Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

First Azulene Liquid Crystal with de Vries behavior and a SmA Re-entrant Phase

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1. General methods

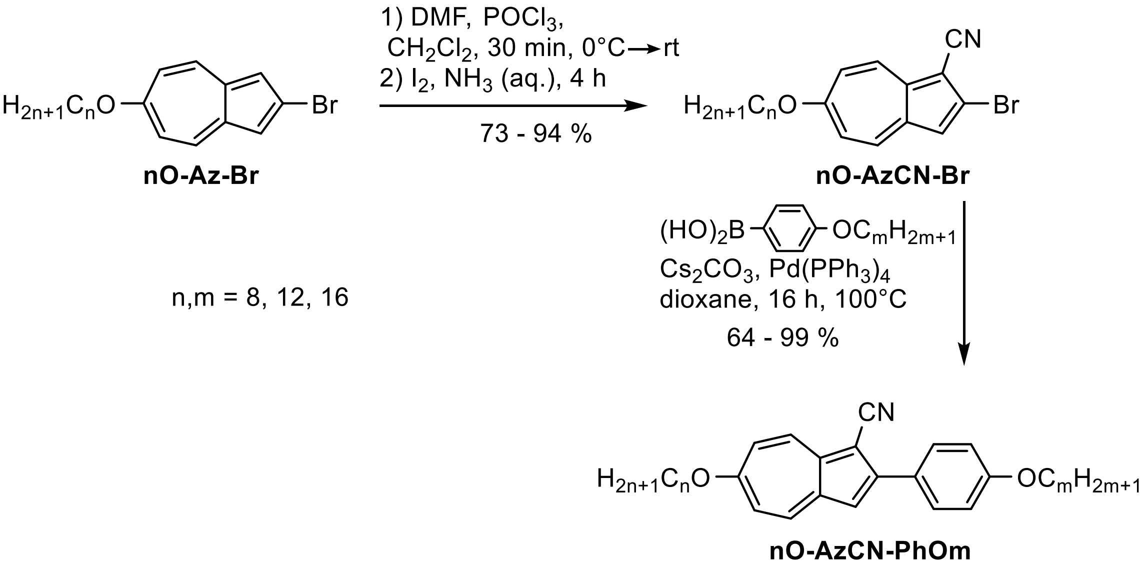
All chemicals were, unless otherwise stated, used without further purification. Anhydrous THF was obtained by refluxing the solvent over potassium. The eluents for chromatography (hexanes, low boiling, and ethyl acetate EtOAc) were distilled prior to use. ^{1}H NMR spectra were measured using the Bruker Avance 500, and Bruker Avance 700 spectrometers at 500 MHz, and 700 MHz as well as ^{13}C NMR spectra at 126 MHz, and 176 MHz, respectively. To assign the signals of the ^{1}H and ^{13}C NMR spectra, COSY, HSQC, and HMBC measurements were carried out. FT-IR spectra were measured on a Bruker Vektor 22 with a MKII Golden Gate Single Reflection Diamond ATR. Absorption bands were rounded to integer wavenumbers / cm^{-1} and the absorption intensities were classified as follows: w (weak), m (medium), s (strong). Mass spectra (MS) and high-resolution mass spectra (HRMS) were measured by electrospray ionisation (ESI) or electron impact ionisation (EI) with a Bruker MicrOTOF-Q spectrometer or electron impact ionisation (EI) with a *Varian MAT 711* spectrometer. For thin layer chromatography, silica gel 60 F254 glass plates (layer thickness of 0.25 mm) on aluminium (pore size 60 Å) from Merck were used. Column chromatography was performed using silica gel (particle diameter of 40 – 60 µm) from Fluka. A polarizing optical microscope Olympus BX 50, equipped with a Linkam LTS heating stage, was used. Temperature regulation was carried out with the control units TP93 and LNP from Linkam ($\Delta T = \pm 1$ K). Photographs were saved with a digital camera ColorView from Soft Imaging System using the software analySIS. For differential scanning calorimetry, a DSC822e from the company Mettler Toledo was employed. The compounds were analysed in 40 µL sealed aluminium pans. Heating and cooling rates of 5 K min^{-1} were employed. Phase transition temperatures and enthalpies were determined by onset values using the software STARe 7.01.

Measurements of the X-ray diffraction were performed using a Bruker AXS Nanostar C with a ceramic tube generator (1500 W) having cross-coupled Goebel mirrors providing monochromatic Cu Kα radiation (1.5405 Å). Diffraction patterns were recorded with Bruker HI-STAR or VÅNTEC 500 detectors. Calibration was carried out using the diffraction pattern of silver behenate at room temperature. The compounds were examined in sealed glass capillaries from Hilgenberg GmbH (external diameter of 0.7 mm, wall thickness 0.01 mm). Measured values were analysed with the software SAXS from Bruker. The diffraction patterns were further processed using the software Datasqueeze and Origin 2018Pro. For UV/Vis spectroscopy solvents were obtained in spectroscopic grade from the supplier and were not further purified. For absorption spectra, a Perkin Elmer Lambda 35 spectrometer was employed. Fits were obtained using origin software and the goodness of fit judged by the reduced χ^2 value and residual plot shape. Optical tilt angles were measured by manually rotating the sample and observing the position of maximum darkness of two opposite tilt domains. Optical birefringence Δn was precisely measured using a Phi-Viz Imaging System from Polaviz (APSYS Inc.) mounted on a Leica DM 2700P polarizing microscope fitted with a HCS 302 hot stage (Instec). Samples were filled in rubbed nylon liquid crystal test cells (AWAT1, Poland) of 3.0 µm thickness in the isotropic phase. The fully automated system uses three liquid crystal variable retarders replacing the polarizer and analyzer of the microscope. Polychromatic light with an average wavelength of 550 nm was used and the intensity of the light detected with a digital camera for a maximum of 1900 x 1200 pixels. By cycling through different polarization states, a 2D map of the optic axis and the retardance of the sample were obtained.

2. Syntheses

The synthesis of phenylboronic acids is well known in the literature and described elsewhere.

The synthesis of 6-alkoxy-2-bromoazulenes is described in our previous paper.[1]



2.1 General Procedures

General procedure for the nitrilation of 6-alkoxy-2-bromoazulenes-bromoazulenes nO-Az-Br via Vilsmeier-Haack reaction at the example of 12O-Az-Br (GP 1)

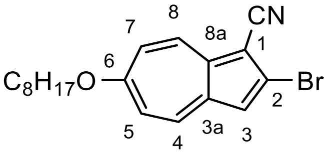
Adapting a procedure of Ushijima,[2] $POCl_3$ (9.5 µL, 16 mg, 102 µmol) was slowly added to dry DMF (1 mL) at 0 C. The solution was then stirred for 30 min. **12O-Az-Br** (40 mg, 102 µmol) in dry CH_2Cl_2 (10 mL) was cooled down to 0 °C and then added slowly to the reaction mixture. After warming up to room temperature overnight, aq. ammonia (30 Vol%, 5 mL) was added dropwise. During the addition, a color change from orange to green to red was observed within seconds. Subsequently, iodine (52 mg. 204 µmol) was added, and the reaction was stirred vigorously for 4 h, and subsequently quenched with water (10 mL). After phase separation, the organic phase was washed with sat. $NaHSO_3$ solution and water (each 2x; 10 mL) and dried over $MgSO_4$. The solution was filtered over a silica pad. Careful elution of the orange spot with CH_2Cl_2, without simultaneously eluting the more polar yellow spot afforded the pure **12O-AzCN-Br** as an orange solid in 94 % yield (40 mg, 96 µmol).

General Procedure for Suzuki-coupling of nO-AzCN-Br with aryl boronic acids at the example of 12O-AzCN-Br (GP2).

C12O-AzCN-Br (38 mg, 91 µmol), (4-dodecyloxyphenyl) boronic acid (42 mg, 137 µmol) and Cs_2CO_3 (89 mg, 274 mmol) were dissolved in dioxane (5 mL). The mixture was degassed for 30 min, then $Pd(PPh_3)_4$ (5 mg, 5 µmol) was added and the reaction was refluxed for 16 h. After cooling down, Celite was added and the solvent was removed under reduced pressured. Purification was performed by column chromatography on silica with an adequate solvent (hexanes / CH_2Cl_2 1 : 1) and subsequent recrystallization from isopropanol. Azulene **12O-AzCN-PhO12** was obtained as an orange solid in 64 % yield (35 mg, 59 µmol).

2.2 Syntheses

2-Bromo-6-octyloxyazulene-1-carbonitrile (8O-AzCN-Br)

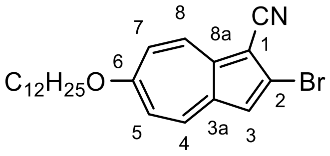


$C_{19}H_{22}BrNO$
(360.30)

Synthesis according to GP1**: 8O-Az-Br** (70 mg, 209 µmol), $POCl_3$ (20 µL, 209 µmol), DMF (3 mL), CH_2Cl_2 (10 mL), I_2 (106 mg, 418 µmol), NH_3 (30 vol%, 10 mL); yield: orange solid (70 mg, 194 µmmol, 93 %); melting point (POM): 88 °C; ^1H NMR (500 MHz, $CDCl_3$):

δ = 0.89 (t, J = 6.8 Hz, 3H, CH_3), 1.24–1.42 (m, 8H, CH_2), 1.46–1.54 (m, 2H, $OCH_2CH_2CH_2$), 1.83–1.93 (m, 2H, OCH_2CH_2), 4.16 (t, J = 6.5 Hz, 2H, OCH_2), 7.09–7.11 (m, 1H, 5-H), 7.11–7.13 (m, 1H, 7-H), 7.16 (s, 1H, 3-H), 8.18 (d, J = 11.2 Hz, 1H, 4-H), 8.36 (d, J = 11.1 Hz, 1H, 8-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.0, 29.0, 29.2, 29.3, 31.8 (CH_2), 69.7 (OCH_2), 99.4 (C-1), 115.4 (C-7), 116.3 (C-2), 116.9 (C-5), 119.9 (C-3), 124.3 (CN), 135.1 (C-8), 137.1 (C-3a, C-4), 138.5 (C-8a), 169.1 (C-6) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3099 (w), 2948 (w), 2923 (m), 2852 (w), 2204 (m), 1581 (m), 1544 (w), 1499 (w), 1440 (w), 1406 (m), 1389 (s), 1294 (w), 1272 (m), 1200 (s), 1127 (w), 1020 (w), 979 (w), 901 (w), 855 (m), 825 (w), 792 (w), 766 (w), 730 (w), 713 (w), 644 (w), 622 (w), 504 (w) cm^{-1}; MS (ESI): *m/z* for $C_{19}H_{23}BrNO^+$ calc.: 360.10 $[M+H]^+$, found.: 360.09; HRMS (ESI): *m/z* for $C_{19}H_{23}BrNO^+$ calc.: 360.0958 $[M+H]^+$, found: 360.0943.

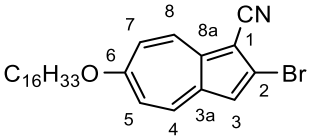
2-Bromo-6-dodecyloxyazulene-1-carbonitrile (12O-AzCN-Br)



$C_{23}H_{30}BrNO$
(415.15)

Synthesis according to GP1; **12O-Az-Br** (40 mg, 102 µmol), $POCl_3$ (10 µL, 102 µmol), DMF (1 mL), CH_2Cl_2 (10 mL), I_2 (52 mg, 204 µmol), NH_3 (30 vol%, 5 mL); yield: orange solid (40 mg, 96 µmmol, 94 %); melting point (POM): 91 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 3H, CH_3), 1.20–1.41 (m, 16H, CH_2), 1.46–1.54 (m, 2H, $OCH_2CH_2CH_2$), 1.84-1.92 (m, 2H, OCH_2CH_2), 4.15 (t, J = 6.5 Hz, 2H, OCH_2), 7.08–7.13 (m, 2H, 5-H, 7-H), 7.15 (s, 1H, 3-H), 8.17 (d, J = 11.3 Hz, 1H, 4-H), 8.35 (d, J = 11.1 Hz, 1H, 8-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (CH_3), 22.7, 26.0, 29.0, 29.3, 29.4, 29.6, 29.6, 29.7, 29.7, 31.9 (CH_2), 69.7 (OCH_2), 99.4 (C-1), 115.5 (C-5/C-7), 116.3 (C-2), 116.8 (C-5/C-7), 119.8 (C-3), 124.2 (CN), 135.1 (C-8), 137.0, 137.1 (C-4, C-3a), 138.5 (C-8a), 169.1 (C-6) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2918 (m), 2849 (m), 2203 (m), 1582 (s), 1546 (w), 1495 (w), 1468 (w), 1435 (w), 1419 (w), 1389 (s), 1288 (w), 1251 (s), 1195 (s), 1127 (w), 1016 (m), 988 (m), 972 (m), 899 (m), 840 (m), 828 (m), 803 (w), 778 (w), 760 (m), 721 (w), 710 (m), 619 (w), 541 (w), 506 (w) cm^{-1}; MS(ESI): *m/z* für $C_{23}H_{31}BrNO^+$ calc.: 416.16 $[M+H]^+$, found: 416.16; HRMS(ESI): *m/z* für $C_{23}H_{31}BrNO^+$ calc.: 416.1584 $[M+H]^+$, found.: 416.1585.

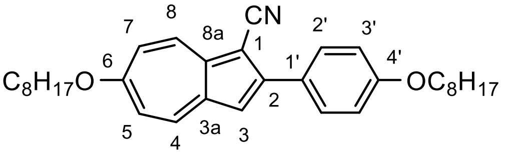
2-Bromo-6-hexadecyloxyazulene-1-carbonitrile (16O-AzCN-Br)



$C_{27}H_{38}BrNO$
(472.51)

Synthesis according to GP1; **16O-Az-Br** (89 mg, 188 µmol), $POCl_3$ (18 µL, 188 µmol), DMF (1 mL), CH_2Cl_2 (10 mL), I_2 (95 mg, 376 µmol), NH_3 (30 vol%, 10 mL); yield: orange solid (65 mg, 188 µmol, 73 %); melting point (POM): 93 °C; ^1H NMR (700 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.1 Hz, 3H, CH_3), 1.21–1.41 (m, 24H, CH_2), 1.47–1.53 (m, 2H, $OCH_2CH_2C\mathit{H}_2$), 1.86–1.91 (m, 2H, $OCH_2C\mathit{H}_2$), 4.15 (t, J = 6.5 Hz, 2H, OCH_2), 7.08–7.12 (m, 2H, 5-H, 7-H), 7.15 (s, 1H, 3-H), 8.17 (d, J = 11.1 Hz, 1H, 4-H), 8.35 (d, J = 11.0 Hz, 1H, 8-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.9, 25.9, 28.9, 29.0, 29.3, 29.4, 29.5, 29.6, 29.7, 29.7, 29.7, 29.7, 29.7, 31.9 (CH_2), 69.7 (OCH_2), 99.4 (C-1), 115.5 (C-7), 116.3 (C-2), 116.8 (C-5), 119.8 (C-3), 124.2 (CN), 135.1 (C-8), 137.0 (C-3a), 137.1 (C-4), 138.5 (C-8a), 169.1 (C-6) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2917 (s), 2848 (s), 2204 (m), 1583 (m), 1546 (w), 1495 (w), 1468 (m), 1436 (m), 1419 (w), 1389 (m), 1287 (w), 1251 (m), 1197 (s), 1038 (w), 1012 (m), 988 (m), 899 (m), 842 (s), 826 (m), 778 (m), 759 (m), 721 (m), 711 (m), 619 (w), 541 (w), 506 (m) cm^{-1}; MS (ESI): *m/z* for $C_{33}H_{43}NO_2^+$ calc.: 472.22 $[M+H]^+$, found.: 472.22; HRMS (ESI): *m/z* for $C_{27}H_{39}BrNO^+$ calc.: 472.2210 $[M+H]^+$, found.: 472.2212.

6-Octyloxy-2-(4-octyloxyphenyl)azulene-1-carbonitrile (8O-AzCN-PhO8)



$C_{33}H_{43}NO_2$
(485.71)

Synthesis according to GP2; **8O-AzCN-Br** (100 mg, 278 µmol), 4-octyloxyphenylboronic acid (208 mg, 833 µmol); $Pd(PPh_3)_4$ (32 mg, 28 µmol), Cs_2CO_3 (271 mg, 833 µmol), dioxane (5 mL); yield: orange solid (114 mg, 235 µmol, 85 %); melting behavior: Cr 101 °C SmA 155 °C I; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87–0.92 (m, 6H, CH_3), 1.24–1.42 (m, 16H, CH_2), 1.44–1.54 (m, 4H, $OCH_2CH_2CH_2$), 1.78–1.91 (m, 4H, OCH_2CH_2), 4.03 (t, J = 6.6 Hz, 2H, 4'-OCH_2), 4.14 (t, J = 6.5 Hz, 2H, 6-OCH_2), 7.00–7.04 (m, 2H, 3'-H), 7.04–7.08 (m, 2H, 5-H, 7-H), 7.34 (s, 1H, 3-H), 7.95–8.00 (m, 2H, 2'-H), 8.18 (d, J = 11.5 Hz, 1H, 4-H), 8.42 (d, J = 10.7 Hz, 1H, 8-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 22.7, 26.0, 26.1, 29.1, 29.2, 29.3, 29.3, 29.4, 31.8, 31.9 (CH_2), 68.2 (4'-OCH_2), 69.4 (6-OCH_2), 93.7 (C-1), 114.0 (C-7), 115.0 (C-3'), 116.4 (C-3), 116.9 (C-5), 118.9 (CN), 127.2 (C-1'), 129.5 (C-2'), 134.6 (C-8), 136.7 (C-4), 138.0 (C-3a), 141.0 (C-8a), 148.0 (C-2), 159.8 (C-4'), 167.9 (C-6) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3085 (w), 3044 (w), 2952 (m), 2918 (s), 2869 (m), 2851 (s), 2730 (w), 2387 (w), 2202 (m), 1605 (m), 1581 (s), 1544 (m), 1526 (m), 1462 (s), 1430 (s), 1408 (m), 1388 (m), 1378 (m), 1318 (w), 1301 (w), 1288 (m), 1269 (m), 1253 (s), 1210 (m), 1196 (s), 1185 (s), 1142 (w), 1129 (w), 1084 (w), 1069 (w), 1031 (m), 1018 (m), 1000 (m), 982 (m), 962 (w), 934 (w), 905 (m), 872 (w), 845 (m), 830 (s), 797 (m), 772 (w), 734 (m), 722 (m), 636 (w), 622 (w), 536 (w), 507 (m) cm^{-1};MS (ESI): m/z for $C_{33}H_{43}NO_2^+$ calc.: 486.3 $[M+H]^+$, found.: 486.3; HRMS (ESI): m/z for $C_{33}H_{44}NO_2^+$ calc.: 486.3367 $[M+H]^+$, found.: 486.3355.

