Double Annulation of *ortho*- and *peri*-C–H Bonds of Fused (Hetero)Arenes to Unusual Oxepino-Pyridines

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SUPPORTING INFORMATION

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General Experimental

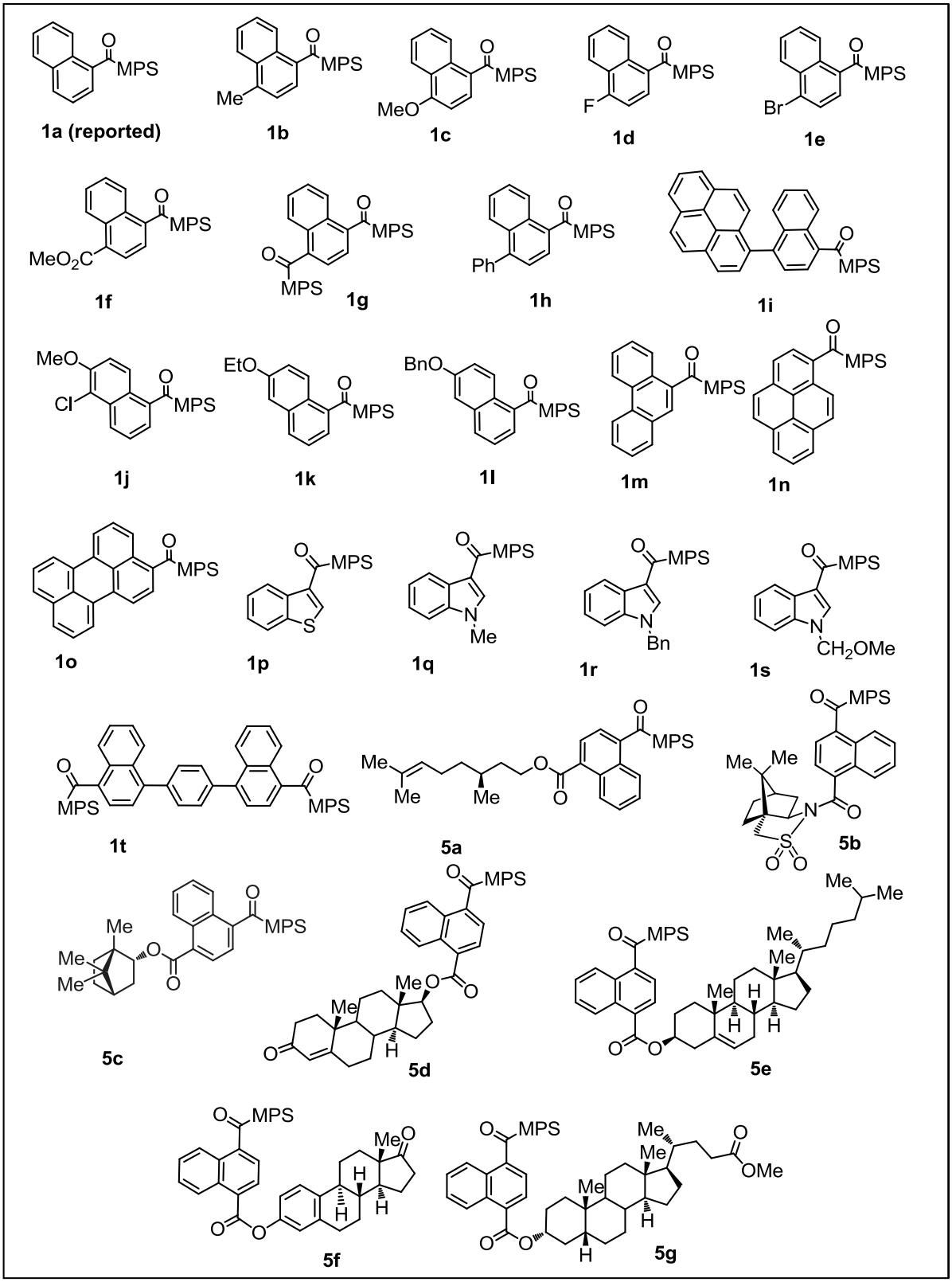
All the reactions were performed in an oven-dried Schlenk flask. Commercial grade solvents were distilled prior to use. Column chromatography was performed using either 100-200 Mesh or 230-400 Mesh silica gel or neutral alumina. Thin layer chromatography (TLC) was performed on silica gel GF254 plates 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) and (^{1}H NMR, 500 MHz; ^{13}C NMR, 126 MHz; ^{19}F NMR, 470 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). Few cases tetramethylsilane (TMS) at 0.00 ppm was used as reference standard. 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, ^{19}F NMR were reported in terms of chemical shift (ppm). IR spectra were reported in cm^{-1}. High resolution mass spectra were obtained in ESI mode. 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).

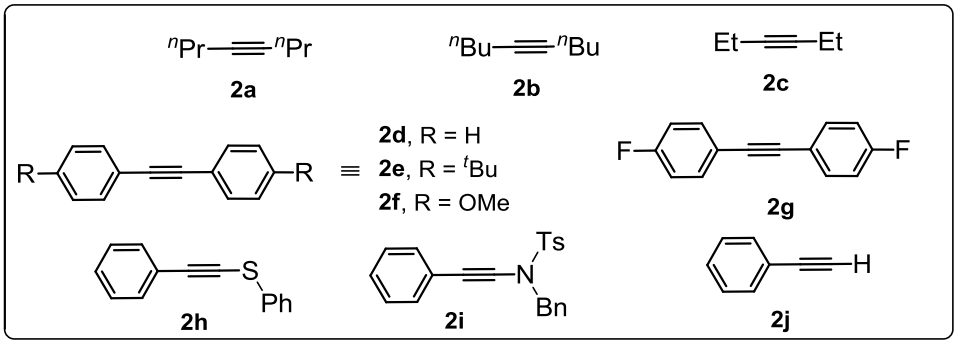
Materials: Unless otherwise noted, all the reagents and intermediates were obtained commercially and used without purification. Dichloromethane (DCM), Chloroform ($CHCl_3$), acetonitrile (CH_3CN), toluene, 1,1,2,2-tetrachloroethane (TCE), 1,2-dichloroethane (DCE) and 1,4-dioxane were distilled over CaH_2. $[RuCl_2(p\text{-cymene})]_2$, $AgSbF_6$, $AgBF_4$, $NaPF_6$ and KPF_6 were purchased and used as received. Analytical and spectral data of all the known compounds are exactly matching with the reported values.

Following the known procedure, compounds **1a** and symmetrical alkynes were prepared.[1-2]

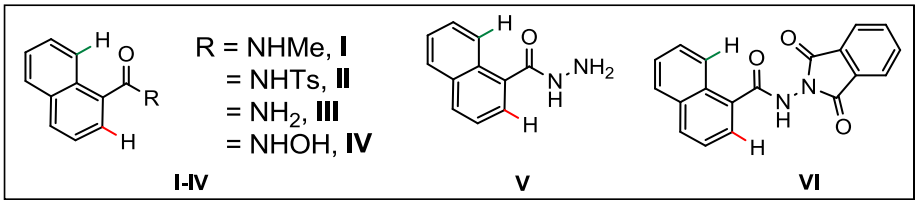
Following a known procedure, compounds **1b, 1c, 1d, 1e, 1f, 1g, 1h, 1i, 1j, 1k, 1l, 1m, 1n, 1o, 1p, 1q, 1r, 1s, 1t, 5a, 5b, 5c, 5d, 5e, 5f** and **5g** were prepared for the first time.[1]



Following the reported method, the alkynes **2e, 2f, 2g, 2h,** and **2i** were prepared.[2] 4-octyne (**2a**), 5-decyne (**2b**), 3-hexyne (**2c**), diphenyl acetylene (**2d**), and phenyl acetylene (**2j**) were purchased and used.

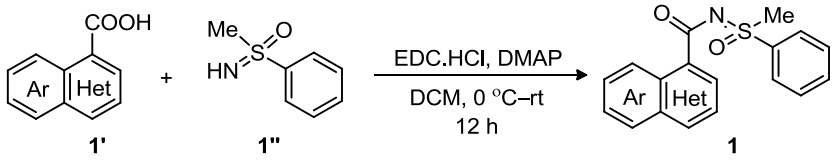


Following a known procedure, the compounds **I, II, III, IV, V** and **VI** were prepared.[3]



Experimental Procedures:

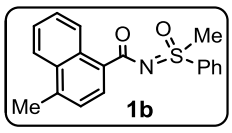
Preparation of *N*-Aroyl/heteroaroylated *S*-Methyl-*S*-Phenylsulfoximine (1): General Procedures (GP-1A): EDC-coupling:[1]



A solution of *N*'-(3-dimethylaminopropyl)-*N*-ethylcarbodimide hydrochloride salt (EDC.HCl) (3.0 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 30 min at 0 °C, and warmed to ambient temperature and continued for 12 h. 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 the reduced pressure. The crude residue was purified using column chromatography on silica gel using hexane/ethyl acetate.

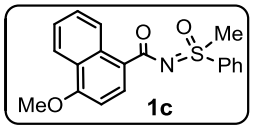
Following this procedure, the compounds **1b, 1c, 1d, 1e, 1f, 1h, 1j, 1k, 1l, 1m, 1n, 1o, 1p, 1q, 1r,** and **1s** were prepared.[1]

***N*-[4-Methyl-1-naphthoyl]-*S*-methyl-*S*-phenylsulfoximine (1b):**



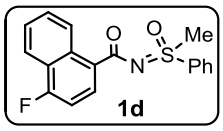
1b (0.81 g, 78%) as colorless thick liquid. R_f = 0.56 (1:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.09 (dd, J = 7.5 & 1.5 Hz, 1H), 8.28 (d, J = 7.5 Hz, 1H), 8.07 (d, J = 8.0 Hz, 2H), 8.02 (dd, J = 7.5 & 1.5 Hz, 1H), 7.65 (t, J = 7.0 Hz, 1H), 7.58 (t, J = 7.75 Hz, 2H), 7.56–7.48 (m, 2H), 7.33 (d, J = 7.0 Hz, 1H), 3.46 (s, 3H), 2.72 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.5, 139.0, 133.6, 132.8, 131.3, 131.1, 129.7, 129.6, 129.2, 127.0, 126.9, 126.7, 125.6, 125.4, 124.1, 44.4, 20.0; IR (Neat) ν_{max} 2924, 1620, 1511, 1475, 1278, 1213, 1194, 1092, 1019, 974 cm^{-1}; **HRMS (ESI)** for $C_{19}H_{18}NO_2S$ $(M+H)^+$: calcd. 324.1053, found 324.1053.

***N*-[4-Methoxy-1-naphthoyl]-*S*-methyl-*S*-phenylsulfoximine (1c):**



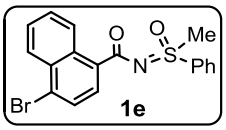
1c (0.69 g, 64%) as colorless crystalline solid. mp = 110–111 °C; R_f = 0.42 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (d, J = 8.8 Hz, 1H), 8.47 (d, J = 8.0 Hz, 1H), 8.30 (dd, J = 8.4 & 0.8 Hz, 1H), 8.09 (d, J = 7.2 Hz, 2H), 7.67 (t, J = 7.2 Hz, 1H), 7.61 (t, J = 7.4 Hz, 2H), 7.59–7.51 (m, 1H), 7.50–7.43 (m, 1H), 6.80 (d, J = 8.4 Hz, 1H), 4.04 (s, 3H), 3.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 158.7, 139.3, 133.6, 132.8, 132.3, 129.6, 127.7, 127.1, 126.4, 125.6, 125.1, 124.5, 121.9, 102.3, 55.6, 44.5; IR (Neat) ν_{max} 2998, 2917, 1620, 1606, 1573, 1511, 1462, 1443, 1390, 1209, 1183, 1090, 1022, 984 cm^{-1}; **HRMS (ESI)** for $C_{19}H_{18}NO_3S$ $(M+H)^+$: calcd. 340.1002, found 340.1002.

***N*-[4-Fluoro-1-naphthoyl]-*S*-methyl-*S*-phenylsulfoximine (1d):**



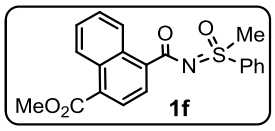
1d (0.95 g, 93%) as colorless crystalline solid. mp = 121–122 °C; R_f = 0.50 (1:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.12 (d, J = 8.5 Hz, 1H), 8.40 (dd, J = 8.5 & 6.0 Hz, 1H), 8.13 (d, J = 9.0 Hz, 1H), 8.07 (d, J = 8.0 Hz, 2H), 7.67 (t, J = 7.3 Hz, 1H), 7.64–7.50 (m, 4H), 7.13 (t, J = 9.0 Hz, 1H), 3.47 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.4, 160.9 (d, J = 258 Hz), 138.8, 133.7, 133.2 (d, J = 5.0 Hz), 131.0 (d, J = 10 Hz), 129.7, 128.6 (d, J = 4.0 Hz), 128.1, 127.0, 126.5 (d, J = 2.5 Hz), 126.1, 123.8 (d, J = 15 Hz), 120.5 (d, J = 7.5 Hz), 108.1 (d, J = 20 Hz), 44.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ –115.84; IR (Neat) ν_{max} 2930, 1644, 1613, 1510, 1443, 1278, 1252, 1210, 1159, 1123, 1055, 885, 973 cm^{-1}; **HRMS (ESI)** for $C_{18}H_{14}FNNaO_2S$ $(M+Na)^+$: calcd. 350.0621, found 350.0626.

***N*-[4-Bromo-1-naphthoyl]-*S*-methyl-*S*-phenylsulfoximine (1e):**



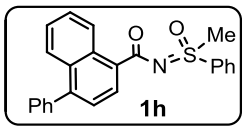
1e (0.75 g, 60%) as colorless crystalline solid. mp = 145–146 °C; R_f = 0.65 (1:1 hexane/EtOAc);^{1}H NMR (500 MHz, $CDCl_3$) δ 9.04–8.98 (m, 1H), 8.32–8.26 (m, 1H), 8.16 (d, J = 8.0 Hz, 1H), 8.07 (d, J = 7.5 Hz, 2H), 7.81 (d, J = 8.0 Hz, 1H), 7.73–7.66 (m, 1H), 7.65–7.54 (m, 4H), 3.49 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 138.8, 133.9, 132.9, 132.4, 132.1, 129.74, 129.68, 128.8, 127.8, 127.4, 127.3, 127.1, 126.9, 44.4; IR (Neat) ν_{max} 2924, 1621, 1561, 1502, 1415, 1274, 1242, 1215, 1160, 1092, 1021, 972 cm^{-1}; **HRMS (ESI)** for $C_{18}H_{15}BrNO_2S$ $(M+H)^+$: calcd. 388.0001, found 388.0015.

N-[Methyl-4-(chlorocarbonyl)-1-naphthoate]-*S*-methyl-*S*-phenylsulfoximine (1f):



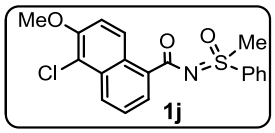
1f (0.82 g, 69%) as colorless crystalline solid. mp = 115–116 °C; R_f = 0.50 (1:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88–8.79 (m, 2H), 8.18 (d, J = 7.5 Hz, 1H), 8.12–8.04 (m, 3H), 7.68 (t, J = 7.5 Hz, 1H), 7.65–7.55 (m, 4H), 4.00 (s, 3H), 3.49 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1, 167.8, 138.7, 138.0, 134.0, 131.6, 131.3, 130.3, 129.8, 128.4, 127.5, 127.12, 127.08, 126.6, 125.8, 52.3, 44.5; IR (Neat) ν_{max} 3022, 3003, 1707, 1607, 1511, 1477, 1325, 1297, 1213, 1199, 1144, 1120, 1037, 980 cm^{-1}; **HRMS (ESI)** for $C_{20}H_{18}NO_4S$ $(M+H)^+$: calcd. 368.0951, found 368.0952.

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



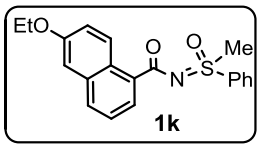
1h (1.06 g, 85%) as colorless crystalline solid. mp = 149–150 °C; R_f = 0.61 (1:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.07 (d, J = 8.5 Hz, 1H), 8.38 (d, J = 7.5 Hz, 1H), 8.15–8.09 (m, 2H), 7.90 (d, J = 8.0 Hz, 1H), 7.74–7.66 (m, 1H), 7.63 (t, J = 7.5 Hz, 2H), 7.58–7.39 (m, 8H), 3.51 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.5, 144.2, 140.5, 139.0, 133.8, 132.4, 132.1, 131.6, 129.9, 129.7, 129.0, 128.2, 127.5, 127.1, 126.9, 126.6, 126.4, 125.9, 125.6, 44.5; IR (Neat) ν_{max} 3005, 1620, 1578, 1492, 1420, 1327, 1266, 1210, 1143, 1091, 1043, 984 cm^{-1}; **HRMS (ESI)** for $C_{24}H_{20}NO_2S$ $(M+H)^+$: calcd. 386.1209, found 386.1209.

N-[5-Chloro-6-methoxy-1-naphthoyl]-*S*-methyl-*S*-phenylsulfoximine (1j):



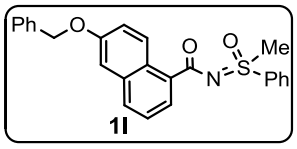
1j (0. 76 g, 63%) as colorless crystalline solid. mp = 175–176 °C; R_f = 0.51 (1:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (d, J = 9.5 Hz, 1H), 8.41 (d, J = 8.5 Hz, 1H), 8.26 (dd, J = 7.0 & 1.0 Hz, 1H), 8.09 (d, J = 7.5 Hz, 2H), 7.70 (br t, J = 7.25 Hz, 1H), 7.63 (br t, J = 7.75 Hz, 2H), 7.57 (t, J = 8.0 Hz, 1H), 7.32 (d, J = 9.5 Hz, 1H), 4.02 (s, 3H), 3.49 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.3, 152.4, 138.7, 133.9, 133.0, 132.4, 129.8, 128.1, 127.5, 127.3, 127.1, 126.7, 126.1, 116.6, 114.3, 56.8, 44.5; IR (Neat) ν_{max} 3025, 2928, 1600, 1579, 1503, 1444, 1261, 1150, 1089, 1045 cm^{-1}; **HRMS (ESI)** for $C_{19}H_{17}ClNO_3S$ $(M+H)^+$: calcd. 374.0612, found 374.0612.

***N*-[6-Ethoxy-1-naphthoyl]-*S*-methyl-*S*-phenylsulfoximine (1k):**



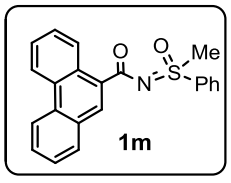
1k (1.01 g, 88%) as colorless crystalline solid. mp = 130–131 °C; R_f = 0.60 (1:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (d, J = 9.5 Hz, 1H), 8.19 (dd, J = 7.5 & 1.0 Hz, 1H), 8.12–8.05 (m, 2H), 7.83 (d, J = 8.0 Hz, 1H), 7.71–7.64 (m, 1H), 7.60 (t, J = 7.5 Hz, 2H), 7.43 (t, J = 7.75 Hz, 1H), 7.19 (dd, J = 9.0 & 2.5 Hz, 1H), 7.13 (d, J = 3.0 Hz, 1H), 4.14 (q, J = 7.0 Hz, 2H), 3.47 (s, 3H), 1.47 (t, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.5, 156.6, 139.1, 135.4, 133.7, 132.8, 131.1, 129.7, 128.0, 127.5, 127.1, 126.7, 125.0, 119.9, 107.0, 63.3, 44.4, 14.7; IR (Neat) ν_{max} 2930, 1615, 1585, 1505, 1460, 1445, 1393, 1248, 1197, 1141, 1112, 1032, 962 cm^{-1}; **HRMS (ESI)** for $C_{20}H_{20}NO_3S$ $(M+H)^+$: calcd. 354.1148, found 354.1158.

***N*-[6-(Benzyloxy)-1-naphthoyl]-*S*-methyl-*S*-phenylsulfoximine (1l):**



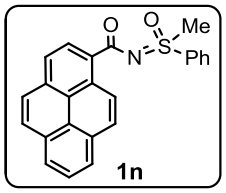
1l (0.98 g, 73%) as colorless crystalline solid. mp = 161–162 °C; R_f = 0.50 (1:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (d, J = 9.5 Hz, 1H), 8.22 (d, J = 7.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.5 Hz, 1H), 7.68 (br t, J = 6.75 Hz, 1H), 7.60 (t, J = 7.25 Hz, 2H), 7.51–7.37 (m, 5H), 7.34 (t, J = 7.5 Hz, 1H), 7.29 (dd, J = 9.25 & 2.25 Hz, 1H), 7.23 (d, J = 2.5 Hz, 1H), 5.18 (s, 2H), 3.47 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.5, 156.4, 138.8, 136.7, 135.3, 133.7, 132.7, 131.2, 129.7, 128.5, 128.1, 127.9, 127.7, 127.5, 127.1, 126.9, 125.1, 120.0, 69.8, 44.4; IR (Neat) ν_{max} 3060, 2925, 1616, 1590, 1507, 1447, 1374, 1248, 1214, 1196, 1133, 1093, 1012, 972, 906, 832, 730 cm^{-1}; **HRMS (ESI)** for $C_{25}H_{22}NO_3S$ $(M+H)^+$: calcd. 416.1315, found 416.1313.

***N*-[Phenanthrene-9-carbonyl]-*S*-methyl-*S*-phenylsulfoximine (1m):**



1m (0.52 g, 45%) as colorless thick liquid. R_f = 0.59 (1:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.00 (d, J = 8.0 Hz, 1H), 8.71 (d, J = 8.0 Hz, 1H), 8.67 (d, J = 8.5 Hz, 1H), 8.62 (s, 1H), 8.12 (d, J = 8.0 Hz, 2H), 7.98 (d, J = 7.5 Hz, 1H), 7.74–7.59 (m, 7H), 3.52 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.5, 138.78, 133.76, 131.85, 131.77, 131.3, 130.6, 130.3, 129.72, 129.68, 129.3, 128.2, 127.13, 127.05, 126.96, 126.7, 126.5, 122.6, 122.5, 44.4; IR (Neat) ν_{max} 3058, 1624, 1493, 1445, 1306, 1288, 1210, 1143, 1032 cm^{-1}; **HRMS (ESI)** for $C_{22}H_{18}NO_2S$ $(M+H)^+$: calcd. 360.1053, found 360.1058.

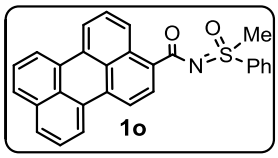
***N*-[Pyrene-1-carbonyl]-*S*-methyl-*S*-phenylsulfoximine (1n):**



1n (0.94 g, 76%) as yellow crystalline solid. mp = 134–136 °C; R_f = 0.38 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (d, J = 9.6 Hz, 1H), 8.84 (d, J = 8.0 Hz, 1H), 8.24–7.97 (m, 9H), 7.71–7.58 (m, 3H), 3.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 138.9, 133.7, 133.6, 131.0, 130.5, 130.4,

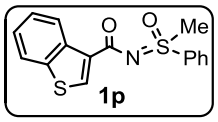
129.7, 129.5, 129.0, 128.7, 128.6, 127.2, 127.1, 126.0, 125.8, 125.7, 125.6, 124.8, 124.3, 123.9, 44.5; IR (Neat) ν_{max} 2927, 1610, 1593, 1578, 1538, 1447, 1403, 1367, 1208, 1094, 845 cm^{-1}; **HRMS (ESI)** for $C_{24}H_{18}NO_2S$ $(M+H)^+$: calcd. 384.1053, found 384.1058.

***N*-[Perylene-3-carbonyl]-*S*-methyl-*S*-phenylsulfoximine (1o):**



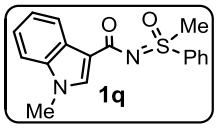
1o (0.83 g, 60%) as orange crystalline solid. mp = 200–202 °C; R_f = 0.50 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, DMSO-D_6) δ 8.71 (d, J = 8.8 Hz, 1H), 8.46–8.37 (m, 4H), 8.26 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 7.2 Hz, 2H), 7.89–7.71 (m, 5H), 7.64–7.53 (m, 3H), 3.69 (s, 3H); ^{13}C NMR (101 MHz, DMSO-D_6) δ175.3, 139.2, 134.6, 134.2, 134.0, 132.9, 132.6, 131.0, 130.8, 130.5, 130.3, 130.1, 129.4, 128.8, 128.6, 128.1, 128.0, 127.6, 127.4, 126.4, 122.5, 121.8, 121.3, 120.1, 43.8; IR (Neat) ν_{max} 2926, 1672, 1605, 1569, 1516, 1475, 1312, 1250, 1205, 1150, 1124, 1090, 972, 918, 808 cm^{-1}; **HRMS (ESI)** for $C_{28}H_{20}NO_2S$ $(M+H)^+$: calcd. 434.1209, found 434.1212.

***N*-[Benzo[b]thiophene-3-carbonyl]-*S*-methyl-*S*-phenylsulfoximine (1p):**



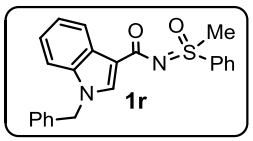
1p (0.97 g, 95%) as colorless crystalline solid. mp = 128–129 °C; R_f = 0.46 (1:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, J = 8.0 Hz, 1H), 8.50 (s, 1H), 8.10–8.05 (m, 2H), 7.84 (d, J = 8.0 Hz, 1H), 7.72–7.65 (m, 1H), 7.64–7.59 (m, 2H), 7.45–7.40 (m, 1H), 7.39–7.34 (m, 1H), 3.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ170.3, 140.2, 138.9, 137.0, 136.2, 133.7, 132.9, 129.6, 127.1, 125.3, 125.0, 124.6, 122.3, 44.5; IR (KBr) ν_{max} 3388, 2927, 1617, 1498, 1419, 1368,1233, 1098, 972 cm^{-1}; **HRMS (ESI)** for $C_{16}H_{14}NO_2S_2$ $(M+H)^+$: calcd. 316.0460, found 316.0467.

***N*-[1-Methyl-1H-indole-3-carbonyl]-*S*-methyl-*S*-phenylsulfoximine (1q):**



1q (0.62 g, 62%) as colorless crystalline solid. mp = 184–185 °C; R_f = 0.48 (100% EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35–8.30 (m, 1H), 8.05 (d, J = 7.2 Hz, 2H), 7.83 (s, 1H), 7.64 (t, J = 8.4 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.32–7.18 (m, 3H), 3.76 (s, 3H), 3.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ171.8, 139.5, 137.2, 135.4, 133.4, 129.5, 127.1, 126.8, 122.3, 122.0, 121.4, 113.0, 109.5, 44.7, 33.2; IR (KBr) ν_{max} 2926, 1607, 1528, 1466, 1385, 1269, 1226, 1110, 973 cm^{-1}; **HRMS (ESI)** for $C_{17}H_{17}N_2O_2S$ $(M+H)^+$: calcd. 313.1005, found 313.1011.

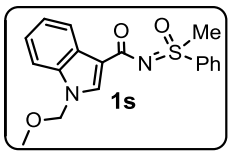
***N*-[1-Benzyl-1H-indole-3-carbony]-*S*-methyl-*S*-phenylsulfoximine (1r):**



1r (0.91 g, 73%) as colorless crystalline solid. mp = 200–201 °C; R_f = 0.30 (3:7 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ8.40 (br d, J = 7.5 Hz, 1H), 8.11 (d, J = 7.5 Hz, 2H), 7.97 (s, 1H), 7.77–7.64 (m, 1H), 7.61 (br t, J =

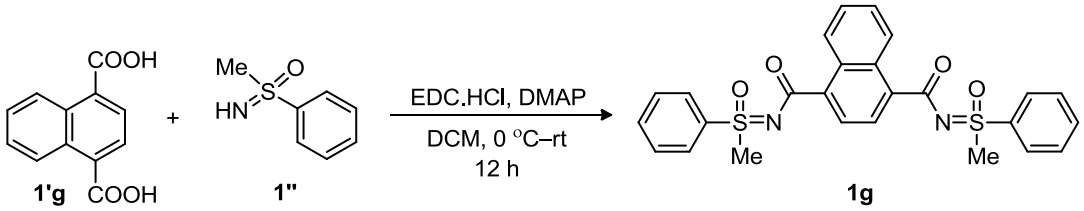
7.3 Hz, 2H), 7.39–7.21 (m, 6H), 7.17 (br d, J = 7.5 Hz, 2H), 5.34 (s, 2H), 3.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 139.6, 136.8, 136.2, 134.9, 133.4, 129.5, 128.8, 127.8, 127.1, 126.9, 122.5, 122.2, 121.6, 113.7, 110.1, 50.5, 44.7; IR (KBr) ν_{max} 1659, 1532, 1463, 1360, 1283, 1185, 1019 cm^{-1}; **HRMS (ESI)** for $C_{23}H_{21}N_2O_2S$ $(M+H)^+$: calcd. 389.1318, found 389.1325.

***N*-[1-(Methoxymethyl)-1H-indole-3-carbonyl]-*S*-methyl-*S*-phenylsulfoximine (1s):**



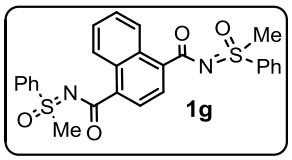
1s (0.90 g, 82%) as colorless crystalline solid. mp = 190–191 °C; R_f = 0.35 (3:2 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37–8.31 (m, 1H), 8.07 (d, J = 7.5 Hz, 2H), 7.95 (s, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.75 Hz, 2H), 7.48 (dd, J = 6.5 & 2.0 Hz, 1H), 7.30–7.21 (m, 2H), 5.44 (s, 2H), 3.47 (s, 3H), 3.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 139.6, 136.8, 134.5, 133.5, 129.5, 127.3, 127.1, 122.9, 122.2, 122.1, 114.5, 110.2, 77.9, 56.0, 44.7; IR (Neat) ν_{max} 2920, 1603, 1523, 1443, 1378, 1260, 1208, 1125, 1092, 1029, 975 cm^{-1}; **HRMS (ESI)** for $C_{18}H_{19}N_2O_3S$ $(M+H)^+$: calcd. 343.1111, found 343.1111.

Preparation of *N*-[Naphthalene-1,4-dicarbonyl]-*S*-methyl-*S*-phenylsulfoximine (1): General Procedure (GP-1B):



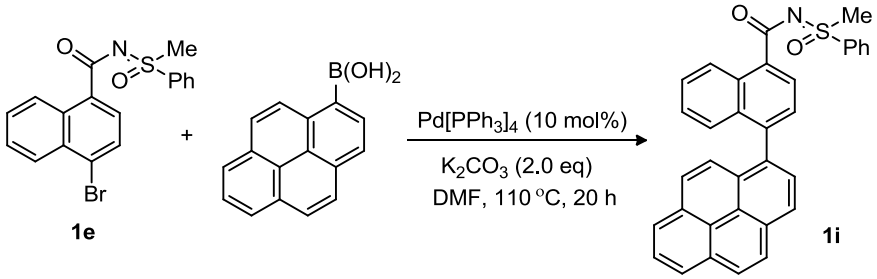
A solution of *N*'-(3-dimethylaminopropyl)-*N*-ethylcarbodimide, hydrochloride salt (EDC.HCl) (4.28 g, 27.6 mmol), 4-*N*,*N*-dimethylaminopyridine (DMAP) (2.25 g, 18.4 mmol) and naphthalene-1,4-dicarboxylic acid (**1'g**) (1.0 g, 4.6 mmol) in CH_2Cl_2 (40 mL) was stirred under an argon atmosphere. Sulfoximine (**1″**) (1.56 g, 10.1 mmol) was introduced dropwise at 0 °C. The resulting reaction mixture was stirred for about 1 h at 0°C, and warmed to ambient temperature and continued for 12 h. Upon complete consumption of carboxylic acid, the reaction mixture was acidified with 2N hydrochloric acid (40 mL). The organic layer was separated; the aqueous layer was extracted with CH_2Cl_2 (4 × 30 mL). 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 using column chromatography on silica gel using hexane/ethyl acetate.

***N*-[Naphthalene-1,4-dicarbonyl]-*S*-methyl-*S*-phenylsulfoximine (1g):**



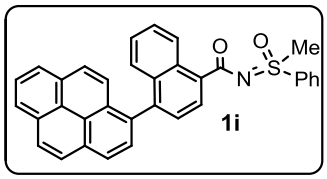
1g (1.75 g, 77%) as colorless crystalline solid. mp = 110–111 °C; R_f = 0.45 (1:4 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (dd, J = 6.75 & 3.25 Hz, 2H), 8.21 (s, 2H), 8.05 (d, J = 8.0 Hz, 4H), 7.65 (t, J = 7.0 Hz, 2H), 7.58 (t, J = 7.5 Hz, 4H), 7.50 (dd, J = 6.75 & 3.25 Hz, 2H), 3.46 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ176.2, 138.6, 136.5, 133.8, 131.4, 129.7, 127.5, 127.0, 126.8, 126.3, 44.4; IR (Neat) ν_{max} 3014, 1618, 1575, 1475, 1446, 1242, 1212, 1145, 1010, 971 cm^{-1}; **HRMS (ESI)** for $C_{26}H_{23}N_2O_4S_2$ $(M+H)^+$: calcd. 491.1094, found 491.1094.

Preparation of *N*-[4-(Pyren-1-yl)-1-naphthoyl]-*S*-methyl-*S*-phenylsulfoximine (1i): Sonogashira-coupling:



A mixture of pyren-1-ylboronic acid (0.22 g, 1.1 mmol), **1e** (0.39 g, 1.0 mmol), $Pd(PPh_3)_4$ (0.119 g 10 mol%), and K_2CO_3 (0.28 g, 2.0 mmol) in *N*,*N*-dimethylformamide (10.0 mL) was taken in a screw capeed tube and heated at 110 °C in a heating block for 20 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite. The reaction mixture was extracted with ethylacetate (4 × 15 mL), dried over Na_2SO_4 and concentrated under vacuum to give a yellow solid. The crude material was purified by silica gel column chromatograpy eluting with hexane: ethyl acetate (1:1) to give compound **1i** as yellow colour gummy liquid.

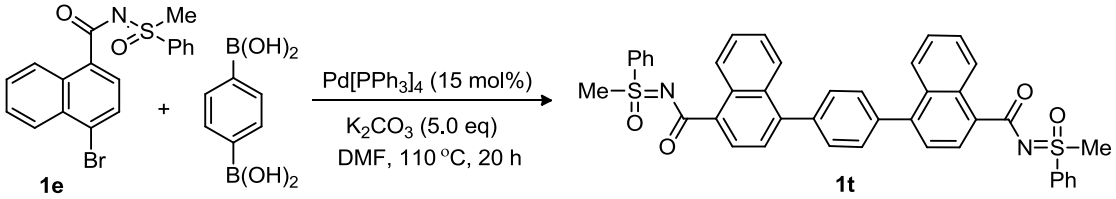
***N*-[4-(Pyren-1-yl)-1-naphthoyl]-*S*-methyl-*S*-phenylsulfoximine (1i):**



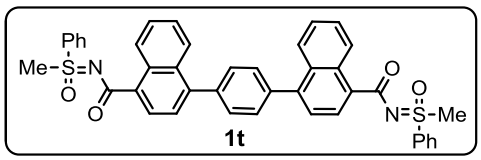
1i (0.35 g, 69%) as yellow colour gummy liquid. R_f = 0.52 (1:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.13 (dd, J = 8.5 & 5.0 Hz, 1H), 8.50 (d, J = 7.5 Hz, 1H), 8.29 (d, J = 7.5 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.20–8.12 (m, 5H), 8.05–7.96 (m, 2H), 7.89 (dd, J = 9.25 & 5.25 Hz, 1H), 7.73 (t, J = 7.25 Hz, 1H), 7.70–7.58 (m, 4H), 7.55 (t, J = 8.0 Hz, 1H), 7.41 (d, J = 8.5 Hz, 1H), 7.31–7.24 (m, 1H), 3.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ176.7, 143.1, 139.1, 135.6, 133.9, 133.6, 133.0, 131.5, 131.4, 131.04, 130.97, 129.83, 129.77, 129.03, 129.01, 128.1, 127.7, 127.6, 127.4, 127.2, 127.14, 127.08, 126.6, 126.1, 125.6, 125.3, 125.2, 124.75, 124.72, 124.5, 44.6; IR

(Neat) ν_{max} 3041, 1620, 1576, 1435, 1242, 1215, 1142, 1092, 973 cm^{-1}; **HRMS (ESI)** for $C_{34}H_{24}NO_2S$ $(M+H)^+$: calcd. 510.1522, found 510.1525.

Preparation of *N*-[4,4'-(1,4-Phenylene)bis(1-naphthoyl)]-*S*-methyl-*S*-phenylsulfoximine (1t): Sonogashira-coupling

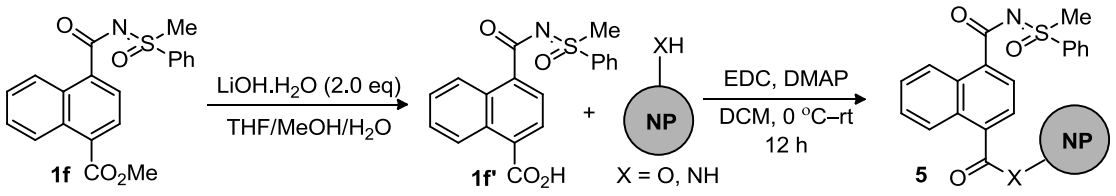


A mixture of 1,4-phenylenediboronic acid (80 mg, 0.48 mmol), **1e** (370 mg, 0.96 mmol), $Pd(PPh_3)_4$ (83 mg, 15 mol%), and K_2CO_3 (333 mg, 2.41 mmol) in *N*,*N*-dimethylformamide (10.0 mL) was taken in a screw capped tube and heated at 110 °C in a heating block for 20 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite. The reaction mixture was extracted with ethylacetate (4 × 15 mL), dried over Na_2SO_4 and concentrated under vacuum to give a yellow solid. The crude material was purified by silica gel column chromatograpy eluting with hexane: ethyl acetate (1:1) to give compound **1t** as yellow colour thick liquid.



1t (247 mg, 74%) as yellow colour thick liquid; R_f = 0.65 (1:4 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 8.4 Hz, 2H), 8.08 (d, J = 7.2 Hz, 2H), 7.80–7.66 (m, 6H), 7.37–7.10 (m, 16H), 3.16 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 143.6, 139.7, 138.7, 133.7, 132.0, 131.9, 131.6, 129.8, 129.6, 129.0, 128.5, 128.3, 127.0, 126.9, 126.3, 126.0, 125.7, 44.4; IR (Neat) ν_{max} 3056, 1623, 1507, 1421, 1360, 1266, 1220, 1143, 1092, 1018, 976 cm^{-1}; **HRMS (ESI)** for $C_{42}H_{33}N_2O_4S_2$ $(M+H)^+$: calcd. 693.1876, found 693.1884.

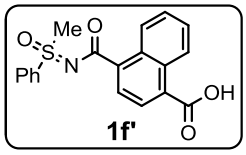
Preparation of Natural products bearing *N*-Aroyl *S*-Methyl-*S*-Phenylsulfoximine (5): EDC-coupling:[1]



General Procedure for the Hydrolysis of 1f (Step-I):

A mixture of the compound **1f** (4.0 g, 10.8 mmol), $LiOH.H_2O$ (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 materials **1f**. 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 **1f'**.

4-(*N*-(*S*-Methyl-*S*-phenylsulfoximine carbamoyl))-1-naphthoic acid (1f'):

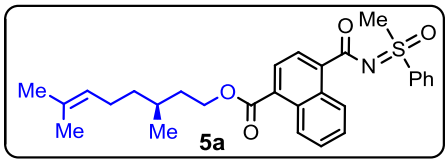


1f' (1.96 g, 51%) as colorless crystalline solid. mp = 233–235 ^oC; ^1H NMR (500 MHz, DMSO-D_6) δ 8.81 (br d, J = 8.5 Hz, 1H), 8.63 (br d, J = 8.0 Hz, 1H), 8.16–8.09 (m, 4H), 7.82–7.59 (m, 5H), 3.69 (s, 3H); ^{13}C NMR (126 MHz, DMSO-D_6) δ175.4 (-**C**OOH), 169.0, 138.8, 138.4, 134.3, 131.3, 130.9, 130.1, 128.6, 128.0, 127.8, 127.6, 127.5, 127.1, 126.5, 126.2, 43.7; IR (Neat) ν_{max} 2925, 2624, 1681, 1625, 1577, 1513, 1263, 1478, 1244, 1215, 1194, 1150, 1096, 1030, 987, 861, 884 cm^{-1}; **HRMS (ESI)** for $C_{19}H_{15}NO_4S$ $(M+Na)^+$: calcd. 376.0614, found 376.0618. No peak for –COOH group has been observed in ^1H NMR.

Step-II

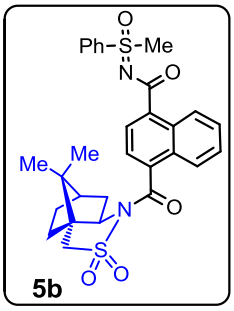
A solution of *N*'-(3-dimethylaminopropyl)-*N*-ethylcarbodimide, hydrochloride salt (EDC.HCl) (3.0 equiv), 4-*N*,*N*-dimethylaminopyridine (DMAP) (2.2 equiv) and sulfoximine-bearing naphthoic acid (**1f'**) (1.2 equiv) in CH_2Cl_2 (5.0 mL, for 1.0 mmol of sulfoximine) was stirred under an argon atmosphere. The respective natural products (1.0 equiv, 0.50 g) were introduced dropwise at 0 °C. The resulting reaction mixture was stirred for about 30 mintus 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 using column chromatography on silica gel using hexane/ethyl acetate.

Synthesis of 5a:



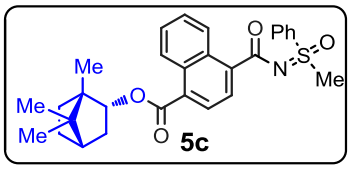
5a (1.20 g, 77%) as colorless liquid; R_f = 0.65 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90–8.79 (m, 2H), 8.19 (d, J = 7.6 Hz, 1H), 8.08 (d, J = 7.6 Hz, 3H), 7.74–7.66 (m, 1H), 7.65–7.52 (m, 4H), 5.15–5.07 (m, 1H), 4.52–4.41 (m, 2H), 3.50 (s, 3H), 2.09–1.96 (m, 2H), 1.93–1.82 (m, 1H), 1.69–1.63 (m, 5H), 1.62 (s, 3H), 1.50–1.37 (m, 1H), 1.32–1.19 (m, 1H), 1.00 (d, J = 6.4 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 176.1, 167.5, 138.6, 137.7, 133.9, 131.5, 131.4, 131.3, 130.7, 129.7, 128.1, 127.3, 127.12, 127.09, 126.5, 125.7, 124.5, 63.9, 44.4, 37.0, 35.5, 29.6, 25.7, 25.4, 19.5, 17.6; IR (Neat) ν_{max} 3854, 3631, 2958, 2922, 2852, 2156, 2027, 1702, 1561, 1460, 1259, 1132 cm^{-1}; **HRMS (ESI)** for $C_{29}H_{34}NO_4S$ $(M+H)^+$: calcd. 492.2203, found 492.2203.

Synthesis of 5b:



5b (1.13 g, 89%) as colorless crystalline solid. mp = 302–303 °C; R_f = 0.39 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00–8.90 (m, 1H), 8.28 (dd, J = 7.6 & 4.0 Hz, 1H), 8.07 (d, J = 7.2 Hz, 2H), 8.05–8.00 (m, 1H), 7.73–7.50 (m, 6H), 4.16 (br s, 1H), 3.51–3.37 (m, 5H), 2.18–1.89 (m, 5H), 1.67–1.23 (m, 5H), 0.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.83, 175.78, 138.61, 138.58, 136.2, 134.2, 133.9, 131.2, 130.7, 129.74, 129.72, 127.4, 127.2, 127.1, 126.7, 125.1, 65.5, 53.2, 48.4, 47.8, 45.0, 44.4, 44.3, 38.5, 33.1, 26.3, 21.2, 19.8; IR (Neat) ν_{max} 2955, 1674, 1624, 1576, 1447, 1291, 1247, 1194, 1165, 1134, 1069, 973, 852 cm^{-1}; **HRMS (ESI)** for $C_{29}H_{31}N_2O_5S_2$ $(M+H)^+$: calcd. 551.1669, found 551.1675.

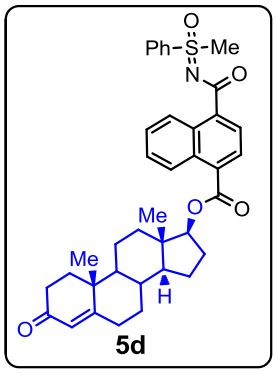
Synthesis of 5c:



5c (1.29 g, 81%) as colorless gummy liquid. R_f = 0.57 (3:2 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91–8.80 (m, 2H), 8.23 (bd, J = 7.6 Hz, 1H), 8.13–8.04 (m, 3H), 7.69 (bt, J = 7.2 Hz, 1H), 7.66–7.52 (m, 4H), 5.27–5.20 (m, 1H), 3.49 (s, 3H), 2.62–2.51 (m, 1H), 2.15–2.04 (m, 1H), 1.87–1.74 (m, 2H), 1.46–1.28 (m, 2H), 1.21 (dd, J = 7.6 & 4.2 Hz, 1H), 1.01 (s, 3H), 0.97 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.1, 167.7, 138.6, 137.5, 133.9, 131.5, 131.3, 131.2, 129.7, 127.9, 127.3, 127.2, 127.1, 126.5, 125.8, 81.1, 49.0, 47.9, 44.9, 44.4, 37.0, 28.0, 27.4, 19.7, 18.9, 13.7; IR (Neat) ν_{max} 2951, 2876, 1708, 1577, 1513, 1448, 1285, 1185, 1095, 973 cm^{-1}; **HRMS (ESI)** for $C_{29}H_{32}NO_4S$ $(M+H)^+$: calcd. 490.2047, found 490.2051.

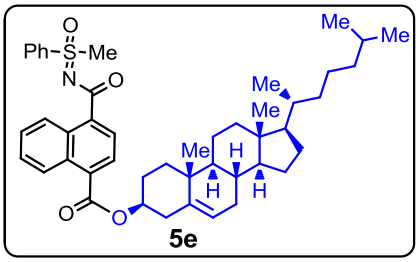
Synthesis of 5d:

5d (0.76 g, 70%) as colorless gummy liquid. R_f = 0.50 (1:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (d, J = 8.5 Hz, 1H), 8.82 (d, J = 8.5 Hz, 1H), 8.19 (d, J = 7.5 Hz, 1H), 8.08 (d, J = 7.5 Hz, 3H), 7.70 (t, J = 7.0 Hz, 1H), 7.67–7.52 (m, 4H), 5.74 (s, 1H), 4.94 (t, J = 8.25 Hz, 1H), 3.50 (s, 3H), 2.46–2.25 (m, 5H), 2.37–1.85 (m, 2H), 1.79–1.58 (m, 5H), 1.50–1.38 (m, 2H), 1.37–1.25 (m, 2H), 1.21–1.10 (m, 4H), 1.07–0.95 (m, 4H), 0.90–0.82 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ199.4, 176.1, 170.8, 167.3, 138.6, 137.7, 133.9, 131.6, 131.3, 130.9, 129.7, 128.1, 127.3, 127.1, 126.5, 125.8, 123.9, 83.5, 53.7, 50.2, 44.4, 42.9, 38.6, 36.8, 35.7, 35.4, 33.9, 32.7, 31.5, 27.7, 23.6, 20.6, 17.4, 12.4; IR (Neat) ν_{max} 2929, 2849, 1709, 1665, 1625, 1576, 1446, 1325, 1223, 1184, 1143, 1037, 1008, 972, 865, 779, 741 cm^{-1}; **HRMS (ESI)** for $C_{38}H_{41}NNaO_5S$ $(M+Na)^+$: calcd. 646.2598, found 646.2599.



5d

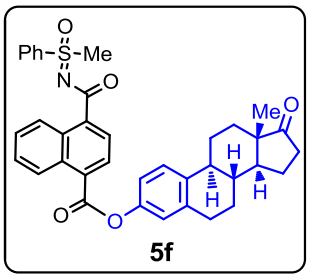
Synthesis of 5e:



5e

5e (0.64 g, 69%) as colorless crystalline solid. mp = 204–205 ^{o}C; R_f = 0.45 (3:2 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (d, J = 8.0 Hz, 1H), 8.79 (dd, J = 7.5 Hz, 1H), 8.19 (d, J = 7.5 Hz, 1H), 8.11–8.04 (m, 3H), 7.71 (t, J = 7.25 Hz, 1H), 7.64 (t, J = 7.75 Hz, 2H), 7.62–7.52 (m, 2H), 5.46 (d, J = 5.0 Hz, 1H), 5.04–4.94 (m, 1H), 3.51 (s, 3H), 2.59–2.49 (m, 2H), 2.12–1.74 (m, 6H), 1.63–1.45 (m, 6H), 1.41–0.97 (m, 17H), 0.93 (d, J = 6.5 Hz, 3H), 0.87 (dd, J = 6.75 & 2.25 Hz, 6H), 0.69 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ176.1, 166.9, 139.6, 138.7, 137.5, 133.9, 131.5, 131.33, 131.28, 129.8, 127.9, 127.3, 127.2, 127.12, 127.06, 126.5, 125.7, 122.9, 75.1, 56.7, 56.1, 50.1, 44.4, 42.3, 39.7, 39.5, 38.2, 37.1, 36.7, 36.2, 35.8, 31.94, 31.88, 28.2, 28.0, 27.9, 24.3, 23.8, 22.8, 22.5, 21.0, 19.4, 18.7, 11.8; IR (Neat) ν_{max} 2931, 2867, 1710, 1624, 1576, 1446, 1285, 1242, 1220, 1185, 1143, 1093, 973, 830, 777 cm^{-1}; **HRMS (ESI)** for $C_{46}H_{60}NO_4S$ $(M+H)^+$: calcd. 722.4238, found 722.4231.

Synthesis of 5f:

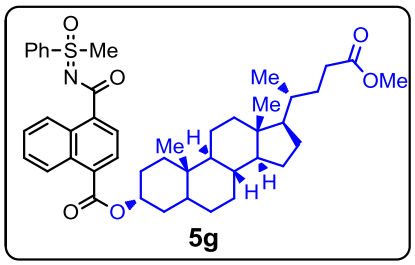


5f

5f (0.49 g, 41%) as colorless crystalline solid. mp = 254–255 ^{o}C; R_f = 0.39 (1:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (d, J = 8.5 Hz, 1H), 8.88 (d, J = 7.5 Hz, 1H), 8.37 (d, J = 7.5 Hz, 1H), 8.23 (d, J = 7.5 Hz, 1H), 8.10 (d, J = 7.5 Hz, 2H), 7.72 (t, J = 7.5 Hz, 1H), 7.69–7.56 (m, 4H), 7.38 (d, J = 8.5 Hz, 1H), 7.07 (dd, J = 8.5 & 2.5 Hz, 1H), 7.03 (d, J = 2.5 Hz, 1H), 3.53 (s, 3H), 2.97 (br t, J = 4.5 Hz, 2H), 2.57–2.41 (m, 2H), 2.38–2.29 (m, 1H), 2.20–2.10 (m, 1H), 2.09–1.96 (m, 3H), 1.71–1.45 (m, 6H), 0.93 (s, 3H); ^{13}C

NMR (126 MHz, $CDCl_3$) δ 176.0, 165.9, 148.8, 138.8, 138.7, 138.2, 137.6, 134.0, 131.9, 131.3, 129.8, 129.3, 129.1, 127.8, 127.2, 127.1, 126.9, 126.6, 126.5, 125.7, 121.7, 118.9, 50.5, 47.9, 44.5, 44.2, 38.0, 35.8, 31.6, 29.7, 29.4, 26.3, 25.8, 21.6, 13.8; IR (Neat) ν_{max} 2923, 2854, 1729, 1617, 1575, 1512, 1447, 1403, 1277, 1240, 1215, 1178, 1137, 1114, 1026, 974 cm^{-1}; **HRMS (ESI)** for $C_{37}H_{36}NO_5S$ $(M+H)^+$: calcd. 606.2309, found 606.2309.

Synthesis of 5g:

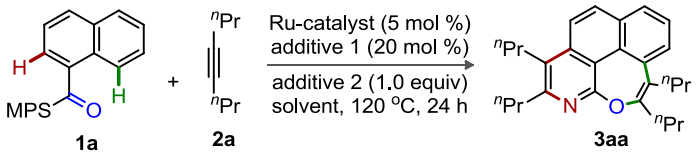


5g (0.59 g, 64%) as colorless thick liquid; R_f = 0.59 (1:1 hexane/EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 8.87 (d, J = 8.0 Hz, 1H), 8.77 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 7.5 Hz, 1H), 8.11–8.03 (m, 3H), 7.74–7.67 (m, 1H), 7.67–7.56 (m, 4H), 5.13–5.07 (m, 1H), 3.65 (s, 3H), 3.51 (s, 3H), 2.42–2.29 (m, 1H), 2.26–2.17 (m, 1H), 2.06–1.73 (m, 8H), 1.64–1.54 (m, 3H), 1.50–1.35 (m, 5H), 1.34–1.24 (m, 4H), 1.21–1.05 (m, 6H), 0.98 (s, 3H), 0.91 (d, J = 6.5 Hz, 3H), 0.65 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.2, 174.8, 167.1, 138.6, 137.4, 133.9, 131.4, 131.3, 129.8, 127.8, 127.3, 127.2, 127.09, 127.06, 126.5, 125.7, 75.5, 56.4, 55.9, 51.4, 44.4, 42.7, 42.0, 40.4, 40.0, 35.8, 35.3, 35.1, 34.6, 32.3, 31.0, 30.9, 28.1, 27.0, 26.8, 26.3, 24.1, 23.3, 20.8, 18.2, 12.0; IR (Neat) ν_{max} 2927, 2863, 1709, 1627, 1577, 1512, 1446, 1376, 1284, 1223, 1184, 1143, 1095, 1032, 974 cm^{-1}; **HRMS (ESI)** for $C_{44}H_{56}NO_6S$ $(M+H)^+$: calcd. 726.3823, found 726.3827.

Optimization of Reaction Conditions; General Procedure (GP-2A):[a]

The annulation reactions were carried out in a 25 mL screw capped tube. The tube was charged with ***N***-[1-naphthoyl]-*S*-methyl-*S*-phenylsulfoximine (**1a**, 0.3 mmol), 4-octyne (**2a**, 0.9 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5.0 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 ^oC 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.

Table S1: Optimization of Reaction Conditions



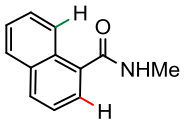
Entry	Additive 1 (20 mol %)	Additive 2 (1.0 equiv)	Solvent	Yield of **3aa** (%)[b]
1	$AgSbF_6$	NaOAc	DCE	08
2	$AgSbF_6$	$Mn(OAc)_2$	DCE	12
3	$AgSbF_6$	AgOAc	DCE	15
4	$AgSbF_6$	$Zn(OAc)_2{\cdot}2H_2O$	DCE	11
5	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	DCE	35
6	KPF_6	$Cu(OAc)_2{\cdot}H_2O$	DCE	<5[c]
7	$NaPF_6$	$Cu(OAc)_2{\cdot}H_2O$	DCE	6
8	$AgBF_4$	$Cu(OAc)_2{\cdot}H_2O$	DCE	30
9	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	MeCN	<5[c]
10	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	toluene	7
11	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	TCE	22
12	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	41
13[d]	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	68
14[e]	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	77
15	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	<5[c]
16	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	<5[c]

[a] Conditions: **1a** (0.3 mmol), **2a** (0.9 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5.0 mol %), additive-1 (20 mol %), additive-2 (0.3 mmol), solvent (2.0 mL) at 120 °C. [b] Isolated yield. [c] ^1H NMR conversion. [d] $[RuCl_2(p\text{-cymene})]_2$ (10 mol %), $AgSbF_6$ (40 mol %) was used. [e] **2a** (1.2 mmol), $[RuCl_2(p\text{-cymene})]_2$ (10 mol %), $AgSbF_6$ (40 mol %), $Cu(OAc)_2{\cdot}H_2O$ (1.5 equiv) was used. DCE = $ClCH_2CH_2Cl$, TCE = 1,1,2,2-Tetrachloroethane.

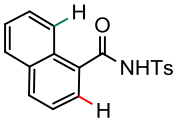
Effect of Directing Groups in the Double-Annulation of 1-Naphthoic Acid Derivative with 4-Octyne: General Procedure (GP-2B):

The annulation reactions were carried out in a 25 mL screw capped tube. The tube was charged with various directing group protected 1-naphthoic acid (**I–VI**, 0.3 mmol), 4-octyne (**2a**, 1.2 mmol), $[RuCl_2(p\text{-cymene})]_2$ (18 mg, 10 mol %), and $Cu(OAc)_2{\cdot}H_2O$ (85 mg, 0.45 mmol). Subsequently, $AgSbF_6$ (41 mg, 40 mol %) was introduced in to the tube in a glove box. The solvent 1,4-dioxane (2.0 mL) was added to the mixture and the resulting mixture was stirred at 120 °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 × 10 mL).

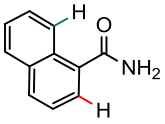
The solvents were evaporated under reduced pressure and the crude material was purified using column chromatography on neutral aluminia (5–10% *n*-hexane/EtOAc eluent) to give the desired product.



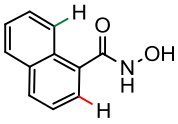
I, 0%



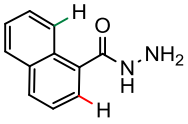
II, 0%



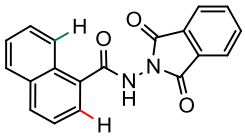
III, 22%



IV, 15%



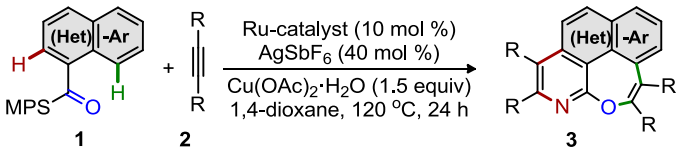
V, 7%



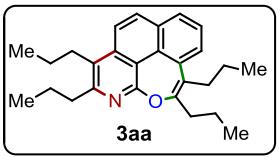
VI, 26%

Synthesis of 6,7-Fused Oxepino-Isoquinoline via the Direct Double-Annulation of *N*-(Hetero)aroylated-*N*-Methylphenyl Sulfoximine (MPS) with Unactivated 1,2-Dialkyl Alkynes (GP-2C):

The annulation reactions were carried out in a 25 mL screw capped tube. The tube was charged with *N*-(hetero)aroylated-MPS (**1**, 0.3 mmol), alkyne (**2**, 1.2 mmol), $[RuCl_2(p\text{-cymene})]_2$ (18 mg, 10 mol %), and $Cu(OAc)_2.H_2O$ (85 mg, 0.45 mmol). Subsequently, $AgSbF_6$ (41 mg, 40 mol %) was introduced in to the tube in a glove box. The solvent 1,4-dioxane (2.0 mL) was added to the mixture and the resulting mixture was stirred at 120 ^oC 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 (5–15% *n*-hexane/EtOAc eluent) to give the desired product. The products **3** were found unstable when kept at the ambient temperature for longer time; thus, these compounds were stored at –20 °C under the inert atmosphere.



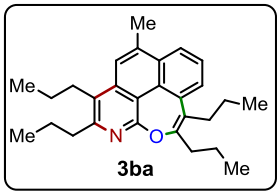
1,2,5,6-Tetrapropyl-4-oxa-3-azacyclohepta[def]phenanthrene (3aa):



3aa (89 mg, 77%); light yellow colour liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 9.2 Hz, 1H), 7.81 (d, J = 9.2 Hz, 1H), 7.75 (t, J = 7.6 Hz, 2H),

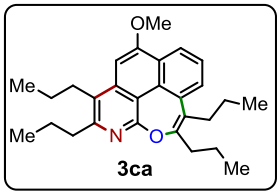
7.61 (t, J = 7.6 Hz, 1H), 3.07–2.97 (m, 2H), 2.93 (br t, J = 7.6 Hz, 2H), 2.69 (t, J = 7.6 Hz, 2H), 2.49 (t, J = 7.6 Hz, 2H), 2.08–1.95 (m, 2H), 1.91–1.78 (m, 2H), 1.77–1.63 (m, 2H), 1.17–1.07 (m, 5H), 1.06–0.98 (m, 6H), 0.67 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 154.5, 154.2, 138.8, 137.4, 131.7, 131.5, 128.2, 126.9, 126.5, 125.9, 123.8, 121.1, 117.1, 36.6, 34.7, 34.2, 30.0, 24.3, 23.0, 22.5, 20.5, 14.4, 14.1, 14.0, 13.9; IR (Neat) ν_{max} 2960, 2930, 2870, 1617, 1573, 1460, 1400, 1378, 1271, 1174, 1087, 830 cm^{-1}; **HRMS (ESI)** for $C_{27}H_{34}NO$ $(M+H)^+$: calcd. 388.2635, found 388.2642.

10-Methyl-1,2,5,6-tetrapropyl-4-oxa-3-azacyclohepta[def]phenanthrene (3ba):



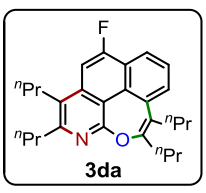
3ba (81 mg, 67%); light yellow colour liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 7.5 Hz, 1H), 7.73 (d, J = 7.0 Hz, 1H), 7.63 (s, 1H), 7.60 (t, J = 7.25 Hz, 1H), 3.00 (t, J = 8.0 Hz, 2H), 2.93 (t, J = 7.75 Hz, 2H), 2.74 (s, 3H), 2.71 (t, J = 7.5 Hz, 2H), 2.48 (t, J = 7.75 Hz, 2H), 2.10–1.99 (m, 2H), 1.93–1.81 (m, 2H), 1.77–1.65 (m, 2H), 1.12 (t, J = 7.5 Hz, 3H), 1.10–1.01 (m, 8H), 0.65 (t, J = 7.25 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 154.4, 154.1, 138.6, 137.7, 137.3, 131.7, 128.4, 126.6, 125.7, 125.2, 123.8, 122.3, 121.3, 116.3, 36.6, 34.6, 34.3, 29.8, 24.2, 23.0, 22.5, 20.9, 20.5, 14.5, 14.2, 14.0, 13.8; IR (Neat) ν_{max} 3396, 2957, 2929, 2869, 1661, 1619, 1571, 1457, 1396, 1374, 1272, 1200, 1146, 1024, 998 cm^{-1}; **HRMS (ESI)** for $C_{28}H_{36}NO$ $(M+H)^+$: calcd. 402.2791, found 402.2794.

10-Methoxy-1,2,5,6-tetrapropyl-4-oxa-3-azacyclohepta[def]phenanthrene (3ca):



3ca (74 mg, 60%); light yellow colour liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, J = 8.0 & 1.2 Hz, 1H), 7.74 (dd, J = 7.6 & 1.2 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 6.99 (s, 1H), 4.09 (s, 3H), 2.99–2.94 (m, 2H), 2.93–2.86 (m, 2H), 2.67 (t, J = 7.6 Hz, 2H), 2.47 (t, J = 7.8 Hz, 2H), 2.07–1.94 (m, 2H), 1.89–1.77 (m, 2H), 1.76–1.67 (m, 2H), 1.15–1.00 (m, 11H), 0.65 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 157.0, 154.5, 154.3, 140.1, 137.4, 129.5, 127.6, 126.5, 125.7, 124.9, 123.7, 120.4, 113.3, 96.9, 55.5, 36.9, 34.7, 34.3, 30.2, 23.7, 23.1, 22.6, 20.6, 14.6, 14.3, 14.1, 13.9; IR (Neat) ν_{max} 2957, 2929, 2869, 1617, 1586, 1502, 1459, 1376, 1355, 1272, 1240, 1159, 1107, 1005 cm^{-1}; **HRMS (ESI)** for $C_{28}H_{36}NO_2$ $(M+H)^+$: calcd. 418.2741, found 418.2744.

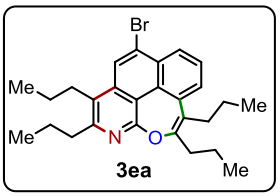
10-Fluoro-1,2,5,6-tetrapropyl-4-oxa-3-azacyclohepta[def]phenanthrene (3da):



3da (105 mg, 87%); light yellow colour liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.65 (t, J = 7.8 Hz, 1H), 7.43 (d, J = 12.4 Hz, 1H), 2.98–2.88 (m, 4H), 2.69 (t, J = 7.6 Hz, 2H), 2.48 (t, J = 7.6 Hz, 2H), 2.09–1.96 (m, 2H), 1.91–1.78 (m, 2H), 1.74–1.60 (m, 2H), 1.17–0.99 (m, 11H), 0.66 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (d, J = 257 Hz), 158.4, 154.8 (d,

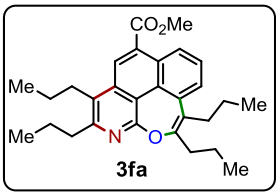
J = 4.0 Hz), 139.1 (d, J = 10 Hz), 137.6 (d, J = 2.0 Hz), 129.8 (d, J = 6.0 Hz), 128.0, 126.2, 125.8 (d, J = 6.0 Hz), 124.0, 123.8, 123.4, 119.1 (d, J = 8.0 Hz), 114.7, 103.3 (d, J = 21 Hz), 36.6, 34.6, 34.1, 30.1, 24.0, 23.0, 22.5, 20.5, 14.4, 14.1, 14.0, 13.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ –117.40; IR (Neat) ν_{max} 2960, 2930, 2871, 1636, 1576, 1457, 1291, 1197, 1086 cm^{-1}; **HRMS (ESI)** for $C_{27}H_{33}FNO$ $(M+H)^+$: calcd. 406.2541, found 406.2543.

10-Bromo-1,2,5,6-tetrapropyl-4-oxa-3-azacyclohepta[def]phenanthrene (3ea):



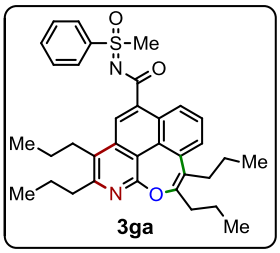
3ea (71 mg, 51%); light yellow colour liquid. ^{1}H NMR (400 MHz, DCl_3) δ 8.27 (dd, J = 8.0 & 1.2 Hz, 1H), 8.17 (s, 1H), 7.79 (dd, J = 7.6 & 1.2 Hz, 1H), 7.68 (t, J = 8.0 Hz, 1H), 3.10–2.87 (m, 4H), 2.67 (t, J = 7.6 Hz, 2H), 2.48 (t, J = 7.8 Hz, 2H), 2.07–1.93 (m, 2H), 1.89–1.79 (m, 2H), 1.75–1.65 (m, 2H), 1.12 (t, J = 7.2 Hz, 3H), 1.07–0.99 (m, 8H), 0.63 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 155.2, 154.9, 138.6, 137.7, 130.2, 129.2, 128.0, 127.5, 126.7, 126.2, 125.6, 125.2, 123.6, 116.6, 36.7, 34.5, 34.3, 29.9, 24.4, 23.0, 22.4, 20.5, 14.5, 14.2, 14.0, 13.8; IR (Neat) ν_{max} 2957, 2928, 2869, 1714, 1600, 1585, 1492, 1397, 1271, 1196, 1169, 1130, 1086 cm^{-1}; **HRMS (ESI)** for $C_{27}H_{33}BrNO$ $(M+H)^+$: calcd. 466.1740, found 466.1740.

Methyl 1,2,5,6-tetrapropyl-4-oxa-3-azacyclohepta[def]phenanthrene-10-carboxylate (3fa):



3fa (79 mg, 60%); light yellow colour liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (dd, J = 8.5 & 1.0 Hz, 1H), 8.40 (s, 1H), 7.77 (dd, J = 7.5 & 0.5 Hz, 1H), 7.66 (t, J = 7.75 Hz, 1H), 4.05 (s, 3H), 3.05 (t, J = 8.25 Hz, 2H), 2.94 (t, J = 7.75 Hz, 2H), 2.69 (t, J = 7.75 Hz, 2H), 2.47 (t, J = 7.75 Hz, 2H), 2.07–1.96 (m, 2H), 1.92–1.81 (m, 2H), 1.77–1.66 (m, 2H), 1.11 (t, J = 7.5 Hz, 3H), 1.07–1.00 (m, 8H), 0.61 (t, J = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 158.4, 155.0, 154.8, 137.6, 136.8, 131.3, 128.7, 128.6, 127.3, 126.8, 126.5, 125.3, 124.2, 123.8, 118.3, 52.5, 36.6, 34.4, 34.2, 29.7, 24.5, 22.9, 22.3, 20.4, 14.3, 14.1, 14.0, 13.7; IR (Neat) ν_{max} 2958, 2929, 2870, 1723, 1609, 1565, 1459, 1434, 1409, 1257, 1196, 1131, 1087 cm^{-1}; **HRMS (ESI)** for $C_{29}H_{36}NO_3$ $(M+H)^+$: calcd. 446.2690, found 446.2694.

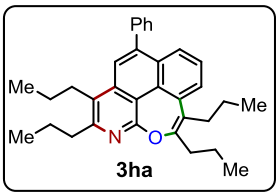
***N*-[1,2,5,6-Tetrapropyl-4-oxa-3-azacyclohepta[def]phenanthrene-10-carbonyl]-S-methyl-S-phenylsulfoximine (3ga):**



3ga (90 mg, 52%); light yellow colour liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (dd, J = 8.0 & 1.0 Hz, 1H), 8.50 (s, 1H), 8.08 (d, J = 7.5 Hz, 2H), 7.72 (dd, J = 7.5 & 1.5 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.64–7.56 (m, 3H), 3.52 (s, 3H), 3.05 (br t, J = 8.0 Hz, 2H), 2.92 (t, J = 7.75 Hz, 2H), 2.67 (t, J = 7.5 Hz, 2H), 2.46 (br t, J = 7.75 Hz, 2H), 2.04–1.94 (m, 2H),

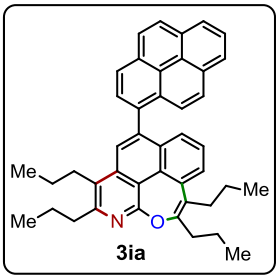
1.90–1.81 (m, 2H), 1.77–1.69 (m, 2H), 1.09 (t, J = 7.5 Hz, 3H), 1.06–1.00 (m, 8H), 0.59 (t, J = 7.5 Hz, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 176.5, 158.4, 154.5, 138.6, 137.3, 137.0, 133.9, 129.7, 129.0, 128.7, 128.2, 128.1, 127.01, 126.96, 126.6, 126.2, 124.7, 124.1, 123.9, 117.9, 44.4, 36.6, 34.4, 34.1, 29.9, 24.5, 22.9, 22.3, 20.4, 14.4, 14.1, 13.9, 13.7; IR (Neat) ν_{max} 2958, 2923, 2869, 1623, 1563, 1445, 1411, 1378, 1270, 1209, 1145, 1088, 978 cm^{-1}; **HRMS (ESI)** for $C_{35}H_{41}N_2O_3S$ $(M+H)^+$: calcd. 569.2832, found 569.2831.

10-Phenyl-1,2,5,6-tetrapropyl-4-oxa-3-azacyclohepta[def]phenanthrene (3ha):



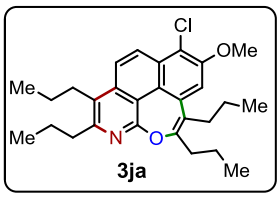
3ha (81 mg, 61%); light yellow colour solid. mp = 137–138 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78–7.71 (m, 3H), 7.56–7.47 (m, 6H), 3.02 (t, J = 8.0 Hz, 2H), 2.95 (t, J = 7.75 Hz, 2H), 2.73 (t, J = 7.5 Hz, 2H), 2.51 (t, J = 7.75 Hz, 2H), 2.11–2.00 (m, 2H), 1.92–1.82 (m, 2H), 1.73–1.66 (m, 2H), 1.14 (q, J = 7.5 Hz, 2H), 1.11–1.01 (m, 9H), 0.70 (t, J = 7.25 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 154.8, 154.5, 143.3, 140.8, 138.2, 137.7, 131.1, 129.9, 128.7, 128.3, 127.7, 126.9, 126.0, 125.7, 125.1, 123.9, 122.1, 116.7, 36.7, 34.7, 34.5, 29.9, 24.3, 23.0, 22.7, 20.5, 14.4, 14.2, 14.03, 13.96; IR (Neat) ν_{max} 3059, 2957, 2928, 2869, 1665, 1568, 1458, 1411, 1392, 1325, 1272, 1198, 1127, 1086, 1028, 883 cm^{-1}; **HRMS (ESI)** for $C_{33}H_{38}NO$ $(M+H)^+$: calcd. 464.2948, found 464.2948.

1,2,5,6-Tetrapropyl-10-(pyren-1-yl)-4-oxa-3-azacyclohepta[def]phenanthrene (3ia):



3ia (79 mg, 45%); light yellow colour liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 8.0 Hz, 1H), 8.25 (d, J = 7.6 Hz, 1H), 8.23–8.12 (m, 3H), 8.08 (d, J = 7.6 Hz, 1H), 8.03 (t, J = 7.6 Hz, 1H), 7.96 (s, 1H), 7.91 (d, J = 9.2 Hz, 1H), 7.75 (dd, J = 7.2 & 1.2 Hz, 1H), 7.67 (d, J = 9.2 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.31 (dd, J = 8.0 & 0.8 Hz, 1H), 3.04–2.95 (m, 4H), 2.79 (bt, J = 7.6 Hz, 2H), 2.60–2.50 (m, 2H), 2.18–2.05 (m, 2H), 1.97–1.85 (m, 2H), 1.75–1.65 (m, 2H), 1.30–1.18 (m, 2H), 1.14–1.04 (m, 6H), 0.99 (bt, J = 7.4 Hz, 3H), 0.77 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 154.8, 154.7, 142.1, 138.2, 137.7, 135.5, 132.2, 131.4, 131.1, 130.9, 129.9, 128.4, 128.0, 127.7, 127.3, 127.0, 126.2, 126.1, 126.0, 125.7, 125.44, 125.37, 125.2, 124.68, 124.67, 124.5, 124.0, 123.6, 36.7, 34.7, 34.6, 29.9, 24.4, 23.1, 22.8, 20.6, 14.4, 14.2, 14.08, 14.07; IR (Neat) ν_{max} 3041, 2956, 2868, 1602, 1570, 1457, 1412, 1392, 1272, 1240, 1168, 1130, 1086, 1038, 966 cm^{-1}; **HRMS (ESI)** for $C_{43}H_{42}NO$ $(M+H)^+$: calcd. 588.3261, found 588.3241.

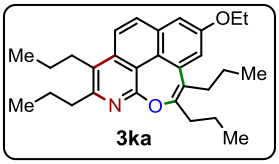
9-Chloro-8-methoxy-1,2,5,6-tetrapropyl-4-oxa-3-azacyclohepta[def]phenanthrene (3ja):



3ja (61 mg, 45%); light yellow colour solid. mp = 151–152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 9.5 Hz, 1H), 7.90 (d, J = 9.5 Hz, 1H), 7.42

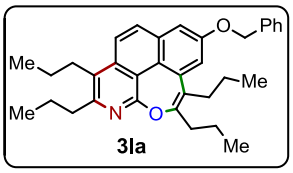
(s, 1H), 4.05 (s, 3H), 3.00 (t, J = 8.0 Hz, 2H), 2.91 (t, J = 7.25 Hz, 2H), 2.67 (t, J = 7.75 Hz, 2H), 2.48 (t, J = 7.75 Hz, 2H), 2.31–1.96 (m, 2H), 1.88–1.79 (m, 2H), 1.73–1.65 (m, 2H), 1.10 (t, J = 7.25 Hz, 5H), 1.06–0.99 (m, 6H), 0.66 (t, J = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 155.0, 154.3, 152.7, 137.2, 137.5, 130.1, 126.7, 126.3, 124.0, 123.2, 123.1, 117.1, 116.9, 112.6, 56.8, 36.6, 34.6, 34.4, 30.0, 24.4, 23.0, 22.5, 20.5, 14.5, 14.2, 14.0, 13.9; IR (Neat) ν_{max} 2958, 2929, 1583, 1460, 1419, 1378, 1350, 1274, 1246, 1185, 1137, 1087 cm^{-1}; **HRMS (ESI)** for $C_{28}H_{35}ClNO_2$ $(M+H)^+$: calcd. 452.2351, found 452.2354.

8-Ethoxy-1,2,5,6-tetrapropyl-4-oxa-3-azacyclohepta[def]phenanthrene (3ka):



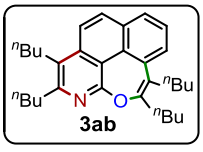
3ka (71 mg, 55%); light yellow colour liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (s, 2H), 7.35 (d, J = 2.5 Hz, 1H), 7.16 (d, J = 2.5 Hz, 1H), 4.19 (q, J = 7.0 Hz, 2H), 2.99 (t, J = 8.25 Hz, 2H), 2.91 (t, J = 7.75 Hz, 2H), 2.68 (t, J = 7.5 Hz, 2H), 2.46 (t, J = 8.0 Hz, 2H), 2.07–1.95 (m, 2H), 1.89–1.78 (m, 2H), 1.73–1.65 (m, 2H), 1.50 (t, J = 7.0 Hz, 3H), 1.15 (q, J = 7.5 Hz, 2H), 1.10 (t, J = 7.25 Hz, 3H), 1.06–0.99 (m, 6H), 0.70 (t, J = 7.25 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 156.8, 154.5, 153.0, 139.1, 137.7, 133.2, 131.1, 126.0, 123.5, 122.7, 121.6, 117.3, 108.2, 63.7, 36.6, 34.8, 34.3, 30.0, 24.3, 23.1, 22.6, 20.5, 14.8, 14.5, 14.2, 14.02, 13.98; IR (Neat) ν_{max} 2958, 2930, 2870, 1663, 1597, 1459, 1397, 1346, 1296, 1244, 1203, 1169, 1135, 1052 cm^{-1}; **HRMS (ESI)** for $C_{29}H_{38}NO_2$ $(M+H)^+$: calcd. 432.2897, found 432.2898.

8-(Benzyloxy)-1,2,5,6-tetrapropyl-4-oxa-3-azacyclohepta[def]phenanthrene (3la):



3la (75 mg, 51%); light yellow colour liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 1.0 Hz, 2H), 7.51 (d, J = 7.0 Hz, 2H), 7.46–7.39 (m, 3H), 7.38–7.36 (m, 1H), 7.26 (d, J = 2.5 Hz, 1H), 5.23 (s, 2H), 2.99 (t, J = 8.0 Hz, 2H), 2.92 (t, J = 7.75 Hz, 2H), 2.69 (t, J = 7.75 Hz, 2H), 2.44 (t, J = 8.0 Hz, 2H), 2.07–1.97 (m, 2H), 1.91–1.80 (m, 2H), 1.76–1.64 (m, 2H), 1.16–1.07 (m, 5H), 1.07–1.00 (m, 6H), 0.68 (t, J = 7.25 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 156.6, 154.6, 153.2, 139.2, 137.7, 136.7, 133.1, 131.1, 128.6, 128.1, 127.5, 126.0, 123.5, 122.9, 121.7, 117.3, 117.2, 108.8, 70.2, 36.5, 34.8, 34.3, 30.0, 24.3, 23.1, 22.6, 20.5, 14.5, 14.2, 14.0, 13.9; IR (Neat) ν_{max} 2957, 2925, 1597, 1456, 1399, 1377, 1296, 1244, 1165, 1135, 1084, 1028 cm^{-1}; **HRMS (ESI)** for $C_{34}H_{40}NO_2$ $(M+H)^+$: calcd. 494.3054, found 494.3056.

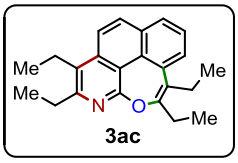
1,2,5,6-Tetrabutyl-4-oxa-3-azacyclohepta[def]phenanthrene (3ab):



3ab (105 mg, 79%); light yellow colour liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.8 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.76–7.69 (m, 2H), 7.58 (t, J = 7.6 Hz, 1H), 3.07–2.93 (m, 4H), 2.74 (t, J = 7.6 Hz, 2H), 2.50 (bt, J = 7.6 Hz, 2H),

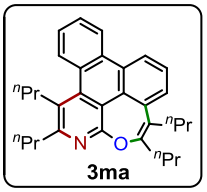
2.06–1.94 (m, 2H), 1.90–1.78 (m, 2H), 1.69–1.43 (m, 8H), 1.17–1.07 (m, 4H), 1.06–0.97 (m, 9H), 0.74 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 154.7, 154.4, 138.9, 137.6, 131.8, 131.6, 128.3, 127.0, 126.6, 126.0, 123.8, 121.1, 117.2, 34.5, 33.3, 32.8, 32.2, 31.8, 29.7, 27.8, 23.2, 23.0, 22.9, 22.7, 14.2, 14.1, 14.0, 13.8; IR (Neat) ν_{max} 2957, 2865, 1665, 1616, 1570, 1462,1400, 1378, 1282, 1246, 1132 cm^{-1}; **HRMS (ESI)** for $C_{31}H_{42}NO$ $(M+H)^+$: calcd. 444.3261, found 444.3265.

1,2,5,6-Tetraethyl-4-oxa-3-azacyclohepta[def]phenanthrene (3ac):



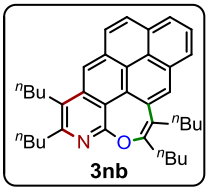
3ac (83 mg, 80%); light yellow colour liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.79 (m, 2H), 7.78–7.72 (m, 2H), 7.61 (t, J = 7.6 Hz, 1H), 3.08 (q, J = 7.6 Hz, 2H), 2.99 (q, J = 7.6 Hz, 2H), 2.75 (q, J = 7.6 Hz, 2H), 2.53 (q, J = 7.6 Hz, 2H), 1.48 (t, J = 7.6 Hz, 3H), 1.39 (t, J = 7.6 Hz, 3H), 1.31 (t, J = 7.6 Hz, 3H), 0.84 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 155.7, 155.2, 138.6, 137.3, 131.75, 131.71, 128.3, 127.0, 126.8, 126.6, 126.1, 124.4, 120.9, 117.2, 27.8, 26.1, 25.4, 21.0, 15.3, 14.4, 14.2, 12.5; IR (Neat) ν_{max} 2967, 2874, 1665, 1616, 1570, 1461, 1401, 1321, 1174, 1056 cm^{-1}; **HRMS (ESI)** for $C_{23}H_{26}NO$ $(M+H)^+$: calcd. 332.2009, found 332.2015.

1,2,5,6-Tetrapropyl-4-oxa-3-azacyclohepta[def]triphenylene (3ma):



3ma (37 mg, 25%); light yellow colour thick liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, J = 8.0 Hz, 1H), 8.37 (d, J = 7.5 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 7.68 (t, J = 7.5 Hz, 1H), 7.64–7.52 (m, 3H), 3.11 (bt, J = 7.75 Hz, 2H), 2.94 (t, J = 7.75 Hz, 2H), 2.66 (t, J = 7.5 Hz, 2H), 2.43 (t, J = 7.75 Hz, 2H), 2.02–1.93 (m, 4H), 1.88 (q, J = 7.5 Hz, 2H), 1.18 (t, J = 7.25 Hz, 3H), 1.10–0.99 (m, 8H), 0.59 (t, J = 7.25 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 158.1, 154.8, 139.6, 138.1, 132.9, 128.4, 128.3, 128.2, 127.7, 127.5, 126.6, 126.4, 125.4, 124.2, 123.5, 120.0, 117.2, 37.2, 34.0, 33.7, 33.2, 24.3, 23.4, 22.2, 20.7, 14.4, 14.3, 14.1, 13.8; IR (Neat) ν_{max} 2958, 2929, 2870, 1719, 1558, 1458, 1387, 1259, 1204, 1168, 1129, 1085 cm^{-1}; **HRMS (ESI)** for $C_{31}H_{36}NO$ $(M+H)^+$: calcd. 438.2791, found 438.2799.

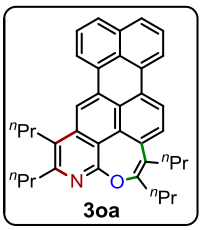
8,9,12,13-Tetrabutyl-11-oxa-10-azabenzo[def]cyclohepta[jkl]triphenylene (3nb):



3nb (47 mg, 54%); yellow colour thick liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.36 (s, 1H), 8.20 (d, J = 8.0 Hz, 1H), 8.02 (bd, J = 7.2 Hz, 1H), 7.98–7.84 (m, 3H), 3.23 (bt, J = 8.0 Hz, 2H), 3.08 (t, J = 8.0 Hz, 2H), 2.85 (t, J = 7.6 Hz, 2H), 2.66 (t, J = 7.6 Hz, 2H), 2.15–2.04 (m, 2H), 1.98–1.73 (m, 4H), 1.67–1.51 (m, 7H), 1.13–1.00 (m, 12H), 0.67 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 155.4, 151.2, 136.9, 136.0, 132.8, 130.5, 130.3, 128.9, 128.1, 127.5, 127.1, 126.4, 126.3, 125.5, 124.9, 124.2, 123.4, 122.8, 119.7, 115.5, 34.5, 33.2, 32.8, 32.7, 32.3, 31.6, 29.7, 28.0, 23.3, 23.0, 22.9, 22.6, 14.14,

14.10, 14.0, 13.6; IR (Neat) ν_{max} 3044, 2954, 1602, 1572, 1463, 1388, 1298, 1174, 1052, 1024, 873 cm^{-1}; **HRMS (ESI)** for $C_{37}H_{44}NO$ $(M+H)^+$: calcd. 518.3417, found 518.3422.

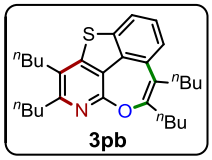
1,2,5,6-Tetrapropyl-3-oxa-4-azacyclohepta[def]phenaleno[1,2,3-jk]phenanthrene (3oa):



3oa

3oa (73 mg, 48%); orange colour thick liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.21 (d, J = 8.0 Hz, 2H), 8.12 (bd, J = 7.0 Hz, 1H), 7.74–7.63 (m, 3H), 7.51–7.41 (m, 2H), 3.08 (br t, J = 8.0 Hz, 2H), 2.94 (t, J = 7.75 Hz, 2H), 2.71 (t, J = 7.25 Hz, 2H), 2.49 (br t, J = 7.75 Hz, 2H), 2.10–1.99 (m, 2H), 1.94–1.84 (m, 2H), 1.83–1.73 (m, 2H), 1.18 (t, J = 7.25 Hz, 3H), 1.16–1.02 (m, 8H), 0.66 (t, J = 7.25 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 155.0, 154.5, 138.9, 137.2, 134.2, 133.1, 130.44, 130.42, 129.5, 128.9, 128.8, 127.9, 127.8, 127.4, 127.1, 126.7, 126.5, 125.8, 123.8, 121.7, 120.9, 120.8, 116.9, 115.3, 36.8, 34.6, 34.1, 30.0, 24.6, 23.0, 22.6, 20.5, 14.6, 14.2, 14.1, 13.9; IR (Neat) ν_{max} 2958, 2927, 2869, 1602, 1572, 1504, 1458, 1414, 1376, 1324, 1265, 1191, 1137, 1091 cm^{-1}; **HRMS (ESI)** for $C_{37}H_{38}NO$ $(M+H)^+$: calcd. 512.2948, found 512.2948.

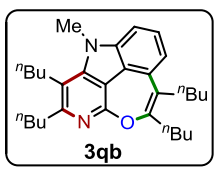
5,6,9,10-Tetrabutyl-8-oxa-4-thia-7-azacyclohepta[def]fluorene (3pb):



3pb

3pb (110 mg, 82%); light yellow colour liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 6.2, 2.9 Hz, 1H), 7.32–7.25 (m, 2H), 2.86–2.74 (m, 4H), 2.57 (bt, J = 7.8 Hz, 2H), 2.45 (bt, J = 7.8 Hz, 2H), 1.89–1.60 (m, 6H), 1.55–1.33 (m, 10H), 1.03–0.89 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 155.3, 153.8, 150.4, 137.9, 135.2, 132.9, 126.5, 125.0, 123.0, 120.9, 120.5, 119.5, 34.6, 34.0, 32.3, 31.9, 31.4, 30.5, 29.9, 22.9, 22.8, 22.7, 22.6, 13.98, 13.97, 13.8; IR (Neat) ν_{max} 2954, 2860, 1720, 1624, 1590, 1547, 1463, 1395, 1265, 1154, 1096, 962 cm^{-1}; **HRMS (ESI)** for $C_{29}H_{40}NOS$ $(M+H)^+$: calcd. 450.2825, found 450.2831.

