Supporting Information

for

Regioselective (thio)carbamoylation of 2,7-di-*tert*-butylpyrene at the 1-position with iso(thio)cyanates

Anna Wrona-Piotrowicz[*,1], Marzena Witalewska[1], Janusz Zakrzewski[*1] and Anna Makal[2]

Address: [1]Department of Organic Chemistry, Faculty of Chemistry, University of Łódź, Tamka 12, 91-403 Łódź, Poland and [2]University of Warsaw, Biological and Chemical Research Center, Żwirki i Wigury 101, 02-089 Warszawa, Poland

Email: Janusz Zakrzewski - janzak@uni.lodz.pl

*Corresponding author

Characterization data, copies of ^{1}H, ^{13}C NMR and IR spectra for synthesized compounds, and crystallographic structure and refinement data of 4.

Content

Characterization data◦

2,7-Di-*tert*-butyl-*N*-butylpyrene-1-carboxamide (3b). White solid (265 mg, 64%); Mp 134 – 136◦C ^{1}H NMR (600 MHz, $CDCl_3$)◦: δ 8.25 (s, 1H), 8.20 (m, 2H), 8.03 (m, 3H), 7.96 (d, *J* = 9.0 Hz, 1H), 5.98 (t, *J* = 5.4 Hz, 1H), 3.67 (m, 1H), 3.52 (m, 1H), 1.67 (m, 13H), 1.60 (s, 9H), 1.45 (m, 2H), 0.99 (t, *J* = 7.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.9, 149.1, 143.9, 131.3, 131.0, 130.9, 130.3, 128.7, 128.3, 128.1, 127.2, 124.4, 123.5, 122.65, 122.63, 122.34, 122.32, 40.0, 37.00, 35.2, 32.3, 31.9, 31.1, 20.3, 13.7. IR (KBr, cm^{-1}): 3430, 2958, 2898, 2870, 1670, 1605, 1393, 1226, 894. Anal. Calcd. for $C_{29}H_{35}NO$: C, 84.22; H, 8.53; N, 3.39; O, 3.87. Found: C, 84.30; H, 8.59; N, 3.27.

2,7-Di-*tert*-butyl-*N*-cyclohexylpyrene-1-carboxamide (3c). White solid (317 mg, 72%). Mp 217 – 218 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.25 (s, 1H), 8.21 (s, 2H), 8.09 (d, *J* = 9.6 Hz, 1H), 8.05 (d, *J* = 9.6 Hz, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 7.94 (d, *J* = 9.0 Hz, 1H), 5.87 (d, *J* = 8.4 Hz, 1H), 4.24 (m, 1H), 2.27 (d, *J* = 9.6 Hz, 1H), 2.10 (d, *J* = 9.0 Hz, 1H), 1.77 (m, 2H), 1.69 (m, 10H), 1.61 (s, 9H), 1.49 (m, 2H), 1.32 (m, 1H), 1.20 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.7, 149.1, 143.8, 131.5, 130.9, 130.8, 130.2, 128.6, 128.2, 128.0, 127.2, 124.3, 123.4, 122.6, 122.6, 122.29, 122.28, 48.9, 37.0, 35.2, 33.1, 32.4, 32.3, 31.9, 25.5, 24.81, 24.80. IR (KBr, cm^{-1}): 3433, 3215, 2958, 2930, 1624, 1602, 1553, 1226, 881. Anal. Calcd. for $C_{31}H_{37}NO$: C, 84.69; H, 8.48; N, 3.19; O, 3.64. Found: C, 84.58; H, 8.47; N, 3.25.

***N*,2,7-Tri-*tert*-butylpyrene-1-carboxamide (3d)**. White solid (281 mg, 84%). Mp 148 – 149 (C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.26 (s, 1H), 8.19 (m, 3H), 8.06 (d, *J* = 9.0 Hz, 1H), 8.03 (d, *J* = 9.0 Hz, 1H), 7.98 (d, *J* = 9.0 Hz, 1H), 5.69 (s, 1H), 1.72 (s, 9H), 1.62 (s, 9H), 1.59 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.0, 149.1, 143.7, 132.2, 130.94, 130.92, 130.3, 128.9, 128.3, 128.1, 127.2, 124.3, 123.5, 122.8, 122.6, 122.4, 122.3, 52.5, 37.16, 35.21, 32.4, 31.9, 28.7. IR (KBr, cm^{-1}): 3243, 3050, 2961, 1625, 1546, 1363, 1226, 878. Anal. Calcd. for $C_{29}H_{35}NO$: C, 84.22; H, 8.53; N, 3.39; O, 3.87. Found: C, 84.25; H, 8.47; N, 3.43.

2,7-Di-*tert*-butyl-*N*-phenylpyrenecarboxamides (3e) (1:1 mixture of 1- and 4-isomers)

(**3e**). White solid (273 mg, 63%). Mp 242 – 275 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.77 (s, 1H), 8.34 (s, 1H), 8.29 (s, 1H), 8.26 (d, *J* = 1.8 Hz, 1H), 8.24 (m, 2H), 8.23 (d, *J* = 1.2 Hz, 1H), 8.20 (d, *J* = 1.8 Hz, 1H), 8.13 (d, *J* = 9.0 Hz, 1H), 8.07 (d, *J* = 9.0 Hz, 1H), 8.04 (m, 2H), 8.00 (d, *J* = 9.0 Hz, 1H), 7.96 (s, 1H), 7.76 (s, 1H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.64 (s, 1H), 7.44 (m, 4H), 7.22 (m, 2H), 1.70 (s, 9H), 1.60 (s, 9H), 1.59 (s, 9H), 1.57 (s, 9H). ^{13}C NMR (150

MHz, $CDCl_3$): δ 170.1, 149.4, 149.3, 149.2, 144.1, 138.2, 138.0, 131.3, 131.0, 130.9, 130.8, 130.3, 129.3, 129.2, 129.1, 128.8, 128.6, 128.5, 127.9, 127.7, 127.2, 127.18, 127.17, 124.7, 124.6, 124.0, 123.7, 123.6, 123.3, 123.2, 123.1, 123.0, 122.9, 122.7, 122.6, 122.3, 120.6, 120.1, 119.8, 37.1, 35.4, 35.25, 35.24, 32.3, 31.92, 31.91, 31.9. IR (KBr, cm^{-1}): 3427, 3275, 2958, 1652, 1599, 1534, 1440, 1316, 1225, 882. Anal. Calcd. for $C_{31}H_{31}NO$: C, 85.87; H, 7.21; N, 3.23; O, 3.69. Found: C, 85.79; H, 7.30; N, 3.27.

2,7-Di-*tert*-butyl-*N*-isopropylpyrene-1-carbothioamide (3g). Pale yellow solid (370 mg, 89%). Mp 216 – 217 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.19 (d, J = 1.8 Hz, 1H), 8.17 (d, J = 1.8 Hz, 1H), 8.11 (d, J = 9.0 Hz, 1H), 8.40 (d, J = 9.6 Hz, 1H), 8.01 (d, J = 9.0 Hz, 1H), 7.95 (d, J = 9.0 Hz, 1H), 7.46 (d, J = 7.8 Hz, 1H), 5.08 (m, 1H), 1.75 (s, 9H), 1.59 (s, 9H), 1.50 (d, J = 6.6 Hz, 3H), 1.40 (d, J = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 202.0, 149.2, 142.3, 137.1, 130.9, 130.8, 130.2, 128.4, 128.0, 127.6, 127.2, 124.2, 124.8, 123.0, 122.7, 122.3, 122.3, 47.6, 37.9, 35.2, 32.7, 31.9, 21.2, 20.7; IR (KBr, cm^{-1}): 3432, 3385, 3195, 2963, 1602, 1533, 1456, 1390, 1227, 991, 881. Anal. Calcd. for $C_{28}H_{33}NS$: C, 80.91; H, 8.00; N, 3.37; S, 7.71. Found: C, 80.82; H, 8.07; N, 3.34, S, 7.63.

2,7-Di-*tert*-butyl-*N*-butylpyrene-1-carbothioamide (3h). Pale yellow solid (391 mg, 91%). Mp 179 – 180 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.19 (d, J = 1.8 Hz, 1H), 8.18 (d, J = 1.8 Hz, 1H), 8.07 (d, J = 9.6 Hz, 1H), 8.03 (d, J = 9.0 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 9.0 Hz, 1H), 7.61 (s, 1H), 4.07 (m, 1H), 3.82 (m, 1H), 1.77 (m, 2H), 1.72 (s, 9H), 1.59 (s, 9H), 1.48 (m, 2H), 1.00 (t, J = 7.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 203.3, 149.2, 142.5, 137.1, 130.9, 130.8, 130.3, 128.4, 128.0, 127.7, 127.2, 124.9, 124.3, 124.2, 122.9, 122.7, 122.29, 122.28, 46.0, 37.7, 35.2, 32.6, 31.9, 29.6, 20.4, 13.7. IR (KBr, cm^{-1}): 3167, 2958, 1600, 1540, 1360, 1224, 883. Anal. Calcd. for $C_{29}H_{35}NS$: C, 81.07; H, 8.21; N, 3.26; S, 7.46. Found: C, 80.99; H, 8.28; N, 3.24, S, 7.40.

***N*,2,7-Tri-*tert*-butylpyrene-1-carbothioamide (3i)**. Pale yellow solid (400 mg, 93%). Mp 121 – 123 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.30 (s, 1H), 8.28 (d, J = 9.0 Hz, 1H), 8.20 (d, J = 1.8 Hz, 1H), 8.19 (d, J = 1.8 Hz, 1H), 8.08 (d, J = 9.0 Hz, 1H), 8.01 (d, J = 9.0 Hz, 1H), 7.96 (d, J = 9.0 Hz, 1H), 7.46 (s, 1H), 1.81 (s, 9H), 1.80 (s, 9H), 1.61 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 202.6, 149.1, 141.7, 138.5, 130.9, 130.6, 130.2, 128.3, 127.9, 127.6, 127.1, 124.4, 124.3, 123.1, 122.6, 122.3, 122.2, 57.0, 37.9, 35.2, 32.8, 31.9, 27.4. IR (KBr, cm^{-1}): 3379, 2955, 1601, 1500, 1456, 1358, 1260, 1225, 880. Anal. cCalcd. for $C_{29}H_{35}NS$: C, 81.07; H, 8.21; N, 3.26; S, 7.46. Found: C, 81.11; H, 8.22; N, 3.19, S, 7.35.

2,7-Di-*tert*-butyl-*N*-hexylpyrene-1-carbothioamide (3j). Pale yellow solid (398 mg, 87%). Mp 168 – 169 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.19 (d, J = 1.8 Hz, 1H), 8.17 (d, J = 1.8 Hz, 1H), 8.07 (d, J = 9.6 Hz, 1H), 8.02 (d, J = 9.0 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 9.0 Hz, 1H), 7.63 (s, 1H), 4.07 (m, 1H), 3.83 (m, 1H), 1.79 (m, 2H), 1.72 (s, 9H), 1.59 (s, 9H), 1.45 (m, 2H), 1.35 (m, 4H), 0.92 (t, J = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 203.3, 149.2, 142.4, 137.1, 130.80, 130.27, 128.3, 128.0, 127.7, 127.2, 124.4, 124.2, 122.9, 122.7, 122.29, 122.27, 46.3, 37.7, 35.2, 32.6, 31.9, 31.4, 27.5, 26.9, 22.5, 14.0. IR (KBr, cm^{-1}): 3221, 2955, 1600, 1533, 1360, 1227, 880. Anal. Calcd. for $C_{31}H_{39}NS$: C, 81.35; H, 8.59; N, 3.06; S, 7.01. Found: C, 81.37; H, 8.53; N, 3.08, S, 7.02.

2,7-Di-*tert*-butyl-*N*-cyclohexylpyrene-1-carbothioamide (3k). Pale yellow solid (415 mg, 91%) Mp 277 – 278 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.18 (d, J = 1.2 Hz, 1H), 8.16 (d, J = 1.8 Hz, 1H), 8.07 (d, J = 9.6 Hz, 1H), 8.02 (d, J = 9.6 Hz, 1H), 8.00 (d, J = 9.0 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.49 (d, J = 7.2 Hz, 1H), 4.84 (m, 1H), 2.44 (m, 1H), 2.24 (m, 1H), 1.81 (m, 2H), 1.74 (s, 9H), 1.71 (m, 1H), 1.58 (s, 9H), 1.55 (m, 2H), 1.41 (m, 1H), 1.35 (m, 1H), 1.27 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 201.8, 149.2, 142.3, 137.2, 131.0, 130.8, 130.3, 128.4, 128.0, 127.6, 127.2, 124.3, 124.2, 123.0, 122.7, 122.31, 122.27, 54.3, 37.9, 35.2, 32.75, 32.4, 31.9, 31.4, 31.0, 25.5, 24.6. IR (KBr, cm^{-1}): 3433, 3386, 3155, 2965, 2927, 1603, 1540, 1385, 1359, 1223, 985, 878. Anal. Calcd. for $C_{31}H_{37}NS$: C, 81.71; H, 8.18; N, 3.07; S, 7.04. Found: C, 81.77; H, 8.15; N, 3.09, S, 6.95.

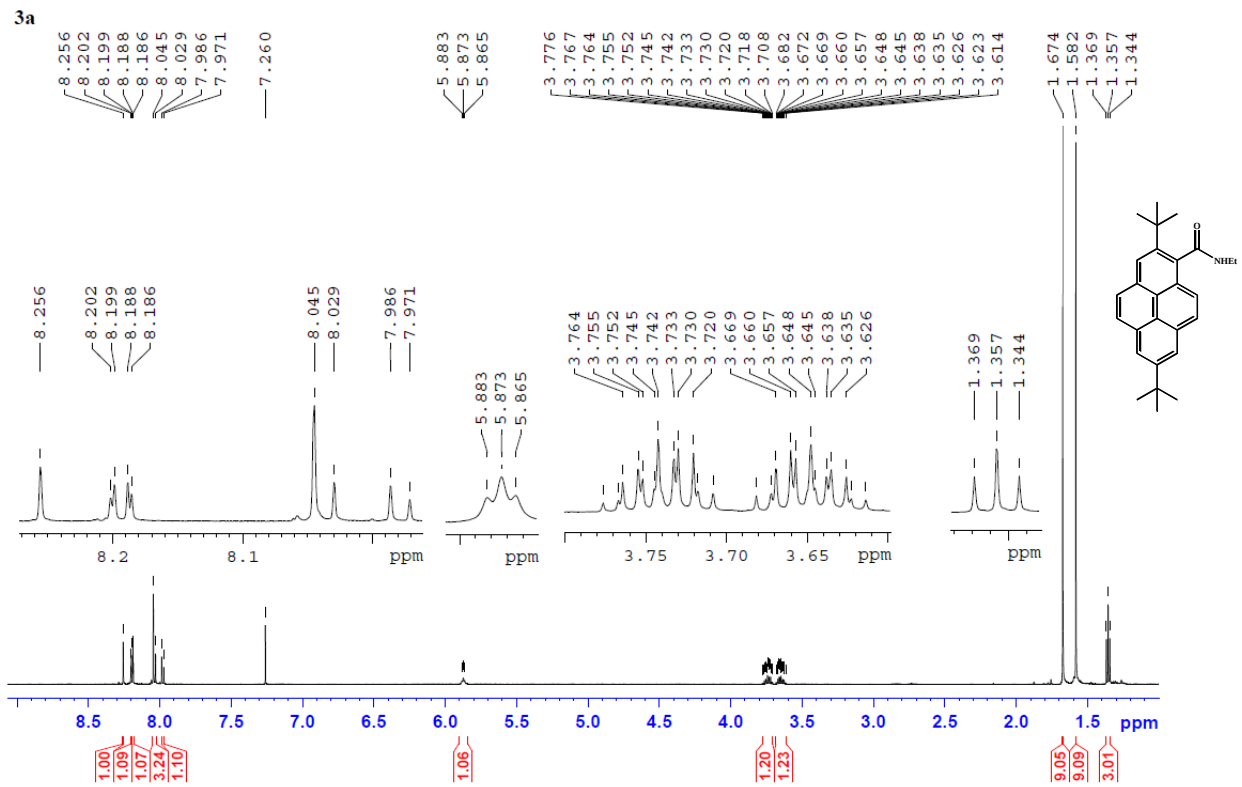
2,7-Di-*tert*-butyl-*N*-benzylpyrene-1-carbothioamide (3l). Yellow solid (415 mg, 87%). Mp 115 – 116 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.20 (d, J = 1.8 Hz, 1H), 8.19 (d, J = 1.8 Hz, 1H), 8.12 (d, J = 9.0 Hz, 1H), 8.04 (d, J = 9.6 Hz, 1H), 8.01 (d, J = 9.0 Hz, 1H), 7.95 (d, J = 9.0 Hz, 1H), 7.79 (t, J = 4.2 Hz, 1H), 7.42 (m, 2H), 7.36 (m, 2H), 7.32 (m, 1H), 5.25 (dd, J_1 = 14.4 Hz, J_2 = 4.8 Hz, 1H), 4.90 (dd, J_1 = 14.4 Hz, J_2 = 4.8 Hz, 1H), 1.74 (s, 9H), 1.60 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 203.1, 149.2, 142.5, 136.7, 135.5, 130.93, 130.86, 130.2, 129.0, 128.8, 128.4, 128.3, 128.05, 127.7, 127.2, 124.3, 124.1, 122.9, 122.7, 122.3, 122.2, 50.9, 37.7, 35.2, 32.6, 31.9. IR (KBr, cm^{-1}): 3395, 3351, 2958, 1602, 1497, 1380, 1360, 1226, 881. Anal. Calcd. for $C_{32}H_{33}NS$: C, 82.89; H, 7.17; N, 3.02; S, 6.92. Found: C, 82.95; H, 7.21; N, 2.94, S, 6.86.

2,7-Di-*tert*-butyl-*N*-phenylpyrenecarbothioamides (3m). (Mixture of 1 and 4- isomers_ (3:1). Pale brown solid (369 mg, 82%). Mp 238 – 247 °C. Main component: ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.34 (s, 1H), 8.27 (d, J = 9.6 Hz, 1H), 8.21 (d, J = 1.8 Hz, 1H), 8.19 (d, J =

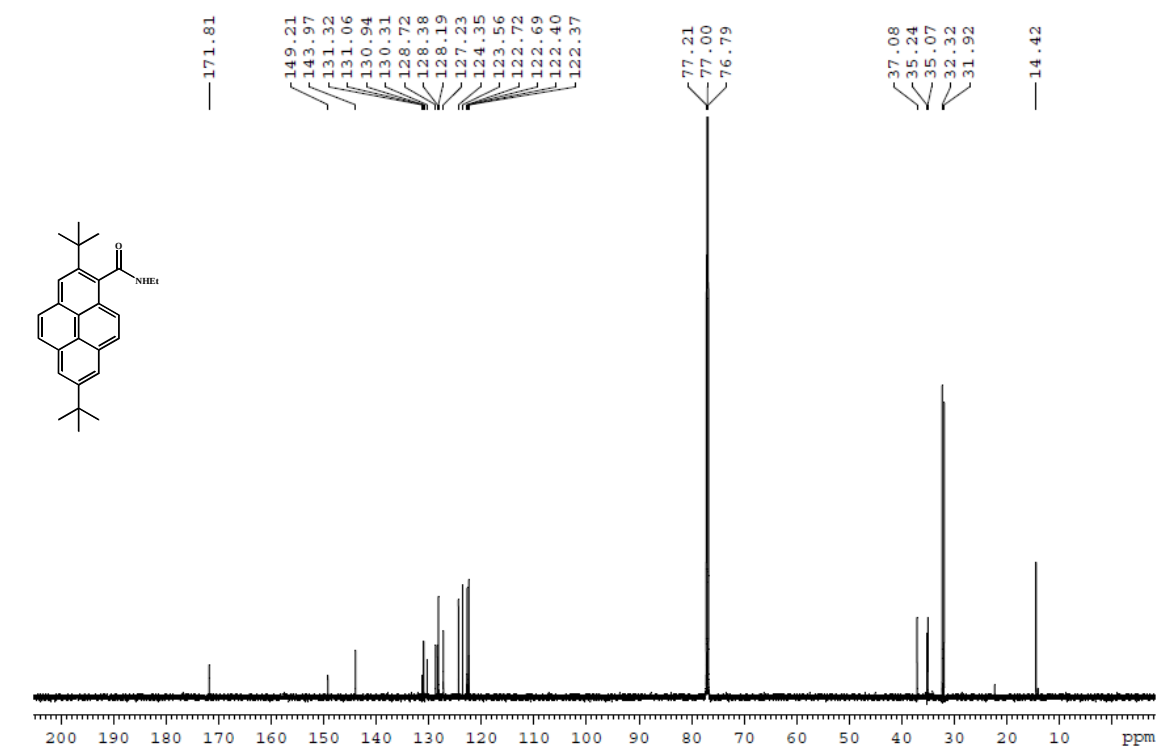
1.8 Hz, 1H), 8.06 (d, *J* = 9.6 Hz, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 7.99 (d, *J* = 9.0 Hz, 1H), 7.96 (m, 2H), 7.49 (m, 2H), 7.35 (m, 1H), 6.88 (m, 1H), 1.79 (s, 9H), 1.60 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 202.1, 149.3, 142.3, 138.5, 137.9, 131.0, 130.3, 129.2, 129.2, 128.7, 128.2, 127.5, 127.2, 127.1, 124.4, 124.1, 123.0, 122.9, 122.8, 122.4, 122.3, 119.8, 37.9, 32.8, 32.5, 31.9. IR (KBr, cm^{-1}): 3436, 3378, 3212, 3050, 2961, 1597, 1549, 1363, 1226, 880. Anal. Calcd. for $C_{31}H_{31}NS$: C, 82.80; H, 6.95; N, 3.12; S, 7.13. Found: C, 82.85; H, 7.01; N, 3.03, S, 7.05.

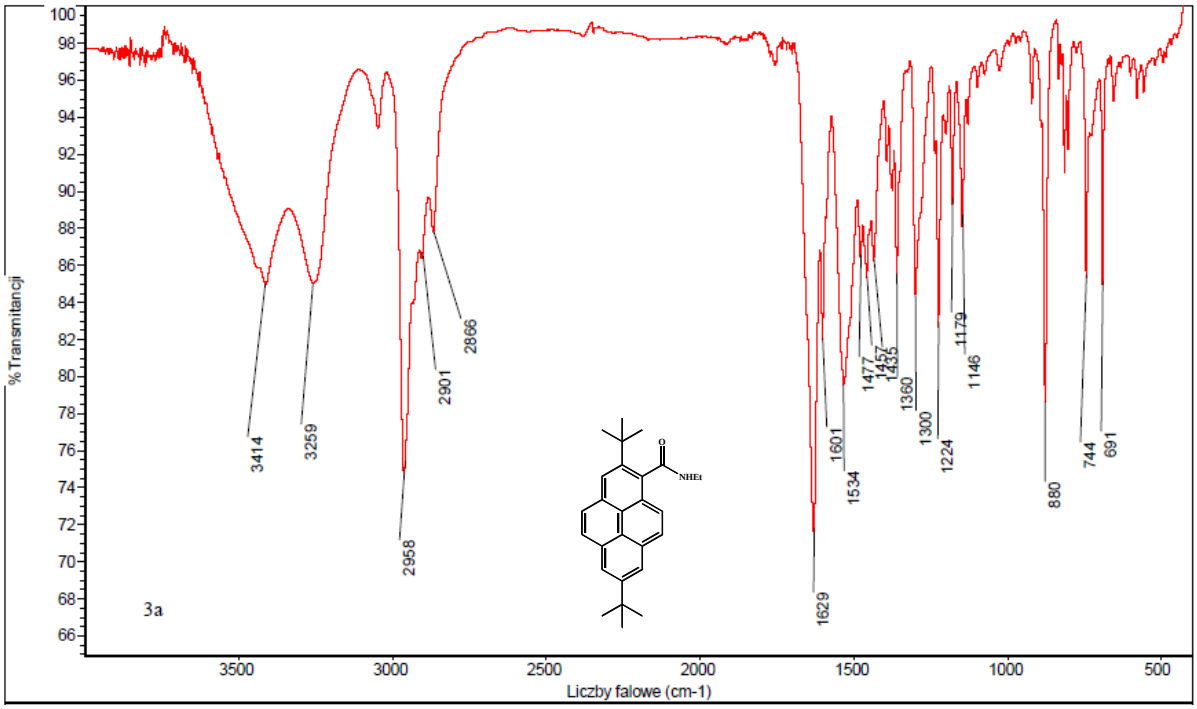
2,7-Di-*tert*-butyl-*N*-(4-methoxyphenyl)pyrene-1-carbothioamide (3n). Yellow solid (427 mg, 89%). Mp 237 – 238 °C. ^{1}H NMR (600 MHz, DMSO): δ 12.36 (s, 1H), 8.47 (s, 1H), 8.36 (d, *J* = 1.2 Hz, 1H), 8.29 (d, *J* = 1.8 Hz, 1H), 8.18 (d, *J* = 9.6 Hz, 1H), 8.14 (m, 3H), 8.04 (m, 2H), 7.08 (m, 2H), 3.82 (s, 1H), 1.73(s, 9H), 1.55 (s, 9H). ^{13}C NMR (150 MHz, DMSO): δ 199.2, 158.0, 149.4, 142.2, 138.5, 133.1, 131.1, 130.4, 130.3, 128.5, 128.1, 127.7, 127.2, 125.01, 124.97, 124.8, 123.1, 122.6, 122.45, 122.1, 114.4, 55.9, 38.1, 35.5, 32.9, 32.2. IR (KBr, cm^{-1}): 3173, 2949, 1602, 1546, 1507, 1378, 1247, 1226, 1037, 835. Anal. Calcd. for $C_{32}H_{33}NOS$: C, 80.13; H, 6.93; N, 2.92; O, 3.34; S, 6.68. Found: C, 80.17; H, 7.02; N, 2.84, S, 6.65.