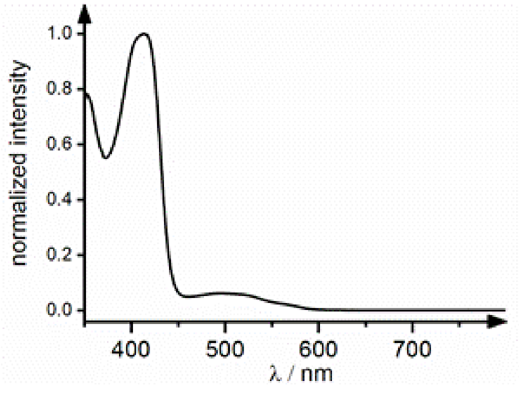
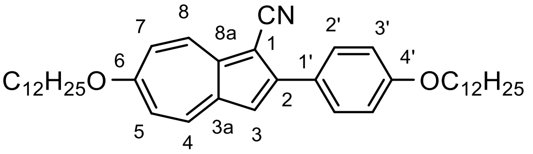


Figure S1: Normalized UV/VIS spectra of **8O-AzCN-PhO8** in chloroform.

6-Dodecyloxy-2-(4-dedecyloxyphenyl)azulene-1-carbonitrile (12O-AzCN-PhO12)



$C_{41}H_{59}NO_2$
(597.45)

Synthesis according to GP2; **12O-AzCN-Br** (38 mg, 91 µmol), 4-dodecyloxyphenyl boronic acid (42 mg, 137 µmol); $Pd(PPh_3)_4$ (5 mg, 5 µmol), Cs_2CO_3 (89 mg, 274 µmol), dioxane (5 mL); yield: orange solid (35 mg, 59 µmol, 64 %); melting behavior: Cr 90 °C SmC 133 °C SmA 150 °C I; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 6H, CH_3), 1.21–1.42 (m, 32H, CH_2), 1.43–1.55 (m, 4H, $OCH_2CH_2CH_2$), 1.76-1.94 (m, 4H, OCH_2CH_2), 4.02 (t, J = 6.6 Hz, 2H, C-4'-OCH_2), 4.13 (t, J = 6.5 Hz, 2H, C-6-OCH_2), 6.99–7.03 (m, 2H, 3'-H), 7.03–7.08 (m, 2H, 5-H, 7-H), 7.33 (s, 1H, 3-H), 7.94–8.00 (m, 2H, 2'-H), 8.17 (d, J = 11.1 Hz, 1H, C-4)), 8.40 (d, J = 10.8 Hz, 1H, C-8) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (CH_3), 22.7, 26.0, 26.1, 29.1, 29.3, 29.4, 29.4, 29.5, 29.6, 29.6, 29.6, 29.7, 29.7, 32.0 (CH_2), 68.2 (C-4'-OCH_2), 69.4 (C-6-OCH_2), 93.7 (C-1), 114.0 (C-5/C-7), 115.0 (C-3'), 116.4 (C-3), 116.8 (C-5/C-7), 118.9 (C-2), 127.2 (C-1'), 129.5 (C-2'), 134.6 (C-8), 136.7 (C-4), 138.0 (C-3a), 141.0 (C-8a), 147.9 (CN), 159.8 (C-4'), 167.9 (C-6) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2953 (m), 2917 (s), 2850 (s), 2198 (m), 1606 (s), 1583 (m), 1545 (m), 1526 (m), 1463 (s), 1431 (s), 1394 (w), 1317 (w), 1288 (m), 1255 (s), 1197 (s), 1183 (s), 1158 (w), 1130 (w), 1022 (m), 1000 (m), 974 (w), 904 (w), 830 (s), 807 (w), 791 (w), 766 (w), 720 (m), 622 (w), 541 (w), 510 (w) cm^{-1}; MS(ESI): m/z for $C_{41}H_{59}NNaO_2^+$ calc.: 620.44 $[M+Na]^+$, found.: 620.43; HRMS(ESI): m/z for $C_{41}H_{59}NNaO_2^+$ calc.: 620.4438 $[M+Na]^+$, found.: 620.4349.

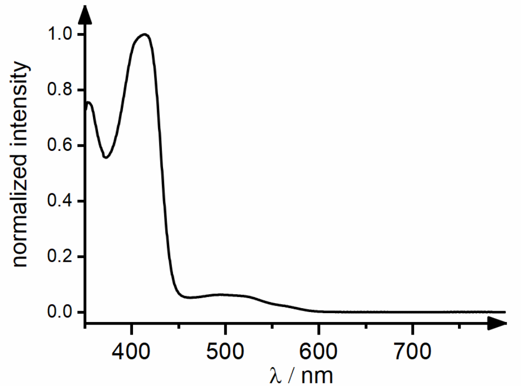
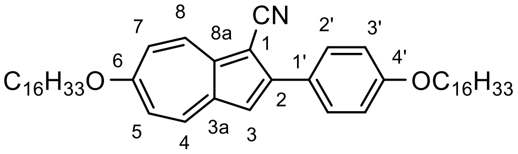


Figure S2: Normalized UV/VIS spectra of **12O-AzCN-PhO12** in chloroform.

6-Hexadecyloxy-2-(4-hexadecyloxyphenyl)azulene-1-carbonitrile (16O-AzCN-PhO16)



$C_{49}H_{75}NO_2$
(710.14)

Synthesis according to GP2; **16O-AzCN-Br** (16 mg, 34 µmol), 4-hexadecyloxyphenyl boronic acid (25 mg, 68 µmol); $Pd(PPh_3)_4$ (4 mg, 3 µmol), Cs_2CO_3 (33 mg, 102 µmol), dioxane (3 mL); yield: orange solid (17 mg, 34 µmol, 71 %); melting behavior: Cr 94 °C SmC 135 °C SmA 138 °C I; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.0 Hz, 6H, CH_3), 1.21–1.41 (m, 48H, CH_2), 1.44–1.53 (m, 4H, $OCH_2CH_2CH_2$), 1.82 (tt, J = 6.8 Hz, 6.6 Hz, 2H, OCH_2CH_2), 1.88 (tt, J = 6.7 Hz, 6.5 Hz, 2H, OCH_2CH_2), 4.03 (t, J = 6.6 Hz, 2H, 4'-OCH_2), 4.14 (t, J = 6.5 Hz, 2H, 6-OCH_2), 7.00–7.03 (m, 2H, 3'-H), 7.05–7.09 (m, 2H, 5-H, 7-H), 7.35 (s, 1H, 3-H), 7.93–8.00 (m, 2H, 2'-H), 8.19 (d, J = 10.9 Hz, 1H, 4-H), 8.42 (d, J = 10.7 Hz, 1H, 8-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.2 (CH_3), 22.7, 26.0, 26.1, 29.1, 29.3, 29.3, 29.4, 29.4, 29.6, 29.6, 29.6, 29.6, 29.7, 29.7, 29.7, 29.7, 29.7, 32.0 (CH_2), 68.2 (4'-OCH_2), 69.4 (6-OCH_2), 93.7 (C-1), 114.0 (C-7), 115.1 (C-3'), 116.4 (C-3), 116.9 (C-5), 118.9 (CN), 127.2 (C-1'), 129.5 (C-2'), 134.6 (C-8), 136.7 (C-4), 138.0 (C-3a), 141.0 (C-8a), 148.0 (C-2), 159.8 (C-4'), 167.9 (C-6) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2954 (w), 2916 (s), 2850 (s), 2204 (w), 1606 (w), 1584 (w), 1546 (w), 1526 (w), 1465 (m), 1432 (m), 1288 (w), 1256 (m), 1199 (m), 1043 (w), 1018 (w), 999 (w), 904 (w), 828 (w), 807 (w), 788 (w), 719 (w), 622 (w), 509 (w) cm^{-1};MS (EI): m/z for $C_{37}H_{52}NO_2^+$ calc.: 709.6 $[M]^+$, found: 709.6; HRMS (ESI): m/z for $C_{37}H_{52}NO_2Na^+$ calc.: 732.5690 $[M+Na]^+$, found.: 732.5690.

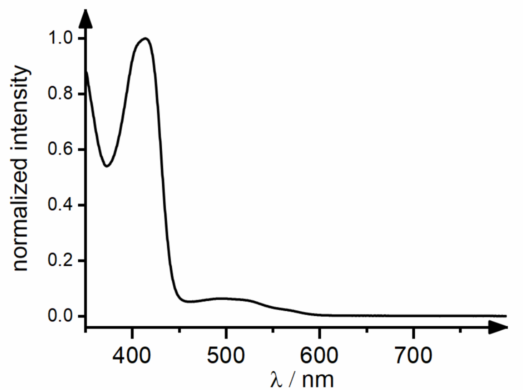
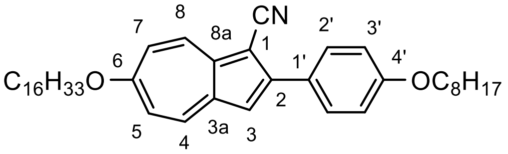


Figure S3: Normalized UV/VIS spectra of **16O-AzCN-PhO16** in chloroform.

6-Hexadecyloxy-2-(4-octyloxyphenyl)azulene-1-carbonitrile (16O-AzCN-PhO8)



$C_{41}H_{59}NO_2$
(597.93)

Synthesis according to GP2; **16O-AzCN-Br** (44 mg, 93 µmol), 4-octyloxyphenylboronic acid (47 mg, 186 µmol); Pd(PPh$_3$)$_4$ (11 mg, 9 µmol), Cs$_2$CO$_3$ (91 mg, 279 µmol), dioxane (5 mL); yield: orange solid (42 mg, 70 µmol, 75 %); melting behavior: Cr 86 °C SmC 137 °C SmA 151 °C I; ^{1}H NMR (700 MHz, CDCl$_3$): δ = 0.86–0.92 (m, 6H, CH$_3$), 1.20–1.42 (m, 32H, CH$_2$), 1.46–1.53 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.79–1.84 (m, 2H, OCH$_2$C*H*$_2$), 1.84–1.89 (m, 2H, OCH$_2$C*H*$_2$), 4.02 (t, *J* = 6.6 Hz, 2H, 6-OCH$_2$), 4.13 (t, *J* = 6.5 Hz, 2H, 4'-OCH$_2$), 7.00–7.03 (m, 2H, 3'-H), 7.04–7.07 (m, 2H, 5-H, 7-H), 7.34 (s, 1H, 3-H), 7.94–8.00 (m, 2H, 2'-H), 8.17 (d, *J* = 11.2 Hz, 1H, 4-H), 8.40 (d, *J* = 10.8 Hz, 1H, 8-H) ppm; ^{13}C NMR (176 MHz, CDCl$_3$): δ = 14.1, 14.1 (CH$_3$), 22.7, 22.7, 26.0, 26.1, 29.1, 29.3, 29.3, 29.3, 29.4, 29.4, 29.6, 29.6, 29.7, 29.7, 29.7, 29.7, 31.9, 32.0 (CH$_2$), 68.2 (4'-O*C*H$_2$), 69.4 (6-O*C*H$_2$), 93.7 (C-1), 114.0 (C-7), 115.1 (C-3'), 116.4 (C-3), 116.8 (C-5), 118.9 (CN), 127.2 (C-1'), 129.5 (C-2'), 134.6 (C-8), 136.7 (C-4), 138.0 (C-3a), 141.0 (C-8a), 147.9 (C-2), 159.8 (C-4'), 167.9 (C-6) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3072 (w), 3042 (w), 2956 (m), 2920 (s), 2871 (m), 2851 (s), 2729 (w), 2196 (m), 1605 (m), 1584 (m), 1546 (w), 1525 (m), 1488 (w), 1463 (m), 1425 (s), 1390 (w), 1287 (m), 1251 (s), 1198 (s), 1182 (m), 1142 (w), 1109 (w), 1087 (w), 1043 (w), 1030 (w), 1002 (w), 999 (w), 906 (w), 834 (m), 795 (w), 764 (w), 736 (m), 723 (w), 622 (w), 540 (w), 511 (w) cm^{-1}; MS (ESI): *m/z* for $C_{41}H_{60}NO_2^+$ calc.: 598.46 [M+H]$^+$, found.: 598.46; HRMS (ESI): *m/z* for $C_{41}H_{60}NO_2^+$ calc.: 598.4619 [M+H]$^+$, found.: 598.4601.

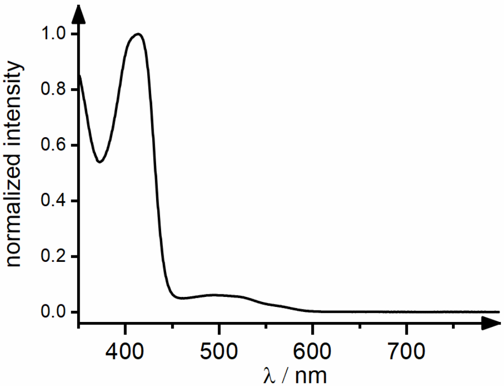
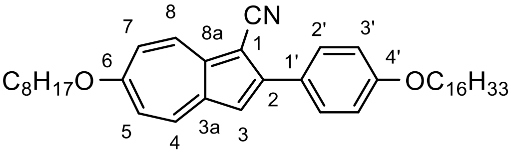


Figure S4: Normalized UV/VIS spectra of **16O-AzCN-PhO8** in chloroform.

2-(4-Hexadecyloxyphenyl)-6-octyloxyazulene-1-carbonitrile (8O-AzCN-PhO16)



$C_{41}H_{59}NO_2$
(597.93)

Synthesis according to GP2; **8O-AzCN-Br** (77 mg, 278 µmol), 4-hexadecyloxyphenyl boronic acid (155 mg, 833 µmol); $Pd(PPh_3)_4$ (25 mg, 21 µmol), Cs_2CO_3 (209 mg, 641 µmol), dioxane (5 mL); yield: orange solid (127 mg, 212 µmol, 99 %); melting behavior: Cr 95 °C SmA 147 °C I; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.92 (m, 6H), 1.21–1.43 (m, 32H, CH_2), 1.43–1.54 (m, 4H, $OCH_2CH_2CH_2$), 1.77–1.91 (m, 4H, OCH_2CH_2), 4.02 (t, J = 6.5 Hz, 2H, 6-OCH_2), 4.13 (t, J = 6.5 Hz, 2H, 4'-OCH_2), 7.00–7.03 (m, 2H, 3'-H), 7.03–7.08 (m, 2H, 5-H, 7-H), 7.34 (s, 1H, 3-H), 7.94–7.99 (m, 2H, 2'-H), 8.17 (d, J = 11.2 Hz, 1H, 4-H), 8.41 (d, J = 10.8 Hz, 1H, 8-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1, 14.2 (CH_3), 22.7, 22.7, 26.0, 26.1, 29.1, 29.2, 29.3, 29.3, 29.4, 29.4, 29.6, 29.6, 29.7, 29.7, 31.8, 32.0 (CH_2), 68.2 (4'-OCH_2), 69.4 (6-OCH_2), 93.7 (C-1), 114.0 (C-7), 115.0 (C-3'), 116.4 (C-3), 116.8 (C-5), 118.9 (CN), 127.2 (C-1'), 129.5 (C-2'), 134.6 (C-8), 136.7 (C-4), 138.0 (C-3a), 141.0 (C-8a), 147.9 (C-2), 159.8 (C-4'), 167.9 (C-6) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2919 (s), 2851 (s), 2197 (w), 1606 (m), 1584 (m), 1546 (w), 1526 (w), 1464 (m), 1431 (m), 1392 (w), 1289 (w), 1257 (m), 1199 (m), 1183 (m), 1027 (w), 1000 (w), 904 (w), 832 (m), 793 (w), 771 (w), 722 (w), 622 (w), 510 (w) cm^{-1}; MS (ESI): *m/z* for $C_{41}H_{60}NO_2^+$ calc.: 598.46 $[M+H]^+$, found.: 598.46; HRMS (ESI): *m/z* for $C_{41}H_{60}NO_2^+$ calc.: 598.4619 $[M+H]^+$, found.: 598.4611.

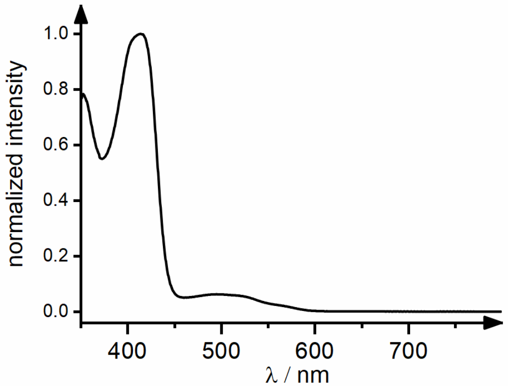


Figure S5: Normalized UV/VIS spectra of **8O-AzCN-PhO16** in chloroform.