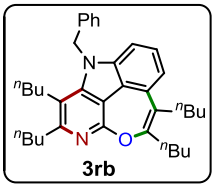
5,6,9,10-Tetrabutyl-4-methyl-4H-8-oxa-4,7-diazacyclohepta[def]fluorene (3qb):



3qb

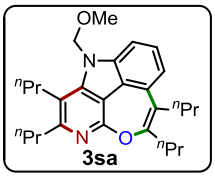
3qb (116 mg, 52%); light yellow colour liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, J = 8.0 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 6.85 (d, J = 7.6 Hz, 1H), 3.86 (s, 3H), 2.87 (br t, J = 8.0 Hz, 2H), 2.73 (br t, J = 8.0 Hz, 2H), 2.37 (br q, J = 7.6 Hz, 4H), 1.78–1.38 (m, 16H), 1.03–0.91 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 155.8, 153.7, 144.9, 139.9, 132.3, 126.1, 120.5, 117.3, 115.6, 114.5, 107.7, 107.5, 35.2, 34.6, 34.4, 33.0, 31.8, 31.7, 30.9, 30.2, 26.5, 23.0, 22.9, 22.8, 22.7, 14.0, 13.91, 13.87; IR (Neat) ν_{max} 2956, 2928, 2860, 1639, 1610, 1565, 1462, 1395, 1373, 1261, 1152, 1099, 774 cm^{-1}; **HRMS (ESI)** for $C_{30}H_{43}N_2O$ $(M+H)^+$: calcd. 447.3370, found 447.3375.

4-Benzyl-5,6,9,10-tetrabutyl-4H-8-oxa-4,7-diazacyclohepta[def]fluorene (3rb):



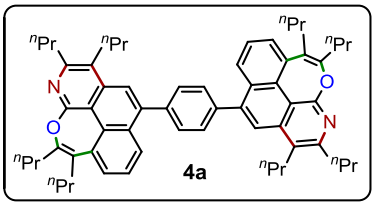
3rb (78 mg, 30%); light yellow colour liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.23 (m, 3H), 7.13 (t, J = 8.0 Hz, 1H), 6.97 (d, J = 6.8 Hz, 2H), 6.93–6.87 (m, 2H), 5.54 (s, 2H), 2.72 (br t, J = 8.2 Hz, 2H), 2.65 (br t, J = 8.4 Hz, 2H), 2.46–2.36 (m, 4H), 1.83–1.34 (m, 16H), 1.03–0.89 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 156.3, 153.9, 144.7, 139.8, 137.5, 132.5, 128.9, 127.4, 126.4, 125.3, 120.8, 117.8, 115.5, 114.5, 108.3, 107.8, 48.1, 35.3, 34.5, 34.3, 32.9, 31.7, 31.0, 30.3, 26.5, 23.0, 22.8, 22.7, 14.1, 14.0, 13.9, 13.8; IR (KBr) ν_{max} 2956, 2863, 1637, 1610, 1564, 1457, 1422, 1375, 1256, 1168, 1099 cm^{-1}; **HRMS (ESI)** for $C_{36}H_{47}N_2O$ $(M+H)^+$: calcd. 523.3683, found 523.3688.

4-(Methoxymethyl)-5,6,9,10-tetrapropyl-4H-8-oxa-4,7-diazacyclohepta[def]fluorene (3sa):



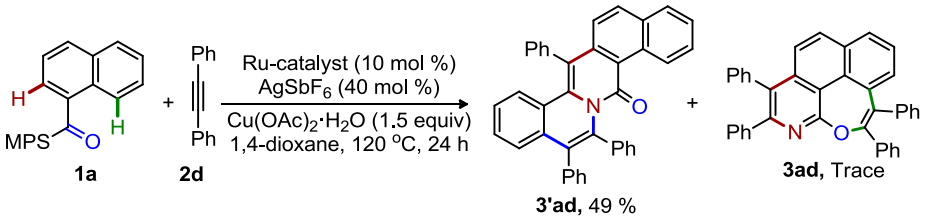
3sa (48 mg, 40%); light yellow colour liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (t, J = 7.75 Hz, 1H), 7.11 (d, J = 8.5 Hz, 1H), 6.89 (d, J = 7.5 Hz, 1H), 5.51 (s, 2H), 3.28 (s, 3H), 2.89–2.83 (m, 2H), 2.77–2.70 (m, 2H), 2.41–2.32 (m, 4H), 1.82–1.68 (m, 4H), 1.62–1.50 (m, 4H), 1.07 (t, J = 7.5 Hz, 3H), 1.31–0.97 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 156.6, 153.8, 144.7, 140.2, 132.7, 126.4, 121.0, 118.3, 115.9, 115.6, 108.6, 108.1, 74.9, 55.9, 37.4, 36.8, 33.4, 28.6, 25.1, 23.9, 22.7, 21.3, 14.3, 14.2, 14.1, 13.9; IR (Neat) ν_{max} 2958, 2928, 2870, 1639, 1611, 1572, 1461, 1423, 1384, 1264, 1220, 1170, 1076, 966 cm^{-1}; **HRMS (ESI)** for $C_{27}H_{37}N_2O_2$ $(M+H)^+$: calcd. 421.2850, found 421.2855.

1,4-Bis(1,2,5,6-tetrapropyl-4-oxa-3-azacyclohepta[def]phenanthren-10-yl)benzene (4a):



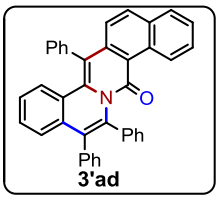
4a (38 mg, 15%); light yellow colour thick liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, J = 5.0 & 1.0 Hz, 2H), 7.91–7.85 (m, 2H), 7.80 (dd, J = 8.0 & 0.5 Hz, 2H), 7.73–7.65 (m, 4H), 7.62 (t, J = 7.25 Hz, 2H), 3.07 (br t, J = 8.0 Hz, 4H), 2.96 (t, J = 7.75 Hz, 4H), 2.73 (t, J = 7.5 Hz, 4H), 2.52 (t, J = 7.25 Hz, 4H), 2.09–2.00 (m, 4H), 1.92–1.84 (m, 4H), 1.81–1.58 (m, 8H), 1.15–1.08 (m, 6H), 1.07–1.02 (m, 12H), 0.72 (t, J = 7.5 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 154.9, 154.7, 142.9, 140.2, 138.3, 137.9, 131.0, 130.1, 128.8, 127.14, 127.10, 126.1, 126.0, 125.1, 124.0, 122.3, 116.8, 36.8, 34.7, 34.6, 30.0, 24.5, 23.2, 22.7, 20.6, 14.6, 14.3, 14.11, 14.08; IR (Neat) ν_{max} 2957, 2926, 1722, 1670, 1607, 1570, 1493, 1458, 1411, 1324, 1260, 1197, 1085 cm^{-1}; **HRMS (ESI)** for $C_{60}H_{69}N_2O_2$ $(M+H)^+$: calcd. 849.5354, found 849.5355.

Double-Annulation of *N*-[1-naphthoyl]methylphenyl sulfoximine (1a) with Diphenyl acetylene (2d) :



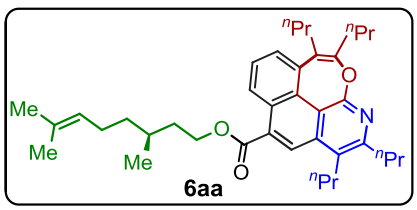
The annulation reactions were carried out in a 10 mL screw capped tube. The tube was charged with N-[1-naphthoyl]methylphenyl sulfoximine (**1a**, 0.3 mmol), diphenyl acetylene (**2d**, 1.2 mmol), $[RuCl_2(p\text{-cymene})]_2$ (18 mg, 10 mol %), and $Cu(OAc)_2{\cdot}H_2O$ (85 mg, 0.45 mmol). Subsequently, $AgSbF_6$ (41 mg, 40 mol %) was introduced in to the tube in a glove box. The solvent 1,4-dioxane (2.0 mL) was added to the mixture and the resulting mixture was stirred at 120 °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 × 10 mL). The solvents were evaporated under reduced pressure and the crude material was purified using column chromatography on neutral aluminia (5–15% *n*-hexane/EtOAc eluent) to give the desired product. The compound **3′ad** (77 mg) in 49% yield was isolated along with trace amount of desired **3ad**.

5,6,15-triphenyl-8H-benzo[h]isoquinolino[2,1-b]isoquinolin-8-one (3'ad):



3′ad (77 mg, 49%); yellow colour solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.40 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 9.0 Hz, 1H), 7.85 (dd, J = 7.0 & 2.0 Hz, 1H), 7.64–7.50 (m, 7H), 7.35–7.27 (m, 3H), 7.25–7.10 (m, 8H), 7.11–7.04 (m, 3H), 6.98–6.90 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7, 139.3, 138.3, 137.3, 136.8, 136.3, 134.8, 133.1, 133.0, 132.3, 131.8, 131.6, 130.8, 129.9, 128.8, 128.6, 128.5, 128.1, 127.9, 127.3, 127.0, 126.8, 126.5, 126.3, 126.2, 125.7, 123.5, 119.1, 116.1.

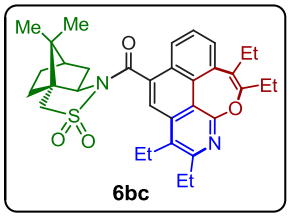
(S)-3,7-Dimethyloct-6-en-1-yl 1,2,5,6-tetrapropyl-4-oxa-3-azacyclohepta[def] phenanthrene-10-carboxylate (6aa):



6aa (30 mg, 18%); light yellow colour liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 7.6 Hz, 1H), 8.38 (s, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.68 (t, J = 7.8 Hz, 1H), 5.14–5.04 (m, 1H), 3.04 (q, J = 4.6 Hz, 2H), 2.93 (t, J = 7.8 Hz, 2H), 2.68 (t, J =

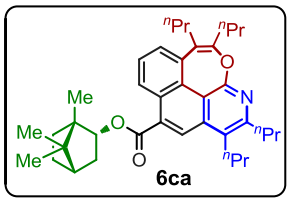
7.4 Hz, 2H), 2.48 (t, J = 7.6 Hz, 2H), 2.34–2.28 (m, 1H), 2.17–2.07 (m, 1H), 2.05–1.93 (m, 2H), 1.90–1.58 (m, 10H), 1.27–1.16 (m, 2H), 1.12 (t, J = 7.2 Hz, 3H), 1.07–0.95 (m, 13H), 0.93–0.91 (m, 3H), 0.62 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 158.5, 154.8, 154.7, 137.6, 137.0, 132.0, 128.8, 128.7, 127.3, 126.7, 126.6, 124.8, 124.2, 123.9, 118.2, 75.6, 47.4, 40.9, 36.6, 34.5, 34.2, 31.5, 30.0, 26.7, 24.6, 23.4, 23.0, 22.4, 22.0, 20.9, 20.5, 16.3, 14.5, 14.2, 14.0, 13.8; IR (Neat) ν_{max} 3363, 2955, 2928, 2869, 1714, 1565, 1456, 1392, 1254, 1131, 1087, 1018, 958 cm^{-1}; **HRMS (ESI)** for $C_{38}H_{52}NO_3$ $(M+H)^+$: calcd. 570.3942, found 570.3942; $[\alpha]_D^{25}$ = –26.7° (c = 0.03, $CHCl_3$).

((3aR,6S)-8,8-Dimethyl-2,2-dioxidohexahydro-1H-3a,6-methanobenzo[c]isothiazol-1-yl)(1,2,5,6-tetraethyl-4-oxa-3-azacyclohepta[def]phenanthren-10-yl)methanone (6bc):



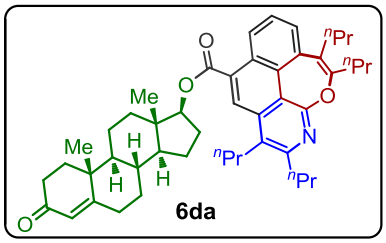
6bc (69 mg, 40%); light yellow colour liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 7.0 Hz, 1H), 7.63 (t, J = 7.75 Hz, 1H), 4.21 (br s, 1H), 3.54–3.40 (m, 2H), 3.11–2.94 (m, 4H), 2.76–2.68 (m, 2H), 2.59–2.43 (m, 2H), 2.25 (br s, 1H), 2.01–1.93 (m, 4H), 1.45 (t, J = 7.5 Hz, 3H), 1.41–1.29 (m, 11H), 1.01 (s, 3H), 0.84 (t, J = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 158.5, 155.93, 155.91, 137.8, 136.4, 134.1, 129.3, 128.5, 128.2, 128.0, 127.4, 126.7, 124.4, 123.8, 118.2, 65.5, 53.3, 48.5, 47.9, 45.0, 38.4, 33.1, 27.8, 26.4, 26.0, 25.6, 21.01, 21.00, 19.8, 15.1, 14.4, 14.1, 12.4; IR (Neat) ν_{max} 2963, 2875, 1677, 1565, 1455, 1375, 1281, 1203, 1134, 1116, 998, 907 cm^{-1}; **HRMS (ESI)** for $C_{34}H_{41}N_2O_4S$ $(M+H)^+$: calcd. 573.2782, found 573.2784; $[\alpha]_D^{25}$ = –149.6° (c = 0.173, $CHCl_3$).

(1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 1,2,5,6-tetrapropyl-4-oxa-3-azacyclohepta[def]phenanthrene-10-carboxylate (6ca):



6ca (56 mg, 32%) as yellow colour thick liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, J = 8.0 Hz, 1H), 8.50 (s, 1H), 7.78 (d, J = 7.5 Hz, 1H), 7.68 (t, J = 7.75 Hz, 1H), 5.29–5.24 (m, 1H), 3.05 (t, J = 8.25 Hz, 2H), 2.94 (t, J = 7.75 Hz, 2H), 2.68 (t, J = 7.5 Hz, 2H), 2.65–2.55 (m, 1H), 2.49 (t, J = 7.75 Hz, 2H), 2.20–2.11 (m, 1H), 2.06–1.95 (m, 2H), 1.90–1.78 (m, 4H), 1.77–1.69 (m, 2H), 1.51–1.43 (m, 1H), 1.40–1.30 (m, 2H), 1.28–1.20 (m, 2H), 1.13 (t, J = 7.25 Hz, 3H), 1.06–0.99 (m, 12H), 0.96 (s, 3H), 0.62 (t, J = 7.25 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 158.5, 154.8, 154.7, 137.6, 136.9, 131.5, 128.8, 128.7, 127.3, 126.8, 126.6, 125.7, 124.3, 123.9, 118.4, 81.3, 49.1, 47.9, 45.0, 37.1, 36.6, 34.5, 34.3, 30.2, 28.1, 27.5, 24.6, 23.0, 22.4, 20.5, 19.7, 18.9, 14.5, 14.2, 14.0, 13.8, 13.7; IR Neat) ν_{max} 2956, 2930, 2870, 1715, 1565, 1454, 1256, 1131, 1087, 1046; **HRMS (ESI)** for $C_{38}H_{50}NO_3$ $(M+H)^+$: calcd. 568.3785, found 568.3788; $[\alpha]_D^{25}$ = –10.0° (c = 0.04, $CHCl_3$).

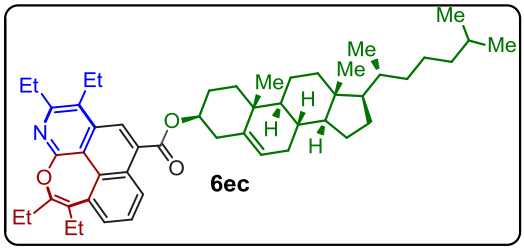
(8R,9S,10R,13S,14S,17S)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 1,2,5,6-tetrapropyl-4-oxa-3-azacyclohepta[def]phenanthrene-10-carboxylate (6da):



6da

6da (47 mg, 33%); light yellow colour solid. mp = 179–180 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (d, J = 8.5 Hz, 1H), 8.47 (s, 1H), 7.77 (d, J = 7.5 Hz, 1H), 7.68 (t, J = 8.0 Hz, 1H), 5.75 (s, 1H), 4.97 (d, J = 8.25 Hz, 1H), 3.04 (br t, J = 8.0 Hz, 2H), 2.93 (t, J = 7.75 Hz, 2H), 2.67 (t, J = 7.5 Hz, 2H), 2.51–2.28 (m, 7H), 2.05–1.65 (m, 16H), 1.54–1.31 (m, 4H), 1.24–1.18 (m, 4H), 1.12 (t, J = 7.25 Hz, 3H), 1.06–0.99 (m, 10H), 0.61 (t, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.3, 170.7, 167.4, 158.5, 154.9, 154.8, 137.6, 136.9, 131.3, 128.80, 128.76, 127.4, 126.7, 126.6, 125.7, 124.3, 124.0, 123.9, 118.4, 83.8, 53.7, 50.3, 42.9, 38.6, 37.0, 36.6, 35.7, 35.5, 34.5, 34.3, 33.9, 32.7, 31.5, 30.1, 27.8, 24.6, 23.7, 23.0, 22.4, 20.6, 20.5, 17.4, 14.5, 14.2, 14.0, 13.8, 12.4; IR (Neat) ν_{max} 2959, 2935, 2871, 1716, 1670, 1612, 1456, 1411, 1377, 1263, 1190, 1131, 1087, 908, 868 cm^{-1}; **HRMS (ESI)** for $C_{47}H_{60}NO_4$ $(M+H)^+$: calcd 702.4517, found 702.4521; $[\alpha]_D^{25}$ = +90.8° (c = 0.179, $CHCl_3$).

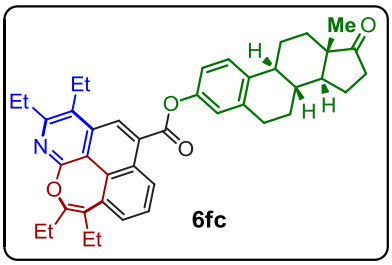
(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 1,2,5,6-tetraethyl-4-oxa-3-azacyclohepta[def]phenanthrene-10-carboxylate (6ec):



6ec

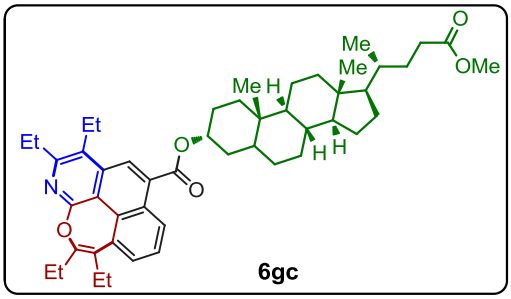
6ec (45 mg, 30%); light yellow colour liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 8.0 Hz, 1H), 8.35 (s, 1H), 7.78 (br d, J = 8.4 Hz, 1H), 7.68 (br t, J = 8.0 Hz, 1H), 5.50 (s, 1H), 5.09–4.99 (m, 1H), 3.12 (br q, J = 6.8 Hz, 2H), 3.00 (br q, J = 6.8 Hz, 2H), 2.73 (br q, J = 6.8 Hz, 2H), 2.62–2.47 (m, 4H), 2.18–2.11 (m, 1H), 2.07–1.94 (m, 3H), 1.88–1.81 (m, 2H), 1.69–1.25 (m, 23H), 1.18–1.00 (m, 10H), 0.93 (br d, J = 6.4 Hz, 3H), 0.90–0.82 (m, 6H), 0.77 (br t, J = 6.8 Hz, 2H), 0.70 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 158.6, 155.9, 155.7, 139.4, 137.5, 136.8, 132.5, 128.8, 128.6, 127.8, 127.2, 126.6, 124.5, 124.4, 124.2, 123.1, 118.3, 75.6, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.2, 37.0, 36.7, 36.1, 35.8, 31.9, 31.8, 28.2, 28.0, 27.9, 27.8, 25.9, 25.5, 24.3, 23.8, 22.8, 22.5, 21.0, 20.9, 19.4, 18.7, 15.5, 14.3, 14.2, 12.4, 11.8; IR (Neat) ν_{max} 2934, 2868, 1714, 1609, 1565, 1463, 1409, 1378, 1252, 1191, 1131, 1057, 975 cm^{-1}; **HRMS (ESI)** for $C_{51}H_{70}NO_3$ $(M+H)^+$: calcd. 744.5350, found 744.5351.

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 1,2,5,6-tetraethyl-4-oxa-3-azacyclohepta[def]phenanthrene-10-carboxylate (6fc):



6fc (47 mg, 23%); light yellow colour liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (dd, J = 8.0 & 0.5 Hz, 1H), 8.68 (s, 1H), 7.80 (d, J = 7.0 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.41 (d, J = 8.5 Hz, 1H), 7.12 (dd, J = 8.5 & 2.5 Hz, 1H), 7.07 (d, J = 2.0 Hz, 1H), 3.09 (br t, J = 8.0 Hz, 2H), 3.03–2.97 (m, 2H), 2.95 (br t, J = 7.75 Hz, 2H), 2.69 (t, J = 7.25 Hz, 2H), 2.58–2.46 (m, 4H), 2.38–2.33 (m, 1H), 2.21–1.97 (m, 6H), 1.91–1.83 (m, 2H), 1.79–1.50 (m, 10H), 1.11 (t, J = 7.25 Hz, 3H), 1.08–1.00 (m, 6H), 0.94 (s, 3H), 0.63 (t, J = 7.25 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 158.5, 155.2, 154.9, 148.8, 138.4, 137.9, 137.7, 136.8, 130.2, 128.8, 128.7, 127.6, 127.1, 126.9, 126.7, 124.2, 123.9, 121.8, 118.9, 118.7, 50.4, 48.0, 44.2, 38.1, 36.7, 35.9, 34.5, 34.3, 31.6, 29.9, 29.5, 26.4, 25.8, 24.7, 23.1, 22.4, 21.6, 20.6, 14.5, 14.3, 14.1, 13.9; IR (Neat) ν_{max} 2957, 2927, 2869, 1735, 1607, 1491, 1455, 1407, 1375, 1206, 1177, 1122, 1081, 1051, 1007 cm^{-1}; **HRMS (ESI)** for $C_{46}H_{54}NO_4$ $(M+H)^+$: calcd 684.4047, found 684.4045; $[\alpha]_D^{25}$ = +42.9° (c = 0.11, $CHCl_3$).

(3R,8R,9S,10S,13R,14S,17R)-17-((R)-5-methoxy-5-oxopentan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 1,2,5,6-tetraethyl-4-oxa-3-azacyclohepta[def]phenanthrene-10-carboxylate (6gc):

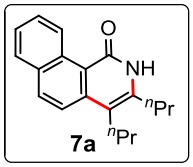


6gc (46 mg, 31%); light yellow colour liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (dd, J = 8.0 & 1.0 Hz, 1H), 8.31 (s, 1H), 7.78 (dd, J = 7.5 & 1.0 Hz, 1H), 7.68 (t, J = 7.75 Hz, 1H), 5.20–5.11 (m, 1H), 3.65 (s, 3H), 3.12 (q, J = 7.5 Hz, 2H), 2.99 (q, J = 7.5 Hz, 2H), 2.72 (q, J = 7.5 Hz, 2H), 2.51 (q, J = 7.5 Hz, 2H), 2.36–2.20 (m, 1H), 2.24–2.18 (m, 1H), 2.01–1.99 (m, 1H), 1.98–1.78 (m, 7H), 1.72–1.54 (m, 4H), 1.49–1.32 (m, 16H), 1.22–1.06 (m, 7H), 0.99 (s, 3H), 0.90 (d, J = 6.5 Hz, 3H), 0.77 (t, J = 7.5 Hz, 3H), 0.65 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.8, 167.8, 158.6, 155.9, 155.7, 137.5, 136.8, 132.8, 128.7, 128.5, 127.8, 127.2, 126.6, 124.4, 124.18, 124.16, 118.2, 76.2, 56.4, 55.9, 51.5, 42.7, 42.1, 40.4, 40.1, 35.8, 35.3, 35.1, 34.7, 32.3, 30.99, 30.94, 28.1, 27.8, 27.0, 26.9, 26.8, 26.3, 25.9, 25.5, 24.1, 23.4, 20.9, 20.8, 18.2, 15.6, 14.3, 14.2; IR (Neat) ν_{max} 2926, 2859, 1713, 1563, 1448, 1257, 1190, 1131, 1059, 976, 806 cm^{-1}; **HRMS (ESI)** for $C_{49}H_{66}NO_5$ $(M+H)^+$: calcd. 748.4936, found 748.4935; $[\alpha]_D^{25}$ = +20.4° (c = 0.05, $CHCl_3$).

A Stepwise Unsymmtrical Double-annulation of *N*-[1-naphthoyl]-*S*-methyl-*S*-phenylsulfoximine with different Alkynes for the Synthesis of 6,7-Fused Oxepino-Isoquinoline (GP-3A):

Step I: First Annulation of *N*-[1-naphthoyl]-*S*-methyl-*S*-phenylsulfoximine with 4-Octyne for the Synthesis of 3,4-Dipropylbenzo[h]isoquinolin-1(2H)-one (7a):

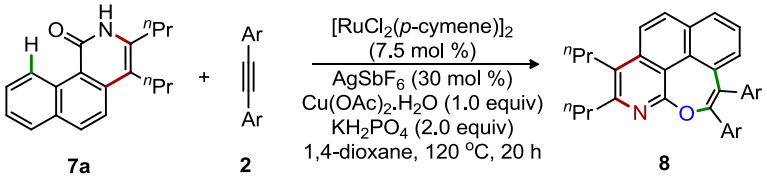
The annulation reactions were carried out in a 25 mL screw capped tube. The tube was charged with *N*-[1-naphthoyl]-*S*-methyl-*S*-phenylsulfoximine (**1a**, 0.5 mmol), 4-octyne (**2a**, 1.0 mmol), $[RuCl_2(p\text{-cymene})]_2$ (15 mg, 5 mol%), and acetic acid (8.0 equiv). Subsequently, $AgSbF_6$ (34 mg, 20 mol %) was introduced in to the tube in a glove box. The solvent DCE (2.5 mL) was added to the mixture and the resulting mixture was stirred at 120 °C for 20 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 (15–20% *n*-hexane/EtOAc eluent) to give **7a** (105 mg, 75%).



7a

7a (105 mg, 75%); colorless crystalline solid. mp = 243–244 °C; ^{1}H NMR (400 MHz, DMSO–D_6) δ 11.51 (br s, 1H), 10.21 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 9.2 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 9.2 Hz, 1H), 7.71–7.64 (m, 1H), 7.62–7.56 (m, 1H), 2.73 (br t, J = 8.0 Hz, 2H), 2.64 (br t, J = 7.6 Hz, 2H), 1.71–1.59 (m, 2H), 1.59–1.47 (m, 2H), 1.01 (t, J = 7.4 Hz, 3H), 0.96 (d, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, DMSO–D_6; patially soluble) δ 163.0, 141.7, 139.9, 133.7, 132.3, 131.4, 128.4, 128.2, 127.1, 126.2, 122.2, 118.0, 112.3, 32.2, 28.7, 24.1, 23.2, 14.5, 14.2; IR (KBr) ν_{max} 3117, 3015, 2868, 1630, 1596, 1495, 1427, 1346, 1293, 1147, 1036, 913, 894, 821 cm^{-1}; **HRMS (ESI)** for $C_{19}H_{22}NO$ $(M+H)^+$: calcd. 280.1696, found. 280.1702.

Step II: Second Annulation of Isoquinolone 7a with Alkynes (GP-3B):

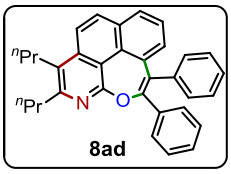


7a **2** **8**

The annulation reactions were carried out in a 25 mL screw capped tube. The tube was charged with 3,4-dipropylbenzo[h]isoquinolin-1(2H)-one (**7a**, 0.3 mmol), alkyne (**2**, 0.6 mmol), $[RuCl_2(p\text{-cymene})]_2$ (13.8 mg, 7.5 mol %), KH_2PO_4 (82 mg, 0.6 mmol), $Cu(OAc)_2.H_2O$ (57.3 mg, 0.3 mmol). 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) was added to the mixture and the resulting mixture was stirred at 120 °C for 20 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite and then washed with

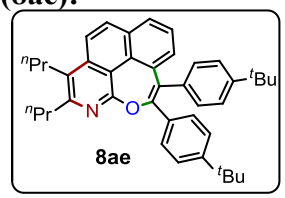
dichloromethane (3 × 10 mL). The solvents were evaporated under reduced pressure and the crude material was purified using column chromatography on neutral aluminia (5–10% *n*-hexane/EtOAc eluent) to give the desired product.

5,6-Diphenyl-1,2-dipropyl-4-oxa-3-azacyclohepta[def]phenanthrene (8ad):



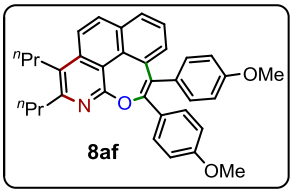
8ad (53 mg, 39%); light yellow thik liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.8 Hz, 1H), 7.93 (d, J = 9.2 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.66–7.58 (m, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.36 (d, J = 7.6 Hz, 1H), 7.32–7.20 (m, 6H), 7.08 (dd, J = 7.6, 2.0 Hz, 2H), 3.07 (br t, J = 8.0 Hz, 2H), 2.89 (t, J = 7.6 Hz, 2H), 1.81–1.65 (m, 4H), 1.15 (t, J = 7.6 Hz, 3H), 0.91 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 155.1, 149.6, 140.8, 138.9, 138.3, 135.5, 131.8, 131.64, 131.61, 131.5, 129.9, 129.6, 128.4, 128.0, 127.9, 127.5, 127.4, 127.3, 126.5, 125.8, 121.3, 117.2, 36.5, 30.0, 24.3, 22.7, 14.5, 14.0; IR (KBr) ν_{max} 3055, 2959, 2870, 1615, 1573, 1491, 1444, 1400, 1378, 1299, 1265, 1204, 1167, 1134, 1087, 967 cm^{-1}; **HRMS (ESI)** for $C_{33}H_{30}NO$ $(M+H)^+$: calcd. 456.2322, found 456.2332.

5,6-Bis(4-(*tert*-butyl)phenyl)-1,2-dipropyl-4-oxa-3-azacyclohepta[def]phenanthrene (8ae):



8ae (82 mg, 52%); light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 9.2 Hz, 1H), 7.89 (d, J = 9.2 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.57–7.46 (m, 3H), 7.38 (d, J = 7.6 Hz, 1H), 7.26 (d, J = 8.4 Hz, 2H), 7.20 (t, J = 8.8 Hz, 2H), 6.99 (t, J = 8.0 Hz, 2H), 3.03 (br t, J = 8.0 Hz, 2H), 2.87 (t, J = 7.6 Hz, 2H), 1.78–1.65 (m, 4H), 1.33 (s, 9H), 1.29 (s, 9H), 1.12 (t, J = 7.6 Hz, 3H), 0.85 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 154.9, 150.7, 150.3, 149.1, 138.9, 138.8, 137.8, 132.5, 131.8, 131.7, 131.6, 131.0, 129.6, 128.9, 128.0, 127.2, 126.3, 125.7, 125.3, 124.2, 121.2, 117.3, 36.4, 34.5, 31.3, 31.2, 30.0, 24.3, 22.5, 14.5, 13.9; IR (KBr) ν_{max} 2962, 2870, 1612, 1574, 1507, 1461, 1400, 1303, 1267, 1206, 1167, 1110 cm^{-1}; **HRMS (ESI)** for $C_{41}H_{46}NO$ $(M+H)^+$: calcd. 568.3574, found 568.3576.

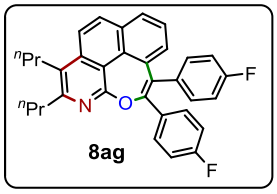
5,6-Bis(4-methoxyphenyl)-1,2-dipropyl-4-oxa-3-azacyclohepta[def]phenanthrene (8af):



8af (54 mg, 35%); light yellow solid. mp = 160–161 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 9.2 Hz, 1H), 7.89 (d, J = 9.2 Hz, 1H), 7.81 (dd, J = 7.5 & 1.0 Hz, 1H), 7.54 (dd, J = 7.0 & 2.0 Hz, 2H), 7.49 (t, J = 7.75 Hz, 1H), 7.35 (dd, J = 7.5 & 1.0 Hz, 1H), 6.95 (d, J = 8.5 Hz, 2H), 6.81–6.72 (m, 4H), 3.80 (s, 6H), 3.07–3.00 (m, 2H), 2.89–2.82 (m, 2H), 1.75–1.65 (m, 4H), 1.11 (t, J = 7.5 Hz, 3H), 0.89 (t, J = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 158.8, 157.5, 155.0, 148.9, 138.93, 138.88, 133.4, 132.7, 131.8, 131.6, 131.45, 131.41, 128.3, 127.9, 127.7, 127.2, 126.3,

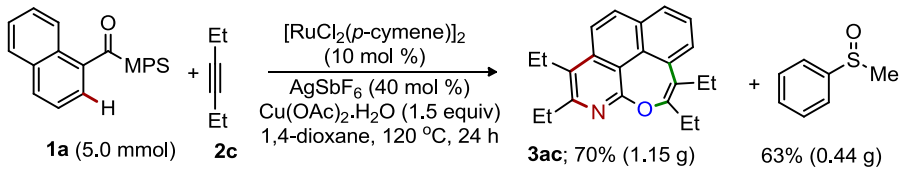
125.7, 121.2, 117.3, 114.0, 112.8, 55.15, 55.14, 36.6, 30.0, 24.3, 22.7, 14.5, 14.1; IR (Neat) ν_{max} 2956, 2927, 1600, 1504, 1457, 1440, 1299, 1243, 1201, 1165, 1133, 1025, 828 cm^{-1}; **HRMS (ESI)** for $C_{35}H_{34}NO_3$ $(M+H)^+$: calcd. 516.2533, found 516.2533.

5,6-Bis(4-fluorophenyl)-1,2-dipropyl-4-oxa-3-azacyclohepta[def]phenanthrene (8ag):



8ag (85 mg, 55%); light yellow solid. mp = 198–199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 9.2 Hz, 1H), 7.90 (d, J = 9.2 Hz, 1H), 7.84 (dd, J = 7.8 & 1.0 Hz, 1H), 7.59–7.52 (m, 2H), 7.50 (d, J = 7.6 Hz, 1H), 7.30 (dd, J = 7.6 & 1.2 Hz, 1H), 7.04–6.88 (m, 6H), 3.04 (t, J = 8.2 Hz, 2H), 2.86 (t, J = 7.8 Hz, 2H), 1.77–1.62 (m, 4H), 1.12 (t, J = 7.4 Hz, 3H), 0.89 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, J = 249 Hz), 162.2 (d, J = 247 Hz), 157.2, 155.2, 148.7, 139.0, 138.0, 136.6, 133.1 (d, J = 8.0 Hz), 131.9 (d, J = 8.0 Hz), 131.7 (d, J = 10.0 Hz), 131.1 (d, J = 16.0 Hz), 128.4, 127.9, 127.7, 126.7, 125.8, 121.4, 117.1, 115.7, 115.5, 114.6, 114.4, 36.5, 30.0, 24.3, 22.6, 14.5, 14.0; ^{19}F NMR (470 MHz, $CDCl_3$) δ –112.41, –113.99; IR (Neat) ν_{max} 2961, 2927, 2870, 1591, 1501, 1460, 1395, 1293, 1215, 1198, 1131, 1081, 1011, 890 cm^{-1}; **HRMS (ESI)** for $C_{33}H_{28}F_2NO$ $(M+H)^+$: calcd. 492.2133, found 492.2133.

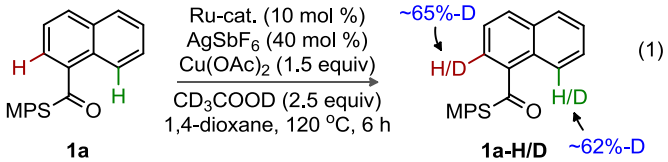
General Procedure for the Gram Scale Synthesis of 3ac:



The gram scale reaction was carried out in a 25 mL screw capped tube. The tube was independently charged with *N*-[naphthoyl]-*S*-methyl-*S*-phenylsulfoximine (**1a**, 5.0 mmol), 3-hexyne (**2c**, 20.0 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.306 g, 10 mol %), and $Cu(OAc)_2 \cdot H_2O$ (1.43 g, 7.5 mmol). Subsequently, $AgSbF_6$ (0.686 g, 40 mol %) was introduced in to the tube in a glove box. The solvent 1,4-dioxane (20.0 mL) was added to the mixture and the resulting mixture was stirred at 120 °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 **3ac** (1.15 g) in 70% yield was isolated along with the isolation of phenyl methyl sulfoxide 63% yield.

Control Experiments:

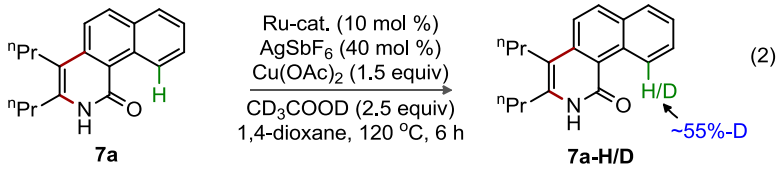
Deuterium-Labelling Experiment (eq 1):



(1)

A mixture of *N*-[1-naphthoyl]-*S*-methyl-*S*-phenylsulfoximine (**1a**, 0.3 mmol), $[RuCl_2(p\text{-cymene})]_2$ (18 mg, 10 mol%), and $Cu(OAc)_2$ (48 mg, 0.45 mmol) was taken in a 25 mL screw capped tube. Subsequently, $AgSbF_6$ (41 mg, 40 mol %) was introduced in to the tube in a glove box. The solvent 1,4-dioxane (2.0 mL) and CD_3COOD (43 μL, 2.5 equiv) were added to the mixture and the resulting mixture was stirred at 120 °C for 6 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite and then washed with dichloromethane (3 × 5.0 mL). The solvents were evaporated under reduced pressure to give the desired product **1a-H/D** with deuterium incorporation at the *o*rtho (65%) and *peri* (62%) of **1a**.

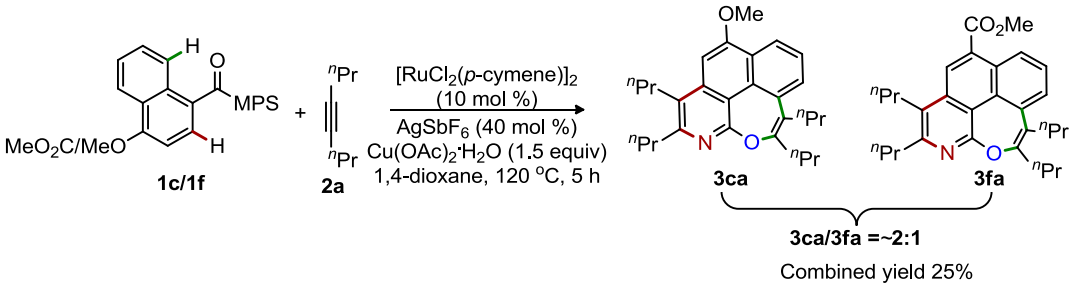
Deuterium-Labelling Experiment (eq 2):



(2)

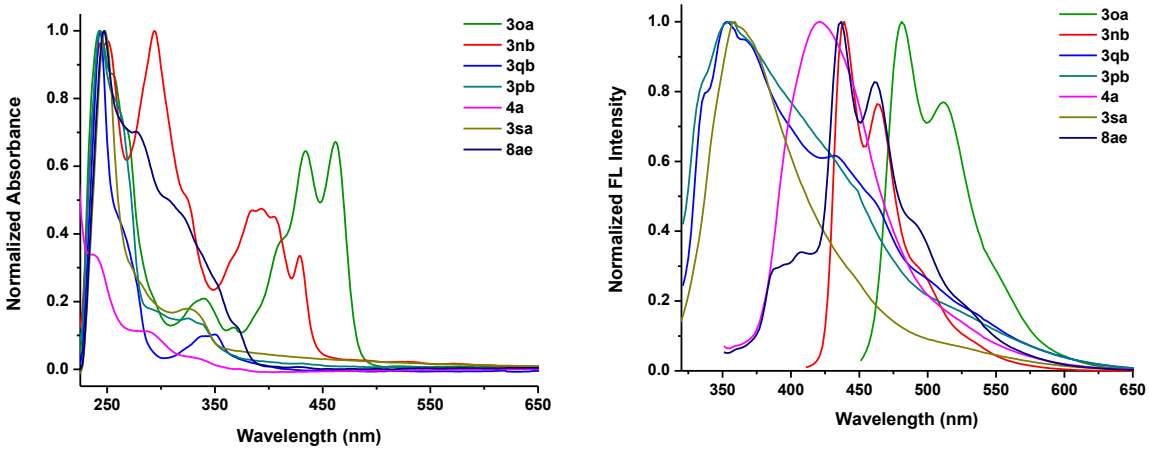
A mixture of 3,4-dipropylbenzo[h]isoquinolin-1(2H)-one (**7a**, 0.3 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (18 mg, 10 mol%) was taken in a 25 mL screw capped tube. Subsequently, $AgSbF_6$ (41 mg, 40 mol%) was introduced in to the tube in a glovebox. The solvent 1,4-dioxane (2.0 mL) and CD_3COOD (43 μL, 2.5 equiv) were added to the mixture and the resulting mixture was stirred at 120 °C for 6 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite and then washed with dichloromethane (3 × 5.0 mL). The solvents were evaporated under reduced pressure to give the desired product **7a-H/D** with 55% deuterium incorporation at the *peri-postion* of **7a**.

Competition Experiment between 1c and 1f with 2a (eq 3):



The competition experiment was carried out in a 25 mL screw capped tube. The tube was charged with **1c** (0.3 mmol), **1f** (0.3 mmol), 4-octyne (**2a**, 1.2 mmol), $[RuCl_2(p\text{-cymene})]_2$ (18 mg, 10 mol %), and $Cu(OAc)_2$ (85 mg, 0.45 mmol). Subsequently, $AgSbF_6$ (41 mg, 40 mol %) was introduced in to the tube in a glove box. The solvent 1,4-dioxane (2.0 mL) was added to the mixture and the resulting mixture was stirred at 120 ^oC for 5 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite and then washed with dichloromethane (3 × 5.0 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 **3ca** and **3fa** (65 mg) as a yellow colour thick liquid. Based on the ^1H NMR spectrum of crude sample, the inseparable mixture of **3ca** and **3fa** was formed in ~2:1 ratio, respectively.

Optical and Photophysical Properties



A **B**

(A) Normalized Absorption (A) and PL spectra (B) of derivatives of **3nb**, **3oa**, **3pb**, **3qb**, **3sa**, **4a**, and **8ae** dispersed in dichloromethane medium (1 X 10^{-5}M).

X-ray crystallography: Single crystal X-ray data for the compound **3ha**, **3ja**, and **8ae** 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 software was used for the intensity data acquisition and the SAINTPLUS Software was used for the data extraction. In each case, absorption correction was performed with the help of SADABS program, an empirical absorption correction using equivalent reflections was performed with the program. The structure was solved using SHELXS-97, and full-matrix least-squares refinement against F^2 was carried out using SHELXL-97. 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.[4]

X-ray crystal structure and data for 3ha, 3ja and 8ae [4]

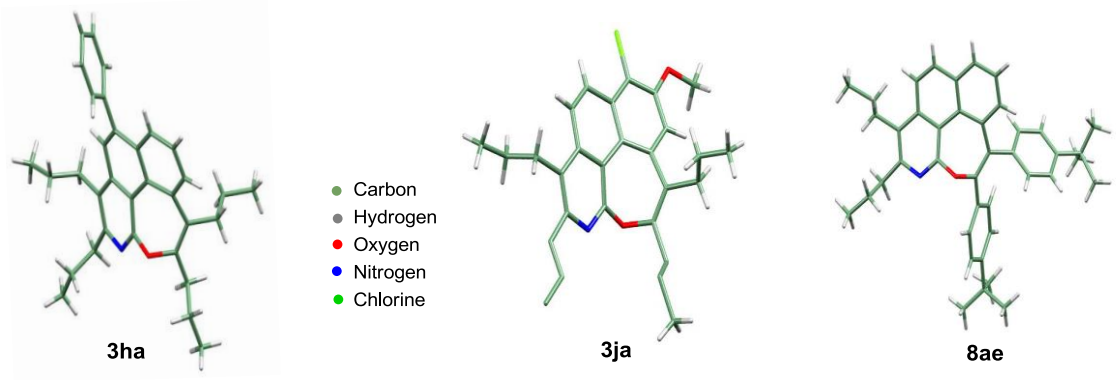


Figure 1. Molecular structures of compounds **3ha**, **3ja**, and **8ae**; thermal ellipsoids are set at 30% probability.

Table S2. Crystal data for 3ha, 3ja, and 8ae

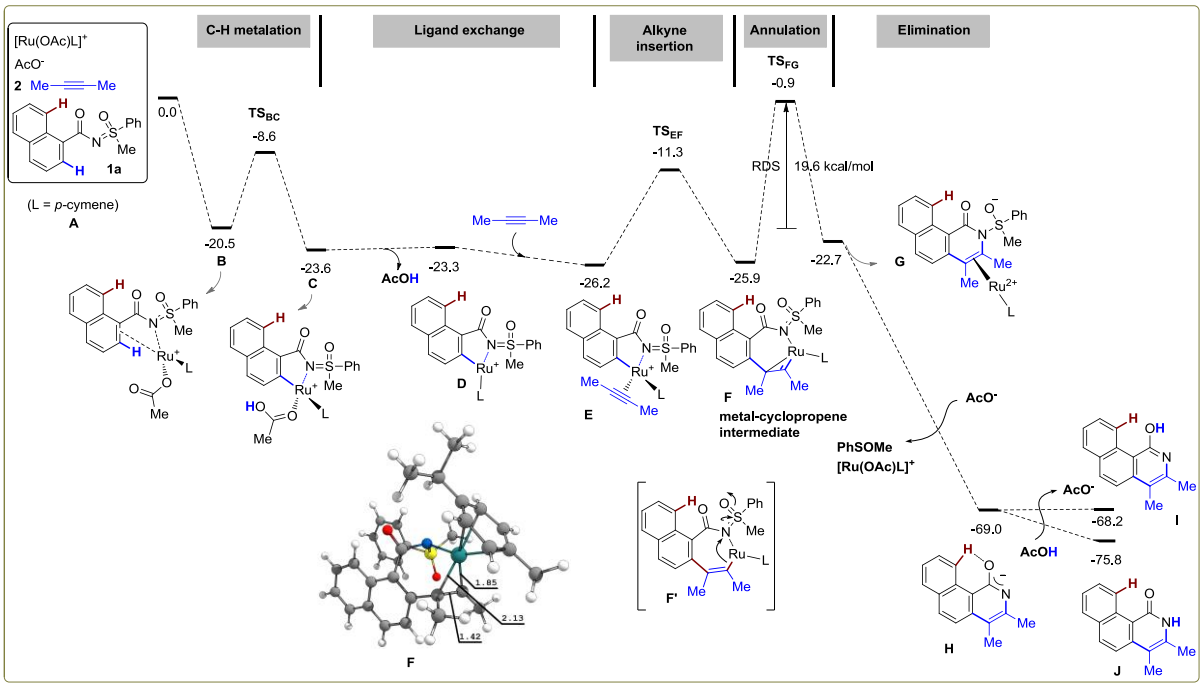
Identification code	**3ha**	**3ja**	**8ae**
Formula	C_{33} H_{37} N O	C_{28} H_{23} Cl N O_2	$C_{41}H_{45}NO$
F_w	463.63	446.72	567.78
T (K)	197 K	296 K	223K
λ (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic
Space group	*P -1*	*P 1 21/n 1*	*P 1 21/n 1*

a(Å)	10.7051(8)	14.5781(4)	15.001(3)
b (Å)	10.9218(9)	9.3138(3)	10.5247(15)
c (Å)	12.9779(4)	18.8307(6)	22.239(4)
α (^{o})	81.166(6)	90	90
β (^{o})	67.584(6)	94.961(3)	94.419(8)
γ(^{o})	72.381(7)	90	90
V (Å^3)	1335.66(17)	2547.21(14)	3500.6(9)
Z	2	4	4
ρ_{calcd} (Mg m^{-3})	1.153	1.165	1.077
μ [mm^{-1}]	0.068	0.173	0.063
total reflns	16862	22700	54795
unique reflns	4712	5299	6175
observed reflns	2928	3016	3200
$R_1[I > 2\sigma(I)]$	0.0841	0.0863	0.0893
wR_2 [all]	0.2861	0.3098	0.2635
GOF	1.128	1.112	1.027
Diffractometer	SMART APEX CCD	SMART APEX CCD	SMART APEX CCD
CCDC Number	1979334	1979335	1979336

Density Functional Theory (DFT) Calculations:

The proposed mechanistic hypothesis was checked computationally using the Gaussian 09 software package.[5] Following a recent report,[6] optimizations were carried out using the M06 functional,[7] the 6-31G(d,p) basis set[8] for all main group elements, and the LANL2DZ+f (ECP) basis set[9] for Ru. Single point calculations were conducted and the M06/6-311++G(d,p)-SDD+f(ECP)[10] level of theory. Solvation energies were obtained at the single point level using the SMD approach[11] for 1,4-dioxane. 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** and 2 equiv of 2-butyne was used as a reference for the free

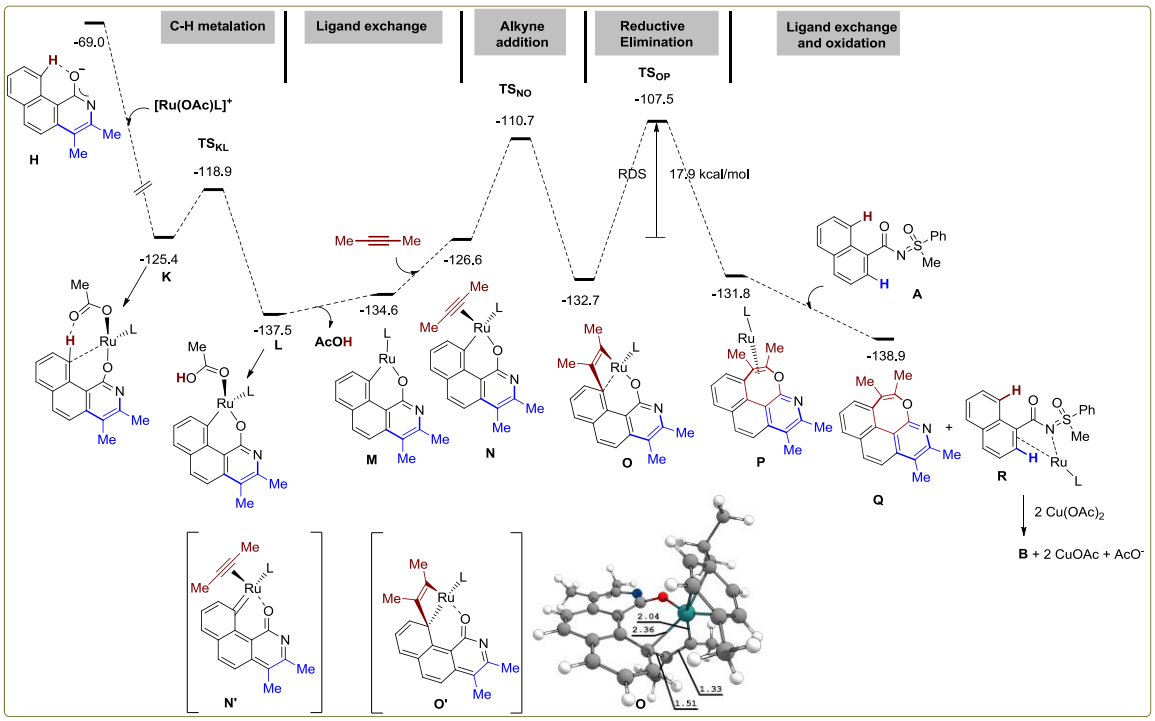
energies, together with $[RuOAcL]^+$ (L = *p*-cymene) and an additional AcO^- to ensure the two deprotonation of **A** with the same Ru complex (Scheme S1). The complexation of the putative active species $[RuOAc(p\text{-cymene})]^+$ to **A** leads to chelate **B** with a release of 20.5 kcal/mol. C-H metalation then occurs through $\mathbf{TS_{BC}}$ lying 11.9 kcal/mol above **B**. A stepwise ligand exchange between acetic acid and 2-butyne was then computed, leading to the alkyne complex **E**, which is more stable than **C** by 2.6 kcal/mol. Alkyne insertion does not yield the metallalkenyl complex **F'** but its valence isomer **F**, which is a metallacyclopropene as witnessed by the distortion of the 7-membered ring and by the short Ru-C distance of 1.85 Å.[12] The formation of this intermediate is slightly endergonic by 0.3 kcal/mol and requires 14.9 kcal/mol of free energy of activation. The next step can be considered as an intramolecular nucleophilic addition to the N=S bond to give the annulated intermediate **G** (see arrows in **F'**). This pathway is the rate-determining step of the catalytic cycle. The barrier is of 25.0 kcal/mol (19.6 kcal/mol from **B**), which is consistent with the temperature of the reaction (120 °C). The resulting complex **G** is less stable than **F** by 3.2 kcal/mol, yet the dissociation of the metallic fragment to regenerate the active species $[Ru(OAc)L]^+$ promotes a spontaneous elimination of PhSOMe from the free ligand to give **H**, located as low as -69.0 kcal/mol on the energy surface. Obviously, the liberation of the stable PhSOMe molecule, the conjugated nature of the anion and the formation of a quite strong H-bond in **H** are



Scheme S1. Free energy profile (ΔG_{393}, kcal/mol), part 1 (first annulation).

favorable thermodynamic factors that explain the straightforward loss of the sulfur moiety. Protonation of **H** by AcOH might give rise to pyridine **I** or pyridone **J**, the latter being significantly more stable, which is in line which its experimental observation.

The second part of the mechanism involves first the reaction of **H** with $[Ru(OAc)L]^+$ (Scheme S2). This step is exergonic by 56.4 kcal/mol and yields **K** at -125.4 kcal/mol. The values on Scheme S2 might seems very low, but this is due to the fact that they correspond to a second reaction; all intermediates are already 69.0 kcal/mol below the reference system shown in Scheme S1. Intermediate **K** shows a H-bond between the acetate ligand and one arene carbon. The acidity of this proton comes from the coordination of Ru to the *ipso*-carbon, as shown by the relatively short Ru-C distance of 2.36 Å. From this pre-organized complex, the C-H metalation step is then easily achieved through $\mathbf{TS_{KL}}$, using only 6.5 kcal/mol of free energy of activation. Complex **L** lies at -137.5 kcal/mol on the energy surface, and the substitution of acetic acid but the second alkyne equivalent is endergonic by 10.9 kcal/mol. Of particular interest, the formation of the 7-membered ring product does not seem to arise from the reductive elimination of a simple 8-membered metallacycle. Formation of a C-C bond from **N** is achieved via $\mathbf{TS_{NO}}$ at the expense of 15.9 kcal/mol, and provides the ruthena-oxabicyclooctene type complex **O** located at -132.7 kcal/mol.

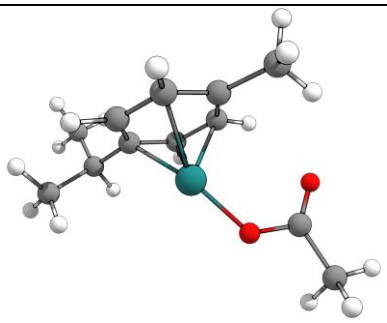


Scheme S2. Free energy profile (ΔG_{393}, kcal/mol), part 2 (second annulation)

The Ru-C^{ipso} distance of 2.35 Å and other geometrical parameters show that **O** is an intermediate structure between the Lewis depiction **O** and **O'**. Its formation can be understood as an intramolecular [2+2] cycloaddition between the alkyne and a Ru=C bond as shown in **N'**, which is a fictive valence isomer of **N**. By doing so, a highly strained phenanthrene-containing 8-membered ring is avoided. The reductive elimination, which is the rate-determining step of this second reaction, demands 25.2 kcal/mol of free energy of activation to give **P** in a slightly endergonic fashion. The transfer of the RuL moiety to the starting compound **A** to give the experimentally observed 7-membered ring product **Q** and chelate **R** is appreciably exergonic by 7.9 kcal/mol. As it is generally accepted,[13] one can then propose that complex **R** transforms into **B** by $Cu(OAc)_2$ mediated oxidation.

The coordinates of all computed species are provided in Table S3 and in a separate file that allow direct visualization: DFT.xyz.

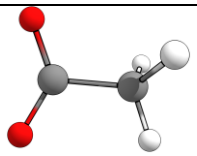
Table S3. Coordinates (x,y,z) and M06 energies (Hartree) of the computed species.



[Ru(OAc)(*p*-cymene)]$^+$

E(RM06) = -712.378891180

Ru	-0.234083	-0.225936	-0.46122
O	-1.888648	-1.137544	-0.438343
C	-2.987895	-0.880759	0.329791
O	-3.012014	0.047014	1.102049
C	-4.086045	-1.858039	0.08254
H	-3.741074	-2.869357	0.321181
H	-4.354627	-1.857571	-0.978614
H	-4.954657	-1.605631	0.691422
C	0.599602	1.730554	-0.988
C	1.720393	0.88377	-0.844478
C	-0.374573	1.887026	0.047662
H	2.38069	0.737411	-1.695036
C	1.876444	0.086239	0.305819
C	-0.205212	1.10238	1.22791

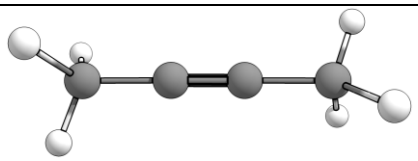


AcO^-

E(RM06) = -228.468688977

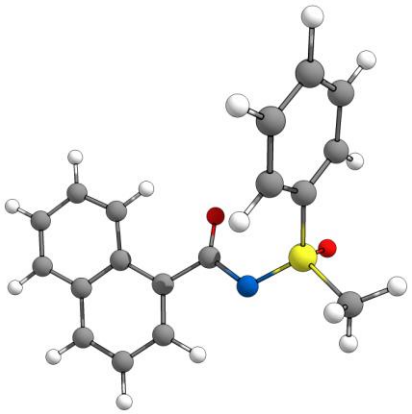
O	-0.682326	1.164656	0.000055
O	-0.809492	-1.099509	-0.000071
C	-0.219223	0.002103	0.000013
C	1.342891	-0.06217	-0.000007
H	1.718645	-1.093568	-0.000616
H	1.736902	0.465827	0.879749
H	1.736983	0.466963	-0.879039

H	-0.995149	1.090848	1.974475
C	0.887847	0.20203	1.331352
H	0.938585	-0.475754	2.182485
H	0.428857	2.227439	-1.941357
C	-1.575668	2.744005	-0.135462
H	-2.449052	2.291448	0.344706
H	-1.399796	3.721522	0.332227
H	-1.78886	2.915019	-1.194663
C	2.987729	-0.916588	0.4631
H	2.592463	-1.731708	1.088796
C	3.478612	-1.507774	-0.850252
H	3.998737	-0.761693	-1.463923
H	4.200067	-2.305002	-0.648593
H	2.66457	-1.941892	-1.443855
C	4.129364	-0.234975	1.225646
H	4.937399	-0.951279	1.404521
H	4.540013	0.597673	0.640894
H	3.803187	0.156722	2.195594



2

E(RM06) = -155.890606795

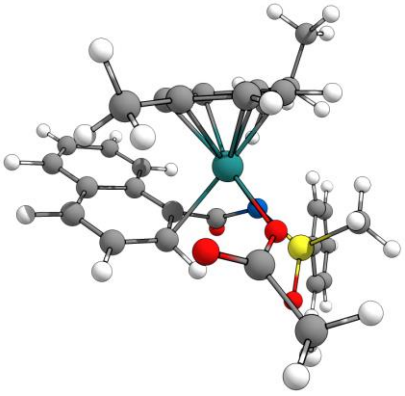
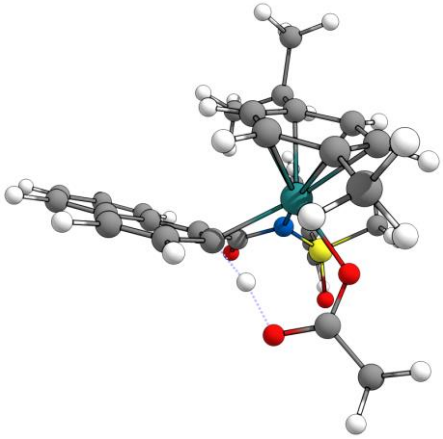


1a

E(RM06) = -1297.84237152

C	-0.603897	0.001574	0.00034
C	0.604098	0.003395	-0.000567
C	-2.057704	-0.001208	0.000055
H	-2.460369	1.003106	0.175561
H	-2.456809	-0.352014	-0.958701
H	-2.458337	-0.656707	0.781855
C	2.057667	-0.001386	-0.000078
H	2.454468	-1.022854	0.030612
H	2.461761	0.481468	-0.89724
H	2.458296	0.532757	0.869403

C	-4.677013	2.234258	-0.285458
C	-4.976551	0.972134	0.153048
C	-3.977098	-0.027508	0.230811
C	-2.634624	0.276267	-0.158202
C	-2.361581	1.595436	-0.606174
C	-3.354838	2.541232	-0.664375
C	-4.303811	-1.323706	0.693305
C	-3.345012	-2.2963	0.789452
C	-2.019265	-2.00469	0.425794
C	-1.64925	-0.761437	-0.048111
C	-0.225141	-0.553531	-0.450189
N	0.636948	-1.508549	0.081865
O	0.151964	0.365774	-1.169617
S	2.131425	-1.351082	-0.388399
O	2.561063	-1.640353	-1.759804

				C	2.948597	-2.486852	0.712067
				C	2.822002	0.226644	0.107232
				C	3.777562	0.807869	-0.714461
				C	4.353882	2.009598	-0.316748
				C	3.969967	2.605616	0.879616
				C	3.003759	2.010883	1.687777
				C	2.419615	0.811293	1.303198
				H	-5.451051	2.995888	-0.342763
				H	-5.9905	0.711113	0.453297
				H	-1.351983	1.837482	-0.915315
				H	-3.116178	3.54383	-1.01233
				H	-5.336864	-1.528594	0.97173
				H	-3.599634	-3.291826	1.144232
				H	-1.255916	-2.772818	0.505206
				H	4.01801	-2.448225	0.49121
				H	2.742503	-2.205163	1.746503
				H	2.542493	-3.477914	0.496935
				H	4.04134	0.324827	-1.651783
				H	5.099935	2.484597	-0.948377
				H	4.421794	3.546549	1.183709
				H	2.698061	2.48807	2.615116
				H	1.645136	0.342728	1.907834
 **B** E(RM06) = -2010.31197599				 **TS_{BC}** Frequency -1431.1698 E(RM06) = -2010.29240859			
C	3.283404	-4.440523	-0.781815	O	-1.087475	-1.259616	-2.935452
C	3.741925	-3.298661	-1.399042	H	-1.364794	-0.441959	-1.875126
C	2.895568	-2.183301	-1.5692	C	-1.678571	0.493034	-1.077476
C	1.557119	-2.254461	-1.089798	C	-3.046574	0.850595	-1.227195
C	1.107573	-3.43817	-0.466158	C	-3.4365	2.159683	-1.15515
C	1.958077	-4.511039	-0.315613	C	-2.487698	3.195152	-0.950626
C	3.361959	-0.989176	-2.20174	C	-2.898452	4.543422	-0.850594
C	2.555136	0.098383	-2.353952	C	-1.975655	5.543334	-0.673478
C	1.212632	0.063716	-1.870787	C	-0.600878	5.234673	-0.593229

C	0.724557	-1.095726	-1.23908	H	-2.300288	6.578013	-0.600124
C	-0.740875	-1.119436	-0.938218	H	-3.960128	4.772502	-0.920403
N	-1.064171	0.044646	-0.198146	C	-1.093669	2.879529	-0.869901
O	-1.511844	-1.989199	-1.262739	C	-0.164597	3.937272	-0.691438
S	-2.354017	0.871156	-0.710396	C	-0.728199	1.506644	-0.934751
O	-2.298274	1.42222	-2.062444	H	0.895664	3.707828	-0.657276
C	-2.564944	2.15143	0.503678	H	0.121271	6.036266	-0.461466
C	-3.800509	-0.147776	-0.548108	H	-4.483418	2.436116	-1.272362
C	-4.676696	-0.185315	-1.625882	H	-3.776748	0.06829	-1.435485
C	-5.837898	-0.942143	-1.502615	Ru	-1.049499	-1.1657	0.278275
C	-6.098854	-1.633796	-0.325015	C	0.685995	1.054767	-0.91334
C	-5.203465	-1.583834	0.743101	N	0.814072	-0.228836	-0.32758
C	-4.037951	-0.839701	0.637422	O	1.631917	1.671083	-1.363213
H	3.944308	-5.294496	-0.659509	S	2.187492	-0.97907	-0.763161
H	4.7641	-3.241234	-1.768438	O	2.359764	-1.338193	-2.168902
H	0.074969	-3.505996	-0.131734	C	2.208921	-2.45138	0.231967
H	1.600992	-5.422469	0.156492	C	3.59306	-0.061709	-0.175972
H	4.384146	-0.973257	-2.577161	H	3.140312	-2.960462	-0.032338
H	2.906748	1.003373	-2.840978	H	2.208012	-2.179521	1.289704
H	0.507092	0.825258	-2.199589	H	1.335823	-3.045243	-0.056848
H	-3.478897	2.68129	0.221835	C	4.72444	-0.050137	-0.981079
H	-2.66663	1.700268	1.494077	C	3.547588	0.559804	1.069182
H	-1.681673	2.792353	0.418853	C	5.858205	0.603855	-0.508652
H	-4.446474	0.361122	-2.536479	H	4.7054	-0.527523	-1.957393
H	-6.537017	-0.991032	-2.332477	C	5.839783	1.224435	0.736051
H	-7.007681	-2.223046	-0.236836	H	6.755272	0.631711	-1.120658
H	-5.412947	-2.13452	1.655946	C	4.688871	1.206231	1.522485
H	-3.319014	-0.81092	1.454208	H	6.728874	1.735027	1.096381
Ru	0.893635	0.779996	0.407574	H	4.679733	1.70613	2.487203
O	0.167557	2.469913	-0.550337	H	2.630065	0.563498	1.656505
C	0.928518	3.263425	-1.268004	O	-0.528578	-2.571169	-1.215607
O	2.135714	3.137492	-1.400157	C	-3.010686	-1.031436	1.273723
C	0.127828	4.354691	-1.935474	C	-0.886849	-0.625992	2.447608
H	-0.35002	4.988017	-1.180096	C	-1.480156	-2.881018	1.614212
H	-0.67333	3.906498	-2.534077	C	-0.640497	-2.329292	-2.471653
H	0.773931	4.967209	-2.566034	C	-0.151635	-3.392179	-3.405251
C	2.664505	-0.188992	1.266294	H	-0.245974	-4.384874	-2.96071
C	1.545991	-0.689814	1.972784	H	0.90952	-3.192731	-3.595557
C	2.969189	1.201417	1.189594	H	-0.684387	-3.336508	-4.356075
H	1.349597	-1.758943	1.959856	C	-2.110755	-0.146248	1.937589
C	0.615139	0.205938	2.553521	C	-2.7156	-2.398018	1.078279
C	2.029256	2.085839	1.768615	H	-3.906499	-0.619288	0.815925
H	2.148912	3.154072	1.599952	H	-2.340147	0.917093	1.964003
C	0.862678	1.608161	2.424383	C	-3.608541	-3.292047	0.284244
H	0.128861	2.316585	2.805032	C	-0.60057	-2.022626	2.293317
H	3.292596	-0.890254	0.716725	C	0.098854	0.243827	3.183083
C	4.176872	1.688726	0.466926	H	-1.179684	-3.906058	1.402872
H	3.993716	2.669207	0.022057	H	0.352019	-2.406553	2.654597

H	5.025267	1.753103	1.159119	H	-3.019695	-3.971258	-0.34104
H	4.448019	0.996811	-0.33777	H	-4.23529	-3.901386	0.946218
C	-0.618437	-0.267224	3.276645	H	-4.270366	-2.71189	-0.366938
H	-1.423747	0.444938	3.028581	H	1.091919	-0.214602	3.033556
C	-1.06592	-1.670329	2.893809	C	0.15777	1.686882	2.704688
H	-0.344511	-2.426138	3.229201	C	-0.234528	0.173883	4.676138
H	-2.01376	-1.905733	3.390763	H	-0.790607	2.213618	2.869843
H	-1.209933	-1.781472	1.81148	H	0.922314	2.23229	3.268917
C	-0.351545	-0.176645	4.782974	H	0.405764	1.760858	1.639569
H	-1.240703	-0.480876	5.344981	H	0.503078	0.734567	5.259699
H	0.469954	-0.846435	5.066581	H	-1.221224	0.614859	4.866795
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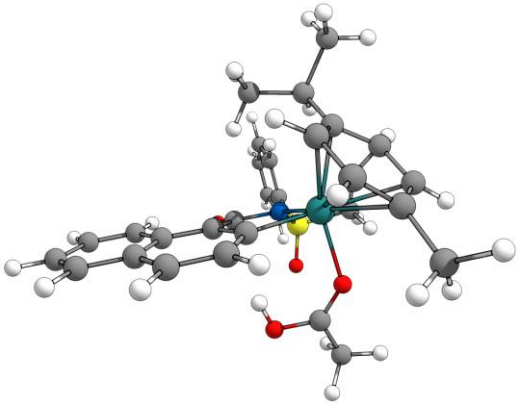
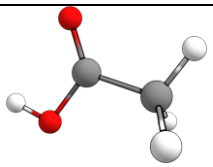


C

E(RM06) = -2010.31635948



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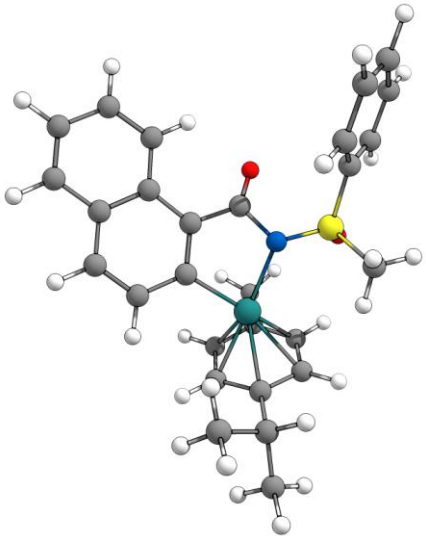
H	-1.664234	0.686219	-1.965855	H	1.703889	-0.811349	0.000028
C	-1.813183	0.41716	0.067574	O	0.651605	1.192477	0.000003
C	-3.227593	0.509937	0.083838	C	0.092231	0.124496	-0.000016
C	-3.847998	1.724228	0.24836	C	-1.386783	-0.100082	-0.000008
C	-3.111227	2.920075	0.409591	H	-1.903728	0.859573	-0.000657
C	-3.776478	4.153879	0.597873	H	-1.675371	-0.682122	0.880486
C	-3.062752	5.316556	0.730616	H	-1.67526	-0.683336	-0.87973
C	-1.655373	5.278722	0.676404				
H	-3.574792	6.264142	0.875304				
H	-4.864406	4.15809	0.633768				
C	-1.685224	2.87771	0.352854				
C	-0.977598	4.096469	0.49087				
C	-1.066035	1.594736	0.160447				
H	0.104392	4.090045	0.439731				
H	-1.092474	6.203073	0.781555				
H	-4.936036	1.784361	0.253254				
H	-3.839476	-0.378684	-0.059426				
Ru	-0.818112	-1.384584	0.001319				
C	0.372534	1.455545	-0.098866				
N	0.75821	0.082132	-0.2174				

O	1.183742	2.345879	-0.282274
S	2.077936	-0.057917	-1.141095
O	1.984163	0.362509	-2.541502
C	2.466137	-1.790717	-1.104409
C	3.49646	0.677351	-0.362518
H	3.370135	-1.891111	-1.712407
H	2.65767	-2.10651	-0.077083
H	1.628116	-2.329185	-1.556137
C	4.490741	1.169766	-1.198917
C	3.609656	0.677964	1.024189
C	5.64938	1.671324	-0.614654
H	4.346957	1.174229	-2.276302
C	5.790306	1.671824	0.769255
H	6.439857	2.068493	-1.245128
C	4.77411	1.180865	1.587581
H	6.69783	2.067372	1.217627
H	4.885469	1.202929	2.668057
H	2.786635	0.328226	1.645403
O	-0.7112	-1.43882	-2.209632
C	-2.460106	-2.472066	0.999712
C	-0.231249	-2.120041	1.989899
C	-0.535341	-3.707783	0.13126
C	-0.897329	-0.60669	-3.107795
C	-0.484465	-0.85979	-4.512194
H	-0.313592	-1.924376	-4.674032
H	0.450939	-0.314707	-4.683498
H	-1.229497	-0.470728	-5.20991
C	-1.622692	-1.851897	1.968607
C	-1.915042	-3.323935	0.015127
H	-3.512532	-2.206791	0.949302
H	-2.043091	-1.103291	2.635851
C	-2.756377	-3.859637	-1.095851
C	0.272279	-3.133994	1.102818
C	0.706788	-1.496747	2.99066
H	-0.110824	-4.3831	-0.609521
H	1.329512	-3.390179	1.151214
H	-2.178564	-3.935394	-2.022571
H	-3.126683	-4.861841	-0.847921
H	-3.622162	-3.21555	-1.281523
H	1.690311	-1.430272	2.493417
C	0.29876	-0.101513	3.439384
C	0.843906	-2.439531	4.188757
H	-0.619872	-0.1243	4.038998
H	1.078057	0.327899	4.07841
H	0.137254	0.576097	2.592551
H	1.55976	-2.037808	4.913789
H	-0.122069	-2.551729	4.697624
H	1.185433	-3.438166	3.892752



D

E(RM06) = -1781.24663062

C	2.741079	5.458732	0.09469
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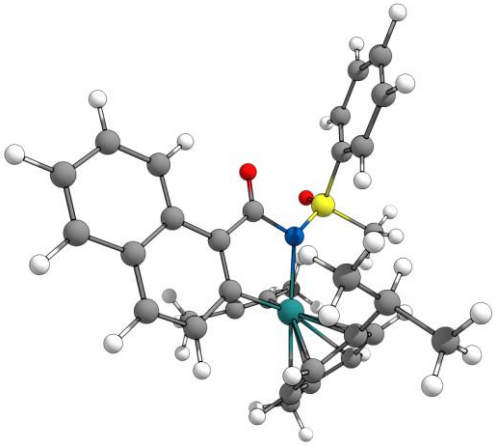
C	0.716713	4.138572	0.206028
C	1.463248	2.9526	-0.076905
C	2.862795	3.065707	-0.272934
C	3.478611	4.290473	-0.189157
C	-0.684446	4.054471	0.393411
C	-1.35285	2.859036	0.302418
C	-0.63873	1.660978	0.062758
C	0.741655	1.722425	-0.1209
C	1.398653	0.429676	-0.38051
N	0.578614	-0.647303	0.112119
O	2.45873	0.224092	-0.932471
S	1.171233	-2.135549	-0.150507
O	0.968352	-2.75251	-1.463886
C	0.337882	-3.094413	1.096329
C	2.871546	-2.238293	0.353331
C	3.731946	-2.944028	-0.477722
C	5.054448	-3.094113	-0.072951
C	5.484046	-2.54272	1.129278
C	4.601577	-1.832773	1.942745
C	3.277081	-1.673897	1.56058
H	3.249744	6.416993	0.159814
H	0.80199	6.273492	0.509136
H	3.439356	2.17597	-0.501622
H	4.552466	4.361433	-0.343238
H	-1.230317	4.972787	0.607863
H	-2.431839	2.840374	0.447505
H	0.71991	-4.114995	1.00797
H	0.55445	-2.674511	2.080871



E

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C	-0.848354	1.538739	0.10646
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C	-1.141646	3.858672	0.737741
C	0.20023	4.160126	0.411317
C	0.70526	5.471072	0.57018
C	2.00485	5.761428	0.243092
C	2.838946	4.741293	-0.254058
H	2.391815	6.769646	0.364786
H	0.040552	6.24189	0.956788
C	1.041151	3.124046	-0.091073
C	2.37797	3.455526	-0.41898
C	0.472817	1.808936	-0.223397
H	3.03328	2.687079	-0.811138
H	3.868976	4.973056	-0.514571
H	-1.775904	4.662114	1.112241
H	-2.707651	2.440297	0.818187
Ru	-1.564517	-0.400071	-0.137088
C	1.244214	0.678722	-0.732716
N	0.567687	-0.557918	-0.528555
O	2.343714	0.697481	-1.264557
S	1.471752	-1.759545	-1.142418
O	1.635962	-1.899015	-2.59004
C	0.712025	-3.250137	-0.538758
C	3.0492	-1.804743	-0.315361
H	1.332759	-4.059253	-0.934044
H	0.72108	-3.258992	0.553195
H	-0.30106	-3.314489	-0.942058
C	4.160329	-2.115195	-1.08753
C	3.119621	-1.590366	1.057954
C	5.390774	-2.22695	-0.44841

H	-0.73356	-3.057696	0.888511	H	4.057835	-2.245538	-2.161696
H	3.371495	-3.350645	-1.418982	C	5.487001	-2.025184	0.924841
H	5.74966	-3.639971	-0.704349	H	6.277422	-2.464339	-1.029501
H	6.519389	-2.662195	1.436911	C	4.357921	-1.704779	1.676299
H	4.948515	-1.398763	2.87625	H	6.452751	-2.110896	1.415716
H	2.585138	-1.104147	2.178099	H	4.44438	-1.53523	2.746054
Ru	-1.465192	-0.186554	-0.174177	H	2.232928	-1.311306	1.626546
C	-2.906188	0.421037	-1.658197	C	-3.513495	-0.044629	0.892562
C	-3.58394	0.383293	-0.423153	C	-1.657991	-1.22547	1.99662
C	-2.174391	-0.718794	-2.12553	C	-2.95129	-2.310717	0.187062
H	-4.040573	1.287638	-0.03082	C	-2.521771	-0.116616	1.900629
C	-3.512587	-0.783247	0.386965	C	-3.705938	-1.116557	-0.015344
C	-2.310725	-1.954745	-1.408176	H	-4.125623	0.848286	0.786292
H	-1.763718	-2.826329	-1.76359	H	-2.347928	0.752912	2.530692
C	-2.969185	-1.981984	-0.183997	C	-4.742354	-1.0346	-1.086524
H	-2.978846	-2.891368	0.41566	C	-1.941318	-2.343246	1.145073
H	-2.828306	1.359214	-2.20441	C	-0.565474	-1.332508	3.030435
C	-1.34011	-0.640222	-3.360248	H	-3.117893	-3.166675	-0.464489
H	-0.493003	-1.331569	-3.306924	H	-1.338116	-3.242011	1.256345
H	-1.940129	-0.905294	-4.240362	H	-4.436425	-1.57899	-1.985442
H	-0.954142	0.373658	-3.508464	H	-5.683192	-1.472949	-0.732303
C	-4.103026	-0.833218	1.772285	H	-4.940419	0.004072	-1.36849
H	-3.564128	-1.629097	2.311239	H	0.194876	-2.012791	2.606834
C	-3.941592	0.462533	2.555749	C	0.110047	-0.004154	3.342057
H	-4.556032	1.270461	2.138554	C	-1.126474	-1.979939	4.297579
H	-4.274904	0.315515	3.588012	H	-0.568889	0.680826	3.865954
H	-2.898118	0.800507	2.581275	H	0.964412	-0.166172	4.008482
C	-5.575485	-1.236468	1.662134	H	0.464477	0.499361	2.433909
H	-6.017148	-1.339756	2.6588	H	-0.33571	-2.121296	5.041988
H	-6.144234	-0.470057	1.120177	H	-1.896108	-1.337203	4.744234
H	-5.701907	-2.188441	1.134015	H	-1.580983	-2.956757	4.094777
				C	-1.714703	-0.613096	-2.366123
				C	-1.950122	0.59065	-2.144706
				C	-1.567249	-1.836602	-3.164772
				H	-0.518999	-2.14718	-3.239151
				H	-2.15595	-2.669675	-2.762566
				H	-1.920899	-1.640165	-4.183874
				C	-2.327001	1.974155	-2.447287
				H	-2.640367	2.035564	-3.495393
				H	-3.155646	2.317211	-1.816663
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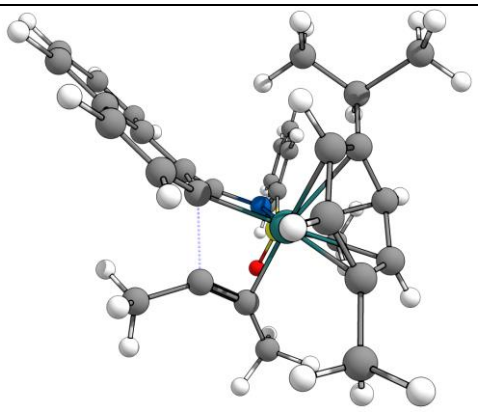

TS_{EF}

Frequency -268.4924

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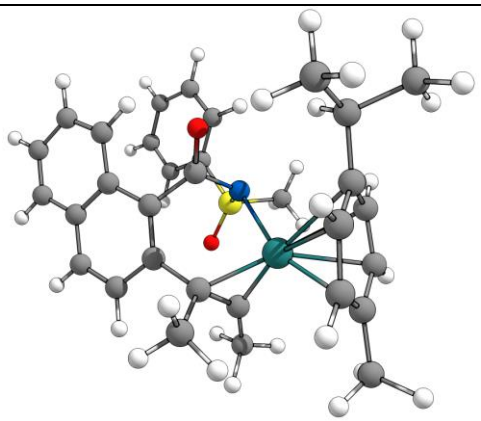
C	-2.401477	2.120101	-0.255295
C	-0.02259	1.781781	-0.545893
Ru	-1.421654	-0.833524	-0.067094
C	-2.191574	3.447067	-0.00187
H	-3.419627	1.735455	-0.278627
C	-0.891578	4.012488	-0.025292
H	-3.035961	4.101514	0.212066
C	-0.694844	5.387544	0.230367
C	0.225637	3.175982	-0.321455
C	0.566115	5.92818	0.203468
H	-1.563022	6.005907	0.45181
C	1.672393	5.104749	-0.08313
H	0.714385	6.986495	0.401203
C	1.514875	3.763274	-0.340012
H	2.66928	5.538139	-0.106441
H	2.374184	3.14678	-0.578211
C	1.064847	0.836494	-0.819976
N	0.724026	-0.484553	-0.434532
C	-2.523566	-0.35786	1.902772
C	-3.269193	-2.055877	0.24765
C	-1.245129	-2.381056	1.581654
C	-1.419641	-1.098095	-2.130582
O	2.14647	1.097148	-1.321927
S	1.841305	-1.519686	-1.003162
O	1.971249	-1.729634	-2.445096
C	1.419929	-3.074456	-0.254166
C	3.419571	-1.171882	-0.258581
H	2.156541	-3.784568	-0.640753
H	1.496236	-2.99615	0.832564
H	0.411763	-3.345991	-0.576967

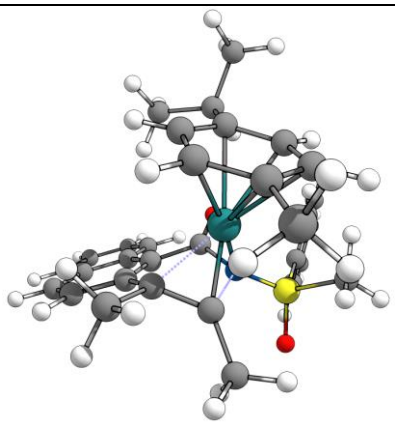


F

E(RM06) = -1937.18058450

C	5.568552	-0.813442	-1.562629
C	4.918239	-1.956222	-1.173448
C	3.512192	-1.969085	-1.013148
C	2.767447	-0.775771	-1.248237
C	3.465767	0.385552	-1.66237
C	4.830286	0.361702	-1.814963
C	2.830341	-3.145018	-0.620876
C	1.468306	-3.159424	-0.478358
C	0.70833	-1.981204	-0.665338
C	1.3572	-0.805084	-1.00322
C	0.610828	0.471839	-0.92973
N	-0.115513	0.669284	0.31776
O	0.590065	1.352185	-1.756028
S	0.690268	0.43985	1.68834
O	0.941005	-0.896432	2.238721
C	-0.258799	1.365694	2.87651
C	2.226829	1.307114	1.503113
C	3.389131	0.64066	1.880155
C	4.604016	1.296859	1.72
C	4.635562	2.591203	1.208945
C	3.460286	3.239007	0.831744
C	2.23734	2.595237	0.966795
H	6.64811	-0.813058	-1.689258
H	5.470597	-2.875656	-0.98695
H	2.909724	1.294008	-1.875182
H	5.348087	1.261065	-2.140793
H	3.410422	-4.050551	-0.450073
H	0.955497	-4.081804	-0.20751
H	0.284897	1.312421	3.823152
H	-0.372128	2.396216	2.532708
H	-1.227164	0.862988	2.956612
H	3.331379	-0.373283	2.268637

C	4.54884	-1.415295	-1.029167	H	5.52701	0.79391	1.994506
C	3.486404	-0.74117	1.063368	H	5.588932	3.100436	1.093564
C	5.79582	-1.229839	-0.44059	H	3.497482	4.244168	0.421339
H	4.446218	-1.723883	-2.066473	H	1.315442	3.071068	0.636995
C	4.740334	-0.560442	1.631177	Ru	-1.929384	-0.432581	0.114365
H	2.578007	-0.52107	1.623616	C	-3.868784	-0.70285	-0.944513
C	5.889312	-0.808574	0.881754	C	-3.403698	0.485596	-1.57919
H	6.695654	-1.409846	-1.021997	C	-4.162294	-0.747662	0.448997
H	6.867206	-0.663957	1.333375	H	-3.260312	0.49414	-2.655152
H	4.822762	-0.216558	2.658554	C	-3.05861	1.590009	-0.804103
C	-3.419829	-0.799177	0.890312	C	-3.850396	0.393949	1.231608
H	-4.250517	-0.162606	0.592977	H	-4.045118	0.39146	2.301752
C	-1.391647	-1.113598	2.233359	C	-3.228704	1.487402	0.6162
C	-0.350003	-0.663755	3.225251	H	-2.895936	2.323288	1.230103
C	-2.175567	-2.874027	0.654254	H	-4.097709	-1.572822	-1.556556
H	-2.019509	-3.842809	0.182532	C	-4.816655	-1.948348	1.053453
H	-2.652794	0.638189	2.319424	H	-4.533998	-2.077687	2.103349
C	-4.24492	-2.502109	-0.791328	H	-5.907256	-1.840173	1.016502
H	-3.793126	-3.209842	-1.493899	H	-4.559269	-2.862783	0.507917
H	-5.101581	-3.000023	-0.321847	C	-2.463003	2.857301	-1.368973
H	-4.624489	-1.648256	-1.362736	H	-1.531588	3.034994	-0.803404
H	-0.374559	-2.983784	1.832458	C	-2.106755	2.762146	-2.843373
H	0.602862	-1.112058	2.891985	H	-3.005226	2.630443	-3.461333
C	-0.174	0.847913	3.273465	H	-1.627484	3.691034	-3.1681
C	-0.682663	-1.22776	4.60732	H	-1.406019	1.945365	-3.044284
H	-1.062523	1.342154	3.687508	C	-3.420546	4.027069	-1.126215
H	0.663778	1.108042	3.929057	H	-2.975174	4.961097	-1.484716
H	0.021411	1.272957	2.280145	H	-4.358551	3.873055	-1.674433
H	0.095851	-0.963522	5.330942	H	-3.670621	4.160669	-0.067562
H	-1.632446	-0.813994	4.970144	C	-0.788895	-2.100016	-0.5462
H	-0.776823	-2.319872	4.592678	C	-1.382062	-2.085809	0.745598
C	-1.251497	-2.280417	-2.997384	C	-1.393624	-2.986484	-1.620617
C	-2.32412	1.181792	-3.015436	H	-2.430458	-3.255296	-1.38281
H	-0.185092	-2.488894	-3.150541	H	-1.385218	-2.47522	-2.59159
H	-1.711746	-3.173316	-2.557312	H	-0.826602	-3.919624	-1.739983
H	-1.702182	-2.111641	-3.983599	C	-1.561633	-3.031926	1.849232
H	-2.38474	0.761858	-4.027005	H	-2.223317	-2.661691	2.639209
H	-3.337597	1.455126	-2.7021	H	-1.927864	-3.999505	1.473849
H	-1.721851	2.096544	-3.046264	H	-0.569097	-3.217682	2.287015



TS_{FG}

Frequency -234.4250

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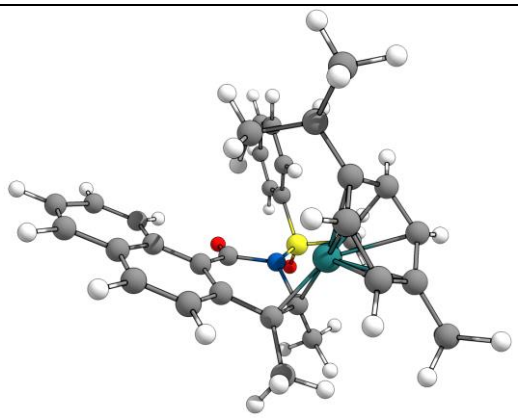

