Systematic Investigation on unsymmetrical mesogenic cyanobiphenyl dimers towards optical storage devices: Synthesis, mesomorphic, photoswitching and DFT studies

Mahima Rabari[a], Vasundhara Hegde[b], Gurumurthy Hegde[b,c],** A. K. Prajapati*[a]

SUPPORTING INFORMATION

➢ *Materials*

All the starting materials and reagents were purchased from (S.R.L. Chemicals, Mumbai) and used without further purification. Solvents like acetone, ethyl acetate and petroleum ether (60-80) were de-moisturized and purified before use.

➢ *Measurements*

Thin-layer chromatography (TLC) was performed on aluminium sheets pre-coated with Kiesel 60F254 silica gel. A Bruker Alpha II spectrometer was used to acquire Fourier Transform Infrared Spectroscopy (FT-IR) spectra of compounds as potassium bromide (KBr) pellets. Using deuterated chloroform ($CDCl_3$) solvent and internal standard tetramethyl silane (TMS), proton and carbon nuclear magnetic resonance (^{1}H and ^{13}C-NMR) spectrum data were obtained on an Advance Bruker 400 spectrometer (400 MHz). The optical textures of various substances were examined using the Leica DM 2500P POM. Thermograms were recorded on DSC-822, Mettler Toledo with Stare software. DSC measurements were investigated using aluminium pans and sample quantities of 2–3 mg. All measurements were taken in a nitrogen atmosphere at 30 mL min^{-1} with a heating rate of 10 °C min^{-1}. SYNAPT-XSHDBA064 TOF-MS in positive ion mode were used for Mass spectrometry. The SII EXSTAR6000 TG-DTA instrument was used to perform TG-DTA analyses. Using an aluminium pan and a heating rate of 10 °C min^{-1}, the experiments were conducted in a N_2 atmosphere between 30 °C and 550 °C. In the UV-Vis spectroscopy, samples were exposed to UV light with an intensity of around 1 mW/cm², provided by an OMNICURE series 2000 UV light source, which was fitted with a heat filter to eliminate heat radiation and a 365 nm UV filter. The molecular properties in the current work are calculated with the help of the Gaussian 09 software using the DFT with method B3LYP, basis set 6-31 G (d, p), polarised, and diffuse functions. The geometrical optimization was

carried out to minimize the energy of the system, and all calculations were done in their respective equilibrium geometry. Visualization of electronic properties with Gauss View in software is the gradient of colours of respective molecules.

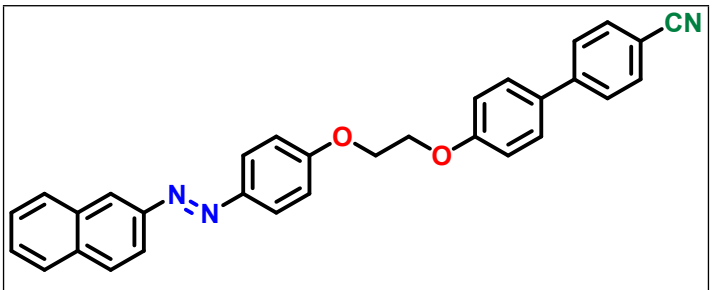
➢ *Synthesis and Characterization:*

Synthesis of (E)-4'-(ω-(4-(naphthalen-2-yldiazenyl)phenoxy)alkoxy)-[1,1'-biphenyl]-4-carbonitrile (CBnAZ):

In a round bottom flask with a reflux system and stirring for 15 minutes, (E)-4-(naphthalen-2-yldiazenyl) phenol (NpAzOH) (0.52 mmol) and CBBr-n (0.5 mmol) were dissolved in acetone. Additions of anhydrous K_2CO_3 (15.7 mmol) and a catalytic amount of KI were made to the reaction mixture, and the system was refluxed for about 48 h (monitored by TLC). The hot solution was filtered and washed with acetone after the reaction was finished. The filtrate was then collected and evaporated in a rotary evaporator. Cold petroleum ether was added to the concentrated extracts, and the resulting precipitate was filtered and washed two times with this same solvent. Column chromatography is used to purify the resulting compound. (96:4 pet ether: ethyl acetate)

Characterization of dimers CBnAZ:

***(E)-4'-(2-(4-(Naphthalen-2-yldiazenyl)phenoxy)ethoxy)-[1,1'-biphenyl]-4-carbonitrile (CB2AZ)*:**

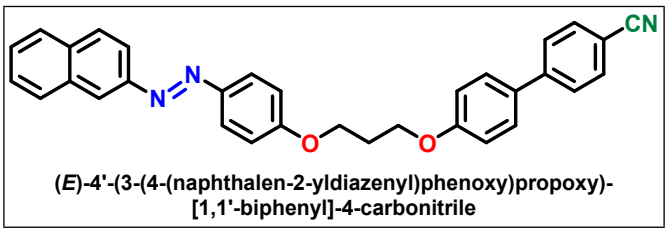


(*E*)-4'-(2-(4-(naphthalen-2-yldiazenyl)phenoxy)ethoxy)-[1,1'-biphenyl]-4-carbonitrile

Orange crystals, Yield: 67%; **IR** ν_{max}/cm^{-1}: 3058.51, 2937.18 (C_{sp3}-H), 2868.76, 2223.41 (C≡N), 1601.95 (-N=N-), 1243.02 (C-O), 1182.79 (C-N), 1069.78, 819.98; **^{1}H NMR (400 MHz, $CDCl_3$): δ (In ppm)**: 8.33 (s, 1H, Ar-H), 7.98 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.92 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.89 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.83 (d, *J* = 9.2 Hz, 2H, Ar-H), 7.61 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.56 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.48 (d, *J* = 2.8 Hz, 2H, Ar-H), 7.45 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.94 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.88 (d, *J* = 8.8 Hz, 2H, Ar-H), 4.01 (t,

J = 6.0 Hz, 2H, -O-C$\underline{H}_2$-), 3.96 (t, *J* = 6.0 Hz, 2H, -O-C$\underline{H}_2$-); **^{13}C NMR (400MHz, $CDCl_3$): δ (In ppm):** 161.31 (Ar $\underline{C}$-O-), 159.44, 150.31, 147.17, 145.15, 134.61, 133.57, 132.65, 131.62, 129.14, 128.42, 127.13, 126.69, 124.81, 119.15, 117.25, 115.16, 114.77, 110.10, 65.26 (Ar-O-$\underline{C}$-); **Elemental Analysis**: $C_{31}H_{23}N_3O_2$:(cal): C, 79.30; H, 4.94; N, 8.95; found C, 79.19; H, 4.91; N, 8.91; %;

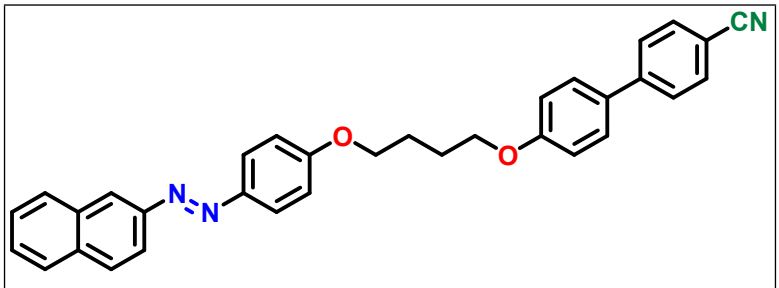
***(E)-4'-(3-(4-(Naphthalen-2-yldiazenyl)phenoxy)propoxy)-[1,1'-biphenyl]-4-carbonitrile* (*CB3AZ*):**



(*E*)-4'-(3-(4-(naphthalen-2-yldiazenyl)phenoxy)propoxy)-[1,1'-biphenyl]-4-carbonitrile