3. Differential Scanning Calorimetry

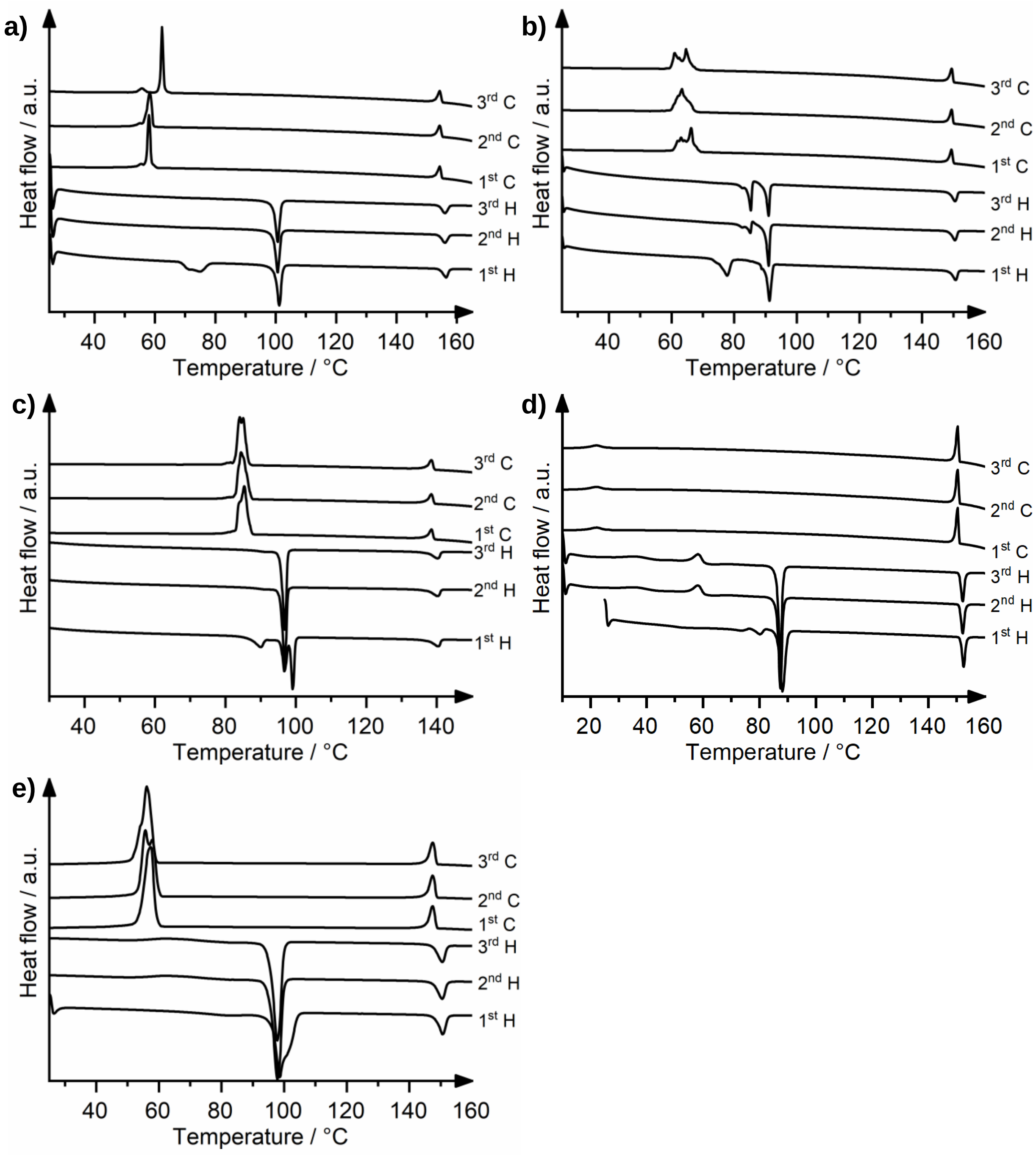


Figure S6: DSC-curves of azulenes **nO-AzCN-PhOm**: a) **8O-AzCN-PhO8** b) **12O-AzCN-PhO12** c) **16O-AzCN-PhO16** d) **16O-AzCN-PhO8** e) **8O-AzCN-PhO16**. The SmA-SmC transition is not visible. Heating / cooling rate: 5 K/min, H = Heating, C = Cooling.

4. Polarizing Optical Microscopy (POM)

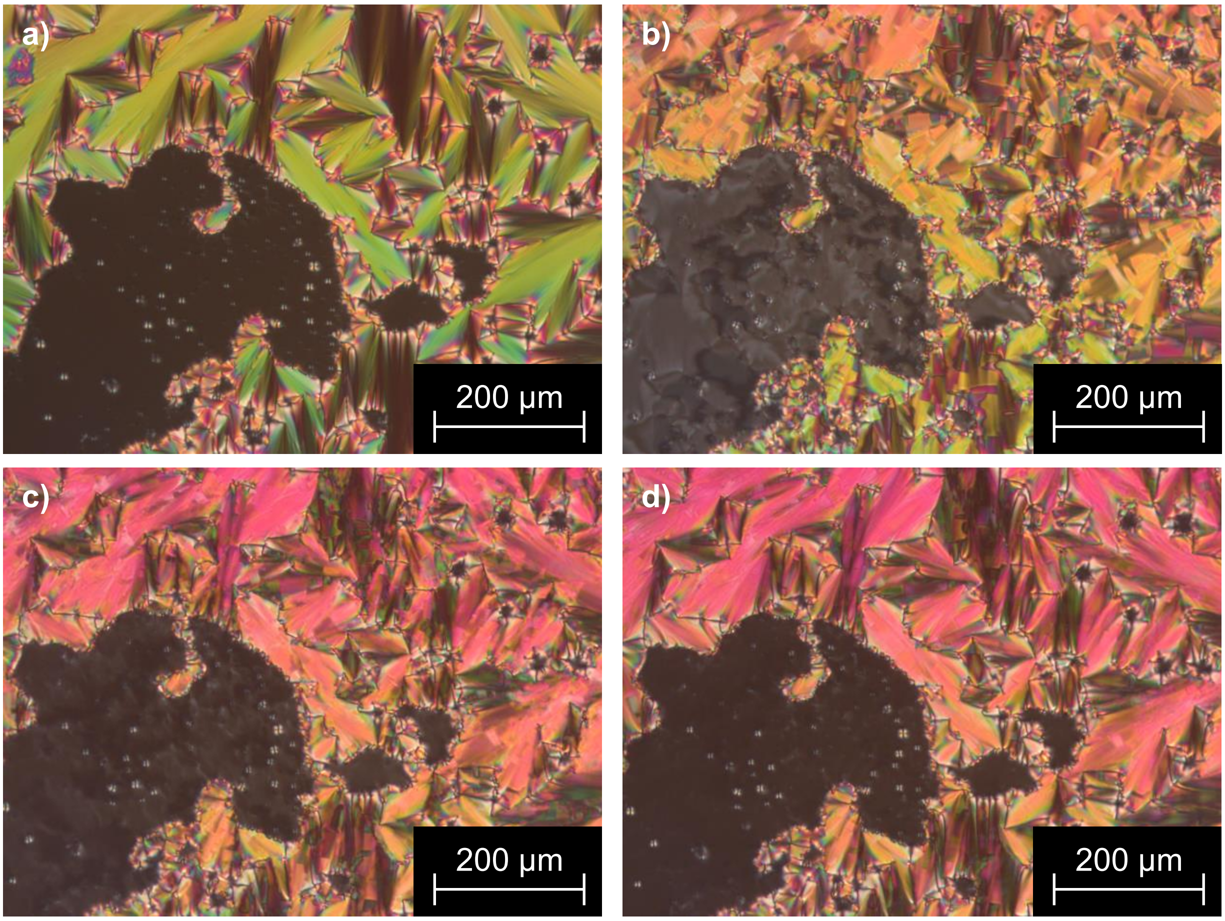


Figure S7: POM micrographs between crossed polarizers of **16O-AzCN-PhO8**: a) Fan textures and Maltese crosses of a SmA phase at 144 °C upon cooling from the isotropic liquid (cooling rate 2 K/min) that transform into b) broken fan and Schlieren textures of a SmC phase at 128 °C. c) shows the same frame of the SmC phase directly before the SmA reentrance phase at 80 °C. d) The Schlieren textures disappear and the broken fans recombine after completion of the reentrance at 75 °C.

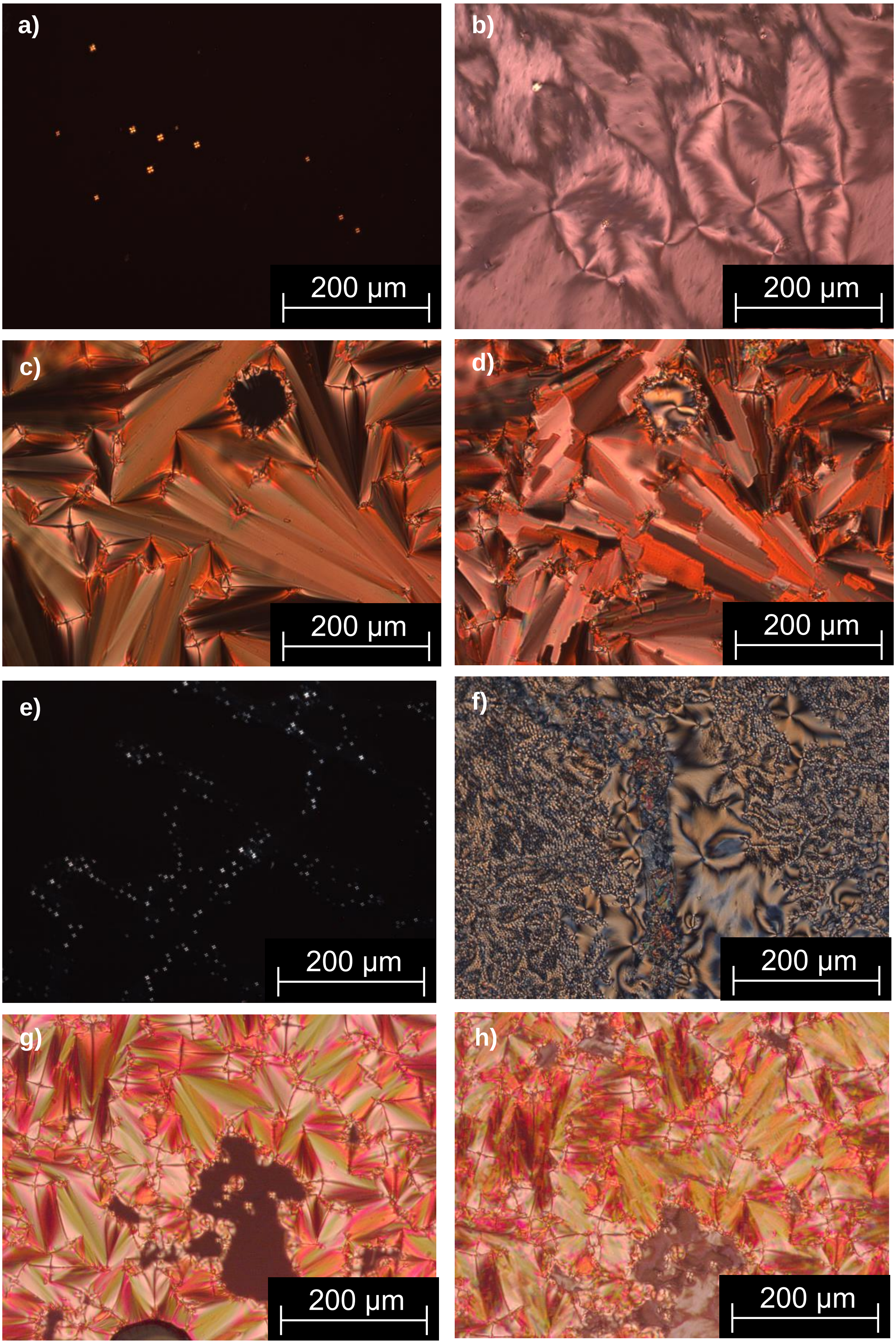


Figure S8: POM micrographs of the observed textures between crossed polarizers upon cooling from the isotropic liquid (2 K/min): a) Maltese crosses of **8O-AzCN-PhO8** at 159 °C and b) Schlieren textures at 86 °C; c) and d) fan- and broken fan textures at the same position for **12O-AzCN-PhO12** at 139 °C and 104 °C, e) and f) Maltese crosse and Schlieren textures of **16O-AzCN-PhO16** at 137 °C and 122 °C; g) and h): fan and broken fan textures of **8O-AzCN-PhO16** at 106 °C and 75 °C.

5. X-Ray Diffractometry

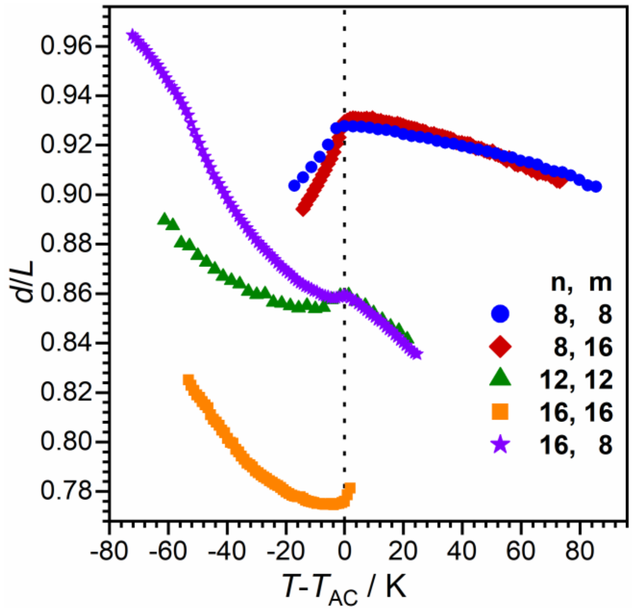


Figure S9: Plot of the relative layer thickness *d/L* as a function of the temperature for all investigated compounds.

6. Single Crystal X-Ray Data

The crystal structures were obtained by allowing the solvent to evaporate slowly in a NMR tube at room temeparture.

Table S1: Refinement data of the single crystal structures

Compound	**8O-AzCN-PhO8**	**8O-AzCN-PhO16**	**12O-AzCN-PhO12**	**16O-AzCN-PhO8**	**16O-AzCN-PhO16**
CCDC number	CCDC 2215784	CCDC 2215785	CCDC 2215787	CCDC 2215788	CCDC 2215789
formula	C33H43NO2	C41H59NO2	C41H59NO2	C41H59NO2	C49H75NO2
formula weight (g/mol)	485.68	597.89	597.89	597.89	710.10
crystal size (mm)	0.567 x 0.455 x 0.144	0.594 x 0.127 x 0.074	0.234 x 0.090 x 0.041	0.352 x 0.146 x 0.120	0.234 x 0.072 x 0.040
temperature (K)	140(2)	140(2)	145(2)	140(2)	145(2)
wavelength λ (Å)	0.71073	0.71073 A	1.54178	0.71073	0.71073
crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic
space group	P-1	P2(1)/c	P-1	P-1	P1
unit cell dimension					
a (Å)	11.2228(11)	31.2817(18)	8.1653(13)	8.1918(6)	7.2017(4)
b (Å)	12.1634(6)	5.5982(3)	9.8958(15)	9.9946(7)	15.2415(9)
c (Å)	12.4879(6)	21.1584(13)	23.177(4)	22.1775(13)	40.140(3)
α (deg)	117.700(2)	90	88.317(12)	93.108(4)	80.771(5)
β (deg)	110.189(3)	105.680(3)	80.397(12)	90.023(4)	87.247(4)
γ (deg)	92.934(3)	90	74.704(13)	104.781(4)	79.223(4)
V (Å^3)	1369.89(17)	3567.4(4)	1780.9(5)	1752.9(2)	4271.5(5)
Z	2	4	2	2	4
D_c (g/cm^3)	1.177	1.113	1.115	1.113	1.104
μ (mm^{-1})	0.072	0.066	0.506	0.068	0.065

F(000)	528	1312	656	656	1568
theta range for data collection	1.955 to 28.467	1.930 to 28.356	3.869 to 64.992	1.839 to 28.374	1.376 to 24.999
index ranges	-15<=h<=15, -16<=k<=16, -16<=l<=16	-41<=h<=41, -7<=k<=7, -28<=l<=28	-9<=h<=9, -11<=k<=11 -26<=l<=24	-10<=h<=10, -13<=k<=13, -29<=l<=29	-8<=h<=8, -18<=k<=18, -47<=l<=47
reflection collected/unique	34547 / 6849 [R(int) = 0.0264]	49204 / 8892 [R(int) = 0.0412]	19439 / 5823 [R(int) = 0.0529]	38246 / 8720 [R(int) = 0.0377]	53692 / 27012 [R(int) = 0.0931]
completeness to theta	100.0 %	99.9 %	96.2 %	100.0 %	99.9 %
max. and min. transmission	0.7457 and 0.7155	0.7457 and 0.7042	0.8642 and 0.7096	0.7444 and 0.7247	0.8619 and 0.8065
refinement methods	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
data/restraints/parameter	6849 / 0 / 327	8892 / 0 / 399	5823 / 0 / 399	8720 / 0 / 399	27012 / 1204 / 1881
GOF on F^2	1.043	1.039	1.013	1.001	1.004
R_1, wR_2 [$I > 2\alpha(I)$]	R1 = 0.0503, wR2 = 0.1125	R1 = 0.0473, wR2 = 0.1140	R1 = 0.0483, wR2 = 0.1154	R1 = 0.0492, wR2 = 0.1080	R1 = 0.0847, wR2 = 0.1274
R_1, wR_2 (all data)	R1 = 0.0726, wR2 = 0.1204	R1 = 0.0816, wR2 = 0.1248	R1 = 0.0795, wR2 = 0.1331	R1 = 0.0968, wR2 = 0.1196	R1 = 0.2623, wR2 = 0.1740
largest diff. peak and hole (e/Å^3)	0.588 and -0.374	0.283 and -0.224	0.158 and -0.208	0.265 and -0.231	0.595 and -0.337

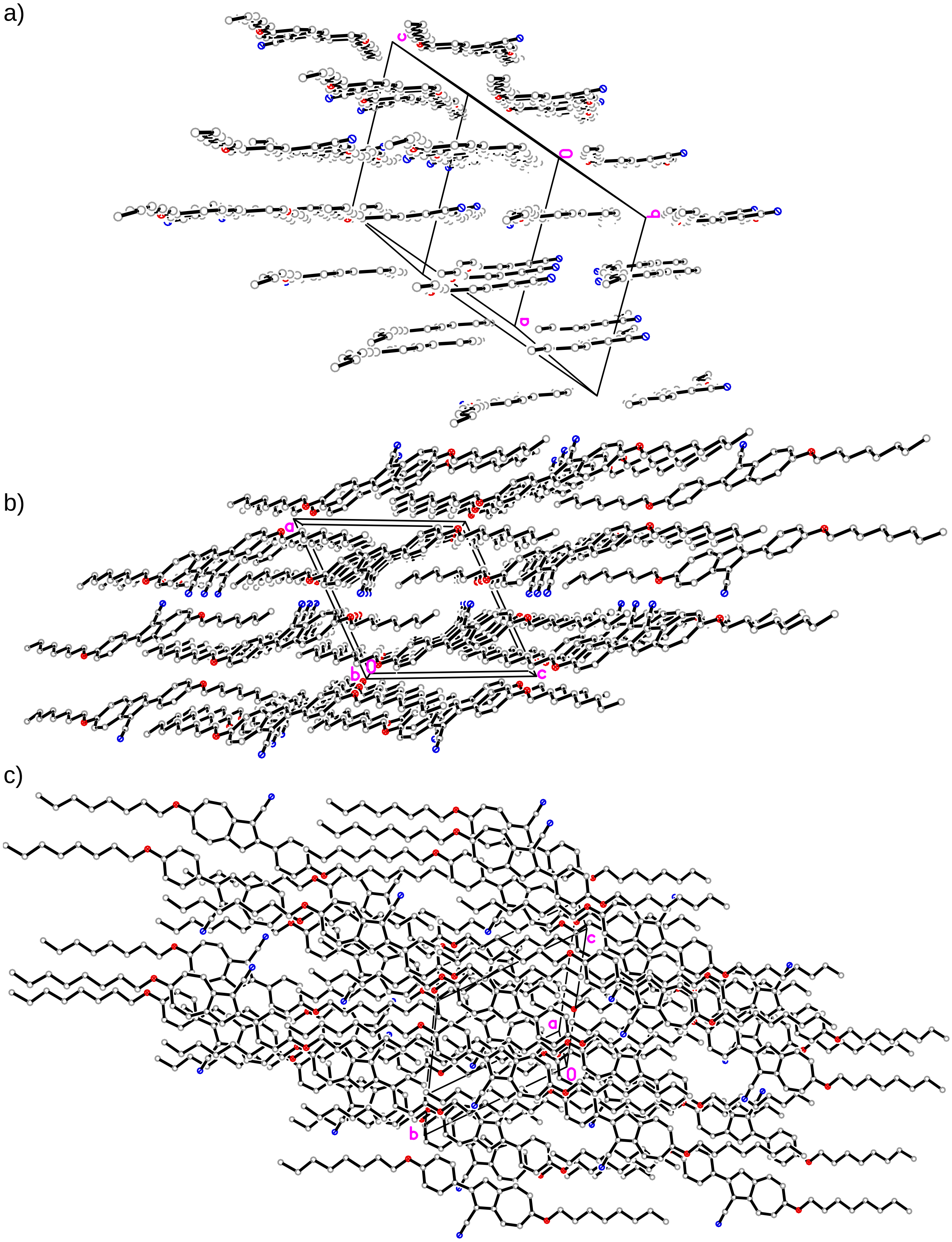


Figure S10: Single crystal X-Ray structure of **8O-AzCN-PhO8**. Point of view a) along the long molecule axis, b) along the b-axis and c) along the a-axis.

