Supporting Information

Tailoring liquid crystalline self-assembly and de Vries behavior of azulenes via lateral and core substitution

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1. General methods

All chemicals were, unless otherwise stated, used without further purification. If not stated otherwise, reactions were performed under inert conditions with nitrogen as an inert gas. 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 and DSC3 from the company Mettler Toledo were 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 16.01.

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 analyzed with the software SAXS from Bruker. The diffraction patterns were further processed using the software Datasqueeze and Origin

2018Pro. Optical tilt angles were measured by manually rotating the sample and observing the position of maximum darkness of two opposite tilt domains.

2. Syntheses

The following compounds have been synthesized according to the literature: 2,6-dibromoazulene,[1] **12O-Az-Br**,[2] **12OAzCN-Br**,[3] 4-dodecyloxyphenylboronic acid,[4] (4-bromophenyl)(dodecyl)sulfane,[5] (4-(dodecyloxy)-2-methylphenyl) boronic acid,[6] 2-bromo-5-dodecylthiophene,[7] 5 dodecylthienyl-2-boronic acid,[8] 2-(dodecyloxy)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaboro-lane-2-yl)pyrimidine[9].

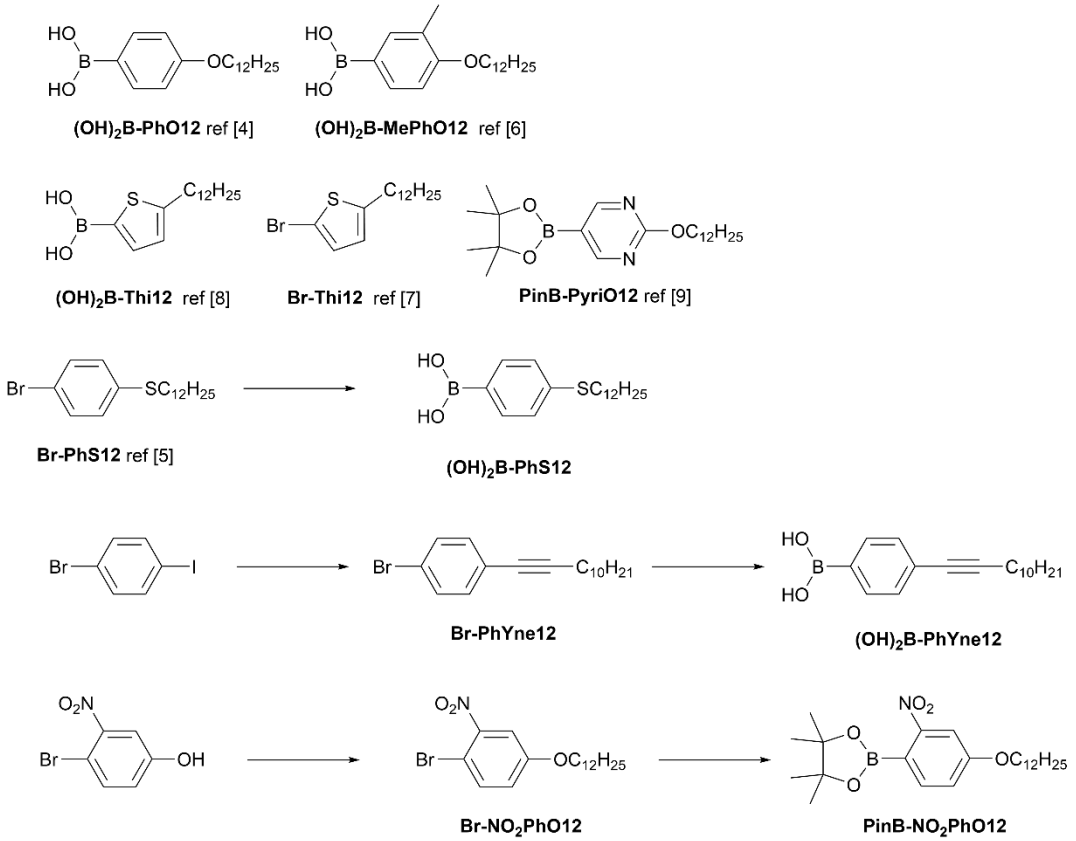


Figure S1: Origin of the coupling partners with the azuelene moeities in Suzuki-Miyaura couplings.

2.1 General Procedures

General procedure for the borylation of bromobenzenes exemplified by (4-dodecylthiophenyl)boronic acid (GP 1)

(4-Bromophenyl)(dodecyl)sulfane (2.93 g, 8.20 mmol) was dissolved in abs. THF (55 mL). At -78 °C *n*-butyllithium (2.5 M in hexane, 4.9 mL, 12.30 mmol) was dropwise added and the reaction was stirred for 30 min. After adding trimethylborate (3.41 g, 32.79 mmol) the mixture was allowed to warm up to room temperature while being stirred for 16 h. Aqueous

HCl (2 M, 50 mL) was added and after 30 min water and CH_2Cl_2 (each 80 mL) were added, and the phases separated. The aqueous phase was extracted with CH_2Cl_2 (2 x 50 mL), and the combined organic phases were washed with water (3 x 100 mL) and dried over $MgSO_4$. After removing the solvent under reduced pressure, the crude product was recrystallized from hexanes to yield 68 % (1.80 g, 5.58 mmol) of a white solid.

General procedure for the Miyaura coupling of arylbromides to pinacolatobronoates exemplified by 2-(4-(dodecyloxy)-2-nitrophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (GP 2)

1-Bromo-4-(dodecyloxy)-2-nitrobenzene (1.00 g, 2.59 mmol), bis(pinacolato)diboron (1.07 g, 5.18 mmol), $Pd(dppf)Cl_2$ (379 mg, 518 µmol) and potassium acetate (0.97 g, 9.84 mmol) were dissolved in dioxane (500 mL).[9] Nitrogen gas was bubbled through the reaction mixture with a syringe for 30 min and the reaction was refluxed for 16 h. After cooling down to room temperature the solvent was removed under reduced pressure. The crude mixture was purified by column chromatography on silica gel (hexanes / CH_2Cl_2 4 / 1 → 1 / 1) to afford the product as a yellow oil in 14 % yield (157 mg, 362 µmol)

General procedure for the nitrile substitution of 2-bromoazulenes *via* Vilsmeier-Haack reaction exemplified by 12S-AzCN-Br (GP 3)

$POCl_3$ (33 µL, 354 µmol) was slowly added to dry DMF (4 mL) at 0 °C. The solution was then stirred for 30 min. **12S-Az-Br** (131 mg, 322 µmol) in dry CH_2Cl_2 (15 mL) was cooled down to 0 °C and then added slowly to the reaction mixture.[10] After warming up to room temperature overnight, aq. ammonia (30 Vol-%, 10 mL) was added dropwise. Subsequently, iodine (163 mg, 643 µmol) was added, and the reaction was stirred vigorously for 4 h, and quenched with water (20 mL). After phase separation, the organic phase was washed with sat. $NaHSO_3$ solution and water (each 2 x, 20 mL) and dried over $MgSO_4$. The solution was filtered over a silica pad. Careful elution of the violet spot with CH_2Cl_2, without simultaneously eluting the more polar red spot afforded the pure **12S-AzCN-Br** as a violet solid in 94 % yield (130 mg, 300 µmol).

General procedure for the Sonogashira coupling of 6-bromo-azulenes with dodecyne exemplified by 12Yne-Az-Br (GP4)

Br-Az-Br (100 mg, 349 µmol), 1-dodecyne (58 mg, 75 µl, 350 mmol), CuI (7 mg, 38 µmol), $Pd(PPh_3)_4$ (20 mg, 17 µmol) and triethylamine (2.6 ml) were suspended in toluene (10 mL).[11] Nitrogen gas was bubbled through the reaction mixture with a syringe for 30 min

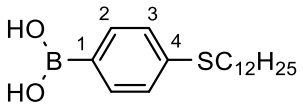
and the reaction was stirred at room temperature for 16 h. Afterwards, the suspension was washed with aqueous NH_4Cl (5 wt%, 3 x 30 mL) and water (2 x 30 mL), dried over $MgSO_4$ and the solvent was removed under reduced pressure. Flash column chromatography on silica gel (hexanes) yielded in the product as a blue sold (85 %, 111 mg, 298µmol).

General Procedure for the Suzuki coupling of 2-bromoazulenes with aryl boronic acids or pincaolato boronates exemplified by 12O-AzCN-PhS12 (GP5)

C12O-AzCN-Br (50 mg, 77 µmol), (4-dodecylthiophenyl)boronic acid (77 mg, 240 µmol), and Cs_2CO_3 (78 mg, 240 mmol) were dissolved in dioxane (10 mL). Nitrogen gas was bubbled through the reaction mixture with a syringe for 30 min, then $Pd(PPh_3)_4$ (14 mg, 12 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 gel (hexanes / CH_2Cl_2 1 / 1) and subsequent recrystallization from ethyl acetate. The product was obtained as a red solid in 94 % yield (69 mg, 112 µmol).

2.2 Syntheses

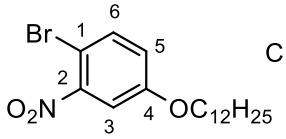
(4-Dodecylthiophenyl)boronic acid



$C_{18}H_{31}BO_2S$
(322.31)

Synthesis according to GP1; (4-Bromophenyl)(dodecyl)sulfane (2.93 g, 8.20 mmol), *n*-butyllithium (4.9 mL, 2.5 M in hexane, 12.30 mmol); trimethylborate (3.41 g, 32.79 mmol); purification: recrystallization from hexanes; yield: white solid (68 %, 1.80 g, 5.58 mmol); melting point (POM): 87 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3H, CH_3), 1.22–1.37 (m, 16H, CH_2), 1.42–1.50 (m, 2H, $SCH_2CH_2CH_2$), 1.72 (tt, J = 7.5 Hz, 7.4 Hz, 2H, SCH_2CH_2), 3.01 (t, J = 7.4 Hz, 2H, SCH_2), 7.35–7.38 (m, 2H, 3-H), 8.04–8.12 (m, 2H, 2-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (CH_3), 22.7, 29.0, 29.0, 29.2, 29.4, 29.5, 29.6, 29.7, 29.7, 31.9 (CH_2), 32.2 (SCH_2), 126.4 (C-3), 135.9 (C-2), 143.6 (C-4) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3398 (w), 2950 (w), 2916 (m), 2849 (m), 1592 (m), 1544 (w), 1469 (w), 1455 (w), 1397 (m), 1346 (s), 1312 (m), 1183 (w), 1112 (w), 1095 (m), 1073 (w), 1014 (w), 822 (w), 777 (w), 738 (m), 719 (w), 687 (m), 645 (w), 484 (w), 471 (w), 455 (w) cm^{-1}; MS (ESI): *m/z* for $C_{18}H_{30}BO_2S^-$ calc.: 321.21 [M-H]$^-$, found: 321.21; HRMS (ESI): *m/z* for $C_{18}H_{30}BO_2S^-$ calc.: 321.2068 [M-H]$^-$, found: 321.2068.

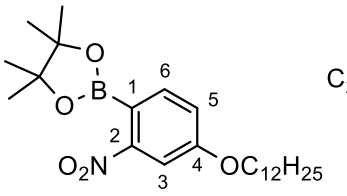
1-Bromo-4-dodecyloxy-2-nitrobenzene



$C_{18}H_{28}BrNO_3$
(386.33)

3-Bromo-4-nitrophenol (2.00 g, 9.17 mmol), potassium carbonate (3.80 g, 27.52 mmol) and dodecyl bromide (2.29 g, 9.17 mmol) were dissolved in MeCN (70 mL) and the reaction mixture was heated to 85 °C and stirred for 16 h. Afterwards, water (50 ml) was added. The mixture was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phases were washed with water (2 x 70 mL) and brine (70 mL), dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The target compound was received as brown crystals without further purification in 83 % yield (2.95 g, 7.64 mmol). Melting point (POM): 47 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 3H, CH_3), 1.18–1.50 (m, 18H, CH_2), 1.79 (tt, J = 6.9 Hz, 6.7 Hz, 2H, OCH_2CH_2), 3.97 (t, J = 6.7 Hz, 2H, OCH_2), 6.97 (dd, J = 8.9 Hz, 2.9 Hz, 1H, 5-H), 7.36 (d, J = 2.9 Hz, 1H, 3-H), 7.58 (d, J = 8.9 Hz, 1H, 6-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (CH_3), 22.7, 25.9, 28.9, 29.3, 29.4, 29.5, 29.6, 29.7, 29.7, 31.9 (CH_2), 69.1 (OCH_2), 104.3 (C-1), 111.3 (C-3), 120.4 (C-5), 135.4 (C-6), 150.51 (C-2) 158.8 (C-4) ppm; FT-IR (ATR): $\tilde{\nu}$ =2923 (s), 2853 (m), 2171 (w), 2140 (w), 1743 (m), 1602 (w), 1568 (w), 1538 (s), 1466 (m), 1352 (m), 1302 (m), 1270 (m), 1232 (m), 1184 (m), 1114 (m), 1020 (m), 851 (w), 811 (w), 750 (w), 722 (w), 683 (w), 643 (w), 503 (w) cm^{-1}; MS(ESI): *m/z* for $C_{18}H_{28}BrNO_3Na^+$ calc.: 408.11 $[M+Na]^+$, found: 408.11; HRMS(ESI): *m/z* for $C_{18}H_{28}BrNO_3Na^+$ calc.: 408.1145 $[M+Na]^+$, found: 408.1143.

2-(4-(Dodecyloxy)-2-nitrophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

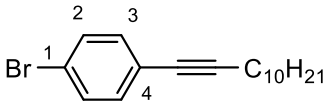


$C_{24}H_{40}BNO_5$
(433.40)

Synthesis according to GP2; 1-bromo-4-(dodecyloxy)-2-nitrobenzene (1.00 g, 2.59 mmol), bis(pinacolato)diboron (1.07 g, 5.18 mmol), Pd(dppf)Cl_2 (379 mg, 518 µmol), potassium acetate (0.97 g, 9.84 mmol), dioxane (500 mL); purification: column chromatography on silica gel (hexanes / CH_2Cl_2 4 / 1 → 1 / 1); yield: yellow oil (14 %, 157 mg, 362 µmol); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.7 Hz, 3H, CH_3), 1.19–1.37 (m, 18H, CH_2), 1.41 (s, 12H, CCH_3), 1.80 (tt, J = 6.7 Hz, 6.5 Hz, 2H, OCH_2CH_2), 4.01 (t, J = 6.5 Hz, 2H, OCH_2), 7.17 (dd, J = 8.2 Hz, 2.4 Hz, 1H, 6-H), 7.43 (d, J = 8.2 Hz, 1H, 6-H), 7.62 (d, J = 2.4 Hz,

1H, 3-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 24.6, 24.7, 25.9, 29.0, 29.4, 29.6, 29.6, 29.7, 29.7, 31.0, 31.9 (CH_2), 68.7 (OCH_2), 84.4 $(CH_3)_2CO$), 108.4 (C-3), 120.9 (C-5), 133.8 (C-6), 152.5 (C-2), 160.5 (C-4) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2923 (m), 2853 (m), 2164 (w), 1624 (w), 1561 (w), 1531 (s), 1504 (w), 1466 (w), 1380 (m), 1352 (s), 1318 (m), 1266 (m), 1228 (m), 1144 (m), 1103 (m), 1021 (w), 962 (w), 856 (m), 821 (w), 763 (w), 721 (w), 670 (w), 658 (w), 631 (w), 576 (w), 422 (w) cm^{-1}; MS(ESI): *m/z* for $C_{24}H_{40}BNO_5Na^+$ calc.: 455.29 $[M+Na]^+$, found: 455.29; HRMS(ESI): *m/z* for $C_{24}H_{40}BNO_5Na^+$ calc.: 455.2928 $[M+Na]^+$, found: 455.2919.

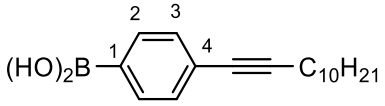
4-(Dodec-1-yne)-bromobenzene



$C_{18}H_{25}Br$
321.30 g/mol

4-Bromoiodobenzene (1.00 g, 3.53 mmol), CuI (27 mg, 0.14 mmol), 1-dodecyne (705 mg, 4.24 mmol) and $Pd(PPh_3)_4$ were dissolved in dry DMF (2 mL).[12] After nitrogen gas was bubbled through the reaction mixture with a syringe for 30 min, freshly distilled diethyl amine (4 mL) was added, and the reaction was warmed to 40 °C for 16 h. Subsequently, sat. NH_4Cl solution (20 mL) was added, and the mixture was extracted with Et_2O (3 x 20 mL). The combined organic phases were dried ($MgSO_4$), and the solvent was removed under reduced pressure. Final purification was performed by column chromatography on silica gel (hexanes, R_f = 0.7) to give the target compound in 72 % yield as a yellow oil (812 mg, 2.53 mmol). ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.26–1.33 (m, 12H, CH_2), 1.40–1.46 (m, 2H, C≡C$CH_2CH_2CH_2$), 1.59 (tt, *J* = 7.2 Hz, 7.2 Hz, 2H, C≡CCH_2CH_2), 2.38 (t, *J* = 7.2 Hz, 2H, C≡CCH_2), 7.23–7.26 (m, 2H, 3-H), 7.38–7.42 (m, 2H, 2-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.3 (CH_3), 19.6 (C≡CCH_2), 22.8, 28.8, 29.1, 29.3, 29.5, 29.7, 29.7, 32.1 (CH_2), 79.7 (4-*C*≡C), 92.0 (4-C≡*C*), 121.7 (C-1), 123.2 (C-4), 131.5 (C-2), 133.2 (C-3) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2924 (s), 2854 (m), 1485 (m), 1465 (w), 1394 (w), 1377 (w), 1330 (w), 1255 (w), 1095 (w), 1071 (w), 1011 (w), 823 (m), 722 (w), 636 (w), 521 (w), 444 (w), 410 (w) cm^{-1}; MS(EI): *m/z* for $C_{18}H_{25}Br^+$ calc.: 320.11 $[M]^+$, found: 320.11; HRMS(EI): *m/z* for $C_{18}H_{25}Br^+$ calc.: 320.1134 $[M]^+$, found: 320.1131.

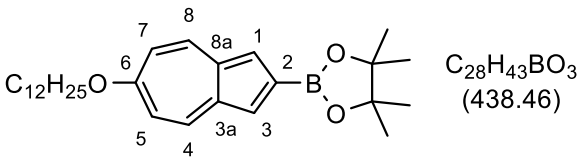
(4-(Dodec-1-yn-1-yl)phenyl)boronic acid



$C_{18}H_{27}BO_2$
(286.22)

Synthesis according to GP1; 4-(Dodec-1-yne)-bromobenzene (812 mg, 2.56 mmol), *n*-butyllithium (1.1 mL, 2.5 M in hexane, 2.81 mmol); trimethylborate (1.1 mL, 10.23 mmol); purification: recrystallization from hexanes; yield: white solid (42 %, 305 mg, 1.07 mmol); Melting point (POM): 135 °C; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.89 (t, J = 6.9 Hz, 3H, CH_3), 1.25–1.35 (m, 12H, CH_2), 1.44–1.50 (m, 2H, C≡C$CH_2CH_2CH_2$), 1.66 (tt, J = 7.3 Hz, 7.2 Hz, 2H, C≡CCH_2CH_2), 2.45 (t, J = 7.2 Hz, 2H, C≡CCH_2), 7.51 (d, J = 7.6 Hz, 2H, 3-H), 8.13 (d, J = 7.6 Hz, 2H, 2-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.2 (CH_3), 19.6 (C≡CCH_2), 22.7, 28.7, 29.0, 29.2, 29.4, 29.6, 29.6, 31.9 (CH_2), 80.8 (4-*C*≡C), 93.2 (4-C≡*C*), 128.5 (C-4), 131.1 (C-3), 133.3 (C-1), 135.4 (C-2) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2921 (w), 2852 (w), 1606 (w), 1402 (m), 1371 (m), 1344 (s), 1307 (m), 1180 (w), 839 (w), 749 (w), 690 (w), 418 (w) cm^{-1}; MS(ESI): *m/z* for $C_{18}H_{27}BO_2Na^+$ calc.: 309.20 $[M+Na]^+$, found: 309.20; HRMS(ESI): *m/z* for $C_{28}H_{27}BO_2Na^+$ calc.: 309.2002 $[M+Na]^+$, found: 309.2000.

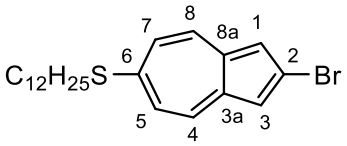
2-(6-(Dodecyloxy)azulen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12O-Az-BPin)



$C_{28}H_{43}BO_3$
(438.46)

Synthesis according to GP2; **12O-Az-Br** (500 mg, 1.28 mmol), bis(pinacolato)diboron (526 mg, 2.55 mmol), Pd(dppf)Cl_2 (187 mg, 256 µmol), potassium acetate (478 mg, 4.85 mmol), dioxane (250 mL); purification: column chromatography on silica gel (hexanes / CH_2Cl_2 1 / 2); yield: violet solid (30 %, 168 mg, 383 µmol); melting point (POM): 28 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, J = 6.8 Hz, 3H, CH_3), 1.19–1.33 (m, 18H, CH_2), 1.36 (s, 12H, CCH_3), 1.78 (tt, J = 6.8 Hz, 6.5 Hz, 2H, OCH_2CH_2), 4.01 (t, J = 6.5 Hz, 2H, OCH_2), 6.67 (d, J = 11.0 Hz, 2H, 5-H, 7-H), 7.62 (s, 2H, 1-H, 3-H), 8.14 (d, J = 11.0 Hz, 2H, 4-H, 8-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (CH_3), 22.8, 24.9, 25.0, 25.1, 26.1, 27.0, 29.2, 29.4, 29.4, 29.6, 29.7, 29.7, 29.7, 32.0 (CH_2), 68.8 (OCH_2), 83.5 ($(CH_3)_2CO$), 110.6 (C-5, C-7), 126.3 (C-1, C-3), 136.3 (C-3a, C-8a), 137.9 (C-4, C-8), 168.3 (C-6) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2976 (w), 2922 (m), 2852 (w), 1578 (m), 1507 (m), 1465 (m), 1413 (w), 1360 (m), 1341 (s), 1308 (m), 1234 (s), 1184 (s), 1079 (w), 1002 (w), 965 (m), 929 (w), 852 (m), 840 (m), 789 (w), 731 (w), 712 (m), 694 (m), 681 (m), 577 (w), 520 (w), 449 (w) cm^{-1}; MS(ESI): *m/z* for $C_{28}H_{44}BO_3^+$ calc.: 439.33 $[M+H]^+$, found: 439.33; HRMS(ESI): *m/z* for $C_{28}H_{44}BO_3^+$ calc.: 439.3383 $[M+H]^+$, found: 439.3378.

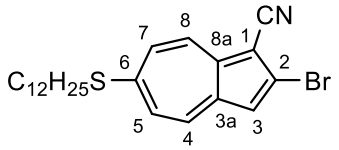
(2-Bromoazulen-6-yl)(dodecyl)sulfane (12S-Az-Br)



$C_{22}H_{31}BrS$
(407.45)

Br-Az-Br (242 mg, 846 µmol) and dodecanethiol (0.8 mL, 3.39 mmol) were dissolved in dry THF (100 mL). NaH (102 mg, 2.54 mol, 60 % on mineral oil) was added and the reaction mixture was heated at 60 °C for 5 h. Afterwards, water (200 mL) was added, the precipitate was filtered off and redissolved in CH_2Cl_2 (30 mL). The organic phase was washed with water and brine (each 30 mL), dried ($MgSO_4$), and the solvent was removed under reduced pressure. **12S-Az-Br** was isolated by column chromatography on silica gel (hexanes) as a violet solid in 56 % yield (192 mg, 471 µmol); melting behavior: Cr 66 °C SmE 101 °C I; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.81 (t, J = 6.9 Hz, 3H, CH_3), 1.13–1.29 (m, 16H, CH_2), 1.37–1.44 (m, 2H, $SCH_2CH_2CH_2$), 1.68 (tt, J = 7.5 Hz, 7.4 Hz, 2H, SCH_2CH_2), 2.99 (t, J = 7.4 Hz, 2H, SCH_2), 7.03–7.06 (m, 2H, 5-H, 7-H), 7.16 (s, 2H, 1-H, 3-H), 7.88–7.94 (m, 2H, 4-H, 8-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 28.4, 29.0, 29.2, 29.4, 29.5, 29.6, 29.6, 31.9 (CH_2), 33.4 (SCH_2), 119.7 (C-1, C-3), 121.8 (C-5, C-7), 125.0 (C-2), 133.2 (C-4, C-8), 137.3 (C-3a, C-8a), 152.1 (C-6) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2955 (w), 2918 (s), 2851 (m), 1782 (w), 1720 (w), 1598 (w), 1577 (w), 1532 (w), 1464 (w), 1438 (w), 1402 (w), 1373 (w), 1283 (w), 1254 (w), 1212 (w), 1171 (w), 1020 (w), 969 (w), 908 (m), 820 (m), 798 (w), 733 (m), 651 (w), 594 (w) cm^{-1}; MS (EI): *m/z* for $C_{22}H_{31}BrS^+$ calc.: 406.1 $[M]^+$, found: 406.1; HRMS (EI): *m/z* for $C_{22}H_{31}BrS^+$ calc.: 406.1330 $[M]^+$, found: 406.1326.

2-Bromo-6-(dodecylthio)azulene-1-carbonitrile (12S-AzCN-Br)

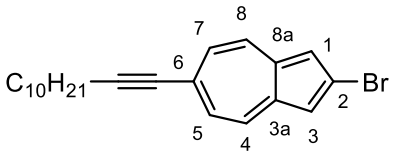


$C_{23}H_{30}BrNS$
(432.46)

Synthesis according to GP3: **12S-Az-Br** (131 mg, 322 µmol), $POCl_3$ (33 µL, 354 µmol), DMF (4 mL), CH_2Cl_2 (16 mL), I_2 (163 mg, 643 µmol), NH_3 (aq, 30 vol%, 10 mL); yield: violet solid (94 %, 130 mg, 300 µmol); melting point: 105 °C; no further purification; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 3H, CH_3), 1.20–1.39 (m, 16H, CH_2), 1.46–1.53 (m, 2H, $SCH_2CH_2CH_2$), 1.78 (tt, J = 7.5 Hz, 7.4 Hz, 2H, SCH_2CH_2), 3.10 (t, J = 7.4 Hz, 2H, SCH_2), 7.18 (s, 1H, C-1), 7.31–7.36 (m, 2H, 5-H, 7-H), 8.04 (d, J = 10.8 Hz, 1H, 4-H), 8.24 (d, J = 10.6 Hz, 1H, 8-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7,

28.0, 29.0, 29.1, 29.4, 29.5, 29.6, 29.6, 31.9 (CH_2), 33.3 (SCH_2), 100.0 (CN), 115.9 (C-2), 120.2 (C-3), 124.5 (C-7), 125.3 (C-5), 126.9 (C-1), 133.1 (C-8), 135.0 (C-4), 138.7 (C-3a), 140.2 (C-8a), 157.6 (C-6) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3115 (w), 2951 (w), 2918 (s), 2849 (m), 2313 (w), 2206 (m), 1571 (m), 1543 (w), 1487 (w), 1465 (w), 1428 (m), 1408 (m), 1393 (s), 1369 (m), 1286 (w), 1240 (w), 1214 (w), 1191 (w), 1127 (w), 1023 (m), 896 (w), 845 (w), 823 (m), 792 (w), 759 (w), 722 (w), 614 (w), 583 (m), 504 (w) cm^{-1}; MS (ESI): *m/z* for $C_{23}H_{31}BrNS^+$ calc.: 432.14 $[M+H]^+$, found: 432.13; HRMS (ESI): *m/z* for $C_{23}H_{31}BrNS^+$ calc.: 432.1355 $[M+H]^+$, found: 432.1343.

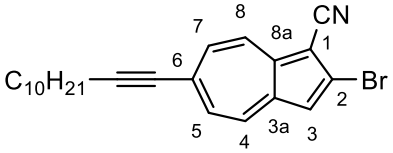
2-Bromo-6-(dodec-1-yn-1-yl)azulene (12Yne-Az-Br)



$C_{22}H_{27}Br$
(371.36)

Synthesis according to GP4: **Br-Az-Br (**100 mg, 349 µmol), 1-Dodecyne (58 mg, 75 µl, 350 mmol), CuI (7 mg, 38 µmol), $Pd(PPh_3)_4$ (20 mg, 17 µmol), triethylamine (2.6 ml); purification: flash column chromatography on silica gel (hexanes); yield: blue solid (85 %, 111 mg, 298 µmol); melting point (POM): 43 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.19–1.40 (m, 12H, CH_2), 1.43–1.51 (m, 2H, C≡C$CH_2CH_2CH_2$), 1.64 (tt, *J* = 7.2 Hz, 7.2 Hz, 2H, C≡CCH_2CH_2), 2.46 (t, *J* = 7.2 Hz, 2H, C≡CCH_2), 7.28 (s, 2H, 1-H, 3-H), 7.33 (d, *J* = 10.3 Hz, 2H, 5-H, 7-H), 8.05–8.11 (m, 2H, 4-H, 8-H) ppm, ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.3 (CH_3), 19.9 (6-C≡CCH_2), 22.8, 28.7, 29.1, 29.2, 29.3, 29.5, 29.7, 29.7, 32.1 (CH_2), 85.4 (6-*C*≡C), 94.9 (6-C≡*C*), 119.6 (C1, C-3), 127.6 (C-2), 128.0 (C-5, C-7), 133.8 (C-4, C-8, C-6), 139.3 (C-3a, C-8a) ppm, FT-IR (ATR): $\tilde{\nu}$ = 2924 (s), 2853 (m), 1570 (m), 1541 (w), 1464 (w), 1438 (w), 1393 (s), 1210 (w), 1073 (w), 1014 (w), 911 (w), 841 (m), 788 (w), 724 (w), 594 (w), 483 (w), 443 (w), 417 (w) cm^{-1}, MS (ESI): *m/z* for $C_{22}H_{26}Br^-$: calc. :371.12 $[M-H]^-$, found: 371.12; MS (ESI): *m/z* for $C_{22}H_{26}Br^-$: calc.: 371.1209 $[M-H]^-$, found: 371.1205.

2-Bromo-6-(dodec-1-yn-1-yl)azulene-1-carbonitrile (12Yne-AzCN-Br)

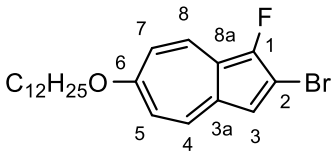


$C_{23}H_{26}BrN$
(396.37)

Synthesis according to GP3: **12Yne-Az-Br** (230 mg, 619 µmol), $POCl_3$ (87 µL, 929 µmol), DMF (15 mL), CH_2Cl_2 (20 mL), I_2 (240 mg, 805 µmol), NH_3 (aq, 30 vol%, 20 mL); purification: column chromatography on silica gel (hexanes / CH_2Cl_2 5 / 1); yield: violet

solid (18 %, 45 mg, 114 µmol); melting point (POM): 60 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 3H, CH_3), 1.21–1.39 (m, 12H, CH_2), 1.42–1.51 (m, 2H, C≡C$CH_2CH_2CH_2$), 1.65 (tt, J = 7.3 Hz, 7.2 Hz, 2H, C≡CCH_2CH_2), 2.49 (t, J = 7.2 Hz, 2H, 6-C≡CCH_2), 7.27 (s, 1H, 3-H), 7.56–7.63 (m, 2H, 5-H, 7-H), 8.17 (d, J = 10.2 Hz, 1H, 4-H), 8.36 (d, J = 10.2 Hz, 1H, 8-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.3 (CH_3), 20.0, 20.0, 22.8, 28.5, 29.1, 29.3, 29.5, 29.7, 29.7, 32.0 (CH_2), 84.9 (6-*C*≡C), 98.9 (6-C≡*C*), 100.2 (C-1), 115.8 (CN), 120.2 (C-3), 129.7 (C-2), 131.8 (C-7), 132.1 (C-5), 133.8 (C-4), 135.8 (C-8), 137.0 (C-6), 141.0 (C-3a), 142.5 (C-8a) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2924 (m), 2852 (w), 1578 (m), 1464 (w), 1435 (w), 1398 (s), 1327 (w), 1290 (w), 1241 (w), 1049 (w), 1016 (w), 909 (w), 848 (w), 806 (w), 731 (w), 649 (w), 622 (w), 499 (w), 434 (w), 416 (w) cm^{-1}; MS (ESI): *m/z* for $C_{23}H_{27}BrN^+$: calc.: 396.13 $[M + H]^+$, found: 396.13; HRMS (ESI): *m/z* for $C_{23}H_{27}BrN^+$: calc.: 396.1321 $[M + H]^+$, found: 396.1312.

2-Bromo-1-fluoro-6-dodecyloxyazulene (12O-AzF-Br)

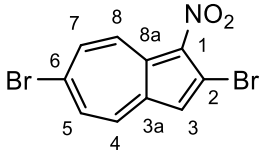


$C_{22}H_{30}BrFO$
(409.38)

Adapting a literature known procedure, **12O-Az-Br** (210 mg, 537 µmol) was dissolved in CH_2Cl_2 (30 mL).[13] Selectfluor (70 mg, 197 µmol) in MeCN (12 mL) was added and the reaction mixture was stirred for 15 min. A saturated solution of $NaHCO_3$ (30 mL) was added, the phases were separated, and the solvent was removed under reduced pressure. Final purification was achieved by column chromatography on silica gel (PE) to yield **12O-AzF-Br** as a violet solid in 48 % yield (106 mg, 259 µmol). Melting point (POM): 67 °C; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.89 (t, J = 7.0 Hz, 3H, CH_3), 1.19–1.42 (m, 16H, CH_2), 1.44–1.51 (m, 2H, $OCH_2CH_2CH_2$), 1.81–1.87 (m, 2H, OCH_2CH_2), 4.07 (t, J = 6.5 Hz, 2H, OCH_2), 6.66 (dd, J = 10.6 Hz, 2.6 Hz, 1H, 7-H), 6.72 (dd, J = 10.9 Hz, 2.6 Hz, 1H, 5-H), 7.03 (d, J = 4.6 Hz, 1H, 3-H), 7.95 (dd, J = 10.6 Hz, 3.1 Hz, 1H, 8-H), 8.08 (d, J = 10.9 Hz, 1H, 4-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.2 (CH_3), 22.7, 26.0, 29.1, 29.4, 29.4, 29.6, 29.6, 29.7, 29.7, 31.9 (CH_2), 69.0 (OCH_2), 106.0 (d, J = 18.6 Hz, C-2), 109.8 (d, J = 3.5 Hz, C-7), 111.9 (d, J = 3.9 Hz, C-5), 114.1 (d, J = 1.4 Hz, C-3), 116.4 (d, J = 9.5 Hz, C-3a), 127.8 (d, J = 5.2 Hz, C-8a), 130.6 (d, J = 3.0 Hz, C-4), 137.1 (d, J = 2.1 Hz, C-8), 148.15 (d, J = 261.8 Hz, C-1), 168.20 (d, J = 2.2 Hz, C-6) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -148.14 (t, J = 3.9 Hz) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2953 (m),

2917 (s), 2850 (s), 1582 (m), 1545 (m), 1509 (m), 1474 (w), 1464 (m), 1434 (w), 1402 (m), 1333 (w), 1293 (w), 1259 (m), 1230 (m), 1199 (s), 1159 (w), 1130 (w), 1033 (m), 993 (w), 975 (w), 900 (w), 837 (m), 813 (w), 763 (w), 728 (w), 707 (w), 682 (w), 604 (w), 522 (w), 461 (w) cm^{-1}; MS (ESI): *m/z* for $C_{22}H_{31}BrFO^+$ calc.: 409.15 $[M+H]^+$, found: 409.15; HRMS (ESI): *m/z* for $C_{22}H_{31}BrFO^+$ calc.: 409.1537 $[M+H]^+$, found: 409.1536.

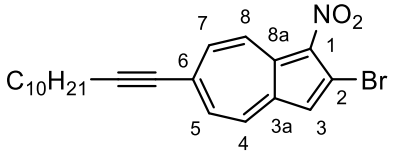
2,6-Dibromo-1-nitroazulene (Br-AzNO$_2$-Br)



$C_{10}H_5Br_2NO_2$
(330.96)

Adapting a literature known procedure,[14] $Cu(NO_3)_2 \cdot 3H_2O$ (358 mg, 1.48 mmol) was suspended in acetic anhydride (2 mL) and treated with an ultrasonic bath for 15 min. The mixture was cooled down to 0 °C and **Br-Az-Br** (212 mg, 0.74 mmol, 0 °C) in Ac_2O (4 mL) was added. After stirring for 30 min, water and CH_2Cl_2 (each 10 mL) were added, and the phases were separated. The organic phase was washed with water and brine (each 10 mL), dried over $MgSO_4$, and the solvent was removed under reduced pressure. Flash column chromatography on silica (hexanes → CH_2Cl_2) afforded **Br-AzNO$_2$-Br** as an orange solid in 91 % yield (223 mg, 0.67 mmol). Melting point (POM): 253 °C; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 7.38 (s, 1H, 3-H), 7.97 (dd, *J* = 10.6 Hz, 2.0 Hz, 1H, 5-H), 8.09 (dd, *J* = 11.0 Hz, 2.0 Hz, 1H, 7-H), 8.14 (d, *J* = 10.6 Hz, 1H, 4-H), 9.32 (d, *J* = 11.0 Hz, 1H, 8-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 121.9 (C-3), 125.3 (C-2), 132.8 (C-3a), 134.1 (C-5), 134.9 (C-7), 135.0 (C-8), 136.9 (C-4), 138.9 (C-6), 139.0 (C-8a) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2922 (m), 2852 (m), 1735 (w), 1568 (w), 1526 (w), 1494 (m), 1466 (w), 1428 (w), 1400 (m), 1359 (m), 1333 (s), 1298 (m), 1269 (w), 1251 (w), 1236 (w), 1191 (m), 1117 (w), 1070 (w), 996 (w), 893 (w), 834 (w), 801 (w), 753 (w), 723 (w), 599 (w), 540 (w) cm^{-1}; MS (EI): *m/z* for $C_{10}H_5Br_2NO_2^+$ calc.: 328.9 $[M]^+$, found.: 328.9; HRMS (EI): *m/z* for $C_{10}H_5Br_2NO_2^+$ calc.: 328.8687 $[M]^+$, found.: 328.8687.

2-Bromo-6-(dodec-1-yn-1-yl)-1-nitroazulene (12Yne-AzNO$_2$-Br)

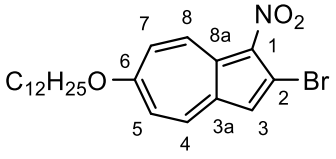


$C_{22}H_{26}BrNO_2$
(416.36)

Synthesis according to GP4: **Br-AzNO$_2$-Br (**175 mg, 529 µmol), 1-Dodecyne (88 mg, 116 µL, 529µmol), CuI (11 mg, 58 µmol), $Pd(PPh_3)_4$ (31 mg, 26 µmol), triethylamine

(4.2 mL); purification: column chromatography on silica gel (hexanes /ethyl acetate 30 / 1); yield: blue solid (16 %, 35 mg, 84 µmol). ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 3H, CH_3), 1.23–1.38 (m, 12H, CH_2), 1.44–1.51 (m, 2H, C≡CCH$_2$CH$_2$C*H*$_2$), 1.66 (tt, J = 7.2 Hz, 7.2 Hz, 2H, C≡CCH$_2$C*H*$_2$), 2.51 (t, J = 7.2 Hz, 2H, 6-C≡CC*H*$_2$), 7.27 (s, 1H, 3-H), 7.68 (dd, J = 10.3 Hz, 1.6 Hz, 1H, 5-H), 7.78 (dd, J = 10.7 Hz, 1.6 Hz, 1H, 7-H), 8.21 (d, J = 10.3 Hz, 1H, 4-H), 9.41 (d, J = 10.7 Hz, 1H, 8-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.3 (CH_3), 20.1 (6-C≡C*C*H$_2$), 22.8, 28.4 (C≡CCH$_2$*C*H$_2$), 29.1 (C≡CCH$_2$CH$_2$*C*H$_2$), 29.2, 29.5, 29.6, 29.7, 32.0 (CH_2), 84.7 (6-*C*≡C), 100.1 (6-C≡*C*), 121.1 (C-3), 124.3 (C-2), 133.7 (C-8a), 133.8 (C-5), 134.9 (C-7), 135.4 (C-8), 137.4 (C-4), 138.3 (C-6), 139.8 (C-3a) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3108 (w), 3033 (w), 2952 (w), 2917 (m), 2850 (m), 2493 (w), 2326 (w), 2221 (w), 1983 (w), 1740 (w), 1578 (m), 1543 (w), 1487 (m), 1465 (w), 1424 (w), 1400 (s), 1359 (m), 1331 (s), 1266 (s), 1242 (s), 1129 (m), 1068 (m), 1013 (w), 942 (w), 900 (w), 867 (m), 850 (m), 789 (m), 755 (w), 721 (m), 647 (w), 603 (m), 442 (w), 411 (w) cm^{-1}; MS (ESI): *m*/*z* for $C_{22}H_{26}BrNO_2Na^+$: calc: 438.10 $[M+Na]^+$: found: 438.10; HRMS (ESI) for $C_{22}H_{27}BrNO_2^+$ calc.: 416.1224 $[M+H]^+$, found: 416.1220.

2-Bromo-6-dodecyloxy-1-nitroazulene (12O-AzNO$_2$-Br)

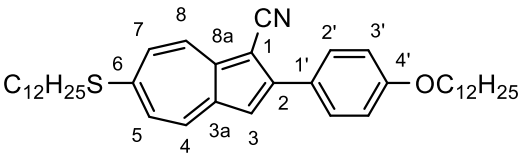


$C_{22}H_{30}BrNO_3$
(436.39)

Adapting a literature known procedure,[14] $Cu(NO_3)_2 \cdot 3H_2O$ (70 mg, 312 µmol) was suspended in acetic anhydride (1 ml) and treated with an ultrasonic bath for 15 min. The mixture was cooled down to 0 °C and **12OAz-Br** (61 mg, 156 µmol, 0 °C) in CH_2Cl_2 (2 mL) was added. After stirring for 30 min, water was added, and the phases were separated. The organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure. Column chromatography on silica (hexanes / CH_2Cl_2 2 / 1) afforded **12O-AzNO$_2$-Br** as a yellow solid in 41 % yield (28 mg, 64 µmol). Melting point (POM): 126 °C; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.0 Hz, 3H, CH_3), 1.19–1.41 (m, 16H, CH_2), 1.47–1.54 (m, 2H, OCH$_2$CH$_2$C*H*$_2$), 1.90 (tt, J = 6.5 Hz, 6.7 Hz, 2H, OCH$_2$C*H*$_2$), 4.20 (t, J = 6.5 Hz, 2H, OCH_2), 7.18 (s, 1H, 3-H), 7.23 (dd, J = 11.1 Hz, 2.9 Hz, 1H, 5-H), 7.30 (dd, J = 11.5 Hz, 2.9 Hz, 1H, 7-H), 8.23 (d, J = 11.1 Hz, 1H, 4-H), 9.48 (d, J = 11.5 Hz, 1H, 8-H) ppm.; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 25.9, 28.9, 29.3, 29.4, 29.5, 29.6, 29.6, 29.7, 31.9 (CH_2), 69.9 (OCH_2), 118.2 (C-7), 118.9 (C-5), 119.0 (C-2), 120.9 (C-3), 130.0 (C-8a), 132.0 (C-1), 136.0 (C-3a), 137.1 (C-8), 138.6 (C-4), 170.0 (C-6) ppm.; FT-IR (ATR):

$\tilde{\nu}$ = 3068 (w), 2950 (w), 2918 (m), 2849 (m), 1587 (m), 1545 (w), 1505 (w), 1477 (w), 1431 (w), 1397 (m), 1355 (w), 1332 (s), 1270 (m), 1247 (s), 1123 (w), 1019 (w), 989 (w), 972 (w), 906 (w), 861 (w), 837 (w), 802 (w), 788 (w), 763 (w), 719 (w), 599 (w), 524 (w) cm^{-1}; MS (ESI): *m/z* for $C_{22}H_{31}BrNO_3^+$ calc.: 436.15 $[M+H]^+$, found: 436.15; HRMS (ESI): *m/z* for $C_{22}H_{31}BrNO_3^+$ calc.: 436.1482 $[M+H]^+$, found: 436.1487.

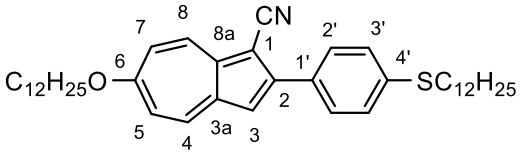
2-(4-Dodecyloxyphenyl)-6-dodecylthioazulene-1-carbonitrile (12S-AzCN-PhO12)



$C_{41}H_{59}NOS$
(613.99)

Synthesis according to GP5; **12S-AzCN-Br** (45 mg, 104 µmol), 4-dodecyloxyphenyl boronic acid (64 mg, 208 µmol), $Pd(PPh_3)_4$ (12 mg, 10 µmol), Cs_2CO_3 (68 mg, 208 µmol), dioxane (10 mL); purification: column chromatography on silica gel (ethyl acetate → CH_2Cl_2) with successive recrystallization from isopropylic alcohol; yield: turquoise solid (58% yield, 37 mg, 60 µmol); melting behavior: Cr 116 °C (51.4 kJ/mol) SmC 129 °C SmA (9.6 kJ/mol)143 C I; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.85–0.90 (m, 6H, CH_3), 1.22–1.40 (m, 32H, CH_2), 1.45–1.52 (m, 4H, $SCH_2CH_2CH_2$, $OCH_2CH_2CH_2$), 1.75–1.85 (m, 4H, SCH_2CH_2, OCH_2CH_2), 3.10 (t, *J* = 7.4 Hz, 2H, SCH_2), 4.03 (t, *J* = 6.5 Hz, 2H, OCH_2), 7.00–7.03 (m, 2H, 3'-H), 7.28 (d, *J* = 10.5 Hz, 1H, 5-H), 7.31 (d, *J* = 10.3 Hz, 1H, 7-H), 7.36 (s, 1H, 3-H), 7.96–8.02 (m, 2H, 2'-H), 8.04 (d, *J* = 10.5 Hz, 1H, 4-H), 8.28 (d, *J* = 10.3 Hz, 1H, 8-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.1, 28.2, 29.0, 29.2, 29.2, 29.4, 29.4, 29.4, 29.5, 29.6, 29.6, 29.6, 29.6, 29.7, 29.7, 29.7, 31.9, 31.9 (CH_2), 33.4 (SCH_2), 68.2 (OCH_2), 94.1 (C-1), 115.1 (C-3'), 116.6 (C-1), 118.5 (CN), 124.0 (C-7), 125.1 (C-5), 126.9 (C-1'), 129.7 (C-2'), 132.7 (C-8), 134.8 (C-4), 139.7 (C-3a), 142.9 (C-8a), 150.1 (C-1), 154.4 (C-6), 160.2 (C-4') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2954 (w), 2916 (s), 2870 (m), 2851 (m), 2202 (w), 1604 (m), 1573 (w), 1537 (w), 1523 (m), 1460 (m), 1424 (m), 1395 (w), 1379 (w), 1316 (w), 1299 (w), 1284 (w), 1254 (m), 1208 (w), 1184 (m), 1029 (m), 825 (w), 794 (w), 825 (s), 621 (w), 586 (w), 539 (w), 506 (w) cm^{-1}; MS (ESI): *m/z* for $C_{41}H_{60}NOS^+$ calc.: 614.44 $[M+H]^+$, found: 614.44; HRMS (ESI): *m/z* for $C_{41}H_{60}NOS^+$ calc.: 614.4390 $[M+H]^+$, found: 614.4385.

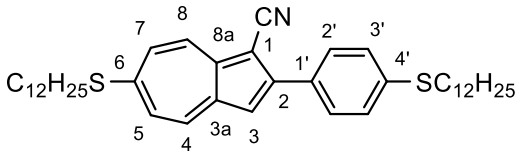
6-Dodecyloxy-2-(4-(dodecylthio)phenyl)azulene-1-carbonitrile (12O-AzCN-PhS12)



$C_{41}H_{59}NOS$
(613.99)

Synthesis according to GP5; **12O-AzCN-Br** (50 mg, 77 µmol), (4-dodecylthiophenyl) boronic acid (77 mg, 240 µmol), $Pd(PPh_3)_4$ (14 mg, 12 µmol), Cs_2CO_3 (78 mg, 240 µmol), dioxane (10 mL); purification: column chromatography on silica gel (hexanes / CH_2Cl_2 1 / 1) with successive recrystallization from ethyl acetate; yield: red solid (94 % yield, 69 mg, 112 µmol); melting behavior: Cr 97 °C (23.4 kJ/mol) SmA 137 °C (8.8 kJ/mol) I; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.86–0.90 (m, 6H, CH_3), 1.22–1.40 (m, 32H, CH_2), 1.42–1.52 (m, 4H, $SCH_2CH_2CH_2$, $OCH_2CH_2CH_2$), 1.70 (tt, J = 7.5 Hz, 7.4 Hz, 2H, SCH_2CH_2), 1.86 (tt, J = 6.9, 6.8 Hz, 2H, OCH_2CH_2), 2.98 (t, J = 7.4 Hz, 2H, SCH_2), 4.12 (t, J = 6.8 Hz, 2H, OCH_2), 7.04–7.07 (m, 2H, 5-H, 7-H), 7.34 (s, 1H, 3-H), 7.38–7.41 (m, 2H, 3'-H), 7.90–7.95 (m, 2H, 2'-H), 8.18 (d, J = 11.0 Hz, 1H, 4-H), 8.41 (d, J = 11.2 Hz, 1H, 8-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.2, 22.7 (CH_3), 26.0, 29.0, 29.1, 29.1, 29.2, 29.4, 29.4, 29.6, 29.6, 29.6, 29.6, 29.7, 29.7, 31.9 (CH_2), 33.0 (SCH_2), 69.5 (OCH_2), 93.9 (C-1), 114.3 (C-5/C-7), 116.6 (C-3), 116.7 (C-5/C-7), 118.6 (CN), 128.39 (C-3'), 128.42 (C-2'), 131.9 (C-1'), 135.1 (C-8), 137.2 (C-4), 137.9 (C-3a), 138.5 (C-4'), 140.9 (C-8a), 147.1 (C-2), 168.3 (C-6) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2952 (w), 2916 (s), 2870 (w), 2849 (s), 2201 (m), 1596 (m), 1581 (m), 1544 (w), 1513 (w), 1469 (m), 1430 (s), 1416 (m), 1379 (w), 1300 (w), 1272 (m), 1257 (w), 1212 (s), 1200 (s), 1145 (w), 1095 (w), 1054 (w), 1011 (w), 978 (w), 940 (w), 903 (w), 844 (m), 823 (s), 793 (m), 775 (w), 733 (m), 718 (m), 535 (w), 489 (s), 417 (w) cm^{-1}; MS (ESI): *m/z* for $C_{41}H_{60}NOS^+$ calc.: 614.44 $[M+H]^+$, found: 614.44; HRMS (ESI): *m/z* for $C_{41}H_{60}NOS^+$ calc.: 614.4390 $[M+H]^+$, found: 614.4391.

