Indium(III) chloride catalyzed highly diastereoselective domino synthesis of indenodithiepines and indenodithiocines

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General Remarks: Melting points were determined on a capillary melting point apparatus and uncorrected. IR spectra were recorded using ATR technique on a Bruker Alpha FT-IR spectrophotometer. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a Bruker Avance at 400 MHz using $CDCl_3$ in ppm (δ) related to tetramethylsilane (δ=0.00) as an internal standard and are reported as follows; chemical shift (ppm), multiplicity (br = broad, s = singlet, d = doublet, m = multiplet), coupling constant (Hz) and integration. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 100 MHz in $CDCl_3$. Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to the center of the triplet at 77.7 ppm for $CDCl_3$. Carbon types were determined from ^{13}C NMR and DEPT experiments. High resolution mass analyses were performed using electrospray ionization technique on a Waters QTof-micromass spectrometer. All solvents were purified by distillation following standard procedure. Thin layer chromatography was performed on silica or alumina plates and components visualized by observation under iodine/UV light at 254 nm. Column chromatography was performed on silica gel (100-200 mesh). All the reactions were conducted in oven-dried glassware under a positive pressure of argon with magnetic stirring. Reagents were added via syringes through septa.

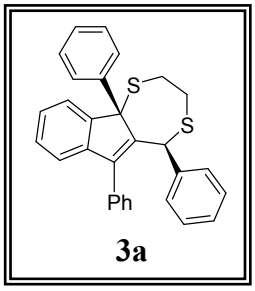
General experimental procedures and physical characterizations: All reactions were carried out under nitrogen atmosphere. All air sensitive reactions were conducted in oven-

dried glassware under a positive pressure of an argon or nitrogen with magnetic stirring. Aldehydes, ethane and propane dithiols, phenyl acetylene, benzophenone derivatives and $InCl_3$ were purchased from M/s Aldrich and used as provided.

Propargylic alcohols 1 and dithioacetals 2: The propargylic alcohols[1] and dithioacetals[2] were prepared according to the literature methods. Dichloromethane (DCM) and 1,2-dichloroethane (DCE) were distilled from CaH_2 under N_2 atmosphere.

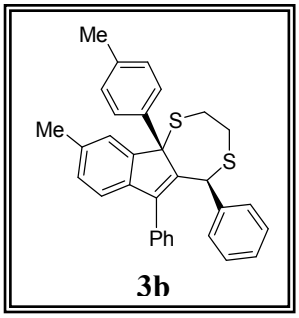
General procedure for synthesis of indenodithiepines and indenodithiocines: To a solution of thioacetal (1 mmol) and propargyl alcohol (1.1 mmol) in dry DCE (10 mL) was added 10 mol% of indium trichloride. The reaction mixture was stirred at 60 °C under an inert atmosphere and monitored using TLC until the disappearance of propargyl alcohol. After the appropriate period, the reaction mixture was diluted with DCM (10 mL) and water (15 mL) was added. The organic phase was separated and the aqueous layer was washed with DCM (10 mL). Concentration of the combined organic layer under reduced pressure afforded the crude product, which was purified by silica gel column chromatography to afford the corresponding product.

Synthesis of (5*S*,10b*S*)-5,6,10b-triphenyl-2,3,5,10b-tetrahydroindeno[1,2-*e*][1,4]dithiepine (3a): White solid; yield: 107 mg (87%); mp 172-174 °C; IR (neat): ν_{max} 3056, 1603, 1486, 1448, 1407, 1262, 1032, 887, 733 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.83-2.89 (m, 1H), 2.99-3.02 (m, 2H), 3.12-3.19 (m, 1H), 5.37 (s, 1H, C*H*), 6.79 (d, 2H, J = 7.2 Hz), 6.86 (d, 1H, J = 7.2 Hz), 6.91-7.01 (m, 5H), 7.13-7.20 (m, 5H), 7.29-7.40 (m, 4H), 7.67 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 33.14 (*C*H_2), 34.29 (*C*H_2), 46.03 (*C*H), 68.38 (*quat-C*), 120.36 (=*C*H), 124.02 (=*C*H), 126.08 (=*C*H), 126.70 (=*C*H), 127.17 (=*C*H), 127.44 (=*C*H), 127.60 (=*C*H), 127.74 (=*C*H), 127.92 (=*C*H), 128.51 (=*C*H), 128.92 (=*C*H), 129.15 (=*C*H), 134.55 (*quat-C*), 139.66 (*quat-C*), 140.89 (*quat-C*), 141.77 (*quat-C*), 144.13 (*quat-C*), 149.87 (*quat-C*), 151.60 (*quat-C*); HRMS (ESI) Calcd for $C_{30}H_{24}S_2$ $[M+H]^+$ 449.1398; found, 449.1406.



3a

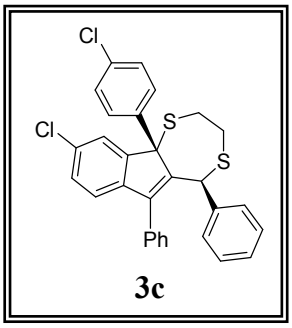
Synthesis of (5*S*,10b*S*)-9-methyl-5,6-diphenyl-10b-*p*-tolyl-2,3,5,10b-tetrahydroindeno[1,2-*e*][1,4]dithiepine (3b): White solid; yield: 123 mg (94%); mp 189-191 °C; IR (neat): ν_{max} 3053, 1599, 1492, 1446, 1406, 1268, 1031, 899, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.92-1.97 (m, 2H), 2.27 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.87-2.94 (m, 2H), 4.97 (s, 1H, C*H*), 6.09 (d, 2H, J = 5.2 Hz), 6.57 (s, 1H), 6.67-6.73 (m, 3H), 7.02-7.11



3b

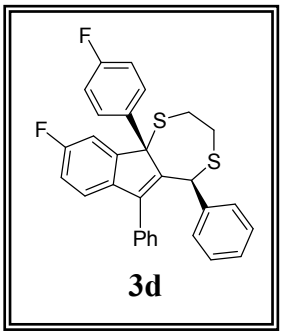
(m, 4H), 7.15-7.48 (m, 5H), 7.53-7.59 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.89 (*C*H_3), 20.93 (*C*H_3), 33.01 (*C*H_2), 33.33 (*C*H_2), 47.17 (*C*H), 68.40 (*quat-C*), 120.84 (=*C*H), 123.96 (=*C*H), 126.54 (=*C*H), 127.24 (=*C*H), 127.37 (=*C*H), 127.69 (=*C*H), 127.81 (=*C*H), 128.66 (=*C*H), 129.50 (=*C*H), 129.67 (=*C*H), 131.46 (*quat-C*), 133.98 (*quat-C*), 136.21 (*quat-C*), 137.20 (*quat-C*), 139.47 (*quat-C*), 142.43 (*quat-C*), 145.36 (*quat-C*), 147.52 (*quat-C*), 151.63 (*quat-C*); HRMS (ESI) Calcd for $C_{32}H_{28}S_2$ $[M+Na]^+$ 499.1525; found, 499.1532.

Synthesis of (5*S*,10b*S*)-9-chloro-10b-(4-chlorophenyl)-5,6-diphenyl-2,3,5,10b-tetrahydroindeno[1,2-*e*][1,4]dithiepine (3c): White solid; yield:120 mg (85%); mp 203-205 °C; IR (neat): ν_{max} 3058, 1592, 1486, 1402, 1264, 1092, 1013, 824, 732 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.84-2.91 (m, 1H), 2.95-3.10 (m, 2H), 3.26-3.32 (m, 1H), 4.80 (s, 1H, C*H*), 6.72-6.80 (m, 4H), 6.95-7.00 (m, 5H), 7.08-7.13 (m, 1H), 7.18-7.22 (m, 1H), 7.30-7.36 (m, 3H), 7.50-7.55 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.94 (*C*H_2), 34.04 (*C*H_2), 46.59 (*C*H), 70.38 (*quat-C*), 120.86 (=*C*H), 124.05 (=*C*H), 126.11 (=*C*H), 127.04 (=*C*H), 127.48 (=*C*H), 127.59 (=*C*H), 127.93 (=*C*H), 128.63 (=*C*H), 129.03 (=*C*H), 129.78 (=*C*H), 130.00 (=*C*H), 133.02 (*quat-C*), 133.22 (*quat-C*), 136.90 (*quat-C*), 138.45 (*quat-C*), 139.28 (*quat-C*), 141.02 (*quat-C*), 143.16 (*quat-C*), 149.44 (*quat-C*), 150.80 (*quat-C*); HRMS (ESI) Calcd for $C_{30}H_{22}Cl_2S_2$ $[M+H]^+$ 517.0613; found, 517.0612.



3c

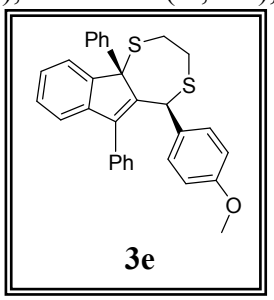
Synthesis of (5*S*,10b*S*)-9-fluoro-10b-(4-fluorophenyl)-5,6-diphenyl-2,3,5,10b-tetrahydroindeno[1,2-*e*][1,4]dithiepine (3d): White solid; yield: 108 mg (81%); mp 185-187 °C; IR (neat): ν_{max} 3058, 1600, 1501, 1456, 1456, 1406, 1226, 1159, 1017, 829, 731 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.89-3.28 (m, 4H), 4.84 (s, 1H, C*H*), 6.51-6.53 (m, 2H), 6.80 (s, 2H), 6.95-7.34 (m, 9H), 7.56-7.57 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.99 (*C*H_2), 34.00 (*C*H_2), 46.66 (*C*H), 70.26 (*quat-C*), 114.60 (d, *J* = 84 Hz), 115.68 (d, *J* = 84 Hz), 120.85 (=*C*H), 124.11 (=*C*H), 126.16 (=*C*H), 126.97 (=*C*H), 127.46 (=*C*H), 128.72 (=*C*H), 130.03 (=*C*H), 130.10 (=*C*H), 130.29 (=*C*H), 130.37 (=*C*H), 136.36 (*quat-C*), 136.70 (*quat-C*), 138.48 (*quat-C*), 143.13 (*quat-C*), 150.08 (*quat-C*), 151.70 (*quat-C*), 160.77 (d, *J* = 84 Hz), 163.22 (d, *J* = 80 Hz); HRMS (ESI) Calcd for $C_{30}H_{22}F_2S_2$ $[M+H]^+$ 485.1204; found, 485.1210.



3d

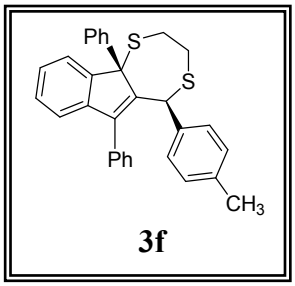
Synthesis of (5*S*,10b*S*)-5-(4-methoxyphenyl)-6,10b-diphenyl-2,3,5,10b-tetrahydroindeno[1,2-*e*][1,4]dithiepine (3e): White solid; yield: 107 mg (95%); mp 194-196 °C; IR (neat): ν_{max} 3057, 2920, 1607, 1506, 1454, 1300, 1245, 1175, 1031, 824, 769, 695

cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.74-2.82 (m, 2H), 2.98-3.09 (m, 2H), 3.80 (s, 3H, OCH_3), 5.16 (s, 1H, C*H*), 6.76-6.78 (m, 1H), 6.81 (s, 1H), 6.83 (s, 1H), 6.94-7.00 (m, 5H), 7.07-7.12 (m, 3H), 7.13-7.18 (m, 5H), 7.25-7.29 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.51 (*C*H_2), 40.24 (*C*H_2), 55.22 (*C*H), 59.04 (O*C*H_3), 73.27 (*quat-C*), 113.56 (=*C*H), 120.36 (=*C*H), 123.45 (=*C*H), 126.07 (=*C*H), 126.19 (=*C*H), 126.61 (=*C*H), 126.74 (=*C*H), 127.11 (=*C*H), 127.17 (=*C*H), 127.47 (=*C*H), 129.48 (=*C*H), 130.63 (=*C*H), 131.55 (*quat-C*), 135.33 (*quat-C*), 144.26 (*quat-C*), 145.84 (*quat-C*), 146.39 (*quat-C*), 148.22 (*quat-C*), 148.65 (*quat-C*), 158.39 (*quat-C*); HRMS (ESI) Calcd for $C_{31}H_{26}OS_2$ $[M+H]^+$ 479.1503; found, 479.1505.



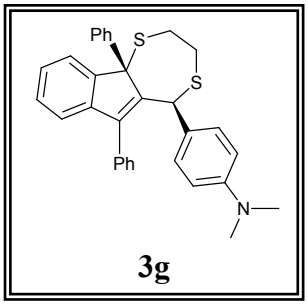
3e

Synthesis of (5*S*,10b*S*)-6,10b-diphenyl-5-*p*-tolyl-2,3,5,10b-tetrahydroindeno[1,2-*e*][1,4]dithiepine (3f): White solid; yield: 108 mg (92%); mp 158-160 °C; IR (neat): ν_{max} 3053, 1593, 1491, 1449, 1407, 1027, 731, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.17 (s, 3H, CH_3), 2.80-2.86 (m, 1H), 2.98-3.01 (m, 2H), 3.09-3.14 (m, 1H), 5.32 (s, 1H, C*H*), 6.63-6.65 (m, 2H), 6.72-6.74 (m, 2H), 6.84-6.86 (m, 1H), 7.00-7.03 (m, 2H), 7.11-7.19 (m, 5H), 7.27-7.39 (m, 4H), 7.65 (d, 2H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.88 (*C*H_3), 32.98 (*C*H_2), 34.26 (*C*H_2), 45.62 (*C*H), 68.28 (*quat-C*), 120.27 (=*C*H), 123.91 (=*C*H), 126.57 (=*C*H), 127.07 (=*C*H), 127.11 (=*C*H), 127.49 (=*C*H), 127.62 (=*C*H), 127.80 (=*C*H), 128.02 (=*C*H), 128.27 (=*C*H), 128.80 (=*C*H), 129.14 (=*C*H), 134.56 (*quat-C*), 135.49 (*quat-C*), 137.75 (*quat-C*), 139.62 (*quat-C*), 141.57 (*quat-C*), 144.18 (*quat-C*), 149.87 (*quat-C*), 151.66 (*quat-C*); HRMS (ESI) Calcd for $C_{31}H_{26}S_2$ $[M+Na]^+$ 485.1368; found, 485.1366.



3f

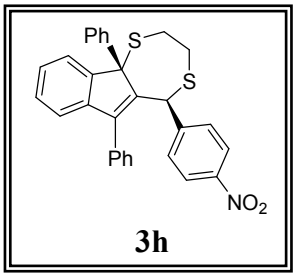
Synthesis of 4-((5*S*,10b*S*)-6,10b-diphenyl-2,3,5,10b-tetrahydroindeno[1,2-*e*][1,4]dithiepin-5-yl)-*N*,*N*-dimethylbenzenamine (3g): White solid; yield: 108 mg (92%); mp 158-160 °C; IR (neat): ν_{max} 2882, 1610, 1519, 1446, 1347, 1229, 1170, 1066, 947, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.69-2.76 (m, 1H), 2.81-2.88 (m, 1H), 2.94 (s, 6H, CH_3), 3.00-3.09 (m, 2H), 5.11 (s, 1H, C*H*), 6.66-6.68 (m, 2H), 6.75-6.77 (m, 1H), 6.94-7.00 (m, 5H), 7.09-7.15 (m, 8H), 7.29-7.30 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.26 (*C*H_2), 40.12 (*C*H_2), 40.69 (N*C*H_3), 58.95 (*C*H), 73.42 (*quat-C*), 112.42 (=*C*H), 120.21 (=*C*H), 123.48 (=*C*H), 125.97 (=*C*H), 126.12 (=*C*H), 126.40 (=*C*H), 126.64 (=*C*H), 126.91 (*quat-C*), 127.10 (=*C*H), 127.23 (=*C*H), 127.43 (=*C*H), 129.53 (=*C*H), 130.29 (=*C*H), 135.52 (*quat-C*), 143.94 (*quat-C*), 145.86



3g

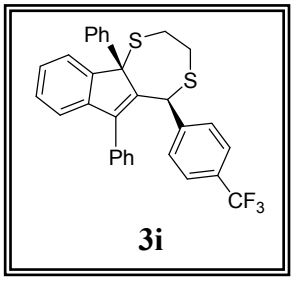
(*quat-C*), 146.44 (*quat-C*), 148.63 (*quat-C*), 148.78 (*quat-C*), 149.48 (*quat-C*); HRMS (ESI) Calcd for $C_{32}H_{29}NS_2$ $[M+H]^+$ 492.1794; found, 492.1814.

Synthesis of (5*S*,10b*S*)-5-(4-nitrophenyl)-6,10b-diphenyl-2,3,5,10b-tetrahydroindeno[1,2-*e*][1,4]dithiepine (3h): White solid; yield: 87 mg (80%); mp 195-197 °C; IR (neat): ν_{max} 3406, 3054, 1739, 1598, 1512, 1451, 1310, 1243, 1000, 746, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.87-3.04 (m, 3H), 3.15-3.21 (m, 1H), 5.44 (s, 1H, C*H*), 6.89 (d, 1H, J_2 = 7.2 Hz), 6.94 (d, 2H, J = 8.8 Hz), 7.01-7.03 (m, 2H), 7.16-7.25 (m, 5H), 7.32-7.42 (m, 4H), 7.67 (d, 2H, J = 7.6 Hz), 7.78 (d, 2H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 33.08 (*C*H_2), 34.36 (*C*H_2), 45.62 (*C*H), 68.29 (*quat-C*), 120.53 (=*C*H), 122.60 (=*C*H), 124.07 (=*C*H), 126.97 (=*C*H), 127.11 (=*C*H), 127.66 (=*C*H), 127.80 (=*C*H), 127.93 (=*C*H), 128.19 (=*C*H), 128.86 (=*C*H), 129.06 (=*C*H), 129.18 (=*C*H), 134.02 (*quat-C*), 139.19 (*quat-C*), 142.39 (*quat-C*), 143.45 (*quat-C*), 145.91 (*quat-C*), 148.37 (*quat-C*), 149.54 (*quat-C*), 150.17 (*quat-C*); HRMS (ESI) Calcd for $C_{30}H_{23}NO_2S_2$ $[M+Na]^+$ 516.1062; found, 516.1075.



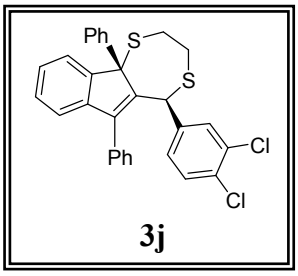
3h

Synthesis of (5*S*,10b*S*)-6,10b-diphenyl-5-(4-(trifluoromethyl)phenyl)-2,3,5,10b-tetrahydroindeno[1,2-*e*][1,4]dithiepine (3i): White solid; yield: 88 mg (85%); mp 165-167 °C; IR (neat): ν_{max} 3060, 1615, 1490, 1450, 1410, 1323, 1163, 1118, 1068, 831. 746 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.84-2.90 (m, 1H), 2.95-3.06 (m, 2H), 3.13-3.19 (m, 1H), 5.39 (s, 1H, C*H*), 6.86 (d, 2H, J = 7.6 Hz), 6.96-6.98 (m, 2H), 7.15-7.22 (m, 7H), 7.31-7.34 (m, 1H), 7.37-7.41 (m, 3H), 7.66 (d, 2H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 33.05(*C*H_2), 34.36 (*C*H_2), 45.60 (*C*H), 68.28 (*quat-C*), 120.46 (=*C*H), 122.78 (*quat-C*), 124.05 (=*C*H), 124.31 (d, $J_{C,F}$ = 16 Hz), 125.48 (*quat-C*), 126.95 (=*C*H), 127.09 (=*C*H), 127.41 (=*C*H), 127.75 (=*C*H), 127.87 (=*C*H), 128.04 (=*C*H), 128.65 (=*C*H), 128.99 (d, $J_{C,F}$ = 16 Hz), 134.21 (*quat-C*), 139.38 (*quat-C*), 142.18 (*quat-C*), 143.85 (*quat-C*), 144.87 (*quat-C*), 149.71 (*quat-C*), 150.89 (*quat-C*); HRMS (ESI) Calcd for $C_{31}H_{23}F_3S_2$ $[M+H]^+$ 517.1266; found, 517.1262.



3i

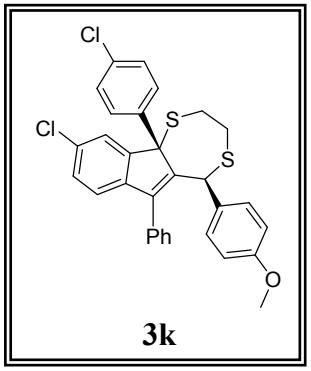
Synthesis of (5*S*,10b*S*)-5-(3,4-dichlorophenyl)-6,10b-diphenyl-2,3,5,10b-tetrahydroindeno[1,2-*e*][1,4]dithiepine (3j): White solid; yield: 81 mg (79%); mp 193-195 °C; IR (neat): ν_{max} 3057, 1590, 1465, 1392, 1264, 1133, 1208, 894, 736 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.57-2.64 (m, 1H), 2.78-2.86 (m, 1H), 2.95-3.03 (m, 1H), 3.17-3.24 (m, 1H), 5.60 (s, 1H, C*H*), 6.89-6.91 (m, 1H), 6.95-7.04 (m, 4H), 7.08-7.12 (m, 3H), 7.17-7.23



3j

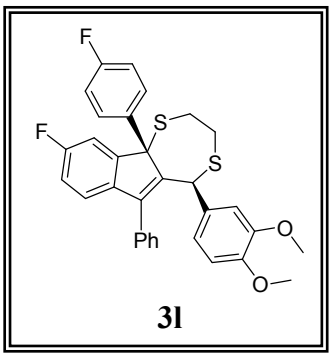
(m, 3H), 7.30 (d, 1H, J = 2.0 Hz), 7.45-7.50 (m, 3H), 7.55-7.59 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.97 (CH_2), 32.24 (CH_2), 46.52 (*C*H), 66.57 (*quat-C*), 120.71 (=*C*H), 123.40 (=*C*H), 126.39 (=*C*H), 126.79 (=*C*H), 127.35 (=*C*H), 127.67 (=*C*H), 127.84 (=*C*H), 128.09 (=*C*H), 128.51 (=*C*H), 128.80 (=*C*H), 129.08 (=*C*H), 129.25 (=*C*H), 130.49 (*quat-C*), 131.16 (=*C*H), 131.35 (*quat-C*), 133.85 (*quat-C*), 138.15 (*quat-C*), 138.24 (*quat-C*), 141.75 (*quat-C*), 144.77 (*quat-C*), 144.83 (*quat-C*), 152.80 (*quat-C*); HRMS (ESI) Calcd for $C_{30}H_{22}Cl_2S_2$ [M-H]$^+$ 515.0462; found, 515.0469.

Synthesis of (5*S*,10b*S*)-9-chloro-10b-(4-chlorophenyl)-5-(4-methoxyphenyl)-6-phenyl-2,3,5,10b-tetrahydroindeno[1,2-*e*][1,4]dithiepine (3k): White solid; yield: 118 mg (92%); mp 203-205 °C; IR (neat): ν_{max} 2922, 1606, 1505, 1455, 1245, 1174, 1090, 1031, 820, 728 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.78 (ddd, 2H, J_1 = 10.8 Hz, J_2 = 9.6 Hz, J_3 = 1.6 Hz), 3.00-3.10 (m, 2H), 3.81 (s, 3H, CH_3), 5.15 (s, 1H, C*H*), 6.64-6.66 (m, 1H), 6.83-6.88 (m, 3H), 6.95-6.99 (m, 3H), 7.04 (s, 1H), 7.07-7.16 (m, 5H), 7.23-7.25 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.56 (CH_2), 40.34 (CH_2), 55.22 (OCH_3), 58.75 (*C*H), 72.82 (*quat-C*), 113.72 (=*C*H), 120.98 (=*C*H), 123.98 (=*C*H), 126.45 (=*C*H), 126.95 (=*C*H), 127.04 (=*C*H), 127.28 (=*C*H), 127.78 (=*C*H), 130.32 (*quat-C*), 130.54 (=*C*H), 132.10 (*quat-C*), 132.93 (*quat-C*), 133.30 (*quat-C*), 142.36 (*quat-C*), 143.81 (*quat-C*), 146.02 (*quat-C*), 149.59 (*quat-C*), 149.99 (*quat-C*), 158.62 (*quat-C*); HRMS (ESI) Calcd for $C_{31}H_{24}Cl_2OS_2$ [M+H]$^+$ 547.0724; found, 547.0728.



3k

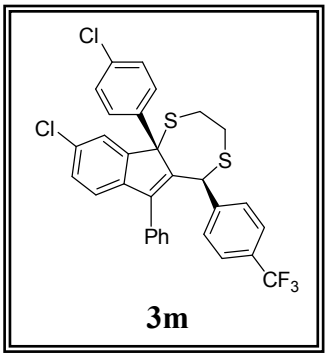
Synthesis of (5*S*,10b*S*)-5-(3,4-dimethoxyphenyl)-9-fluoro-10b-(4-fluorophenyl)-6-phenyl-2,3,5,10b-tetrahydroindeno[1,2-*e*][1,4]dithiepine (3l): White solid; yield: 100 mg (89%); mp 220-222 °C; IR (neat): ν_{max} 3055, 1599, 1498, 1460, 1405, 1283, 1222, 1160, 1091, 1006, 829, 729, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.15-3.30 (m, 3H), 3.52-3.60 (m, 1H), 3.67 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 6.04 (s, 1H, C*H*), 6.32 (s, 1H), 6.39-6.48 (m, 6H), 6.86-7.04 (m, 6H), 7.80 (dd, 2H, J_1 = 8.4 Hz, J_2 = 5.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 34.31 (CH_2), 36.42 (CH_2), 55.23 (*C*H), 56.04 (OCH_3), 56.07 (OCH_3), 65.72 (*quat-C*), 106.93 (=*C*H), 107.15 (=*C*H), 113.50 (d, $J_{C,F}$ = 84 Hz), 114.56 (d, $J_{C,F}$ = 84 Hz), 126.17 (=*C*H), 126.27 (=*C*H), 127.98 (=*C*H), 130.83 (*quat-C*), 130.92 (d, $J_{C,F}$ = 32 Hz), 131.16 (d, $J_{C,F}$ = 32 Hz), 135.35 (*quat-C*), 140.07 (d, $J_{C,F}$ = 16 Hz), 141.91 (d, $J_{C,F}$ = 12 Hz), 142.03 (*quat-C*), 142.29 (*quat-C*), 149.51 (*quat-C*), 150.39 (*quat-C*), 159.88 (d, $J_{C,F}$ =



3l

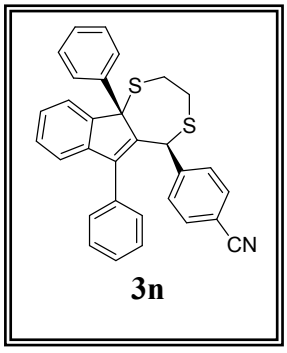
312 Hz), 160.37 (*quat-C*), 162.32 (d, $J_{C,F}$ = 316 Hz); HRMS (ESI) Calcd for $C_{32}H_{26}F_2O_2S_2$ $[M+H]^+$ 545.1421; found, 545.1428.

Synthesis of (5*S*,10b*S*)-9-chloro-10b-(4-chlorophenyl)-6-phenyl-5-(4-(trifluoromethyl)phenyl)-2,3,5,10b-tetrahydroindeno[1,2-*e*][1,4]dithiepine (3m): White solid; yield: 102 mg (87%); mp 187-189 °C; IR (neat): ν_{max} 2911, 1615, 1487, 1408, 1324, 1163, 1122, 1067, 1015, 828, 751 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.80-2.86 (m, 1H), 3.01-3.14 (m, 2H), 3.23-3.28 (m, 1H), 4.79 (s, 1H, C*H*), 6.70-6.80 (m, 4H), 7.10-7.15 (m, 3H), 7.21-7.26 (m, 3H), 7.31-7.38 (m, 3H), 7.51-7.57 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.98 (CH_2), 34.00 (CH_2), 46.31 (*C*H), 70.51 (*quat-C*), 121.06 (=*C*H), 122.62 (*quat-C*), 124.03 (=*C*H), 124.37 (d, $J_{C,F}$ = 16 Hz), 125.32 (*quat-C*), 127.33 (=*C*H), 127.71 (=*C*H), 128.08 (=*C*H), 128.22 (*quat-C*), 128.92 (=*C*H), 129.13 (=*C*H), 129.77 (d, $J_{C,F}$ = 60 Hz), 133.39 (*quat-C*), 137.19 (*quat-C*), 138.98 (*quat-C*), 140.52 (*quat-C*), 142.61 (*quat-C*), 142.98 (*quat-C*), 149.29 (*quat-C*), 150.62 (*quat-C*); HRMS (ESI) Calcd for $C_{31}H_{21}Cl_2F_3S_2$ $[M-H]^+$ 583.0336; found, 583.0346.