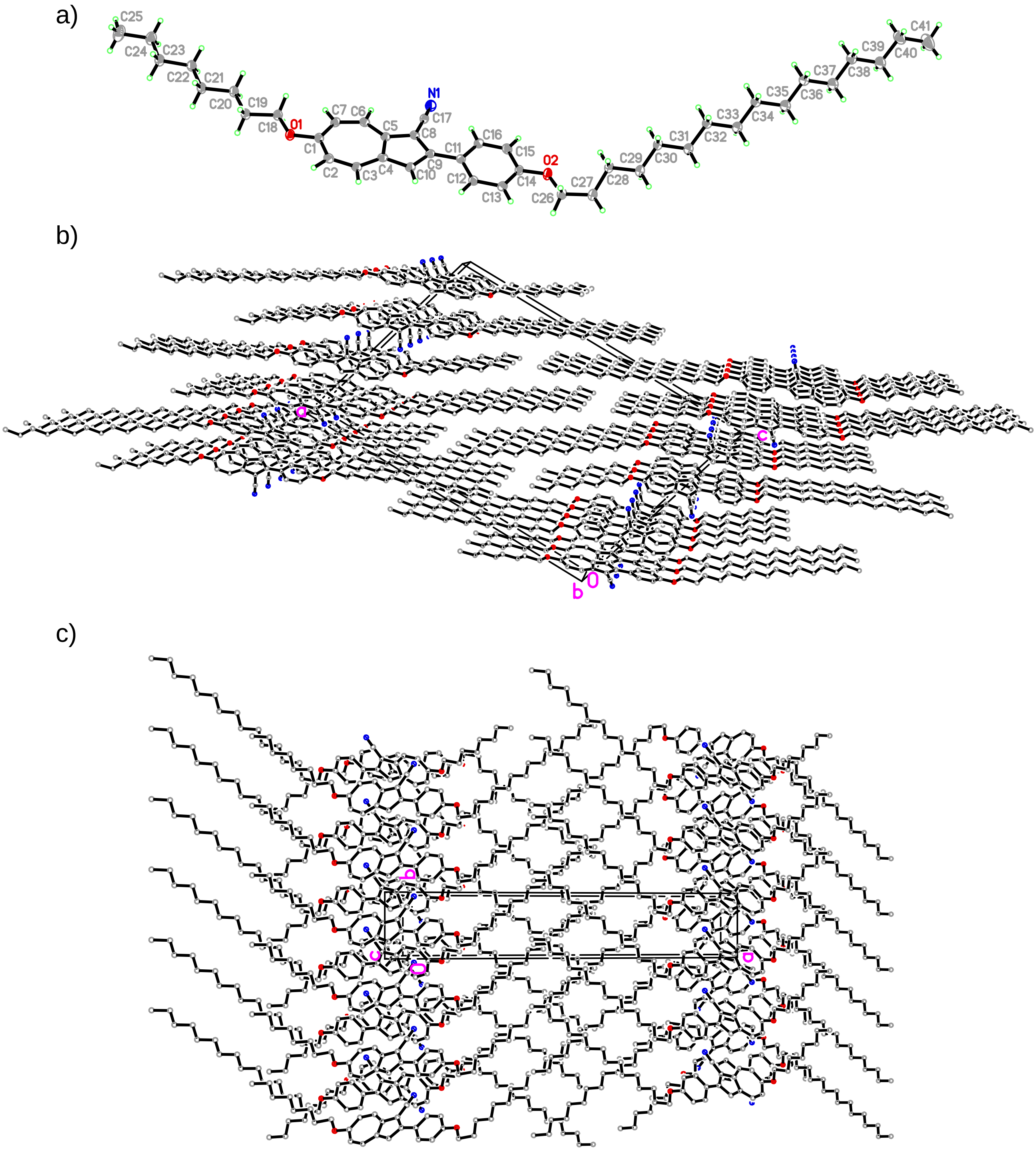


Figure S11: Single crystal X-Ray structure of **8O-AzCN-PhO16**. a) single molecule, b) point of view along the b-axis and c) along the c-axis.

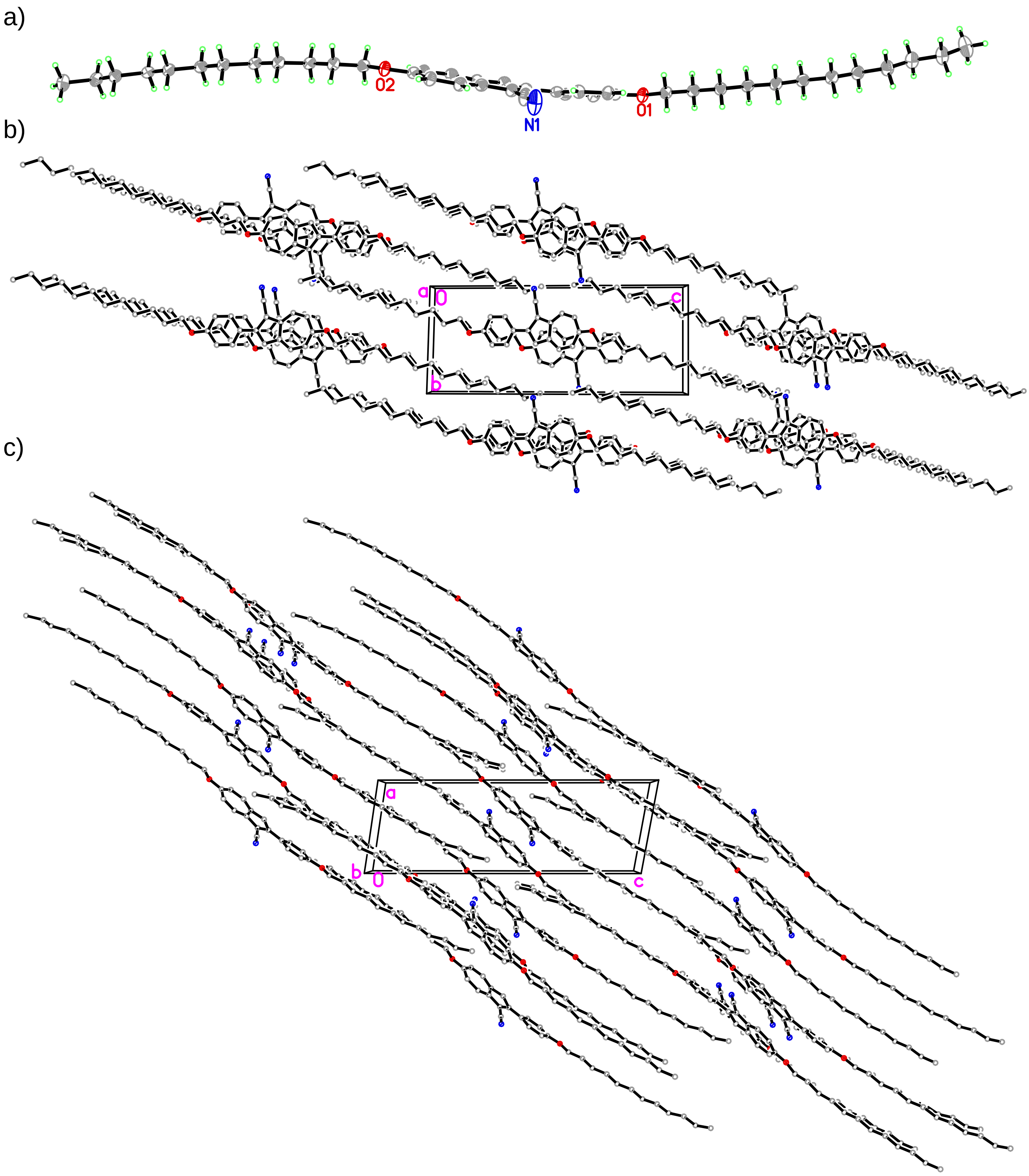


Figure S12: Single crystal X-Ray structure of **12O-AzCN-PhO12**. a) single molecule, b) point of view along the a-axis, and c) along the b-axis.

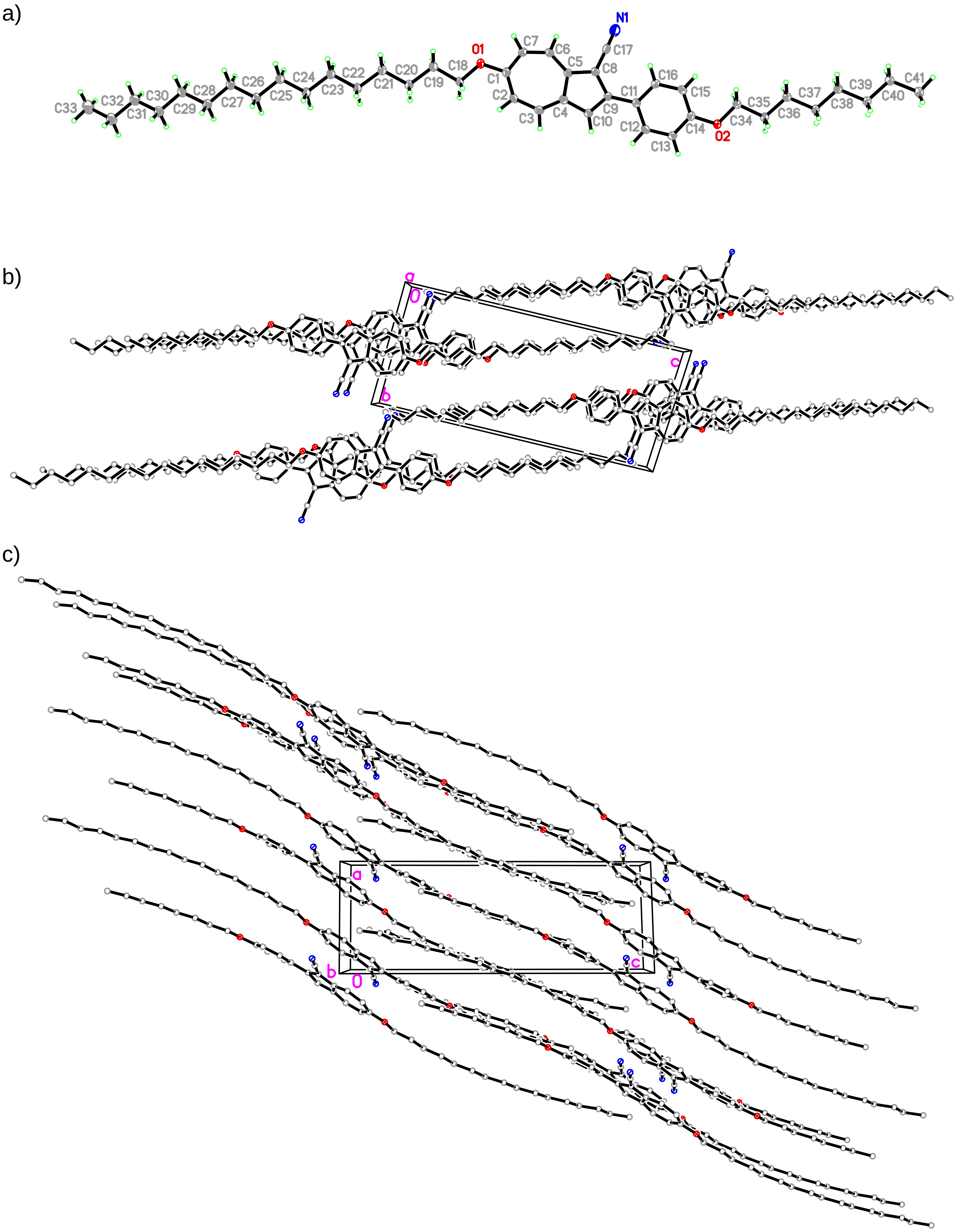


Figure S13: Single crystal X-Ray structure of **16O-AzCN-PhO8**. a) single molecule, b) point of view along the a-axis and c) along the b-axis.