Orange crystals, Yield: 65%; **IR** ν_{max}/cm^{-1}: 3066.43, 2933.33 (C_{sp3}-H), 2868.38, 2224.00 (C≡N), 1598.77 (-N=N-), 1245.98 (C-O), 1181.69 (C-N), 1048.64, 822.09; **^{1}H NMR (400 MHz, $CDCl_3$): δ (In ppm)**: 8.33 (s, 1H, Ar-$\underline{H}$), 8.08 (d, *J* = 8.4 Hz, 1H, Ar-$\underline{H}$), 8.06 (d, *J* = 8.4 Hz, 1H, Ar-$\underline{H}$), 8.0 (d, *J* = 8.8 Hz, 2H, Ar-$\underline{H}$), 7.91 (d, *J* = 9.2 Hz, 2H, Ar-$\underline{H}$), 7.71 (d, *J* = 8.0 Hz, 2H, Ar-$\underline{H}$), 7.65 (d, *J* = 8.0 Hz, 2H, Ar-$\underline{H}$), 7.58 (d, *J* = 3.2 Hz, 2H, Ar-$\underline{H}$), 7.56 (d, *J* = 8.8 Hz, 2H, Ar-$\underline{H}$), 7.08 (d, *J* = 8.8 Hz, 2H, Ar-$\underline{H}$), 7.05 (d, *J* = 8.0 Hz, 2H, Ar-$\underline{H}$), 4.31 (t, *J* = 6.0 Hz, 2H, -O-C$\underline{H}_2$-), 4.27 (t, *J* = 6.0 Hz, 2H, -O-C$\underline{H}_2$-), 2.40-2.34 (m, 2H, -O-C-C$\underline{H}_2$-); **^{13}C NMR (400MHz, $CDCl_3$): δ (In ppm):** 161.32 (Ar $\underline{C}$-O-), 159.45, 150.30, 147.15, 145.19, 134.57, 133.61, 132.61, 131.65, 129.15, 128.43, 127.14, 126.69, 124.81, 119.16, 117.25, 115.11, 114.78, 110.11, 64.55 (Ar-O-$\underline{C}$-), 29.23; **Elemental Analysis**: $C_{32}H_{25}N_3O_2$:(cal): C, 79.48; H, 5.21; N, 8.69; found C, 79.39; H, 5.19; N, 8.61; %;

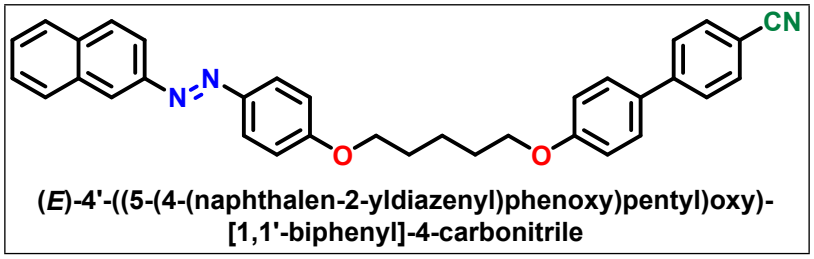
***(E)-4'-(4-(4-(Naphthalen-2-yldiazenyl)phenoxy)butoxy)-[1,1'-biphenyl]-4-carbonitrile* (*CB4AZ*):**



(*E*)-4'-(4-(4-(naphthalen-2-yldiazenyl)phenoxy)butoxy)-[1,1'-biphenyl]-4-carbonitrile

Orange crystals, Yield: 69%; **IR** ν_{max}/cm^{-1}: 3055.39, 2941.96 (Csp3-H), 2869.95, 2222.95 (C≡N), 1601.40 (-N=N-), 1257.46 (C-O), 1177.44 (C-N), 1027.12, 819.32; **^{1}H NMR (400 MHz, $CDCl_3$): δ (In ppm)**: 8.33 (s, 1H, Ar-H), 8.08 (d, *J* = 8.4 Hz, 1H, Ar-H), 8.05 (d, *J* = 8.4 Hz, 1H, Ar-H), 8.02 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.91 (d, *J* = 9.2 Hz, 2H, Ar-H), 7.72 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.66 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.58 (d, *J* = 3.2 Hz, 2H, Ar-H), 7.56 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.06 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.03 (d, *J* = 8.0 Hz, 2H, Ar-H), 4.31 (t, *J* = 6.0 Hz, 2H, -O-CH_2-), 4.18 (t, J = 6.0 Hz, 2H, -O-CH2-), 4.14 (t, J = 6.0 Hz, 2H, -O-CH2-), 2.12-2.08 (m, 4H, 2 X -O-C-CH_2-); **^{13}C NMR (400MHz, $CDCl_3$): δ (In ppm):** 161.35 (Ar C-O-), 159.43, 150.30, 147.11, 145.20, 134.53, 133.71, 132.61, 131.60, 129.15, 128.43, 127.15, 126.69, 124.82, 119.10, 117.25, 115.16, 114.78, 110.14, 64.70 (Ar-O-C-), 27.20; **Elemental Analysis**: $C_{33}H_{27}N_3O_2$:(cal): C, 79.66; H, 5.47; N, 8.44; found C, 79.72; H, 5.45; N, 8.39; %;

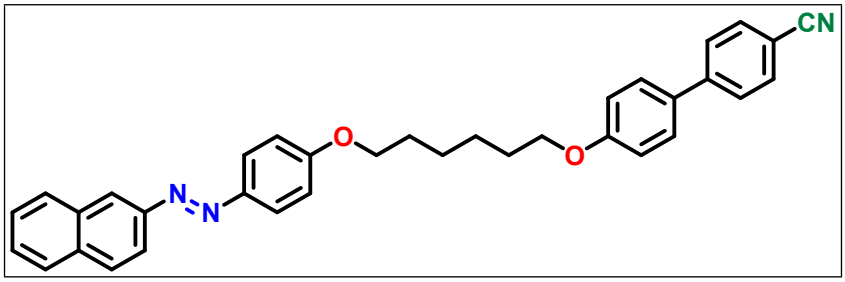
***(E)-4'-((5-(4-(Naphthalen-2-yldiazenyl)phenoxy)pentyl)oxy)-[1,1'-biphenyl]-4-carbonitrile* (*CB5AZ*):**



(*E*)-4'-((5-(4-(naphthalen-2-yldiazenyl)phenoxy)pentyl)oxy)-[1,1'-biphenyl]-4-carbonitrile

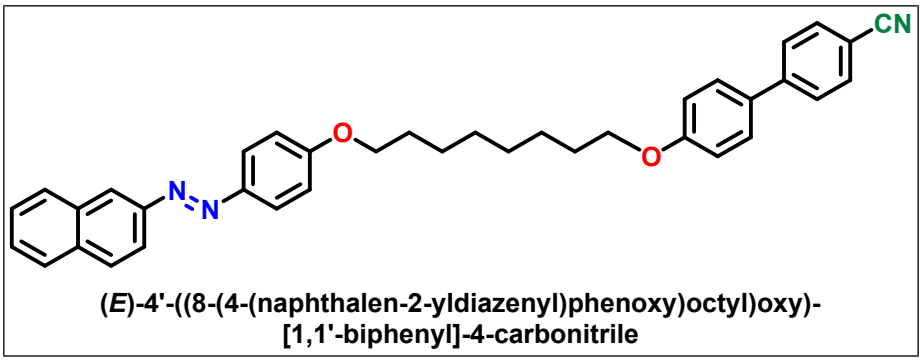
Orange crystals, Yield: 65%; **IR** ν_{max}/cm^{-1}: 3055.32, 2941.91 (C_{sp3}-H), 2868.99, 2222.98 (C≡N), 1601.48 (-N=N-), 1259.46 (C-O), 1177.44 (C-N), 1027.12, 819.39; **^{1}H NMR (400 MHz, $CDCl_3$): δ (In ppm)**: 8.32 (s, 1H, Ar-H), 7.97 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.92 (d, *J* = 8.4 Hz, 1H, Ar-H) 7.89 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.82 (d, *J* = 9.2 Hz, 2H, Ar-H), 7.59 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.54 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.47 (d, *J* = 3.2 Hz, 2H, Ar-H), 7.44 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.95 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.90 (d, *J* = 9.4 Hz, 2H, Ar-H), 3.97 (t, J = 6.0 Hz, 2H, -O-CH_2-), 3.93 (t, J = 6.0 Hz, 2H, -O-CH_2-), 1.75-1.74 (m, 4H, 2 X -O-C-CH_2-), 1.58 (m, 2H, -O-C-C-CH_2-); **^{13}C NMR (400MHz, $CDCl_3$): δ (In ppm):** 161.66 (Ar C-O-), 158.72, 149.25, 145.86, 144.23, 133.45, 132.54, 131.51, 130.18, 128.19, 127.29, 126.87, 126.10, 125.60, 116.24, 113.99, 113.68, 109.01, 65.21 (Ar-O-C-), 28.31, 24.43; **Elemental Analysis**: $C_{34}H_{29}N_3O_2$:(cal): C, 79.82; H, 5.71; N, 8.21; found C, 79.80 H, 5.70; N, 8.31; %;