6-(Dodecylthio)-2-(4-(dodecylthio)phenyl)azulene-1-carbonitrile (12S-AzCN-PhS12)

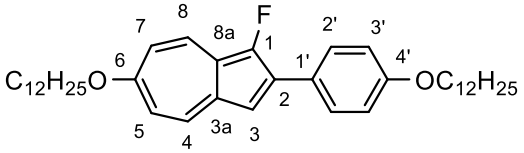


$C_{41}H_{59}NS_2$
(630.05)

Synthesis according to GP5; **12S-AzCN-Br** (40 mg, 92 µmol), (4-dodecylthiophenyl) boronic acid (60 mg, 185 µmol), $Pd(PPh_3)_4$ (11 mg, 9 µmol), Cs_2CO_3 (60 mg, 185 µmol), dioxane (10 mL); purification: column chromatography on silica gel (hexanes / CH_2Cl_2 1 / 1) with successive recrystallization from ethyl acetate; yield: brown solid (69 % yield, 40 mg, 63 µmol); melting behavior: Cr 128 °C (49.0 kJ/mol) SmA 137 °C (9.8 kJ/mol) I; ^{1}H

NMR (700 MHz, $CDCl_3$): δ = 0.85–0.89 (m, 6H, CH_3), 1.21–1.38 (m, 32H, CH_2), 1.43–1.53 (4H, $SCH_2CH_2CH_2$), 1.71 (tt, J = 7.5 Hz, 7.5 Hz, 2H, SCH_2CH_2), 1.79 (tt, J = 7.5 Hz, 7.5 Hz, 2H, SCH_2CH_2), 2.99 (t, J = 7.4 Hz, 2H, 4'-SCH_2), 3.11 (t, J = 7.4 Hz, 2H, 6-SCH_2), 7.30 (dd, J = 10.5 Hz, 1.8 Hz, 1H, 5-H), 7.33 (dd, J = 10.4 Hz, 1.8 Hz, 1H, 7-H), 7.38–7.42 (m, 3H, 3-H, 3'-H), 7.93–7.99 (m, 2H, 2'-H), 8.08 (d, J = 10.5 Hz, 1H, 4-H), 8.31 (d, J = 10.4 Hz, 1H, 8-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.2 (CH_3), 22.7, 28.1, 28.9, 29.0, 29.1, 29.2, 29.2, 29.4, 29.4, 29.5, 29.6, 29.6, 29.6, 29.6, 29.7, 29.7, 31.9, 31.9 (CH_2), 32.9 (4'-SCH_2), 33.3 (6-SCH_2), 94.4 (C-1), 116.9 (C-3), 118.3 (CN), 124.0 (C-7), 125.0 (C-5), 128.2 (C-3'), 128.5 (C-2'), 131.5 (C-1'), 133.2 (C-8), 135.3 (C-4), 139.2 (C-4'), 139.6 (C-3a), 142.8 (C-8a), 149.4 (C-2), 155.4 (C-6) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2954 (w), 2918 (s), 2851 (m), 2201 (w), 1595 (w), 1568 (w), 1467 (w), 1427 (w), 1096 (w), 1026 (w), 817 (w), 792 (w), 721 (w), 490 (w), 412 (w) cm^{-1}; MS (EI): *m/z* for $C_{41}H_{59}NS_2^+$ calc.: 629.4 $[M]^+$, found: 629.4; HRMS (EI): *m/z* for $C_{41}H_{59}NS_2^+$ calc.: 629.4083 $[M]^+$, found: 629.4087.

6-Dodecyloxy-2-(4-dodecyloxyphenyl)-1-fluoroazulene (12O-AzF-PhO12)

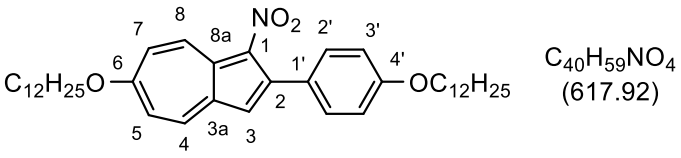


$C_{40}H_{59}FO_2$
(590.91)

Synthesis according to GP5; **12O-AzF-Br** (78 mg, 191 µmol), 4-dodecyloxyphenylboronic acid (117 mg, 381 µmol), $Pd(PPh_3)_4$ (22 mg, 19 µmol), Cs_2CO_3 (124 mg, 381 µmol), dioxane (10 mL); purification: recrystallization from isopropylic alcohol and toluene; yield: turquoise powder (68 %, 77 mg, 130 µmol); melting behavior: Cr 105 °C (58.0 kJ/mol) SmC 173 °C (14.5 kJ/mol) I; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.0 Hz, 6H, CH_3), 1.22–1.40 (m, 32H, CH_2), 1.45–1.51 (m, 4H, $OCH_2CH_2CH_2$), 1.77–1.87 (m, 4H, OCH_2CH_2), 4.01 (t, J = 6.6 Hz, 2H, 4'-OCH_2), 4.07 (t, J = 6.5 Hz, 2H, 6-OCH_2), 6.63 (dd, J = 10.5 Hz, 2.6 Hz, 1H, 5-H), 6.68 (dd, J = 10.8 Hz, 2.6 Hz, 1H, 6-H), 6.97–7.00 (m, 2H, 3'-H), 7.23 (d, J = 5.5 Hz, 1H, 3-H), 7.86–7.91 (m, 2H, 2'-H), 7.95 (dd, J = 10.5 Hz, 3.0 Hz, 1H, 4-H), 8.06 (d, J = 10.8 Hz, 1H, 8-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 29.4, 29.6, 29.7, 29.7, 29.7, 31.9 (CH_2), 68.1 (4'-OCH_2), 68.8 (6-OCH_2), 109.6 (d, J = 3.3 Hz, C-5), 110.2 (C-3), 110.9 (d, J = 3.7 Hz, C-7), 114.9 (C-3'), 118.9 (d, J = 10.7 Hz, C-8a), 126.6 (d, J = 3.8 Hz, C-1'), 128.4 (d, J = 6.3 Hz, C-3a), 129.0 (d, J = 9.9 Hz, C-2), 129.2 (d, J = 4.7 Hz, C-2'), 130.2 (C-8), 136.6 (C-4), 148.8 (d, J = 265.5 Hz, C-1), 158.9 (C-4'), 167.1 (d, J = 2.1 Hz, C-6) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -147.71 (t, J = 4.5 Hz) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2955 (w), 2917 (s), 2872 (w), 2850 (m), 1609 (w), 1585 (w), 1532 (w), 1474

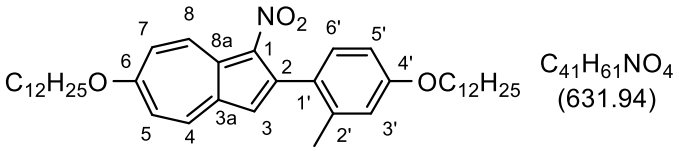
(w), 1464 (w), 1418 (w), 1403 (w), 1284 (w), 1252 (m), 1188 (m), 1109 (w), 1022 (w), 1005 (w), 825 (m), 777 (w), 729 (w), 625 (w), 532 (w) cm^{-1}; MS (ESI): *m/z* for $C_{40}H_{60}FO_2^+$ calc.: 591.46 $[M+H]^+$, found: 591.46; HRMS (ESI): *m/z* for $C_{40}H_{60}FO_2^+$ calc.: 591.4572 $[M+H]^+$, found: 591.4560.

6-Dodecyloxy-2-(4-dodecyloxyphenyl)-1-nitroazulene (12O-AzNO$_2$-PhO12)



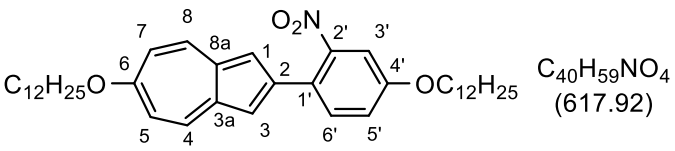
Synthesis according to GP5; **12O-AzNO$_2$-Br** (37 mg, 85 µmol), 4-dodecyloxyphenylboronic acid (52 mg, 170 µmol), $Pd(PPh_3)_4$ (10 mg, 8 µmol), Cs_2CO_3 (55 mg, 170 µmol), dioxane (5 mL); purification: silica gel column chromatography (hexanes / CH_2Cl_2 1 / 1); yield: orange solid (95 %, 50 mg, 81 µmol); melting behavior: Cr 94 °C (47.1 kJ/mol) SmA 152 °C (11.1 kJ/mol) I; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.0 Hz, 6H, CH_3), 1.22–1.42 (m, 32H, CH_2), 1.45–1.54 (m, 4H, $OCH_2CH_2CH_2$), 1.78–1.84 (m, 2H, 4'-OCH_2CH_2), 1.86–1.91 (m, 2H, 6-OCH_2CH_2), 4.01 (t, *J* = 6.6 Hz, 2H, 4'-OCH_2), 4.17 (t, *J* = 6.5 Hz, 2H, 6-OCH_2), 6.95–6.98 (m, 2H, 3'-H), 7.04 (s, 1H, 3-H), 7.17 (dd, *J* = 11.0 Hz, 2.8 Hz, 1H, 5-H), 7.25 (dd, *J* = 11.4 Hz, 2.2 Hz, 1H, 7-H), 7.50–7.54 (m, 2H, 2'-H), 8.24 (d, *J* = 11.0 Hz, 1H, 4-H), 9.35 (d, *J* = 11.4 Hz, 1H, 8-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 22.7, 26.0, 26.1, 29.0, 29.3, 29.4, 29.4, 29.4, 29.6, 29.6, 29.6, 29.6, 29.7, 29.7, 29.7, 31.9, 32.0 (CH_2), 68.1 (4'-O*C*H_2), 69.6 (6-O*C*H_2), 114.3 (C-3'), 117.5 (C-7), 118.0 (C-5), 119.0 (C-3), 127.8 (C-1'), 130.6 (C-2'), 131.4 (C-8a), 132.0 (C-1), 136.5 (C-3a), 136.8 (C-8), 138.6 (C-4), 143.9 (C-2), 159.3 (C-4'), 169.0 (C-6) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2954 (w), 2915 (s), 2851 (s), 1608 (m), 1589 (m), 1551 (w), 1533 (w), 1488 (m), 1472 (m), 1418 (m), 1395 (w), 1380 (m), 1363 (m), 1338 (s), 1308 (w), 1274 (s), 1264 (s), 1209 (s), 1175 (s), 1129 (w), 1107 (w), 1061 (w), 1020 (m), 997 (m), 973 (w), 909 (w), 851 (m), 826 (m), 813 (w), 786 (m), 771 (w), 716 (m), 676 (w), 649 (w), 626 (w), 616 (w), 558 (w), 521 (w), 443 (w), 413 (w) cm^{-1}; MS (ESI): *m/z* for $C_{40}H_{60}NO_4^+$ calc.: 618.45 $[M+H]^+$, found: 618.45; HRMS (ESI): *m/z* for $C_{40}H_{60}NO_4^+$ calc.: 618.4517 $[M+H]^+$, found: 618.4518.

6-Dodecyloxy-2-(4-(dodecyloxy)-2-methylphenyl)-1-nitroazulene (12O-AzNO$_2$-MePhO12)



Synthesis according to GP5; **12O-AzNO$_2$-Br** (50 mg, 115 µmol), 4-dodecyloxy-2-methyl-phenylboronic acid (55 mg, 172 µmol), $Pd(PPh_3)_4$ (13 mg, 11 µmol), Cs_2CO_3 (93 mg, 286 µmol), dioxane (10 mL); purification: column chromatography on silica gel (hexanes / CH_2Cl_2 1 / 1); yield: orange solid (88 %, 64 mg, 101 µmol); melting behavior: Cr 70 °C (64.4 kJ/mol) SmA 79 °C (4.4 kJ/mol) I; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.79–0.93 (m, 6H, CH_3), 1.15–1.56 (m, 36H, CH_2), 1.74–1.92 (m, 4H, OCH_2CH_2), 2.14 (s, 3H, 2'-CH_3), 3.98 (t, *J* = 6.5 Hz, 2H, 4'-OCH_2), 4.19 (t, *J* = 6.5 Hz, 2H, 6-OCH_2), 6.78 (dd, *J* = 8.3 Hz, 2.6 Hz, 1H, 5'-H), 6.83 (d, *J* = 2.6 Hz, 1H, 3'-H), 6.94 (s, 1H, 3-H), 7.16 (d, *J* = 8.3 Hz, 1H, 6'-H), 7.21 (dd, *J* = 11.1 Hz, 2.8 Hz, 1H, 5-H), 7.30 (dd, *J* = 11.5 Hz, 2.8 Hz, 1H, 7-H), 8.28 (d, *J* = 11.1 Hz, 1H, 4-H), 9.51 (d, *J* = 11.5 Hz, 1H, 8-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 20.2, 22.7, 25.9, 26.1, 29.0, 29.3, 29.4, 29.4, 29.4, 29.5, 29.6, 29.6, 29.6, 29.7, 29.7, 29.7, 30.9, 31.9, 31.9 (CH_2), 67.9 (4'-OCH_2), 69.7 (6-OCH_2), 111.3 (C-5'), 115.9 (C-3'), 117.6 (C-7), 118.0 (C-5), 119.7 (C-3), 128.7 (C-1'),130.1 (C-6'), 130.5 (C-2), 133.3 (C-8a), 136.5 (C-3a), 137.3 (C-8), 137.8 (C-1), 138.9 (C-4), 144.5 (C-2'), 158.8 (C-4'), 169.3 (C-6) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2920 (s), 2851 (m), 2393 (w), 1960 (w), 1604 (m), 1586 (m), 1549 (w), 1486 (m), 1468 (m), 1415 (s), 1377 (w), 1361 (m), 1329 (s), 1246 (s), 1169 (m), 1136 (w), 1103 (w), 1047 (w), 1001 (w), 980 (w), 906 (w), 846 (m), 811 (w), 761 (w), 721 (w), 682 (w), 627 (w), 581 (w), 460 (w) cm^{-1}; MS(ESI): *m/z* for $C_{41}H_{62}NO_4^+$ calc.: 632.46 $[M+H]^+$, found: 632.46; HRMS(ESI): *m/z* for $C_{41}H_{62}NO_4^+$ calc.: 632.4673 $[M+H]^+$, found: 632.4671.

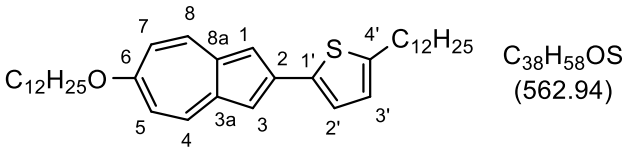
6-Dodecyloxy-2-(4-dodecyloxy-2-nitrobenzol-1-yl)-azulene (12O-Az-NO$_2$PhO12)



Synthesis according to GP5; **12O-Az-Br** (88 mg, 225 µmol), 2-(4-(dodecyloxy)-2-nitrophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (146 mg, 337 µmol), $Pd(PPh_3)_4$ (26 mg, 23 µmol), Cs_2CO_3 (183 mg, 562 µmol), dioxane (10 mL); purification: column

chromatography on silica gel (hexanes / CH_2Cl_2 1 / 1) with successive recrystallization from isopropylic alcohol; yield: dark red solid (71 %, 26 mg, 23 μmol); melting behavior: Cr 75 °C (5.1 kJ/mol) SmC 86 °C (7.1 kJ/mol) I; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.94 (t, J = 7.0 Hz, 6H, CH_3), 1.25–1.56 (m, 36H, CH_2), 1.86 (m, 4H, OCH_2CH_2), 4.04 (t, J = 6.5 Hz, 2H, 4'-OCH_2), 4.10 (t, J = 6.5 Hz, 2H, 6-OCH_2), 6.83 (d, J = 10.6 Hz, 2H, 5-H, 7-H) 7.14 (dd, J = 8.7 Hz, 2.6 Hz, 1H, 5'-H), 7.27 (s, 2H, 1-H, 3-H), 7.28 (d, J = 2.6 Hz, 1H, 3'-H), 7.62 (d, J = 8.7 Hz, 1H, 6'-H), 8.15 (d, J = 10.6 Hz, 2H, 4-H, 8-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.2 (CH_3), 22.8, 26.0, 26.1, 29.1, 29.2, 29.4, 29.4, 29.6, 29.7, 29.7, 29.7, 32.0 (CH_2), 68.8 (4'-OCH_2), 68.9 (6-OCH_2), 109.3 (C-3'), 111.7 (C-5, C-7), 116.8 (C-1, C-3), 118.7 (C-5'), 124.1 (C-1'), 133.1 (C-6'), 136.2 (C-3a, C-8a), 136.4 (C-4, C-8), 140.1 (C-2), 149.9 (C-2'), 158.4 (C-4'), 167.2 (C-6) ppm FT-IR (ATR): $\tilde{\nu}$ = 2920 (m), 2851 (m), 1614 (w), 1579 (m), 1527 (m), 1467 (m), 1412 (m), 1365 (m), 1289 (m), 1250 (m), 1186 (s), 1083 (w), 1019 (w), 999 (w), 906 (s), 875 (w), 836 (m), 823 (m), 811 (m), 767 (w), 729 (s), 675 (w), 649 (w), 572 (w), 535 (w), 475 (w) cm^{-1}; MS(ESI): *m/z* for $C_{40}H_{60}NO_4^+$ calc.: 618.45 $[M+H]^+$, found: 618.45; HRMS(ESI): *m/z* for $C_{40}H_{60}NO_4^+$ calc.: 618.4517 $[M+H]^+$, found: 618.4495.

6-Dodecyloxy-2-(5-dodecylthiophene-2-yl)azulene (12O-Az-Thi12)

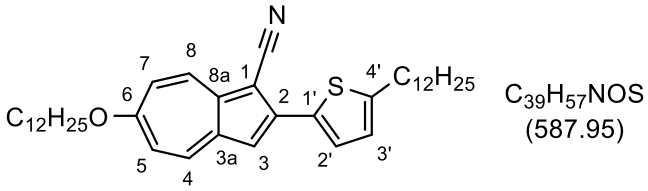


$C_{38}H_{58}OS$
(562.94)

Synthesis according to GP5; **12O-Az-BPin** (100 mg, 228 μmol), 2-bromo-5-dodecylthiophene (162 mg, 342 μmol), $Pd(PPh_3)_4$ (27 mg, 23 μmol), Cs_2CO_3 (186 mg, 570 μmol), dioxane (20 mL); purification: column chromatography on silica gel (hexanes / CH_2Cl_2 1 / 1) and successive recrystallization from chloroform; yield: brown solid (33 %, 42 mg, 75 μmol); melting behavior: Cr 91 °C (25.1 kJ/mol) SmE 156 °C (14.7 kJ/mol) SmA (16.4 kJ/mol) 160 °C I; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.83–0.95 (m, 6H, CH_3), 1.15–1.51 (m, 36H, CH_2), 1.71 (tt, J = 7.6 Hz, 7.6 Hz, 2H, 4'-CH_2CH_2), 1.83 (tt, J = 6.8 Hz, 6.5 Hz, 2H, OCH_2CH_2), 2.83 (t, J = 7.6 Hz, 2H, 4'-CH_2), 4.07 (t, J = 6.5 Hz, 2H, OCH_2), 6.73–6.80 (m, 3H, 5-H, 7-H, 3'-H), 7.29 (d, J = 3.5 Hz, 1H, 2'-H), 7.35 (s, 2H, 1-H, 3-H), 8.03 (d, J = 11.1 Hz, 2H, 4-H, 8-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.2 (CH_3), 22.7, 26.1, 29.1, 29.3, 29.4, 29.4, 29.6, 29.7, 29.7, 29.7, 29.7, 30.4, 31.7, 31.9 (CH_2), 68.8 (6-OCH_2), 111.9 (C-5, C-7), 114.5 (C-1, C-3), 124.2 (C-2'), 125.3 (C-3'), 134.6 (C-4,

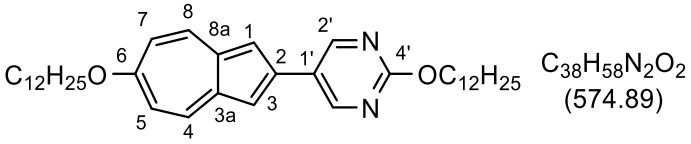
C-8), 137.0 (C-3a, C-8a), 138.8 (C-2), 139.7 (C-1'), 146.4 (C-4'), 165.8 (C-6) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2955 (w), 2918 (s), 2850 (m), 2334 (w), 2276 (w), 2174 (w), 2065 (w), 1975 (w), 1593 (m), 1545 (w), 1464 (w), 1418 (w), 1392 (w), 1355 (m), 1327 (m), 1273 (w), 1249 (w), 1190 (w), 1142 (w), 1121 (w), 1029 (w), 962 (w), 855 (w), 836 (w), 810 (w), 798 (w), 725 (w), 693 (w), 671 (w), 575 (w), 536 (w), 513 (w), 493 (w), 462 (w), 448 (w), 432 (w), 421 (w), 406 (w) cm^{-1}; MS(ESI): *m/z* for $C_{38}H_{59}OS^+$ calc.: 563.42 $[M+H]^+$, found: 563.42; HRMS(ESI): *m/z* for $C_{38}H_{59}OS^+$ calc.: 563.4281 $[M+H]^+$, found: 563.4280.

6-Dodecyloxy-2-(5-dodecylthiophene-2-yl)azulene-1-carbonitrile (12O-AzCN-Thi12)



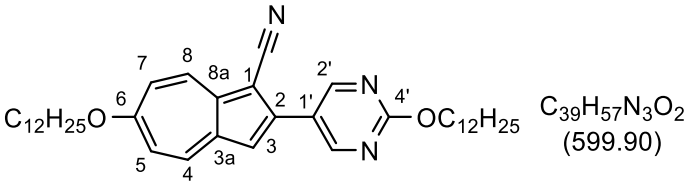
Synthesis according to GP5; **12O-AzCN-Br** (50 mg, 120 µmol), 2-bromo-5-dodecylthiophene (53 mg, 180 mmol), $Pd(PPh_3)_4$ (14 mg, 12 µmol), Cs_2CO_3 (59 mg, 180 mmol), dioxane (15 mL); purification: flash column chromatography on silica gel (hexanes) and successive recrystallization from isopropylic alcohol; yield: red solid (26%, 18 mg, 31 µmol); melting behavior: Cr 59 °C (26.9 kJ/mol) SmA 109 °C (8.0 kJ/mol) I; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.88 (m, *J* = 7.1 Hz, 4.0 Hz, 6H, CH_3), 1.18–1.77 (m, 38H, CH_2), 1.86 (tt, *J* = 7.1 Hz, 7.6 Hz, 6.5 Hz, 2H, OCH_2CH_2), 2.85 (t, *J* = 7.6 Hz, 2H, 4'-CH_2), 4.11 (t, *J* = 6.5 Hz, 2H, OCH_2), 6.83 (d, *J* = 3.7 Hz, 1H, 3'-H), 7.01-7.05 (m, 2H, 5-H, 7-H), 7.24 (s, 1H, 3-H), 7.76 (d, *J* = 3.7 Hz, 1H, 2'-H), 8.09 (d, *J* = 11.2 Hz, 1H, 4-H), 8.31 (d, *J* = 10.9 Hz, 1H, 8-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.0, 29.1, 29.2, 29.3, 29.4, 29.4, 29.4, 29.6, 29.6, 29.6, 29.7, 29.7, 29.7, 29.7, 30.4, 31.6, 31.9 (CH_2), 69.4 (OCH_2), 92.6 (C-1), 114.3 (C-7), 115.7 (C-3), 117.2 (C-5), 118.5 (CN), 125.8 (C-3'), 127.0 (C-2'), 134.2 (C-8), 135.5 (C-1'), 136.3 (C-4), 138.0 (C-3a), 140.8 (C-8a), 141.4 (C-2), 148.6 (C-4'), 167.7 (C-6) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2953 (w), 2919 (s), 2850 (m), 2198 (m), 1589 (m), 1543 (w), 1494 (w), 1467 (m), 1423 (m), 1397 (w), 1367 (m), 1300 (w), 1271 (m), 1204 (s), 1114 (w), 1093 (w), 993 (w), 902 (w), 847 (w), 806 (w), 789 (w), 722 (w), 530 (w), 494 (w) cm^{-1}; MS(ESI): *m/z* for $C_{39}H_{58}NOS^+$ calc.: 588.42 $[M+H]^+$, found: 588.42; HRMS(ESI): *m/z* for $C_{39}H_{58}NOS^+$ calc.: 588.4234 $[M+H]^+$, found: 588.4238.

2-(Dodecyloxy)-5-(6-(dodecyloxy)azulen-2-yl)pyrimidine (12O-Az-PyriO12)



Synthesis according to GP5; **12O-Az-Br** (541 mg, 1.38 mmol), 2-(dodecyloxy)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrimidine (540 mg, 1.38 mmol), $Pd(PPh_3)_4$ (160 mg, 138 µmol), Cs_2CO_3 (901 mg, 2.77 mmol), dioxane (100 mL); purification: column chromatography on silica gel (hexanes / CH_2Cl_2 2 / 1 → CH_2Cl_2) and successive recrystallization from ethyl acetate; yield: orange-red solid (30 %, 242 mg, 421 µmol); melting behavior: Cr 147 °C (18.2 kJ/mol) SmC 179 °C (0.8 kJ/mol) SmA 185 °C (12.0 kJ/mol) I; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.87–0.89 (m, 6H, CH_3), 1.20–1.42 (m, 32H, CH_2), 1.44–1.53 (m, 4H, 6-$OCH_2CH_2CH_2$, 4'-$OCH_2CH_2CH_2$), 1.79–1.89 (m, 4H, 6-OCH_2CH_2, 4'-OCH_2CH_2), 4.11 (t, J = 6.5 Hz, 2H, 6-OCH_2), 4.40 (t, J = 6.7 Hz, 2H, 4'-OCH_2), 6.85 (d, J = 10.5 Hz, 2H, 5-H, 7-H), 7.47 (s, 2H, 1-H, 3-H), 8.17 (d, J = 10.5 Hz, 2H, 4-H, 8-H), 8.97 (s, 2H, 2'-H) ppm; ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 14.3 (CH_3), 22.8, 26.1, 26.2, 29.1, 29.3, 29.5, 29.5, 29.5, 29.7, 29.7, 29.8, 29.8, 29.8, 29.8, 32.1, 68.1 (4'-OCH_2), 69.1 (6'-OCH_2), 112.3 (C-5, C-7), 114.3 (C-1, C-3), 124.7 (C-1'), 136.2 (C-4, C-8), 137.0 (C-3a, C-8a), 138.3 (C-2), 157.3 (C-2'), 164.7 (C-4'), 167.3 (C-6) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2955 (w), 2917 (s), 2872 (m), 2849 (s), 1598 (m), 1583 (m), 1547 (m), 1509 (m), 1463 (m), 1437 (m), 1418 (m), 1385 (m), 1346 (m), 1334 (m), 1285 (w), 1253 (m), 1195 (s), 1160 (w), 1061 (w), 1019 (m), 997 (w), 945 (w), 839 (s), 825 (m), 810 (m), 773 (m), 729 (w), 719 (m), 656 (w), 665 (m), 572 (w), 552 (w), 499 (w), 421 (w) cm^{-1}; MS(ESI): *m*/*z* for $C_{38}H_{59}N_2O_2^+$ calc.: 574.45 $[M+H]^+$, found: 574.46; HRMS(ESI): *m*/*z* for $C_{41}H_{56}NO_3^+$ calc.: 575.4576 $[M+H]^+$, found: 575.4571.

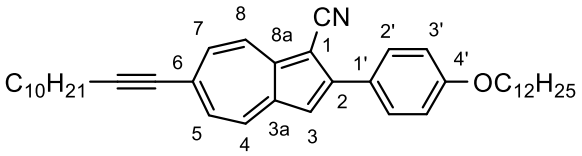
6-(Dodecyloxy)-2-(2-(dodecyloxy)pyrimidin-5-yl)azulene-1-carbonitrile (12O-AzCN-PyriO12)



Synthesis according to GP5; **12O-AzCN-Br** (50 mg, 120 µmol), 2-(dodecyloxy)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrimidine (70 mg, 180 µmol), $Pd(PPh_3)_4$ (14 mg,

12 µmol), Cs_2CO_3 (98 mg, 300 µmol), dioxane (20 mL); purification: column chromatography on silica gel (hexanes / CH_2Cl_2 1 / 2 → CH_2Cl_2) and successive recrystallization from isopropylic alcohol; yield: orange-red solid (86 %, 62 mg, 103 µmol); melting behavior: Cr 83 °C (54.9 kJ/mol) SmA 151 °C (10.1 kJ/mol) I; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.86–0.93 (m, 6H, CH_3), 1.20–1.41 (m, 32H, CH_2), 1.46–1.55 (m, 4H, $OCH_2CH_2CH_2$), 1.81–1.94 (m, 4H, OCH_2CH_2), 4.18 (t, J = 6.5 Hz, 2H, 6-OCH_2), 4.44 (t, J = 6.7 Hz, 2H, 4'-OCH_2), 7.11–7.17 (m, 2H, 5-H, 7-H), 7.34 (s, 1H, 3-H), 8.28 (d, J = 10.8 Hz, 1H, 4-H), 8.49 (d, J = 10.7 Hz, 1H, 8-H), 9.10 (s, 2H, 2'-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.0, 26.0, 28.9, 29.0, 29.3, 29.4, 29.4, 29.4, 29.5, 29.6, 29.6, 29.6, 29.7, 29.7, 29.7, 29.7, 31.9, 31.9 (CH_2), 68.3 (6-OCH_2), 69.7 (4'-OCH_2), 93.9 (C-1), 115.1 (C-7), 115.9, (C-3), 116.9 (C-5), 117.9 (CN), 122.8 (C-3'), 136.0 (C-8), 137.8 (C-3a), 138.0 (C-4), 140.58 (C-8a), 140.7 (C-2), 158.1 (C-2'), 165.1 (C-1'), 169.2 (C-6) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2953 (w), 2920 (s), 2851(m), 2196 (w), 1600 (m), 1583 (w), 1547 (w), 1501 (w), 1468 (w), 1428 (m), 1386 (w), 1336 (w), 1296 (w), 1270 (w), 1205 (m), 1050 (w), 1021 (w), 946 (w), 848 (w), 803 (w), 766 (w), 723 (w) cm^{-1}; MS(ESI): *m/z* for $C_{39}H_{58}N_3O_2^+$ calc.: 600.45 $[M+H]^+$, found: 600.45; HRMS(ESI): *m/z* for $C_{39}H_{58}N_3O_2^+$ calc.: 600.4524 $[M+H]^+$, found: 600.4522; elemental analysis: calc. (%) for $C_{39}H_{57}N_3O_2$ (599.90): C 78.08, H 9.58, N 7.00; found: C 78.25, H 9.72, N 6.84.

6-(Dodec-1-yn-1-yl)-2-(4-(dodecyloxy)phenyl)azulene-1-carbonitrile (12Yne-AzCN-PhO12)

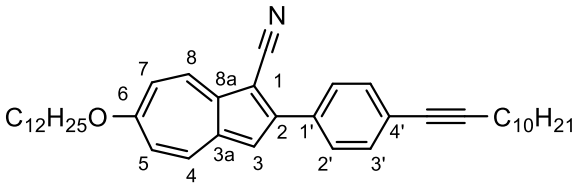


$C_{41}H_{55}NO$
(577.90)

Synthesis according to GP5; **12Yne-AzCN-Br** (14 mg, 35 µmol), 2-bromo-5-4-dodecyloxyphenylboronic acid (32 mg, 105 µmol), $Pd(PPh_3)_4$ (4 mg, 4 µmol), Cs_2CO_3 (46 mg, 141 µmol), dioxane (5 mL); purification: column chromatography on silica gel (hexanes / CH_2Cl_2 2 / 1); yield: green solid (44%, 9 mg, 15 µmol); melting behavior: Cr 70 °C (58.5 kJ/mol) SmC 94 °C (5.6 kJ/mol) I; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.85–0.92 (m, 6H, CH_3), 1.20–1.40 (m, 28H, CH_2), 1.44–1.51 (m, 4H, $OCH_2CH_2CH_2$, $C{\equiv}CCH_2CH_2CH_2$), 1.66 (tt, J = 7.3 Hz, 7.3 Hz, 2H, $C{\equiv}CCH_2CH_2$), 1.79–1.84 (m, 2H, OCH_2CH_2), 2.50 (t, J = 7.3 Hz, 2H, $C{\equiv}CCH_2$), 4.03 (t, J = 6.6 Hz, 2H, OCH_2), 7.01–7.05

(m, 2H, 3'-H), 7.43 (s, 1H, 3-H), 7.47–7.51 (m, 1H, 5-H), 7.55–7.58 (m, 1H, 7-H), 8.01–8.06 (m, 2H, 2'-H), 8.15 (d, *J* = 10.4 Hz, 1H, 4-H), 8.38 (d, *J* = 10.1 Hz, 1H, 8-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) δ = 14.3 (CH_2), 20.0, 22.8, 26.2, 28.6, 29.1, 29.3, 29.3, 29.5, 29.5, 29.5, 29.7, 29.7, 29.8, 29.8, 29.8, 32.1, 32.1 (CH_2), 68.3 (OCH_2), 85.1 (6-*C*≡C), 94.1 (C-1), 97.0 (6-C≡*C*), 115.3 (C-3'), 116.4 (C-3), 118.5 (CN), 126.8 (C-1'), 130.1 (C-2'), 131.1 (C-7), 131.2 (C-5), 133.2 (C-8), 134.8 (C-6), 135.4 (C-4), 141.8 (C-3a), 145.4 (C-8a), 151.8 (C-2), 160.7 (C-4') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2921 (s), 2851 (m), 1604 (m), 1574 (w), 1542 (w), 1524 (w), 1458 (m), 1425 (m), 1388 (w), 1288 (w), 1258 (m), 1203 (w), 1183 (m), 1138 (w), 1106 (w), 1021 (w), 899 (w), 852 (w), 834 (m), 795 (w), 722 (w), 621 (w), 540 (w), 510 (w), 451 (w), 421 (w) cm^{-1}; MS (ESI): *m/z* for $C_{41}H_{56}NO^+$ calc.: 578.44 $[M + H]^+$, found: 578.43; HRMS (ESI): *m/z* for $C_{41}H_{55}NONa^+$ calc.: 600.4176 $[M + Na]^+$, found: 600.4166.

2-(4-(Dodec-1-yn-1-yl)phenyl)-6-(dodecyloxy)azulene-1-carbonitrile (12O-AzCN-PhYne12)

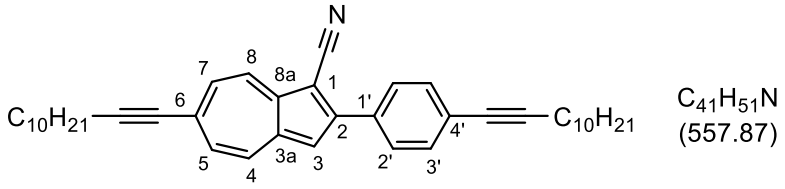


$C_{41}H_{55}NO$ (577.90)

Synthesis according to GP5; **12O-AzCN-Br** (60 mg, 144 µmol), (4-(dodec-1-yn-1-yl)phenyl)boronic acid (41 mg, 144 µmol), $Pd(PPh_3)_4$ (17 mg, 14 µmol), Cs_2CO_3 (84 mg, 259 µmol), dioxane (20 mL); purification: column chromatography on silica gel (hexanes / CH_2Cl_2 2 / 1); yield: red solid (92%, 69 mg, 130 µmol); melting behavior: Cr 80 °C (25.8 kJ/mol) SmA 143 °C (7.5 kJ/mol) I; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.85–0.92 (m, 6H, CH_3), 1.22–1.43 (m, 28H, CH_2), 1.44–1.54 (m, 4H, C≡C$CH_2CH_2CH_2$), 1.64 (tt, *J* = 7.3 Hz, 7.2 Hz, 2H, C≡CCH_2CH_2), 1.81–1.91 (m, 2H, 6-OCH_2CH_2), 2.44 (t, *J* = 7.2 Hz, 2H, 4'-C≡CCH_2), 4.11 (t, *J* = 6.6 Hz, 2H, 6-OCH_2), 7.00–7.09 (m, 2H, 5-H, 7-H), 7.35 (d, *J* = 2.3 Hz, 1H, 3-H), 7.50 (d, *J* = 8.2 Hz, 2H, 3'-H), 7.94 (d, *J* = 8.1 Hz, 2H, 2'-H), 8.18 (d, *J* = 11.0 Hz, 2.4 Hz, 1H, 4-H), 8.41 (d, *J* = 10.9 Hz, 2.1 Hz, 1H, 8-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.3 (CH_3), 19.7 (4'-C≡CCH_2), 22.8, 26.1, 28.9 (C≡CCH_2CH_2), 29.1, 29.2, 29.3, 29.5, 29.5, 29.5, 29.7, 29.7, 29.7, 29.7, 29.8, 29.8, 32.1, 69.6 (6-OCH_2), 80.7 (4'-*C*≡C), 92.4 (4'-C≡*C*), 94.1 (C-1), 114.6 (C-5), 116.7 (C-7), 117.0 (C-3), 118.6 (CN), 124.5 (C-2), 128.0 (C-2'), 132.3 (C-3'), 133.9 (C-1'), 135.5 (C-8), 137.6 (C-4), 137.8 (C-3a), 141.0 (C-8a), 146.9 (C-4'), 168.7 (C-6) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2921 (m), 2852 (m), 2250 (w), 2197 (w), 1605 (w), 1582 (m), 1547 (w), 1523 (w), 1487 (w), 1465

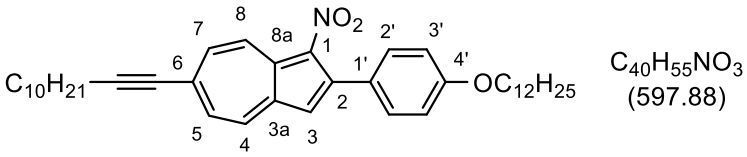
(w), 1426 (m), 1330 (w), 1270 (m), 1195 (m), 1090 (w), 1007 (w), 985 (w), 905 (s), 840 (m), 796 (w), 766 (w), 730 (s), 649 (w), 545 (w), 519 (w), 440 (w), 408 (w) cm^{-1}; MS(ESI): *m*/*z* for $C_{41}H_{56}NO^+$ calc.: 578.43 $[M+H]^+$ found: 578.44; HRMS (ESI): *m*/*z* for $C_{41}H_{56}NO^+$ calc.: 578.4357 $[M+H]^+$, found: 578.4356.

6-(Dodec-1-yn-1-yl)-2-(4-(dodec-1-yn-1-yl)phenyl)azulene-1-carbonitrile (12Yne-AzCN-PhYne12)



Synthesis according to GP5; **12Yne-AzCN-Br** (42 mg, 106 µmol), (4-(dodec-1-yn-1-yl)phenyl)boronic acid (30 mg, 106 µmol), $Pd(PPh_3)_4$ (12 mg, 11 µmol), Cs_2CO_3 (69 mg, 211 µmol), dioxane (15 mL); purification: column chromatography on silica gel (hexanes / CH_2Cl_2 2 / 1) and subsequent recrystallization from isopropylic alcohol; yield: green solid (69%, 41 mg, 75 µmol); melting behavior: Cr 55 °C (9.7 kJ/mol) SmC 73 °C SmA 78 °C (5.0 kJ/mol) I; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.85–0.92 (m, 6H, CH_3), 1.22–1.39 (m, 24H, CH_2), 1.41–1.51 (m, 4H, 6-C≡CCH$_2$CH$_2$C*H*$_2$, 4'-C≡CCH$_2$CH$_2$C*H*$_2$), 1.60–1.70 (m, 4H, 6-C≡CCH$_2$C*H*2, 4'-C≡CCH$_2$C*H*$_2$), 2.44 (t, *J* = 7.2 Hz, 2H, 4'-C≡CC*H*$_2$), 2.50 (t, *J* = 7.2 Hz, 2H, 6-C≡CC*H*$_2$), 7.47 (s, 1H, 3-H), 7.50–7.54 (m, 3H, 5-H, 3'-H), 7.57–7.62 (m, 1H, 7-H), 7.97–8.01 (m, 2H, 2'-H), 8.20 (d, *J* = 10.4 Hz, 1H, 4-H), 8.43 (d, *J* = 10.1 Hz, 1H, 8-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.3 (CH_3), 19.7 (4'-C≡C*C*H$_2$), 20.0 (6-C≡C*C*H$_2$), 22.8, 28.6, 28.8, 29.1, 29.1, 29.3, 29.3, 29.5, 29.5, 29.7, 29.7, 29.7, 29.7, 32.1 (CH_2), 80.6 (4'-*C*≡C), 85.1 (6-*C*≡C), 93.1 (4'-C≡*C*), 94.7 (C-1), 97.8 (6-C≡*C*), 117.0 (C-3), 118.1 (CN), 125.6 (C-4'), 128.4 (C-2'), 131.2 (C-7), 131.3 (C-5), 132.4 (C-3'), 133.3 (C-1'), 134.1 (C-8), 135.9 (C-6), 136.3 (C-4), 141.7 (C-3a), 145.2 (C-8a), 150.9 (C-2) ppm; FT-IR (ATR): $\tilde{\nu}$ = 3035 (w), 2953 (m), 2921 (s), 2852 (s), 2202 (m), 1730 (w), 1603 (w), 1576 (w), 1544 (w), 1521 (w), 1456 (m), 1425 (s), 1378 (w), 1352 (w), 1299 (w), 1232 (w), 1188 (w), 1104 (w), 1054 (w), 1017 (w), 900 (w), 843 (m), 799 (w), 722 (w), 649 (w), 546 (w), 518 (w), 441 (w) cm^{-1}; MS (EI): *m/z* for $C_{41}H_{61}N^+$ calc.: 557.4 $[M]^+$, found: 557.4; HRMS (EI): *m/z* for $C_{41}H_{61}N^+$: calc.: 557.4019 $[M]^+$, found: 557.4016.

6-(Dodec-1-yn-1-yl)-2-(4-(dodecyloxy)phenyl)-1-nitroazulene (12Yne-AzNO$_2$-PhO12)



Synthesis according to GP5; **12Yne-AzNO$_2$-Br** (29 mg, 70 µmol), 2-bromo-5-4-dodecyloxyphenylboronic acid (21 mg, 70 µmol), Pd(PPh$_3$)$_4$ (8 mg, 7 µmol), Cs$_2$CO$_3$ (45 mg, 139 µmol), dioxane (10 mL); purification: column chromatography on silica gel (hexanes / CH_2Cl_2 2 / 1) with subsequent recrystallization from ispropylic alcohol; yield: brown solid (31%, 13 mg, 22 µmol); melting behavior: Cr 70 °C (24.5 kJ/mol) SmC 94 °C (5.8 kJ/mol) I; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.0 Hz, 6H, CH_3), 1.20–1.40 (m, 28H, CH_2), 1.44–1.52 (m, 4H, $OCH_2CH_2CH_2$, $C{\equiv}CCH_2CH_2CH_2$), 1.66 (tt, J = 7.4 Hz, 7.1 Hz, 2H, $C{\equiv}CCH_2CH_2$), 1.81 (tt, J = 6.7 Hz, 6.5 Hz, 2H, OCH_2CH_2), 2.51 (t, J = 7.1 Hz, 2H, $C{\equiv}CCH_2$), 4.02 (t, J = 6.5 Hz, 2H, OCH_2), 6.98 (d, J = 8.6 Hz, 2H, 2'-H), 7.15 (s, 1H, 3-H), 7.55 (d, J = 8.6 Hz, 2H, 3'-H), 7.61 (d, J = 10.4 Hz, 1.5 Hz, 1H, 5-H), 7.74 (d, J = 10.6 Hz, 1.5 Hz, 1H, 7-H), 8.22 (d, J = 10.4 Hz, 1H, 4-H), 9.24 (d, J = 10.6 Hz, 1H, 8-H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.3 (CH_3), 20.0 ($C{\equiv}CCH_2$), 22.8, 22.8, 26.2, 28.5 ($C{\equiv}CCH_2CH_2$), 29.1, 29.3, 29.4, 29.5, 29.5, 29.6, 29.7, 29.7, 29.8, 29.8, 29.8, 32.1, 32.1 (CH_2), 68.2 (OCH_2), 84.8 (6-$C{\equiv}$C), 98.4 (6-C$\equiv$C), 114.6 (C-2'), 118.8 (C-3), 127.2 (C-2), 131.0 (C-3'), 132.2 (C-1), 132.6 (C-5), 134.1 (C-7), 135.0 (C-8), 135.3 (C-8a), 136.5 (C-6), 137.4 (C-4), 140.3 (C-3a), 147.7 (C-1'), 160.0 (C-4') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2954 (m), 2920 (s), 2852 (m), 2220 (w), 1605 (m), 1577 (w), 1545 (w), 1494 (s), 1467 (m), 1413 (s), 1373 (w), 1330 (s), 1272 (s), 1248 (s), 1178 (m), 1111 (w), 1070 (w), 1026 (w), 852 (w), 835 (m), 806 (w), 722 (w), 624 (w), 531 (w), 415 (w) cm^{-1}; MS(ESI): m/z for $C_{40}H_{56}NO_3^+$ calc.: 598.42 $[M+H]^+$, found: 598.43; HRMS(ESI): m/z for $C_{40}H_{56}NO_3^+$ calc.: 598.4255, found: 598.4255

3. Polarized Optical Microscopy

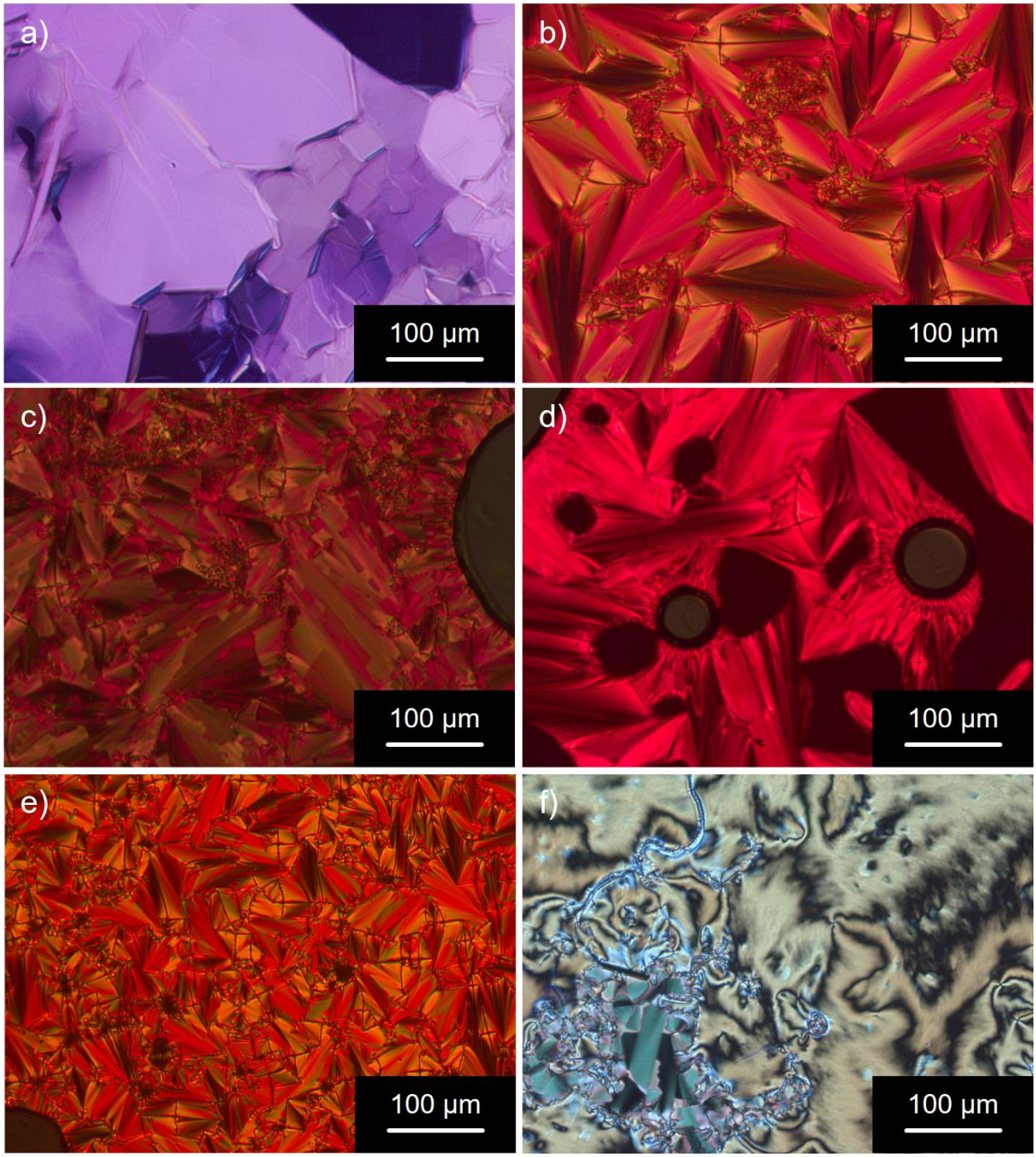


Figure S2: Optical micrographs between crossed polarizers upon cooling from the isotropic yield in 5 K/min: a) The SmE phase of **12S-Az-Br** at 100 °C. SmA (b) and SmC (c) phase of **12S-AzCN-PhO12** at 143 °C and 124 °C. SmA phases of **12O-AzCN-PhS12** at 137 °C (d) and **12S-AzCN-PhS12** at135 °C (e). f) SmC phase of **12O-AzF-PhO12** at 133 °C.

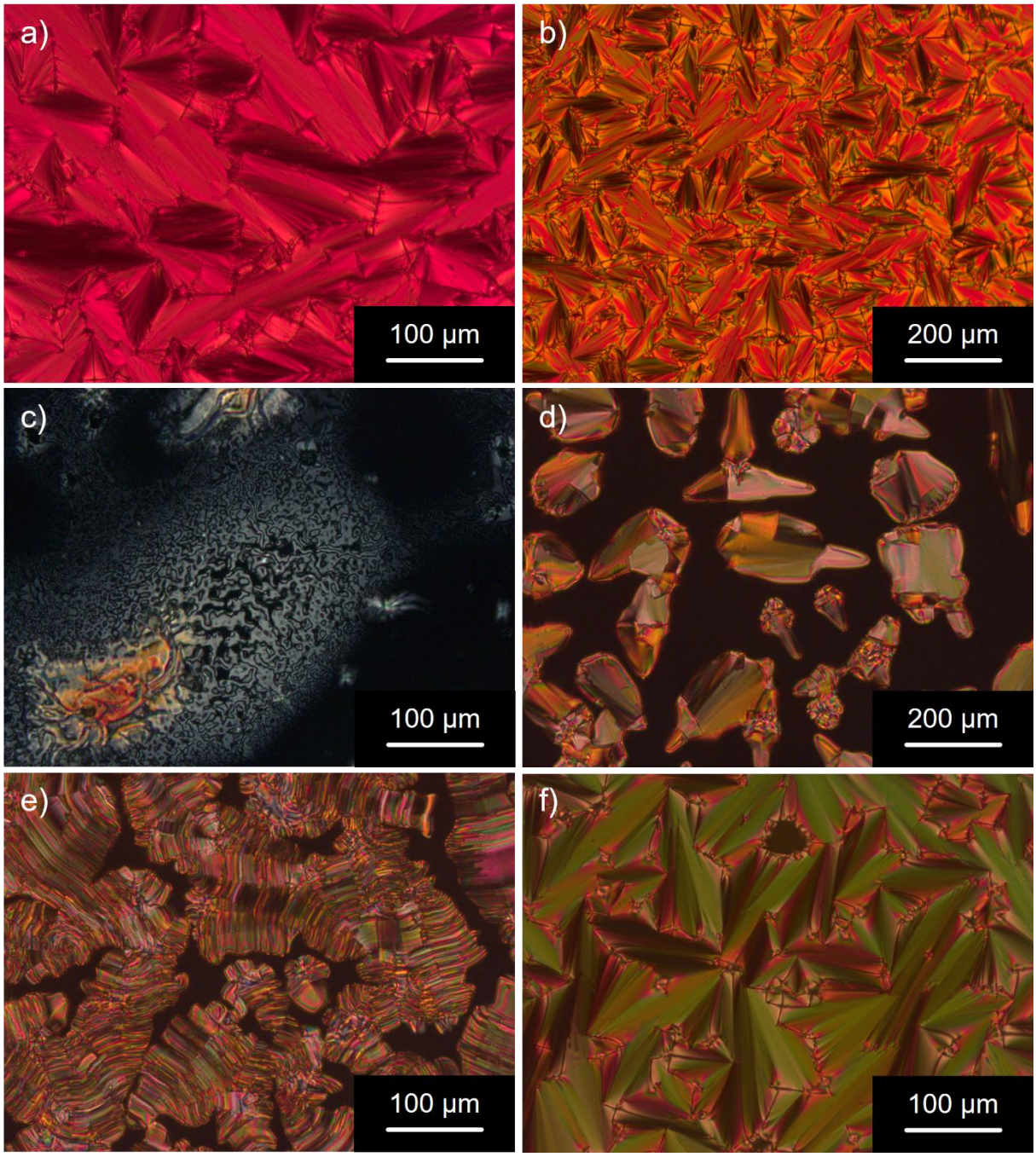


Figure S3: Optical micrographs between crossed polarizers upon cooling from the isotropic yield in 5 K/min.: SmA phases of **12O-AzNO$_2$-PhO12** at 152 °C (a) and **12O-AzNO$_2$MePhO12** at 73 °C (b). c) The SmC phase of **12O-Az-NO$_2$PhO12** at 77 °C. SmA (d) and SmE (e) phase of **12S-Az-Thi12** at 158 °C and 153 °C. f) SmA phases of **12O-AzCN-Thi12** at 93 °C.