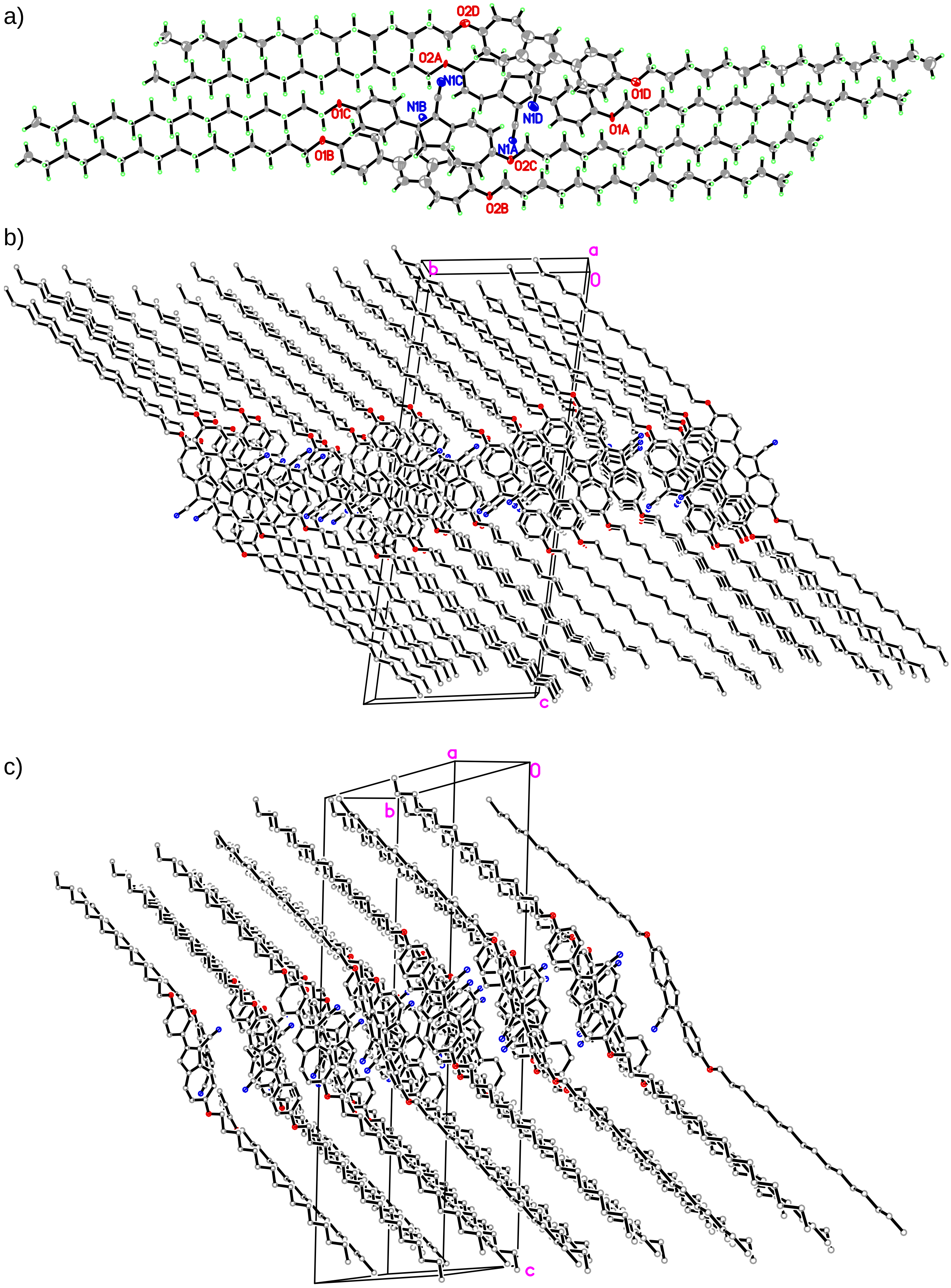


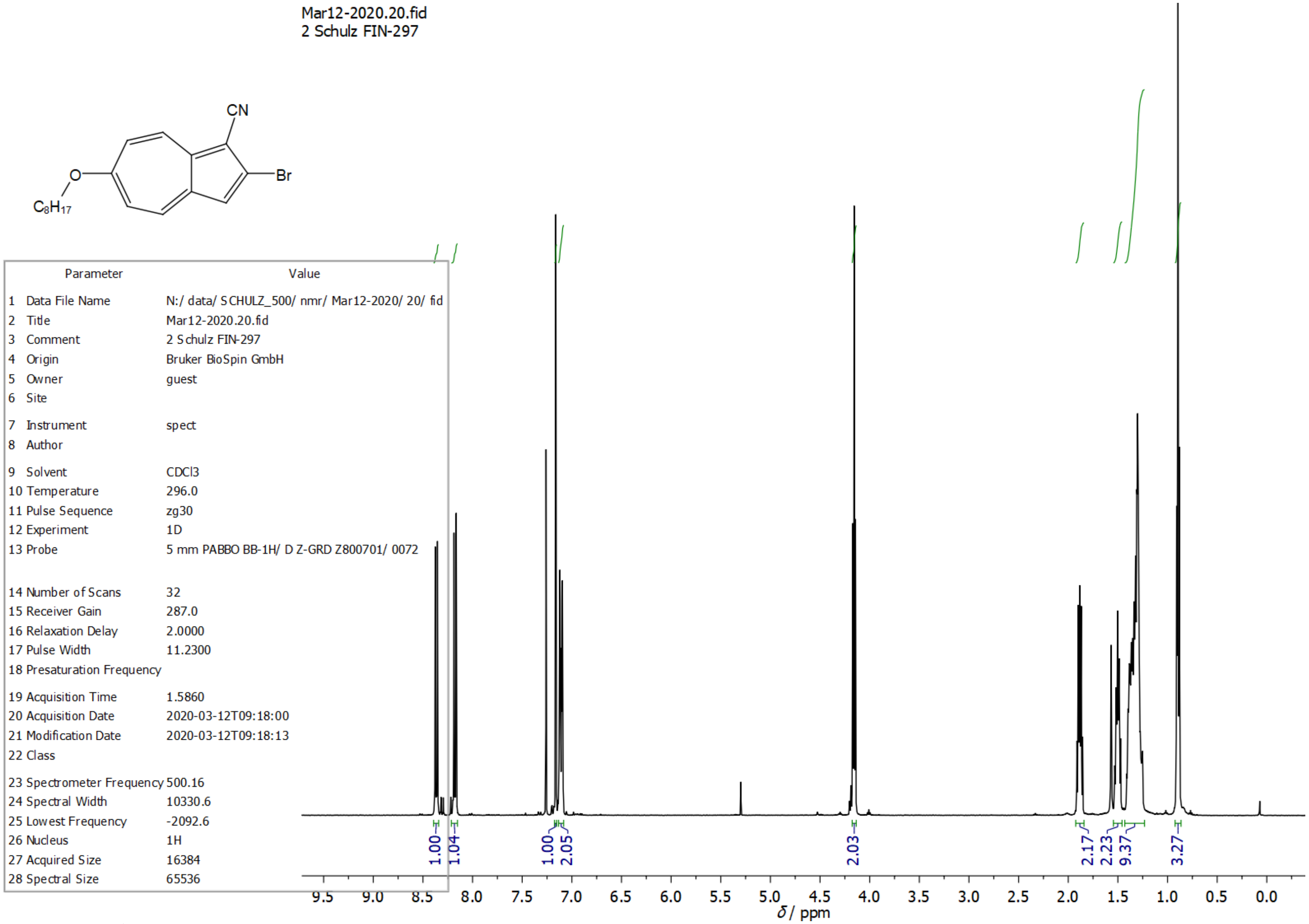
Figure S14: Single crystal X-Ray structure of **16O-AzCN-PhO16**. a) All four independent molecules of the unit cell, b) point of view along the a-axis, parallel to the ab-plane.

7. Literature

1 F. Schulz, P. Ehni, B. Wank, A. Bauer, W. Frey and S. Laschat, *Liq. Cryst.*, 2021, **48**, 832–843.

2 S. Ushijima and H. Togo, *Synlett*, 2010, **2010**, 1067–1070.

8. NMR-spectra



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6	Site	
7	Instrument	spect
8	Author	
9	Solvent	CDCl3
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24	Spectral Width	10330.6
25	Lowest Frequency	-2092.6
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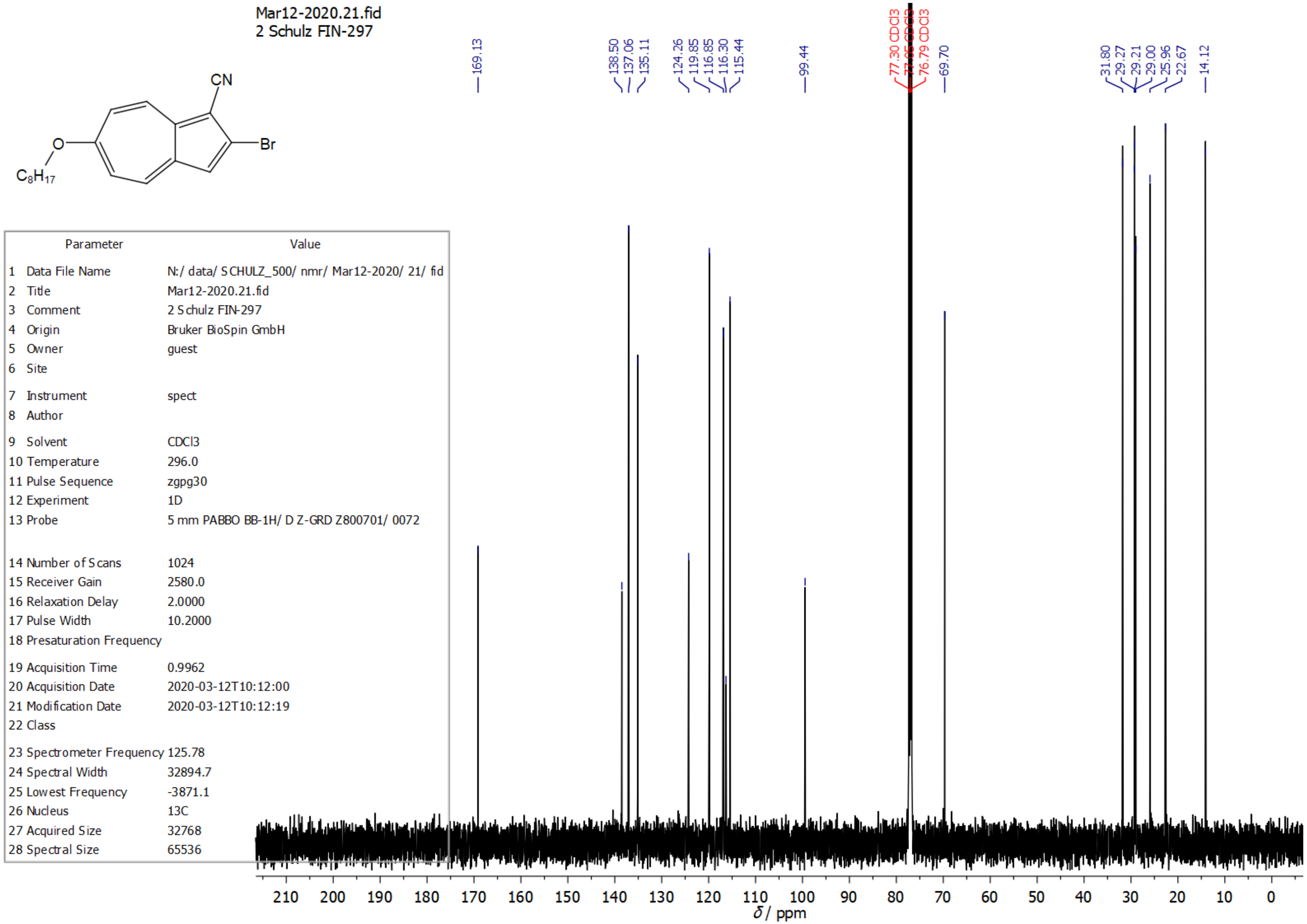
27	Acquired Size	16384
28	Spectral Size	65536

Figure S15: ^{1}H NMR spectrum of compound **8O-AzCN-Br**



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5 Owner	guest
6 Site	
7 Instrument	spect
8 Author	
9 Solvent	CDCl3
10 Temperature	296.0
11 Pulse Sequence	zgpg30
12 Experiment	1D
13 Probe	5 mm PABBO BB-1H/ D Z-GRD Z800701/ 0072
14 Number of Scans	1024
15 Receiver Gain	2580.0
16 Relaxation Delay	2.0000
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23 Spectrometer Frequency	125.78
24 Spectral Width	32894.7
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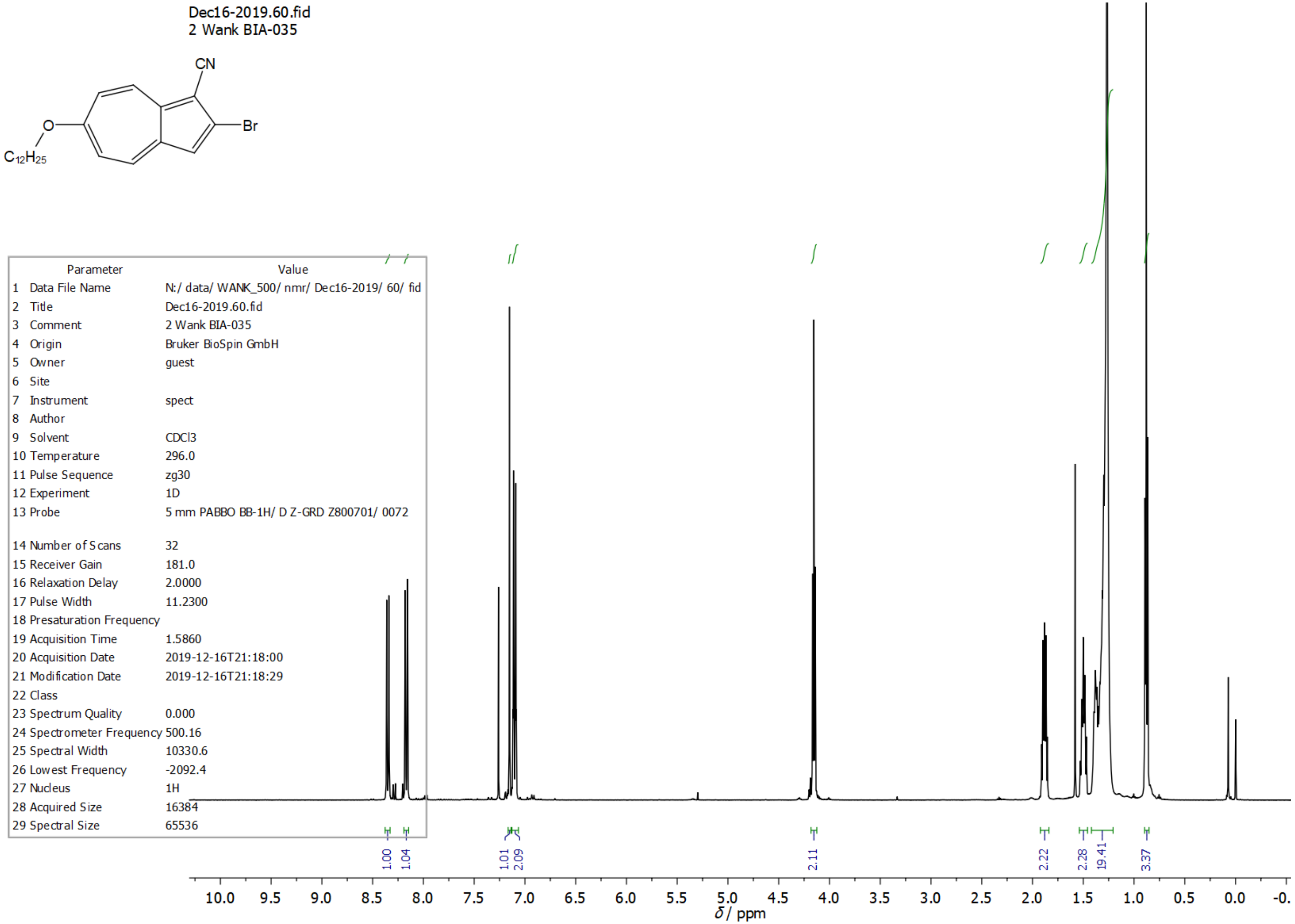
26 Nucleus	13C
27 Acquired Size	32768
28 Spectral Size	65536

Figure S16: ^{13}C NMR spectrum of compound **8O-AzCN-Br**



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8	Author	
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26	Lowest Frequency	-2092.4
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28	Acquired Size	16384
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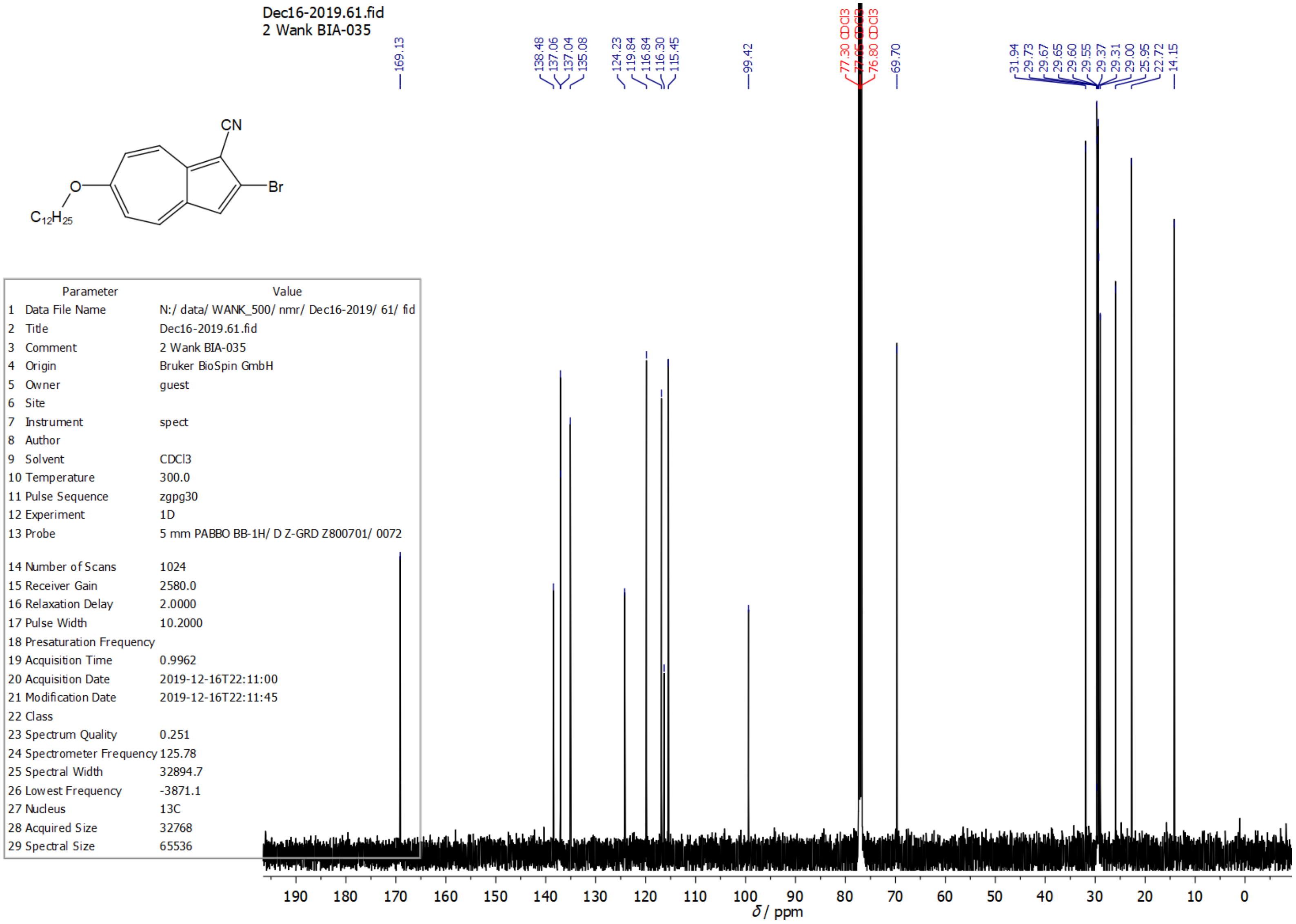
Figure S17: ^{1}H NMR spectrum of compound **12O-AzCN-Br**



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8	Author	
9	Solvent	CDCl3
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12	Experiment	1D
13	Probe	5 mm PABBO BB-1H/ D Z-GRD Z800701/ 0072
14	Number of Scans	1024
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16	Relaxation Delay	2.0000
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19	Acquisition Time	0.9962
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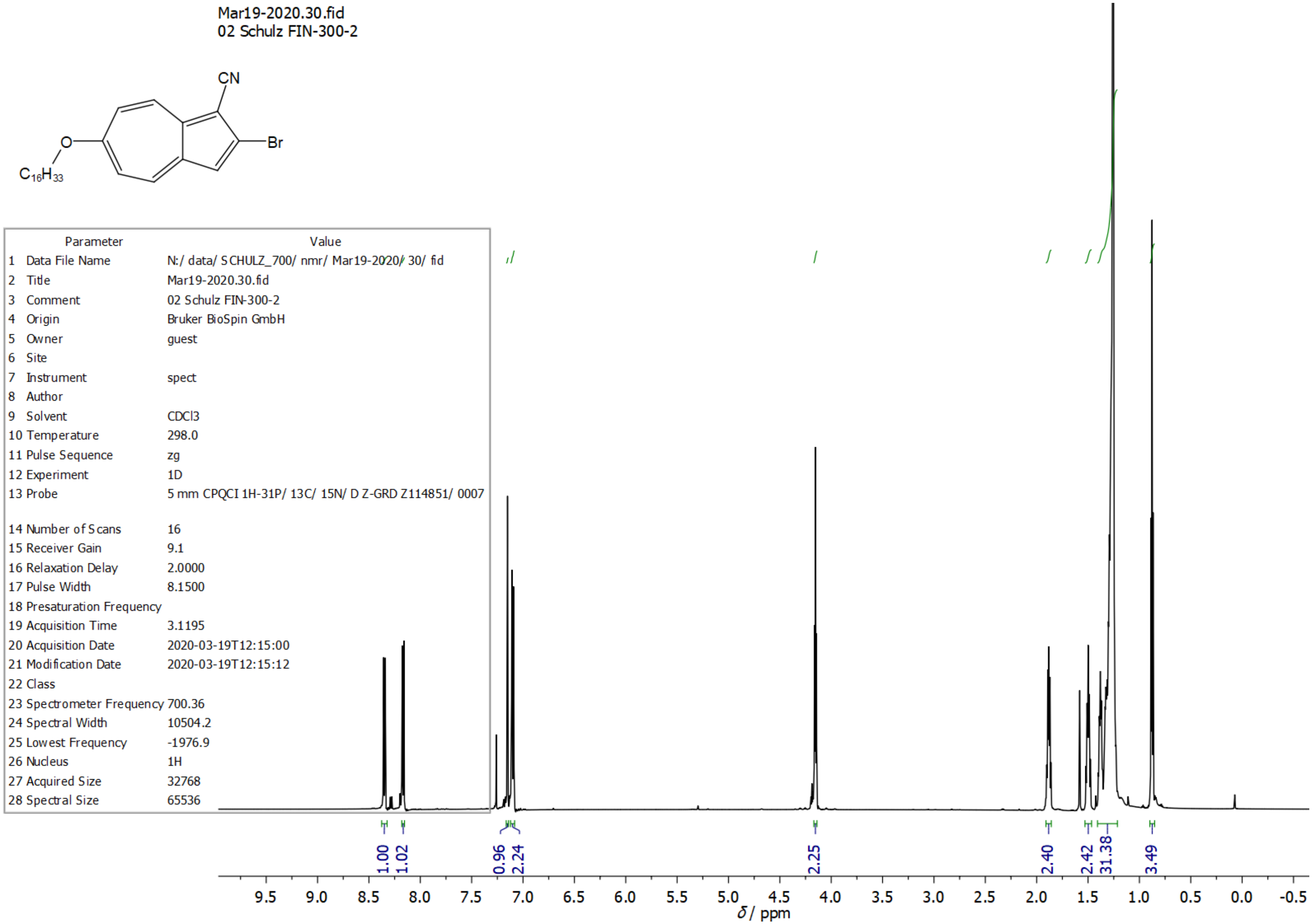
22	Class	
23	Spectrum Quality	0.251
24	Spectrometer Frequency	125.78
25	Spectral Width	32894.7
26	Lowest Frequency	-3871.1
27	Nucleus	13C
28	Acquired Size	32768
29	Spectral Size	65536

