Palladium-Catalyzed Three-Component Domino Reaction for the Preparation of Benzo[*b*]thiophene and Related Compounds

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Supporting Information

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General Information

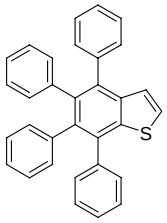
All reagents were used as received and used directly without further purification. Silica gel (200-300 mesh) for purification and silica gel TLC (F254) were purchased from Qing Dao Hai Yang Chemical Industry Co. of China. 1H NMR and 13C NMR spectra were recorded on a Bruker DPX-300 spectrometer. Mass spectra were obtained on a Waters Q-Tof MicroTM spectrometer. Element analytic data were obtained on a Thermo Electron Corporation flash EA 1112 element spectrometer. Melting points (uncorrected) were obtained on a X-4 micro-melting point apparatus. IR spectra were recorded on a Thermo Nicolet IR 200 spectrometer.Ultraviolet data were recorded in a Varian Cary 100 UV-visible spectrophotometer at room temperature in diluted dichloromethane solution (*ca.* 10^{-5} mol L^{-1}).

Reaction procedure :

General procedure: a reaction vessel was charged with 3 mmol diphenylacetylene, 10 mol% $Pd(OAc)_2$, 20 mol % Cy_3P, 2 mmol Na_2CO_3, 0.7 mmol LiBr in 5 mL DMF under N_2. Then 1mmol 3-bromothiophene was added to the vessel. The mixture was stirred at 120 ºC for 20 hours. The suspension was cooled down to r.t., diluted with 20 mL EtOAc and washed with 60 mL H_2O. The aqueous layer was extracted twice with EtOAc (10 mL) and the combined organic layers were dried over Na_2SO_4. After evaporation of the solvents the residue

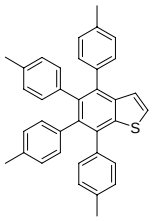
was subjected to silica gel chromatography or thin layer chromatography (TLC) (hexane).

3aa: 4,5,6,7-Tetraphenylbenzo[*b*]thiophene



Yield: 82%. Purple solid. m.p.: 206-207 ºC. ^{1}H NMR (300MHz, CDCl3): 6.82~6.90 (m, 10H), 7.15~7.32 (m, 11H), 7.36 (d, *J*=5.7Hz, 1H).^{13}C NMR (75MHz, $CDCl_3$): 124.68(CH), 125.44(CH), 125.55(CH), 126.50(CH), 126.73(CH), 126.76(CH), 127.13(CH), 127.16(CH), 127.61(CH), 128.02(CH), 129.99(CH), 130.64(CH), 131.70(CH), 131.73(CH), 135.02, 135.97, 137.00, 137.78, 138.47, 139.93, 139.99, 140.12, 140.21, 140.65. IR (KBr): 3056, 3022, 1600, 1503, 1490, 1441, 1415, 1279, 1109, 1072, 1026, 914, 835, 735, 699, 660, 587, 555, 543 cm^{-1}.HRMS m/z (M^{+}+H) Calcd for $C_{32}H_{22}S$: 439.1521, Found: 439.1518.

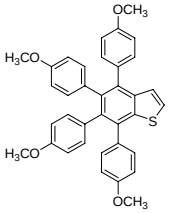
3ab: 4,5,6,7-Tetra*p*-tolylbenzo[*b*]thiophene



Yield: 54%. Purple solid. m.p.: 230-231 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): 2.10 (s, 6H,CH_3), 2.29 (s, 6H,CH_3), 6.66~6.73 (m, 8H), 6.99~7.18 (m, 9H), 7.30 (d, *J*=5.7Hz, 1H). ^{13}C NMR (75MHz, $CDCl_3$): 21.15(CH_3), 21.27(CH_3), 21.36(CH_3), 124.83(CH), 126.65(CH), 127.45(CH), 127.47(CH), 128.29(CH), 128.73(CH), 129.80(CH), 130.50(CH), 131.52(CH), 131.54(CH), 134.47, 134.59, 134.90, 135.72, 135.90, 136.43, 137.11, 137.25, 137.30, 137.55, 137.89, 138.46, 140.67. IR (KBr): 3021, 2920, 1890, 1611, 1516, 1448, 1421, 1373, 1182, 111

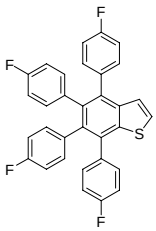
1, 1020, 819, 738, 665, 543 cm^{-1} .HMRS m/z(M^++Na) Calcd for $C_{36}H_{30}S$: 517.1965, found: 517.1962.

3ac:4,5,6,7-Tetrakis(4-methoxyphenyl)benzo[*b*]thiophene



Yield: 61%. White solid. m.p.: 259-261 ºC. ^{1}H NMR (300M Hz, $CDCl_3$): 3.53 (s, 6H,CH_3), 3.66~3.67 (d, 6H,CH_3), 6.35 ~6.37 (m, 3H), 6.61~6.70(m, 9H), 6.99~7.14 (m, 5H), 7.23 (d, *J*=5.7Hz, 1H). ^{13}C NMR (75MHz, $CDCl_3$): 54.91(CH_3), 55.09(CH_3),5 5.12(CH_3), 112.34(CH), 113.07(CH), 113.44(CH), 124.81(CH), 126.68(C H), 131.10(CH), 131.69(CH), 132.65, 132.69(CH), 132.89, 132.91, 134.6 7, 135.66, 137.04, 137.80, 138.59, 140.84, 157.04, 157.12, 157.95, 158.3 2. IR (KBr): 2996, 2931, 2834, 2361, 1608, 1514, 1461, 1423, 1373, 128 7, 1245, 1177, 1033, 833, 806, 766, 551 cm^{-1}.HMRS m/z (M^++Na) Calcd for $C_{36}H_{30}O_4S$: 587.1762, found: 581.1766.

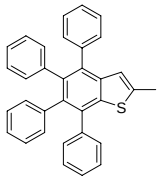
3ad: 4,5,6,7-Tetrakis(4-fluorophenyl)benzo[*b*]thiophene



Yield: 73%. White solid. m.p.: 232-233 ºC. ^{1}H NMR (300M Hz, $CDCl_3$): 6.61~6.79 (m, 8H), 6.91~6.99 (m, 4H), 7.12~7.2 6 (m, 5H), 7.42 (d, *J*=5.4Hz, 1H). ^{13}C NMR (75MHz, $CDCl_3$) : 114.01(J_{C-F}=2.6Hz,CH), 114.3(J_{C-F}=2.7Hz,CH), 114.86(J_{C-F} =21.2Hz,CH), 115.3(J_{C-F}=21.4Hz,CH),124.44(CH), 127.74(CH), 131.5(J_{C-F}=8Hz,CH), 132.0(J_{C-F}=8Hz,CH), 132.94(J_{C-F}=7.9Hz,CH), 134.38, 13 5.28, 135.5(J_{C-F}=3.5Hz,2C), 135.7(J_{C-F}=3.1Hz), 135.71(J_{C-F}=4.1Hz), 13

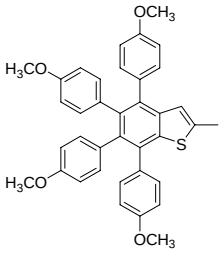
6.12, 136.95, 138.68, 140.92, 160.8(J_{C-F}=244Hz,CF), 160.9(J_{C-F}=244Hz, CF), 161.6(J_{C-F}=245Hz,CF), 161.9(J_{C-F}=245Hz,CF). HMRS m/z(M^++H) IR (KBr): 3072, 1886, 1687, 1603, 1514, 1454, 1426, 1399, 1326, 1297, 1227, 1156, 1095, 1014, 934, 856, 838, 816, 765, 740, 708, 667, 542, 533, 515 cm^{-1}. Calcd for $C_{32}H_{18}F_4S$:511.1144, found: 511.1106. Anal. Calcd. For $C_{32}H_{18}F_4S$: C, 75.28; H, 3.55. Found: C, 74.84; H. 3.44.

3ca: 2-Methyl-4,5,6,7-tetraphenylbenzo[*b*]thiophene



Yield: 71%. Purple solid. m.p.: 190-191 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): 2.35 (s, 3H,CH_3), 6.70~6.76 (m, 11H), 7.04~7.20 (m, 10H), ^{13}C NMR (75MHz, $CDCl_3$): 16.24(CH_3), 122.26(CH), 125.39(CH), 125.48(CH), 126.41(CH), 126.72(CH), 126.75(CH), 127.07(CH), 127.61(CH), 127.99(CH), 129.98(CH), 130.67(CH), 131.80(2CH), 134.66, 135.05, 136.16, 137.69, 139.22, 140.09, 140.29, 140.31, 140.39, 140.42, 141.76. IR (KBr): 3055, 3024, 2916, 1600, 1496, 1442, 1418, 1375, 1128, 1073, 1027, 758, 702, 574, 543 cm^{-1} . HMRS m/z (M^++Na) Calcd for $C_{33}H_{24}S$: 475.1496,found: 475.1495.

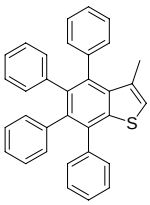
3cc: 2-Methyl -4,5,6,7-tetrakis(4-methoxyphenyl)benzo[*b*]thiophene



Yield: 57%. White solid. m.p.: 200-203 ºC. ^{1}H NMR (300MHz, $CDCl_3$): 2.46(s, 3H,CH_3), 3.62 (s, 6H,OCH_3), 3.76 (s, 6H,OCH_3), 6.42~6.46 (m, 4H), 6.70~6.78(m, 9H), 7.

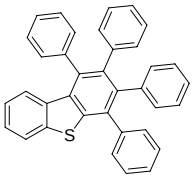
08 (d, *J*=8.7Hz, 2H), 7.18 (d, *J*=8.7Hz, 2H). ^{13}C NMR (75MHz, $CDCl_3$): 16.16(CH_3),54.91(OCH_3), 55.08(OCH_3), 55.10(OCH_3), 112.26(CH), 112.29(CH), 113.01(CH), 113.37(CH), 122.36(CH), 131.03(CH), 131.65(CH), 132.69(CH), 132.71(CH), 132.78, 132.88, 133.03, 133.04, 134.24, 134.69, 136.14, 137.65, 139.27, 140.51, 141.15, 156.97, 157.04, 157.85, 158.26. IR (KBr): 2924, 2835, 1608, 1514, 1461, 1378, 1286, 1245, 1175, 1107, 1032, 833, 768, 620, 551 cm^{-1}.HMRS m/z (M^++Na) Calcd for $C_{37}H_{32}O_4S$: 595.1918,found: 595.1923.

3da: 3-Methyl 4,5,6,7-tetrakis(4-methoxyphenyl) benzo[*b*]thiophene



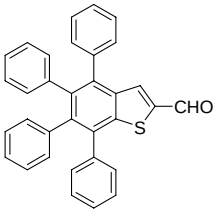
Yield: 64%. Purple solid. m.p.: 251-252 ºC. ^{1}H NMR (300MHz, $CDCl_3$): 1.80(s, 3H,CH_3), 6.92~6.94 (m, 10H), 7.09 (d, *J*=0.9Hz, 1H), 7.21~7.34 (m, 8H), 7.39~7.42 (m, 2H). ^{13}C NMR (75MHz, $CDCl_3$): 17.78(CH_3), 124.35(CH), 125.30(CH), 125.52(CH), 126.50(CH),126.60(CH), 126.72(CH), 126.87(CH),127.15(CH), 128.01(CH), 130.16(CH), 131.24(CH), 131.59(CH), 131.63(CH), 134.43, 135.39, 136.01, 136.58, 136.65, 138.90, 139.90, 140.04, 140.11, 140.20, 142.09. IR (KBr): 3055, 3024, 2960, 2920, 2851, 1600, 1497, 1442, 1369, 1277, 1144, 1063, 1024, 913, 851, 771, 732, 698, 590, 557 cm^{-1}. HMRS m/z (M^++H) Calcd for $C_{33}H_{24}S$: 453.1678, found: 453.1669.

3ea: 1, 2, 3, 4-Tetraphenyldibenzothiophene



Yield: 52%. Purple solid. m.p.: 215-217 ºC ^{1}H NMR (300 MHz, $CDCl_3$): 6.62 (d, *J*=8.1Hz, 1H), 6.84~6.90 (m, 10H), 6.97~7.03 (m, 2H),7.23~7.34 (m, 10H), 7.36 (d, *J*=1.8Hz, 1H). ^{13}C NMR (75MHz, $CDCl_3$): 122.30(CH), 123.76(CH), 125.14(CH), 125.40(CH), 125.62(CH), 125.97(CH), 126.54(CH), 126.72(CH), 127.05(CH), 127.26(CH), 128.07(CH), 128.27(CH), 130.06(CH), 130.23(CH), 131.37(CH), 131.53(CH), 132.46, 135.18, 136.28, 137.35, 138.76, 139.00, 139.71, 139.74, 139.90, 140.11, 140.45. IR (KBr): 3055, 2921, 2362, 1633, 1441, 1382, 1071, 1028, 734, 699, 569 cm^{-1}.HMRS m/z (M^{+}+Na) Calcd for $C_{36}H_{24}S$: 511.1496, found: 511.1494.

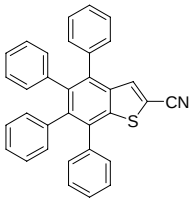
3fa: 4,5,6,7-Tetraphenylbenzo[*b*]thiophene-2-carbaldehyde



Yield: 47%. yellow solid. m.p.: 269-270 ºC ^{1}H NMR (300MHz, $CDCl_3$): 6.73~6.82 (m, 10H), 7.10~7.19 (m, 10H), 7.73 (s, 1H), 9.83 (s, 1H,CHO), ^{13}C NMR (75MHz, $CDCl_3$): 125.83(CH), 126.01(CH), 126.94(CH), 127.09(CH), 127.57(CH), 127.89(CH), 128.27(CH), 129.80(CH), 130.47(CH), 131.28(CH), 131.50(CH), 135.37(CH), 135.77, 137.81, 138.50, 138.92, 138.95, 139.10, 139.27, 139.31, 140.89, 143.54, 143.86, 184.75(CHO).IR (KBr): 3053, 3023, 2809, 1670, 1599, 1546, 1486, 1422, 1344, 1245, 1177, 1144, 1106, 856, 779, 740, 699, 655, 568cm^{-1}.HMRS m/z(M^{+}+Na) Calcd for $C_{33}H_{22}OS$:489.1288,found:489.1250. Anal.Calcd. For $C_{33}H_{22}OS$: C, 84.95;

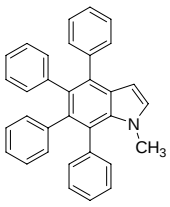
H, 4.75. Found: C, 84.79; H. 4.83.

3ga: 4,5,6,7-Tetraphenylbenzo[*b*]thiophene-2-carbonitrile



Yield: 43%. Yellow solid. m.p.: 298-299 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): 6.80~6.91 (m, 10H), 7.14~7.23 (m, 10H), 7.69 (s, 1H). ^{13}C NMR (75MHz, $CDCl_3$): 110.10(CN), 114.60, 125.91(CH), 126.09(CH), 126.96(CH), 126.98(CH), 127.21(CH), 127.80(CH), 127.94(CH), 128.41(CH), 129.59(CH), 130.35(CH), 131.24(CH), 131.42(CH), 135.02, 136.09(CH), 136.71, 137.60, 138.63, 138.94, 139.02, 139.07, 139.37, 140.55, 142.64. R (KBr): 3026, 2215, 1598, 1485, 1443, 1417, 1230, 1101, 1073, 1026, 882, 777, 761, 735, 713, 698, 572, 556, 535cm^{-1}.HMRS m/z(M^{+}+Na) Calcd for $C_{33}H_{21}NS$: 486.1293, found: 486.1254.Anal. Calcd. For $C_{33}H_{21}NS$: C, 85.50; H, 4.57; N, 3.02; Found: C, 84.98; H. 4.41; N, 2.70.

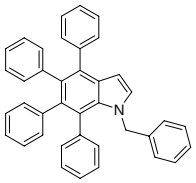
5aa: 1-Methyl-4,5,6,7-tetraphenyl-1*H*-indole



Yield: 66%. White solid. m.p.: 189-190 ºC. ^{1}H NMR (300MHz, $CDCl_3$): 3.17 (s, 3H,CH_3), 6.38~6.39 (m, 1H), 6.83~6.84 (m, 10H), 6.98(d, *J*=3Hz, 1H), 7.14~7.25 (m, 10H). ^{13}C NMR (75MHz, $CDCl_3$): 36.62(CH_3), 100.98(CH), 124.88(CH), 124.92(CH), 125.96(CH), 126.26(CH), 126.44(CH), 126.63(CH), 126.95(CH), 127.39(CH), 128.42, 130.75(CH), 131.71(CH), 131.88(CH), 132.17(CH), 132.76, 1

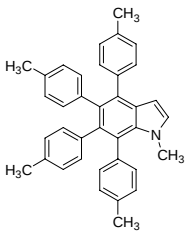
33.38, 136.24, 138.57, 140.18, 140.72, 140.98. IR (KBr): 3055, 3019, 1600 , 1518, 1494, 1469, 1440, 1425, 1391, 1374, 1334, 1069, 1027, 761, 744, 73 3, 694, 594, 574cm^{-1}. HRMS m/z(M^++H) Calcd for $C_{33}H_{25}N$: 436.2066, Fou nd: 436.2060.

5ba: 1-Benzyl-4,5,6,7-tetraphenyl-1*H*-indole



Yield: 53%. White solid. m.p.: 231-232 ºC. ^{1}H NMR (300MH z, $CDCl_3$): 4.73 (s, 2H,CH_2), 6.48 (d, *J*=3Hz, 1H), 6.60~6.63 (m, 2H), 6.71~6.87 (m, 10H), 6.91~7.01 (m, 6H), 7.11~7.21 (m, 6H), 7.28~7.31 (m, 2H). ^{13}C NMR (75MHz, $CDCl_3$): 51.62(CH_2), 102.27 (CH), 124.98(CH), 125.00(CH), 125.15, 126.12(CH), 126.22(CH), 126.31(C H), 126.58(CH), 126.65(CH), 127.05(CH), 127.13(CH), 127.54(CH), 128.32 (CH), 128.84, 130.93(CH), 131.24(CH), 131.42(CH), 131.94(CH), 132.26(C H), 132.47, 132.93, 133.10, 136.73, 138.27, 138.93, 140.30, 140.85, 141.09. IR (KBr): 3056, 3022, 1600, 1519, 1494, 1453, 1440, 1380, 1328, 1240, 11 55, 1070, 1028, 760, 744, 704, 697, 593cm^{-1}. HRMS m/z(M^++H) Calcd for $C_{39}H_{29}N$: 512.2379, Found: 512.2374.

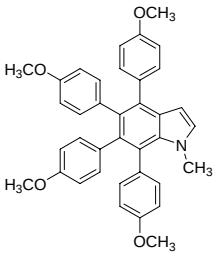
5ab: 1-Methyl-4,5,6,7-tetra*p*-tolyl-1*H*-indole



Yield: 47%. White solid. m.p.: 232-233 ºC. ^{1}H NMR (300MH z, $CDCl_3$): 2.08(s, 3H,CH_3),2.10(s, 3H,CH_3), 2.28(s, 3H,CH_3), 2.29 (s, 3H,CH_3), 3.13 (s, 3H,NCH_3), 6.34 (d, *J*=3.3Hz, 1H), 6

.61~6.73 (m, 8H), 6.92~7.01 (m, 5H), 7.10~7.15 (m, 4H). ^{13}C NMR (75MHz , $CDCl_3$): 21.08(CH_3), 21.24(CH_3), 21.26(CH_3), 36.60(NCH_3), 100.98(CH), 124.93, 126.96(CH), 127.18(CH), 127.63(CH), 128.11(CH), 128.40,130.62(CH),131.43(CH), 131.55(CH), 131.66(CH), 131.96(CH), 132.25, 132.61, 13 3.57, 133.81, 133.83, 135.11, 135.68, 135.89, 136.44, 137.43, 137.89, 138.1 5. IR (KBr): 3018, 2921, 2861, 1897, 1525, 1513, 1452, 1429, 1372, 1331, 1263, 1210, 1180, 1110, 1091, 1019, 854, 818, 803, 771, 750, 736, 697, 676, 543, 530cm^{-1}. HRMS m/z(M^++H) Calcd for $C_{37}H_{33}N$: 492.2692, Found: 492 .268.