3m

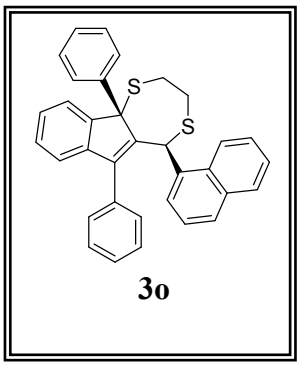
Synthesis of 4-((5*S*,10b*S*)-6,10b-diphenyl-2,3,5,10b-tetrahydroindeno[1,2-*e*][1,4]dithiepin-5-yl)benzonitrile (3n): White solid; yield: 102 mg (89%); mp 171-173 °C; IR (neat): ν_{max} 3055, 1600, 1492, 1448, 1407, 1265, 1176, 1024, 731, 694 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.85-3.02 (m, 3H), 3.16 (ddd, 1H, J_1 = 15.2 Hz, J_2 = 8.8 Hz, J_3 = 2.8 Hz), 5.39 (s, 1H, C*H*), 6.87-6.91 (m, 3H), 6.99-7.01 (m, 2H), 7.15-7.24 (m, 7H), 7.30-7.41 (m, 4H), 7.65-7.67 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 33.08 (CH_2), 34.24 (CH_2), 45.83 (*C*H), 68.26 (*quat-C*), 109.63 (*quat-C*), 118.88 (*quat-C*), 120.47 (=*C*H), 124.03 (=*C*H), 126.95 (=*C*H), 127.03 (=*C*H), 127.55 (=*C*H), 127.73 (=*C*H), 127.89 (=*C*H), 128.15 (=*C*H), 128.84 (=*C*H), 129.01 (=*C*H), 129.09 (=*C*H), 131.19 (=*C*H), 134.05 (*quat-C*), 139.23 (*quat-C*), 142.26 (*quat-C*), 143.45 (*quat-C*), 146.29 (*quat-C*), 149.51 (*quat-C*), 150.26 (*quat-C*); HRMS (ESI) Calcd for $C_{31}H_{23}NS_2$ $[M+Na]^+$ 496.117; found, 496.1165.



3n

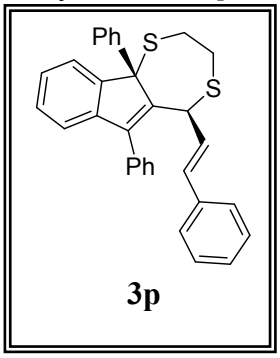
Synthesis of (5*S*,10b*S*)-5-(naphthalen-1-yl)-6,10b-diphenyl-2,3,5,10b-tetrahydroindeno[1,2-*e*][1,4]dithiepine (3o): White solid; yield: 103 mg (96%); mp 214-216 °C; IR (neat): ν_{max} 3406, 3054, 1739, 1598, 1512, 1451, 1310, 1243, 1000, 746, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.84-2.90 (m, 1H), 3.01-3.08 (m, 2H), 3.14-3.20 (m, 1H), 5.49 (s, 1H, C*H*), 6.67 (dd, 1H, J_1 = 8.4 Hz, J_2 = 1.6 Hz), 6.86 (d, 1H, J = 7.2 Hz), 6.96-6.97

(m, 2H), 7.03-7.11 (m, 3H), 7.14-7.22 (m, 2H), 7.28 (s, 1H), 7.33-7.42 (m, 7H), 7.45-7.48 (m, 1H), 7.63-7.65 (m, 1H), 7.68 (d, 2H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.96 (CH_2), 34.51 (CH_2), 45.98 (*C*H), 68.41 (*quat-C*), 120.39 (=*C*H), 124.01 (=*C*H), 125.42 (=*C*H), 125.54 (=*C*H), 126.66 (=*C*H), 126.75 (=*C*H), 127.01 (=*C*H), 127.20 (=*C*H), 127.22 (=*C*H), 127.26 (=*C*H), 127.58 (=*C*H), 127.64 (=*C*H), 127.70 (=*C*H), 127.82 (=*C*H), 127.98 (=*C*H), 128.09 (=*C*H), 128.92 (=*C*H), 129.08 (=*C*H), 131.92 (*quat-C*), 132.68 (*quat-C*), 134.43 (*quat-C*), 137.95 (*quat-C*), 139.63 (*quat-C*), 142.03 (*quat-C*), 144.28 (*quat-C*), 150.08 (*quat-C*), 151.20 (*quat-C*); HRMS (ESI) Calcd for $C_{34}H_{26}S_2$ $[M+H]^+$ 499.1549; found, 499.1550.



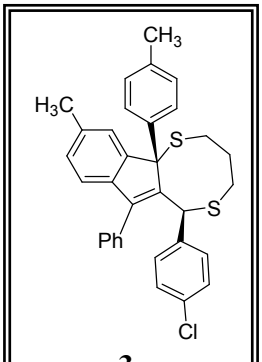
3o

Synthesis of (5*S*,10b*S*,*E*)-6,10b-diphenyl-5-styryl-2,3,5,10b-tetrahydroindeno[1,2-*e*][1,4]dithiepine (3p): White solid; yield: 78 mg (68%); mp 114-116 °C; IR (neat): ν_{max} 3048, 2950, 1649, 1602, 1504, 1460, 1301, 1241, 1168, 1039, 770, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.00-3.14 (m, 2H), 3.21-3.32 (m, 2H), 4.86 (d, 1H, J = 9.6 Hz), 6.05 (dd, 1H, J_1 = 15.6 Hz, J_2 = 9.2 Hz), 6.73 (d, 1H, J = 15.6 Hz), 6.80-6.82 (m, 1H), 6.98-7.03 (m, 4H), 7.17-7.24 (m, 6H), 7.29-7.42 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.12 (CH_2), 40.54 (CH_2), 57.85 (*C*H), 73.37 (*quat-C*), 120.52 (=*C*H), 123.83 (=*C*H), 125.91 (=*C*H), 126.23 (=*C*H), 126.37 (=*C*H), 126.85 (=*C*H), 127.13 (=*C*H), 127.34 (=*C*H), 127.51 (=*C*H), 128.54 (=*C*H), 129.39 (=*C*H), 133.21 (=*C*H), 135.32 (*quat-C*), 137.83 (*quat-C*), 142.98 (*quat-C*), 144.56 (*quat-C*), 146.13 (*quat-C*), 146.34 (*quat-C*), 147.56 (*quat-C*); HRMS (ESI) Calcd for $C_{32}H_{26}S_2$ $[M+H]^+$ 475.1554; found, 475.1541.



3p

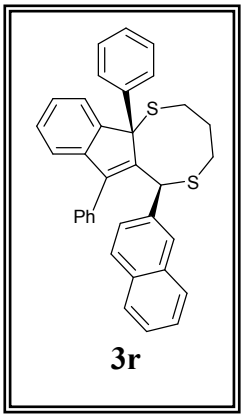
Synthesis of (6*S*,11b*S*)-6-(4-chlorophenyl)-10-methyl-7-phenyl-11b-*p*-tolyl-3,4,6,11b-tetrahydro-2*H*-indeno[1,2-*b*][1,5]dithiocine (3q): White solid; yield: 83 mg (77%); mp 189-191 °C; IR (neat): ν_{max} 2917, 1602, 1488, 1263, 1092, 1015, 888, 810, 733, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.87-1.94 (m, 2H), 2.27 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.48 (ddd, 1H, J_1 = 14.4 Hz, J_2 = 12.0 Hz, J_3 = 5.2 Hz), 2.78 (dt, 1H, J_1 = 14.4 Hz, J_2 = 3.6 Hz), 3.12 (dt, 1H, J_1 = 15.2Hz, J_2 = 3.6 Hz), 3.64 (ddd, 1H, J_1 = 15.2 Hz, J_2 = 11.2 Hz, J_3 = 3.6 Hz), 4.73 (s, 1H, C*H*), 6.00 (d, 2H, J = 8.8 Hz), 6.61 (s, 1H), 6.67-6.69 (m, 2H), 7.02-7.11 (m, 5H), 7.23-7.30 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.03(CH_3), 21.42 (CH_3), 26.72 (CH_2), 29.88 (CH_2), 33.33 (CH_2), 48.17 (*C*H), 68.43 (*quat-C*), 120.86 (=*C*H), 123.94 (=*C*H), 126.89



3q

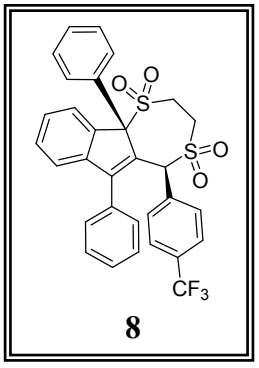
(=*C*H), 127.28 (=*C*H), 127.46 (=*C*H), 127.75 (=*C*H), 127.83 (=*C*H), 128.65 (=*C*H), 129.32 (=*C*H), 129.62 (=*C*H), 131.46 (*quat-C*), 134.54 (*quat-C*), 136.01 (*quat-C*), 137.43 (*quat-C*), 137.68 (*quat-C*), 139.53 (*quat-C*), 142.17 (*quat-C*), 145.52 (*quat-C*), 147.82 (*quat-C*), 151.92 (*quat-C*); HRMS (ESI) Calcd for $C_{33}H_{29}ClS_2$ $[M+H]^+$ 525.1477; found, 525.1476.

Synthesis of (6*S*,11b*S*)-6-(naphthalen-2-yl)-7,11b-diphenyl-3,4,6,11b-tetrahydro-2*H*-indeno[1,2-*b*][1,5]dithiocine (3r): White solid; yield: 106 mg (93%); mp 213-215 °C; IR (neat): ν_{max} 3052, 1599, 1492, 1438, 1415, 1023, 748, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.91-2.03 (m, 2H), 2.53-2.61 (m, 1H), 2.82 (dt, 1H, J_1 = 18.4 Hz, J_2 = 4.0 Hz), 3.15 (dt, 1H, J_1 = 19.2 Hz, J_2 = 4.0 Hz), 3.65-3.73 (m, 1H), 4.93 (s, 1H, C*H*), 6.04 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.0 Hz), 6.59 (s, 1H), 6.80-6.82 (m, 1H), 7.02-7.04 (m, 2H), 7.10-7.17 (m, 3H), 7.18-7.25 (m, 4H), 7.26-7.29 (m, 2H), 7.30-7.39 (m, 4H), 7.44-7.46 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.83 (*C*H_2), 30.03 (*C*H_2), 33.55 (*C*H_2), 49.11 (*C*H), 69.15 (*quat-C*), 120.30 (=*C*H), 124.28 (=*C*H), 125.30 (=*C*H), 125.33 (=*C*H), 125.81 (=*C*H), 126.34 (=*C*H), 126.53 (=*C*H), 126.94 (=*C*H), 127.04 (=*C*H), 127.40 (=*C*H), 127.62 (=*C*H), 127.80 (=*C*H), 127.83 (=*C*H), 128.00 (=*C*H), 128.02 (=*C*H), 128.78 (=*C*H), 129.73 (=*C*H), 131.77 (*quat-C*), 132.57 (*quat-C*), 134.47 (*quat-C*), 138.30 (*quat-C*), 139.07 (*quat-C*), 142.52 (*quat-C*), 145.62 (*quat-C*), 150.79 (*quat-C*), 151.70 (*quat-C*); HRMS (ESI) Calcd for $C_{35}H_{28}S_2$ $[M+H]^+$ 513.1691; found, 513.1705.



3r

Synthesis of sulfone 8: In a 50-mL, round-bottomed flask fitted with a magnetic stirrer, condenser is placed 50 mg(0.14 mol) of **3i** and peroxide (0.6 mol) dissolved in 5 mL of dry DCM stirred at 0°C for 1 h. One hour later, saturated $NaHCO_3$ was added, and the mixture was extracted with DCM. The combined organic layers were dried over Na_2SO_4 and evaporated to afford 39 mg (70%) of sulfone **8** as a white solid. Although this material is sufficiently pure for most purposes, recrystallization from DCM affords colourless crystal. White solid; yield: 88 mg (85%); mp 231-233 °C; IR (neat): ν_{max} 3063, 1616, 1492, 1448, 1418, 1315, 1117, 1068, 837, 726 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.73-3.94 (m, 4H), 5.61 (s, 1H, C*H*), 6.84-6.88 (m, 3H), 7.22-7.24 (m, 2H), 7.28-7.36 (m, 4H), 7.41-7.47 (m, 5H), 7.66-7.64 (m, 2H), 7.73-7.75 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 48.43 (*C*H_2), 50.93 (*C*H_2), 67.68 (*C*H), 86.47 (*quat-C*), 122.57 (=*C*H), 124.73 (d, $J_{C,F}$ = 16 Hz), 126.37 (=*C*H), 127.43 (=*C*H), 128.12 (*quat-C*), 128.77 (=*C*H), 128.93 (=*C*H), 129.51 (=*C*H), 129.76 (*quat-C*), 129.86 (=*C*H), 130.79 (*quat-C*), 131.12 (=*C*H), 132.45 (*quat-C*), 133.37 (*quat-C*), 134.17 (*quat-C*),

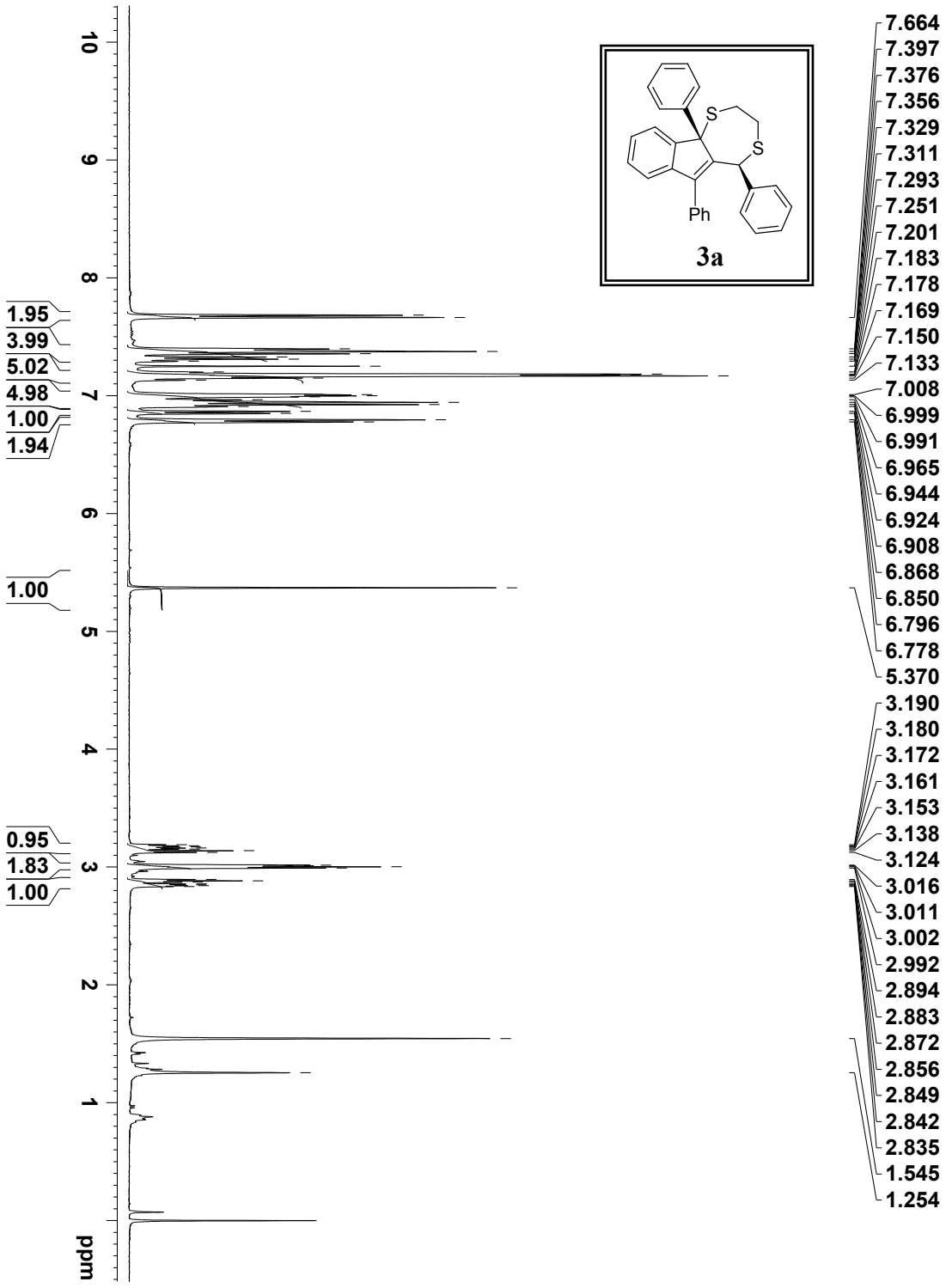


8

140.83 (*quat-C*), 144.98 (*quat-C*), 155.55 (*quat-C*); HRMS (ESI) Calcd for $C_{31}H_{23}F_3O_4S_2$ $[M+Na]^+$ 603.0888; found, 603.0890.

References

1. (*a*) D. A. Engel and G. B. Dudley, *Org. Lett*., 2006, **8**, 4027; (*b*) Y. Zhu, G. Yin, D. Hong, P. Lu, and Y. Wang, *Org. Lett*., 2011, **13**, 1024.
2. S. Muthusamy, S. A. Babu and C. Gunanathan, *Tetrahedron*, 2002, **58**, 7897.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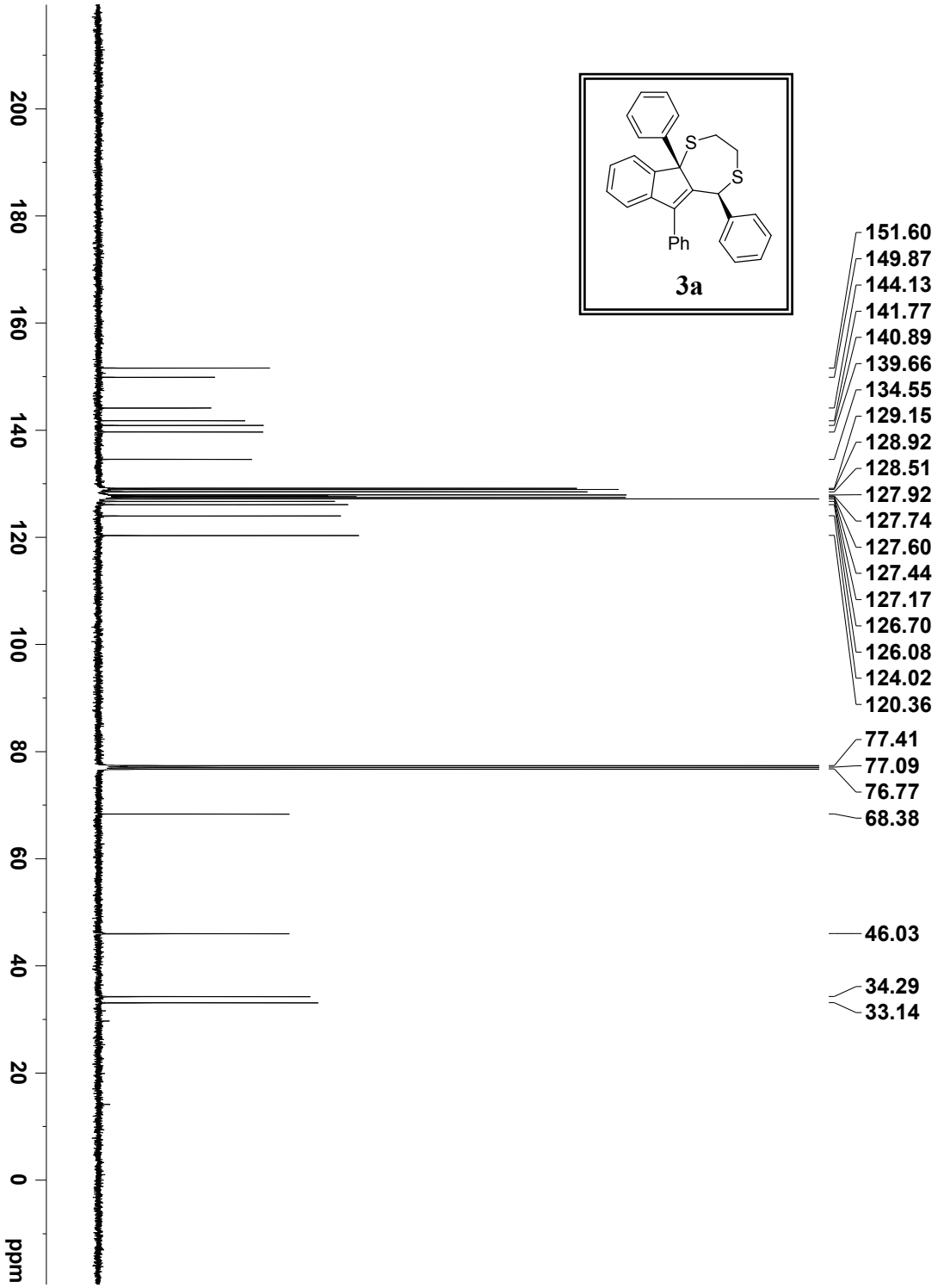
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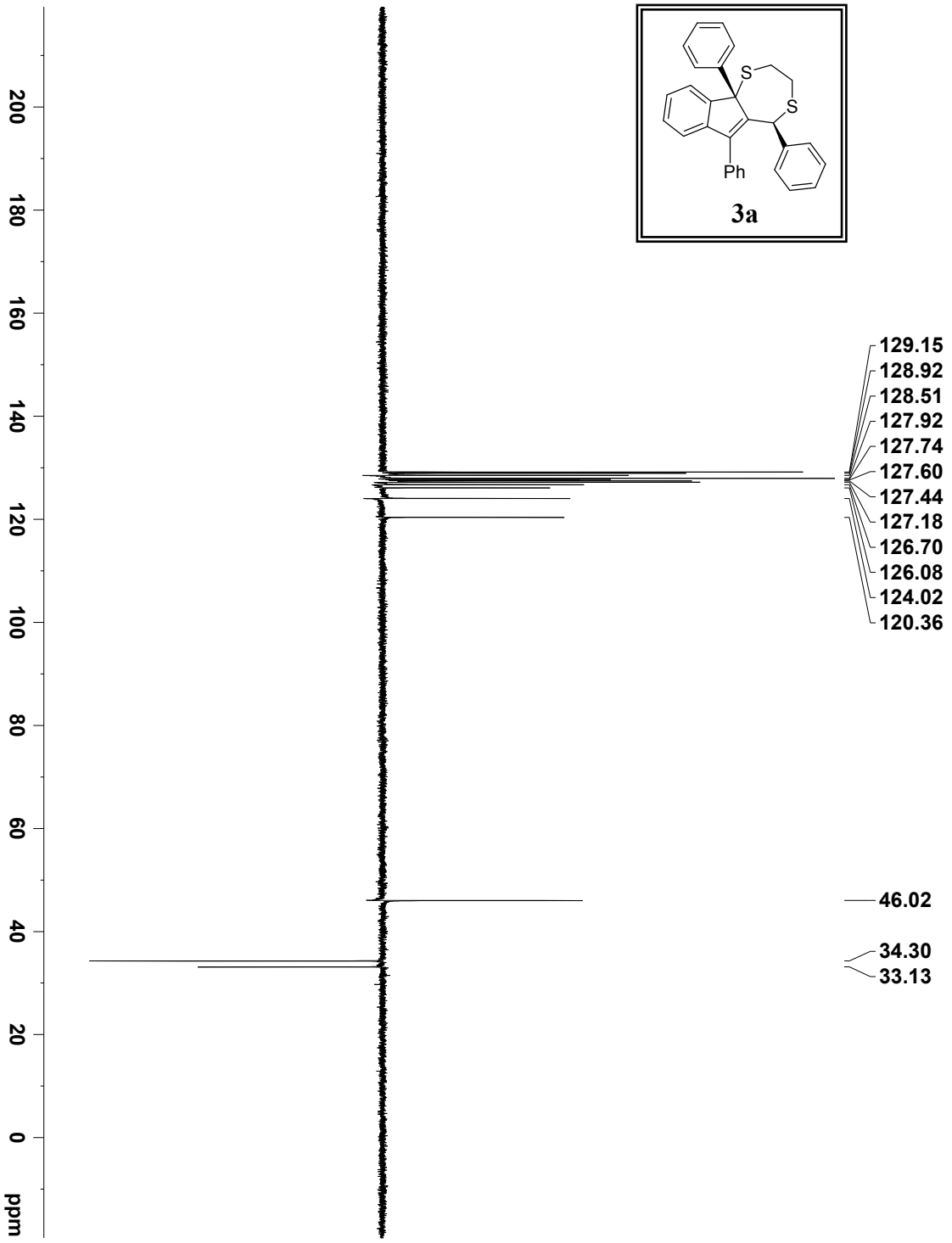
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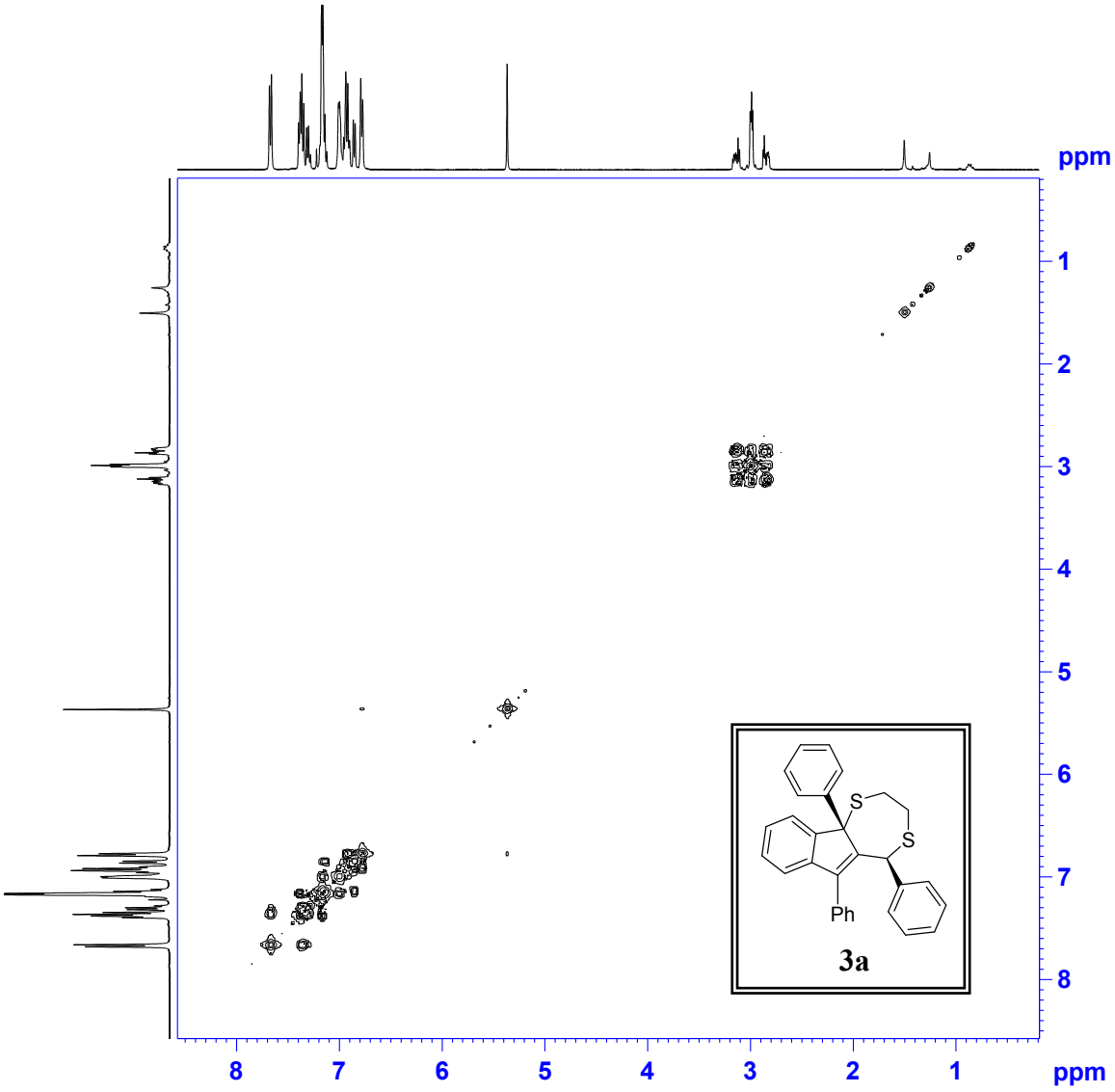
ppm
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2
3
4
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8
S
S
Ph
3a
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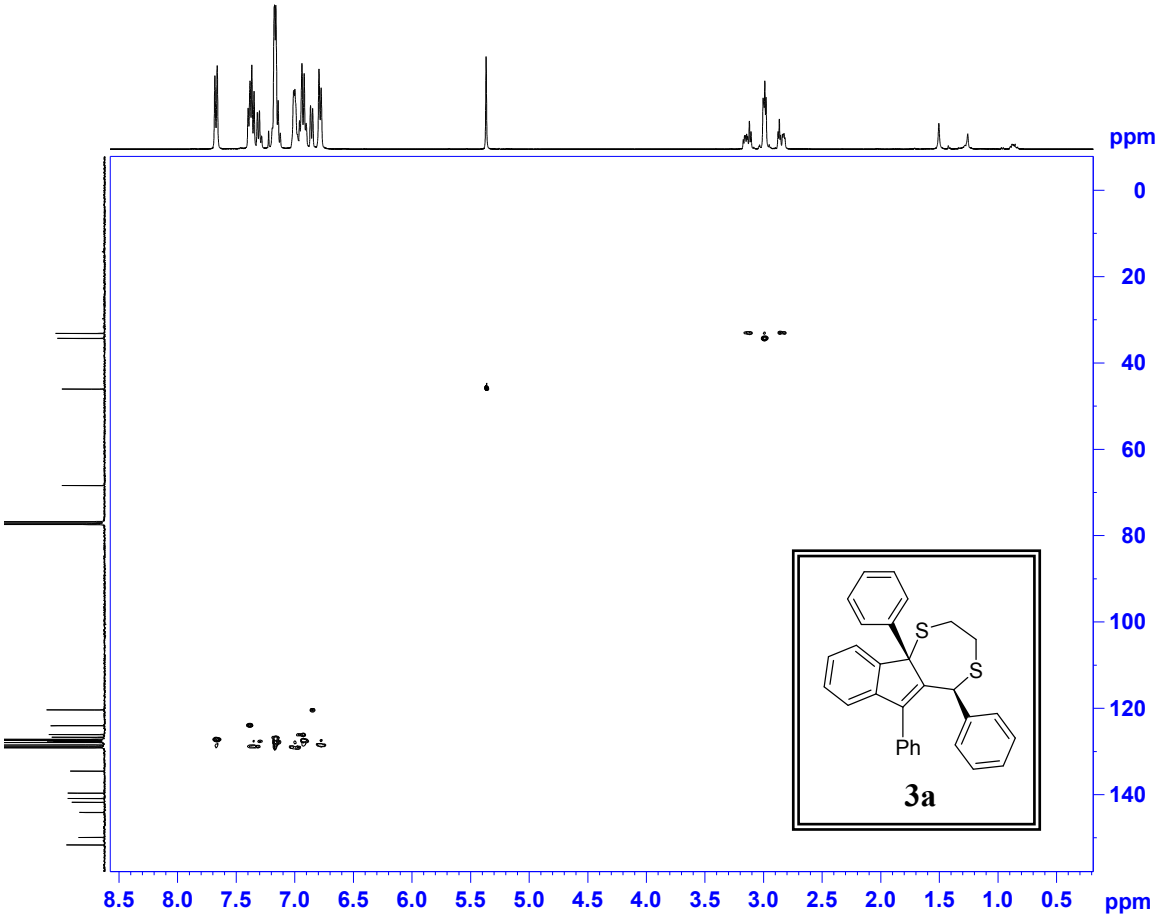
7
6
5
4
3
2
1
ppm