Figure S18: ^{13}CNMR spectrum of compound **12O-AzCN-Br**



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6	Site	
7	Instrument	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.0
11	Pulse Sequence	zg
12	Experiment	1D
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14	Number of Scans	16
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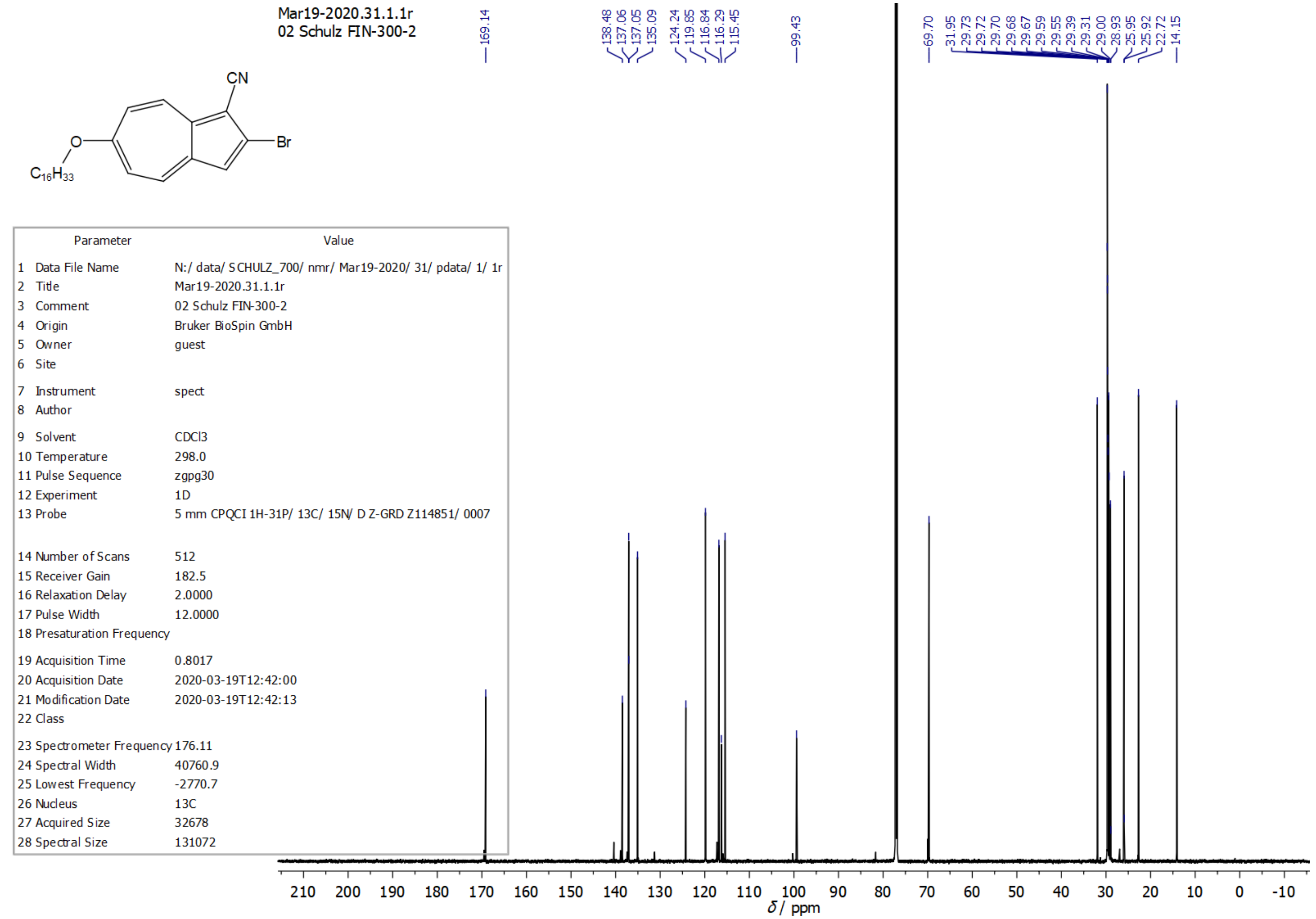
20	Acquisition Date	2020-03-19T12:15:00
21	Modification Date	2020-03-19T12:15:12
22	Class	
23	Spectrometer Frequency	700.36
24	Spectral Width	10504.2
25	Lowest Frequency	-1976.9
26	Nucleus	1H
27	Acquired Size	32768
28	Spectral Size	65536

Figure S19: ^{1}H NMR spectrum of compound **16O-AzCN-Br**



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8	Author	
9	Solvent	CDCl3
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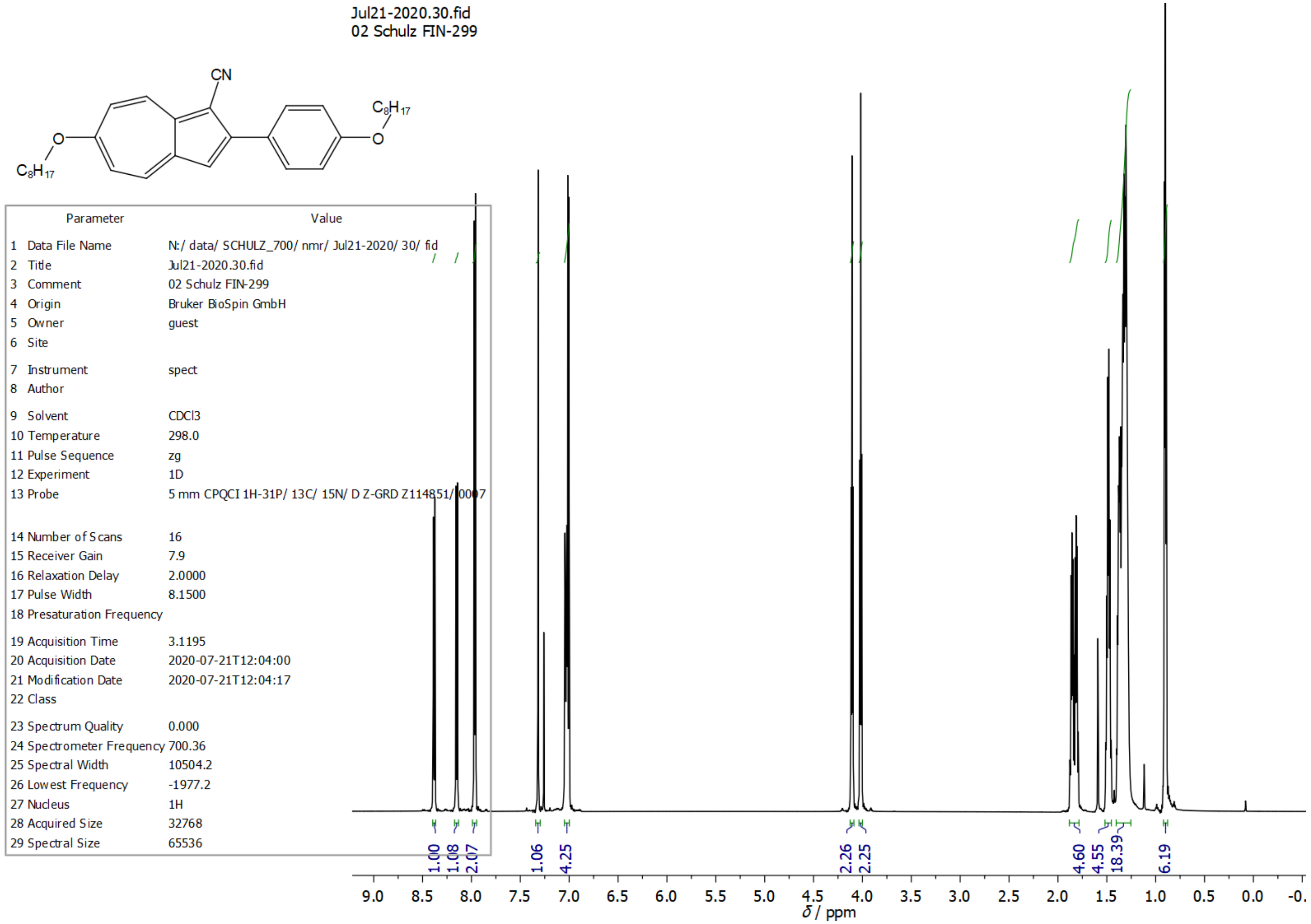
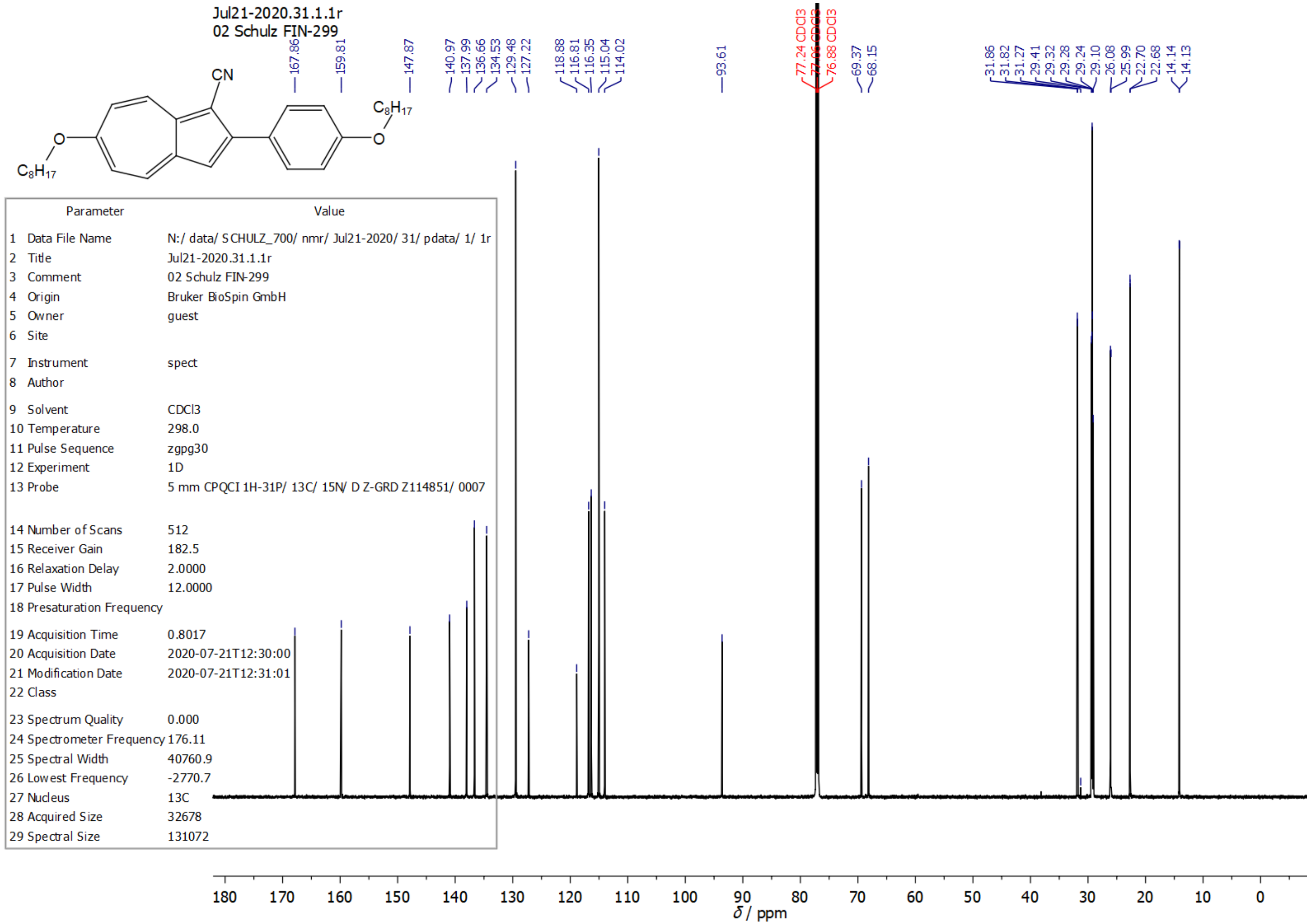
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114851/ 0007
14	Number of Scans	512
15	Receiver Gain	182.5
16	Relaxation Delay	2.0000
17	Pulse Width	12.0000
18	Presaturation Frequency	
19	Acquisition Time	0.8017
20	Acquisition Date	2020-03-19T12:42:00
21	Modification Date	2020-03-19T12:42:13
22	Class	
23	Spectrometer Frequency	176.11
24	Spectral Width	40760.9
25	Lowest Frequency	-2770.7
26	Nucleus	13C
27	Acquired Size	32678
28	Spectral Size	131072

Figure S20: ^{13}C NMR spectrum of compound **16O-AzCN-Br**



Parameter	Value
1 Data File Name	N:/ data/ SCHULZ_700/ nmr/ Jul21-2020/ 30/ fid
2 Title	Jul21-2020.30.fid
3 Comment	02 Schulz FIN-299
4 Origin	Bruker BioSpin GmbH
5 Owner	guest
6 Site	
7 Instrument	spect
8 Author	
9 Solvent	CDCl3
10 Temperature	298.0
11 Pulse Sequence	zg
12 Experiment	1D
13 Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114851/ 0007
14 Number of Scans	16
15 Receiver Gain	7.9
16 Relaxation Delay	2.0000
17 Pulse Width	8.1500
18 Presaturation Frequency	
19 Acquisition Time	3.1195
20 Acquisition Date	2020-07-21T12:04:00
21 Modification Date	2020-07-21T12:04:17
22 Class	
23 Spectrum Quality	0.000
24 Spectrometer Frequency	700.36
25 Spectral Width	10504.2
26 Lowest Frequency	-1977.2
27 Nucleus	1H
28 Acquired Size	32768
29 Spectral Size	65536

Figure S21: ^1H NMR spectrum of compound **8O-AzCN-PhO8**



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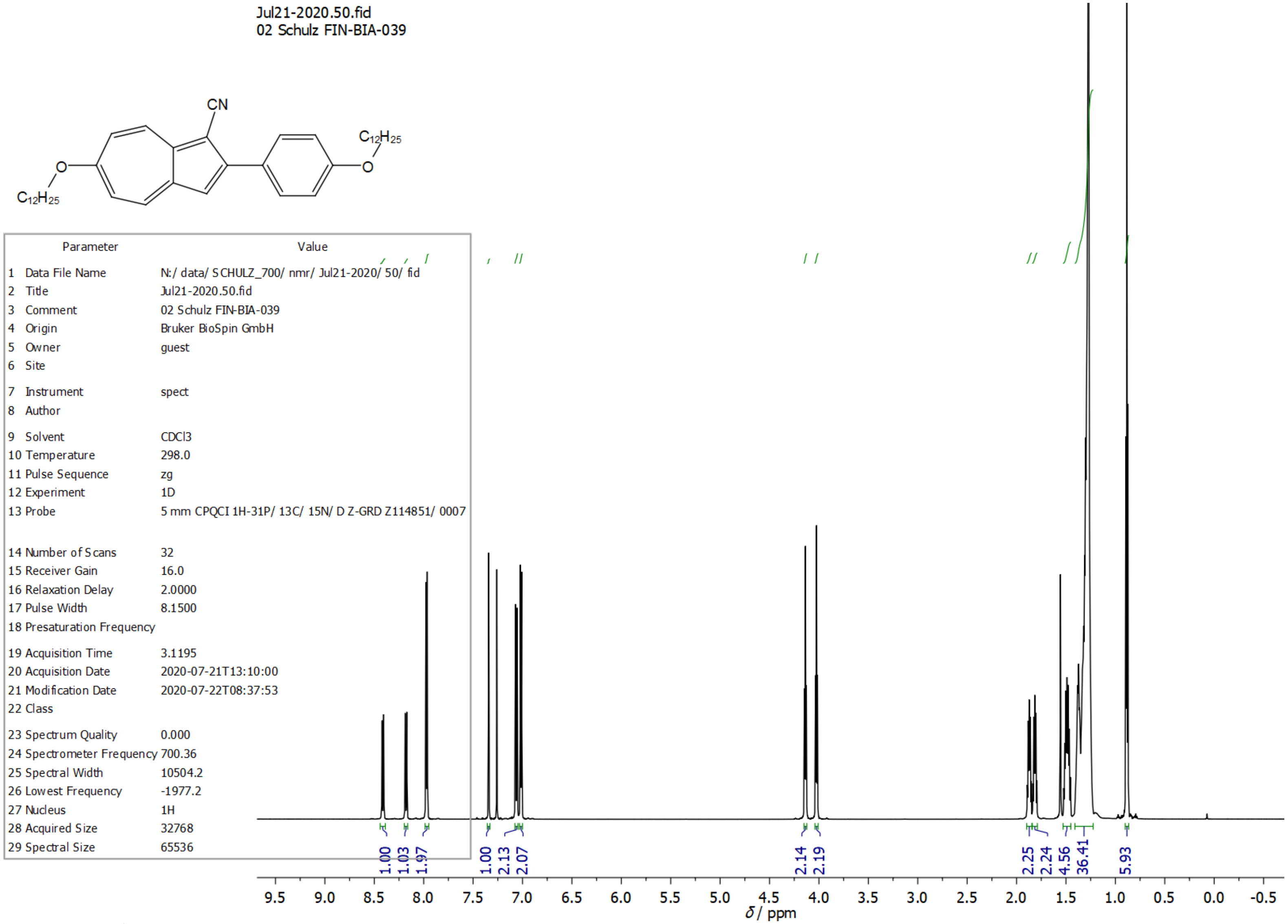
1	Data File Name	N:/ data/ SCHULZ_700/ nmr/ Jul21-2020/ 31/ pdata/ 1/ 1r
2	Title	Jul21-2020.31.1.1r
3	Comment	02 Schulz FIN-299
4	Origin	Bruker BioSpin GmbH
5	Owner	guest
6	Site	
7	Instrument	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.0
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114851/ 0007
14	Number of Scans	512
15	Receiver Gain	182.5
16	Relaxation Delay	2.0000
17	Pulse Width	12.0000
18	Presaturation Frequency	
19	Acquisition Time	0.8017
20	Acquisition Date	2020-07-21T12:30:00
21	Modification Date	2020-07-21T12:31:01
22	Class	
23	Spectrum Quality	0.000
24	Spectrometer Frequency	176.11
25	Spectral Width	40760.9
26	Lowest Frequency	-2770.7
27	Nucleus	13C
28	Acquired Size	32678
29	Spectral Size	131072