5ac: 1-Methyl-4,5,6,7-tetrakis(4-methoxyphenyl)- 1*H*-indole



Yield: 47%. Yellow solid. m.p.: 253-254 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): 3.16 (s, 3H,NCH_3), 3.61 (s, 3H,OCH_3),3.63 (s , 3H,OCH_3), 3.76(s, 3H,OCH_3), 3.77(s, 3H,OCH_3), 6.35~6.4 4 (m, 5H), 6.70~6.77 (m, 8H), 6.94 (d, *J*=3Hz, 1H), 7.12~7. 18 (m, 4H). ^{13}C NMR (75MHz, $CDCl_3$): 36.69(NCH_3), 54.87(OCH_3), 54.89(OCH_3), 55.08(OCH_3), 100.93(CH), 111.85(CH), 112.06(CH), 112.40(CH), 1 12.88(CH), 124.71, 128.48, 131.02, 131.50(CH), 131.78(CH), 132.14, 132.4 1, 132.61(CH), 132.71(CH), 132.82, 133.04(CH), 133.53, 133.73, 133.77, 1 36.49, 156.60, 156.64, 157.56, 158.09. IR (KBr): 2930, 2834, 1609, 1574, 1 514, 1458, 1429, 1393, 1373, 1333, 1285, 1244, 1176, 1106, 1035, 832, 808, 776, 740, 588, 552cm^{-1}. HRMS m/z(M^++H) Calcd for $C_{37}H_{33}NO_4$: 556.2488 , Found: 556.2484.

huanghn318p3

7.374
7.355
7.320
7.314
7.307
7.293
7.288
7.259
7.253
7.239
7.220
7.214
7.203
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7.190
7.188
7.169
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6.896
6.888
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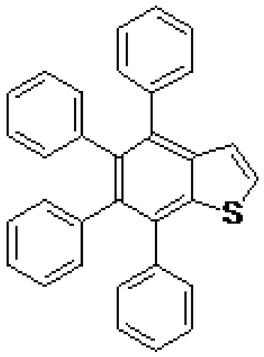
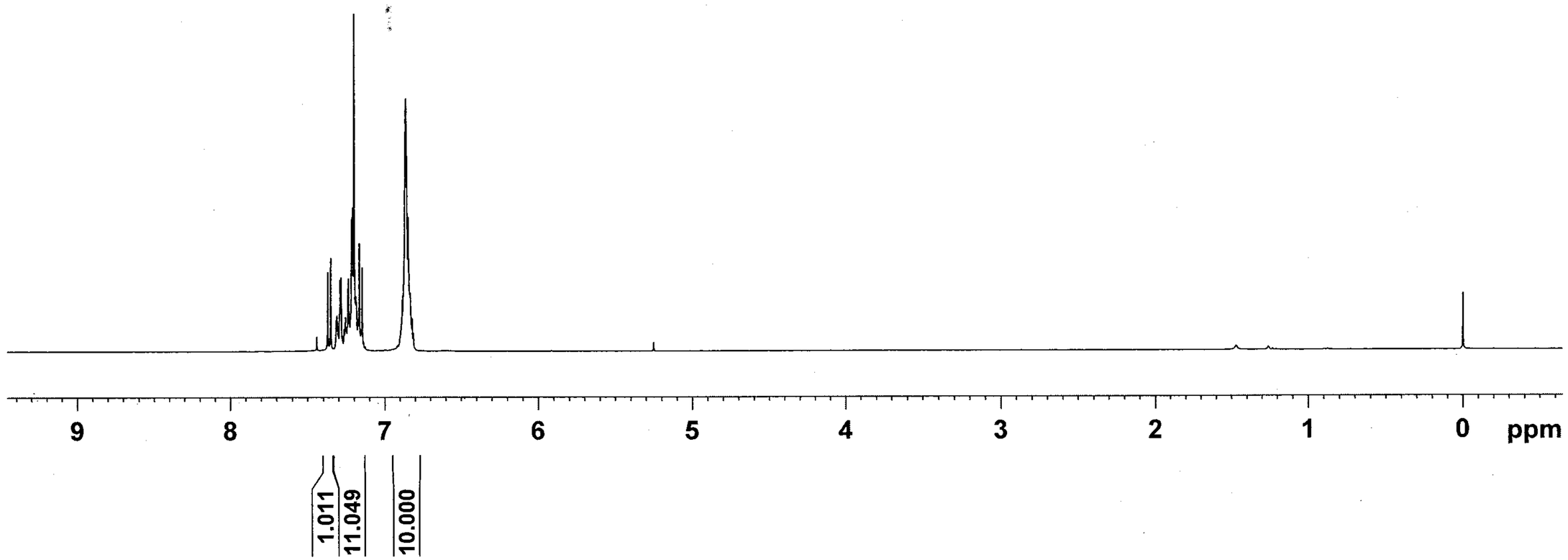
6.866
6.849
6.839
6.836
6.824
6.816

-0.000



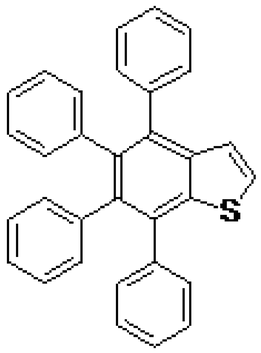
3aa



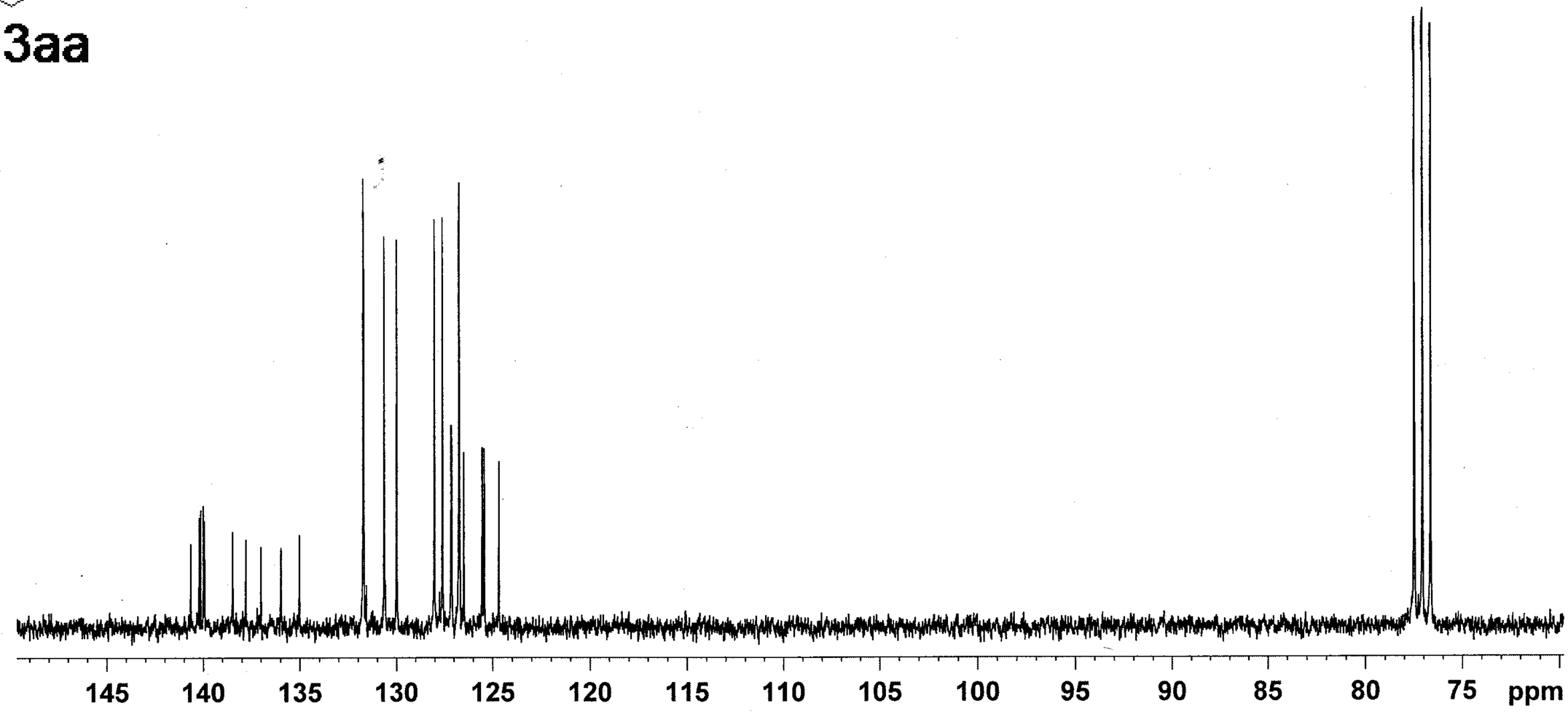
huanghn318p3 C13CPD

140.650
140.205
140.124
139.985
139.927
138.466
137.783
136.995
135.973
135.021
131.733
131.702
130.637
129.989
128.023
127.607
127.163
127.131
126.756
126.731
126.499
125.545
125.440
124.677

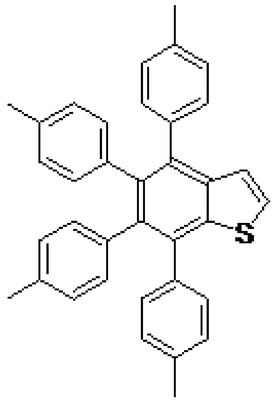
77.491
77.068
76.644



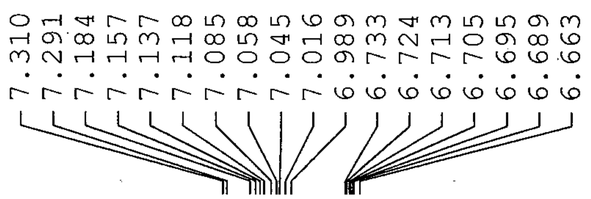
3aa

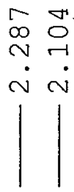


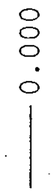
huanghn212 p3proton



3ab





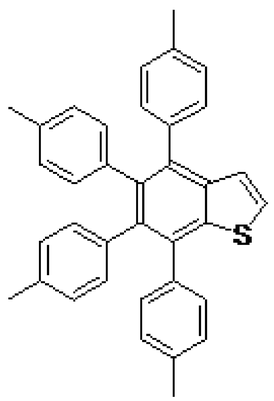


huanghn212 p3 C13CPD

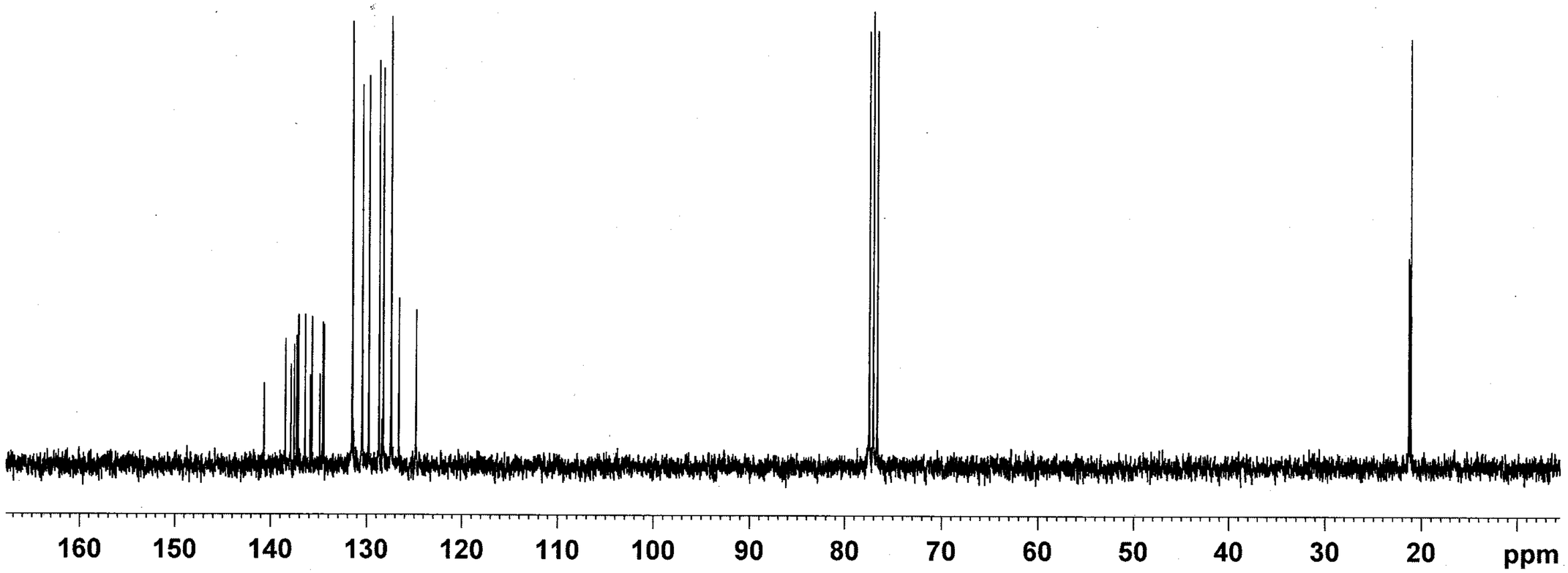
140.672
138.456
137.892
137.551
137.302
137.245
137.114
136.427
135.898
135.720
134.902
134.592
134.465
131.543
131.516
130.497
129.803
128.728
128.286
127.474
127.449
126.652
124.834

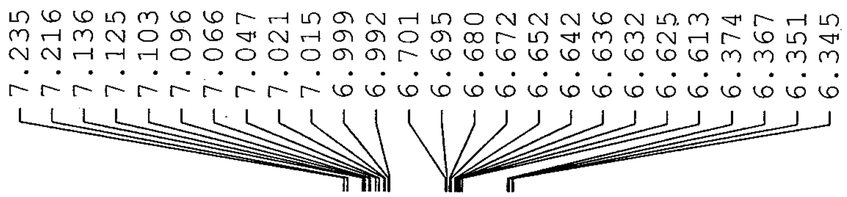
77.492
77.069
76.645

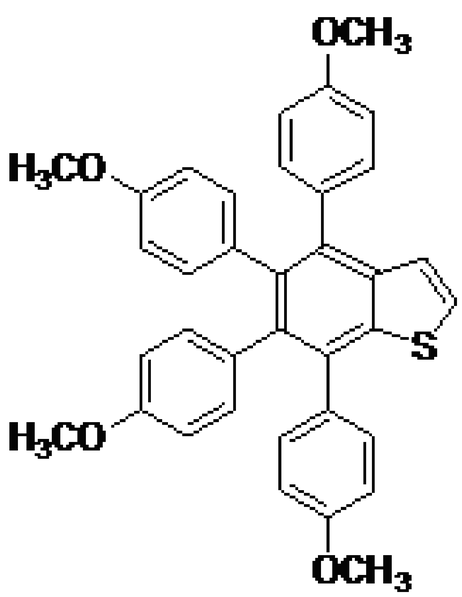
21.362
21.272
21.150



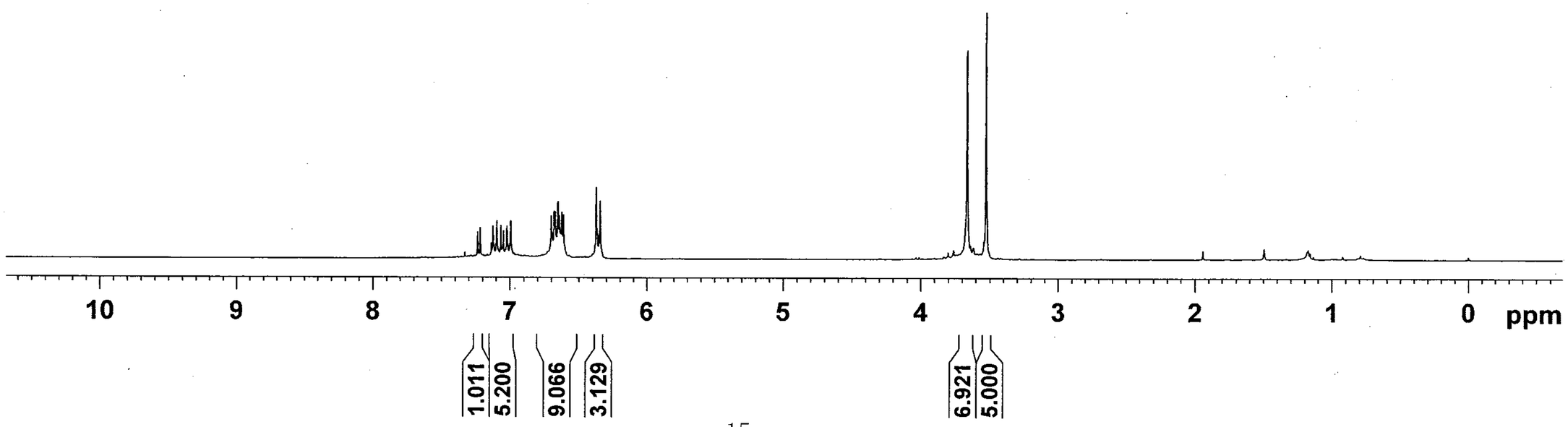
3ab







3ac



huanghn 228 p3 C13CPD

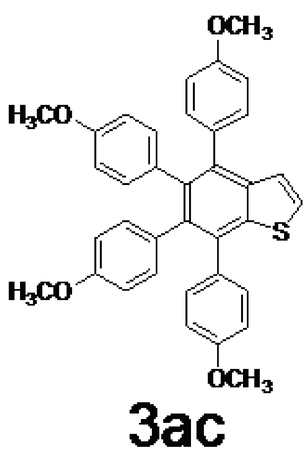
158.324
157.949
157.116
157.043

140.837
138.587
137.803
137.042
135.663
134.669
132.913
132.893
132.683
132.646
131.690
131.103
126.677
124.808

