Electronic Supplementary Material (ESI) for Chemical Science.

Harnessing Sulfur and Nitrogen in the Cobalt (III)-Catalyzed Unsymmetrical Double Annulation of Thioamides: Probing the Origin of Chemo- and Regioselectivity

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SUPPORTING INFORMATION

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General Experimental Methods

All the reactions were performed in an oven-dried Schlenk flask. Commercial grade solvents were distilled prior to use. Column chromatography was performed using either 100-200 Mesh or 230-400 Mesh silica gel or neutral alumina. Thin layer chromatography (TLC) was performed on silica gel GF254 plates and alumina plates.

Proton, carbon, and fluorine nuclear magnetic resonance spectra (^{1}H NMR, ^{13}C NMR and ^{19}F NMR) were recorded based on the resonating frequencies as follows: (^{1}H NMR, 400 MHz; ^{13}C NMR, 101 MHz; ^{19}F NMR, 376 MHz), (^{1}H NMR, 500 MHz; ^{13}C NMR, 126 MHz; ^{19}F NMR, 470 MHz) and (^{1}H NMR, 600 MHz; ^{13}C NMR, 150 MHz) having the solvent resonance as internal standard (^{1}H NMR, $CDCl_3$ at 7.26 ppm; ^{13}C NMR, $CDCl_3$ at 77.0 ppm). In a few cases, tetramethylsilane (TMS) was used as reference standard at 0.00 ppm. Data for ^{1}H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet; bs = broad singlet; d = doublet; bd = broad doublet, t = triplet; bt = broad triplet; q = quartet; m = multiplet), coupling constants, J, in (Hz), and integration. Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (ppm). IR spectra are reported in cm^{-1}. High resolution mass spectra were obtained in ESI mode in Maxis-TOF analyzer. Melting points were determined by electro-thermal heating and are uncorrected. X-ray data was collected at 293 K using graphite monochromated Mo-Kα radiation (0.71073 Å).

Materials: Unless otherwise noted, all the reagents and intermediates were obtained commercially and used without purification. Dichloromethane (DCM), methanol (MeOH), acetonitrile (CH_3CN), toluene, dimethoxyethane (DME), tetrachloroethylene (TCE), 1,4-dioxane, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and 1,2-dichloroethane (DCE) were distilled over CaH_2. $AgSbF_6$, $AgBF_4$, $NaPF_6$, KPF_6, $[RuCl_2(p\text{-cymene})]_2$, and $[Cp^*RhCl_2]_2$ were purchased and used as received. Analytical and spectral data of all the known compounds are exactly matching with the reported values. The complex $[Cp^*Co(CO)I_2]$ was prepared following the known procedure.[1] Compounds **1', 1'aa, 1'bb**, and **7'** were prepared following known procedures.[2] The symmetrical alkynes **2b–n, 2s** and **2v** were synthesized following reported procedures.[3] Analytical and spectral data of these compounds are exactly matching with the reported values. Diphenyl acetylene (**2a**), 1-phenyl-1-propyne (**2l**), phenylacetylene (**2m**), 2-butyne (**2o**), 3-hexyne (**2p**), 4-octyne (**2q**), 5-decyne (**2r**), dimethyl acetylenedicarboxylate (**2t**) and 1-phenyl-2-trimethylsilylacetylene (**2u**) were purchased and used as received.

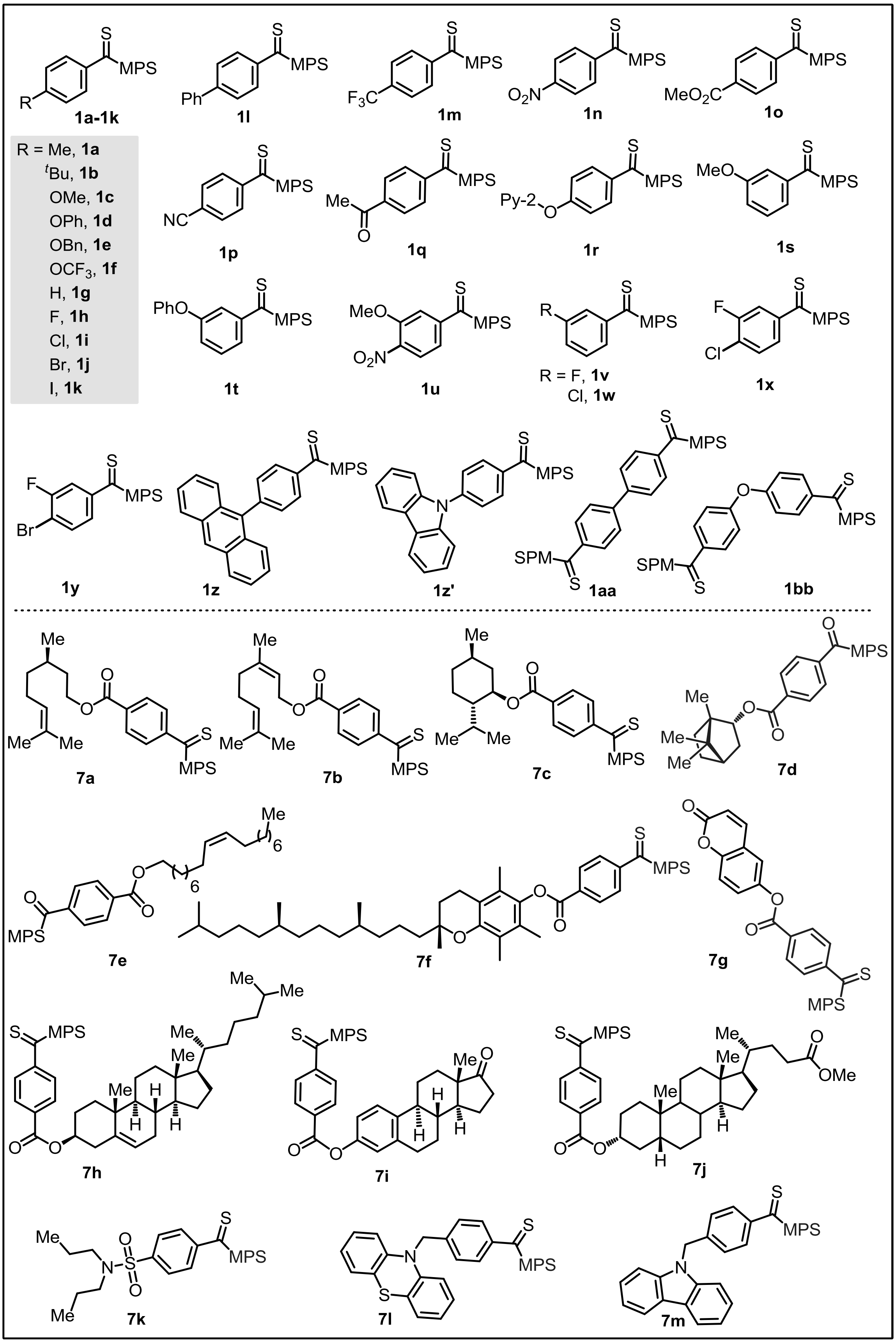


Figure S1: List of *N*-[arenethioyl]-*S*-Methyl-*S*-Phenylsulfoximine (**1** & **7**).

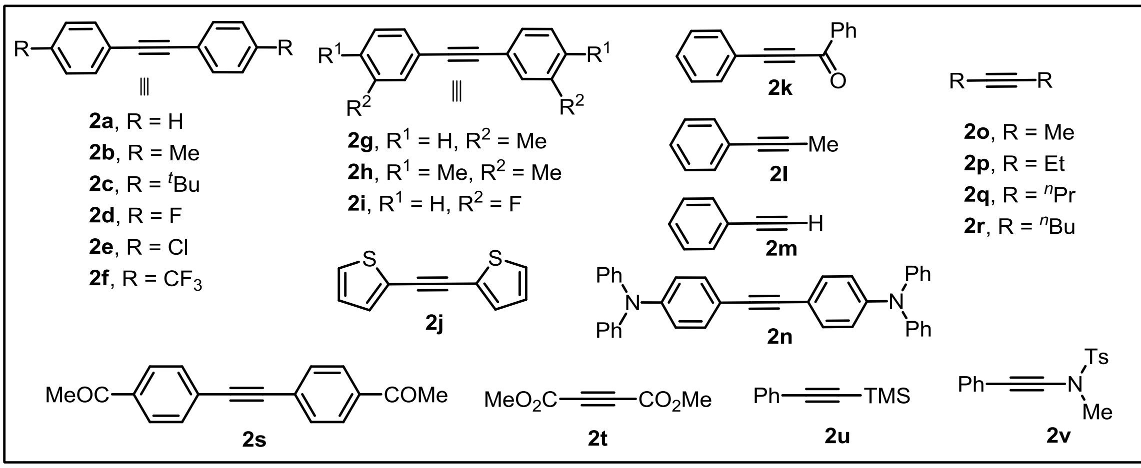
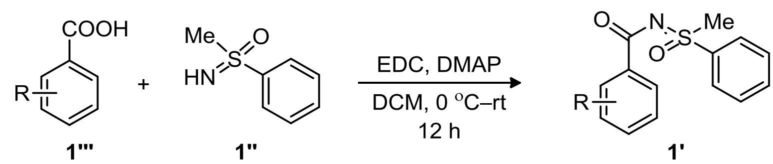


Figure S2: List of alkynes **2**.

Experimental Procedures:

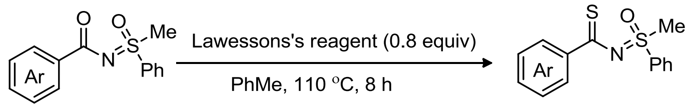
Preparation of *N*-[arenethioyl]-*S*-Methyl-*S*-Phenylsulfoximine (1): General Procedure (GP-1):[2]



Step-I

A solution of *N'*-(3-dimethylaminopropyl)-*N*-ethylcarbodimide, hydrochloride salt (EDC·HCl) (2.0 equiv), 4-*N,N*-dimethylaminopyridine (DMAP) (2.2 equiv) and benzoic acids (**1'''**) (1.1 equiv) in CH_2Cl_2 (5.0 mL, for 1.0 mmol of sulfoximine) was stirred under an argon atmosphere. Sulfoximine (**1''**) (1.0 equiv, 0.50 g) was introduced dropwise at 0 °C. The resulting reaction mixture was stirred for about 1 h at 0 °C and then 12 h at ambient temperature. Upon complete consumption of sulfoximine, the reaction mixture was acidified with hydrochloric acid (HCl, 2N). The organic layer was separated; the aqueous layer was extracted with CH_2Cl_2 (3 times). The combined extracts were washed with 10% aqueous $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4. Solvent was filtered and evaporated under reduced pressure. The crude residue was purified using column chromatography on silica gel using hexane/ethyl acetate.[2]

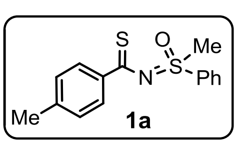
Step-II:



1'   1

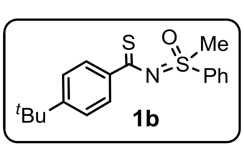
The oven dried reaction tube was charged with *N*-aroylated-MPS (**1'**; 1.0 equiv, 0.5 g) and Lawessons's reagent (0.8 equiv). The reaction tube was evacuated and dry toluene (10 mL) was added and the resulting mixture was stirred at 110 °C for 8 h. Progress of the reaction was monitored by TLC. After complete consumption of **1'**, the reaction mixture was cooled to room temperature. The solvents were evaporated under the reduced pressure and the crude material was extracted with ethylacetate (3 × 10 mL). The organic layer was dried over Na_2SO_4. Solvent was filtered and evaporated under the reduced pressure. The crude residue was purified over a small pad of silica gel using hexane/ethyl acetate (2:3) to provide **1**. The freshly prepared compounds **1** were used for annulations. The compounds **1** were stored under inert conditions at −20 °C.[4a]

N-[4-Methylbenzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1a):



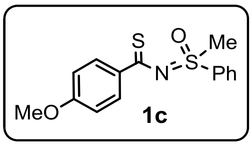
1a (401 mg, 76%); yellow crystalline solid; R_f = 0.57(1:1 hexane/EtOAc; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, J = 8.5 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H), 7.64 (bt, J = 7.0 Hz, 1H), 7.57 (bt, J = 7.5 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 3.46 (s, 3H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 210.8, 142.6, 139.7, 137.4, 133.5, 129.7, 128.3, 128.2, 127.3, 44.6, 21.4; IR (Neat) ν_{max} 2921, 1602, 1446, 1319, 1309, 1220, 1172, 1090, 1027 cm^{-1}; **HRMS (ESI) for** $C_{15}H_{15}NNaOS_2$ $(M+Na)^+$: calcd. 312.0487, found 312.0490.

N-[4-(Tertbutyl)benzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1b):



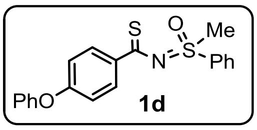
1b (390 mg, 75%); yellow solid; R_f = 0.48 (7:3 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dt, J = 8.8 & 2.0 Hz, 2H), 8.01–7.97 (m, 2H), 7.70–7.63 (m, 1H), 7.63–7.58 (m, 2H), 7.38 (dt, J = 8.8 & 2.2 Hz, 2H), 3.48 (s, 3H), 1.33 (s, 9H); $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$) δ 211.0, 155.6, 139.8, 137.6, 133.6, 129.7, 128.0, 127.4, 124.7, 44.7, 34.9, 31.1; IR (Neat) ν_{max} 2951, 1601, 1410, 1317, 1276, 1233, 1206, 1172, 1108, 1004, 956 cm^{-1}; **HRMS (ESI)** for $C_{18}H_{22}NOS_2$ $(M+H)^+$: calcd. 332.1137, found 332.1143.

N-[4-Methoxybenzothioyl]-S-methyl-S-phenylsulfoximine (1c):



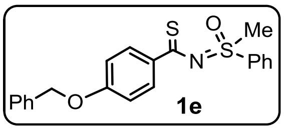
1c (390 mg, 74%); yellow crystalline solid; R_f = 0.42 (3:2 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 7.2 Hz, 2H), 7.97 (d, J = 6.0 Hz, 2H), 7.66 (t, J = 5.8 Hz, 1H), 7.59 (t, J = 6.0 Hz, 2H), 6.85 (d, J = 7.2 Hz, 2H), 3.85 (s, 3H), 3.48 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 209.7, 163.2, 137.9, 135.5, 133.5, 130.4, 129.7, 127.4, 112.8, 55.4, 44.7; IR (Neat) ν_{max} 3001, 2918, 1594, 1474, 1417, 1301, 1157, 970 cm^{-1}; **HRMS (ESI)** for $C_{15}H_{16}NO_2S_2$ $(M+H)^+$: calcd. 306.0617, found 306.0632.

N-[4-Phenoxybenzothioyl]-S-methyl-S-phenylsulfoximine (1d):



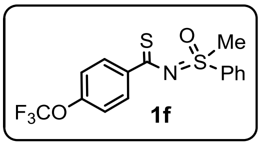
1d (381 mg, 73%); yellow crystalline solid; R_f = 0.45 (3:2 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 7.2 Hz, 2H), 7.97 (d, J = 6.0 Hz, 2H), 7.66 (bt, J = 5.8 Hz, 1H), 7.59 (bt, J = 6.2 Hz, 2H), 7.37 (bt, J = 6.6 Hz, 2H), 7.17 (t, J = 6.0 Hz, 1H), 7.06 (d, J = 6.0 Hz, 2H), 6.92 (d, J = 7.2 Hz, 2H), 3.47 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 209.6, 161.2, 155.9, 137.4, 137.1, 133.6, 130.3, 129.8, 129.7, 127.3, 124.1, 119.7, 116.7, 44.7; IR (Neat) ν_{max} 3363, 3192, 1651, 1572, 1508, 1486, 1322, 1248, 1140 cm^{-1}; **HRMS (ESI)** for $C_{20}H_{18}NO_2S_2$ $(M+H)^+$: calcd. 368.0773, found 368.0775.

N-[4-(Benzyloxy)benzothioyl]-S-methyl-S-phenylsulfoximine (1e):



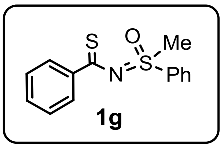
1e (376 mg, 72%); yellow crystalline solid; R_f = 0.54 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.8 Hz, 2H), 7.98 (d, J = 8.4 Hz, 2H), 7.65 (t, J = 6.4 Hz, 1H), 7.59 (t, J = 7.2 Hz, 2H), 7.46–7.33 (m, 5H), 6.92 (d, J = 8.8 Hz, 2H), 5.12 (s, 2H), 3.48 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 209.7, 162.4, 137.9, 136.5, 135.7, 133.6, 130.5, 129.7, 128.6, 128.1, 127.43, 127.40, 113.8, 70.1, 44.7; IR (Neat) ν_{max} 3032, 2914, 1598, 1501, 1446, 1322, 1214, 996, 883 cm^{-1}; **HRMS (ESI)** for $C_{21}H_{20}NO_2S_2$ $(M+H)^+$: calcd. 382.0930, found 382.0930.

N-[4-(trifluoromethoxy)benzothioyl]-S-methyl-S-phenylsulfoximine (1f):



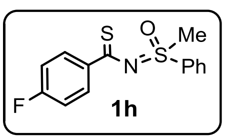
1f (388 mg, 74%); yellow crystalline solid; R_f = 0.42 (3:2 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 7.2 Hz, 2H), 7.95 (d, J = 6.0 Hz, 2H), 7.65 (t, J = 6.0 Hz, 1H), 7.58 (t, J = 6.2 Hz, 2H), 7.16 (d, J = 6.4 Hz, 2H), 3.47 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 209.0, 151.92, 151.90, 140.4, 136.9, 133.7, 129.9, 129.7, 127.2, 119.4, 44.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ −57.54; IR (Neat) ν_{max} 2931, 1592, 1500, 1445, 1412, 1299, 1260, 1206, 1164, 1120, 1101, 1084, 1009, 959 cm^{-1}; **HRMS (ESI)** for $C_{15}H_{13}F_3NO_2S_2$ $(M+H)^+$: calcd. 360.0334, found 306.0335.

***N*-[Benzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1g):**



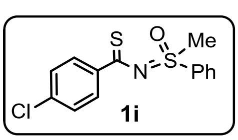
1g (378 mg, 71%); yellow crystalline solid; R_f = 0.67 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (dd, J = 7.6 & 1.2 Hz, 2H), 7.97 (bd, J = 7.6 Hz, 2H), 7.66 (bt, J = 6.8 Hz, 1H), 7.62–7.54 (m, 2H), 7.53–7.46 (m, 1H), 7.36 (t, J = 7.8 Hz, 2H), 3.47 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 211.2, 142.1, 137.2, 133.6, 131.9, 129.7, 128.1, 127.7, 127.3, 44.6; IR (Neat) ν_{max} 2923, 1602, 1576, 1447, 1320, 1269, 1220, 1172, 1089, 965cm^{-1}; **HRMS (ESI)** for $C_{14}H_{14}NOS_2$ $(M+H)^+$: calcd. 276.0511, found 276.0518.

***N*-[4-Fluorobenzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1h):**



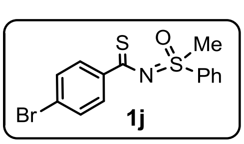
1h (320 mg, 61%); yellow crystalline solid; R_f = 0.62 (1:1 hexane/EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 8.38 (dd, J = 8.5 & 6.0 Hz, 2H), 7.97 (d, J = 7.5 Hz, 2H), 7.67 (bt, J = 7.2 Hz, 1H), 7.60 (t, J = 7.2 Hz, 2H), 7.01 (t, J = 8.2 Hz, 2H), 3.48 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 209.4, 165.6 (d, J = 253 Hz), 138.5, 137.4, 133.7, 130.6 (d, J = 8.8 Hz), 129.8, 127.3, 114.5 (d, J = 21 Hz), 44.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ −108.22; IR (Neat) ν_{max} 3063, 2923, 1672, 1598, 1498, 1446, 1320, 1273, 1222, 1095, 1010, 964, 892 cm^{-1}; **HRMS (ESI)** for $C_{14}H_{13}FNOS_2$ $(M+H)^+$: calcd. 294.0417, found 294.0419.

***N*-[4-Chlorobenzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1i):**



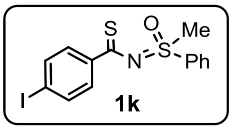
1i (398 mg, 88%); yellow crystalline solid; R_f = 0.59 (1:1 hexane/EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, J = 8.5 Hz, 2H), 7.96 (d, J = 7.5 Hz, 2H), 7.68 (bt, J = 7.5 Hz, 1H), 7.61 (t, J = 7.5 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 3.48 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 209.5, 140.5, 138.4, 137.3, 133.8, 129.8, 129.5, 127.8, 127.4, 44.7; IR (Neat) ν_{max} 3010, 2923, 1586, 1480, 1446, 1321, 1220, 1167, 1101, 1087, 1007, 965 cm^{-1}; **HRMS (ESI)** for $C_{14}H_{13}ClNOS_2$ $(M+H)^+$: calcd. 310.0122, found 310.0127.

***N*-[4-Bromobenzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1j):**



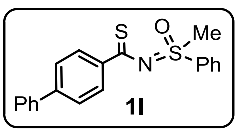
1j (360 mg, 69%); yellow crystalline solid; R_f = 0.62 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 7.2 Hz, 2H), 7.99–7.94 (m, 2H), 7.72–7.65 (m, 1H), 7.64–7.58 (m, 2H), 7.48 (d, J = 6.8 Hz, 2H), 3.49 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 209.6, 140.9, 137.2, 133.8, 130.8, 129.8, 129.7, 127.4, 127.2, 44.7; IR (Neat) ν_{max} 3181, 2922, 1579, 1476, 1394, 1319, 1269, 1218, 1168, 1101, 1068, 1004, 834cm^{-1}; **HRMS (ESI)** for $C_{14}H_{12}BrNNaOS_2$ $(M+Na)^+$: calcd. 375.9436, found 375.9435.

***N*-[4-Iodobenzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1k):**



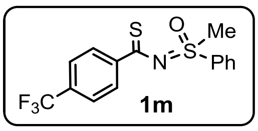
1k (342 mg, 65%); yellow crystalline solid; R_f = 0.56 (1:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 8.5 Hz, 2H), 7.94 (d, J = 7.5 Hz, 2H), 7.69 (d, J = 9.0 Hz, 2H), 7.65 (d, J = 7.5 Hz, 1H), 7.58 (t, J = 7.75 Hz, 2H), 3.47 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 209.7, 141.4, 137.0, 136.8, 133.8, 129.8, 129.6, 127.3, 99.9, 44.6; IR (Neat) ν_{max} 3014, 2963, 1599, 1504, 1390, 1306, 1281, 1209, 1056, 1018 cm^{-1}; **HRMS (ESI)** for $C_{14}H_{12}INNaOS_2$ $(M+Na)^+$: calcd. 423.9297, found 423.9301.

***N*-[[1,1'-Biphenyl]-4-carbothioyl]-*S*-methyl-*S*-phenylsulfoximine (1l):**



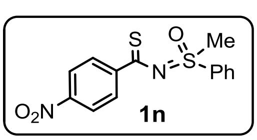
1l (392 mg, 64%); yellow crystalline solid; R_f = 0.56 (1:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, J = 8.5 Hz, 2H), 8.00 (d, J = 7.5 Hz, 2H), 7.71–7.57 (m, 7H), 7.46 (bt, J = 7.75 Hz, 2H), 7.38 (bt, J = 7.25 Hz, 1H), 3.51 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 210.5, 144.6, 141.1, 140.2, 137.4, 133.7, 129.8, 128.8, 128.7, 127.9, 127.4, 127.1, 126.4, 44.7; IR (Neat) ν_{max} 3058, 2163, 1736, 1469, 1312, 1279, 1206, 1115, 1003, 856, 731 cm^{-1}; **HRMS (ESI)** for $C_{20}H_{18}NOS_2$ $(M+H)^+$: calcd. 352.0824, found 352.0834.

***N*-[4-(Trifluoromethyl)benzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1m):**



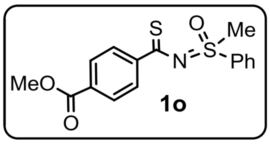
1m (381 mg, 72%); yellow crystalline solid; R_f = 0.54 (1:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, J = 8.0 Hz, 2H), 7.97 (d, J = 7.5 Hz, 2H), 7.69 (bt, J = 7.5 Hz, 1H), 7.61 (bt, J = 8.5 Hz, 4H), 3.50 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 209.5, 144.9, 137.0, 133.9, 132.9 (q, J = 32 Hz), 129.9, 128.3, 127.4, 126.1 (q, J = 268 Hz), 124.7 (q, J = 4.0 Hz), 44.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ –62.76; IR (Neat) ν_{max} 3005, 2914, 1609, 1446, 1409, 1324, 1213, 1163, 1060, 981 cm^{-1}; **HRMS (ESI)** for $C_{15}H_{13}F_3NOS_2$ $(M+H)^+$: calcd. 344.0385, found 344.0392.

***N*-[4-Nitrobenzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1n):**



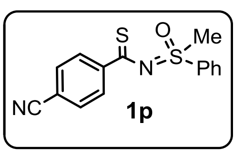
1n (341 mg, 66%); red crystalline solid; R_f = 0.46 (1:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (d, J = 9.0 Hz, 2H), 8.17 (d, J = 9.0 Hz, 2H), 7.97 (d, J = 7.5 Hz, 2H), 7.71 (t, J = 7.25 Hz, 1H), 7.63 (t, J = 7.75 Hz, 2H), 3.52 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 208.3, 149.4, 146.5, 136.5, 134.1, 129.9, 128.9, 127.4, 122.9, 44.6; IR (Neat) ν_{max} 3010, 2917, 1736, 1511, 1476, 1344, 1299, 1162, 106, 758 cm^{-1}; **HRMS (ESI)** for $C_{14}H_{12}N_2NaO_3S_2$ $(M+Na)^+$: calcd. 343.0182, found 343.0186.

***N*-[4-Methoxycarbonylbenzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1o):**



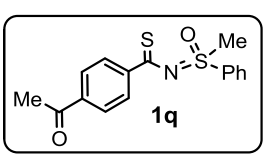
1o (425 mg, 80%); yellow crystalline solid; R_f = 0.50 (3:2 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 6.8 Hz, 2H), 8.03–7.95 (m, 4H), 7.68 (t, J = 6.0 Hz, 1H), 7.61 (t, J = 6.0 Hz, 2H), 3.93 (s, 3H), 3.50 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 210.1, 166.7, 145.5, 137.2, 133.8, 132.5, 129.8, 129.0, 128.0, 127.4, 52.2, 44.6; IR (Neat) ν_{max} 3188, 3054, 2917, 1721, 1656, 1473, 1402, 1324, 1274, 1213, 1105, 894 cm^{-1}; **HRMS (ESI)** for $C_{16}H_{16}NO_3S_2$ $(M+H)^+$: calcd. 334.0566, found 334.0568.

***N*-[4-Cyanobenzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1p):**



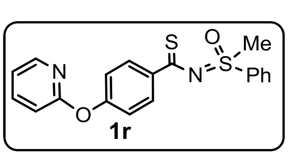
1p (380 mg, 72%); red colour solid; R_f = 0.50 (1:1 hexane/EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, J = 8.5 Hz, 2H), 7.97 (d, J = 7.5 Hz, 2H), 7.70 (t, J = 7.25 Hz, 1H), 7.67–7.59 (m, 4H), 3.51 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 208.7, 145.2, 136.8, 134.0, 131.6, 129.9, 128.5, 127.4, 118.6, 114.7, 44.6; IR (Neat) ν_{max} 3023, 2217, 1452, 1411, 1308, 1209, 1085, 1010, 965, 891, 844 cm^{-1}; **HRMS (ESI)** for $C_{15}H_{13}N_2OS_2$ $(M+H)^+$: calcd. 301.0464, found 301.0464.

***N*-[4-Acetylbenzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1q):**



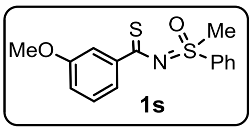
1q (400 mg, 77%); orange colour solid; R_f = 0.50 (1:1 hexane/EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, J = 8.5 Hz, 2H), 7.97 (d, J = 7.5 Hz, 2H), 7.90 (d, J = 8.5 Hz, 2H), 7.67 (t, J = 7.25 Hz, 1H), 7.60 (t, J = 7.75 Hz, 2H), 3.50 (s, 3H), 2.61 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 209.9, 197.8, 145.5, 138.9, 137.0, 133.8, 129.8, 128.2, 127.7, 127.4, 44.6, 26.8; IR (Neat) ν_{max} 3011, 2913, 1678, 1489, 1265, 1085, 956 cm^{-1}; **HRMS (ESI)** for $C_{16}H_{16}NO_2S_2$ $(M+H)^+$: calcd. 318.0617, found 318.0616.

***N*-[4-(pyridin-2-yloxy)benzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1r):**



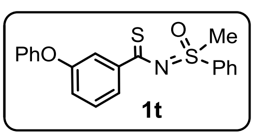
1r (350 mg, 67%); yellow colour solid; R_f = 0.52 (2:3 hexane/EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 8.41 (bd, J = 7.0 Hz, 2H), 8.21 (bs, 1H), 8.00–7.92 (m, 2H), 7.70 (bt, J = 7.25 Hz, 1H), 7.69–7.56 (m, 3H), 7.09 (dd, J = 8.75 & 2.25 Hz, 2H), 7.03 (bt, J = 6.0 Hz, 1H), 6.94 (dd, J = 8.0 & 1.0 Hz, 1H), 3.47 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 209.7, 163.0, 157.9, 147.7, 139.6, 138.5, 137.4, 133.6, 130.1, 129.7, 127.4, 119.6, 119.1, 112.0, 44.7; IR (Neat) ν_{max} 3069, 2910, 1577, 1493, 1464, 1424, 1325, 1236, 1222, 1152, 1084 cm^{-1}; **HRMS (ESI)** for $C_{19}H_{17}N_2O_2S_2$ $(M+H)^+$: calcd. 369.0726, found 369.0728.

***N*-[3-Methoxybenzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1s):**


1s

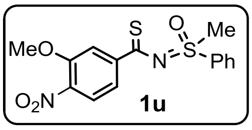
1s (427 mg, 81%); yellow crystalline solid; R_f = 0.41 (3:2 hexane/EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, J = 7.2 Hz, 2H), 7.92 (d, J = 7.8 Hz, 1H), 7.89 (bs, 1H), 7.66–7.61 (m, 1H), 7.60–7.54 (m, 2H), 7.28–7.23 (m, 1H), 7.04 (d, J = 9.6 Hz, 1H), 3.83 (s, 3H), 3.46 (s, 3H); $^{13}C\{^1H\}$ NMR (600 MHz, $CDCl_3$) δ 210.9, 159.0, 143.6, 137.2, 133.7, 129.8, 128.6, 127.3, 120.5, 118.1, 113.3, 55.4, 44.7; IR (Neat) ν_{max} 2914, 2835, 1590, 1508, 1412, 1371, 1331, 1259, 1199, 1129, 1087, 1017 cm^{-1}; **HRMS (ESI)** for $C_{15}H_{16}NO_2S_2$ $(M+H)^+$: calcd. 306.0617, found 306.0621.

***N*-[3-Phenoxybenzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1t):**


1t

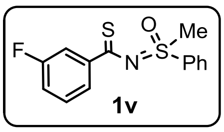
1t (421 mg, 80%); yellow crystalline solid; R_f = 0.59 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15–8.08 (m, 1H), 8.02 (bt, J = 2.0 Hz, 1H), 7.98–7.92 (m, 2H), 7.71–7.63 (m, 1H), 7.59 (bt, J = 7.6 Hz, 2H), 7.38–7.28 (m, 3H), 7.18–7.07 (m, 2H), 7.06–6.98 (m, 2H), 3.46 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 210.1, 157.1, 156.5, 144.0, 137.1, 133.7, 129.8, 129.7, 128.9, 127.3, 123.5, 123.2, 122.3, 118.6, 118.4, 44.5; IR (Neat) ν_{max} 3017, 1650, 1578, 1486, 1327, 1245, 1213, 1162, 1083, 973, 856 cm^{-1}; **HRMS (ESI)** for $C_{20}H_{18}NO_2S_2$ $(M+H)^+$: calcd. 368.0773, found 368.0770.

***N*-[3-Methoxy-4-nitrobenzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1w):**


1u

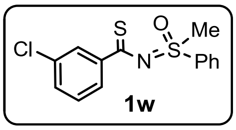
1u (410 mg, 79%); red colour crystalline solid; R_f = 0.44 (1:1 hexane/ EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11–8.05 (m, 1H), 7.99–7.94 (m, 2H), 7.94–7.88 (m, 1H), 7.81–7.73 (m, 1H), 7.73–7.66 (m, 1H), 7.67–7.59 (m, 2H), 3.99 (s, 3H), 3.51 (s, 3H); $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$) δ 208.2, 152.1, 146.4, 141.1, 136.6, 134.1, 129.9, 127.4, 124.9, 119.14, 119.07, 114.04, 113.97, 56.6, 44.6; IR (Neat) ν_{max} 3017, 2931, 1606, 1512, 1398, 1334, 1306, 1251, 1212, 1194, 1172, 1141, 1051, 1082, 964 cm^{-1}; **HRMS (ESI)** for $C_{15}H_{15}N_2O_4S_2$ $(M+H)^+$: calcd. 351.0468, found 351.0466.

***N*-[3-Fluorobenzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1v):**


1v

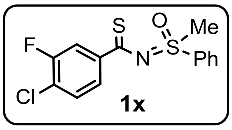
1v (410 mg, 79%); yellow crystalline solid; R_f = 0.52 (3:2 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dt, J = 7.6 & 1.2 Hz, 1H), 8.06–8.00 (m, 1H), 7.96 (d, J = 8.4 Hz, 2H), 7.68 (t, J = 7.0 Hz, 1H), 7.60 (t, J = 7.8 Hz, 2H), 7.36–7.28 (m, 1H), 7.18 (td, J = 8.0 & 2.5 Hz, 1H), 3.48 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 209.3, 162.2 (d, J = 246 Hz), 144.2 (d, J = 7.0 Hz), 137.0, 133.8, 129.8, 129.1 (d, J = 8.0 Hz), 127.3, 123.9 (d, J = 3.0 Hz), 118.5 (d, J = 22.2 Hz), 114.7 (d, J = 23.2 Hz), 44.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ −113.69; IR (Neat) ν_{max} 3167, 1655, 1624, 1581, 1534, 1446, 1392, 1285, 1266, 1225, 1129, 1020, 913 cm^{-1}; **HRMS (ESI)** for $C_{14}H_{13}FNOS_2$ $(M+H)^+$: calcd. 294.0417, found 294.0421.

N-[3-Chlorobenzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1w):



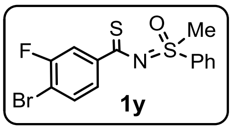
1w (412 mg, 79%); yellow crystalline solid; R_f = 0.53 (3:2 hexane/EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 8.31 (t, J = 2.0 Hz, 1H), 8.25–8.19 (m, 1H), 7.96 (d, J = 7.5 Hz, 2H), 7.68 (t, J = 7.25 Hz, 1H), 7.61 (d, J = 7.5 Hz, 2H), 7.49–7.43 (m, 1H), 7.29 (t, J = 7.75 Hz, 1H), 3.48 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 209.3, 143.7, 137.1, 133.8, 131.6, 129.8, 128.9, 127.9, 127.4, 126.6, 44.7; IR (Neat) ν_{max} 3016, 2922, 1562, 1458, 1321, 1272, 1205, 1081 cm^{-1}; **HRMS (ESI)** for $C_{14}H_{13}ClNOS_2$ $(M+H)^+$: calcd. 310.0122, found 310.0124.

N-[4-Chloro-3-fluorobenzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1x):



1x (400 mg, 77%); yellow crystalline solid; R_f = 0.57 (3:2 hexane/EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 8.15–8.06 (m, 2H), 7.97–7.93 (m, 2H), 7.69 (t, J = 9.25 Hz, 1H), 7.65–7.57 (m, 2H), 7.40–7.34 (m, 1H), 3.49 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 207.8 (d, J = 3.8 Hz), 157.3 (d, J = 310 Hz), 142.3 (d, J = 7.5 Hz), 136.8, 133.9, 129.7 (d, J = 31.5 Hz), 127.3, 124.9 (d, J = 22.7 Hz), 124.5 (d, J = 3.8 Hz), 115.9 (d, J = 29.0 Hz), 44.7; ^{19}F NMR (470 MHz, $CDCl_3$) δ −115.74; IR (Neat) ν_{max} 3173, 3056, 2913, 1658, 1475, 1323, 1284, 1247, 1216, 1168, 1084, 1062, 1029, 980 cm^{-1}; **HRMS (ESI)** for $C_{14}H_{12}ClFNOS_2$ $(M+H)^+$: calcd. 328.0027, found 328.0031.

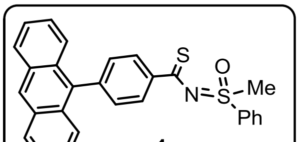
N-[4-Bromo-3-fluorobenzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1y):



1y (380 mg, 73%); yellow crystalline solid; R_f = 0.55 (3:2 hexane/EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 8.09 (dd, J = 10.0 & 2.0 Hz, 1H), 8.02 (dd, J = 8.5 & 2.0 Hz, 1H), 7.95 (d, J = 7.5 Hz, 2H), 7.69 (t, J = 7.25 Hz, 1H), 7.61 (t, J = 7.5 Hz, 2H), 7.52 (dd, J = 8.5 & 7.0 Hz, 1H), 3.49 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 207.9 (d, J = 2.5 Hz), 158.3 (d, J = 247.0 Hz), 143.2 (d, J = 6.3 Hz), 136.8, 133.9, 132.6, 129.9, 127.3, 124.9 (d, J = 2.5 Hz), 115.6 (d, J = 23.9 Hz), 113.5 (d, J = 21.4 Hz), 44.7; ^{19}F NMR (470 MHz,

$CDCl_3$) δ −107.74; IR (Neat) ν_{max} 3012, 2912, 1625, 1472, 1324, 1400, 1246, 1218, 1083 cm^{-1}; **HRMS (ESI)** for $C_{14}H_{12}BrFNOS_2$ $(M+H)^+$: calcd. 371.9522, found 371.9518.

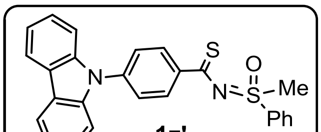
***N*-[4-(Anthracen-9-yl)benzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1z):**



1z

1z (356 mg, 67%); yellow solid; R_f = 0.43 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 8.4 Hz, 2H), 8.51 (bs, 1H), 8.06 (t, J = 8.8 Hz, 4H), 7.73–7.61 (m, 5H), 7.50–7.43 (m, 4H), 7.39–7.31 (m, 2H), 3.56 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 210.9, 142.9, 141.6, 137.4, 136.2, 133.8, 131.3, 130.9, 129.9, 129.8, 128.3, 128.2, 127.5, 126.8, 126.6, 125.5, 125.1, 44.8; IR (Neat) ν_{max} 3014, 2924, 1662, 1601, 1270, 1011 cm^{-1}; **HRMS (ESI)** for $C_{28}H_{22}NOS_2$ $(M+H)^+$: calcd. 452.1137, found 452.1143.

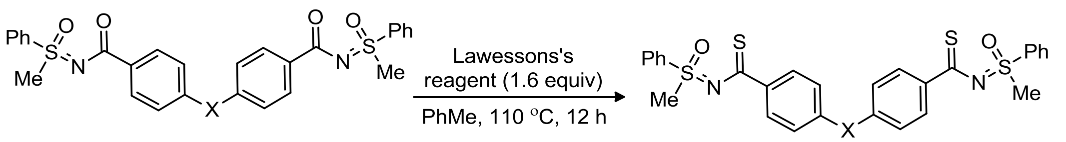
***N*-[4-(9H-Carbazol-9-yl)benzothioyl]-*S*-methyl-*S*-phenylsulfoximine (1z'):**



1z'

1z' (362 mg, 70%); yellow crystalline solid; R_f = 0.52 (1:1 hexane/EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 8.65 (d, J = 8.5 Hz, 2H), 8.17 (d, J = 8.0 Hz, 2H), 8.04 (d, J = 7.5 Hz, 2H), 7.71–7.64 (m, 1H), 7.65–7.59 (m, 4H), 7.53 (d, J = 8.0 Hz, 2H), 7.48–7.41 (m, 2H), 7.37–7.30 (m, 2H), 3.52 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 209.4, 140.9, 140.6, 140.1, 137.1, 133.7, 129.8, 129.7, 127.2, 125.9, 125.4, 123.5, 120.2, 109.7, 44.5; IR (Neat) ν_{max} 3015, 2913, 1597, 1472, 1390, 1355, 1282, 1169, 996 cm^{-1}; **HRMS (ESI)** for $C_{26}H_{21}N_2OS_2$ $(M+Na)^+$: calcd. 441.1090, found 441.1095.

Preparation of 1aa and 1bb: General Procedure (GP-2):[2b,4]

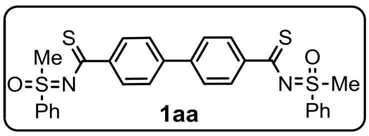


1'aa–1'bb **1aa–1bb**

The oven dried reaction tube was charged with *N*-aroylated-MPS (**1'aa** or **1'bb**; 1.0 equiv, 0.5 g) and Lawessons's reagent (1.6 equiv). The reaction tube was evacuated and dry toluene (15 mL) was added and the resulting mixture was stirred at 110 °C for 12 h. Progress of the reaction was monitored by TLC. After complete consumption of **1'aa** or **1'bb**, the reaction mixture was cooled to room temperature. The solvents were evaporated under the reduced pressure and the crude material was extracted with ethylacetate (3 × 10 mL). The organic layer was dried over Na_2SO_4. Solvent was filtered and evaporated under reduced pressure. The crude residue was purified over a small pad of silica gel using hexane/ethyl acetate (2:3).

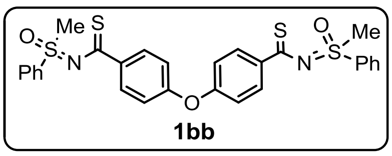
The freshly prepared compounds **1aa** or **1bb** were used for annulations. The compounds **1aa** and **1bb** were stored under inert conditions at –20 °C.

Synthesis of 1aa:



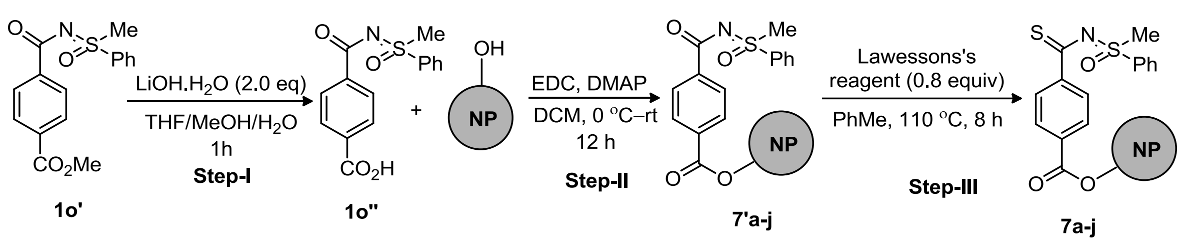
The compound has been isolated by filtration from the reaction mixture followed by washing with MeOH and dichloromethane mixture. **1aa** (356 mg, 67%); yellow colour solid. The compound is insoluble in deuterated $CHCl_3$, THF, DMSO, MeOH, and CH_3CN. Thus, it is impossible to record respective ^{1}H NMR and ^{13}C NMR spectra; IR (Neat) ν_{max} 3002, 2911, 1737, 1598, 1444, 1396, 1328, 1311, 1210, 1173, 1083, 999, 978 cm^{-1}; **HRMS (ESI)** for $C_{28}H_{25}N_2O_2S_4$ $(M+H)^+$: calcd. 549.0793, found 549.0800.

Synthesis of 1bb:



1bb (402 mg, 76%); yellow colour solid; R_f = 0.42 (2:3 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (bd, J = 8.8 Hz, 4H), 7.98 (bd, J = 8.8 Hz, 4H), 7.67 (bt, J = 7.4 Hz, 2H), 7.60 (bt, J = 8.8 Hz, 4H), 6.98 (bd, J = 8.8 Hz, 4H), 3.49 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.6, 160.0, 138.0, 137.5, 133.7, 130.4, 129.8, 127.4, 117.8, 44.7; IR (Neat) ν_{max} 3005, 2919, 1581, 1451, 1410, 1267, 1209, 1154, 1085, 1004 cm^{-1}; **HRMS (ESI)** for $C_{28}H_{25}N_2O_3S_4$ $(M+H)^+$: calcd. 565.0743, found 565.0749.

Preparation of natural products bearing *N*-[arenethioyl]-*S*-methyl-*S*-phenylsulfoximine (7a-j): EDC-coupling (General Procedure-3):[2c,4]



Step-I

A mixture of compound **1o'** (4.0 g, 10.8 mmol), $LiOH\cdot H_2O$ (0.82 g, 19.6 mmol) in THF (80 mL), water (10 mL), and MeOH (5 mL) was stirred at RT. The crude mixture was stirred for 20 h; upon completion of the reaction, THF was removed. The reaction mixture was diluted with water (200 mL) and extracted with EtOAc (3 × 50 mL). The organic layer was dried over Na_2SO_4, and concentrated under vacuum to give the unreacted starting material **1o'**. The aqueous layer was acidified with 1N HCl and extracted with EtOAc (5 × 50 mL). The organic layer was dried over Na_2SO_4, and concentrated under vacuum to give the corresponding acid **1o''**.

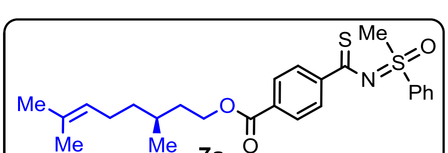
Step-II

A solution of *N'*-(3-dimethylaminopropyl)-*N*-ethylcarbodimide, hydrochloride salt (EDC·HCl) (3.0 equiv), 4-*N,N*-dimethylaminopyridine (DMAP) (2.2 equiv) and sulfoximine-bearing aryl acid (**1o''**; 1.1 equiv) in CH_2Cl_2 (5.0 mL, for 1.0 mmol of sulfoximine) was stirred under an argon atmosphere. The respective natural product (1.0 equiv, 0.50 g) was introduced dropwise at 0 °C. The resulting reaction mixture was stirred for about 30 minutes at 0 °C, and warmed to ambient temperature and continued for 12 h. The reaction mixture was acidified with hydrochloric acid (HCl, 2N). The organic layer was separated; the aqueous layer was extracted with CH_2Cl_2 (3 times). The combined extracts were washed with 10% aqueous $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4. Solvent was filtered and evaporated under the reduced pressure. The crude residue was purified by column chromatography on silica gel using hexane/ethyl acetate eluent. The freshly prepared compound **7'a-j** was used for the next step.[2c]

Step-III

The oven dried reaction tube was charged with natural product bearing *N*-aroylated-MPS (**7'a-j**; 1.0 equiv, 0.5 g) and Lawessons's reagent (0.8 equiv). The reaction tube was evacuated and dry toluene (10 mL) was added. The resulting mixture was stirred at 110 °C for 8 h. Progress of the reaction was monitored by TLC. After complete consumption of **7'a-j**, the reaction mixture was cooled to room temperature. The solvents were evaporated under the reduced pressure and the crude material was extracted with ethylacetate (3 × 10 mL). The organic layer was dried over Na_2SO_4. Solvent was filtered and evaporated under the reduced pressure. The crude residue was purified over a small pad of silica gel using hexane/ethyl acetate (2:3) eluent. The compounds **7a-j** were stored under inert conditions at –20 °C.[4a]

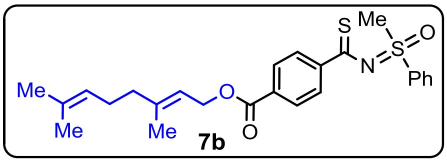
Synthesis of 7a:



7a

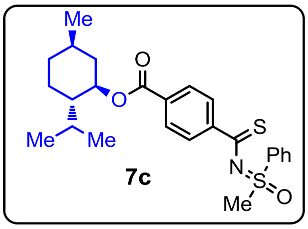
7a (374 mg, 72%); orange colour solid; R_f = 0.54 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 8.8 Hz, 2H), 8.03–7.97 (m, 4H), 7.68 (t, J = 7.4 Hz, 1H), 7.61 (t, J = 7.8 Hz, 2H), 5.13–5.07 (m, 1H), 4.41–4.33 (m, 2H), 3.50 (s, 3H), 2.07–1.95 (m, 2H), 1.87–1.77 (m, 1H), 1.67 (bs, 3H), 1.60 (bs, 3H), 1.45–1.34 (m, 1H), 1.30–1.10 (m, 2H), 0.97 (d, J = 6.4 Hz, 3H), 0.90–0.81 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 210.1, 166.3, 145.4, 137.1, 133.9, 132.9, 131.4, 129.9, 128.9, 128.0, 127.4, 124.5, 63.7, 44.6, 36.9, 35.4, 29.6, 25.7, 25.4, 19.5, 17.6; IR (Neat) ν_{max} 2958, 2920, 2359, 1712, 1598, 446, 1405, 1378, 1321, 1263, 1216, 1097, 1025, 1009, 963, 889 cm^{-1}; **HRMS (ESI)** for $C_{25}H_{32}NO_3S_2$ $(M+H)^+$: calcd. 458.1818, found 458.1811.

Synthesis of 7b:



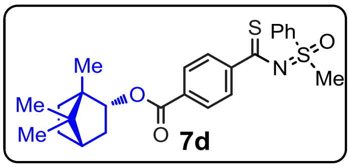
7b (370 g, 71%); orange colour solid; R_f = 0.54 (3:2 hexane/EtOAc); ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.35 (d, J = 8.5 Hz, 2H), 8.01 (d, J = 7.5 Hz, 2H), 7.97 (d, J = 7.5 Hz, 2H), 7.68 (t, J = 7.25 Hz, 1H), 7.61 (t, J = 8.0 Hz, 2H), 5.47 (t, J = 7.0 Hz, 1H), 5.09 (t, J = 6.75 Hz, 1H), 4.85 (d, J = 7.0 Hz, 2H), 3.50 (s, 3H), 2.17–2.04 (m, 4H), 1.77 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 210.1, 166.2, 145.4, 142.5, 137.2, 133.8, 132.9, 131.8, 129.8, 129.0, 127.9, 127.4, 123.7, 118.3, 62.1, 44.6, 39.5, 26.3, 25.6, 17.6, 16.5; IR (Neat) ν_{max} 2928, 2852, 1701, 1448, 1411, 1322, 1266, 1211, 1094, 1004, 965, 922 cm^{-1}; **HRMS (ESI)** for $C_{25}H_{30}NO_3S_2$ $(M+H)^+$: calcd. 456.1662, found 456.1667.

Synthesis of 7c:



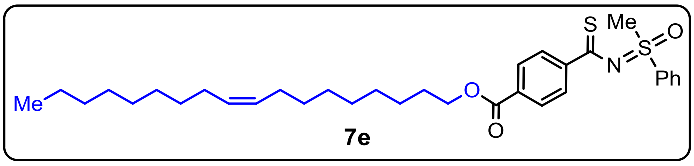
7c (372 mg, 72%); yellow crystalline solid; R_f = 0.54 (1:1 hexane/EtOAc); ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.36 (d, J = 8.5 Hz, 2H), 8.04–7.95 (m, 4H), 7.69 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.25 Hz, 2H), 4.98–4.90 (m, 1H), 3.51 (s, 3H), 2.13 (bd, J = 11.5 Hz, 1H), 1.98–1.90 (m, 1H), 1.73 (d, J = 11.0 Hz, 2H), 1.60–1.52 (m, 2H), 1.19–1.06 (m, 2H), 0.96–0.89 (m, 7H), 0.79 (d, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 210.2, 165.7, 145.4, 137.2, 133.9, 133.3, 129.9, 129.0, 128.0, 127.4, 75.2, 47.3, 44.6, 40.9, 34.3, 31.4, 26.6, 23.7, 22.0, 20.7, 16.6; IR (Neat) ν_{max} 3021, 2924, 2360, 1698, 1568, 1406, 1327, 1264, 1101, 1009, 962 cm^{-1}; **HRMS (ESI)** for $C_{25}H_{32}NO_3S_2$ $(M+H)^+$: calcd. 458.1818, found 458.1816.

Synthesis of 7d:



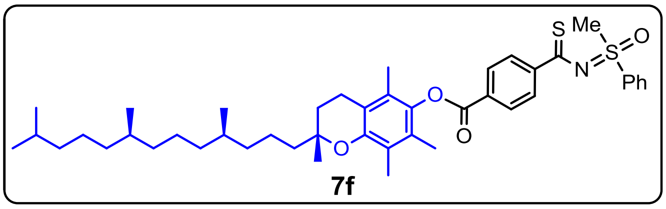
7d (451 mg, 87%); colorless gummy liquid. R_f = 0.57 (3:2 hexane/EtOAc); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.37 (bd, J = 8.4 Hz, 2H), 8.01 (bd, J = 8.4 Hz, 2H), 7.95 (bd, J = 7.6 Hz, 2H), 7.65 (bt, J = 7.2 Hz, 1H), 7.58 (bt, J = 7.6 Hz, 2H), 5.11 (bd, J = 8.8 Hz, 1H), 3.49 (bs, 3H), 2.51–2.39 (m, 1H), 2.18–2.06 (m, 1H), 1.85–1.71 (m, 2H), 1.45–1.21 (m, 2H), 1.12 (dd, J = 13.8 & 3.0 Hz, 1H), 0.95 (s, 3H), 0.90 (s, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 209.9, 166.3, 145.3, 136.9, 133.8, 133.1, 129.7, 128.8, 127.9, 127.3, 80.6, 49.0, 47.7, 44.8, 44.5, 36.7, 27.9, 27.2, 19.6, 18.8, 13.5; IR (Neat) ν_{max} 2927, 1704, 1595, 1404, 1442, 1323, 1299, 1215, 1115, 1005, 967 cm^{-1}; **HRMS (ESI)** for $C_{25}H_{30}NO_3S_2$ $(M+H)^+$: calcd. 456.1662, found 456.1680.

Synthesis of 7e:



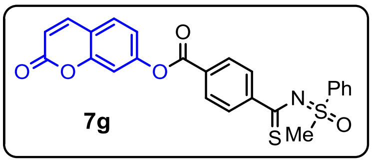
7e (324 mg, 63%); yellow crystalline solid; R_f = 0.54 (1:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, J = 8.5 Hz, 2H), 8.01 (d, J = 8.5 Hz, 2H), 7.99 (d, J = 7.5 Hz, 2H), 7.69 (t, J = 7.25 Hz, 1H), 7.62 (t, J = 7.75 Hz, 2H), 5.35 (t, J = 5.5 Hz, 2H), 4.33 (t, J = 6.75 Hz, 2H), 3.51 (s, 3H), 2.09–1.95 (m, 4H), 1.82–1.73 (m, 2H), 1.50–1.38 (m, 3H), 1.38–1.23 (m, 19H), 0.87 (t, J = 6.75 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 209.6, 166.0, 145.2, 136.9, 133.6, 132.7, 129.7, 129.6, 129.5, 128.7, 127.8, 127.2, 65.1, 55.3, 44.3, 32.3, 31.6, 29.51, 29.48, 29.3, 29.2, 29.05, 29.01, 28.9, 28.4, 27.0, 26.9, 25.8, 22.4, 13.9; IR (Neat) ν_{max} 3006, 2920, 2850, 1715, 1597, 1570, 1502, 1444, 1405, 1329, 1221, 1205, 1117, 1010, 982, 894 cm^{-1}; **HRMS (ESI)** for $C_{33}H_{48}NO_3S_2$ $(M+H)^+$: calcd. 570.3070, found 570.3073.

Synthesis of 7f:



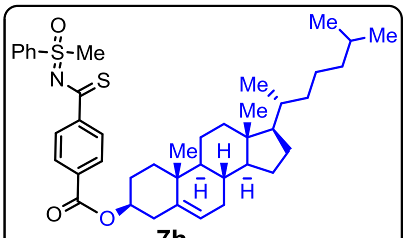
7f (360 mg, 72%); orange colour solid; R_f = 0.61 (3:2 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, J = 8.5 Hz, 2H), 8.23 (d, J = 8.5 Hz, 2H), 8.00 (d, J = 7.5 Hz, 2H), 7.70 (t, J = 7.5 Hz, 1H), 7.63 (t, J = 7.75 Hz, 2H), 3.53 (s, 3H), 2.62 (t, J = 6.75 Hz, 2H), 2.13 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.88–1.76 (m, 2H), 1.65–1.50 (m, 3H), 1.42–1.24 (m, 15H), 1.18–1.04 (m, 6H), 0.90–0.83 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.1, 164.8, 149.5, 146.1, 140.6, 137.2, 133.9, 132.0, 129.9, 129.6, 128.2, 127.5, 126.8, 125.1, 123.2, 117.5, 75.1, 44.7, 39.4, 37.6, 37.55, 37.50, 37.46, 37.42, 37.39, 37.3, 32.8, 32.7, 28.0, 24.80, 24.79, 24.4, 22.7, 22.6, 21.0, 20.6, 19.74, 19.68, 19.65, 19.63, 19.59, 13.0, 12.2; IR (Neat) ν_{max} 2954, 2921, 2865, 1736, 1445, 1405, 1378, 1324, 1267, 1237, 1212, 1090, 1009 cm^{-1}; **HRMS (ESI)** for $C_{44}H_{62}NO_4S_2$ $(M+H)^+$: calcd. 732.4115, found 732.4114.

Synthesis of 7g:



7g (403 mg, 76%); yellow crystalline solid; solubility of compound is poor in $CDCl_3$, DMSO–d6 and other solvents. R_f = 0.31 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, DMSO–d6) δ 8.37 (d, J = 8.4 Hz, 2H), 8.16 (d, J = 8.4 Hz, 2H), 8.08 (d, J = 9.6 Hz, 1H), 8.02 (d, J = 7.2 Hz, 2H), 7.82 (d, J = 8.4 Hz, 1H), 7.76 (t, J = 7.2 Hz, 1H), 7.69 (t, J = 7.4 Hz, 2H), 7.48 (d, J = 9.6 Hz, 1H), 7.34 (dd, J = 8.4 2.0 Hz, 1H), 6.49 (d, J = 4.8 Hz, 1H), 7.35 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, DMSO–d6) δ 208.3, 164.1, 160.0, 154.3, 153.1, 146.5, 144.1, 136.3, 134.2, 131.0, 129.93, 129.85, 129.69, 128.3, 127.9, 119.0, 117.1, 115.9, 110.5, 43.9; IR (Neat) ν_{max} 2919, 1737, 1708, 1616, 1566, 1505, 1403, 1332, 1305, 1228, 1210, 1124, 1009, 977, 890, 872 cm^{-1}; **HRMS (ESI)** for $C_{24}H_{18}NO_5S_2$ $(M+H)^+$: calcd. 464.0621, found 464.0625.

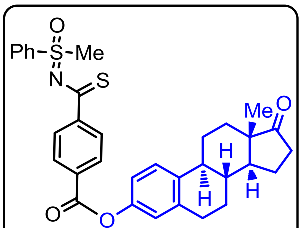
Synthesis of 7h:



7h

7h (348 mg, 68%); yellow crystalline solid; R_f = 0.54 (1:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, J = 9.0 Hz, 2H), 8.04–7.96 (m, 4H), 7.69 (t, J = 7.5 Hz, 1H), 7.62 (t, J = 7.75 Hz, 2H), 5.43 (s, 1H), 4.92–4.82 (m, 1H), 3.51 (s, 3H), 2.47 (bd, J = 7.5 Hz, 2H), 2.06–1.72 (m, 6H), 1.57–1.32 (m, 7H), 1.31–1.07 (m, 13H), 1.05–0.97 (m, 3H), 0.92 (d, J = 6.5 Hz, 3H), 0.87 (dd, J = 6.5 & 2.5 Hz, 6H), 0.69 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 210.2, 165.7, 145.3, 139.6, 137.1, 133.9, 133.3, 129.9, 129.0, 127.9, 127.4, 122.8, 74.9, 56.7, 56.1, 50.0, 44.7, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 31.93, 31.87, 28.2, 28.0, 27.8, 24.3, 23.8, 22.8, 22.5, 21.0, 19.4; IR (Neat) ν_{max} 3894, 3762, 3564, 3495, 3433, 2961, 2717, 2442, 1976, 1705, 1406, 1269, 891 cm^{-1}; **HRMS (ESI)** for $C_{42}H_{58}NO_3S_2$ $(M+H)^+$: calcd. 688.3853, found 688.3866.

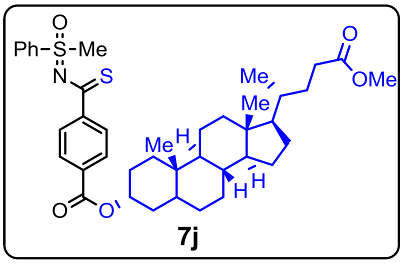
Synthesis of 7i:



7i

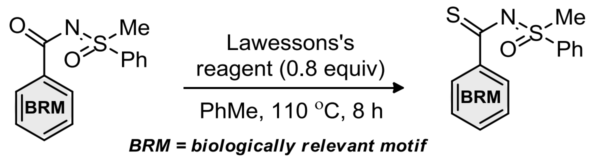
7i (309 mg, 61%); light yellow crystalline solid. R_f = 0.52 (3:7 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, J = 8.5 Hz, 2H), 8.16 (d, J = 8.5 Hz, 2H), 8.00 (d, J = 7.5 Hz, 2H), 7.70 (t, J = 7.25 Hz, 1H), 7.63 (t, J = 7.5 Hz, 2H), 7.34 (d, J = 8.5 Hz, 1H), 7.00 (dd , J = 8.25 & 2.5 Hz, 1H), 6.96 (d, J = 2.0 Hz, 1H), 3.53 (s, 3H), 2.94 (bt, J = 4.5 Hz, 2H), 2.51 (dd , J = 18.75 & 8.75 Hz, 1H), 2.47–2.40 (m, 1H), 2.37–2.29 (m, 1H), 2.22–2.12 (m, 1H), 2.09–2.02 (m, 2H), 2.01–1.96 (m, 1H), 1.67–1.58 (m, 3H), 1.57–1.45 (m, 3H), 0.93 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 209.7, 165.0, 148.6, 145.8, 138.0, 137.4, 136.9, 133.8, 131.9, 129.8, 129.5, 128.0, 127.3, 126.4, 121.5, 118.7, 50.3, 47.8, 44.5; 44.0, 37.9, 35.7, 31.4, 29.3, 26.2, 25.7, 21.5, 13.7; IR (Neat) ν_{max} 2926, 2856, 1729, 1504, 1470, 1260, 1215, 1152, 1071, 1007, 964, 886, 770 cm^{-1}; **HRMS (ESI)** for $C_{33}H_{34}NO_4S_2$ $(M+H)^+$: calcd. 572.1924; found: 572.1929.

Synthesis of 7j:



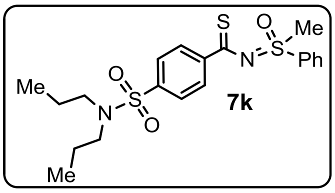
7j (380 mg, 74%); orange colour gummy compound; R_f = 0.55 (1:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.5 (d, J = 8.5 Hz, 2H), 8.04–7.96 (m, 4H), 7.69 (t, J = 7.25 Hz, 1H), 7.62 (t, J = 7.75 Hz, 2H), 5.20–4.93 (m, 1H), 3.66 (s, 3H), 3.51 (s, 3H), 2.39–2.29 (m, 1H), 2.26–2.17 (m, 1H), 2.01–1.95 (m, 2H), 1.92–1.77 (m, 5H), 1.71–1.65 (m, 2H), 1.61–1.40 (m, 7H), 1.32–1.20 (m, 5H), 1.15–1.05 (m, 5H), 0.96 (s, 3H), 0.91 (d, J = 6.5 Hz, 3H), 0.65 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.2, 174.7, 165.8, 145.3, 137.2, 133.9, 133.4, 129.9, 128.9, 127.9, 127.4, 75.3, 56.4, 56.0, 51.4, 44.6, 42.7, 42.0, 40.5, 40.1, 35.8, 35.3, 35.1, 34.6, 32.3, 31.04, 31.00, 28.2, 27.0, 26.7, 26.3, 24.2, 23.3, 20.9, 18.3, 12.0; IR (Neat) ν_{max} 2927, 2863, 1719, 1445, 1405, 1320, 1267, 1220, 1168, 806 cm^{-1}; **HRMS (ESI)** for $C_{40}H_{54}NO_5S_2$ $(M+H)^+$: calcd. 692.3438, found 692.3445.

Preparation of 7k, **7l,** and **7m:**[4a]



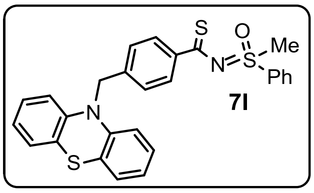
The oven dried reaction tube was charged with *N*-aroylated-MPS (**7'k–m**; 1.0 equiv, 0.5 g) and Lawessons's reagent (0.8 equiv). The reaction tube was evacuated and dry toluene (10 mL) was added and the resulting mixture was stirred at 110 °C for 8 h. Progress of the reaction was monitored by TLC. After complete consumption of **7'k–m**, the reaction mixture was cooled to room temperature. The solvents were evaporated under the reduced pressure and the crude material was extracted with ethylacetate (3 × 10 mL). The organic layer was dried over Na_2SO_4. Solvent was filtered and evaporated under the reduced pressure. The crude residue was purified over a small pad of silica gel using hexane/ethyl acetate (2:3) to provide **7k–m**. The freshly prepared compounds **7k–m** were further used for annulations. The compounds **7k–m** were stored under inert conditions at −20 °C.

N-[4-(N,N-Dipropylsulfamoyl)benzothioyl]-S-methyl-S-phenylsulfoximine (7k):



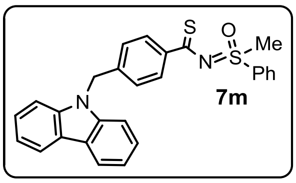
7k (380 mg, 74%); yellow crystalline solid; R_f = 0.38 (3:2 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, J = 8.5 Hz, 2H), 7.95 (d, J = 7.5 Hz, 2H), 7.74 (bd, J = 9.0 Hz, 2H), 7.67 (t, J = 7.25 Hz, 1H), 7.59 (t, J = 7.75 Hz, 2H), 3.49 (s, 3H), 3.05 (t, J = 7.75 Hz, 4H), 1.58–1.47 (m, 4H), 0.84 (t, J = 7.25 Hz, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 209.0, 144.8, 142.3, 136.8, 133.9, 129.8, 128.5, 127.3, 126.3, 50.0, 44.5, 21.9, 11.0; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 209.0, 144.8, 142.3, 136.8, 133.9, 129.8, 128.5, 127.3, 126.3, 50.0, 44.5, 21.9, 11.0; IR (Neat) ν_{max} 2973, 2919, 1683, 1473, 1334, 1267, 1213, 1095, 965 cm^{-1}; **HRMS (ESI)** for $C_{20}H_{27}N_2O_3S_3$ $(M+H)^+$: calcd. 439.1178, found 439.1179.

N-[4-((10H-phenothiazin-10-yl)methyl)benzothioyl]-S-methyl-S-phenylsulfoximine (7l):



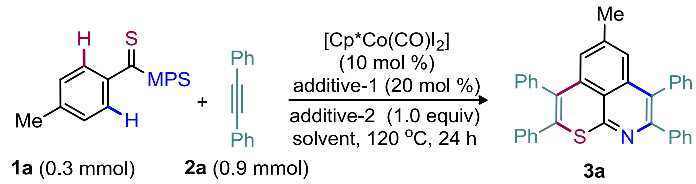
The corresponding acid is synthesized from the literature report.[4b] **7l** (375 mg, 71%); yellow crystalline solid; R_f = 0.53 (3:2 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J = 8.5 Hz, 2H), 7.96 (d, J = 7.5 Hz, 2H), 7.65 (t, J = 7.5 Hz, 1H), 7.58 (t, J = 7.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.09 (dd, J = 7.5 & 1.5 Hz, 2H), 6.99–6.92 (m, 2H), 6.90–6.83 (m, 2H), 6.60 (d, J = 8.0 Hz, 2H), 5.08 (s, 2H), 3.46 (s, 3H); $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$) δ 210.5, 144.2, 141.2, 141.0, 137.2, 133.7, 129.7, 128.6, 127.3, 127.2, 126.8, 126.0, 123.1, 122.5, 115.3, 52.4, 44.6; IR (Neat) ν_{max} 3056, 2919, 1893, 1671, 1592, 1569, 1488, 1460, 1442, 1411, 1317, 1129, 1026, 1008, 961, 889 cm^{-1}; **HRMS (ESI)** for $C_{27}H_{23}N_2OS_3$ $(M+H)^+$ calcd. 487.0967, found 487.0978.

N-[4-(9H-Carbazol-9-yl)methyl)benzothioyl)]-S-methyl-S-phenylsulfoximine (7m):



The corresponding acid has been synthesized from the literature report.[4c] **7m** (372 mg, 71%); yellow crystalline solid; R_f = 0.53 (3:12 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, J = 8.0 Hz, 2H), 8.14 (d, J = 8.0 Hz, 2H), 7.95–7.86 (m, 2H), 7.63 (bt, J = 7.5 Hz, 1H), 7.55 (t, J = 7.75 Hz, 2H), 7.43 (td, J = 8.0 & 1.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.29–7.24 (m, 2H), 7.11 (d, J = 8.5 Hz, 2H), 5.52 (s, 2H), 3.41 (s, 3H); $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$) δ 210.4, 141.7, 141.2, 140.5, 137.4, 133.7, 129.7, 128.7, 127.3, 125.9, 125.8, 123.0, 120.4, 119.3, 108.8, 46.4, 44.5; IR (Neat) ν_{max} 3044, 3017, 2920, 2361, 1626, 1599, 1483, 1455, 1416, 1324, 1217, 1173, 1008 cm^{-1}; **HRMS (ESI)** for $C_{27}H_{23}N_2OS_2$ $(M+H)^+$: calcd. 455.1246, found 455.1258.

Table S1: Optimization of Reaction Conditions

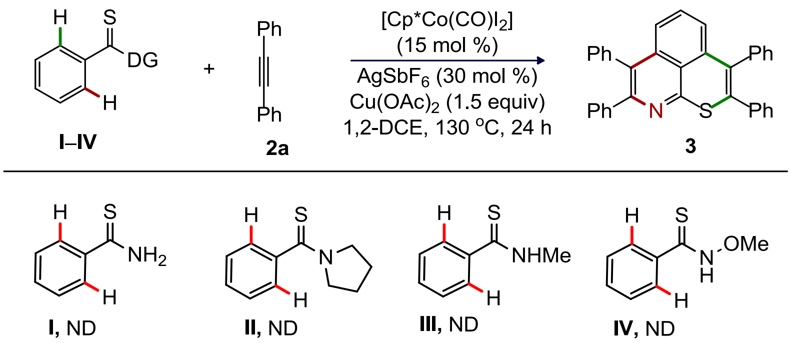


entry	additive 1 (20 mol %)	additive 2 (1.0 equiv)	solvent	yield of **3a** (%)[b]
1	$AgSbF_6$	$Cu(OAc)_2 \cdot H_2O$	$ClCH_2CH_2Cl$	59
2	$AgSbF_6$	NaOAc	$ClCH_2CH_2Cl$	9
3	$AgSbF_6$	KOAc	$ClCH_2CH_2Cl$	5
4	$AgSbF_6$	CsOAc	$ClCH_2CH_2Cl$	trace
5	$AgSbF_6$	$Zn(OAc)_2.2H_2O$	$ClCH_2CH_2Cl$	12
6	$AgSbF_6$	AgOAc	$ClCH_2CH_2Cl$	40
7	$AgSbF_6$	-	$ClCH_2CH_2Cl$	trace
8	$AgSbF_6$	$Cu(OAc)_2$	$ClCH_2CH_2Cl$	68
9	$AgBF_4$	$Cu(OAc)_2$	$ClCH_2CH_2Cl$	55
10	$NaSbF_6$	$Cu(OAc)_2$	$ClCH_2CH_2Cl$	trace
11	KPF_6	$Cu(OAc)_2$	$ClCH_2CH_2Cl$	trace
12	$AgSbF_6$	$Cu(OAc)_2$	PhMe	25
13	$AgSbF_6$	$Cu(OAc)_2$	DME	39
14	$AgSbF_6$	$Cu(OAc)_2$	HFIP	30
15	$AgSbF_6$	$Cu(OAc)_2$	CH_3CN	NR
16	$AgSbF_6$	$Cu(OAc)_2$	Dioxane	60
17	$AgSbF_6$	$Cu(OAc)_2$	TCE	41
18[c]	$AgSbF_6$	$Cu(OAc)_2$	$ClCH_2CH_2Cl$	76
19[c,d]	**$AgSbF_6$**	**$Cu(OAc)_2$**	**$ClCH_2CH_2Cl$**	**87**
20[c,d,e]	$AgSbF_6$	$Cu(OAc)_2$	$ClCH_2CH_2Cl$	76
21[c,d,f]	$AgSbF_6$	$Cu(OAc)_2$	$ClCH_2CH_2Cl$	55
22[c,d,g]	$AgSbF_6$	$Cu(OAc)_2$	$ClCH_2CH_2Cl$	49

[a]Conditions: **1a** (0.3 mmol), **2a** (0.9 mmol), $[Cp^*Co(CO)I_2]$ (10.0 mol %), additive-1 (20 mol %), additive-2 (0.3 mmol), solvent (2.0 mL) at 120 °C. [b]Isolated yield. [c]$[Cp^*Co(CO)I_2]$ (15.0 mol %), $AgSbF_6$ (30 mol %), $Cu(OAc)_2$ (1.5 equiv) was used. [d]Reaction conducted at 130 °C. [e]**2a** (0.75 mmol) used. [f]$[RuCl_2(p\text{-cymene})]_2$ (10 mol%), [g]$[Cp^*RhCl_2]_2$ (5.0 mol%).

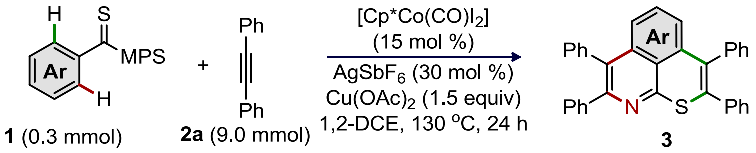
The annulation reactions were carried out in a 15 mL screw capped tube. The tube was charged with *N*-[4-methylbenzothioyl]-*S*-methyl-*S*-phenylsulfoximine (**1a**, 0.3 mmol), diphenyl acetylene (**2a**, 0.9 mmol), $[Cp^*Co(CO)I_2]$ (10.0 mol %), and additive-2 (0.3 mmol). Subsequently, additive-1 (20 mol %) was introduced in to the tube in a glove box. Solvent (2.0 mL) was added to the mixture and the resulting mixture was stirred at 120 °C in a heating block for 24 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite and then washed with dichloromethane (3 × 10 mL). The solvents were evaporated under reduced pressure and the crude material was purified using column chromatography on neutral aluminia (5-10% *n*-hexane/EtOAc eluent) to give the desired product.

<u>Effect of directing groups in the double-annulation of 4-methylbenzothioamide derivatives (I–IV) with diphenyl acetylene (2a) (GP-4):</u>



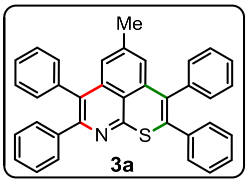
The annulation reactions were carried out in a 15 mL screw capped tube. The tube was charged with various directing group protected 4-methylbenzothioamide (**I–IV**, 0.3 mmol), diphenyl acetylene (**2a**, 0.9 mmol), [Cp*Co(CO)I_2] (21.5 mg, 15.0 mol %), and Cu$(OAc)_2$ (81 mg, 0.45 mmol). Subsequently, $AgSbF_6$ (31 mg, 30 mol %) was introduced in to the tube in a glove box. Freshely dried 1,2-DCE (2.0 mL) was added to the mixture and the resulting mixture was stirred at 130 °C in a heating block for 24 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite and then washed with dichloromethane (3 × 10 mL). The solvents were evaporated under reduced pressure and the crude material was purified using column chromatography on neutral aluminia (5−10% *n*-hexane/EtOAc eluent) to give the desired product.

<u>Synthesis of 6,6-fused thiopyrano-isoquinoline via direct double-annulation of *N*-[arenethioyl]-*S*-methyl-*S*-phenylsulfoximine (1) with diphenyl acetylene (2a) (GP-4A):</u>



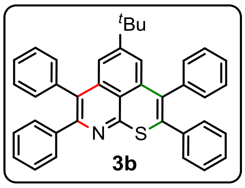
The annulation reactions were carried out in a 15 mL screw capped tube. The tube was charged with freshly prepared **1** (0.3 mmol), diphenyl acetylene (**2a**, 0.9 mmol), [Cp*Co(CO)I_2] (21.5 mg, 15 mol %), and Cu$(OAc)_2$ (81 mg, 0.45 mmol). Subsequently, $AgSbF_6$ (31 mg, 30 mol %) was introduced in to the tube in a glove box. Freshely dried 1,2-DCE (2.0 mL) was added to the mixture and the resulting mixture was stirred at 130 °C in a heating block for 24 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite and then washed with dichloromethane (3 × 10 mL). The solvents were evaporated under reduced pressure and the crude material was purified using column chromatography on neutral aluminia (5−10% *n*-hexane/EtOAc eluent) to give the desired products **3**.

5-Methyl-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3a):



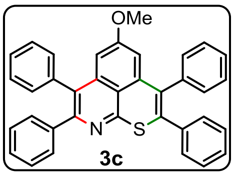
3a (131 mg, 87%); yellow crystalline solid; mp = 255–256 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.31 (m, 5H), 7.29 (t, J = 7.25 Hz, 2H), 7.25–7.20 (m, 5H), 7.19–7.16 (m, 6H), 7.14 (d, J = 7.0 Hz, 2H), 7.04 (s, 1H), 6.65 (s, 1H), 2.17 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 158.1, 150.7, 141.3, 140.2, 138.0, 137.8, 137.6, 137.4, 136.4, 136.1, 131.9, 131.1, 130.9, 130.0, 129.5, 128.6, 128.0, 127.9, 127.5, 127.15, 127.13, 127.10, 126.6, 125.0, 122.7, 122.6, 22.3; IR (Neat) ν_{max} 3053, 2921, 2851, 2359, 1736, 1441, 1313, 1276, 1196, 911 cm^{-1}; **HRMS (ESI)** for $C_{36}H_{26}NS$ $(M+H)^+$: calcd.: 504.1780; found: 504.1780.

5-(*tert*-Butyl)-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3b):



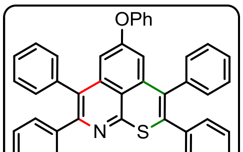
3b (127 mg, 78%); yellow colour solid; mp = 298–302 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.27 (m, 8H), 7.25–7.21 (m, 6H), 7.20–7.16 (m, 5H), 7.15 (bs, 1H), 7.14 (s, 1H), 6.90 (bd, J = 1.5 Hz, 1H), 1.04 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 158.0, 153.9, 150.6, 140.3, 137.9, 137.7, 137.6, 137.5, 136.2, 135.5, 132.3, 131.1, 130.8, 130.0, 129.5, 128.53, 128.50, 128.0, 127.9, 127.5, 127.24, 127.17, 127.14, 127.08, 122.5, 122.2, 118.9, 35.1, 30.6; IR (Neat) ν_{max} 3020, 2958, 1746, 1599, 1482, 1381, 1259, 1197, 1127, 1025, 991, 896 cm^{-1}; **HRMS (ESI)** for $C_{39}H_{32}NS$ $(M+H)^+$: calcd. 546.2250; found: 546.2257.

5-Methoxy-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3c):



3c (143 mg, 92%); pale yellow crystalline solid. mp = 178–179 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.28 (m, 6H), 7.27 (d, J = 7.5 Hz, 2H), 7.25–7.20 (m, 5H), 7.19–7.15 (m, 5H), 7.14–7.11 (m, 2H), 6.60 (d, J = 2.5 Hz, 1H), 6.45 (d, J = 3.0 Hz, 1H), 3.55 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126MHz, $CDCl_3$) δ 161.3, 157.6, 151.1, 140.2, 140.1, 138.7, 137.8, 137.6, 137.3, 137.0, 131.7, 131.0, 130.8, 130.0, 129.4, 128.7, 128.6, 128.0, 127.5, 127.24, 127.20, 127.1, 126.6, 120.2, 114.4, 102.7, 54.9; IR (Neat) ν_{max} 3056, 2927, 1598, 1535, 1486, 1312, 1233, 1166, 1052, 991, 899 cm^{-1}; **HRMS (ESI)** for $C_{36}H_{26}NOS$ $(M+H)^+$: calcd. 520.1730; found: 520.1730.

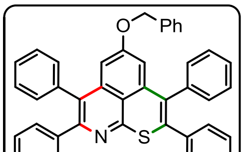
5-Phenoxy-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3d):



3d

3d (157 mg, 90%); yellow crystalline solid. mp = 309–310 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.31 (dd, J = 6.5 & 3.0 Hz, 2H), 7.25–7.13 (m, 16H), 7.10 (d, J = 7.0 Hz, 2H), 7.07 (d, J = 7.0 Hz, 2H), 7.03 (t, J = 7.25 Hz, 1H), 6.86 (d, J = 7.5 Hz, 2H), 6.67 (bd, J = 7.0 Hz, 1H), 6.50 (d, J = 2.0 Hz, 1H); ^{13}C{^{1}H} NMR (126MHz, CDCl$_3$) δ 159.6, 157.9, 155.4, 151.1, 140.1, 140.0, 139.3, 137.43, 137.39, 137.3, 137.2, 131.8, 130.9, 130.7, 130.0, 129.6, 129.4, 128.6, 128.5, 128.1, 128.0, 127.5, 127.3, 127.2, 126.7, 123.9, 121.0, 119.4, 115.4, 109.3; IR (Neat) ν_{max} 2359, 1605, 1568, 1486, 1312, 1209, 1167, 1154, 1028, 940 cm^{-1}; **HRMS (ESI)** for $C_{41}H_{28}NOS$ (M+H)$^+$: calcd.: 582.1886; found: 582.1885.

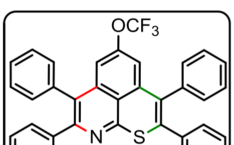
5-(Benzyloxy)-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3e):



3e

3e (148 mg, 83%); red crystalline solid; mp = 257–258 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36–7.30 (m, 5H), 7.29–7.24 (m, 5H), 7.23–7.13 (m, 12H), 7.13–7.12 (m, 1H), 7.11–7.08 (m, 2H), 6.63 (d, J = 2.5 Hz, 1H), 6.45 (d, J = 2.5 Hz, 1H), 4.81 (s, 2H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 160.2, 157.6, 151.0, 140.2, 139.9, 138.7, 137.7, 137.6, 137.3, 137.0, 135.9, 131.7, 131.0, 130.8, 130.0, 129.4, 128.7, 128.69, 128.5, 128.03, 127.98, 127.7, 127.5, 127.2, 127.15, 127.13, 126.5, 120.1, 114.7, 104.3, 69.7; IR (Neat) ν_{max} 3026, 2360, 1595, 1536, 1441, 1320, 1216, 1167, 1022, 993, 723 cm^{-1}; **HRMS (ESI)** for $C_{42}H_{30}ONS$ (M+H)$^+$: calcd. 596.2043; found: 596.2047.

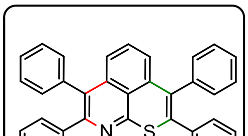
2,3,7,8-Tetraphenyl-5-(trifluoromethoxy)thiopyrano[4,3,2-ij]isoquinoline (3f):



3f

3f (151 mg, 89%); pale yellow crystalline solid. mp = 230–231 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.45–7.36 (m, 5H), 7.33 (d, J = 7.5 Hz, 2H), 7.30–7.27 (m, 1H), 7.26–7.20 (m, 10H), 7.16 (d, J = 6.5 Hz, 2H), 7.08 (bs, 1H), 6.67 (s, 1H); ^{13}C{^{1}H} NMR (126MHz, CDCl$_3$) δ 158.3, 151.6, 151.1, 139.8, 139.63, 139.56, 138.5, 136.93, 136.87, 136.7, 131.5, 130.8, 130.6, 130.0, 129.3, 128.9, 128.8, 128.3, 128.1, 127.63, 127.60, 127.5, 127.1, 122.5, 120.1 (q, J = 256.6 Hz), 115.8, 112.8; ^{19}F NMR (376 MHz, CDCl$_3$) δ –57.50; IR (Neat) ν_{max} 3395, 2921, 2851, 1735, 1607, 1561, 1535, 1442, 1376, 1308, 1255, 1167, 1026 cm^{-1}; **HRMS (ESI)** for $C_{36}H_{23}F_3NOS$ (M+H)$^+$: calcd. 574.1447; found: 574.1450.

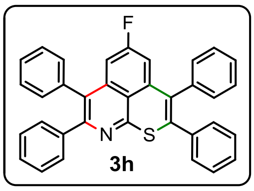
2,3,7,8-Tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3g):



3g

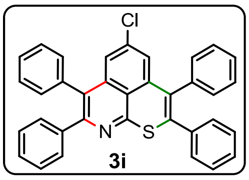
3g (121 mg, 82%); yellow crystalline solid. mp = 321–322 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.42–7.33 (m, 6H), 7.32–7.28 (m, 4H), 7.27–7.19 (m, 10H), 7.18–7.14 (m, 2H), 6.83 (dd, J = 6.25 & 2.25 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 158.5, 150.5, 140.1, 137.84, 137.76, 137.51, 137.3, 136.6, 136.0, 132.1, 131.1, 131.0, 130.9, 130.1, 129.5, 128.6, 128.02, 127.98, 127.5, 127.24, 127.20, 127.1, 124.2, 123.28, 123.26; IR (Neat) ν_{max} 3009, 1649, 1587, 1478, 1427, 1303, 1071, 987, 890 cm^{-1}; **HRMS (ESI)** for $C_{35}H_{24}NS$ $(M+H)^+$: calcd. 490.1624, found 490.1628.

5-Fluoro-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3h):



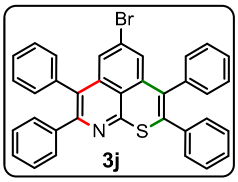
3h (120 mg, 79%); light yellow crystalline solid. mp = 264–265 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.35 (m, 2H), 7.35–7.32 (m, 3H), 7.30 (bt, J = 7.5 Hz, 2H), 7.25–7.23 (m, 1H), 7.22–7.17 (m, 10H), 7.12 (dd, J = 8.25 & 1.25 Hz, 2H), 6.84 (dd, J = 10.5 & 2.0 Hz, 1H), 6.53 (dd, J = 10.75 & 2.25 Hz, 1H); ^{13}C{^{1}H} NMR (101MHz, $CDCl_3$) δ 164.1 (d, J = 200.0 Hz), 158.2, 151.4, 140.4, 140.3, 140.2, 139.8, 138.4, 137.2, 137.1, 137.0, 131.6 (d, J = 2.0 Hz), 130.9, 130.7, 130.0, 129.4, 128.8 (d, J = 4.0 Hz), 128.3, 128.1, 127.6, 127.5, 127.4, 126.9 (d, J = 4.0 Hz), 121.7, 112.4, 112.2, 107.4, 107.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −105.21; IR (Neat) ν_{max} 3050, 2359, 1530, 1439, 1416, 1378, 1306, 1210, 1156, 857cm^{-1}; **HRMS (ESI)** for $C_{35}H_{23}FNS$ $(M+H)^+$: calcd. 508.1530; found: 508.1528.

5-Chloro-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3i):



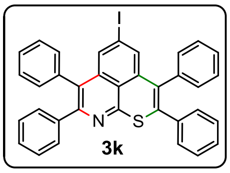
3i (134 mg, 85%); pale-yellow crystalline solid. mp = 282–283 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.28 (m, 8H), 7.27–7.23 (m, 1H), 7.22–7.16 (m, 10H), 7.12 (d, J = 7.0 Hz, 2H), 6.74 (bd, J = 2.0 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.3, 151.6, 139.7, 139.1, 138.7, 138.3, 137.9, 137.05, 137.00, 136.9, 131.4, 131.0, 130.7, 130.0, 129.4, 128.9, 128.8, 128.2, 128.1, 127.6, 127.4, 126.4, 123.3, 122.6, 122.0; IR (Neat) ν_{max} 3053, 2921, 2850, 1725, 1672, 1591, 1524, 1440, 1328, 1206, 1072, 990 cm^{-1}; **HRMS (ESI)** for $C_{35}H_{23}ClNS$ $(M+H)^+$: calcd. 524,1234; found: 524.1232.

5-Bromo-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3j):



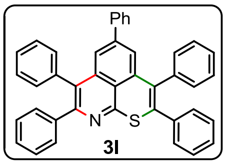
3j (147 mg, 86%); yellow crystalline solid; mp = 298–299 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (bd, J = 2.0 Hz, 1H), 7.31 (bt, J = 6.75 Hz, 2H), 7.29–7.25 (m, 2H), 7.24 (d, J = 7.5 Hz, 2H), 7.19 (d, J = 7.5 Hz, 1H), 7.17–7.10 (m, 11H), 7.06 (d, J = 7.0 Hz, 2H), 6.84 (bd, J = 1.5 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.4, 151.5, 139.6, 139.1, 138.5, 138.2, 136.9, 136.7, 131.2, 130.9, 130.7, 130.0, 129.3, 128.84, 128.81, 128.2, 128.0, 127.5, 127.4, 126.8, 126.1, 125.9, 125.2, 122.7; IR (Neat) ν_{max} 3051, 2360, 1738, 1588, 1527, 1485, 1356, 1327, 1206, 1072, 989 cm^{-1}; **HRMS (ESI)** for $C_{35}H_{23}BrNS$ $(M+H)^+$: calcd. 568.0729; found: 568.0725.

5-Iodo-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3k):



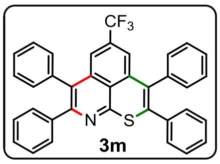
3k (167 mg, 91%); yellow crystalline solid. mp = 345–347 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (bd, J = 1.5 Hz, 1H), 7.41–7.28 (m, 7H), 7.27–7.22 (m, 1H), 7.21–7.16 (m, 10H), 7.10 (d, J = 6.5 Hz, 2H), 7.06 (bd, J = 1.5 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.6, 151.5, 139.8, 139.1, 138.1, 138.0, 137.03, 136.98, 136.7, 131.9, 131.6, 131.0, 130.7, 130.0, 129.3, 128.83, 128.82, 128.2, 128.1, 127.6, 127.4, 125.7, 123.0, 99.8; IR (Neat) ν_{max} 3050, 1584, 1523, 1486, 1439, 1354, 1304, 1205, 1071, 987, 896 cm^{-1}; **HRMS (ESI)** for $C_{35}H_{23}INS$ $(M+H)^+$: calcd. 616.0590, found 616.0594.

2,3,5,7,8-Pentaphenylthiopyrano[4,3,2-ij]isoquinoline (3l):



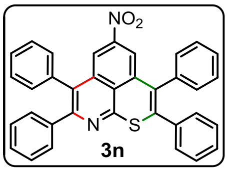
3l (141 mg, 83%); light yellow crystalline solid. mp = 305–306 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (bd, J = 1.5 Hz, 2H), 7.36–7.32 (m, 4H), 7.29 (d, J = 7.0 Hz, 1H), 7.25–7.23 (m, 3H), 7.23–7.19 (m, 4H), 7.17–7.13 (m, 11H), 7.06 (bd, J = 2.0 Hz, 2H); ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 158.3, 151.0, 143.4, 140.4, 140.1, 138.2, 137.6, 137.4, 137.3, 137.2, 136.5, 132.2, 131.1, 130.8, 130.0, 129.4, 128.73, 128.69, 128.67, 128.0, 127.9, 127.5, 127.31, 127.26, 127.21, 123.2, 122.7, 121.2; IR (Neat) ν_{max} 3023, 2918, 2849, 1600, 1571, 1534, 1485, 1310, 1202, 1088, 1051 cm^{-1}; **HRMS (ESI)** for $C_{41}H_{28}NS$ $(M+H)^+$: calcd. 566.1937; found: 566.1930.

2,3,7,8-Tetraphenyl-5-(trifluoromethyl)thiopyrano[4,3,2-ij]isoquinoline (3m):



3m (140 mg, 84%); yellow crystalline solid; mp = 269–270 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 2H), 7.48–7.42 (m, 5H), 7.42–7.38 (m, 4H), 7.36 (d, J = 9.5 Hz, 3H), 7.34–7.30 (m, 2H), 7.21–7.16 (m, 4H), 7.02 (bs, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.5, 151.8, 139.5, 138.2, 137.7, 136.9, 136.8, 136.5, 132.8, 132.5, 131.7, 130.9, 130.7, 130.0, 129.4, 128.9, 128.3, 128.1, 127.67 (q, J = 7.5 Hz), 124.9, 124.5, 122.4, 120.2, 118.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.62; IR (Neat) ν_{max} 3052, 2921, 2359, 2339, 1560, 1486,1390, 1303, 1269, 1161, 1123, 1106, 894, 693 cm^{-1}; **HRMS (ESI)** for $C_{36}H_{23}F_3NS$ $(M+H)^+$: calcd. 558.1498; found: 558.1499.

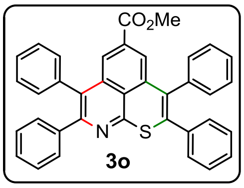
5-Nitro-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3n):



3n (127 mg, 79%); reddish crystalline solid. mp = 299–300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (bd, J = 2.0 Hz, 2H), 7.55 (d, J = 2.0 Hz, 2H), 7.48–7.45 (m, 4H), 7.41–7.36 (m, 4H), 7.32 (s, 1H), 7.28–7.26 (m, 5H), 7.19 (bd, J = 1.6 Hz, 2H), 7.17 (bt, J = 0.8 Hz, 2H); ^{13}C{^{1}H} NMR (101MHz, $CDCl_3$) δ 158.8, 152.5, 149.4, 139.4, 139.3, 139.1, 138.3, 136.6, 136.4, 136.0, 131.7, 130.8, 130.6, 130.0, 129.3, 129.14, 129.11, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 127.7, 125.5, 118.4, 115.7; IR (Neat) ν_{max}

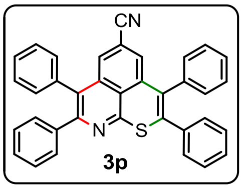
3051, 2921, 1737, 1521, 1484, 1330, 1204, 1101, 1024 cm^{-1}; **HRMS (ESI)** for $C_{35}H_{23}N_2O_2S$ $(M+H)^+$: calcd. 535.1475; found: 535.1473.

Methyl 2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline-5-carboxylate (3o):



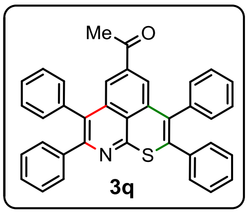
3o (113 mg, 69%); pale yellow solid. mp = 318–320 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.41–7.27 (m, 8H), 7.25–7.16 (m, 11H), 7.13 (bd, J = 7.5 Hz, 2H), 3.73 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 166.4, 158.6, 151.4, 139.7, 137.6, 137.22, 137.17, 137.1, 137.0, 136.7, 132.13, 132.07, 131.0, 130.7, 130.0, 129.4, 128.8, 128.2, 127.9, 127.5, 127.4, 125.5, 125.2, 52.3; IR (Neat) ν_{max} 2954, 1722, 1535, 1432, 1383, 1257, 1217, 1115, 1001 cm^{-1}; **HRMS (ESI)** for $C_{37}H_{26}NO_2S$ $(M+H)^+$: calcd. 548.1679, found 548.1687.

2,3,7,8-Tetraphenylthiopyrano[4,3,2-ij]isoquinoline-5-carbonitrile (3p):



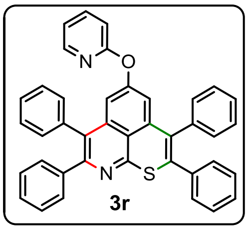
3p (105 mg, 68%); yellow crystalline solid. mp = >350 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (bs, 1H), 7.44–7.36 (m, 3H), 7.35–7.30 (m, 4H), 7.29–7.25 (m, 1H), 7.22–7.15 (m, 10H), 7.09 (d, J = 7.0 Hz, 2H), 6.89 (bd, J = 1.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 158.7, 152.1, 139.2, 139.0, 138.3, 137.7, 136.6, 136.5, 136.1, 131.2, 130.8, 130.6, 130.0, 129.3, 129.12, 129.08, 128.5, 128.2, 128.04, 127.98, 127.89, 127.78, 127.70, 126.96, 124.7, 123.4, 118.4, 114.9; IR (Neat) ν_{max} 3019, 2921, 2851, 2227,l 1734, 1598, 1574, 1532, 1485, 1456, 1439, 1333, 1308, 1203, 1154, 1063, 1026, 991 cm^{-1}; **HRMS (ESI)** for $C_{36}H_{23}N_2S$ $(M+H)^+$: calcd. 515.1578, found 515.1581.

1-(2,3,7,8-Tetraphenylthiopyrano[4,3,2-ij]isoquinolin-5-yl)ethanone (3q):



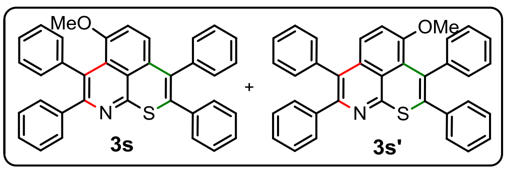
3q (115 mg, 72%); yellow crystalline solid. mp = 286–287 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (bs, 1H), 7.42–7.32 (m, 7H), 7.30 (d, J = 7.5 Hz, 2H), 7.25–7.17 (m, 10H), 7.14 (d, J = 7.5 Hz, 2H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 197.8, 158.5, 151.3, 139.5, 138.5, 137.7, 137.3, 137.1, 137.0, 136.7, 132.1, 130.9, 130.7, 130.0, 129.3, 128.8, 128.2, 128.1, 128.0, 127.65, 127.58, 127.53, 127.46, 125.3, 124.0, 121.2, 26.5; IR (Neat) ν_{max} 2954, 1686, 1537, 1486, 1385, 1247, 1316, 1177 cm^{-1}; **HRMS (ESI)** for $C_{37}H_{26}NOS$ $(M+H)^+$: calcd. 532.1730, found 532.1738.

2,3,7,8-Tetraphenyl-5-(pyridin-2-yloxy)thiopyrano[4,3,2-ij]isoquinoline (3r):



3r (107 mg, 61%); yellow crystalline solid. mp = 335–336 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (bd, J = 3.5 Hz, 1H), 7.58 (bt, J = 7.0 Hz, 1H), 7.39–7.07 (m, 20H), 7.10–6.88 (m, 2H), 6.77 (d, J = 8.0 Hz, 1H), 6.61 (bs, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 162.6, 158.1, 156.2, 151.1, 147.5, 140.0, 139.8, 139.3, 139.0, 137.4, 137.3, 137.2, 131.8, 131.0, 130.8, 130.0, 129.4, 128.6, 128.1, 128.0, 127.5, 127.24, 127.21, 126.9, 121.8, 118.9, 117.6, 113.1, 111.8; IR (Neat) ν_{max} 1604, 1559, 1435, 1315, 1168, 987, 946 cm^{-1}; **HRMS (ESI)** for $C_{40}H_{27}N_2OS$ $(M+H)^+$: calcd. 583.1839, found 583.1840.

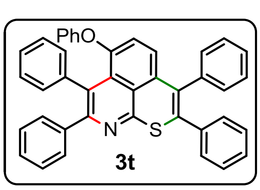
6-Methoxy-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3s)/ 4-Methoxy-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3s′):



Inseparable mixture of **3s** and **3s′** (10 : 1, 90 mg, 57%) was obtained; yellow crystalline solid; mp = >350 °C; **major isomer 3s (structure is elucidated by x-ray analysis)**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.46–7.35 (m, 3H), 7.35–7.18 (m, 18H), 6.94–6.88 (m, 1H), 6.84 (d, J = 8.5 Hz, 1H), 3.42 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 158.6, 154.1, 152.6, 141.0, 140.60, 140.59, 138.1, 137.3, 132.1, 132.0, 130.9, 130.3, 130.0, 129.7, 129.5, 129.3, 128.6, 128.1, 128.0, 127.8, 127.5, 127.2, 126.8, 126.4, 125.7, 124.5, 111.7, 55.6; **Representative peaks for minor isomer 3s'**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.35–7.23 (m, 1.46 H), 7.17–7.10 (m, 0.41 H), 3.27 (s, 0.34 H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 157.7, 153.3, 148.8, 141.4, 139.9, 137.6, 137.4, 135.5, 132.6, 131.1, 128.2, 127.9, 127.4, 127.0, 125.9, 125.6, 123.4, 121.2, 56.9; IR (Neat) ν_{max} 3052, 2925, 1527, 1456, 1349, 1327, 1302, 1257, 1201, 1158, 1070 cm^{-1}; **HRMS (ESI)** for $C_{36}H_{26}NOS$ $(M+H)^+$: calcd. 520.1730, found 520.1735.

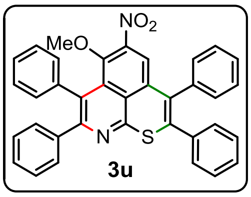
*As **3s** and **3s′** are inseparable, thus, independent proton counts for major isomer **3s** and minor isomer **3s′** does not properly match. Ratio of the both regioisomers **3s:3s′** was determined based on the characteristic Me-H^1 proton integretion. H^1 NMR (500 MHz, CDCl$_3$) H^1 for **3s/3s′:** δ = 3.42 (s, 3H, major)/ 3.27 (s, 3H, minor).*

6-Phenoxy-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3t):



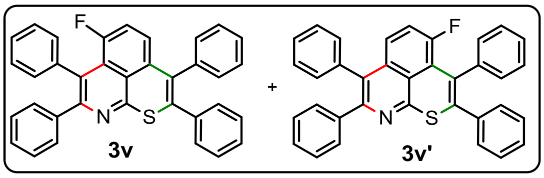
3t (99 mg, 66%); yellow crystalline solid. mp = 329–330 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.29 (t, J = 7.6 Hz, 2H), 7.24–7.09 (m, 13H), 7.03 (t, J = 8.0 Hz, 2H), 7.00–6.93 (m, 6H), 6.89–6.80 (m, 2H), 6.30 (bd, J = 8.0 Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 158.9, 157.5, 152.9, 149.1, 140.3, 139.2, 137.7, 137.1, 134.8, 133.6, 132.0, 130.8, 130.6, 130.4, 129.9, 129.4, 128.9, 128.7, 128.05, 128.01, 127.3, 127.2, 126.9, 126.6, 126.0, 124.8, 124.3, 123.4, 121.8, 116.1; IR (Neat) ν_{max} 1586, 1525, 1485, 1459, 1349, 1317, 1244, 1202, 1071, 1049, 879 cm^{-1}; **HRMS (ESI)** for $C_{41}H_{28}NOS$ $(M+H)^+$: calcd. 582.1886, found 582.1890.

6-Methoxy-5-nitro-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3u):



3u (54 mg, 32%); red crystalline solid. mp = >350 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, J = 7.25 Hz, 2H), 7.26–7.14 (m, 16H), 7.11 (bd, J = 7.0 Hz, 2H), 6.98 (s, 1H), 3.03 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 159.0, 154.8, 146.7 145.8, 139.8, 138.2, 137.4, 136.4, 134.5, 132.9, 131.2, 130.9, 130.6, 129.9, 129.2, 129.1, 128.4, 128.2, 127.9, 127.5, 127.3, 127.0, 126.8, 126.6, 126.0, 117.5, 63.0; IR (Neat) ν_{max} 3053, 2919, 1710, 1610, 1527, 1491, 1442, 1350, 1306, 1264, 1088, 1046 cm^{-1}; **HRMS (ESI)** for $C_{36}H_{25}N_2O_3S$ $(M+H)^+$: calcd. 565.1580, found 565.1584.

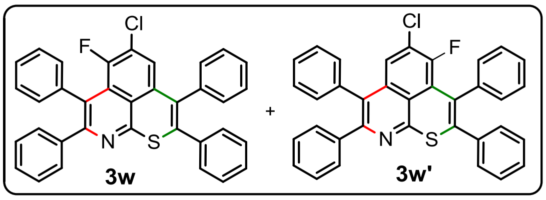
6-Fluoro-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3v)/ 4-Fluoro-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3v'):



Inseparable mixture of **3v** and **3v'** (5 : 1, 90 mg, 57%) was obtained; yellow crystalline solid; mp = 323–324 °C; **major isomer 3v**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.26 (m, 7.24H), 7.25–7.12 (m, 16.29H), 7.09 (dd, J = 15.5 & 6.5 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 157.7 (d, J = 5.0 Hz), 155.6 (d, J = 255.5 Hz), 152.6, 149.9 (d, J = 2.0 Hz), 139.6, 139.3 (d, J = 5.0 Hz), 137.6, 137.0, 136.8, 134.7 (d, J = 7.0 Hz), 131.0, 130.8, 130.0, 129.3, 129.8 (d, J = 4.0 Hz), 129.4, 128.7, 128.05, 128.0, 127.9, 127.7, 127.6, 127.5, 127.3, 126.5, 125.7 (d, J = 9.0 Hz), 122.4, 122.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −105.56; **Representative peaks for minor isomer 3v'**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (dd, J = 15.5 & 10.5 Hz, 0.30H), 7.00 (dd, J = 10.75 & 5.75 Hz, 0.23H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 158.9 (d, J = 3.0 Hz), 156.1 (d, J = 255.5 Hz), 139.8, 138.9 (d, J = 4.0 Hz), 137.5, 133.3 (d, J = 5.0 Hz), 131.8, 130.4 (d, J = 4.0 Hz), 129.9, 129.4, 127.6 (d, J = 2.0 Hz), 127.5, 127.4, 127.3, 127.2, 127.1 (d, J = 1.0 Hz), 126.8, 125.4 (d, J = 3.0 Hz), 124.0 (d, J = 7.0 Hz), 123.1, 121.3 (d, J = 7.0 Hz), 117.0 (d, J = 2.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −107.35; IR (Neat) ν_{max} 2921, 2851, 1598, 1560, 1527, 1494, 1440, 1371, 1318, 1298, 1154, 1088, 1027 cm^{-1}; **HRMS (ESI)** for $C_{35}H_{23}FNS$ $(M+H)^+$: calcd. 508.1530, found 508.1534.

*As **3v** and **3v'** are inseparable, thus, independent proton counts for major isomer **3v** and minor isomer **3v'** does not properly match. Ratio of the both regioisomers **3v:3v'** was determined based on the characteristic F^{19} integretion. F^{19} NMR (376 MHz, $CDCl_3$) F^{19} for **3v/3v'**: δ = –105.56 (1.00; major)/ –107.35 (0.19; minor).*

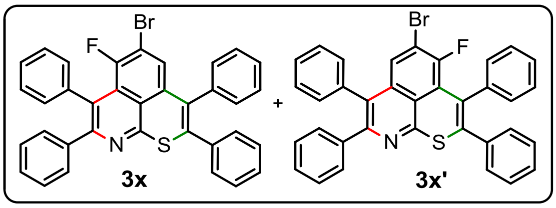
5-Chloro-6-fluoro-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3w)/ 5-Chloro-4-fluoro-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3w'):



Inseparable mixture of **3w/3w′** (5:1, 110 mg, 69%) was obtained; yellow crystalline solid; mp = 343–345 °C; **major isomer 3w:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.33 (m, 4H), 7.32–7.28 (m, 2.50H), 7.32–7.28 (m, 2.50H), 7.27–7.25 (m, 1.61H), 7.24–7.08 (m, 18H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 158.86, 150.87 (d, J = 257.0 Hz), 139.5, 139.3, 138.7 (d, J = 5.0 Hz), 136.5 (d, J = 19.0 Hz), 134.7, 130.9, 130.7, 129.9, 129.9, 129.7 (d, J = 3.8 Hz), 129.3, 128.9, 128.1 (d, J = 5.0 Hz), 128.0, 127.8, 127.6 (d, J = 2.0 Hz), 127.53, 127.47, 127.0, 124.9, 123.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ −108.63; **Representative peaks for minor isomer 3w'**: ^{1}H NMR (500 MHz, $CDCl_3$) 6.80 (d, J = 6.0 Hz, 0.22H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 158.8, 157.6 (d, J = 5.0 Hz), 158.6, 152.5, 138.4, 136.7 (d, J = 16.4 Hz), 134.0, 130.3 (d, J = 3.8 Hz), 128.5, 128.4, 128.3, 127.7, 127.4, 127.0, 126.1, 124.4, 123.1 (d, J = 5.0 Hz); δ ^{19}F NMR (376 MHz, $CDCl_3$) δ −109.87; IR (Neat) ν_{max} 3055, 3021, 1592, 1554, 1522, 1488, 1440, 1377, 1319, 1232, 1201, 1106, 1027, 895 cm^{-1}; **HRMS (ESI)** for $C_{35}H_{22}ClFNS$ $(M+H)^+$: calcd. 542.1140, found 542.1144.

*As **3w** and **3w′** are inseparable, thus, independent proton counts for major isomer **3w** and minor isomer **3w′** does not properly match.* Ratio of the both regioisomers **3w:3w'** was determined based on the characteristic F^{19} integretion. F^{19} NMR (376 MHz, $CDCl_3$) F^{19} for **3w/3w':** δ = −108.63 (1.00; major)/ −109.87 (0.23; minor).

5-Bromo-6-fluoro-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3x)/ 5-Bromo-4-fluoro-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3x′):

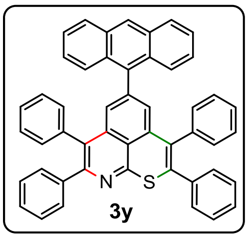


Inseparable mixture of **3x/3x′** (13:1, 92 mg, 52%); yellow crystalline solid. mp = 348–349 °C; The compounds solubility in chloroform/DMSO is poor. **Major isomer 3x:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 7.5 Hz, 1H), 7.43–7.34 (m, 3H), 7.33–7.25 (m, 3H), 7.22–7.10 (m, 18H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 157.7 (d, J = 6.3 Hz), 153.6, 151.8 (d, J = 239.4 Hz), 139.5, 139.3, 138.8 (d, J = 5.0 Hz), 136.6, 136.4, 135.1, 131.0, 130.9, 130.6, 129.7 (d, J = 5.0 Hz), 129.3, 128.9, 128.3, 128.1 (d, J = 5.0 Hz), 128.0, 127.7, 126.5, 124.4, 122.8 (d, J = 8.8 Hz), 117.7, 117.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −99.67; **Minor isomer 3x′:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (d, J = 7.5 Hz, 0.27H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 130.4 (d, J = 6.3 Hz), 129.9, 129.4, 128.7, 127.4, 127.0 (d, J = 10.1 Hz), 112.9, 112.7; ^{19}F NMR (376 MHz,

$CDCl_3$) δ −100.47; IR (Neat) ν_{max} 1586, 1522, 1486, 1370, 1317, 1190, 1123, 1089, 1026, 852 cm^{-1}; **HRMS (ESI)** for $C_{35}H_{22}BrFNS$ $(M+H)^+$: calcd. 586.0635, found 586.0637.

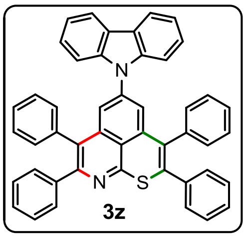
*As **3x** and **3x'** are inseparable, thus, independent proton counts for major isomer **3x** and minor isomer **3x'** does not properly match. Ratio of the both regioisomers **3x:3x'** was determined based on the characteristic F^{19} integretion. F^{19} NMR (376 MHz, $CDCl_3$) for **3x/3x':** δ = –99.67 (1.00; major)/ –100.47 (0.07; minor).*

5-(Anthracen-9-yl)-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3y):



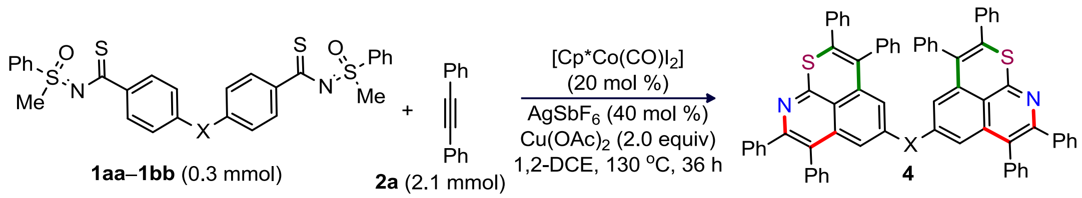
3y (139 mg, 70%); yellow crystalline solid. mp = >350 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.96 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H), 7.43–7.38 (m, 2H), 7.37–7.29 (m, 5H), 7.23–7.15 (s, 12H), 7.14–7.06 (m, 5H), 7.10–6.95 (m, 1H), 6.94 (bd, J = 1.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 158.5, 151.3, 141.9, 140.1, 137.9, 137.4, 137.1, 136.9, 136.7, 136.0, 132.1, 131.2, 131.0, 130.6, 130.1, 129.7, 129.4, 128.59, 128.58, 128.3, 128.1, 128.0, 127.6, 127.3, 127.2, 127.1, 126.9, 126.7, 126.3, 125.8, 125.5, 125.1, 123.6; IR (Neat) ν_{max} 1597, 1536, 1440, 1332, 1259, 1205, 1071, 1026, 888 cm^{-1}; **HRMS (ESI)** for $C_{49}H_{32}NS$ $(M+H)^+$: calcd. 666.2250, found 666.2251.

5-(9H-carbazol-9-yl)-2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline (3z):



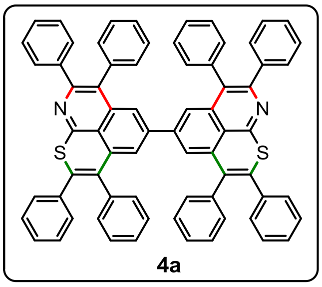
3z (166 mg, 84%); yellow colour solid; mp = 284–286 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (bd, J = 7.6 Hz, 2H), 7.45–7.40 (m, 3H), 7.37–7.30 (m, 7H), 7.29–7.27 (m, 2H), 7.25–7.17 (m, 13H), 7.11 (bt, J = 6.4 Hz, 2H), 7.05 (bd, J = 2.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 158.4, 151.3, 140.2, 139.8, 139.7, 139.5, 139.0, 137.8, 137.3, 137.0, 131.9, 130.8, 130.5, 130.0, 129.4, 128.82, 128.79, 128.2, 128.1, 127.62, 127.58, 127.5, 127.0, 125.9, 123.6, 122.7, 121.4, 120.4, 120.2, 119.5, 109.6; IR (Neat) ν_{max} 2960, 1598, 1535, 1485, 1441, 1376, 1310, 1225, 1198, 1127, 1070, 990; cm^{-1}; **HRMS (ESI)** for $C_{47}H_{31}N_2S$ $(M+H)^+$: calcd.: 655.2202; found: 655.2201.

<u>Synthesis of 6,6-fused bis-thiopyrano-isoquinoline via direct double-annulation of 1aa</u> or <u>1bb with diphenyl acetylene (2a) (GP-4B):</u>



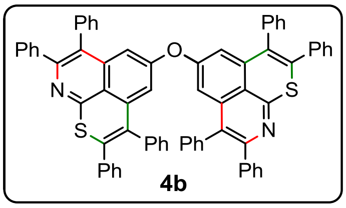
The annulation reactions were carried out in a 15 mL screw capped tube. The tube was charged with freshly prepared **1aa** or **1bb** (0.3 mmol), diphenyl acetylene (**2a**, 2.1 mmol), [Cp*Co(CO)I_2] (29 mg, 20 mol %), and Cu(OAc)$_2$ (108 mg, 0.6 mmol). Subsequently, $AgSbF_6$ (41 mg, 40 mol %) was introduced in to the tube in a glove box. Freshly dried 1,2-DCE (3.0 mL) was added to the mixture and the resulting mixture was stirred at 130 °C in a heating block for 36 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite and then washed with dichloromethane (3 × 10 mL). The solvents were evaporated under reduced pressure and the crude material was purified using column chromatography on neutral aluminia (5–20% *n*-hexane/EtOAc eluent) to give the desired product.

2,2',3,3',7,7',8,8'-octaphenyl-5,5'-bithiopyrano[4,3,2-ij]isoquinoline (4a):



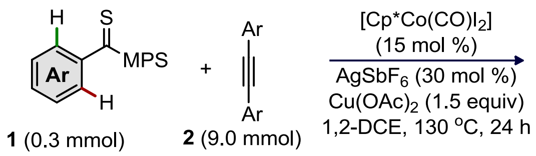
The solubility of compound **4a** in chloroform/DMSO is poor. **4a** (153 mg, 52%); yellow crystalline solid; mp = 333–334 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (bd, J = 8.5 Hz, 2H), 7.42 (bd, J = 1.5 Hz, 1H), 7.40–7.27 (m, 16H), 7.25–7.21 (m, 10H), 7.20–7.14 (m, 14H), 6.99 (d, J = 2.0 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.4, 151.5, 144.9, 141.4, 139.9, 138.3, 137.8, 137.5, 137.2, 132.6, 132.0, 131.1, 130.8, 130.0, 129.4, 128.84, 128.82, 128.1, 127.8, 127.6, 127.5, 127.4, 123.6, 122.0, 121.6, 118.6, 111.6; IR (Neat) ν_{max} 3449, 3054, 2916, 1594, 1532, 1441, 1306, 1220, 1177, 1030, 901 cm^{-1}; **HRMS (ESI)** for $C_{70}H_{45}N_2S_2$ $(M+H)^+$: calcd. 977.3019; found: 977.3017.

5,5'-Oxybis(2,3,7,8-tetraphenylthiopyrano[4,3,2-ij]isoquinoline) (4b):



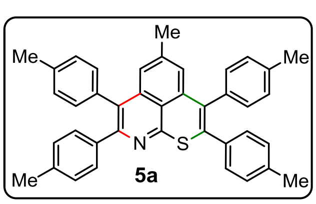
4b (181 mg, 61%); yellow crystalline solid. mp = >350 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.26 (m, 11H), 7.22–7.20 (m, 21H), 7.05 (d, J = 6.5 Hz, 4H), 6.98 (d, J = 7.0 Hz, 4H), 6.60 (bd, J = 2.0 Hz, 2H), 6.29 (d, J = 2.0 Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.0, 157.9, 151.2, 139.9, 139.7, 139.3, 137.6, 137.2, 137.15, 137.08, 131.6, 130.9, 130.6, 130.0, 129.4, 128.7, 128.6, 128.2, 128.1, 127.6, 127.4, 126.6, 121.3, 115.7, 110.0; IR (Neat) ν_{max} 1593, 1562, 1531, 1461, 1441, 1373, 1309, 1197, 1171, 1071, 1030, 992 cm^{-1}; **HRMS (ESI)** for $C_{70}H_{45}N_2OS_2$ $(M+H)^+$: calcd. 993.2968, found 993.2973.

Synthesis of 6,6-fused thiopyrano-isoquinoline via direct double-annulation of *N*-[arenethioyl]-*S*-methyl-*S*-phenylsulfoximine (1) with various 1,2-diaryl alkyne (2) (GP-4C):



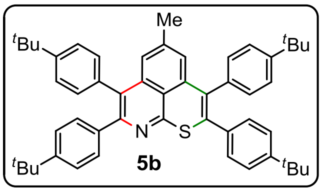
The annulation reactions were carried out in a 15 mL screw capped tube. The tube was charged with freshly prepared *N*-[arenethioyl]-S- methyl-S-phenylsulfoximine (**1**, 0.3 mmol), 1,2-diaryl alkyne (**2**, 0.9 mmol), [Cp*Co(CO)I_2] (21.5 mg, 15 mol %), and $Cu(OAc)_2$ (81 mg, 0.45 mmol). Subsequently, $AgSbF_6$ (31 mg, 30 mol %) was introduced in to the tube in a glove box. Freshly dried 1,2-DCE (2.0 mL) was added to the reaction and the resulting mixture was stirred at 130 °C in a heating block for 24 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite and then washed with dichloromethane (3 × 10 mL). The solvents were evaporated under reduced pressure and the crude material was purified using column chromatography on neutral aluminia (5−10% *n*-hexane/EtOAc eluent) to give the desired product.

2,3,7,8-Tetrakis(4-methoxyphenyl)-5-methylthiopyrano[4,3,2-ij]isoquinoline (5a):



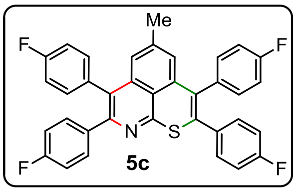
5a (157 mg, 93%); yellow crystalline solid. mp = 288–289 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (bd, J = 8.0 Hz, 2H), 7.17 (bd, J = 8.0 Hz, 2H), 7.11–7.05 (m, 6H), 7.01–7.04 (m, 7H), 6.60 (bd, J = 1.0 Hz, 1H), 2.39 (s, 3H), 2.32 (s, 3H), 2.27 (s, 3H), 2.25 (s, 3H), 2.14 (s, 3H); ^{13}C{^{1}H} NMR (101MHz, $CDCl_3$) δ 158.0, 150.6, 141.1, 138.2, 137.6, 136.8, 136.7, 136.60, 136.58, 136.0, 135.0, 134.84, 134.80, 131.7, 131.0, 130.7, 130.0, 129.3, 128.7, 128.2, 126.3, 124.8, 122.6, 122.5, 22.3, 21.31, 21.25, 21.20, 21.15; IR (Neat) ν_{max} 2915, 1737, 1604, 1502, 1443, 1372, 1314, 1212, 1106, 1020, 994 cm^{-1}; **HRMS (ESI)** for $C_{40}H_{34}NS$ $(M+H)^+$: calcd. 560.2406, found 560.2403.

2,3,7,8-Tetrakis(4-(*tert*-butyl)phenyl)-5-methylthiopyrano[4,3,2-ij]isoquinoline (5b):



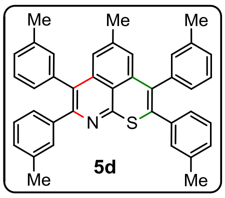
5b (179 mg, 82%); yellow crystalline solid. mp = >350 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36 (d, J = 8.0 Hz, 2H), 7.25–7.19 (m, 4H), 7.15 (bd, J = 8.5 Hz, 2H), 7.14–7.10 (m, 4H), 7.08–7.03 (m, 3H), 7.00 (bd, J = 8.0 Hz, 2H), 6.74 (bs, 1H), 2.19 (s, 3H), 1.35 (s, 9H), 1.27 (s, 9H), 1.24 (s, 9H), 1.22 (s, 9H); ^{13}C{^{1}H} NMR (101MHz, CDCl$_3$) δ 158.0, 150.6, 150.0, 149.9 149.8, 141.2, 138.1, 137.4, 136.5, 136.0, 134.9, 134.7, 131.9, 130.7, 130.8, 130.6, 129.6, 129.1, 126.4, 125.3, 125.2, 124.8, 124.6, 124.3, 122.6, 122.5, 34.5, 34.44, 34.36, 31.4, 31.3, 31.2, 31.1, 22.3; IR (Neat) ν_{max} 2955, 2901, 1605, 1553, 1503, 1459, 1390, 1361, 1268, 1110, 1020, 858 cm^{-1}; **HRMS (ESI)** for $C_{52}H_{58}NS$ (M+H)$^+$: calcd. 728.4284, found 728.4285.

2,3,7,8-Tetrakis(4-fluorophenyl)-5-methylthiopyrano[4,3,2-ij]isoquinoline (5c):



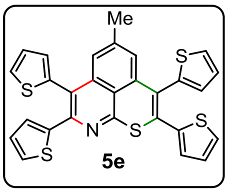
5c (95 mg, 55%); yellow crystalline solid. mp = 334–335 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.27 (s, 1H), 7.25–7.22 (m, 1H), 7.16–6.95 (m, 11H), 6.92–6.83 (m, 4H), 6.58 (d, J = 1.0 Hz, 1H), 2.18 (s, 3H); ^{13}C{^{1}H} NMR (101MHz, CDCl$_3$) δ 163.3, 160.9, 160.8, 160.6, 158.1, 150.0, 141.8, 138.0, 136.3, 135.9, 135.6, 133.3, 133.2, 133.1, 132.7, 132.6, 132.5, 132.4, 131.8, 131.7, 131.3, 131.2, 125.6, 125.1, 122.6, 116.0, 115.8, 115.5, 115.2, 114.7, 114.5, 22.3 (*The ^{13}C NMR is complex due to the presence of four F-atoms on the periphery of arene moiety; it is therefore difficult to assign the corresponding peaks of ^{13}C-attached to the fluorine-bearing arenes. Hence, complete list of the representative peaks of ^{13}C is shown*); ^{19}F NMR (376 MHz, CDCl$_3$) δ −112.44, −114.01, −114.26, −114.54; IR (Neat) ν_{max} 2920, 1599, 139, 1501, 1388, 1314, 1220, 1156, 1064, 996, 899 cm^{-1}; **HRMS (ESI)** for $C_{36}H_{22}F_4NS$ (M+H)$^+$: calcd. 576.1404, found 576.1396.

5-Methyl-2,3,7,8-tetra-*m*-tolylthiopyrano[4,3,2-ij]isoquinoline (5d):



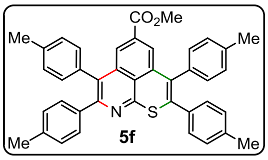
5d (132 mg, 79%); yellow crystalline solid. mp = 225–227 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.25–7.21 (m, 2H), 7.17 (bt, J = 7.75 Hz, 1H), 7.12 (bd, J = 8.0 Hz, 1H), 7.05–6.89 (m, 13H), 6.63 (bs, 1H), 2.32 (s, 3H), 2.28 (s, 3H), 2.25 (s, 3H), 2.22 (s, 3H), 2.17 (s, 3H); ^{13}C{^{1}H} NMR (101MHz, CDCl$_3$) δ 158.0, 150.5, 141.2, 140.0, 138.02, 137.98, 137.8, 137.6, 137.4, 137.3, 136.9, 136.5, 135.9, 131.8, 131.7, 131.4, 130.7, 130.1, 128.6, 128.4, 128.3, 128.2, 127.9, 127.83, 127.78, 127.7, 127.14, 127.1, 126.6, 126.5, 125.0, 122.60, 122.57, 22.3, 21.5, 21.4, 21.2; IR (Neat) ν_{max} 2915, 1606, 1559, 1533, 1481, 1370, 1333, 1313, 1234, 1150, 1092, 988, 957 cm^{-1}; **HRMS (ESI)** for $C_{40}H_{34}NS$ (M+H)$^+$: calcd. 560.2406, found 560.2406.

5-Methyl-2,3,7,8-tetra(thiophen-2-yl)thiopyrano[4,3,2-ij]isoquinoline (5e):



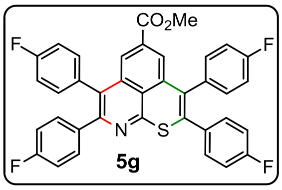
5e (55 mg, 35%); gray crystalline solid. mp = 321–322 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (bd, J = 4.5 Hz, 1H), 7.48 (bd, J = 5.0 Hz, 1H), 7.29–7.21 (m, 4H), 7.14 (bt, J = 4.0 Hz, 1H), 7.02 (dd, J = 10.75 & 2.75 Hz, 2H), 6.96 (s, 1H), 6.92 (bt, J = 4.25 Hz, 1H), 6.87 (bt, J = 4.25 Hz, 1H), 6.74 (bt, J = 4.25 Hz, 2H), 2.20 (s, 3H); ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 158.1, 145.6, 143.7, 142.0, 139.1, 138.5, 137.9, 137.8, 136.5, 132.0, 130.2, 128.93, 128.86, 128.5, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.4, 126.3, 125.5, 123.5, 123.0, 121.4, 116.3, 22.4; IR (Neat) ν_{max} 3094, 1600, 1519, 1456, 1431, 1370, 1305, 1229, 1175, 1135, 1038 cm^{-1}; **HRMS (ESI)** for $C_{28}H_{18}NS_5$ $(M+H)^+$: calcd. 528.0037, found 528.0040.

Methyl 2,3,7,8-tetra-*p*-tolylthiopyrano[4,3,2-ij]isoquinoline-5-carboxylate (5f):



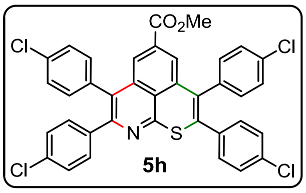
5f (108 mg, 60%); yellow crystalline solid. mp = 345–346 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (bd, J = 1.5 Hz, 1H), 7.38 (bd, J = 1.5 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.13–7.06 (m, 6H), 7.03–6.95 (m, 6H), 3.74 (s, 3H), 2.40 (s, 3H), 2.32 (s, 3H), 2.28 (s, 3H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (101MHz, $CDCl_3$) δ 166.6, 158.4. 151.2, 137.85, 137.76, 137.5, 137.05, 136.99, 136.9, 136.8, 134.4, 134.3, 133.8, 131.9, 131.7, 130.8, 130.5, 129.9, 129.5, 129.2, 128.8, 128.3, 127.5, 125.3, 125.0, 122.3, 52.3, 21.33, 21.27, 21.21, 21.16; IR (Neat) ν_{max} 2954, 2918, 1722, 1552, 1503, 1435, 1331, 1249, 1180, 1110, 1020, 994 cm^{-1}; **HRMS (ESI)** for $C_{41}H_{34}NO_2S$ $(M+H)^+$: calcd. 604.2305, found 604.2307.

Methyl 2,3,7,8-tetrakis(4-fluorophenyl)thiopyrano[4,3,2-ij]isoquinoline-5-carboxylate (5g):



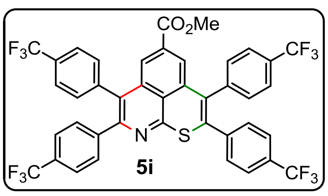
5g (135 mg, 73%); yellow crystalline solid. mp = >350 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (bd, J = 1.6 Hz, 1H), 7.36 (bd, J = 1.6 Hz, 1H), 7.30–7.23 (m, 2H), 7.19–6.99 (m, 10H), 6.89 (t, J = 8.8 Hz, 4H), 3.77 (s, 3H); ^{13}C{^{1}H} NMR (101MHz, $CDCl_3$) δ 166.2, 163.53, 163.49, 163.46, 163.2, 161.05, 161.02, 160.99, 160.8, 158.5, 150.6, 137.6, 137.0, 136.5, 135.42, 135.39, 132.75, 132.73, 132.72, 132.68, 132.60, 132.40, 132.37, 131.8, 131.7, 131.4, 131.2, 131.1, 126.8, 125.4, 125.0, 122.6, 116.3, 116.0, 115.6, 115.3, 114.9, 114.6, 52.52; (*The ^{13}C NMR is complex due to the presence of four F-atoms on the periphery of arene moiety; it is therefore difficult to assign the corresponding peaks of ^{13}C-attached to the fluorine-bearing arenes. Hence, complete list of the representative peaks of ^{13}C is shown*); ^{19}F NMR (376 MHz, $CDCl_3$) δ −111.95, −113.46, −113.49, −113.86; IR (Neat) ν_{max} 3041, 2919, 1721, 1598, 1537, 1500, 1435, 1379, 1258, 1219, 1155, 1090, 998 cm^{-1}; **HRMS (ESI)** for $C_{37}H_{22}F_4NO_2S$ $(M+H)^+$: calcd. 620.1302, found 620.1306.

Methyl 2,3,7,8-tetrakis(4-chlorophenyl)thiopyrano[4,3,2-ij]isoquinoline-5-carboxylate (5h):



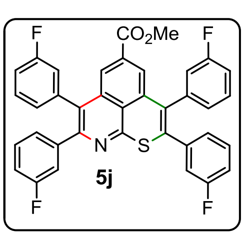
5i (149 mg, 73%); yellow crystalline solid. mp = >350 °C. The compound is insoluble in deuterated $CHCl_3$, THF, DMSO, MeOH, and CH_3CN. Thus, it is impossible to record respective ^1H NMR and ^{13}C NMR spectra; the structure was confirmed by single crystal X-ray analaysis; IR (Neat) ν_{max} 2923, 2852, 1723, 1631, 1554, 1535, 1554, 1488, 1441, 1398, 1260, 1151, 1089, 1015, 997 cm^{-1}; **HRMS (ESI)** for $C_{37}H_{22}Cl_4NO_2S$ $(M+H)^+$: calcd. 684.0120, found 684.0120.

Methyl 2,3,7,8-tetrakis(4-(trifluoromethyl)phenyl)thiopyrano[4,3,2-ij]isoquinoline-5-carboxylate (5i):



5i (161 mg, 66%); yellow crystalline solid. mp = 312–313 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 1.5 Hz, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.51–7.45 (m, 4H), 7.40 (d, J = 8.0 Hz, 2H), 7.38–7.33 (m, 3H), 7.32–7.27 (m, 4H), 3.78 (s, 3H); $^{13}C\{^1H\}$ NMR (101MHz, $CDCl_3$) δ 165.8, 158.9, 150.3, 142.5, 140.3, 139.8, 137.1, 136.6, 136.4, 132.8, 131.5, 131.4, 131.1, 130.9, 130.7, 130.5, 130.4, 130.3, 130.2, 130.1, 129.8, 129.7, 127.2, 126.20, 126.17, 126.1, 125.6, 125.53, 125.50, 125.3, 125.01, 124.98, 124.87, 124.84, 124.81, 124.63, 123.3, 122.8, 122.7, 122.5, 52.7; (*The ^{13}C NMR is complex due to the presence of four CF_3-atoms on the periphery of arene moiety; it is therefore difficult to assign the corresponding peaks of ^{13}C-attached to the fluorine-bearing arenes. Hence, complete list of the representative peaks of ^{13}C is shown*); ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.59, –62.71, –62.73, –62.93; IR (Neat) ν_{max} 2958, 1737, 1616, 1534, 1382, 1316, 1210, 1107, 996, 1068 cm^{-1}; **HRMS (ESI)** for $C_{41}H_{22}F_{12}NO_2S$ $(M+H)^+$: calcd. 820.1174, found 820.1175.

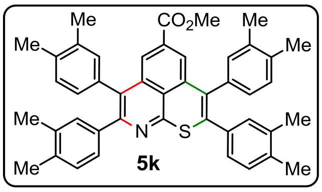
Methyl 2,3,7,8-tetrakis(3-fluorophenyl)thiopyrano[4,3,2-ij]isoquinoline-5-carboxylate (5j):



5j (155 mg, 84%); yellow crystalline solid. mp = >335 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.43–7.36 (m, 2H), 7.31 (q, J = 7.2 Hz, 1H), 7.22–7.14 (m, 2H), 7.21–6.89 (m, 11H), 6.84 (d, J = 8.5 Hz, 1H), 3.77 (s, 3H); $^{13}C\{^1H\}$ NMR (126MHz, $CDCl_3$) δ 166.0, 164.1, 163.25, 163.24, 162.1, 161.30, 161.27, 158.7, 150.1, 141.4, 141.3, 138.8, 138.7, 138.5, 138.4, 138.3, 137.3, 136.5, 136.2, 132.5, 131.3, 130.70, 130.67, 130.64, 130.61, 130.03, 129.97, 129.23, 129.17, 127.0, 126.7, 126.4, 125.63, 125.61, 125.5, 125.3, 125.09, 125.07, 123.0, 117.9, 117.8, 117.6, 117.4, 117.0, 116.8, 116.5, 116.3, 115.7, 115.6, 115.2, 115.1, 115.04, 115.0, 114.94, 114.88, 114.7, 52.5; (*The ^{13}C NMR is complex due to the presence of four F-atoms on the periphery of arene moiety; it is therefore difficult to assign the corresponding peaks of ^{13}C-attached to the fluorine-bearing arenes. Hence, complete list of the representative peaks of ^{13}C is shown*); ^{19}F NMR (376 MHz, $CDCl_3$) δ –111.71 (d, J = 15.0), –111.79

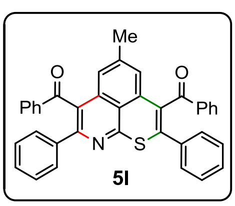
(d, J = 15.8), −112.11, 113.43; IR (Neat) ν_{max} 2920, 2850, 1724, 1609, 1580, 1557, 1531, 1434, 1332, 1267, 1199, 1173, 1153, 873, 819 cm^{-1}; HRMS (ESI) for $C_{37}H_{22}F_4NO_2S$ (M+H)$^+$: calcd. 620.1302, found 620.1302.

Methyl 2,3,7,8-tetrakis(3,4-dimethylphenyl)thiopyrano[4,3,2-ij]isoquinoline-5-carboxylate (5k):



5k (148 mg, 75%); yellow crystalline solid. mp = 313–315 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (bd, J = 1.0 Hz, 1H), 7.37 (bs, 1H), 7.24 (bs, 1H), 7.13 (d, J = 7.5 Hz, 1H), 7.04 (d, J = 7.5 Hz, 1H), 7.02 (bs, 1H), 6.97 (bd, J = 6.5 Hz, 2H), 6.94–6.86 (m, 5H), 6.84 (d, J = 7.5 Hz, 1H), 3.74 (s, 3H), 2.30 (s, 3H), 2.24 (s, 3H), 2.22 (s, 3H), 2.20–2.14 (m, 12H), 2.13 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.8, 158.3, 151.1, 137.8, 137.6, 137.4, 136.73, 136.67, 136.63, 136.4, 136.0, 135.65, 135.61, 135.56, 135.4, 134.9, 134.8, 134.4, 132.0, 131.8, 131.7, 131.6, 131.2, 130.5, 130.0, 129.9, 129.2, 128.6, 128.4, 128.1, 127.6, 127.5, 126.8, 125.2, 125.1, 122.3, 52.3, 19.8, 19.74, 19.70, 19.60, 19.57, 19.55, 19.51, 19.4; IR (Neat) ν_{max} 2917, 2852, 1720, 1600, 1552, 1495, 1380, 1228, 1112, 989, 818 cm^{-1}; **HRMS (ESI)** for $C_{45}H_{42}NO_2S$ (M+H)$^+$: calcd. 660.2931, found 660.2949.

(5-Methyl-2,8-diphenylthiopyrano[4,3,2-ij]isoquinoline-3,7-diyl)bis(phenylmethanone) (5l)/ minor isomers::

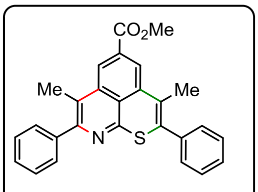


5l (108 mg, 65%); yellow solid. mp = 233–235 °C; **Major isomer 5l:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, J = 7.0 Hz, 2H), 7.73 (d, J = 7.0 Hz, 2H), 7.55 (d, J = 7.0 Hz, 2H), 7.50–7.40 (m, 3H), 7.39–7.35 (m, 2H), 7.34–7.27 (m, 4H), 7.24–7.19 (m, 6H), 6.86 (s, 1H), 2.22 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 197.7, 196.4, 159.9, 150.6, 143.2, 138.8, 137.7, 137.3, 136.5, 136.1, 135.2, 133.9, 133.6, 133.2, 131.2, 130.3, 129.50, 129.46, 129.36, 129.3, 129.1, 128.62, 128.58, 128.5, 128.2, 125.0, 124.4, 122.4, 121.7, 22.2; IR (Neat) ν_{max} 3056, 2920, 1736, 1659, 1595, 1553, 1536, 1489, 1376, 1335, 1309, 1256, 1173, 1073, 999 cm^{-1}; **HRMS (ESI)** for $C_{38}H_{26}NO_2S$ (M+H)$^+$: calcd. 560.1679, found 560.1684.

Representative peaks for minor isomers:

minor isomers (25 mg, 15%); yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 8.5 Hz, 2H), 7.78 (d, J = 9.0 Hz, 2H), 7.51–7.43 (m, 2H), 7.40–7.28 (m, 10H), 7.27 (s, 1H), 7.23–7.17 (m, 3H), 7.11 (s, 1H), 6.91 (s, 1H), 2.22 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 196.5, 194.9, 157.7, 149.2, 142.6, 137.9, 137.3, 136.6, 136.5, 135.3, 134.7, 133.9, 133.2, 133.15, 131.06, 130.3, 130.2, 129.5, 129.4, 129.0, 128.64, 128.58, 128.2, 128.0, 127.9, 124.9, 123.6, 123.2, 22.2.

Methyl 3,7-dimethyl-2,8-diphenylthiopyrano[4,3,2-ij]isoquinoline-5-carboxylate (5m)/ minor isomers:



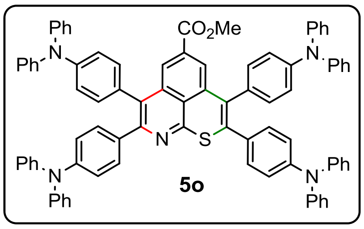
5m + other isomers

Inseparable mixture of **5m** and **minior isomers** (5:1, 89 mg, 70%); yellow solid. mp = 249–250 °C; **Major isomer 5m:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.57–7.49 (m, 5H), 7.48–7.37 (m, 6H), 7.20 (d, J = 7.0 Hz, 2H), 7.16 (bd, J = 1.0 Hz, 1H), 3.84 (s, 3H), 2.45 (s, 3H), 1.91 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.6, 156.1, 152.4, 140.4, 137.9, 137.7, 137.4, 132.7, 132.0, 131.1, 129.8, 129.7, 129.6, 129.4, 128.1, 127.8, 125.0, 122.5, 121.6, 120.9, 52.3, 21.1, 15.7; IR (Neat) ν_{max} 3055, 2949, 2921, 1722, 1610, 1563, 1543, 1491, 1437, 1384, 1328, 1308, 1251, 1155, 1117, 1072 cm^{-1}; **HRMS (ESI)** for $C_{27}H_{22}NO_2S$ $(M+H)^+$: calcd. 424.1366, found 424.1377.

Representative peaks for other isomer: ^{1}H NMR (500 MHz, $CDCl_3$) 8.37 (s, 0.21H), 7.95 (s, 0.22 H), 4.01 (s, 0.63H), 2.50 (s, 0.61H), 2.13 (s, 0.62H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.8, 156.3, 135.5, 130.0, 129.7, 129.1, 128.71, 128.67, 123.9, 123.3, 119.4, 52.5, 22.8, 17.5.

*As **5m** and **minor isomers** are inseparable, independent protons count for major isomer **5m** and minor isomer are not feasible. Ratio of the both regioisomers **5m: minor isomers** was determined based on the characteristic Me-H^{1} proton integration. H^{1} NMR (500 MHz, $CDCl_3$) H^{1} for **5m/minor isomers:** δ = 3.84 (s, 3H, major)/ 4.01 (s, 0.63H, minor).*

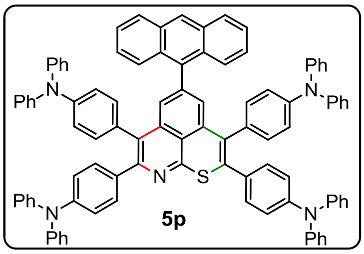
Methyl 2,3,7,8-tetrakis(4-(diphenylamino)phenyl)thiopyrano[4,3,2-ij]isoquinoline-5-carboxylate (5o):



5o

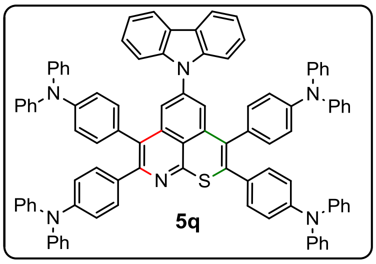
5o (281 mg, 77%); yellow crystalline solid; mp = 333–335 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 1.2 Hz, 1H), δ 7.60 (d, J = 1.2 Hz, 1H), 7.31–7.23 (m, 12H), 7.18–7.00 (m, 40H), 6.96 (d, J = 7.75 Hz, 2H), 6.91 (d, J = 7.75 Hz, 2H), 3.87 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.6, 158.4, 151.2, 147.63, 147.60, 147.53, 147.25, 147.16, 147.11, 146.9, 137.7, 137.4, 136.9, 133.7, 132.0, 131.8, 131.5, 131.0, 130.9, 130.6, 130.3, 129.4, 129.27, 129.23, 127.3, 125.3, 125.0, 124.9, 124.6, 124.4, 124.3, 123.9, 123.8, 123.4, 123.0, 122.93, 122.86, 122.23, 122.15, 121.7, 52.4; IR (Neat) ν_{max} 3043, 3016, 2920, 2360, 1722, 1592, 1483, 1456, 1416, 1324, 1279, 1218, 1174, 1109, 894, 847; **HRMS (ESI)** for $C_{85}H_{62}N_5O_2S$ $(M+H)^+$: calcd. 1216.4619; found: 1216.7528.

4,4',4'',4'''-(5-(Anthracen-9-yl)thiopyrano[4,3,2-ij]isoquinoline-2,3,7,8-tetrayl)tetrakis(N,N-diphenylaniline) (5p):



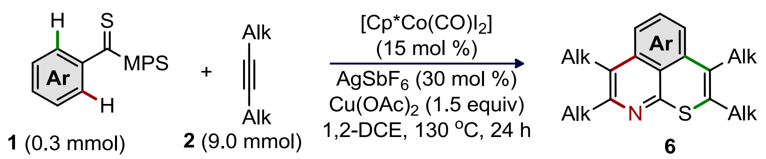
5p (259 mg, 65%); yellow crystalline solid. mp = 205–206 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.06 (d, J = 8.5 Hz, 2H), 7.72 (d, J = 8.5 Hz, 2H), 7.58 (s, 1H), 7.47 (t, J = 7.25 Hz, 2H), 7.36 (t, J = 7.75 Hz, 2H), 7.32–7.22 (m, 8H), 7.19 (bs, 1H), 7.16–6.88 (m, 46H), 6.84 (t, J = 8.5 Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.4, 151.3, 147.6, 147.53, 147.47, 147.3, 146.9, 146.8, 146.7, 141.6, 137.9, 136.8, 136.4, 134.4, 132.0, 131.7, 131.64, 131.56, 131.3, 131.1, 130.3, 129.8, 129.4, 129.2, 129.1, 128.3, 126.9, 126.6, 126.5, 125.6, 125.2, 124.8, 124.5, 124.35, 124.31, 123.6, 123.4, 123.3, 122.9, 122.8, 122.5, 121.9; IR (Neat) ν_{max} 1586, 1487, 1312, 1262, 1174, 1074, 1017, 884, 799 cm^{-1}; **HRMS (ESI)** for $C_{97}H_{68}N_5S$ $(M+H)^+$: calcd. 1334.5190, found 1334.5180.

4,4',4'',4'''-(5-(9H-Carbazol-9-yl)thiopyrano[4,3,2-ij]isoquinoline-2,3,7,8-tetrayl)tetrakis(N,N-diphenylaniline) (5q):



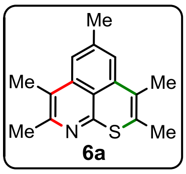
5q (326 mg, 82%); yellow crystalline solid; mp = >350 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.0 Hz, 2H), 7.56 (bd, J = 2.0 Hz, 1H), 7.42 (d, J = 7.5 Hz, 2H), 7.38–7.27 (m, 12H), 7.23 (bd, J = 1.5 Hz, 1H), 7.21–6.91 (m, 48H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.3, 151.1, 147.8, 147.60, 147.57, 147.53, 147.30, 147.17, 147.09, 147.0, 140.1, 139.8, 139.73, 139.3, 137.6, 133.8, 131.8, 131.7, 131.6, 131.5, 131.3, 131.1, 130.5, 130.4, 129.4, 129.3, 126.4, 126.2, 125.0, 124.6, 124.3, 124.2, 124.1, 124.0, 123.8, 123.5, 123.0, 122.9, 122.8, 122.3, 121.7, 120.6, 120.5, 120.3, 118.7, 109.9; IR (Neat) ν_{max} 3054, 2952, 2159, 2028, 1742, 1592, 1535, 1489, 1445, 1312, 1277, 1026, 991, 875, 748, 693, 618 cm^{-1}; **HRMS (ESI)** for $C_{95}H_{67}N_6S$ $(M+H)^+$: calcd. 1323.5142; found: 1323.5148.

<u>Synthesis of 6,6-fused thiopyrano-isoquinoline (6) via direct double-annulation of *N*-[arenethioyl]-*S*-methyl-*S*-phenylsulfoximine (1) with 1,2-dialkyl alkyne (2) (GP-4D):</u>



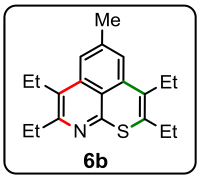
The annulation reactions were carried out in a 15 mL screw capped tube. The tube was charged with freshly prepared **1** (0.3 mmol), 1,2-dialkyl alkyne (**2**, 0.9 mmol), [Cp*Co(CO)I$_2$] (21.5 mg, 15 mol %), and Cu(OAc)$_2$ (81 mg, 0.45 mmol). Subsequently, AgSbF$_6$ (31 mg, 30 mol %) was introduced in to the tube in a glove box. Freshly dried 1,2-DCE (2.0 mL) was added to the mixture and the resulting mixture was stirred at 130 °C in a heating block for 24 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite and then washed with dichloromethane (3 × 10 mL). The solvents were evaporated under reduced pressure and the crude material was purified using column chromatography on neutral aluminia (5–10% *n*-hexane/EtOAc eluent) to give the desired product **6**.

2,3,5,7,8-Pentamethylthiopyrano[4,3,2-ij]isoquinoline (6a):



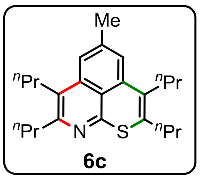
6a (39 mg, 52%); pale yellow solid. mp = 188–189 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.18 (s, 1H), 6.90 (s, 1H), 2.50 (s, 3H), 2.43 (s, 3H), 2.27 (s, 3H), 2.16 (m, 3H), 2.03 (m, 3H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 154.8, 148.5, 140.8, 137.3, 136.1, 128.5, 122.7, 121.6, 119.8, 118.9, 118.8, 22.6, 22.4, 20.6, 15.4, 14.0; IR (Neat) ν_{max} 2918, 2852, 1735, 1613, 1541, 1435, 1368, 1299, 1226, 1103, 1073, 971 cm^{-1}; **HRMS (ESI)** for $C_{16}H_{18}NS$ (M+H)$^{+}$: calcd. 256.1154, found 256.1153.

2,3,7,8-Tetraethyl-5-methylthiopyrano[4,3,2-ij]isoquinoline (6b):



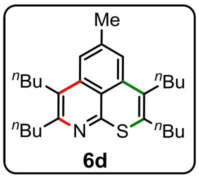
6b (65 mg, 70%); yellow crystalline solid. mp = 128–129 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.29 (s, 1H), 7.04 (s, 1H), 2.86–2.75 (m, 4H), 2.64 (q, J = 7.5 Hz, 2H), 2.54–2.48 (m, 2H), 2.47 (s, 3H), 1.31–1.14 (m, 12H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 155.5, 153.6, 140.7, 137.2, 135.6, 135.3, 128.0, 124.2, 122.5, 120.2, 119.1, 28.0, 27.4, 22.7, 21.6, 20.7, 14.4, 14.3, 13.9, 12.8; IR (Neat) ν_{max} 2960, 2868, 1610, 1540, 1485, 1389, 1296, 1222, 1094, 987 cm^{-1}; **HRMS (ESI)** for $C_{20}H_{26}NS$ (M+H)$^{+}$: calcd. 312.1780, found 312.1780.

5-Methyl-2,3,7,8-tetrapropylthiopyrano[4,3,2-ij]isoquinoline (6c):



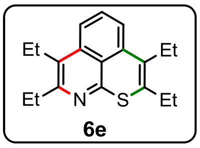
6c (80 mg, 73%); yellow crystalline solid. mp = 82–83 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (s, 1H), 6.99 (s, 1H), 2.74 (q, J = 7.75 Hz, 4H), 2.56 (t, J = 7.5 Hz, 4H), 2.48–2.41 (m, 5H), 1.76–1.51 (m, 8H), 1.09–0.96 (m, 12H); $^{13}C\{^1H\}$NMR (126 MHz, $CDCl_3$) δ 155.4, 152.6, 140.5, 137.4, 135.6, 134.6, 127.1, 123.2, 122.4, 120.3, 119.3, 36.9, 36.1, 30.9, 29.8, 23.3, 22.9, 22.75, 22.69, 21.3, 14.4, 14.3, 14.2, 13.9; IR (Neat) ν_{max} 2955, 2927, 2869, 1611, 1567, 1454, 1328, 1273, 1087, 1035, 981, 887 cm^{-1}; **HRMS (ESI)** for $C_{24}H_{34}NS$ $(M+H)^+$: calcd. 368.2406, found 368.2407.

2,3,7,8-Tetrabutyl-5-methylthiopyrano[4,3,2-ij]isoquinoline (6d):



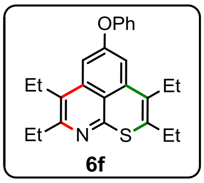
6d (90 mg, 71%); orange colour semi solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.03 (s, 1H), 2.82–2.74 (m, 4H), 2.60 (bt, J = 6.75 Hz, 2H), 2.52–2.45 (m, 5H), 1.74–1.41 (m, 16H), 1.02 (bt, J = 7.25 Hz, 6H), 0.98 (bt, J = 7.75 Hz, 6H); $^{13}C\{^1H\}$ NMR (101MHz, $CDCl_3$) δ 155.3, 152.7, 140.5, 137.4, 135.6, 134.7, 127.1, 123.2, 122.4, 120.2, 119.2, 34.7, 33.8, 32.3, 31.8, 31.6, 30.1, 28.5, 27.4, 23.1, 22.95, 22.92, 22.8, 22.5, 14.0, 13.92, 13.88, 13.81; IR (Neat) ν_{max} 2953, 2925, 2857, 1737, 1612, 1566, 1543, 1459, 1375, 1311, 1216, 1102, 1034, 980, 843 cm^{-1}; **HRMS (ESI)** for $C_{28}H_{42}NS$ $(M+H)^+$: calcd. 424.3032, found 424.3032.

2,3,7,8-Tetraethylthiopyrano[4,3,2-ij]isoquinoline (6e):



6e (76 mg, 85%); pale-yellow crystalline solid. mp = 112–113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.49 (m, 2H), 7.24 (dd, J = 6.4 & 2.4 Hz, 1H), 2.89–2.77 (m, 4H), 2.65 (q, J = 7.6 Hz, 2H), 2.51 (q, J = 7.4 Hz, 2H), 1.32–1.13 (m, 12H); $^{13}C\{^1H\}$ NMR (101MHz, $CDCl_3$) δ 155.8, 153.1, 136.9, 135.5, 131.0, 128.3, 124.8, 124.1, 119.7, 118.4, 27.8, 27.4, 21.7, 20.7, 14.5, 14.3, 13.8, 12.8; IR (Neat) ν_{max} 2965, 2931, 2871, 1609, 1575, 1542, 1375, 1309, 1161, 1055, 984, 848 cm^{-1}; **HRMS (ESI)** for $C_{19}H_{24}NS$ $(M+H)^+$: calcd. 298.1624, found 298.1630.

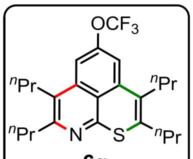
2,3,7,8-Tetraethyl-5-phenoxythiopyrano[4,3,2-ij]isoquinoline (6f):



6f (95 mg, 81%); yellow crystalline solid; mp = 80–81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.35 (m, 2H), 7.17 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 7.6 Hz, 2H), 6.95 (d, J = 5.6 Hz, 2H), 2.78 (q, J = 7.6 Hz, 2H), 2.68 (q, J = 7.6 Hz, 2H), 2.57 (q, J = 7.6 Hz, 2H), 2.52 (q, J = 7.6 Hz, 2H), 1.29–1.22 (m, 6H), 1.15–1.06 (m, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.4, 156.3, 155.4, 154.2, 138.9, 138.3, 137.2, 129.9, 128.0, 124.4, 123.8, 121.1, 119.3, 111.1, 106.4, 28.1, 27.5, 21.8, 20.9, 14.44, 14.37, 13.6, 12.6; IR (Neat)

ν_{max} 2960, 2927, 2868, 1609, 1592, 1542, 1486, 1390, 1295, 1212, 1177, 1121, 1021, 977 cm^{-1}; **HRMS (ESI)** for $C_{25}H_{28}NOS$ (M+H)$^+$: calcd. 390.1886, found 390.1885.

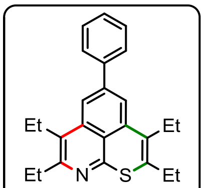
2,3,7,8-Tetrapropyl-5-(trifluoromethoxy)thiopyrano[4,3,2-ij]isoquinoline (6g):



6g

6g (95 mg, 83%); yellow crystalline solid; mp = 223–224 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (s, 1H), 6.96 (s, 1H), 2.75 (q, J = 8.25 Hz, 4H), 2.55 (bt, J = 8.0 Hz, 2H), 2.49 (t, J = 7.75 Hz, 2H), 1.77–1.65 (m, 4H), 1.63–1.52 (s, 4H), 1.09–0.97 (m, 12H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 155.6, 154.0, 151.2, 138.9, 138.6, 137.4, 126.9, 123.9, 122.3, 120.8 (q, J = 257 Hz), 111.5, 109.9, 37.0, 36.2, 31.0, 29.9, 23.2, 23.0, 22.6, 21.0, 14.3, 14.20, 14.18, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ −57.26 IR (Neat) ν_{max} 2958, 2928, 2871, 1741, 1610, 1578, 1542, 1451, 1375, 1253, 1213, 1144, 1012, 983 cm^{-1}; **HRMS (ESI)** for $C_{24}H_{31}F_3NOS$ (M+H)$^+$: calcd. 438.2073, found 438.2083.

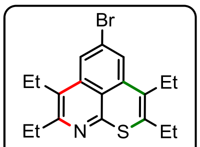
2,3,7,8-Tetraethyl-5-phenylthiopyrano[4,3,2-ij]isoquinoline (6h):



6h

6h (94 mg, 84%); yellow crystalline solid; mp = 158–160 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 7.0 Hz, 3H), 7.52 (t, J = 7.5 Hz, 2H), 7.44 (t, J = 8.0 Hz, 2H), 2.92 (q, J = 7.5 Hz, 2H), 2.85 (q, J = 7.75 Hz, 2H), 2.73 (q, J = 7.5 Hz, 2H), 2.55 (q, J = 7.5 Hz, 2H), 1.35–1.20 (m, 12H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 155.7, 153.9, 143.6, 141.6, 137.3, 136.3, 136.1, 128.9, 128.3, 127.9, 127.5, 125.0, 123.2, 118.2, 118.0, 28.1, 27.5, 21.8, 20.8, 14.4, 14.3, 14.0, 12.9; IR (Neat) ν_{max} 2962, 2926, 1604, 1578, 1542, 1444, 1328, 1258, 1181, 1098, 858, 794 cm^{-1}; **HRMS (ESI)** for $C_{25}H_{28}NS$ (M+H)$^+$: calcd. 374.1937, found 374.1943.

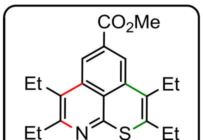
5-Bromo-2,3,7,8-tetraethylthiopyrano[4,3,2-ij]isoquinoline (6i):



6i

6i (97 mg, 86%); light yellow crystalline solid. mp = 151–152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (bd, J = 1.6 Hz, 1H), 7.28 (bd, J = 1.6 Hz, 1H), 2.86–2.75 (m, 4H), 2.62 (q, J = 7.4 Hz, 2H), 2.53 (q, J = 7.6 Hz, 2H), 1.30–1.23 (m, 6H), 1.23–1.14 (m, 6H); $^{13}C\{^1H\}$ NMR (101MHz, $CDCl_3$) δ 155.9, 154.7, 138.4, 138.0, 137.7, 127.6, 126.8, 124.1, 122.6, 121.9, 121.4, 28.1, 27.6, 21.7, 20.8, 14.3, 13.8, 12.6; IR (Neat) ν_{max} 2966, 2931, 2871, 1600, 1565, 1536, 1358, 1308, 1212, 1182, 1054, 987, 897 cm^{-1}; **HRMS (ESI)** for $C_{19}H_{23}BrNS$ (M+H)$^+$: calcd. 376.0729, found 376.0736.

Methyl 2,3,7,8-tetraethylthiopyrano[4,3,2-ij]isoquinoline-5-carboxylate (6j):

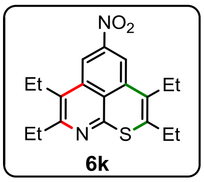


6j

6j (83 mg, 78%); yellow crystalline solid; mp = 139–140 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.79 (s, 1H), 3.98 (s, 3H), 2.90 (q, J = 7.5 Hz, 2H), 2.83 (q, J = 7.5 Hz, 2H), 2.70 (q, J = 7.5 Hz, 2H), 2.53 (q, J = 7.5 Hz, 2H), 1.31–1.16

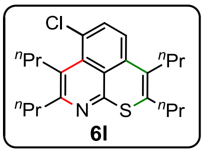
(m, 12H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 167.1, 156.0, 154.5, 136.8, 136.7, 136.2, 131.8, 128.4, 126.0, 125.6, 121.9, 117.8, 52.4, 28.0, 27.5, 21.8, 20.8, 14.30, 14.27, 14.2, 12.8; IR (Neat) ν_{max} 2961, 2930, 2870, 1719, 1566, 1431, 1251, 1181, 1140, 1004 cm^{-1}; **HRMS (ESI)** for $C_{21}H_{26}NO_2S$ $(M+H)^+$: calcd. 356.1679, found 356.1679.

2,3,7,8-Tetraethyl-5-nitrothiopyrano[4,3,2-ij]isoquinoline (6k):



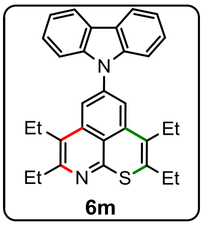
6k (98 mg, 95%); red crystalline solid; mp = 163–165 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.34 (bd, J = 2.0 Hz, 1H), 7.89 (bd, J = 1.5 Hz, 1H), 2.89 (d, J = 6.5 Hz, 2H), 2.85 (q, J = 7.5 Hz, 2H), 2.71 (q, J = 7.5 Hz, 2H), 2.57 (q, J = 7.5 Hz, 2H), 1.32–1.17 (m, 12H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 156.2, 155.8, 149.4, 139.3, 138.3, 137.1, 128.1, 126.7, 125.6, 115.0, 111.0, 28.1, 27.6, 21.9, 21.0, 14.3, 14.2, 14.1, 12.5; IR (Neat) ν_{max} 2964, 1612, 1578, 1520, 1478, 1367, 1309, 1207, 1054 cm^{-1}; **HRMS (ESI)** for $C_{19}H_{23}N_2O_2S$ $(M+H)^+$: calcd. 343.1475, found 343.1485.

6-Chloro-2,3,7,8-tetrapropylthiopyrano[4,3,2-ij]isoquinoline (6l):



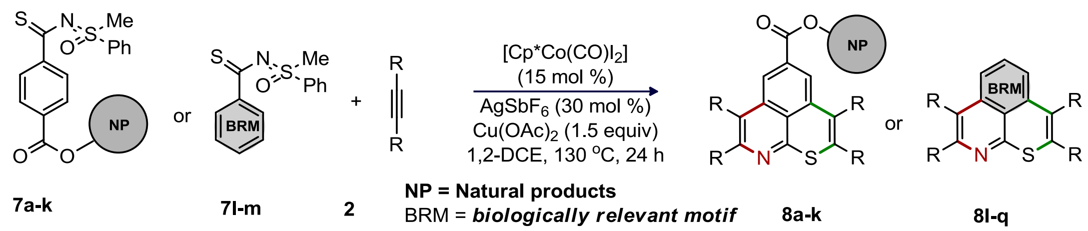
6l (86 mg, 75%); light yellow crystalline solid; mp = 89–90 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51 (bd, J = 8.0 Hz, 1H), 7.05 (bd, J = 8.0 Hz, 1H), 3.17 (bs, 2H), 2.77 (t, J = 8.0 Hz, 2H), 2.52 (bt, J = 7.75 Hz, 2H), 2.44 (bt, J = 7.75 Hz, 2H), 1.77–1.58 (m, 6H), 1.56–1.47 (m, 2H), 1.06–0.98 (m, 12H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 156.2, 155.3, 135.4, 135.1, 134.61, 134.57, 127.0, 126.4, 125.4, 124.0, 119.3, 37.5, 35.8, 31.2, 31.1, 25.45, 23.4, 22.8, 21.1, 14.3, 14.2, 13.9; IR (Neat) ν_{max} 2957, 2927, 2869, 1714, 1634, 1535, 1457, 1374, 1300, 1261, 1204, 1089, 1018 cm^{-1}; **HRMS (ESI)** for $C_{23}H_{31}ClNS$ $(M+H)^+$: calcd. 388.1860, found 388.1860.

5-(9H-Carbazol-9-yl)-2,3,7,8-tetraethylthiopyrano[4,3,2-ij]isoquinoline (6m):



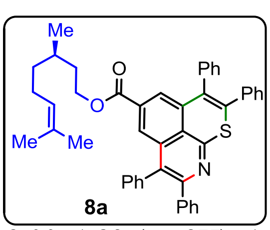
6l (112 mg, 81%); yellow crystalline solid; mp = 231–232 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 7.5 Hz, 2H), 7.72 (bd, J = 1.5 Hz, 1H), 7.54 (dd, J = 8.5 & 0.5 Hz, 2H), 7.47 (t, J = 7.5 Hz, 2H), 7.42 (bd, J = 1.5 Hz, 1H), 7.35 (t, J = 7.25 Hz, 2H), 2.94–2.81 (m, 4H), 2.68–2.55 (m, 4H), 1.39–1.29 (m, 6H), 1.24 (t, J = 7.5 Hz, 3H), 1.85 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 155.9, 154.7, 140.5, 140.0, 138.4, 138.1, 137.7, 128.0, 126.1, 124.8, 123.6, 123.0, 120.4, 120.2, 117.1, 117.0, 109.7, 28.2, 27.5, 21.8, 20.9, 14.43, 14.39, 14.1, 12.8; IR (Neat) ν_{max} 2962, 2868, 1605, 1541, 1481, 1449, 1372, 1258, 1120, 1027, 990 cm^{-1}; **HRMS (ESI)** for $C_{31}H_{31}N_2S$ $(M+H)^+$: calcd. 463.2202, found 463.2208.

The Direct Double-Annulation of 7 with symmetrical alkyne (2) (GP-4E):



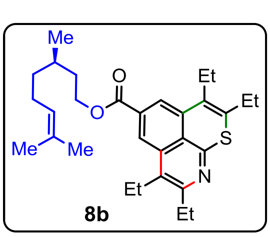
The annulation reactions were carried out in a 15 mL screw capped tube. The tube was charged with freshly prepared **7** (0.3 mmol), symmetrical alkyne (**2**, 0.9 mmol), [Cp*Co(CO)I$_2$] (21.5 mg, 15 mol %), and Cu(OAc)$_2$ (81 mg, 0.45 mmol). Subsequently, AgSbF$_6$ (31 mg, 30 mol %) was introduced in to the tube in a glove box. Freshly dried 1,2-DCE (2.0 mL) was added to the mixture and the resulting mixture was stirred at 130 °C in a heating block for 24 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite and then washed with dichloromethane (3 × 10 mL). The solvents were evaporated under reduced pressure and the crude material was purified using column chromatography on neutral aluminia (5−10% *n*-hexane/EtOAc eluent) to give the desired product.

Synthesis of 8a:



8a (149 mg, 74%); yellow crystalline solid; mp = 190–191 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.96 (bd, J = 1.5 Hz, 1H), 7.39 (bd, J = 1.5 Hz, 1H), 7.38 (bs, 1H), 7.38–7.27 (m, 7H), 7.25 (t, J = 1.75 Hz, 1H), 7.24–7.16 (m, 9H), 7.13 (d, J = 8.5 Hz, 2H), 5.10–4.98 (m, 1H), 4.24–4.13 (m, 2H), 2.00–1.83 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.42–1.33 (s, 1H), 1.31–1.22 (m, 2H), 1.18–1.09 (m, 1H), 0.95–0.84 (m, 1H), 0.81 (d, J = 8.0 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 165.9, 158.6, 151.3, 139.7, 137.6, 137.2, 137.15, 137.07, 136.8, 136.7, 132.4, 132.1, 131.2, 131.0, 130.7, 130.0, 129.4, 128.7, 128.15, 128.1, 127.9, 127.59, 127.55, 127.4, 125.2, 124.6, 122.6, 63.6, 36.8, 35.0, 29.5, 25.7, 25.4, 19.3, 17.6; IR (Neat) ν_{max} 3831, 3435, 3224, 2996, 2763, 2540, 2266, 1622, 1441, 1256, 1122, 1027, 991 cm^{-1}; **HRMS (ESI)** for $C_{46}H_{42}NO_2S$ (M+H)$^+$: calcd. 672.2931; found: 672.2912.

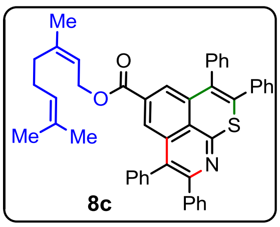
Synthesis of 8b:



8b (115 mg, 80%); yellow crystalline solid; mp = 166–167 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.23 (s, 1H), 7.81 (s, 1H), 5.12 (bt, J = 7.5 Hz, 1H), 4.46–4.39 (m, 2H), 2.90 (q, J = 7.5 Hz, 2H), 2.83 (q, J = 7.5 Hz, 2H), 2.70 (q, J = 7.5 Hz, 2H), 2.53 (q, J = 7.5 Hz, 2H), 2.08–1.97 (m, 2H), 1.91–1.82

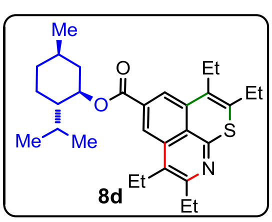
(m, 1H), 1.76–1.63 (m, 6H), 1.62 (s, 3H), 1.49–1.38 (m, 1H), 1.30–1.16 (m, 12H), 1.01 (d, J = 6.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.6, 156.0, 154.4, 136.6, 136.58, 136.0, 132.1, 131.4, 128.3, 125.9, 125.5, 124.5, 121.8, 117.8, 64.0, 37.1, 35.5, 29.9, 28.1, 27.5, 25.7, 25.5, 21.8, 20.8, 19.5, 17.6, 14.4, 14.3, 14.1, 12.7; IR (Neat) ν_{max} 2965, 2926, 1722, 1544, 1457, 1259, 1117, 972, 766 cm^{-1}; **HRMS (ESI)** for $C_{30}H_{42}NO_2S$ $(M+H)^+$: calcd. 480.2931; found: 480.2939.