Figure S22: ^{13}C NMR spectrum of compound **8O-AzCN-PhO8**



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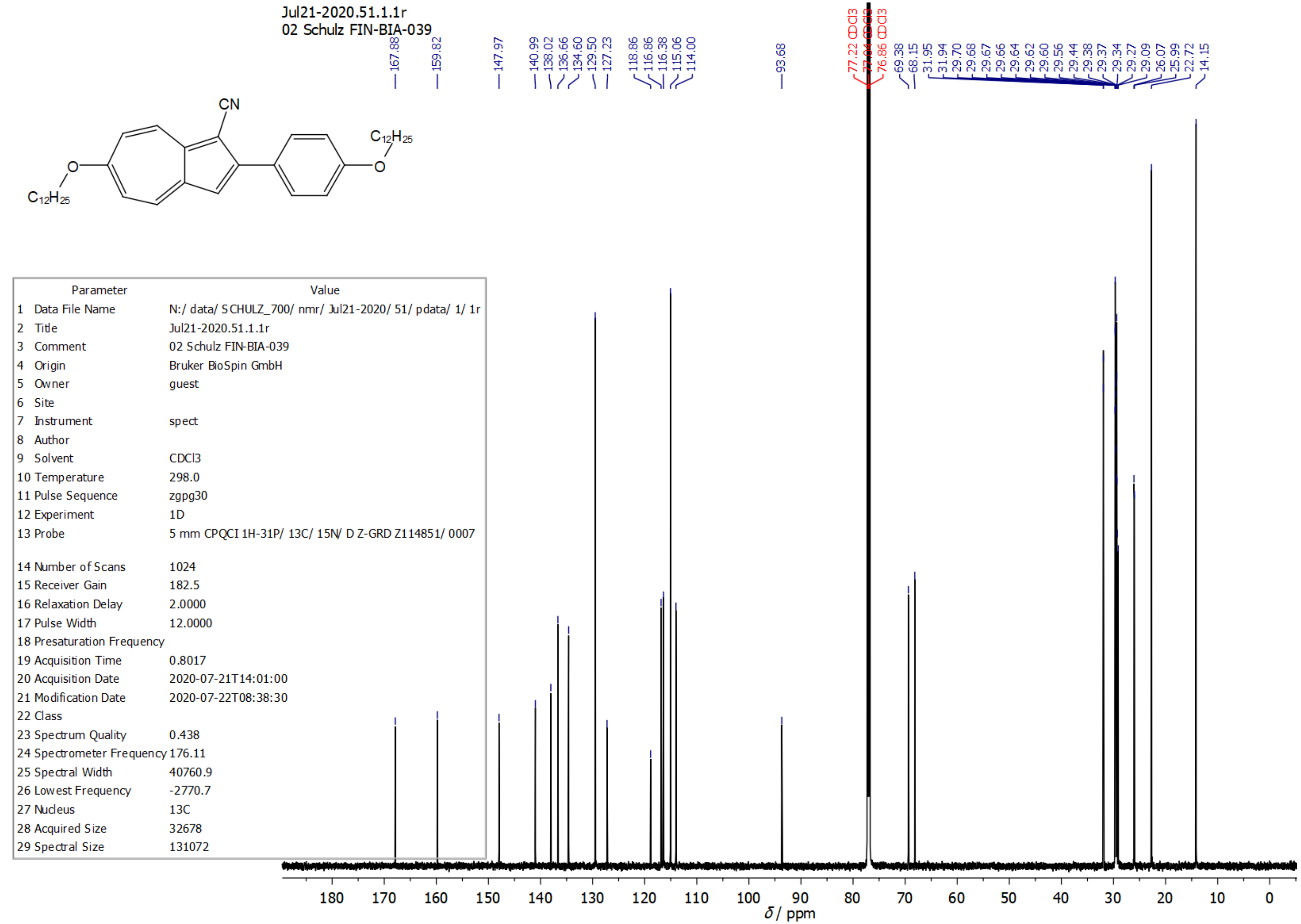
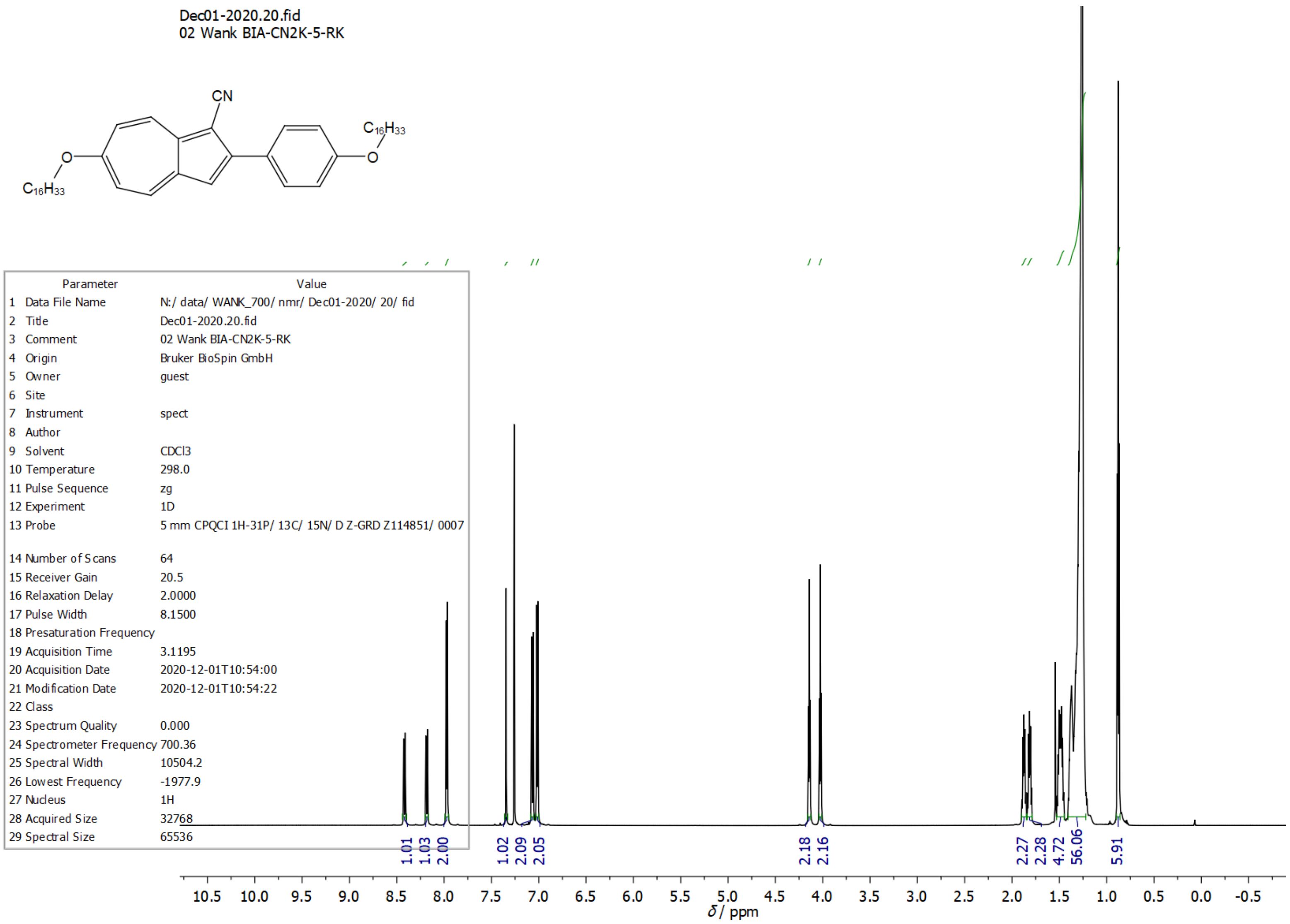
1	Data File Name	N:/ data/ SCHULZ_700/ nmr/ Jul21-2020/ 50/ fid
2	Title	Jul21-2020.50.fid
3	Comment	02 Schulz FIN-BIA-039
4	Origin	Bruker BioSpin GmbH
5	Owner	guest
6	Site	
7	Instrument	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.0
11	Pulse Sequence	zg
12	Experiment	1D
13	Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114851/ 0007
14	Number of Scans	32
15	Receiver Gain	16.0
16	Relaxation Delay	2.0000
17	Pulse Width	8.1500
18	Presaturation Frequency	
19	Acquisition Time	3.1195
20	Acquisition Date	2020-07-21T13:10:00
21	Modification Date	2020-07-22T08:37:53
22	Class	
23	Spectrum Quality	0.000
24	Spectrometer Frequency	700.36
25	Spectral Width	10504.2
26	Lowest Frequency	-1977.2
27	Nucleus	1H
28	Acquired Size	32768
29	Spectral Size	65536

Figure S23: ^{1}H NMR spectrum of compound **12O-AzCN-PhO12**



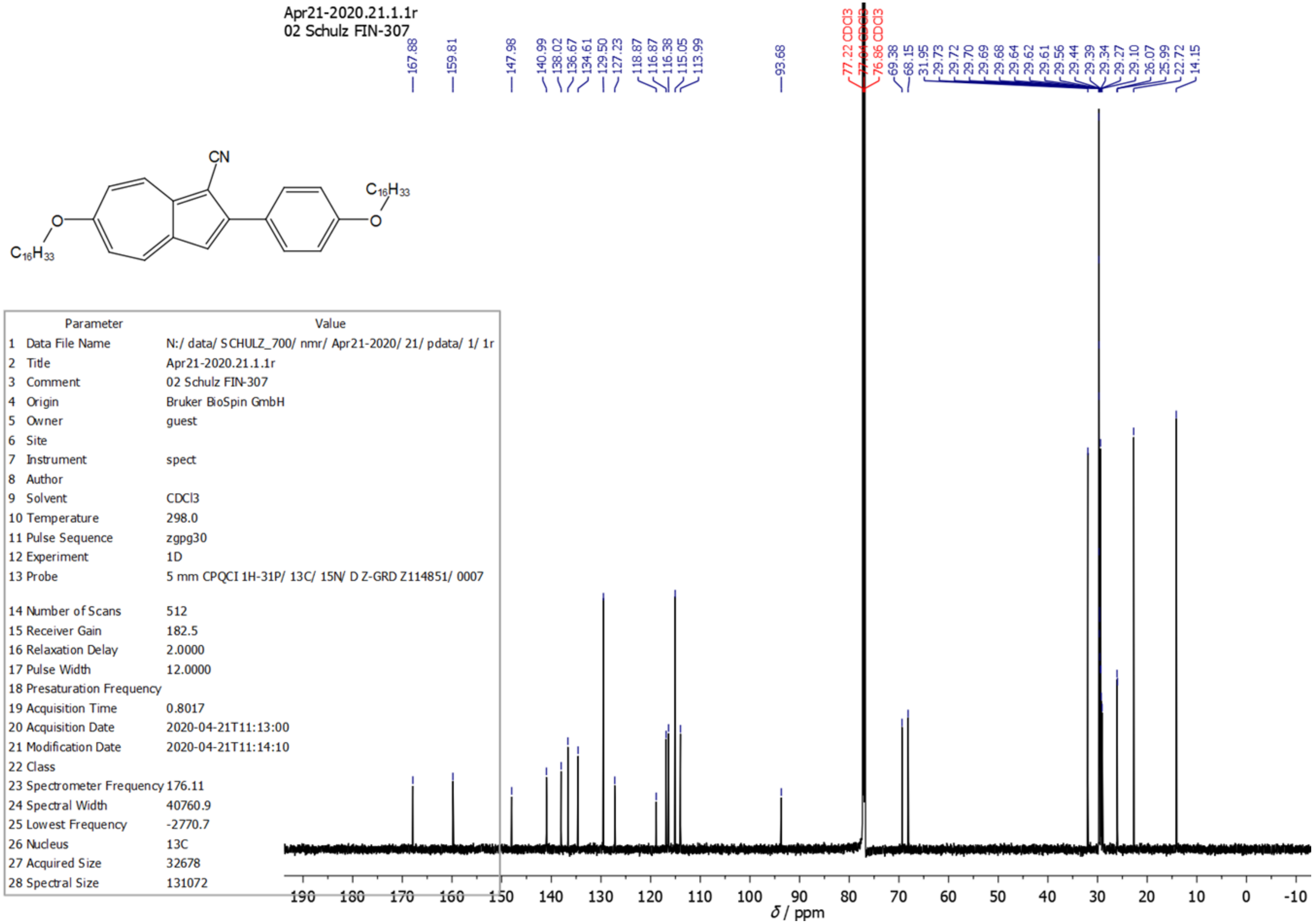
	Parameter	Value
1	Data File Name	N:/ data/ SCHULZ_700/ nmr/ Jul21-2020/ 51/ pdata/ 1/ 1r
2	Title	Jul21-2020.51.1.1r
3	Comment	02 Schulz FIN-BIA-039
4	Origin	Bruker BioSpin GmbH
5	Owner	guest
6	Site	
7	Instrument	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.0
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114851/ 0007
14	Number of Scans	1024
15	Receiver Gain	182.5
16	Relaxation Delay	2.0000
17	Pulse Width	12.0000
18	Presaturation Frequency	
19	Acquisition Time	0.8017
20	Acquisition Date	2020-07-21T14:01:00
21	Modification Date	2020-07-22T08:38:30
22	Class	
23	Spectrum Quality	0.438
24	Spectrometer Frequency	176.11
25	Spectral Width	40760.9
26	Lowest Frequency	-2770.7
27	Nucleus	13C
28	Acquired Size	32678
29	Spectral Size	131072

Figure S24: ^{13}C NMR spectrum of compound **12O-AzCN-PhO12**



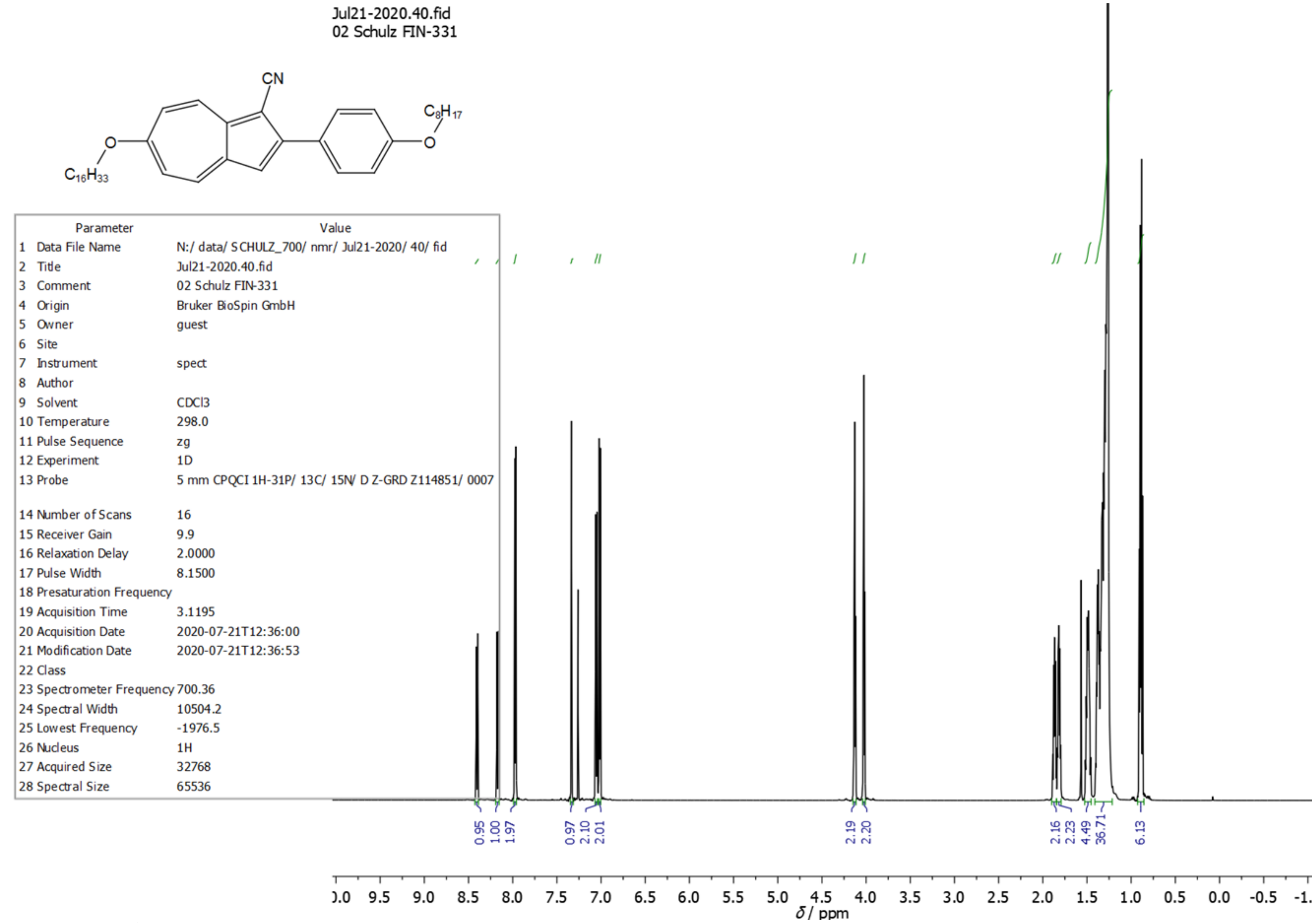
Parameter	Value
1 Data File Name	N:/ data/ WANK_700/ nmr/ Dec01-2020/ 20/ fid
2 Title	Dec01-2020.20.fid
3 Comment	02 Wank BIA-CN2K-5-RK
4 Origin	Bruker BioSpin GmbH
5 Owner	guest
6 Site	
7 Instrument	spect
8 Author	
9 Solvent	CDCl3
10 Temperature	298.0
11 Pulse Sequence	zg
12 Experiment	1D
13 Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114851/ 0007
14 Number of Scans	64
15 Receiver Gain	20.5
16 Relaxation Delay	2.0000
17 Pulse Width	8.1500
18 Presaturation Frequency	
19 Acquisition Time	3.1195
20 Acquisition Date	2020-12-01T10:54:00
21 Modification Date	2020-12-01T10:54:22
22 Class	
23 Spectrum Quality	0.000
24 Spectrometer Frequency	700.36
25 Spectral Width	10504.2
26 Lowest Frequency	-1977.9
27 Nucleus	1H
28 Acquired Size	32768
29 Spectral Size	65536