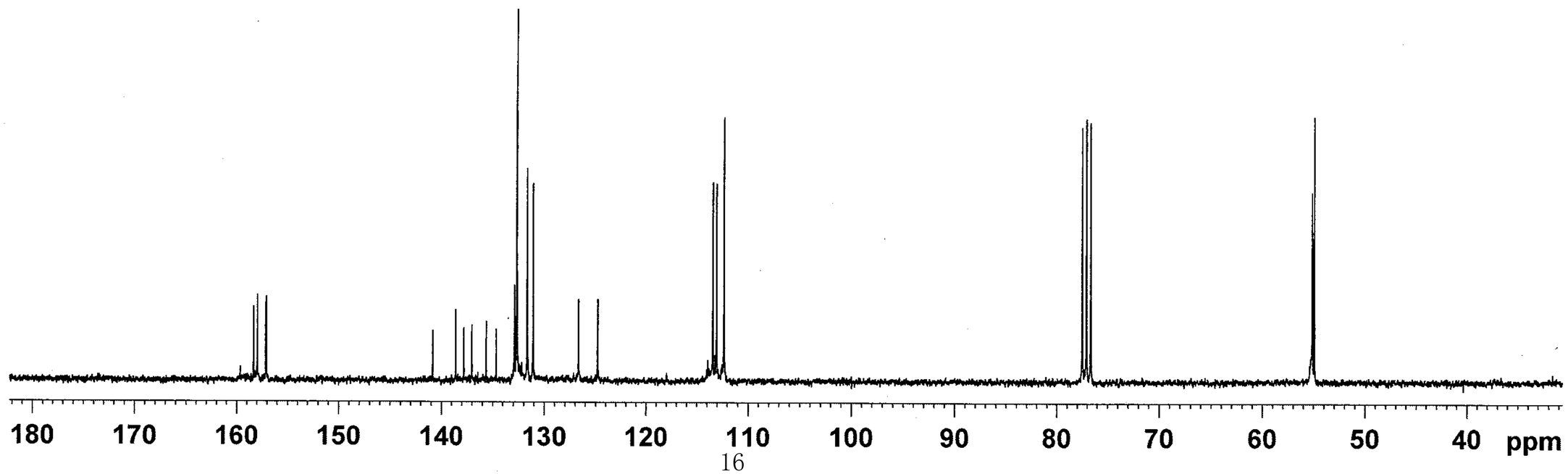
113.444
113.066
112.329

77.503
77.079
76.656

55.117
55.091
54.911



3ac



7.426
7.408
7.259
7.253
7.241
7.231
7.219
7.213
7.171
7.160
7.136
7.117
6.991
6.962
6.938
6.910
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6.760
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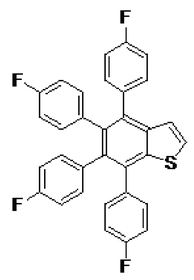
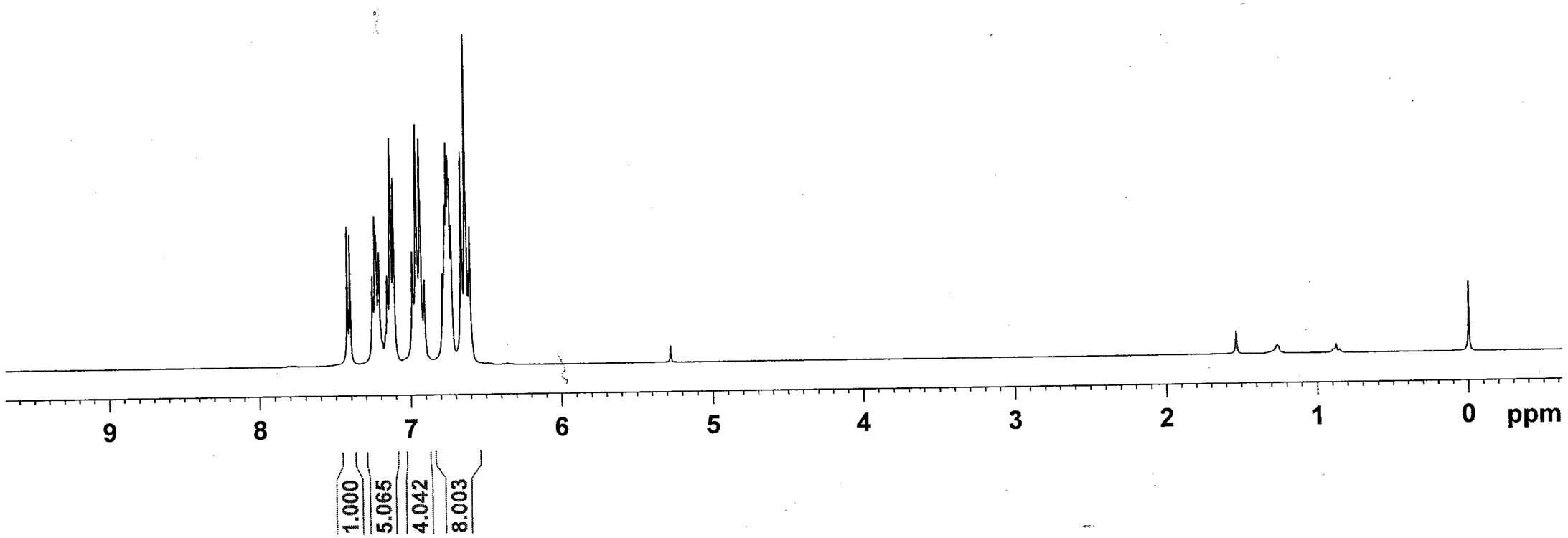
6.743
6.730
6.664
6.635
6.606

-0.000



3ad

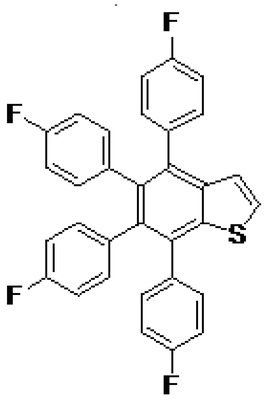


huanghn317 p3 C13CPD

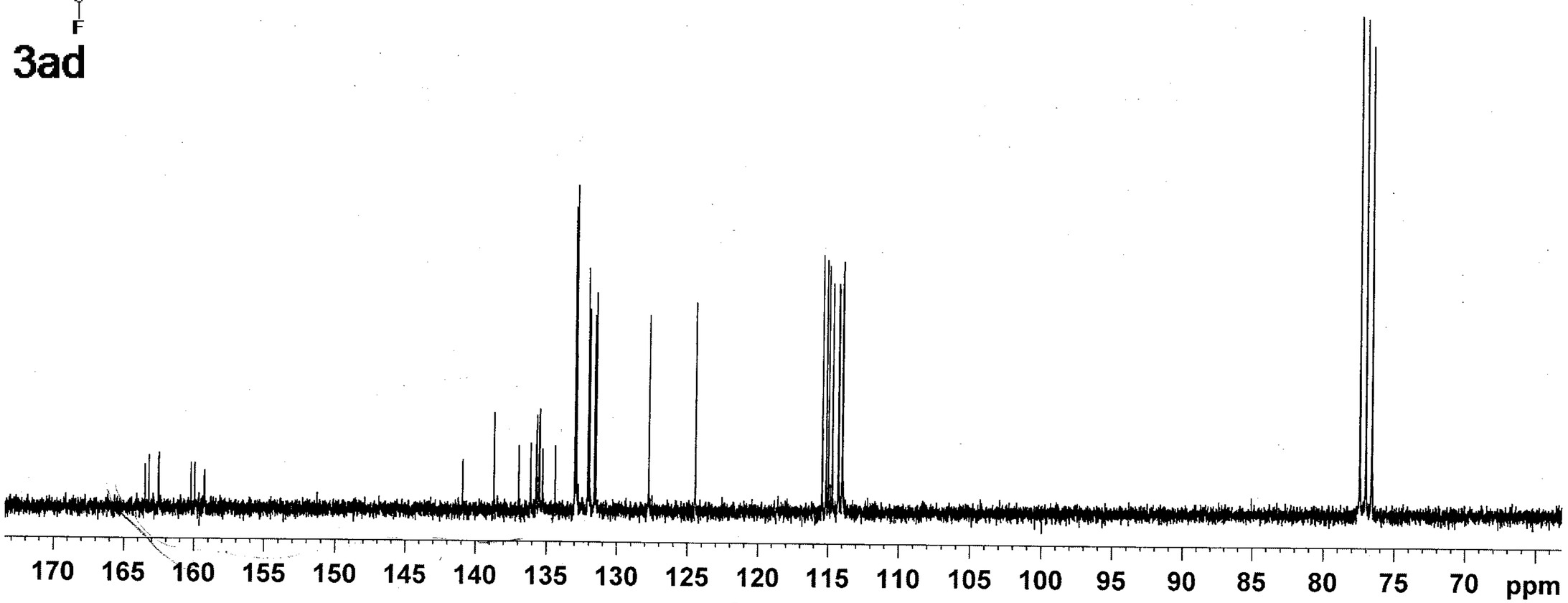
163.503
163.227
162.549
162.498
160.230
159.962
159.292
159.242

140.912
138.685
136.949
136.114
135.721
135.680
135.528
135.482
135.271
134.382
132.990
132.886
132.067
131.959
131.595
131.489
127.738
124.442
115.438
115.153
114.994
114.710
114.307
114.270
114.024
113.987

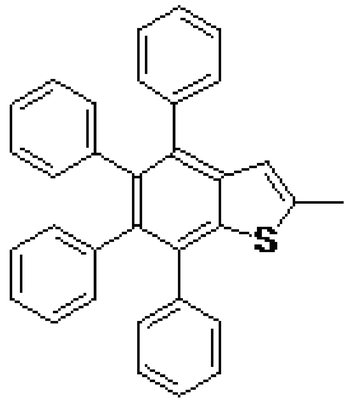
77.459
77.035
76.611



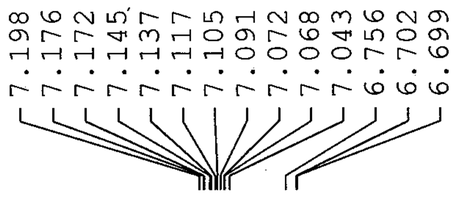
3ad

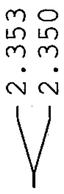


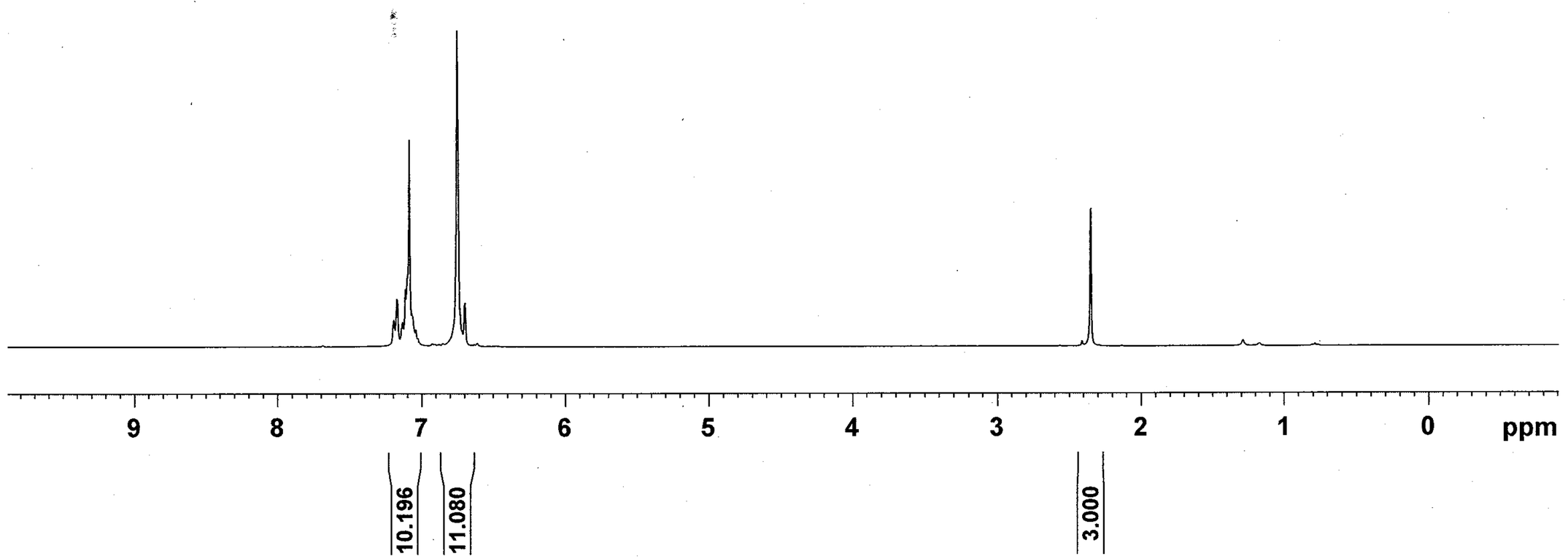
huanghn230P32



3ca





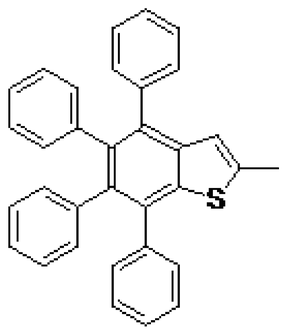


huanghn230P32 C13CPD

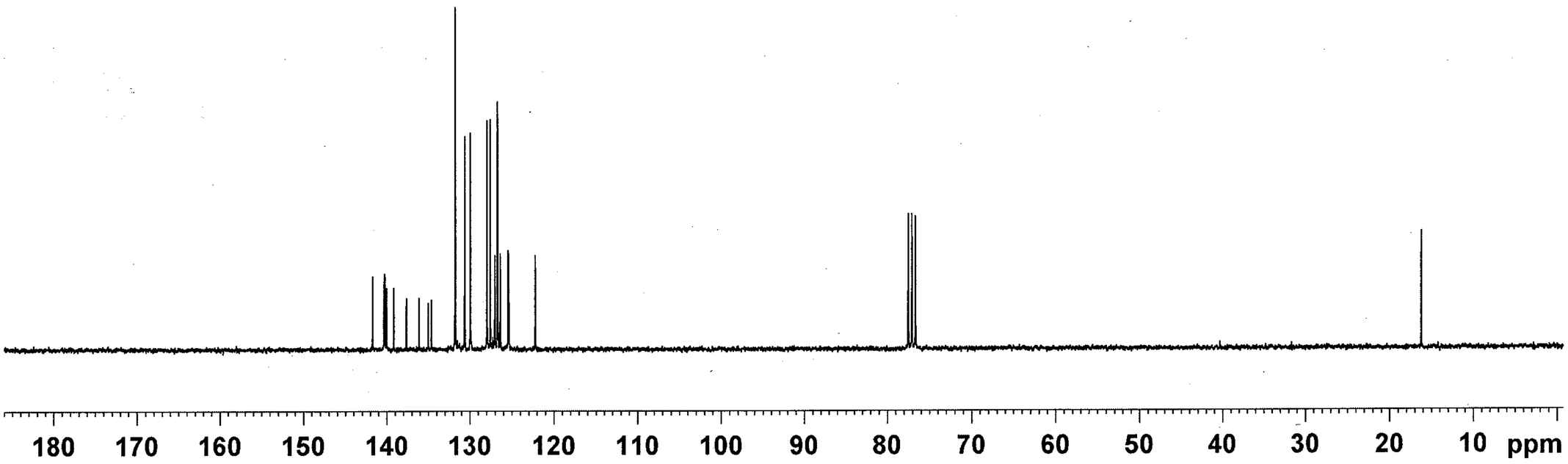
141.761
140.421
140.393
140.313
140.287
140.091
139.221
137.690
136.158
135.053
134.664
131.796
130.665
129.981
127.992
127.606
127.065
126.753
126.721
126.413
125.484
125.394
122.263

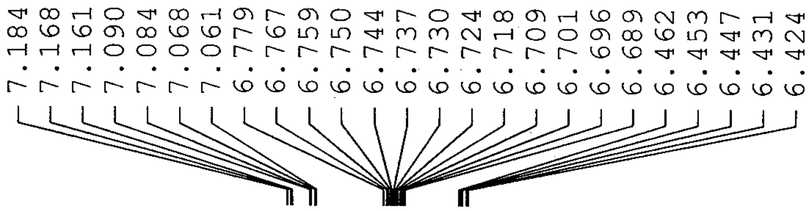
77.534
77.111
76.688

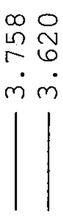
16.244

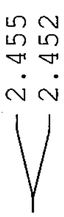


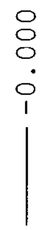
3ca

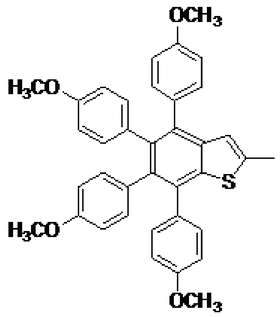




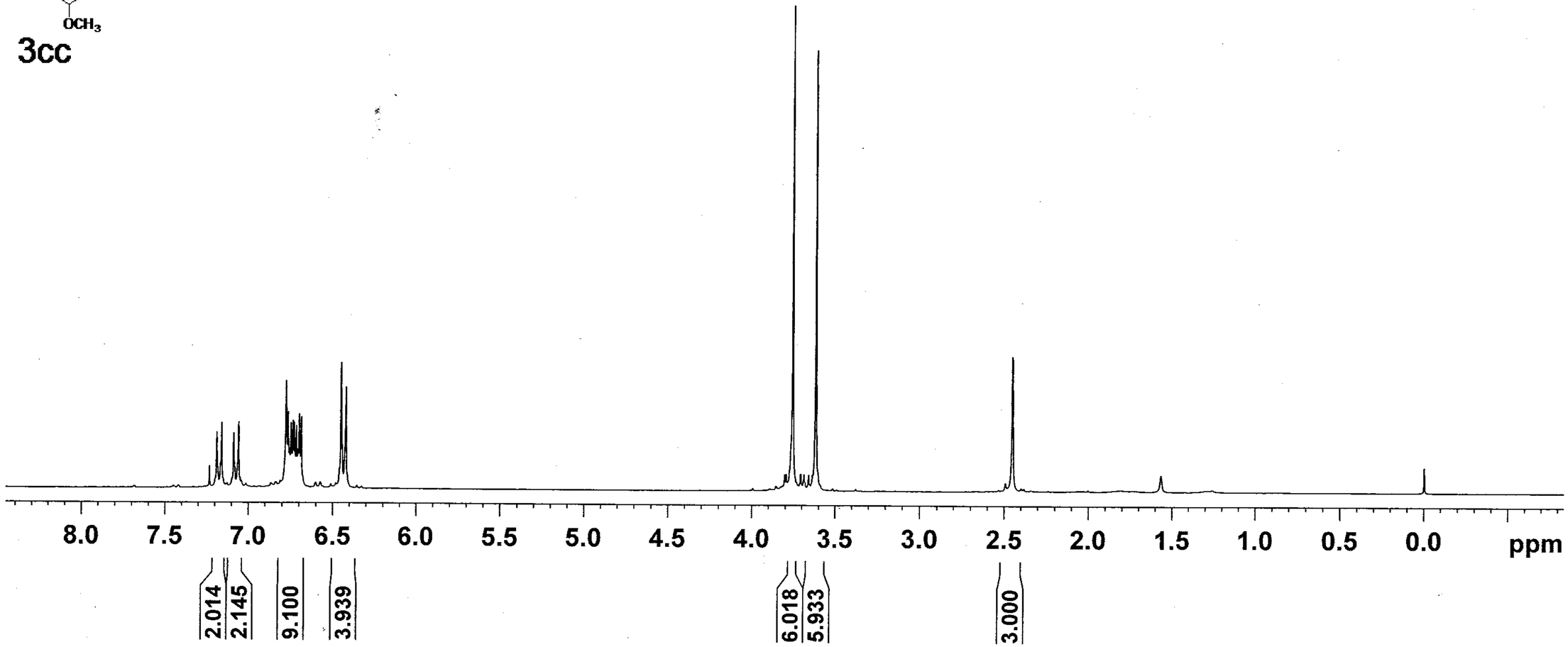








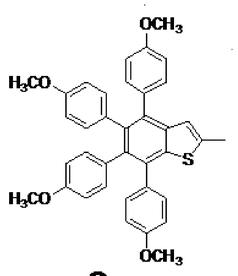
3cc



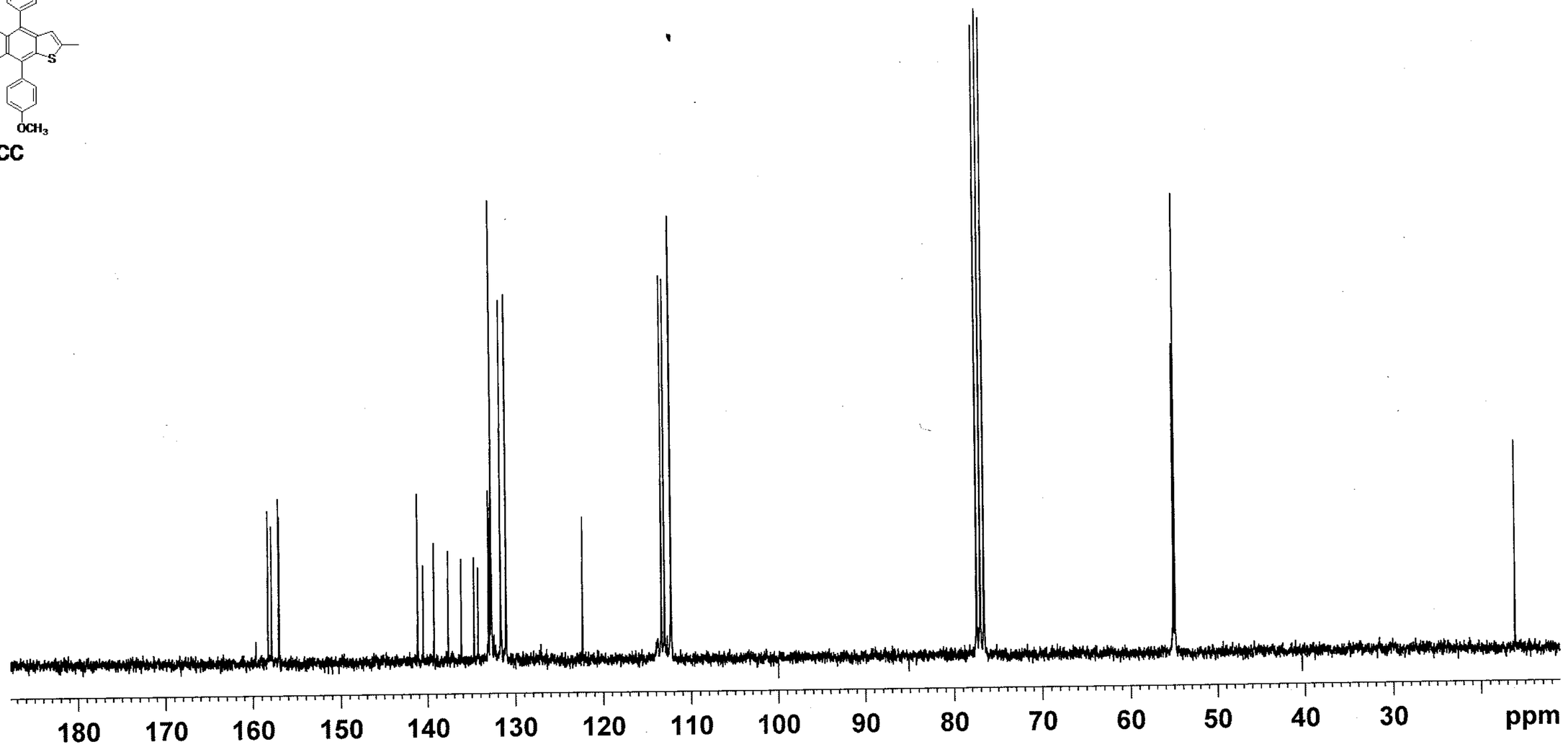
158.255
157.850
157.038
156.974
141.145
140.511
139.270
137.647
136.139
134.691
134.244
133.037
133.025
132.875
132.784
132.707
132.688
131.649
131.030
122.360
113.369
113.011
112.287
112.263