ppm
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60
80
100
120
140
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7.5
7.0
6.5
6.0
5.5
5.0
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2.5
2.0
1.5
1.0
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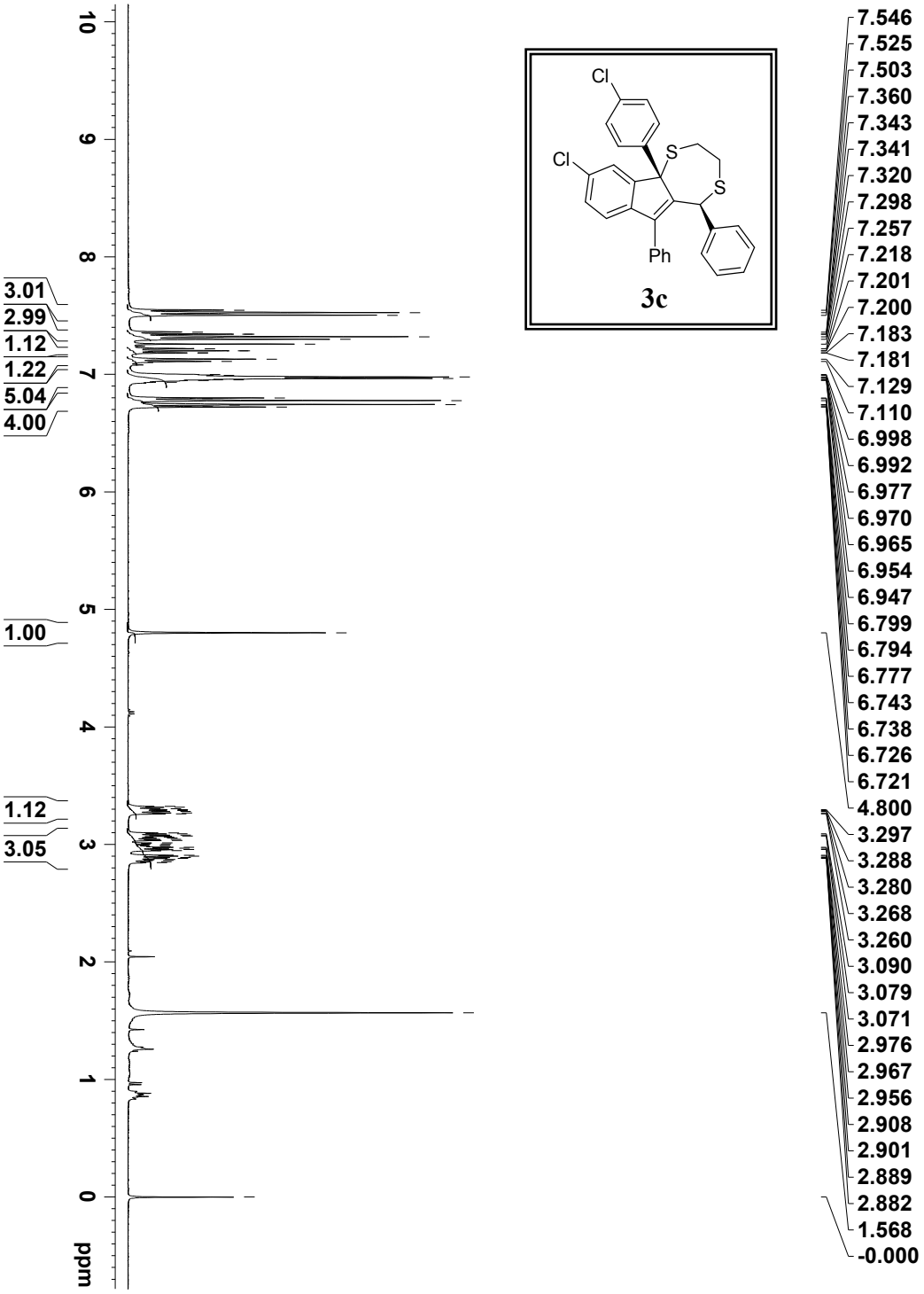
ppm
S
S
Ph
3a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2.99
1.12
1.22
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4.00
1.00
1.12
3.05
10
9
8
7
6
5
4
3
2
1
0
ppm
Cl
Cl
S
S
Ph
3c
7.546
7.525
7.503
7.360
7.343
7.341
7.320
7.298
7.257
7.218
7.201
7.200
7.183
7.181
7.129
7.110
6.998
6.992
6.977
6.970
6.965
6.954
6.947
6.799
6.794
6.777
6.743
6.738
6.726
6.721
4.800
3.297
3.288
3.280
3.268
3.260
3.090
3.079
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2.901
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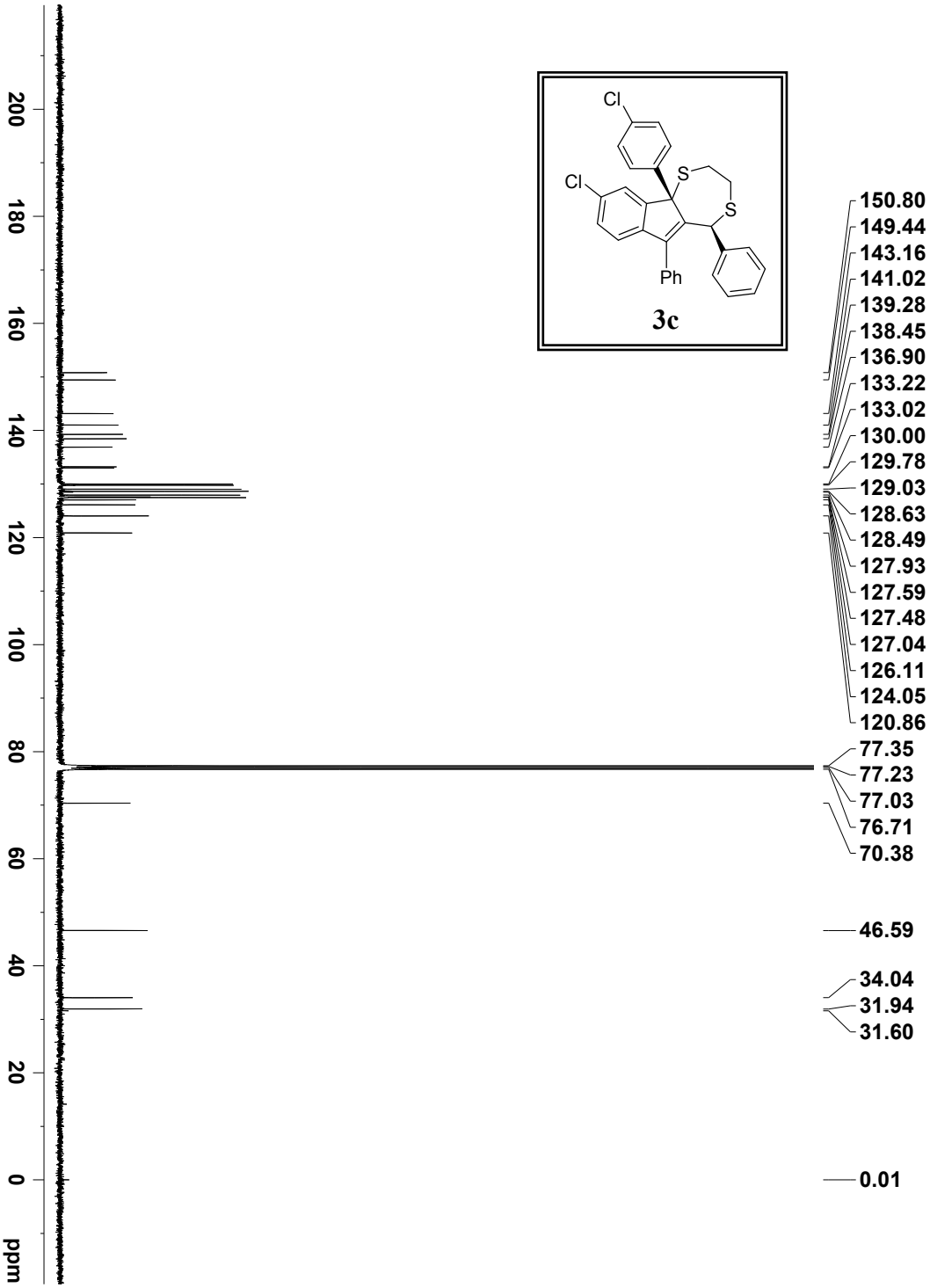
Cl
Cl
S
S
Ph
3c
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149.44
143.16
141.02
139.28
138.45
136.90
133.22
133.02
130.00
129.78
129.03
128.63
128.49
127.93
127.59
127.48
127.04
126.11
124.05
120.86
77.35
77.23
77.03
76.71
70.38
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120
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40
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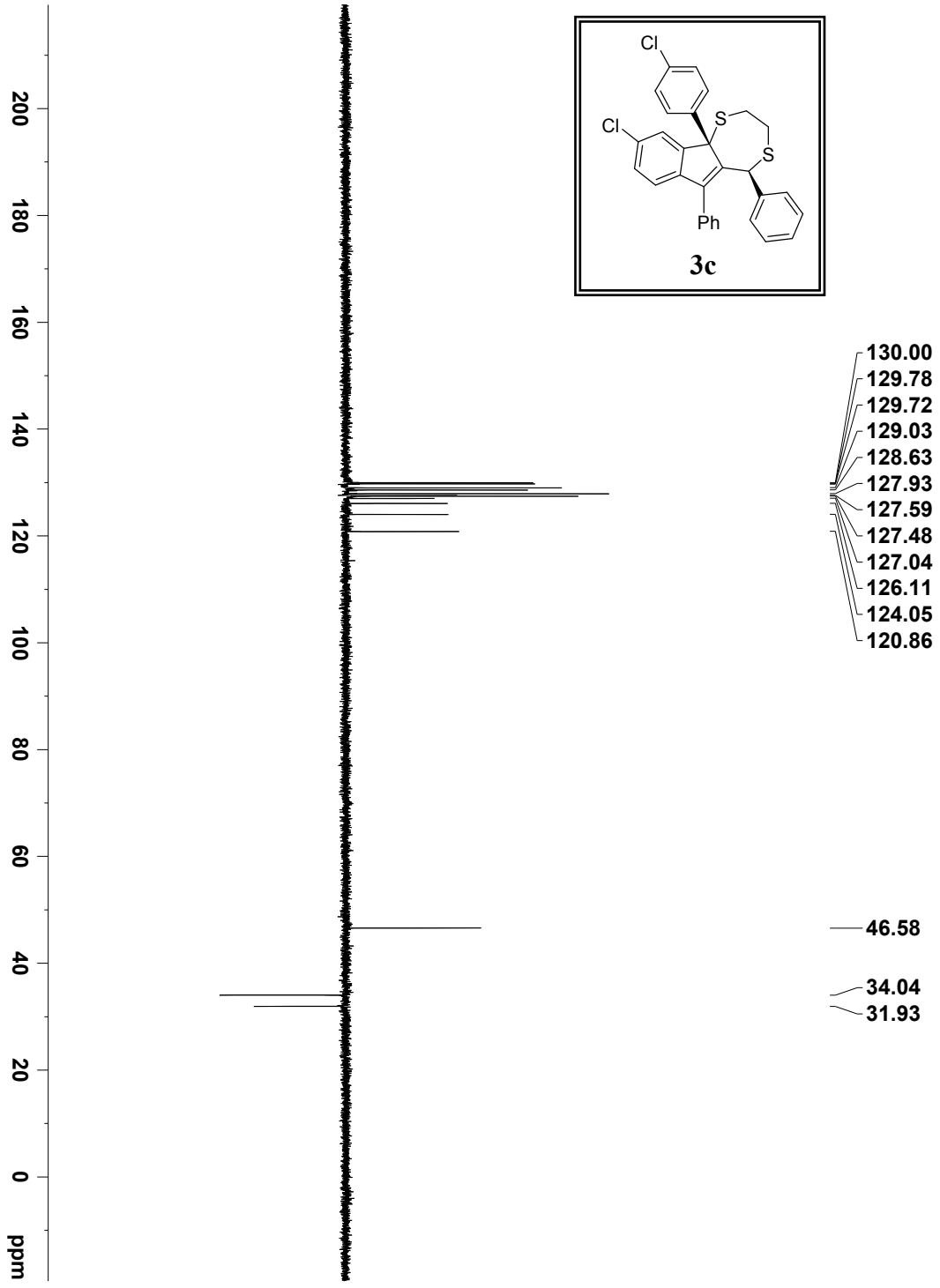
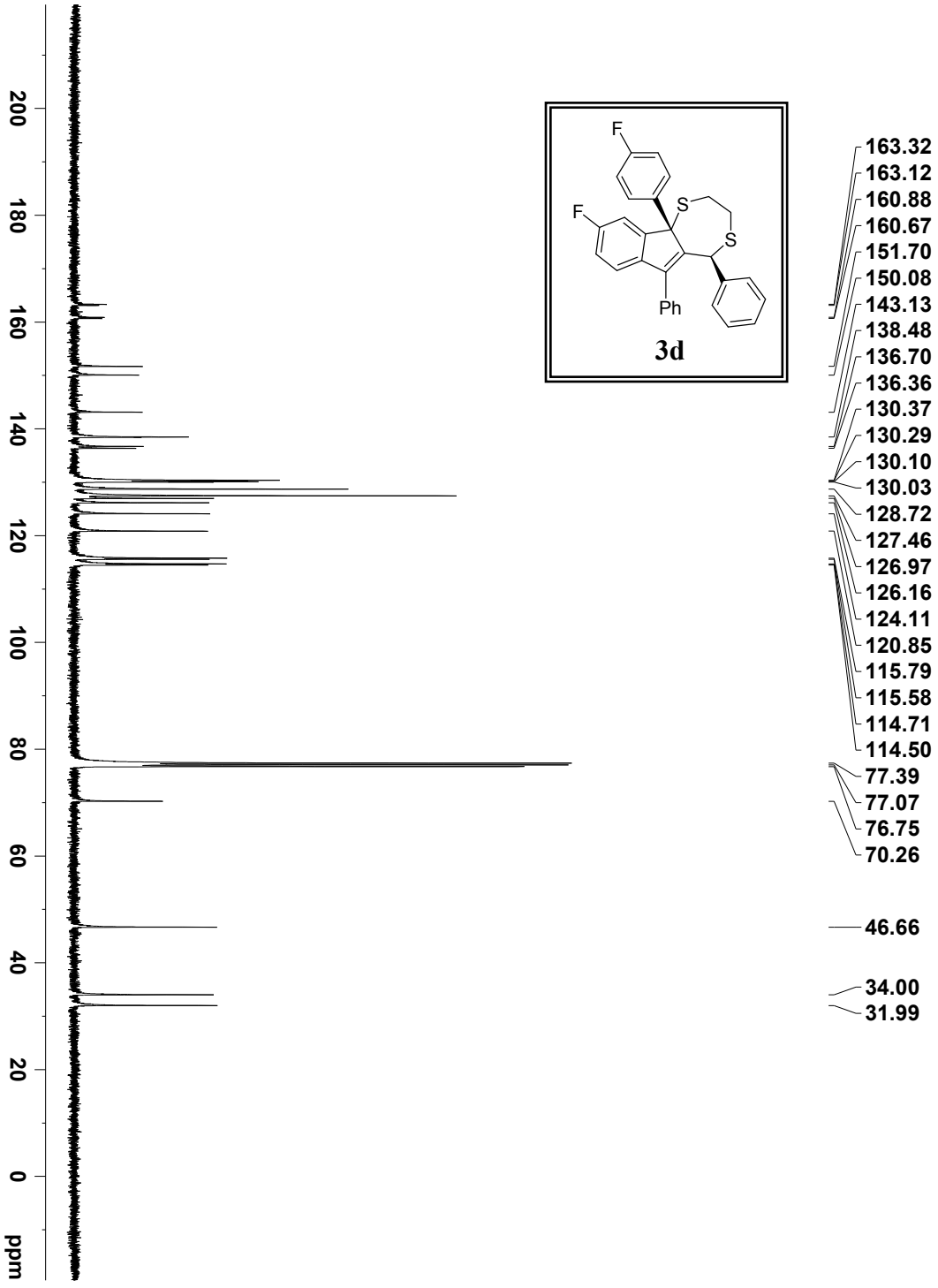
0
ppm


Cl
Cl
S
S
Ph
3c
130.00
129.78
129.72
129.03
128.63
127.93
127.59
127.48
127.04
126.11
124.05
120.86
46.58
34.04
31.93
200
180
160
140
120
100
80
60
40
20
0
ppm


F
F
S
S
Ph
3d
163.32
163.12
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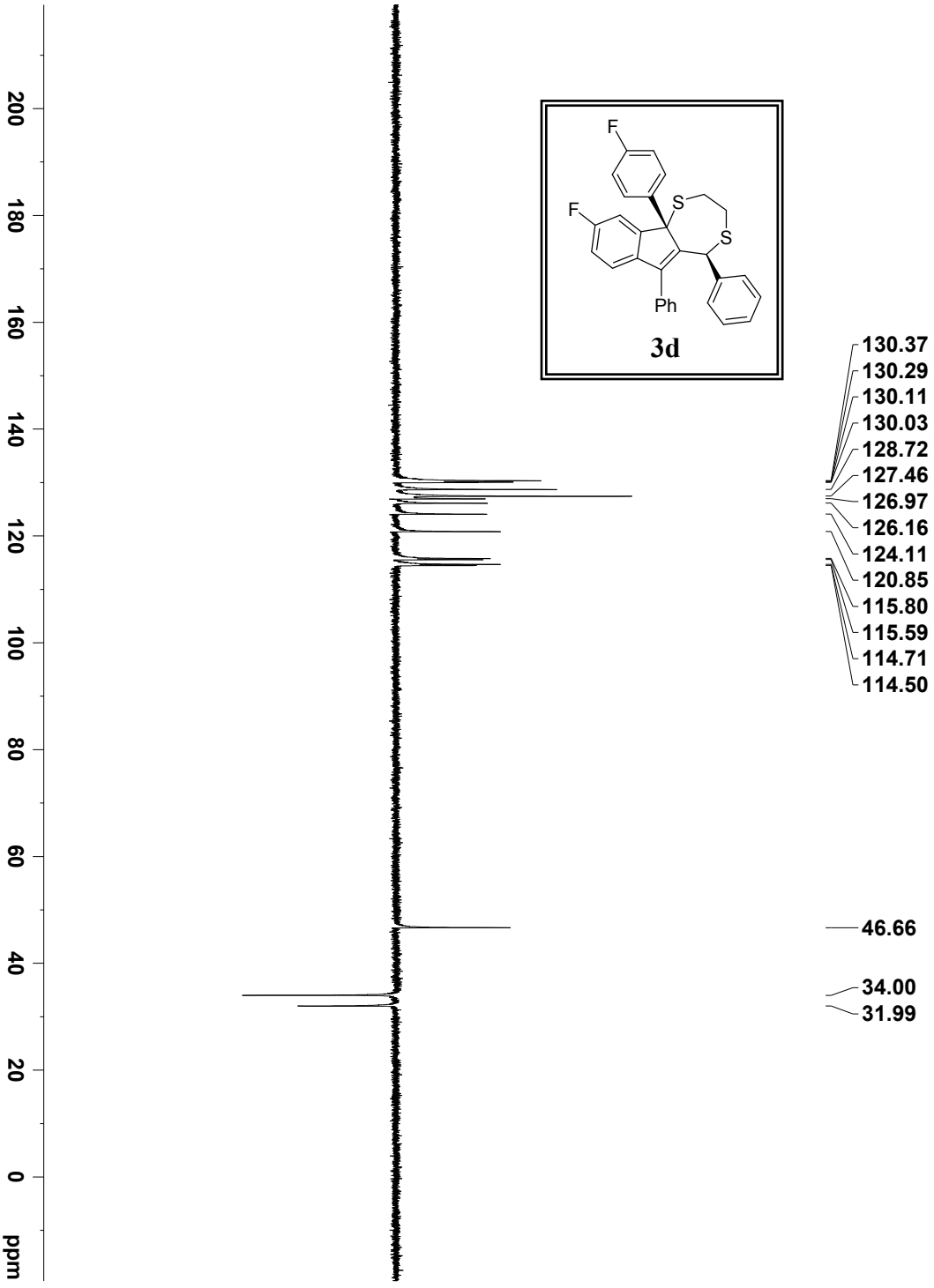
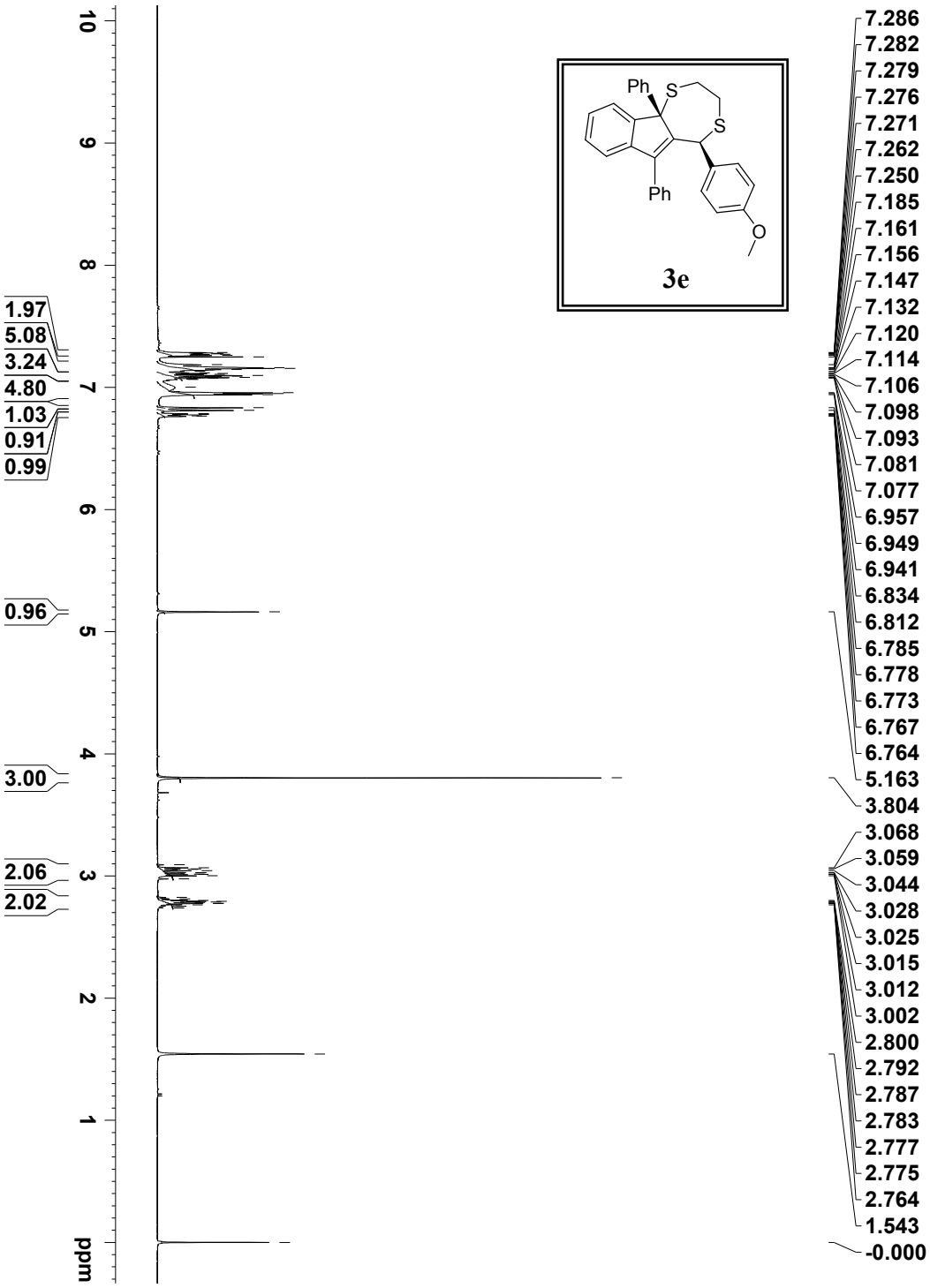
160.67
151.70
150.08
143.13
138.48
136.70
136.36
130.37
130.29
130.10
130.03
128.72
127.46
126.97
126.16
124.11
120.85
115.79
115.58
114.71
114.50
77.39
77.07
76.75
70.26
46.66
34.00
31.99
200
180
160
140
120
100
80
60
40
20
0
ppm


F
F
S
S
Ph
3d
130.37
130.29
130.11
130.03
128.72
127.46
126.97
126.16
124.11
120.85
115.80
115.59
114.71
114.50
46.66
34.00
31.99
200
180
160
140
120
100
80
60
40
20
0
ppm