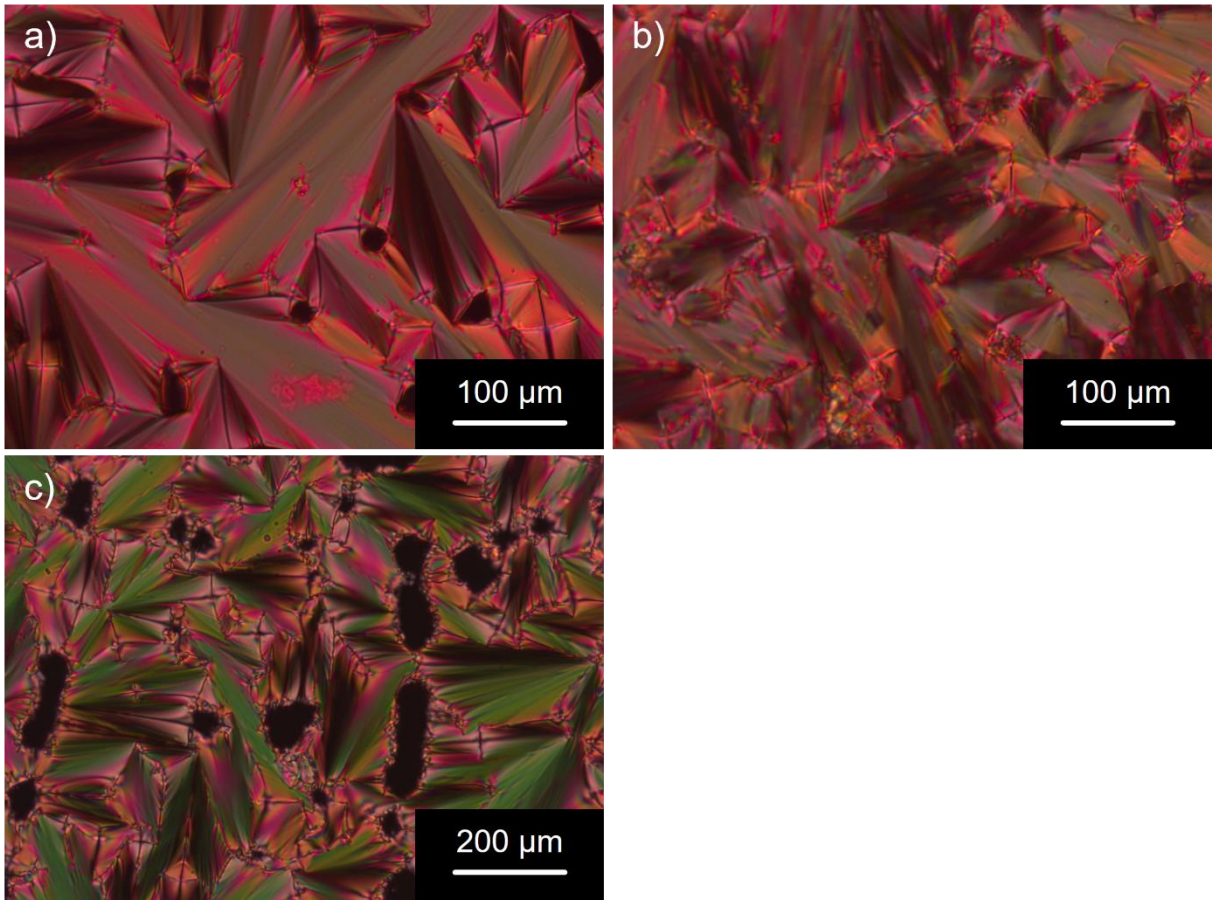


Figure S4: Optical micrographs between crossed polarizers upon cooling from the isotropic yield in 5 K/min: SmA (a) and SmC (b) phase of **12O-Az-PyriO12** at 190 °C and 185 °C. c) SmA phases of **12O-AzCN-PyriO12** at 142 °C.

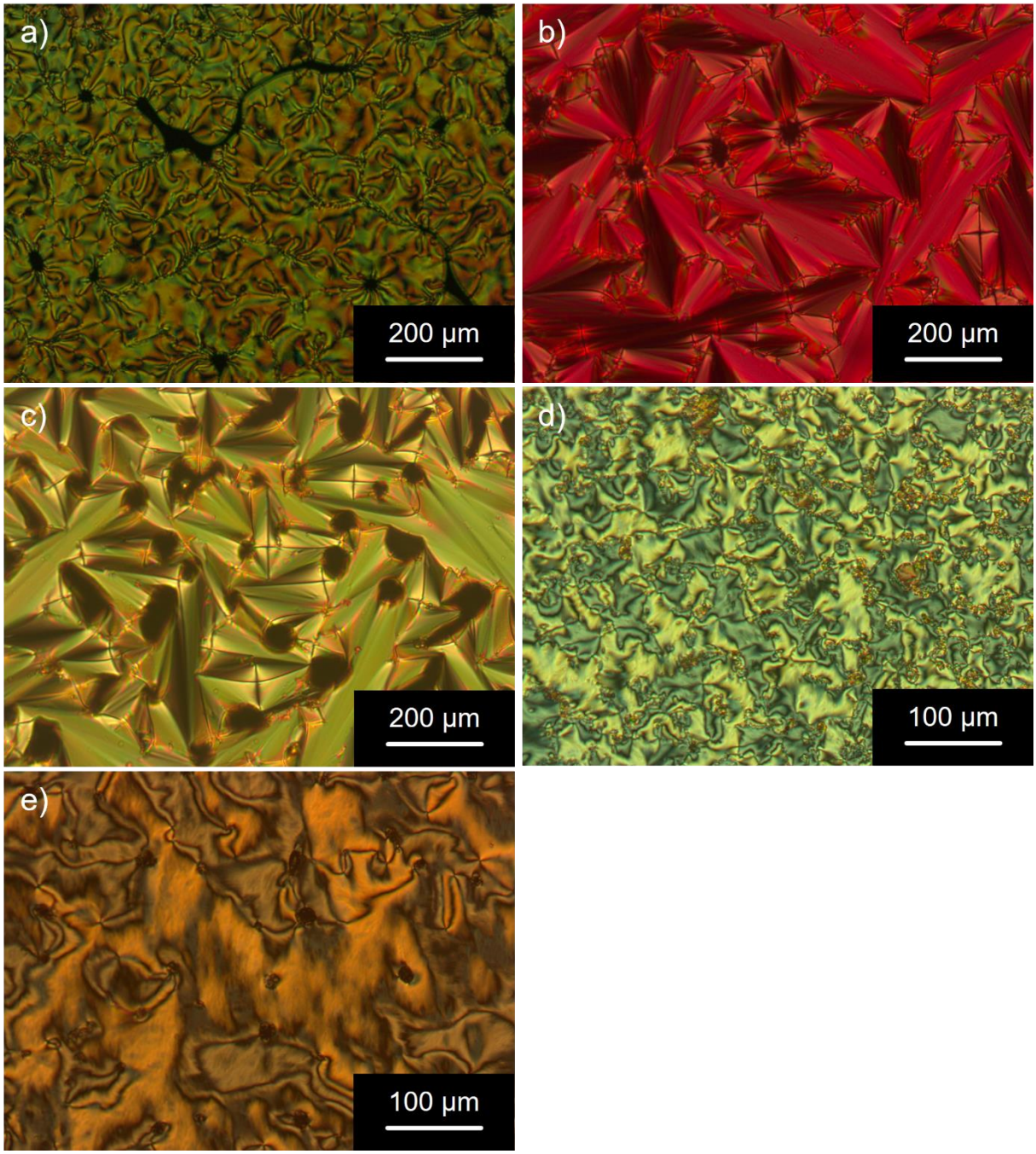


Figure S5: Optical micrographs between crossed polarizers upon cooling from the isotropic yield in 5 K/min: a) SmC phase of **12Yne-AzCN-PhO12** at 90 °C. b) SmA phase of **12O-AzCN-PhYne12** at 146 °C. SmA (c) and SmC (d) phase of **12Yne-AzCN-PhYne12** at 78 °C and 70 °C. e) SmC phase of **12Yne-AzNO$_2$-PhO12** at 76 °C.

4. DSC spectra

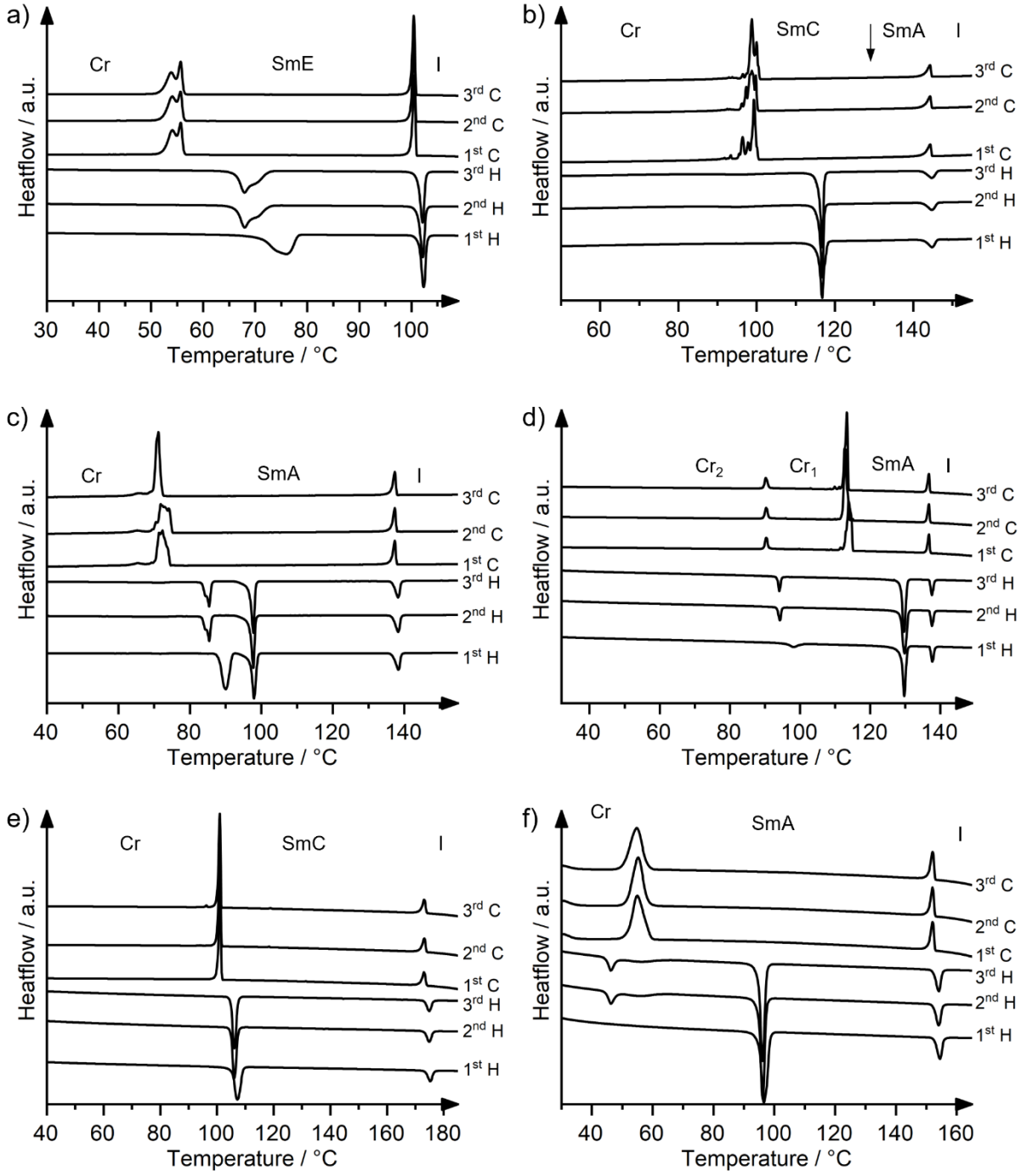


Figure S6: DSC-curves of azulenes: a) **12S-Az-Br**, b)**12S-AzCN-PhO12,** c) **12O-AzCN-PhS12**, d) **12S-AzCN-PhS12**, e) **12O-AzF-PhO12**, f)**12O-AzNO$_2$-PhO12.** Heating / cooling rate: 5 K/min, H = Heating, C = Cooling.

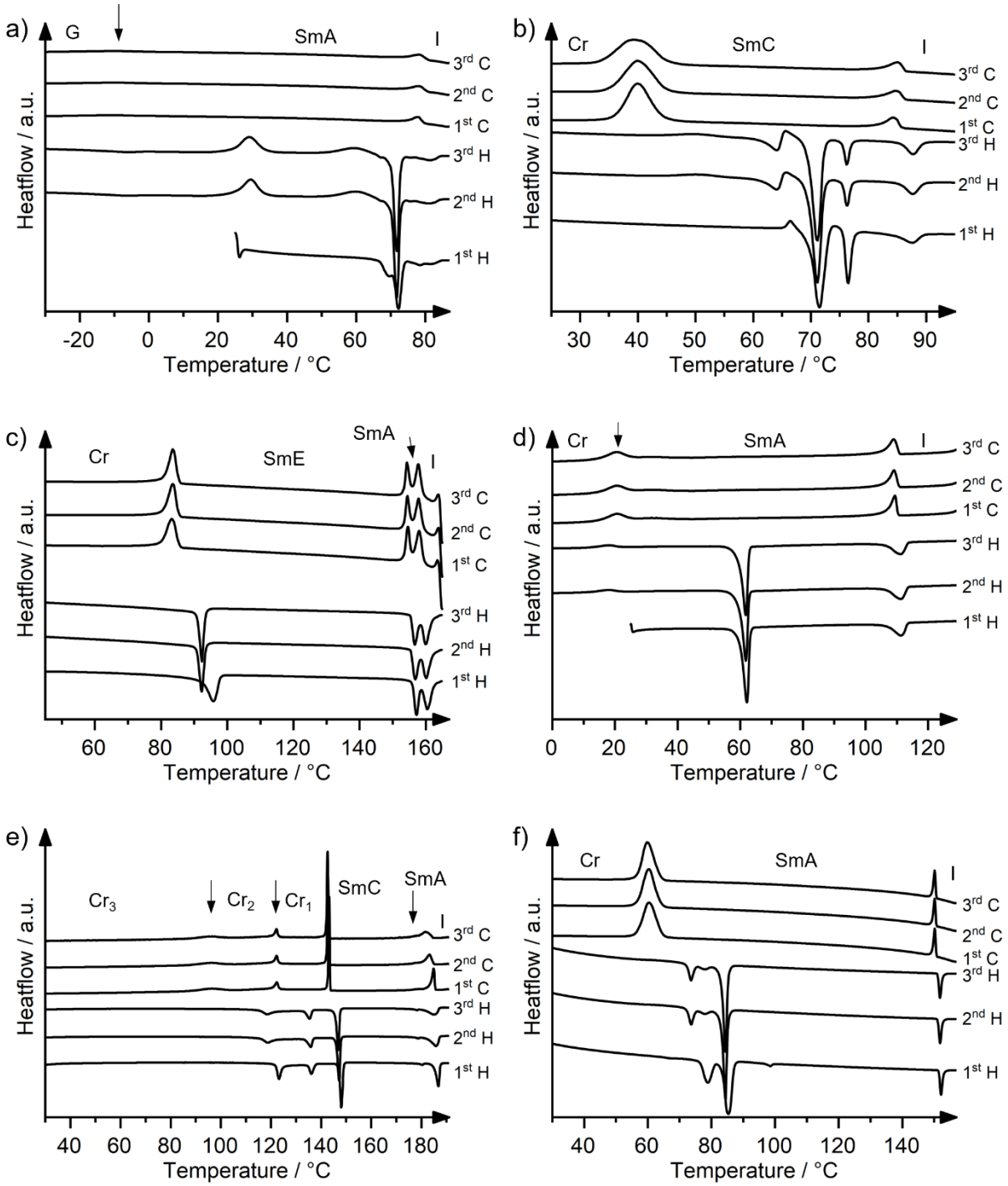


Figure S7: DSC-curves of azulenes: a) **12O-AzNO$_2$-MePhO12**, b)**12O-Az-NO$_2$PhO12**, c) **12O-Az-Thi12**, d) **12O-AzCN-Thi12**, e) **12O-Az-PyriO12**, f) **12O-AzCN-PyriO12**.
Heating / cooling rate: 5 K/min, H = Heating, C = Cooling.

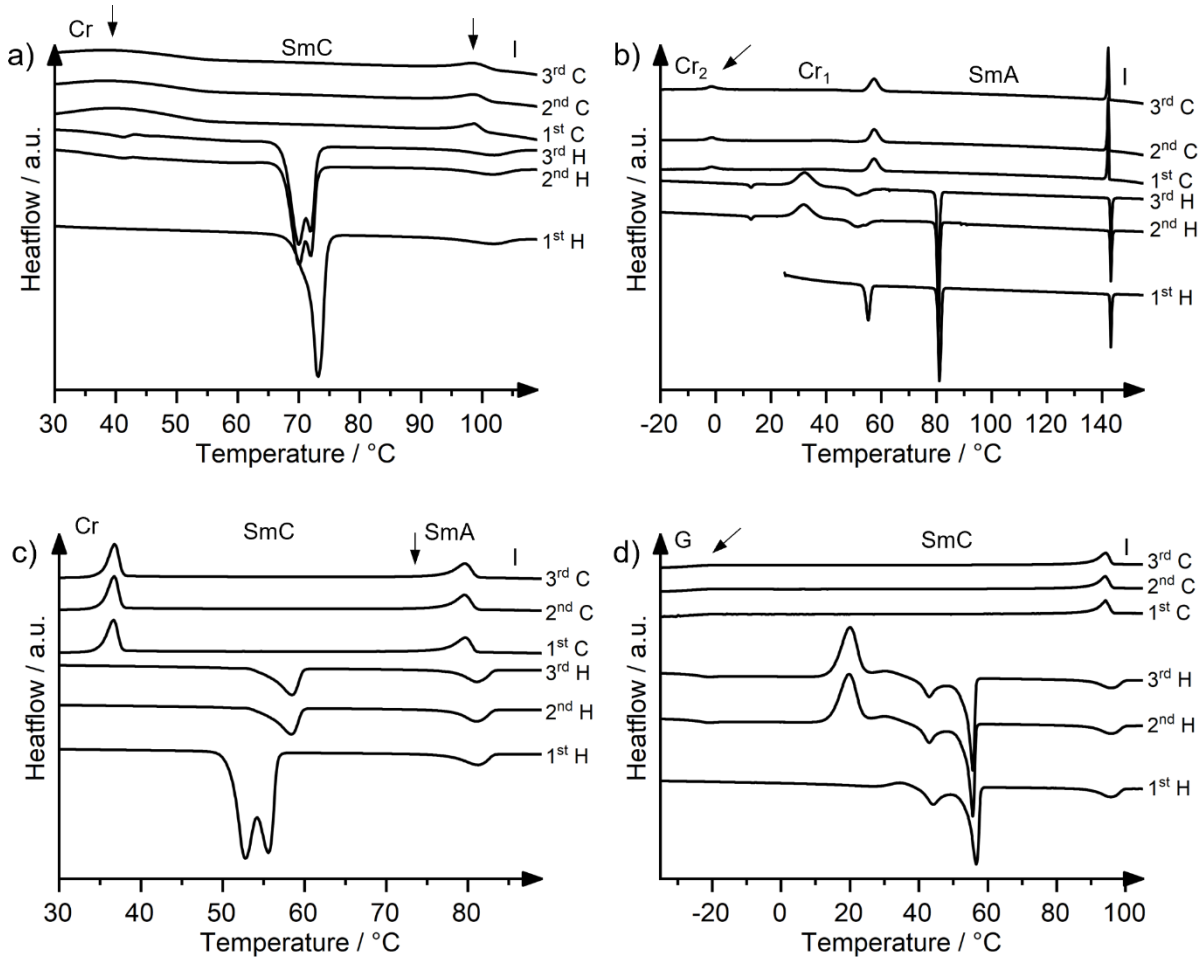


Figure S8: DSC-curves of azulenes: a) **12Yne-AzCN-PhO12**, b**) 12O-AzCN-PhYne12**, c) **12Yne-AzCN-PhYne12**, d) **12Yne-AzNO$_2$-PhO12**.

Heating / cooling rate: 5 K/min, H = Heating, C = Cooling.

Table S1: Phase transition temperatures [°C] and enthalpies [kJ/mol] azulene mesogens determined by DSC.

Compound	Transition temperatures / °C (and enthalpies / kJ/mol)						
12S-Az-Br	Cr	66 (22.9)	SmE	101 (15.8)		I	h
	Cr	56 (–21.8)	SmE	101 (–15.7)		I	c
12S-AzCN-PhO12	Cr	116 (51.4)	SmC	129[a]	SmA 143 (9.6)	I	h
	Cr	100 (–56.4)	SmC	129[a]	SmA 144 (–9.7)	I	c
12O-AzCN-PhS12	Cr	97 (23.4)			SmA 137 (8.8)	I	h
	Cr	72 (–35.3)			SmA 138 (–8.8)	I	c
12S-AzCN-PhS12	Cr	128 (49.0)			SmA 137 (9.8)	I	h
	Cr	114 (–51.6)			SmA 137 (–9.8)	I	c
12O-AzF-PhO12	Cr	105 (58.0)	SmC	173 (14.5)		I	h
	Cr	102 (–56.4)	SmC	174 (–14.1)		I	c
12O-AzNO_2-PhO12	Cr	94 (47.1)			SmA 152 (11.1)	I	h
	Cr	58 (–52.3)			SmA 153 (–11.0)	I	c
12O-AzNO_2-MePhO12	Cr	70 (64.4)			SmA 79 (4.4)	I	h
	Cr	–9[b]			SmA 80 (–8.2)	I	c
12O-Az-NO_2PhO12	Cr	75 (5.1)	SmC	85 (7.1)		I	h
	Cr	45 (–41.7)	SmC	86 (–6.4)		I	c
12O-Az-Thi12	Cr	91 (25.1)	SmE	155 (14.7)	SmA 158 (16.4)	I	h
	Cr	85 (–29.0)	SmE	156 (–14.8)	SmA 159 (–21.0)	I	c
12O-AzCN-Thi12	Cr	59 (26.9)			SmA 109 (8.0)	I	h
	Cr	25 (–5.1)			SmA 110 (–8.2)	I	c
12O-Az-PyriO12	Cr	147 (18.2)	SmC	179 (0.4)	SmA 185 (12.0)	I	h[c]
	Cr	144 (–18.9)	SmC	179[a]	SmA 185 (–11.9)	I	c[c]
12O-AzCN-PyriO12	Cr	83 (54.9)			SmA 151 (10.1)	I	h
	Cr	64 (–71.1)			SmA 151 (–10.3)	I	c
12Yne-AzCN-PhO12	Cr	67 (58.5)	SmC	95 (5.6)		I	h
	Cr	51 (–8.8)	SmC	102 (–5.2)		I	c
12O-AzCN-PhYne12	Cr	80 (25.8)			SmA 143 (7.5)	I	h
	Cr	61 (–10.7)			SmA 143 (–7.5)	I	c
12Yne-AzCN-PhYne12	Cr	55 (9.7)	SmC	73[a]	SmA 78 (5.0)	I	h
	Cr	38 (–6.7)	SmC	73[a]	SmA 81 (–4.7)	I	c
12Yne-AzNO_2-PhO12	Cr	53 (24.5)	SmC	94 (5.8)		I	h
	Cr	-22[b]	SmC	96 (–5.8)		I	c

Heating/Cooling rate: 5 K/min, h: 2nd heating, c: 2nd cooling. Crystal-crystal transitions are not listed. [a] Determined *via* POM. [b] Glass transition. [c] First heating cycle was used.

5. X-Ray Diffractometry

Table S2: Lattice constants and observed reflexes in WAXS and SAXS measurements of azulene mesogens

Compound	Lattice constants / Å	Spacing / Å Observed	/(Calc.)	Miller indices (hkl)
12S-Az-Br	(SmE at 75 °C)	27.15	(27.15)	(001)
	a = 7.72	4.67	(4.67)	(110)
	b = 5.86	3.86	(3.86)	(200)
	c = 27.15	3.24	(3.24)	(210)
	Z = 2.0 ρ = 1.1[a]	4.01		halo
12O-AzCN-PhS12	(SmA at 126 °C)	38.15		(001)
		4.35		halo
12S-AzCN-PhO12	(SmA at 137 °C)	37.62		(001)
		4.14		halo
	(SmC at 112 °C)	37.88		(001)
		4.12		
12S-AzCN-PhS12	(SmA at 131 °C)	39.69		(001)
		4.34		(halo)
12O-AzF-PhO12	(SmC at 140 °C)	35.78		(001)
		4.44		halo
12O-AzNO$_2$-PhO12	(SmA at 137 °C)	37.80		(001)
		4.28		halo
12O-AzNO$_2$-MePhO12	(SmA at 65 °C)	36.62		(001)
		4.39		halo
12O-Az-NO$_2$PhO12	(SmC at 70 °C)	31.04		(001)
		4.38		halo
12O-Az-Thi12	(SmE at 131 °C)	34.86	(34.86)	(001)
	a = 8.32	17.35	(17.43)	(002)
	b = 5.73	11.60	(11.62)	(003)
	c = 34.86	8.66	(8.71)	(004)
	Z = 2.0 ρ = 1.12[a]	4.72	(4.72)	(110)
		4.16	(4.16)	(200)
		3.51	(3.37)	(210)
12O-AzCN-Thi12	(SmA at 98 °C)	37.39		(001)
		4.34		halo
12O-Az-PyriO12	(SmA at 183°C)	37.48		(001)
		4.51		halo
	(SmC at 154°C)	36.17		(001)
		4.46		halo
12O-AzCN-PyriO12	(SmA at 120 °C)	37.60		(001)
		4.27		halo
12Yne-AzCN-PhO12	(SmC at 88 °C)	32.63		(001)
		4.22		halo
12O-AzCN-PhYne12	(SmA at 131 °C)	37.04		(001)
		4.37		halo
12Yne-AzCN-PhYne12	(SmA at 79 °C)	36.06		(001)
		4.31		halo
	(SmC at 60 °C)	36.12		(001)
		4.27		halo
12Yne-AzNO$_2$-PhO12	(SmC at rt)	34.36		(001)
		4.22		halo

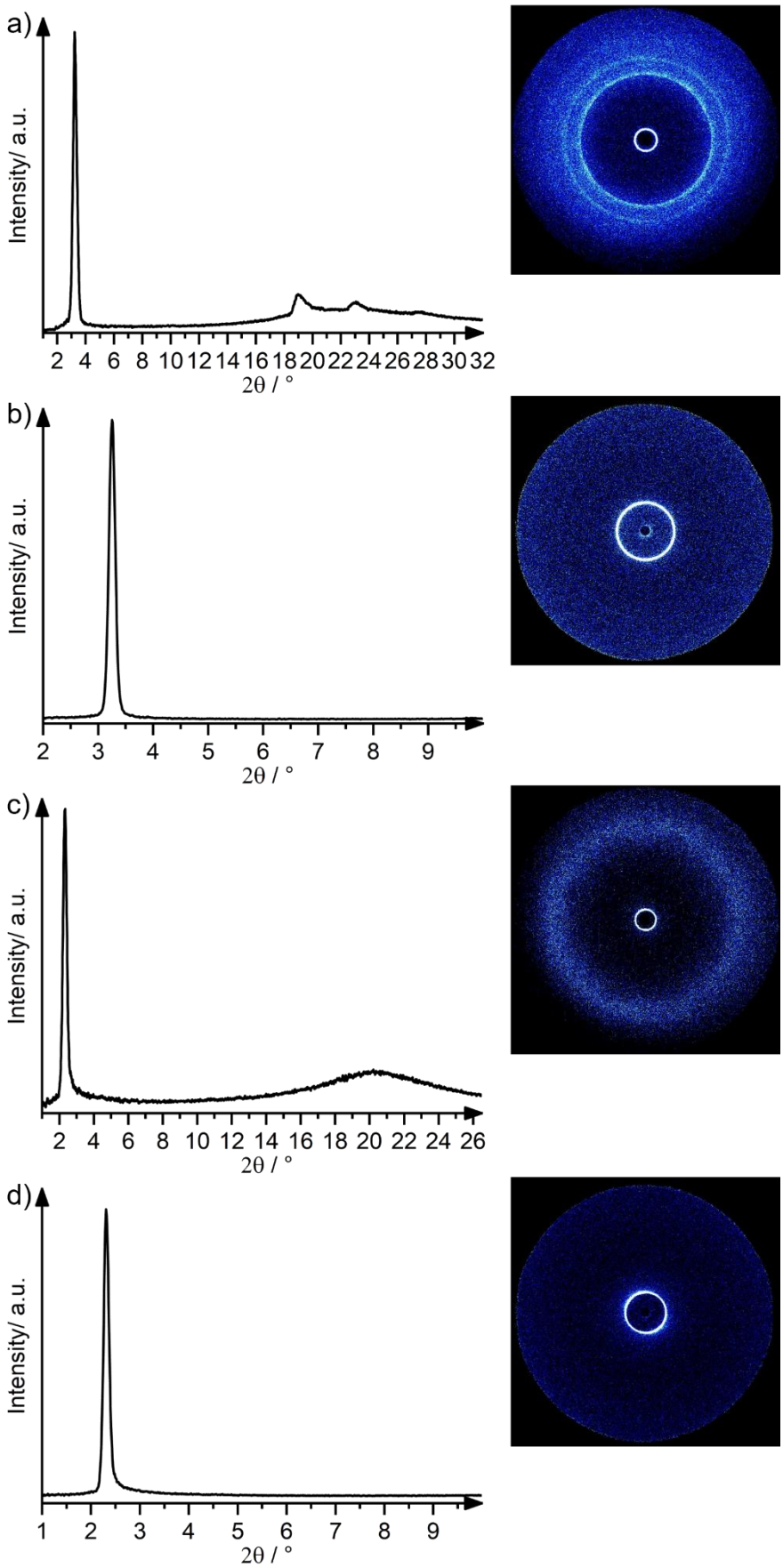


Figure S9: WAXS (a) and SAXS (b) diffraction pattern and diffractogram of the SmE phase of **12S-Az-Br** at 75 °C and WAXS (c) and SAXS (d) of the SmA phase of **12O-AzCN-PhS12** at 126 °C

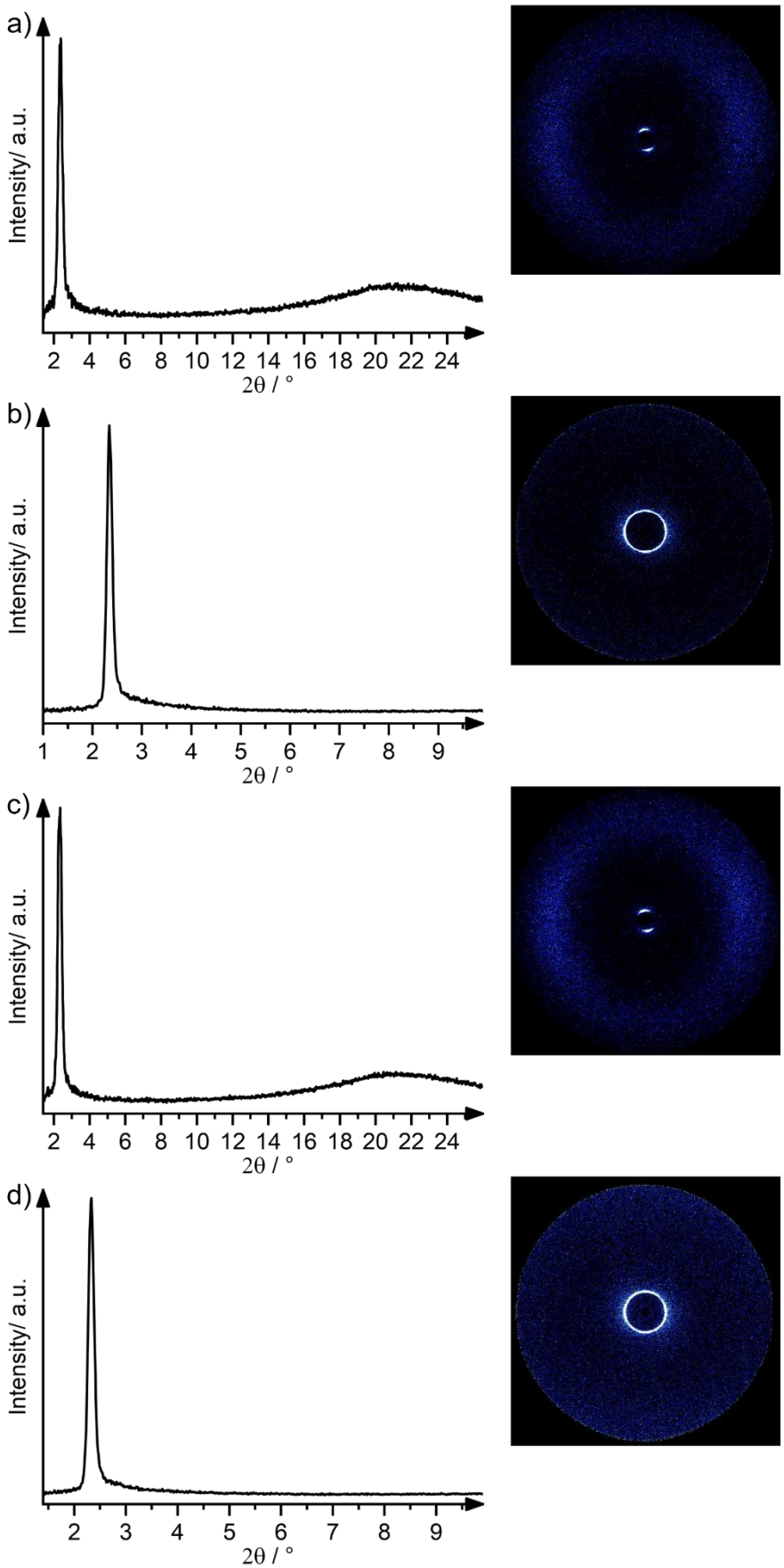


Figure S10: WAXS (a) and SAXS (b) diffraction pattern and diffractogram of the SmA phase of **12S-AzCN-PhO12** at 137 °C and WAXS (c) and SAXS (d) of the SmC phase of **12S-AzCN-PhO12** at 112 °C.

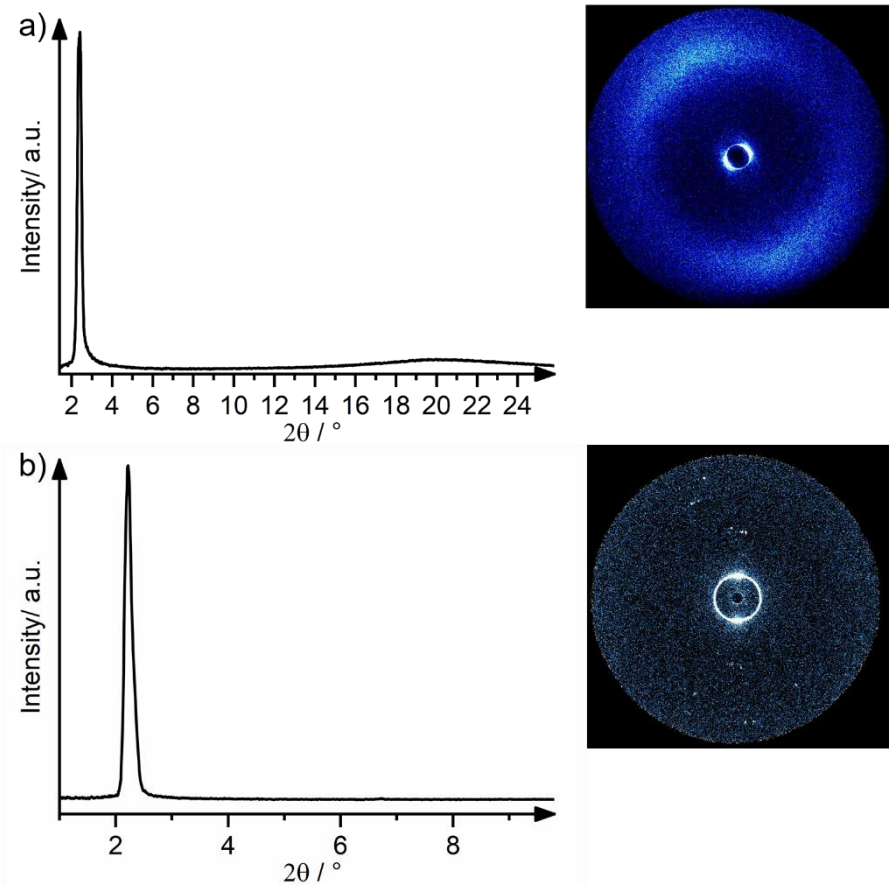


Figure S11: WAXS (a) and SAXS (b) diffraction pattern and diffractogram of the SmA phase of **12S-AzCN-PhS12** at 1313 °C.

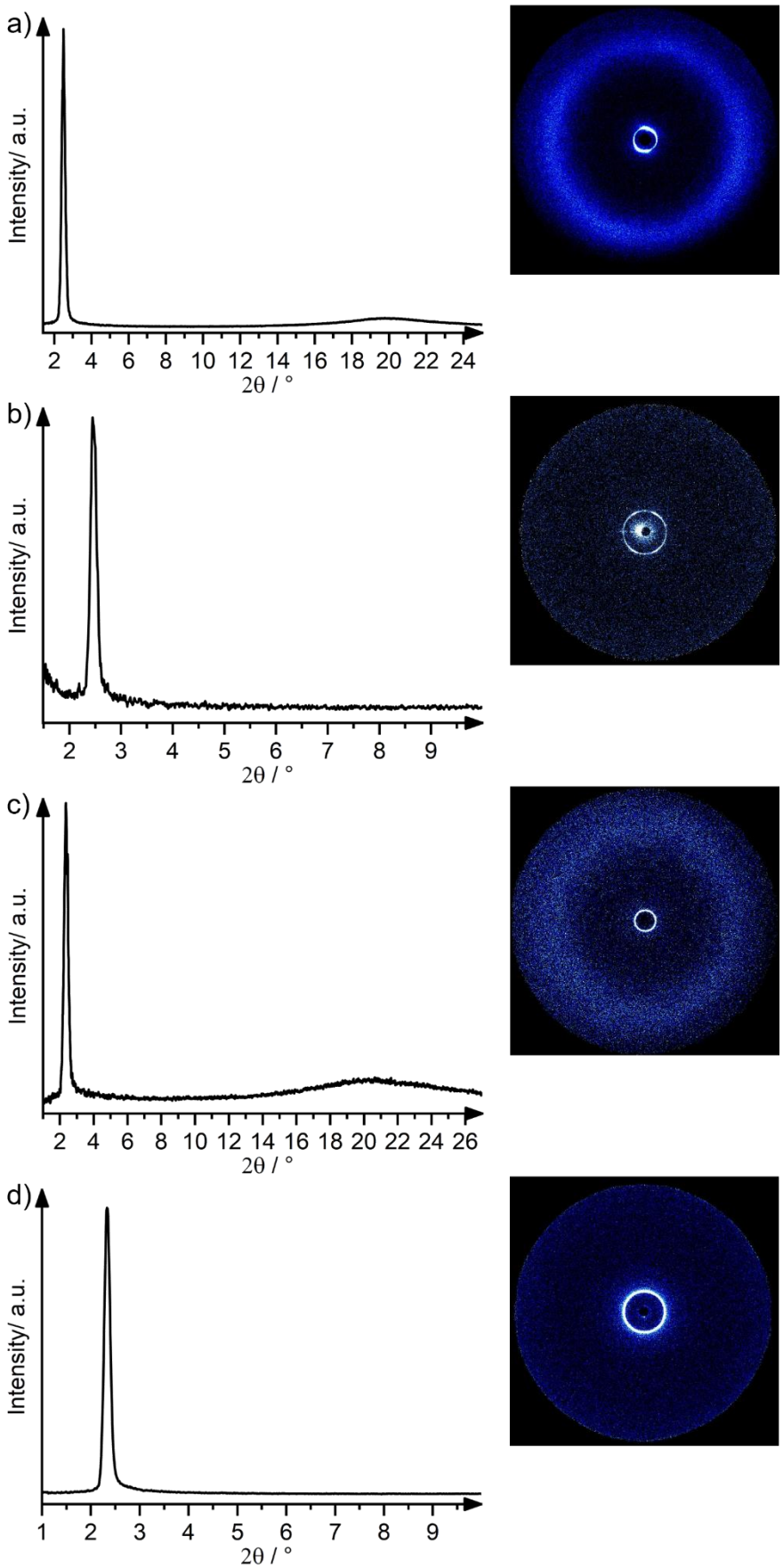


Figure S12: WAXS (a) and SAXS (b) diffraction pattern and diffractogram of the SmA phase of **12O-AzF-PhO12** at 140 °C and WAXS (c) and SAXS (d) of the SmA phase of **12O-AzNO$_2$-PhO12** at 137 °C.

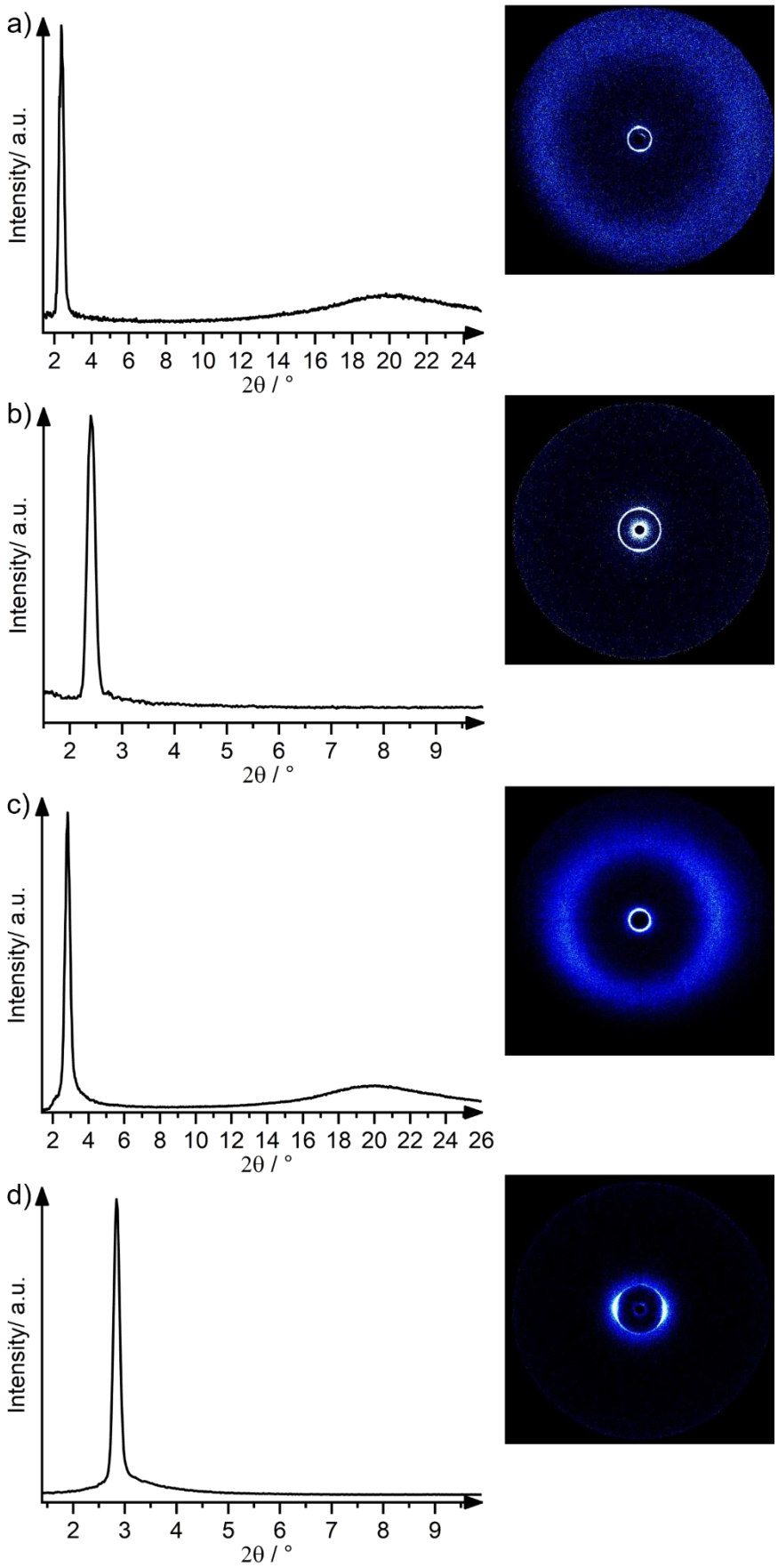


Figure S13: WAXS (a) and SAXS (b) diffraction pattern and diffractogram of the SmA phase of **12O-AzNO$_2$-MePhO12** at 74 °C and WAXS (c) and SAXS (d) of the SmC phase of **12O-Az-NO$_2$PhO12** at 137 °C.

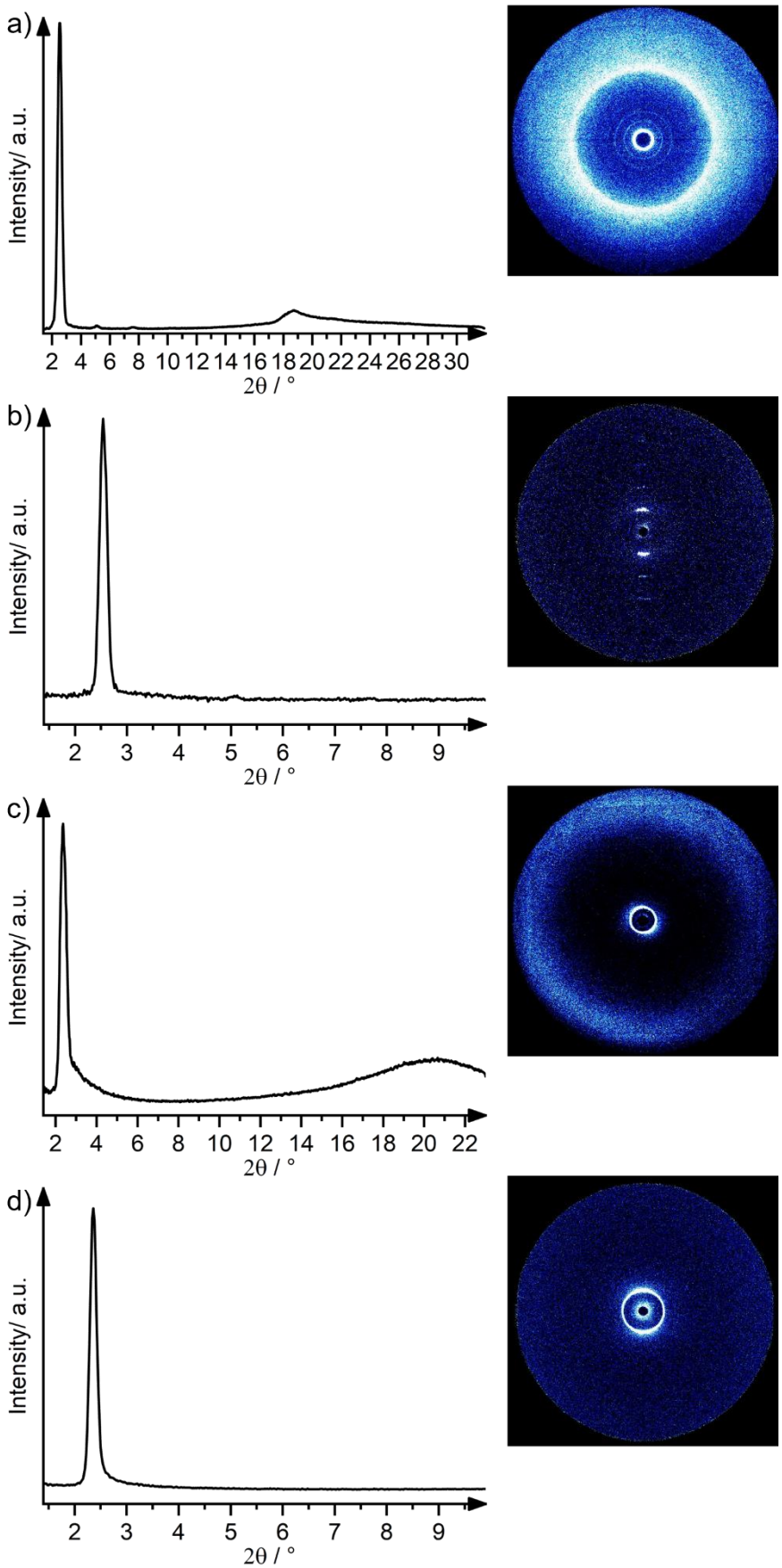


Figure S14: WAXS (a) and SAXS (b) diffraction pattern and diffractogram of the SmE phase of **12O-Az-Thi12** at 131 °C and WAXS (c) and SAXS (d) of the SmA phase of **12O-AzCN-Thi12** at 98 °C.

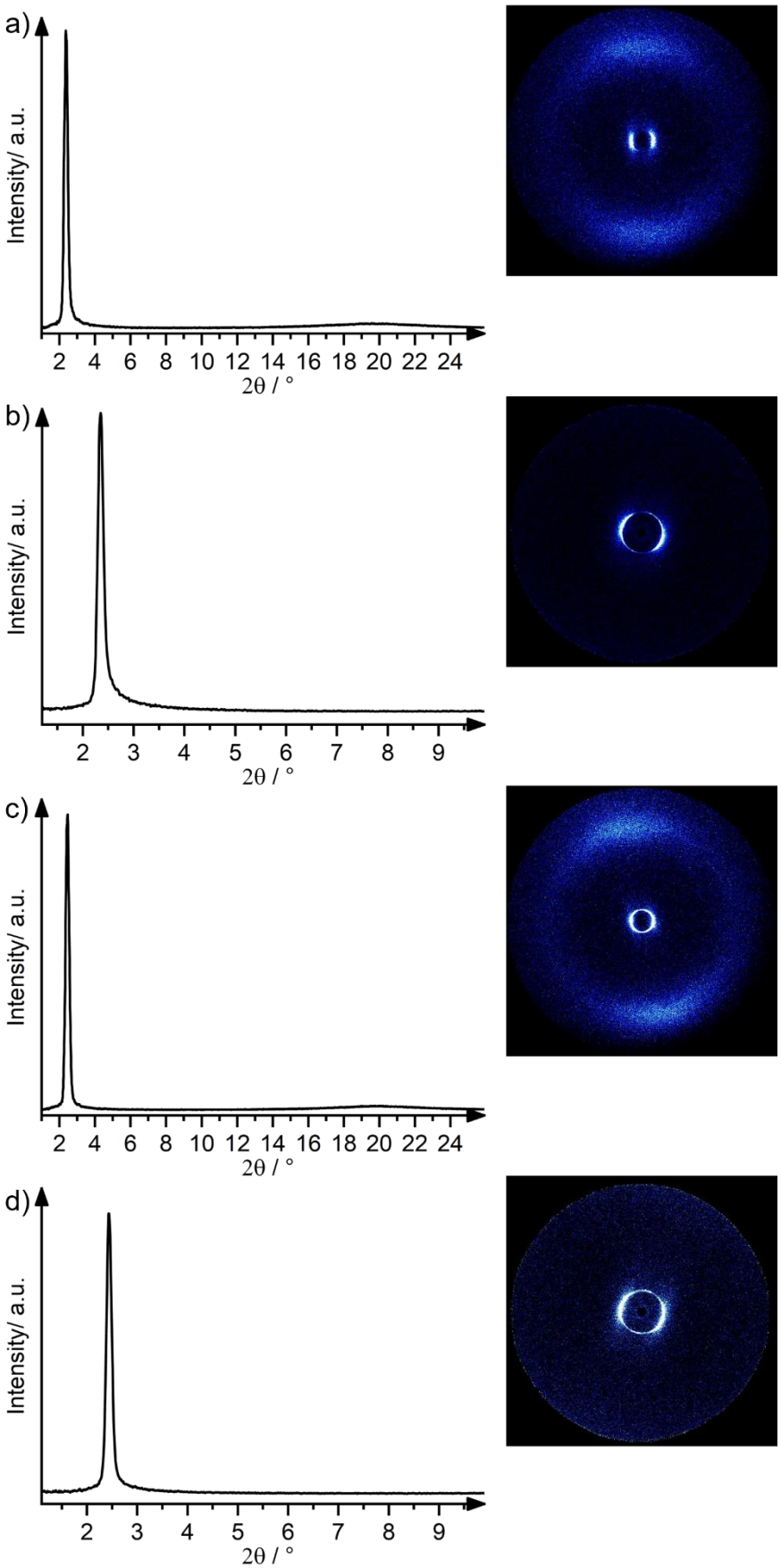


Figure S15: WAXS (a) and SAXS (b) diffraction pattern and diffractogram of the SmA phase of **12O-Az-PyriO12** at 183 °C and WAXS (c) and SAXS (d) of the SmC phase of **12O-Az-PyriO12** at 154 °C.