3a

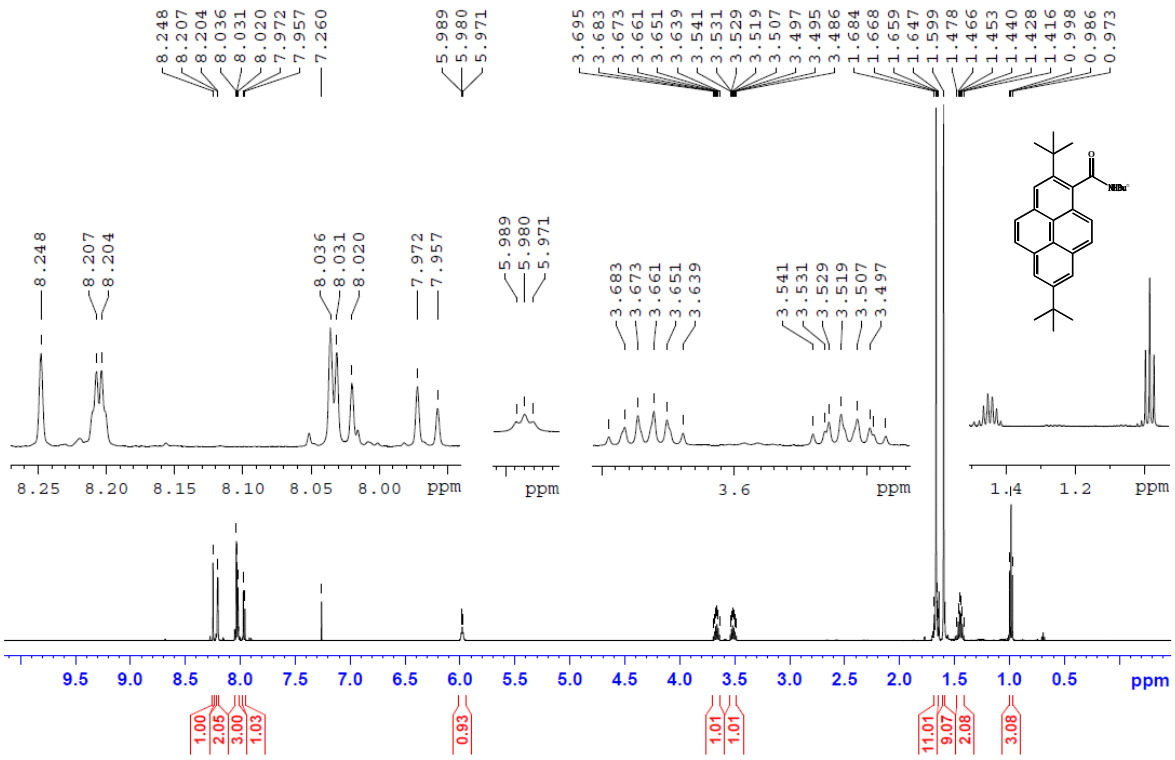


3a

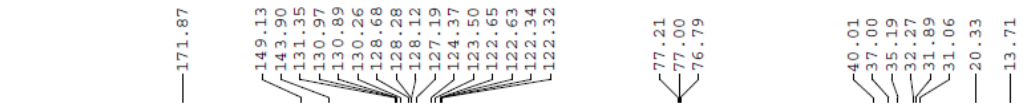


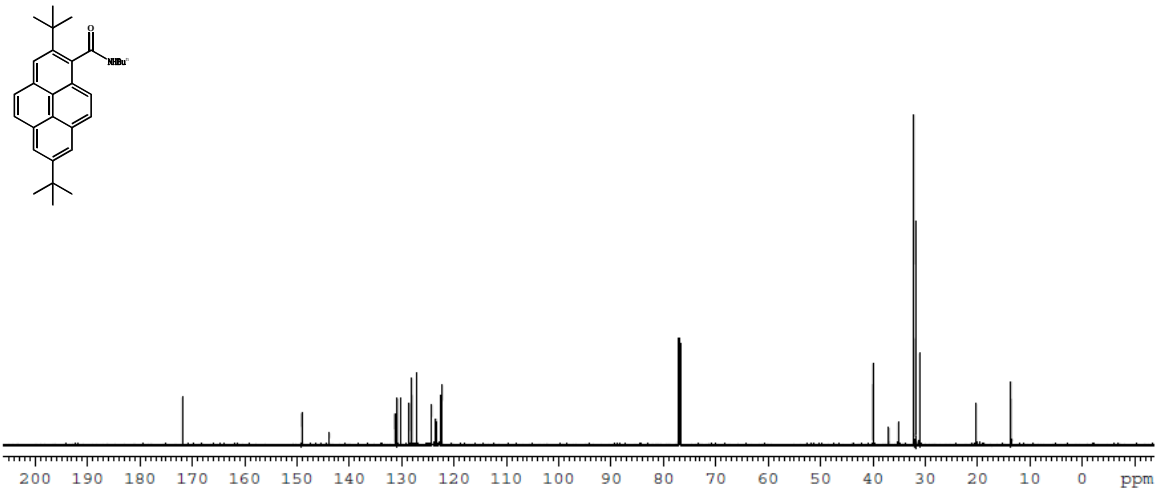

% Transmitancji
Liczby falowe (cm-1)
3a
3414
3259
2958
2901
2866
1629
1601
1534
1477
1457
1435
1360
1300
1224
1179
1146
880
744
691

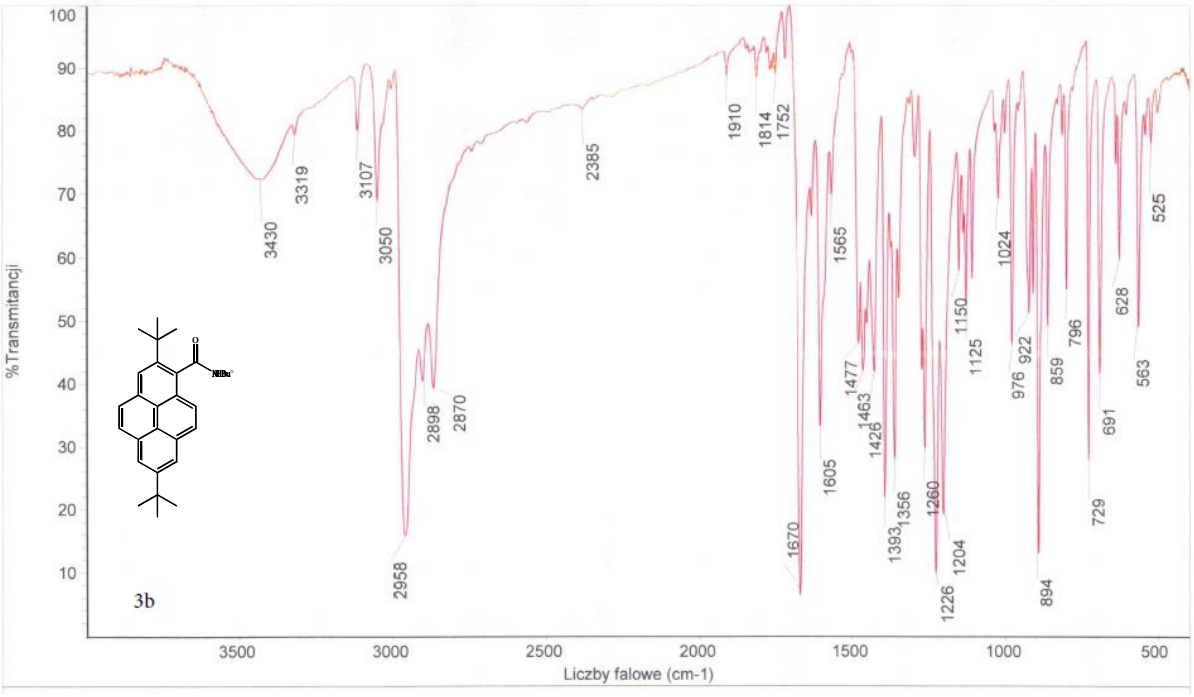
3b


8.248
8.207
8.204
8.036
8.031
8.020
7.972
7.957
7.260
5.989
5.980
5.971
3.695
3.683
3.673
3.661
3.651
3.639
3.541
3.531
3.529
3.519
3.507
3.497
3.495
3.486
1.684
1.668
1.659
1.647
1.599
1.478
1.466
1.453
1.440
1.428
1.416
0.998
0.986
0.973
ppm

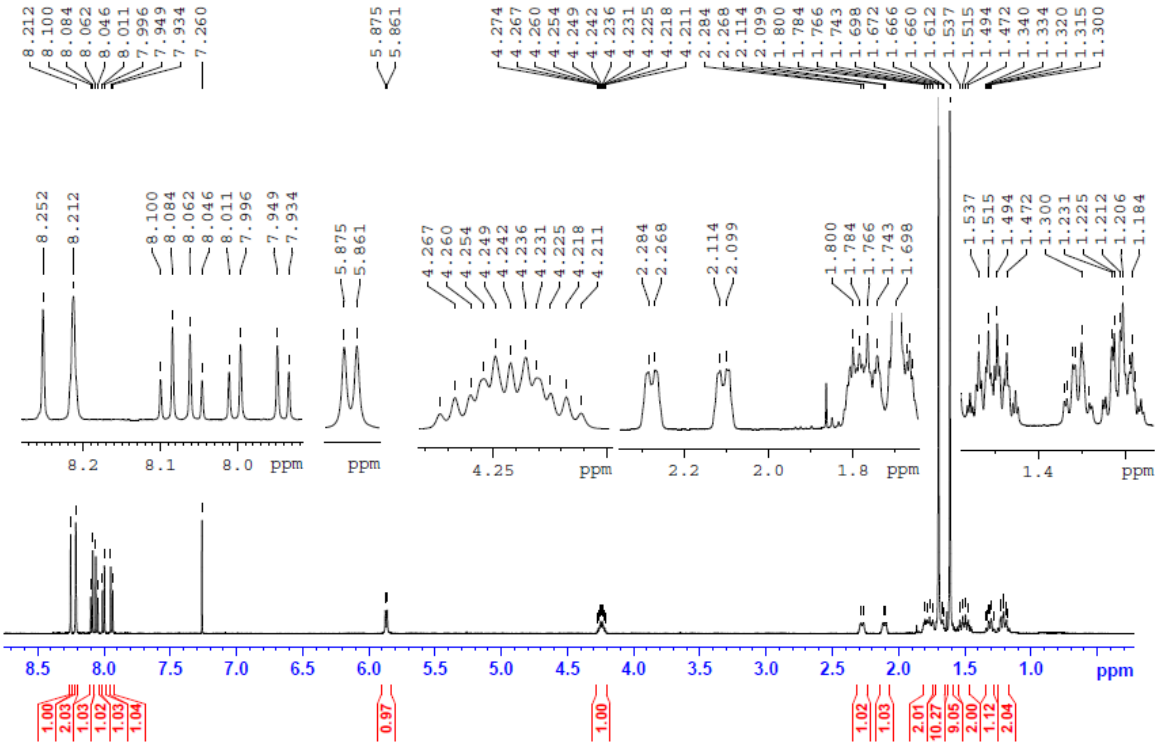
3b


171.87
149.13
143.90
131.35
130.97
130.89
130.26
128.68
128.28
128.12
127.19
124.37
123.50
122.65
122.63
122.34
122.32
77.21
77.00
76.79
40.01
37.00
35.19
32.27
31.89
31.06
20.33
13.71

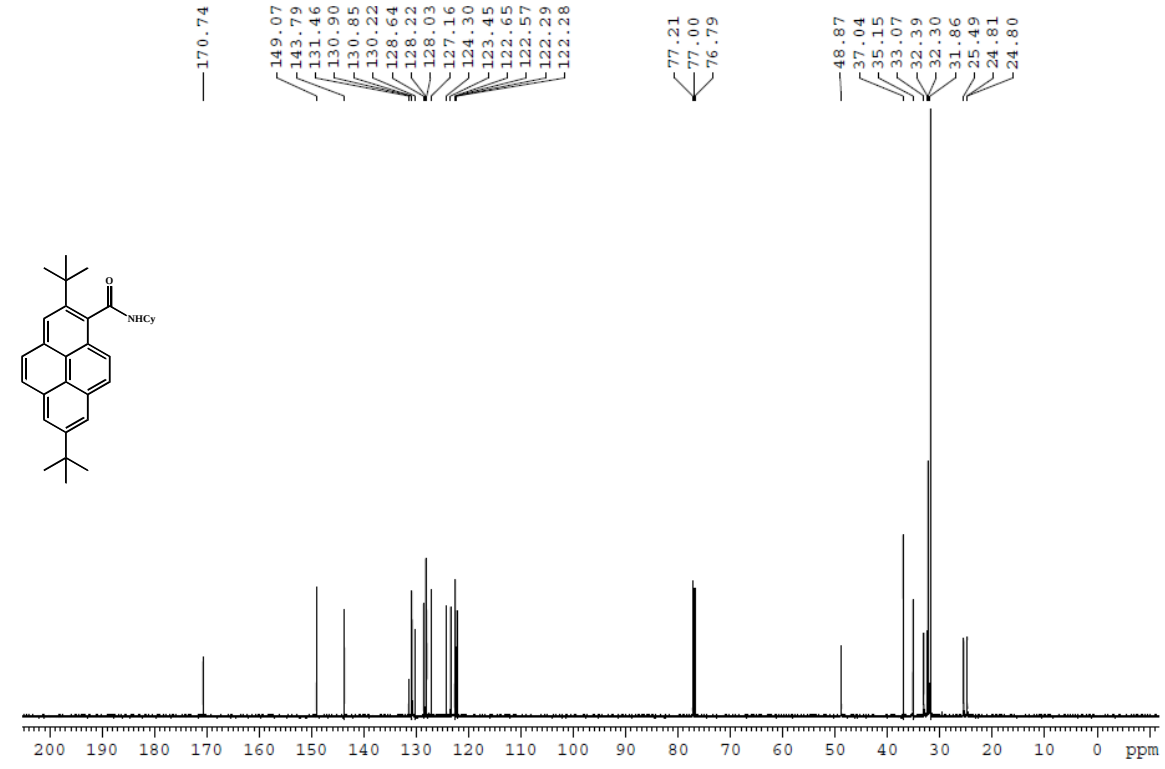

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

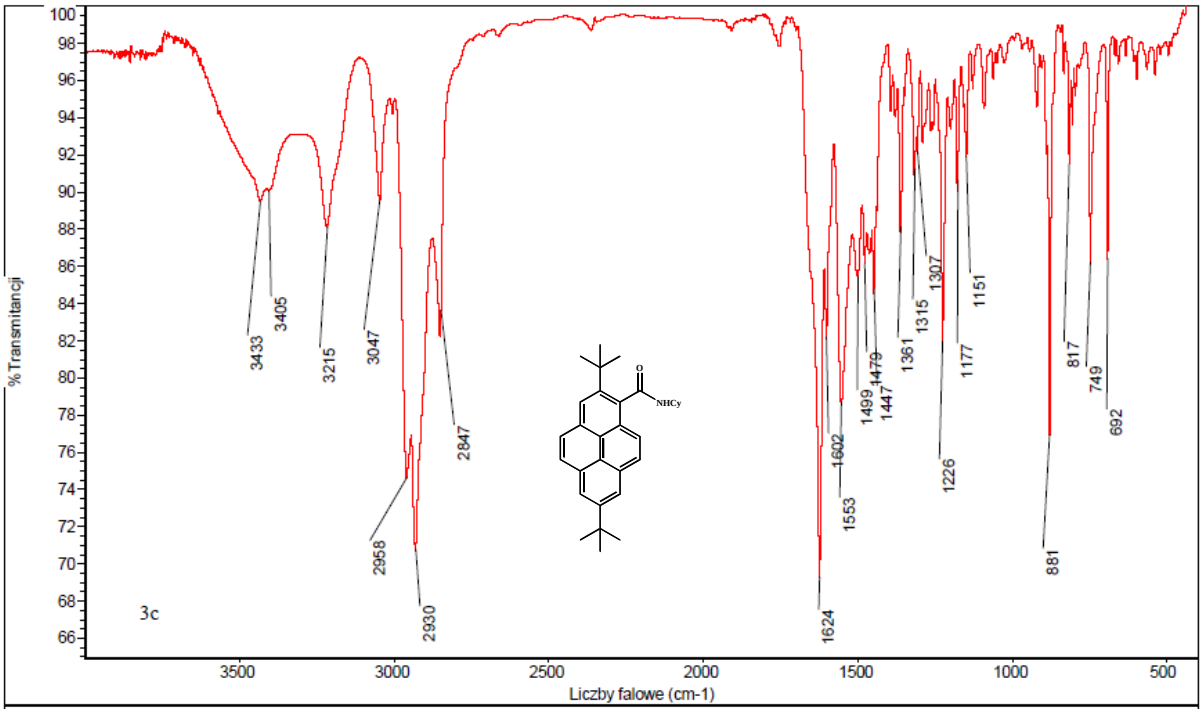

%Transmitancji
Liczby falowe (cm-1)
3b
3430
3319
3107
3050
2958
2898
2870
2385
1910
1814
1752
1670
1605
1565
1477
1463
1426
1393
1356
1260
1226
1204
1150
1125
1024
976
922
894
859
796
729
691
628
563
525