***(E)-4'-((6-(4-(Naphthalen-2-yldiazenyl)phenoxy)hexyl)oxy)-[1,1'-biphenyl]-4-carbonitrile* (*CB6AZ*):**



Orange crystals, Yield: 67%; **IR** ν_{max}/cm^{-1}: 3056.36, 2938.38 (C_{sp3}-H), 2868.08, 2220.20 (C≡N), 1600.49 (-N=N-), 1247.71 (C-O), 1177.28 (C-N), 1027.70, 818.60; **^{1}H NMR (400 MHz, $CDCl_3$): δ (In ppm)**: 8.42 (s, 1H, Ar-H), 7.98 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.92 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.89 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.83 (d, *J* = 9.2 Hz, 2H, Ar-H), 7.60 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.55 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.47 (d, *J* = 3.2 Hz, 2H, Ar-H), 7.44 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.95 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.91 (d, *J* = 9.4 Hz, 2H, Ar-H), 4.01 (t, J = 6.0 Hz, 2H, -O-CH_2-), 3.96 (t, J = 6.0 Hz, 2H, -O-CH_2-), 1.81-1.80 (m, 4H, 2 X -O-C-CH_2-), 1.53-1.52 (m, 4H, 2 X -O-C-C-CH_2-); **^{13}C NMR (400MHz, $CDCl_3$): δ (In ppm):** 161.56 (Ar C-O-), 158.65, 149.25, 145.91, 144.19, 133.46, 132.54, 131.54, 130.26, 128.10, 127.31, 126.87, 126.10, 125.61, 118.13, 116.19, 113.67, 108.94, 66.90 (Ar-O-C-), 29.95, 28.10, 24.80; **Elemental Analysis**: $C_{35}H_{31}N_3O_2$:(cal): C, 79.97; H, 5.94; N, 7.99; found C, 79.91; H, 5.92; N, 7.94; %;

***(E)-4'-((8-(4-(Naphthalen-2-yldiazenyl)phenoxy)octyl)oxy)-[1,1'-biphenyl]-4-carbonitrile* (*CB8AZ*):**

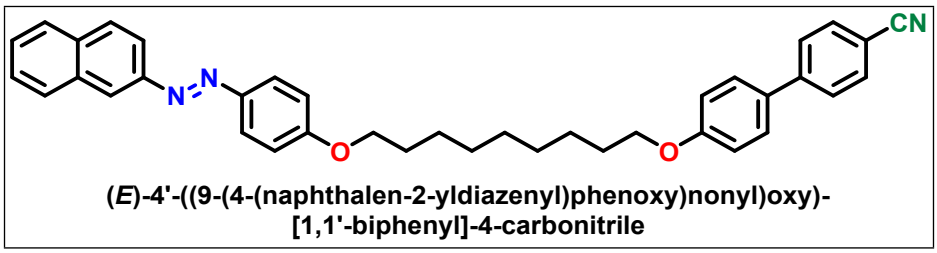


(*E*)-4'-((8-(4-(naphthalen-2-yldiazenyl)phenoxy)octyl)oxy)-[1,1'-biphenyl]-4-carbonitrile

Orange crystals, Yield: 64%; **IR** ν_{max}/cm^{-1}: 3052.31, 2936.43 (C_{sp3}-H), 2851.05, 2219.72 (C≡N), 1600.67 (-N=N-), 1251.29 (C-O), 1177.29 (C-N), 1018.16, 820.49; **^{1}H NMR (400 MHz, $CDCl_3$): δ (In ppm)**: 8.32 (s, 1H, Ar-H), 7.97 (d, *J* = 8 .0 Hz, 1H, Ar-H), 7.92 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.89 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.82 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.59 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.55 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.47 (d, *J* = 3.2 Hz, 2H, Ar-H), 7.45 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.94 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.90 (d, *J* = 8.0 Hz, 2H, Ar-H), 3.97 (t, J = 6.0 Hz, 2H, -O-CH_2-), 3.93 (t, J = 6.0 Hz, 2H, -O-CH_2-), 1.76-1.74 (m, 4H, 2 X -O-C-CH_2-),

1.43-1.35 (m, 8H, -O-C-C-($\underline{CH_2}$)$_4$-); **^{13}C NMR (400MHz, $CDCl_3$): δ (In ppm):** 160.61 (Ar $\underline{C}$-O-), 158.69, 149.25, 145.87, 144.19, 133.59, 132.54, 131.52, 130.19, 128.18, 127.28, 126.87, 126.11, 125.60, 118.13, 116.06, 113.67, 108.91, 67.13 (Ar-O-$\underline{C}$-), 29.94, 28.24, 28.13, 24.91; **Elemental Analysis**: $C_{37}H_{35}N_3O_2$:(cal): C, 80.26; H, 6.37; N, 7.59; found C, 80.23; H, 6.35; N, 7.53; %;

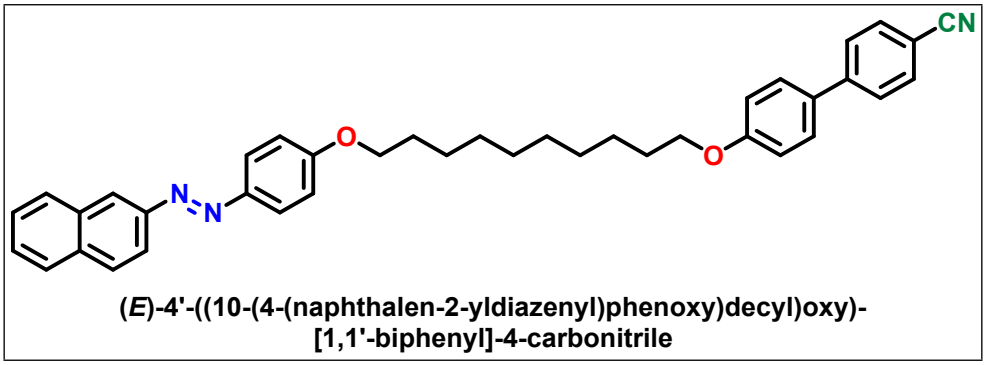
***(E)-4'-((9-(4-(Naphthalen-2-yldiazenyl)phenoxy)nonyl)oxy)-[1,1'-biphenyl]-4-carbonitrile* (*CB9AZ*):**



(*E*)-4'-((9-(4-(naphthalen-2-yldiazenyl)phenoxy)nonyl)oxy)-[1,1'-biphenyl]-4-carbonitrile

Orange crystals, Yield: 66%; **IR** ν_{max}/cm^{-1}: 3060.86, 2941.07 (C_{sp3}-H), 28750.51, 2225.19 (C≡N), 1600.24 (-N=N-), 1257.66 (C-O), 1182.03 (C-N), 1028.58, 821.41; **^{1}H NMR (400 MHz, $CDCl_3$): δ (In ppm)**: 8.32 (s, 1H, Ar-$\underline{H}$), 8.08 (d, *J* = 8.4 Hz, 1H, Ar-$\underline{H}$), 8.06 (d, *J* = 8.4 Hz, 1H, Ar-$\underline{H}$), 8.00 (d, *J* = 8.8 Hz, 2H, Ar-$\underline{H}$), 7.91 (d, *J* = 9.2 Hz, 2H, Ar-$\underline{H}$), 7.69 (d, *J* = 8.0 Hz, 2H, Ar-$\underline{H}$), 7.63 (d, *J* = 8.4 Hz, 2H, Ar-$\underline{H}$), 7.57 (d, *J* = 3.2 Hz, 2H, Ar-$\underline{H}$), 7.55 (d, *J* = 8.0 Hz, 2H, Ar-$\underline{H}$), 7.05 (d, *J* = 8.8 Hz, 2H, Ar-$\underline{H}$), 7.00 (d, *J* = 8.4 Hz, 2H, Ar-$\underline{H}$), 4.07 (t, J = 6.0 Hz, 2H, -O-C$\underline{H_2}$-), 4.01 (t, J = 6.4 Hz, 2H, -O-C$\underline{H_2}$-), 1.87-1.80 (m, 4H, 2 X -O-C-$\underline{CH_2}$-), 1.52-1.41 (m, 10H, -O-C-C-($\underline{CH_2}$)$_5$-); **^{13}C NMR (400MHz, $CDCl_3$): δ (In ppm):** 160.72 (Ar $\underline{C}$-O-), 159.81, 150.37, 146.99, 145.27, 133.64, 132.57, 131.26, 129.24, 128.33, 127.24, 126.93, 126.65, 124.78, 119.15, 117.36, 115.09, 110.03, 68.24 (Ar-O-$\underline{C}$-), 29.45, 29.27, 29.19, 26.01; **Elemental Analysis**: $C_{38}H_{37}N_3O_2$:(cal): C, 80.39; H, 6.57; N, 7.40; found C, 80.32; H, 6.55; N, 7.37; %;

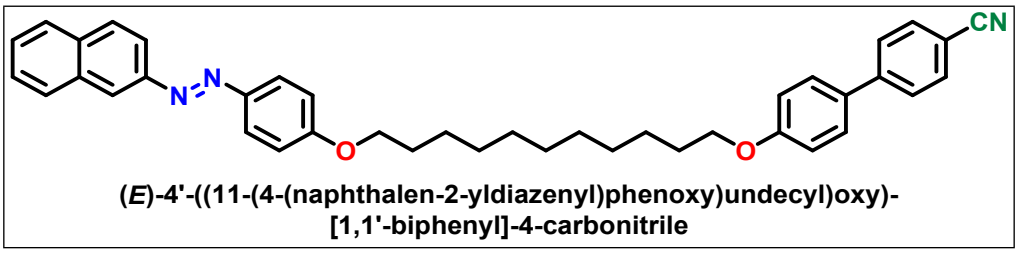
***(E)-4'-((10-(4-(Naphthalen-2-yldiazenyl)phenoxy)decyl)oxy)-[1,1'-biphenyl]-4-carbonitrile* (*CB10AZ*):**