Synthesis of 8c:



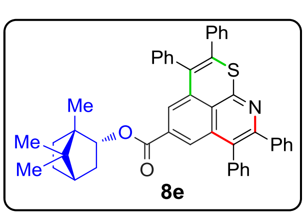
8c (60 mg, 30%); orange colour solid; mp = 140–141 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (bs, 1H), 7.41–7.27 (m, 8H), 7.25–7.15 (m, 11H), 7.13 (bt, J = 7.5 Hz, 2H), 5.27 (bt, J = 7.0 Hz, 1H), 5.06 (bt, J = 6.75 Hz, 1H), 4.65 (bt, J = 7.0 Hz, 2H), 2.10–1.95 (m, 4H), 1.67 (s, 3H), 1.60 (bt, J = 5.5 Hz, 6H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 165.9, 158.6, 151.3, 142.9, 139.7, 137.6, 137.2, 137.1, 136.8, 136.7, 132.6, 132.1, 131.8, 131.0, 130.8, 130.0, 129.4, 128.75, 128.73, 128.15, 128.08, 128.0, 127.6, 127.5, 127.4, 125.4, 125.2, 123.7, 122.7, 117.8, 62.0, 39.4, 26.3, 25.6, 17.7, 16.5; IR (Neat) ν_{max} 2967, 2926, 2849, 1719, 1604, 1537, 1499, 1379, 1251, 1207, 1119, 1028, 994 cm^{-1}; **HRMS (ESI)** for $C_{46}H_{40}NO_2S$ $(M+H)^+$: calcd. 670.2774, found 670.2745.

Synthesis of 8d:



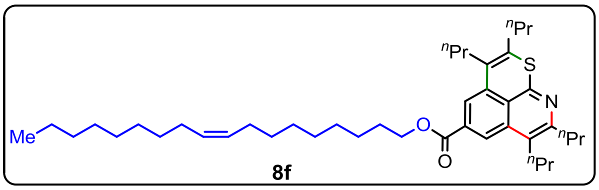
8d (111 mg, 77%); yellow crystalline solid; mp = 174-175 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.83 (s, 1H), 5.00–4.91 (m, 1H), 2.96–2.87 (m, 2H), 2.84 (q, J = 7.5 Hz, 2H), 2.71 (q, J = 7.5 Hz, 2H), 2.54 (q, J = 7.5 Hz, 2H), 2.24–2.17 (m, 1H), 2.02–1.96 (m, 1H), 1.79–1.72 (m, 3H), 1.63–1.58 (m, 1H), 1.32–1.15 (m, 12H), 0.98–0.91 (m, 9H), 0.84 (d, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.0, 156.0, 136.7, 136.5, 136.0, 132.5, 128.4, 126.0, 125.4, 121.8, 118.0, 75.6, 47.3, 40.9, 34.3, 31.4, 27.9, 27.5, 27.0, 24.1, 22.0, 21.8, 20.8, 20.5, 17.1, 14.4, 14.3, 14.1, 12.6; IR (Neat) ν_{max} 2958, 2870, 2360, 1716, 1610, 1545, 1454, 1251, 1144, 1097, 980, 766 cm^{-1}; **HRMS (ESI)** for $C_{30}H_{42}NO_2S$ $(M+H)^+$: calcd. 480.2931; found: 480.2930.

Synthesis of 8e:



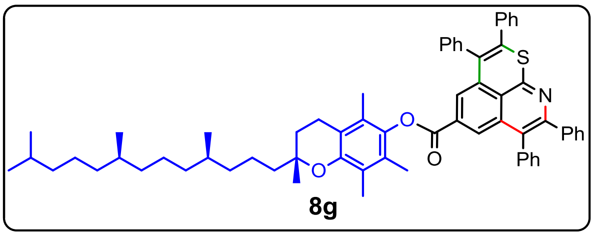
8e (132 mg, 66%); pale-yellow crystalline solid. mp = 318–320 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.98 (bd, J = 1.5 Hz, 1H), 7.42–7.35 (m, 5H), 7.34 (d, J = 7.0 Hz, 1H), 7.30 (t, J = 7.5 Hz, 2H), 7.25–7.17 (m, 11H), 7.15 (d, J = 7.5 Hz, 2H), 4.91 (d, J = 9.0 Hz, 1H), 2.38–2.28 (m, 1H), 1.72–1.66 (m, 1H), 1.65 (bt, J = 4.5 Hz, 1H), 1.57–1.47 (m, 1H), 1.19–1.10 (m, 1H), 1.09–1.00 (m, 1H), 0.96–0.89 (m, 1H), 0.88 (s, 3H), 0.86 (s, 3H), 0.72 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, CDCl$_3$) δ 165.9, 158.5, 151.1, 139.7, 137.7, 137.3, 137.2, 137.1, 136.82, 136.77, 132.7, 132.1, 131.0, 130.7, 130.1, 129.4, 128.8, 128.7, 128.2, 128.1, 128.0, 127.6, 127.5, 127.43, 127.40, 125.34, 125.2, 122.7, 80.7, 48.9, 47.7, 44.9, 36.7, 27.8, 27.0, 19.6, 18.8, 13.3; IR (Neat) ν_{max} 2950, 1716, 1604, 1557, 1533, 1487, 1441, 1386, 1258, 1118, 1074, 992, 898 cm^{-1}; **HRMS (ESI)** for $C_{46}H_{40}NO_2S$ (M+H)$^+$: calcd. 670.2774; found: 670.2781.

Synthesis of 8f:



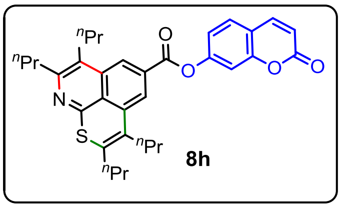
8f (144 mg, 74%); pale yellow gummy liquid; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.21 (s, 1H), 7.78 (s, 1H), 5.37–5.31 (m, 2H), 4.37 (t, J = 6.5 Hz, 2H), 2.84 (bt, J = 8.0 Hz, 2H), 2.77 (bt, J = 8.0 Hz, 2H), 2.63 (t, J = 8.25 Hz, 2H), 2.48 (t, J = 8.0 Hz, 2H), 2.04–1.95 (m, 4H), 1.83–1.77 (m, 2H), 1.76–1.67 (m, 4H), 1.64–1.57 (m, 4H), 1.54–1.47 (m, 2H), 1.36–1.23 (m, 20H), 1.11–0.97 (m, 12H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 166.6, 155.9, 153.5, 136.8, 136.2, 135.5, 131.9, 129.9, 129.7, 129.1, 127.4, 125.3, 124.9, 122.0, 118.0, 65.4, 36.9, 36.2, 31.9, 31.0, 29.8, 29.7, 29.5, 29.3, 29.2, 28.7, 27.2, 27.1, 26.1, 23.3, 23.1, 23.0, 22.6, 21.2, 14.4, 14.3, 14.2; IR (Neat) ν_{max} 2958, 2915, 2848, 2783, 1716, 1654, 1546, 1464, 1248, 1145, 981 cm^{-1}; **HRMS (ESI)** for $C_{42}H_{66}NO_2S$ (M+H)$^+$: calcd. 648.4809; found: 648.4810.

Synthesis of 8g:



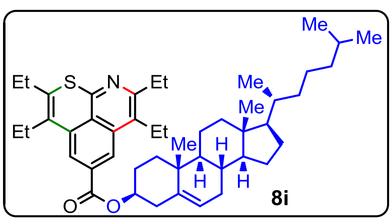
8g (202 mg, 73%); orange colour solid. mp = 205–206 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.19 (bd, J = 1.5 Hz, 1H), 7.60 (bd, J = 1.5 Hz, 1H), 7.40–7.14 (m, 20H), 2.57 (bt, J = 6.75 Hz, 2H), 2.09 (s, 3H), 1.91 (s, 3H), 1.87 (s, 3H), 1.85–1.73 (m, 2H), 1.60–1.05 (m, 24H), 0.92–8.05 (m, 12H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 164.5, 158.6, 151.5, 149.4, 140.6, 139.7, 137.8, 137.5, 137.2, 137.13, 137.12, 136.7, 132.4, 132.1, 131.8, 131.0, 130.7, 130.1, 129.4, 128.8, 128.2, 128.1, 128.0, 127.7, 127.60, 127.57, 127.47, 126.7, 125.8, 125.6, 124.9, 123.0, 122.9, 117.4, 75.1, 39.4, 37.54, 37.52, 37.44, 37.38, 37.33, 37.28, 32.8, 32.76, 32.70, 32.68, 31.10, 31.06, 27.9, 24.78, 24.77, 24.4, 22.7, 22.6, 21.0, 20.5, 19.74, 19.67, 19.62, 19.60, 19.56, 12.9; IR (Neat) ν_{max} 2921, 2851, 1734, 1566, 1613, 1537, 1459, 1377, 1229, 1203, 1177, 1101, 1060, 930 cm^{-1}; **HRMS (ESI)** for $C_{65}H_{72}NO_3S$ (M+H)$^+$: calcd. 946.5227, found 946.5230.

Synthesis of 8h:



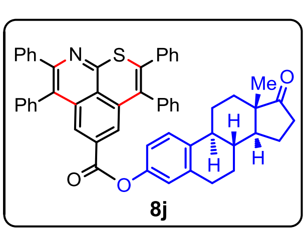
8h (104 mg, 64%); yellow solid; mp = 128–129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (bd, J = 0.8 Hz, 1H), 7.86 (bd, J = 1.2 Hz, 1H), 7.74 (d, J = 9.6 Hz, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.31 (d, J = 2 Hz, 1H), 7.24 (d, J = 2.4 Hz, 1H), 6.43 (d, J = 9.6 Hz, 1H), 2.87 (t, J = 8.0 Hz, 2H), 2.79 (t, J = 7.8 Hz, 2H), 2.66 (t, J = 8.0 Hz, 2H), 2.51 (d, J = 8.0 Hz, 2H), 1.80–1.58 (m, 8H), 1.11–1.02 (m, 12H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.6, 160.2, 156.0, 154.8, 154.1, 153.5, 142.8, 136.9, 136.8, 136.4, 130.2, 128.6, 127.3, 125.7, 125.0, 123.0, 118.5, 117.9, 116.8, 116.2, 110.6, 37.0, 36.3, 30.9, 29.8, 23.2, 23.1, 23.0, 21.2, 14.4, 14.3, 14.2, 14.0; IR (Neat) ν_{max} 3084, 2955, 2925, 2869, 2359, 1729, 1614, 1540, 1385, 1227, 1122, 984, 887, 751 cm^{-1}; **HRMS (ESI)** for $C_{33}H_{36}NO_4S$ $(M+H)^+$: calcd. 542.2360; found: 542.2367.

Synthesis of 8i:



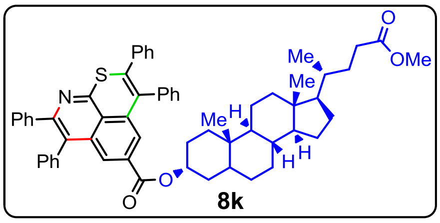
8i (156 mg, 73%); yellow crystalline solid; mp = 191–192 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.81 (s, 1H), 5.44 (s, 1H), 4.93–4.85 (m, 1H), 2.91 (q, J = 7.5 Hz, 2H), 2.83 (q, J = 7.5 Hz, 2H), 2.70 (q, J = 7.5 Hz, 2H), 2.53 (q, J = 7.5 Hz, 4H), 2.08–1.90 (m, 5H), 1.87–1.73 (m, 3H), 1.60–1.44 (m, 6H), 1.40–1.30 (m, 3H), 1.29–1.19 (m, 12H), 1.16–1.04 (m, 9H), 1.03–0.95 (m, 3H), 0.92 (d, J = 6.5 Hz, 3H), 0.86 (dd, J = 6.5 & 2.0 Hz, 6H), 0.68 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.0, 155.9, 154.4, 139.5, 136.6, 136.5, 136.0, 132.4, 128.4, 125.9, 125.5, 122.9, 121.7, 117.9, 75.2, 56.6, 56.1, 50.0, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.1, 35.8, 31.9, 31.8, 28.2, 28.1, 28.0, 27.9, 27.5, 24.3, 23.8, 22.8, 22.5, 21.8, 21.0; IR (Neat) ν_{max} 3612, 3469, 3370, 3317, 3192, 2858, 2573, 2444, 2148, 1631, 1462, 1232, 766 cm^{-1}; **HRMS (ESI)** for $C_{47}H_{68}NO_2S$ $(M+H)^+$: calcd. 710.4985; found: 710.4977.

Synthesis of 8j:



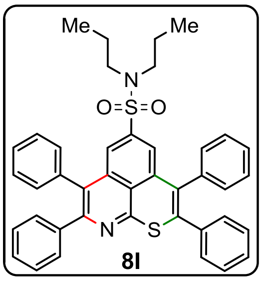
8j (166 mg, 72%); light yellow crystalline solid. mp = 235–237 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (bd, J = 1.5 Hz, 1H), 7.51 (bd, J = 1.5 Hz, 1H), 7.40–7.27 (m, 7H), 7.25–7.12 (m, 14H), 6.84–6.78 (m, 2H), 2.89–2.84 (m, 2H), 2.54–2.46 (m, 1H), 2.43–2.36 (m, 1H), 2.32–2.24 (m, 1H), 2.19–2.09 (m, 1H), 2.08–1.95 (m, 3H), 1.66–1.40 (m, 6H), 0.90 (s, 3H); ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 164.8, 158.6, 151.5, 148.6, 139.6, 138.0, 137.6, 137.5, 137.4, 137.2, 137.0, 136.6, 132.0, 131.6, 131.0, 130.7, 130.0, 129.4, 128.8, 128.2, 128.1, 128.0, 127.7, 127.54, 127.50, 126.3, 125.8, 125.6, 122.8, 121.5, 118.6, 50.4, 47.9, 44.1, 38.0, 35.8, 31.5, 29.6, 29.3, 26.2, 25.7, 21.5, 13.8; IR (Neat) ν_{max} 3338, 2921, 2853, 1719, 1607, 1580, 1494, 1441, 1376, 1247, 1205, 1053, 897 cm^{-1}; **HRMS (ESI)** for $C_{54}H_{44}NO_3S$ $(M+H)^+$: calcd. 786.3036; found: 786.3047.

Synthesis of 8k:



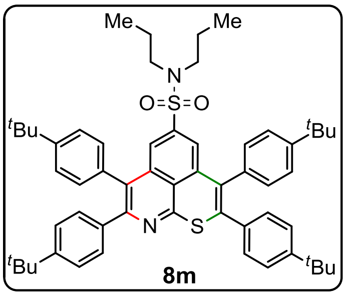
8k (201 mg, 70%); yellow solid. mp = 181–182 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (bd, J = 1.0 Hz, 1H), 7.41–7.28 (m, 8H), 7.25–7.16 (m, 11H), 7.15 (d, J = 7.0 Hz, 2H), 4.77–4.67 (m, 1H), 3.67 (s, 3H), 2.41–2.32 (m, 1H), 2.30–2.19 (m, 1H), 1.99 (bd, J = 11.0 Hz, 1H), 1.93–1.49 (m, 9H), 1.46–1.08 (m, 16H), 0.94 (d, J = 6.5 Hz, 3H), 0.91 (s, 3H), 0.66 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.7, 165.4, 158.5, 151.3, 139.7, 137.5, 137.3, 137.1, 137.0, 136.8, 136.7, 133.0, 132.1, 131.1, 130.8, 130.0, 129.4, 128.69, 128.66, 128.15, 128.08, 127.9, 127.6, 127.5, 127.4, 125.4, 125.0, 122.8, 75.6, 56.6, 56.2, 51.4, 42.7, 41.7, 40.4, 40.2, 35.7, 35.4, 34.9, 34.5, 31.9, 31.1, 31.0, 28.2, 26.9, 26.3, 26.2, 24.2, 23.3, 20.8, 18.3, 12.0; IR (Neat) ν_{max} 2926, 2852, 1718, 1610, 1531, 1451, 1381, 1321, 1214, 1166, 1124, 991, 908 cm^{-1}; **HRMS (ESI)** for $C_{61}H_{64}NO_4S$ $(M+H)^+$: calcd. 906.4551, found 906.4551.

2,3,7,8-Tetraphenyl-*N,N*-dipropylthiopyrano[4,3,2-ij]isoquinoline-5-sulfonamide (8l):



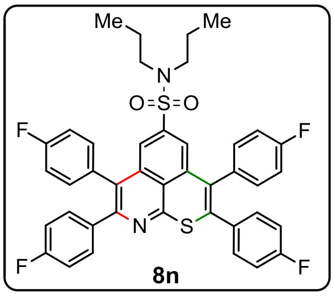
8l (142 mg, 60%); yellow crystalline solid. mp = 270–271 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (bs, 1H), 7.41–7.27 (m, 7H), 7.25–7.14 (m, 11H), 7.11 (d, J = 8.0 Hz, 2H), 7.05 (bs, 1H), 2.85 (bt, J = 7.75 Hz, 4H), 1.37 (bq, J = 7.5 Hz, 4H), 0.76 (t, J = 7.25 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.5, 151.9, 142.8, 139.4, 138.4, 138.2, 137.9, 136.9, 136.7, 136.4, 131.7, 130.8, 130.6, 130.0, 129.3, 129.0, 128.9, 128.4, 128.1, 127.9, 127.7, 127.65, 127.62, 124.7, 121.9, 119.4, 49.8, 21.7, 11.1; IR (Neat) ν_{max} 3056, 2925, 1555, 1531, 1487, 1457, 1364, 1305, 1148, 1107, 1073, 987 cm^{-1}; **HRMS (ESI)** for $C_{41}H_{36}N_2NaO_2S_2$ $(M+Na)^+$: calcd. 675.2110, found 675.2125.

2,3,7,8-Tetrakis(4-(tert-butyl)phenyl)-N,N-dipropylthiopyrano[4,3,2-ij]isoquinoline-5-sulfonamide (8m):



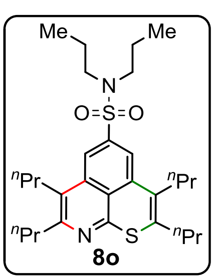
8m (104 mg, 40%); yellow crystalline solid. mp = 337–338 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (bd, J = 1.5 Hz, 1H), 7.38 (d, J = 8.0 Hz, 2H), 7.30–7.22 (m, 4H), 7.21–7.14 (m, 4H), 7.13–7.05 (m, 5H), 7.00 (d, J = 8.0 Hz, 2H), 2.88 (t, J = 7.75 Hz, 4H), 1.40 (bq, J = 7.5 Hz, 4H), 1.35 (s, 9H), 1.27 (s, 9H), 1.26 (s, 9H), 1.23 (s, 9H), 0.77 (t, J = 7.5 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.3, 151.9, 151.5, 150.6, 150.43, 150.38, 142.6, 138.5, 138.2, 138.0, 136.6, 134.1, 134.0, 133.5, 131.6, 130.5, 130.3, 129.6, 128.9, 127.6, 125.7, 125.5, 124.7, 124.6, 124.4, 121.7, 118.9, 49.9, 34.6, 34.5, 34.4, 31.3, 31.20, 31.18, 31.1, 21.8, 11.1; IR (Neat) ν_{max} 2958, 2867, 1590, 1549, 1500, 1461, 1362, 1343, 1326, 1266, 1188, 1152, 1056, 1017, 986 cm^{-1}; **HRMS (ESI)** for $C_{57}H_{69}N_2O_2S_2$ $(M+H)^+$: calcd. 877.4795, found 877.4800.

2,3,7,8-Tetrakis(4-fluorophenyl)-N,N-dipropylthiopyrano[4,3,2-ij]isoquinoline-5-sulfonamide (8n):



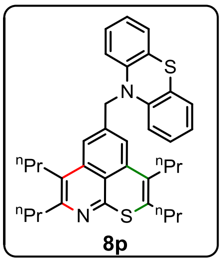
8n (174 mg, 80%); yellow crystalline solid. mp = 247–248 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (bd, J = 1.5 Hz, 1H), 7.31–7.25 (m, 2H), 7.18–7.00 (m, 11H), 6.95–6.87 (m, 4H), 2.87 (bt, J = 7.75 Hz, 4H), 1.42–1.32 (m, 4H), 0.76 (t, J = 7.75 Hz, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 163.4, 163.34, 163.31, 163.1, 161.42, 161.37, 161.34, 161.1, 158.5, 151.2, 143.2, 138.2, 137.9, 137.8, 135.2, 135.1, 132.8, 132.5, 132.4, 132.3, 132.2, 132.04, 132.01, 131.8, 131.7, 131.2, 131.1, 127.5, 126.8, 124.6, 121.8, 119.4, 116.43, 116.41, 116.3, 116.2, 115.6, 115.4, 114.9, 114.7, 49.6, 21.6, 11.0 cm^{-1}; (*The ^{13}C NMR is complex due to the presence of four F-atoms on the periphery of arene moiety; it is therefore difficult to assign the corresponding peaks of ^{13}C-attached to the fluorine-bearing arenes. Hence, complete list of the representative peaks of ^{13}C is shown*); ^{19}F NMR (376 MHz, $CDCl_3$) δ −111.55, −112.93, −112.96, −113.52; IR (Neat) ν_{max} 2970, 2922, 2859, 1595, 1500, 1342, 1222, 1155, 1095, 1010, 988, 833 cm^{-1}; **HRMS (ESI)** for $C_{41}H_{33}F_4N_2O_2S_2$ $(M+H)^+$: calcd. 725.1914, found 725.1915.

***N,N*,2,3,7,8-Hexapropylthiopyrano[4,3,2-ij]isoquinoline-5-sulfonamide (8o):**



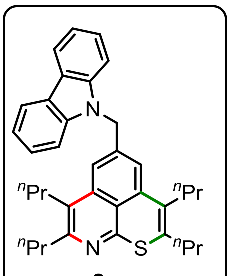
8o (114 mg, 73%); yellow crystalline solid. mp = 95–96 °C; ^{1}H NMR (126 MHz, $CDCl_3$) δ 7.93 (bd, J = 1.0 Hz, 1H), 7.45 (bd, J = 1.0 Hz, 1H), 3.12 (t, J = 7.75 Hz, 4H), 2.83 (t, J = 8.0 Hz, 2H), 2.78 (t, J = 7.75 Hz, 2H), 2.61 (t, J = 8.0 Hz, 2H), 2.50 (t, J = 8.0 Hz, 2H), 1.79–1.65 (m, 4H), 1.63–1.51 (m, 8H), 1.09–0.97 (m, 11H), 0.91–0.84 (m, 7H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 155.8, 154.4, 141.9, 137.5, 137.2, 137.0, 127.1, 124.9, 124.7, 119.0, 114.9, 50.2, 36.3, 30.9, 29.7, 23.2, 23.04, 22.98, 22.1, 21.2, 14.3, 14.23, 14.22, 13.9, 11.1; IR (Neat) ν_{max} 2956, 2927, 1603, 1568, 1463, 1366, 1341, 1231, 1159, 1134, 1036, 993 cm^{-1}; **HRMS (ESI)** for $C_{29}H_{45}N_2O_2S_2$ $(M+H)^+$: calcd. 517.2917, found 517.2927.

<u>Synthesis of 8p:</u>



8p (122 mg, 72%); pale yellow crystalline solid. mp = 166–168 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.15 (bd, J = 1.0 Hz, 1H), 7.14–7.11 (m, 2H), 7.03–6.95 (m, 2H), 6.88 (td, J = 7.5 & 1.0 Hz, 2H), 6.69 (dd, J = 8.0 & 0.5 Hz, 2H), 5.19 (s, 2H), 2.72 (t, J = 7.25 Hz, 2H), 2.67 (t, J = 8.25 Hz, 2H), 2.44 (q, J = 8.0 Hz, 4H), 1.74–1.62 (m, 4H), 1.42–1.29 (m, 4H), 1.04–0.97 (m, 6H), 0.93 (t, J = 7.25 Hz, 3H), 0.89 (t, J = 7.25 Hz, 3H); $^{13}C\{^1H\}$ NMR (126MHz, $CDCl_3$) δ 155.5, 153.0, 144.5, 139.1, 137.4, 136.4, 135.3, 127.4, 127.2, 127.0, 123.8, 123.6, 123.2, 122.7, 117.7, 117.0, 115.6, 52.6, 37.0, 36.2, 31.0, 29.9, 23.3, 23.0, 22.8, 21.2, 14.4, 14.23, 14.20, 14.0; IR (Neat) ν_{max} 2953, 2924, 2866, 2360, 1745, 1612, 1544, 1460, 1441, 1358, 1252, 1211, 1005, 863, 739; cm^{-1}; **HRMS (ESI)** for $C_{36}H_{41}N_2S_2$ $(M+H)^+$: calcd. 565.2706; found: 565.2707.

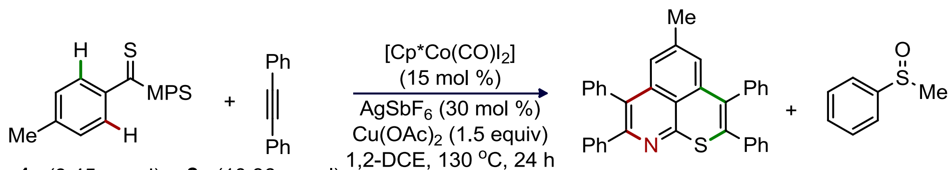
Synthesis of 8q:



8q

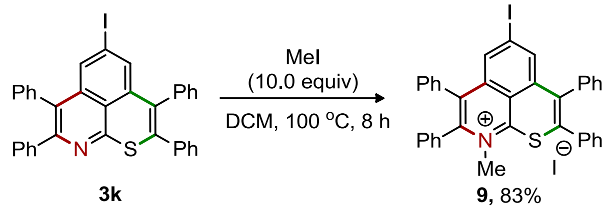
8q (135 mg, 85%); pale yellow crystalline solid. mp = 184–186 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, J = 7.5 Hz, 2H), 7.43 (td, J = 8.5 & 1.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.27(bd, J = 1.0 Hz, 1H), 7.24 (bd, J = 1.0 Hz, 1H), 7.12 (s, 1H), 6.78 (s, 1H), 5.64 (s, 2H), 2.69 (t, J = 7.75 Hz, 2H), 2.54 (t, J = 8.0 Hz, 2H), 2.37 (t, J = 7.75 Hz, 2H), 2.23 (t, J = 8.0 Hz, 2H), 1.70–1.56 (m, 4H), 1.37–1.30 (m, 2H), 1.20–1.12 (m, 2H), 0.96 (t, J = 7.25 Hz, 6H), 0.83 (t, J = 7.25 Hz, 3H), 0.69 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (126MHz, $CDCl_3$) δ 155.5, 140.5, 137.3, 136.5, 135.2, 127.3, 125.9, 123.7, 123.1, 123.0, 120.4, 119.4, 117.0, 116.5, 108.7, 46.7, 36.1, 30.9, 29.8, 23.34, 23.0, 22.5, 20.9, 14.25, 14.20, 14.0, 13.9; IR (Neat) ν_{max} 2952, 2925, 2867, 1730, 1610, 1568, 1484, 1323, 1259, 1207, 1151, 981, 887 cm^{-1}; **HRMS (ESI)** for $C_{36}H_{41}N_2S$ $(M+H)^+$: calcd. 533.2985; found: 533.2997.

General procedure for the gram scale synthesis of 3a:

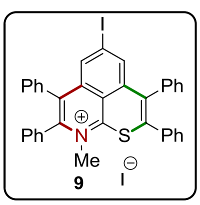


The gram scale reaction was carried out in a 50 mL screw capped tube. The tube was independently charged with *N*-[4-methylbenzothioyl]-S-methyl-S-phenylsulfoximine (**1a**, 1.00 gram, 3.45 mmol), diphenylacetylene (**2a**, 1.85 gram, 10.36 mmol), [Cp*Co(CO)I_2] (0.25 g, 15 mol %), and $Cu(OAc)_2$ (0.94 g, 5.18 mmol). Subsequently, $AgSbF_6$ (0.35 g, 30 mol %) was introduced in to the tube in a glove box. Freshly prepared 1,2-DCE (20.0 mL) was added to the mixture and the resulting mixture was stirred at 130 °C for 24 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite and then washed with dichloromethane (3 × 20 mL). The solvents were evaporated under reduced pressure and the crude material was purified using column chromatography on neutral aluminia (5–10% *n*-hexane/EtOAc eluent). The **3a** (1.6 g) in 84% yield was isolated along with the isolation of phenyl methyl sulfoxide 51% yield.

Synthesis of compound 9:

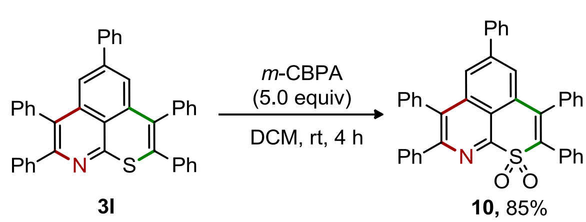


To a solution of **3k** (100 mg, 0.162 mmol) in dry CH_2Cl_2 (1.5 mL) was added MeI (10.0 equiv, 1.62 mmol) under an argon atmosphere. The resulting mixture was stirred at room temperature for 12 hours. The reaction progress was monitored by TLC. Upon completion of the reaction, the crude mixture was concentrated under reduced pressure. The crude residue was washed three times with hexane/ethyl acetate (2:1, 3 × 5 mL). The compound **9** was obtained 102 mg in 83% yield as brown colour solid.

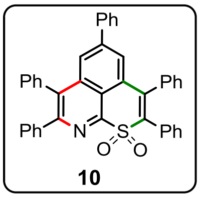


9 (102 mg, 83%); brown colour solid. mp = >350 °C; ^{1}H NMR (400 MHz, DMSO-d6) δ 7.57 (bd, J = 1.2 Hz, 1H), 7.50 (bd, J = 1.6 Hz, 1H), 7.47 (bd, J = 6.8 Hz, 2H), 7.44–7.38 (m, 13H), 7.37–7.29 (m, 3H), 7.21 (d, J = 8.5 Hz, 2H), 3.71 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, DMSO-d6) δ 157.2, 144.4, 135.4, 134.7, 132.9, 132.6, 132.4, 132.2, 132.0, 131.5, 130.7, 129.7, 128.5, 128.2, 128.0, 127.95, 127.89, 127.8, 127.3, 127.0, 126.6, 120.6, 41.5; IR (Neat) ν_{max} 1620, 1591, 1553, 1518, 1483, 1445, 1407, 1343, 1229, 1156, 1114, 1070 cm^{-1}; **HRMS (ESI)** for $C_{36}H_{25}INS$ (M-I)$^+$: calcd. 630.0747, found 630.0750.

2,3,5,7,8-pentaphenylthiopyrano[4,3,2-ij]isoquinoline 1,1-dioxide (10):

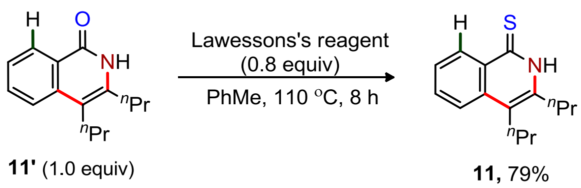


To a solution of **3l** (100 mg, 0.176 mmol) in dry CH_2Cl_2 (1.5 mL) was added *m*-CBPA (5.0 equiv, 0.88 mmol) under an argon atmosphere. The resulting mixture was stirred at room temperature for 4 hours. The reaction progress was monitored by TLC. Upon completion of the reaction, the crude mixture was concentrated under reduced pressure. The crude residue was purified using column chromatography on silica gel eluting with hexane:ethyl acetate (3:2) to afford **10** (89 mg) in 85% yield as colorless crystalline solid.



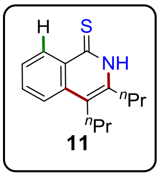
10 (89 mg, 85%); colorless crystalline solid. mp = >350 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (bd, J = 1.5 Hz, 1H), 7.59 (bd, J = 1.5 Hz, 1H), 7.54–7.49 (m, 2H), 7.48–7.42 (m, 5H), 7.39–7.35 (m, 3H), 7.34–7.29 (m, 7H), 7.28–7.22 (m, 8H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.3, 152.0, 143.5, 141.7, 139.9, 139.0, 138.6, 137.3, 136.0, 135.6, 135.3, 131.9, 131.8, 131.0, 130.6, 130.0, 129.1, 128.9, 128.7, 128.7, 128.32, 128.28, 128.05, 127.99, 127.7, 127.3, 125.8, 118.5; IR (Neat) ν_{max} 1577, 1440, 1301, 1378, 1141, 1117, 1070, 1025, 911 cm^{-1}; **HRMS (ESI)** for $C_{41}H_{28}NO_2S$ $(M+H)^+$: calcd. 598.1835, found 598.1843.

Synthesis of 3,4-dipropylisoquinoline-1(2H)-thione (11):[4a]



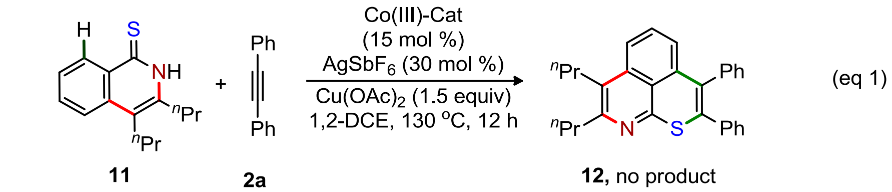
The oven dried sealed tube was charged with **11′** (0.5 g, 1.0 equiv) and Lawesson’s reagent (0.8 equiv). The reaction tube was evacuated several times and purged with nitrogen followed by dry toluene (15 mL) was added and the resulting mixture was stirred at 110 °C for 8 h until complete consumption of **11'**. Progress of the reaction was monitored by TLC. The reaction mixture was then cooled to room temperature until the formation of lighte yellow solid precipitate. Yellow precipitate was filtered and washed three times with hexane/ethyl acetate (1:1, 3 × 20 mL). The compound **11** was obtained 0.42 g in 79% yield as light yellow solid. The compound **11** was stored under inert conditions at −20 °C.

3,4-dipropylisoquinoline-1(2H)-thione (11):



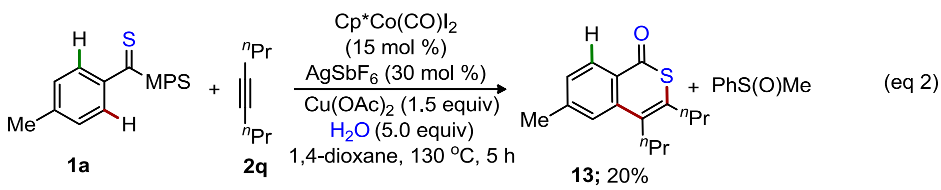
11 (420 mg, 79%); lighte yellow crystalline solid. ^{1}H NMR (400 MHz, DMSO-d6) δ 13.07 (bs, 1H), 8.84 (dd, J = 8.0 & 0.8 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.82–7.74 (m, 1H), 7.58–7.50 (m, 1H), 2.72 (q, J = 7.6 Hz, 4H), 1.66–1.45 (m, 4H), 1.09–0.96 (m, 6H); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d6) δ 181.1, 141.4, 134.5, 133.4, 131.71, 131.70, 127.1, 124.1, 119.4, 31.8, 28.4, 23.8, 23.6, 14.5, 14.1; IR (Neat) ν_{max} 2952, 2862, 1620, 1572, 1468, 1249, 1232, 1151, 992 cm^{-1}; **HRMS (ESI)** for $C_{15}H_{20}NS$ $(M+H)^+$: calcd. 246.1311, found 246.1311.

Annulation of 3,4-dipropylisoquinoline-1(2H)-thione (11) with diphenylacetylene (2a, eq 1):



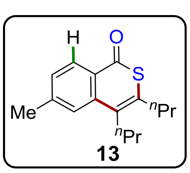
The oven dried 15 mL screw capped tube was charged with thioamide (**11**, 0.3 mmol), diphenylacetylene (**2a**, 0.6 mmol), Cp*Co(CO)I_2 (15 mol %), and Cu(OAc)$_2$ (1.5 equiv). Subsequently, $AgSbF_6$ (30 mol %) was introduced in to the tube in glove box. Dry 1,2-dichloroethane (2.0 mL) was added to the tube under nitrogen atmosphere and the resulting mixture was stirred at 130 °C for 12 h. The product **12** was not obtained.

Synthesis of 6-methyl-3,4-dipropyl-1H-isothiochromen-1-one (13, eq 2):



A mixture of *N*-[4-methylbenzothioyl]-S-methyl-S-phenylsulfoximine (**1a**, 0.3 mmol), 4-octyne (**2q**, 0.9 mmol), and Cp*Co(CO)I_2 (21 mg, 15 mol%) was taken in a 15 mL screw capped tube. Subsequently, $AgSbF_6$ (31 mg, 30 mol%) was introduced in to the tube in a glove box. The solvent 1,4-dioxane (2.0 mL) and H_2O (27 μL, 5.0 equiv) were added to the mixture and the resulting mixture was stirred at 130 °C in a heating block for 5 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite, and then washed with dichloromethane (3 × 10 mL). The solvents were evaporated under reduced pressure and the crude material was purified by flash chromatography on silica gel (5−10% *n*-hexane/EtOAc eluent) to afford the product **13**. The compound **13** was obtained 16 mg in 20% yield as colour less solid.

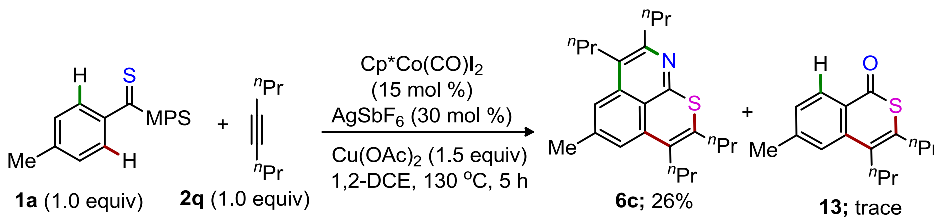
6-Methyl-3,4-dipropyl-1H-isothiochromen-1-one (13):



13 (16 mg, 20%); colorless solid. mp = 106–107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.0 Hz, 1H), 7.56 (s, 1H), 7.31 (d, J = 8.5 Hz, 1H), 2.79 (t, J = 8.0 Hz, 2H), 2.62 (t, J = 8.0 Hz, 2H), 2.50 (s, 3H), 1.73–1.65 (m, 2H), 1.64–1.58 (m, 2H), 1.08 (t, J = 7.25 Hz, 3H), 1.02 (t, J = 7.25 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz,

$CDCl_3$) δ 187.3, 144.3, 138.7, 136.8, 128.4, 126.9, 126.8, 126.3, 126.2, 36.6, 30.9, 23.6, 23.2, 22.3, 14.3, 13.9; IR (Neat) ν_{max} 2954, 2925, 2861, 1714, 1621, 1603, 1574, 1545, 1472, 1456, 1377, 1329, 1278, 1261, 1228, 1211, 1139, 1087, 1035, 973, 887 cm^{-1}; **HRMS (ESI)** for $C_{16}H_{21}OS$ $(M+H)^+$: calcd. 261.1308, found 261.1310.

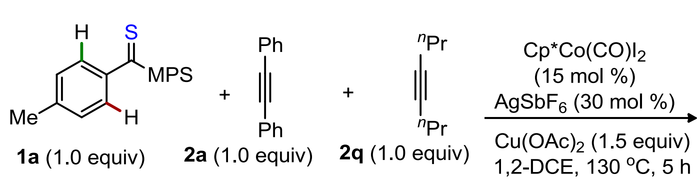
Reaction of 1a with 2q (eq 3):



(eq 3)

A mixture of *N*-[4-methylbenzothioyl]-S-methyl-S-phenylsulfoximine (**1a**, 0.3 mmol), 4-octyne (**2q**, 0.3 mmol), and $Cp^*Co(CO)I_2$ (21 mg, 15 mol%) was taken in a 15 mL screw capped tube. Subsequently, $AgSbF_6$ (31 mg, 30 mol%) was introduced into the tube in a glove box. The solvent 1,2-DCE (2.0 mL) was added to the mixture and the resulting mixture was stirred at 130 °C in a heating block for 5 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite, and then washed with dichloromethane (3 × 10 mL). The solvents were evaporated under reduced pressure and the crude material was purified by flash chromatography on silica gel (5−10% *n*-hexane/EtOAc eluent) to afford the product **6c** and **13**. The compound **6c** was obtained in 26% yield as yellow colour solid along with trace amount of product **13**.

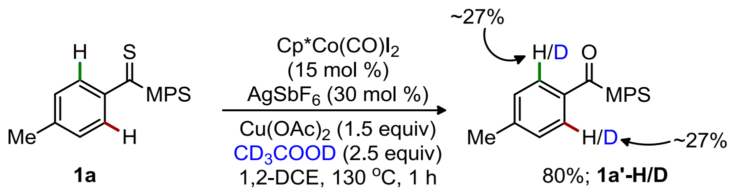
Reaction of 1a with 2a and 2q (eq 4):



(eq 4)

A mixture of *N*-[4-methylbenzothioyl]-S-methyl-S-phenylsulfoximine (**1a**, 0.3 mmol), 4-octyne (**2q**, 0.3 mmol), diphenylacetylene (**2a**, 0.3 mmol), and $Cp^*Co(CO)I_2$ (21 mg, 15 mol%) was taken in a 15 mL screw capped tube. Subsequently, $AgSbF_6$ (31 mg, 30 mol%) was introduced in to the tube in a glove box. The solvent 1,2-DCE (2.0 mL) was added to the mixture and the resulting mixture was stirred at 130 °C in a heating block for 5 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite, and then washed with dichloromethane (3 × 10 mL). The solvents were evaporated under reduced pressure and the purification of the crude material proved highly difficult due to the formation of a mixture of products.

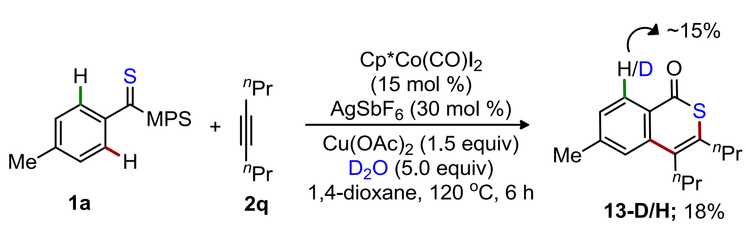
Deuterium labelling experiment-1 (eq 5):



(eq 5)

A mixture of *N*-[4-methylbenzothioyl]-S-methyl-S-phenylsulfoximine (**1a**, 0.3 mmol), $Cp^*Co(CO)I_2$ (21 mg, 15 mol%), and $Cu(OAc)_2$ (81 mg, 0.45 mmol) was taken in a 15 mL screw capped tube. Subsequently, $AgSbF_6$ (31 mg, 30 mol %) was introduced in to the tube in a glove box. The solvent 1,2-dichloroethane (2.0 mL) and CD_3COOD (48 µL, 2.5 equiv) were added to the mixture and the resulting mixture was stirred at 130 °C in a heating block for 1 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite and then washed with dichloromethane (3 × 10 mL). The solvents were evaporated under reduced pressure to give the desired *o*-deuterium incorporated product **1'a-H/D** with 33% D-incorporation in both the *ortho*-H of **1'a**.

Deuterium labelling experiment-2 (eq 6):

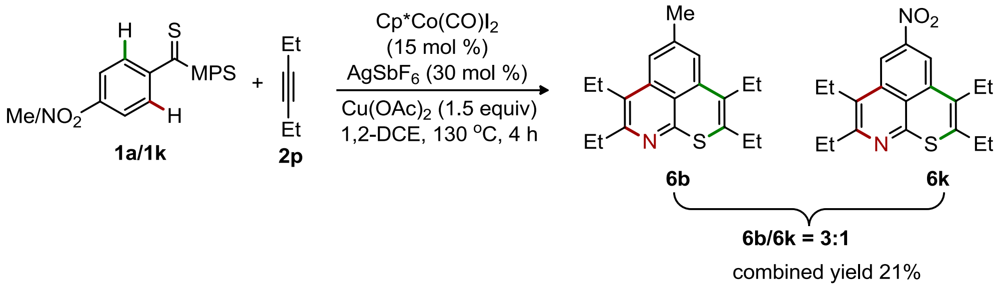


(eq 6)

A mixture of *N*-[4-methylbenzothioyl]-S-methyl-S-phenylsulfoximine (**1a**, 0.3 mmol), 4-octyne (**2q**, 0.9 mmol), and $Cp^*Co(CO)I_2$ (21 mg, 15.0 mol%) was taken in a 15 mL screw capped tube. Subsequently, $AgSbF_6$ (31 mg, 30 mol%) was introduced in to the tube in a glove box. The solvent 1,4-dioxane (2.0 mL) and D_2O (27 µL, 5.0 equiv) were added to the mixture and the resulting mixture was stirred at 130 °C in a heating block for 6 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite and then washed with dichloromethane (3 × 10 mL). The solvents were evaporated under reduced pressure and the crude material was purified using column chromatography on silica gel (5−10% *n*-hexane/EtOAc eluent) to give **13-D/H** (14 mg, 18%) with 15% deuterium incorporation in the *peri*-C–H bond of isothiochromenone.

Competition experiments:

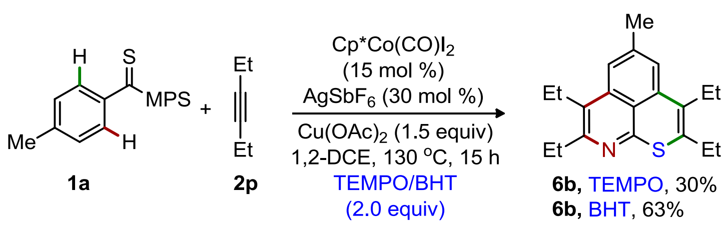
Competition experiment between **1a** *and* **1k** with **2m** (eq 7):



(eq 7)

The competition experiment was carried out in a 15 mL screw capped tube. The tube was charged with **1a** (0.3 mmol), **1k** (0.3 mmol), 3-hexyne (**2p**, 0.9 mmol), Cp*Co(CO)I_2 (21 mg, 10 mol %), and $Cu(OAc)_2$ (85 mg, 0.45 mmol). Subsequently, $AgSbF_6$ (31 mg, 30 mol %) was introduced in to the tube in a glove box. The solvent 1,2-dichloroethane (2.0 mL) (2.0 mL) was added to the mixture and the resulting mixture was stirred at 130 °C in a heating block for 4 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite and then washed with dichloromethane (3 × 10 mL). The solvents were evaporated under reduced pressure and the crude material was purified using column chromatography on neutral aluminia (5−10% *n*-hexane/EtOAc eluent) to provide a mixture of the desired products **6b** and **6k** (42 mg) as red solid. Based on the ^{1}H NMR spectrum, the respective compounds **6b** and **6k** (~3:1) were formed as inseparable mixture.

Reaction in presence of TEMPO/BHT (eq 8)



(eq 8)

The annulation reactions were carried out in a 15 mL screw capped tube. The tube was independently charged with *N*-[4-methylbenzothioyl]-S-methyl-S-phenylsulfoximine (**1a**, 3.0 mmol), 3-hexyne (**2p**, 9.0 mmol), Cp*Co(CO)I_2 (21 mg, 10 mol %), TEMPO/BHT (2.0 equiv), and $Cu(OAc)_2$ (85 mg, 0.45 mmol). Subsequently, $AgSbF_6$ (31 mg, 30 mol %) was introduced in to the tube in a glove box. The solvent 1,2-dichloroethane (2.0 mL) was added to the mixture and the resulting mixture was stirred at 130 °C for 15 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite and then washed with dichloromethane (3 × 20 mL). The solvents were evaporated under reduced pressure and the crude material was purified using column chromatography on neutral alumina (5−10% *n*-hexane/EtOAc eluent). The desired product **6b** was isolated in 30% yield (when conducted in presence of TEMPO) and 63% yield (when conducted in presence of BHT).

Photophysical Properties

UV-Vis and fluorescence Spectra of the represented thiopyrano-isoquinoline derivatives were recorded in dichloromethane solvent with a fixed concentration of 10^{-5} M.

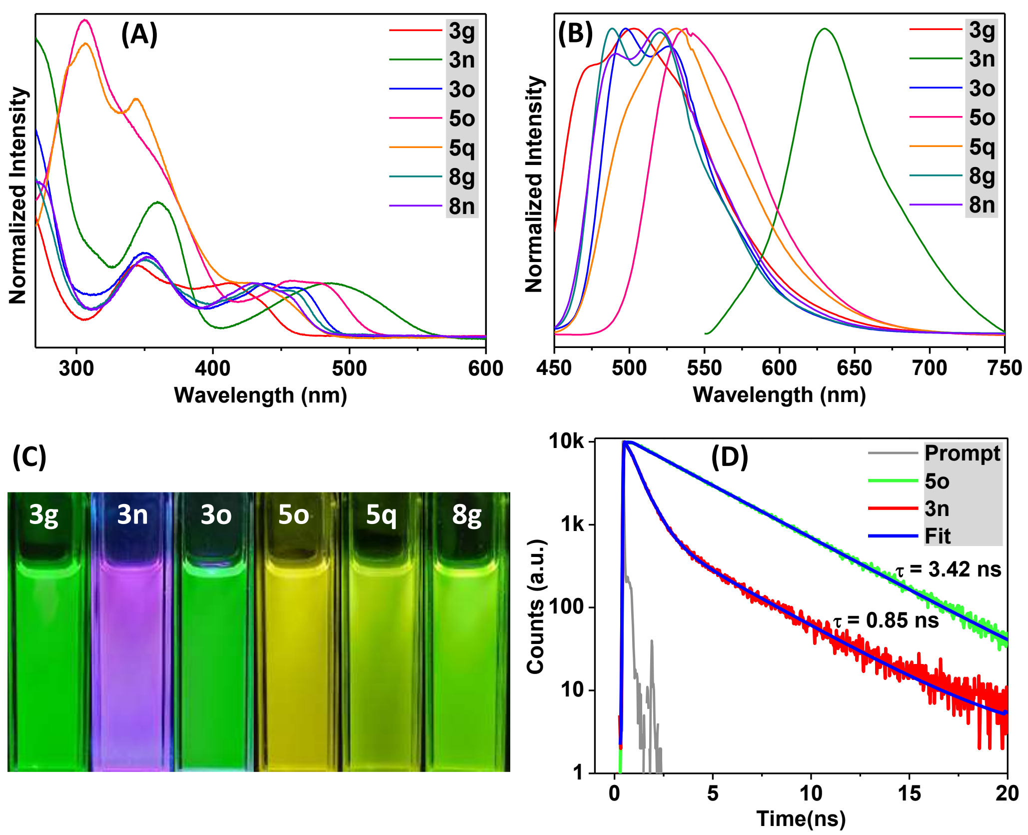


Figure S3: Normalized absorption (A) and fluorescence (B) spectra in DCM at RT; (10^{-5} M); Observer fluorescence under UV excitation (365 nm); (C); Life time measurements (D).

Table S2: **Absorpotion, Emission Maxima and Stokes Shifts**

Compounds	**λ_{ab}(nm)**	**λ_{fl}(nm)**	**λ_{ss}(nm)**
3g	412/344	503	91
3o	438/350	526	88
3n	486/360	630	144

8g	433/351	520	87
5p	457/360	538	81
5q	429/344	531	102
8n	431/354	520	89

X-ray crystallography: Single crystal X-ray data for the compound **3o**, **5f**, and **5h** were collected using the Bruker D8 Quest CMOS detector system [λ(Mo-Kα) = 0.71073 Å] at 298K, graphite monochromator with a ω scan width of 0.3°, crystal-detector distance 60 mm, collimator 0.5 mm. The SMART softwar[5] was used for the intensity data acquisition and the SAINTPLUS Software[5] was used for the data extraction. In each case, absorption correction was performed with the help of SADABS program,[5] an empirical absorption correction using equivalent reflections was performed with the program. The structure was solved using SHELXS-97,[6] and full-matrix least-squares refinement against F^2 was carried out using SHELXL-97.[6] All non-hydrogen atoms were refined anisotropically. Aromatic and methyl hydrogens were introduced on calculated positions and included in the refinement riding on their respective parent atoms.

X-ray crystal structure and data for 3s, 5h and 5l

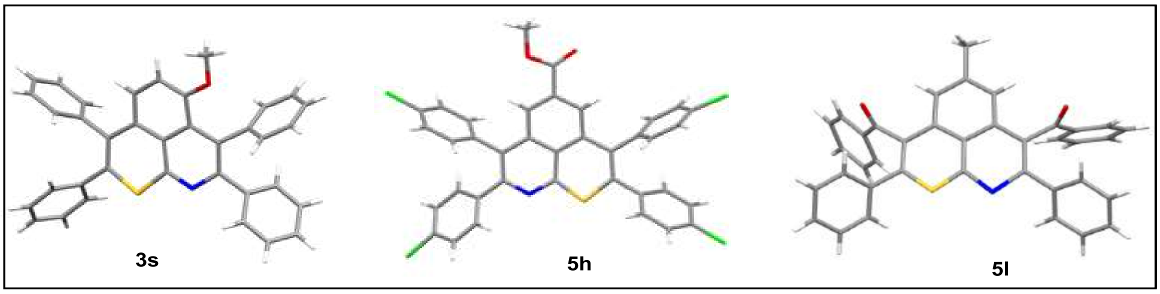


Figure S4. Thermal ellipsoidal plot of compound **3s, 5h**, and **5l** with atom labeling scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius**.**

Table S3. Crystal data for 3s, 5h, **and 5l**

Identification code	**3s**	**5h**	**5l**
Formula	$C_{36}H_{25}NOS$	$C_{37}H_{21}Cl_4NO_2S$	$C_{38}H_{25}N_{1.75}O_2S$
F_w	519.63	685.41	570.16
T (K)	296	298	306
λ (Å)	0.71073	0.71073	0.71073

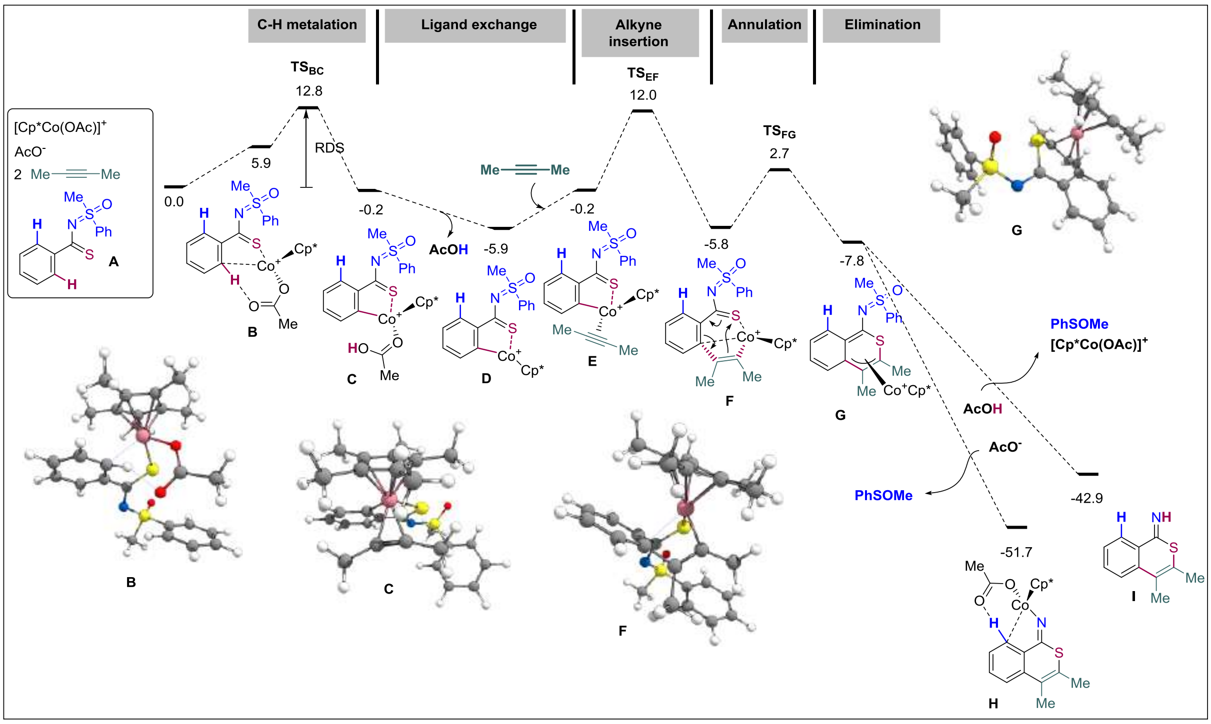
Crystal system	monoclinic	triclinic	triclinic
Space group	*P 21/c*	*P -1*	*P -1*
a(Å)	13.5770(4)	9.0387(7)	9.3410(2)
b (Å)	9.7186(3)	12.2872(11)	11.8743(2)
c (Å)	21.3735(8)	15.4499(13)	14.2000(2)
α (°)	90	70.572(4)	103.803(1)
β (°)	102.957(1)	83.642(3)	92.000(2)
γ(°)	90	86.486(4)	108.233(2)
V (Å^3)	2748.41(16)	1607.7(2)	1442.47(5)
Z	4	2	2
ρ_{calcd} (Mg m^{-3})	1.256	1.416	1.313
μ [mm^{-1}]	0.148	0.469	0.150
total reflns	18167	67192	21430
unique reflns	6620	7393	6282
observed reflns	3931	5708	3836
$R_1[I > 2\sigma(I)]$	0.0674	0.0746	0.0855
wR_2 [all]	0.2153	0.2330	0.3122
GOF	1.037	1.030	1.115
Diffractometer	SMART APEX CCD	SMART APEX CCD	SMART APEX CCD
CCDC Number	2045976	2045977	2045975

DFT calculations:

DFT computations were carried out to validate the proposed mechanism. The Gaussian 09 software package was used[7] with its implemented M06 functional,[8] the 6-31G(d,p) basis set[9] for all main group elements, and the LANL2DZ (ECP) basis set[10] for Co. Single point calculations were conducted at the M06/6-311++G(d,p)-SDD(ECP)[11] level of theory. Solvation energies were obtained at the single point level using the SMD approach[12] for 1,2-dichloroethane. The discussed values are solvent-corrected Gibbs free energies at 393.15 K in kcal/mol (ΔG_{393}). The molecular system composed of substrate **A**, 2 equiv of 2-butyne, $[Cp^*Co(OAc)]^+$, and an additional AcO^- to ensure a second deprotonation of **A** with the same Co complex, was used as a reference for the free energies (Scheme 1).

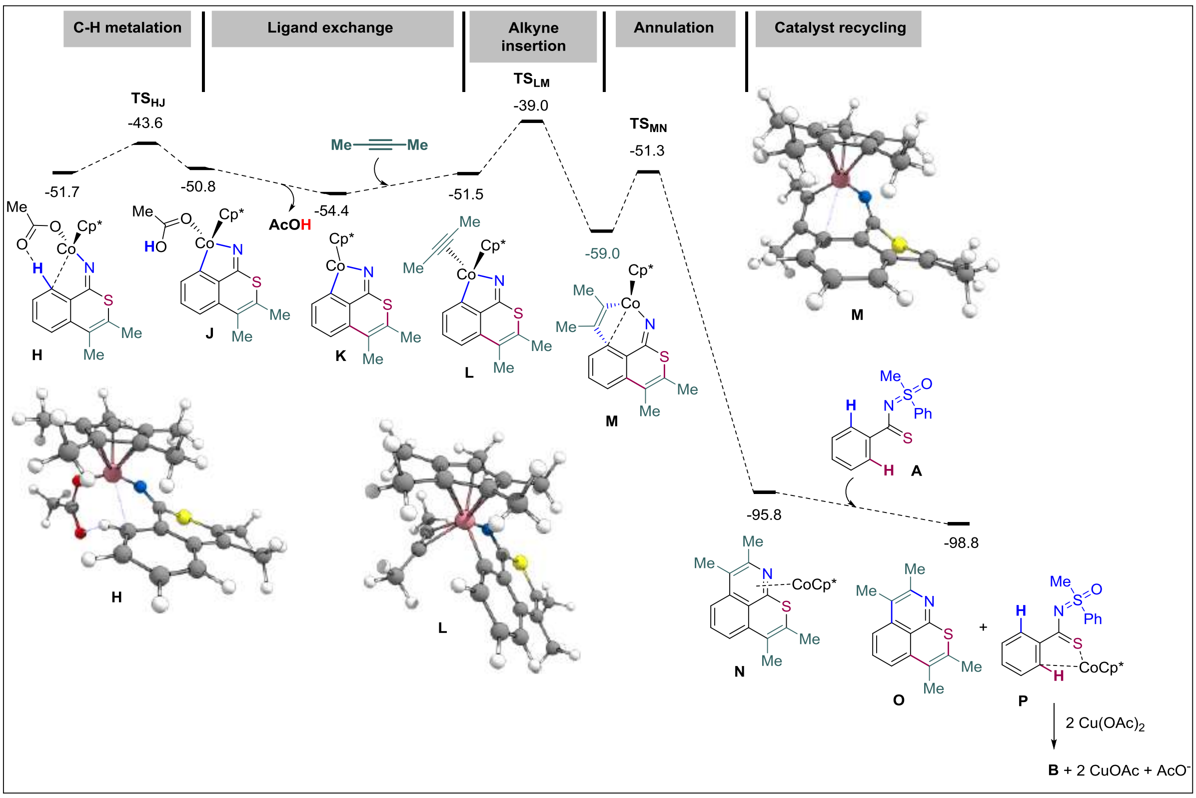
Cp-cobalt(III) complexes can adopt different spin states, i.e. singlet (S), triplet (T) and quintet (Q). In agreement with our previous studies,[13] 16-electrons complexes are more stable in the triplet state. For instance, for complex **D** in Scheme 1, we found $\Delta E_{S\text{-}T}$ = -3.8 kcal/mol and $\Delta E_{S\text{-}Q}$ = 20.0 kcal/mol. On the other hand, 18-electron complexes are usually more stable in singlet state, as it is the case for instance for complex **E**, for which we found $\Delta E_{S\text{-}T}$ = 7.8 kcal/mol and $\Delta E_{S\text{-}Q}$ = 25.9 kcal/mol. Since all major steps involve 18-electron complexes (16-electron species are only involved in dissociative ligand exchanges such as from **C** to **E**), we did not compute the minimum energy crossing points (MECP) of the singlet and triplet energy surfaces.

Coordination of **A** to $[Cp^*Co(OAc)]^+$ gives complex **B**, which is already pre-organized for a concerted metallation-deprotonation process (CMD), as shown by a hydrogen bond with the acetate ligand and a η^1-coordination between Co and the *ipso* carbon, at the expense of 5.9 kcal/mol (-12.1 kcal/mol without solvent effect). C-H metalation then occurs through **TS_{BC}**, lying 12.8 kcal/mol above the reference system. The resulting metallacycle **C** is only 0.2 kcal/mol more stable than **B**. A stepwise ligand exchange between acetic acid and 2-butyne then takes place, leading to the alkyne complex **E**, which was also located at -0.2 kcal/mol on the free energy surface.



Scheme 1. Free energy profile (ΔG_{393}, kcal/mol), part 1 (first annulation).

Alkyne insertion yields the seven-membered complex **F** in which the metal receives electron density from an aryl carbon. This intermediate is formed in an exergonic fashion (-5.8 kcal/mol) through **TS_{EF}** lying at 12.0 kcal/mol. The annulation step can be described as a 6π-electrocyclization to give the π-allyl intermediate **G** at -7.8 kcal/mol. The corresponding transition state, **TS$_{FG}$**, was found as low as 2.8 kcal/mol on the surface. Complex **G** might then react with AcO^- to give species **H** at -51.7 kcal/mol, which is ready for another CMD step, or with AcOH to give compound **I** at -42.9 kcal/mol.[14]

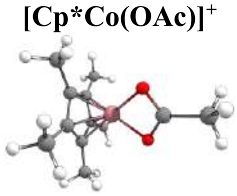


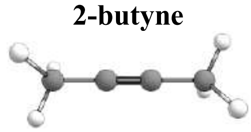
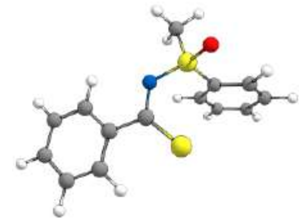
Scheme 2. Free energy profile (ΔG_{393}, kcal/mol), part 2 (second annulation)

The second part of the mechanism is shown in Scheme 2. It starts in a similar fashion, the computed pathway between **H** and the alkyne complex **L** being rather flat. The insertion step requires 12.0 kcal/mol of free energy of activation and is exergonic by 7.5 kcal/mol to provide **M**. The reductive elimination step is achieved through **TS$_{MN}$**, which was found at -51.3 kcal/mol. This irreversible step leads to the experimentally observed tricyclic product with a release of 36.8 kcal/mol. Liberation of the final product **O** by ligand exchange with **A** further lowers the free energy by 3.0 kcal/mol (-98.8 kcal/mol for the reference system in Scheme 1). It is then likely that complex **P** transforms into **B** for a new turn-over by $Cu(OAc)_2$ mediated oxidation.[15]

Density Functional Theory (DFT) Calculations:

Table S4. Coordinates (x,y,z), energies (Hartree) and imaginary frequencies (cm^{-1}) of the computed species.

$[Cp^{*}Co(OAc)]^{+}$  Thermal correction to Gibbs Free Energy= 0.203311 E(RM06) = -763.966307256 E(SCRF) = -764.046700803				**AcO^{-}**  Thermal correction to Gibbs Free Energy= 0.012493 E(RM06) = -228.468666314 E(SCRF) = -228.557009978			
Co	-0.295866	0.000415	-0.203279	O	0.81005	1.099263	-0.000018
O	-1.859548	-1.070374	-0.280903	C	0.219497	-0.00208	0.000075
C	-2.543994	0.009533	-0.371343	O	0.682323	-1.164733	-0.000015
O	-1.854738	1.084007	-0.286552	C	-1.343042	0.062187	0.000025
C	-4.00702	0.004082	-0.558784	H	-1.738991	-0.464279	-0.881793
H	-4.475497	-0.500854	0.292674	H	-1.739344	-0.46759	0.879686
H	-4.25748	-0.58066	-1.449608	H	-1.719382	1.094985	0.001772
H	-4.390496	1.021142	-0.649616				
C	1.553671	-0.737411	-0.674358				
C	1.557066	0.723676	-0.680675				
C	1.171993	1.176262	0.599624				
C	0.872139	0.003796	1.392266				
C	1.164657	-1.177272	0.609176				
C	0.932624	2.573171	1.039587				
H	1.624664	2.84345	1.84619				
H	1.0688	3.287486	0.224794				
H	-0.087442	2.695413	1.422347				
C	0.333353	0.011254	2.768893				
H	1.1639	0.00846	3.48924				
H	-0.265777	0.905403	2.966242				
H	-0.276499	-0.874348	2.971993				
C	0.91649	-2.569032	1.060349				
H	1.049234	-3.290571	0.251369				
H	1.605259	-2.837065	1.87046				
H	-0.105134	-2.682054	1.441714				
C	1.819757	-1.568358	-1.872086				
H	1.562151	-2.617629	-1.712294				
H	1.256599	-1.207897	-2.741214				
H	2.883375	-1.51501	-2.139042				
C	1.83006	1.544051	-1.88391				
H	1.319501	1.141238	-2.76616				
H	1.517809	2.582883	-1.755202				

H	2.904942	1.53783	-2.108159				
2-butyne  Thermal correction to Gibbs Free Energy= 0.045795 E(RM06) = -155.890566811 E(SCRF) = -155.897968660				**A**  Thermal correction to Gibbs Free Energy= 0.170973 E(RM06) = -1467.24063733 E(SCRF) = -1467.26886336			
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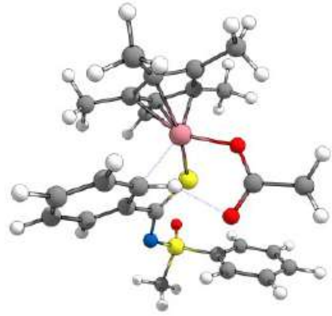
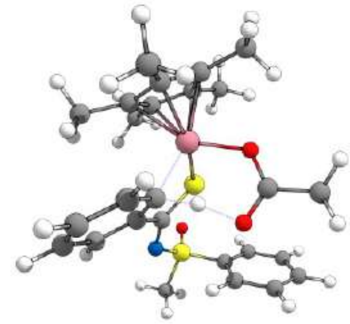
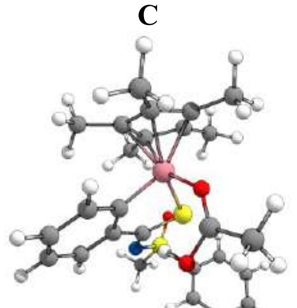
C	0.603933	0.000764	-0.001137	C	3.01645	-0.761669	-0.772949
C	2.058312	-0.000294	0.000358	C	5.081312	0.476807	-0.714544
H	2.462601	0.601976	-0.823881	C	4.51009	1.377178	0.180812
H	2.459783	0.412485	0.935107	C	3.199207	1.207892	0.600134
H	2.459779	-1.01643	-0.108832	C	2.430889	0.137405	0.12847
C	-2.058168	-0.000198	0.000254	C	1.022482	-0.040491	0.568941
H	-2.460639	-0.359948	0.956278	S	0.320436	0.922924	1.739564
H	-2.460605	1.007546	-0.166832	N	0.399058	-1.055634	-0.103485
H	-2.460576	-0.648556	-0.78933	S	-1.116146	-1.384412	0.237098
				O	-1.544768	-1.957378	1.514749
				C	-1.45319	-2.575944	-1.042453
				C	-2.198091	-0.026564	-0.205645
				C	-3.332633	0.180552	0.567264
				C	-4.209448	1.195066	0.199955
				C	-3.941629	1.978426	-0.918387
				C	-2.795262	1.757876	-1.67827
				C	-1.909989	0.74796	-1.324743
				H	6.111492	0.609393	-1.041571
				H	5.091531	2.217923	0.555159
				H	-2.502278	-2.871819	-0.946609
				H	-1.250885	-2.137675	-2.023245
				H	-0.792492	-3.428578	-0.859593
				H	-3.501038	-0.433441	1.449275
				H	-5.100411	1.380794	0.796085
				H	-4.628923	2.774467	-1.198305
				H	-2.583744	2.381513	-2.544303
				H	-0.994595	0.579198	-1.891103
				H	2.426877	-1.598718	-1.137415
				H	4.771	-1.305621	-1.884903
				H	2.745011	1.904307	1.302185
B				**TS$_{BC}$**			

 Thermal correction to Gibbs Free Energy= 0.415026 E(RM06) = -2231.26691649 E(SCRF) = -2231.34690154				 Thermal correction to Gibbs Free Energy= 0.414080 E(RM06) = -2231.25736895 E(SCRF) = -2231.33497869 Frequency -795.5507			
H	-0.807361	0.134419	-1.620748	H	-0.502465	-0.117329	-1.616229
C	-1.10907	1.190213	-1.411965	O	0.251447	-1.17158	-2.170008
C	-2.065672	1.779765	-2.238711	C	-0.992653	0.974524	-1.345484
C	-2.155311	3.165026	-2.330961	C	-1.860139	1.465096	-2.330192
C	-1.269804	3.968422	-1.612383	C	-0.081923	1.882661	-0.75733
C	-0.279771	3.395123	-0.821698	Co	-1.591515	-0.426974	0.155206
H	-1.338228	5.050578	-1.687606	C	-1.872763	2.813257	-2.67134
C	-0.198395	2.006067	-0.714603	H	-2.509283	0.767949	-2.858127
H	-2.898445	3.622384	-2.97929	C	-0.993788	3.697925	-2.044085
H	-2.714008	1.14804	-2.841653	H	-2.552839	3.179466	-3.436918
Co	-1.591072	-0.496388	0.103476	C	-0.078939	3.233882	-1.104834
C	0.859457	1.371371	0.090252	H	-1.004354	4.751694	-2.31095
O	-0.928016	-2.073978	-0.749082	H	0.637081	3.908174	-0.641381
C	-2.382833	-0.01058	1.987378	C	0.917026	1.320221	0.162097
C	-3.689943	-0.371406	0.103639	O	-1.013636	-2.114955	-0.595213
C	0.000302	-2.114762	-1.661656	C	-3.674843	-0.272144	0.061696
O	0.467596	-1.14108	-2.248059	C	-2.472751	-1.129915	1.838588
C	0.500491	-3.512094	-1.934833	S	0.508366	-0.11872	0.977747
H	-0.315831	-4.239019	-1.916558	N	2.081955	1.971731	0.21566
H	1.206864	-3.787255	-1.142735	C	-0.183553	-2.174567	-1.565401
H	1.018548	-3.544615	-2.895526	C	-2.431465	0.310604	1.93109
C	-2.385621	-1.425779	1.68363	C	-3.141913	0.836696	0.822915
C	-3.294588	-1.639243	0.584272	C	-1.790087	1.116102	3.002755
C	-1.685403	-2.505859	2.42265	C	-3.328695	-1.470519	0.739146
C	-3.134032	0.641714	0.983734	C	-4.544195	-0.187834	-1.14312
C	-1.714107	0.649601	3.137549	C	0.291192	-3.54603	-1.949298
C	-3.423079	2.098102	0.932944	H	-0.51385	-4.278136	-1.850583
C	-4.609547	-0.136496	-1.041423	H	1.092662	-3.839649	-1.262168
C	-3.620443	-2.957489	-0.005592	H	0.685318	-3.541225	-2.967276
H	-4.386238	2.300319	1.419604	C	-1.845001	-2.108585	2.765055
H	-2.661479	2.680672	1.459889	C	-3.678561	-2.850569	0.32912
H	-3.484265	2.475799	-0.091851	H	-1.482294	-2.984507	2.216157
H	-5.635343	-0.411286	-0.764138	H	-0.995219	-1.673258	3.299689
H	-4.622012	0.913317	-1.3455	H	-2.56671	-2.45959	3.513973
H	-4.334144	-0.743358	-1.911488	C	-3.407039	2.277476	0.576598

H	-3.981215	-3.644698	0.768541	H	-1.05507	0.540445	3.571376
H	-4.389437	-2.876664	-0.778377	H	-1.281604	1.999174	2.60018
H	-2.716884	-3.392717	-0.452401	H	-2.556454	1.468172	3.705547
H	-1.306908	-3.258938	1.723729	H	-4.376621	2.55005	1.013512
H	-0.836958	-2.121831	2.996981	H	-2.650113	2.916859	1.04038
H	-2.367401	-3.004448	3.123604	H	-3.44377	2.518025	-0.489566
H	-0.920379	0.032181	3.565953	H	-5.584742	-0.422875	-0.885692
H	-1.270968	1.609377	2.852209	H	-4.531683	0.813244	-1.582666
H	-2.452564	0.843364	3.926333	H	-4.228091	-0.900492	-1.914153
S	0.512998	-0.103866	0.862058	H	-4.182976	-3.371904	1.15164
H	0.433159	4.013347	-0.282439	H	-4.343146	-2.859678	-0.538811
N	2.019251	2.030253	0.109441	H	-2.772612	-3.413131	0.074872
S	3.290711	1.396701	0.880957	S	3.336763	1.297266	0.969973
O	3.263394	1.249019	2.334594	O	3.321598	1.072781	2.41365
H	4.603974	2.589049	-0.686203	C	4.615931	2.449417	0.546788
C	4.548264	2.550794	0.404155	C	3.733923	-0.207269	0.104412
H	4.264757	3.522993	0.815411	H	4.675706	2.537032	-0.540365
H	5.487265	2.200702	0.840521	H	4.347155	3.406387	1.001618
C	3.736132	-0.138909	0.102692	H	5.547793	2.065842	0.969946
C	4.382636	-1.07849	0.901922	C	4.353892	-1.213774	0.838493
H	4.566951	-0.869123	1.952928	C	3.404512	-0.3507	-1.241975
C	4.75697	-2.284703	0.322949	H	4.56383	-1.070174	1.895733
H	5.264763	-3.035034	0.922502	C	4.665662	-2.402743	0.189362
C	4.472015	-2.53321	-1.017992	H	5.153329	-3.204021	0.737507
H	4.762697	-3.482133	-1.461742	C	4.341489	-2.569146	-1.154964
H	3.565499	-1.79072	-2.831906	H	4.580604	-3.505444	-1.653209
C	3.810821	-1.583854	-1.794019	C	3.708404	-1.552337	-1.867389
C	3.436952	-0.367315	-1.238151	H	3.435006	-1.695498	-2.909228
H	2.888104	0.362902	-1.828545	H	2.892948	0.443513	-1.782159

C



Thermal correction to Gibbs Free Energy=
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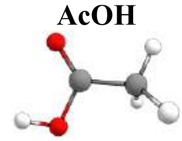
E(RM06) = -2231.28366811
E(SCRF) = -2231.35863210

AcOH



Thermal correction to Gibbs Free Energy=
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E(RM06) = -229.030900998
E(SCRF) = -229.039875448

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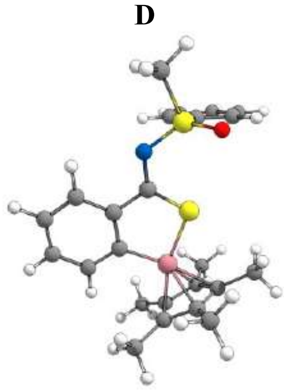
O	-0.704031	-1.038953	-2.920656	O	-0.762292	-1.047155	-0.000002
C	-1.35934	1.141645	-0.977051	C	-0.0925	0.125019	0.000022
C	-2.339091	1.686161	-1.80843	O	-0.653138	1.192221	0
C	-0.109867	1.796737	-0.916617	C	1.38729	-0.099363	0.000019
Co	-1.643737	-0.351294	0.201134	H	1.904989	0.861789	0.000338

C	-2.111306	2.877278	-2.495243	H	1.678354	-0.682237	0.881165
H	-3.303193	1.185088	-1.911313	H	1.678316	-0.681441	-0.881701
C	-0.898861	3.558012	-2.357561				
H	-2.887417	3.287144	-3.138455				
C	0.107884	3.017266	-1.575036				
H	-0.739157	4.496881	-2.880899				
H	1.073653	3.508832	-1.479627				
C	0.953214	1.096781	-0.20477				
O	-2.033676	-1.701622	-1.240247				
C	-3.573255	-0.360057	0.926219				
C	-1.771589	-0.995705	2.236328				
S	0.614582	-0.530101	0.237981				
N	2.101562	1.75222	0.001208				
C	-1.560172	-1.863691	-2.366628				
C	-1.750426	0.448139	2.067259				
C	-2.933258	0.833175	1.357011				
C	-0.801399	1.394855	2.712924				
C	-2.87318	-1.487606	1.520054				
C	-4.807483	-0.480322	0.105869				
C	-1.917427	-3.027843	-3.221583				
H	-2.638557	-3.666305	-2.711276				
H	-1.013205	-3.597782	-3.457052				
H	-2.328873	-2.674459	-4.171939				
C	-0.779317	-1.781605	3.017613				
C	-3.277359	-2.904819	1.333578				
H	-0.661196	-2.796571	2.625025				
H	0.207197	-1.305704	3.015645				
H	-1.102086	-1.863983	4.063231				
C	-3.377707	2.236886	1.151857				
H	0.189699	0.955523	2.865418				
H	-0.676479	2.302337	2.110955				
H	-1.184118	1.705548	3.694272				
H	-3.785413	2.625478	2.094125				
H	-2.550746	2.891536	0.854673				
H	-4.160565	2.321163	0.393251				
H	-5.659535	-0.791725	0.723911				
H	-5.076885	0.468255	-0.36886				
H	-4.685526	-1.231562	-0.682923				
H	-4.242529	-3.094838	1.820132				
H	-3.392686	-3.14015	0.269544				
H	-2.547525	-3.599456	1.758384				
S	3.24267	1.080347	0.917731				
O	2.941371	0.738653	2.308474				
C	4.478144	2.349165	0.856873				
C	3.974491	-0.308422	0.082083				
H	4.744198	2.544953	-0.184284				
H	4.041971	3.238531	1.318903				
H	5.338517	1.993275	1.429019				

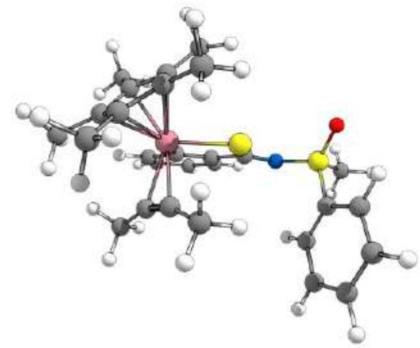
C	4.379735	-1.387146	0.860418
C	4.140033	-0.273227	-1.301008
H	4.209039	-1.376304	1.934009
C	4.98251	-2.466385	0.22405
H	5.307299	-3.322949	0.808093
C	5.164294	-2.449919	-1.155762
H	5.63761	-3.296605	-1.646112
C	4.744094	-1.360631	-1.917529
H	4.884368	-1.360785	-2.994794
H	3.791806	0.577791	-1.883383

D



Thermal correction to Gibbs Free Energy= 0.356758
E(RM06) = -2002.21201071
E(SCRF) = -2002.29234377

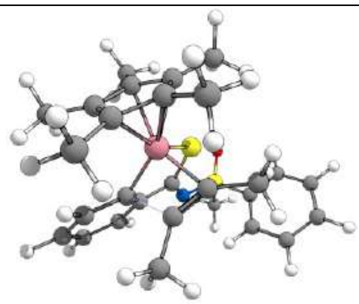
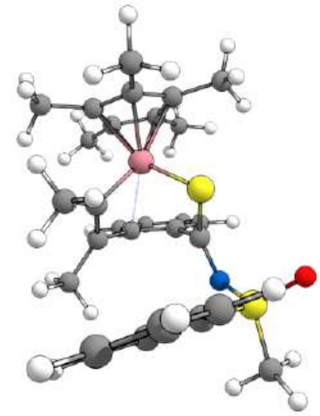
E



Thermal correction to Gibbs Free Energy= 0.440386
E(RM06) = -2158.14132509
E(RM06) = -2158.21912771

C	-0.822254	4.26672	-0.943591	C	0.706791	4.205708	1.205508
C	0.149408	3.431941	-0.407852	C	-0.267156	3.42636	0.614028
C	-2.082674	3.750667	-1.224947	C	1.95498	3.639774	1.471338
C	-2.381665	2.412312	-0.953752	C	2.221554	2.314614	1.142032
C	-1.43463	1.548818	-0.406039	C	1.265601	1.500128	0.528091
C	-0.15252	2.090858	-0.155088	C	0.006458	2.08811	0.278301
C	0.864491	1.175513	0.3437	C	-1.018532	1.263476	-0.328281
S	0.383511	-0.482336	0.514643	S	-0.563349	-0.328413	-0.734158
N	2.069997	1.662955	0.60919	N	-2.236458	1.799378	-0.507656
S	3.252204	0.698313	1.15142	S	-3.430205	0.911662	-1.101274
O	3.08718	-0.048168	2.395031	O	-3.34001	0.313954	-2.432599
C	4.556309	1.886193	1.324436	C	-4.757526	2.086686	-1.055561
C	3.765543	-0.376897	-0.168404	C	-3.880856	-0.331734	0.094991
C	4.118793	-1.678612	0.169284	C	-4.302485	-1.565476	-0.38829
C	4.553889	-2.523481	-0.845993	C	-4.69373	-2.534936	0.52968
C	4.625322	-2.060733	-2.156758	C	-4.657677	-2.258966	1.893523
C	4.259686	-0.753241	-2.473249	C	-4.225136	-1.01715	2.357376
C	3.821707	0.106163	-1.474813	C	-3.829266	-0.037014	1.456015
H	-2.846172	4.395652	-1.65489	H	2.730804	4.239441	1.943594
H	-3.383808	2.057384	-1.185286	H	3.204504	1.915618	1.385579
H	5.446276	1.342201	1.650421	H	-5.655912	1.572879	-1.406467
H	4.72219	2.38878	0.369119	H	-4.8808	2.458162	-0.036048
H	4.233289	2.599423	2.08733	H	-4.483628	2.898929	-1.733656
H	4.039882	-2.014165	1.200344	H	-4.311088	-1.753428	-1.459249

H	4.836296	-3.545935	-0.61118	H	-5.030162	-3.505982	0.176844
H	4.968883	-2.726931	-2.943802	H	-4.97082	-3.018716	2.605018
H	4.313534	-0.403931	-3.500486	H	-4.19735	-0.811974	3.423995
H	3.51798	1.124986	-1.707501	H	-3.475164	0.932184	1.802463
Co	-1.729716	-0.317251	-0.027627	Co	1.571777	-0.353602	0.012275
H	1.146764	3.805149	-0.186631	H	-1.253294	3.828709	0.39512
H	-0.598023	5.310649	-1.145156	H	0.505455	5.242001	1.462379
C	-2.278535	-2.203594	0.711794	C	2.104327	-1.694723	-1.558932
C	-2.921507	-1.097846	1.368845	C	2.293735	-0.301759	-1.912779
C	-3.744709	-0.389695	0.411277	C	3.307705	0.23805	-1.067734
C	-3.493204	-0.963146	-0.852274	C	3.627041	-0.750871	-0.093763
C	-2.572625	-2.077743	-0.662288	C	2.921956	-1.964113	-0.443032
C	-4.669583	0.718496	0.765291	C	3.953961	1.559802	-1.278318
H	-5.46763	0.341158	1.416939	H	4.603453	1.497811	-2.161579
H	-4.155071	1.521471	1.304305	H	3.220918	2.351955	-1.461206
H	-5.146477	1.156822	-0.115674	H	4.578245	1.864325	-0.434526
C	-4.038038	-0.558939	-2.1744	C	4.668055	-0.663291	0.965404
H	-4.643313	-1.366318	-2.605597	H	5.623442	-1.062341	0.599493
H	-4.671045	0.329797	-2.104231	H	4.852121	0.368711	1.283579
H	-3.232895	-0.338321	-2.886002	H	4.392167	-1.248479	1.850012
C	-1.99129	-2.856869	-1.783176	C	3.100978	-3.258687	0.265129
H	-1.14446	-3.469347	-1.461716	H	2.422242	-4.031887	-0.105988
H	-2.743767	-3.522582	-2.226113	H	4.124733	-3.626915	0.121814
H	-1.644073	-2.188106	-2.580656	H	2.943681	-3.152697	1.345315
C	-1.38913	-3.208061	1.355004	C	1.251208	-2.660444	-2.303861
H	-0.657593	-3.614118	0.648837	H	1.014734	-3.548649	-1.709245
H	-0.83349	-2.779793	2.195346	H	0.30586	-2.213623	-2.629858
H	-1.97742	-4.048641	1.742117	H	1.773495	-3.002259	-3.20652
C	-2.806023	-0.735558	2.801834	C	1.711005	0.407228	-3.083564
H	-1.854927	-1.063455	3.231244	H	0.8242	-0.097793	-3.47521
H	-2.886905	0.347563	2.941081	H	1.422287	1.432612	-2.82372
H	-3.615091	-1.204201	3.379127	H	2.449219	0.469187	-3.894246
				C	1.42775	-0.659014	2.141752
				C	0.756922	-1.535254	1.578203
				C	-0.106701	-2.697415	1.358364
				H	0.202329	-3.283062	0.485632
				H	-0.075666	-3.350992	2.237536
				H	-1.144806	-2.387268	1.193417
				C	2.043607	0.085037	3.241883
				H	1.544196	1.045343	3.404211
				H	1.962426	-0.508275	4.159353
				H	3.104941	0.28971	3.067018
TS$_{EF}$				**F**			

 Thermal correction to Gibbs Free Energy= 0.444350 E(RM06) = -2158.12604730 E(SCRF) = -2158.20329388 Frequency -243.8195				 Thermal correction to Gibbs Free Energy= 0.441945 E(RM06) = -2158.15189480 E(SCRF) = -2158.22956772			
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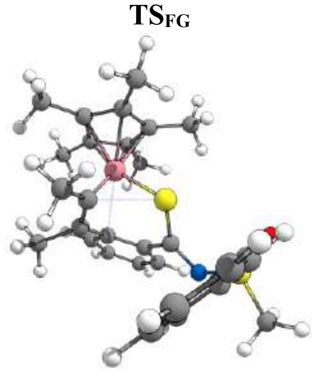
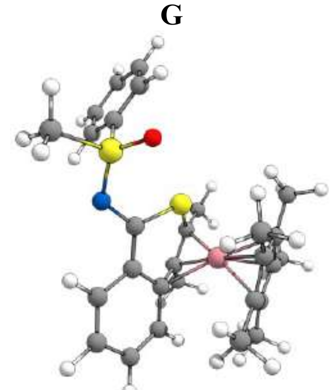
C	1.240485	1.41975	0.636389	C	0.829294	1.223917	1.507277
C	2.25731	2.224294	1.183983	C	1.818954	1.935082	2.215607
C	2.115582	3.596813	1.303632	C	2.354691	3.111212	1.7289
C	0.926961	4.228273	0.921404	C	1.926631	3.623448	0.495948
C	-0.09723	3.470966	0.387259	C	0.950196	2.962431	-0.221151
H	0.814727	5.302596	1.036476	H	2.343366	4.552828	0.116075
C	0.063033	2.087178	0.20494	C	0.389143	1.770229	0.274982
H	-1.026384	3.931367	0.060132	H	0.573423	3.370643	-1.157337
H	2.932219	4.185444	1.715981	H	3.105043	3.645991	2.306458
H	3.166983	1.754982	1.553696	H	2.14528	1.546128	3.17898
Co	1.525884	-0.398289	-0.077019	Co	1.424756	-0.415057	-0.187731
C	-0.965576	1.313664	-0.457343	C	-0.794578	1.221841	-0.450121
S	-0.499993	-0.212506	-1.054534	S	-0.499049	-0.173654	-1.356631
N	-2.195407	1.852445	-0.537096	N	-1.913273	1.92122	-0.298846
S	-3.412547	0.974394	-1.091758	S	-3.272682	1.32564	-0.963753
O	-3.433013	0.458254	-2.459494	O	-3.372668	1.144276	-2.409162
C	-4.758872	2.103537	-0.852128	C	-4.446728	2.530702	-0.406077
C	-3.712308	-0.354775	0.063613	C	-3.680867	-0.178729	-0.104726
H	-5.671746	1.587487	-1.159583	H	-5.430701	2.206811	-0.754
H	-4.801234	2.403671	0.196949	H	-4.407892	2.600565	0.683005
H	-4.56471	2.9657	-1.495309	H	-4.164022	3.481736	-0.865043
C	-4.157055	-1.566934	-0.451987	C	-4.213373	-1.222697	-0.8528
C	-3.522461	-0.146642	1.42868	C	-3.477103	-0.264517	1.271439
C	-4.432261	-2.602382	0.436068	C	-4.565552	-2.39304	-0.18838
H	-4.270405	-1.688881	-1.526545	H	-4.335021	-1.116245	-1.928
C	-4.261476	-2.411638	1.80448	C	-4.385519	-2.495735	1.188291
H	-4.78321	-3.558126	0.056558	H	-4.983472	-3.22471	-0.748582
C	-3.80486	-1.1909	2.300154	C	-3.841732	-1.438351	1.916683
H	-4.484974	-3.222192	2.493387	H	-4.66976	-3.410825	1.701322
H	-3.669766	-1.052252	3.369625	H	-3.70103	-1.52928	2.990817
H	-3.149104	0.806712	1.798947	H	-3.026486	0.560838	1.820092
C	2.495017	-0.594148	-1.899812	C	2.627319	-0.739876	-1.918218
C	3.555227	-0.839945	0.129178	C	3.45887	-0.591078	0.232197

C	0.445273	-1.124731	1.369483	C	0.302483	-1.053631	1.247913
C	2.140298	-1.895553	-1.354933	C	2.255656	-1.941586	-1.179629
C	2.843979	-2.056421	-0.134009	C	2.879083	-1.8772	0.113606
C	1.267349	-2.907458	-2.012161	C	1.533283	-3.112407	-1.745051
C	3.390204	0.033253	-1.001835	C	3.343362	0.089505	-1.046691
C	2.078472	-0.02023	-3.20805	C	2.266767	-0.438238	-3.330287
C	4.048445	1.342882	-1.255058	C	3.907054	1.430566	-1.348522
C	4.414386	-0.624545	1.325657	C	4.222959	-0.116515	1.415756
C	2.870456	-3.249455	0.753573	C	2.959675	-2.942759	1.147935
H	4.768467	1.242373	-2.077145	H	4.974951	1.35213	-1.590235
H	3.323402	2.112704	-1.543893	H	3.407511	1.900617	-2.201902
H	4.596835	1.711715	-0.384429	H	3.815857	2.109481	-0.493186
H	5.247545	-1.338826	1.337933	H	5.235322	-0.542677	1.409039
H	4.850999	0.378319	1.349148	H	4.323275	0.972805	1.432747
H	3.848918	-0.774225	2.254426	H	3.74187	-0.428892	2.350198
H	2.154411	-4.014655	0.43867	H	2.373414	-3.826295	0.880857
H	3.865616	-3.711806	0.730798	H	4.001866	-3.268868	1.258288
H	2.662783	-2.987208	1.798862	H	2.624453	-2.588568	2.129816
H	0.711598	-3.499153	-1.276215	H	1.080038	-3.726026	-0.959977
H	0.533892	-2.440701	-2.677513	H	0.73441	-2.810212	-2.430845
H	1.863137	-3.602071	-2.617339	H	2.220967	-3.753679	-2.312059
H	1.229378	-0.549971	-3.647645	H	1.384804	-0.997472	-3.657767
H	1.7942	1.033875	-3.104932	H	2.049836	0.626315	-3.472934
H	2.909641	-0.070048	-3.923619	H	3.091531	-0.704311	-4.003168
C	1.023391	0.607325	3.214088	C	-0.51386	0.103624	3.389626
C	-0.336103	-2.356081	1.551291	C	-0.371201	-2.372736	1.341427
H	0.238285	-3.251171	1.290295	H	0.333064	-3.212689	1.351328
H	-0.667202	-2.453688	2.593511	H	-0.997531	-2.45735	2.240876
H	-1.22958	-2.338119	0.912804	H	-1.029318	-2.511862	0.469663
H	0.542108	1.590733	3.273262	H	-1.285154	0.888139	3.375923
H	0.584891	-0.056088	3.968636	H	-0.983228	-0.843064	3.675407
H	2.082133	0.744029	3.462231	H	0.181851	0.374291	4.195042
TS$_{FG}$  Thermal correction to Gibbs Free Energy= 0.443255 E(RM06) = -2158.13981513 E(SCRF) = -2158.21737849 Frequency -85.9033				**G**  Thermal correction to Gibbs Free Energy= 0.445419 E(RM06) = -2158.15934355 E(SCRF) = -2158.23626483			
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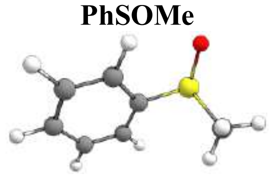
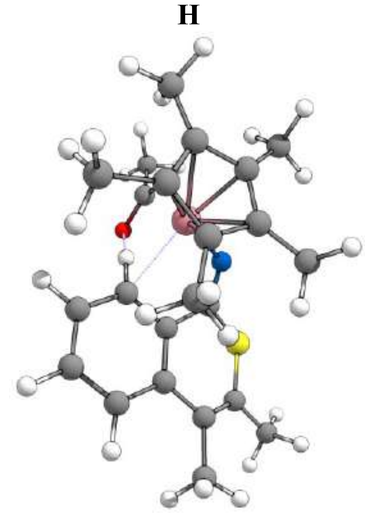
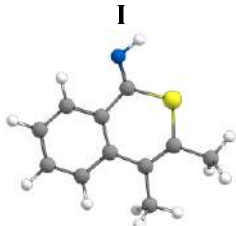
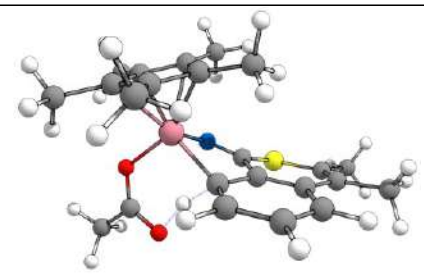
S	-0.587732	-0.391482	-0.627223	S	-0.589831	-0.521076	0.051351
C	0.962632	0.181085	1.939534	C	1.301453	0.15491	1.904457
C	1.055651	1.482614	1.217115	C	1.375646	1.354672	1.092286
C	1.408232	0.183131	3.385027	C	2.173414	-0.055679	3.111593
C	2.052221	2.38175	1.671289	C	2.514778	2.227075	1.307569
C	0.053128	2.038815	0.356664	C	0.184065	2.001634	0.507945
Co	1.598035	-0.524633	-0.104565	Co	1.640809	-0.508404	-0.017706
C	2.068437	3.715114	1.313138	C	2.465078	3.559933	1.064205
H	2.829213	2.008198	2.334118	H	3.428801	1.788652	1.701207
C	1.054988	4.249329	0.509817	C	1.264384	4.18393	0.590937
H	2.870056	4.354663	1.675234	H	3.345208	4.171875	1.248012
C	0.052412	3.414547	0.06327	C	0.165693	3.428616	0.346276
H	1.060705	5.300033	0.235523	H	1.246714	5.256252	0.419127
H	-0.745336	3.792699	-0.570343	H	-0.750472	3.867814	-0.039549
C	-0.985077	1.222533	-0.228201	C	-0.902989	1.257106	0.119189
C	3.632082	-0.515125	-0.258629	C	3.641842	-0.685312	-0.435665
C	2.275786	-2.030446	-1.311432	C	2.031023	-2.05532	-1.327104
N	-2.194444	1.794931	-0.388108	N	-2.128778	1.786049	-0.160124
S	-3.394281	0.978363	-1.063068	S	-3.17115	0.999376	-1.042483
O	-3.283876	0.45772	-2.425783	O	-2.749776	0.311692	-2.26996
C	-4.695743	2.17898	-0.966675	C	-4.366019	2.260717	-1.40449
C	-3.882022	-0.330172	0.04462	C	-4.066969	-0.166834	-0.02891
H	-5.598272	1.71088	-1.36746	H	-5.188326	1.782597	-1.943034
H	-4.829918	2.482884	0.073669	H	-4.710075	2.706891	-0.468894
H	-4.391528	3.028831	-1.582913	H	-3.867615	3.00416	-2.031257
C	-4.349731	-1.511227	-0.520546	C	-4.534909	-1.332896	-0.627214
C	-3.766296	-0.15167	1.42198	C	-4.285919	0.122065	1.316455
C	-4.720192	-2.547448	0.329988	C	-5.248395	-2.235933	0.153404
H	-4.402383	-1.613417	-1.601661	H	-4.328279	-1.524897	-1.677302
C	-4.138145	-1.198501	2.25493	C	-5.003205	-0.790221	2.08028
H	-3.377779	0.780037	1.829415	H	-3.89005	1.037621	1.752938
C	-4.613295	-2.390185	1.708927	C	-5.481615	-1.962986	1.498475
H	-5.090027	-3.480433	-0.086308	H	-5.622763	-3.154729	-0.289777
H	-4.904098	-3.20476	2.367218	H	-6.042978	-2.671645	2.10189
H	-4.05954	-1.084814	3.332752	H	-5.188905	-0.587411	3.131568
C	2.241394	-0.77202	-2.057866	C	1.97641	-0.769979	-2.016033
C	3.096051	0.150257	-1.420534	C	2.997885	0.056839	-1.496123
C	1.468894	-0.539701	-3.308016	C	1.013023	-0.388889	-3.0863
C	3.1987	-1.881166	-0.243777	C	3.094039	-2.010323	-0.392984
C	4.561542	0.090212	0.731407	C	4.816306	-0.224809	0.352273
C	0.251209	-2.314378	1.959654	C	0.229239	-2.183784	2.188365
C	1.514576	-3.256546	-1.673239	C	1.155266	-3.223582	-1.616986
C	3.603568	-2.894785	0.768734	C	3.534008	-3.096974	0.524275
H	1.456328	-3.955984	-0.832827	H	1.100514	-3.911096	-0.766067
H	0.489502	-3.019679	-1.981372	H	0.134101	-2.91975	-1.871973
H	1.988695	-3.783613	-2.511296	H	1.54197	-3.794431	-2.470988
C	3.324917	1.573155	-1.793448	C	3.32104	1.441652	-1.930369
H	0.609157	-1.210723	-3.394756	H	0.121035	-1.022444	-3.083351

H	1.09487	0.487408	-3.373219	H	0.674749	0.646964	-2.965306
H	2.110865	-0.716218	-4.180491	H	1.478996	-0.473168	-4.076159
H	4.30373	1.713494	-2.269126	H	4.117946	1.43979	-2.684815
H	2.561547	1.926308	-2.494172	H	2.447838	1.934829	-2.371997
H	3.286788	2.229243	-0.914201	H	3.65627	2.064316	-1.093678
H	5.599255	-0.176164	0.491015	H	5.734221	-0.677191	-0.045574
H	4.494385	1.18232	0.737313	H	4.94142	0.860507	0.301572
H	4.363859	-0.272966	1.747034	H	4.752846	-0.515514	1.407505
H	2.933961	-3.761013	0.775385	H	2.722028	-3.796061	0.752281
H	4.615302	-3.269447	0.567338	H	4.349347	-3.681362	0.07848
H	3.61706	-2.47121	1.781478	H	3.90997	-2.698407	1.473924
H	1.128557	1.118366	3.883192	H	2.514318	0.896533	3.525995
H	0.952599	-0.651173	3.927522	H	1.611492	-0.574325	3.895417
H	2.496351	0.068821	3.483746	H	3.05826	-0.66835	2.89204
H	1.138498	-2.901485	2.235525	H	1.183113	-2.608392	2.522265
H	-0.379263	-2.197469	2.85046	H	-0.417893	-2.060626	3.066103
H	-0.305757	-2.906504	1.223301	H	-0.24715	-2.911431	1.522861
PhSOMe  Thermal correction to Gibbs Free Energy= 0.084214 E(RM06) = -744.752363361 E(SCRF) = -744.768611573				**H**  Thermal correction to Gibbs Free Energy= 0.365529 E(RM06) = -1642.05466419 E(SCRF) = -1642.08657482			
S	1.676724	-0.143615	-0.469103	H	0.49177	-0.122071	1.785422
O	2.195908	1.258264	-0.348631	C	-0.35941	0.557752	1.557399
C	2.032289	-0.953476	1.12669	C	-0.507626	1.729478	2.293416
C	-0.116072	-0.066849	-0.204918	C	-1.72862	2.396621	2.261547
C	-0.664492	1.150177	0.172414	C	-2.78566	1.890307	1.513804
C	-2.040275	1.238343	0.361735	C	-2.674599	0.698519	0.775213
C	-2.845072	0.119998	0.165771	H	-3.729933	2.428401	1.517215
C	-2.281482	-1.092467	-0.225958	C	-1.426319	0.044791	0.804616
C	-0.908256	-1.189143	-0.420398	H	-1.870596	3.308568	2.837439
H	1.678622	-0.292589	1.926333	H	0.312044	2.093269	2.909665
H	1.532538	-1.927206	1.177726	Co	1.274699	-0.034903	-0.08644
H	3.117214	-1.080237	1.19908	C	-1.103402	-1.130312	-0.019669
H	-0.000566	2.005085	0.299838	N	0.047472	-1.420957	-0.451434
H	-2.48739	2.185207	0.65977	O	2.448165	-1.290247	0.751148

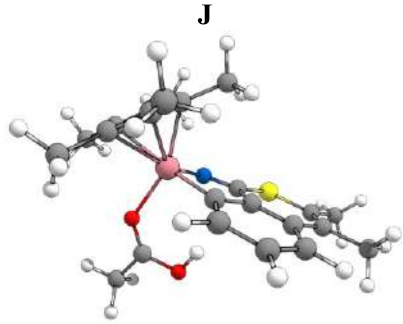
H	-3.921411	0.1941	0.310461	C	1.013657	0.625353	-2.050801
H	-2.915618	-1.962218	-0.388203	C	2.123773	1.898159	-0.449186
H	-0.458083	-2.129914	-0.742322	C	2.164706	-1.953172	1.830781
				O	1.217094	-1.745573	2.581085
				C	3.158755	-3.060931	2.111466
				H	4.184825	-2.691034	2.016759
				H	3.028661	-3.854667	1.368094
				H	2.99616	-3.471651	3.109998
				C	2.298995	0.029533	-1.779241
				C	3.015744	0.903797	-0.868161
				C	2.855349	-1.210943	-2.375538
				C	0.87354	1.727328	-1.179301
				C	-0.004216	0.090064	-2.991587
				C	-0.285965	2.655925	-1.102638
				C	2.392923	2.968689	0.551033
				C	4.388978	0.648825	-0.367663
				H	-0.073109	3.572878	-1.668423
				H	-1.193506	2.208176	-1.519915
				H	-0.50924	2.94559	-0.069851
				H	2.884979	3.83138	0.082508
				H	1.464845	3.326938	1.007682
				H	3.043385	2.609619	1.355909
				H	5.086921	0.508504	-1.201846
				H	4.755388	1.475643	0.248072
				H	4.389429	-0.268943	0.235558
				H	3.311901	-1.820747	-1.587966
				H	2.069773	-1.80933	-2.845093
				H	3.619476	-0.984293	-3.131042
				H	-0.069794	-1.000392	-2.911336
				H	-1.001674	0.489683	-2.775986
				H	0.25178	0.351811	-4.026106
				S	-2.485027	-2.231833	-0.403227
				C	-3.833869	-1.09938	-0.460103
				C	-3.812803	0.166968	0.025051
				C	-5.013682	1.059348	-0.131813
				H	-4.719661	2.057972	-0.479979
				H	-5.728944	0.665829	-0.857184
				H	-5.551676	1.197444	0.817028
				C	-5.034455	-1.720131	-1.120235
				H	-5.952881	-1.526375	-0.556244
				H	-5.173793	-1.330965	-2.137338
				H	-4.922094	-2.805775	-1.205704

I 	**TS$_{HJ}$**

Thermal correction to Gibbs Free Energy= 0.137052 E(RM06) = -878.467412469 E(SCRF) = -878.483632672				 Thermal correction to Gibbs Free Energy= 0.361824 E(RM06) = -1642.04224088 E(SCRF) = -1642.06998028 Frequency -1509.2993			
C	3.303598	-0.006018	0.000171	H	0.41398	-0.268125	1.802298
C	2.934215	-1.349017	0.000245	O	0.805952	-1.225117	2.675705
C	1.596255	-1.698459	0.000154	C	1.809535	-1.745249	2.125189
C	0.567056	-0.736741	-0.000009	O	2.264031	-1.390298	0.998879
C	0.957711	0.623438	-0.000052	Co	1.262252	-0.090298	-0.070878
C	2.317794	0.961431	0.000023	C	-0.248112	0.647412	1.186025
C	-0.825695	-1.19165	-0.000127	C	-0.313998	1.841073	1.910232
C	-1.877237	-0.343522	0.000101	C	-1.431262	0.156708	0.592661
S	-1.72941	1.408766	0.000445	C	-1.519449	2.529793	2.010136
C	0.019072	1.758122	-0.000219	H	0.572434	2.215172	2.421791
C	-1.077501	-2.674523	-0.000517	C	-2.670308	2.026743	1.412944
C	-3.322792	-0.761641	0.000088	H	-1.576216	3.457668	2.576337
N	0.434674	2.965257	-0.000671	C	-2.668579	0.815141	0.697309
H	4.353207	0.281168	0.000233	H	-3.597365	2.583748	1.523838
H	3.693309	-2.129511	0.000381	C	-3.895292	0.276339	0.106445
H	1.339866	-2.754221	0.000225	C	-1.17717	-1.05632	-0.185101
H	2.56759	2.019602	-0.000034	N	-0.008838	-1.433257	-0.50427
H	-2.143648	-2.914059	-0.001045	C	2.600551	-0.212382	-1.608078
H	-0.637329	-3.158	-0.884045	C	1.053313	1.474669	-1.412331
H	-0.638098	-3.158378	0.883192	S	-2.594282	-2.059682	-0.661355
H	-3.568854	-1.359472	-0.887155	C	1.382909	0.297438	-2.144183
H	-3.56876	-1.360012	0.886989	C	0.560253	-0.380414	-3.178477
H	-3.992052	0.106549	0.000382	C	2.173073	1.789037	-0.540409
H	-0.332236	3.640765	-0.0007	C	3.119862	0.760339	-0.669804
				C	2.312927	3.016092	0.292515
				C	2.508811	-2.870756	2.833869
				H	3.528972	-2.992552	2.464285
				H	1.955736	-3.795678	2.638566
				H	2.502606	-2.700227	3.912915
				C	3.265491	-1.483499	-1.995844
				C	4.400047	0.611456	0.070684
				H	3.746151	-1.948695	-1.129301
				H	2.535339	-2.197848	-2.389594
				H	4.032424	-1.318265	-2.765054
				C	-0.14505	2.32985	-1.63606
				H	0.249521	-1.371924	-2.821962
				H	-0.345443	0.187115	-3.413969

H	1.135304	-0.504674	-4.104235
H	0.050749	3.089014	-2.405039
H	-1.002611	1.732747	-1.965751
H	-0.44878	2.849029	-0.720525
H	2.927256	3.764601	-0.22538
H	1.341438	3.474391	0.500491
H	2.793029	2.804056	1.254824
H	5.242768	0.520197	-0.626324
H	4.595182	1.468292	0.722841
H	4.377787	-0.294237	0.688767
C	-3.954279	-0.95399	-0.45779
C	-5.217188	-1.563017	-1.005777
C	-5.127021	1.135162	0.183897
H	-4.944324	2.12789	-0.248408
H	-5.973514	0.702517	-0.352701
H	-5.4453	1.29461	1.223621
H	-6.031973	-1.527082	-0.274375
H	-5.552488	-1.039657	-1.910094
H	-5.067347	-2.612761	-1.277575

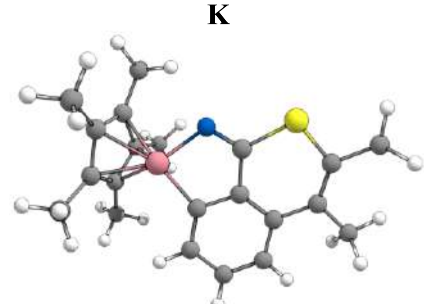
J



Thermal correction to Gibbs Free Energy= 0.367005
E(RM06) = -1642.05993041
E(SCRF) = -1642.08651171

H	-0.510104	1.938583	0.697692
O	-0.276159	2.537674	1.444305
C	0.962669	2.300643	1.806271
O	1.689592	1.45581	1.291374
Co	1.262346	-0.078968	0.036658
C	-0.240423	0.699699	-0.894237
C	-0.288875	1.652511	-1.912174
C	-1.467804	0.209288	-0.39611
C	-1.520319	2.0472	-2.442079
H	0.628991	2.094639	-2.302873
C	-2.710846	1.51399	-1.965926
H	-1.553286	2.786762	-3.24099
C	-2.723342	0.585306	-0.909778
H	-3.646629	1.844957	-2.408572
C	-3.977477	0.058278	-0.367075
C	-1.218042	-0.624366	0.778688
N	-0.043764	-0.801588	1.226168

K

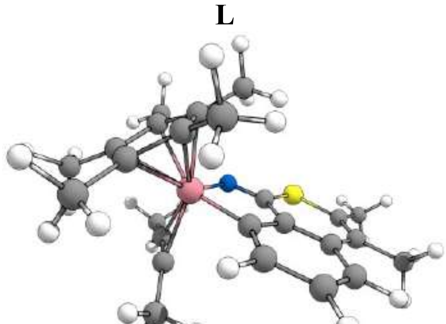


Thermal correction to Gibbs Free Energy= 0.311163
E(RM06) = -1412.99266437
E(SCRF) = -1413.02144893

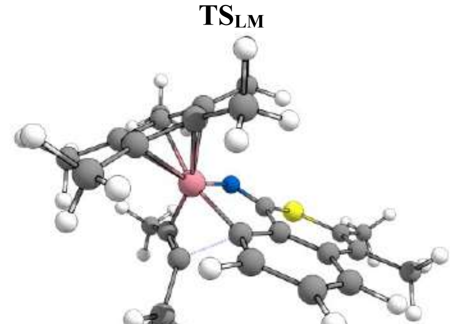
C	0.17402	1.13021	-0.220719
C	0.207789	2.514722	-0.301574
C	1.436225	3.192779	-0.250734
C	2.629021	2.503287	-0.129528
C	2.651915	1.092113	-0.087533
H	3.559362	3.063597	-0.082063
C	1.407162	0.452784	-0.13162
H	1.454423	4.280482	-0.302334
H	-0.710791	3.093405	-0.403774
Co	-1.295022	-0.116542	-0.317938
C	1.167817	-0.982386	-0.219081
N	-0.017483	-1.449762	-0.320791
C	-2.263939	-0.242188	1.385344
C	-3.254827	0.599133	-0.50751
C	-2.731198	-1.371722	0.614169
C	-3.252467	-0.853749	-0.581773
C	-2.457723	-2.795161	0.93832

C	3.215111	-0.886703	0.364275	C	-2.709411	0.974398	0.733373
C	1.620451	-1.721122	-1.059961	C	-1.556929	-0.324447	2.690773
S	-2.631003	-1.347002	1.625974	C	-2.615961	2.337129	1.321914
C	2.317767	-1.950118	0.182914	C	-3.74537	1.494972	-1.590838
C	1.993715	-3.015812	1.163161	C	-3.657771	-1.624901	-1.788325
C	2.263254	-0.613967	-1.729779	H	-3.376456	2.460457	2.10444
C	3.188871	-0.053411	-0.824972	H	-1.636504	2.518451	1.776884
C	2.004917	-0.205586	-3.136678	H	-2.786288	3.119883	0.575324
C	1.423888	3.172196	2.926357	H	-4.842605	1.54175	-1.61123
H	2.488479	3.022179	3.107296	H	-3.36822	2.516181	-1.472146
H	0.858302	2.918079	3.828716	H	-3.418921	1.138482	-2.575371
H	1.215038	4.220966	2.696909	H	-4.742547	-1.576465	-1.95267
C	4.03185	-0.637132	1.585202	H	-3.176582	-1.220473	-2.688041
C	4.009848	1.172509	-1.022845	H	-3.366169	-2.676111	-1.709114
H	4.344202	0.409651	1.649805	H	-3.135718	-3.46733	0.403006
H	3.457767	-0.866039	2.490491	H	-1.422898	-3.037695	0.647899
H	4.939529	-1.255154	1.59522	H	-2.573564	-2.986308	2.011058
C	0.57885	-2.612609	-1.639802	H	-0.874061	-1.180943	2.70501
H	1.062903	-2.751384	1.688672	H	-0.960964	0.57634	2.87268
H	1.84753	-3.981	0.664618	H	-2.264475	-0.437147	3.524252
H	2.789938	-3.133378	1.905451	S	2.570417	-2.079002	-0.252093
H	1.027125	-3.457044	-2.181637	C	3.963197	-1.004537	-0.097137
H	-0.066637	-3.02217	-0.854409	C	3.909405	0.348146	-0.026315
H	-0.063696	-2.06626	-2.339147	C	5.176426	1.147817	0.102625
H	2.528688	-0.885524	-3.822054	H	5.135354	1.815424	0.972917
H	0.938791	-0.241059	-3.384075	H	6.059994	0.517694	0.220142
H	2.363044	0.808185	-3.345373	H	5.342215	1.782314	-0.778398
H	5.069798	0.931148	-1.178313	C	5.242636	-1.797256	-0.059116
H	3.669454	1.747199	-1.891131	H	5.939753	-1.474327	-0.840854
H	3.945724	1.83099	-0.148355	H	5.750275	-1.690075	0.907576
C	-4.022592	-0.765331	0.707958	H	5.056584	-2.865439	-0.210135
C	-5.302105	-1.305794	1.28988				
C	-5.247054	0.480755	-1.053348				
H	-5.22085	0.232854	-2.122835				
H	-6.13283	0.002043	-0.631725				
H	-5.399277	1.566545	-0.982966				
H	-5.969267	-0.497047	1.611075				
H	-5.846047	-1.918366	0.560809				
H	-5.108972	-1.935491	2.16409				

L



TS_{LM}



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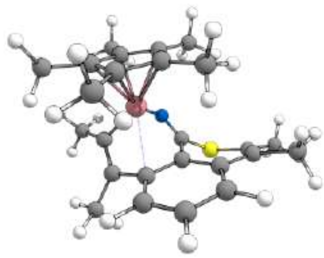
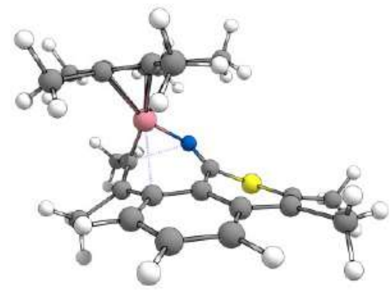
<tr><td colspan="4">Thermal correction to Gibbs Free Energy= 0.392531
E(RM06) = -1568.92470447
E(SCRF) = -1568.95033108</td><td colspan="4">Thermal correction to Gibbs Free Energy= 0.395495
E(RM06) = -1568.90778299
E(SCRF) = -1568.93331360
Frequency -261.7897</td></tr>
<tr><td>C</td><td>-0.310487</td><td>1.132327</td><td>0.100108</td><td>C</td><td>0.7569</td><td>0.547981</td><td>1.944776</td></tr>
<tr><td>C</td><td>-0.336928</td><td>2.524653</td><td>0.087929</td><td>C</td><td>-0.250175</td><td>1.100572</td><td>0.390646</td></tr>
<tr><td>C</td><td>-1.55791</td><td>3.199313</td><td>0.044492</td><td>C</td><td>-0.266369</td><td>2.499663</td><td>0.287526</td></tr>
<tr><td>C</td><td>-2.760669</td><td>2.505986</td><td>0.017142</td><td>C</td><td>-1.471901</td><td>0.408744</td><td>0.216692</td></tr>
<tr><td>C</td><td>-2.786411</td><td>1.102067</td><td>0.037835</td><td>Co</td><td>1.224069</td><td>-0.150755</td><td>0.066655</td></tr>
<tr><td>H</td><td>-3.689603</td><td>3.068478</td><td>-0.020437</td><td>C</td><td>-1.460417</td><td>3.164233</td><td>0.047871</td></tr>
<tr><td>C</td><td>-1.538787</td><td>0.450252</td><td>0.083775</td><td>H</td><td>0.653432</td><td>3.069601</td><td>0.414698</td></tr>
<tr><td>H</td><td>-1.571522</td><td>4.288347</td><td>0.029163</td><td>C</td><td>-2.660629</td><td>2.469829</td><td>-0.07647</td></tr>
<tr><td>H</td><td>0.586491</td><td>3.104485</td><td>0.113448</td><td>H</td><td>-1.463741</td><td>4.249676</td><td>-0.03766</td></tr>
<tr><td>Co</td><td>1.190216</td><td>-0.093637</td><td>0.125912</td><td>C</td><td>-2.700112</td><td>1.069471</td><td>0.005853</td></tr>
<tr><td>C</td><td>-1.314106</td><td>-0.985542</td><td>0.115114</td><td>H</td><td>-3.573946</td><td>3.032377</td><td>-0.246722</td></tr>
<tr><td>N</td><td>-0.147233</td><td>-1.48284</td><td>0.148917</td><td>C</td><td>-3.96022</td><td>0.335871</td><td>-0.143406</td></tr>
<tr><td>C</td><td>1.61423</td><td>-0.545556</td><td>-1.818725</td><td>C</td><td>-1.26542</td><td>-1.025694</td><td>0.167786</td></tr>
<tr><td>C</td><td>2.976787</td><td>0.83906</td><td>-0.579582</td><td>N</td><td>-0.106537</td><td>-1.541607</td><td>0.087688</td></tr>
<tr><td>C</td><td>2.465228</td><td>-1.378465</td><td>-1.005999</td><td>C</td><td>1.74391</td><td>-0.639319</td><td>-1.85706</td></tr>
<tr><td>C</td><td>3.288764</td><td>-0.52346</td><td>-0.240228</td><td>C</td><td>2.879911</td><td>0.963612</td><td>-0.652217</td></tr>
<tr><td>C</td><td>2.390818</td><td>-2.861976</td><td>-0.967177</td><td>C</td><td>1.184927</td><td>-0.659825</td><td>1.923186</td></tr>
<tr><td>C</td><td>1.990192</td><td>0.817956</td><td>-1.603676</td><td>S</td><td>-2.701819</td><td>-2.103988</td><td>0.275105</td></tr>
<tr><td>C</td><td>0.612403</td><td>-1.0323</td><td>-2.80466</td><td>C</td><td>2.620073</td><td>-1.310836</td><td>-0.921304</td></tr>
<tr><td>C</td><td>1.508213</td><td>1.973108</td><td>-2.406834</td><td>C</td><td>1.920216</td><td>0.758896</td><td>-1.703056</td></tr>
<tr><td>C</td><td>3.695395</td><td>2.032141</td><td>-0.050535</td><td>C</td><td>0.828703</td><td>-1.304209</td><td>-2.823148</td></tr>
<tr><td>C</td><td>4.312363</td><td>-0.908958</td><td>0.769688</td><td>C</td><td>3.348113</td><td>-0.311109</td><td>-0.218092</td></tr>
<tr><td>H</td><td>2.074317</td><td>2.025387</td><td>-3.346807</td><td>C</td><td>3.399477</td><td>2.267496</td><td>-0.149186</td></tr>
<tr><td>H</td><td>0.447205</td><td>1.881068</td><td>-2.660364</td><td>C</td><td>2.706764</td><td>-2.787422</td><td>-0.763818</td></tr>
<tr><td>H</td><td>1.64355</td><td>2.927751</td><td>-1.889164</td><td>C</td><td>4.356602</td><td>-0.502072</td><td>0.861472</td></tr>
<tr><td>H</td><td>4.616258</td><td>2.230669</td><td>-0.616628</td><td>H</td><td>3.354955</td><td>-3.067354</td><td>0.074039</td></tr>
<tr><td>H</td><td>3.081741</td><td>2.939427</td><td>-0.105395</td><td>H</td><td>1.706927</td><td>-3.19674</td><td>-0.567392</td></tr>
<tr><td>H</td><td>3.987917</td><td>1.889083</td><td>0.997105</td><td>H</td><td>3.102538</td><td>-3.26684</td><td>-1.668503</td></tr>
<tr><td>H</td><td>4.417635</td><td>-1.995638</td><td>0.850498</td><td>C</td><td>1.2256</td><td>1.805437</td><td>-2.502418</td></tr>
<tr><td>H</td><td>5.295239</td><td>-0.500747</td><td>0.501687</td><td>H</td><td>0.518983</td><td>-2.287941</td><td>-2.458309</td></tr>
<tr><td>H</td><td>4.056449</td><td>-0.518119</td><td>1.764598</td><td>H</td><td>-0.083035</td><td>-0.713323</td><td>-2.972405</td></tr>
<tr><td>H</td><td>3.124703</td><td>-3.291902</td><td>-0.276813</td><td>H</td><td>1.309922</td><td>-1.433279</td><td>-3.802146</td></tr>
<tr><td>H</td><td>1.385965</td><td>-3.16573</td><td>-0.640743</td><td>H</td><td>1.69448</td><td>1.921677</td><td>-3.488398</td></tr>
<tr><td>H</td><td>2.573327</td><td>-3.293129</td><td>-1.959579</td><td>H</td><td>0.170441</td><td>1.549431</td><td>-2.659426</td></tr>
<tr><td>H</td><td>0.159821</td><td>-1.970463</td><td>-2.468086</td><td>H</td><td>1.246491</td><td>2.780973</td><td>-2.005828</td></tr>
<tr><td>H</td><td>-0.198851</td><td>-0.306938</td><td>-2.934237</td><td>H</td><td>4.414403</td><td>2.460941</td><td>-0.52295</td></tr>
<tr><td>H</td><td>1.071171</td><td>-1.202834</td><td>-3.78831</td><td>H</td><td>2.773119</td><td>3.107652</td><td>-0.467466</td></tr>
<tr><td>S</td><td>-2.734623</td><td>-2.086087</td><td>0.077447</td><td>H</td><td>3.454222</td><td>2.284403</td><td>0.947255</td></tr>
<tr><td>C</td><td>-4.117102</td><td>-0.989204</td><td>0.016259</td><td>H</td><td>4.558096</td><td>-1.561786</td><td>1.049553</td></tr>
<tr><td>C</td><td>-4.05151</td><td>0.362955</td><td>0.005318</td><td>H</td><td>5.310973</td><td>-0.028785</td><td>0.596393</td></tr>
<tr><td>C</td><td>-5.313319</td><td>1.178779</td><td>-0.047745</td><td>H</td><td>4.022291</td><td>-0.049339</td><td>1.806331</td></tr>
<tr><td>H</td><td>-5.335426</td><td>1.818479</td><td>-0.940504</td><td>C</td><td>-4.051294</td><td>-1.010376</td><td>-0.019383</td></tr>
<tr><td>H</td><td>-6.213276</td><td>0.561383</td><td>-0.066284</td><td>C</td><td>-5.344014</td><td>-1.775484</td><td>-0.124711</td></tr>
</table>

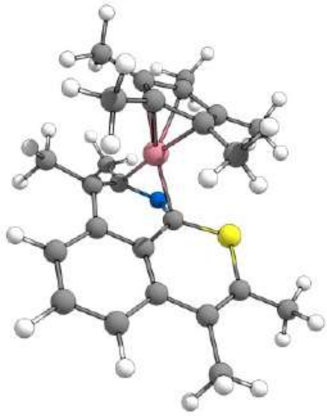
H	-5.391326	1.846213	0.82104	C	-5.192011	1.150624	-0.426772
C	-5.406281	-1.766782	-0.024084	H	-5.069317	1.751072	-1.337998
H	-6.038518	-1.54032	0.842948	H	-6.081016	0.532836	-0.566072
H	-5.9846	-1.539211	-0.92771	H	-5.407215	1.853275	0.38993
H	-5.222373	-2.845927	-0.019214	H	-6.089349	-1.406028	0.589051
C	1.38244	-0.700245	2.121943	H	-5.775308	-1.697066	-1.130444
C	1.321297	0.538871	2.129694	H	-5.1948	-2.840457	0.080202
C	1.323641	1.898871	2.673336	C	1.587733	-1.901172	2.588853
H	2.03953	2.5447	2.150245	C	0.738464	1.710492	2.870114
H	0.336221	2.362333	2.576314	H	1.456921	2.480782	2.560736
H	1.598511	1.874485	3.733911	H	-0.247621	2.185084	2.926249
C	1.487334	-2.109448	2.488852	H	1.030894	1.369647	3.869988
H	1.348555	-2.233226	3.569092	H	1.401676	-1.856446	3.669195
H	0.724495	-2.684606	1.95396	H	1.026416	-2.74447	2.169433
H	2.471596	-2.514465	2.221634	H	2.654177	-2.106538	2.431073
M  Thermal correction to Gibbs Free Energy= 0.392920 E(RM06) = -1568.93693454 E(SCRF) = -1568.96273468				**TS$_{MN}$**  Thermal correction to Gibbs Free Energy= 0.394213 E(RM06) = -1568.92600824 E(SCRF) = -1568.95171465 Frequency -135.7552			
C	0.934793	2.08111	1.230443	C	-1.365244	0.020283	-1.845101
C	-0.103994	1.893965	0.171389	N	0.032072	-1.335278	-0.856101
C	-0.155926	2.78662	-0.914499	C	-0.737318	1.226986	-1.751752
C	-1.113991	0.895074	0.264277	C	0.356911	1.532347	-0.794965
Co	1.084223	-0.232999	0.149554	C	-1.257076	2.384823	-2.568986
C	-1.1548	2.69789	-1.866398	C	0.491583	2.855904	-0.330248
H	0.613411	3.553515	-0.994661	C	1.414998	0.620448	-0.503335
C	-2.160254	1.739905	-1.745593	Co	-1.310129	-0.203762	-0.058948
H	-1.173094	3.392599	-2.703766	C	1.616819	3.249692	0.375507
C	-2.180794	0.84305	-0.674257	H	-0.295821	3.579892	-0.526595
H	-2.959336	1.715305	-2.482436	C	2.594583	1.03953	0.154011
C	-3.313034	-0.071995	-0.497482	C	1.173069	-0.775399	-0.83167
C	-1.061077	-0.147248	1.320179	C	-2.595917	0.611139	1.318339
N	-0.026001	-0.815339	1.571078	C	-2.457066	-1.611203	0.807319
C	1.128549	-2.153241	-0.734094	C	2.661843	2.366451	0.60811
C	2.036314	-0.27204	-1.731038	H	1.690721	4.273707	0.736833
C	1.691522	1.00286	1.457145	H	3.540192	2.716612	1.141269
S	-2.642657	-0.458943	2.159936	C	3.728531	0.136208	0.364945
C	2.328986	-1.765146	-0.011603	C	3.852684	-1.055836	-0.269714
C	0.933985	-1.218601	-1.759447	C	4.831688	0.616113	1.268784

C	0.208321	-3.248688	-0.325352	S	2.609446	-1.772763	-1.283808
C	2.935502	-0.659344	-0.717863	C	-1.351356	-1.280843	1.704193
C	2.209998	0.870688	-2.669867	C	-1.450202	0.082387	2.029277
C	2.87693	-2.498246	1.160363	C	-0.277136	-2.229519	2.107336
C	4.238106	0.002712	-0.426915	C	-3.276772	-0.449862	0.660196
H	3.674336	-1.933869	1.655213	C	-2.998019	2.046433	1.318711
H	2.087616	-2.670893	1.901692	C	-2.168604	-0.6182	-2.90111
H	3.286799	-3.474057	0.866861	C	-2.670708	-2.956226	0.208745
C	-0.205239	-1.146547	-2.713964	C	-0.497015	0.904375	2.82654
H	0.170734	-3.334761	0.765596	H	-0.069459	-2.944126	1.303818
H	-0.817092	-3.052018	-0.661083	H	0.662775	-1.704164	2.317472
H	0.523972	-4.216375	-0.73653	H	-0.558267	-2.796061	3.004924
H	0.095578	-1.489226	-3.713306	C	-4.524614	-0.31367	-0.14286
H	-1.045295	-1.76779	-2.384895	H	-3.598414	2.296382	2.204217
H	-0.57645	-0.118353	-2.817126	H	-2.118319	2.701646	1.327485
H	2.6747	0.548155	-3.611984	H	-3.595656	2.298793	0.434079
H	1.247532	1.335015	-2.916778	H	-3.496674	-2.951785	-0.511232
H	2.847129	1.648797	-2.232794	H	-1.765231	-3.279368	-0.320108
H	4.716994	-0.417035	0.463409	H	-2.900072	-3.708243	0.975492
H	4.934538	-0.129808	-1.264731	H	-4.680888	-1.179343	-0.796294
H	4.115112	1.081335	-0.26456	H	-5.412733	-0.224095	0.496479
C	-3.640325	-0.600978	0.709456	H	-4.492724	0.579509	-0.781767
C	-4.898903	-1.374359	0.97693	H	-0.949035	1.251574	3.765735
C	-4.201035	-0.309106	-1.691373	H	0.403791	0.336606	3.081679
H	-3.608015	-0.440883	-2.604695	H	-0.174387	1.79504	2.268739
H	-4.808151	-1.210007	-1.574768	C	5.071001	-1.933845	-0.182388
H	-4.889685	0.5287	-1.875526	H	5.993946	-1.365419	-0.3401
H	-5.740846	-1.019673	0.374779	H	5.140899	-2.425024	0.797026
H	-4.756025	-2.444044	0.772599	H	5.039708	-2.727397	-0.936157
H	-5.185982	-1.291523	2.031192	H	4.428406	0.981545	2.221569
C	2.682673	0.766946	2.533013	H	5.545693	-0.175993	1.503792
C	0.978504	3.413316	1.924823	H	5.396942	1.446616	0.822323
H	1.17554	4.236209	1.223827	H	-2.012515	-0.180664	-3.896249
H	0.020156	3.637281	2.41373	H	-1.884995	-1.678155	-2.943212
H	1.763082	3.439145	2.688036	H	-3.240401	-0.585808	-2.662498
H	2.766739	1.616667	3.225222	H	-1.947067	3.013213	-1.987362
H	2.382687	-0.113706	3.117667	H	-0.43915	3.029872	-2.914138
H	3.684963	0.561141	2.135708	H	-1.813399	2.026273	-3.441294

N

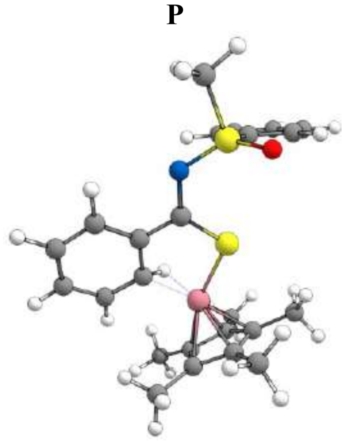
O

Thermal correction to Gibbs Free Energy=

 Thermal correction to Gibbs Free Energy= 0.402170 E(RM06) = -1569.00698176 E(SCRF) = -1569.03058325				0.201764 E(RM06) = -1033.24426264 E(SCRF) = -1033.26316370			
C	-1.015251	0.83156	-1.834228	C	1.453905	2.411831	0.000021
N	-0.209471	-0.276278	-1.875294	C	0.286007	3.130383	0.000037
C	-0.777775	1.798698	-0.797849	C	-0.960439	2.493756	0.000025
C	0.609686	2.023336	-0.358869	C	-1.063938	1.108883	0.000007
C	-1.729061	2.948709	-0.634589	C	0.151955	0.349886	0.000008
C	1.101899	3.234683	0.114708	C	1.429857	0.996158	0.000004
C	1.447995	0.894491	-0.398331	C	-2.38483	0.478273	-0.00002
Co	-1.138096	-0.128627	-0.142326	C	-2.572615	-0.861564	-0.000001
C	2.419617	3.306133	0.566317	S	-1.284266	-2.047371	0.00007
H	0.466159	4.116263	0.147983	C	0.184021	-1.067498	0.000009
C	2.779589	0.952324	0.042069	C	-3.578732	1.392006	-0.00007
C	0.753465	-0.299986	-0.887853	C	-3.91995	-1.531771	-0.000029
C	-1.835974	0.101736	1.76361	N	1.271145	-1.796979	-0.000013
C	-2.853524	-1.370153	0.272089	C	2.475292	-1.178569	-0.00003
C	3.238917	2.192006	0.532142	C	2.615559	0.196944	-0.000016
H	2.806131	4.244542	0.958279	C	3.632794	-2.130861	-0.00004
H	4.255361	2.280833	0.904104	C	3.989995	0.807673	-0.000011
C	3.669819	-0.212881	0.024802	H	2.400482	2.944029	0.000025
C	3.253757	-1.445338	-0.341021	H	0.324631	4.21872	0.000056
C	5.098178	0.003811	0.440053	H	-1.853774	3.110934	0.00003
S	1.626081	-1.85853	-0.872637	H	-4.524713	0.845054	-0.000107
C	-1.635631	-1.950042	0.727011	H	-3.58145	2.046826	0.883109
C	-1.029844	-1.061643	1.693487	H	-3.581376	2.046833	-0.883242
C	-1.156002	-3.304965	0.329475	H	-3.824724	-2.623881	-0.000046
C	-2.960615	-0.084951	0.863125	H	-4.505665	-1.257059	0.88671
C	-1.563081	1.293086	2.618879	H	-4.505635	-1.257032	-0.886779
C	-2.104409	0.905121	-2.854452	H	4.608595	-1.637542	-0.000215
C	-3.763291	-1.980323	-0.738262	H	3.574641	-2.785946	0.878768
C	0.240837	-1.288881	2.436926	H	3.574431	-2.786168	-0.878667
H	-1.123493	-3.413033	-0.762845	H	3.977081	1.899903	-0.000005
H	-0.150327	-3.511053	0.706904	H	4.567217	0.499457	0.882252
H	-1.828523	-4.082298	0.717461	H	4.567216	0.499472	-0.882281
C	-4.105302	0.855122	0.690937				
H	-1.770252	1.087956	3.677641				

H	-0.513995	1.609692	2.538986	
H	-2.181567	2.14886	2.326237	
H	-4.488797	-1.255	-1.122493	
H	-3.197991	-2.367202	-1.5964	
H	-4.331847	-2.82203	-0.318643	
H	-4.455288	0.891189	-0.348688	
H	-4.959806	0.545636	1.307653	
H	-3.847662	1.876756	0.988118	
H	0.067847	-1.803682	3.391603	
H	0.943862	-1.896173	1.853111	
H	0.740645	-0.337107	2.656068	
C	4.131173	-2.66827	-0.356379	
H	4.931698	-2.57528	-1.100433	
H	4.597843	-2.84166	0.620001	
H	3.559603	-3.567727	-0.608558	
H	5.171894	0.310708	1.492453	
H	5.707706	-0.893756	0.32022	
H	5.567478	0.79725	-0.156075	
H	-1.830975	1.586437	-3.671062	
H	-2.272636	-0.090005	-3.2776	
H	-3.045225	1.270421	-2.42919	
H	-1.722449	3.320341	0.398272	
H	-1.449827	3.793998	-1.282065	
H	-2.758992	2.6782	-0.881766	

P



Thermal correction to Gibbs Free Energy= 0.366716
E(RM06) = -2003.00239782
E(SCRF) = -2003.03638881

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C	-1.351193	1.472449	-0.731329	
C	-2.35609	2.349453	-1.228122	
C	-2.186302	3.714552	-1.24105	
C	-0.968757	4.2926	-0.823692	
C	0.054171	3.482008	-0.391987	
H	-0.839715	5.371906	-0.855177	
C	-0.116252	2.082525	-0.319806	
H	-2.991779	4.355123	-1.596091	

H	-3.278377	1.922559	-1.61799	
Co	-1.676986	-0.351834	-0.096816	
C	0.889466	1.228178	0.212505	
C	-2.645315	-1.113089	1.529574	
C	-3.603347	-0.881824	-0.546357	
C	-2.184228	-2.200834	0.68373	
C	-2.8052	-2.075723	-0.579753	
C	-1.242148	-3.273945	1.11118	
C	-3.5636	-0.330058	0.778997	
C	-2.261005	-0.910524	2.955227	
C	-4.309669	0.87143	1.24526	
C	-4.463931	-0.413676	-1.672651	
C	-2.652142	-2.9693	-1.762256	
H	-5.38484	0.666784	1.340046	
H	-3.949689	1.206291	2.223468	
H	-4.191354	1.716364	0.553547	
H	-5.233893	-1.159552	-1.912758	
H	-4.983154	0.517983	-1.422391	
H	-3.885814	-0.240454	-2.590492	
H	-3.482148	-3.687072	-1.835853	
H	-2.6358	-2.395221	-2.69611	
H	-1.72195	-3.545823	-1.717114	
H	-0.747718	-3.739633	0.25118	
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H	-1.233083	-1.237521	3.144029	
H	-2.316534	0.146381	3.238026	
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N	2.146446	1.757114	0.418029	
S	3.308699	0.871684	0.978736	
O	3.30928	0.281388	2.322998	
H	4.78386	2.335737	-0.179425	
C	4.67666	2.00277	0.854711	
H	4.443861	2.846873	1.508102	
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H	4.263829	-1.785241	1.374619	
C	4.554711	-2.626958	-0.60636	
H	4.91472	-3.586064	-0.242643	
C	4.43529	-2.397987	-1.973867	
H	4.705944	-3.181125	-2.678018	
H	3.861537	-1.008067	-3.517649	
C	3.963693	-1.1759	-2.448589	
C	3.610458	-0.172928	-1.555015	
H	3.213691	0.778739	-1.904494	

The coordinates of all computed species are provided in Table S4 and in a separate file that allow direct visualization: DFT.xyz.

References

1. B. Sun, T. Yoshino, S. Matsunaga and M. Kanai, *Adv. Synth. Catal.,* 2014, **356**, 1491-1495

2. (a) M. R. Yadav, R. K. Rit and A. K. Sahoo, *Chem. Eur. J.,* 2012, **18**, 5541-5545; (b) M. Shankar, K. Ghosh, K. Mukherjee, R. K. Rit and A. K. Sahoo, *Org. Lett.*, 2018, **20**, 5144; (c) M. Shankar, R. K. Rit, S. Sau, K. Mukherjee, V. Gandon and A. K. Sahoo, *Chem. Sci.,* 2020, **11**, 10770.

3. (a) M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth and P. A. Grieco, *Org. Lett.,* **2002**, **4**, 3199-3202; (b) S. Dutta, R. K. Mallick, R. Prasad, V. Gandon and A. K. Sahoo, *Angew. Chem., Int. Ed.,* 2019, **58**, 2289.

4. (a) T. Ozturk, E. Ertas and O. Mert, *Chem. Rev.*, 2007, **107**, 5210–5278; (b) K. Vogerl, N. Ong, J. Senger, D. Herp, K. Schmidtkunz, M. Marek, M. Muller, K. Bartel, T. B. Shaik, N. J. Porter, D. Robaa, D. W. Christianson, C. Romier, W. Sippl, M. Jung and F. Bracher, *J. Med. Chem.,* 2019, **62**, 1138–1166; (c) J.Z. Liu, S.E. Zhang, F. Nie, Y. Yang, Y.B. Tang, W. Yin, J.Y. Tian, F. Ye and Z. Xiao, Bioorg. *Med. Chem. Lett*, 2013, **23**, 6217-6222.

5. Bruker SMART V5.630 and SAINT-PLUS V6.45, Bruker-Nonius Analytical X-ray Systems Inc.: Madison, Wisconsin, USA 2003. SADABS, Empirical absorption correction program, Bruker AXS Inc., Madison, Wisconsin, USA, 1997.

6. G M, Sheldrick *Acta Crystallogr* 64A, **112**, 2008.

7. M. J. Frisch, *Gaussian 09*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.

8. Y. Zhao and D. G. Truhlar, *J. Chem. Phys.,* 2006, **125**, 194101.

9. A. D. MacLean and Chandler, G. S. *J. Chem. Phys.,*1980.**72**, 5639

10. T. H. Jr. Dunning and P. J. Hay, *Modern Theoretical Chemistry*; Schaeffer, H. F., III, Ed.; Plenum: New York, vol. **3** ,1997.

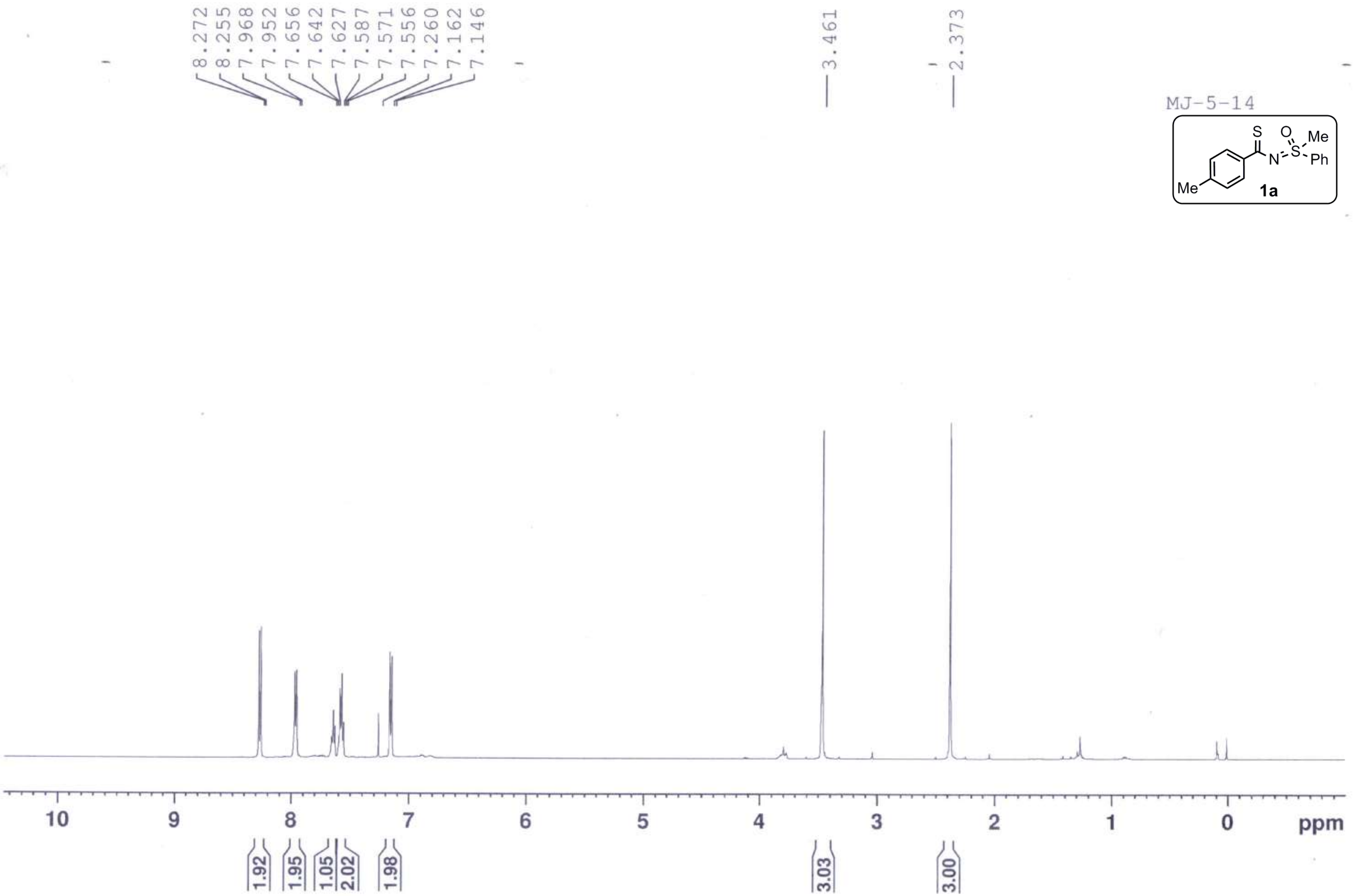
11. D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim. Acta*, 1990, **77**, 123–141.

12. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B.* 2009, **113**, 6378–6396.

13. V. Gandon, N. Agenet, K. P. C. Vollhardt, M. Malacria and C. Aubert, *J. Am. Chem. Soc.* 2006, **128**, 8509–8520

14. There is no spontaneous elimination of PhSOMe when the Cp^*Co^{2+} moiety is removed, nor when **G** or its free ligand are protonated.