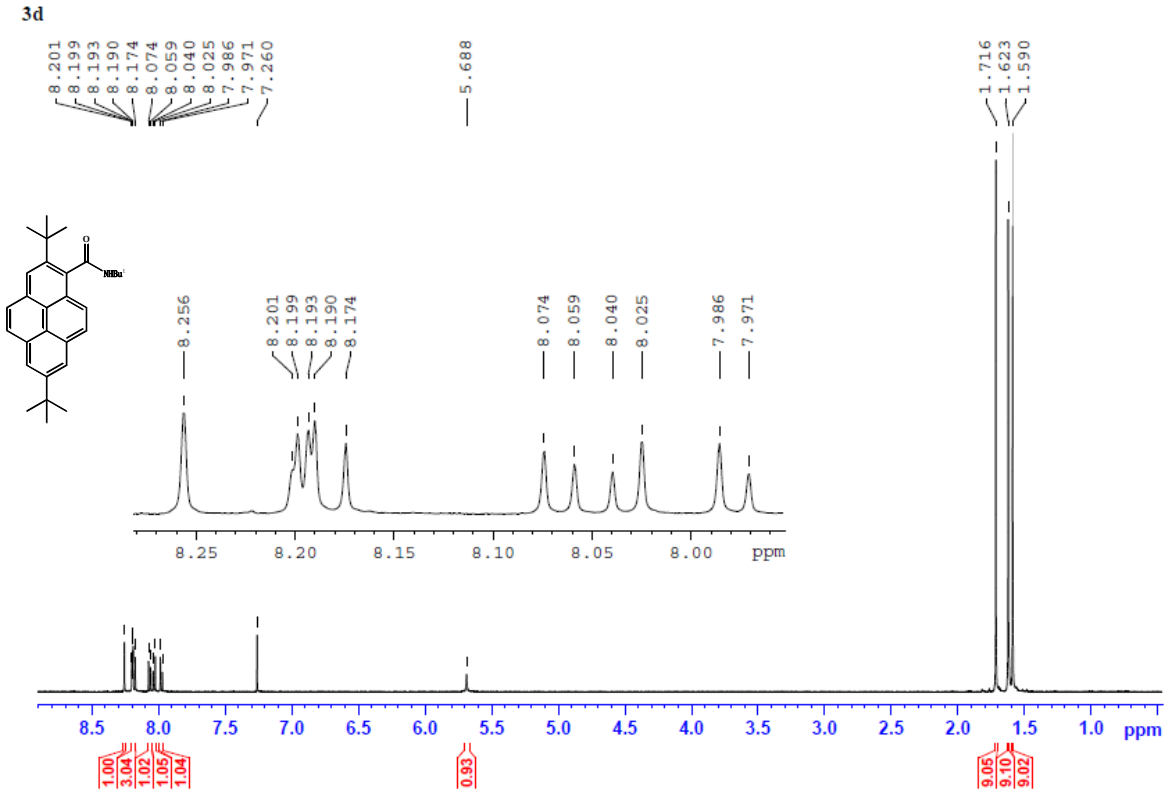
3c



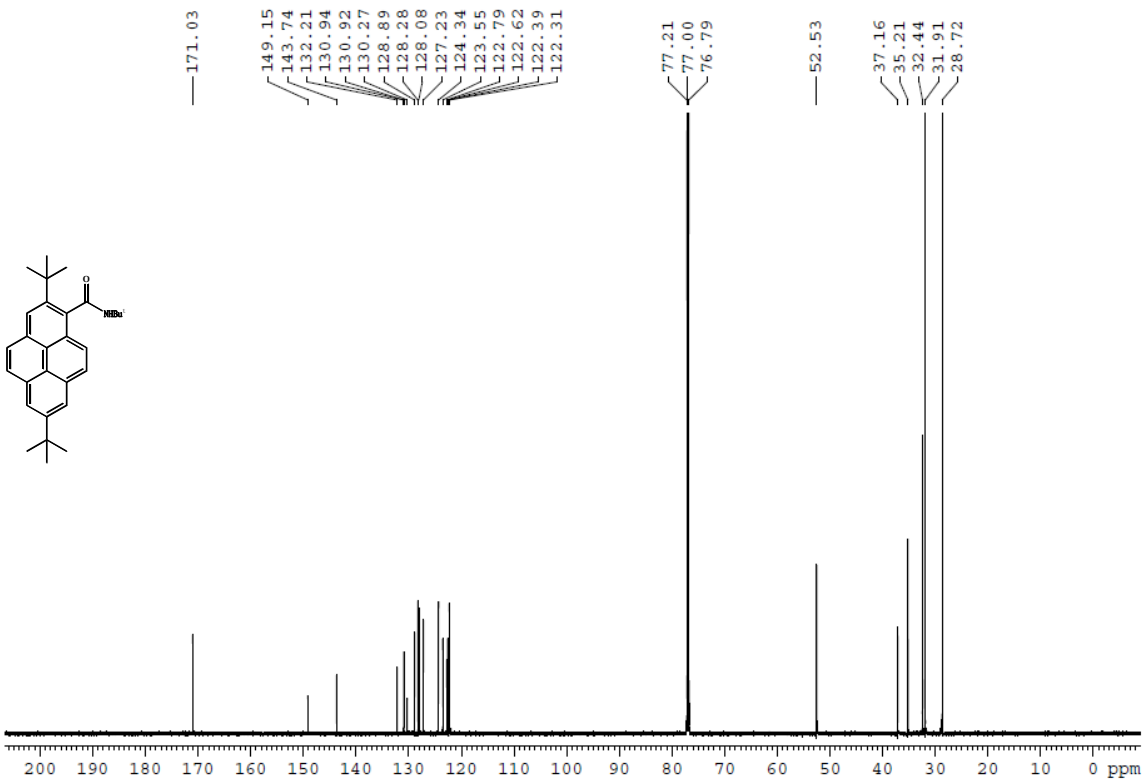
3c

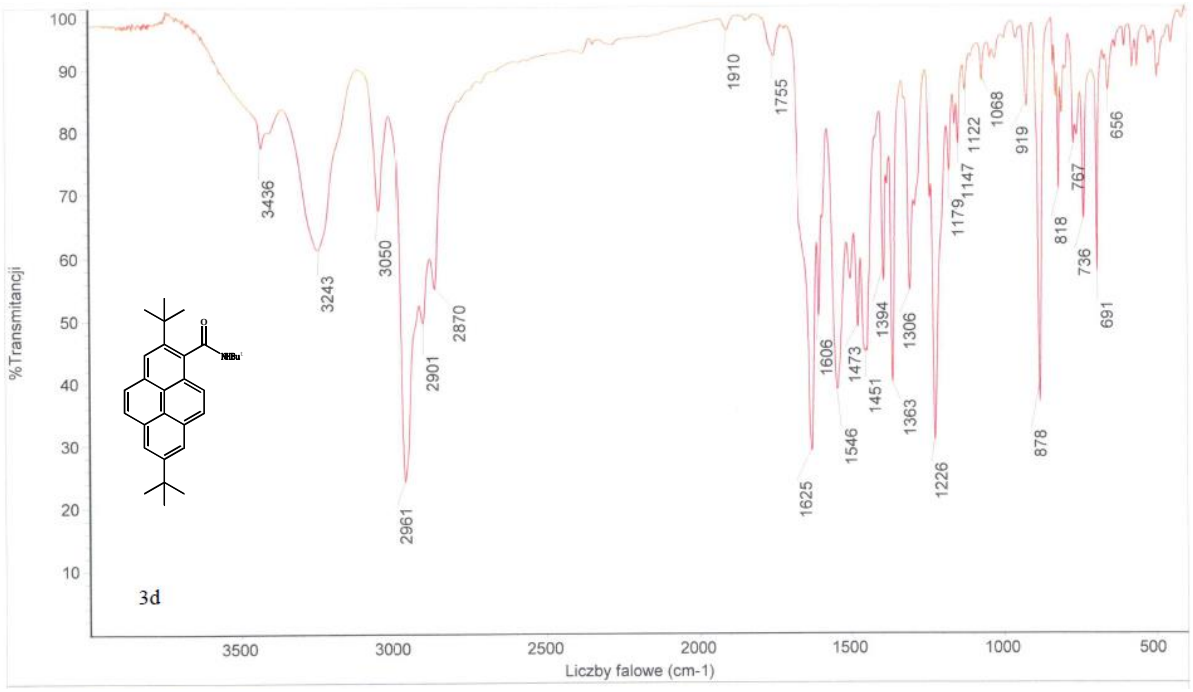


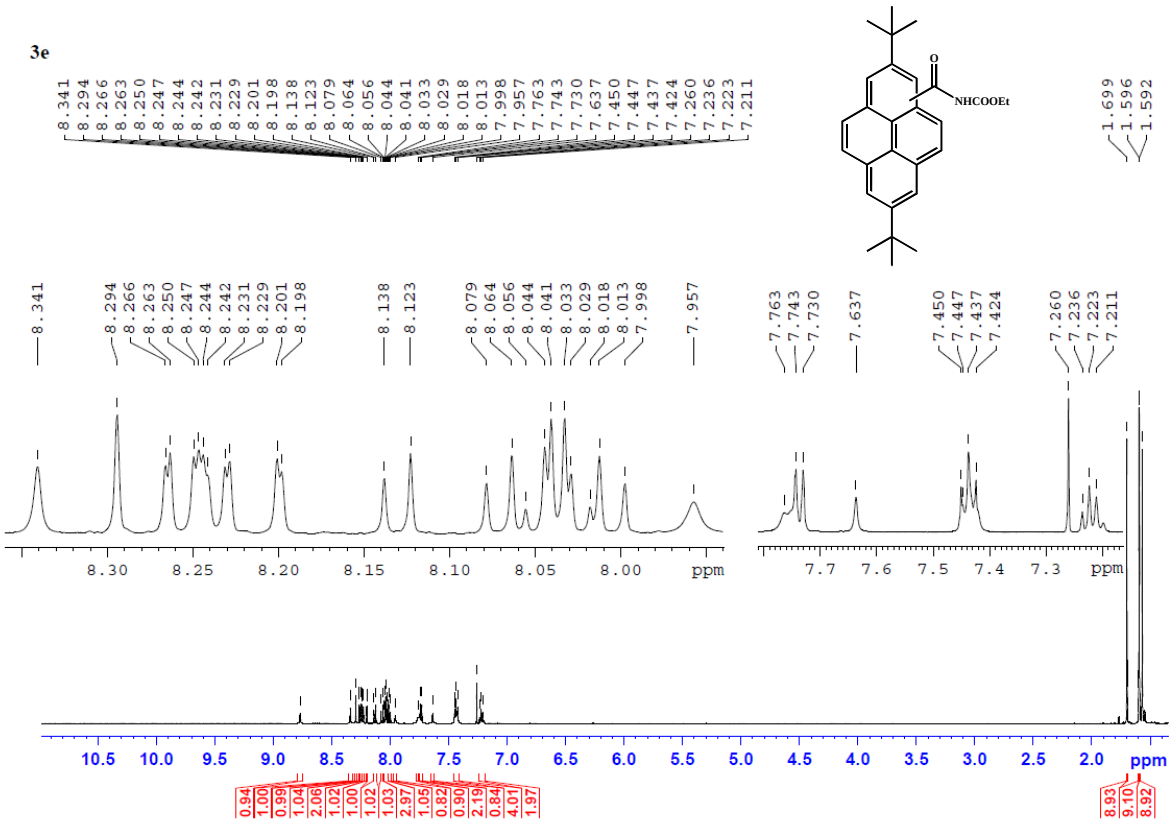

% Transmitancji
Liczby falowe (cm-1)
3c
3433
3405
3215
3047
2958
2930
2847
1624
1602
1553
1499
1479
1447
1361
1315
1307
1226
1177
1151
881
817
749
692
NHCy

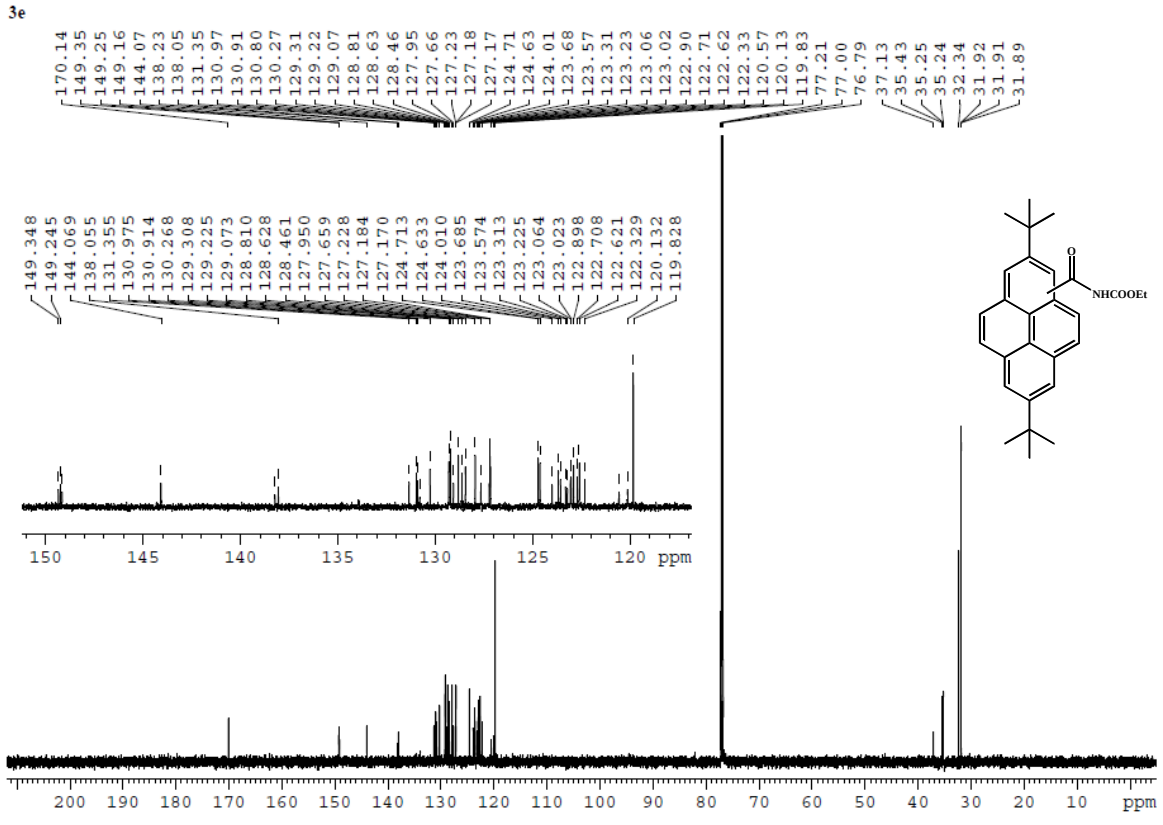

3d
8.201
8.199
8.193
8.190
8.174
8.074
8.059
8.040
8.025
7.986
7.971
7.260
5.688
1.716
1.623
1.590
8.256
ppm
1.00
3.04
1.02
1.05
1.04
0.93
9.05
9.10
9.02

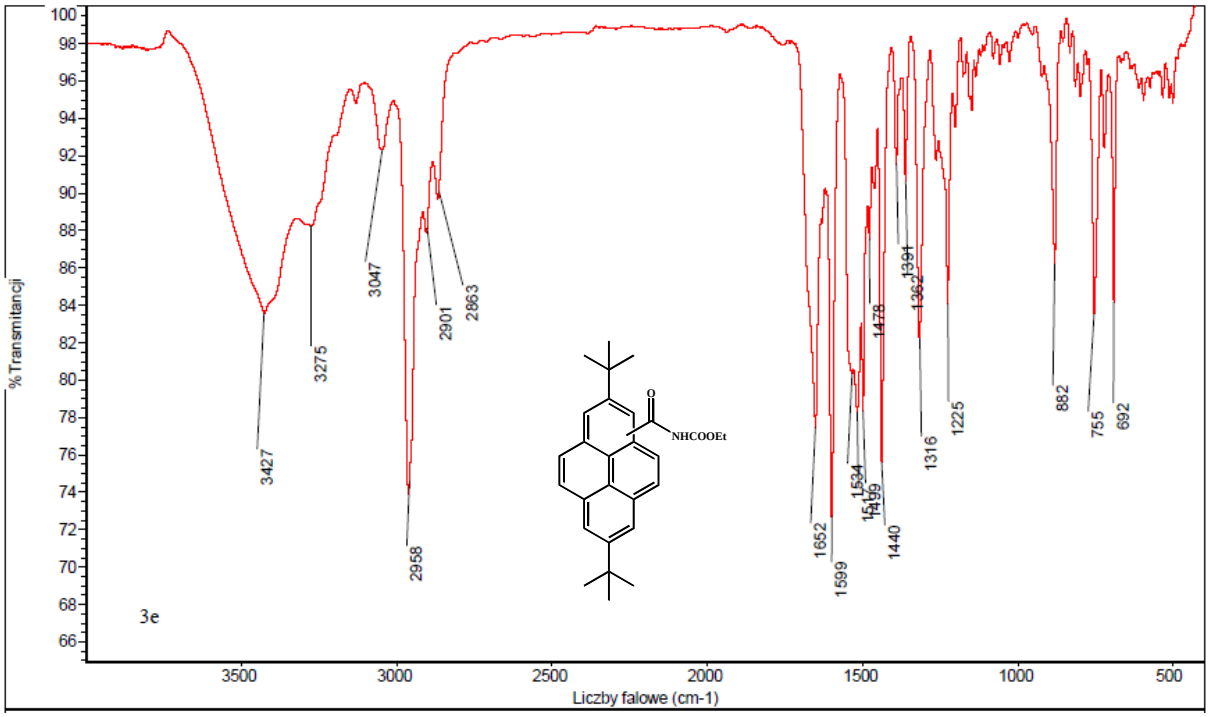
3d

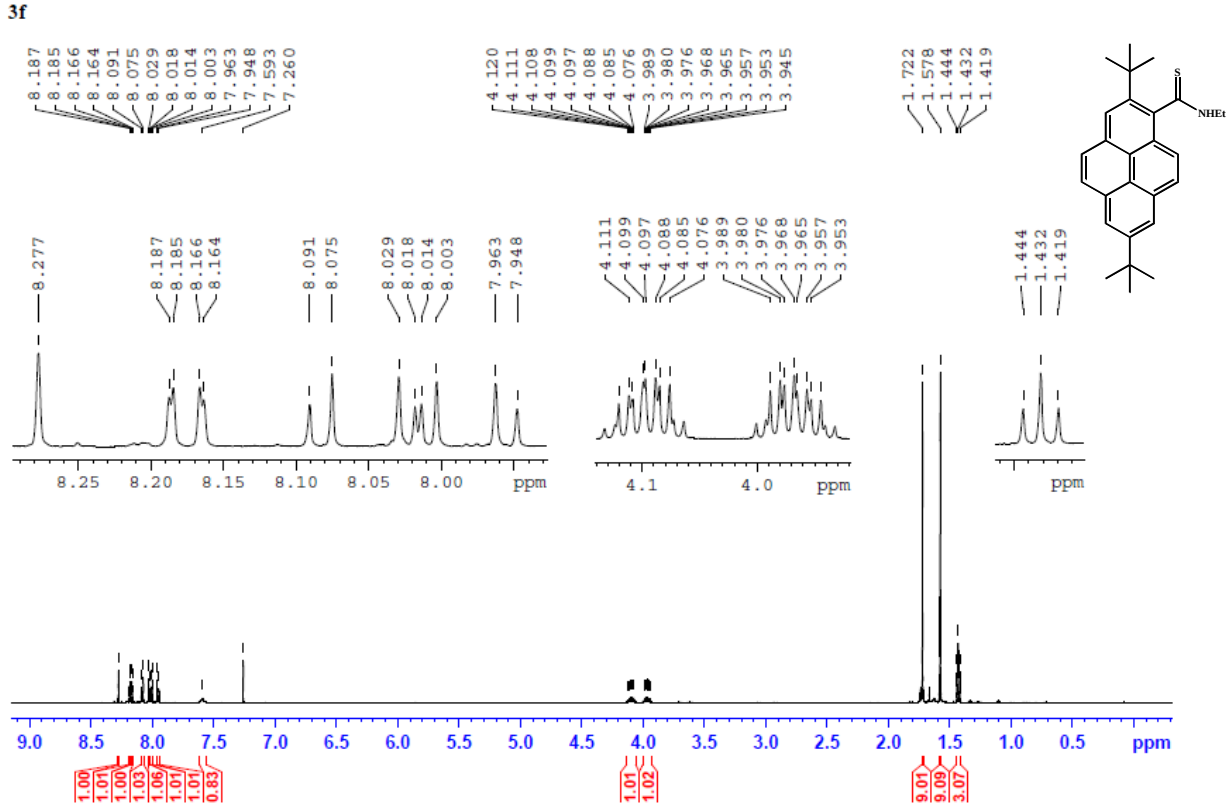

171.03
149.15
143.74
132.21
130.94
130.92
130.27
128.89
128.28
128.08
127.23
124.34
123.55
122.79
122.62
122.39
122.31
77.21
77.00
76.79
52.53
37.16
35.21
32.44
31.91
28.72
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

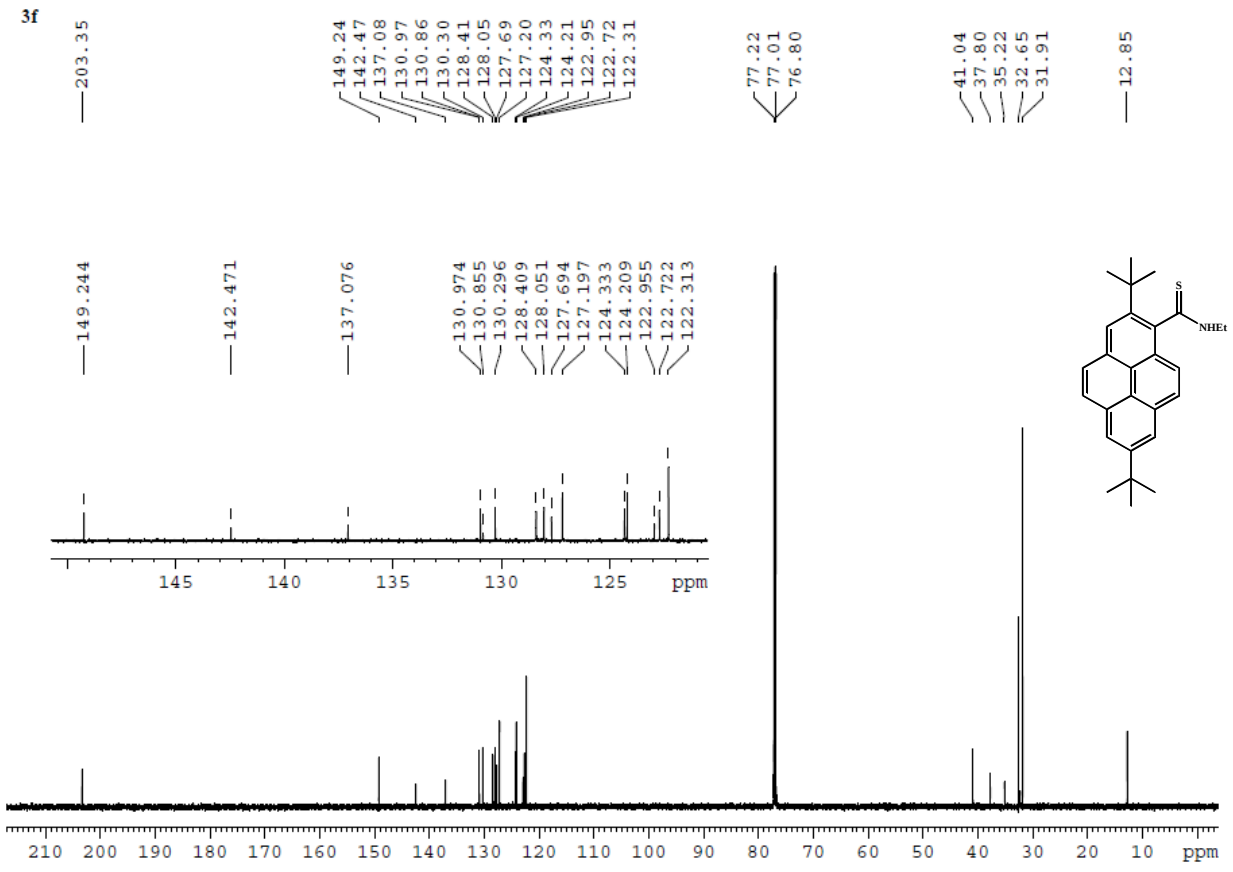

%Transmitancji
100 90 80 70 60 50 40 30 20 10
3436
3243
3050
2961
2901
2870
1910
1755
1625
1606
1546
1473
1451
1394
1363
1306
1226
1179
1147
1122
1068
919
878
818
767
736
691
656
3d
3500 3000 2500 2000 1500 1000 500
Liczby falowe (cm-1)

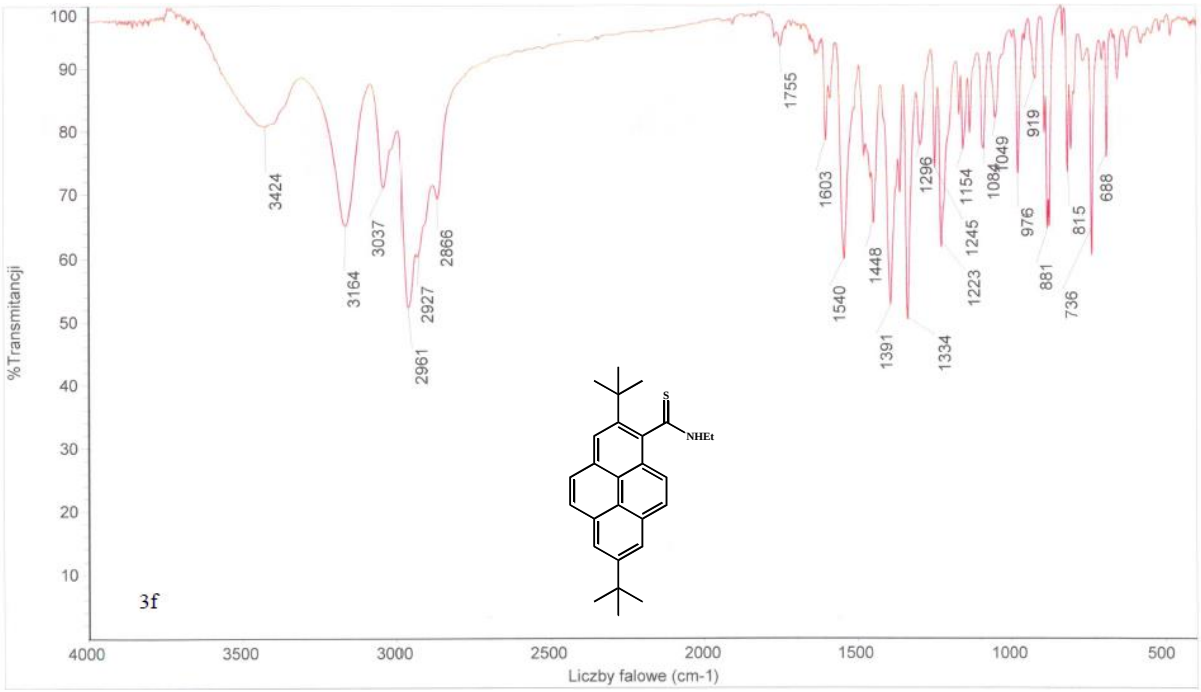

3e
8.341
8.294
8.266
8.263
8.250
8.247
8.244
8.242
8.231
8.229
8.201
8.198
8.138
8.123
8.079
8.064
8.056
8.044
8.041
8.033
8.029
8.018
8.013
7.998
7.957
7.763
7.743
7.730
7.637
7.450
7.447
7.437
7.424
7.260
7.236
7.223
7.211
1.699
1.596
1.592
NHCOOEt
ppm


3e
170.14
149.35
149.25
149.16
144.07
138.23
138.05
131.35
130.97
130.91
130.80
130.27
129.31
129.22
129.07
128.81
128.63
128.46
127.95
127.66
127.23
127.18
127.17
124.71
124.63
124.01
123.68
123.57
123.31
123.23
123.06
123.02
122.90
122.71
122.62
122.33
120.57
120.13
119.83
77.21
77.00
76.79
37.13
35.43
35.25
35.24
32.34
31.92
31.91
31.89
NHCOOEt
ppm