55.101
55.083
54.905

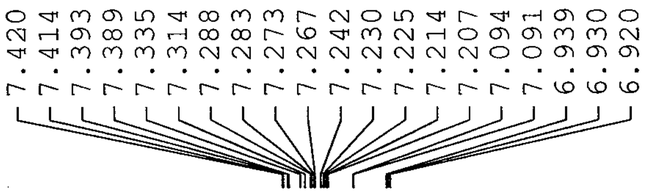
16.156

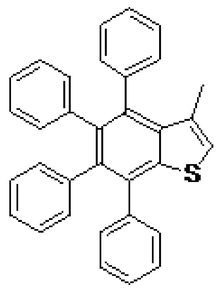


3cc

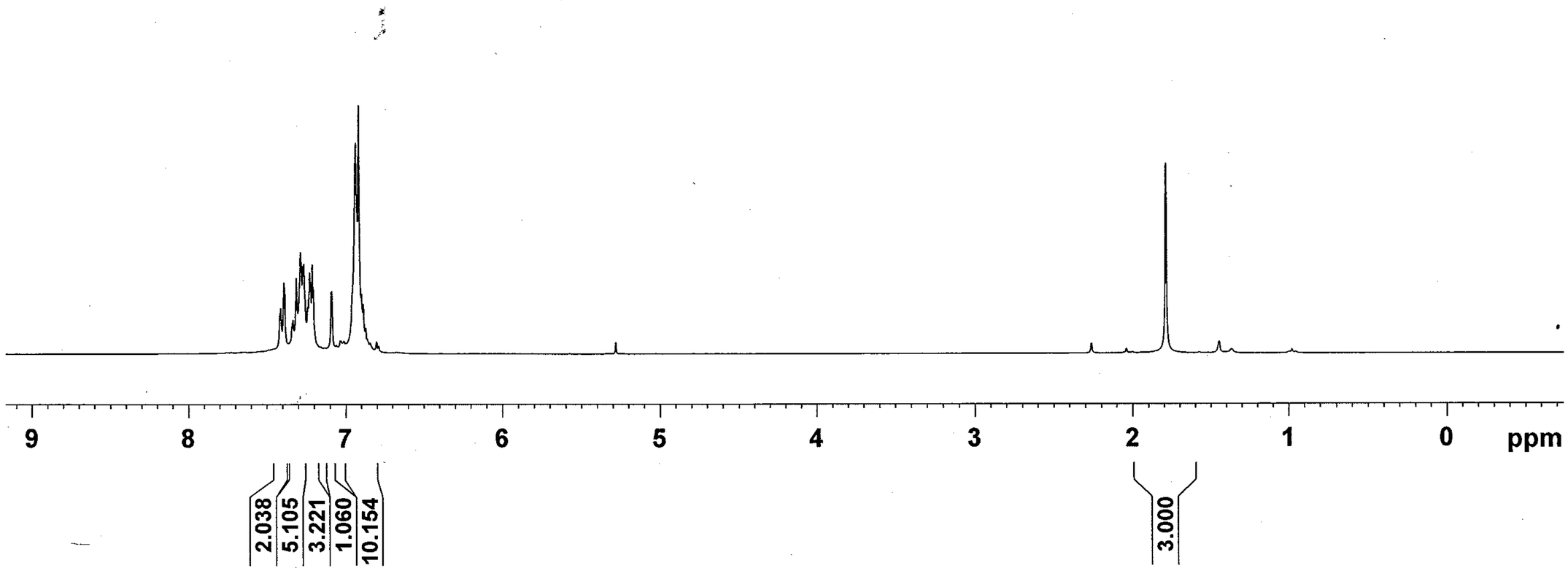


huanghn231P32





3da

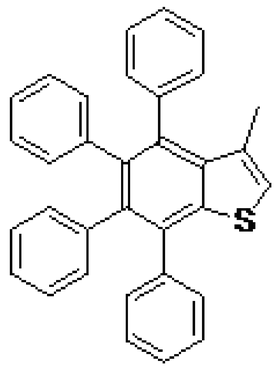


huanghn231P32 C13CPD

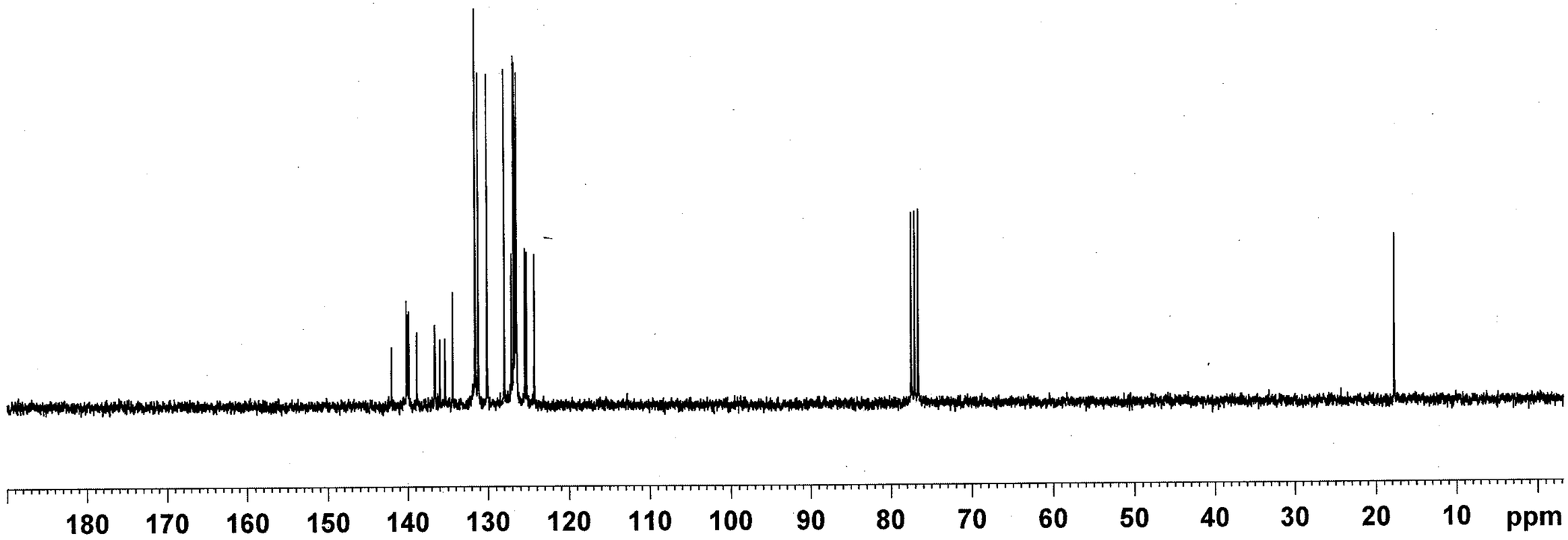
142.085
140.204
140.113
140.041
139.903
138.902
136.652
136.582
136.005
135.387
134.434
131.625
131.593
131.244
130.156
128.013
127.152
126.869
126.720
126.595
126.500
125.515
125.302
124.348

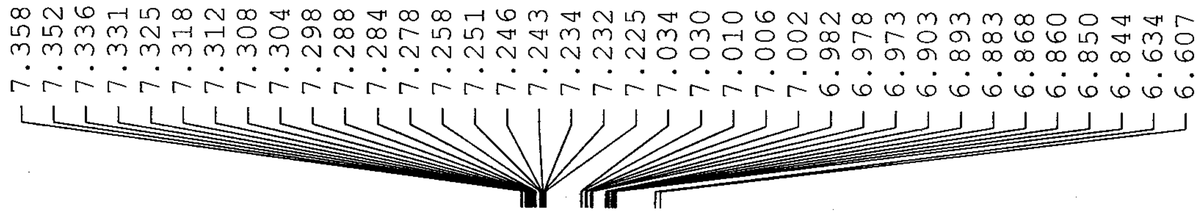
77.541
77.116
76.694

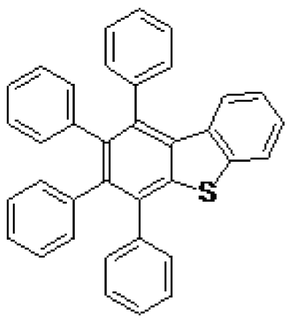
17.775



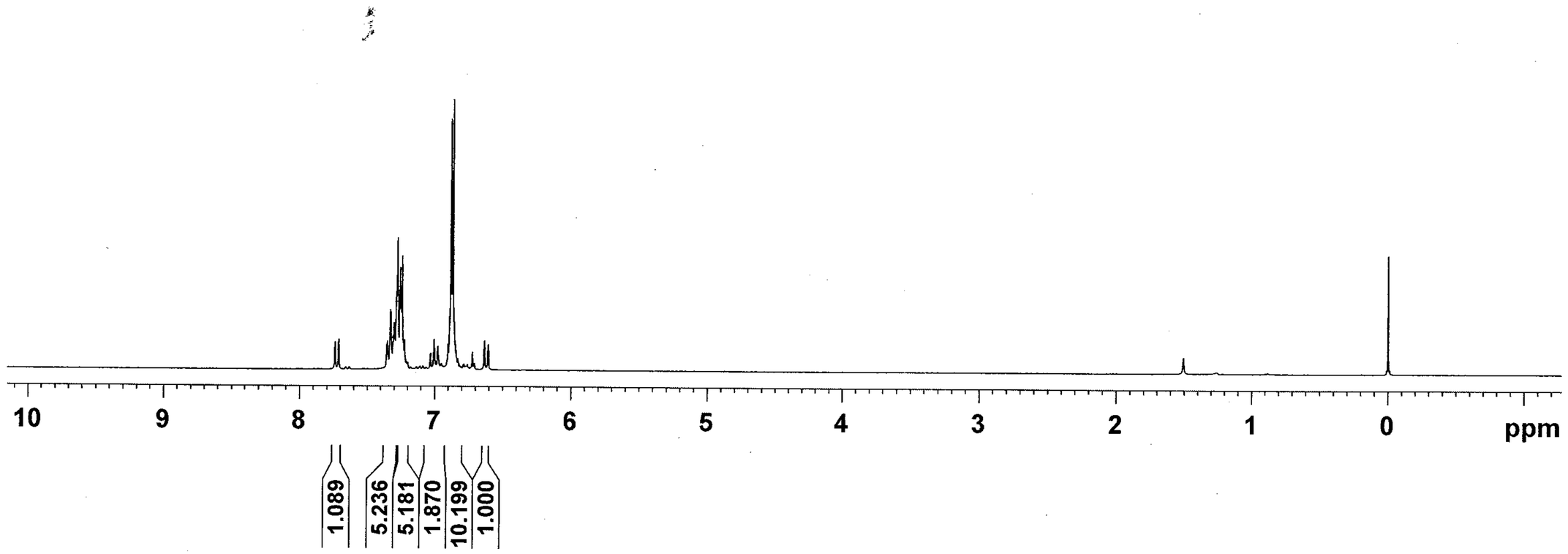
3da



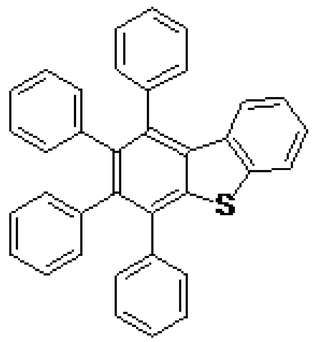




3ea

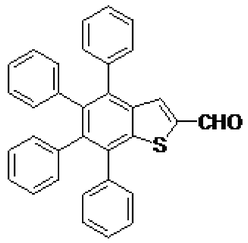


140.447
140.105
139.898
139.744
139.714
139.002
138.759
137.348
136.284
135.182
132.455
131.525
131.374
130.231
130.055
128.267
128.071
127.257
127.045
126.722
126.541
125.973
125.618
125.399
125.142
123.764
122.304

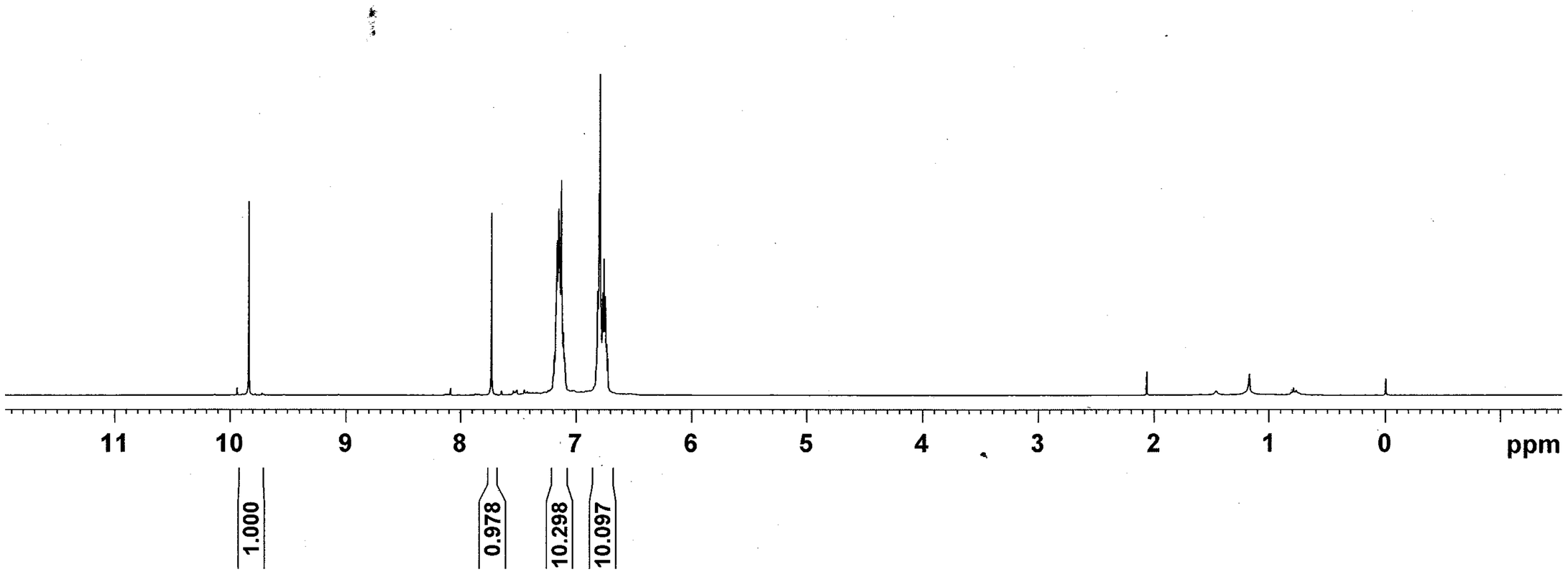


3ea

9.833
7.733
7.191
7.180
7.174
7.169
7.165
7.160
7.153
7.148
7.141
7.137
7.130
7.112
7.107
7.103
6.817
6.811
6.803
6.795
6.772
6.768
6.759
6.747
6.739
6.734



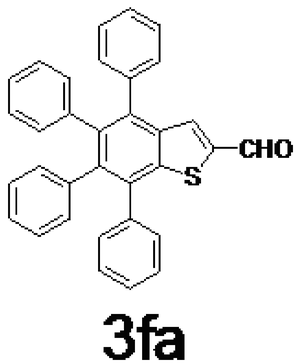
3fa



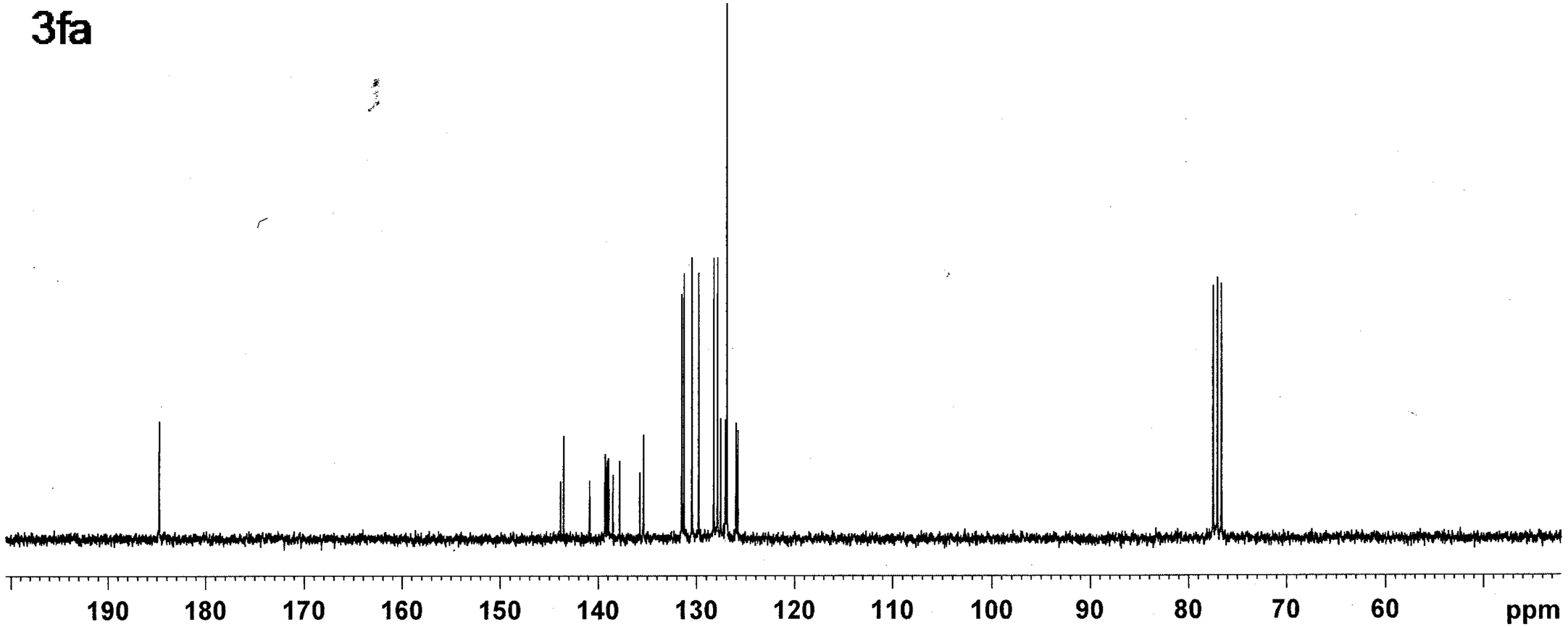
184.751

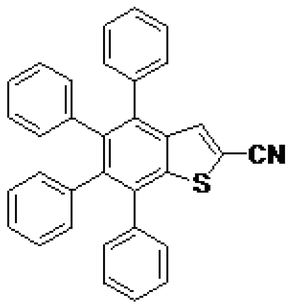
143.857
143.535
140.893
139.309
139.273
139.098
138.948
138.917
138.497
137.813
135.765
135.372
131.497
131.275
130.471
129.799
128.270
127.892
127.570
127.087
126.936
126.012
125.830