Ph
S
S
Ph
O
3e
10
9
8
7
6
5
4
3
2
1
ppm
1.97
5.08
3.24
4.80
1.03
0.91
0.99
0.96
3.00
2.06
2.02
7.286
7.282
7.279
7.276
7.271
7.262
7.250
7.185
7.161
7.156
7.147
7.132
7.120
7.114
7.106
7.098
7.093
7.081
7.077
6.957
6.949
6.941
6.834
6.812
6.785
6.778
6.773
6.767
6.764
5.163
3.804
3.068
3.059
3.044
3.028
3.025
3.015
3.012
3.002
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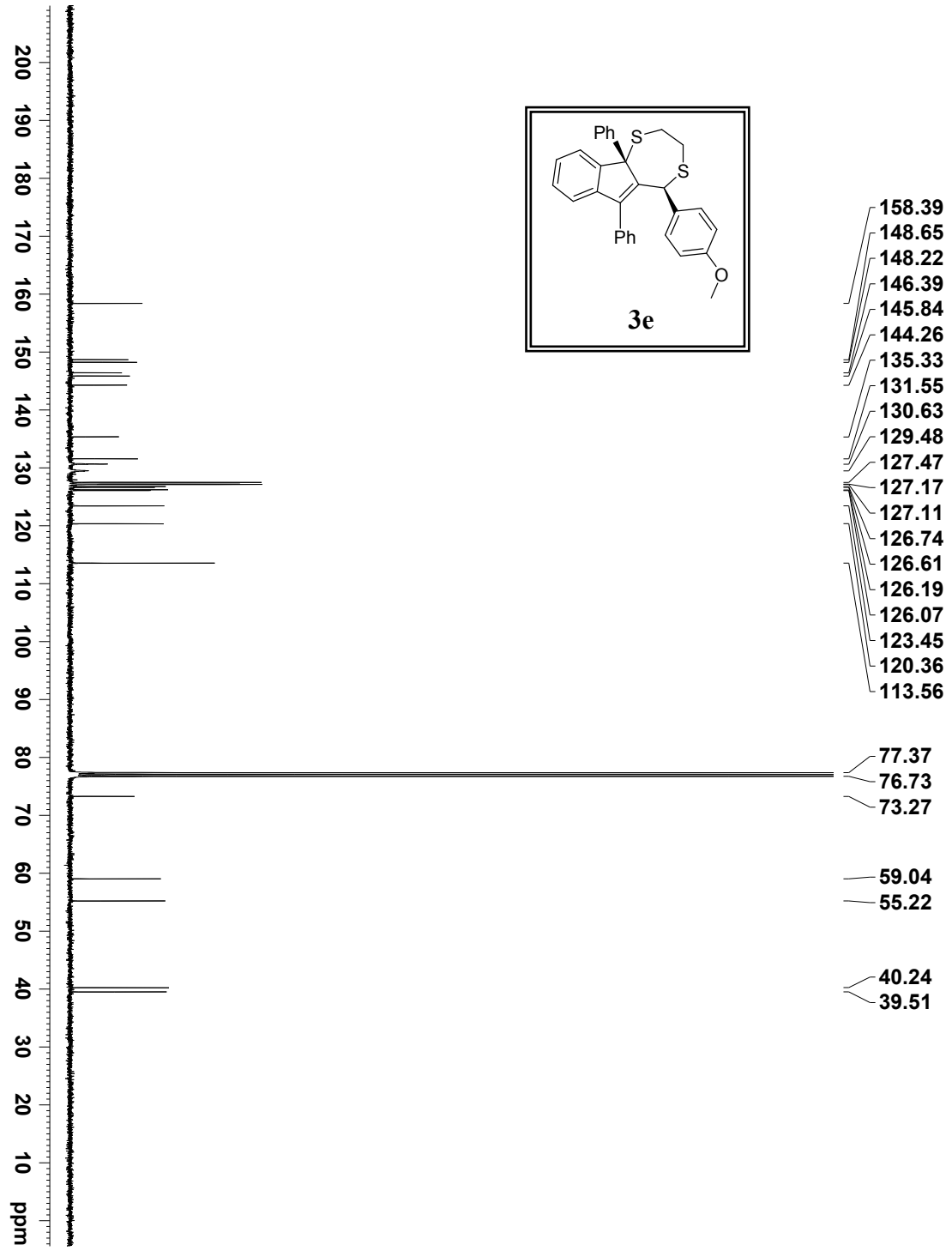
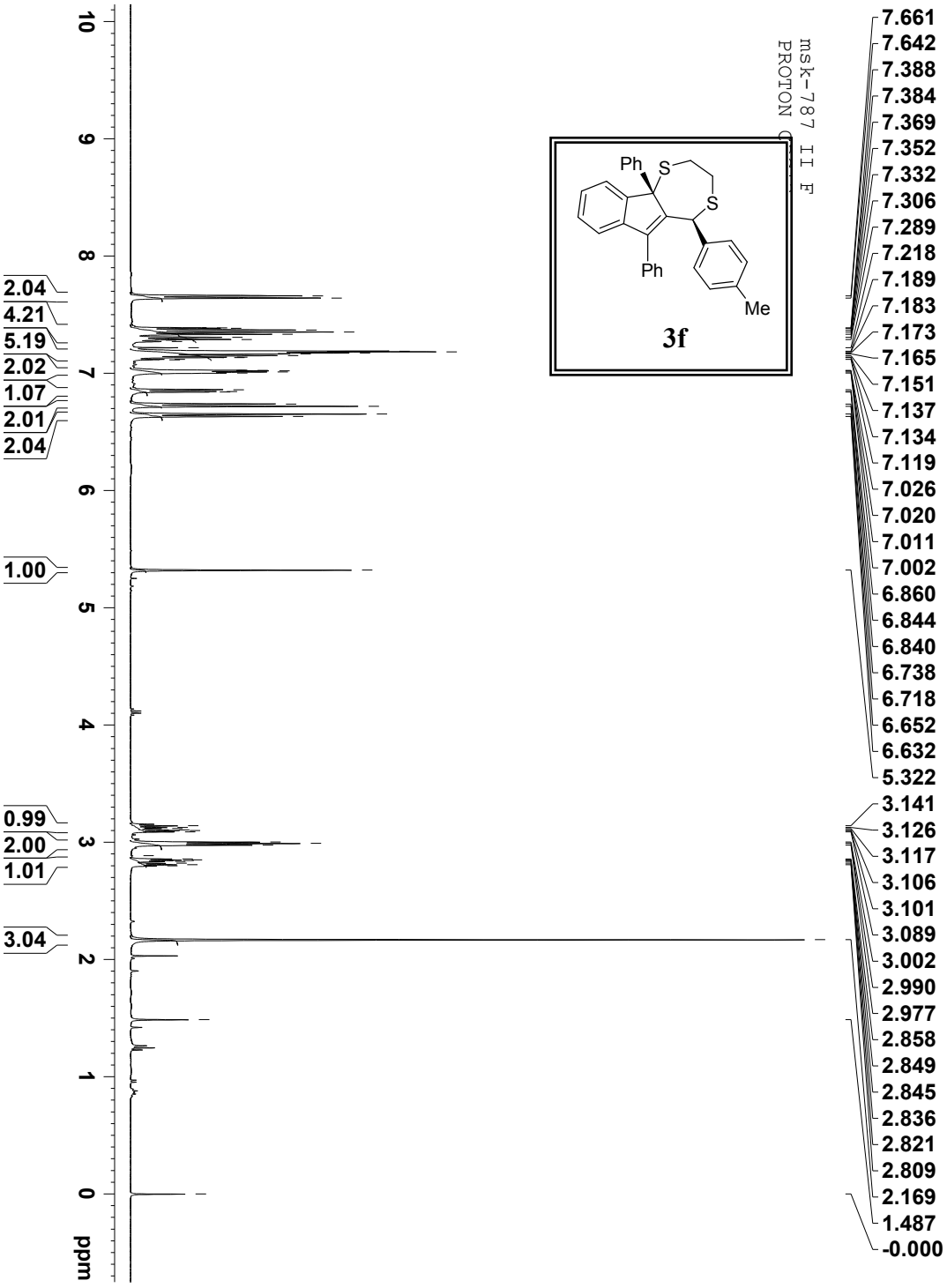
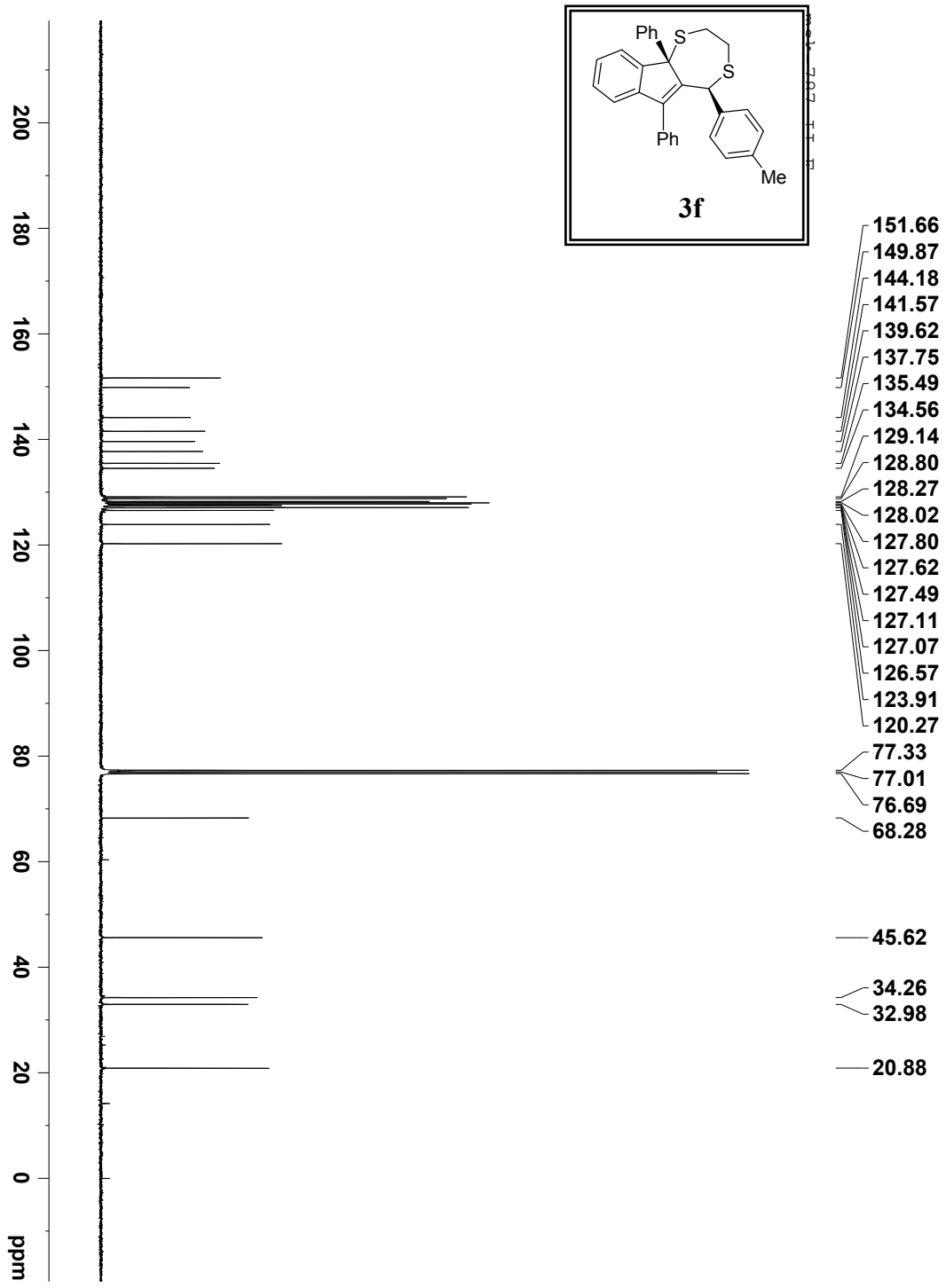
2.792
2.787
2.783
2.777
2.775
2.764
1.543
-0.000


Ph
S
S
Ph
O
3e
158.39
148.65
148.22
146.39
145.84
144.26
135.33
131.55
130.63
129.48
127.47
127.17
127.11
126.74
126.61
126.19
126.07
123.45
120.36
113.56
77.37
76.73
73.27
59.04
55.22
40.24
39.51
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


msk-787 II F
PROTON
Ph
S
S
Ph
Me
3f
7.661
7.642
7.388
7.384
7.369
7.352
7.332
7.306
7.289
7.218
7.189
7.183
7.173
7.165
7.151
7.137
7.134
7.119
7.026
7.020
7.011
7.002
6.860
6.844
6.840
6.738
6.718
6.652
6.632
5.322
3.141
3.126
3.117
3.106
3.101
3.089
3.002
2.990
2.977
2.858
2.849
2.845
2.836
2.821
2.809
2.169
1.487
-0.000
2.04
4.21
5.19
2.02
1.07
2.01
2.04
1.00
0.99
2.00
1.01
3.04
10
9
8
7
6
5
4
3
2
1
0
ppm


Ph
S
S
Ph
Me
3f
151.66
149.87
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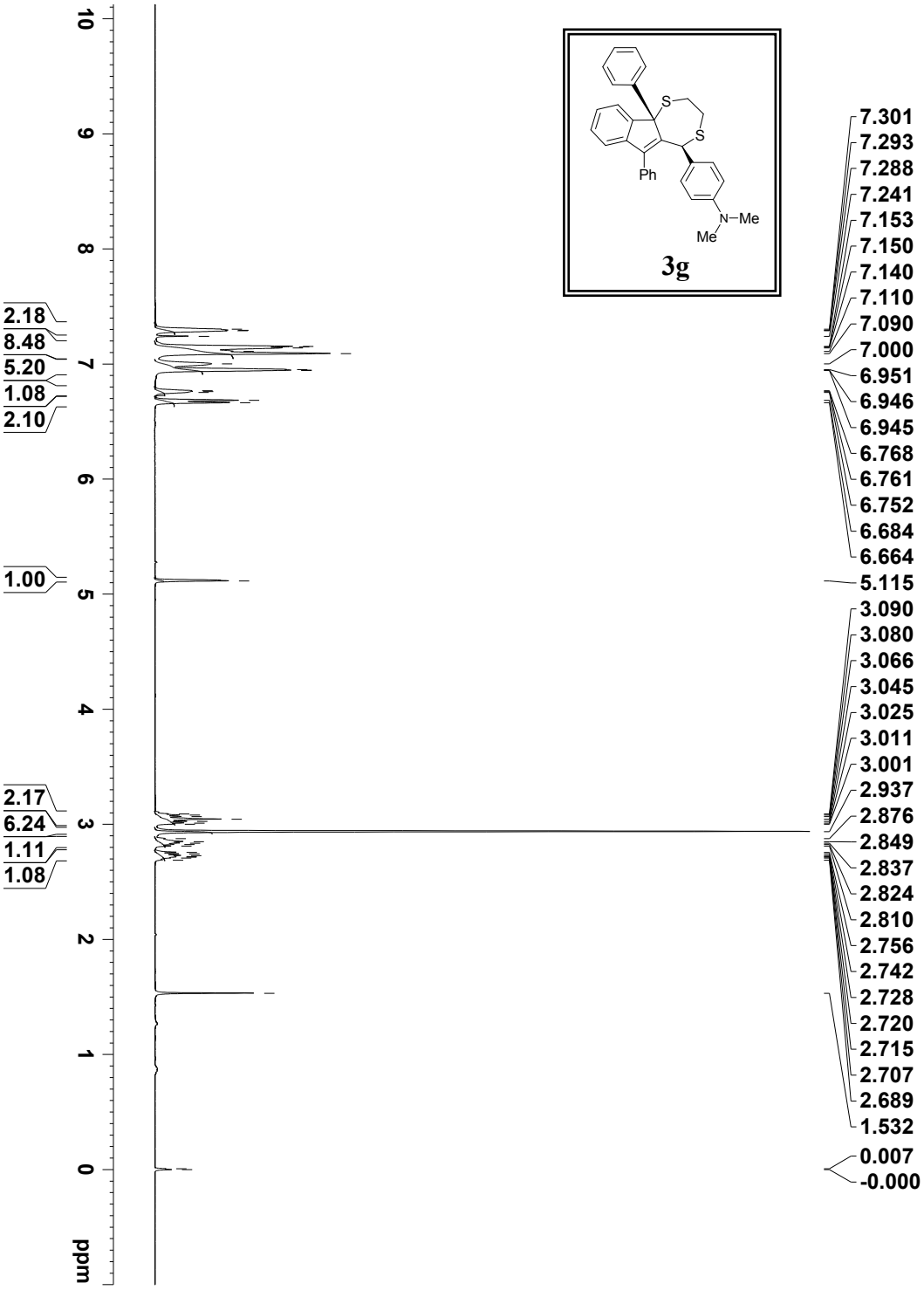
141.57
139.62
137.75
135.49
134.56
129.14
128.80
128.27
128.02
127.80
127.62
127.49
127.11
127.07
126.57
123.91
120.27
77.33
77.01
76.69
68.28
45.62
34.26
32.98
20.88
200
180
160
140
120
100
80
60
40
20
0
ppm


S
S
Ph
N–Me
Me
3g
7.301
7.293
7.288
7.241
7.153
7.150
7.140
7.110
7.090
7.000
6.951
6.946
6.945
6.768
6.761
6.752
6.684
6.664
5.115
3.090
3.080
3.066
3.045
3.025
3.011
3.001
2.937
2.876
2.849
2.837
2.824
2.810
2.756
2.742
2.728
2.720
2.715
2.707
2.689
1.532
0.007
-0.000
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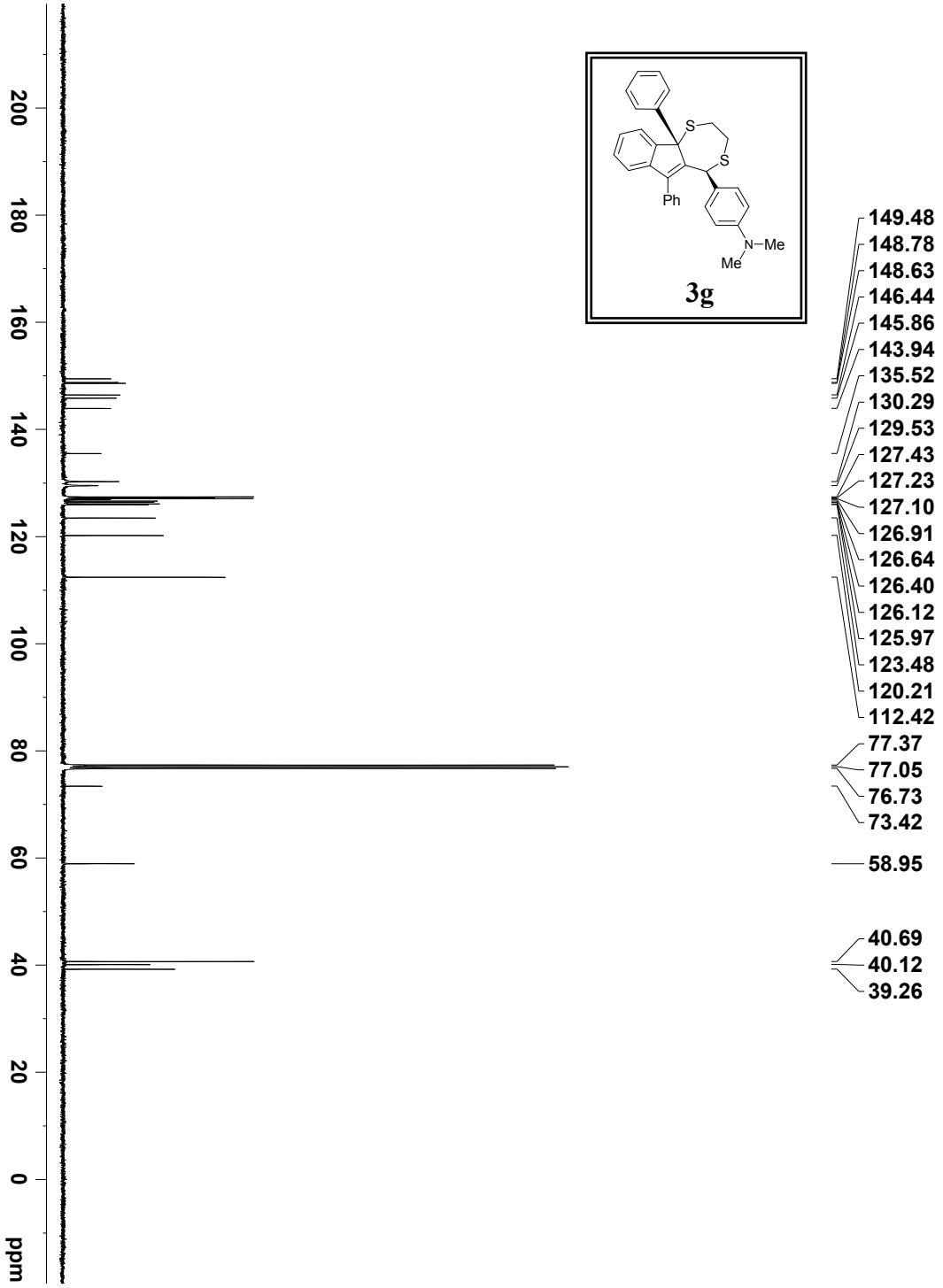
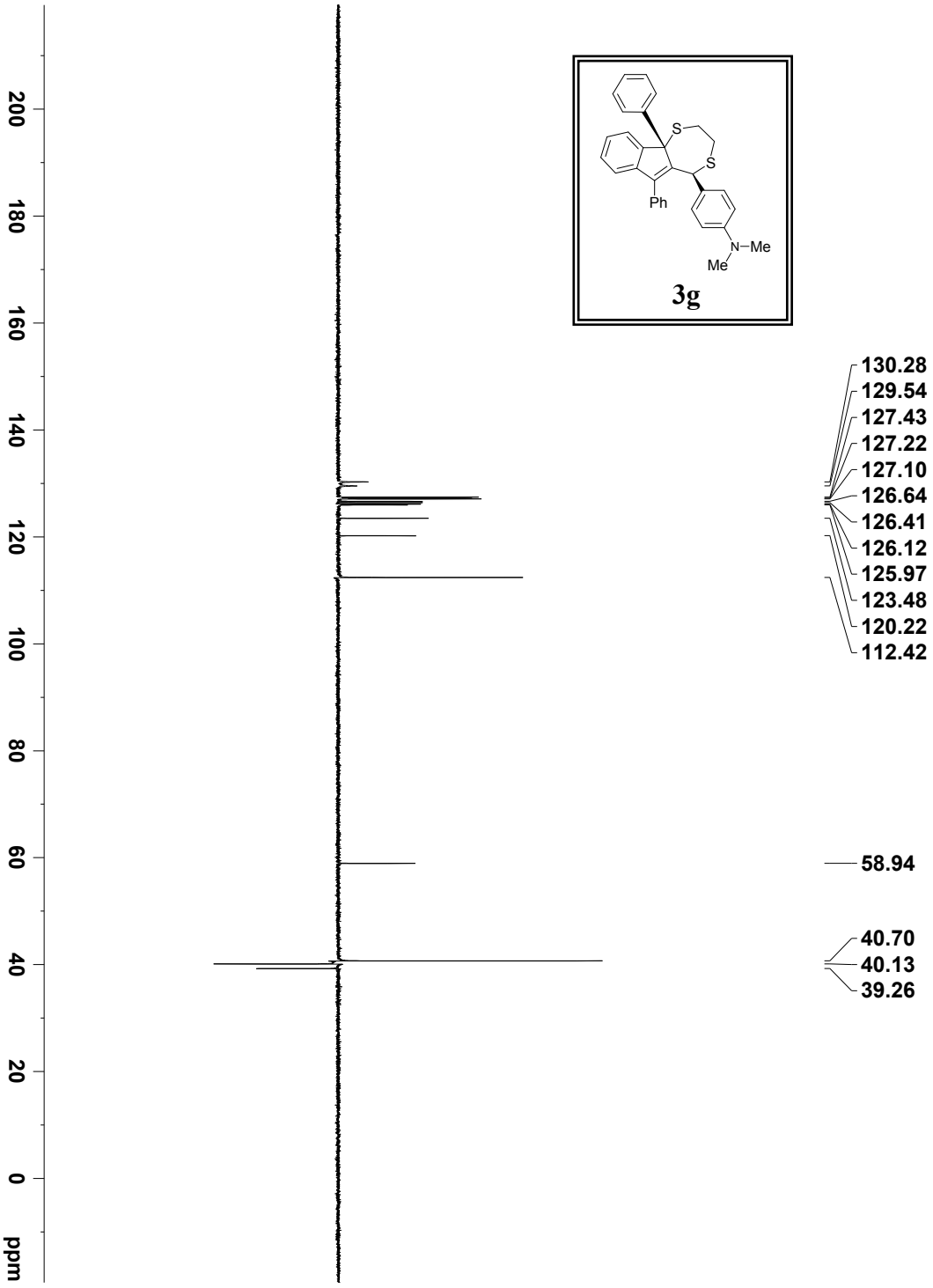
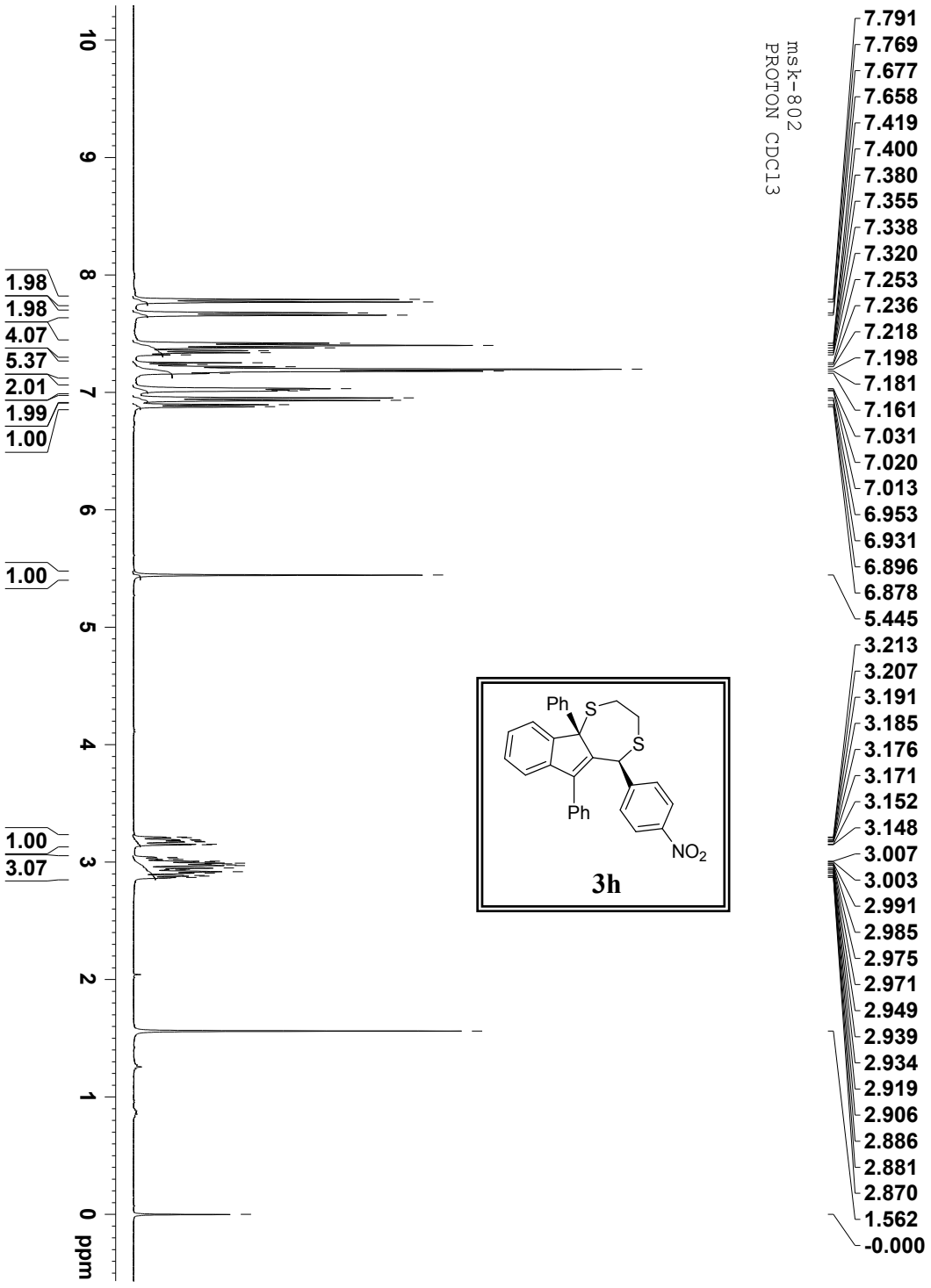
8.48
5.20
1.08
2.10
1.00
2.17
6.24
1.11
1.08
ppm


200
180
160
140
120
100
80
60
40
20
0
ppm
S
S
Ph
N–Me
Me
3g
149.48
148.78
148.63
146.44
145.86
143.94
135.52
130.29
129.53
127.43
127.23
127.10
126.91
126.64
126.40
126.12
125.97
123.48
120.21
112.42
77.37
77.05
76.73
73.42
58.95
40.69
40.12
39.26