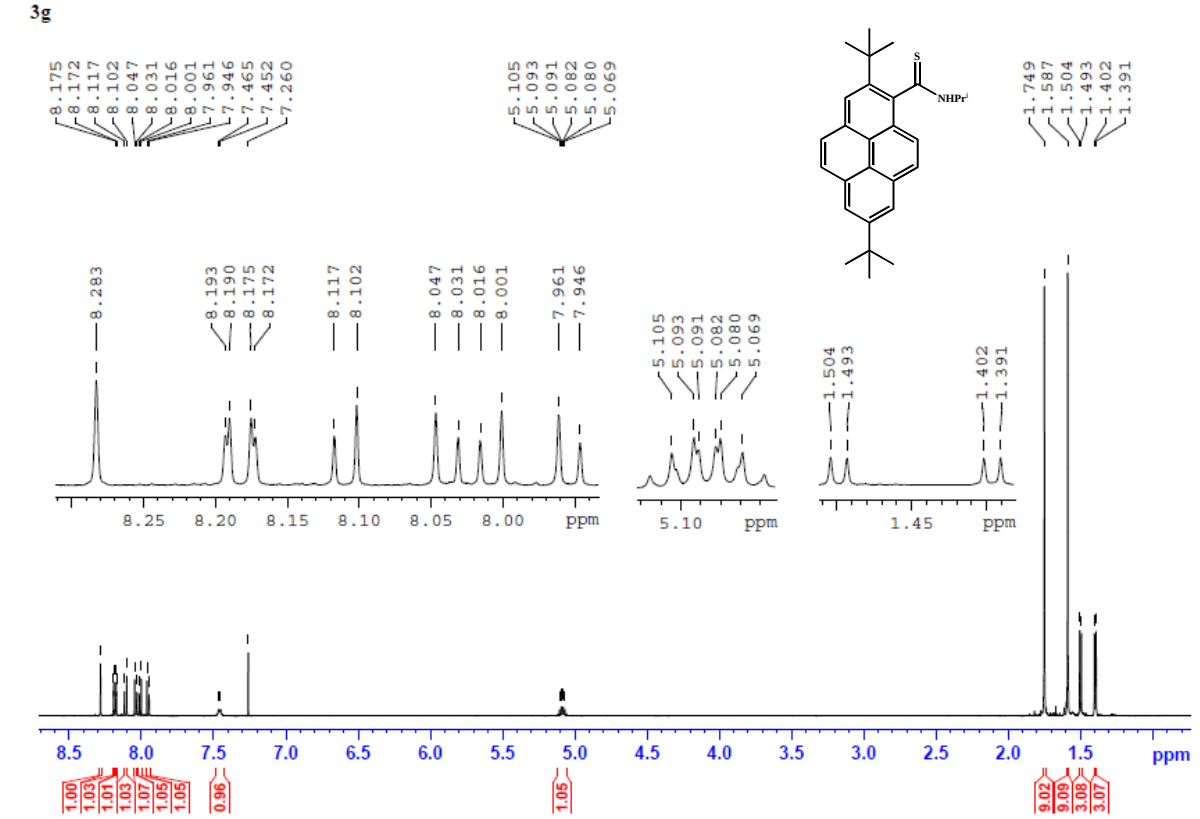

% Transmitancji
Liczby falowe (cm-1)
3427
3275
3047
2958
2901
2863
1652
1599
1534
1517
1499
1478
1440
1391
1362
1316
1225
882
755
692
NHCOOEt
3e


3f
NHEt
ppm

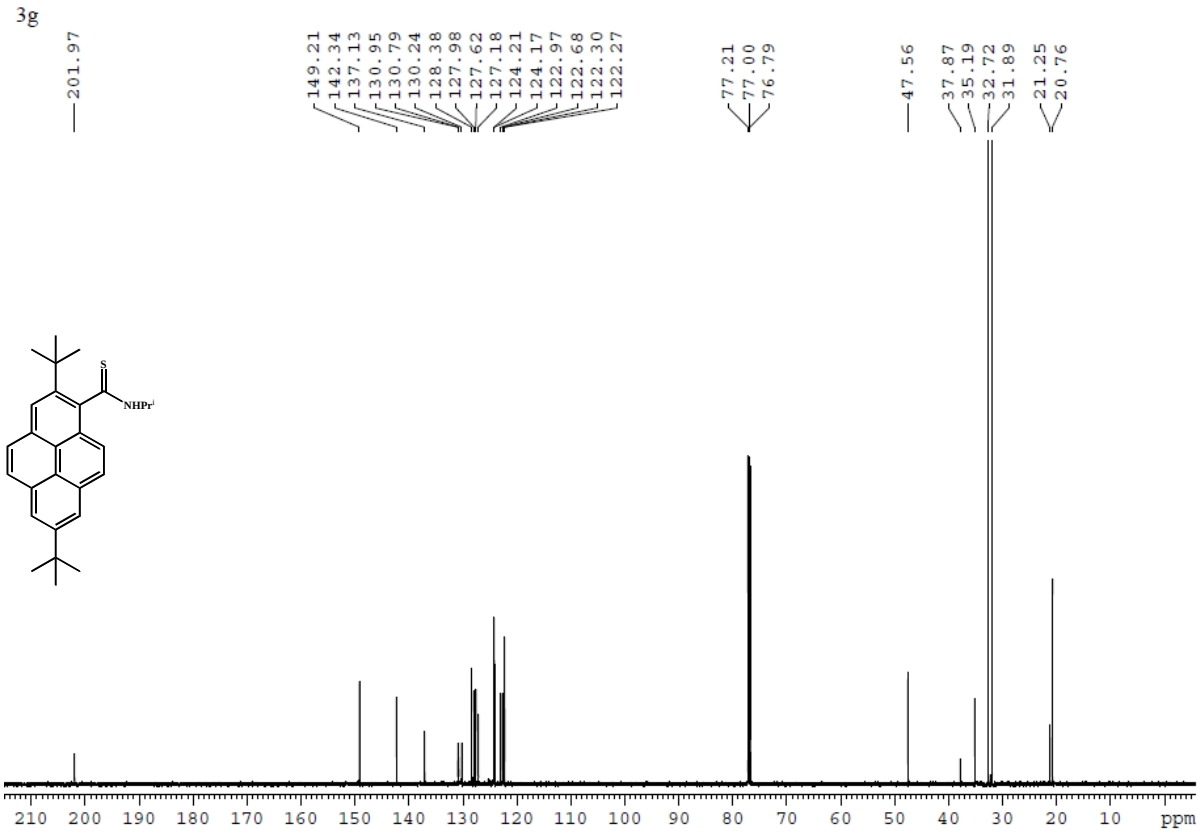

3f
203.35
149.24
142.47
137.08
130.97
130.86
130.30
128.41
128.05
127.69
127.20
124.33
124.21
122.95
122.72
122.31
77.22
77.01
76.80
41.04
37.80
35.22
32.65
31.91
12.85
149.244
142.471
137.076
130.974
130.855
130.296
128.409
128.051
127.694
127.197
124.333
124.209
122.955
122.722
122.313
S
NHEt
145
140
135
130
125
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

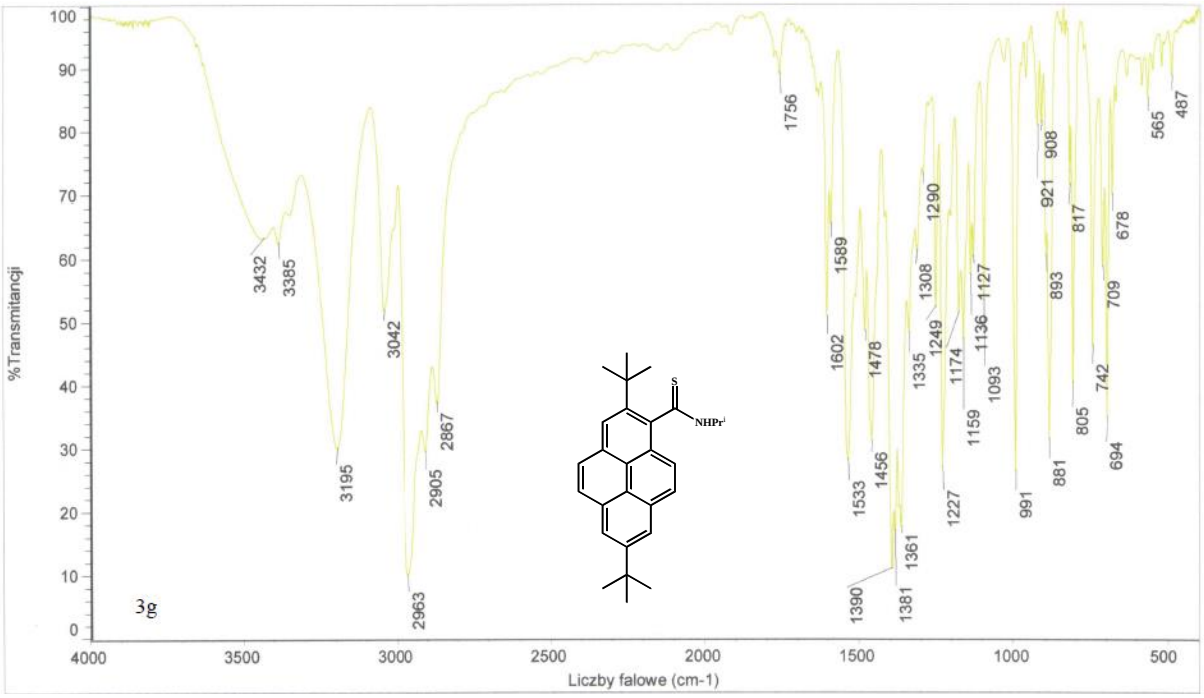

%Transmitancji
100
90
80
70
60
50
40
30
20
10
3424
3164
3037
2961
2927
2866
1755
1603
1540
1448
1391
1334
1296
1245
1223
1154
1084
1049
976
919
881
815
736
688
S
NHEt
3f
4000
3500
3000
2500
2000
1500
1000
500
Liczby falowe (cm-1)

3g

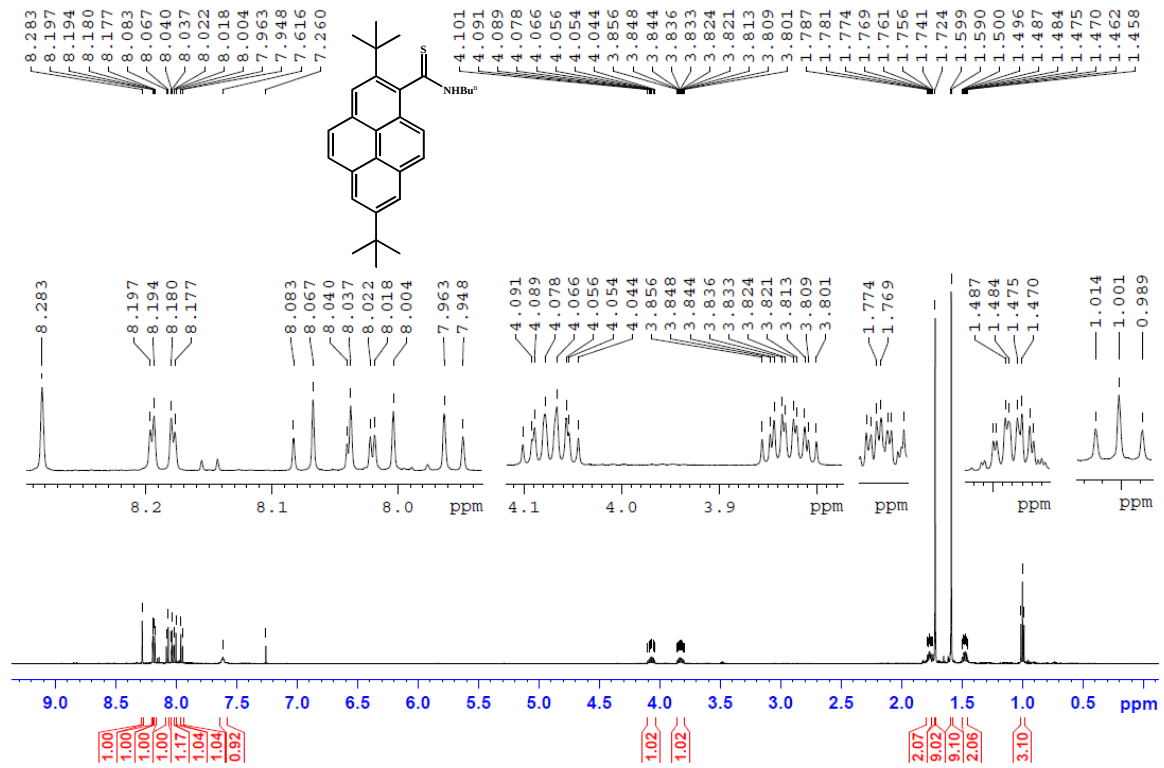

8.175
8.172
8.117
8.102
8.047
8.031
8.016
8.001
7.961
7.946
7.465
7.452
7.260
5.105
5.093
5.091
5.082
5.080
5.069
1.749
1.587
1.504
1.493
1.402
1.391
S
NHPr^{i}
8.283
8.193
8.190
8.175
8.172
8.117
8.102
8.047
8.031
8.016
8.001
7.961
7.946
5.105
5.093
5.091
5.082
5.080
5.069
1.504
1.493
1.402
1.391
8.25
8.20
8.15
8.10
8.05
8.00
ppm
5.10
ppm
1.45
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.00
1.03
1.01
1.03
1.07
1.05
1.05
0.96
1.05
9.02
9.09
3.08
3.07

3g

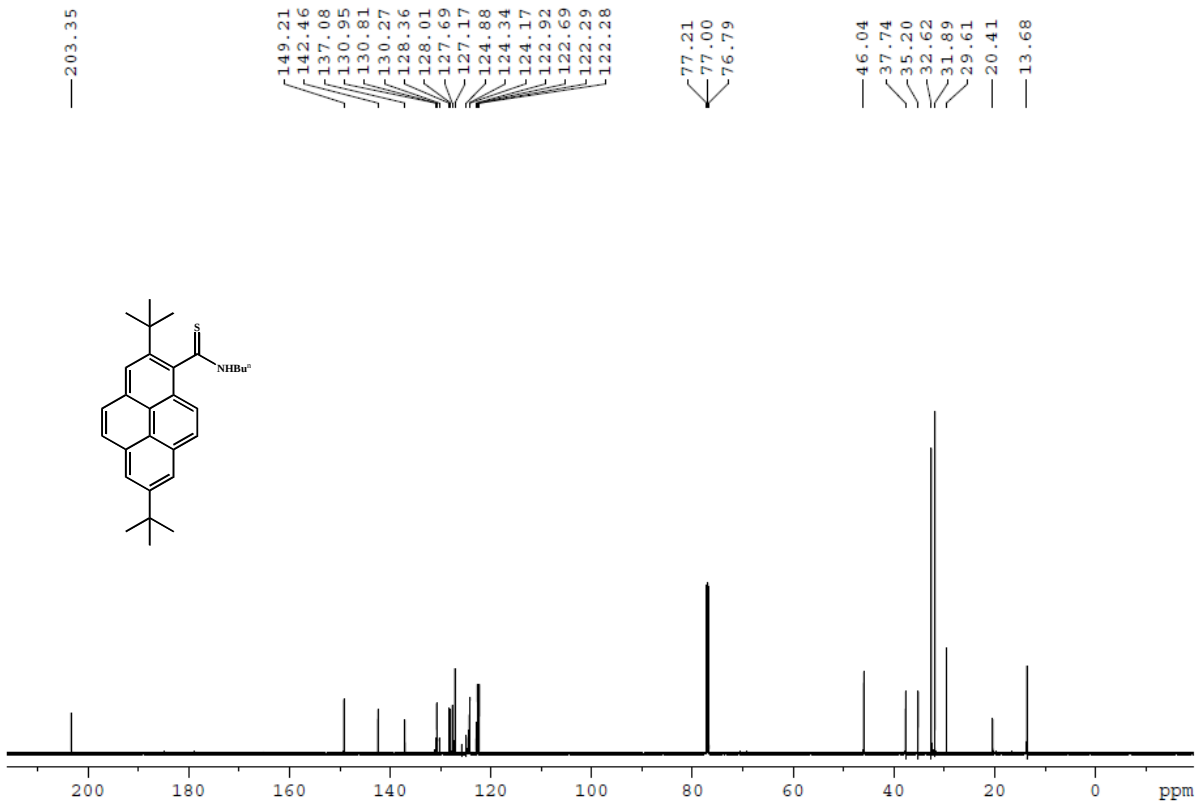

201.97
149.21
142.34
137.13
130.95
130.79
130.24
128.38
127.98
127.62
127.18
124.21
124.17
122.97
122.68
122.30
122.27
77.21
77.00
76.79
47.56
37.87
35.19
32.72
31.89
21.25
20.76
S
NHPr^{i}
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

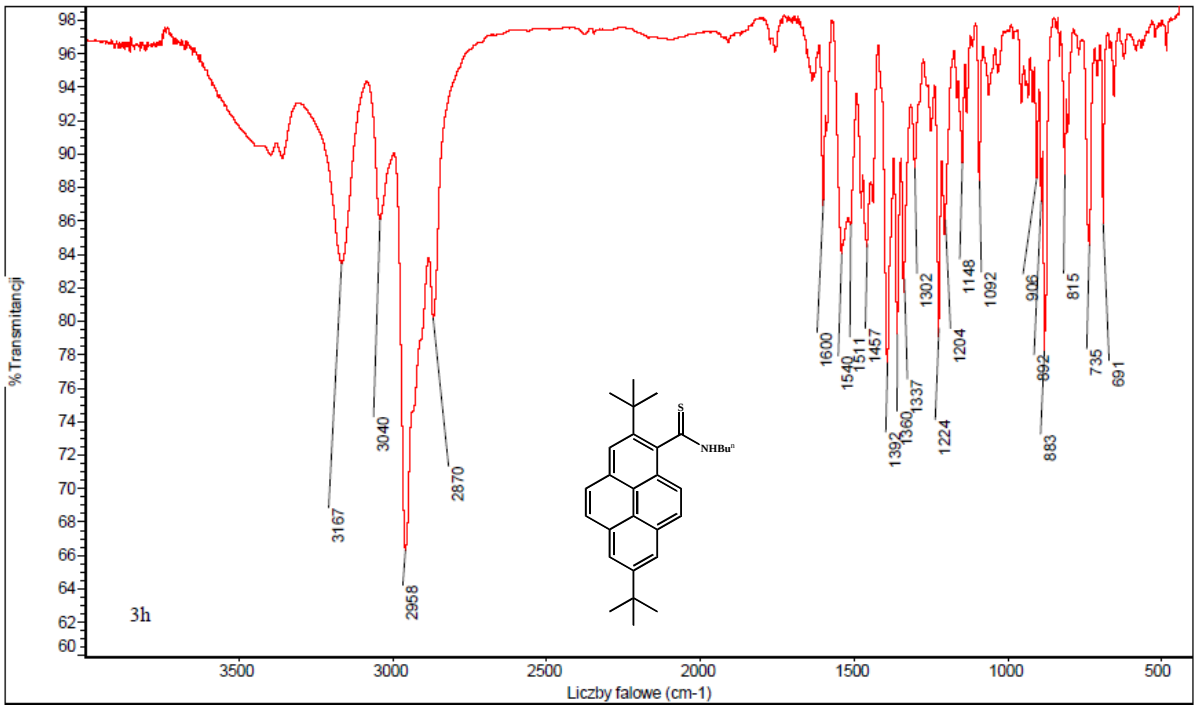

%Transmitancji
Liczby falowe (cm-1)
3g
NHPr^{i}
3432
3385
3195
3042
2963
2905
2867
1756
1602
1589
1533
1478
1456
1390
1381
1361
1335
1308
1290
1249
1227
1174
1159
1136
1127
1093
991
921
908
893
881
817
805
742
709
694
678
565
487

3h

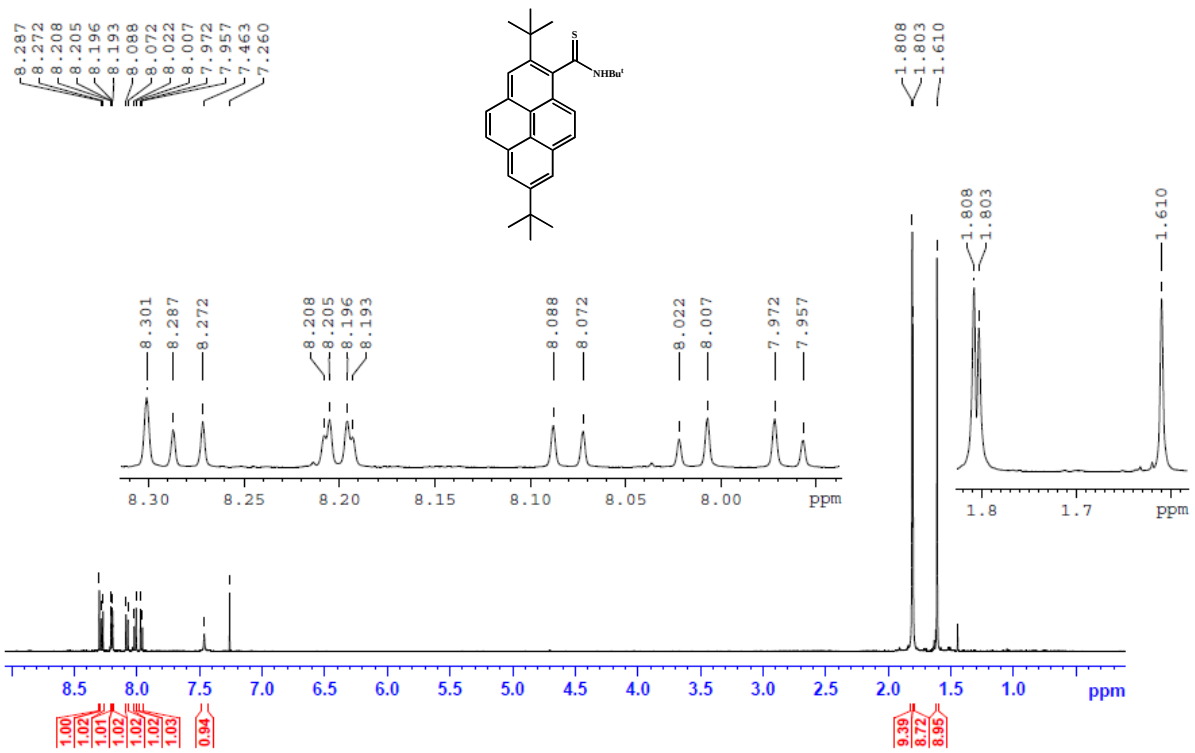

NHBu^{n}
8.283
8.197
8.194
8.180
8.177
8.083
8.067
8.040
8.037
8.022
8.018
8.004
7.963
7.948
7.616
7.260
4.101
4.091
4.089
4.078
4.066
4.056
4.054
4.044
3.856
3.848
3.844
3.836
3.833
3.824
3.821
3.813
3.809
3.801
1.787
1.781
1.774
1.769
1.761
1.756
1.741
1.724
1.599
1.590
1.500
1.496
1.487
1.484
1.475
1.470
1.462
1.458
ppm
1.014
1.001
0.989
1.00
1.00
1.00
1.00
1.17
1.04
1.04
0.92
1.02
1.02
2.07
9.02
9.10
2.06
3.10