G

E(RM06) = -1937.17269842

C	1.219587	-0.741281	-1.9139	C	0.99676	0.085835	-1.937099
N	-0.099446	0.509364	-0.939657	N	-0.064833	0.863358	-1.214711
C	-1.0292	-0.049722	0.0214	C	-1.495178	0.43383	-1.2799
C	-1.400751	-1.455346	-0.239185	C	-1.674191	-0.979487	-1.065562
C	-2.7185	-1.887888	0.131898	C	-2.95562	-1.490294	-0.642301
C	-3.06072	-3.259917	-0.06835	C	-3.052975	-2.883378	-0.35553
C	-4.353969	-3.732536	0.26139	C	-4.276103	-3.44141	0.074788
C	-5.301387	-2.8831	0.765163	C	-5.390577	-2.654661	0.224038
C	-4.97867	-1.522871	0.950666	C	-5.300743	-1.279705	-0.055021
H	-6.294427	-3.246651	1.015037	H	-6.332417	-3.085825	0.551823
H	-4.575423	-4.785548	0.096735	H	-4.31383	-4.50923	0.283456
C	-2.092265	-4.135439	-0.594312	C	-1.907242	-3.700397	-0.508402
C	-3.731779	-1.035299	0.646974	C	-4.120494	-0.705835	-0.474048
H	-3.522017	0.014556	0.811139	H	-4.0913	0.354009	-0.693566
H	-5.731975	-0.843321	1.342128	H	-6.182109	-0.652599	0.056407
C	-0.843639	-3.694945	-0.944852	C	-0.71097	-3.198718	-0.936302
H	-2.353235	-5.184687	-0.723243	H	-1.999609	-4.762814	-0.285931
C	-0.468554	-2.338049	-0.796275	C	-0.557578	-1.82002	-1.233794
H	-0.137467	-4.414449	-1.343669	H	0.136406	-3.868385	-1.046839
C	0.918552	-1.940842	-1.193282	C	0.737417	-1.332759	-1.72761
O	-1.431514	0.624337	0.945865	O	-2.31311	1.316248	-1.419147
S	-0.38987	1.952286	-1.614556	S	0.020184	2.552095	-1.184871
Ru	1.82131	-0.301788	-0.149726	Ru	1.670915	-0.391018	-0.075716
O	-0.916312	1.853846	-2.974362	O	-0.316705	3.275072	-2.401496
C	1.162351	2.822413	-1.637204	C	1.689377	2.957525	-0.69807
C	-1.461104	3.004422	-0.656121	C	-0.939187	3.04089	0.223999
H	0.985131	3.732334	-2.217551	H	1.701586	4.050857	-0.766556
H	1.472373	3.052823	-0.616137	H	1.872108	2.613712	0.320529
H	1.904701	2.177511	-2.114525	H	2.403673	2.512763	-1.392422
C	-2.674966	3.34297	-1.244274	C	-1.789456	4.1249	0.047254
C	-1.069339	3.488725	0.590839	C	-0.796887	2.368984	1.436526

C	-3.52032	4.207317	-0.554291	C	-2.517515	4.562828	1.1482
H	-2.937732	2.950761	-2.222956	H	-1.888796	4.592205	-0.929352
C	-3.140246	4.713879	0.683011	C	-2.394673	3.912882	2.372771
H	-4.472843	4.489838	-0.993223	H	-3.191819	5.407706	1.042772
C	-1.918159	4.35828	1.255397	C	-1.543065	2.818254	2.517222
H	-3.801705	5.394214	1.21275	H	-2.974152	4.258157	3.224714
H	-1.634133	4.752914	2.226703	H	-1.463927	2.306913	3.473322
H	-0.135108	3.170788	1.047679	H	-0.139489	1.503574	1.526062
C	2.5911	-1.187582	1.834125	C	2.233028	-1.966087	1.510558
C	4.050617	-0.166696	0.083396	C	3.827338	-0.686803	0.064881
C	2.557408	1.195256	1.442044	C	2.618401	0.404948	1.884944
C	3.531236	-1.305884	0.766776	C	3.124187	-1.888961	0.400919
H	3.879152	-2.294272	0.473251	H	3.293289	-2.775472	-0.208768
H	2.220083	-2.086629	2.31791	H	1.715555	-2.898955	1.721454
C	2.071081	0.067127	2.175638	C	1.915427	-0.797879	2.217651
C	3.576104	1.11277	0.474194	C	3.59067	0.461338	0.873058
C	5.077373	-0.317883	-0.992347	C	4.812189	-0.649263	-1.059167
C	0.995666	0.273712	3.213312	C	0.872595	-0.784545	3.311445
H	3.950783	2.00712	-0.019056	H	4.123383	1.388411	0.666423
H	2.122019	2.169596	1.670759	H	2.371018	1.310777	2.44055
H	4.962339	0.455029	-1.759961	H	4.786268	0.320944	-1.56998
H	6.08842	-0.230099	-0.576404	H	5.833586	-0.807562	-0.691387
H	5.004428	-1.297277	-1.476237	H	4.604648	-1.431347	-1.797247
H	0.284003	0.999722	2.784199	H	0.665671	0.275224	3.539985
C	0.213678	-0.988865	3.541269	C	-0.439317	-1.44267	2.89515
C	1.612927	0.874465	4.477653	C	1.436229	-1.430979	4.576745
H	0.843475	-1.730148	4.050993	H	-0.309091	-2.515736	2.706199
H	-0.61263	-0.749971	4.218003	H	-1.184252	-1.345889	3.693158
H	-0.215484	-1.453134	2.644756	H	-0.852305	-0.995884	1.979917
H	0.838478	1.082177	5.223929	H	0.717365	-1.364576	5.40076
H	2.328623	0.17164	4.923262	H	1.649217	-2.493677	4.404278
H	2.147415	1.810375	4.27573	H	2.367472	-0.950236	4.896334
C	1.848769	-3.078448	-1.590379	C	1.546432	-2.292148	-2.571798
C	1.185998	-0.430946	-3.349365	C	1.489246	0.657158	-3.238111
H	2.842161	-2.69749	-1.851078	H	2.529539	-1.877683	-2.815021
H	1.974319	-3.792056	-0.766907	H	1.73228	-3.240587	-2.058703
H	1.473871	-3.633038	-2.46217	H	1.035228	-2.529448	-3.515467
H	1.581261	0.552417	-3.619699	H	1.89837	1.669948	-3.16252
H	1.827143	-1.190523	-3.82245	H	2.287344	0.026185	-3.637071
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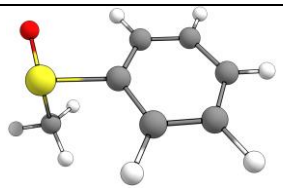

PhSOMe

E(RM06) = -744.752413725

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C	2.034718	-0.960235	1.119735
C	-0.116437	-0.067043	-0.20482
C	-0.664774	1.150148	0.171395
C	-2.040409	1.238012	0.360753
C	-2.844637	0.119363	0.166094
C	-2.280937	-1.093222	-0.224364
C	-0.907947	-1.1899	-0.419076
H	1.681013	-0.304755	1.921603
H	1.535308	-1.932809	1.162158
H	3.118254	-1.086191	1.187844
H	0.000046	2.003256	0.297488
H	-2.487432	2.183934	0.657342
H	-3.919726	0.193025	0.310837
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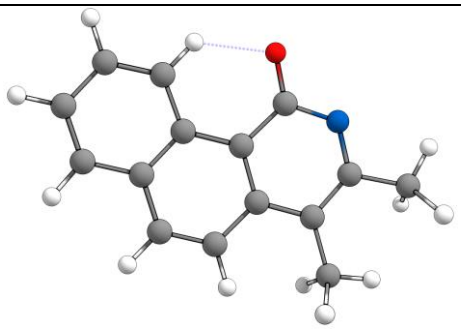
H	-0.457912	-2.129858	-0.739333



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E(RM06) = -708.544236337

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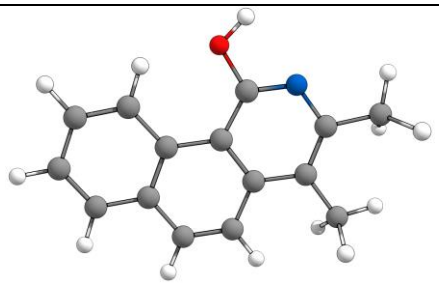
C	-0.747936	-1.655165	-0.000155
C	-0.042571	-0.353476	-0.000047
C	1.394157	-0.251712	-0.000015
C	2.015889	1.036232	-0.000123
C	3.420272	1.155629	-0.000039
C	4.230388	0.04417	0.000162
C	3.632317	-1.22815	0.000283
H	5.314741	0.147691	0.000253
H	3.849114	2.159566	-0.000164
C	1.197922	2.199672	-0.000272
C	2.263104	-1.377656	0.000175
H	1.786956	-2.353606	0.00021
H	4.263141	-2.117098	0.000464
C	-0.155266	2.101638	-0.000181
H	1.686123	3.176111	-0.000538
C	-0.821518	0.831121	0.000002
H	-0.759194	3.007496	-0.0003
C	-2.237154	0.769129	0.000148
O	-0.149344	-2.74773	-0.000278
C	-3.062525	2.023101	0.00028
C	-4.305164	-0.687065	0.000055
H	-4.133925	1.798991	0.00146
H	-2.873291	2.659018	0.880565
H	-2.875031	2.658171	-0.881012
H	-4.517854	-1.759246	-0.000611
H	-4.779316	-0.235954	0.883127
H	-4.779724	-0.234684	-0.882134



I

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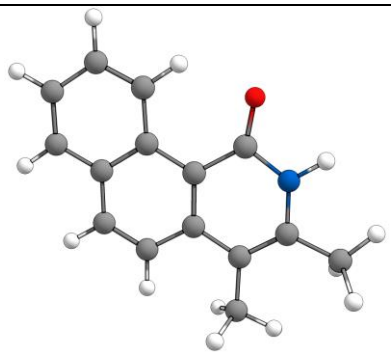
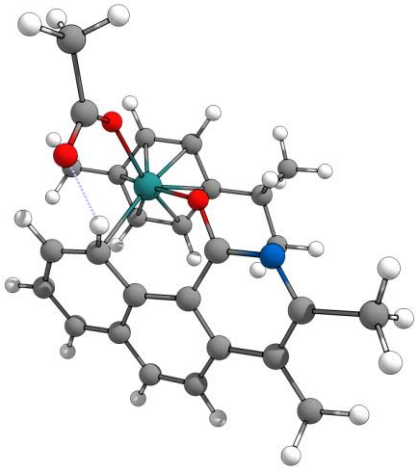
C	-0.143117	2.124012	0.000415
C	1.208344	2.204493	0.000162
C	2.025457	1.036784	-0.000069
C	1.420438	-0.251909	0.000143
C	-0.789287	-1.530439	0.000251
N	-2.099446	-1.586833	-0.00022
C	-2.826243	-0.449467	-0.000345
C	-2.228989	0.798419	0.000095
O	-0.168154	-2.728545	0.000822
C	2.287834	-1.367995	0.000005
C	3.658023	-1.211495	-0.000242
C	4.242325	0.061901	-0.000472
C	3.427391	1.168578	-0.000419
H	-0.738397	3.032262	0.000693
H	1.702902	3.175063	0.000078
H	4.291067	-2.09591	-0.000189
H	5.323906	0.17138	-0.000793
H	3.850304	2.172295	-0.000665
C	-4.313577	-0.646677	-0.00091
H	-4.786765	-0.198634	0.881403
H	-4.786201	-0.198035	-0.883211
H	-4.532473	-1.716662	-0.001318
C	-3.042944	2.058483	0.000281
H	-2.835932	2.678338	-0.881771
H	-4.114428	1.846786	0.00037
H	-2.835757	2.678123	0.882447
H	1.8737	-2.366058	0.000076
H	-0.891754	-3.373692	0.000718



J

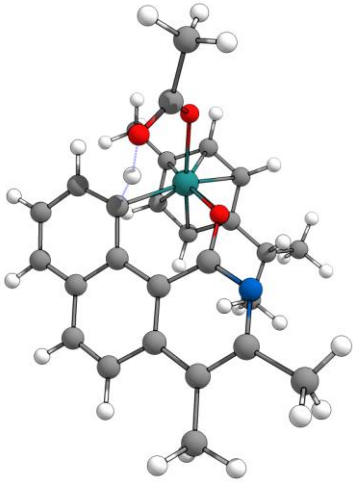
E(RM06) = -709.102737995

C	-0.006085	-0.333792	0.001715
C	-0.785092	0.839891	0.002622
C	-0.124866	2.104073	0.002873
C	1.231862	2.19131	0.001977
C	2.046985	1.031464	0.000613
C	1.432972	-0.255249	0.000676
C	-0.686028	-1.629809	0.00114
N	-2.074722	-1.544715	0.002095
C	-2.845421	-0.411286	0.003228
C	-2.228824	0.802272	0.002476
O	-0.185064	-2.749549	0.000524
C	2.289699	-1.385099	-0.000664
C	3.657399	-1.234919	-0.002277
C	4.253468	0.038028	-0.002544
C	3.452915	1.152215	-0.001051
H	-0.719733	3.012576	0.00364
H	1.719425	3.165557	0.002122
H	4.287229	-2.121801	-0.003375
H	5.336269	0.136428	-0.00393
H	3.884834	2.152167	-0.001157
C	-4.326255	-0.63175	-0.003689
H	-4.81345	-0.127111	0.837309
H	-4.784695	-0.252421	-0.924128
H	-4.56933	-1.696417	0.068883
C	-3.022201	2.073894	-0.00394
H	-2.803251	2.68684	-0.888042
H	-4.097785	1.880582	-0.007457
H	-2.808251	2.694343	0.87617
H	1.844321	-2.371851	-0.000531
H	-2.515179	-2.456935	0.002704



K

E(RM06) = -1421.13171487



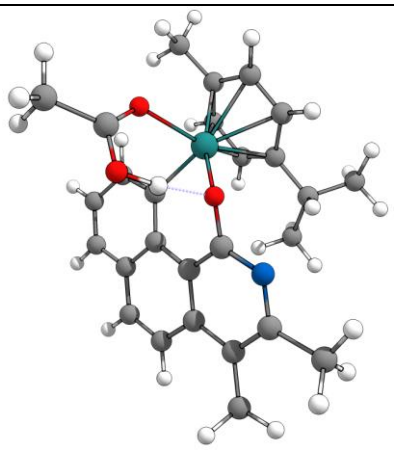
TS_{KL}

Frequency -1511.0173

E(RM06) = -1421.11777635

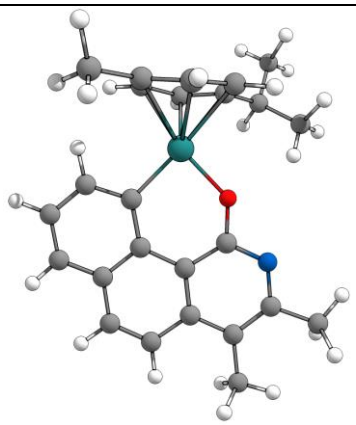
C	-0.703595	1.776807	0.229701	C	-0.774612	1.726193	-0.266606
C	1.575712	2.635098	0.49429	C	1.464134	2.698015	-0.239085
C	-1.719025	0.814419	0.508662	C	-1.754115	0.767493	0.167485
C	-0.98268	2.863681	-0.641711	C	-1.175533	2.78897	-1.125501
C	-3.056352	1.060885	0.114237	C	-3.118462	0.942863	-0.183785
C	-1.41905	-0.469428	1.095653	C	-1.427801	-0.390311	0.967485
C	-3.315917	2.200811	-0.722678	C	-3.471534	2.018865	-1.065309
C	-4.078433	0.174052	0.518469	C	-4.10833	0.074997	0.332489
N	-2.408488	-1.255487	1.522168	N	-2.388945	-1.155891	1.485844
O	-0.214856	-0.949383	1.158174	O	-0.21338	-0.788546	1.204091
C	-2.31912	3.032758	-1.121436	C	-2.541487	2.88872	-1.529214
H	-4.332596	2.379719	-1.064457	H	-4.511784	2.133793	-1.35928
C	-3.688271	-0.925424	1.287191	C	-3.679595	-0.921234	1.20509
C	-5.508563	0.429391	0.141955	C	-5.553468	0.257947	-0.028755
H	-2.530141	3.869702	-1.786434	H	-2.825521	3.701909	-2.196807
C	0.050124	3.760277	-0.973649	C	-0.235142	3.747069	-1.54619
C	1.325734	3.641603	-0.442316	C	1.074987	3.721756	-1.104026
H	-0.180594	4.579552	-1.655163	H	-0.575448	4.539964	-2.212475
C	-4.695857	-1.875843	1.870138	C	-4.647361	-1.849444	1.884529
H	-5.44352	-1.356393	2.481574	H	-5.394633	-1.302783	2.472856
H	-5.241005	-2.421697	1.088718	H	-5.195845	-2.469119	1.163087
H	-4.173516	-2.603707	2.494553	H	-4.090477	-2.509997	2.552597
H	-5.655877	0.422268	-0.947201	H	-5.715943	0.206944	-1.114104
H	-6.178014	-0.32883	0.55543	H	-6.182912	-0.513119	0.422399
H	-5.865503	1.402943	0.504967	H	-5.945787	1.228373	0.306248
H	2.530997	2.573689	1.0155	H	2.481293	2.679317	0.158698
H	2.098748	4.359152	-0.707971	H	1.776888	4.494682	-1.408987
C	0.588724	1.704144	0.83031	C	0.587051	1.685115	0.162227
H	0.736765	1.154193	1.771406	H	0.77426	1.437462	1.409119

O	1.814889	0.600389	3.227131	O	1.068499	1.436476	2.712598
C	2.516009	-0.29748	2.777098	C	1.991731	0.595752	2.843095
C	3.431149	-1.093727	3.685765	C	2.625947	0.443092	4.197119
H	2.99807	-2.08877	3.835032	H	1.990763	-0.215224	4.799462
H	3.524606	-0.596877	4.653775	H	2.675588	1.410983	4.701323
H	4.415566	-1.230712	3.228816	H	3.617172	-0.007677	4.117756
Ru	1.355754	-0.328501	-0.085141	Ru	1.434467	-0.351384	0.054481
O	2.593448	-0.693552	1.539863	O	2.430948	-0.150881	1.914766
H	4.636356	0.775642	-0.683368	H	4.73837	0.75752	-0.335694
H	4.709047	0.824076	-2.455952	H	5.110622	0.346248	-2.020891
C	4.051043	0.967583	-1.590066	C	4.315019	0.683279	-1.344878
H	3.735364	2.015792	-1.578555	H	4.009317	1.685953	-1.661429
C	2.871915	0.051641	-1.655211	C	3.156501	-0.261381	-1.358588
H	1.442689	1.559079	-2.29478	H	1.817815	1.014007	-2.495252
C	1.581452	0.501551	-2.069624	C	1.935389	0.039766	-2.020874
C	0.456264	-0.362284	-2.125386	C	0.822201	-0.846378	-2.001862
H	-0.511289	0.048993	-2.399806	H	-0.107639	-0.534223	-2.467851
C	0.556261	-1.693882	-1.645163	C	0.884904	-2.061051	-1.264025
H	1.905858	-3.120107	-0.693832	H	2.134639	-3.241779	0.071989
C	1.826319	-2.143369	-1.16505	C	2.096708	-2.374634	-0.582307
C	2.957562	-1.283863	-1.192243	C	3.186748	-1.469587	-0.608999
H	3.871476	-1.605912	-0.696624	H	4.040445	-1.655709	0.041375
C	-0.634072	-2.610739	-1.499799	C	-0.306619	-2.971894	-1.077467
H	-0.685295	-2.859095	-0.426337	H	-0.46872	-3.027484	0.011804
H	0.504816	-4.423243	-2.006994	H	0.902573	-4.808017	-1.13387
H	-1.249442	-4.576576	-2.166054	H	-0.824273	-5.044581	-1.436388
C	-0.405726	-3.891792	-2.304516	C	0.019924	-4.368405	-1.610926
H	-0.32953	-3.667471	-3.376667	H	0.204271	-4.335584	-2.692944
H	-1.980687	-1.758328	-2.979349	H	-1.507776	-2.444142	-2.813639
C	-1.955065	-1.973162	-1.901768	C	-1.588749	-2.460374	-1.717649
H	-2.778187	-2.661709	-1.682107	H	-2.418787	-3.126288	-1.45772
H	-2.156024	-1.04481	-1.355548	H	-1.861529	-1.456909	-1.371921



L

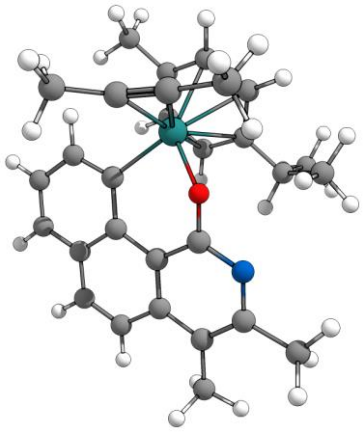
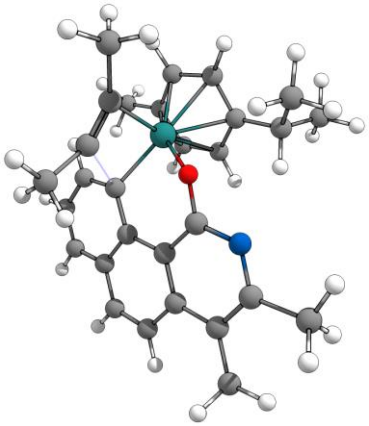
E(RM06) = -1421.15243093



M

E(RM06) = -1192.08123075

C	-0.820222	1.581187	-0.662429	C	0.113288	1.656309	0.231245
C	1.422338	2.233933	-1.29044	C	1.529491	1.401926	0.232357
C	-1.788564	0.751692	0.02	Ru	-1.326701	0.263839	-0.168438
C	-1.309323	2.70115	-1.397104	C	-0.304081	2.969487	0.504655
C	-3.176926	0.928617	-0.189564	C	2.136806	0.113498	0.012183
C	-1.415219	-0.243155	0.974761	C	2.417921	2.503202	0.481279
C	-3.613293	2.030084	-0.993437	C	3.552948	-0.053802	0.043106
C	-4.105758	0.037589	0.408969	C	1.383028	-1.076089	-0.237723
N	-2.285625	-1.085084	1.505677	C	4.381763	1.088883	0.280975
O	-0.167888	-0.333808	1.420182	C	4.132985	-1.324755	-0.151034
C	-2.717679	2.89401	-1.53292	N	1.945886	-2.27398	-0.403085
H	-4.678074	2.186601	-1.146179	O	0.082892	-1.086322	-0.327037
C	-3.598871	-0.970684	1.214705	C	3.83204	2.305709	0.489882
C	-5.576567	0.202658	0.163884	H	5.461439	0.970092	0.29882
H	-3.059158	3.750427	-2.114385	C	3.273536	-2.404043	-0.361748
C	-0.416333	3.596146	-2.015553	C	5.623478	-1.496233	-0.120302
C	0.939359	3.381272	-1.94011	H	4.463505	3.173883	0.677233
H	-0.822459	4.450524	-2.55577	C	1.925156	3.78855	0.726321
C	-4.47789	-2.00963	1.853075	C	0.565429	4.026928	0.744627
H	-5.207661	-1.566122	2.542366	H	2.637673	4.592205	0.909252
H	-5.045517	-2.583613	1.109342	C	3.784165	-3.803462	-0.559986
H	-3.850793	-2.700691	2.421051	H	4.419194	-3.885522	-1.451271
H	-5.817602	0.184026	-0.907464	H	4.380558	-4.147665	0.294281
H	-6.159491	-0.589652	0.639707	H	2.931336	-4.474791	-0.681601
H	-5.950962	1.158315	0.556223	H	6.050645	-1.203997	0.848642
H	2.499915	2.062648	-1.275664	H	5.915837	-2.533321	-0.299701
H	1.636962	4.075762	-2.405162	H	6.122086	-0.884669	-0.884241
C	0.578784	1.314449	-0.67767	C	-2.984172	-1.068419	-1.041433
H	0.25688	0.896551	2.195414	C	-3.061098	0.084045	1.092692
O	0.696135	1.709733	2.642835	C	-3.061987	1.426727	-0.959708
C	1.925015	1.805119	2.247115	H	-1.369143	3.186609	0.535443
C	2.676716	2.966163	2.81038	H	0.177965	5.023986	0.944572
H	2.370347	3.165543	3.839621	C	-3.025864	-1.149486	0.354814
H	2.429532	3.848399	2.20845	C	-2.911877	-2.446953	1.113608
H	3.751764	2.79219	2.746524	C	-2.879948	0.201676	-1.675892
Ru	1.445853	-0.385238	0.088131	H	-2.695337	0.247637	-2.7478
O	2.467343	1.032761	1.442743	C	-3.180141	1.341233	0.442779
H	4.817805	0.05681	0.542905	H	-3.233084	2.249813	1.038245
H	5.561196	-0.928796	-0.734785	H	-2.807532	-1.964945	-1.628833
C	4.698691	-0.297521	-0.486806	H	-3.032088	0.042285	2.180343
H	4.714952	0.57579	-1.147239	H	-2.331988	-2.214917	2.021836
C	3.420043	-1.056951	-0.631448	C	-4.306944	-2.909442	1.536491
H	2.828808	-0.112675	-2.491216	C	-2.171453	-3.538094	0.353575
C	2.561082	-0.846978	-1.734127	C	-3.068131	2.729183	-1.691621
C	1.280268	-1.474371	-1.776671	H	-2.86496	3.571959	-1.024144
H	0.585332	-1.214774	-2.570791	H	-2.306696	2.733113	-2.479537
C	0.865007	-2.334622	-0.726874	H	-4.043981	2.901235	-2.162687
H	1.478584	-3.272673	1.144896	H	-4.245678	-3.81713	2.147779

C	1.807743	-2.648305	0.316684	H	-4.835393	-2.142707	2.11602
C	3.048422	-2.026834	0.365906	H	-4.914915	-3.140255	0.651559
H	3.697934	-2.169771	1.227105	H	-1.186249	-3.194603	0.014927
C	-0.489614	-3.000488	-0.686339	H	-2.032344	-4.411017	1.000998
H	-0.882031	-2.853532	0.333981	H	-2.748373	-3.877237	-0.517825
H	0.359903	-4.97005	-0.217927				
H	-1.284297	-5.010742	-0.8762				
C	-0.316885	-4.499685	-0.940269				
H	0.09103	-4.674789	-1.945131				
H	-1.222789	-2.643939	-2.705608				
C	-1.49901	-2.420378	-1.665609				
H	-2.48366	-2.867499	-1.487175				
H	-1.60719	-1.334494	-1.559126				
 **N** E(RM06) = -1347.99650658				 **TS_{NO}** Frequency -291.1541 E(RM06) = -1347.97068619			
C	2.213927	0.842497	2.057256	C	-0.849535	-1.38272	2.011665
C	0.42285	1.716569	-0.031615	C	-0.15608	-1.745064	0.135792
C	-0.996655	1.834167	-0.102831	C	1.245649	-1.599492	-0.118989
Ru	1.395041	-0.114842	0.175056	Ru	-1.41831	-0.04072	0.126015
C	1.194083	2.830619	-0.337839	C	-0.776869	-2.970126	-0.102202
C	2.082187	-0.37108	2.29507	C	-1.825362	-0.570861	2.096418
C	2.535136	2.233514	2.391096	C	0.151019	-2.165688	2.762587
C	-1.919151	0.754661	0.171071	C	1.990022	-0.372123	0.059288
C	-1.548945	3.083295	-0.524651	C	1.936483	-2.747732	-0.610079
C	-3.307295	0.898478	-0.066378	C	3.374052	-0.326027	-0.255575
C	-1.500952	-0.479188	0.765677	C	1.409683	0.84668	0.574798
C	-3.799057	2.162284	-0.523589	C	4.017796	-1.511248	-0.735263
C	-4.195763	-0.182791	0.17322	C	4.117	0.871173	-0.097397
N	-2.342906	-1.490827	0.966186	N	2.12288	1.97036	0.671114
O	-0.284654	-0.669536	1.19919	O	0.188732	0.929733	1.006682
C	-2.958286	3.207522	-0.712359	C	3.329918	-2.665891	-0.899985
H	-4.864854	2.285821	-0.697955	H	5.0779	-1.475406	-0.972037
C	-3.650115	-1.355007	0.67286	C	3.429095	1.986932	0.357472

C	-5.66424	-0.036053	-0.09836	C	5.58184	0.912915	-0.422512
H	-3.343133	4.173281	-1.04018	H	3.828759	-3.56124	-1.270395
C	-0.722578	4.188114	-0.800128	C	1.263518	-3.965867	-0.835662
C	0.641611	4.067935	-0.702035	C	-0.0857	-4.081681	-0.595132
H	-1.187044	5.123787	-1.109171	H	1.840928	-4.812166	-1.206029
C	-4.481236	-2.580172	0.938853	C	4.098166	3.322221	0.532897
H	-5.246132	-2.400624	1.705276	H	4.913539	3.278087	1.266173
H	-5.003968	-2.929586	0.039283	H	4.529172	3.694228	-0.405388
H	-3.82481	-3.379601	1.292161	H	3.356909	4.042506	0.886585
H	-5.863603	0.278365	-1.131953	H	5.781486	0.684514	-1.479027
H	-6.199814	-0.975644	0.059546	H	6.009384	1.89905	-0.224681
H	-6.132041	0.713225	0.555889	H	6.158015	0.190588	0.172116
C	2.2699	-2.18867	-0.486143	C	-3.001613	1.532721	-0.259358
C	0.981097	-0.707253	-1.917253	C	-1.262325	0.976951	-1.892395
C	3.239842	-0.001771	-1.189018	C	-2.994354	-0.701919	-1.352259
H	2.280719	2.750855	-0.302698	H	-1.831215	-3.070916	0.152526
H	1.293847	4.910436	-0.925234	H	-0.60592	-5.021874	-0.766215
C	1.95801	-1.670779	2.949585	C	-2.776215	0.045229	3.040311
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H	2.683909	-2.398805	2.566241	H	-3.815867	-0.075946	2.710914
H	2.121477	-1.566452	4.029138	H	-2.687008	-0.37947	4.048467
C	1.094976	-1.948172	-1.223674	C	-1.816009	1.890164	-0.93288
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C	3.271846	-1.186237	-0.401137	C	-3.537331	0.222345	-0.424652
H	4.113559	-1.335431	0.276021	H	-4.394079	-0.084375	0.175072
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H	4.797199	1.052332	-0.160653	H	-4.104791	-2.417243	-0.684489
H	5.186912	0.635314	-1.836721	H	-4.433672	-1.933208	-2.355989
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H	0.98304	-4.356081	-2.533567	H	-2.619303	4.42802	-1.638199
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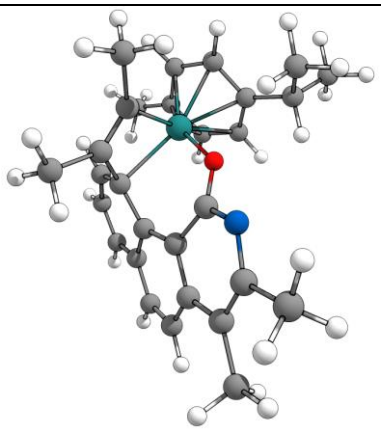

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N	-2.339325	1.998021	-0.583392
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C	-4.228877	0.849911	0.387675
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C	-0.191652	-1.705757	-0.764244
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C	0.294285	-3.789495	0.439979
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C	-0.042661	-1.055785	-2.120621
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H	-3.367132	-3.32861	2.163624
H	1.456504	-2.993635	-1.202309
H	0.933996	-4.656437	0.589992
H	-1.23161	-4.466606	1.793536
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H	1.026641	0.493782	-4.159115
C	-0.956565	-1.494524	-3.223524
H	-0.861548	-2.570809	-3.425036
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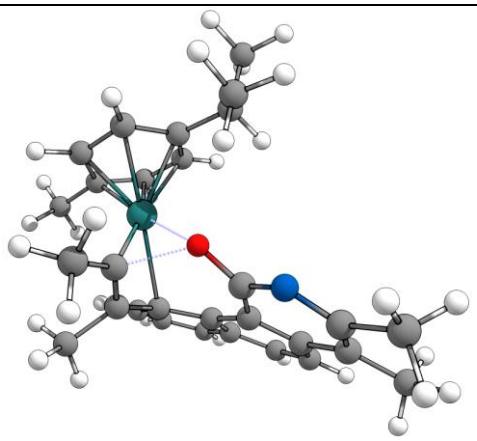

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C	1.273686	-1.621866	-0.234198
C	3.916183	-1.472546	-1.299509
C	4.330841	0.620021	-0.059131
C	3.073318	-2.445763	-1.713005
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C	1.750941	-2.5677	-1.18893
H	3.40516	-3.199096	-2.426727
C	0.989097	-3.684916	-1.584662
C	0.034933	-1.938646	0.434211
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C	3.796458	1.653846	0.691667
C	4.624156	2.804491	1.190425
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Ru	-1.513194	0.091493	0.228022
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C	-0.457585	-1.371799	1.734879
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H	-1.600088	-3.317383	0.52751
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C	-0.822577	-2.37131	2.808933
C	-0.944916	0.722828	3.221841
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H	-1.93646	0.504778	3.642188
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H	-6.148601	1.813357	0.612299	H	5.861883	0.699354	-1.591035
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Ru	1.402866	-0.088295	-0.123277	H	6.281585	-0.310986	-0.207192
C	3.145024	1.20137	-0.170729	C	-2.093585	1.75783	-1.100348
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C	2.49047	-0.680976	1.843151	H	-4.160902	0.53939	1.367244
H	2.180448	-1.427405	2.572852	C	-3.510887	-0.592596	-0.378532
H	3.360419	1.912067	-0.964534	H	-1.57241	0.663208	-2.910459
C	3.687147	-2.528855	0.574123	C	-4.189147	-1.858082	0.045914
H	2.956138	-3.221244	1.006386	H	-2.836049	-1.386151	-2.296375
H	3.852692	-2.810702	-0.471838	H	-3.697101	-2.731957	-0.395246
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C	1.813079	2.996217	1.092138	H	-5.240911	-1.871873	-0.26905
H	0.84493	2.900429	1.606262	H	-0.329036	2.522089	-1.954584
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H	2.387536	4.790501	2.172466	C	-0.808709	3.821737	-0.332882
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H	3.753934	3.883557	1.49763	H	-2.260145	3.162021	-3.426895
C	1.559647	3.726309	-0.218525	H	-2.9082	4.176603	-2.125802
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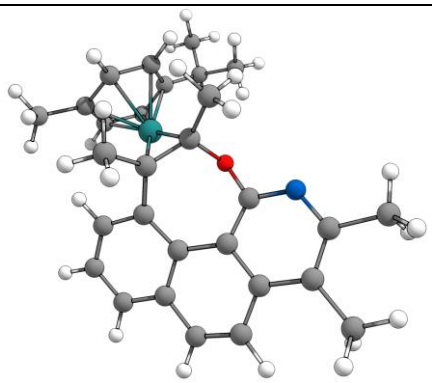
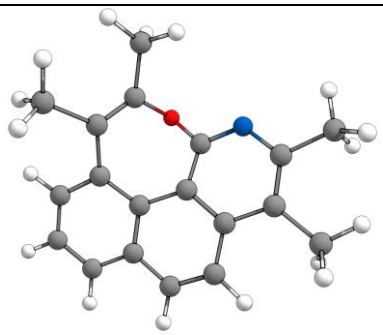
 **P** E(RM06) = -1348.00775144				 **Q** E(RM06) = -863.817248933			
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C	1.989773	1.119777	0.109373	C	-1.279423	2.55895	0.231883
C	2.679064	-0.096692	-0.106714	C	-0.03627	3.063475	0.043744
C	4.079221	0.029376	-0.294271	C	1.105132	2.220784	-0.136143
C	2.017922	-1.371453	-0.270743	C	0.943892	0.807794	-0.138325
C	4.810171	-1.098134	-0.78901	C	-0.745529	-1.020001	-0.500154
C	4.714666	1.274253	-0.061592	N	-1.941255	-1.538307	-0.428296
C	4.16523	-2.24134	-1.122432	C	-2.971945	-0.756707	-0.036074
H	5.881004	-1.009271	-0.950526	C	-2.818538	0.602107	0.202813
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C	0.69636	-1.665112	0.191652	C	3.499306	1.998585	-0.280815
N	2.569243	2.278896	0.298517	C	2.381817	2.79832	-0.239201
C	3.915537	2.361944	0.263478	C	2.098047	-1.450461	0.280461
C	4.478856	3.723626	0.549957	C	1.156232	-2.282951	-0.186225
C	6.202154	1.402935	-0.207333	H	-2.116316	3.226596	0.416562
Ru	-1.692379	-0.200051	-0.011212	H	0.130139	4.139604	0.067991
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H	-0.860828	-3.125022	0.210802	C	0.945811	-3.731903	0.068788
H	0.384763	-4.843656	-1.060423	H	-0.07769	-3.884327	0.435605
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H	5.031578	4.127122	-0.307734	C	-3.989202	1.485475	0.516344
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C	-3.471378	1.105006	-0.768648				
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C	-3.386542	0.965042	0.641445				
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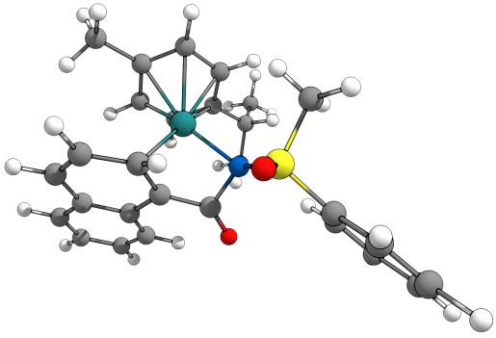 **R** E(RM06) = -1782.04950523				
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C	-1.809055	2.127354	0.293773	
C	-1.716645	2.590774	1.614977	
C	-2.78563	3.232269	2.223384	
C	-3.152113	1.882982	-1.78143	
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C	-0.886417	0.952711	-1.757033	
C	-0.734528	1.380162	-0.369623	
C	0.585448	1.207125	0.238297	
N	1.173529	-0.01336	-0.321701	
O	1.086002	1.758626	1.201706	
S	2.417126	-0.104091	-1.258064	
O	2.462331	0.447477	-2.620792	
C	2.679065	-1.863515	-1.364416	
C	3.840382	0.499719	-0.367571	
C	4.922139	0.97047	-1.10664	
C	6.05814	1.393173	-0.42632	
C	6.094206	1.343409	0.964685	
C	4.99743	0.880504	1.687326	
C	3.85424	0.451654	1.02388	

H	-4.814784	3.940965	2.004737	
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H	-0.006242	0.926164	-2.400102	
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H	2.803302	-2.270267	-0.357963	
H	1.781636	-2.271333	-1.841748	
H	4.855881	1.015788	-2.191045	
H	6.913254	1.768018	-0.982783	
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H	2.965672	0.131097	1.562996	
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C	-2.136079	-1.412933	1.207078	
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H	-2.424264	-0.78122	2.045903	
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C	-1.394727	-2.918881	-1.092826	
H	-1.079072	-3.487582	-1.964295	
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H	-1.030444	-0.803928	3.770854	
H	0.667201	-1.110103	4.129932	
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H	-1.518711	-3.339468	3.76134	
H	-0.499748	-4.428861	2.804562	

References

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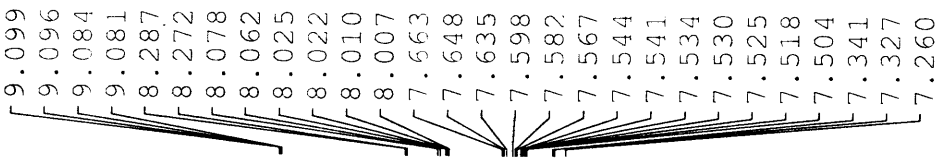
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7.635
7.598
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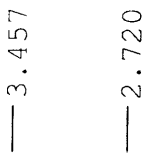
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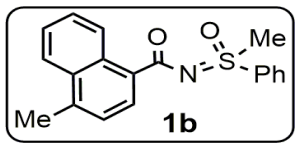
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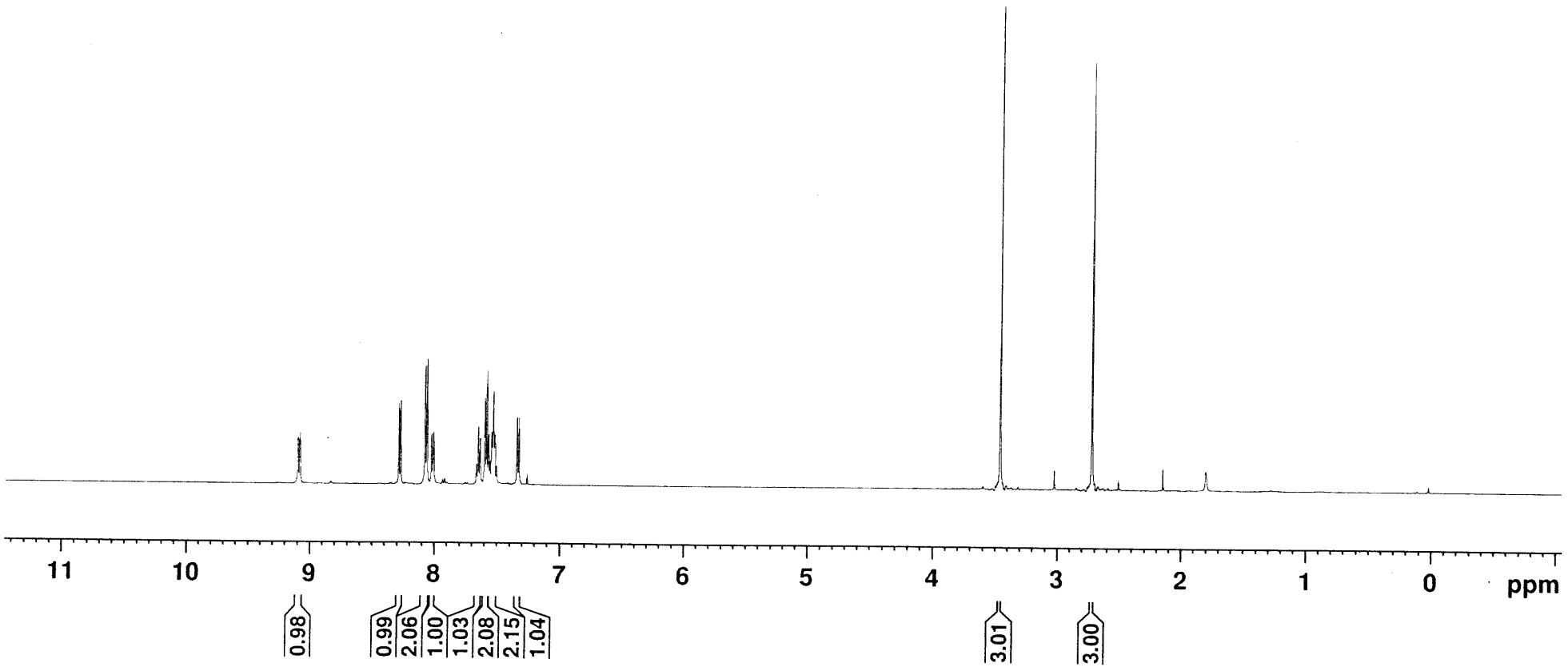
N
S
Ph
Me
1b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2.08
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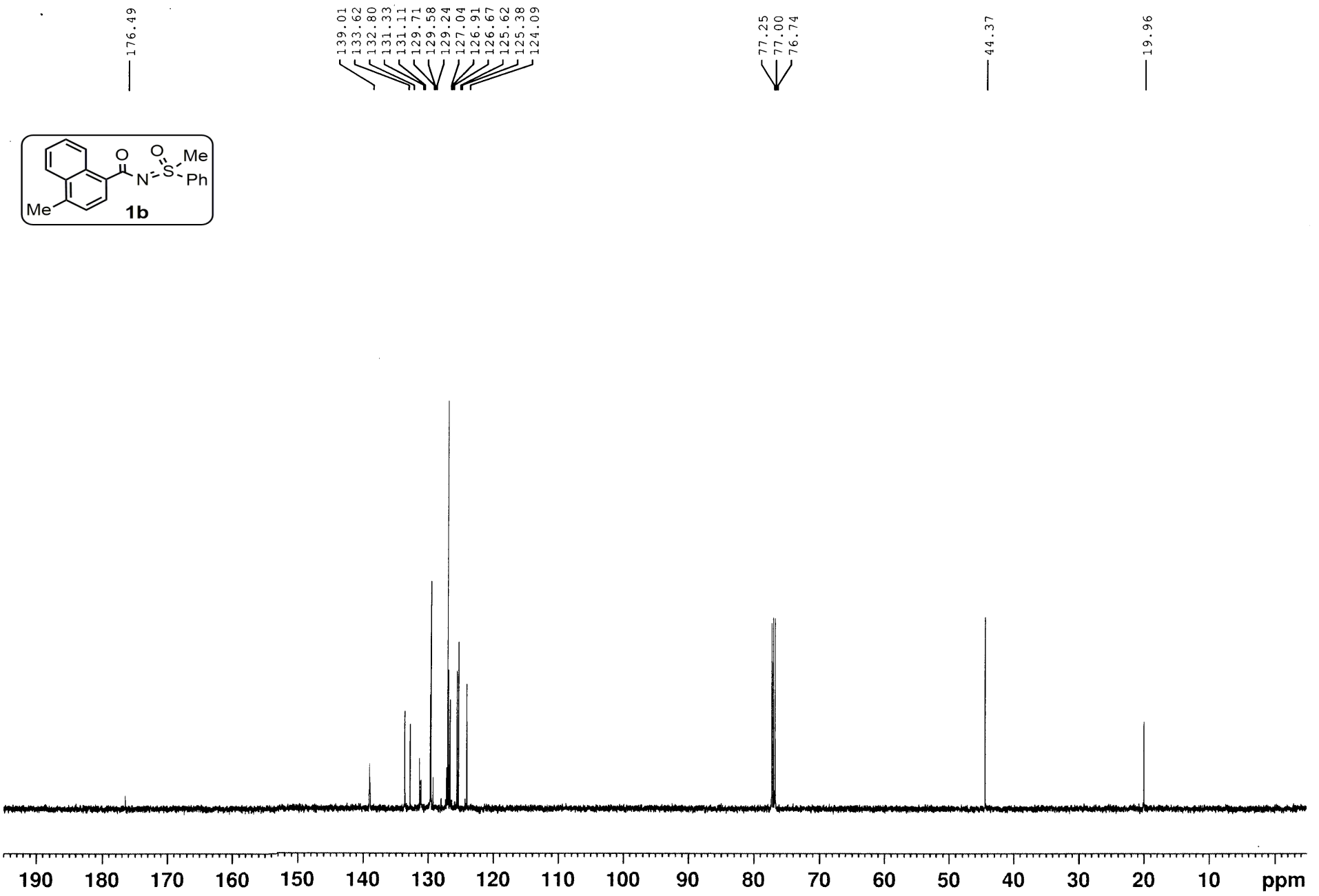
1.04
3.01
3.00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129.58
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127.04
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126.67
125.62
125.38
124.09
77.25
77.00
76.74
44.37
19.96
O
O
Me
N
S
Ph
Me
1b
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10
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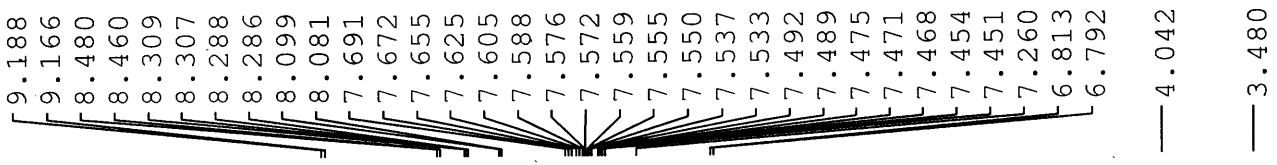
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7.655
7.625
7.605
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7.576
7.572
7.559
7.555
7.550
7.537
7.533
7.492
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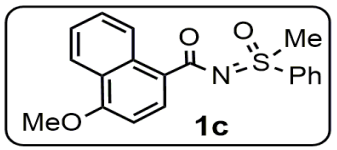
MJ-Tome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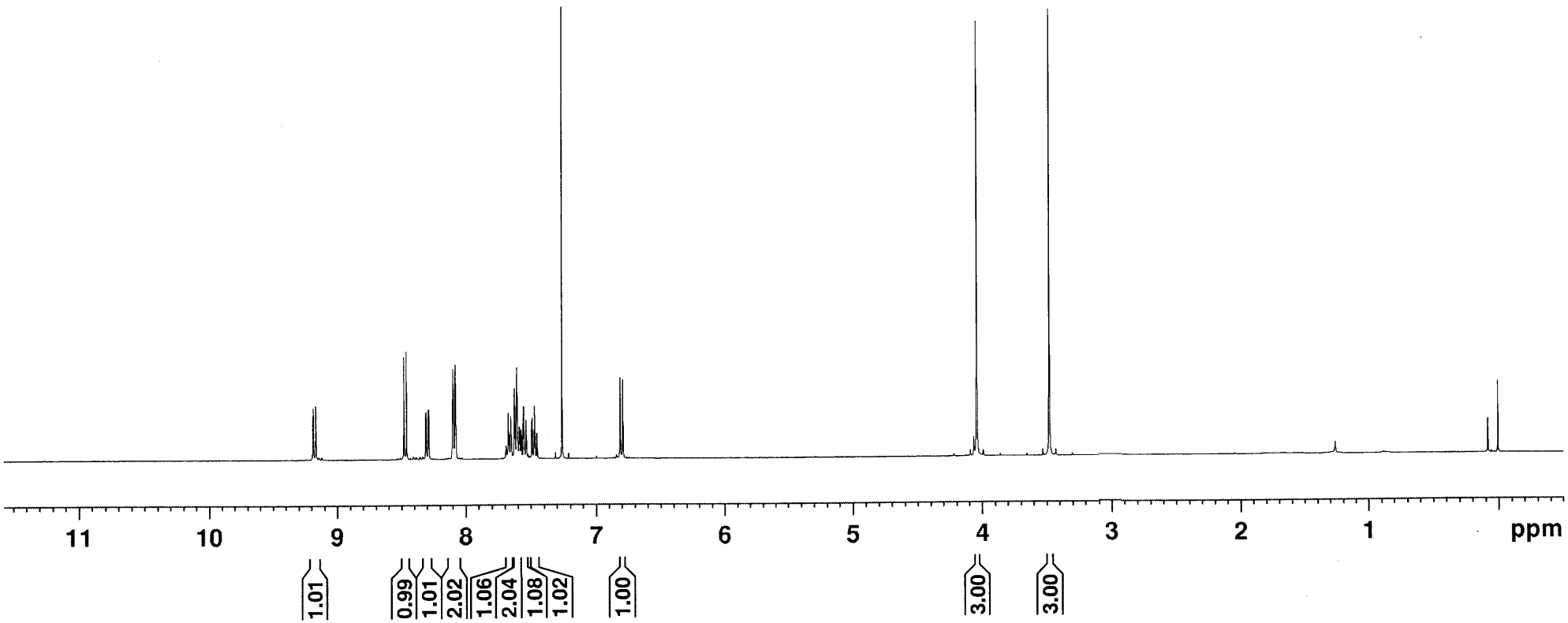
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5
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2.04
1.08
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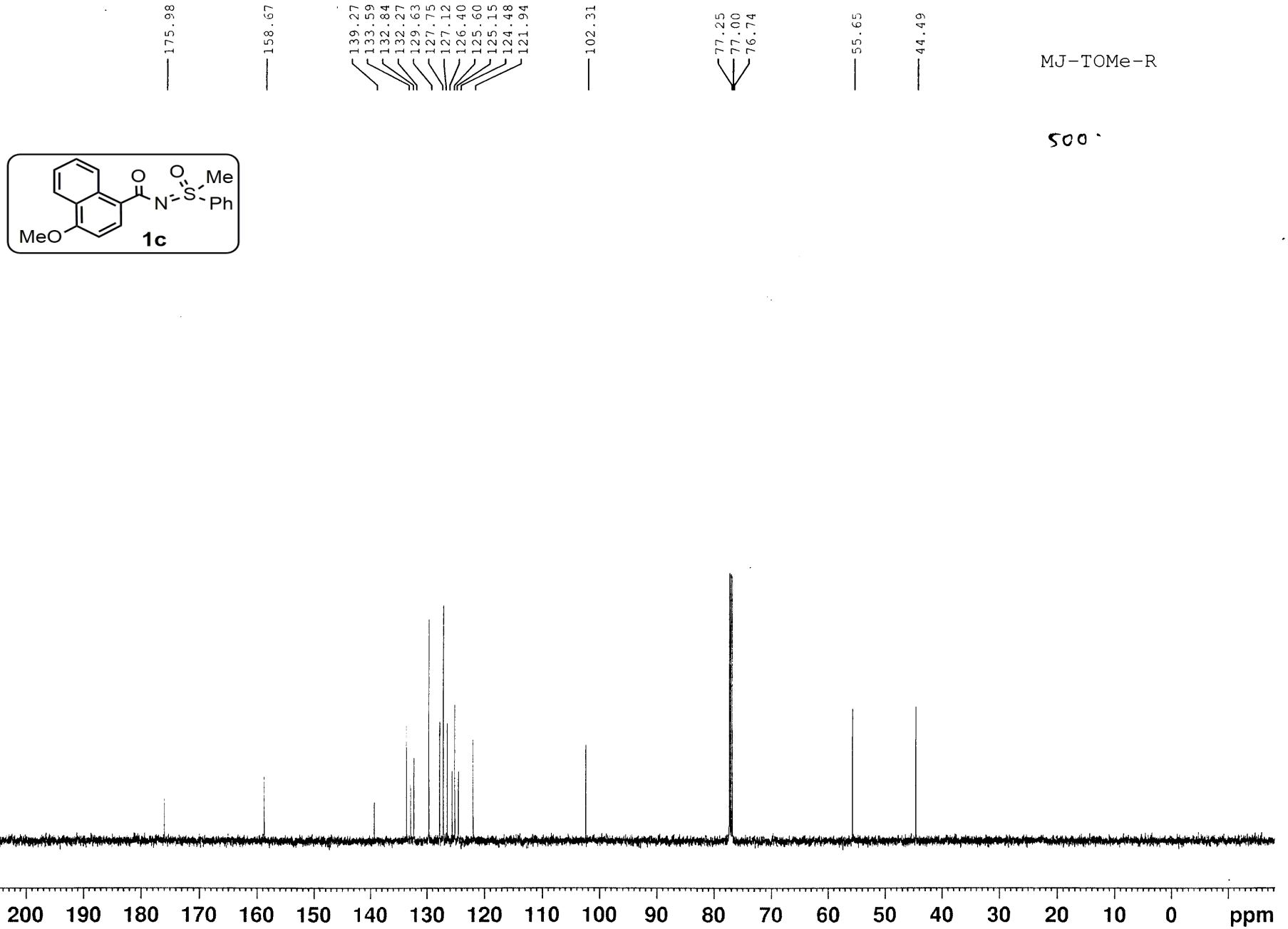
3.00
3.00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121.94
102.31
77.25
77.00
76.74
55.65
44.49
MJ-TOMe-R
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O
Me
N
S
Ph
MeO
1c
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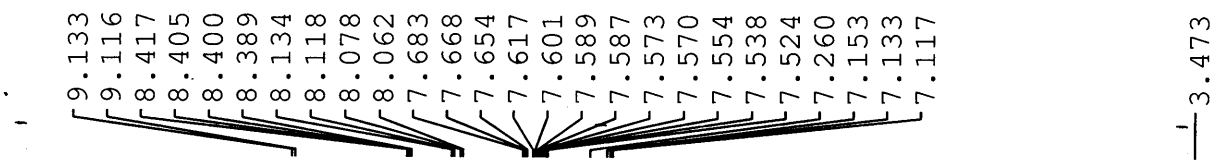
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7.654
7.617
7.601
7.589
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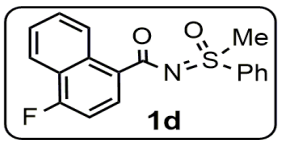
7.133
7.117
3.473

MJ- 34-13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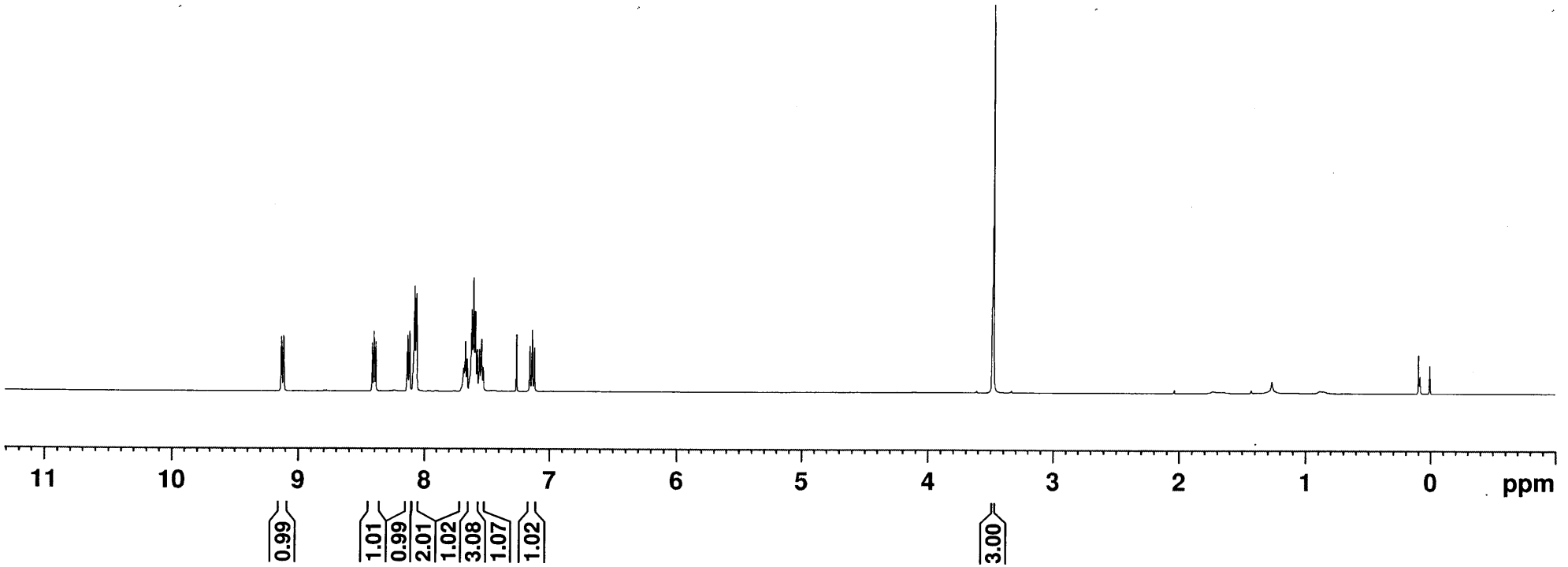
Me
N
S
Ph
F

1d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1.01
0.99
2.01
1.02
3.08
1.07
1.02
3.00

175.43
161.97
159.92
138.79
133.74
133.19
133.15
131.00
130.92
129.66
128.64
128.61
128.13
127.01
126.55
126.53
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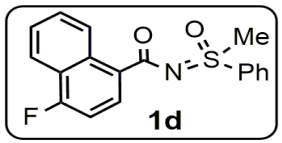
44.40

MJ- 34-7



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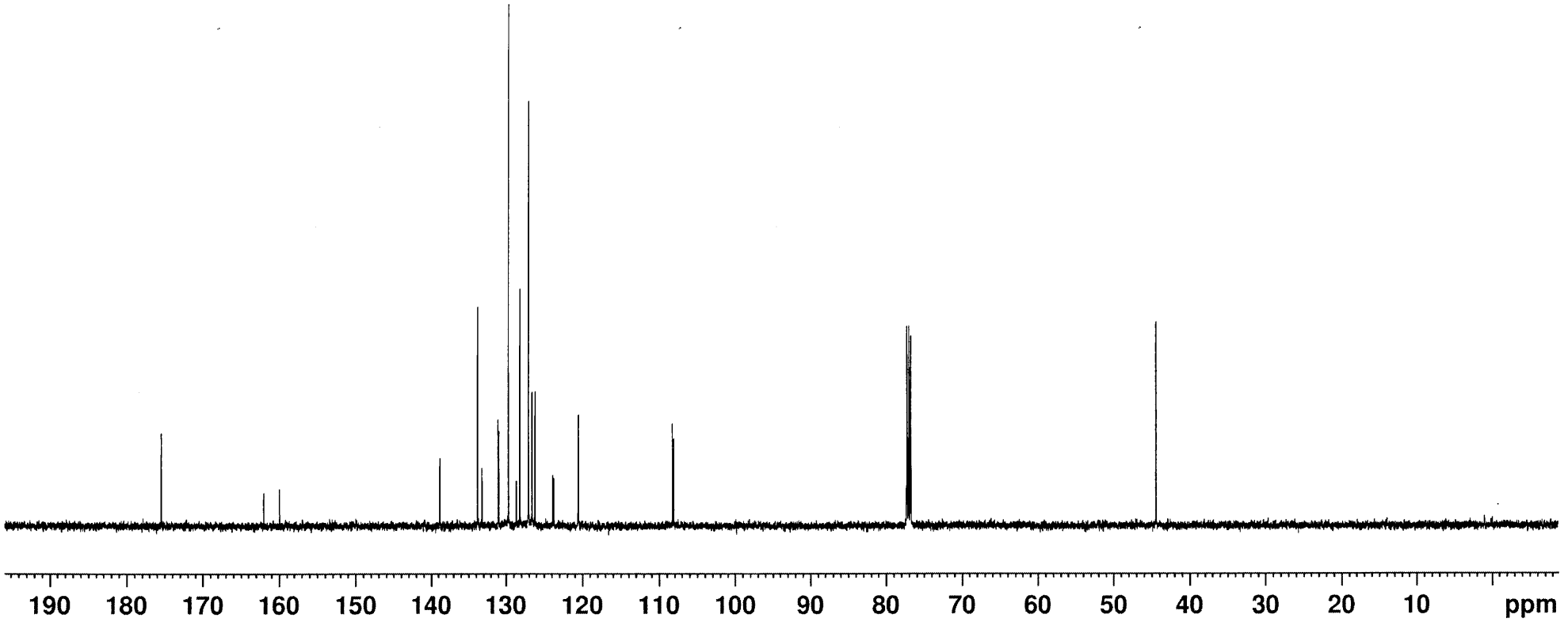

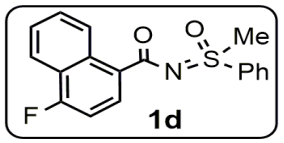
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O
Me
N
S
Ph
F
1d

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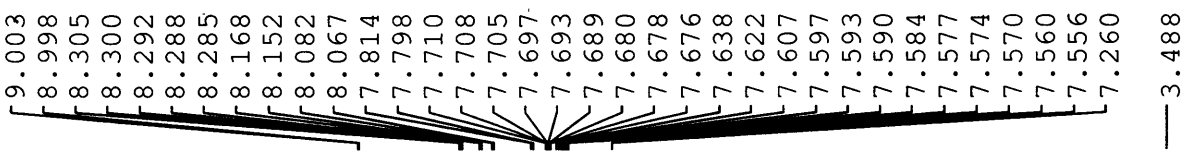
-180
-200
ppm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7.705
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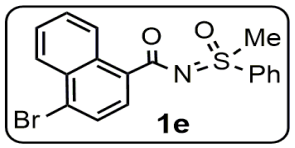
MJ-197-14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S
Ph
Br
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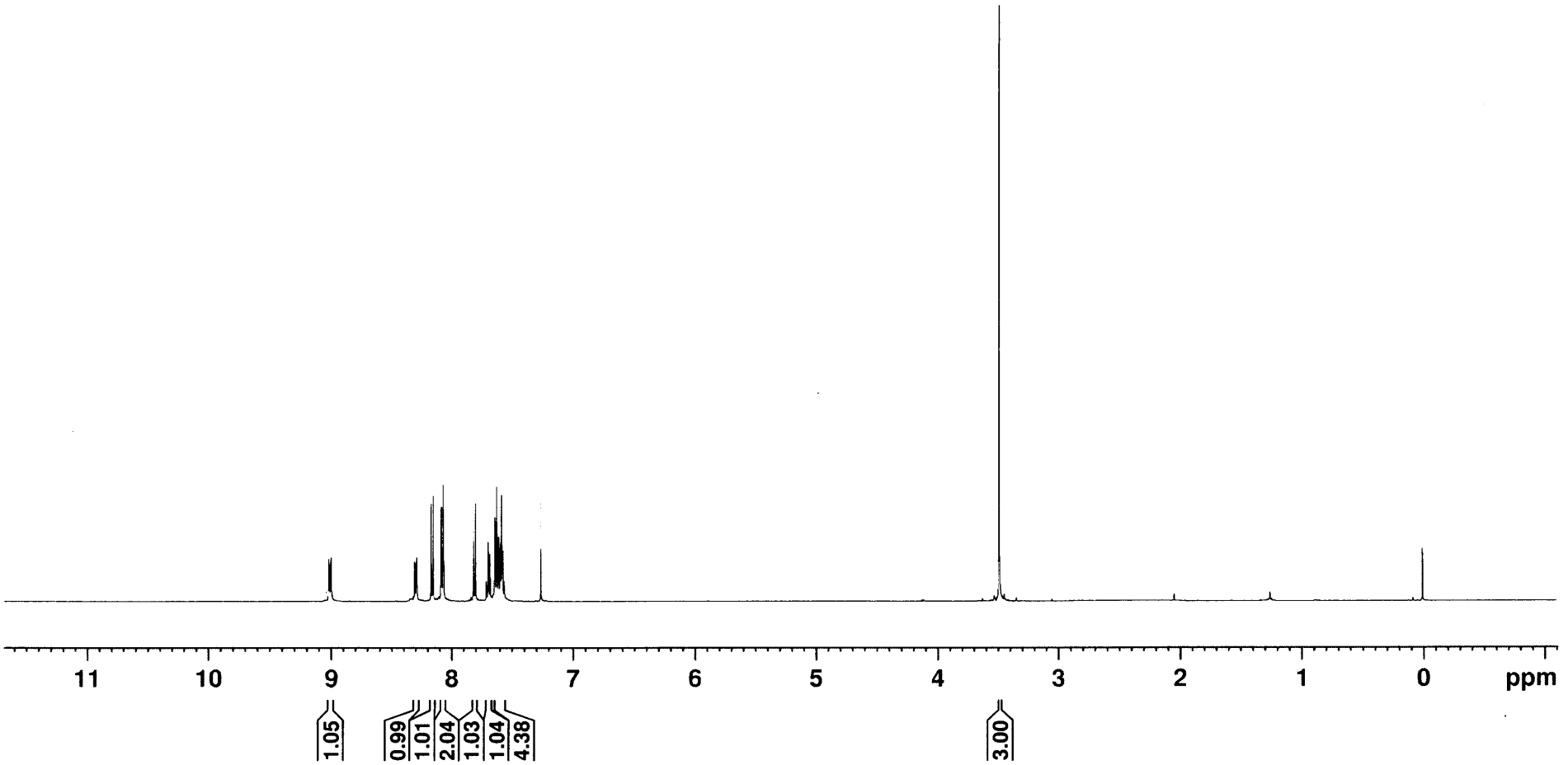
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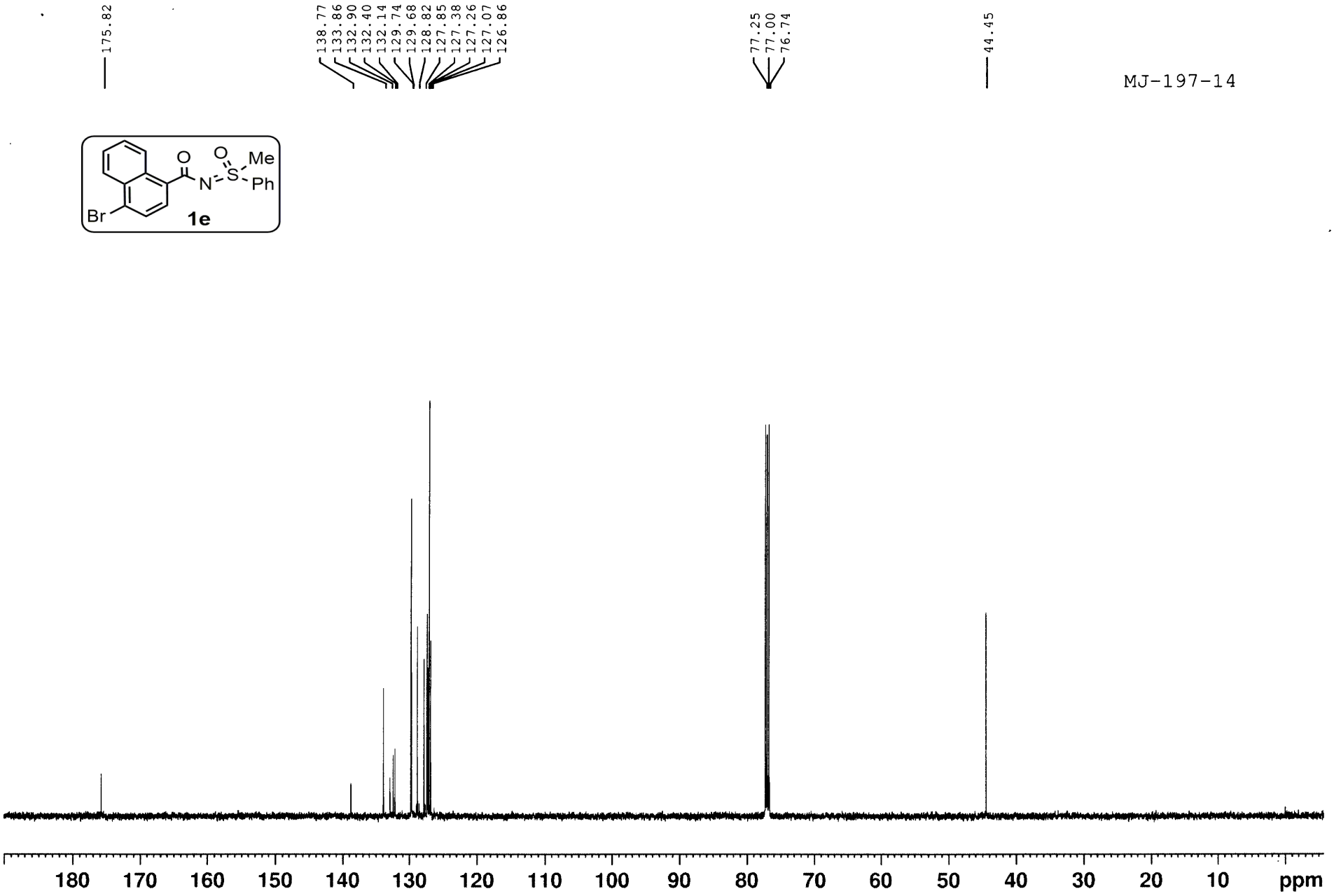
1.03
1.04
4.38
3.00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MJ-197-14
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N
S
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Br
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70
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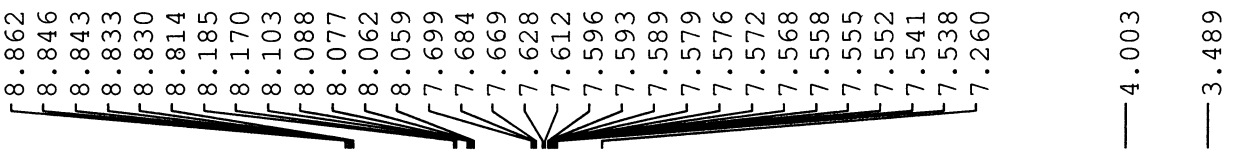
10
ppm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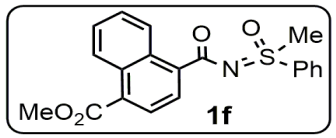
MJ-190-14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Me
N
S
Ph
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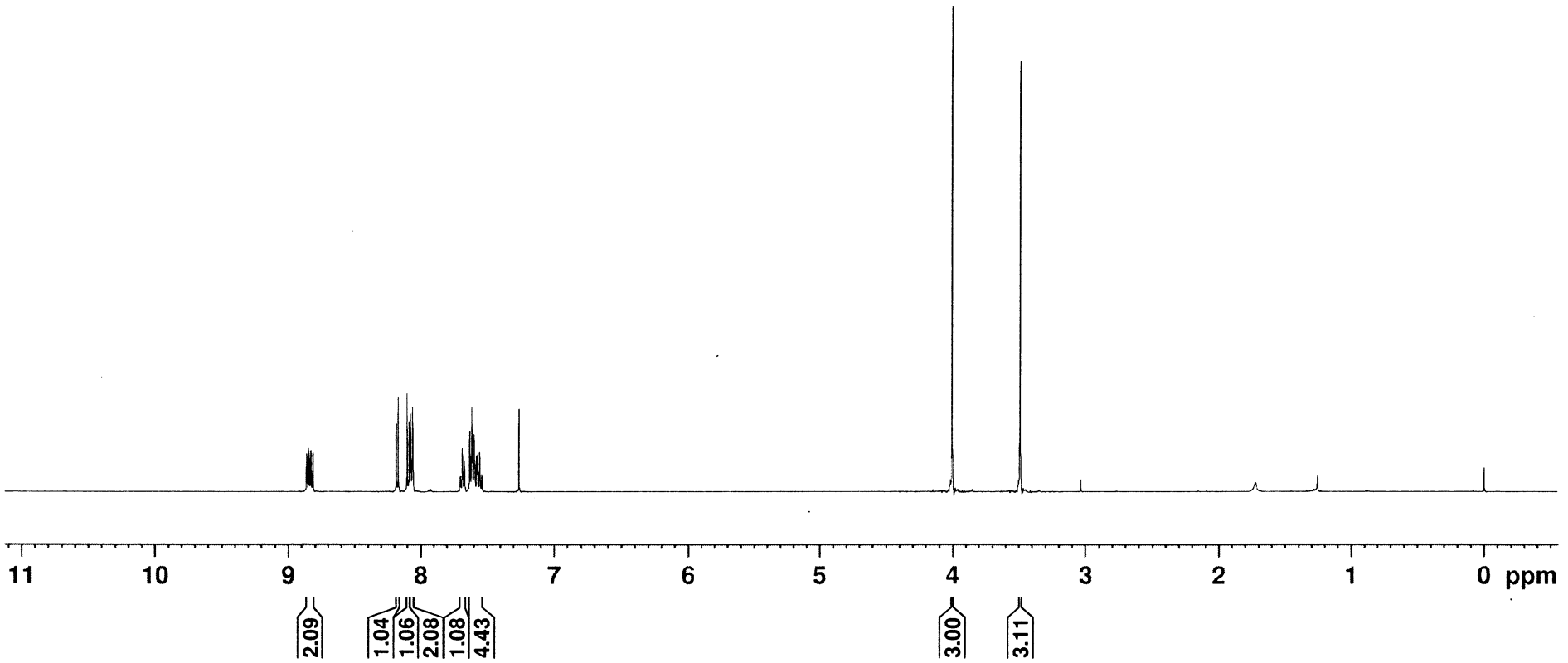
1f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2.08
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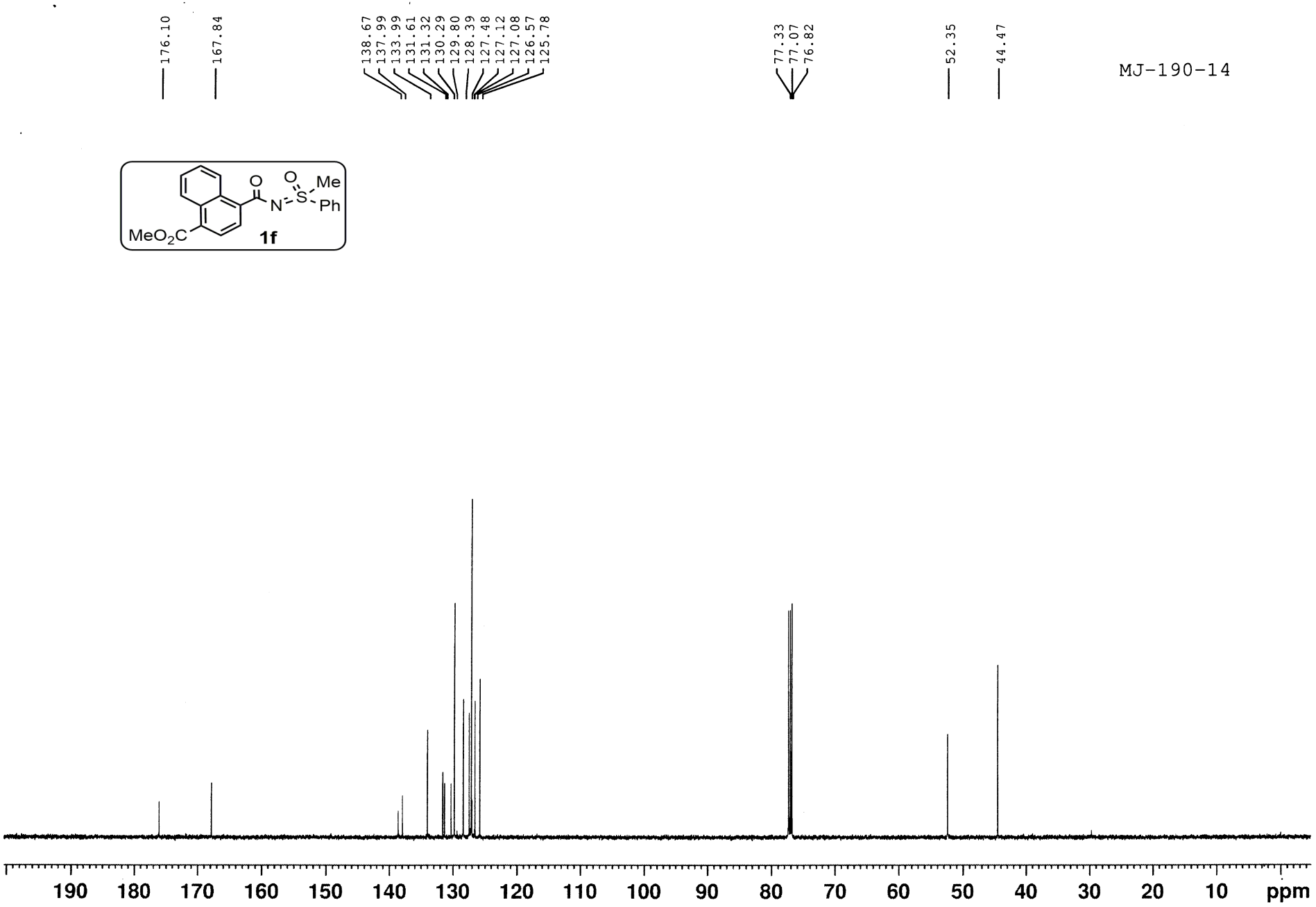
3.11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S
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10
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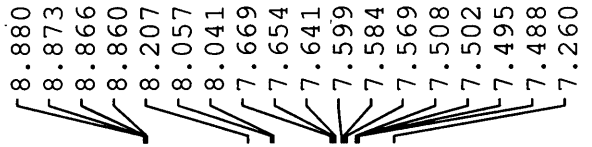
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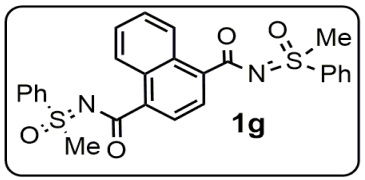
MJ- 188-14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Ph
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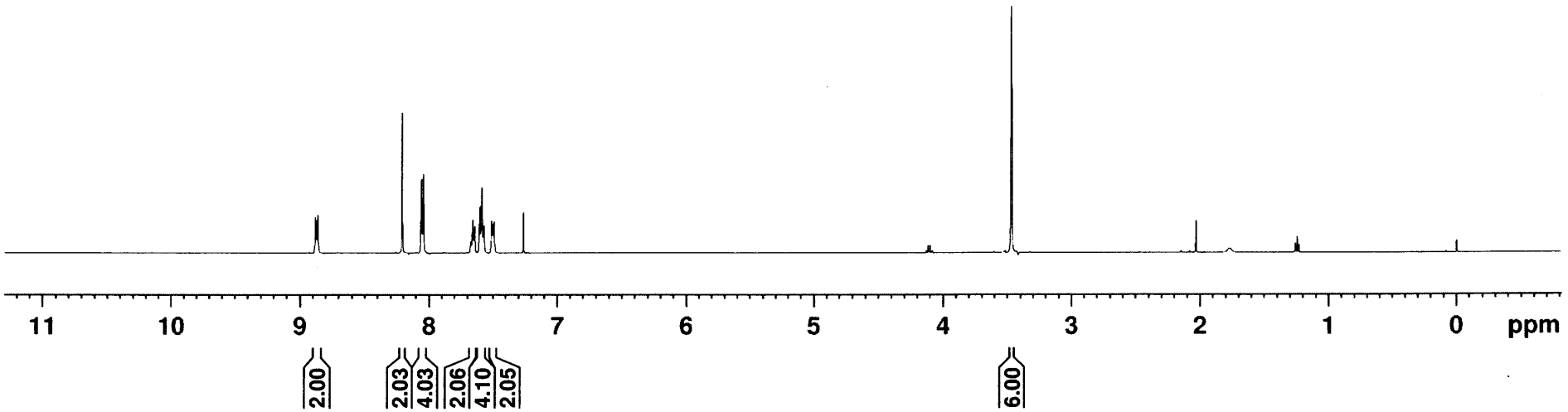
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ppm
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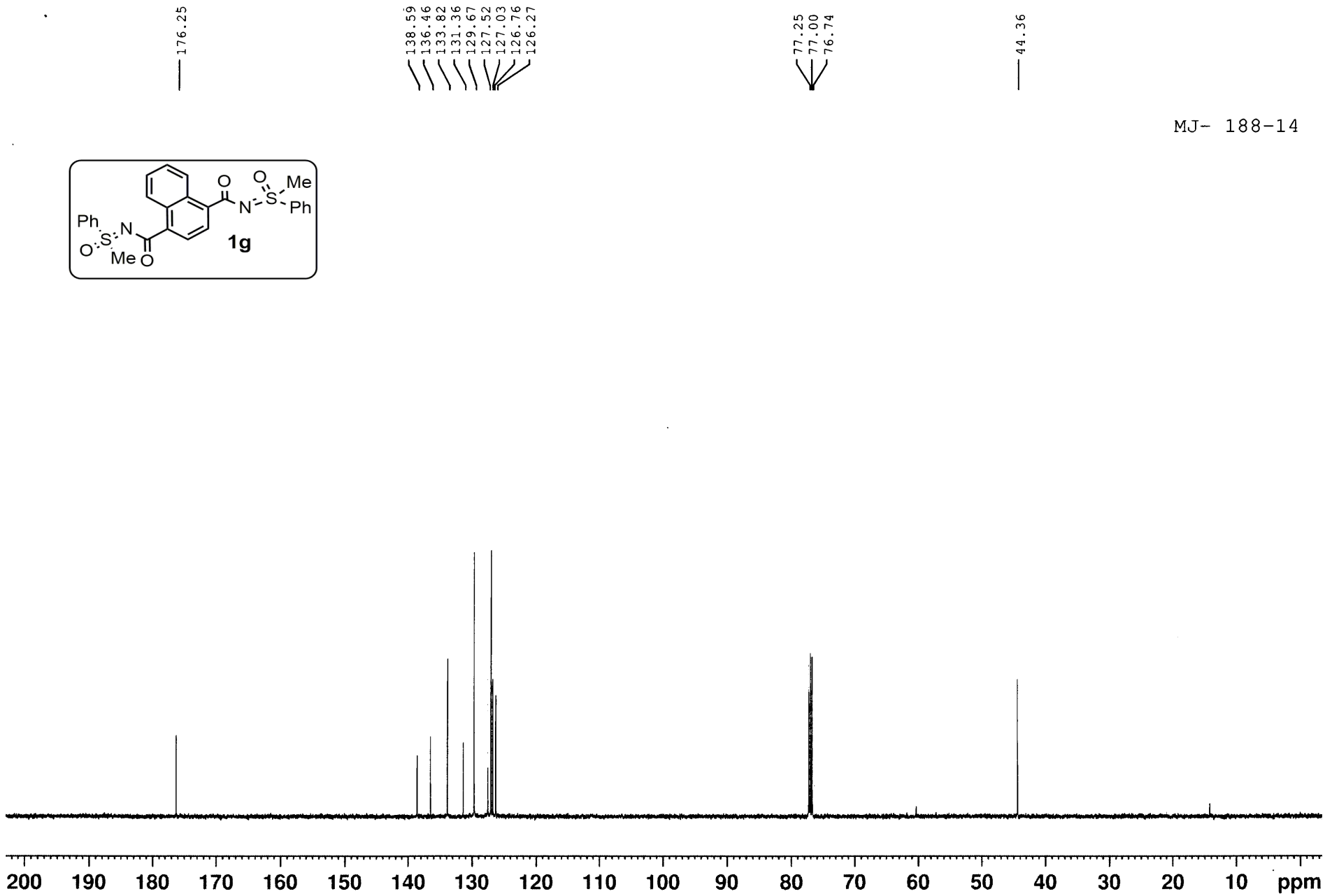
4.03
2.06
4.10
2.05
6.00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150
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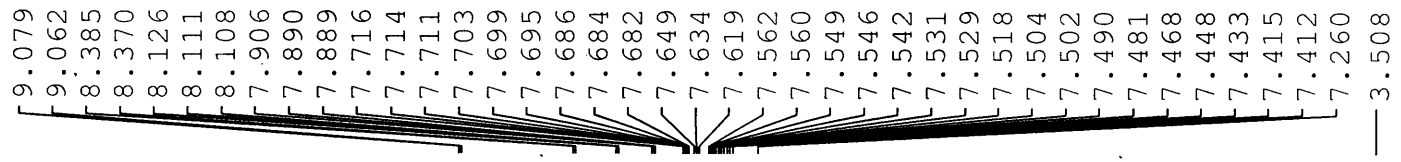
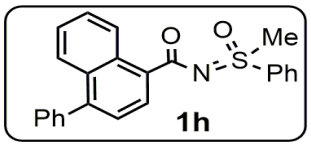
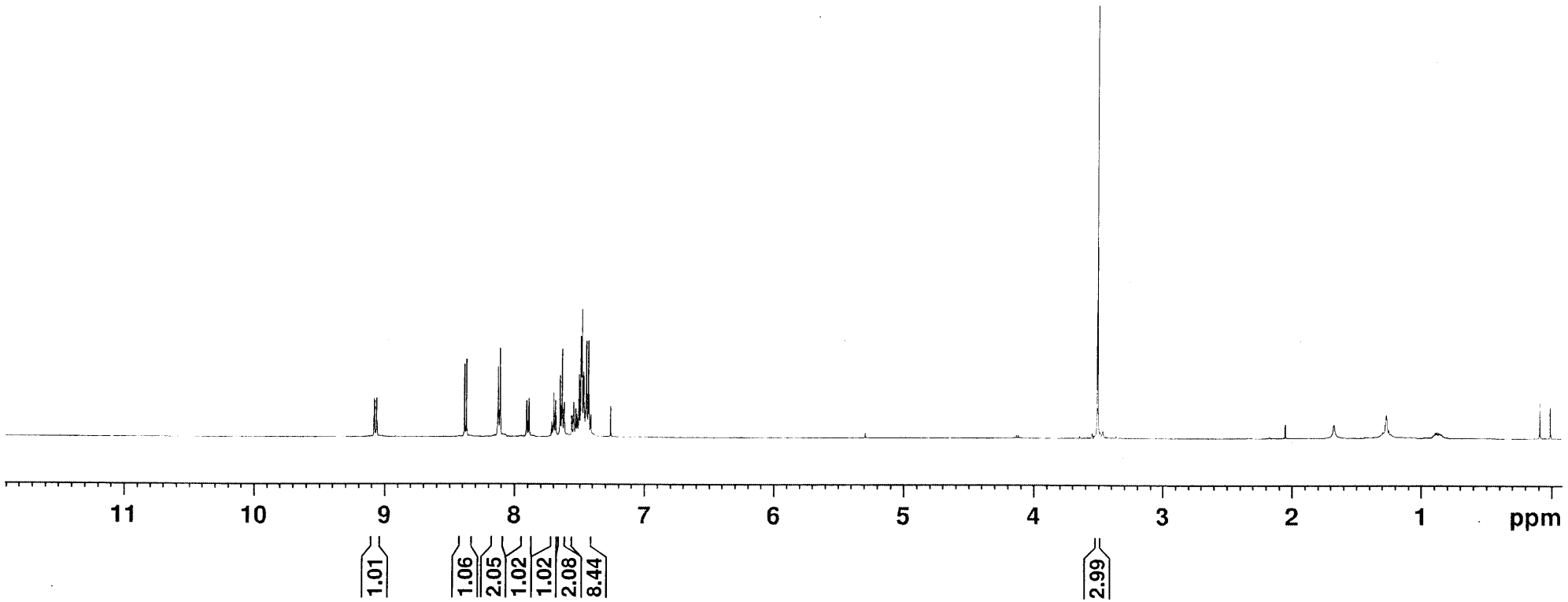
10
ppm

