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N-Fused Quinoxalines and Benzoquinoxalines as Attractive Emitters for Organic Light Emitting Diodes

- Supporting Information -

Benjamin D. Lindner,[a,‖] Yexiang Zhang,[b,‖] Stefan Höfle,[c] Nancy Berger,[d] Claudia Teusch,[a,e] Malte Jesper,[a,e] Kenneth I. Hardcastle,[d] Xuhong Qian,[b] Uli Lemmer,[c] Alexander Colsmann,[d] Uwe H.F. Bunz,[a,]* Manuel Hamburger[a,e,]*

a) Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany; b) Shanghai Key Laboratory of Chemical Biology, State Key Laboratory of Bioreactor Engineering, School of Pharmacy, East China University of Science and Technology, Shanghai 200237, People's Republic of China; c) Light Technology Institute, Karlsruhe Institute of Technology (KIT), Engesserstr. 13, 76131 Karlsruhe, Germany; d) School of Chemistry and Biochemistry, Georgia Institute of Technology, 901 Atlantic Drive, Atlanta, GA 30332, United States; e) Competence Center Synthesis, InnovationLab GmbH, Speyerer Str. 4, 69115 Heidelberg, Germany

‖ These authors contributed equally to the work presented in this publication.

CONTENTS

1. GENERAL METHODS

All reagents and solvents were obtained from Fisher Scientific, ABCR, Alfa Aesar, Sigma-Aldrich or VWR and were used without further purification unless otherwise noted. All of the other absolute solvents were dried by a MB SPS-800 using drying columns. Preparation of air- and moisture-sensitive materials was carried out in oven dried flasks under an atmosphere of nitrogen using Schlenk-techniques. For thin layer chromatography Polygram Sil G/UV 254 plates from Macherey, Nagel & Co. KG, Düren (Germany) were used and examined under UV-light irradiation (254 nm and 365 nm). Flash column chromatography was performed on silica gel from Macherey, Nagel & Co. KG, Düren (Germany) (particle size: 0.04-0.063 mm). Melting points were determined with a Melting Point Apparatus MEL-TEMP (Electrothermal, Rochford, UK) and are uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker Avance 300 (300 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to traces of $CHCl_3$ in the corresponding deuterated solvent.[1] MS spectra were recorded on a Vakuum Generators ZAB-2F, Finnigan MAT TSQ 700 or JEOL JMS-700 spectrometer. Crystal structure analysis was accomplished on Bruker Smart CCD or Bruker APEX diffractometers. Infrared (IR) spectra were recorded on a Jasco FT/IR-4100 spectrometer. Absorption spectra were recorded on a Jasco UV-VIS V-660 or Jasco UV-VIS V-670. Emission spectra were recorded on a Jasco FP-6500. Elemental Analysis was performed by the Microanalytical Laboratory of the University of Heidelberg using an Elementar Vario EL machine. Computational studies were carried out using DFT calculations on Spartan ´10. Geometry optimization was found by B3LYP functional and 6-311+G** basis set. Using this geometry the absolute energy and FMO energies were assigned on frequency analysis by employing B3LYP/6-311+G**. Cyclic voltammetry was performed with a VERSASTAT3-200 potentiostat (Princeton Applied Research) using a glassy carbon working electrode, a 0.1 mol/l NBu_4PF_6 solution in THF as solvent and ferrocene/ferrocenium as reference redox system and internal standard. Nomenclature of all new compounds described in the supporting information was determined according to IUPAC-rules.

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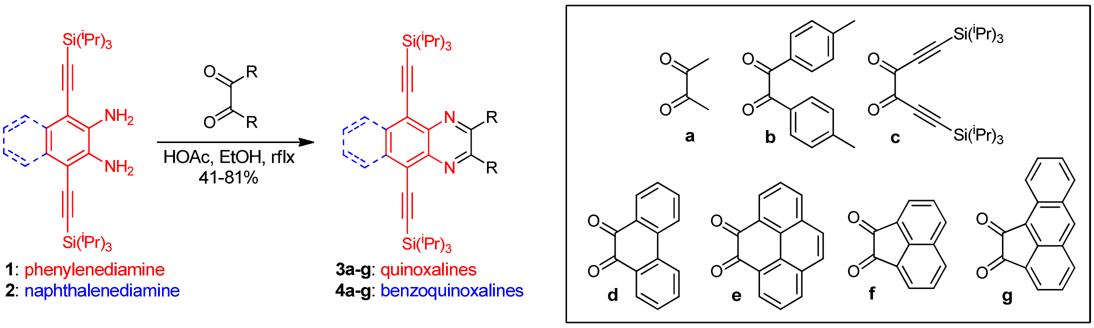
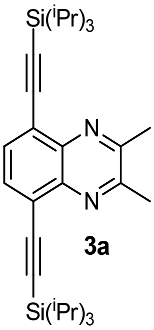
[1] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*,2176.

2. SYNTHESIS AND ANALYTICAL DATA

General procedure (GP)

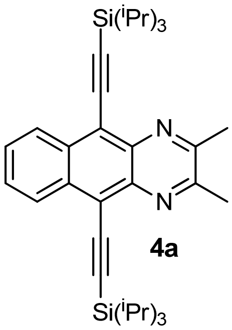


To a solution of the TIPS substituted benzo- or naphtodiamin in EtOH (3.5 mL per 100 mg diamin) and acetic acid (1.5 mL per 100 mg diamin) was added the corresponding dione. The mixture was stirred over night under reflux. After cooling down to room temperature water was added to the reaction-mixture and was extracted three times with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. Purification by flash column chromatography furnished the designated products.



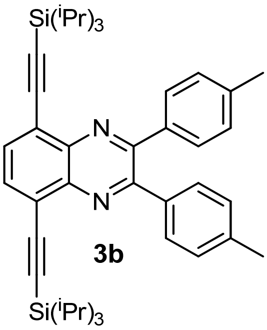
3a

2,3-dimethyl-5,8-bis{[tri(propan-2-yl)silyl]ethynyl}quinoxaline (3a): Starting from 3,6-bis{[tri(propan-2-yl)silyl]ethynyl}benzene-1,2-diamine **1** (0.200 g, 0.427 mmol, 1.0 equiv.) and biacetyl **a** (0.044 g, 0.512 mmol, 1.2 equiv.) according to **GP** a slightly yellow solid (0.179 g, 81 %) was isolated after flash column chromatography (silica gel, hexane/dichloromethane, 2/1, *v/v*). m.p. = 81 °C ; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (s, 2H), 2.72 (s, 6H), 1.21 (m, 42H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 154.20, 141.79, 132.14, 123.23, 103.76, 99.17, 23.18, 18.78, 11.49; IR (cm^{-1}) 3165, 2939, 2923, 2891, 2864, 2149, 1673, 1573, 1463, 1454, 1445, 1395, 1365, 1329, 1321, 1257, 1203, 1180, 1073, 1016; accurate mass for $C_{32}H_{50}N_2Si_2$: *m/z* = 518.3517 [M+], calc. *m/z* = 518.3513.



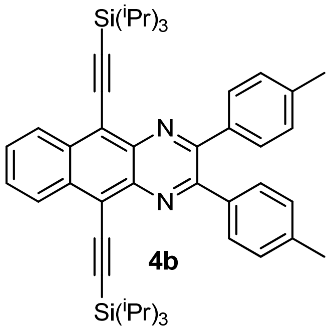
2,3-dimethyl-5,10-bis{[tri(propan-2-yl)silyl]ethynyl}benzo[*g*]quinoxaline (4a): Starting from 1,4-bis{[tri(propan-2-yl)silyl]ethynyl}naphthalene-2,3-diamine **2** (0.200 g, 0.386 mmol, 1.0 equiv.) and biacetyl **a** (0.040 g, 0.462 mmol, 1.2 equiv.) according to **GP** a yellow solid (0.195 g, 89 %) was isolated after flash column chromatography (silica gel, hexane/dichloromethane, 5/1, *v/v*). m.p.= 164 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.65 (m, 2H), 7.62 (m, 2H), 2.75 (s, 6H), 1.25 (m, 42H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 155.33, 140.17, 133.94, 127.63, 120.07, 106.16, 102.69, 100.12, 23.89, 19.15, 11.81; IR (cm^{-1}) 2909, 2849, 2710, 2605, 2555, 2453, 2376, 2189, 2131, 1969, 1917, 1821, 1726, 1579, 1503, 1456, 1364, 1227, 1174, 1039; accurate mass for $C_{36}H_{52}N_2Si_2$: *m/z* = 568.36604 [M+], calc. *m/z* = 568.37520; calcd. for $C_{36}H_{52}N_2Si_2$: C 75.99, H 9.21, N 4.92, found: C 75.99, H 8.98, N 4.86.

4a



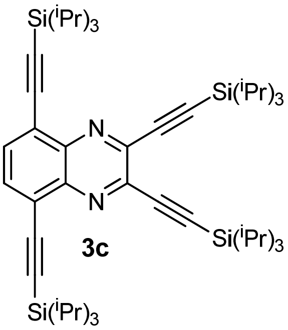
3b

2,3-bis(4-methylphenyl)-5,8-bis{[tri(propan-2-yl)silyl]ethynyl}quinoxaline (3b): Starting from 3,6-bis{[tri(propan-2-yl)silyl]ethynyl}benzene-1,2-diamine **1** (0.285 g, 0.608 mmol, 1.0 equiv.) and 1,2-di-*p*-tolylethane-1,2-dione **b** (0.174 g, 0.729 mmol, 1.2 equiv.) w according to **GP** a yellow solid (0.310g, 76 %) was isolated after flash column chromatography (silica gel, hexane/dichloromethane, 3/1, *v/v*). m.p. = 130 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (s, 2H), 7.64 (d, 4H), 7.13 (d, 4H), 2.40 (s, 6H), 1.23 (m, 42H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 152.90, 141.14, 139.11, 136.09, 133.13, 130.33, 128.68, 123.66, 103.57, 99.46, 21.43, 18.86, 11.50; IR (cm^{-1}) 3055, 3029, 2956, 2939, 2924, 2889, 2862, 2158, 1901, 1790, 1687, 1612, 1462, 1443, 1380, 1329, 1305, 1225, 1211, 1182, 1154, 1062; accurate mass for $C_{44}H_{58}N_2Si_2$: *m/z* = 670.4131, [M+], calc. *m/z* =670.4139.



4b

2,3-bis(4-methylphenyl)-5,10-bis{[tri(propan-2-yl)silyl]ethynyl}benzo[*g*]quinoxaline (4b): Starting from 1,4-bis{[tri(propan-2-yl)silyl]ethynyl}naphthalene-2,3-diamine **2** (0.200 g, 0.385 mmol, 1.0 equiv.) and 1,2-di-*p*-tolylethane-1,2-dione **b** (0.110 g, 0.462 mmol, 1.2 equiv.) according to **GP** a yellow solid (0.261 g, 94 %) was isolated after flash column chromatography (silica gel, hexane/dichloromethane, 6/1, *v/v*). (0.110 g, 41%). m.p.= 212 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.68 (m, 2H), 7.64 (m, 6H), 7.11 (d, 4H), 2.38 (s, 6H), 1.26 (m, 42H); $^{13}C\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ = 153.78, 139.58, 139.33, 136.38, 134.71, 130.57, 128.86, 127.83, 127.67, 120.45, 106.58, 102.62, 21.68, 19.18, 11.78; IR (cm^{-1}) 2913, 2849, 2712, 2613, 2557, 2442, 2349, 2133, 1906, 1898, 1812, 1715, 1605, 1529, 1453, 1381, 1341; accurate mass for $C_{48}H_{60}N_2Si_2$: *m/z* = 720.42485 [M+], calc. *m/z* = 720.43780; calcd. for $C_{48}H_{60}N_2Si_2$: C 79.94, H 8.39, 3.88, found: C 79.94, H 8.15, N 3.71.



3c

2,3,5,8-tetrakis{[tri(propan-2-yl)silyl]ethynyl}quinoxaline (3c): Starting from 3,6-bis{[tri(propan-2-yl)silyl]ethynyl}benzene-1,2-diamine **1** (0.150 g, 0.320 mmol, 1.0 equiv.) and 1,6-bis(triisopropylsilyl)hexa-1,5-diyne-3,4-dione **c**[2] (0.174 g, 0.416 mmol, 1.3 equiv.) according to **GP** a yellow solid (0.128 g, 47 %) was isolated after flash column chromatography (silica gel, hexane/dichloromethane, 3/1, *v/v*). m.p.= 145 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81 (s, 2H), 1.21 (m, 84H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 140.95, 140.38, 134.18, 123.44, 103.62, 102.88, 100.53, 99.13, 18.77, 11.40; IR (cm^{-1}) 2941, 2927, 2889, 2864, 2756, 2724, 2153, 1561, 1462, 1383, 1366, 1318, 1193, 1164, 1073, 1017; accurate mass for $C_{52}H_{86}N_2Si_2$: *m/z* = 850.5864 [M+], calc. *m/z* = 850.5868.

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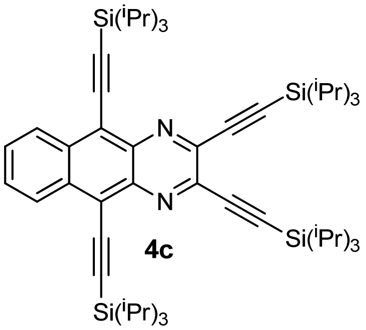
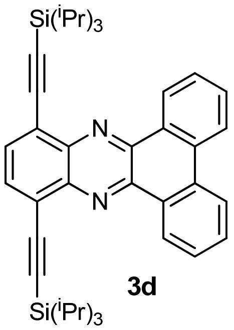
[2] R. Faust, C. Weber, V. Fiandanese, G. Marchese, A. Punzi, *Tetrahedron* **1997**, *53*, 14655-14670.



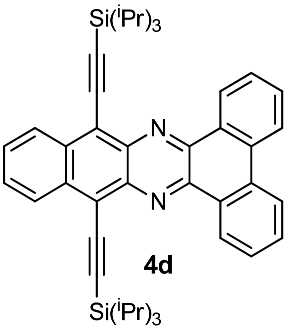
4c

2,3,5,10-tetrakis{[tri(propan-2-yl)silyl]ethynyl}benzo[*g*]quinoxaline (4c): Starting from 1,4-bis{[tri(propan-2-yl)silyl]ethynyl}naphthalene-2,3-diamine **2** (0.200 g, 0.385 mmol, 1.0 equiv.) and 1,6-bis(triisopropylsilyl)hexa-1,5-diyne-3,4-dione **c**[2] (0.193 g, 0.501 mmol, 1.3 equiv.) according to **GP** a orange solid (0.188 g, 54 %) was isolated after flash column chromatography (silica gel, hexane/dichloromethane, 8/1, *v/v*). m.p. = 206 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.60 (m, 2H), 7.64 (m, 2H), 1.23 (m, 42H), 1.17 (m, 42H); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ = 140.63, 138.74, 135.05, 128.46, 127.93, 120.47, 107.81, 104.21, 102.02, 99.67, 19.13, 19.03, 11.72, 11.67; IR (cm^{-1}) 3063, 2941, 2923, 2864, 2757, 2724, 2164, 2137, 1514, 1462, 1384, 1329, 1271, 1213, 1166, 1017; accurate mass for $C_{56}H_{88}N_2Si_2$: *m/z* = 900.603 [M+], calc. *m/z* = 900.609; calcd. for $C_{56}H_{88}N_2Si_4$: C 74.60, H 9.84, N 3.11, found: C 76.61, H 9.62, N 3.00.



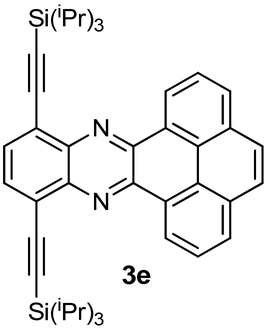
3d

10,13-bis{[tri(propan-2-yl)silyl]ethynyl}dibenzo[*a*,*c*]phenazine (3d): Starting from 3,6-bis{[tri(propan-2-yl)silyl]ethynyl}benzene-1,2-diamine **1** (0.200 g, 0.427 mmol, 1.0 equiv.) and phenanthrene-9,10-dione **d** (0.107 g, 0.512 mmol, 1.2 equiv.) according to **GP** a yellow solid (0.252 g, 92 %) was isolated after flash column chromatography (silica gel, hexane/dichloromethane, 1/1, *v/v*). m.p.= 108 °C ; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.49 (d, 2H), 8.48 (d, 2H), 7.94 (s, 2H), 7.74 (t, 2H), 7.65 (t, 2H), 1.27 (m, 42H); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ = 142.81, 142.48, 133.74, 132.50, 130.79, 130.40, 127.91, 127.18, 124.33, 123.01, 104.04, 99.85, 19.08, 11.92; IR (cm^{-1}) 3071, 2923, 2918, 2889, 2862, 2148, 1604, 1562, 1493, 1462, 1372, 1365, 1351, 1269, 1259, 1221, 1166, 1148, 1111, 1088, 1064; accurate mass for $C_{42}H_{52}N_2Si_2$: *m/z* = 640.3681 [M+], calc. *m/z* = 640.3669.



4d

10,13-bis{[tri(propan-2-yl)silyl]ethynyl}dibenzo[a,c]phenazine (4d): Starting from 1,4-bis{[tri(propan-2-yl)silyl]ethynyl}naphthalene-2,3-diamine **2** (0.200 g, 0.385 mmol, 1.0 equiv.) and phenanthrene-9,10-dione **d** (0.096 g, 0.463 mmol, 1.2 equiv.) according to **GP** a red solid (0.261 g, 98 %) was isolated after flash column chromatography (silica gel, hexane/dichloromethane, 3/1, *v/v*). m.p.= 179 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.74 (m, 2H), 8.37 (m, 2H), 8.10 (d, 2H), 7.84 (t, 2H), 7.67 (m, 4H), 1.24 (m, 42H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 143.76, 140.13, 134.81, 132.59, 130.99, 130.44, 127.85, 127.76, 127.54, 127.31, 122.94, 120.55, 106.77, 102.83, 18.97, 11.67; IR (cm^{-1}) 2351, 2214, 2136, 1985, 1391, 1192, 1160, 1069, 1049; accurate mass for $C_{46}H_{54}N_2Si_2$: *m/z* = 690.37776 [M+], calc. *m/z* = 690.38256.