3h

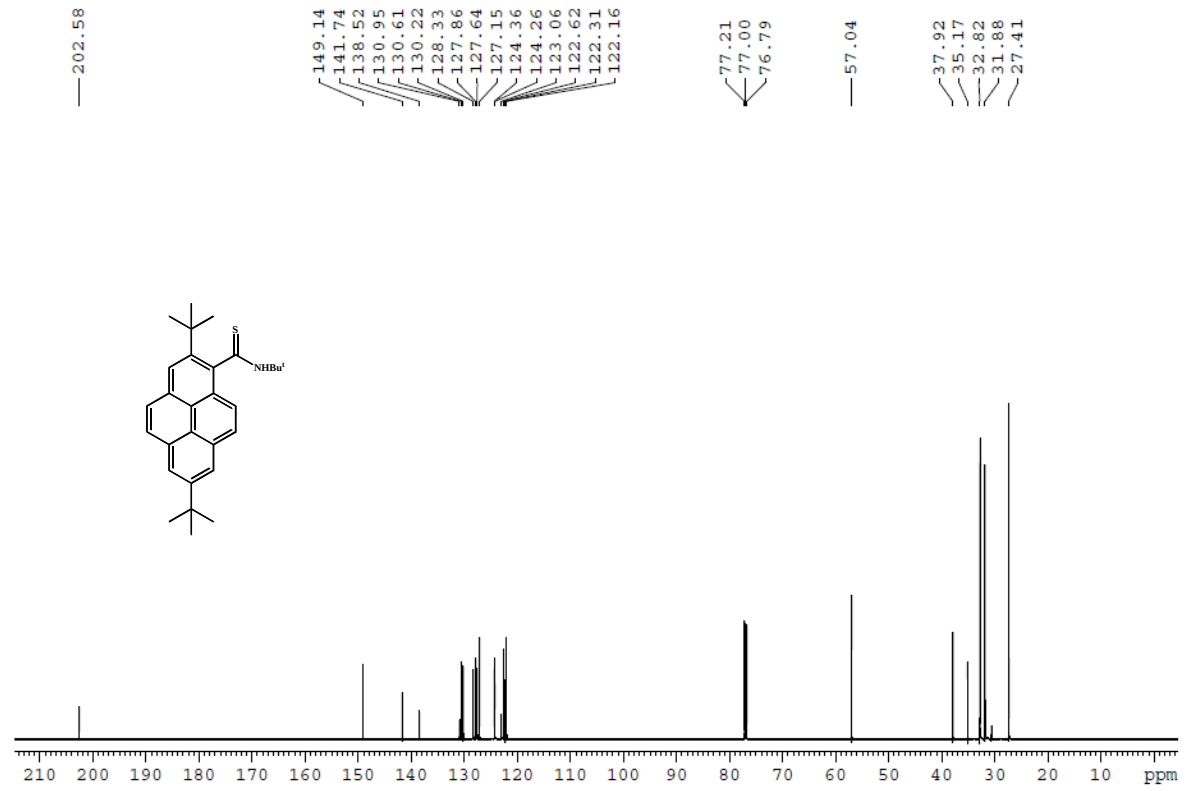

203.35
149.21
142.46
137.08
130.95
130.81
130.27
128.36
128.01
127.69
127.17
124.88
124.34
124.17
122.92
122.69
122.29
122.28
77.21
77.00
76.79
46.04
37.74
35.20
32.62
31.89
29.61
20.41
13.68
S
NHBu^n
200
180
160
140
120
100
80
60
40
20
0
ppm

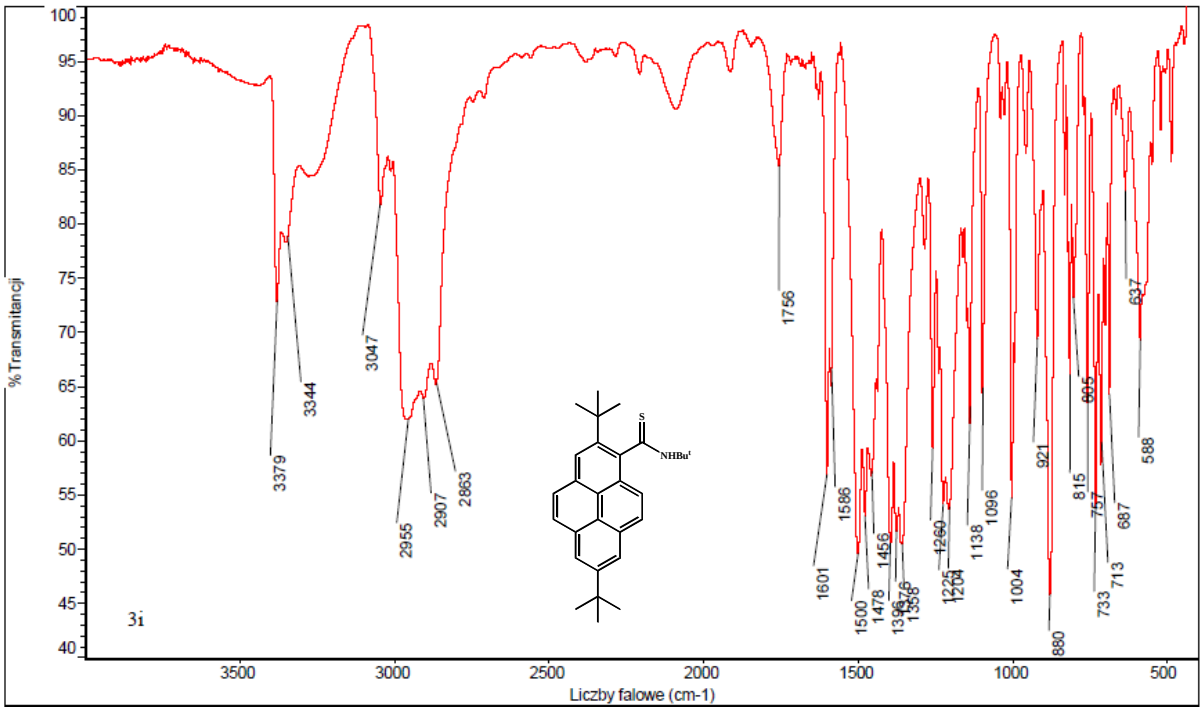

% Transmitancji
3167
3040
2958
2870
1600
1540
1511
1457
1392
1360
1337
1302
1224
1204
1148
1092
906
892
883
815
735
691
S
NHBu^n
3h
Liczby falowe (cm-1)

3i

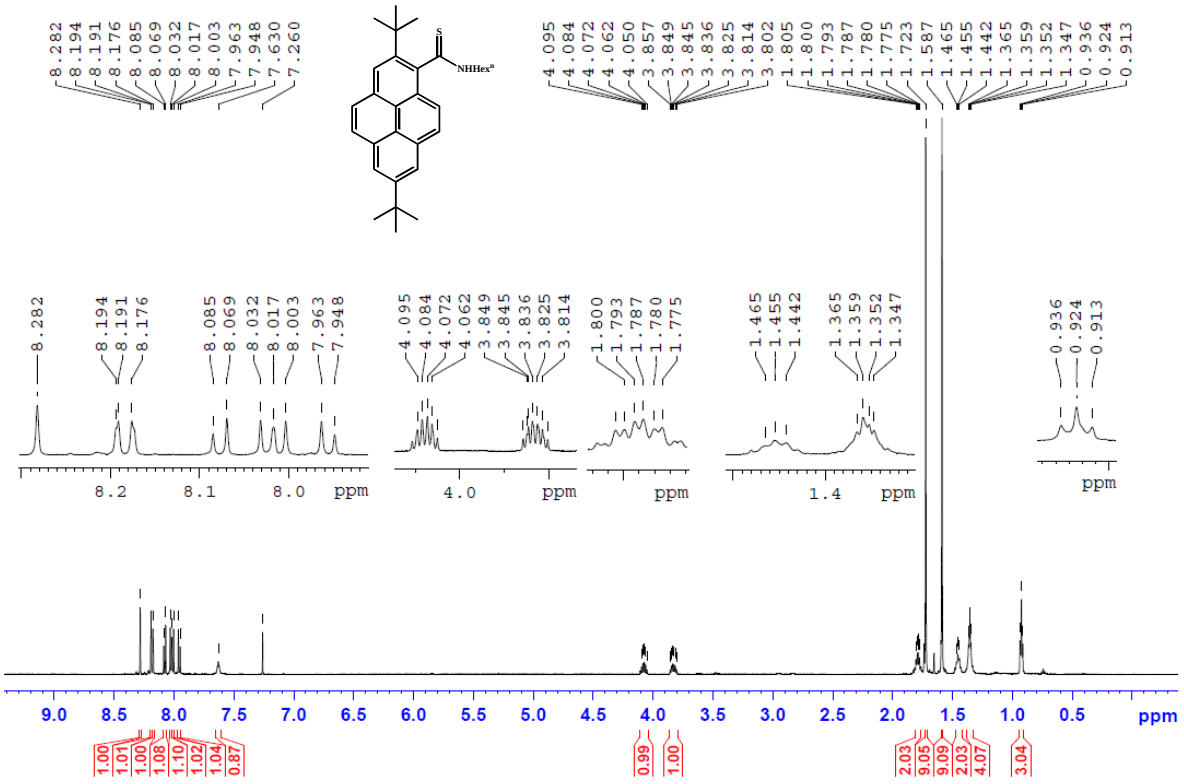

8.287
8.272
8.208
8.205
8.196
8.193
8.088
8.072
8.022
8.007
7.972
7.957
7.463
7.260
1.808
1.803
1.610
8.30
8.25
8.20
8.15
8.10
8.05
8.00
1.8
1.7
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
1.00
1.02
1.01
1.02
1.02
1.02
1.03
0.94
9.39
8.72
8.85

3i

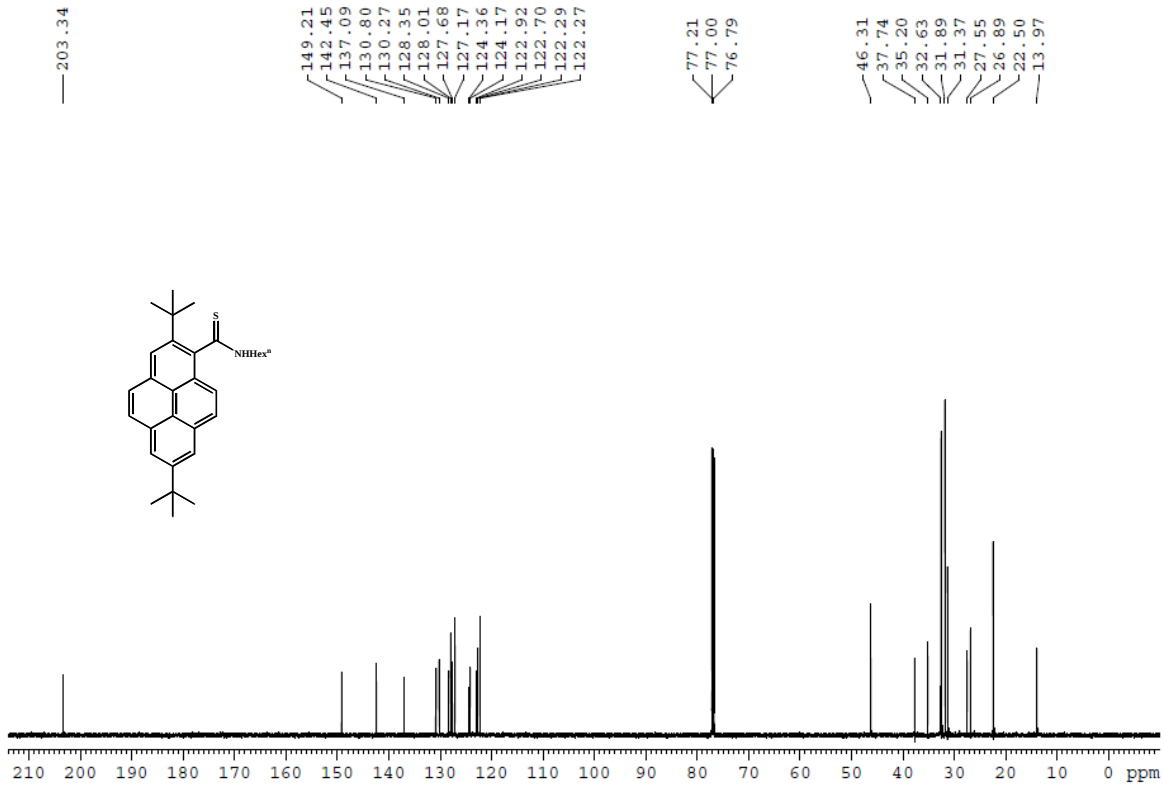

202.58
149.14
141.74
138.52
130.95
130.61
130.22
128.33
127.86
127.64
127.15
124.36
124.26
123.06
122.62
122.31
122.16
77.21
77.00
76.79
57.04
37.92
35.17
32.82
31.88
27.41
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

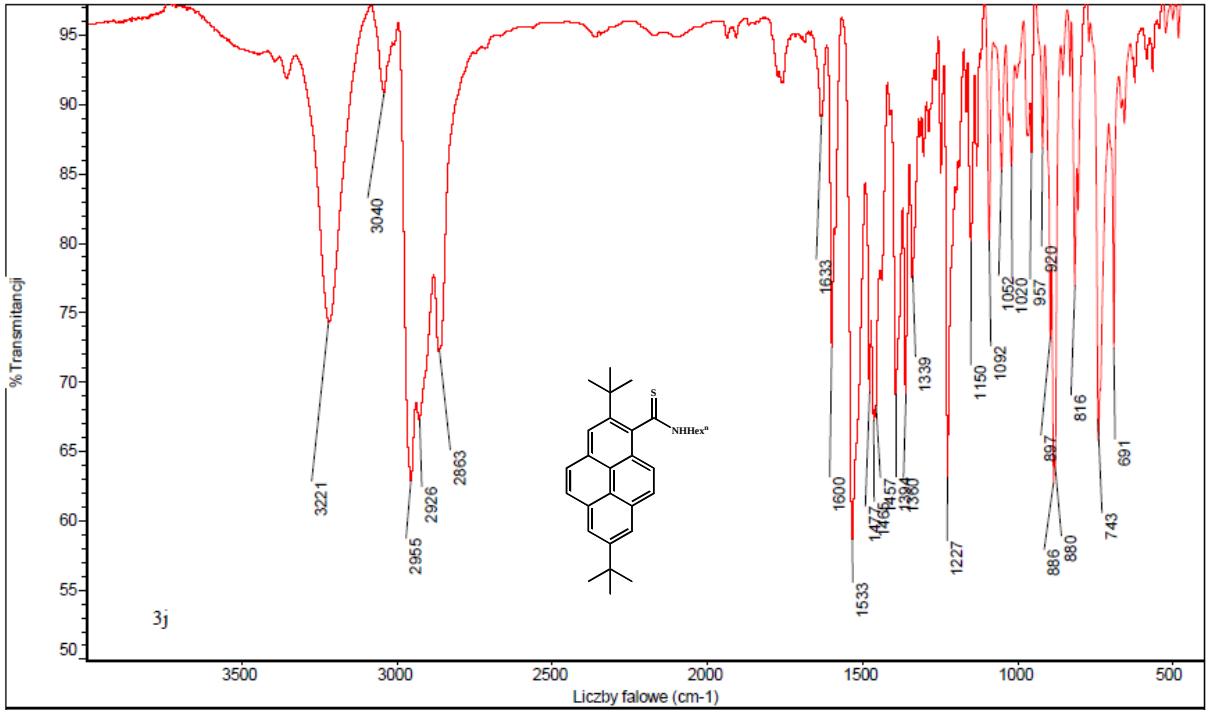

% Transmitancji
Liczby falowe (cm-1)
3i
3379
3344
3047
2955
2907
2863
1756
1601
1586
1500
1478
1456
1396
1378
1358
1260
1225
1204
1138
1096
1004
921
880
815
805
757
733
713
687
637
588
NHBu^t

3j

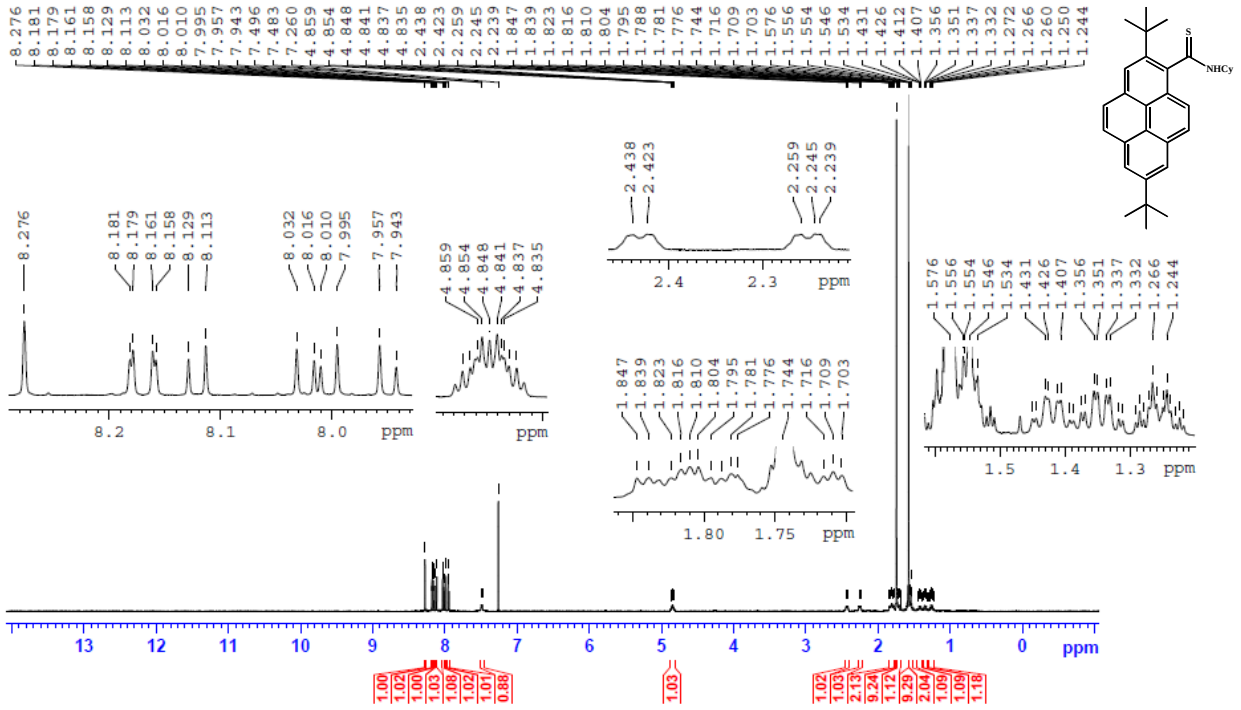

NHHex^n
8.282
8.194
8.191
8.176
8.085
8.069
8.032
8.017
8.003
7.963
7.948
7.630
7.260
4.095
4.084
4.072
4.062
4.050
3.857
3.849
3.845
3.836
3.825
3.814
3.802
1.805
1.800
1.793
1.787
1.780
1.775
1.723
1.587
1.465
1.455
1.442
1.365
1.359
1.352
1.347
0.936
0.924
0.913
ppm
1.00
1.01
1.00
1.08
1.10
1.02
1.04
0.87
0.99
1.00
2.03
9.05
9.09
2.03
4.07
3.04

3j

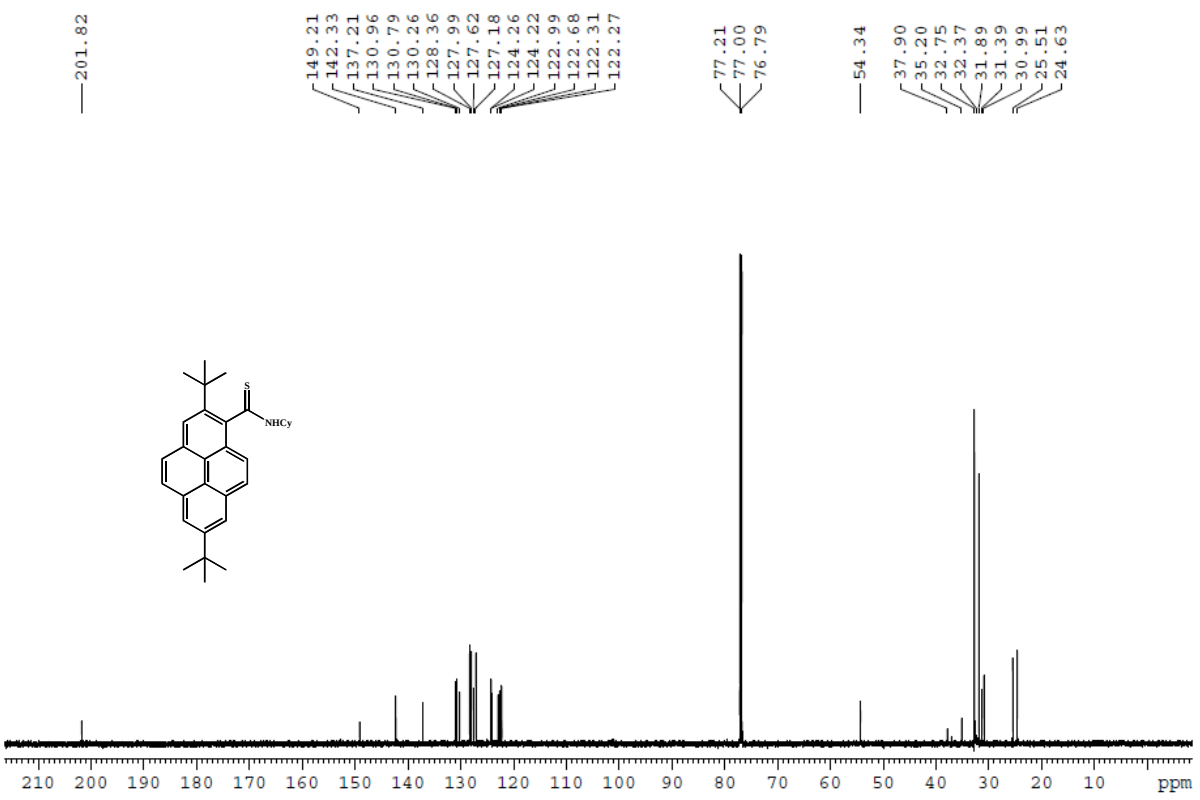

203.34
149.21
142.45
137.09
130.80
130.27
128.35
128.01
127.68
127.17
124.36
124.17
122.92
122.70
122.29
122.27
77.21
77.00
76.79
46.31
37.74
35.20
32.63
31.89
31.37
27.55
26.89
22.50
13.97
S
NHHex^n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

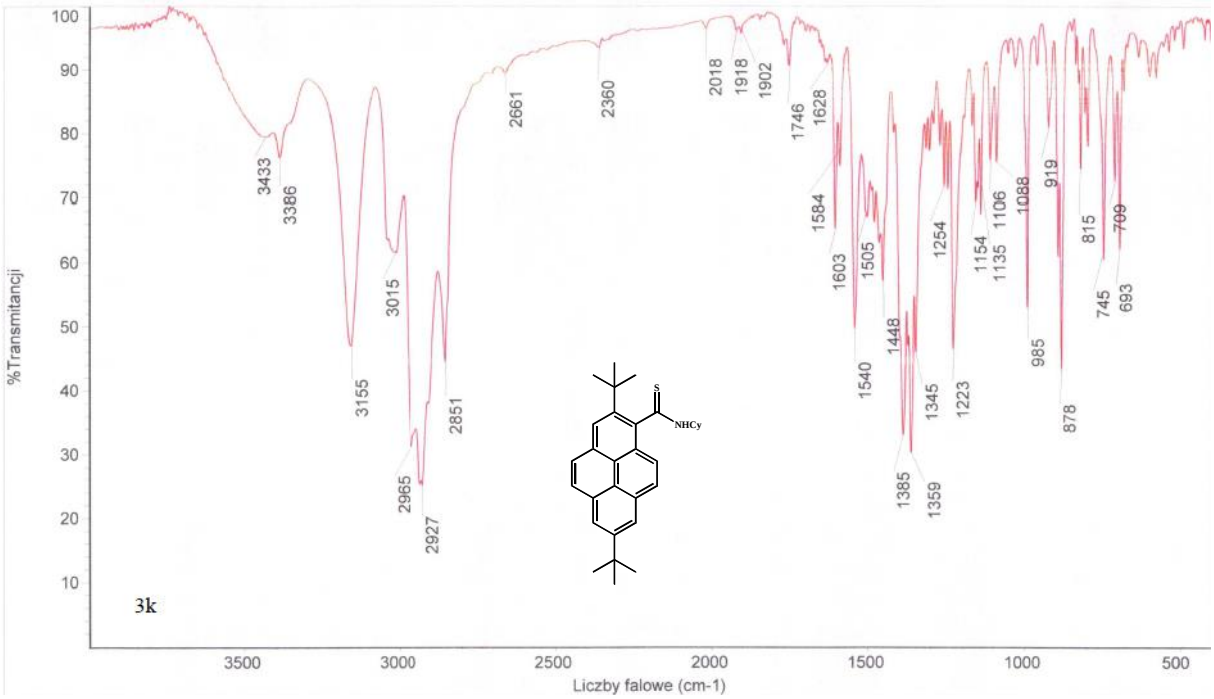

% Transmitancji
95
90
85
80
75
70
65
60
55
50
3500
3000
2500
2000
1500
1000
500
Liczby falowe (cm-1)
3221
3040
2955
2926
2863
1633
1600
1533
1477
1457
1380
1339
1227
1150
1092
1052
1020
957
920
897
886
880
816
743
691
S
NHHex^n
3j