(*E*)-4'-((10-(4-(naphthalen-2-yldiazenyl)phenoxy)decyl)oxy)-[1,1'-biphenyl]-4-carbonitrile

Orange crystals, Yield: 69%; **IR** ν_{max}/cm^{-1}: 3058.20, 2924.34 (C_{sp3}-H), 2853.42, 2219.34 (C≡N), 1600.33 (-N=N-), 1257.71 (C-O), 1181.17 (C-N), 1028.29, 822.54; **^{1}H NMR (400 MHz, $CDCl_3$): δ (In ppm)**: 8.34 (s, 1H, Ar-H), 7.96 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.90 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.89 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.82 (d, *J* = 9.2 Hz, 2H, Ar-H), 7.60 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.54 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.45 (d, *J* = 3.2 Hz, 2H, Ar-H), 7.44 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.95 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.90 (d, *J* = 8.4 Hz, 2H, Ar-H), 3.97 (t, J = 6.0 Hz, 2H, -O-CH_2-), 3.92 (t, J = 6.0 Hz, 2H, -O-CH_2-), 1.75-1.73 (m, 4H, 2 X -O-C-CH_2-), 1.40-1.28 (m, 12H, -O-C-C-(CH_2)$_6$-); **^{13}C NMR (400MHz, $CDCl_3$): δ (In ppm):** 161.64 (Ar C-O-), 158.71, 149.26, 145.87, 144.21, 133.45, 132.54, 131.53, 130.17, 128.18, 127.28, 126.87, 126.09, 125.60, 116.21, 113.99, 113.68, 108.91, 67.19 (Ar-O-C-), 29.49, 28.43, 28.17, 24.97; **Elemental Analysis**: $C_{39}H_{39}N_3O_2$:(cal): C, 80.52; H, 6.76; N, 7.22; found C, 80.51; H, 6.72; N, 7.18; %;

***(E)-4'-((11-(4-(Naphthalen-2-yldiazenyl)phenoxy)undecyl)oxy)-[1,1'-biphenyl]-4-carbonitrile* (*CB11AZ*):**

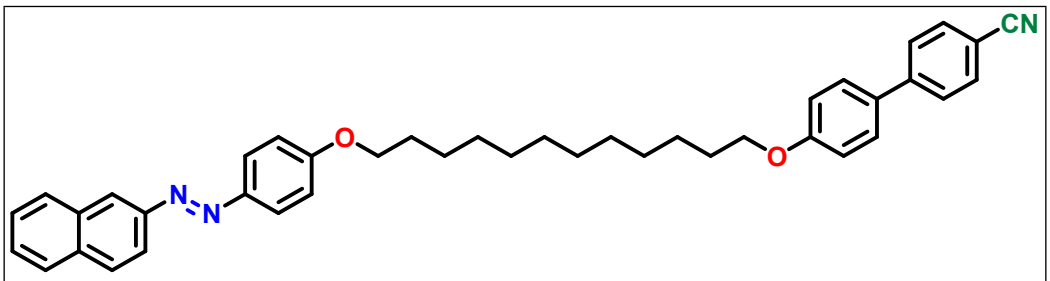


(*E*)-4'-((11-(4-(naphthalen-2-yldiazenyl)phenoxy)undecyl)oxy)-[1,1'-biphenyl]-4-carbonitrile

Orange crystals, Yield: 68%; **IR** ν_{max}/cm^{-1}: 3067.60, 2920.86 (C_{sp3}-H), 2856.29, 2223.37 (C≡N), 1600.78 (-N=N-), 1256.02 (C-O), 1182.12 (C-N), 1022.63, 820.68; **^{1}H NMR (400 MHz, $CDCl_3$): δ (In ppm)**: 8.32 (s, 1H, Ar-H), 7.96 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.90 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.89 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.83 (d, *J* = 9.2 Hz, 2H, Ar-H), 7.60 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.54 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.47 (d, *J* = 3.2 Hz, 2H, Ar-H), 7.44 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.95 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.91 (d, *J* = 8.4 Hz, 2H, Ar-H), 3.97 (t, J = 6.0 Hz, 2H, -O-CH_2-), 3.92 (t, J = 6.0 Hz, 2H, -O-CH_2-), 1.74-1.72 (m, 4H, 2 X -O-C-CH_2-),

1.40-1.29 (m, 14H, -O-C-C-($\underline{CH_2}$)$_{\underline{7}}$-); **^{13}C NMR (400MHz, CDCl$_3$): δ (In ppm):** 161.74 (Ar $\underline{C}$-O-), 159.80, 150.32, 146.94, 145.27, 134.51, 132.59, 131.22, 129.23, 128.34, 127.24, 126.98, 126.65, 124.78, 119.19, 117.31, 115.07, 110.03, 67.93 (Ar-O-$\underline{C}$-), 29.42, 29.29, 26.58, 26.43; **Elemental Analysis**: $C_{40}H_{41}N_3O_2$:(cal): C, 80.64; H, 6.94; N, 7.05; found C, 80.63; H, 6.89; N, 7.02; %;

***(E)-4'-((12-(4-(Naphthalen-2-yldiazenyl)phenoxy)dodecyl)oxy)-[1,1'-biphenyl]-4-carbonitrile* (*CB12AZ*):**



(*E*)-4'-((12-(4-(naphthalen-2-yldiazenyl)phenoxy)dodecyl)oxy)-[1,1'-biphenyl]-4-carbonitrile

Orange crystals, Yield: 66%; **IR** ν_{max}/cm^{-1}: 3058.63, 2920.27 (C_{sp3}-H), 2850.16, 2223.62 (C≡N), 1599.79 (-N=N-), 1256.02 (C-O), 1182.66 (C-N), 1028.23, 821.26; **^{1}H NMR (400 MHz, CDCl$_3$): δ (In ppm)**: 8.32 (s, 1H, Ar-$\underline{H}$), 7.97 (d, *J* = 8.4 Hz, 1H, Ar-$\underline{H}$), 7.91 (d, *J* = 8.4 Hz, 1H, Ar-$\underline{H}$), 7.89 (d, *J* = 8.8 Hz, 2H, Ar-$\underline{H}$), 7.83 (d, *J* = 9.2 Hz, 2H, Ar-$\underline{H}$), 7.60 (d, *J* = 8.0 Hz, 2H, Ar-$\underline{H}$), 7.55 (d, *J* = 8.0 Hz, 2H, Ar-$\underline{H}$), 7.47 (d, *J* = 3.2 Hz, 2H, Ar-$\underline{H}$), 7.44 (d, *J* = 8.0 Hz, 2H, Ar-$\underline{H}$), 6.95 (d, *J* = 8.4 Hz, 2H, Ar-$\underline{H}$), 6.91 (d, *J* = 8.4 Hz, 2H, Ar-$\underline{H}$), 3.97 (t, J = 6.4 Hz, 2H, -O-C$\underline{H_2}$-), 3.92 (t, J = 6.0 Hz, 2H, -O-C$\underline{H_2}$-), 1.77-1.72 (m, 4H, 2 X -O-C-$\underline{CH_2}$-), 1.41-1.23 (m, 16H, -O-C-C-($\underline{CH_2}$)$_{\underline{8}}$-); **^{13}C NMR (400MHz, CDCl$_3$): δ (In ppm):** 161.73 (Ar $\underline{C}$-O-), 159.80, 150.34, 146.94, 145.29, 134.52, 132.59, 131.24, 129.24, 128.34, 127.24, 126.98, 126.65, 124.77, 119.19, 117.31, 115.07, 110.00, 68.24 (Ar-O-$\underline{C}$-), 29.58, 29.39, 29.24, 26.05; **Elemental Analysis**: $C_{41}H_{43}N_3O_2$:(cal): C, 80.75; H, 7.11; N, 6.89; found C, 80.72; H, 7.09; N, 6.84; %;