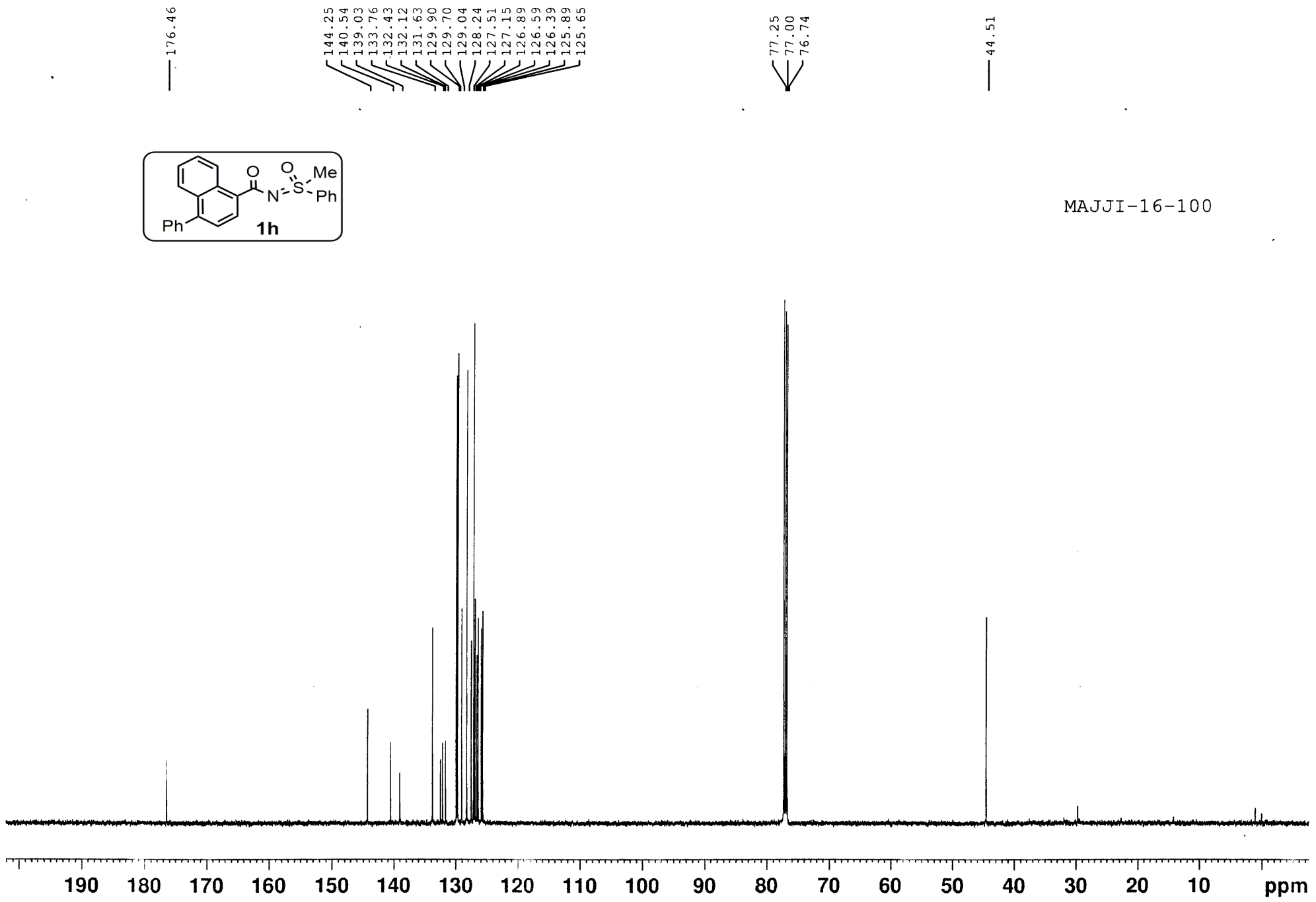


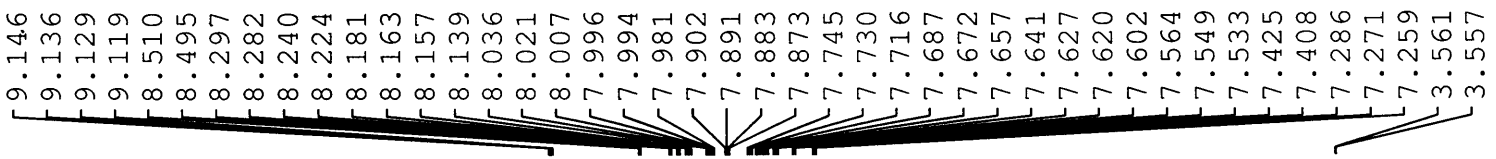
MAJJI-16-100

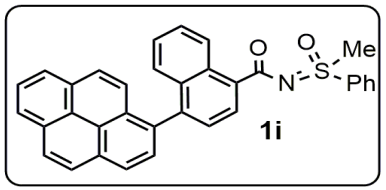


1h

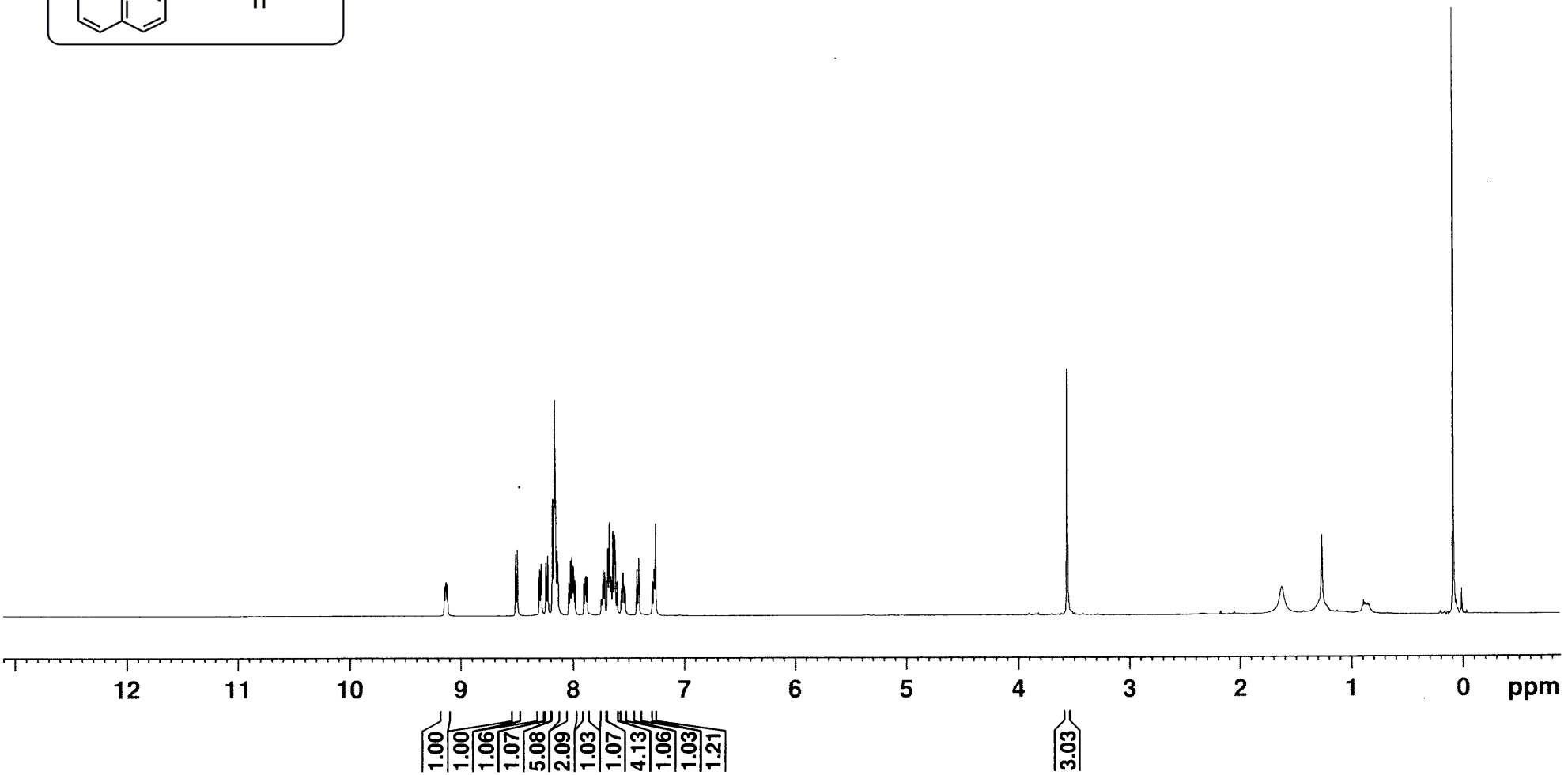


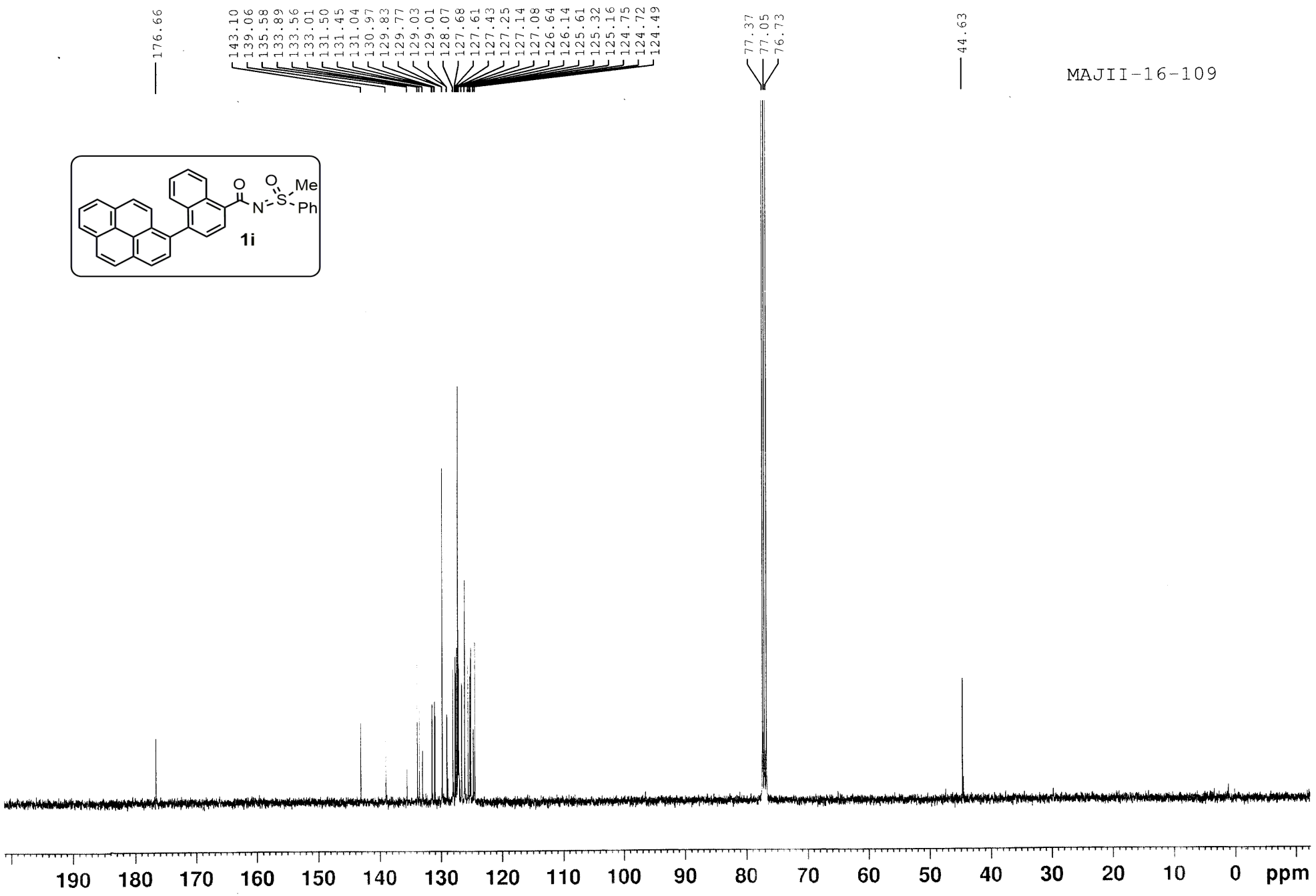

176.46
144.25
140.54
139.03
133.76
132.43
132.12
131.63
129.90
129.70
129.04
128.24
127.51
127.15
126.89
126.59
126.39
125.89
125.65
77.25
77.00
76.74
44.51
O
O
Me
N
S
Ph
Ph
1h
MAJJI-16-100
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

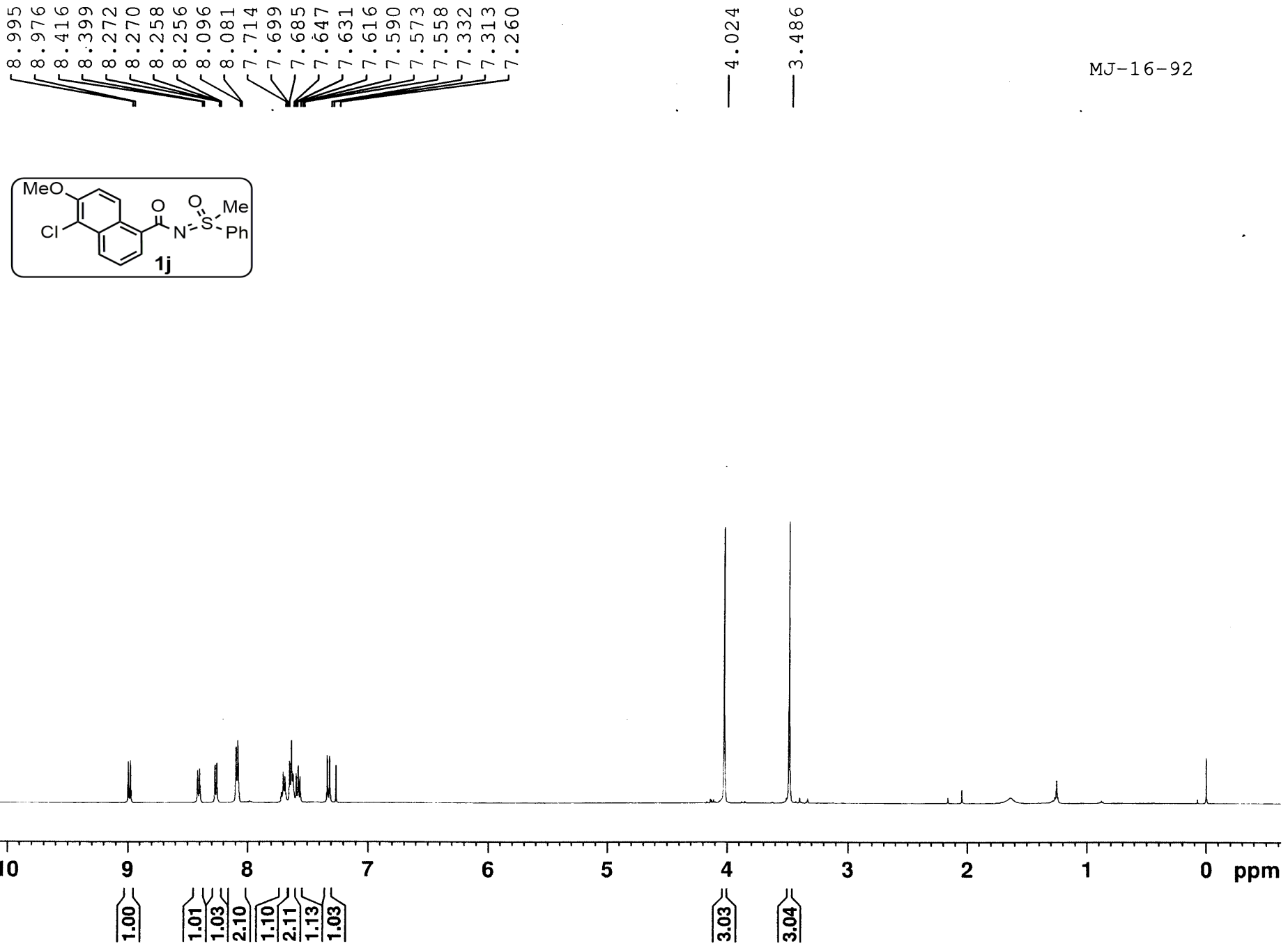


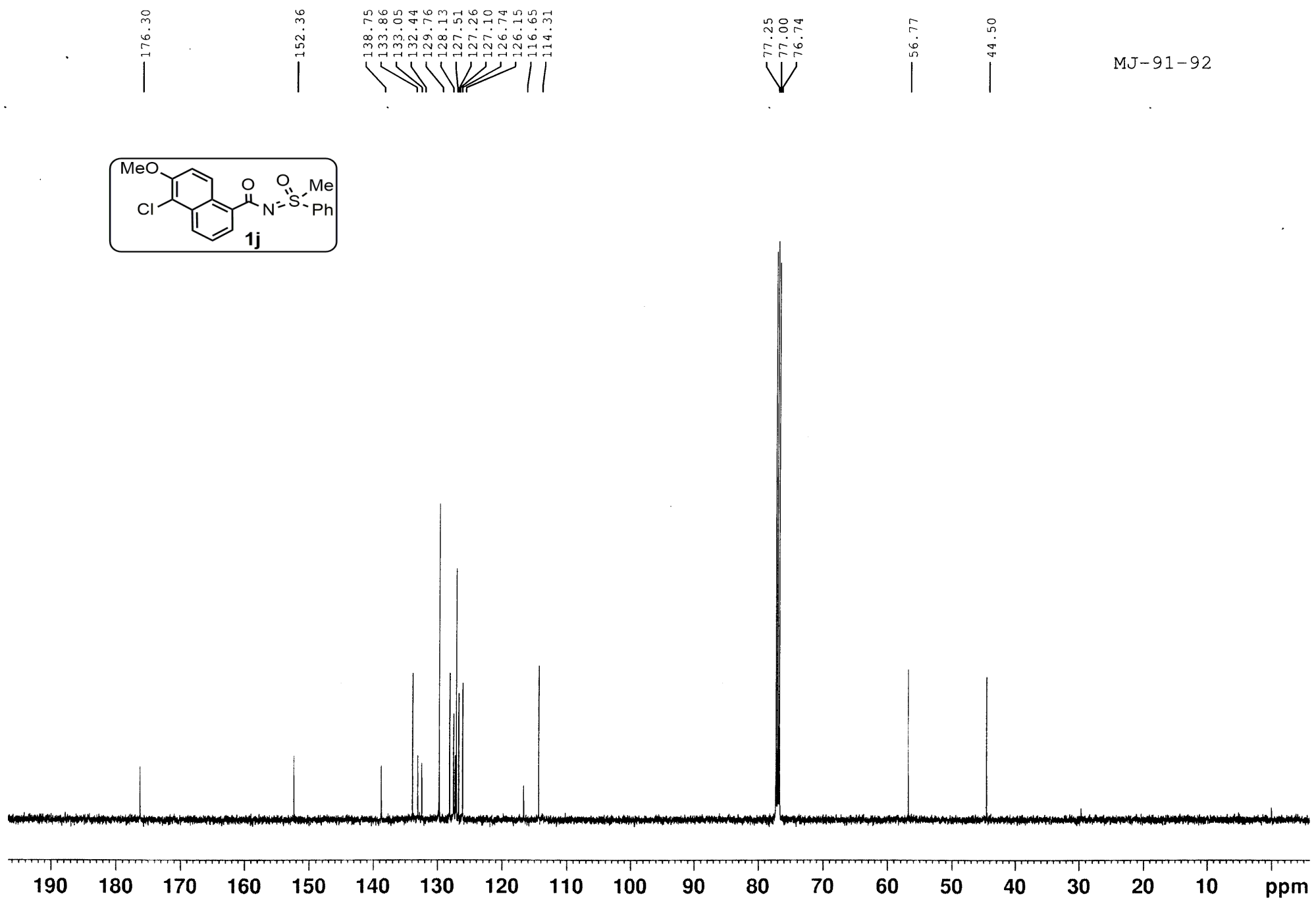


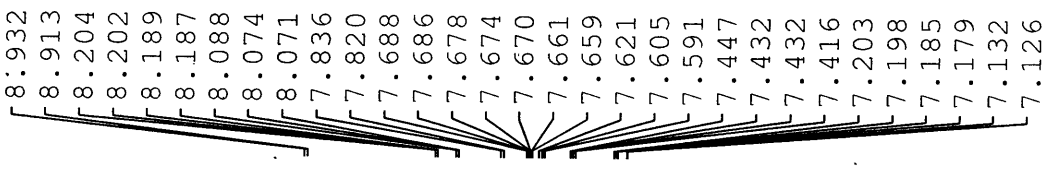
MAJJI-MJ-16-109 R



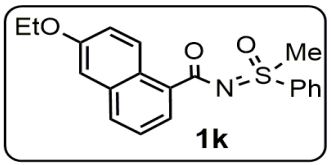

176.66
143.10
139.06
135.58
133.89
133.56
133.01
131.50
131.45
131.04
130.97
129.83
129.77
129.03
129.01
128.07
127.68
127.61
127.43
127.25
127.14
127.08
126.64
126.14
125.61
125.32
125.16
124.75
124.72
124.49
77.37
77.05
76.73
44.63
MAJII-16-109
O
O
Me
N
S
Ph
1i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.995
8.976
8.416
8.399
8.272
8.270
8.258
8.256
8.096
8.081
7.714
7.699
7.685
7.647
7.631
7.616
7.590
7.573
7.558
7.332
7.313
7.260
4.024
3.486
MJ-16-92
MeO
Cl
O
N
O
S
Me
Ph
1j
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.03
2.10
1.10
2.11
1.13
1.03
3.03
3.04

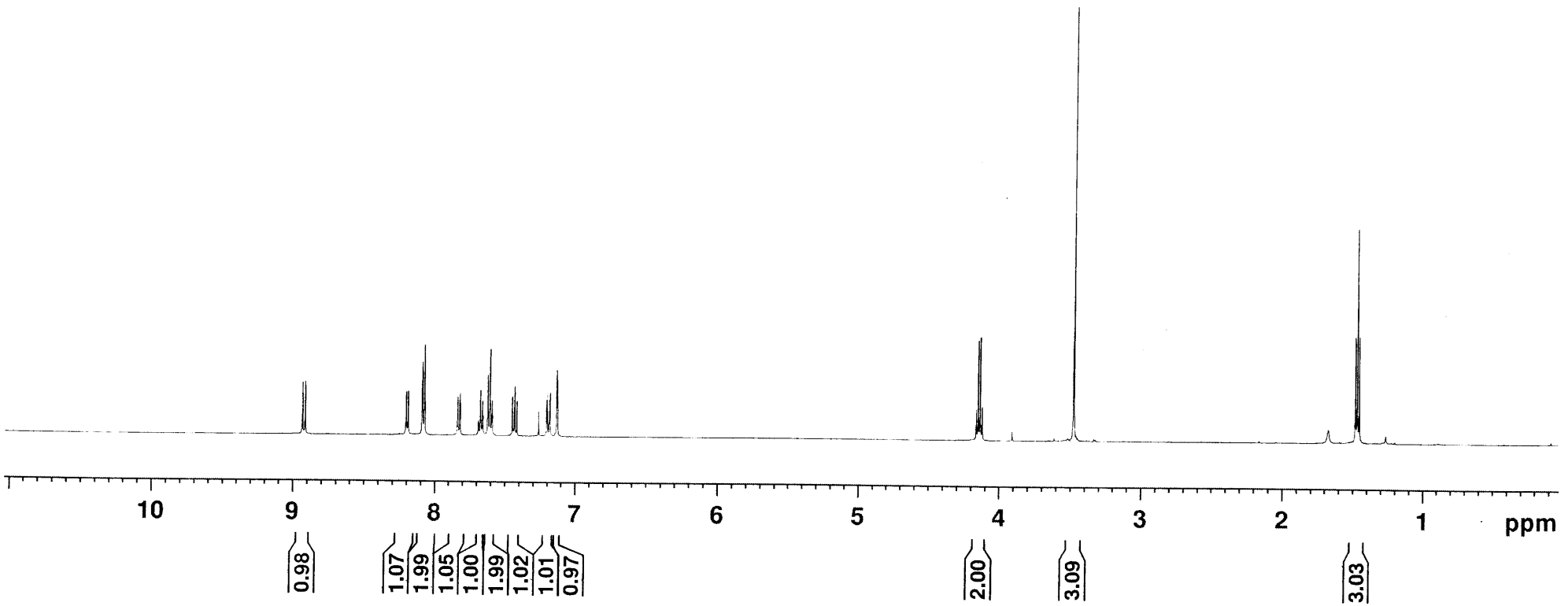

176.30
152.36
138.75
133.86
133.05
132.44
129.76
128.13
127.51
127.26
127.10
126.74
126.15
116.65
114.31
77.25
77.00
76.74
56.77
44.50
MJ-91-92
MeO
Cl
O
N
S
O
Me
Ph
1j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

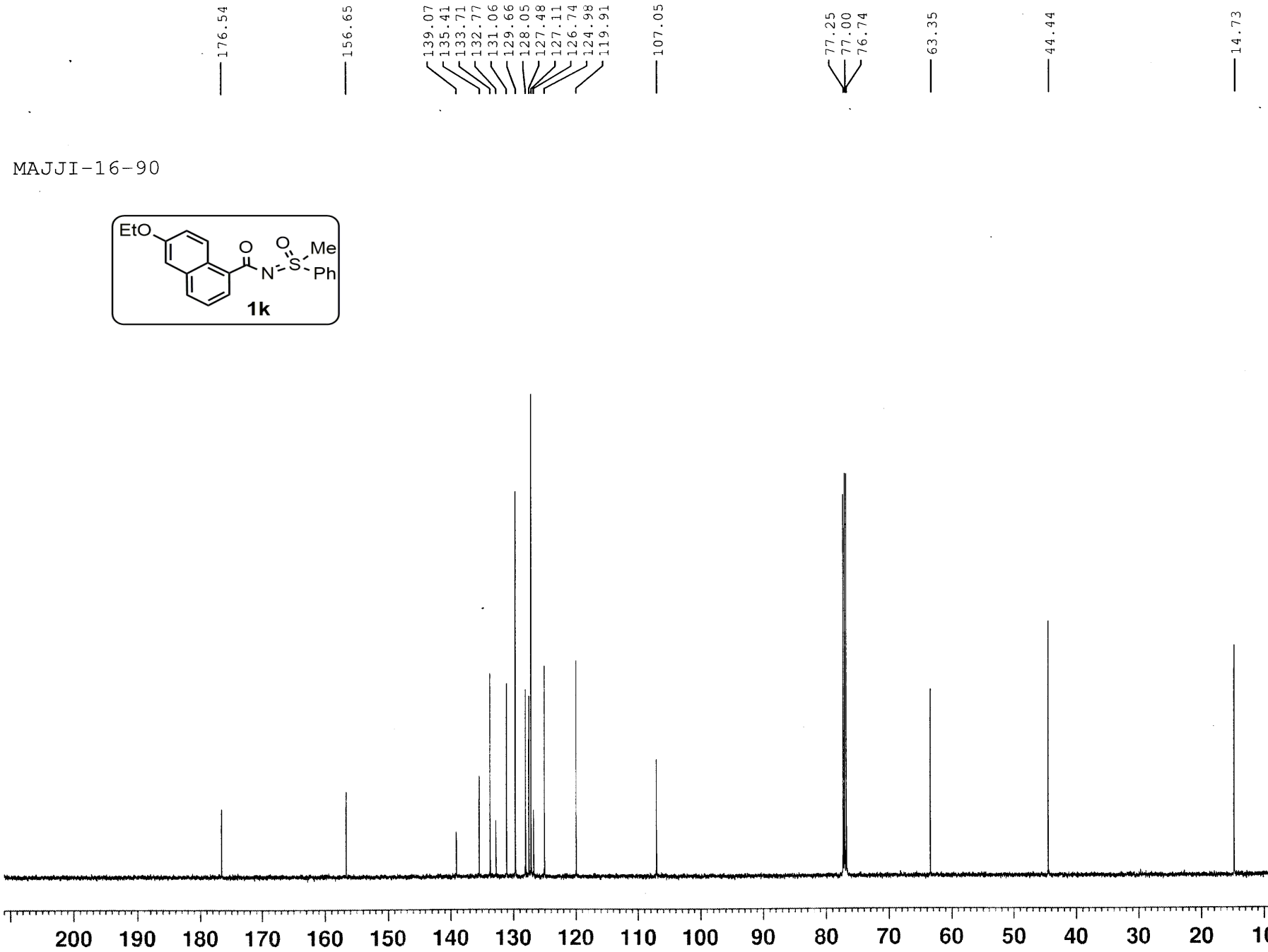


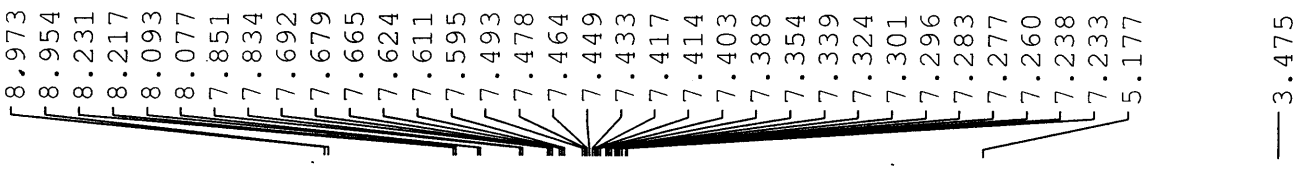
MAJJI-16-90



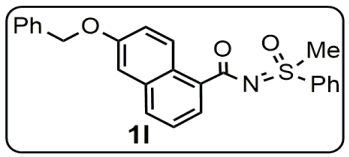
1k



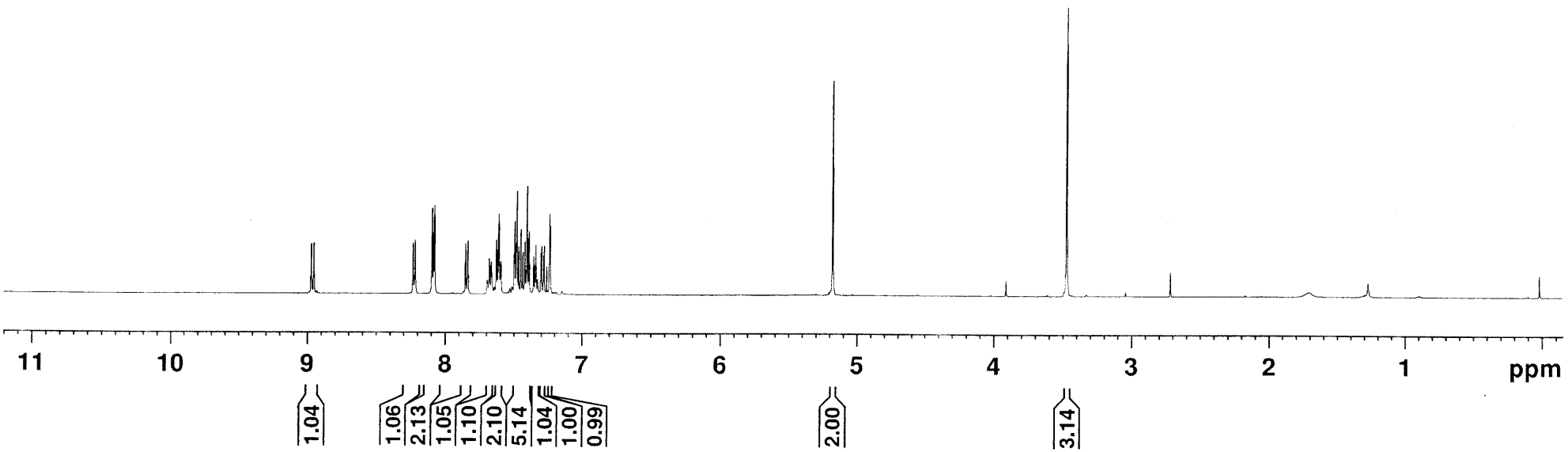

176.54
156.65
139.07
135.41
133.71
132.77
131.06
129.66
128.05
127.48
127.11
126.74
124.98
119.91
107.05
77.25
77.00
76.74
63.35
44.44
14.73
MAJJI-16-90
EtO
O
O
Me
N
S
Ph
1k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

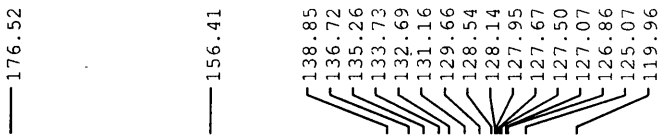

8.973
8.954
8.231
8.217
8.093
8.077
7.851
7.834
7.692
7.679
7.665
7.624
7.611
7.595
7.493
7.478
7.464
7.449
7.433
7.417
7.414
7.403
7.388
7.354
7.339
7.324
7.301
7.296
7.283
7.277
7.260
7.238
7.233
5.177
3.475

MJ-91-16 R

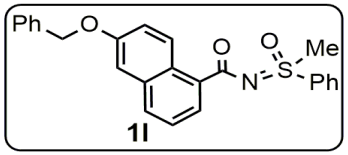

Ph
O
O
Me
N
S
Ph

1l

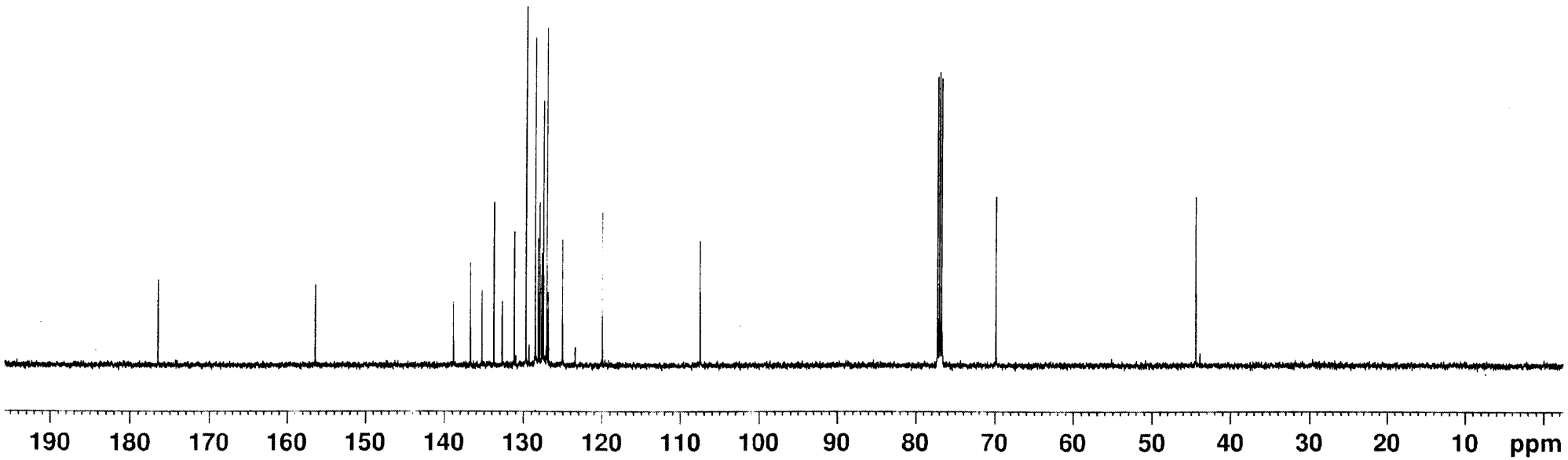

11
10
9
8
7
6
5
4
3
2
1
ppm
1.04
1.06
2.13
1.05
1.10
2.10
5.14
1.04
1.00
0.99
2.00
3.14

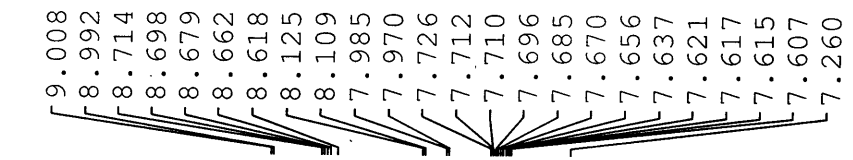

176.52
156.41
138.85
136.72
135.26
133.73
132.69
131.16
129.66
128.54
128.14
127.95
127.67
127.50
127.07
126.86
125.07
119.96
77.25
77.00
76.74
69.83
44.40

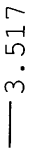
MJ-91-16 R


Ph
O
O
O
N
S
Me
Ph

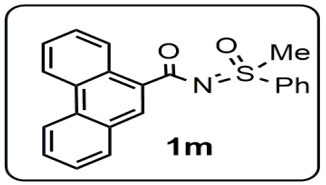
1l

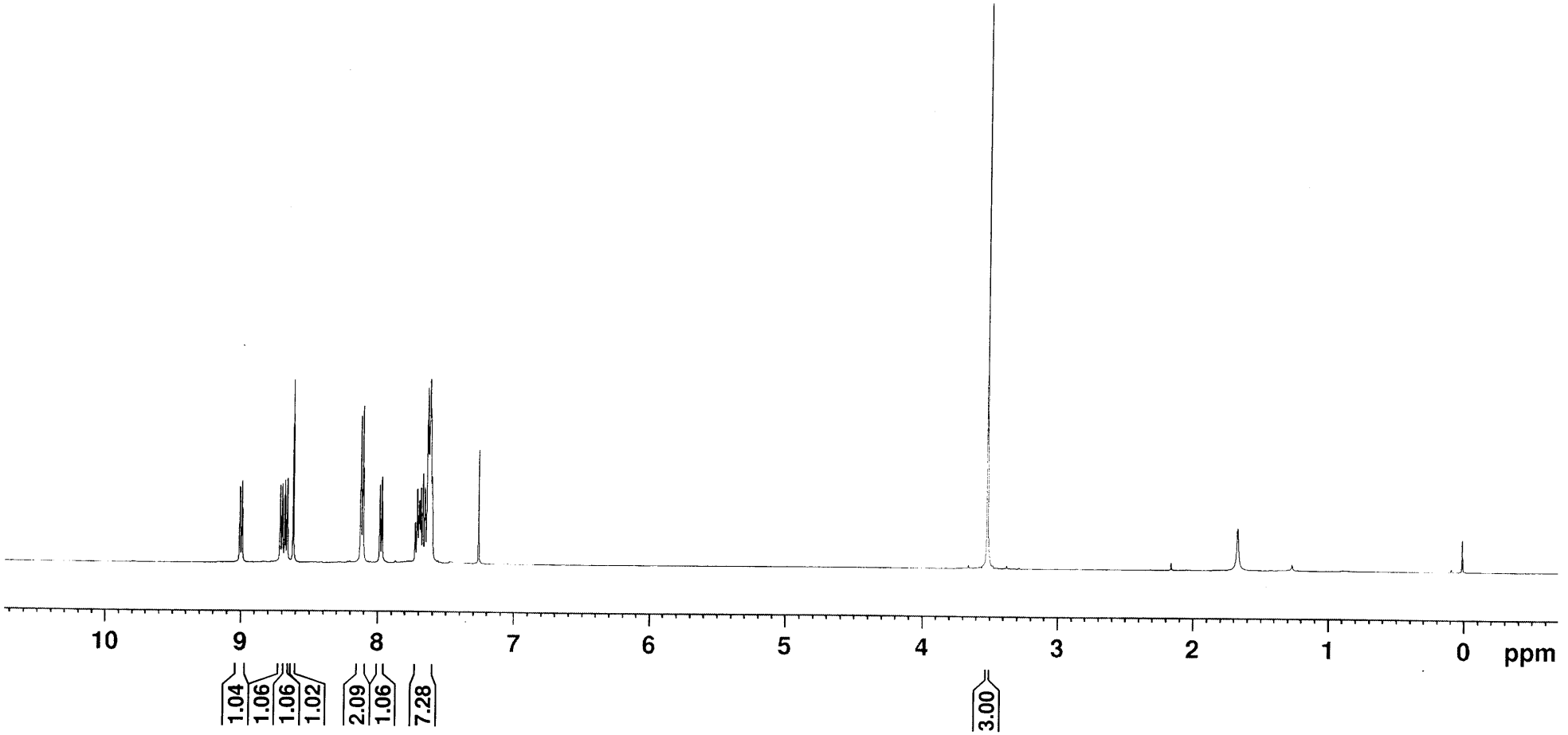

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


9.008
8.992
8.714
8.698
8.679
8.662
8.618
8.125
8.109
7.985
7.970
7.726
7.712
7.710
7.696
7.685
7.670
7.656
7.637
7.621
7.617
7.615
7.607
7.260


3.517

MJ-198-14


O
O
Me
N
S
Ph
1m


10
9
8
7
6
5
4
3
2
1
0
ppm
1.04
1.06
1.06
1.02
2.09
1.06
7.28
3.00

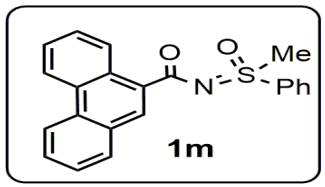
MJ- 198-14

176.50

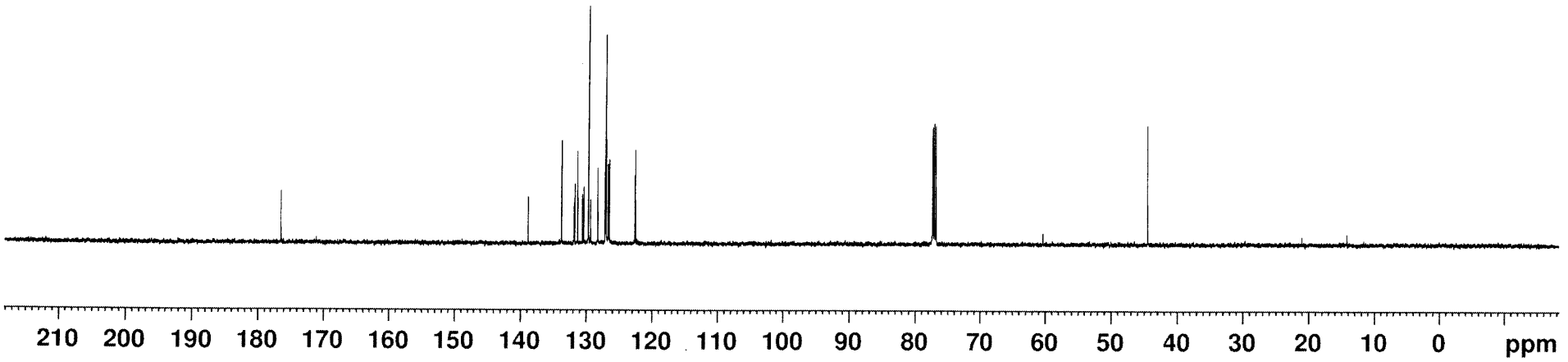
138.78
133.76
131.85
131.77
131.32
130.64
130.34
129.72
129.68
129.33
128.23
127.13
127.05
126.96
126.71
126.51
122.58
122.51

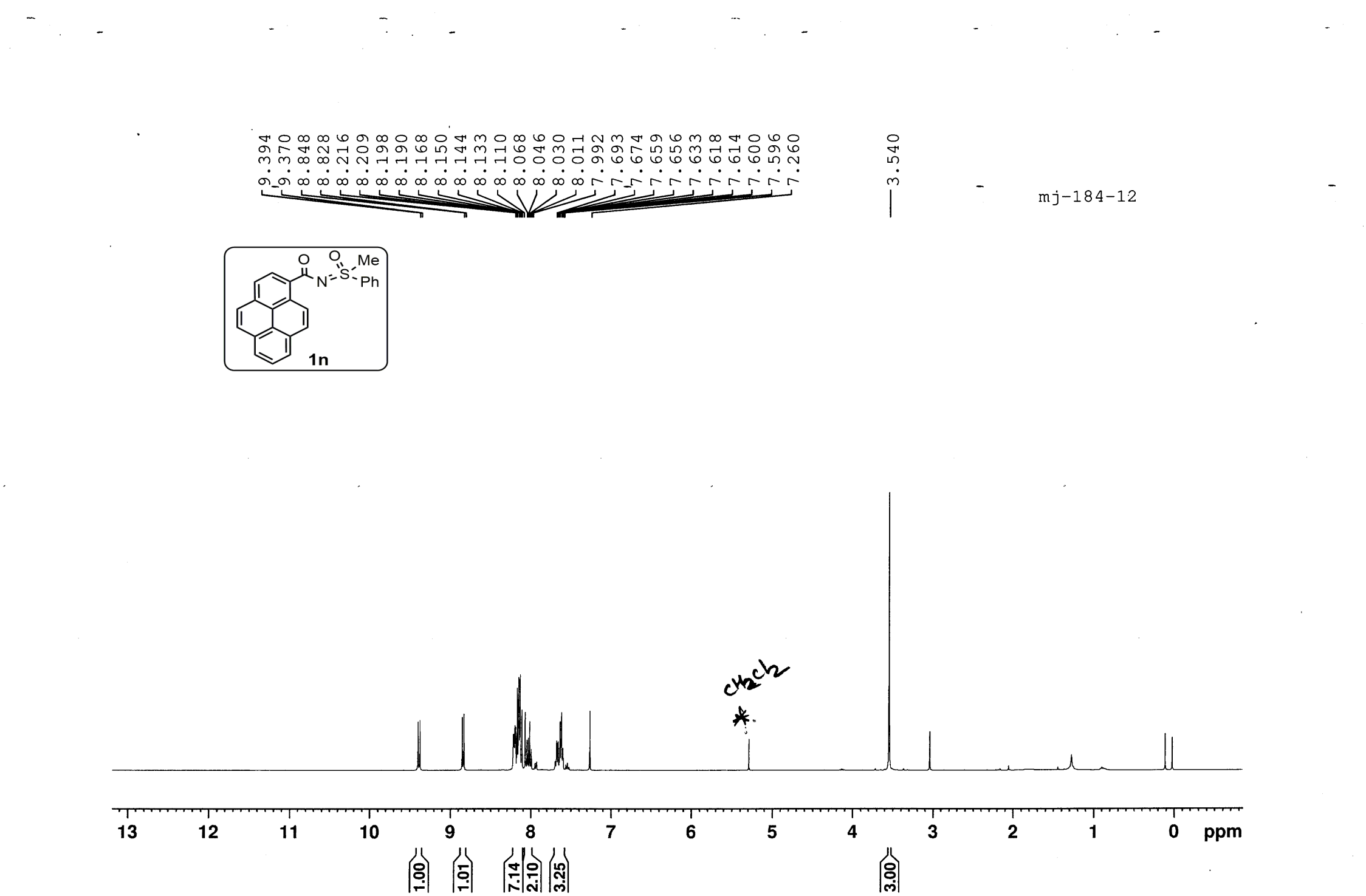
77.25
77.00
76.75

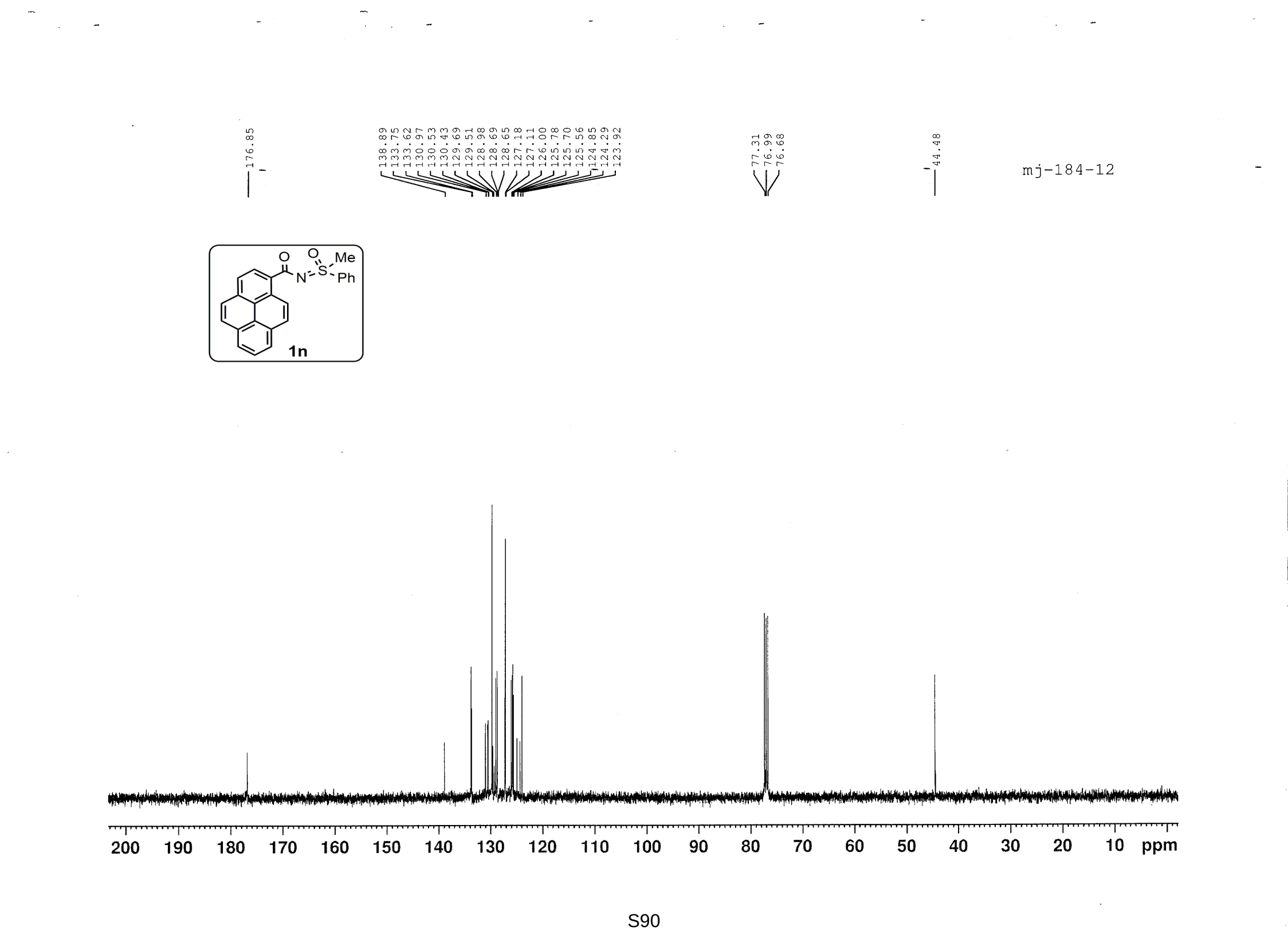
44.42

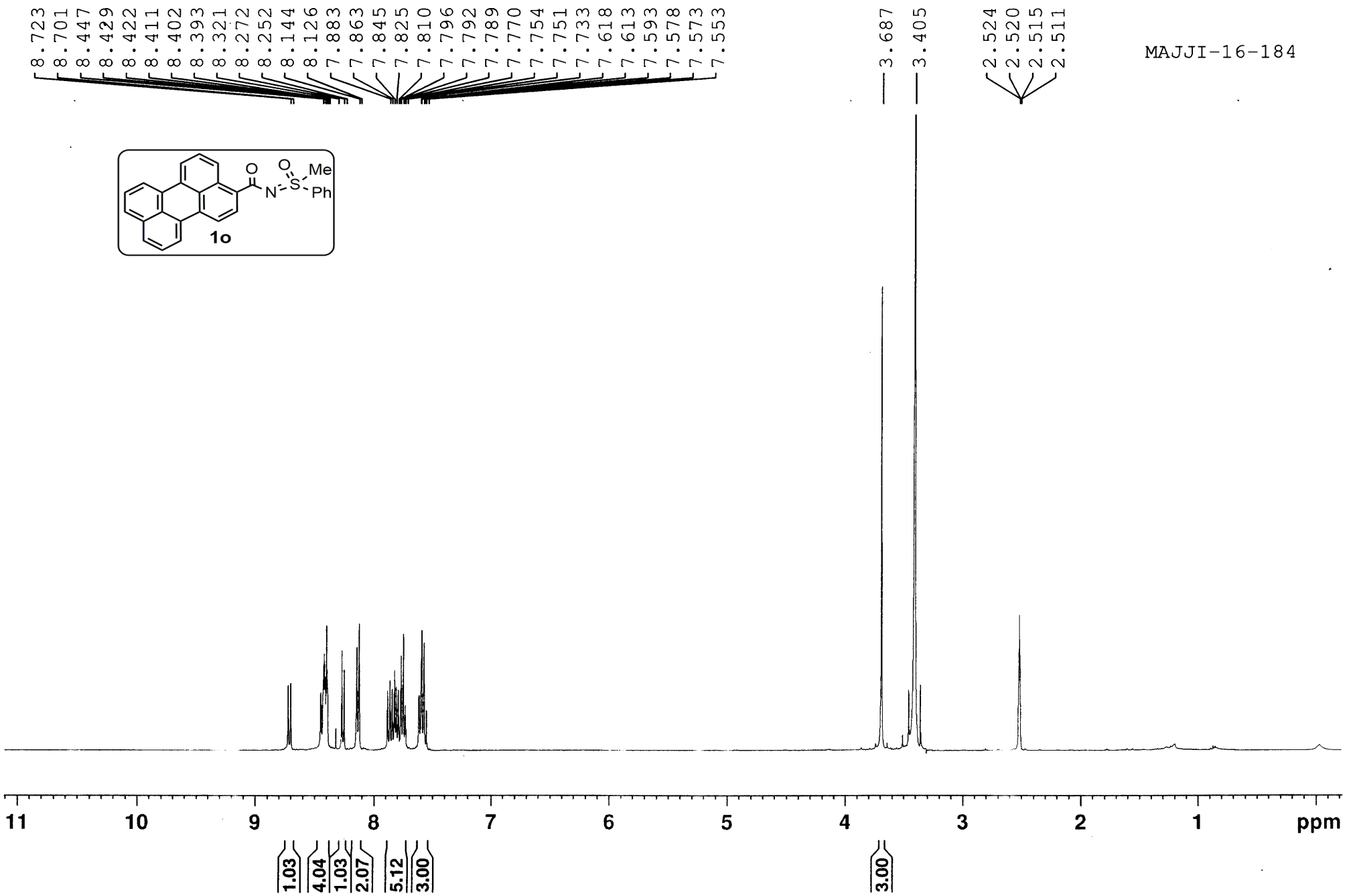


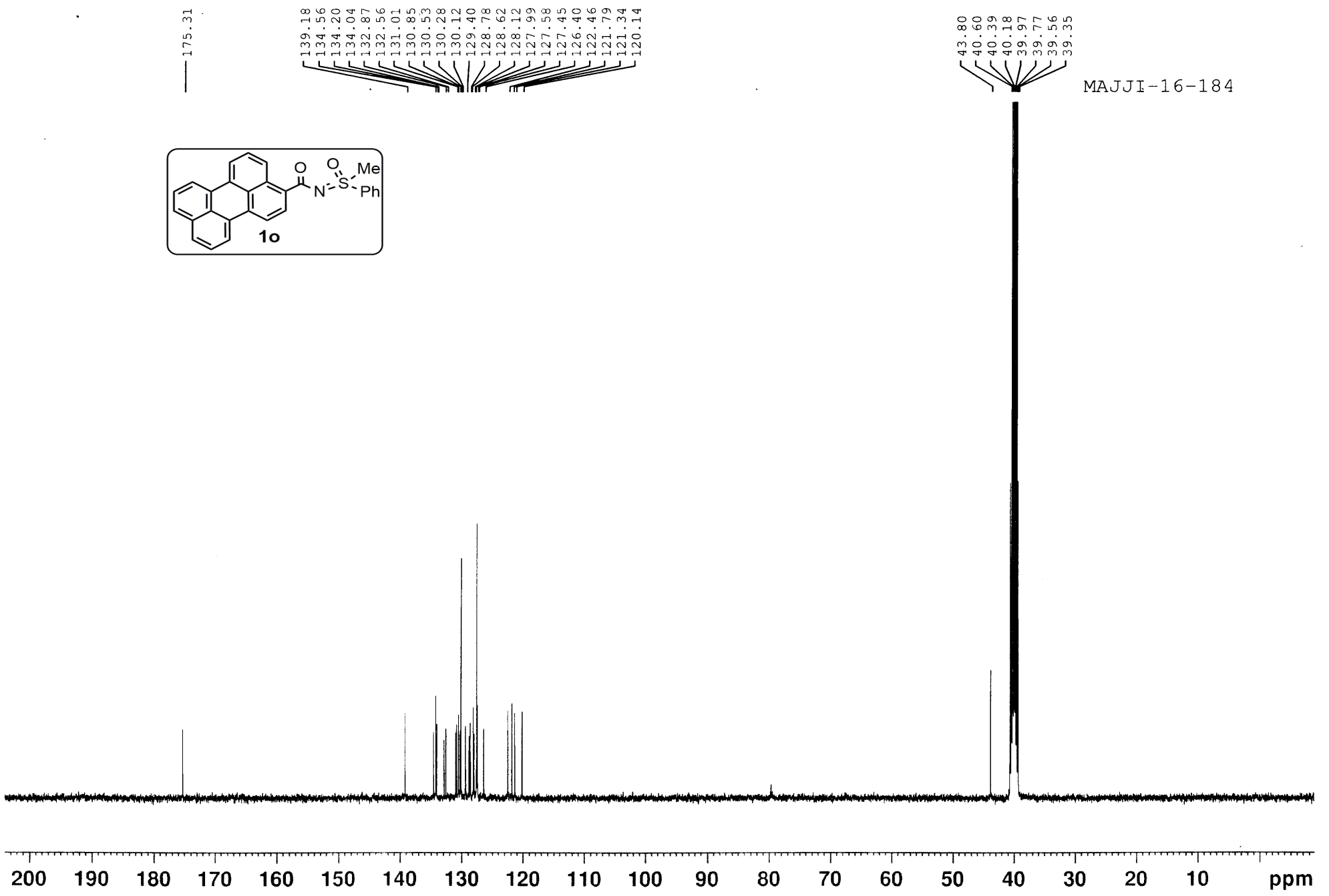
1m

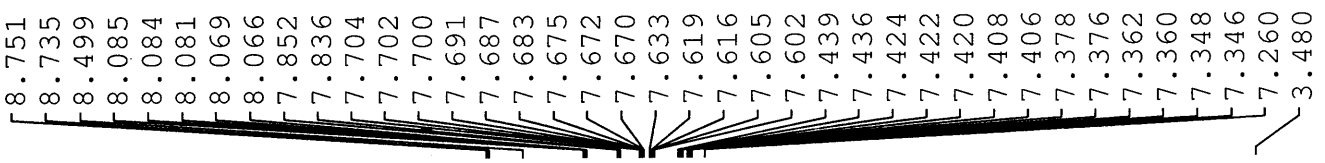


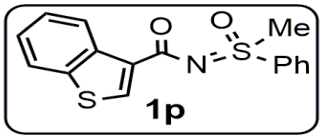

9.394
9.370
8.848
8.828
8.216
8.209
8.198
8.190
8.168
8.150
8.144
8.133
8.110
8.068
8.046
8.030
8.011
7.992
7.693
7.674
7.659
7.656
7.633
7.618
7.614
7.600
7.596
7.260
3.540
mj-184-12
O
O
Me
N
S
Ph
1n
CH2Cl2
*
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
7.14
2.10
3.25
3.00


176.85
138.89
133.75
133.62
130.97
130.53
130.43
129.69
129.51
128.98
128.69
128.65
127.18
127.11
126.00
125.78
125.70
125.56
124.85
124.29
123.92
77.31
76.99
76.68
44.48
mj-184-12
O
O
Me
N
S
Ph
1n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.723
8.701
8.447
8.429
8.422
8.411
8.402
8.393
8.321
8.272
8.252
8.144
8.126
7.883
7.863
7.845
7.825
7.810
7.796
7.792
7.789
7.770
7.754
7.751
7.733
7.618
7.613
7.593
7.578
7.573
7.553
3.687
3.405
2.524
2.520
2.515
2.511
MAJJI-16-184
O
O
Me
N
S
Ph
1o
11
10
9
8
7
6
5
4
3
2
1
ppm
1.03
4.04
1.03
2.07
5.12
3.00
3.00

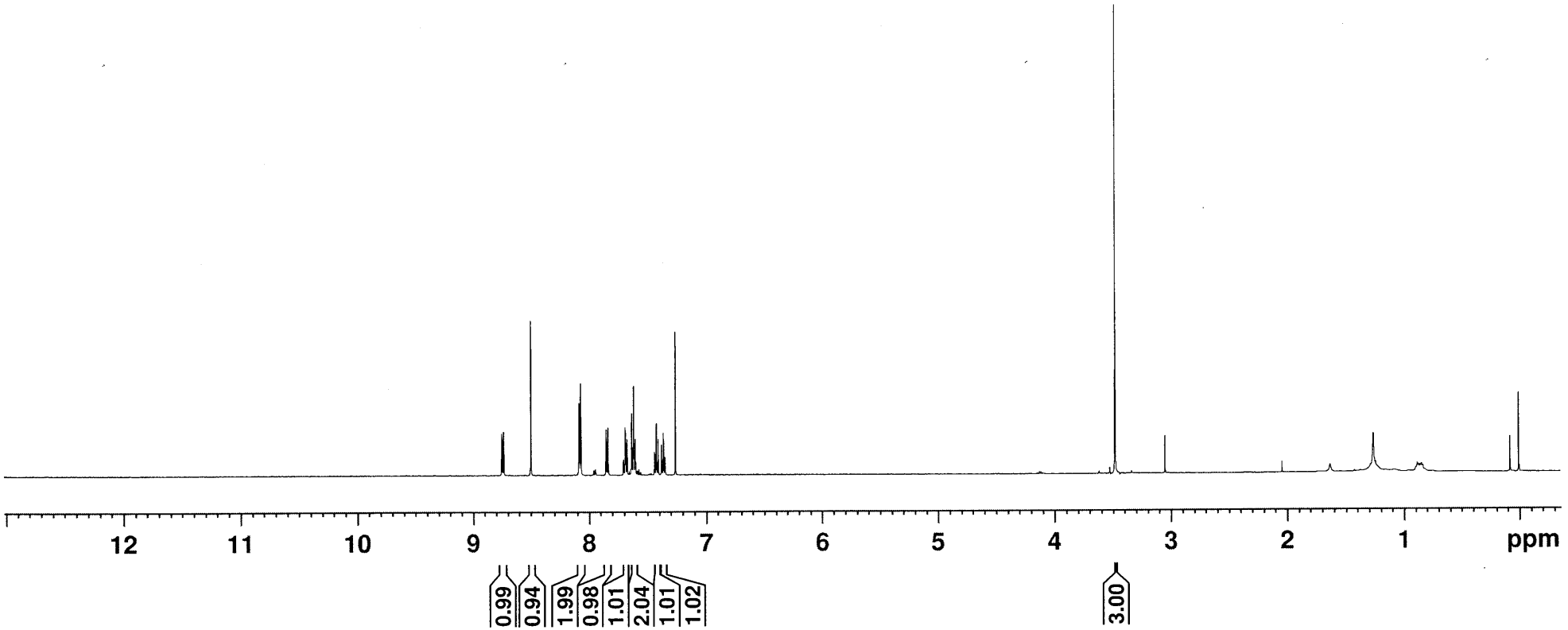

175.31
139.18
134.56
134.20
134.04
132.87
132.56
131.01
130.85
130.53
130.28
130.12
129.40
128.78
128.62
128.12
127.99
127.58
127.45
126.40
122.46
121.79
121.34
120.14
43.80
40.60
40.39
40.18
39.97
39.77
39.56
39.35
MAJJI-16-184
O
O
Me
N
S
Ph
1o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

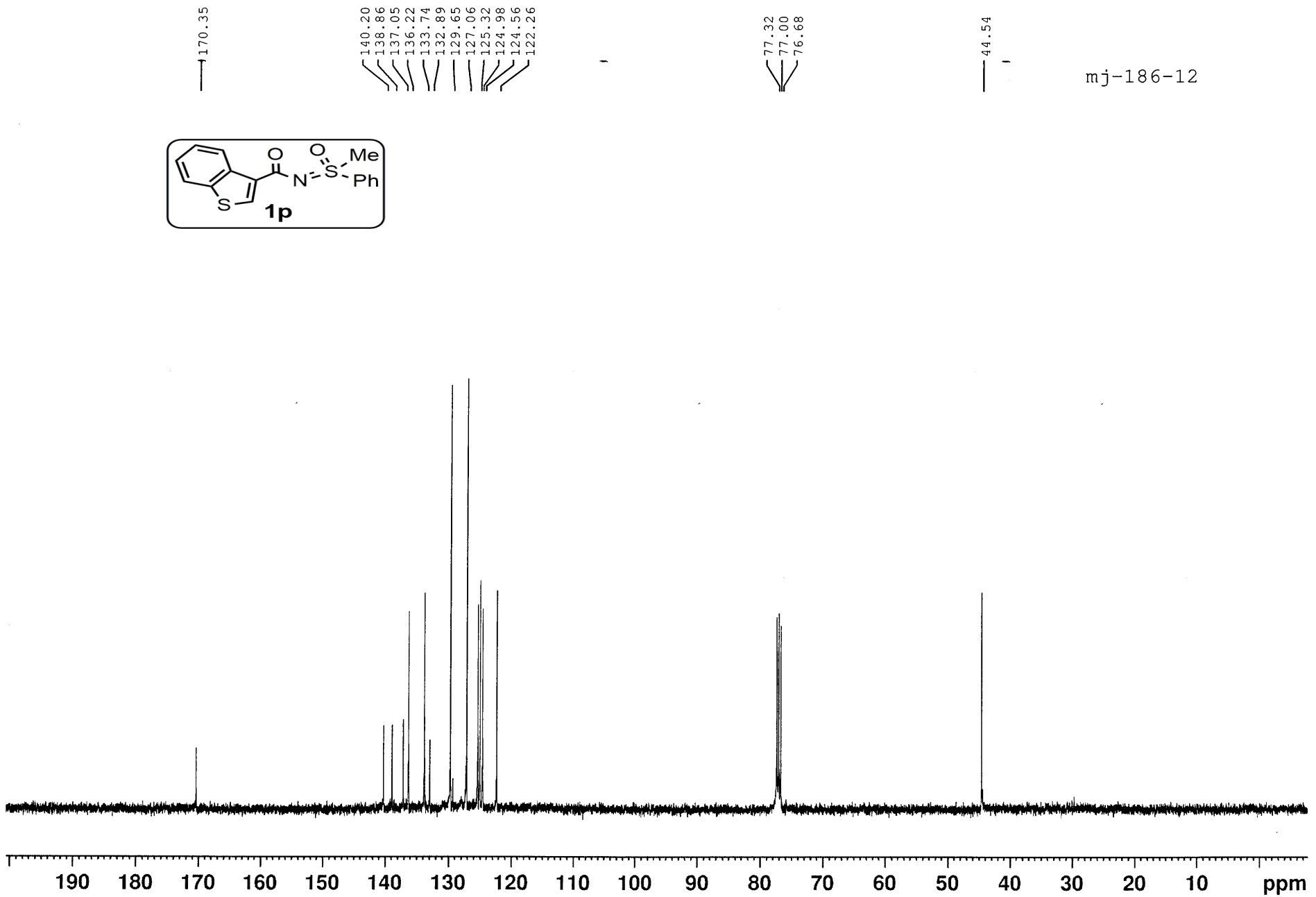

8.751
8.735
8.499
8.085
8.084
8.081
8.069
8.066
7.852
7.836
7.704
7.702
7.700
7.691
7.687
7.683
7.675
7.672
7.670
7.633
7.619
7.616
7.605
7.602
7.439
7.436
7.424
7.422
7.420
7.408
7.406
7.378
7.376
7.362
7.360
7.348
7.346
7.260
3.480

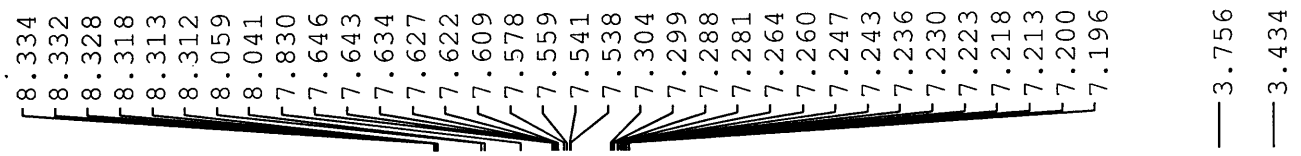

O
O
Me
N
S
Ph
S

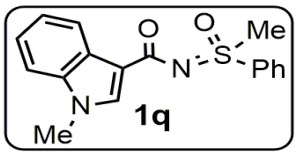
1p

MJ- 186-12

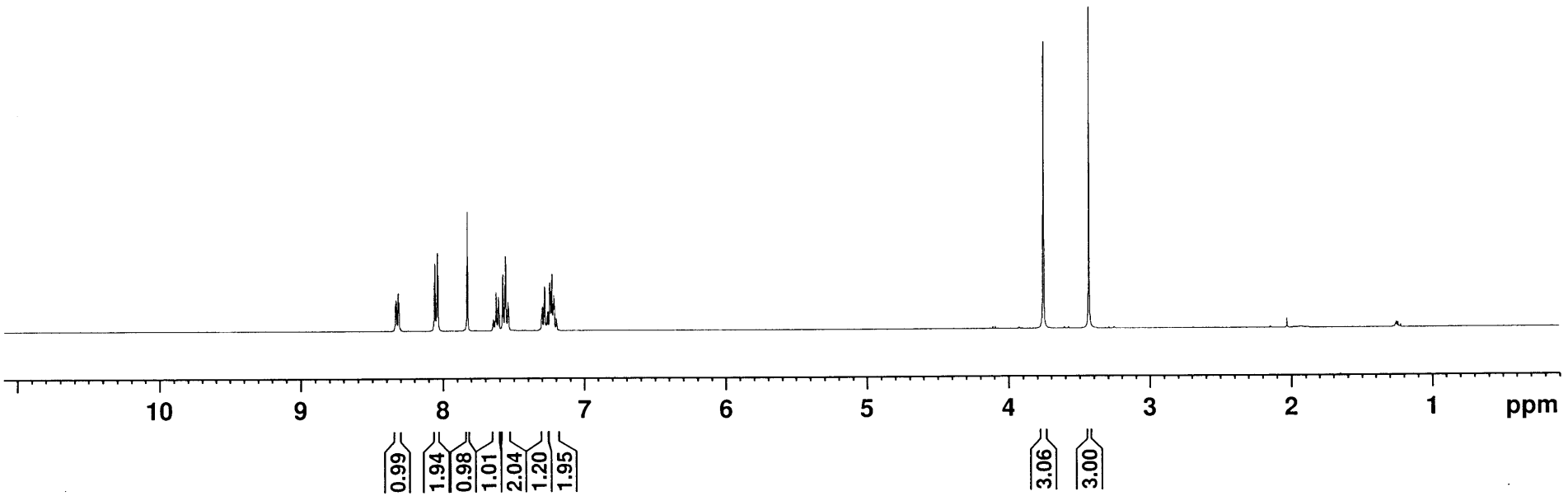

12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.99
0.94
1.99
0.98
1.01
2.04
1.01
1.02
3.00

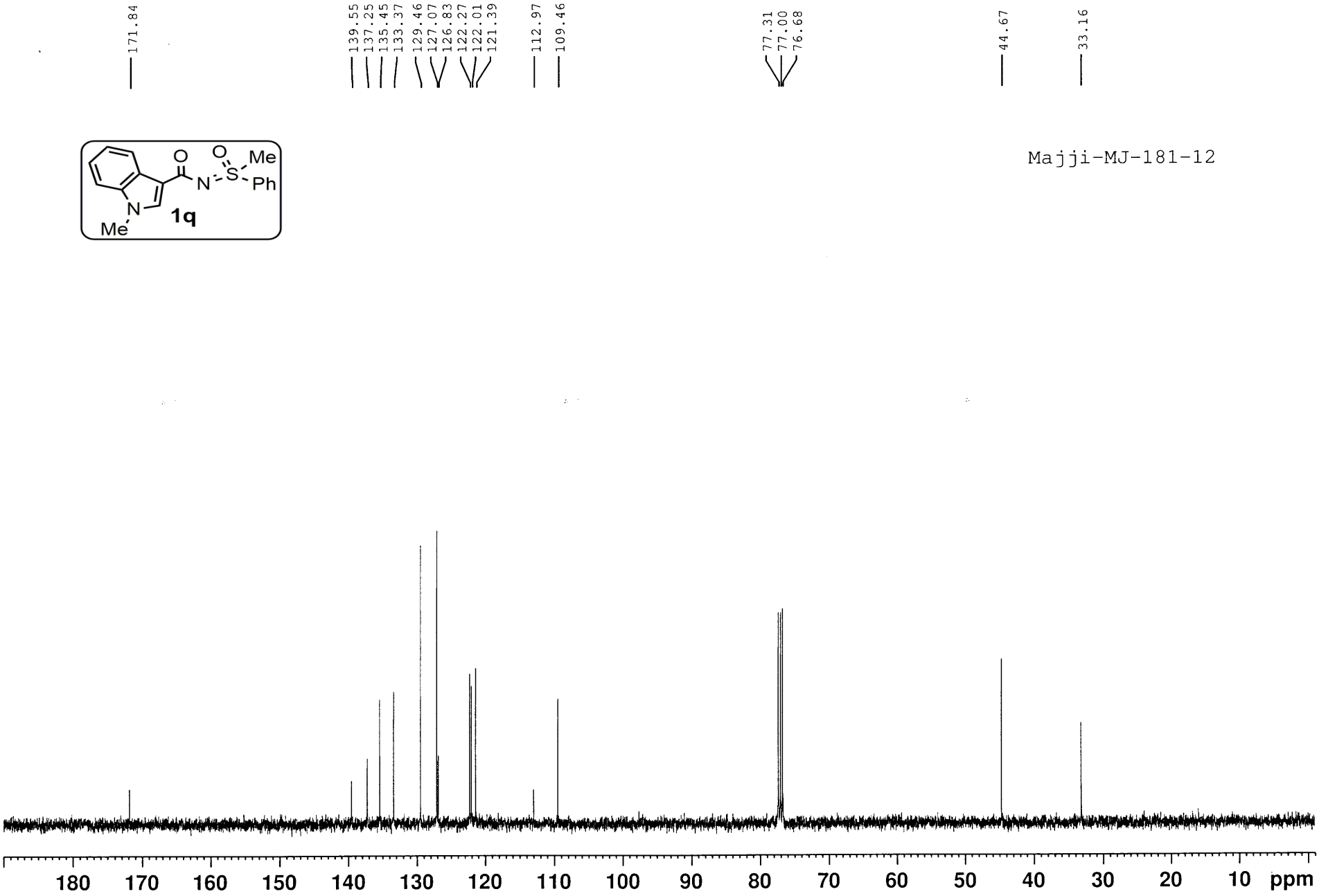

170.35
140.20
138.86
137.05
136.22
133.74
132.89
129.65
127.06
125.32
124.98
124.56
122.26
77.32
77.00
76.68
44.54
mj-186-12
O
O
Me
N
S
Ph
S
1p
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

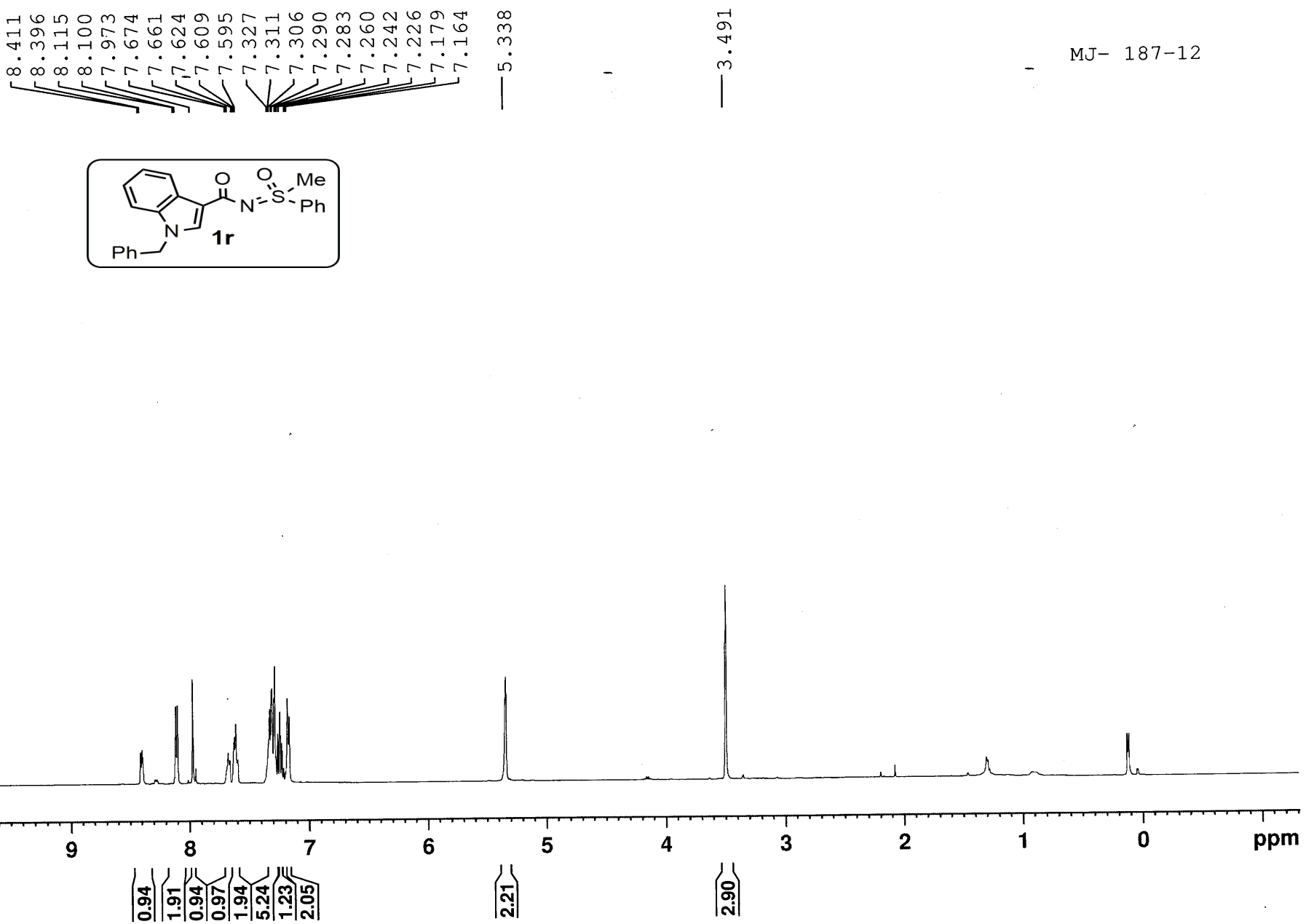




Majji-MJ-181-12

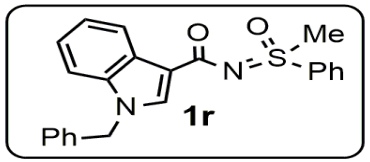



171.84
139.55
137.25
135.45
133.37
129.46
127.07
126.83
122.27
122.01
121.39
112.97
109.46
77.31
77.00
76.68
44.67
33.16
Me
Ph
1q
Majji-MJ-181-12
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

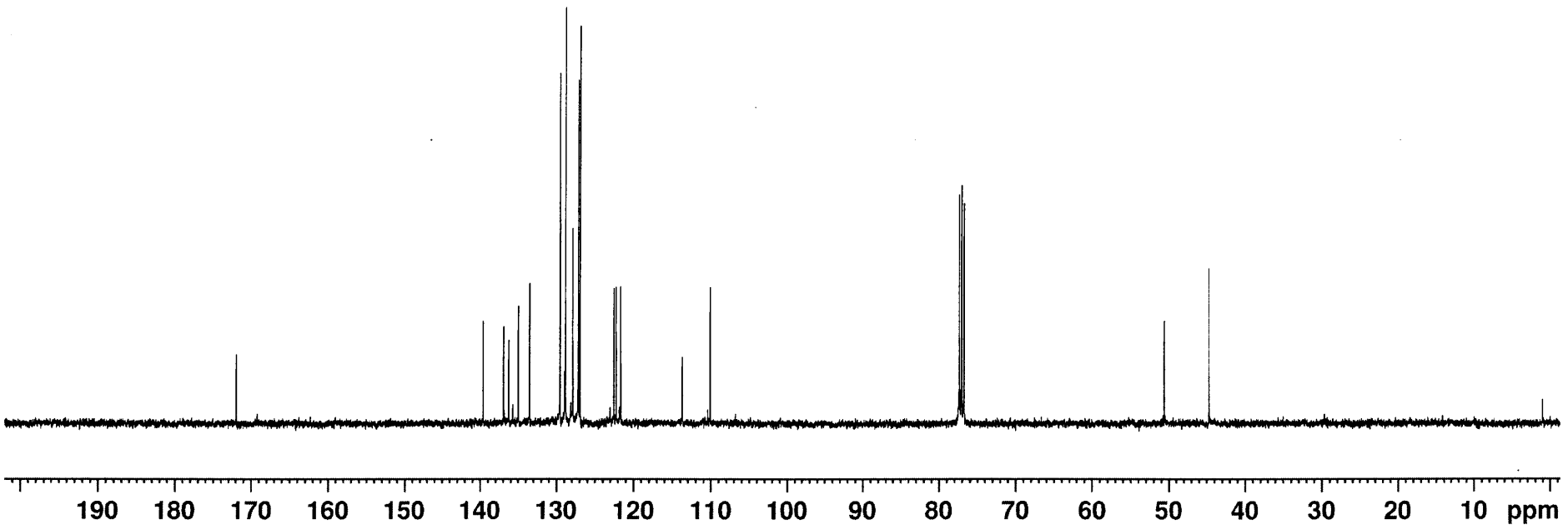

8.411
8.396
8.115
8.100
7.973
7.674
7.661
7.624
7.609
7.595
7.327
7.311
7.306
7.290
7.283
7.260
7.242
7.226
7.179
7.164
5.338
3.491
MJ- 187-12
Me
Ph
Ph
1r
10
9
8
7
6
5
4
3
2
1
0
ppm
0.94
1.91
0.94
0.97
1.94
5.24
1.23
2.05
2.21
2.90

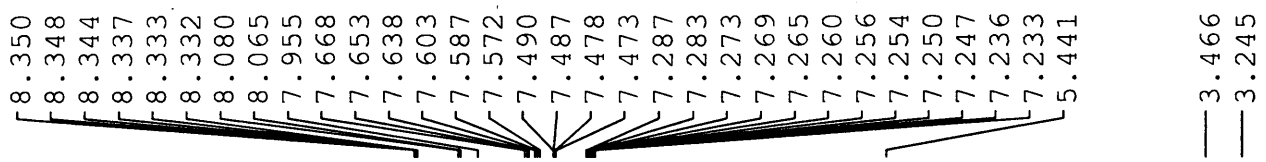
171.93
139.56
136.85
136.19
134.93
133.44
129.52
128.80
127.85
127.13
126.87
122.52
122.22
121.62
113.69
110.07
77.32
77.00
76.68
50.53
44.68

mj-187-12

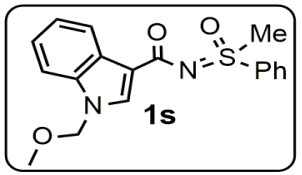


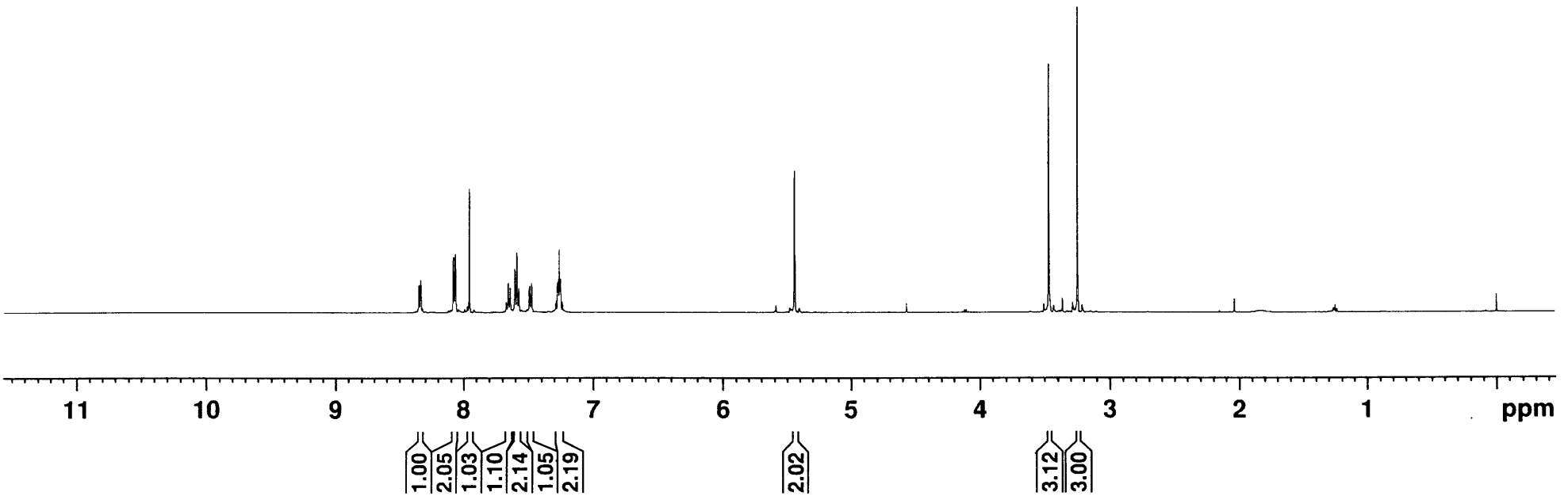
1r

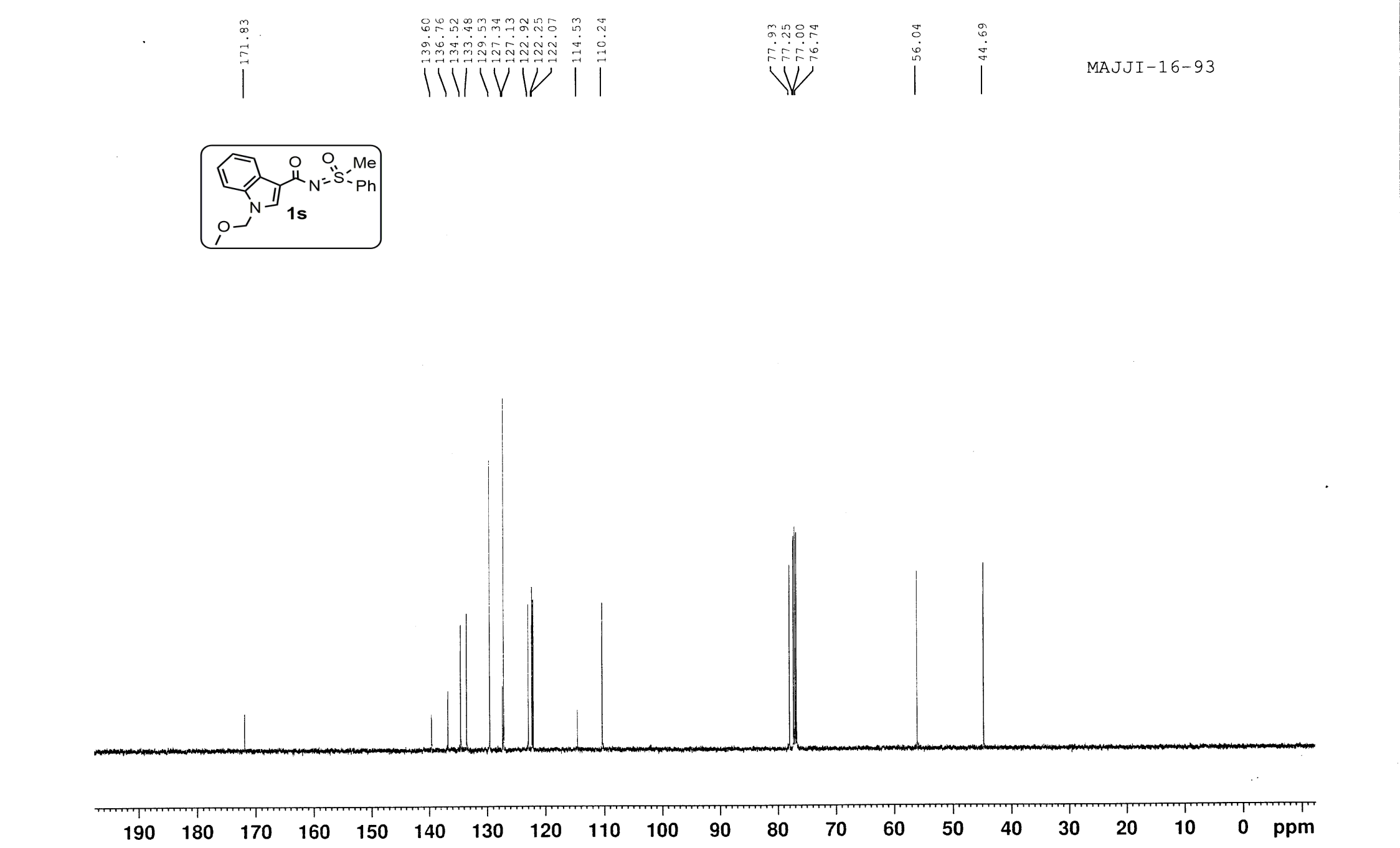


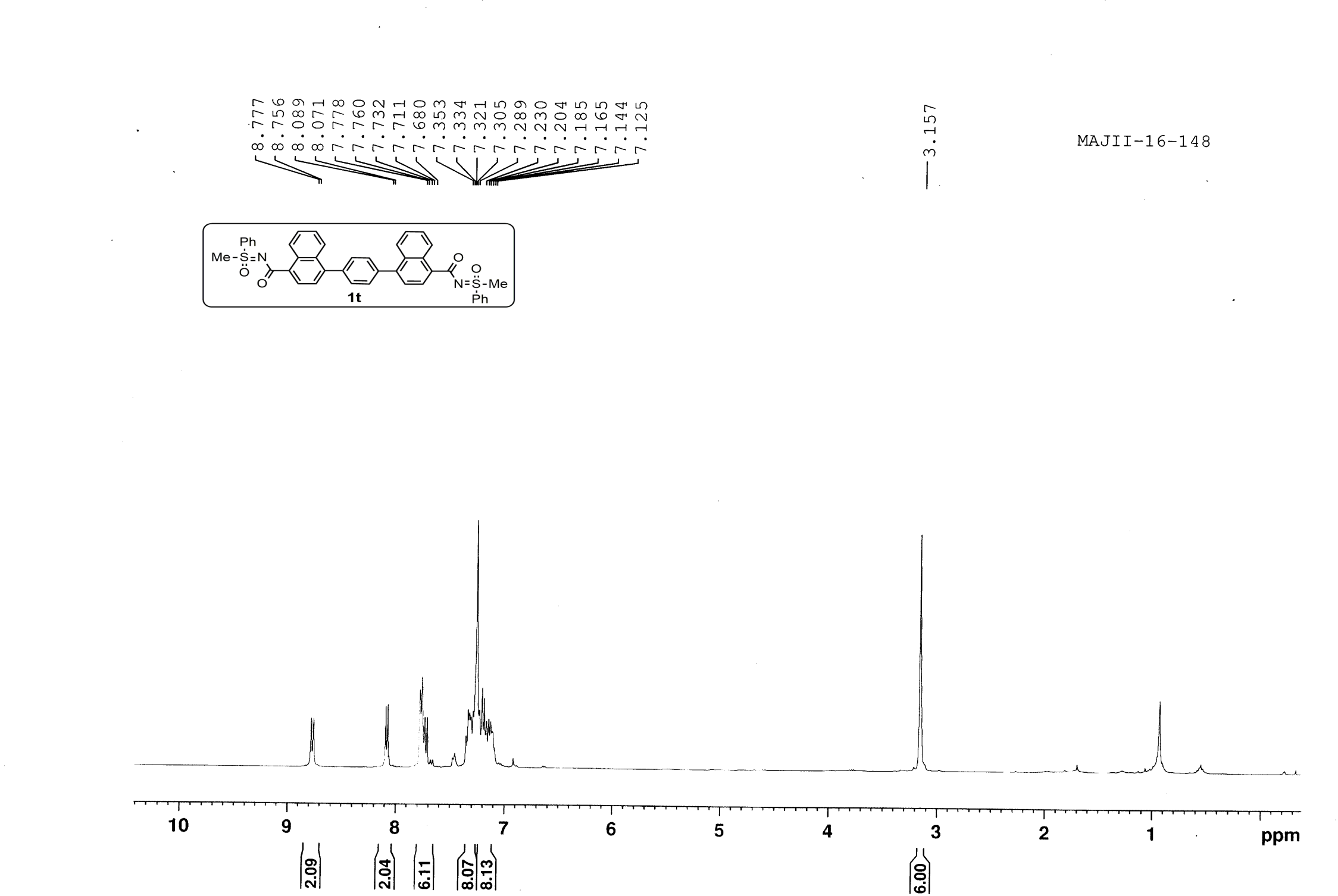

8.350
8.348
8.344
8.337
8.333
8.332
8.080
8.065
7.955
7.668
7.653
7.638
7.603
7.587
7.572
7.490
7.487
7.478
7.473
7.287
7.283
7.273
7.269
7.265
7.260
7.256
7.254
7.250
7.247
7.236
7.233
5.441
3.466
3.245