3e

10,13-bis{[tri(propan-2-yl)silyl]ethynyl}phenanthro[4,5-*abc*]phenazine (3e): Starting from 3,6-bis{[tri(propan-2-yl)silyl]ethynyl}benzene-1,2-diamine **1** (0.100 g, 0.213 mmol, 1.0 equiv.) and pyren-4,5-dione **e**[3] (0.59 g, 0.256 mmol, 1.2 equiv.) according to **GP** a orange solid (0.065 g, 46 %) was isolated after flash column chromatography (silica gel, hexane/dichloromethane, 4/1, *v/v*). m.p.= 198 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.47 (d, 2H), 8.13 (d, 2H), 7.98 (s, 2H), 7.92 (t, 2H), 7.78 (s, 2H), 1.34 (s, 42H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 143.26, 142.40, 133.59, 131.15, 129.40, 129.17, 126.89, 126.59, 126.05, 124.59, 124.19, 103.99, 99.57, 18.98, 11.68; IR (cm^{-1}) 2955, 2938, 2923, 2889, 2862, 2148, 1624, 1483, 1461, 1371, 1352, 1335, 1308, 1251, 1152, 1113, 1084, 1066, 1041, 1017; accurate mass for $C_{44}H_{52}N_2Si_2$: *m/z* = 664.3644 [M+], calc. *m/z* = 664.3669.

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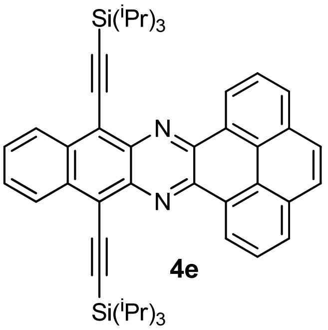
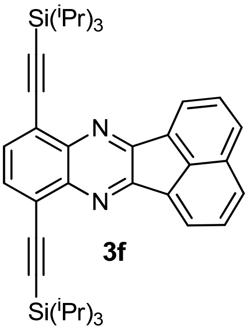
[3] J. Hu, D. Zhang, F. W. Harris, *J. Org. Chem.* **2005**, *70*, 707-708.



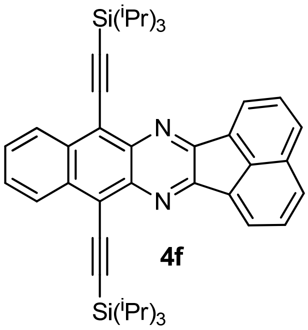
4e

10,15-bis{[tri(propan-2-yl)silyl]ethynyl}benzo[*i*]phenanthro[4,5-*abc*]phenazine (4e): Starting from 1,4-bis{[tri(propan-2-yl)silyl]ethynyl}naphthalene-2,3-diamine **2** (0.100 g, 0.193 mmol, 1.0 equiv.) and pyren-4,5-dione **e**[3] (0.054 g, 0.231 mmol, 1.2 equiv.) according to **GP** a red solid (0.068 g, 49 %) was isolated after flash column chromatography (silica gel, hexane/dichloromethane, 8/1, *v/v*). m.p.= 265 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.66 (d, 2H), 8.82 (m, 2H), 8.19 (d, 2H), 7.96 (t, 2H), 7.88 (s, 2H), 7.71 (m, 2H), 1.38 (m, 42H); $^{13}C\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ = 144.45, 140.27, 134.86, 131.27, 129.92, 129.43, 127.78, 127.60, 126.90, 126.70, 126.31, 125.08, 120.59, 106.71, 102.96, 19.06, 11.76; IR (cm^{-1}) 3060, 2939, 2923, 2889, 2862, 2130, 1623, 1493, 1462, 1383, 1353, 1315, 1229, 1125, 1045; accurate mass for $C_{48}H_{54}N_2Si_2$: *m/z* = 714.3824 [M+], calc. *m/z* = 714.3826.



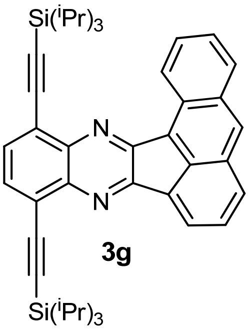
3f

8,11-bis{[tri(propan-2-yl)silyl]ethynyl}acenaphtho[1,2-*b*]quinoxaline (3f): Starting from 3,6-bis{[tri(propan-2-yl)silyl]ethynyl}benzene-1,2-diamine **1** (0.200 g, 0.427 mmol, 1.0 equiv.) and acenaphthylene-1,2-dione **f** (0.093 g, 0.512 mmol, 1.2 equiv.) according to **GP** a yellow solid (0.212 g, 81 %) was isolated after flash column chromatography (silica gel, hexane/dichloromethane, 3/1, *v/v*). m.p. = 168 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.34 (d, 2H), 8.06 (d, 2H), 7.86 (s, 2H), 7.83 (t, 2H), 1.31 (m, 42H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 154.39, 142.22, 136.90, 132.55, 131.95, 129.89, 129.55, 128.67, 124.31, 122.27, 103.97, 99.47, 18.88, 11.55; IR (cm^{-1}) 3587, 3552, 3495, 3047, 3019, 2952, 2939, 2931, 2921, 2885, 2864, 2752, 2722, 2622, 2566, 2354, 2149, 1925, 1881, 1812, 1670, 1629, 1614, 1462, 1164; accurate mass for $C_{40}H_{50}N_2Si_2$: *m/z* = 614.3511 [M+], calc. *m/z* = 614.3513.



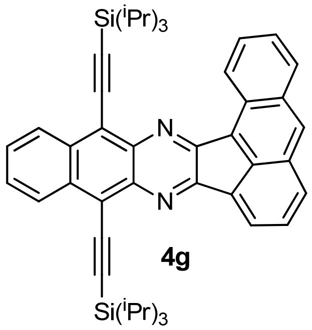
4f

8,13-bis{[tri(propan-2-yl)silyl]ethynyl}acenaphtho[1,2-*b*]benzo[*g*]quinoxaline (4f): Starting from 1,4-bis{[tri(propan-2-yl)silyl]ethynyl}naphthalene-2,3-diamine **2** (0.200 g, 0.385 mmol, 1.0 equiv.) and acenaphthylene-1,2-dione **f** (0.084 g, 0.462 mmol, 1.2 equiv.) according to **GP** a orange solid (0.155 g, 60 %) was isolated after flash column chromatography (silica gel, hexane/dichloromethane, 5/1, *v/v*). m.p.= 220 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.73 (m, 2H), 8.37 (d, 2H), 8.11 (d, 2H), 7.85 (t, 2H), 7.69 (m, 2H), 1.24 (m, 42H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 155.32, 140.57, 138.78, 134.25, 132.40, 130.46, 129.82, 129.12, 128.08, 127.86, 122.23, 121.57, 106.60, 103.02, 19.38, 12.02; IR (cm^{-1}) 3537, 3485, 3053, 2932, 2858, 2710, 2134, 1912, 1812, 1718, 1612, 1555, 1460, 1379, 1300, 1239, 1134, 1127, 1044; accurate mass for $C_{44}H_{52}N_2Si_2$: *m/z* = 664.36261 [M+], calc. *m/z* = 664.36691.



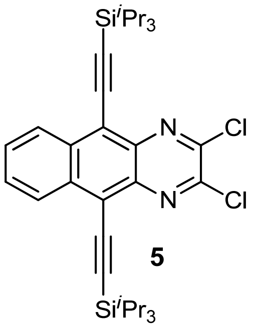
3g

10,13-bis{[tri(propan-2-yl)silyl]ethynyl}aceanthryleno[1,2-*b*]quinoxaline (3g): Starting from 3,6-bis{[tri(propan-2-yl)silyl]ethynyl}benzene-1,2-diamine **1** (0.200 g, 0.427 mmol, 1.0 equiv.) and aceanthrenequinone **g** (0.119 g, 0.512 mmol, 1.2 equiv.) according to **GP** a orange solid (0.173 g, 61 %) was isolated after flash column chromatography (silica gel, hexane/dichloromethane, 2/1, *v/v*). m.p.= 168 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.49 (d, 1H), 8.41 (s, 1H), 8.22 (d, 1H), 7.99 (m, 2H), 7.88 (m, 2H), 7.67 (m, 2H), 7.83 (t, 1H), 1.33 (m, 42H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 155.31, 153.93, 141.93, 141.34, 135.72, 133.94, 133.36, 132.08, 131.47, 130.30, 129.70, 129.56, 129.04, 128.56, 127.63, 127.30, 126.21, 125.98, 125.33, 124.43, 124.33, 122.44, 104.64, 104.25, 99.31, 98.65, 18.99, 11.65, 11.63; IR (cm^{-1}) 3066 3044, 2939, 2927, 2889, 2863, 2721, 2150, 1878. 1760, 1579, 1479, 1462, 1433, 1170, 1167, 1135, 1096; accurate mass for $C_{44}H_{52}N_2Si_2$: *m/z* =664.3675 [M+], calc. *m/z* = 664.3669.



4g

10,15-bis{[tri(propan-2-yl)silyl]ethynyl}aceanthryleno[1,2-*b*]benzo[*g*]quinoxaline (4g): Starting from 1,4-bis{[tri(propan-2-yl)silyl]ethynyl}naphthalene-2,3-diamine **2** (0.200 g, 0.385 mmol, 1.0 equiv.) and aceanthrenequinone **f** (0.108 g, 0.462 mmol, 1.2 equiv.) according to **GP** a red solid (0.196 g, 71 %) was isolated after flash column chromatography (silica gel, hexane/dichloromethane, 2/1, *v/v*). m.p. = 115 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.86 (d, 1H), 8.86 (m, 1H), 8.81 (m, 1H), 8.75 (s, 1H), 8.47 (d, 1H), 8.29 (d, 1H), 8.25 (d, 1H), 8.24 (d, 1H), 7.89 (m,1H), 7.82 (m, 2H), 7.74 (m, 1H), 1.32 (m, 42H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 11.84, 19.19, 19.23, 102.91, 103.29, 105.98, 106.39, 121.15, 121.59, 122.07, 126.02, 126.44, 126.60, 127.65, 127.68, 127.74, 127.88, 127.92, 128.00, 128.84, 129.20, 129.82, 129.86, 130.50, 132.03, 133.84, 134.32, 134.50, 137.91, 139.72, 140.32, 155.01, 156.21; IR (cm^{-1}) 3061, 2954, 2940, 2891, 2862, 2754, 2721, 2612, 2555, 2517, 2359, 2160, 2128, 1945, 1916, 1828, 1714, 1622, 1579, 1528, 1464, 1381, 1292, 1234, 1173, 1040, 1015; accurate mass for $C_{48}H_{54}N_2Si_2$: *m/z* = 714.38445 [M+], calc. *m/z* = 714.38905.



5

2,3-dichloro-5,10-bis{[tri(propan-2-yl)silyl]ethynyl}benzo[g]quinoxaline (5): A mixture of 1,4-bis{[tri(propan-2-yl)silyl]ethynyl}naphthalene-2,3-diamine **2** (1.60 g, 3.08 mmol) and diethyloxalate (7.50 mL) was heated to reflux. After 19 h the mixture was evaporated at 90°C and dried under vacuum. The dark brown solid was dissolved in $POCl_3$ (10.0 mL) and heated to reflux for 20 h. The orange-black solution was evaporated and purified by flash column chromatography (silica gel, petrolether, 677 mg, 36% over two steos) to obtain **5** as orange crystals. m.p. = 143 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.60 (m, 2H), 7,66 (m, 2H), 1,16-1,25 (m, 42H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 11.62, 18.96, 101.07, 108.36, 120.29, 127.76, 128.85, 134.59, 138.95, 146.21; IR (cm^{-1}) 3061, 2954, 2940, 2889, 2862, 2325, 2166, 2144, 1978, 1700, 1552; accurate mass for $C_{34}H_{47}Cl_2N_2Si_2$: *m/z* = 609.26493 [M+], calc. *m/z* = 609.26493.

3. UV-VIS SPECTRA

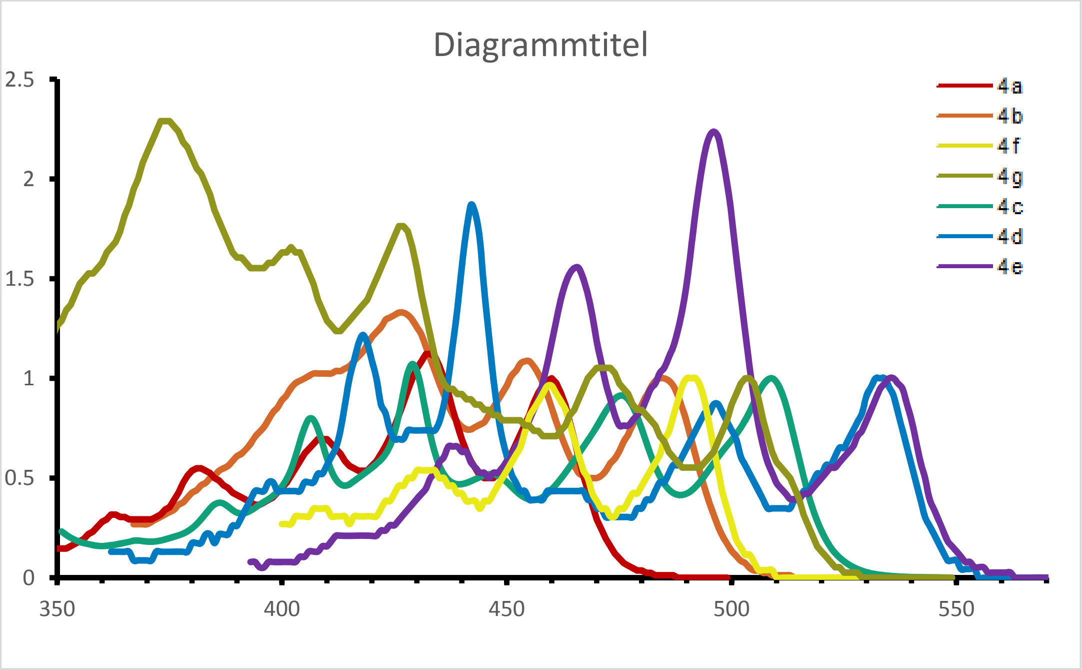


Figure 1: UV/Vis spectra of the benzoquinoxaline-derivatives **4a**-**g** in hexanes.

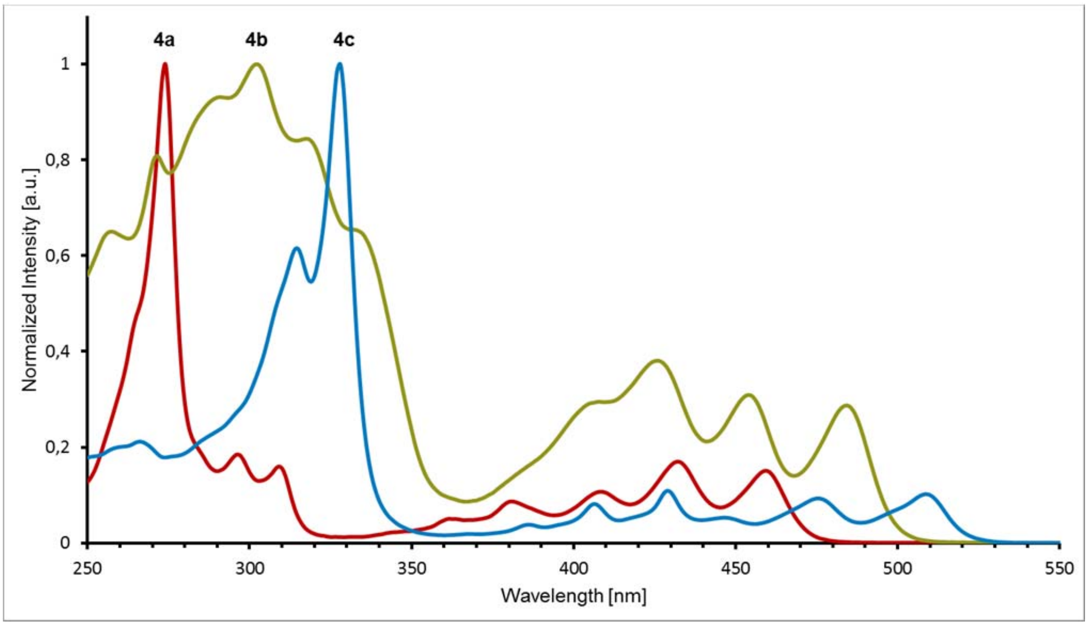


Figure 2: UV/Vis spectra of the benzoquinoxaline-derivatives **4a**-**c** in hexanes.