15. V. S. Thirunavukkarasu and M. Donati and L. Ackermann, *Org. Lett.,* 2012, **14**, 3416–3419.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3.461
2.373
MJ-5-14
S
O
Me
N
S
Ph
Me
1a
10
9
8
7
6
5
4
3
2
1
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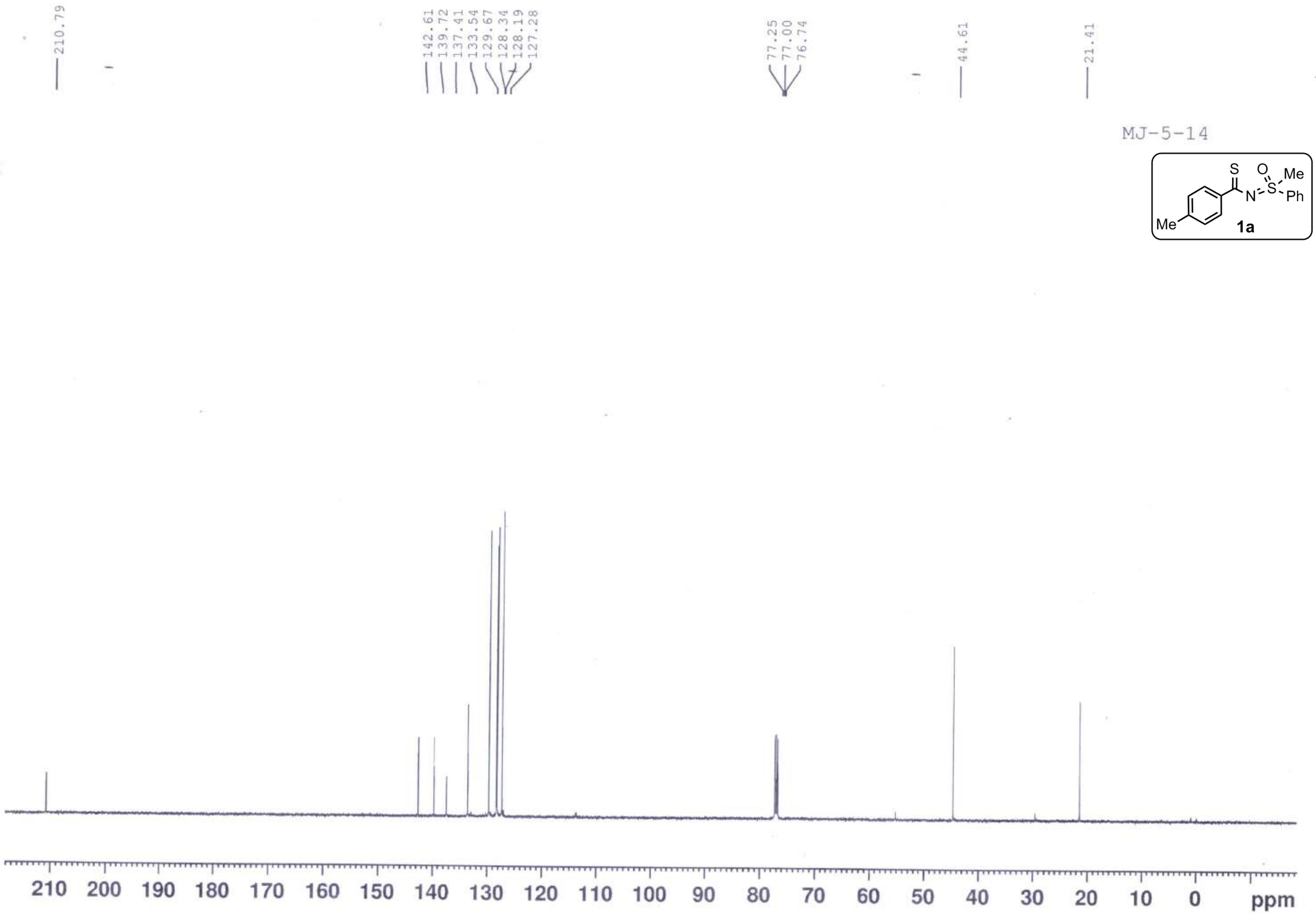
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44.61
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Me
N
S
Ph
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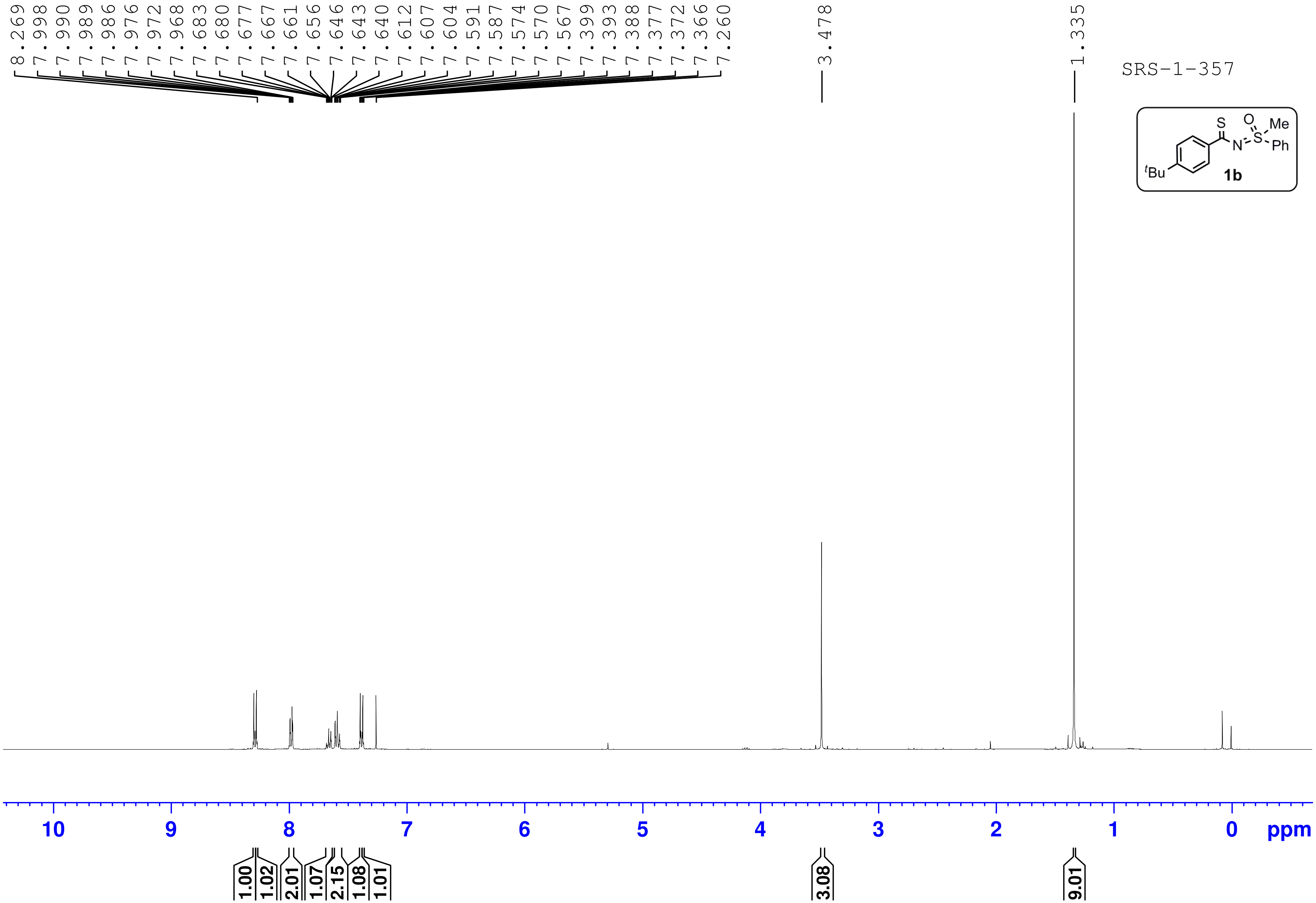
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1.335
SRS-1-357
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Me
N
S
Ph
tBu
1b
10
9
8
7
6
5
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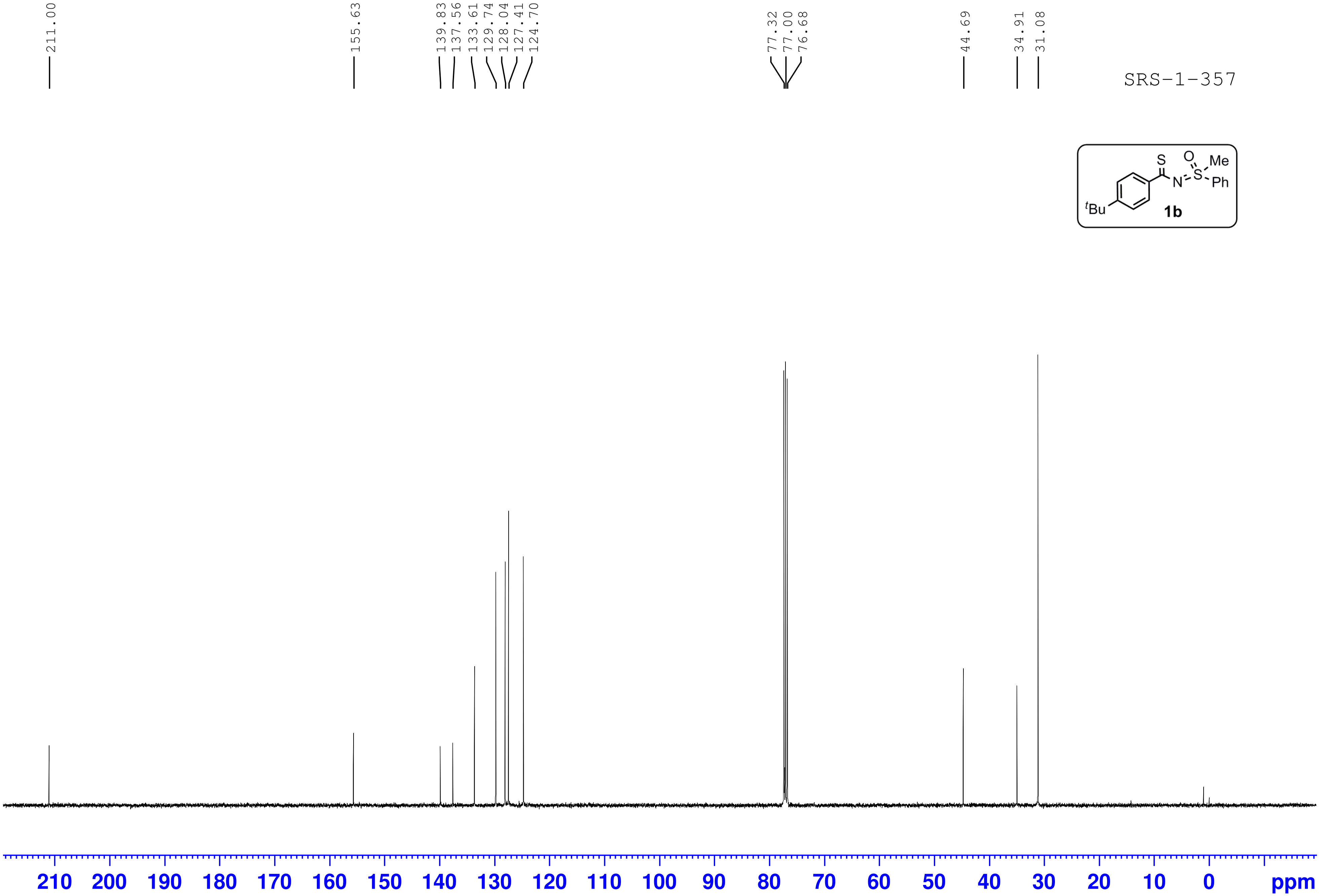
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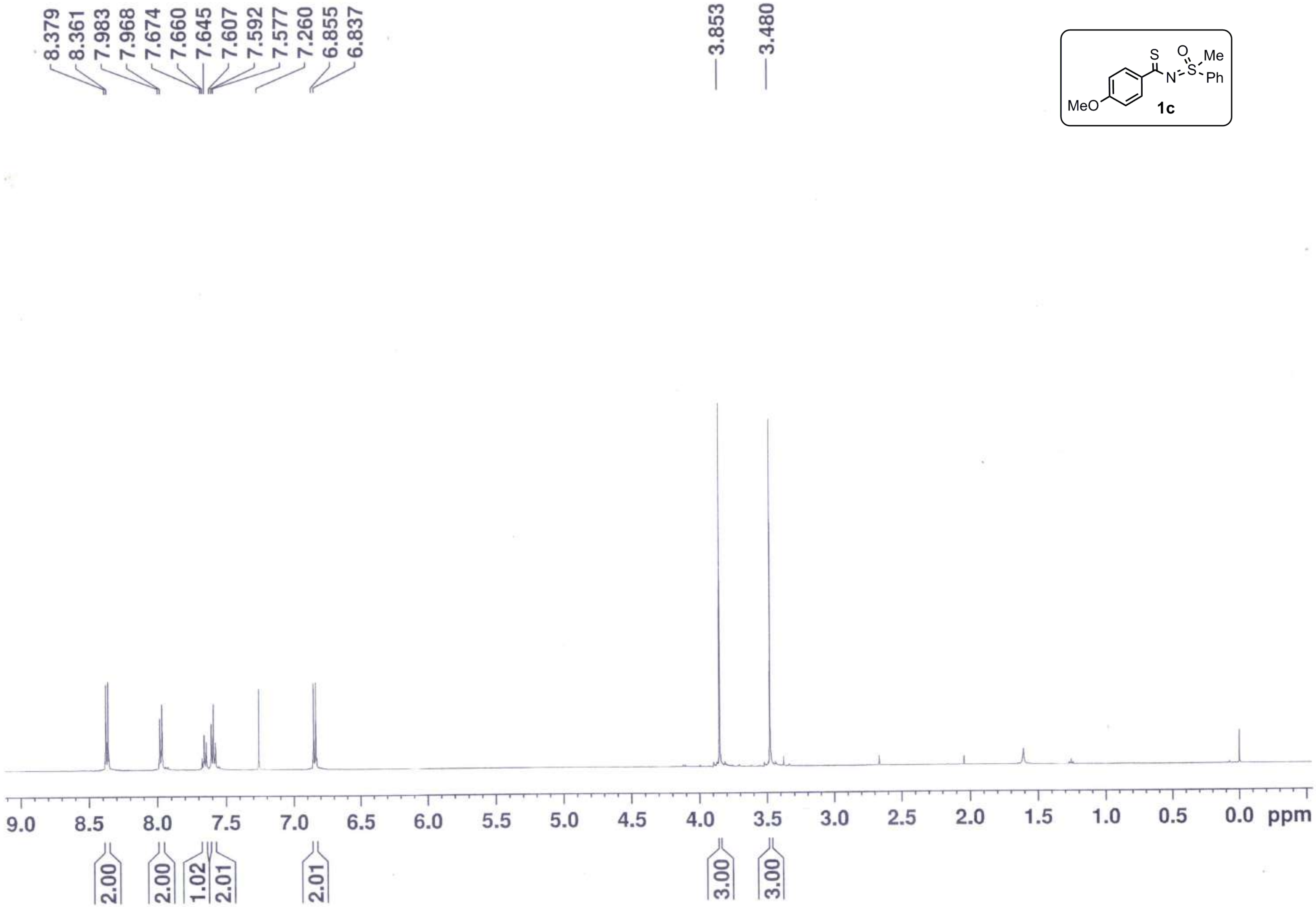
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3.853
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Me
N
S
Ph
MeO
1c
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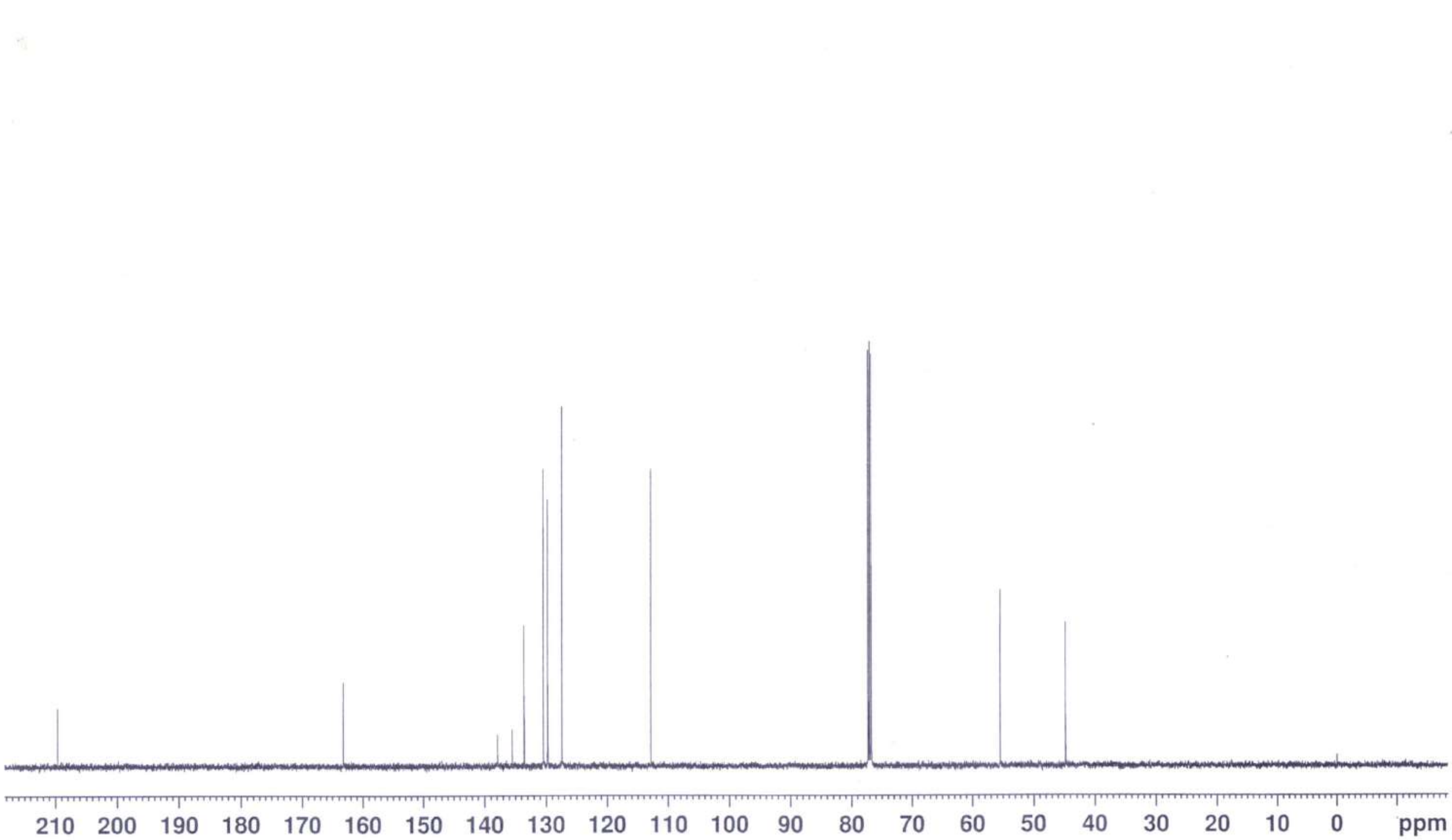
3.00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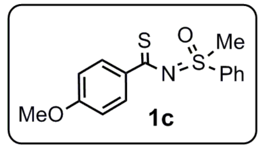
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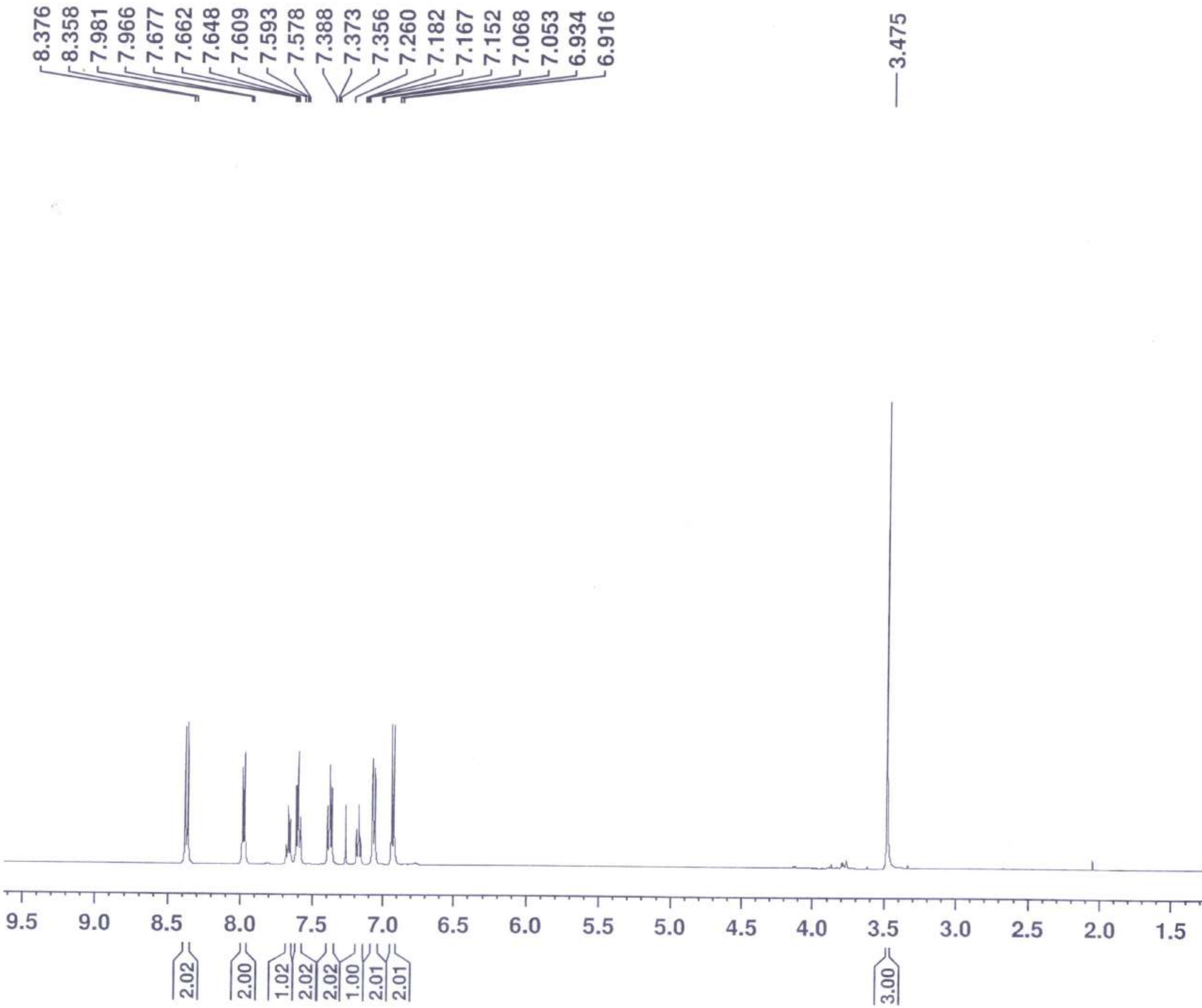
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6.916
3.475
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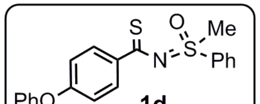

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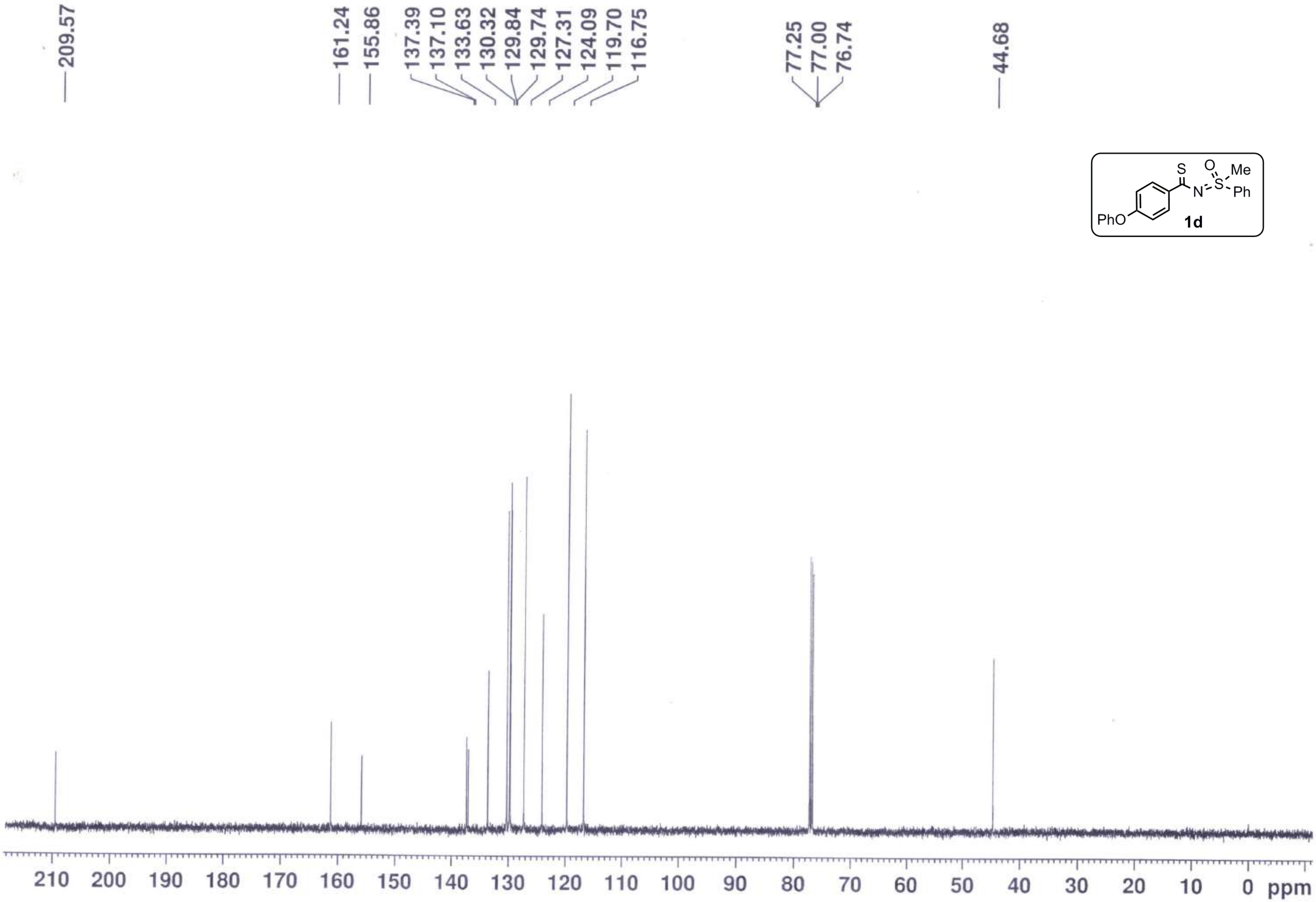
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77.00
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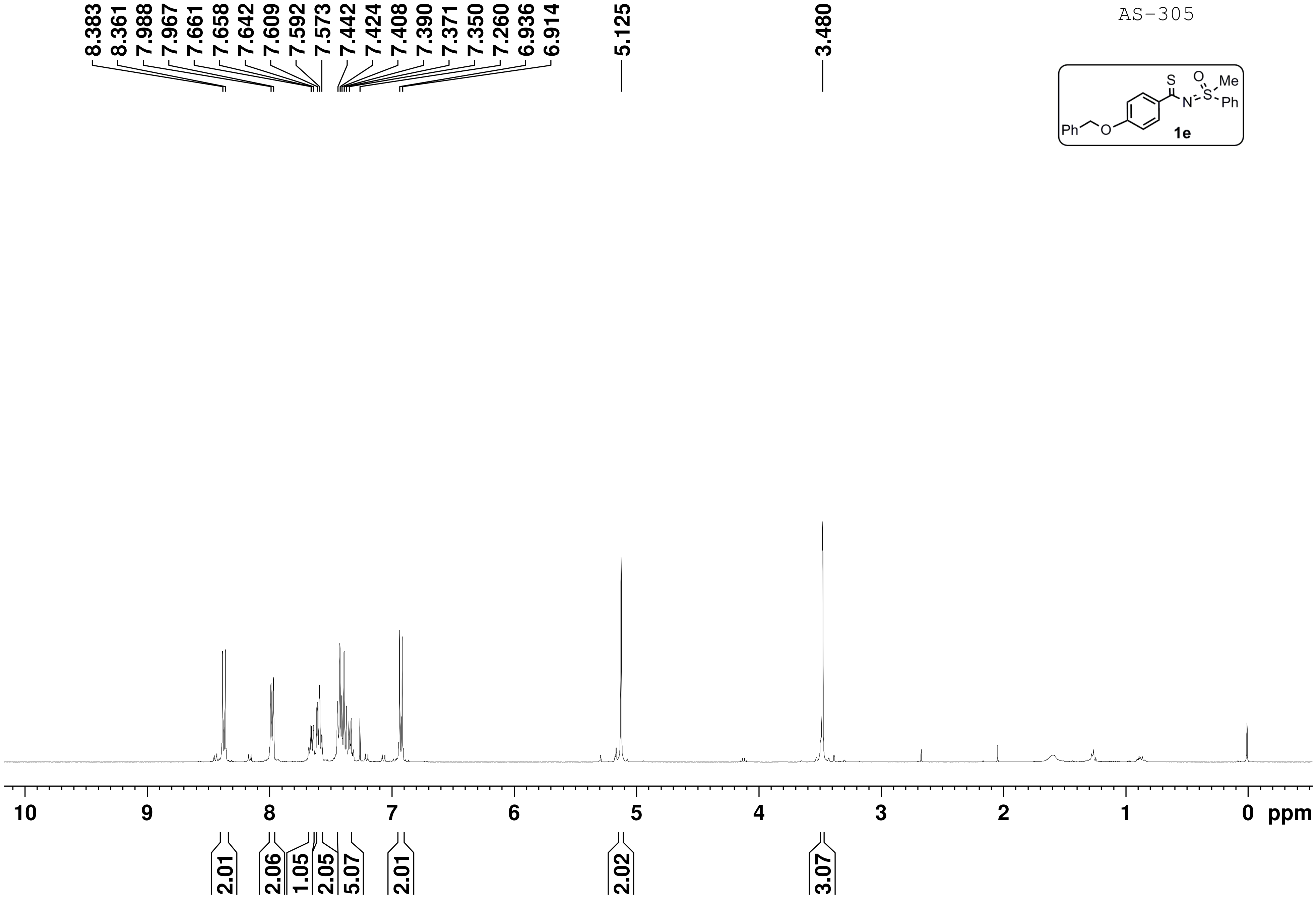
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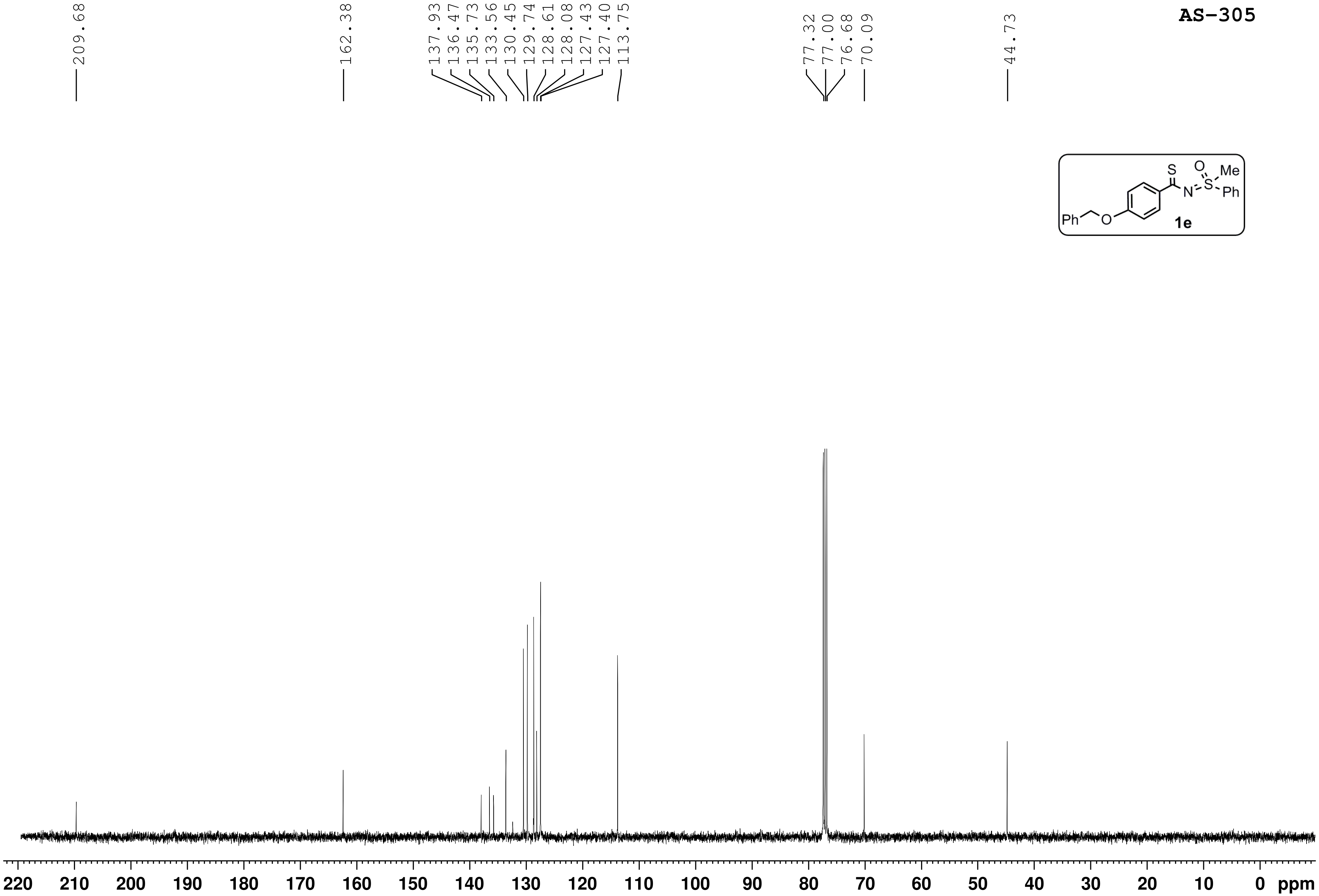
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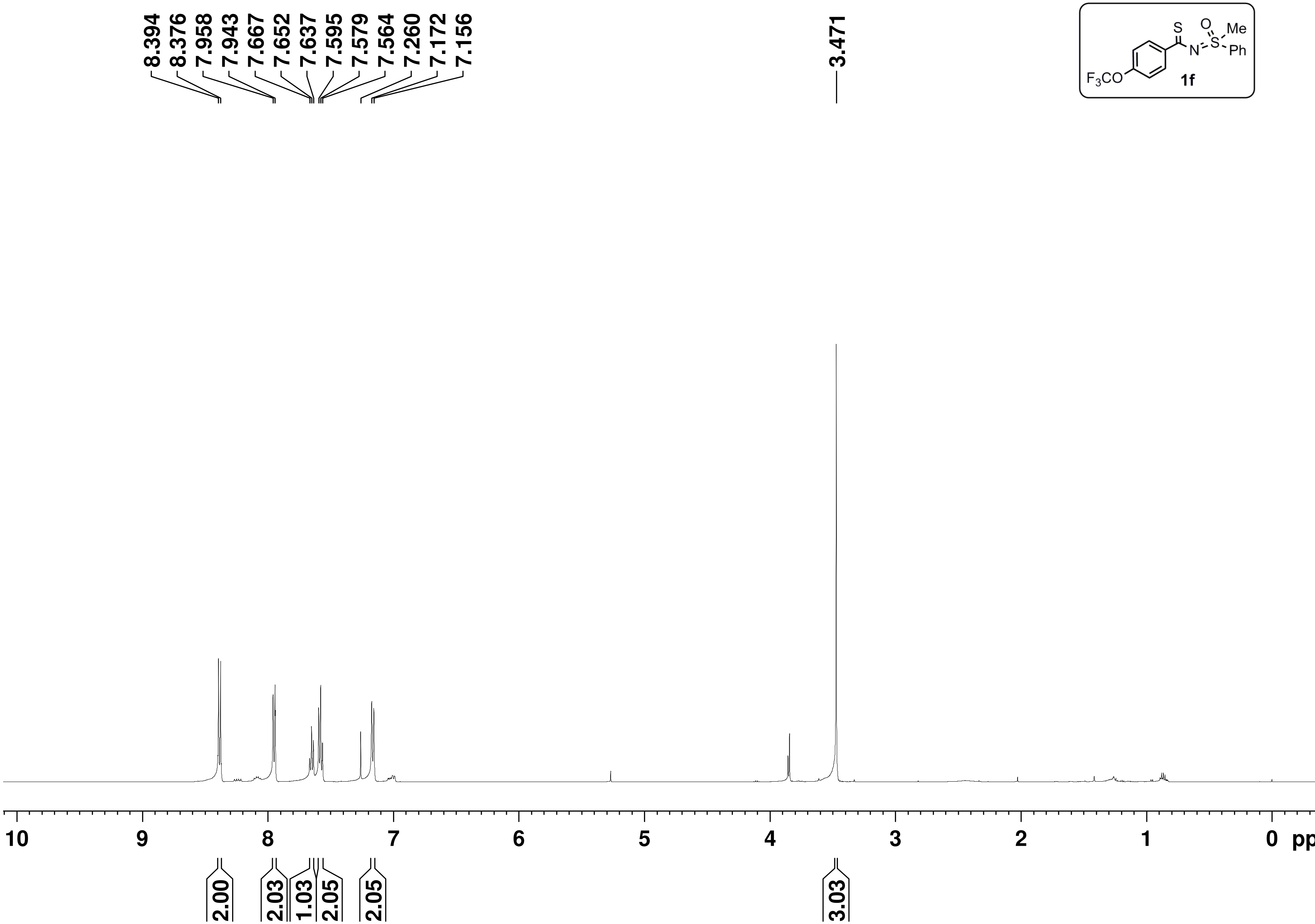
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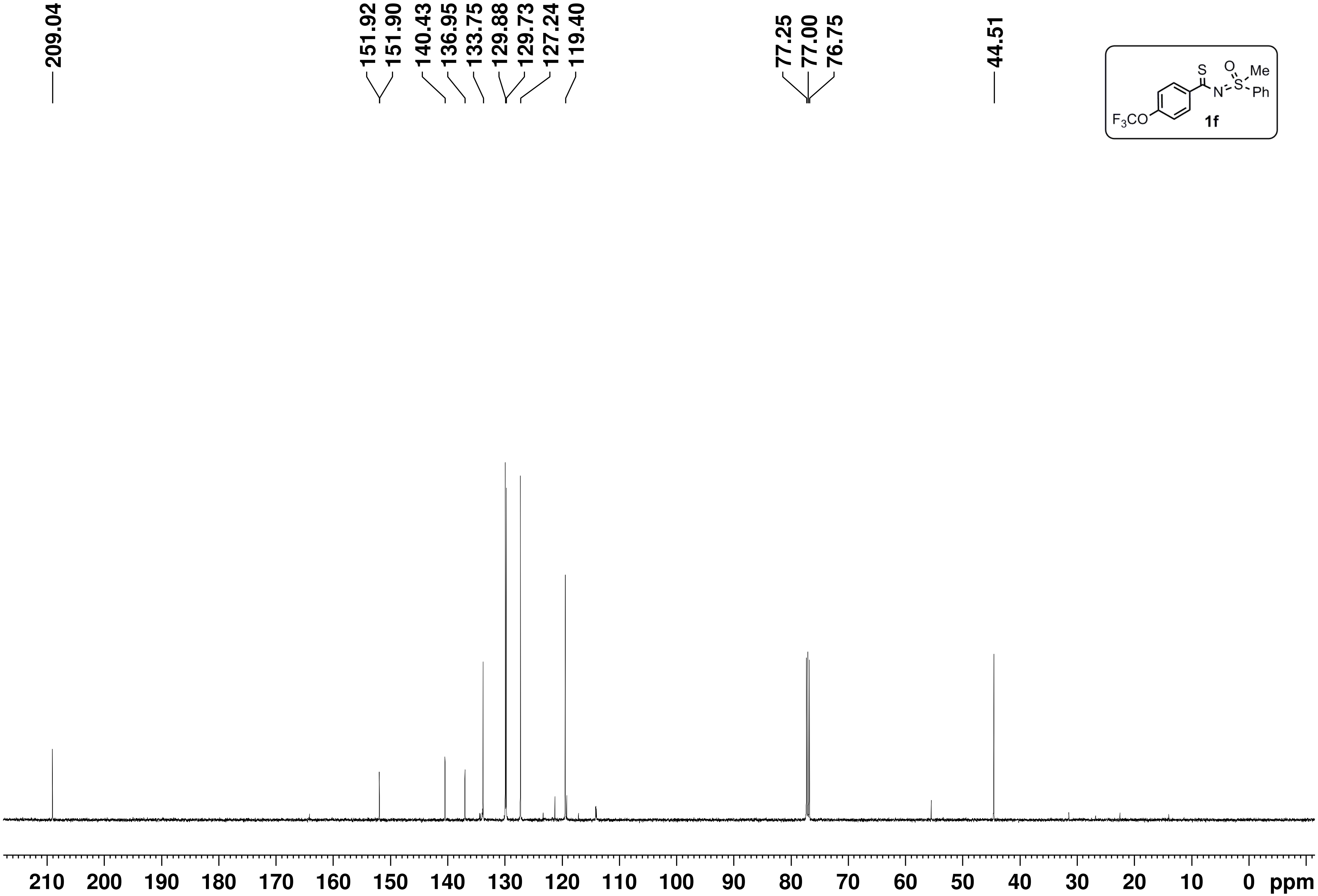
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44.51
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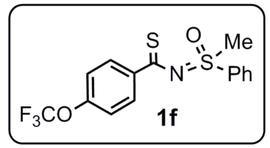
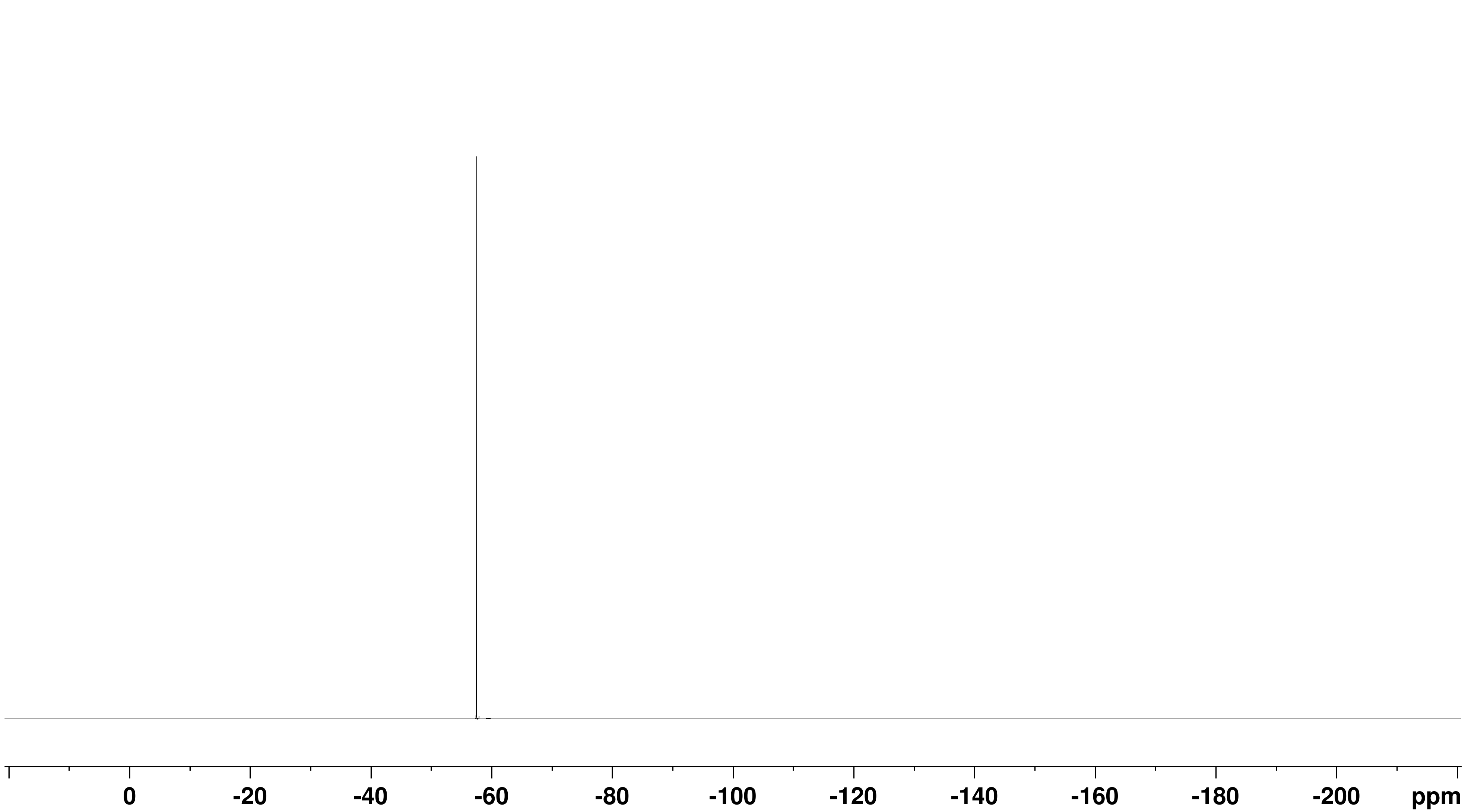
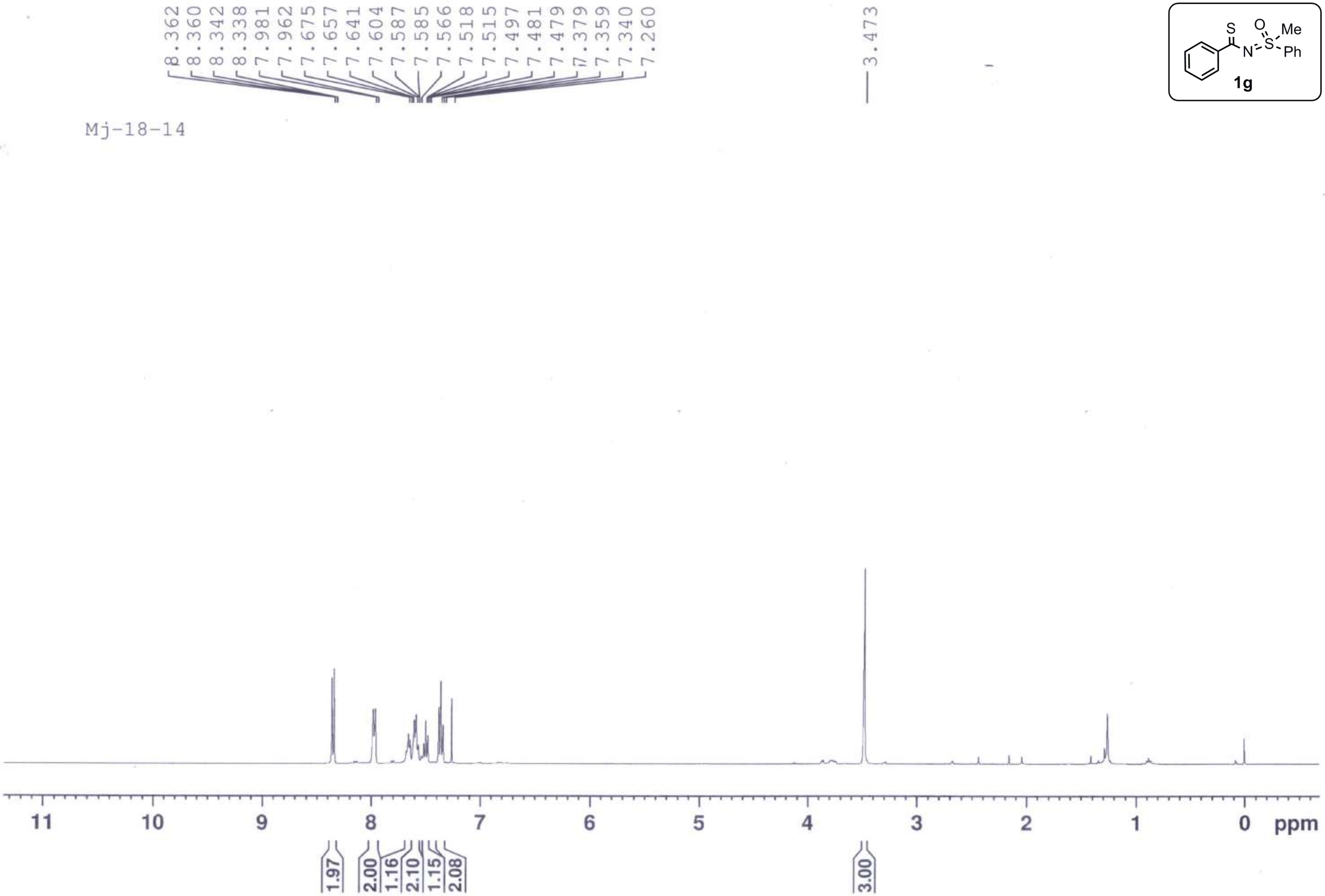
AS-OCF3



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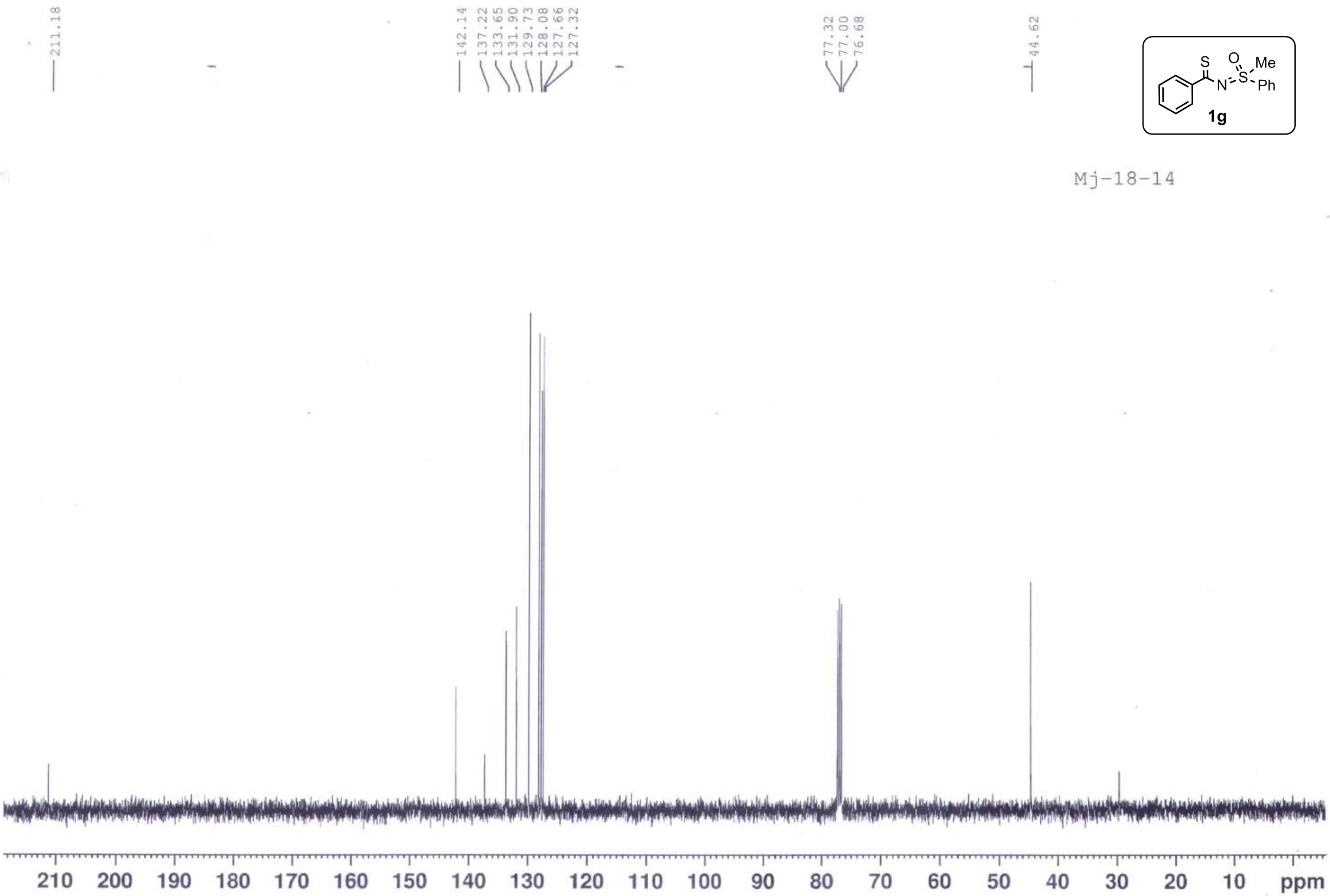

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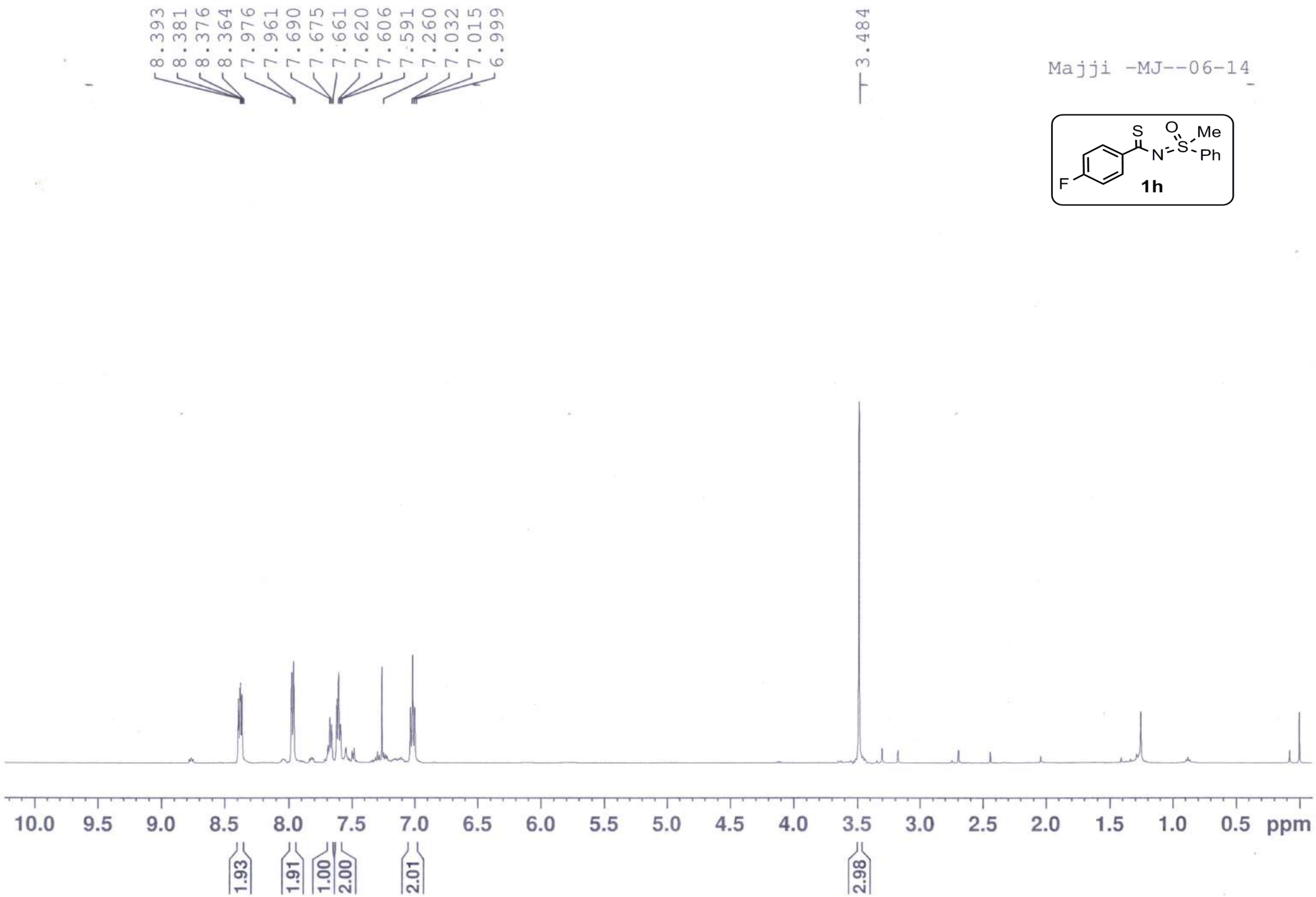
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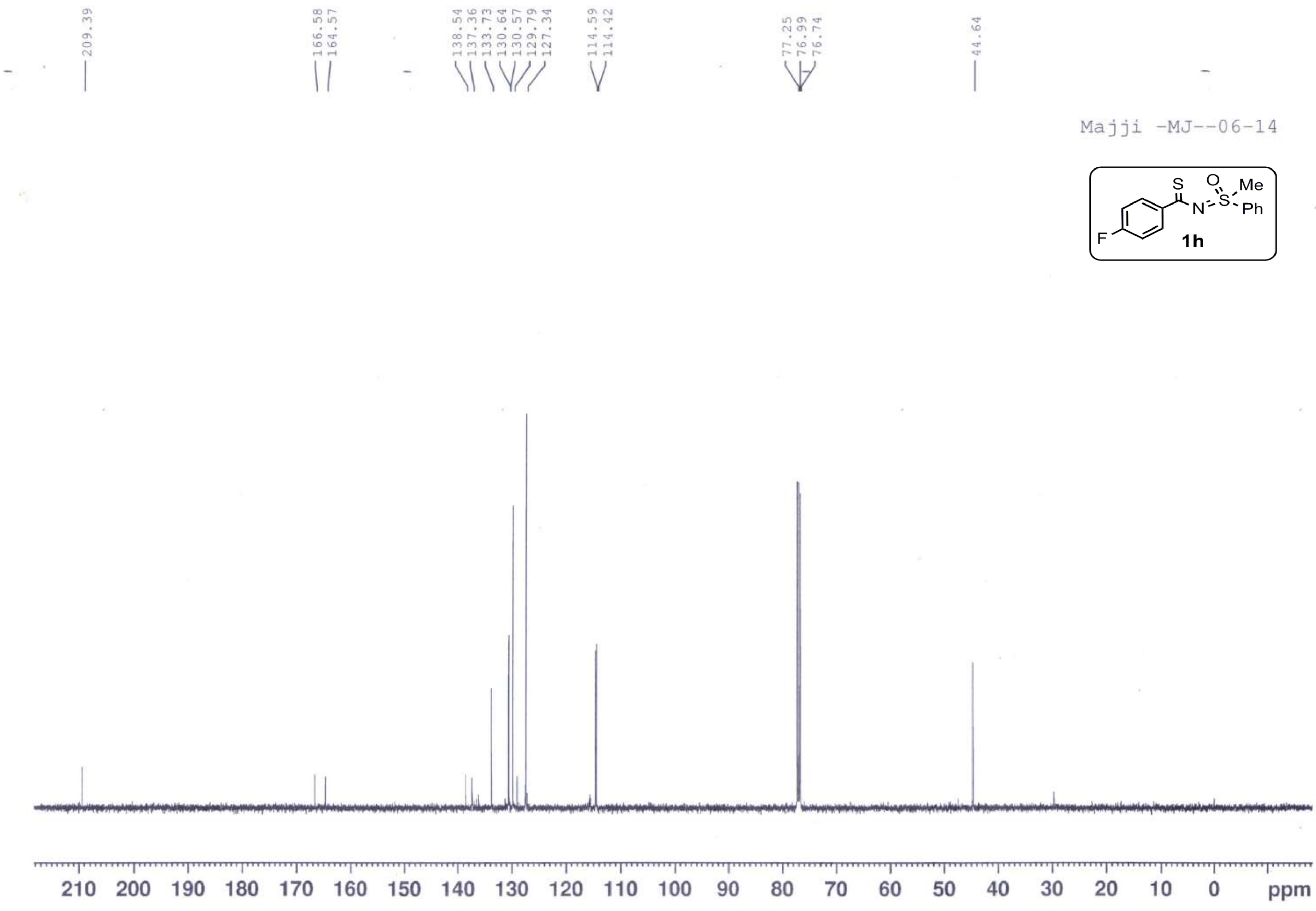
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76.99
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44.64
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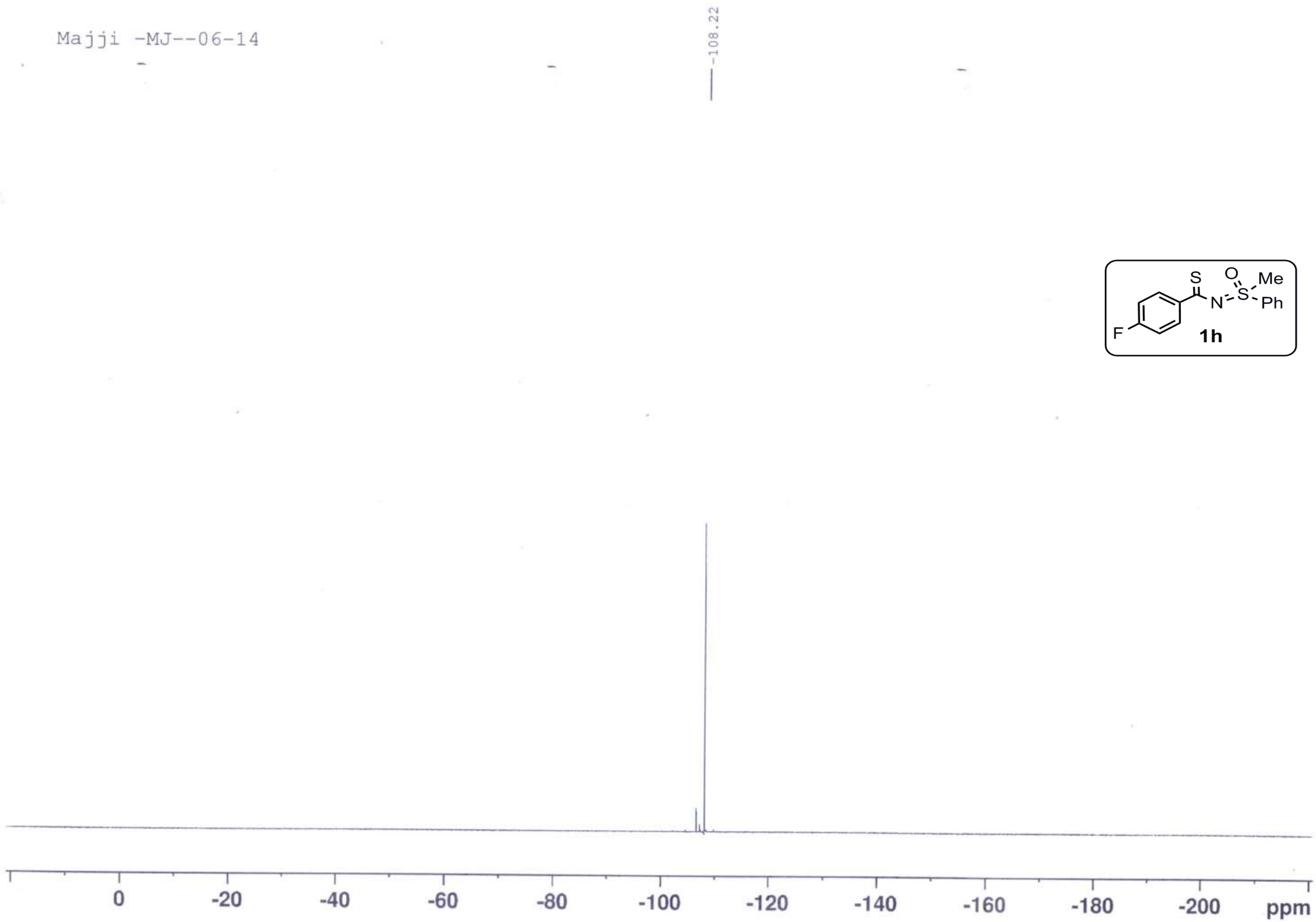
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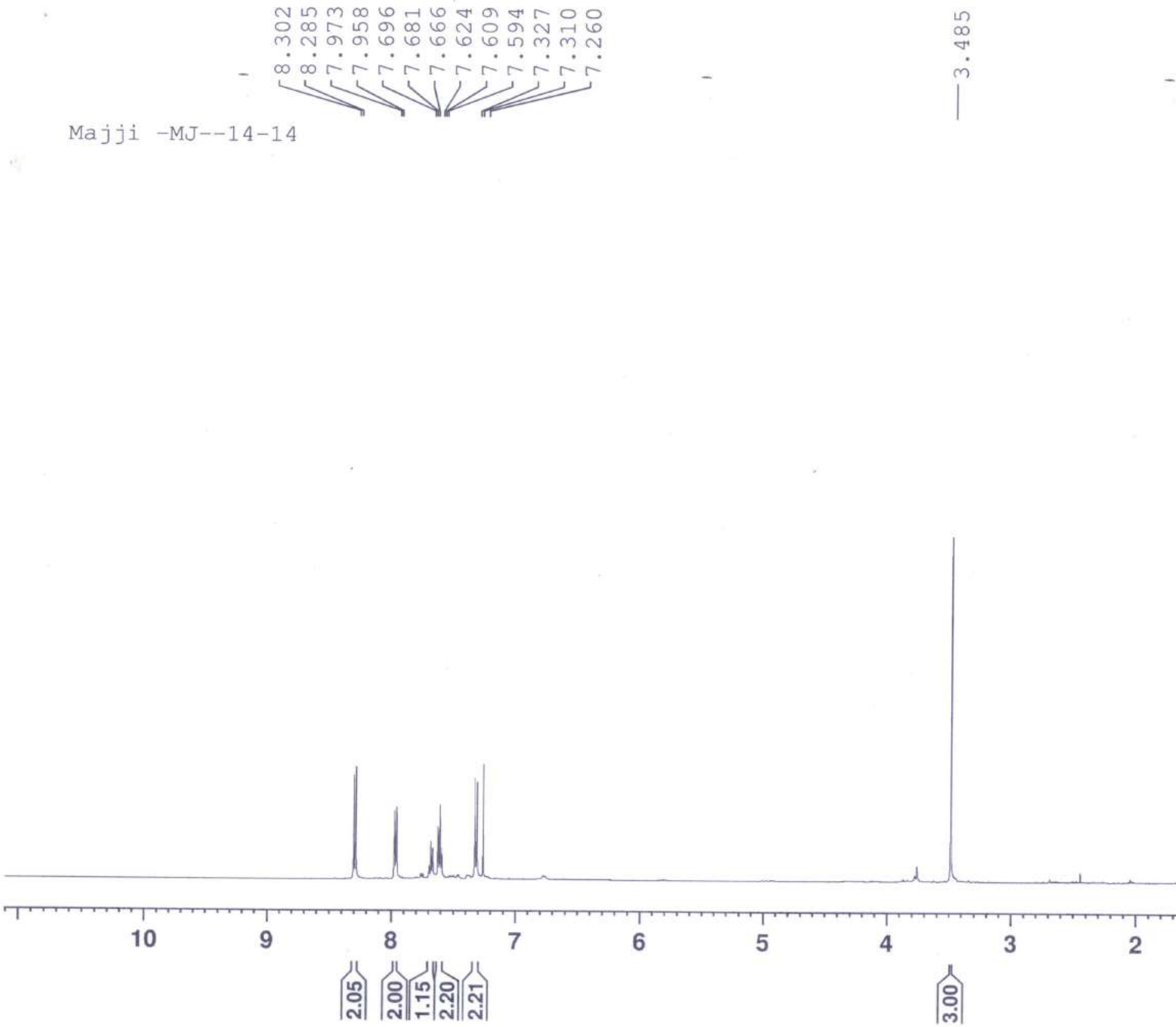

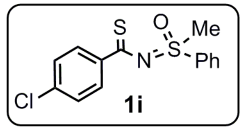

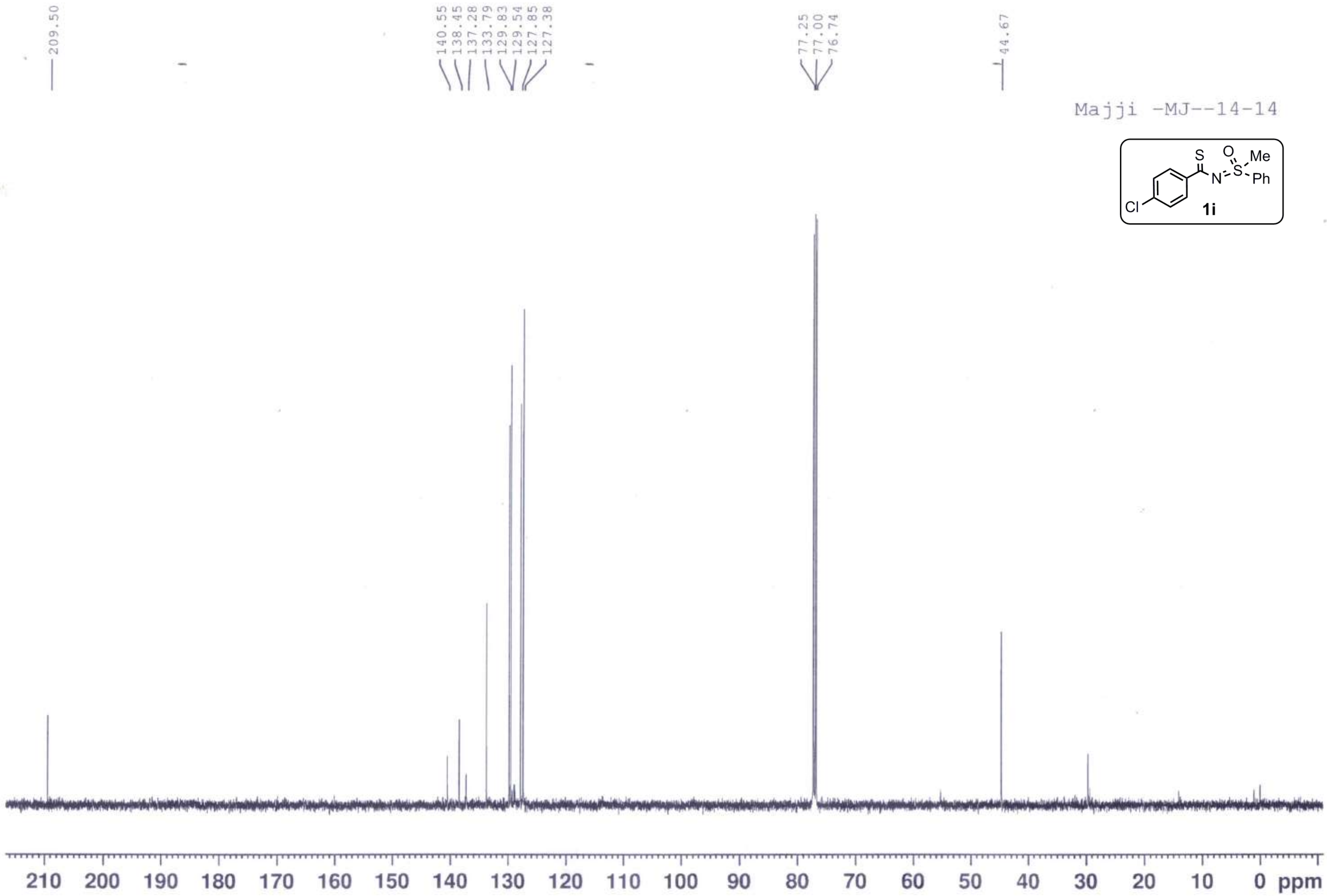
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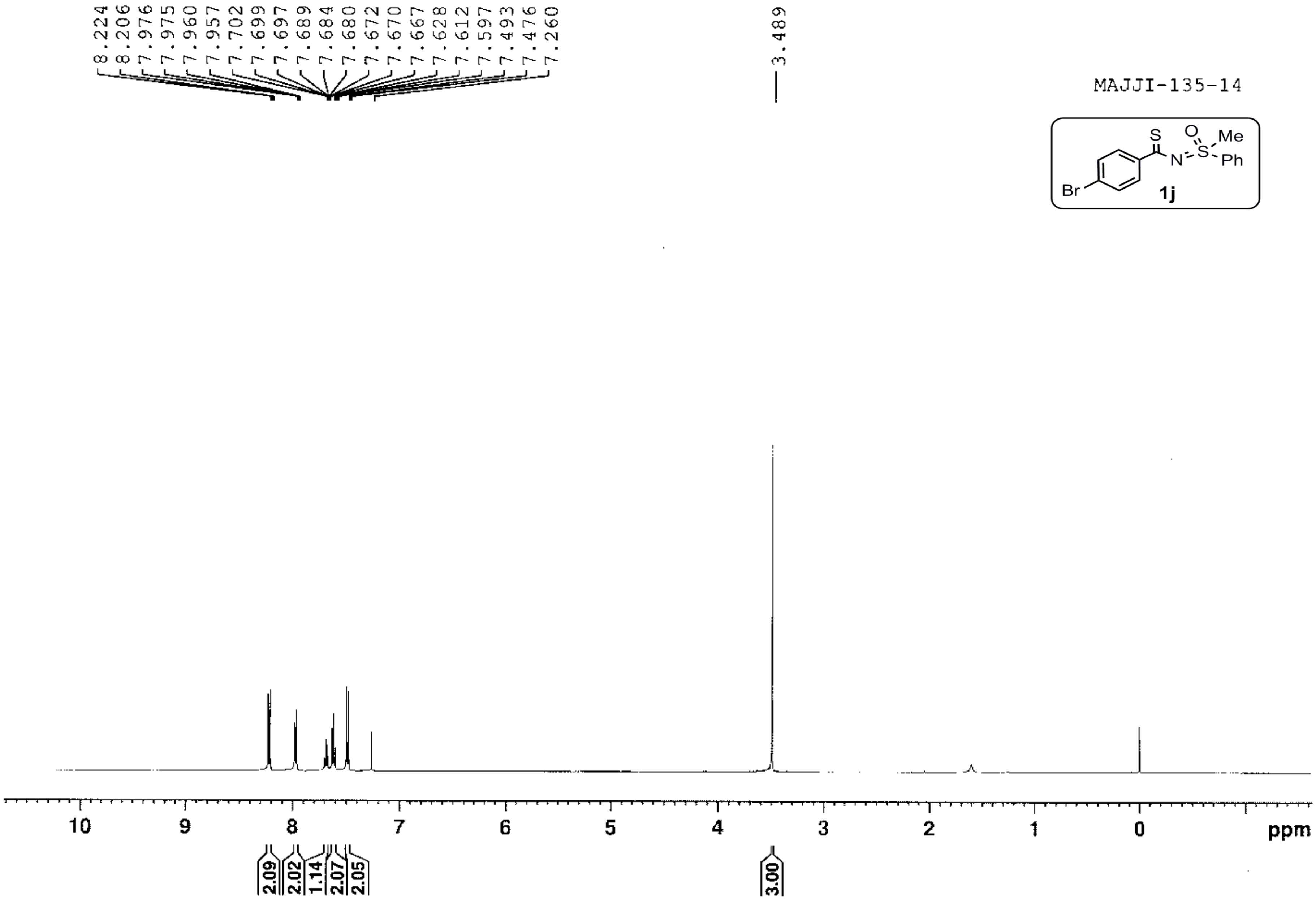
44.67
Majji -MJ--14-14
S
O
Me
N
S
Ph
Cl
1i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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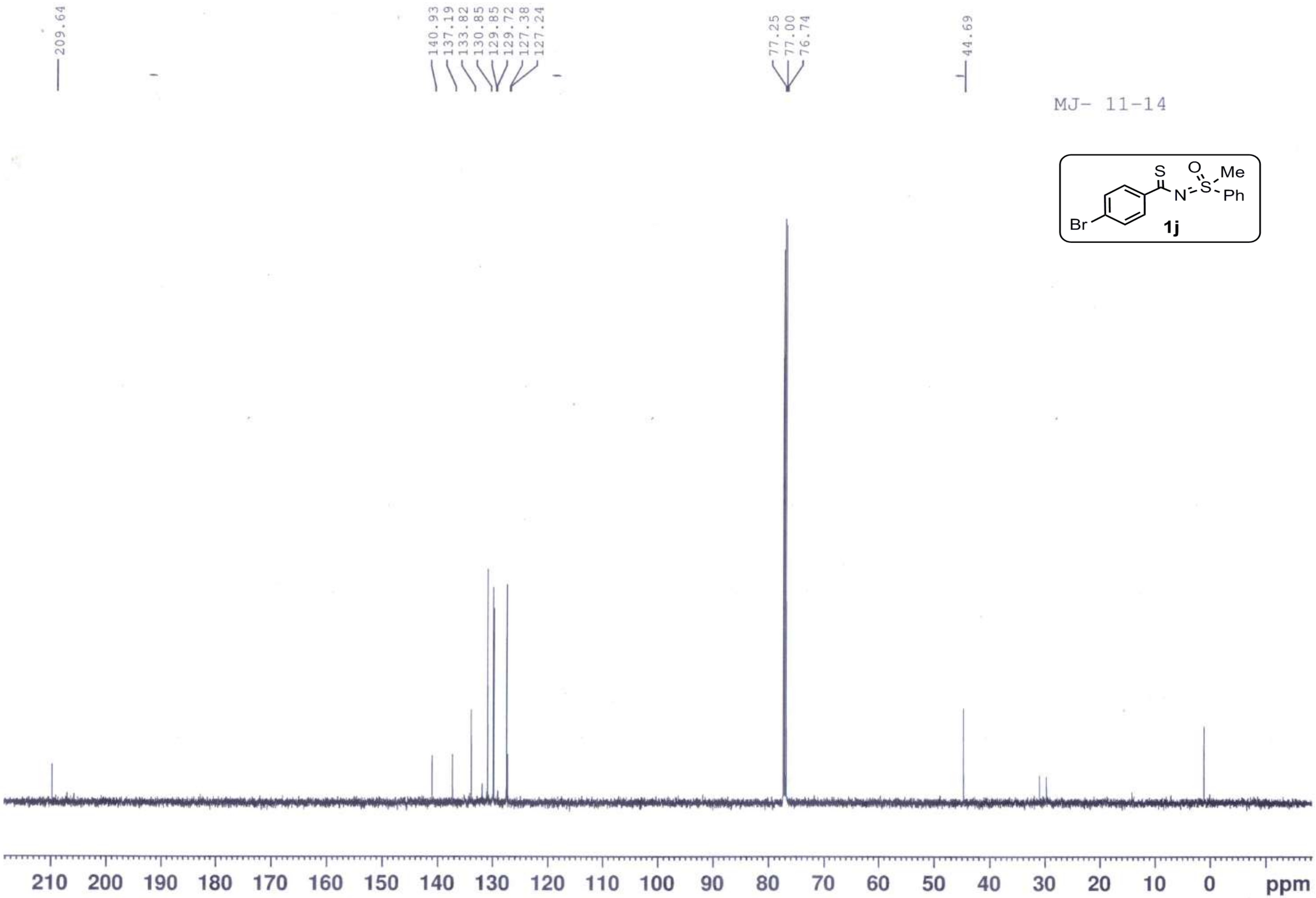
8.206
7.976
7.975
7.960
7.957
7.702
7.699
7.697
7.689
7.684
7.680
7.672
7.670
7.667
7.628
7.612
7.597
7.493
7.476
7.260
3.489
MAJJI-135-14
S
O
Me
N
S
Ph
Br
1j
10
9
8
7
6
5
4
3
2
1
0
ppm
2.09
2.02
1.14
2.07
2.05
3.00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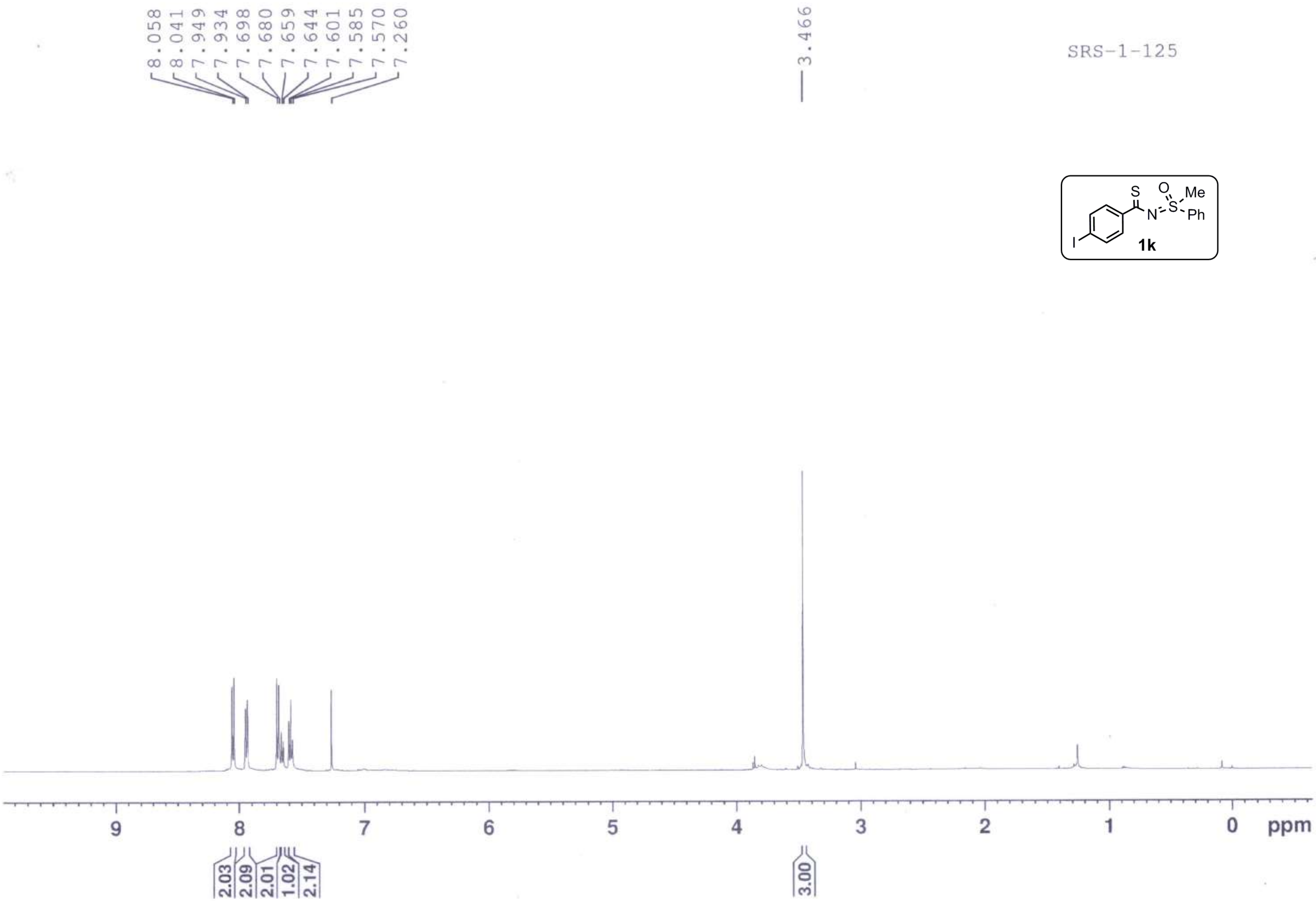
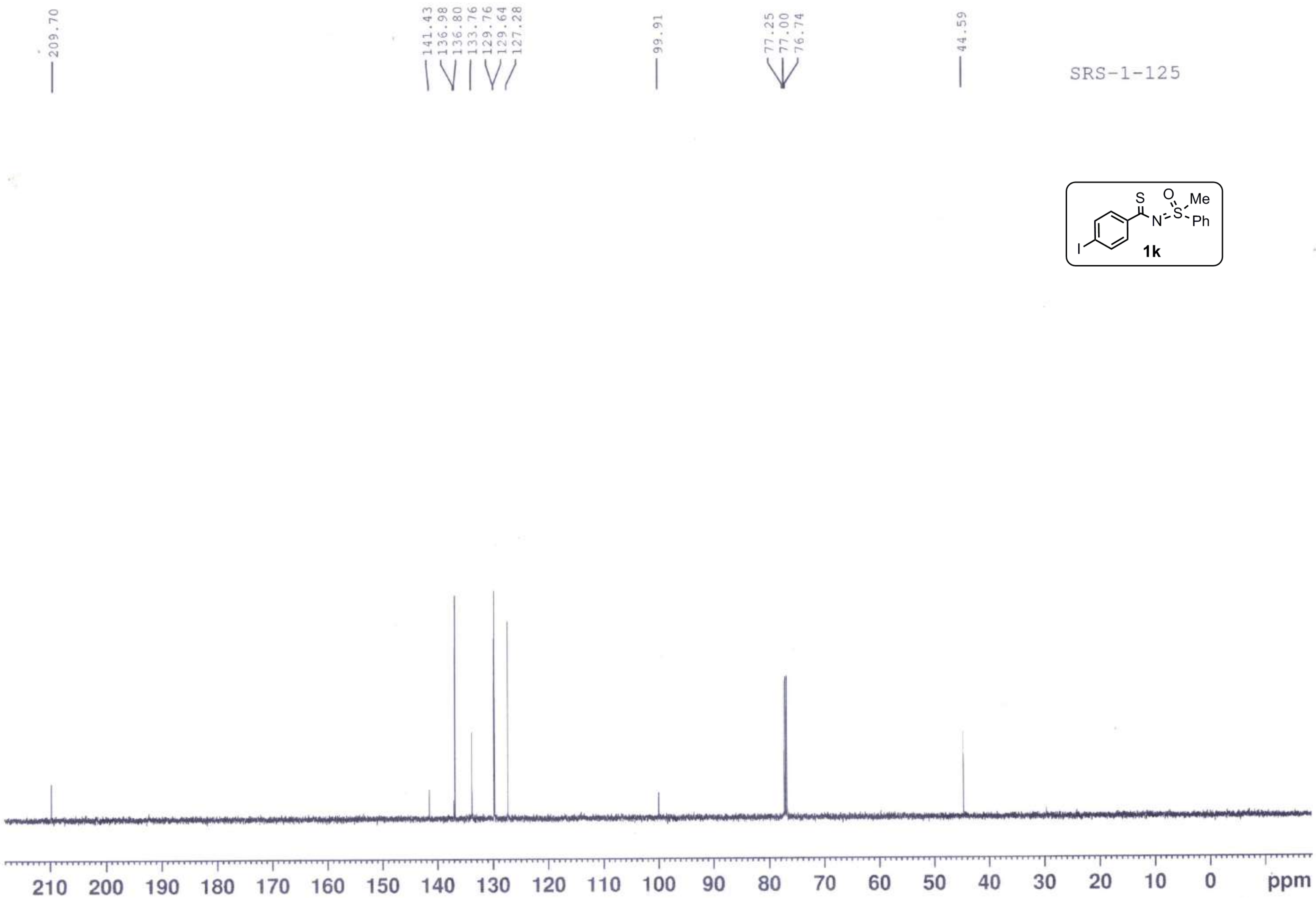
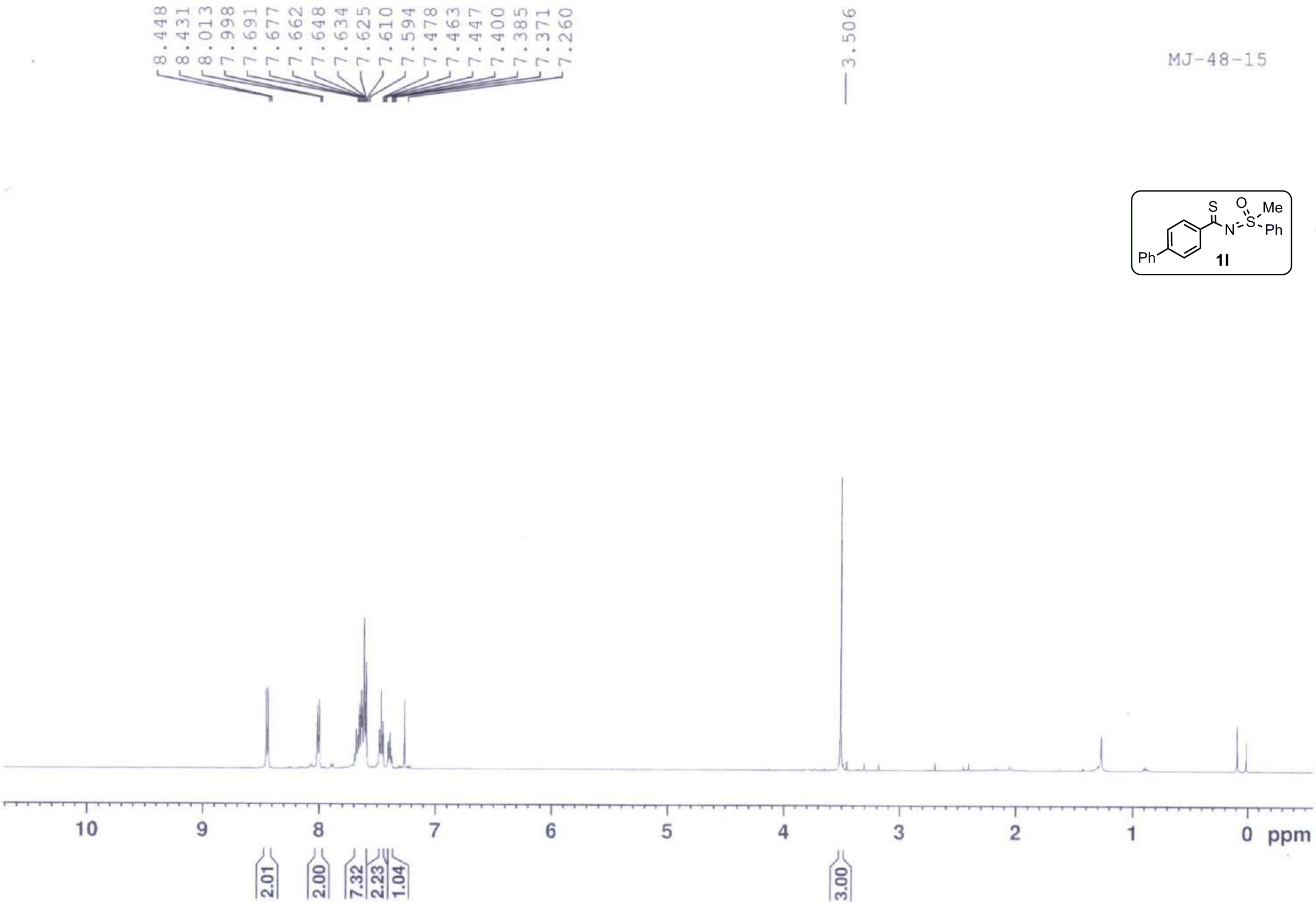
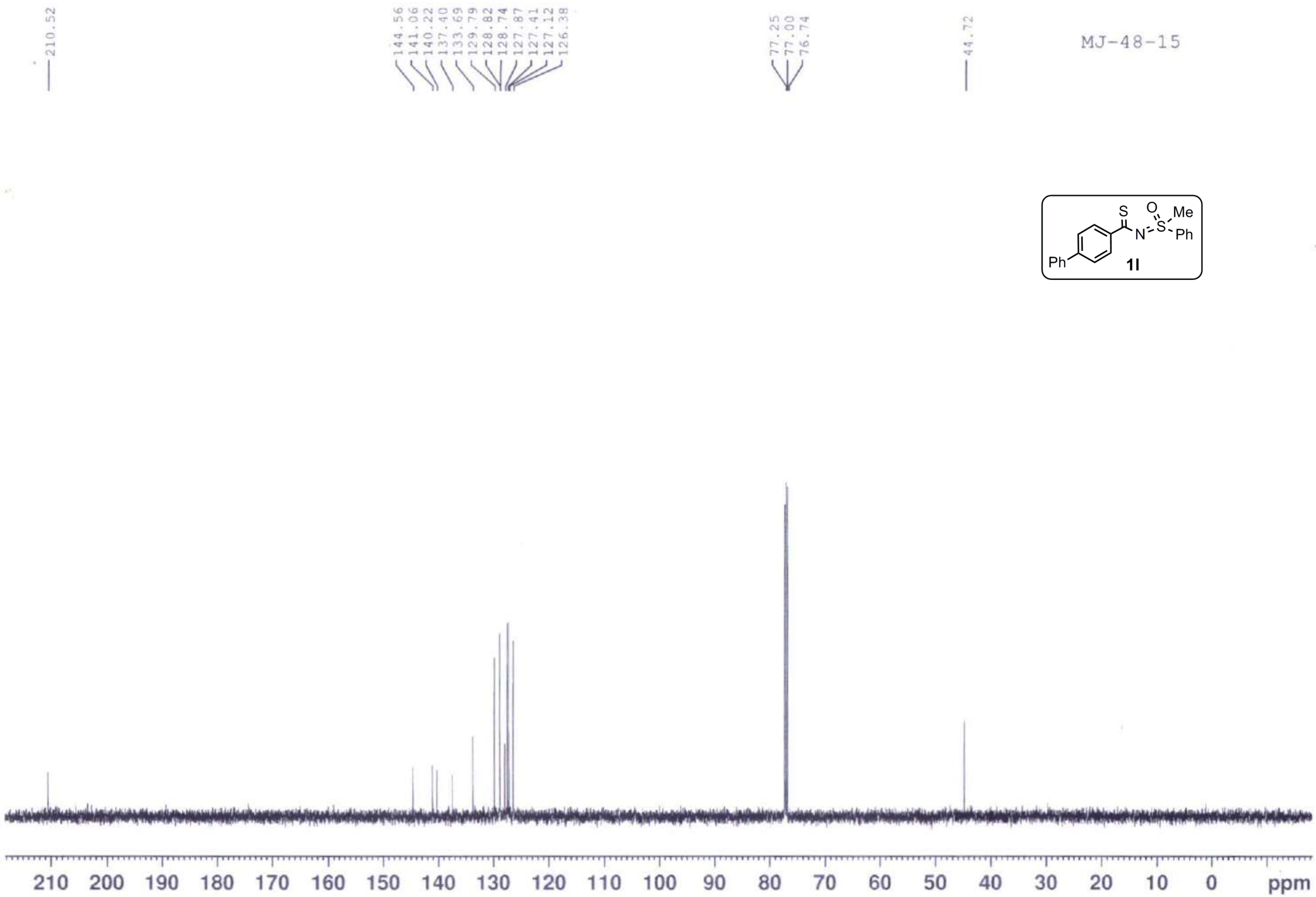
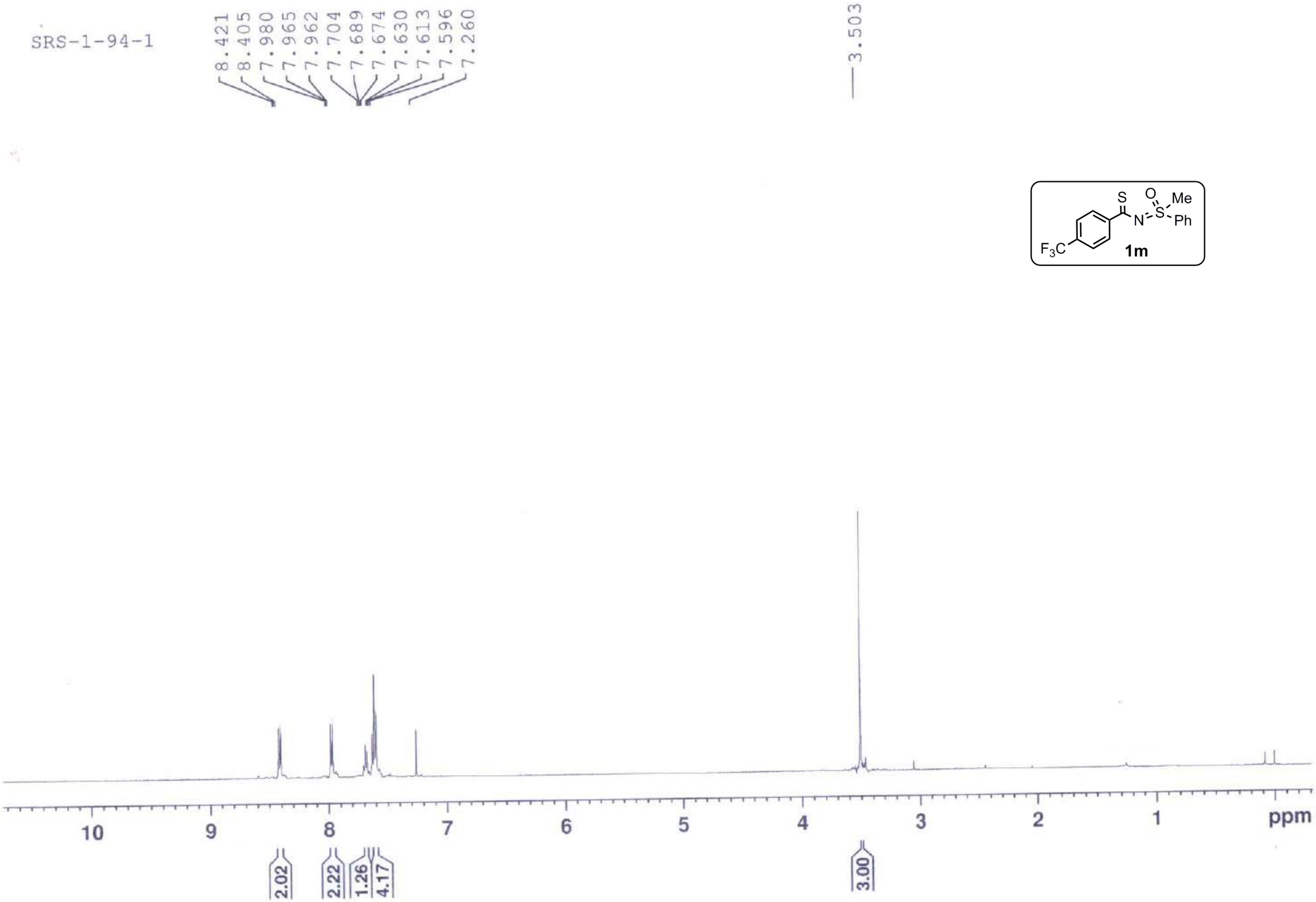
140.93
137.19
133.82
130.85
129.85
129.72
127.38
127.24
77.25
77.00
76.74
44.69
MJ- 11-14
S
O
Me
N
S
Ph
Br
1j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

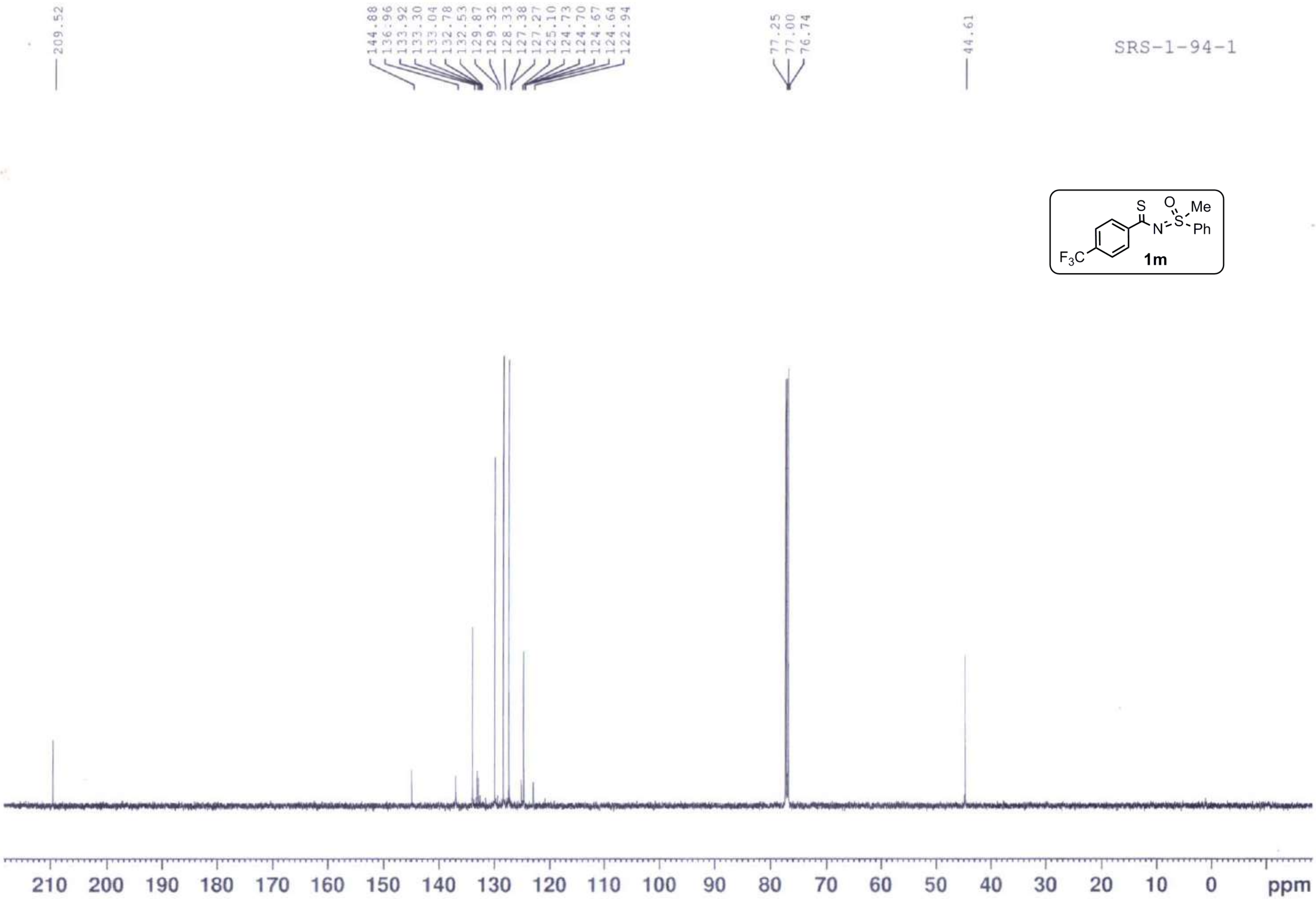

8.058
8.041
7.949
7.934
7.698
7.680
7.659
7.644
7.601
7.585
7.570
7.260
3.466
SRS-1-125
S
O
Me
N
S
Ph
I
1k
9
8
7
6
5
4
3
2
1
0
ppm
2.03
2.09
2.01
1.02
2.14
3.00

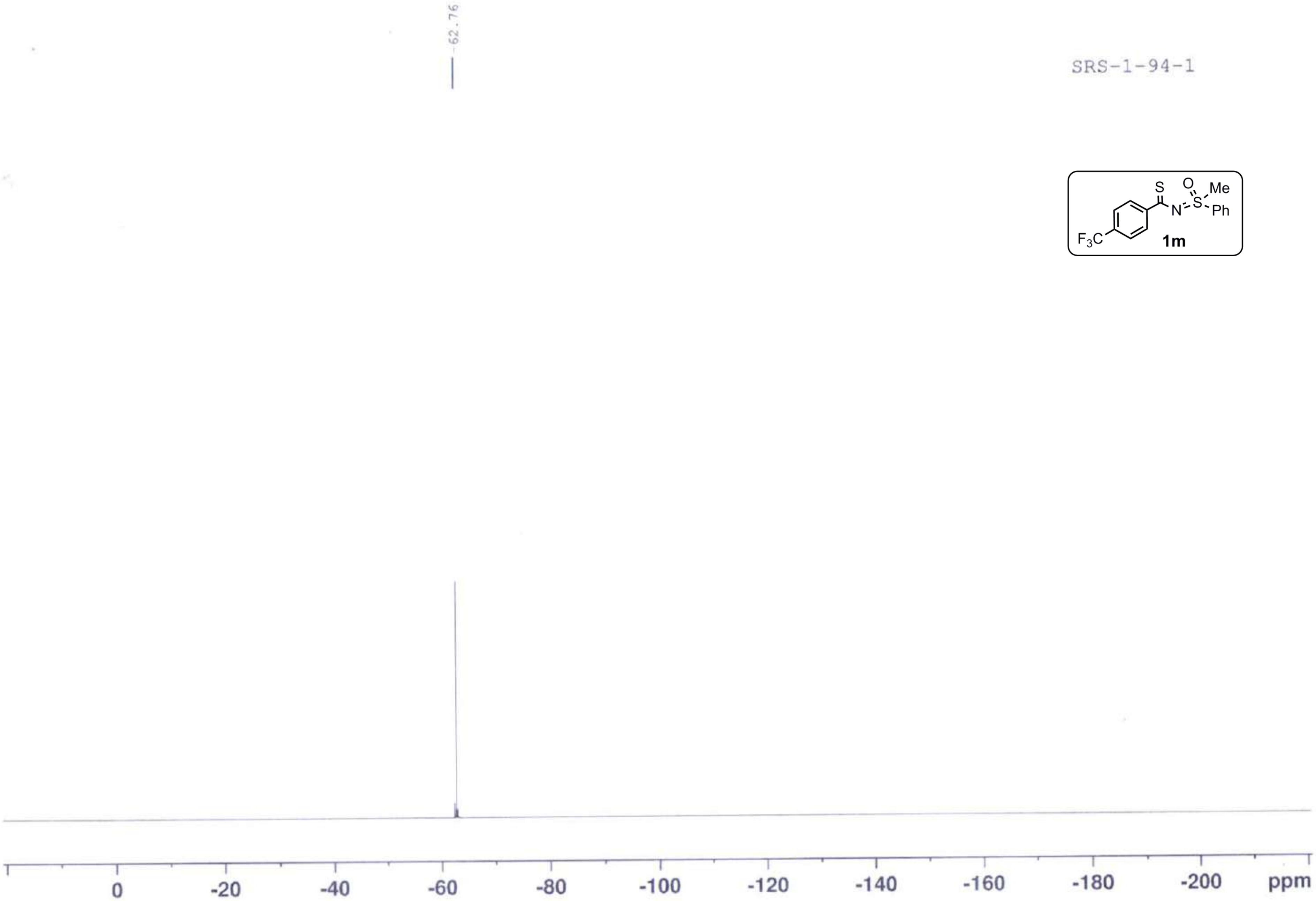

209.70
141.43
136.98
136.80
133.76
129.76
129.64
127.28
99.91
77.25
77.00
76.74
44.59
SRS-1-125
S
O
Me
N
S
Ph
I
1k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.448
8.431
8.013
7.998
7.691
7.677
7.662
7.648
7.634
7.625
7.610
7.594
7.478
7.463
7.447
7.400
7.385
7.371
7.260
3.506
MJ-48-15
10
9
8
7
6
5
4
3
2
1
0 ppm
2.01
2.00
7.32
2.23
1.04
3.00
S
O
Me
N
S
Ph
Ph
1l


210.52
144.56
141.06
140.22
137.40
133.69
129.79
128.82
128.74
127.87
127.41
127.12
126.38
77.25
77.00
76.74
44.72
MJ-48-15
S
O
Me
N
S
Ph
Ph
1l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

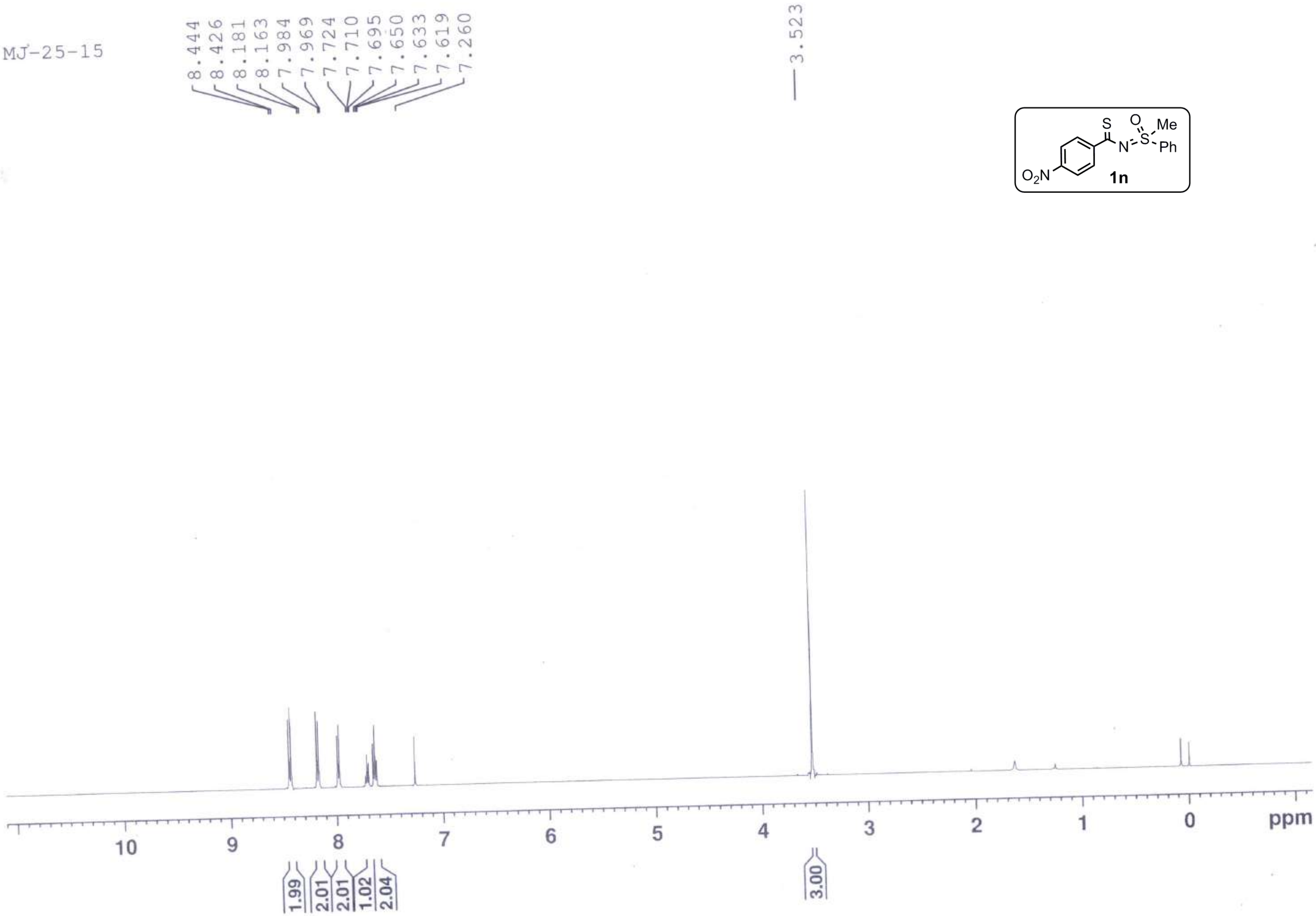

SRS-1-94-1
8.421
8.405
7.980
7.965
7.962
7.704
7.689
7.674
7.630
7.613
7.596
7.260
3.503
S
O
Me
N
S
Ph
F3C
1m
10
9
8
7
6
5
4
3
2
1
ppm
2.02
2.22
1.26
4.17
3.00


209.52
144.88
136.96
133.92
133.30
133.04
132.78
132.53
129.87
129.32
128.33
127.38
127.27
125.10
124.73
124.70
124.67
124.64
122.94
77.25
77.00
76.74
44.61
SRS-1-94-1
S
O
Me
N
S
Ph
F_3C
1m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

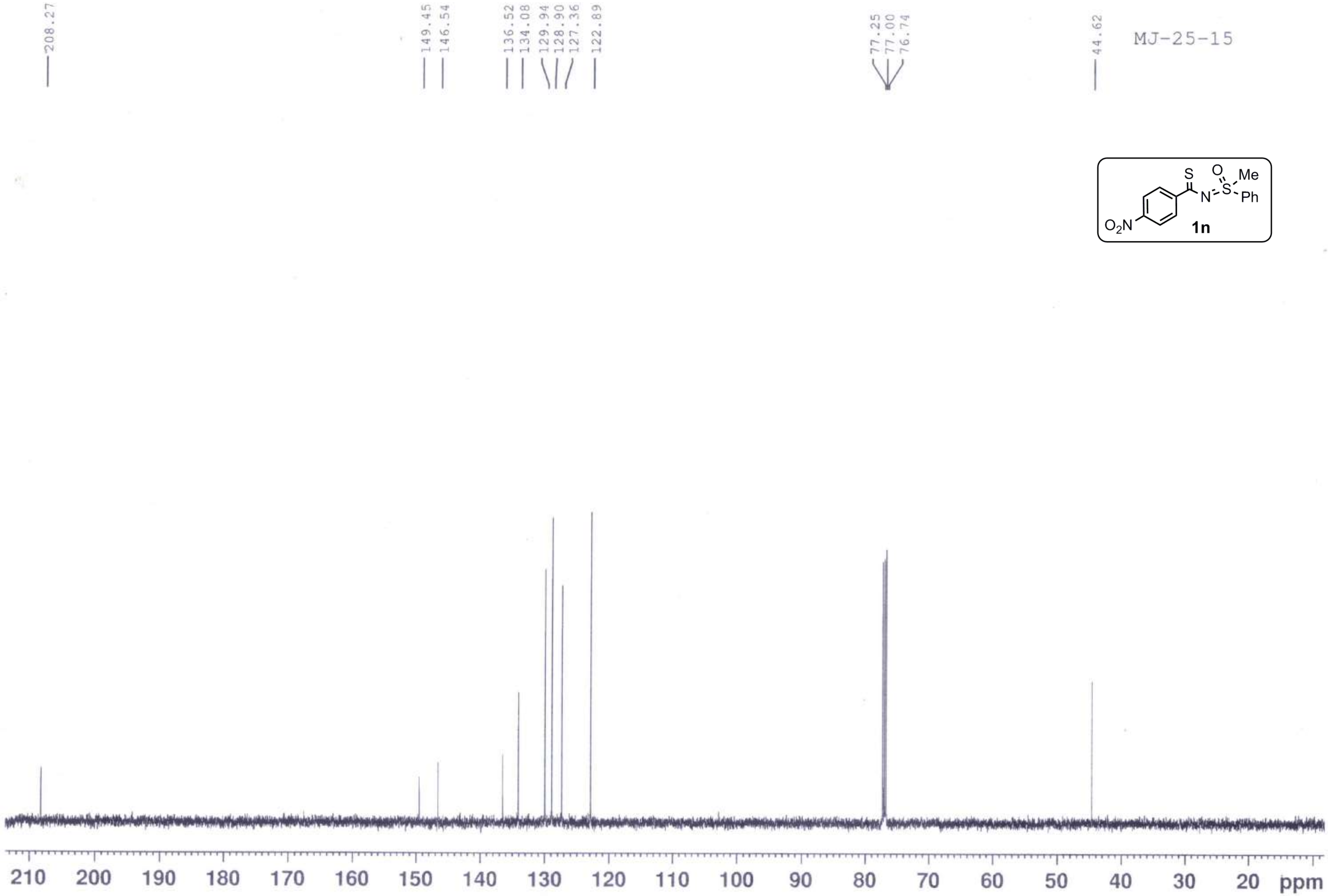


SRS-1-94-1

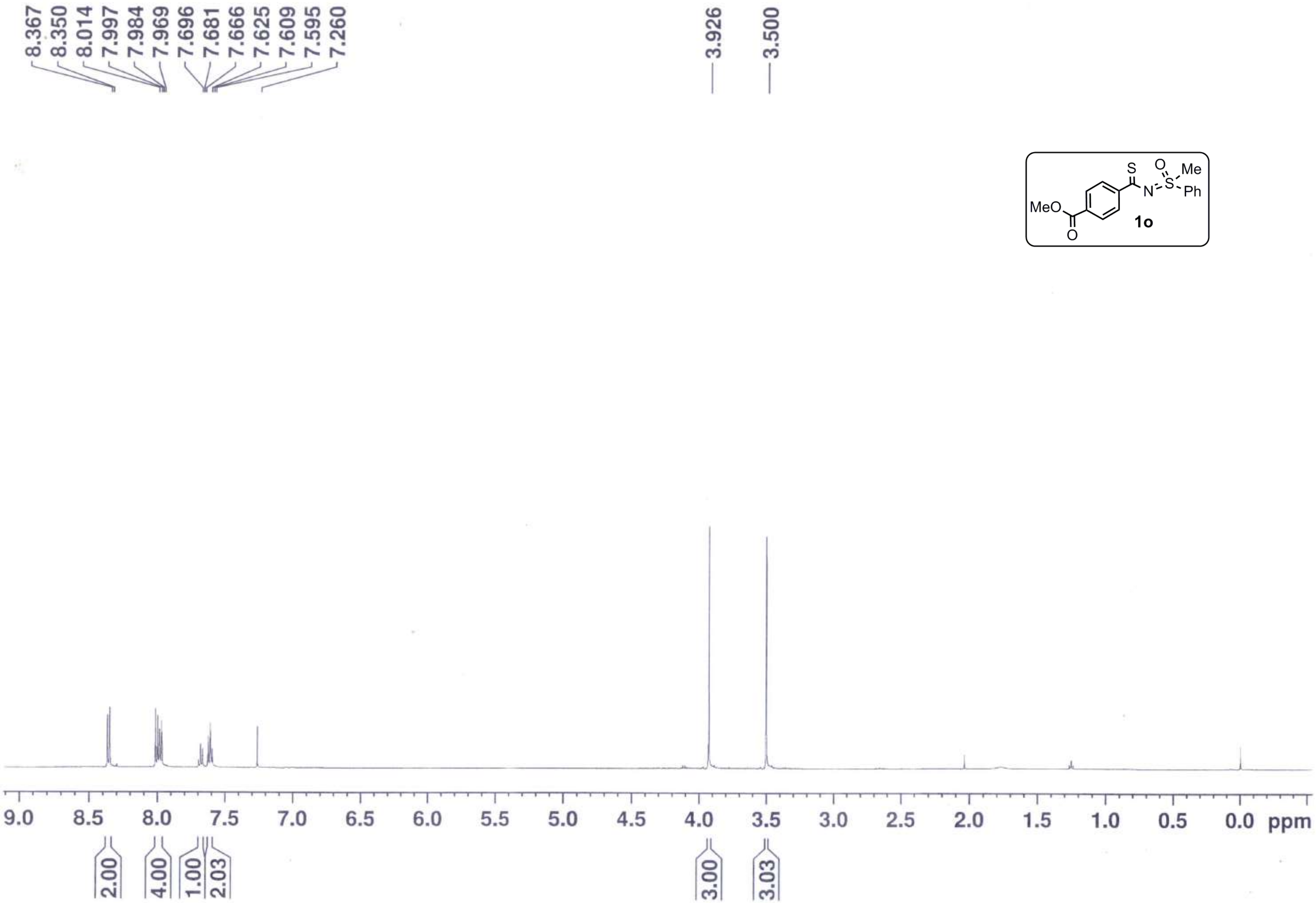
1m


MJ-25-15
8.444
8.426
8.181
8.163
7.984
7.969
7.724
7.710
7.695
7.650
7.633
7.619
7.260
3.523
S
O
Me
N
S
Ph
O2N
1n
10
9
8
7
6
5
4
3
2
1
0
ppm
1.99
2.01
2.01
1.02
2.04
3.00

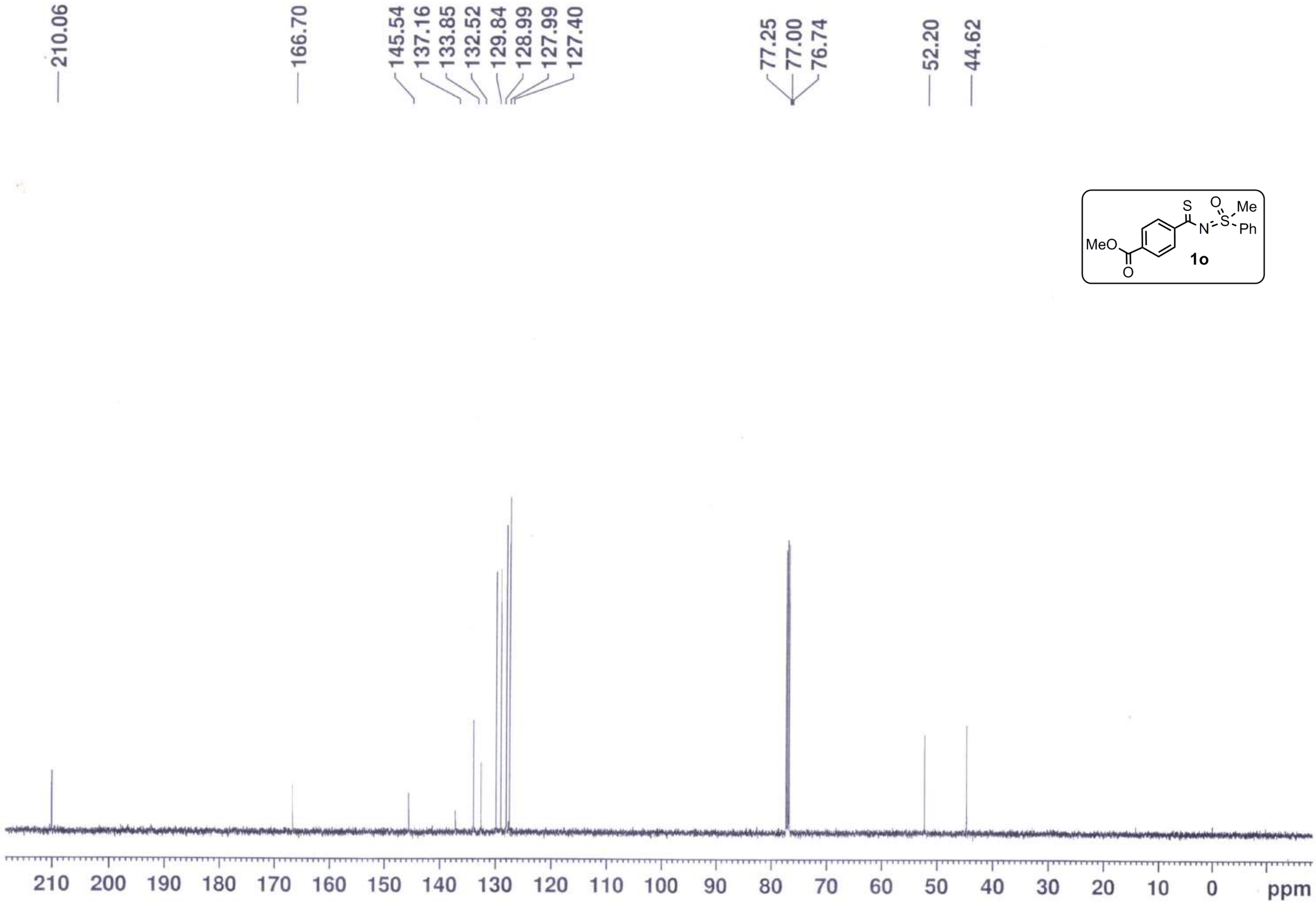
MJ-25-15

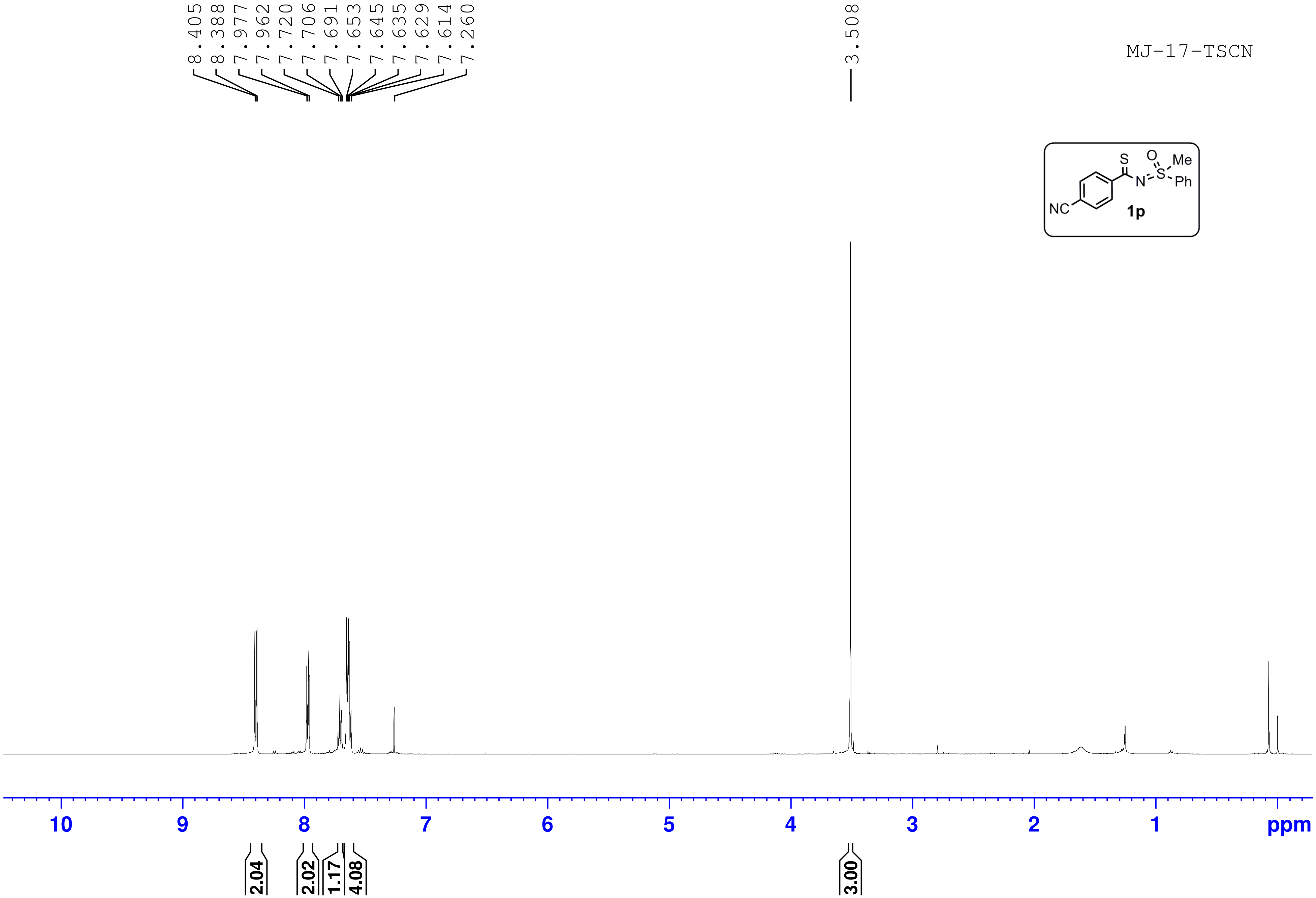


208.27
149.45
146.54
136.52
134.08
129.94
128.90
127.36
122.89
77.25
77.00
76.74
44.62
S
O
Me
N
S
Ph
O_2N
1n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

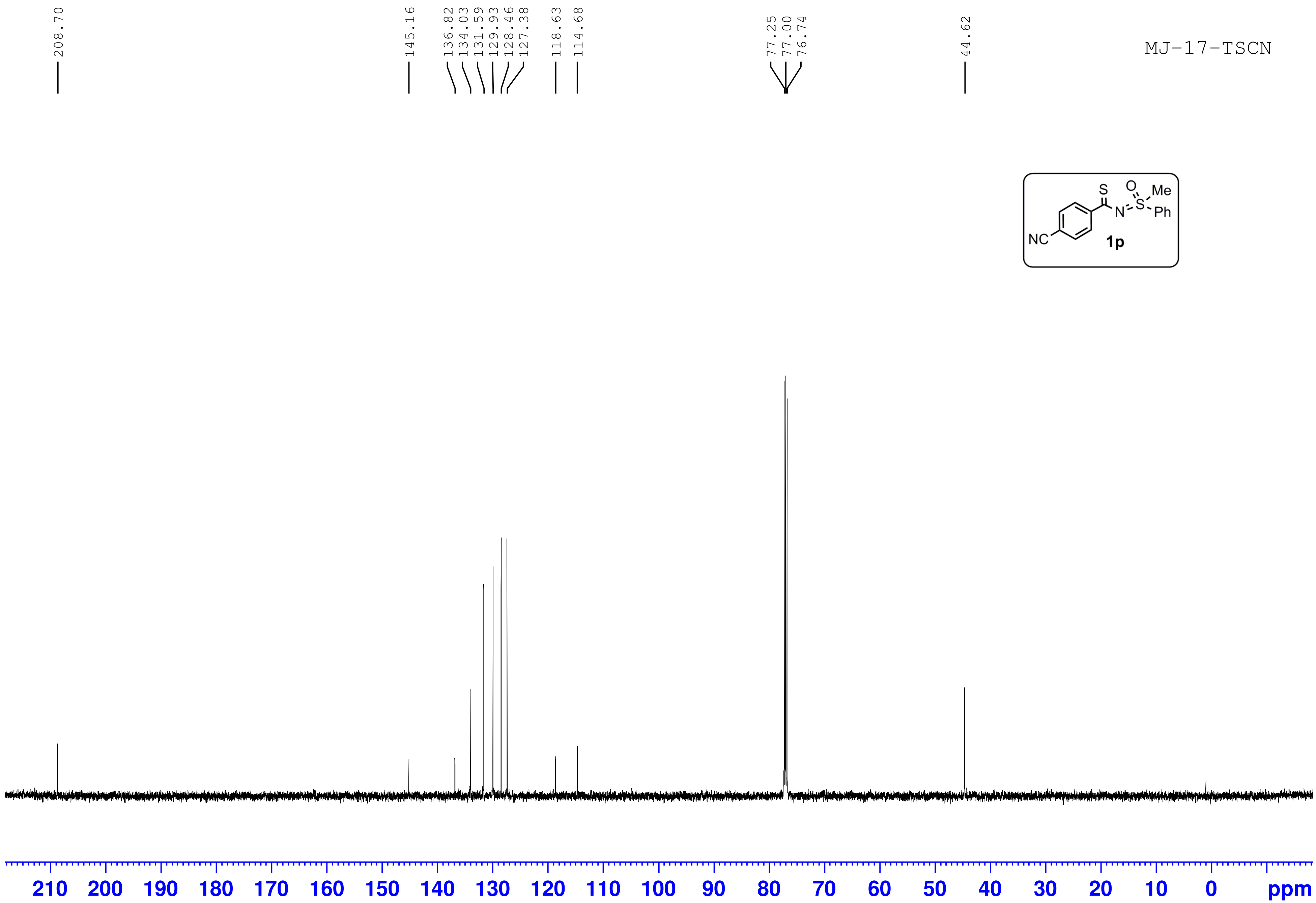


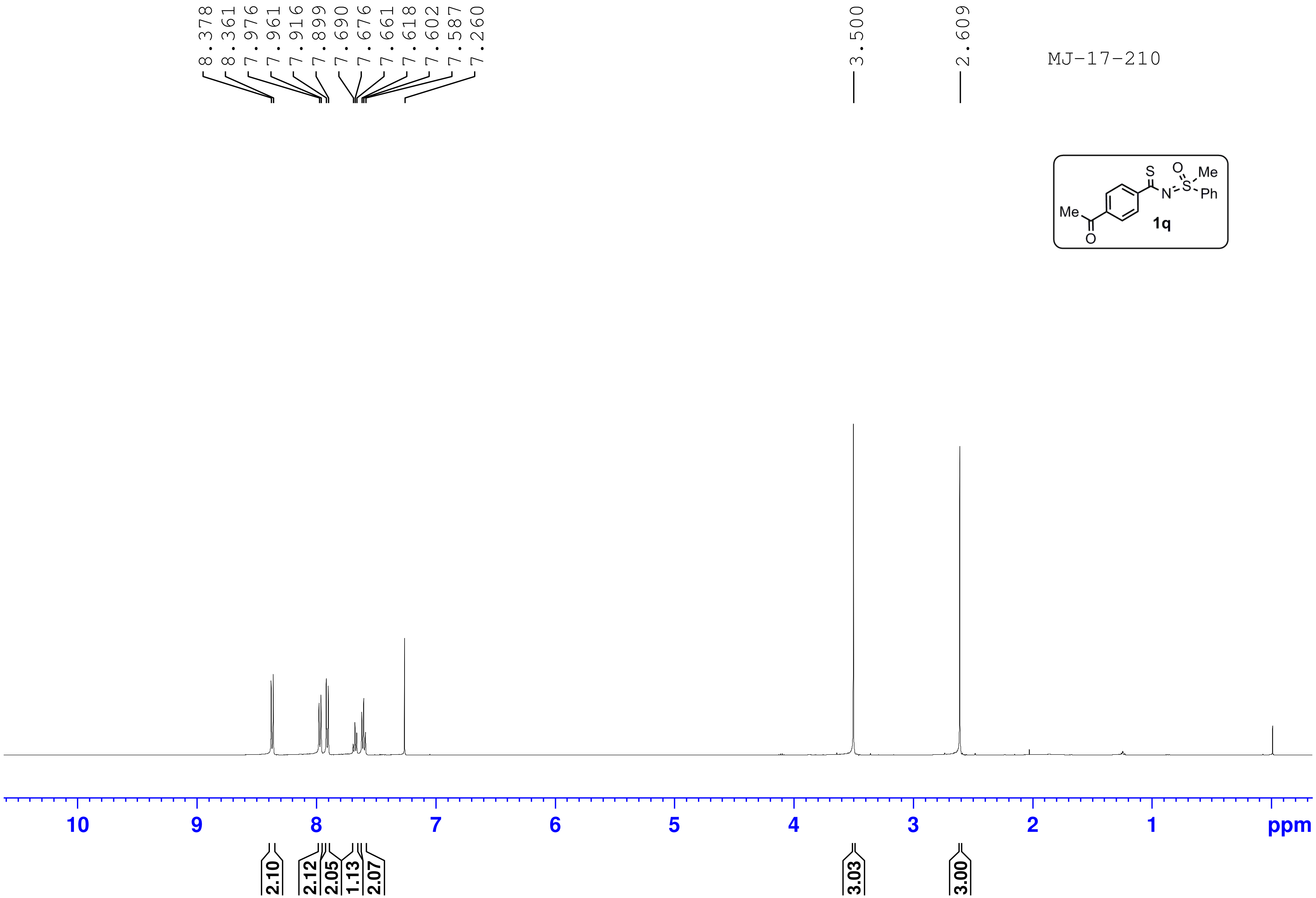
8.367
8.350
8.014
7.997
7.984
7.969
7.696
7.681
7.666
7.625
7.609
7.595
7.260
3.926
3.500
S
O
Me
N
S
Ph
MeO
O
1o
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.00
4.00
1.00
2.03
3.00
3.03

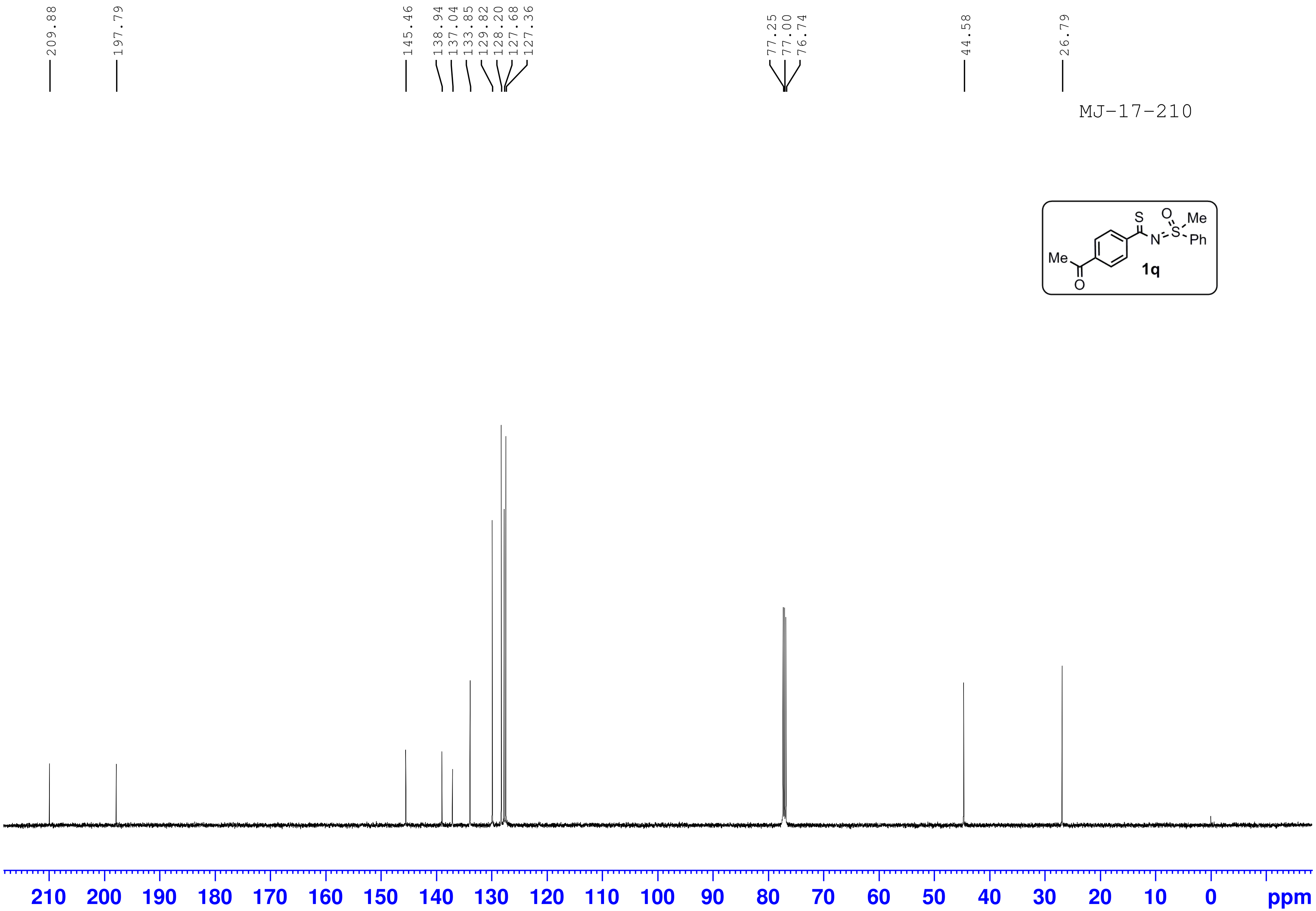

210.06
166.70
145.54
137.16
133.85
132.52
129.84
128.99
127.99
127.40
77.25
77.00
76.74
52.20
44.62
MeO
O
S
N
S
O
Me
Ph
1o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

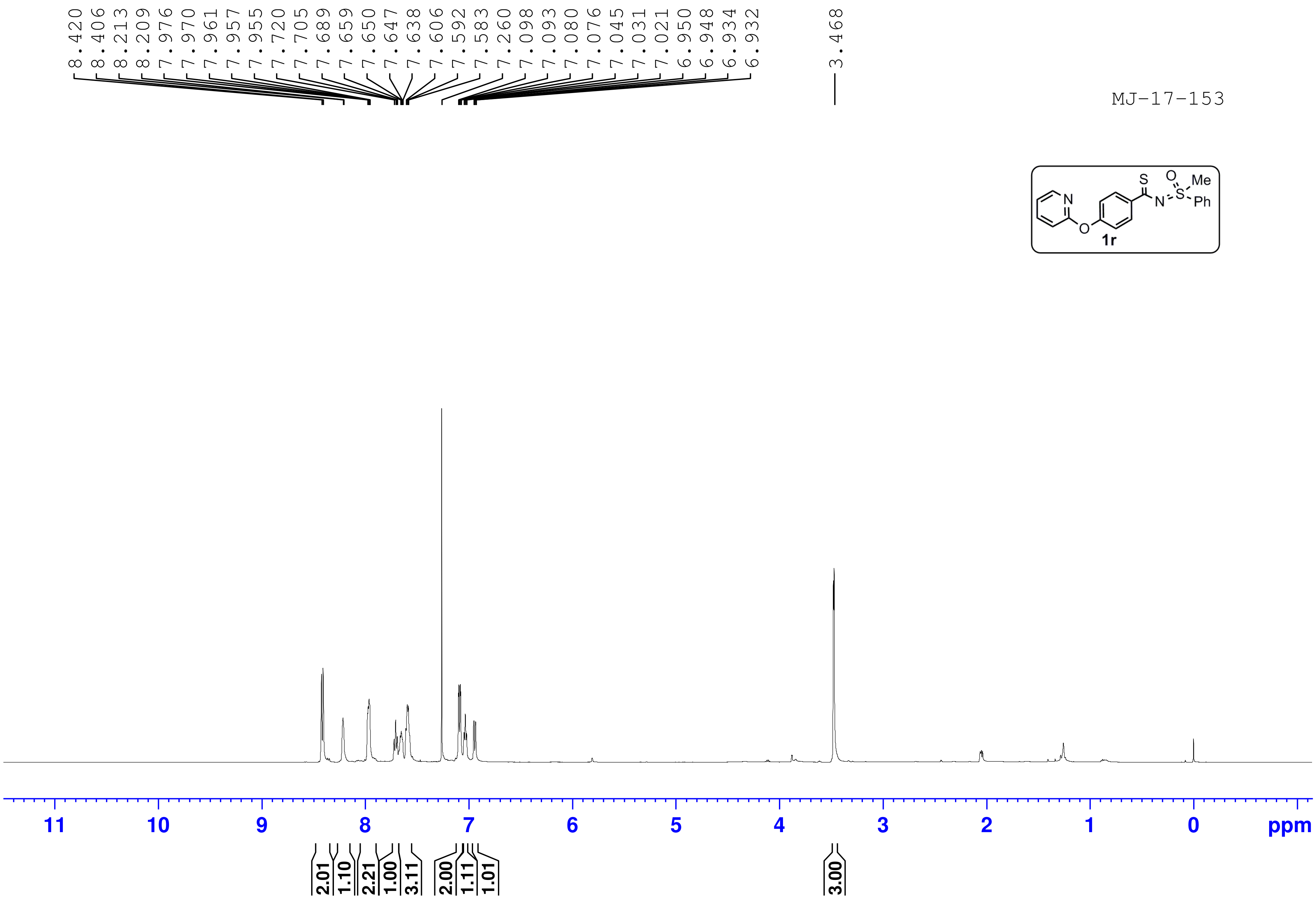


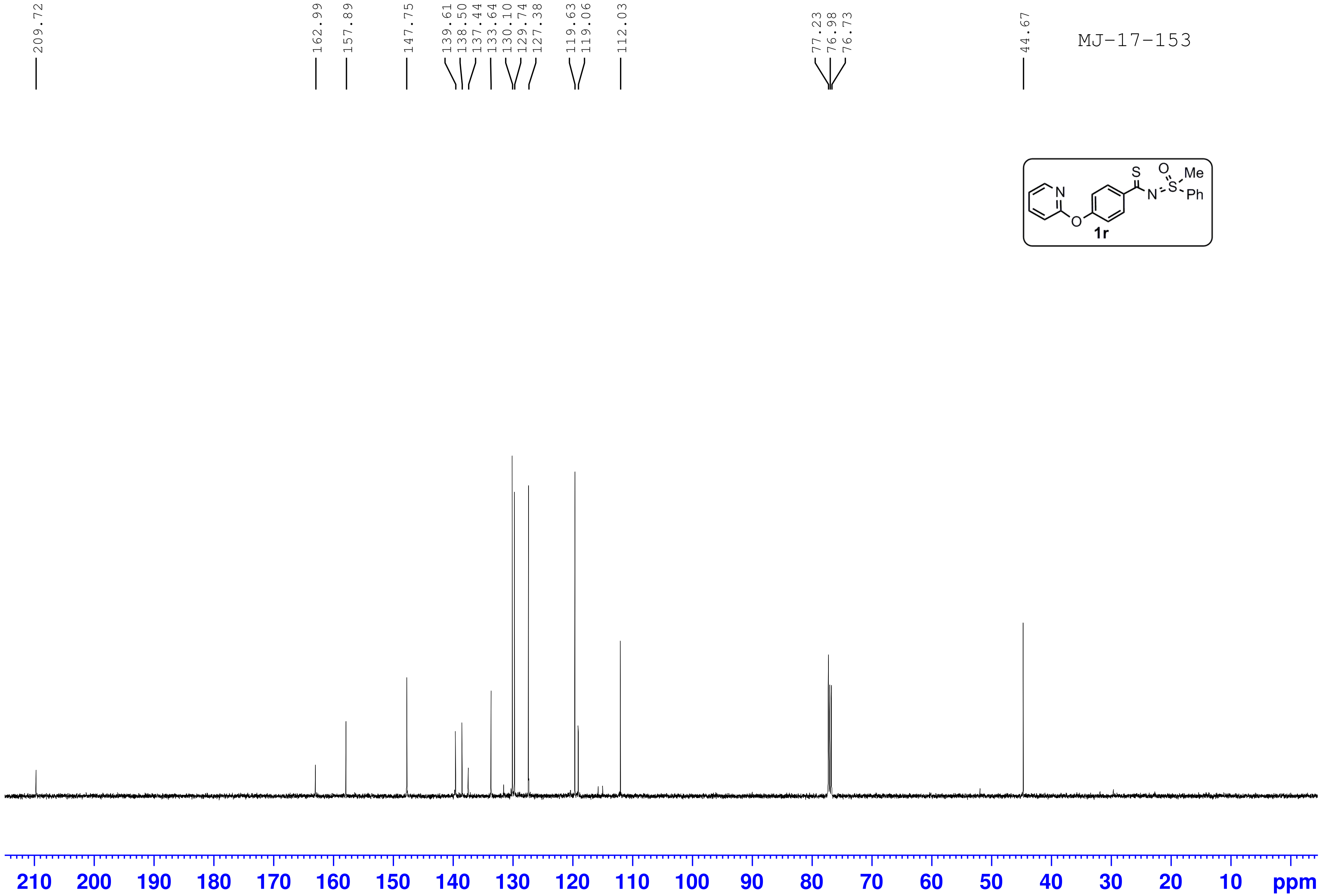
8.405
8.388
7.977
7.962
7.720
7.706
7.691
7.653
7.645
7.635
7.629
7.614
7.260
3.508
MJ-17-TSCN
1p
10
9
8
7
6
5
4
3
2
1
ppm
2.04
2.02
1.17
4.08
3.00

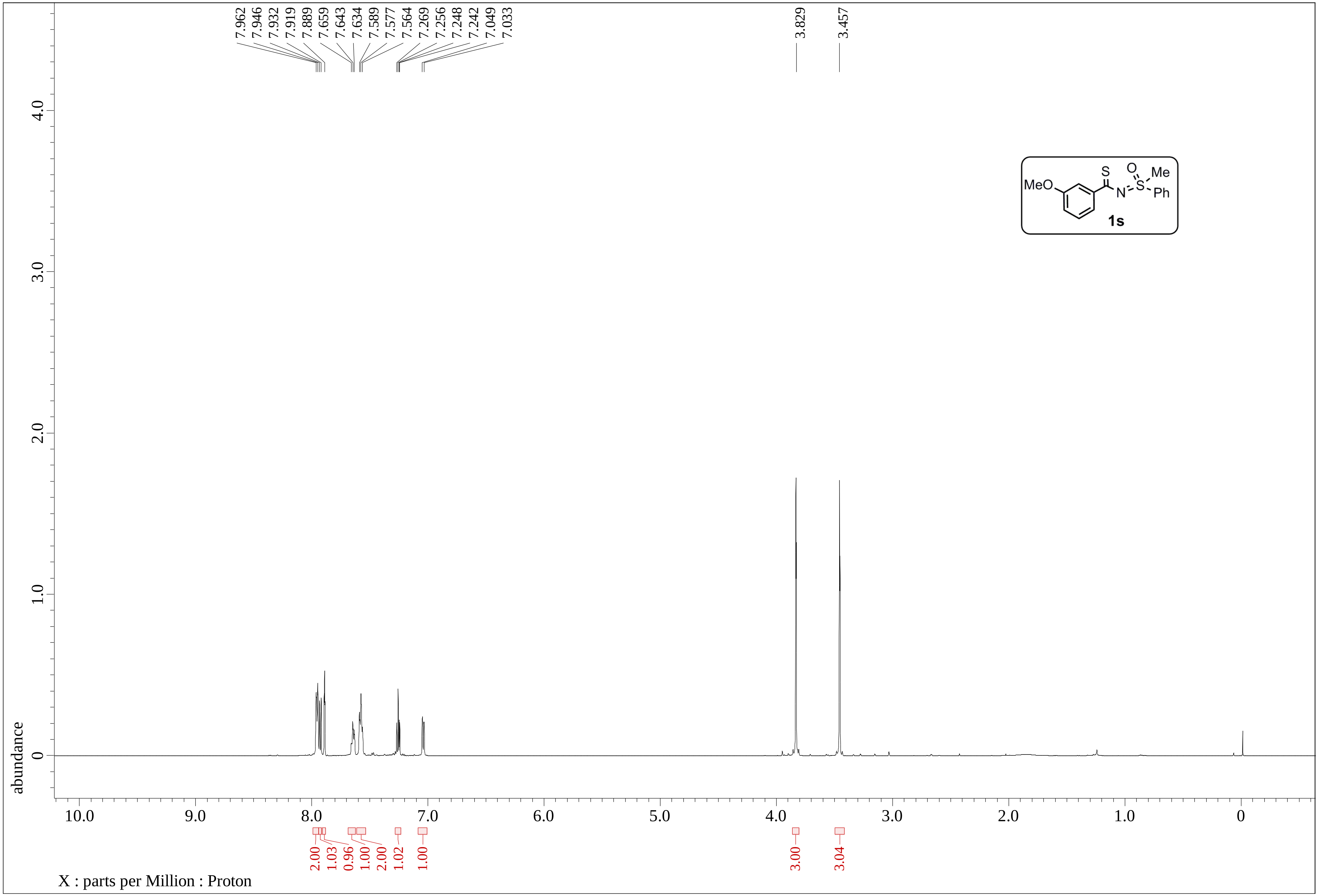

208.70
145.16
136.82
134.03
131.59
129.93
128.46
127.38
118.63
114.68
77.25
77.00
76.74
44.62
MJ-17-TSCN
S
O
Me
N
S
Ph
NC
1p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.378
8.361
7.976
7.961
7.916
7.899
7.690
7.676
7.661
7.618
7.602
7.587
7.260
3.500
2.609
MJ-17-210
S
O
Me
N
S
Ph
Me
O
1q
10
9
8
7
6
5
4
3
2
1
ppm
2.10
2.12
2.05
1.13
2.07
3.03
3.00

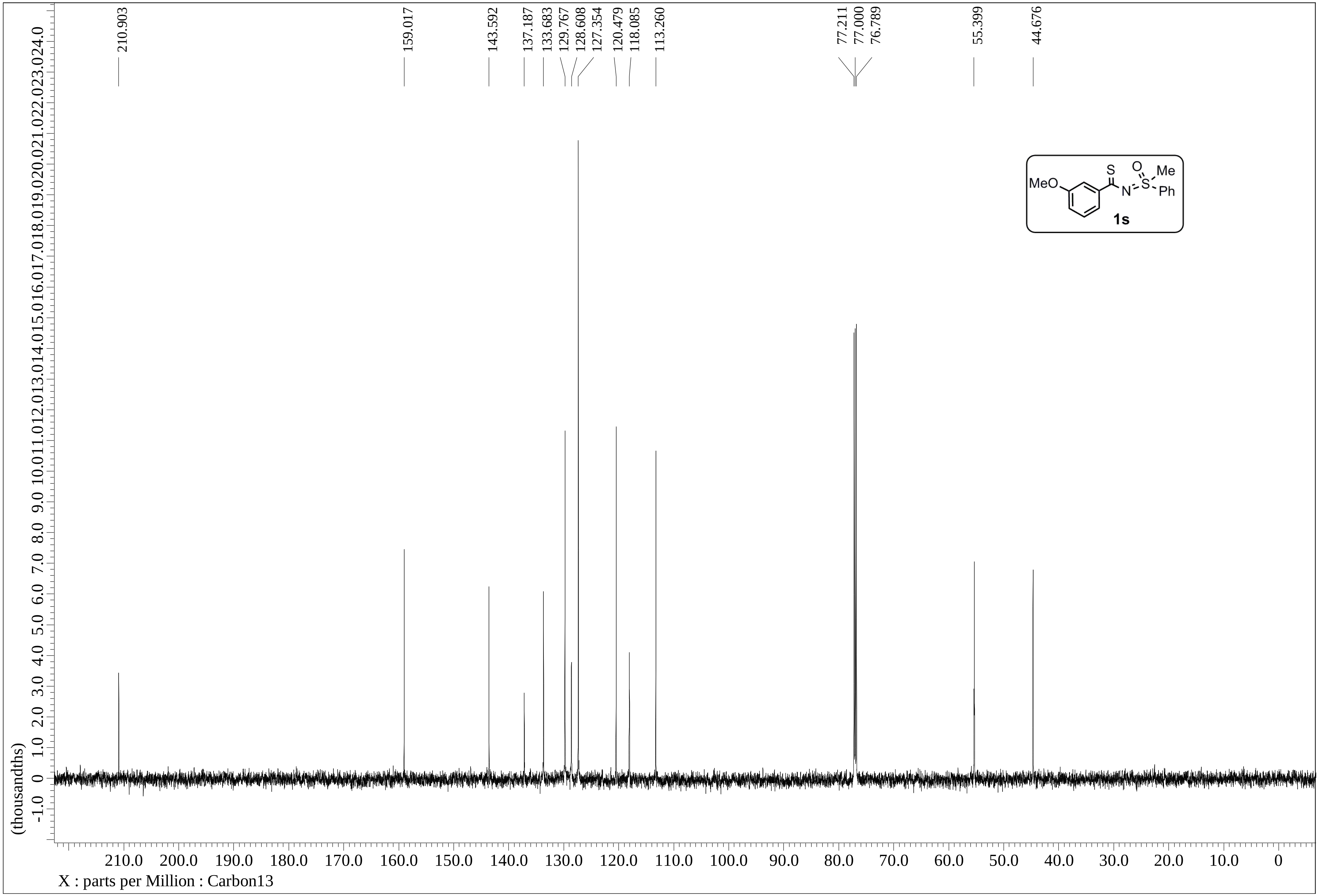

209.88
197.79
145.46
138.94
137.04
133.85
129.82
128.20
127.68
127.36
77.25
77.00
76.74
44.58
26.79
MJ-17-210
S
O
Me
N
S
Ph
Me
O
1q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

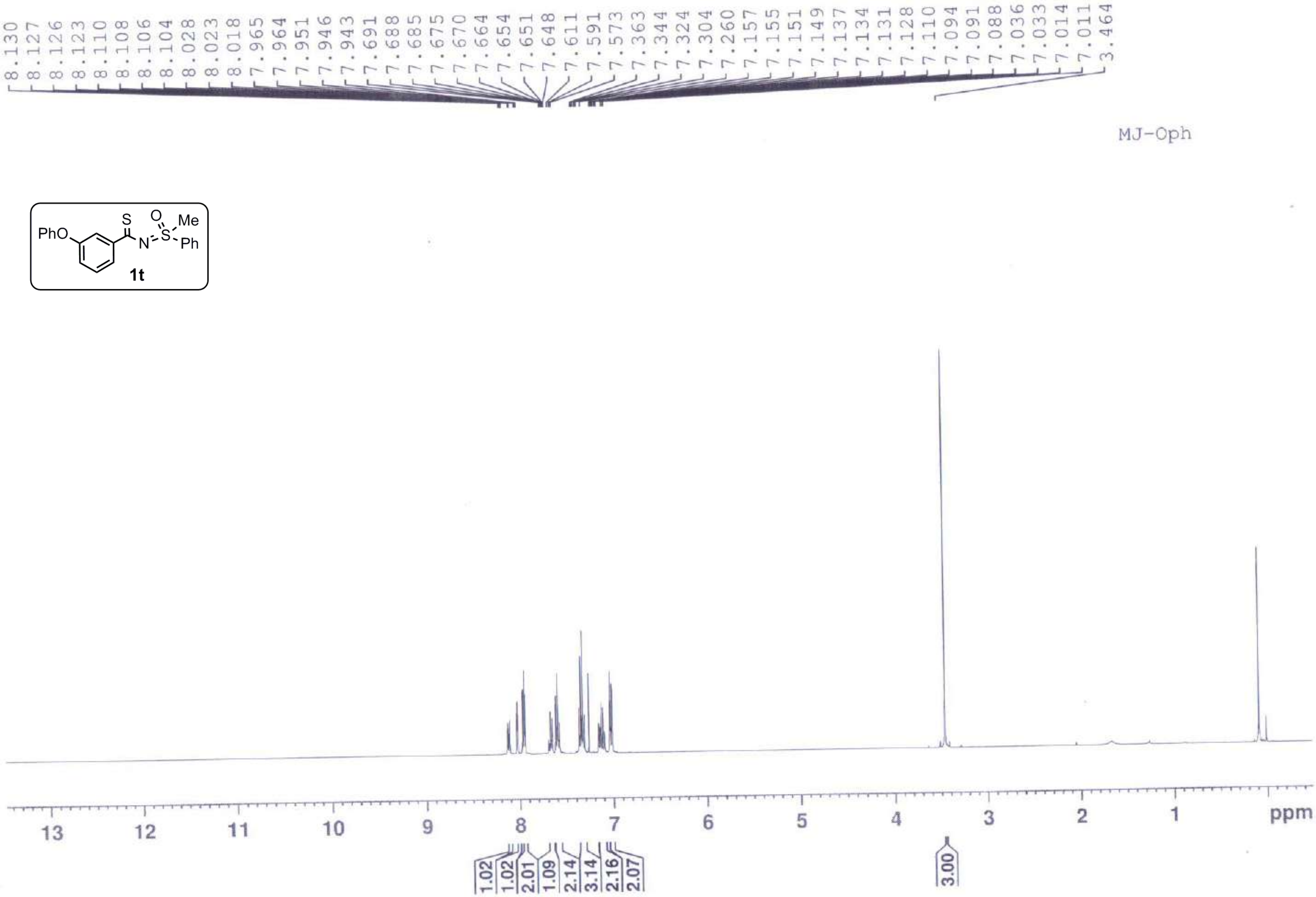

8.420
8.406
8.213
8.209
7.976
7.970
7.961
7.957
7.955
7.720
7.705
7.689
7.659
7.650
7.647
7.638
7.606
7.592
7.583
7.260
7.098
7.093
7.080
7.076
7.045
7.031
7.021
6.950
6.948
6.934
6.932
3.468
MJ-17-153
S
O
Me
N
S
Ph
N
O
1r
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
1.10
2.21
1.00
3.11
2.00
1.11
1.01
3.00

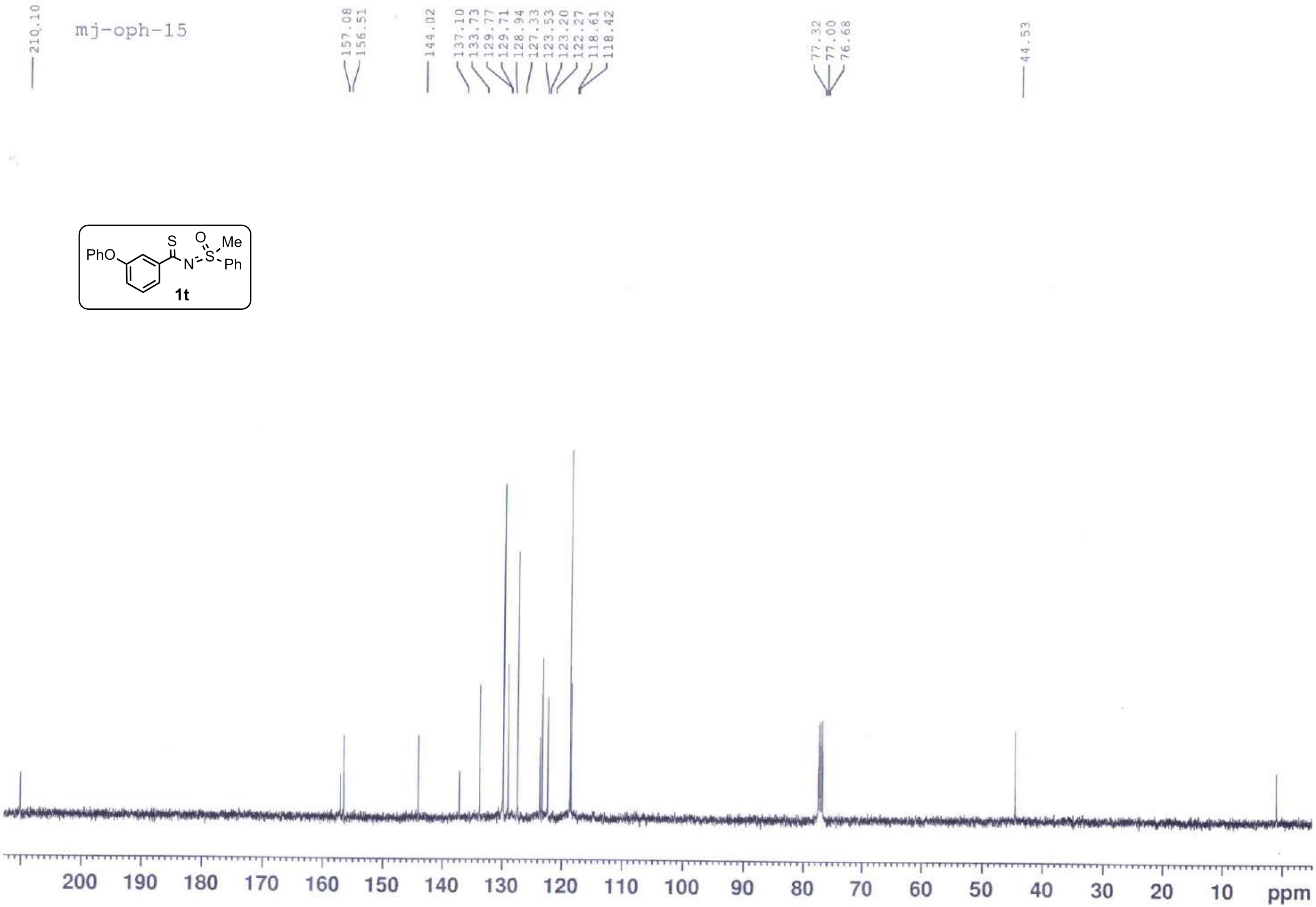

209.72
162.99
157.89
147.75
139.61
138.50
137.44
133.64
130.10
129.74
127.38
119.63
119.06
112.03
77.23
76.98
76.73
44.67
MJ-17-153
S
O
Me
N
S
Ph
N
O
1r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

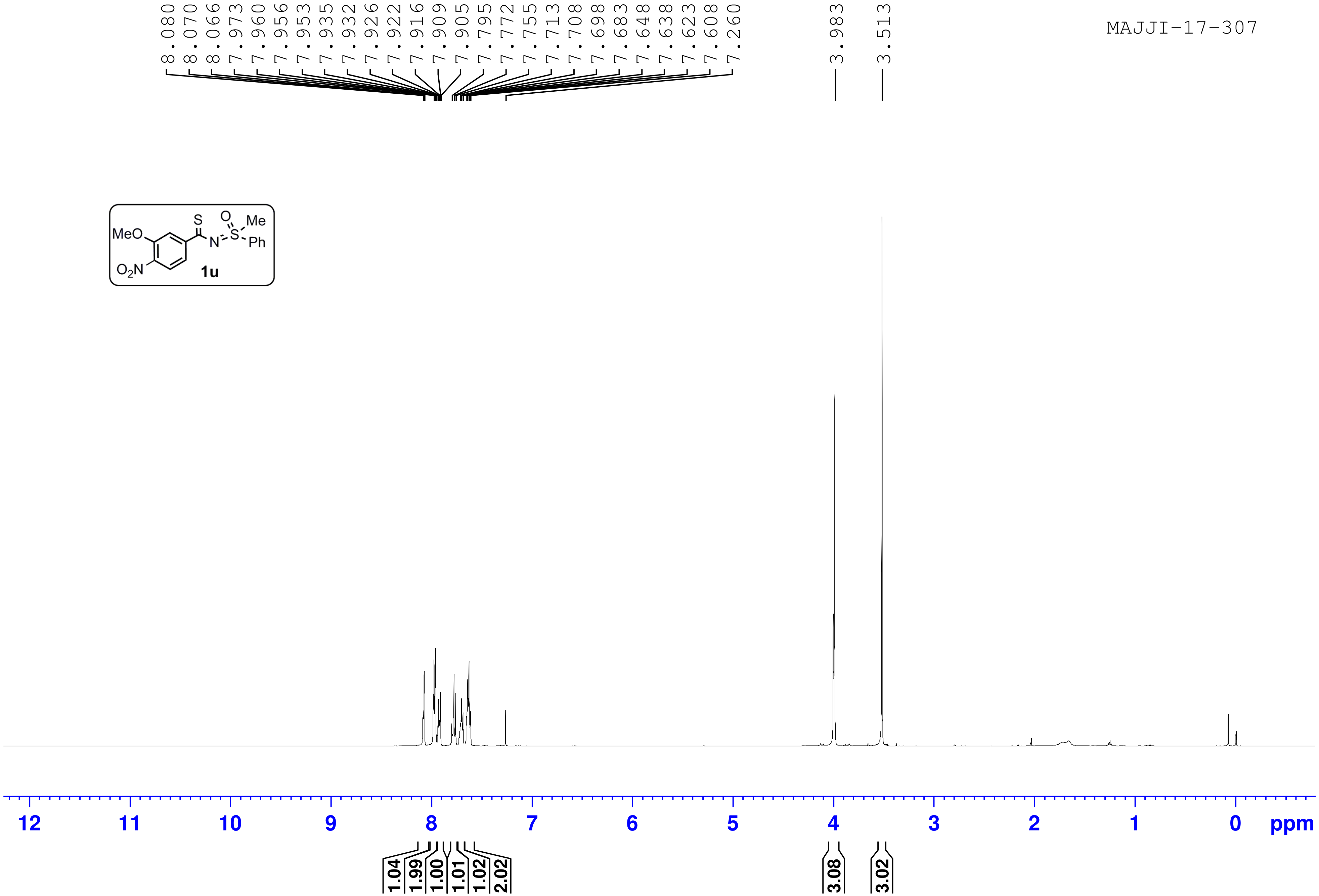


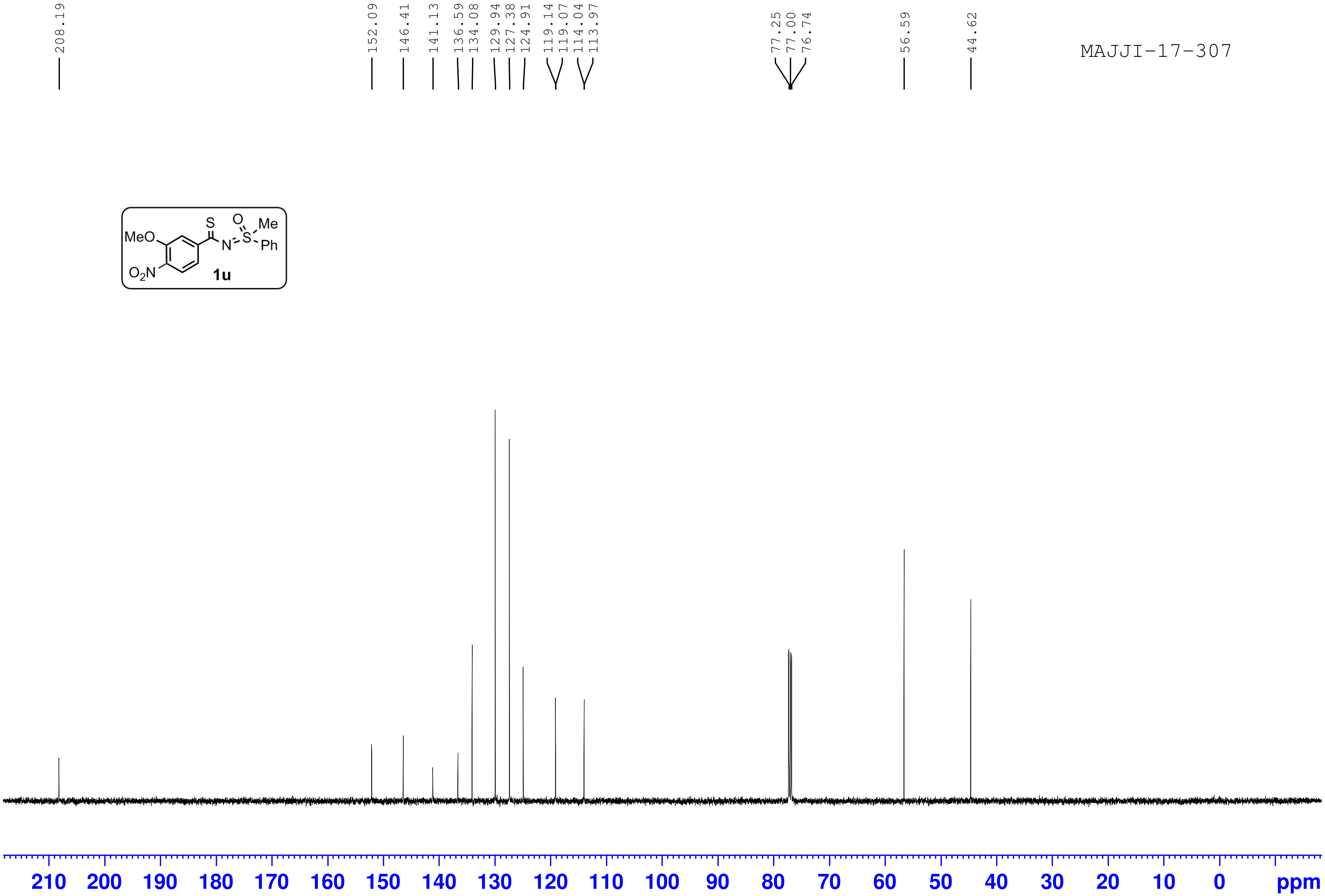
7.962
7.946
7.932
7.919
7.889
7.659
7.643
7.634
7.589
7.577
7.564
7.269
7.256
7.248
7.242
7.049
7.033
3.829
3.457
MeO
S
N
O
S
Me
Ph
1s
abundance
X : parts per Million : Proton
2.00
1.03
0.96
1.00
2.00
1.02
1.00
3.00
3.04

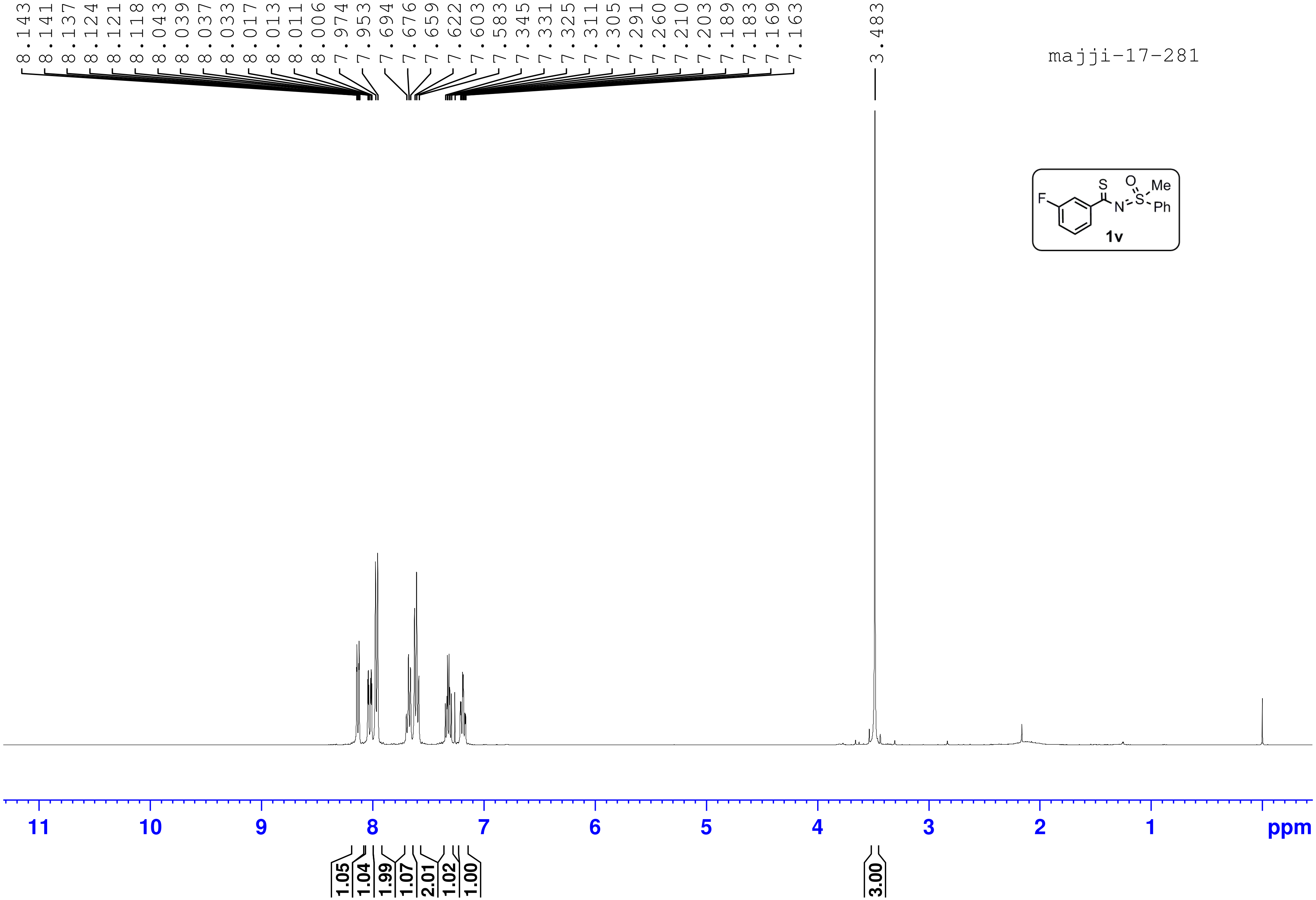

210.903
159.017
143.592
137.187
133.683
129.767
128.608
127.354
120.479
118.085
113.260
77.211
77.000
76.789
55.399
44.676
MeO
S
O
Me
N
S
Ph
1s
(thousandths)
X : parts per Million : Carbon13

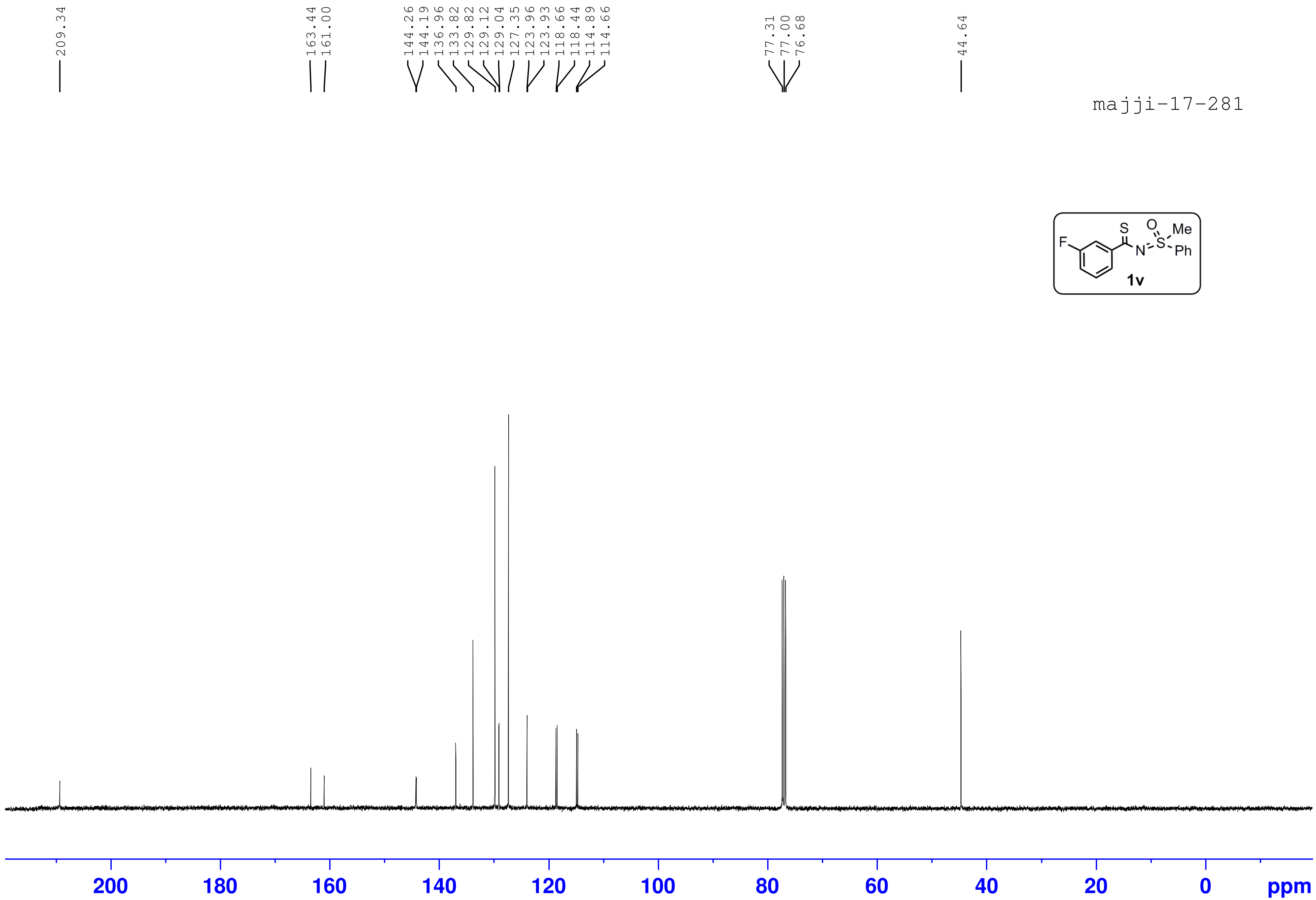

8.130 8.127 8.126 8.123 8.110 8.108 8.106 8.104 8.028 8.023 8.018 7.965 7.964 7.951 7.946 7.943 7.691 7.688 7.685 7.675 7.670 7.664 7.654 7.651 7.648 7.611 7.591 7.573 7.363 7.344 7.324 7.304 7.260 7.157 7.155 7.151 7.149 7.137 7.134 7.131 7.128 7.110 7.094 7.091 7.088 7.036 7.033 7.014 7.011 3.464
MJ-Oph
PhO
S
O
Me
N
S
Ph
1t
13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.02 1.02 2.01 1.09 2.14 3.14 2.16 2.07
3.00

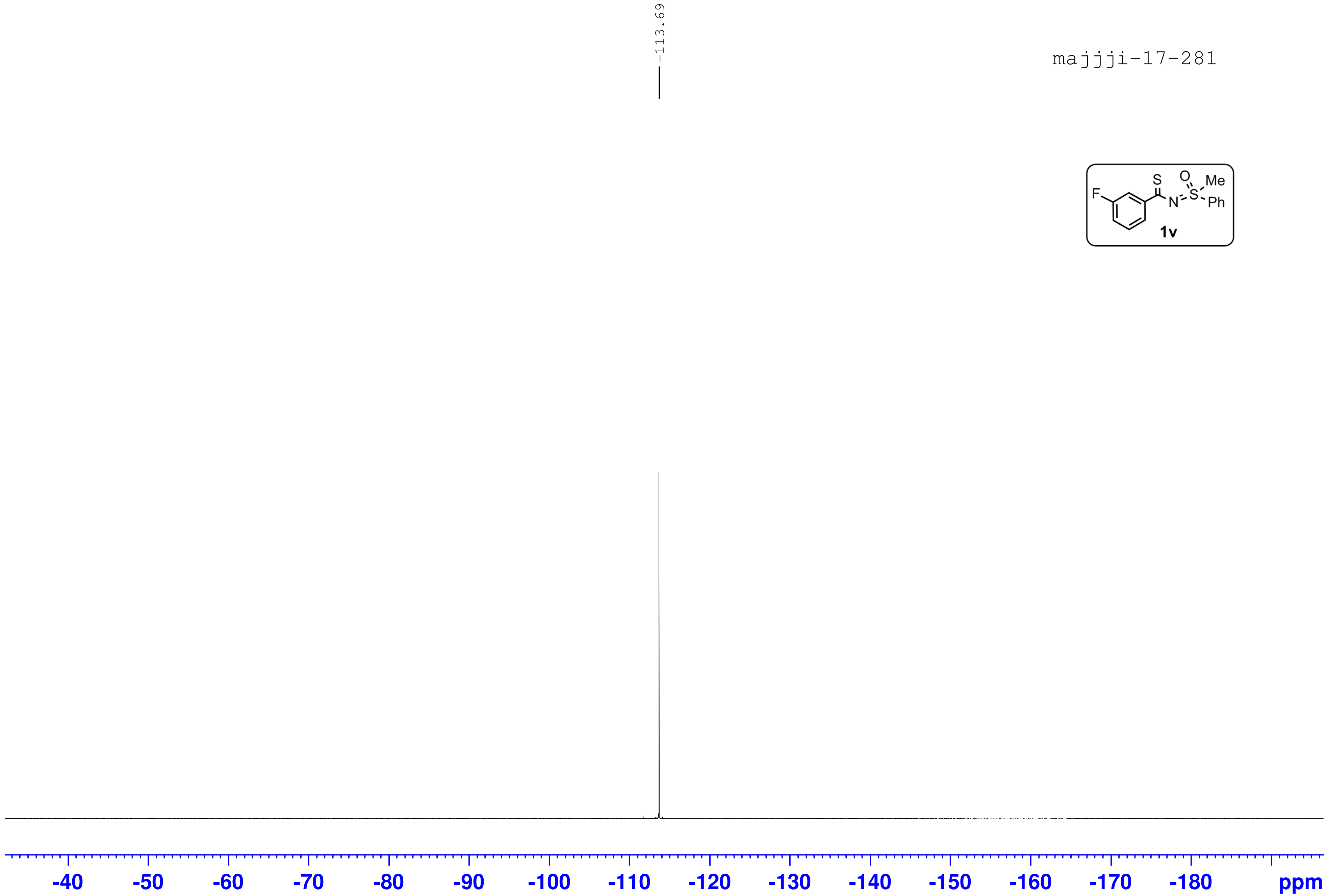

210.10
mj-oph-15
157.08
156.51
144.02
137.10
133.73
129.77
129.71
128.94
127.33
123.53
123.20
122.27
118.61
118.42
77.32
77.00
76.68
44.53
PhO
S
O
Me
N
S
Ph
1t
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

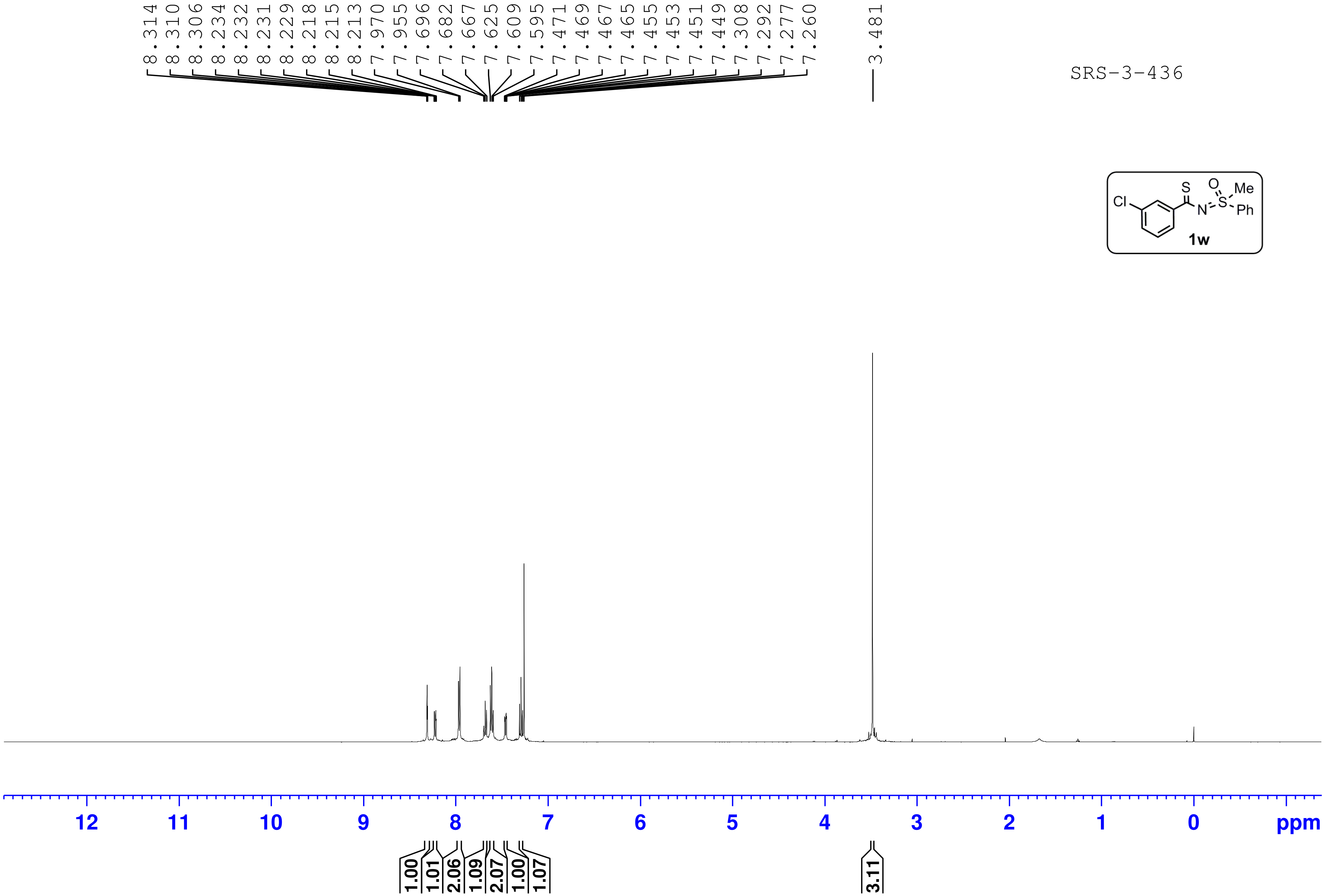

8.080
8.070
8.066
7.973
7.960
7.956
7.953
7.935
7.932
7.926
7.922
7.916
7.909
7.905
7.795
7.772
7.755
7.713
7.708
7.698
7.683
7.648
7.638
7.623
7.608
7.260
3.983
3.513
MAJJI-17-307
MeO
O2N
S
O
Me
N
S
Ph
1u
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.04
1.99
1.00
1.01
1.02
2.02
3.08
3.02

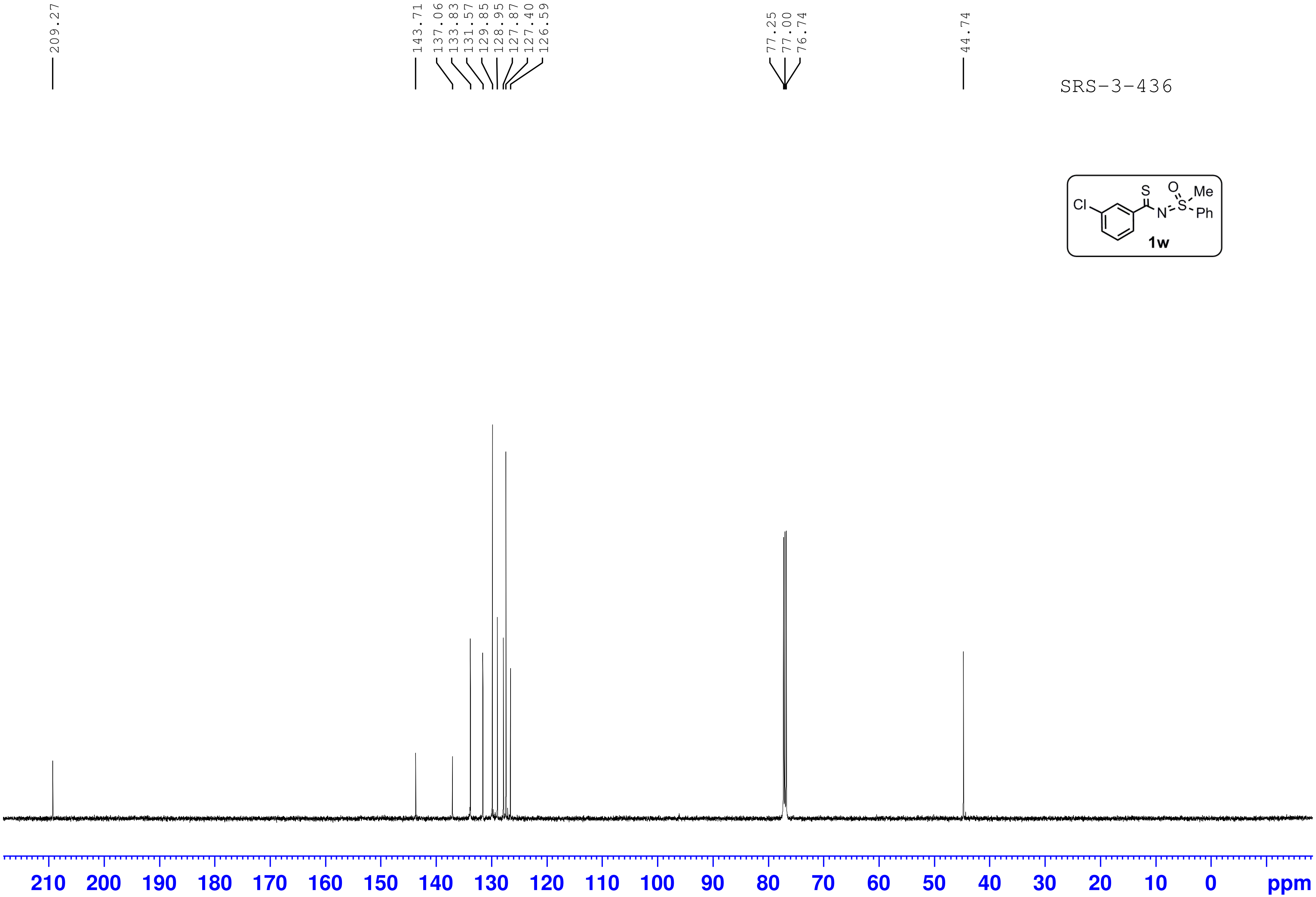

208.19
152.09
146.41
141.13
136.59
134.08
129.94
127.38
124.91
119.14
119.07
114.04
113.97
77.25
77.00
76.74
56.59
44.62
MAJJI-17-307
MeO
O2N
S
O
Me
N
S
Ph
1u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.143
8.141
8.137
8.124
8.121
8.118
8.043
8.039
8.037
8.033
8.017
8.013
8.011
8.006
7.974
7.953
7.694
7.676
7.659
7.622
7.603
7.583
7.345
7.331
7.325
7.311
7.305
7.291
7.260
7.210
7.203
7.189
7.183
7.169
7.163
3.483
majji-17-281
S
O
Me
F
N
S
Ph
1v
11
10
9
8
7
6
5
4
3
2
1
ppm
1.05
1.04
1.99
1.07
2.01
1.02
1.00
3.00

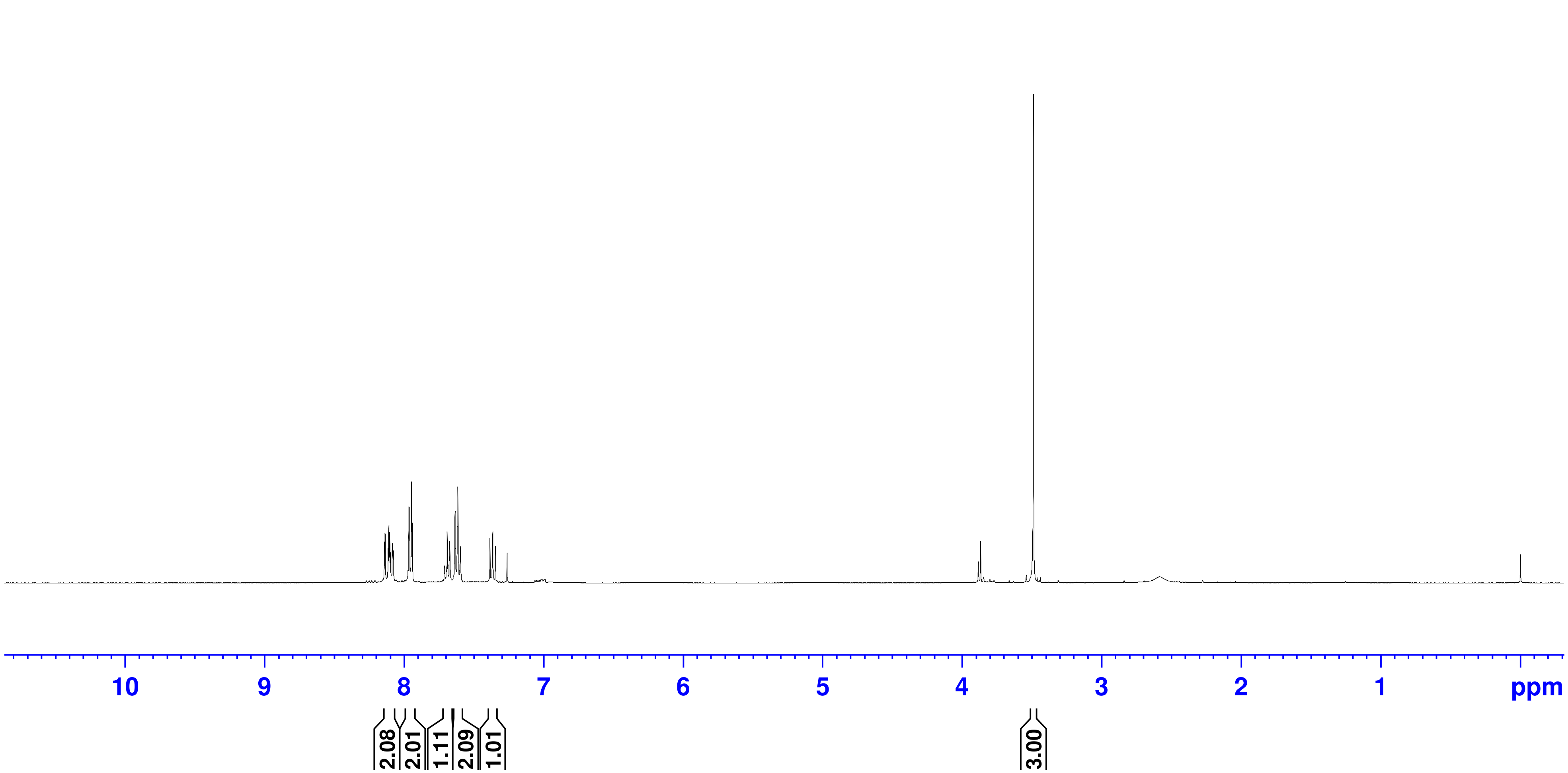

209.34
163.44
161.00
144.26
144.19
136.96
133.82
129.82
129.12
129.04
127.35
123.96
123.93
118.66
118.44
114.89
114.66
77.31
77.00
76.68
44.64
majji-17-281
S
O
Me
F
N
S
Ph
1v
200
180
160
140
120
100
80
60
40
20
0
ppm