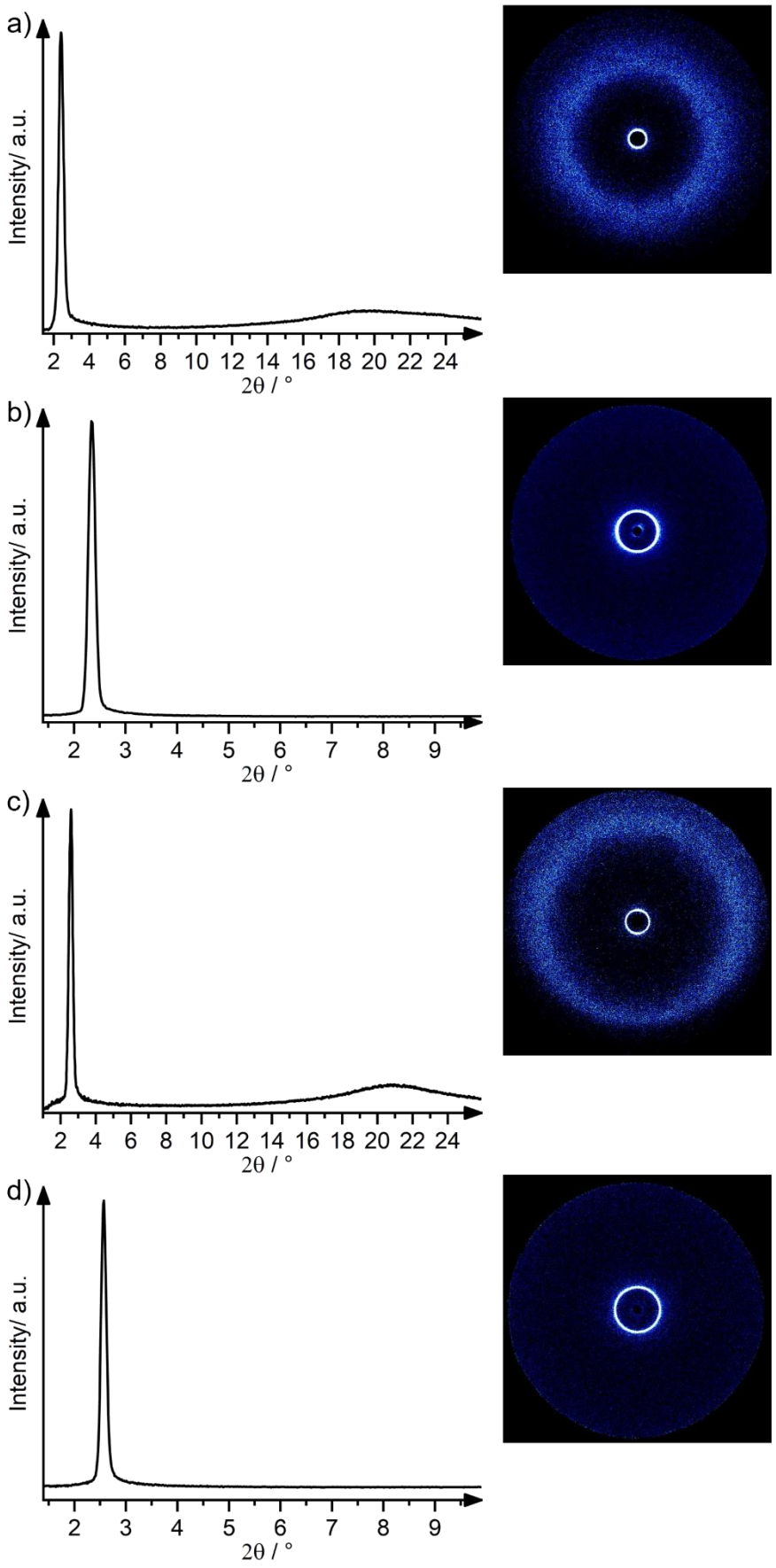


Figure S16: WAXS (a) and SAXS (b) diffraction pattern and diffractogram of the the SmA phase of **12O-AzCN-PyriO12** at 120 and WAXS (c) and SAXS (d) of the SmC phase of **12Yne-AzNO$_2$-PhO12** at room temperature.

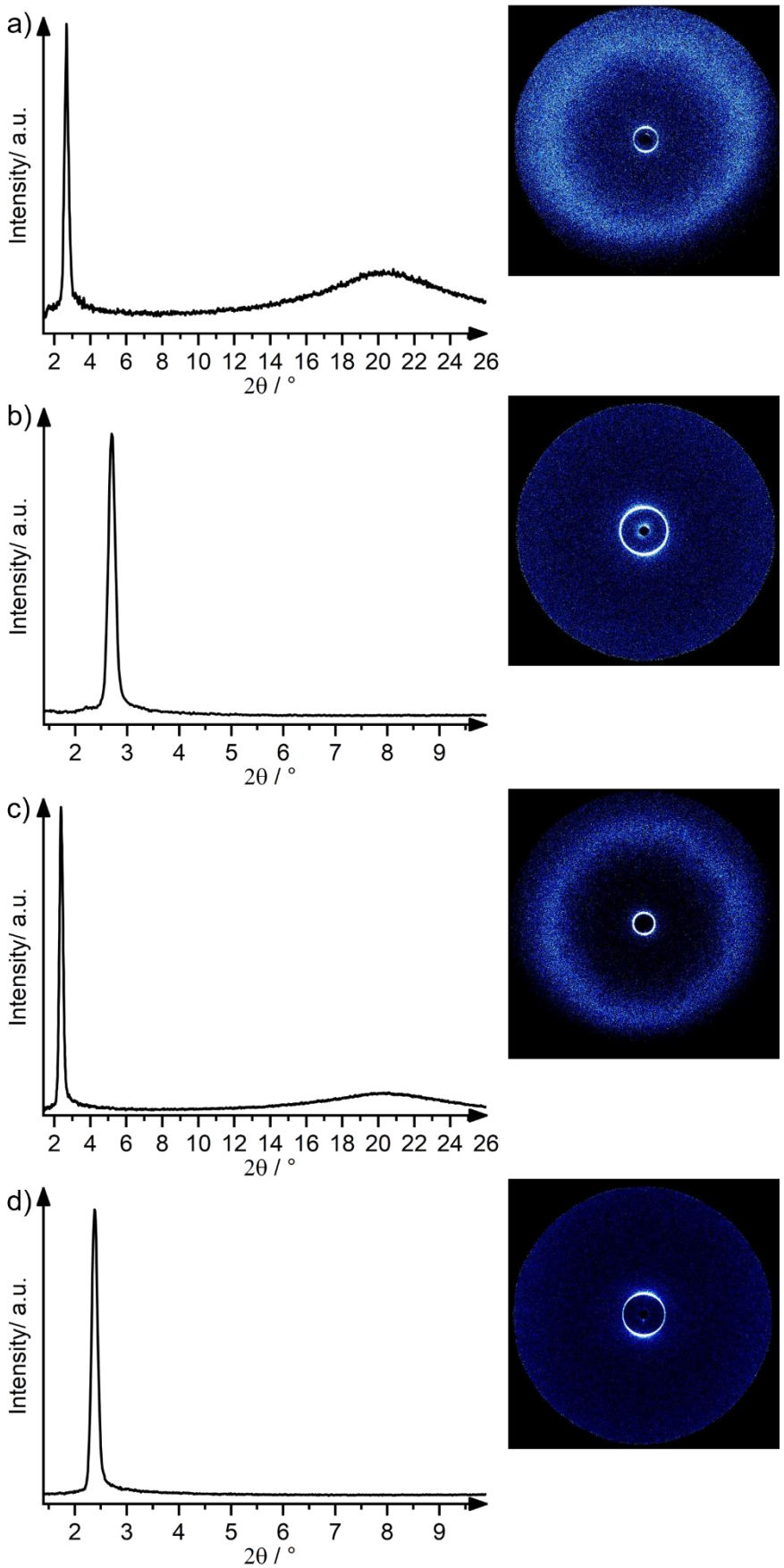


Figure S17: WAXS (a) and SAXS (b) diffraction pattern and diffractogram of the SmC phase of **12Yne-AzCN-PhO12** at 88 °C and WAXS (c) and SAXS (d) of the SmA phase of **12O-AzCN-PhYne12** at 131 °C.

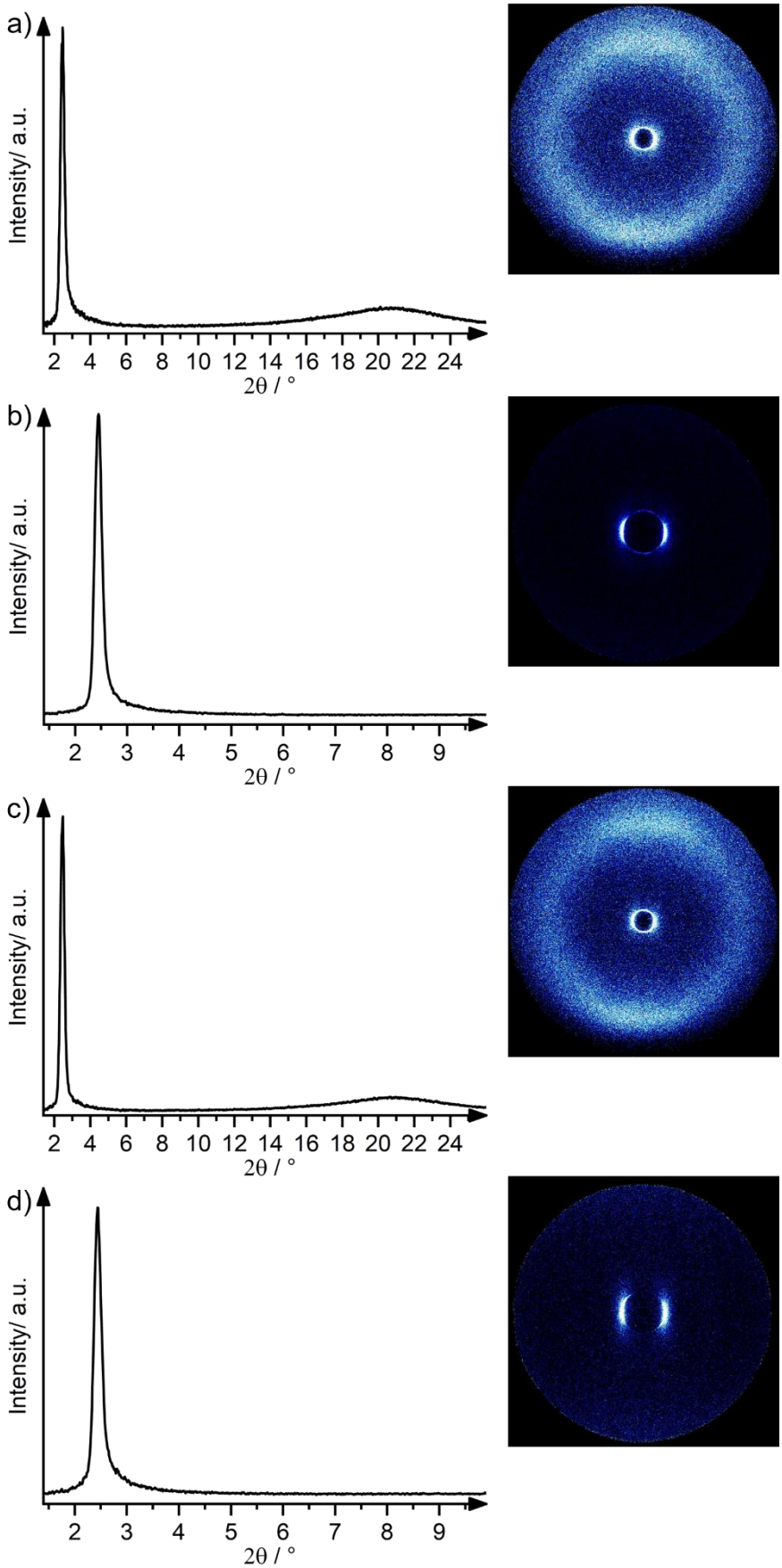


Figure S18: WAXS (a) and SAXS (b) diffraction pattern and diffractogram of the SmA phase of **12Yne-AzCN-PhYne12** at 79 °C and WAXS (c) and SAXS (d) of the SmC phase of **12Yne-AzCN-PhYne12** at 60 °C.

6. Single Crystal X-Ray Data

Table S3: Crystallographic data of the obtained single crystal structures.

Compound	**12S-AzCN-PhO12**	**12O-AzCN-PhS12**	**12O-AzNO$_2$-PhO12**
CCDC number	2242094	2242093	2242092
formula	C41H59NOS	C41H59NOS	C40H59NO4
formula weight (g/mol)	613.95	613.95	617.88
crystal size (mm)	0.317 x 0.260 x 0.026	0.353 x 0.104 x 0.066	0.345 x 0.278 x 0.054
temperature (K)	140(2)	140(2)	145(2)
wavelength λ (Å)	0.71073	1.54178	0.71073
crystal system	Monoclinic	Monoclinic	Triclinic
space group	P2(1)/c	C2/c	P-1
unit cell dimension			
a (Å)	36.366(2)	63.421(5)	4.0571(2)
b (Å)	14.4460(8)	5.4344(4)	32.9255(13)
c (Å)	6.8454(4)	22.0542(15)	42.2251(16)
α (deg)	90	90	110.788(2)
β (deg)	90.421(4)	107.341(4)°	91.124(2)
γ (deg)	90	90	91.507(2)
V (Å^3)	3596.1(4)	7255.6(9)	5269.0(4)
Z	4	8	6
D_c (g/cm^3)	1.134	1.124	1.168
μ (mm^{-1})	0.122	1.011	0.074
F(000)	1344	2688	2028
theta range for data collection	1.120 to 26.498	2.920 to 65.557	1.238 to 28.429
index ranges	-45<=h<=45, -18<=k<=17, -8<=l<=8	-72<=h<=74, -6<=k<=6, -18<=l<=25	-5<=h<=5, -43<=k<=42 -49<=l<=56
reflection collected/unique	50591 / 7321 [R(int) = 0.0768]	31585 / 6083 [R(int) = 0.0532]	107148 / 26370 [R(int) = 0.0563]
completeness to theta	98.7 %	96.9 %	99.8 %
max. and min. transmission	0.7400 and 0.6980	0.7528 and 0.5264	0.7457 and 0.6534
refinement methods	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
data/restraints/parameter	7321 / 0 / 399	6083 / 0 / 399	26370 / 0 / 1222
GOF on F^2	1.028	1.035	1.033
R_1, wR_2 [I > 2σ(I)]	R1 = 0.0609, wR2 = 0.1203	R1 = 0.0465, wR2 = 0.1177	R1 = 0.0883, wR2 = 0.1921
R_1, wR_2 (all data)	R1 = 0.1143, wR2 = 0.1338	R1 = 0.0594, wR2 = 0.1234	R1 = 0.1483, wR2 = 0.2094
largest diff. peak and hole (e/Å^3)	0.231 and -0.341	0.200 and -0.256	0.453 and -0.473

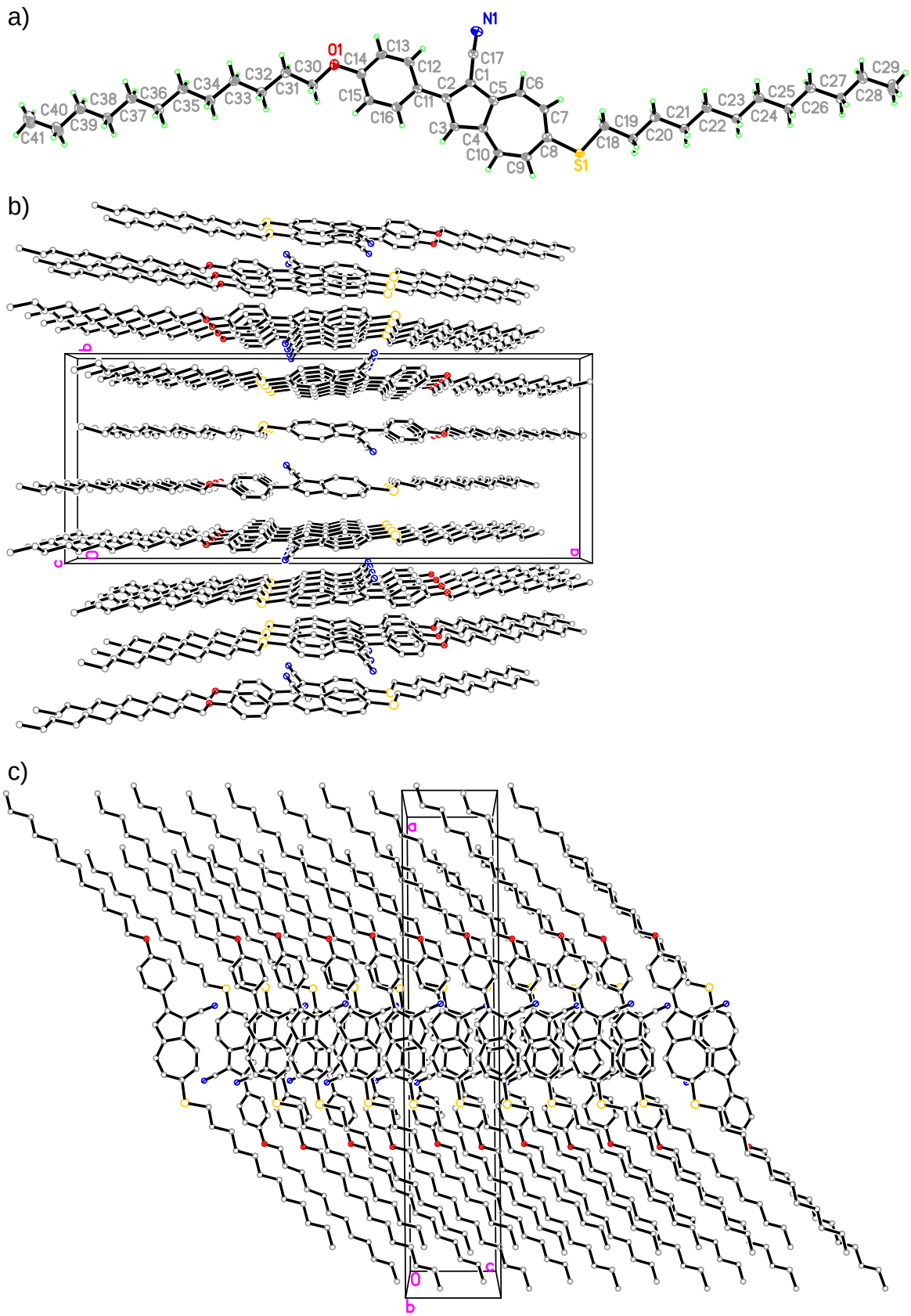


Figure S19: Single crystal X-Ray structure of **12S-AzCN-PhO12**. a) Single molecule, b) view parallel along the c-axis, c) view along the b-axis.

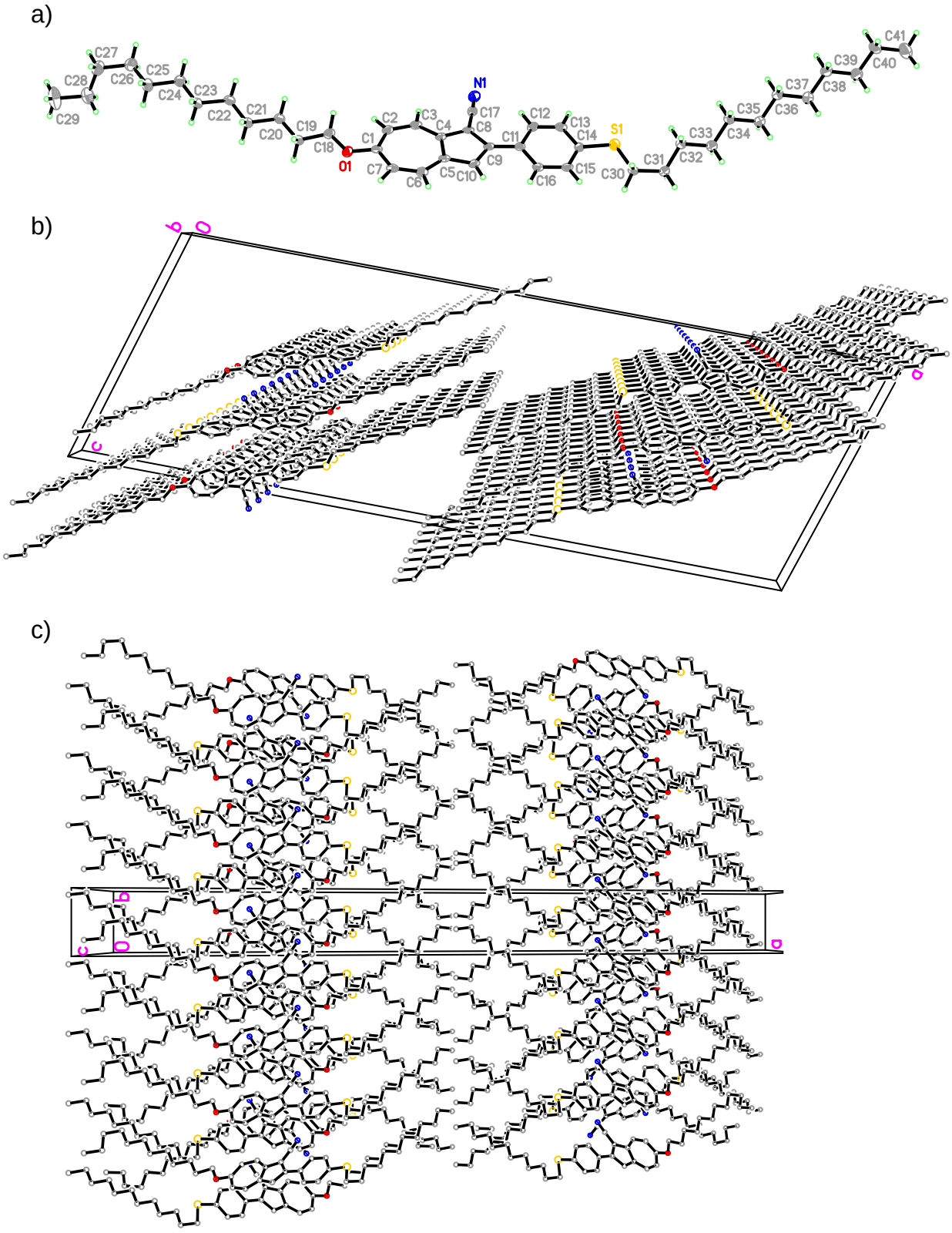


Figure S20: Single crystal X-Ray structure of **12O-AzCN-PhS12**. a) Single molecule, b) view along the b-axis, c) view along the c-axis.

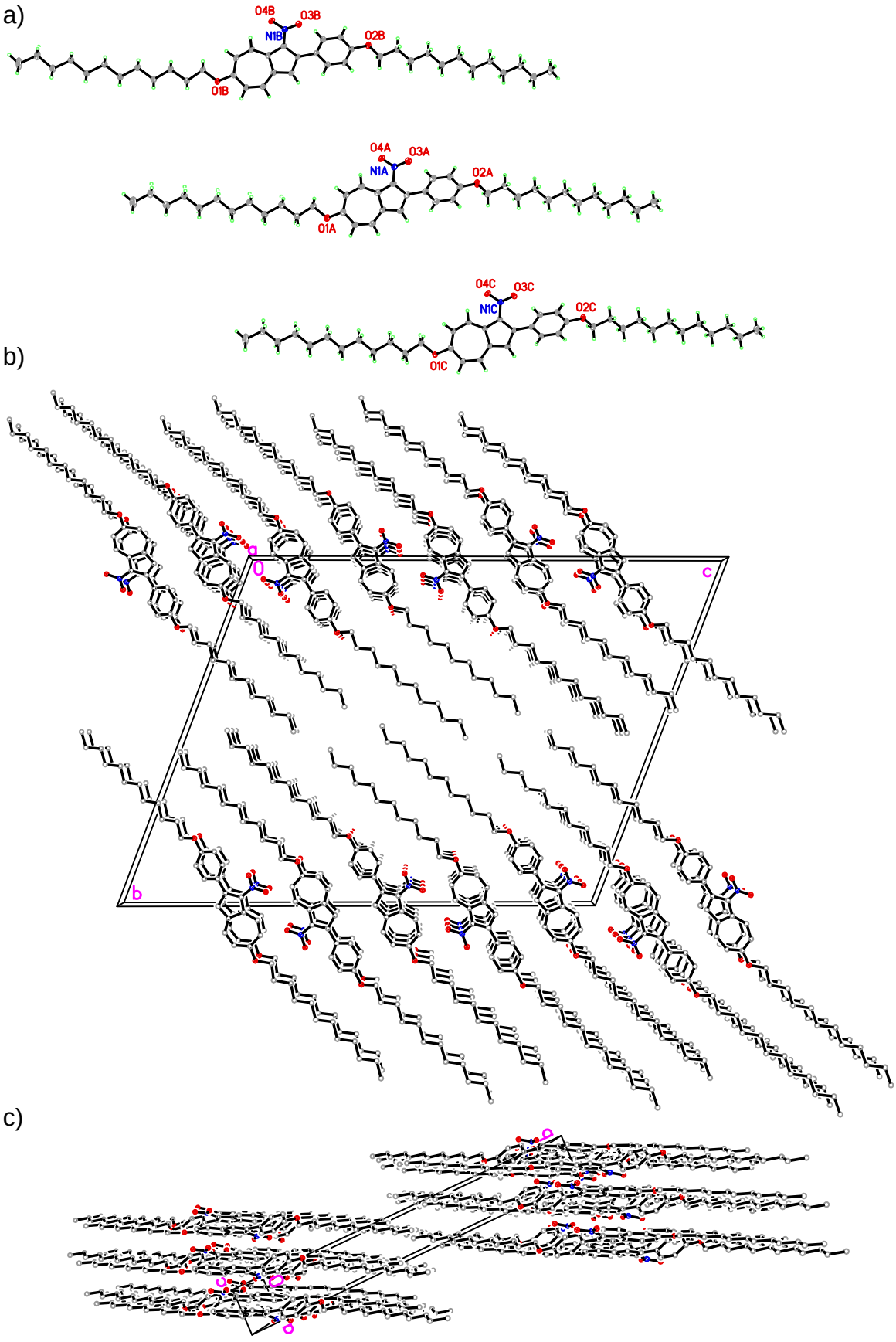


Figure S21: Single crystal X-Ray structure of **12O-AzNO$_2$-PhO12**. a) The three independent molecules, b) view along to the a-axis, c) view along the c-axis.

7. References

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8. NMR spectra

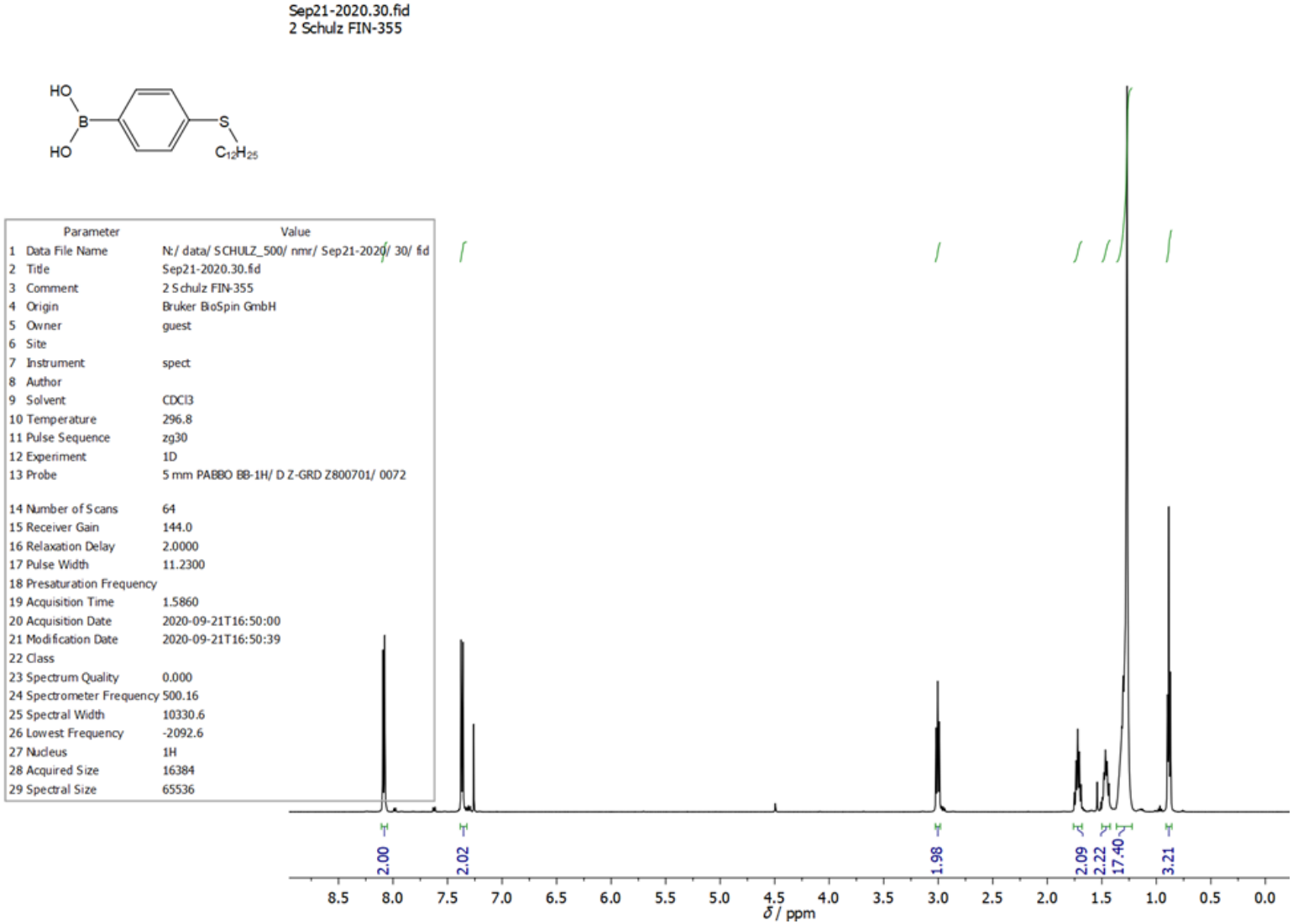


Figure S22: ^{1}H NMR spectrum of (4-dodecylthiophenyl)boronic acid in $CDCl_3$ at 500 MHz.

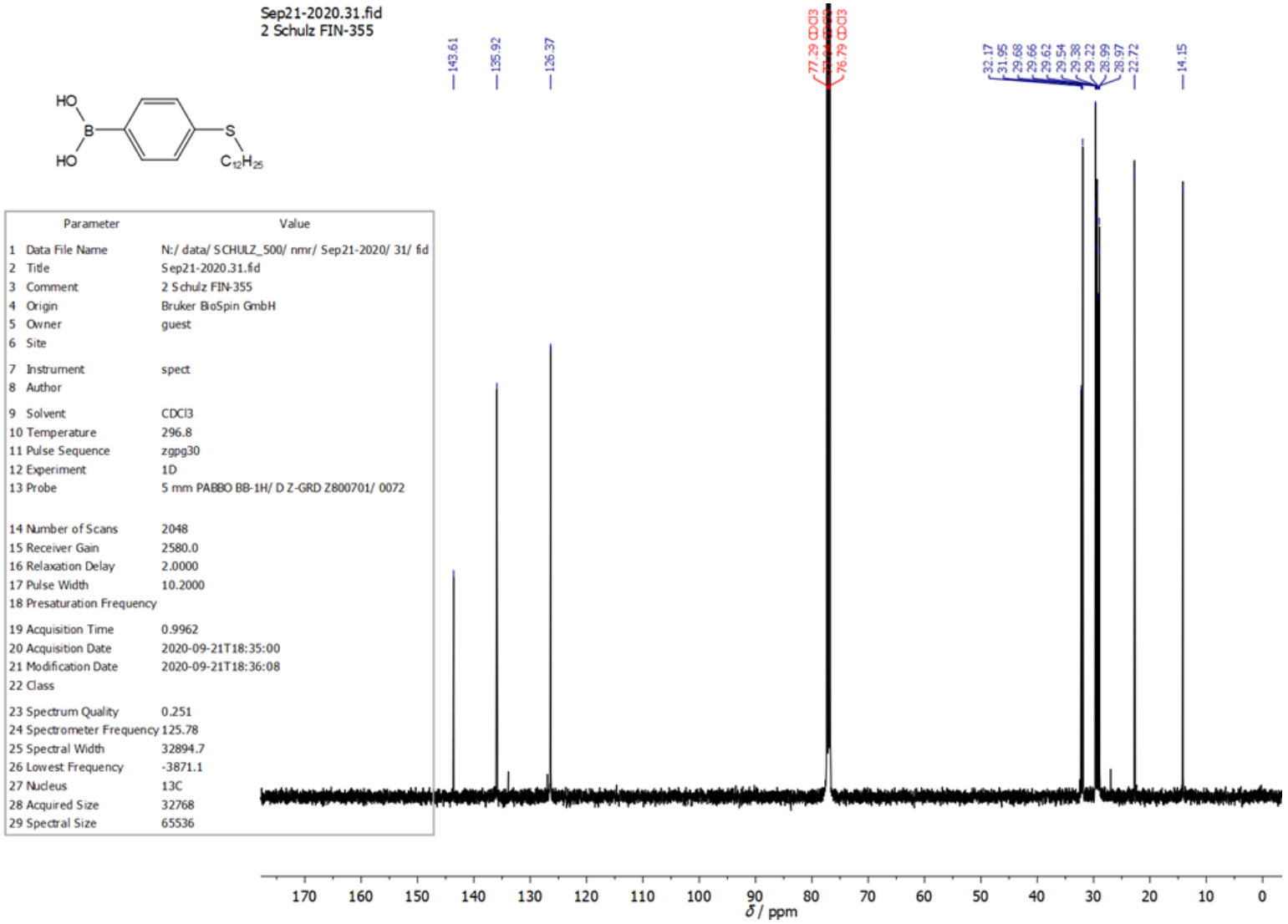


Figure S23: ^{13}C NMR-spectrum of (4-dodecylthiophenyl)boronic acid in $CDCl_3$ at 126 MHz.

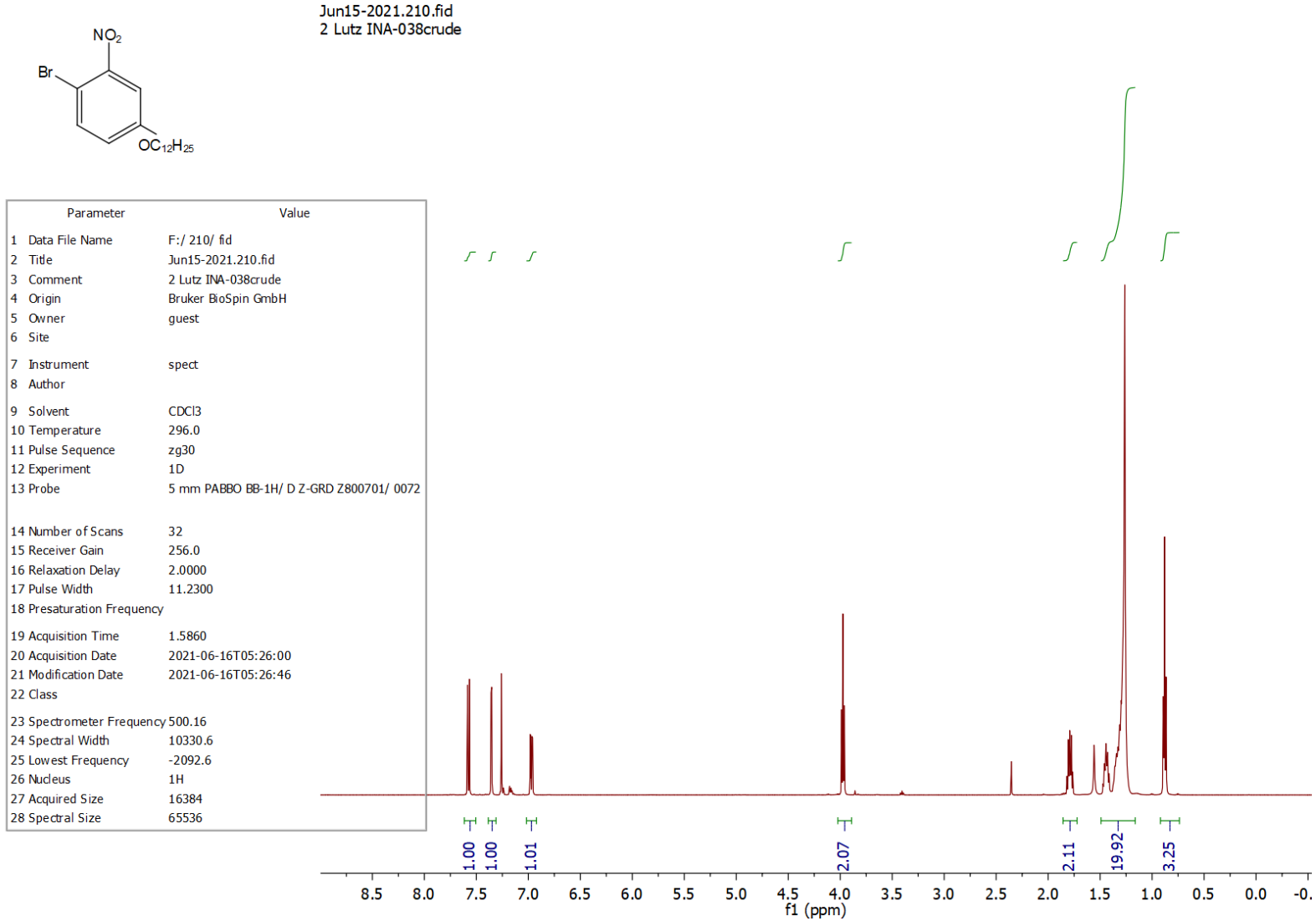


Figure S24: ^{1}H NMR spectrum of 1-bromo-4-dodecyloxy-2-nitrobenzene in $CDCl_3$ at 700 MHz.

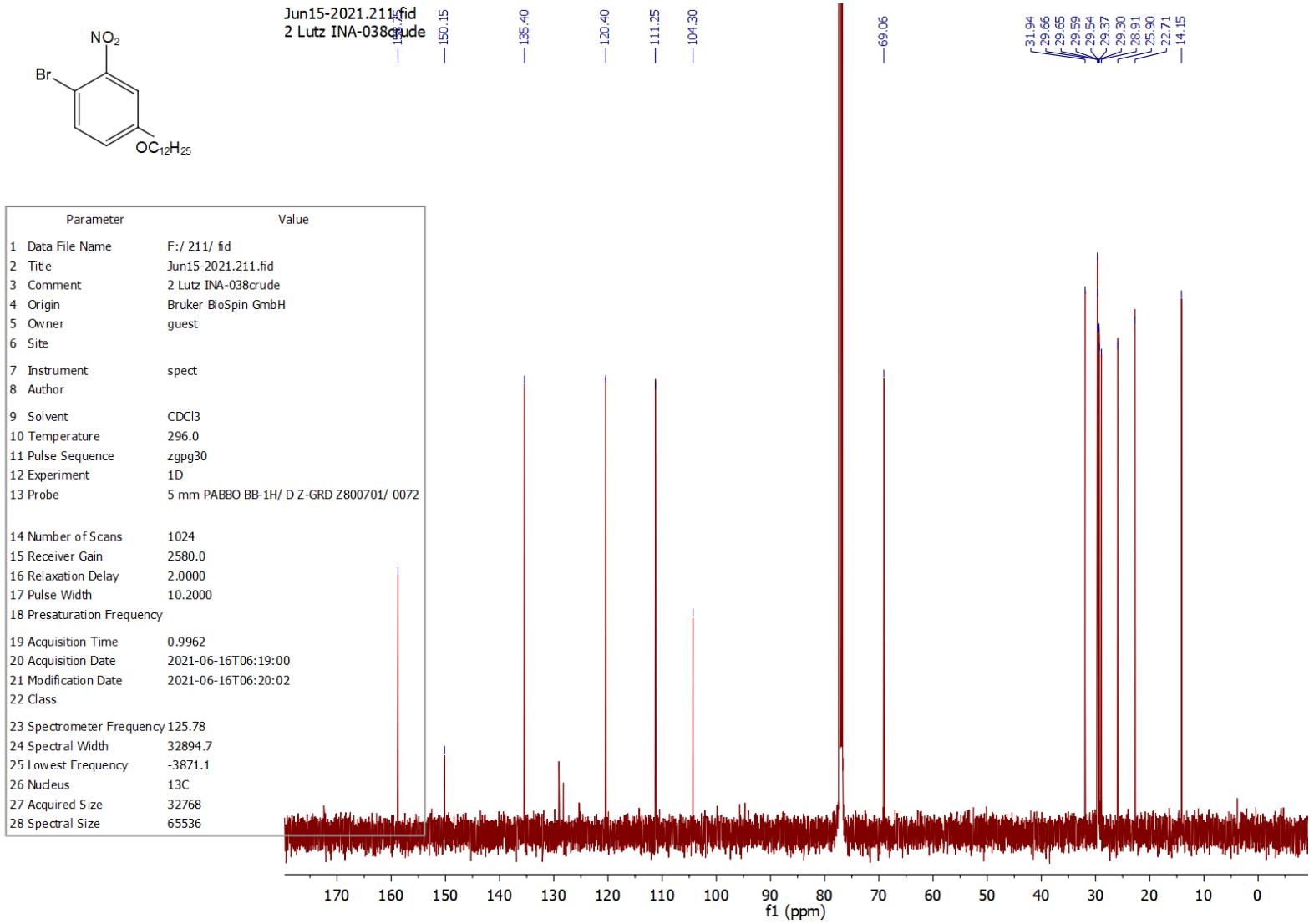


Figure S25: ^{13}C NMR spectrum of 1-bromo-4-dodecyloxy-2-nitrobenzene in $CDCl_3$ at 126 MHz.

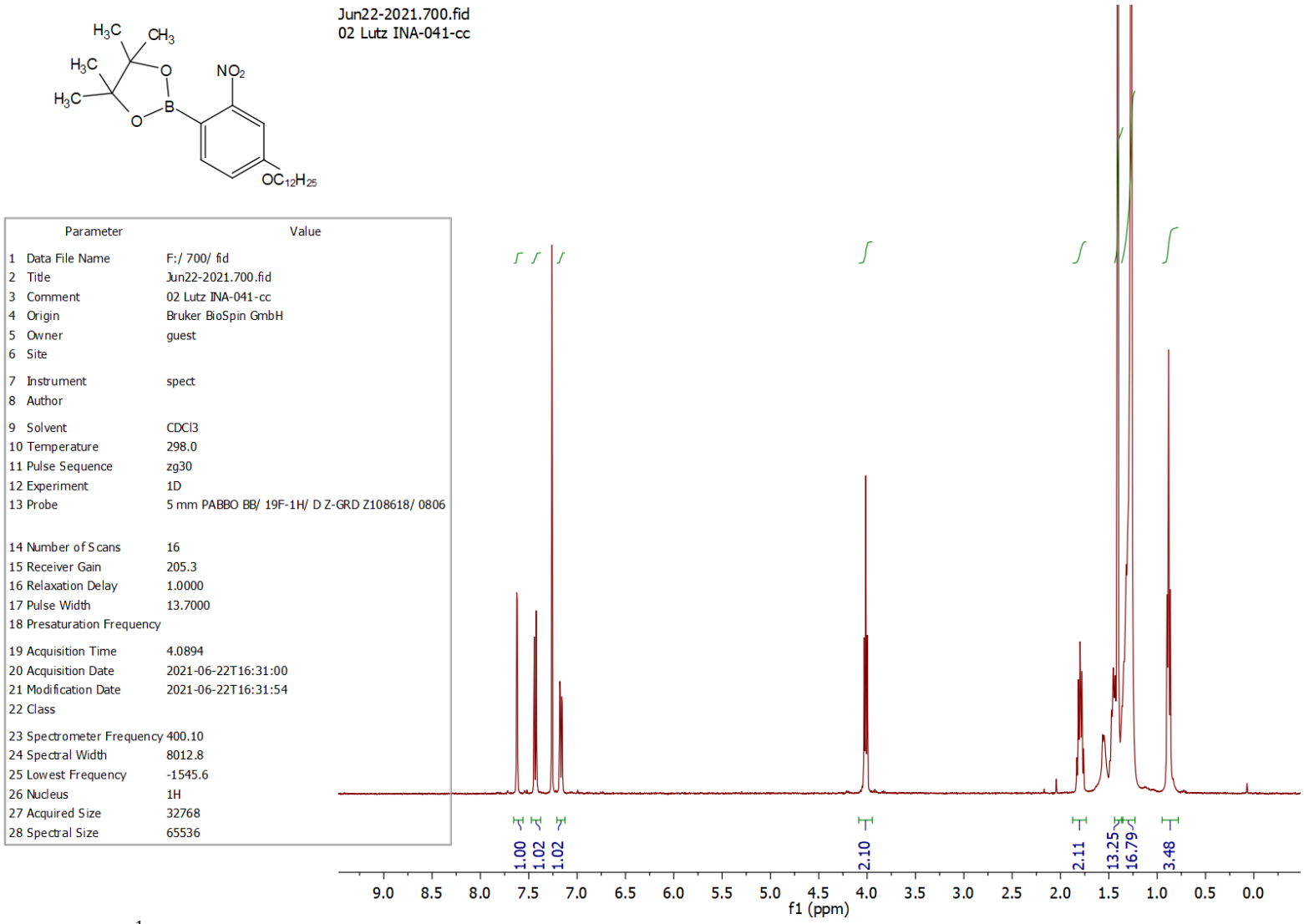
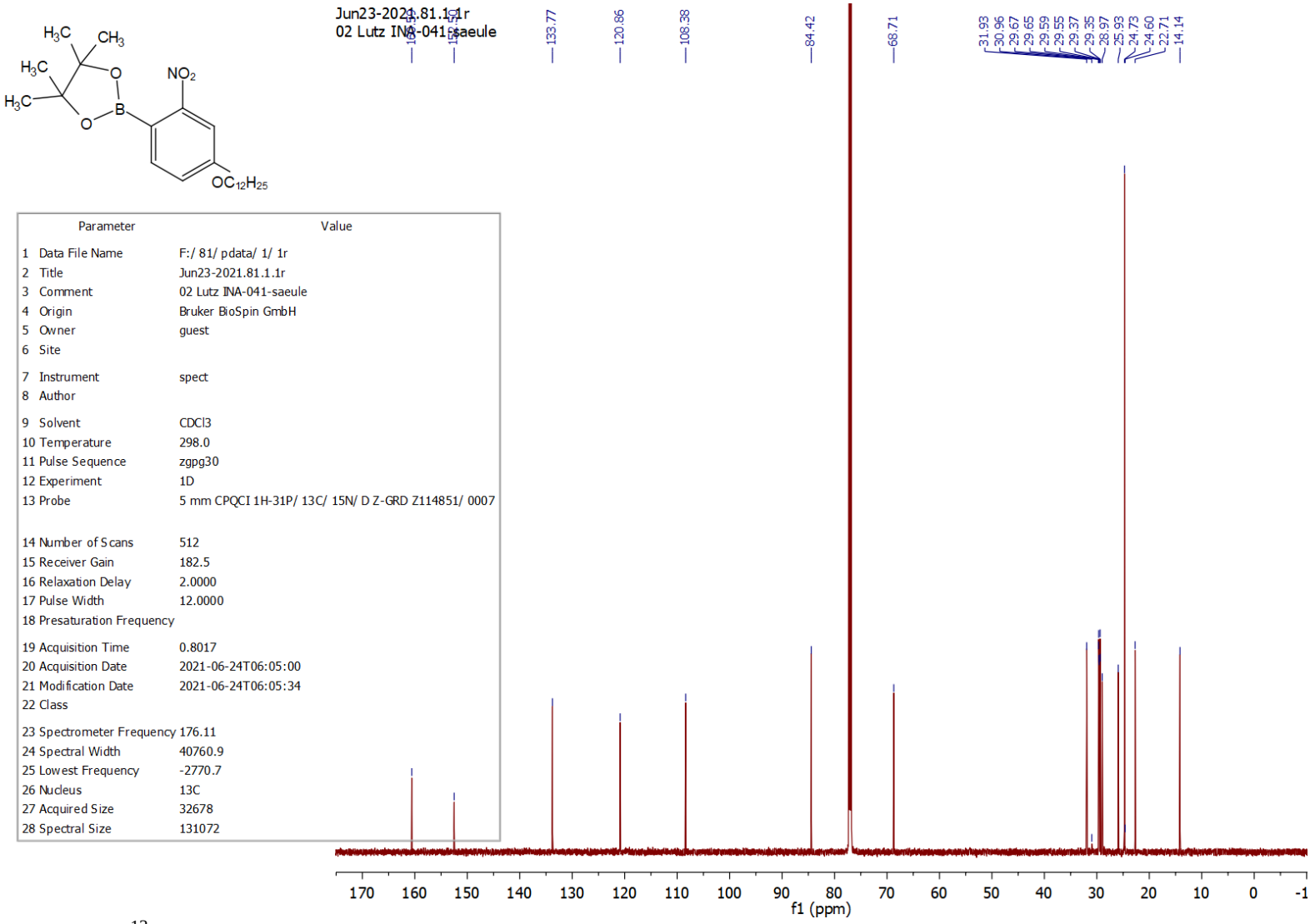


Figure S26: ^{1}H NMR spectrum of 2-(4-(dodecyloxy)-2-nitrophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in $CDCl_3$ at 400 MHz.



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8 Author	
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10 Temperature	298.0
11 Pulse Sequence	zgpg30
12 Experiment	1D
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26 Nucleus	13C
27 Acquired Size	32678
28 Spectral Size	131072

Figure S27: ^{13}C NMR spectrum of 2-(4-(dodecyloxy)-2-nitrophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in $CDCl_3$ at 176 MHz.