➢ ***Spcetras for dimers of Series CBnAZ:***

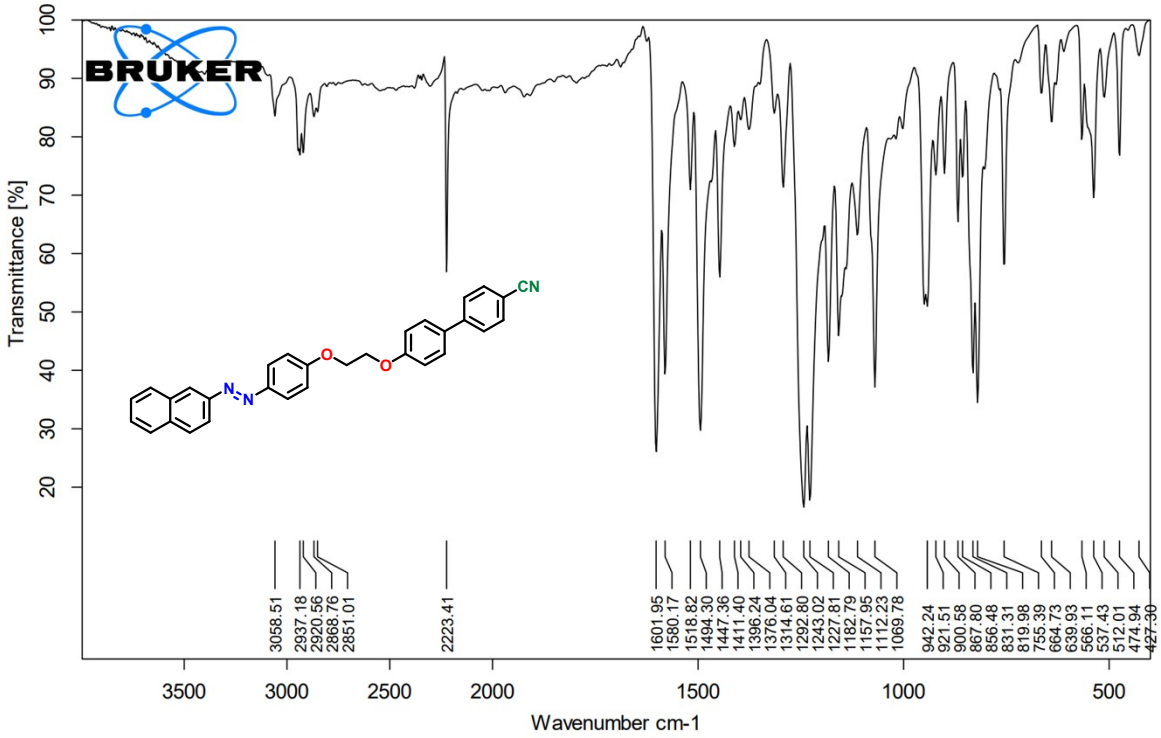


Fig. S1: FT-IR spectra of *CB2AZ*

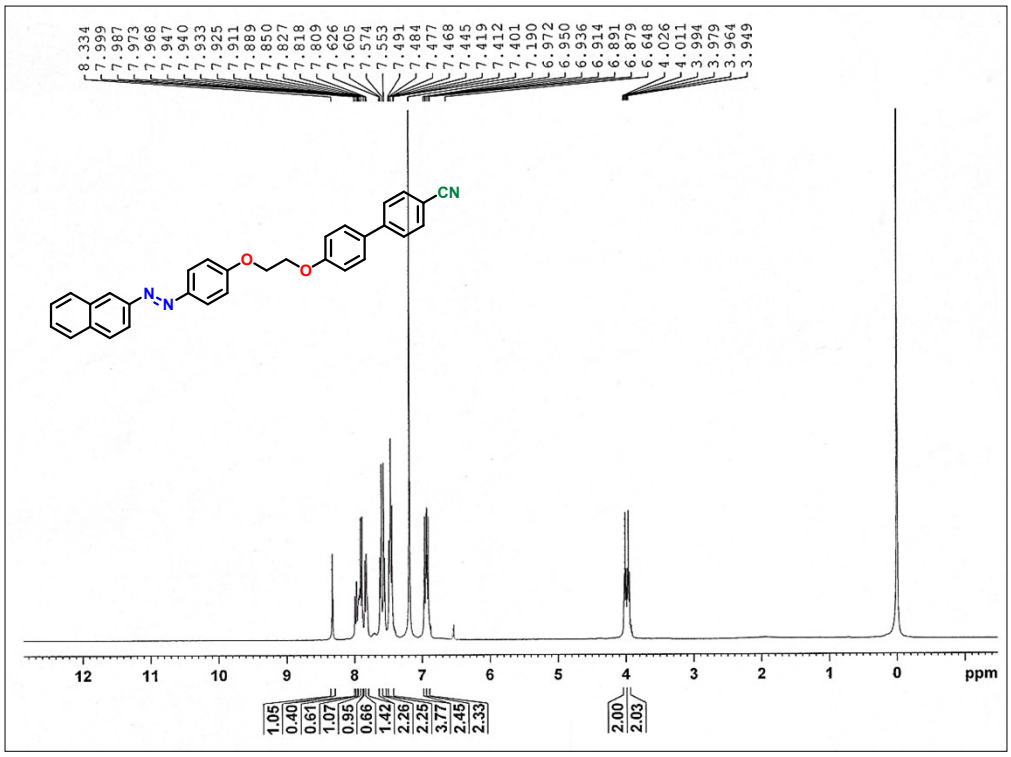


Fig. S2: ^{1}H-NMR spectra of *CB2AZ*

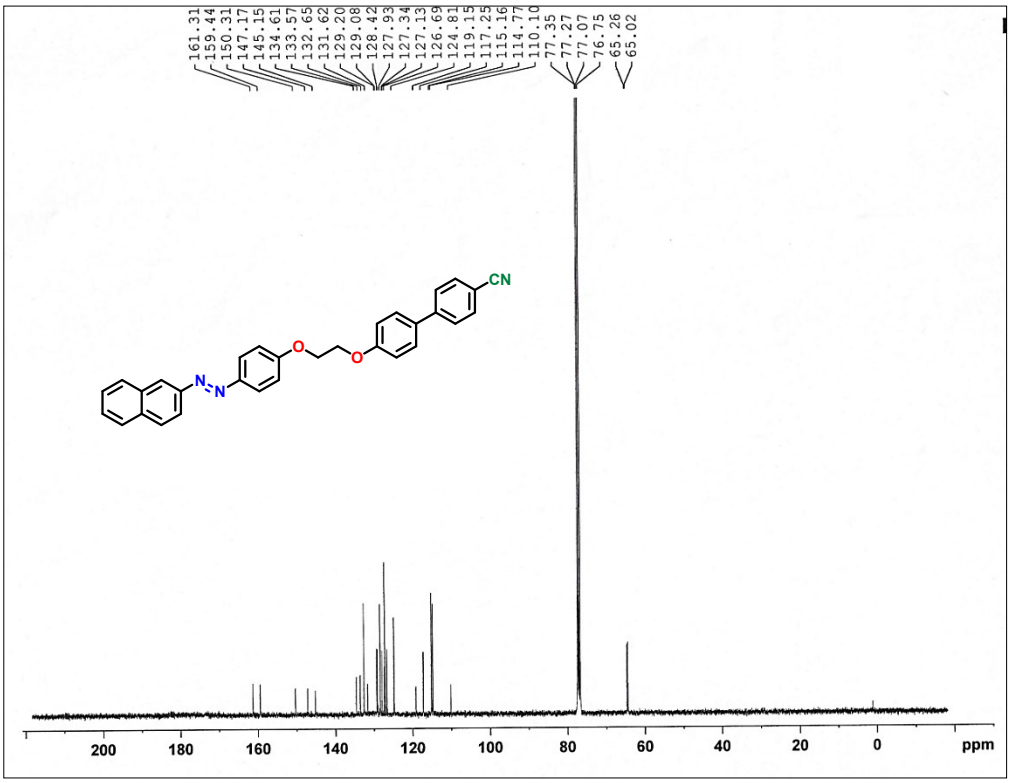


Fig. S3: ^{13}C-NMR spectra of *CB2AZ*