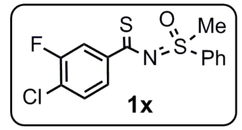

-113.69
majjji-17-281
F
S
O
Me
N
S
Ph
1v
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

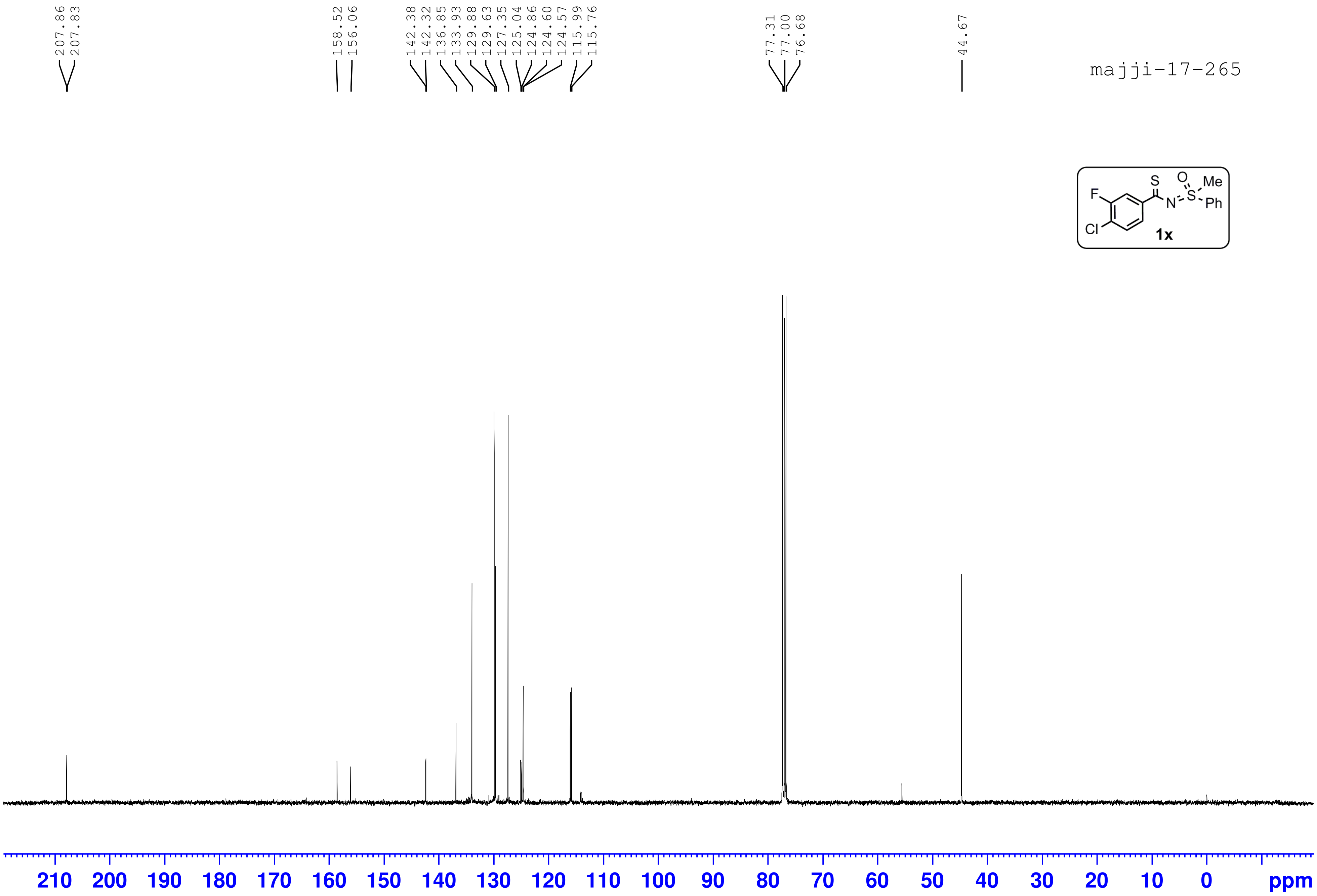

8.314 8.310 8.306 8.234 8.232 8.231 8.229 8.218 8.215 8.213 7.970 7.955 7.696 7.682 7.667 7.625 7.609 7.595 7.471 7.469 7.467 7.465 7.455 7.453 7.451 7.449 7.308 7.292 7.277 7.260
3.481
SRS-3-436
S O Me Cl N S Ph
1w
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00 1.01 2.06 1.09 2.07 1.00 1.07
3.11

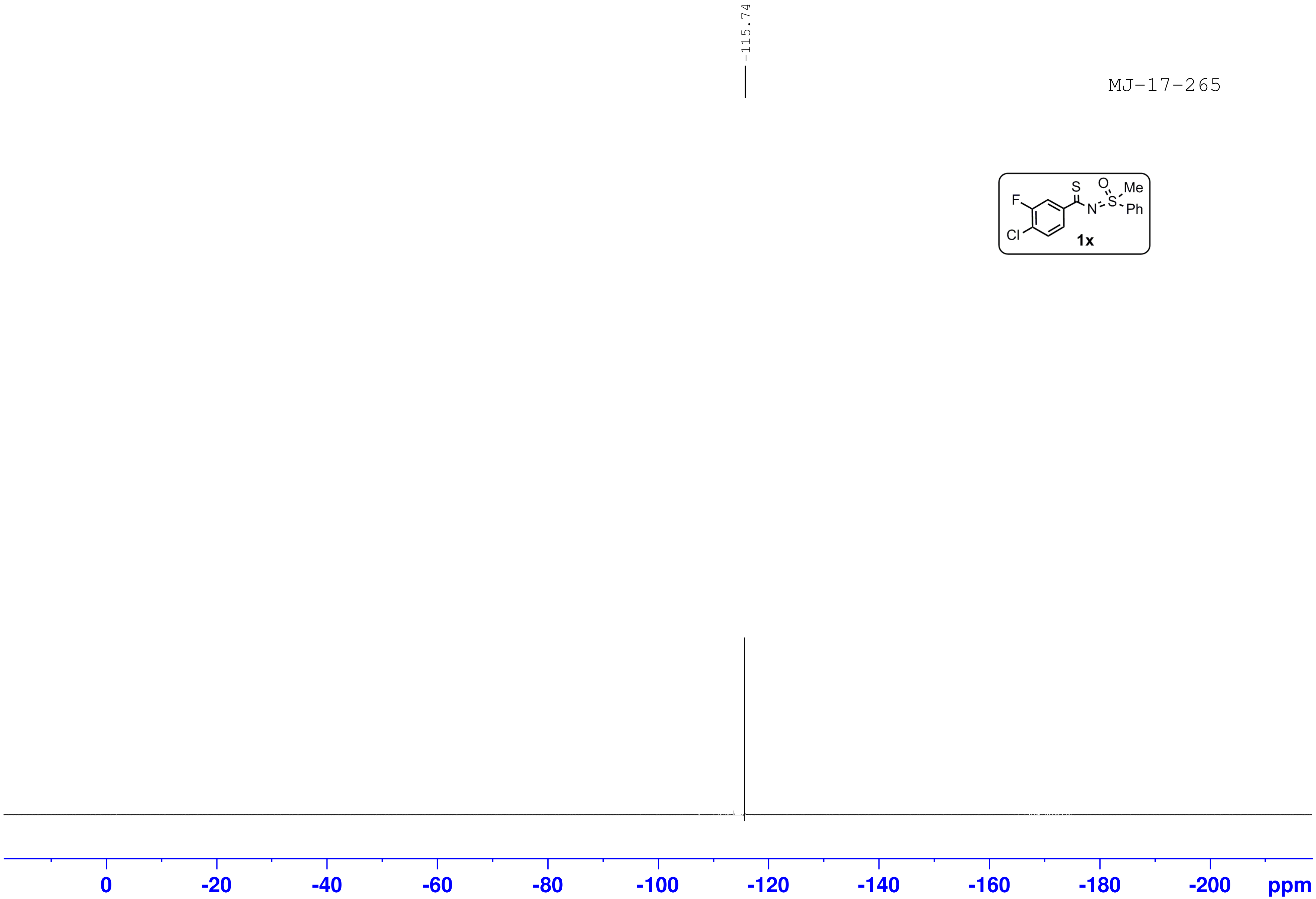

209.27
143.71
137.06
133.83
131.57
129.85
128.95
127.87
127.40
126.59
77.25
77.00
76.74
44.74
SRS-3-436
Cl
S
O
Me
N
S
Ph
1w
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

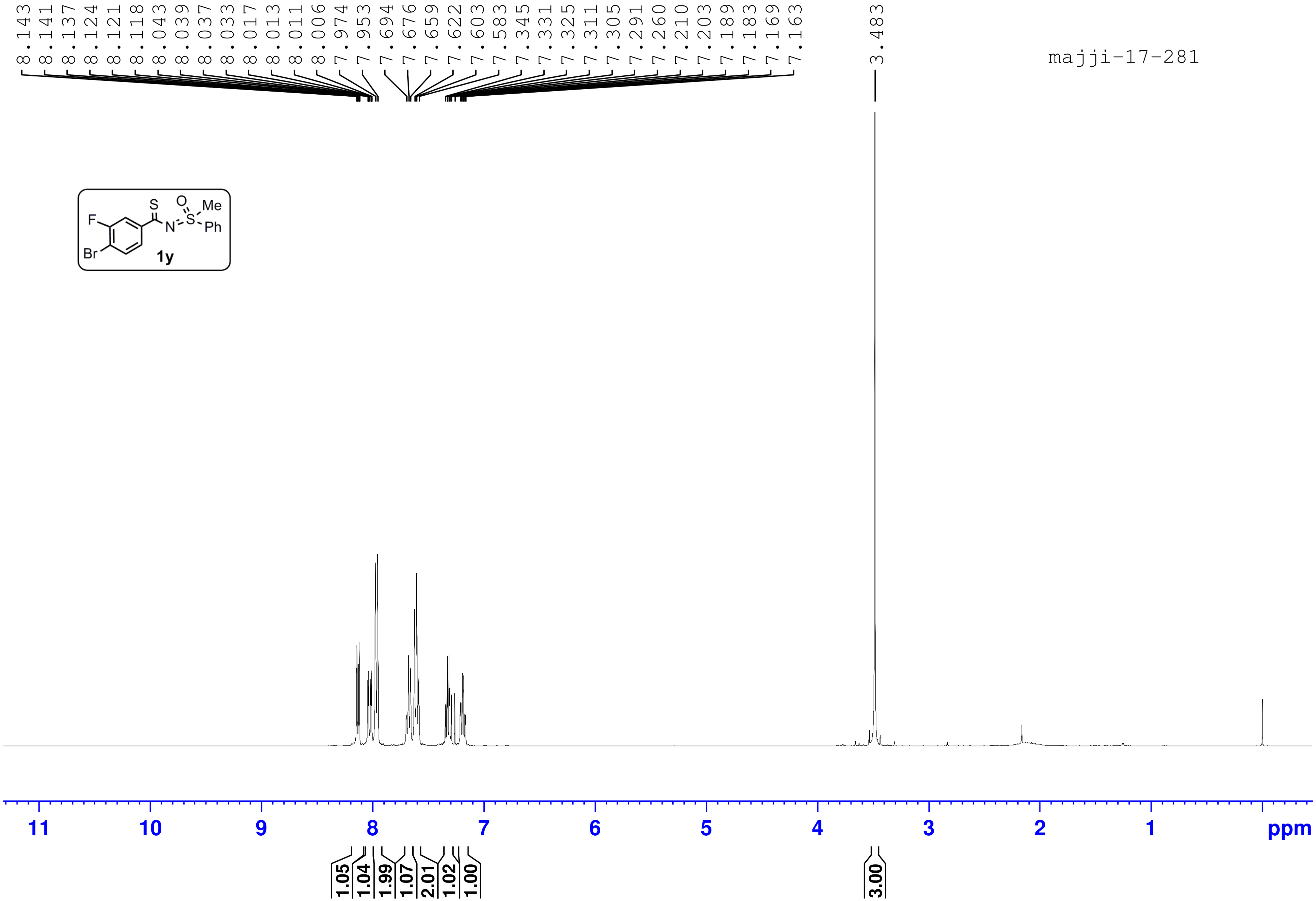
majji-17-265

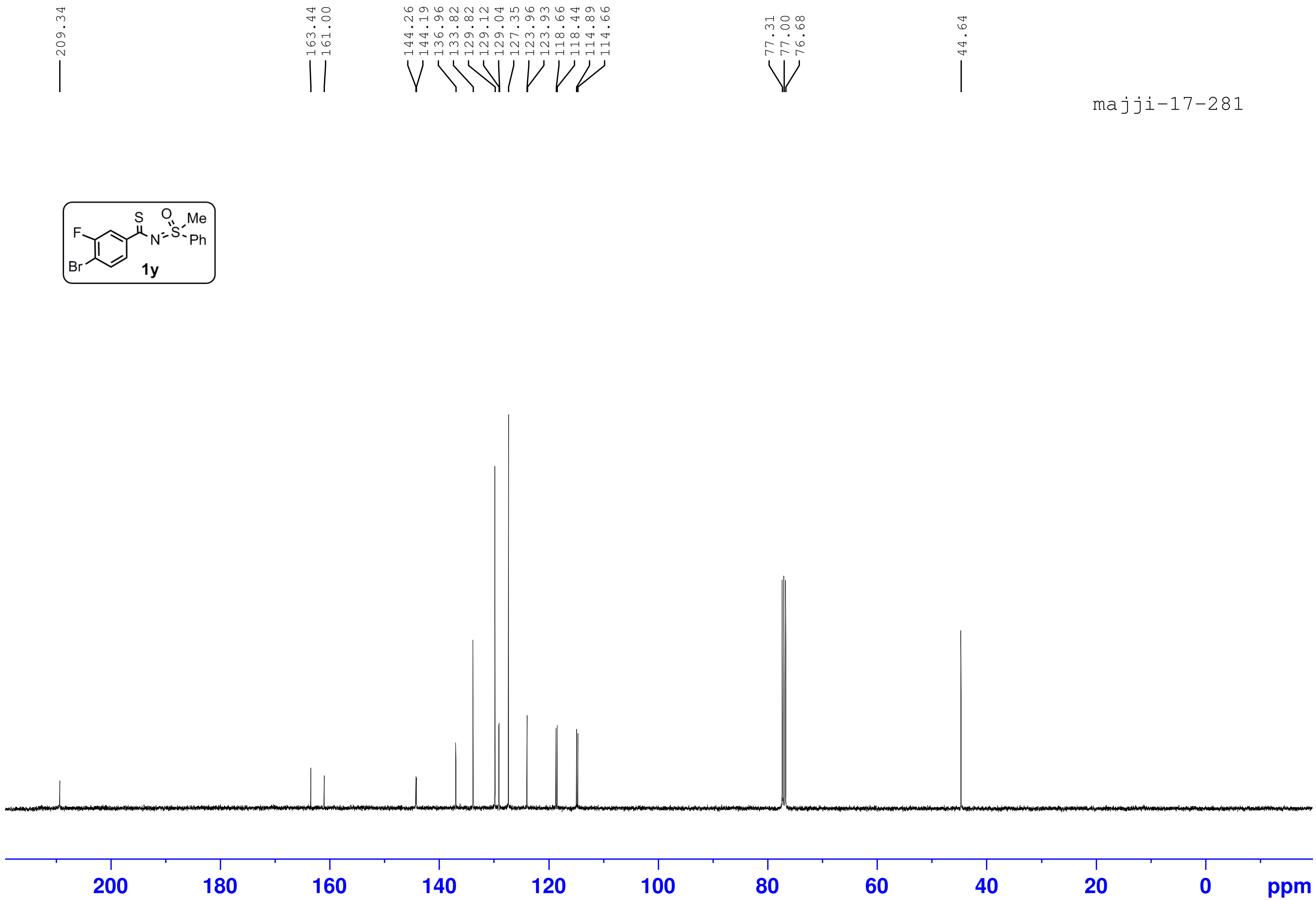

8.139
8.134
8.113
8.108
8.103
8.097
8.083
8.081
8.077
8.076
7.963
7.959
7.945
7.941
7.708
7.690
7.671
7.633
7.617
7.614
7.596
7.593
7.383
7.364
7.344
7.260
3.488
10
9
8
7
6
5
4
3
2
1
ppm
2.08
2.01
1.11
2.09
1.01
3.00

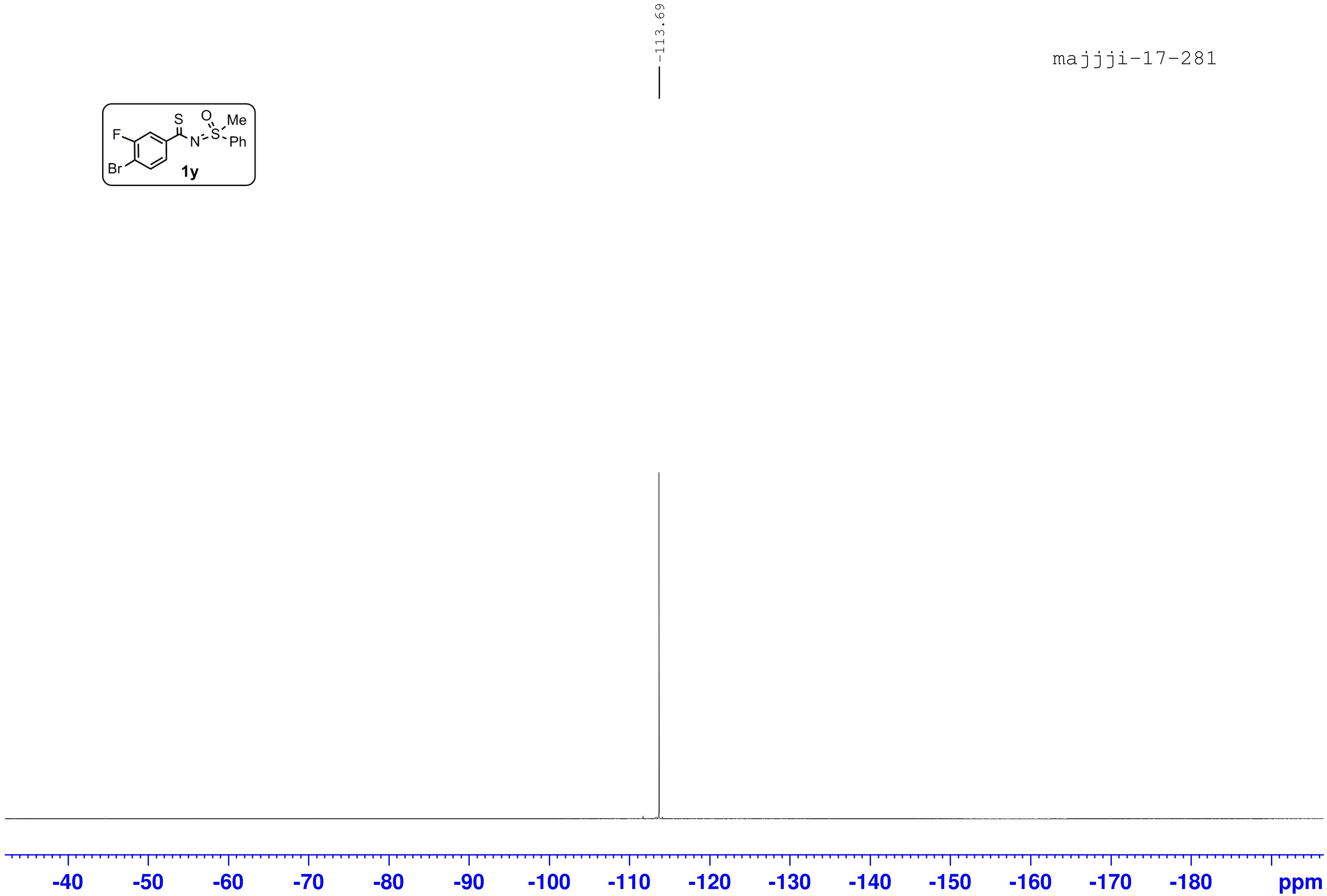

F
Cl
S
O
Me
N
S
Ph
1x


207.86
207.83
158.52
156.06
142.38
142.32
136.85
133.93
129.88
129.63
127.35
125.04
124.86
124.60
124.57
115.99
115.76
77.31
77.00
76.68
44.67
majji-17-265
F
Cl
S
N
O
S
Me
Ph
1x
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

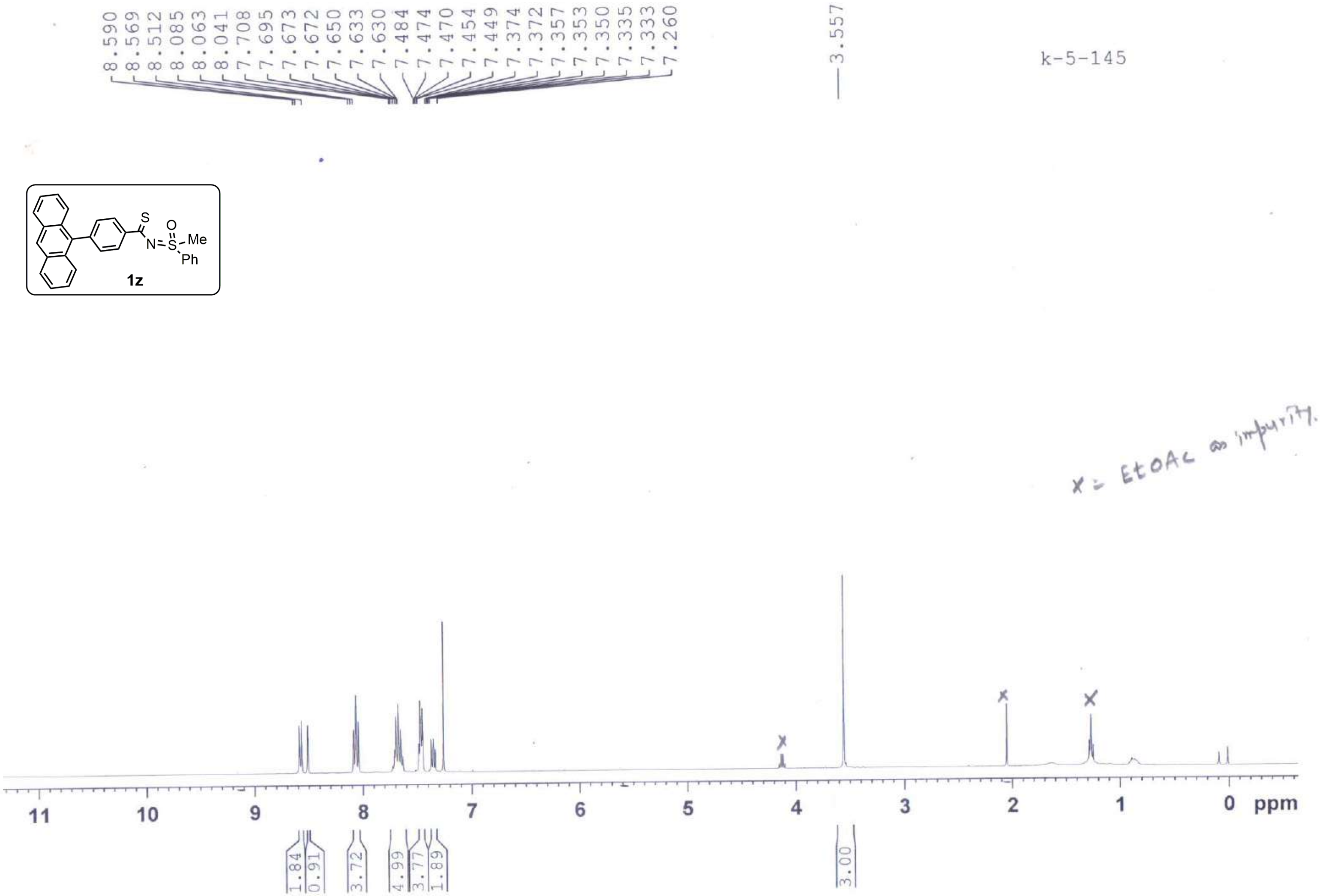

-115.74
MJ-17-265
F
Cl
S
O
Me
N
S
Ph
1x
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

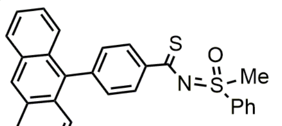

8.143
8.141
8.137
8.124
8.121
8.118
8.043
8.039
8.037
8.033
8.017
8.013
8.011
8.006
7.974
7.953
7.694
7.676
7.659
7.622
7.603
7.583
7.345
7.331
7.325
7.311
7.305
7.291
7.260
7.210
7.203
7.189
7.183
7.169
7.163
3.483
majji-17-281
F
Br
S
O
Me
N
S
Ph
1y
11
10
9
8
7
6
5
4
3
2
1
ppm
1.05
1.04
1.99
1.07
2.01
1.02
1.00
3.00


209.34
163.44
161.00
144.26
144.19
136.96
133.82
129.82
129.12
129.04
127.35
123.96
123.93
118.66
118.44
114.89
114.66
77.31
77.00
76.68
44.64
majji-17-281
S
O
Me
F
N
S
Ph
Br
1y
200
180
160
140
120
100
80
60
40
20
0
ppm

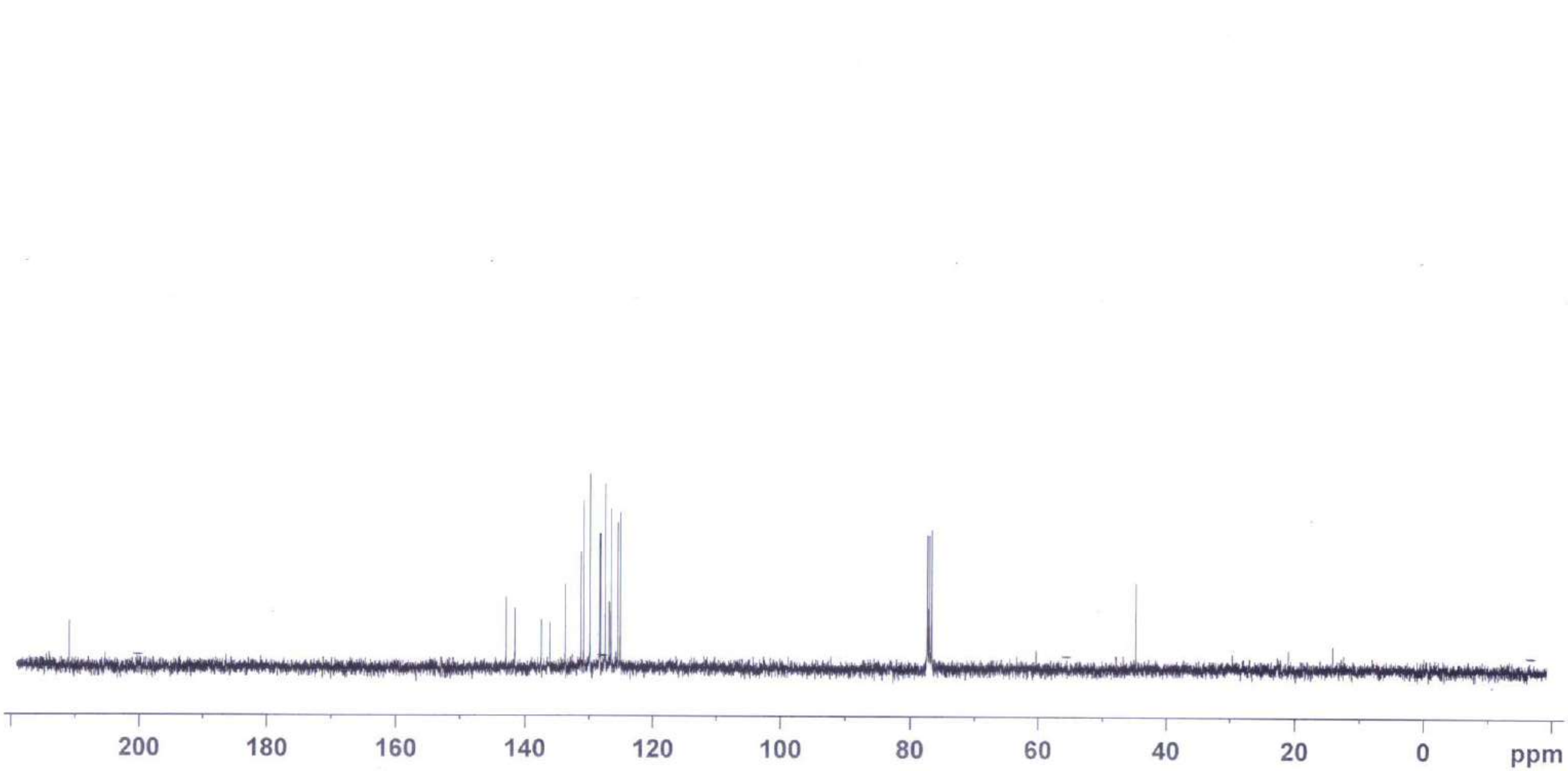


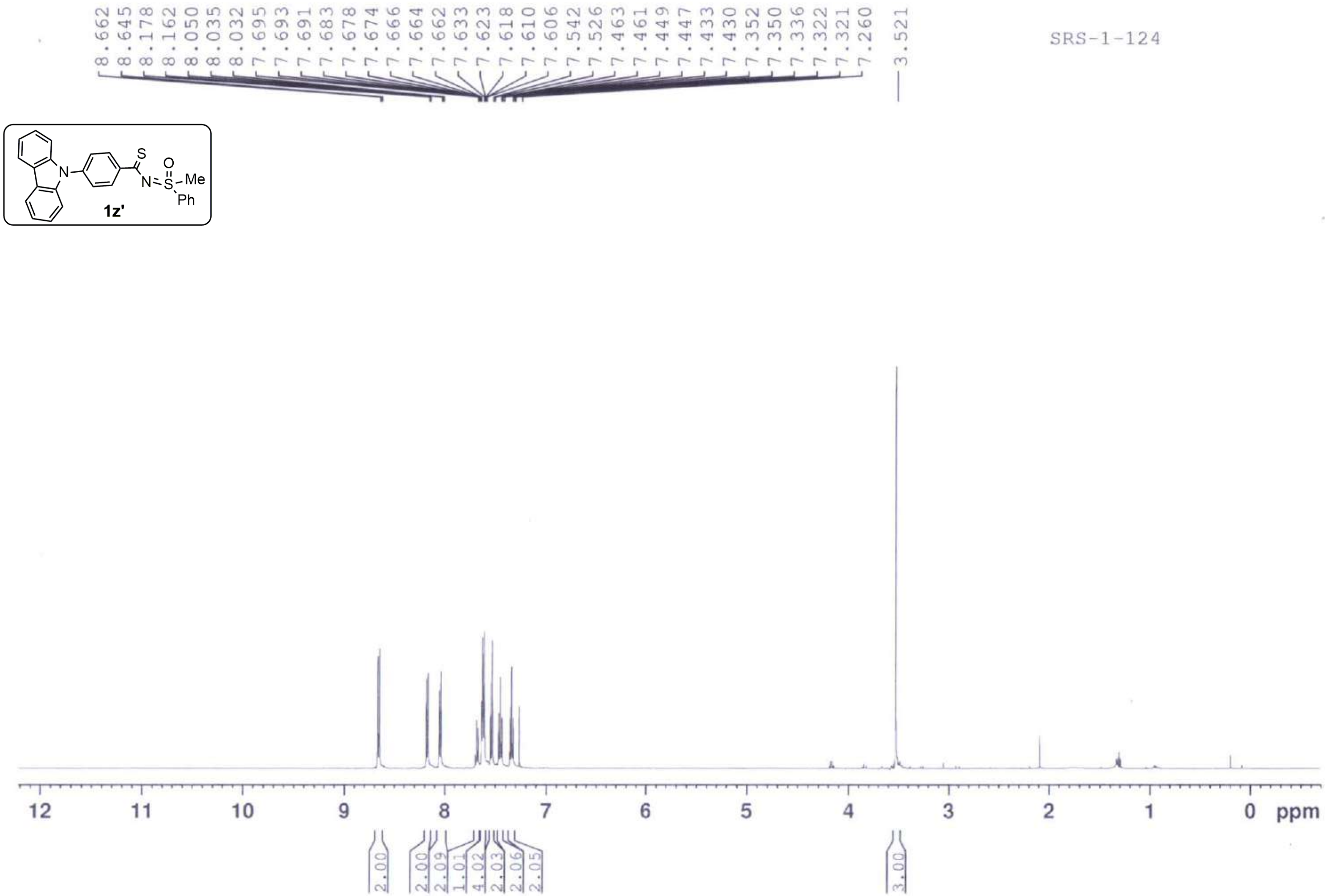
-113.69
majjji-17-281
F
Br
S
O
Me
N
S
Ph
1y
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

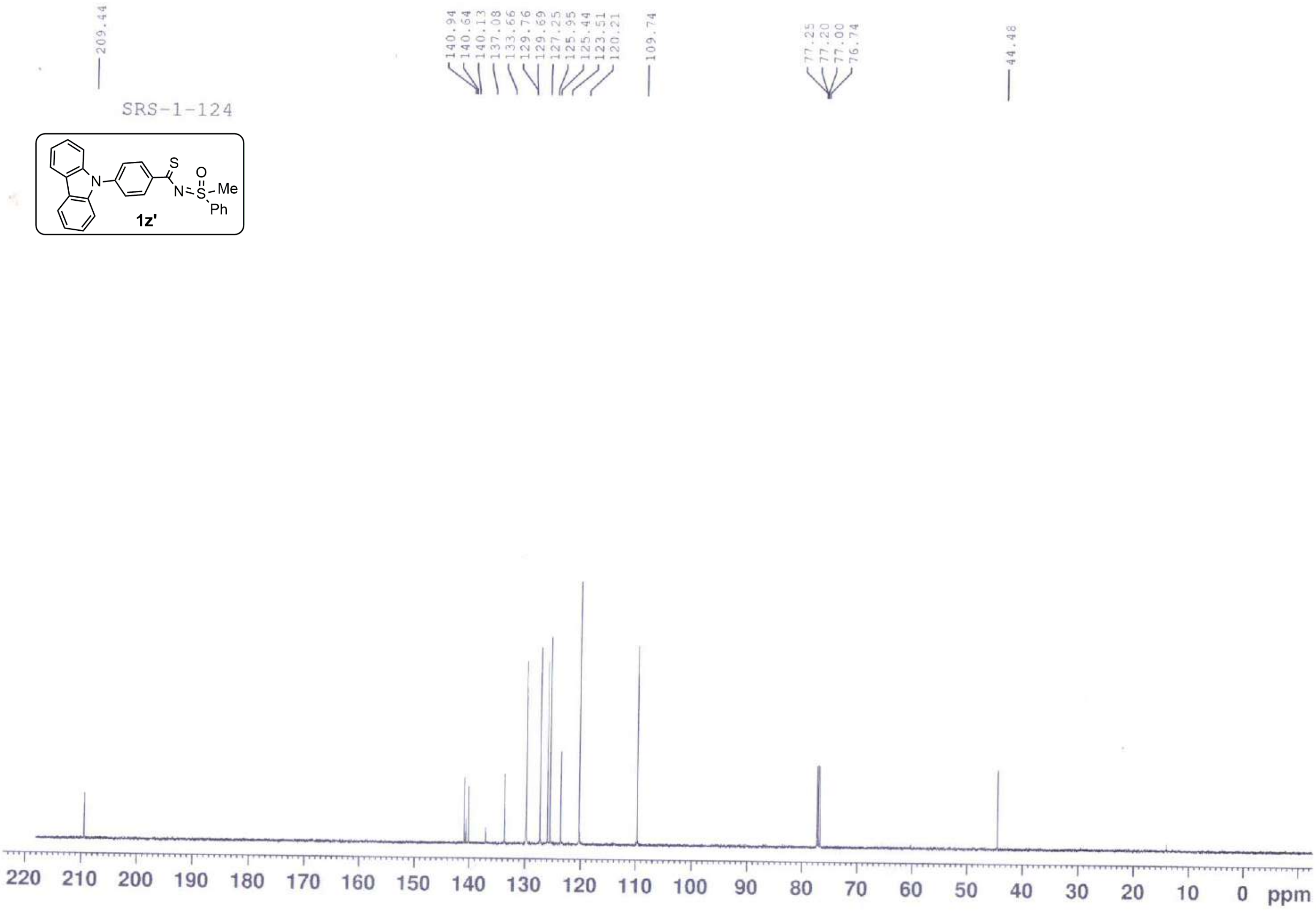

8.590
8.569
8.512
8.085
8.063
8.041
7.708
7.695
7.673
7.672
7.650
7.633
7.630
7.484
7.474
7.470
7.454
7.449
7.374
7.372
7.357
7.353
7.350
7.335
7.333
7.260
3.557
k-5-145
S
O
N
S
Me
Ph
1z
x = EtOAc as impurity.
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.84
0.91
3.72
4.99
3.77
1.89
3.00


S
O
N
S
Me
Ph

1z

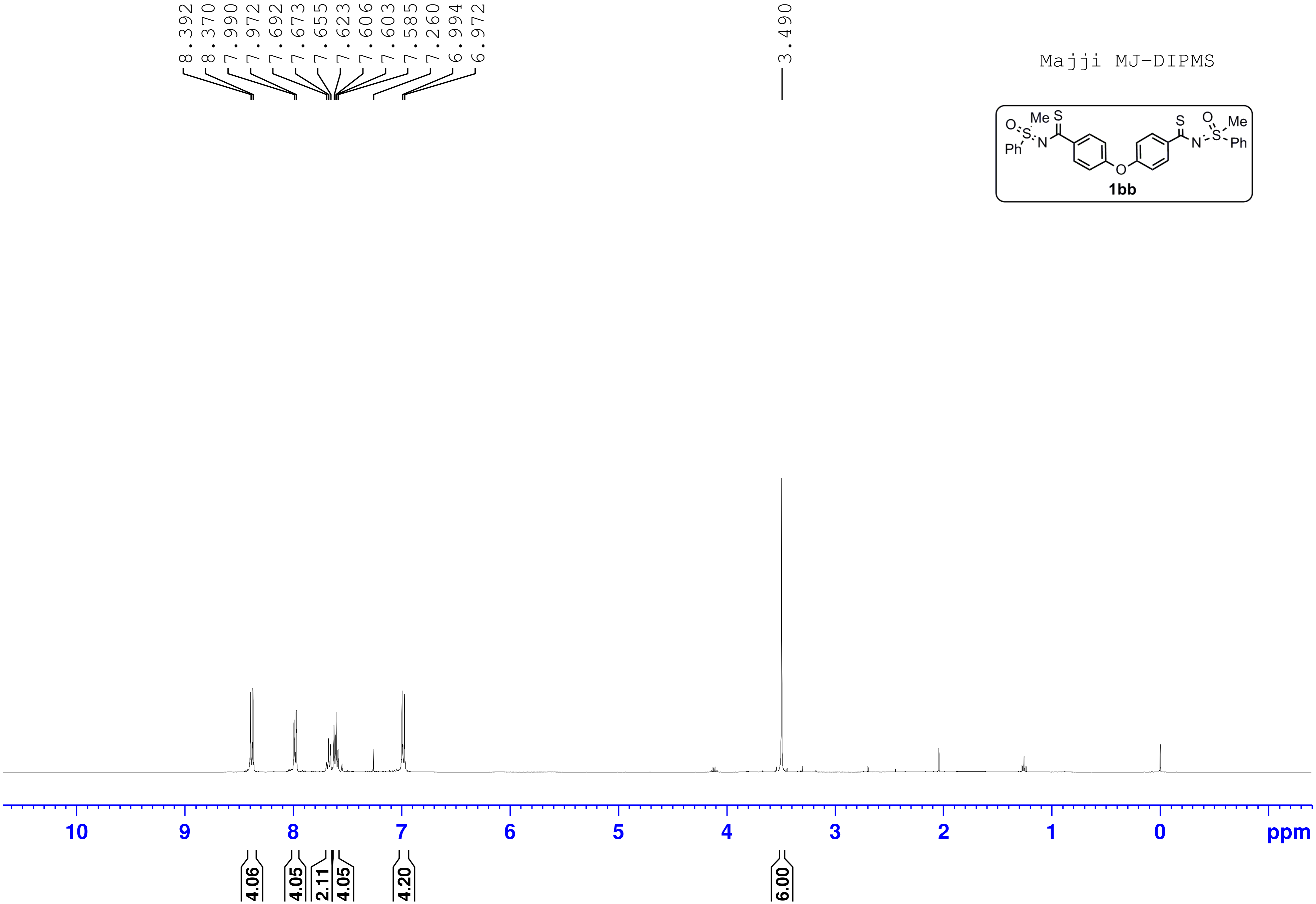

210.92
142.91
141.56
137.45
136.16
133.76
131.26
130.86
129.87
129.83
128.34
128.22
127.48
126.85
126.60
125.49
125.14
77.31
77.00
76.68
44.77
k-5-145
200
180
160
140
120
100
80
60
40
20
0
ppm

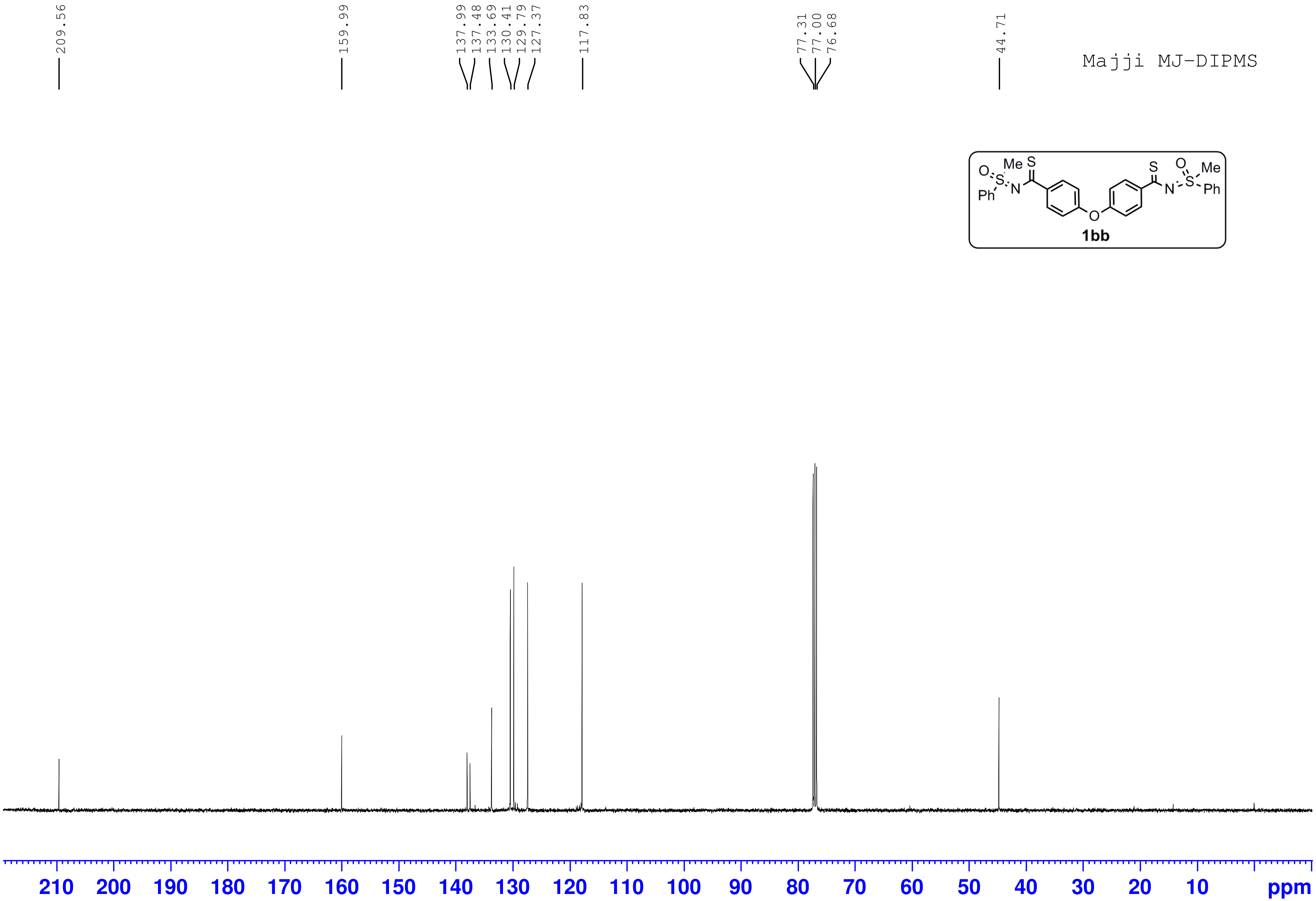

8.662
8.645
8.178
8.162
8.050
8.035
8.032
7.695
7.693
7.691
7.683
7.678
7.674
7.666
7.664
7.662
7.633
7.623
7.618
7.610
7.606
7.542
7.526
7.463
7.461
7.449
7.447
7.433
7.430
7.352
7.350
7.336
7.322
7.321
7.260
3.521
SRS-1-124
1z'
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.00
2.00
2.09
1.01
4.02
2.03
2.06
2.05
3.00

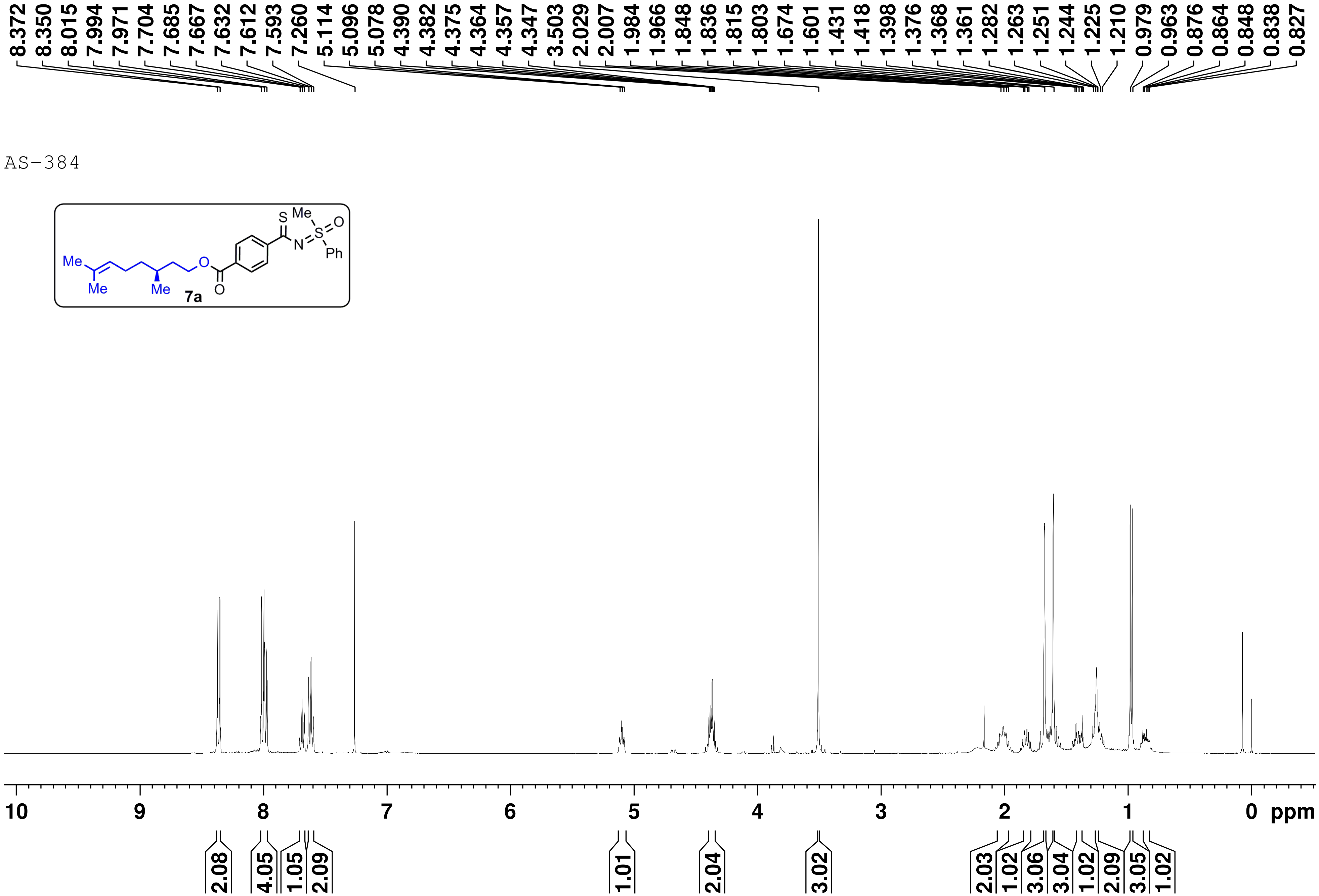

209.44
140.94
140.64
140.13
137.08
133.66
129.76
129.69
127.25
125.95
125.44
123.51
120.21
109.74
77.25
77.20
77.00
76.74
44.48
SRS-1-124
S
O
N
Me
Ph
1z'
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

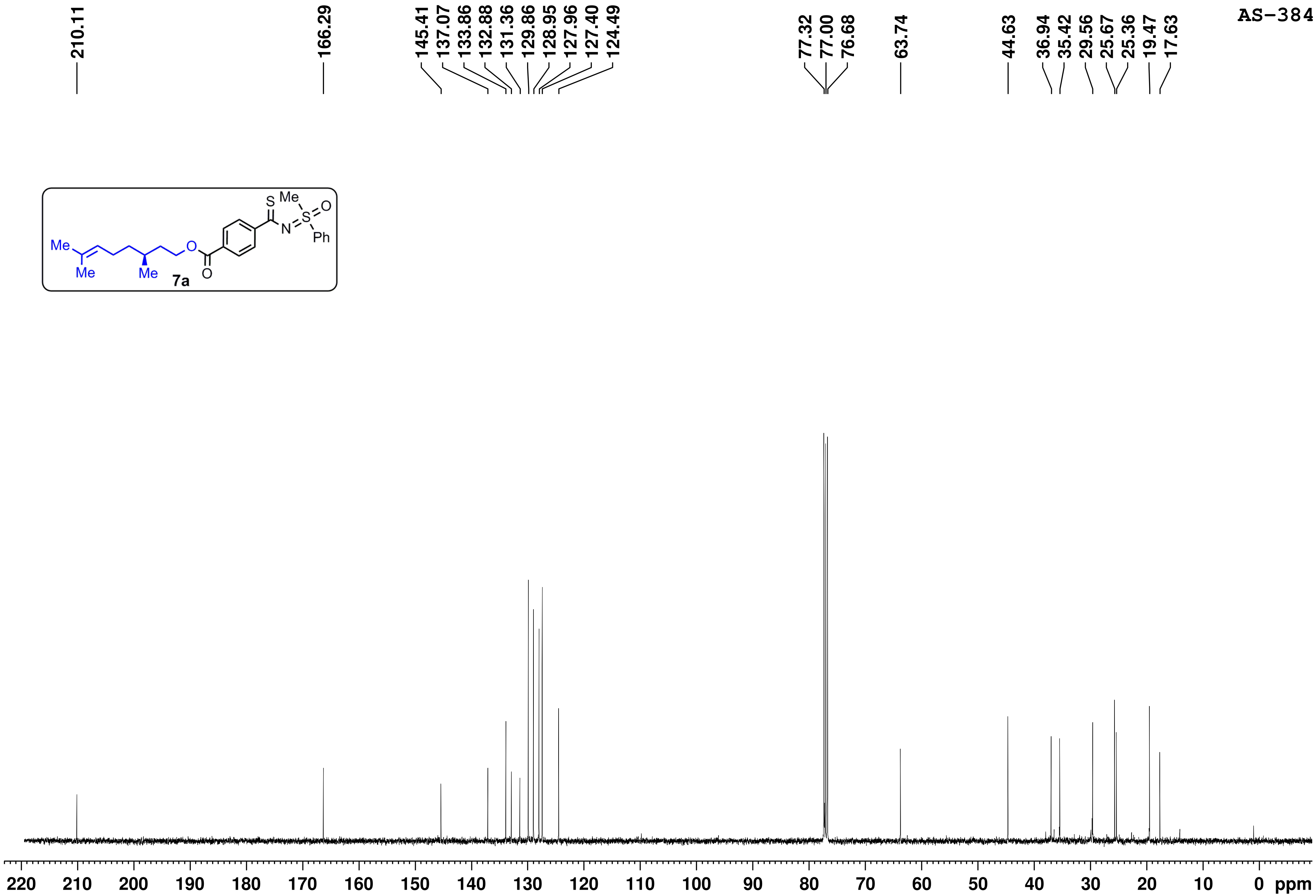
Majji MJ-DIPMS

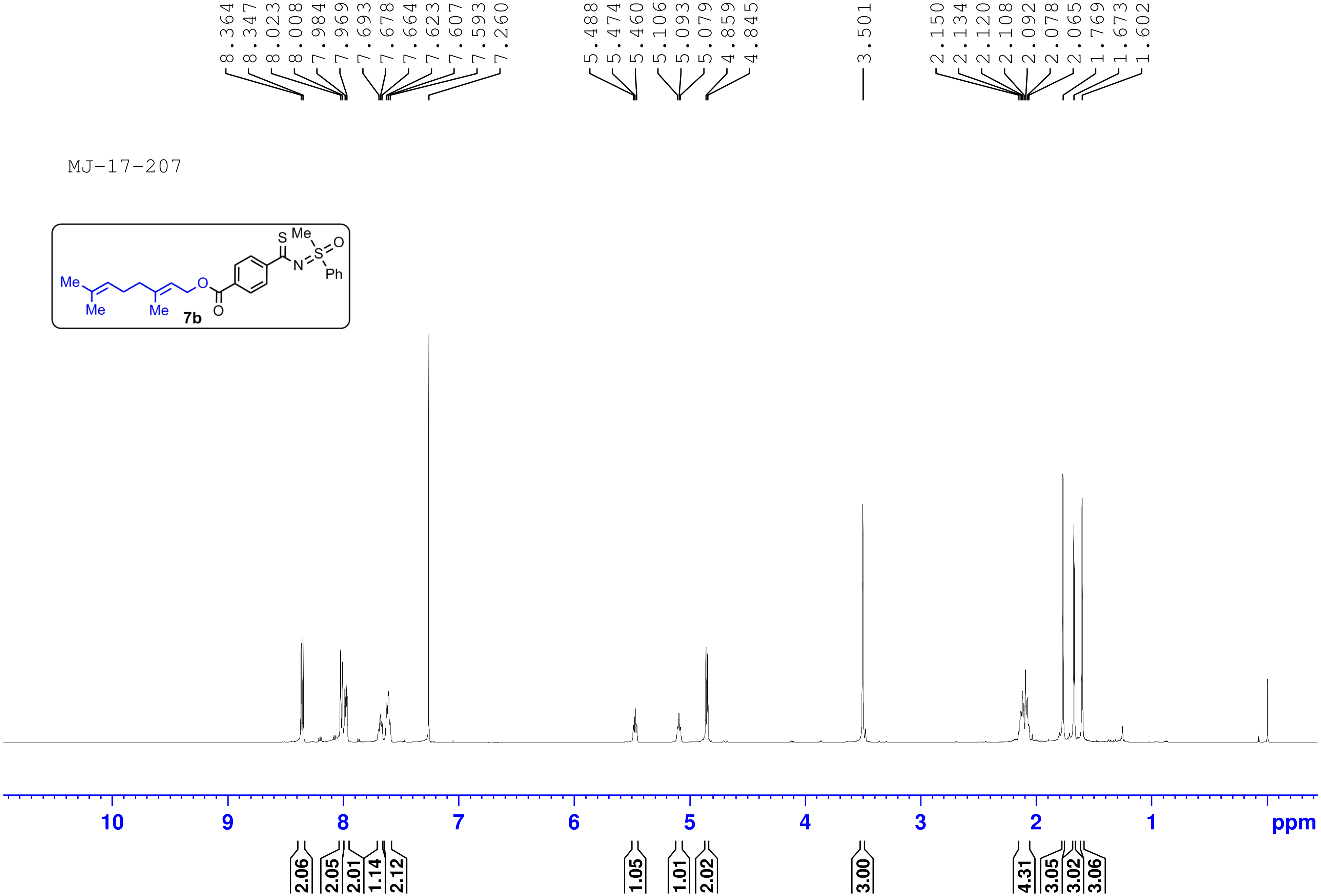
1bb

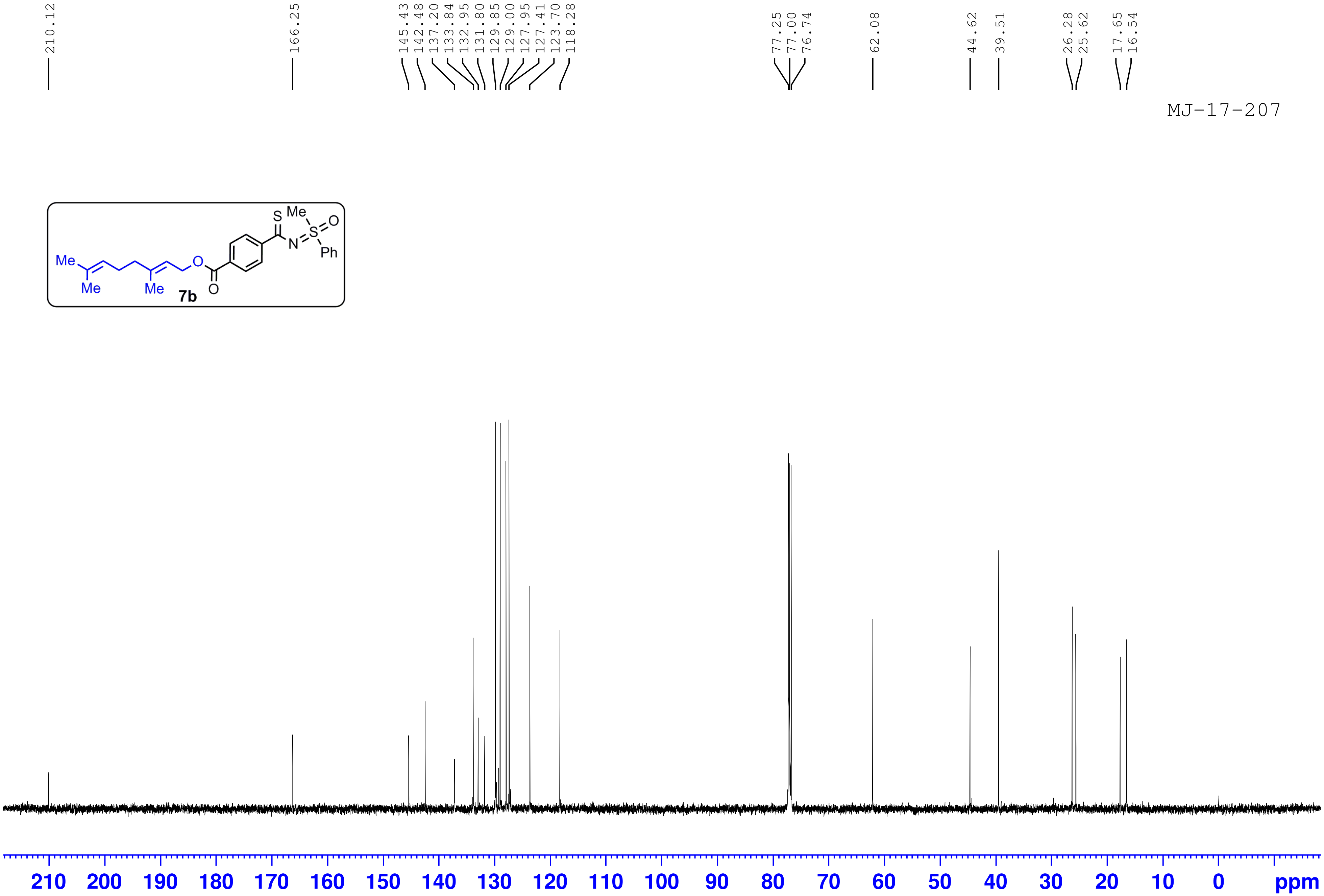



209.56
159.99
137.99
137.48
133.69
130.41
129.79
127.37
117.83
77.31
77.00
76.68
44.71
Majji MJ-DIPMS
1bb
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

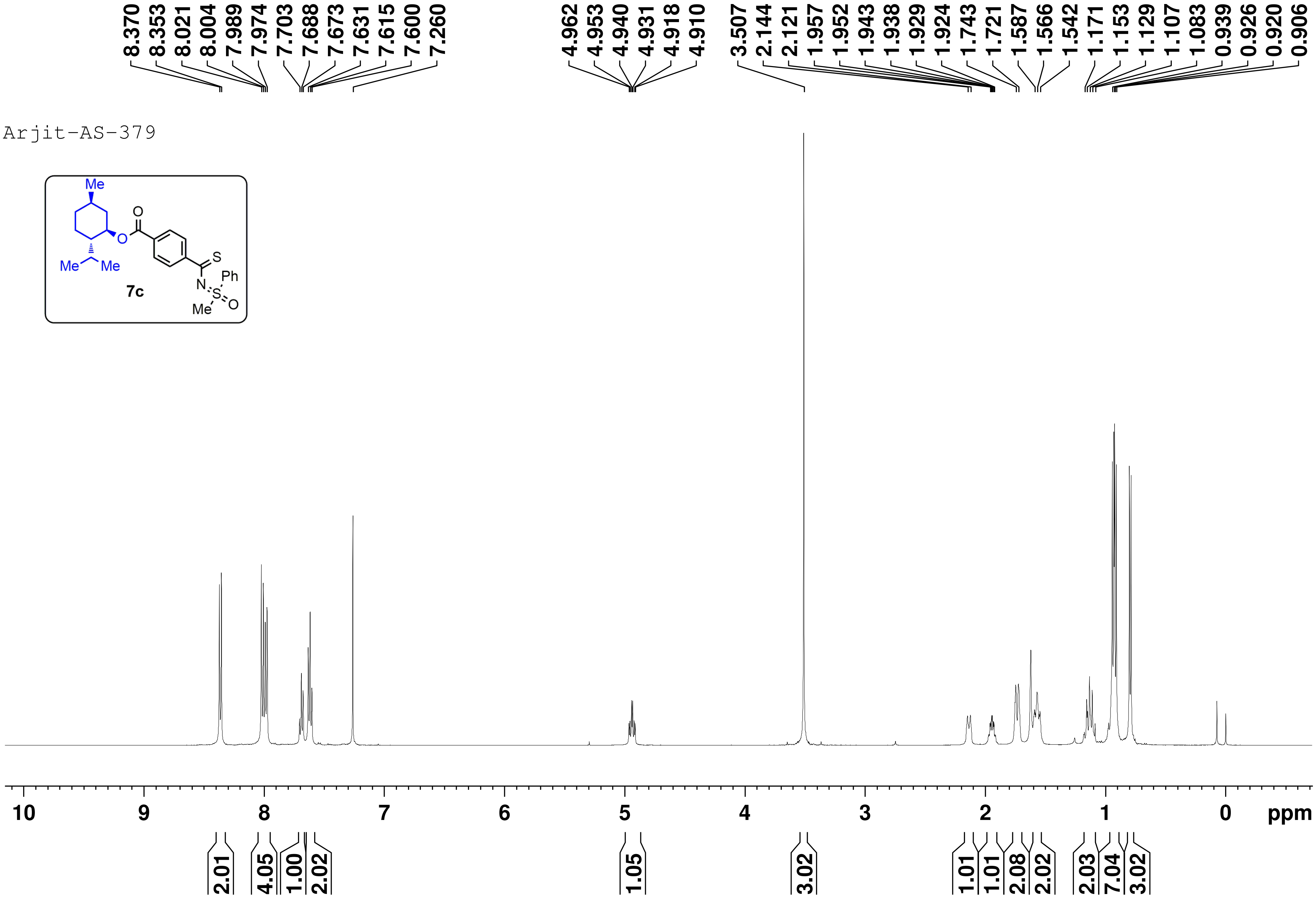

8.372 8.350 8.015 7.994 7.971 7.704 7.685 7.667 7.632 7.612 7.593 7.260 5.114 5.096 5.078 4.390 4.382 4.375 4.364 4.357 4.347 3.503 2.029 2.007 1.984 1.966 1.848 1.836 1.815 1.803 1.674 1.601 1.431 1.418 1.398 1.376 1.368 1.361 1.282 1.263 1.251 1.244 1.225 1.210 0.979 0.963 0.876 0.864 0.848 0.838 0.827
AS-384
S
Me
O
N
S
Ph
Me
Me
Me
O
O
7a
10 9 8 7 6 5 4 3 2 1 0 ppm
2.08 4.05 1.05 2.09 1.01 2.04 3.02 2.03 1.02 3.06 3.04 1.02 2.09 3.05 1.02

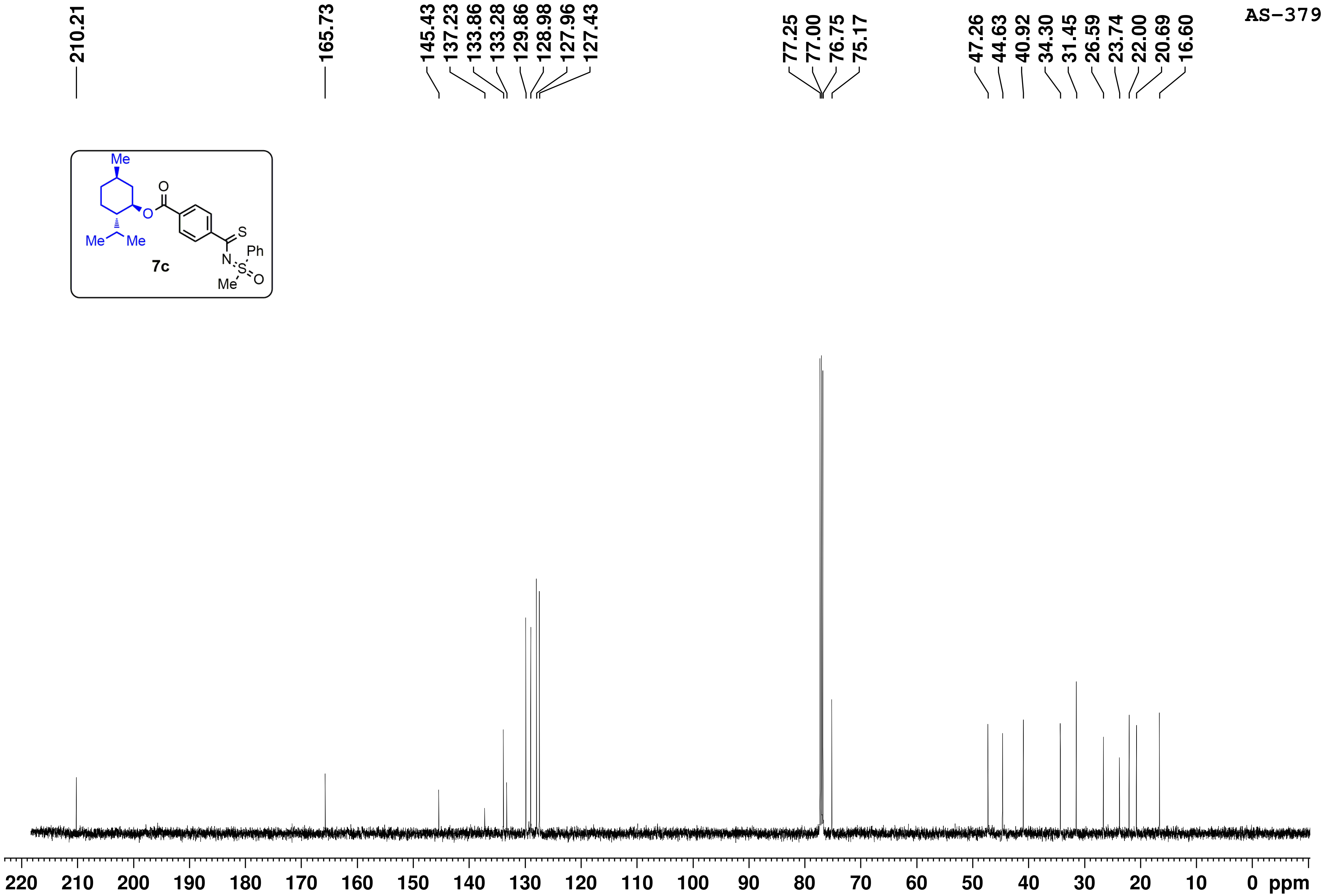

AS-384
210.11
166.29
145.41
137.07
133.86
132.88
131.36
129.86
128.95
127.96
127.40
124.49
77.32
77.00
76.68
63.74
44.63
36.94
35.42
29.56
25.67
25.36
19.47
17.63
Me
S
O
N
Ph
O
7a
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

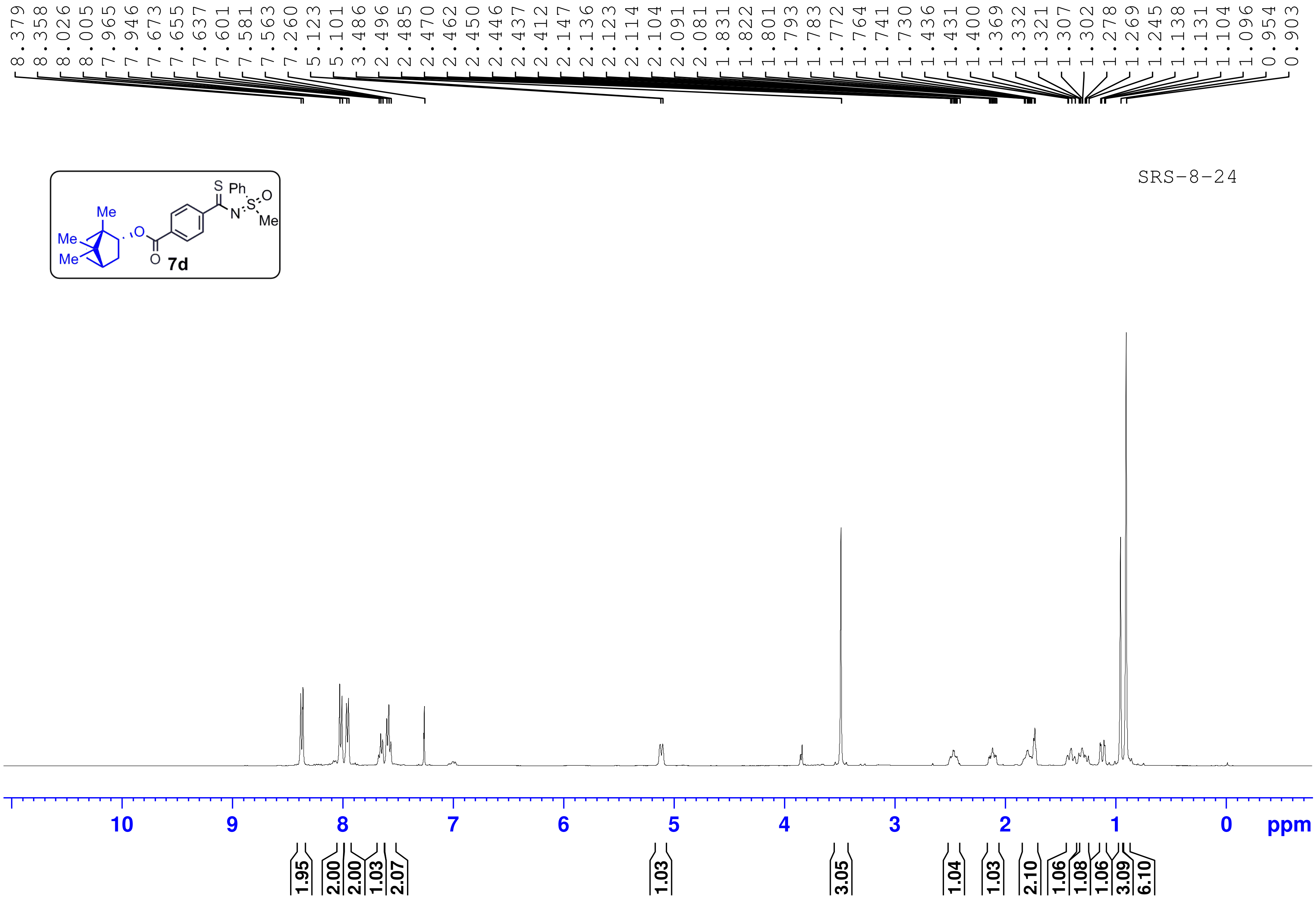

8.364
8.347
8.023
8.008
7.984
7.969
7.693
7.678
7.664
7.623
7.607
7.593
7.260
5.488
5.474
5.460
5.106
5.093
5.079
4.859
4.845
3.501
2.150
2.134
2.120
2.108
2.092
2.078
2.065
1.769
1.673
1.602
MJ-17-207
7b
10 9 8 7 6 5 4 3 2 1 ppm
2.06 2.05 2.01 1.14 2.12 1.05 1.01 2.02 3.00 4.31 3.05 3.02 3.06

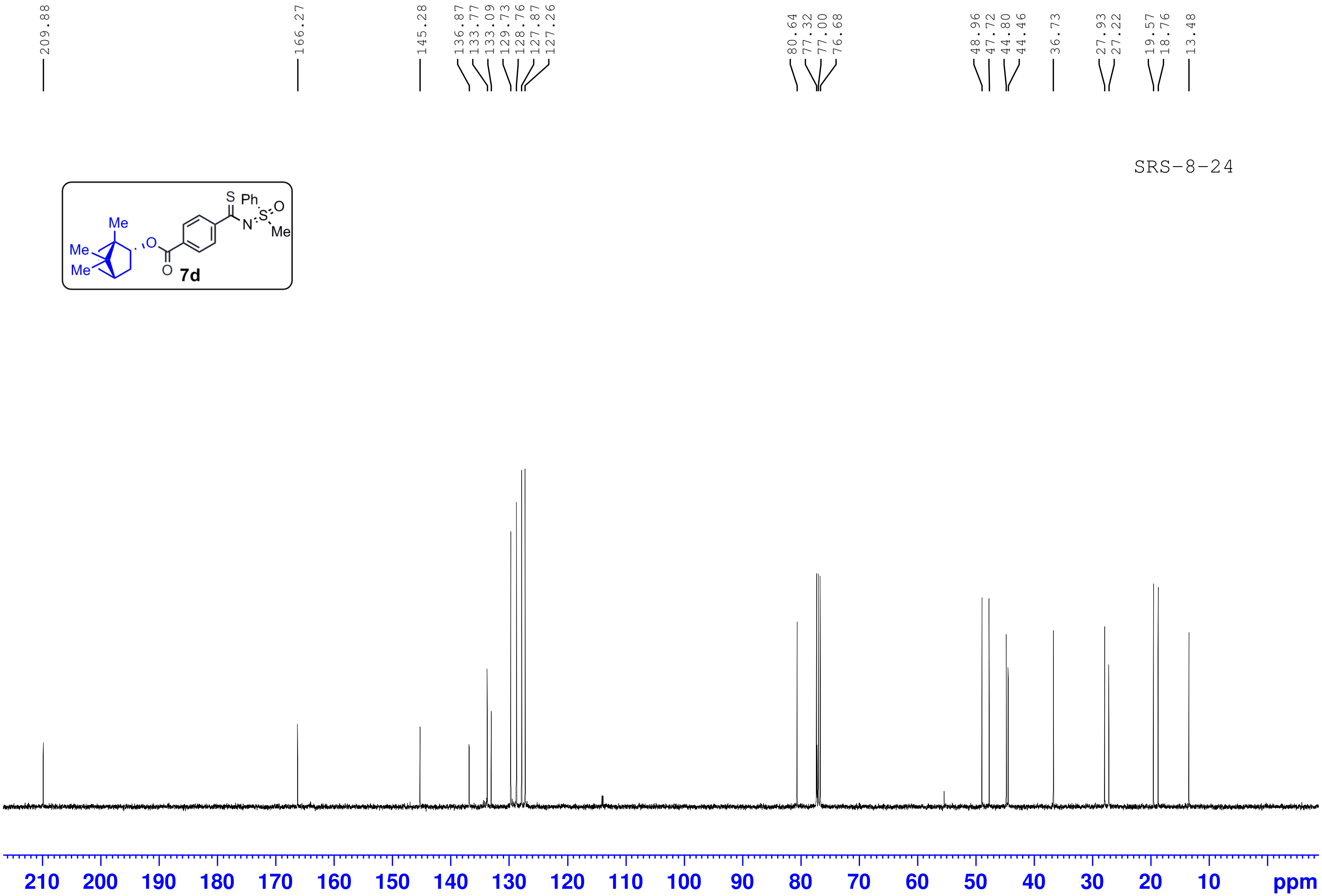

210.12
166.25
145.43
142.48
137.20
133.84
132.95
131.80
129.85
129.00
127.95
127.41
123.70
118.28
77.25
77.00
76.74
62.08
44.62
39.51
26.28
25.62
17.65
16.54
MJ-17-207
Me
Me
Me
O
O
S
Me
S
O
N
Ph
7b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

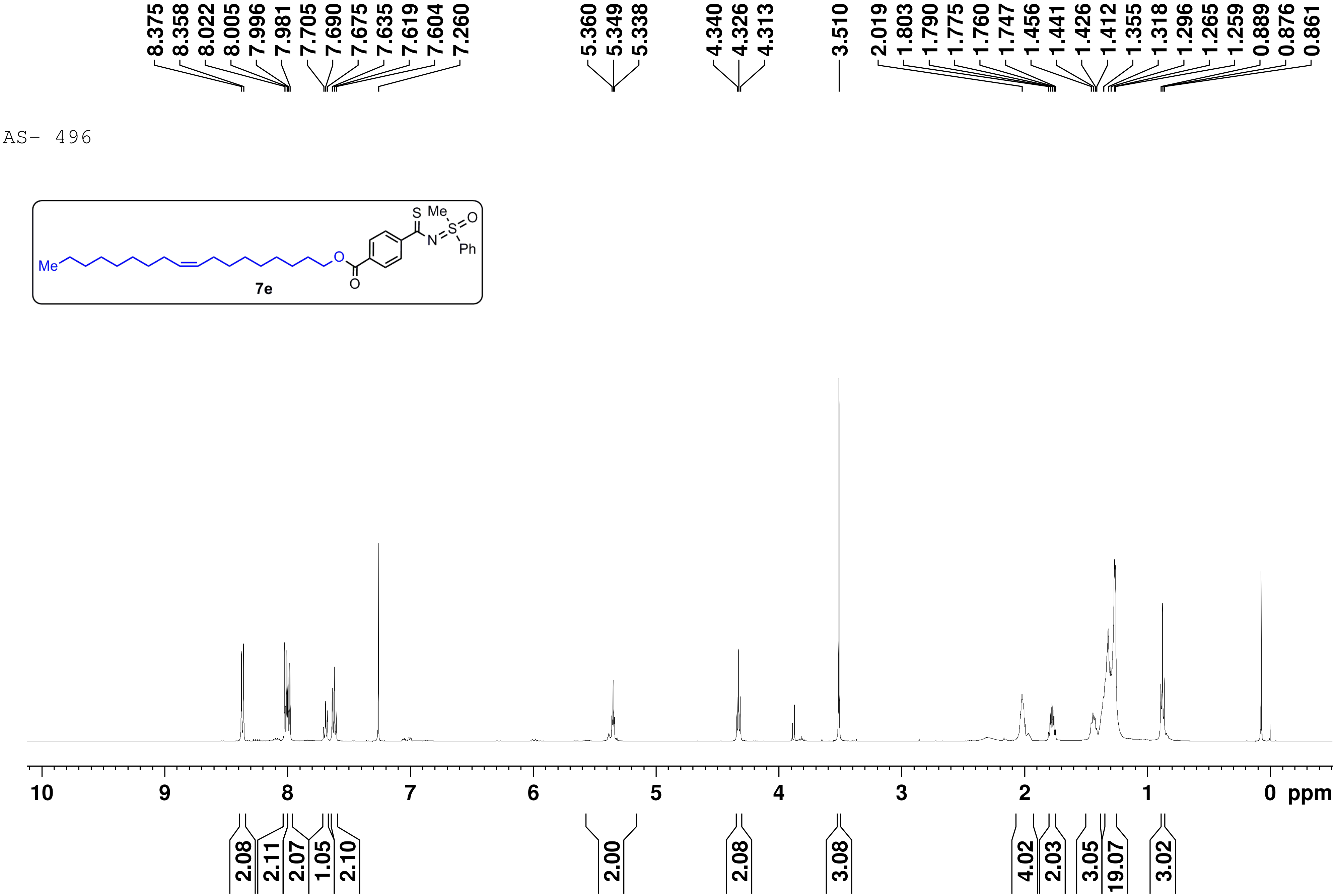
Arjit-AS-379

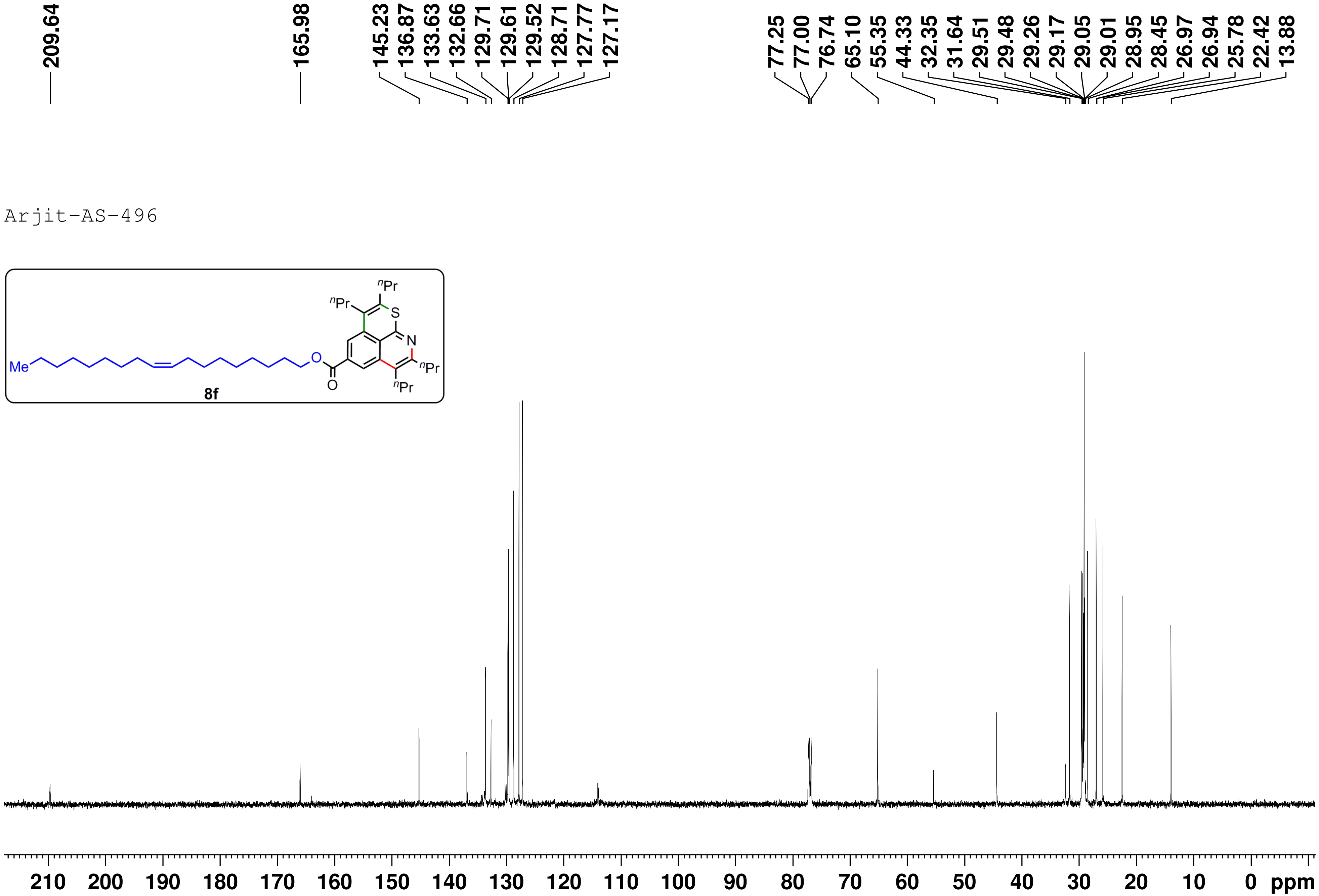

8.370
8.353
8.021
8.004
7.989
7.974
7.703
7.688
7.673
7.631
7.615
7.600
7.260
4.962
4.953
4.940
4.931
4.918
4.910
3.507
2.144
2.121
1.957
1.952
1.943
1.938
1.929
1.924
1.743
1.721
1.587
1.566
1.542
1.171
1.153
1.129
1.107
1.083
0.939
0.926
0.920
0.906
Me
O
O
S
Ph
N
S
O
Me
Me
Me
7c
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
4.05
1.00
2.02
1.05
3.02
1.01
1.01
2.08
2.02
2.03
7.04
3.02

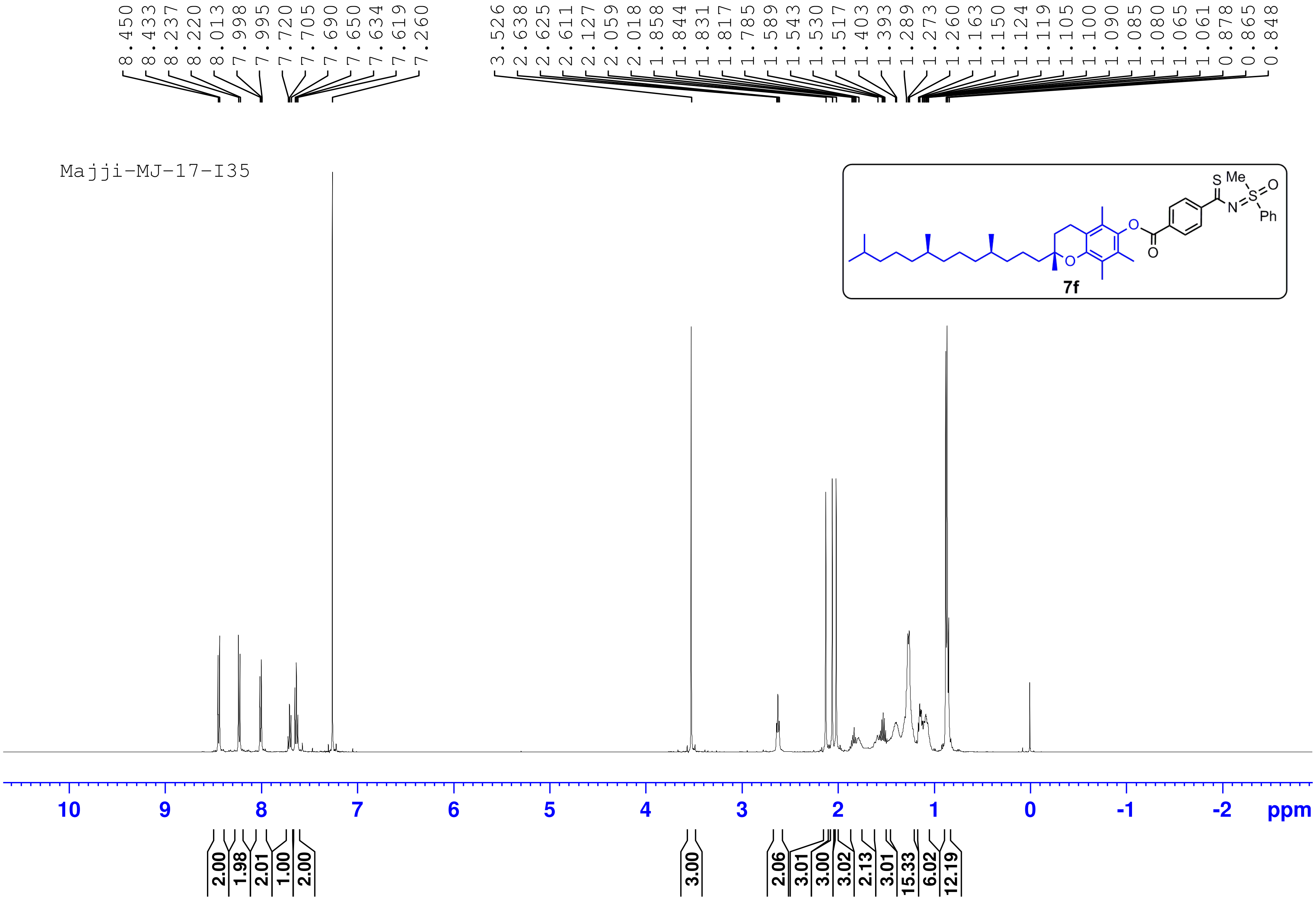

AS-379
210.21
165.73
145.43
137.23
133.86
133.28
129.86
128.98
127.96
127.43
77.25
77.00
76.75
75.17
47.26
44.63
40.92
34.30
31.45
26.59
23.74
22.00
20.69
16.60
Me
O
O
S
Ph
N
S
O
Me
Me
Me
7c
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

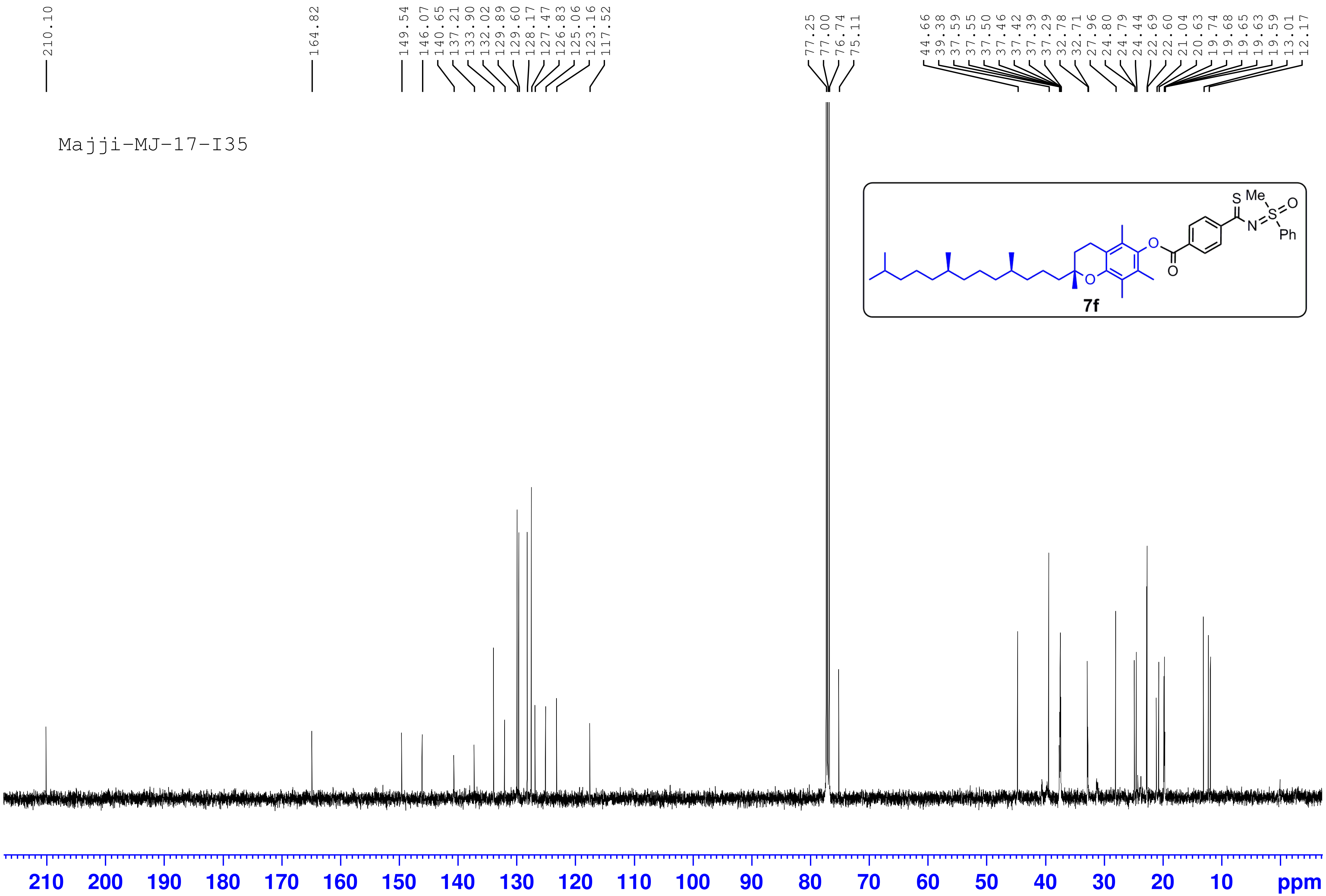

8.379
8.358
8.026
8.005
7.965
7.946
7.673
7.655
7.637
7.601
7.581
7.563
7.260
5.123
5.101
3.486
2.496
2.485
2.470
2.462
2.450
2.446
2.437
2.412
2.147
2.136
2.123
2.114
2.104
2.091
2.081
1.831
1.822
1.801
1.793
1.783
1.772
1.764
1.741
1.730
1.436
1.431
1.400
1.369
1.332
1.321
1.307
1.302
1.278
1.269
1.245
1.138
1.131
1.104
1.096
0.954
0.903
SRS-8-24
S
Ph
N
S
O
Me
Me
Me
Me
O
O
7d
10
9
8
7
6
5
4
3
2
1
0
ppm
1.95
2.00
2.00
1.03
2.07
1.03
3.05
1.04
1.03
2.10
1.06
1.08
1.06
3.09
6.10

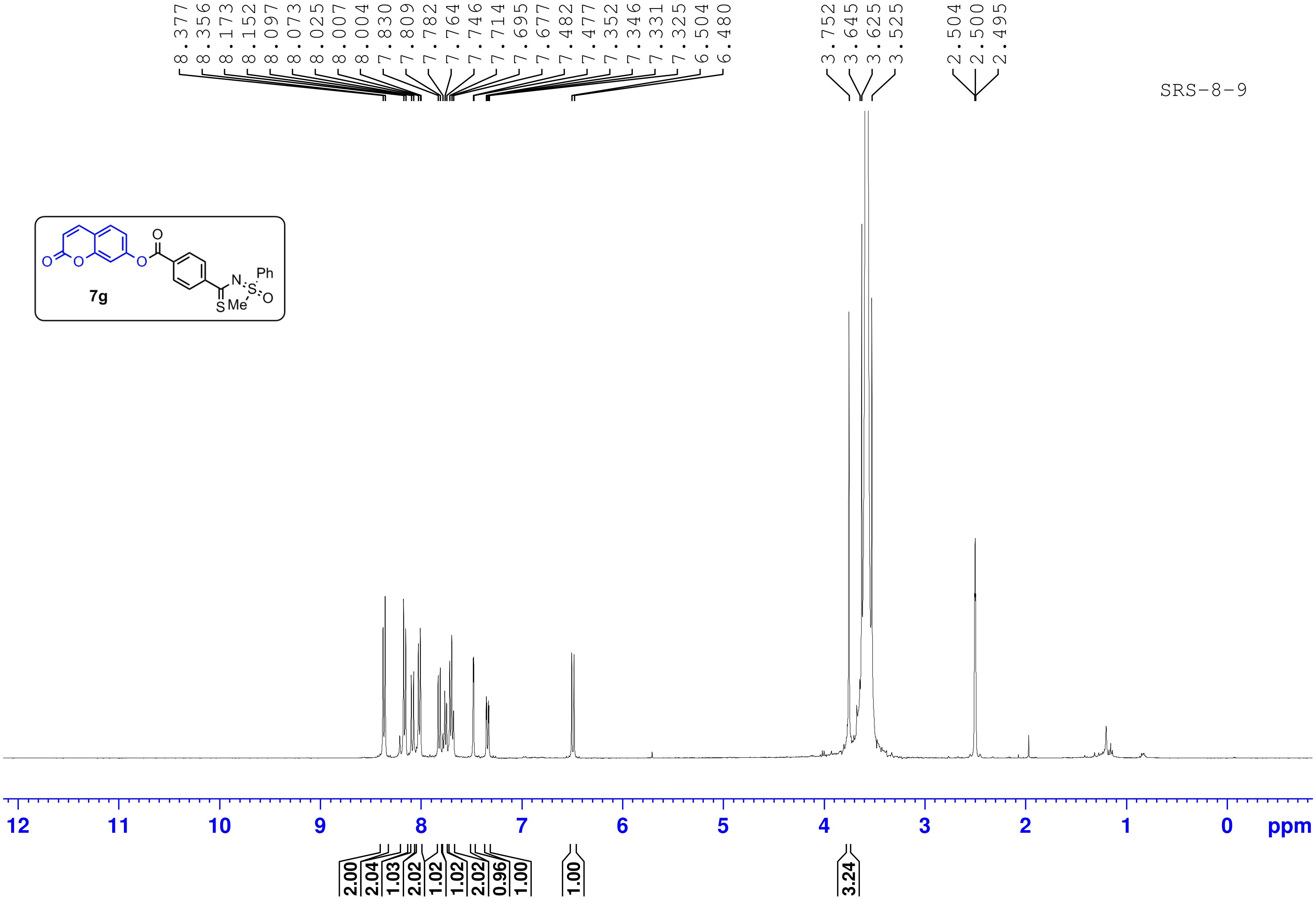

S
Ph
O
S
N
Me
Me
Me
Me
O
O
7d
209.88
166.27
145.28
136.87
133.77
133.09
129.73
128.76
127.87
127.26
80.64
77.32
77.00
76.68
48.96
47.72
44.80
44.46
36.73
27.93
27.22
19.57
18.76
13.48
SRS-8-24
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.375
8.358
8.022
8.005
7.996
7.981
7.705
7.690
7.675
7.635
7.619
7.604
7.260
5.360
5.349
5.338
4.340
4.326
4.313
3.510
2.019
1.803
1.790
1.775
1.760
1.747
1.456
1.441
1.426
1.412
1.355
1.318
1.296
1.265
1.259
0.889
0.876
0.861
AS- 496
Me
S
Me
O
N
S
Ph
O
O
7e
10
9
8
7
6
5
4
3
2
1
0
ppm
2.08
2.11
2.07
1.05
2.10
2.00
2.08
3.08
4.02
2.03
3.05
19.07
3.02


209.64
165.98
145.23
136.87
133.63
132.66
129.71
129.61
129.52
128.71
127.77
127.17
77.25
77.00
76.74
65.10
55.35
44.33
32.35
31.64
29.51
29.48
29.26
29.17
29.05
29.01
28.95
28.45
26.97
26.94
25.78
22.42
13.88
Arjit-AS-496
Me
O
O
S
N
^{n}Pr
^{n}Pr
^{n}Pr
^{n}Pr
8f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


Majji-MJ-17-I35
8.450
8.433
8.237
8.220
8.013
7.998
7.995
7.720
7.705
7.690
7.650
7.634
7.619
7.260
3.526
2.638
2.625
2.611
2.127
2.059
2.018
1.858
1.844
1.831
1.817
1.785
1.589
1.543
1.530
1.517
1.403
1.393
1.289
1.273
1.260
1.163
1.150
1.124
1.119
1.105
1.100
1.090
1.085
1.080
1.065
1.061
0.878
0.865
0.848
S
Me
S
O
N
Ph
O
O
O
7f
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm
2.00
1.98
2.01
1.00
2.00
3.00
2.06
3.01
3.00
3.02
2.13
3.01
15.33
6.02
12.19


210.10
164.82
149.54
146.07
140.65
137.21
133.90
132.02
129.89
129.60
128.17
127.47
126.83
125.06
123.16
117.52
77.25
77.00
76.74
75.11
44.66
39.38
37.59
37.55
37.50
37.46
37.42
37.39
37.29
32.78
32.71
27.96
24.80
24.79
24.44
22.69
22.60
21.04
20.63
19.74
19.68
19.65
19.63
19.59
13.01
12.17
Majji-MJ-17-I35
7f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



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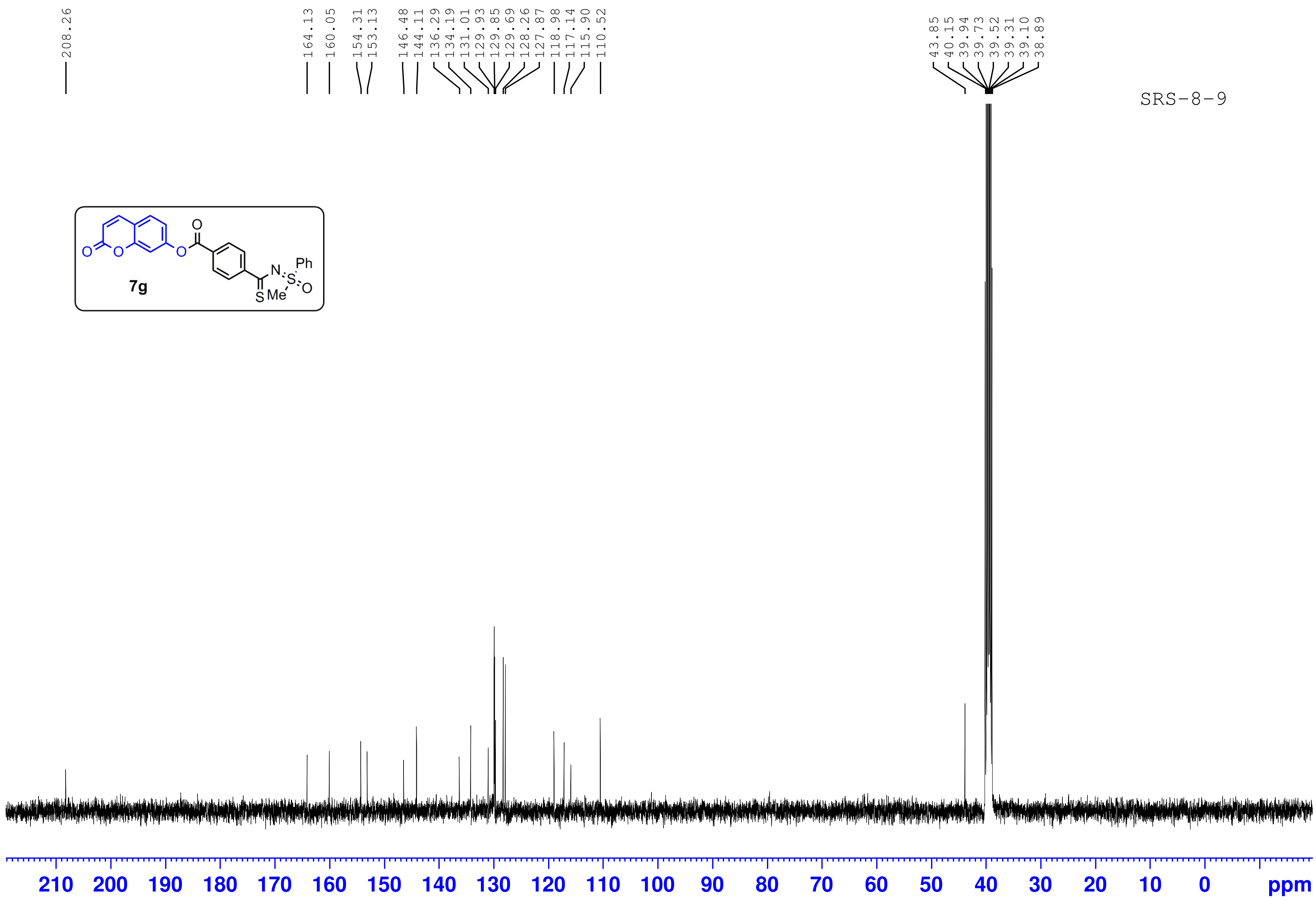
8.356
8.173
8.152
8.097
8.073
8.025
8.007
8.004
7.830
7.809
7.782
7.764
7.746
7.714
7.695
7.677
7.482
7.477
7.352
7.346
7.331
7.325
6.504
6.480
3.752
3.645
3.625
3.525
2.504
2.500
2.495
SRS-8-9
7g
Ph
N
S
O
Me
S
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.04
1.03
2.02
1.02
1.02
2.02
0.96
1.00
1.00
3.24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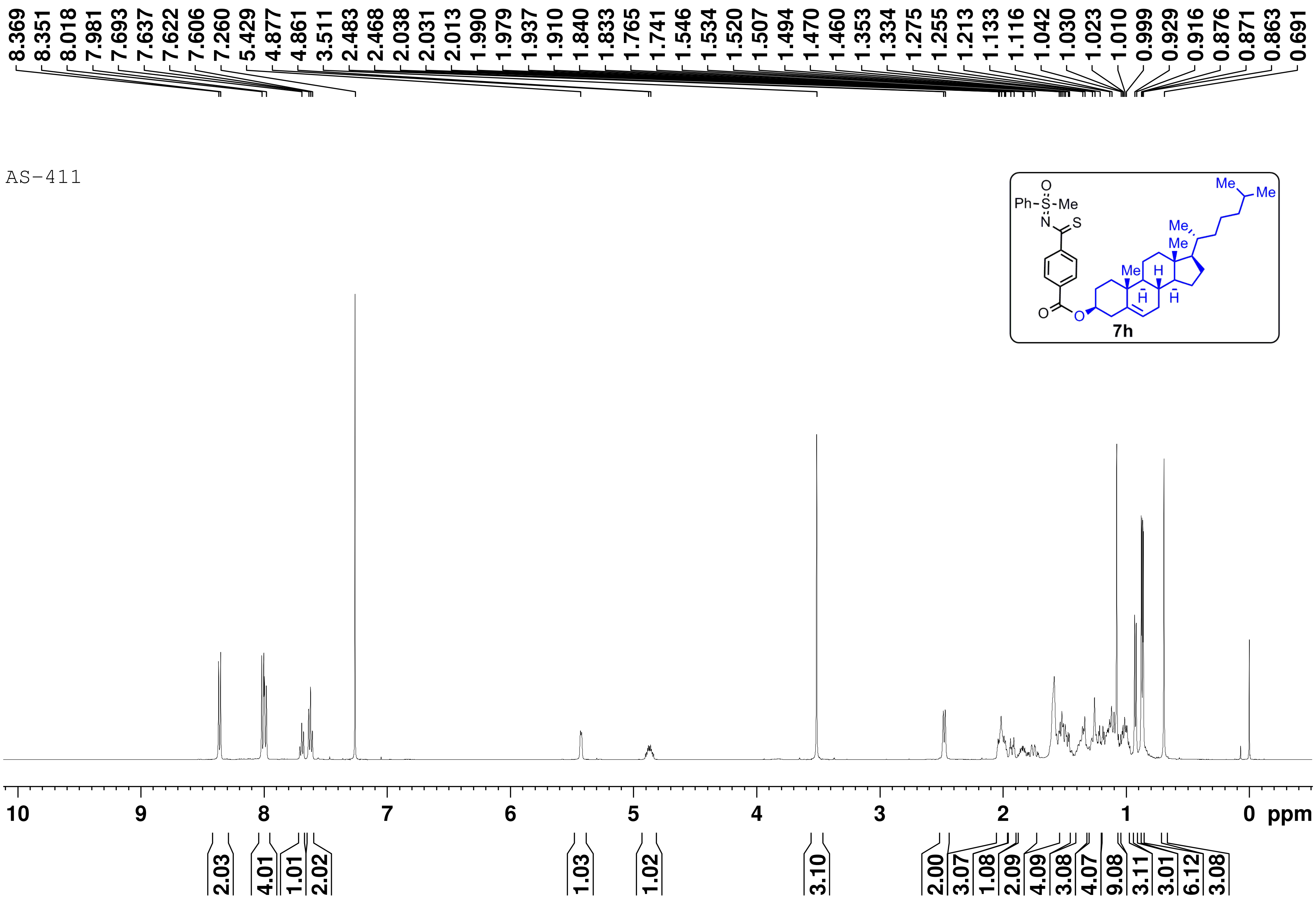
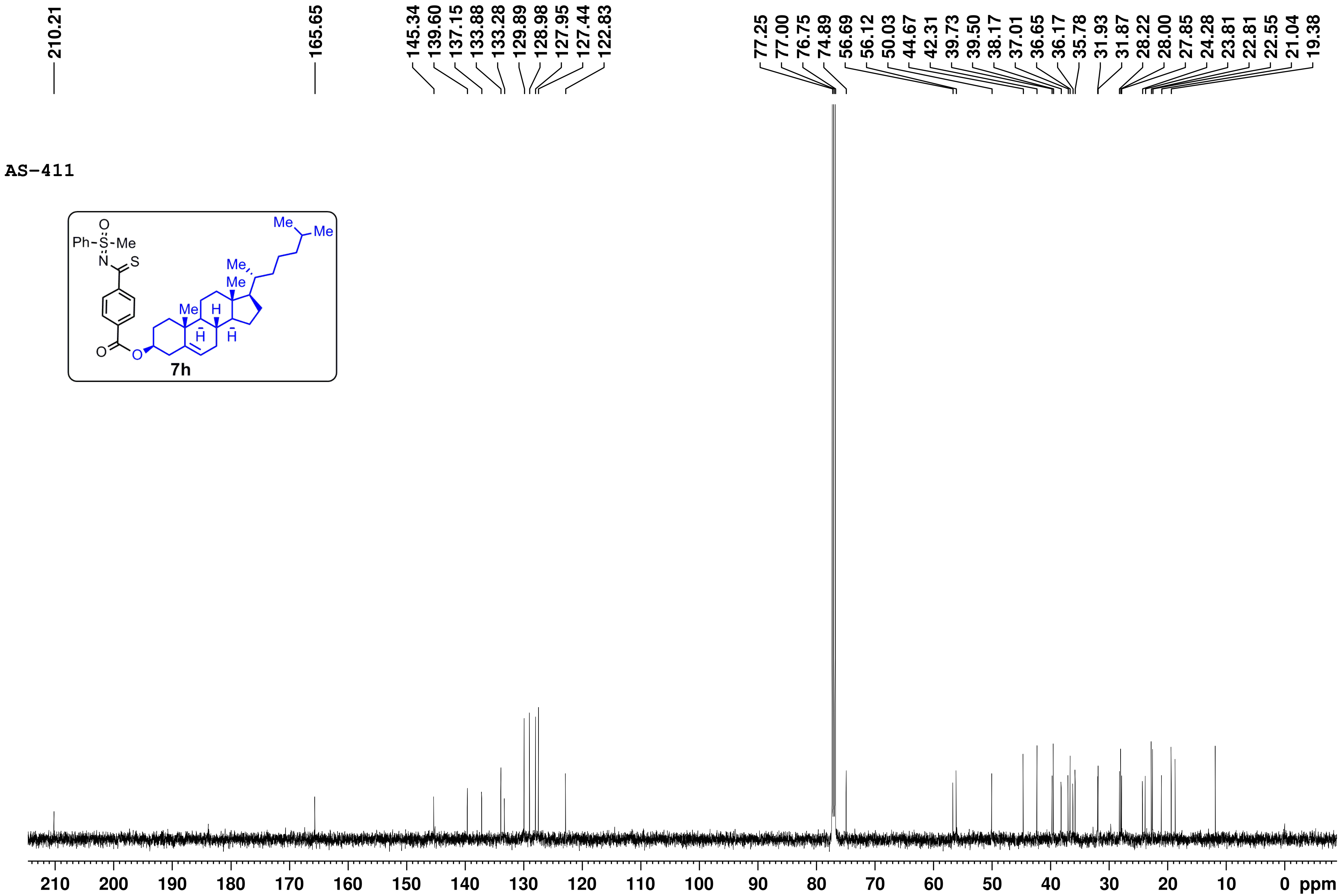
160.05
154.31
153.13
146.48
144.11
136.29
134.19
131.01
129.93
129.85
129.69
128.26
127.87
118.98
117.14
115.90
110.52
43.85
40.15
39.94
39.73
39.52
39.31
39.10
38.89
SRS-8-9
7g
Ph
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.369 8.351 8.018 7.981 7.693 7.637 7.622 7.606 7.260 5.429 4.877 4.861 3.511 2.483 2.468 2.038 2.031 2.013 1.990 1.979 1.937 1.910 1.840 1.833 1.765 1.741 1.546 1.534 1.520 1.507 1.494 1.470 1.460 1.353 1.334 1.275 1.255 1.213 1.133 1.116 1.042 1.030 1.023 1.010 0.999 0.929 0.916 0.876 0.871 0.863 0.691
AS-411
Ph
S
O
N
Me
S
O
O
Me
Me
Me
Me
Me
H
H
H
7h
10 9 8 7 6 5 4 3 2 1 0 ppm
2.03 4.01 1.01 2.02 1.03 1.02 3.10 2.00 3.07 1.08 2.09 4.09 3.08 4.07 9.08 3.11 3.01 6.12 3.08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145.34
139.60
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129.89
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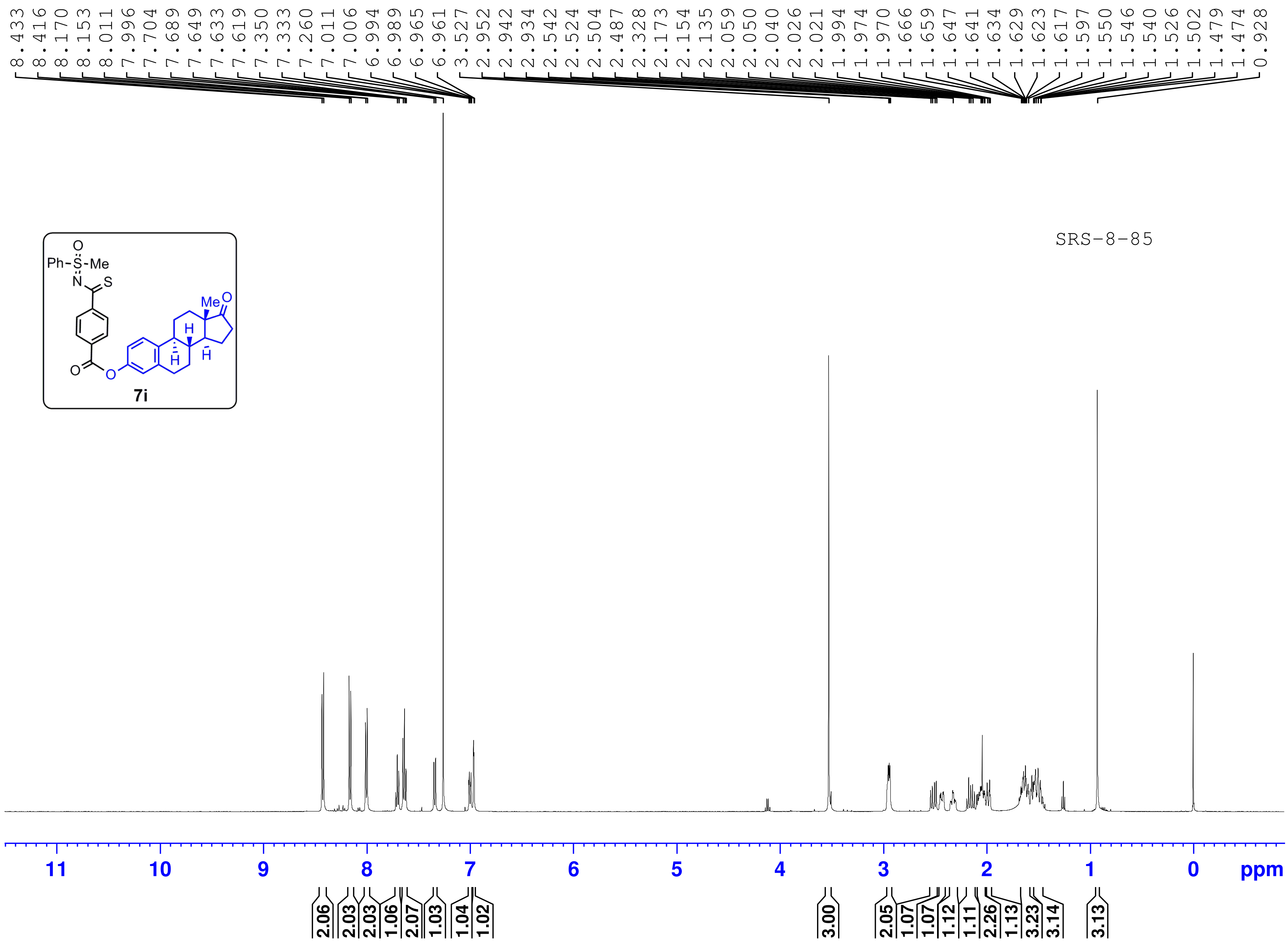
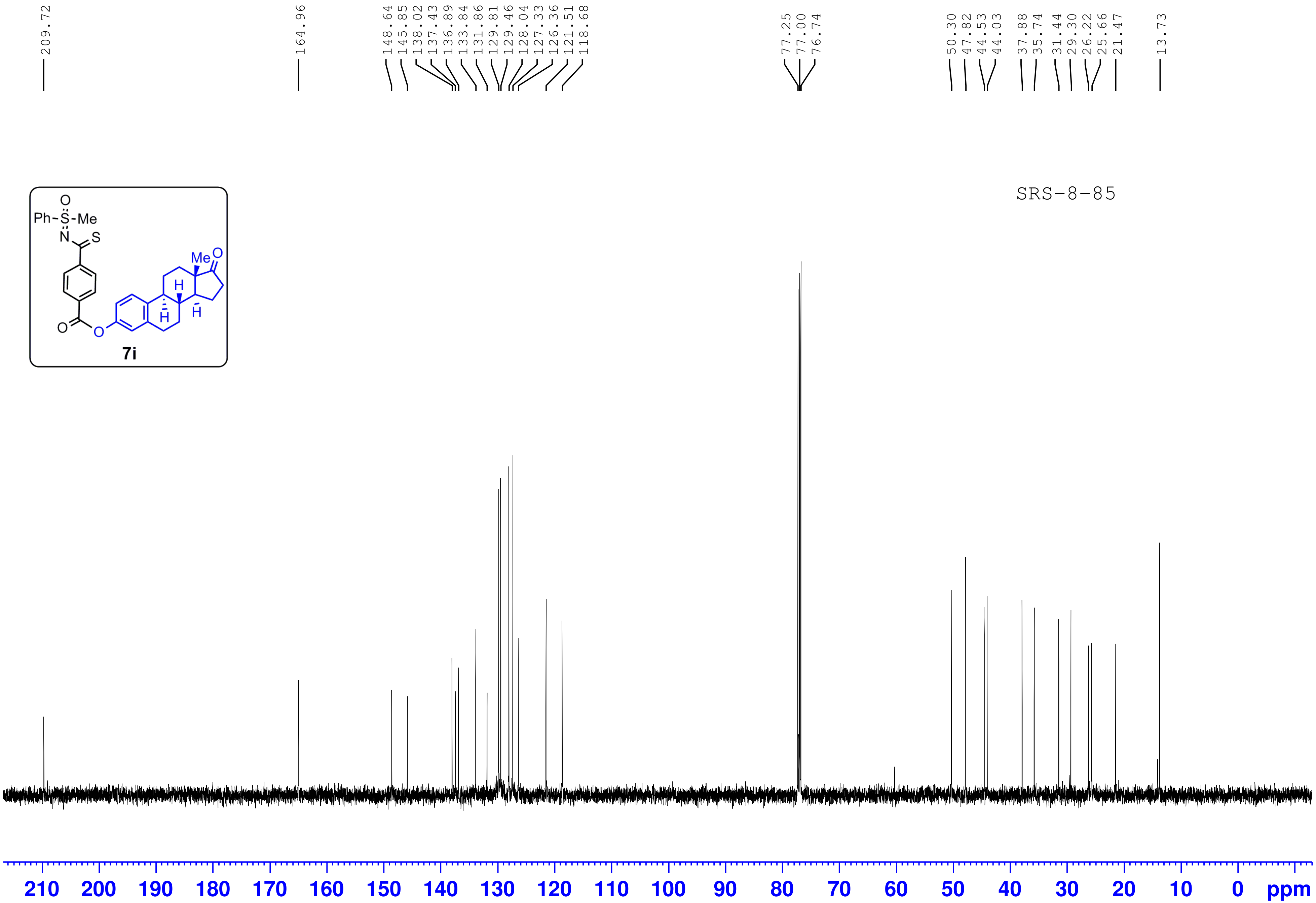
127.95
127.44
122.83
77.25
77.00
76.75
74.89
56.69
56.12
50.03
44.67
42.31
39.73
39.50
38.17
37.01
36.65
36.17
35.78
31.93
31.87
28.22
28.00
27.85
24.28
23.81
22.81
22.55
21.04
19.38
AS-411
O
Ph
S
Me
N
S
Me
Me
Me
Me
Me
H
H
H
O
O
7h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.433
8.416
8.170
8.153
8.011
7.996
7.704
7.689
7.649
7.633
7.619
7.350
7.333
7.260
7.011
7.006
6.994
6.989
6.965
6.961
3.527
2.952
2.942
2.934
2.542
2.524
2.504
2.487
2.328
2.173
2.154
2.135
2.059
2.050
2.040
2.026
2.021
1.994
1.974
1.970
1.666
1.659
1.647
1.641
1.634
1.629
1.623
1.617
1.597
1.550
1.546
1.540
1.526
1.502
1.479
1.474
0.928
SRS-8-85
Ph-S-Me
O
N
S
Me
O
H
H
H
O
O
7i
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.06
2.03
2.03
1.06
2.07
1.03
1.04
1.02
3.00
2.05
1.07
1.07
1.12
1.11
2.26
1.13
3.23
3.14
3.13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148.64
145.85
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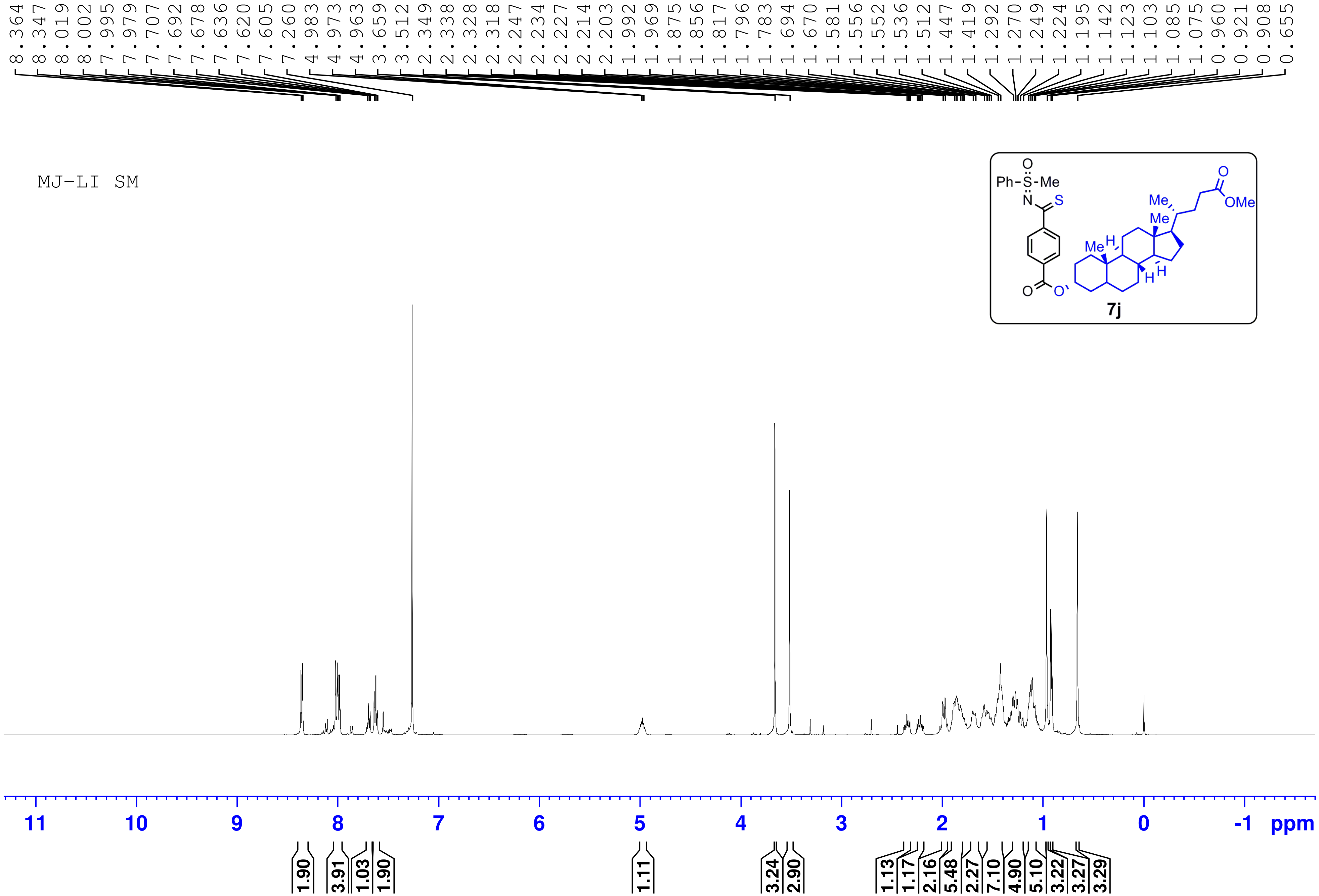
136.89
133.84
131.86
129.81
129.46
128.04
127.33
126.36
121.51
118.68
77.25
77.00
76.74
50.30
47.82
44.53
44.03
37.88
35.74
31.44
29.30
26.22
25.66
21.47
13.73
SRS-8-85
Ph
Me
O
S
N
7i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



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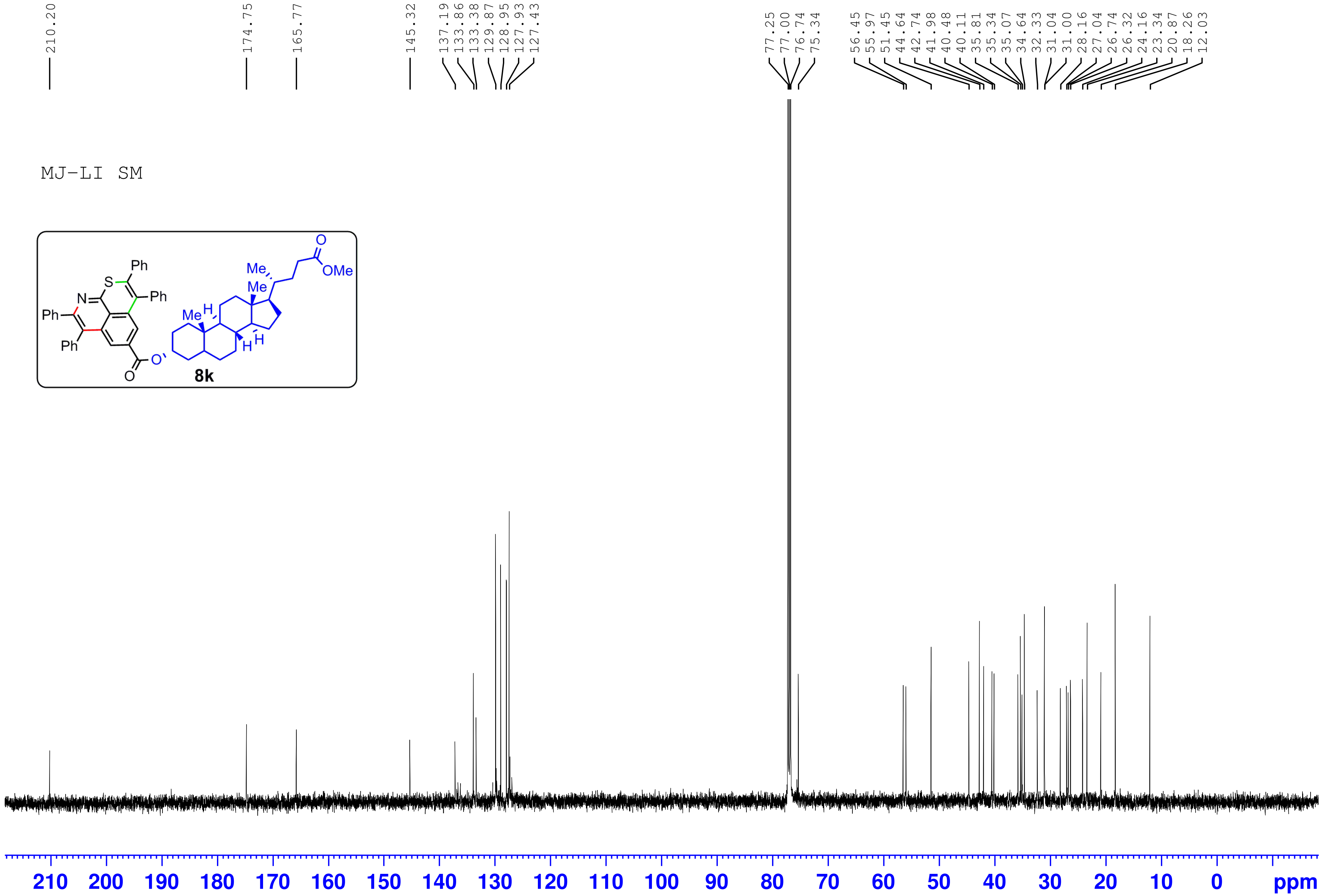
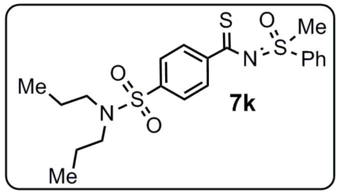
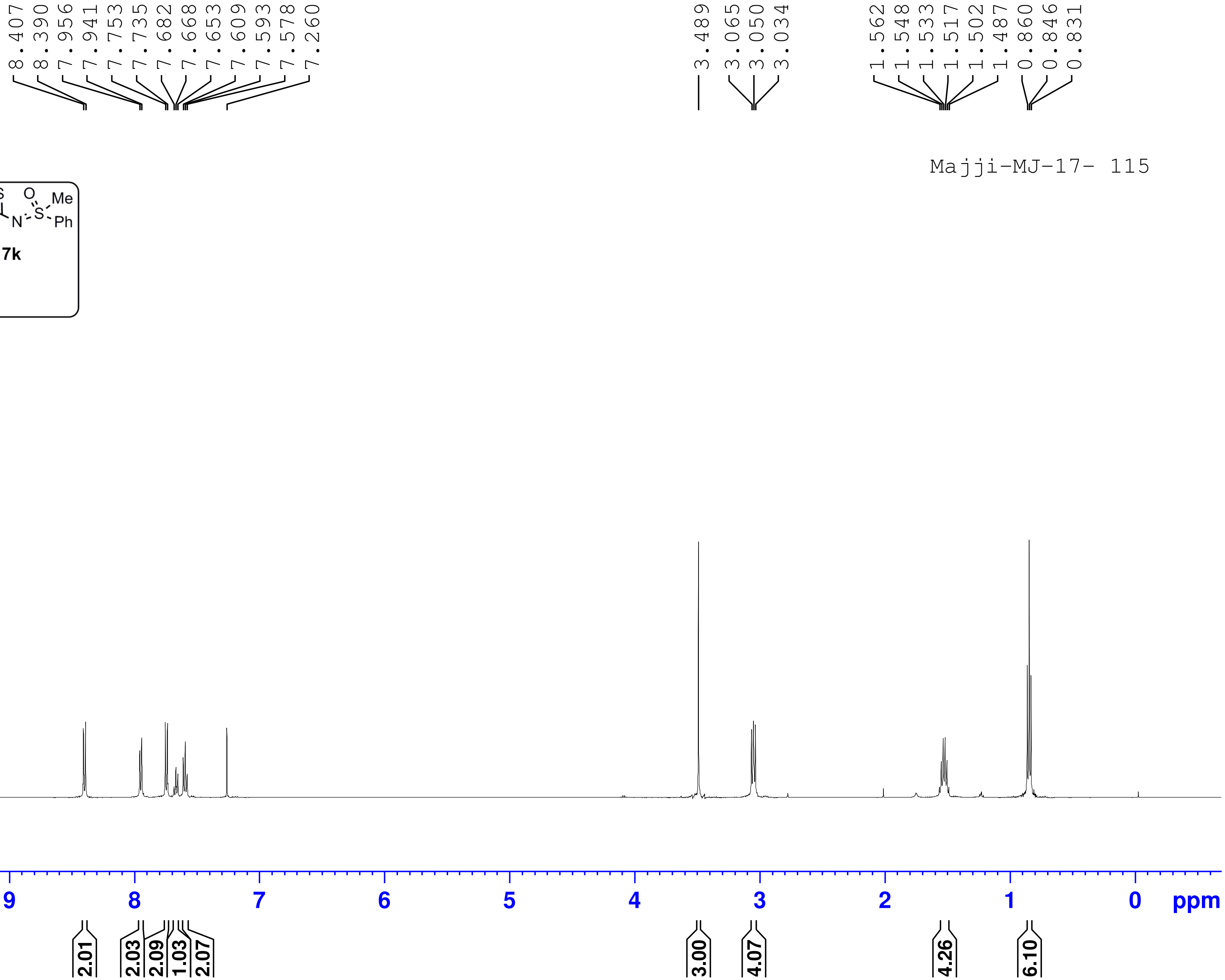
8.347
8.019
8.002
7.995
7.979
7.707
7.692
7.678
7.636
7.620
7.605
7.260
4.983
4.973
4.963
3.659
3.512
2.349
2.338
2.328
2.318
2.247
2.234
2.227
2.214
2.203
1.992
1.969
1.875
1.856
1.817
1.796
1.783
1.694
1.670
1.581
1.556
1.552
1.536
1.512
1.447
1.419
1.292
1.270
1.249
1.224
1.195
1.142
1.123
1.103
1.085
1.075
0.960
0.921
0.908
0.655
MJ-LI SM
Ph-S-Me
O
N
S
O
O
Me
Me
Me
H
H
H
O
OMe
7j
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.90
3.91
1.03
1.90
1.11
3.24
2.90
1.13
1.17
2.16
5.48
2.27
7.10
4.90
5.10
3.22
3.27
3.29



210.20
174.75
165.77
145.32
137.19
133.86
133.38
129.87
128.95
127.93
127.43
77.25
77.00
76.74
75.34
56.45
55.97
51.45
44.64
42.74
41.98
40.48
40.11
35.81
35.34
35.07
34.64
32.33
31.04
31.00
28.16
27.04
26.74
26.32
24.16
23.34
20.87
18.26
12.03
MJ-LI SM
Ph
S
N
Ph
Ph
Ph
O
O
Me
H
Me
Me
H
H
O
OMe
8k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


S
O
Me
N
S
Ph
Me
N
S
O
O
Me

7k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8.390
7.956
7.941
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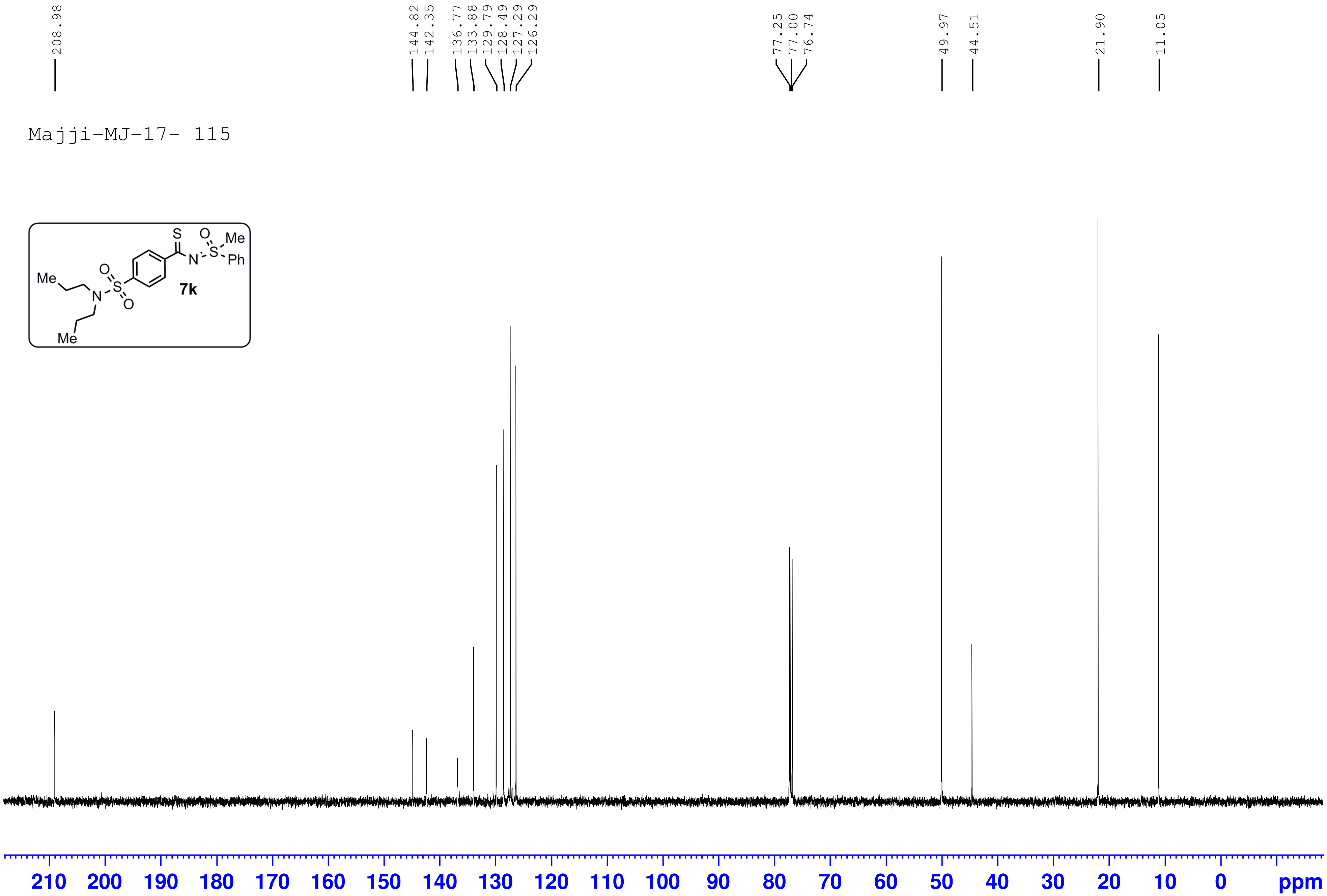
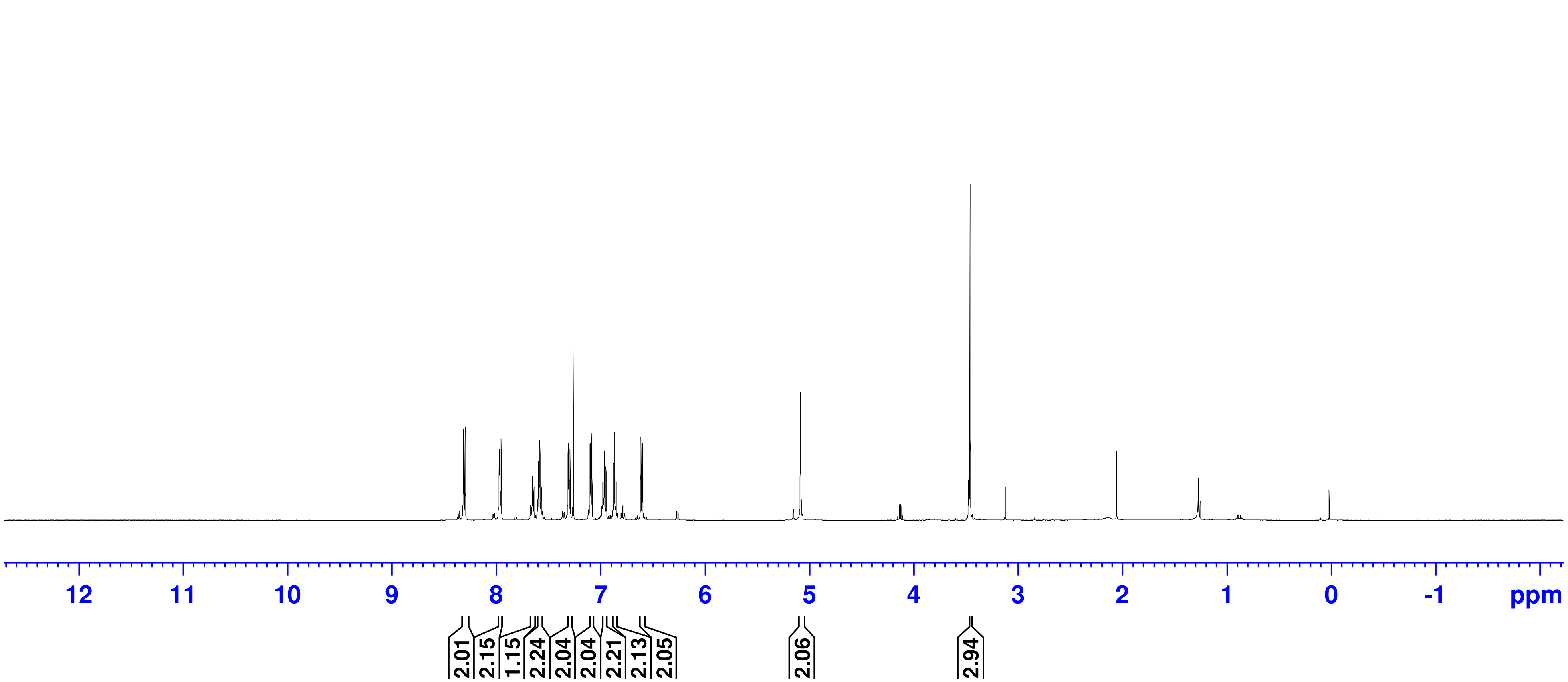
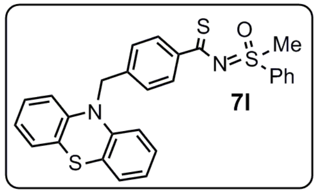
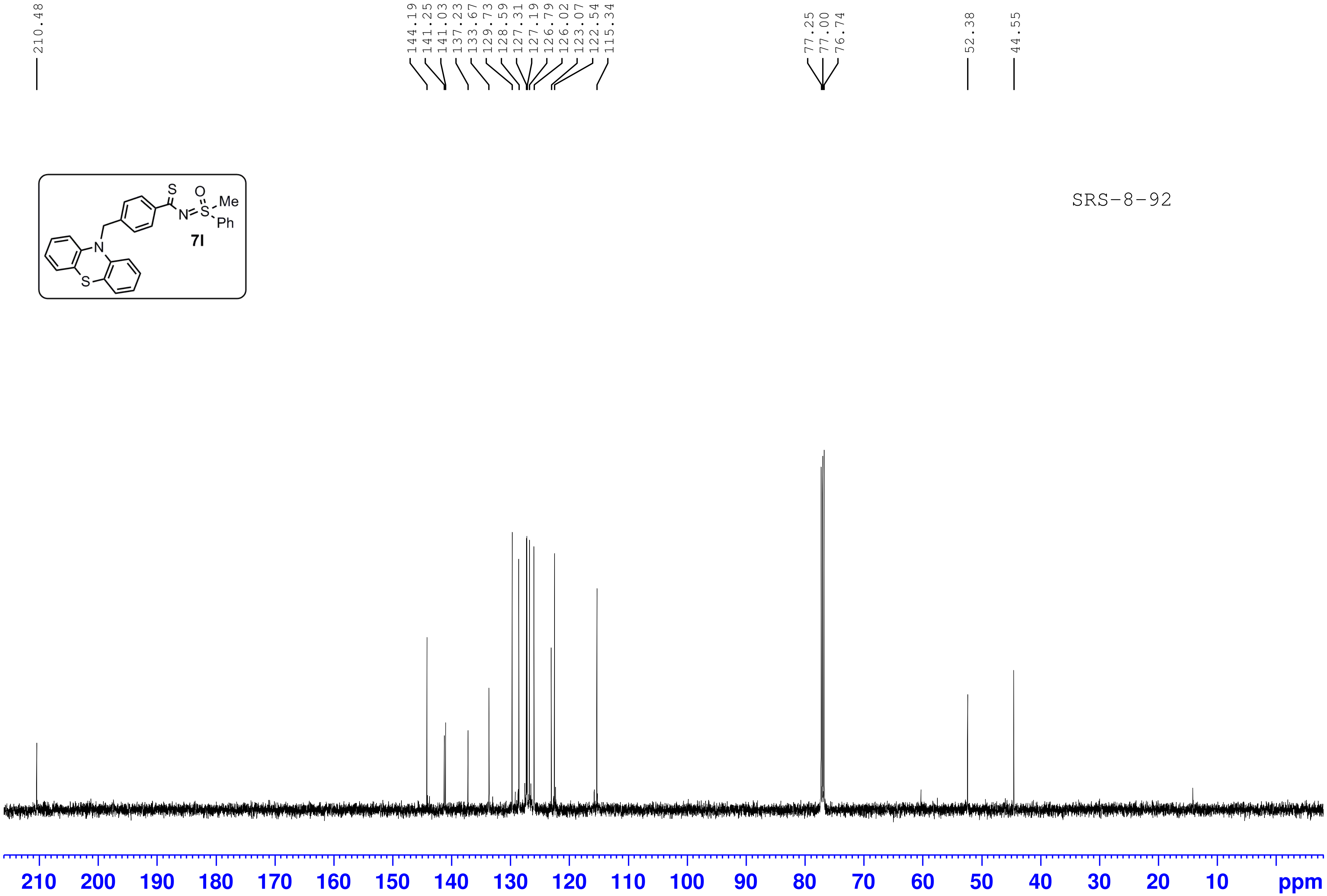
7.668
7.653
7.609
7.593
7.578
7.260
3.489
3.065
3.050
3.034
1.562
1.548
1.533
1.517
1.502
1.487
0.860
0.846
0.831
Majji-MJ-17- 115
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
2.03
2.09
1.03
2.07
3.00
4.07
4.26
6.10


208.98
144.82
142.35
136.77
133.88
129.79
128.49
127.29
126.29
77.25
77.00
76.74
49.97
44.51
21.90
11.05
Majji-MJ-17- 115
7k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.312
8.295
7.967
7.952
7.666
7.651
7.636
7.594
7.578
7.564
7.308
7.291
7.260
7.098
7.095
7.083
7.080
6.978
6.974
6.962
6.960
6.947
6.943
6.878
6.876
6.863
6.861
6.848
6.846
6.611
6.609
6.595
6.593
5.080
3.456
SRS-8-92
12 11 10 9 8 7 6 5 4 3 2 1 0 -1 ppm
2.01 2.15 1.15 2.24 2.04 2.04 2.21 2.13 2.05 2.06 2.94


S
O
N
S
Me
Ph
N
S
7l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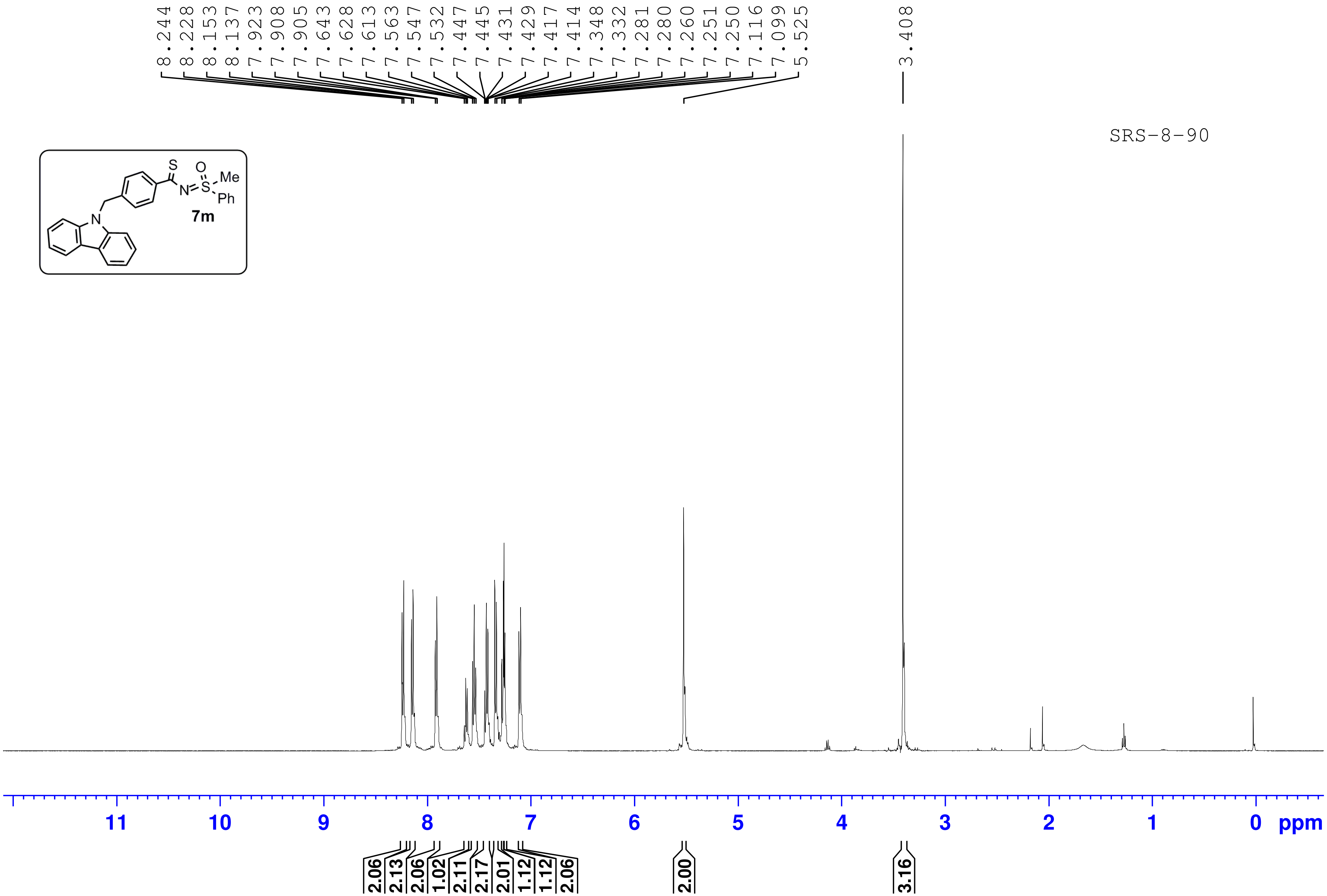
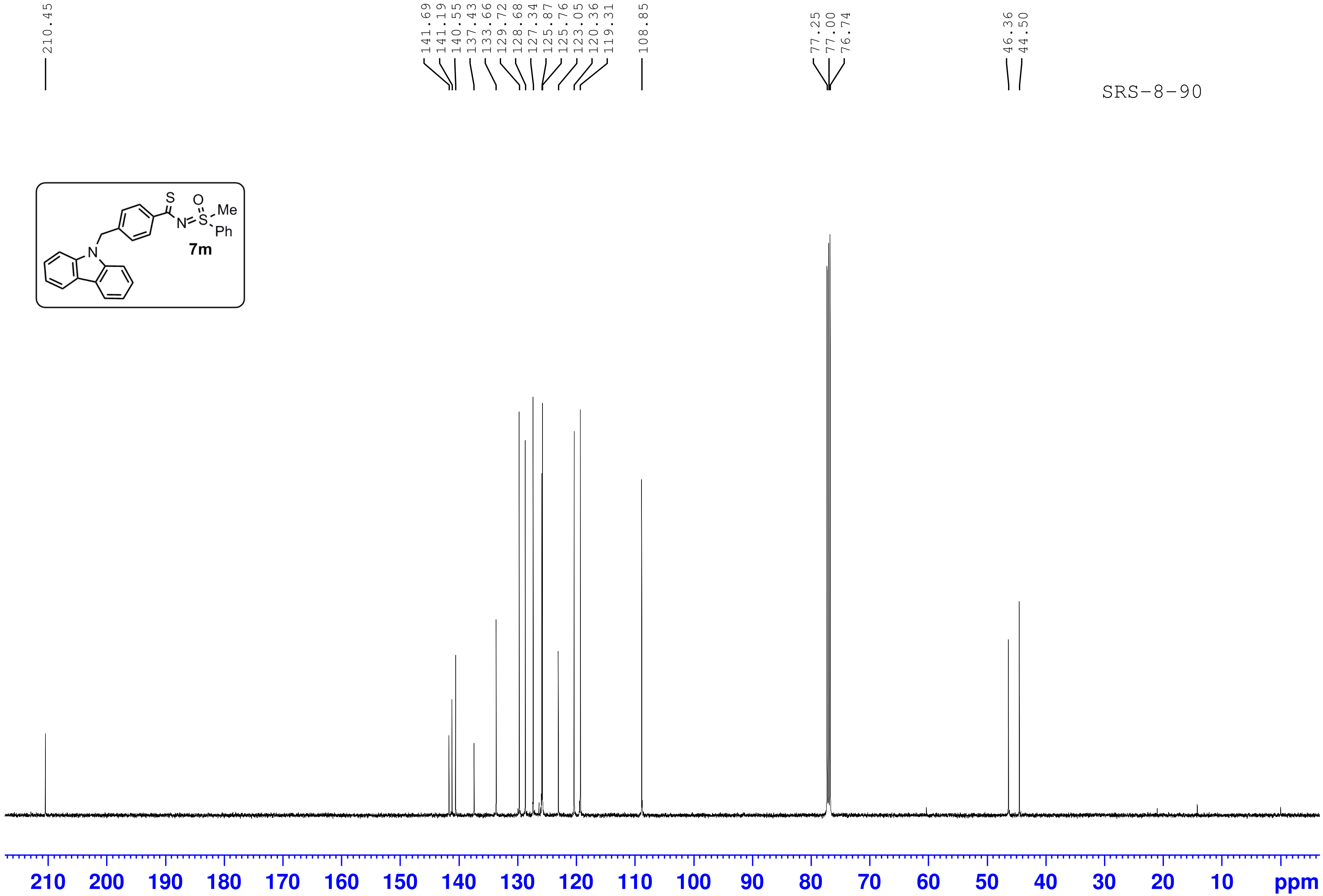
144.19
141.25
141.03
137.23
133.67
129.73
128.59
127.31
127.19
126.79
126.02
123.07
122.54
115.34
77.25
77.00
76.74
52.38
44.55
S
O
N
S
Me
Ph
N
S
7l
SRS-8-92
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.244
8.228
8.153
8.137
7.923
7.908
7.905
7.643
7.628
7.613
7.563
7.547
7.532
7.447
7.445
7.431
7.429
7.417
7.414
7.348
7.332
7.281
7.280
7.260
7.251
7.250
7.116
7.099
5.525
3.408
SRS-8-90
S
O
N
S
Me
Ph
N
7m
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.06
2.13
2.06
1.02
2.11
2.17
2.01
1.12
1.12
2.06
2.00
3.16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141.69
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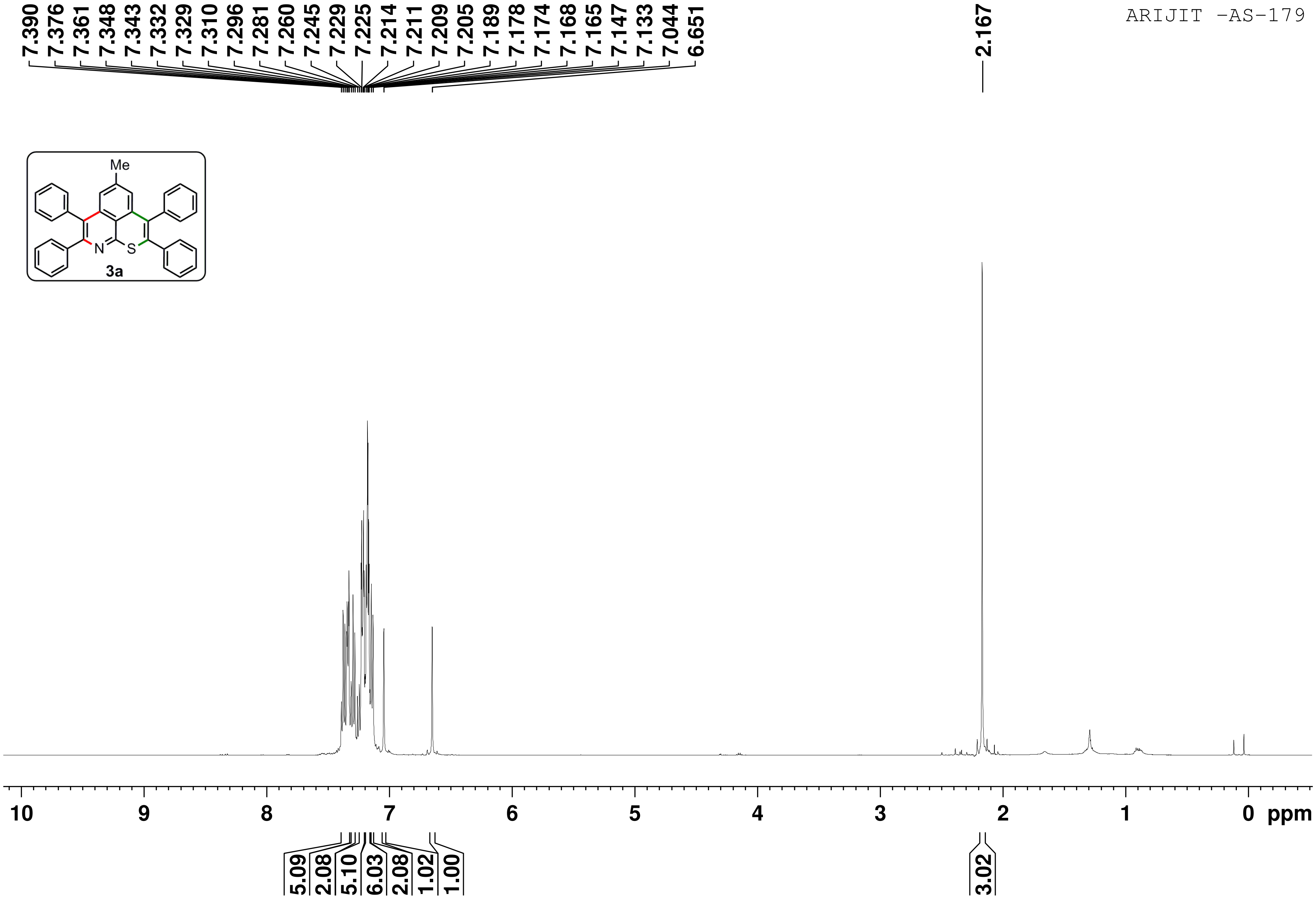
128.68
127.34
125.87
125.76
123.05
120.36
119.31
108.85
77.25
77.00
76.74
46.36
44.50
SRS-8-90
S
O
Me
N
S
Ph
N
7m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


ARIJIT -AS-179
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7.376
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7.348
7.343
7.332
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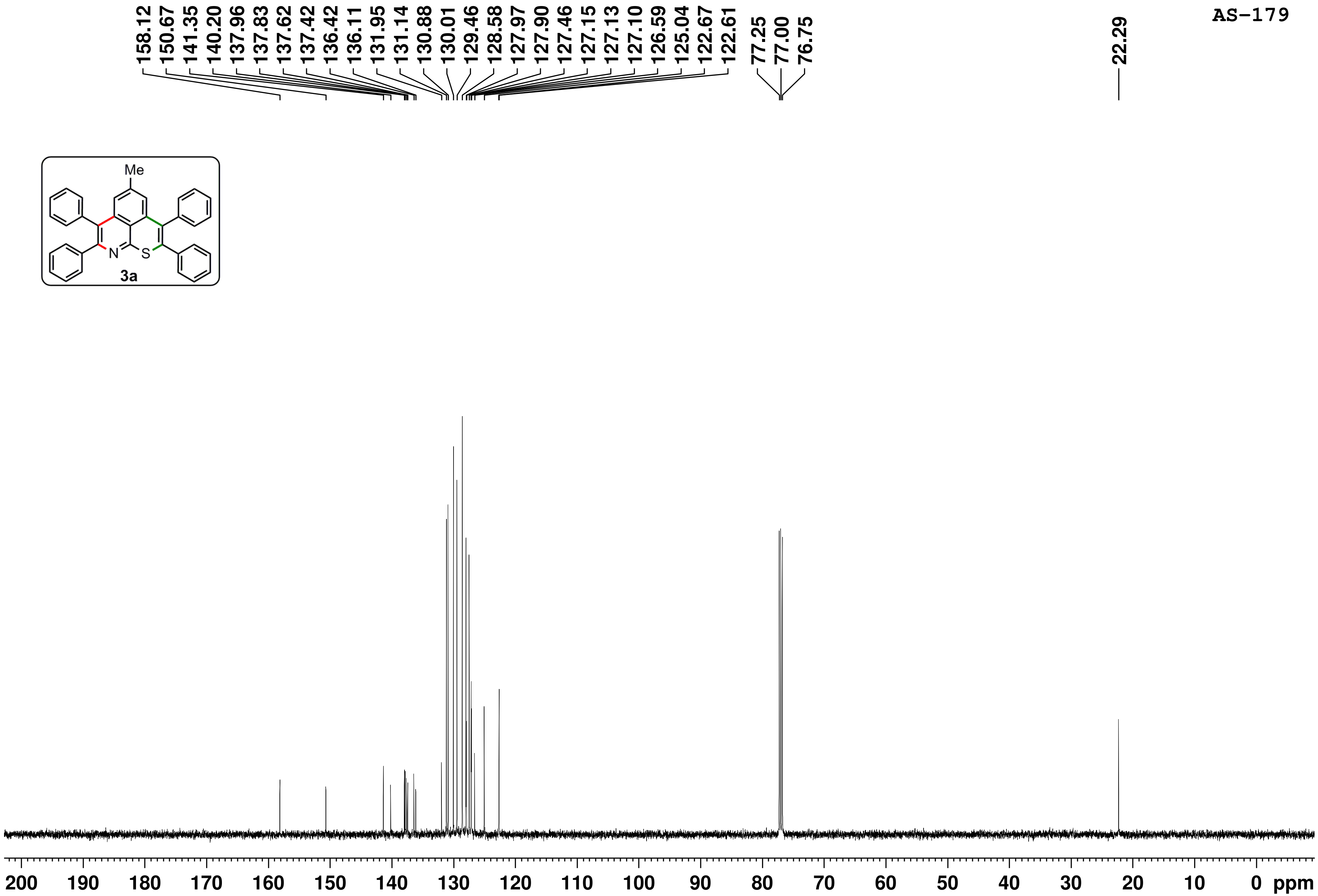
7.310
7.296
7.281
7.260
7.245
7.229
7.225
7.214
7.211
7.209
7.205
7.189
7.178
7.174
7.168
7.165
7.147
7.133
7.044
6.651
2.167
Me
N
S
3a
10
9
8
7
6
5
4
3
2
1
0
ppm
5.09
2.08
5.10
6.03
2.08
1.02
1.00
3.02


AS-179
158.12
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140.20
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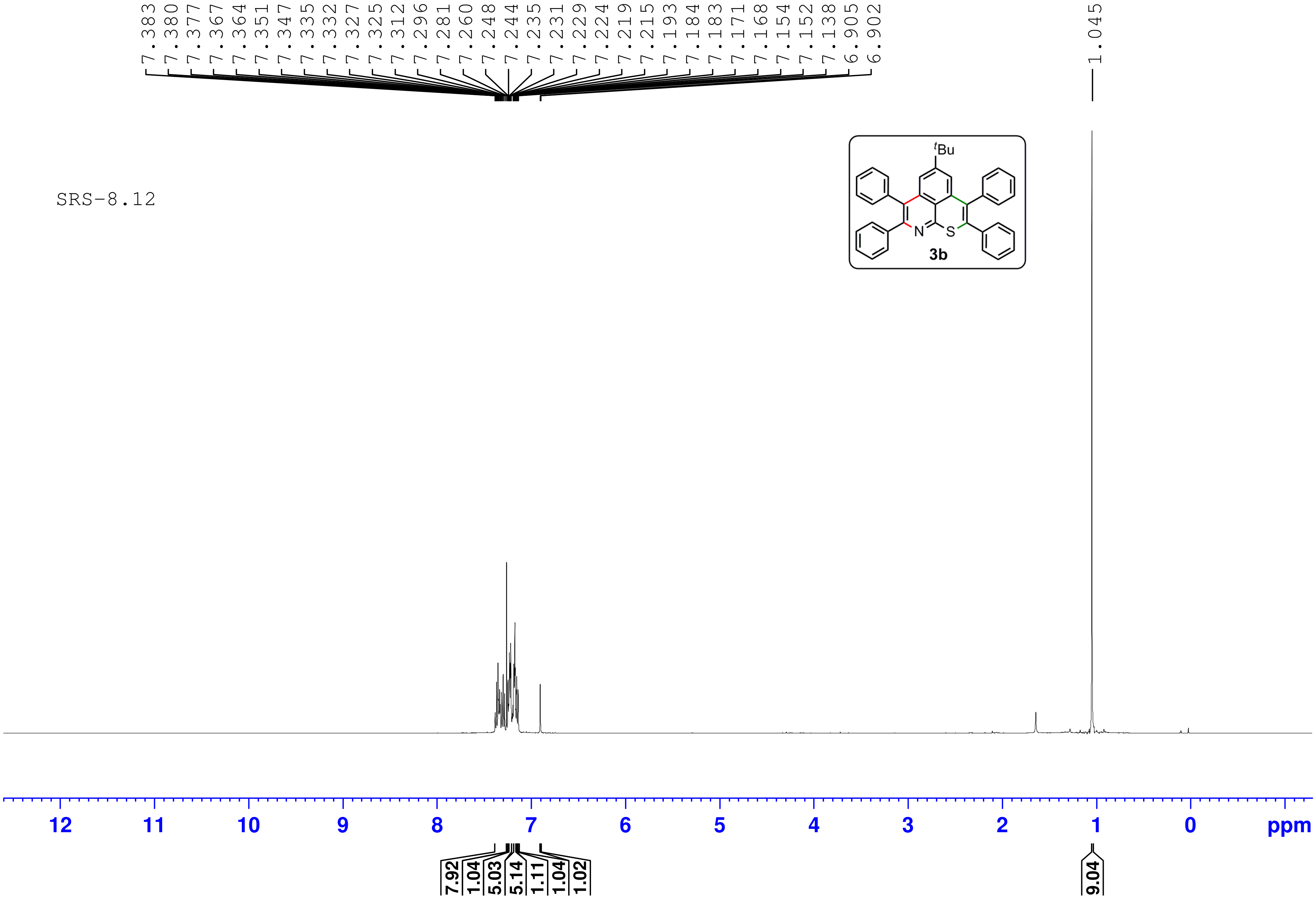
137.83
137.62
137.42
136.42
136.11
131.95
131.14
130.88
130.01
129.46
128.58
127.97
127.90
127.46
127.15
127.13
127.10
126.59
125.04
122.67
122.61
77.25
77.00
76.75
22.29
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
Me
N
S