S
S
Ph
N–Me
Me
3g
130.28
129.54
127.43
127.22
127.10
126.64
126.41
126.12
125.97
123.48
120.22
112.42
58.94
40.70
40.13
39.26
200
180
160
140
120
100
80
60
40
20
0
ppm


msk-802
PROTON CDC13
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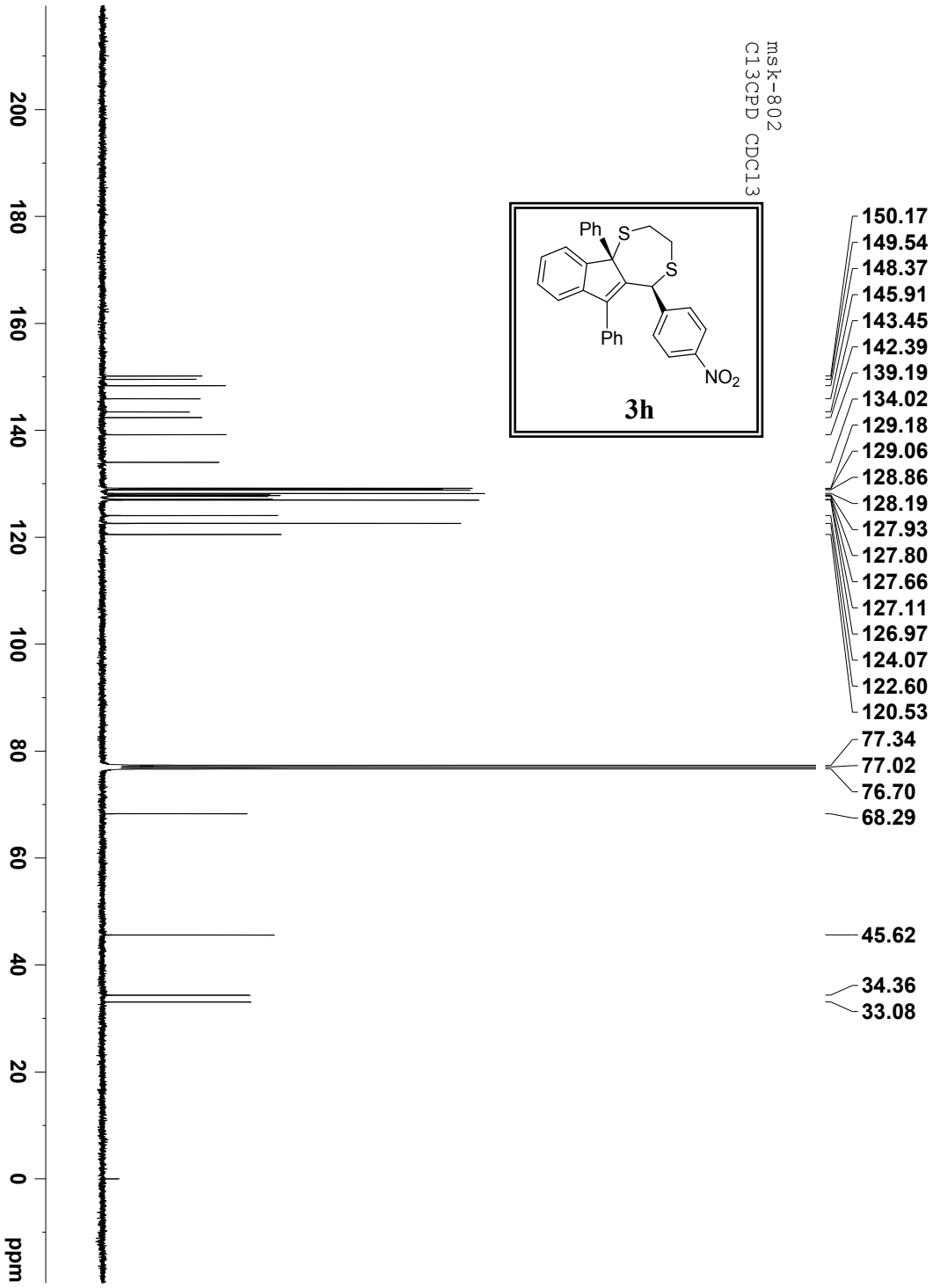
7.677
7.658
7.419
7.400
7.380
7.355
7.338
7.320
7.253
7.236
7.218
7.198
7.181
7.161
7.031
7.020
7.013
6.953
6.931
6.896
6.878
5.445
3.213
3.207
3.191
3.185
3.176
3.171
3.152
3.148
3.007
3.003
2.991
2.985
2.975
2.971
2.949
2.939
2.934
2.919
2.906
2.886
2.881
2.870
1.562
-0.000
1.98
1.98
4.07
5.37
2.01
1.99
1.00
1.00
1.00
3.07
ppm
Ph
S
S
Ph
NO2
3h


msk-802
C13CPD CDC13
Ph
S
S
Ph
NO2
3h
150.17
149.54
148.37
145.91
143.45
142.39
139.19
134.02
129.18
129.06
128.86
128.19
127.93
127.80
127.66
127.11
126.97
124.07
122.60
120.53
77.34
77.02
76.70
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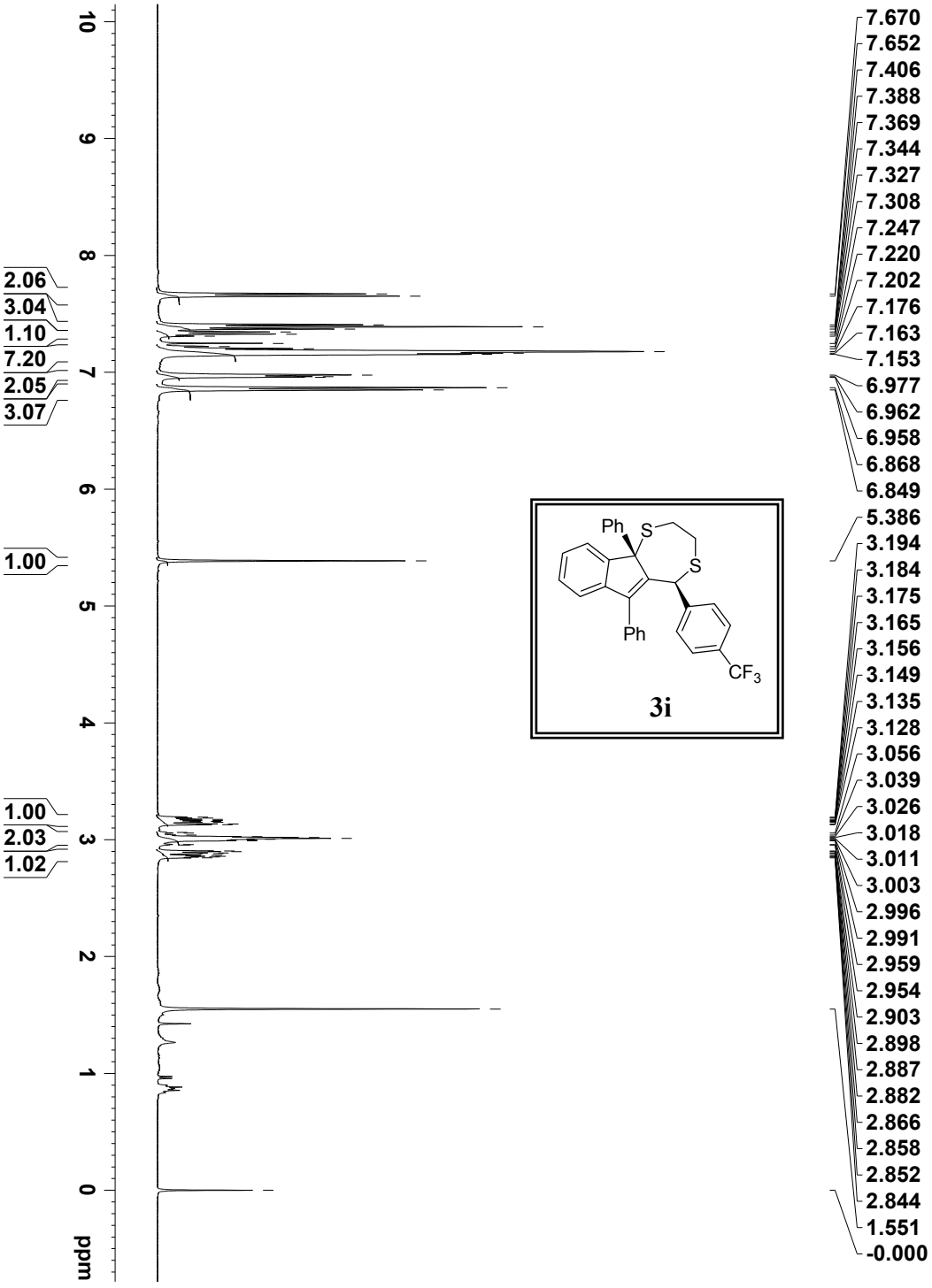
34.36
33.08
200
180
160
140
120
100
80
60
40
20
0
ppm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3.07
1.00
1.00
2.03
1.02
ppm
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7.406
7.388
7.369
7.344
7.327
7.308
7.247
7.220
7.202
7.176
7.163
7.153
6.977
6.962
6.958
6.868
6.849
5.386
3.194
3.184
3.175
3.165
3.156
3.149
3.135
3.128
3.056
3.039
3.026
3.018
3.011
3.003
2.996
2.991
2.959
2.954
2.903
2.898
2.887
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2.858
2.852
2.844
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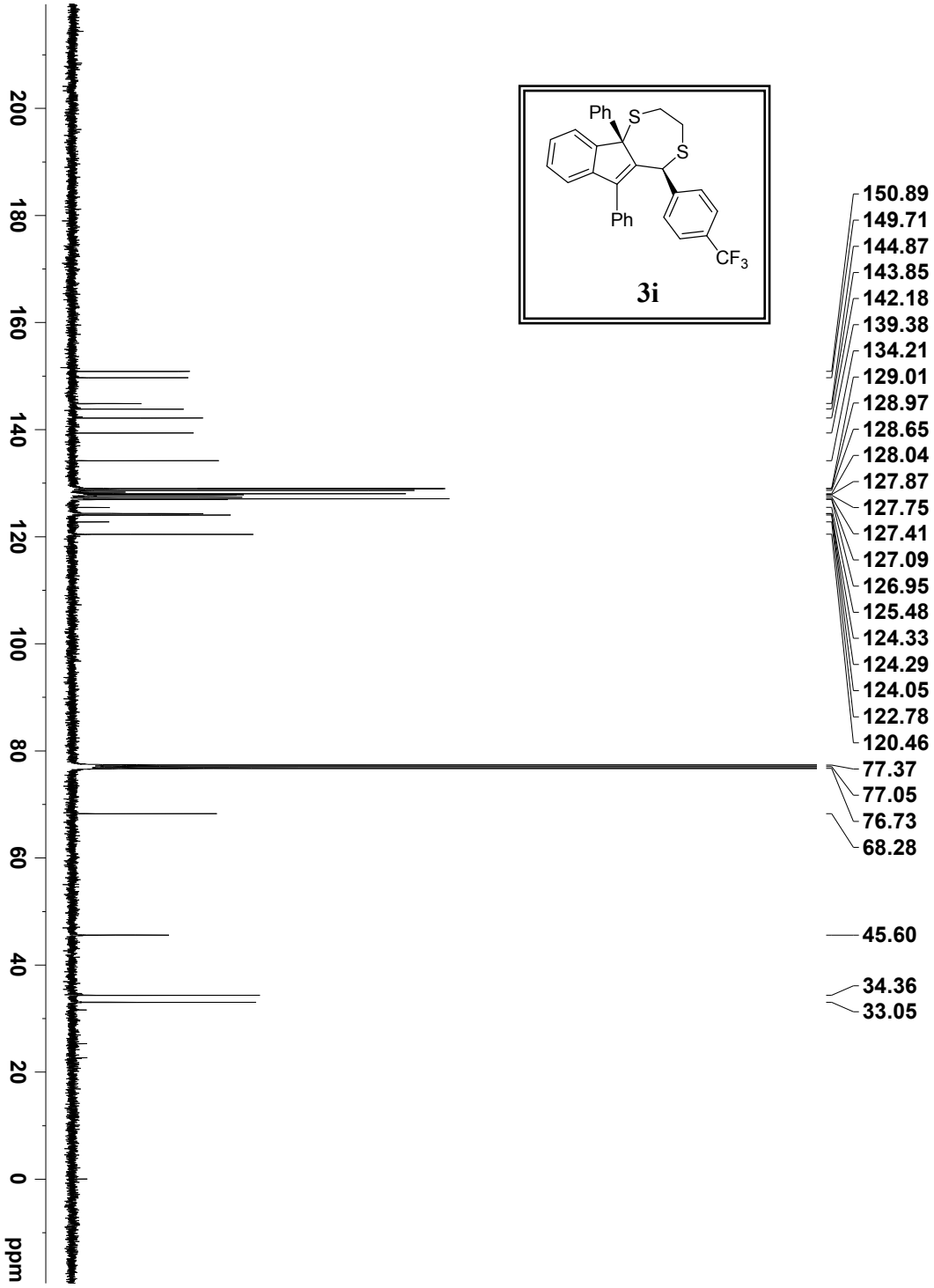
Ph
S
S
Ph
CF3
3i


Ph
S
S
Ph
CF3
3i
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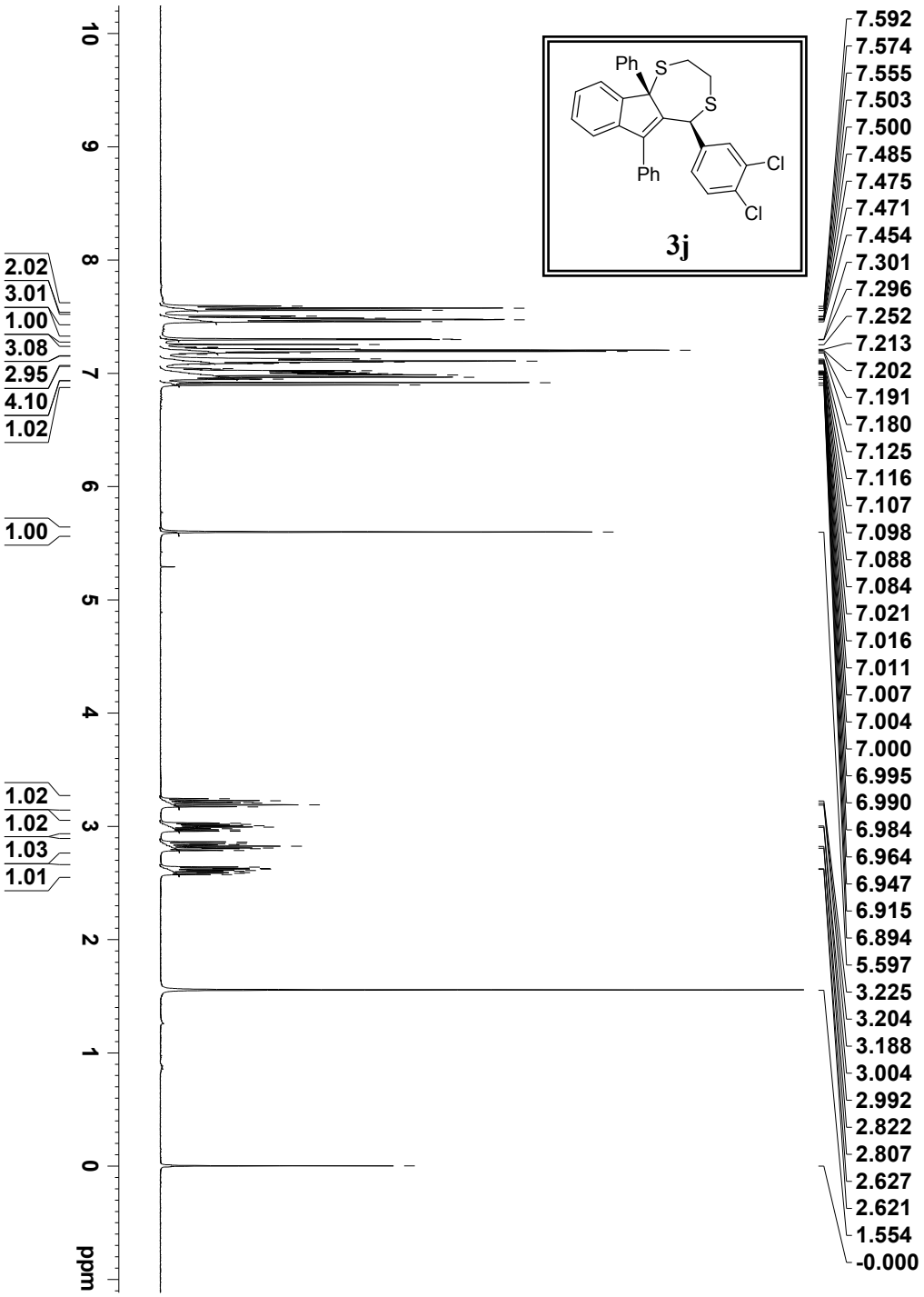
149.71
144.87
143.85
142.18
139.38
134.21
129.01
128.97
128.65
128.04
127.87
127.75
127.41
127.09
126.95
125.48
124.33
124.29
124.05
122.78
120.46
77.37
77.05
76.73
68.28
45.60
34.36
33.05
200
180
160
140
120
100
80
60
40
20
0
ppm


Ph
S
S
Ph
Cl
Cl
3j
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3.01
1.00
3.08
2.95
4.10
1.02
1.00
1.02
1.02
1.03
1.01
ppm
7.592
7.574
7.555
7.503
7.500
7.485
7.475
7.471
7.454
7.301
7.296
7.252
7.213
7.202
7.191
7.180
7.125
7.116
7.107
7.098
7.088
7.084
7.021
7.016
7.011
7.007
7.004
7.000
6.995
6.990
6.984
6.964
6.947
6.915
6.894
5.597
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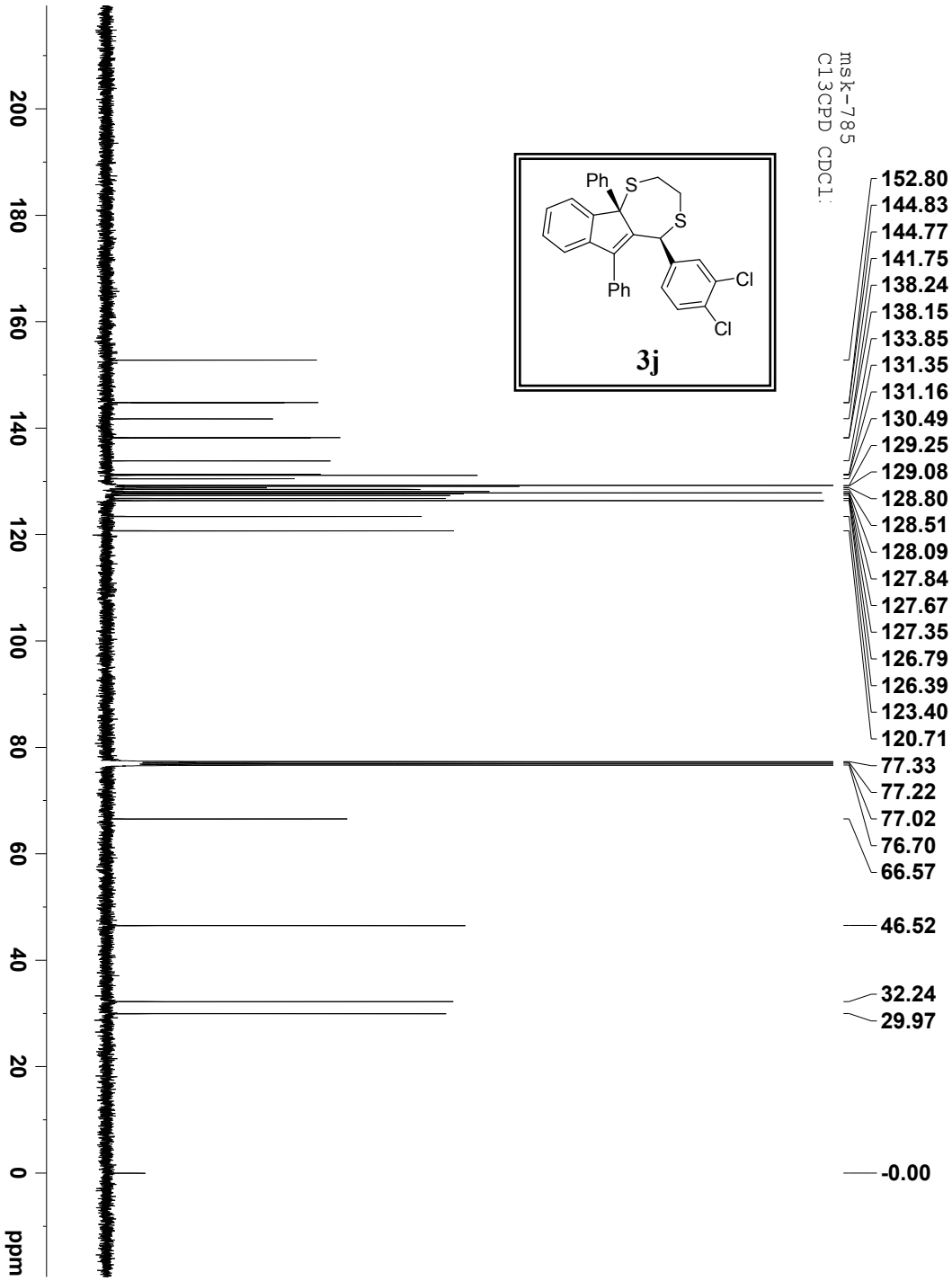
msk-785
C13CPD CDCl3
Ph
S
S
Ph
Cl
Cl
3j
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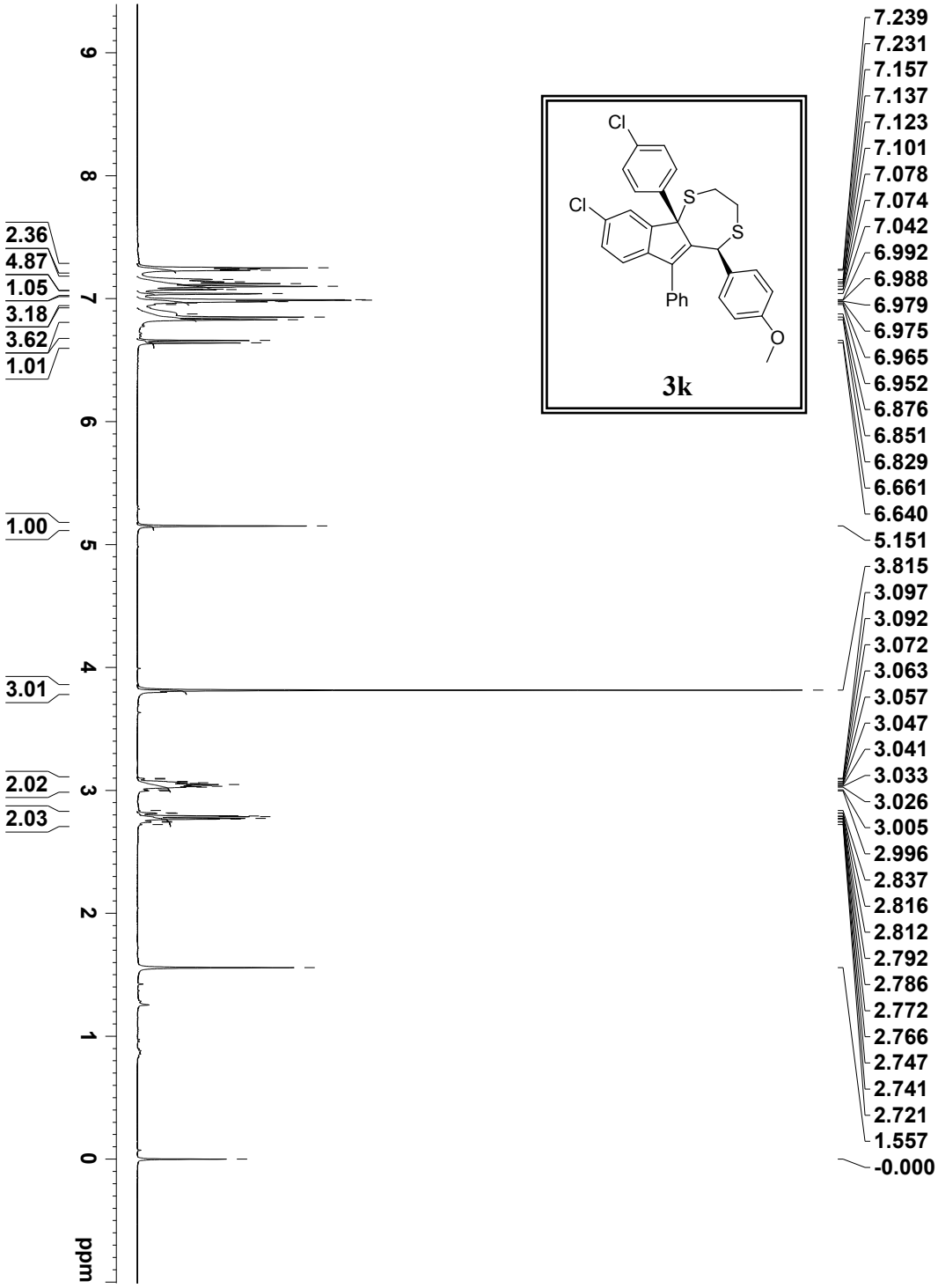
144.77
141.75
138.24
138.15
133.85
131.35
131.16
130.49
129.25
129.08
128.80
128.51
128.09
127.84
127.67
127.35
126.79
126.39
123.40
120.71
77.33
77.22
77.02
76.70
66.57
46.52
32.24
29.97
-0.00
200
180
160
140
120
100
80
60
40
20
0
ppm


Cl
Cl
S
S
Ph
O
3k
7.239
7.231
7.157
7.137
7.123
7.101
7.078
7.074
7.042
6.992
6.988
6.979
6.975
6.965
6.952
6.876
6.851
6.829
6.661
6.640
5.151
3.815
3.097
3.092
3.072
3.063
3.057
3.047
3.041
3.033
3.026
3.005
2.996
2.837
2.816
2.812
2.792
2.786
2.772
2.766
2.747
2.741
2.721
1.557
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4.87
1.05
3.18
3.62
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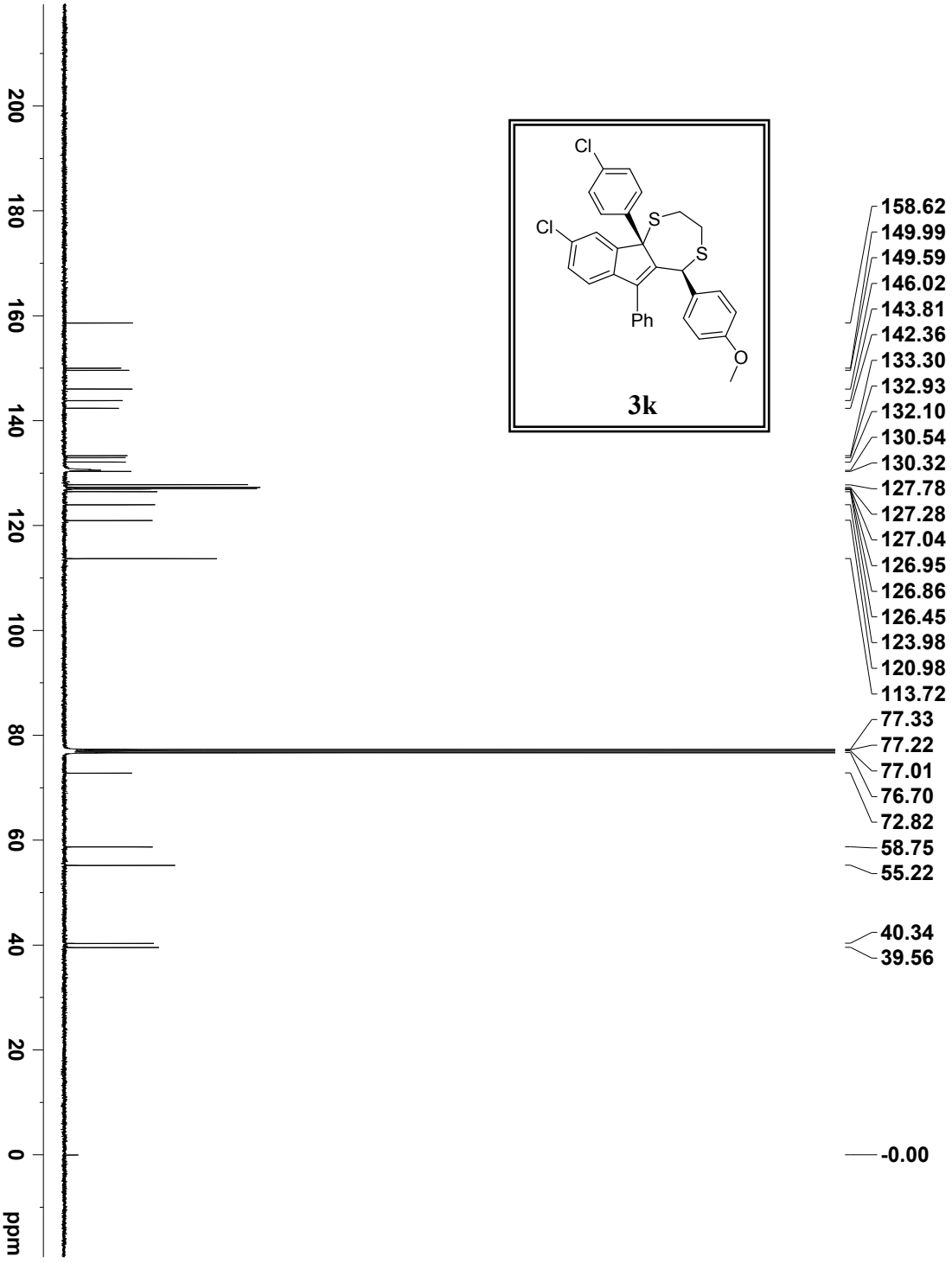
1.00
3.01
2.02
2.03
ppm