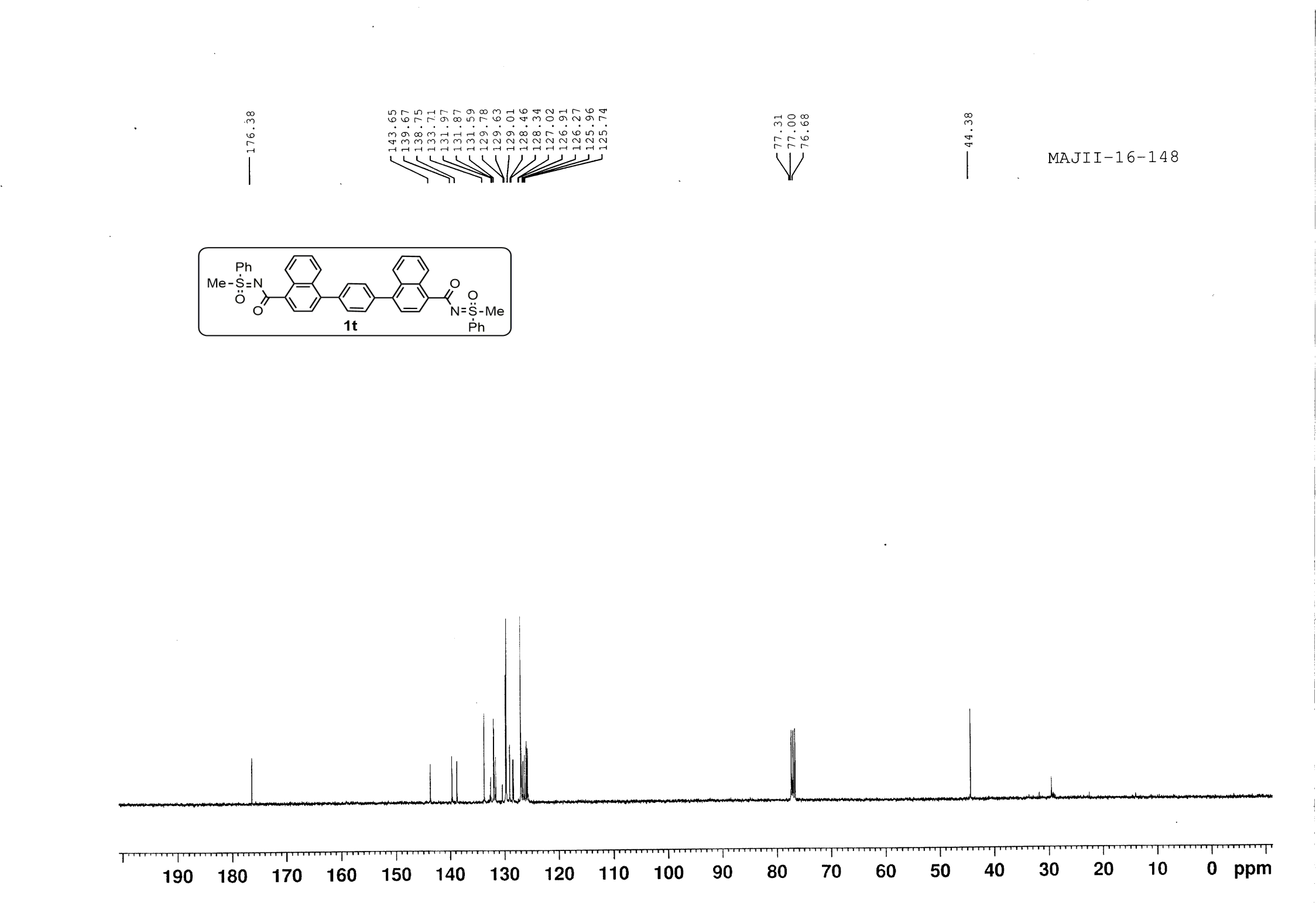
MAJJI-16-93

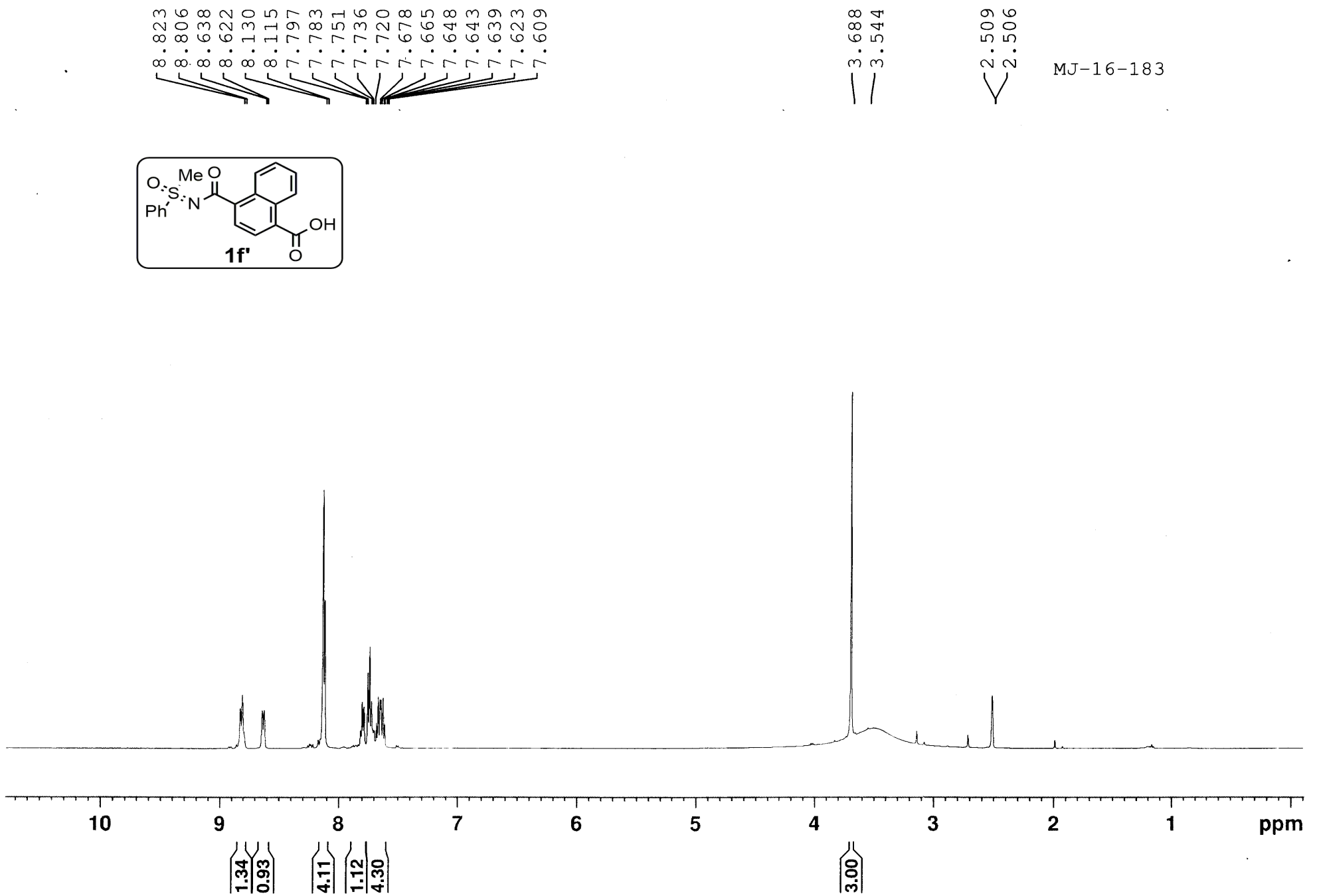

O
O
Me
N
S
Ph
N
O
1s

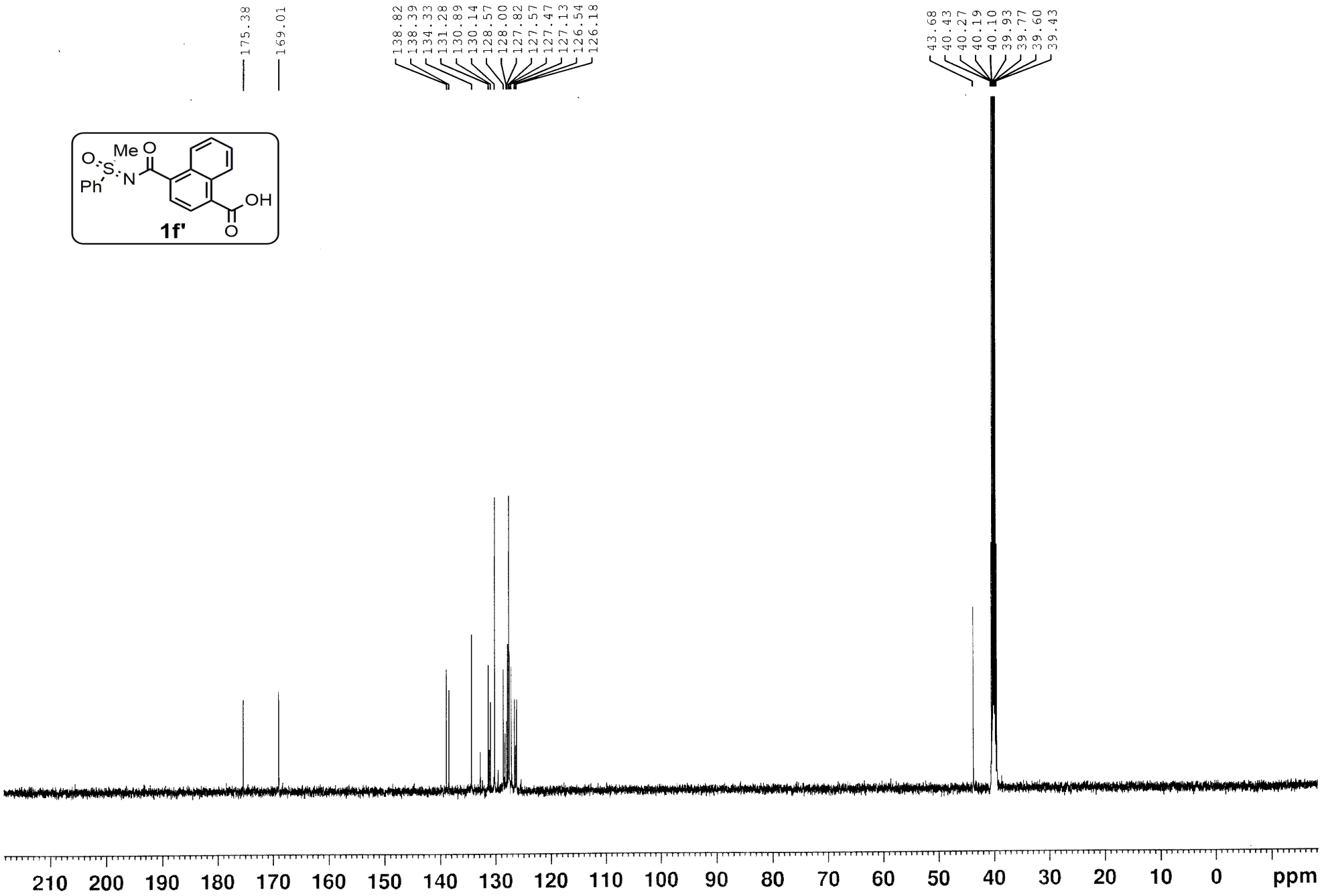

11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.05
1.03
1.10
2.14
1.05
2.19
2.02
3.12
3.00

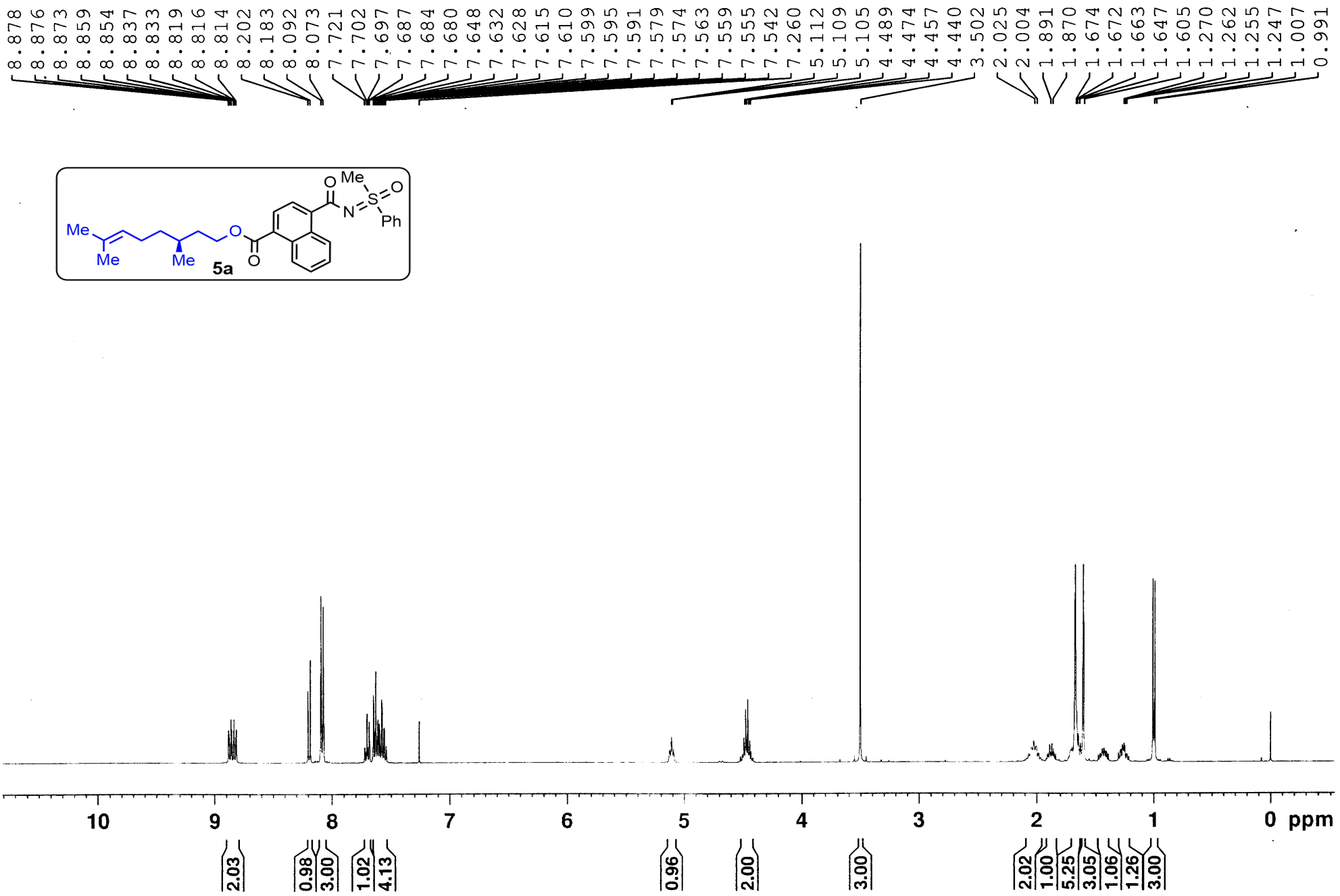

171.83
139.60
136.76
134.52
133.48
129.53
127.34
127.13
122.92
122.25
122.07
114.53
110.24
77.93
77.25
77.00
76.74
56.04
44.69
MAJJI-16-93
1s
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

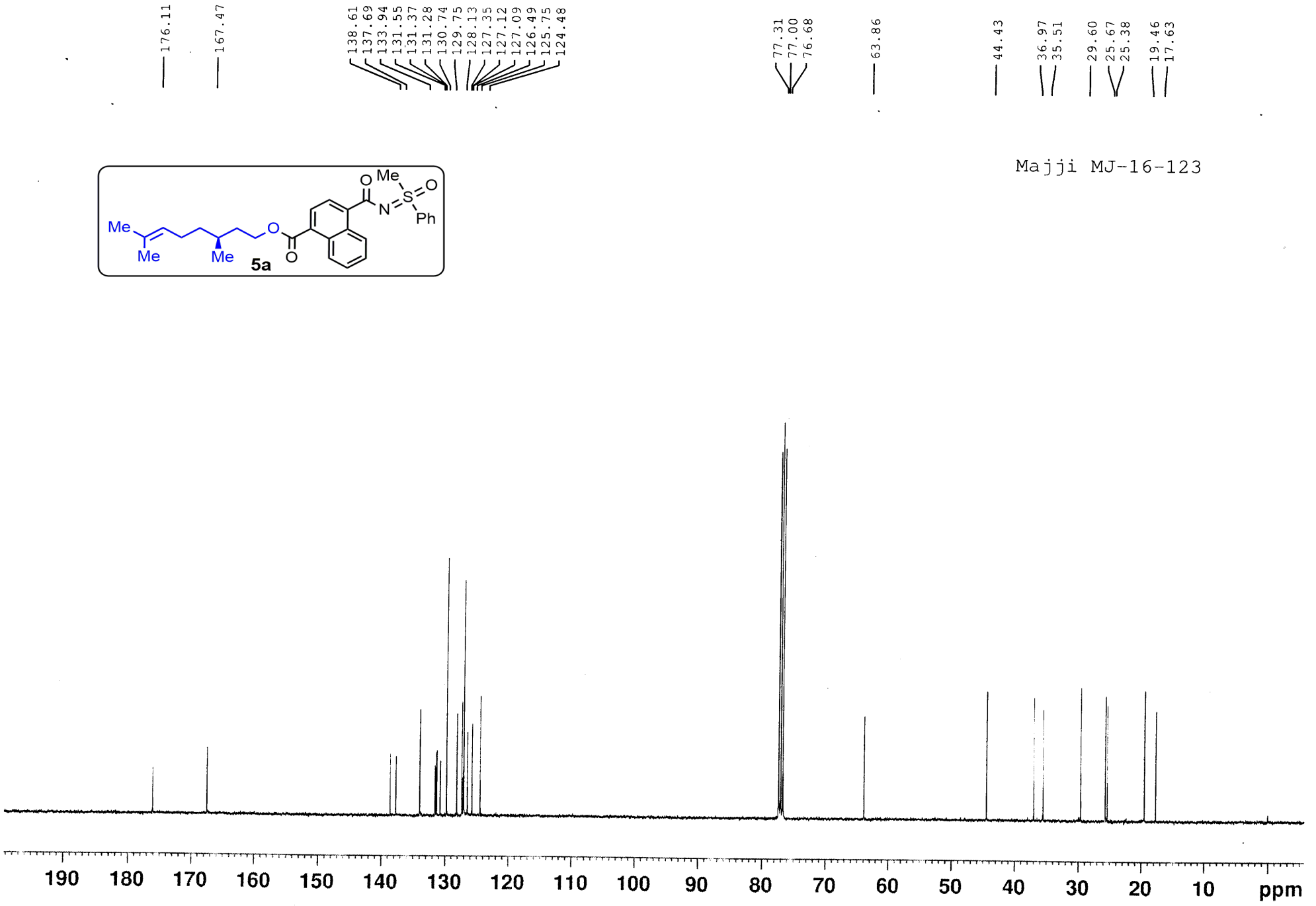

8.777
8.756
8.089
8.071
7.778
7.760
7.732
7.711
7.680
7.353
7.334
7.321
7.305
7.289
7.230
7.204
7.185
7.165
7.144
7.125
3.157
MAJII-16-148
Ph
Me-S=N
O
O
O
N=S-Me
O
Ph
1t
10
9
8
7
6
5
4
3
2
1
ppm
2.09
2.04
6.11
8.07
8.13
6.00

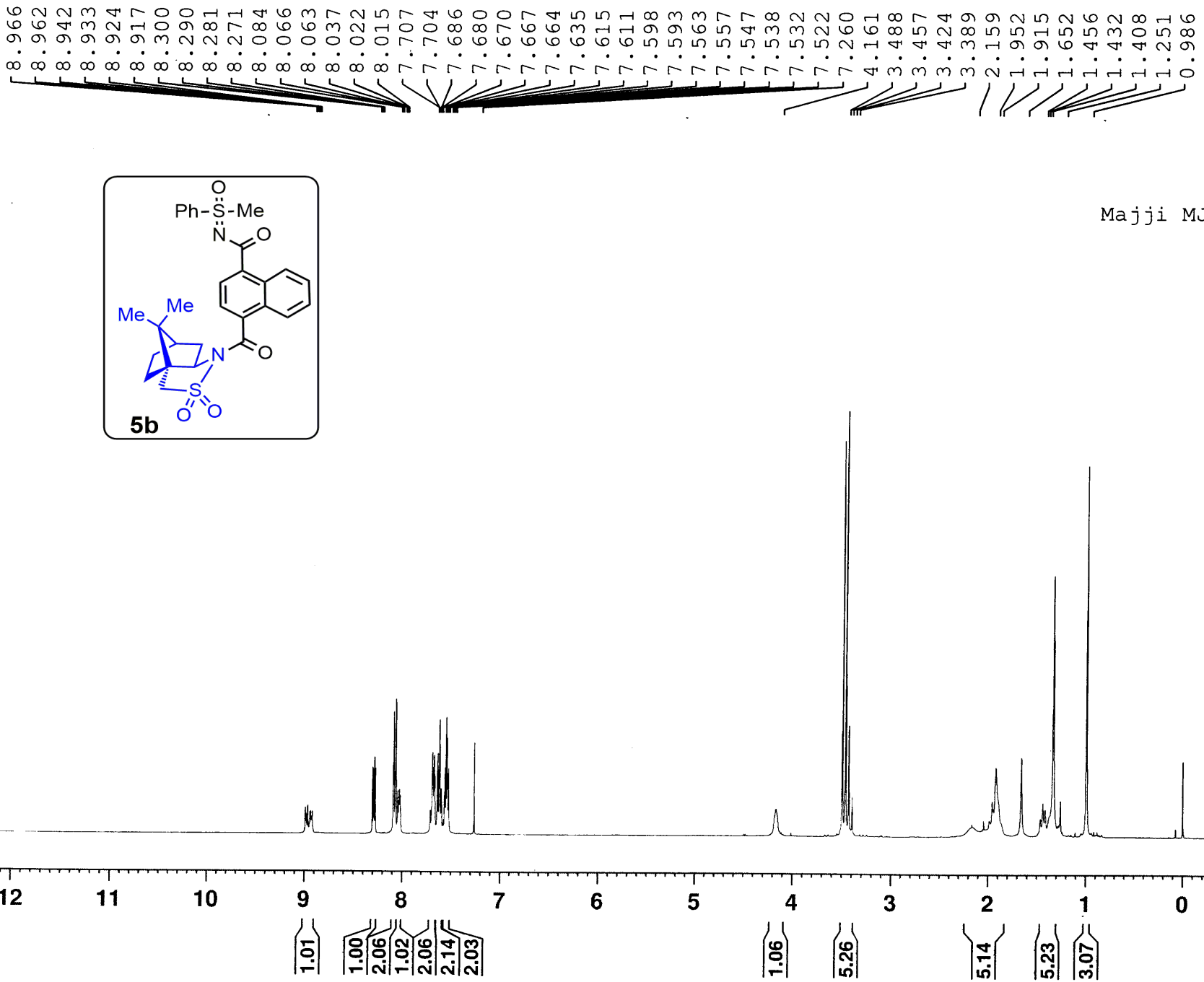

176.38
143.65
139.67
138.75
133.71
131.97
131.87
131.59
129.78
129.63
129.01
128.46
128.34
127.02
126.91
126.27
125.96
125.74
77.31
77.00
76.68
44.38
MAJII-16-148
Ph
Me-S=N
O
O
O
O
N=S-Me
O
Ph
1t
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

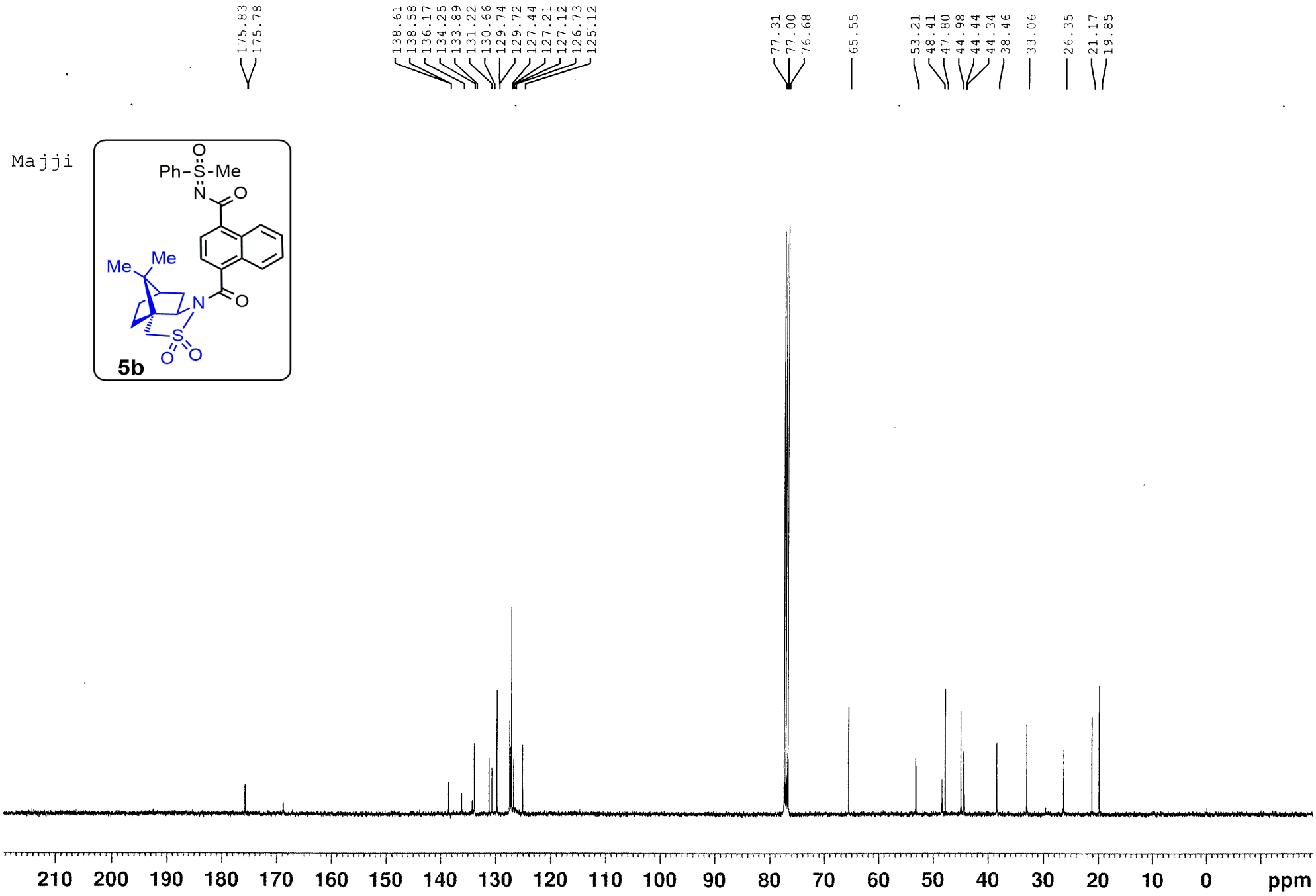

8.823
8.806
8.638
8.622
8.130
8.115
7.797
7.783
7.751
7.736
7.720
7.678
7.665
7.648
7.643
7.639
7.623
7.609
3.688
3.544
2.509
2.506
MJ-16-183
Me
O
O
S
N
Ph
OH
O
1f'
10
9
8
7
6
5
4
3
2
1
ppm
1.34
0.93
4.11
1.12
4.30
3.00

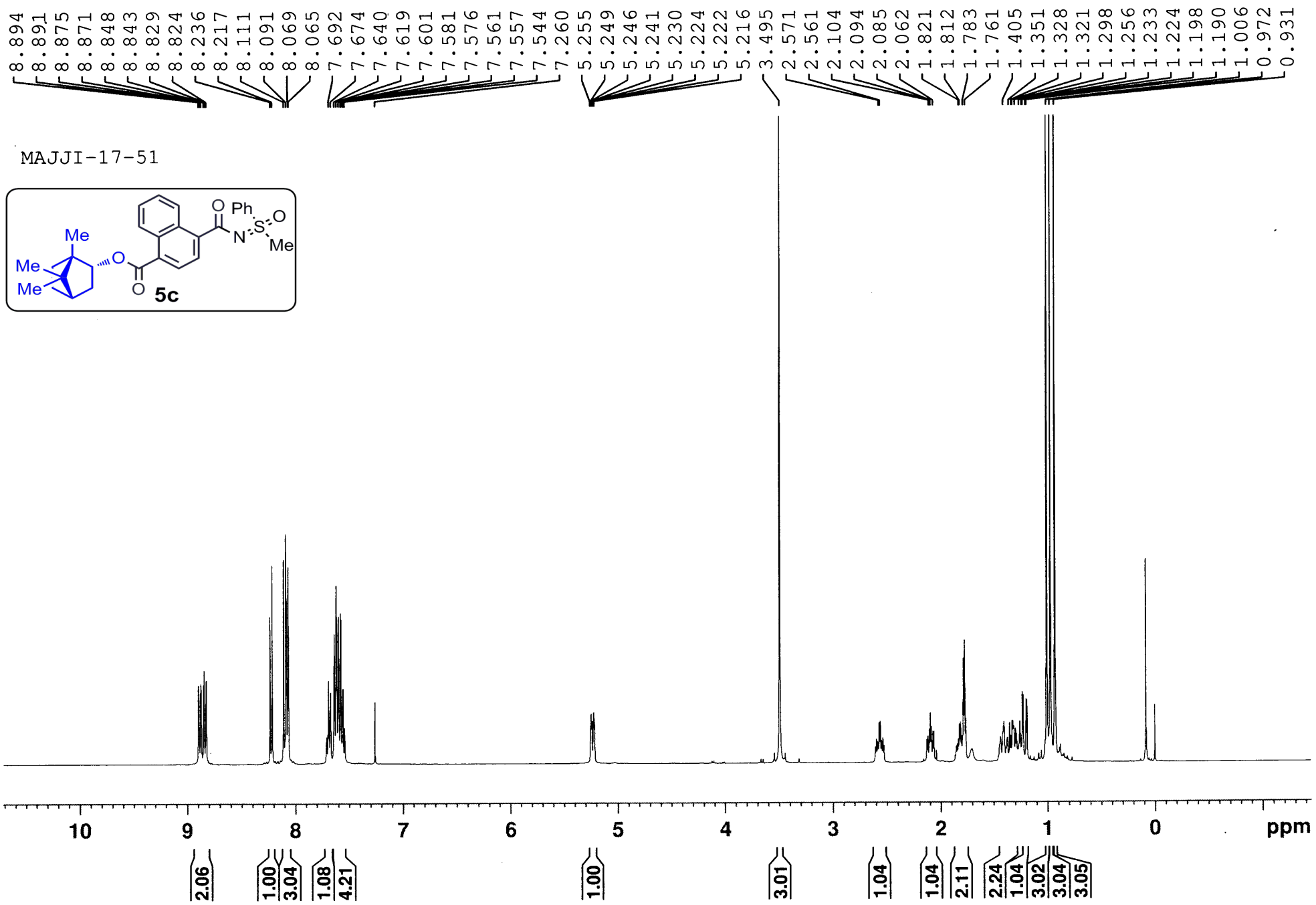

175.38
169.01
138.82
138.39
134.33
131.28
130.89
130.14
128.57
128.00
127.82
127.57
127.47
127.13
126.54
126.18
43.68
40.43
40.27
40.19
40.10
39.93
39.77
39.60
39.43
Me
O
O
S
N
Ph
OH
O
1f'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.878
8.876
8.873
8.859
8.854
8.837
8.833
8.819
8.816
8.814
8.202
8.183
8.092
8.073
7.721
7.702
7.697
7.687
7.684
7.680
7.648
7.632
7.628
7.615
7.610
7.599
7.595
7.591
7.579
7.574
7.563
7.559
7.555
7.542
7.260
5.112
5.109
5.105
4.489
4.474
4.457
4.440
3.502
2.025
2.004
1.891
1.870
1.674
1.672
1.663
1.647
1.605
1.270
1.262
1.255
1.247
1.007
0.991
Me
O
Me
S
O
N
Ph
Me
Me
Me
O
O
5a
10
9
8
7
6
5
4
3
2
1
0 ppm
2.03
0.98
3.00
1.02
4.13
0.96
2.00
3.00
2.02
1.00
5.25
3.05
1.06
1.26
3.00


176.11
167.47
138.61
137.69
133.94
131.55
131.37
131.28
130.74
129.75
128.13
127.35
127.12
127.09
126.49
125.75
124.48
77.31
77.00
76.68
63.86
44.43
36.97
35.51
29.60
25.67
25.38
19.46
17.63
Majji MJ-16-123
Me
O
Me
S
O
N
Ph
Me
Me
Me
O
O
5a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.966
8.962
8.942
8.933
8.924
8.917
8.300
8.290
8.281
8.271
8.084
8.066
8.063
8.037
8.022
8.015
7.707
7.704
7.686
7.680
7.670
7.667
7.664
7.635
7.615
7.611
7.598
7.593
7.563
7.557
7.547
7.538
7.532
7.522
7.260
4.161
3.488
3.457
3.424
3.389
2.159
1.952
1.915
1.652
1.456
1.432
1.408
1.251
0.986
Ph-S-Me
N
O
O
Me
Me
N
O
S
O
O
5b
Majji MJ-16-125
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.01
1.00
2.06
1.02
2.06
2.14
2.03
1.06
5.26
5.14
5.23
3.07


175.83
175.78
138.61
138.58
136.17
134.25
133.89
131.22
130.66
129.74
129.72
127.44
127.21
127.12
126.73
125.12
77.31
77.00
76.68
65.55
53.21
48.41
47.80
44.98
44.44
44.34
38.46
33.06
26.35
21.17
19.85
Majji
Ph-S-Me
O
N
O
Me
Me
N
O
S
O
O
5b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.894
8.891
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8.871
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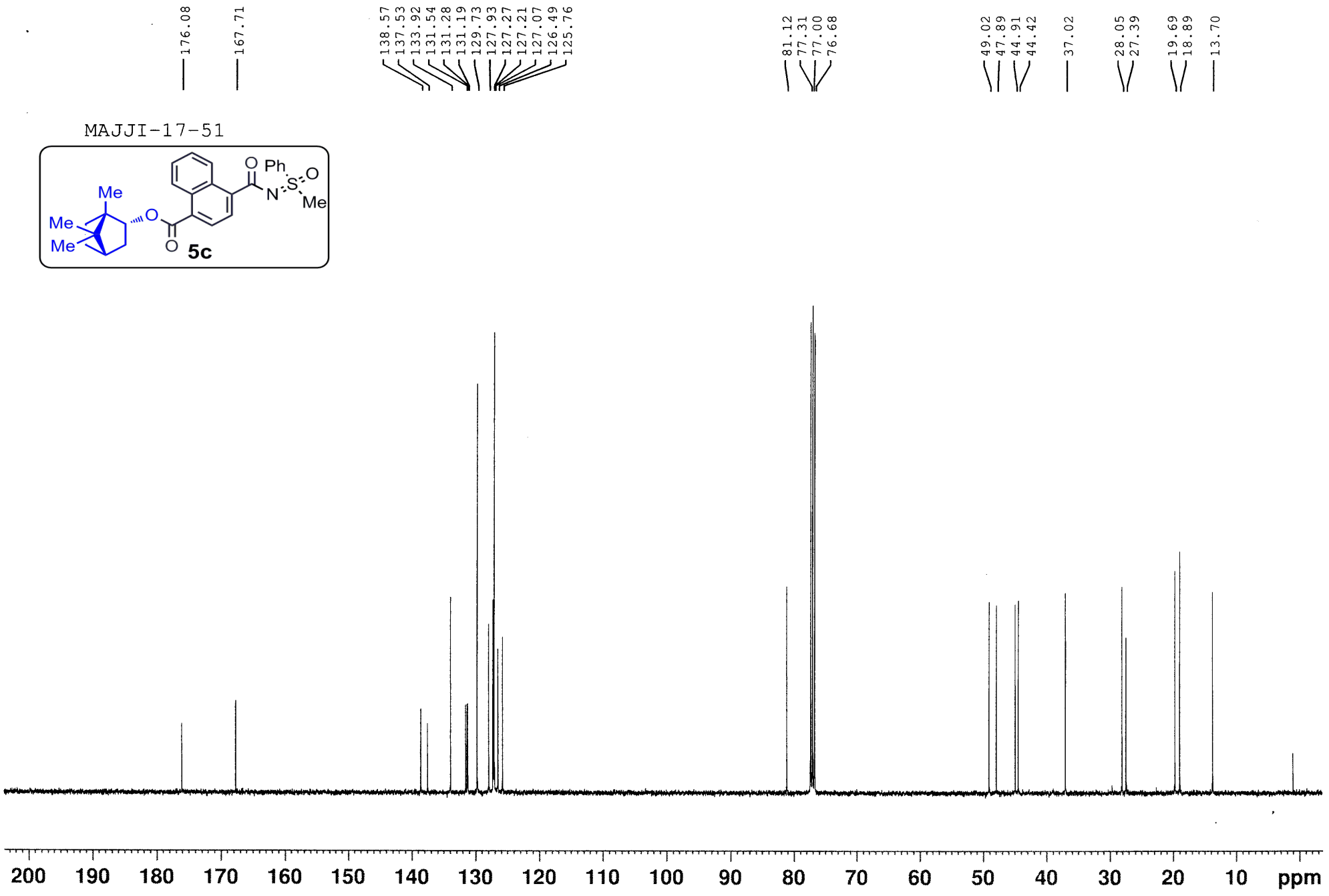
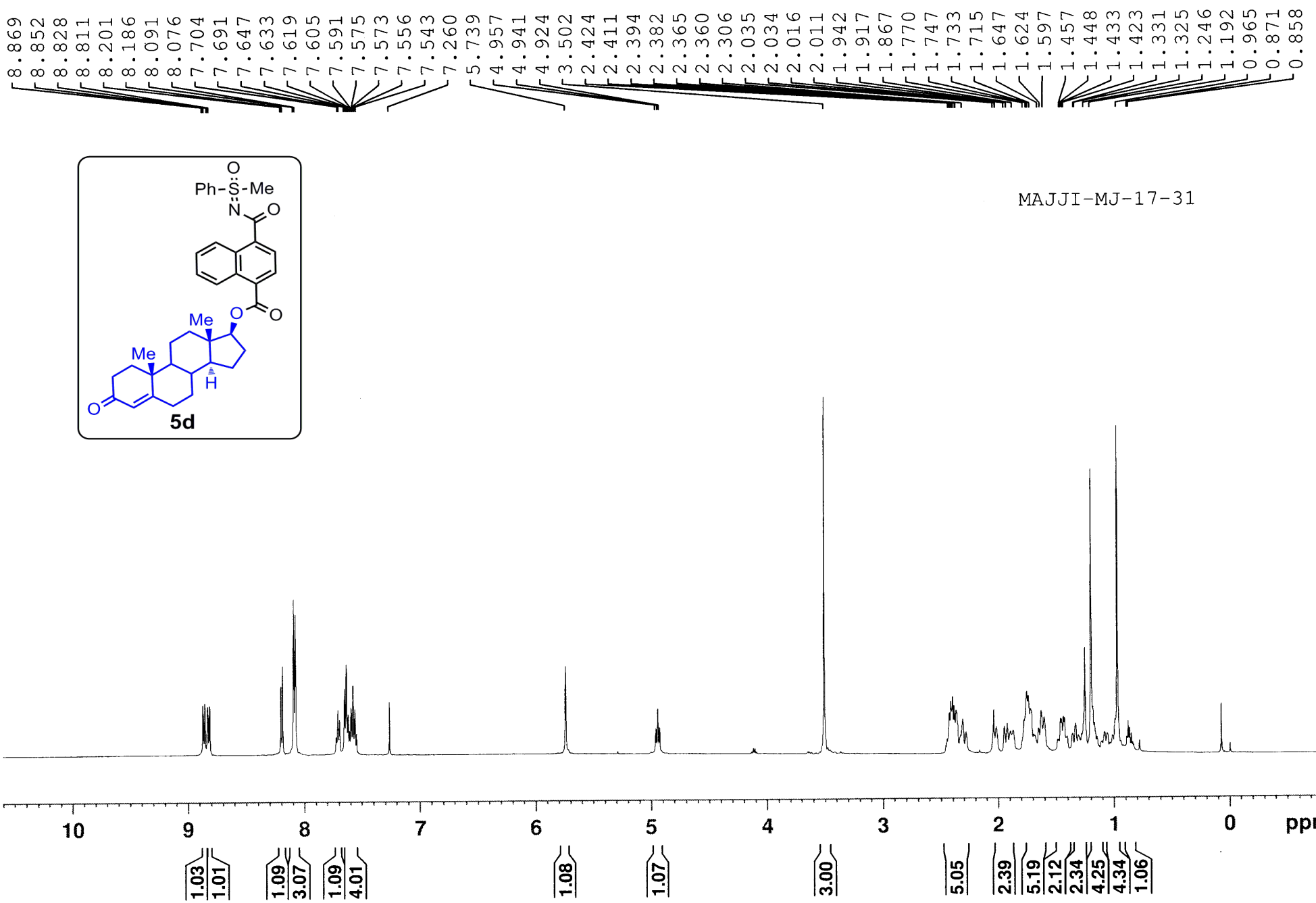
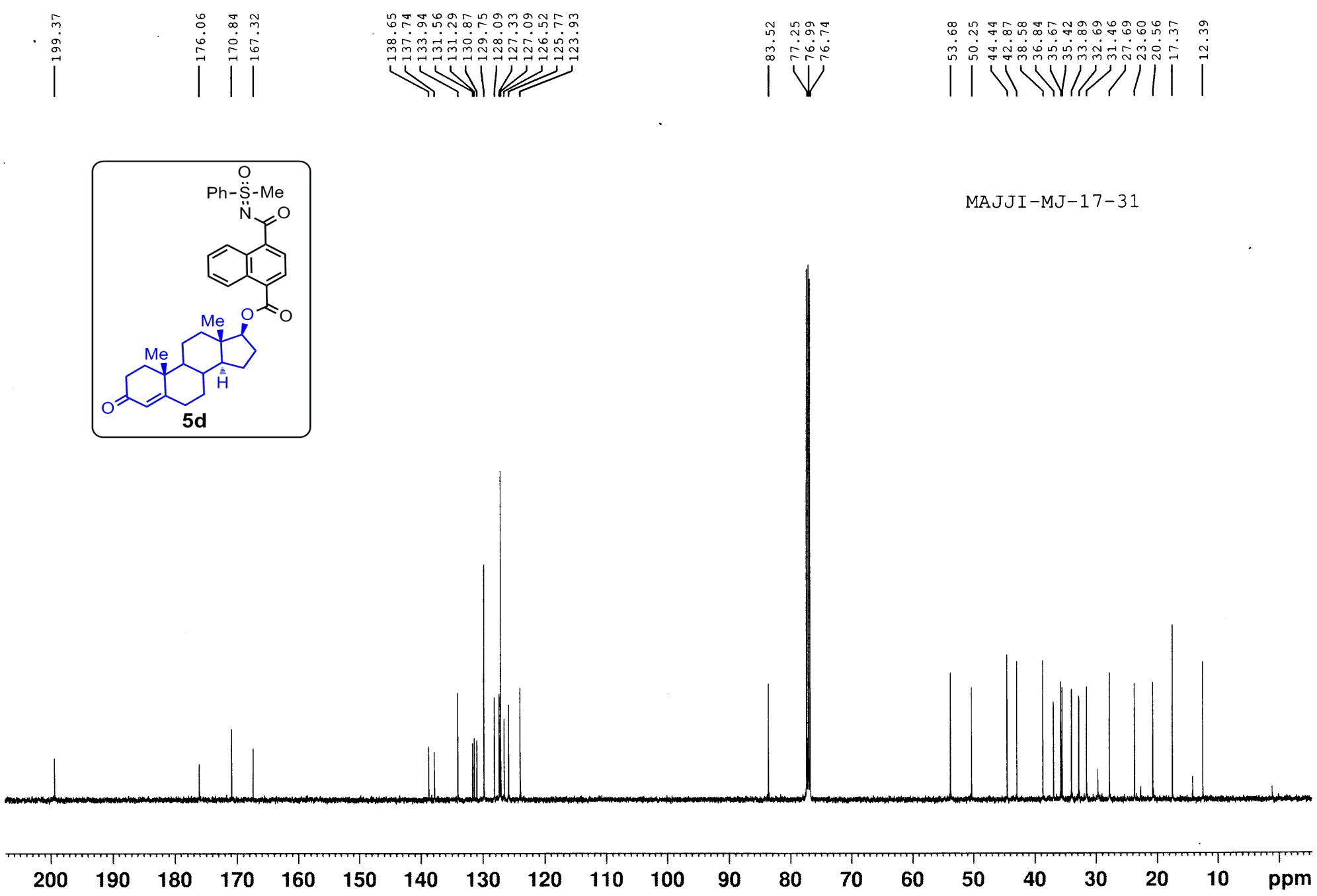
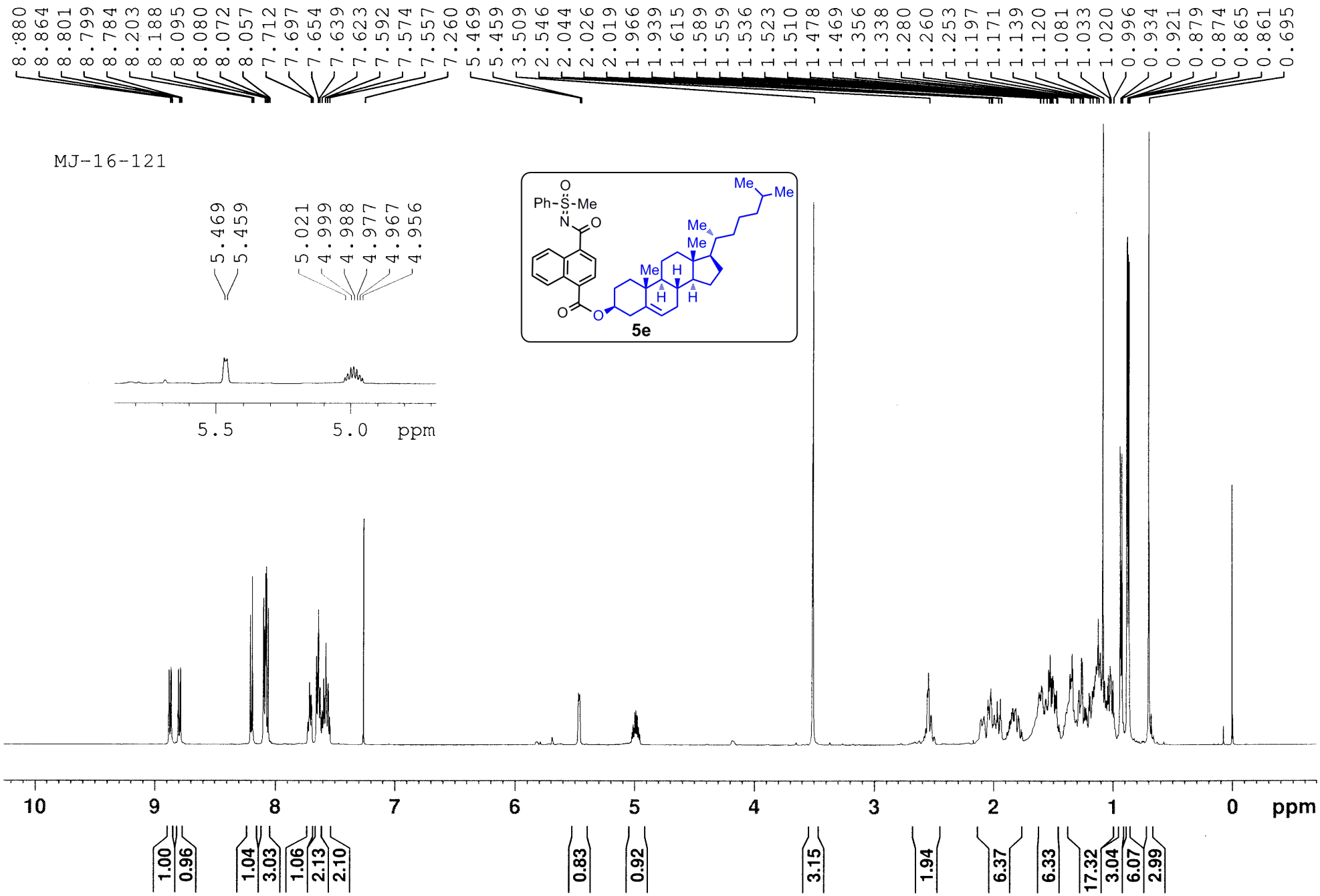
8.843
8.829
8.824
8.236
8.217
8.111
8.091
8.069
8.065
7.692
7.674
7.640
7.619
7.601
7.581
7.576
7.561
7.557
7.544
7.260
5.255
5.249
5.246
5.241
5.230
5.224
5.222
5.216
3.495
2.571
2.561
2.104
2.094
2.085
2.062
1.821
1.812
1.783
1.761
1.405
1.351
1.328
1.321
1.298
1.256
1.233
1.224
1.198
1.190
1.006
0.972
0.931
MAJJI-17-51
Me
Me
Me
O
O
O
Ph
N
S
O
Me
5c
10
9
8
7
6
5
4
3
2
1
0
ppm
2.06
1.00
3.04
1.08
4.21
1.00
3.01
1.04
1.04
2.11
2.24
1.04
3.02
3.04
3.05


176.08
167.71
138.57
137.53
133.92
131.54
131.28
131.19
129.73
127.93
127.27
127.21
127.07
126.49
125.76
81.12
77.31
77.00
76.68
49.02
47.89
44.91
44.42
37.02
28.05
27.39
19.69
18.89
13.70
MAJJI-17-51
Me
Me
Me
O
O
O
Ph
N
S
O
Me
5c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.869
8.852
8.828
8.811
8.201
8.186
8.091
8.076
7.704
7.691
7.647
7.633
7.619
7.605
7.591
7.575
7.573
7.556
7.543
7.260
5.739
4.957
4.941
4.924
3.502
2.424
2.411
2.394
2.382
2.365
2.360
2.306
2.035
2.034
2.016
2.011
1.942
1.917
1.867
1.770
1.747
1.733
1.715
1.647
1.624
1.597
1.457
1.448
1.433
1.423
1.331
1.325
1.246
1.192
0.965
0.871
0.858
Ph-S-Me
N
O
O
O
Me
Me
H
O
5d
MAJJI-MJ-17-31
10
9
8
7
6
5
4
3
2
1
0
ppm
1.03
1.01
1.09
3.07
1.09
4.01
1.08
1.07
3.00
5.05
2.39
5.19
2.12
2.34
4.25
4.34
1.06


199.37
176.06
170.84
167.32
138.65
137.74
133.94
131.56
131.29
130.87
129.75
128.09
127.33
127.09
126.52
125.77
123.93
83.52
77.25
76.99
76.74
53.68
50.25
44.44
42.87
38.58
36.84
35.67
35.42
33.89
32.69
31.46
27.69
23.60
20.56
17.37
12.39
Ph-S-Me
N
O
O
O
O
Me
Me
H
O
5d
MAJJI-MJ-17-31
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.880
8.864
8.801
8.799
8.784
8.203
8.188
8.095
8.080
8.072
8.057
7.712
7.697
7.654
7.639
7.623
7.592
7.574
7.557
7.260
5.469
5.459
3.509
2.546
2.044
2.026
2.019
1.966
1.939
1.615
1.589
1.559
1.536
1.523
1.510
1.478
1.469
1.356
1.338
1.280
1.260
1.253
1.197
1.171
1.139
1.120
1.081
1.033
1.020
0.996
0.934
0.921
0.879
0.874
0.865
0.861
0.695
MJ-16-121
5.469
5.459
5.021
4.999
4.988
4.977
4.967
4.956
5.5
5.0
ppm
Ph-S-Me
O
N
O
Me
Me
Me
Me
H
H
H
O
O
5e
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.96
1.04
3.03
1.06
2.13
2.10
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0.92
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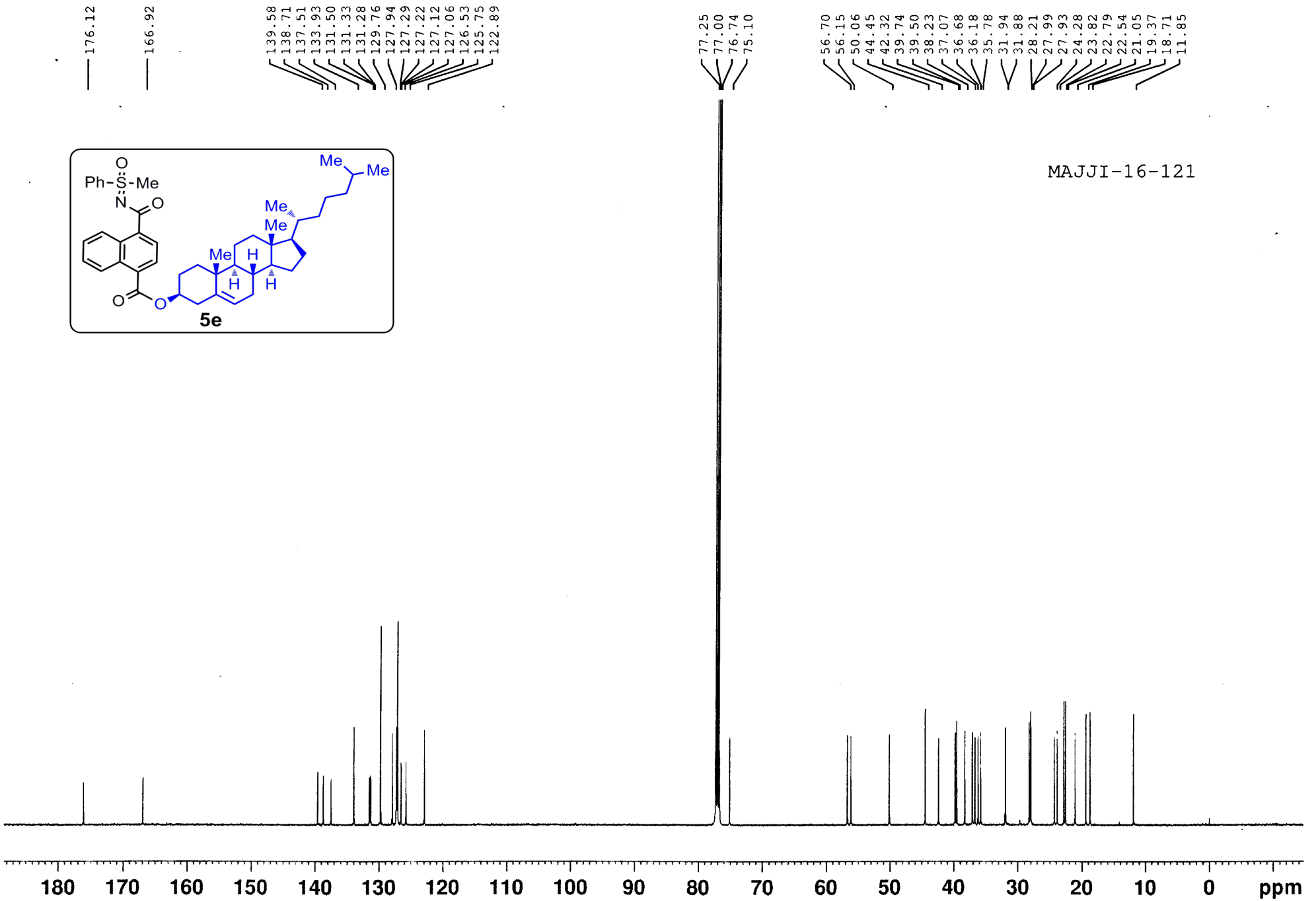
1.94
6.37
6.33
17.32
3.04
6.07
2.99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137.51
133.93
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131.33
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129.76
127.94
127.29
127.22
127.12
127.06
126.53
125.75
122.89
77.25
77.00
76.74
75.10
56.70
56.15
50.06
44.45
42.32
39.74
39.50
38.23
37.07
36.68
36.18
35.78
31.94
31.88
28.21
27.99
27.93
24.28
23.82
22.79
22.54
21.05
19.37
18.71
11.85
MAJJI-16-121
Ph-S-Me
Me
Me
Me
Me
H
H
H
5e
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140
130
120
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100
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60
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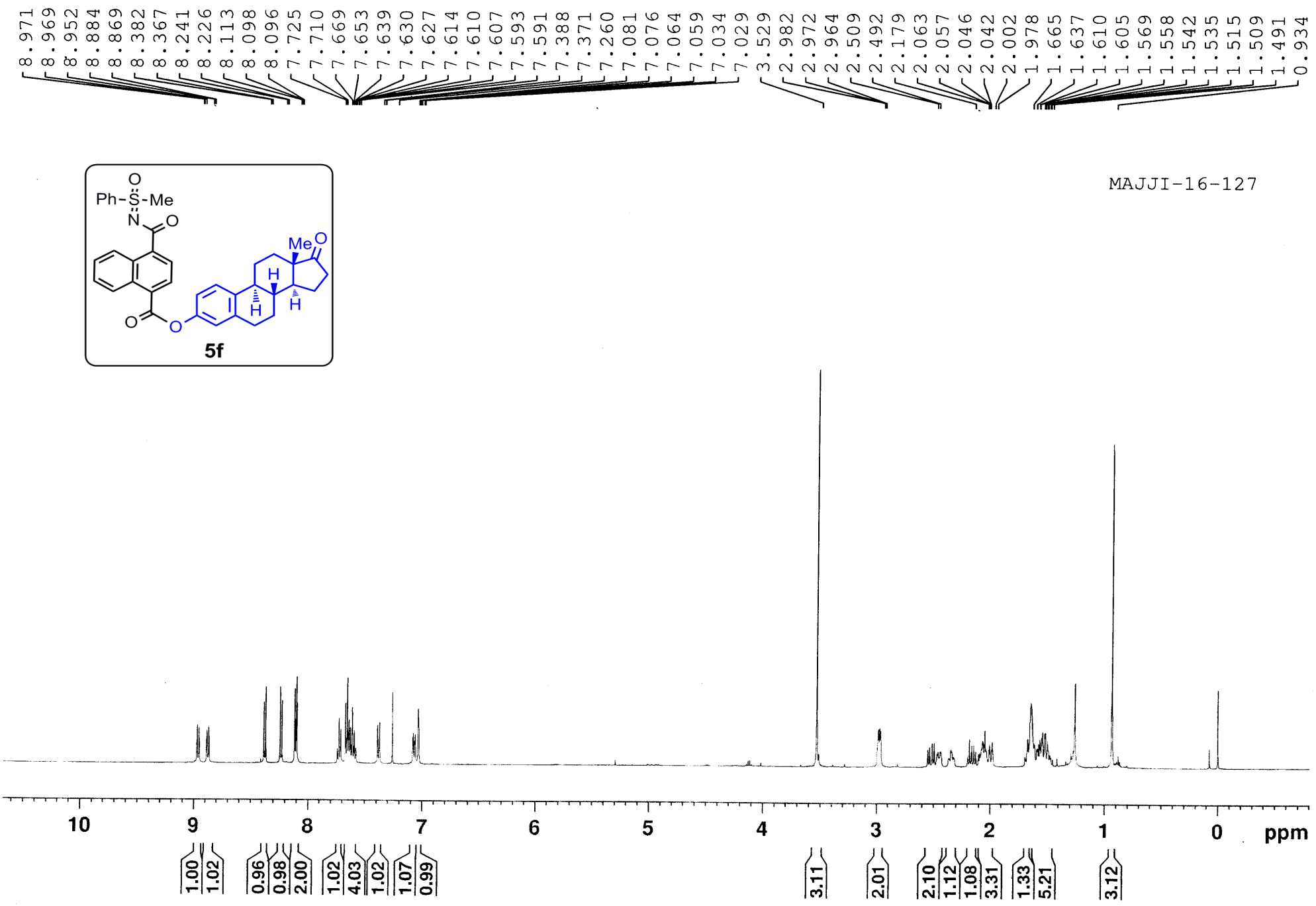
10
0
ppm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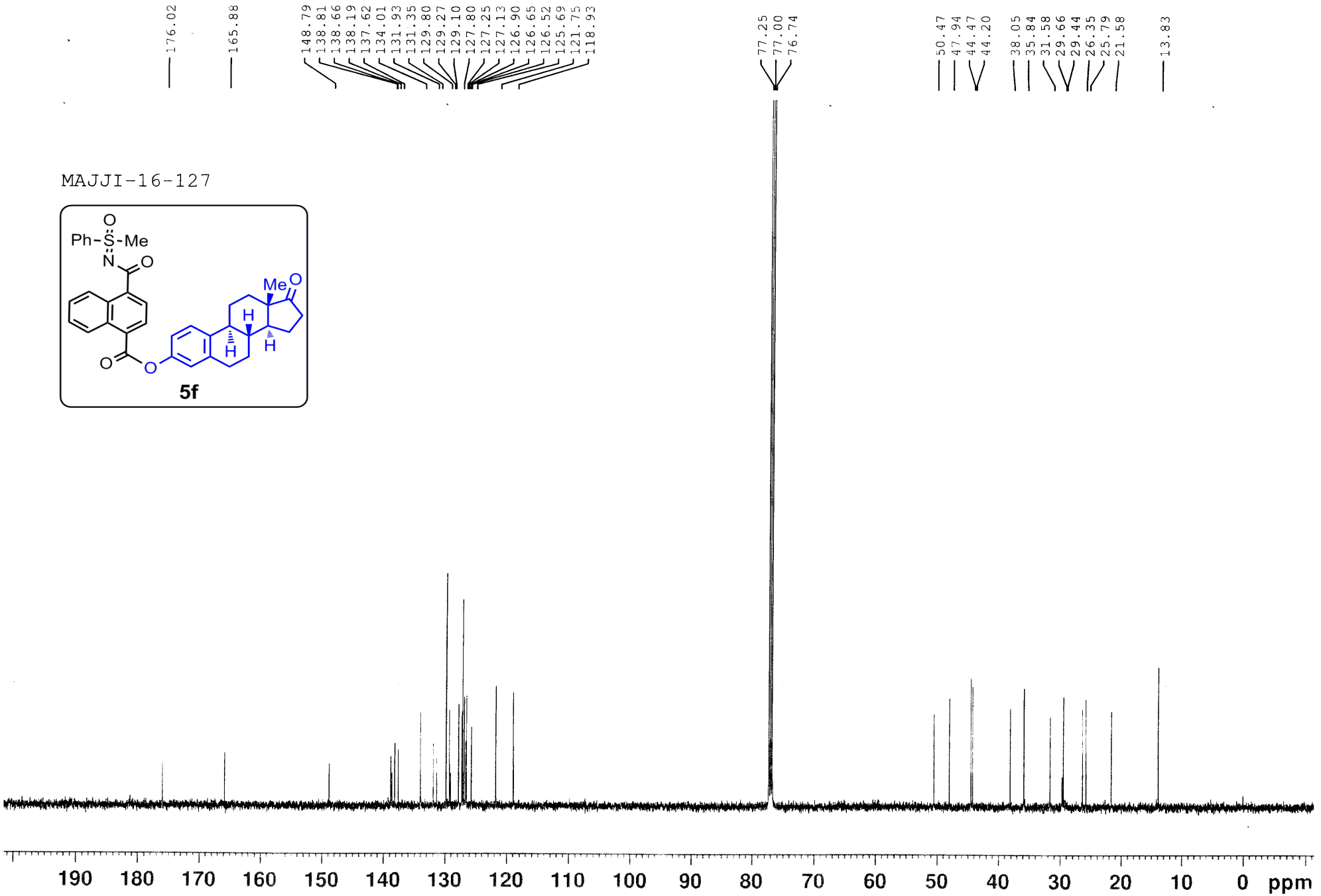
8.241
8.226
8.113
8.098
8.096
7.725
7.710
7.669
7.653
7.639
7.630
7.627
7.614
7.610
7.607
7.593
7.591
7.388
7.371
7.260
7.081
7.076
7.064
7.059
7.034
7.029
3.529
2.982
2.972
2.964
2.509
2.492
2.179
2.063
2.057
2.046
2.042
2.002
1.978
1.665
1.637
1.610
1.605
1.569
1.558
1.542
1.535
1.515
1.509
1.491
0.934
Ph-S-Me
Me
H
H
H
5f
MAJJI-16-127
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.02
0.96
0.98
2.00
1.02
4.03
1.02
1.07
0.99
3.11
2.01
2.10
1.12
1.08
3.31
1.33
5.21
3.12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148.79
138.81
138.66
138.19
137.62
134.01
131.93
131.35
129.80
129.27
129.10
127.80
127.25
127.13
126.90
126.65
126.52
125.69
121.75
118.93
77.25
77.00
76.74
50.47
47.94
44.47
44.20
38.05
35.84
31.58
29.66
29.44
26.35
25.79
21.58
13.83
MAJJI-16-127
Ph-S-Me
N
O
O
O
O
Me
O
H
H
H
5f
190
180
170
160
150
140
130
120
110
100
90
80
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60
50
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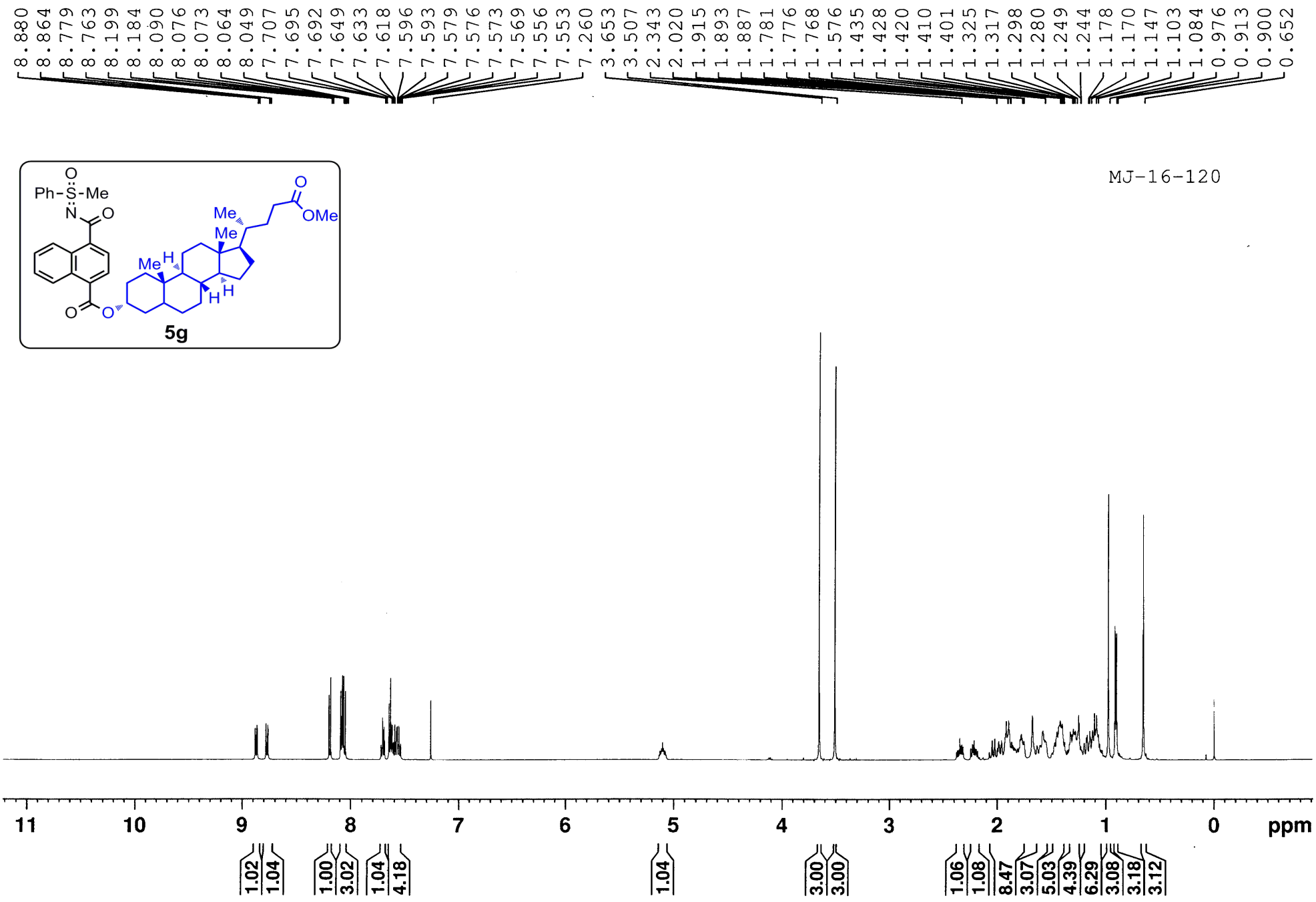
30
20
10
0
ppm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8.076
8.073
8.064
8.049
7.707
7.695
7.692
7.649
7.633
7.618
7.596
7.593
7.579
7.576
7.573
7.569
7.556
7.553
7.260
3.653
3.507
2.343
2.020
1.915
1.893
1.887
1.781
1.776
1.768
1.576
1.435
1.428
1.420
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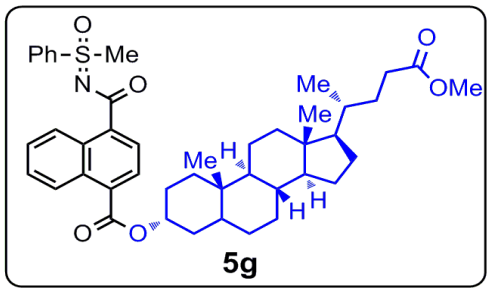
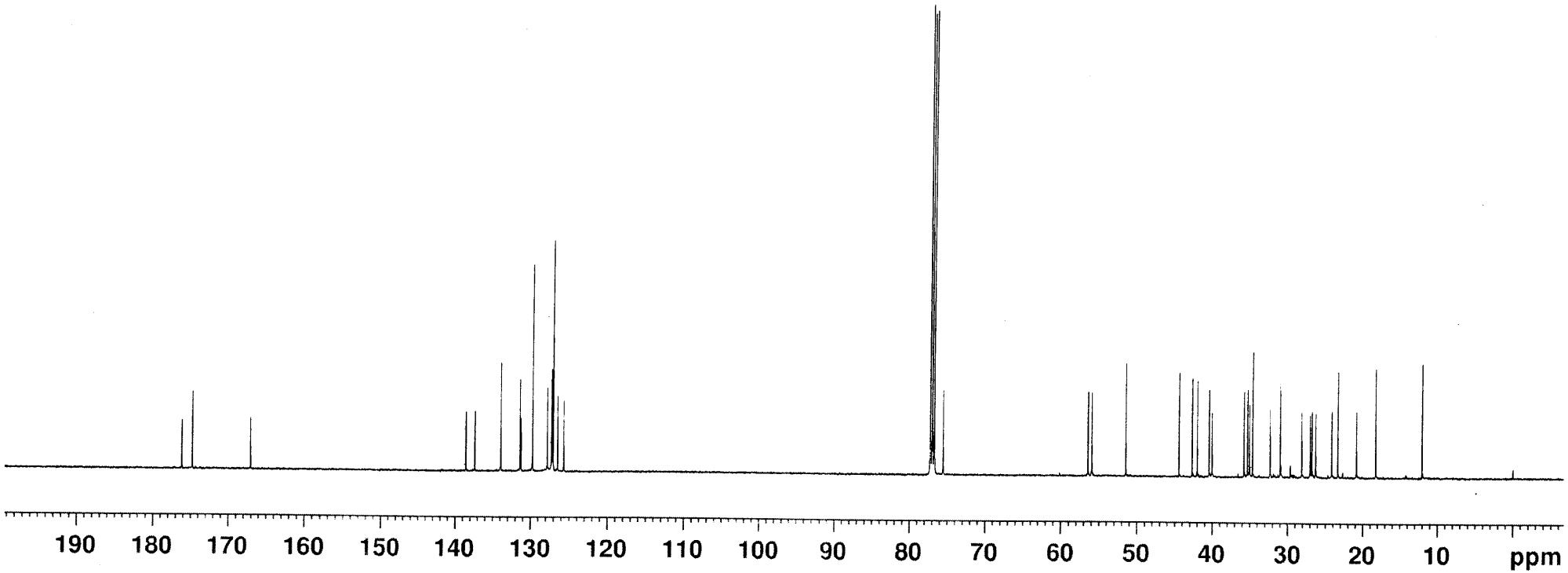
1.325
1.317
1.298
1.280
1.249
1.244
1.178
1.170
1.147
1.103
1.084
0.976
0.913
0.900
0.652
MJ-16-120
Ph-S-Me
N
O
O
O
O
O
Me
Me
Me
H
H
OMe
5g
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.04
1.00
3.02
1.04
4.18
1.04
3.00
3.00
1.06
1.08
8.47
3.07
5.03
4.39
6.29
3.08
3.18
3.12

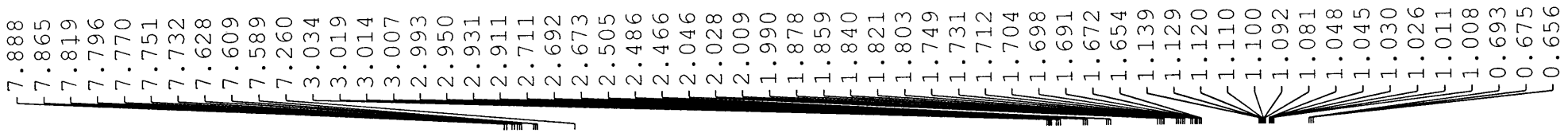

176.16
174.76
167.08
138.58
137.38
133.95
131.41
131.28
129.76
127.83
127.28
127.23
127.09
127.06
126.49
125.70
77.25
76.99
76.74
75.54
56.39
55.89
51.45
44.42
42.69
42.01
40.42
40.05
35.77
35.31
35.08
34.64
32.33
31.00
30.95
28.14
27.02
26.77
26.30
24.13
23.33
20.83
18.22
12.00

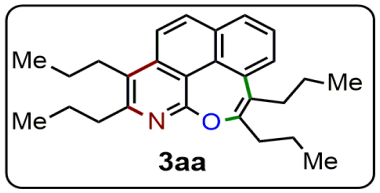

Ph-S-Me
N
O
O
O
O
Me
Me
Me
H
H
H
OMe

5g

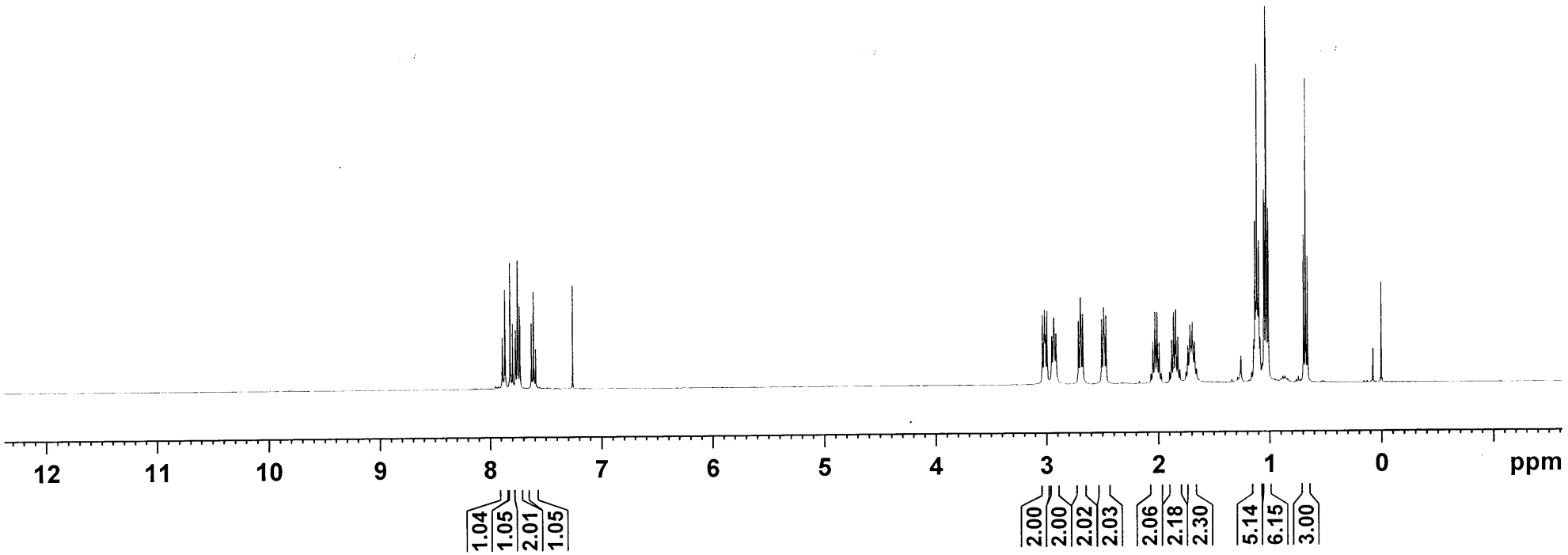
MJ-16-120


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





Majji-MJ-165-12



Majji-MJ-165-12

158.66
154.50
154.20
138.80
137.40
131.70
131.49
128.21
126.94
126.51
125.94
123.79
121.07
117.14
77.32
77.00
76.68
36.61
34.68
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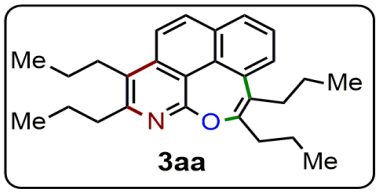
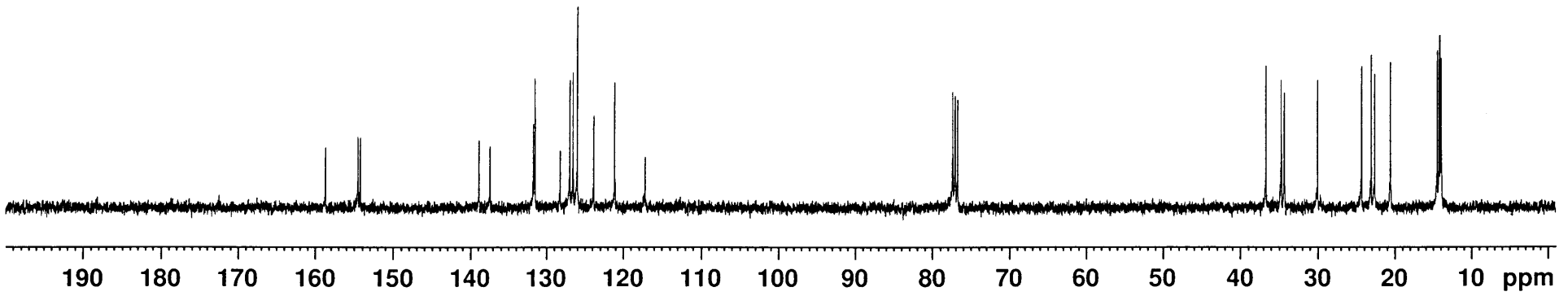
29.97
24.26
23.02
22.55
20.50
14.42
14.14
13.98
13.86

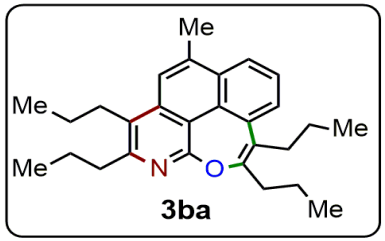


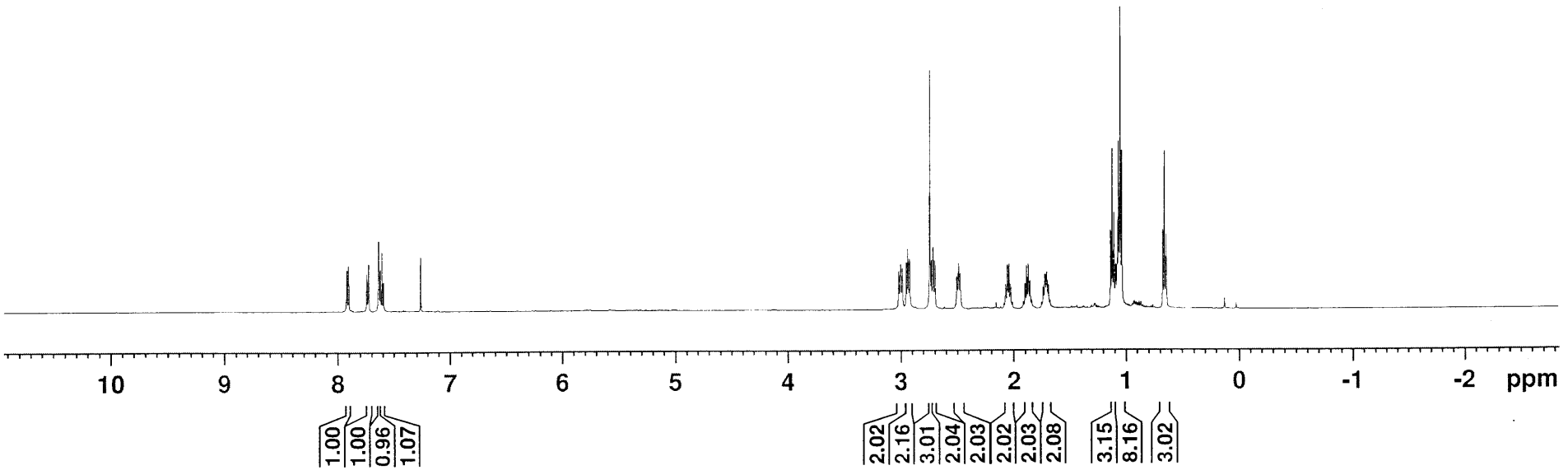
3aa



MJ-200-15

7.917 7.902 7.902 7.739 7.725 7.634 7.620 7.605 7.589 7.260 3.013 2.997 2.981 2.947 2.932 2.916 2.737 2.722 2.707 2.692 2.501 2.485 2.470 2.082 2.067 2.052 2.037 2.022 2.008 1.910 1.895 1.880 1.865 1.850 1.835 1.747 1.732 1.717 1.700 1.685 1.671 1.132 1.117 1.102 1.087 1.070 1.062 1.047 1.032 0.668