3a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7.335
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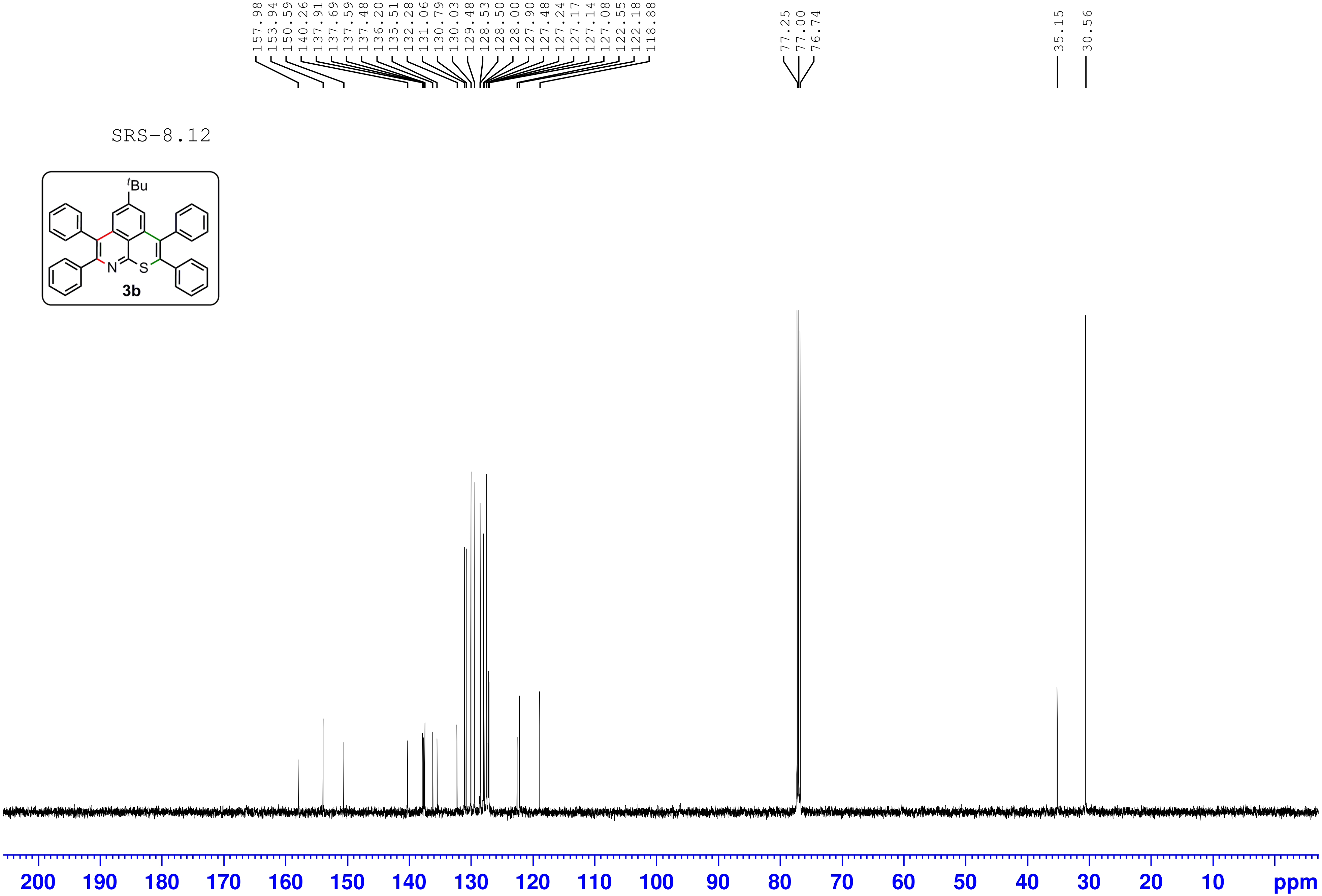
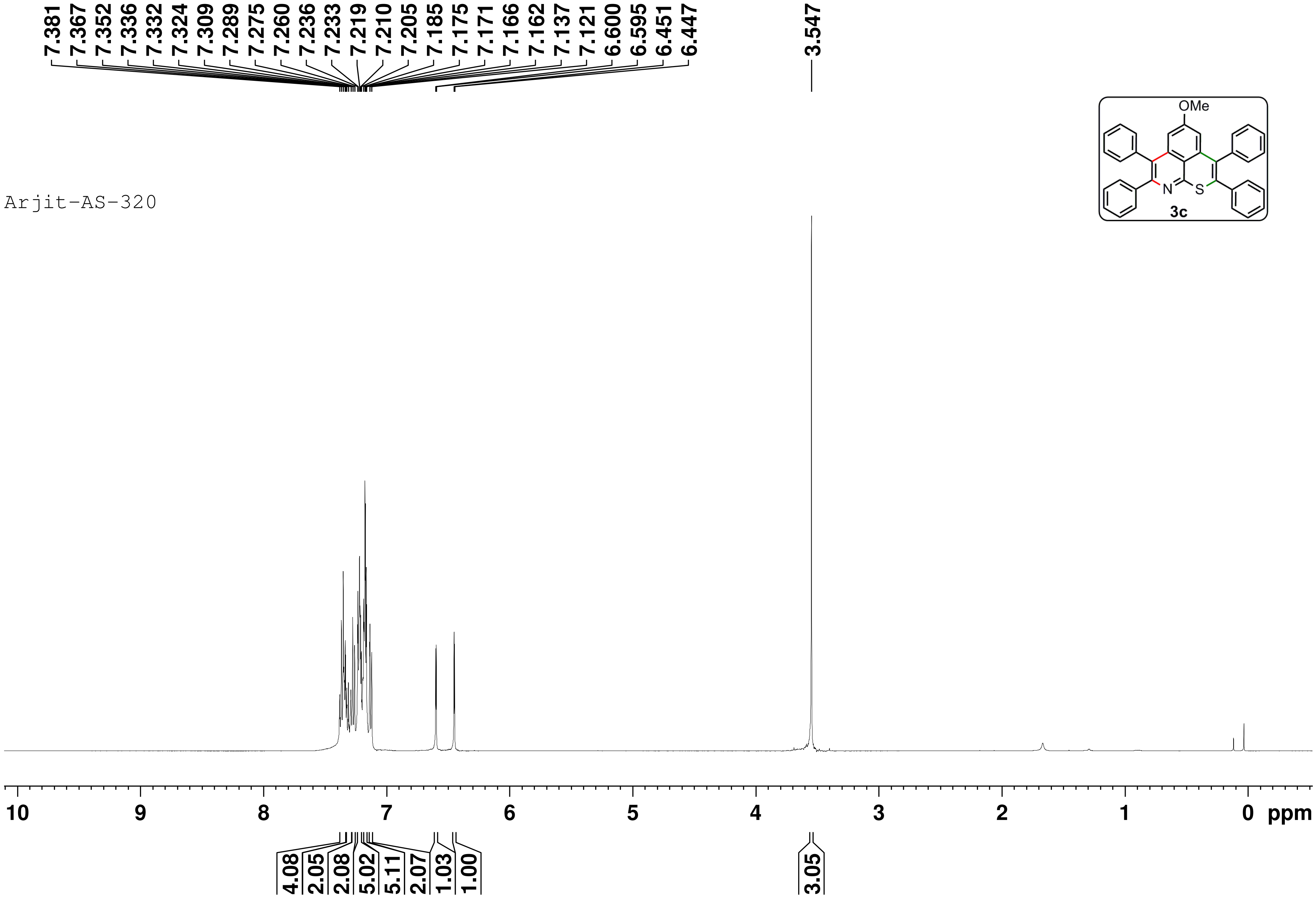
7.327
7.325
7.312
7.296
7.281
7.260
7.248
7.244
7.235
7.231
7.229
7.224
7.219
7.215
7.193
7.184
7.183
7.171
7.168
7.154
7.152
7.138
6.905
6.902
1.045
SRS-8.12
tBu
N
S
3b
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
7.92
1.04
5.03
5.14
1.11
1.04
1.02
9.04


157.98
153.94
150.59
140.26
137.91
137.69
137.59
137.48
136.20
135.51
132.28
131.06
130.79
130.03
129.48
128.53
128.50
128.00
127.90
127.48
127.24
127.17
127.14
127.08
122.55
122.18
118.88
77.25
77.00
76.74
35.15
30.56
SRS-8.12
tBu
N
S
3b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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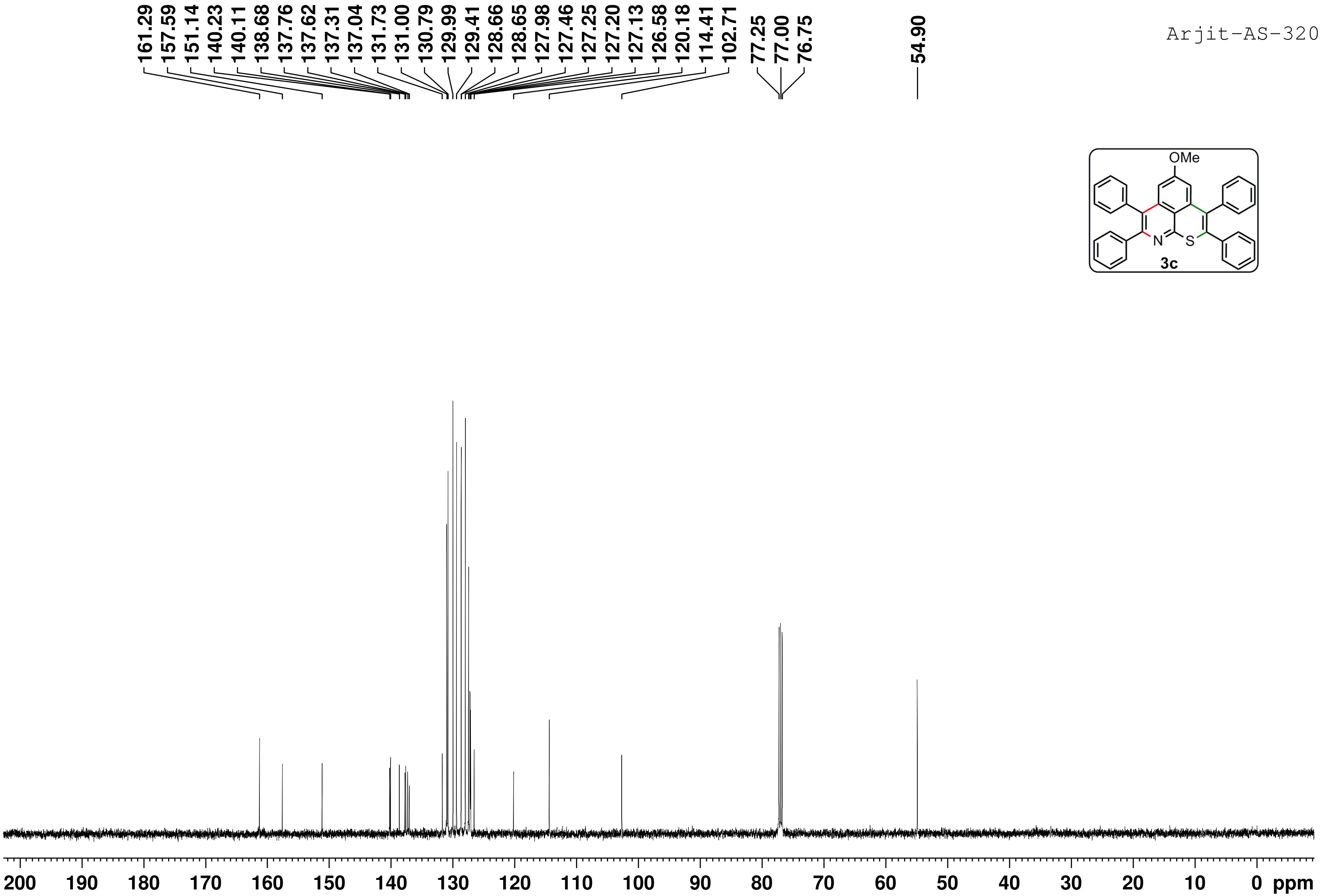
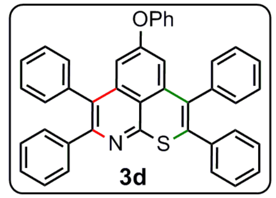
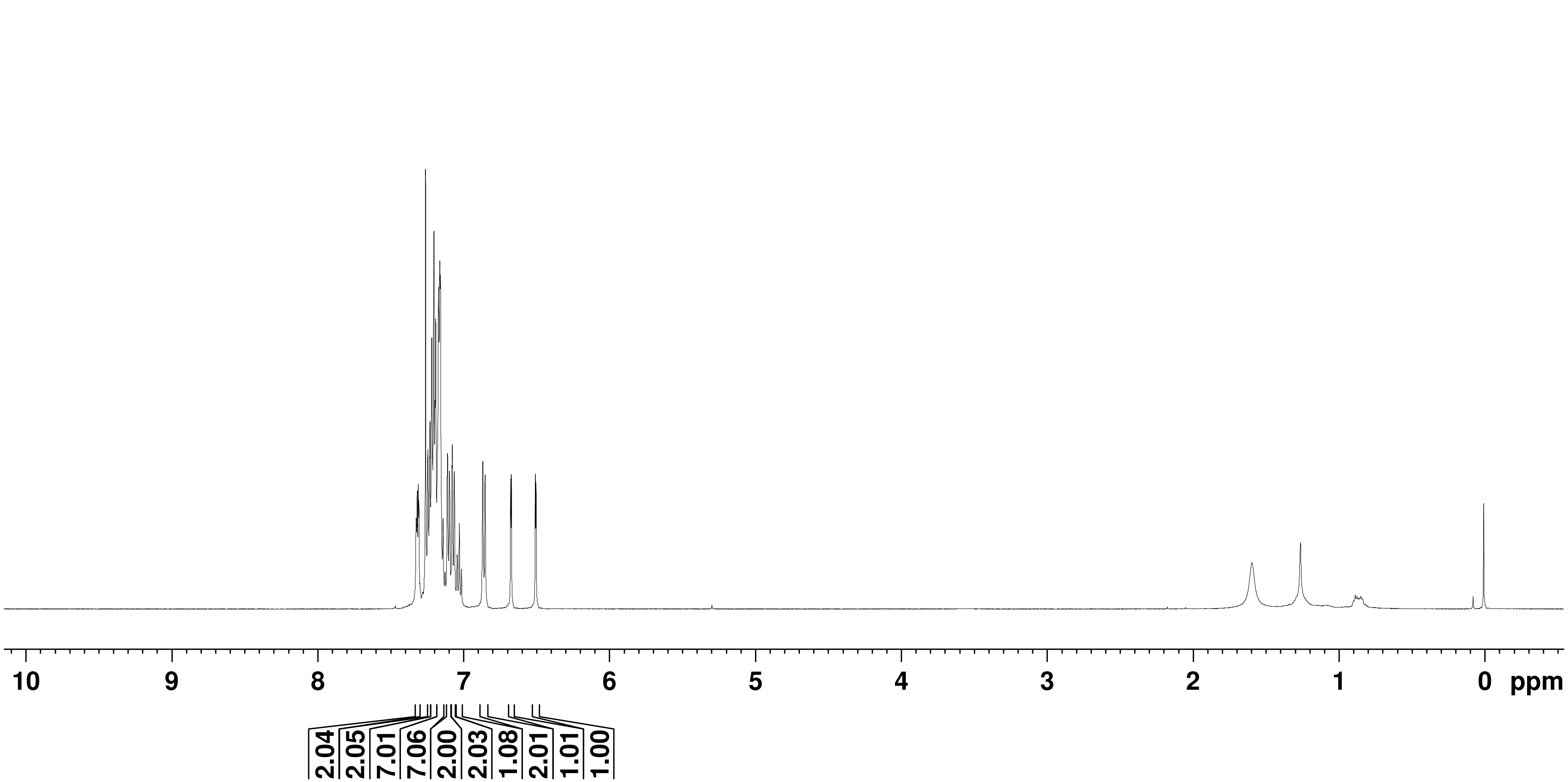
7.309
7.289
7.275
7.260
7.236
7.233
7.219
7.210
7.205
7.185
7.175
7.171
7.166
7.162
7.137
7.121
6.600
6.595
6.451
6.447
3.547
Arjit-AS-320
OMe
N
S
3c
10
9
8
7
6
5
4
3
2
1
0
ppm
4.08
2.05
2.08
5.02
5.11
2.07
1.03
1.00
3.05

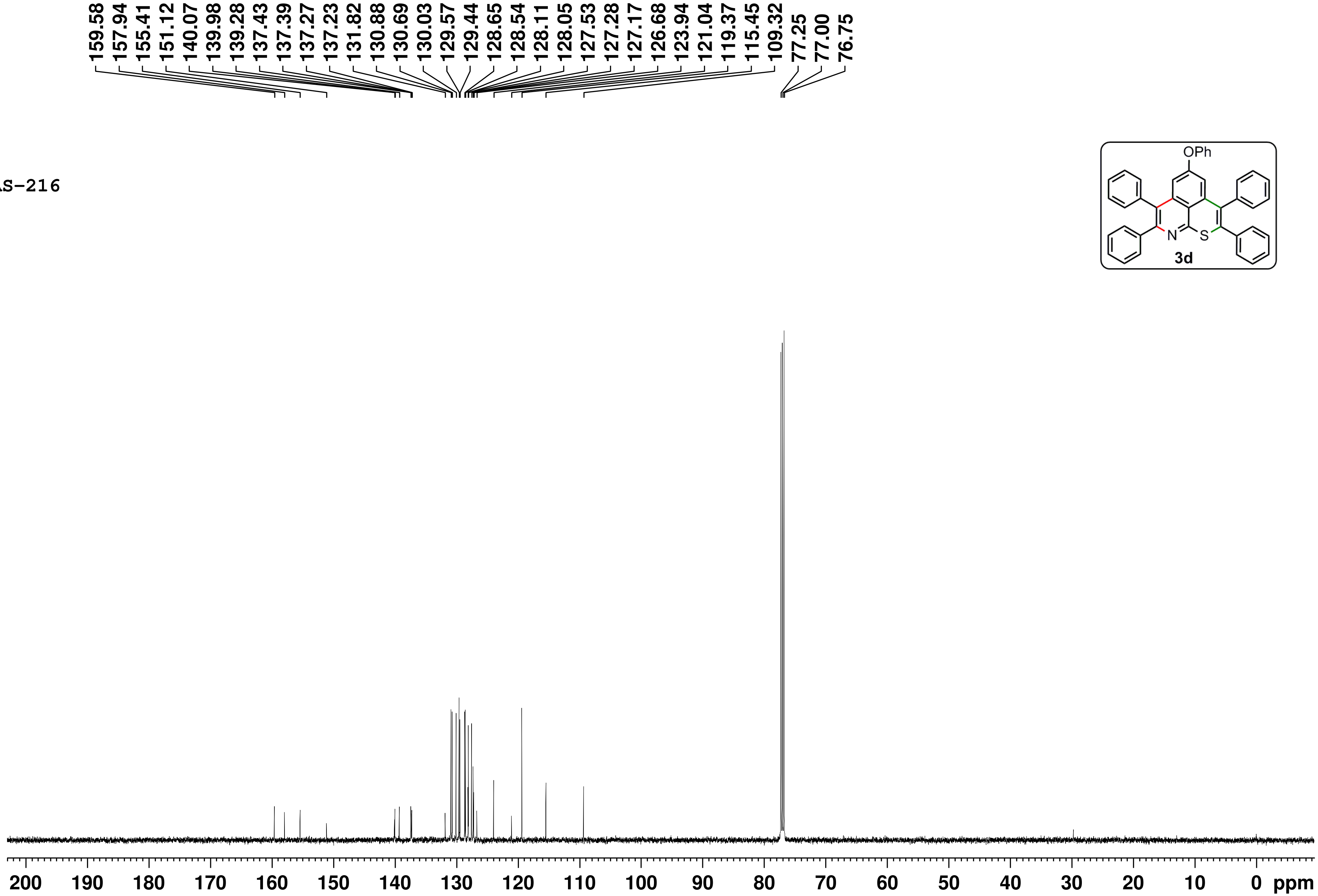

161.29
157.59
151.14
140.23
140.11
138.68
137.76
137.62
137.31
137.04
131.73
131.00
130.79
129.99
129.41
128.66
128.65
127.98
127.46
127.25
127.20
127.13
126.58
120.18
114.41
102.71
77.25
77.00
76.75
54.90
Arjit-AS-320
OMe
N
S
3c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

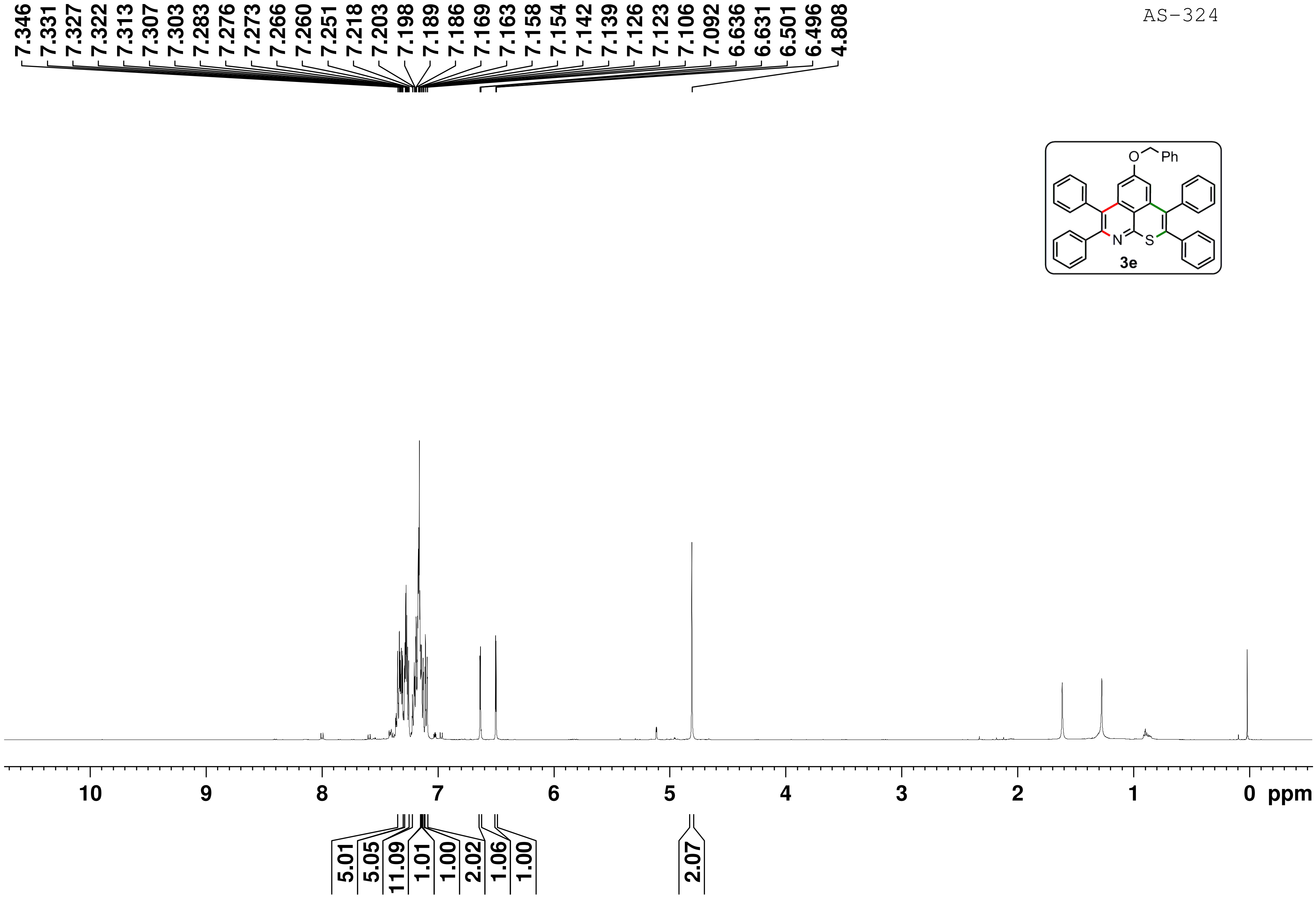
AS-216

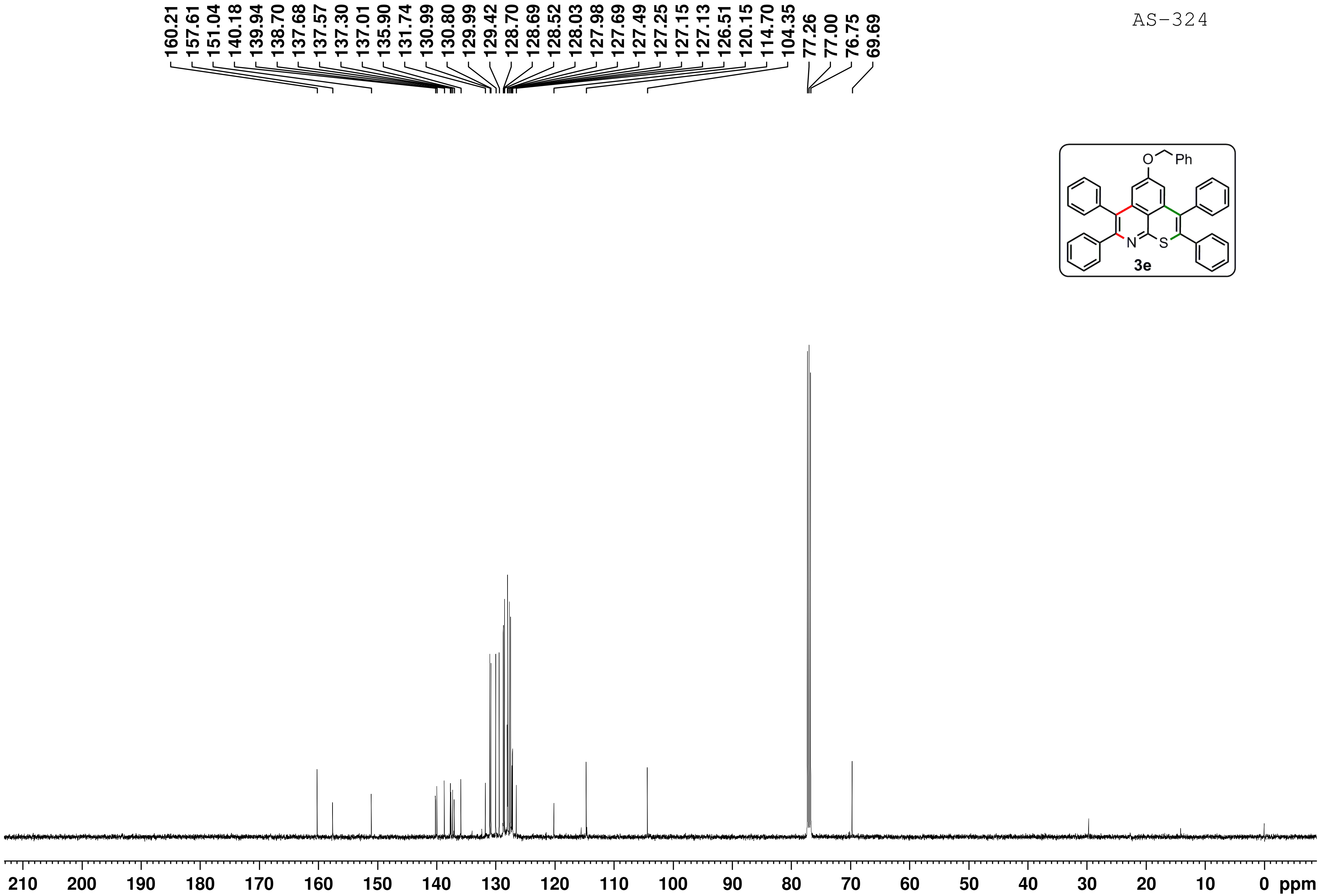

OPh
N
S
3d


7.325
7.317
7.310
7.306
7.260
7.244
7.230
7.217
7.202
7.191
7.171
7.158
7.140
7.109
7.095
7.079
7.077
7.063
7.043
7.029
7.014
6.867
6.852
6.676
6.672
6.507
6.503
10 9 8 7 6 5 4 3 2 1 0 ppm
2.04
2.05
7.01
7.06
2.00
2.03
1.08
2.01
1.01
1.00

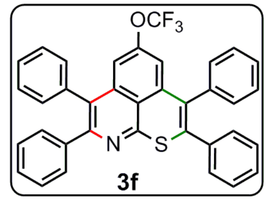
AS-216

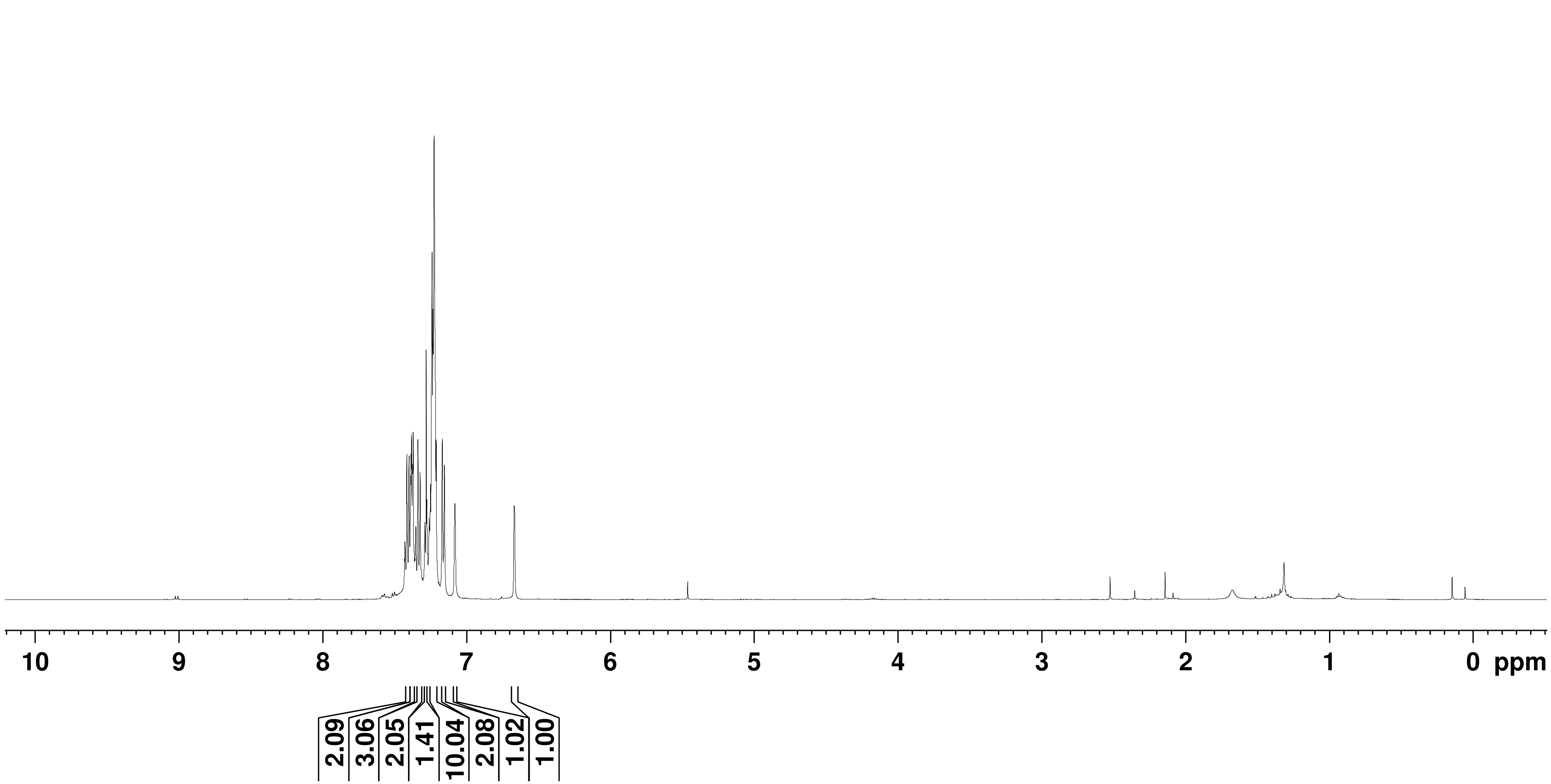

159.58
157.94
155.41
151.12
140.07
139.98
139.28
137.43
137.39
137.27
137.23
131.82
130.88
130.69
130.03
129.57
129.44
128.65
128.54
128.11
128.05
127.53
127.28
127.17
126.68
123.94
121.04
119.37
115.45
109.32
77.25
77.00
76.75
OPh
N
S
3d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.346
7.331
7.327
7.322
7.313
7.307
7.303
7.283
7.276
7.273
7.266
7.260
7.251
7.218
7.203
7.198
7.189
7.186
7.169
7.163
7.158
7.154
7.142
7.139
7.126
7.123
7.106
7.092
6.636
6.631
6.501
6.496
4.808
AS-324
O
Ph
N
S
3e
10
9
8
7
6
5
4
3
2
1
0 ppm
5.01
5.05
11.09
1.01
1.00
2.02
1.06
1.00
2.07

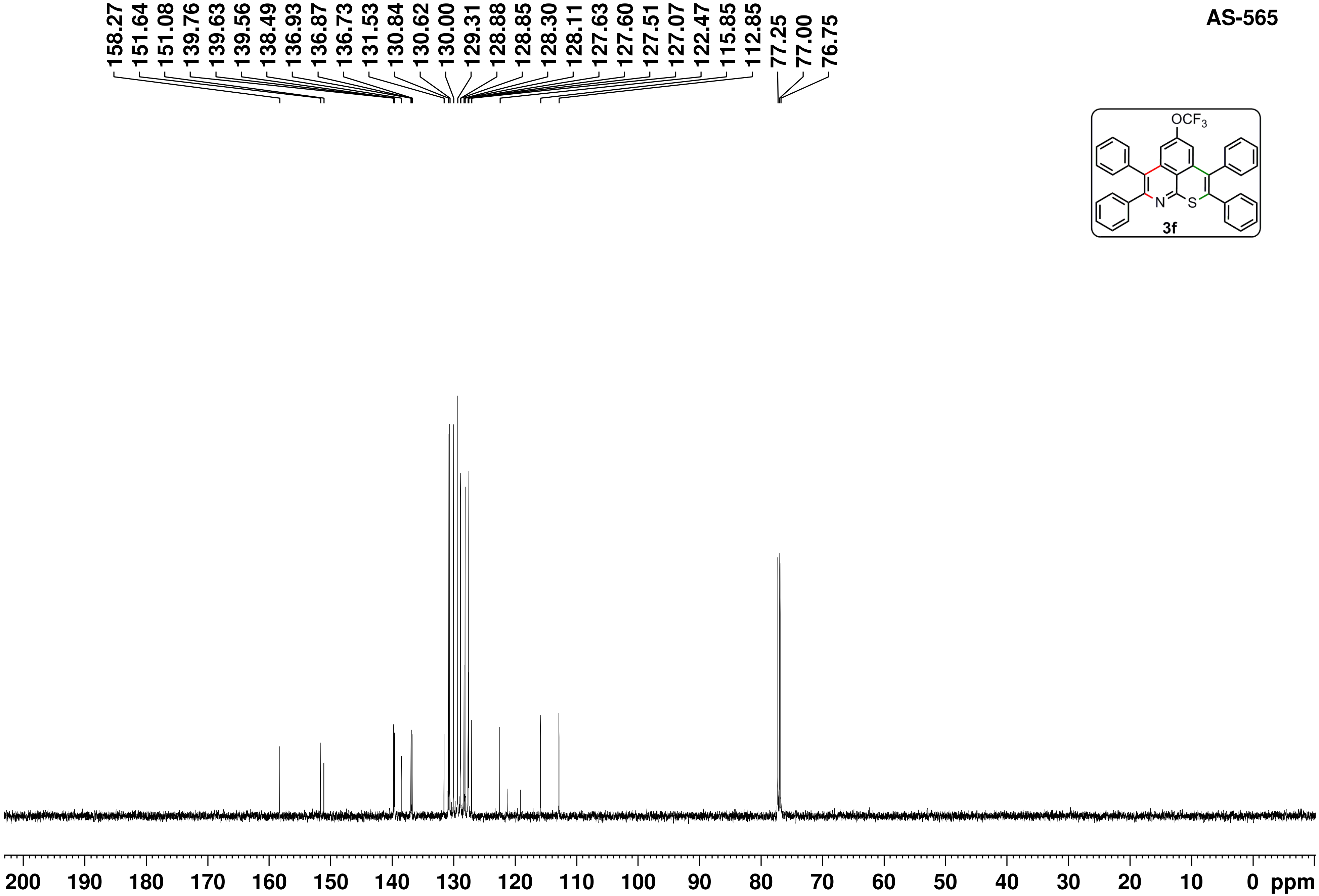

AS-324
160.21
157.61
151.04
140.18
139.94
138.70
137.68
137.57
137.30
137.01
135.90
131.74
130.99
130.80
129.99
129.42
128.70
128.69
128.52
128.03
127.98
127.69
127.49
127.25
127.15
127.13
126.51
120.15
114.70
104.35
77.26
77.00
76.75
69.69
O
Ph
N
S
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

AS-565

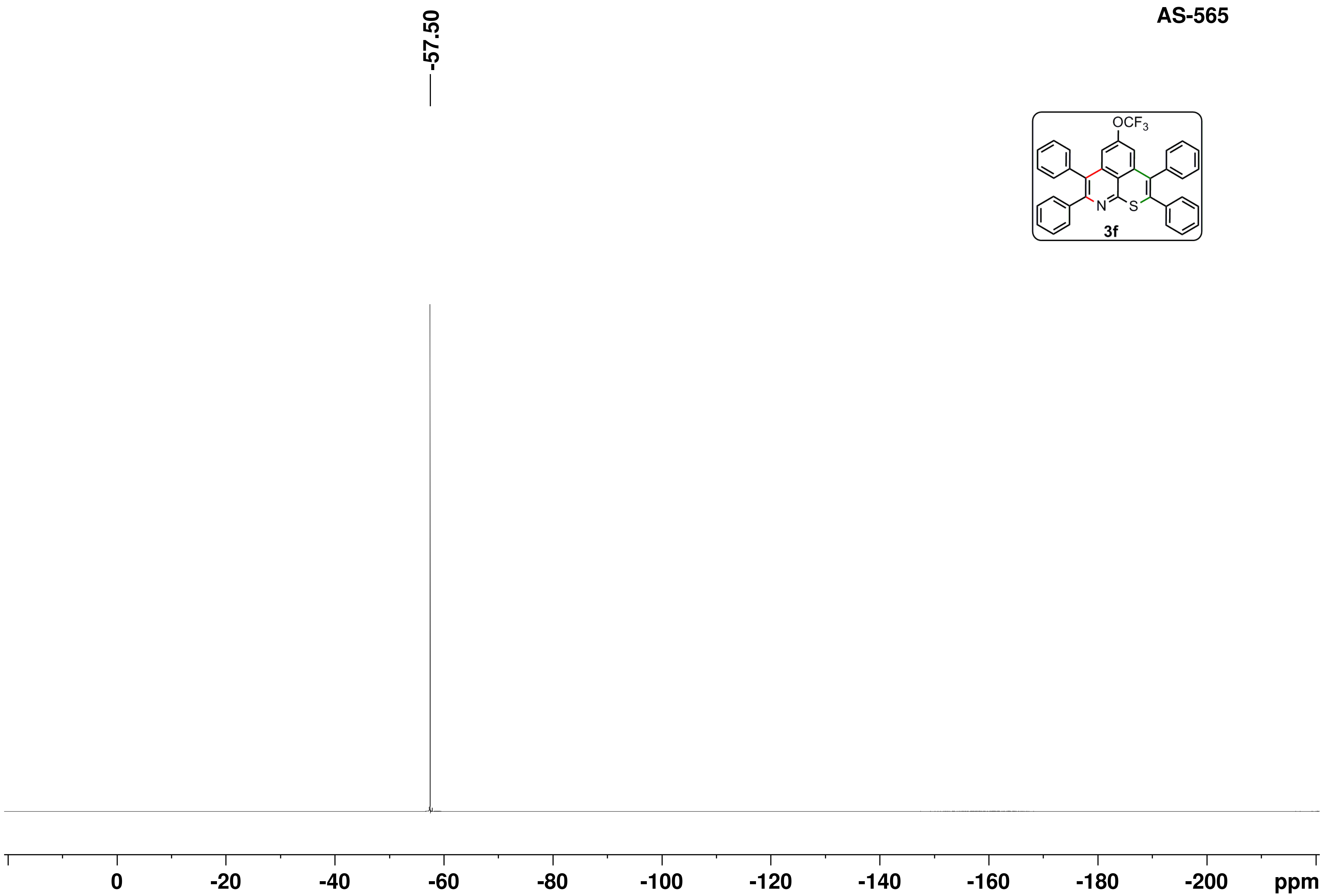

OCF3
N
S
3f


7.428
7.414
7.399
7.389
7.385
7.382
7.379
7.375
7.370
7.352
7.337
7.322
7.289
7.280
7.275
7.260
7.251
7.239
7.233
7.225
7.210
7.167
7.154
7.081
6.668
10
9
8
7
6
5
4
3
2
1
0 ppm
2.09
3.06
2.05
1.41
10.04
2.08
1.02
1.00

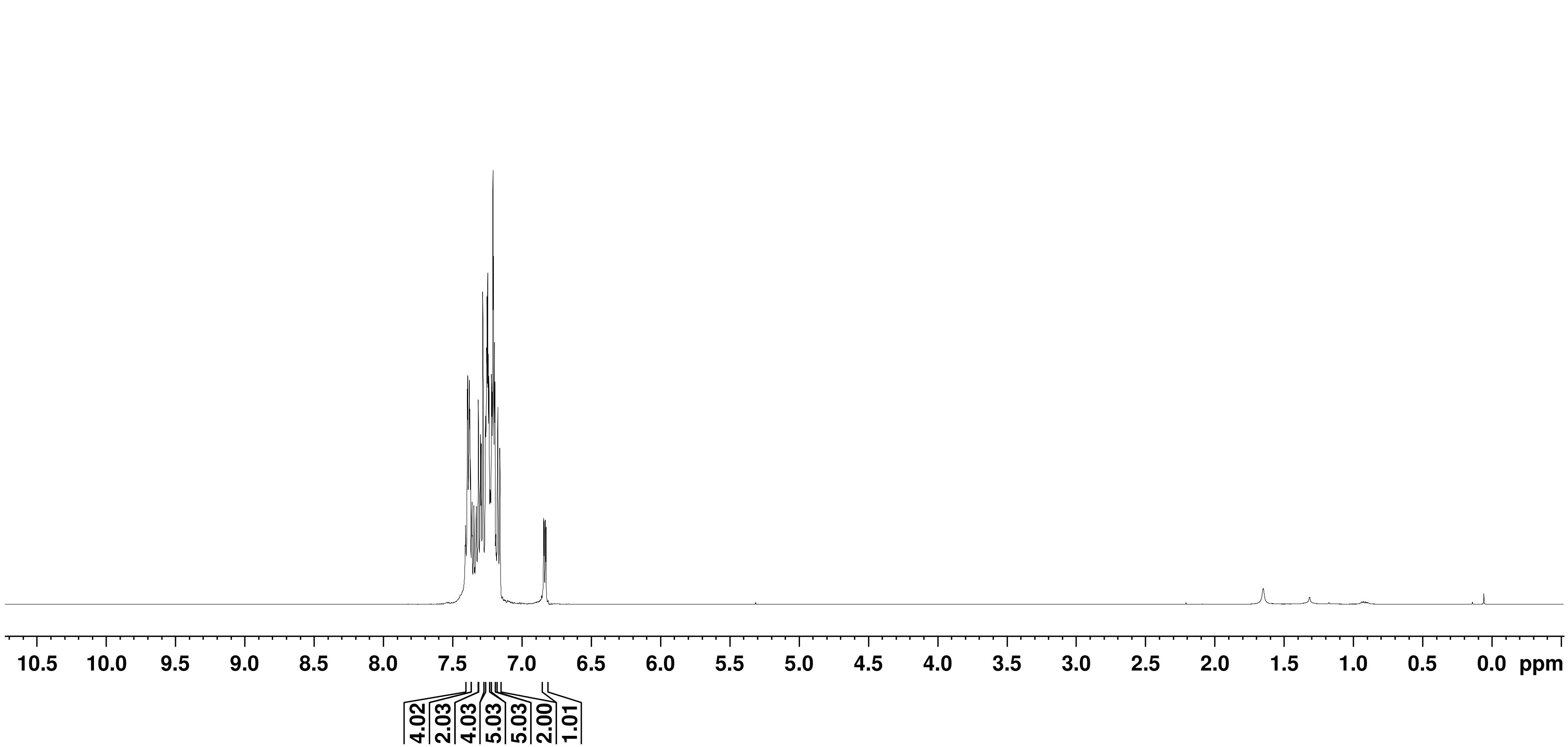
AS-565

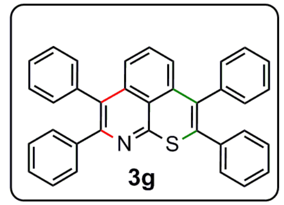


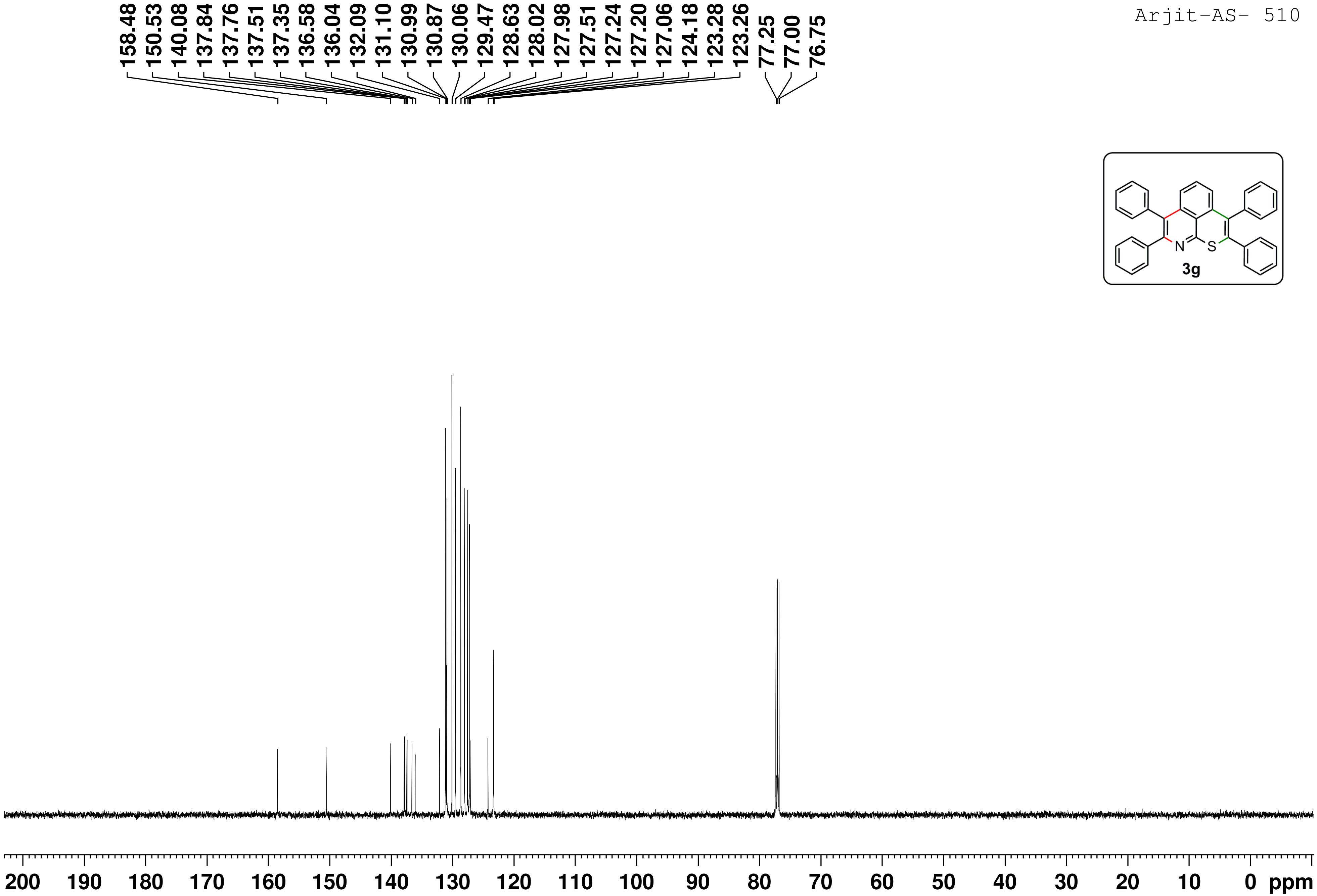
OCF3
N
S
3f
158.27
151.64
151.08
139.76
139.63
139.56
138.49
136.93
136.87
136.73
131.53
130.84
130.62
130.00
129.31
128.88
128.85
128.30
128.11
127.63
127.60
127.51
127.07
122.47
115.85
112.85
77.25
77.00
76.75
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


AS-565
-57.50
OCF3
N
S
3f
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

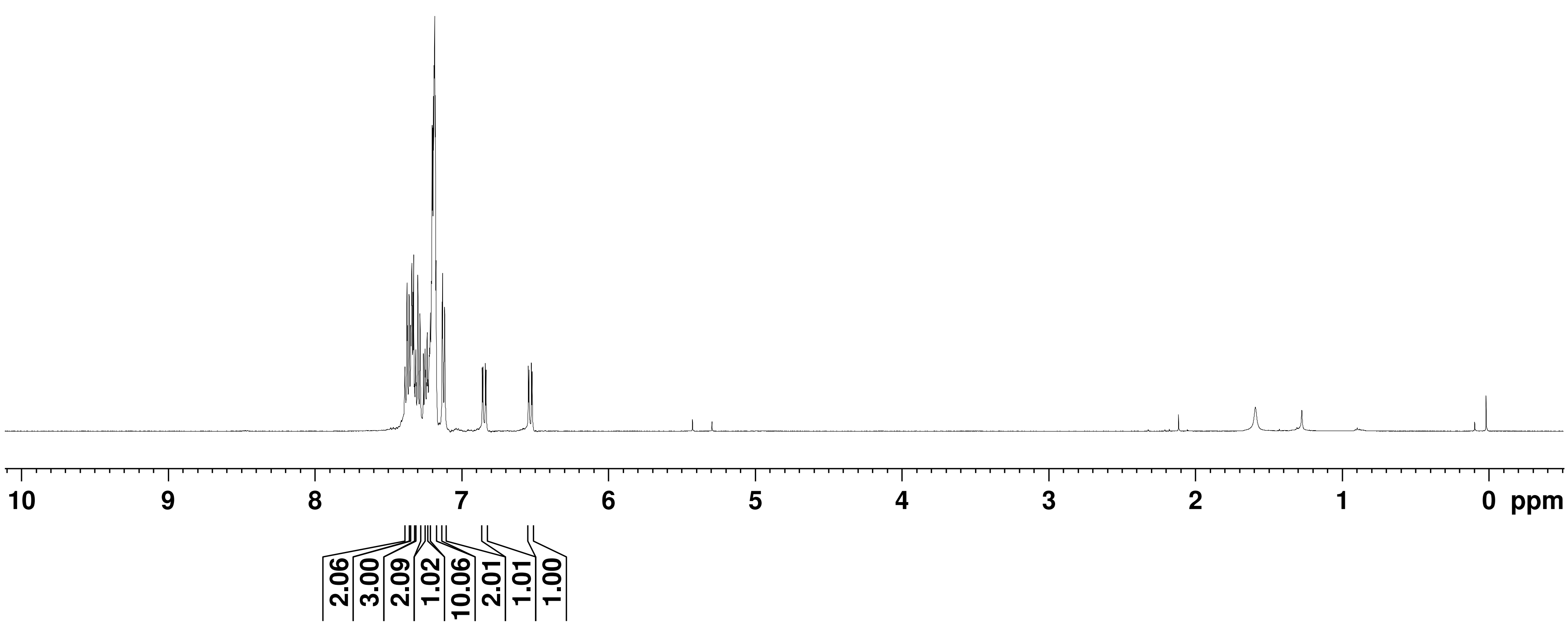
AS- 510

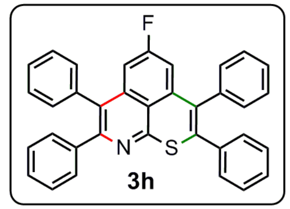

7.405 7.392 7.389 7.379 7.377 7.373 7.369 7.362 7.359 7.356 7.350 7.345 7.329 7.313 7.298 7.292 7.281 7.279 7.277 7.260 7.257 7.253 7.250 7.245 7.241 7.236 7.218 7.214 7.207 7.204 7.197 7.193 7.172 7.158 6.841 6.837 6.829 6.824
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.02 2.03 4.03 5.03 5.03 2.00 1.01


N
S
3g

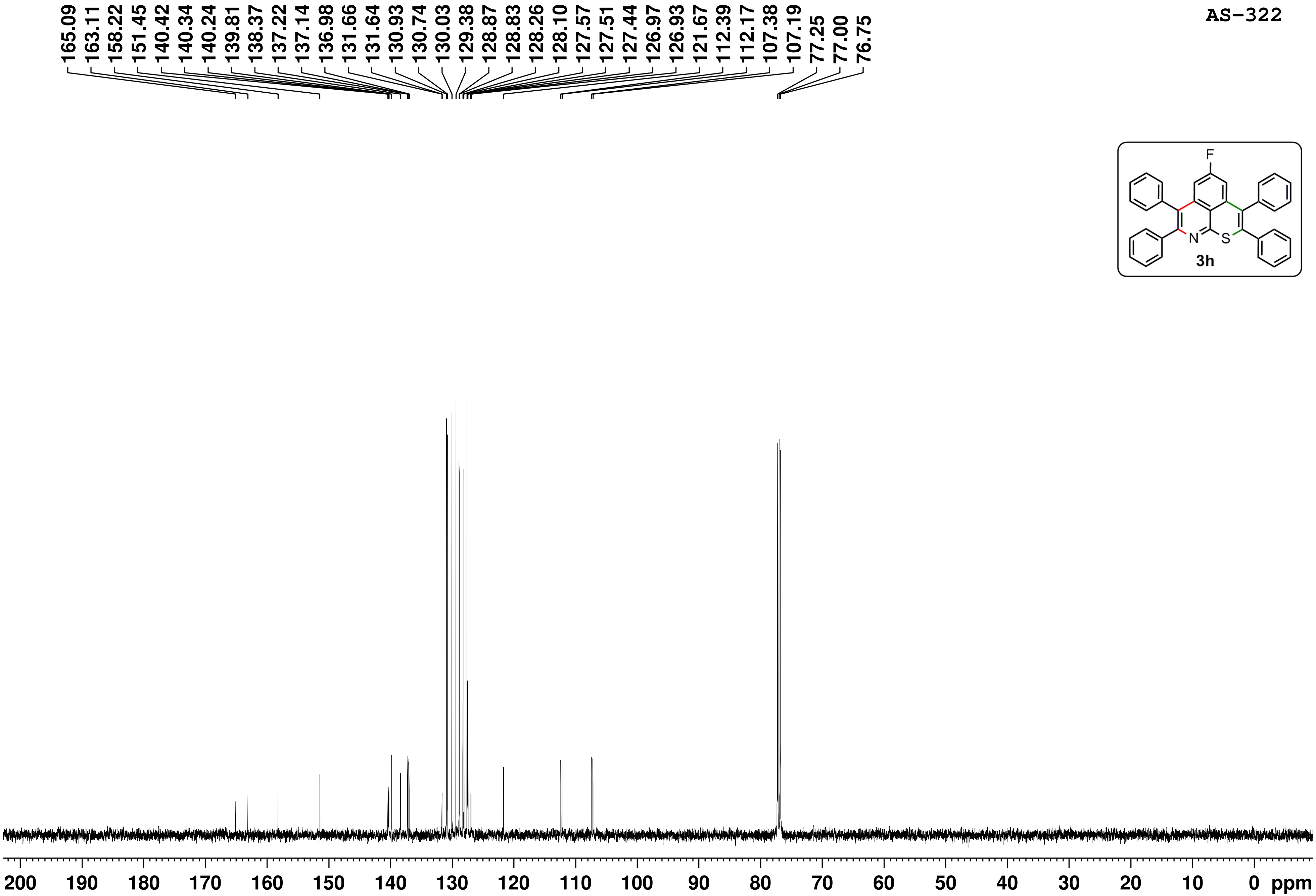

158.48
150.53
140.08
137.84
137.76
137.51
137.35
136.58
136.04
132.09
131.10
130.99
130.87
130.06
129.47
128.63
128.02
127.98
127.51
127.24
127.20
127.06
124.18
123.28
123.26
77.25
77.00
76.75
Arjit-AS- 510
N
S
3g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

AS-322

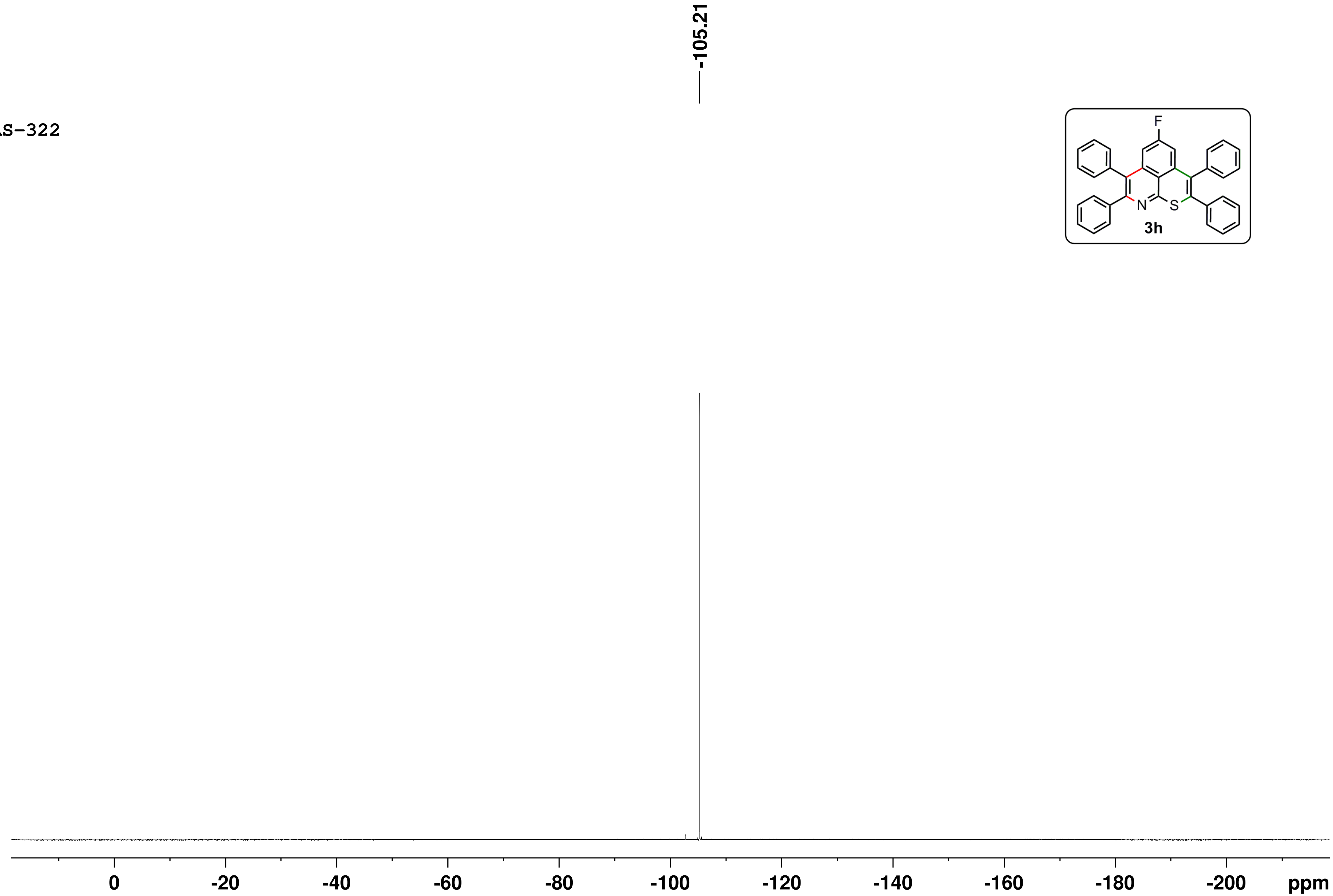

7.386
7.372
7.357
7.339
7.331
7.326
7.312
7.298
7.282
7.260
7.249
7.234
7.200
7.197
7.191
7.187
7.183
7.178
7.132
7.129
7.115
7.113
6.858
6.854
6.837
6.833
6.544
6.540
6.523
6.518
10 9 8 7 6 5 4 3 2 1 0 ppm
2.06
3.00
2.09
1.02
10.06
2.01
1.01
1.00


F
N
S
3h

AS−322

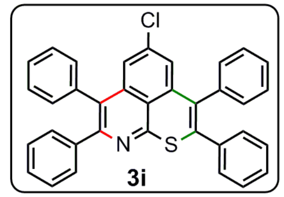

165.09
163.11
158.22
151.45
140.42
140.34
140.24
139.81
138.37
137.22
137.14
136.98
131.66
131.64
130.93
130.74
130.03
129.38
128.87
128.83
128.26
128.10
127.57
127.51
127.44
126.97
126.93
121.67
112.39
112.17
107.38
107.19
77.25
77.00
76.75
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
F
N
S
3h

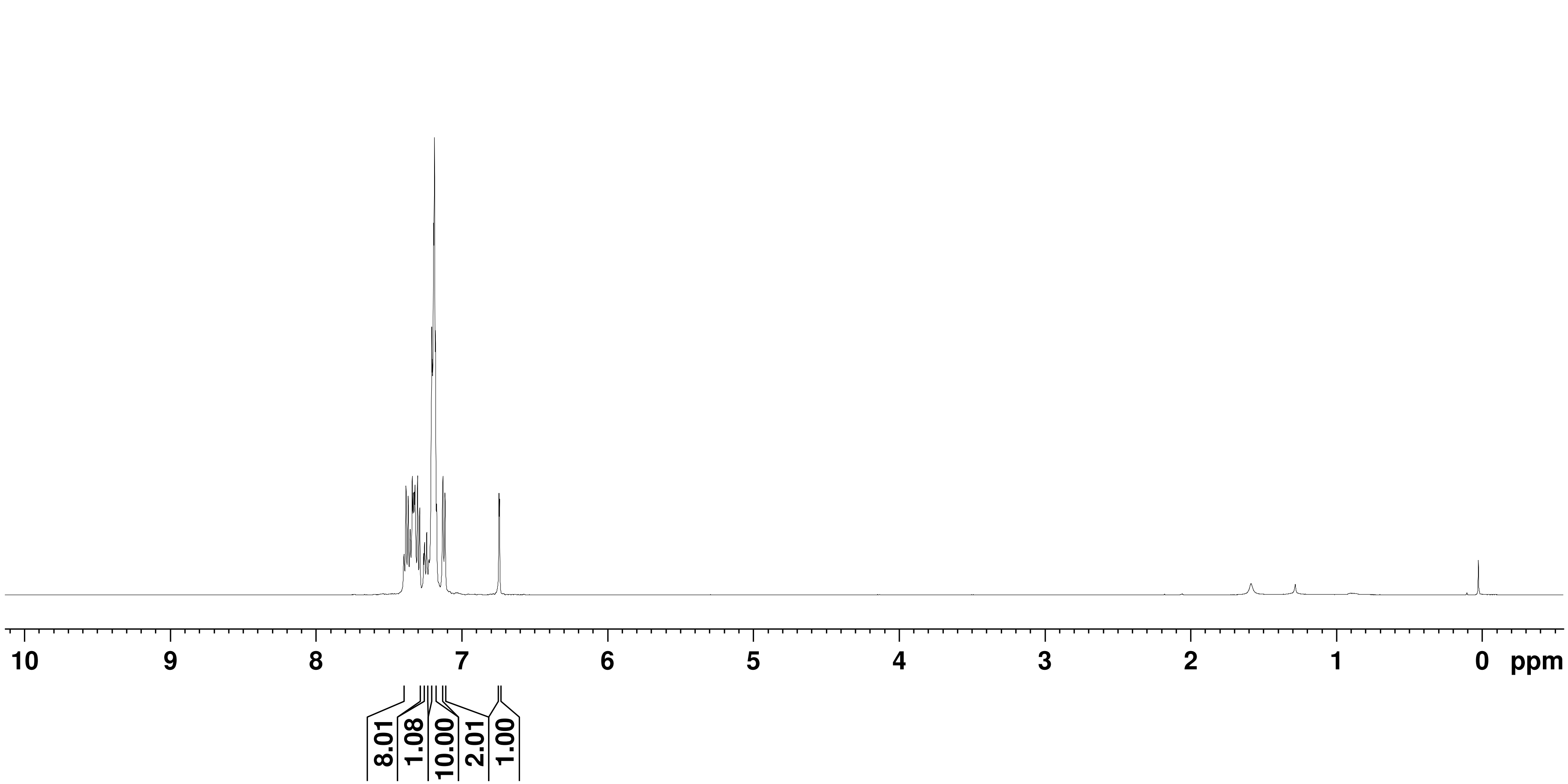
AS-322



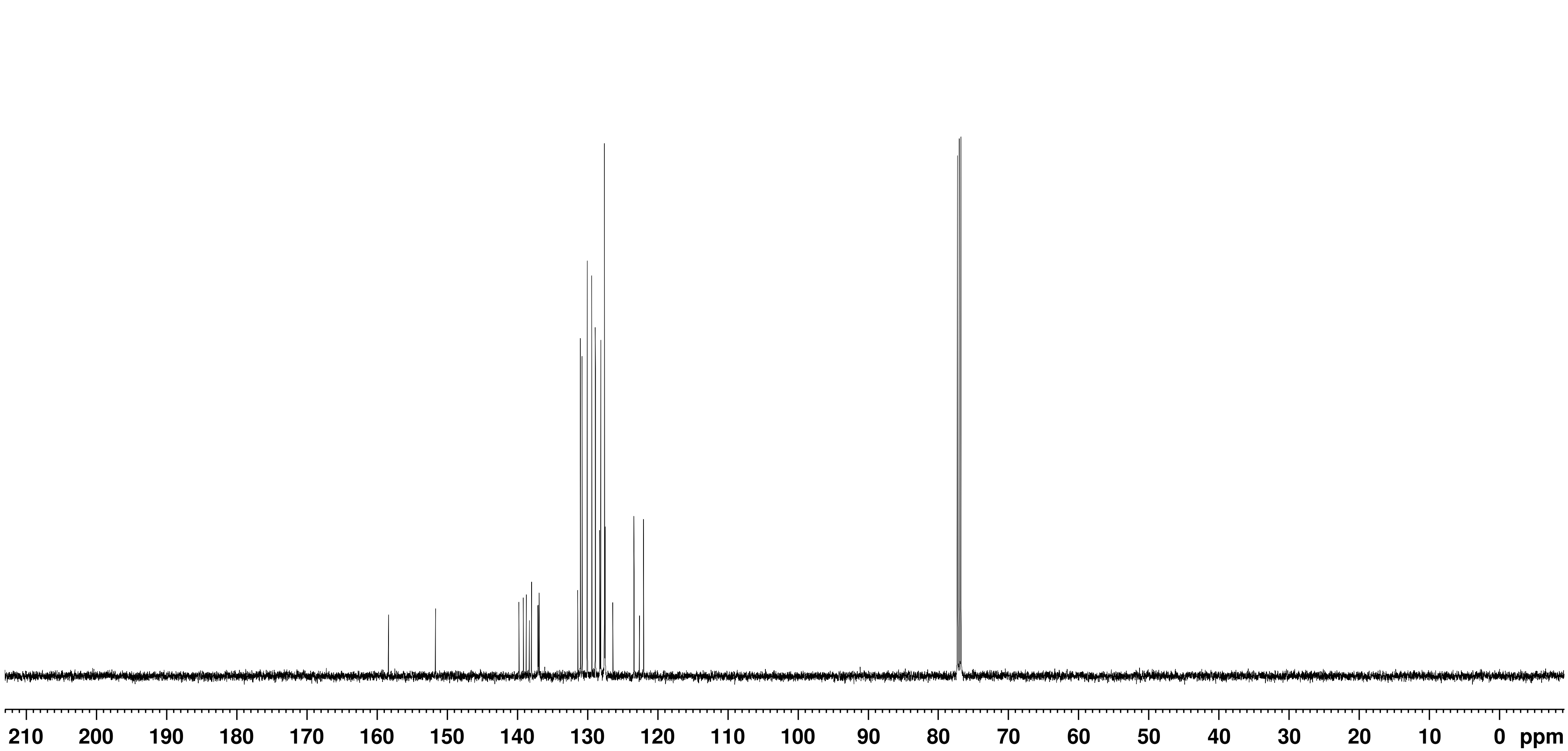
3h

Arjit-AS-217

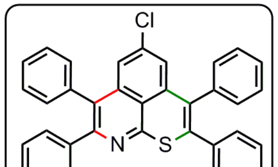

Cl
N
S
3i


7.395
7.381
7.366
7.352
7.338
7.331
7.324
7.319
7.302
7.287
7.260
7.253
7.239
7.204
7.200
7.192
7.186
7.179
7.128
7.114
6.743
6.739
10 9 8 7 6 5 4 3 2 1 0 ppm
8.01
1.08
10.00
2.01
1.00

AS-217

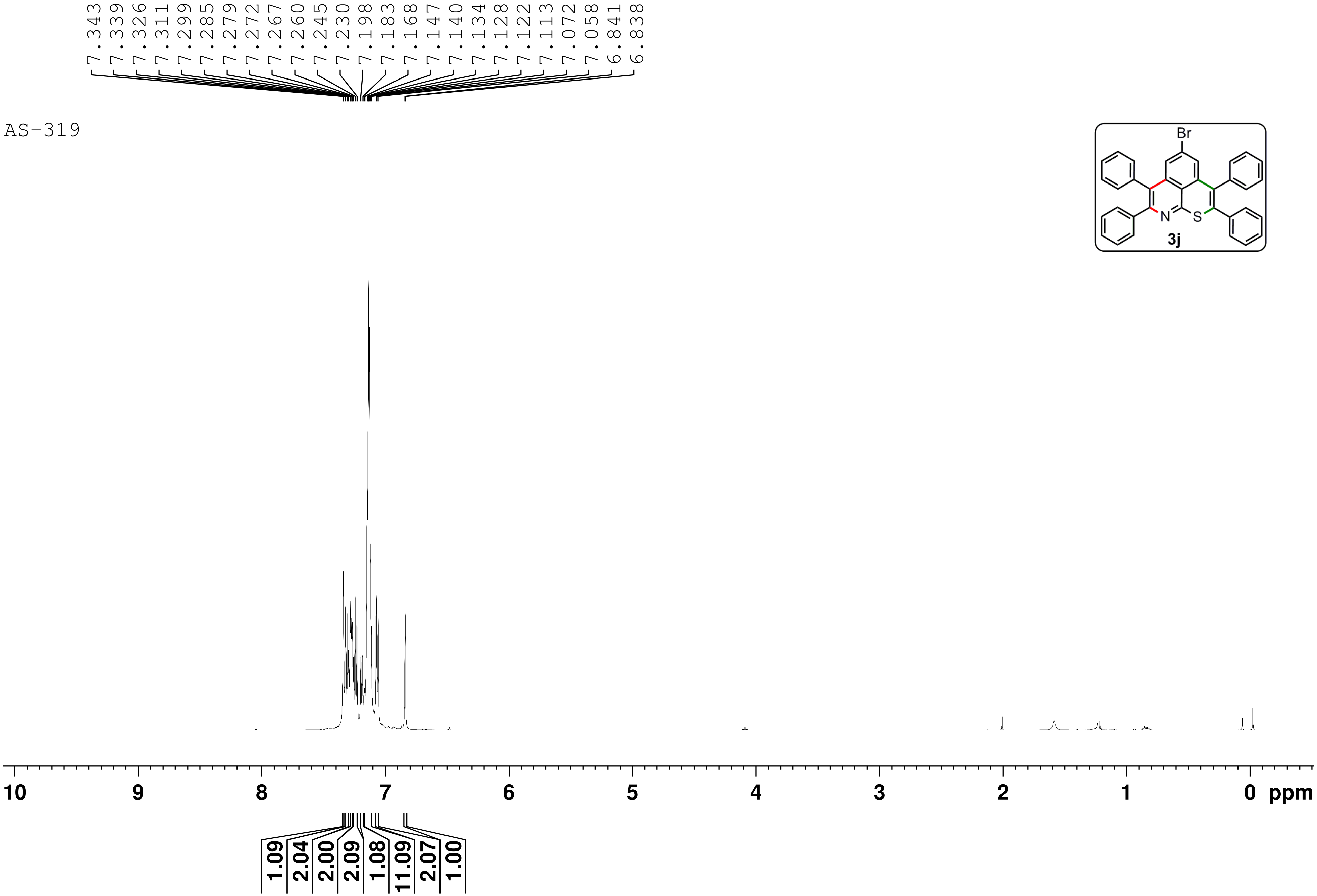


158.35
151.64
139.75
139.12
138.71
138.27
137.94
137.05
137.00
136.86
131.37
130.99
130.74
130.01
129.36
128.86
128.84
128.23
128.09
127.57
127.45
126.36
123.35
122.57
121.99
77.25
77.00
76.74
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

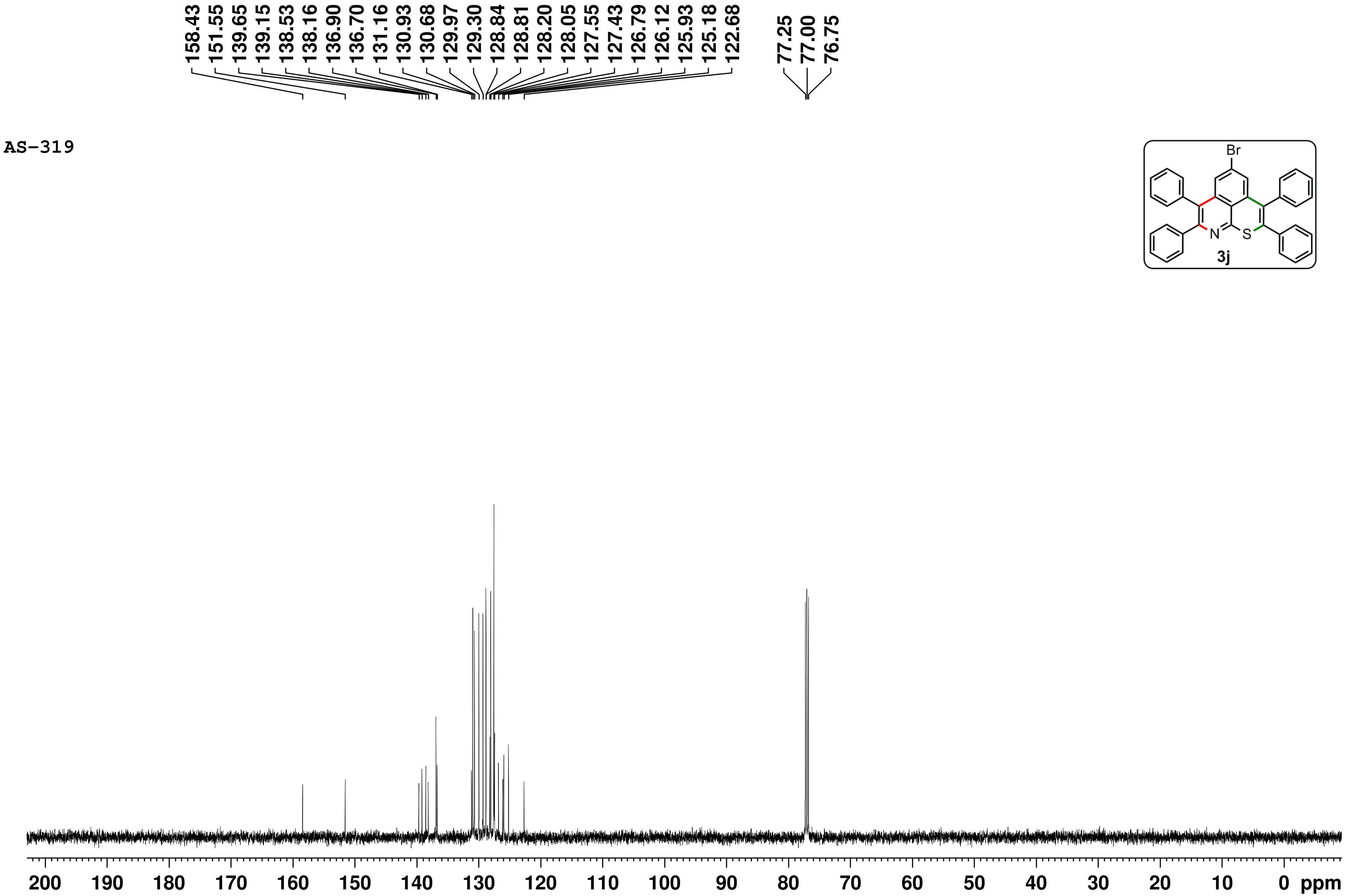


Cl
N
S

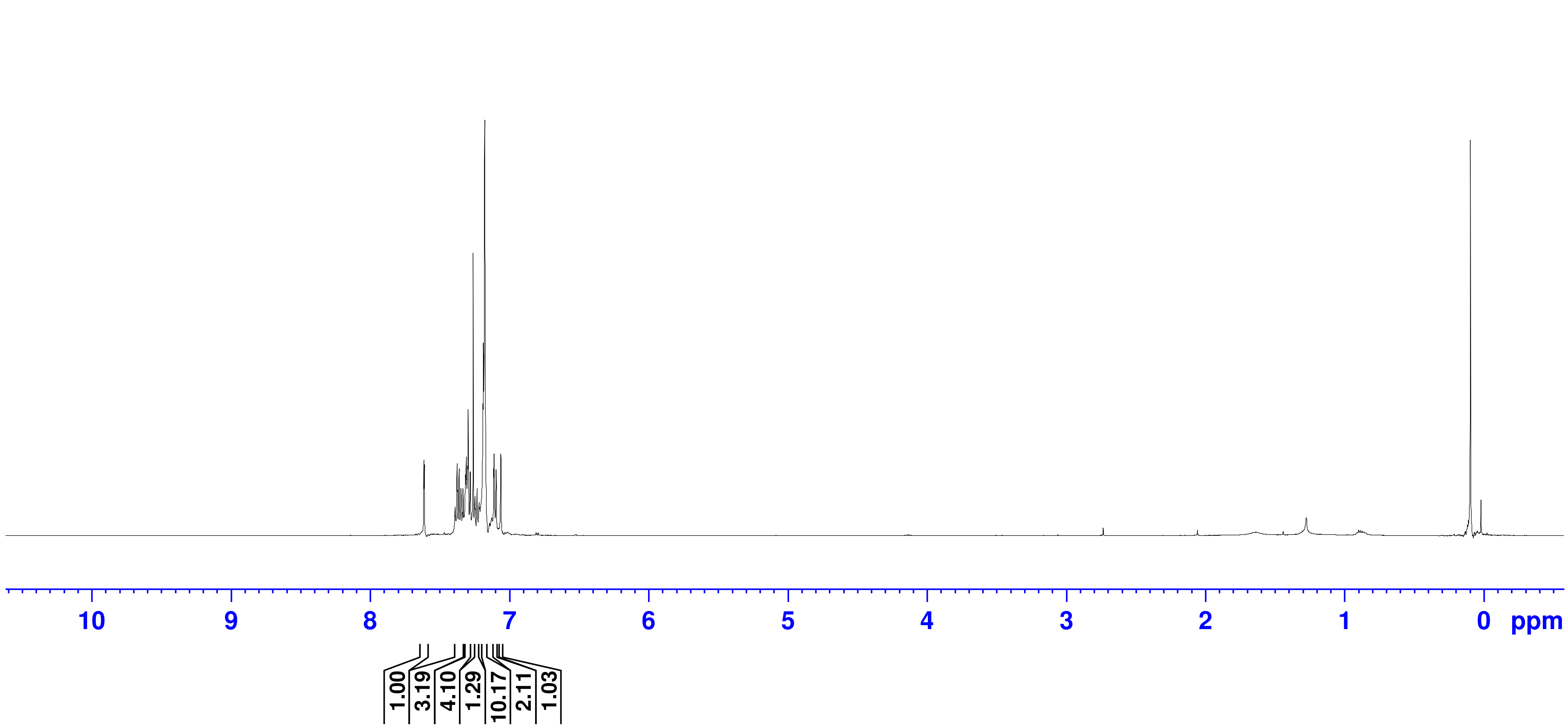
3i

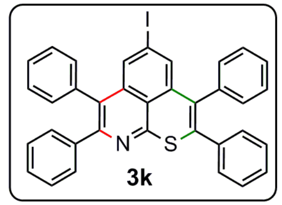


7.343
7.339
7.326
7.311
7.299
7.285
7.279
7.272
7.267
7.260
7.245
7.230
7.198
7.183
7.168
7.147
7.140
7.134
7.128
7.122
7.113
7.072
7.058
6.841
6.838
AS-319
Br
N
S
3j
10
9
8
7
6
5
4
3
2
1
0 ppm
1.09
2.04
2.00
2.09
1.08
11.09
2.07
1.00

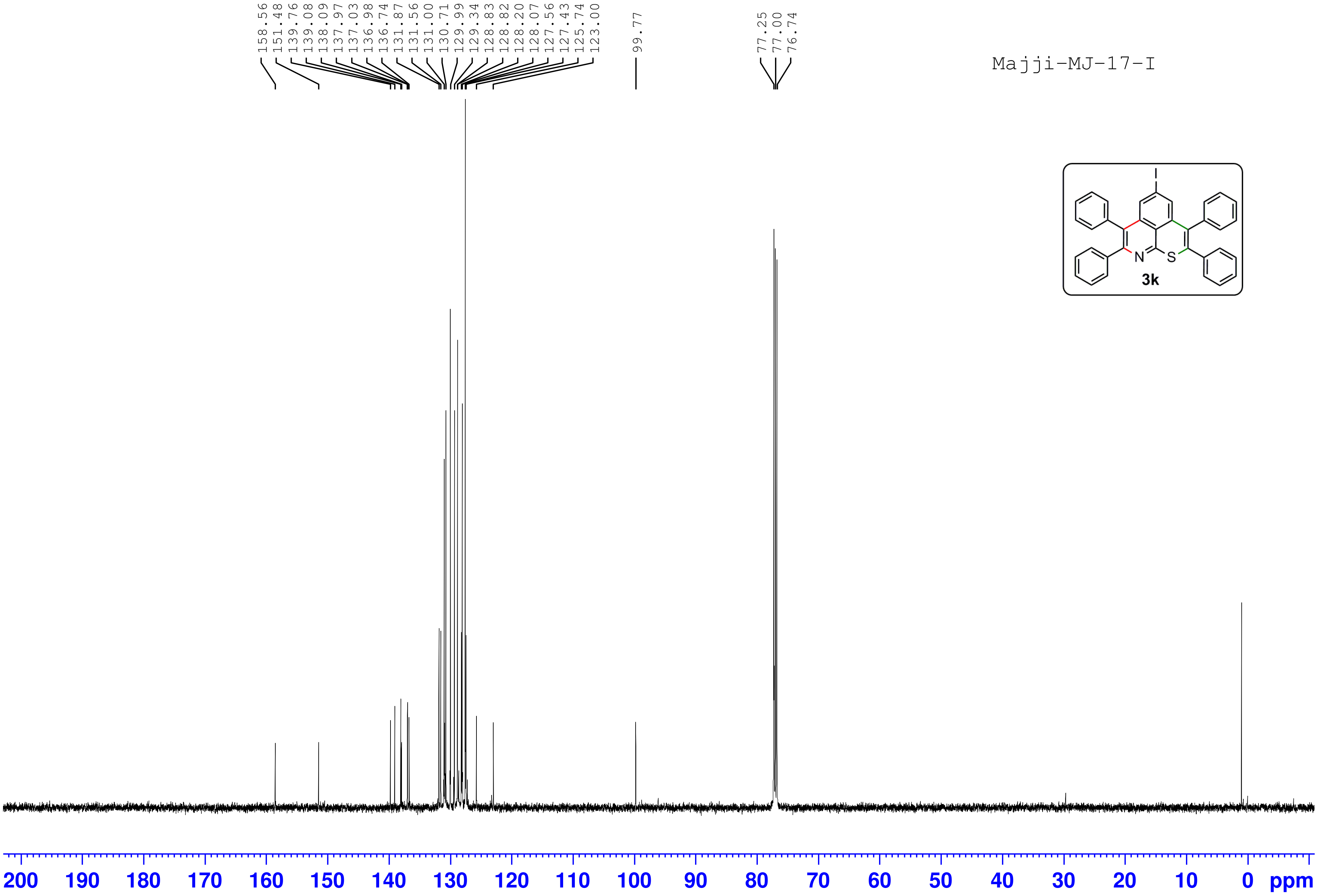

158.43
151.55
139.65
139.15
138.53
138.16
136.90
136.70
131.16
130.93
130.68
129.97
129.30
128.84
128.81
128.20
128.05
127.55
127.43
126.79
126.12
125.93
125.18
122.68
77.25
77.00
76.75
AS-319
Br
N
S
3j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

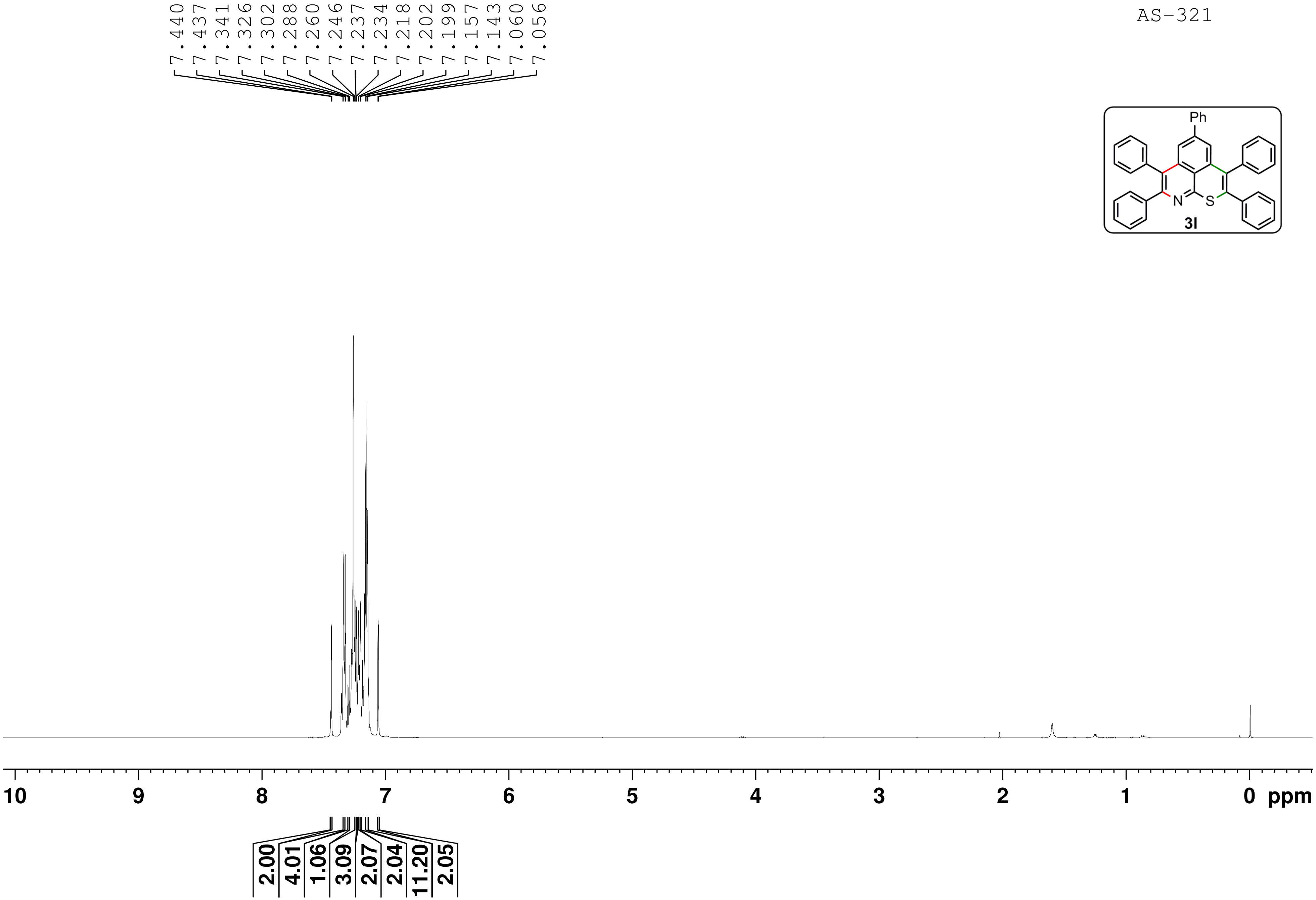
Majji-MJ-17-I


7.614
7.611
7.389
7.375
7.372
7.361
7.347
7.333
7.316
7.309
7.296
7.281
7.260
7.249
7.246
7.244
7.235
7.231
7.190
7.186
7.177
7.109
7.096
7.063
7.060
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
3.19
4.10
1.29
10.17
2.11
1.03

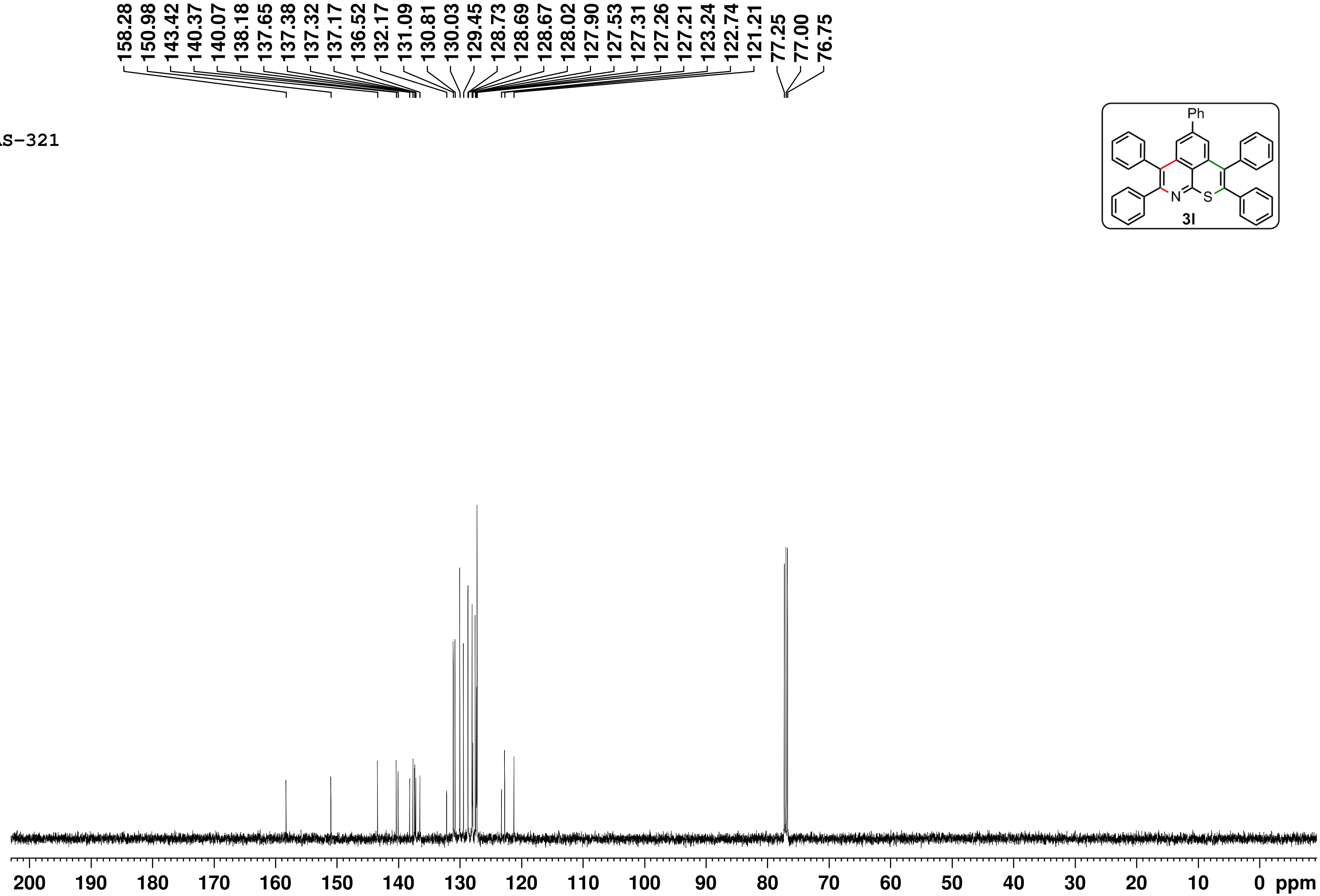

I
N
S
3k

Majji-MJ-17-I

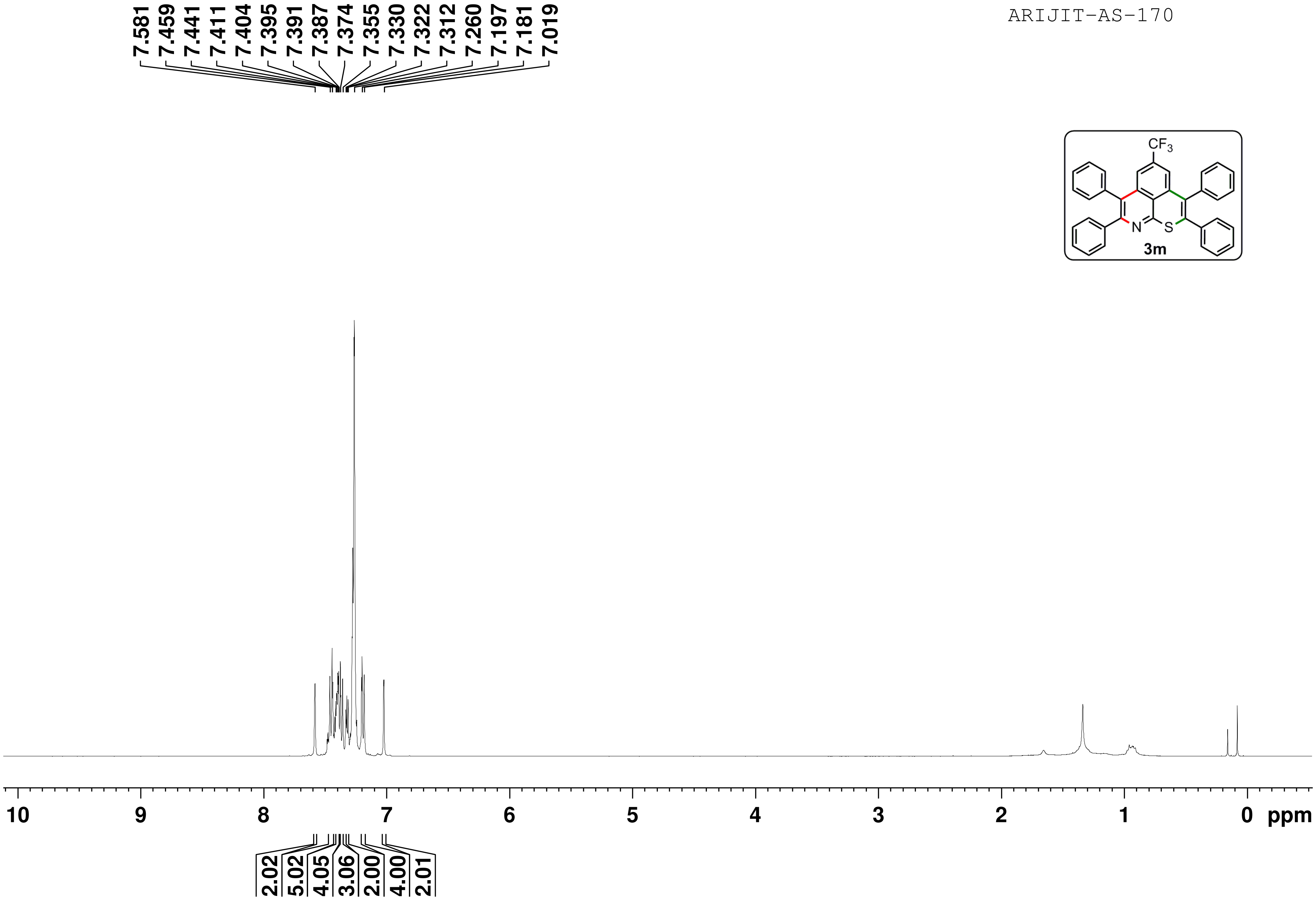

158.56
151.48
139.76
139.08
138.09
137.97
137.03
136.98
136.74
131.87
131.56
131.00
130.71
129.99
129.34
128.83
128.82
128.20
128.07
127.56
127.43
125.74
123.00
99.77
77.25
77.00
76.74
I
N
S
3k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


AS-321
7.440
7.437
7.341
7.326
7.302
7.288
7.260
7.246
7.237
7.234
7.218
7.202
7.199
7.157
7.143
7.060
7.056
Ph
N
S
3l
10
9
8
7
6
5
4
3
2
1
0 ppm
2.00
4.01
1.06
3.09
2.07
2.04
11.20
2.05

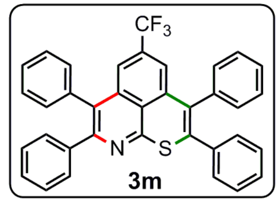
AS-321

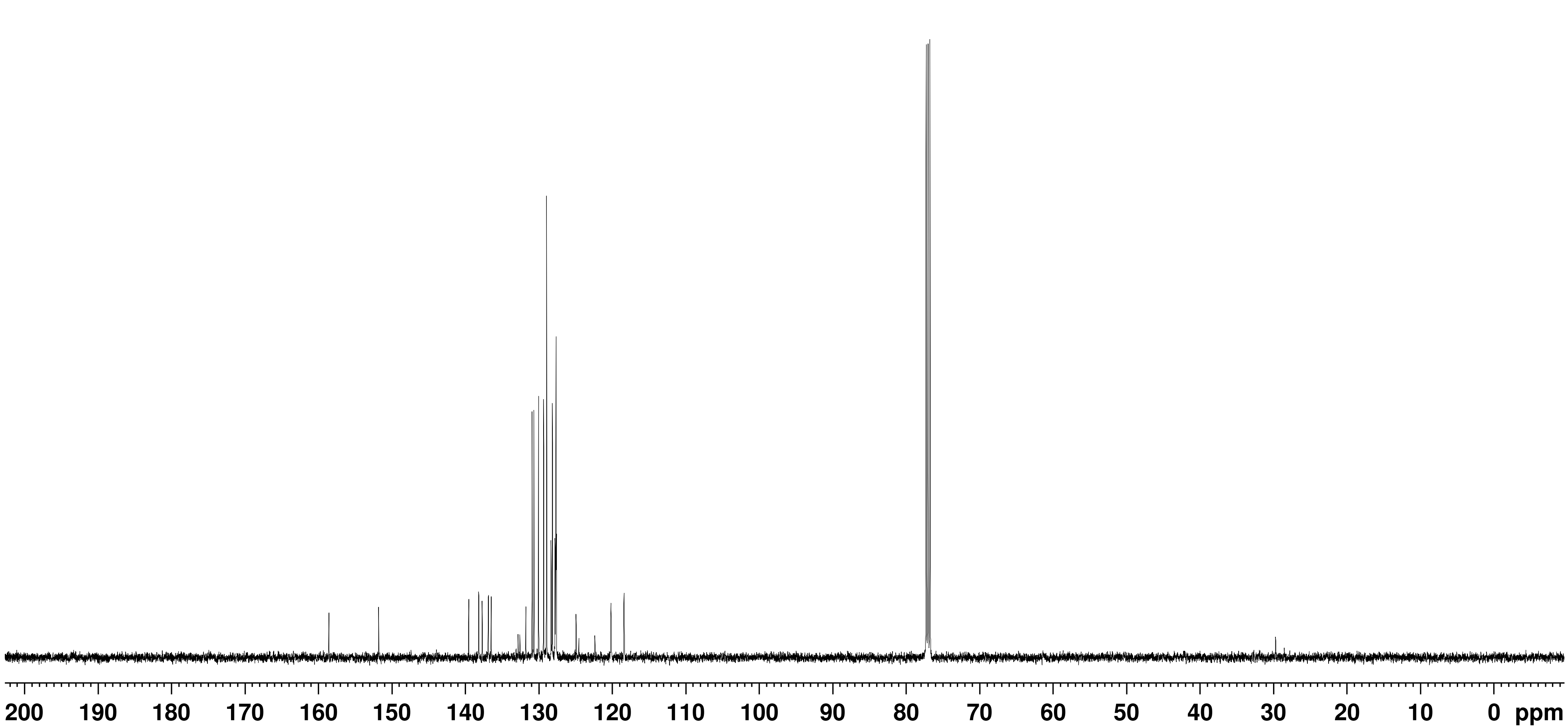

158.28
150.98
143.42
140.37
140.07
138.18
137.65
137.38
137.32
137.17
136.52
132.17
131.09
130.81
130.03
129.45
128.73
128.69
128.67
128.02
127.90
127.53
127.31
127.26
127.21
123.24
122.74
121.21
77.25
77.00
76.75
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
Ph
N
S

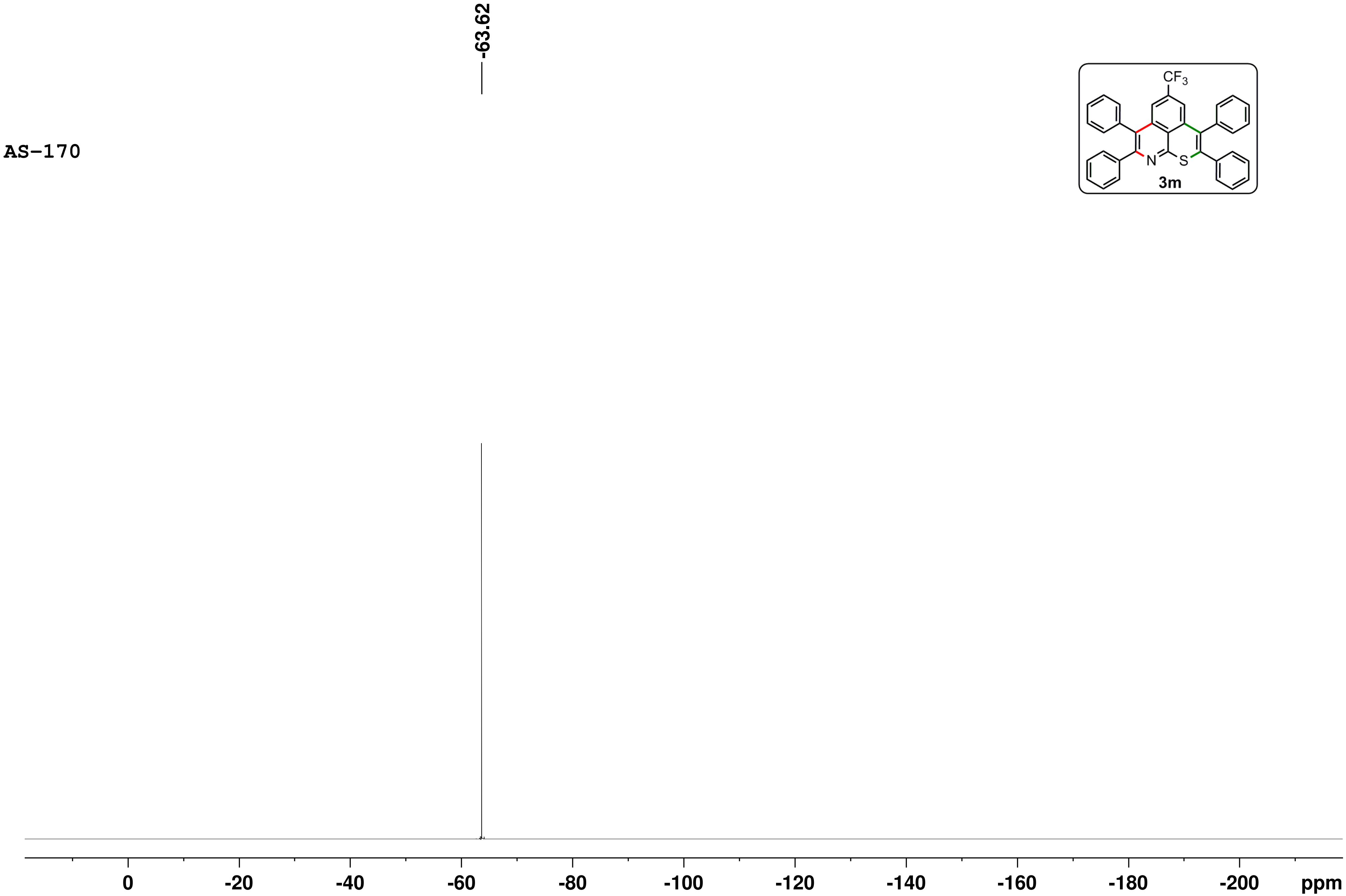
3l

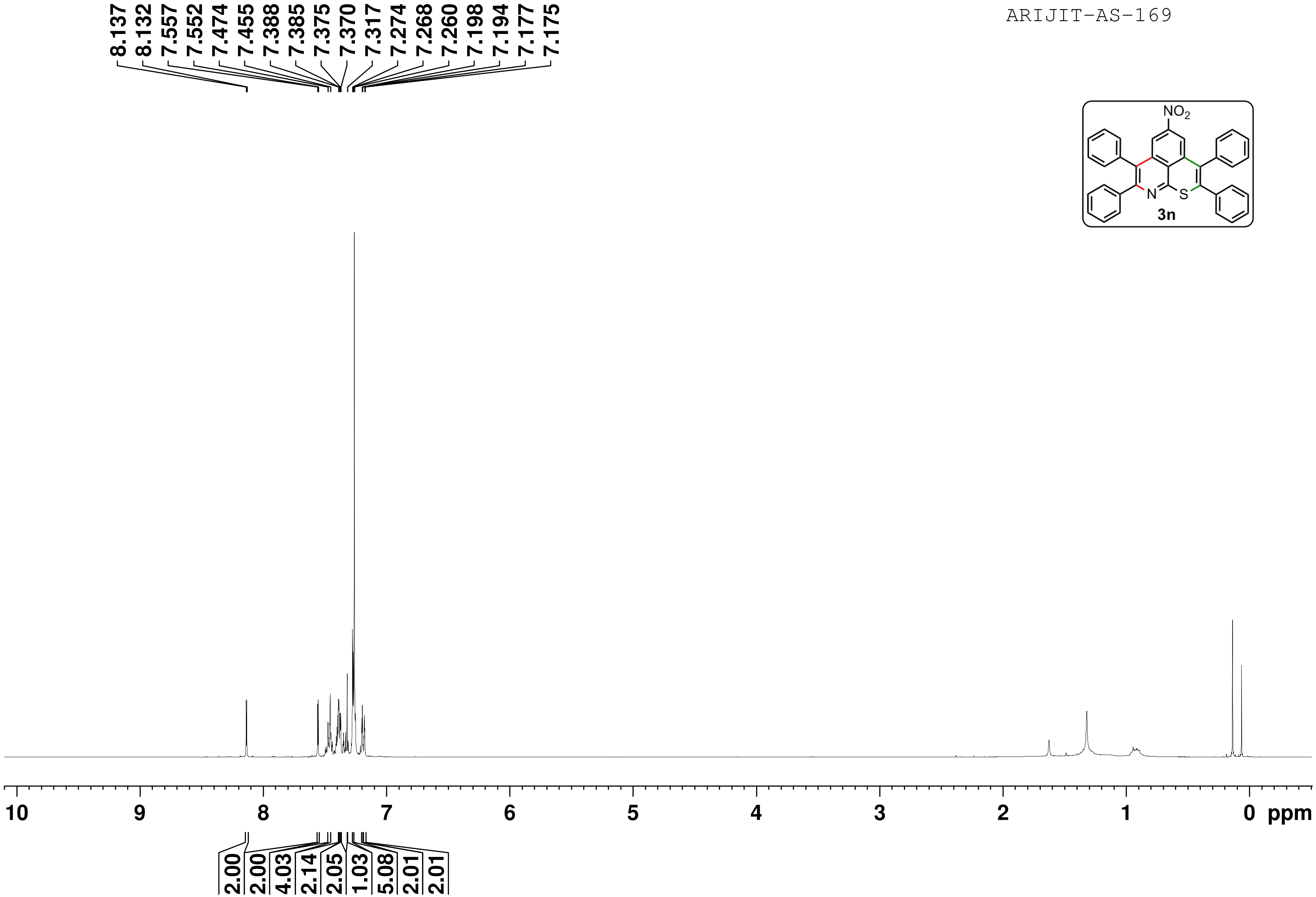

ARIJIT-AS-170
7.581
7.459
7.441
7.411
7.404
7.395
7.391
7.387
7.374
7.355
7.330
7.322
7.312
7.260
7.197
7.181
7.019
CF3
N
S
3m
10
9
8
7
6
5
4
3
2
1
0 ppm
2.02
5.02
4.05
3.06
2.00
4.00
2.01

AS-170

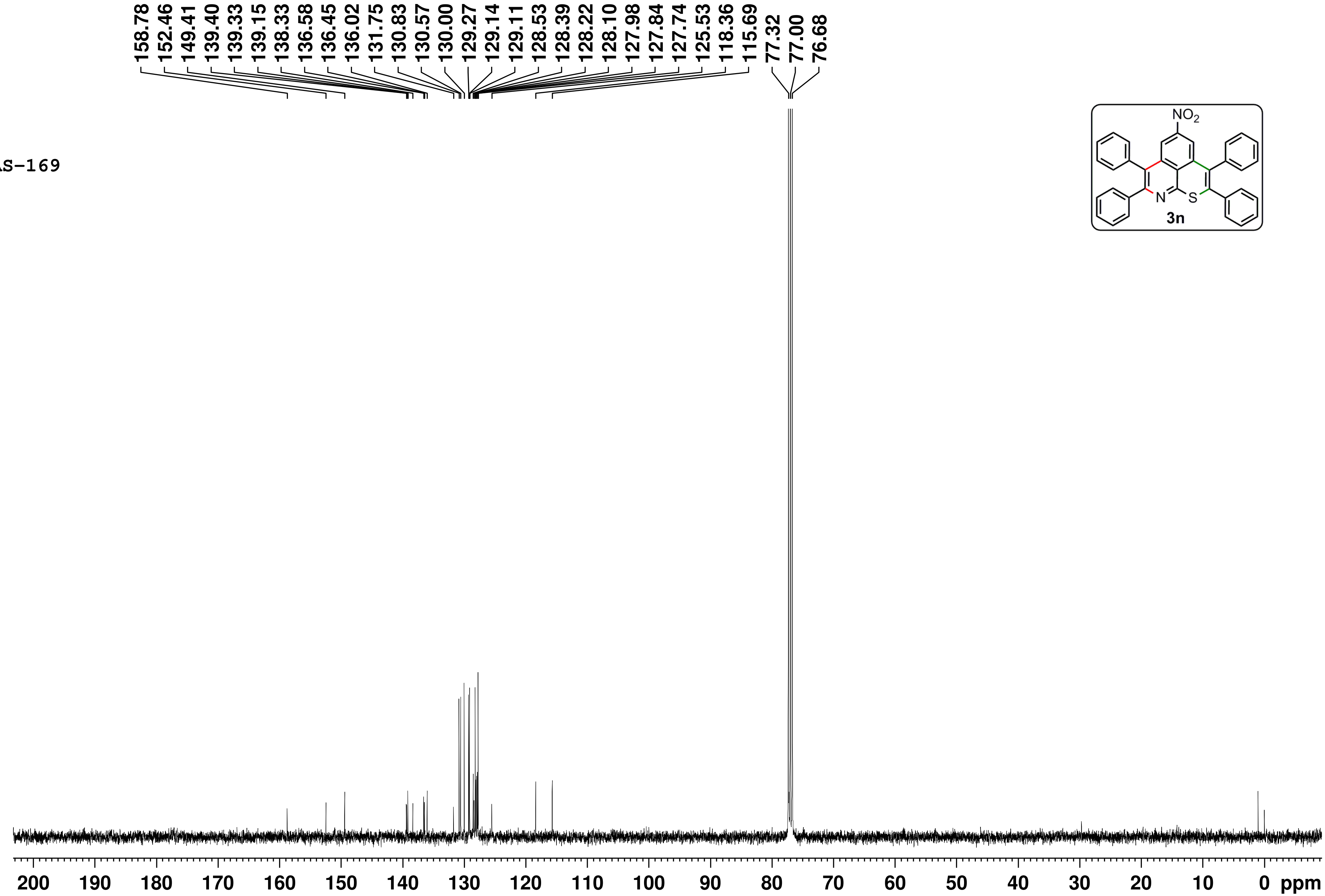

CF3
N
S
3m


158.55
151.79
139.52
138.17
137.69
136.88
136.84
136.46
132.81
132.55
131.74
130.90
130.66
130.02
129.33
128.92
128.31
128.13
127.77
127.69
127.64
127.59
124.91
124.53
122.36
120.17
118.38
77.25
77.00
76.75
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

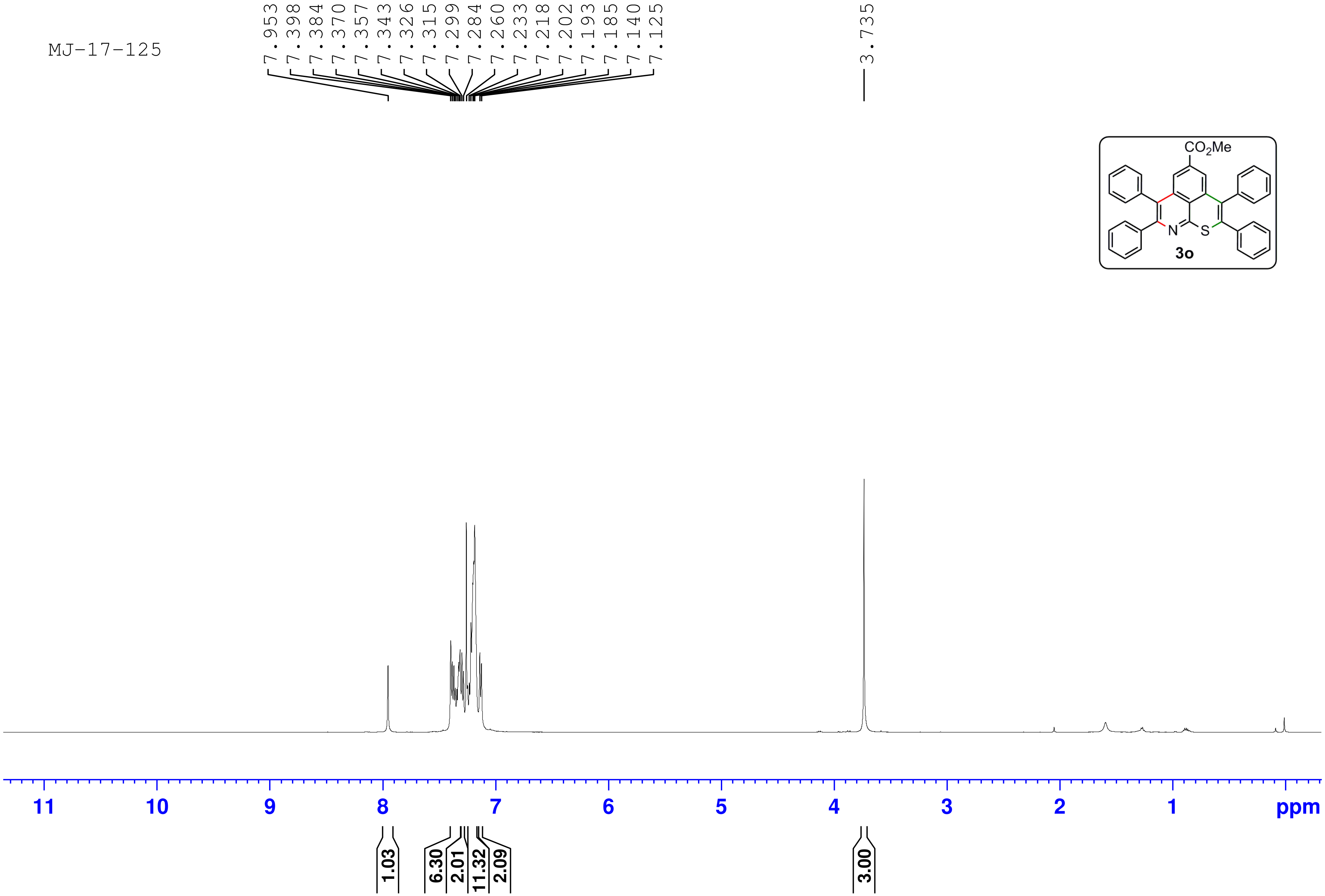

AS-170
-63.62
CF_3
N
S
3m
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

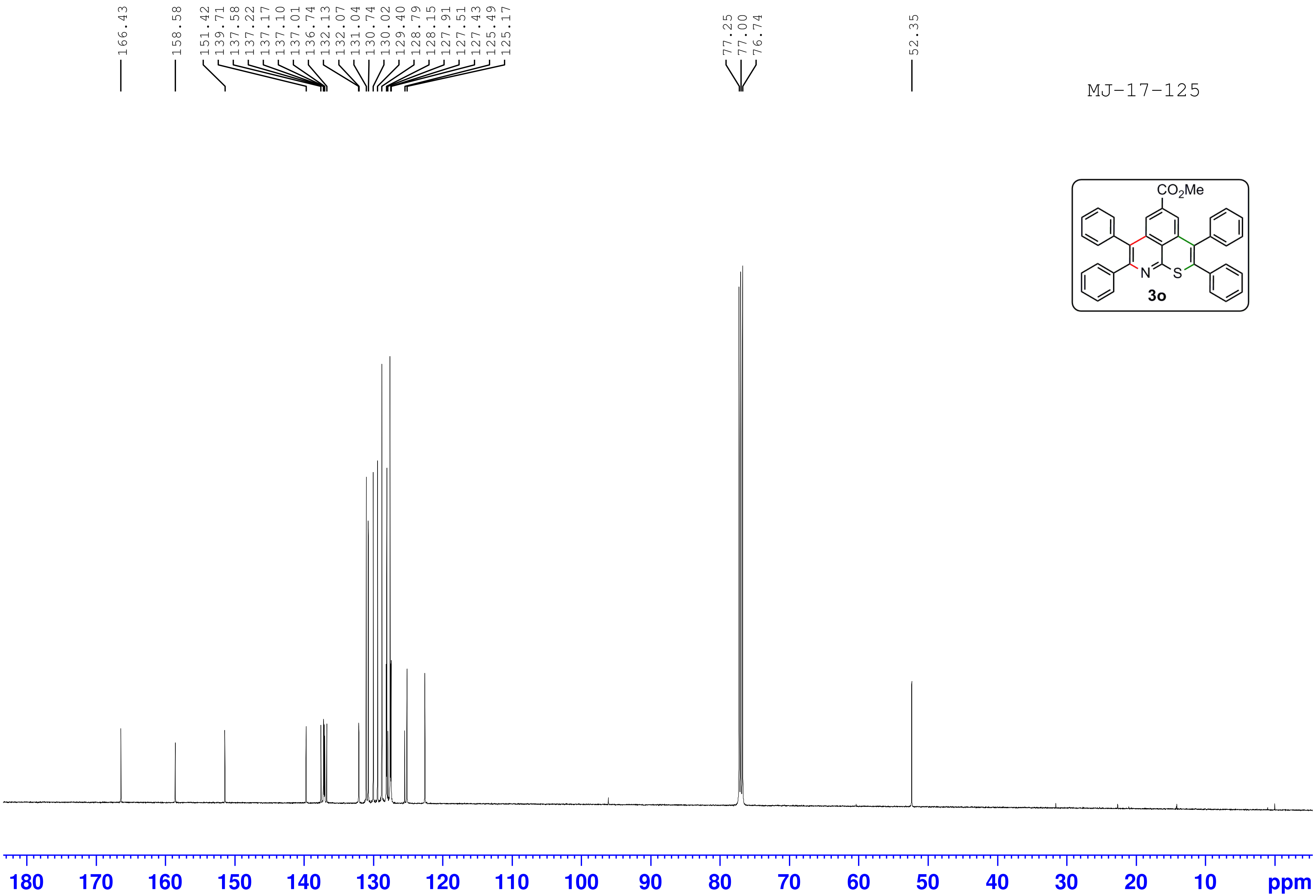

ARIJIT-AS-169
8.137
8.132
7.557
7.552
7.474
7.455
7.388
7.385
7.375
7.370
7.317
7.274
7.268
7.260
7.198
7.194
7.177
7.175
NO_2
N
S
3n
10 9 8 7 6 5 4 3 2 1 0 ppm
2.00
2.00
4.03
2.14
2.05
1.03
5.08
2.01
2.01

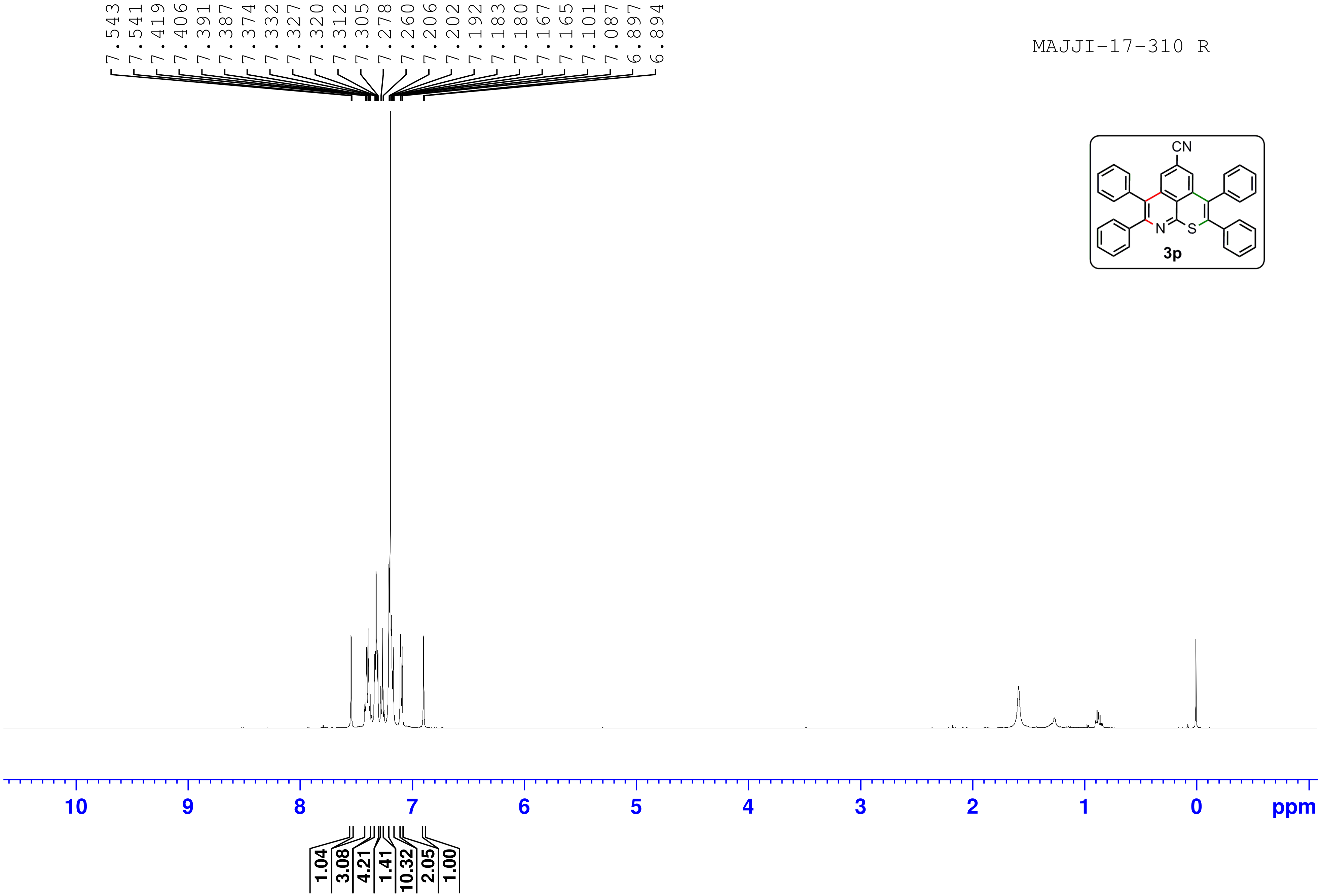
AS-169



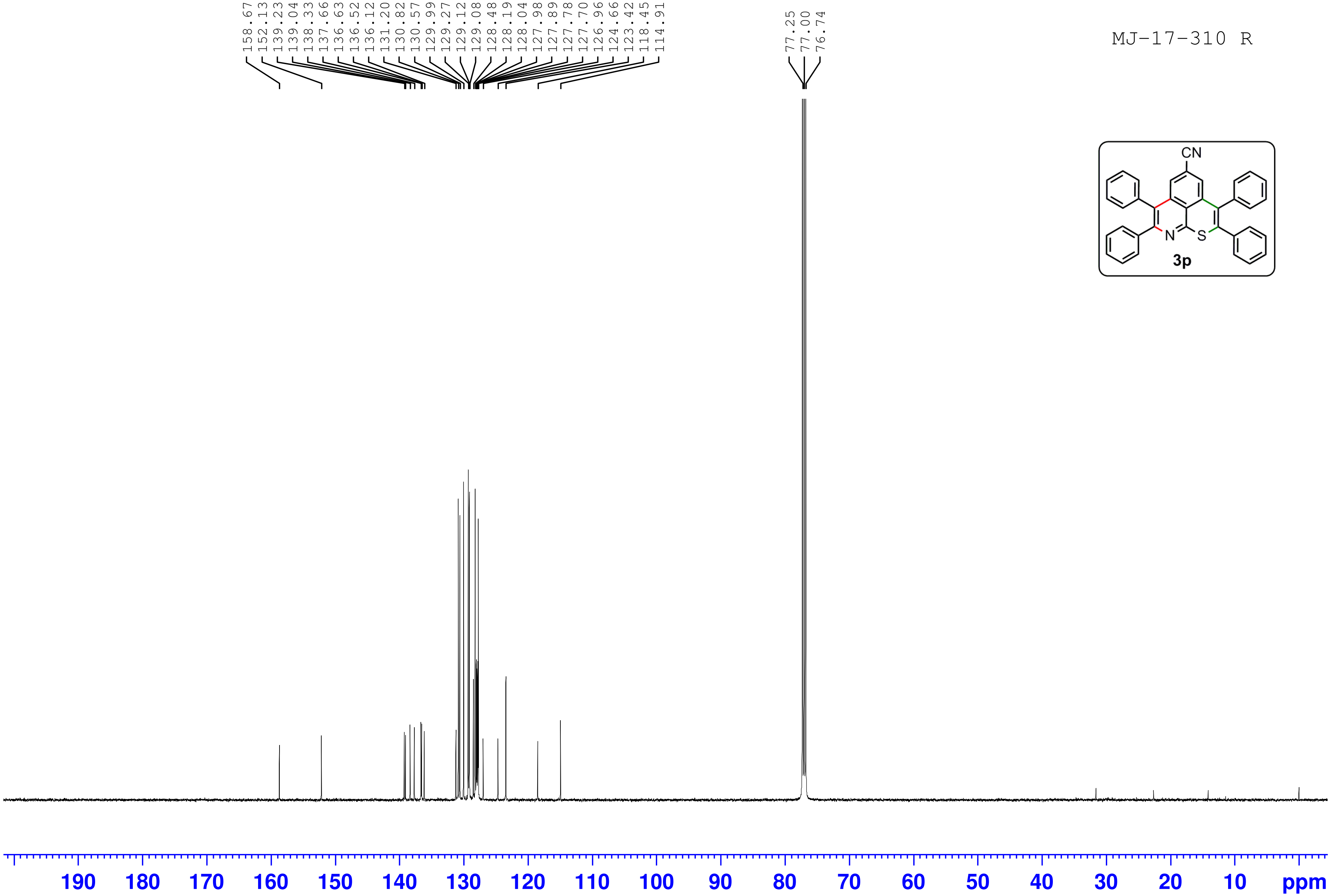
158.78
152.46
149.41
139.40
139.33
139.15
138.33
136.58
136.45
136.02
131.75
130.83
130.57
130.00
129.27
129.14
129.11
128.53
128.39
128.22
128.10
127.98
127.84
127.74
125.53
118.36
115.69
77.32
77.00
76.68
NO_2
N
S
3n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


MJ-17-125
7.953
7.398
7.384
7.370
7.357
7.343
7.326
7.315
7.299
7.284
7.260
7.233
7.218
7.202
7.193
7.185
7.140
7.125
3.735
CO2Me
N
S
3o
11
10
9
8
7
6
5
4
3
2
1
ppm
1.03
6.30
2.01
11.32
2.09
3.00


166.43
158.58
151.42
139.71
137.58
137.22
137.17
137.10
137.01
136.74
132.13
132.07
131.04
130.74
130.02
129.40
128.79
128.15
127.91
127.51
127.43
125.49
125.17
77.25
77.00
76.74
52.35
MJ-17-125
CO_2Me
N
S
3o
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.543
7.541
7.419
7.406
7.391
7.387
7.374
7.332
7.327
7.320
7.312
7.305
7.278
7.260
7.206
7.202
7.192
7.183
7.180
7.167
7.165
7.101
7.087
6.897
6.894
MAJJI-17-310 R
CN
N
S
3p
10
9
8
7
6
5
4
3
2
1
0
ppm
1.04
3.08
4.21
1.41
10.32
2.05
1.00

MJ-17-310 R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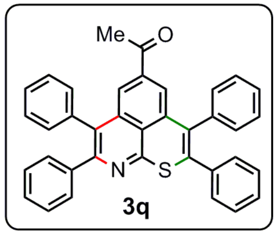
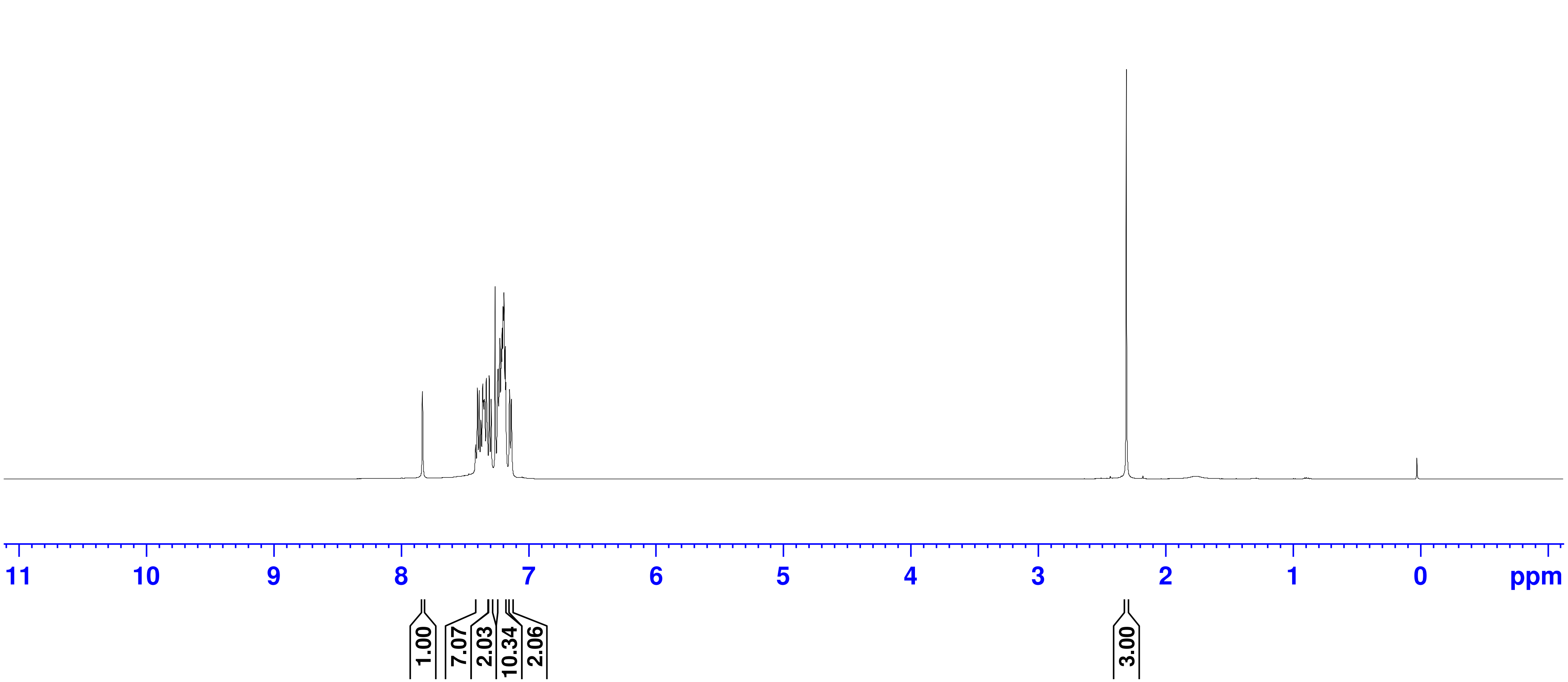
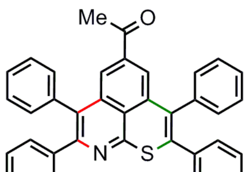
152.13
139.23
139.04
138.33
137.66
136.63
136.52
136.12
131.20
130.82
130.57
129.99
129.27
129.12
129.08
128.48
128.19
128.04
127.98
127.89
127.78
127.70
126.96
124.66
123.42
118.45
114.91
77.25
77.00
76.74
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
CN
N
S

3p


Me
O
N
S

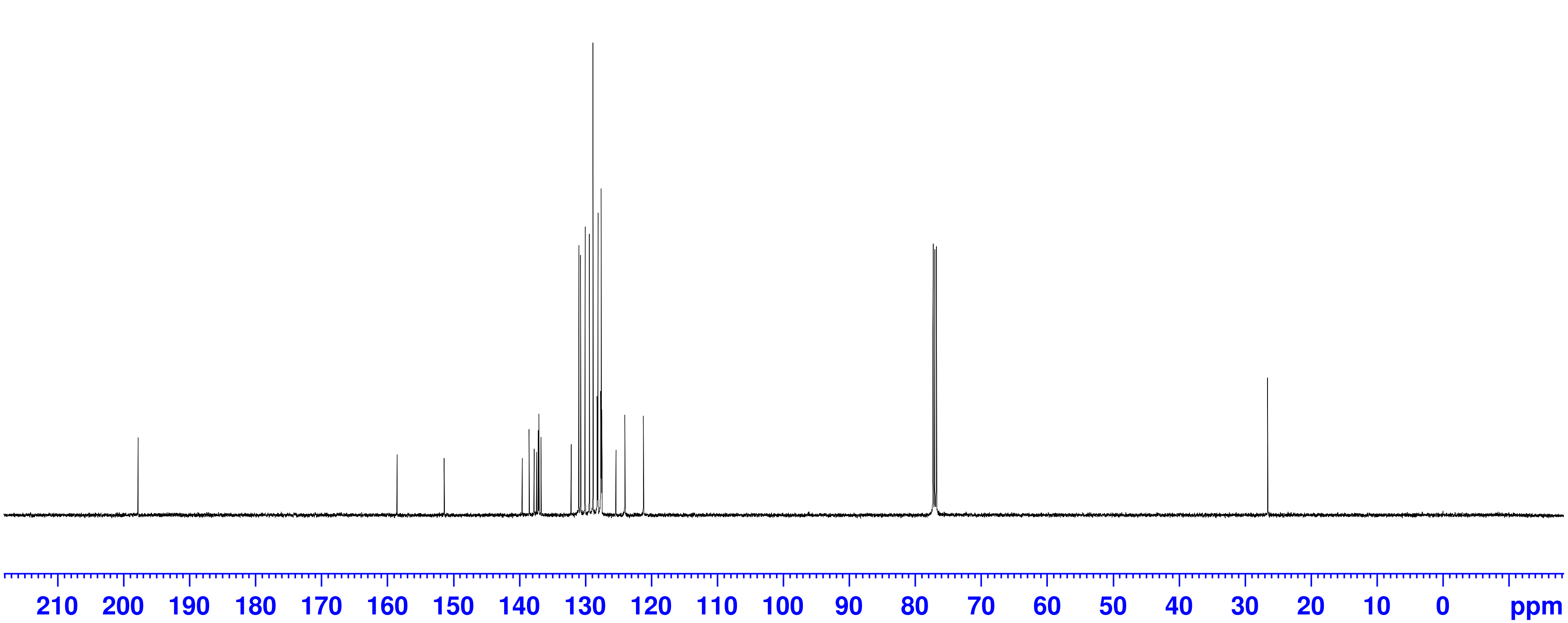
3q


7.829
7.413
7.399
7.384
7.371
7.357
7.353
7.345
7.329
7.327
7.306
7.291
7.260
7.237
7.223
7.205
7.198
7.191
7.181
7.176
7.147
7.132
2.305
MAJJI-17-214
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
7.07
2.03
10.34
2.06
3.00

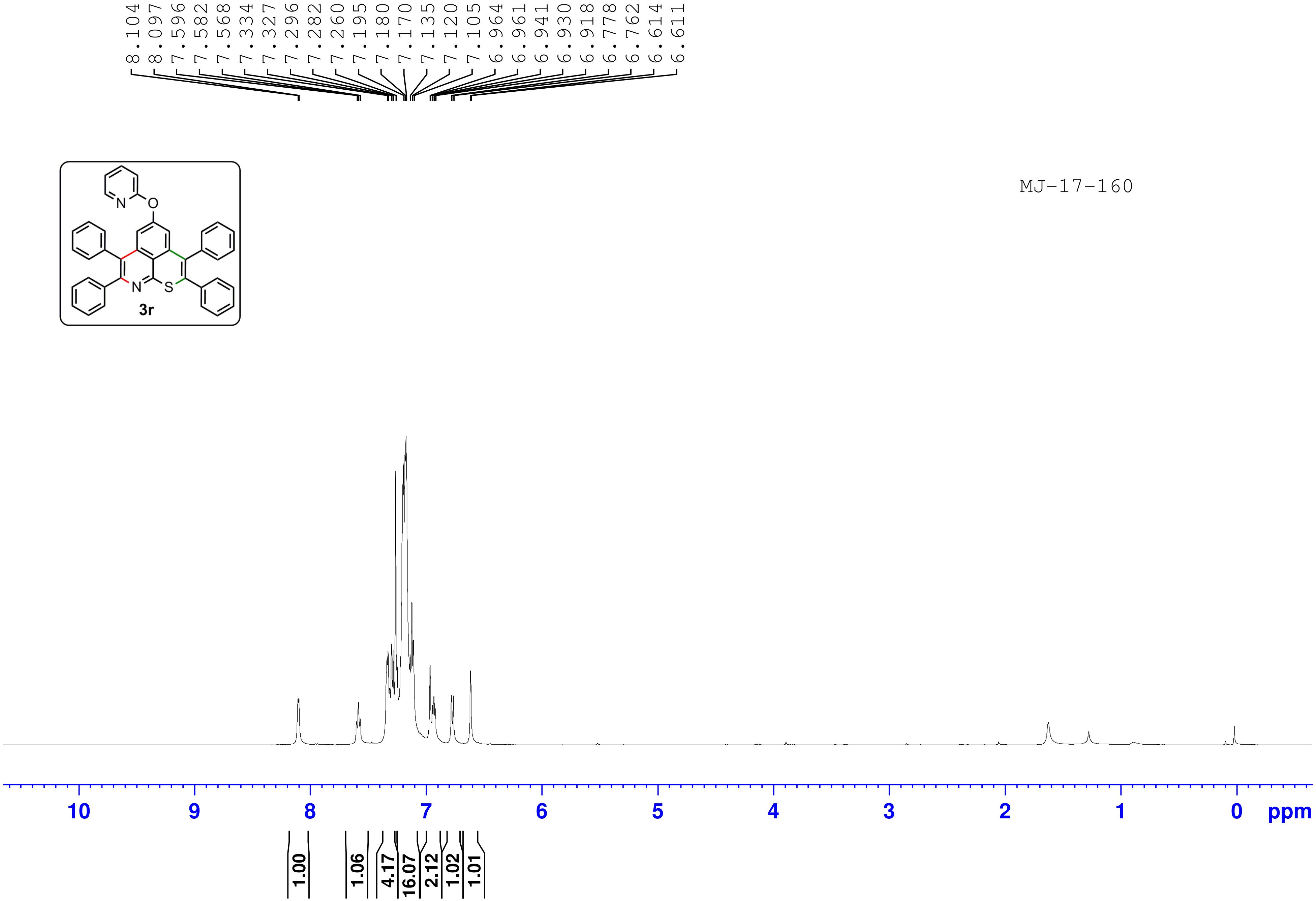


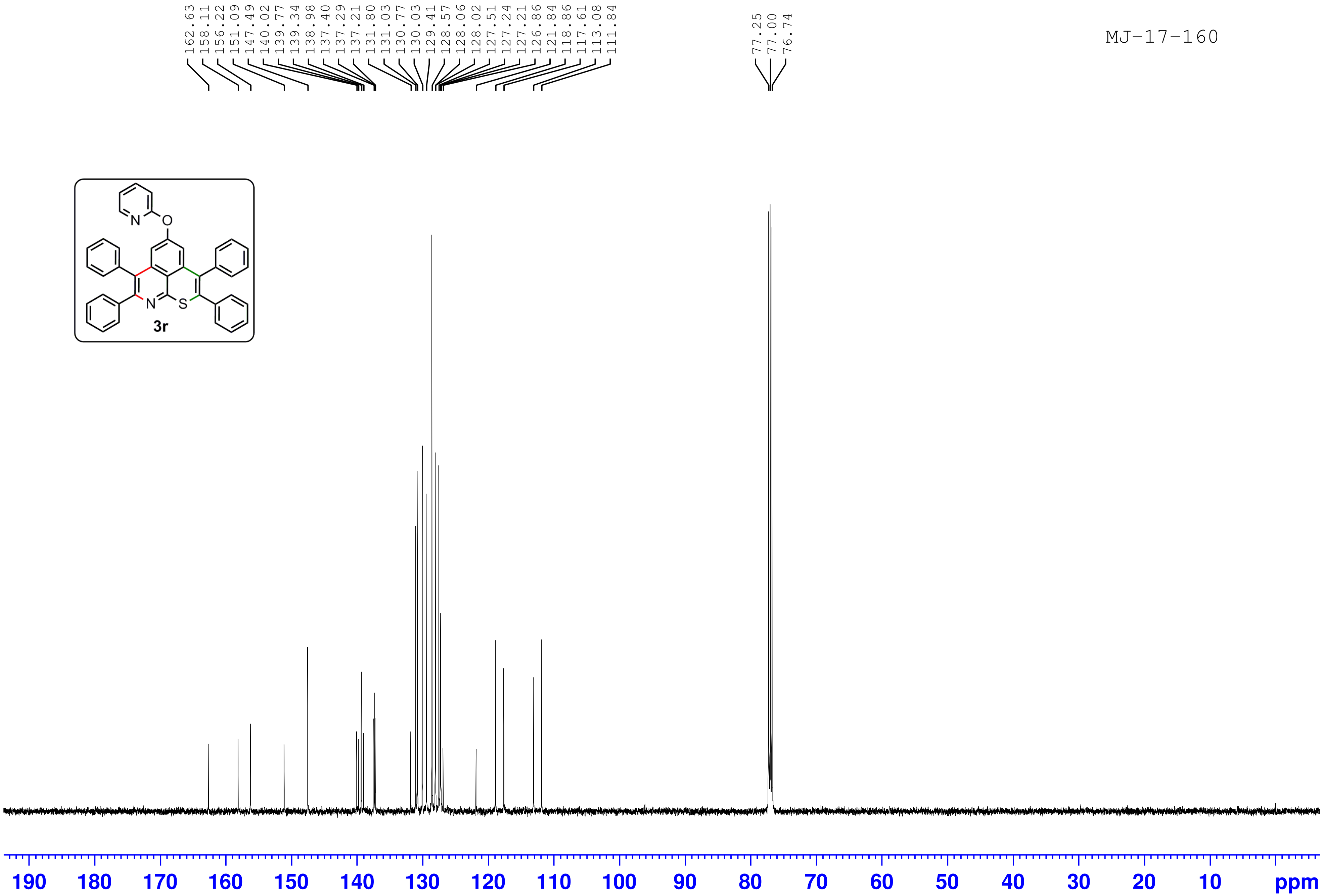
Me
O
N
S

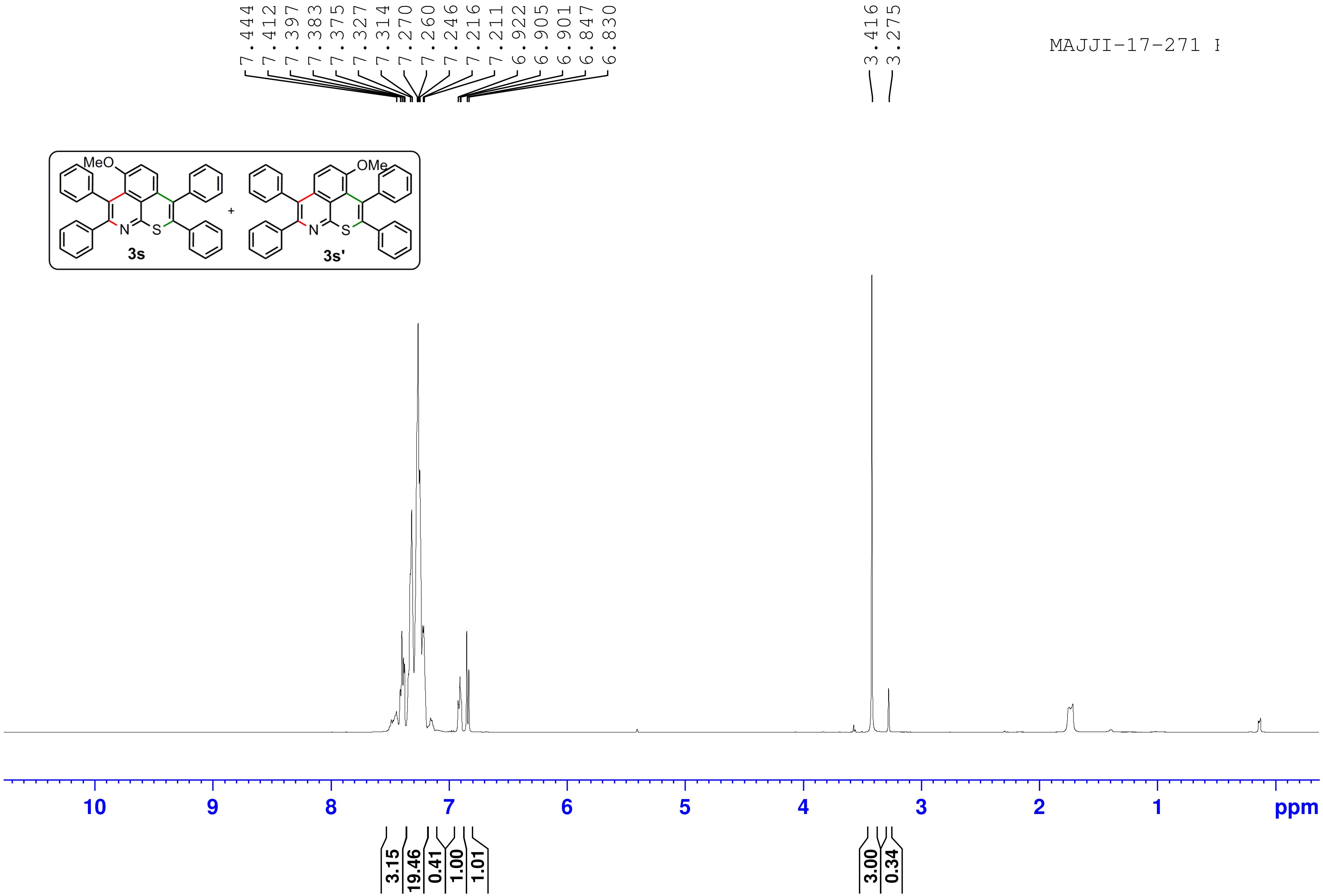
3q

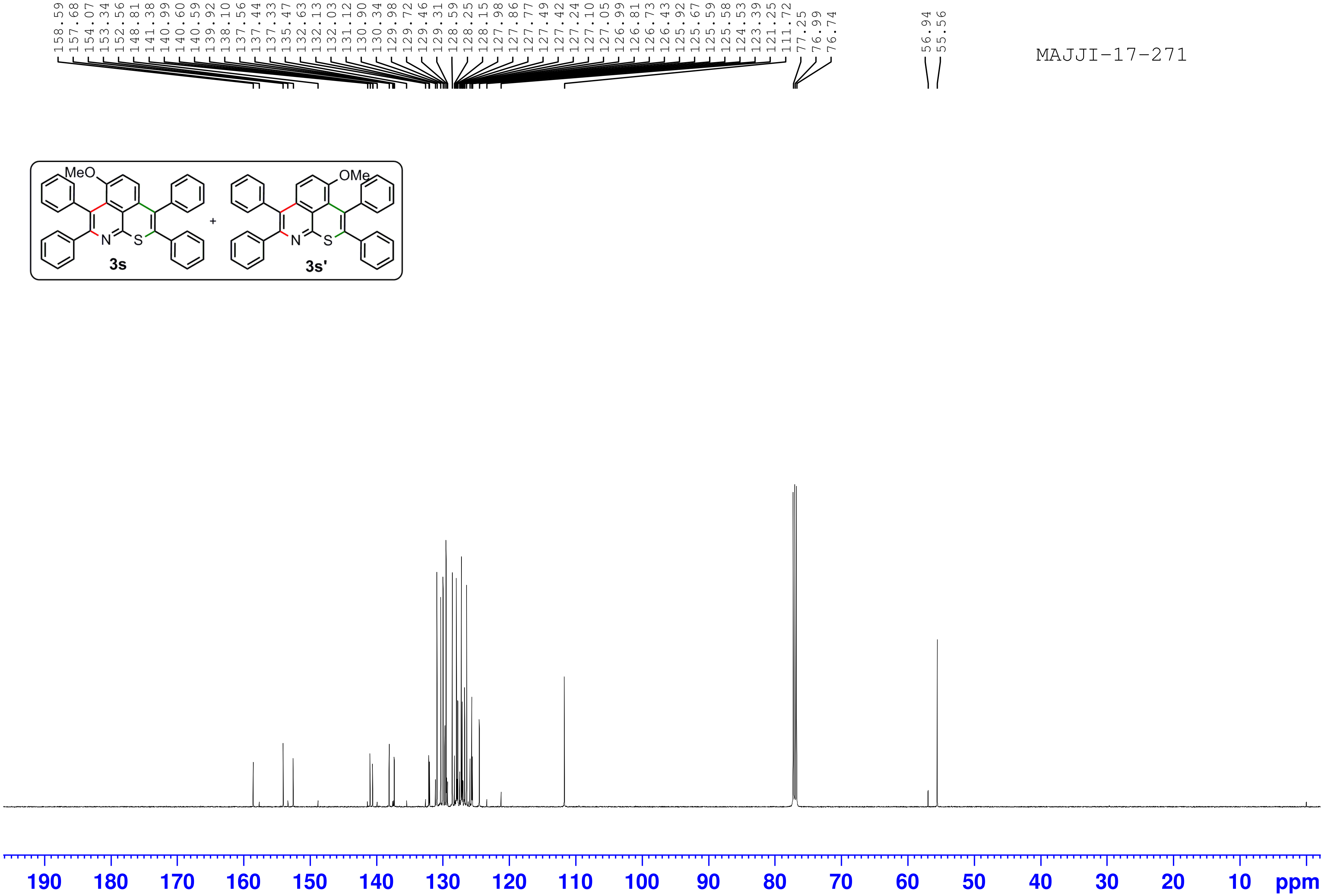


197.76
158.51
151.35
139.54
138.48
137.72
137.35
137.11
137.00
136.69
132.12
130.95
130.67
129.99
129.35
128.79
128.16
128.06
128.03
127.65
127.58
127.53
127.46
125.34
123.98
121.16
77.25
77.00
76.74
26.52
MAJJI-17-214
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.104
8.097
7.596
7.582
7.568
7.334
7.327
7.296
7.282
7.260
7.195
7.180
7.170
7.135
7.120
7.105
6.964
6.961
6.941
6.930
6.918
6.778
6.762
6.614
6.611
MJ-17-160
N
O
N
S
3r
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.06
4.17
16.07
2.12
1.02
1.01


162.63
158.11
156.22
151.09
147.49
140.02
139.77
139.34
138.98
137.40
137.29
137.21
131.80
131.03
130.77
130.03
129.41
128.57
128.06
128.02
127.51
127.24
127.21
126.86
121.84
118.86
117.61
113.08
111.84
77.25
77.00
76.74
MJ-17-160
N
O
N
S
3r
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.444
7.412
7.397
7.383
7.375
7.327
7.314
7.270
7.260
7.246
7.216
7.211
6.922
6.905
6.901
6.847
6.830
3.416
3.275
MAJJI-17-271 H
MeO
N
S
3s
+
OMe
N
S
3s'
10
9
8
7
6
5
4
3
2
1
ppm
3.15
19.46
0.41
1.00
1.01
3.00
0.34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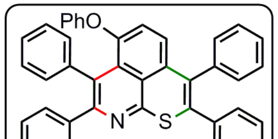
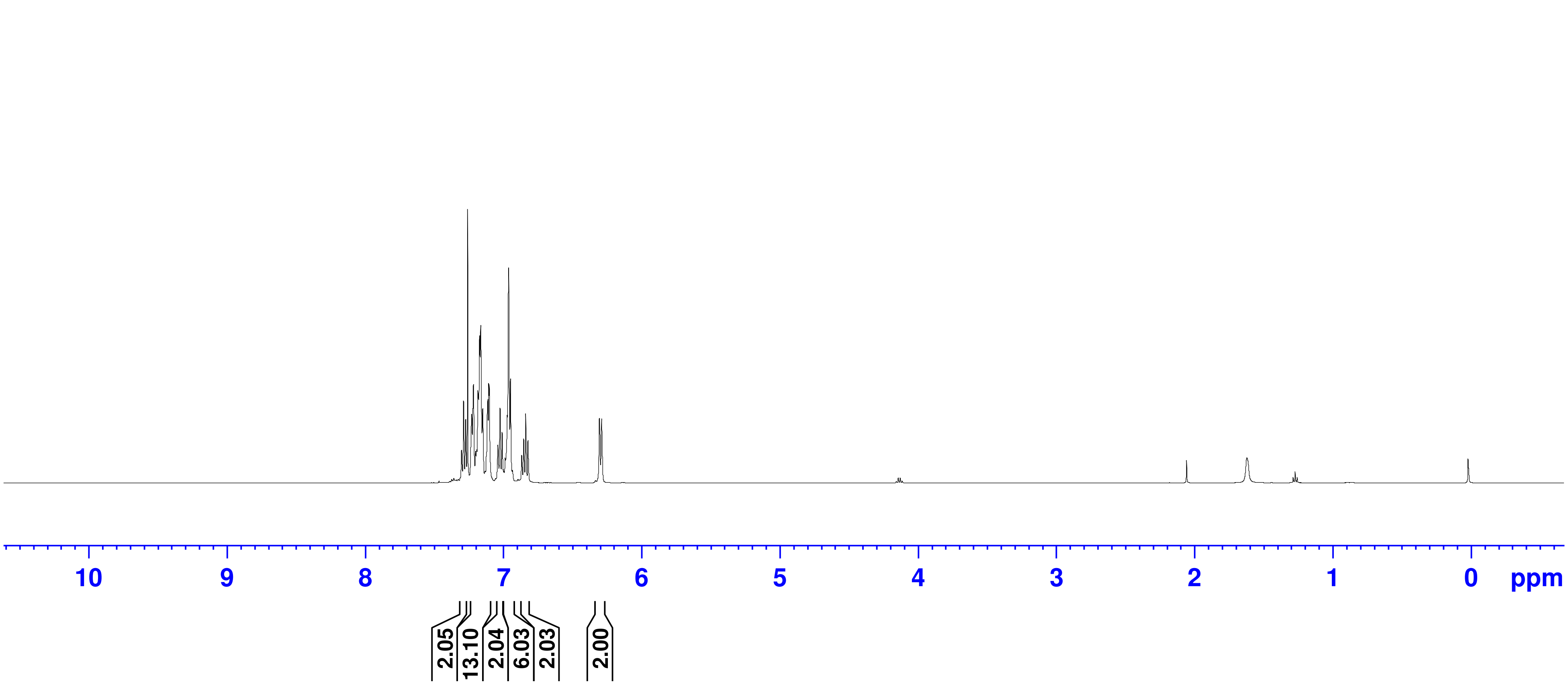
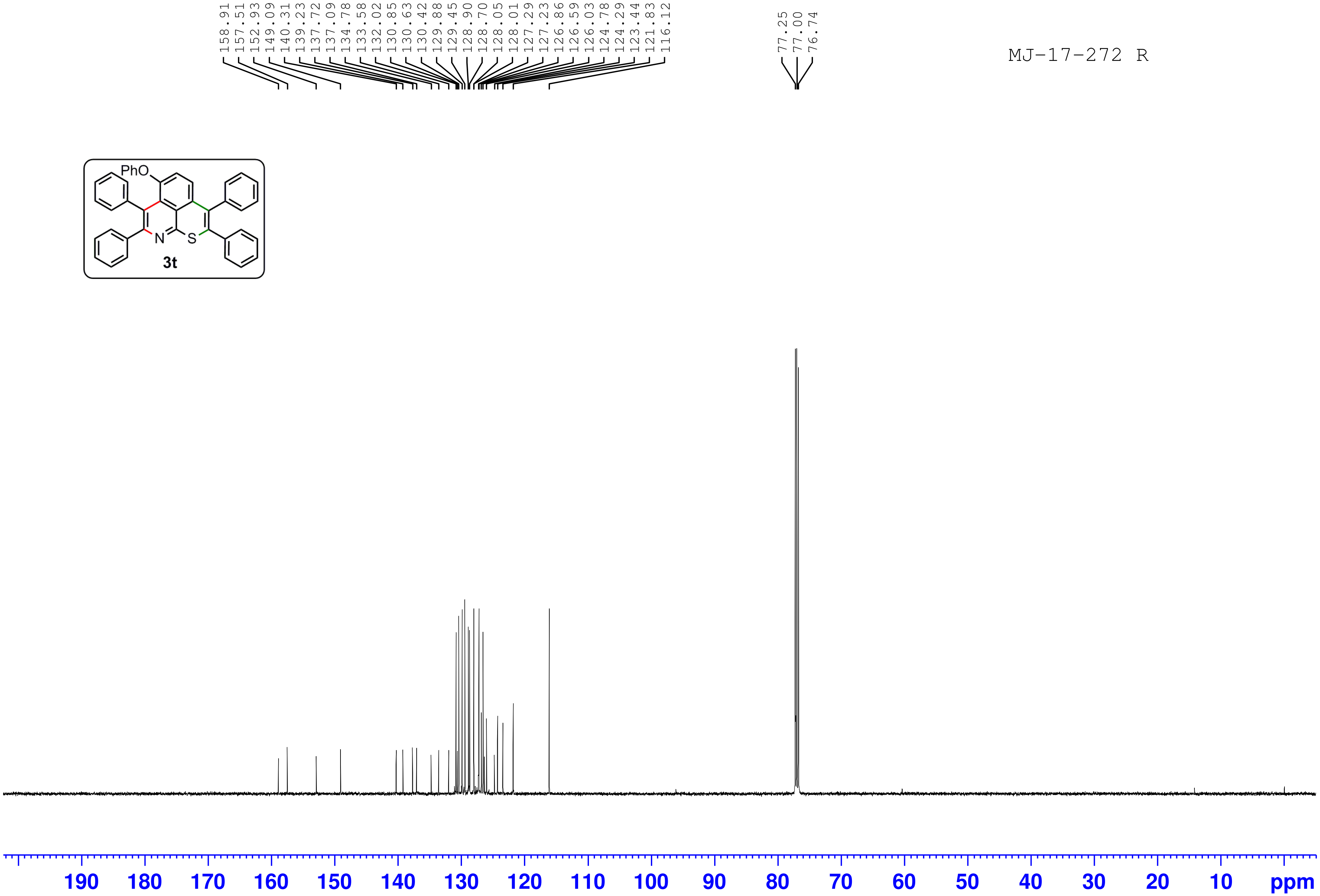
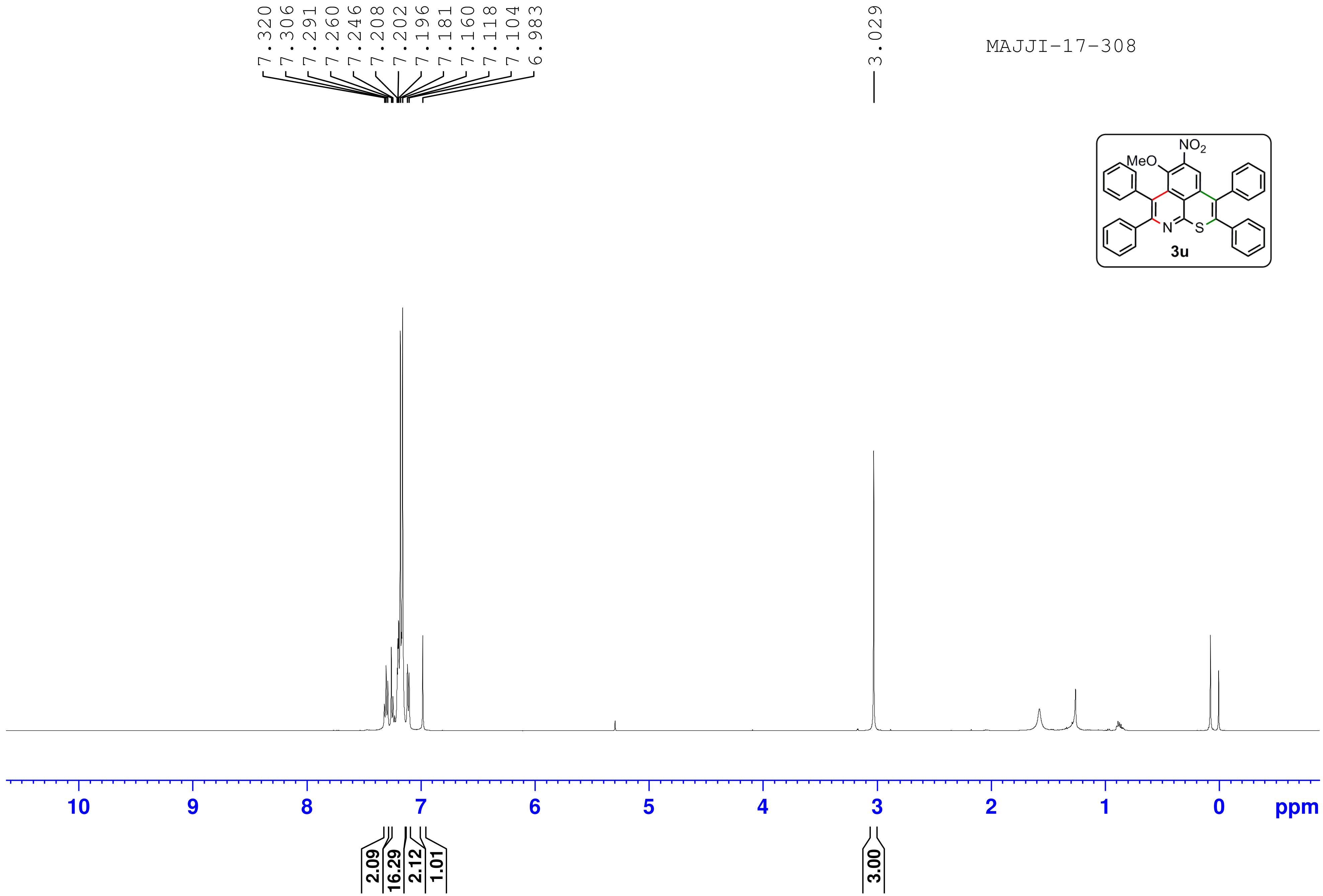
157.68
154.07
153.34
152.56
148.81
141.38
140.99
140.60
140.59
139.92
138.10
137.56
137.44
137.33
135.47
132.63
132.13
132.03
131.12
130.90
130.34
129.98
129.72
129.46
129.31
128.59
128.25
128.15
127.98
127.86
127.77
127.49
127.42
127.24
127.10
127.05
126.99
126.81
126.73
126.43
125.92
125.67
125.59
125.58
124.53
123.39
121.25
111.72
77.25
76.99
76.74
56.94
55.56
MAJJI-17-271
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
MeO
N
S
3s
+
OMe
N
S
3s'

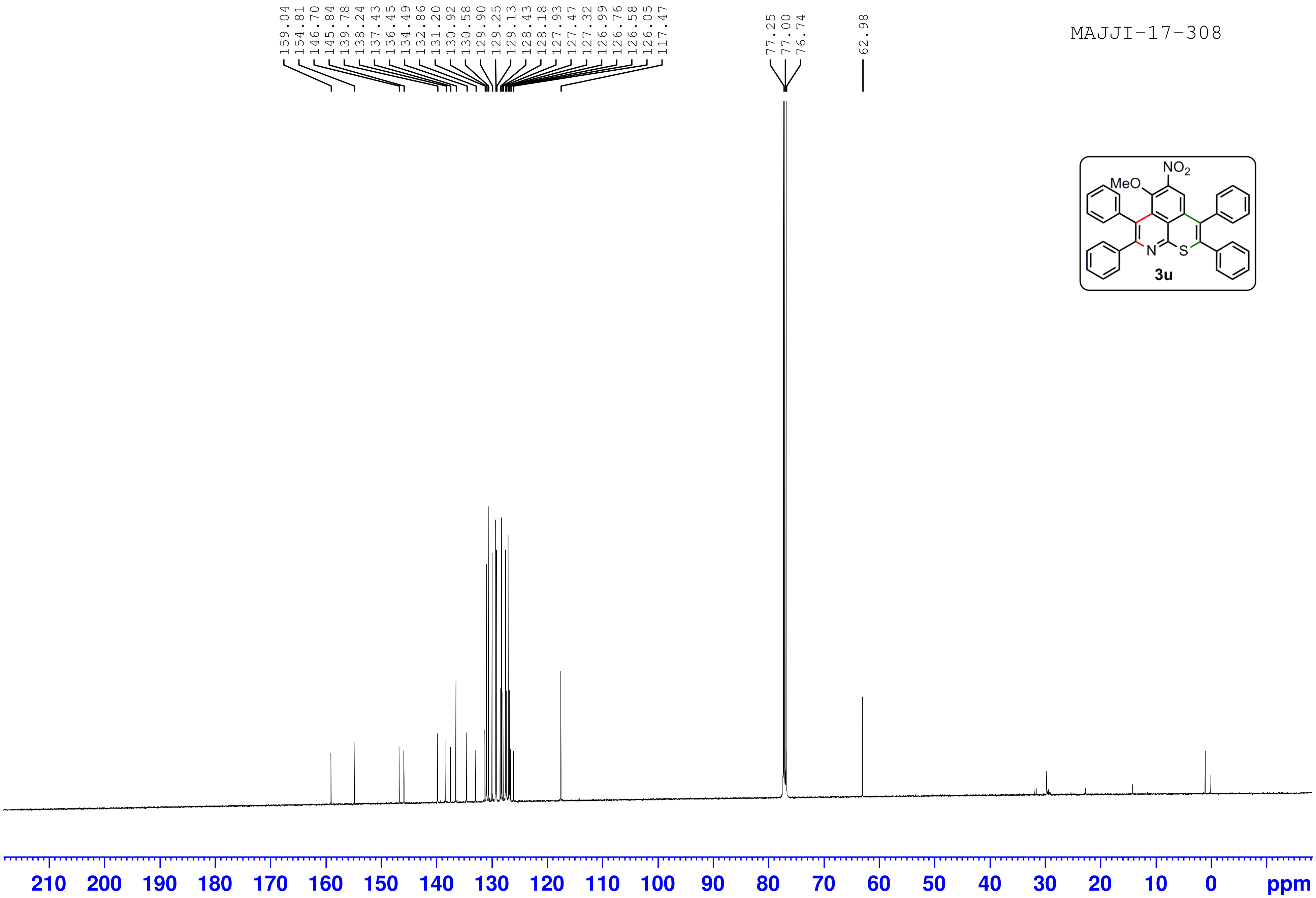

PhO
N
S

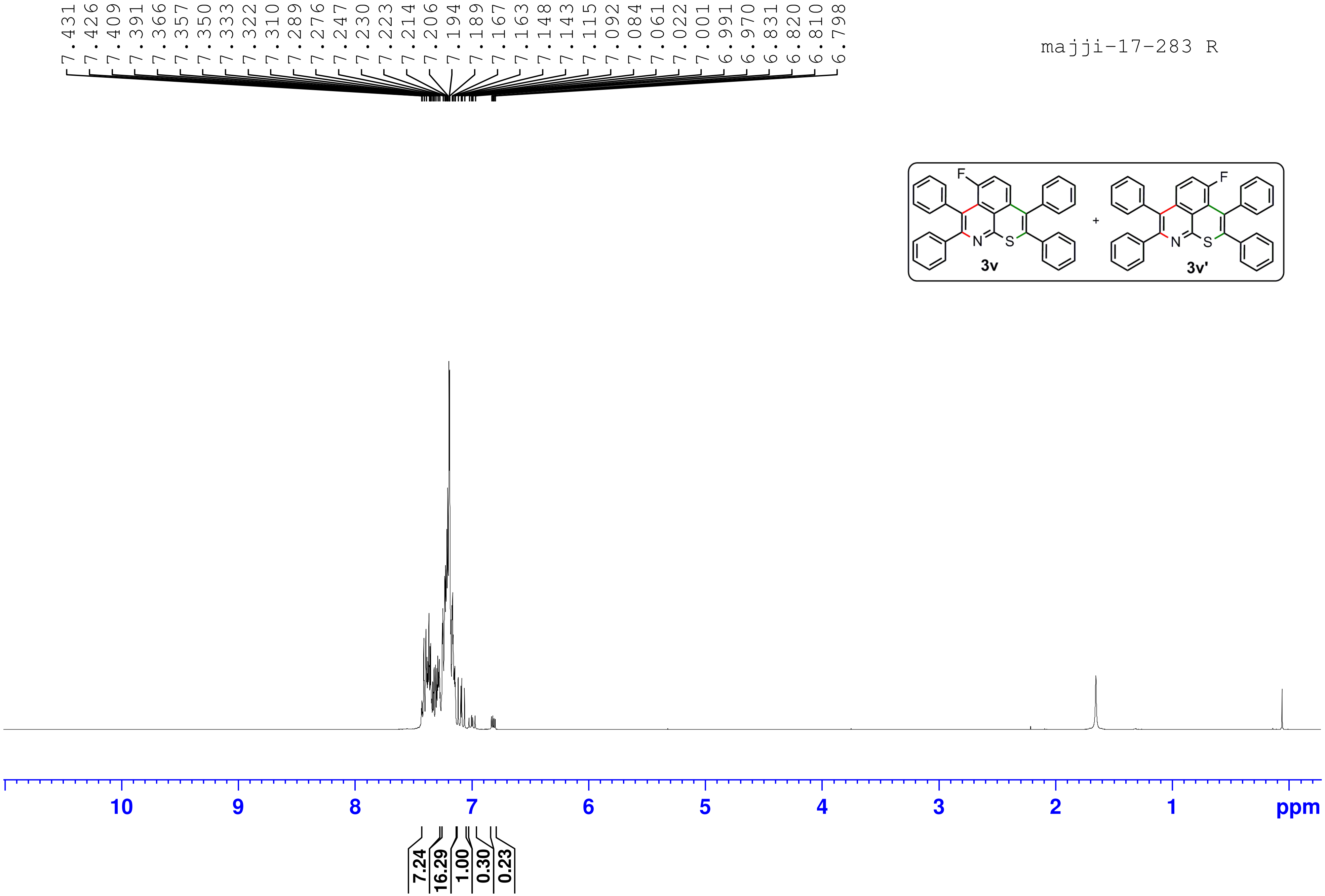
3t

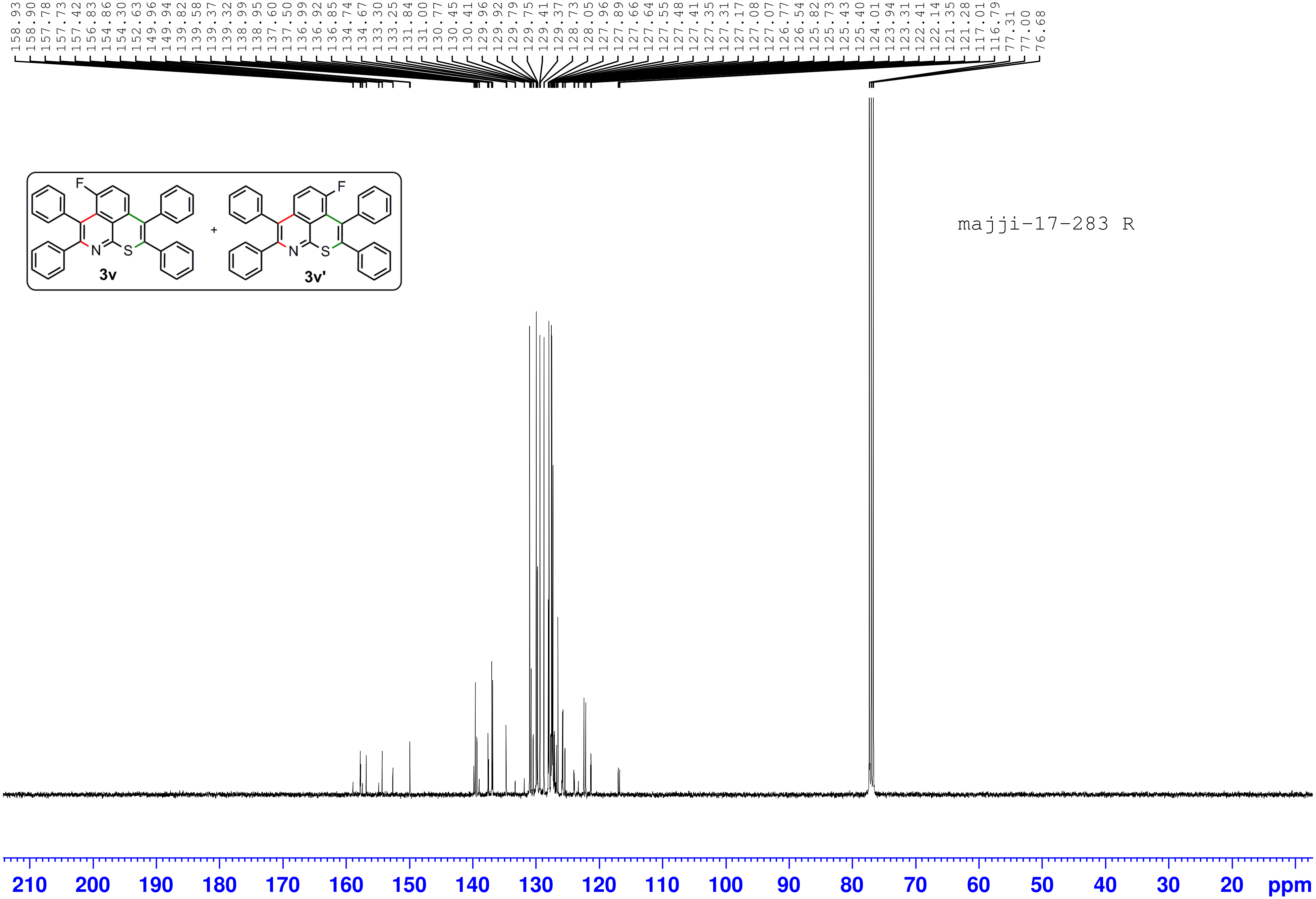

7.304
7.289
7.274
7.260
7.232
7.222
7.218
7.202
7.186
7.182
7.172
7.166
7.151
7.125
7.114
7.107
7.104
7.042
7.025
7.010
6.973
6.963
6.950
6.869
6.854
6.840
6.824
6.306
6.290
MAJJI-17-272 R
10
9
8
7
6
5
4
3
2
1
0
ppm
2.05
13.10
2.04
6.03
2.03
2.00