77.513
77.089
76.666

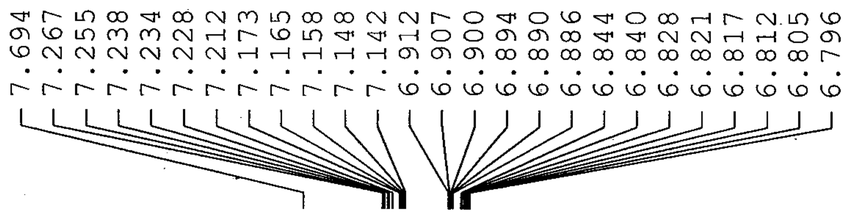


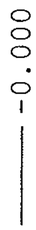
3fa

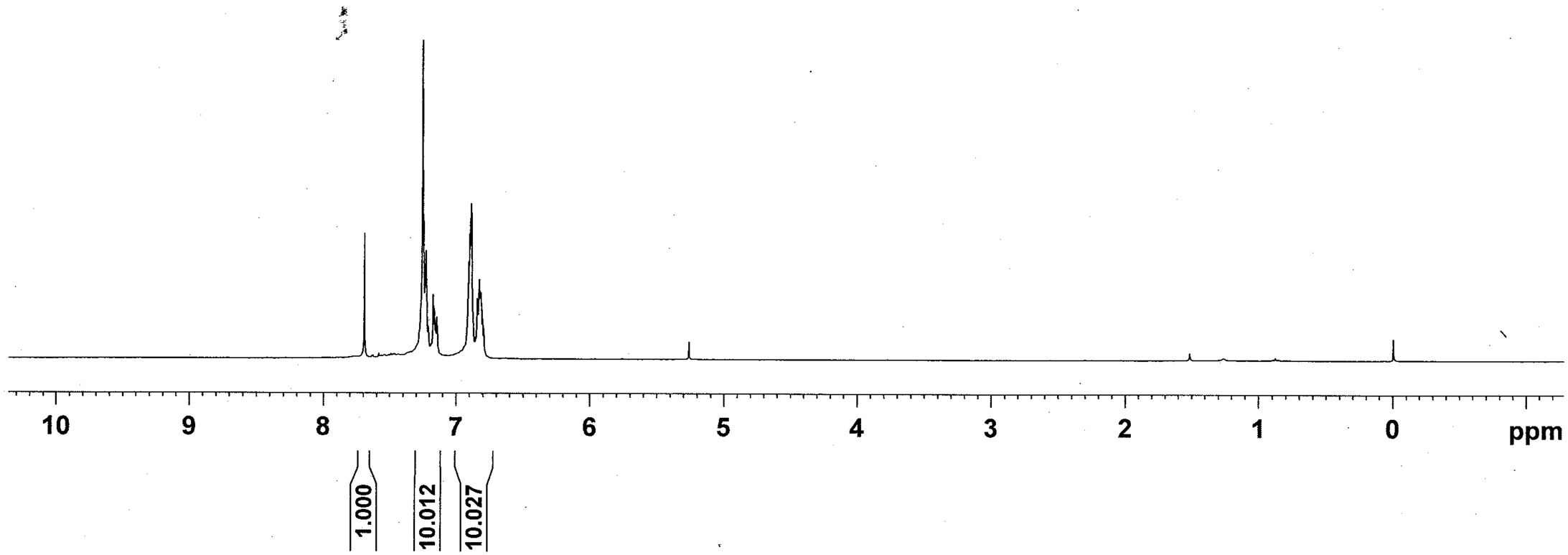


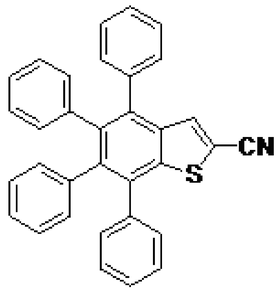


3ga





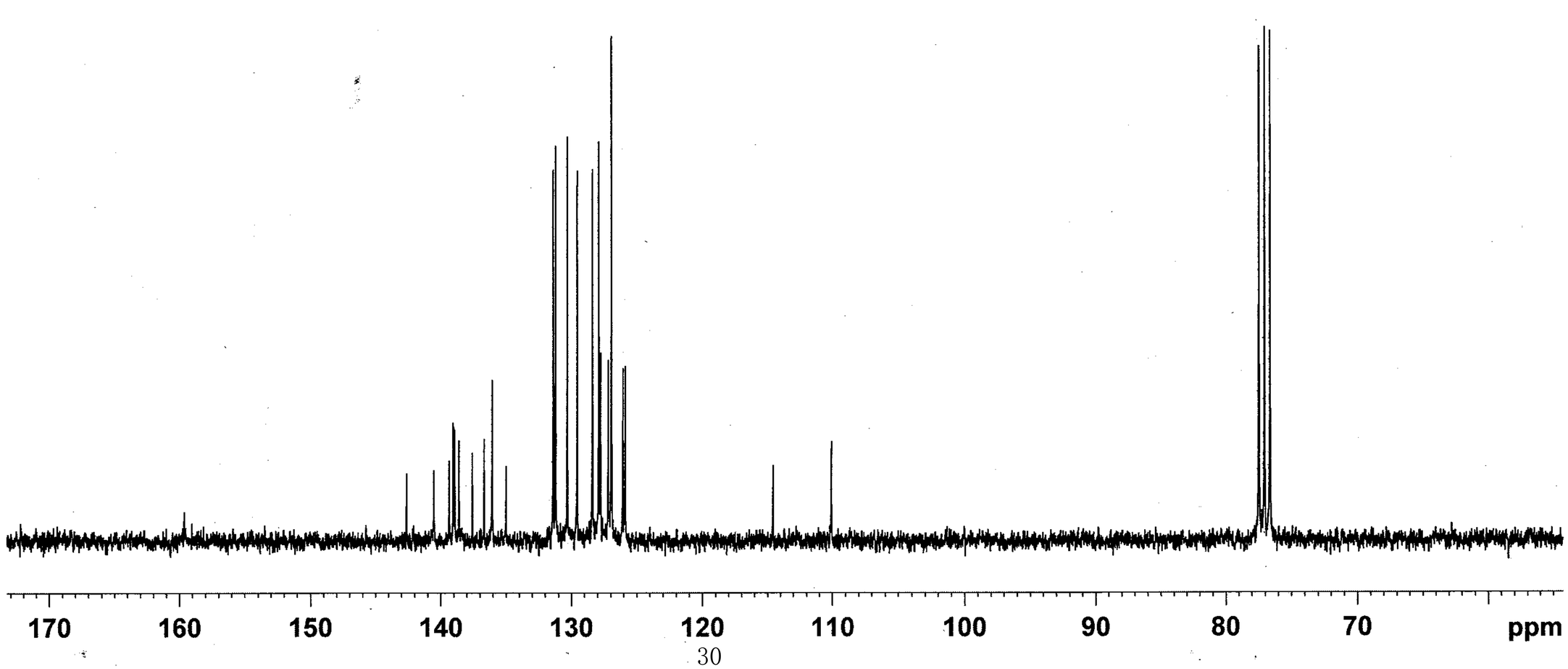


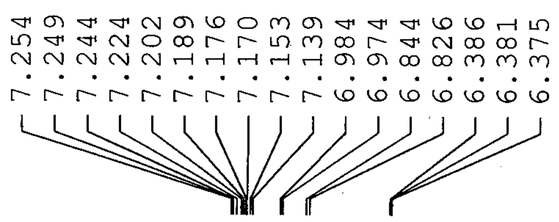


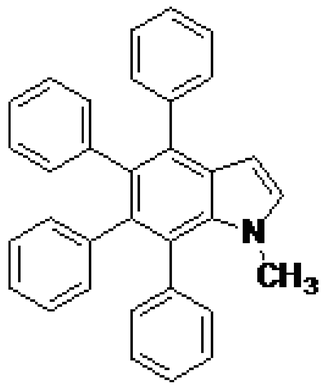
3ga

142.637
140.553
139.371
139.074
139.023
138.941
138.627
137.595
136.705
136.089
135.018
131.416
131.237
130.347
129.585
128.412
127.941
127.797
127.213
126.977
126.964
126.088
125.913
114.601
110.097

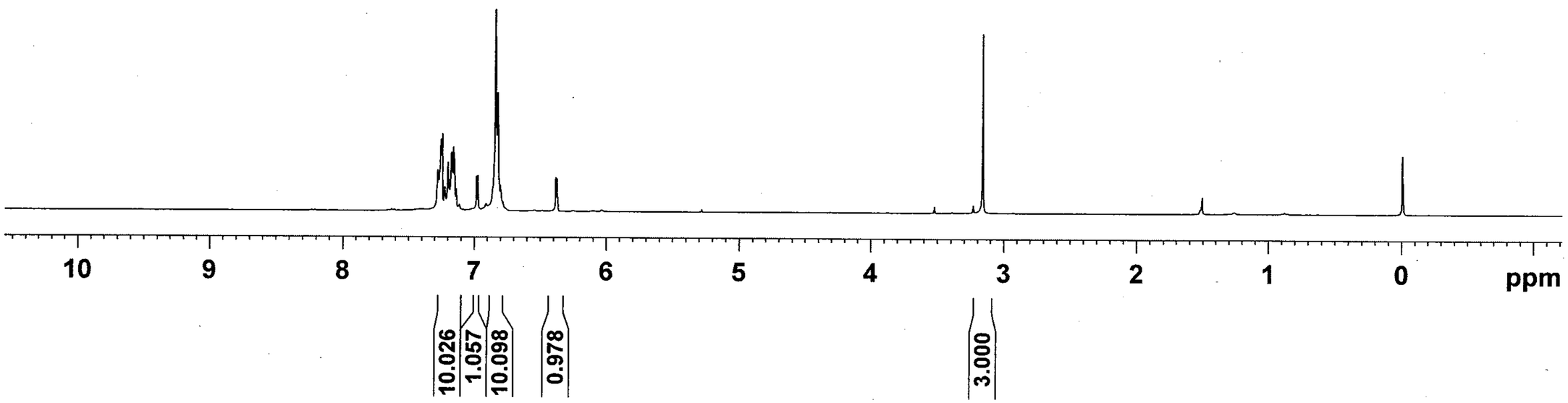
77.495
77.071
76.648







5aa

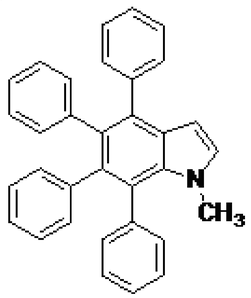


140.982
140.717
140.183
138.565
136.238
133.379
132.759
132.170
131.875
131.708
130.752
128.423
127.385
126.953
126.633
126.438
126.256
125.961
124.916
124.875

100.983

77.433
77.009
76.586

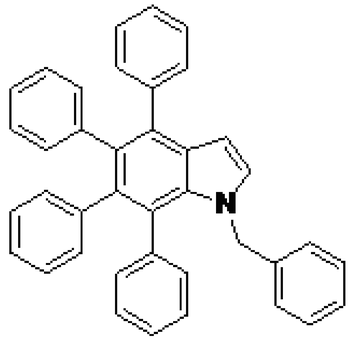
36.624



5aa

huanghn300p3

7.303
7.281
7.277
7.214
7.209
7.186
7.181
7.161
7.155
7.141
7.135
7.130
7.120
7.107
7.012
7.002
6.987
6.956
6.936
6.933
6.908
6.869
6.859
6.850
6.845
6.822
6.815
6.810
6.802
6.797
6.771
6.754
6.739
6.730
6.711
6.632
6.619
6.614
6.609
6.600
6.482
6.471
4.733



5ba

10 9 8 7 6 5 4 3 2 1 0 ppm

2.056 6.036 6.089 10.013 2.017 1.029 2.000

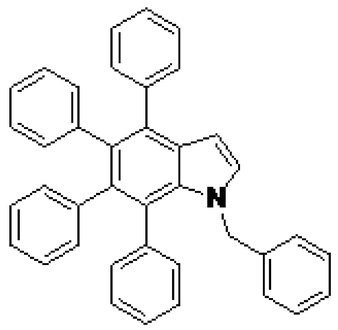
huanghn300p3 C13CPD

141.088
140.849
140.297
138.929
138.271
136.731
133.103
132.929
132.469
132.260
131.940
131.421
131.238
130.926
128.839
128.316
127.542
127.131
127.052
126.647
126.579
126.313
126.219
126.122
125.152
125.002
124.984

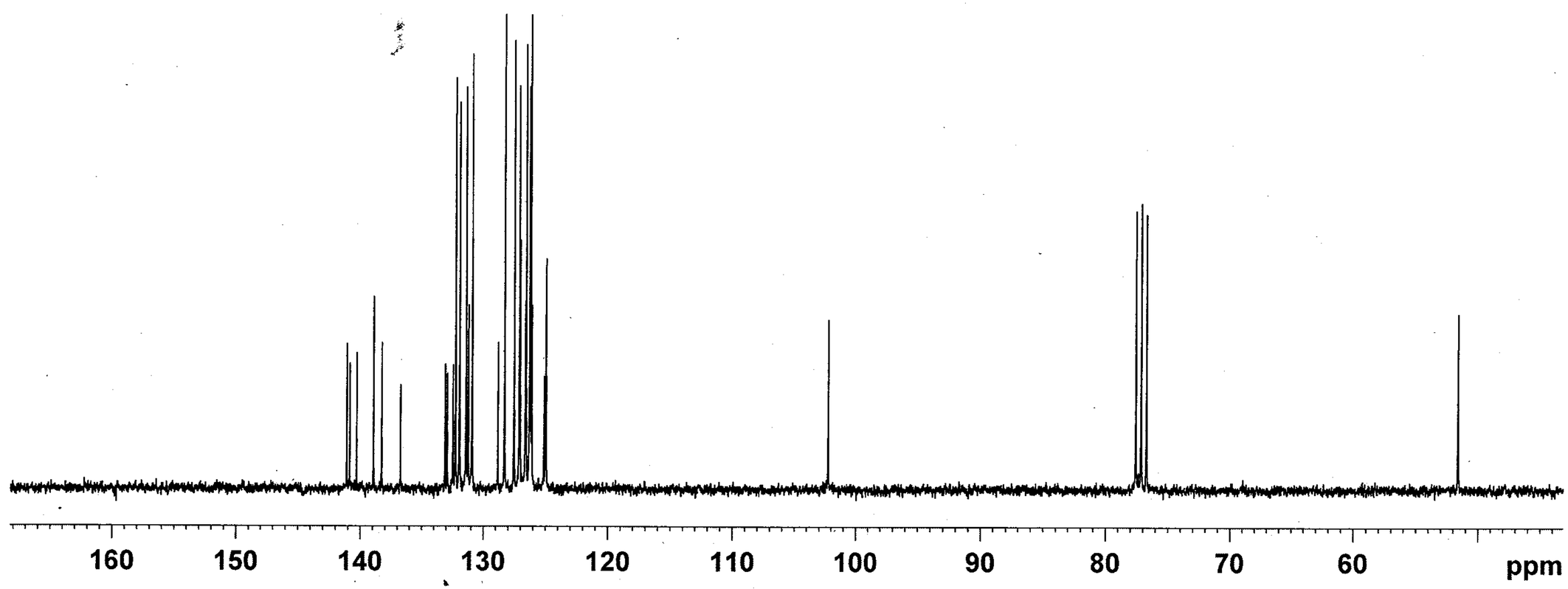
102.271

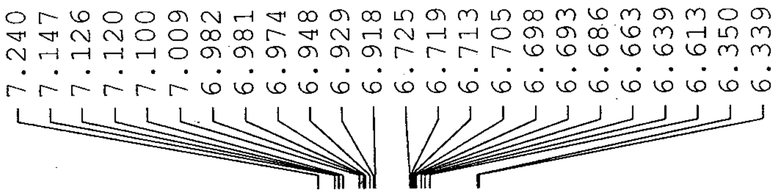
77.586
77.163
76.739

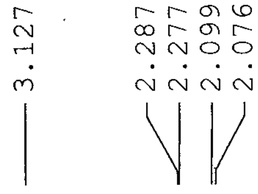
51.618

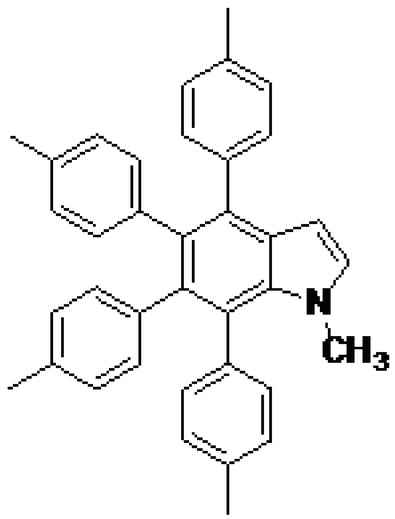


5ba









5ab

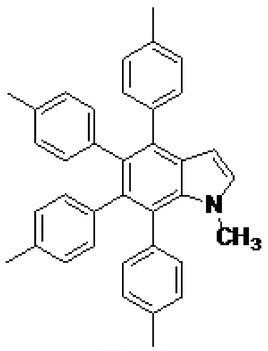
138.149
137.885
137.425
136.442
135.890
135.680
135.113
133.832
133.813
133.573
132.608
132.250
131.961
131.658
131.549
131.425
130.619
128.396
128.107
127.626
127.176
126.963
124.926

100.984

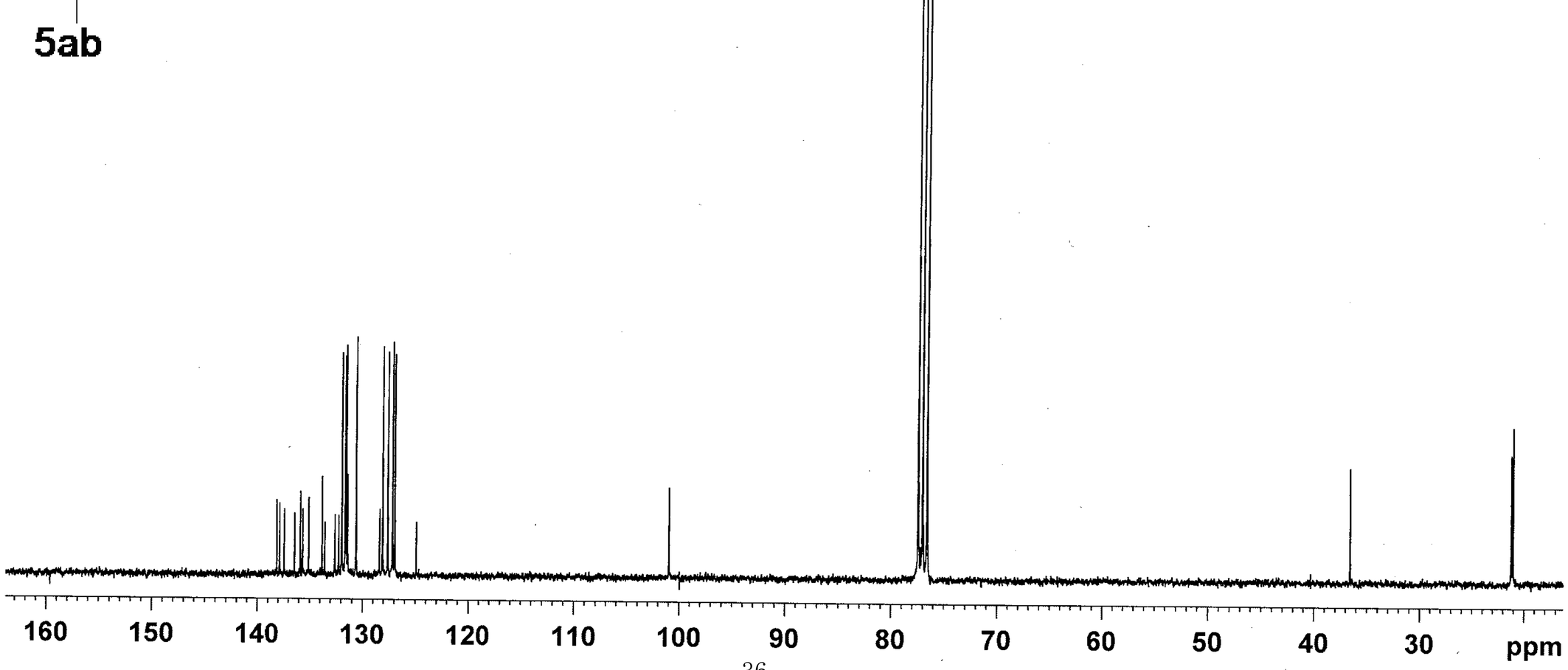
77.454
77.030
76.607

36.599

21.261
21.237
21.083



5ab



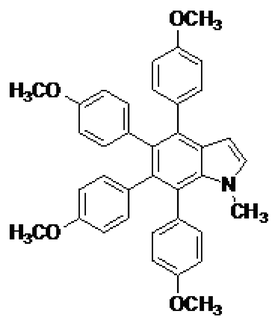
huanghn p2 PROTON

7.178
7.171
7.155
7.149
7.143
7.127
7.120
6.948
6.938
6.768
6.761
6.738
6.733
6.729
6.722
6.715
6.708
6.704
6.699
6.441
6.434
6.426
6.417
6.412
6.395
6.388
6.363
6.352