Cl
Cl
S
S
Ph
O
3k
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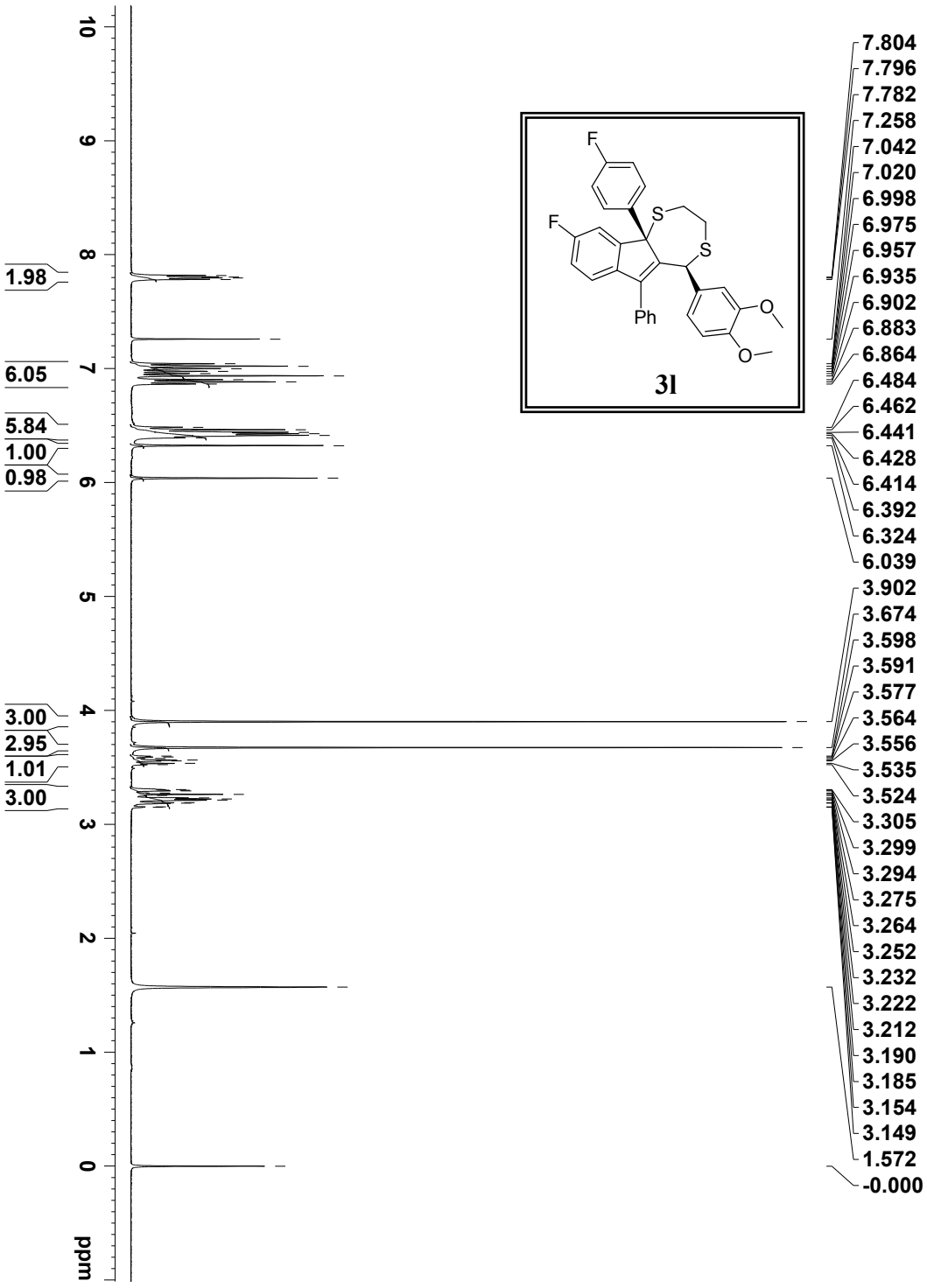
146.02
143.81
142.36
133.30
132.93
132.10
130.54
130.32
127.78
127.28
127.04
126.95
126.86
126.45
123.98
120.98
113.72
77.33
77.22
77.01
76.70
72.82
58.75
55.22
40.34
39.56
-0.00
200
180
160
140
120
100
80
60
40
20
0
ppm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7.042
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6.902
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6.864
6.484
6.462
6.441
6.428
6.414
6.392
6.324
6.039
3.902
3.674
3.598
3.591
3.577
3.564
3.556
3.535
3.524
3.305
3.299
3.294
3.275
3.264
3.252
3.232
3.222
3.212
3.190
3.185
3.154
3.149
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-0.000
1.98
6.05
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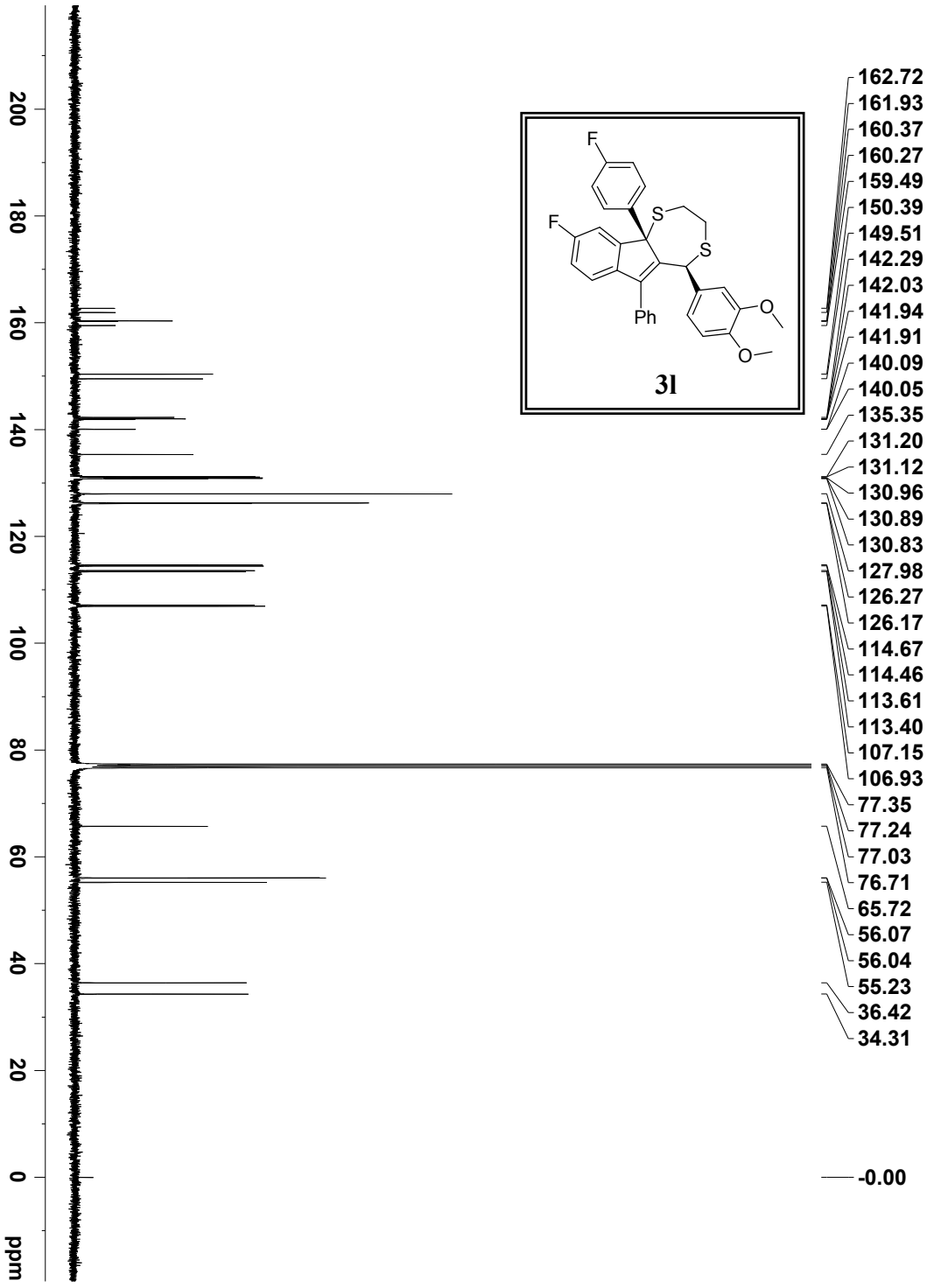
3.00
2.95
1.01
3.00
ppm
F
F
S
S
Ph
O
O
3l


F
F
S
S
Ph
O
O
3l
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142.29
142.03
141.94
141.91
140.09
140.05
135.35
131.20
131.12
130.96
130.89
130.83
127.98
126.27
126.17
114.67
114.46
113.61
113.40
107.15
106.93
77.35
77.24
77.03
76.71
65.72
56.07
56.04
55.23
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34.31
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120
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60
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0
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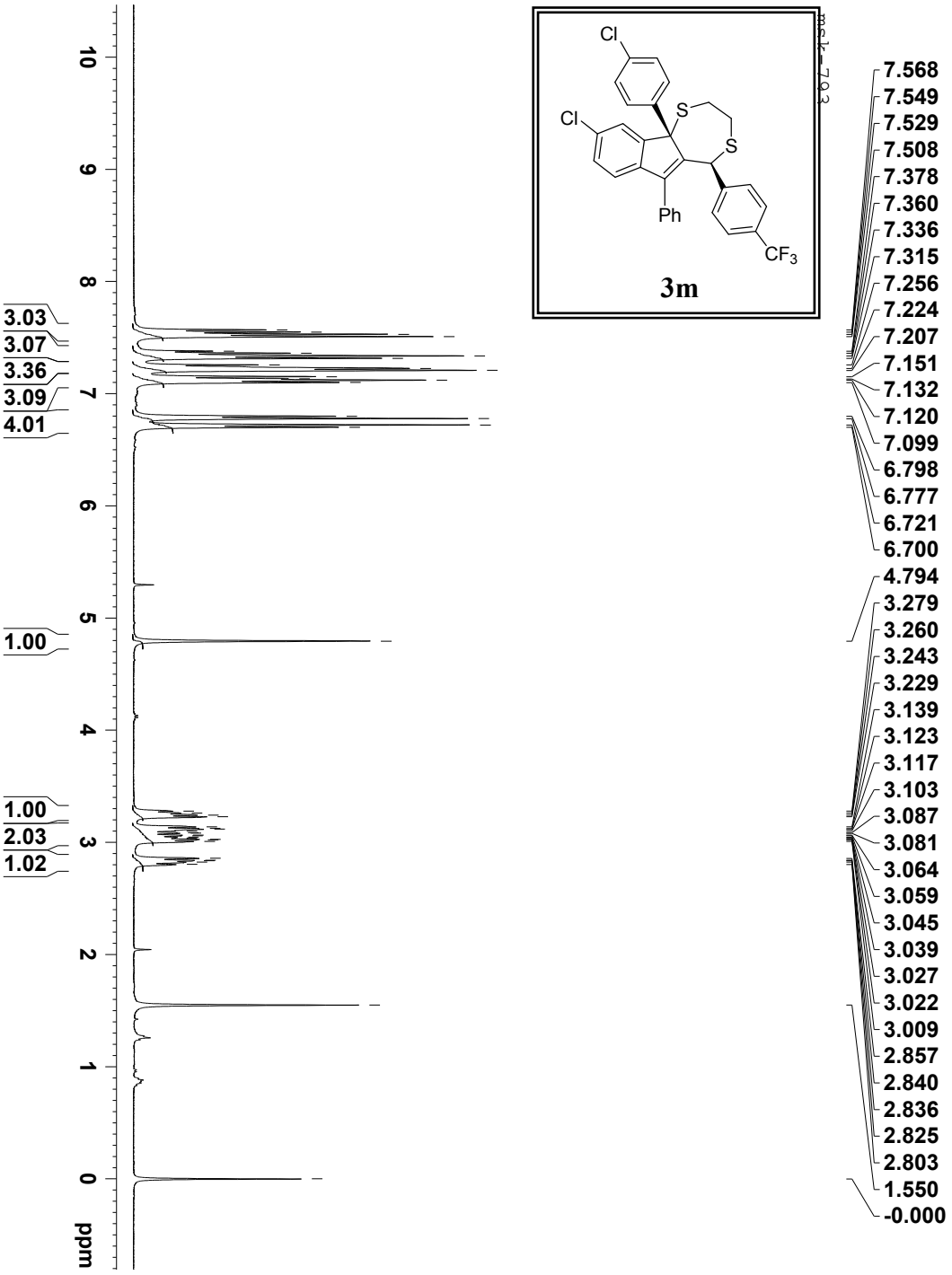
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Cl
S
S
Ph
CF3
3m
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7.378
7.360
7.336
7.315
7.256
7.224
7.207
7.151
7.132
7.120
7.099
6.798
6.777
6.721
6.700
4.794
3.279
3.260
3.243
3.229
3.139
3.123
3.117
3.103
3.087
3.081
3.064
3.059
3.045
3.039
3.027
3.022
3.009
2.857
2.840
2.836
2.825
2.803
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3.07
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3.09
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1.00
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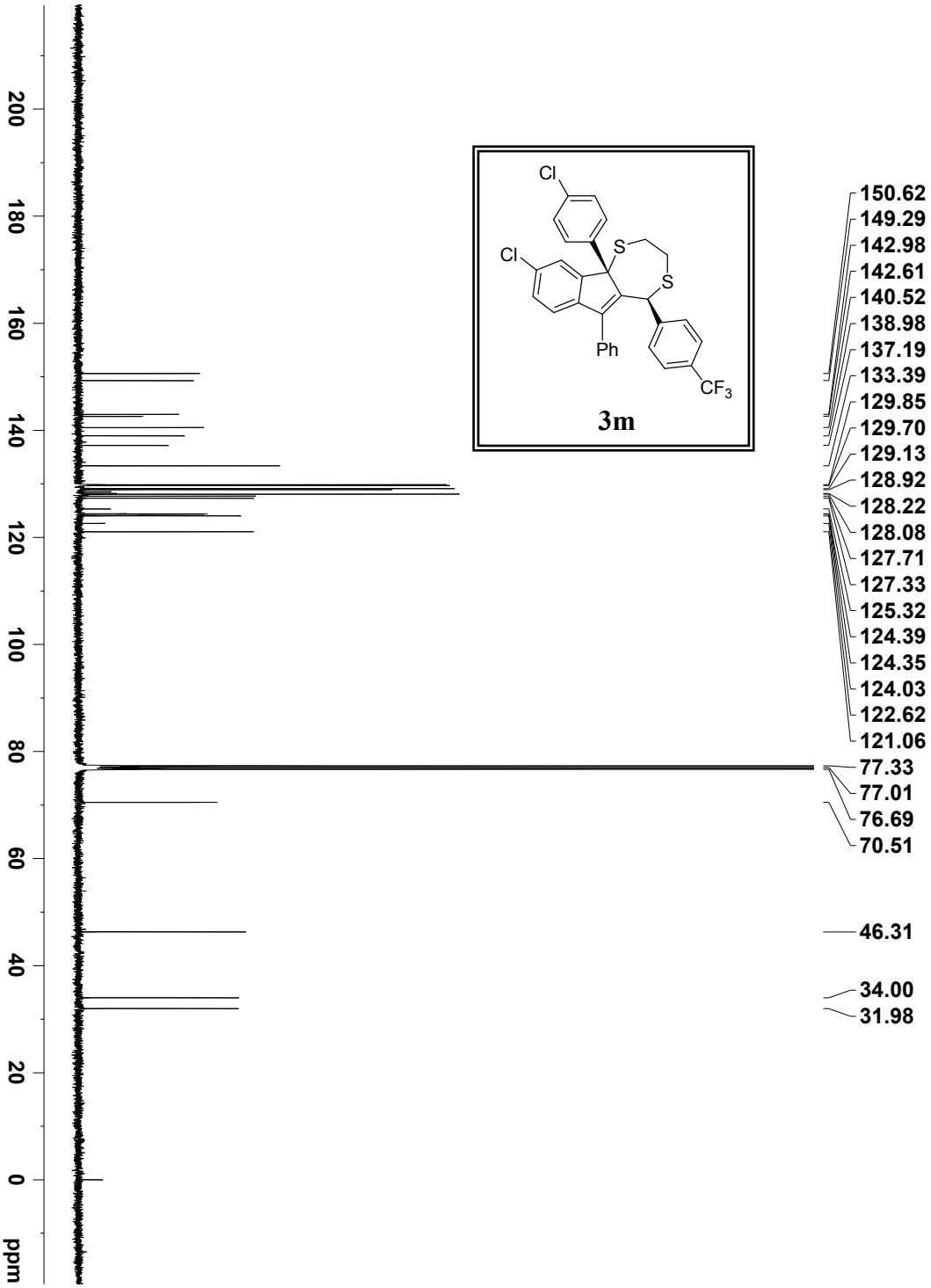
2.03
1.02
ppm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Cl
S
S
Ph
CF3
3m
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149.29
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138.98
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133.39
129.85
129.70
129.13
128.92
128.22
128.08
127.71
127.33
125.32
124.39
124.35
124.03
122.62
121.06
77.33
77.01
76.69
70.51
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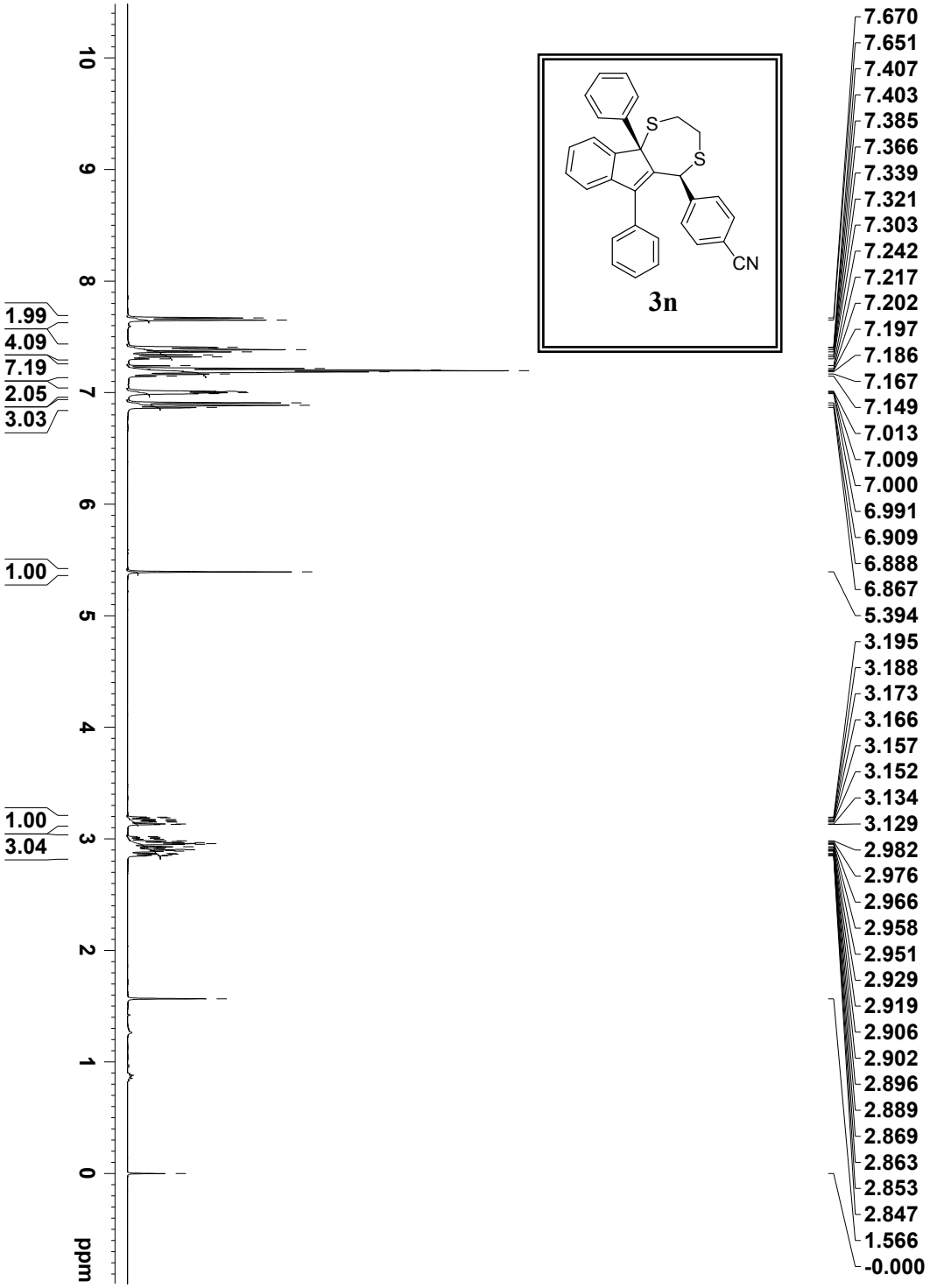
34.00
31.98
200
180
160
140
120
100
80
60
40
20
0
ppm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S
S
CN
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3.04
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7.407
7.403
7.385
7.366
7.339
7.321
7.303
7.242
7.217
7.202
7.197
7.186
7.167
7.149
7.013
7.009
7.000
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6.909
6.888
6.867
5.394
3.195
3.188
3.173
3.166
3.157
3.152
3.134
3.129
2.982
2.976
2.966
2.958
2.951
2.929
2.919
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2.902
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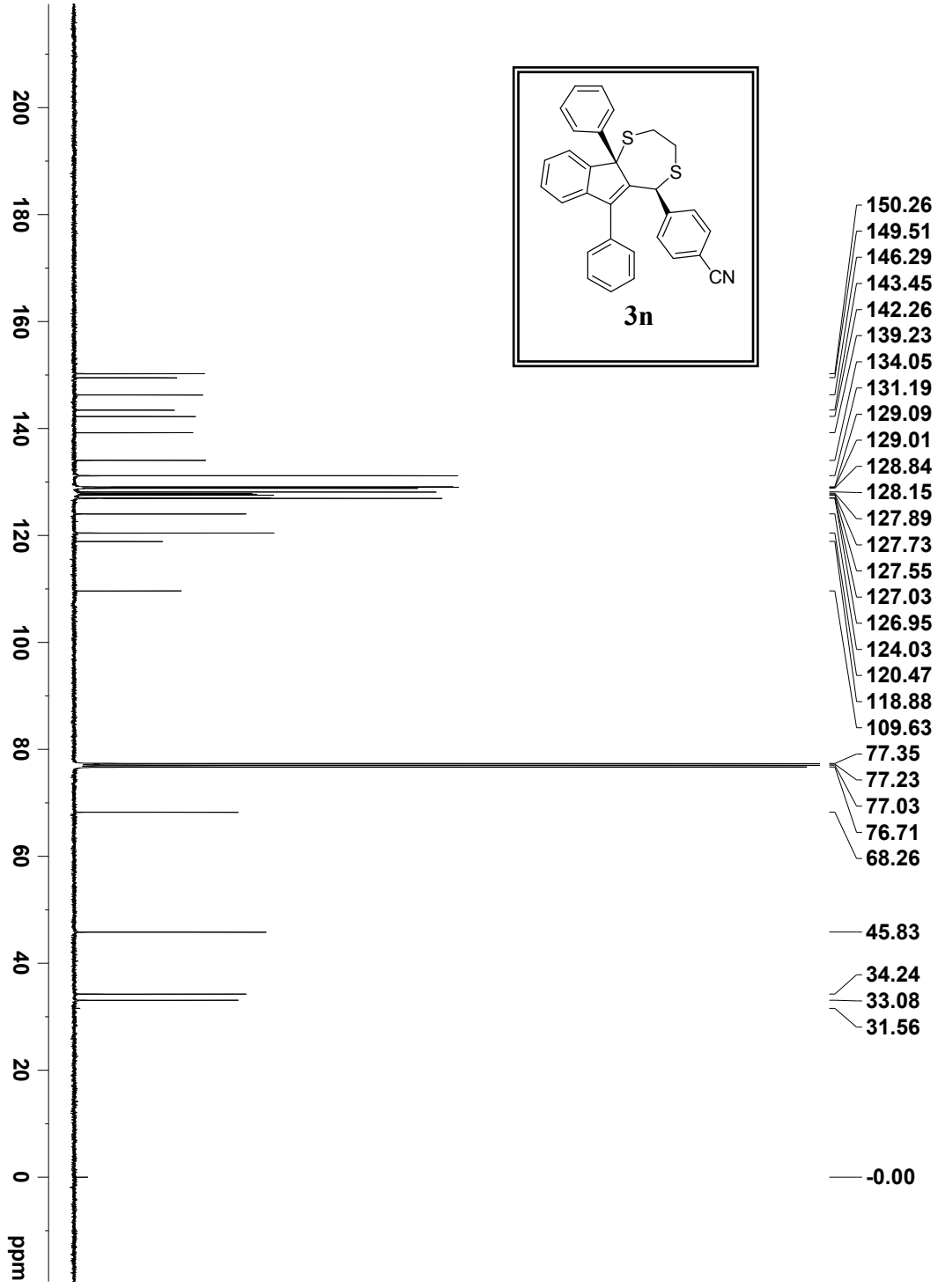
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S
CN
3n
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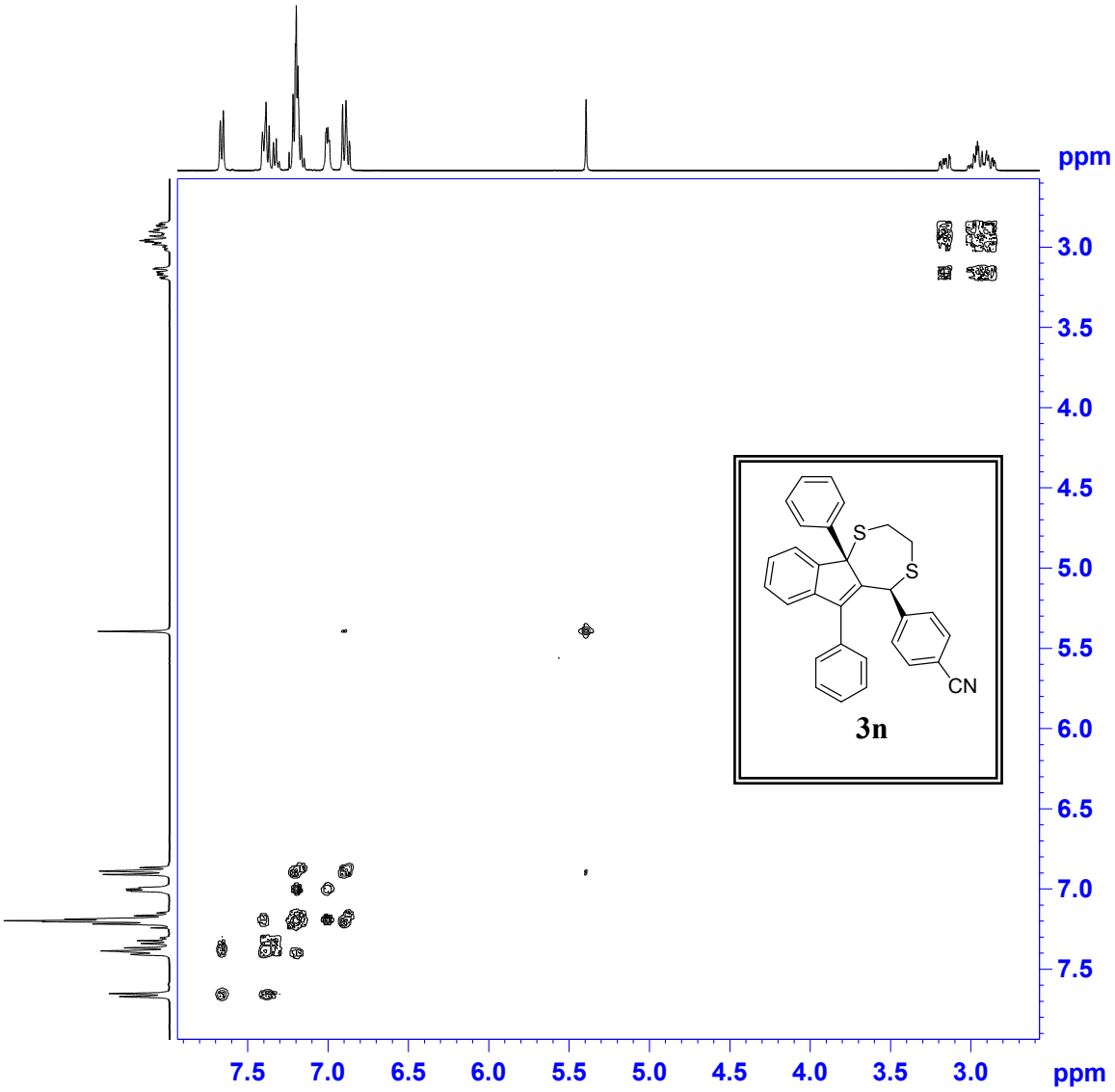
146.29
143.45
142.26
139.23
134.05
131.19
129.09
129.01
128.84
128.15
127.89
127.73
127.55
127.03
126.95
124.03
120.47
118.88
109.63
77.35
77.23
77.03
76.71
68.26
45.83
34.24
33.08
31.56
-0.00
200
180
160
140
120
100
80
60
40
20
0
ppm


ppm
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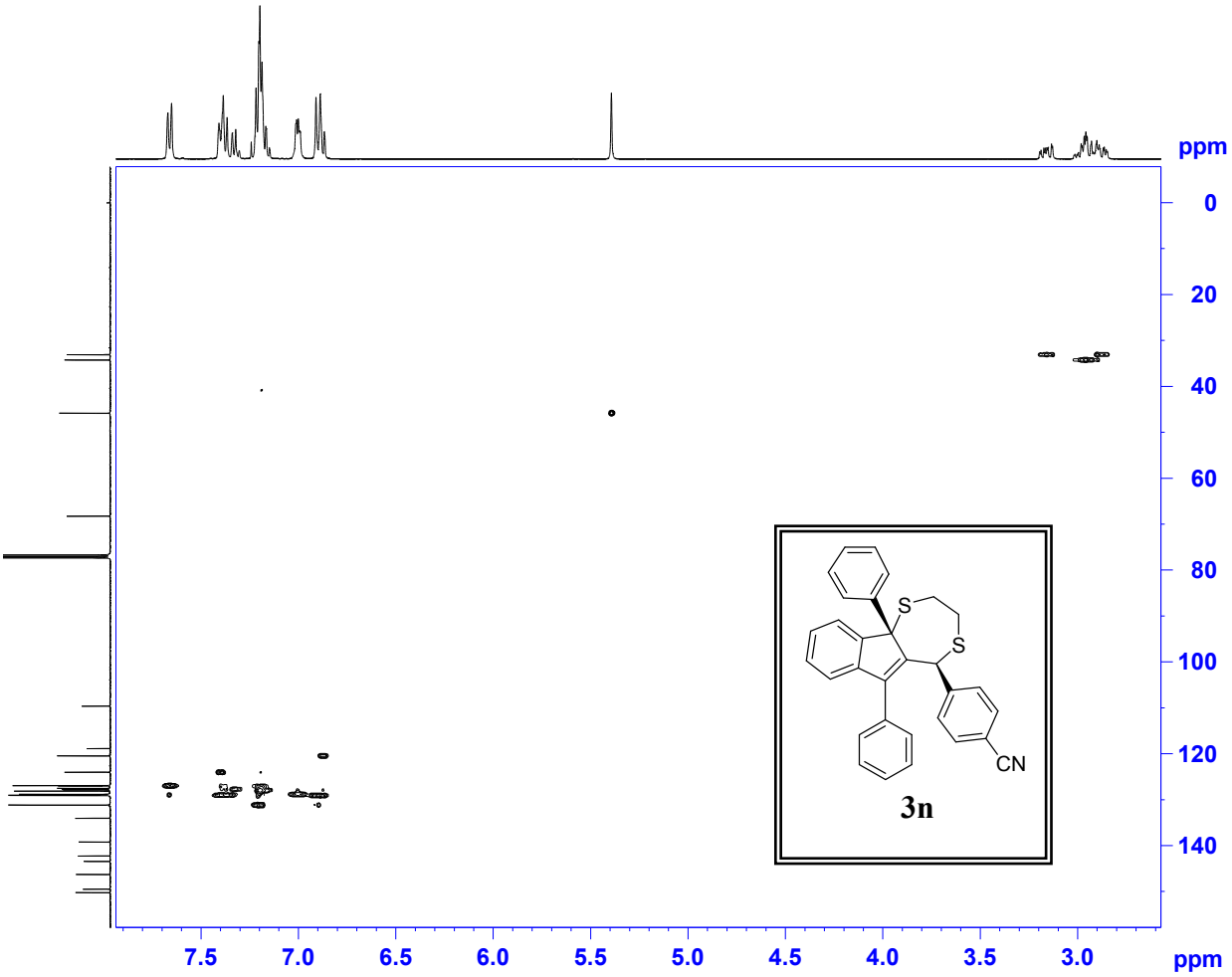
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
S
S
CN
3n
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm