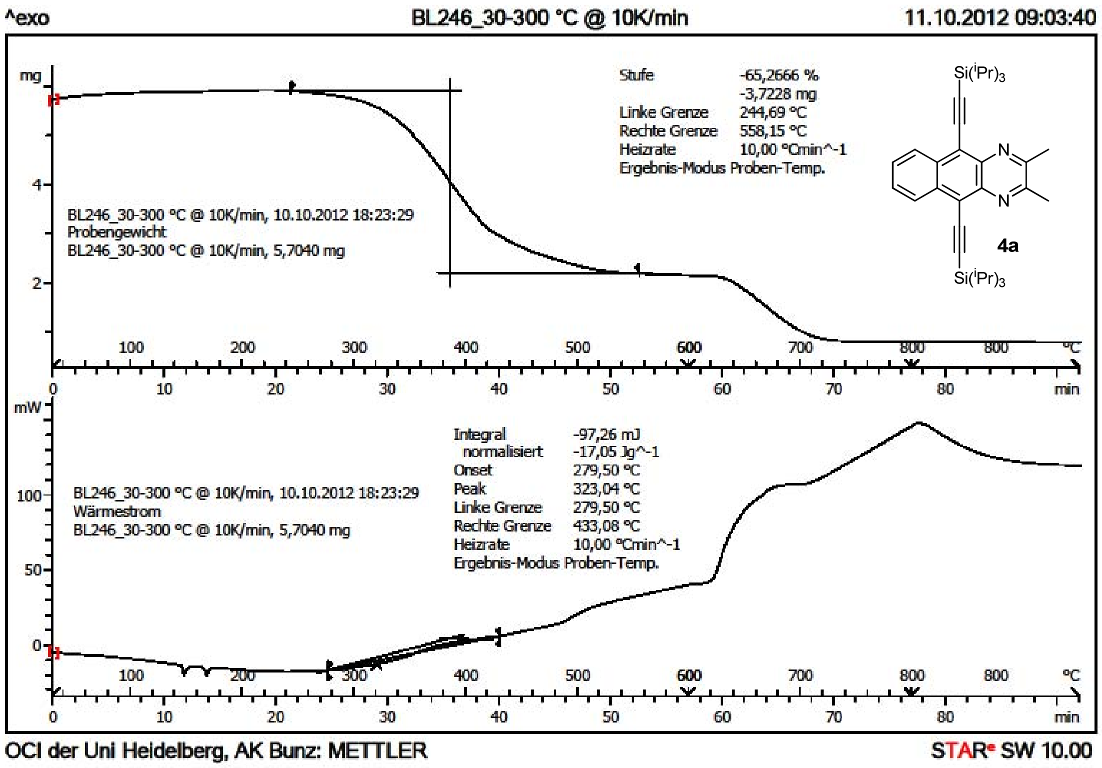
4. SUMMARY OF OPTICAL AND ELECTRONICAL DATA

Table 1: optical, electronical and computational data of the quinoxaline- and benzoquinoxalines-derivatives

	CV[a)] (1. Red)	LUMO$_{CV}$[c)] [eV]	HOMO[f)] [eV]	Gap$_{UV}$[d)] [eV]	LUMO$_{DFT}$[e)] [eV]	HOMO$_{DFT}$[e)] [eV]	Gap$_{DFT}$[e)] [eV]	Abs$_{Max}$[b)] [nm]	Abs$_{edge}$[b)] [nm]	Abs$_{Max}$[g)] [nm]	Emm$_{Max}$[b)] [nm]	Emm$_{Max}$[g)] [nm]	QY[b)]	QY[g)]
3a	–2.08	-3,02	-6,15	-3,13	-2,43	-6,06	-3,63	366	396	342	405	415	0,022	0,033
3b	–1.89	-3,21	-6,19	-2,98	-2,54	-6,02	-3,48	385	416	375	417	433	0,019	0,075
3c	–1.64	-3,46	-6,36	-2,90	-2,82	-6,14	-3,32	405	427	411	426	458	0,053	0,158
3d	–1.64	-3,46	-6,24	-2,78	-2,84	-6,04	-3,20	407	446	409	437	467	0,007	0,022
3e	–1.61	-3,49	-6,11	-2,62	-2,84	-5,99	-3,15	458	473	456	461	497	0,303	0,09
3f	–1.84	-3,26	-6,23	-2,97	-2,58	-5,99	-3,41	401	417	399	411	448	0,005	0,023
3g	–1.65	-3,45	-6,04	-2,59	-2,80	-5,79	-2,99	467	479	466	470	485	0,066	0,082
4a	–1.75	-3,35	-5,93	-2,58	-2,76	-5,64	-2,88	460	481	459	471	483	0,353	0,471
4b	–1.58	-3,52	-5,97	-2,45	-2,84	-5,59	-2,75	485	506	487	496	510	0,127	0,563
4c	–1.38	-3,72	-6,32	-2,60	-3,09	-5,72	-2,63	459	476	511	517	540	0,248	0,207
4d	–1.36	-3,74	-5,97	-2,23	-3,10	-5,61	-2,51	533	556	533	540	563	0,244	0,134
4e	–1.33	-3,77	-5,99	-2,22	-3,10	-5,61	-5,61	535	558	537	541	565	0,05	0,341
4f	–1.56	-3,54	-5,99	-2,45	-2,86	-5,60	-2,74	487	507	492	497	514	0,123	0,127
4g	–1.55	-3,55	-5,91	-2,36	-2,85	-5,52	-2,67	503	525	508	516	534	0,124	0,112

a) measured in THF(Bu_4NPF_6) against Fc/Fc$^+$ @ 50 mV/s; b) in hexanes; c) from CV measurement; d) from UV/Vis spectra in hexanes; e) Spartan 10, B3LYP, 6-311+G**; f) Gap$_{UV}$-LUMO$_{CV}$; g) in DCM.

5. TGA DSC DATA


^exo BL246_30-300 °C @ 10K/min 11.10.2012 09:03:40

Stufe -65,2666 %
-3,7228 mg
Linke Grenze 244,69 °C
Rechte Grenze 558,15 °C
Heizrate 10,00 °Cmin^-1
Ergebnis-Modus Proben-Temp.

BL246_30-300 °C @ 10K/min, 10.10.2012 18:23:29
Probengewicht
BL246_30-300 °C @ 10K/min, 5,7040 mg

Integral -97,26 mJ
normalisiert -17,05 Jg^-1
Onset 279,50 °C
Peak 323,04 °C
Linke Grenze 279,50 °C
Rechte Grenze 433,08 °C
Heizrate 10,00 °Cmin^-1
Ergebnis-Modus Proben-Temp.

BL246_30-300 °C @ 10K/min, 10.10.2012 18:23:29
Wärmestrom
BL246_30-300 °C @ 10K/min, 5,7040 mg

OCI der Uni Heidelberg, AK Bunz: METTLER STAR^e SW 10.00

Figure 3: TGA DSC of compound **4a**

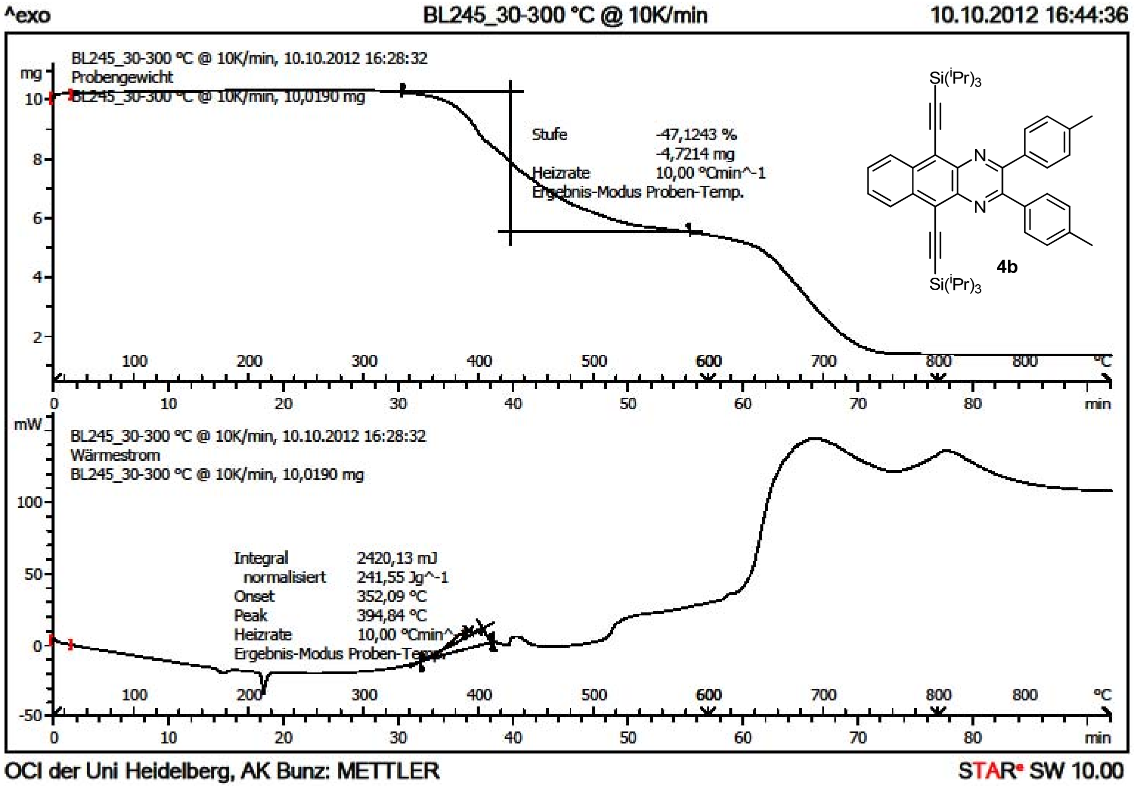


Figure 4: TGA DSC of compound **4b**

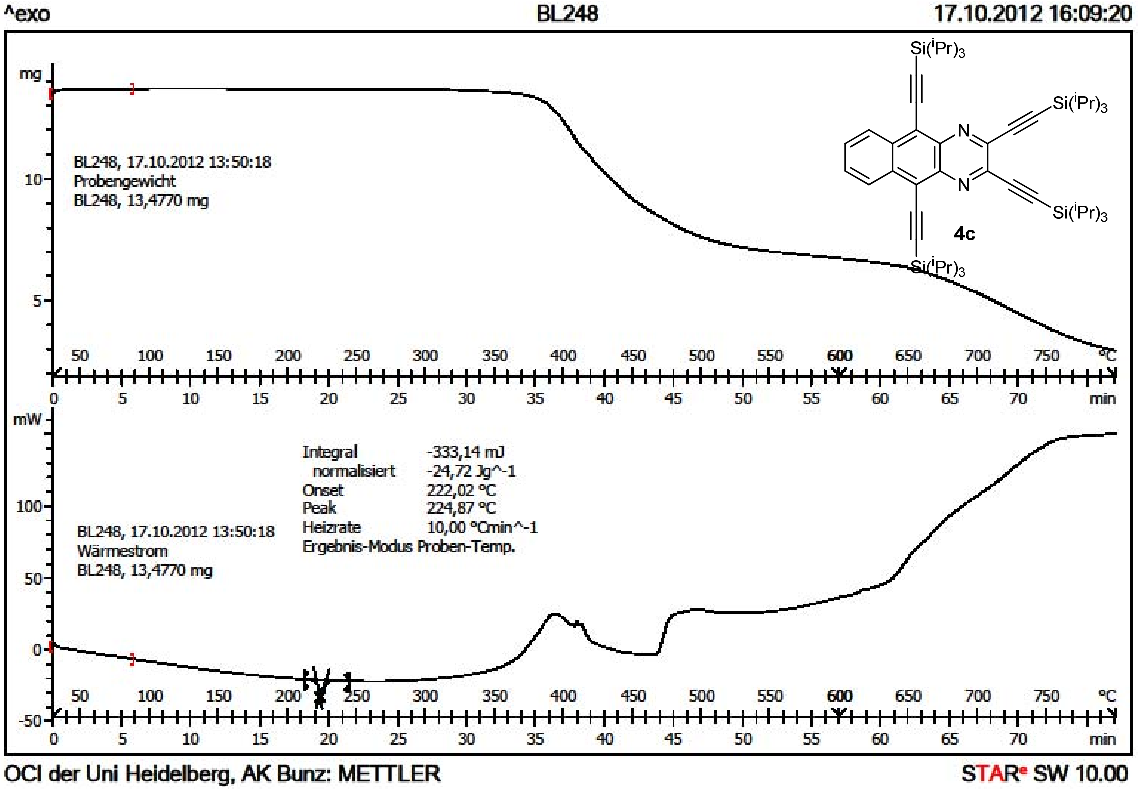
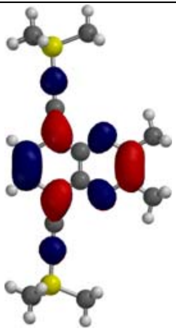
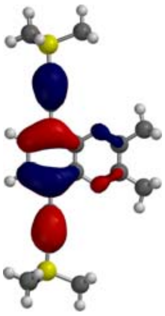
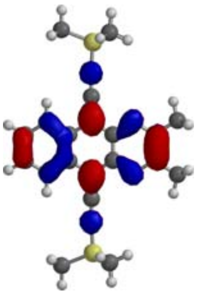
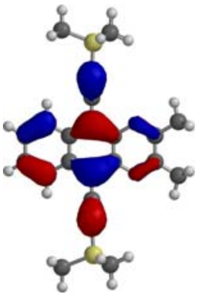
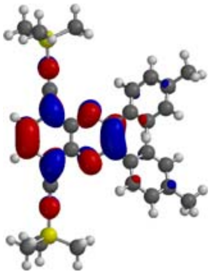
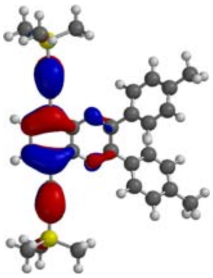
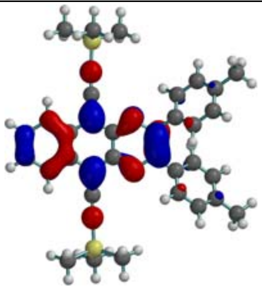
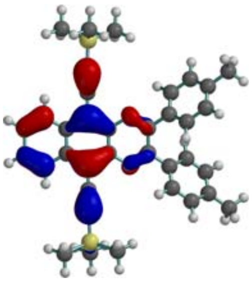
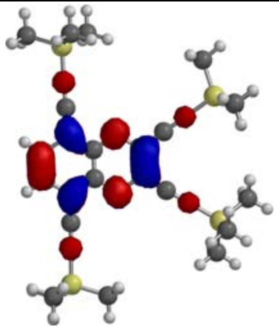
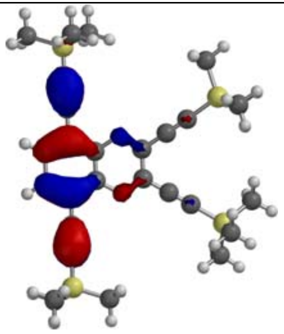
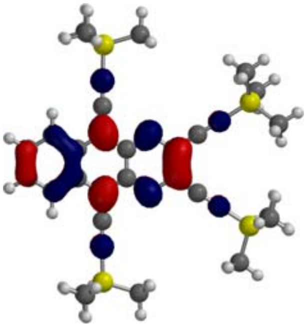
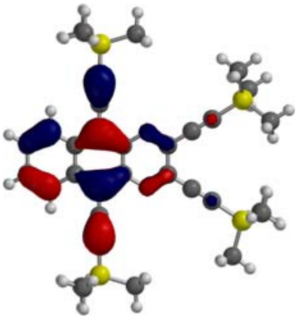
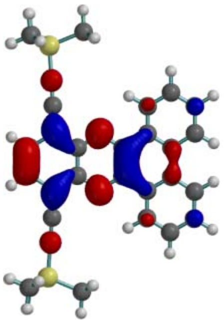
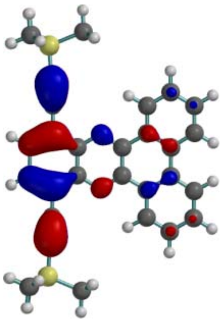
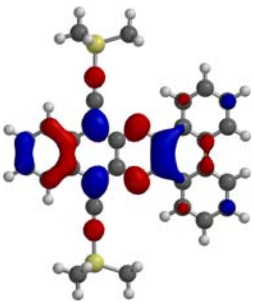
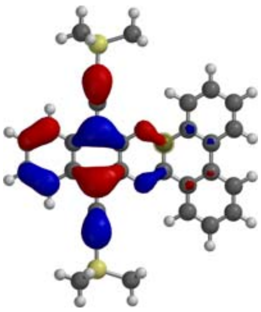


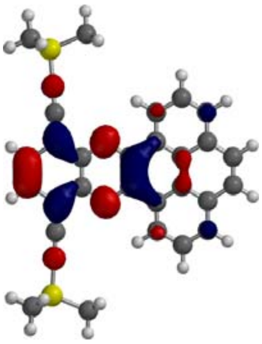
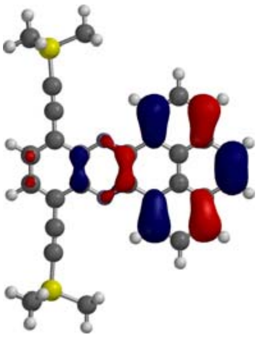
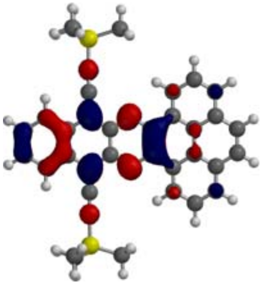
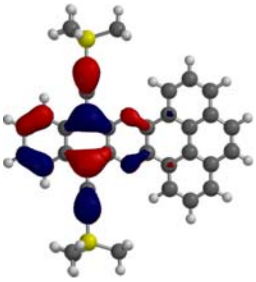
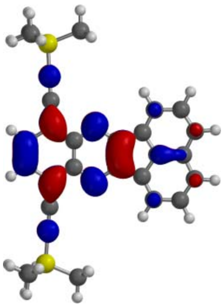
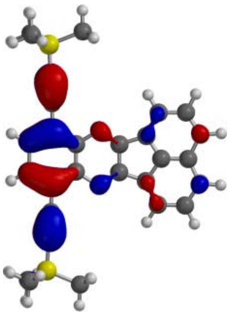
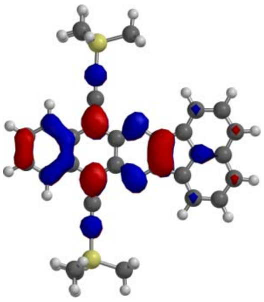
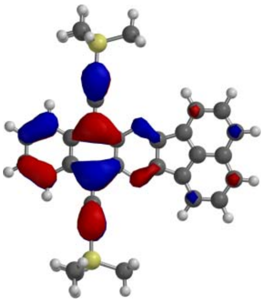
Figure 5: TGA DSC of compound **4c**