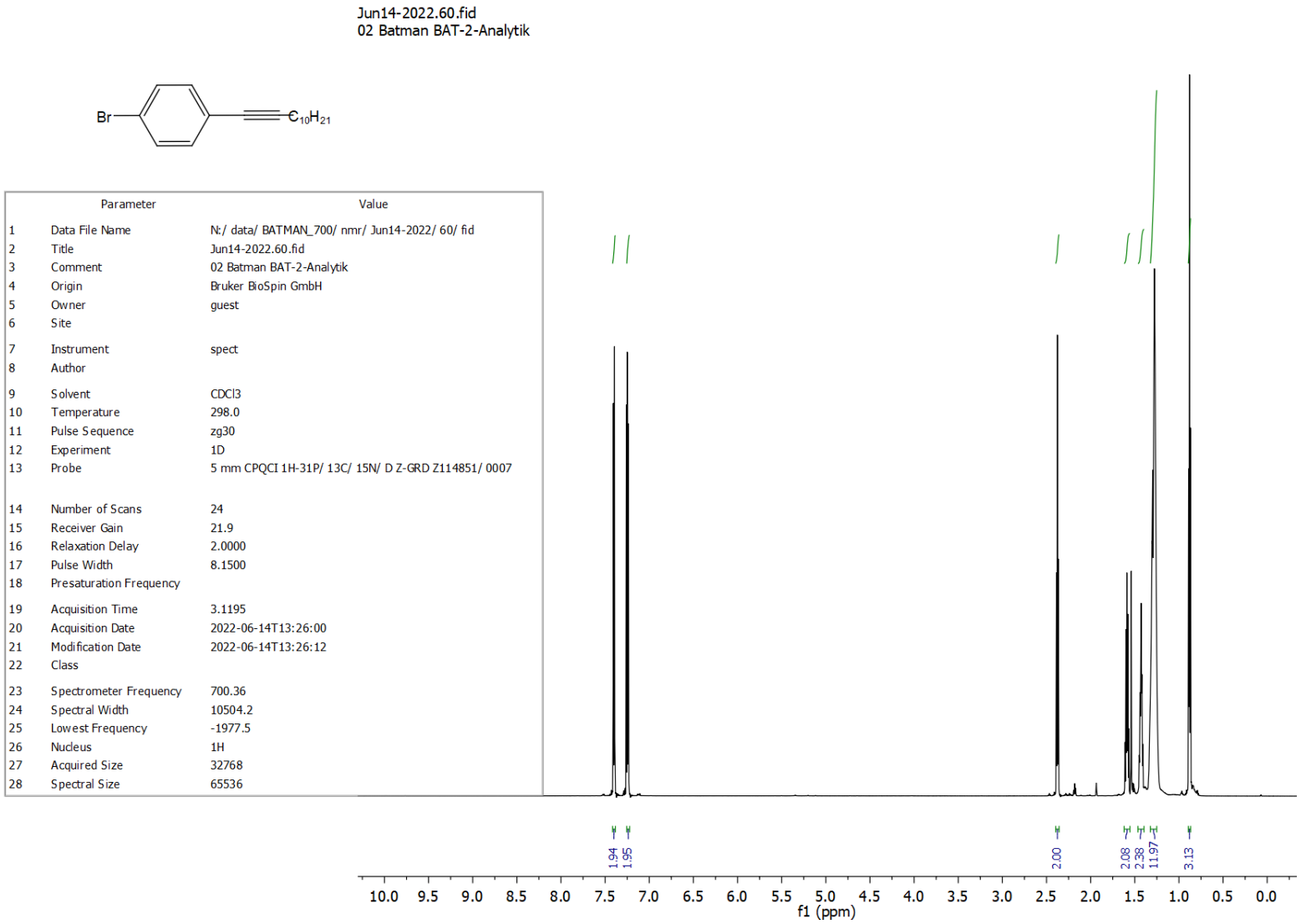


Figure S28: ^{1}H NMR spectrum of 4-(dodec-1-yne)-bromobenzene in $CDCl_3$ at 700 MHz.

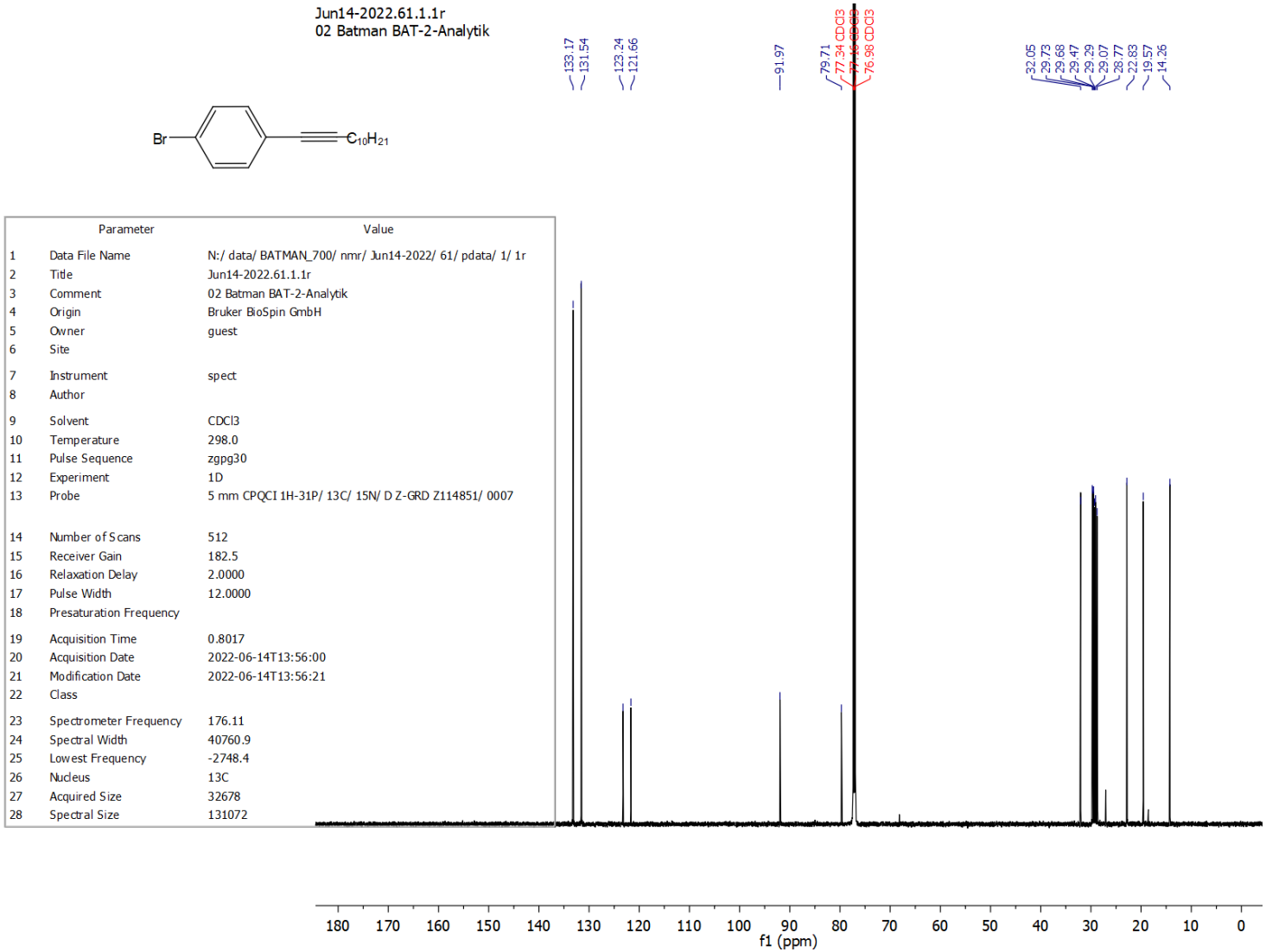


Figure S29: ^{13}C NMR spectrum of 4-(dodec-1-yne)-bromobenzene in $CDCl_3$ at 176 MHz.

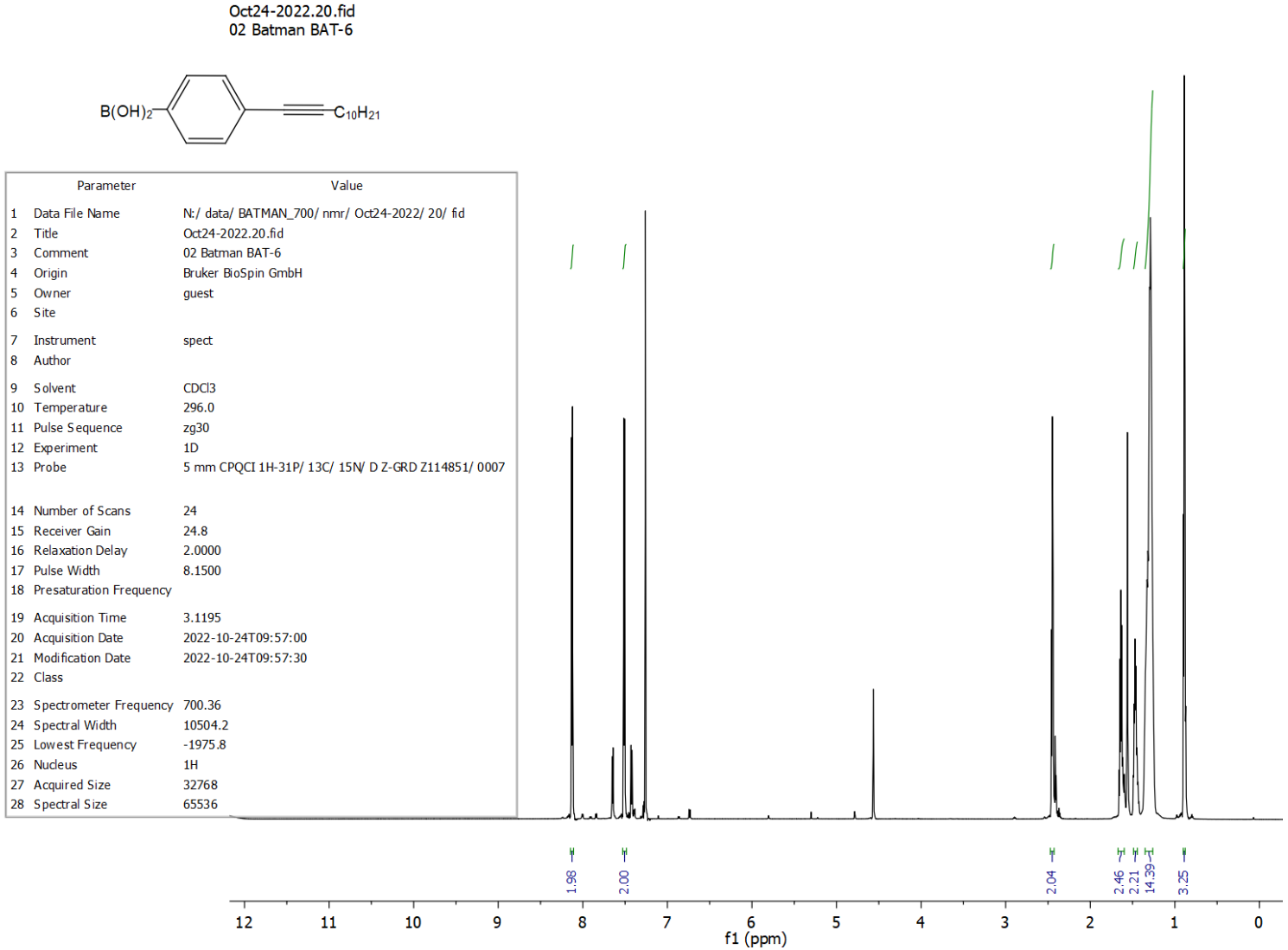


Figure S30: ^{1}H NMR spectrum of (4-(dodec-1-yn-1-yl)phenyl)boronic acid in $CDCl_3$ at700 MHz.

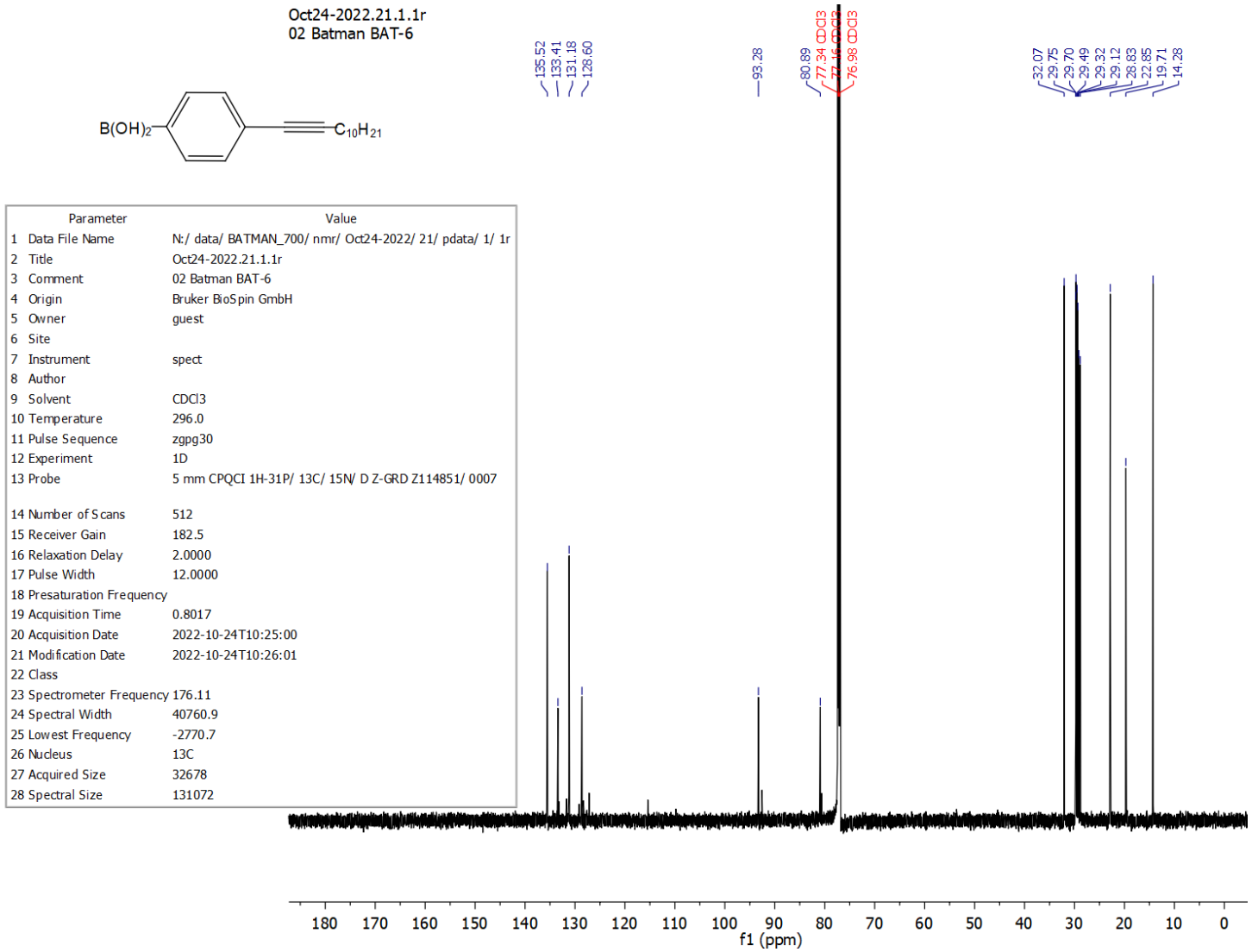


Figure S31: ^{13}C NMR spectrum of (4-(dodec-1-yn-1-yl)phenyl)boronic acid in $CDCl_3$ at176 MHz.

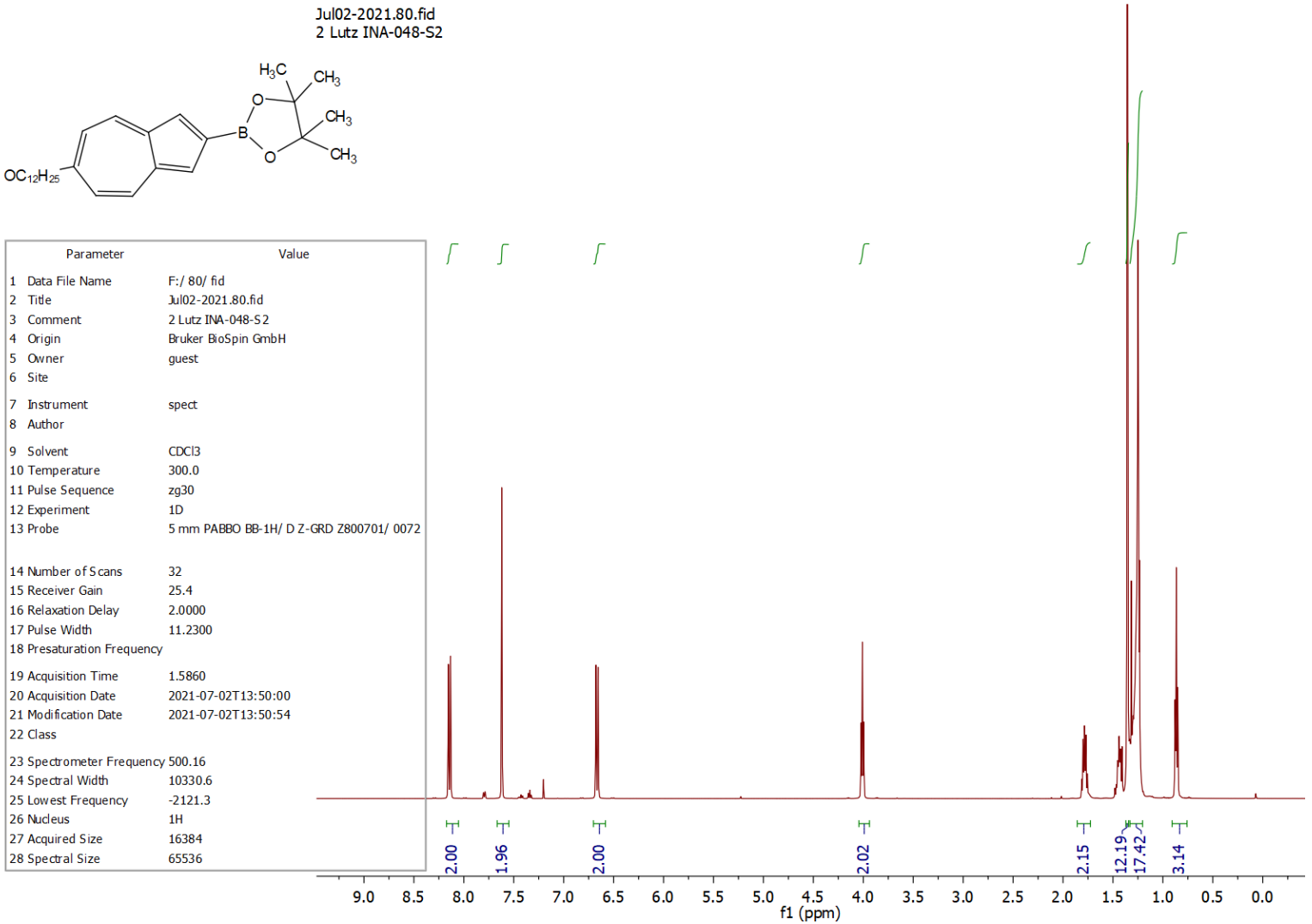


Figure S32: ^{1}H NMR-spectrum of **12O-Az-BPin** in $CDCl_3$ at 500 MHz.

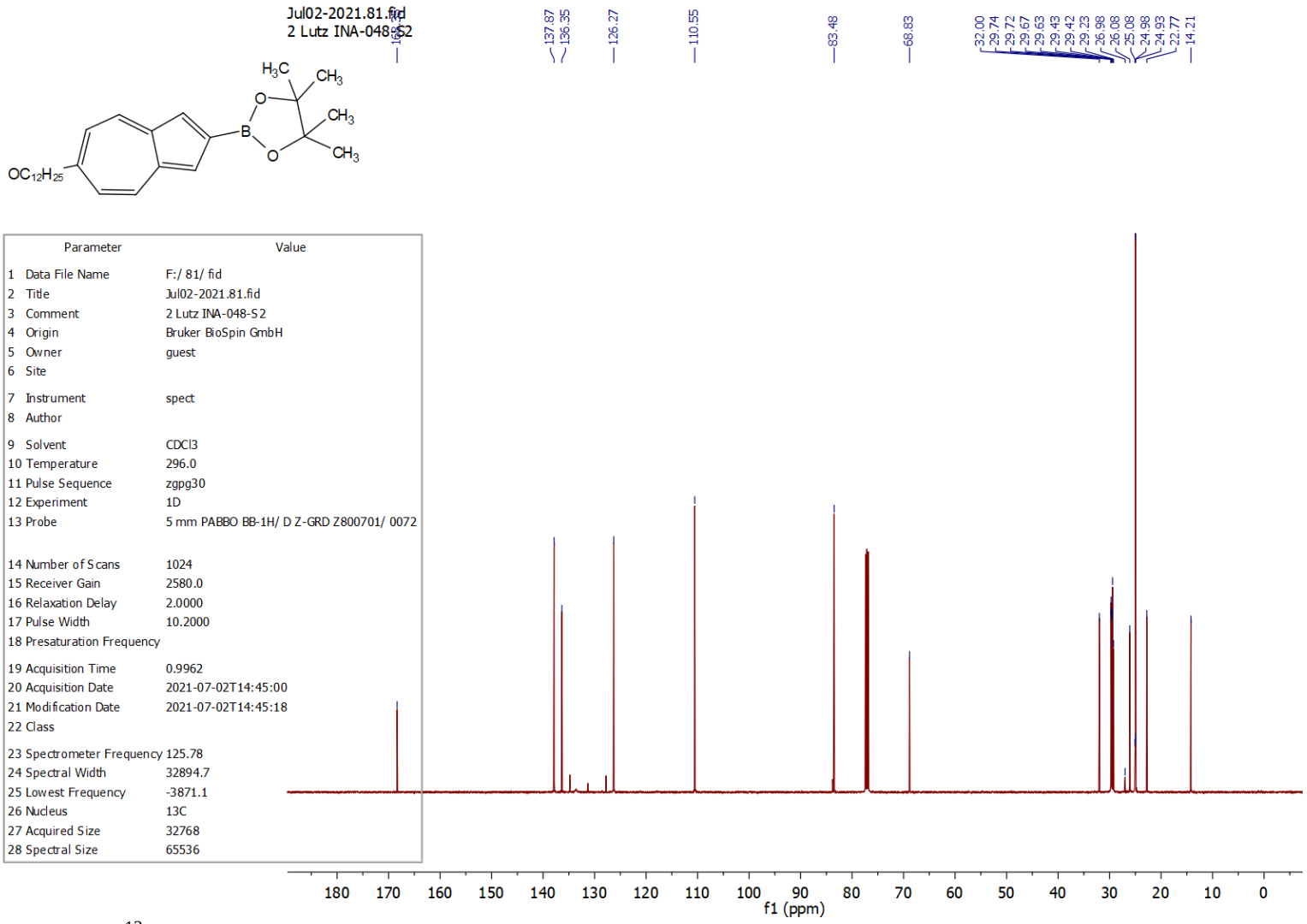


Figure S33: ^{13}C NMR spectrum of **12O-Az-BPin** in $CDCl_3$ at 126 MHz.

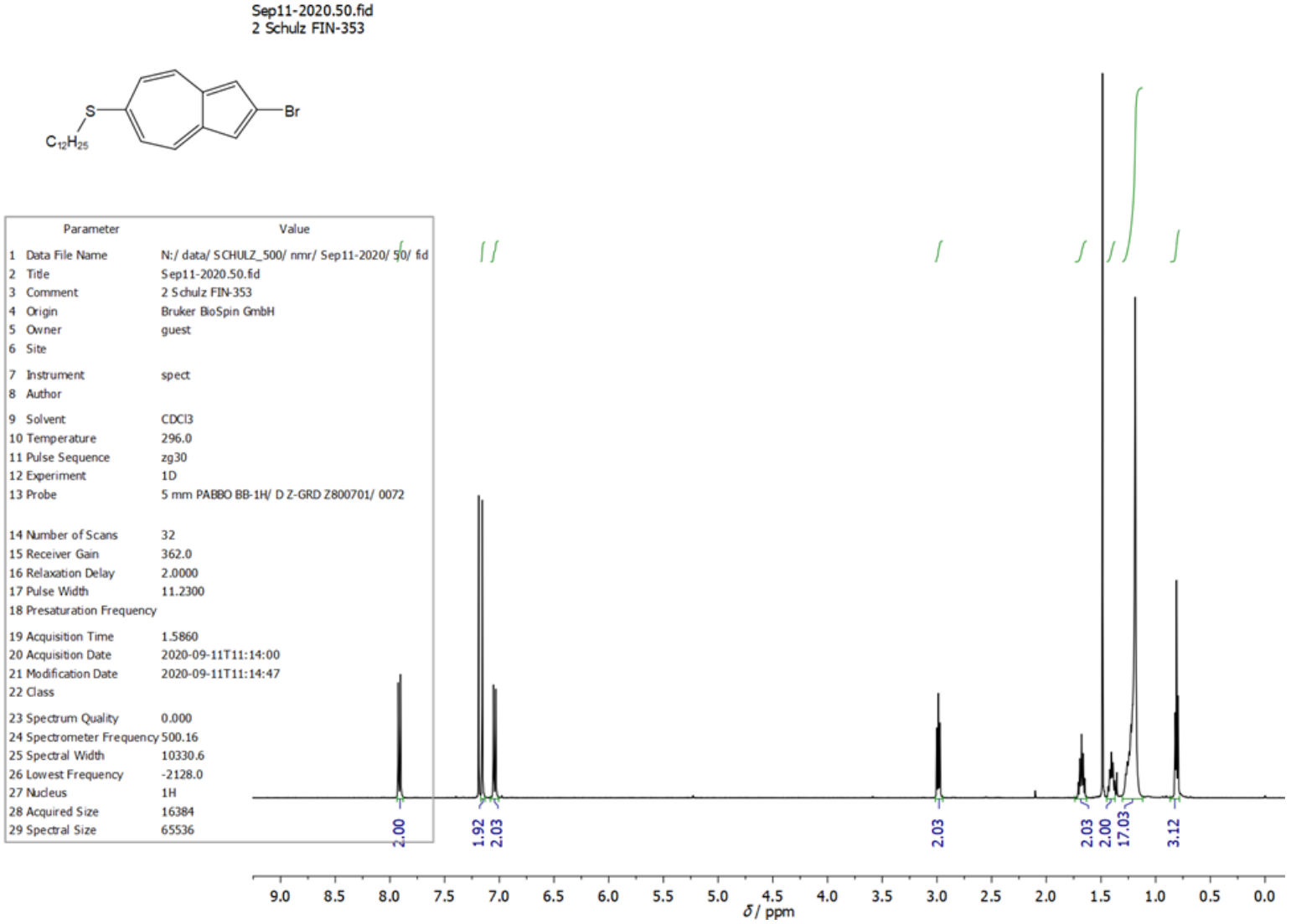


Figure S34: ^{1}H NMR spectrum of **12S-Az-Br** in $CDCl_3$ at 500 MHz.

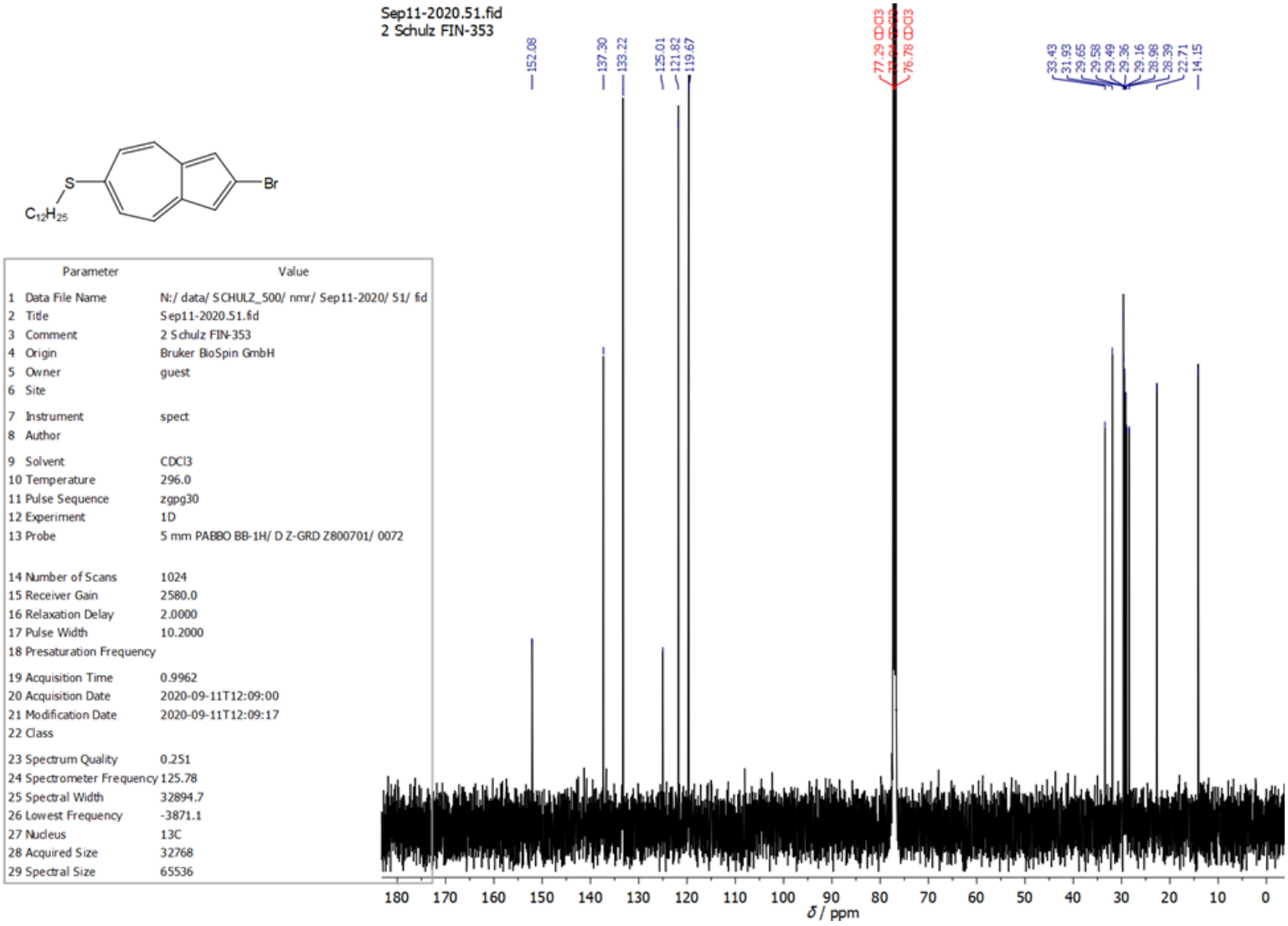


Figure S35: ^{13}C NMR spectrum of **12S-Az-Br** in $CDCl_3$ at 126 MHz.

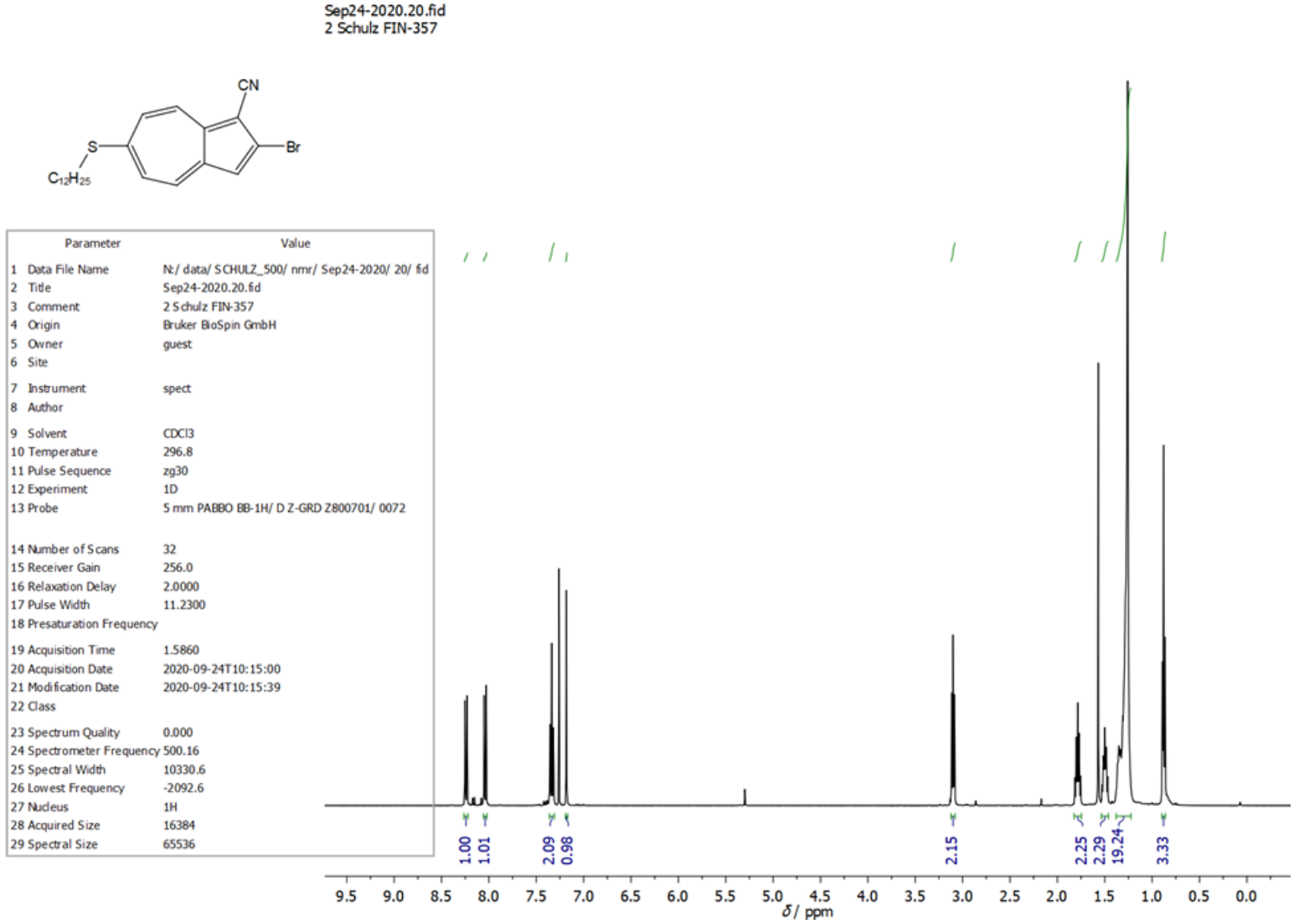


Figure S36: ^{1}H NMR spectrum of **12S-AzCN-Br** in $CDCl_3$ at 500 MHz.

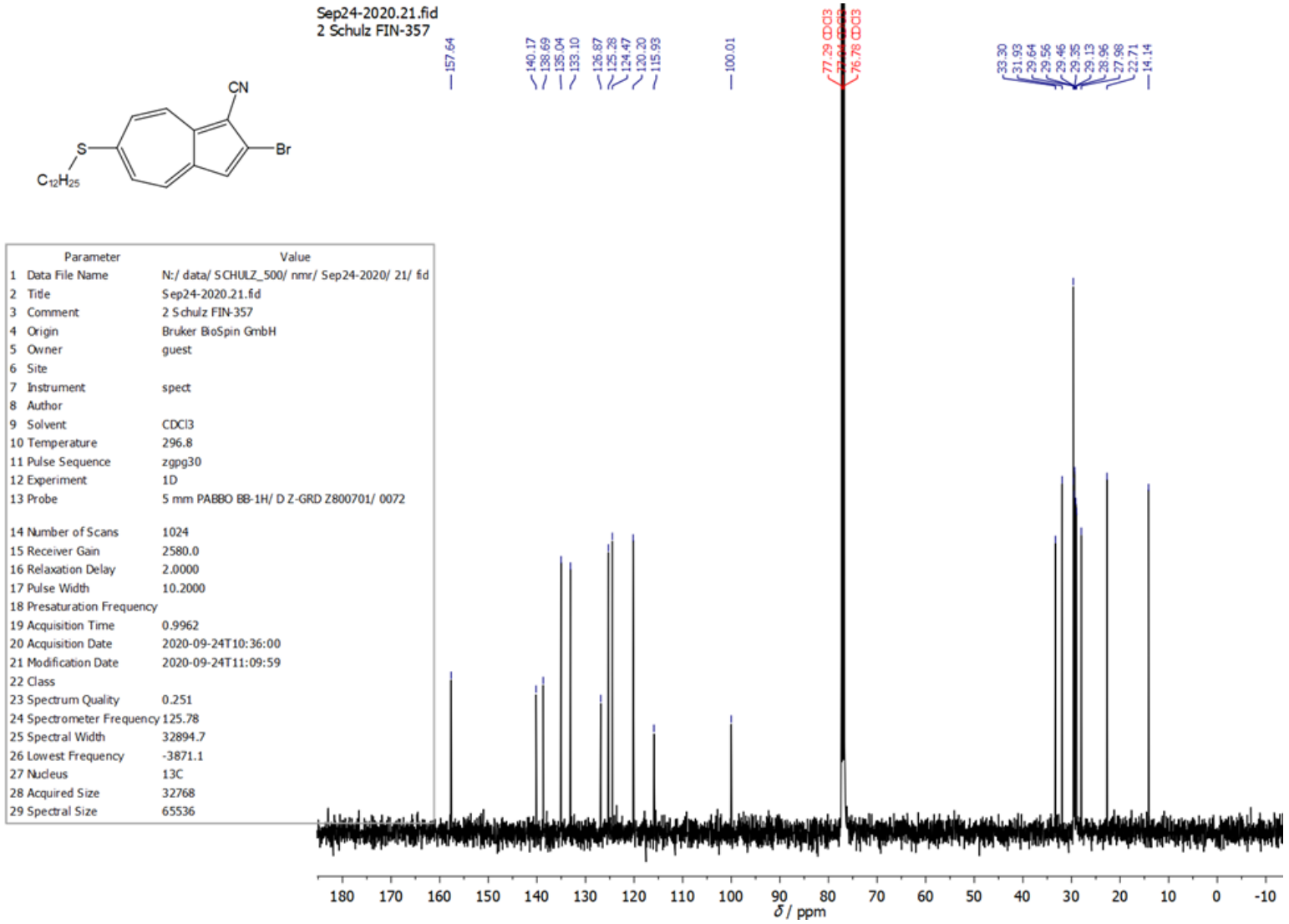


Figure S37: ^{13}C NMR spectrum of **12S-AzCN-Br** in $CDCl_3$ at 126 MHz.

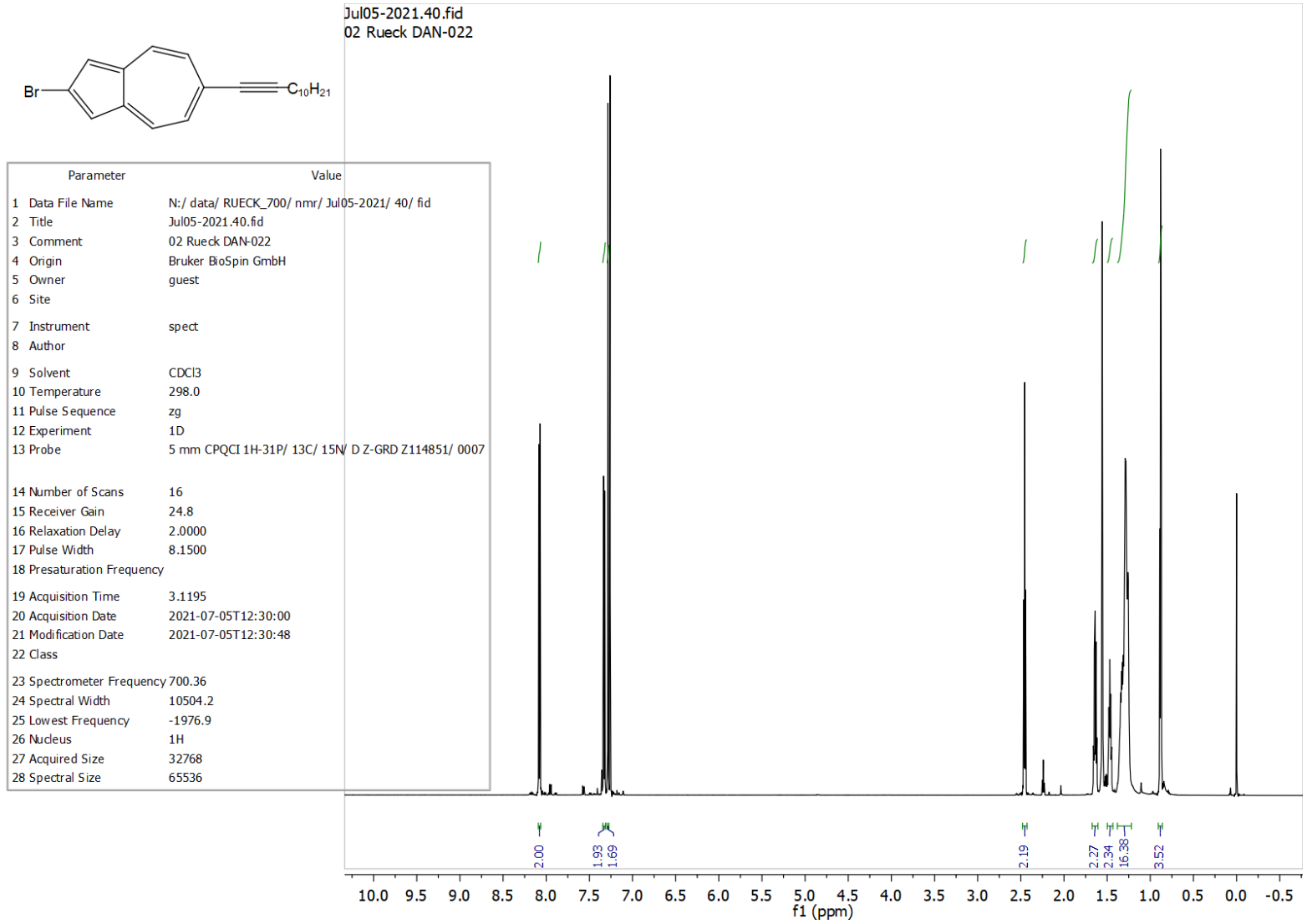


Figure S38: ^{1}H NMR-spectrum of **12Yne-Az-Br** in $CDCl_3$ at 700 MHz.

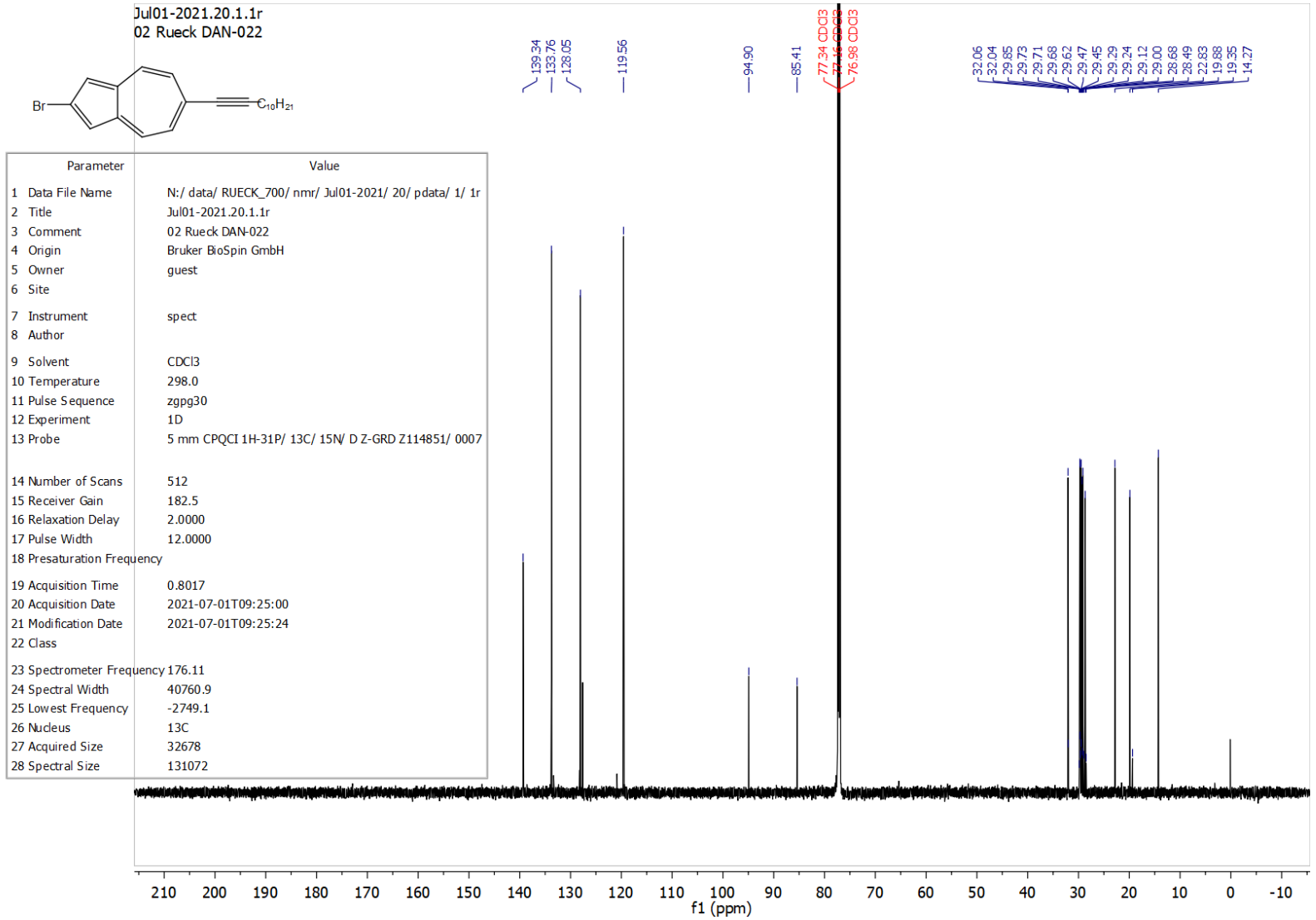


Figure S39: ^{13}C NMR spectrum of **12Yne-Az-Br** in $CDCl_3$ at 176 MHz.

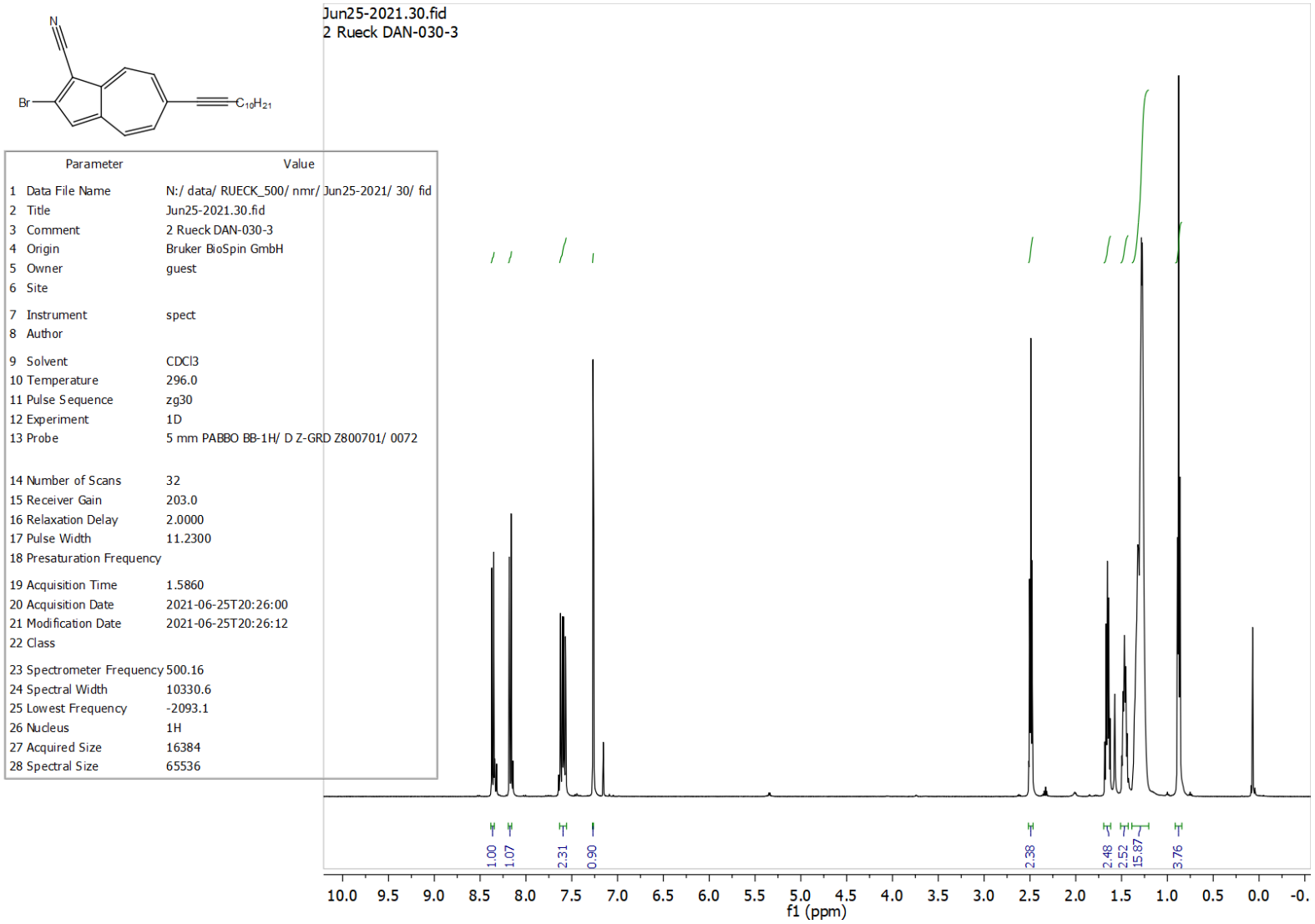


Figure S40: ^{1}H NMR spectrum of **12Yne-AzCN-Br** in $CDCl_3$ at 500 MHz.

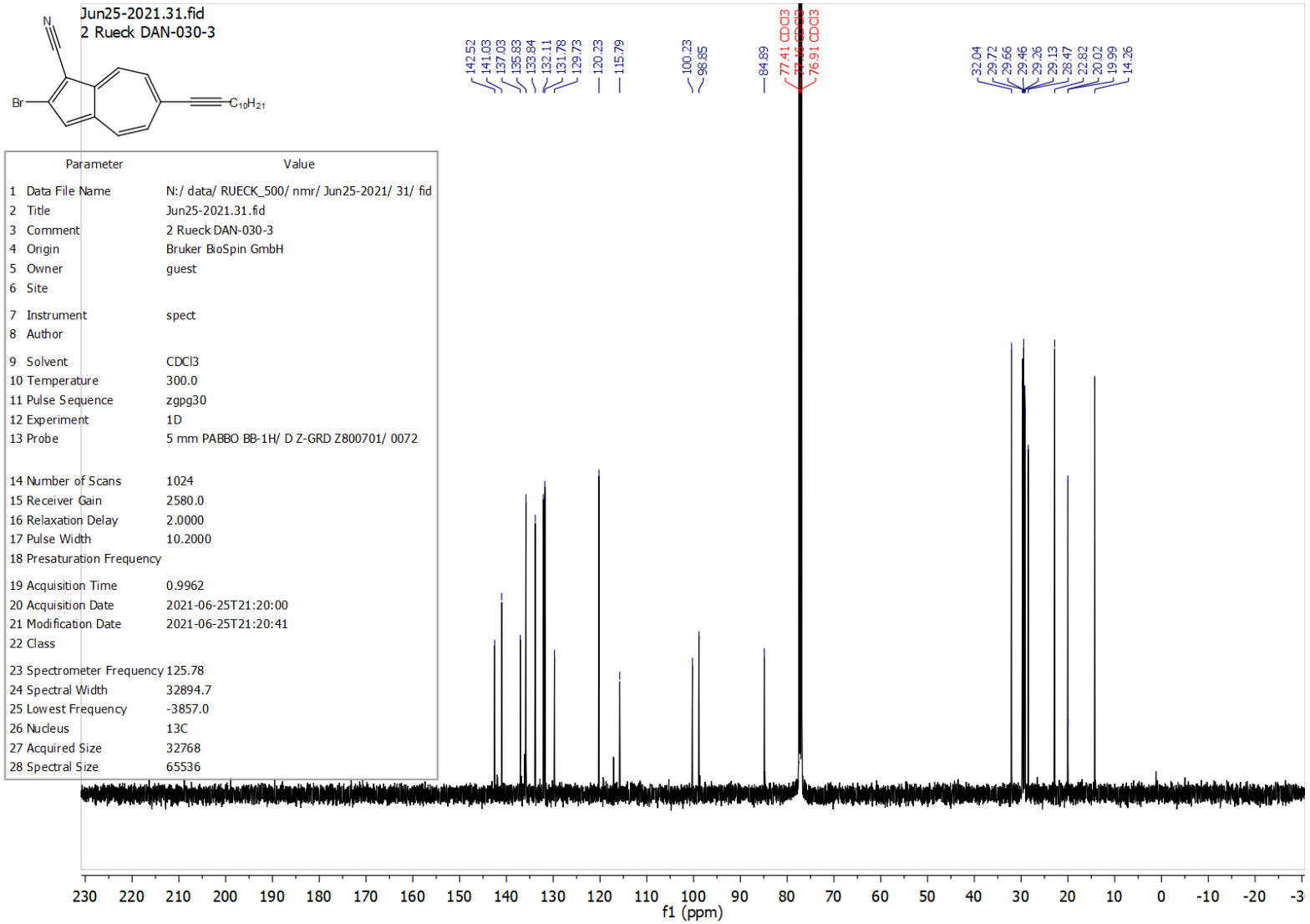


Figure S41: ^{13}C NMRspectrum of **12Yne-AzCN-Br** in $CDCl_3$ at 126 MHz.