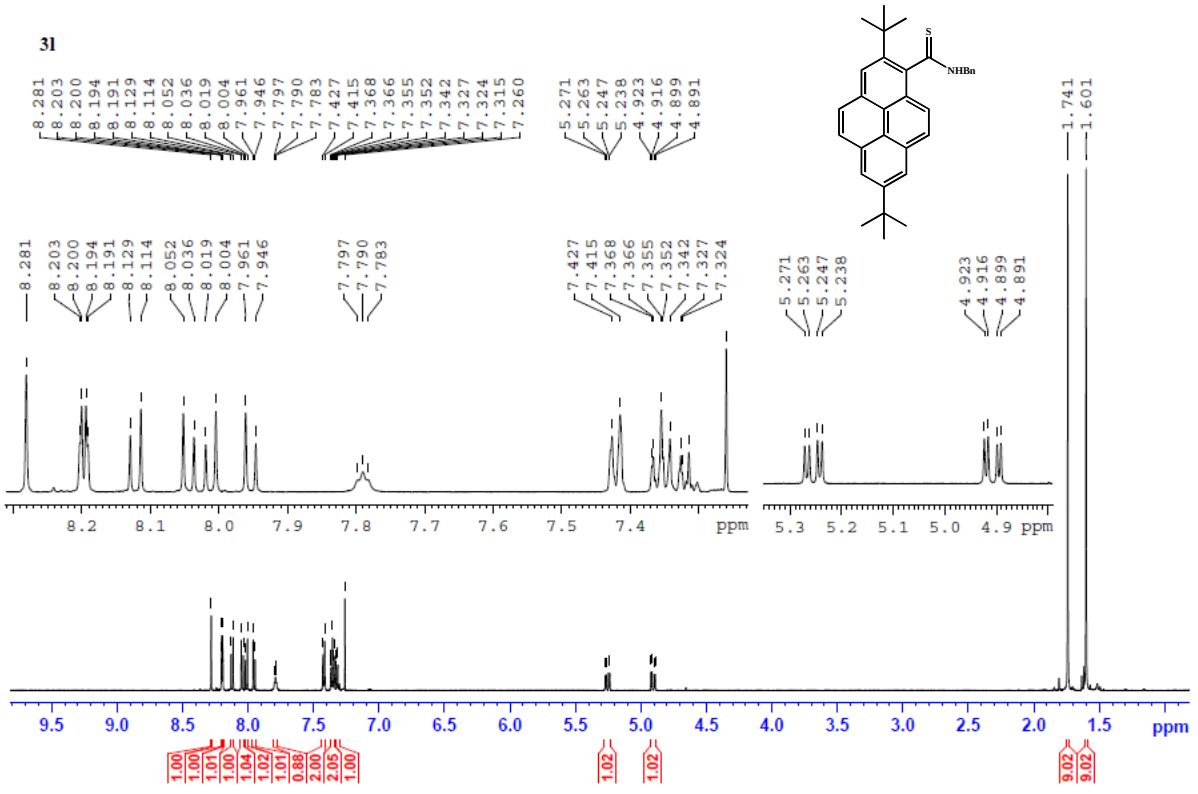
3k

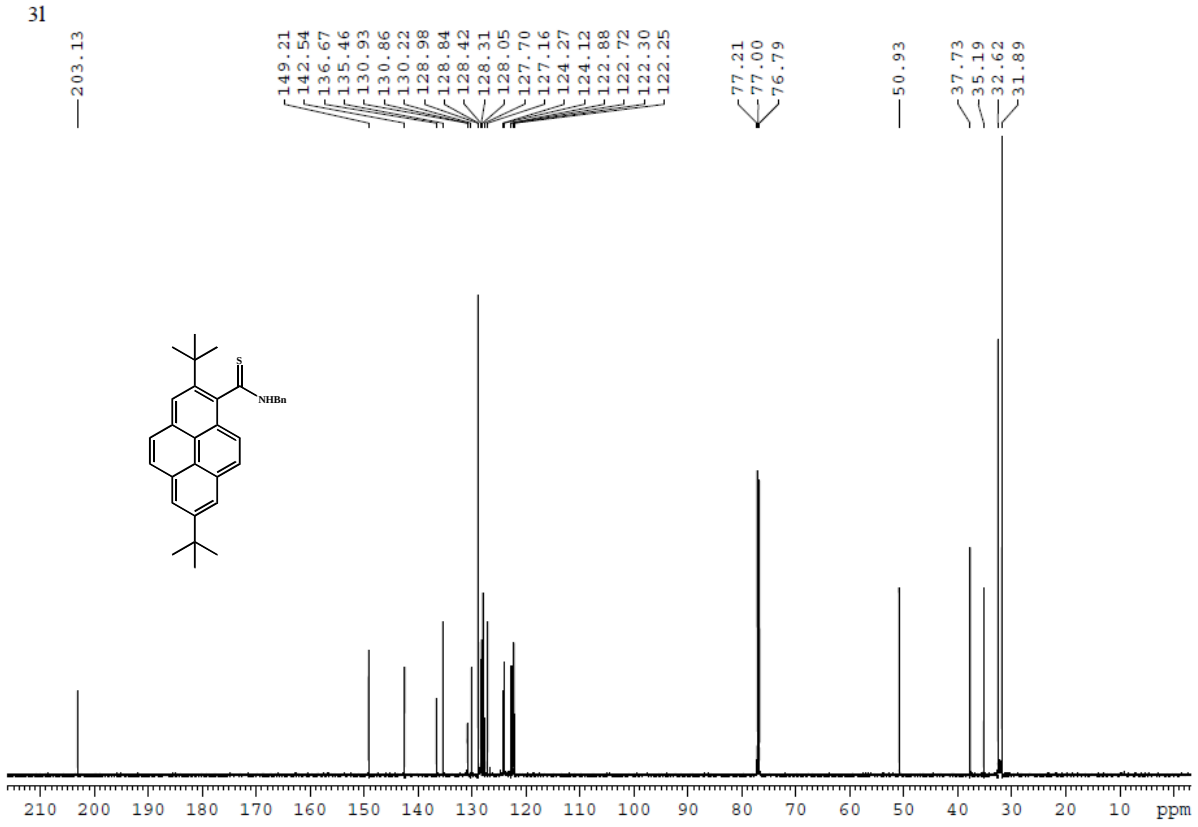


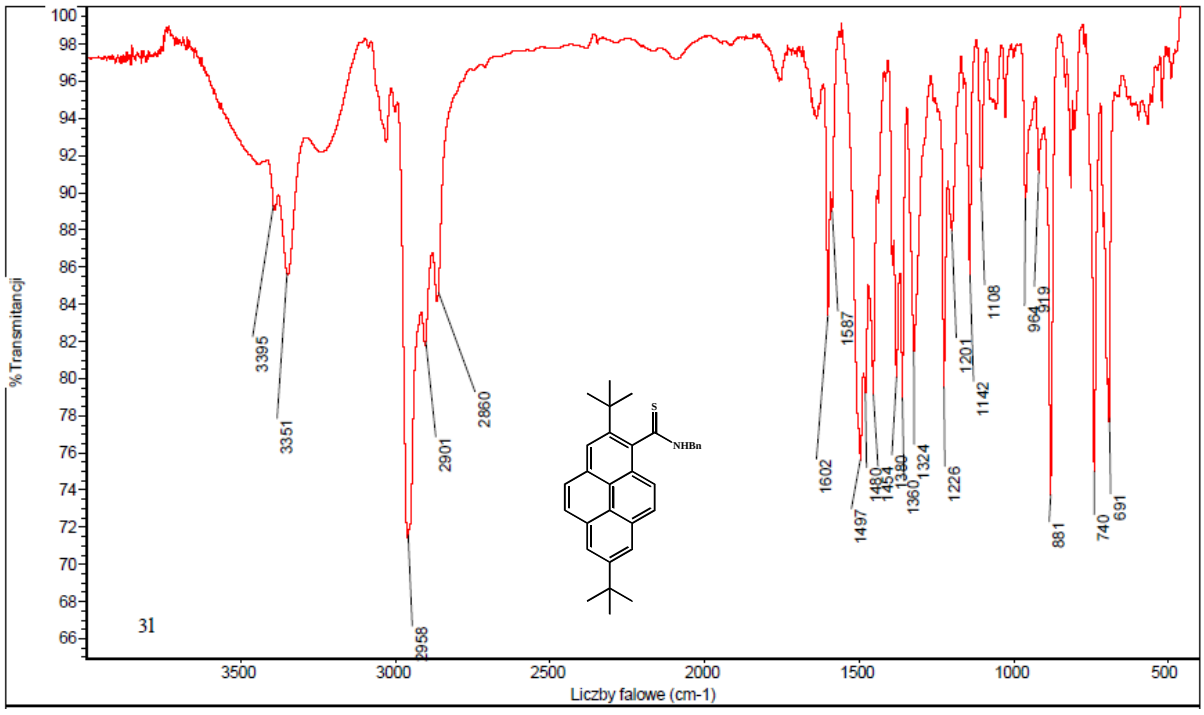
3k



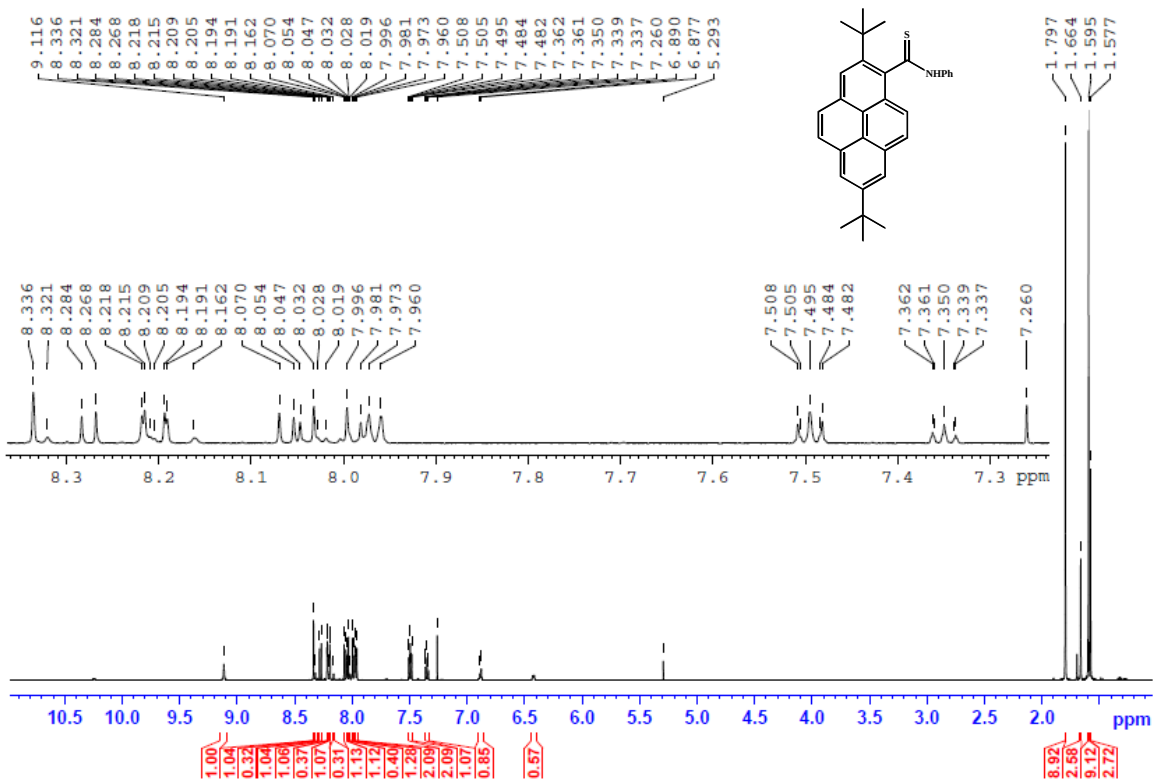

%Transmitancji
Liczby falowe (cm-1)
3k
3433
3386
3155
3015
2965
2927
2851
2661
2360
2018
1918
1902
1746
1628
1584
1603
1505
1540
1448
1385
1359
1345
1254
1223
1154
1135
1106
1088
985
919
878
815
745
709
693
NHCy


3l
NHBn
ppm

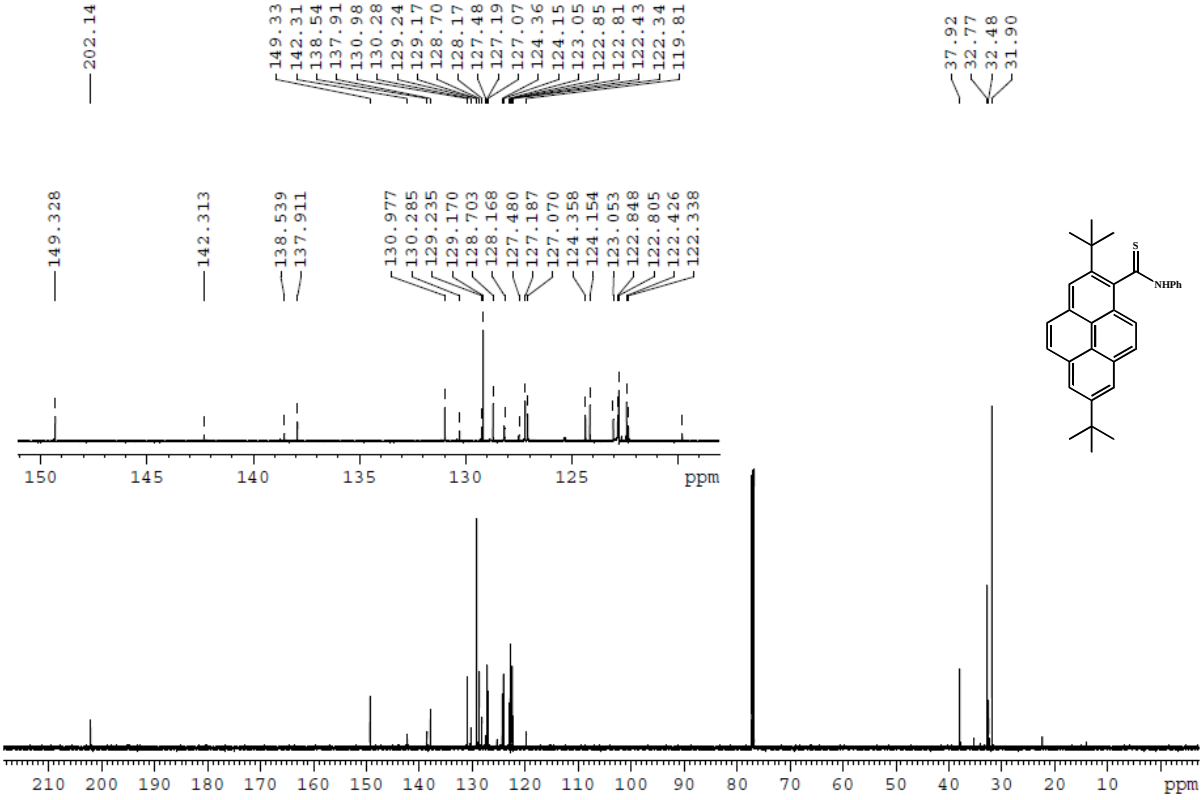

31
203.13
149.21
142.54
136.67
135.46
130.93
130.86
130.22
128.98
128.84
128.42
128.31
128.05
127.70
127.16
124.27
124.12
122.88
122.72
122.30
122.25
77.21
77.00
76.79
50.93
37.73
35.19
32.62
31.89
S
NHBn
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

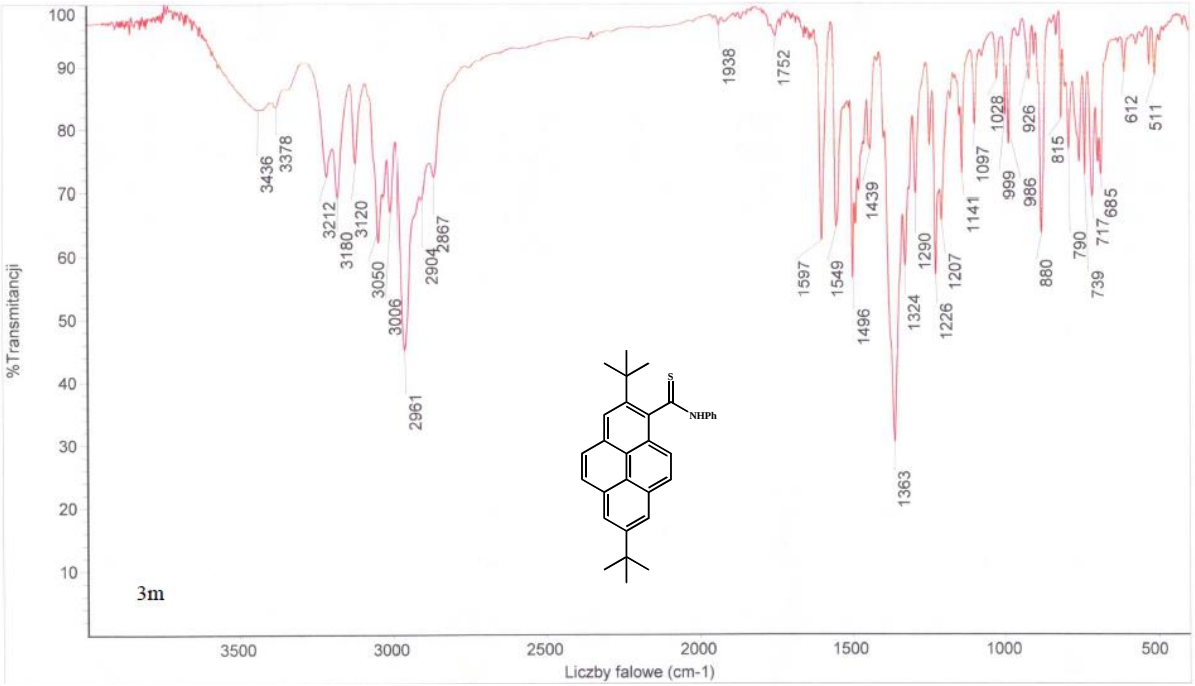

% Transmitancji
100 98 96 94 92 90 88 86 84 82 80 78 76 74 72 70 68 66
3395
3351
2958
2901
2860
1602
1587
1497
1480
1454
1390
1360
1324
1226
1201
1142
1108
964
919
881
740
691
S
NHBn
31
3500 3000 2500 2000 1500 1000 500
Liczby falowe (cm-1)

3m

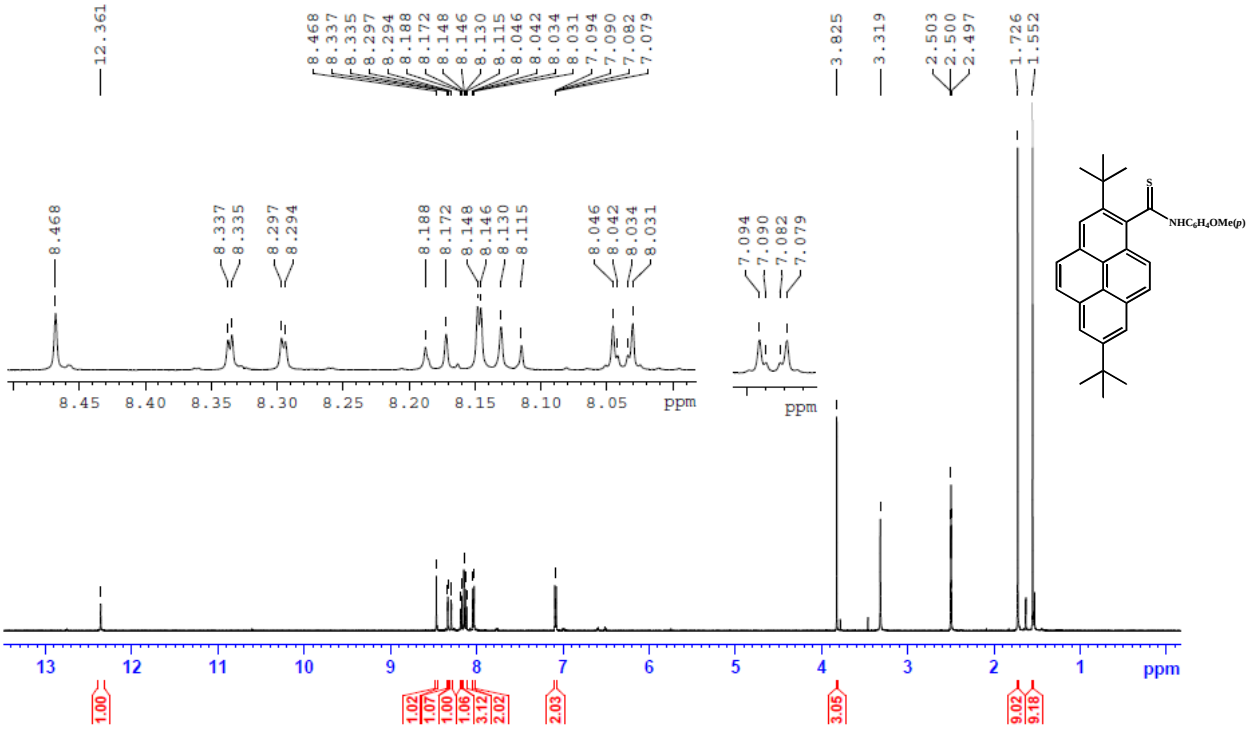

9.116
8.336
8.321
8.284
8.268
8.218
8.215
8.209
8.205
8.194
8.191
8.162
8.070
8.054
8.047
8.032
8.028
8.019
7.996
7.981
7.973
7.960
7.508
7.505
7.495
7.484
7.482
7.362
7.361
7.350
7.339
7.337
7.260
6.890
6.877
5.293
1.797
1.664
1.595
1.577
S
NHPh
ppm