Figure S25: ^{1}H NMR spectrum of compound **16O-AzCN-PhO16**



	Parameter	Value
1	Data File Name	N:/ data/ SCHULZ_700/ nmr/ Apr21-2020/ 21/ pdata/ 1/ 1r
2	Title	Apr21-2020.21.1.1r
3	Comment	02 Schulz FIN-307
4	Origin	Bruker BioSpin GmbH
5	Owner	guest
6	Site	
7	Instrument	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.0
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114851/ 0007
14	Number of Scans	512
15	Receiver Gain	182.5
16	Relaxation Delay	2.0000
17	Pulse Width	12.0000
18	Presaturation Frequency	
19	Acquisition Time	0.8017
20	Acquisition Date	2020-04-21T11:13:00
21	Modification Date	2020-04-21T11:14:10
22	Class	
23	Spectrometer Frequency	176.11
24	Spectral Width	40760.9
25	Lowest Frequency	-2770.7
26	Nucleus	13C
27	Acquired Size	32678
28	Spectral Size	131072

Figure S26: ^{13}C NMR spectrum of compound **16O-AzCN-PhO16**



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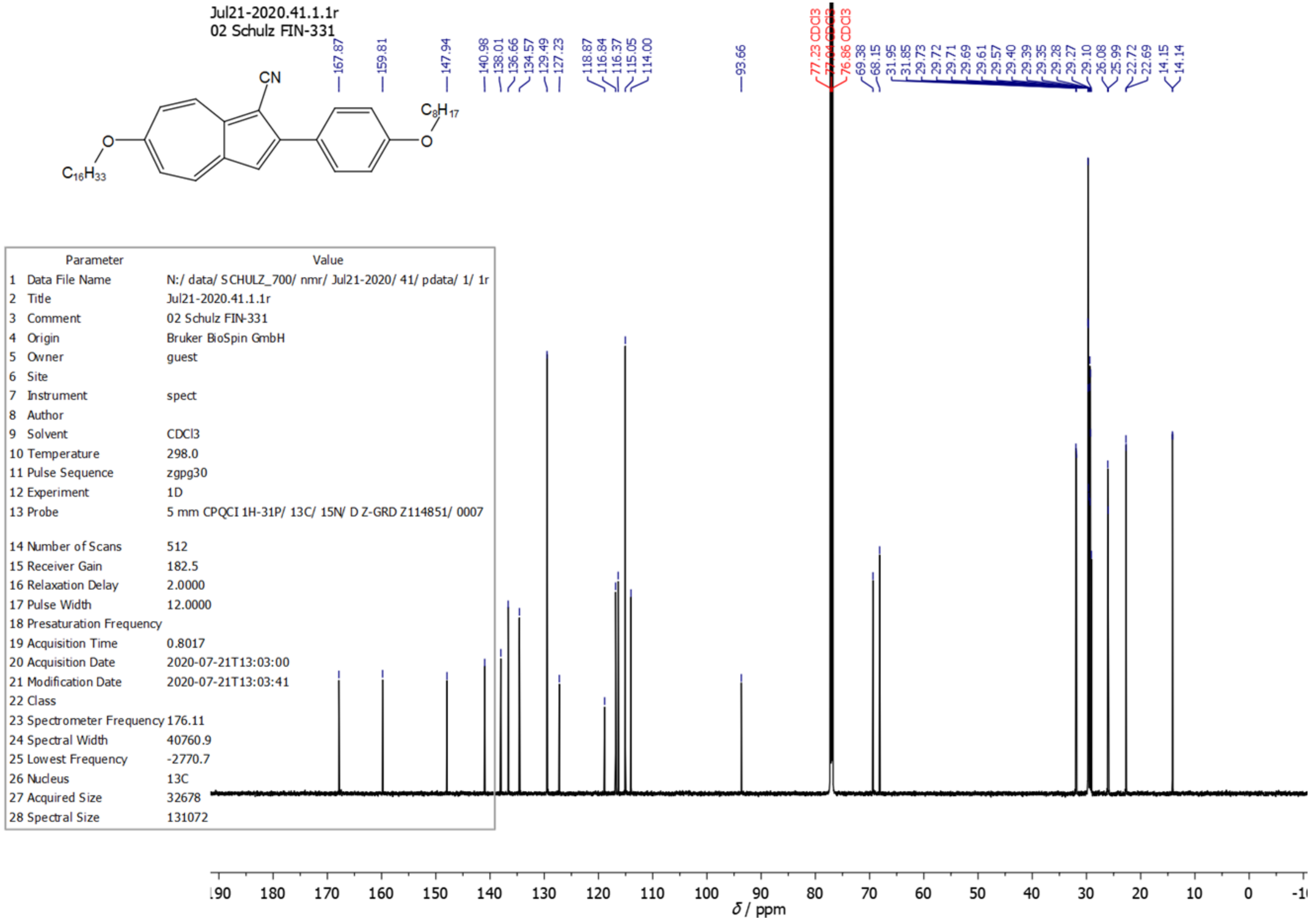
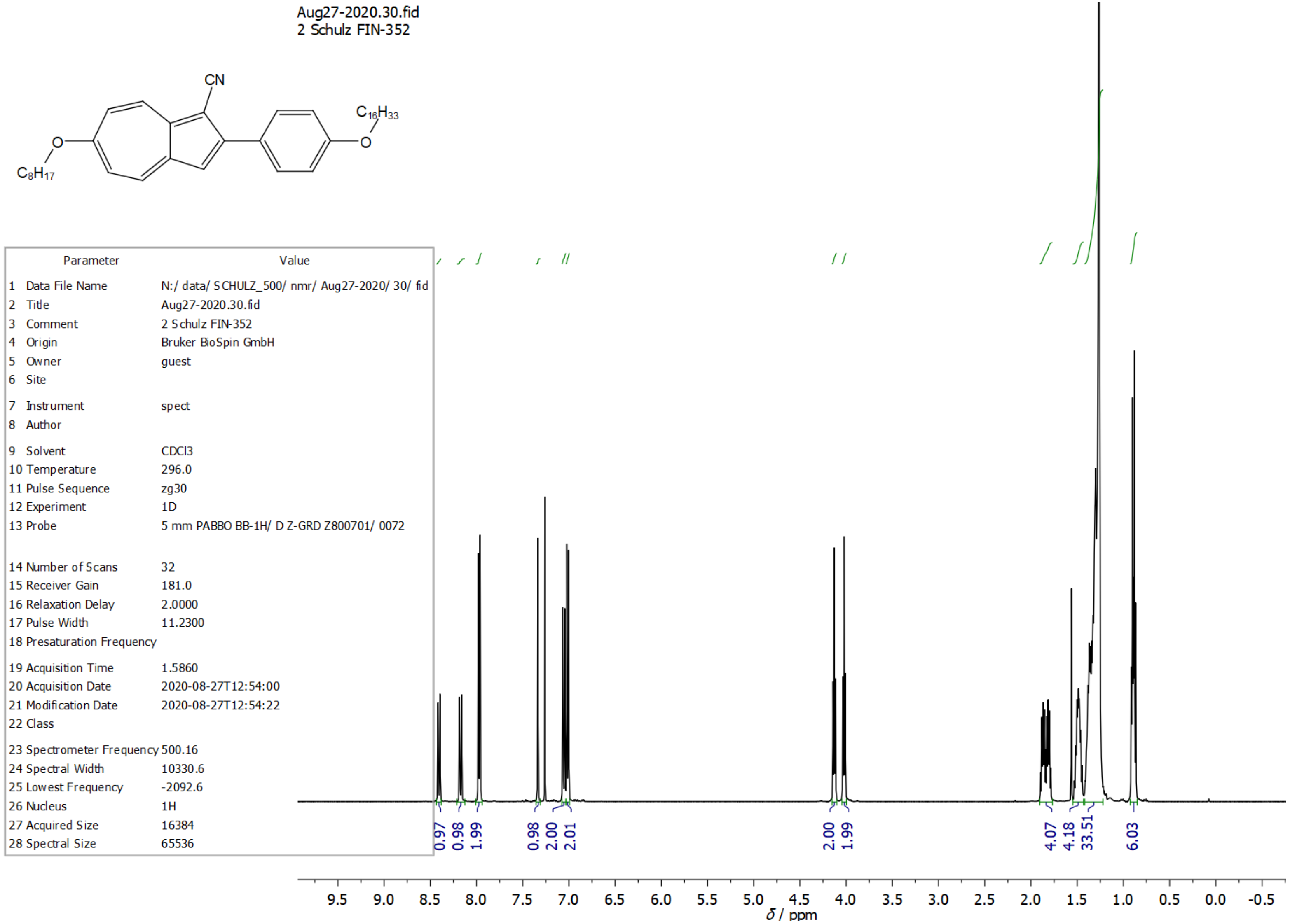
1	Data File Name	N:/ data/ SCHULZ_700/ nmr/ Jul21-2020/ 40/ fid
2	Title	Jul21-2020.40.fid
3	Comment	02 Schulz FIN-331
4	Origin	Bruker BioSpin GmbH
5	Owner	guest
6	Site	
7	Instrument	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.0
11	Pulse Sequence	zg
12	Experiment	1D
13	Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114851/ 0007
14	Number of Scans	16
15	Receiver Gain	9.9
16	Relaxation Delay	2.0000
17	Pulse Width	8.1500
18	Presaturation Frequency	
19	Acquisition Time	3.1195
20	Acquisition Date	2020-07-21T12:36:00
21	Modification Date	2020-07-21T12:36:53
22	Class	
23	Spectrometer Frequency	700.36
24	Spectral Width	10504.2
25	Lowest Frequency	-1976.5
26	Nucleus	1H
27	Acquired Size	32768
28	Spectral Size	65536

Figure S27: ^{1}H NMR spectrum of compound **16O-AzCN-PhO8**



	Parameter	Value
1	Data File Name	N:/ data/ SCHULZ_700/ nmr/ Jul21-2020/ 41/ pdata/ 1/ 1r
2	Title	Jul21-2020.41.1.1r
3	Comment	02 Schulz FIN-331
4	Origin	Bruker BioSpin GmbH
5	Owner	guest
6	Site	
7	Instrument	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.0
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114851/ 0007
14	Number of Scans	512
15	Receiver Gain	182.5
16	Relaxation Delay	2.0000
17	Pulse Width	12.0000
18	Presaturation Frequency	
19	Acquisition Time	0.8017
20	Acquisition Date	2020-07-21T13:03:00
21	Modification Date	2020-07-21T13:03:41
22	Class	
23	Spectrometer Frequency	176.11
24	Spectral Width	40760.9
25	Lowest Frequency	-2770.7
26	Nucleus	13C
27	Acquired Size	32678
28	Spectral Size	131072

Figure S28: ^{13}C NMR spectrum of compound **16O-AzCN-PhO8**



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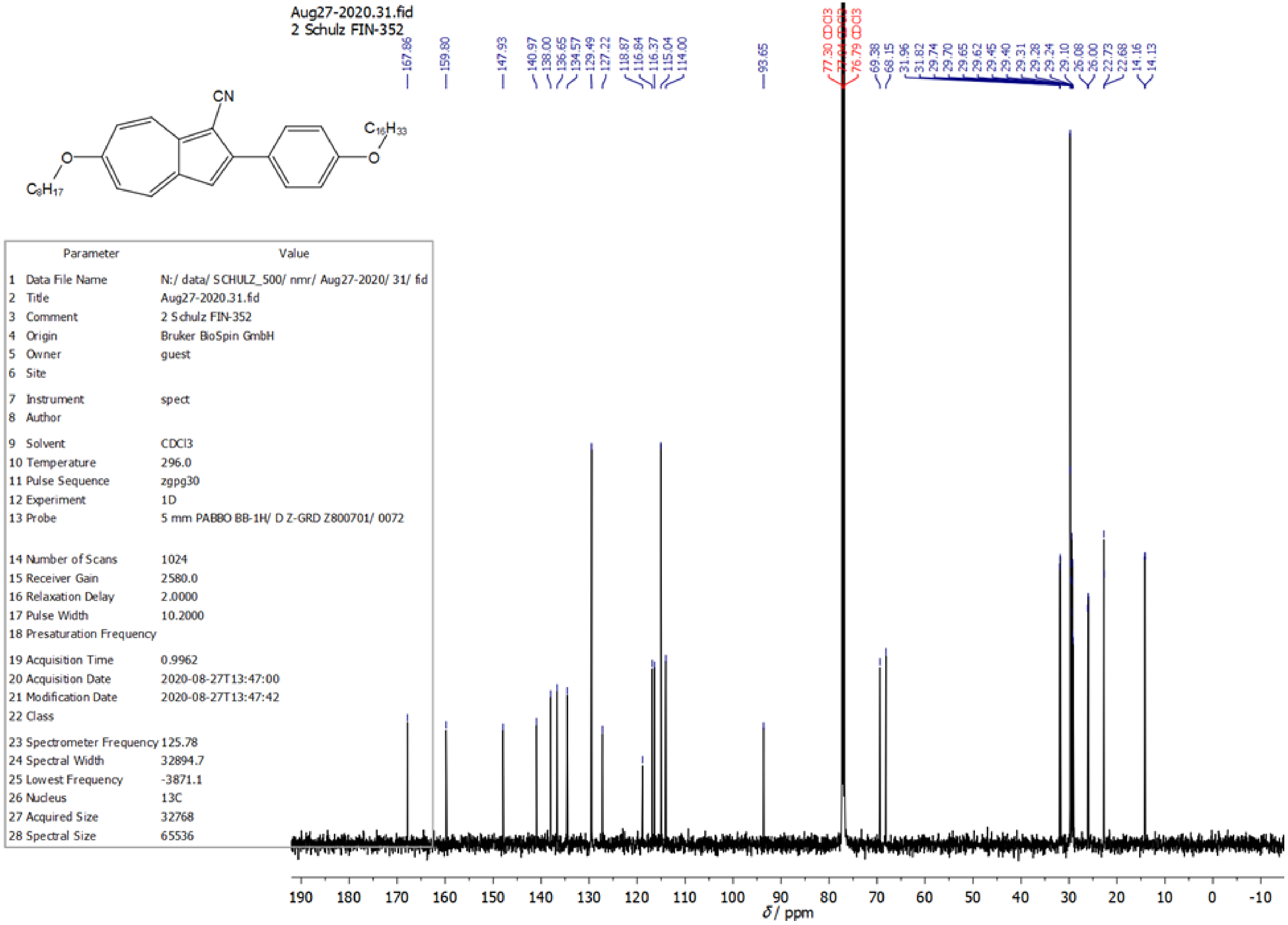
1	Data File Name	N:/ data/ SCHULZ_500/ nmr/ Aug27-2020/ 30/ fid
2	Title	Aug27-2020.30.fid
3	Comment	2 Schulz FIN-352
4	Origin	Bruker BioSpin GmbH
5	Owner	guest
6	Site	
7	Instrument	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	296.0
11	Pulse Sequence	zg30
12	Experiment	1D
13	Probe	5 mm PABBO BB-1H/ D Z-GRD Z800701/ 0072
14	Number of Scans	32
15	Receiver Gain	181.0
16	Relaxation Delay	2.0000
17	Pulse Width	11.2300
18	Presaturation Frequency	
19	Acquisition Time	1.5860
20	Acquisition Date	2020-08-27T12:54:00
21	Modification Date	2020-08-27T12:54:22
22	Class	
23	Spectrometer Frequency	500.16
24	Spectral Width	10330.6
25	Lowest Frequency	-2092.6
26	Nucleus	1H
27	Acquired Size	16384
28	Spectral Size	65536

Figure S29: ^{1}H NMR spectrum of compound **8O-AzCN-PhO16**



	Parameter	Value
1	Data File Name	N:/ data/ SCHULZ_500/ nmr/ Aug27-2020/ 31/ fid
2	Title	Aug27-2020.31.fid
3	Comment	2 Schulz FIN-352
4	Origin	Bruker BioSpin GmbH
5	Owner	guest
6	Site	
7	Instrument	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	296.0
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Probe	5 mm PABBO BB-1H/ D Z-GRD Z800701/ 0072
14	Number of Scans	1024
15	Receiver Gain	2580.0
16	Relaxation Delay	2.0000
17	Pulse Width	10.2000
18	Presaturation Frequency	
19	Acquisition Time	0.9962
20	Acquisition Date	2020-08-27T13:47:00
21	Modification Date	2020-08-27T13:47:42
22	Class	
23	Spectrometer Frequency	125.78
24	Spectral Width	32894.7
25	Lowest Frequency	-3871.1
26	Nucleus	13C
27	Acquired Size	32768
28	Spectral Size	65536

Figure S30: ^{13}C NMR spectrum of compound **8O-AzCN-PhO16**