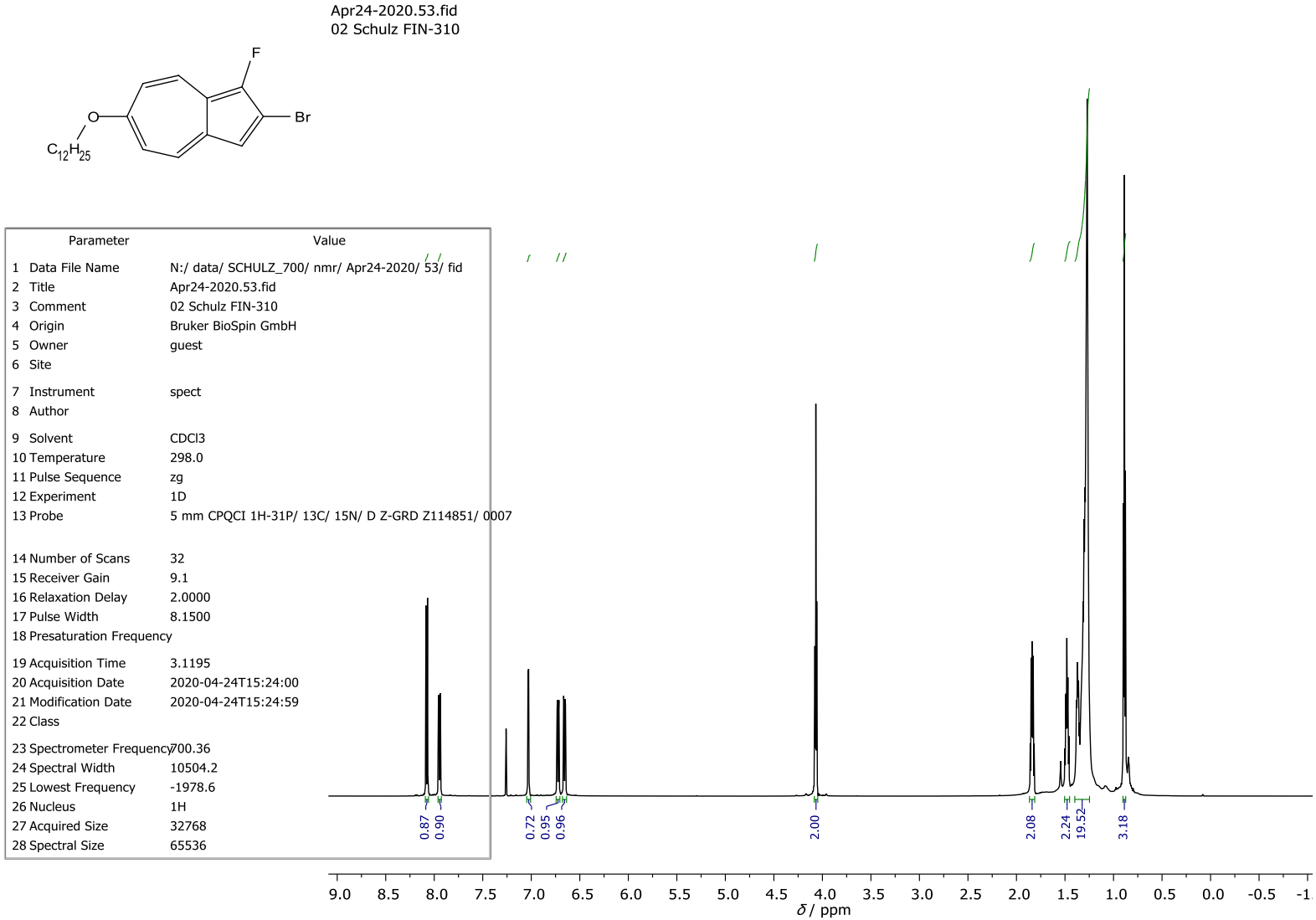


Figure S42: ^{1}H NMR spectrum of **12O-AzF-Br** in $CDCl_3$ at 700 MHz.

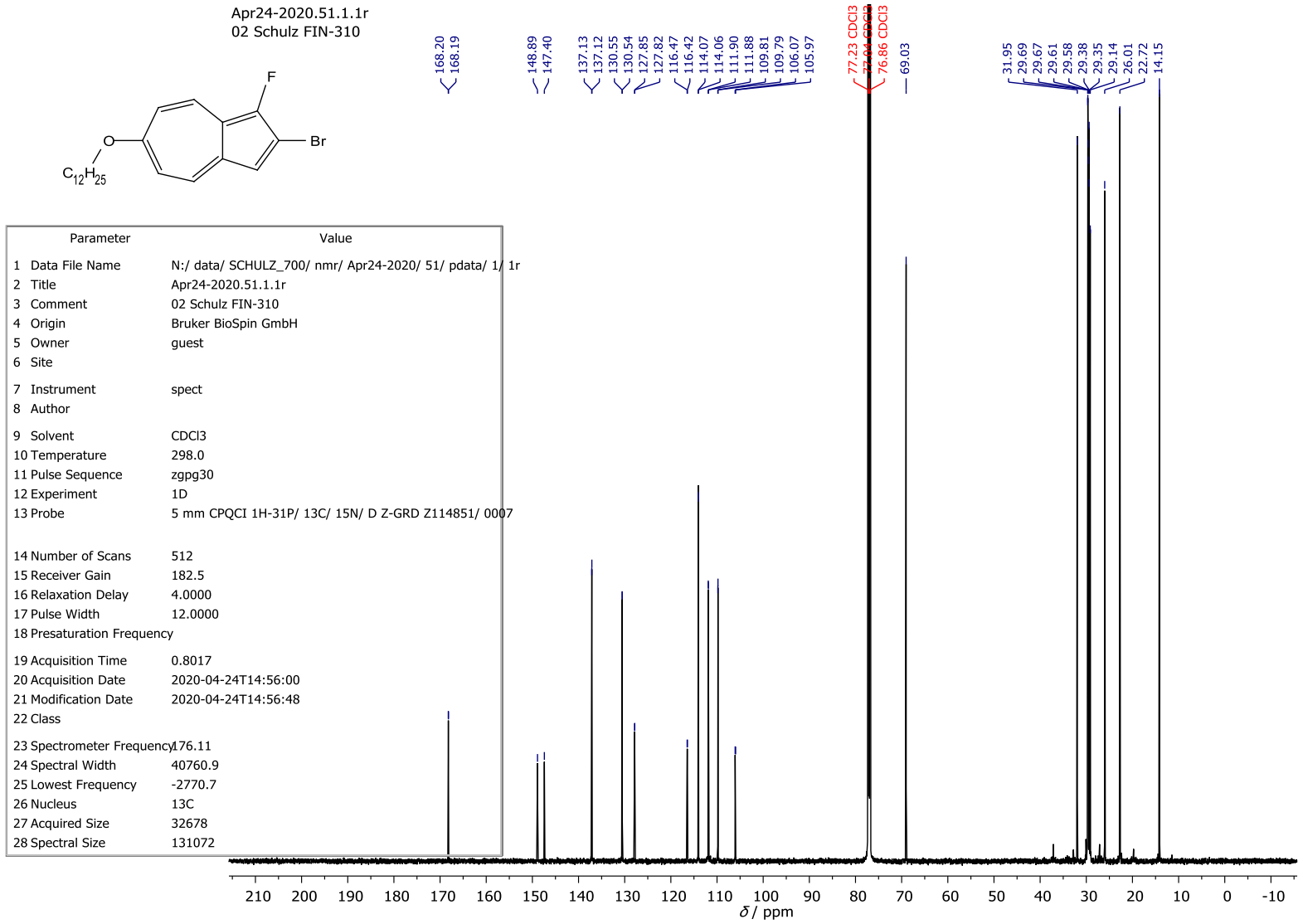
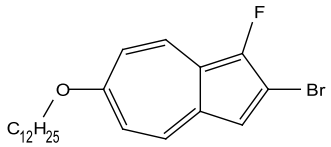


Figure S43: ^{13}C NMR spectrum of **12O-AzF-Br** in $CDCl_3$ at 176 MHz.

Apr23-2020.431.fid
02 Schulz FIN-310-cc-2



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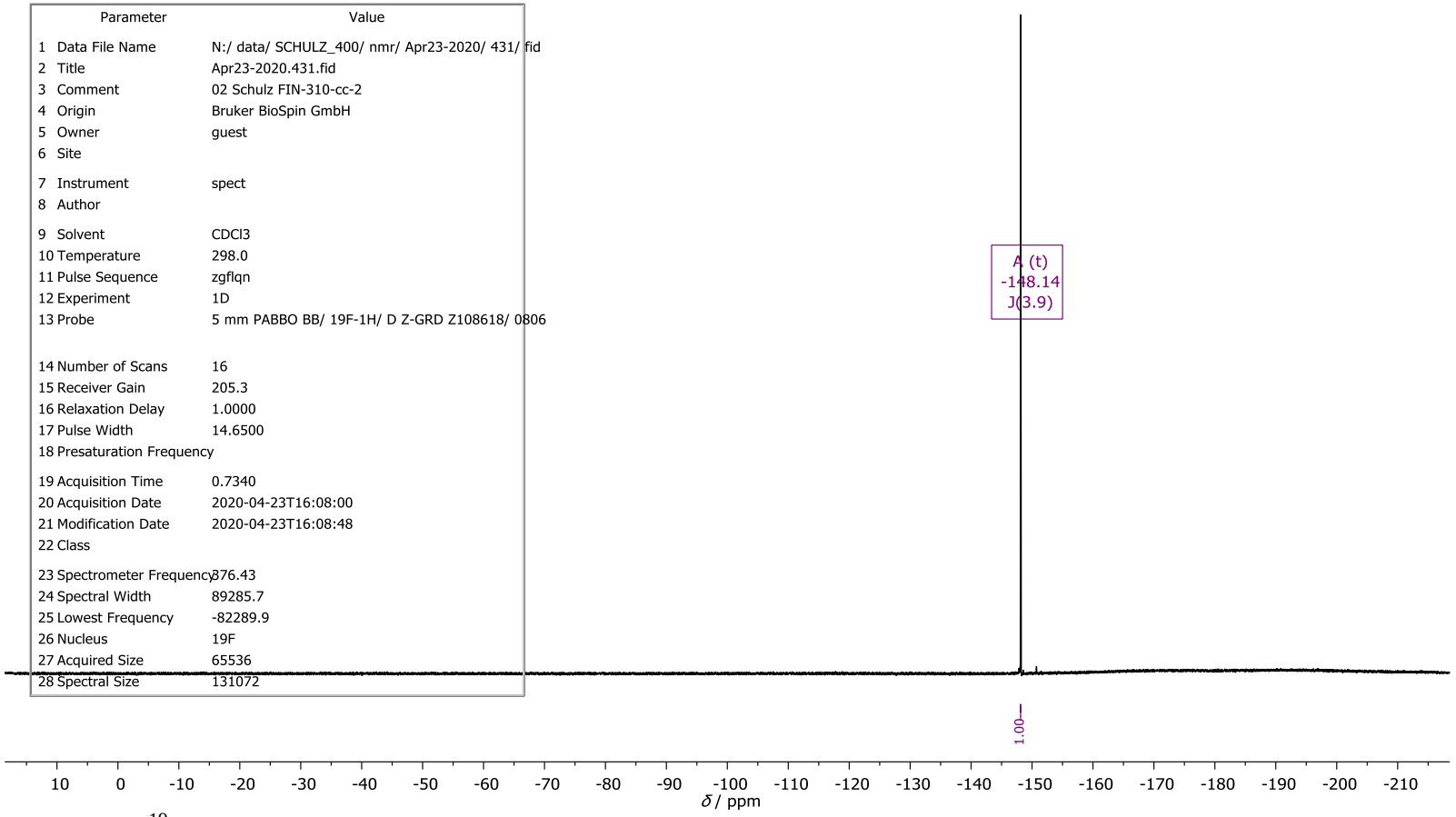

Figure S44: ^{19}F NMR-spectrum of **12O-AzF-Br** in $CDCl_3$ at 376 MHz.

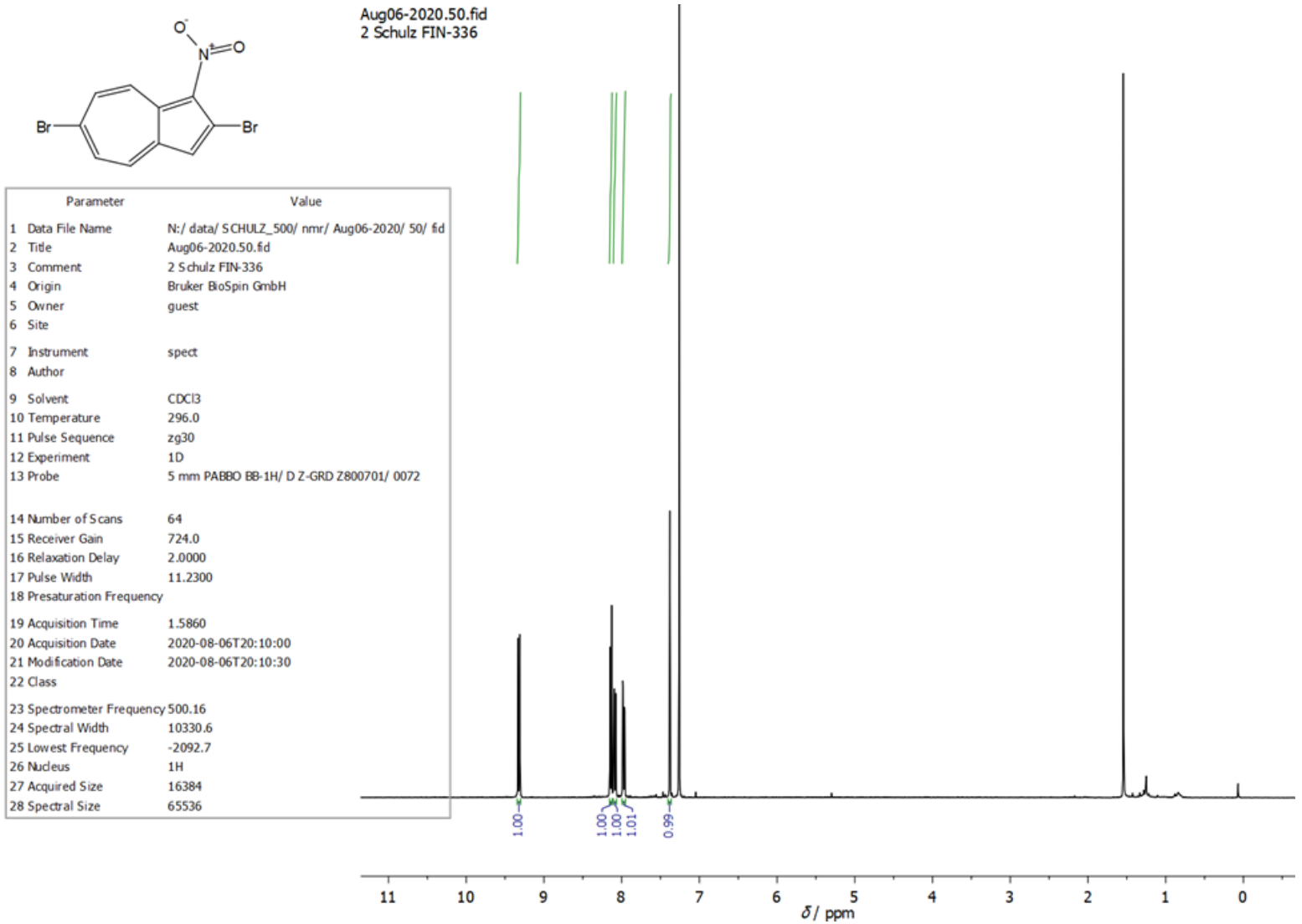

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Figure S45: ^{1}H NMR spectrum of **Br-AzNO$_2$-Br** in $CDCl_3$ at 500 MHz.

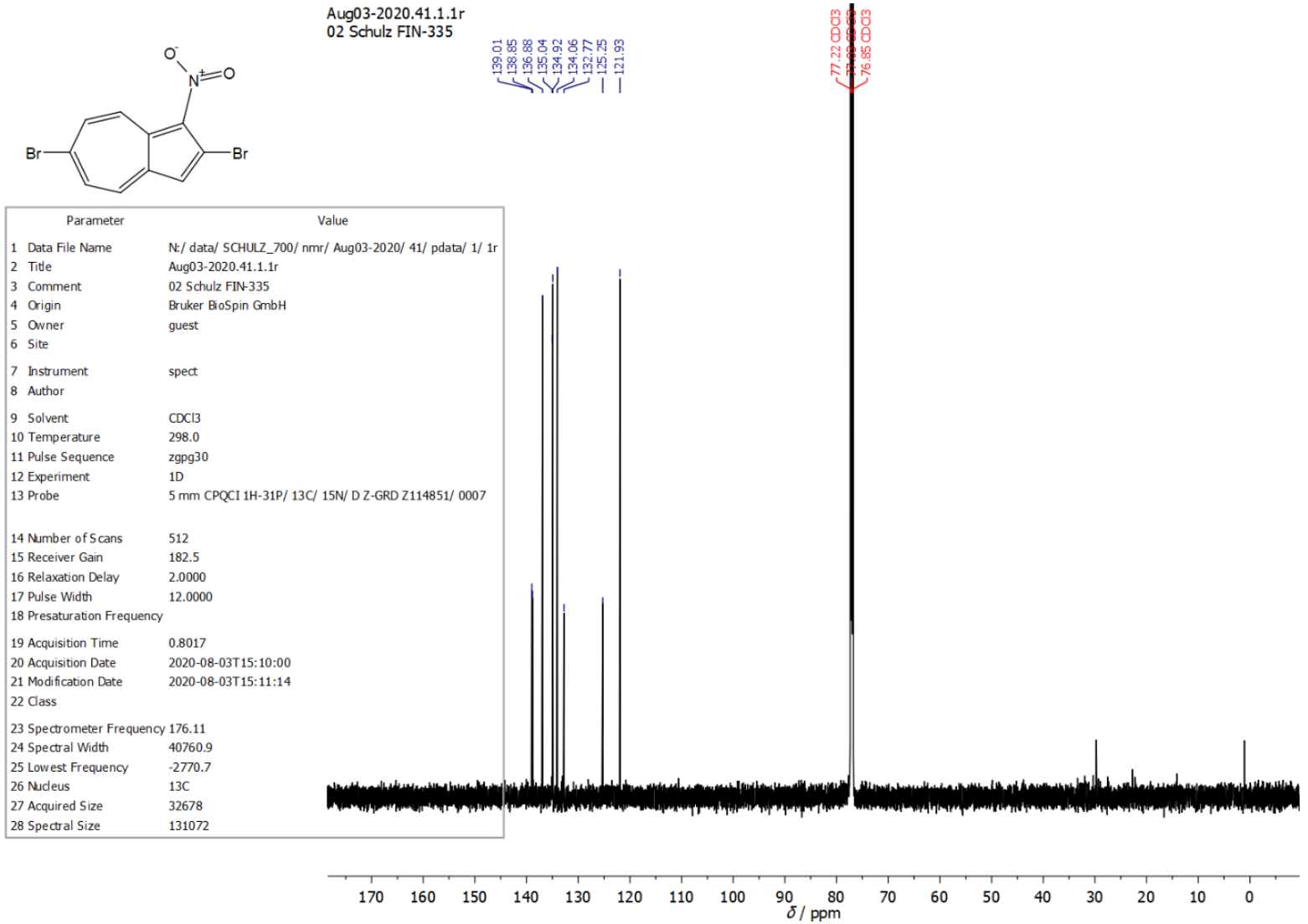


Figure S46: ^{13}C NMR spectrum of **Br-AzNO$_2$-Br** in $CDCl_3$ at 176 MHz.

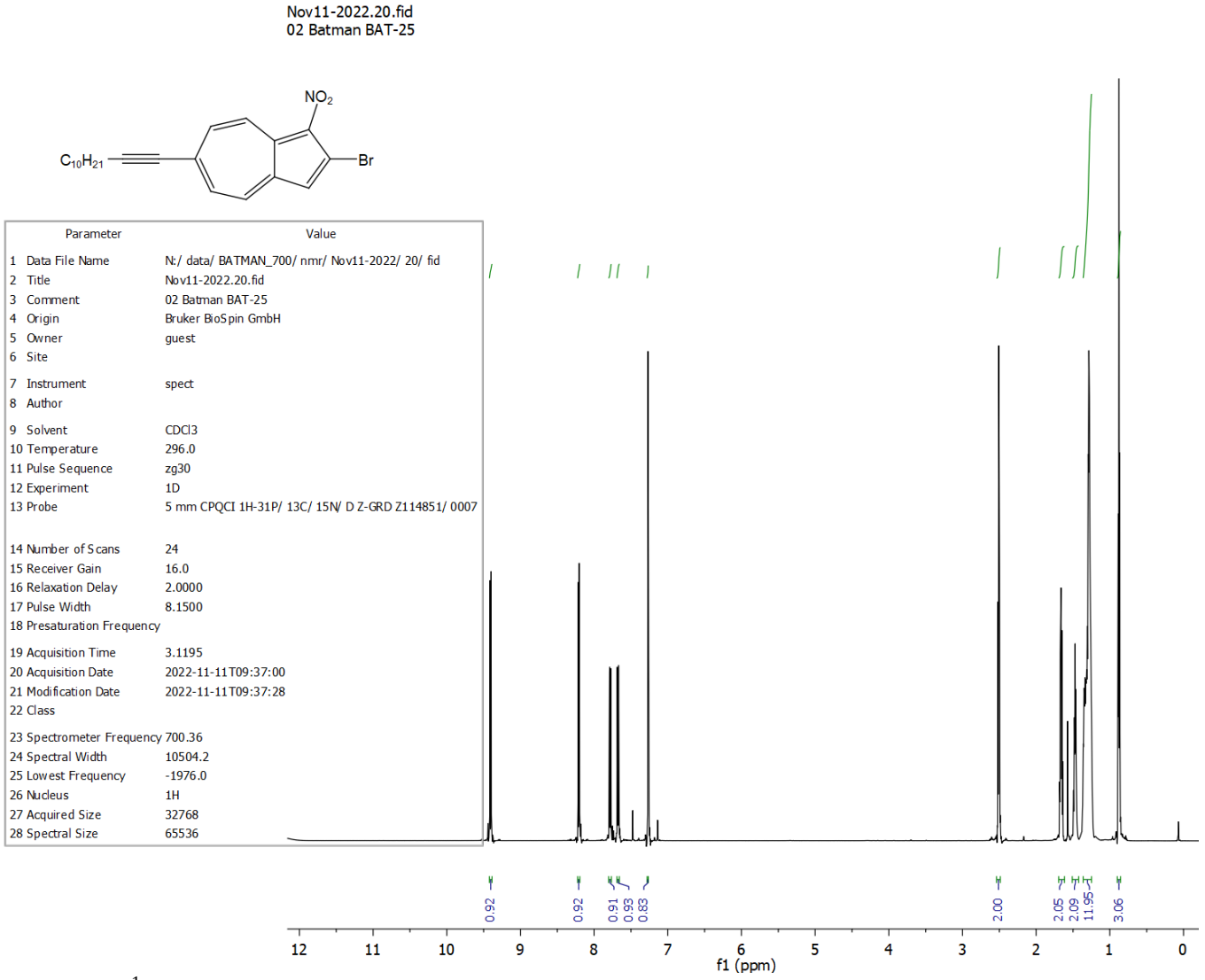


Figure S47: ^{1}H NMR spectrum of **12Yne-AzCN-Br** in $CDCl_3$ at 700 MHz.

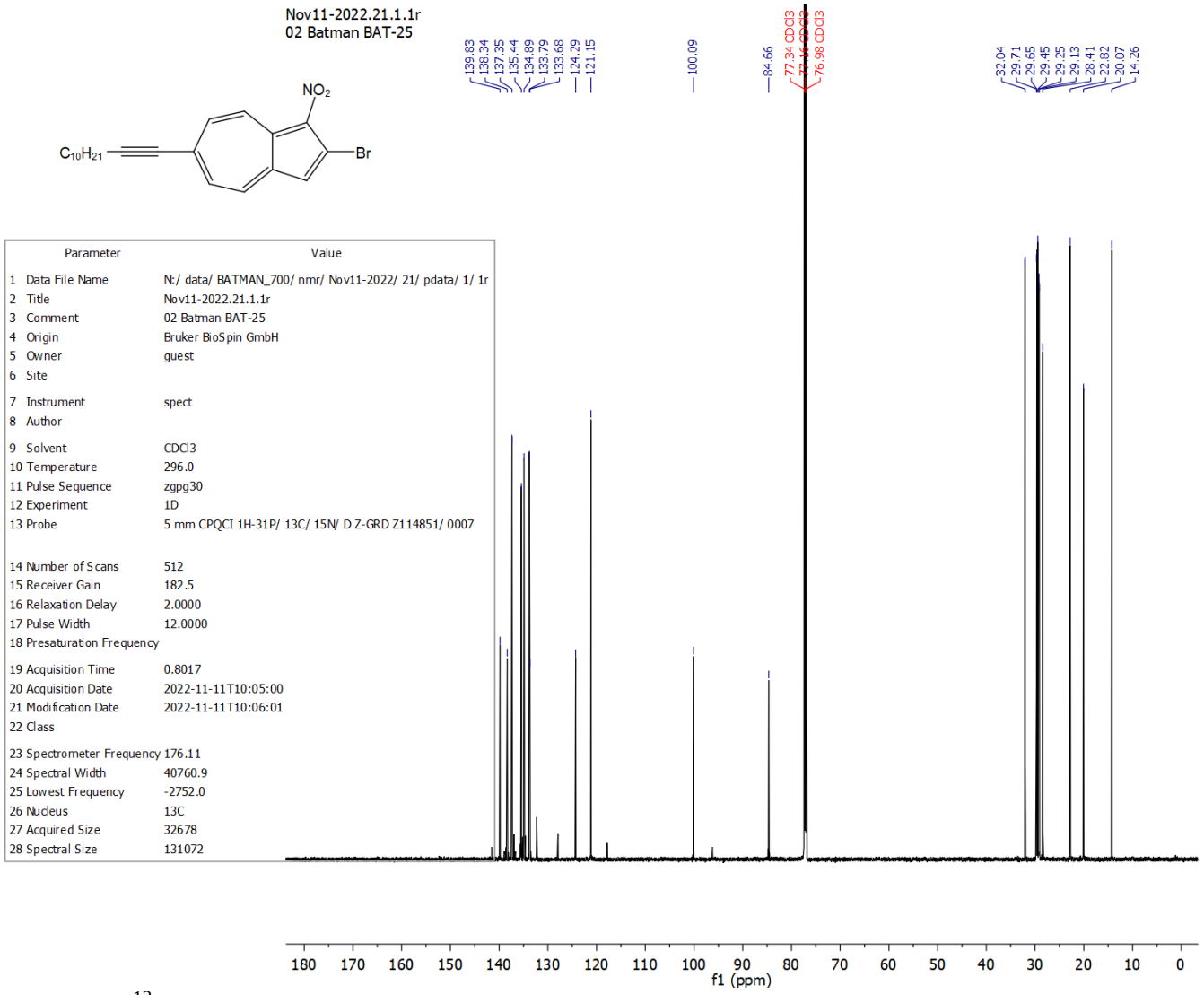


Figure S48: ^{13}C NMR spectrum of **12Yne-AzCN-Br** in $CDCl_3$ at 176 MHz.

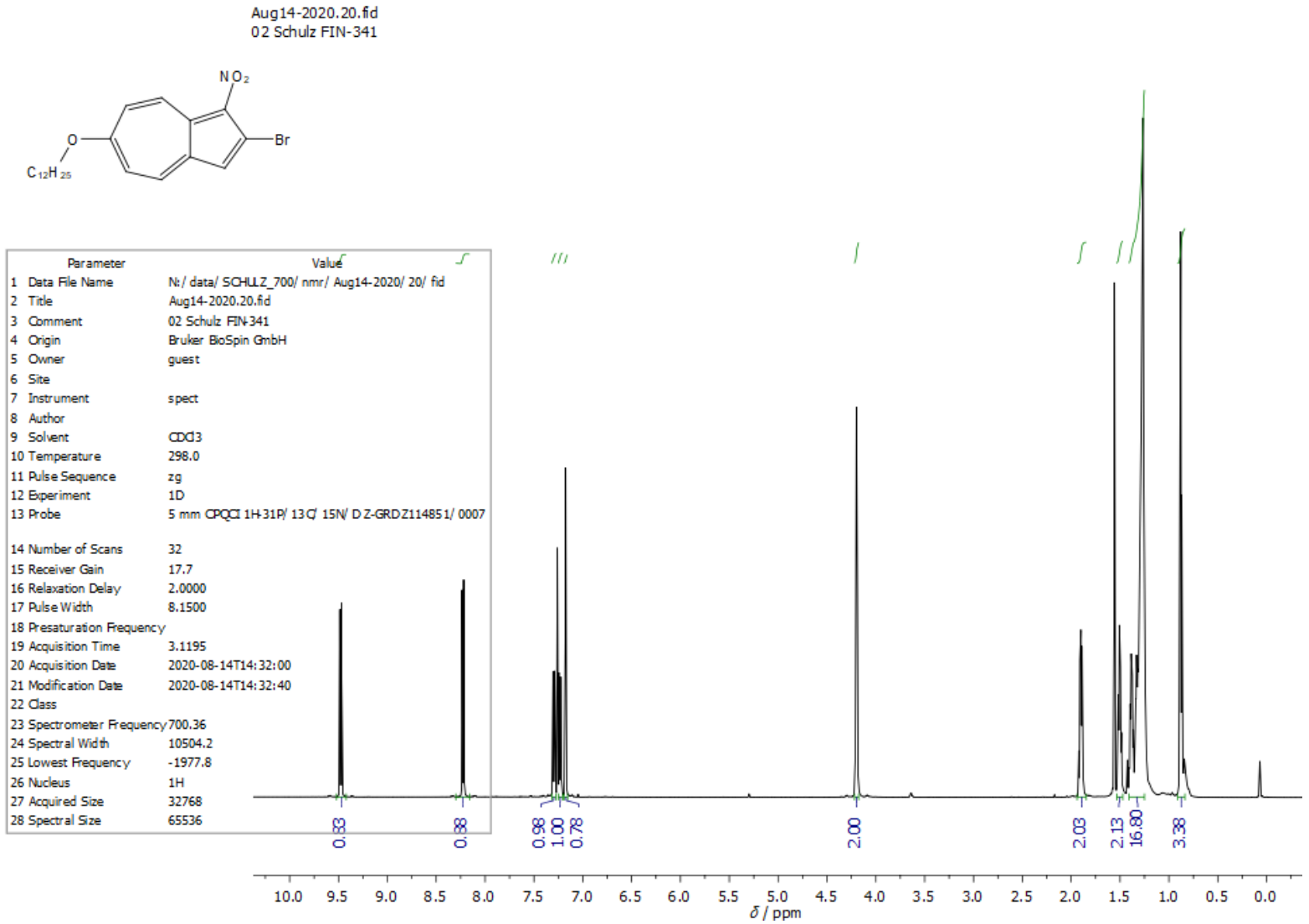


Figure S49: ^{1}H NMR spectrum of **12O-AzNO$_2$-Br** in $CDCl_3$ at 700 MHz.

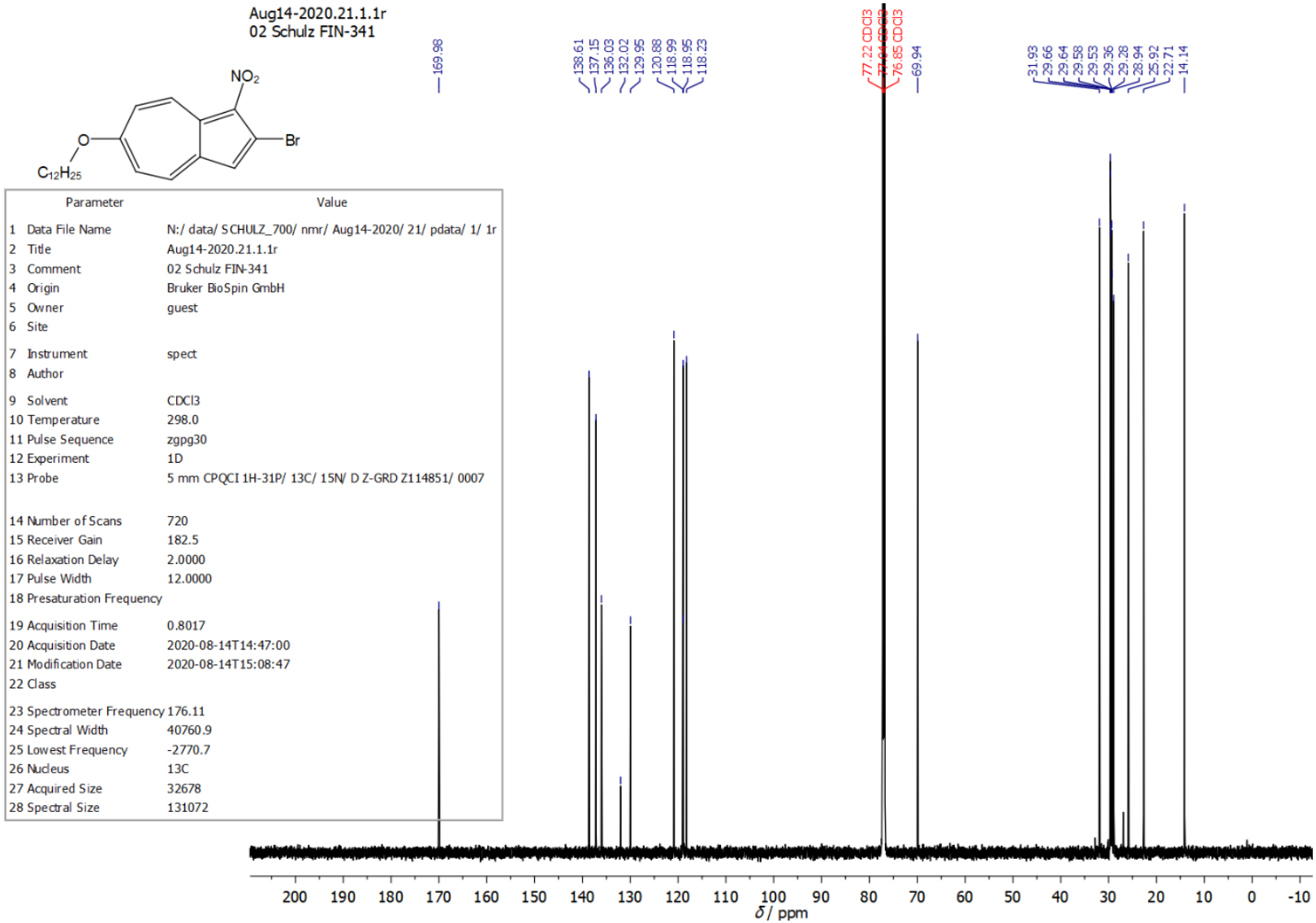


Figure S50: ^{13}C NMR spectrum of **12O-AzNO$_2$-Br** in $CDCl_3$ at 176 MHz.

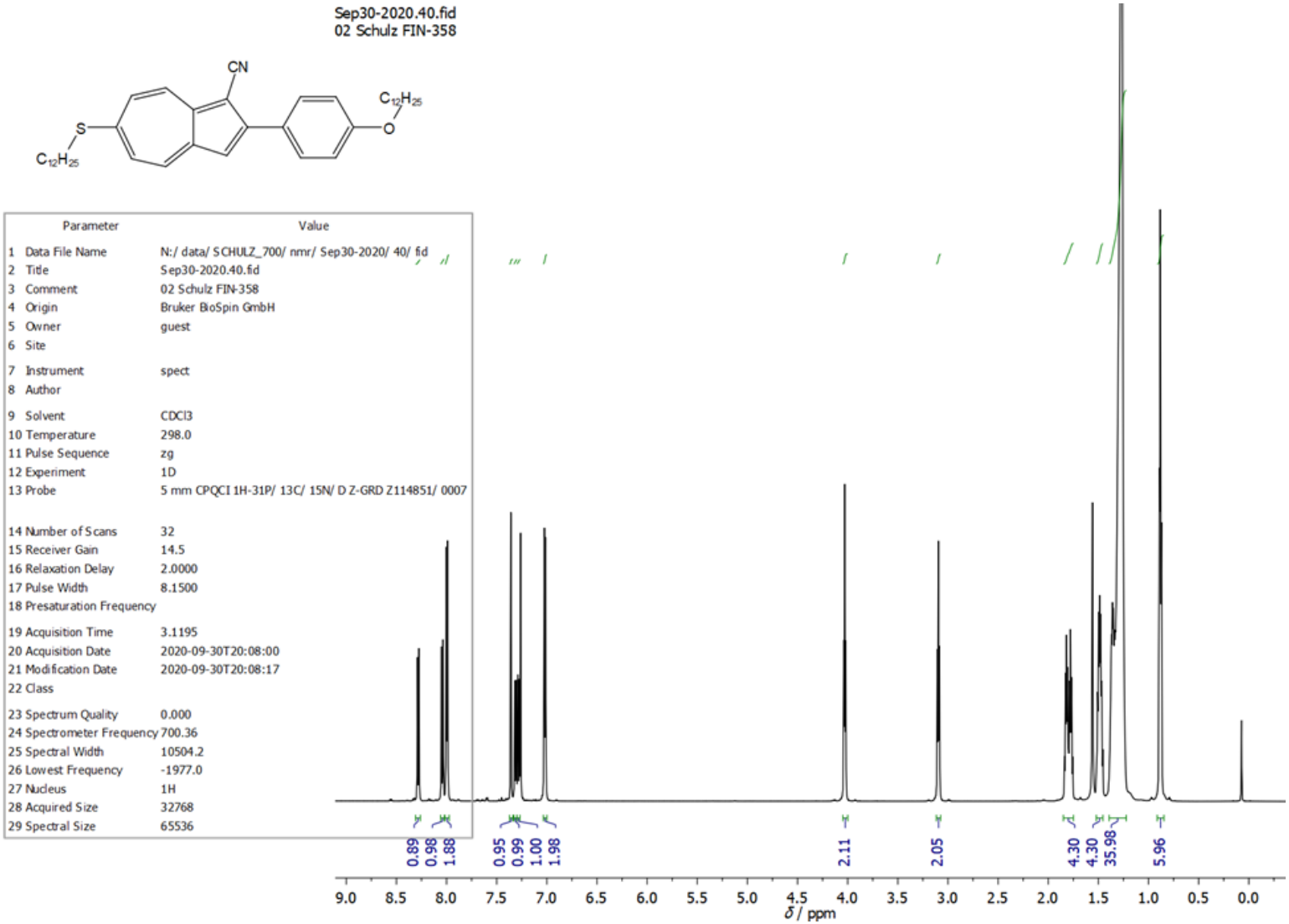


Figure S51: ^{1}H NMR spectrum of **12S-AzCN-PhO12** in $CDCl_3$ at 700 MHz.

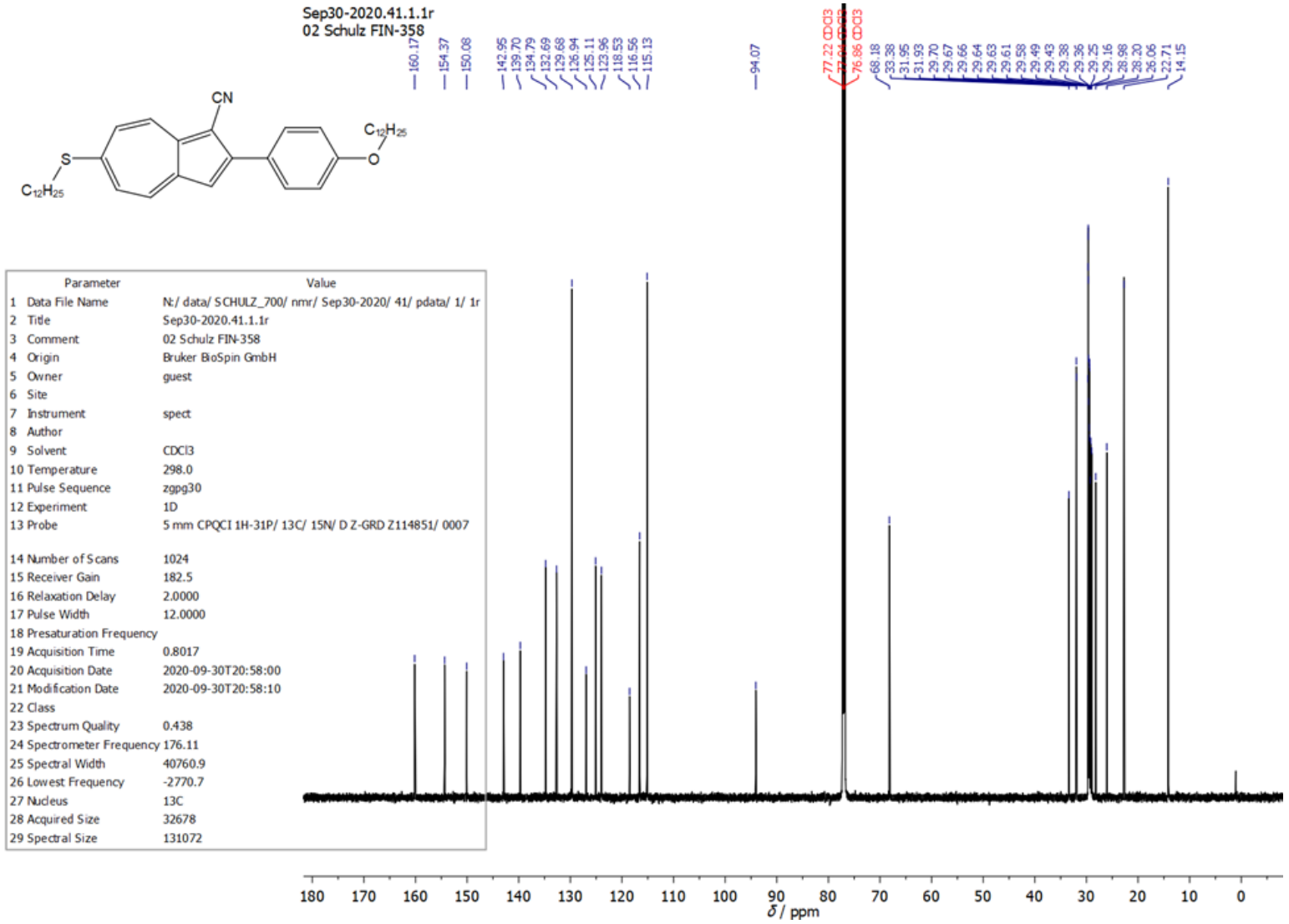


Figure S52: ^{13}C NMR spectrum of **12S-AzCN-PhO12** in $CDCl_3$ at 176 MHz.

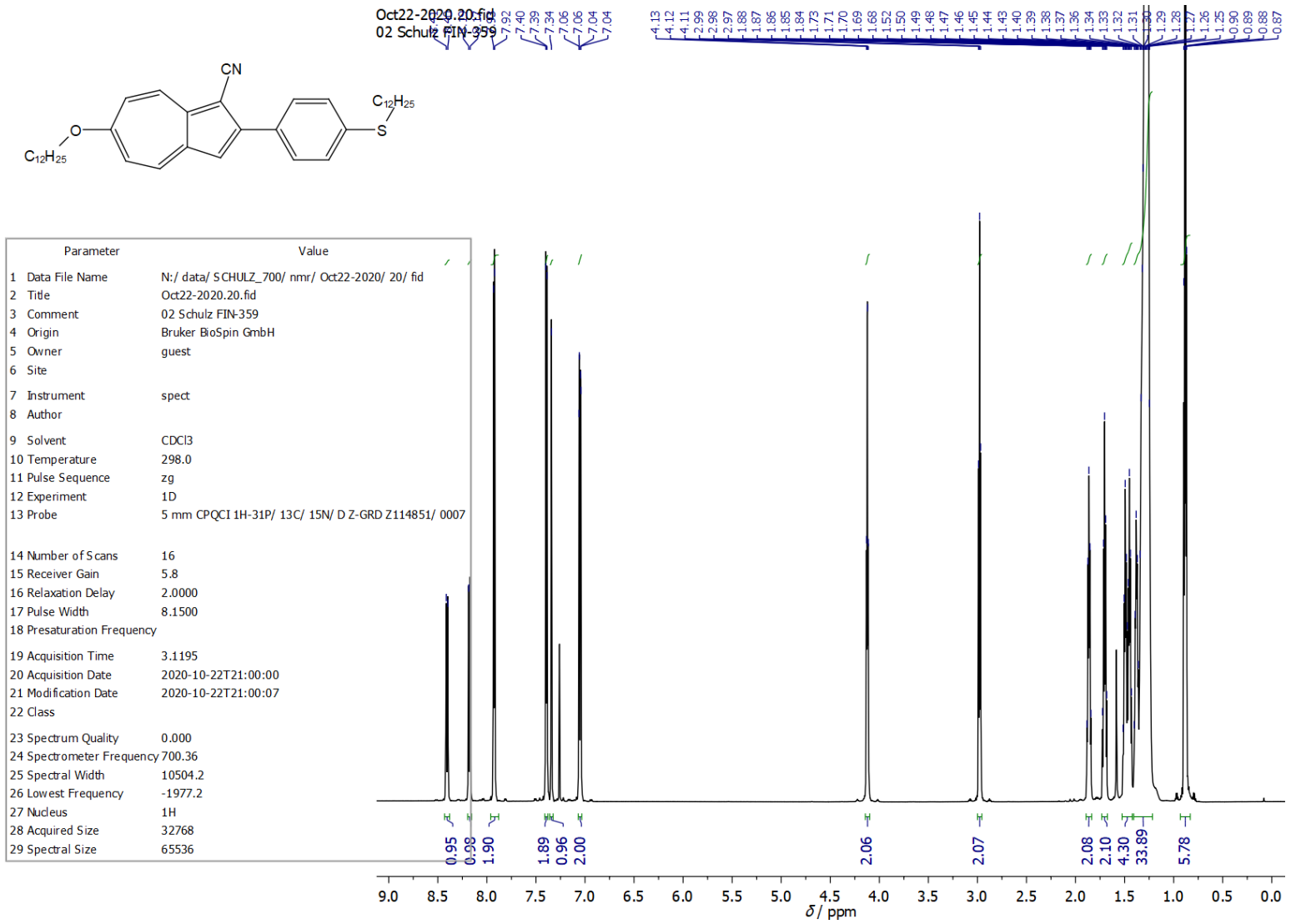


Figure S53: ^{1}H NMR spectrum of **12O-AzCN-PhS12** in $CDCl_3$ at 700 MHz.

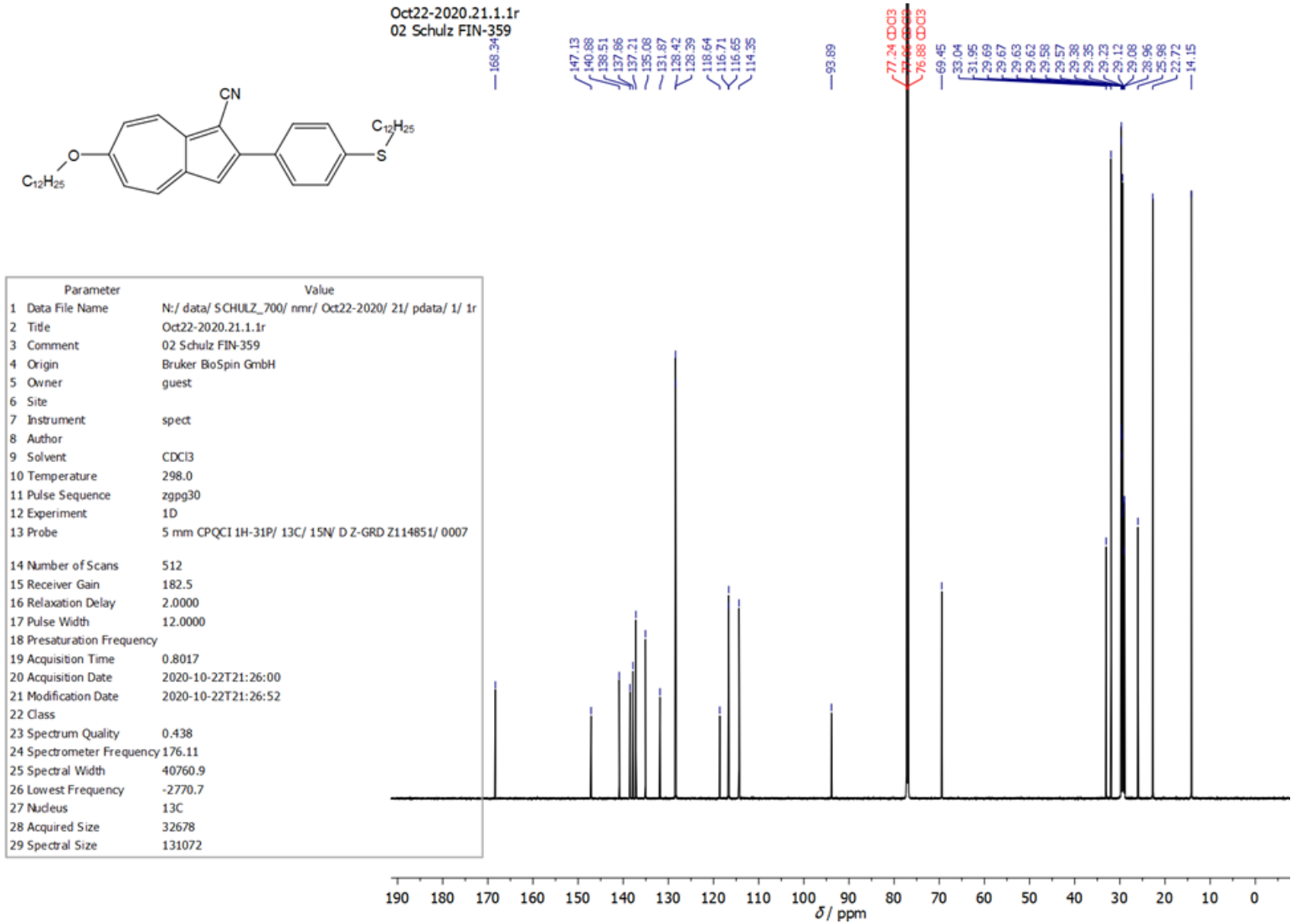


Figure S54: ^{13}C NMR spectrum of **12O-AzCN-PhS12** in $CDCl_3$ at 176 MHz.