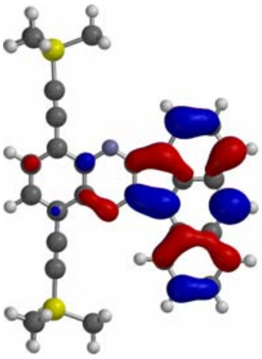
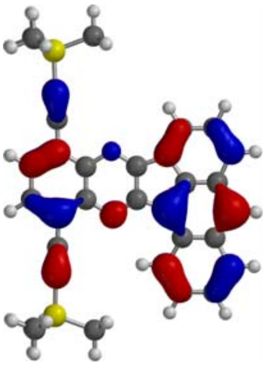
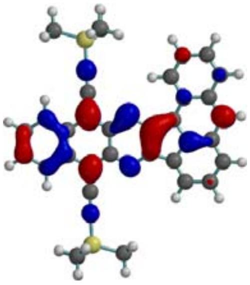
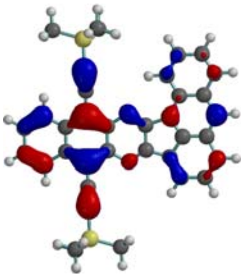
6. COMPUTATIONAL STUDIES

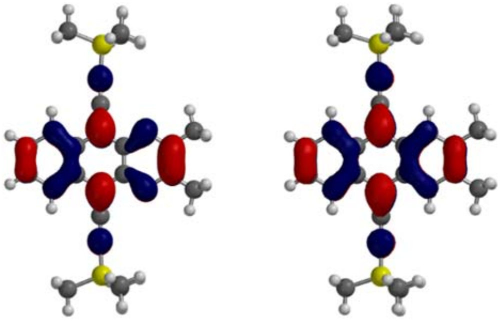
Table 2 FMOs of the quinoxaline- and benzoquinoxalines-derivatives (Spartan´10; B3LYP-6-311+G**)

 LUMO: -2,43 eV **3a**	 HOMO: -6,06 eV
 LUMO: -2,76 eV **4a**	 HOMO: -5,64 eV
 LUMO: -2,54 eV **3b**	 HOMO: -6,02 eV
 LUMO: -2,84 eV **4b**	 HOMO: -5,59 eV

 LUMO: -2,82 eV **3c**	 HOMO: -6,14 eV
 LUMO: -3,09 eV **4c**	 HOMO: -5,72 eV
 LUMO: -2,84 eV **3d**	 HOMO: -6,04 eV
 LUMO: -3,10 eV **4d**	 HOMO: -5,61 eV

 LUMO: -2,84 eV **3e**	 HOMO: -5,99 eV
 LUMO: -3,10 eV **4e**	 HOMO: -5,61 eV
 LUMO: -2,58 eV **3f**	 HOMO: -5,99 eV
 LUMO: -2,86 eV **4f**	 HOMO: -5,60 eV

 LUMO: -2,80 eV **3g**	 HOMO: -5,79 eV
 LUMO: -2,85 eV **4g**	 HOMO: -5,52 eV



Benzoquinoxaline-derivative **4a´**

Anthraceno-derivative

Figure 6: Comparison of the calculated LUMO (Spartan´10 B3LYP-6-311+G**) for the TMS-benzoquinoxaline-derivative **4a**´(lefit) and the all-Carbon-analogon (right)

Here the exemplarily comparison of the frontier orbitals of TMS-benzoquinoxaline-derivative **4a**´ to the all-carbon anthracene derivative shows that the LUMO energies are lowered from -2.44 eV to -2.76 eV by introduction of two nitrogen atoms into the acenecore.

7. OLED FABRICATION

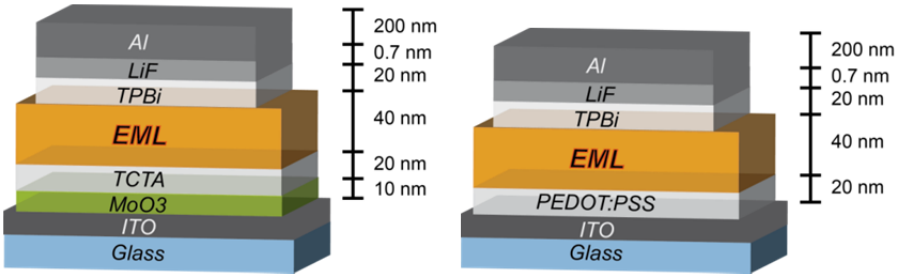


Figure 7 Device architectures of vacuum processed OLEDs (left) and solution deposited OLEDs (right) comprising the compounds 4a-c as emission layers.

According to Figure 1, all OLEDs were fabricated on indium tin oxide (ITO) coated glass substrates ($R_\square \approx 13\ \Omega/\square$) that had been structured using hydrochloric acid. The substrates were cleaned with acetone and isopropanol for 15 min in an ultrasonic bath. Afterwards the substrates were exposed to oxygen plasma for 2 min in order to remove organic residues and to polarize the ITO surface for better PEDOT:PSS adhesion. Then the samples were moved to a glovebox with nitrogen atmosphere and kept there for the remaining fabrication and characterization process.

For partly solution processed devices (Fig 1 left) a PEDOT:PSS (VPAi 4083, Heraeus) layer was spincast at 4000 rpm for 30 s from a 1:1 water diluted solution and then annealed for 10 min in a vacuum oven at 120 °C. Each **4a**, **4b** and **4c** were dissolved in tetrahydrofuran (THF, 3 mg/ml) and spincast at 1000 rpm for 20 s (40nm).

The fully evaporated devices (Figure 7) comprise 10 nm MoO_3 for enhanced hole injection, followed by 20 nm TCTA as an electron blocking layer and a 40nm **4a**, **4b** or **4c** emission layer.

All devices (Figure 7) were capped by a TPBi (20nm) hole blocking layer and a LiF / Al (0.7 nm / 200 nm) counter electrode. All thermal evaporation steps were done in a high vacuum chamber (10^{-6} mbar).

The OLED current density–voltage (J-V) characteristics were recorded with a source measure unit (Keithley 238). The device luminance was calculated from the emission spectrum. The respective spectrometer had been calibrated with a secondary standard calibration halogen lamp (Philips FEL-1000W). Current efficiencies (cd/A) and power efficiencies (lm/W) were calculated from the electrical and optical properties. For this calculation we assumed a lambertian light distribution.

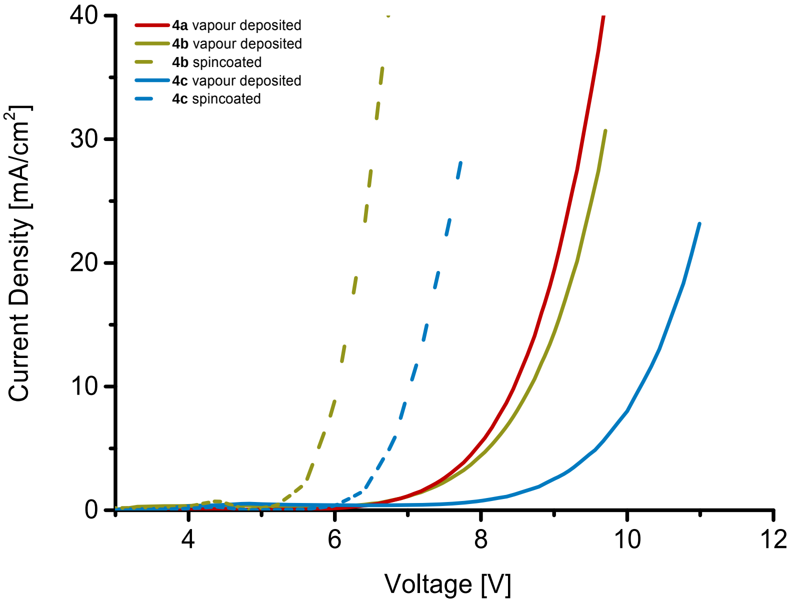


Figure 8: Current Density-Volltage plot for OLEDs with **4a**-**c** as EML.

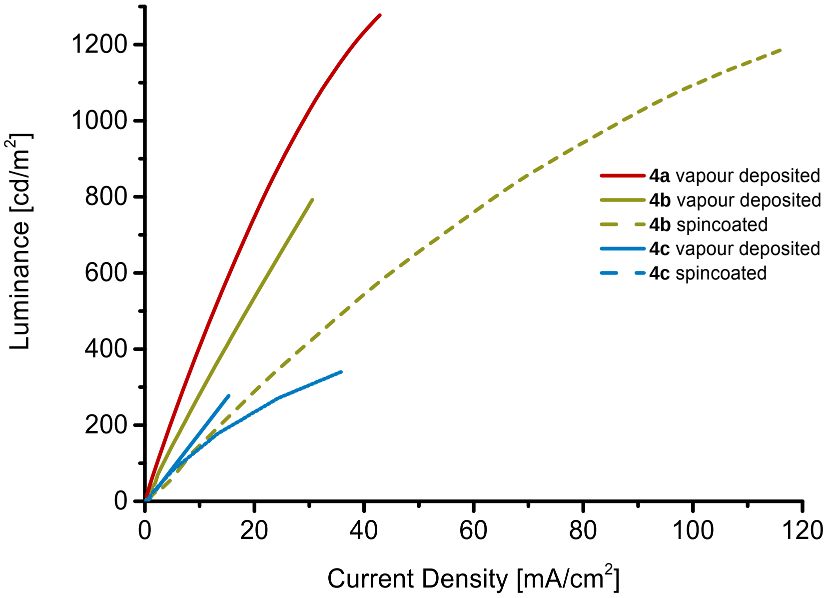


Figure 9: Luminance-Current Density plot for OLEDs with **4a**-**c** as EML.

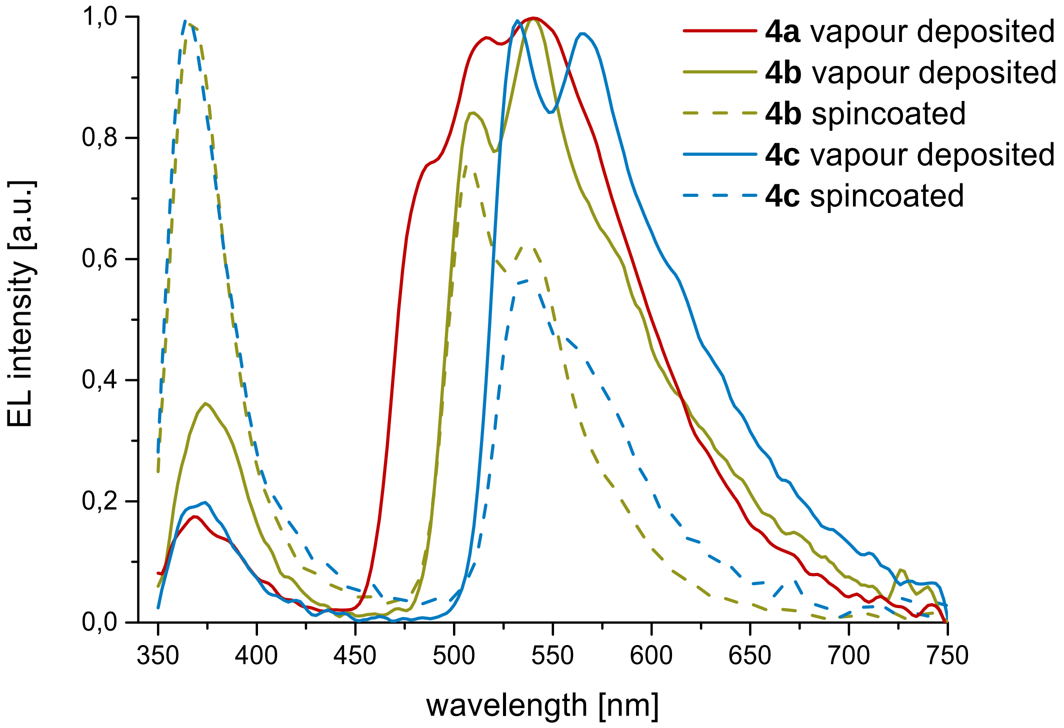


Figure 10: EL spectra of OLEDs prepared with **4a**-**c** as EML.

8. ^{1}H- AND ^{13}C-NMR SPECTRA

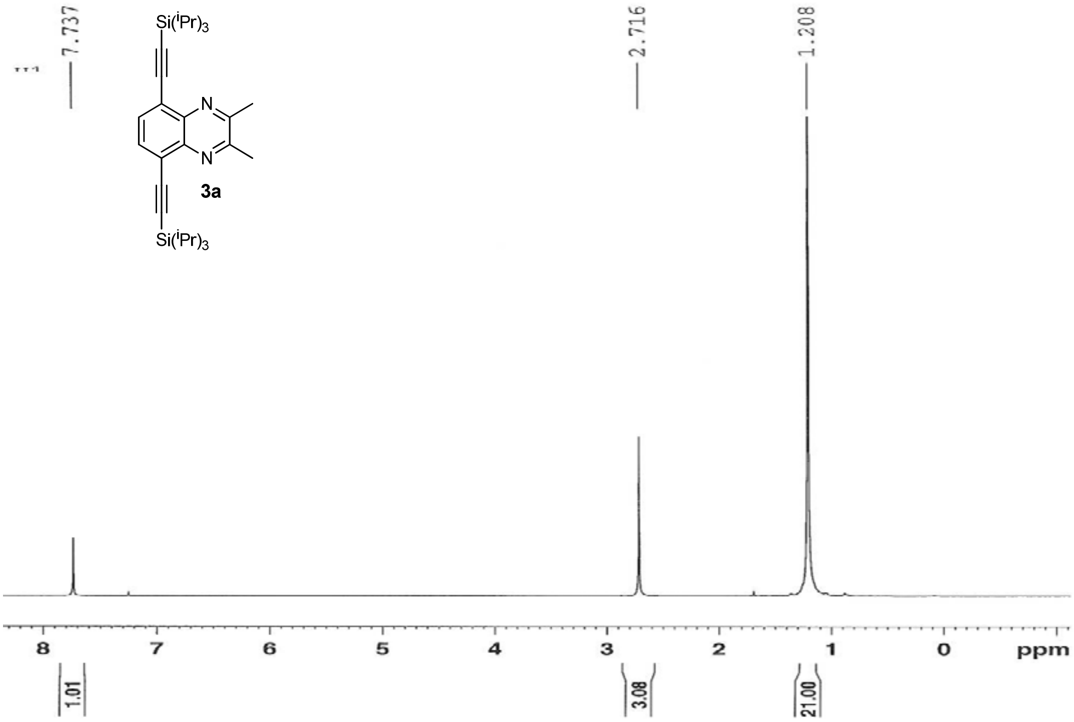


Figure 11: ^{1}H-NMR of compound **3a**.

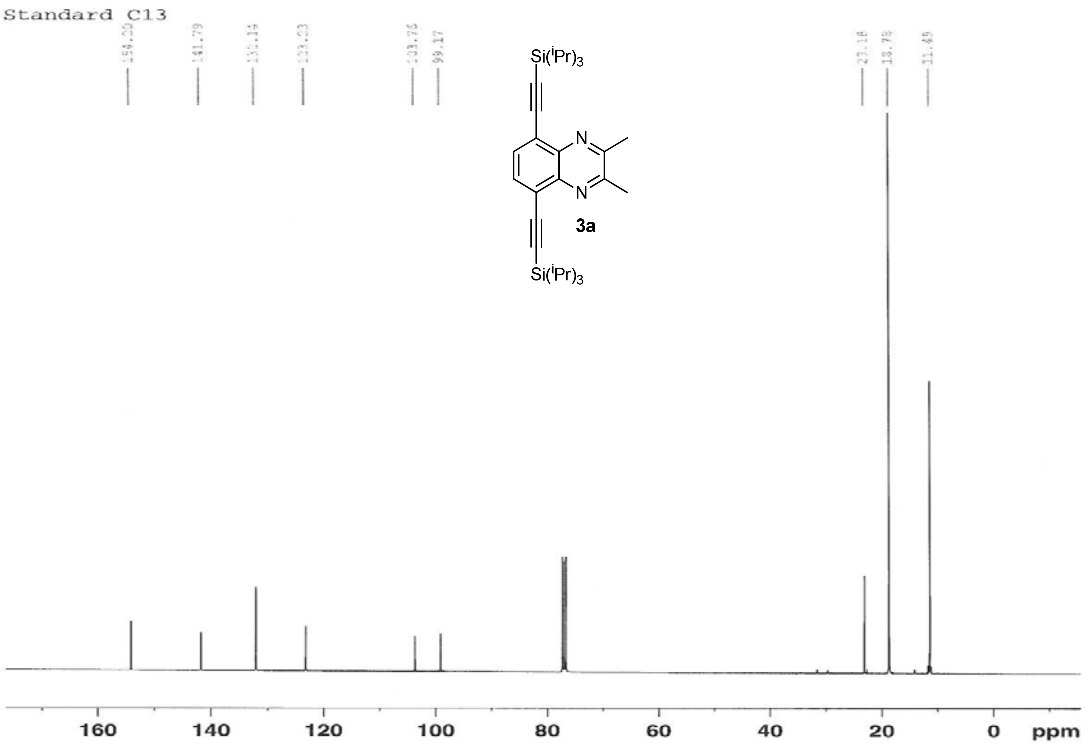


Figure 12: ^{13}C-NMR of compound **3a**.