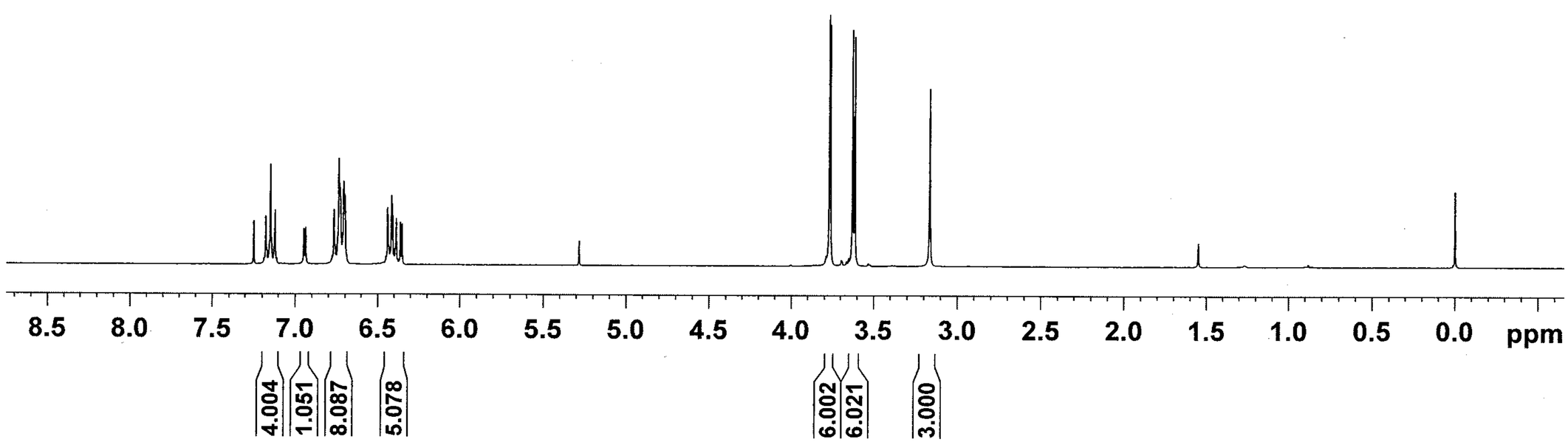
3.770
3.764
3.628
3.614

3.164

0.000

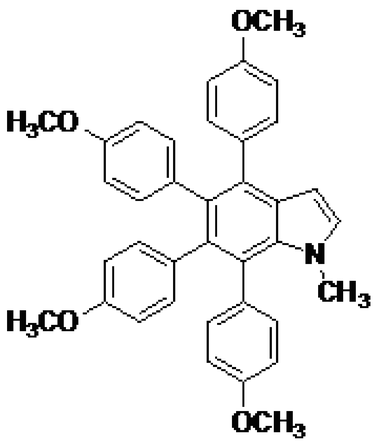


5ac

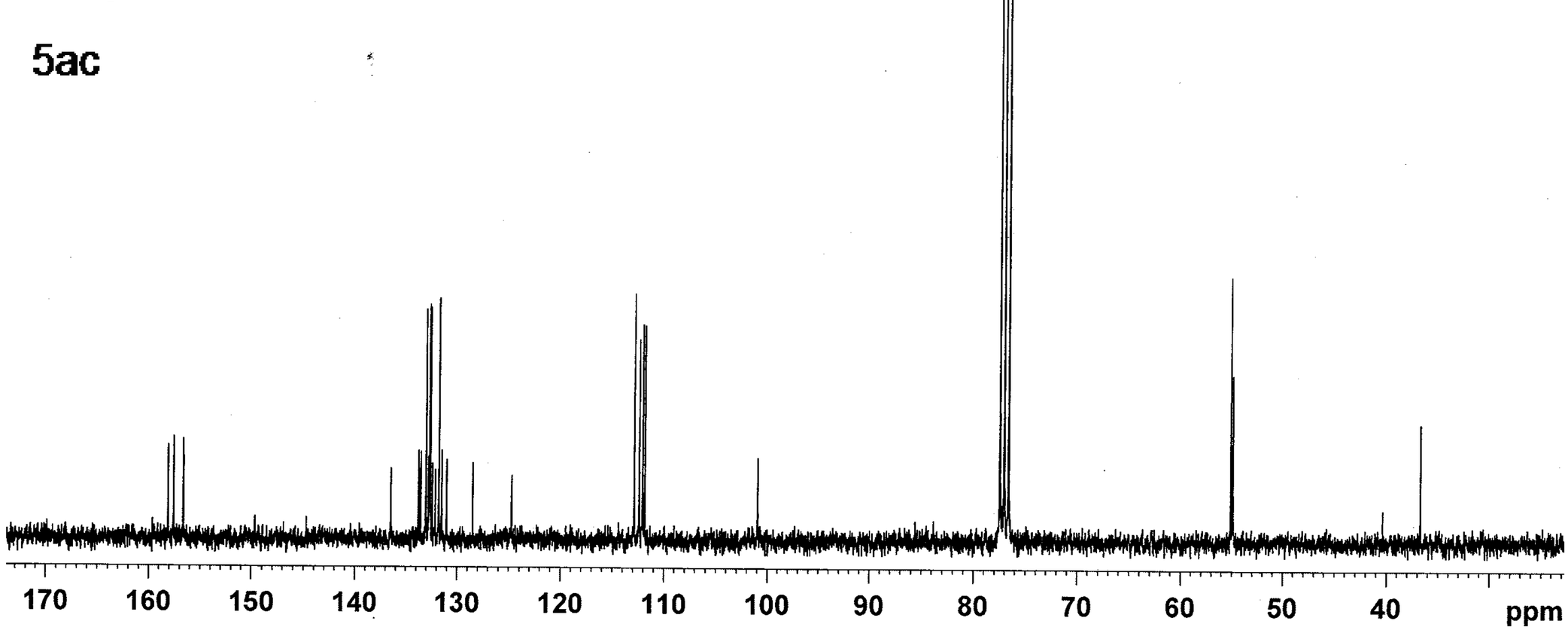


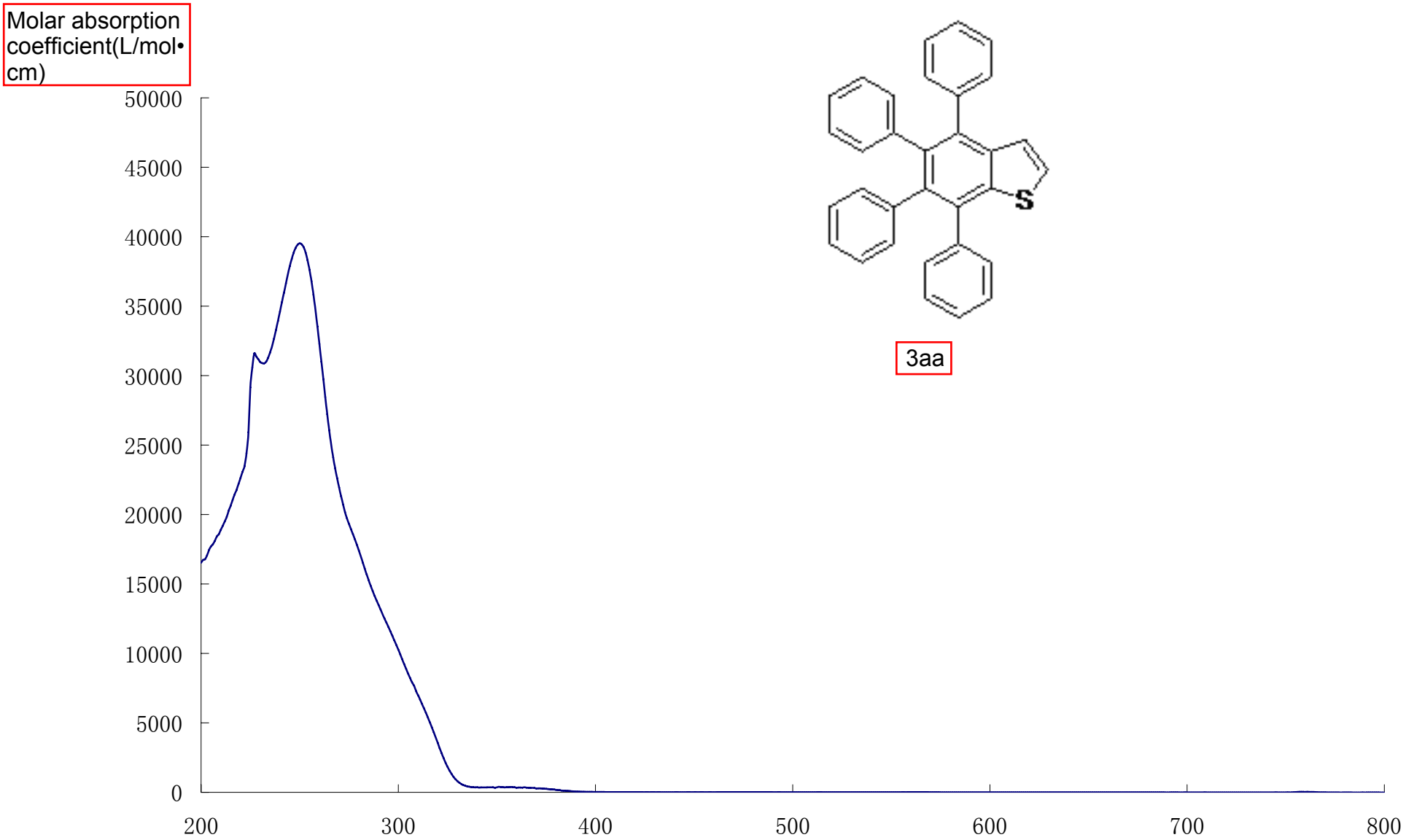
Huang/hn310pz -C31 CDCl3

158.092
157.555
156.636
156.599
136.486
133.766
133.733
133.528
133.038
132.819
132.705
132.608
132.413
132.135
131.779
131.496
131.019
128.478
124.707
112.879
112.395
112.060
111.847
100.930
77.457
77.034
76.610
55.079
54.890
54.865
36.685

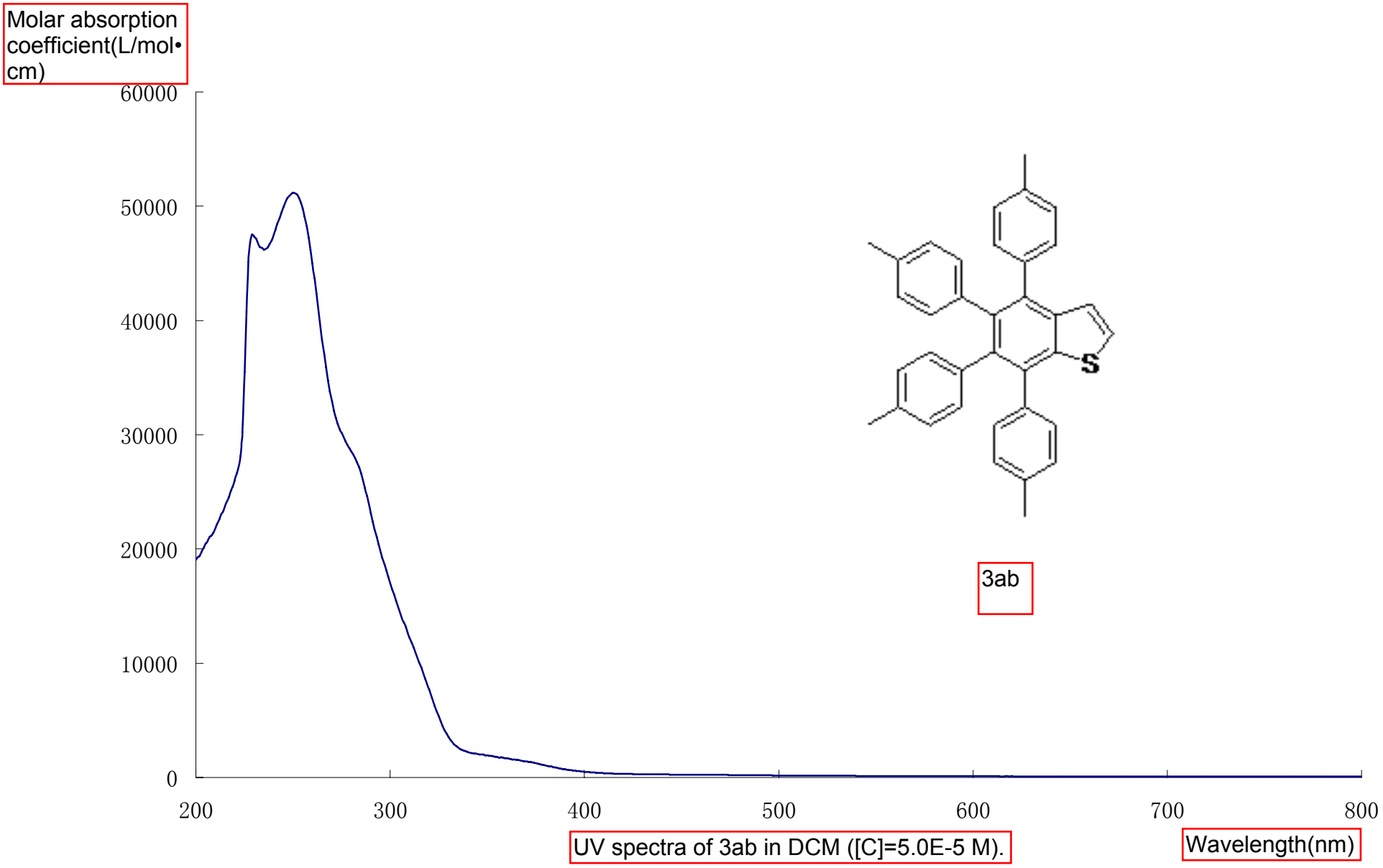


5ac

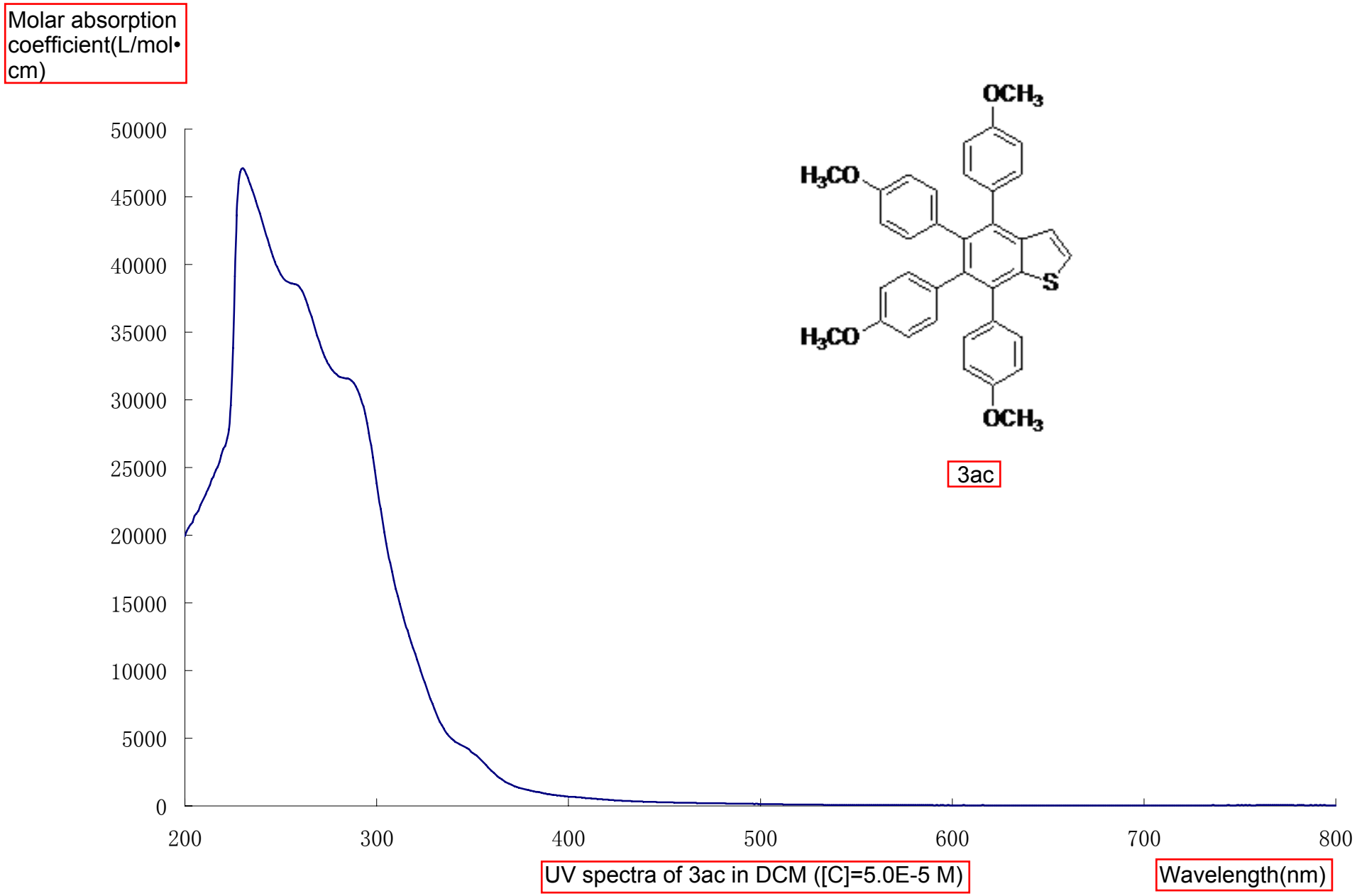




UV spectra of 3aa in DCM ([C]=5.0E-5 M).