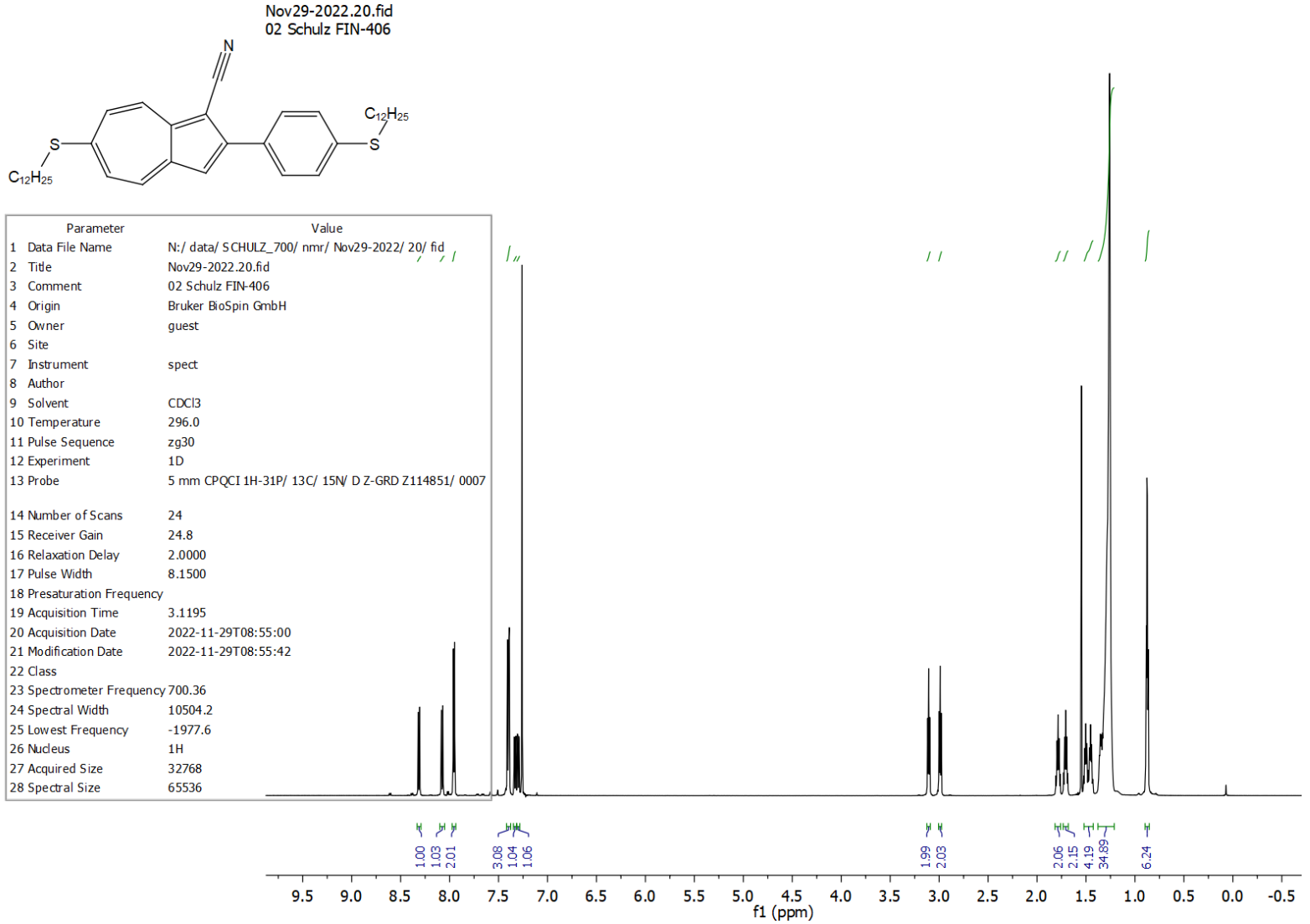


Figure S55: ^{1}H NMR spectrum of **12S-AzCN-PhS12** in $CDCl_3$ at 700 MHz.

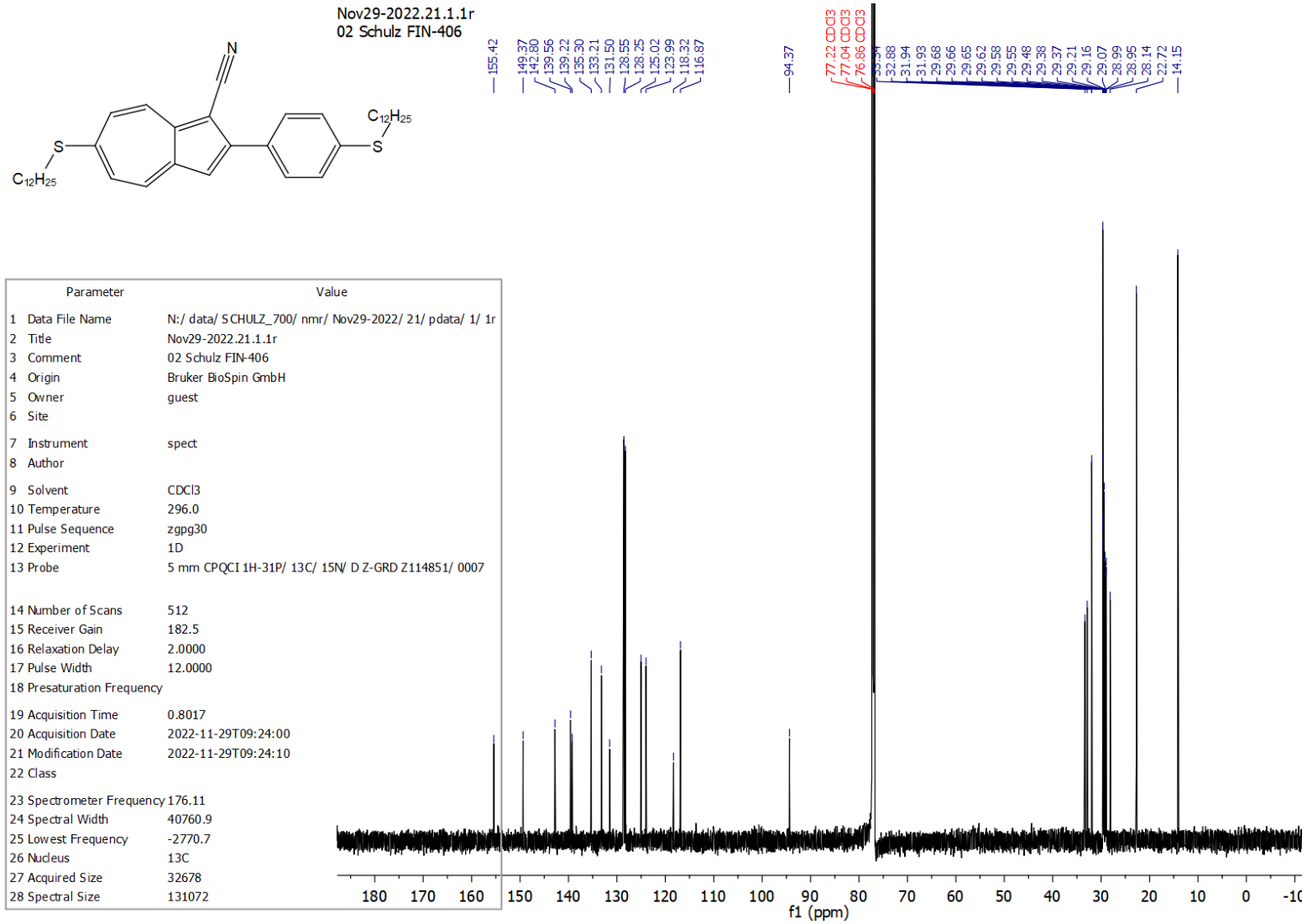


Figure S56: ^{13}C NMR-spectrum of **12S-AzCN-PhS12** in $CDCl_3$ at 176 MHz.

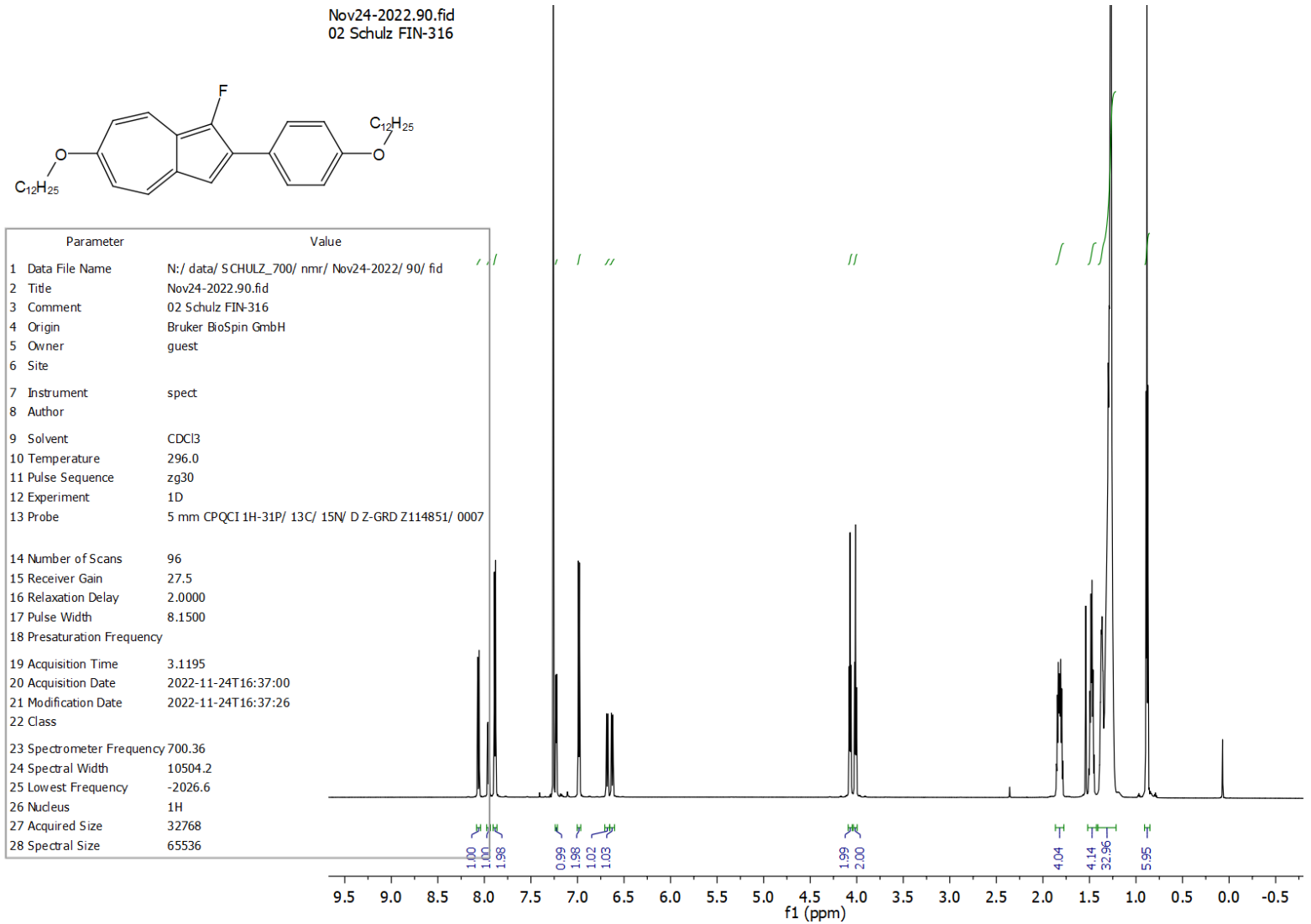
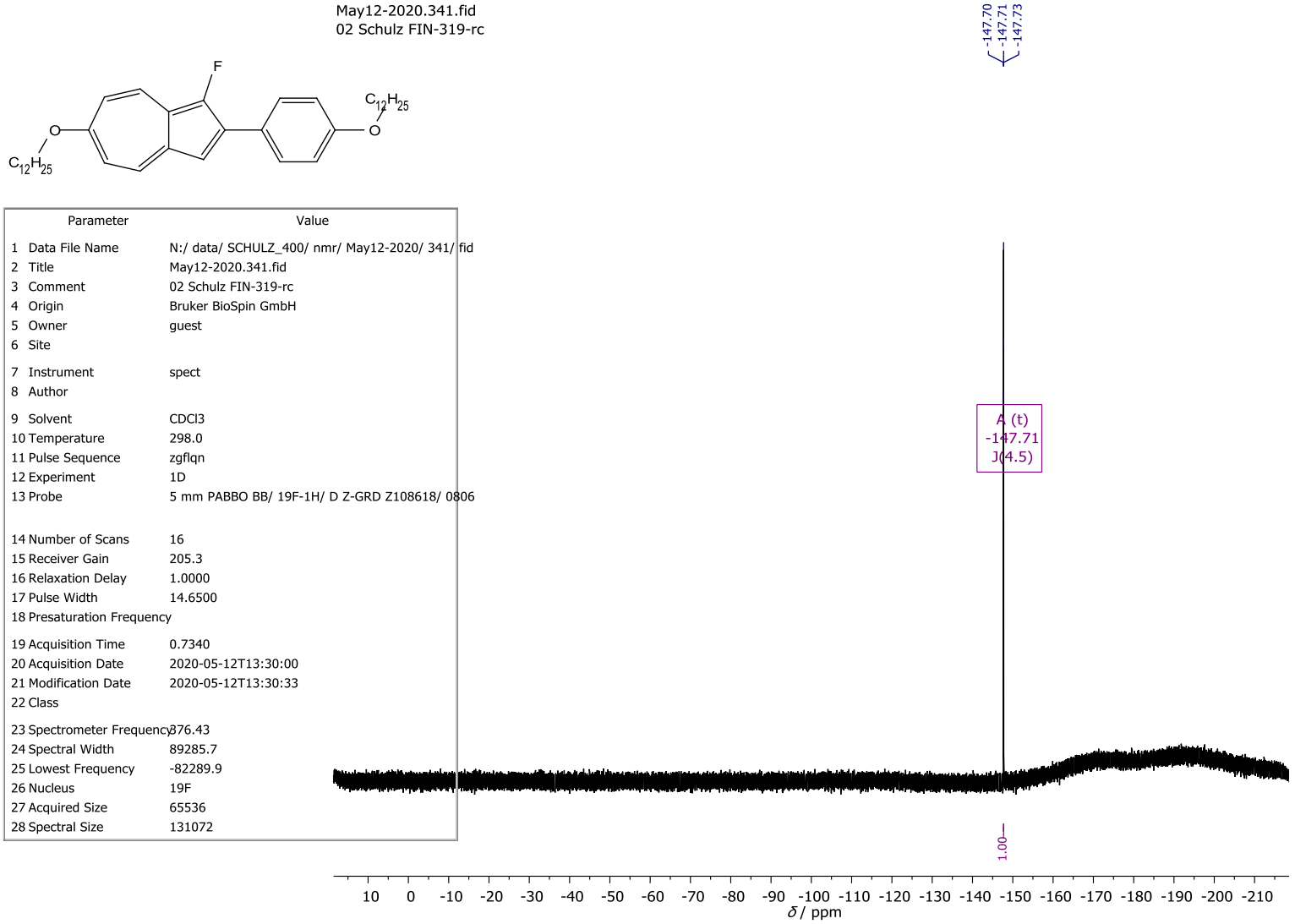


Figure S57: ^{1}H NMR-spectrum of **12O-AzF-PhO12** in $CDCl_3$ at 700 MHz.



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5 Owner	guest
6 Site	
7 Instrument	spect
8 Author	
9 Solvent	CDCl3
10 Temperature	298.0
11 Pulse Sequence	zgflqn
12 Experiment	1D
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18 Presaturation Frequency	
19 Acquisition Time	0.7340
20 Acquisition Date	2020-05-12T13:30:00
21 Modification Date	2020-05-12T13:30:33
22 Class	
23 Spectrometer Frequency	376.43
24 Spectral Width	89285.7
25 Lowest Frequency	-82289.9
26 Nucleus	19F
27 Acquired Size	65536
28 Spectral Size	131072

Figure S58: ^{19}F NMR-spectrum of **12O-AzF-PhO12** in $CDCl_3$ at 376 MHz.

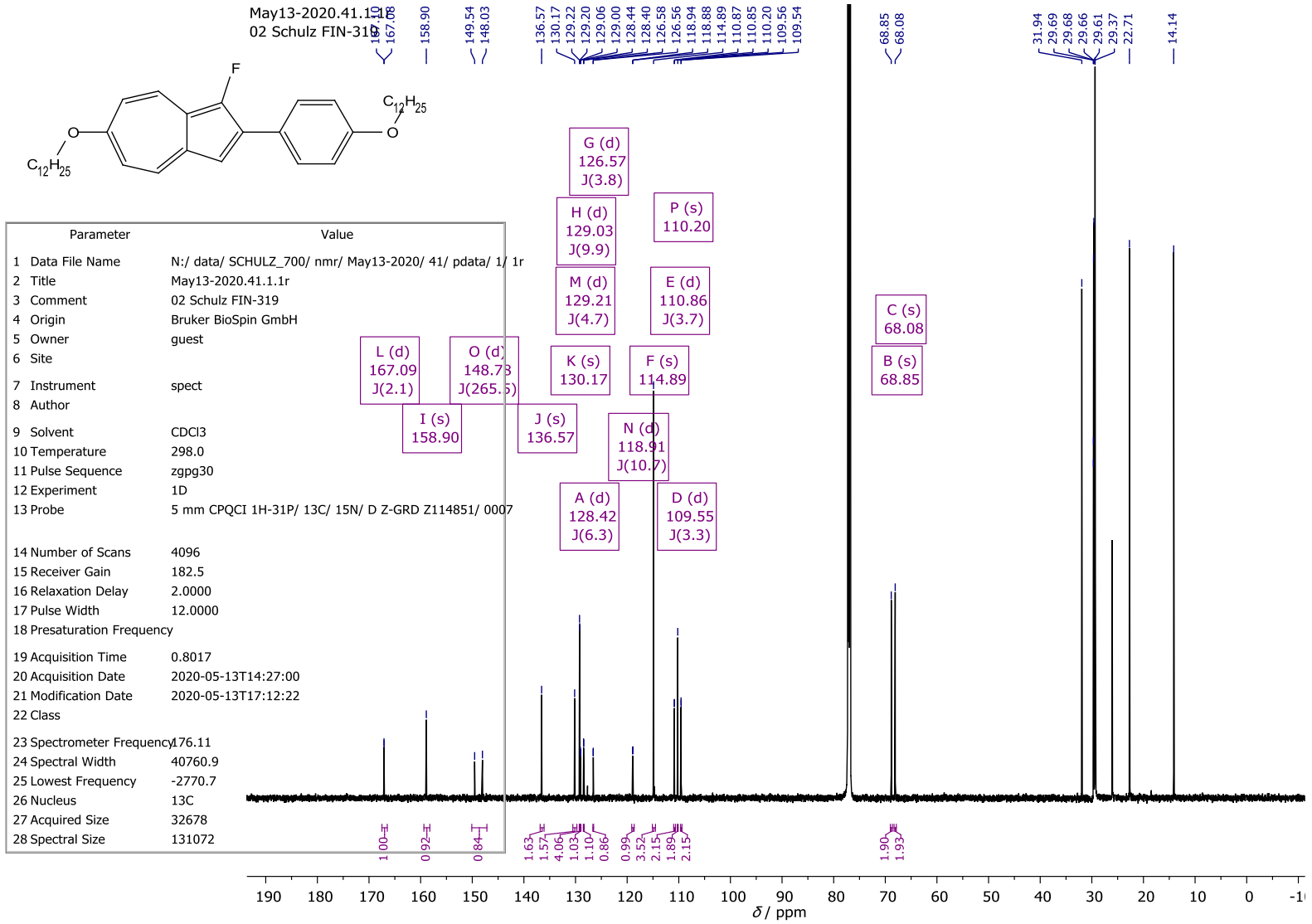


Figure S59: ^{13}C NMR spectrum of **12O-AzF-PhO12** in $CDCl_3$ at 176 MHz.

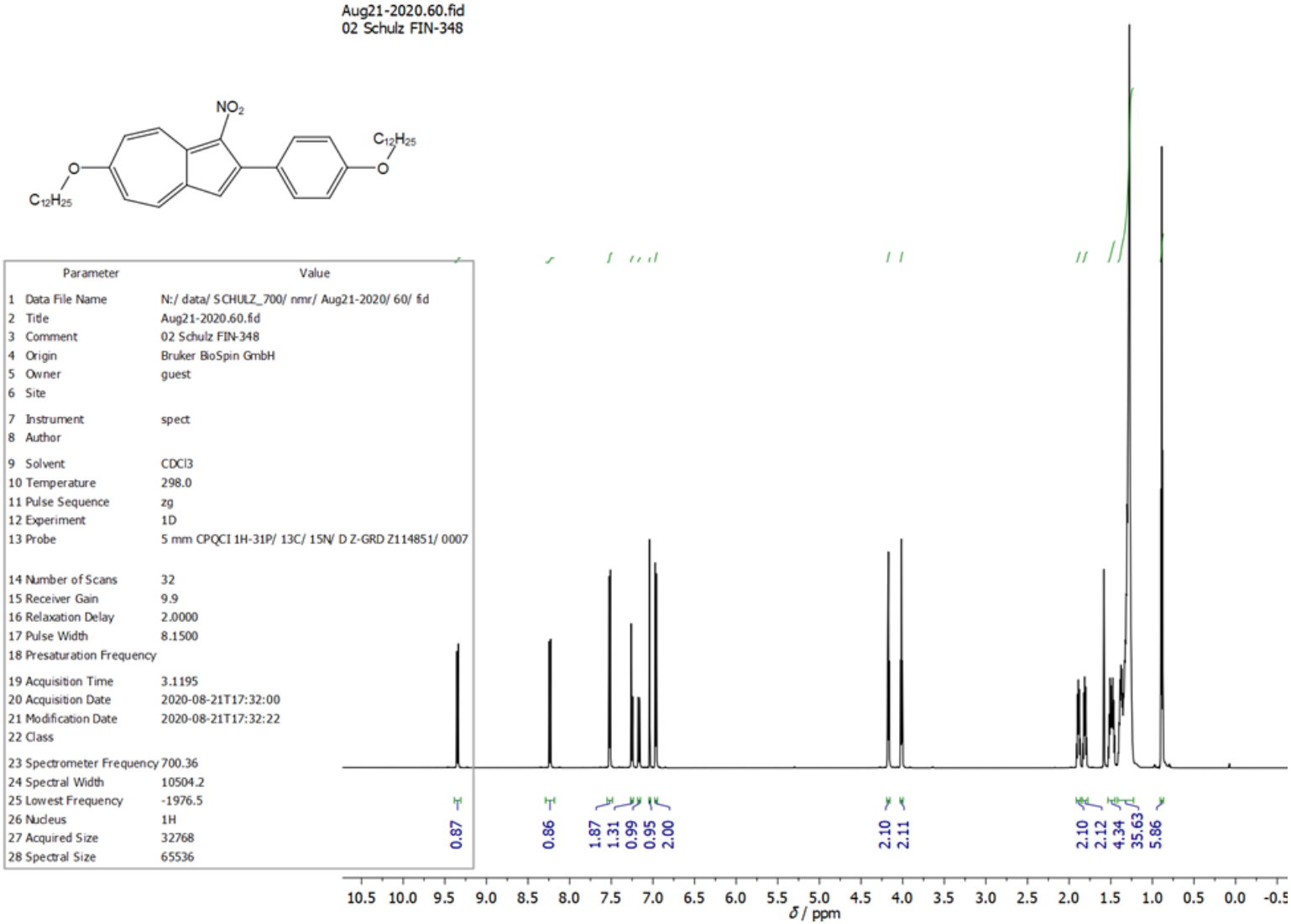


Figure S60: ^{1}H NMR spectrum of **12O-AzNO$_2$-PhO12** in $CDCl_3$ at 700 MHz.

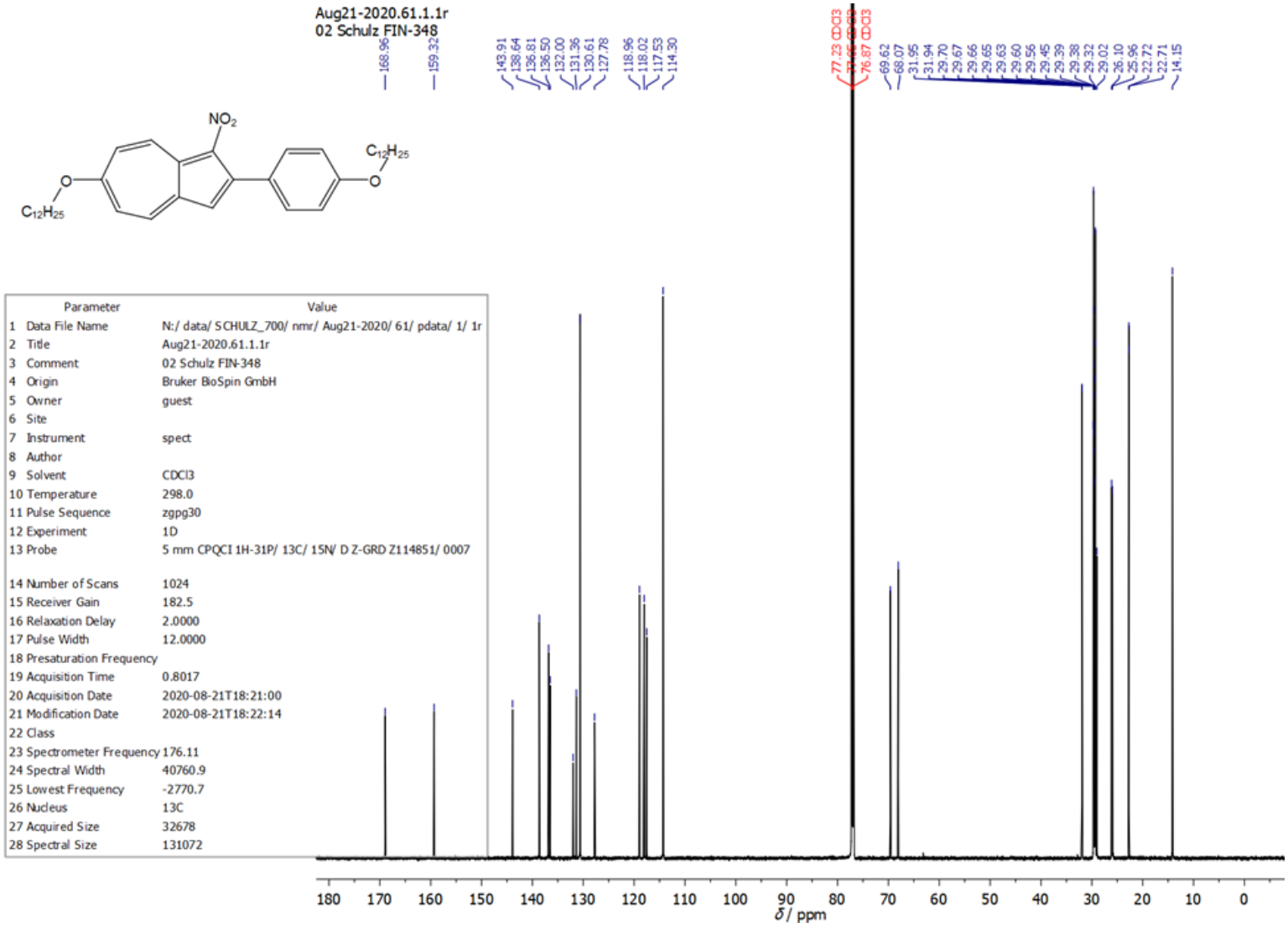


Figure S61: ^{13}C NMR spectrum of **12O-AzNO$_2$-PhO12** in $CDCl_3$ at 700 MHz.

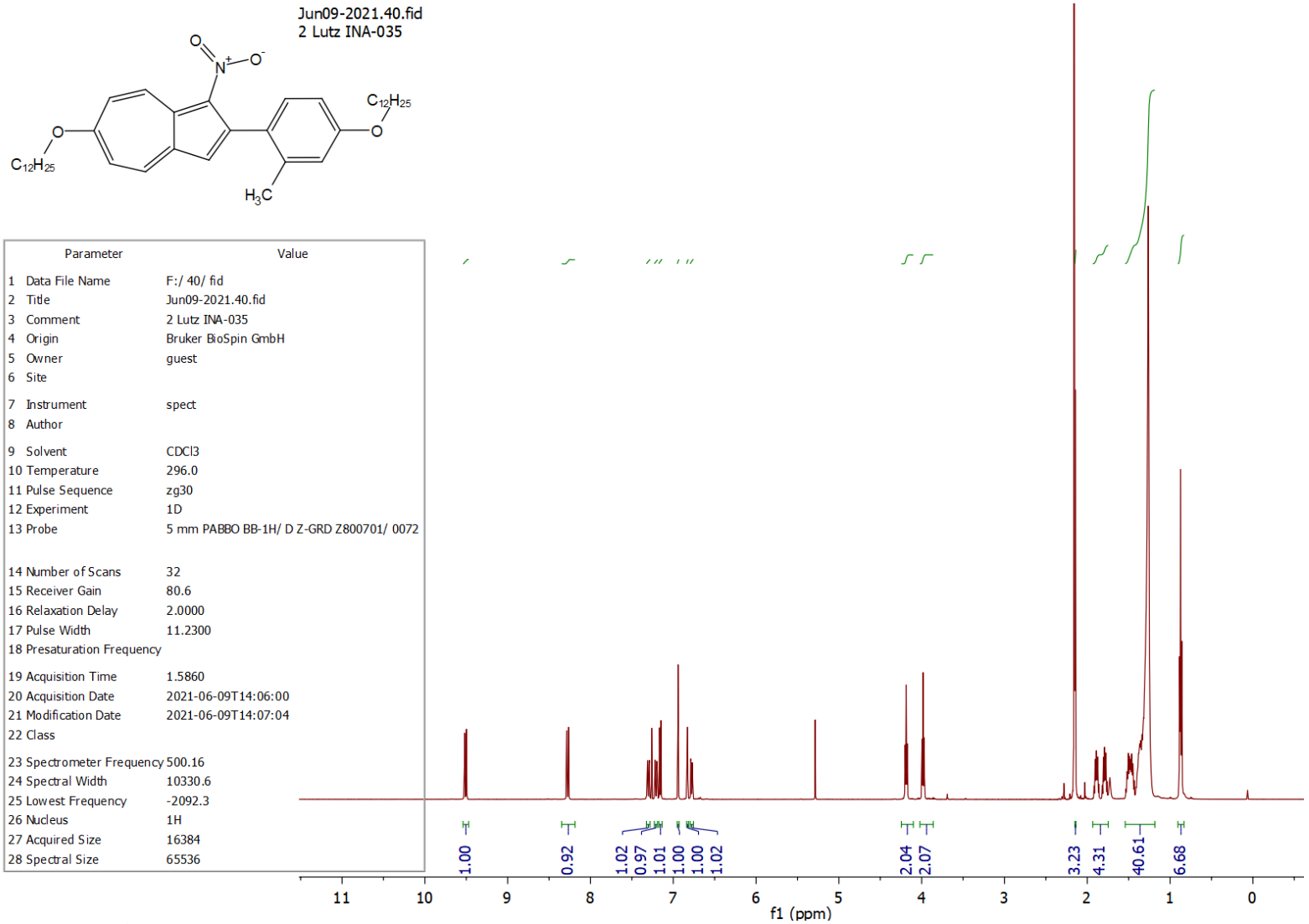


Figure S62: ^{1}H NMR spectrum of **12O-AzNO$_2$-MePhO12** in $CDCl_3$ at 500 MHz.

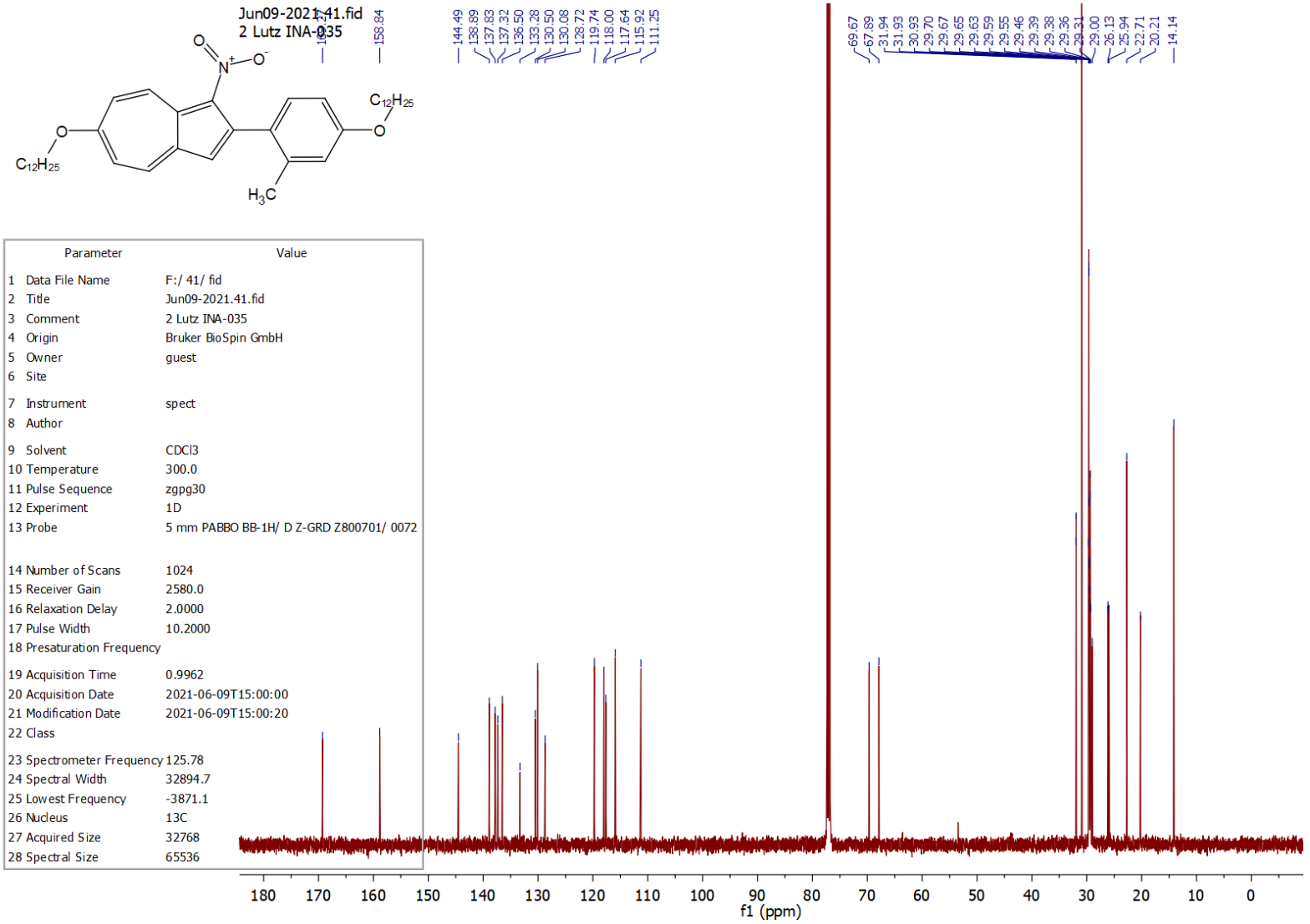


Figure S63: ^{13}C NMR spectrum of **12O-AzNO$_2$-MePhO12** in $CDCl_3$ at 126 MHz.

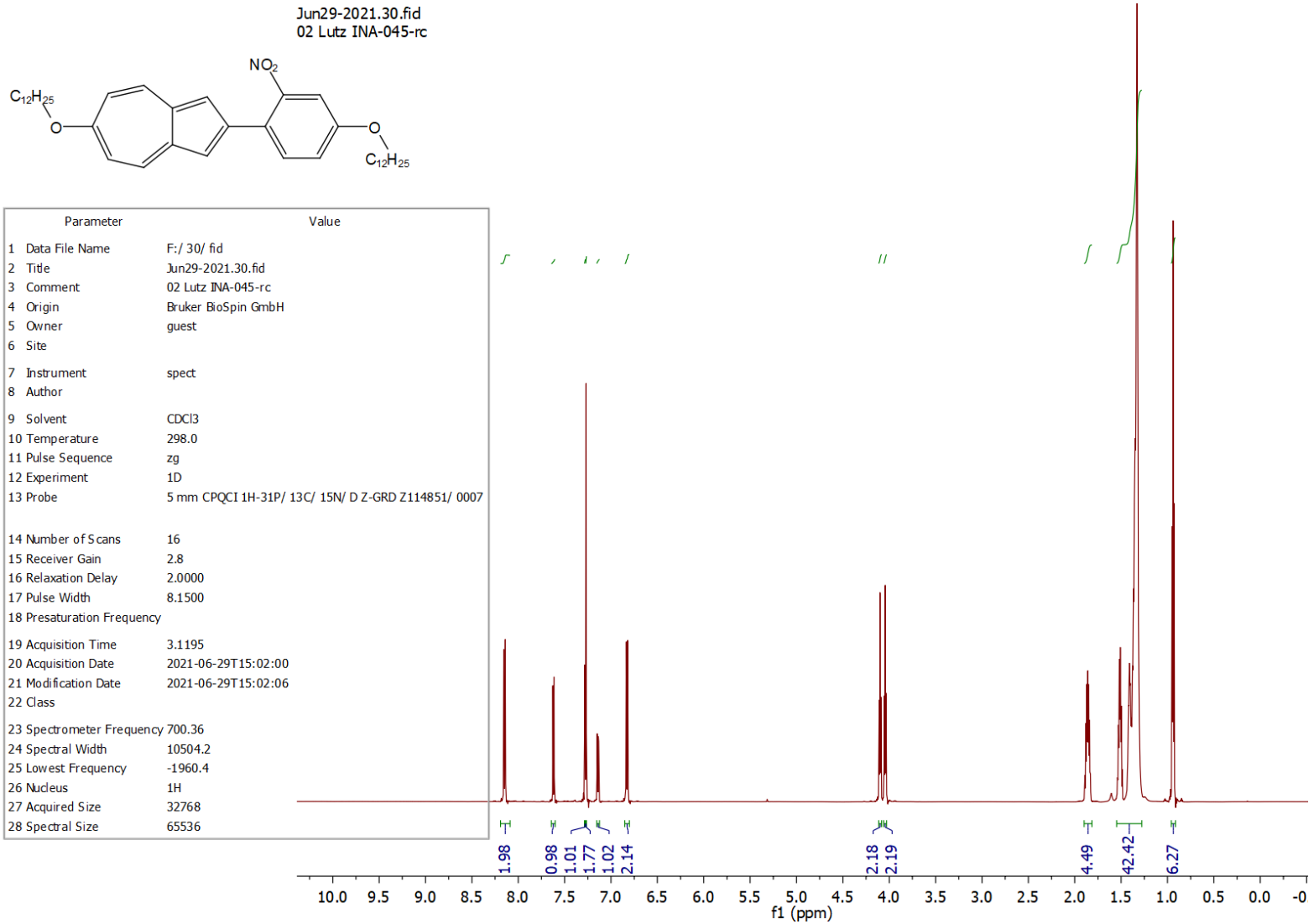


Figure S64: ^{1}H NMR spectrum of **12O-Az-NO$_2$PhO12** in $CDCl_3$ at 700 MHz.

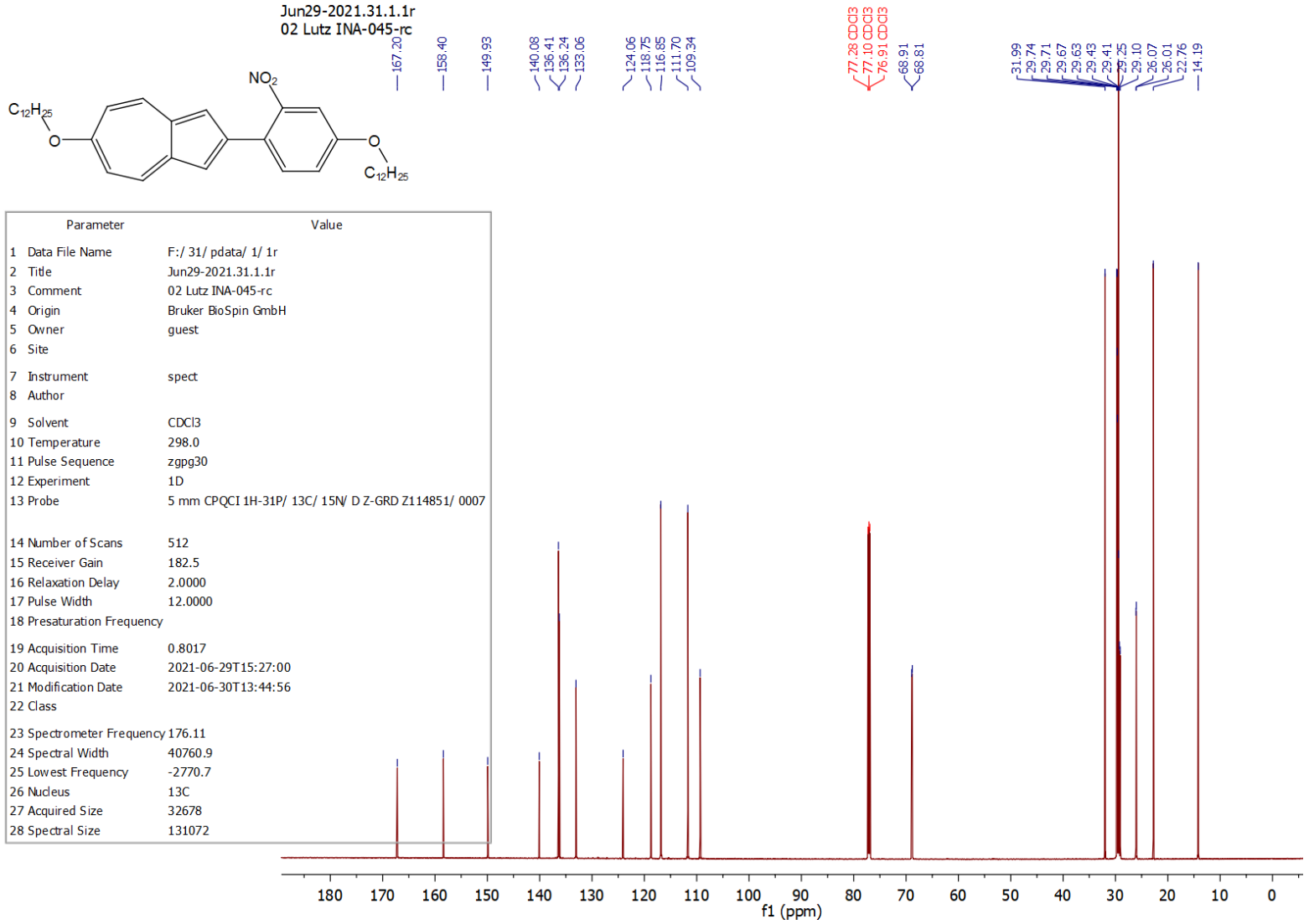


Figure S65: ^{13}C NMR spectrum of **12O-Az-NO_2PhO12** in $CDCl_3$ at 176 MHz.

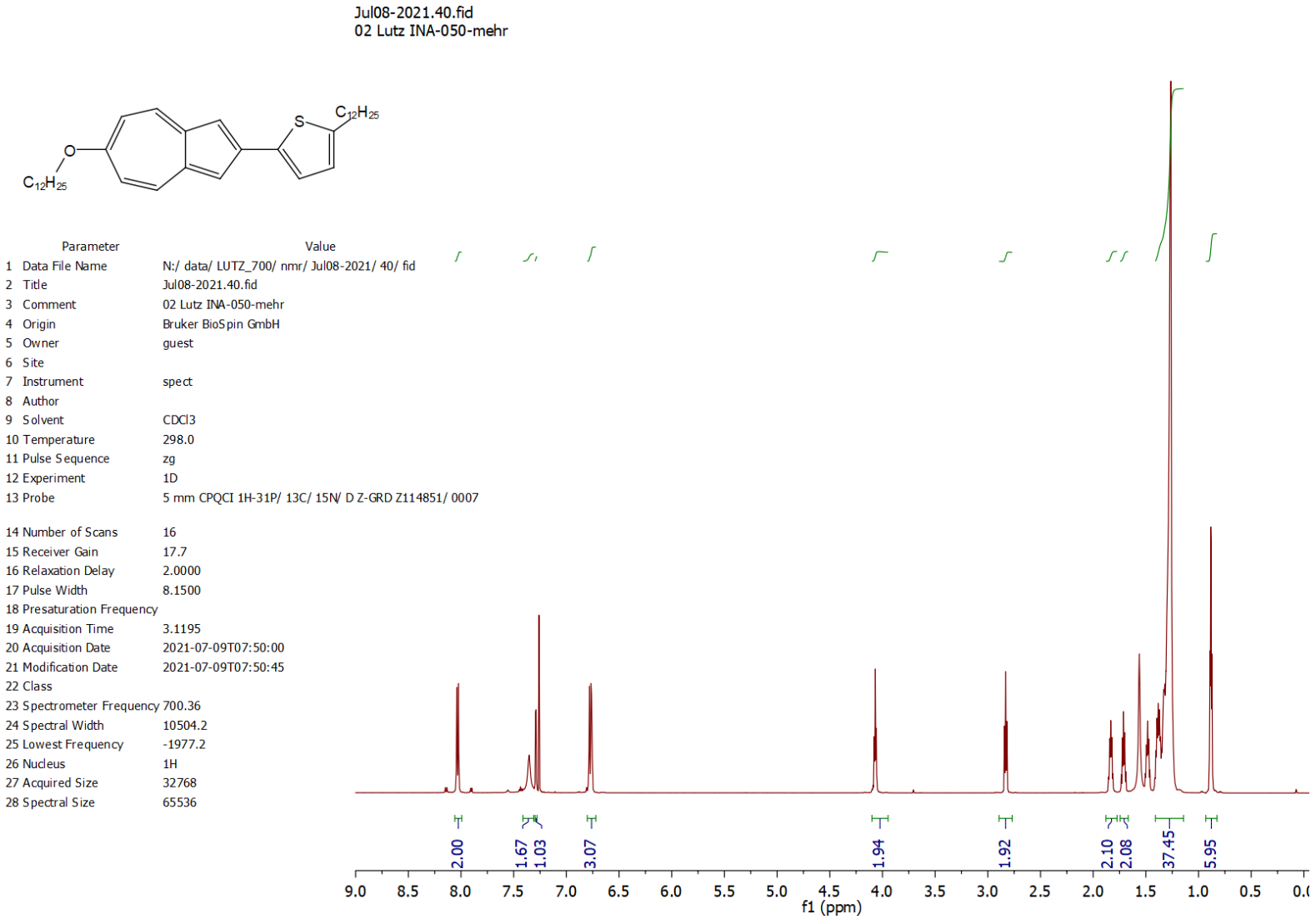


Figure S66: ^{1}H NMR spectrum of **12O-Az-Thi12** in $CDCl_3$ at 700 MHz.

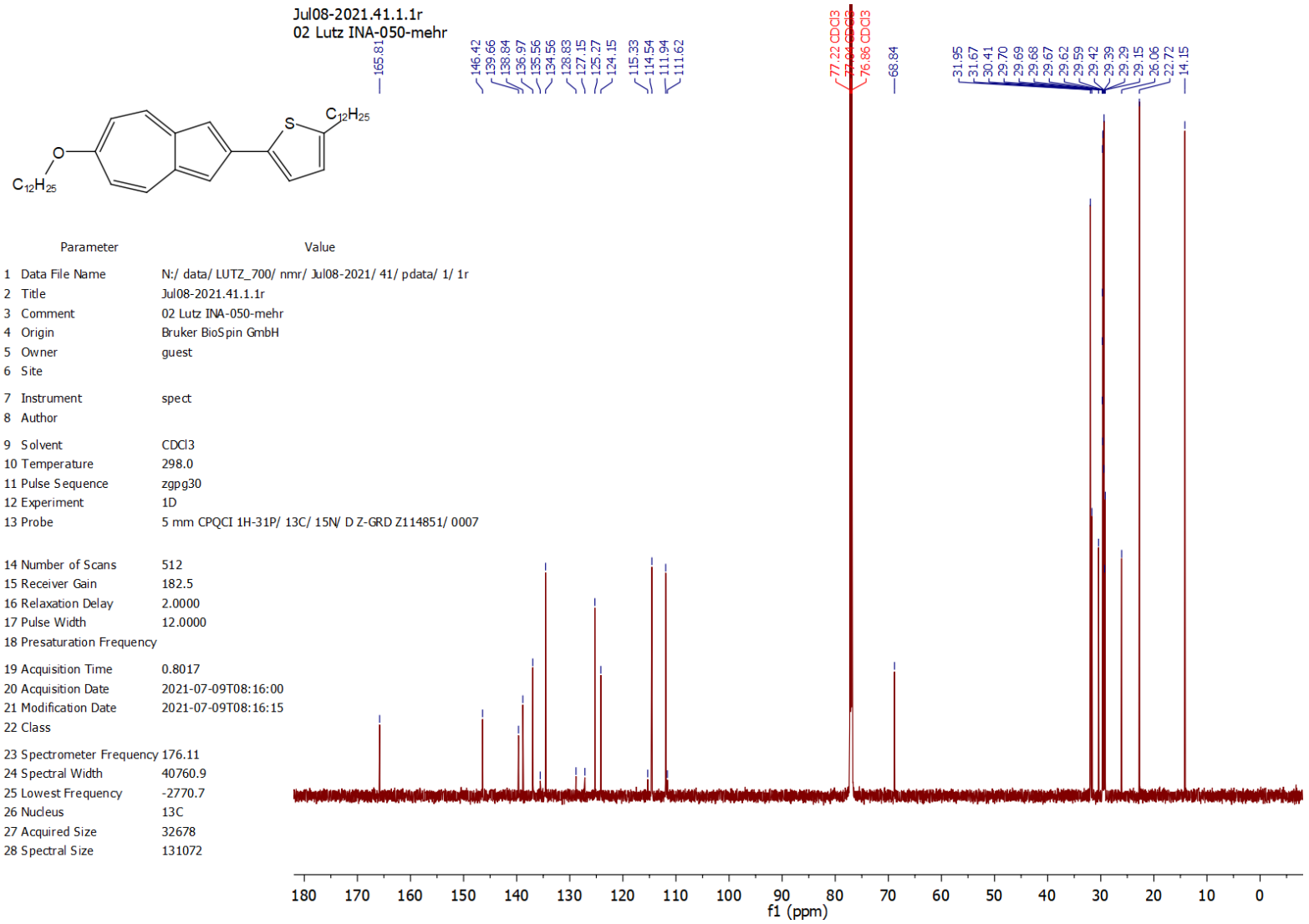


Figure S67: ^{13}C NMR spectrum of **12O-Az-Thi12** in $CDCl_3$ at 176 MHz.