MJ-200-15

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154.12
138.56
137.69
137.34
131.73
128.42
126.64
125.72
125.23
123.78
122.35
121.32
116.35
77.25
77.00
76.74
36.64
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34.31
29.84
24.22
23.04
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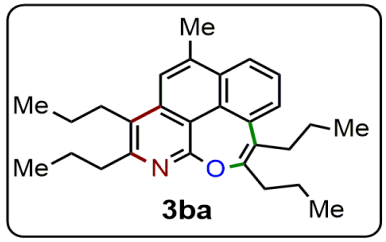
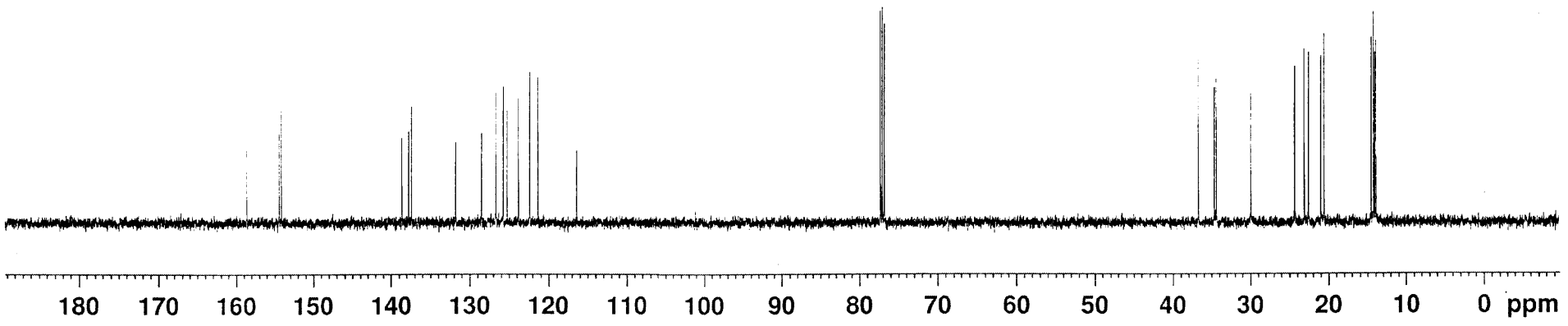
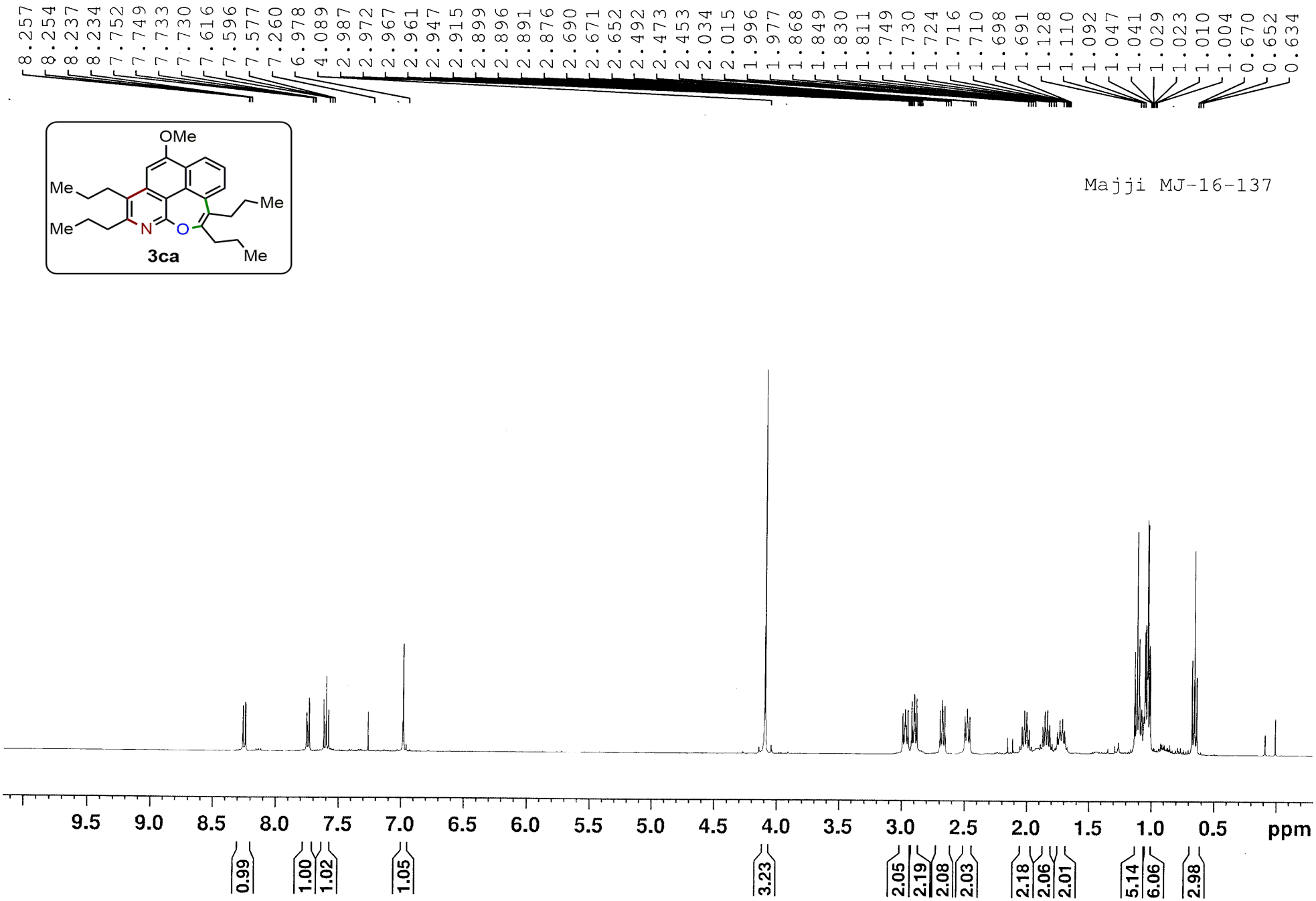
20.93
20.53
14.46
14.16
13.99
13.84



3ba

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7.730
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7.577
7.260
6.978
4.089
2.987
2.972
2.967
2.961
2.947
2.915
2.899
2.896
2.891
2.876
2.690
2.671
2.652
2.492
2.473
2.453
2.034
2.015
1.996
1.977
1.868
1.849
1.830
1.811
1.749
1.730
1.724
1.716
1.710
1.698
1.691
1.128
1.110
1.092
1.047
1.041
1.029
1.023
1.010
1.004
0.670
0.652
0.634
OMe
Me
Me
Me
Me
N
O
3ca
Majji MJ-16-137
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
ppm
0.99
1.00
1.02
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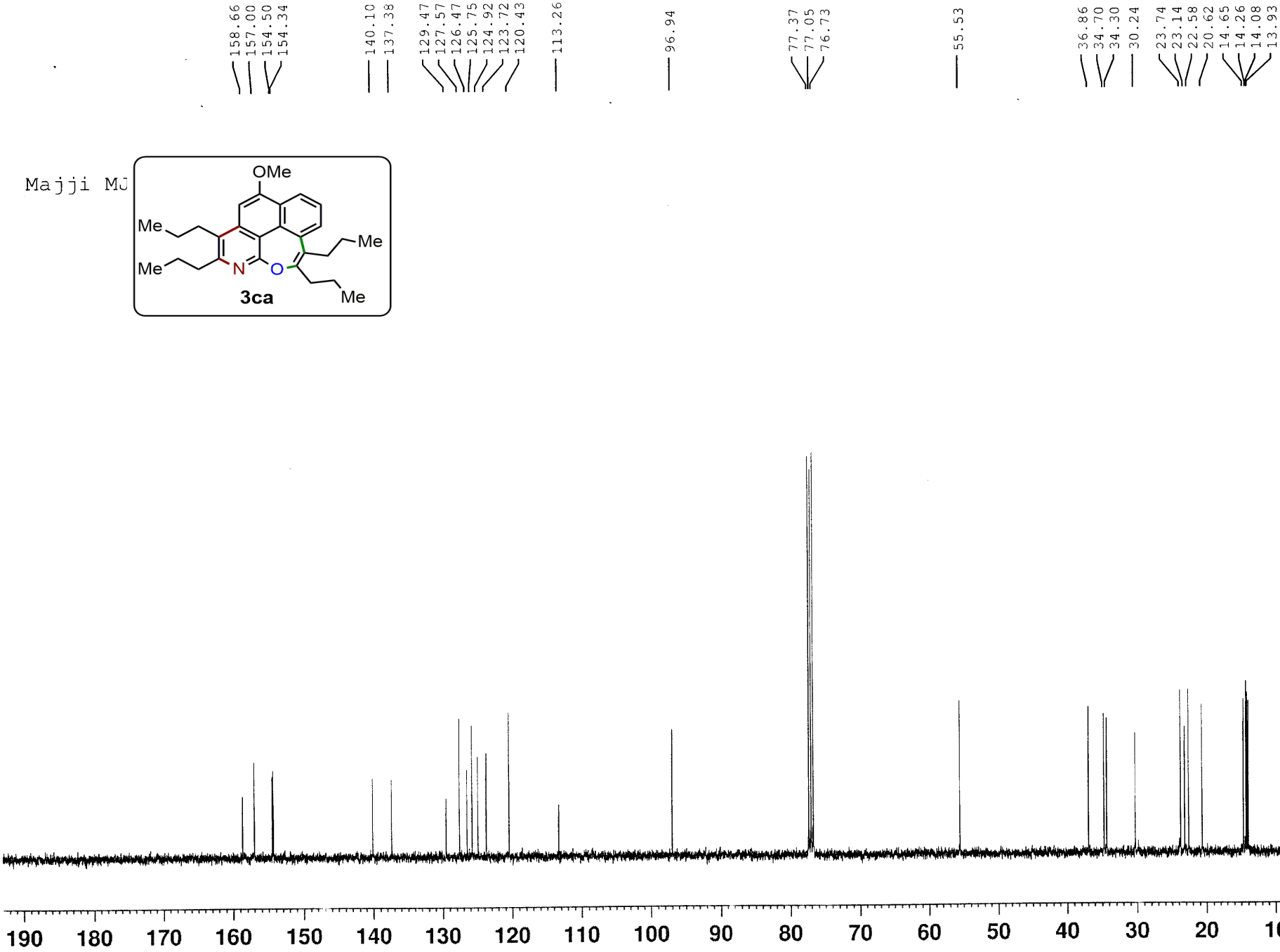
3.23
2.05
2.19
2.08
2.03
2.18
2.06
2.01
5.14
6.06
2.98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127.57
126.47
125.75
124.92
123.72
120.43
113.26
96.94
77.37
77.05
76.73
55.53
36.86
34.70
34.30
30.24
23.74
23.14
22.58
20.62
14.65
14.26
14.08
13.93
Majji MJ
OMe
Me
Me
Me
Me
N
O
3ca
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160
150
140
130
120
110
100
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80
70
60
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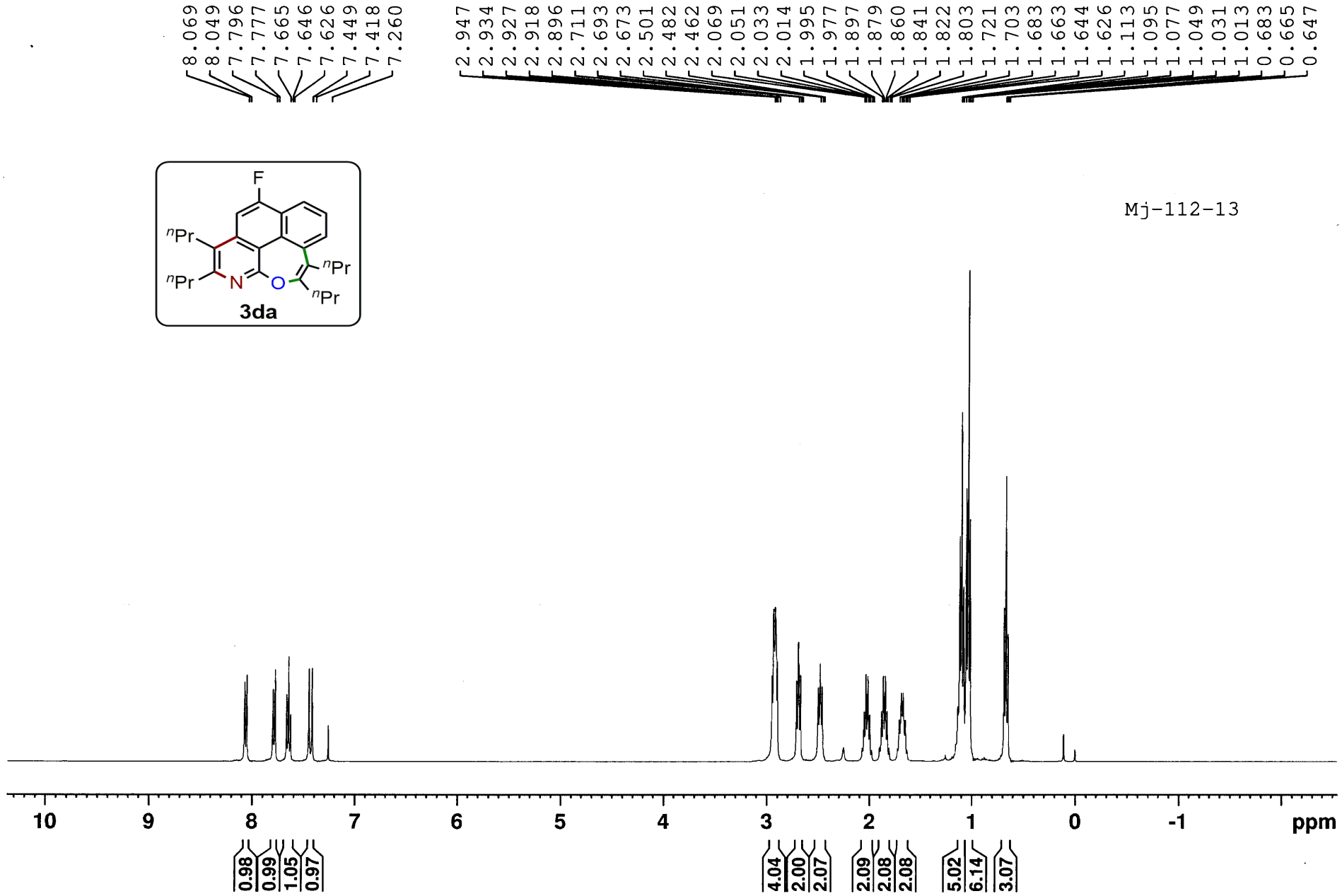
30
20
10
ppm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7.418
7.260
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2.934
2.927
2.918
2.896
2.711
2.693
2.673
2.501
2.482
2.462
2.069
2.051
2.033
2.014
1.995
1.977
1.897
1.879
1.860
1.841
1.822
1.803
1.721
1.703
1.683
1.663
1.644
1.626
1.113
1.095
1.077
1.049
1.031
1.013
0.683
0.665
0.647
F
nPr
nPr
N
O
nPr
nPr
3da
Mj-112-13
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.98
0.99
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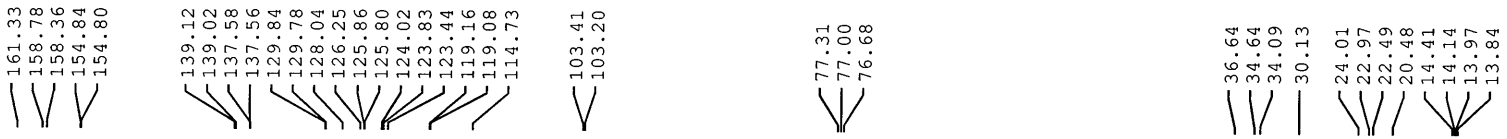
2.00
2.07
2.09
2.08
2.08
5.02
6.14
3.07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129.84
129.78
128.04
126.25
125.86
125.80
124.02
123.83
123.44
119.16
119.08
114.73
103.41
103.20
77.31
77.00
76.68
36.64
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30.13
24.01
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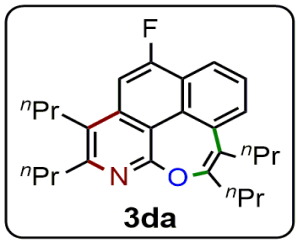
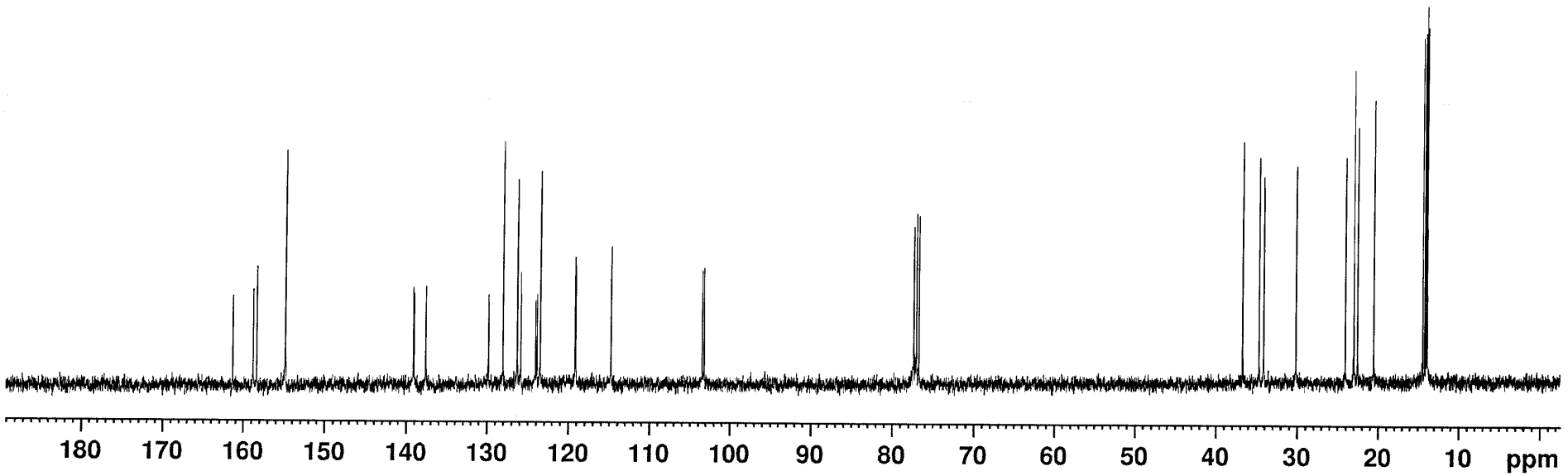
20.48
14.41
14.14
13.97
13.84


F
nPr
nPr
N
O
nPr
nPr
3da

Mj-112-13


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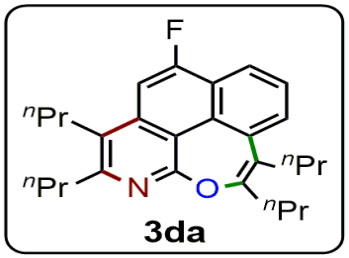
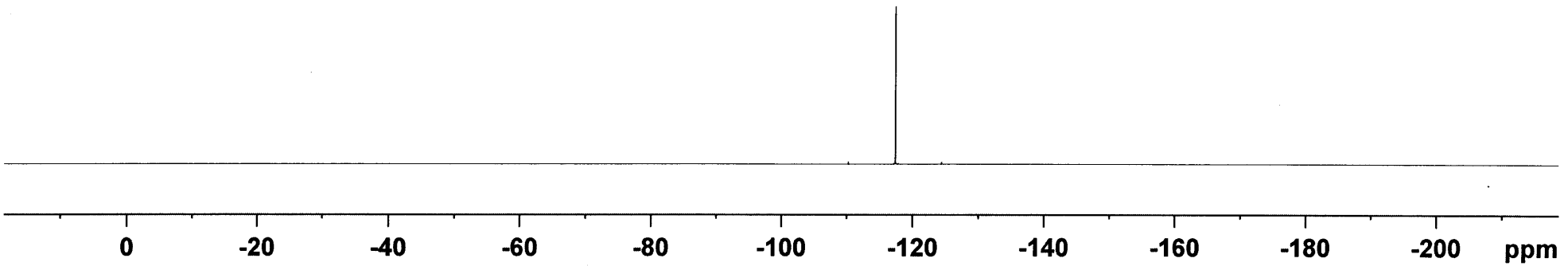
100
90
80
70
60
50
40
30
20
10
ppm

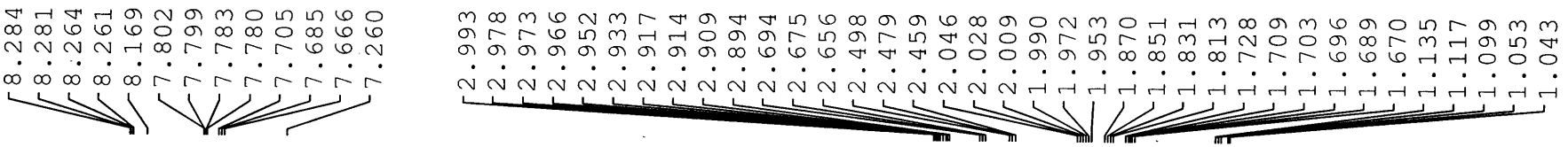


3da

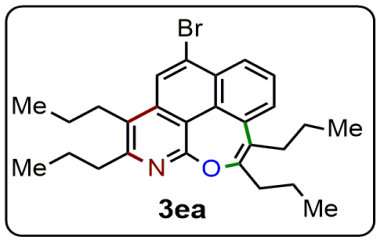
-117.40

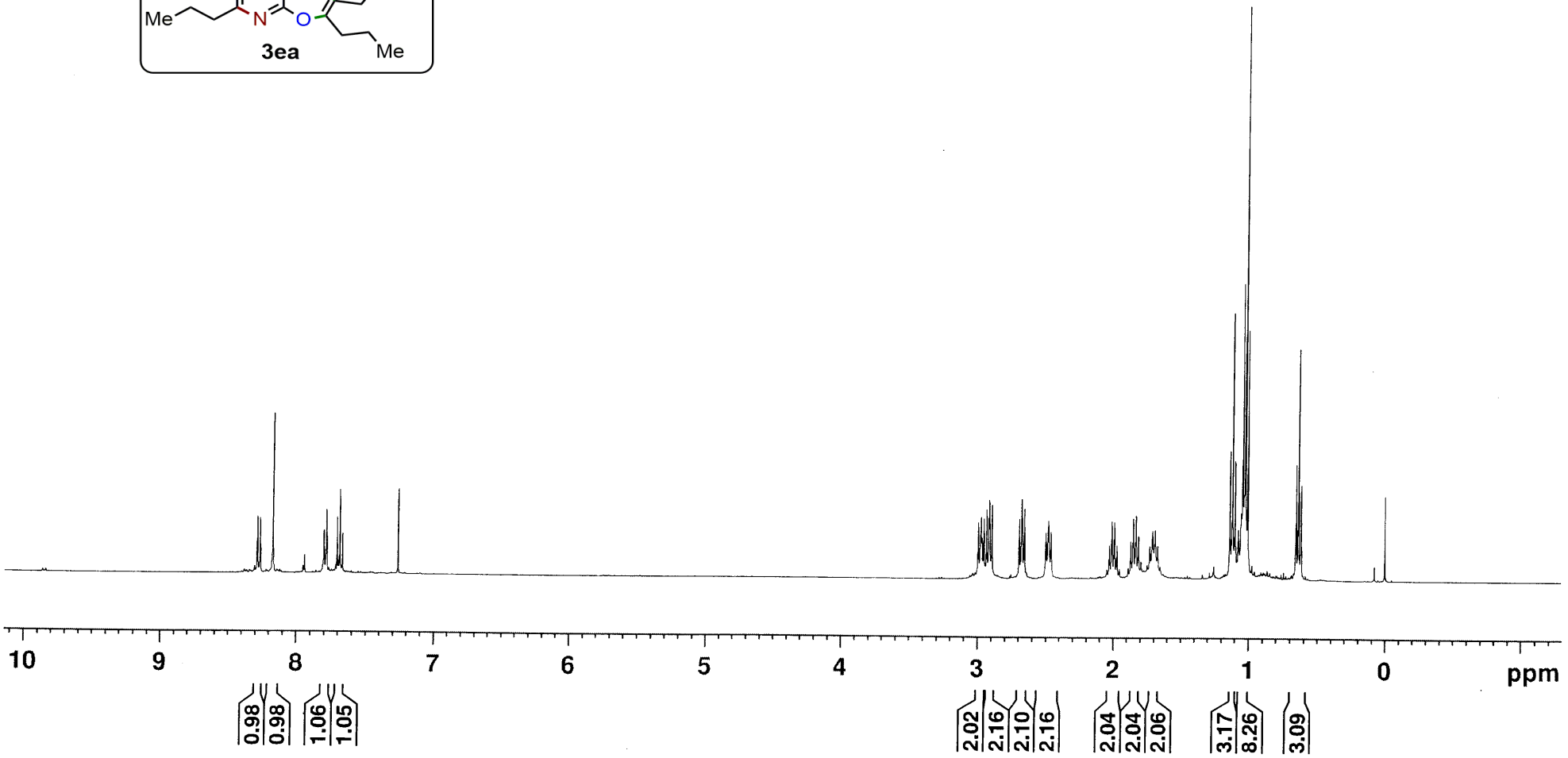
Majji-MJ-112-1



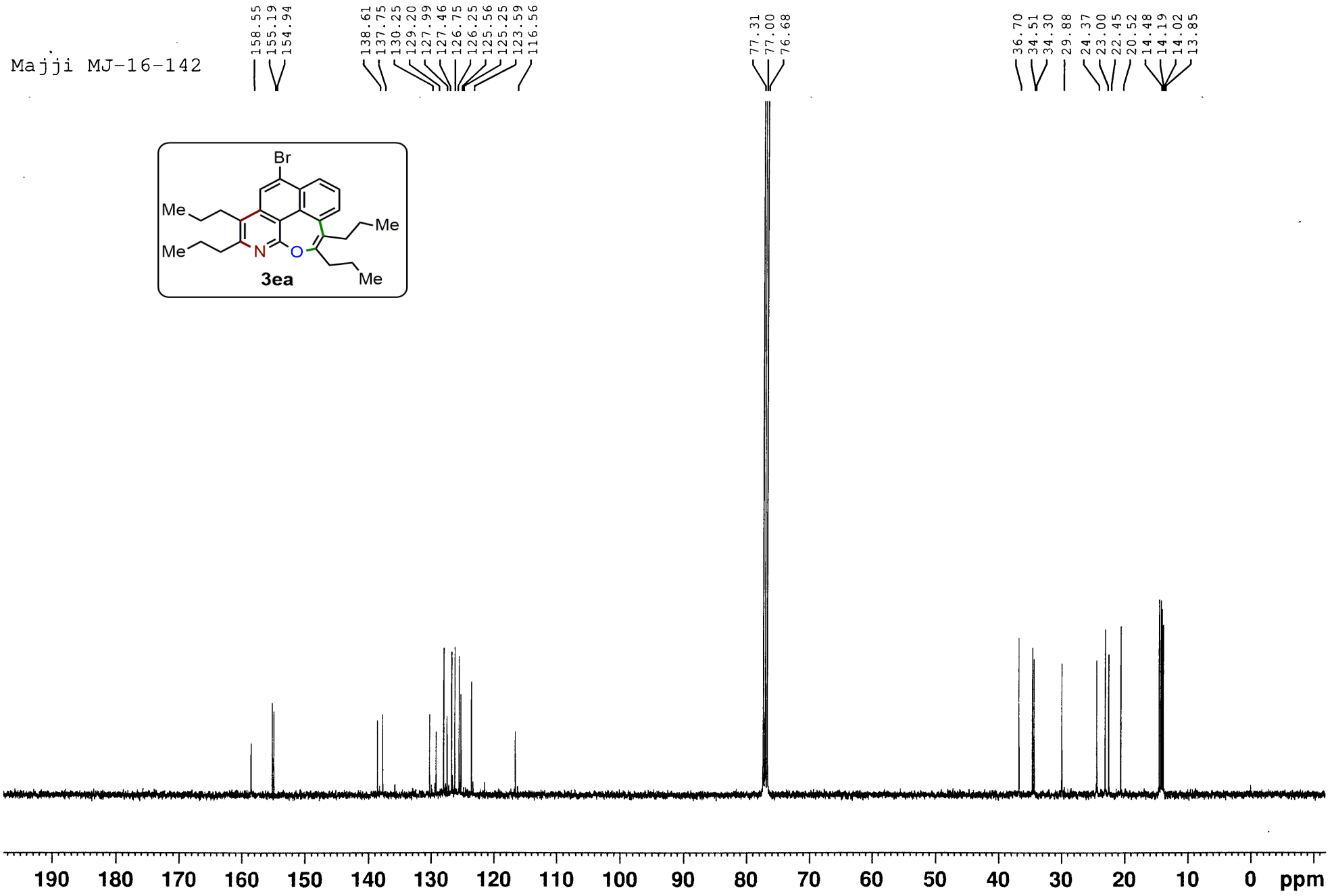


Majji MJ-16-142 R





Majji MJ-16-142



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7.759
7.678
7.663
7.647
7.260
4.054
3.068
3.052
3.035
2.954
2.939
2.923
2.704
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2.476
2.460
2.054
2.039
2.024
2.009
1.994
1.979
1.902
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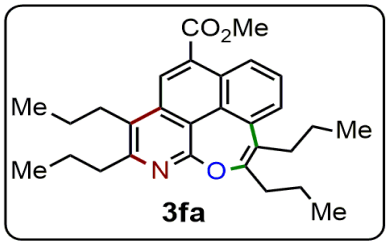
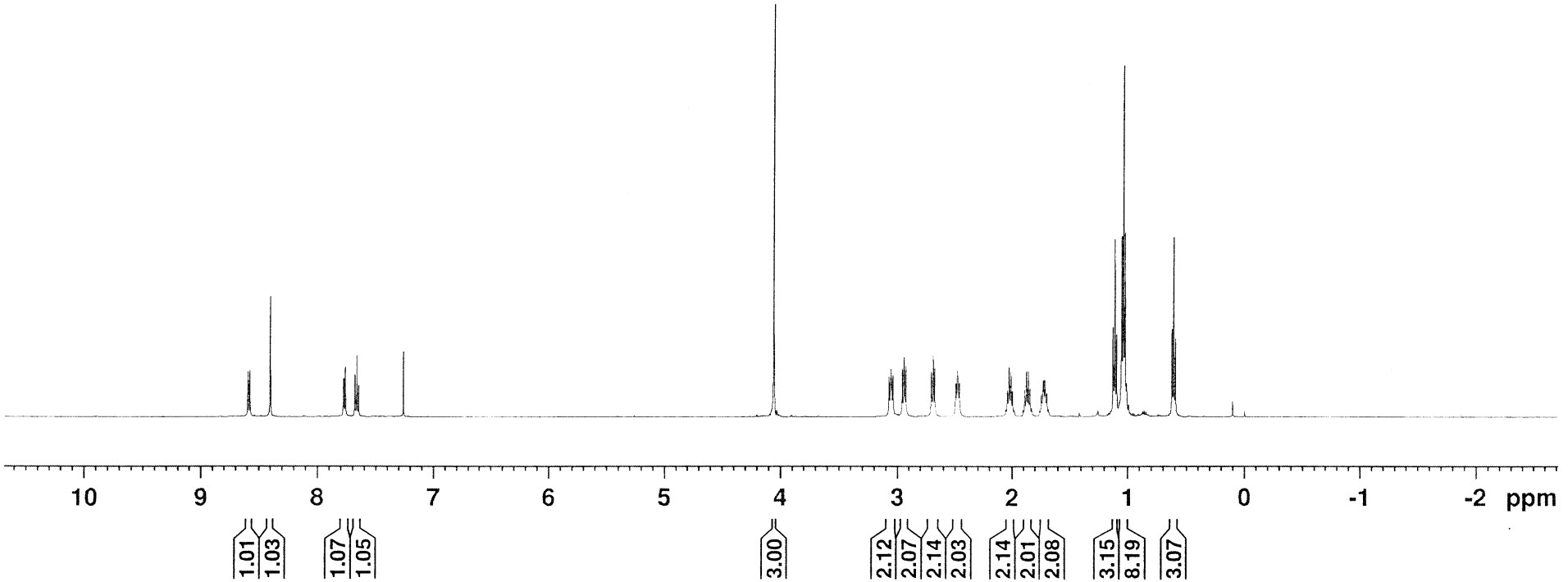


MJ-198-15



168.14
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154.77
137.63
136.83
131.30
128.67
128.58
127.32
126.83
126.51
125.34
124.22
123.80
118.32
77.25
77.00
76.74
52.53
36.60
34.40
34.18
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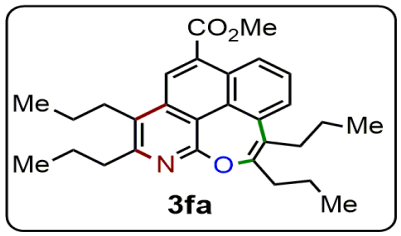
24.53
22.88
22.35
20.45
14.35
14.10
13.97
13.70

MJ-198-



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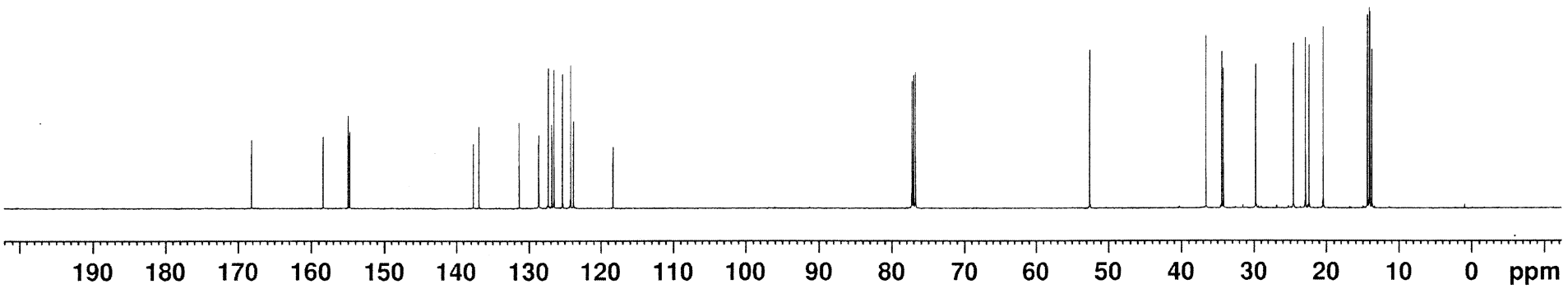

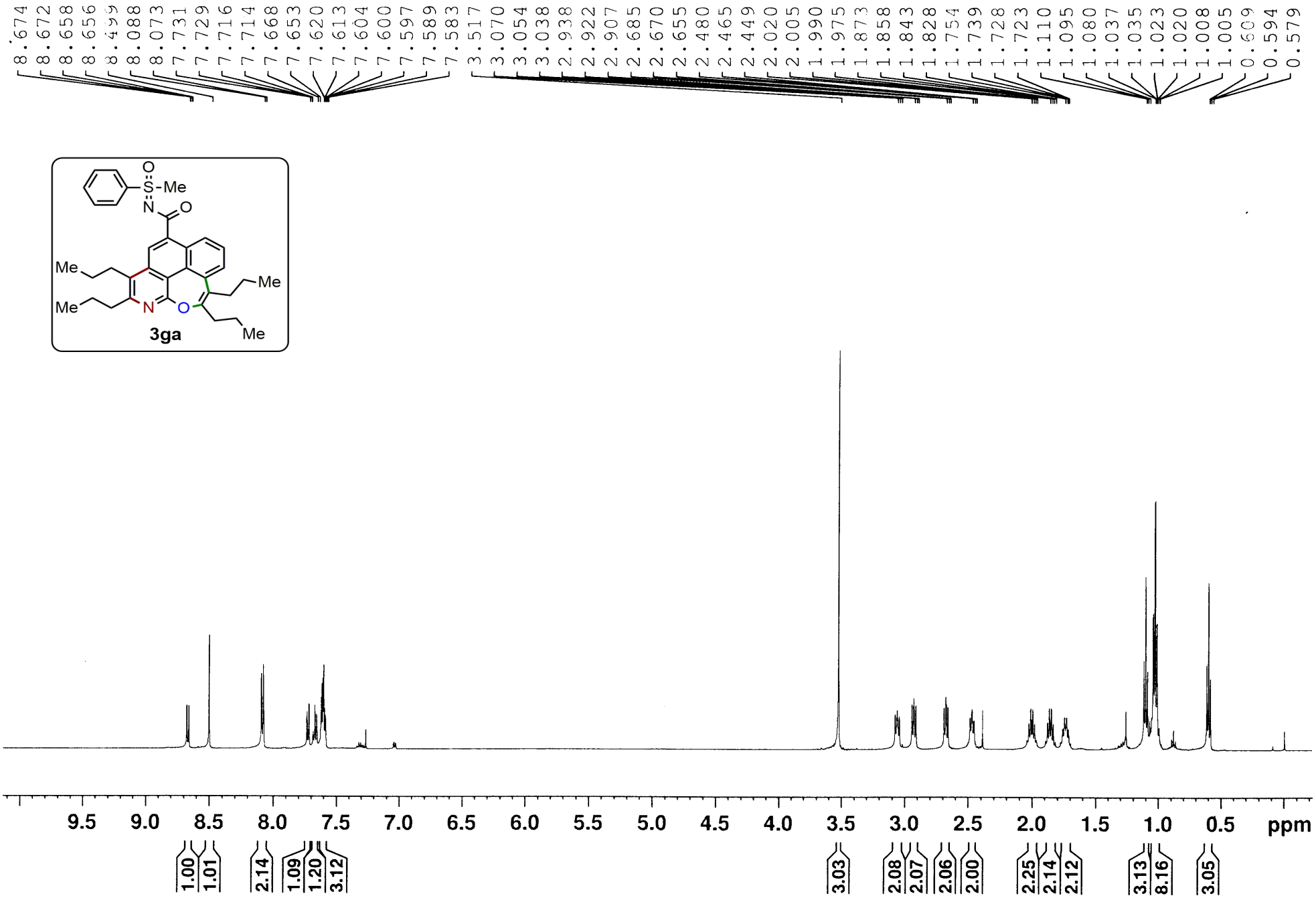
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7.653
7.620
7.613
7.604
7.600
7.597
7.589
7.583
3.517
3.070
3.054
3.038
2.938
2.922
2.907
2.685
2.670
2.655
2.480
2.465
2.449
2.020
2.005
1.990
1.975
1.873
1.858
1.843
1.828
1.754
1.739
1.728
1.723
1.110
1.095
1.080
1.037
1.035
1.023
1.020
1.008
1.005
0.609
0.594
0.579
O
S-Me
N
O
Me
Me
Me
Me
N
O
3ga
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
ppm
1.00
1.01
2.14
1.09
1.20
3.12
3.03
2.08
2.07
2.06
2.00
2.25
2.14
2.12
3.13
8.16
3.05

MAJJI-16-55

158.43
154.48
138.59
137.34
137.04
133.92
129.66
128.98
128.72
128.14
127.01
126.96
126.62
126.16
124.69
123.97
77.25
77.00
76.74
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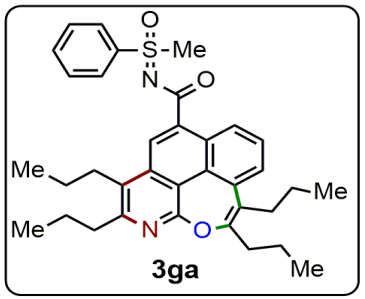
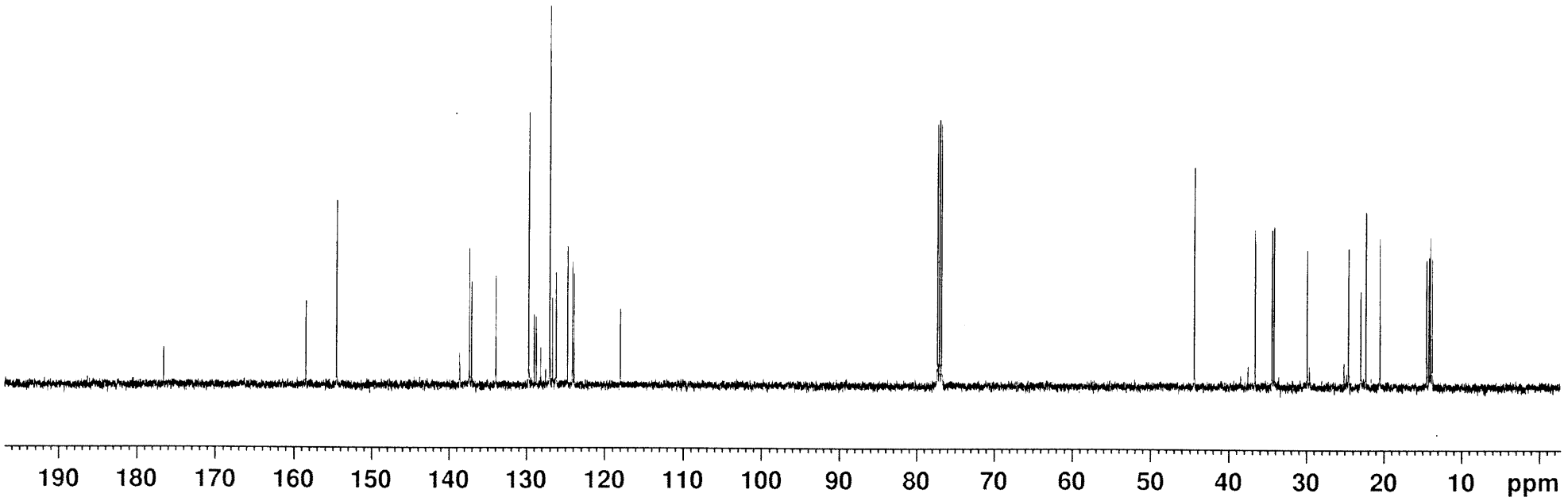
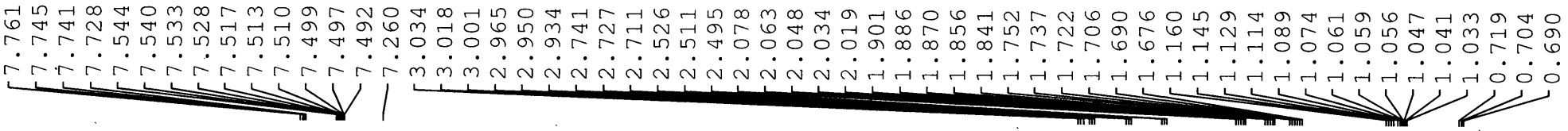
22.92
22.28
20.45
14.43
13.95
13.70



3ga

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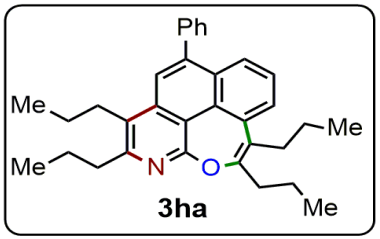
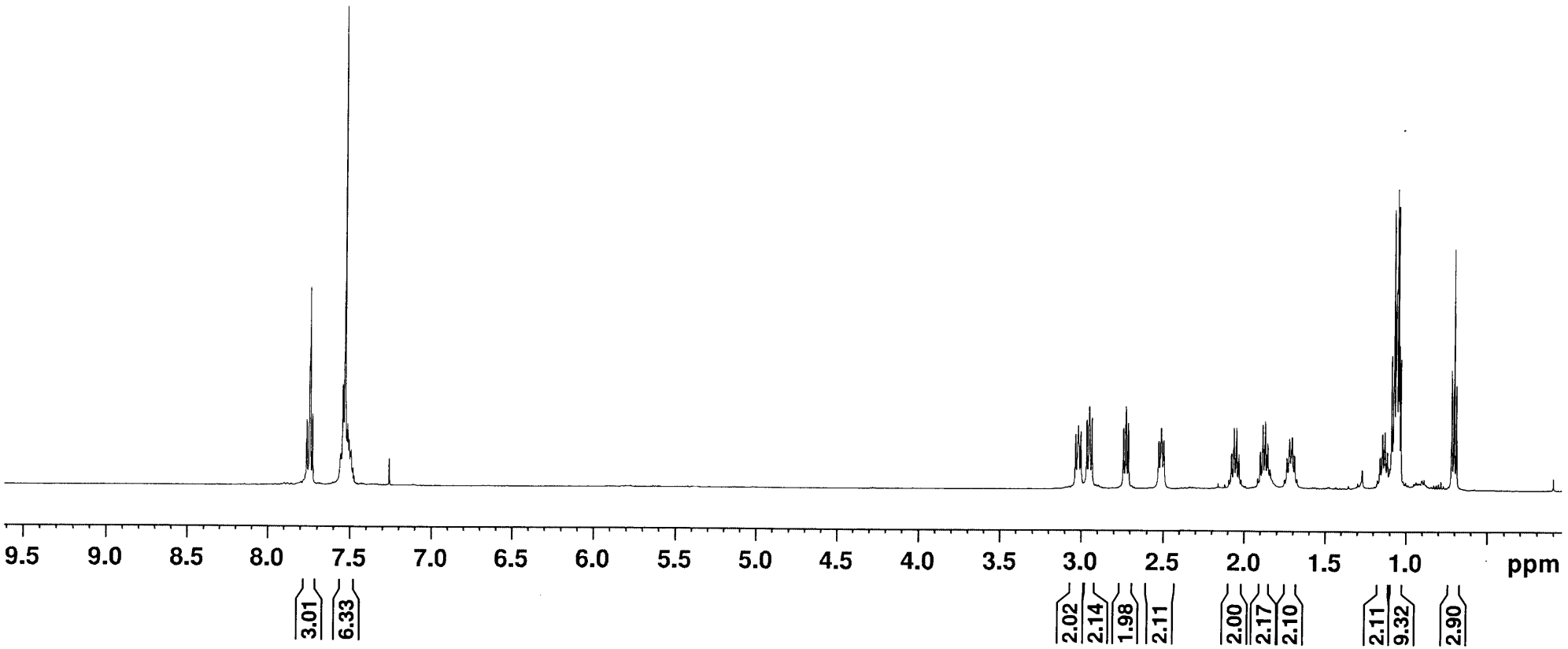
7.741
7.728
7.544
7.540
7.533
7.528
7.517
7.513
7.510
7.499
7.497
7.492
7.260
3.034
3.018
3.001
2.965
2.950
2.934
2.741
2.727
2.711
2.526
2.511
2.495
2.078
2.063
2.048
2.034
2.019
1.901
1.886
1.870
1.856
1.841
1.752
1.737
1.722
1.706
1.690
1.676
1.160
1.145
1.129
1.114
1.089
1.074
1.061
1.059
1.056
1.047
1.041
1.033
0.719
0.704
0.690


Ph
Me
Me
Me
Me
N
O
3ha

MAJJI-16-138


9.5
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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
ppm
3.01
6.33
2.02
2.14
1.98
2.11
2.00
2.17
2.10
2.11
9.32
2.90

MAJJI-16-138

158.62
154.78
154.55
143.28
140.80
138.22
137.72
131.09
129.95
128.71
128.32
127.68
126.90
125.97
125.75
125.08
123.92
122.06
116.72
77.25
77.00
76.74
36.70
34.66
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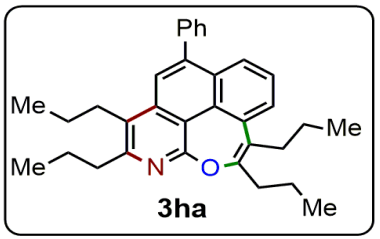
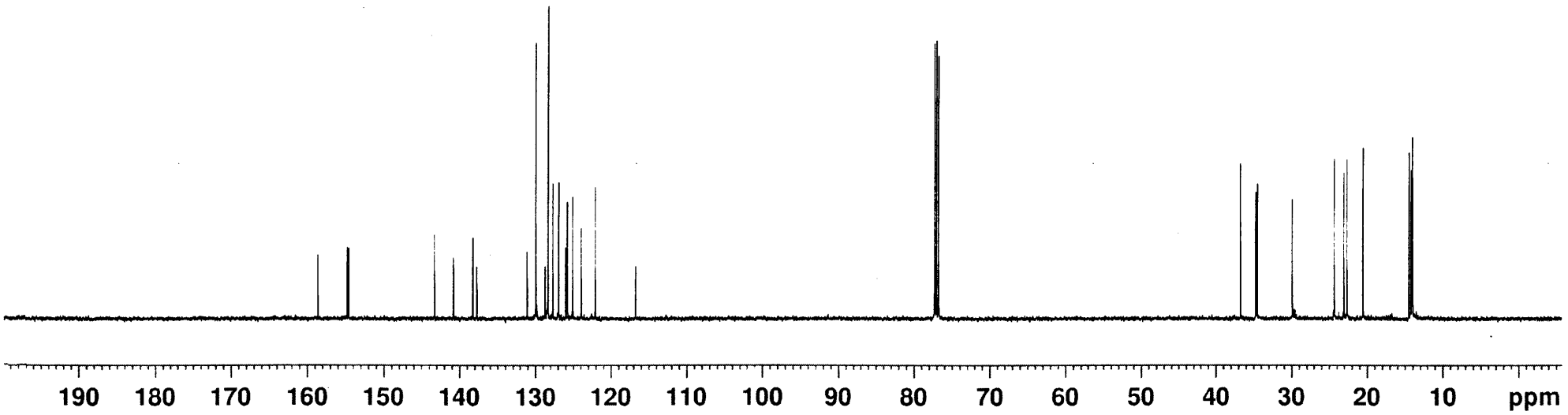
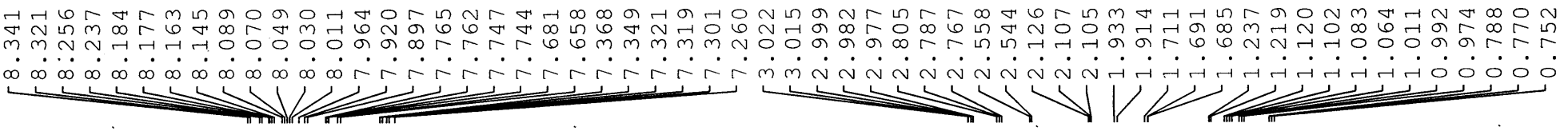
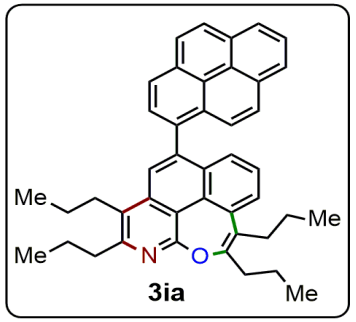
22.66
20.53
14.45
14.18
14.03
13.96

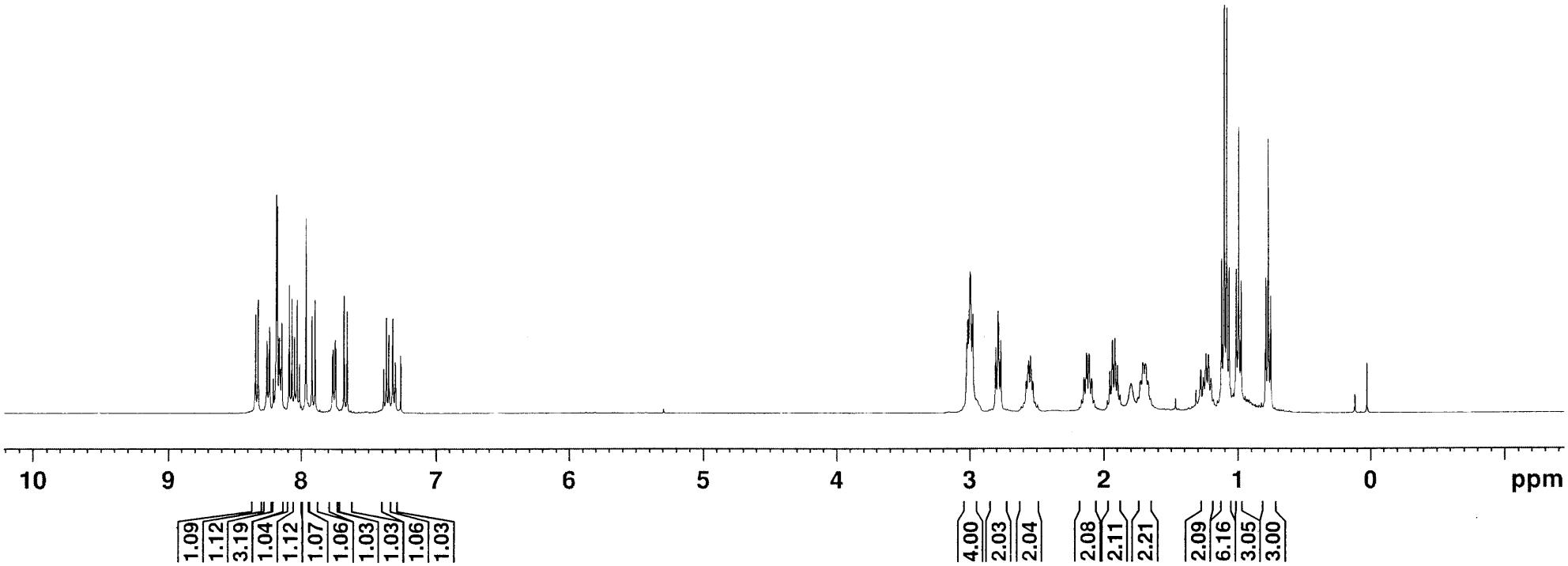


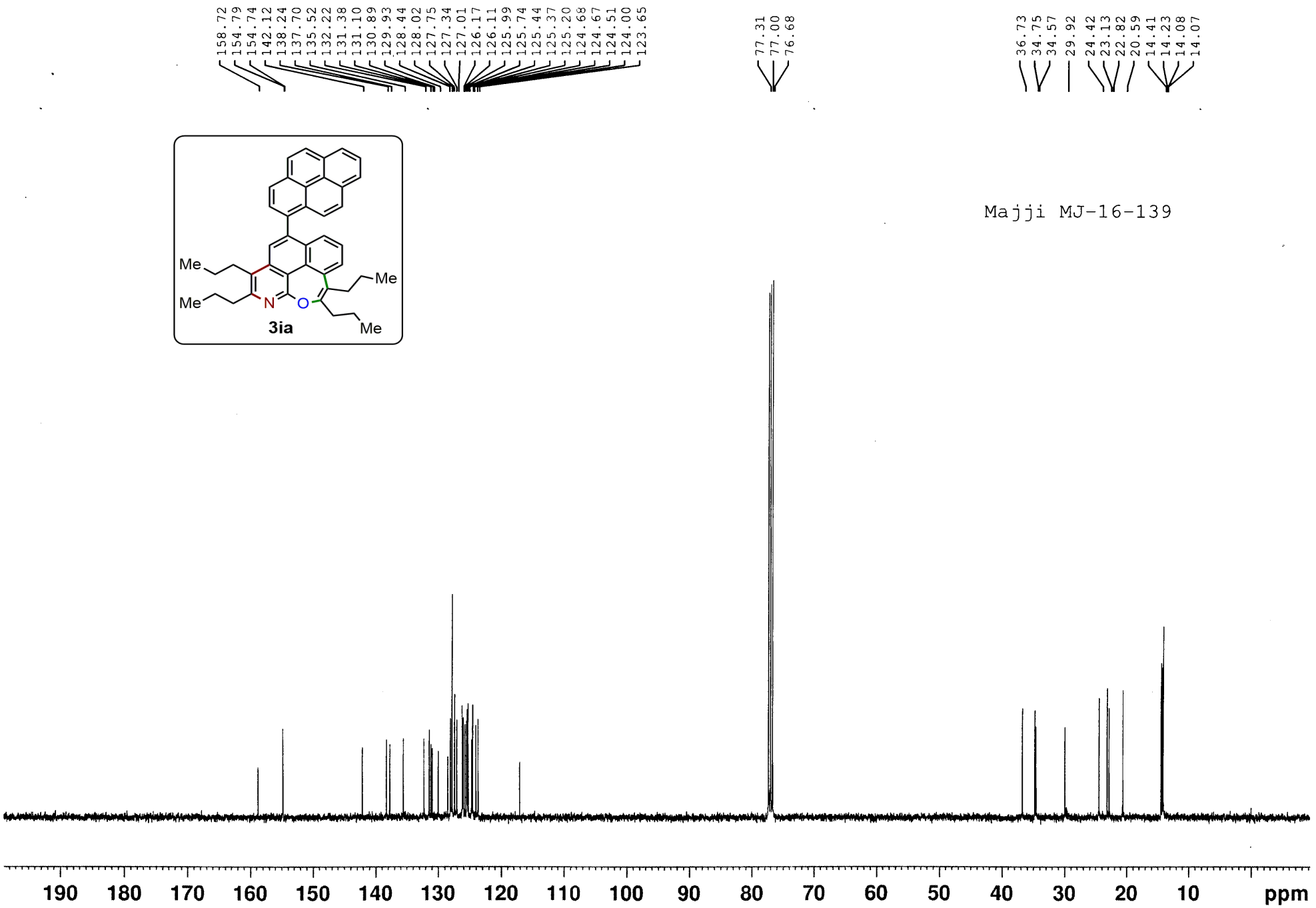






Majji MJ-16-139

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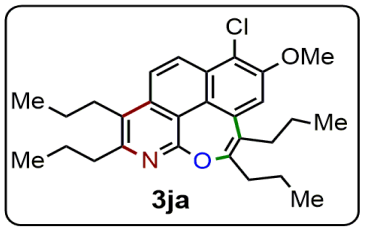
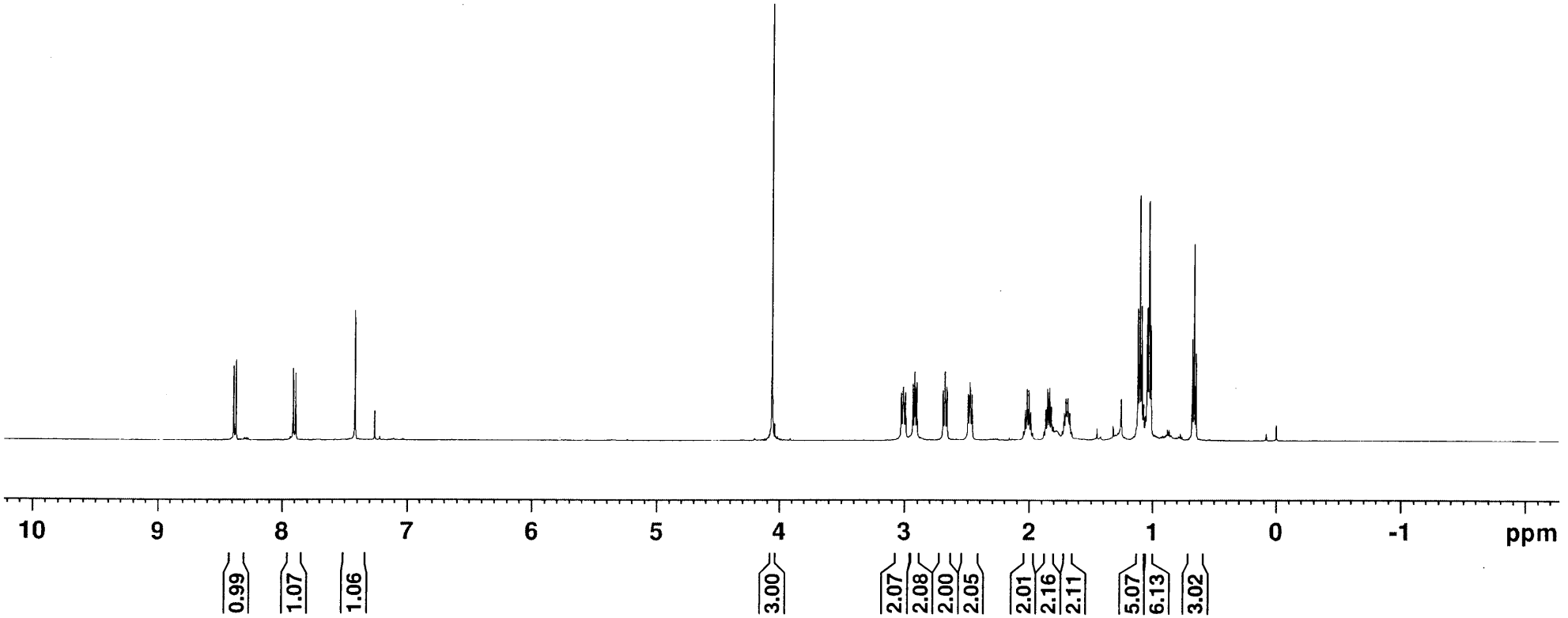
154.79
154.74
142.12
138.24
137.70
135.52
132.22
131.38
131.10
130.89
129.93
128.44
128.02
127.75
127.34
127.01
126.17
126.11
125.99
125.74
125.44
125.37
125.20
124.68
124.67
124.51
124.00
123.65
77.31
77.00
76.68
36.73
34.75
34.57
29.92
24.42
23.13
22.82
20.59
14.41
14.23
14.08
14.07
Me
Me
Me
Me
N
O
3ia
Majji MJ-16-139
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

8.385
8.366
7.910
7.891
7.416
7.260

4.055
3.021
3.005
2.989
2.930
2.915
2.899
2.691
2.676
2.660
2.493
2.477
2.462
2.029
2.014
1.999
1.984
1.863
1.848
1.833
1.818
1.715
1.699
1.688
1.683
1.668
1.115
1.100
1.086
1.043
1.039
1.028
1.024
1.013
1.009
0.673
0.658
0.643

MAJJI-16-144





MAJJI-16-144

157.84
154.99
154.27
152.70
137.72
137.55
130.09
126.74
126.28
123.96
123.24
123.12
117.15
116.90
112.60
77.25
77.00
76.74
56.79
36.59
34.59
34.38
29.98
24.39
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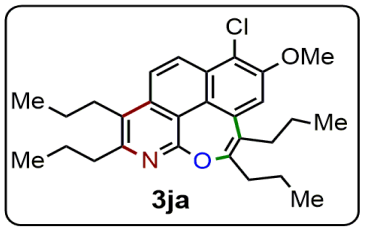
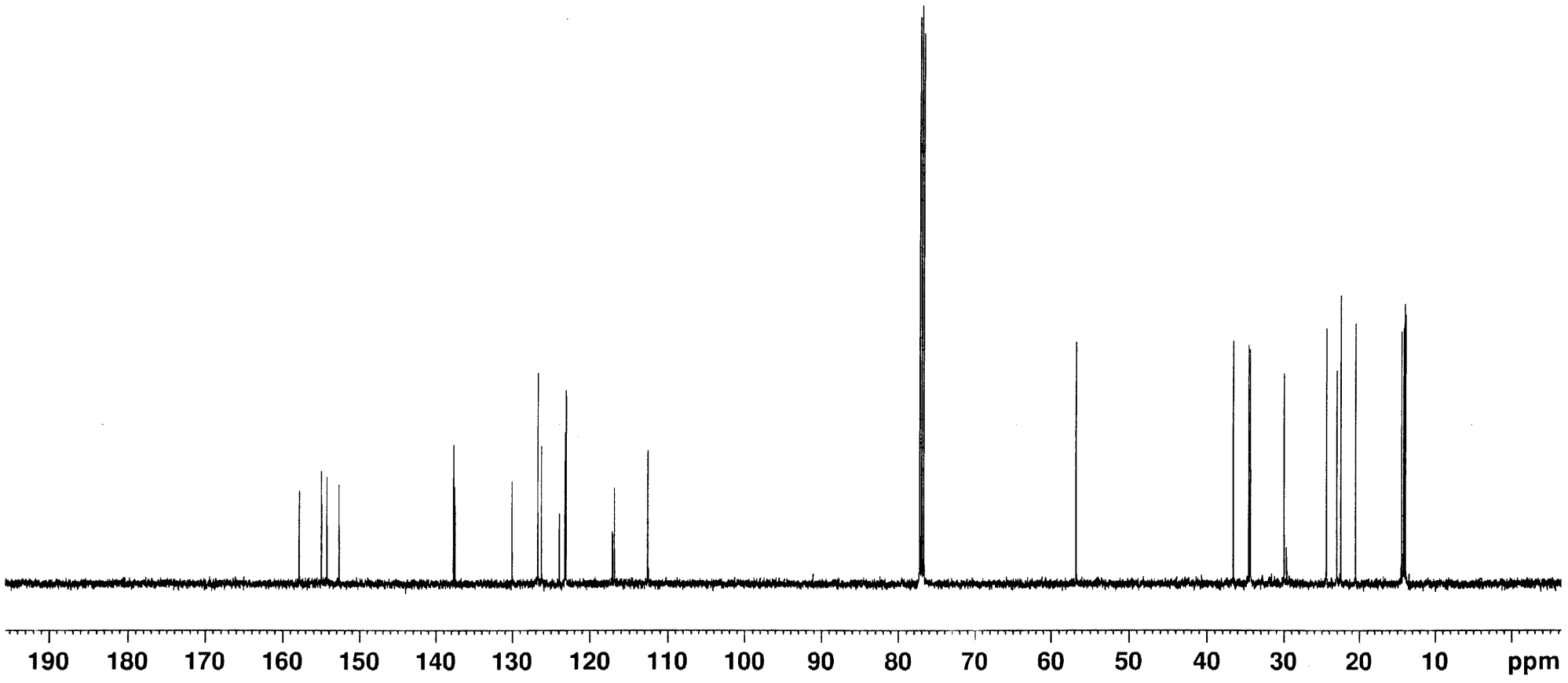
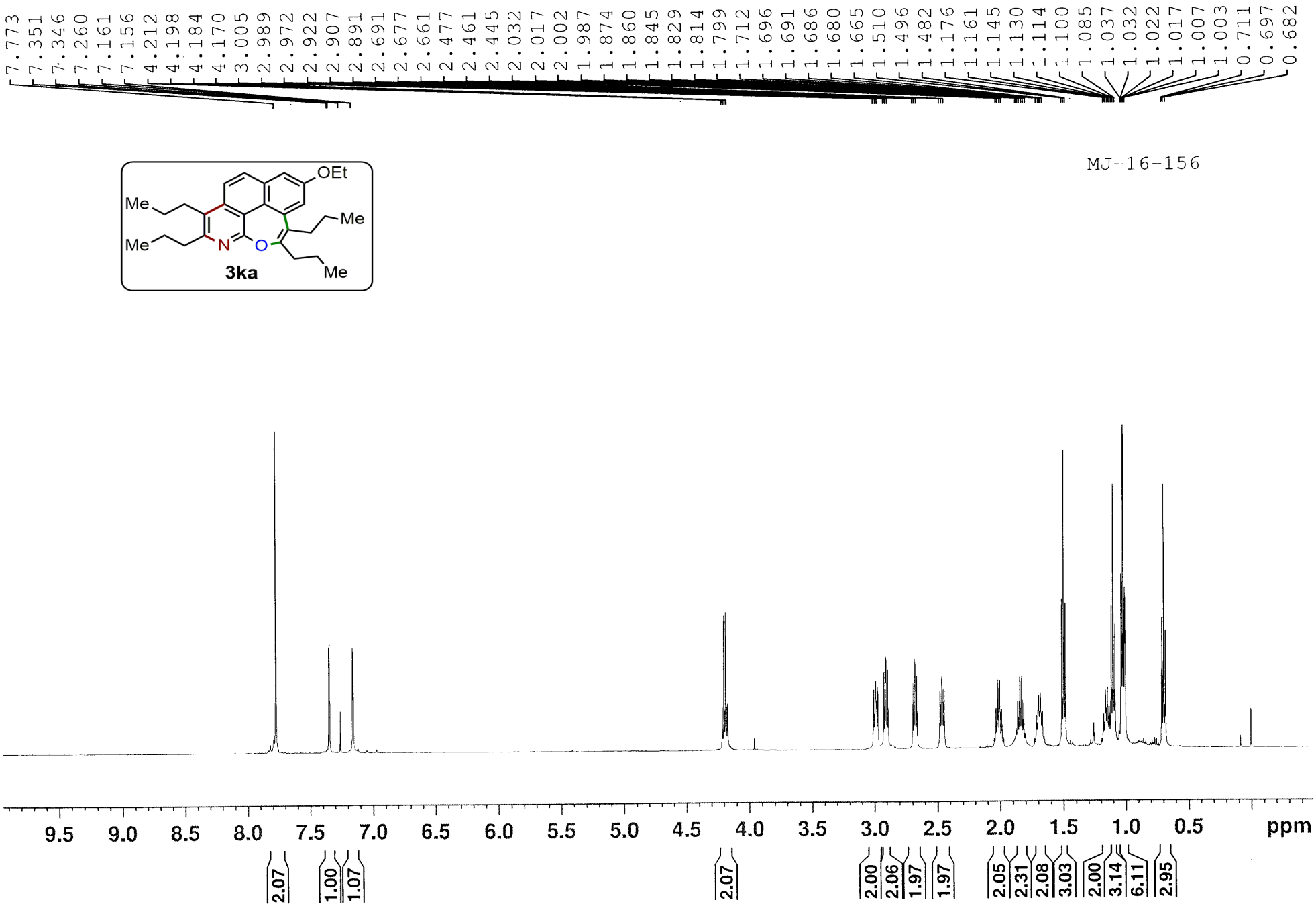
22.49
20.54
14.46
14.17
14.04
13.88



3ja

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7.156
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4.198
4.184
4.170
3.005
2.989
2.972
2.922
2.907
2.891
2.691
2.677
2.661
2.477
2.461
2.445
2.032
2.017
2.002
1.987
1.874
1.860
1.845
1.829
1.814
1.799
1.712
1.696
1.691
1.686
1.680
1.665
1.510
1.496
1.482
1.176
1.161
1.145
1.130
1.114
1.100
1.085
1.037
1.032
1.022
1.017
1.007
1.003
0.711
0.697
0.682
MJ-16-156
OEt
Me
Me
Me
Me
N
O
3ka
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
ppm
2.07
1.00
1.07
2.07
2.00
2.06
1.97
1.97
2.05
2.31
2.08
3.03
2.00
3.14
6.11
2.95

MJ-16-156

158.03
156.83
154.53
153.03
139.09
137.69
133.16
131.11
125.96
123.49
122.70
121.65
117.31
108.18
77.25
76.99
76.74
63.66
36.56
34.78
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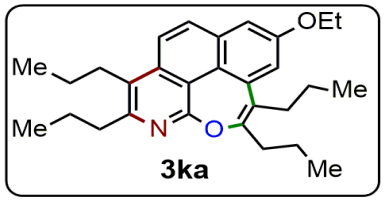
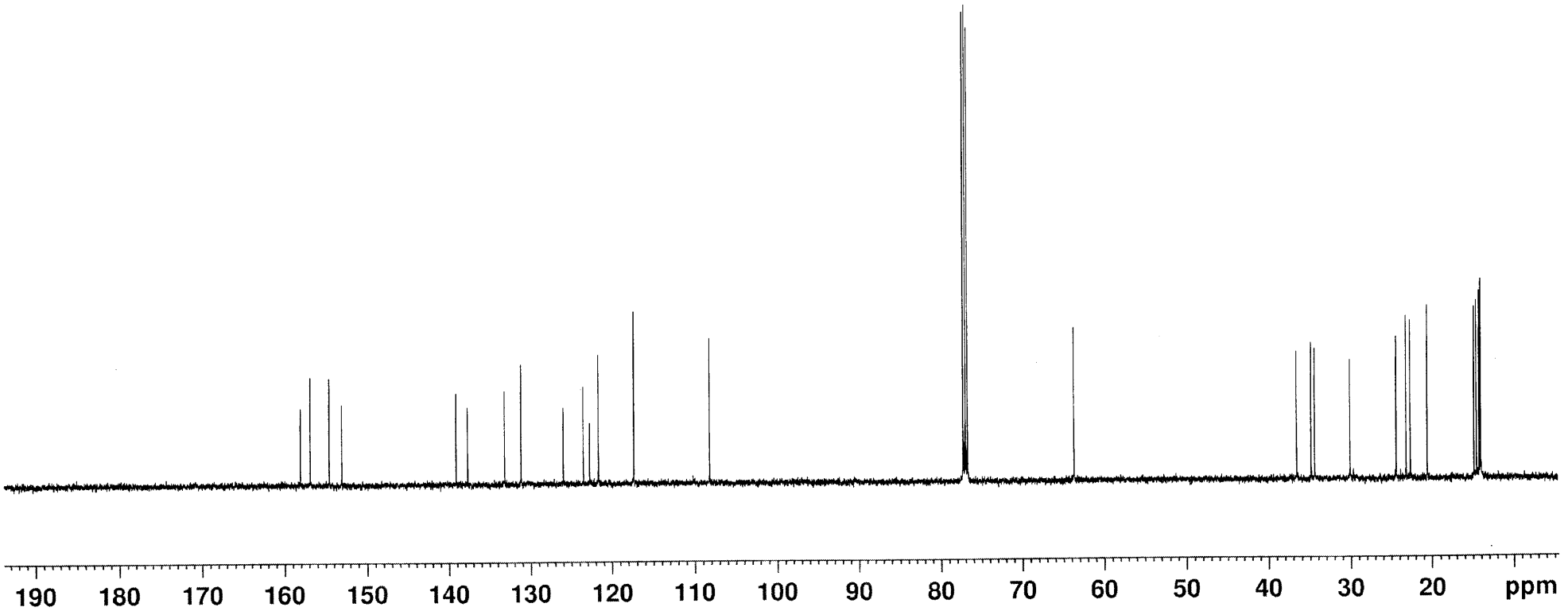
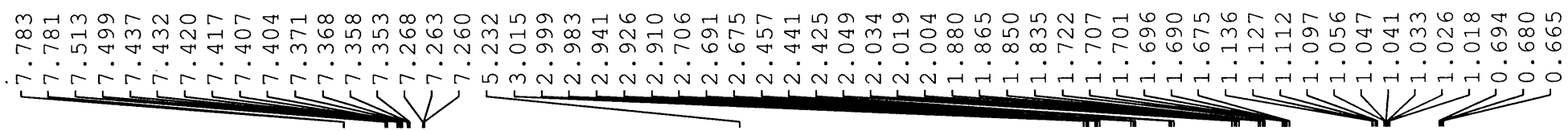
30.04
24.35
23.13
22.62
20.54
14.82
14.52
14.18
14.02
13.98



3ka

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7.432
7.420
7.417
7.407
7.404
7.371
7.368
7.358
7.353
7.268
7.263
7.260
5.232
3.015
2.999
2.983
2.941
2.926
2.910
2.706
2.691
2.675
2.457
2.441
2.425
2.049
2.034
2.019
2.004
1.880
1.865
1.850
1.835
1.722
1.707
1.701
1.696
1.690
1.675
1.136
1.127
1.112
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1.047
1.041
1.033
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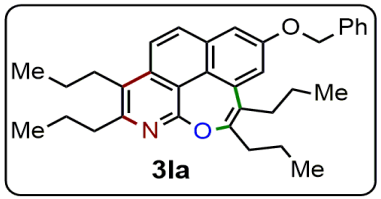
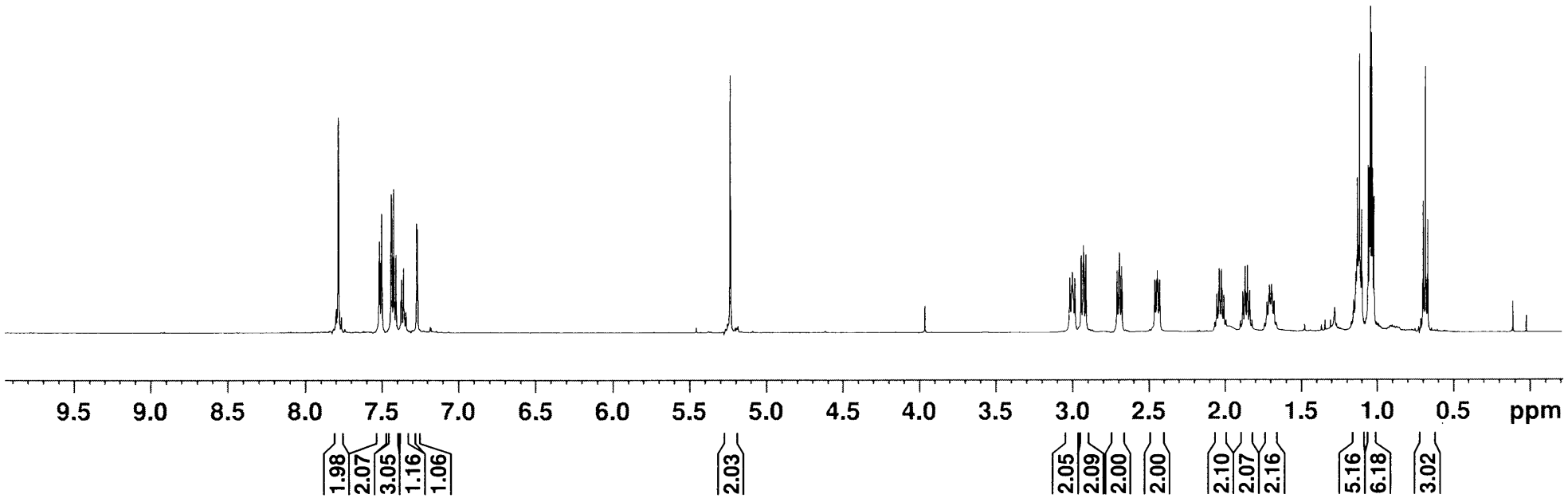
0.694
0.680
0.665

MJ-16-155


O
Ph
Me
Me
Me
N
O
Me

3la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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.98
2.07
3.05
1.16
1.06
2.03
2.05
2.09
2.00
2.00
2.10
2.07
2.16
5.16
6.18
3.02

158.03
156.61
154.60
139.17
137.75
136.68
131.16
128.62
128.32
127.49
125.98
123.48
122.93
121.72
117.35
108.80
77.25
76.74
70.17
36.55
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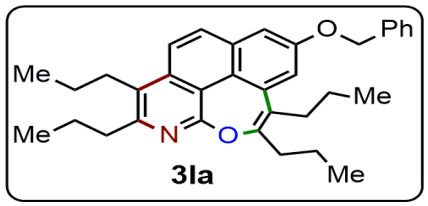
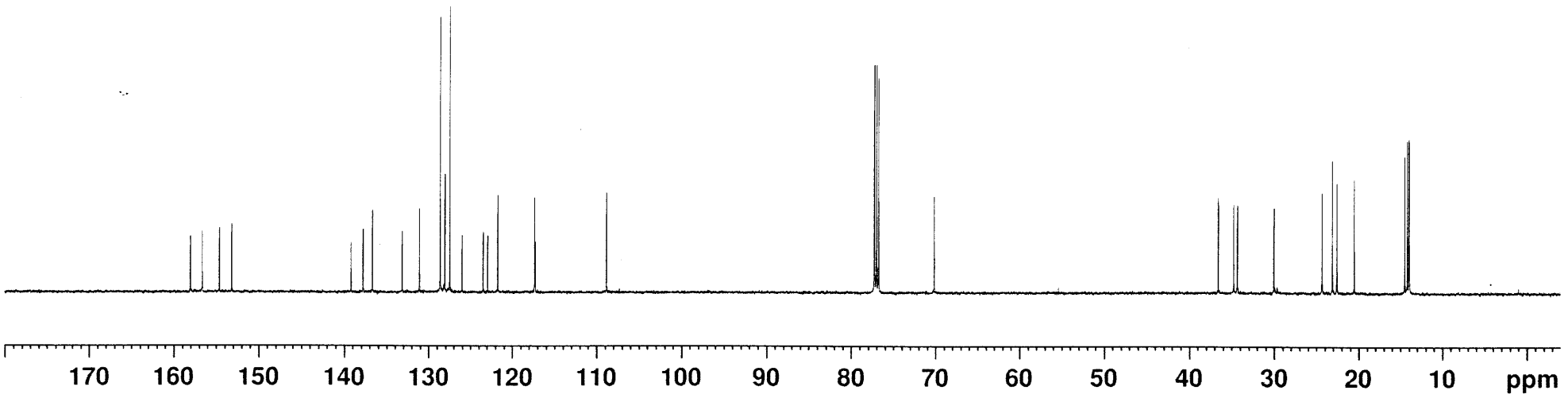
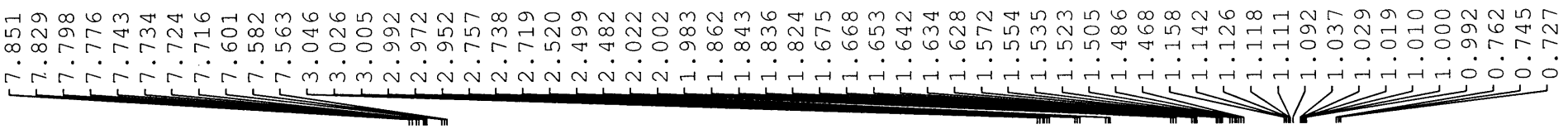
14.56
14.19
14.01
13.95

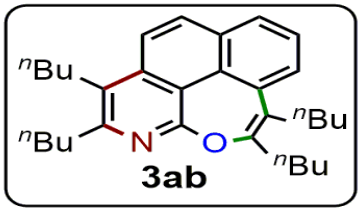
MJ-16-155



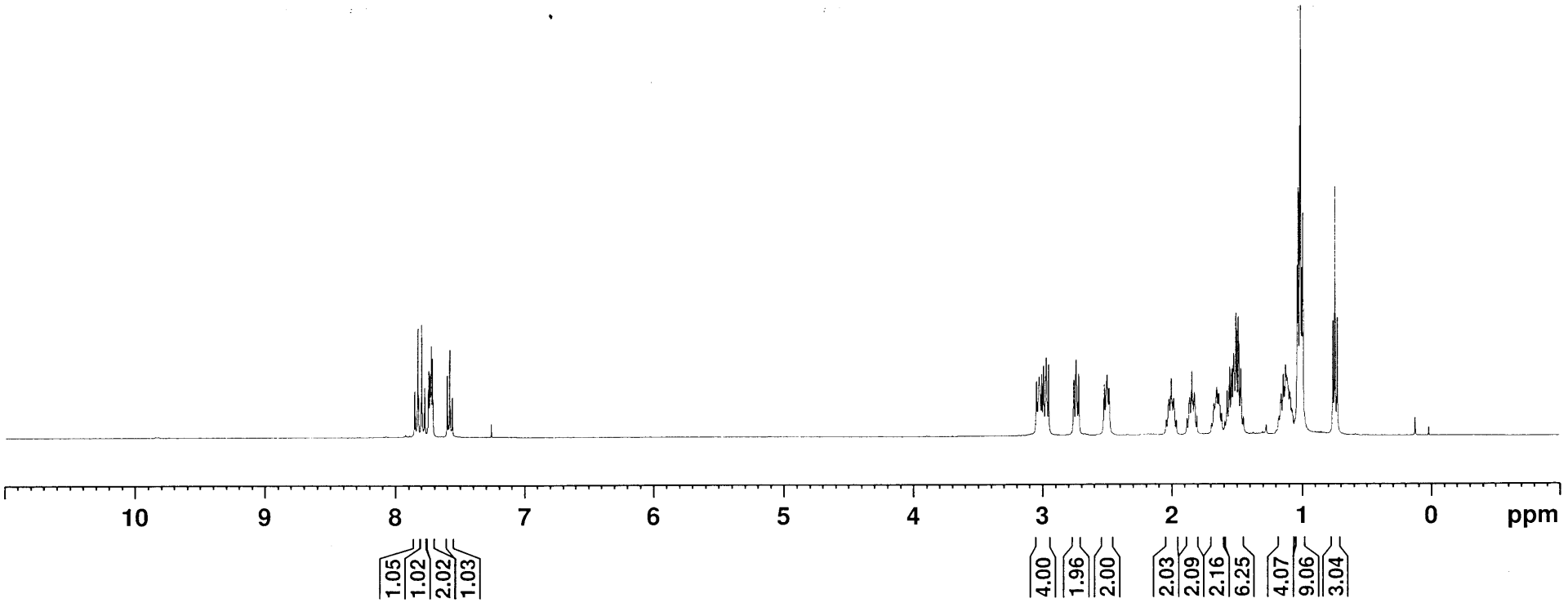
3la







Majji-MJ-166-12



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126.99
126.62
126.05
123.77
121.12
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77.42
77.10
76.78
34.53
33.31
32.79
32.17
31.81
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27.77
23.22
22.98
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22.72
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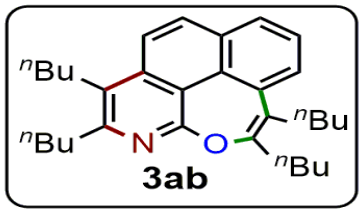
14.10
14.00
13.77



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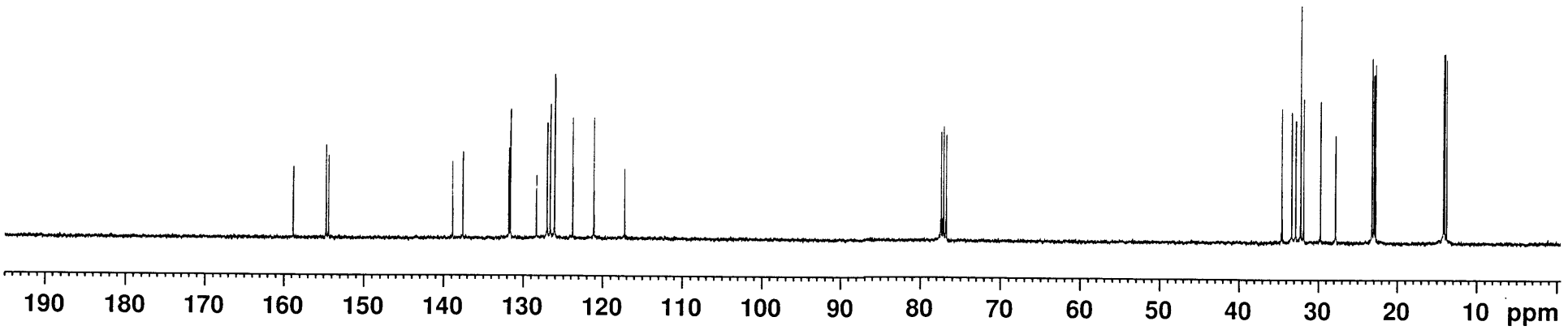
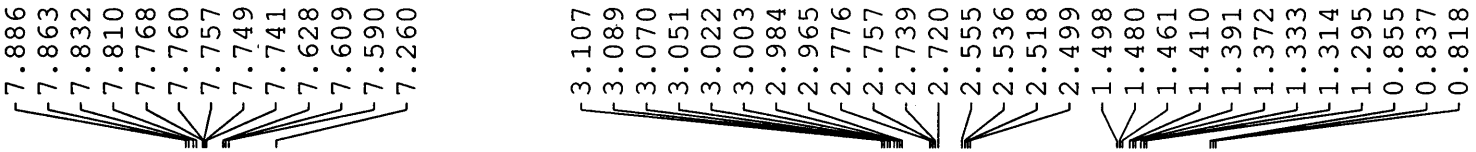
Majji-MJ-166-12

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7.757
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7.741
7.628
7.609
7.590
7.260
3.107
3.089
3.070
3.051
3.022
3.003
2.984
2.965
2.776
2.757
2.739
2.720
2.555
2.536
2.518
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1.498
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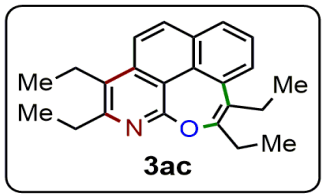
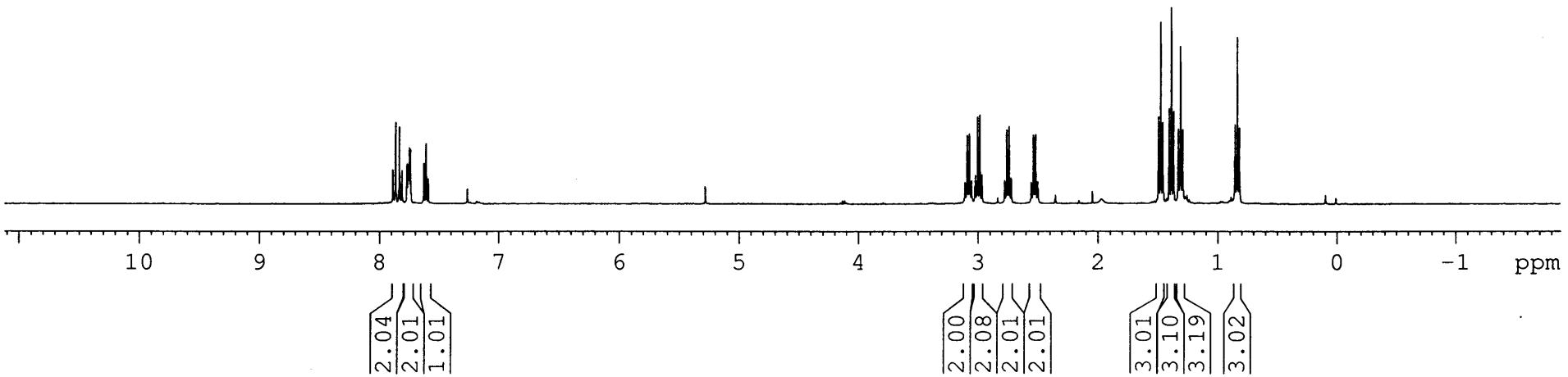
1.372
1.333
1.314
1.295
0.855
0.837
0.818