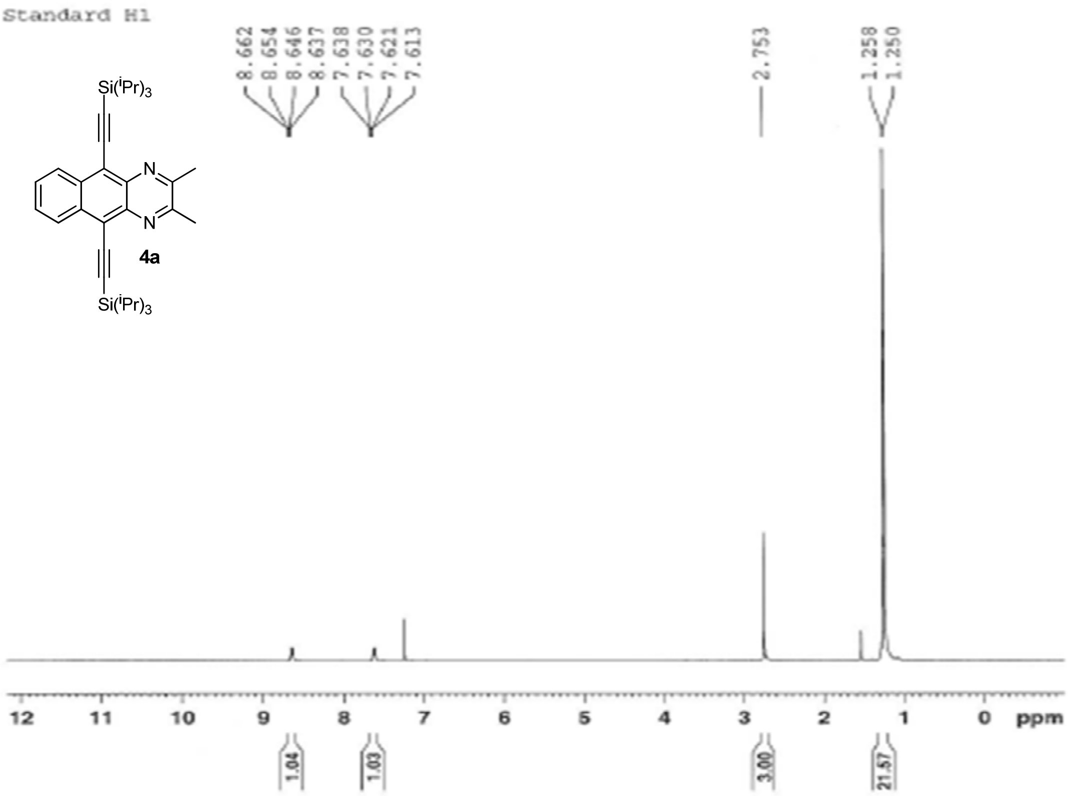


Figure 13: ^{1}H-NMR of compound **4a**.

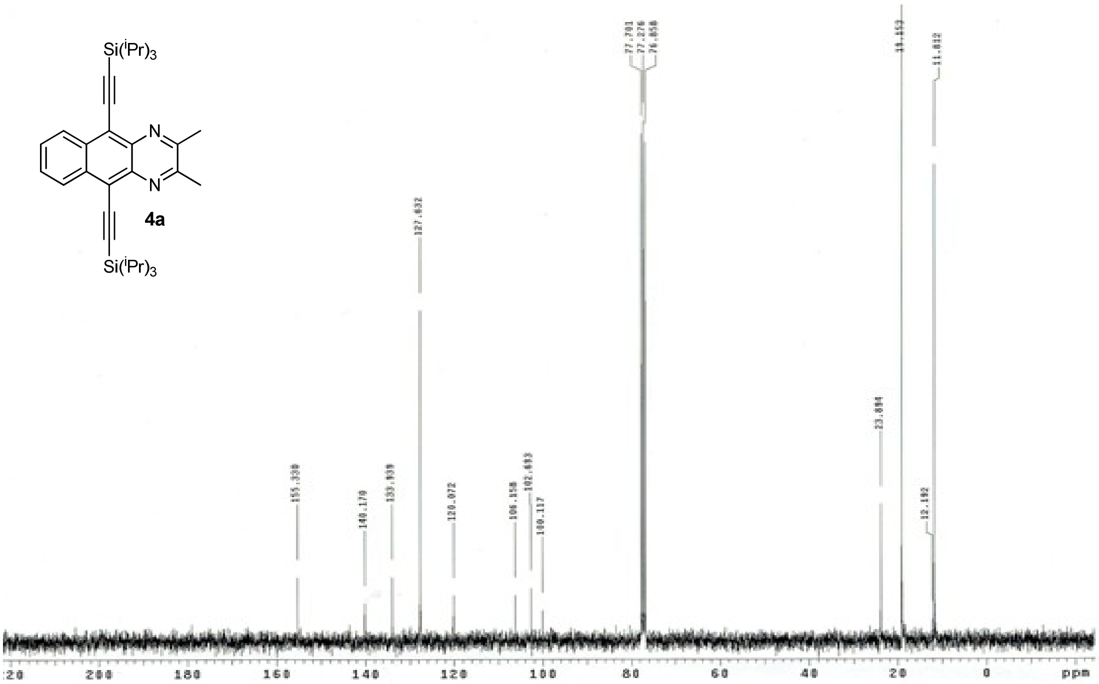


Figure 14: ^{13}C-NMR of compound **4a**.

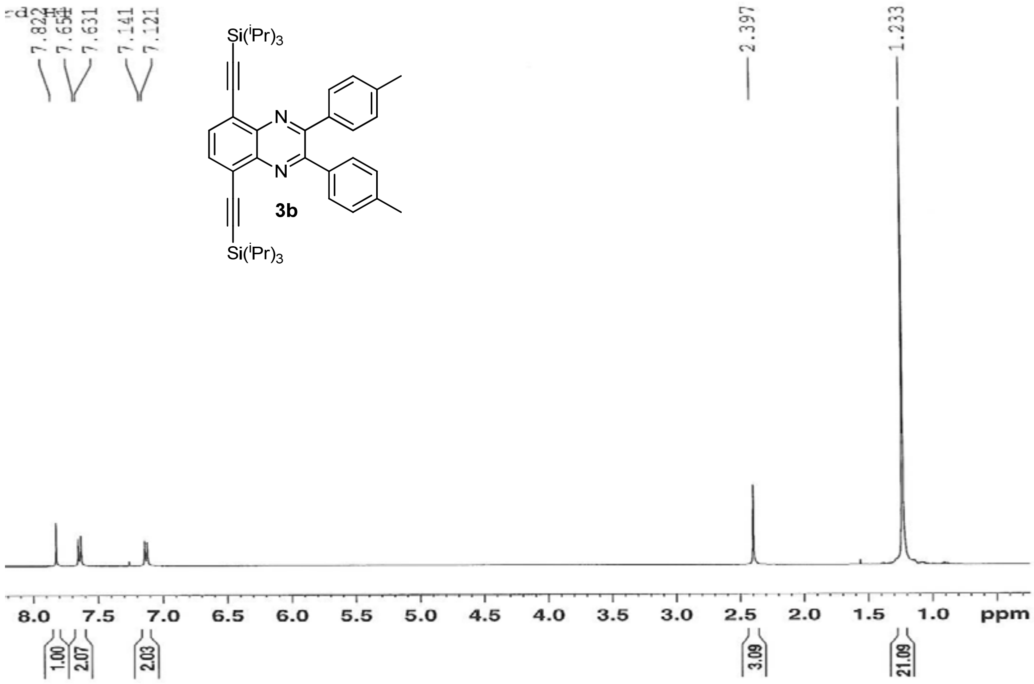


Figure 15: ^{1}H-NMR of compound **3b**.

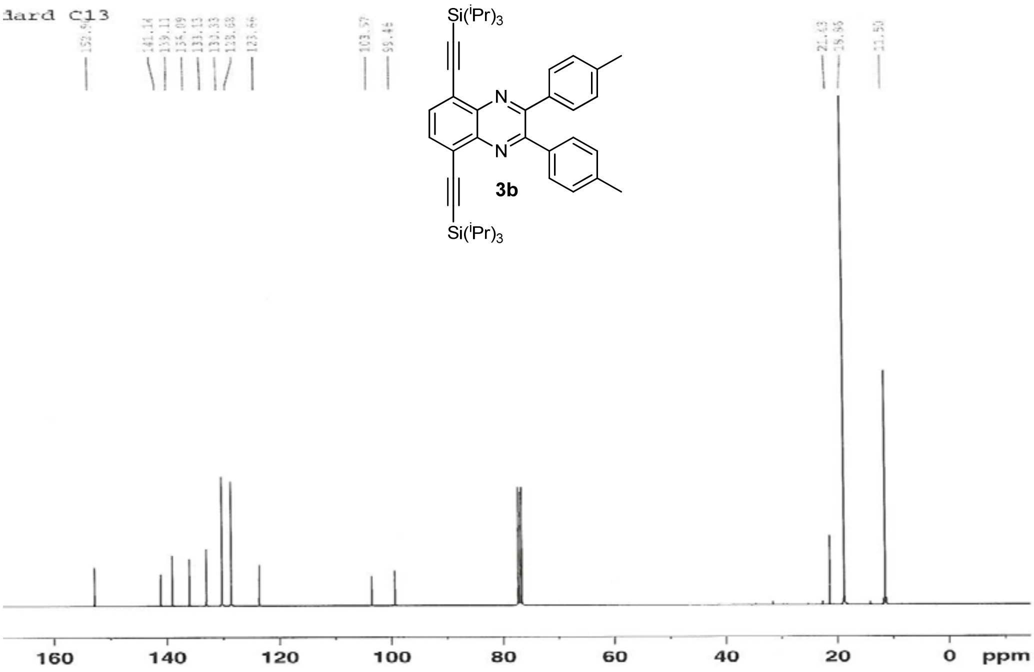


Figure 16: ^{13}C-NMR of compound **3b**.

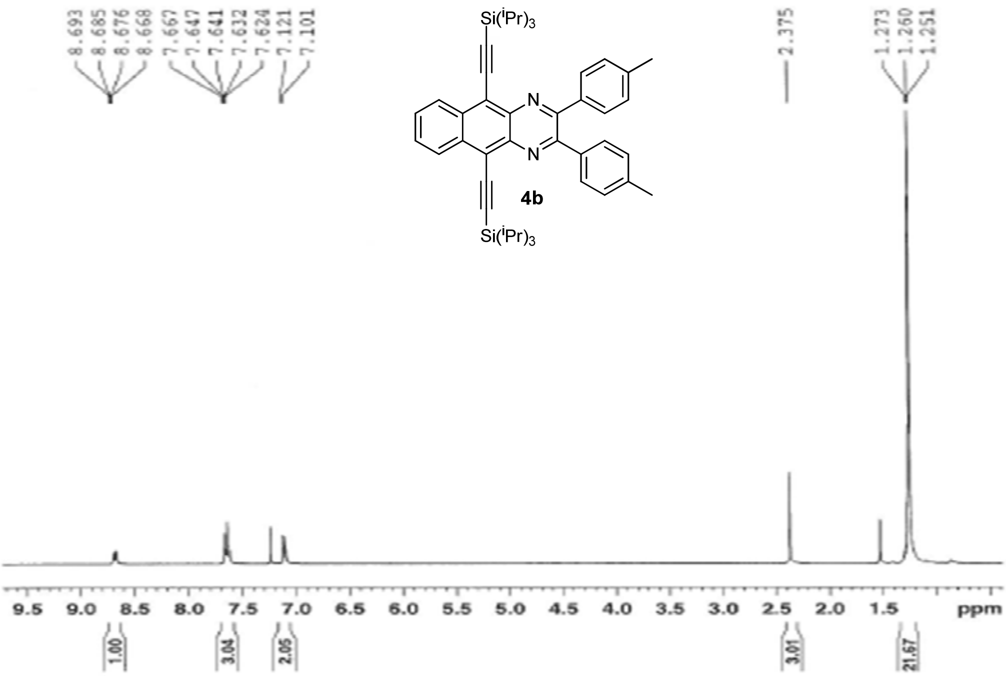


Figure 17: ^{1}H-NMR of compound **4b**.

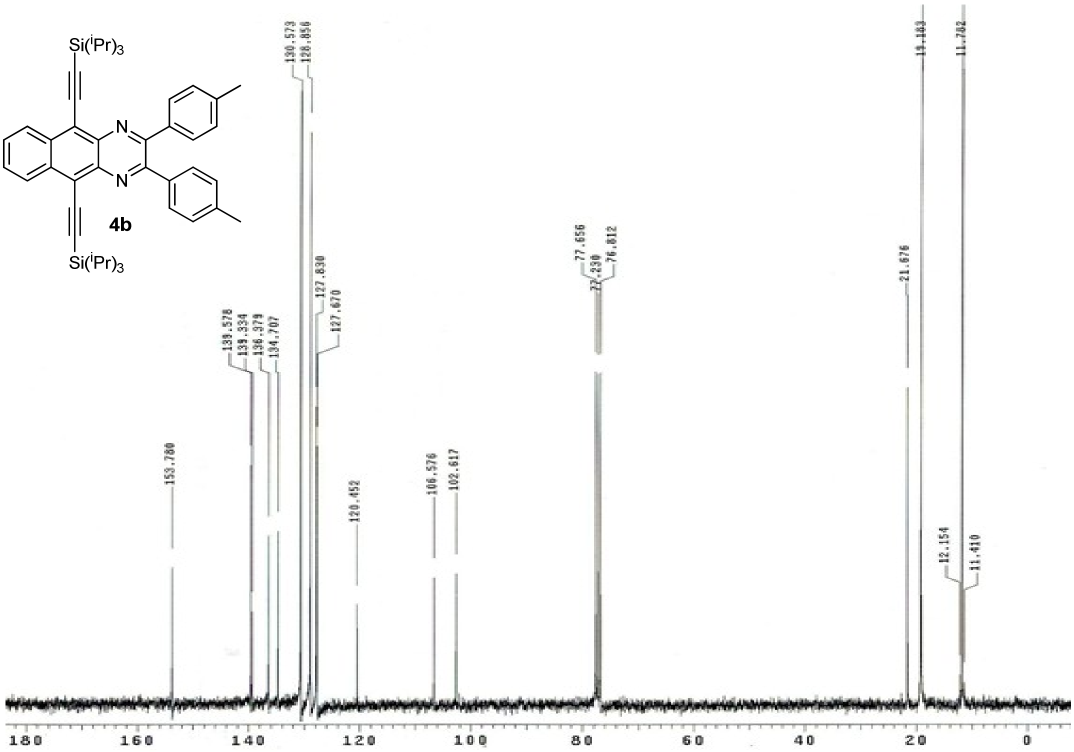


Figure 18: ^{1}H-NMR of compound **4b**.

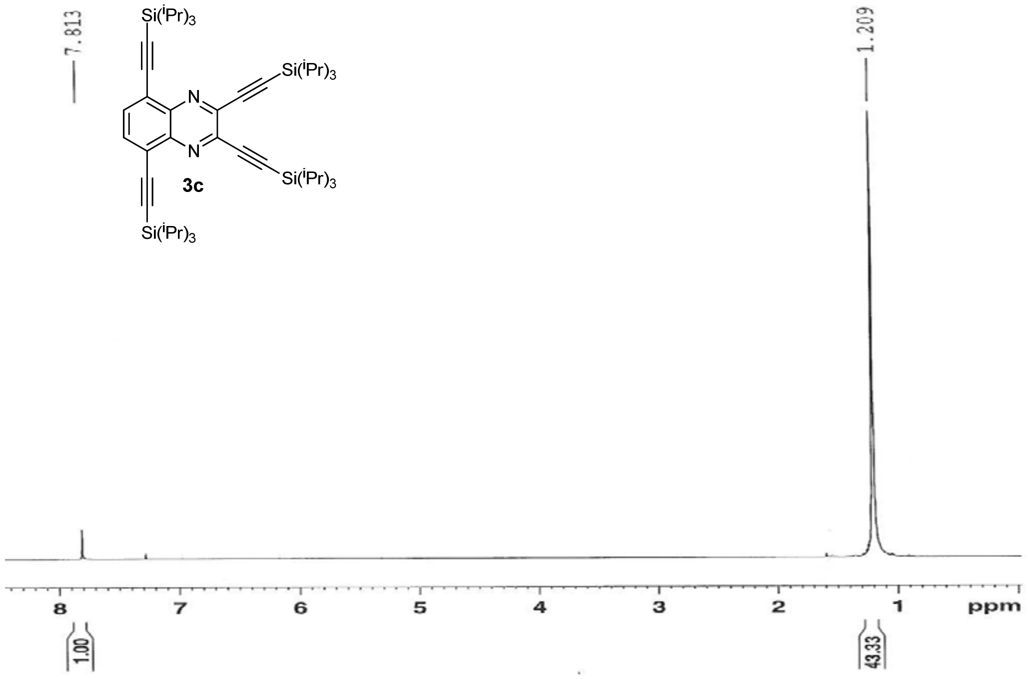


Figure 19: ^{1}H-NMR of compound **3c**.

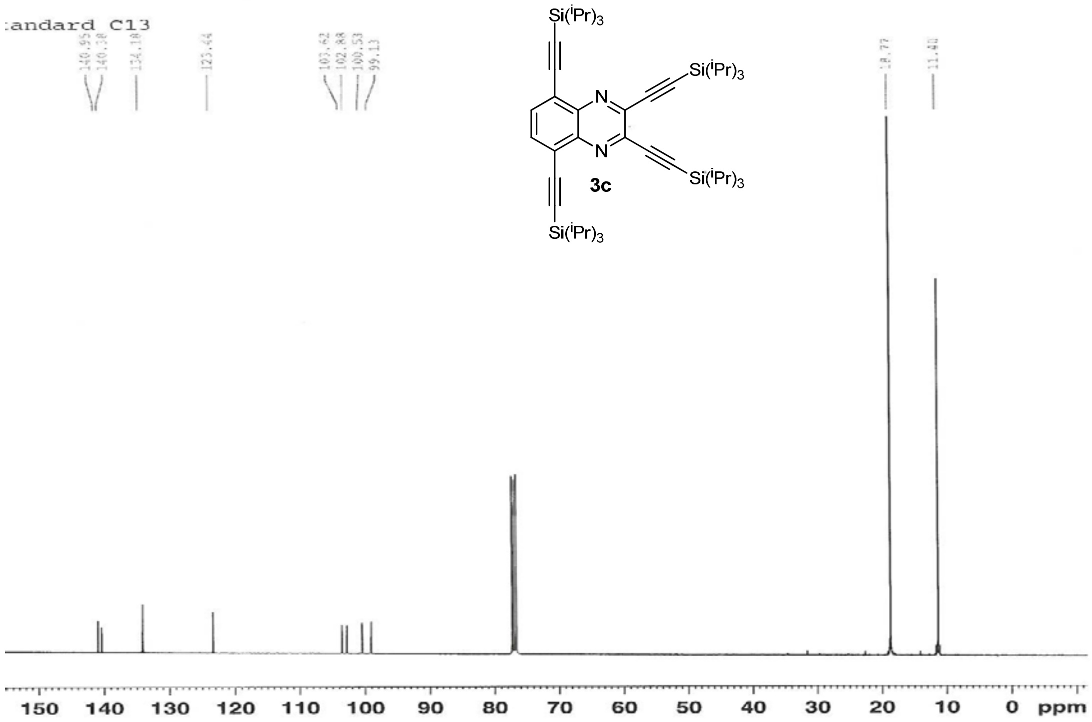


Figure 20: ^{13}C-NMR of compound **3c**.