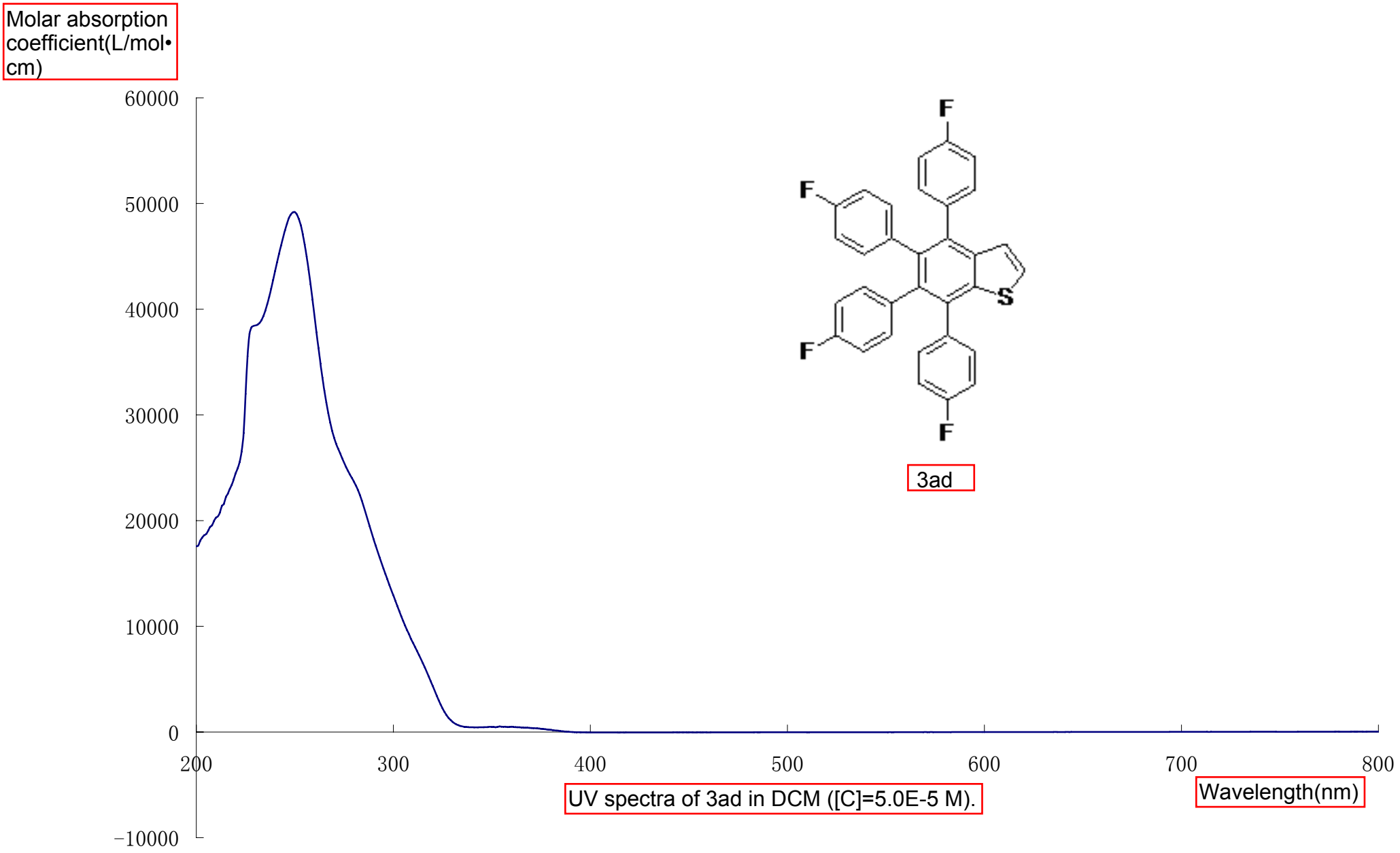


UV spectra of 3ab in DCM ([C]=5.0E-5 M).



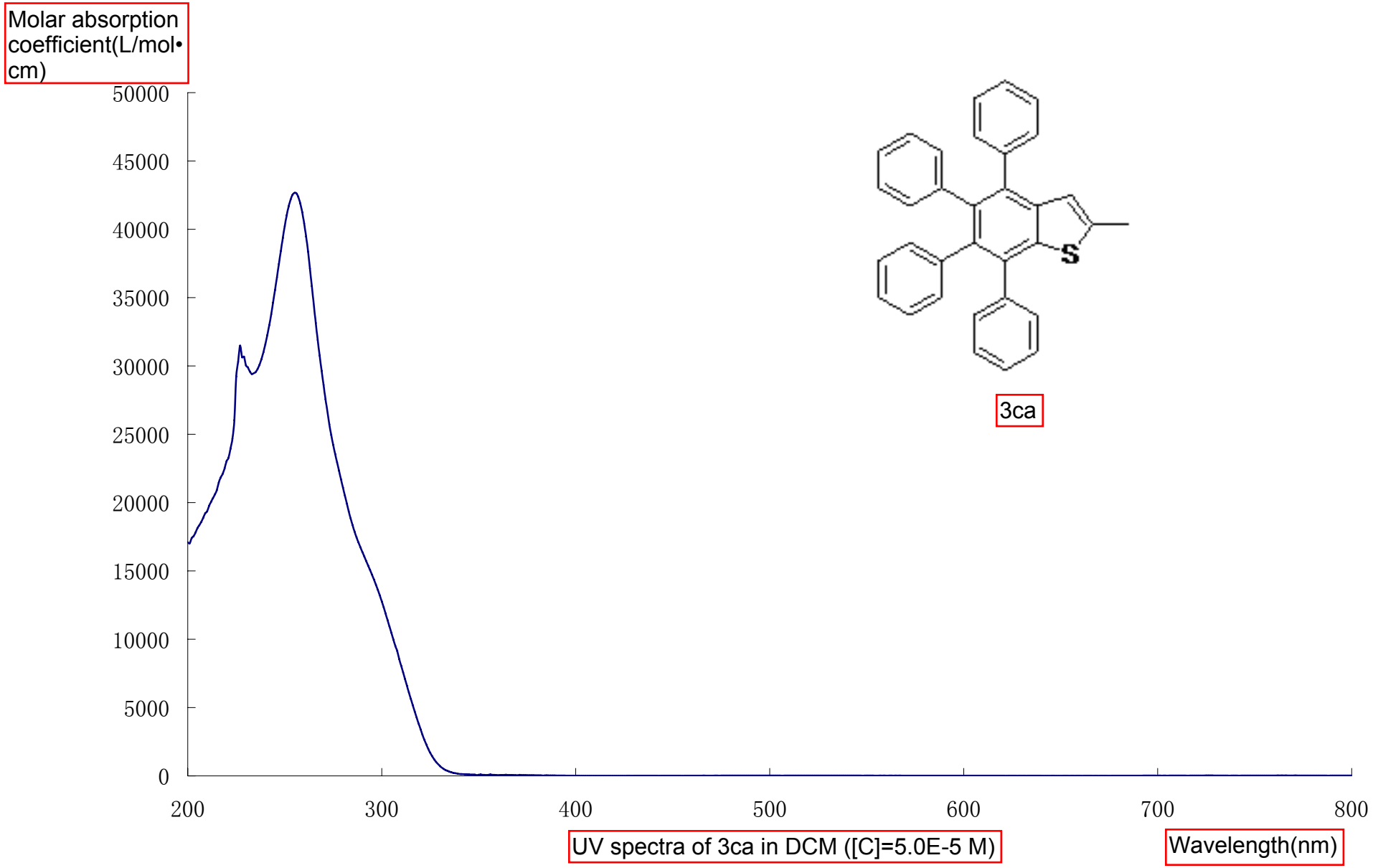
3ac

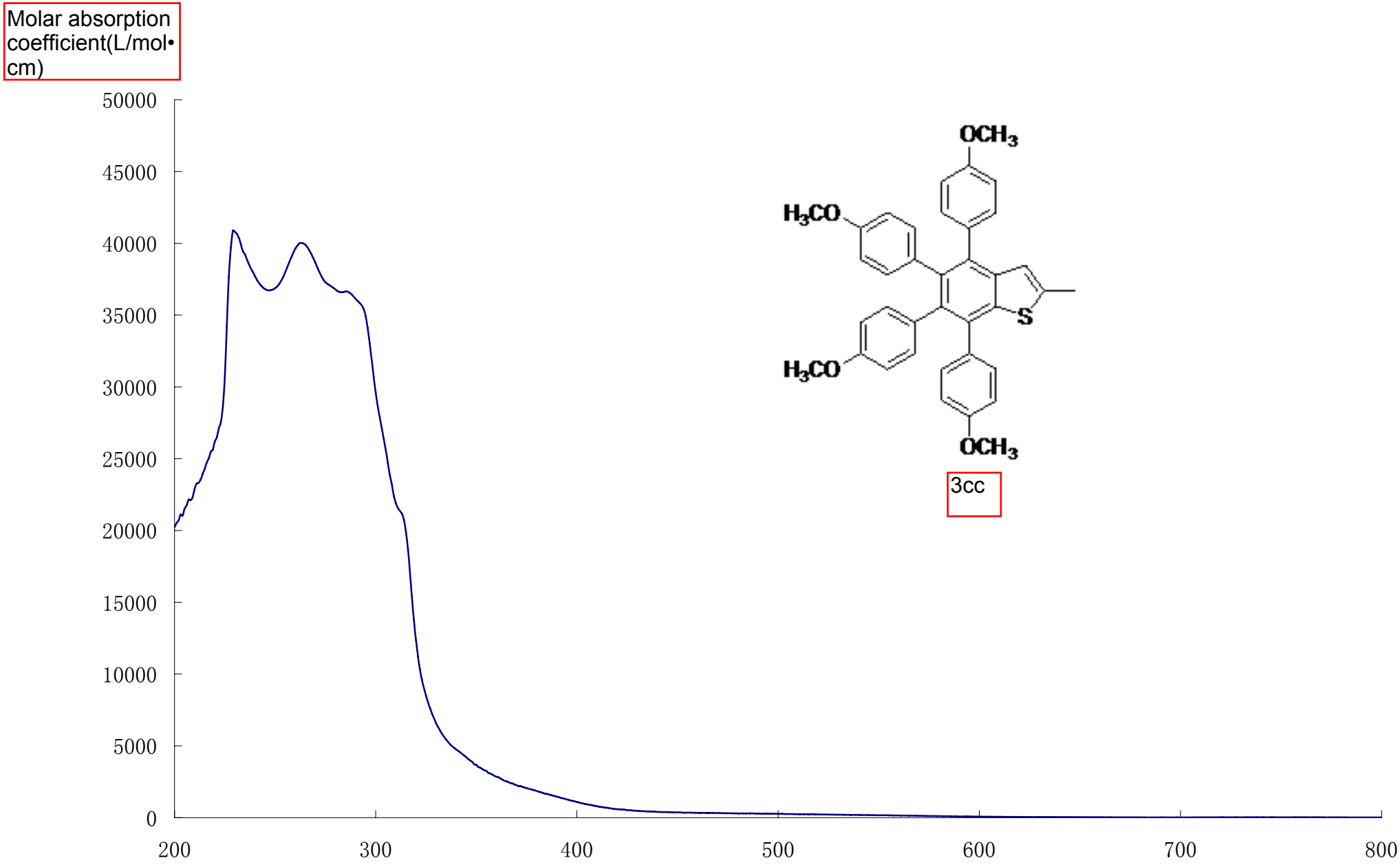
UV spectra of 3ac in DCM ([C]=5.0E-5 M)



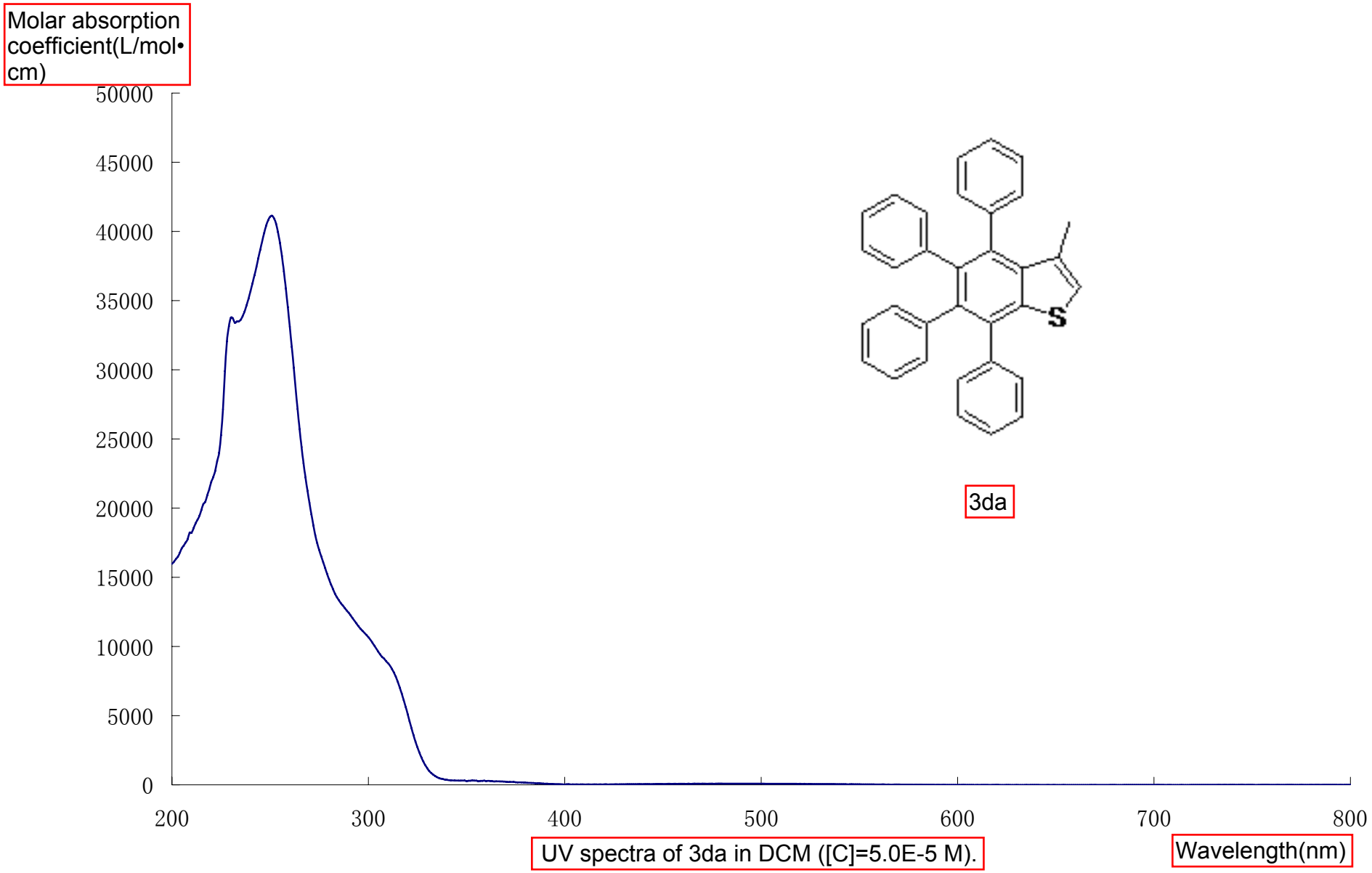
3ad

UV spectra of 3ad in DCM ([C]=5.0E-5 M).

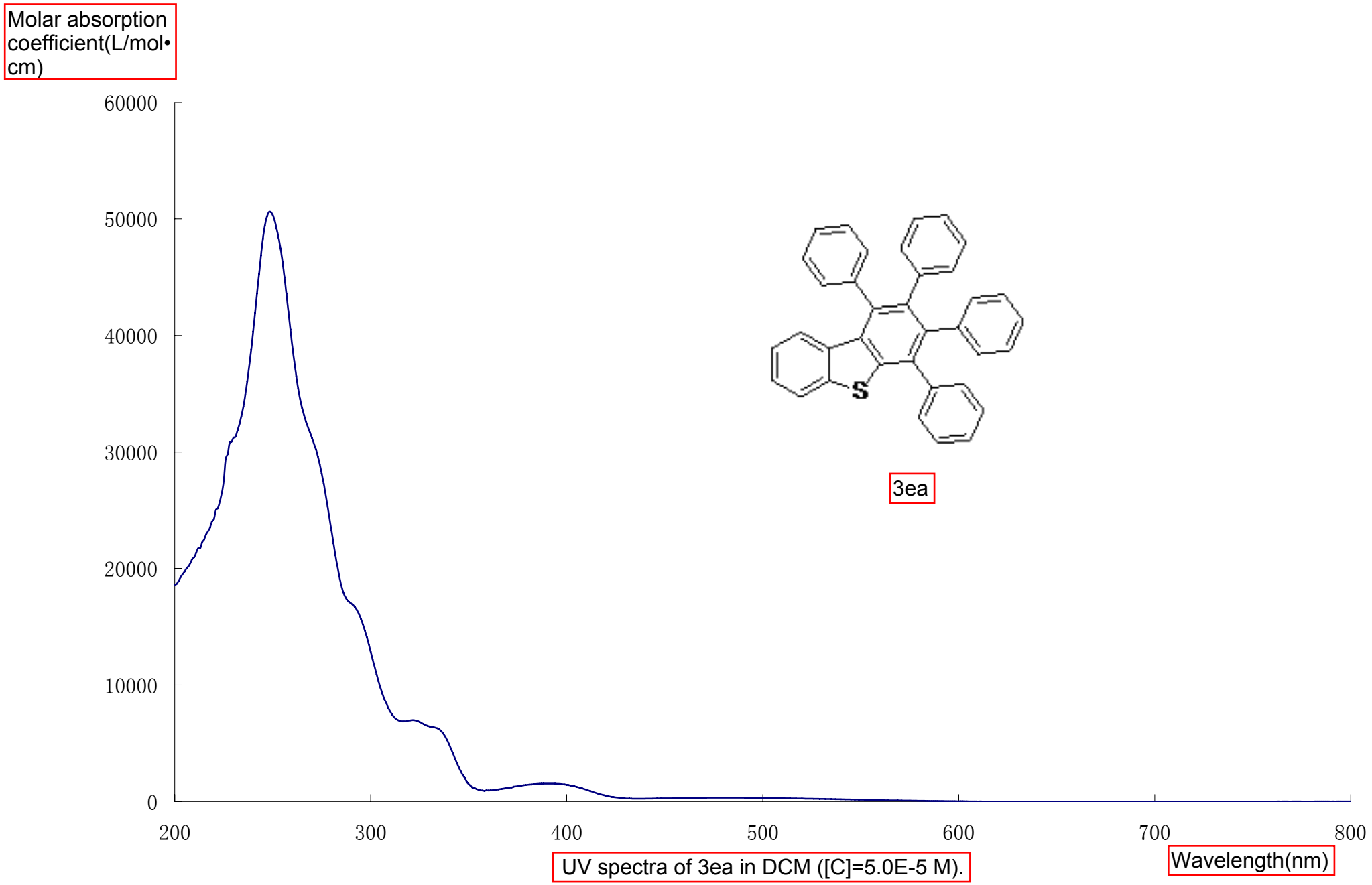




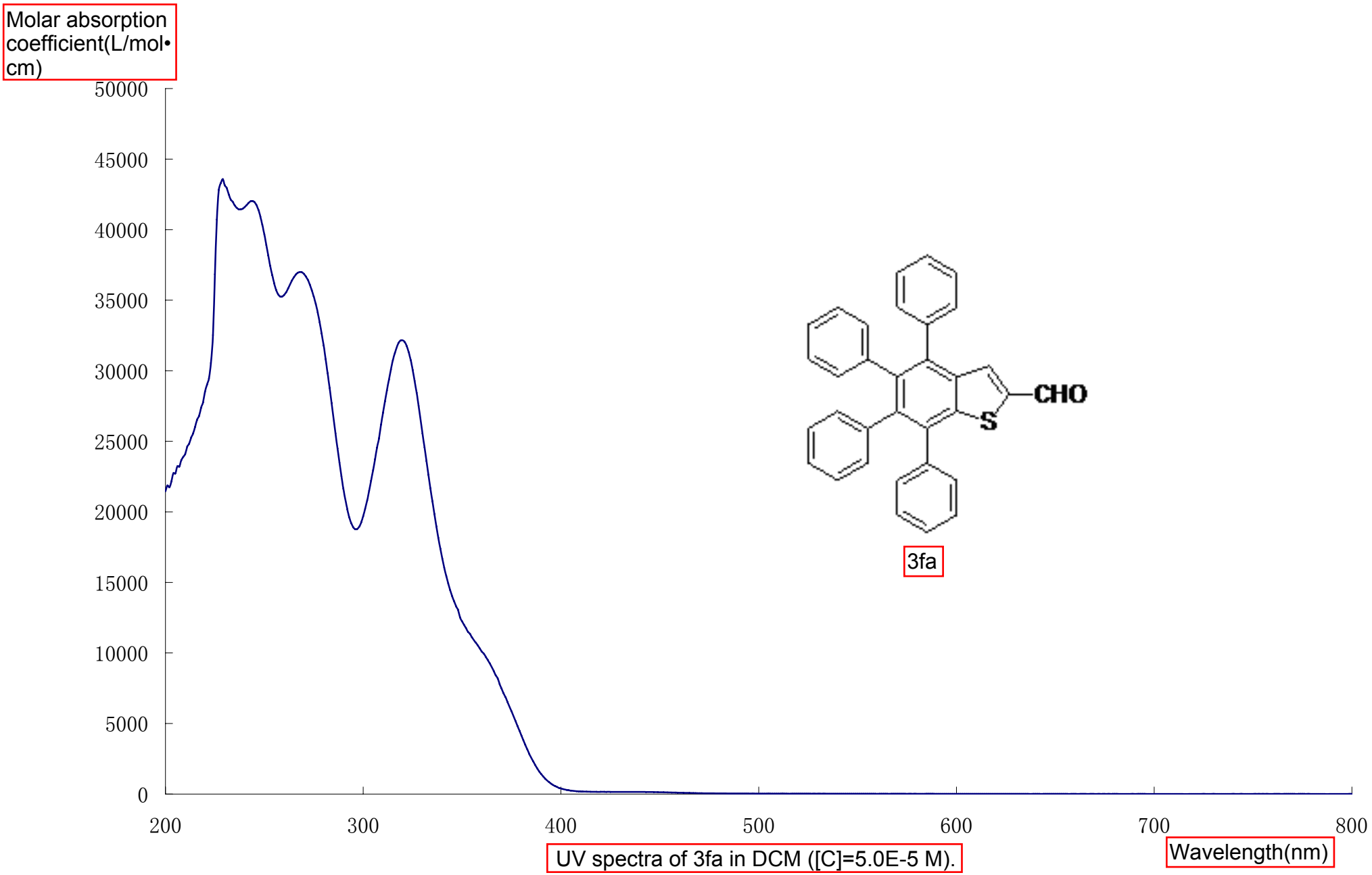
UV spectra of 3cc in DCM ([C]=5.0E-5 M).