158.91
157.51
152.93
149.09
140.31
139.23
137.72
137.09
134.78
133.58
132.02
130.85
130.63
130.42
129.88
129.45
128.90
128.70
128.05
128.01
127.29
127.23
126.86
126.59
126.03
124.78
124.29
123.44
121.83
116.12
77.25
77.00
76.74
MJ-17-272 R
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
PhO
N
S
3t

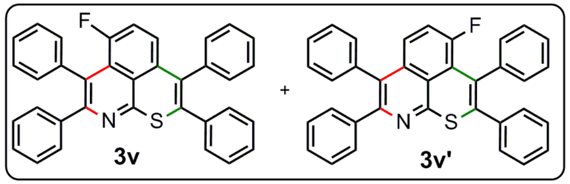

7.320
7.306
7.291
7.260
7.246
7.208
7.202
7.196
7.181
7.160
7.118
7.104
6.983
3.029
MAJJI-17-308
MeO
NO2
N
S
3u
10
9
8
7
6
5
4
3
2
1
0
ppm
2.09
16.29
2.12
1.01
3.00

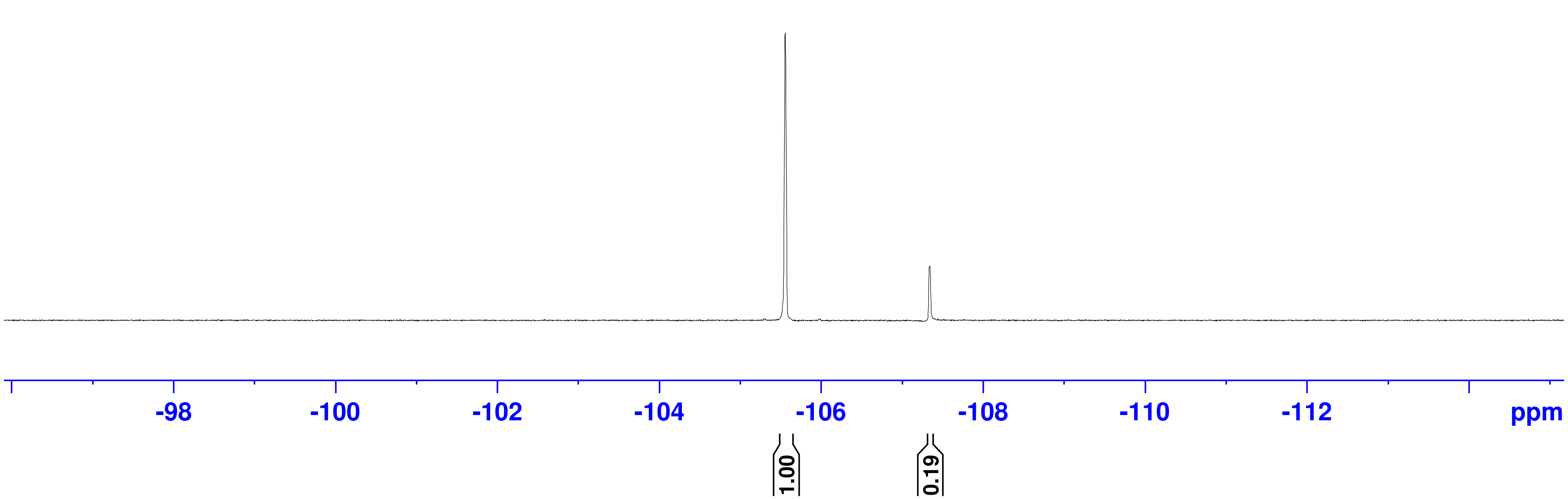

159.04
154.81
146.70
145.84
139.78
138.24
137.43
136.45
134.49
132.86
131.20
130.92
130.58
129.90
129.25
129.13
128.43
128.18
127.93
127.47
127.32
126.99
126.76
126.58
126.05
117.47
77.25
77.00
76.74
62.98
MAJJI-17-308
NO2
MeO
N
S
3u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


majji-17-283 R
7.431
7.426
7.409
7.391
7.366
7.357
7.350
7.333
7.322
7.310
7.289
7.276
7.247
7.230
7.223
7.214
7.206
7.194
7.189
7.167
7.163
7.148
7.143
7.115
7.092
7.084
7.061
7.022
7.001
6.991
6.970
6.831
6.820
6.810
6.798
10 9 8 7 6 5 4 3 2 1 ppm
7.24
16.29
1.00
0.30
0.23
F
N
S
3v
+
3v'

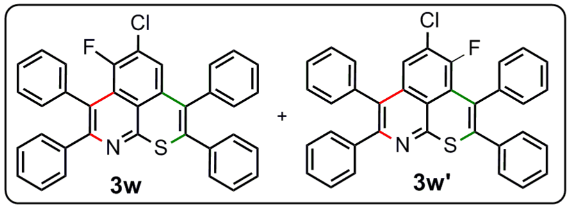

158.93
158.90
157.78
157.73
157.42
156.83
154.86
154.30
152.63
149.96
149.94
139.82
139.58
139.37
139.32
138.99
138.95
137.60
137.50
136.99
136.92
136.85
134.74
134.67
133.30
133.25
131.84
131.00
130.77
130.45
130.41
129.96
129.92
129.79
129.75
129.41
129.37
128.73
128.05
127.96
127.89
127.66
127.64
127.55
127.48
127.41
127.35
127.31
127.17
127.08
127.07
126.77
126.54
125.82
125.73
125.43
125.40
124.01
123.94
123.31
122.41
122.14
121.35
121.28
117.01
116.79
77.31
77.00
76.68
F
N
S
3v
+
F
N
S
3v'
majji-17-283 R
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

majji-17-283

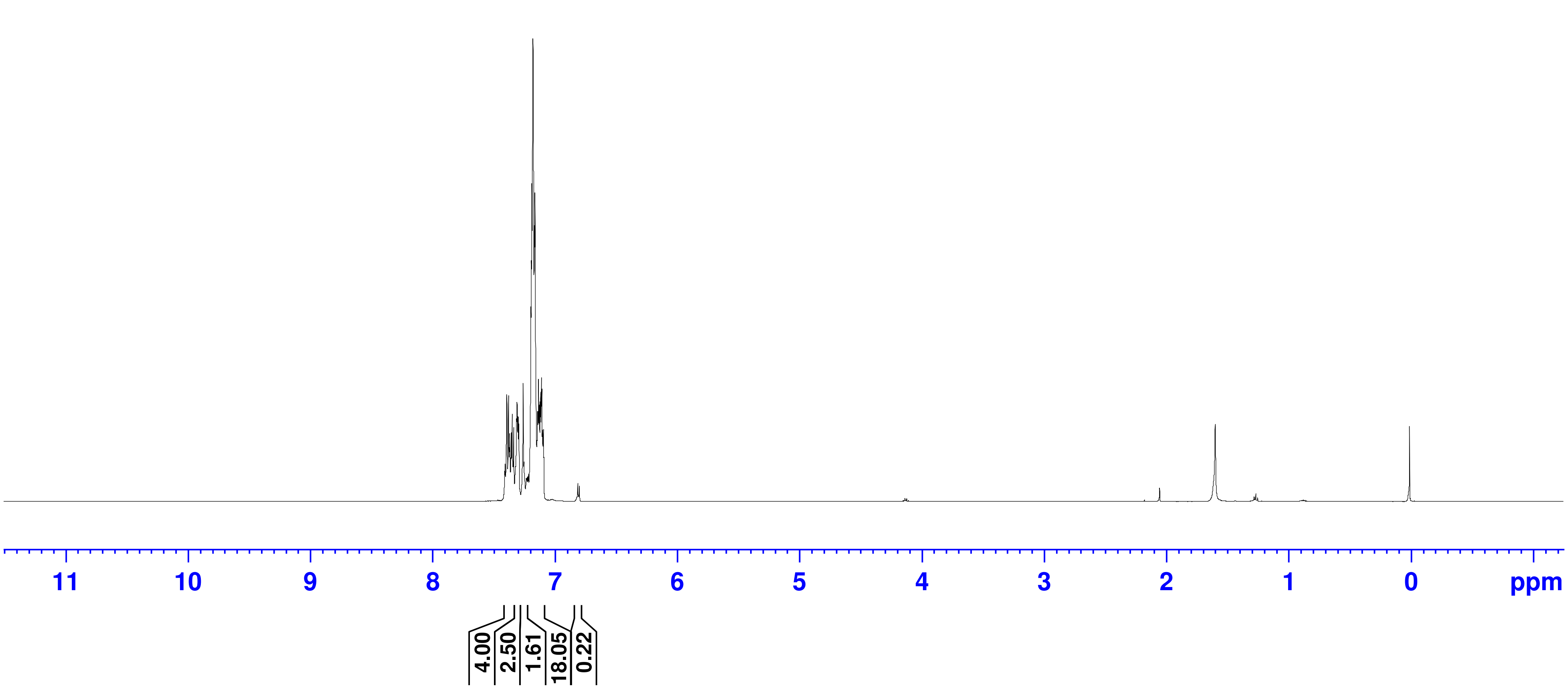

F
N
S
3v
+
F
N
S
3v'


-105.56
-107.35
-98
-100
-102
-104
-106
-108
-110
-112
ppm
1.00
0.19

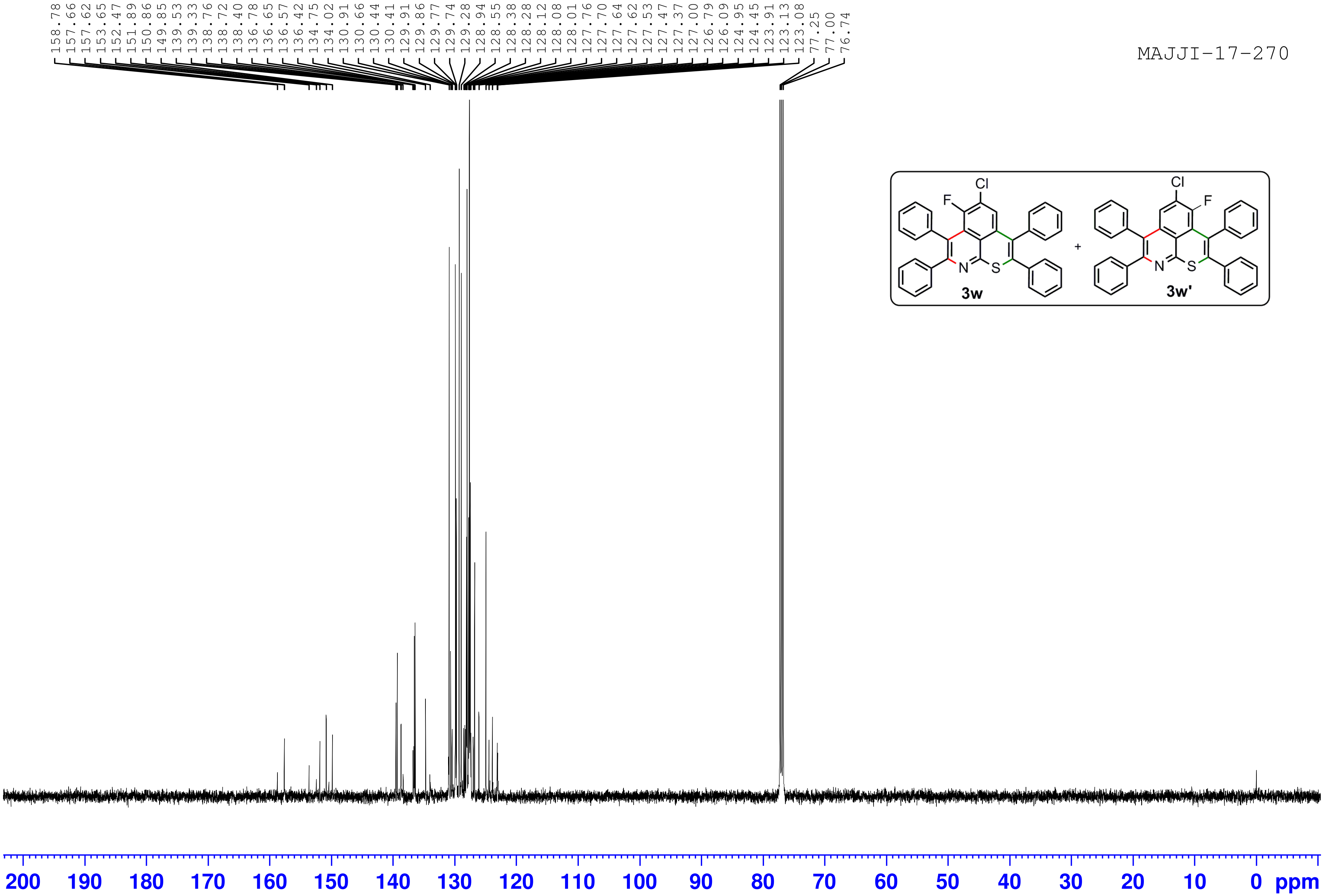
MAJJI-17-270



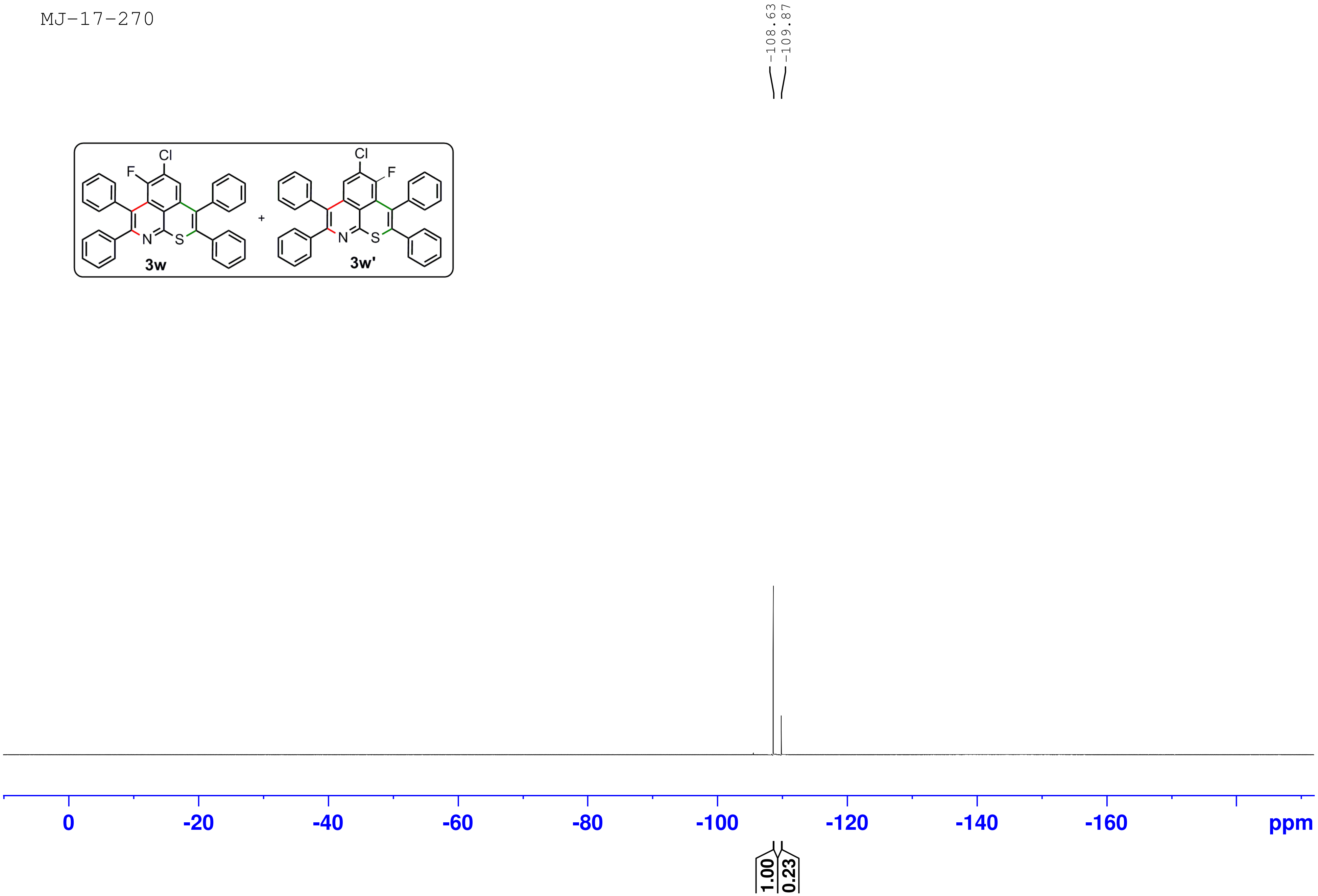
3w
3w'

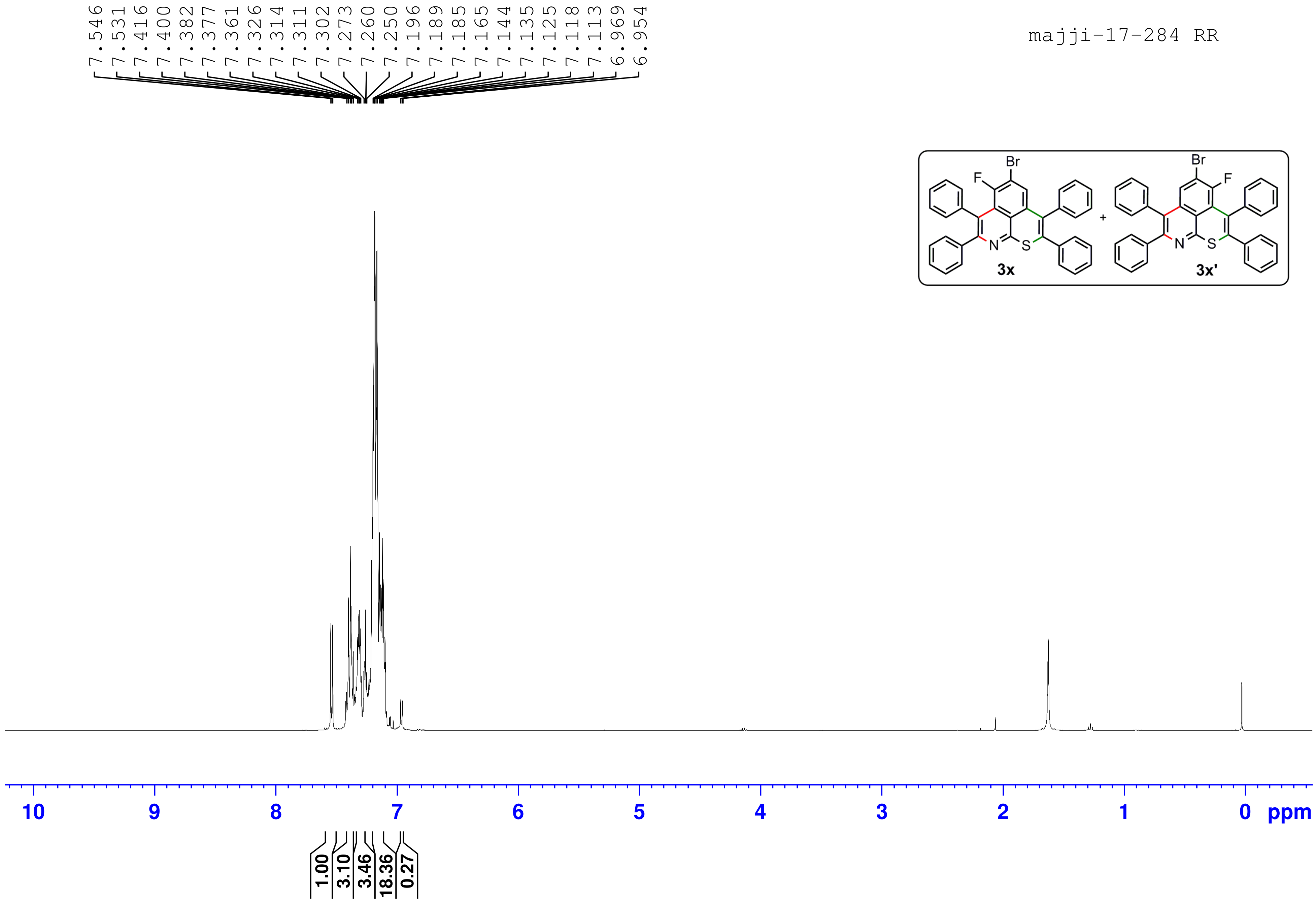


7.406
7.393
7.379
7.368
7.355
7.348
7.335
7.312
7.309
7.307
7.303
7.300
7.293
7.260
7.188
7.181
7.179
7.174
7.163
7.135
7.128
7.127
7.119
7.115
7.109
7.106
7.094
6.811
6.799
11 10 9 8 7 6 5 4 3 2 1 0 ppm
4.00
2.50
1.61
18.05
0.22

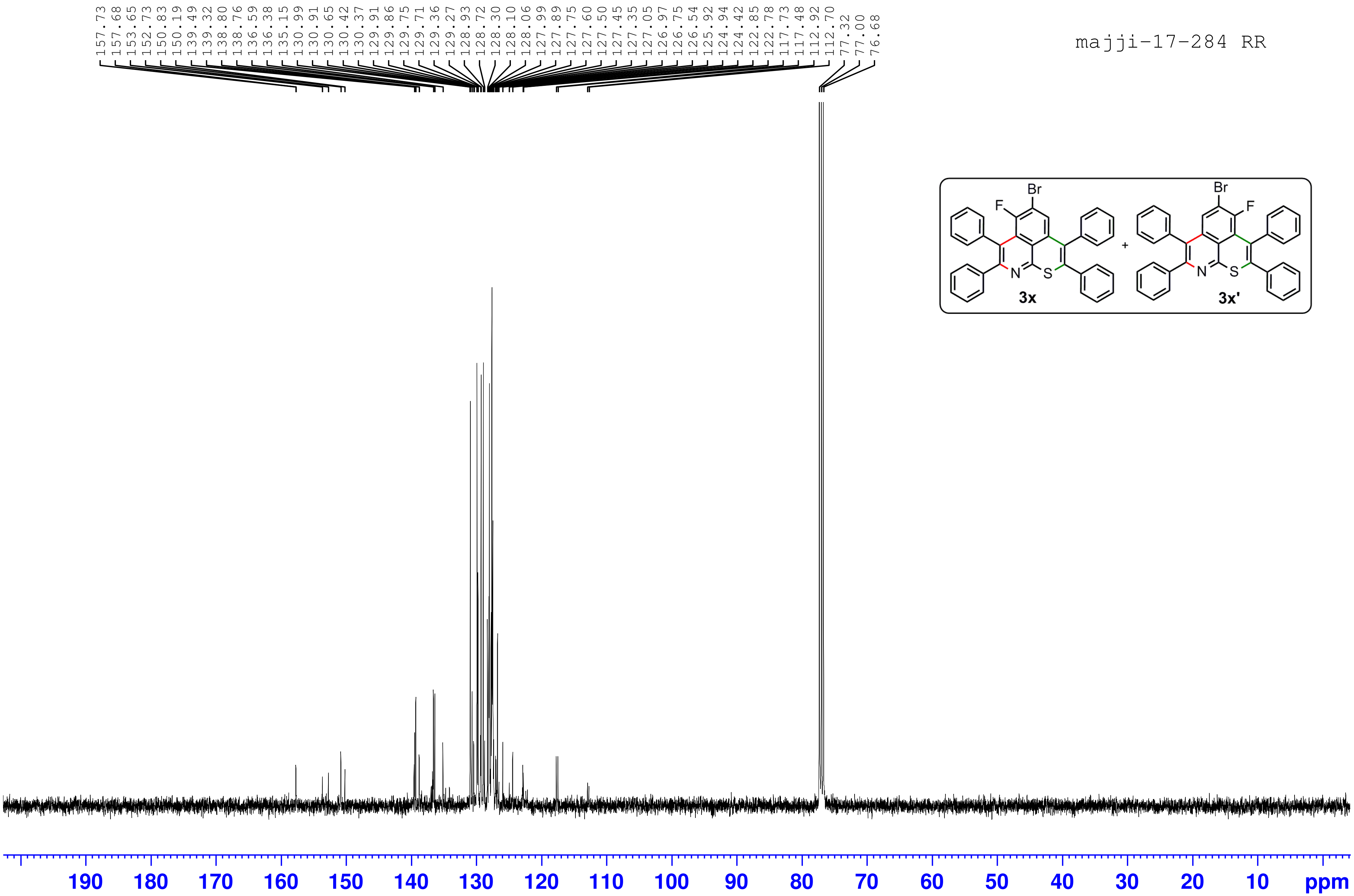

158.78
157.66
157.62
153.65
152.47
151.89
150.86
149.85
139.53
139.33
138.76
138.72
138.40
136.78
136.65
136.57
136.42
134.75
134.02
130.91
130.66
130.44
130.41
129.91
129.86
129.77
129.74
129.28
128.94
128.55
128.38
128.28
128.12
128.08
128.01
127.76
127.70
127.64
127.62
127.53
127.47
127.37
127.00
126.79
126.09
124.95
124.45
123.91
123.13
123.08
77.25
77.00
76.74
MAJJI-17-270
Cl
F
N
S
3w
+
3w'
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

MJ-17-270





7.546
7.531
7.416
7.400
7.382
7.377
7.361
7.326
7.314
7.311
7.302
7.273
7.260
7.250
7.196
7.189
7.185
7.165
7.144
7.135
7.125
7.118
7.113
6.969
6.954
majji-17-284 RR
Br
F
N
S
+
3x
3x'
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
3.10
3.46
18.36
0.27


majji-17-284 RR
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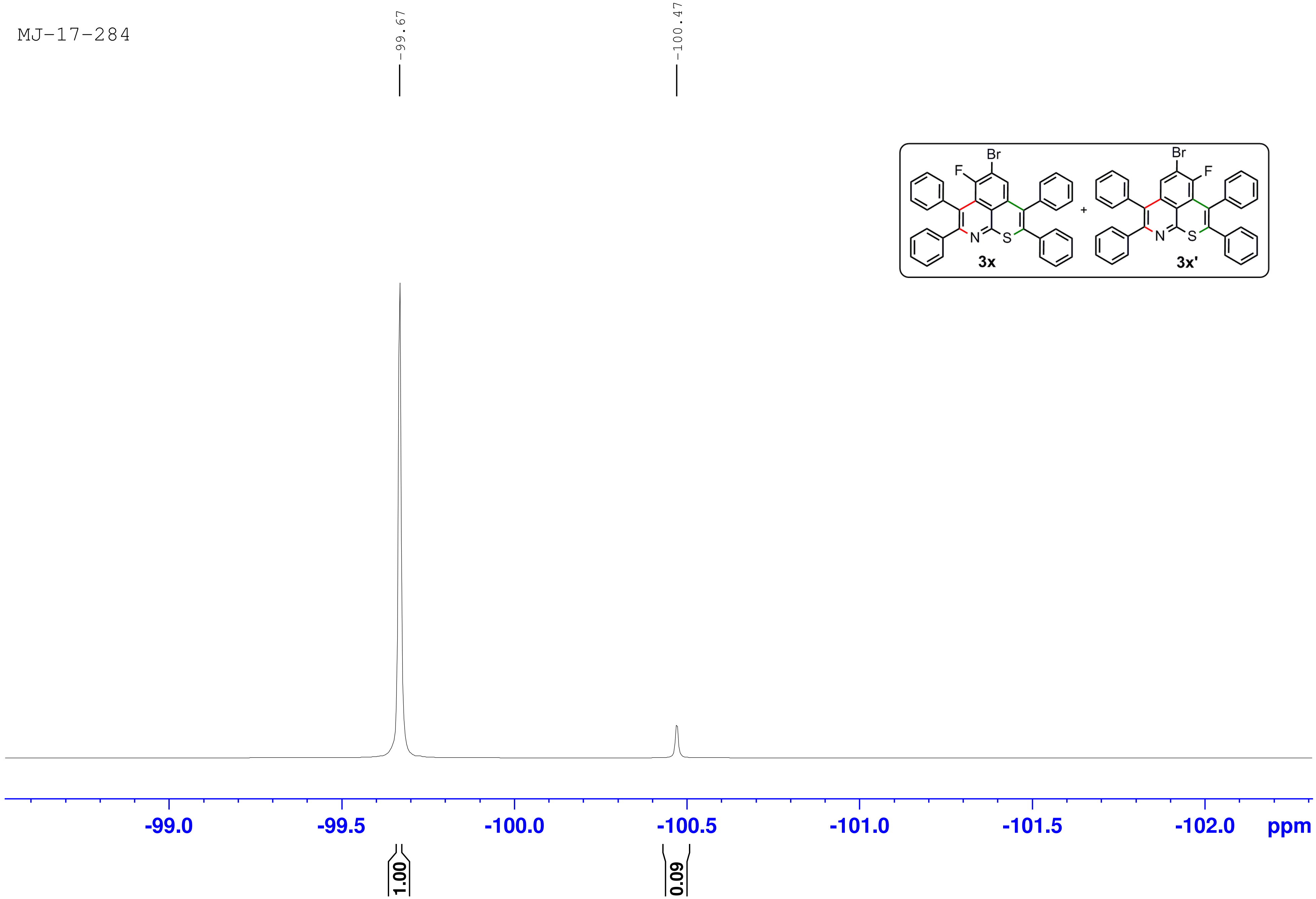
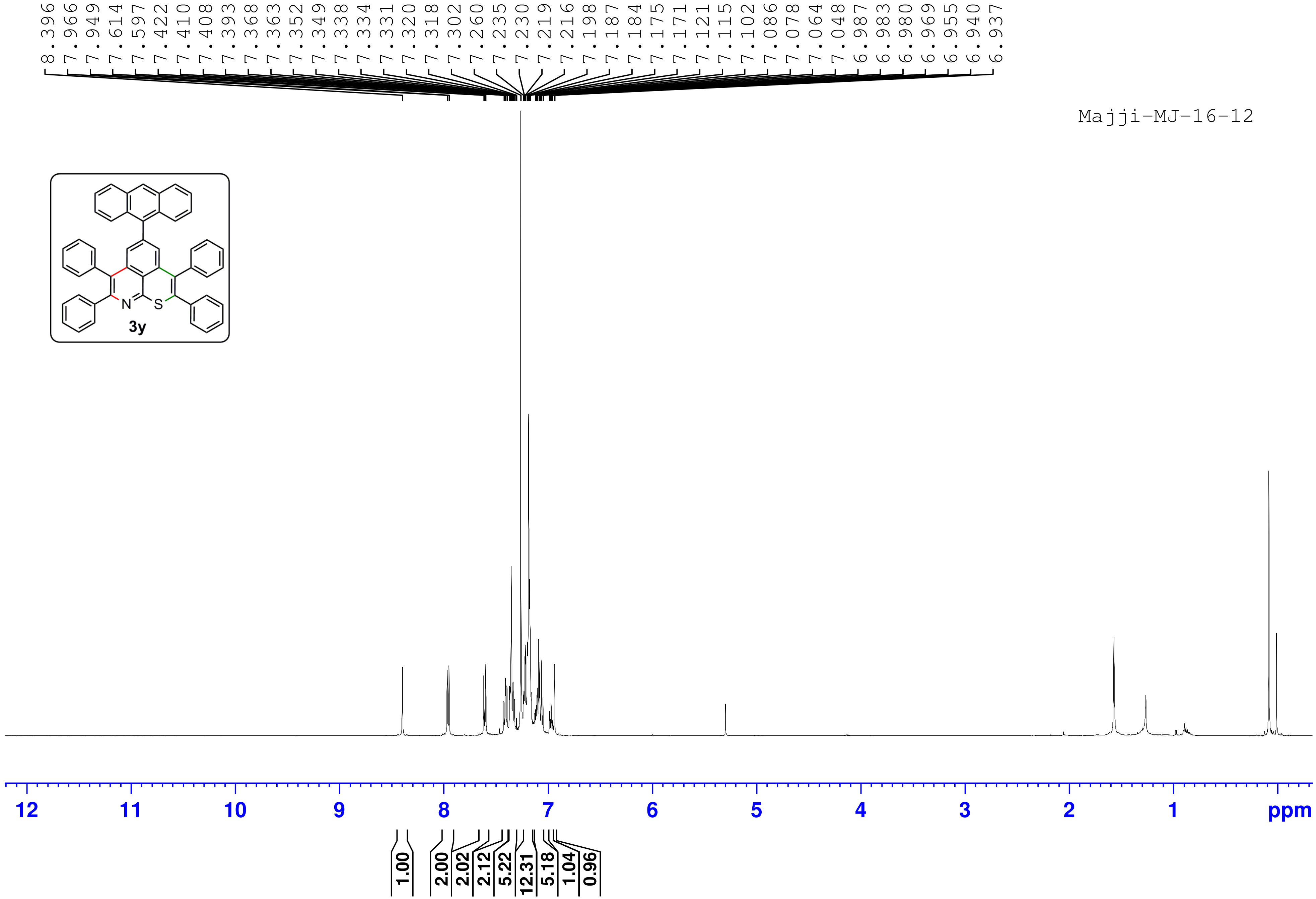
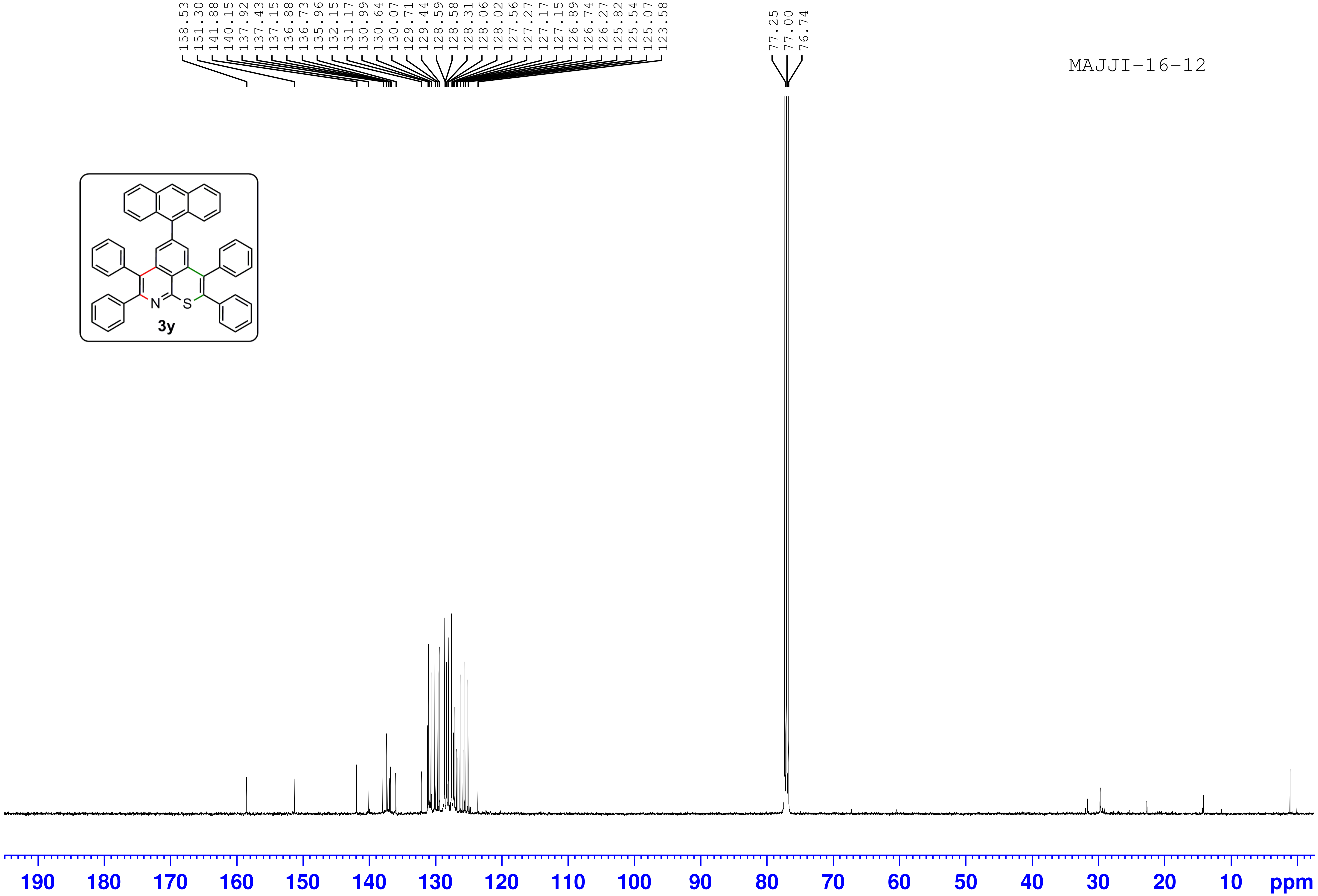
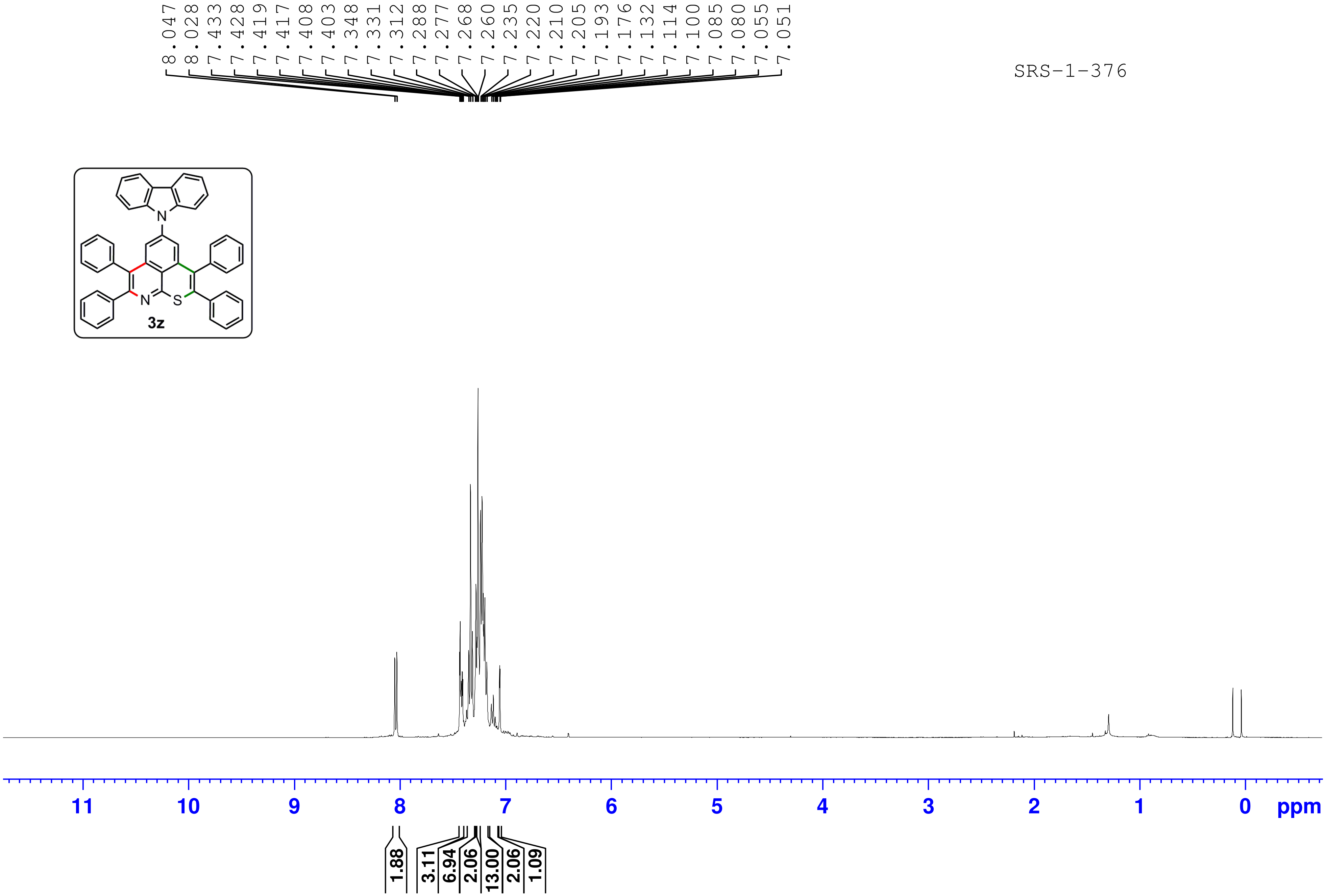
157.68
153.65
152.73
150.83
150.19
139.49
139.32
138.80
138.76
136.59
136.38
135.15
130.99
130.91
130.65
130.42
130.37
129.91
129.86
129.75
129.71
129.36
129.27
128.93
128.72
128.30
128.10
128.06
127.99
127.89
127.75
127.60
127.50
127.45
127.35
127.05
126.97
126.75
126.54
125.92
124.94
124.42
122.85
122.78
117.73
117.48
112.92
112.70
77.32
77.00
76.68
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
Br
F
N
S
3x
+
3x'

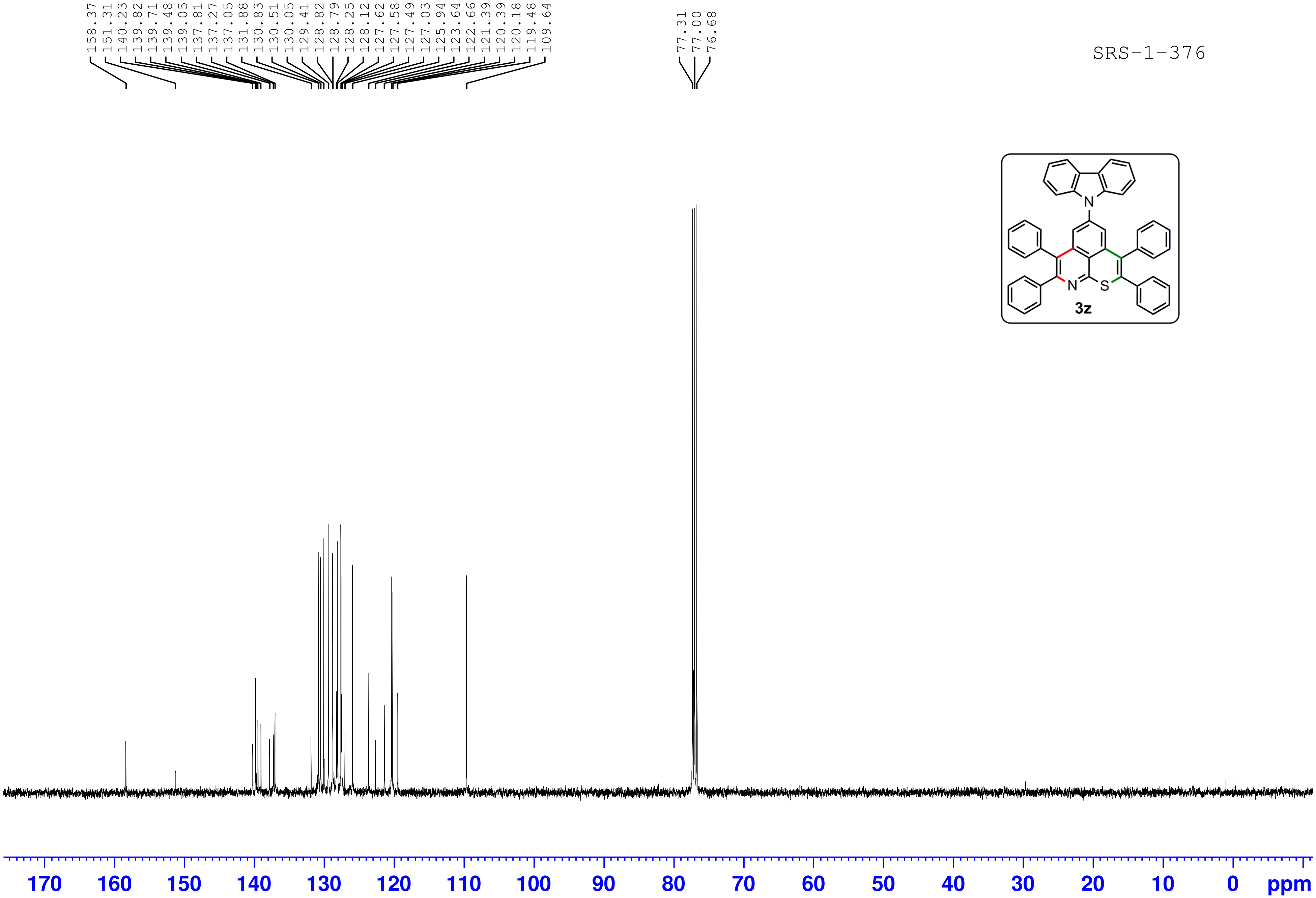

MJ-17-284
-99.67
-100.47
Br
F
N
S
3x
+
3x'
-99.0
-99.5
-100.0
-100.5
-101.0
-101.5
-102.0
ppm
1.00
0.09



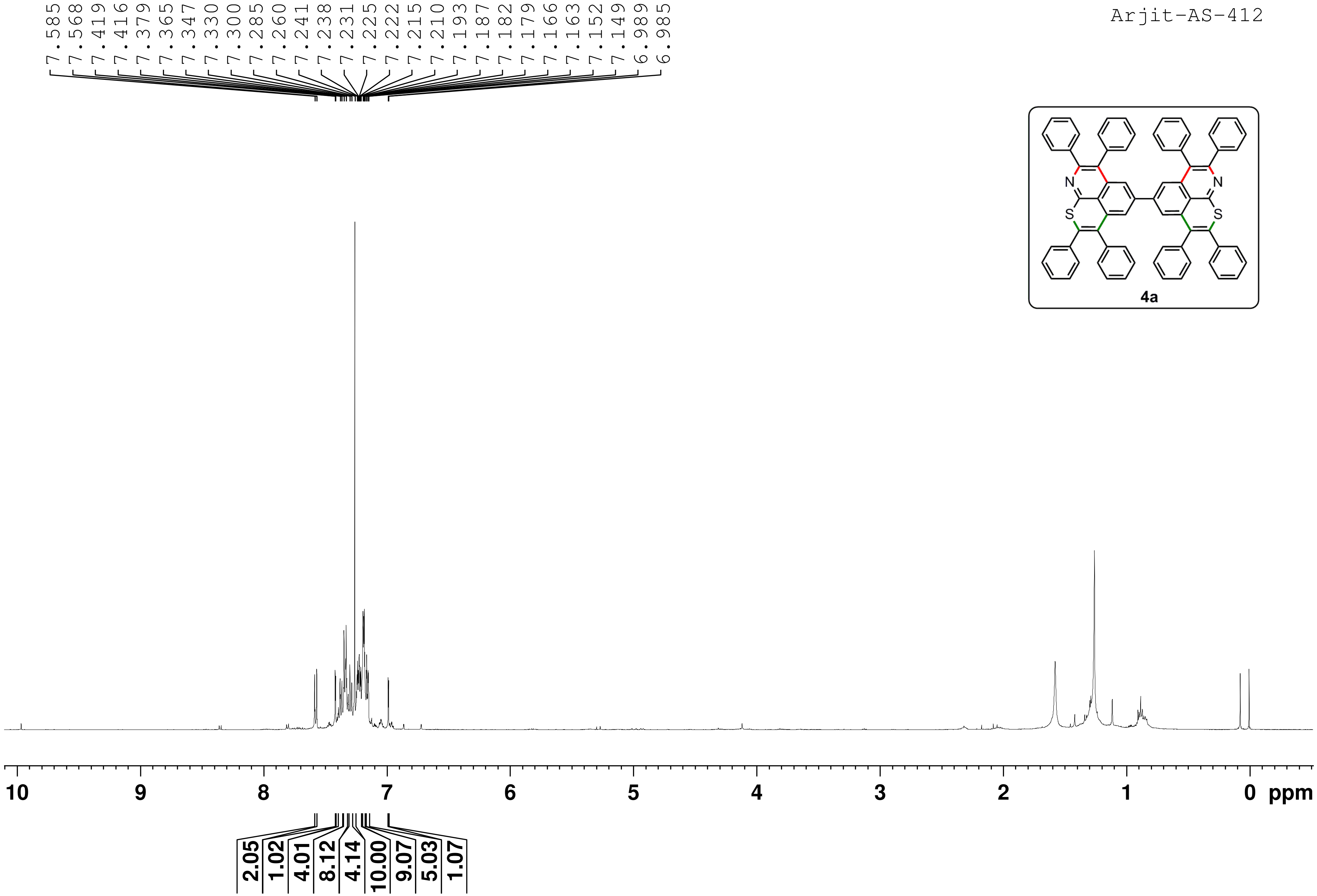
8.396
7.966
7.949
7.614
7.597
7.422
7.410
7.408
7.393
7.368
7.363
7.352
7.349
7.338
7.334
7.331
7.320
7.318
7.302
7.260
7.235
7.230
7.219
7.216
7.198
7.187
7.184
7.175
7.171
7.121
7.115
7.102
7.086
7.078
7.064
7.048
6.987
6.983
6.980
6.969
6.955
6.940
6.937
Majji-MJ-16-12
N
S
3y
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.00
2.02
2.12
5.22
12.31
5.18
1.04
0.96


158.53
151.30
141.88
140.15
137.92
137.43
137.15
136.88
136.73
135.96
132.15
131.17
130.99
130.64
130.07
129.71
129.44
128.59
128.58
128.31
128.06
128.02
127.56
127.27
127.17
127.15
126.89
126.74
126.27
125.82
125.54
125.07
123.58
77.25
77.00
76.74
MAJJI-16-12
N
S
3y
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.047
8.028
7.433
7.428
7.419
7.417
7.408
7.403
7.348
7.331
7.312
7.288
7.277
7.268
7.260
7.235
7.220
7.210
7.205
7.193
7.176
7.132
7.114
7.100
7.085
7.080
7.055
7.051
SRS-1-376
N
S
N
3z
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.88
3.11
6.94
2.06
13.00
2.06
1.09

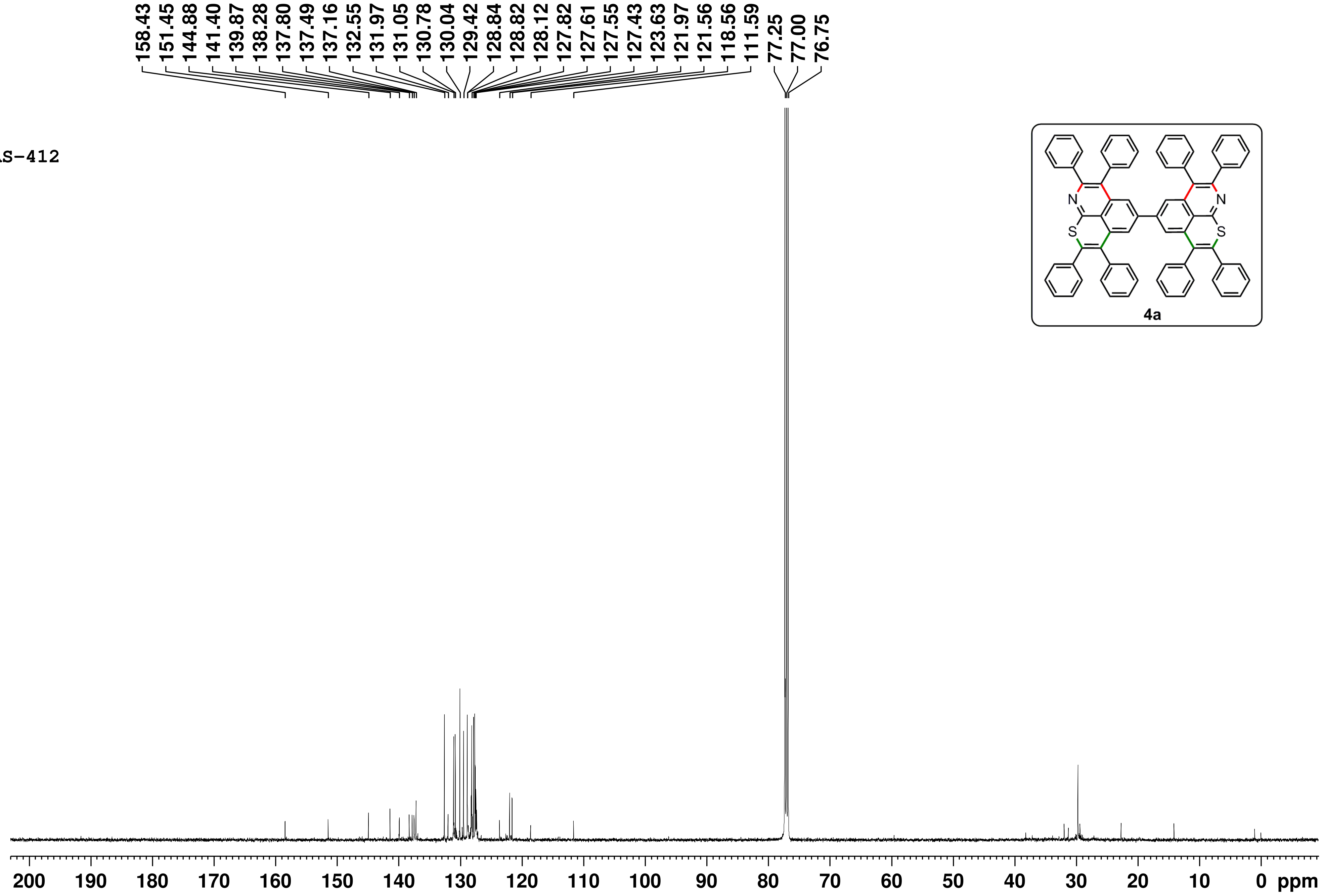

158.37
151.31
140.23
139.82
139.71
139.48
139.05
137.81
137.27
137.05
131.88
130.83
130.51
130.05
129.41
128.82
128.79
128.25
128.12
127.62
127.58
127.49
127.03
125.94
123.64
122.66
121.39
120.39
120.18
119.48
109.64
77.31
77.00
76.68
SRS-1-376
N
N
S
3z
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Arjit-AS-412

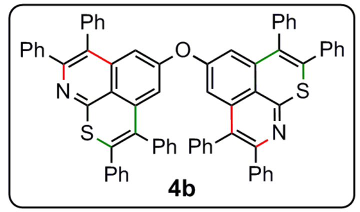


4a

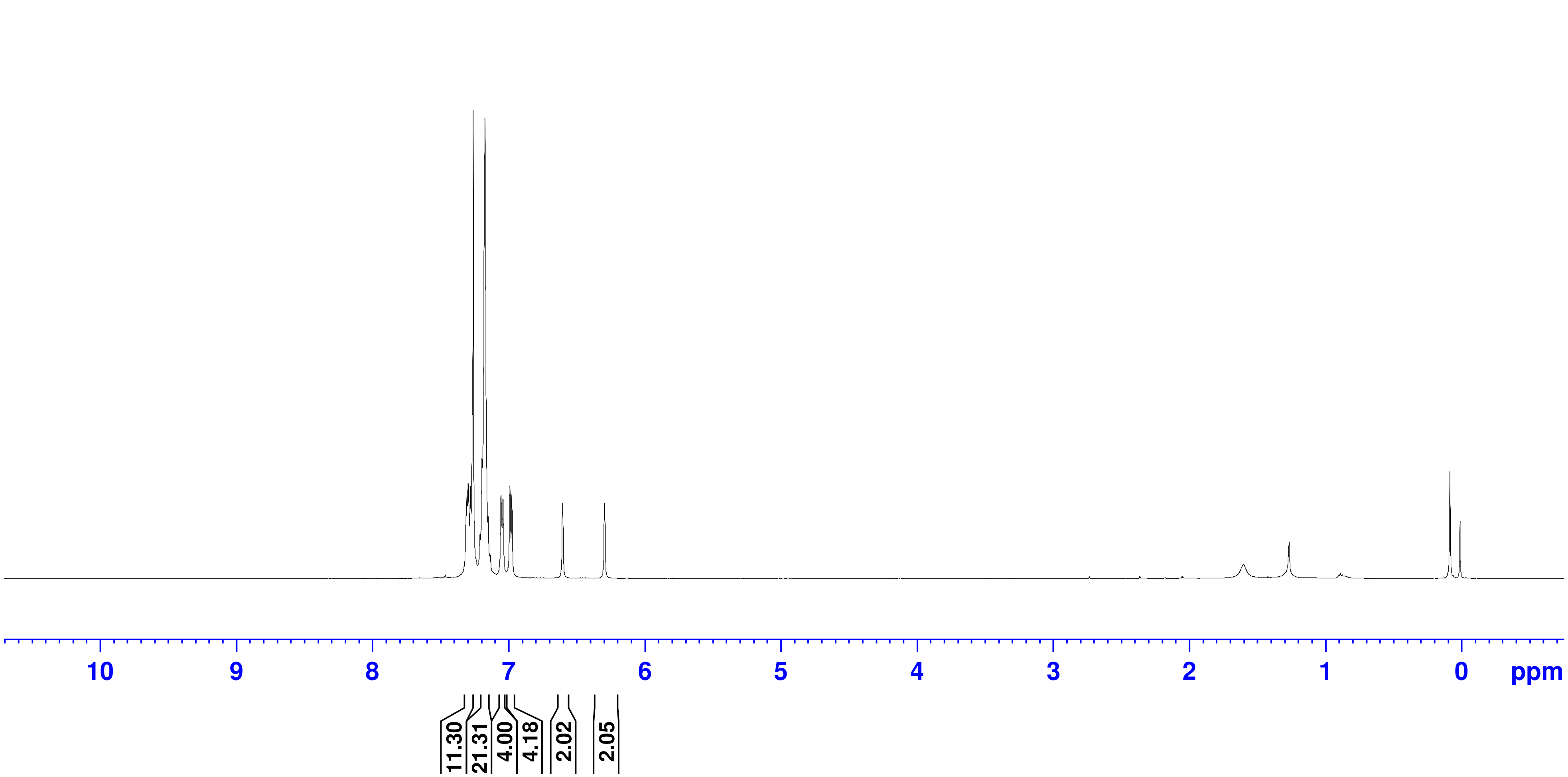
AS-412

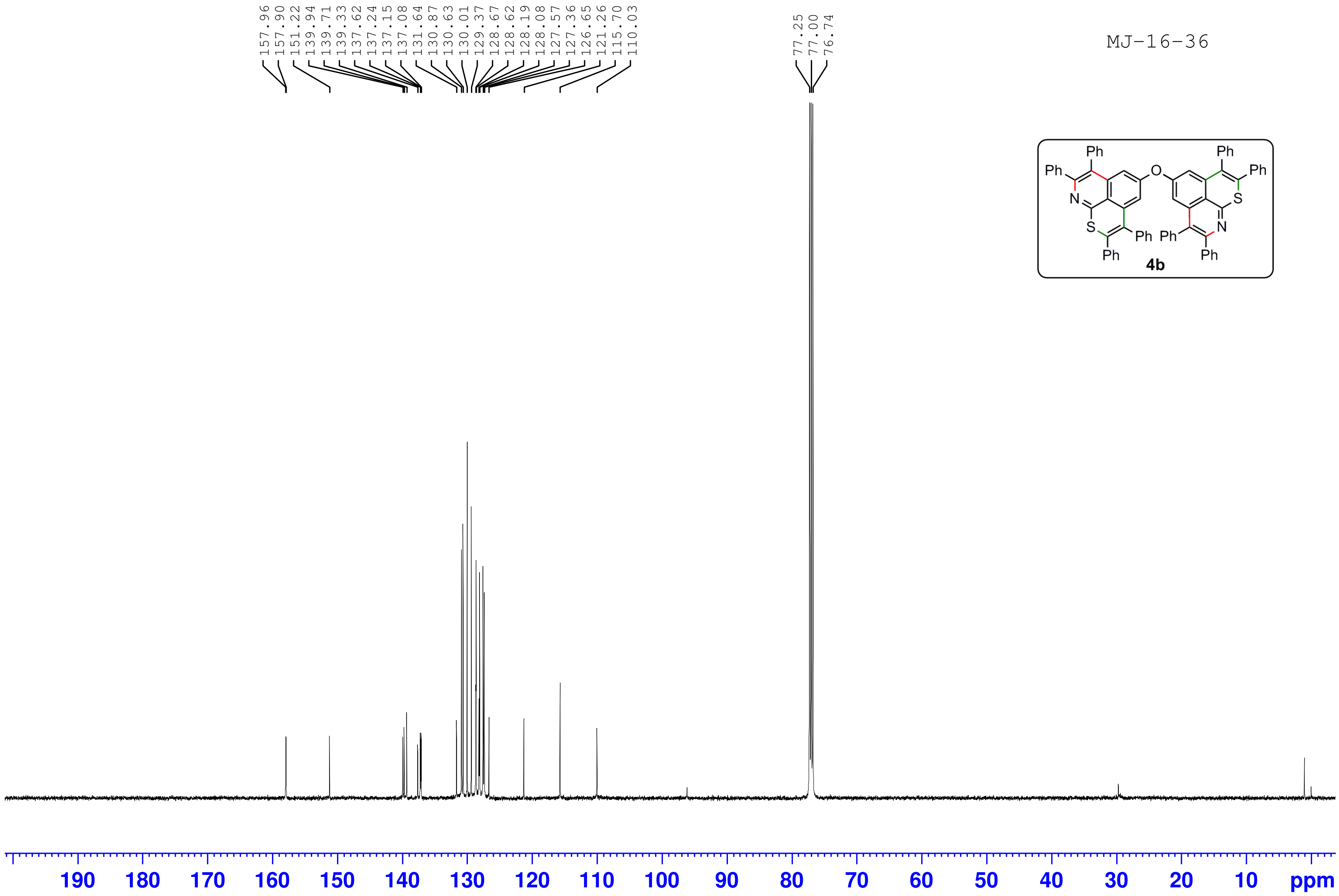

158.43
151.45
144.88
141.40
139.87
138.28
137.80
137.49
137.16
132.55
131.97
131.05
130.78
130.04
129.42
128.84
128.82
128.12
127.82
127.61
127.55
127.43
123.63
121.97
121.56
118.56
111.59
77.25
77.00
76.75
N
S
4a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

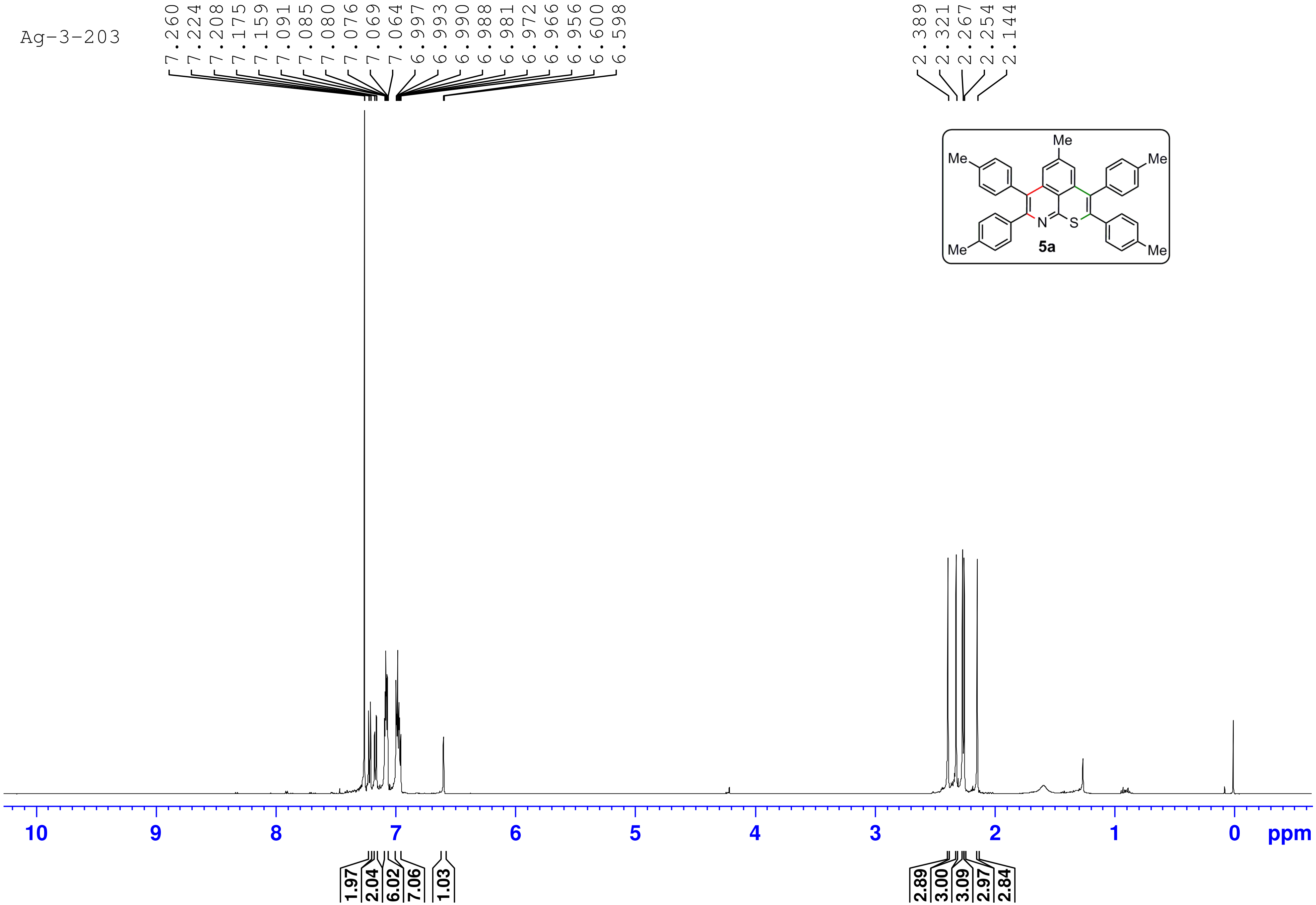
MJ-16-36

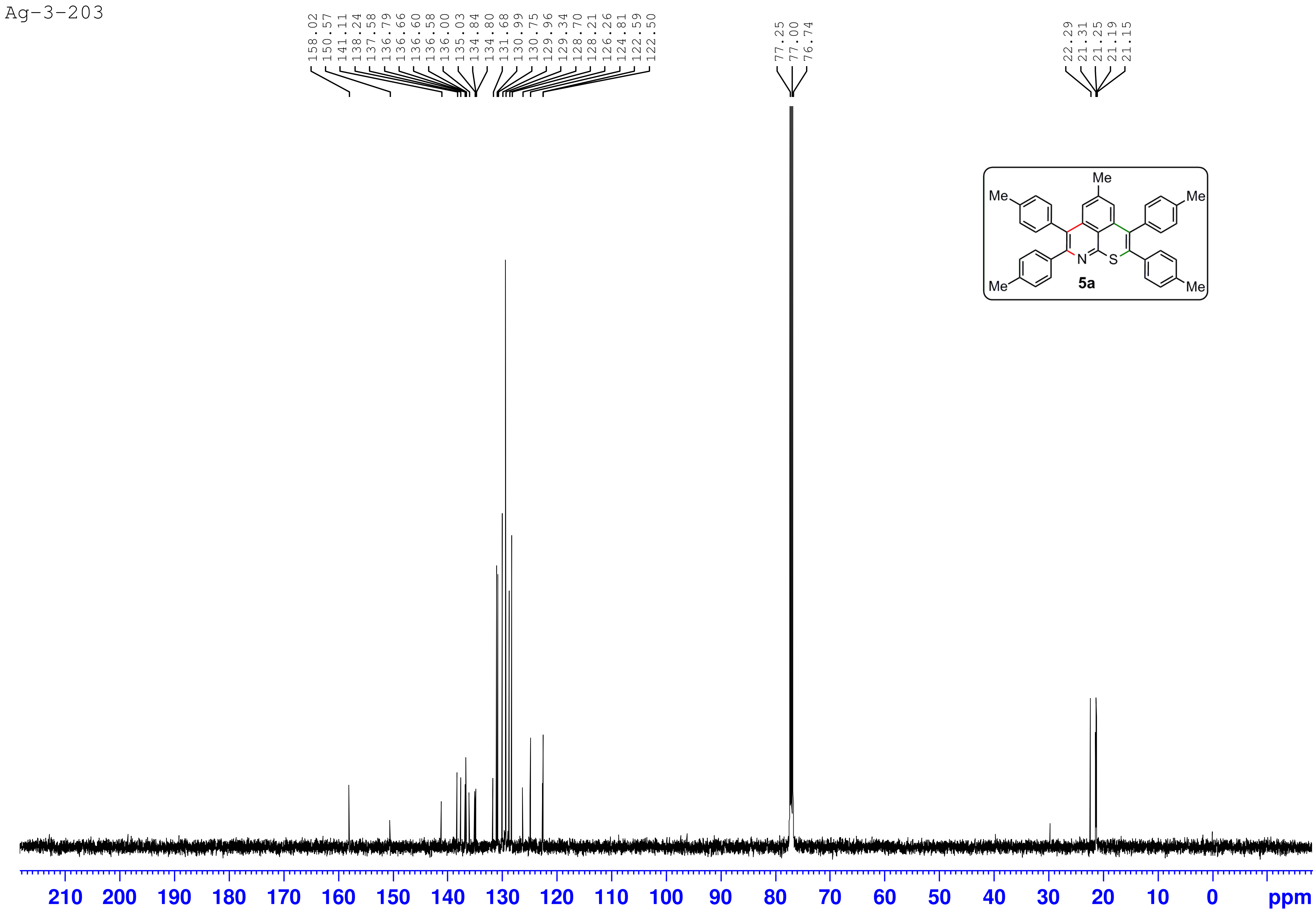

Ph
Ph
N
S
Ph
Ph
O
Ph
Ph
S
N
Ph
Ph

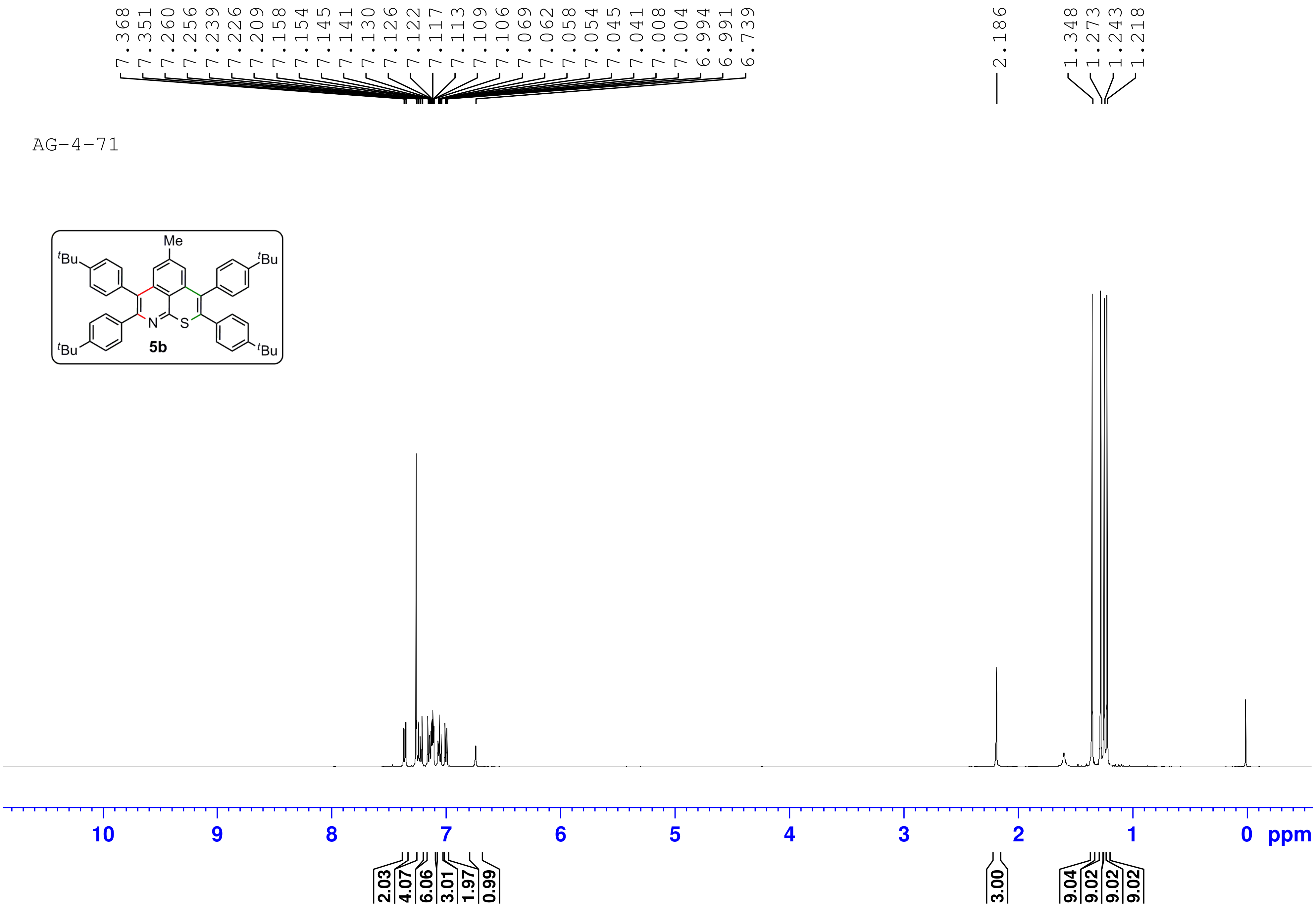
4b


7.306
7.299
7.295
7.282
7.260
7.196
7.174
7.150
7.054
7.041
6.990
6.976
6.605
6.601
6.297
6.293
10
9
8
7
6
5
4
3
2
1
0
ppm
11.30
21.31
4.00
4.18
2.02
2.05

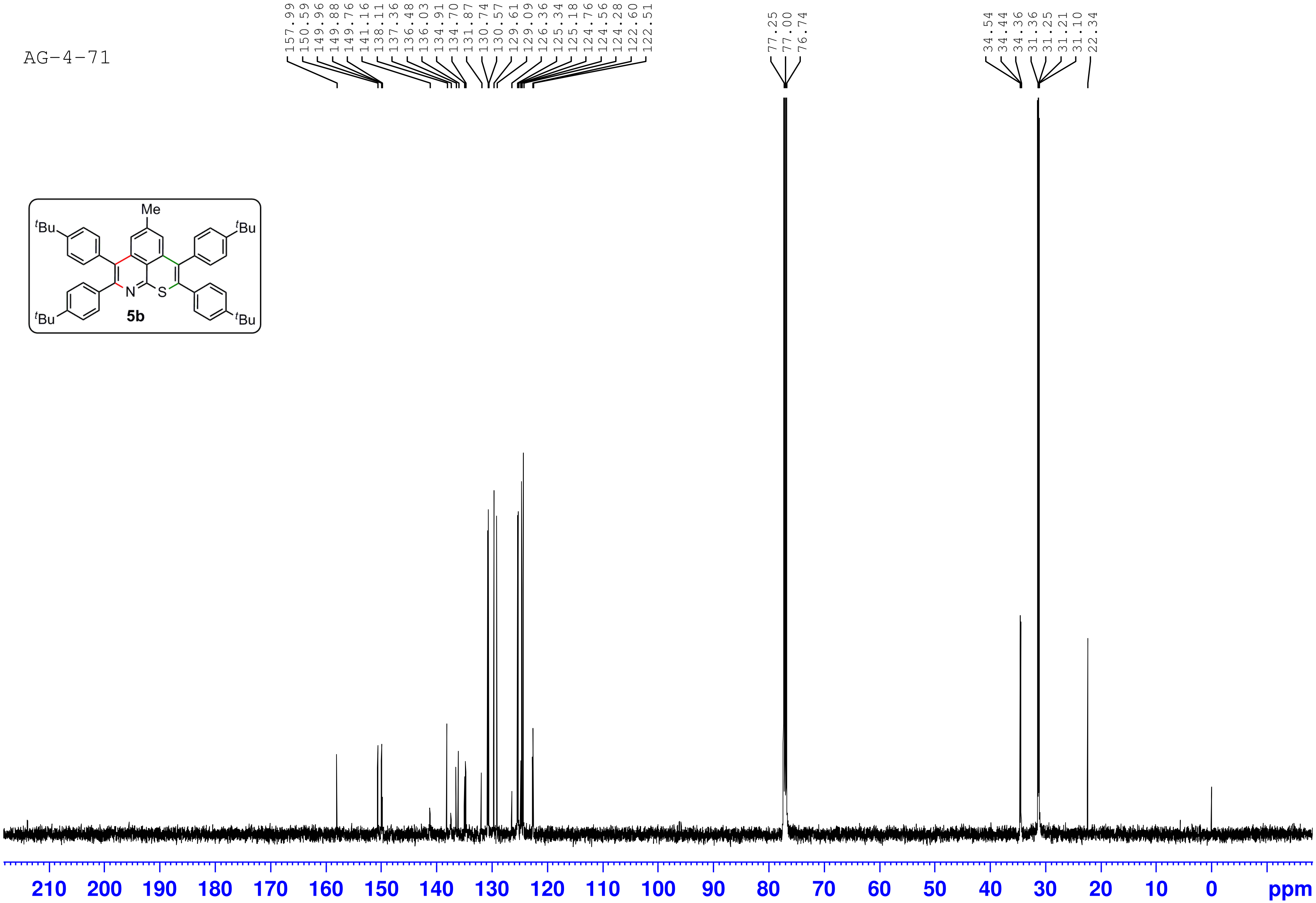

157.96
157.90
151.22
139.94
139.71
139.33
137.62
137.24
137.15
137.08
131.64
130.87
130.63
130.01
129.37
128.67
128.62
128.19
128.08
127.57
127.36
126.65
121.26
115.70
110.03
77.25
77.00
76.74
MJ-16-36
Ph
Ph
N
S
Ph
Ph
O
Ph
Ph
S
N
Ph
Ph
4b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ag-3-203
7.260
7.224
7.208
7.175
7.159
7.091
7.085
7.080
7.076
7.069
7.064
6.997
6.993
6.990
6.988
6.981
6.972
6.966
6.956
6.600
6.598
2.389
2.321
2.267
2.254
2.144
Me
Me
Me
Me
Me
N
S
5a
10
9
8
7
6
5
4
3
2
1
0
ppm
1.97
2.04
6.02
7.06
1.03
2.89
3.00
3.09
2.97
2.84

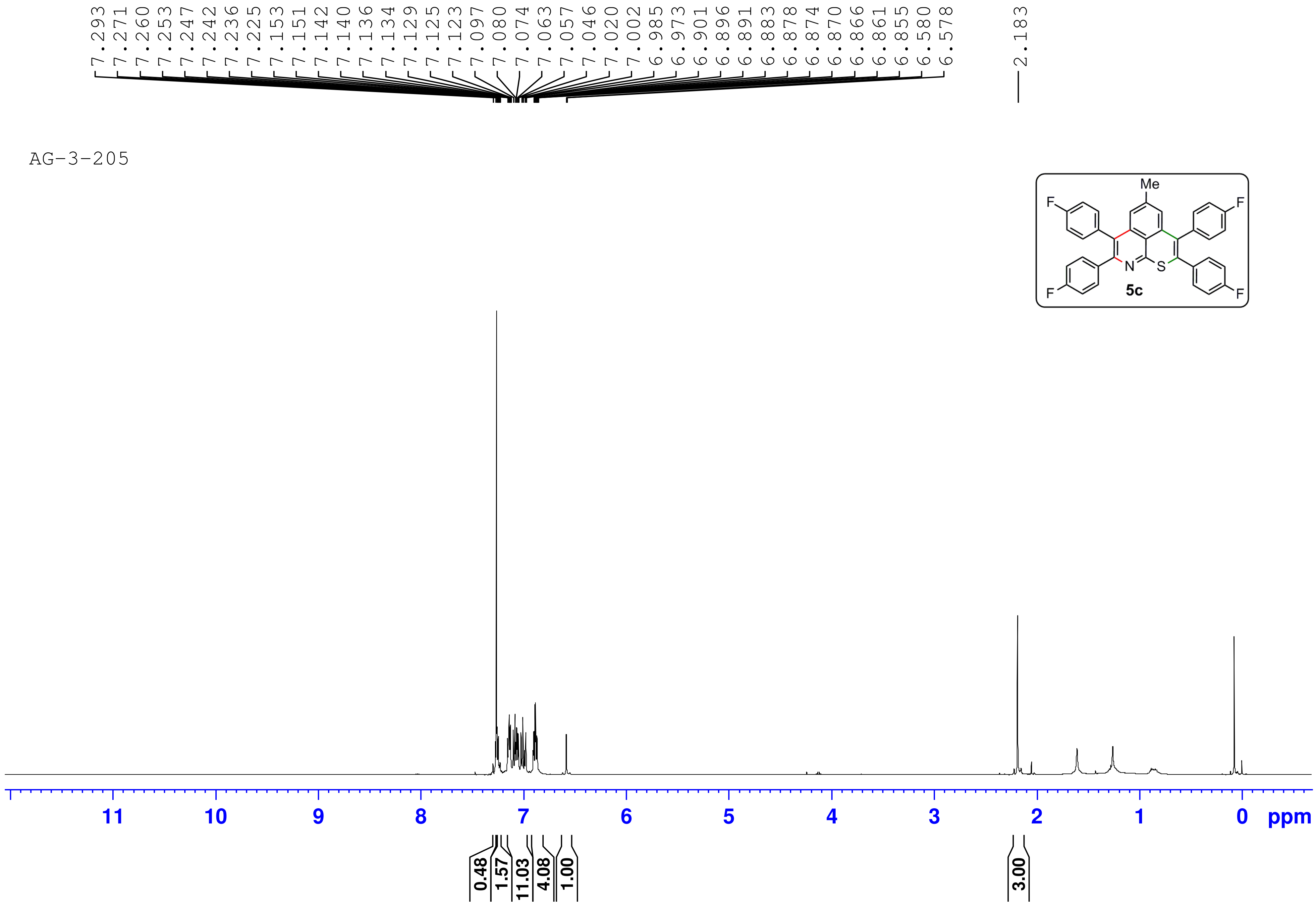

Ag-3-203
158.02
150.57
141.11
138.24
137.58
136.79
136.66
136.60
136.58
136.00
135.03
134.84
134.80
131.68
130.99
130.75
129.96
129.34
128.70
128.21
126.26
124.81
122.59
122.50
77.25
77.00
76.74
22.29
21.31
21.25
21.19
21.15
Me
Me
Me
Me
Me
N
S
5a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.368
7.351
7.260
7.256
7.239
7.226
7.209
7.158
7.154
7.145
7.141
7.130
7.126
7.122
7.117
7.113
7.109
7.106
7.069
7.062
7.058
7.054
7.045
7.041
7.008
7.004
6.994
6.991
6.739
2.186
1.348
1.273
1.243
1.218
AG-4-71
Me
^{t}Bu
N
S
5b
2.03
4.07
6.06
3.01
1.97
0.99
3.00
9.04
9.02
9.02
9.02
10
9
8
7
6
5
4
3
2
1
0
ppm

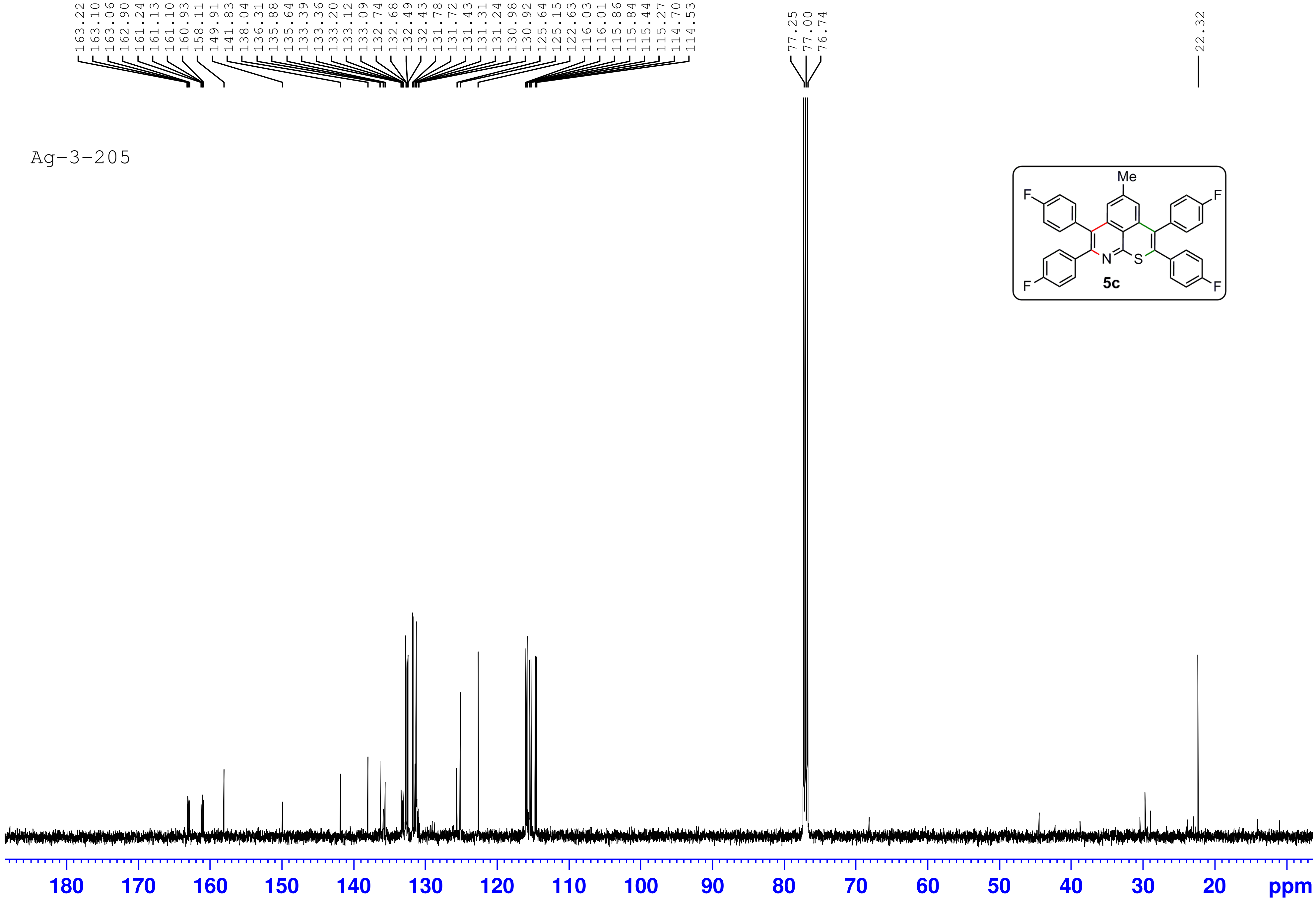
AG-4-71


157.99
150.59
149.96
149.88
149.76
141.16
138.11
137.36
136.48
136.03
134.91
134.70
131.87
130.74
130.57
129.61
129.09
126.36
125.34
125.18
124.76
124.56
124.28
122.60
122.51
77.25
77.00
76.74
34.54
34.44
34.36
31.36
31.25
31.21
31.10
22.34
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
Me
tBu
tBu
N
S
tBu
tBu

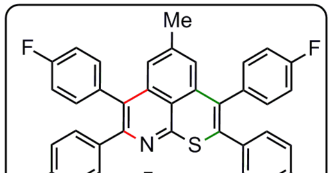
5b



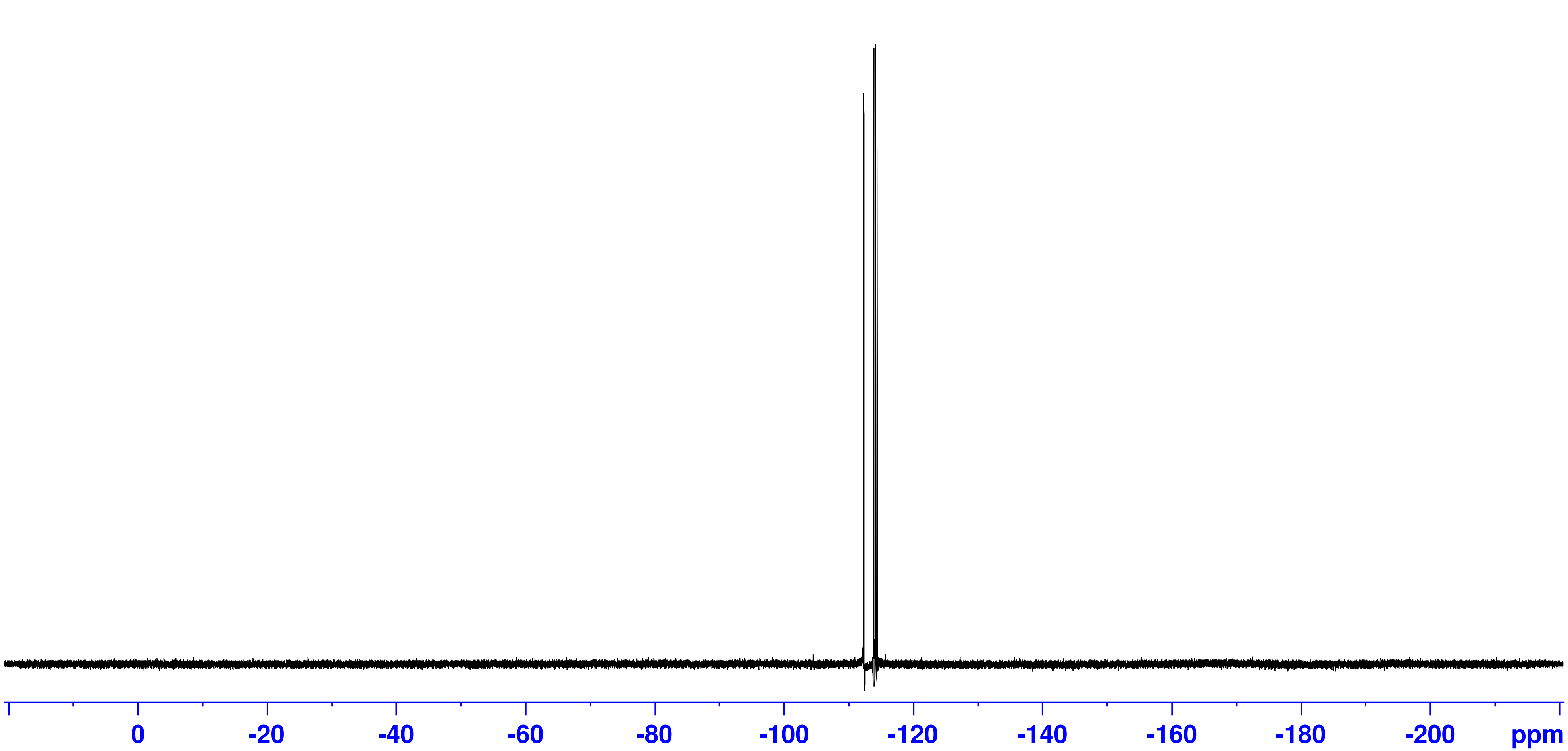
7.293
7.271
7.260
7.253
7.247
7.242
7.236
7.225
7.153
7.151
7.142
7.140
7.136
7.134
7.129
7.125
7.123
7.097
7.080
7.074
7.063
7.057
7.046
7.020
7.002
6.985
6.973
6.901
6.896
6.891
6.883
6.878
6.874
6.870
6.866
6.861
6.855
6.580
6.578
2.183
AG-3-205
Me
F
F
N
S
F
F
5c
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.48
1.57
11.03
4.08
1.00
3.00

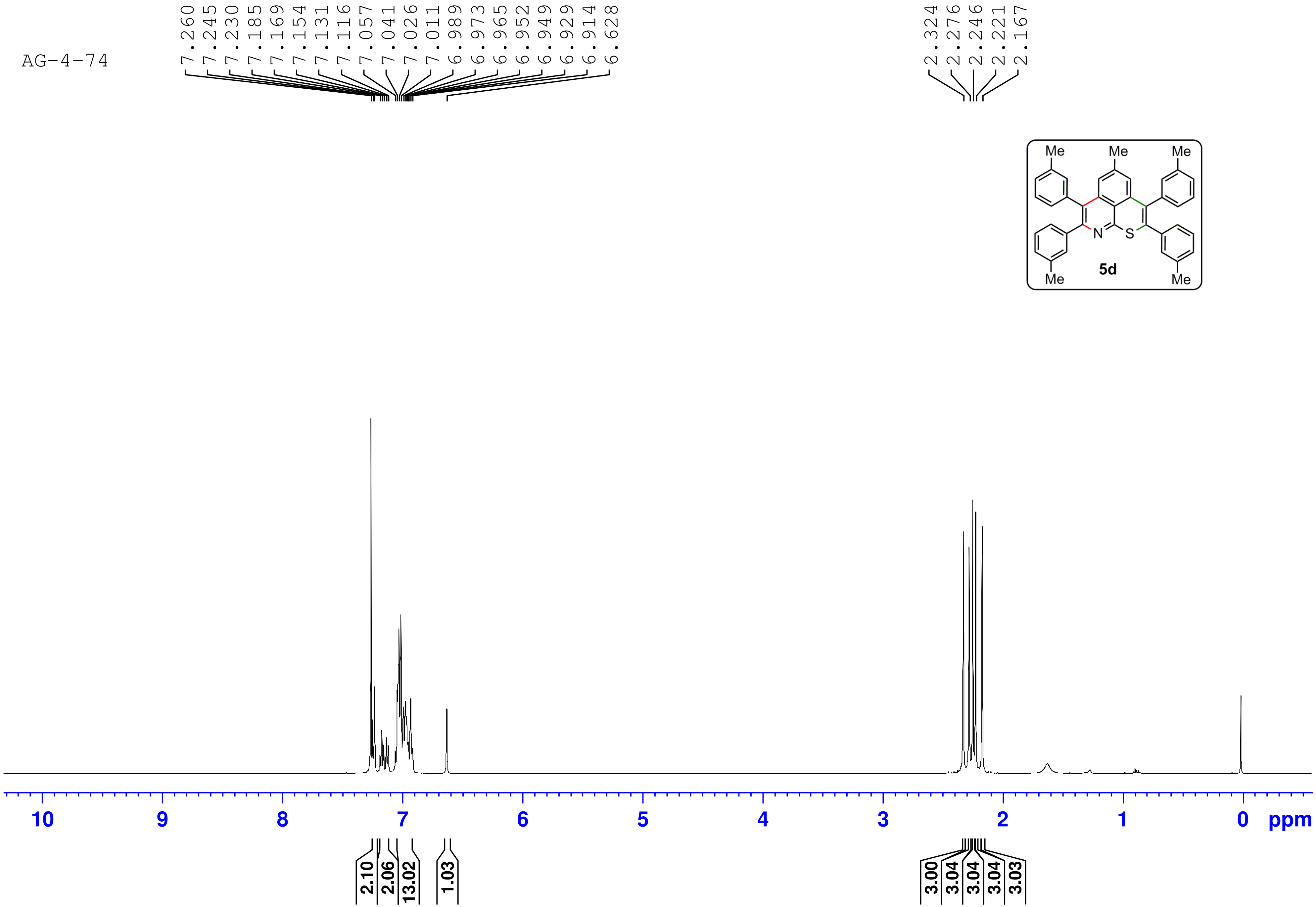

163.22
163.10
163.06
162.90
161.24
161.13
161.10
160.93
158.11
149.91
141.83
138.04
136.31
135.88
135.64
133.39
133.36
133.20
133.12
133.09
132.74
132.68
132.49
132.43
131.78
131.72
131.43
131.31
131.24
130.98
130.92
125.64
125.15
122.63
116.03
116.01
115.86
115.84
115.44
115.27
114.70
114.53
77.25
77.00
76.74
22.32
Ag-3-205
Me
F
F
N
S
F
F
5c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

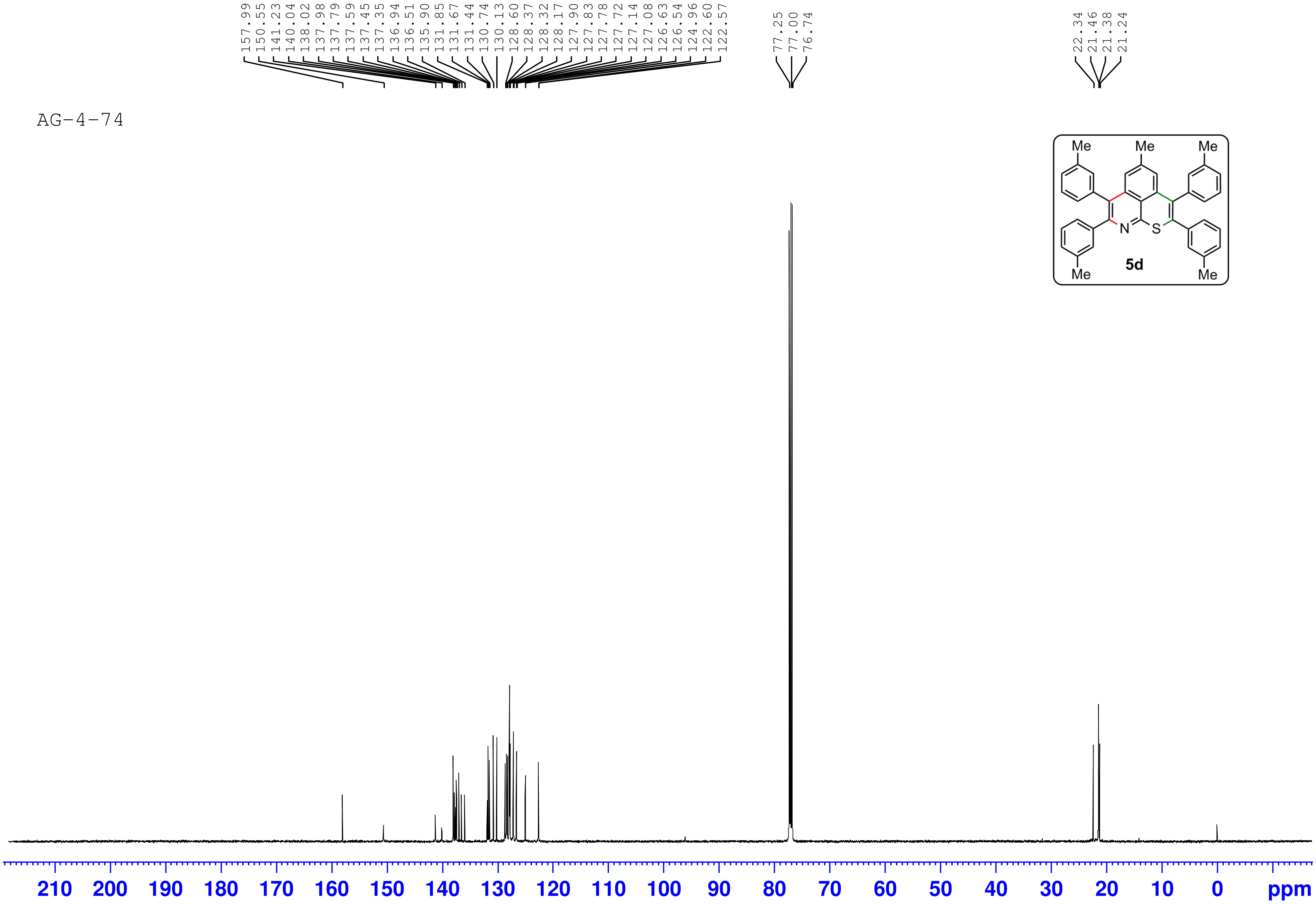
Ag-3-205

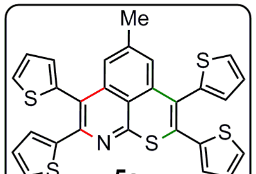

Me
F
F
F
F
N
S

5c

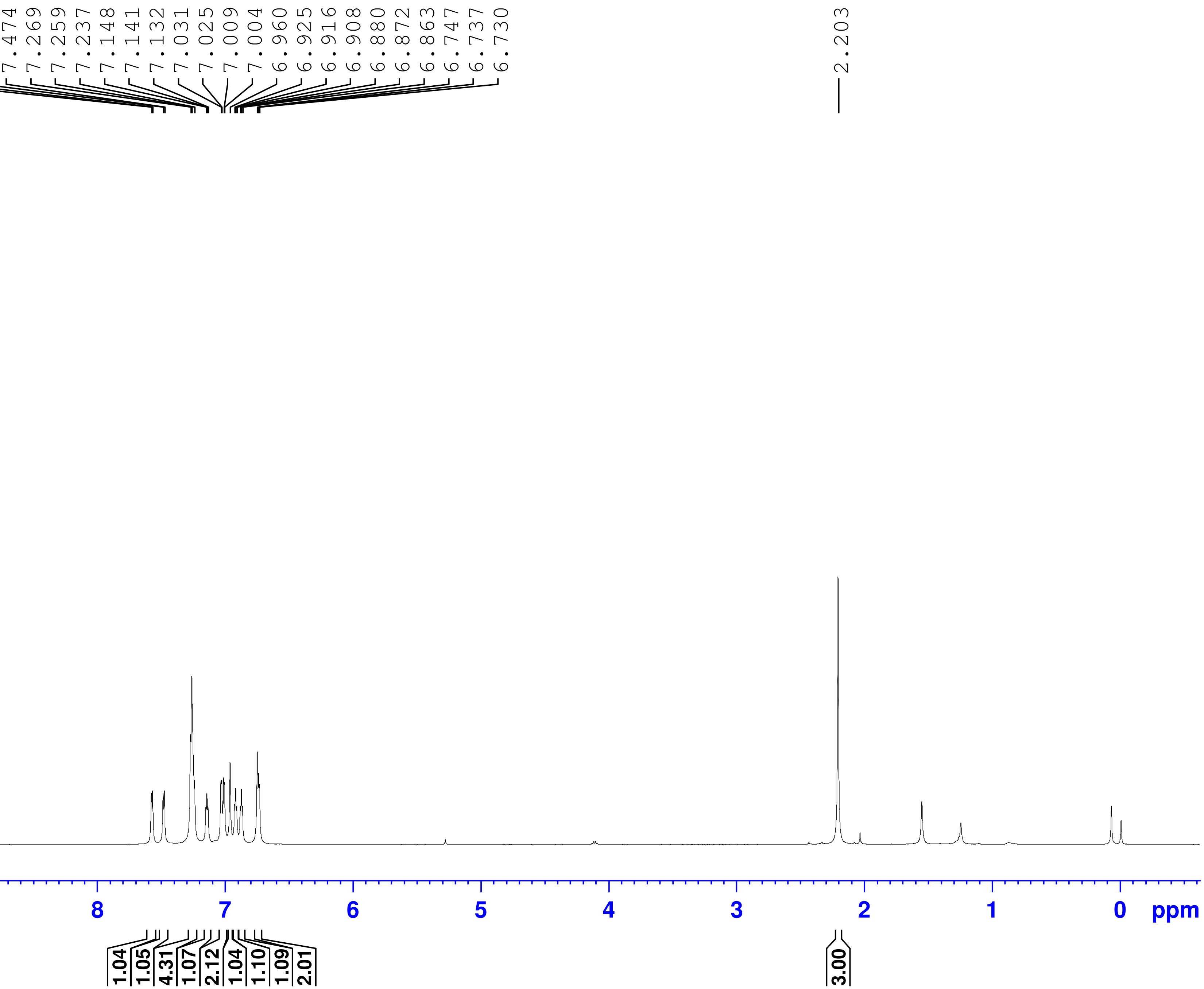

-112.44
-114.01
-114.26
-114.54
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm


AG-4-74
7.260
7.245
7.230
7.185
7.169
7.154
7.131
7.116
7.057
7.041
7.026
7.011
6.989
6.973
6.965
6.952
6.949
6.929
6.914
6.628
2.324
2.276
2.246
2.221
2.167
Me
Me
Me
N
S
Me
Me
5d
10
9
8
7
6
5
4
3
2
1
0
ppm
2.10
2.06
13.02
1.03
3.00
3.04
3.04
3.04
3.03

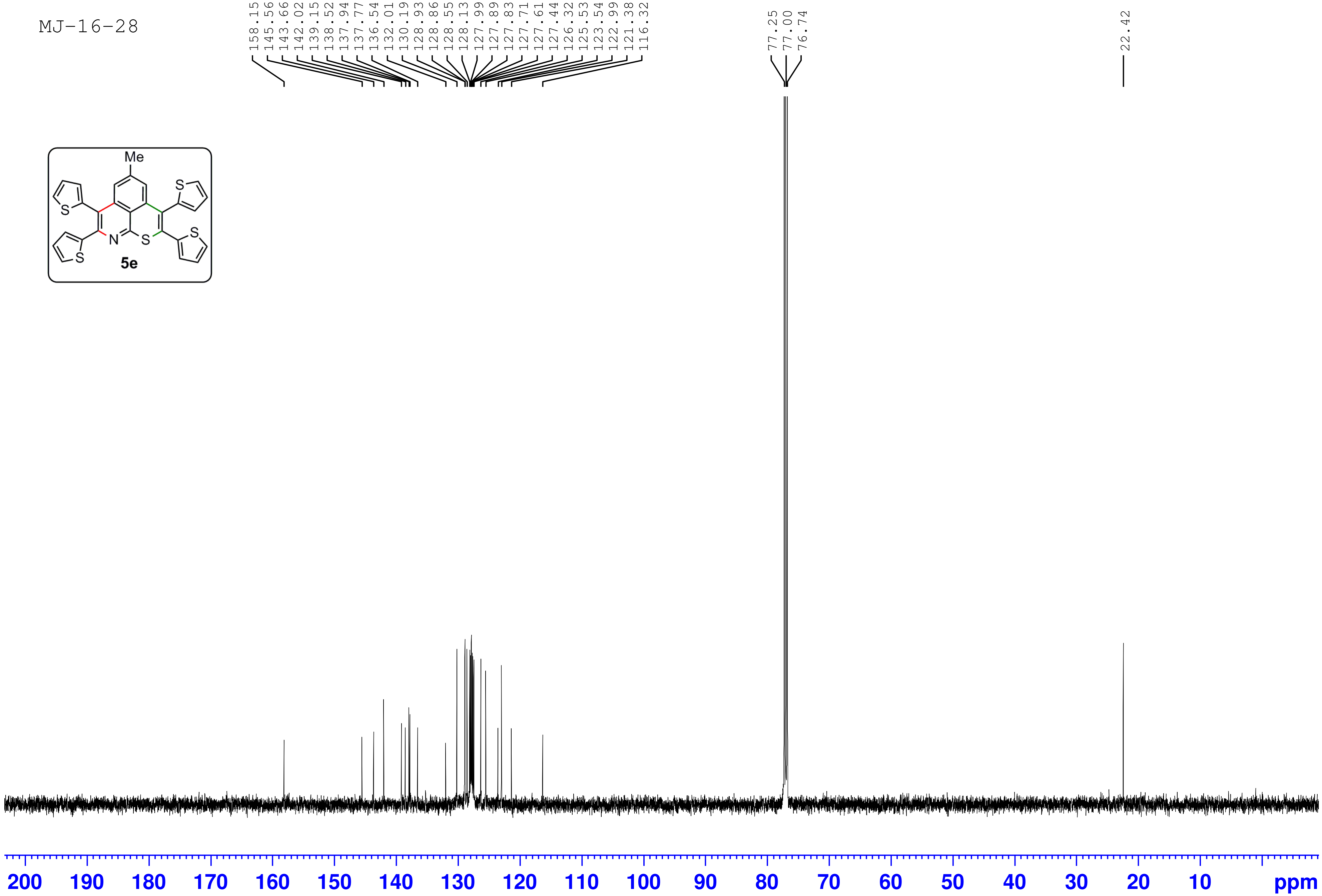

157.99
150.55
141.23
140.04
138.02
137.98
137.79
137.59
137.45
137.35
136.94
136.51
135.90
131.85
131.67
131.44
130.74
130.13
128.60
128.37
128.32
128.17
127.90
127.83
127.78
127.72
127.14
127.08
126.63
126.54
124.96
122.60
122.57
77.25
77.00
76.74
22.34
21.46
21.38
21.24
AG-4-74
Me
Me
Me
N
S
Me
Me
5d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

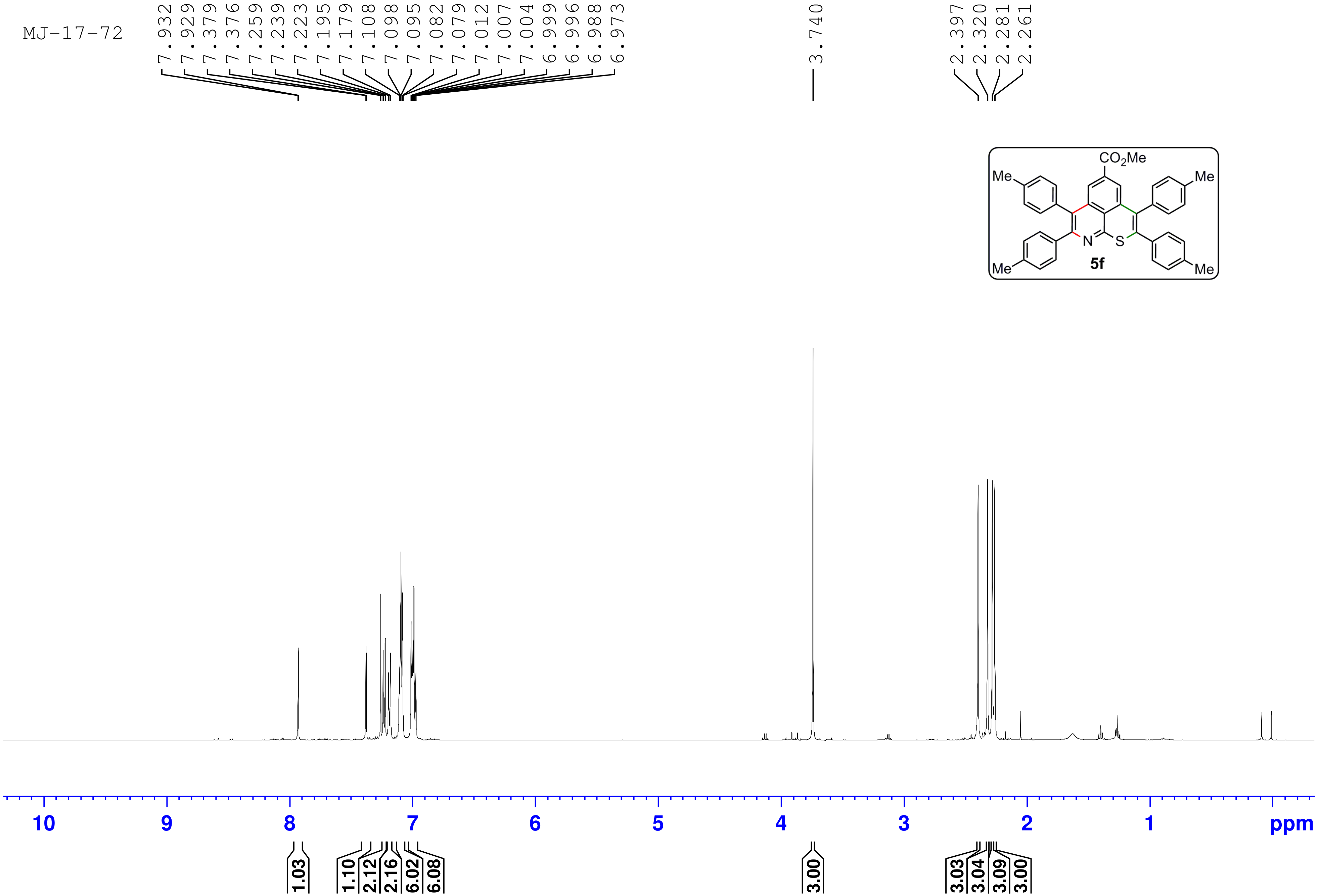

Me
S
S
N
S
S
S

5e


MJ-16-28
7.575
7.566
7.484
7.474
7.269
7.259
7.237
7.148
7.141
7.132
7.031
7.025
7.009
7.004
6.960
6.925
6.916
6.908
6.880
6.872
6.863
6.747
6.737
6.730
2.203
10
9
8
7
6
5
4
3
2
1
0
ppm
1.04
1.05
4.31
1.07
2.12
1.04
1.10
1.09
2.01
3.00

MJ-16-28


158.15
145.56
143.66
142.02
139.15
138.52
137.94
137.77
136.54
132.01
130.19
128.93
128.86
128.55
128.13
127.99
127.89
127.83
127.71
127.61
127.44
126.32
125.53
123.54
122.99
121.38
116.32
77.25
77.00
76.74
22.42
Me
S
N
5e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


MJ-17-72
7.932
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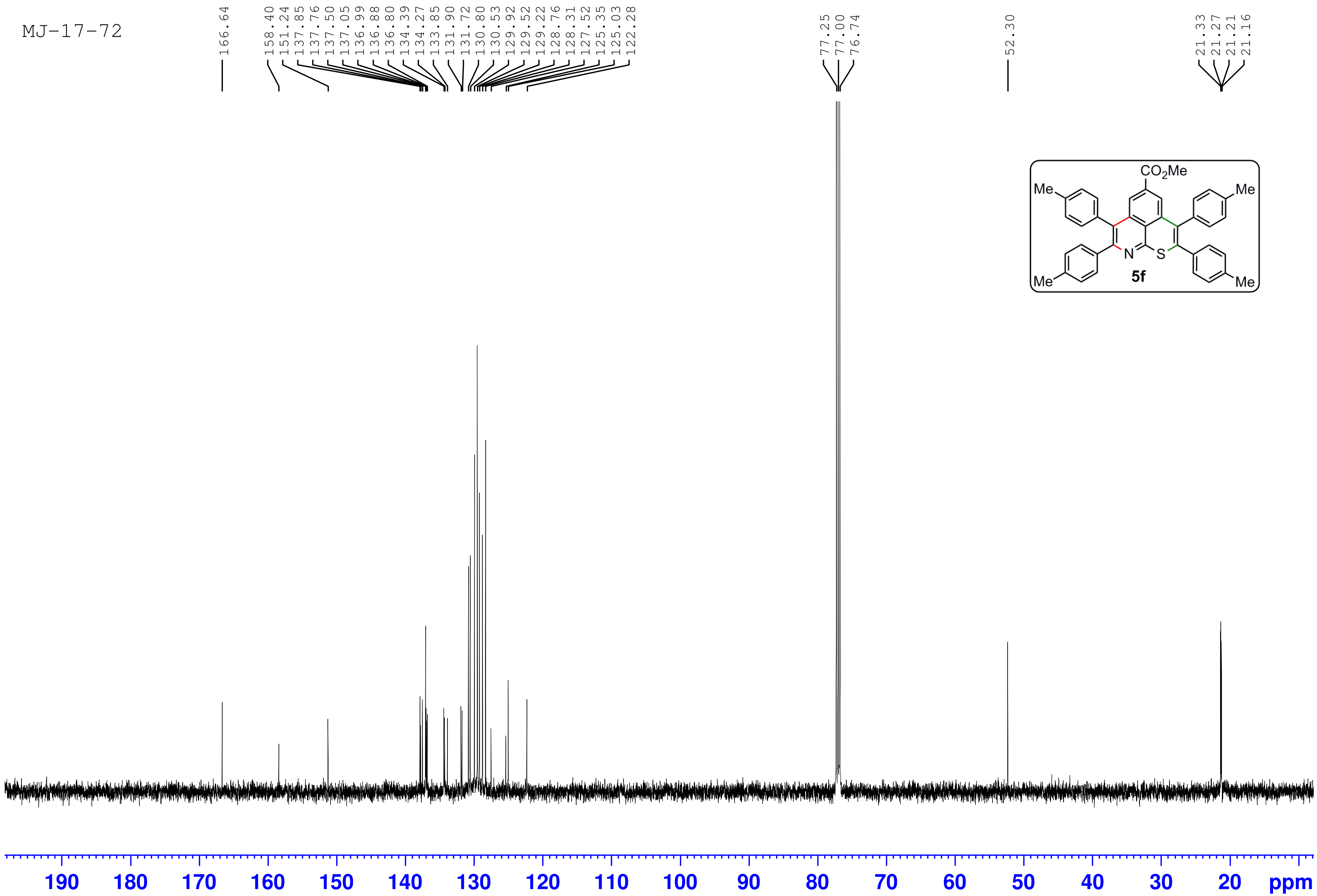
7.379
7.376
7.259
7.239
7.223
7.195
7.179
7.108
7.098
7.095
7.082
7.079
7.012
7.007
7.004
6.999
6.996
6.988
6.973
3.740
2.397
2.320
2.281
2.261
CO2Me
Me
N
S
5f
1.03
1.10
2.12
2.16
6.02
6.08
3.00
3.03
3.04
3.09
3.00
ppm


MJ-17-72
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158.40
151.24
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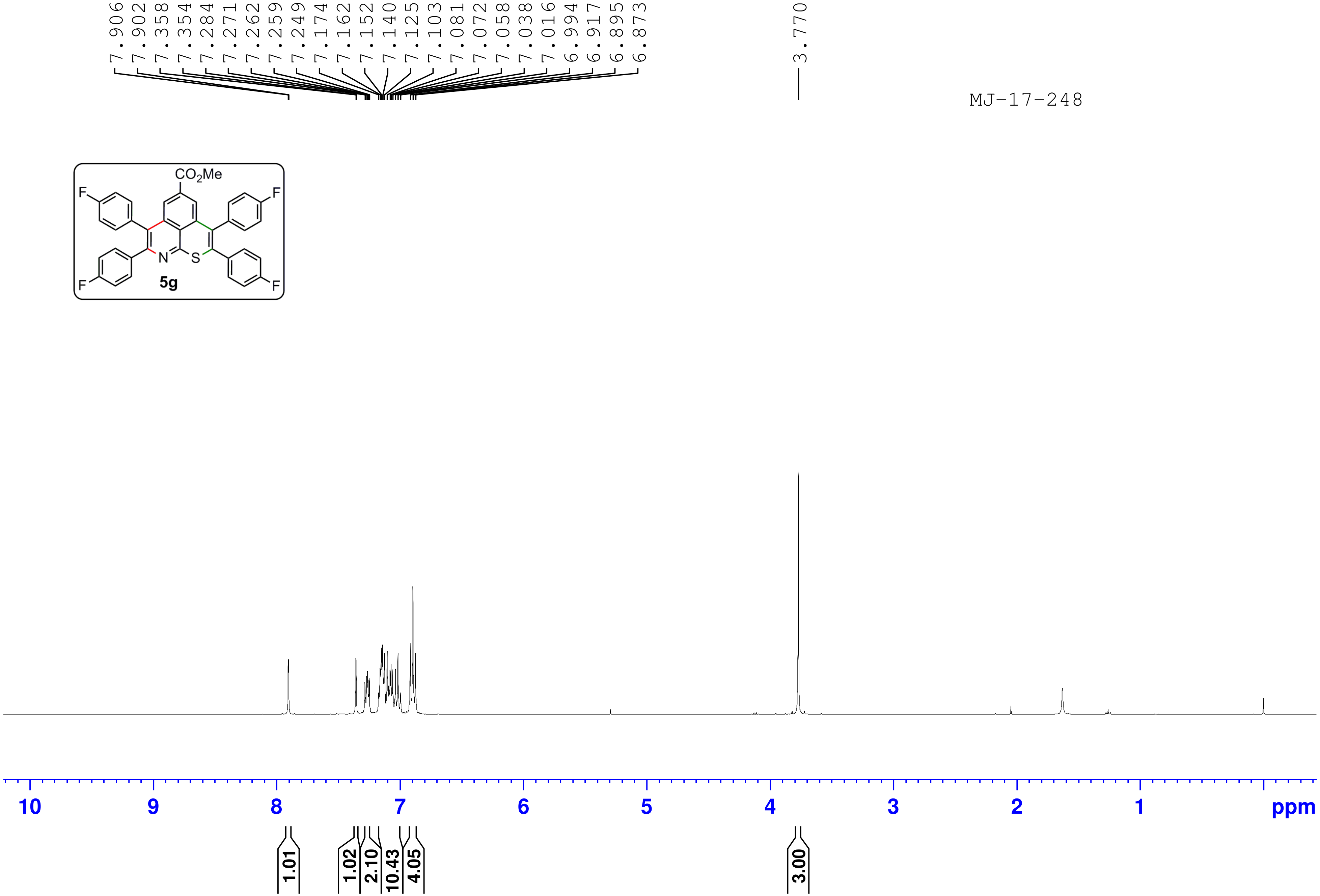
137.76
137.50
137.05
136.99
136.88
136.80
134.39
134.27
133.85
131.90
131.72
130.80
130.53
129.92
129.52
129.22
128.76
128.31
127.52
125.35
125.03
122.28
77.25
77.00
76.74
52.30
21.33
21.27
21.21
21.16
CO2Me
Me
Me
Me
Me
N
S
5f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.906
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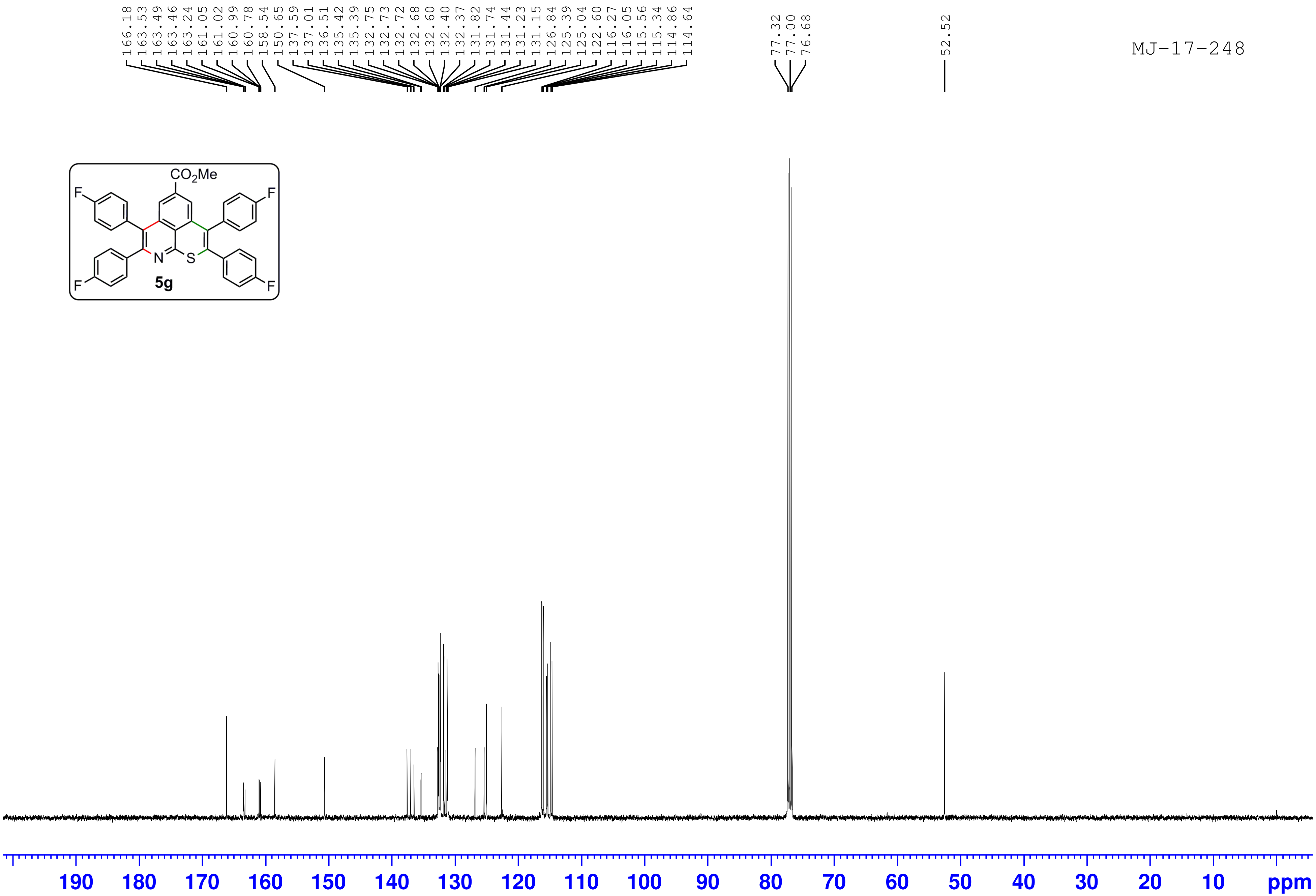
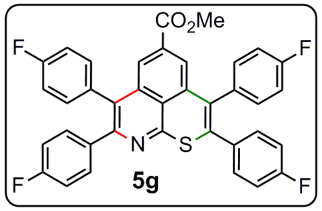
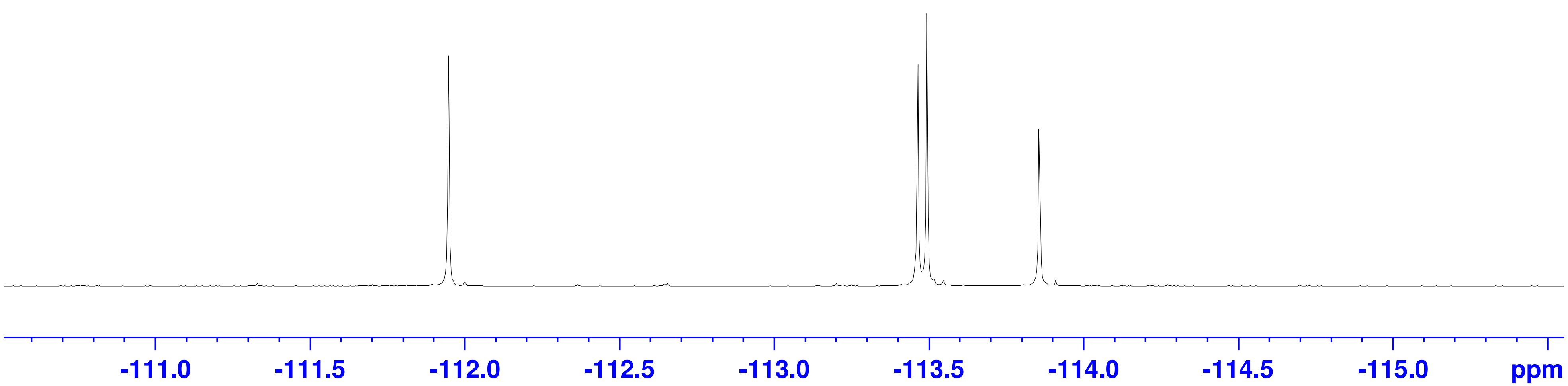
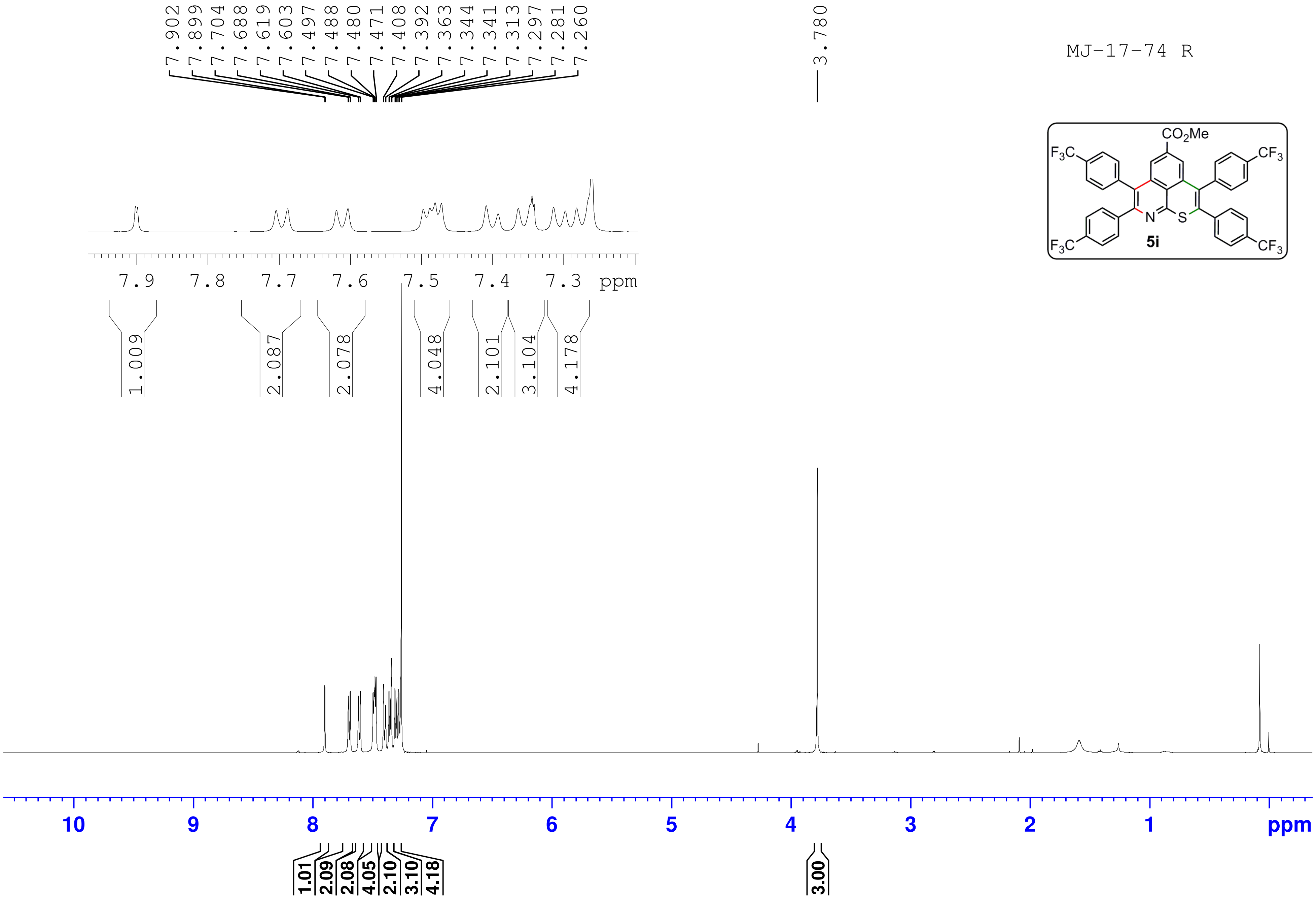
7.354
7.284
7.271
7.262
7.259
7.249
7.174
7.162
7.152
7.140
7.125
7.103
7.081
7.072
7.058
7.038
7.016
6.994
6.917
6.895
6.873
3.770
MJ-17-248
CO_2Me
F
F
F
F
N
S
5g
10
9
8
7
6
5
4
3
2
1
ppm
1.01
1.02
2.10
10.43
4.05
3.00

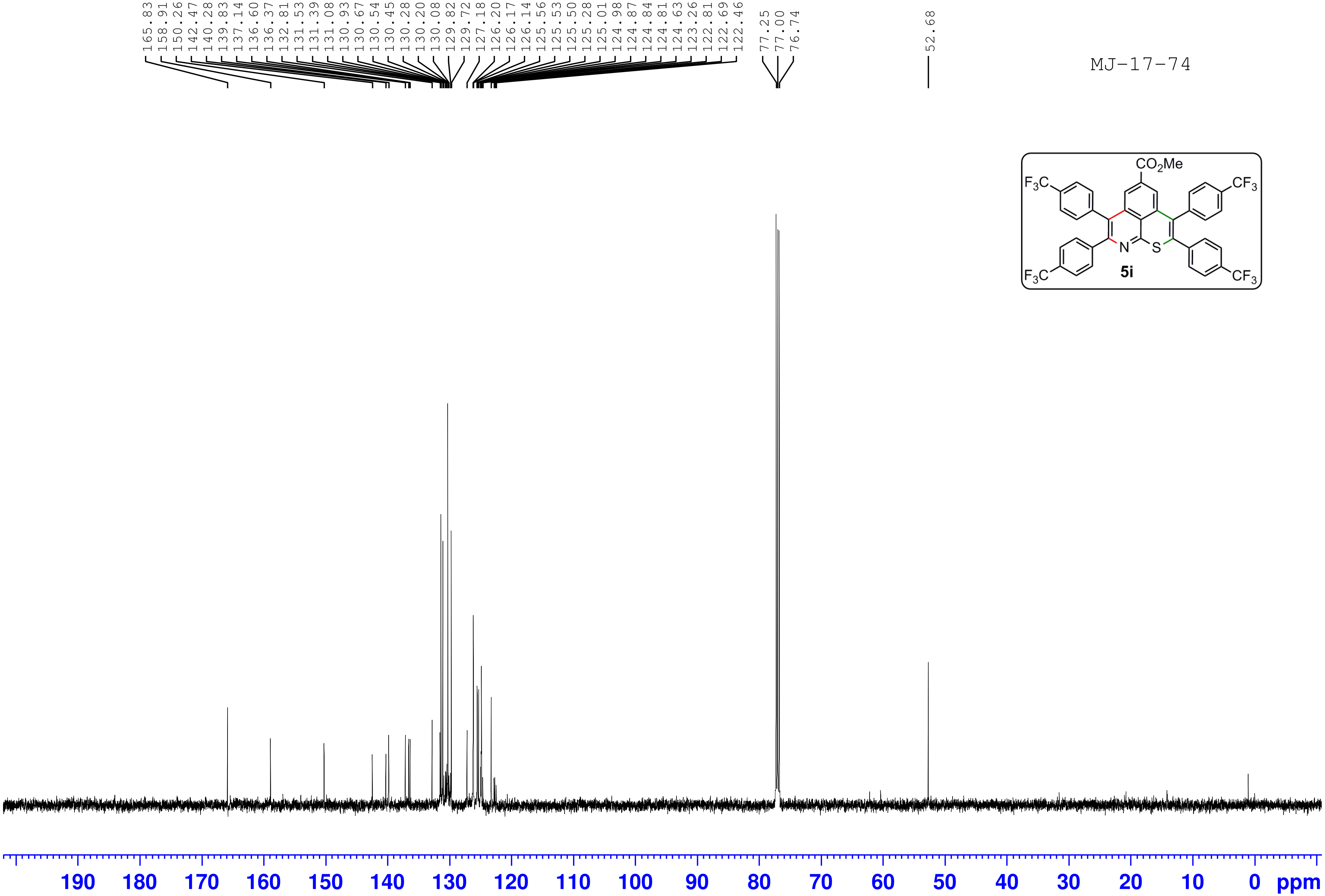

166.18
163.53
163.49
163.46
163.24
161.05
161.02
160.99
160.78
158.54
150.65
137.59
137.01
136.51
135.42
135.39
132.75
132.73
132.72
132.68
132.60
132.40
132.37
131.82
131.74
131.44
131.23
131.15
126.84
125.39
125.04
122.60
116.27
116.05
115.56
115.34
114.86
114.64
77.32
77.00
76.68
52.52
MJ-17-248
CO2Me
F
F
F
F
N
S
5g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

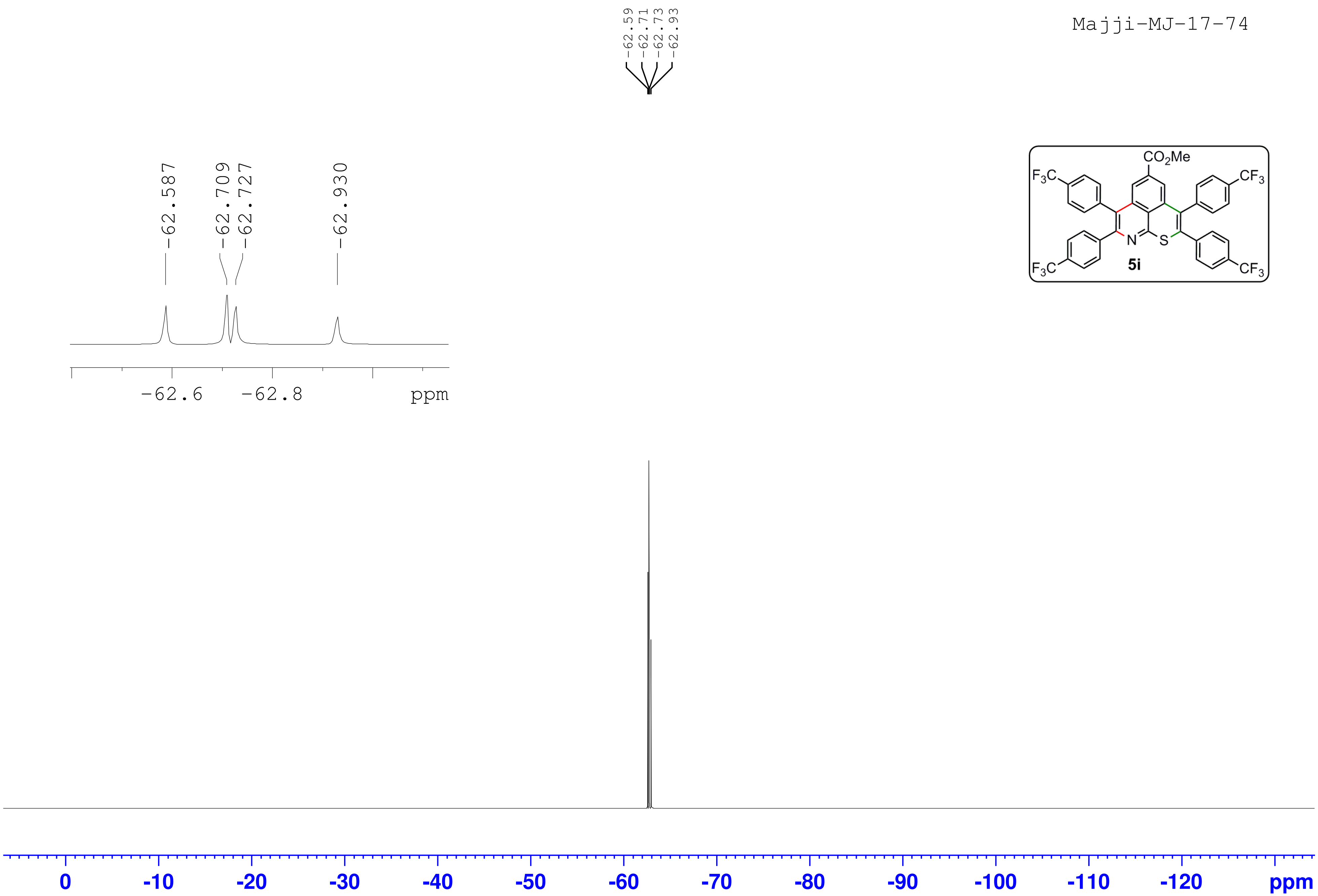
MJ-17-248


CO2Me
F
F
F
F
N
S
5g

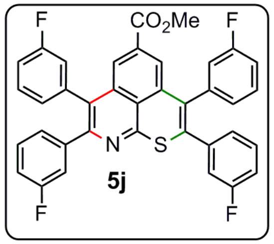

-111.95
-113.46
-113.49
-113.86
-111.0
-111.5
-112.0
-112.5
-113.0
-113.5
-114.0
-114.5
-115.0
ppm

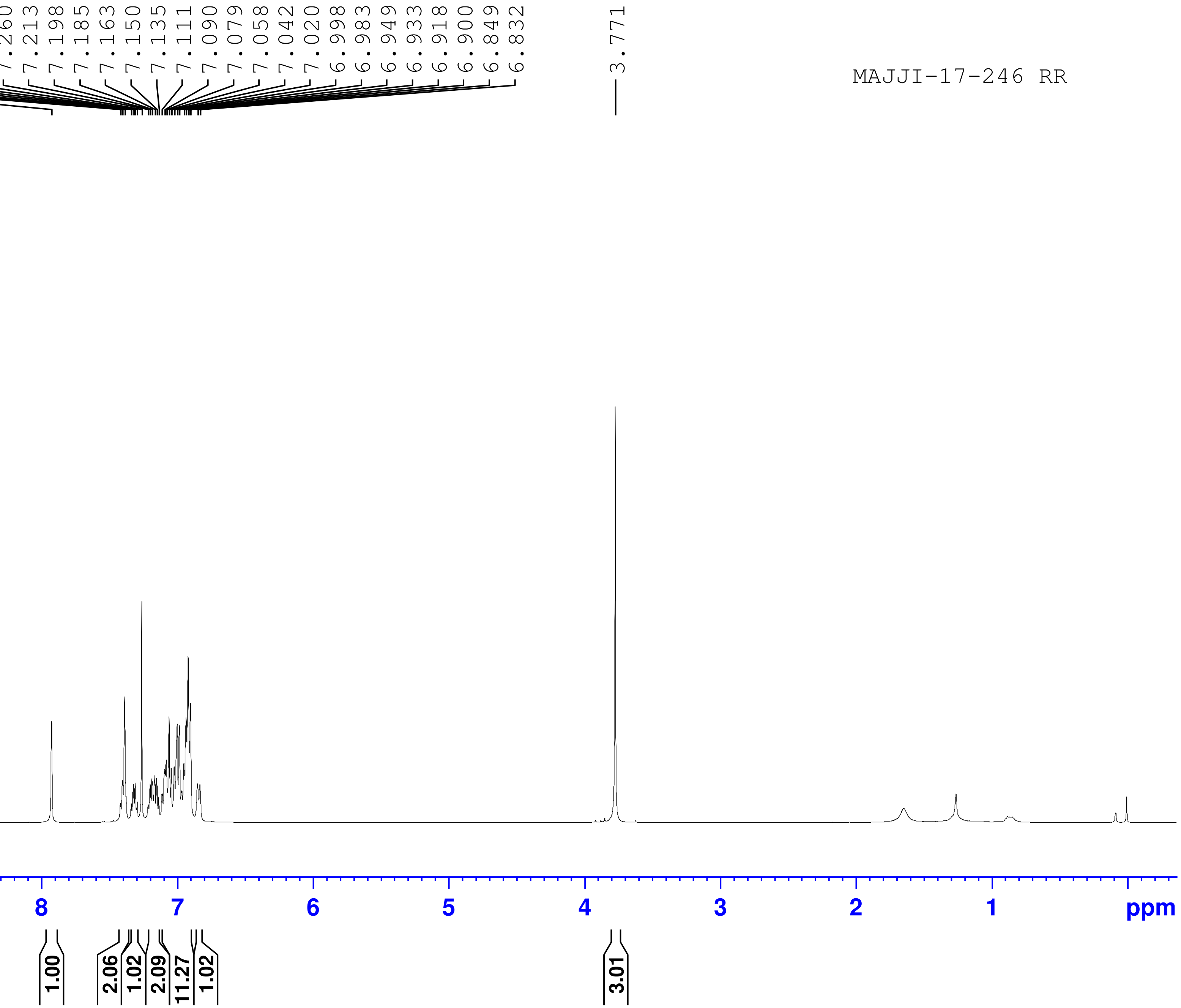

7.902
7.899
7.704
7.688
7.619
7.603
7.497
7.488
7.480
7.471
7.408
7.392
7.363
7.344
7.341
7.313
7.297
7.281
7.260
3.780
MJ-17-74 R
CO2Me
F3C
CF3
F3C
CF3
N
S
5i
7.9
7.8
7.7
7.6
7.5
7.4
7.3
ppm
1.009
2.087
2.078
4.048
2.101
3.104
4.178
10
9
8
7
6
5
4
3
2
1
ppm
1.01
2.09
2.08
4.05
2.10
3.10
4.18
3.00

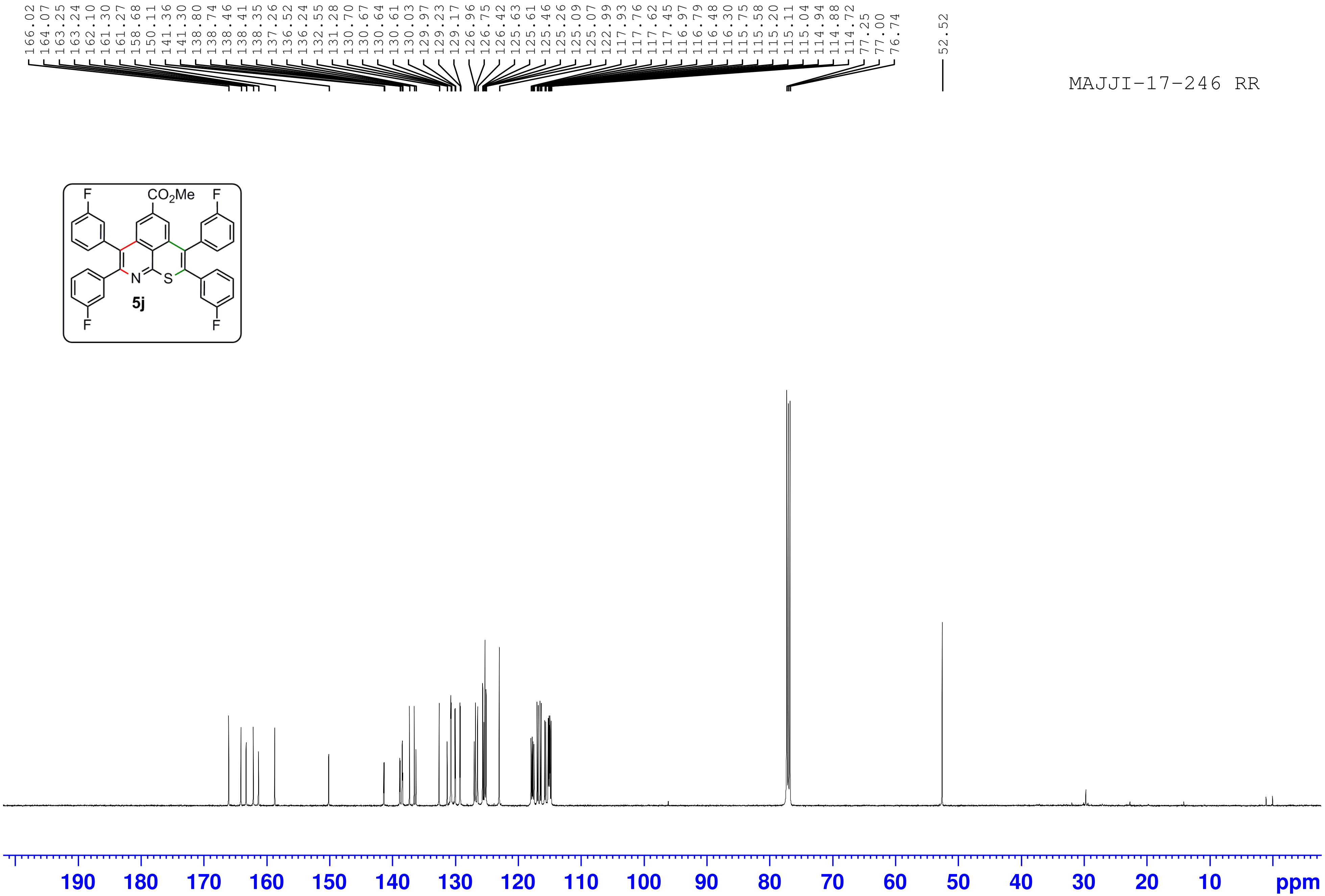

165.83
158.91
150.26
142.47
140.28
139.83
137.14
136.60
136.37
132.81
131.53
131.39
131.08
130.93
130.67
130.54
130.45
130.28
130.20
130.08
129.82
129.72
127.18
126.20
126.17
126.14
125.56
125.53
125.50
125.28
125.01
124.98
124.87
124.84
124.81
124.63
123.26
122.81
122.69
122.46
77.25
77.00
76.74
52.68
MJ-17-74
CO_2Me
F_3C
CF_3
N
S
F_3C
CF_3
5i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



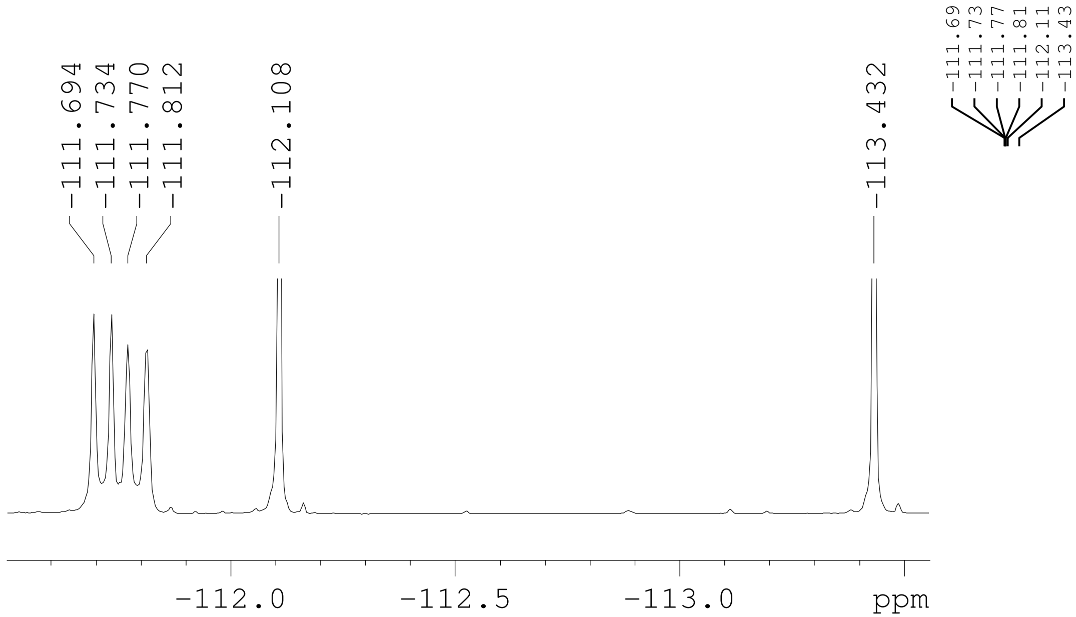
Majji-MJ-17-74
-62.59
-62.71
-62.73
-62.93
-62.587
-62.709
-62.727
-62.930
-62.6
-62.8
ppm
CO2Me
F3C
CF3
N
S
5i
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
ppm

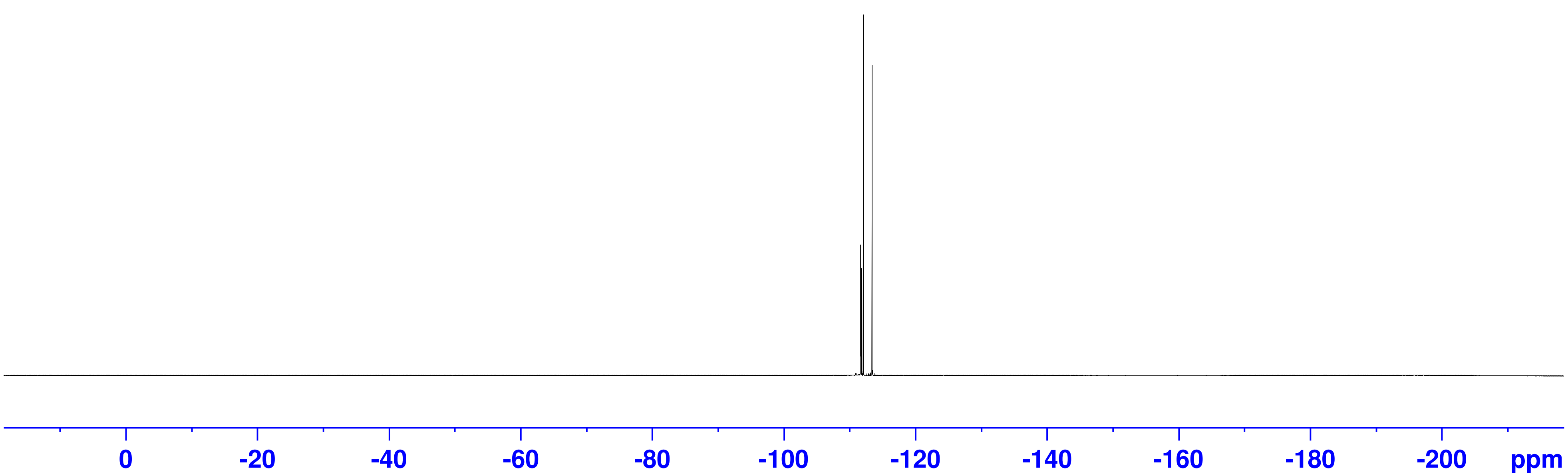


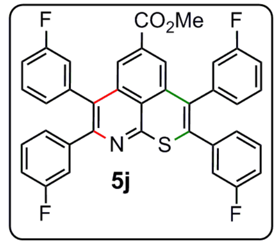

7.924
7.417
7.402
7.385
7.337
7.322
7.309
7.294
7.260
7.213
7.198
7.185
7.163
7.150
7.135
7.111
7.090
7.079
7.058
7.042
7.020
6.998
6.983
6.949
6.933
6.918
6.900
6.849
6.832
3.771
MAJJI-17-246 RR
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.06
1.02
2.09
11.27
1.02
3.01

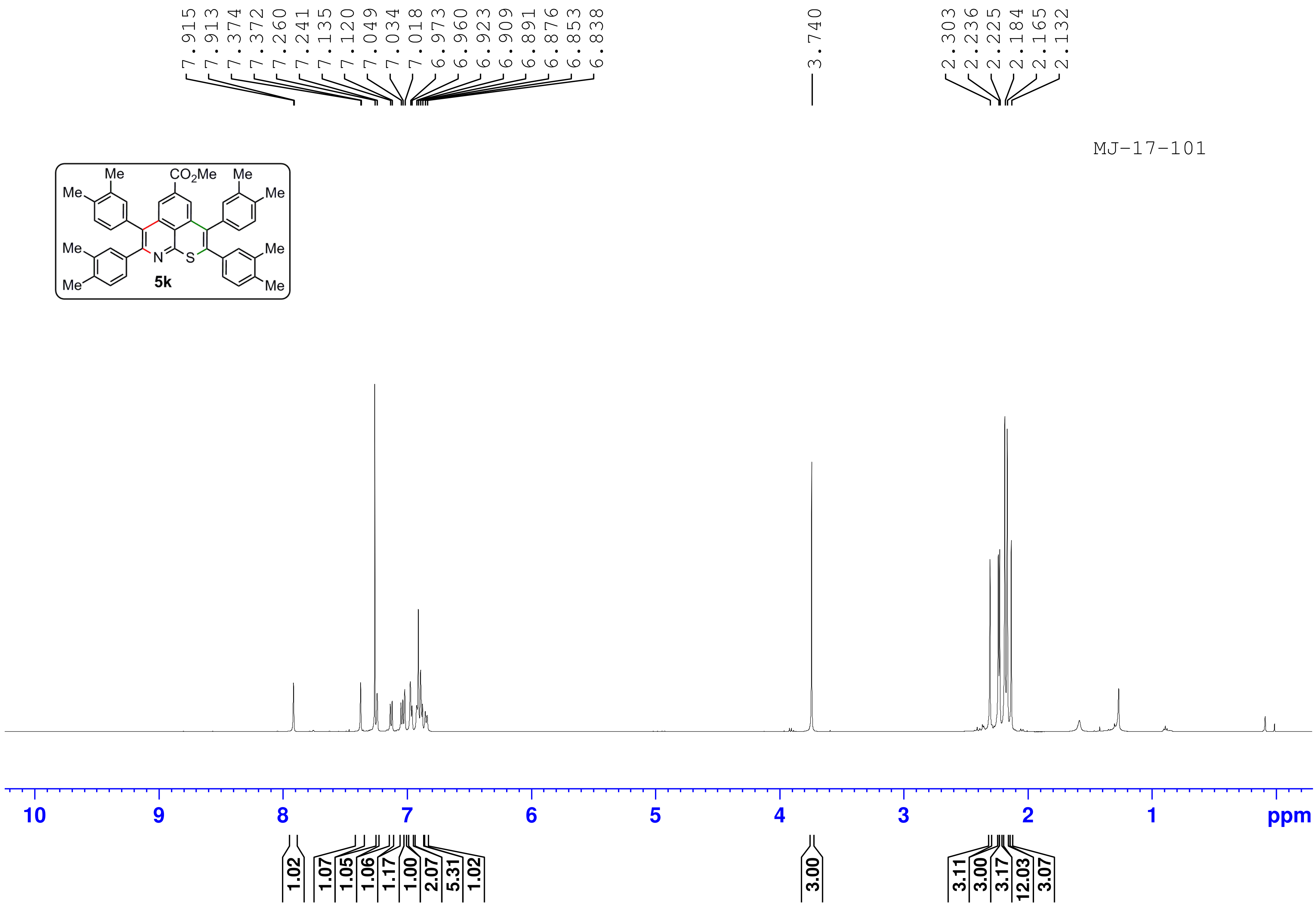

166.02
164.07
163.25
163.24
162.10
161.30
161.27
158.68
150.11
141.36
141.30
138.80
138.74
138.46
138.41
138.35
137.26
136.52
136.24
132.55
131.28
130.70
130.67
130.64
130.61
130.03
129.97
129.23
129.17
126.96
126.75
126.42
125.63
125.61
125.46
125.26
125.09
125.07
122.99
117.93
117.76
117.62
117.45
116.97
116.79
116.48
116.30
115.75
115.58
115.20
115.11
115.04
114.94
114.88
114.72
77.25
77.00
76.74
52.52
MAJJI-17-246 RR
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

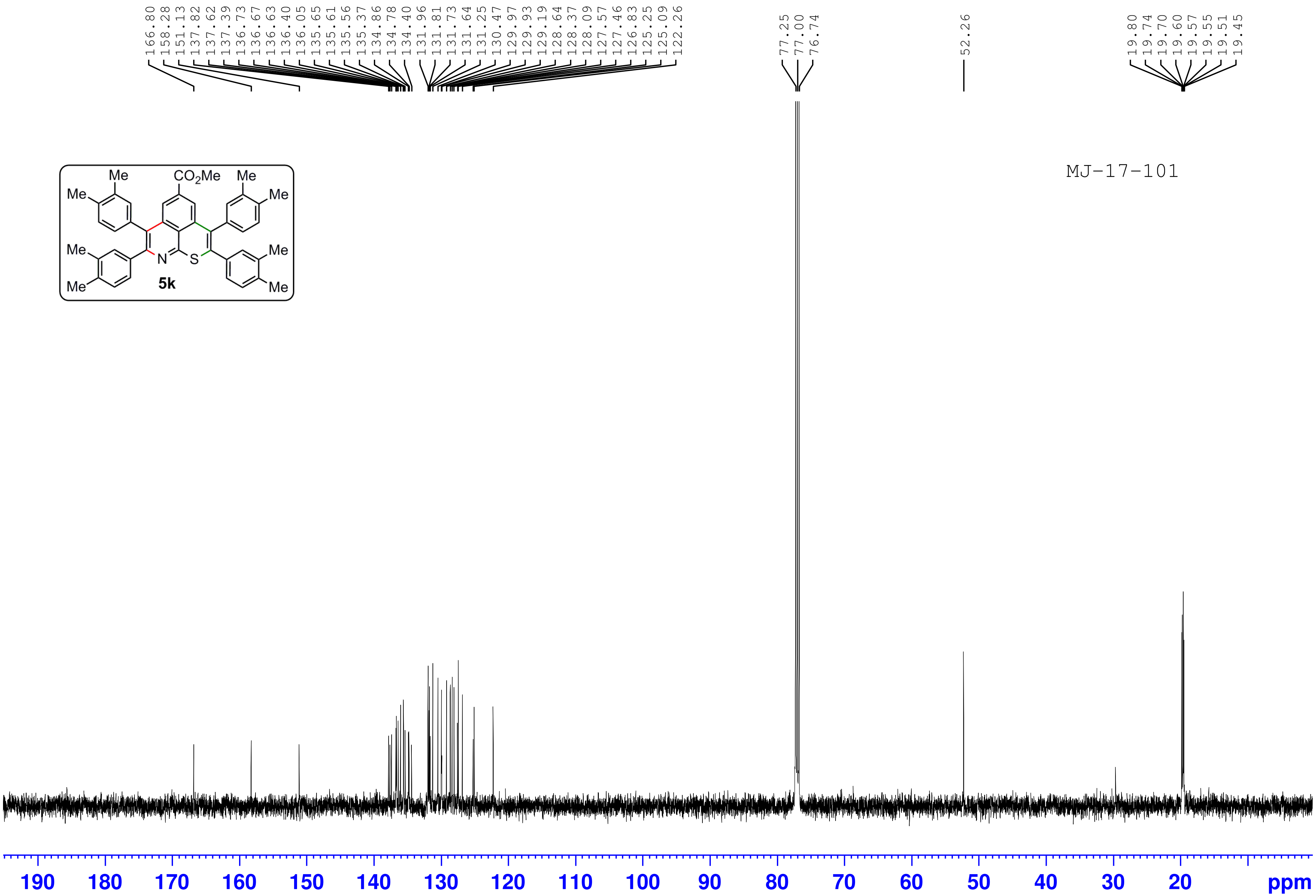
MJ-17-246 R

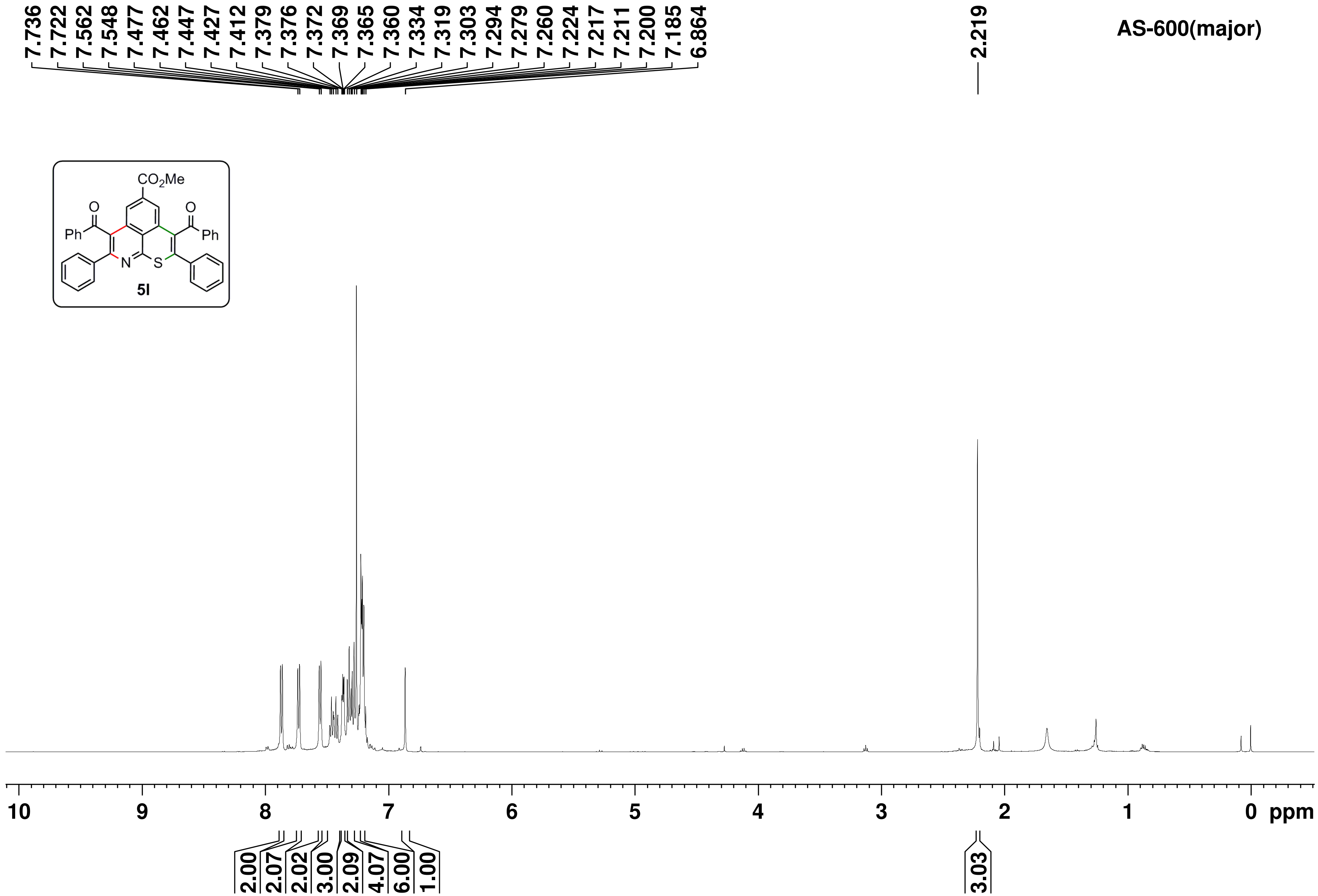

-111.694
-111.734
-111.770
-111.812
-112.108
-113.432
-111.69
-111.73
-111.77
-111.81
-112.11
-113.43
-112.0
-112.5
-113.0
ppm