ppm
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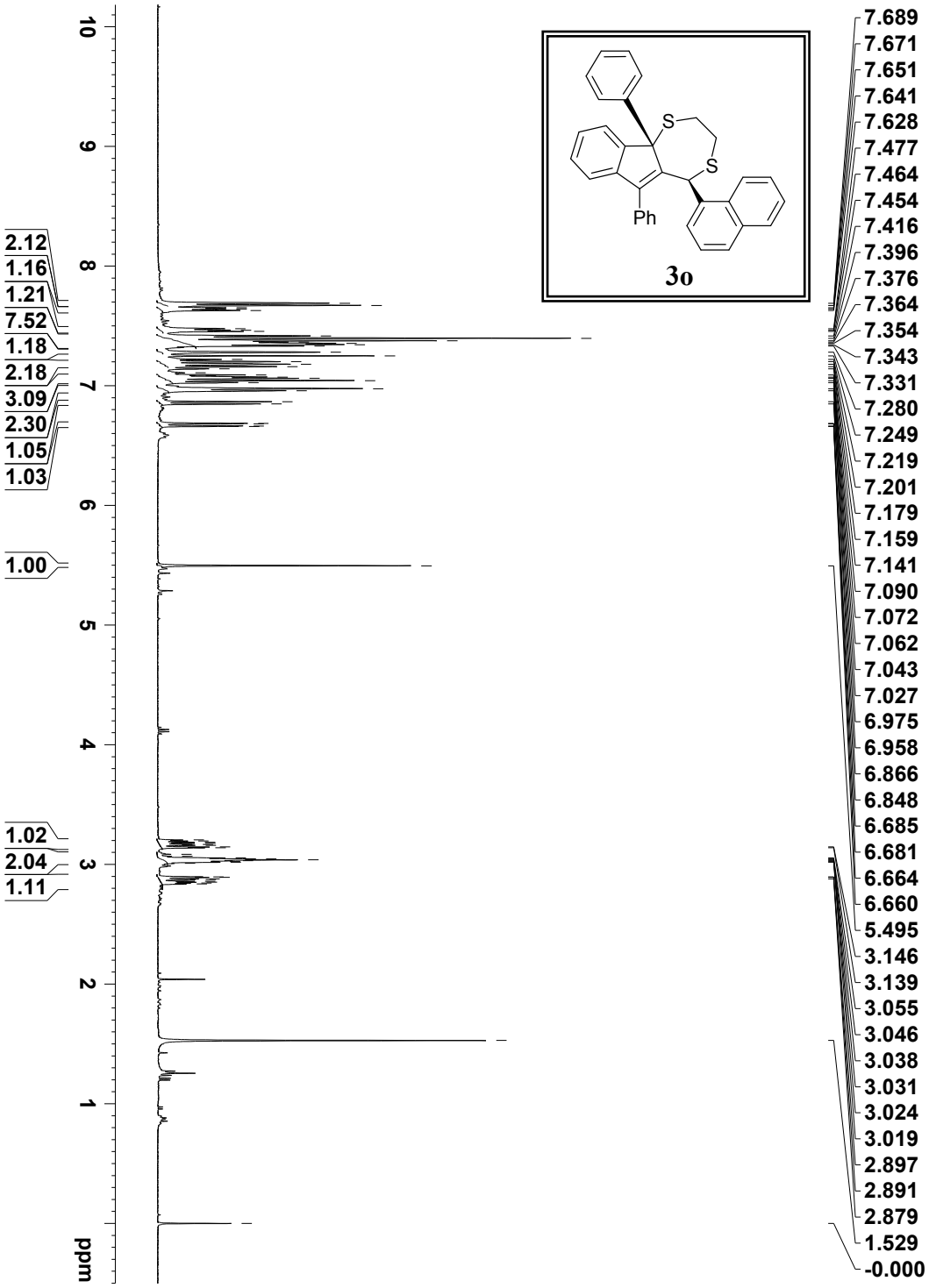
20
40
60
80
100
120
140
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
S
S
CN
3n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S
Ph
3o
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1.21
7.52
1.18
2.18
3.09
2.30
1.05
1.03
1.00
1.02
2.04
1.11
7.689
7.671
7.651
7.641
7.628
7.477
7.464
7.454
7.416
7.396
7.376
7.364
7.354
7.343
7.331
7.280
7.249
7.219
7.201
7.179
7.159
7.141
7.090
7.072
7.062
7.043
7.027
6.975
6.958
6.866
6.848
6.685
6.681
6.664
6.660
5.495
3.146
3.139
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3.038
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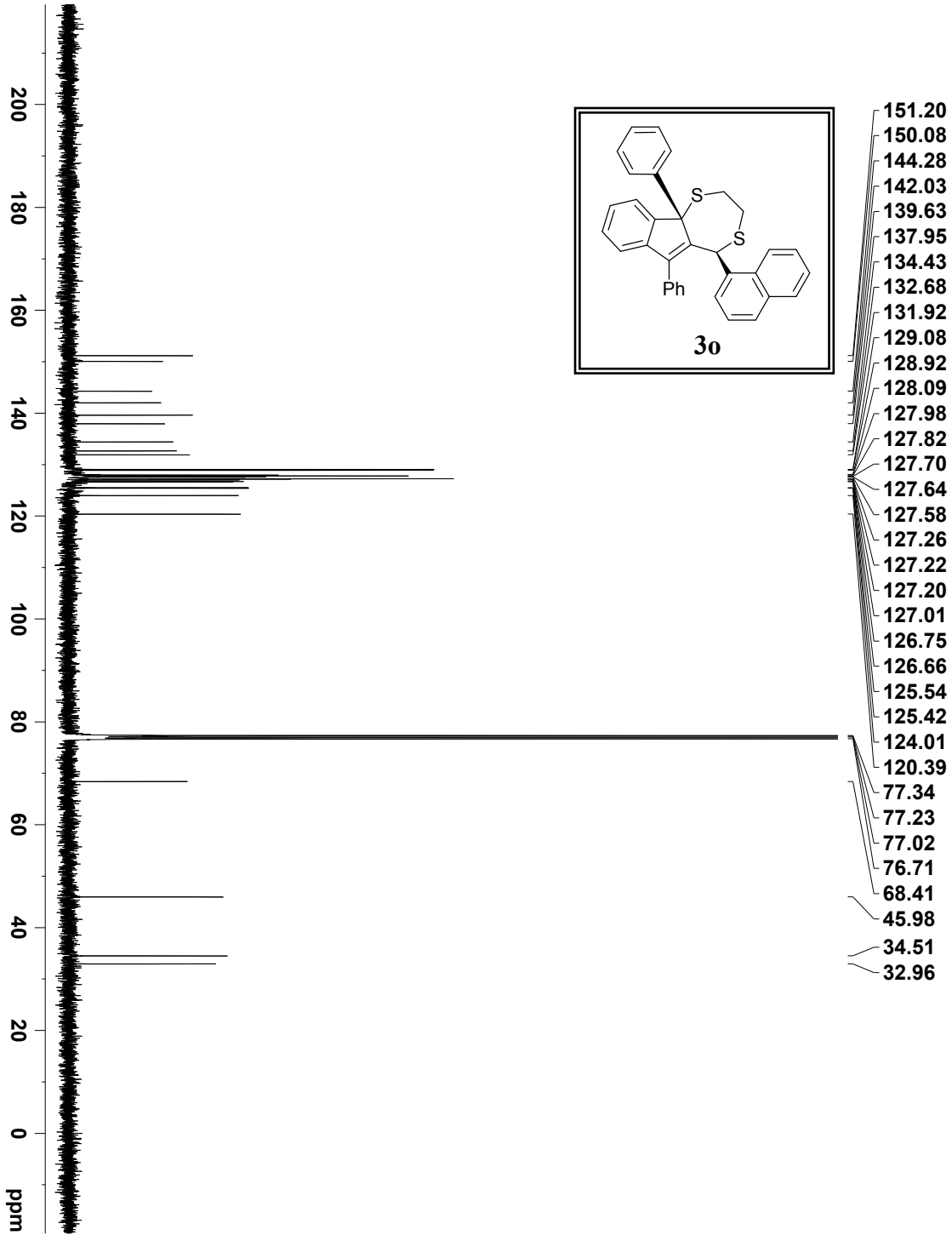
2.879
1.529
-0.000
ppm


200
180
160
140
120
100
80
60
40
20
0
ppm
S
S
Ph
3o
151.20
150.08
144.28
142.03
139.63
137.95
134.43
132.68
131.92
129.08
128.92
128.09
127.98
127.82
127.70
127.64
127.58
127.26
127.22
127.20
127.01
126.75
126.66
125.54
125.42
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120.39
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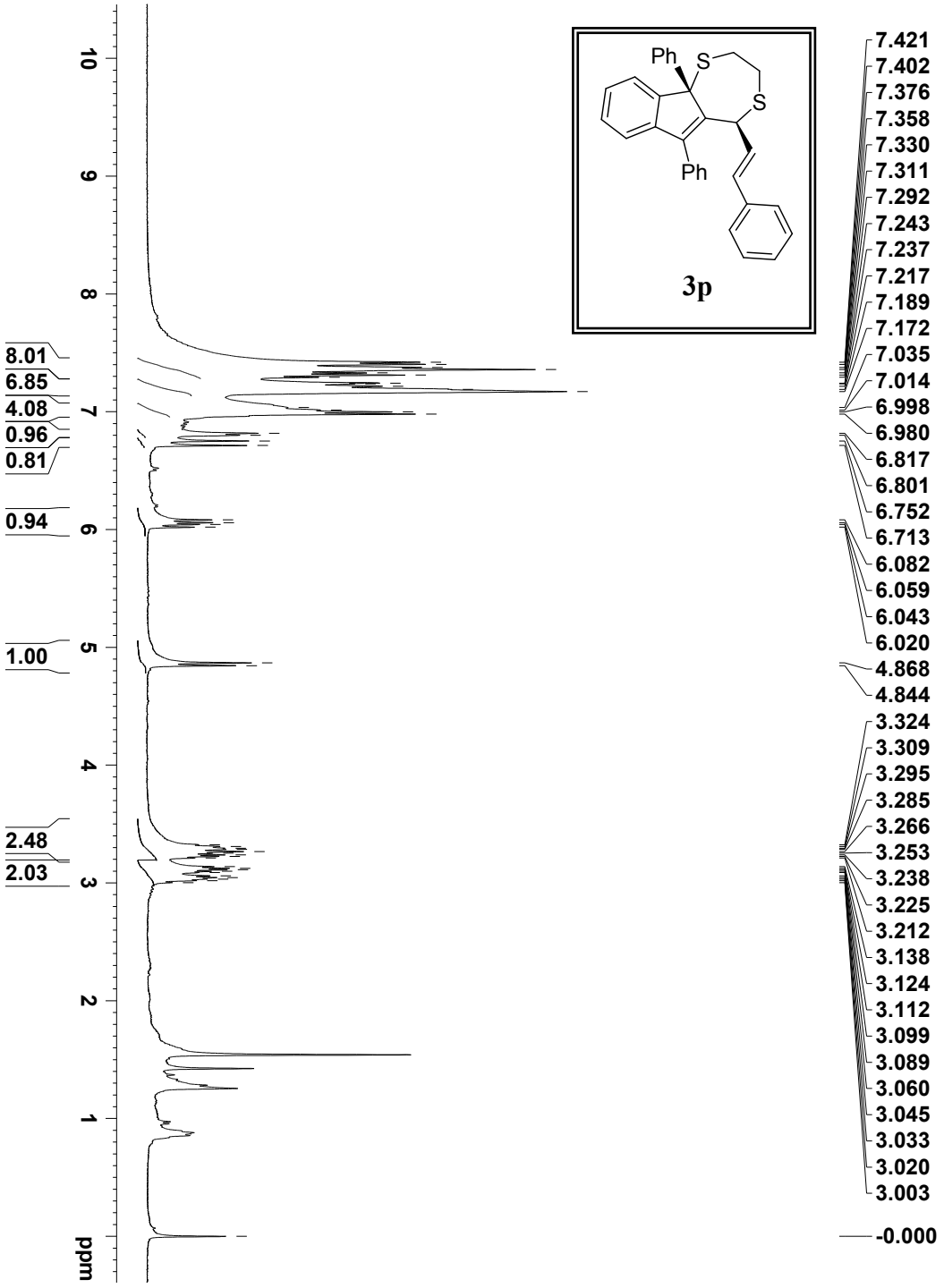
77.23
77.02
76.71
68.41
45.98
34.51
32.96


Ph
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S
Ph
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4.08
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0.81
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2.48
2.03
ppm
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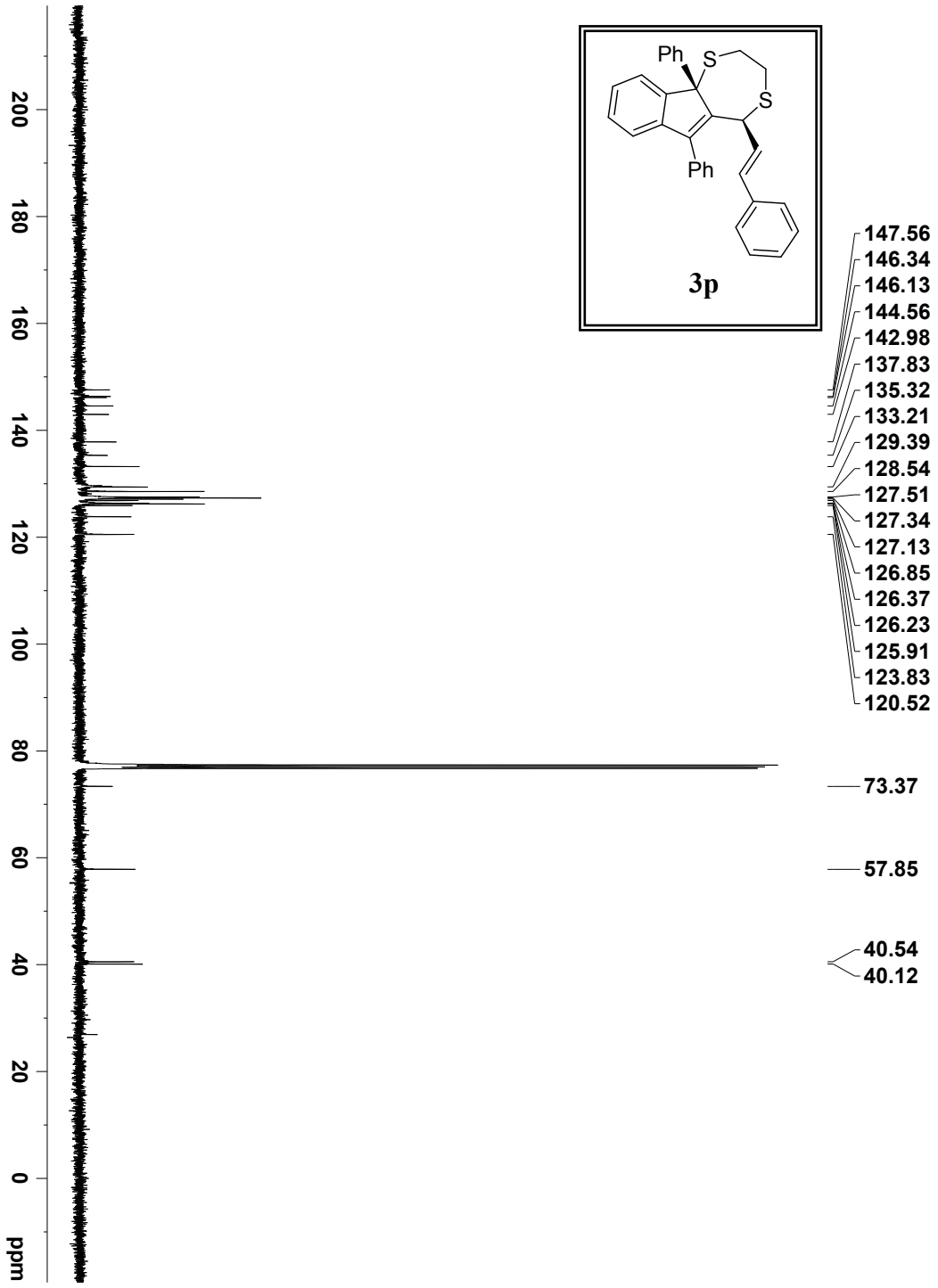
7.402
7.376
7.358
7.330
7.311
7.292
7.243
7.237
7.217
7.189
7.172
7.035
7.014
6.998
6.980
6.817
6.801
6.752
6.713
6.082
6.059
6.043
6.020
4.868
4.844
3.324
3.309
3.295
3.285
3.266
3.253
3.238
3.225
3.212
3.138
3.124
3.112
3.099
3.089
3.060
3.045
3.033
3.020
3.003
-0.000


Ph
S
S
Ph
3p
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146.13
144.56
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135.32
133.21
129.39
128.54
127.51
127.34
127.13
126.85
126.37
126.23
125.91
123.83
120.52
73.37
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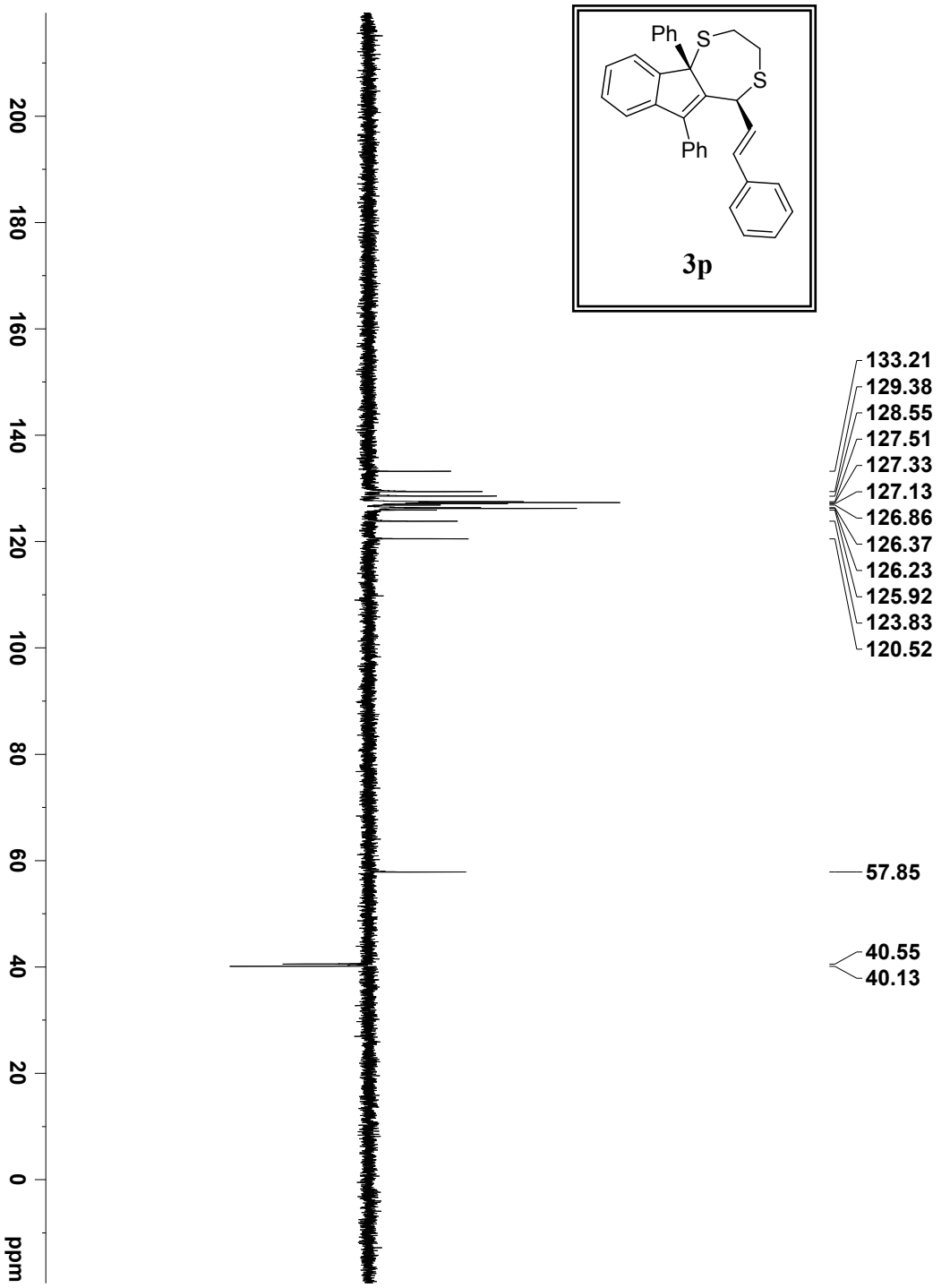
40.54
40.12
200
180
160
140
120
100
80
60
40
20
0
ppm


Ph
S
S
Ph
3p
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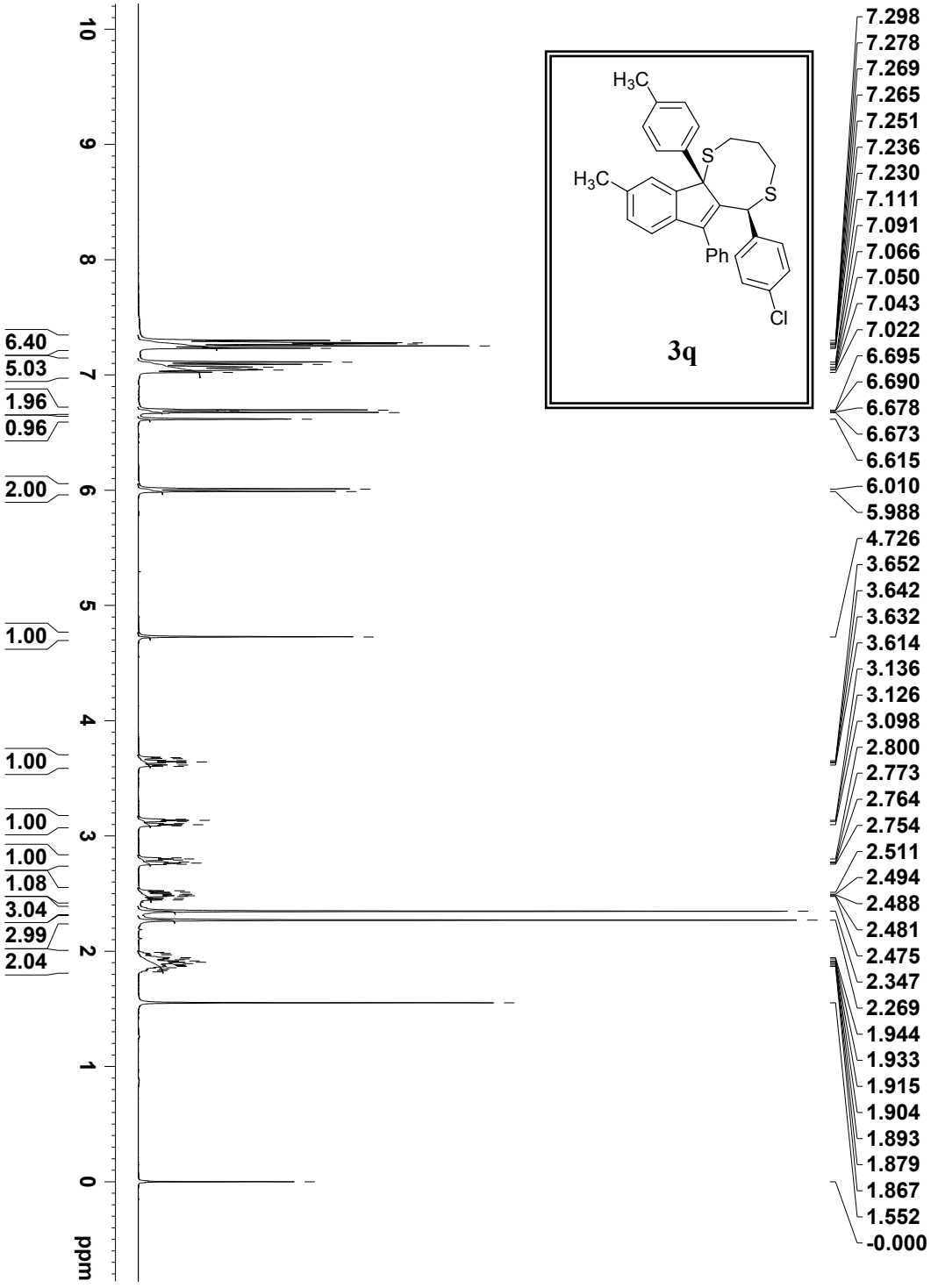
128.55
127.51
127.33
127.13
126.86
126.37
126.23
125.92
123.83
120.52
57.85
40.55
40.13
200
180
160
140
120
100
80
60
40
20
0
ppm