UV spectra of 3da in DCM ([C]=5.0E-5 M).

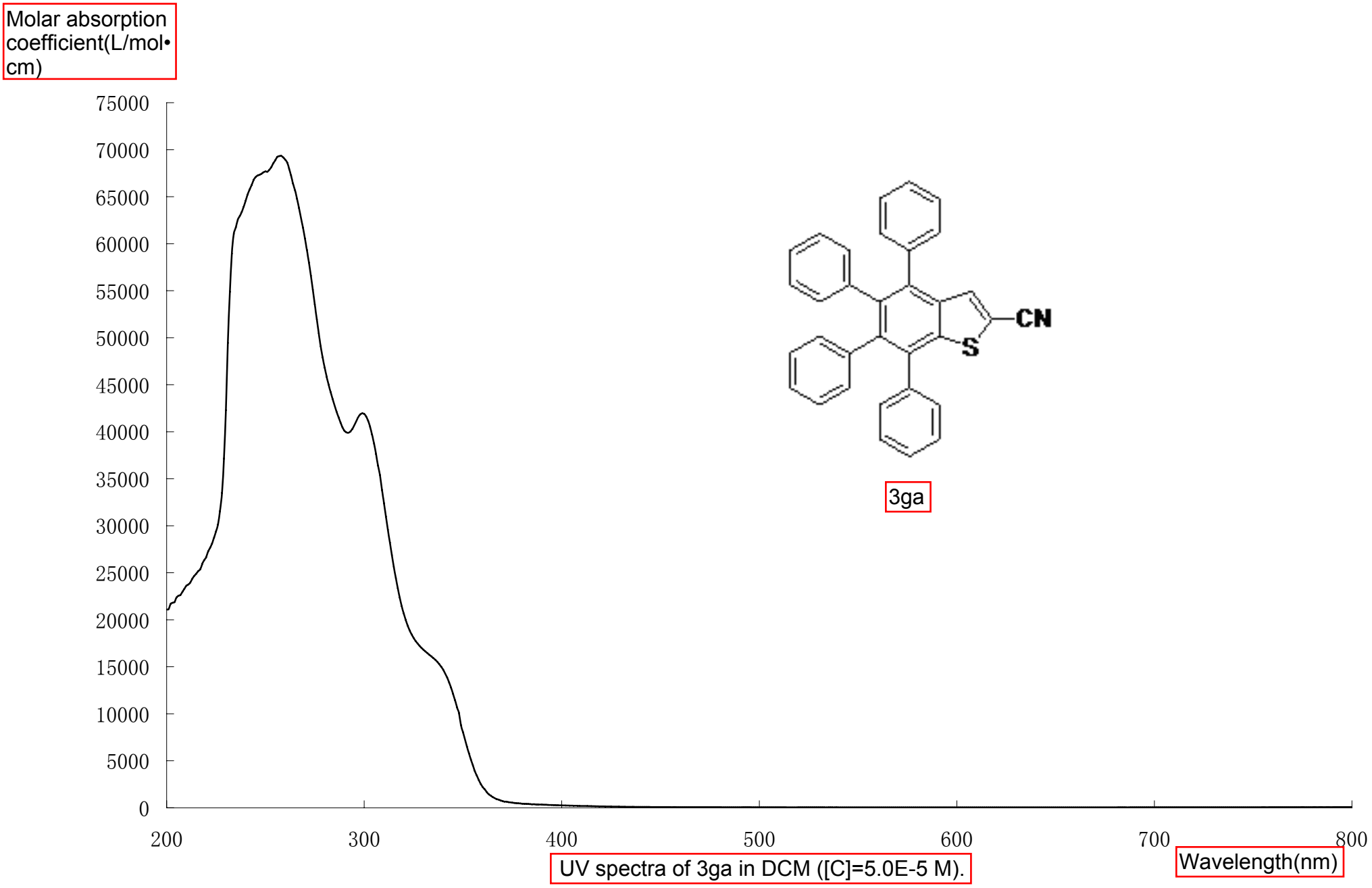


UV spectra of 3ea in DCM ([C]=5.0E-5 M).

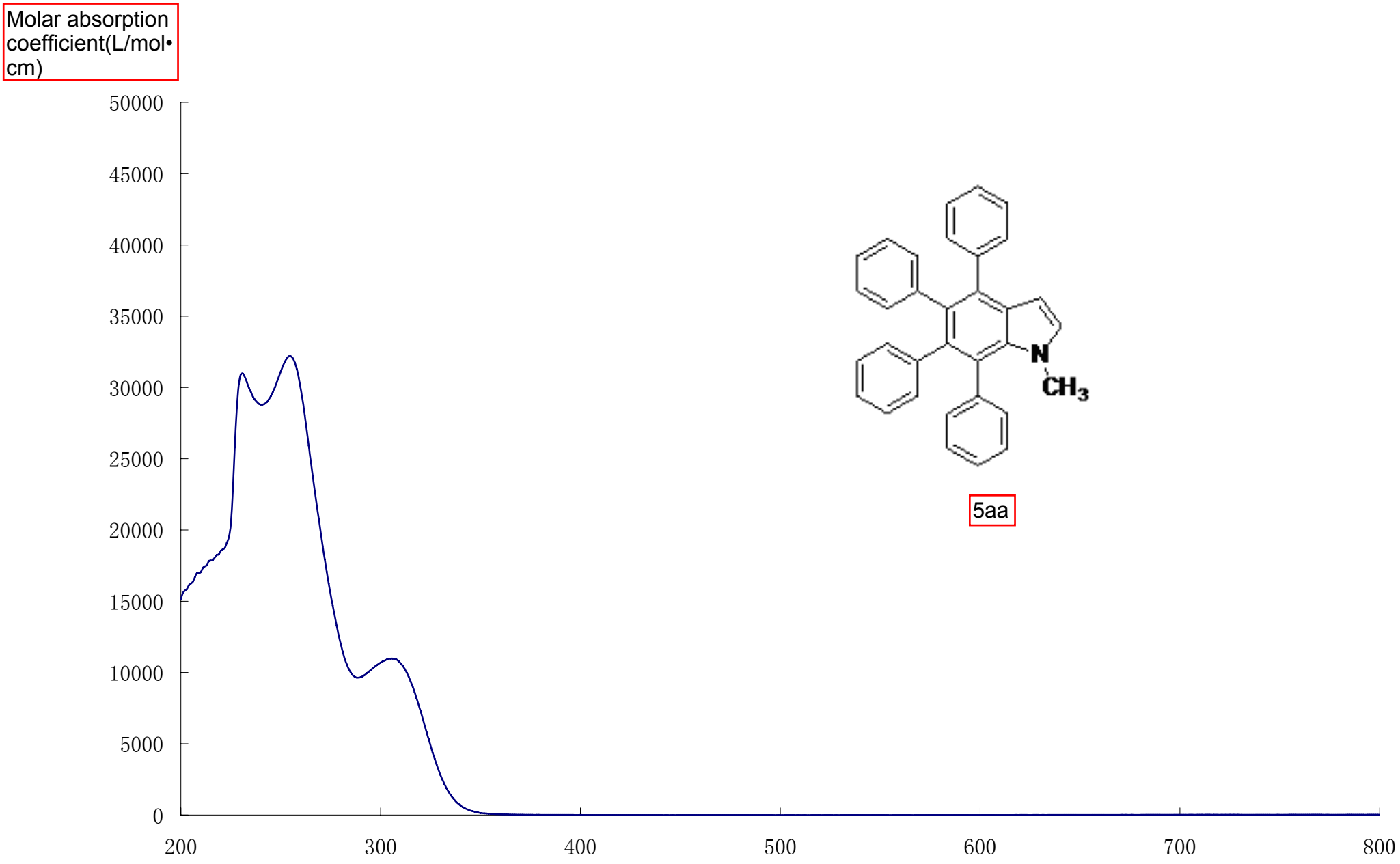


3fa

UV spectra of 3fa in DCM ([C]=5.0E-5 M).

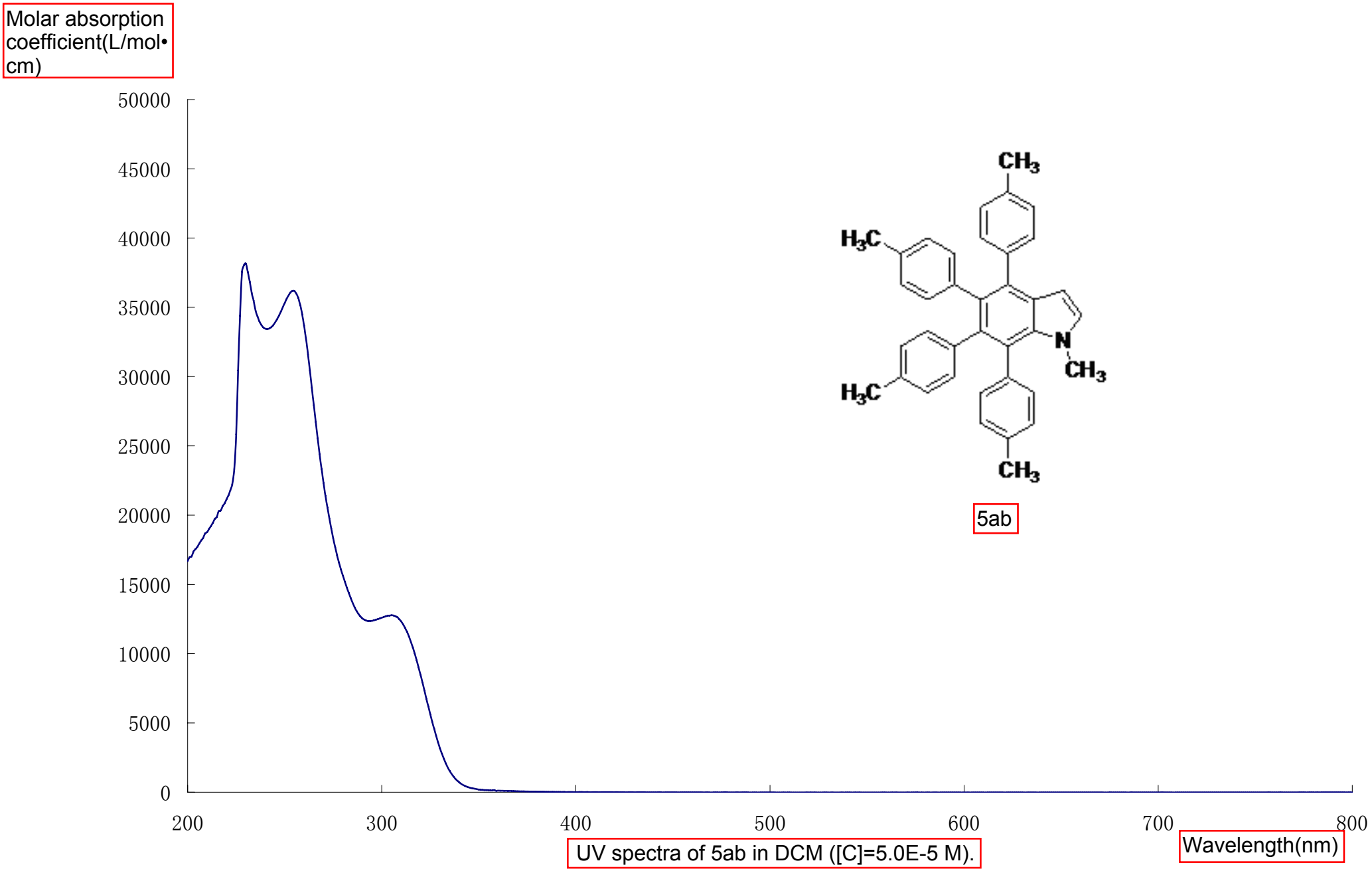


UV spectra of 3ga in DCM ([C]=5.0E-5 M).

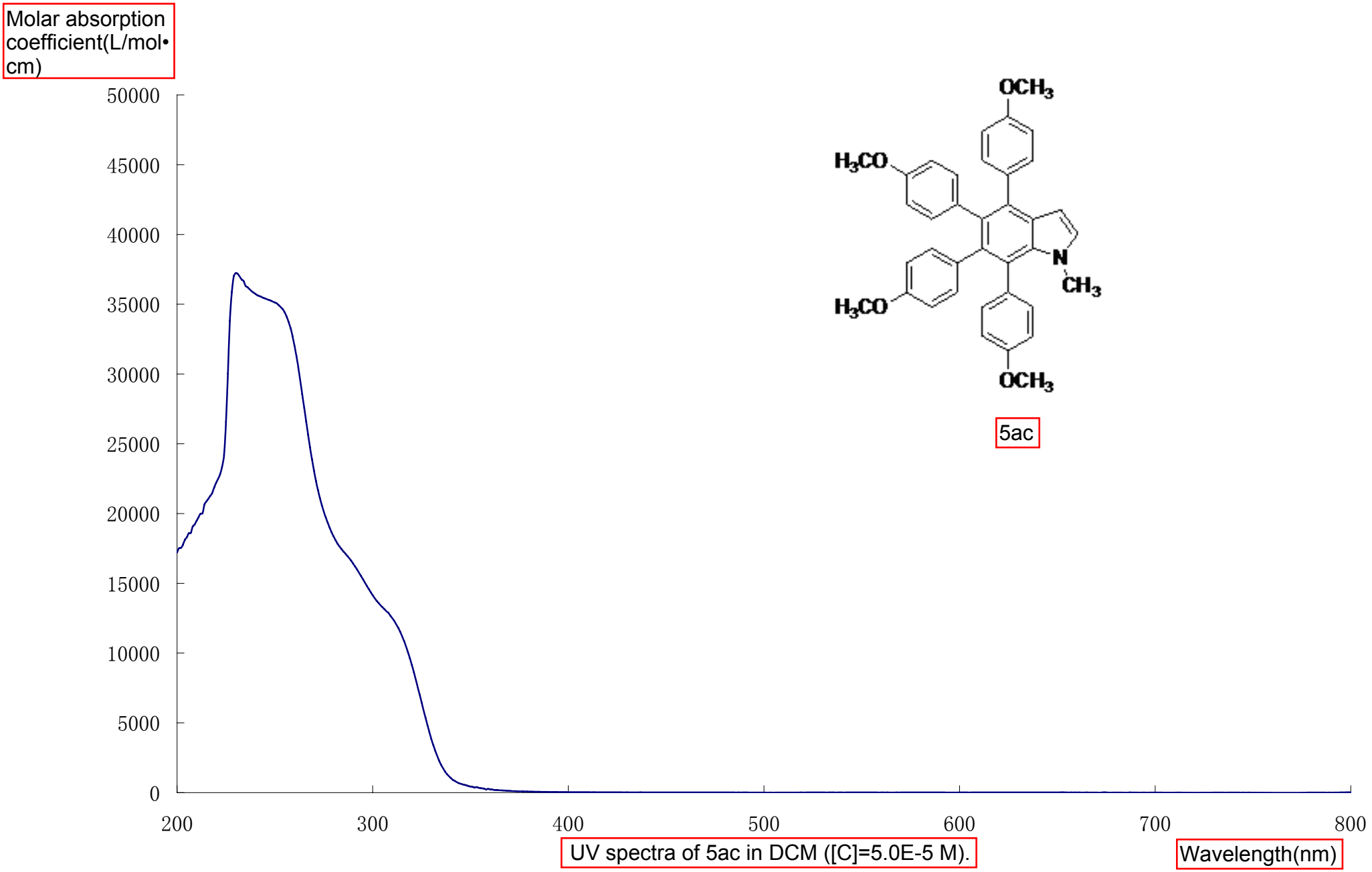


5aa

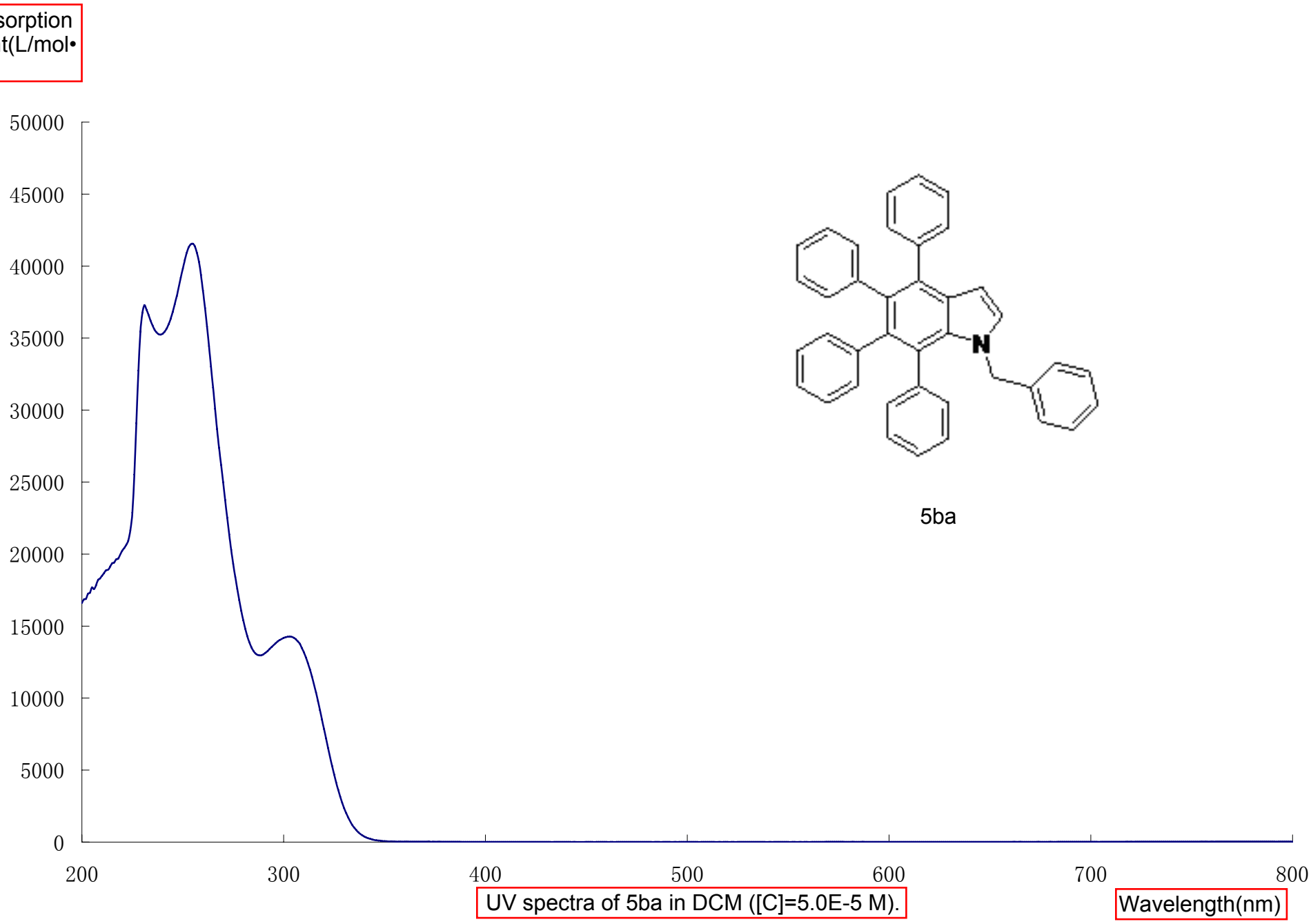
UV spectra of 5aa in DCM ([C]=5.0E-5 M).



UV spectra of 5ab in DCM ([C]=5.0E-5 M).



UV spectra of 5ac in DCM ([C]=5.0E-5 M).



UV spectra of 5ba in DCM ([C]=5.0E-5 M).