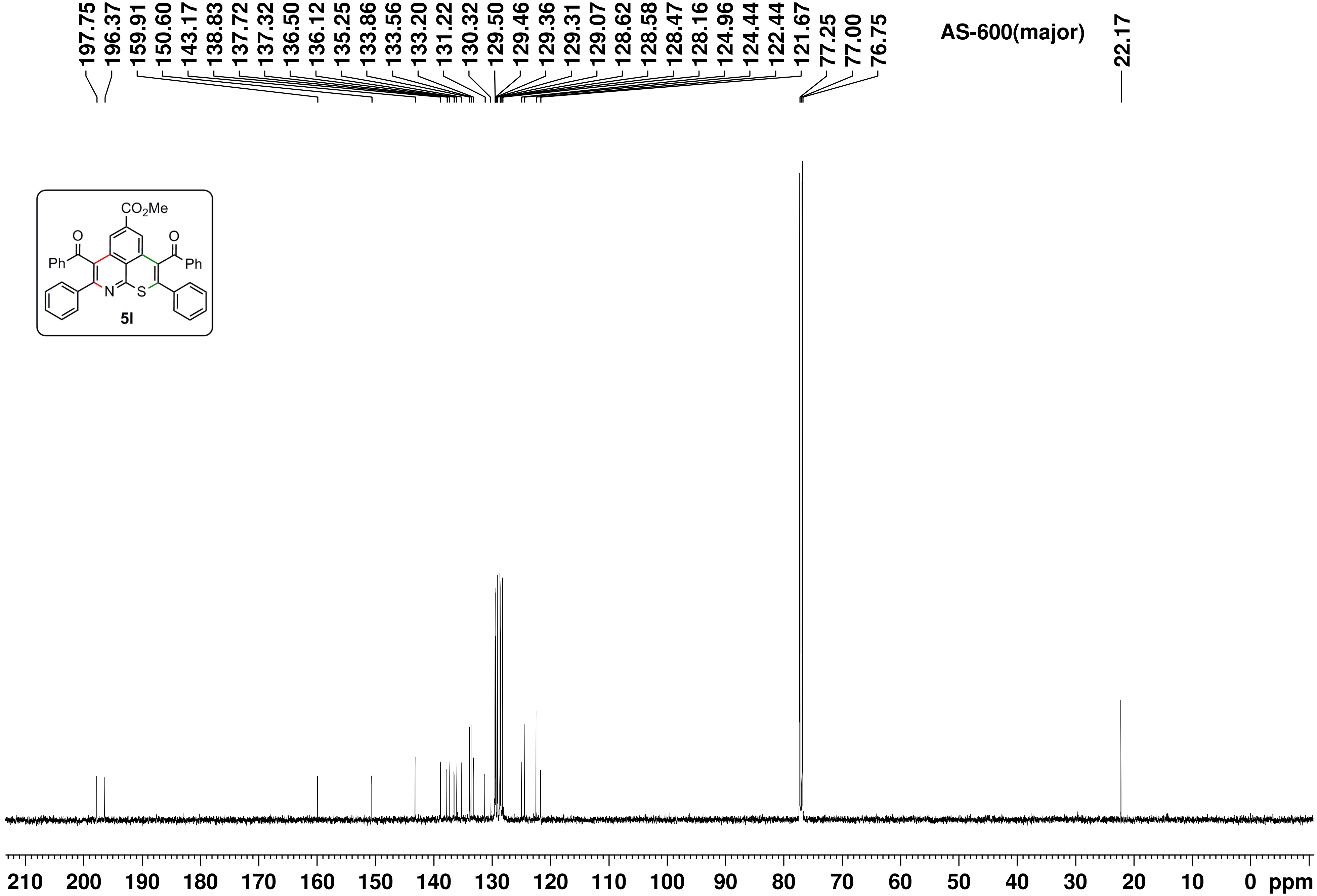

0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm


F
CO_2Me
F
N
S
F
F
5j


7.915
7.913
7.374
7.372
7.260
7.241
7.135
7.120
7.049
7.034
7.018
6.973
6.960
6.923
6.909
6.891
6.876
6.853
6.838
3.740
2.303
2.236
2.225
2.184
2.165
2.132
MJ-17-101
Me
Me
CO2Me
Me
Me
Me
N
S
Me
Me
Me
5k
10
9
8
7
6
5
4
3
2
1
ppm
1.02
1.07
1.05
1.06
1.17
1.00
2.07
5.31
1.02
3.00
3.11
3.00
3.17
12.03
3.07

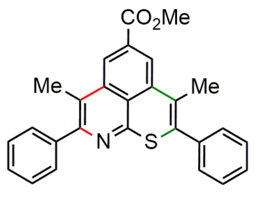

166.80
158.28
151.13
137.82
137.62
137.39
136.73
136.67
136.63
136.40
136.05
135.65
135.61
135.56
135.37
134.86
134.78
134.40
131.96
131.81
131.73
131.64
131.25
130.47
129.97
129.93
129.19
128.64
128.37
128.09
127.57
127.46
126.83
125.25
125.09
122.26
77.25
77.00
76.74
52.26
19.80
19.74
19.70
19.60
19.57
19.55
19.51
19.45
MJ-17-101
Me
Me
CO_2Me
Me
Me
Me
Me
N
S
Me
Me
5k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.736
7.722
7.562
7.548
7.477
7.462
7.447
7.427
7.412
7.379
7.376
7.372
7.369
7.365
7.360
7.334
7.319
7.303
7.294
7.279
7.260
7.224
7.217
7.211
7.200
7.185
6.864
2.219
AS-600(major)
CO2Me
O
O
Ph
Ph
N
S
5l
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.07
2.02
3.00
2.09
4.07
6.00
1.00
3.03

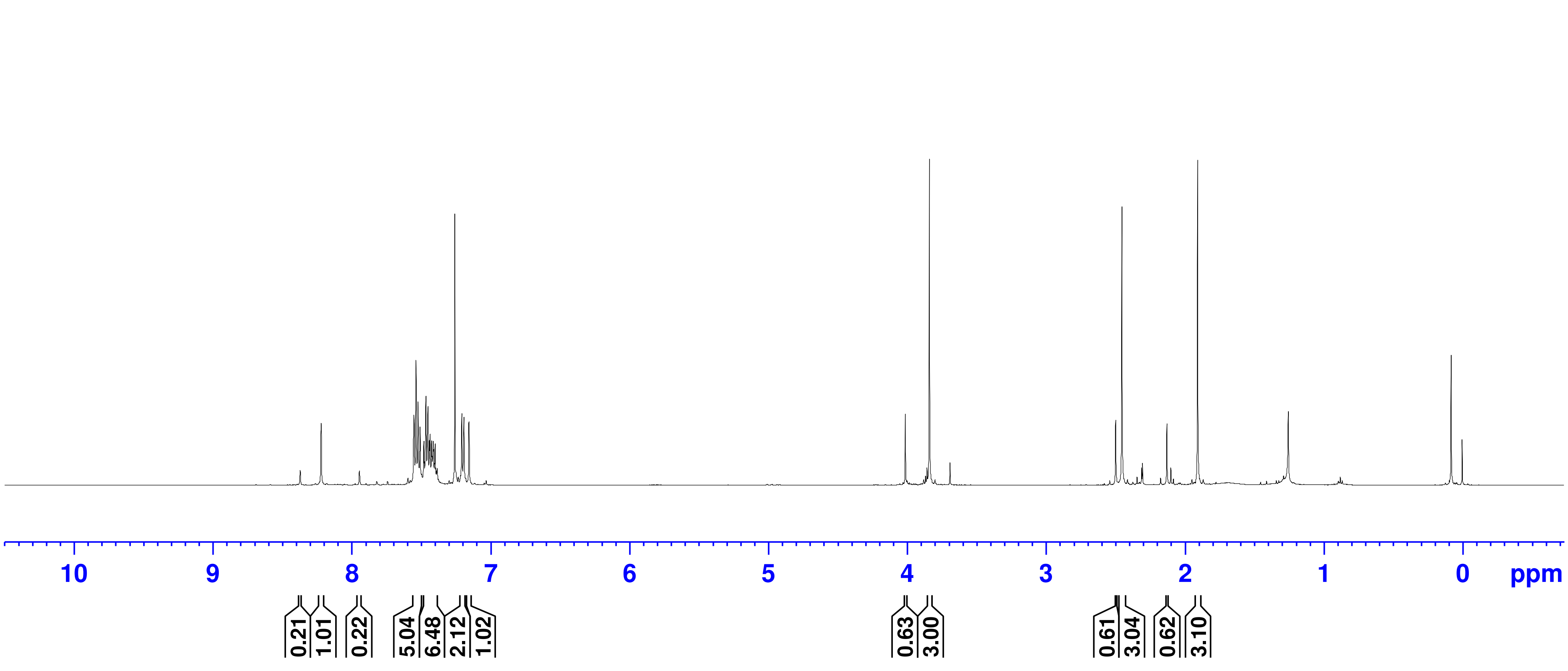

197.75
196.37
159.91
150.60
143.17
138.83
137.72
137.32
136.50
136.12
135.25
133.86
133.56
133.20
131.22
130.32
129.50
129.46
129.36
129.31
129.07
128.62
128.58
128.47
128.16
124.96
124.44
122.44
121.67
77.25
77.00
76.75
AS-600(major)
22.17
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
CO2Me
O
Ph
O
Ph
N
S

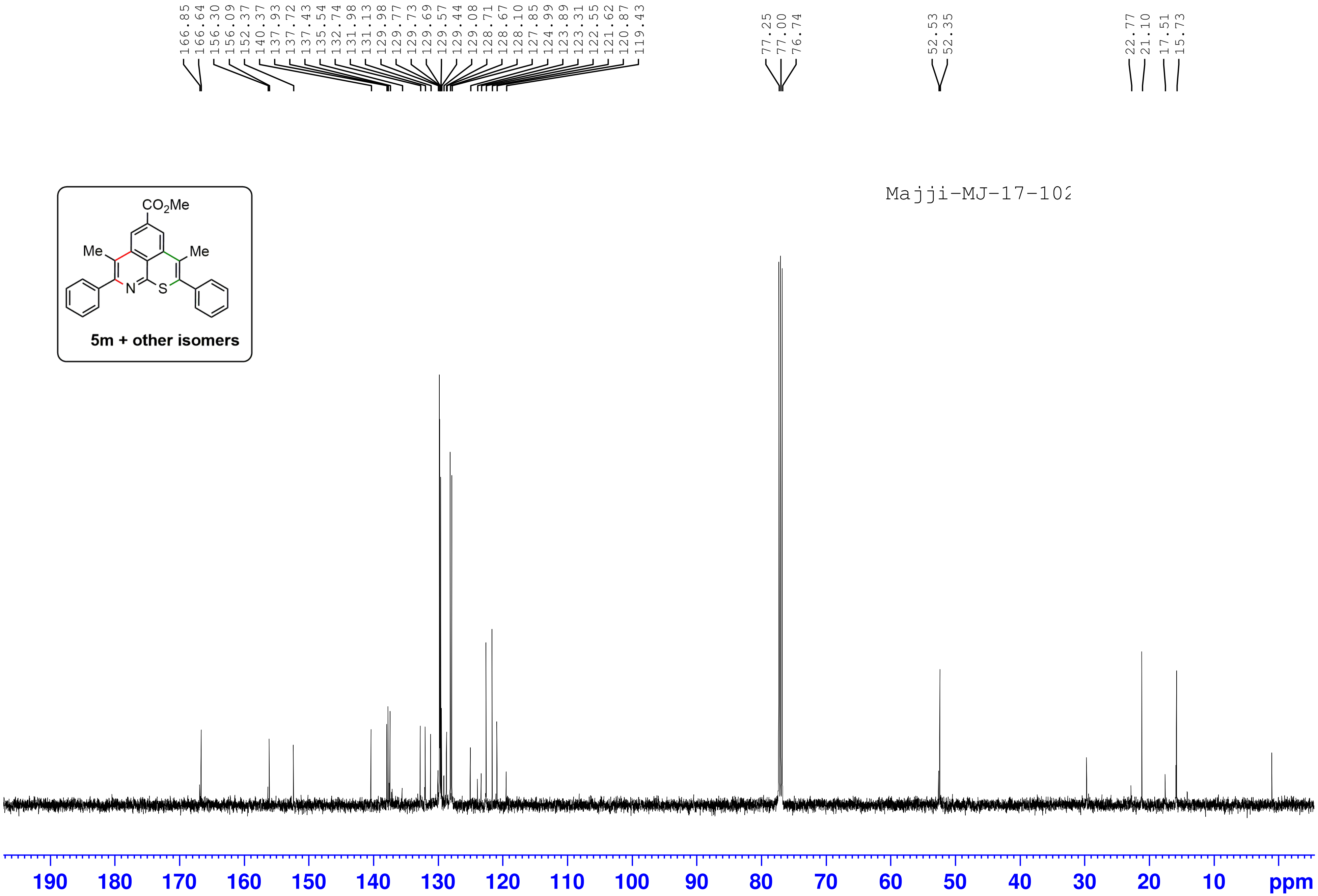
5l

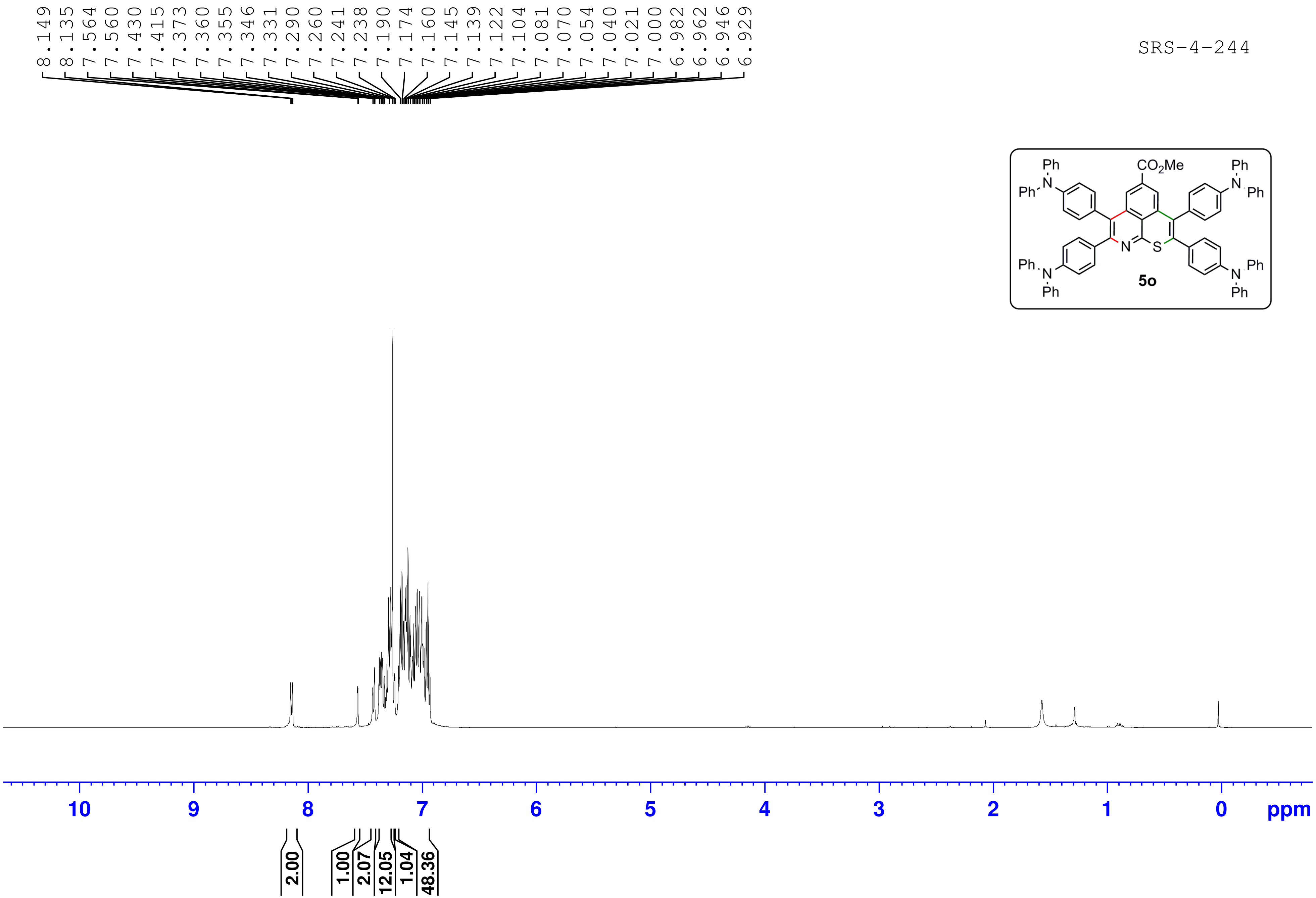
Majji-MJ-17-102

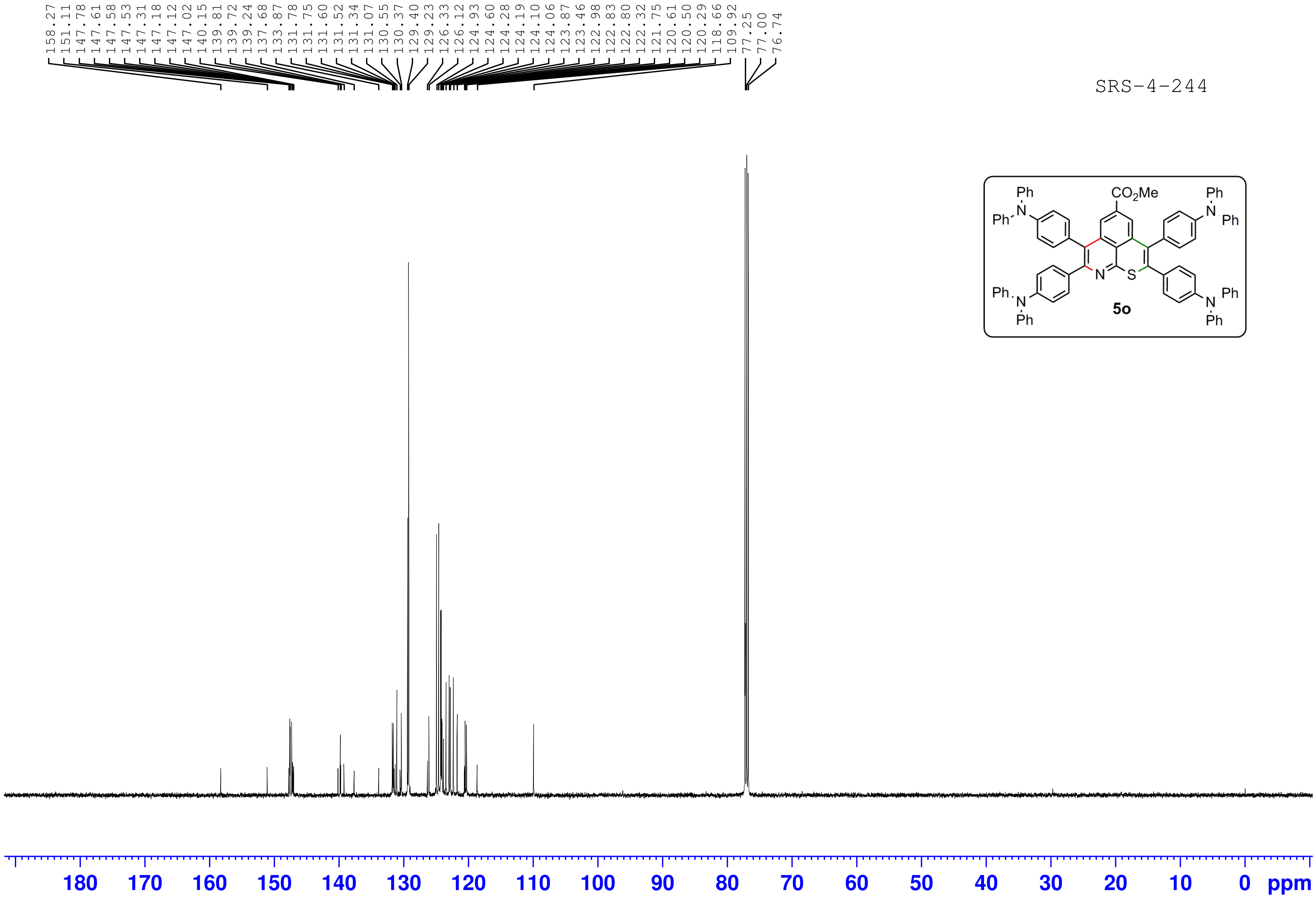


5m + other isomers

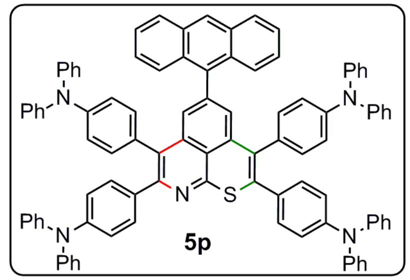


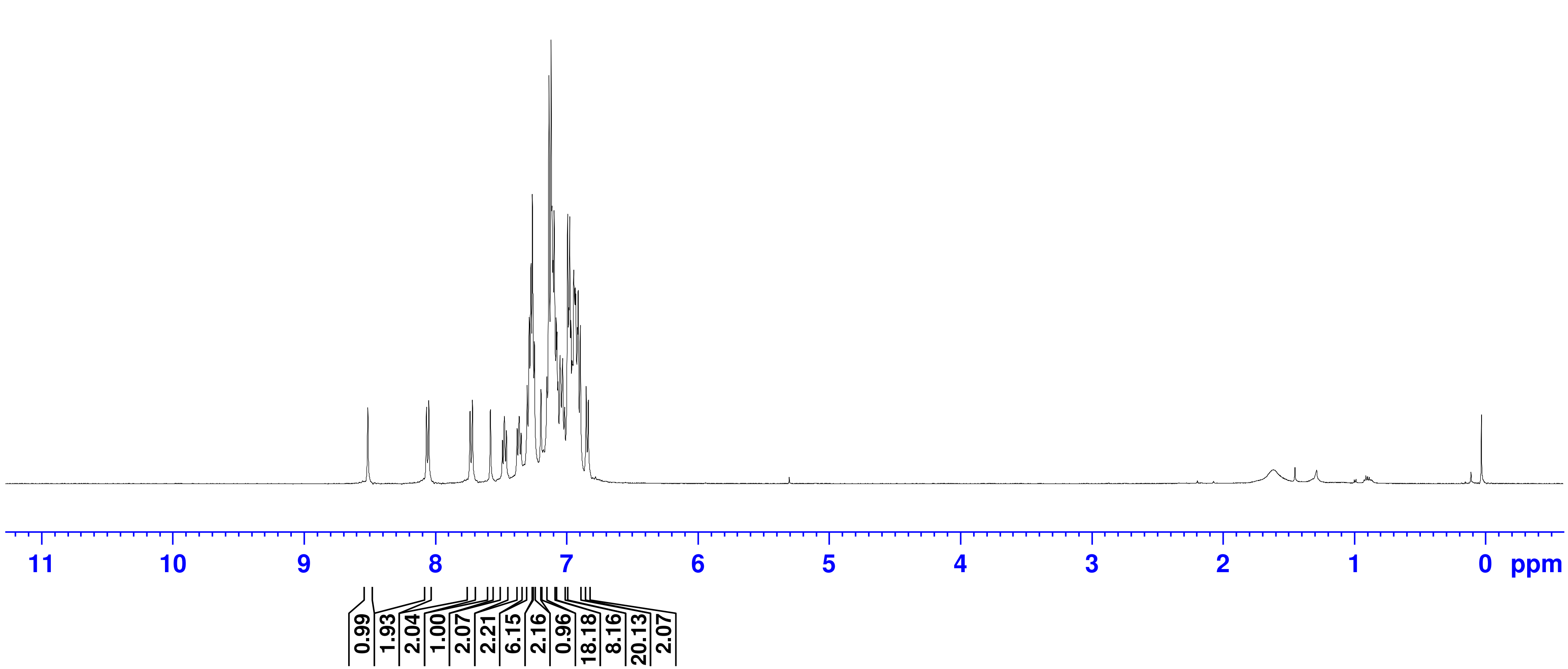

166.85
166.64
156.30
156.09
152.37
140.37
137.93
137.72
137.43
135.54
132.74
131.98
131.13
129.98
129.77
129.73
129.69
129.57
129.44
129.08
128.71
128.67
128.10
127.85
124.99
123.89
123.31
122.55
121.62
120.87
119.43
77.25
77.00
76.74
52.53
52.35
22.77
21.10
17.51
15.73
Majji-MJ-17-10
CO2Me
Me
Me
N
S
5m + other isomers
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

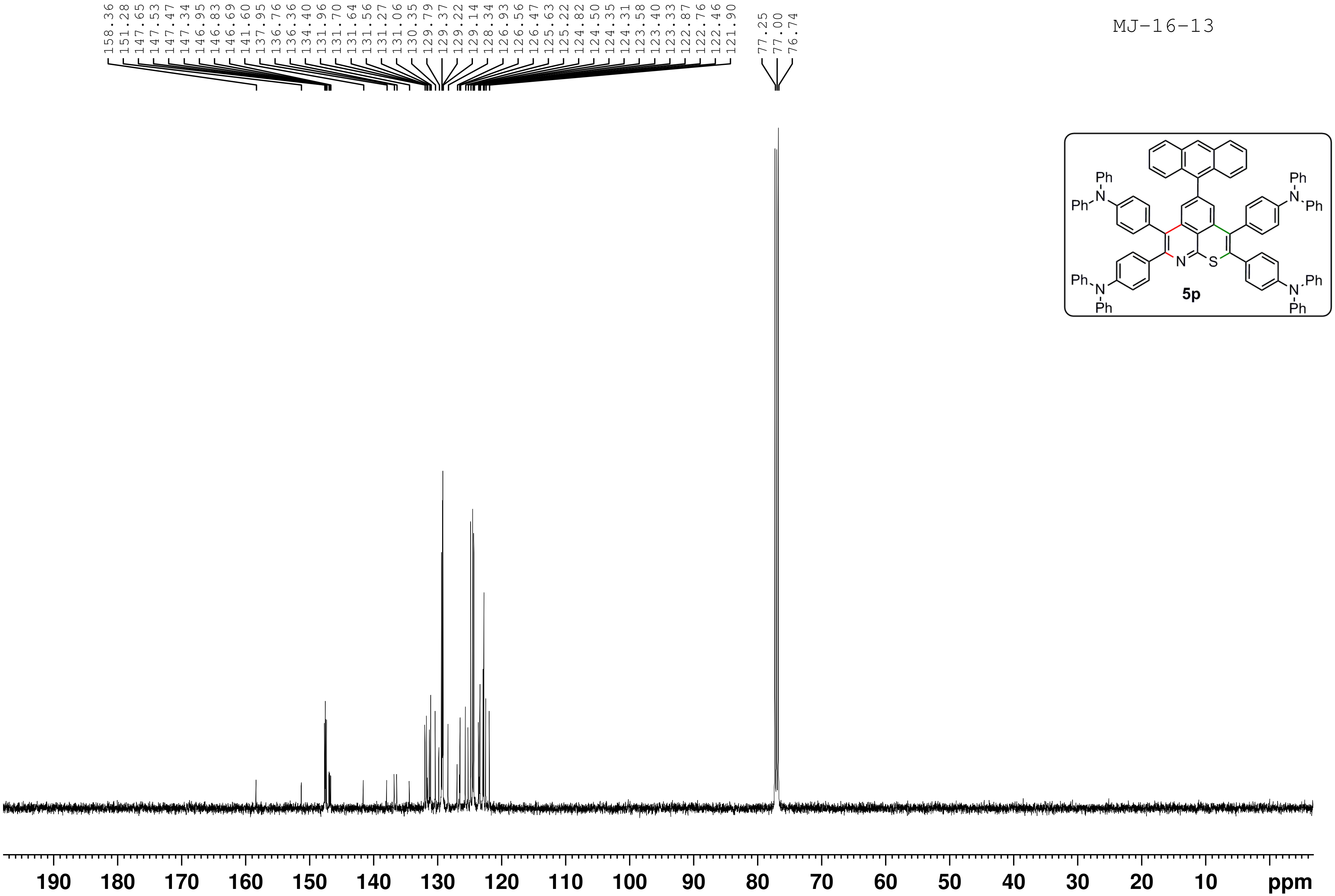

8.149
8.135
7.564
7.560
7.430
7.415
7.373
7.360
7.355
7.346
7.331
7.290
7.260
7.241
7.238
7.190
7.174
7.160
7.145
7.139
7.122
7.104
7.081
7.070
7.054
7.040
7.021
7.000
6.982
6.962
6.946
6.929
SRS-4-244
Ph
Ph
N
CO2Me
Ph
N
Ph
Ph
N
Ph
N
S
Ph
N
Ph
5o
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.00
2.07
12.05
1.04
48.36

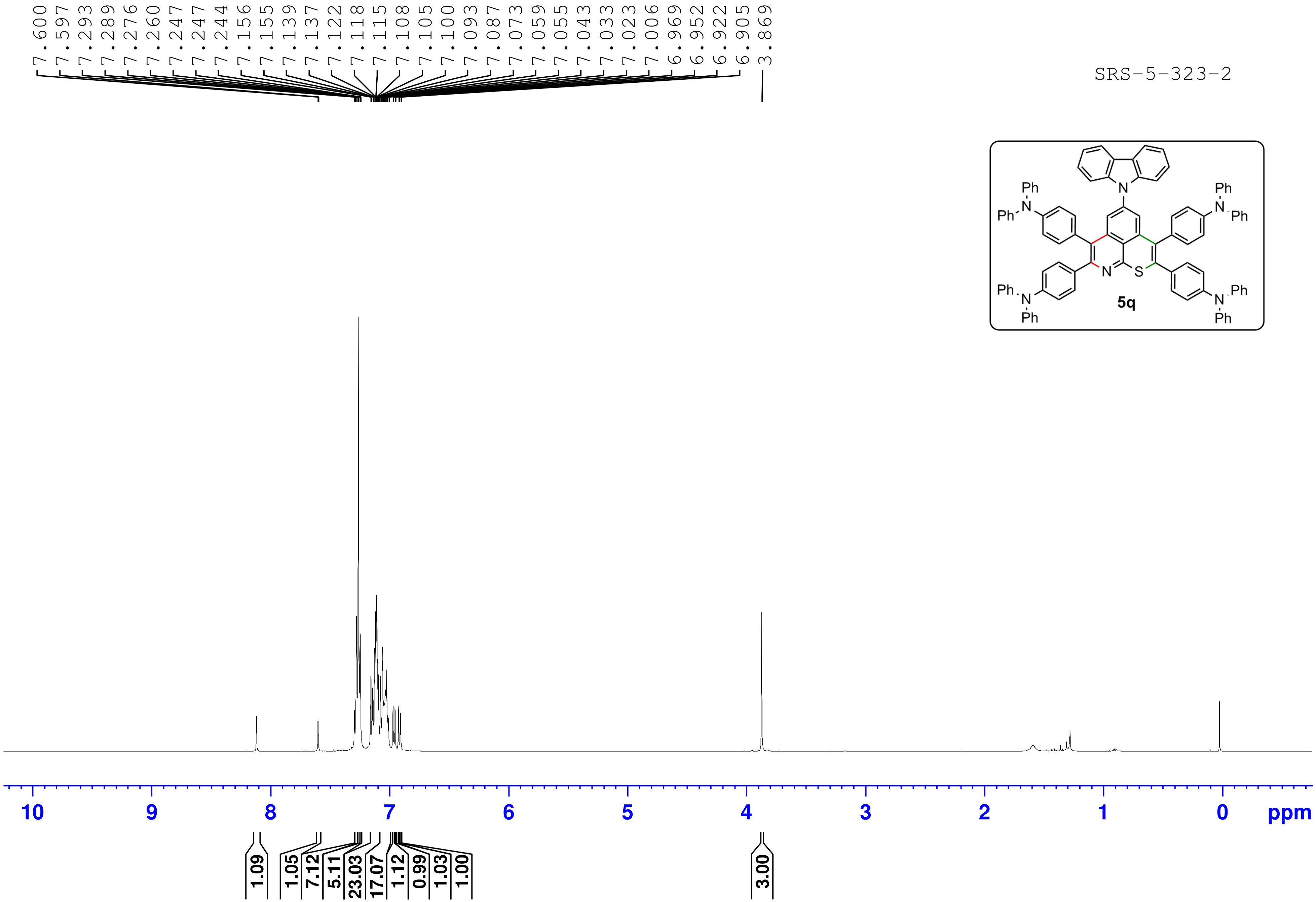

158.27
151.11
147.78
147.61
147.58
147.53
147.31
147.18
147.12
147.02
140.15
139.81
139.72
139.24
137.68
133.87
131.78
131.75
131.60
131.52
131.34
131.07
130.55
130.37
129.40
129.23
126.33
126.12
124.93
124.60
124.28
124.19
124.10
124.06
123.87
123.46
122.98
122.83
122.80
122.32
121.75
120.61
120.50
120.29
118.66
109.92
77.25
77.00
76.74
SRS-4-244
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
CO2Me
Ph
N
Ph
S
5o

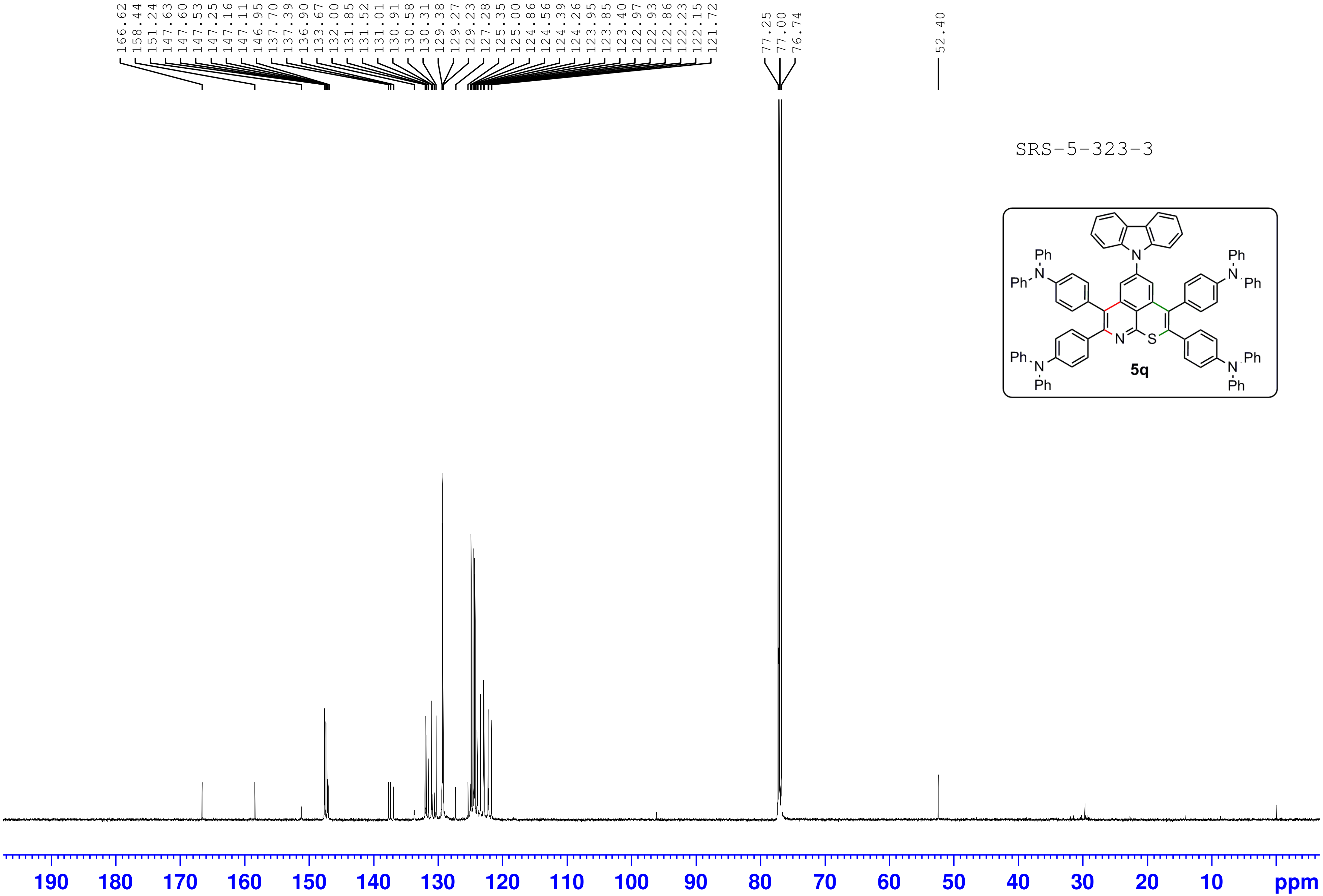
MJ-16-13

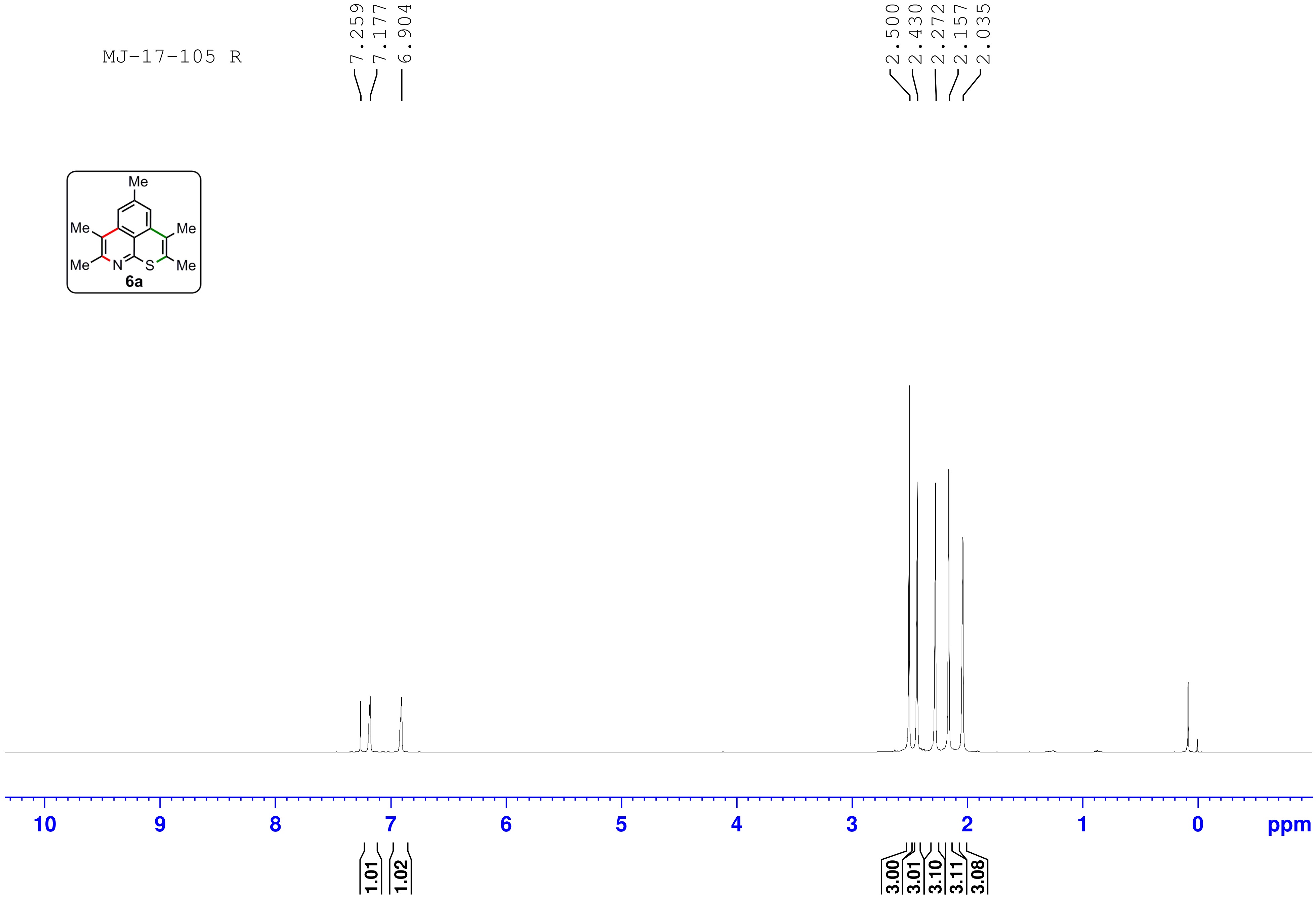

Ph
N
Ph
Ph
N
Ph
N
S
Ph
N
Ph
Ph
N
Ph
5p

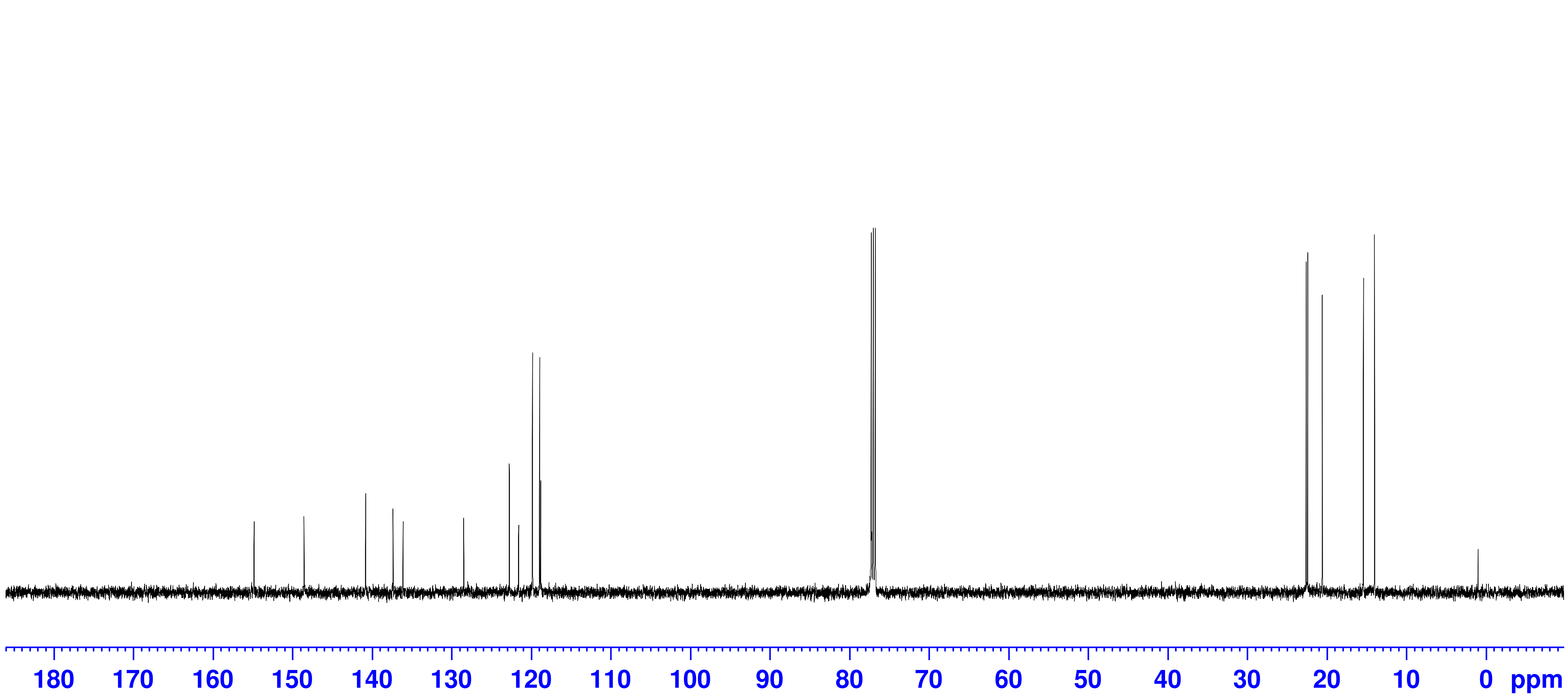

8.513
8.066
8.049
7.734
7.716
7.579
7.487
7.473
7.458
7.376
7.360
7.345
7.299
7.282
7.270
7.259
7.243
7.195
7.149
7.133
7.117
7.109
7.094
7.077
7.072
7.048
7.028
7.013
6.991
6.974
6.944
6.934
6.928
6.910
6.894
6.850
6.833
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.99
1.93
2.04
1.00
2.07
2.21
6.15
2.16
0.96
18.18
8.16
20.13
2.07

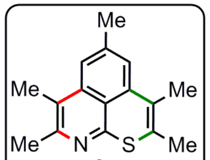

158.36
151.28
147.65
147.53
147.47
147.34
146.95
146.83
146.69
141.60
137.95
136.76
136.36
134.40
131.96
131.70
131.64
131.56
131.27
131.06
130.35
129.79
129.37
129.22
129.14
128.34
126.93
126.56
126.47
125.63
125.22
124.82
124.50
124.35
124.31
123.58
123.40
123.33
122.87
122.76
122.46
121.90
77.25
77.00
76.74
MJ-16-13
Ph
N
Ph
Ph
N
Ph
N
S
Ph
N
Ph
Ph
N
Ph
5p
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.600
7.597
7.293
7.289
7.276
7.260
7.247
7.247
7.244
7.156
7.155
7.139
7.137
7.122
7.118
7.115
7.108
7.105
7.100
7.093
7.087
7.073
7.059
7.055
7.043
7.033
7.023
7.006
6.969
6.952
6.922
6.905
3.869
SRS-5-323-2
Ph
N
Ph
Ph
N
Ph
N
N
S
Ph
N
Ph
Ph
N
Ph
5q
10
9
8
7
6
5
4
3
2
1
0
ppm
1.09
1.05
7.12
5.11
23.03
17.07
1.12
0.99
1.03
1.00
3.00


166.62
158.44
151.24
147.63
147.60
147.53
147.25
147.16
147.11
146.95
137.70
137.39
136.90
133.67
132.00
131.85
131.52
131.01
130.91
130.58
130.31
129.38
129.27
129.23
127.28
125.35
125.00
124.86
124.56
124.39
124.26
123.95
123.85
123.40
122.97
122.93
122.86
122.23
122.15
121.72
77.25
77.00
76.74
52.40
SRS-5-323-3
Ph
N
Ph
S
5q
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

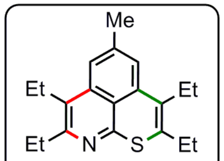

MJ-17-105 R
7.259
7.177
6.904
2.500
2.430
2.272
2.157
2.035
Me
Me
Me
Me
Me
N
S
6a
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
1.02
3.00
3.01
3.10
3.11
3.08


MJ-17-105 R
154.82
148.53
140.78
137.35
136.08
128.47
122.74
121.57
119.83
118.93
118.78
77.25
77.00
76.74
22.58
22.40
20.58
15.40
13.99
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

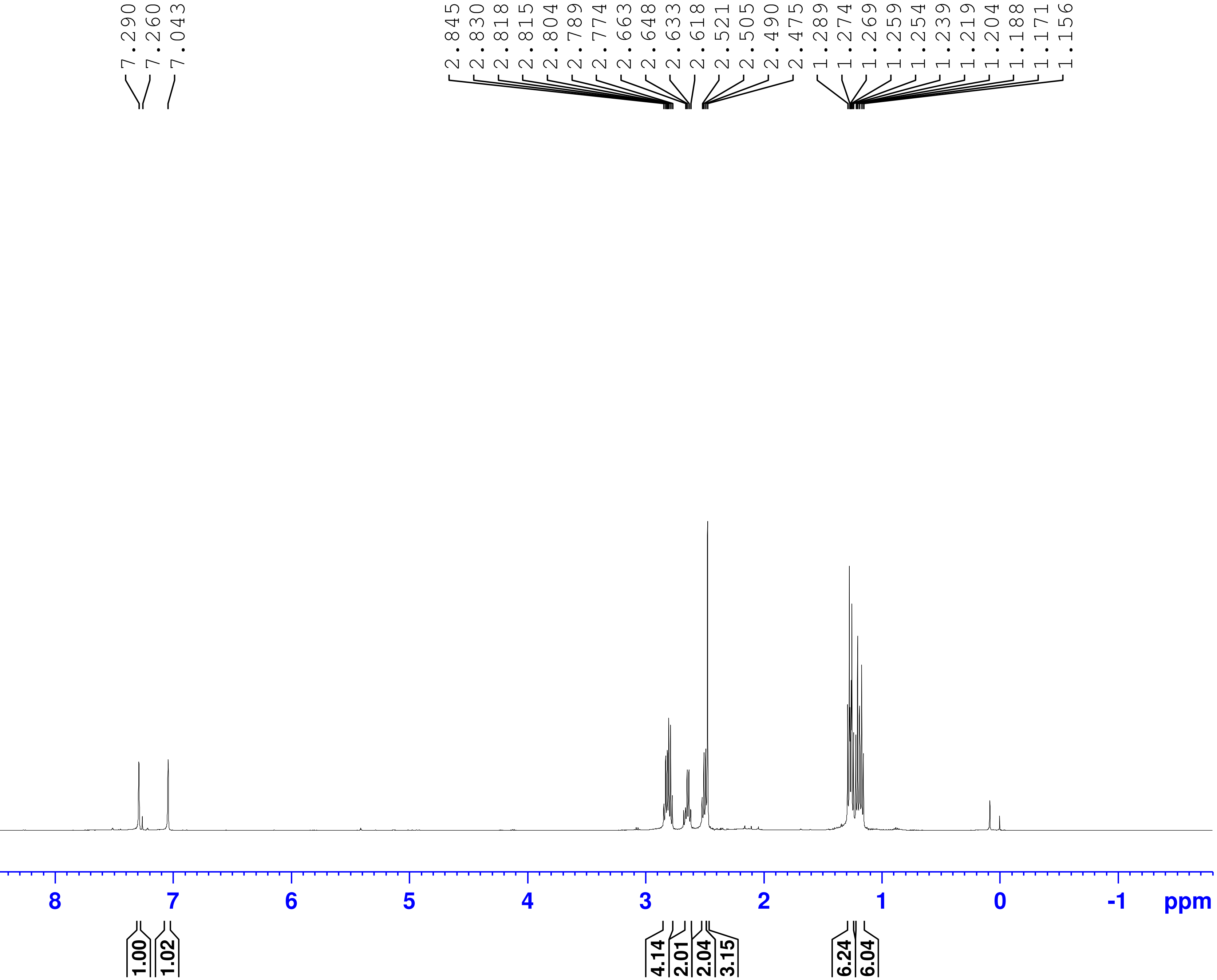

Me
Me
Me
Me
Me
N
S

6a

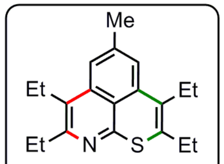
MAJJI-16-18



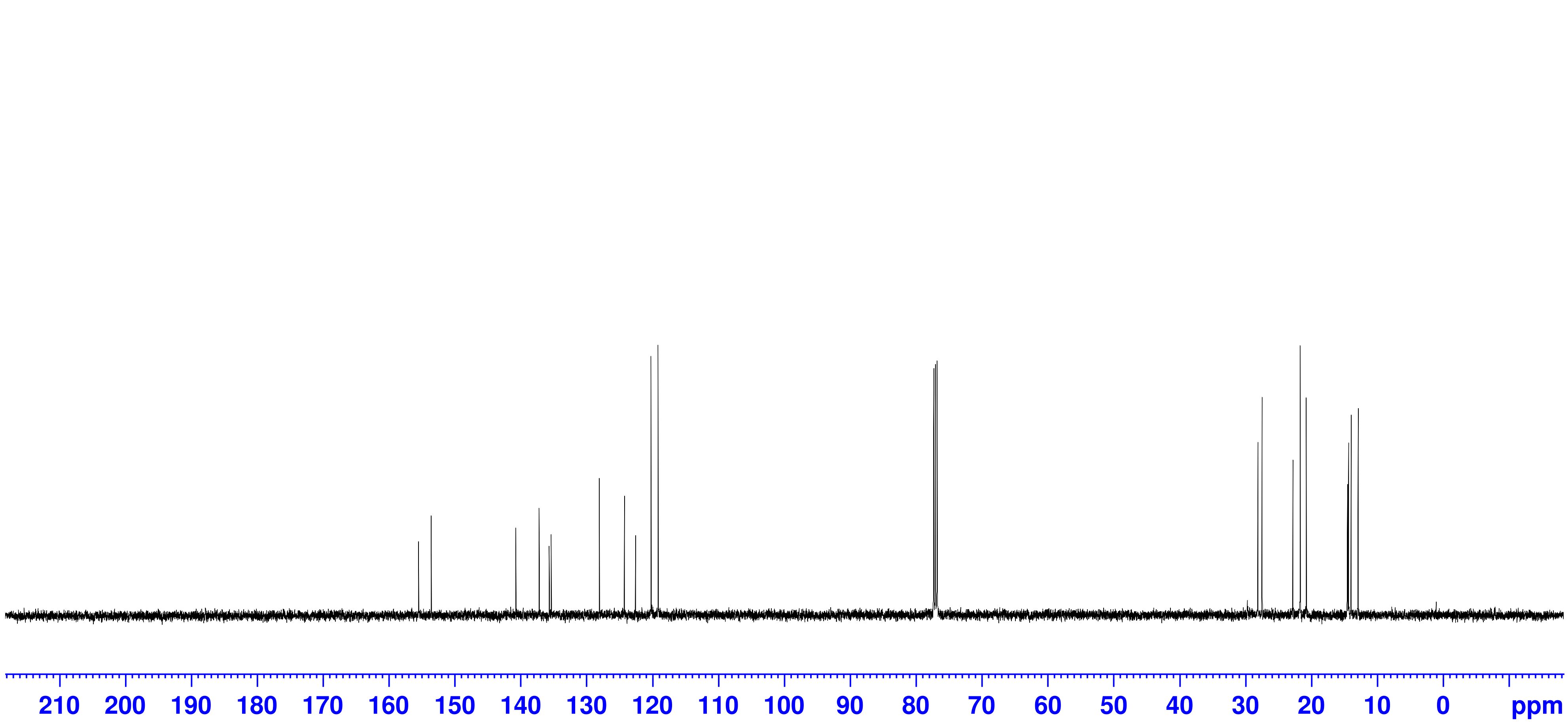
6b



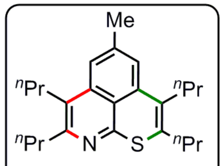
MAJJI-16-18



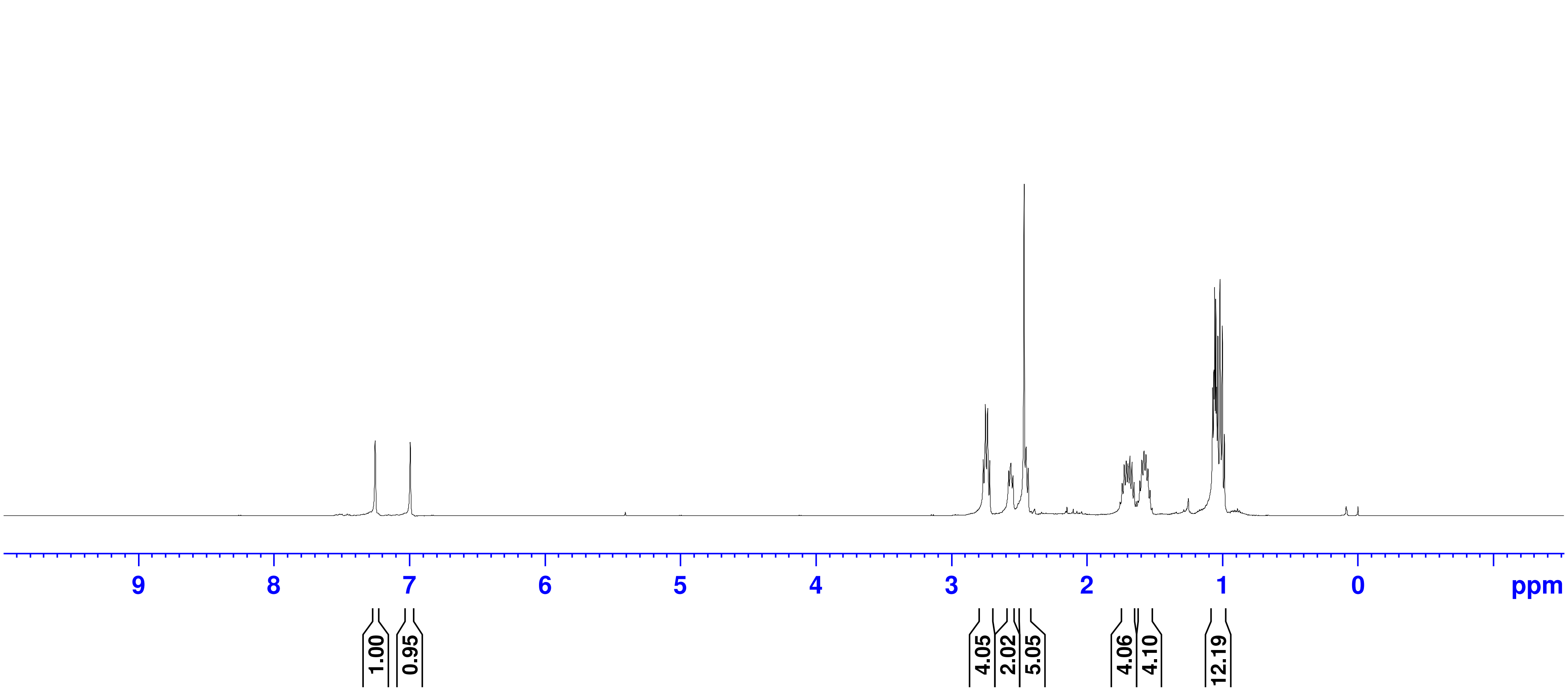
6b

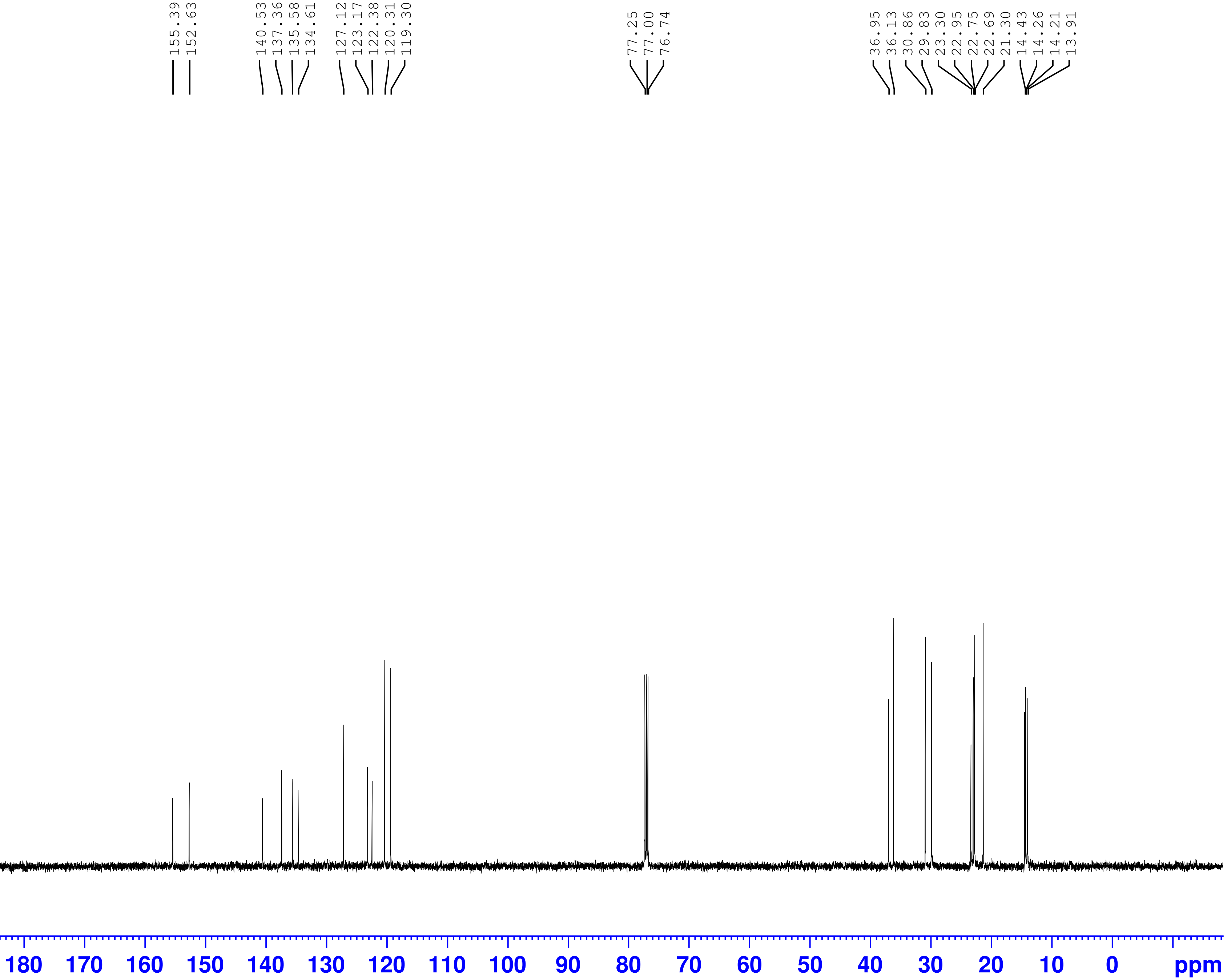


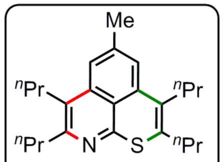
MAJJI-16-19



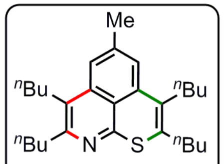
6c



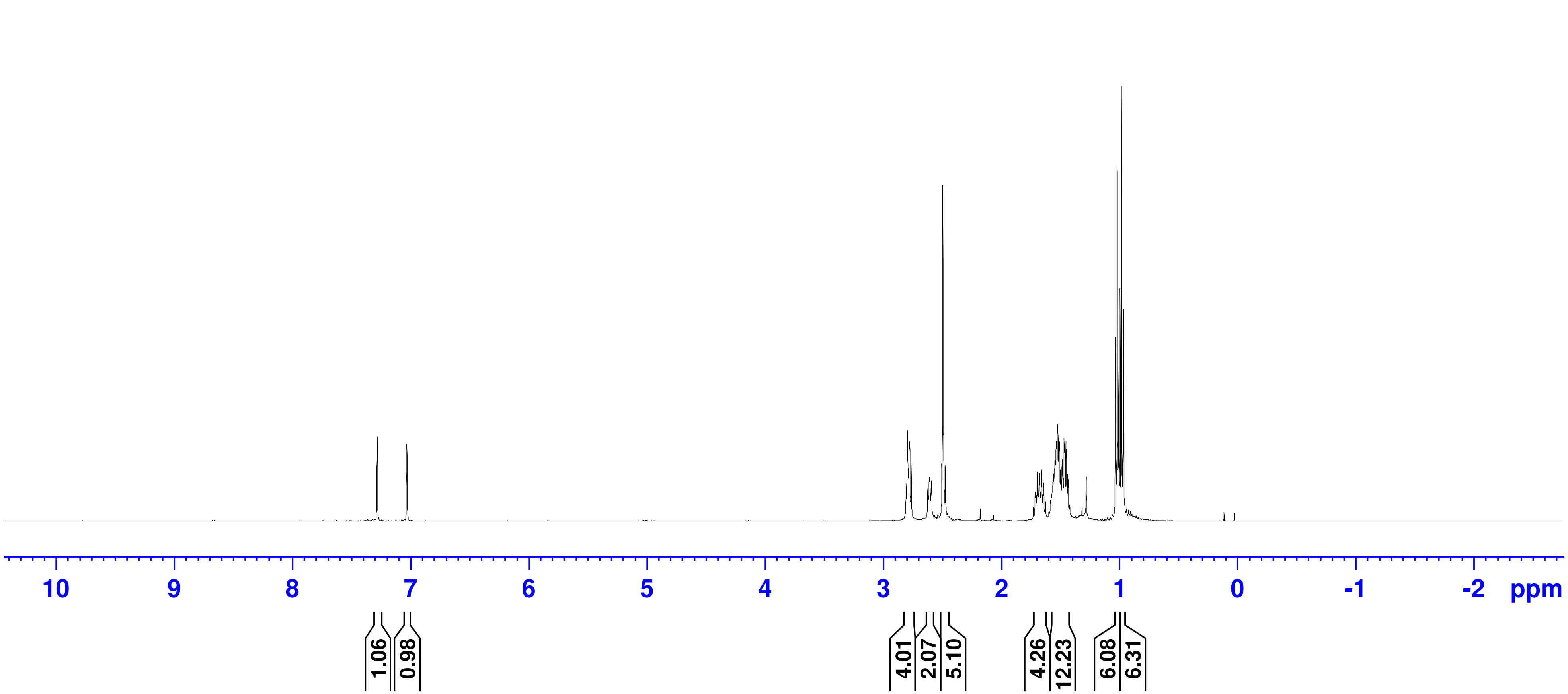

MAJJI-16-19
155.39
152.63
140.53
137.36
135.58
134.61
127.12
123.17
122.38
120.31
119.30
77.25
77.00
76.74
36.95
36.13
30.86
29.83
23.30
22.95
22.75
22.69
21.30
14.43
14.26
14.21
13.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


Me
^{n}Pr
^{n}Pr
^{n}Pr
^{n}Pr
N
S

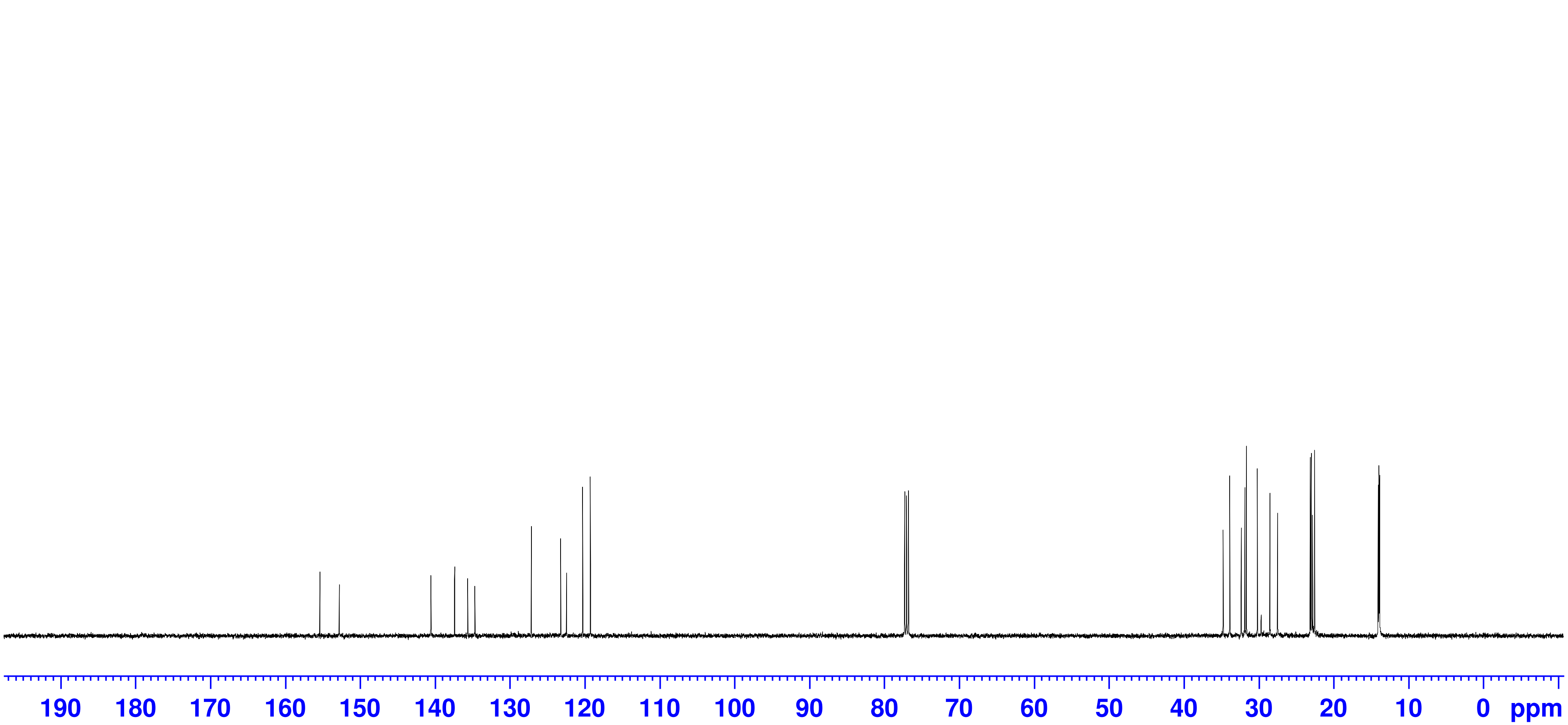
6c

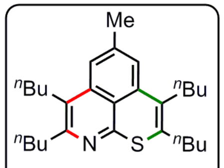

Me
nBu
nBu
nBu
nBu
N
S

6d


MAJJI-16-20
7.281
7.030
2.804
2.792
2.775
2.773
2.760
2.620
2.606
2.589
2.501
2.492
2.469
1.724
1.709
1.693
1.673
1.655
1.640
1.625
1.580
1.554
1.542
1.531
1.518
1.505
1.491
1.480
1.476
1.465
1.461
1.451
1.446
1.436
1.432
1.031
1.016
1.002
0.991
0.977
0.962
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm
1.06
0.98
4.01
2.07
5.10
4.26
12.23
6.08
6.31

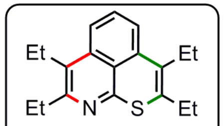
MAJJI-16-20



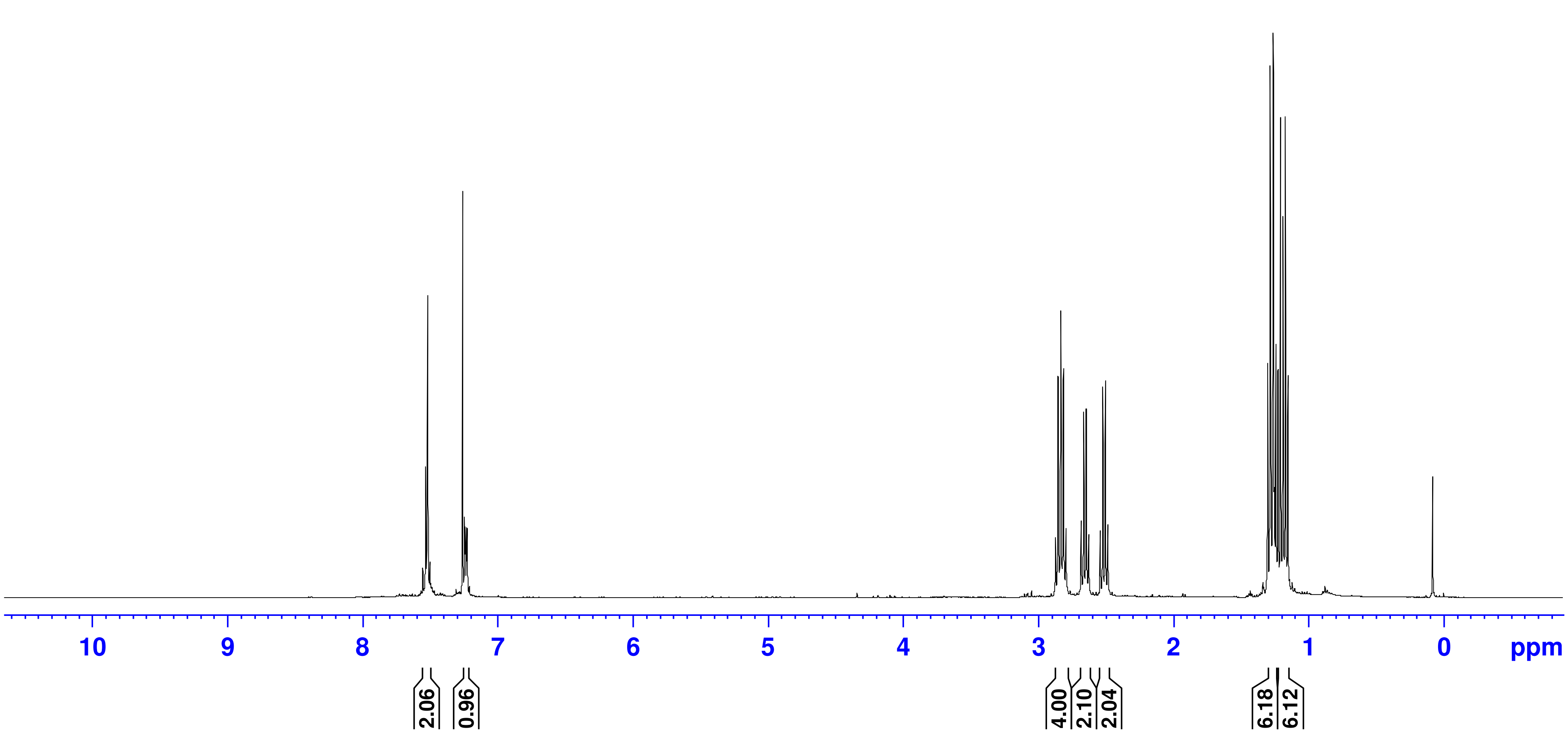


6d

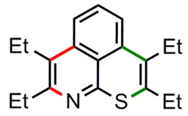
AG-6-143


Et
Et
Et
Et
N
S

6e

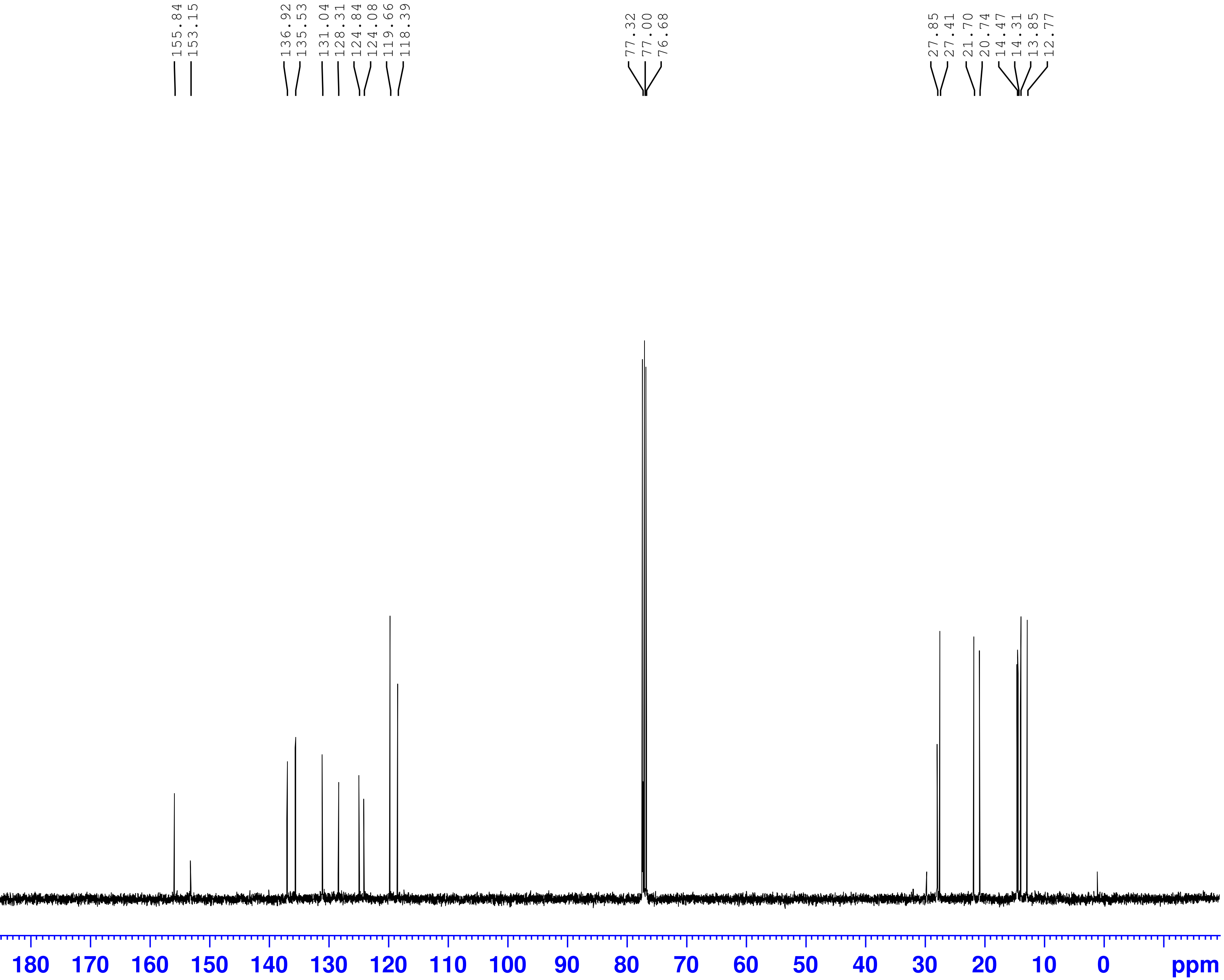

7.555
7.534
7.523
7.518
7.502
7.260
7.247
7.241
7.231
7.225
2.871
2.852
2.832
2.812
2.793
2.681
2.662
2.643
2.624
2.539
2.520
2.501
2.483
1.300
1.281
1.277
1.262
1.258
1.251
1.239
1.224
1.205
1.187
1.169
1.150
10
9
8
7
6
5
4
3
2
1
0
ppm
2.06
0.96
4.00
2.10
2.04
6.18
6.12

AG-6-143

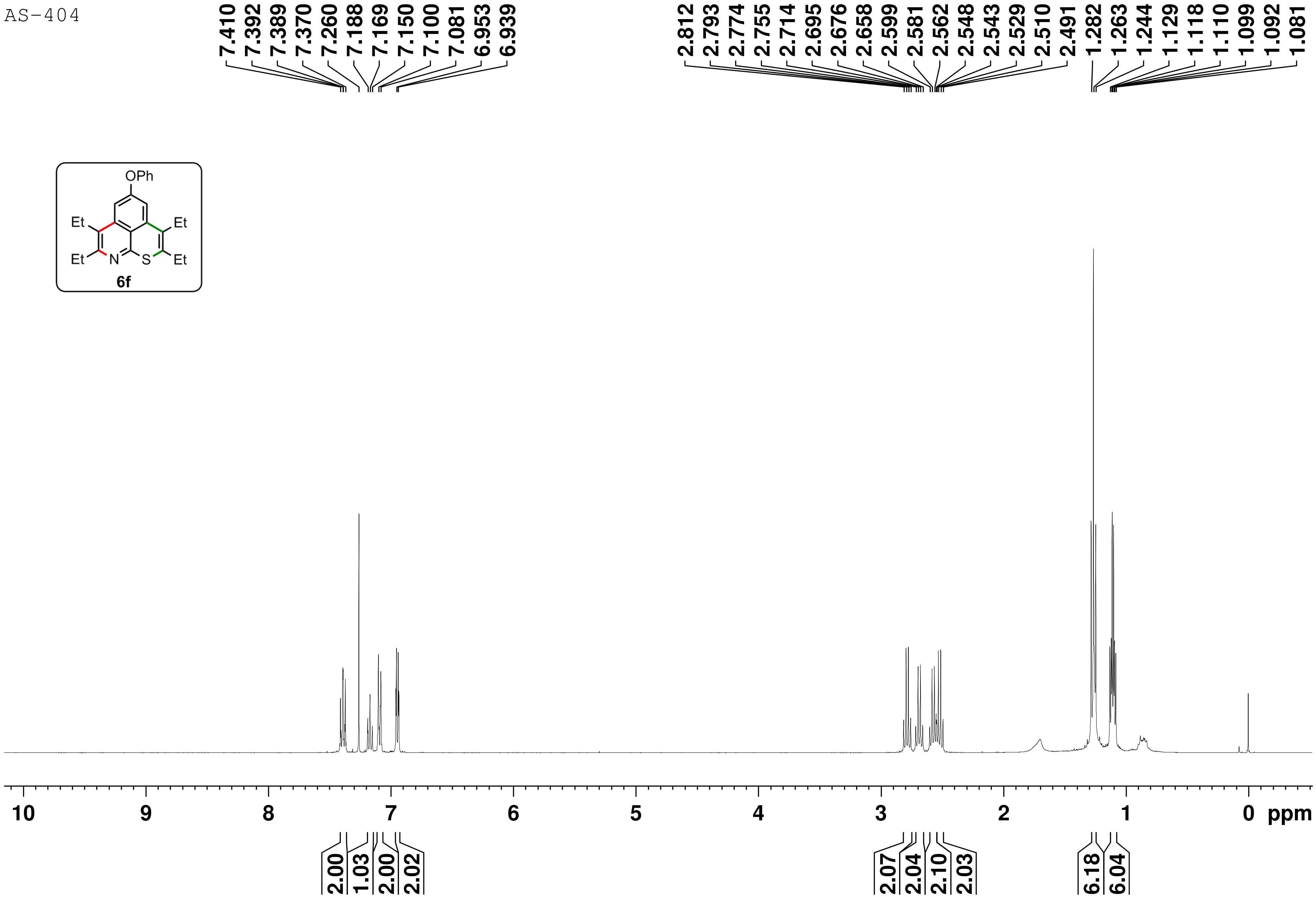


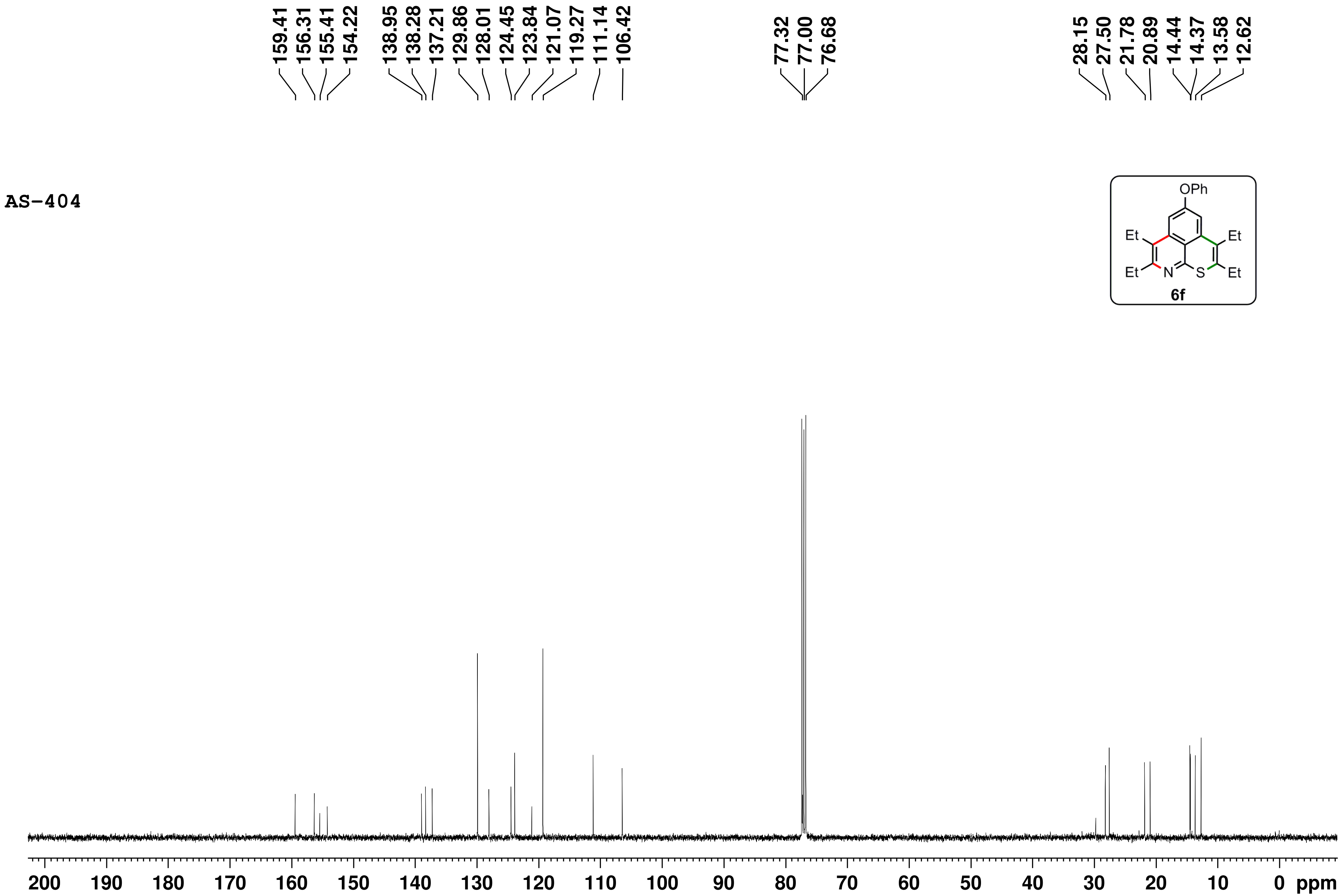
Et
Et
Et
Et
N
S

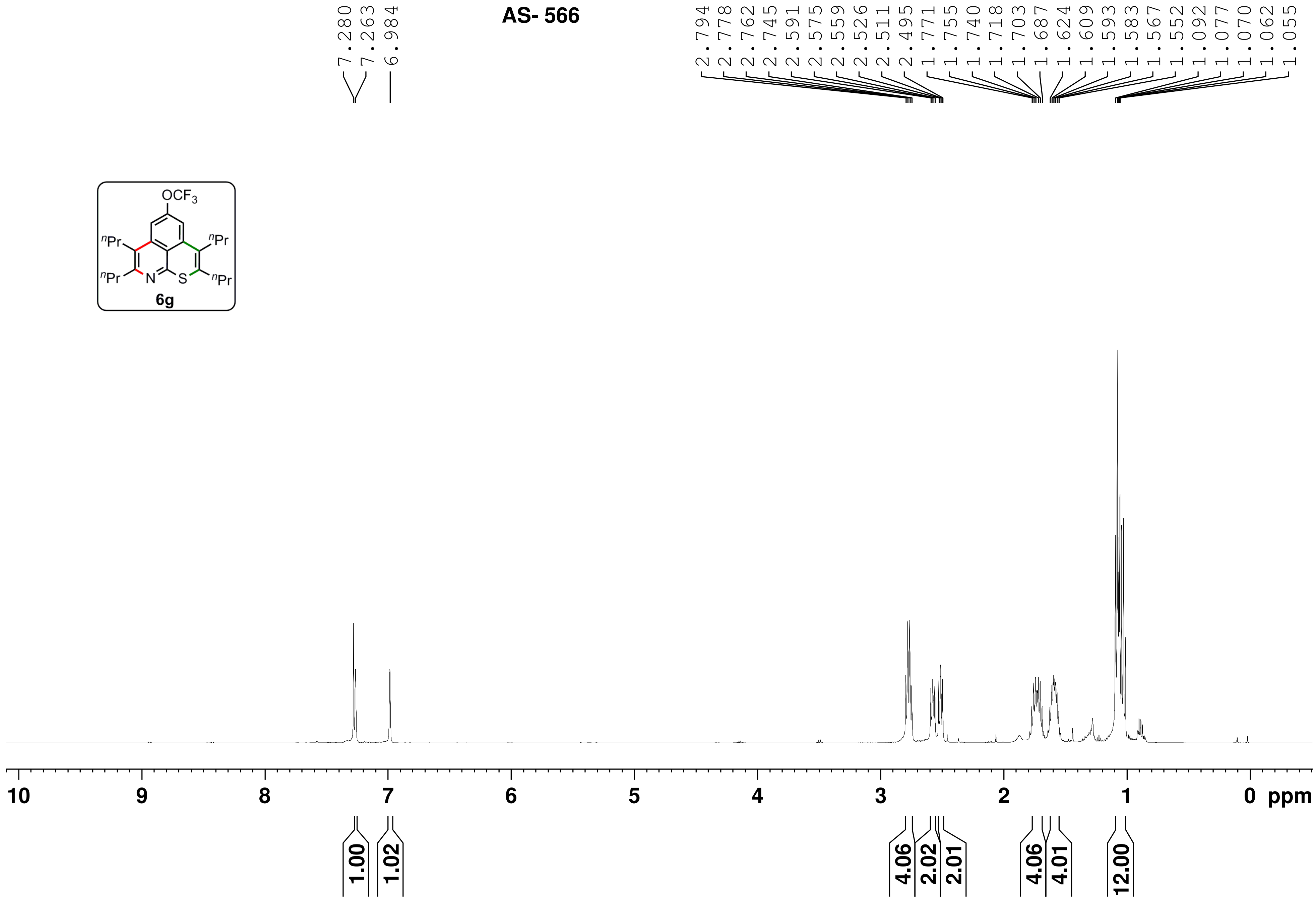
6e



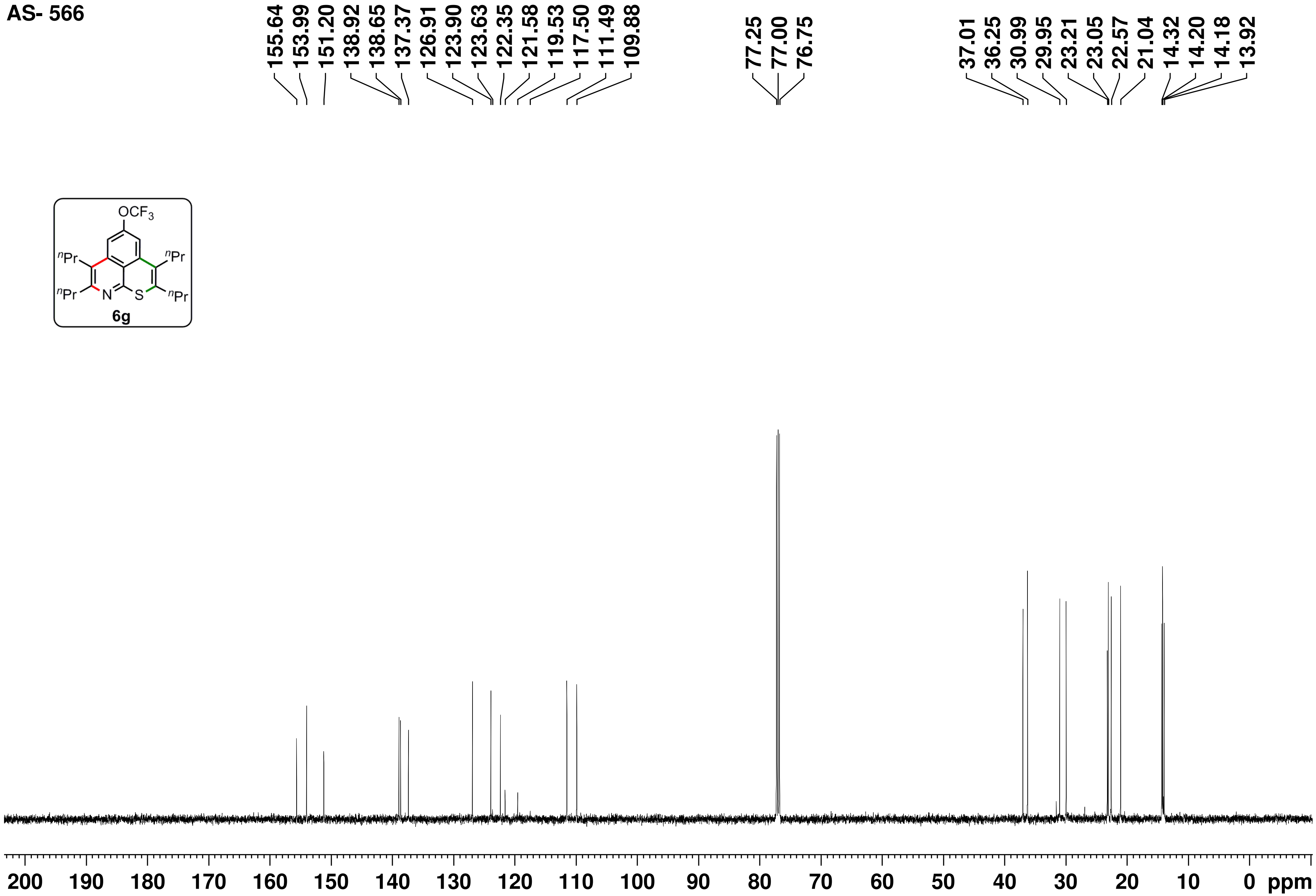
155.84
153.15
136.92
135.53
131.04
128.31
124.84
124.08
119.66
118.39
77.32
77.00
76.68
27.85
27.41
21.70
20.74
14.47
14.31
13.85
12.77
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


AS-404
7.410 7.392 7.389 7.370 7.260 7.188 7.169 7.150 7.100 7.081 6.953 6.939
2.812 2.793 2.774 2.755 2.714 2.695 2.676 2.658 2.599 2.581 2.562 2.548 2.543 2.529 2.510 2.491 1.282 1.263 1.244 1.129 1.118 1.110 1.099 1.092 1.081
OPh
Et
Et
Et
Et
N
S
6f
10 9 8 7 6 5 4 3 2 1 0 ppm
2.00 1.03 2.00 2.02
2.07 2.04 2.10 2.03
6.18 6.04

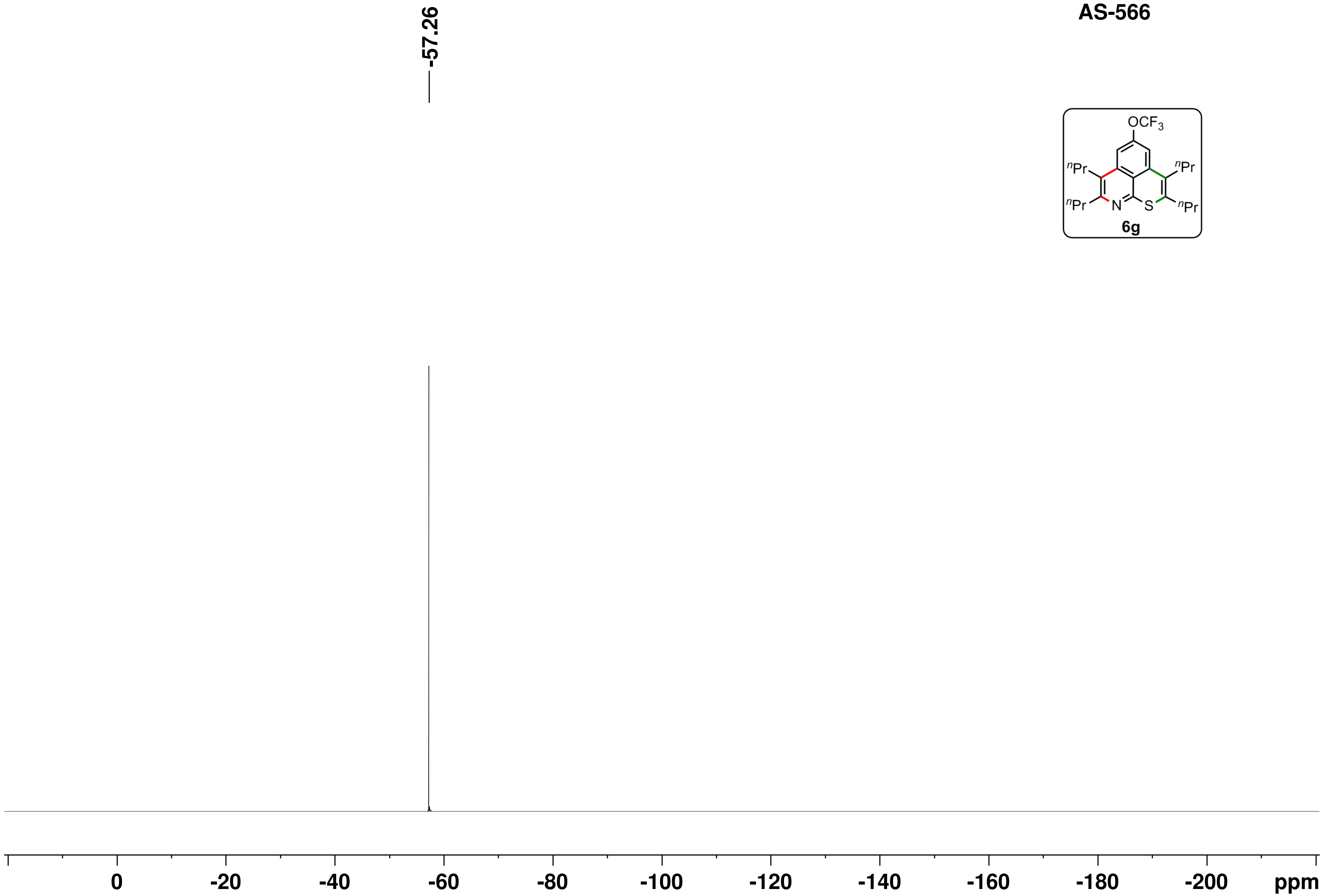

159.41
156.31
155.41
154.22
138.95
138.28
137.21
129.86
128.01
124.45
123.84
121.07
119.27
111.14
106.42
77.32
77.00
76.68
28.15
27.50
21.78
20.89
14.44
14.37
13.58
12.62
AS-404
OPh
Et
Et
Et
Et
N
S
6f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

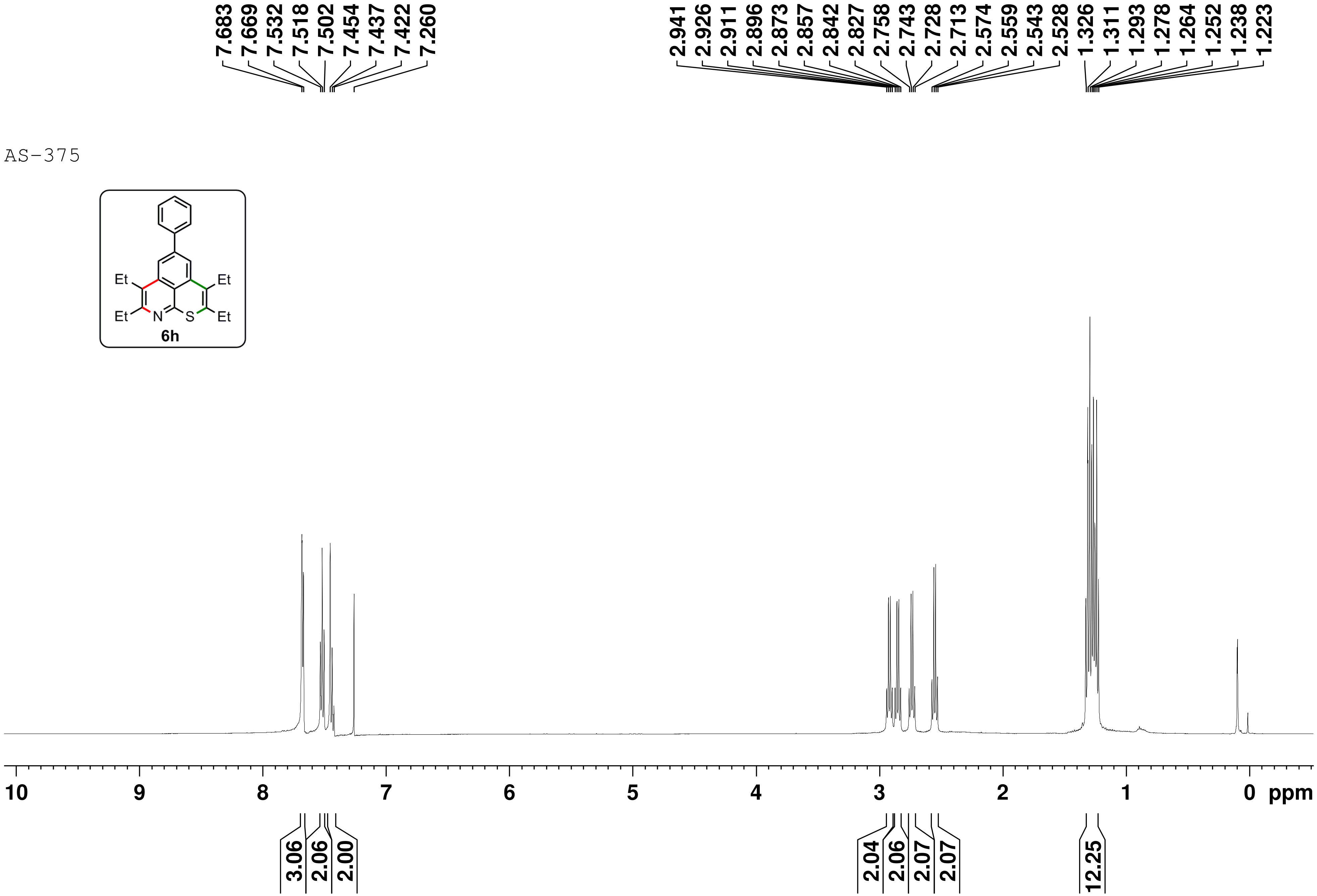

AS- 566
7.280
7.263
6.984
2.794
2.778
2.762
2.745
2.591
2.575
2.559
2.526
2.511
2.495
1.771
1.755
1.740
1.718
1.703
1.687
1.624
1.609
1.593
1.583
1.567
1.552
1.092
1.077
1.070
1.062
1.055
OCF3
nPr
nPr
N
S
nPr
nPr
6g
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.02
4.06
2.02
2.01
4.06
4.01
12.00

AS- 566

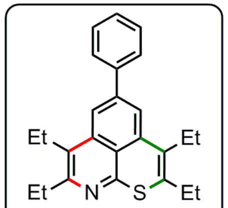


OCF3
nPr
nPr
nPr
nPr
N
S
6g
155.64
153.99
151.20
138.92
138.65
137.37
126.91
123.90
123.63
122.35
121.58
119.53
117.50
111.49
109.88
77.25
77.00
76.75
37.01
36.25
30.99
29.95
23.21
23.05
22.57
21.04
14.32
14.20
14.18
13.92
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

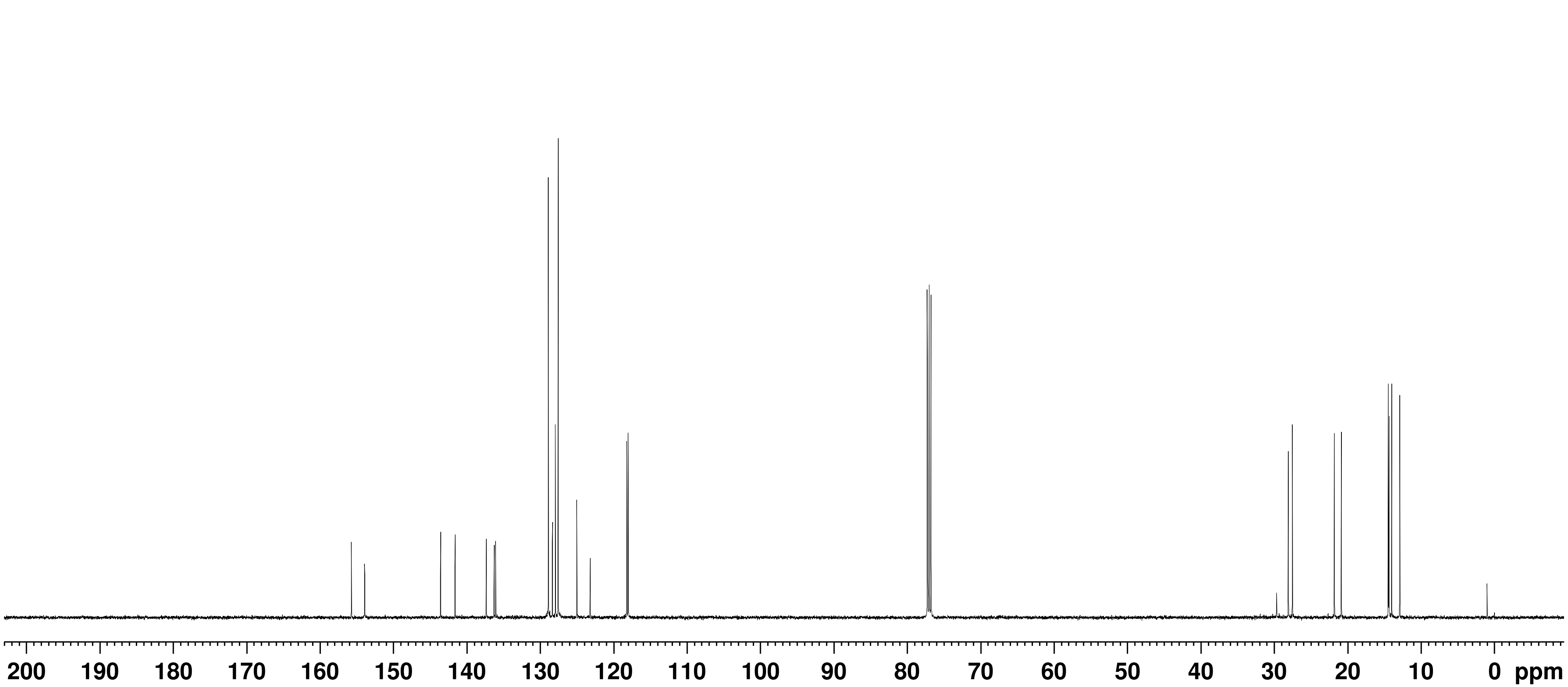

-57.26
AS-566
OCF3
nPr
nPr
nPr
nPr
N
S
6g
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

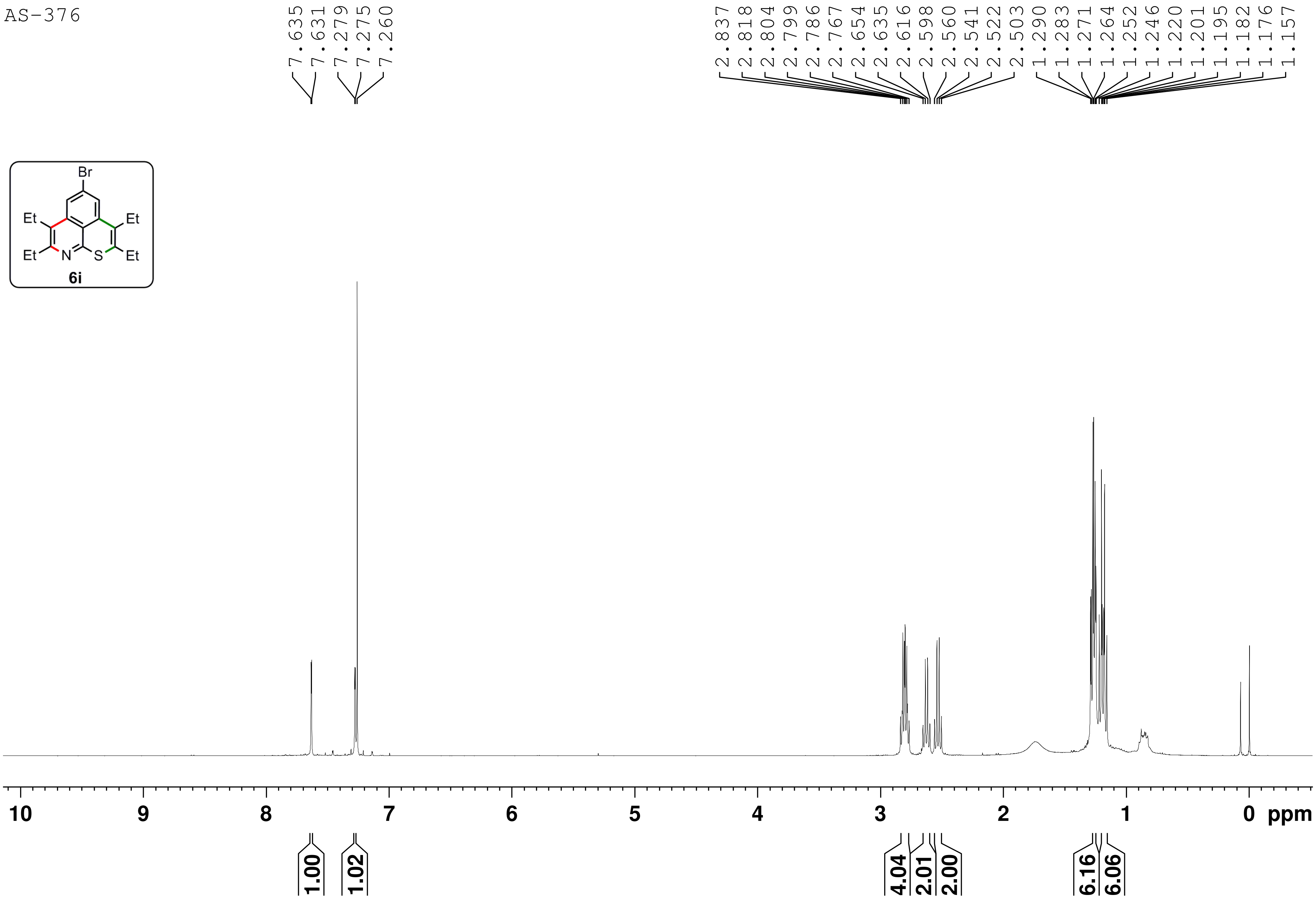

7.683
7.669
7.532
7.518
7.502
7.454
7.437
7.422
7.260
2.941
2.926
2.911
2.896
2.873
2.857
2.842
2.827
2.758
2.743
2.728
2.713
2.574
2.559
2.543
2.528
1.326
1.311
1.293
1.278
1.264
1.252
1.238
1.223
AS-375
Et
Et
Et
Et
N
S
6h
10 9 8 7 6 5 4 3 2 1 0 ppm
3.06
2.06
2.00
2.04
2.06
2.07
2.07
12.25

AS-375

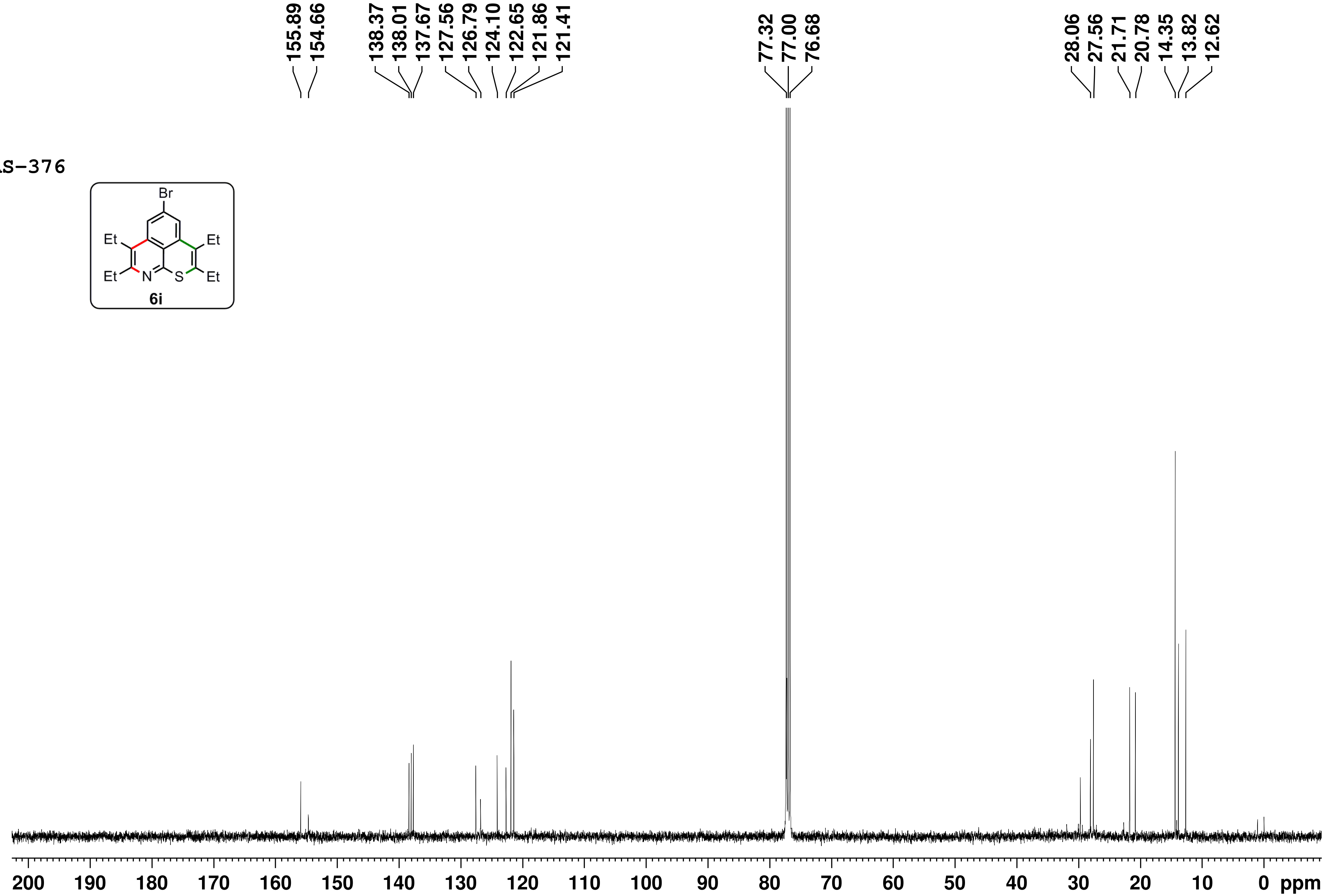


6h

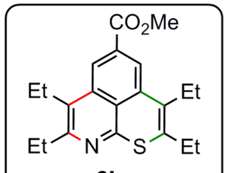

155.72
153.90
143.56
141.59
137.33
136.27
136.06
128.88
128.33
127.92
127.54
124.99
123.18
118.18
118.00
77.25
77.00
76.75
28.06
27.52
21.79
20.84
14.44
14.34
13.97
12.88
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


AS-376
7.635
7.631
7.279
7.275
7.260
2.837
2.818
2.804
2.799
2.786
2.767
2.654
2.635
2.616
2.598
2.560
2.541
2.522
2.503
1.290
1.283
1.271
1.264
1.252
1.246
1.220
1.201
1.195
1.182
1.176
1.157
Br
Et
Et
Et
Et
N
S
6i
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.02
4.04
2.01
2.00
6.16
6.06

AS-376

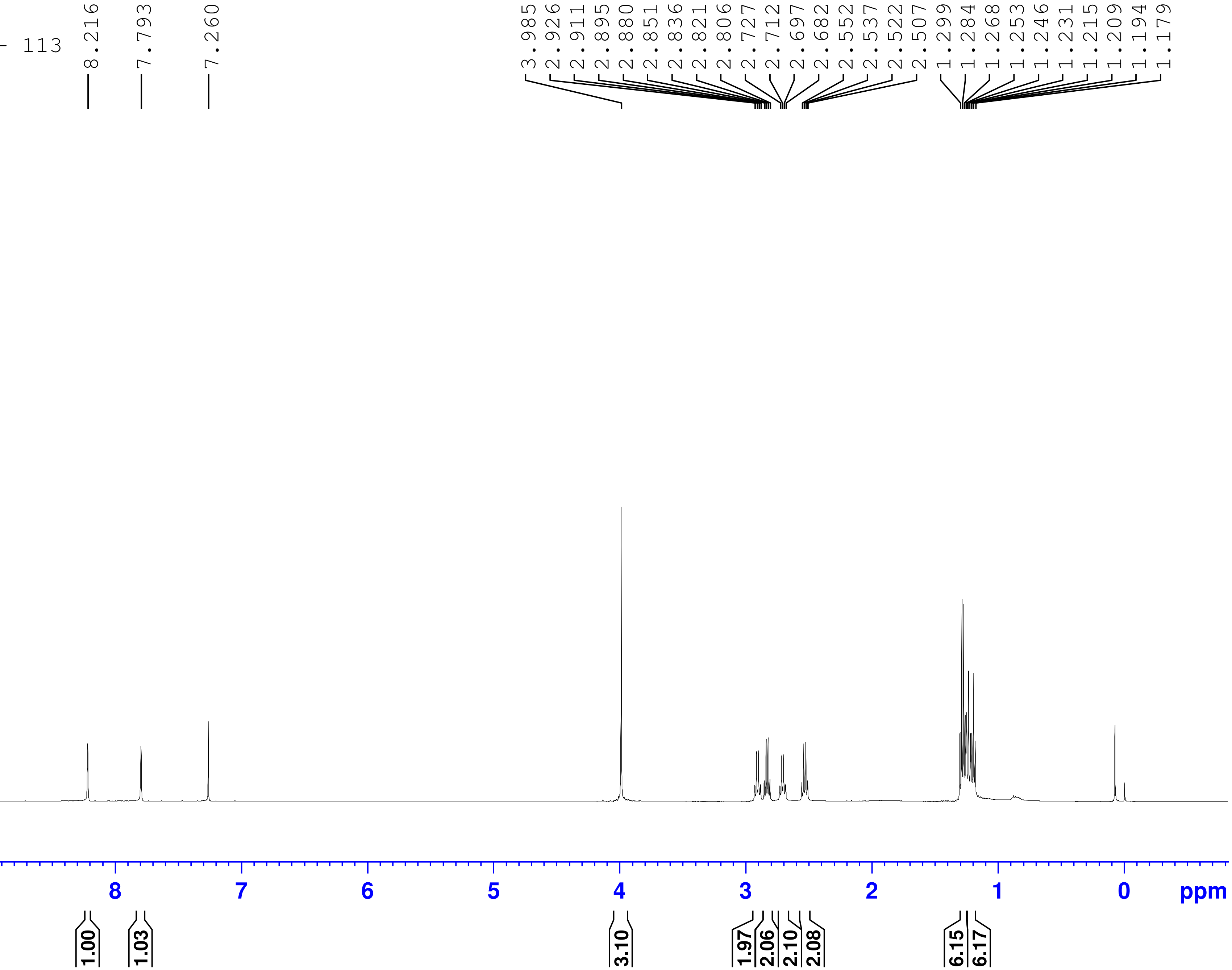


155.89
154.66
138.37
138.01
137.67
127.56
126.79
124.10
122.65
121.86
121.41
77.32
77.00
76.68
28.06
27.56
21.71
20.78
14.35
13.82
12.62
Br
Et
Et
N
S
Et
Et
6i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



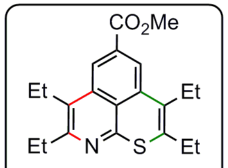
CO2Me
Et
Et
Et
Et
N
S

6j

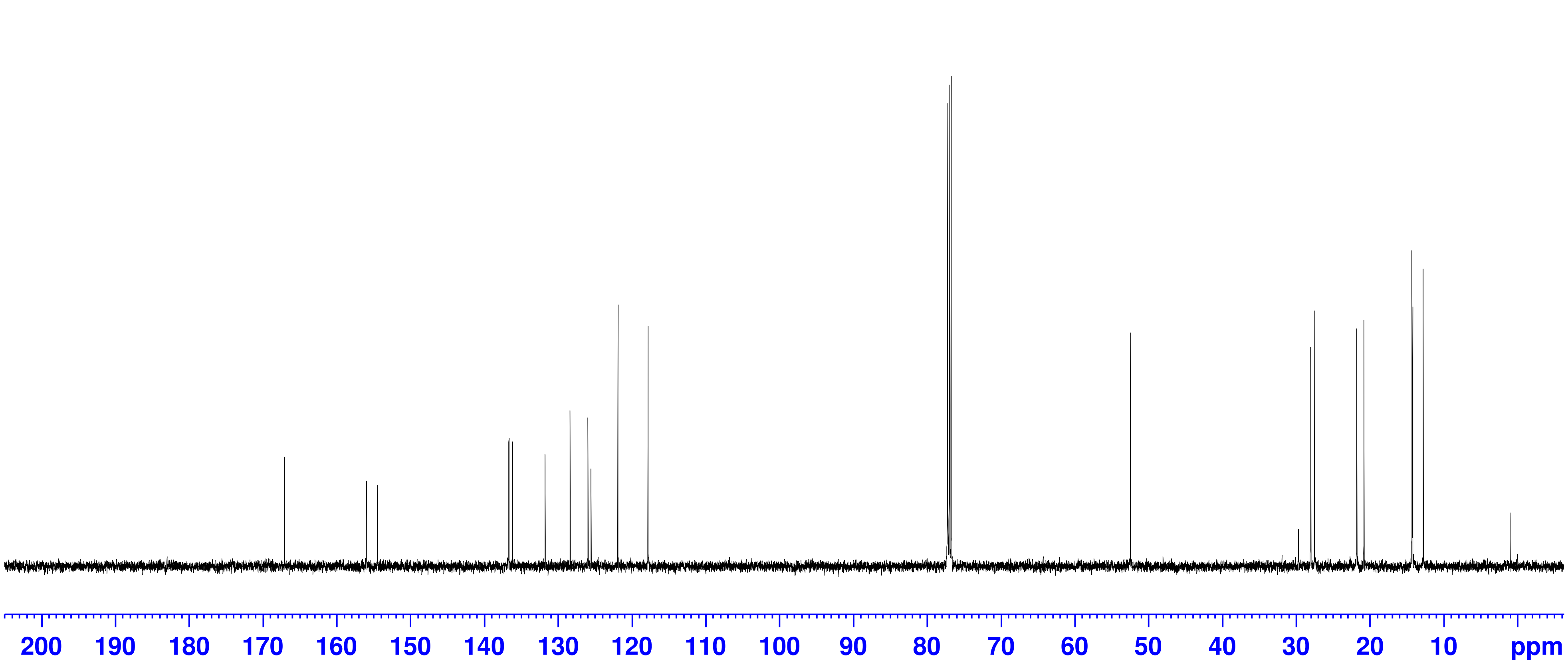


Majji-MJ-16- 113
8.216
7.793
7.260
3.985
2.926
2.911
2.895
2.880
2.851
2.836
2.821
2.806
2.727
2.712
2.697
2.682
2.552
2.537
2.522
2.507
1.299
1.284
1.268
1.253
1.246
1.231
1.215
1.209
1.194
1.179
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
3.10
1.97
2.06
2.10
2.08
6.15
6.17

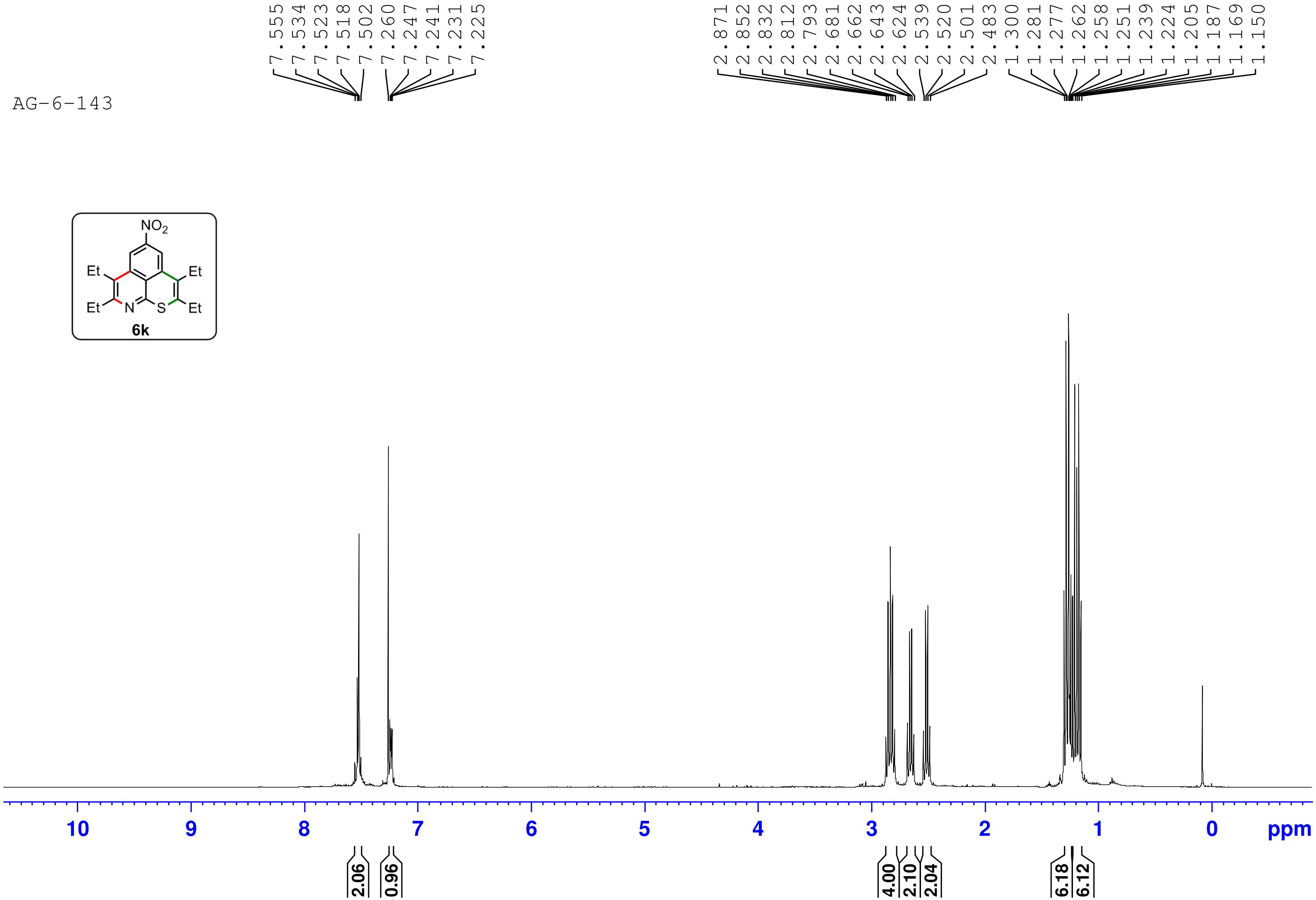
Majji-MJ-16- 113

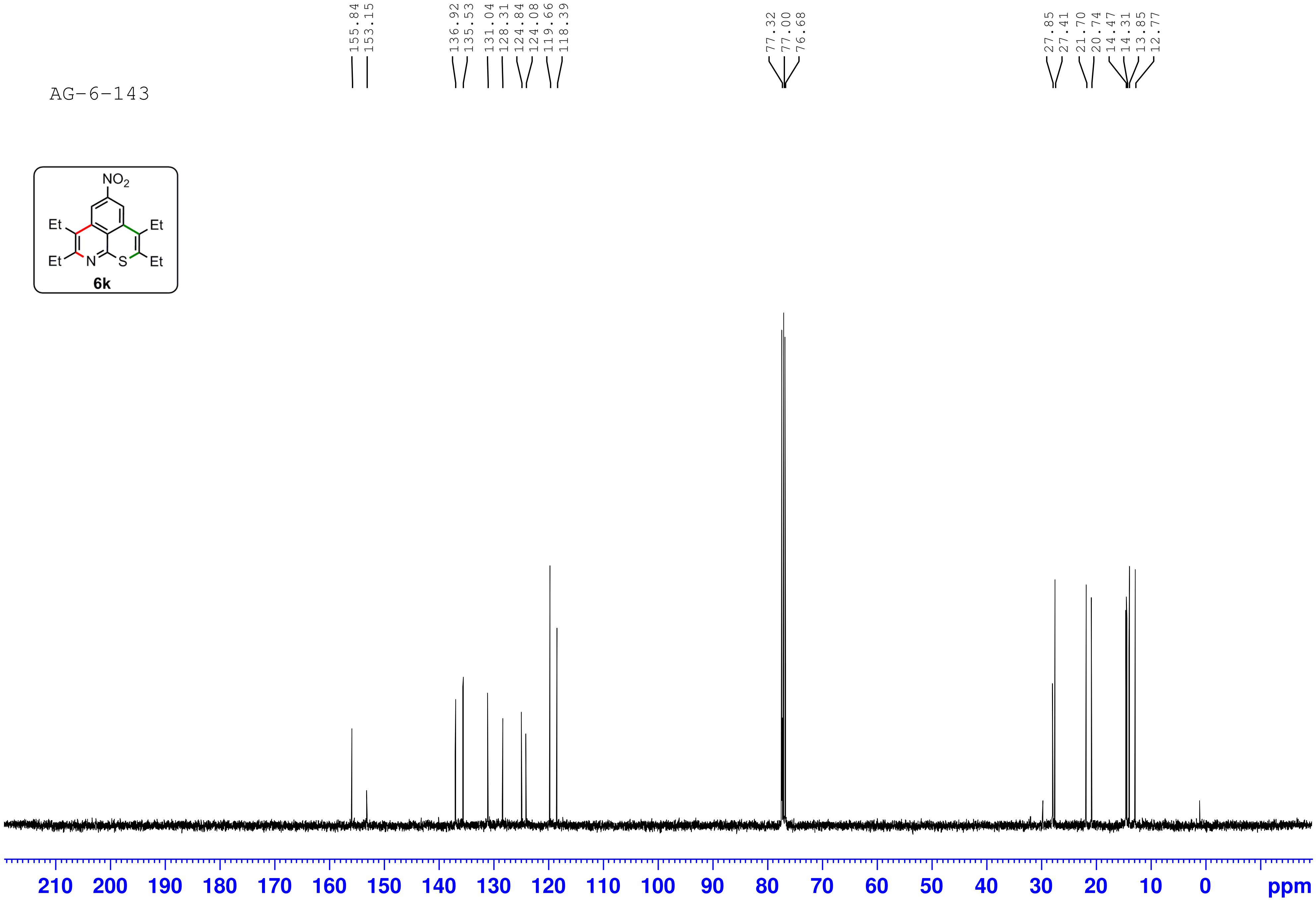


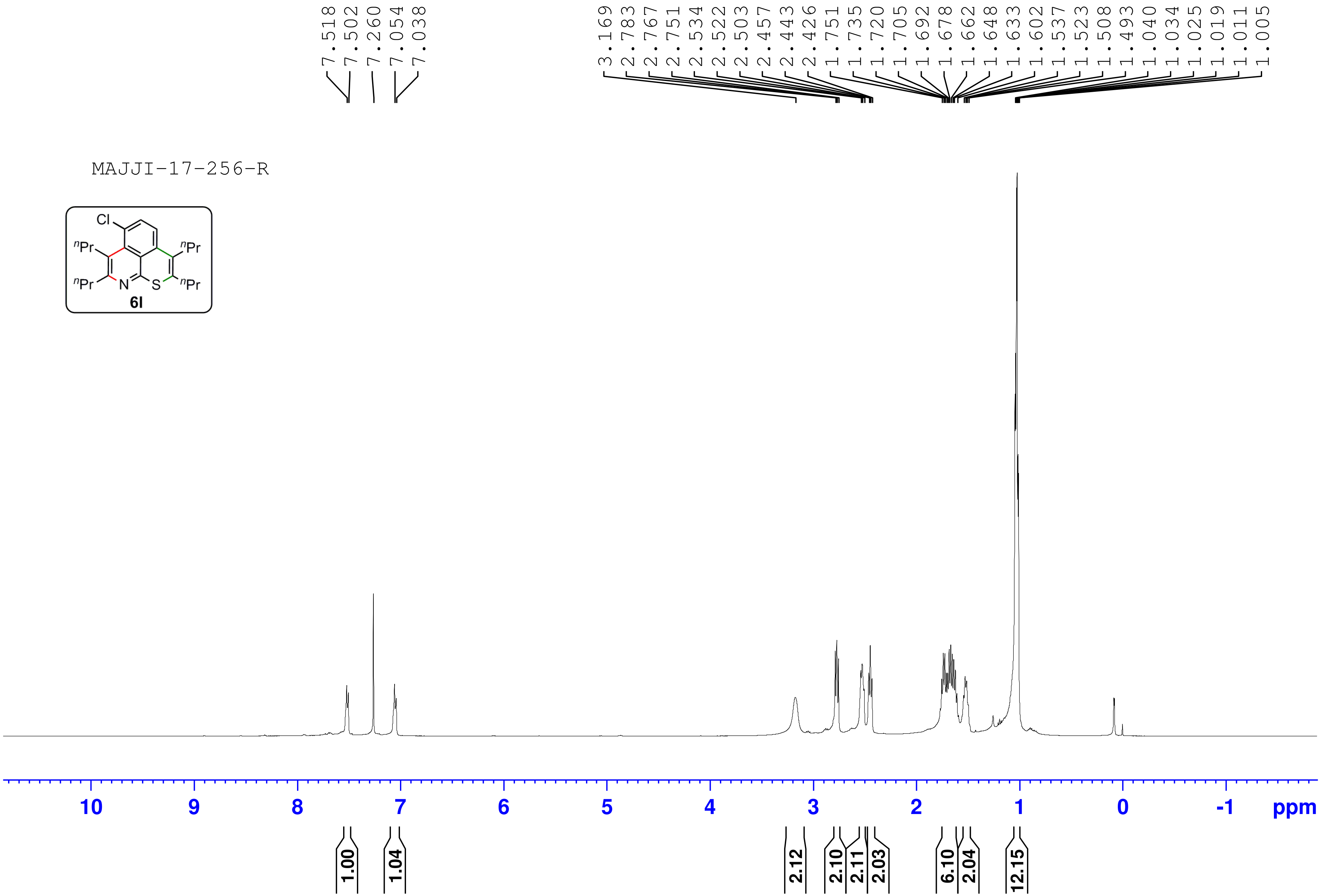
6j

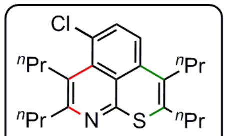


AG-6-143

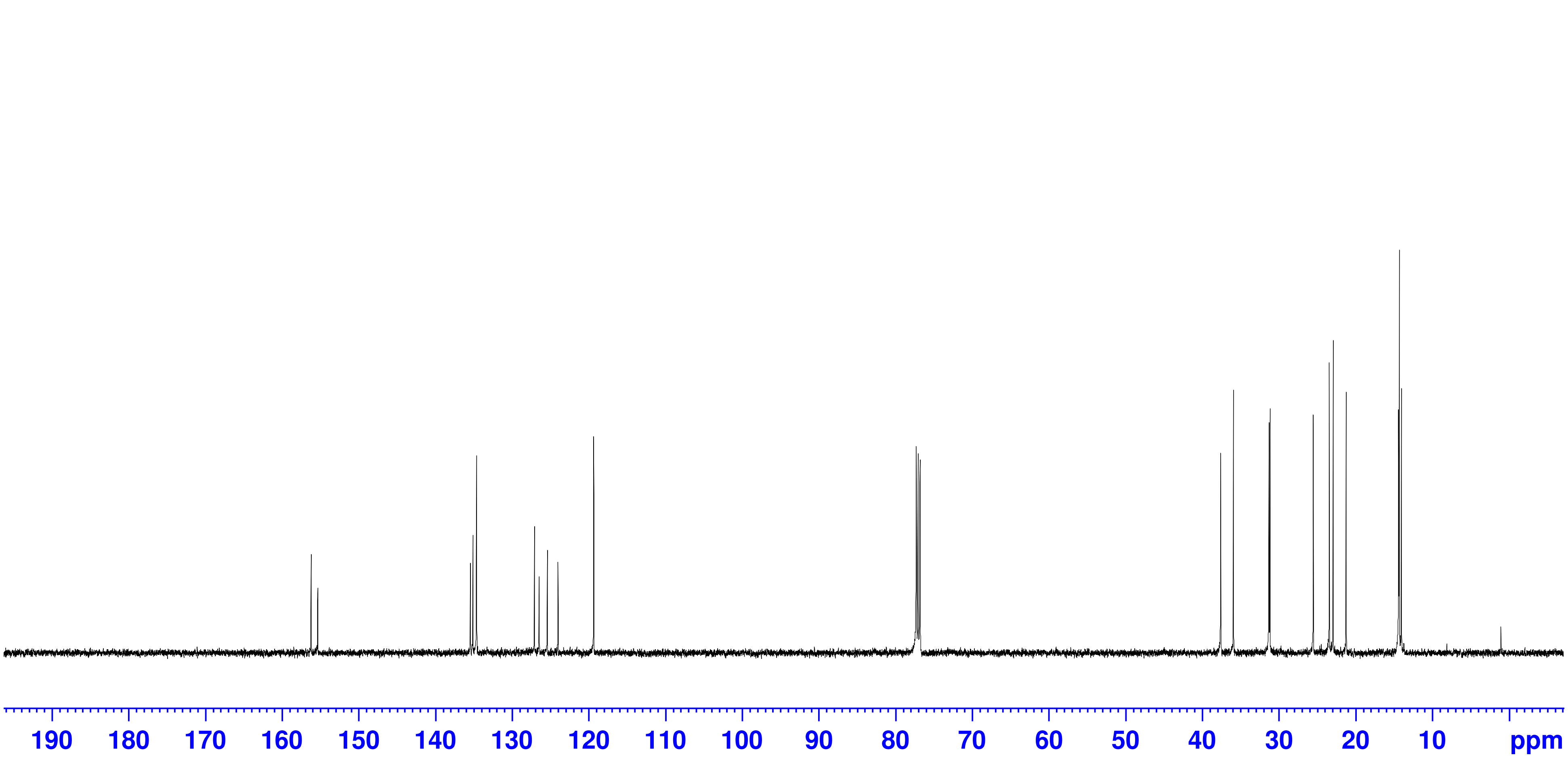

7.555
7.534
7.523
7.518
7.502
7.260
7.247
7.241
7.231
7.225
2.871
2.852
2.832
2.812
2.793
2.681
2.662
2.643
2.624
2.539
2.520
2.501
2.483
1.300
1.281
1.277
1.262
1.258
1.251
1.239
1.224
1.205
1.187
1.169
1.150
NO2
Et
Et
Et
Et
N
S
6k
10
9
8
7
6
5
4
3
2
1
0
ppm
2.06
0.96
4.00
2.10
2.04
6.18
6.12

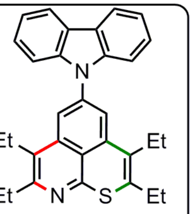

AG-6-143
155.84
153.15
136.92
135.53
131.04
128.31
124.84
124.08
119.66
118.39
77.32
77.00
76.68
27.85
27.41
21.70
20.74
14.47
14.31
13.85
12.77
NO2
Et
Et
N
S
Et
Et
6k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.518
7.502
7.260
7.054
7.038
3.169
2.783
2.767
2.751
2.534
2.522
2.503
2.457
2.443
2.426
1.751
1.735
1.720
1.705
1.692
1.678
1.662
1.648
1.633
1.602
1.537
1.523
1.508
1.493
1.040
1.034
1.025
1.019
1.011
1.005
MAJJI-17-256-R
Cl
nPr
nPr
nPr
nPr
N
S
6l
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
1.04
2.12
2.10
2.11
2.03
6.10
2.04
12.15

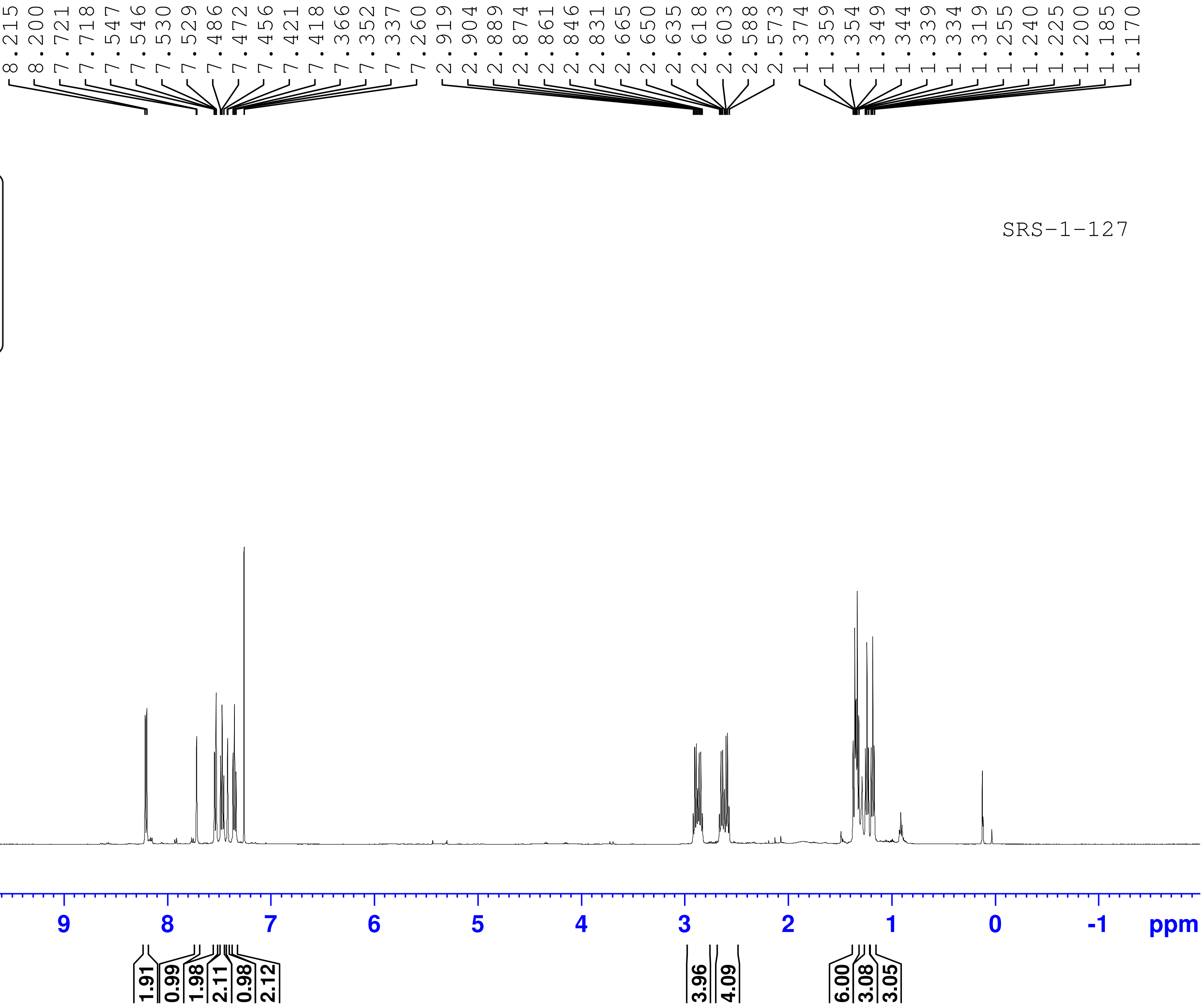

Cl
nPr
nPr
nPr
nPr
N
S

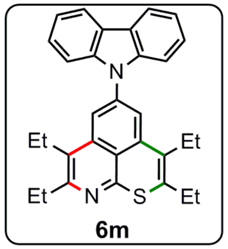
6l


156.19
155.30
135.38
135.06
134.61
134.57
127.04
126.40
125.36
123.96
119.30
77.25
77.00
76.75
37.53
35.85
31.23
31.09
25.45
23.37
22.85
21.14
14.32
14.23
13.95
MAJJI-17-256-R
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

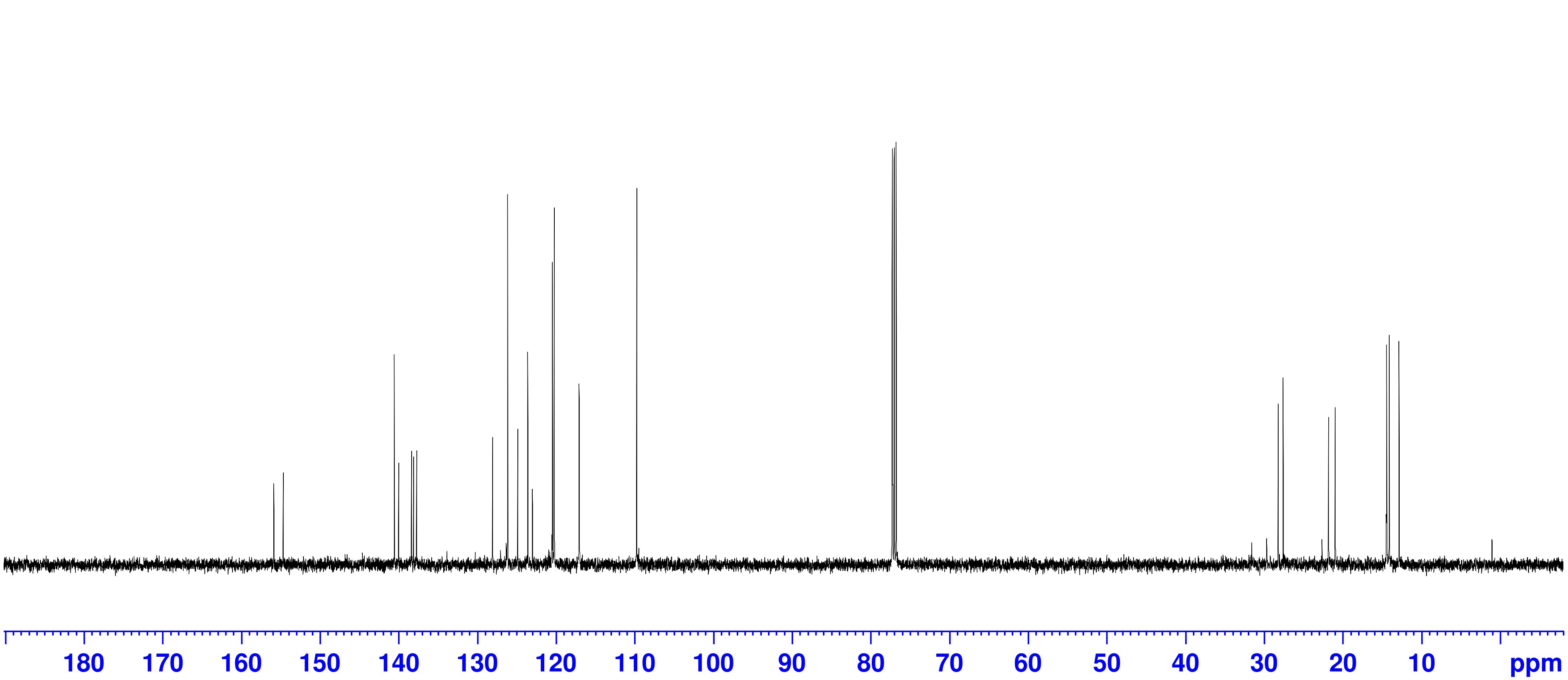

Et
Et
N
S
Et
Et
N

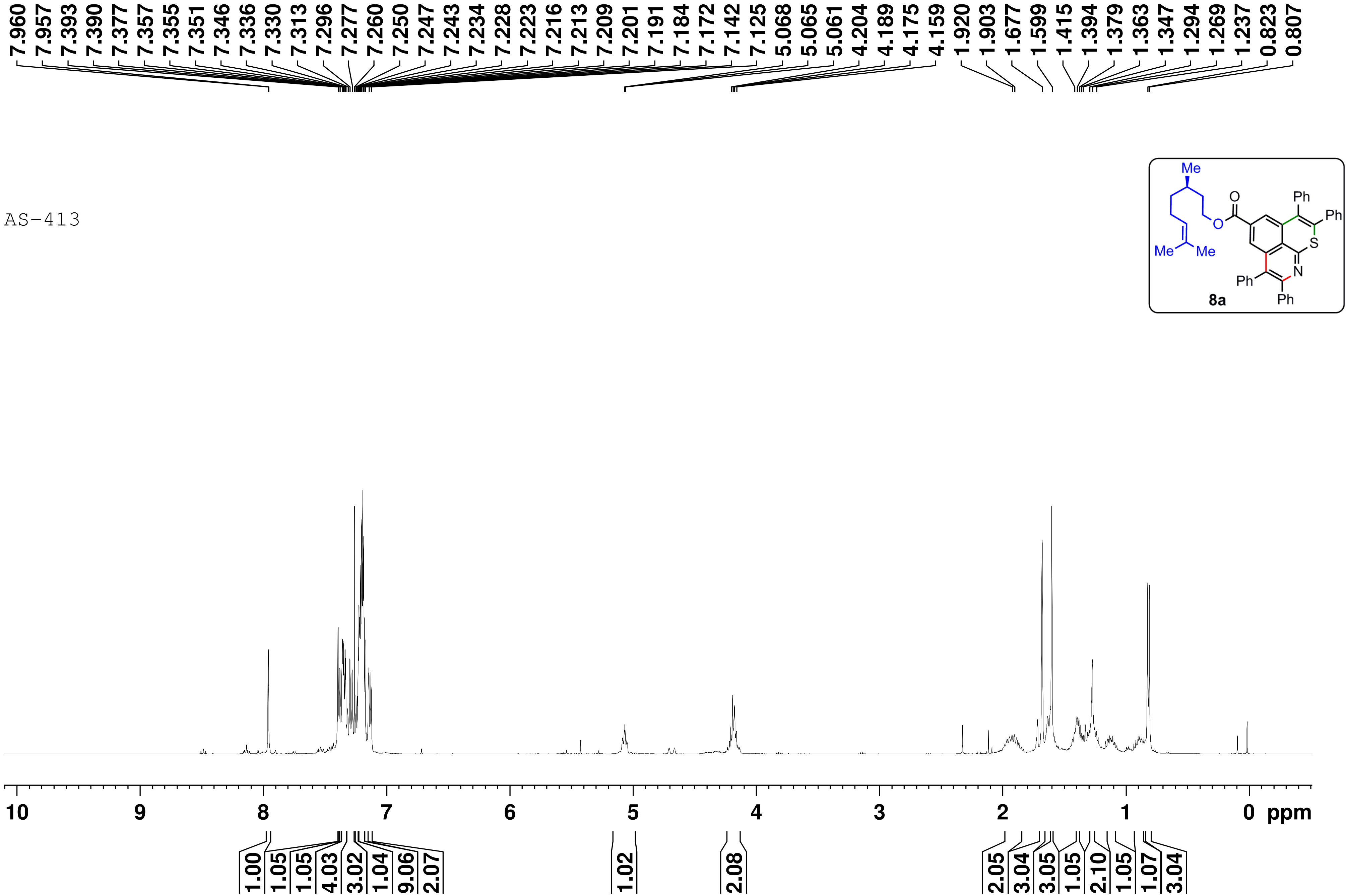
6m


8.215
8.200
7.721
7.718
7.547
7.546
7.530
7.529
7.486
7.472
7.456
7.421
7.418
7.366
7.352
7.337
7.260
2.919
2.904
2.889
2.874
2.861
2.846
2.831
2.665
2.650
2.635
2.618
2.603
2.588
2.573
1.374
1.359
1.354
1.349
1.344
1.339
1.334
1.319
1.255
1.240
1.225
1.200
1.185
1.170
SRS-1-127
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.91
0.99
1.98
2.11
0.98
2.12
3.96
4.09
6.00
3.08
3.05


Et
Et
Et
Et
N
N
S
6m

SRS-1-127


155.87
154.68
140.55
140.01
138.38
138.09
137.72
128.04
126.14
124.85
123.58
122.98
120.45
120.21
117.06
117.01
109.73
77.25
77.00
76.74
28.17
27.55
21.78
20.93
14.43
14.39
14.08
12.81
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.377
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7.355
7.351
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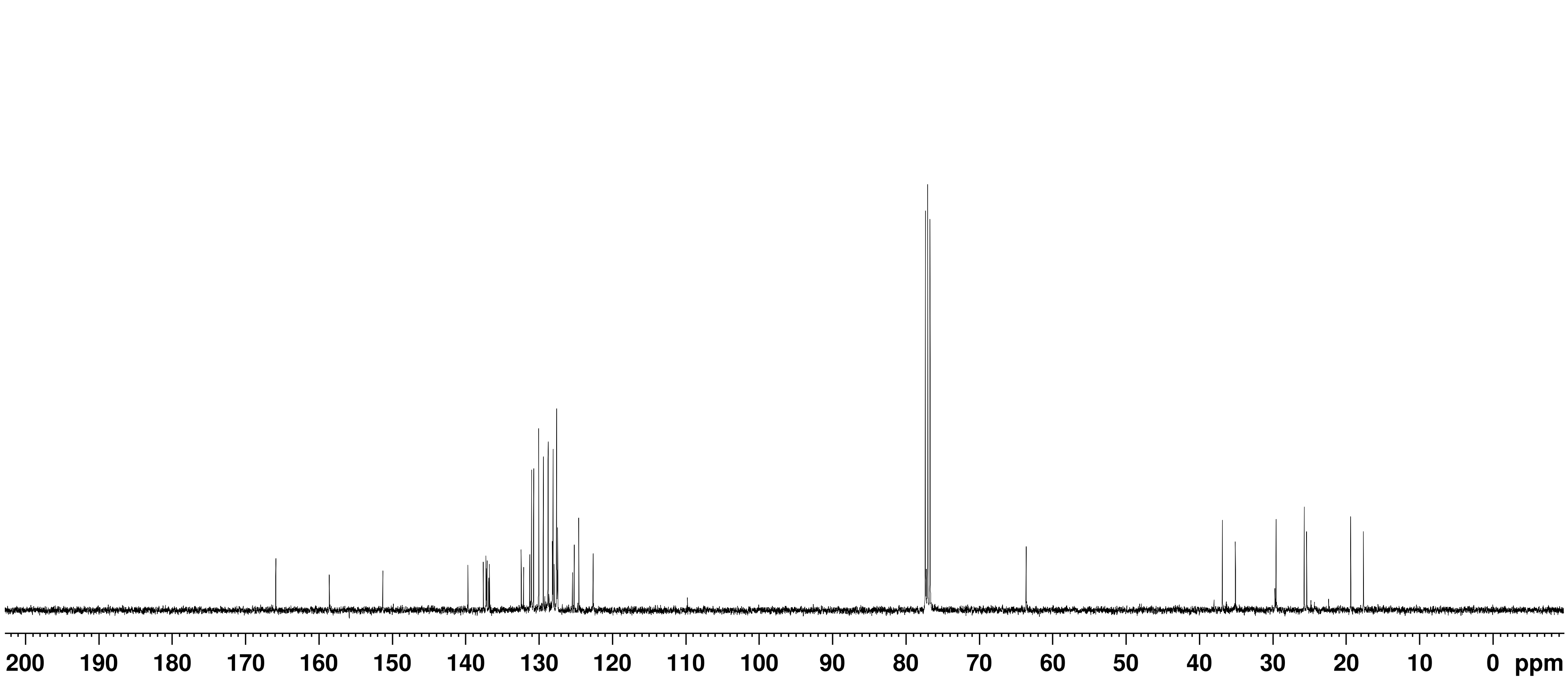
7.336
7.330
7.313
7.296
7.277
7.260
7.250
7.247
7.243
7.234
7.228
7.223
7.216
7.213
7.209
7.201
7.191
7.184
7.172
7.142
7.125
5.068
5.065
5.061
4.204
4.189
4.175
4.159
1.920
1.903
1.677
1.599
1.415
1.394
1.379
1.363
1.347
1.294
1.269
1.237
0.823
0.807
AS-413
Me
O
Ph
Ph
O
S
Me
Me
N
Ph
Ph
8a
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.05
1.05
4.03
3.02
1.04
9.06
2.07
1.02
2.08
2.05
3.04
3.05
1.05
2.10
1.05
1.07
3.04

AS-413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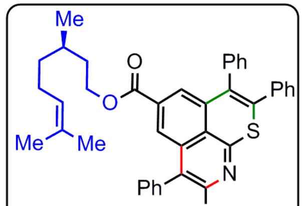
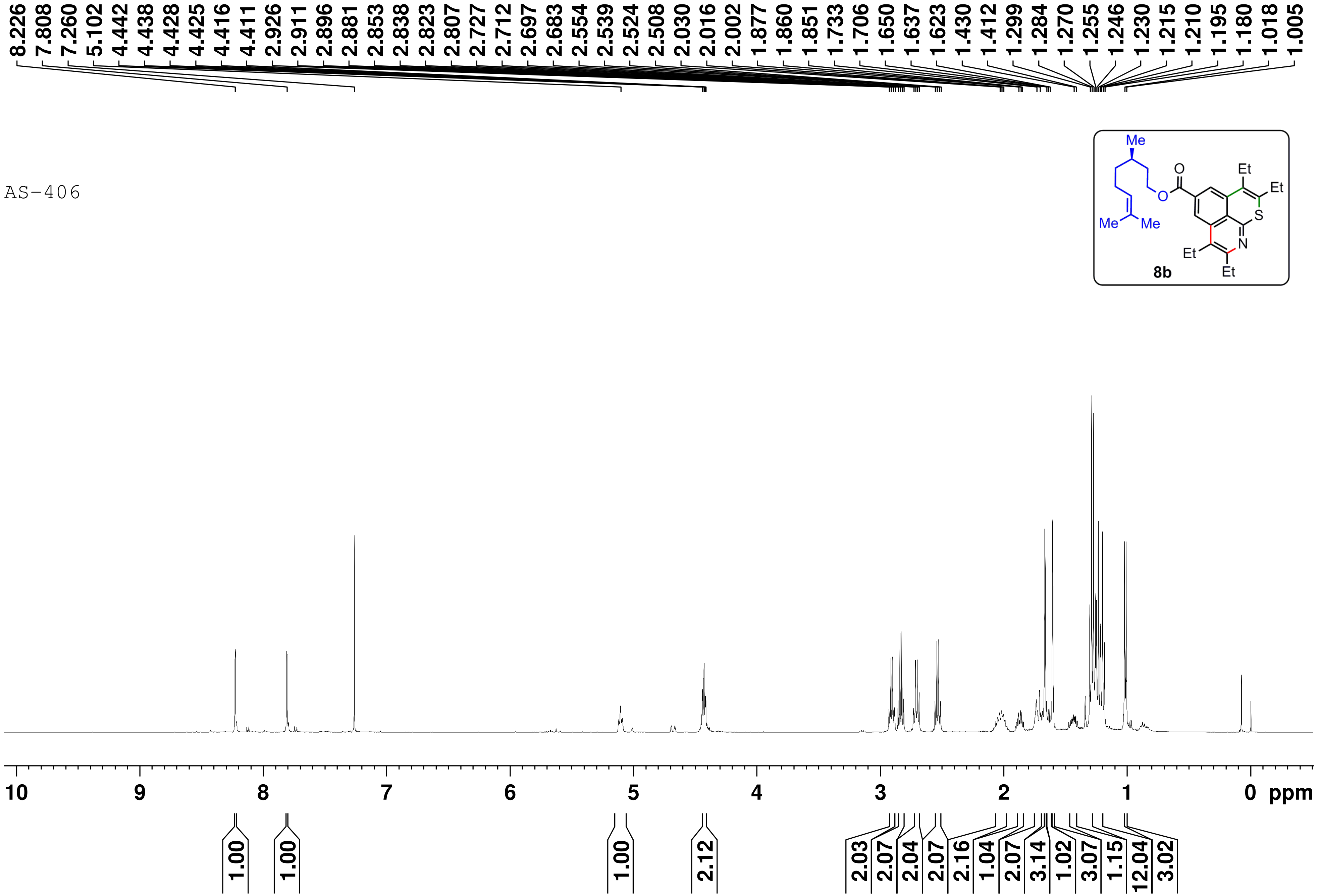
137.20
137.15
137.07
136.84
136.73
132.40
132.08
131.24
130.99
130.72
130.02
129.40
128.73
128.15
128.07
127.93
127.59
127.55
127.45
125.42
125.19
124.57
122.60
77.32
77.00
76.68
63.58
36.82
35.05
29.51
25.68
25.36
19.34
17.63
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


Me
O
O
Me
Me
Ph
Ph
S
N
Ph
Ph

8a

AS-406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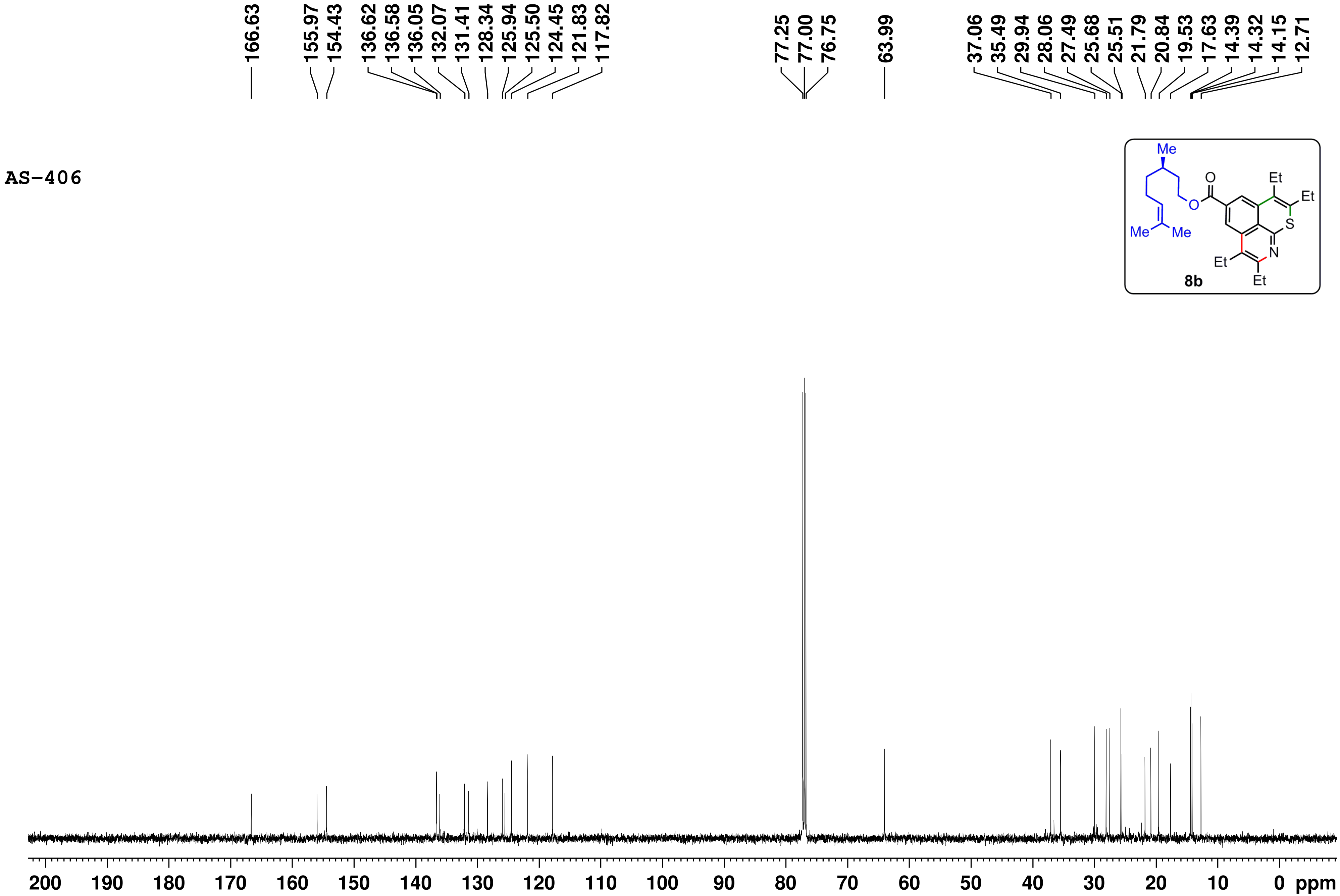
Me
O
Et
Et
S
N
Me
Me
Et
Et
8b
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00 1.00 1.00 2.12 2.03 2.07 2.04 2.07 2.16 1.04 2.07 3.14 1.02 3.07 1.15 12.04 3.02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136.05
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131.41
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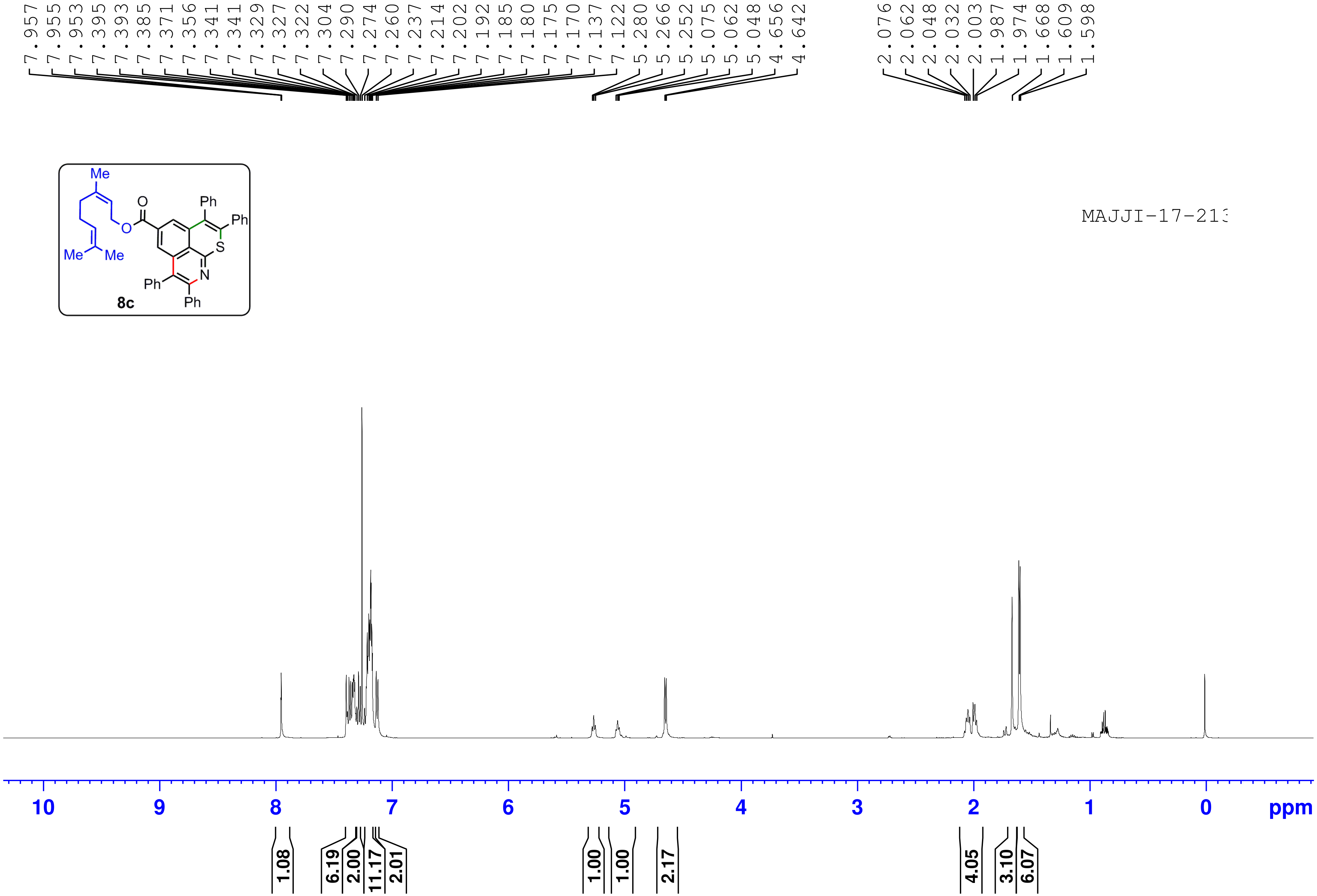
125.94
125.50
124.45
121.83
117.82
77.25
77.00
76.75
63.99
37.06
35.49
29.94
28.06
27.49
25.68
25.51
21.79
20.84
19.53
17.63
14.39
14.32
14.15
12.71
AS-406
Me
O
Et
Et
O
S
Me
Me
N
Et
Et
8b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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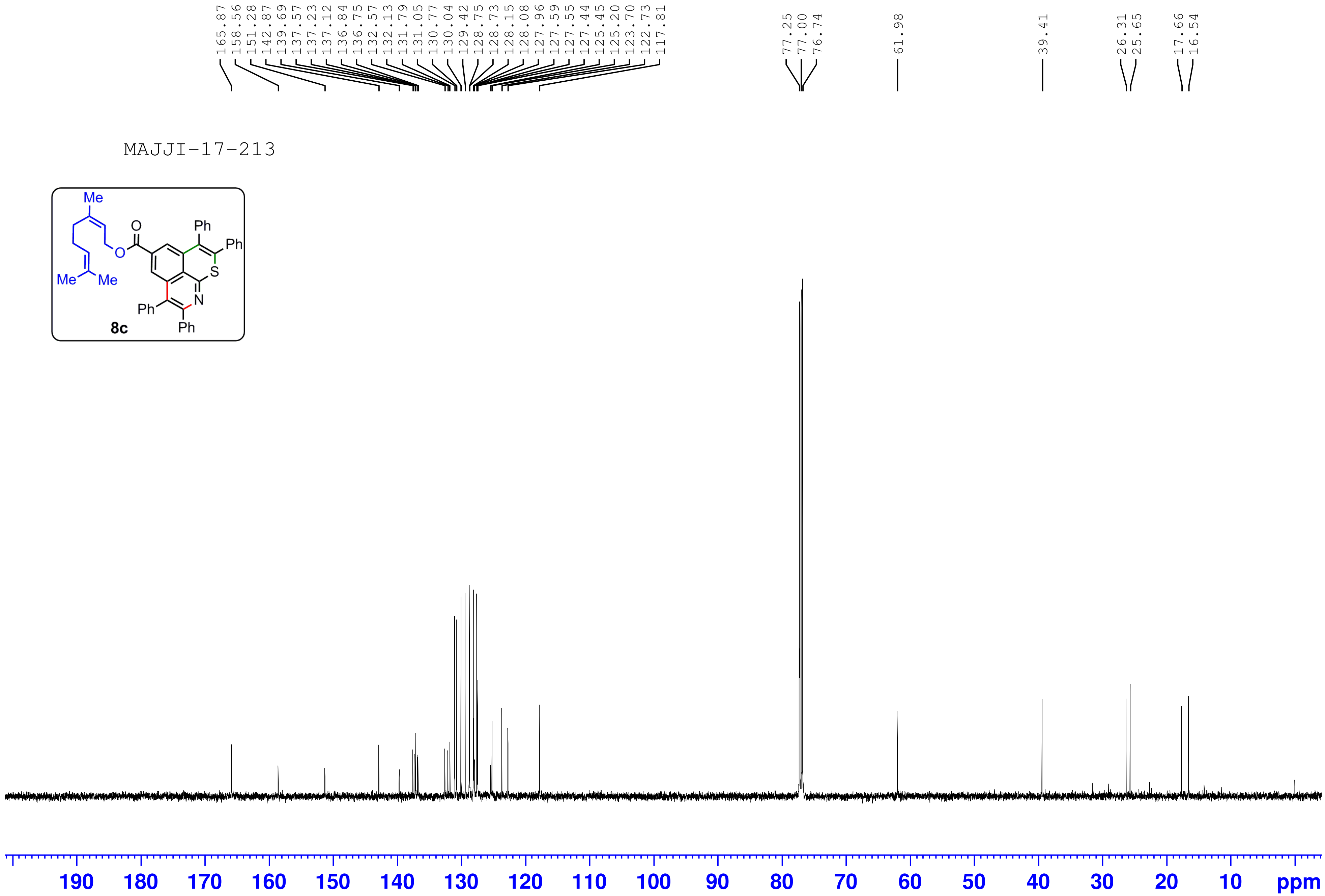
7.955
7.953
7.395
7.393
7.385
7.371
7.356
7.341
7.341
7.329
7.327
7.322
7.304
7.290
7.274
7.260
7.237
7.214
7.202
7.192
7.185
7.180
7.175
7.170
7.137
7.122
5.280
5.266
5.252
5.075
5.062
5.048
4.656
4.642
2.076
2.062
2.048
2.032
2.003
1.987
1.974
1.668
1.609
1.598
MAJJI-17-21
10
9
8
7
6
5
4
3
2
1
0
ppm
1.08
6.19
2.00
11.17
2.01
1.00
1.00
2.17
4.05
3.10
6.07
Me
O
Ph
Ph
O
S
Me
Me
N
Ph
Ph
8c