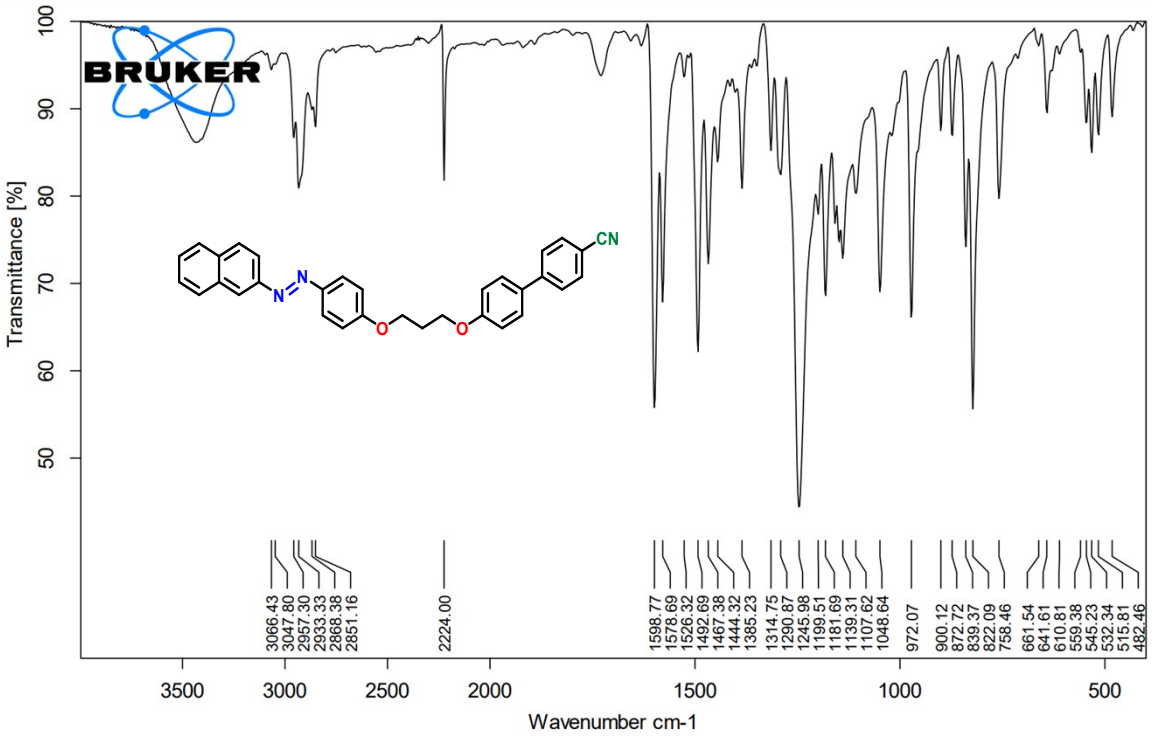


Fig. S4: FT-IR spectra of *CB3AZ*

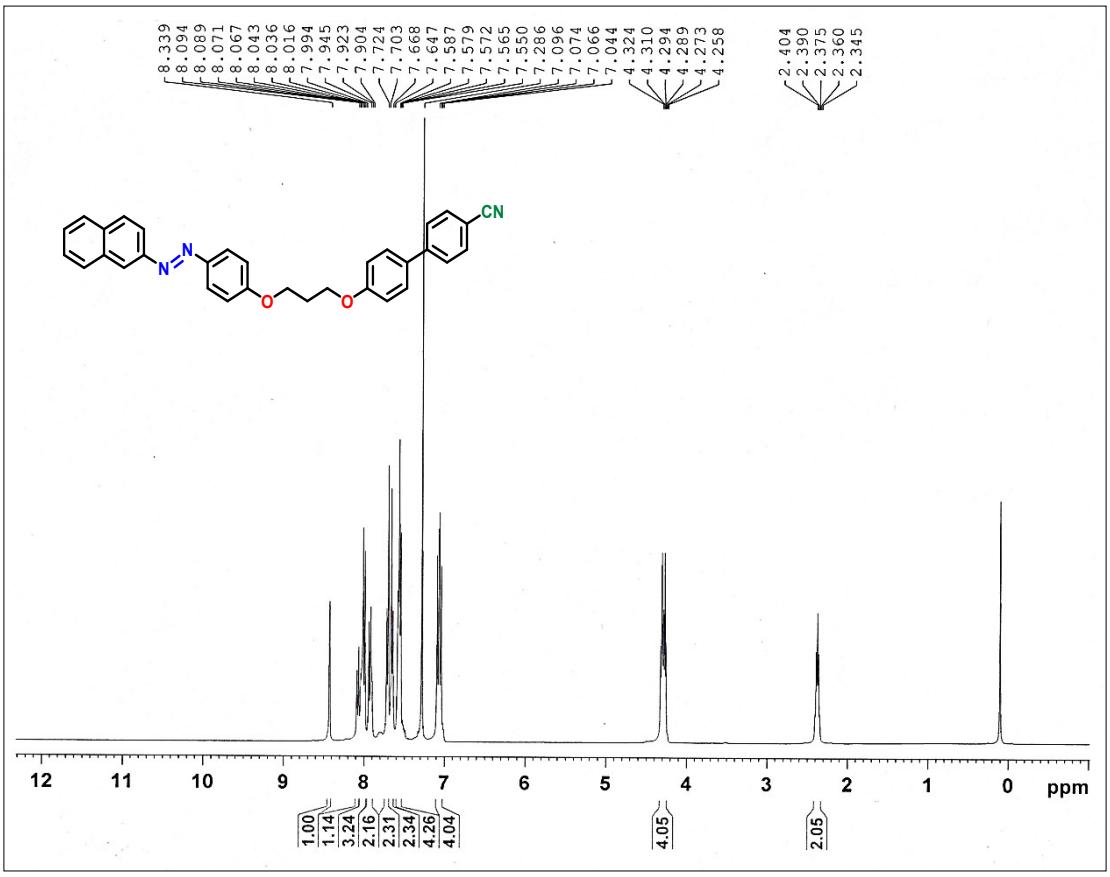


Fig. S5: ^{1}H-NMR spectra of *CB3AZ*

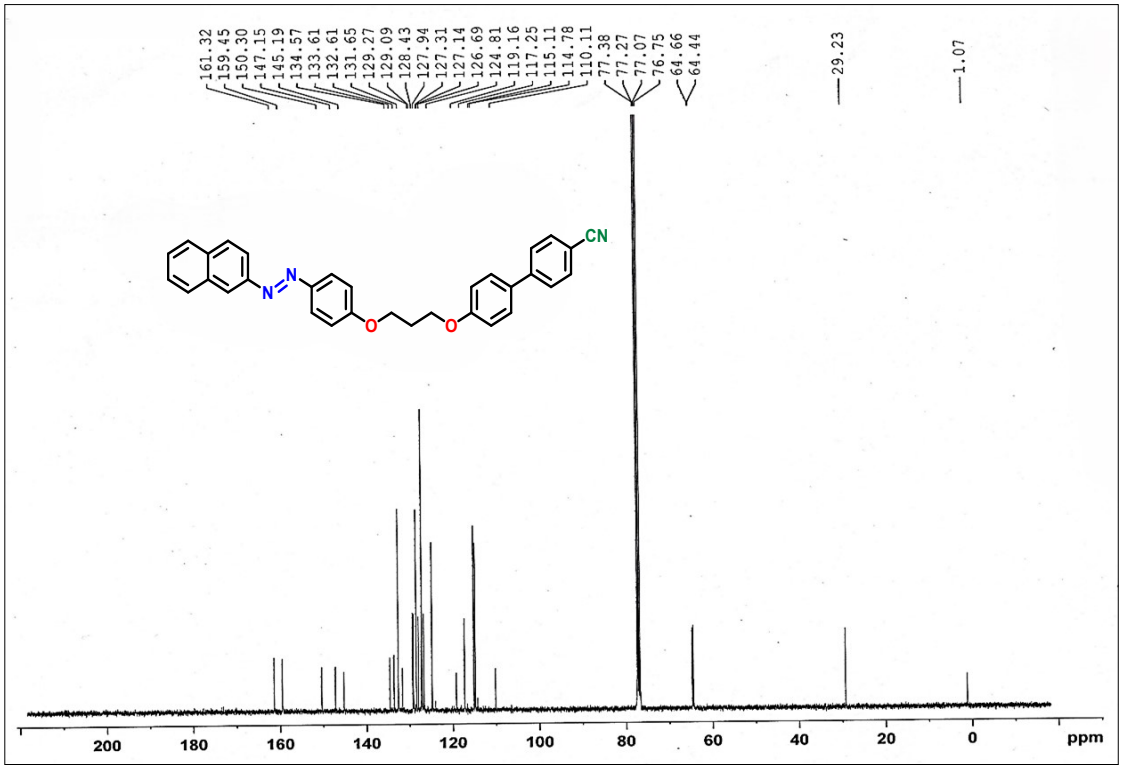


Fig. S6: ^{13}C-NMR spectra of *CB3AZ*