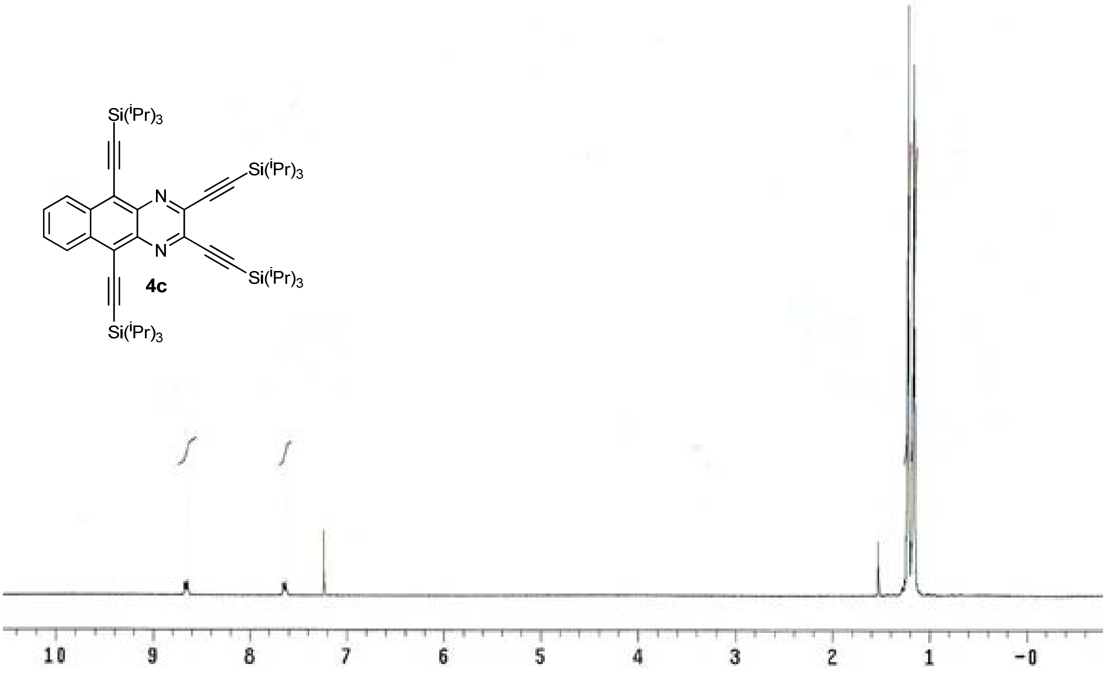


Figure 21: ^{1}H-NMR of compound **4c**.

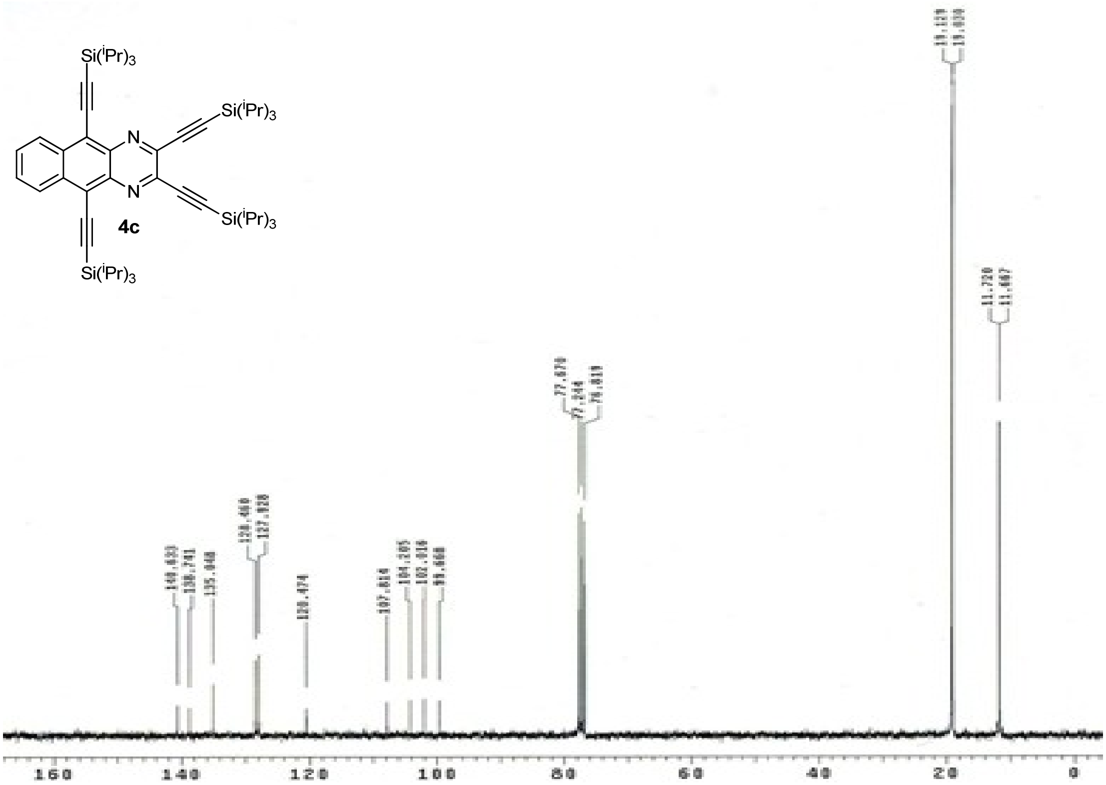


Figure 22: ^{13}C-NMR of compound **4c**.

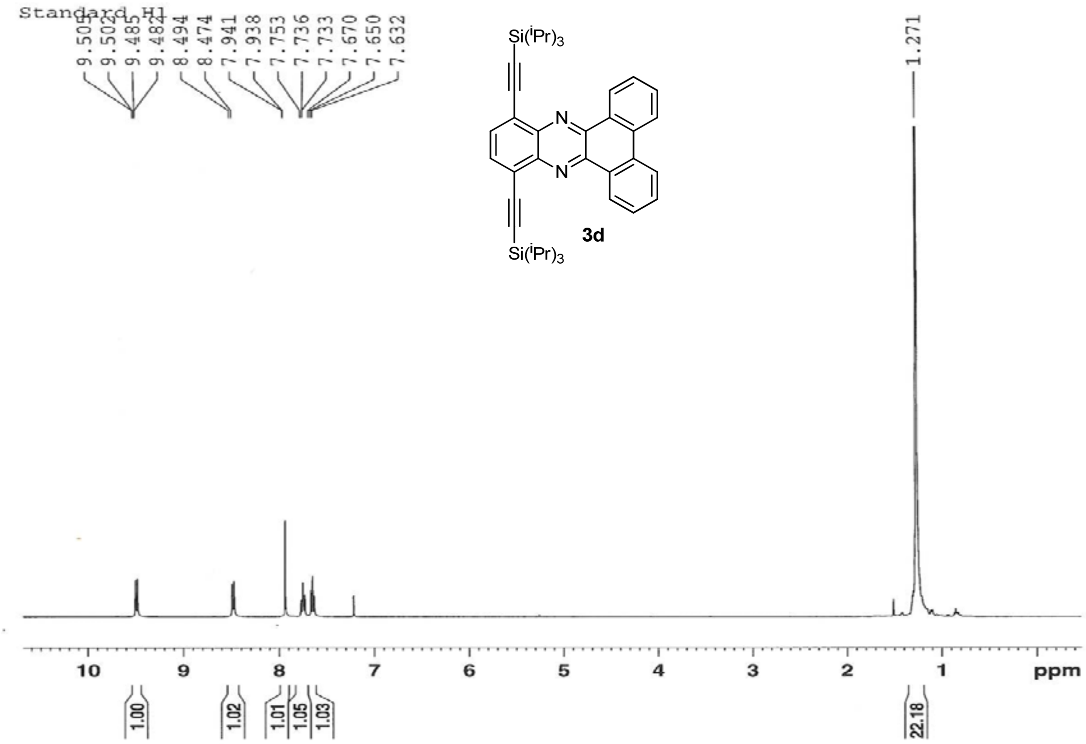


Figure 23: ^{1}H-NMR of compound **3d**.

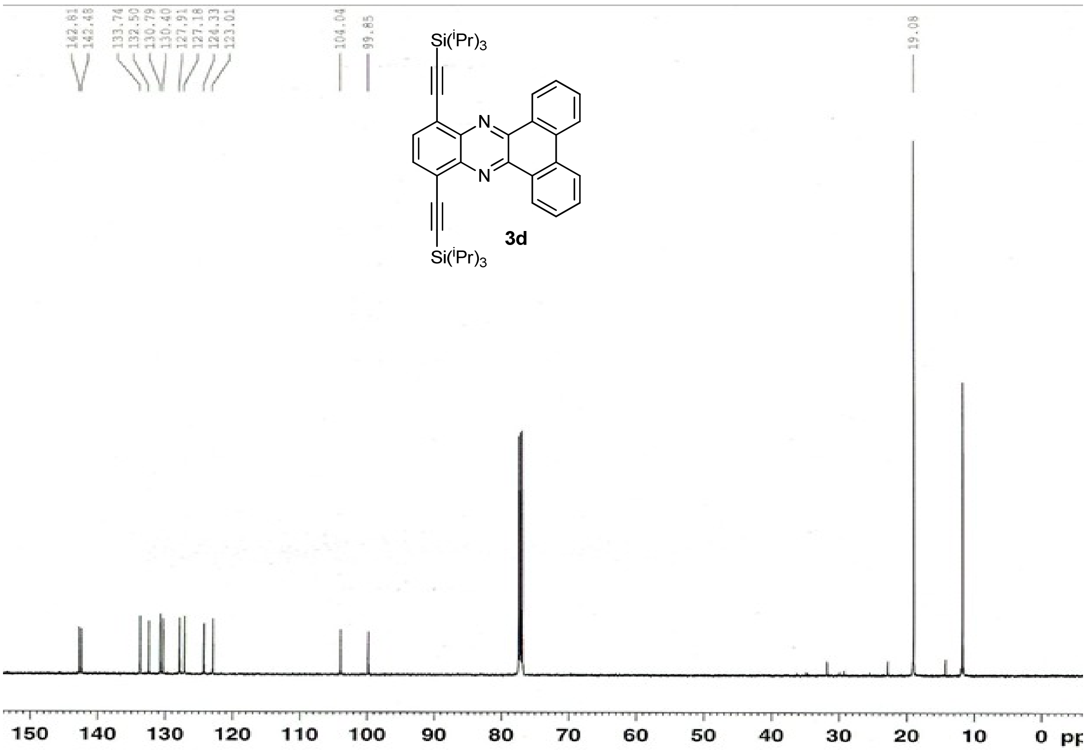


Figure 24: ^{13}C-NMR of compound **3d.**

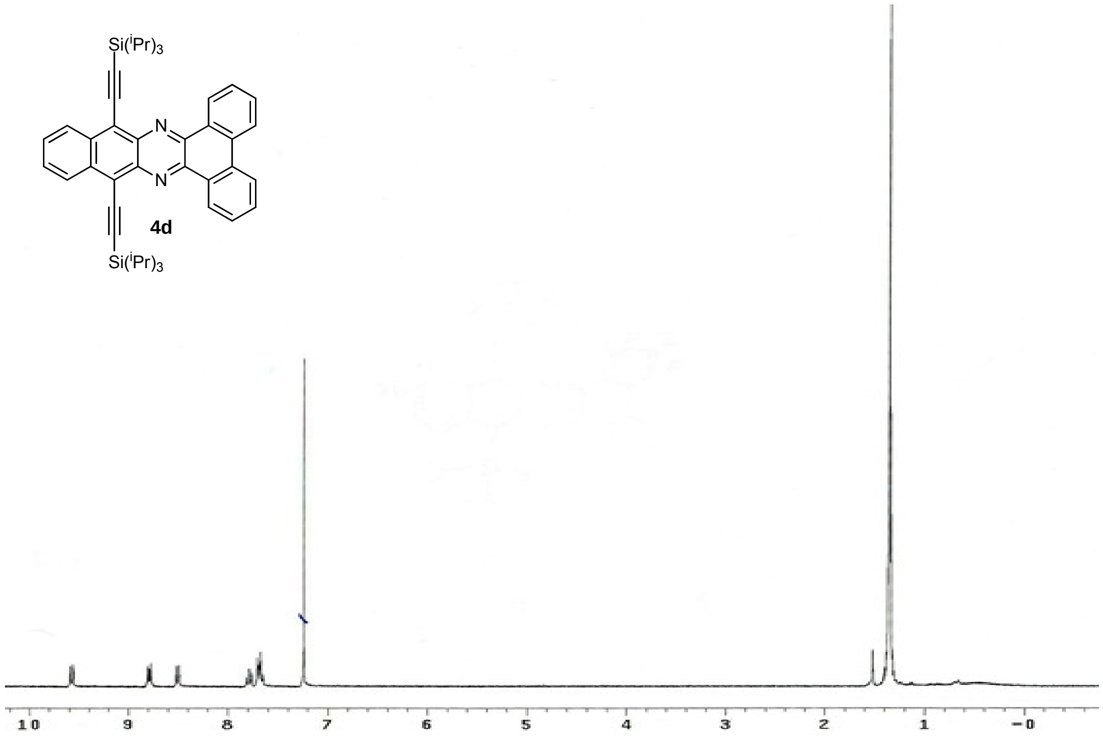


Figure 25: ^{1}H-NMR of compound **4d**.

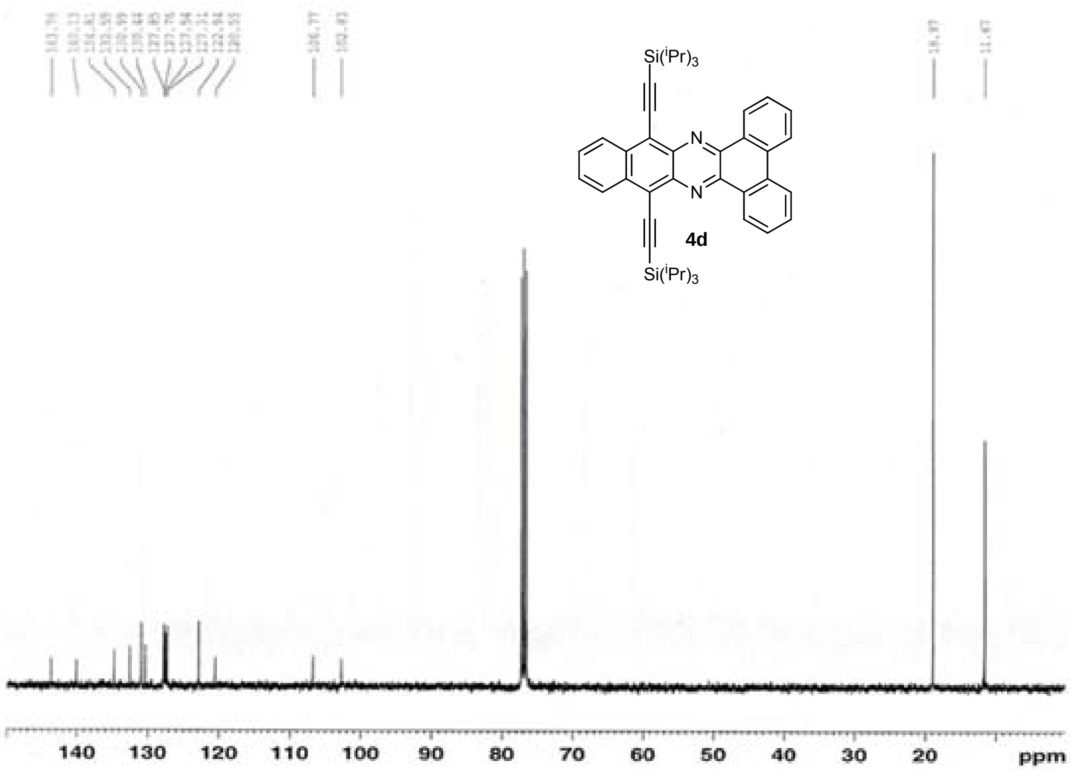


Figure 26: ^{13}C-NMR of compound **4d**.