Me
Me
N
O
Me
Me

3ac

mj -171-12


10
9
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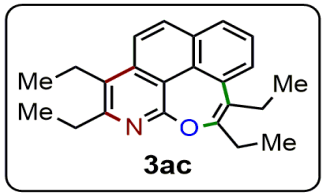
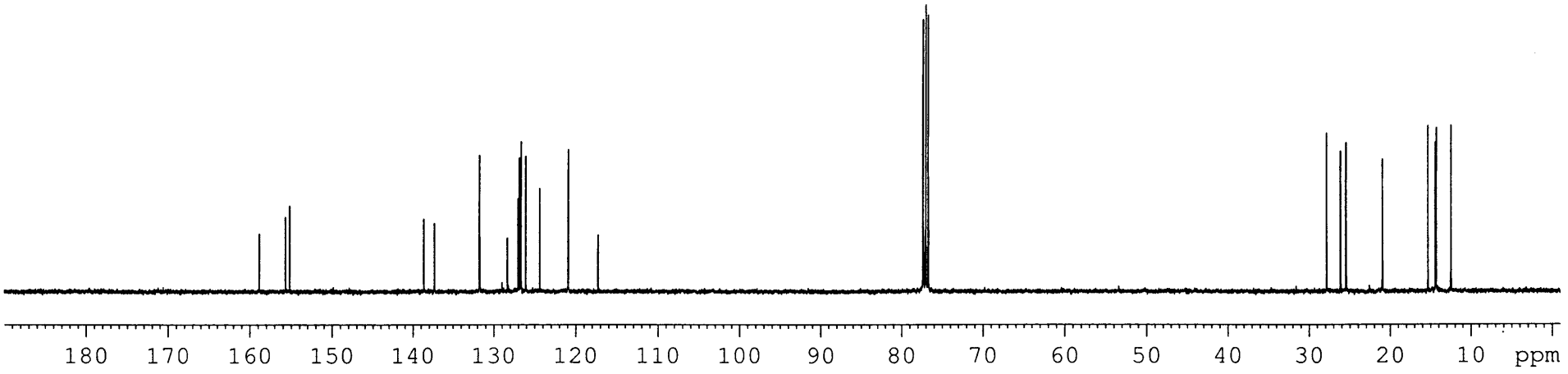
6
5
4
3
2
1
0
-1
ppm
2.04
2.01
1.01
2.00
2.08
2.01
2.01
3.01
3.10
3.19
3.02

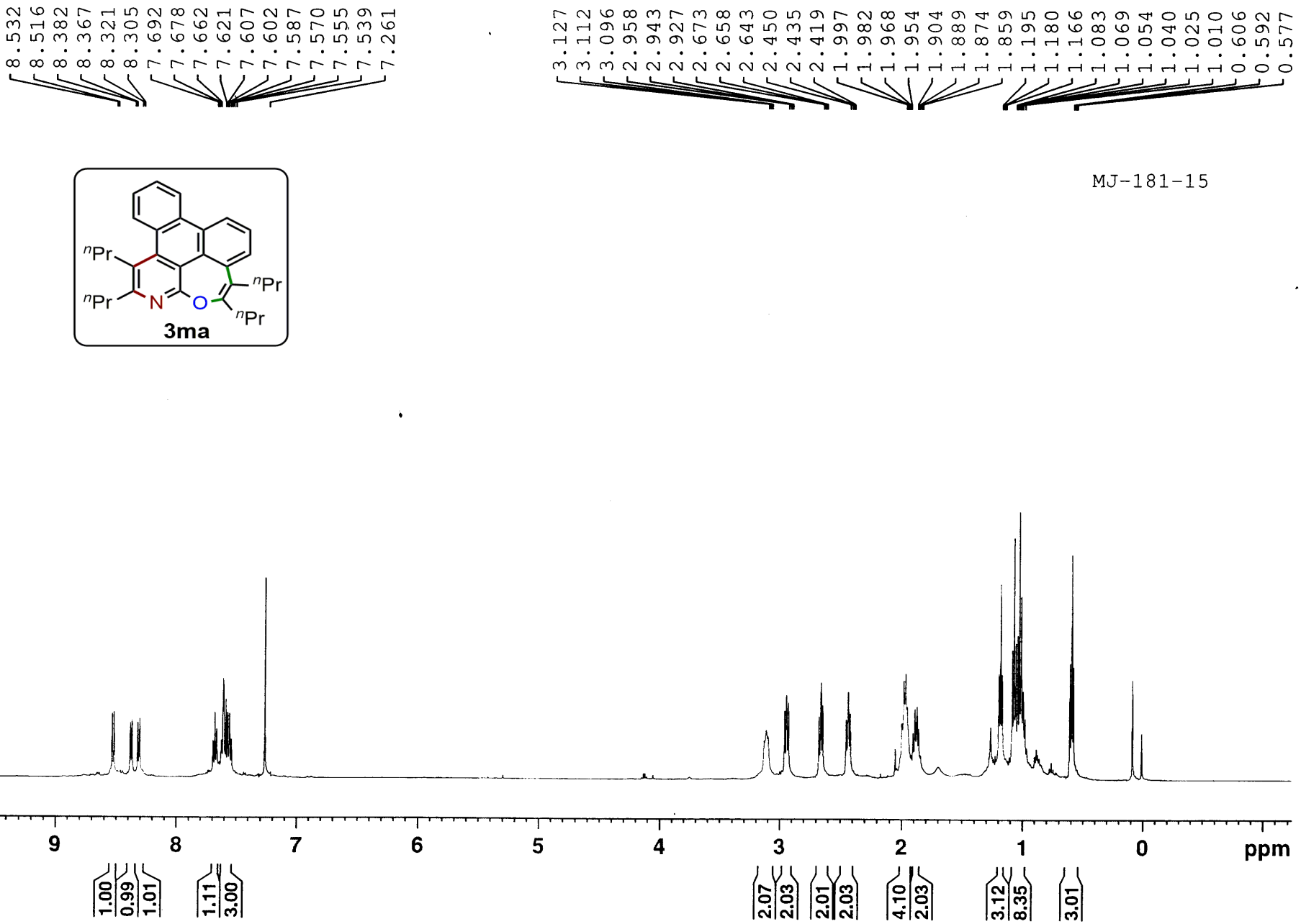
158.84
155.69
155.17
138.65
137.33
131.75
131.71
128.31
127.01
126.84
126.64
126.08
124.38
120.90
117.25
77.32
77.00
76.68
27.83
26.13
25.45
20.97
15.31
14.39
14.25
12.47

mj -171-12



3ac

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8.305
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7.678
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7.602
7.587
7.570
7.555
7.539
7.261
3.127
3.112
3.096
2.958
2.943
2.927
2.673
2.658
2.643
2.450
2.435
2.419
1.997
1.982
1.968
1.954
1.904
1.889
1.874
1.859
1.195
1.180
1.166
1.083
1.069
1.054
1.040
1.025
1.010
0.606
0.592
0.577
nPr
nPr
nPr
nPr
N
O
3ma
MJ-181-15
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.99
1.01
1.11
3.00
2.07
2.03
2.01
2.03
4.10
2.03
3.12
8.35
3.01

mj-181-15

160.17
158.09
154.80
139.63
138.14
132.94
128.45
128.30
128.21
127.68
127.52
126.56
126.38
125.38
124.25
123.47
120.05
117.16
77.32
77.00
76.68
37.16
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22.24
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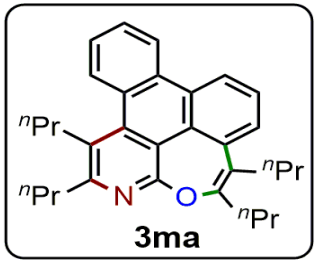
14.30
14.06
13.77



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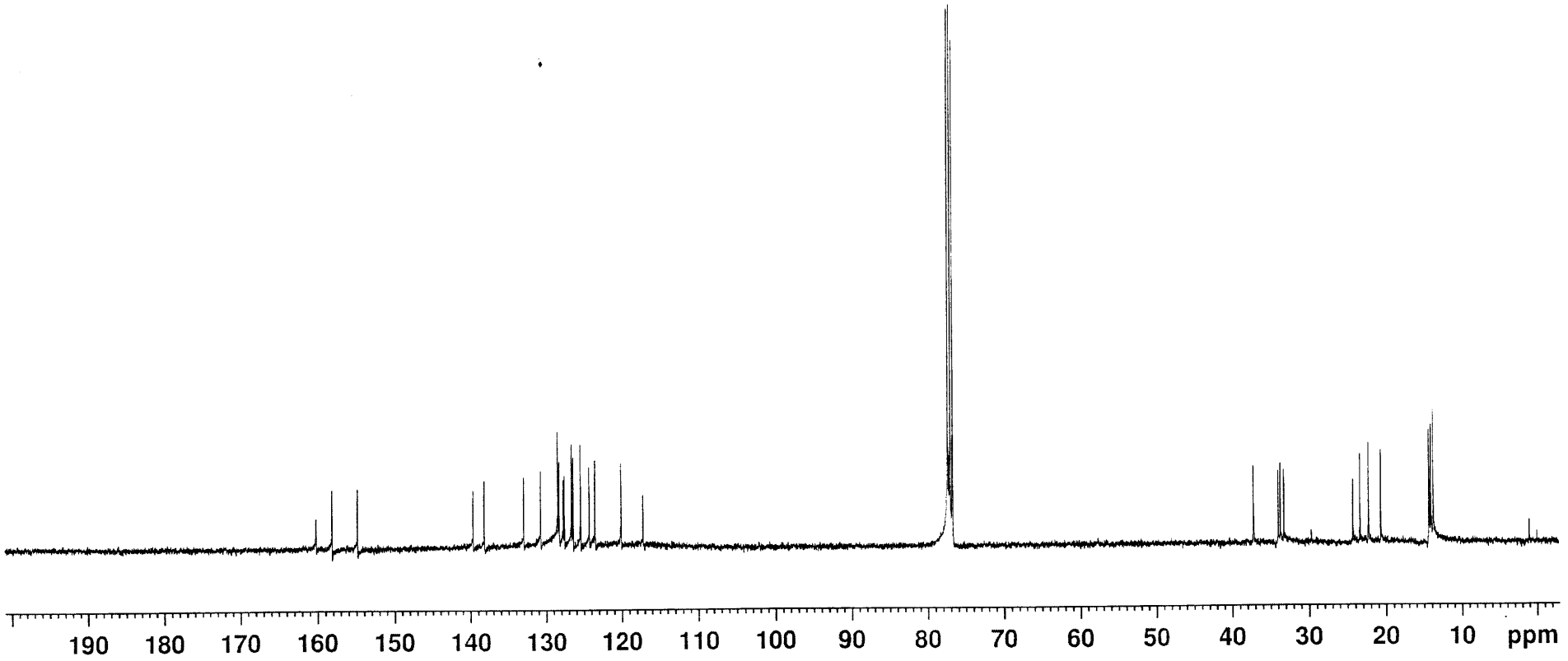

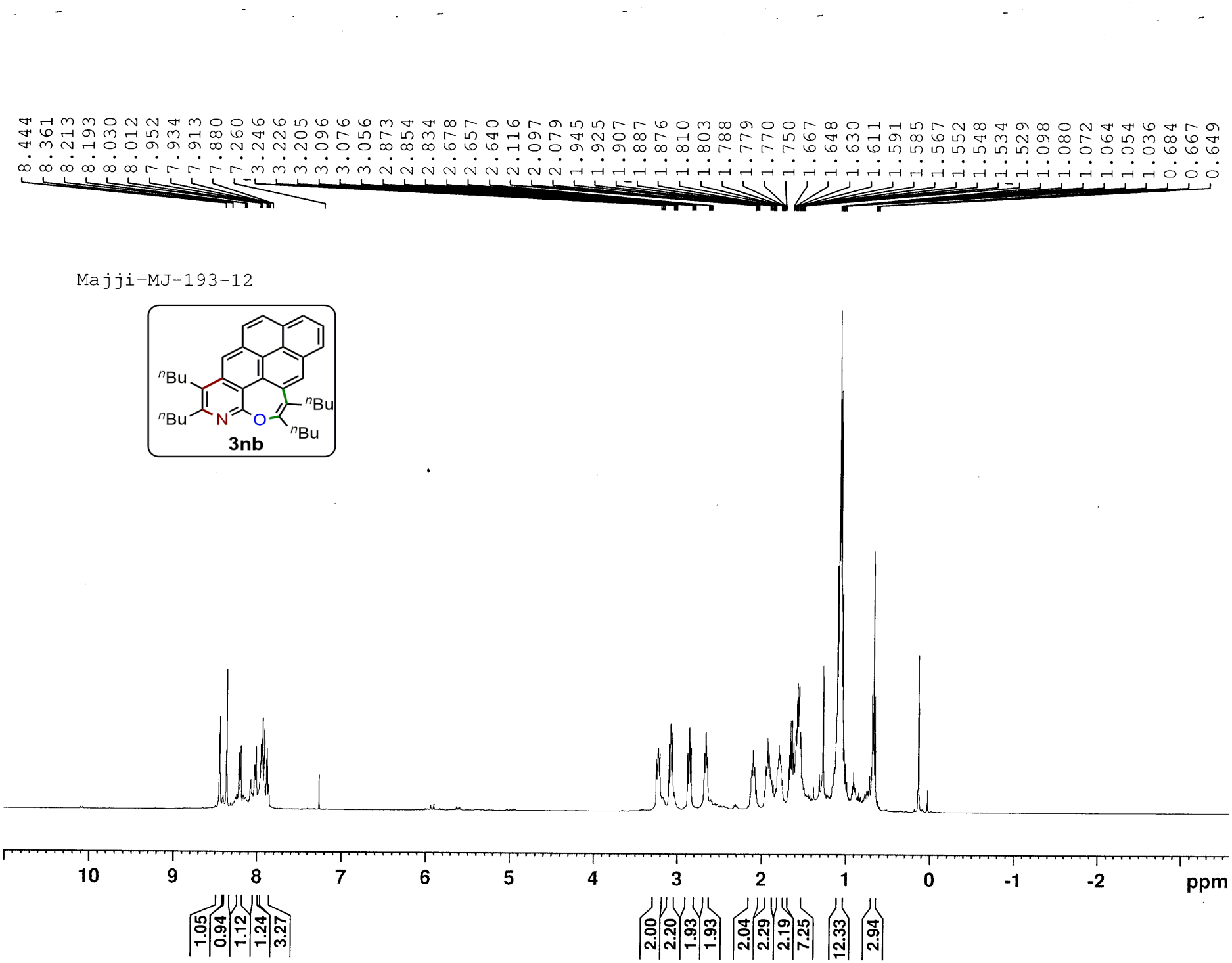
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8.012
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7.934
7.913
7.880
7.260
3.246
3.226
3.205
3.096
3.076
3.056
2.873
2.854
2.834
2.678
2.657
2.640
2.116
2.097
2.079
1.945
1.925
1.907
1.887
1.876
1.810
1.803
1.788
1.779
1.770
1.750
1.667
1.648
1.630
1.611
1.591
1.585
1.567
1.552
1.548
1.534
1.529
1.098
1.080
1.072
1.064
1.054
1.036
0.684
0.667
0.649
Majji-MJ-193-12
nBu
nBu
N
O
nBu
nBu
3nb
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm
1.05
0.94
1.12
1.24
3.27
2.00
2.20
1.93
1.93
2.04
2.29
2.19
7.25
12.33
2.94

159.09
155.42
151.24
136.86
135.99
132.84
130.52
130.27
128.86
128.15
127.52
127.12
126.40
126.31
125.55
124.86
124.23
123.42
122.85
119.67
115.47

77.32
77.00
76.68

34.49
33.19
32.79
32.66
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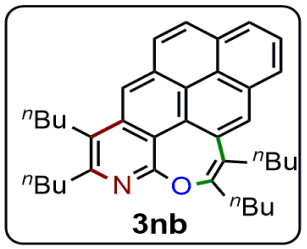
22.99
22.89
22.59
14.14
14.10
14.02
13.64



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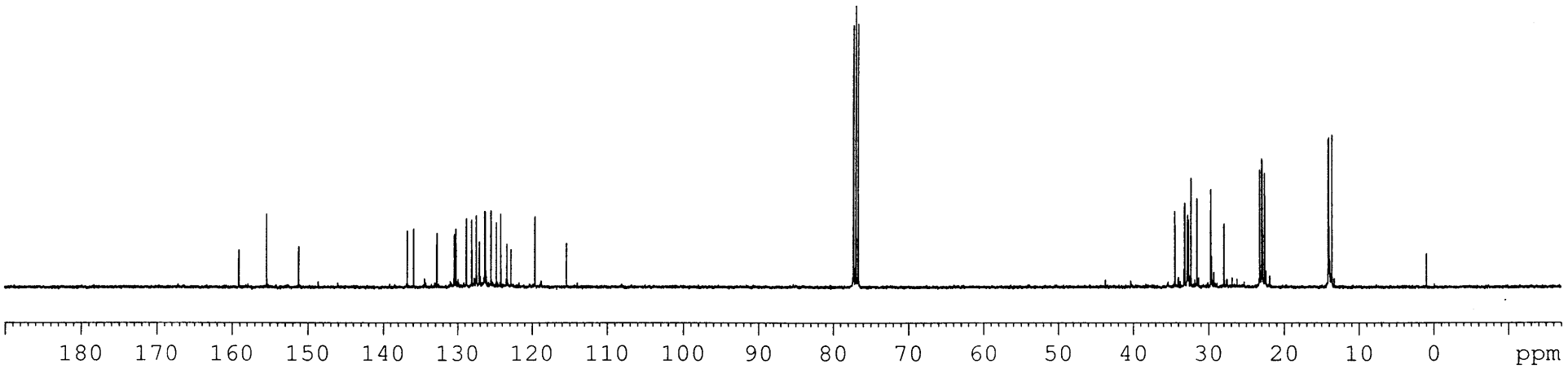

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8.112
7.723
7.706
7.699
7.683
7.663
7.647
7.493
7.478
7.462
7.446
7.430
7.260
3.095
3.079
3.063
2.956
2.941
2.925
2.721
2.707
2.691
2.503
2.487
2.472
2.065
2.050
2.035
2.021
1.909
1.894
1.878
1.863
1.808
1.792
1.777
1.761
1.199
1.185
1.170
1.142
1.127
1.112
1.097
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1.074
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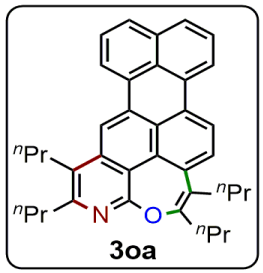
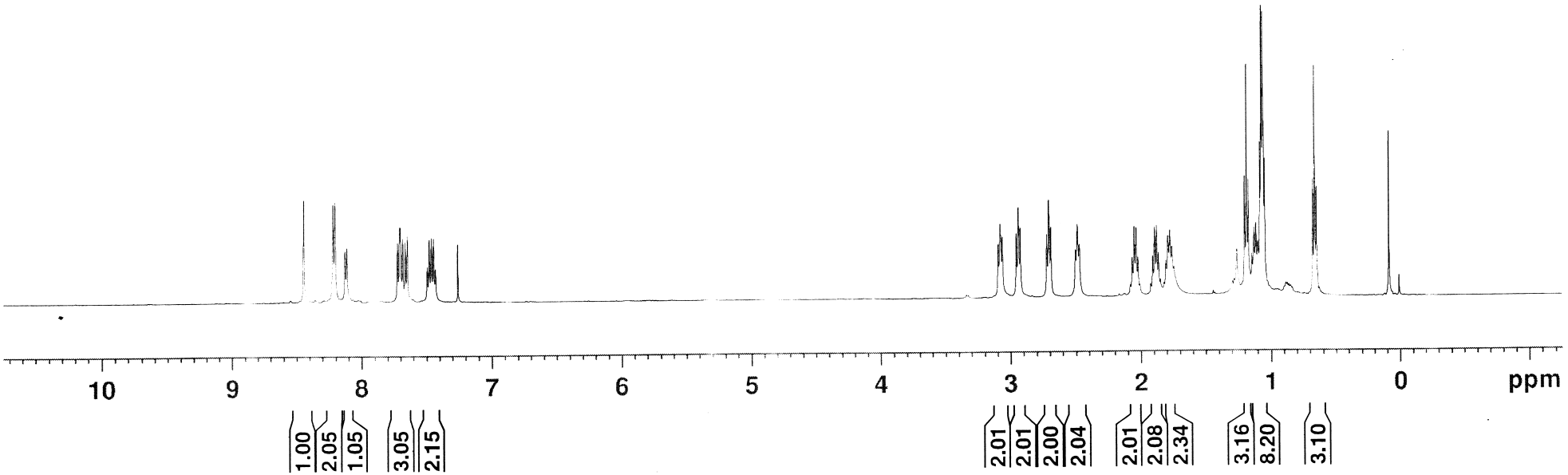
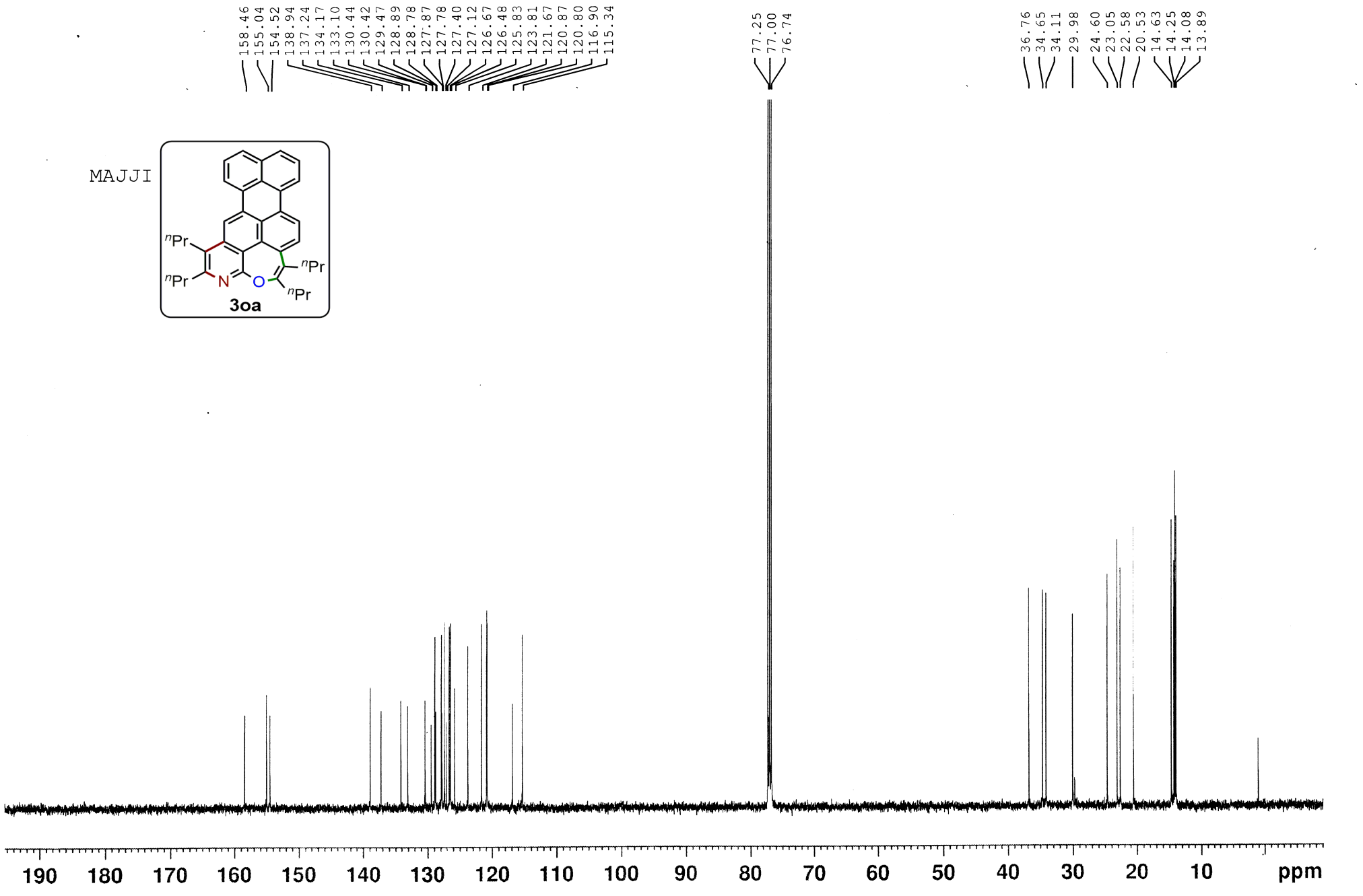
1.060
1.054
1.045
0.679
0.664
0.650

MAJJI-



3oa

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134.17
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130.44
130.42
129.47
128.89
128.78
127.87
127.78
127.40
127.12
126.67
126.48
125.83
123.81
121.67
120.87
120.80
116.90
115.34
77.25
77.00
76.74
36.76
34.65
34.11
29.98
24.60
23.05
22.58
20.53
14.63
14.25
14.08
13.89
MAJJI
nPr
nPr
N
O
nPr
nPr
3oa
190
180
170
160
150
140
130
120
110
100
90
80
70
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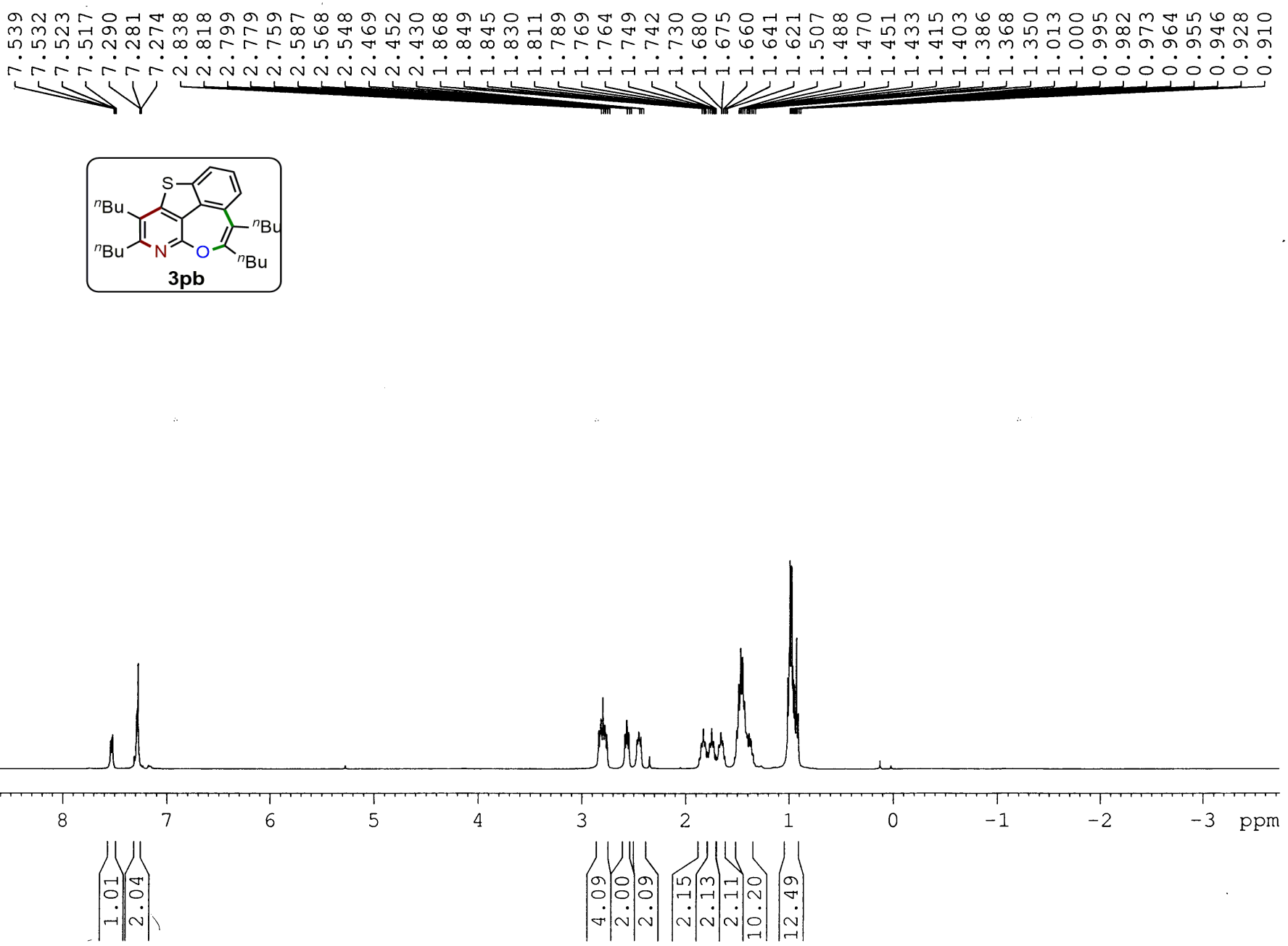
50
40
30
20
10
ppm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7.281
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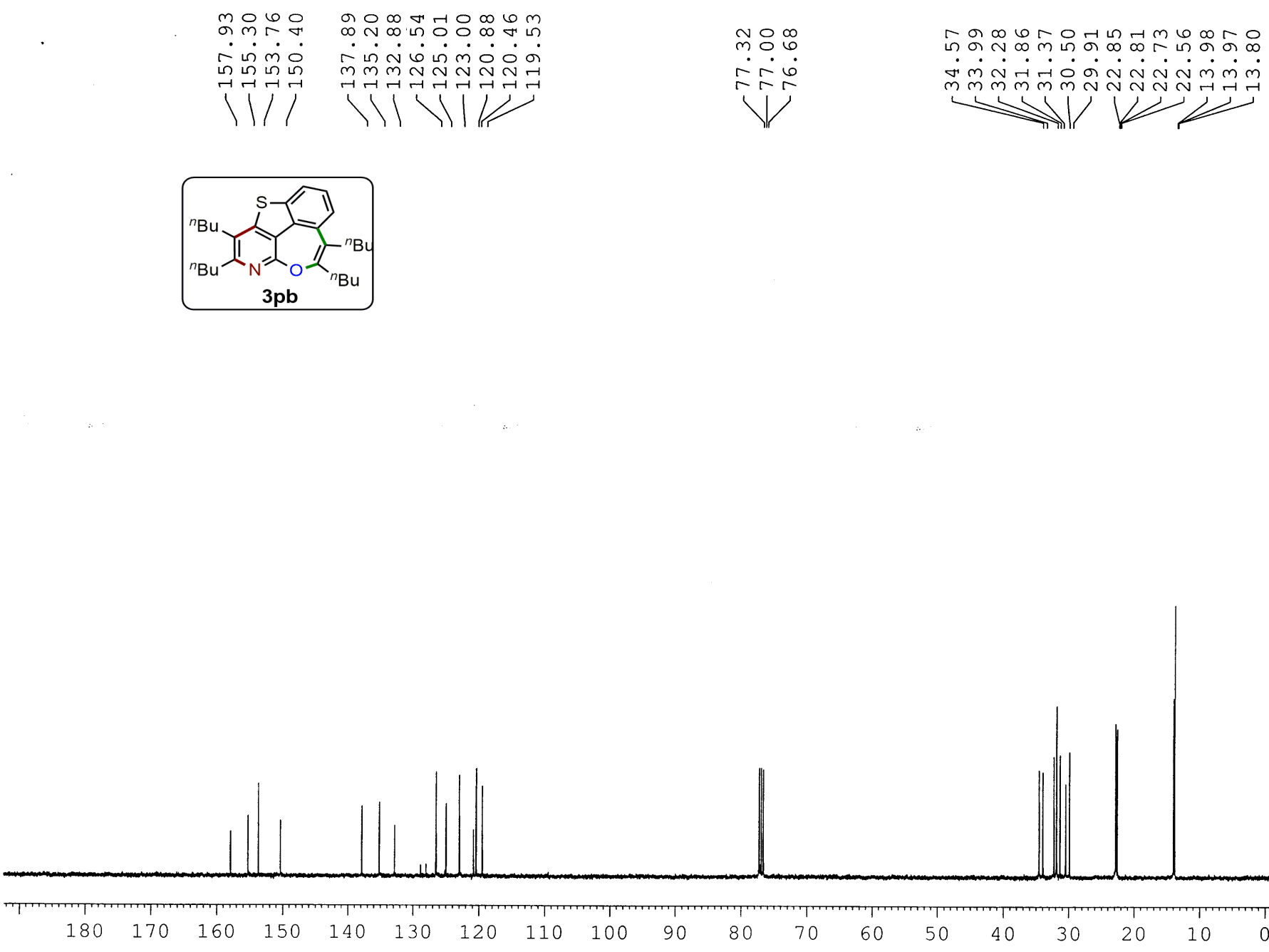
2.838
2.818
2.799
2.779
2.759
2.587
2.568
2.548
2.469
2.452
2.430
1.868
1.849
1.845
1.830
1.811
1.789
1.769
1.764
1.749
1.742
1.730
1.680
1.675
1.660
1.641
1.621
1.507
1.488
1.470
1.451
1.433
1.415
1.403
1.386
1.368
1.350
1.013
1.000
0.995
0.982
0.973
0.964
0.955
0.946
0.928
0.910
S
nBu
nBu
N
O
nBu
nBu
3pb
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
ppm
1.01
2.04
4.09
2.00
2.09
2.15
2.13
2.11
10.20
12.49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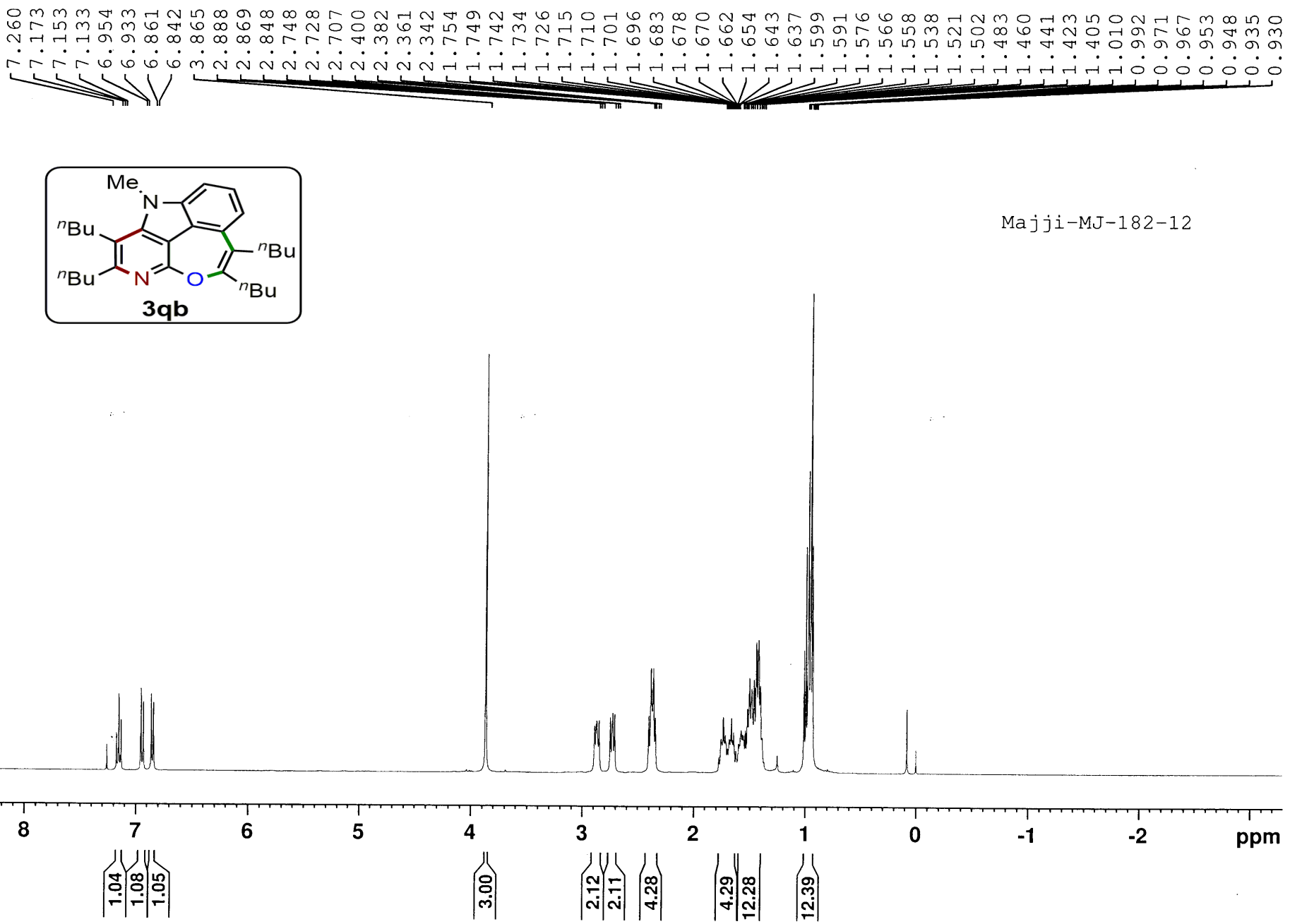
153.76
150.40
137.89
135.20
132.88
126.54
125.01
123.00
120.88
120.46
119.53
77.32
77.00
76.68
34.57
33.99
32.28
31.86
31.37
30.50
29.91
22.85
22.81
22.73
22.56
13.98
13.97
13.80
S
nBu
nBu
N
O
nBu
nBu
3pb
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.153
7.133
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6.933
6.861
6.842
3.865
2.888
2.869
2.848
2.748
2.728
2.707
2.400
2.382
2.361
2.342
1.754
1.749
1.742
1.734
1.726
1.715
1.710
1.701
1.696
1.683
1.678
1.670
1.662
1.654
1.643
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1.566
1.558
1.538
1.521
1.502
1.483
1.460
1.441
1.423
1.405
1.010
0.992
0.971
0.967
0.953
0.948
0.935
0.930
Me
N
nBu
nBu
nBu
nBu
N
O
3qb
Majji-MJ-182-12
8
7
6
5
4
3
2
1
0
-1
-2
ppm
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1.08
1.05
3.00
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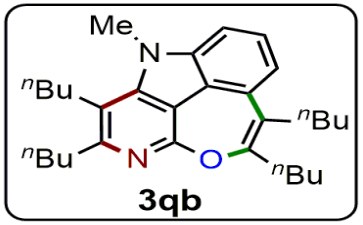
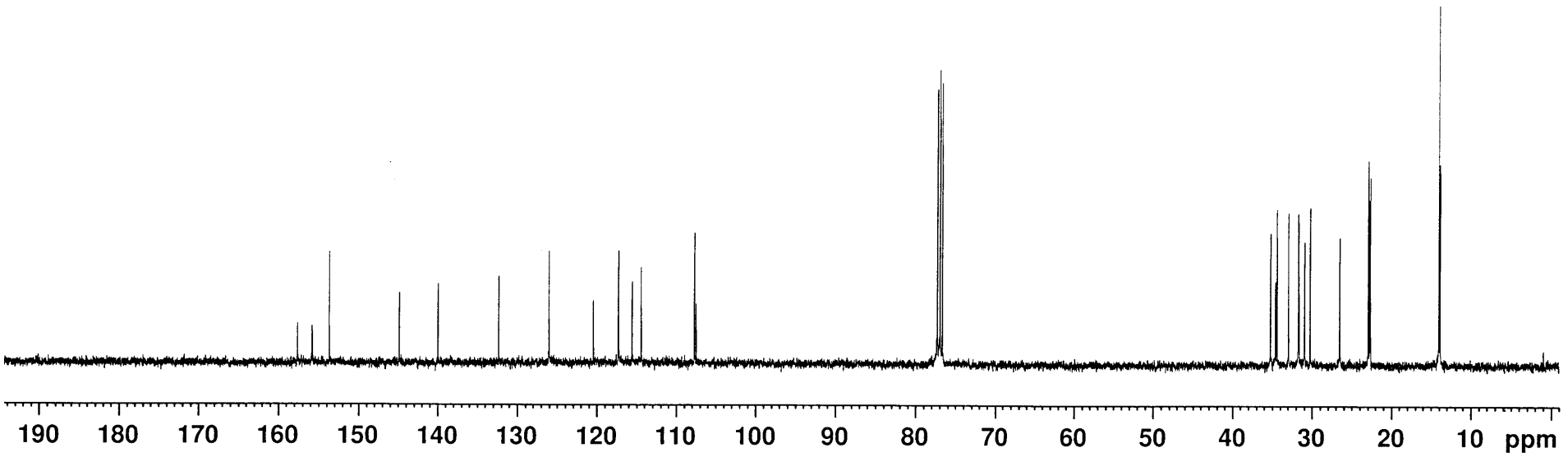
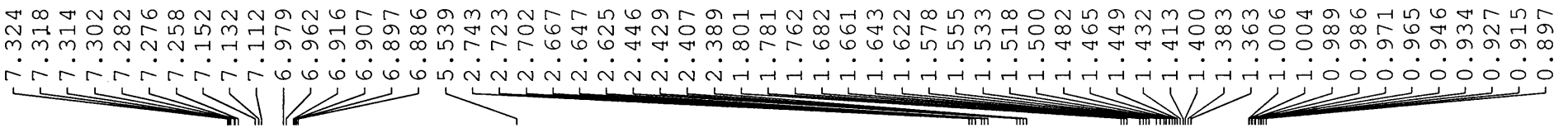
2.11
4.28
4.29
12.28
12.39

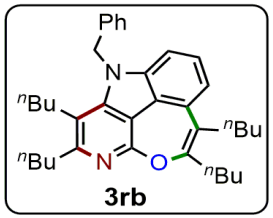


3qb

Majji-MJ-182-12

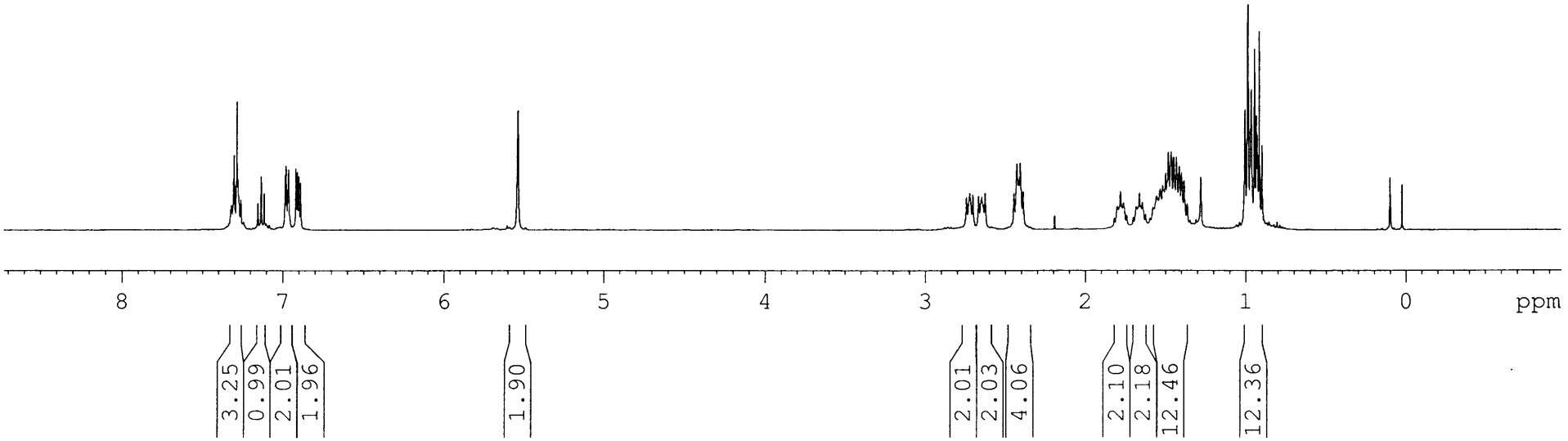






3rb

Majji-MJ-192-12



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137.54
132.54
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127.43
126.42
125.27
120.76
117.76
115.48
114.50
108.26
107.80
77.32
77.00
76.68
48.07
35.28
34.55
34.33
32.94
31.70
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30.28
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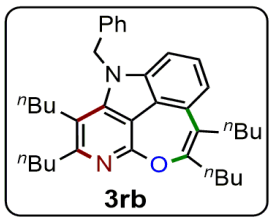
14.02
13.95
13.82

Majji-MJ-192-12



3rb

MAJJI-16-143

7.260
7.190
7.174
7.159
7.116
7.099
6.898
6.883

5.511

3.280
2.880
2.868
2.863
2.857
2.846
2.750
2.739
2.734
2.729
2.718
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2.374
2.370
2.358
2.342
1.800
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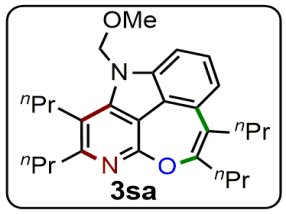
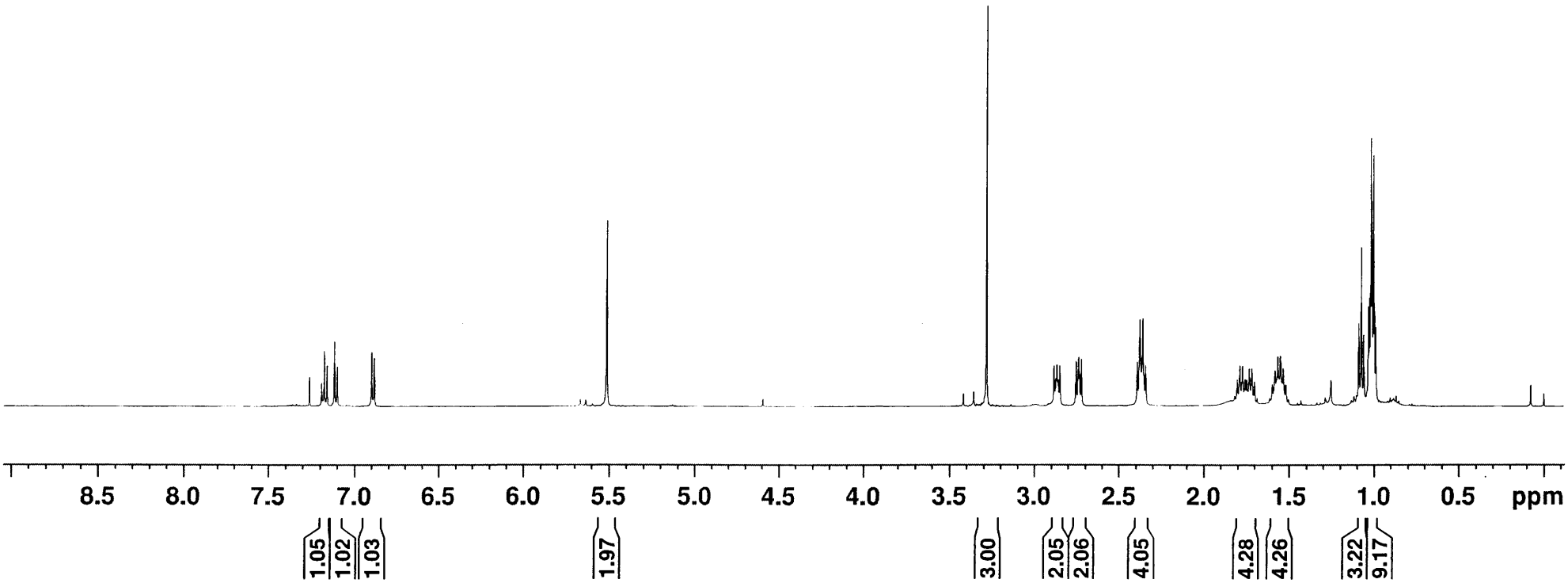
1.087
1.072





MAJJI-16-143

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115.86
115.57
108.56
108.10
77.25
77.00
76.74
74.90
55.87
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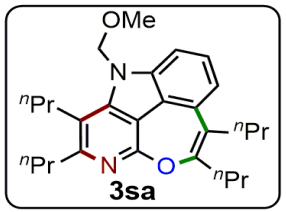
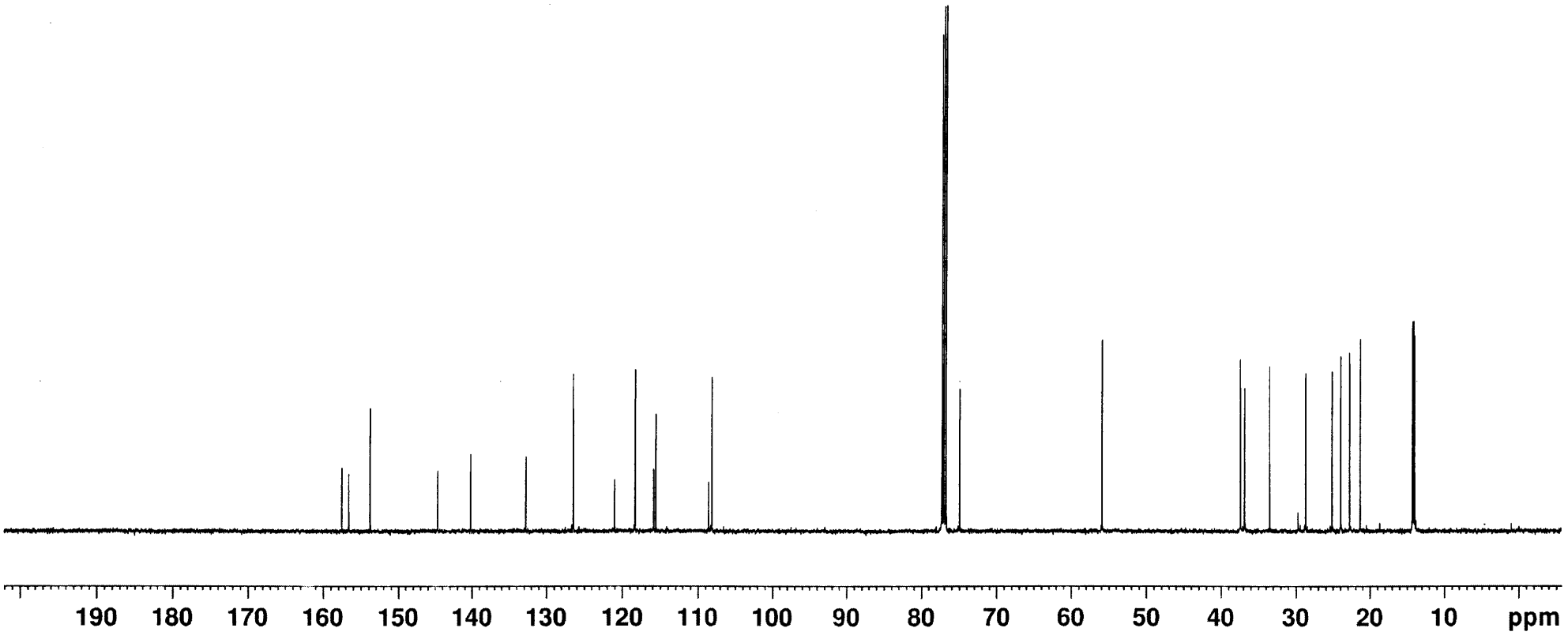
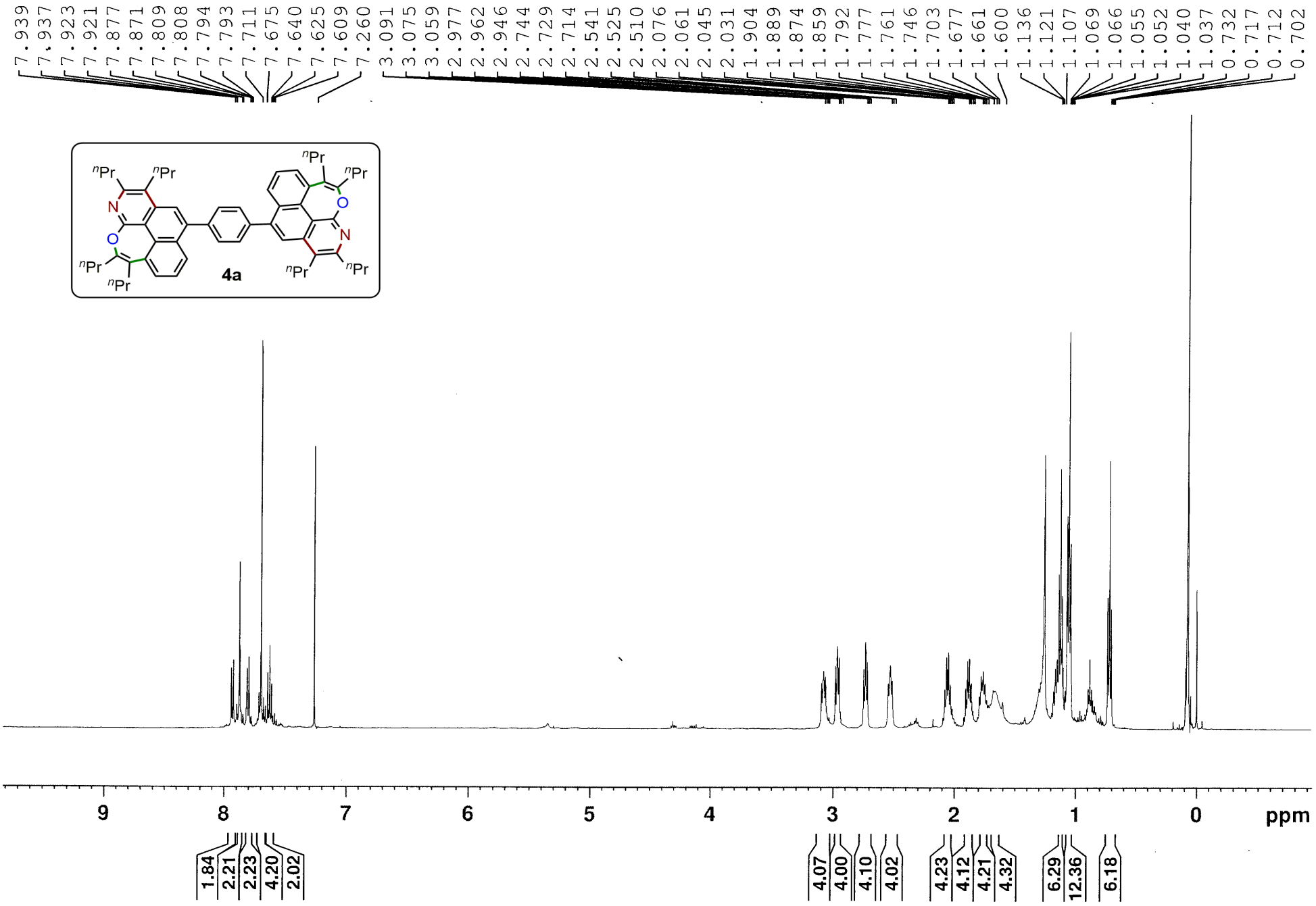
33.45
28.62
25.07
23.92
22.73
21.30
14.26
14.23
14.08
13.94



3sa

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7.921
7.877
7.871
7.809
7.808
7.794
7.793
7.711
7.675
7.640
7.625
7.609
7.260
3.091
3.075
3.059
2.977
2.962
2.946
2.744
2.729
2.714
2.541
2.525
2.510
2.076
2.061
2.045
2.031
1.904
1.889
1.874
1.859
1.792
1.777
1.761
1.746
1.703
1.677
1.661
1.600
1.136
1.121
1.107
1.069
1.066
1.055
1.052
1.040
1.037
0.732
0.717
0.712
0.702
nPr
nPr
nPr
nPr
nPr
nPr
nPr
nPr
N
O
O
N
4a
9
8
7
6
5
4
3
2
1
0
ppm
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2.21
2.23
4.20
2.02
4.07
4.00
4.10
4.02
4.23
4.12
4.21
4.32
6.29
12.36
6.18

MJ-16-152

158.68
154.88
154.71
142.89
140.24
138.28
137.86
131.02
130.06
128.81
127.14
127.10
126.08
125.95
125.10
123.99
122.31
116.83
77.29
77.04
76.78
36.77
34.72
34.56
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20.60
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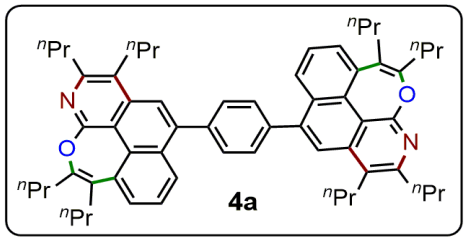
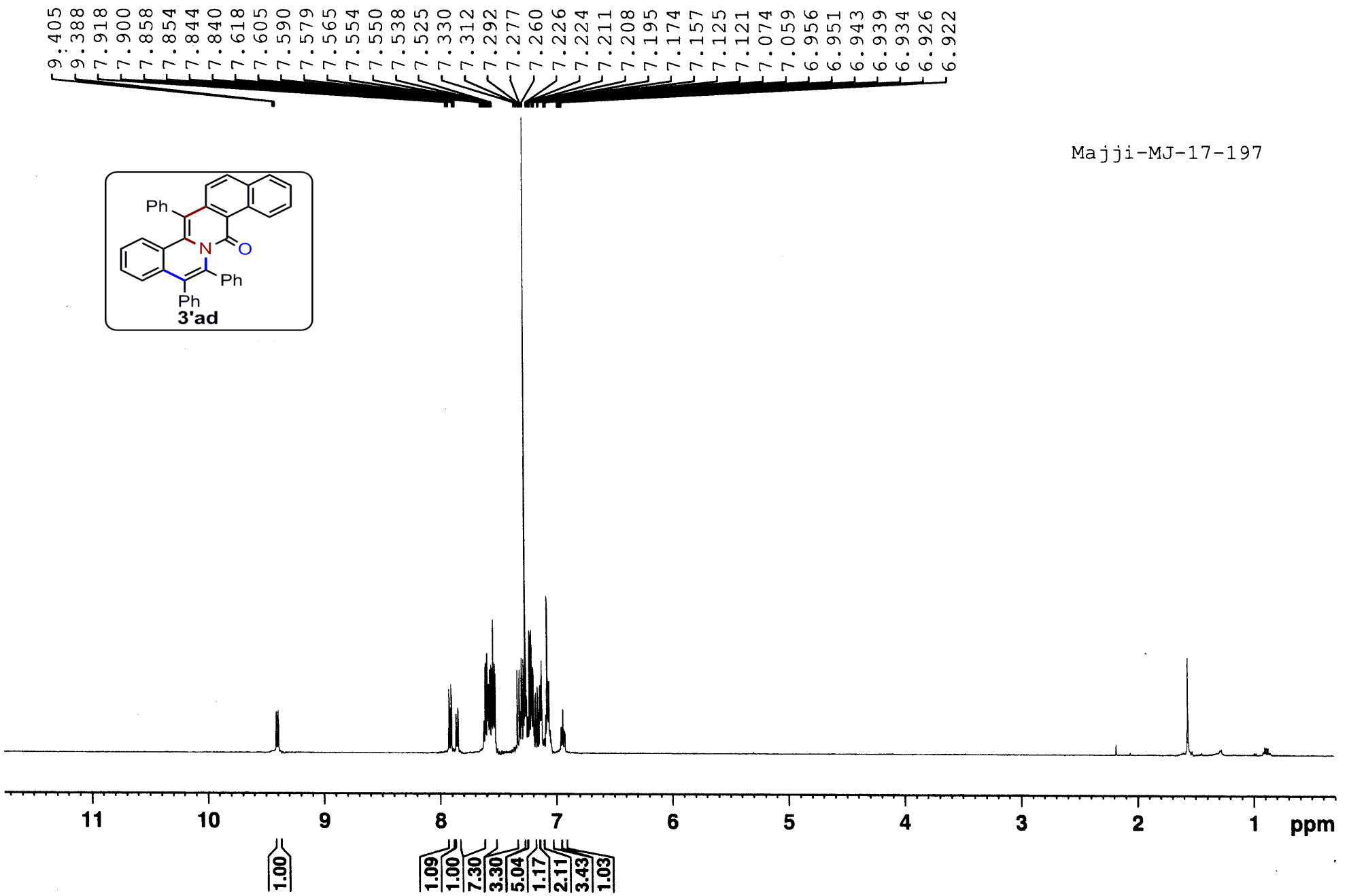
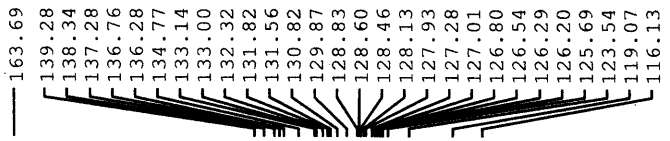
14.28
14.11
14.08



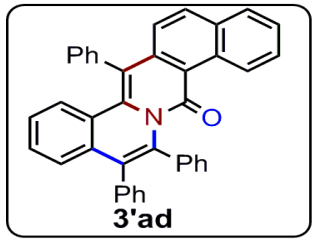
4a

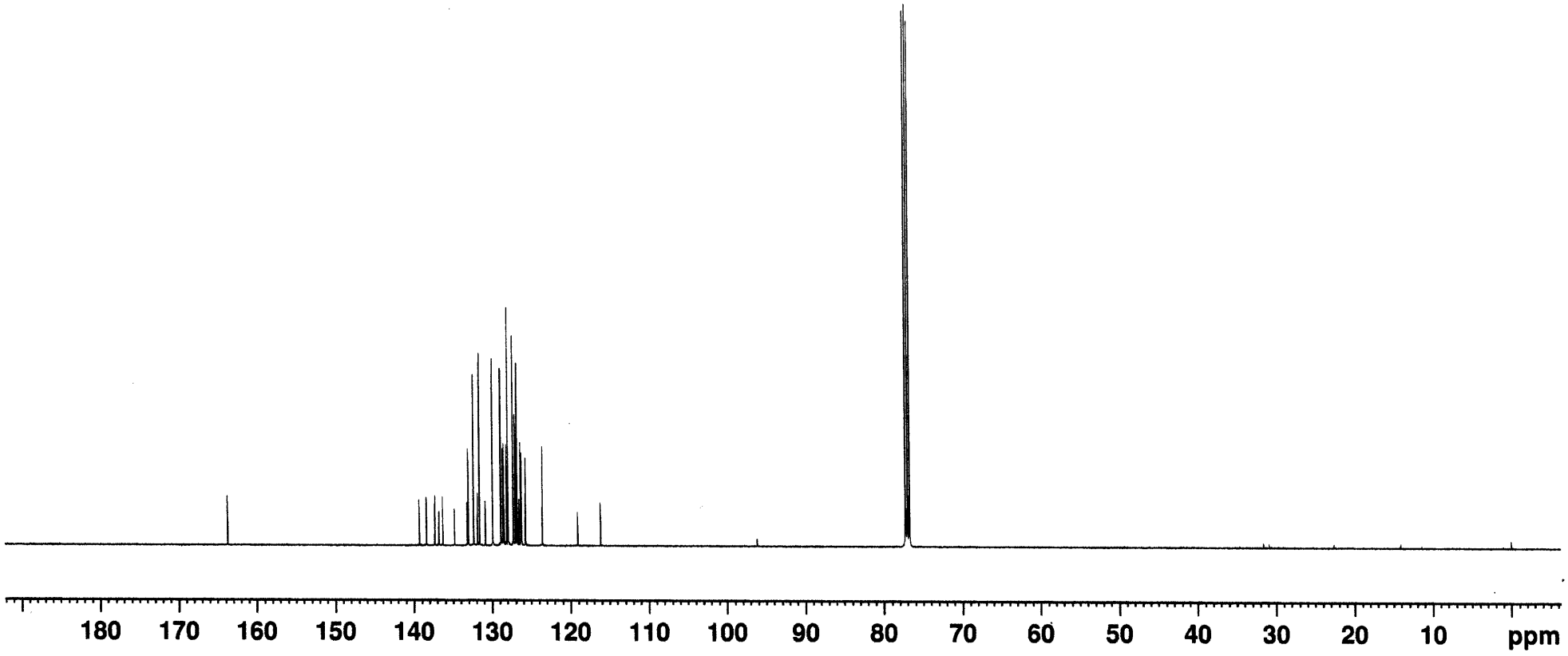
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

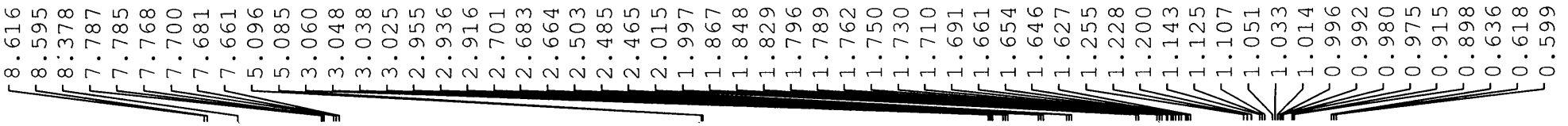

9.405
9.388
7.918
7.900
7.858
7.854
7.844
7.840
7.618
7.605
7.590
7.579
7.565
7.554
7.550
7.538
7.525
7.330
7.312
7.292
7.277
7.260
7.226
7.224
7.211
7.208
7.195
7.174
7.157
7.125
7.121
7.074
7.059
6.956
6.951
6.943
6.939
6.934
6.926
6.922
Majji-MJ-17-197
Ph
N
O
Ph
Ph
3'ad
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.09
1.00
7.30
3.30
5.04
1.17
2.11
3.43
1.03



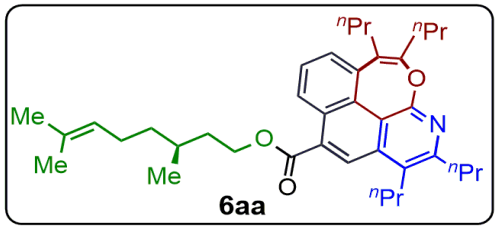
Majji-MJ-17-197



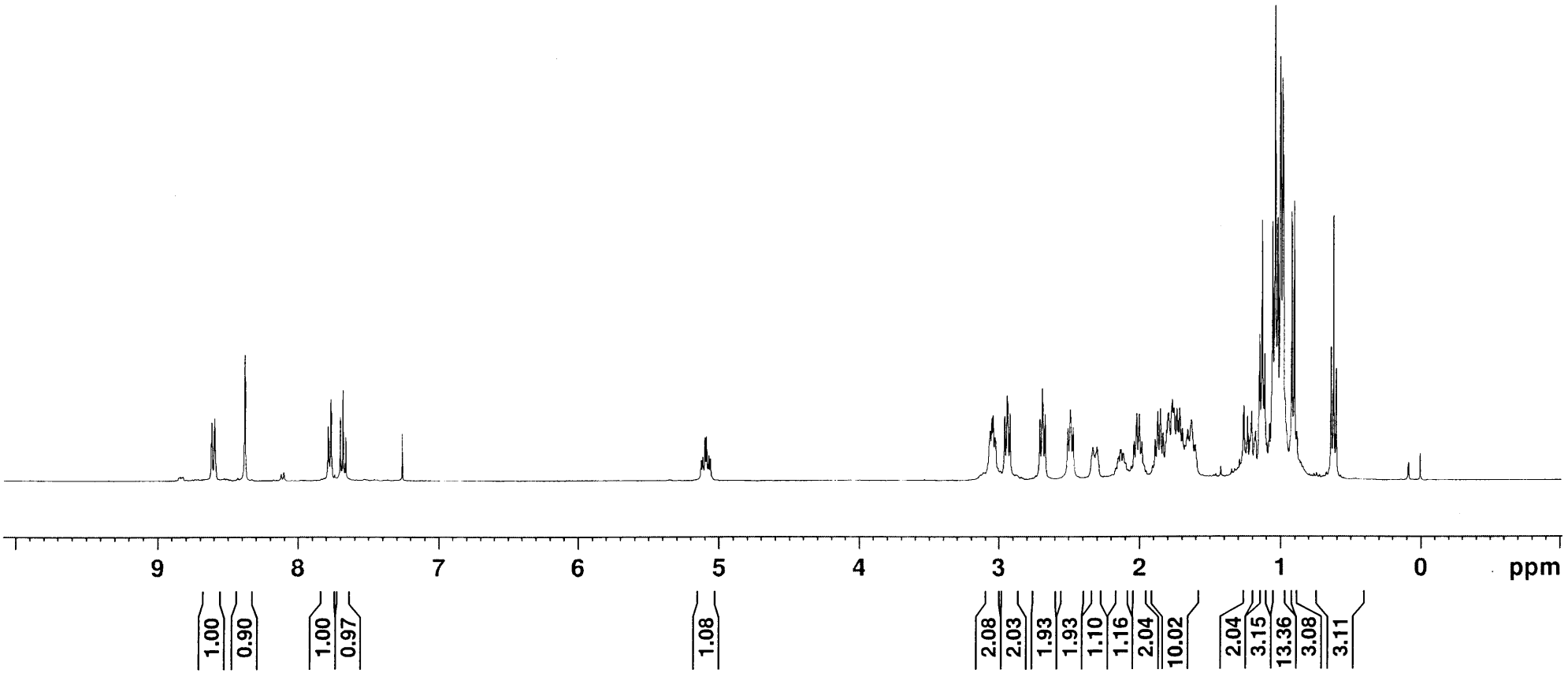


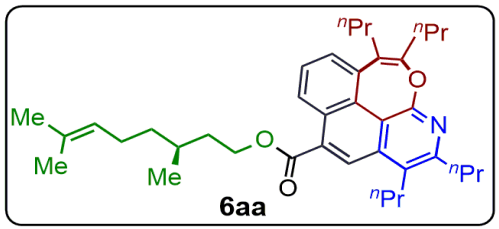


Majji MJ-16-150

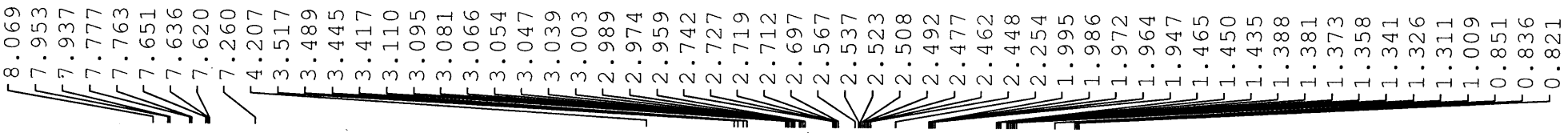


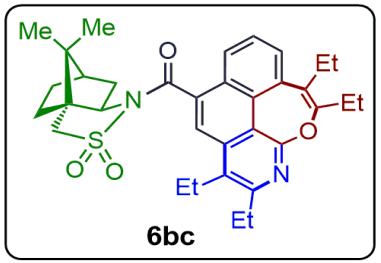
6aa





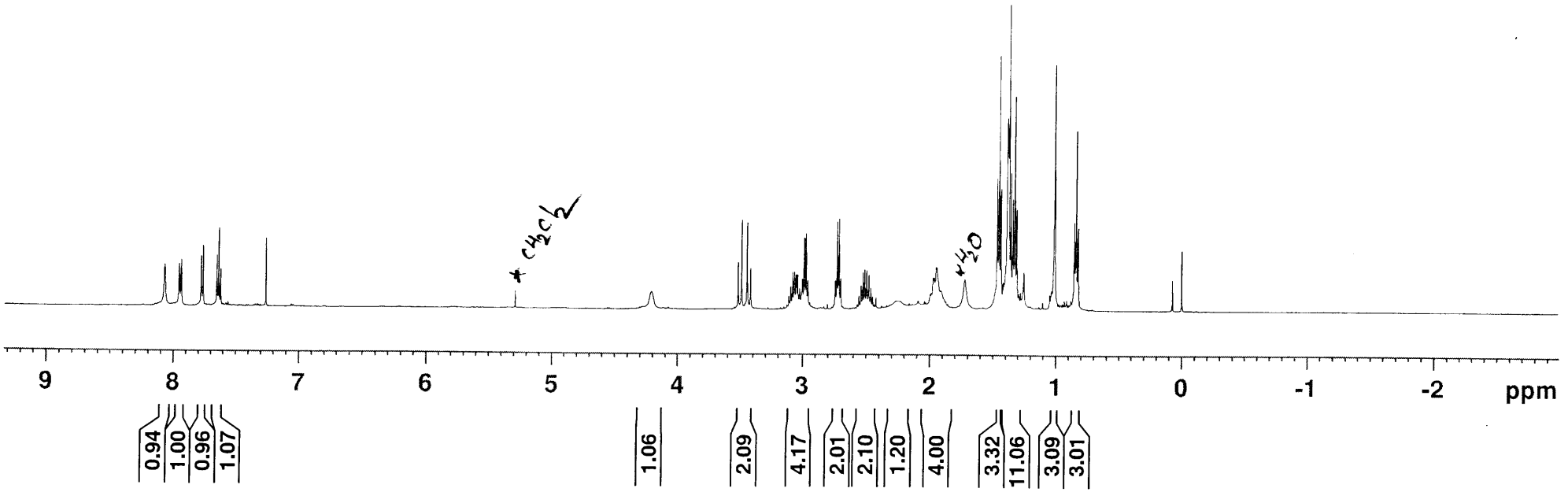
Majji MJ-16-150

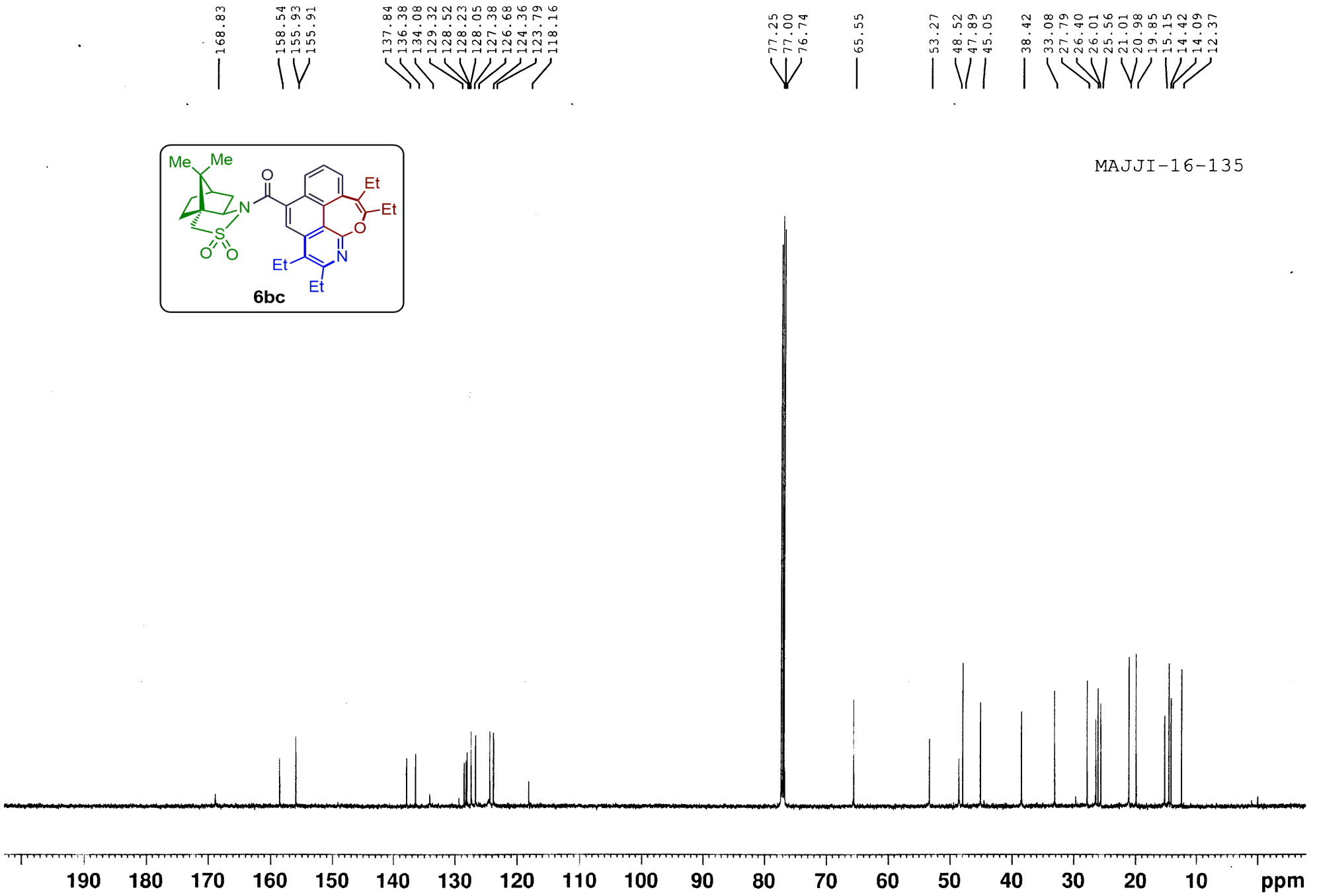


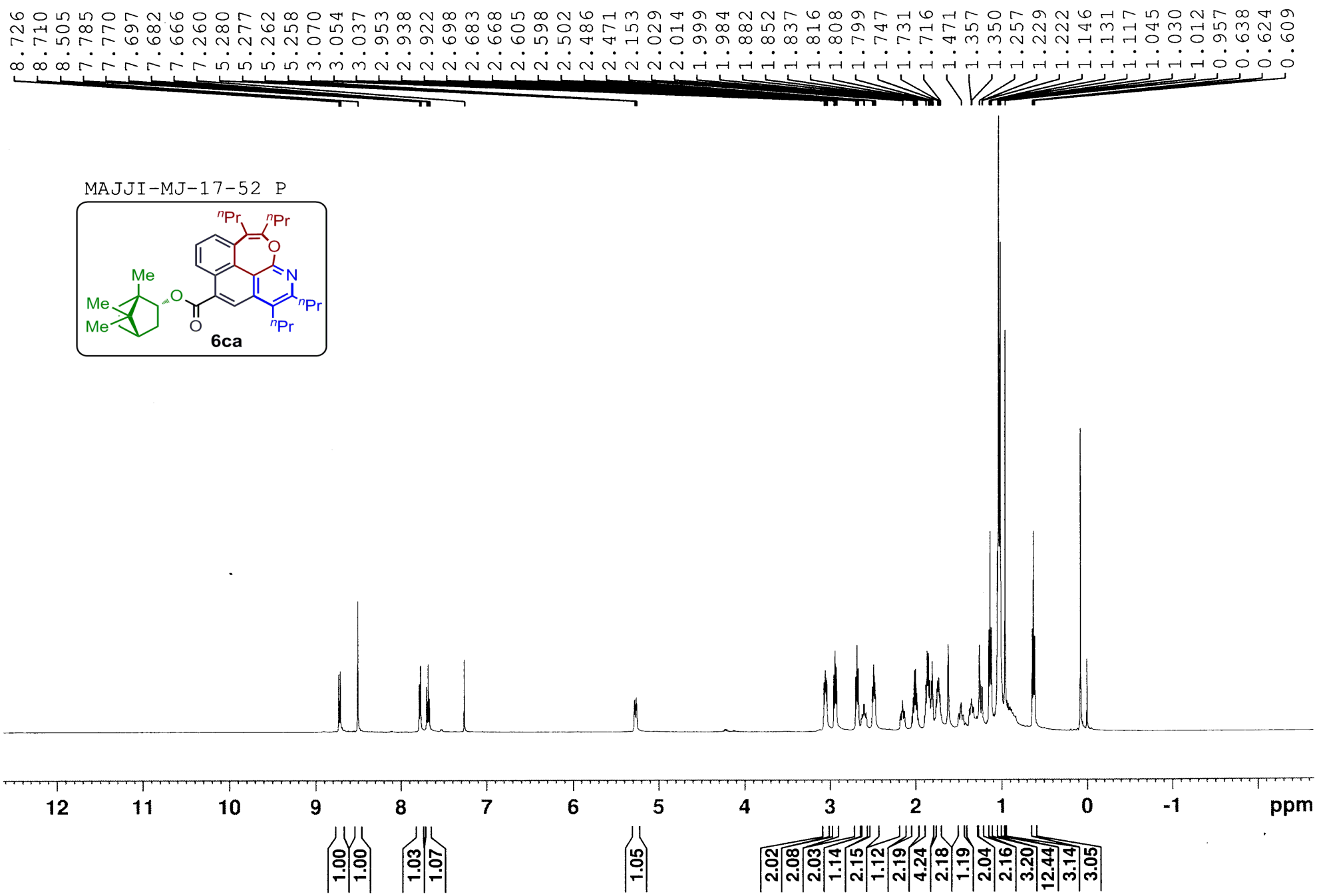


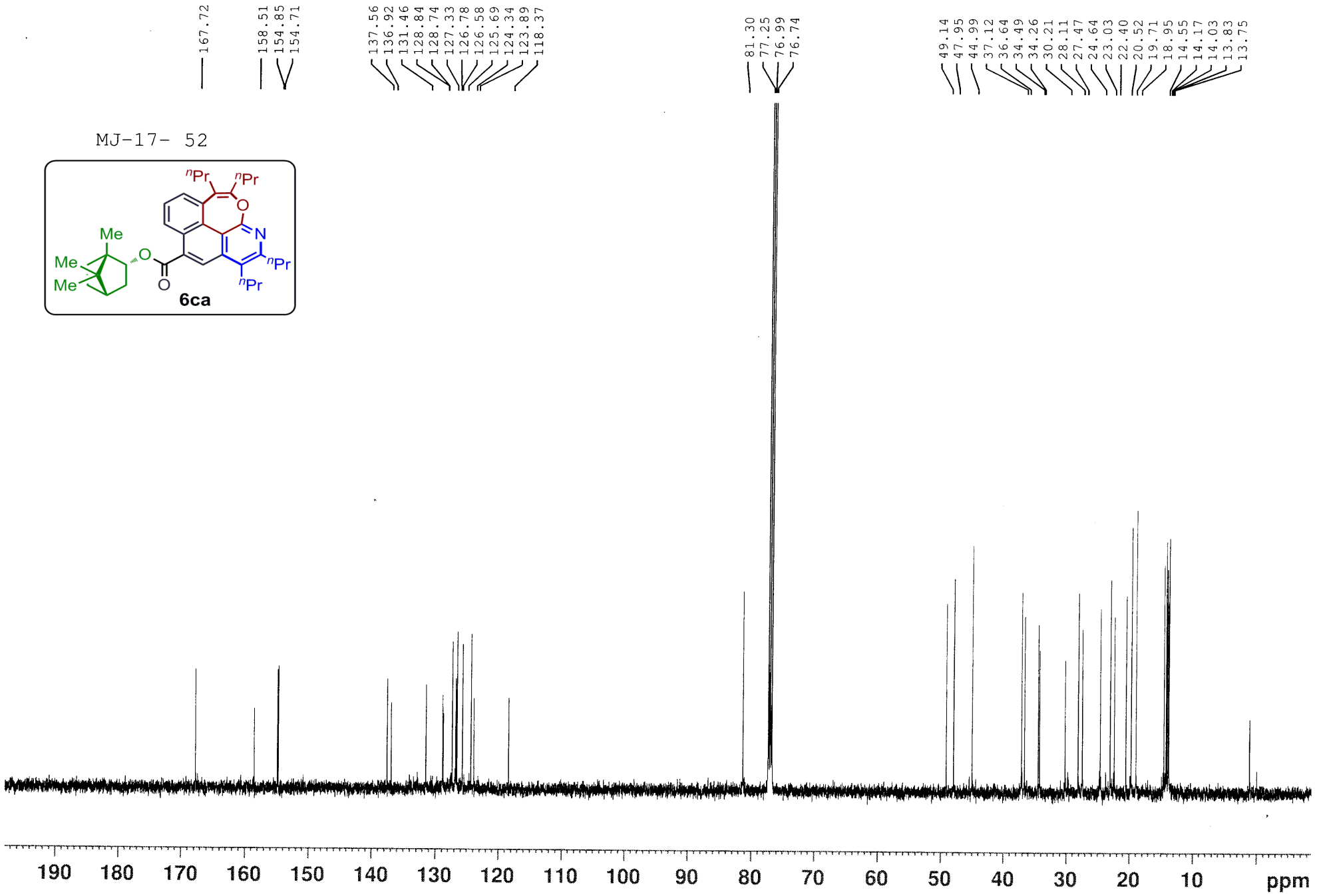
6bc

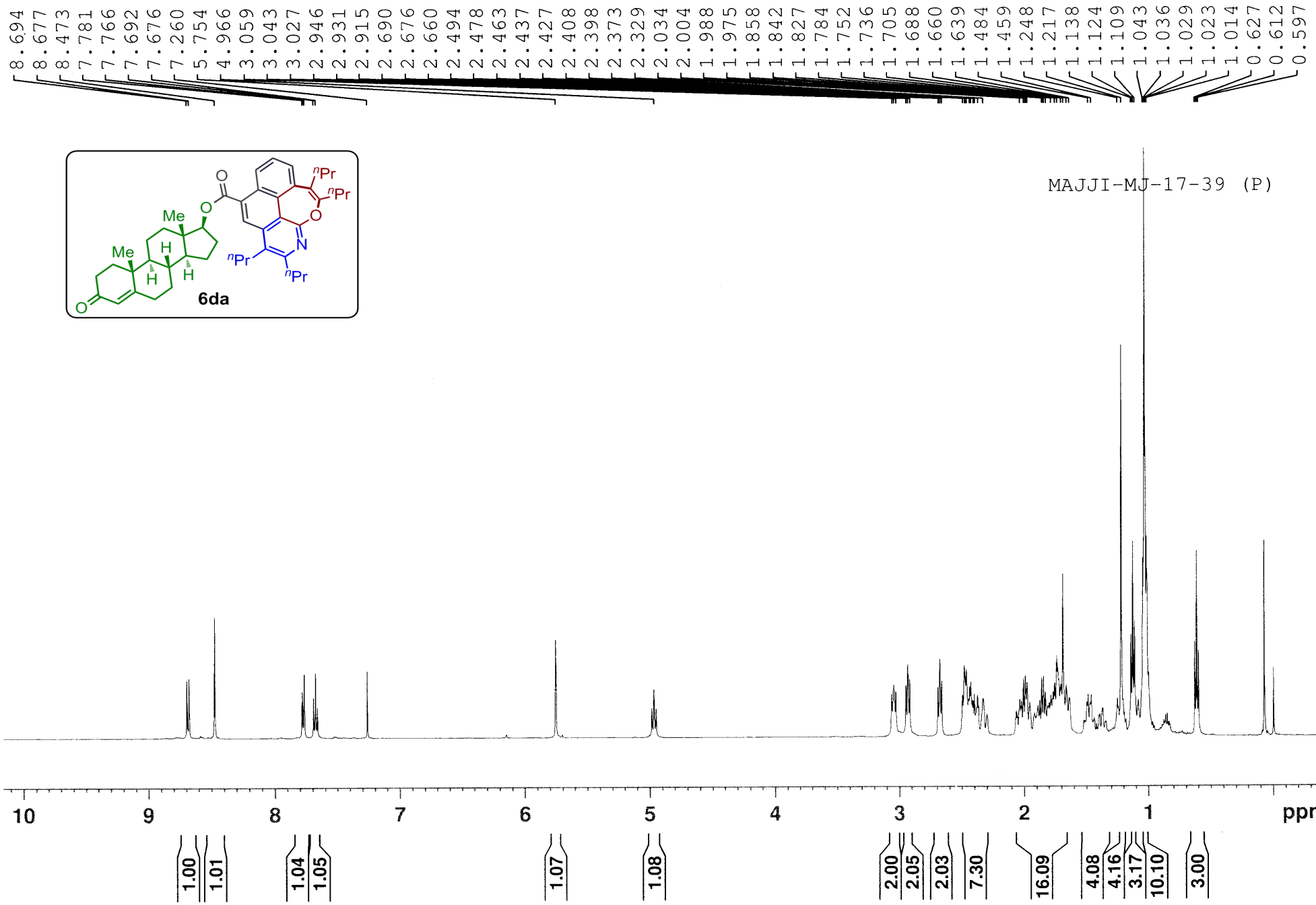
MAJJI-16-135

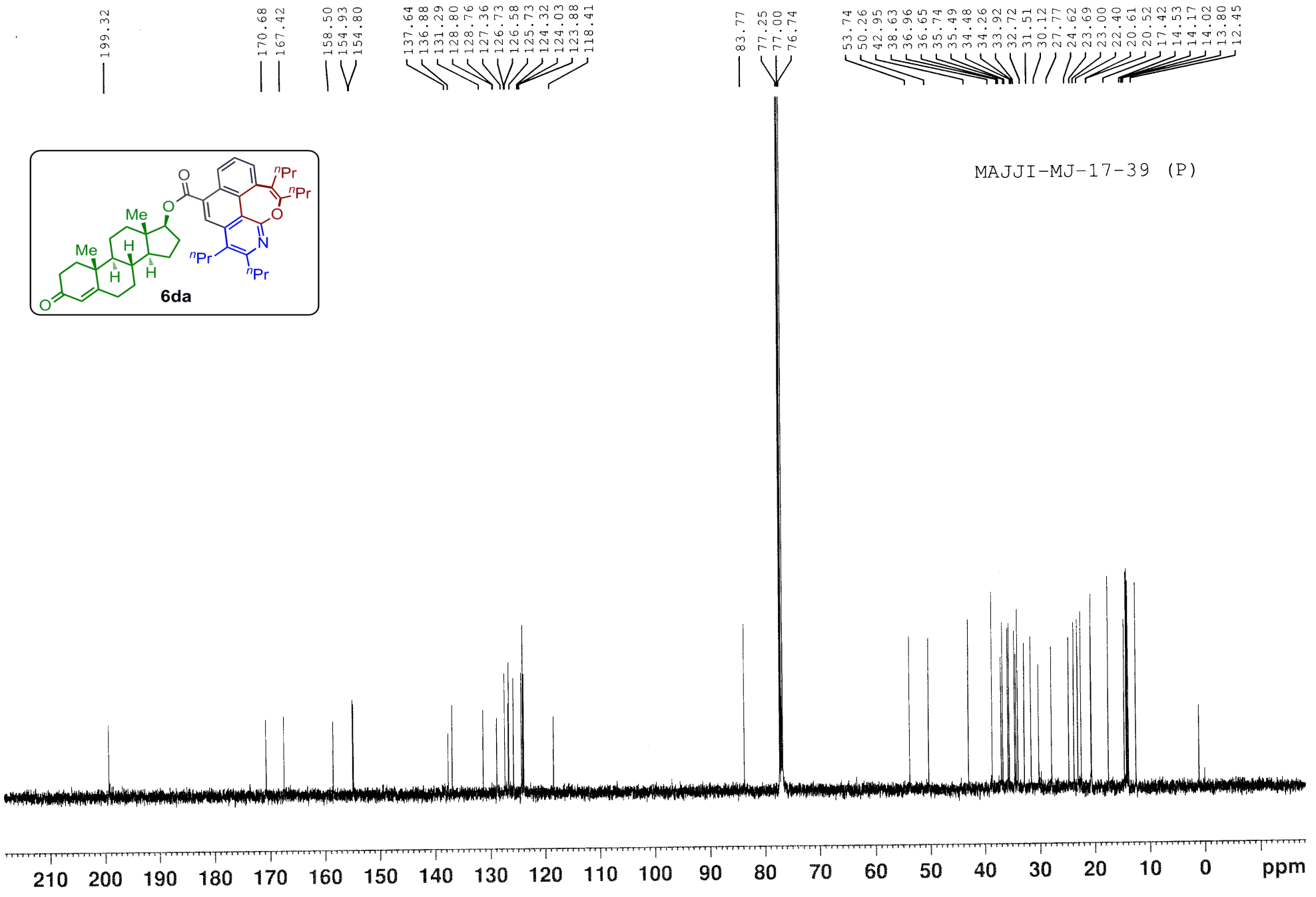


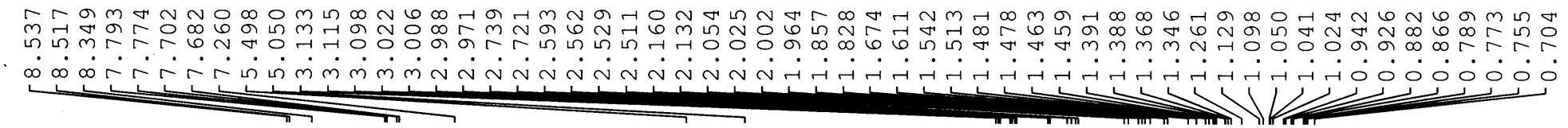

168.83
158.54
155.93
155.91
137.84
136.38
134.08
129.32
128.52
128.23
128.05
127.38
126.68
124.36
123.79
118.16
77.25
77.00
76.74
65.55
53.27
48.52
47.89
45.05
38.42
33.08
27.79
26.40
26.01
25.56
21.01
20.98
19.85
15.15
14.42
14.09
12.37
Me
Me
O
N
Et
Et
S
O
O
O
Et
N
Et
6bc
MAJJI-16-135
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.726
8.710
8.505
7.785
7.770
7.697
7.682
7.666
7.260
5.280
5.277
5.262
5.258
3.070
3.054
3.037
2.953
2.938
2.922
2.698
2.683
2.668
2.605
2.598
2.502
2.486
2.471
2.153
2.029
2.014
1.999
1.984
1.882
1.852
1.837
1.816
1.808
1.799
1.747
1.731
1.716
1.471
1.357
1.350
1.257
1.229
1.222
1.146
1.131
1.117
1.045
1.030
1.012
0.957
0.638
0.624
0.609
MAJJI-MJ-17-52 P
nPr
nPr
O
N
Me
Me
Me
O
O
nPr
nPr
6ca
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
1.00
1.03
1.07
1.05
2.02
2.08
2.03
1.14
2.15
1.12
2.19
4.24
2.18
1.19
2.04
2.16
3.20
12.44
3.14
3.05