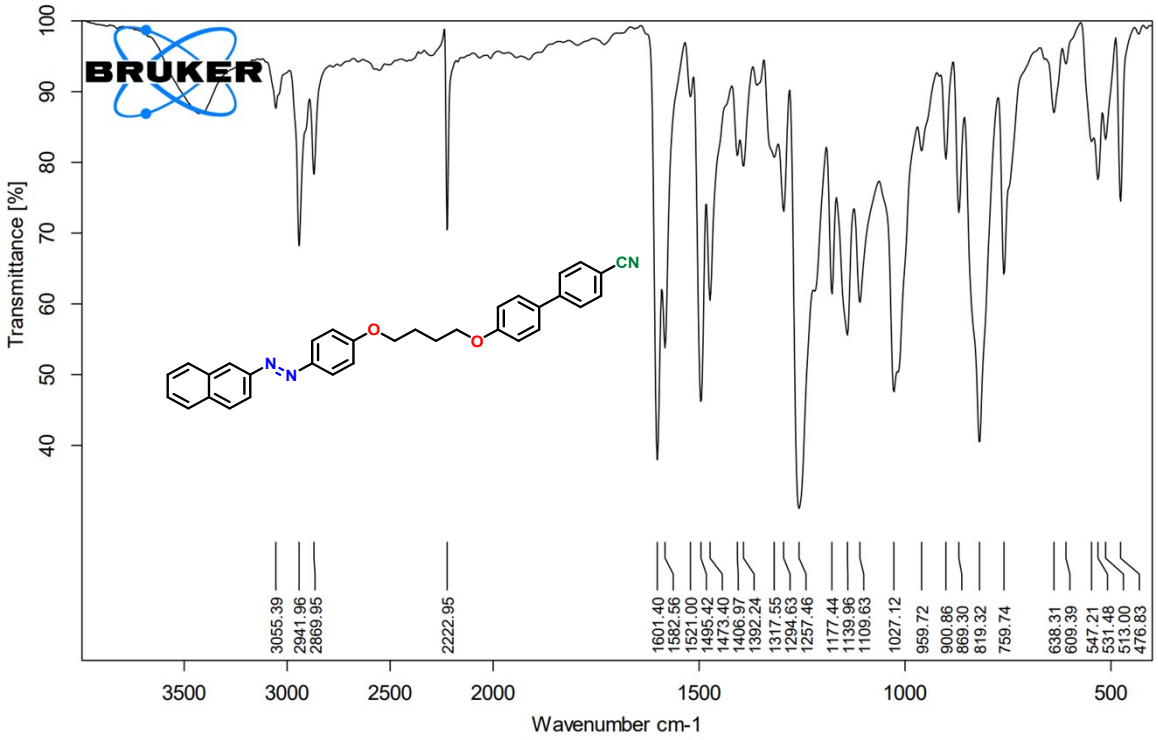


Fig. S7: FT-IR spectra of *CB4AZ*

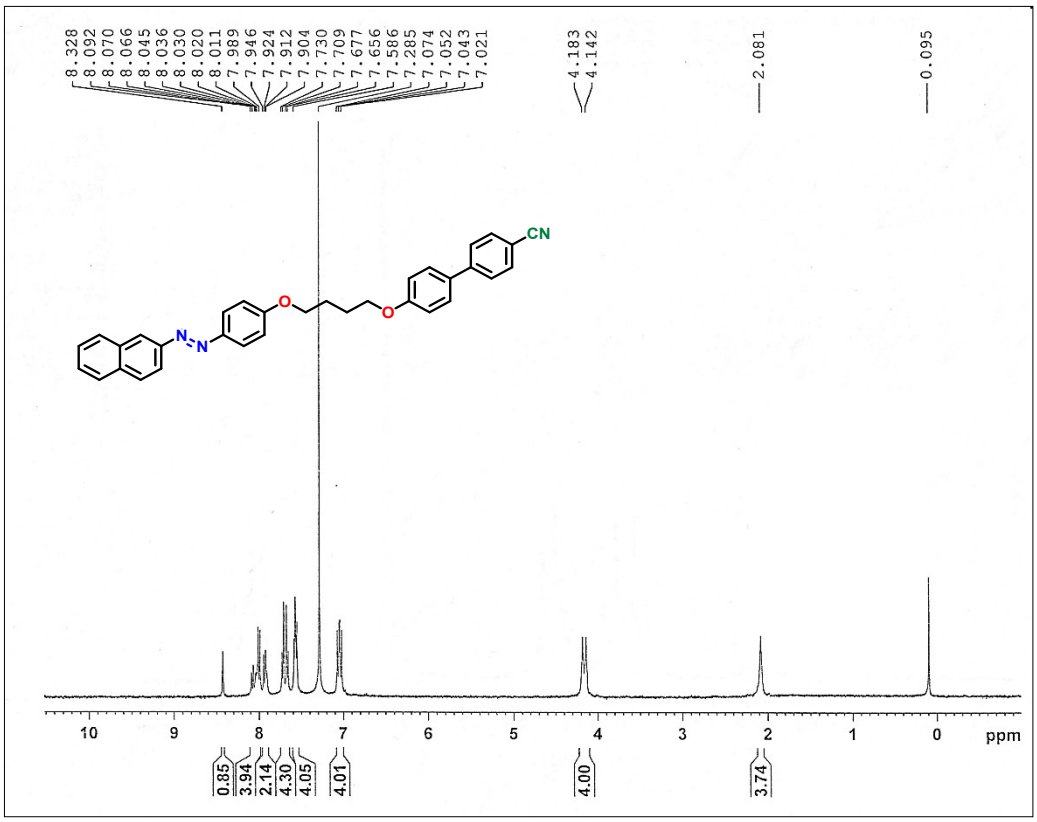


Fig. S8: ^{1}H-NMR spectra of *CB4AZ*

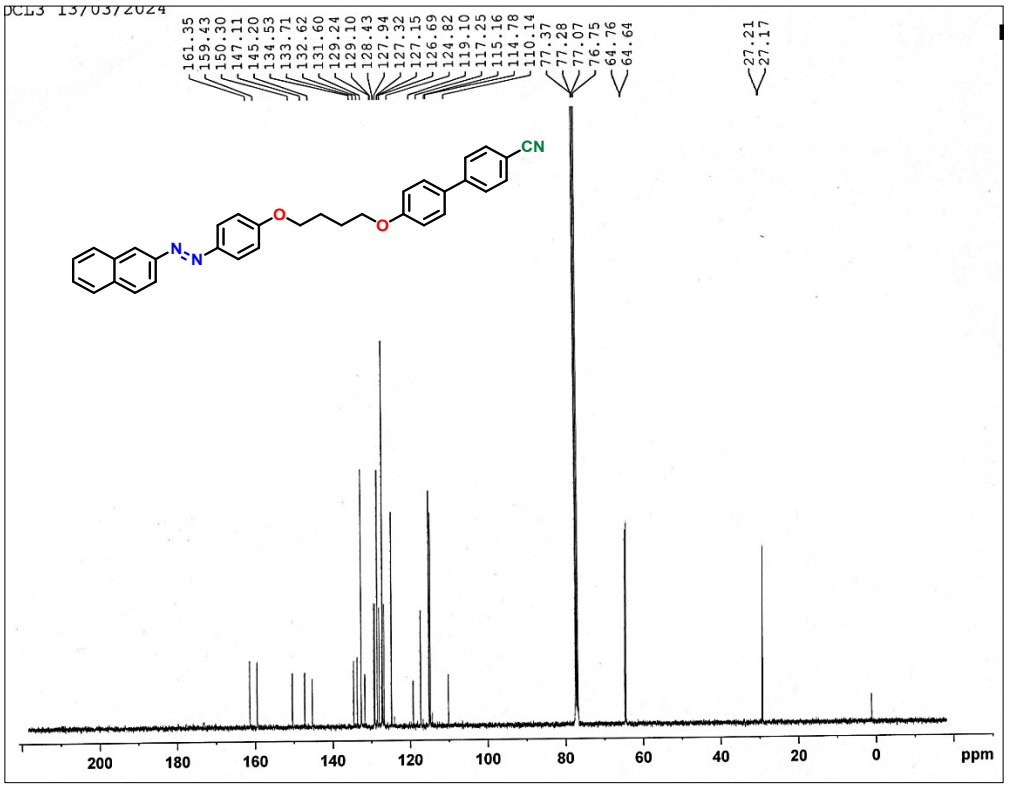


Fig. S9: ^{13}C-NMR spectra of *CB4AZ*

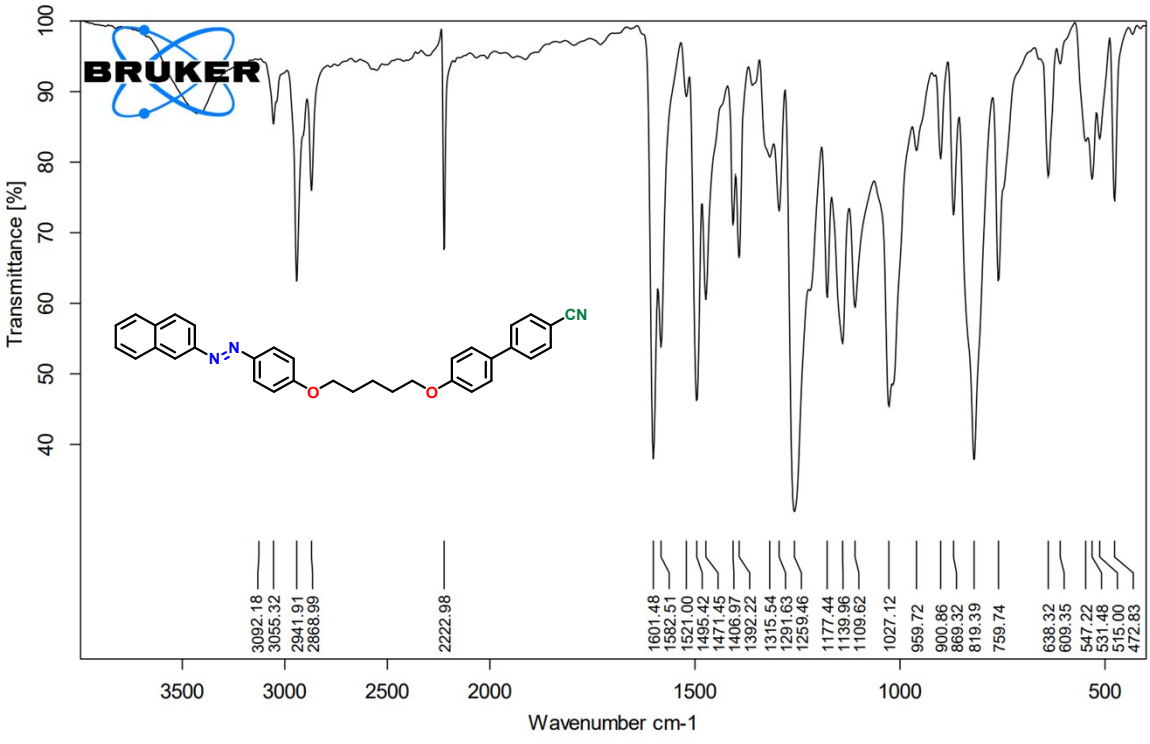