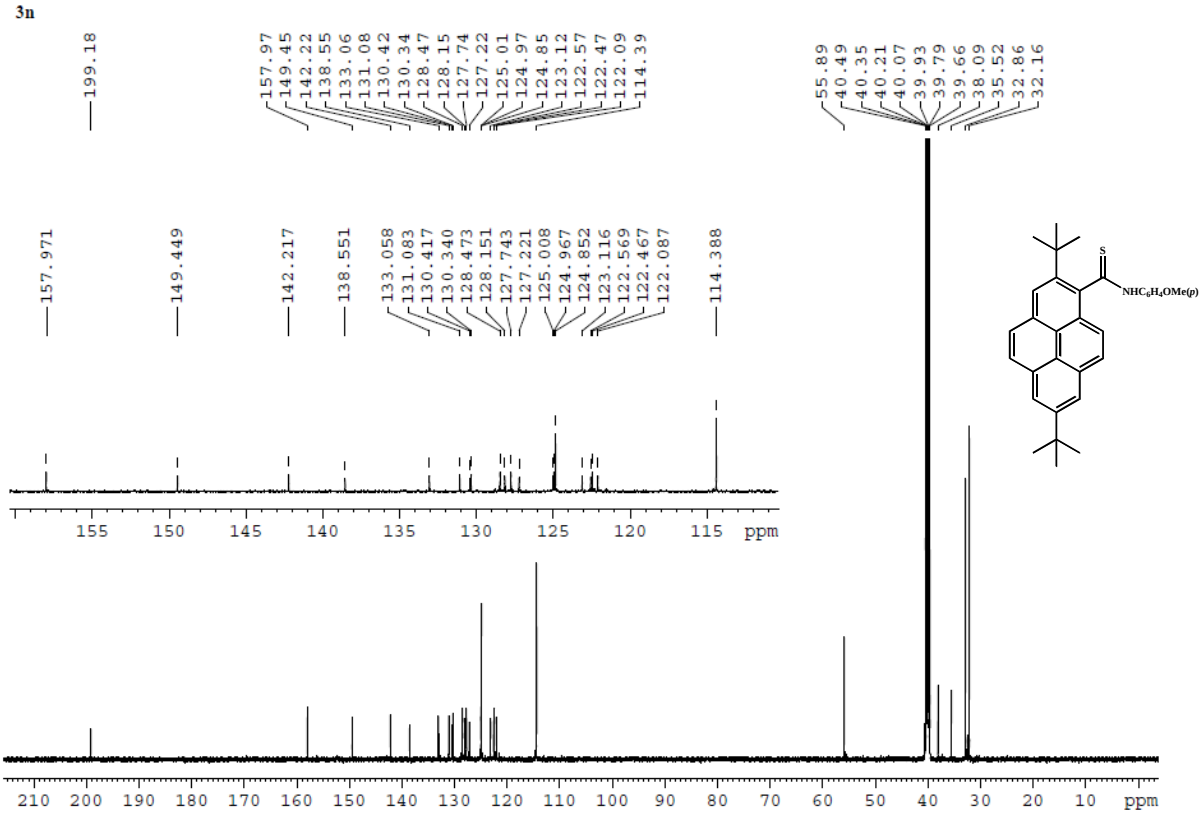
3m

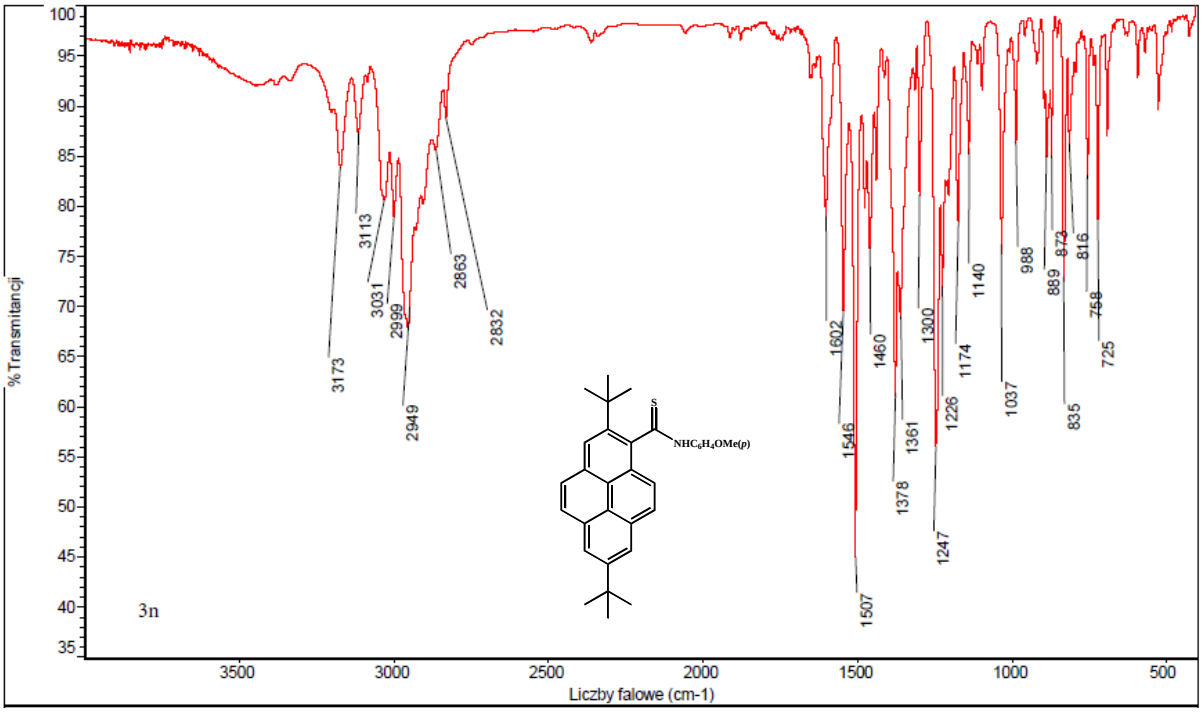

202.14
149.33
142.31
138.54
137.91
130.98
130.28
129.24
129.17
128.70
128.17
127.48
127.19
127.07
124.36
124.15
123.05
122.85
122.81
122.43
122.34
119.81
37.92
32.77
32.48
31.90
149.328
142.313
138.539
137.911
130.977
130.285
129.235
129.170
128.703
128.168
127.480
127.187
127.070
124.358
124.154
123.053
122.848
122.805
122.426
122.338
S
NHPh
ppm

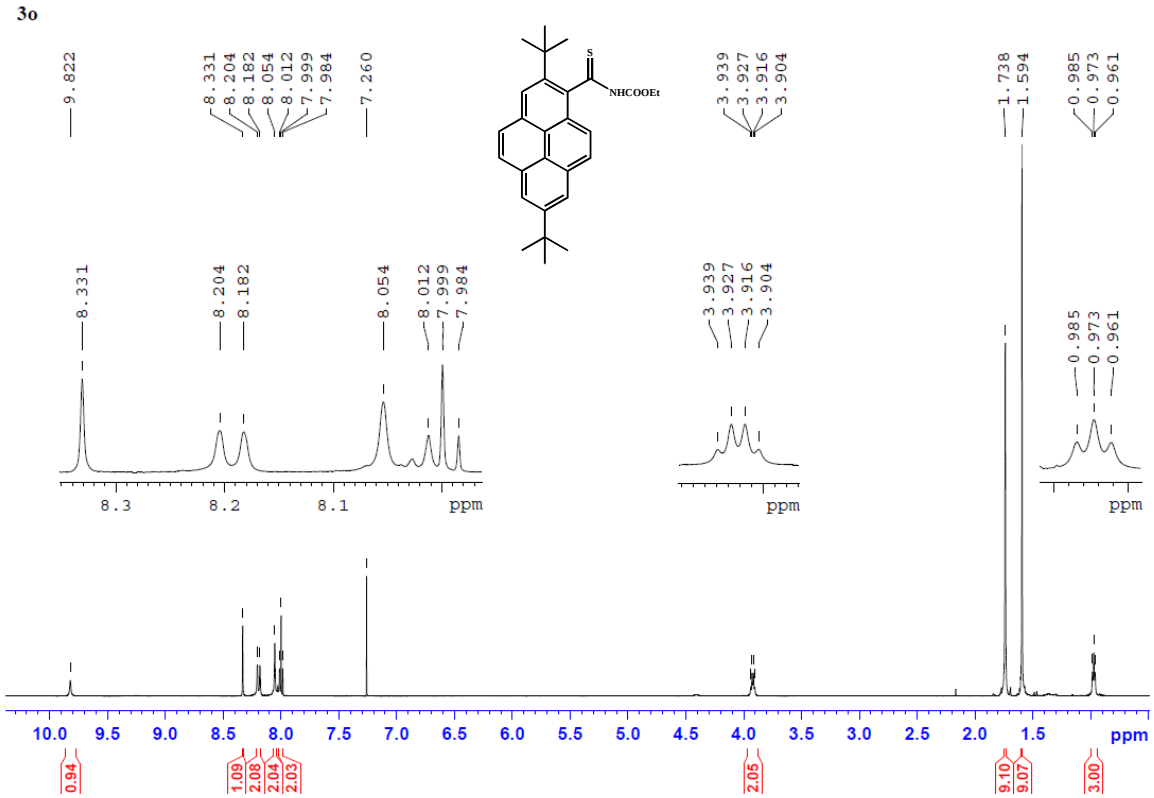

%Transmitancji
Liczby falowe (cm-1)
3m
NHPh
3436
3378
3212
3180
3120
3050
3006
2961
2904
2867
1938
1752
1597
1549
1496
1439
1363
1324
1290
1226
1207
1141
1097
1028
999
986
926
880
815
790
739
717
685
612
511

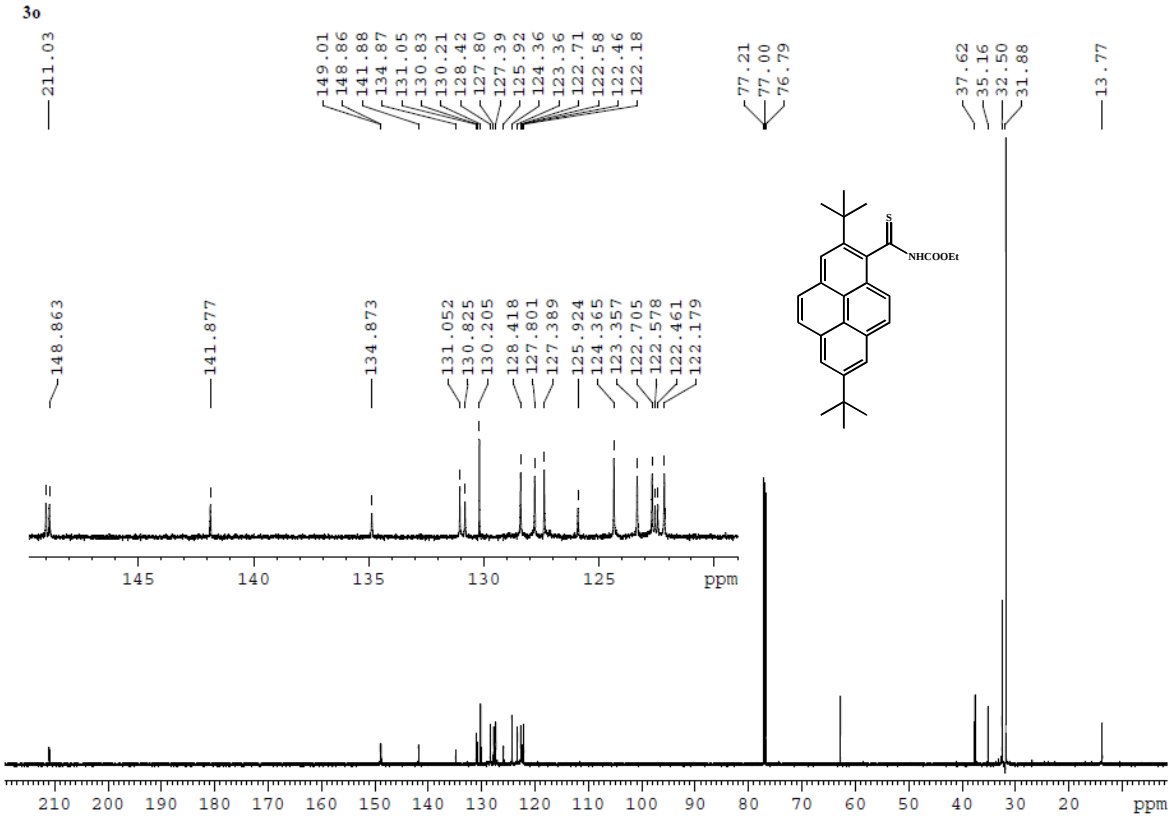
3n

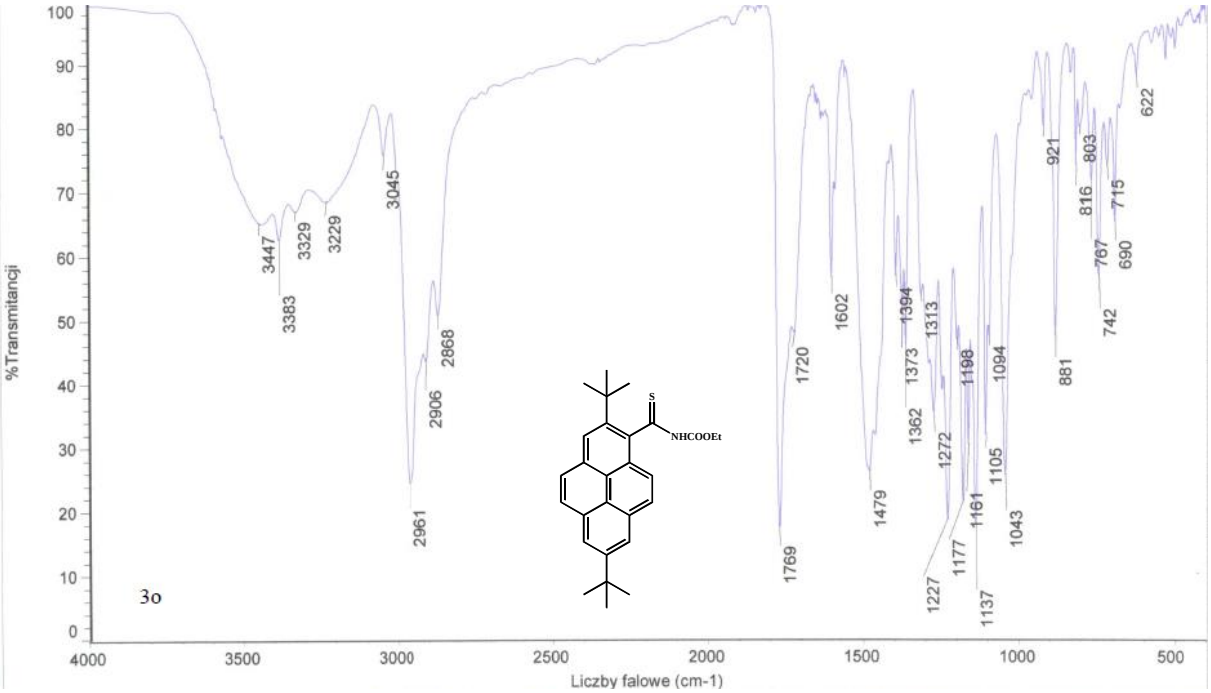

12.361
8.468
8.337
8.335
8.297
8.294
8.188
8.172
8.148
8.146
8.130
8.115
8.046
8.042
8.034
8.031
7.094
7.090
7.082
7.079
3.825
3.319
2.503
2.500
2.497
1.726
1.552
NHC6H4OMe(p)
ppm

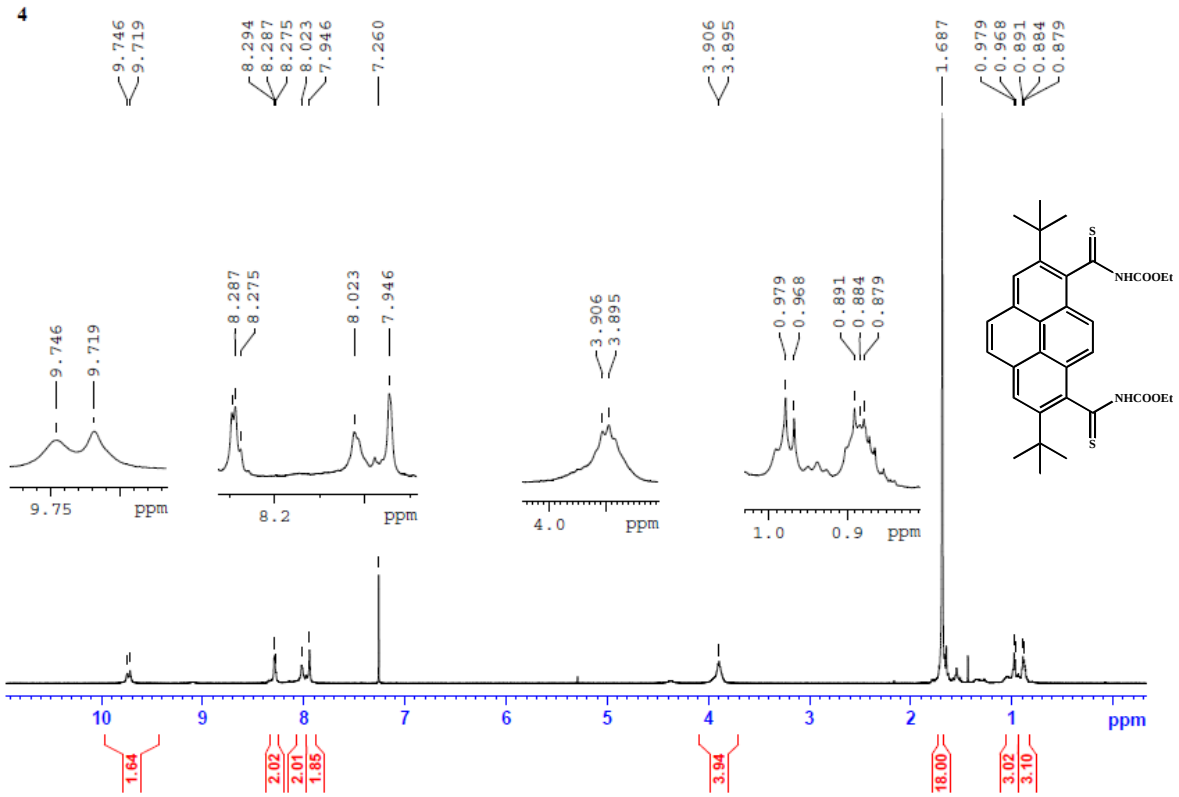

3n
199.18
157.97
149.45
142.22
138.55
133.06
131.08
130.42
130.34
128.47
128.15
127.74
127.22
125.01
124.97
124.85
123.12
122.57
122.47
122.09
114.39
55.89
40.49
40.35
40.21
40.07
39.93
39.79
39.66
38.09
35.52
32.86
32.16
157.971
149.449
142.217
138.551
133.058
131.083
130.417
130.340
128.473
128.151
127.743
127.221
125.008
124.967
124.852
123.116
122.569
122.467
122.087
114.388
NHC6H4OMe(p)
155 150 145 140 135 130 125 120 115 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

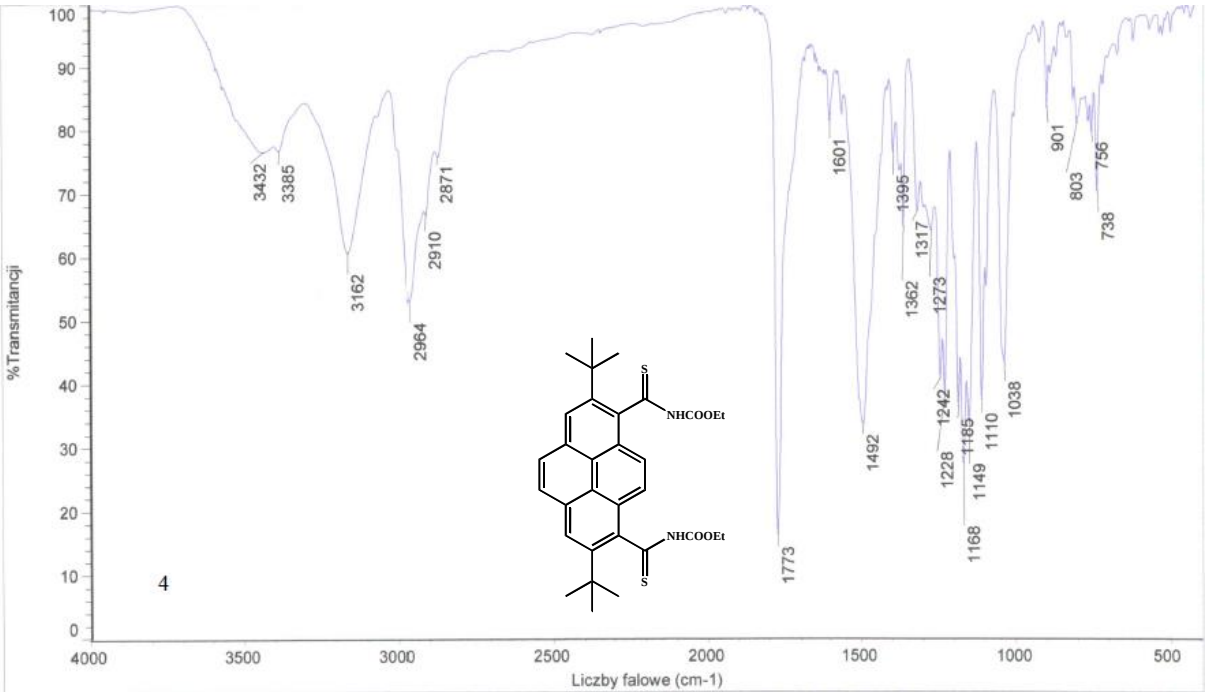

% Transmitancji
100 95 90 85 80 75 70 65 60 55 50 45 40 35
3173
3113
3031
2999
2949
2863
2832
1602
1546
1507
1460
1378
1361
1300
1247
1226
1174
1140
1037
988
889
872
835
816
768
725
NHC6H4OMe(p)
3n
3500 3000 2500 2000 1500 1000 500
Liczby falowe (cm-1)


3o
9.822
8.331
8.204
8.182
8.054
8.012
7.999
7.984
7.260
3.939
3.927
3.916
3.904
1.738
1.594
0.985
0.973
0.961
NHCOOEt
ppm
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
0.94
1.09
2.08
2.04
2.03
2.05
9.10
9.07
3.00

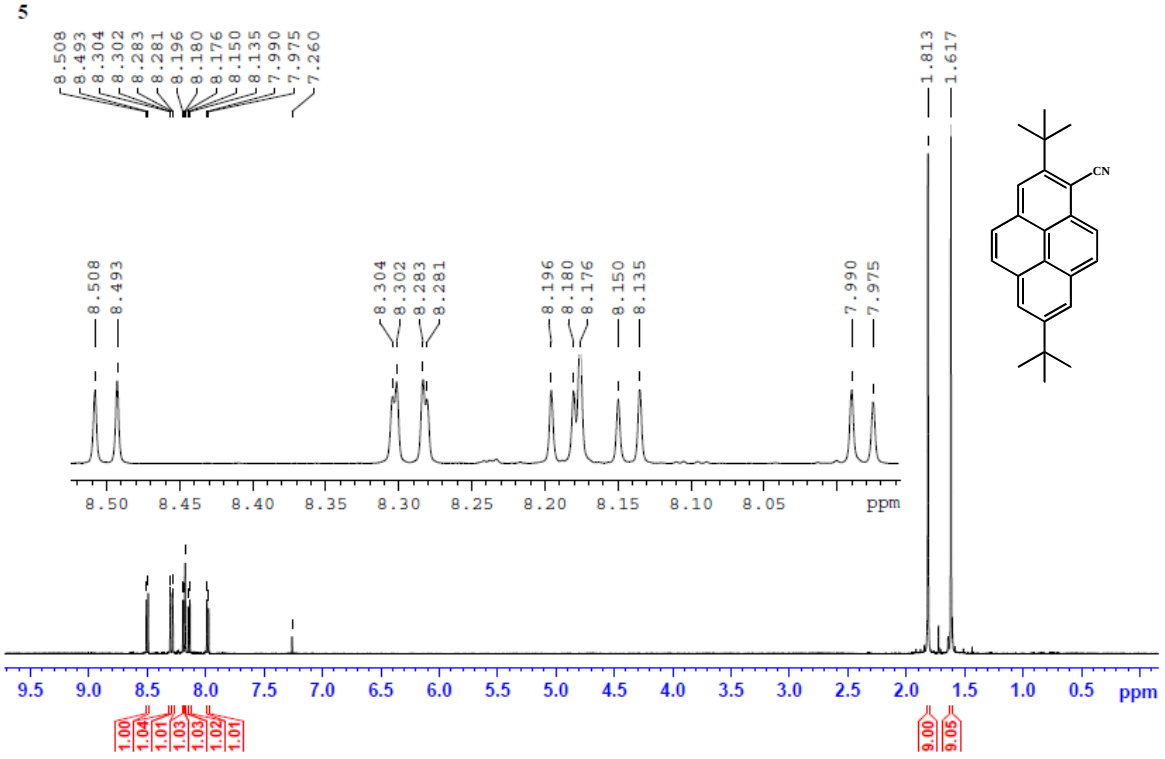

3o
211.03
149.01
148.86
141.88
134.87
131.05
130.83
130.21
128.42
127.80
127.39
125.92
124.36
123.36
122.71
122.58
122.46
122.18
77.21
77.00
76.79
37.62
35.16
32.50
31.88
13.77
148.863
141.877
134.873
131.052
130.825
130.205
128.418
127.801
127.389
125.924
124.365
123.357
122.705
122.578
122.461
122.179
NHCOOEt
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20