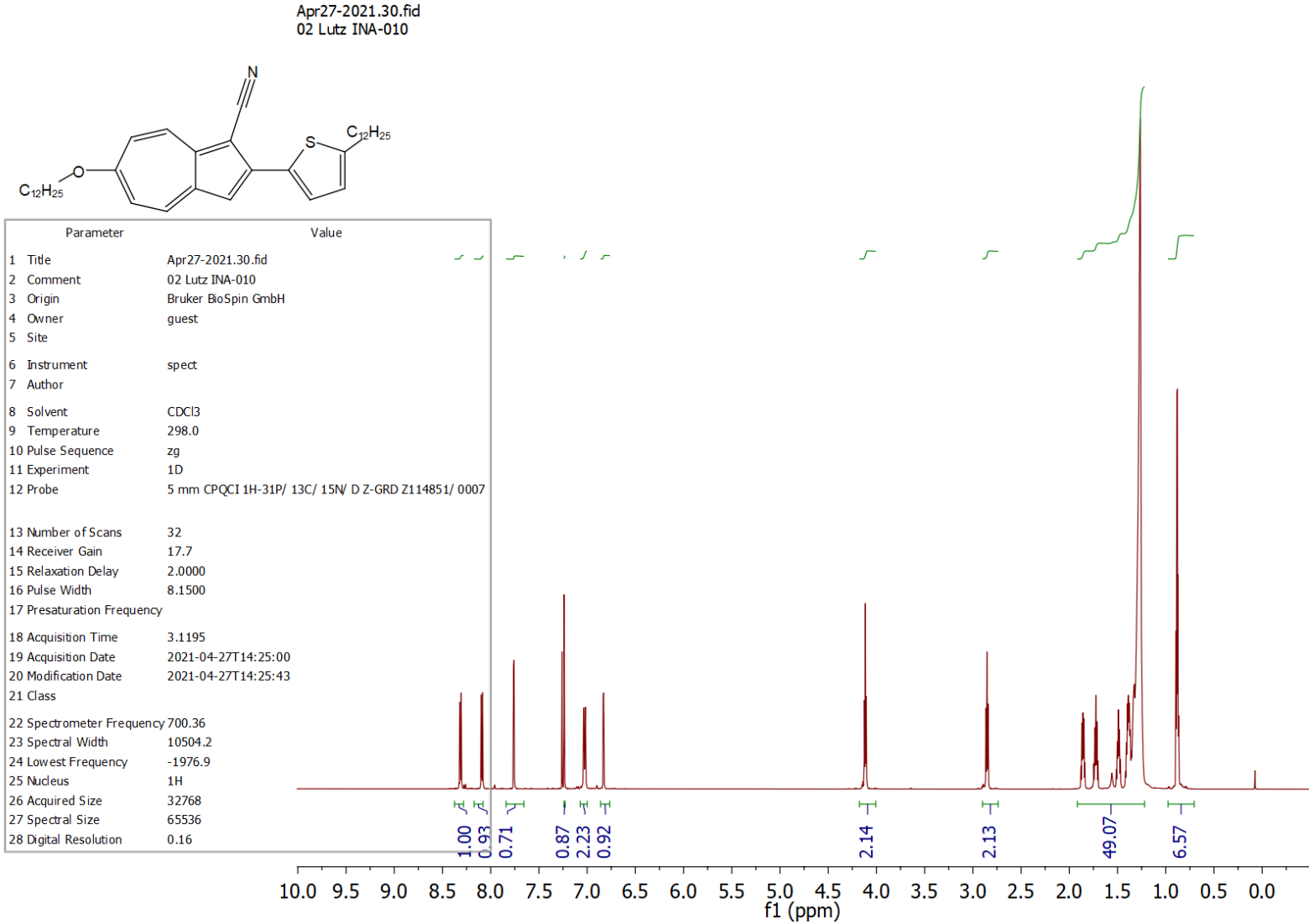


Figure S68: ^{1}H NMR spectrum of **12O-AzCN-Thi12** in $CDCl_3$ at 700 MHz.

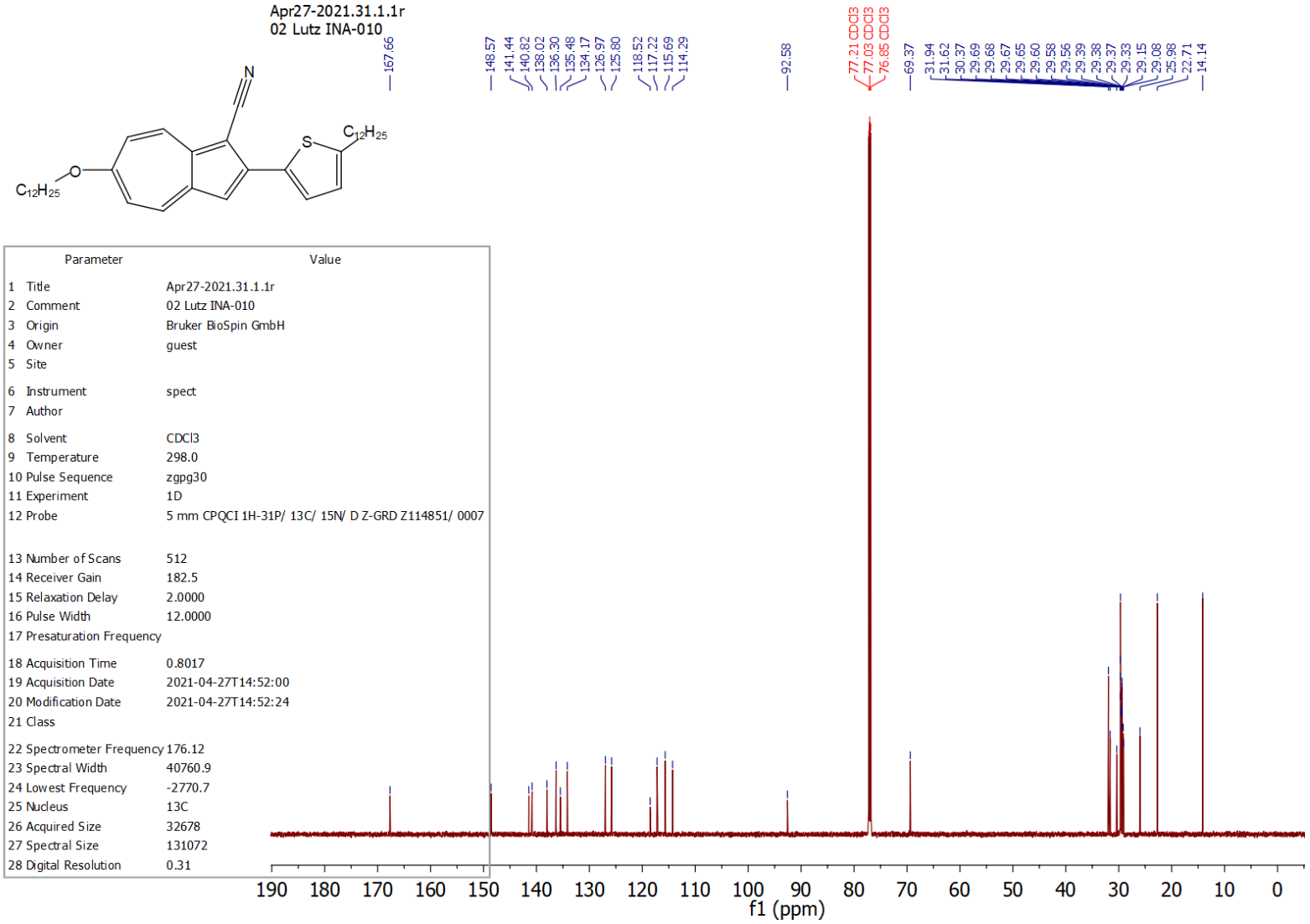


Figure S69: ^{13}C NMR spectrum of **12O-AzCN-Thi12** in $CDCl_3$ at 176 MHz.

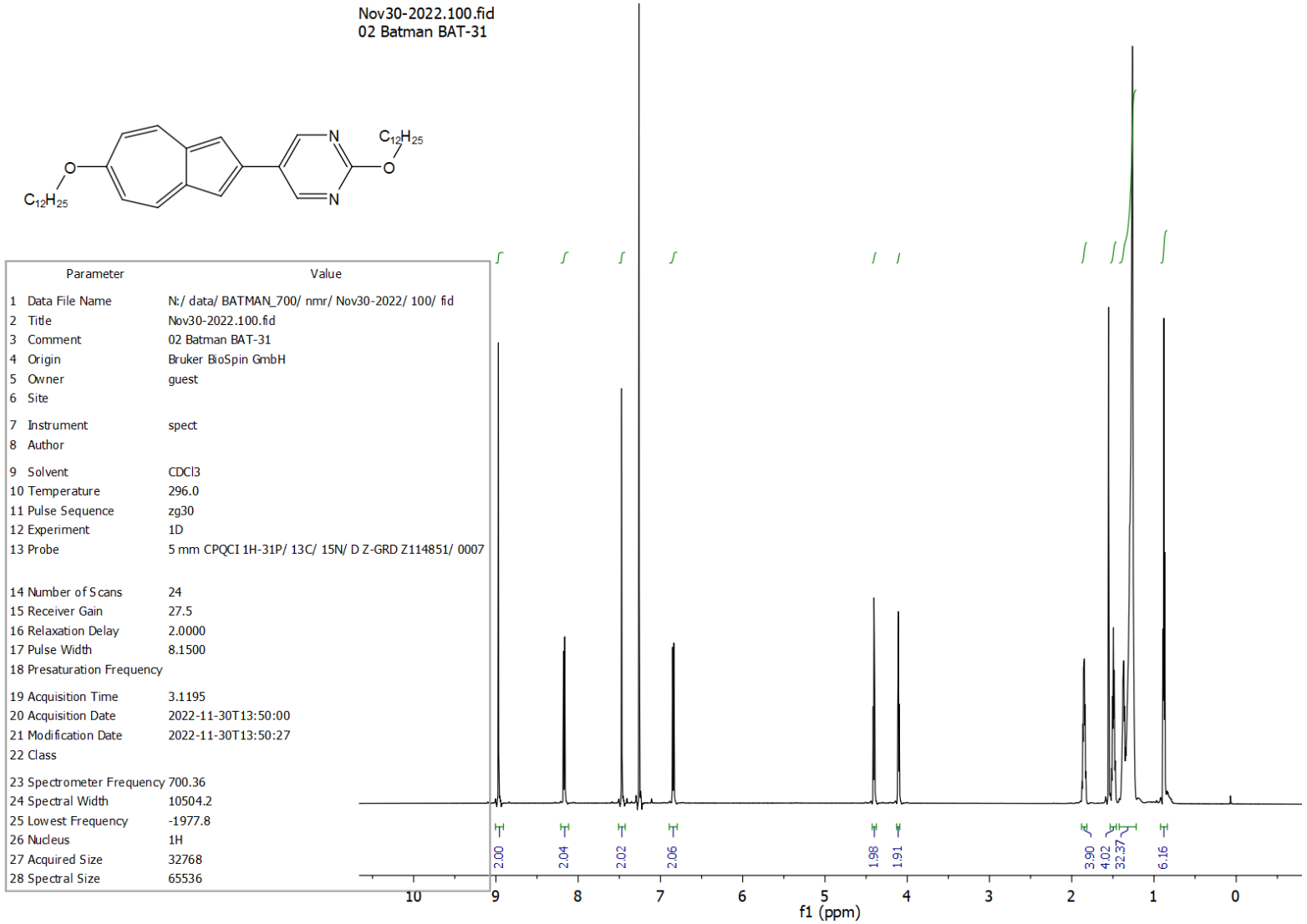


Figure S70: ^{1}H NMR spectrum of **12O-Az-PyriO12** in $CDCl_3$ at 700 MHz.

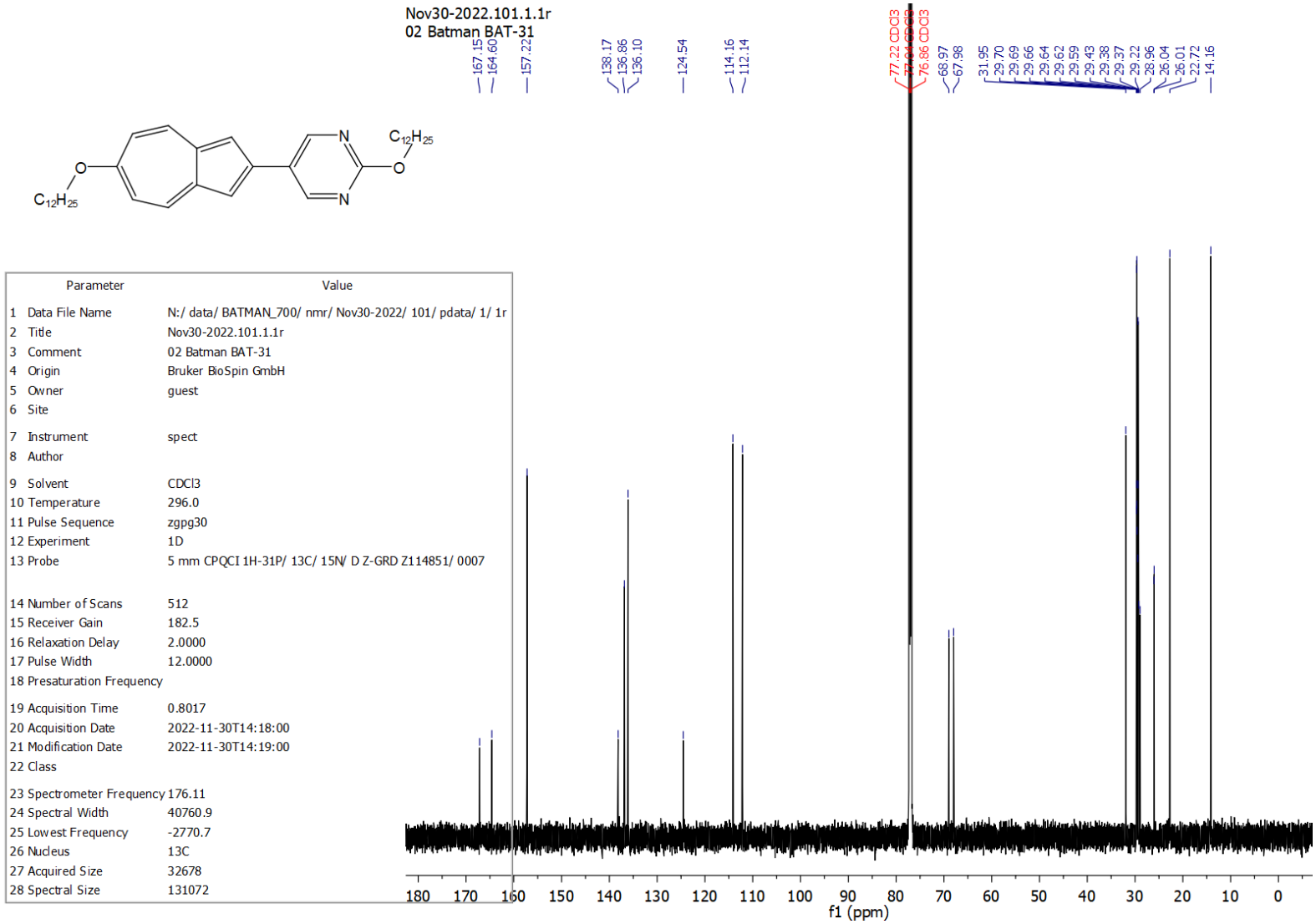


Figure S71: ^{13}C NMR spectrum of **12O-Az-PyriO12** in $CDCl_3$ at 176 MHz.

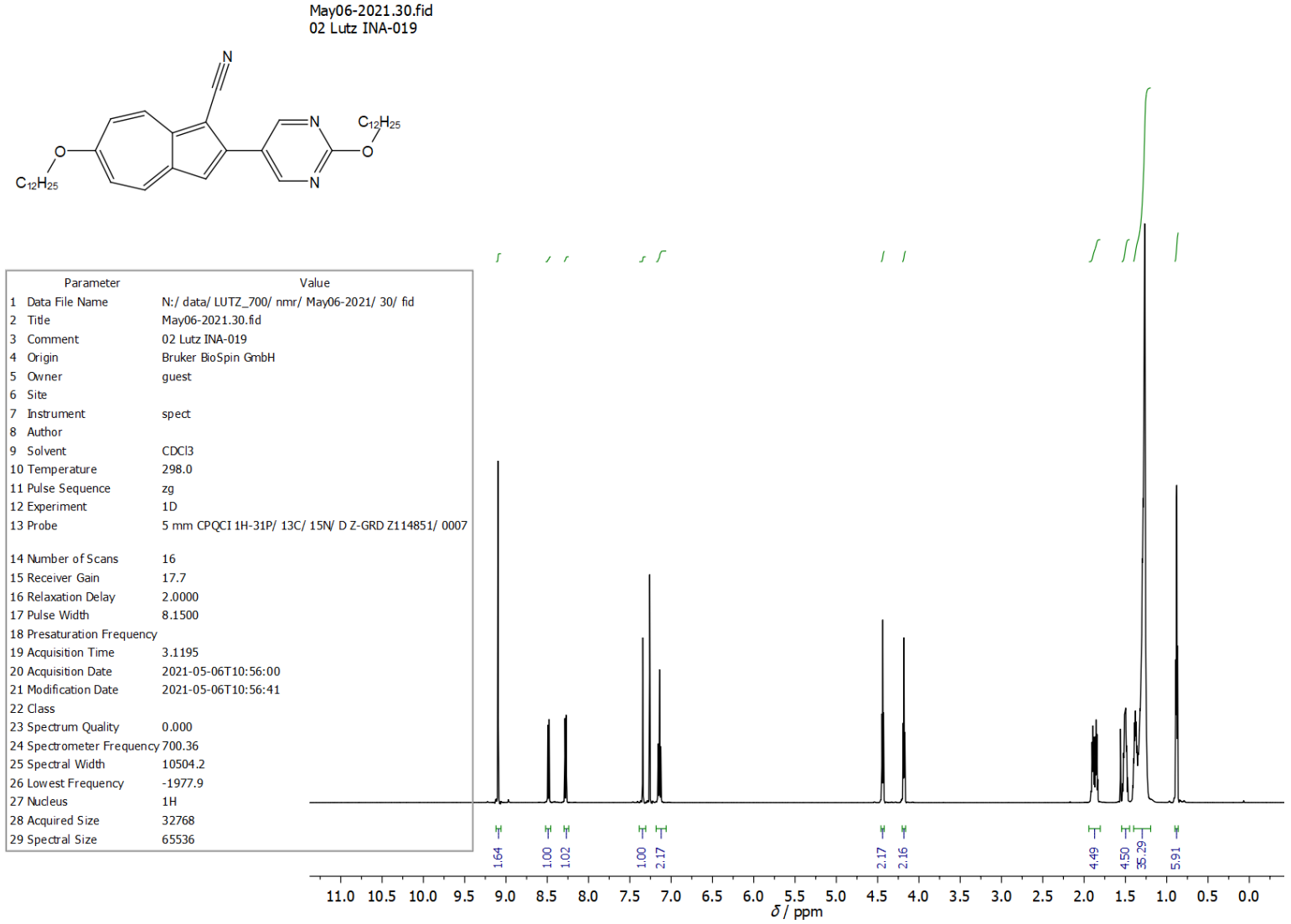


Figure S72: ^{1}H NMR spectrum of **12O-AzCN-PyriO12** in $CDCl_3$ at 700 MHz.

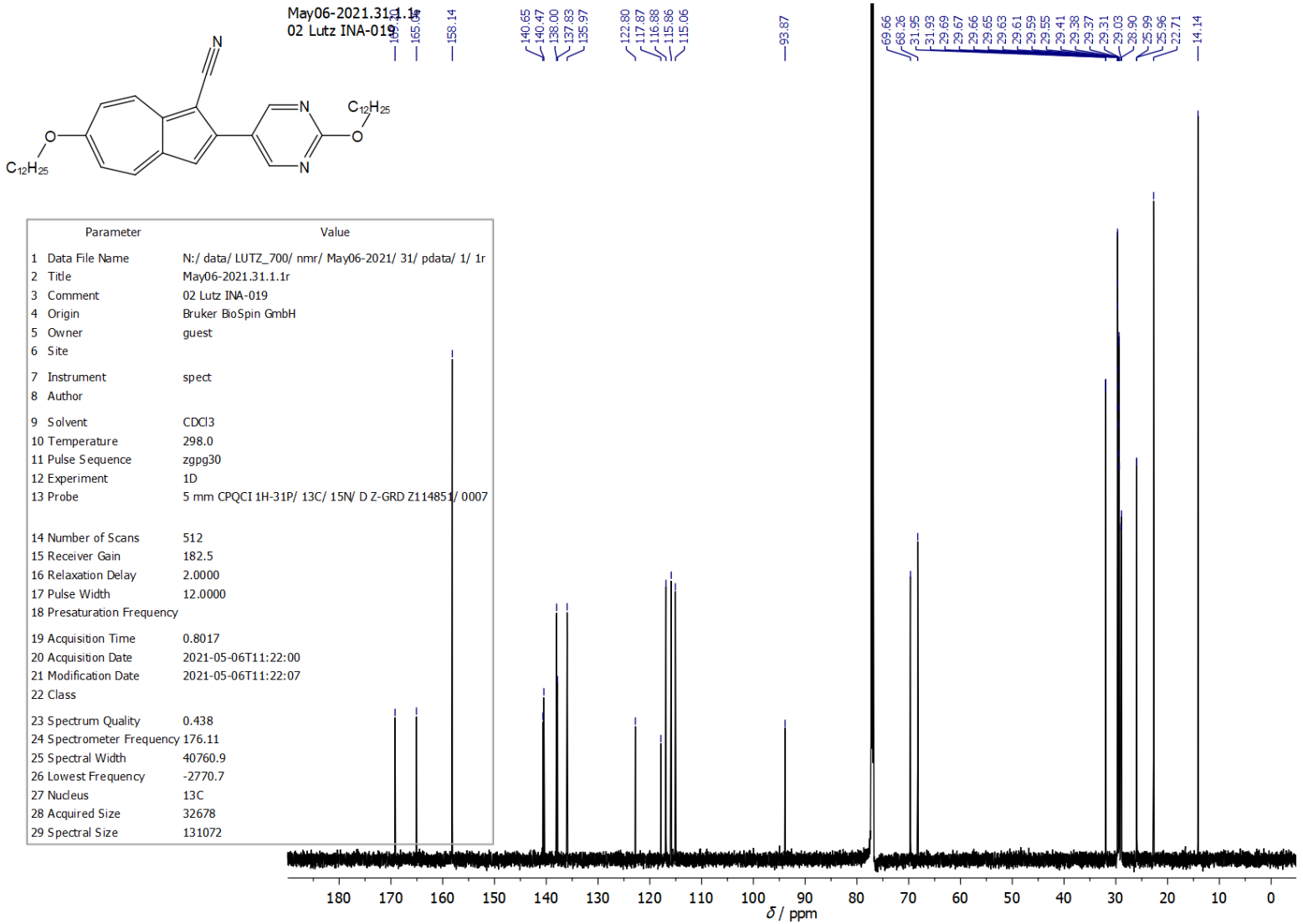


Figure S73: ^{13}C NMR spectrum of **12O-AzCN-PyriO12** in $CDCl_3$ at 176 MHz.

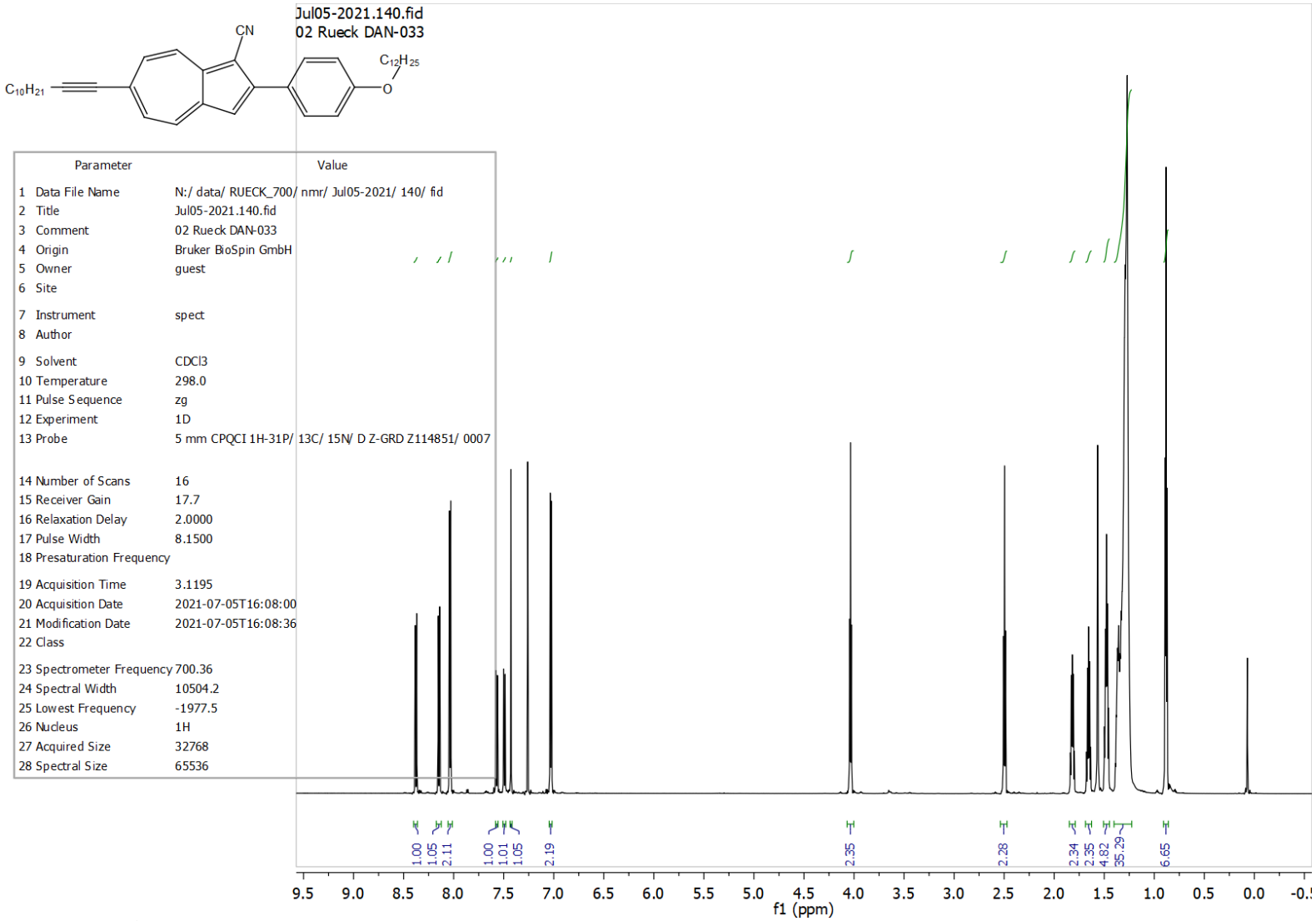


Figure S74: ^{1}H NMR spectrum of **12Yne-AzCN-PhO12** in $CDCl_3$ at 700 MHz.

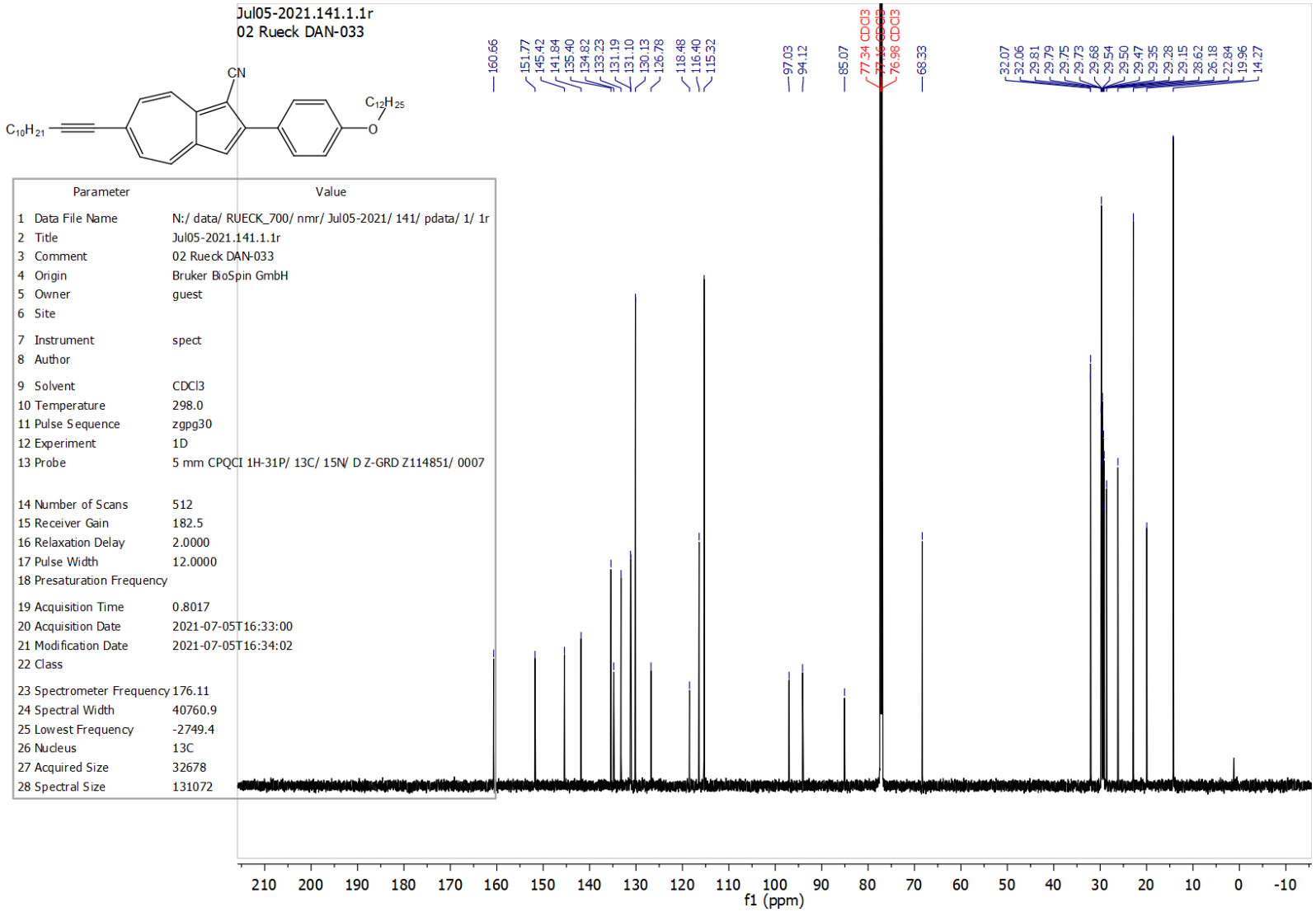


Figure S75: ^{13}C NMR spectrum of **12Yne-AzCN-PhO12** in $CDCl_3$ at 176 MHz.

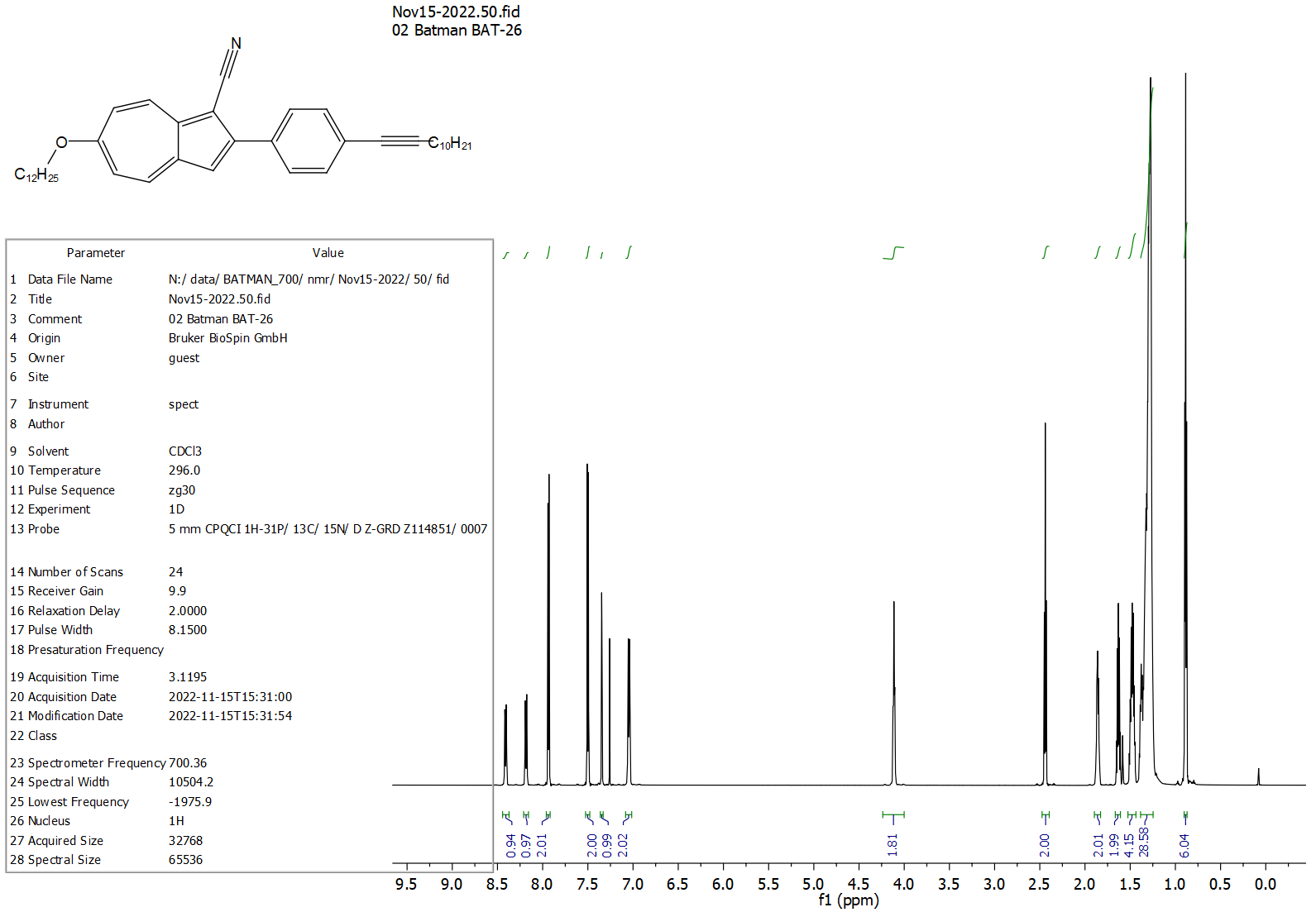


Figure S76: ^{1}H NMR spectrum of **12O-AzCN-PhYne12** in $CDCl_3$ at 700 MHz.

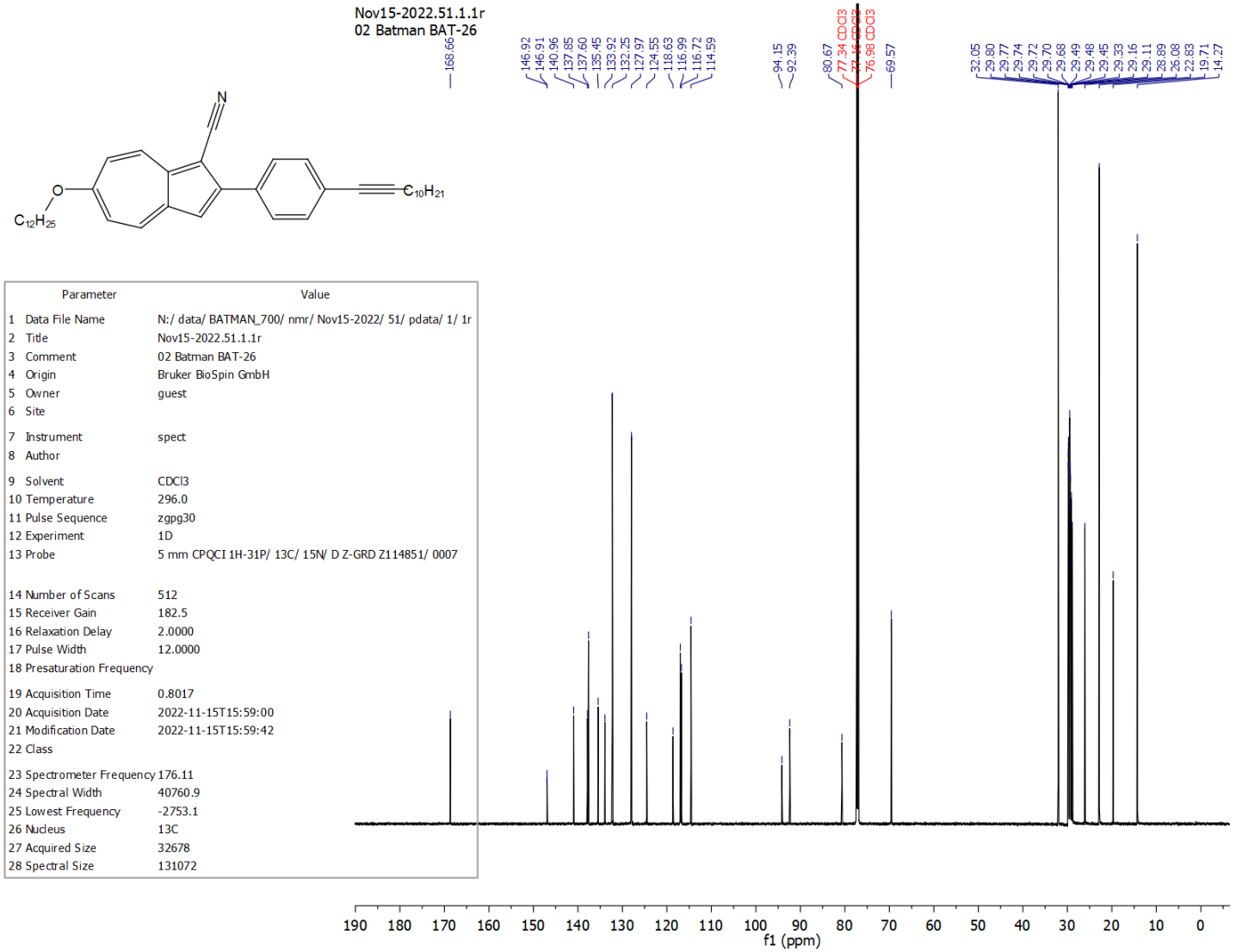


Figure S77: ^{13}C NMR spectrum of **12O-AzCN-PhYne12** in $CDCl_3$ at 176 MHz.

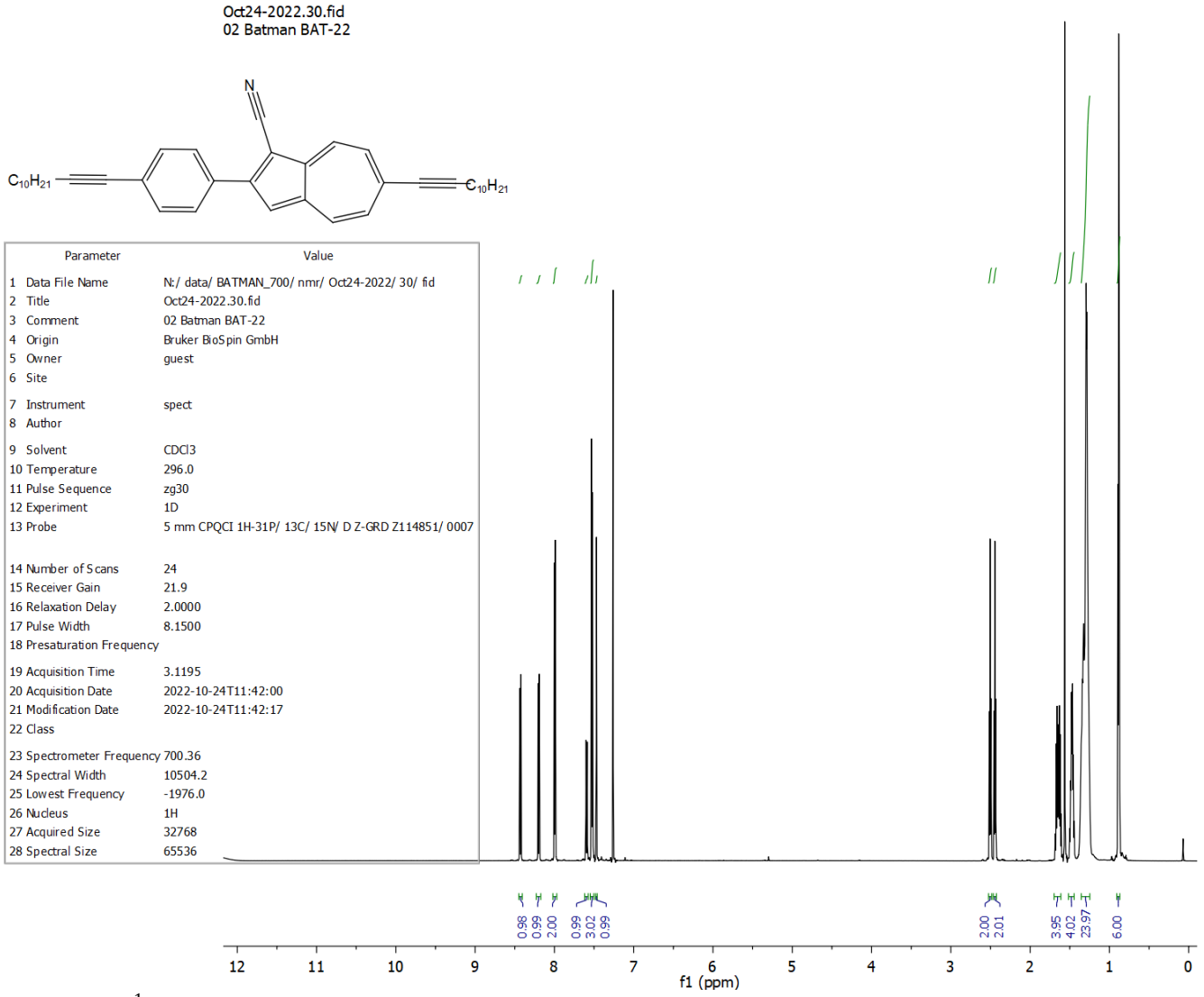
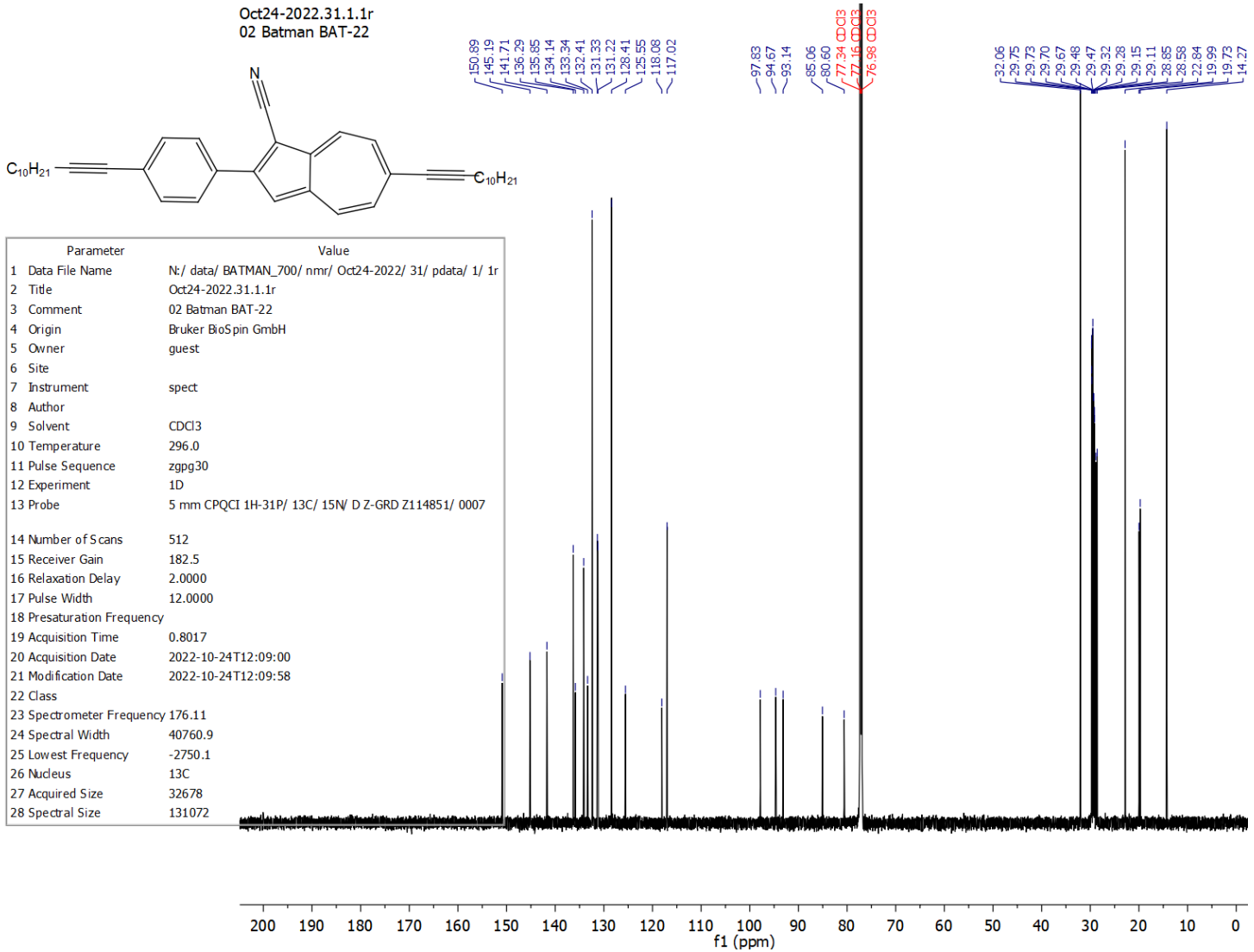


Figure S78: ^{1}H NMR spectrum of **12Yne-AzCN-PhYne12** in $CDCl_3$ at 700 MHz.



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8	Author	
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Figure S79: ^{13}C NMR spectrum of **12Yne-AzCN-PhYne12** in $CDCl_3$ at 176 MHz.

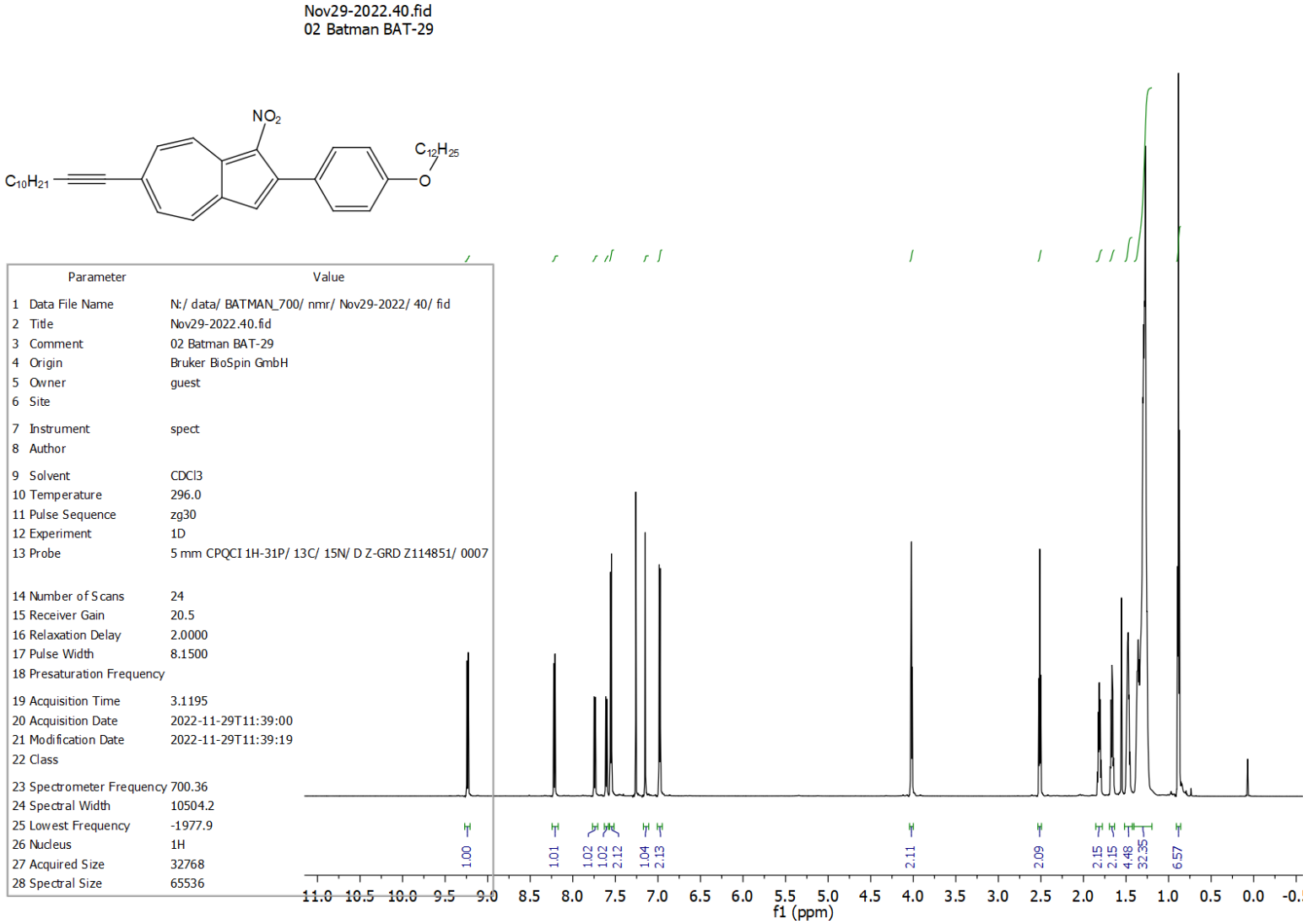

Figure S80: ^{1}H NMR spectrum of **12Yne-AzNO$_2$-PhO12** in $CDCl_3$ at 700 MHz.

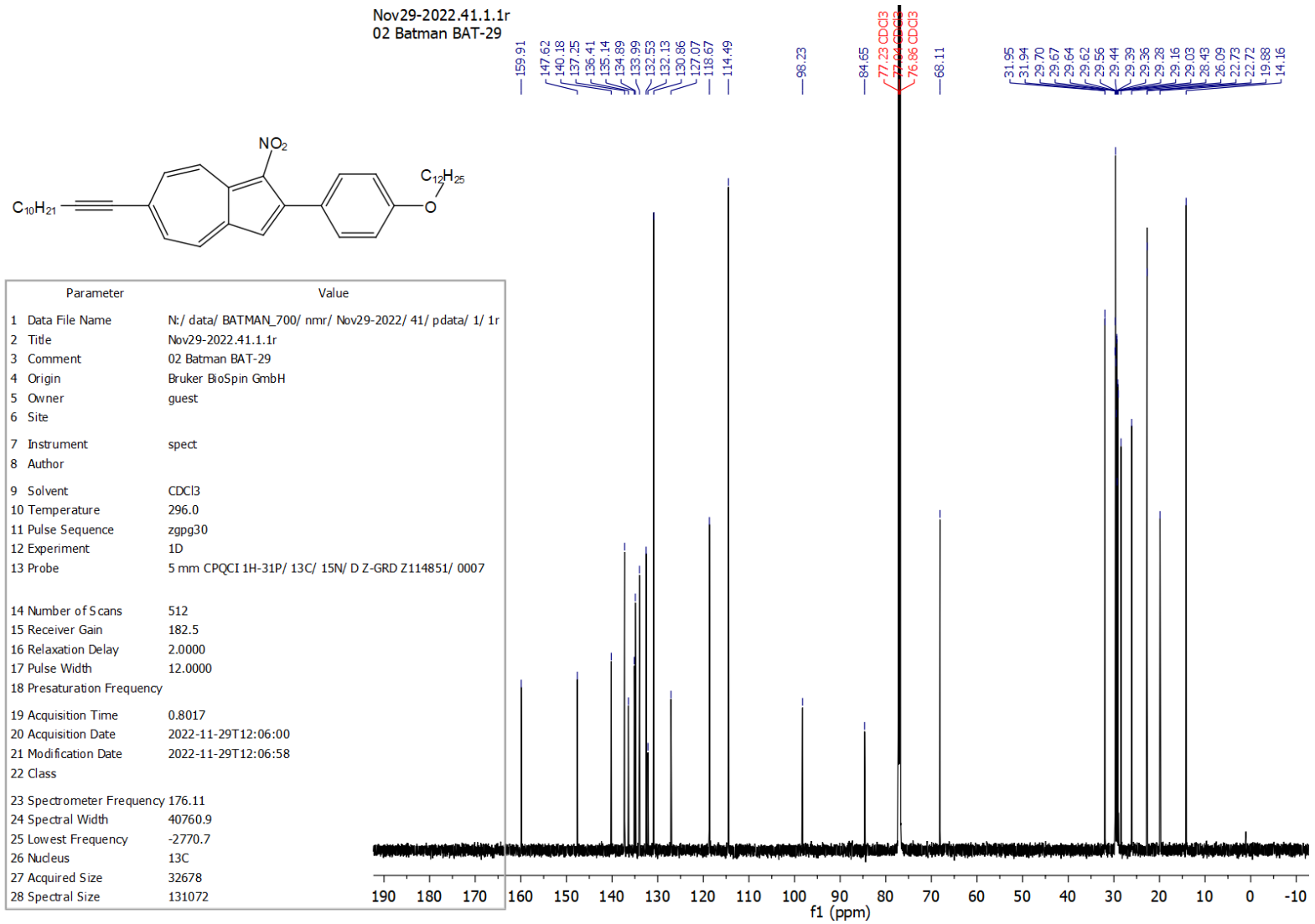

Figure S81: ^{13}C NMR spectrum of **12Yne-AzNO$_2$-PhO12** in $CDCl_3$ at 176 MHz.