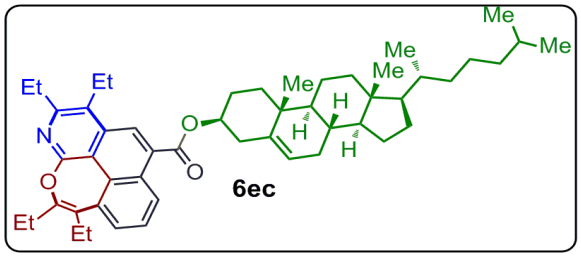

167.72
158.51
154.85
154.71
137.56
136.92
131.46
128.84
128.74
127.33
126.78
126.58
125.69
124.34
123.89
118.37
81.30
77.25
76.99
76.74
49.14
47.95
44.99
37.12
36.64
34.49
34.26
30.21
28.11
27.47
24.64
23.03
22.40
20.52
19.71
18.95
14.55
14.17
14.03
13.83
13.75
MJ-17- 52
nPr
nPr
O
N
Me
Me
Me
O
O
nPr
nPr
6ca
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

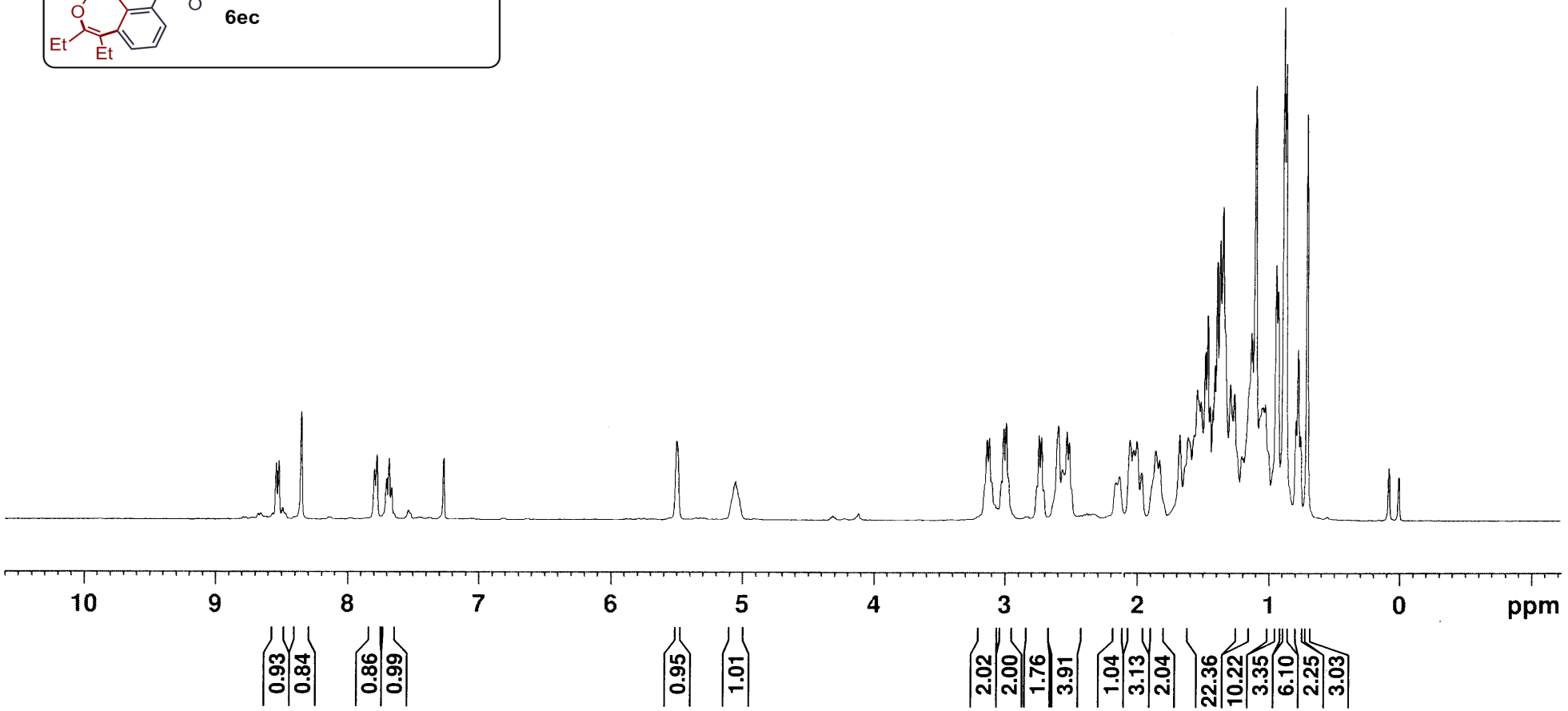

8.694
8.677
8.473
7.781
7.766
7.692
7.676
7.260
5.754
4.966
3.059
3.043
3.027
2.946
2.931
2.915
2.690
2.676
2.660
2.494
2.478
2.463
2.437
2.427
2.408
2.398
2.373
2.329
2.034
2.004
1.988
1.975
1.858
1.842
1.827
1.784
1.752
1.736
1.705
1.688
1.660
1.639
1.484
1.459
1.248
1.217
1.138
1.124
1.109
1.043
1.036
1.029
1.023
1.014
0.627
0.612
0.597
6da
MAJJI-MJ-17-39 (P)
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
1.04
1.05
1.07
1.08
2.00
2.05
2.03
7.30
16.09
4.08
4.16
3.17
10.10
3.00

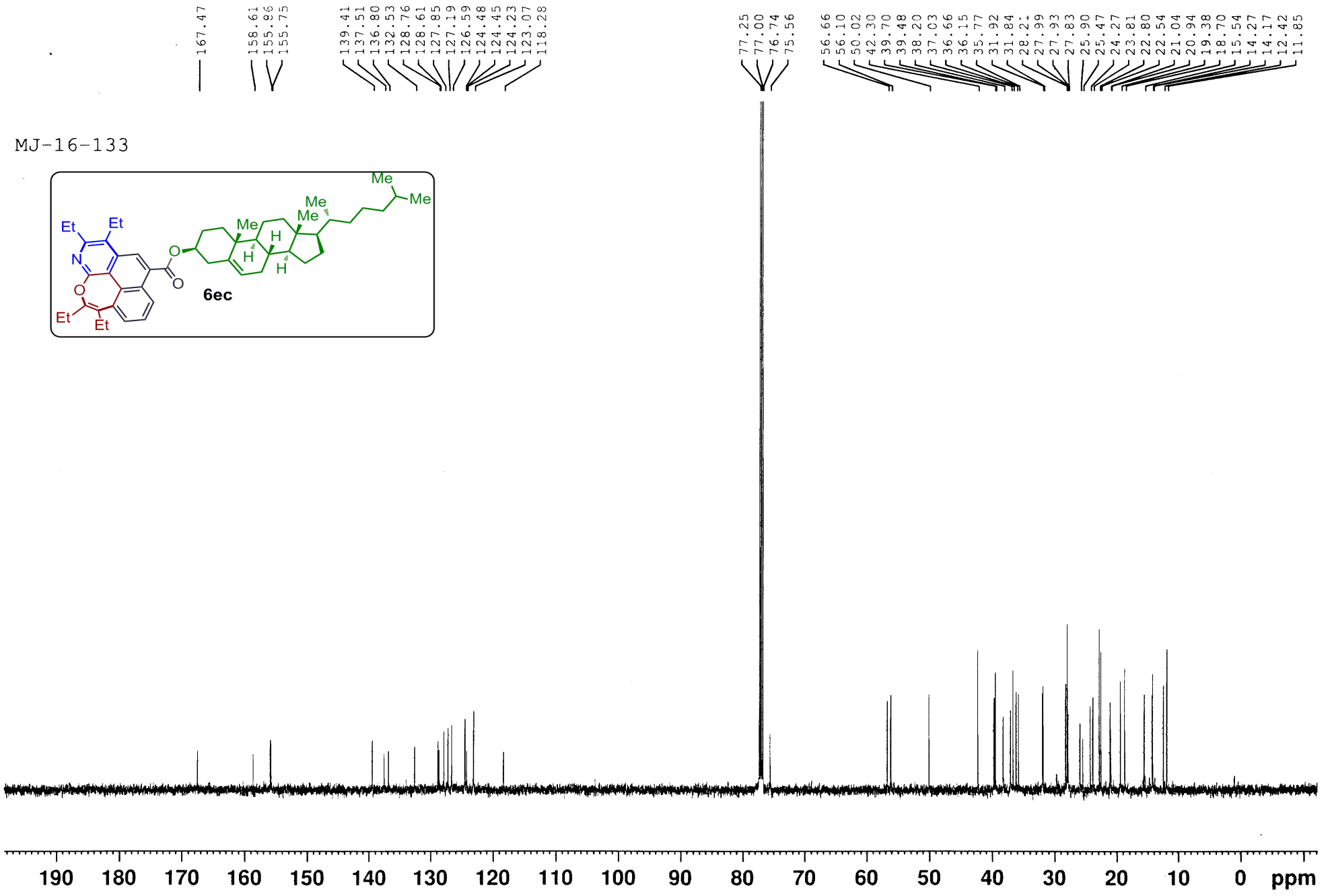

199.32
170.68
167.42
158.50
154.93
154.80
137.64
136.88
131.29
128.80
128.76
127.36
126.73
126.58
125.73
124.32
124.03
123.88
118.41
83.77
77.25
77.00
76.74
53.74
50.26
42.95
38.63
36.96
36.65
35.74
35.49
34.48
34.26
33.92
32.72
31.51
30.12
27.77
24.62
23.69
23.00
22.40
20.61
20.52
17.42
14.53
14.17
14.02
13.80
12.45
MAJJI-MJ-17-39 (P)
6da
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.537
8.517
8.349
7.793
7.774
7.702
7.682
7.260
5.498
5.050
3.133
3.115
3.098
3.022
3.006
2.988
2.971
2.739
2.721
2.593
2.562
2.529
2.511
2.160
2.132
2.054
2.025
2.002
1.964
1.857
1.828
1.674
1.611
1.542
1.513
1.481
1.478
1.463
1.459
1.391
1.388
1.368
1.346
1.261
1.129
1.098
1.050
1.041
1.024
0.942
0.926
0.882
0.866
0.789
0.773
0.755
0.704

majji-16-133

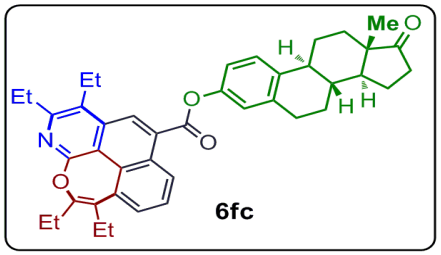

Et
Et
N
O
O
Et
Et
O
Me
H
H
H
Me
Me
Me
Me
6ec

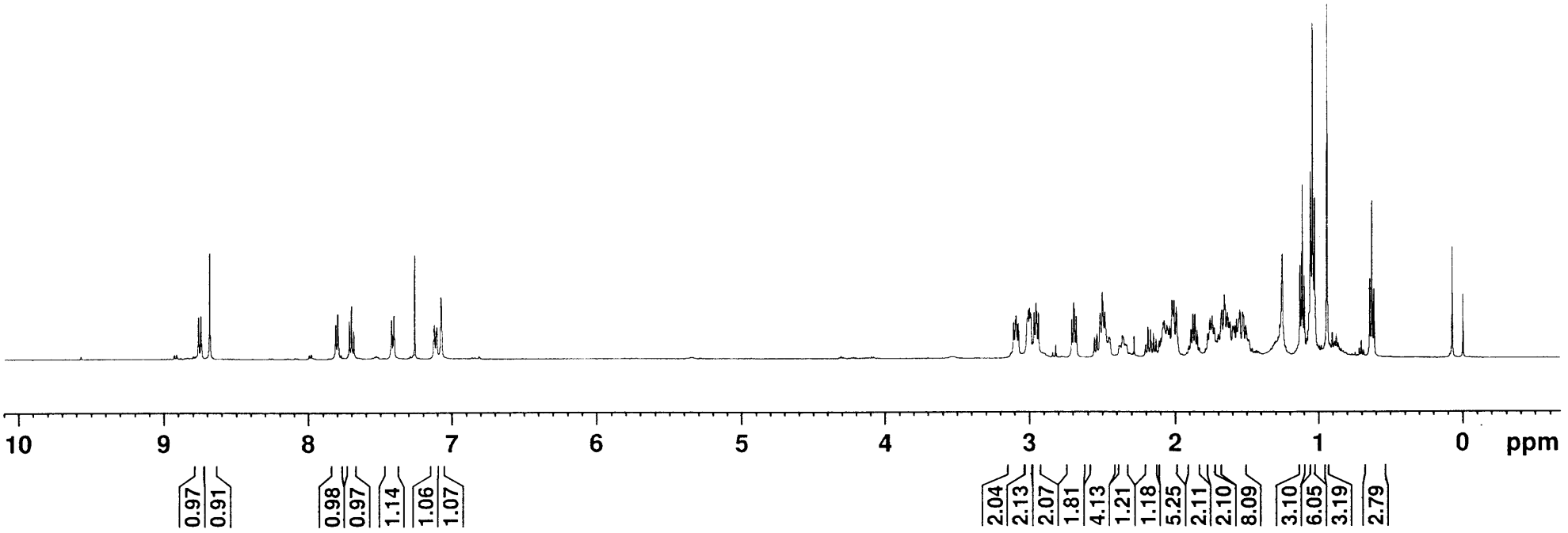

10
9
8
7
6
5
4
3
2
1
0
ppm
0.93
0.84
0.86
0.99
0.95
1.01
2.02
2.00
1.76
3.91
1.04
3.13
2.04
22.36
10.22
3.35
6.10
2.25
3.03

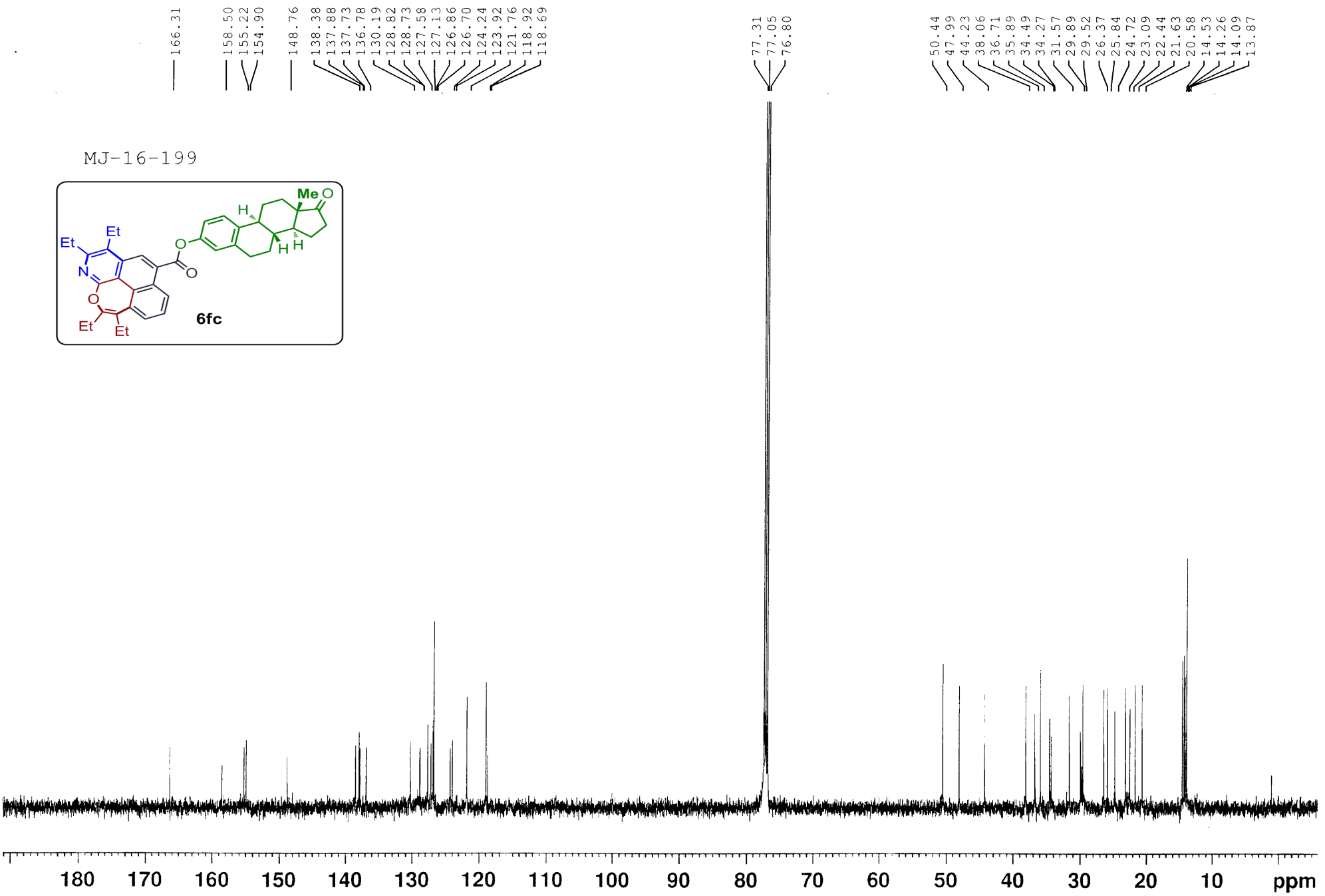

167.47
158.61
155.86
155.75
139.41
137.51
136.80
132.53
128.76
128.61
127.85
127.19
126.59
124.48
124.45
124.23
123.07
118.28
77.25
77.00
76.74
75.56
56.66
56.10
50.02
42.30
39.70
39.48
38.20
37.03
36.66
36.15
35.77
31.92
31.84
28.21
27.99
27.93
27.83
25.90
25.47
24.27
23.81
22.80
22.54
21.04
20.94
19.38
18.70
15.54
14.27
14.17
12.42
11.85
MJ-16-133
Et
Et
N
O
O
Et
Et
O
O
Me
H
H
H
Me
Me
Me
Me
6ec
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

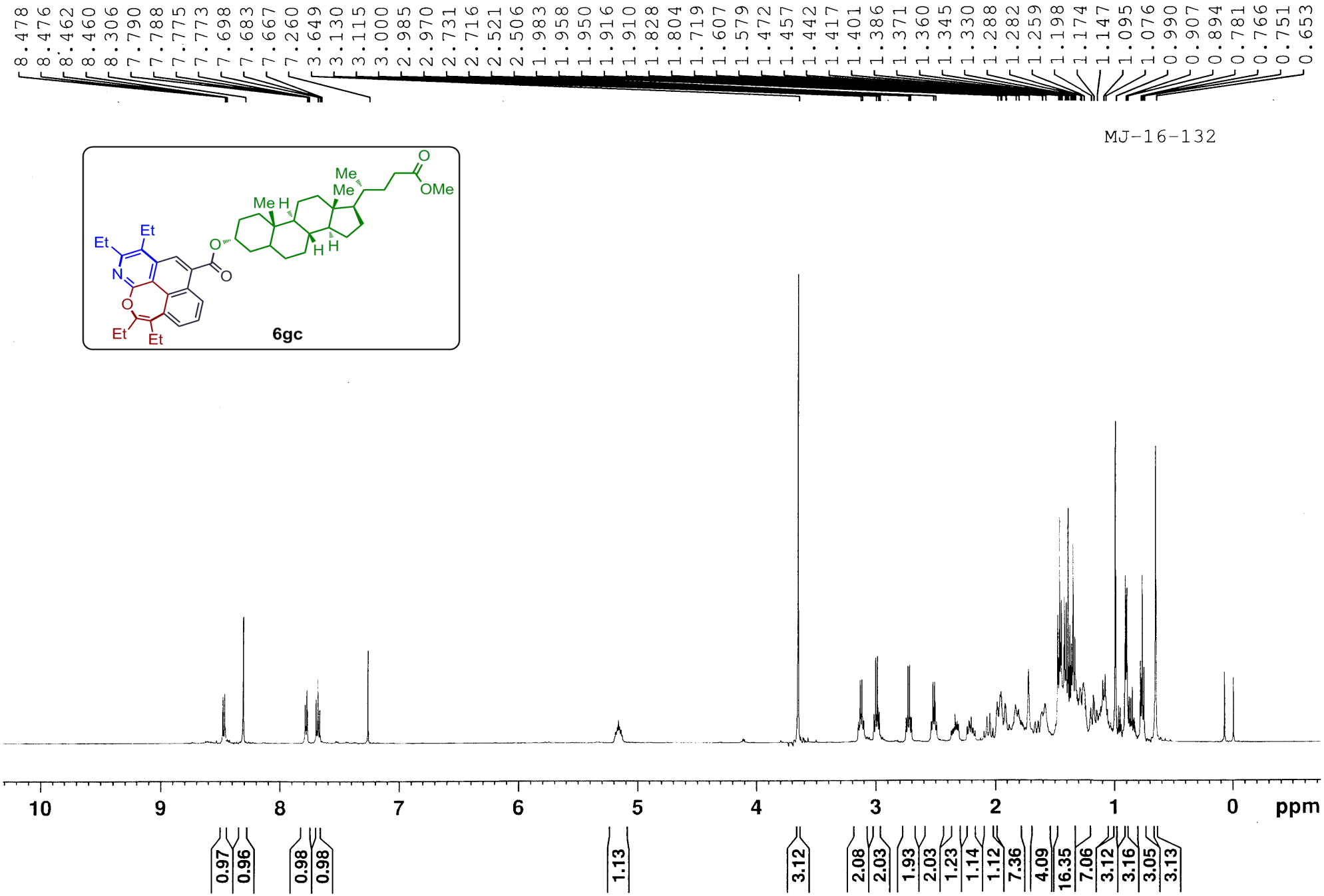
8.762
8.761
8.746
8.745
8.684
7.797
7.717
7.701
7.422
7.405
7.259
7.122
7.077
7.073
3.108
3.092
3.076
3.014
3.007
2.998
2.990
2.967
2.952
2.936
2.709
2.694
2.678
2.516
2.500
2.483
2.080
2.075
2.021
2.007
1.991
1.876
1.861
1.758
1.742
1.675
1.634
1.623
1.616
1.572
1.549
1.530
1.524
1.129
1.114
1.100
1.057
1.042
1.028
0.941
0.642
0.628
0.613

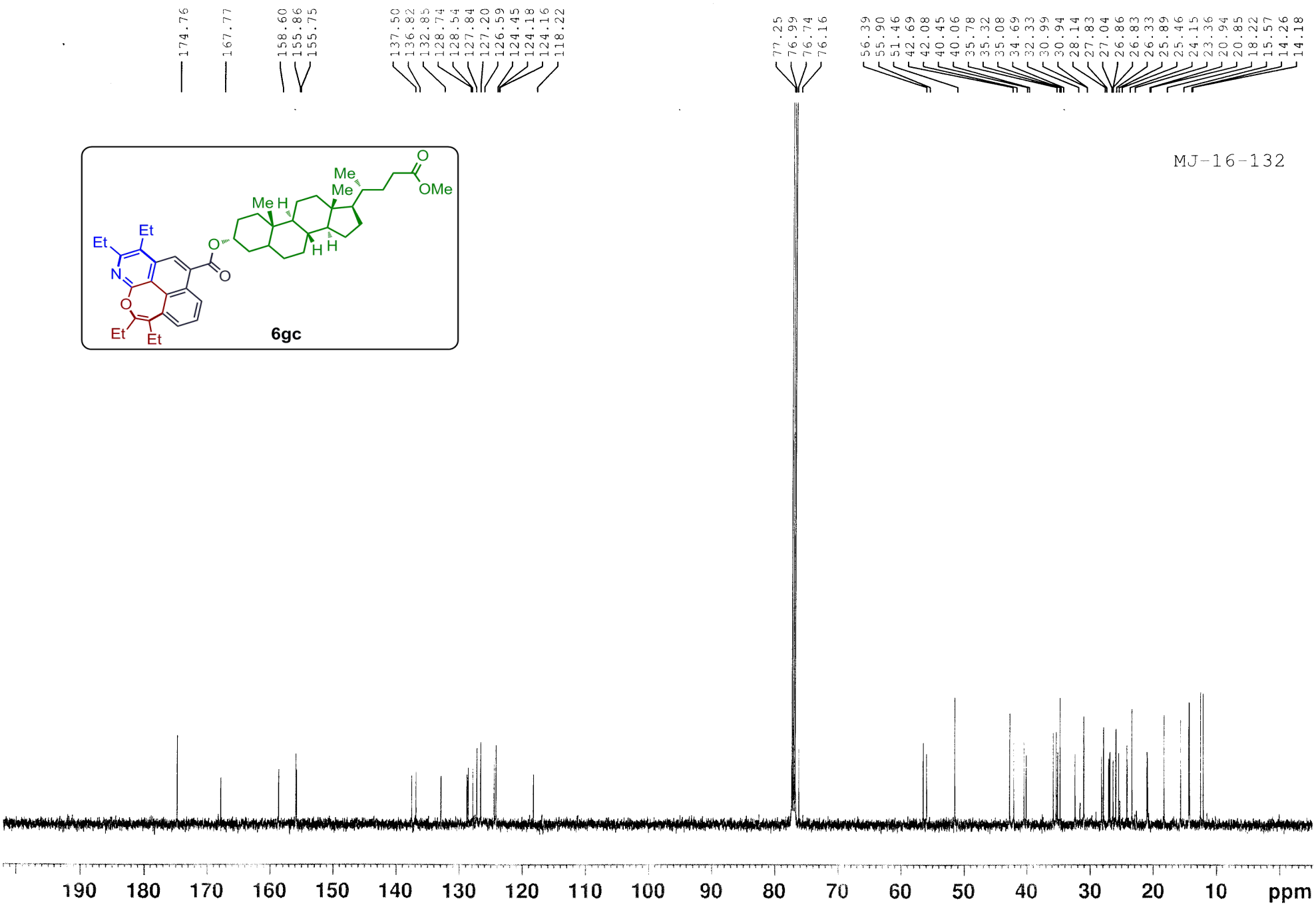
MJ-16-199

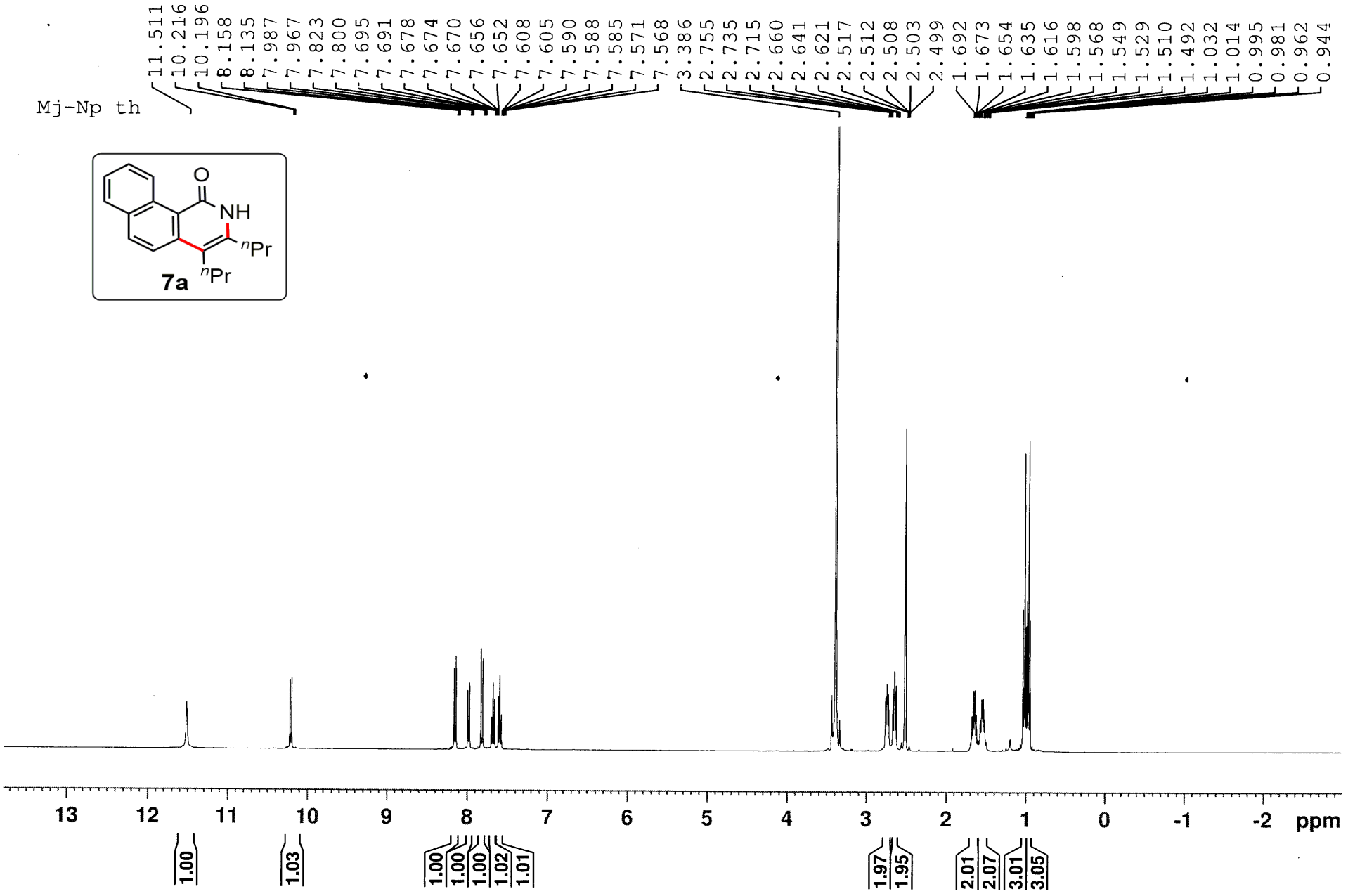




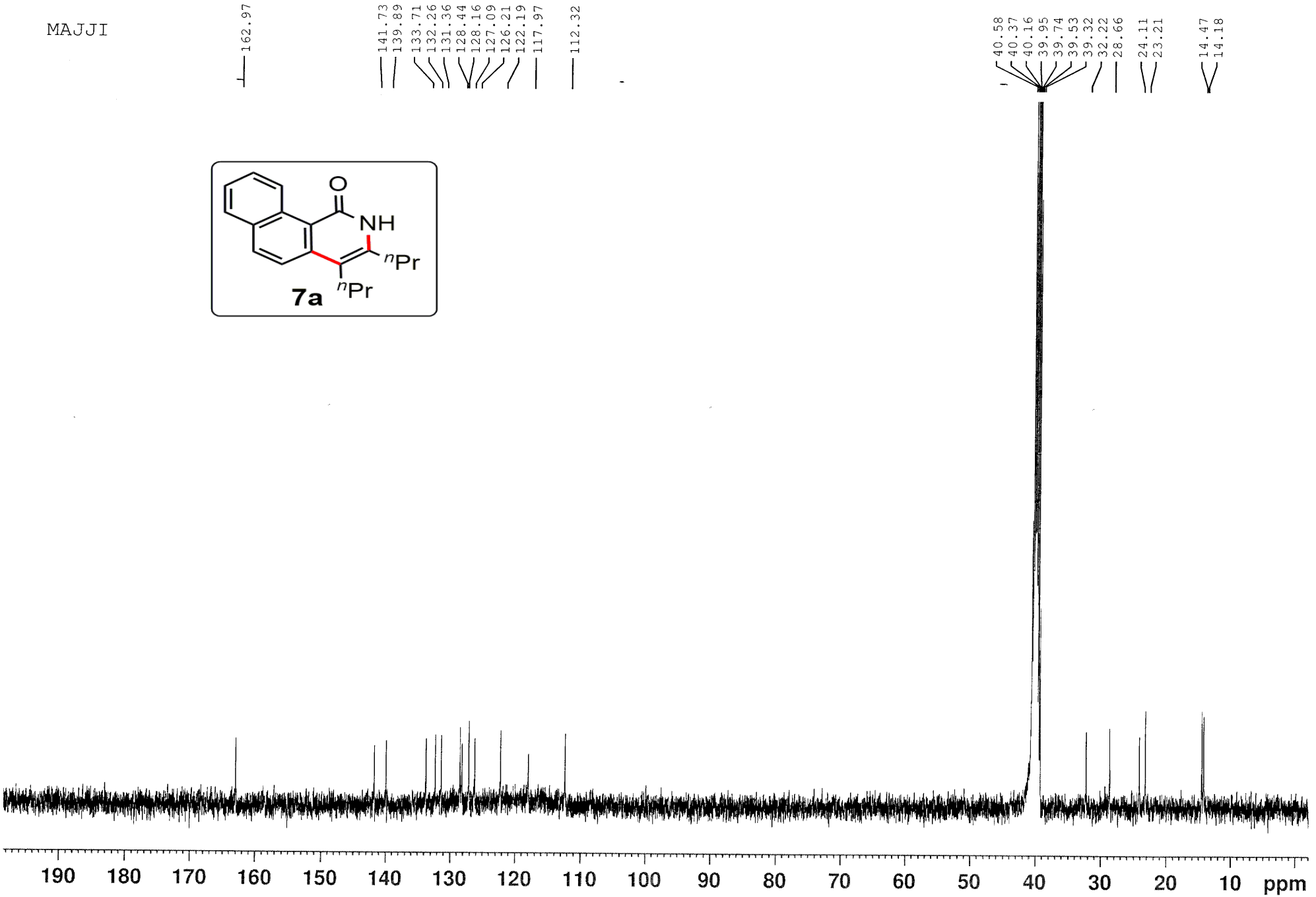

166.31
158.50
155.22
154.90
148.76
138.38
137.88
137.73
136.78
130.19
128.82
128.73
127.58
127.13
126.86
126.70
124.24
123.92
121.76
118.92
118.69
77.31
77.05
76.80
50.44
47.99
44.23
38.06
36.71
35.89
34.49
34.27
31.57
29.89
29.52
26.37
25.84
24.72
23.09
22.44
21.63
20.58
14.53
14.26
14.09
13.87
MJ-16-199
Me
O
H
H
H
Et
Et
N
O
O
Et
Et
6fc
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

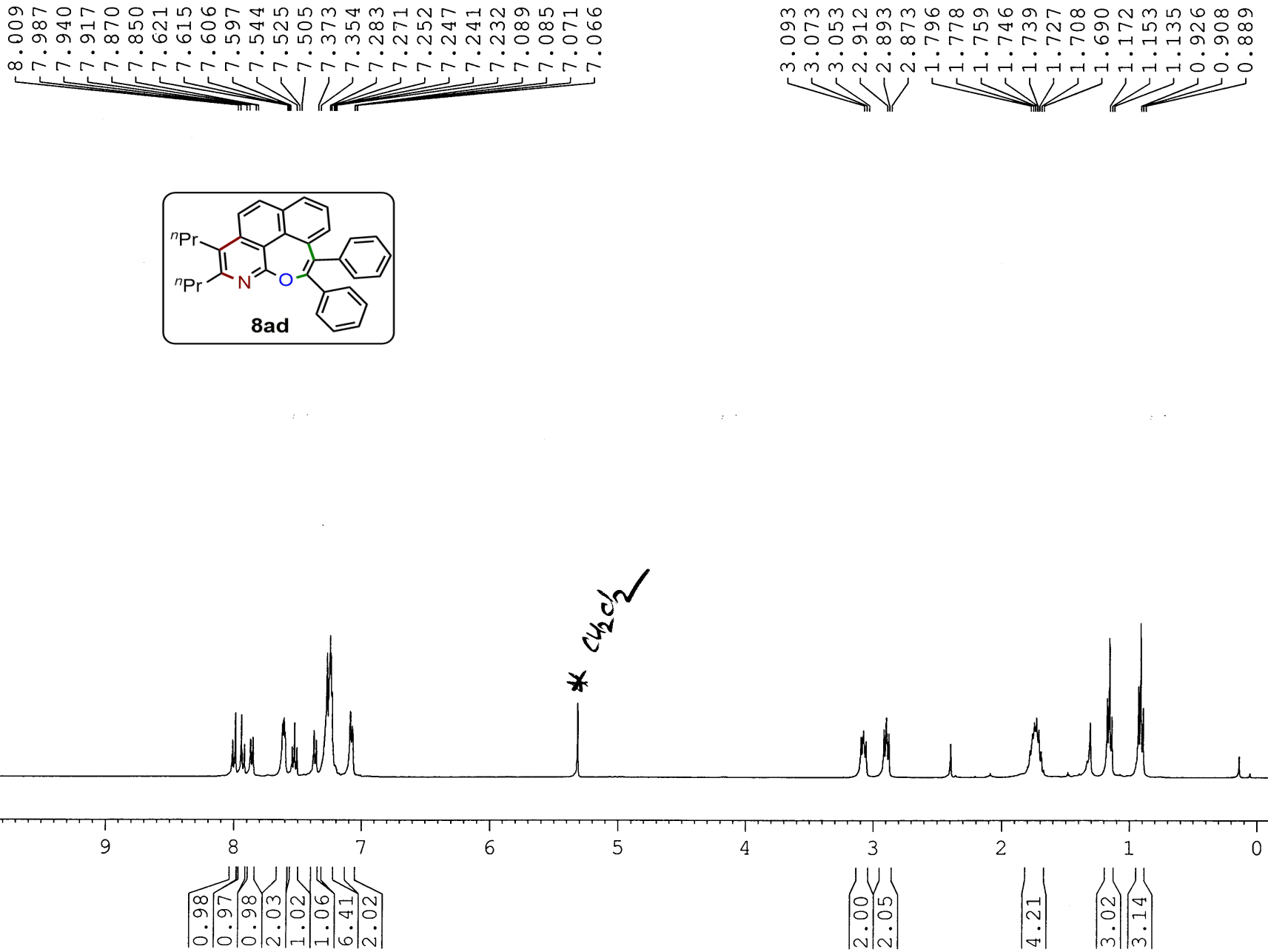

8.478
8.476
8.462
8.460
8.306
7.790
7.788
7.775
7.773
7.698
7.683
7.667
7.260
3.649
3.130
3.115
3.000
2.985
2.970
2.731
2.716
2.521
2.506
1.983
1.958
1.950
1.916
1.910
1.828
1.804
1.719
1.607
1.579
1.472
1.457
1.442
1.417
1.401
1.386
1.371
1.360
1.345
1.330
1.288
1.282
1.259
1.198
1.174
1.147
1.095
1.076
0.990
0.907
0.894
0.781
0.766
0.751
0.653
MJ-16-132
Et
Et
N
O
Et
Et
O
O
Me H
Me
Me
H H
O
OMe
6gc
10
9
8
7
6
5
4
3
2
1
0
ppm
0.97
0.96
0.98
0.98
1.13
3.12
2.08
2.03
1.93
2.03
1.23
1.14
1.12
7.36
4.09
16.35
7.06
3.12
3.16
3.05
3.13


174.76
167.77
158.60
155.86
155.75
137.50
136.82
132.85
128.74
128.54
127.84
127.20
126.59
124.45
124.18
124.16
118.22
77.25
76.99
76.74
76.16
56.39
55.90
51.46
42.69
42.08
40.45
40.06
35.78
35.32
35.08
34.69
32.33
30.99
30.94
28.14
27.83
27.04
26.86
26.83
26.33
25.89
25.46
24.15
23.36
20.94
20.85
18.22
15.57
14.26
14.18
MJ-16-132
6gc
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Mj-Np th
11.511
10.216
10.196
8.158
8.135
7.987
7.967
7.823
7.800
7.695
7.691
7.678
7.674
7.670
7.656
7.652
7.608
7.605
7.590
7.588
7.585
7.571
7.568
3.386
2.755
2.735
2.715
2.660
2.641
2.621
2.517
2.512
2.508
2.503
2.499
1.692
1.673
1.654
1.635
1.616
1.598
1.568
1.549
1.529
1.510
1.492
1.032
1.014
0.995
0.981
0.962
0.944
O
NH
nPr
nPr
7a
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm
1.00
1.03
1.00
1.00
1.00
1.02
1.01
1.97
1.95
2.01
2.07
3.01
3.05

MAJJI


162.97
141.73
139.89
133.71
132.26
131.36
128.44
128.16
127.09
126.21
122.19
117.97
112.32
40.58
40.37
40.16
39.95
39.74
39.53
39.32
32.22
28.66
24.11
23.21
14.47
14.18
O
NH
nPr
nPr
7a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

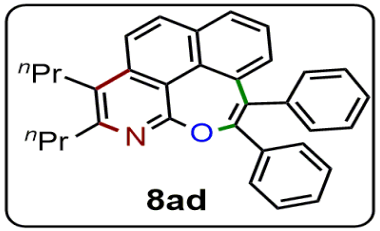

8.009
7.987
7.940
7.917
7.870
7.850
7.621
7.615
7.606
7.597
7.544
7.525
7.505
7.373
7.354
7.283
7.271
7.252
7.247
7.241
7.232
7.089
7.085
7.071
7.066
3.093
3.073
3.053
2.912
2.893
2.873
1.796
1.778
1.759
1.746
1.739
1.727
1.708
1.690
1.172
1.153
1.135
0.926
0.908
0.889
nPr
nPr
N
O
8ad
* CH2Cl2
9
8
7
6
5
4
3
2
1
0
ppm
0.98
0.97
0.98
2.03
1.02
1.06
6.41
2.02
2.00
2.05
4.21
3.02
3.14

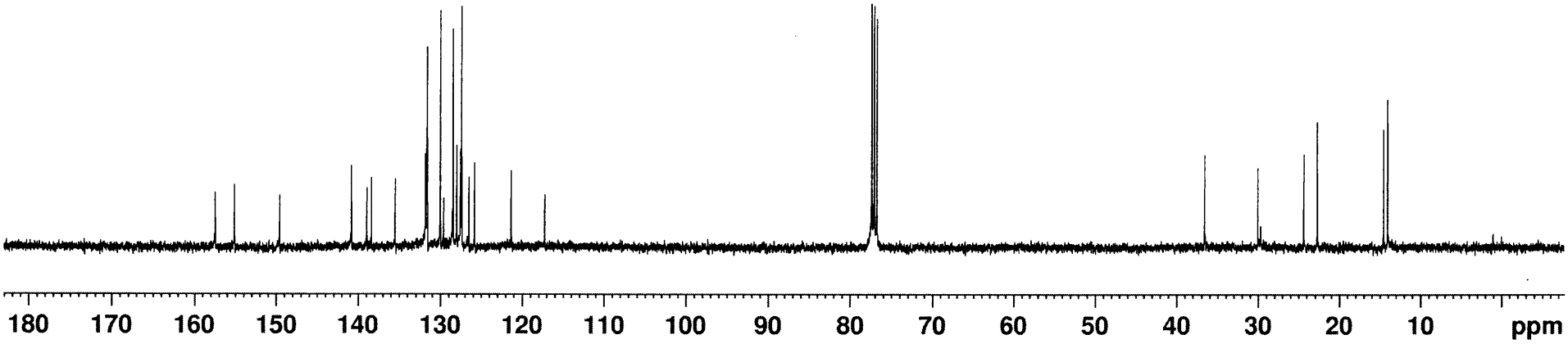
157.43
155.07
149.56
140.80
138.92
138.34
135.49
131.78
131.64
131.61
131.54
129.95
129.58
128.42
127.96
127.94
127.52
127.40
127.33
126.48
125.79
121.28
117.21

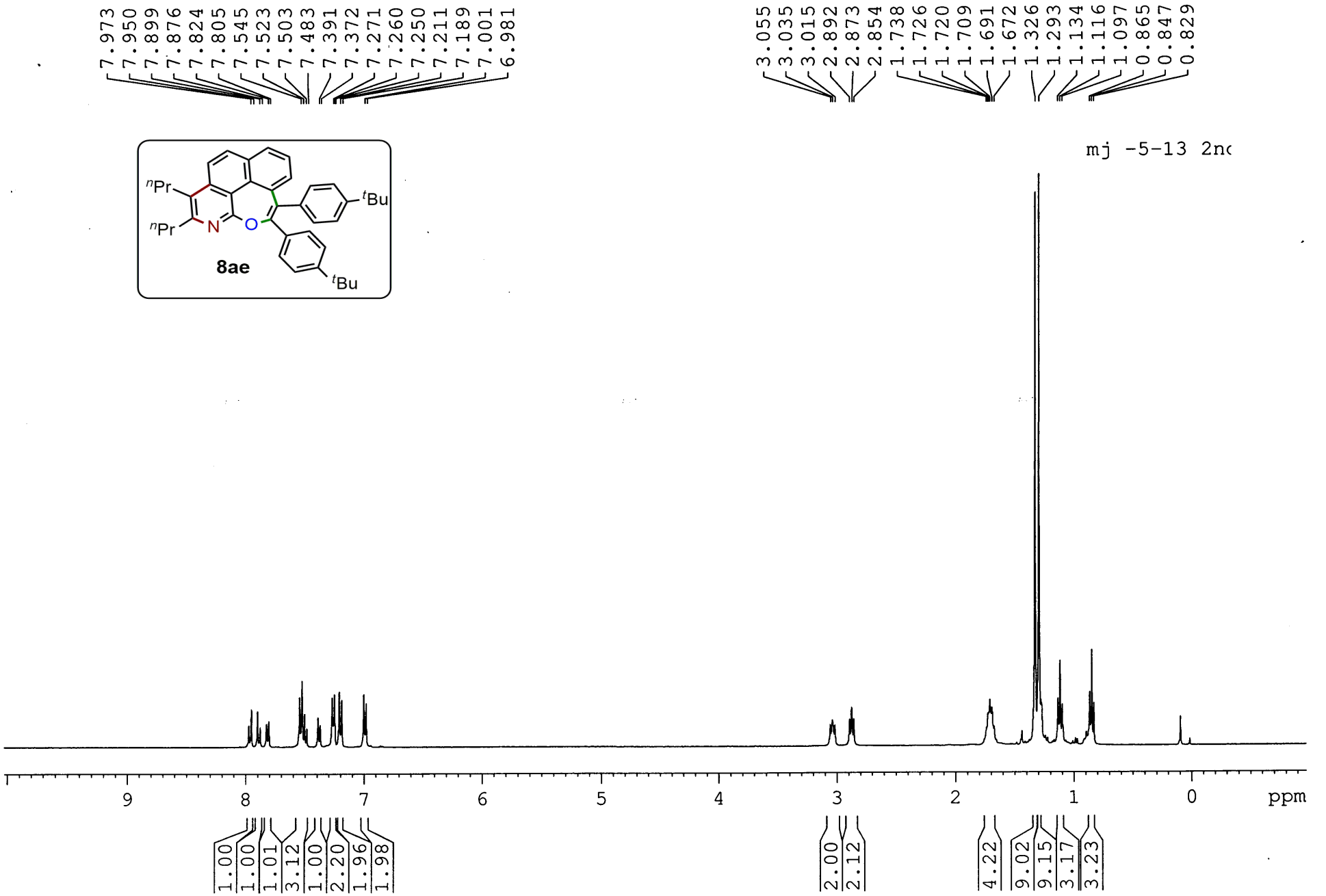
77.32
77.00
76.68

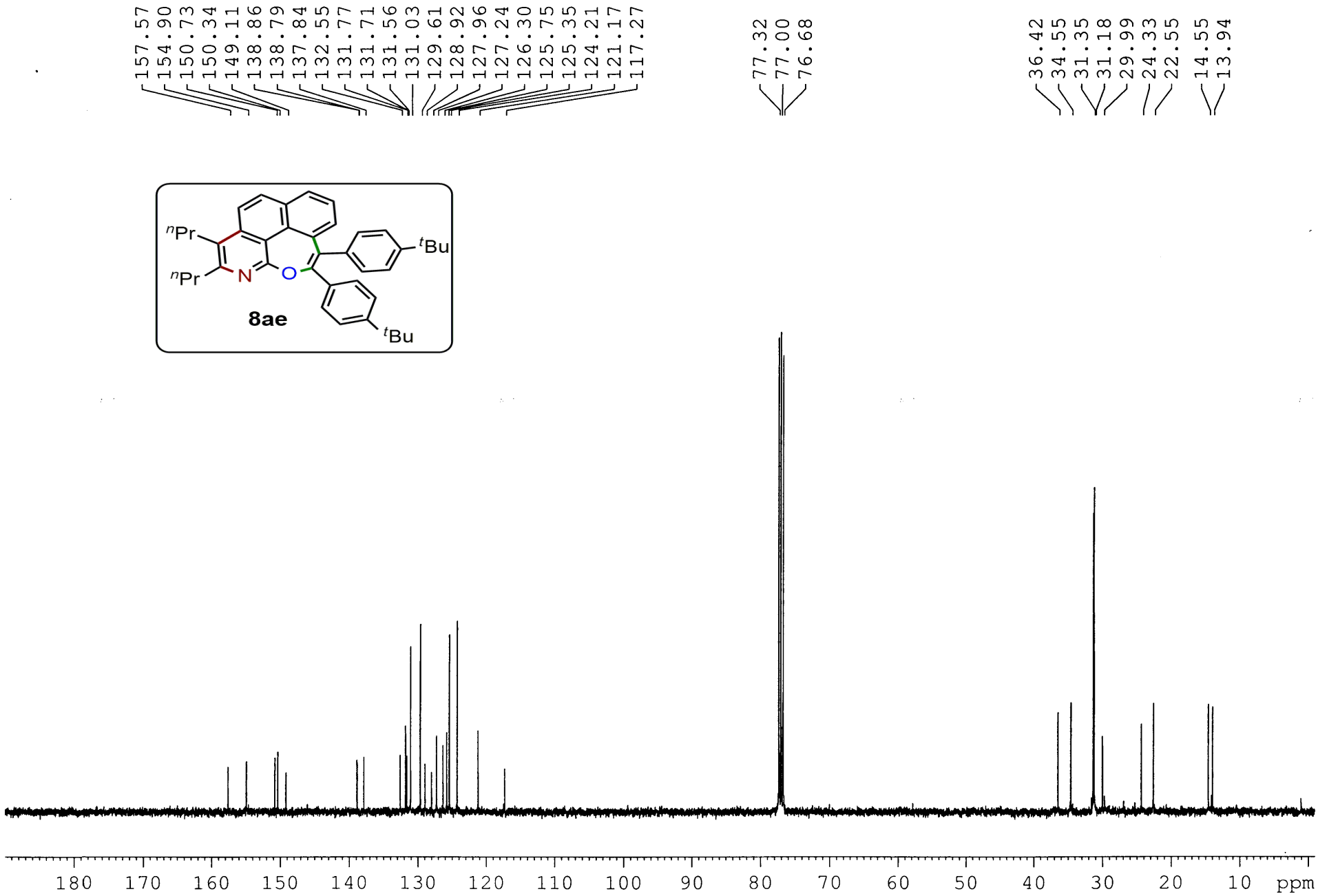
36.53
30.00
24.34
22.70
14.55
14.03

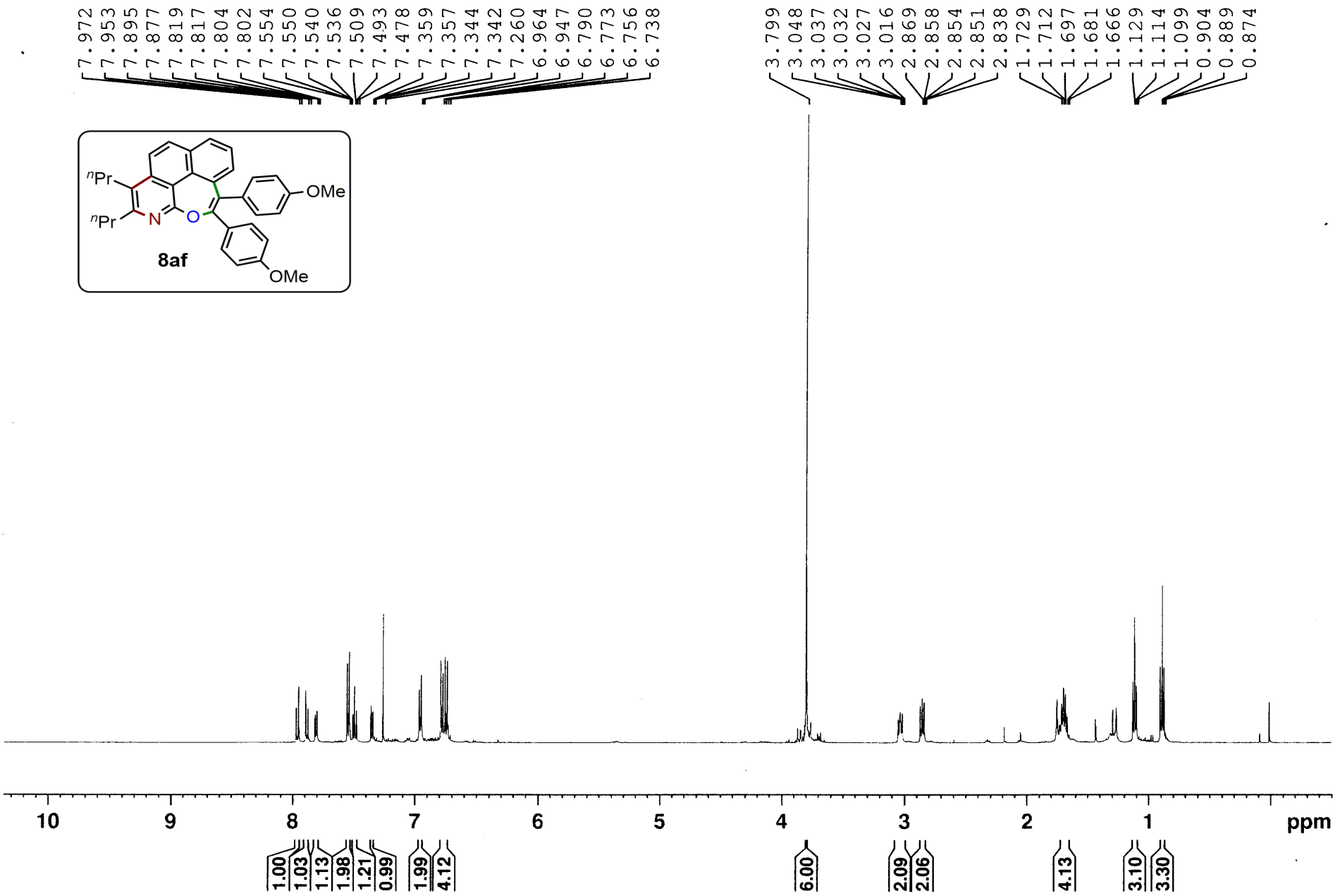
majji-6-13





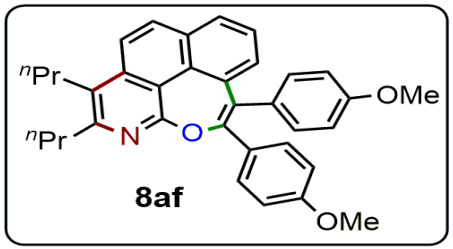

7.973
7.950
7.899
7.876
7.824
7.805
7.545
7.523
7.503
7.483
7.391
7.372
7.271
7.260
7.250
7.211
7.189
7.001
6.981
3.055
3.035
3.015
2.892
2.873
2.854
1.738
1.726
1.720
1.709
1.691
1.672
1.326
1.293
1.134
1.116
1.097
0.865
0.847
0.829
mj -5-13 2nd
nPr
nPr
tBu
tBu
N
O
8ae
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.01
3.12
1.00
2.20
1.96
1.98
2.00
2.12
4.22
9.02
9.15
3.17
3.23


157.57
154.90
150.73
150.34
149.11
138.86
138.79
137.84
132.55
131.77
131.71
131.56
131.03
129.61
128.92
127.96
127.24
126.30
125.75
125.35
124.21
121.17
117.27
77.32
77.00
76.68
36.42
34.55
31.35
31.18
29.99
24.33
22.55
14.55
13.94
nPr
nPr
N
O
tBu
tBu
8ae
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

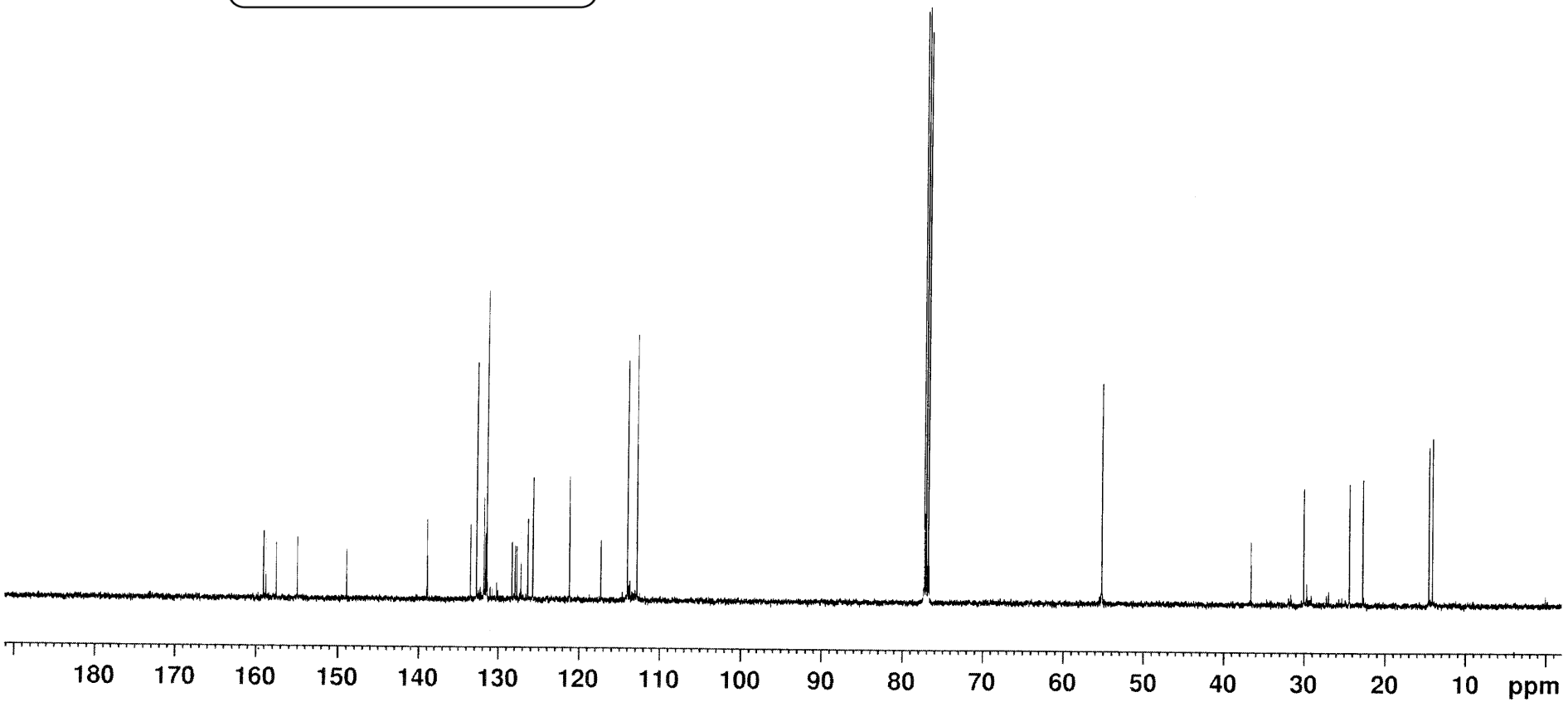

7.972
7.953
7.895
7.877
7.819
7.817
7.804
7.802
7.554
7.550
7.540
7.536
7.509
7.493
7.478
7.359
7.357
7.344
7.342
7.260
6.964
6.947
6.790
6.773
6.756
6.738
3.799
3.048
3.037
3.032
3.027
3.016
2.869
2.858
2.854
2.851
2.838
1.729
1.712
1.697
1.681
1.666
1.129
1.114
1.099
0.904
0.889
0.874
nPr
nPr
N
O
OMe
OMe
8af
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.03
1.13
1.98
1.21
0.99
1.99
4.12
6.00
2.09
2.06
4.13
3.10
3.30

MJ-182-14

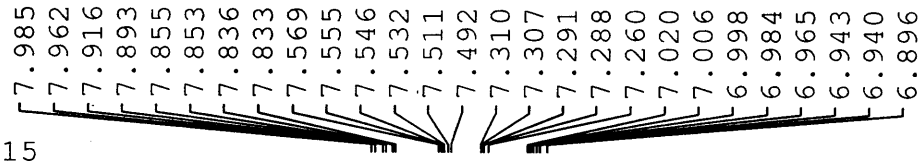
159.08
158.81
157.55
154.98
148.91
138.93
138.88
133.45
132.70
131.78
131.60
131.45
131.41
128.29
127.90
127.70
127.19
126.33
125.71
121.18
117.27
113.98
112.80
77.25
76.99
76.74
55.15
55.14
36.57
30.01
24.33
22.69
14.51
14.06

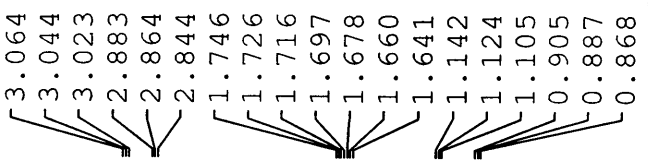


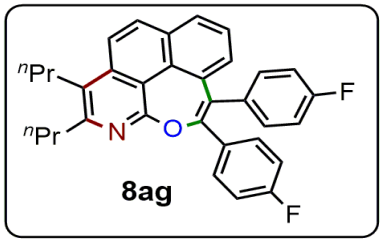
8af

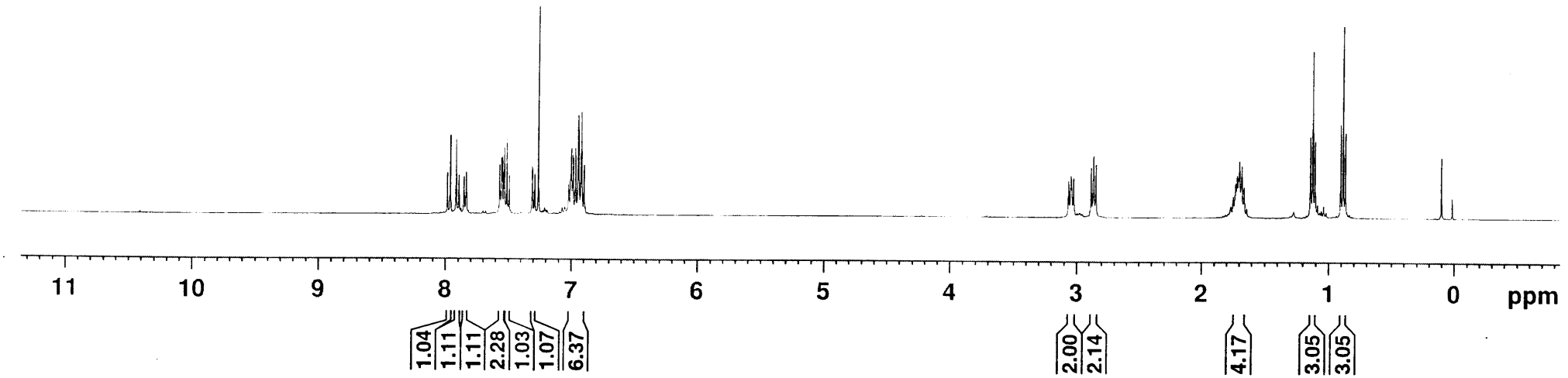


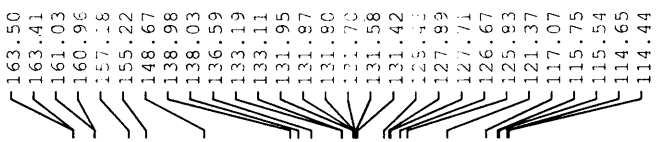
Mj-203-15


7.985
7.962
7.916
7.893
7.855
7.853
7.836
7.833
7.569
7.555
7.546
7.532
7.511
7.492
7.310
7.307
7.291
7.288
7.260
7.020
7.006
6.998
6.984
6.965
6.943
6.940
6.896

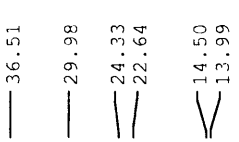

3.064
3.044
3.023
2.883
2.864
2.844
1.746
1.726
1.716
1.697
1.678
1.660
1.641
1.142
1.124
1.105
0.905
0.887
0.868

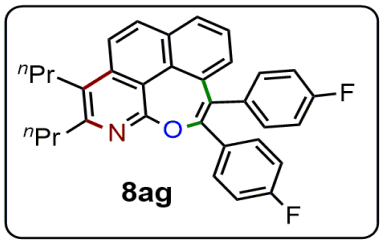

nPr
nPr
N
O
F
F
8ag


11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.04
1.11
1.11
2.28
1.03
1.07
6.37
2.00
2.14
4.17
3.05
3.05

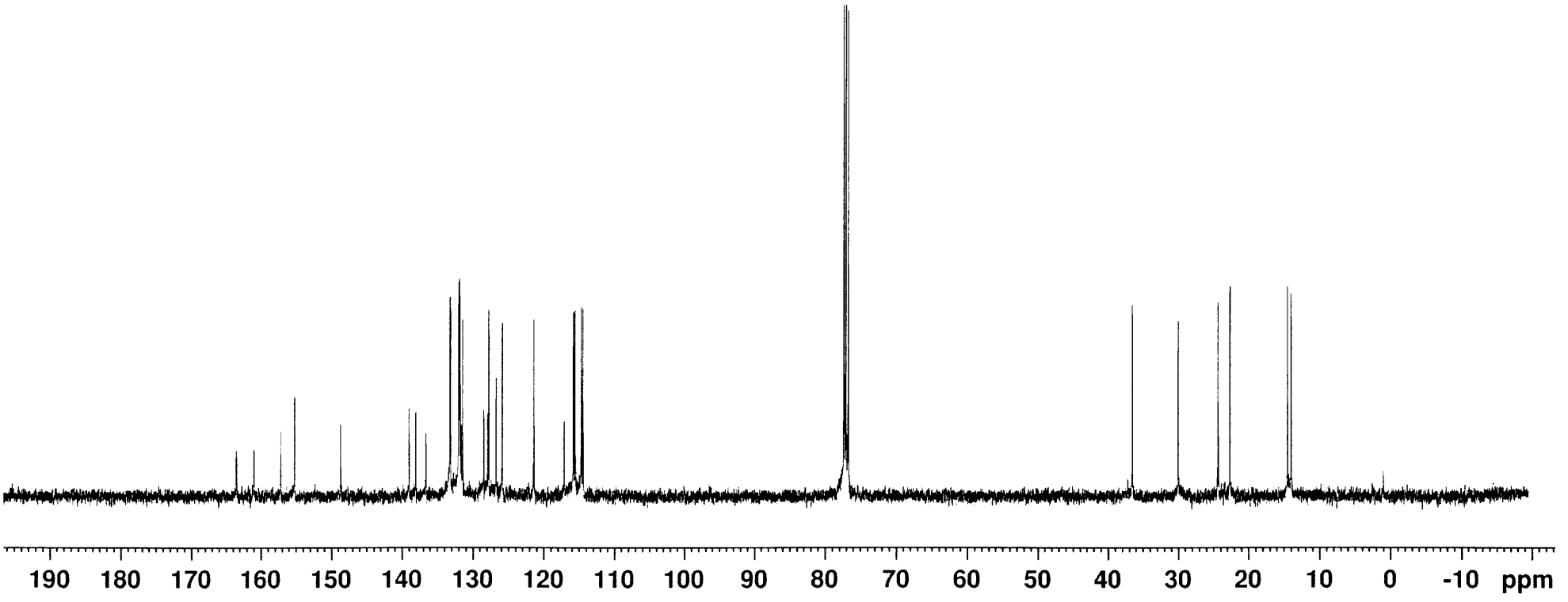

163.50
163.41
161.03
155.22
148.67
138.98
138.03
136.59
133.19
133.11
131.95
131.87
131.58
131.42
127.99
126.67
125.83
121.37
117.07
115.75
115.54
114.65
114.44


77.31
77.00
76.68

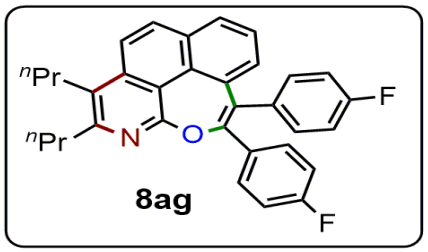

36.51
29.98
24.33
22.64
14.50
13.99


nPr
nPr
N
O
F
F
8ag

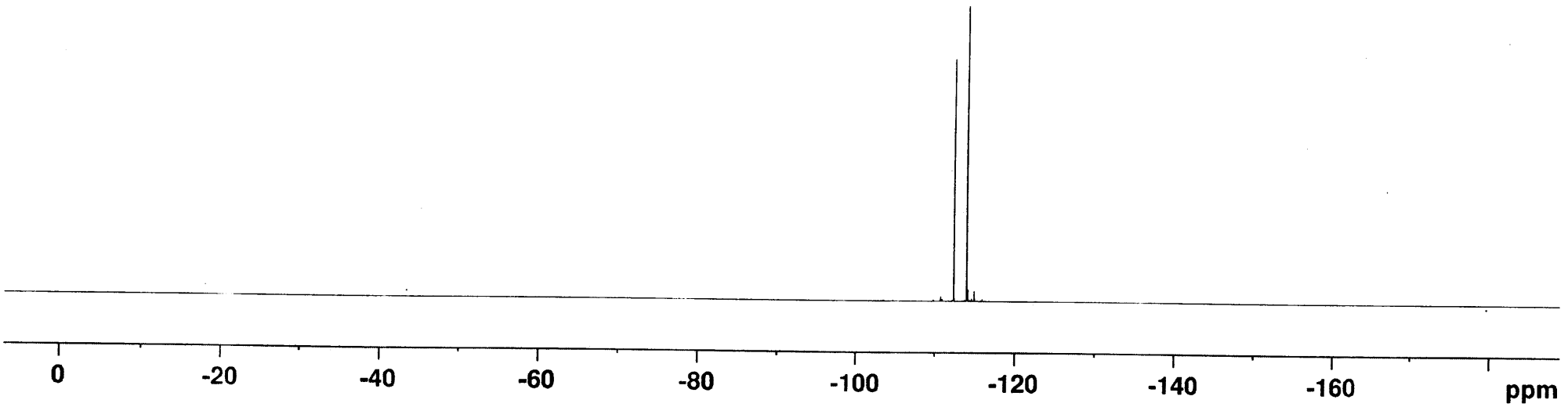
Mj-203-15

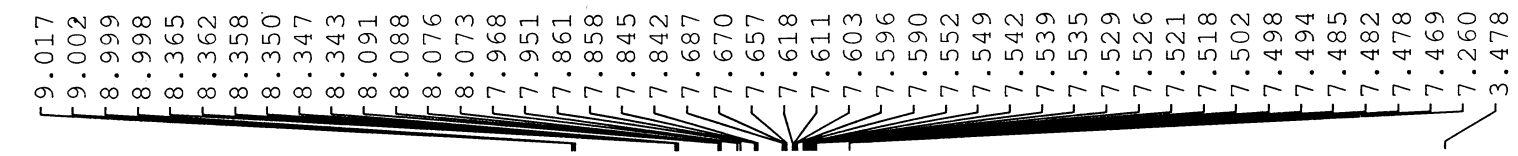

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

Mj-203-15

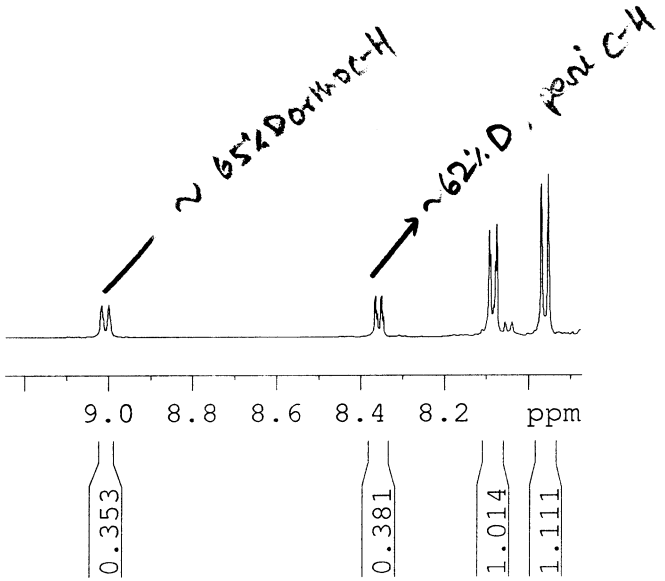


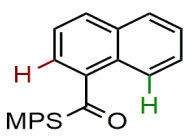
-112.41
-113.99





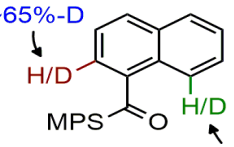
MJ-187-15





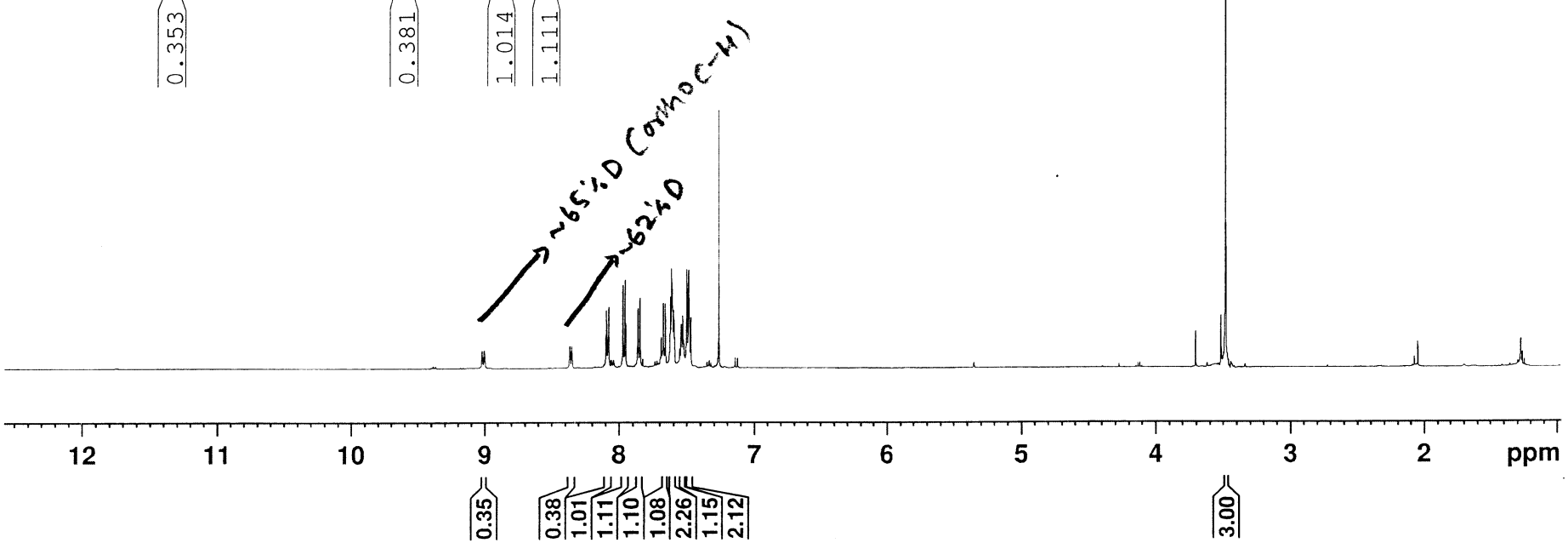
1a

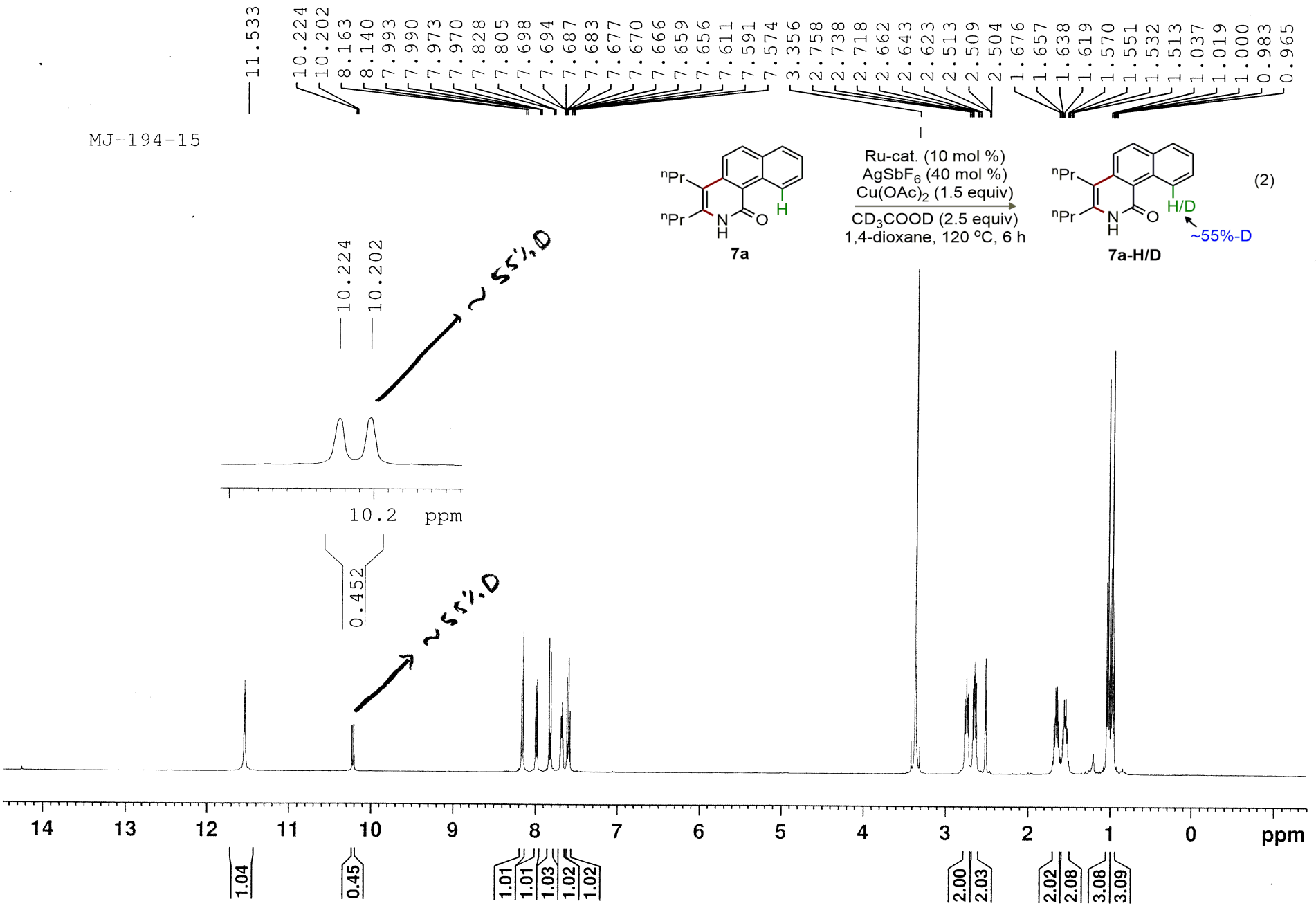
Ru-cat. (10 mol %)
$AgSbF_6$ (40 mol %)
$Cu(OAc)_2$ (1.5 equiv)
CD_3COOD (2.5 equiv)
1,4-dioxane, 120 °C, 6 h

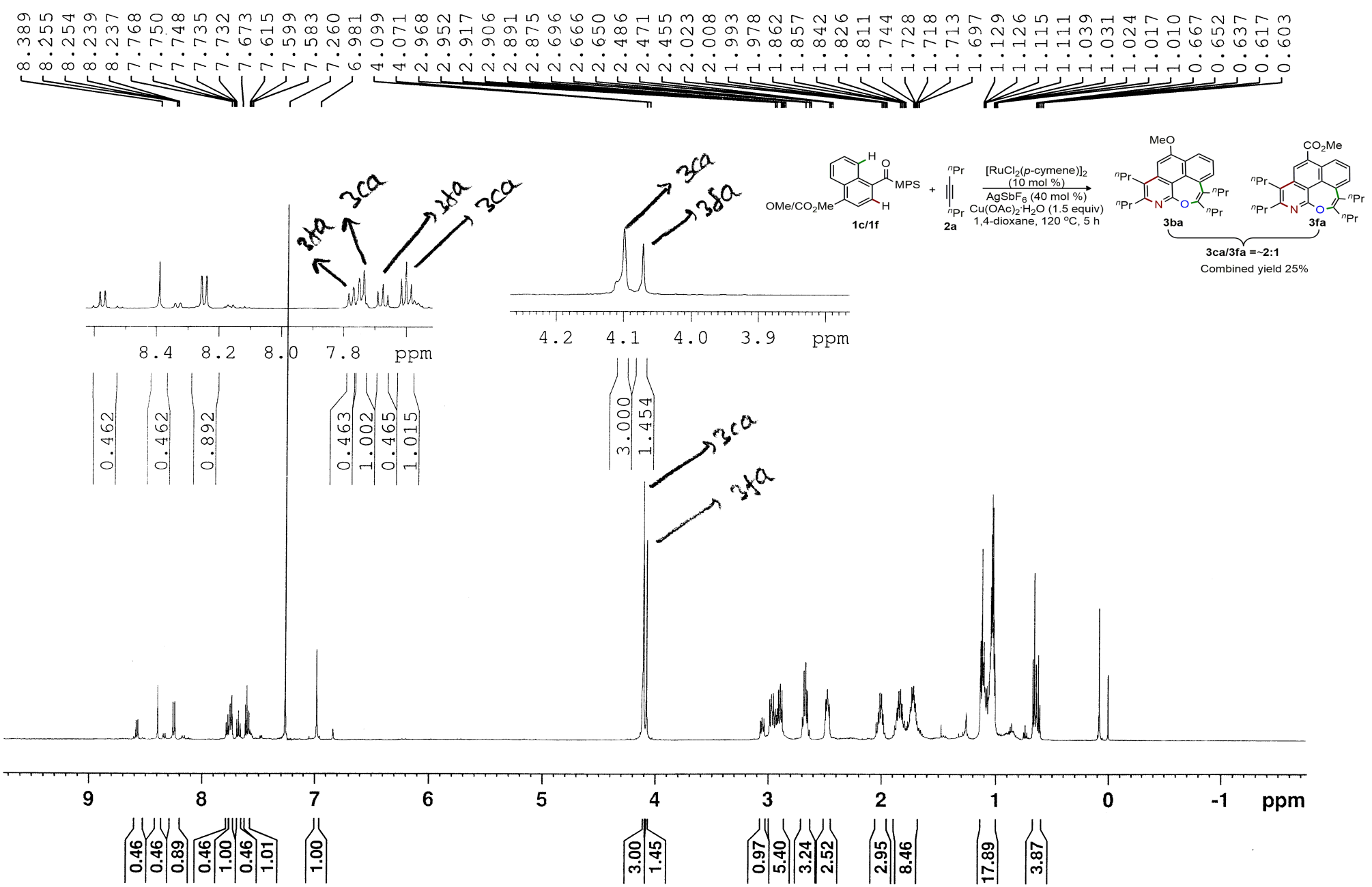


1a-H/D ~62%-D

(1)




MJ-194-15
11.533
10.224
10.202
8.163
8.140
7.993
7.990
7.973
7.970
7.828
7.805
7.698
7.694
7.687
7.683
7.677
7.670
7.666
7.659
7.656
7.611
7.591
7.574
3.356
2.758
2.738
2.718
2.662
2.643
2.623
2.513
2.509
2.504
1.676
1.657
1.638
1.619
1.570
1.551
1.532
1.513
1.037
1.019
1.000
0.983
0.965
nPr
nPr
N
H
O
H
7a
Ru-cat. (10 mol %)
AgSbF6 (40 mol %)
Cu(OAc)2 (1.5 equiv)
CD3COOD (2.5 equiv)
1,4-dioxane, 120 °C, 6 h
H/D
~55%-D
7a-H/D
(2)
~55%D
~55%D
10.2 ppm
0.452
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.04
0.45
1.01
1.01
1.03
1.02
1.02
2.00
2.03
2.02
2.08
3.08
3.09


8.389 8.255 8.254 8.239 8.237 7.768 7.750 7.748 7.735 7.732 7.673 7.615 7.599 7.583 7.260 6.981 4.099 4.071 2.968 2.952 2.917 2.906 2.891 2.875 2.696 2.666 2.650 2.486 2.471 2.455 2.023 2.008 1.993 1.978 1.862 1.857 1.842 1.826 1.811 1.744 1.728 1.718 1.713 1.697 1.129 1.126 1.115 1.111 1.039 1.031 1.024 1.017 1.010 0.667 0.652 0.637 0.617 0.603
3ha 3ca
3ha 3ca
3ca
3da
3ca
3ha
8.4 8.2 8.0 7.8 ppm
4.2 4.1 4.0 3.9 ppm
0.462 0.462 0.892 0.463 1.002 0.465 1.015
3.000 1.454
OMe/CO2Me
MPS
1c/1f
nPr nPr
2a
[RuCl2(p-cymene)]2 (10 mol %)
AgSbF6 (40 mol %)
Cu(OAc)2·H2O (1.5 equiv)
1,4-dioxane, 120 °C, 5 h
MeO
CO2Me
3ba
3fa
3ca/3fa =~2:1
Combined yield 25%
9 8 7 6 5 4 3 2 1 0 -1 ppm
0.46 0.46 0.89 0.46 1.00 0.46 1.01 1.00 3.00 1.45 0.97 5.40 3.24 2.52 2.95 8.46 17.89 3.87