H3C
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H3C
S
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Cl
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7.230
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7.043
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6.690
6.678
6.673
6.615
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4.726
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3.642
3.632
3.614
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3.126
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1.933
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1.00
1.00
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6
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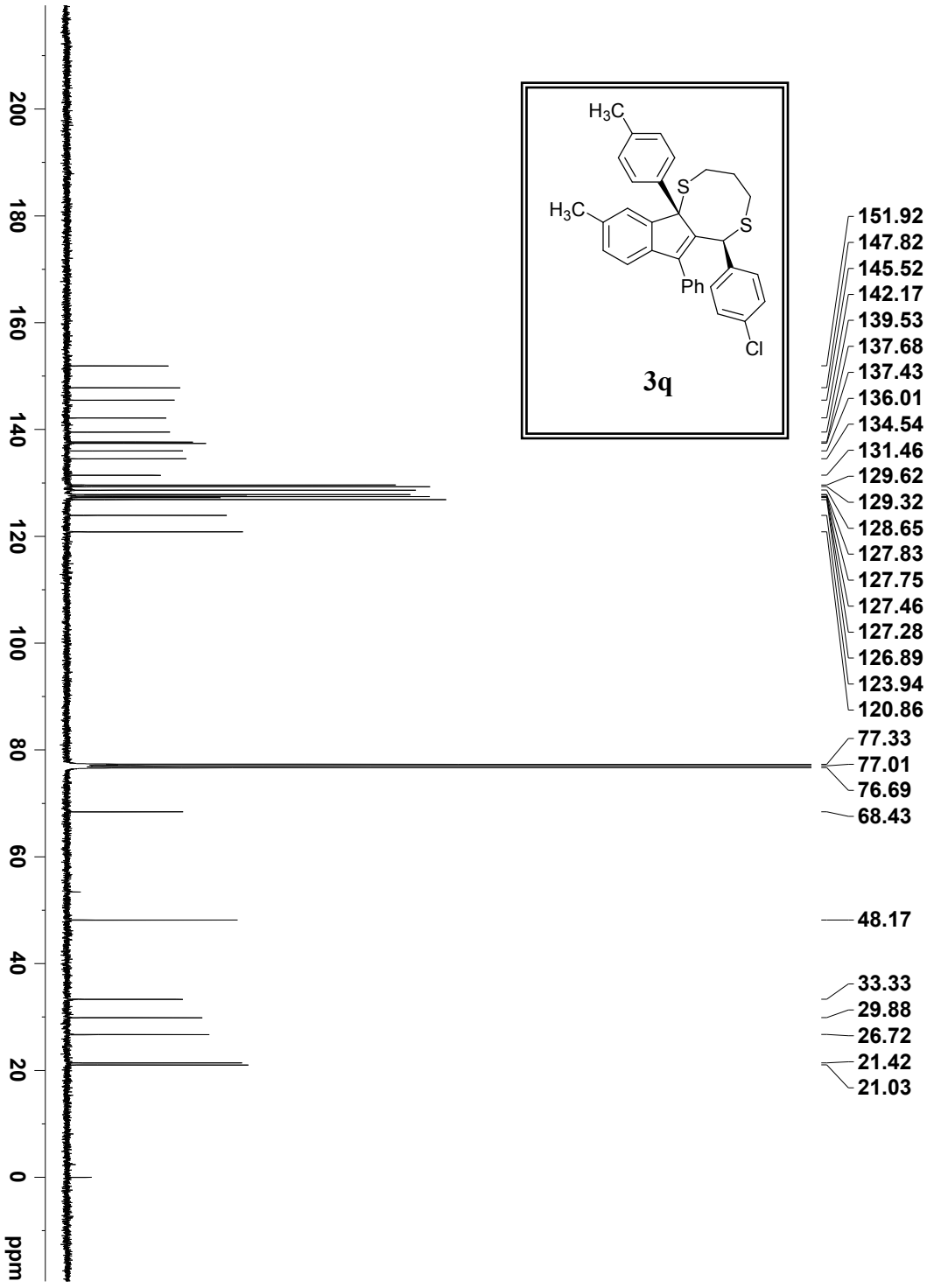
H3C
S
H3C
S
Ph
Cl
3q
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139.53
137.68
137.43
136.01
134.54
131.46
129.62
129.32
128.65
127.83
127.75
127.46
127.28
126.89
123.94
120.86
77.33
77.01
76.69
68.43
48.17
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200
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120
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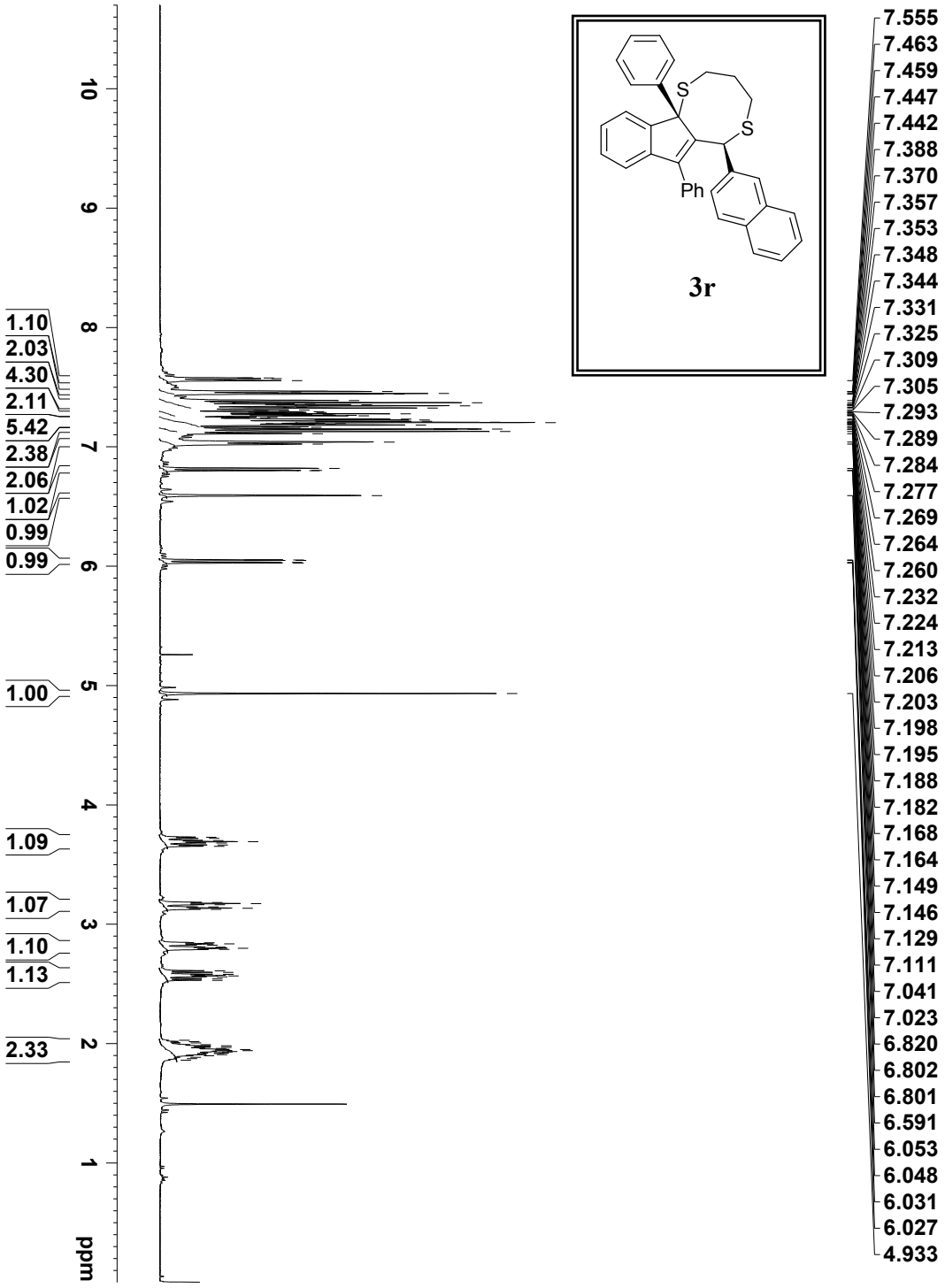
40
20
0
ppm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S
Ph
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1.02
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0.99
1.00
1.09
1.07
1.10
1.13
2.33
ppm
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7.447
7.442
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7.370
7.357
7.353
7.348
7.344
7.331
7.325
7.309
7.305
7.293
7.289
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7.277
7.269
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7.260
7.232
7.224
7.213
7.206
7.203
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7.195
7.188
7.182
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7.164
7.149
7.146
7.129
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7.041
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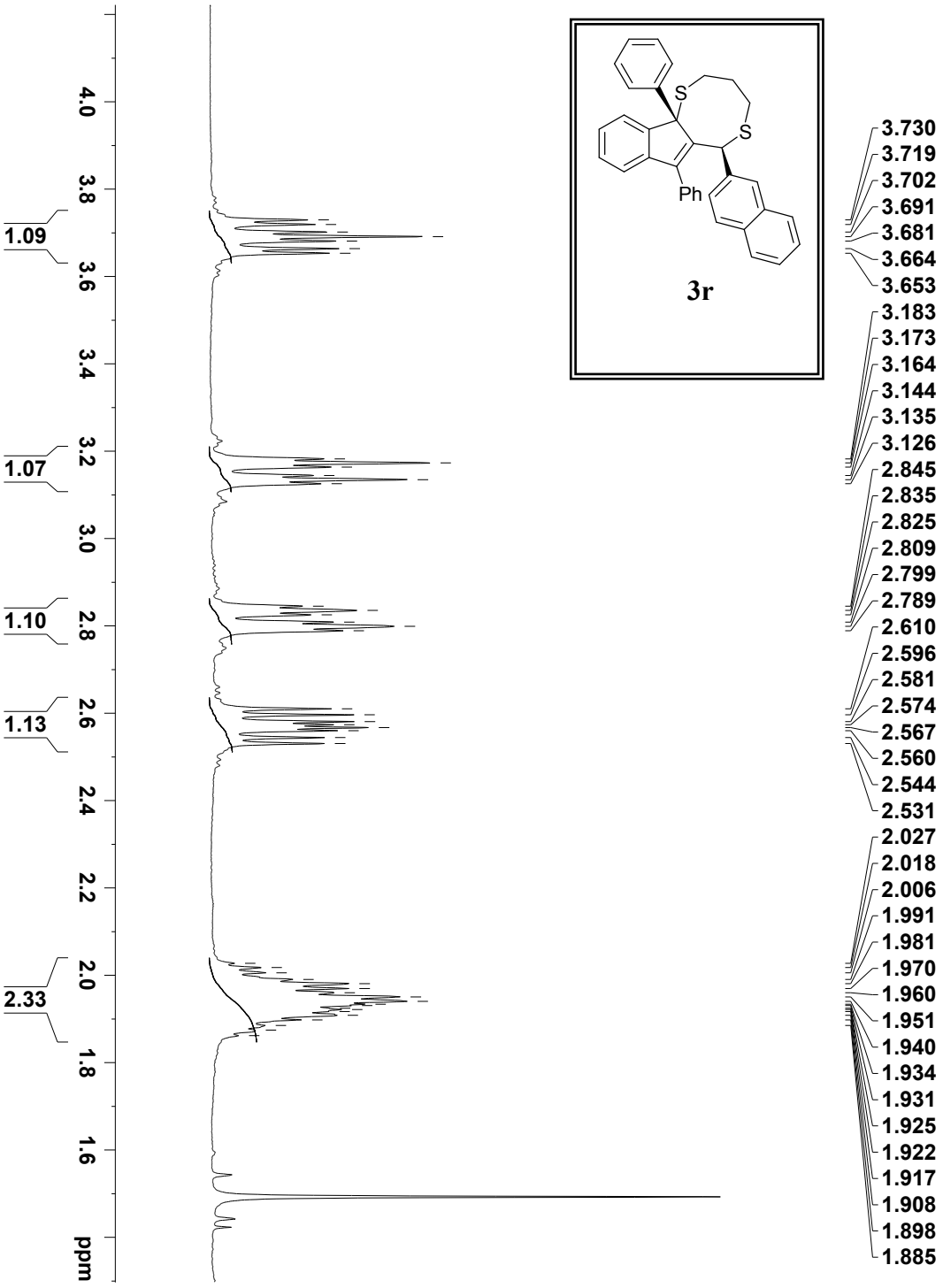
6.031
6.027
4.933


S
S
Ph
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3.144
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2.835
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2.799
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2.567
2.560
2.544
2.531
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2.018
2.006
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1.981
1.970
1.960
1.951
1.940
1.934
1.931
1.925
1.922
1.917
1.908
1.898
1.885
1.09
1.07
1.10
1.13
2.33
4.0
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2.6
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2.2
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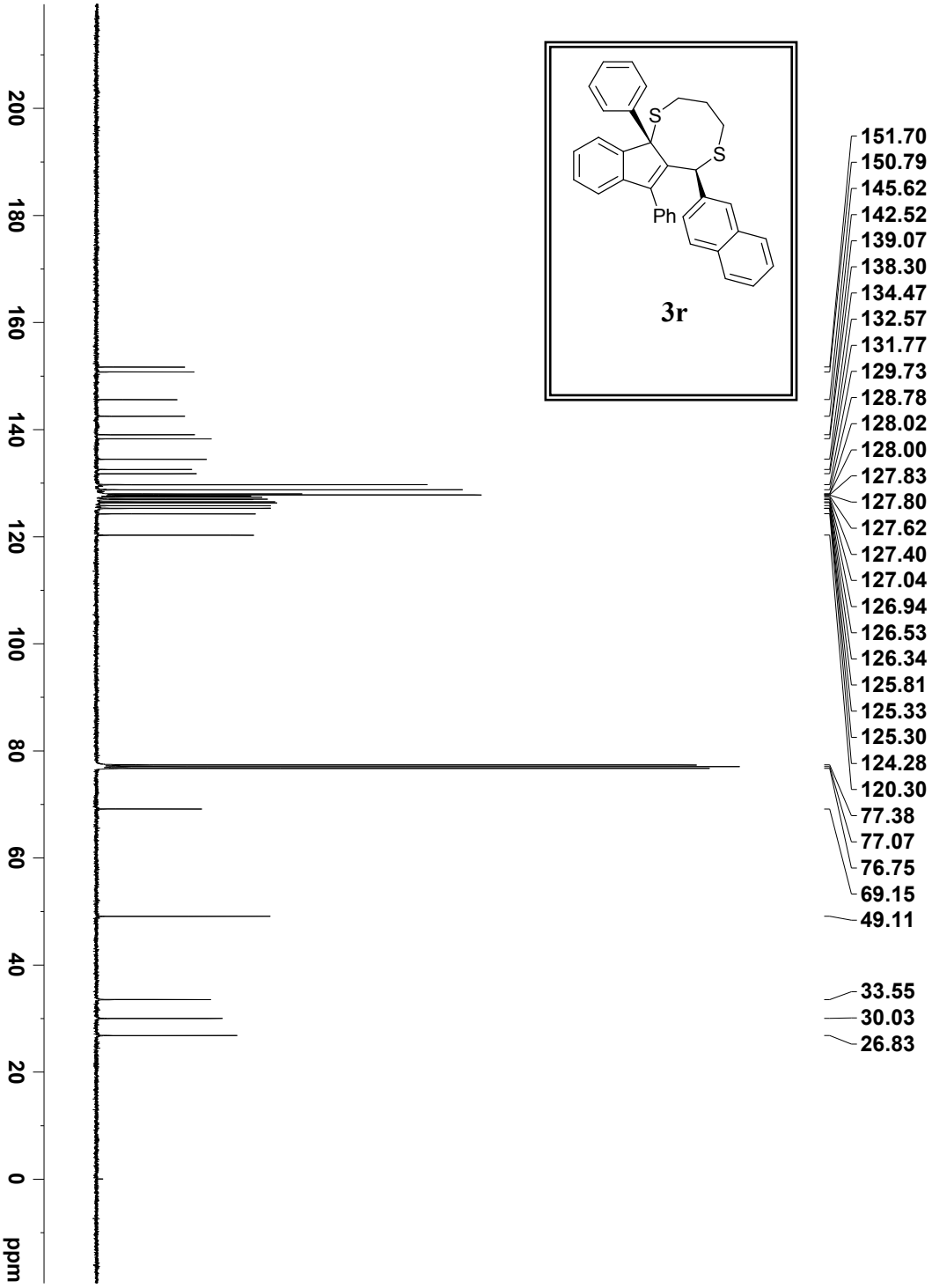
1.8
1.6
ppm


S
S
Ph
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134.47
132.57
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128.78
128.02
128.00
127.83
127.80
127.62
127.40
127.04
126.94
126.53
126.34
125.81
125.33
125.30
124.28
120.30
77.38
77.07
76.75
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200
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120
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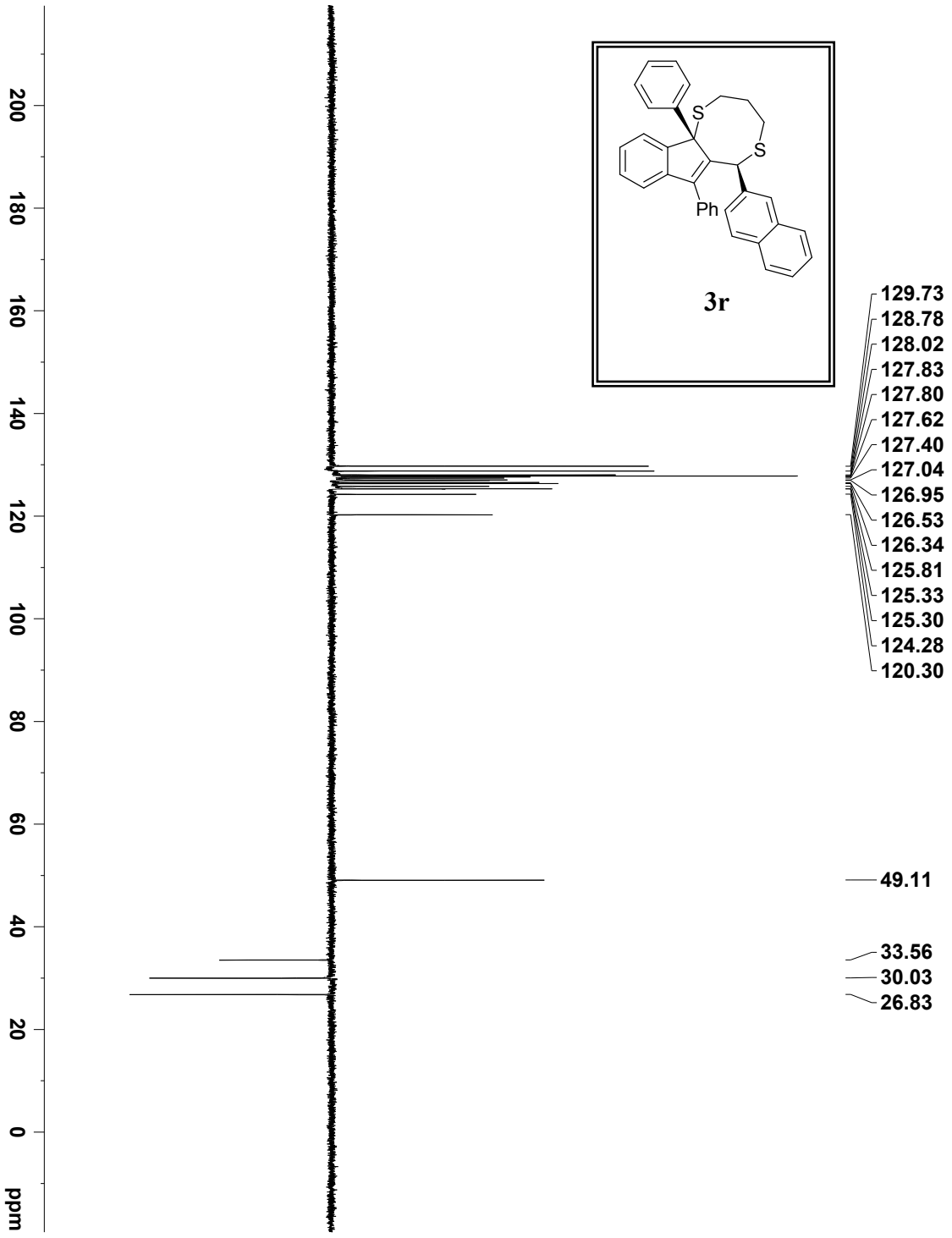
40
20
0
ppm


S
S
Ph
3r
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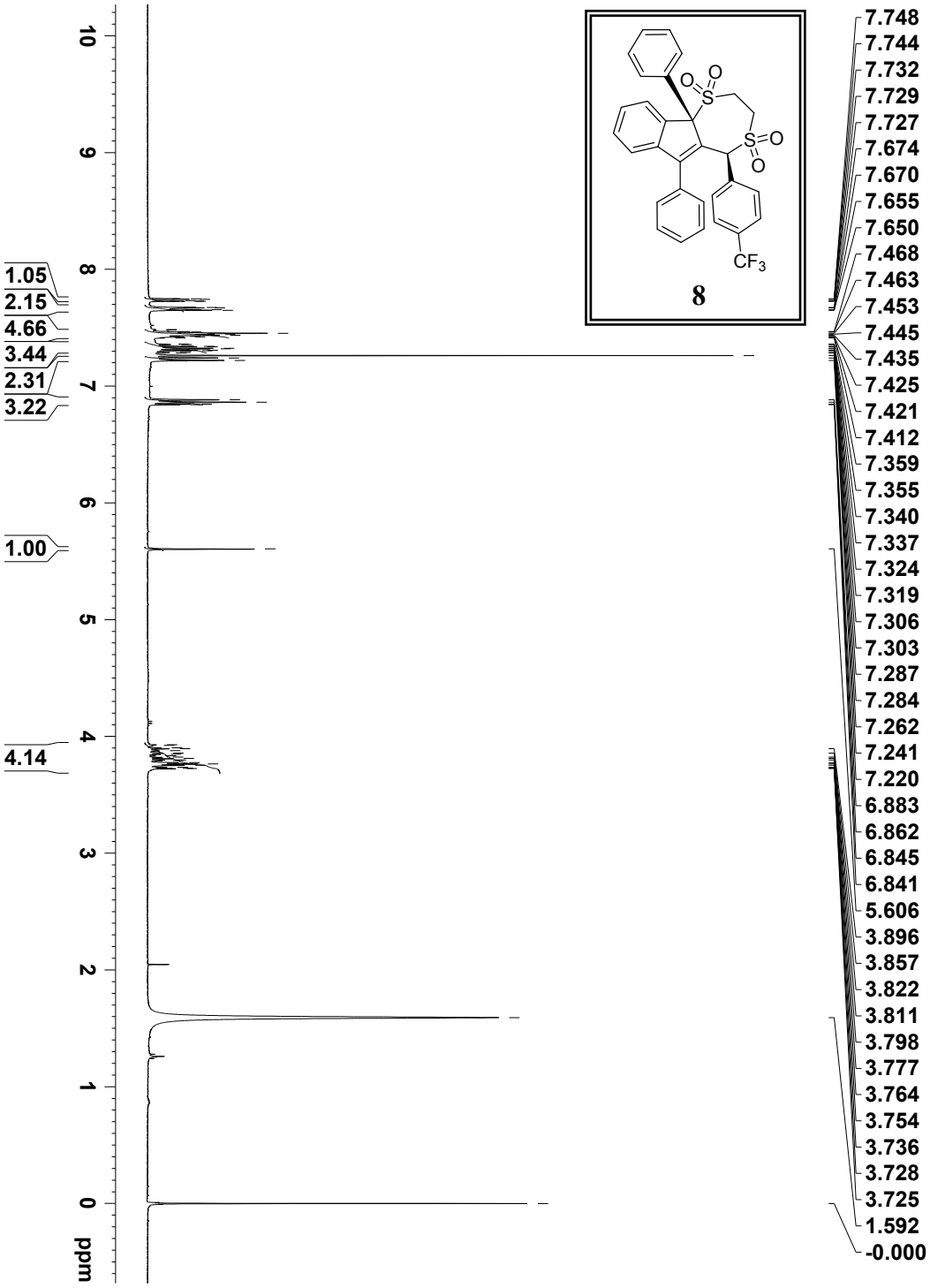
127.80
127.62
127.40
127.04
126.95
126.53
126.34
125.81
125.33
125.30
124.28
120.30
49.11
33.56
30.03
26.83
200
180
160
140
120
100
80
60
40
20
0
ppm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4.14
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7.729
7.727
7.674
7.670
7.655
7.650
7.468
7.463
7.453
7.445
7.435
7.425
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7.287
7.284
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6.862
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3.857
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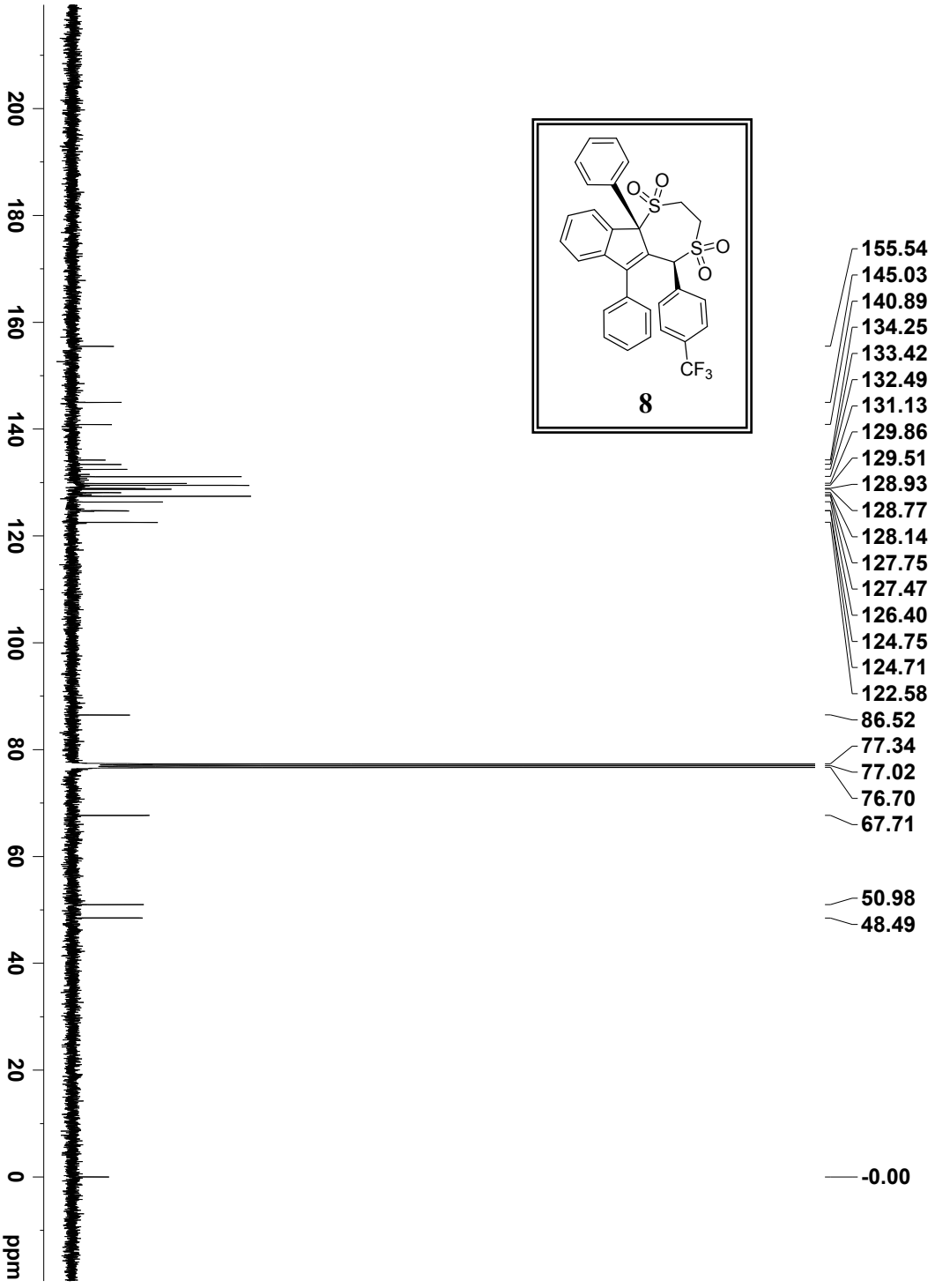
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132.49
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129.86
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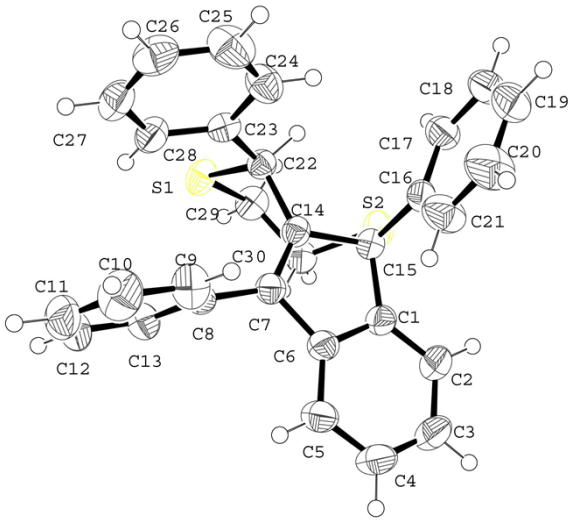
128.93
128.77
128.14
127.75
127.47
126.40
124.75
124.71
122.58
86.52
77.34
77.02
76.70
67.71
50.98
48.49
-0.00
200
180
160
140
120
100
80
60
40
20
0
ppm
O
O
S
S
O
O
CF3
8

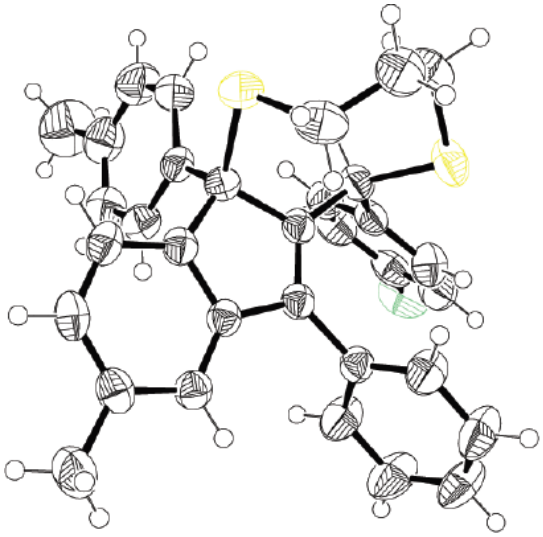
Crystal data and ORTEP for indenodithiepine 3a (CCDC 1019959)



ORTEP diagram for **3a.**

Data	Product **3a**
Molecular Formula	$C_{30}H_{24}S_2$
Molecular weight	448.13
size	0.35x 0.25x 0.20
Temperature/K	273(2)
Radiation	MoKα
Wavelength/Å	0.71073
a (Å)	8.6410(12)
b (Å)	10.6699(15)
c (Å)	25.373(4)
α (°)	90.00
β (°)	97.159(2)
γ (°)	90.00
Volume (Å^3)	2321.2(6)
z	3
Density (mg cm^{-3})	1.284
F(000)	944
μ (1/mm)	0.245
No of unique reflections	5343
No of parameters	4563
*R*_obs, *wR*2_obs	0.0450, 0.1146
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^3)	0.382, -0.147

Crystal data and ORTEP for indenodithiocine 3q (CCDC 1019960)



Data	Product **3q**
Molecular Formula	$C_{33}H_{29}ClS_2$
Molecular weight	525.13
space group	triclinic, P-1
colour	Yellow
size	0.22x 0.22x 0.11
Temperature/K	293(2)
Radiation	MoKα
Wavelength/Å	0.71073
a (Å)	9.901(2)
b (Å)	11.029(3)
c (Å)	14.297(3)
α (°)	74.650(4)
β (°)	76.568(4)
γ (°)	68.378(4)
Volume (Å^3)	1383.6(5)
z	2
Density (mg cm^{-3})	1.260
F(000)	552
μ (1/mm)	0.309
No of unique reflections	5382
No of parameters	4235
*R*_obs, *wR*2_obs	0.0619, 0.1434
$\Delta\rho_{max}$ $\Delta\rho_{min}$ (eÅ^3)	0.376, -0.230