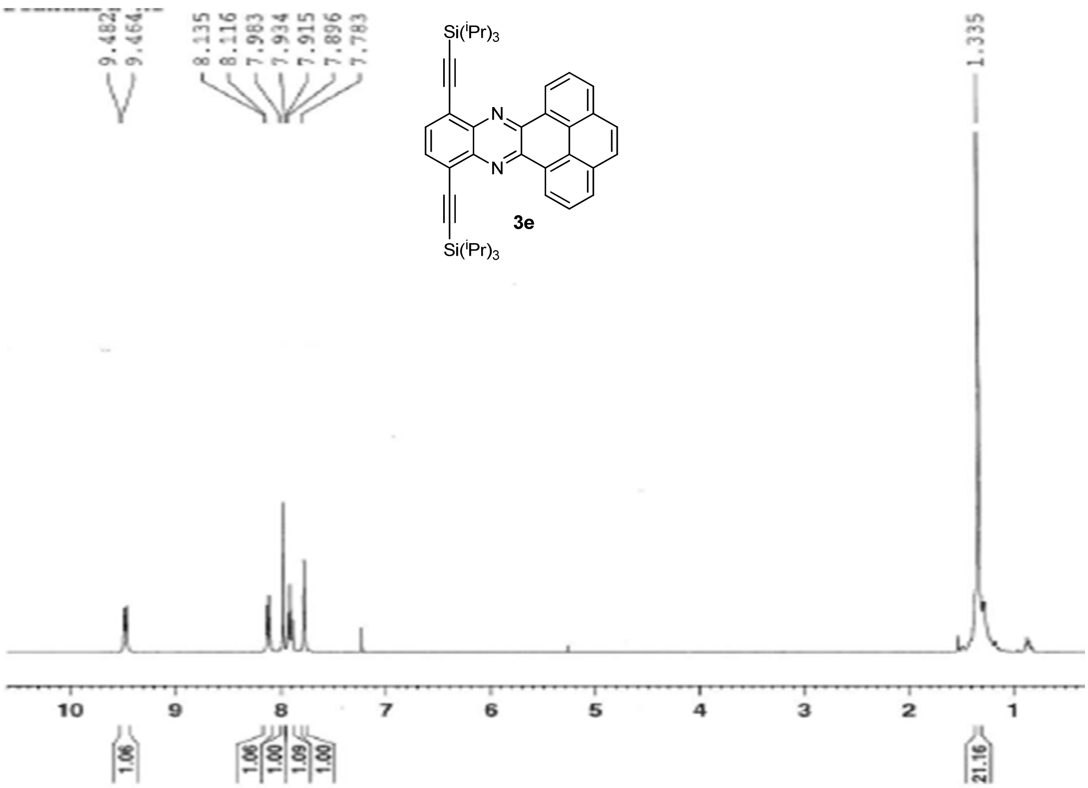


Figure 27: ^{1}H-NMR of compound **3e**.

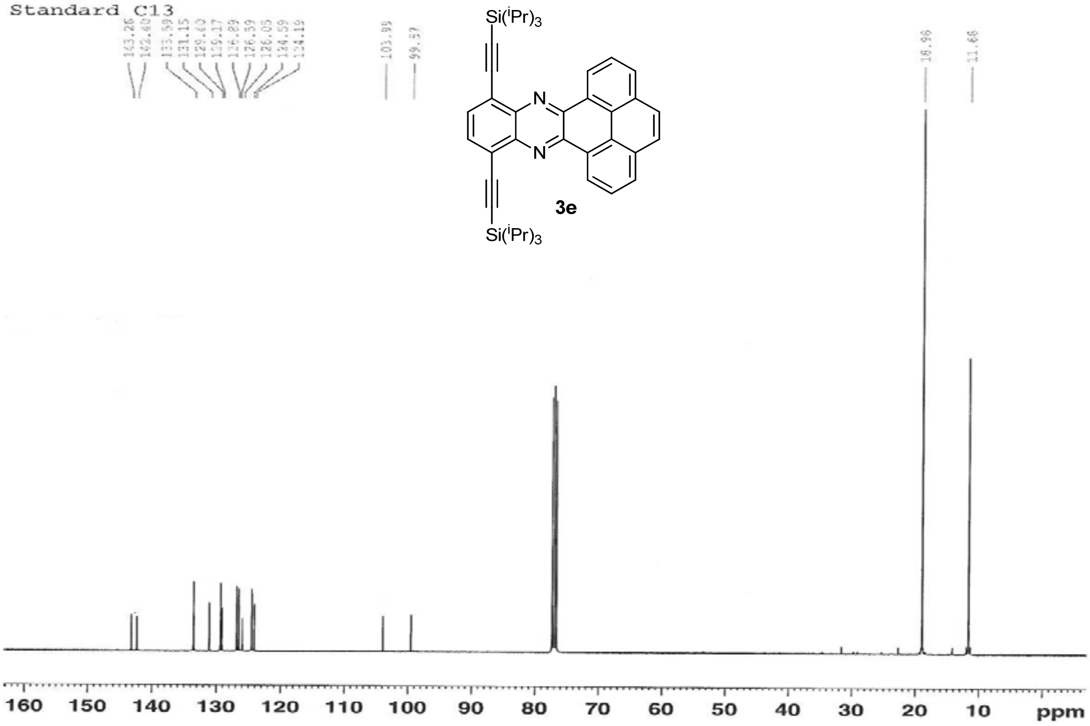


Figure 28: ^{13}C-NMR of compound **3e**.

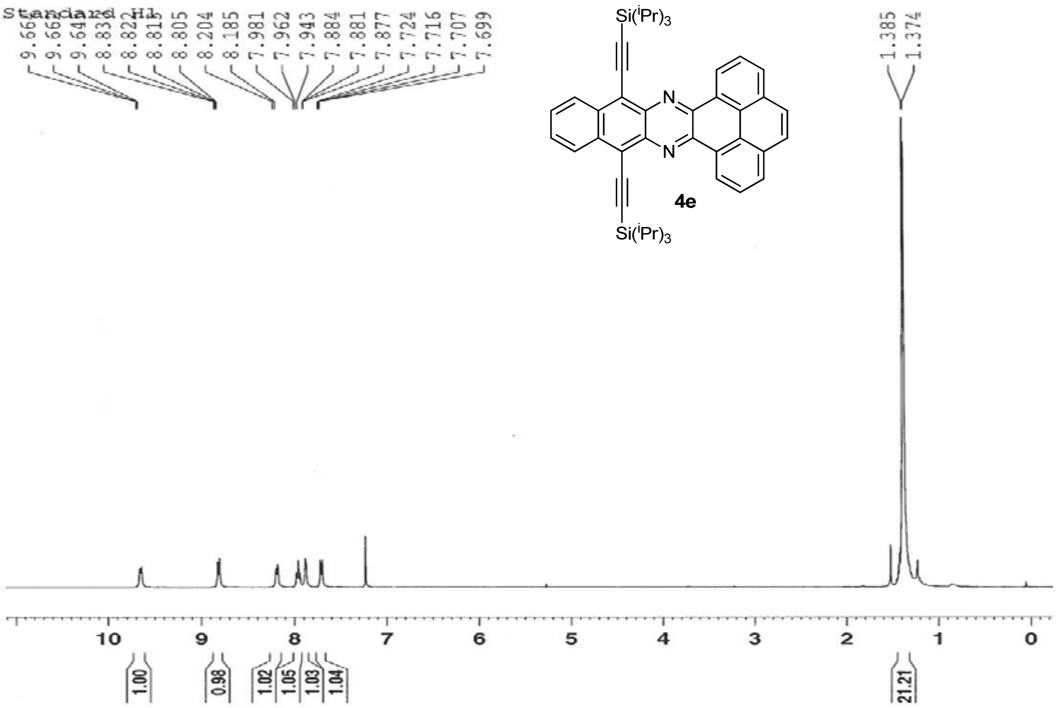


Figure 29: ^{1}H-NMR of compound **4e**.

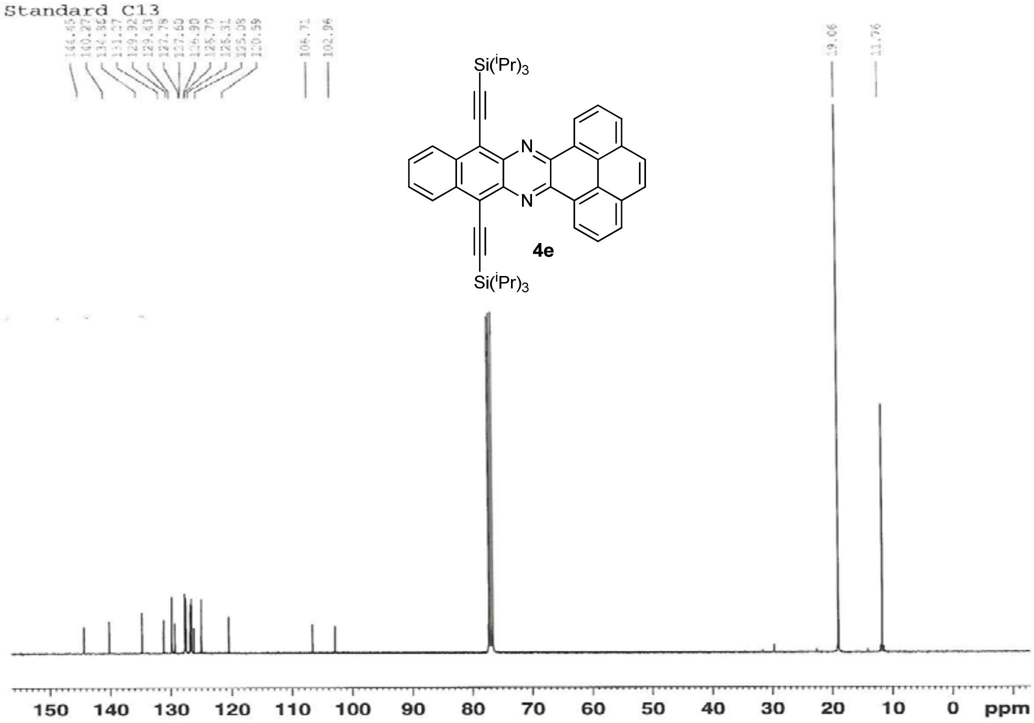


Figure 30: ^{13}C-NMR of compound **4e**.

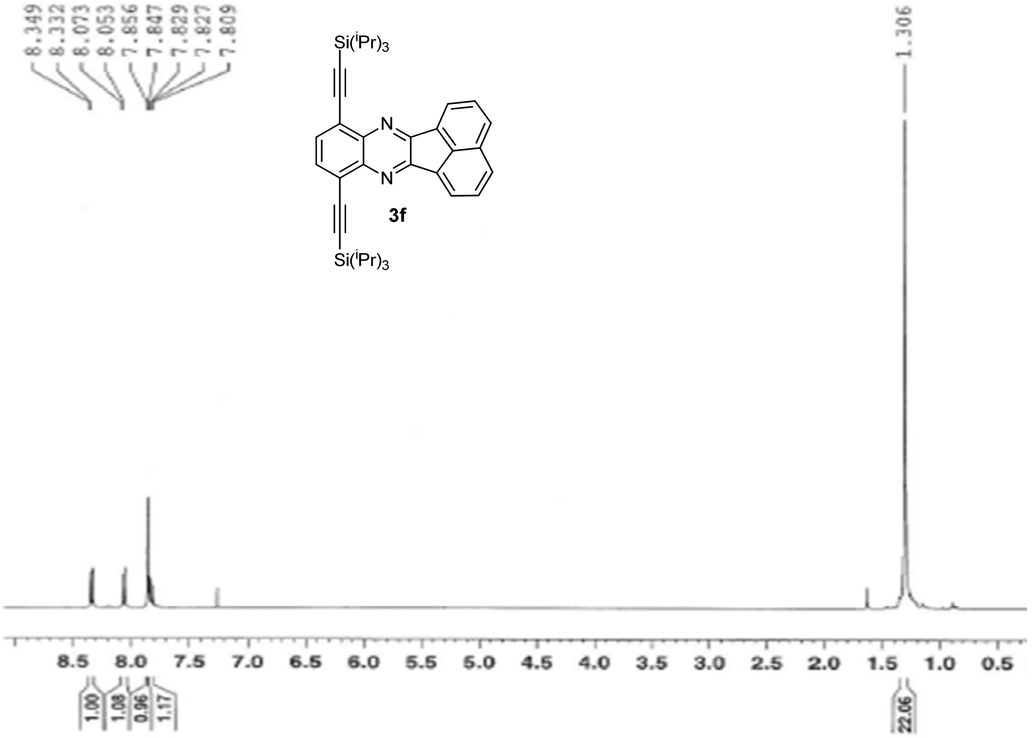


Figure 31: ^{1}H-NMR of compound **3f**.

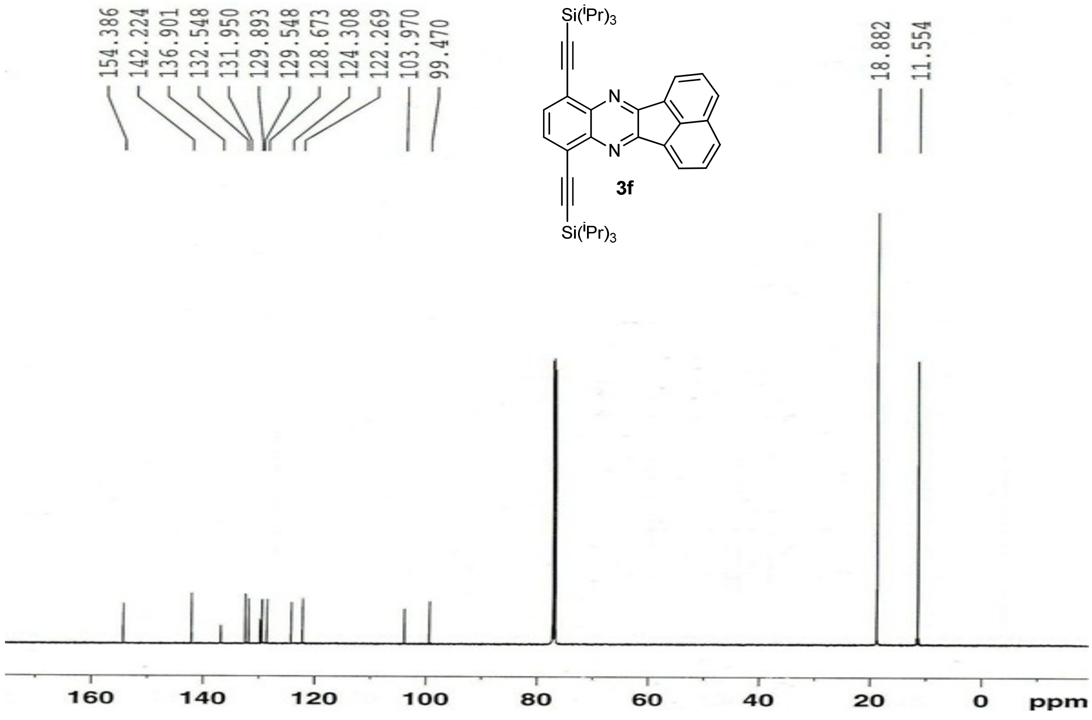


Figure 32: ^{13}C-NMR of compound **3f**.

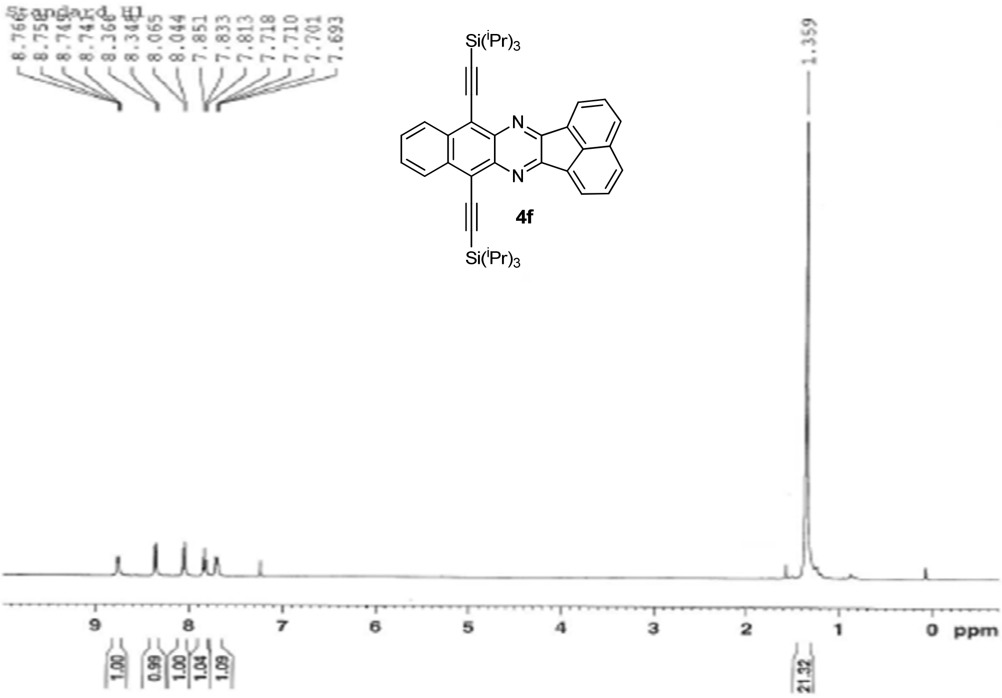


Figure 33: ^{1}H-NMR of compound **4f**.