%Transmitancji
Liczby falowe (cm-1)
3o
NHCOOEt
3447
3383
3329
3229
3045
2961
2906
2868
1769
1720
1602
1479
1394
1373
1362
1313
1272
1227
1198
1177
1161
1137
1105
1094
1043
921
881
816
803
767
742
715
690
622

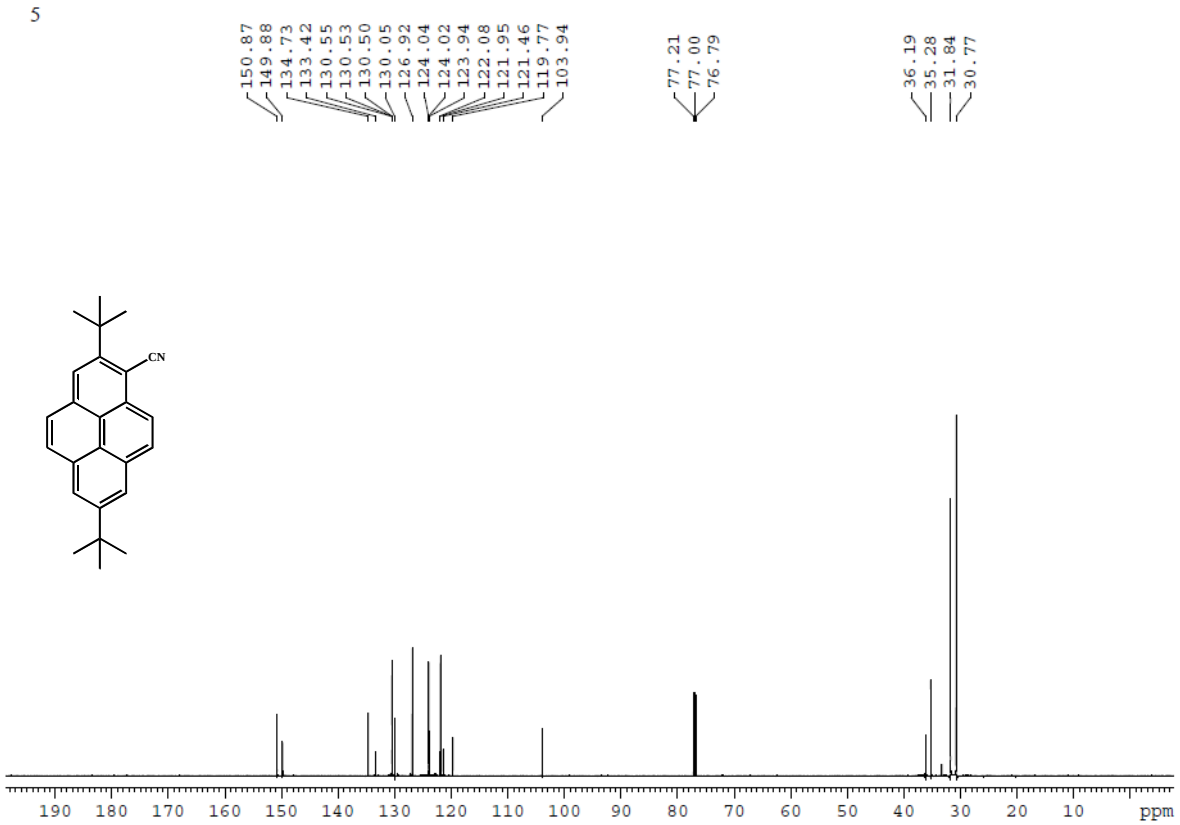

4
NHCOOEt
NHCOOEt
ppm
1.64
2.02
2.01
1.85
3.94
18.00
3.02
3.10

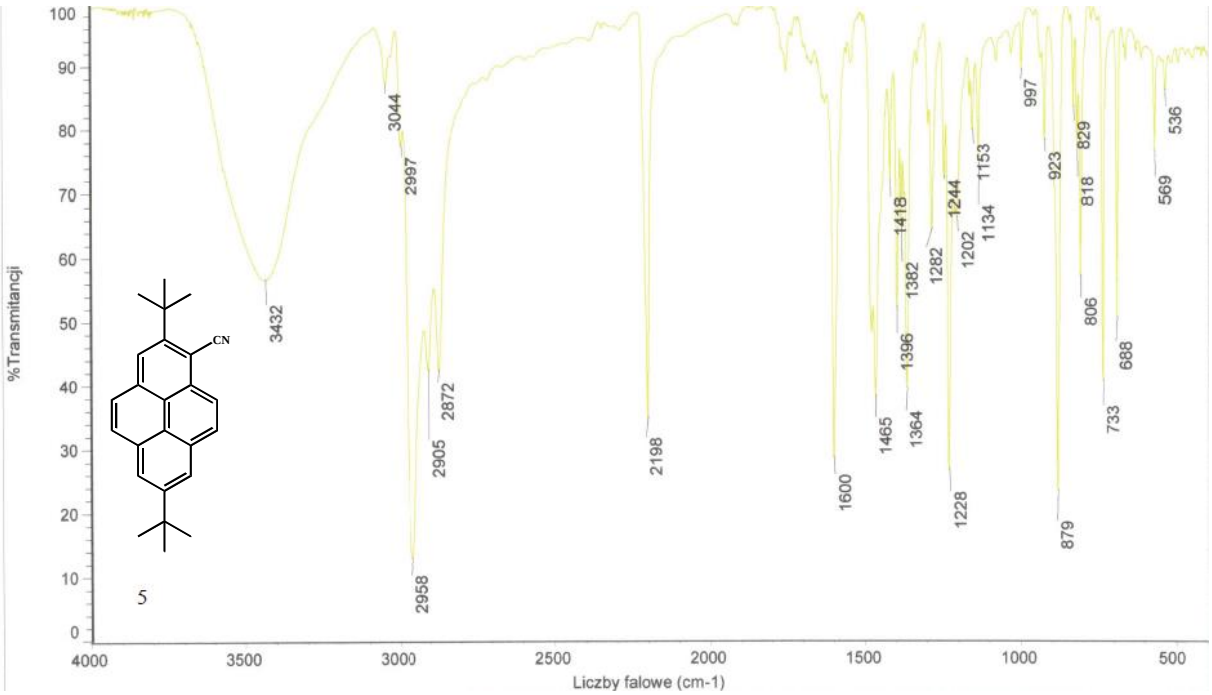

%Transmitancji
Liczby falowe (cm-1)
4
NHCOOEt
NHCOOEt
3432
3385
3162
2964
2910
2871
1773
1601
1492
1396
1362
1317
1273
1242
1228
1185
1168
1149
1110
1038
901
803
756
738

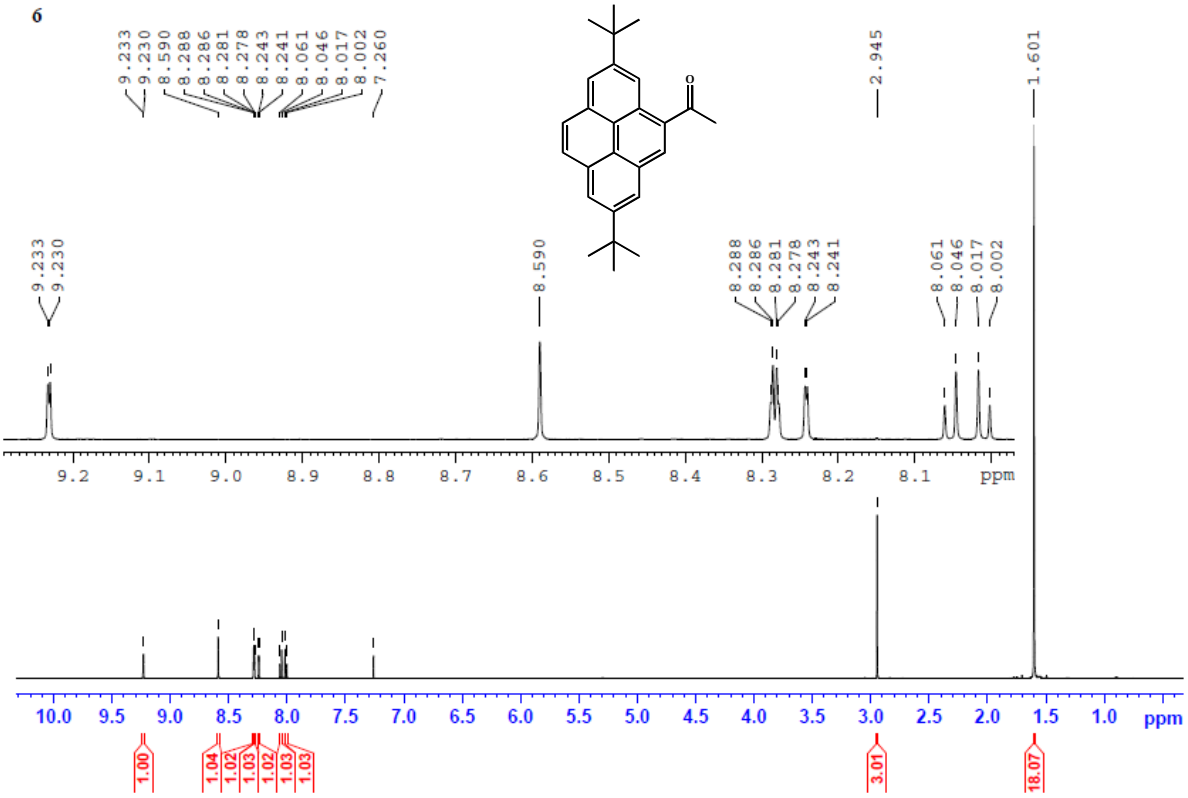
5

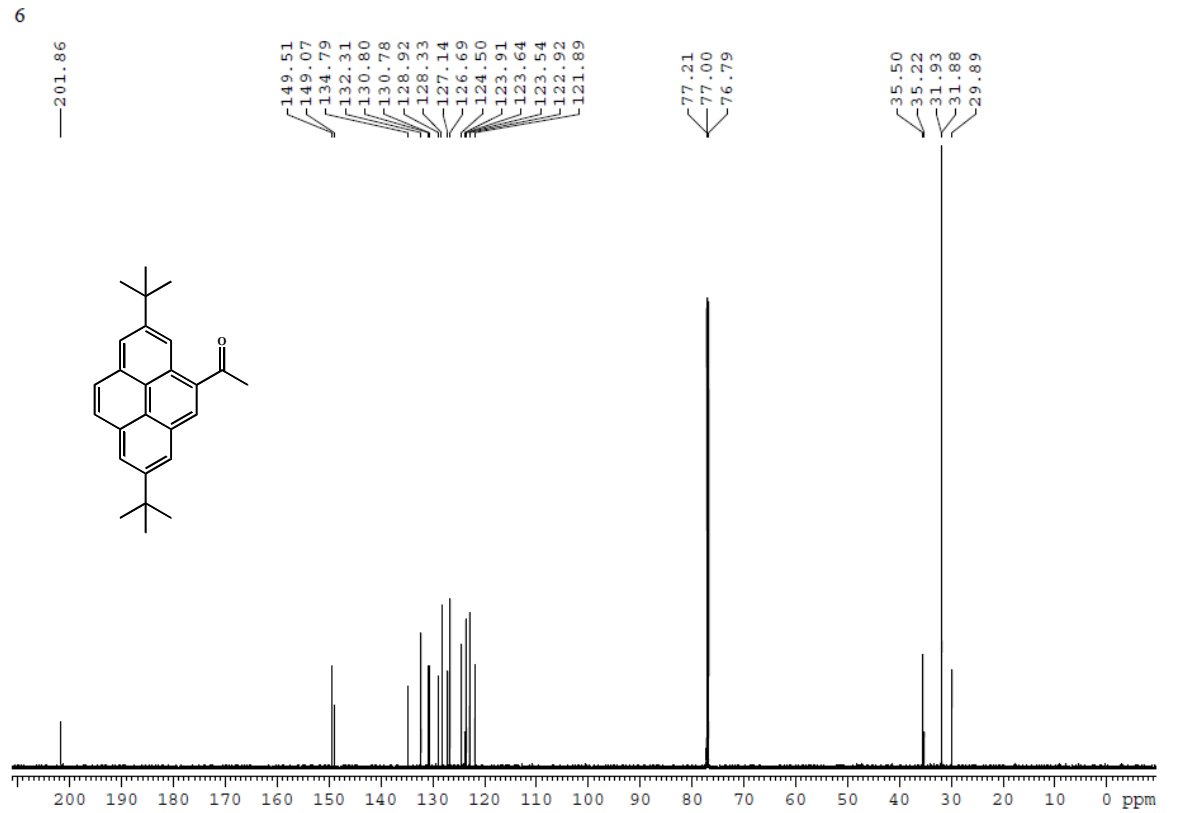

8.508
8.493
8.304
8.302
8.283
8.281
8.196
8.180
8.176
8.150
8.135
7.990
7.975
7.260
1.813
1.617
CN
ppm

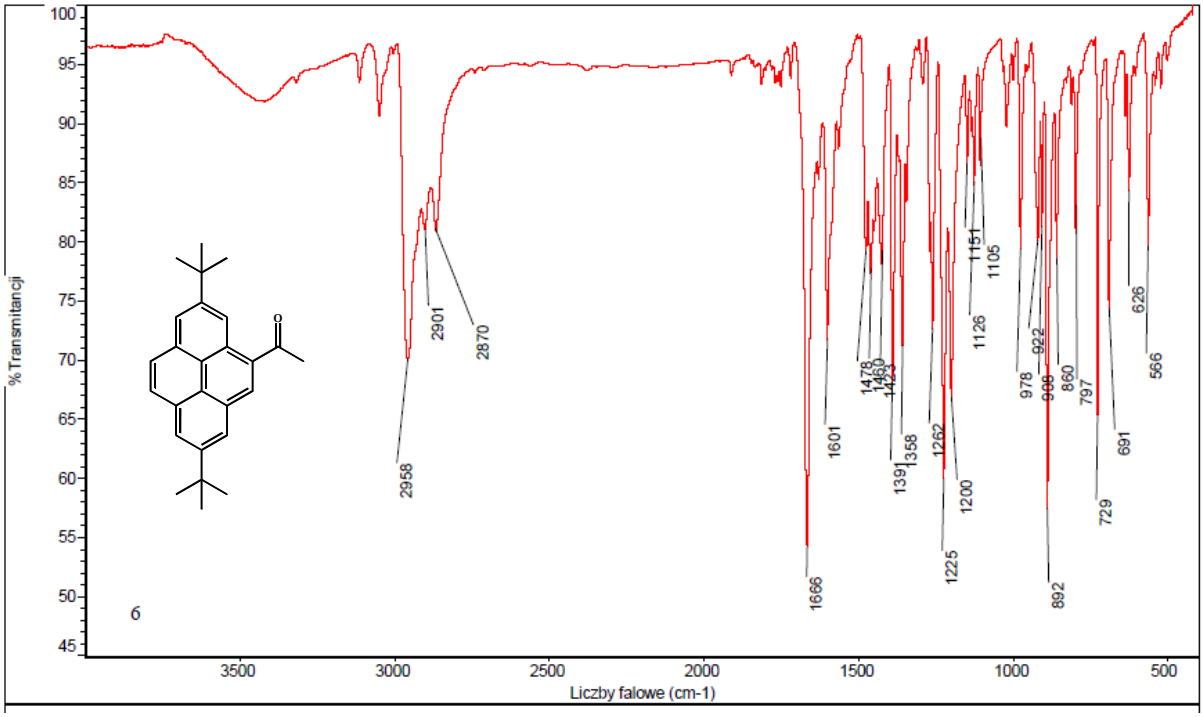
5


150.87
149.88
134.73
133.42
130.55
130.53
130.50
130.05
126.92
124.04
124.02
123.94
122.08
121.95
121.46
119.77
103.94
77.21
77.00
76.79
36.19
35.28
31.84
30.77
CN
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


%Transmitancji
100 90 80 70 60 50 40 30 20 10 0
4000 3500 3000 2500 2000 1500 1000 500
Liczby falowe (cm-1)
3432
3044
2997
2958
2905
2872
2198
1600
1465
1418
1396
1382
1364
1282
1244
1228
1202
1153
1134
997
923
879
829
818
806
733
688
569
536
CN
5


6
9.233
9.230
8.590
8.288
8.286
8.281
8.278
8.243
8.241
8.061
8.046
8.017
8.002
7.260
2.945
1.601
ppm
1.00
1.04
1.02
1.03
1.02
1.03
1.03
3.01
18.07


6
201.86
149.51
149.07
134.79
132.31
130.80
130.78
128.92
128.33
127.14
126.69
124.50
123.91
123.64
123.54
122.92
121.89
77.21
77.00
76.79
35.50
35.22
31.93
31.88
29.89
O
ppm


% Transmitancji
Liczby falowe (cm-1)
6
2958
2901
2870
1666
1601
1478
1460
1423
1391
1358
1262
1225
1200
1151
1126
1105
978
922
892
860
797
729
691
626
566

Crystallographic and Structure Refinement Data for 4.

Table S1. X-ray crystallographic data for **4**.

Identification code	**4**
solvent	CH_2Cl_2
Empirical formula	$C_{32}H_{36}N_2O_4S_2$
Formula weight /gmol^{-1}	589.48
Temperature/K	89.9(2)
Crystal system	monoclinic
Space group	P21/n
a/Å	13.8947(6)
b/Å	11.5388(5)
c/Å	20.3238(10)
α/°	90
β/°	107.084(5)
γ/°	90
Volume/Å^3	3114.7(3)
Z	4
ρ_{calc} mg/mm^3	1.257
F(000)	1249
Θ range for data collection	28.819-1.583
μ /mm^{-1}	0.235
Transmission max/min	1.000
	0.478
Absorption correction type	gaussian
Crystal color	yellow
Crystal habit	needle
Crystal size max/mid/min /mm^3	0.3163
	0.1705

	0.0572
Rint	0.0765
Rsigma	0.0312
Completeness	0.999
Diffractometer / detector	Supernova / Eos
Radiation / wavelength /Å	MoKα 0.71073
Friedel pairs coverage	n/a
Reflections collected I>=2σ (I)	6718
Reflections collected	11128
Largest diff. peak/hole/rms /eÅ^{-3}	0.661
	-0.544
	0.102
Flack parameter	n/a
Extinction coefficient	n/a
Goodness-of-fit on F^2	0.963
Parameters	448
Data	11128
restraints	114
Final R1 indexes [I>=2σ (I)]	0.1025 / 0.0676
Final wR2 indexes [I>=2σ (I)]	0.1721 / 0.1630

Diffraction data were collected on Agilent Supernova 4 circle diffractometer system equipped with molybdenum microsource (Kα, 0.71073Å) and EOS CCD detector. The data were collected withCrysAlis171[1] software and integrated with the CrysAlisPRO[2] software. Data were corrected for absorption effects using the numerical method (SCALE3 ABSPACK).
All the crystals of **4a** were twinned, with two components and the initial twin fractions estimated to be 0.54 and 0.46 for the collected data.

The structure was solved by direct methods using SXELXS[3] and refined by full-matrix least squares procedure with SHELXL[3] within OLEX2[4] graphical interface. Figures were produced

with Mercury_3.5[5]. Most of the H atoms were visible in the residual density map, but all were finally added geometrically and refined in riding approximation. The structure contains solvent molecule with partial occupation, disordered over 2 positions close to the crystallographic symmetry... This results in disorder affecting the **4a** molecule. Each of the two ethyl fragments adapt two alternative positions, with occupancies of 0.65 for the major conformer and 0.35 for the minor.

Additional restraints were necessary in order to properly model the disorder of the ethyl groups and the solvent molecules. The applied restraints were similarity restraints between the major and minor conformers, concerning C-C distances and atomic displacement parameters.

Crystallographic data for 4 have been deposited at the Cambridge Crystallographic Data Centre (Deposition No. 1517030). Copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK. [Fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk].

References

1.CrysAlisPro, Agilent Technologies, Version 1.171.36.20 (release 01-02-2013 CrysAlis171.NET)

2. CrysAlisRED, Agilent Technologies, Version 1.171.36.20 (release 01-02-2013 CrysAlis171.NET)

3. SHELX: G. Sheldrick, A short history of SHELX, Acta Cryst. Section A, *64* (2008) 112.

4. OLEX2: O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, J.Appl. Cryst., *42* (2009), 339.

5 MERCURY: C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Cryst.*, *39* (2006), 45.

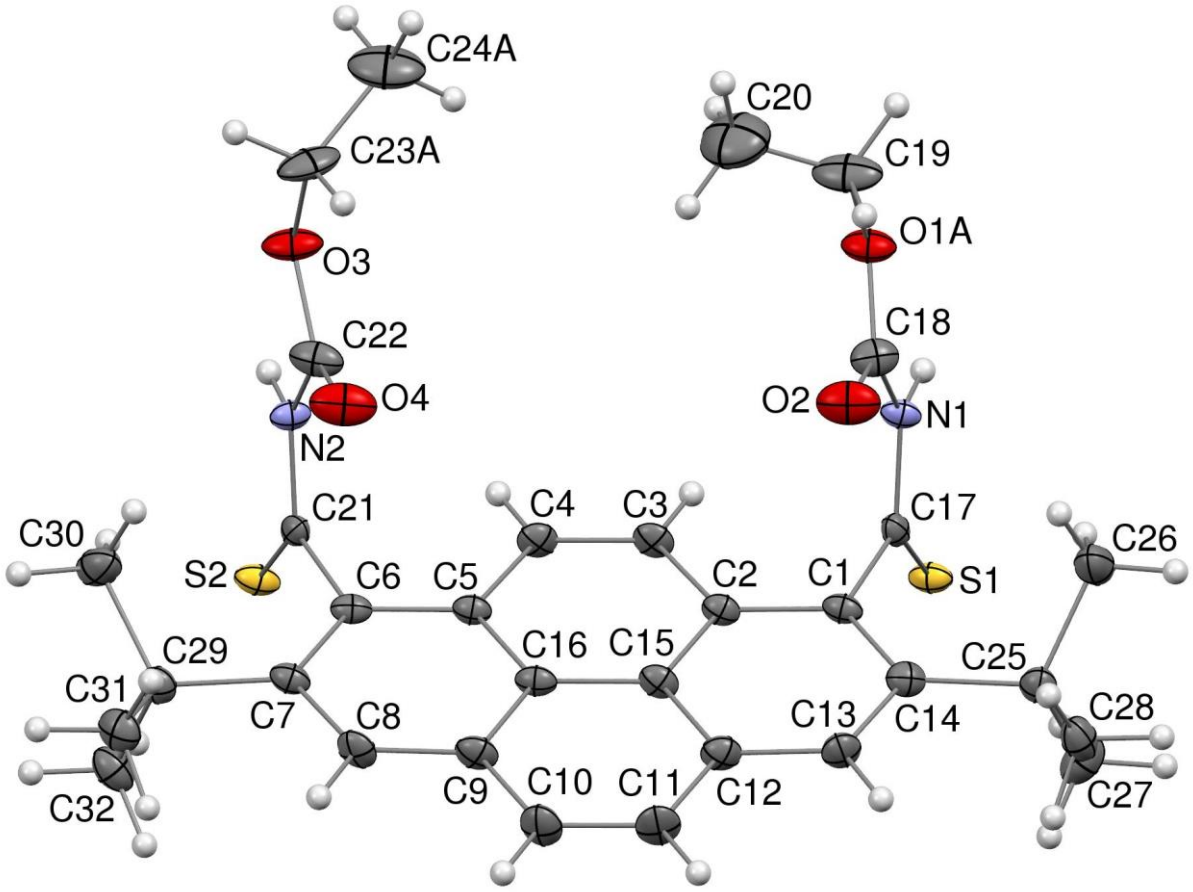


Figure S1. X-ray crystallographic structure of **4** (50% probability level). Only major conformer of the disorder is shown, for clarity.