MAJJI-17-213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142.87
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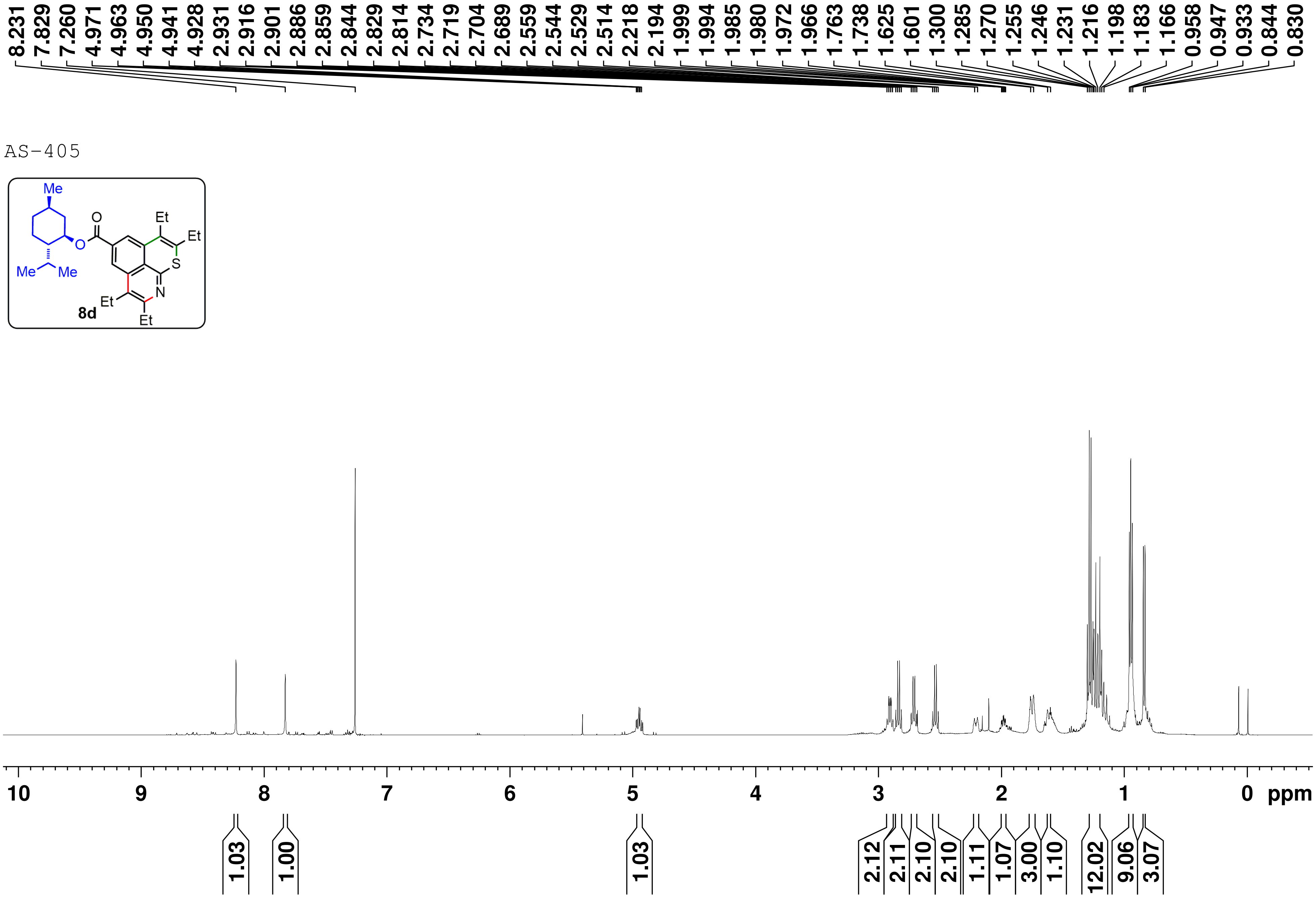
137.57
137.23
137.12
136.84
136.75
132.57
132.13
131.79
131.05
130.77
130.04
129.42
128.75
128.73
128.15
128.08
127.96
127.59
127.55
127.44
125.45
125.20
123.70
122.73
117.81
77.25
77.00
76.74
61.98
39.41
26.31
25.65
17.66
16.54
Me
O
O
Ph
Ph
S
N
Me
Me
Ph
Ph
8c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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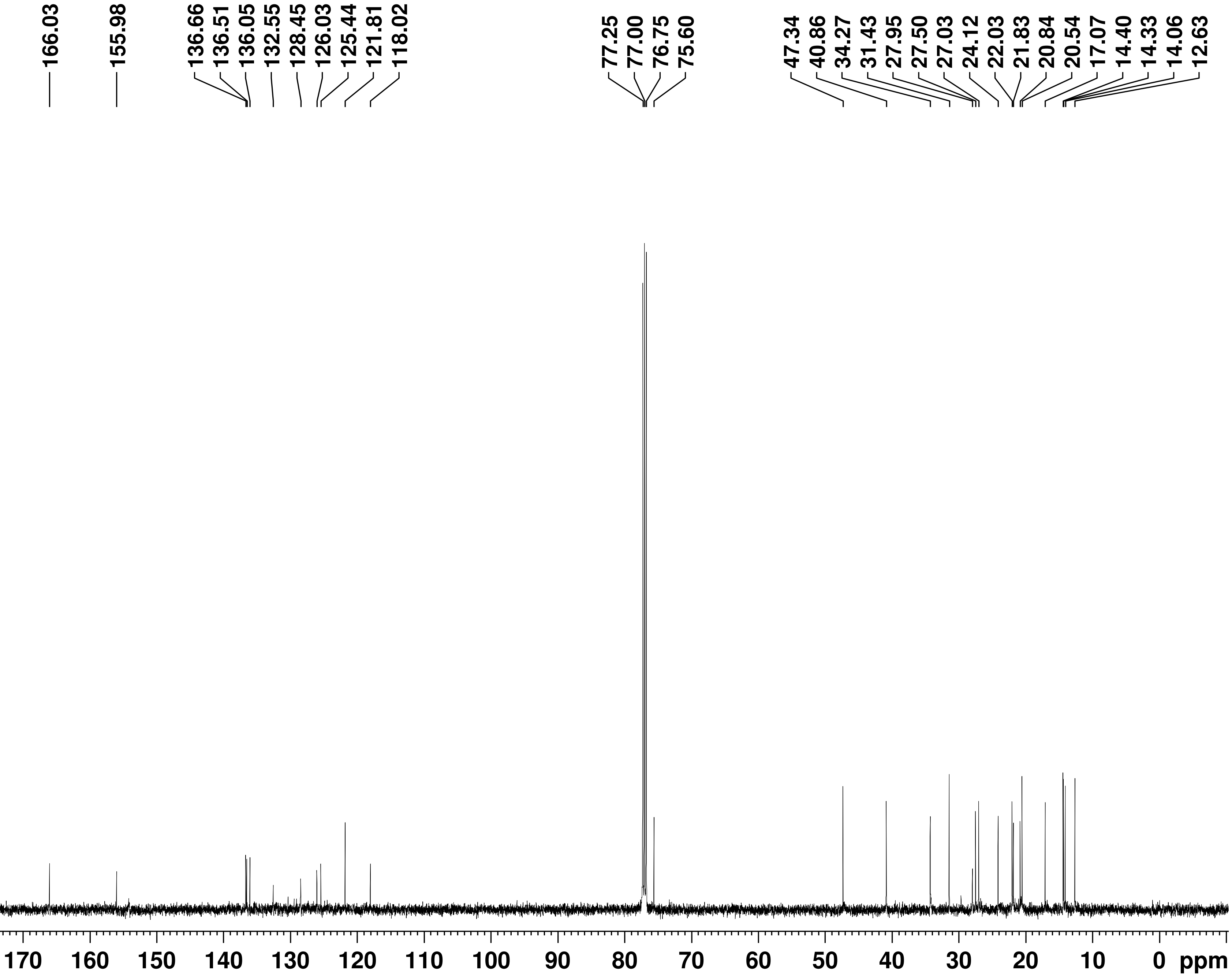
AS-405
Me
O
Et
Et
O
S
Me
Me
N
Et
8d
Et
10
9
8
7
6
5
4
3
2
1
0 ppm
1.03
1.00
1.03
2.12
2.11
2.10
2.10
1.11
1.07
3.00
1.10
12.02
9.06
3.07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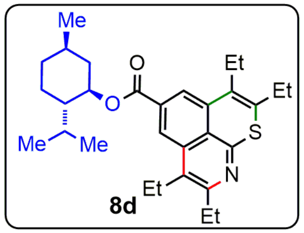
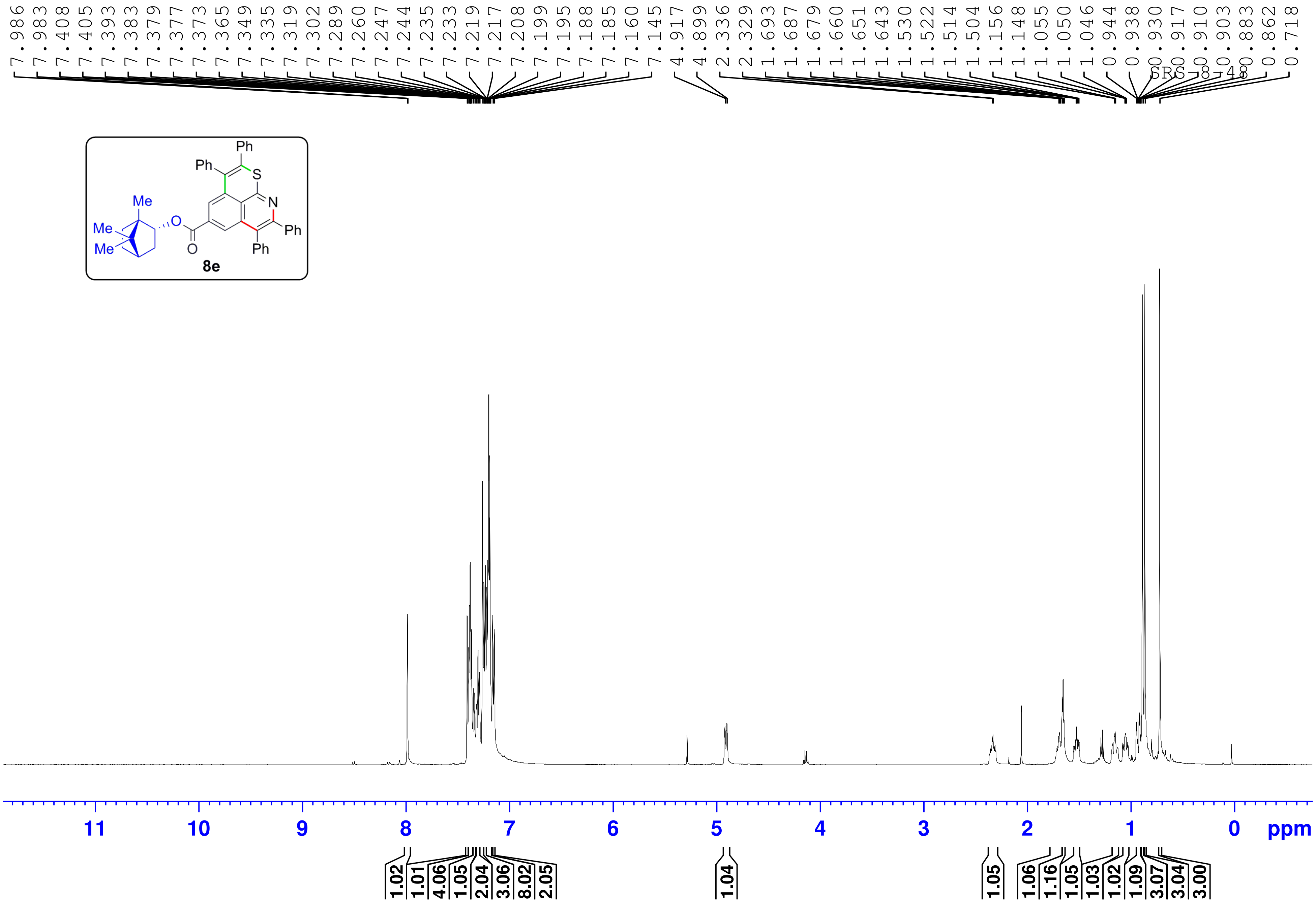
136.66
136.51
136.05
132.55
128.45
126.03
125.44
121.81
118.02
77.25
77.00
76.75
75.60
47.34
40.86
34.27
31.43
27.95
27.50
27.03
24.12
22.03
21.83
20.84
20.54
17.07
14.40
14.33
14.06
12.63
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

AS-405


Me
O
Et
Et
O
S
N
Me
Me
Et
Et
8d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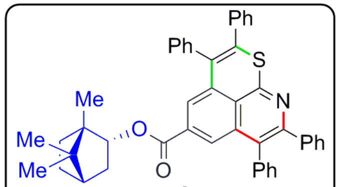
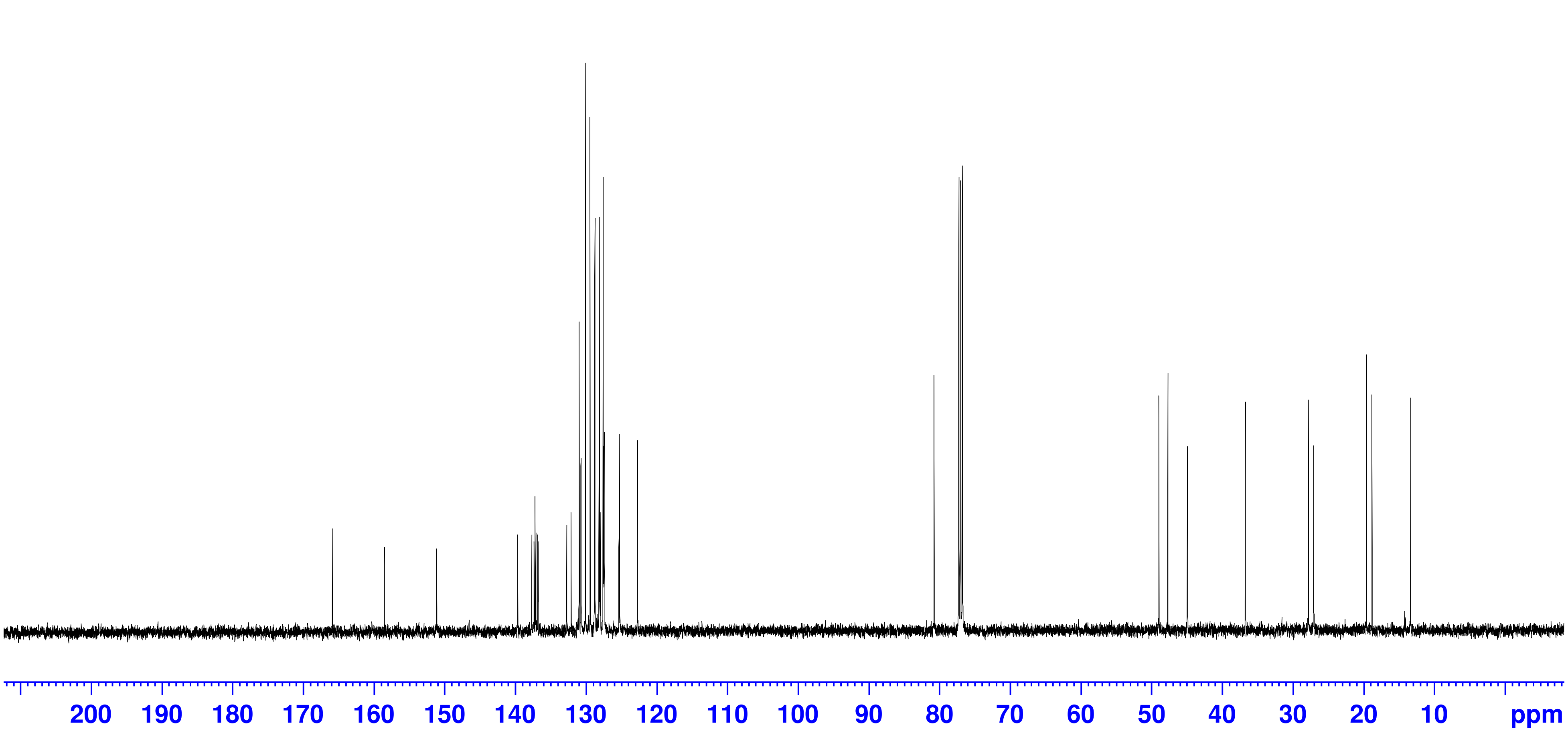
7.377
7.373
7.365
7.349
7.335
7.319
7.302
7.289
7.260
7.247
7.244
7.235
7.233
7.219
7.217
7.208
7.199
7.195
7.188
7.185
7.160
7.145
4.917
4.899
2.336
2.329
1.693
1.687
1.679
1.660
1.651
1.643
1.530
1.522
1.514
1.504
1.156
1.148
1.055
1.050
1.046
0.944
0.938
0.930
0.917
0.910
0.903
0.883
0.862
0.718
SRS-8-48
Ph
Ph
S
N
Ph
Ph
Me
Me
Me
O
O
8e
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.01
4.06
1.05
2.04
3.06
8.02
2.05
1.04
1.05
1.06
1.16
1.05
1.03
1.02
1.09
3.07
3.04
3.00



Ph
Ph
S
N
Ph
Ph
Me
Me
Me
O
O

8e



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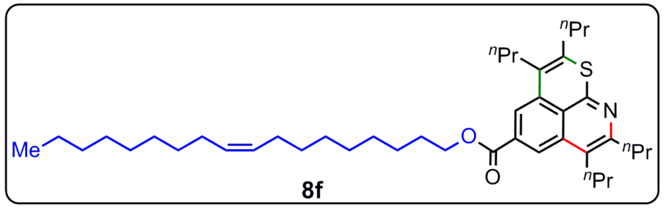
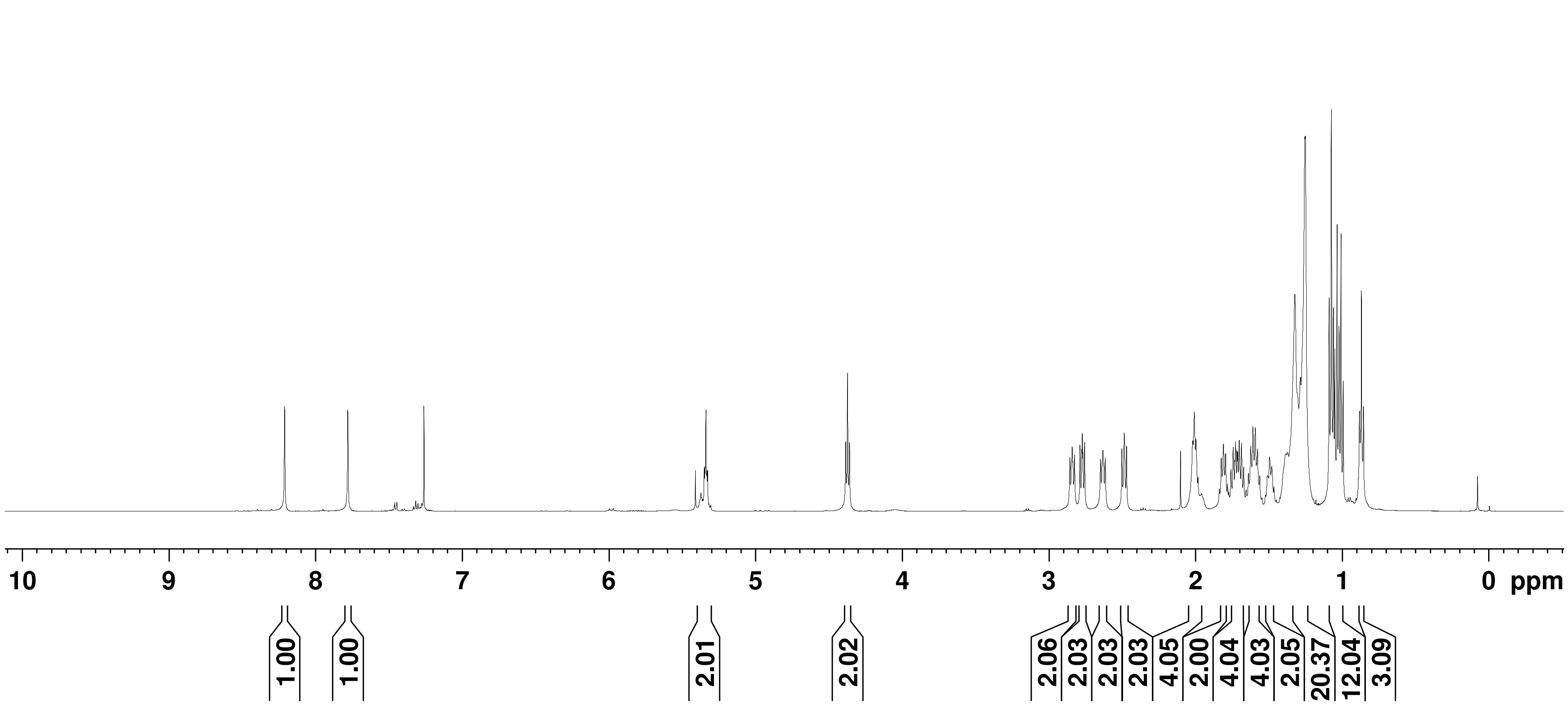
158.54
151.15
139.70
137.67
137.35
137.21
137.09
136.82
136.77
136.73
132.14
130.98
130.70
130.07
129.44
128.78
128.73
128.17
128.07
127.98
127.57
127.50
127.43
127.40
125.34
125.25
122.71
80.75
77.25
77.00
76.74
48.94
47.69
44.90
36.70
27.77
27.03
19.57
18.78
13.31
SRS-8-48
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



Me
O
O
S
N
nPr
nPr
nPr
nPr
8f



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7.260
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4.371
4.358
2.856
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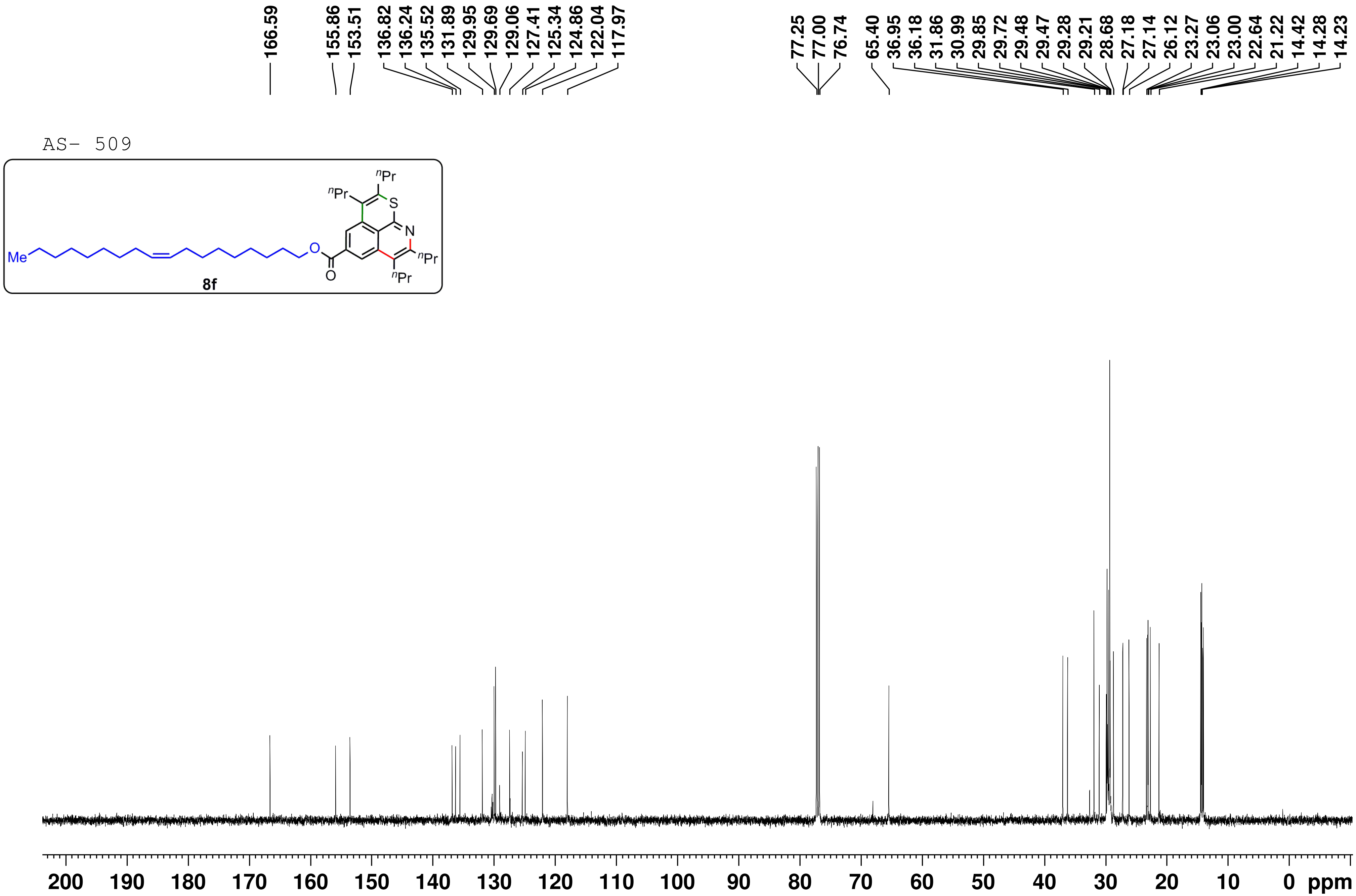
2.824
2.787
2.771
2.755
2.647
2.631
2.614
2.501
2.485
2.469
2.017
2.007
1.996
1.823
1.809
1.794
1.742
1.731
1.726
1.716
1.711
1.701
1.685
1.623
1.607
1.592
1.577
1.494
1.321
1.253
1.087
1.073
1.058
1.048
1.034
1.021
1.019
1.007
0.992
0.881
0.867
0.853
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.00
2.01
2.02
2.06
2.03
2.03
2.03
4.05
2.00
4.04
4.03
2.05
20.37
12.04
3.09

AS- 509



^{n}Pr
^{n}Pr
S
N
^{n}Pr
^{n}Pr
Me
O
O
8f
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136.82
136.24
135.52
131.89
129.95
129.69
129.06
127.41
125.34
124.86
122.04
117.97
77.25
77.00
76.74
65.40
36.95
36.18
31.86
30.99
29.85
29.72
29.48
29.47
29.28
29.21
28.68
27.18
27.14
26.12
23.27
23.06
23.00
22.64
21.22
14.42
14.28
14.23
200
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150
140
130
120
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100
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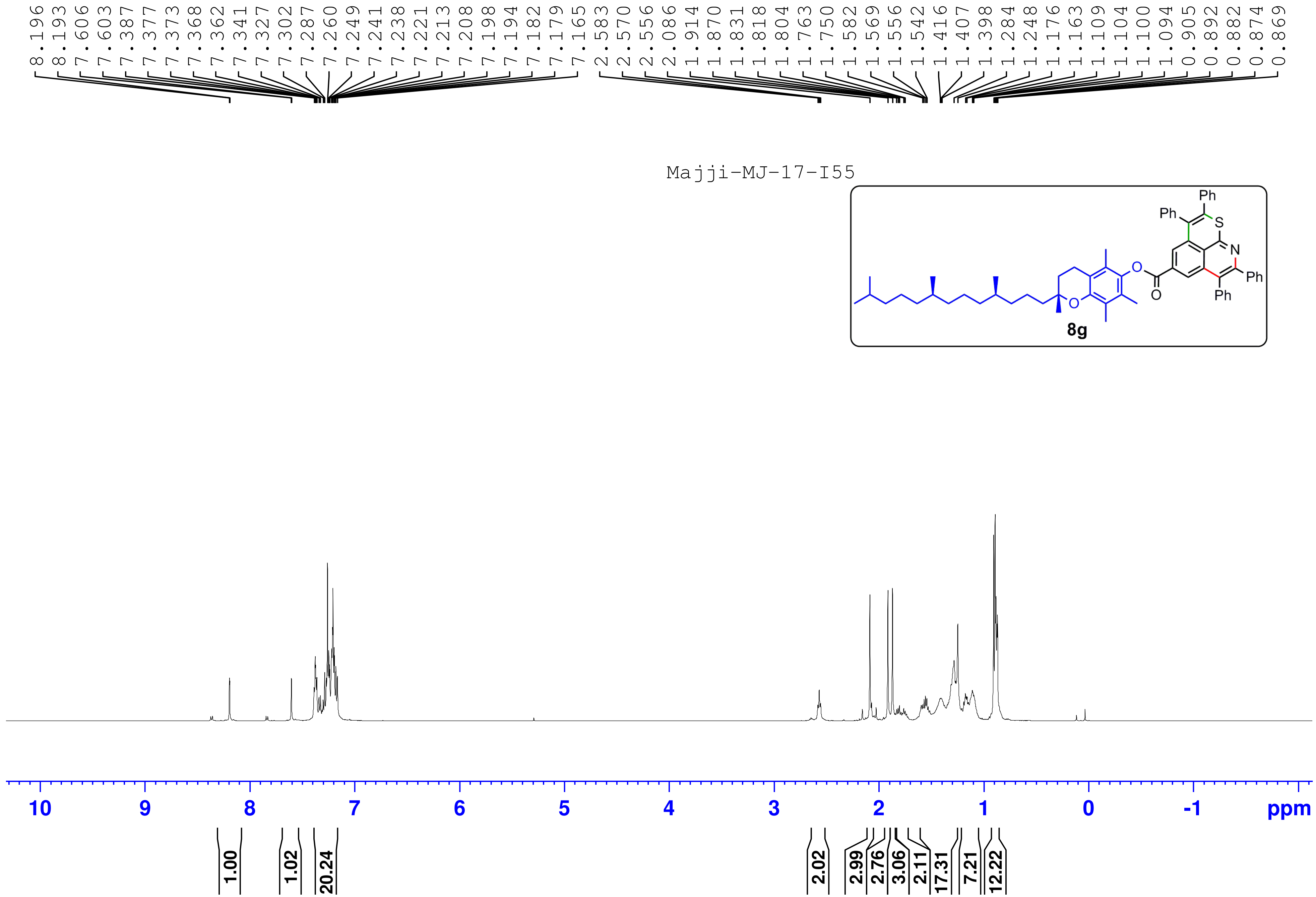
60
50
40
30
20
10
0
ppm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7.341
7.327
7.302
7.287
7.260
7.249
7.241
7.238
7.221
7.213
7.208
7.198
7.194
7.182
7.179
7.165
2.583
2.570
2.556
2.086
1.914
1.870
1.831
1.818
1.804
1.763
1.750
1.582
1.569
1.556
1.542
1.416
1.407
1.398
1.284
1.248
1.176
1.163
1.109
1.104
1.100
1.094
0.905
0.892
0.882
0.874
0.869
Majji-MJ-17-I55
Ph
Ph
S
N
Ph
Ph
O
O
O
8g
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
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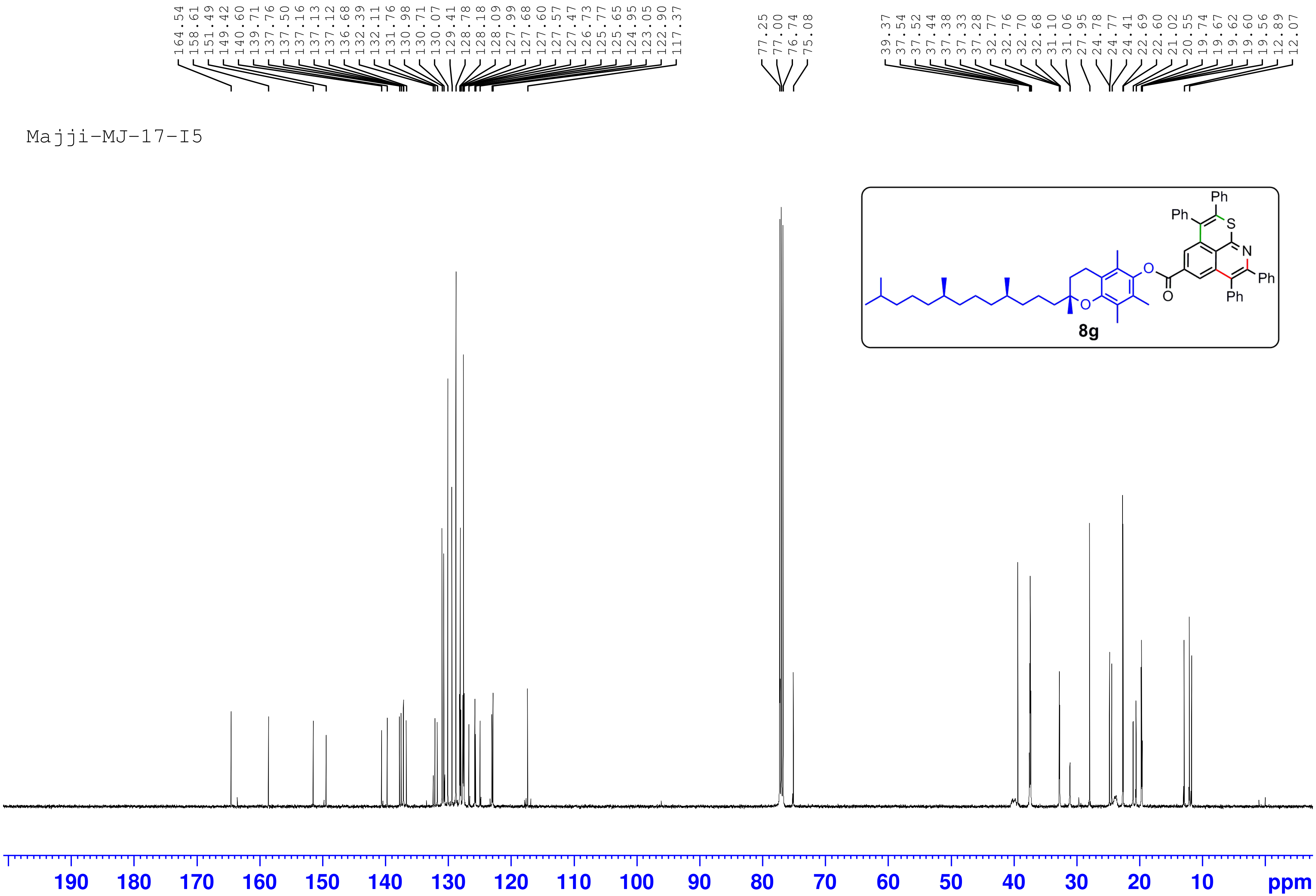
7.21
12.22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137.13
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131.76
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130.71
130.07
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128.78
128.18
128.09
127.99
127.68
127.60
127.57
127.47
126.73
125.77
125.65
124.95
123.05
122.90
117.37
77.25
77.00
76.74
75.08
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37.54
37.52
37.44
37.38
37.33
37.28
32.77
32.76
32.70
32.68
31.10
31.06
27.95
24.78
24.77
24.41
22.69
22.60
21.02
20.55
19.74
19.67
19.62
19.60
19.56
12.89
12.07
Majji-MJ-17-I5
Ph
Ph
S
N
Ph
Ph
O
O
O
8g
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150
140
130
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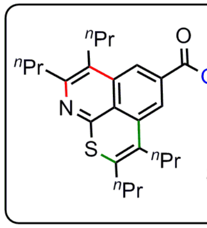
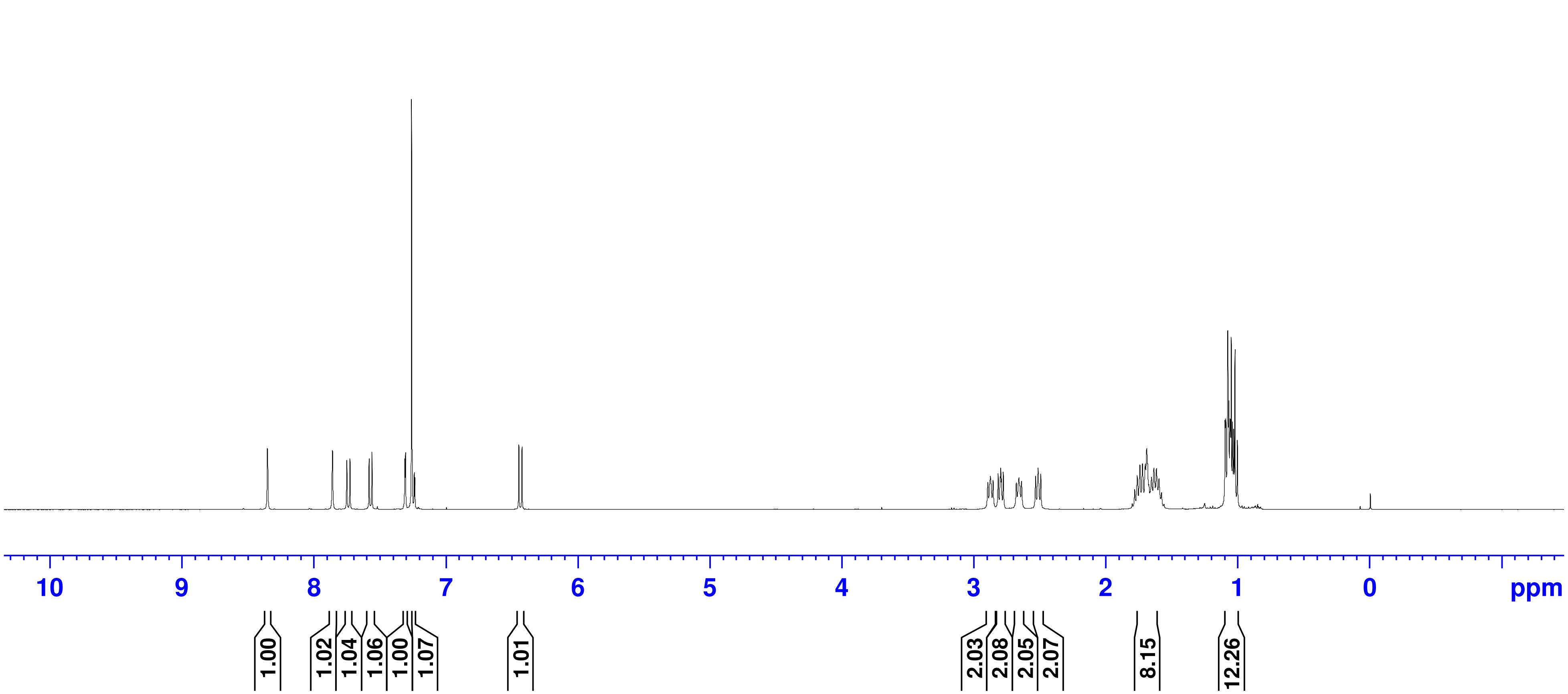
70
60
50
40
30
20
10
ppm


ⁿPr
ⁿPr
ⁿPr
ⁿPr
N
S
O
O
O
O

8h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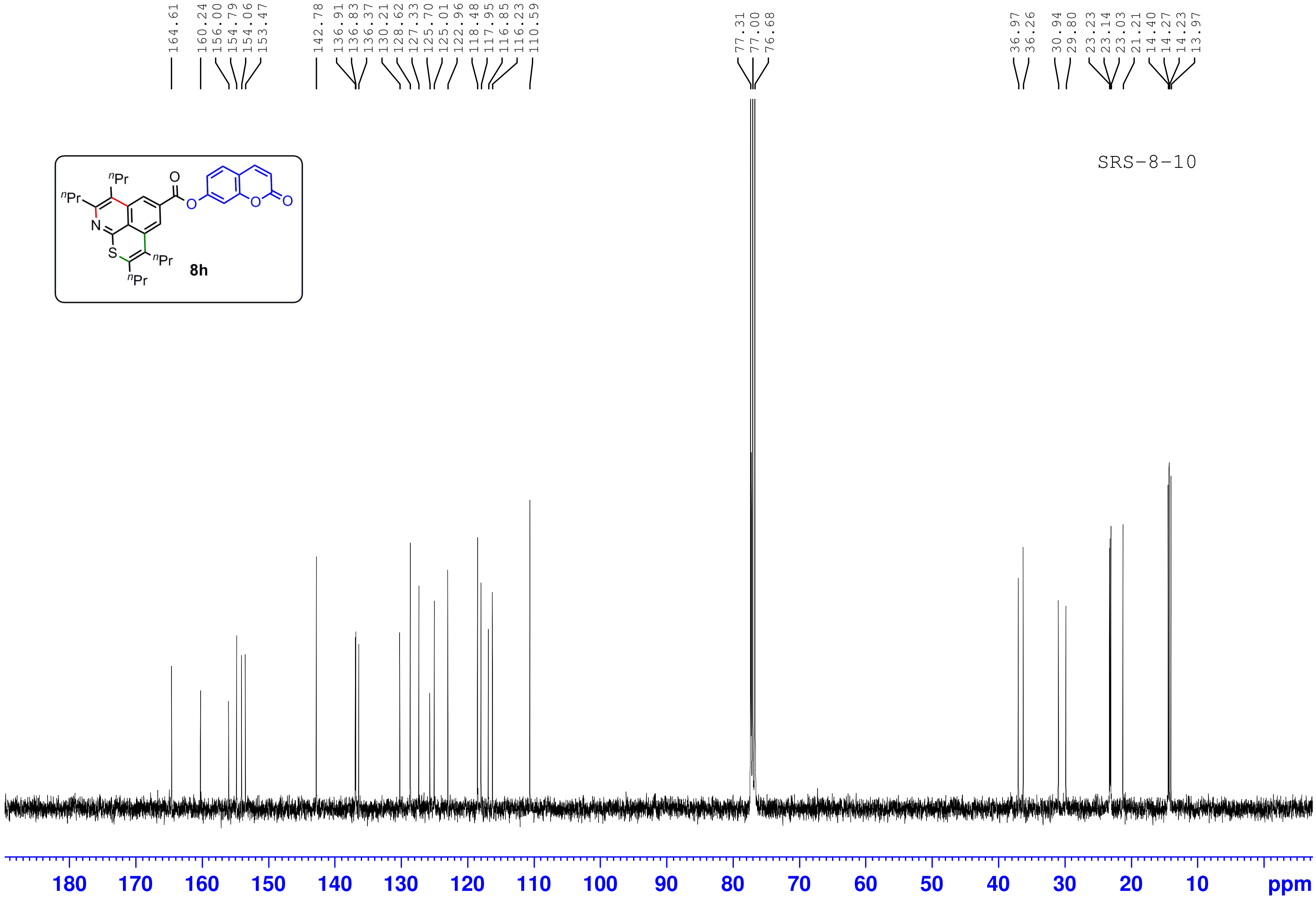
7.306
7.240
7.234
6.447
6.423
2.893
2.873
2.853
2.814
2.795
2.775
2.676
2.656
2.636
2.531
2.511
2.491
1.779
1.760
1.740
1.720
1.699
1.688
1.652
1.633
1.614
1.595
1.576
1.094
1.090
1.076
1.072
1.065
1.057
1.047
1.037
1.029
SRS-8-10
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.02
1.04
1.06
1.00
1.07
1.01
2.03
2.08
2.05
2.07
8.15
12.26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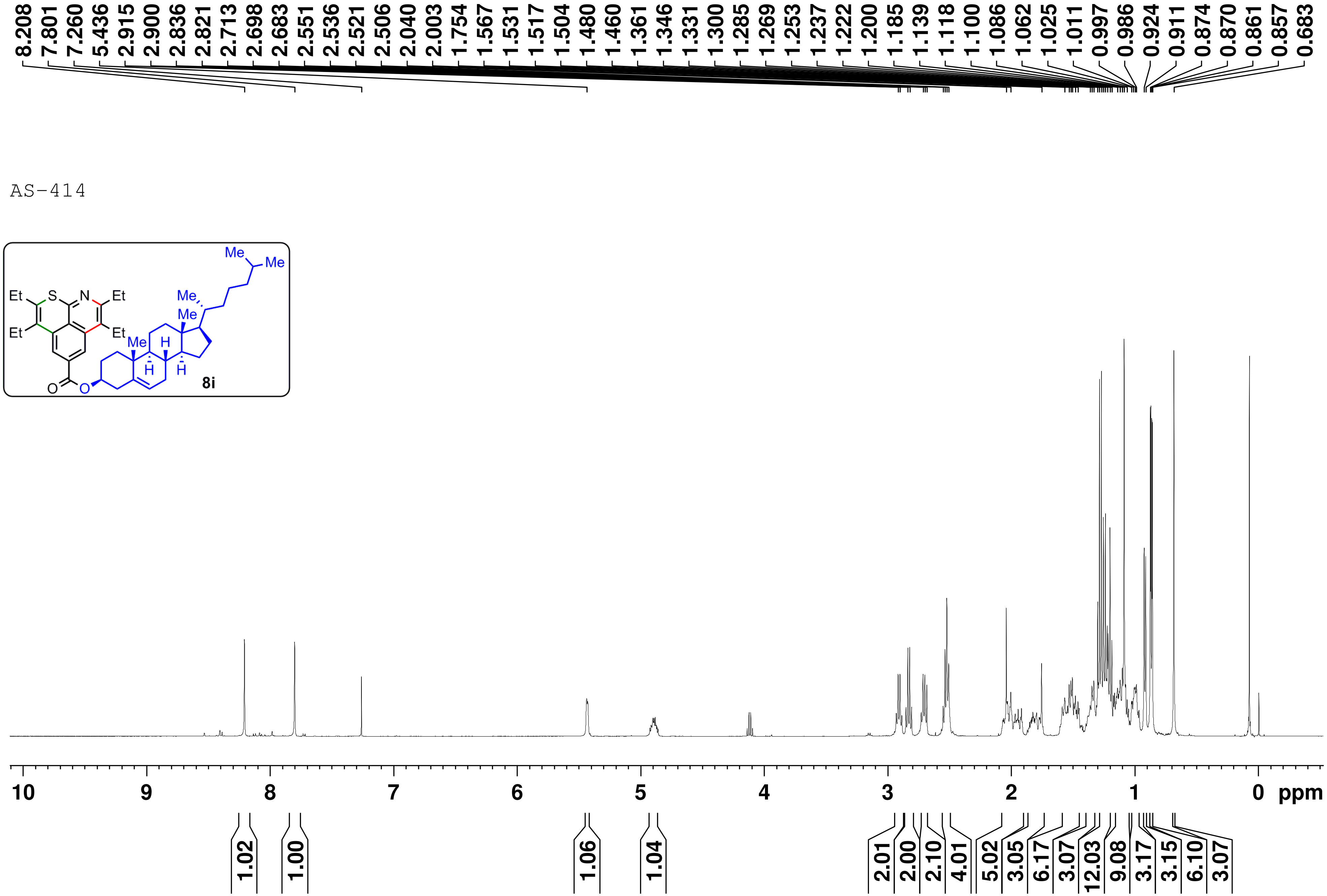
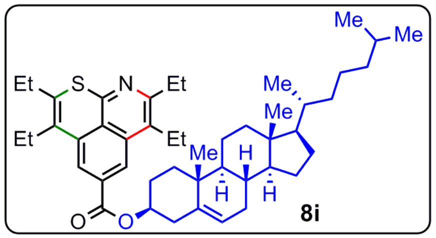
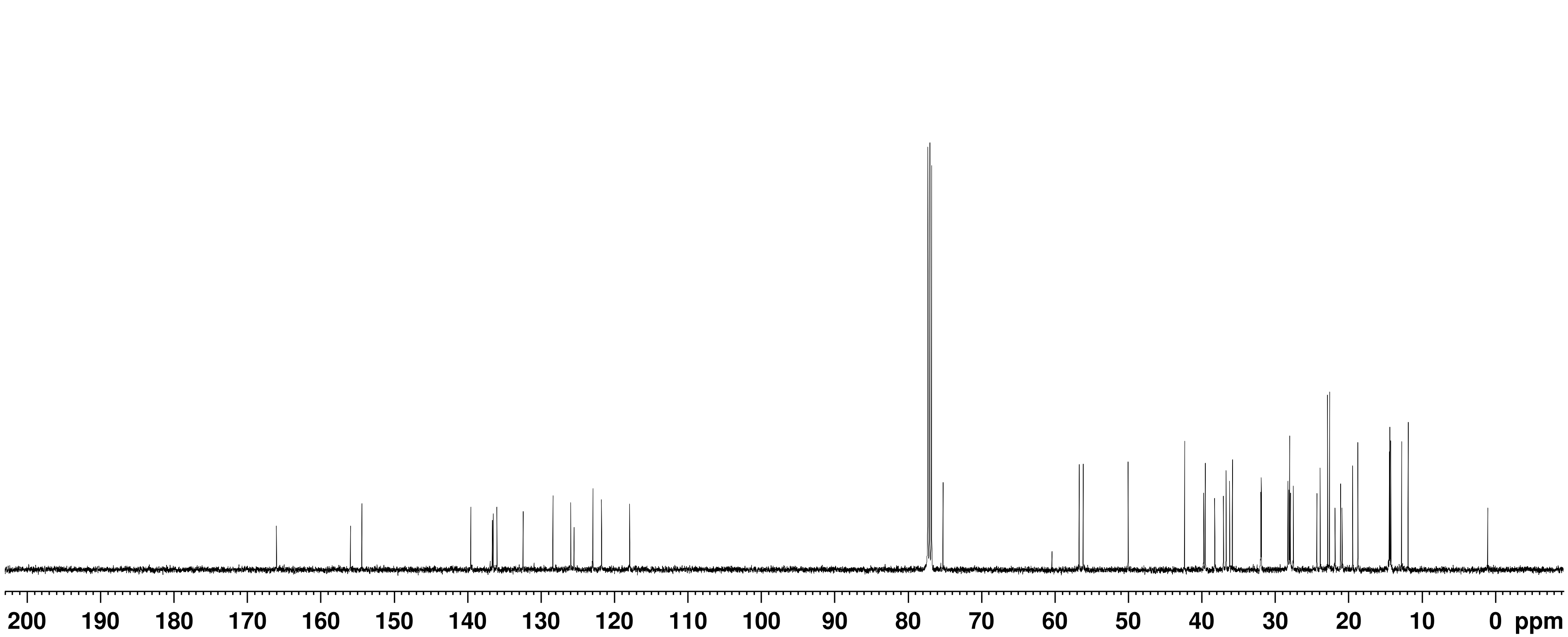
154.06
153.47
142.78
136.91
136.83
136.37
130.21
128.62
127.33
125.70
125.01
122.96
118.48
117.95
116.85
116.23
110.59
77.31
77.00
76.68
36.97
36.26
30.94
29.80
23.23
23.14
23.03
21.21
14.40
14.27
14.23
13.97
SRS-8-10
8h
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.208 7.801 7.260 5.436 2.915 2.900 2.836 2.821 2.713 2.698 2.683 2.551 2.536 2.521 2.506 2.040 2.003 1.754 1.567 1.531 1.517 1.504 1.480 1.460 1.361 1.346 1.331 1.300 1.285 1.269 1.253 1.237 1.222 1.200 1.185 1.139 1.118 1.100 1.086 1.062 1.025 1.011 0.997 0.986 0.924 0.911 0.874 0.870 0.861 0.857 0.683
AS-414
Et
S
N
Me
H
O
10 9 8 7 6 5 4 3 2 1 0 ppm
1.02 1.00 1.06 1.04 2.01 2.00 2.10 4.01 5.02 3.05 6.17 3.07 12.03 9.08 3.17 3.15 6.10 3.07
8i

AS-414


Et
S
N
Et
Et
Et
Me
Me
Me
Me
Me
H
H
H
O
O
8i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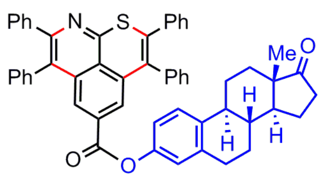
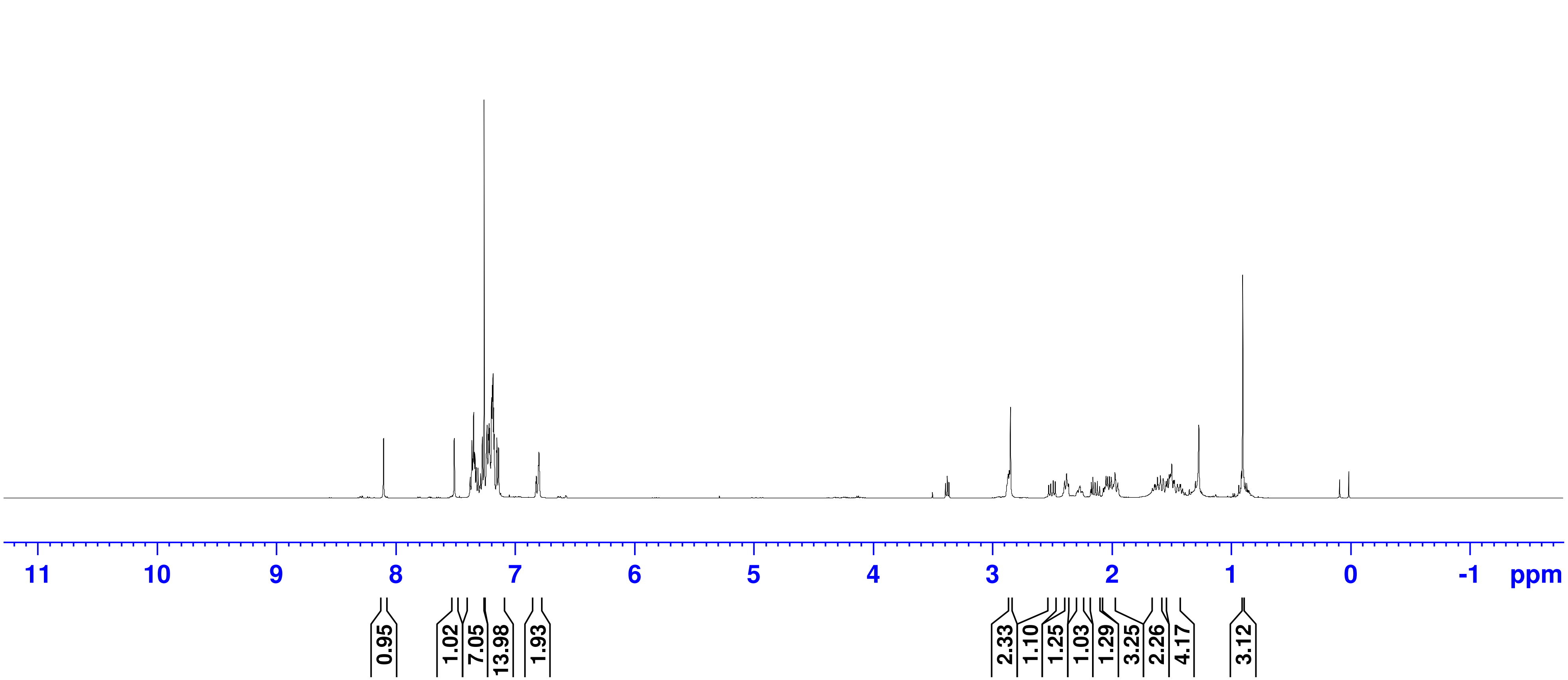
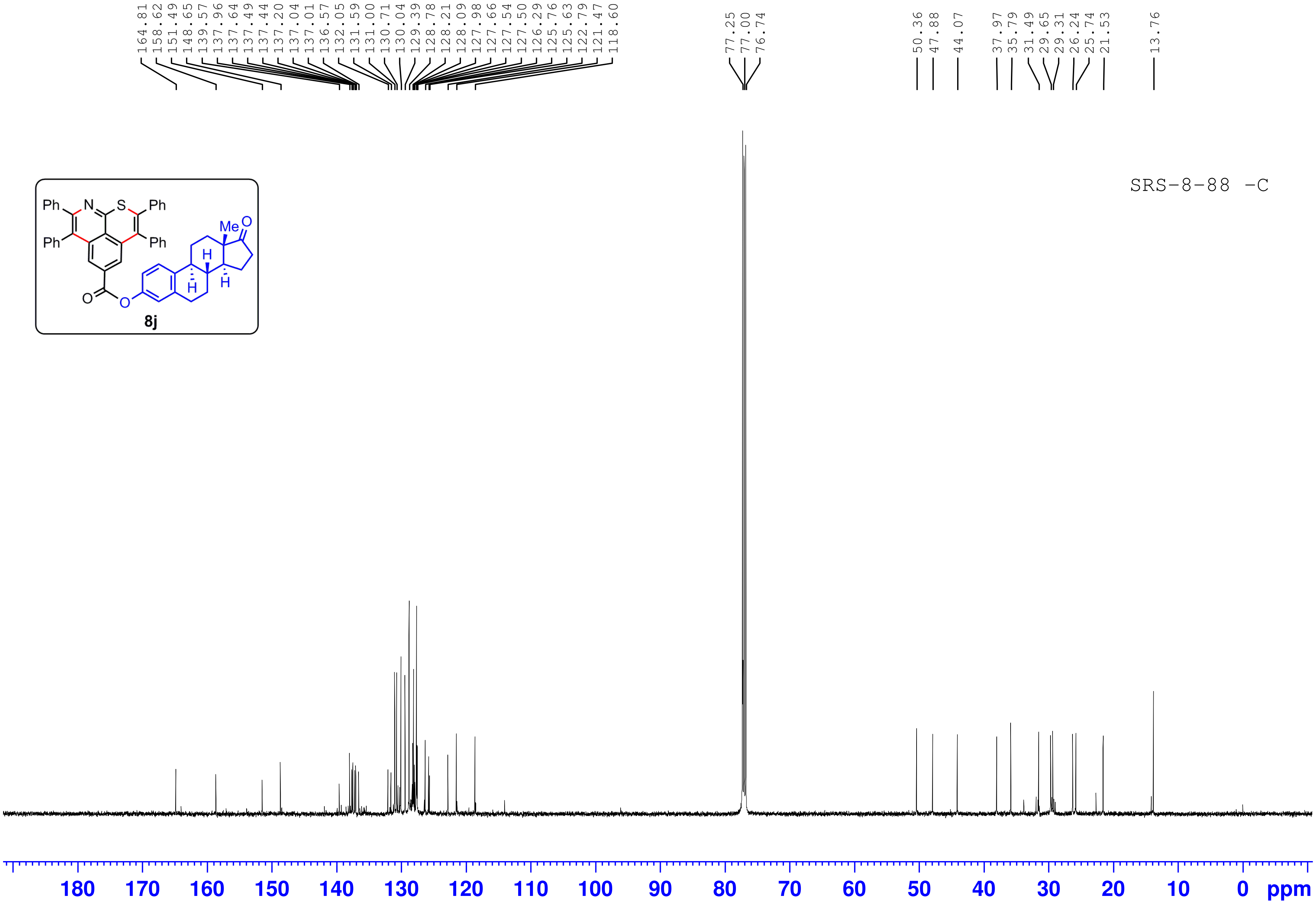
154.38
139.53
136.59
136.48
135.97
132.39
128.36
125.93
125.47
122.88
121.72
117.89
77.25
77.00
76.75
75.20
56.65
56.10
49.99
42.28
39.69
39.48
38.18
37.00
36.64
36.15
35.77
31.91
31.83
28.21
28.06
27.99
27.86
27.48
24.26
23.82
22.80
22.54
21.79
21.02
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

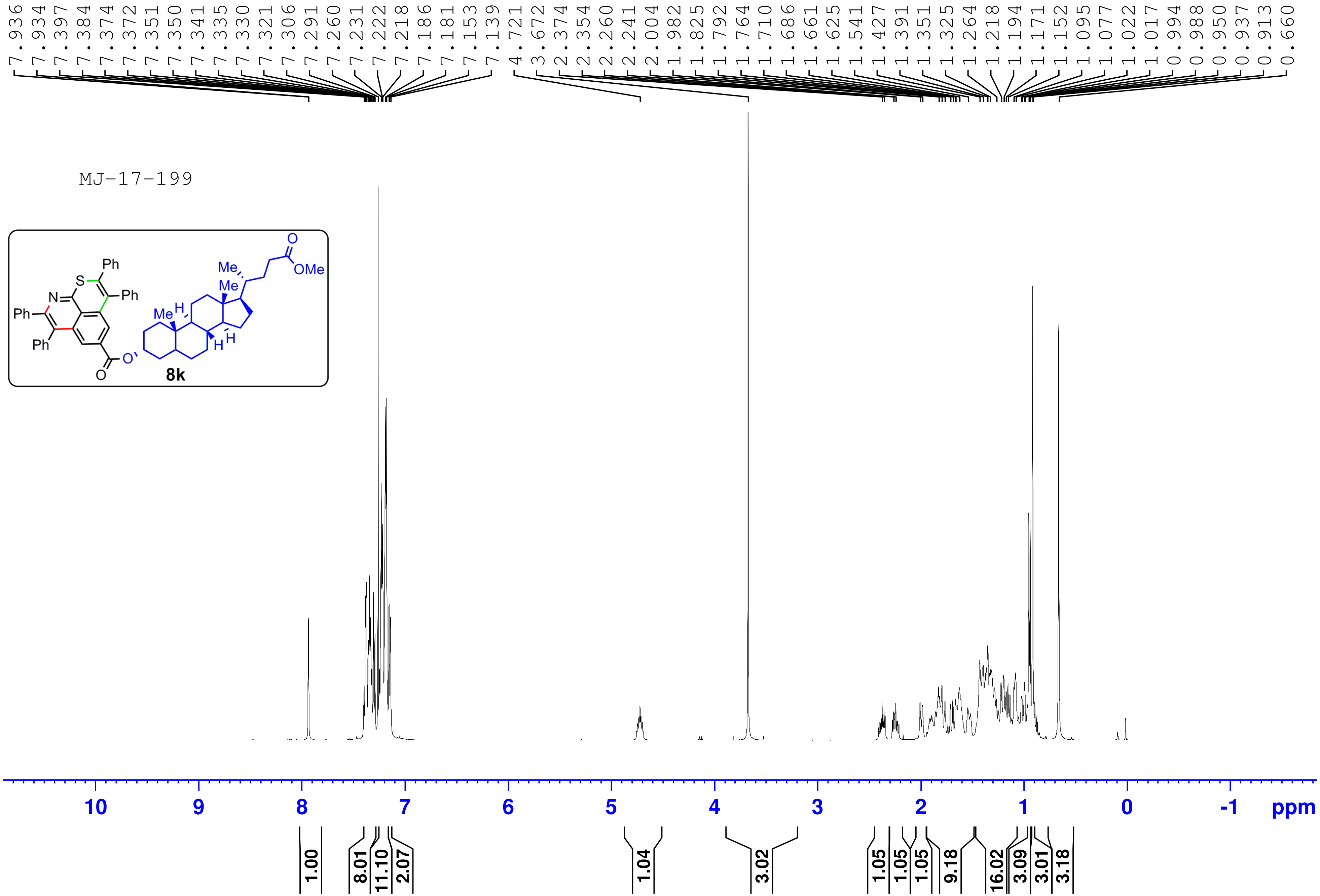

Ph
N
S
Ph
Ph
Ph
Me
O
H
H
H
O
O

8j


8.104
8.101
7.511
7.508
7.379
7.376
7.362
7.348
7.341
7.336
7.326
7.311
7.289
7.274
7.260
7.238
7.235
7.222
7.219
7.214
7.196
7.189
7.185
7.179
7.155
7.152
7.138
6.821
6.804
6.800
2.867
2.857
2.847
2.489
2.472
2.394
2.377
2.169
2.157
2.139
2.119
2.046
2.034
2.018
2.003
1.972
1.948
1.616
1.591
1.568
1.529
1.518
1.496
1.481
1.473
1.422
0.901
SRS-8-88-N
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.95
1.02
7.05
13.98
1.93
2.33
1.10
1.25
1.03
1.29
3.25
2.26
4.17
3.12



164.81
158.62
151.49
148.65
139.57
137.96
137.64
137.49
137.44
137.20
137.04
137.01
136.57
132.05
131.59
131.00
130.71
130.04
129.39
128.78
128.21
128.09
127.98
127.66
127.54
127.50
126.29
125.76
125.63
122.79
121.47
118.60
77.25
77.00
76.74
50.36
47.88
44.07
37.97
35.79
31.49
29.65
29.31
26.24
25.74
21.53
13.76
SRS-8-88 -C
Ph
N
S
Ph
Ph
Ph
Me
O
H
H
H
O
O
8j
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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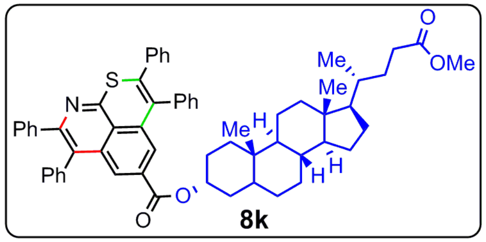
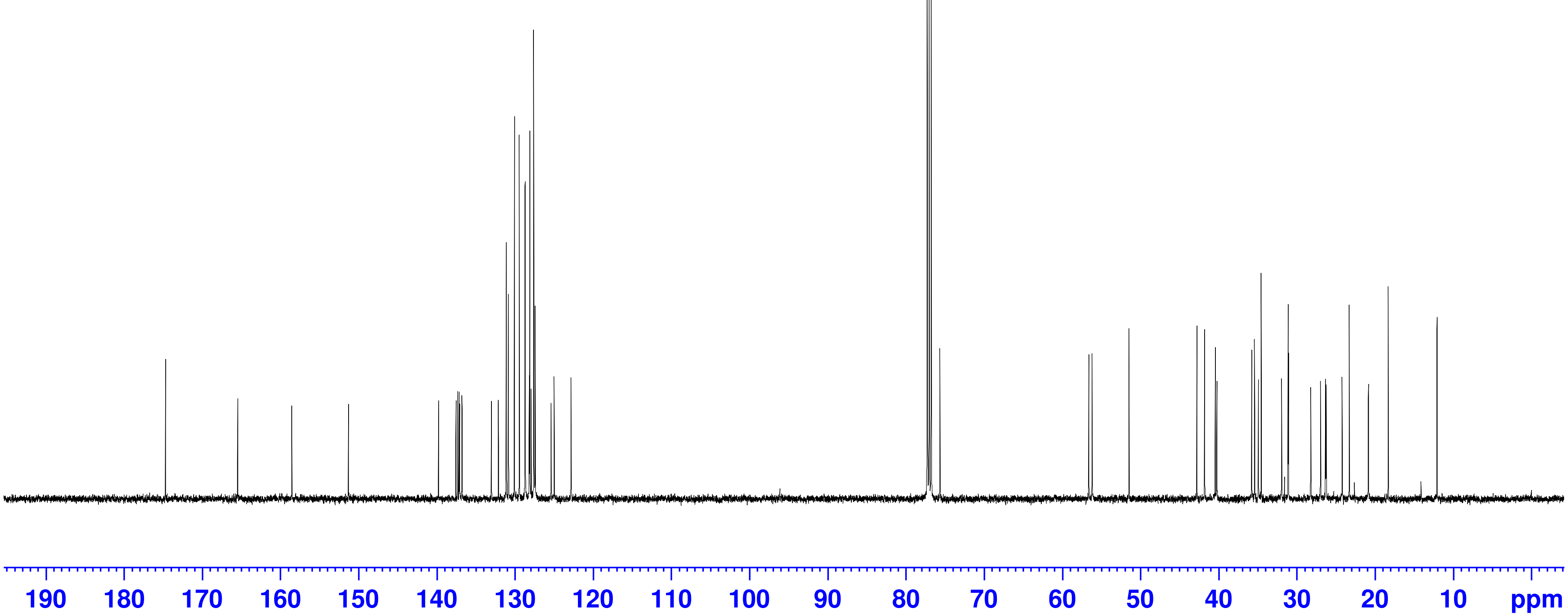
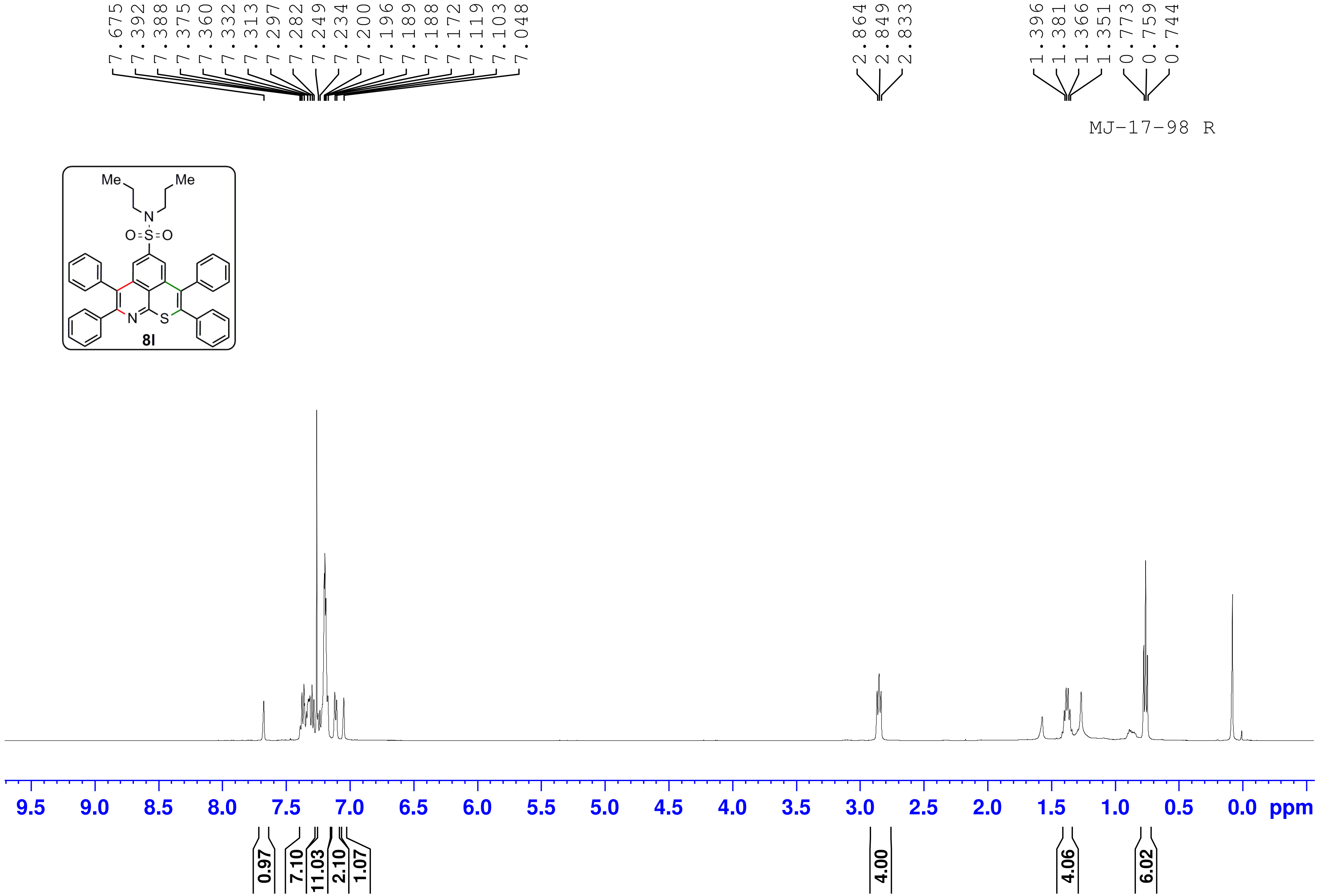
7.934
7.397
7.384
7.374
7.372
7.351
7.350
7.341
7.335
7.330
7.321
7.306
7.291
7.260
7.231
7.222
7.218
7.186
7.181
7.153
7.139
4.721
3.672
2.374
2.354
2.260
2.241
2.004
1.982
1.825
1.792
1.764
1.710
1.686
1.661
1.625
1.541
1.427
1.391
1.351
1.325
1.264
1.218
1.194
1.171
1.152
1.095
1.077
1.022
1.017
0.994
0.988
0.950
0.937
0.913
0.660
MJ-17-199
Ph
S
N
Ph
Ph
Ph
O
O
O
OMe
Me
Me
Me
H
H
H
8k
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
8.01
11.10
2.07
1.04
3.02
1.05
1.05
1.05
9.18
16.02
3.09
3.01
3.18

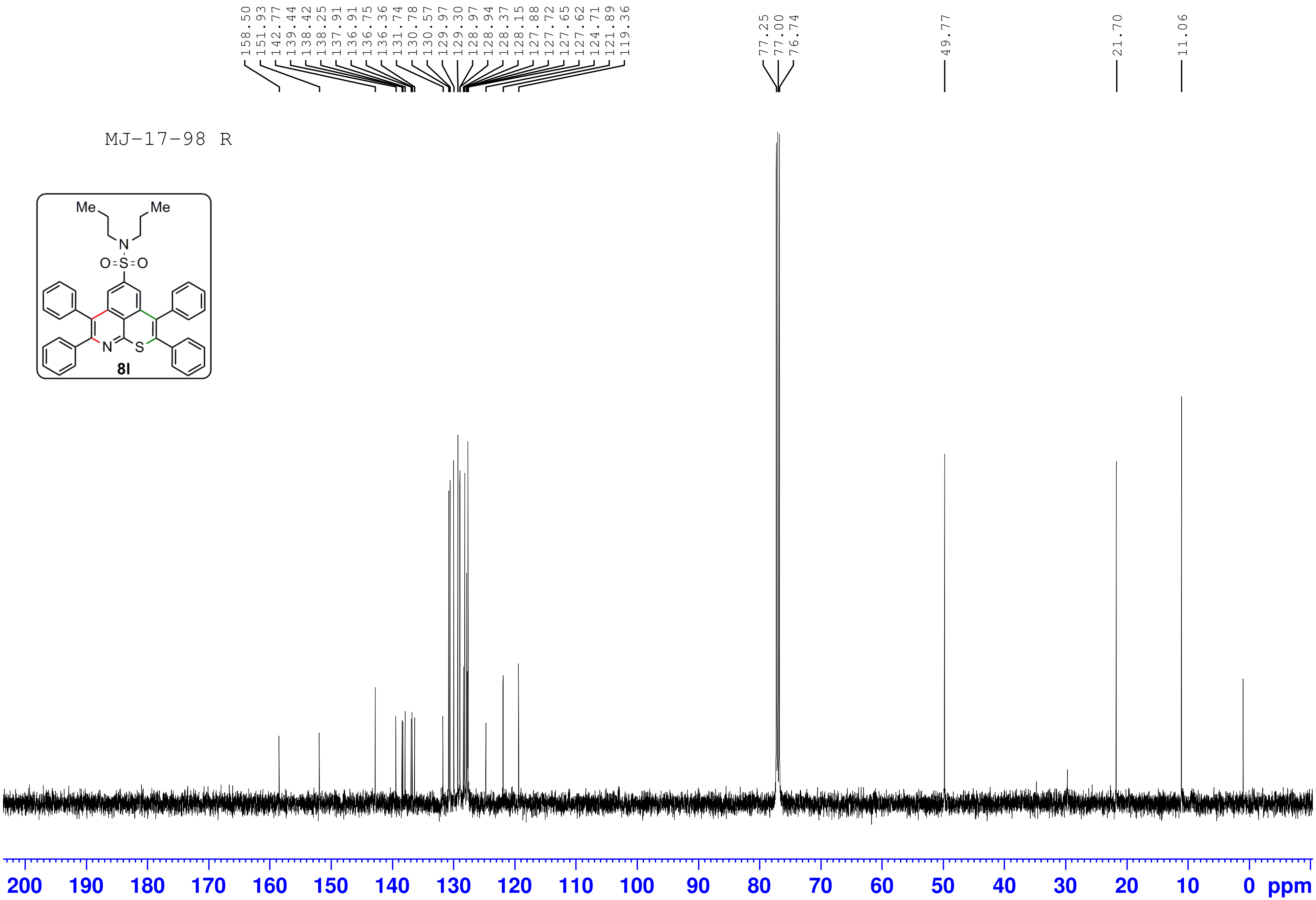

174.66
165.45
158.53
151.27
139.75
137.53
137.30
137.12
137.05
136.78
136.74
132.98
132.10
131.09
130.82
130.05
129.42
128.69
128.66
128.15
128.08
127.91
127.58
127.53
127.39
125.38
124.96
122.82
77.25
77.00
76.74
75.62
56.57
56.17
51.44
42.75
41.75
40.39
40.20
35.73
35.36
34.88
34.51
31.91
31.08
31.03
28.19
26.92
26.29
26.21
24.17
23.26
20.81
18.28
12.03

MJ-17-199

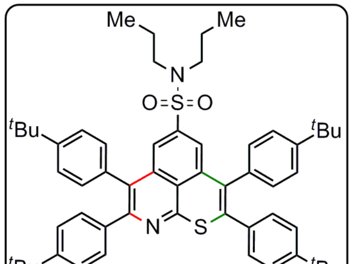

Ph
S
Ph
N
Ph
Ph
O
O
Me
H
Me
Me
H
H
O
OMe
8k


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

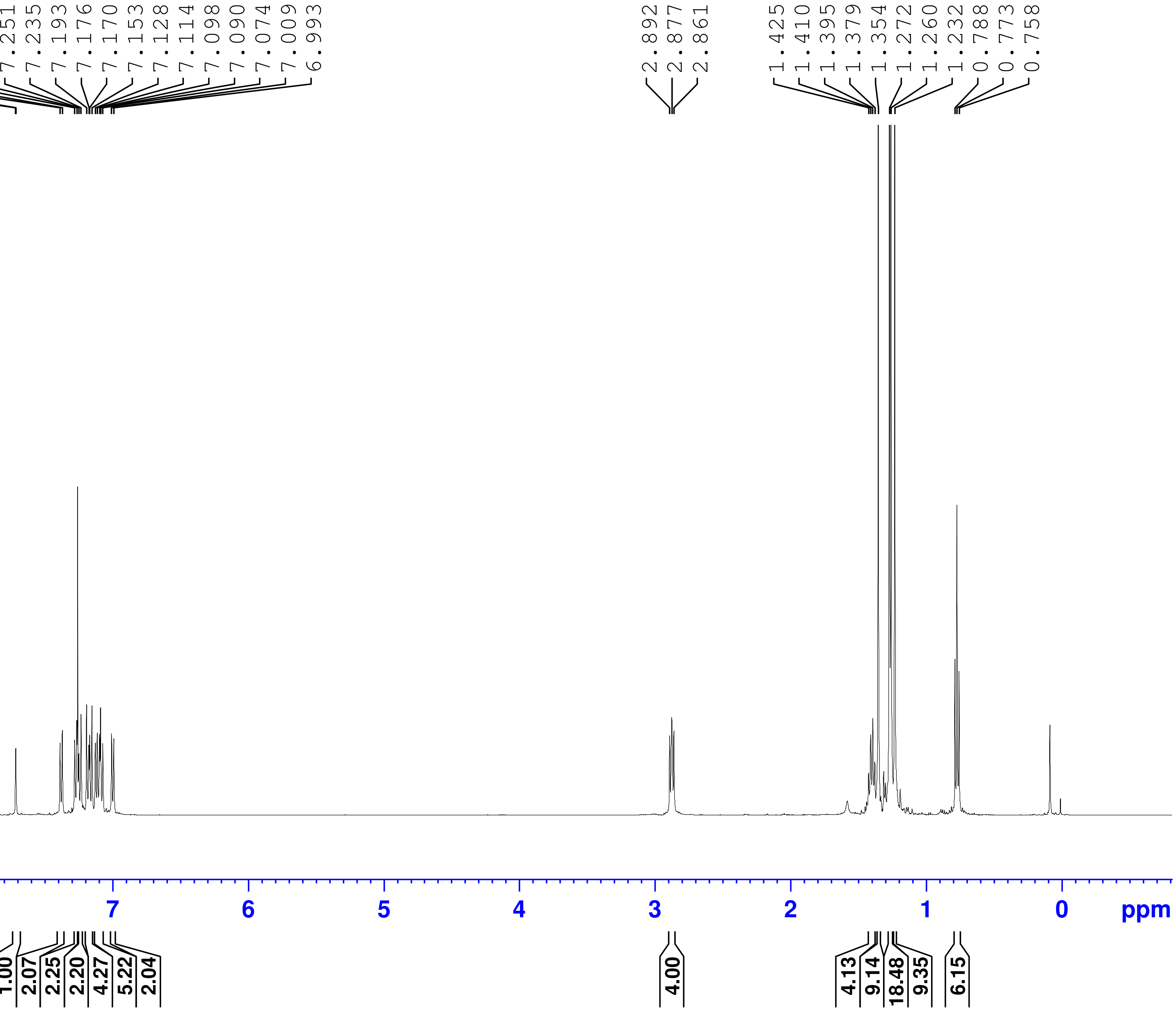

7.675
7.392
7.388
7.375
7.360
7.332
7.313
7.297
7.282
7.249
7.234
7.200
7.196
7.189
7.188
7.172
7.119
7.103
7.048
2.864
2.849
2.833
1.396
1.381
1.366
1.351
0.773
0.759
0.744
MJ-17-98 R
Me
Me
N
O=S=O
N
S
8l
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.97
7.10
11.03
2.10
1.07
4.00
4.06
6.02

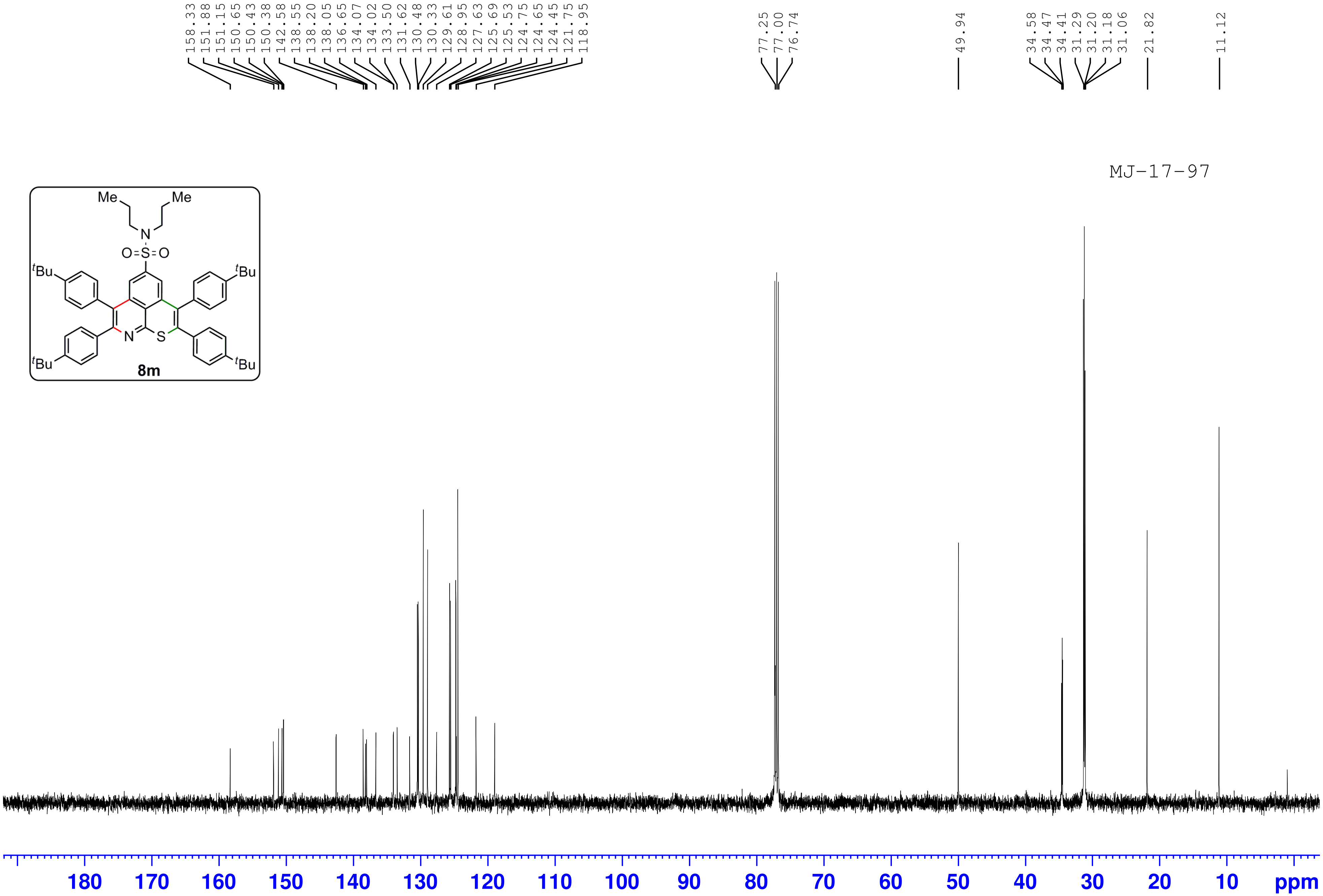

158.50
151.93
142.77
139.44
138.42
138.25
137.91
136.91
136.75
136.36
131.74
130.78
130.57
129.97
129.30
128.97
128.94
128.37
128.15
127.88
127.72
127.65
127.62
124.71
121.89
119.36
77.25
77.00
76.74
49.77
21.70
11.06
MJ-17-98 R
Me
Me
N
O=S=O
N
S
8l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

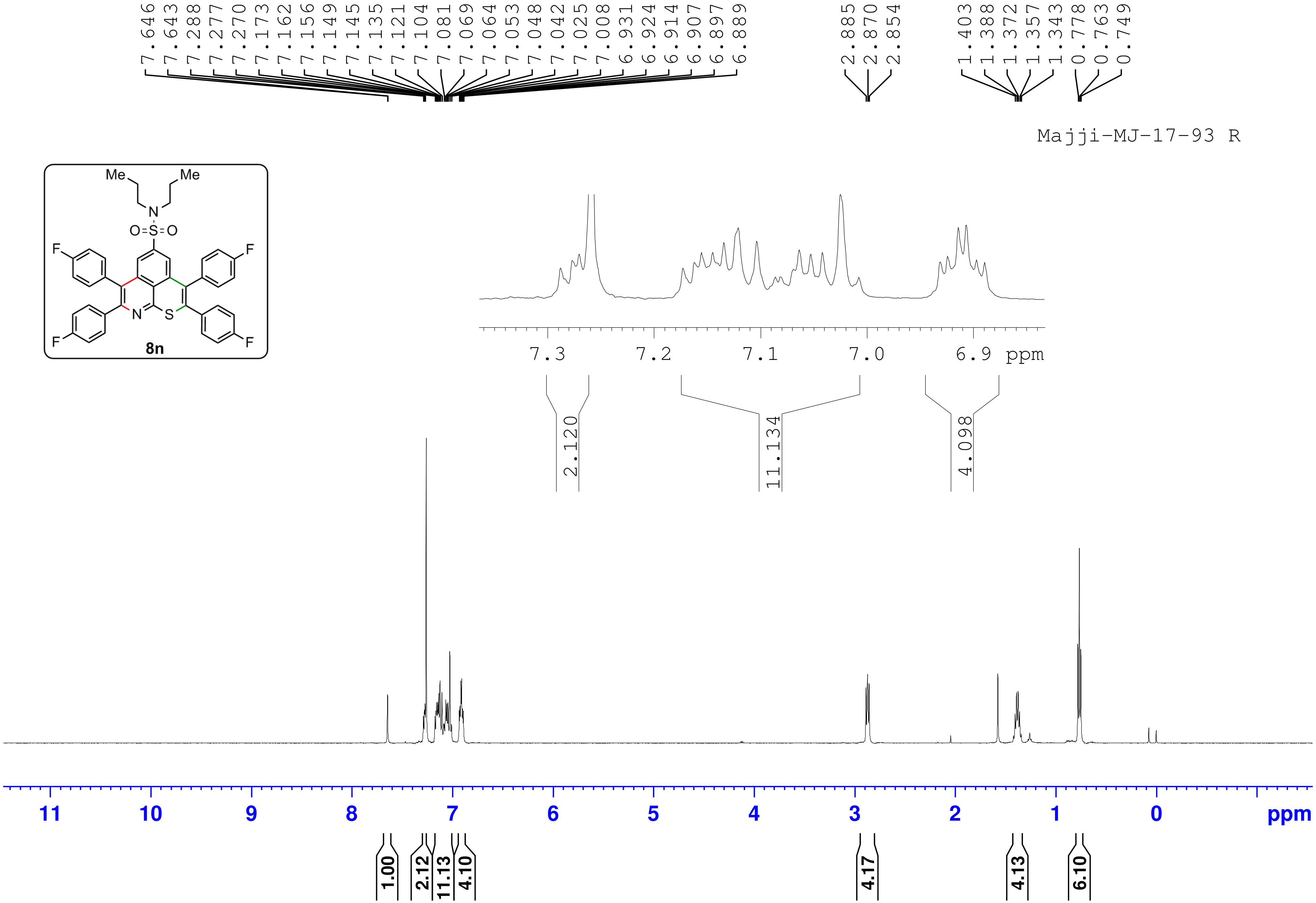
Majji-MJ-17-97

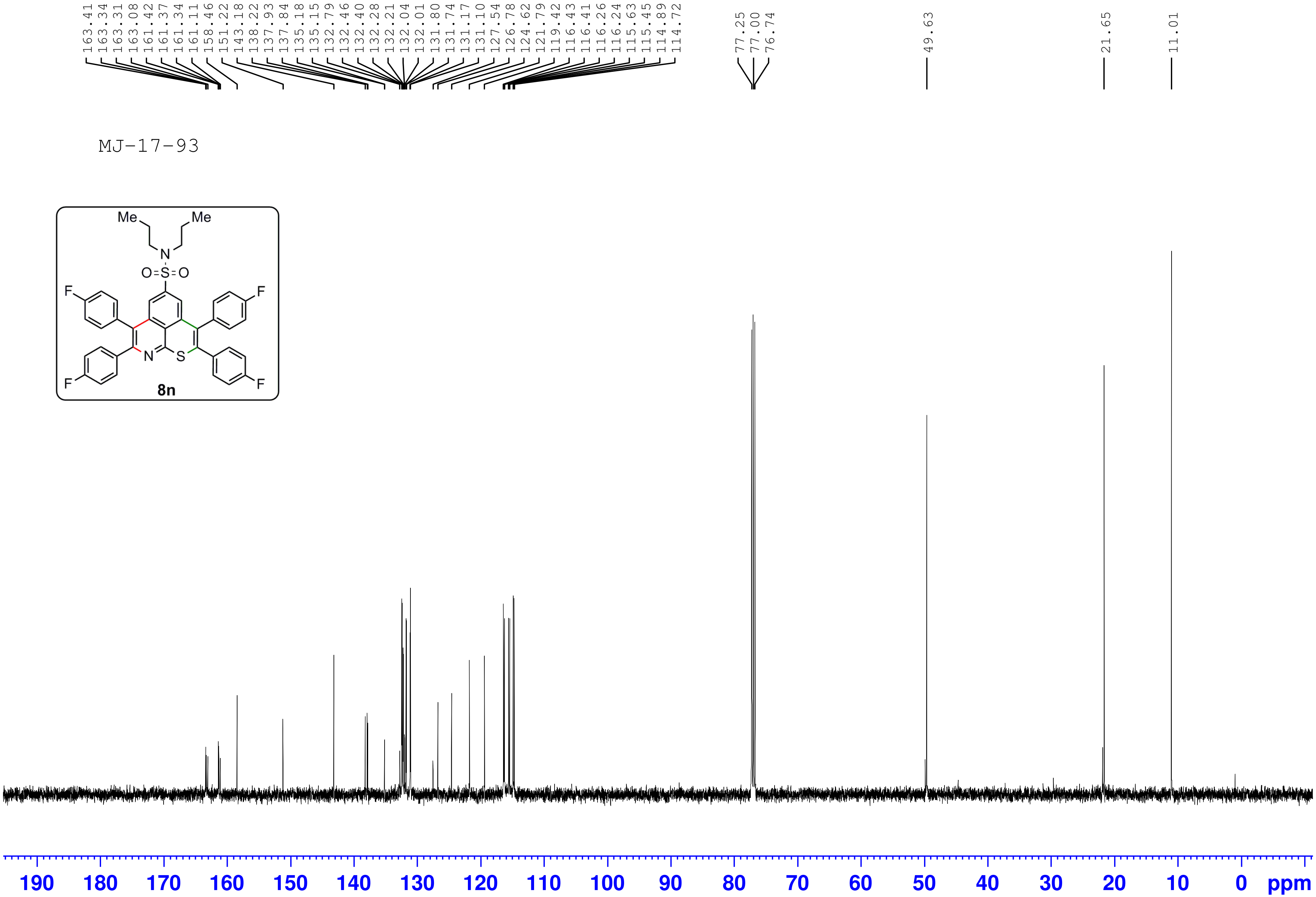


8m

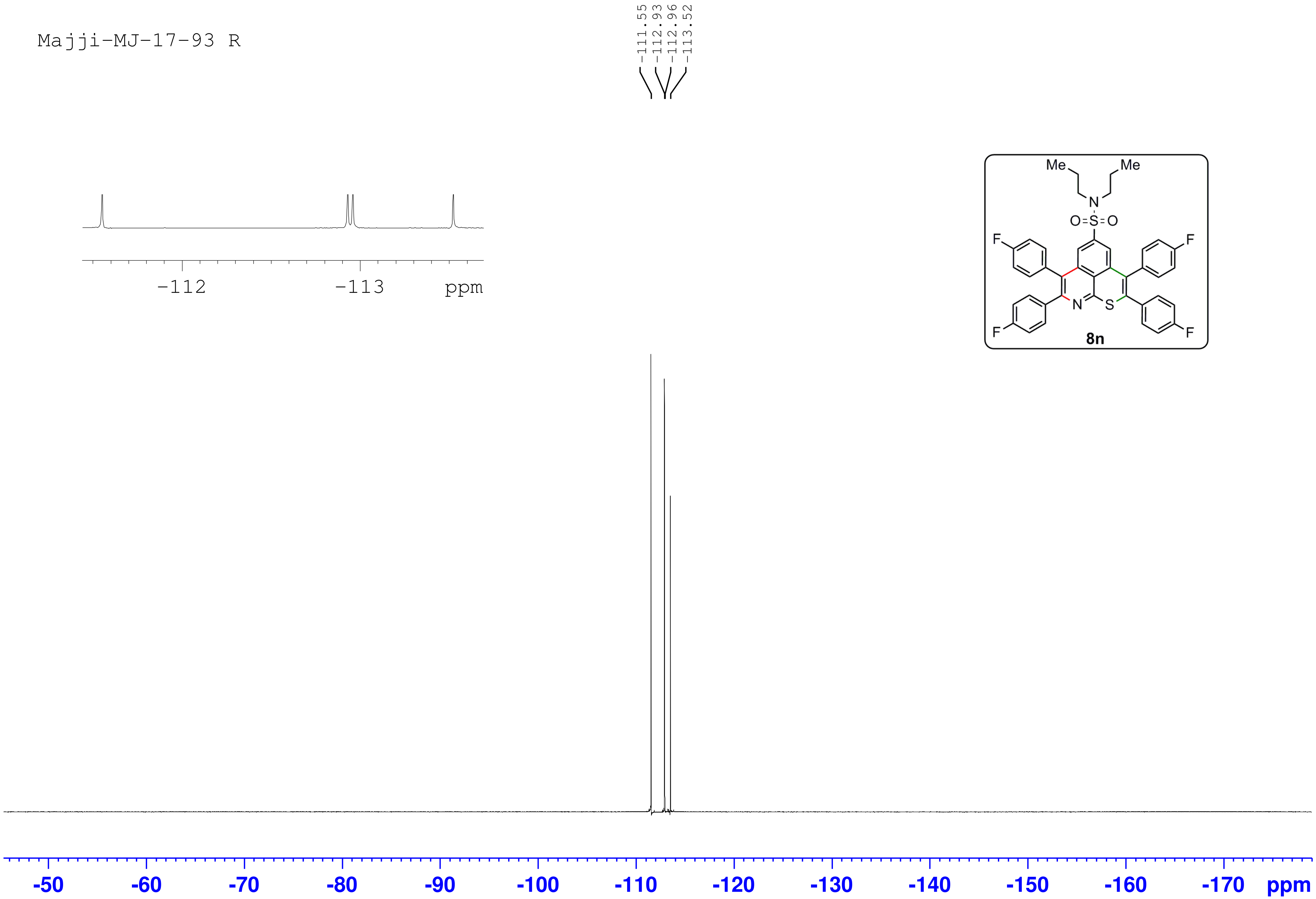



158.33
151.88
151.15
150.65
150.43
150.38
142.58
138.55
138.20
138.05
136.65
134.07
134.02
133.50
131.62
130.48
130.33
129.61
128.95
127.63
125.69
125.53
124.75
124.65
124.45
121.75
118.95
77.25
77.00
76.74
49.94
34.58
34.47
34.41
31.29
31.20
31.18
31.06
21.82
11.12
MJ-17-97
Me
Me
N
O=S=O
tBu
tBu
tBu
tBu
N
S
8m
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

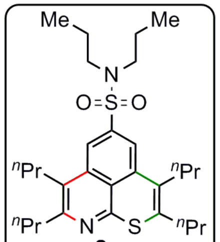

7.646 7.643 7.288 7.277 7.270 7.173 7.162 7.156 7.149 7.145 7.135 7.121 7.104 7.081 7.069 7.064 7.053 7.048 7.042 7.025 7.008 6.931 6.924 6.914 6.907 6.897 6.889
2.885 2.870 2.854
1.403 1.388 1.372 1.357 1.343 0.778 0.763 0.749
Majji-MJ-17-93 R
Me
Me
N
O=S=O
F
F
F
F
N
S
8n
7.3 7.2 7.1 7.0 6.9 ppm
2.120
11.134
4.098
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
2.12
11.13
4.10
4.17
4.13
6.10


163.41
163.34
163.31
163.08
161.42
161.37
161.34
161.11
158.46
151.22
143.18
138.22
137.93
137.84
135.18
135.15
132.79
132.46
132.40
132.28
132.21
132.04
132.01
131.80
131.74
131.17
131.10
127.54
126.78
124.62
121.79
119.42
116.43
116.41
116.26
116.24
115.63
115.45
114.89
114.72
77.25
77.00
76.74
49.63
21.65
11.01
MJ-17-93
Me
Me
N
O=S=O
F
F
F
F
N
S
8n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Majji-MJ-17-93 R

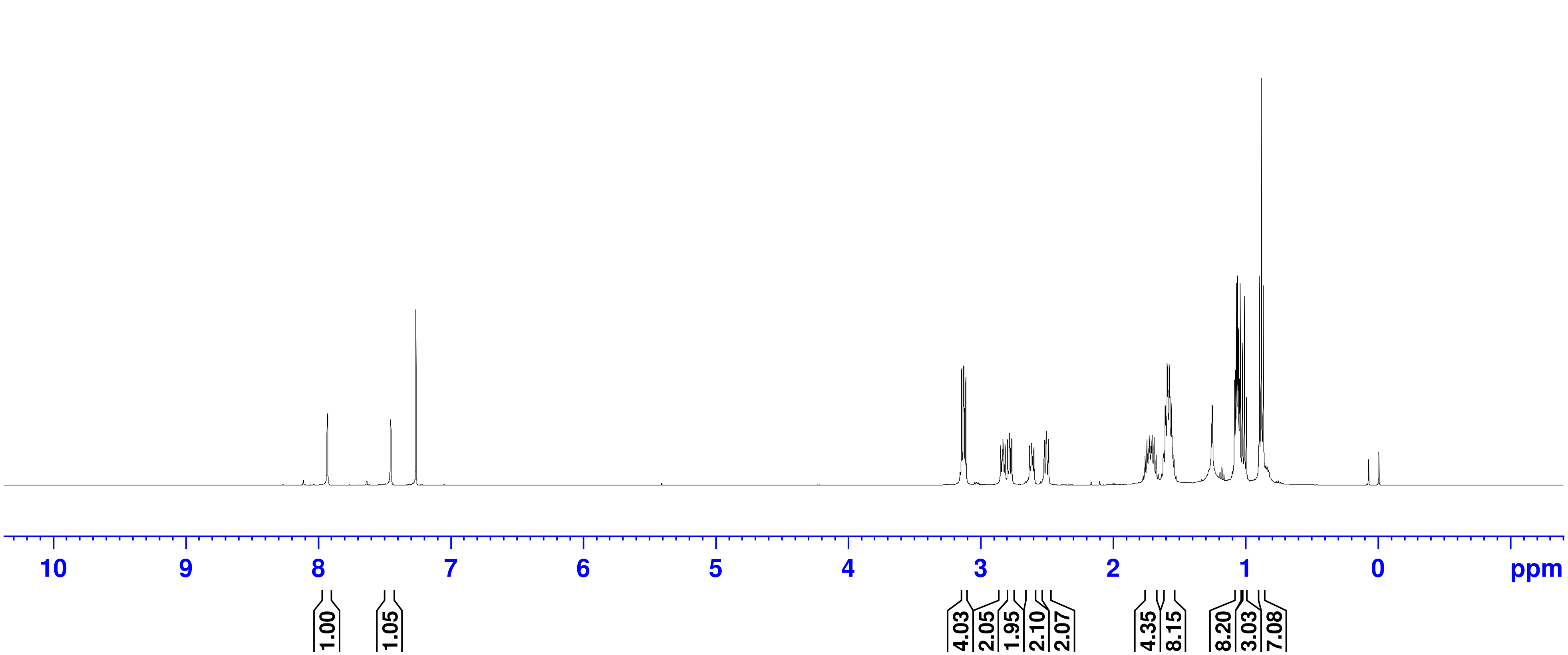


MJ-17-94

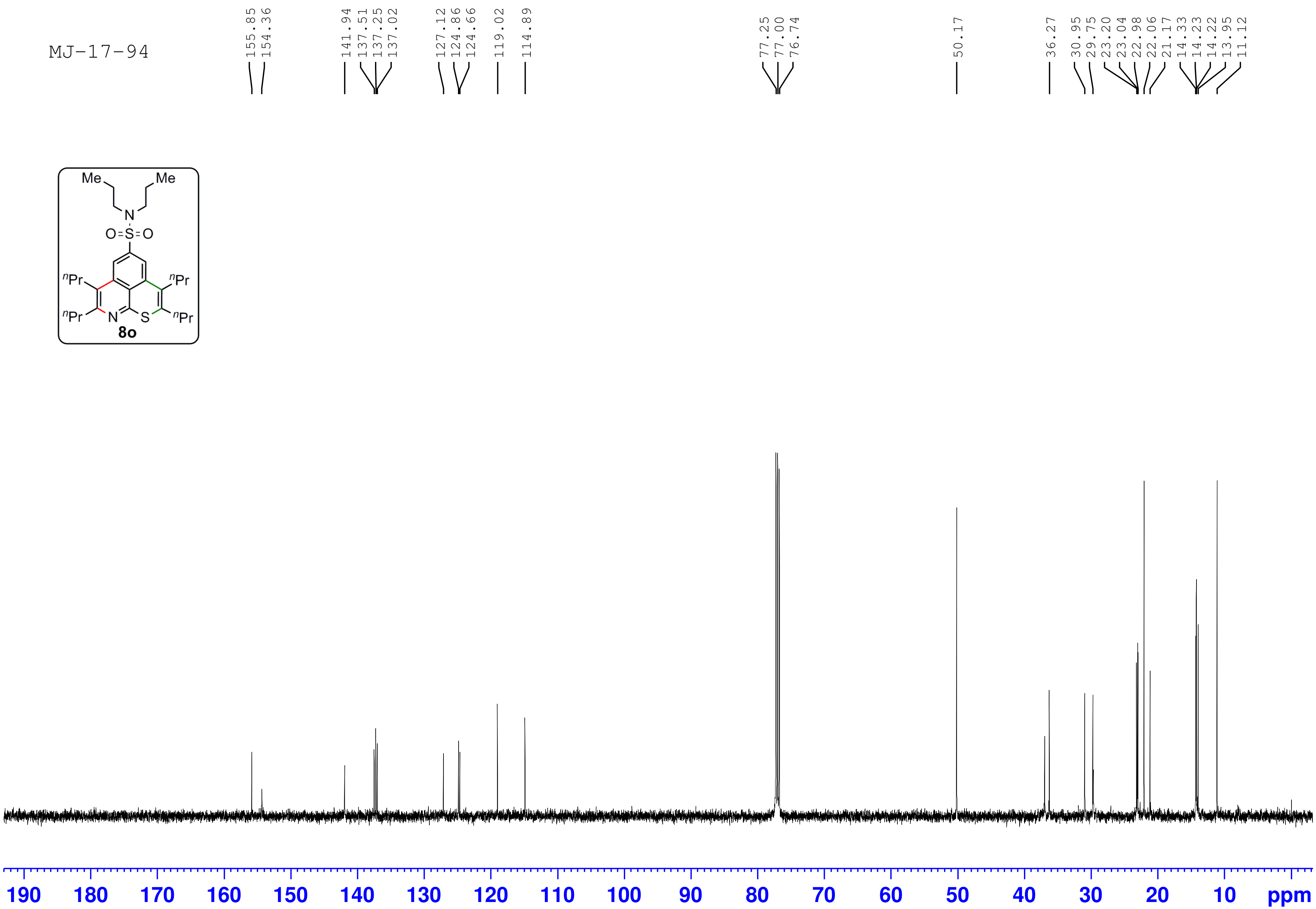


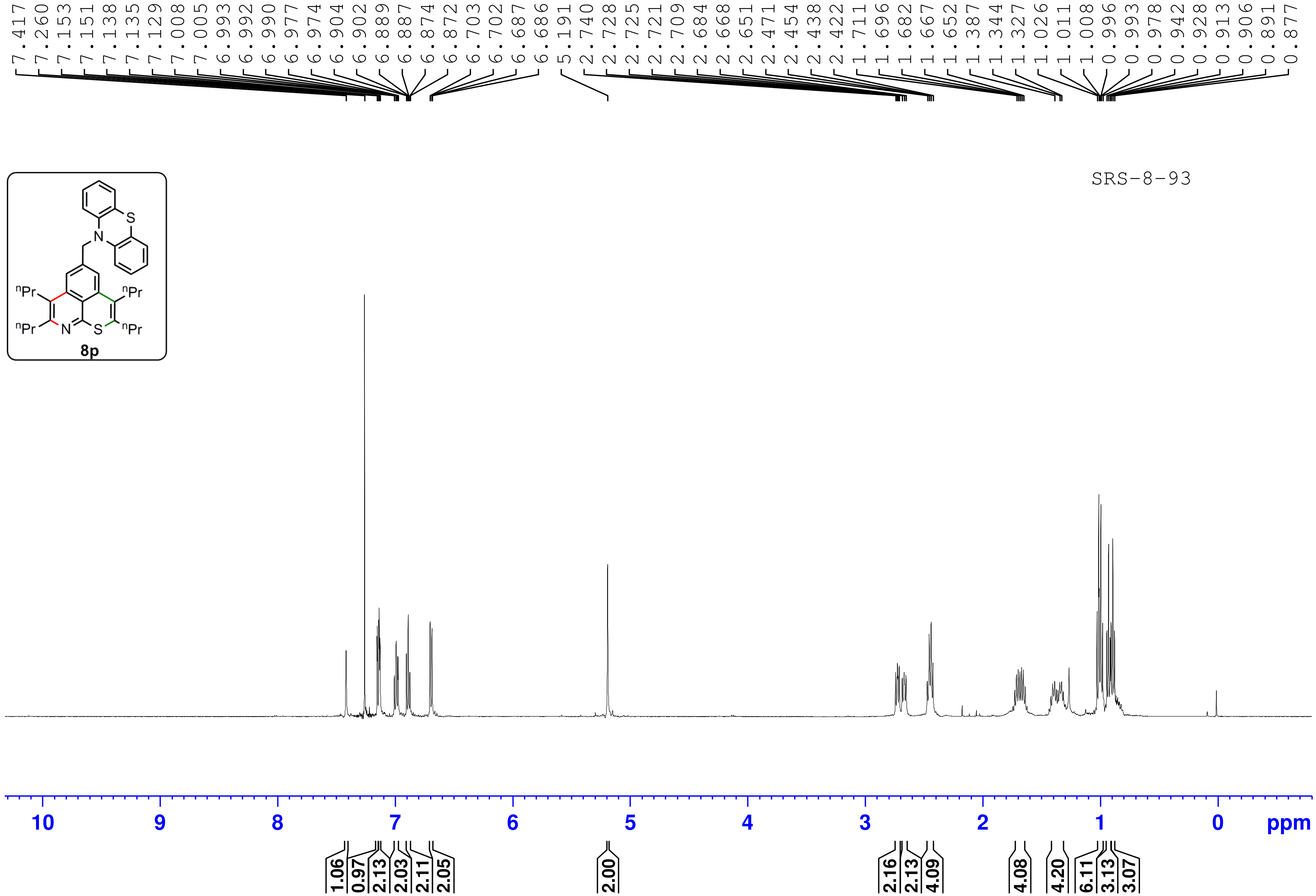
Me
Me
N
O=S=O
^{n}Pr
^{n}Pr
^{n}Pr
^{n}Pr
N
S

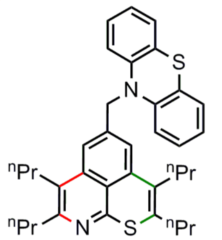
8o



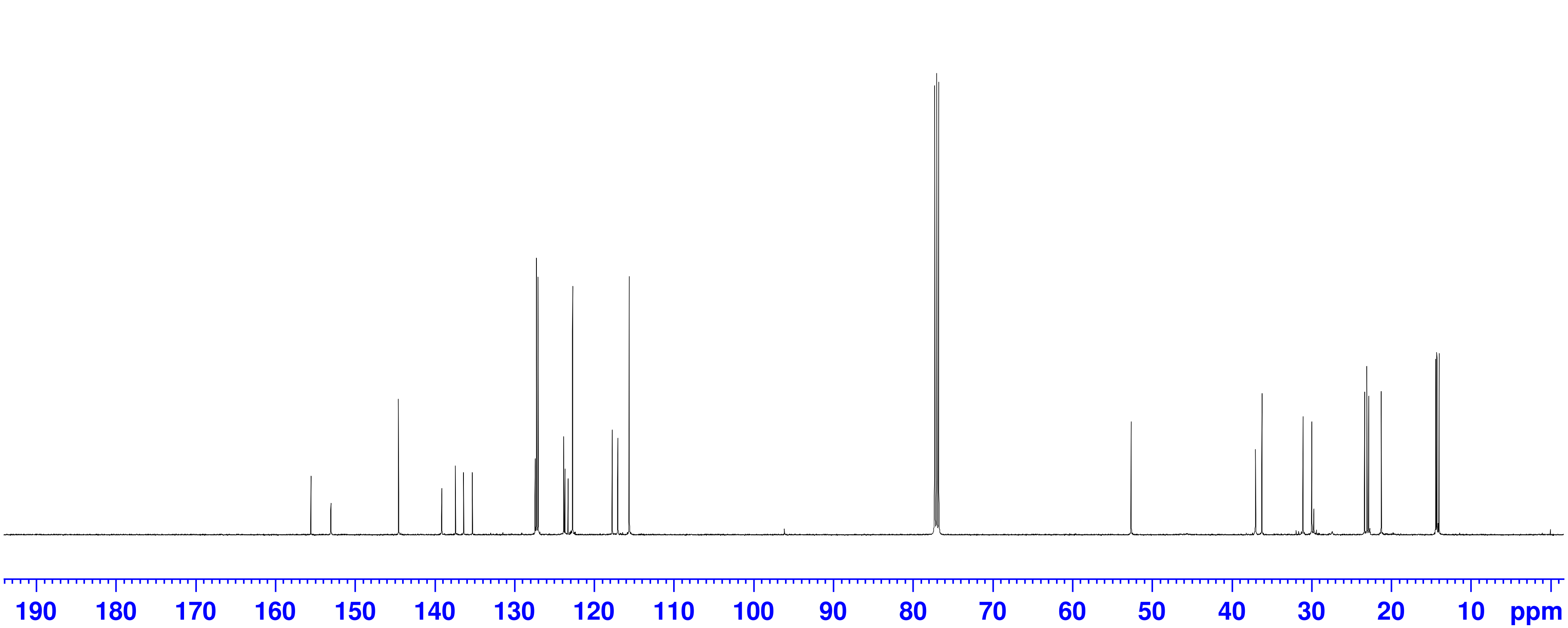
7.930
7.928
7.452
7.450
7.260
3.139
3.124
3.108
2.844
2.828
2.812
2.792
2.777
2.761
2.626
2.610
2.594
2.516
2.500
2.484
1.770
1.755
1.740
1.724
1.701
1.686
1.671
1.617
1.614
1.603
1.587
1.583
1.572
1.568
1.557
1.535
1.078
1.071
1.064
1.056
1.036
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.05
4.03
2.05
1.95
2.10
2.07
4.35
8.15
8.20
3.03
7.08

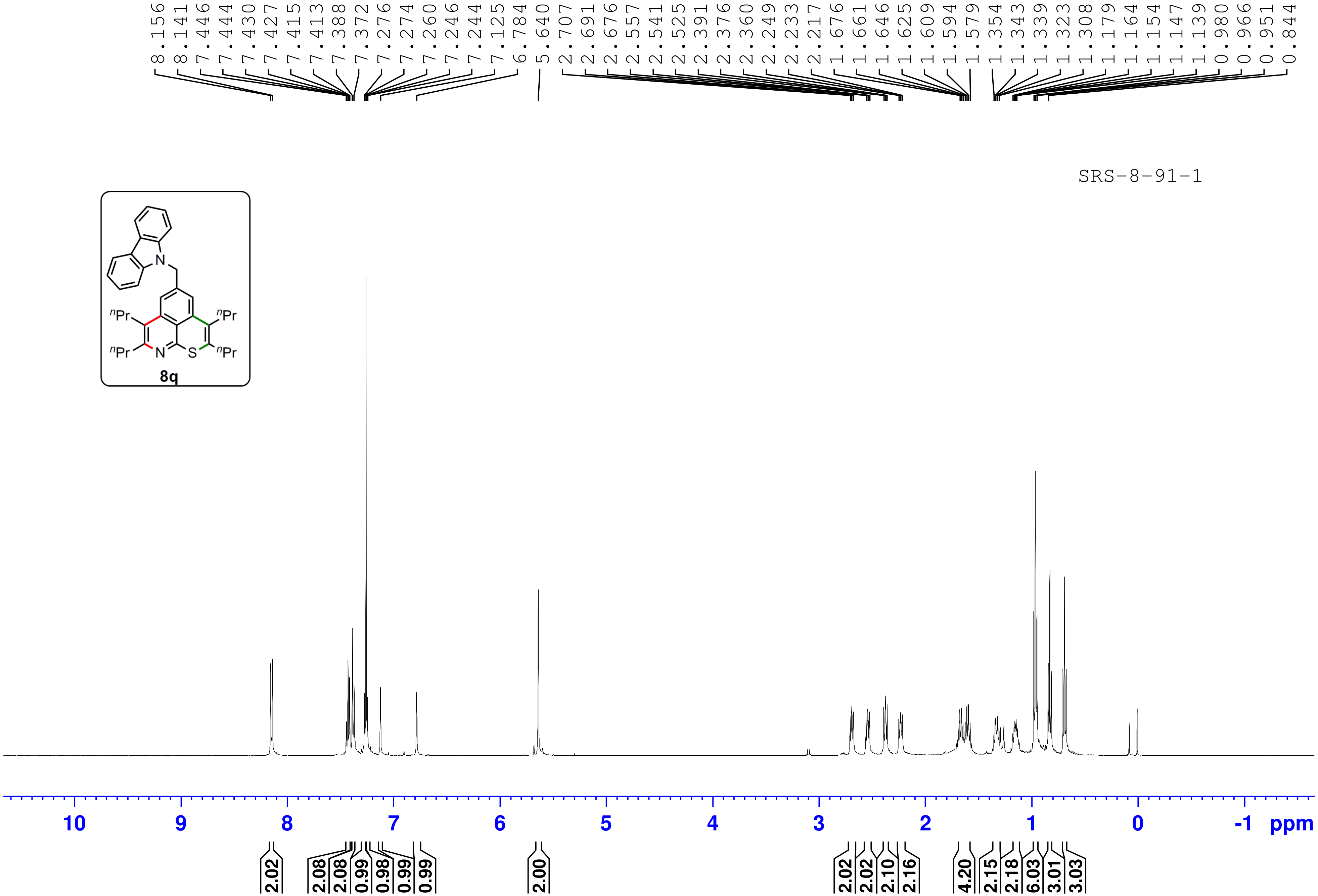

MJ-17-94
155.85
154.36
141.94
137.51
137.25
137.02
127.12
124.86
124.66
119.02
114.89
77.25
77.00
76.74
50.17
36.27
30.95
29.75
23.20
23.04
22.98
22.06
21.17
14.33
14.23
14.22
13.95
11.12
Me
Me
N
O=S=O
^{n}Pr
^{n}Pr
^{n}Pr
^{n}Pr
N
S
8o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

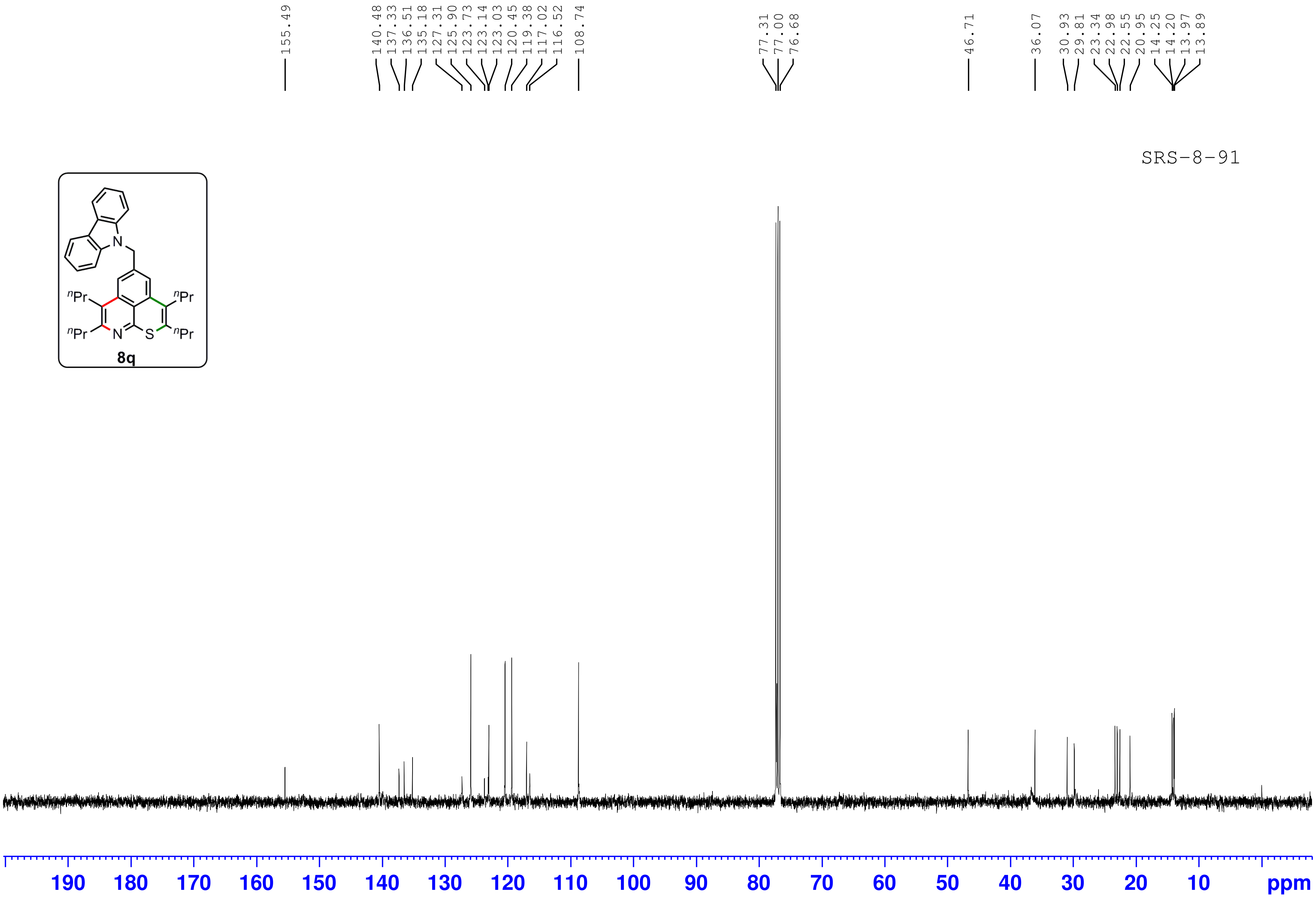

7.417
7.260
7.153
7.151
7.138
7.135
7.129
7.008
7.005
6.993
6.992
6.990
6.977
6.974
6.904
6.902
6.889
6.887
6.874
6.872
6.703
6.702
6.687
6.686
5.191
2.740
2.728
2.725
2.721
2.709
2.684
2.668
2.651
2.471
2.454
2.438
2.422
1.711
1.696
1.682
1.667
1.652
1.387
1.344
1.327
1.026
1.011
1.008
0.996
0.993
0.978
0.942
0.928
0.913
0.906
0.891
0.877
SRS-8-93
S
N
^{n}Pr
^{n}Pr
N
S
^{n}Pr
^{n}Pr
8p
10
9
8
7
6
5
4
3
2
1
0
ppm
1.06
0.97
2.13
2.03
2.11
2.05
2.00
2.16
2.13
4.09
4.08
4.20
6.11
3.13
3.07

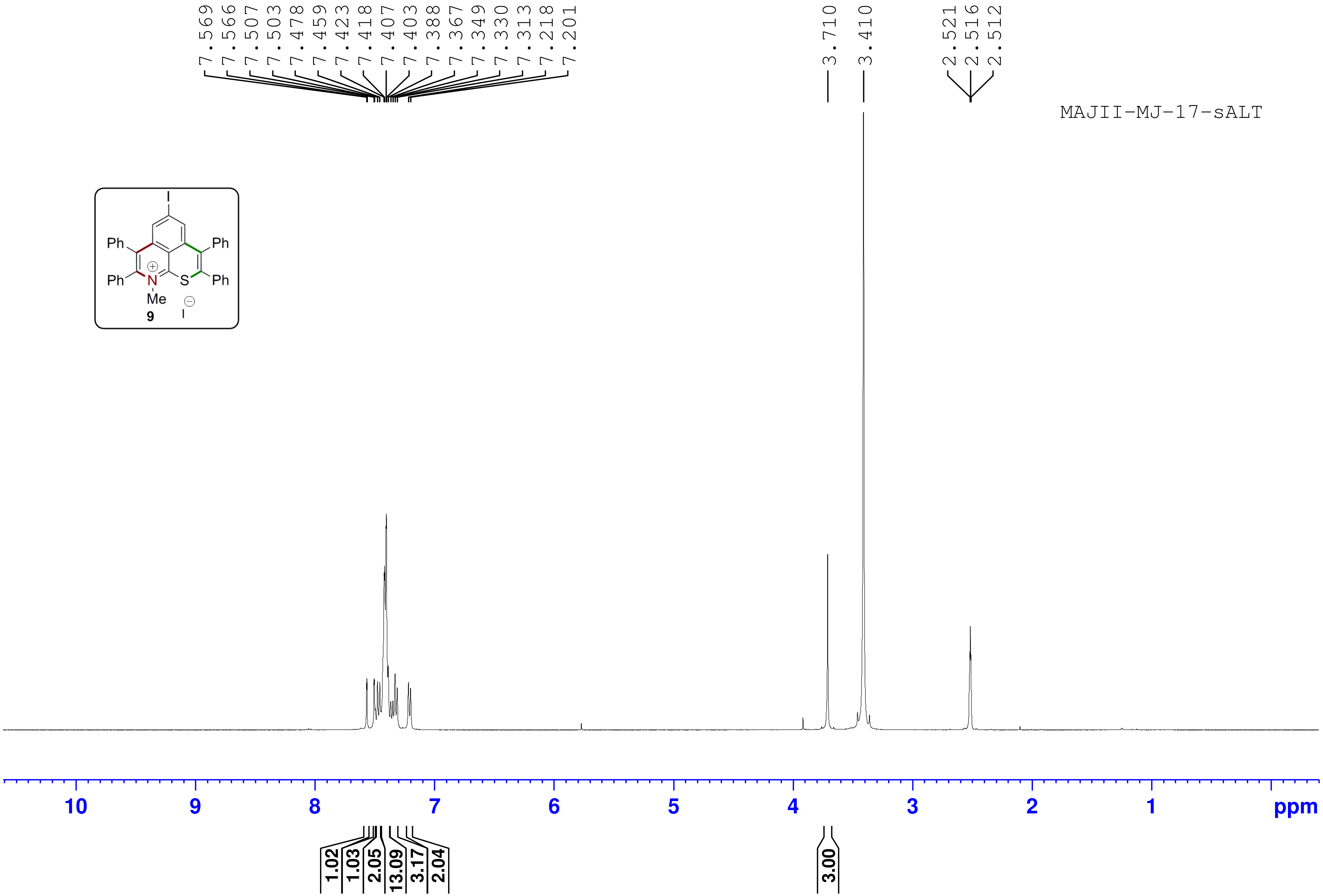

S
N
ⁿPr
ⁿPr
ⁿPr
ⁿPr
N
S

8p

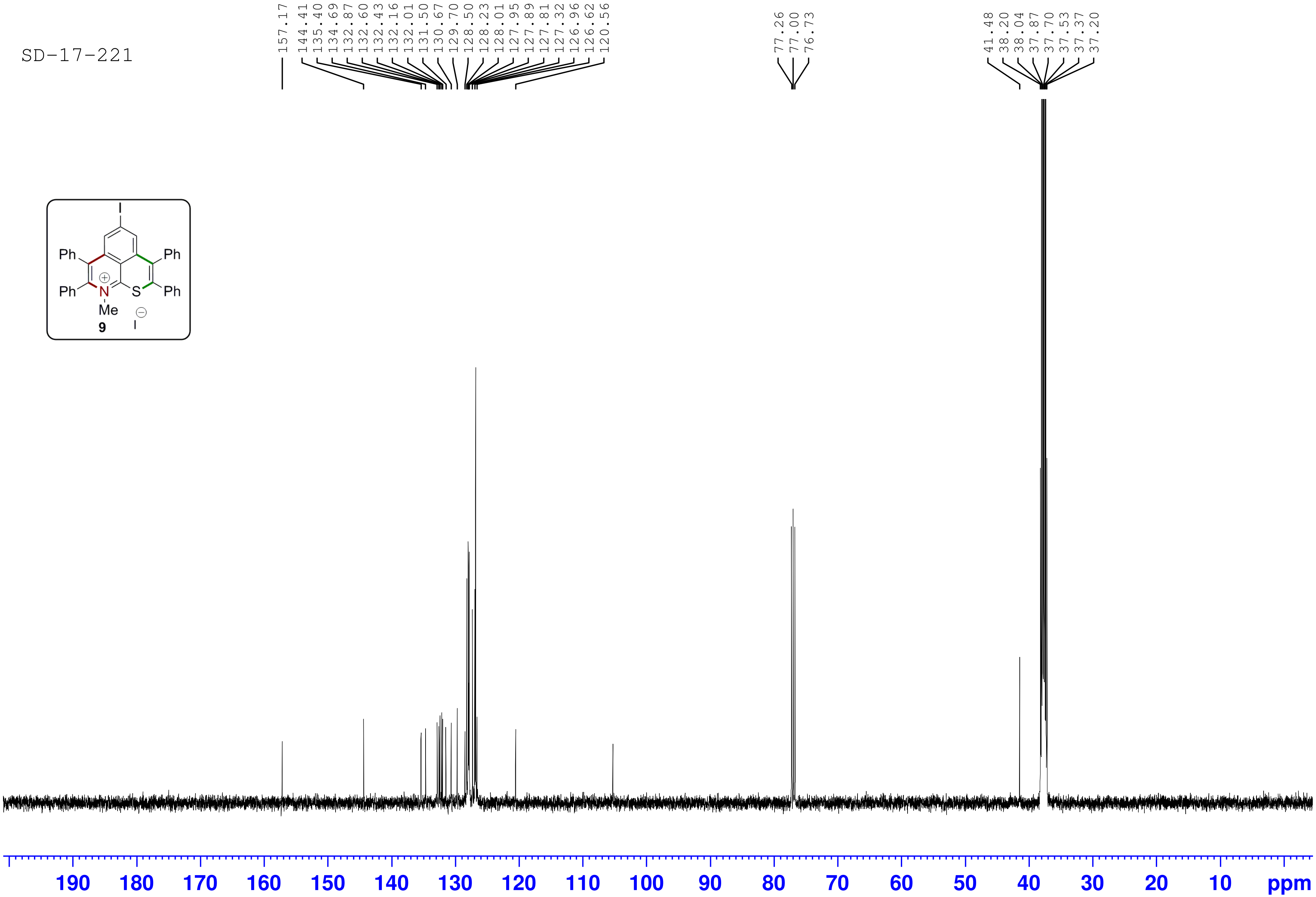

155.53
153.02
144.54
139.11
137.40
136.38
135.28
127.39
127.22
127.02
123.81
123.64
123.25
122.69
117.72
117.02
115.58
77.25
77.00
76.74
52.60
36.99
36.19
31.02
29.91
23.30
22.99
22.77
21.20
14.37
14.23
14.20
13.95
SRS-8-93
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.156
8.141
7.446
7.444
7.430
7.427
7.415
7.413
7.388
7.372
7.276
7.274
7.260
7.246
7.244
7.125
6.784
5.640
2.707
2.691
2.676
2.557
2.541
2.525
2.391
2.376
2.360
2.249
2.233
2.217
1.676
1.661
1.646
1.625
1.609
1.594
1.579
1.354
1.343
1.339
1.323
1.308
1.179
1.164
1.154
1.147
1.139
0.980
0.966
0.951
0.844
SRS-8-91-1
N
^{n}Pr
^{n}Pr
^{n}Pr
^{n}Pr
N
S
8q
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.02
2.08
2.08
0.99
0.98
0.99
0.99
2.00
2.02
2.02
2.10
2.16
4.20
2.15
2.18
6.03
3.01
3.03


155.49
140.48
137.33
136.51
135.18
127.31
125.90
123.73
123.14
123.03
120.45
119.38
117.02
116.52
108.74
77.31
77.00
76.68
46.71
36.07
30.93
29.81
23.34
22.98
22.55
20.95
14.25
14.20
13.97
13.89
SRS-8-91
nPr
nPr
nPr
nPr
N
S
N
8q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

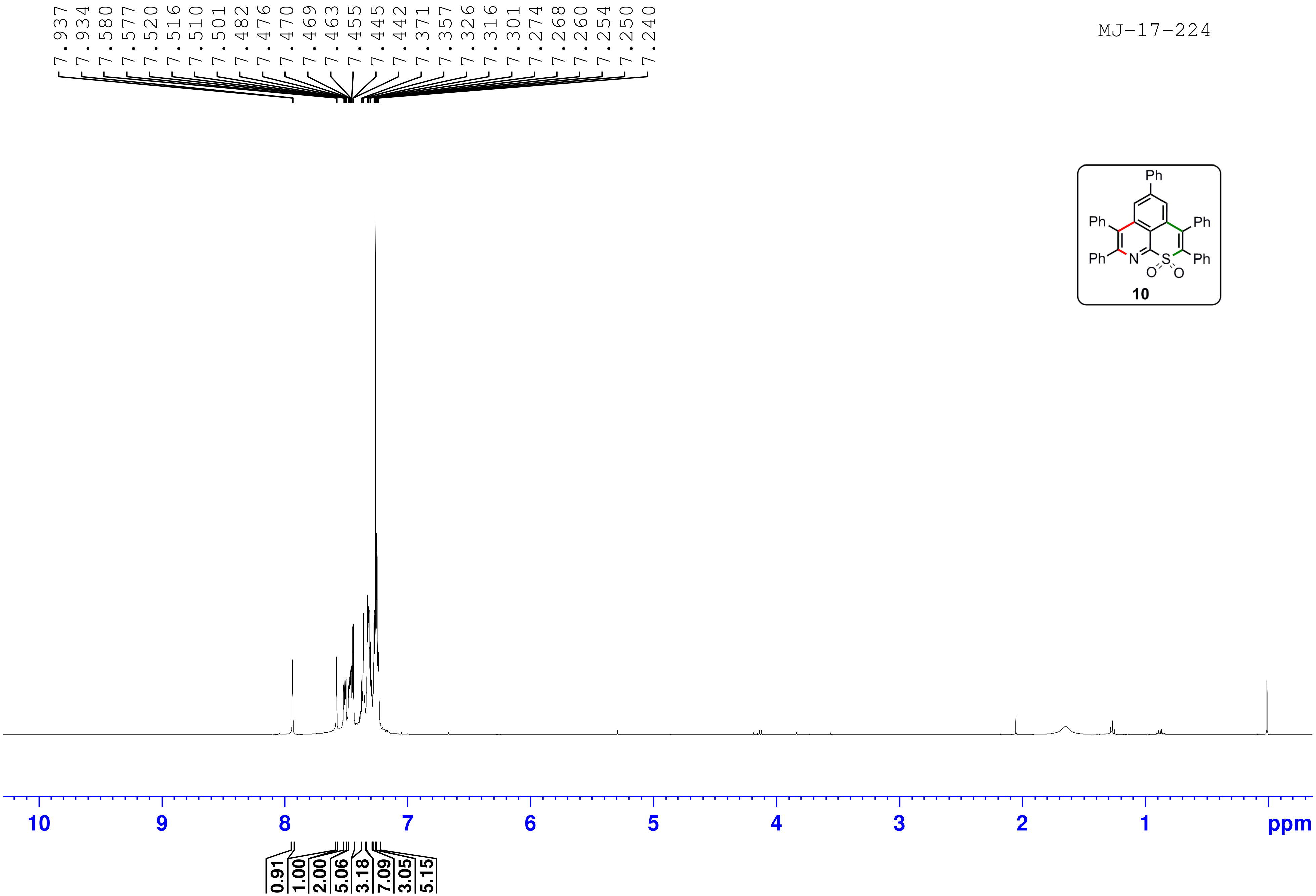

7.569
7.566
7.507
7.503
7.478
7.459
7.423
7.418
7.407
7.403
7.388
7.367
7.349
7.330
7.313
7.218
7.201
3.710
3.410
2.521
2.516
2.512
MAJII-MJ-17-sALT
I
Ph
Ph
Ph
Ph
N
S
Me
I
9
10
9
8
7
6
5
4
3
2
1
ppm
1.02
1.03
2.05
13.09
3.17
2.04
3.00

SD-17-221

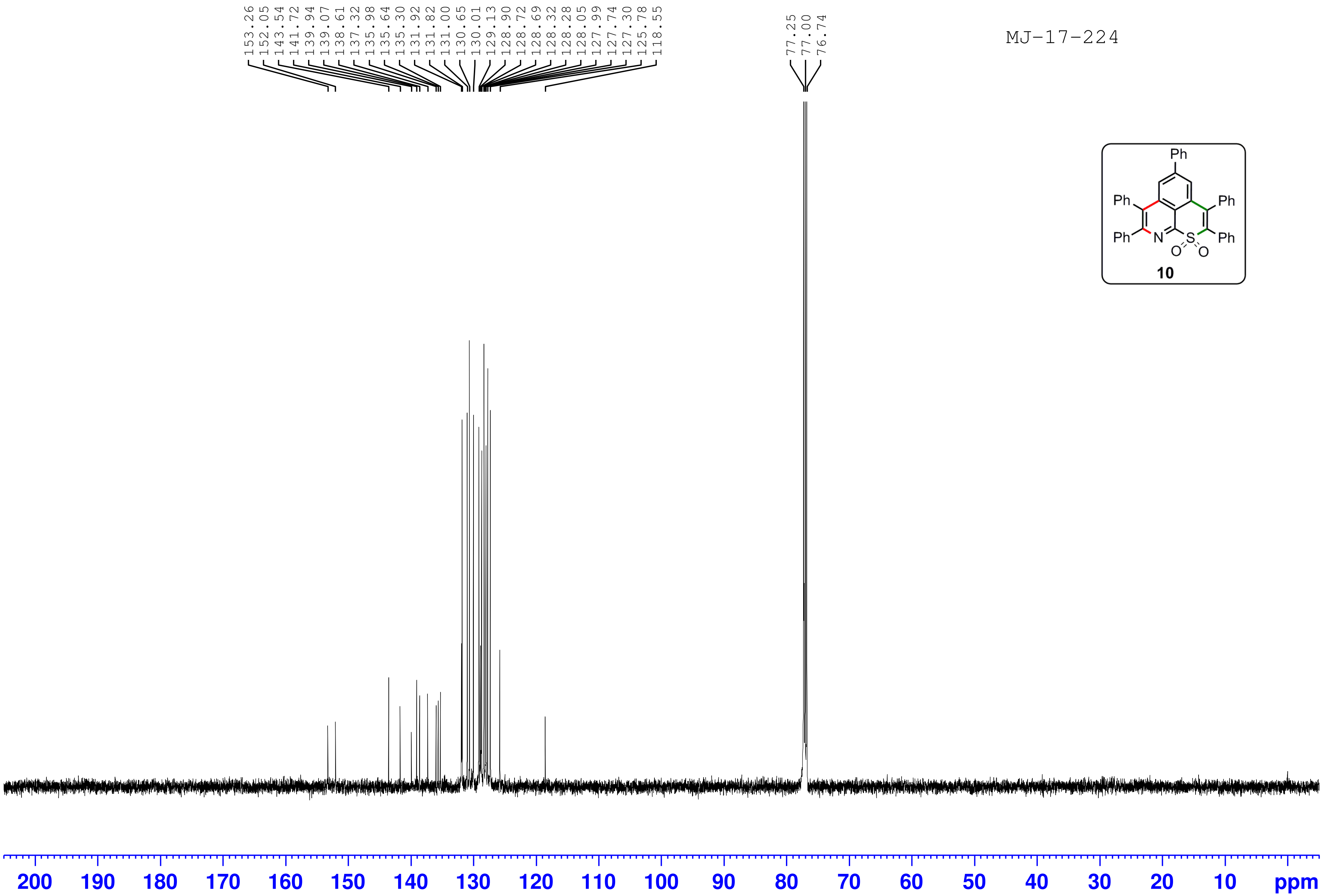


157.17
144.41
135.40
134.69
132.87
132.60
132.43
132.16
132.01
131.50
130.67
129.70
128.50
128.23
128.01
127.95
127.89
127.81
127.32
126.96
126.62
120.56
77.26
77.00
76.73
41.48
38.20
38.04
37.87
37.70
37.53
37.37
37.20
Ph
Ph
N
S
Ph
Ph
Me
I
9
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

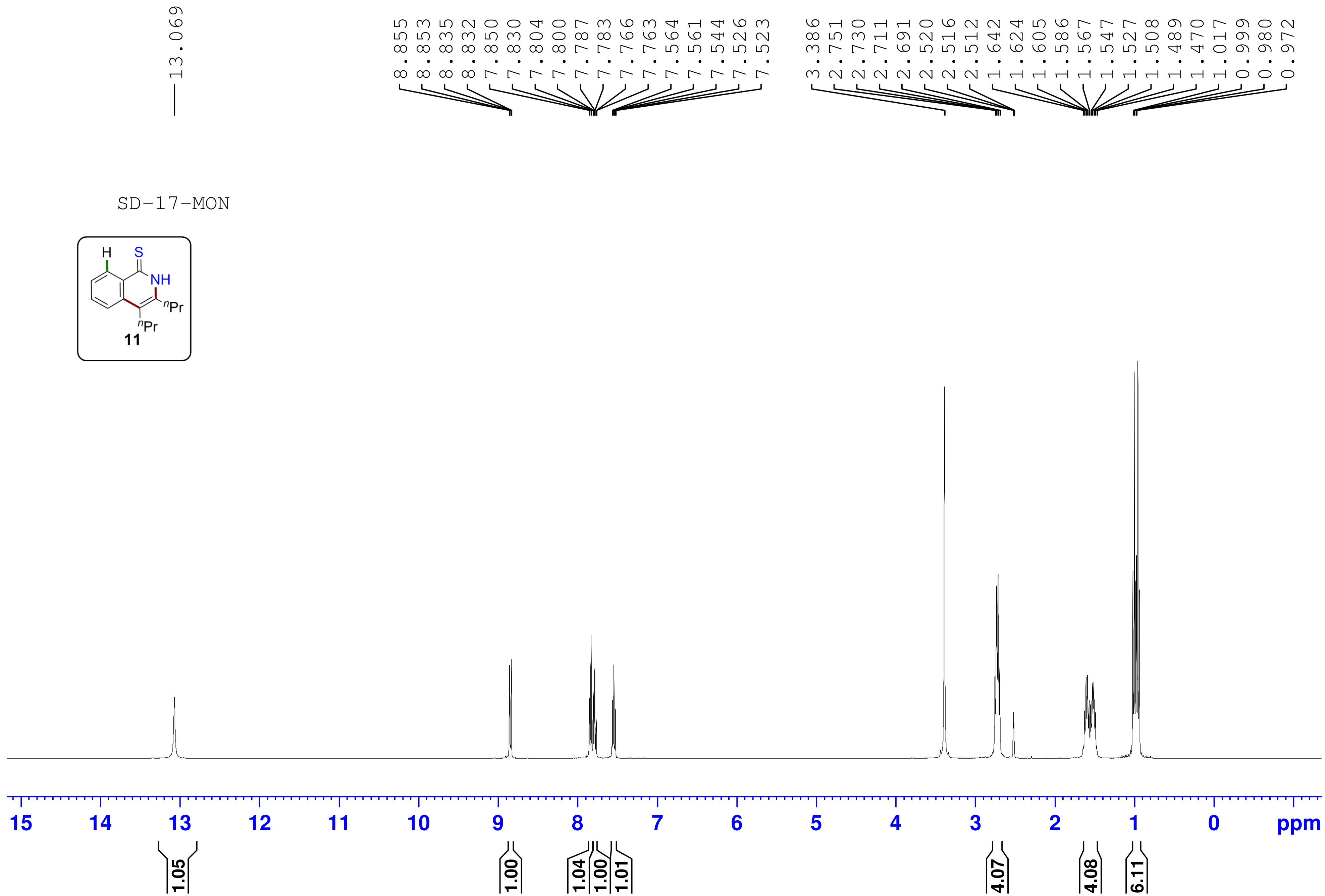
MJ-17-224


7.937
7.934
7.580
7.577
7.520
7.516
7.510
7.501
7.482
7.476
7.470
7.469
7.463
7.455
7.445
7.442
7.371
7.357
7.326
7.316
7.301
7.274
7.268
7.260
7.254
7.250
7.240
10
9
8
7
6
5
4
3
2
1
ppm
0.91
1.00
2.00
5.06
3.18
7.09
3.05
5.15
Ph
Ph
Ph
Ph
Ph
N
S
O
O

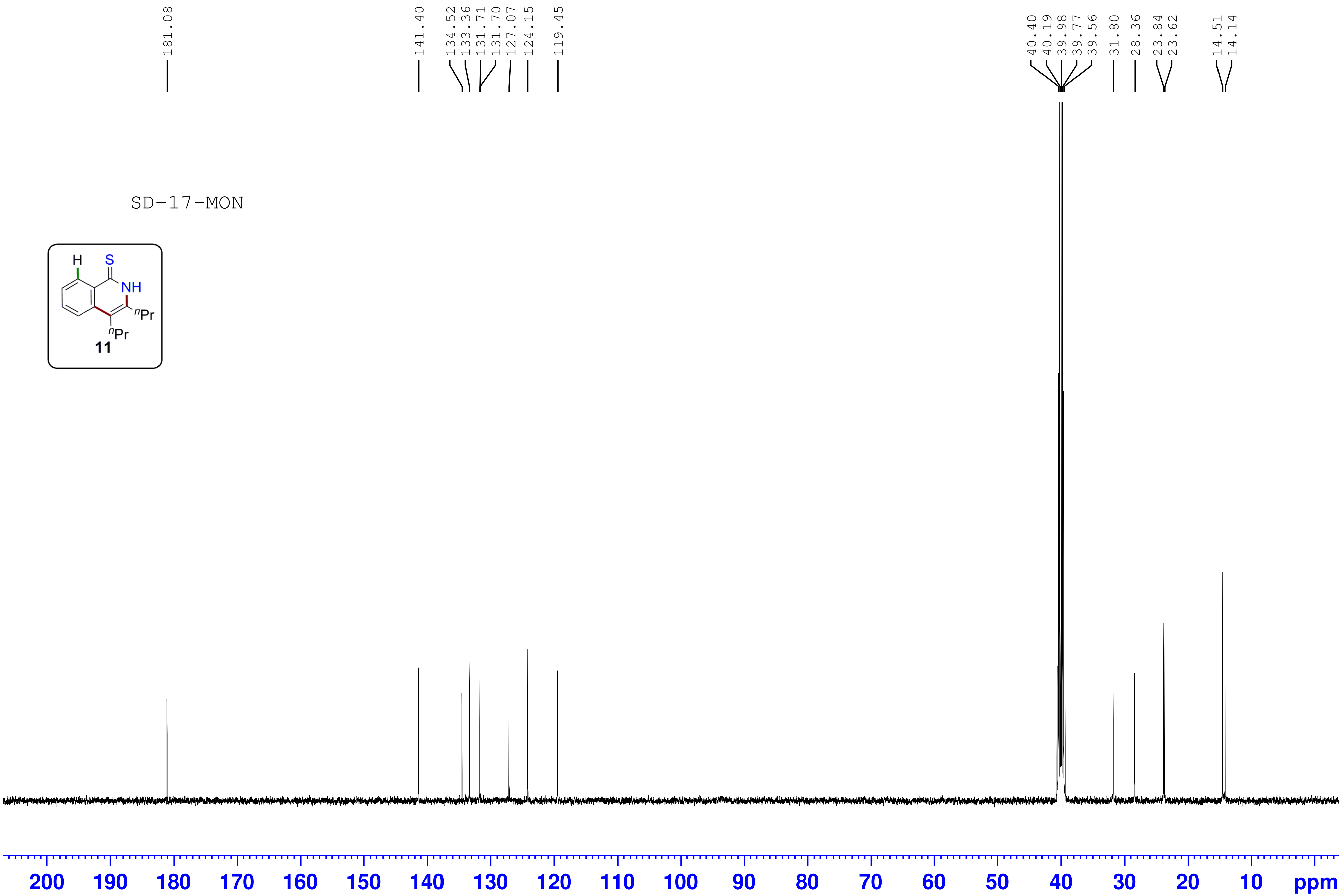
10


153.26
152.05
143.54
141.72
139.94
139.07
138.61
137.32
135.98
135.64
135.30
131.92
131.82
131.00
130.65
130.01
129.13
128.90
128.72
128.69
128.32
128.28
128.05
127.99
127.74
127.30
125.78
118.55
77.25
77.00
76.74
MJ-17-224
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
Ph
Ph
Ph
Ph
Ph
N
S
O
O

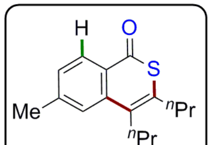
10


13.069
8.855 8.853 8.835 8.832 7.850 7.830 7.804 7.800 7.787 7.783 7.766 7.763 7.564 7.561 7.544 7.526 7.523
3.386 2.751 2.730 2.711 2.691 2.520 2.516 2.512 1.642 1.624 1.605 1.586 1.567 1.547 1.527 1.508 1.489 1.470 1.017 0.999 0.980 0.972
SD-17-MON
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.05 1.00 1.04 1.00 1.01 4.07 4.08 6.11
H
S
NH
^{n}Pr
^{n}Pr

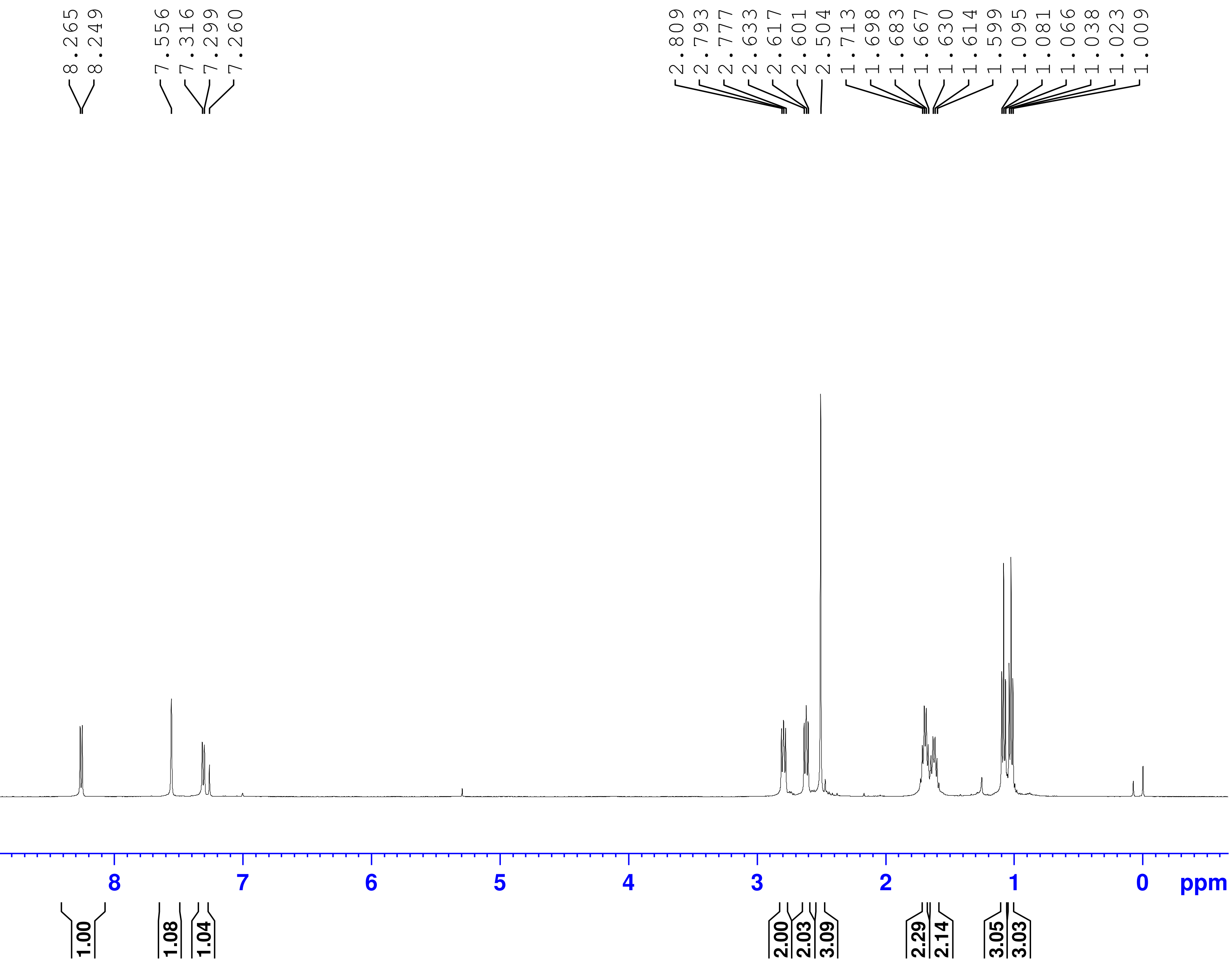
11


181.08
141.40
134.52
133.36
131.71
131.70
127.07
124.15
119.45
40.40
40.19
39.98
39.77
39.56
31.80
28.36
23.84
23.62
14.51
14.14
SD-17-MON
S
NH
H
nPr
nPr
11
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

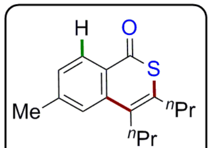
MJ-17-251


H
O
S
Me
nPr
nPr

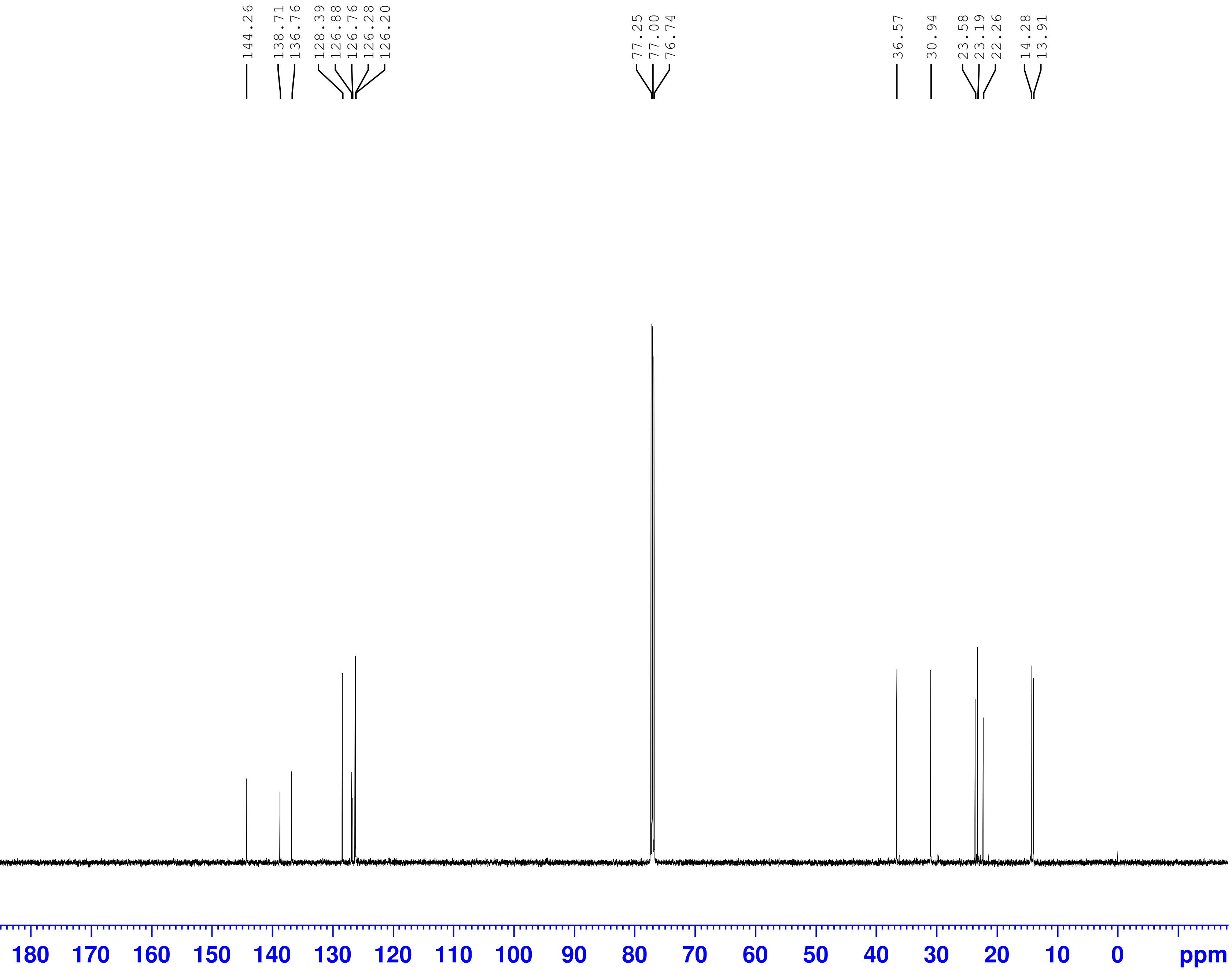
13

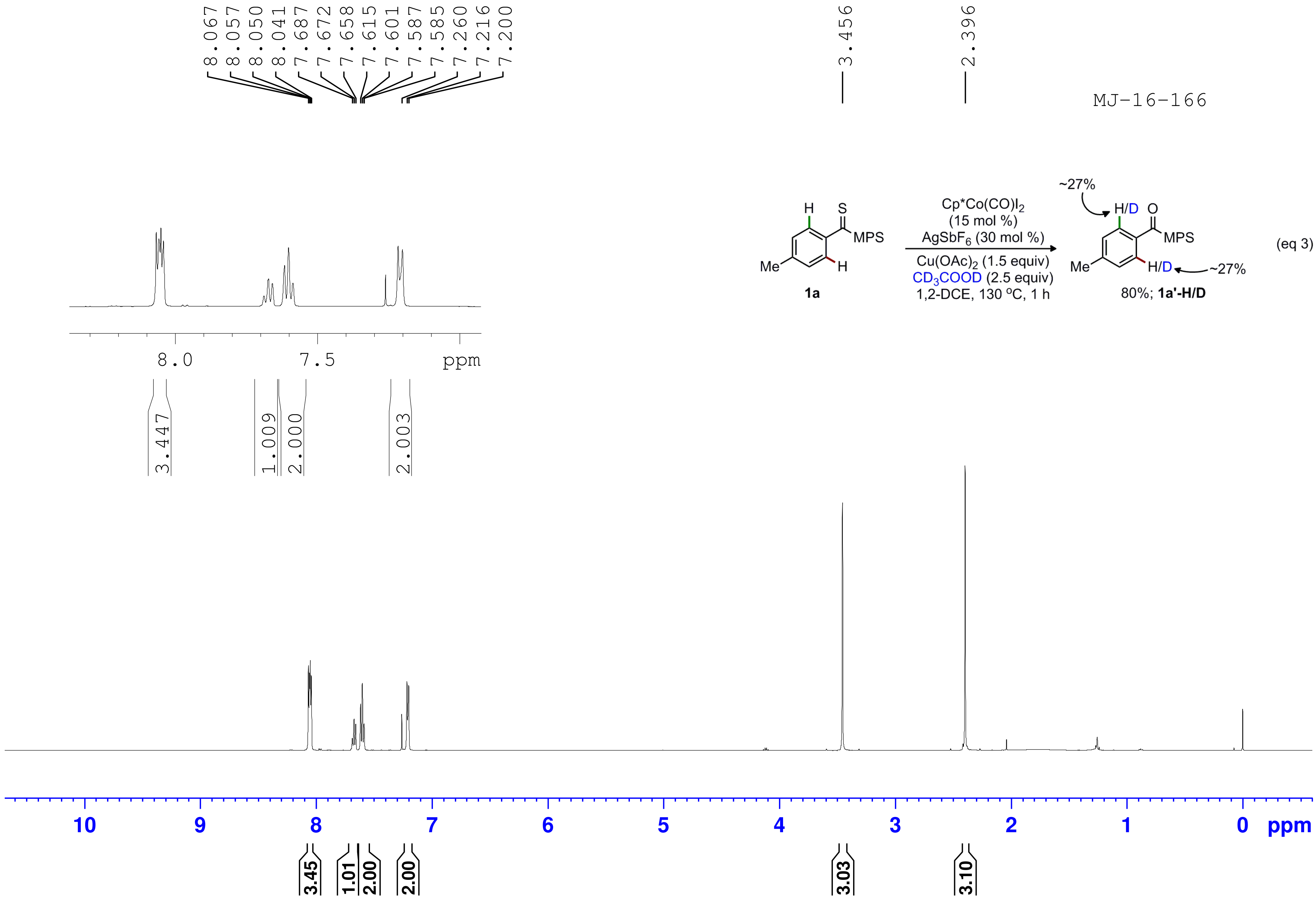

8.265
8.249
7.556
7.316
7.299
7.260
2.809
2.793
2.777
2.633
2.617
2.601
2.504
1.713
1.698
1.683
1.667
1.630
1.614
1.599
1.095
1.081
1.066
1.038
1.023
1.009
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.08
1.04
2.00
2.03
3.09
2.29
2.14
3.05
3.03

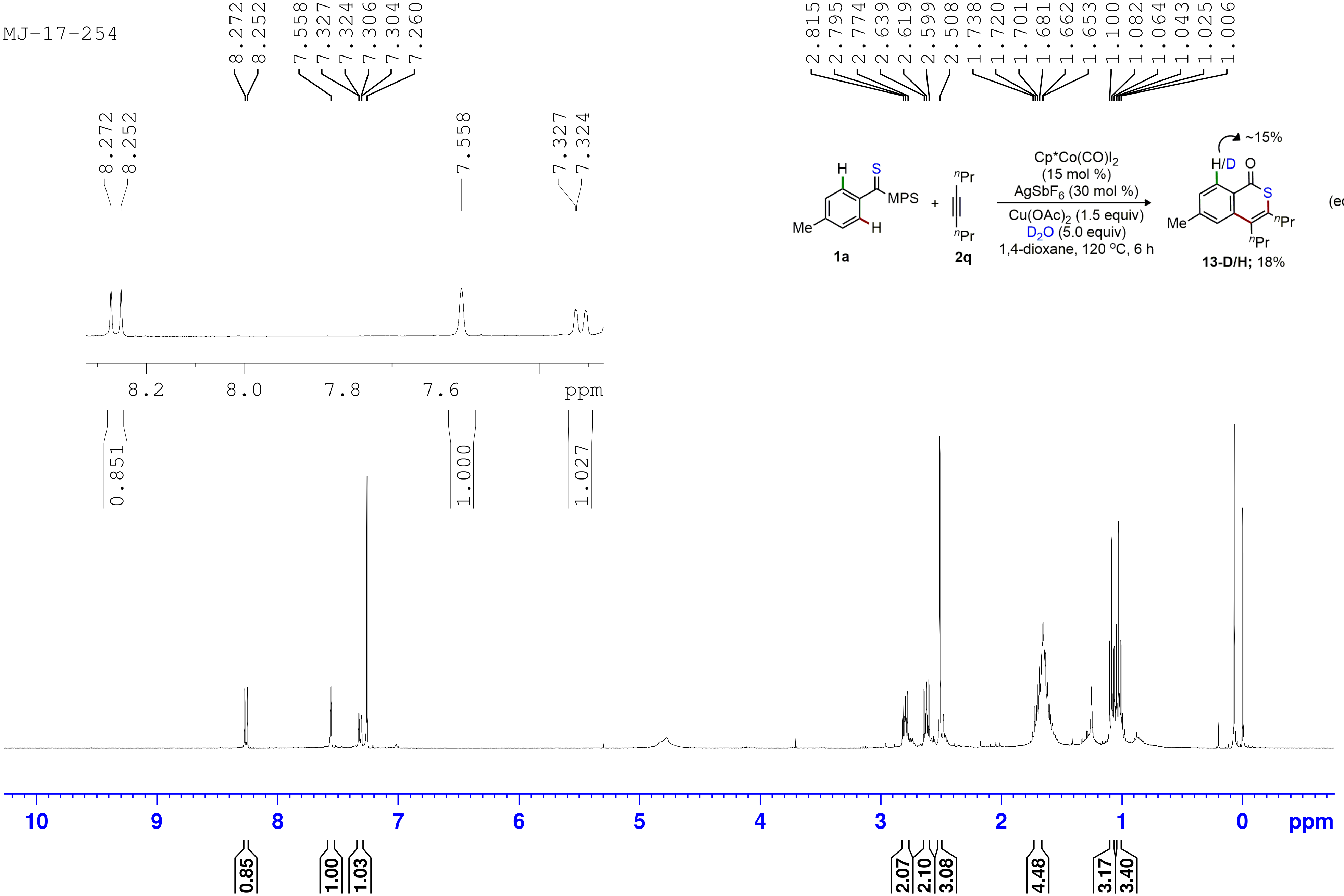
MJ-17-251


H
O
S
Me
nPr
nPr

13

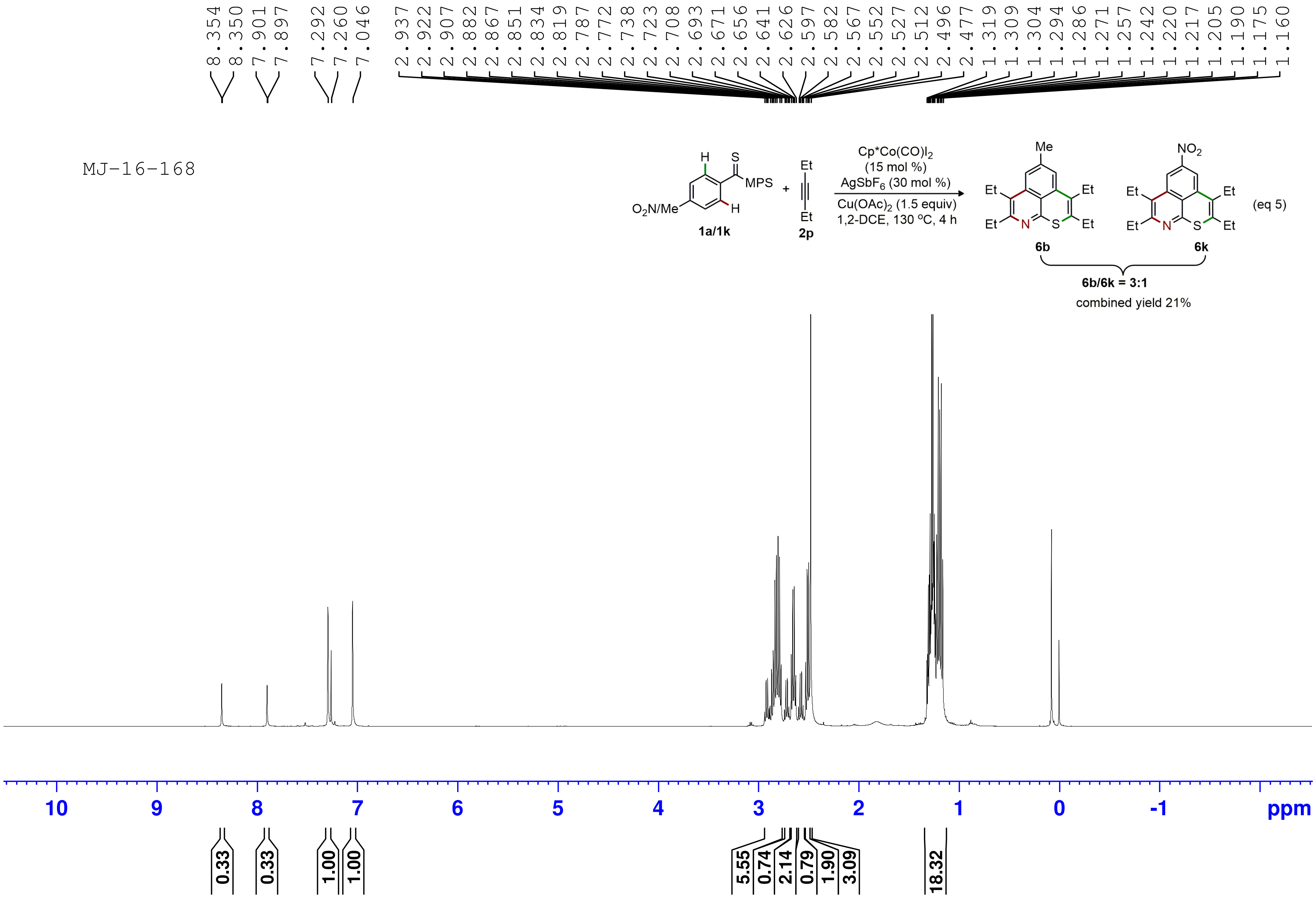

187.26
144.26
138.71
136.76
128.39
126.88
126.76
126.28
126.20
77.25
77.00
76.74
36.57
30.94
23.58
23.19
22.26
14.28
13.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.067
8.057
8.050
8.041
7.687
7.672
7.658
7.615
7.601
7.587
7.585
7.260
7.216
7.200
3.456
2.396
MJ-16-166
8.0
7.5
ppm
3.447
1.009
2.000
2.003
~27%
H/D
O
MPS
H
S
MPS
Me
H
1a
Cp*Co(CO)I2
(15 mol %)
AgSbF6 (30 mol %)
Cu(OAc)2 (1.5 equiv)
CD3COOD (2.5 equiv)
1,2-DCE, 130 °C, 1 h
Me
H/D
~27%
80%; 1a'-H/D
(eq 3)
10
9
8
7
6
5
4
3
2
1
0
ppm
3.45
1.01
2.00
2.00
3.03
3.10


MJ-17-254
8.272
8.252
7.558
7.327
7.324
7.306
7.304
7.260
2.815
2.795
2.774
2.639
2.619
2.599
2.508
1.738
1.720
1.701
1.681
1.662
1.653
1.100
1.082
1.064
1.043
1.025
1.006
0.851
1.000
1.027
8.2
8.0
7.8
7.6
ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
0.85
1.00
1.03
2.07
2.10
3.08
4.48
3.17
3.40
H
S
MPS
Me
H
1a
+
^{n}Pr
^{n}Pr
2q
Cp*Co(CO)I$_2$
(15 mol %)
AgSbF$_6$ (30 mol %)
Cu(OAc)$_2$ (1.5 equiv)
D$_2$O (5.0 equiv)
1,4-dioxane, 120 °C, 6 h
~15%
H/D
O
S
^{n}Pr
Me
^{n}Pr

13-D/H; 18%

(eq 4)


8.354
8.350
7.901
7.897
7.292
7.260
7.046
2.937
2.922
2.907
2.882
2.867
2.851
2.834
2.819
2.787
2.772
2.738
2.723
2.708
2.693
2.671
2.656
2.641
2.626
2.597
2.582
2.567
2.552
2.527
2.512
2.496
2.477
1.319
1.309
1.304
1.294
1.286
1.271
1.257
1.242
1.220
1.217
1.205
1.190
1.175
1.160
MJ-16-168
H
S
MPS
H
O2N/Me
1a/1k
+
Et
Et
2p
Cp*Co(CO)I2
(15 mol %)
AgSbF6 (30 mol %)
Cu(OAc)2 (1.5 equiv)
1,2-DCE, 130 ºC, 4 h
Me
Et
Et
Et
Et
N
S
6b
NO2
Et
Et
Et
Et
N
S
6k
(eq 5)
6b/6k = 3:1
combined yield 21%
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.33
0.33
1.00
1.00
5.55
0.74
2.14
0.79
1.90
3.09
18.32