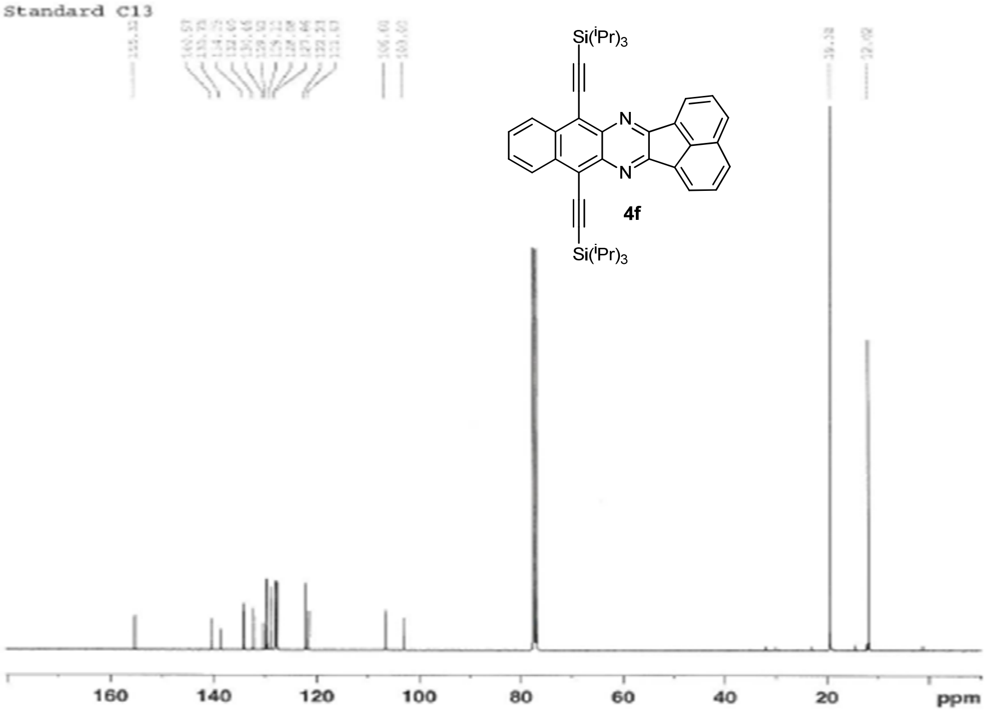


Figure 34: ^{1}H-NMR of compound **4f**.

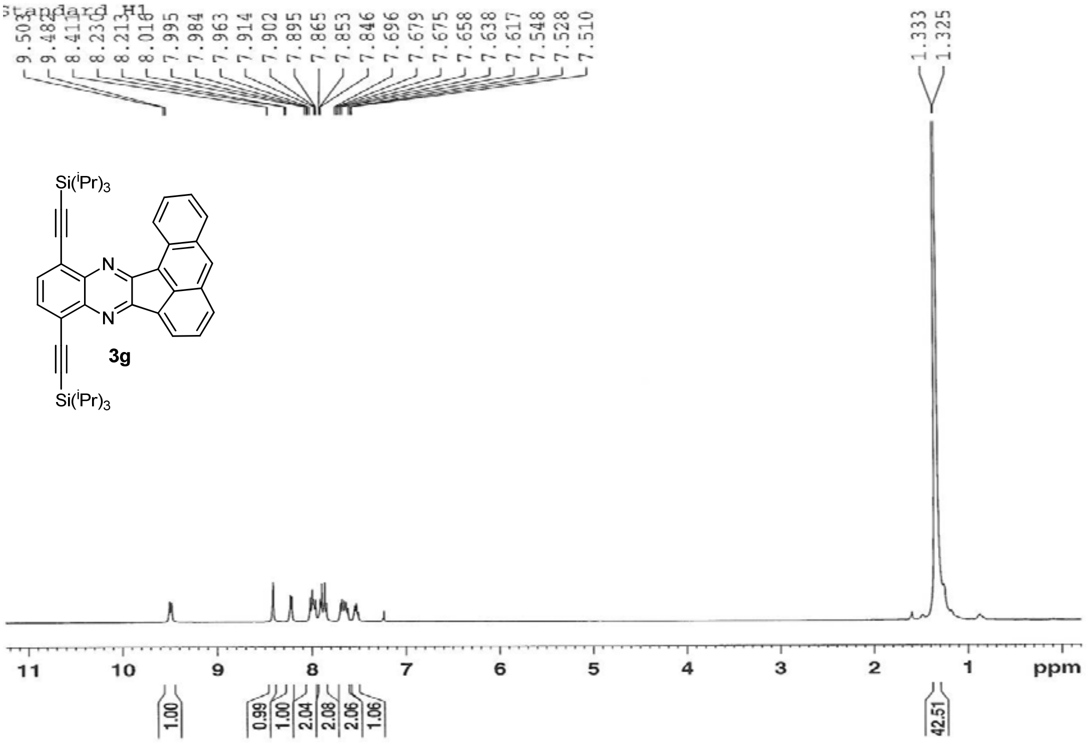


Figure 35: ^{1}H-NMR of compound **3g**.

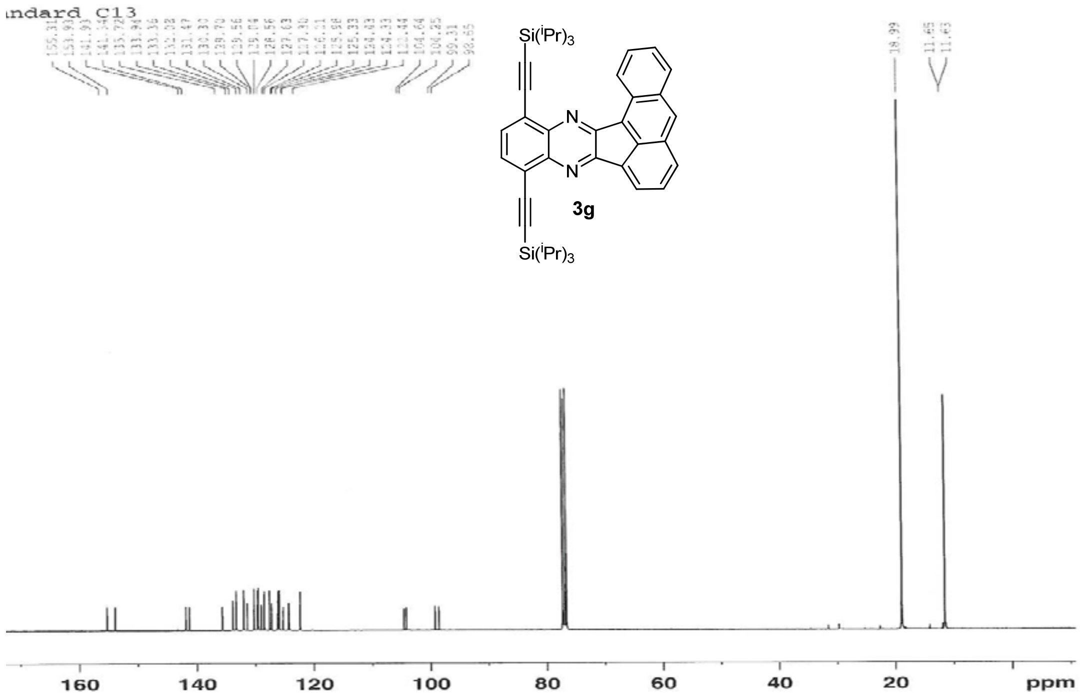


Figure 36: ^{13}C-NMR of compound **3g**.

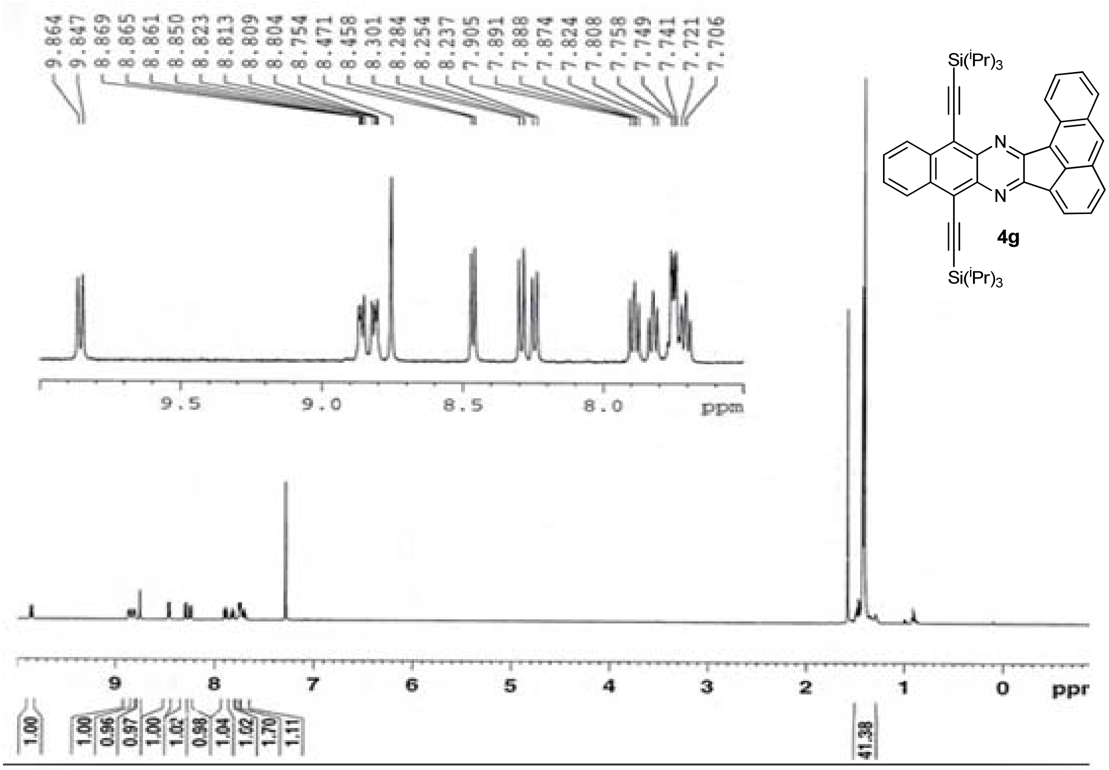


Figure 37: ^{1}H-NMR of compound **4g.**

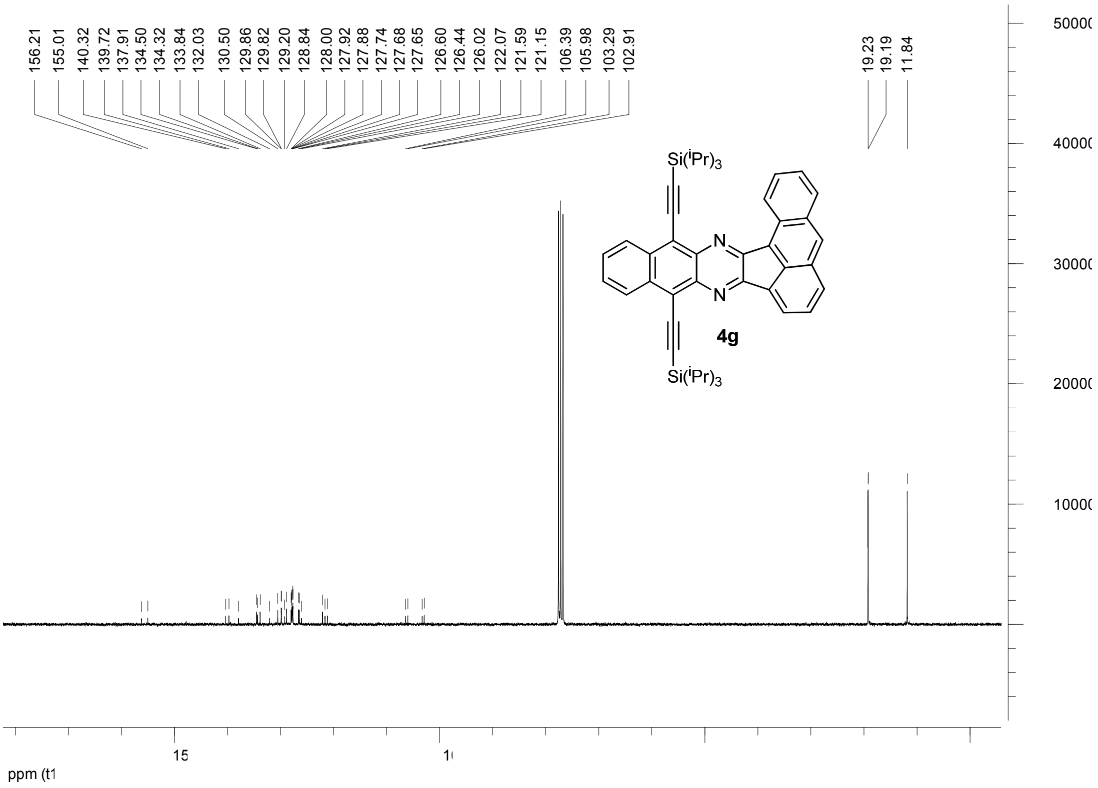


Figure 38: ^{13}C-NMR of compound **4g**.

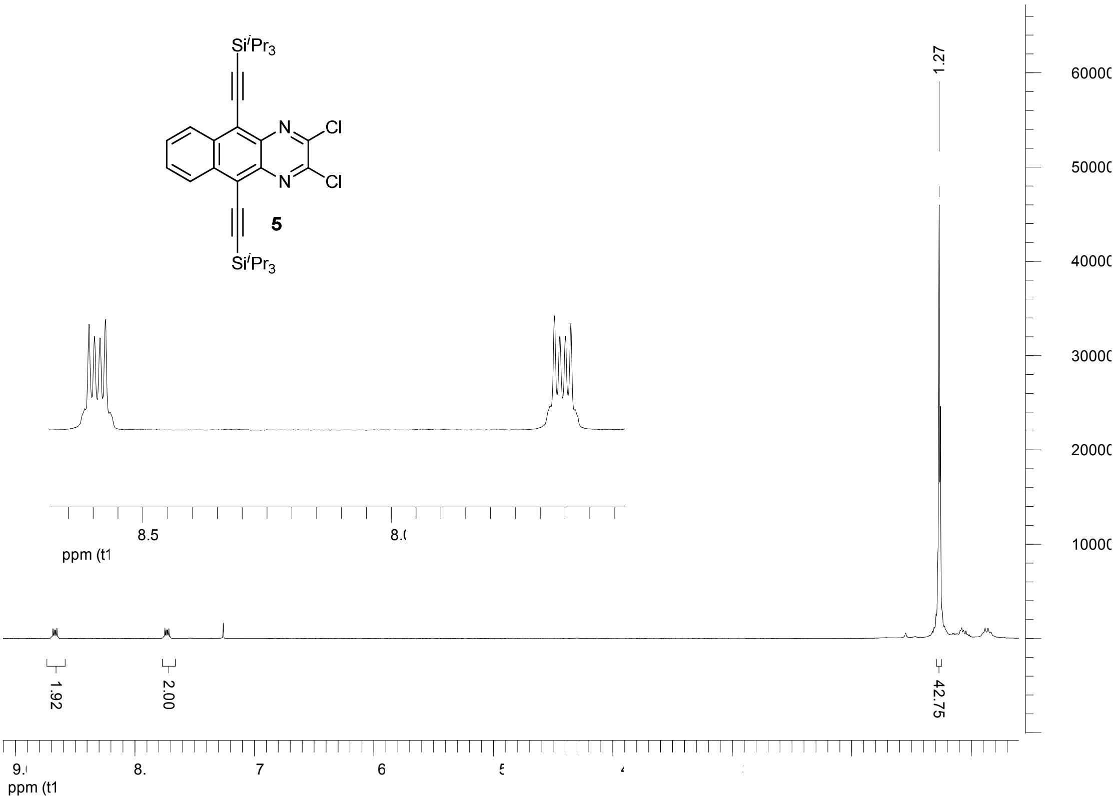


Figure 39: ^{1}H-NMR of compound **5.**

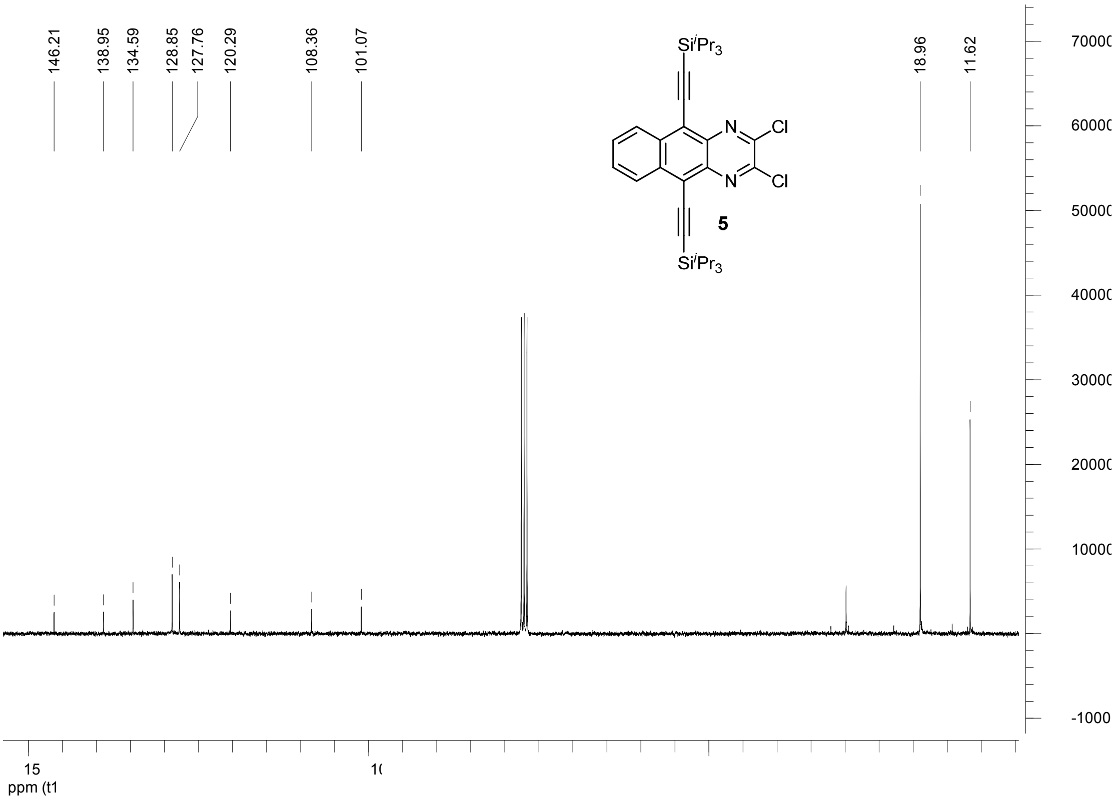


Figure 40: ^{13}C-NMR of compound **5.**