Fig. S10: FT-IR spectra of *CB5AZ*

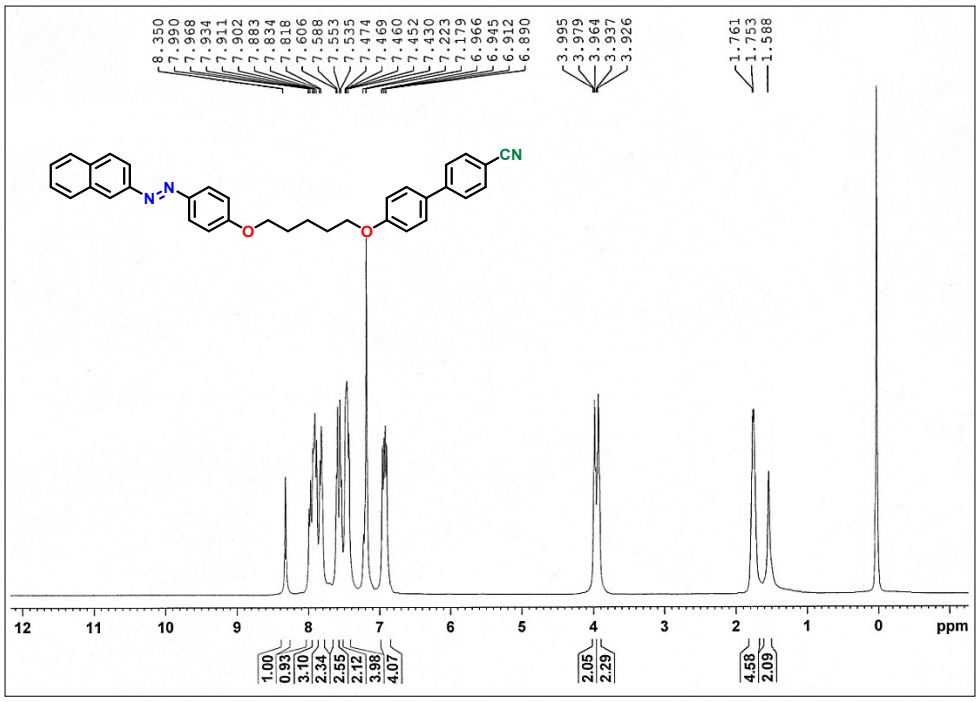


Fig. S11: ^{1}H-NMR spectra of *CB5AZ*

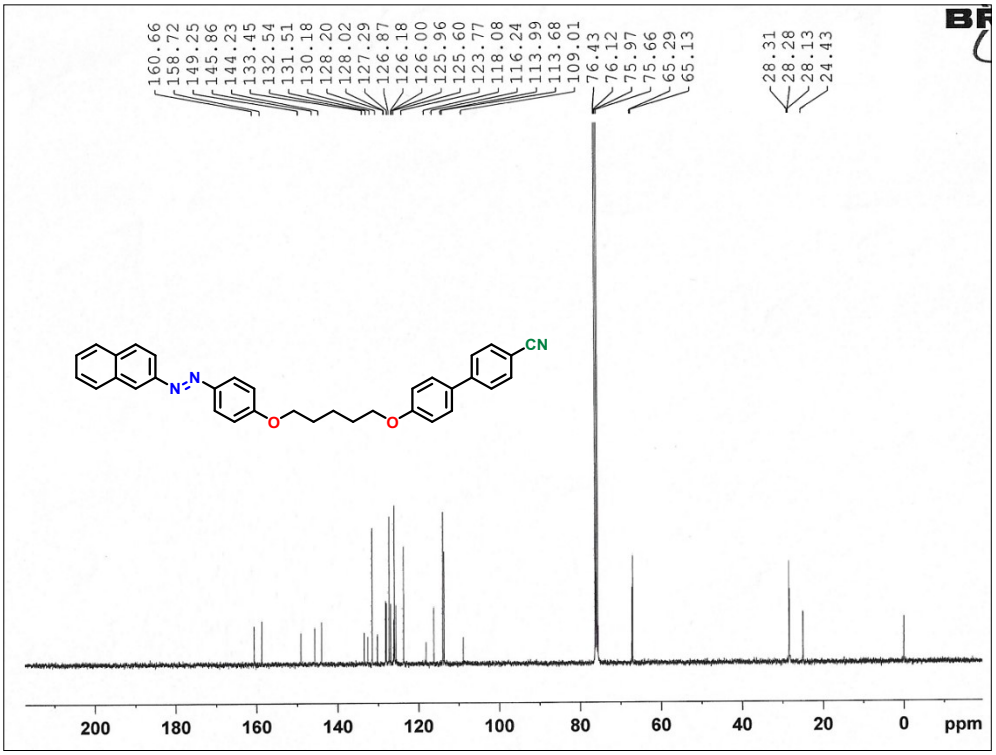


Fig. S12: ^{13}C-NMR spectra of *CB5AZ*

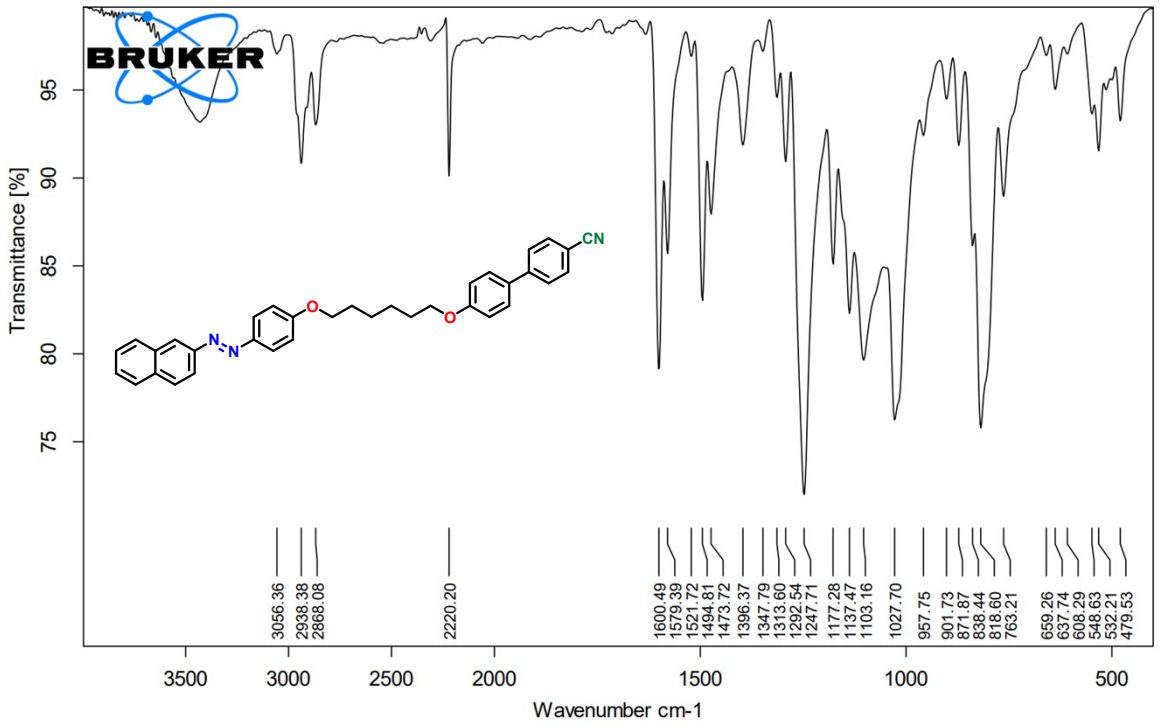


Fig. S13: FT-IR spectra of *CB6AZ*

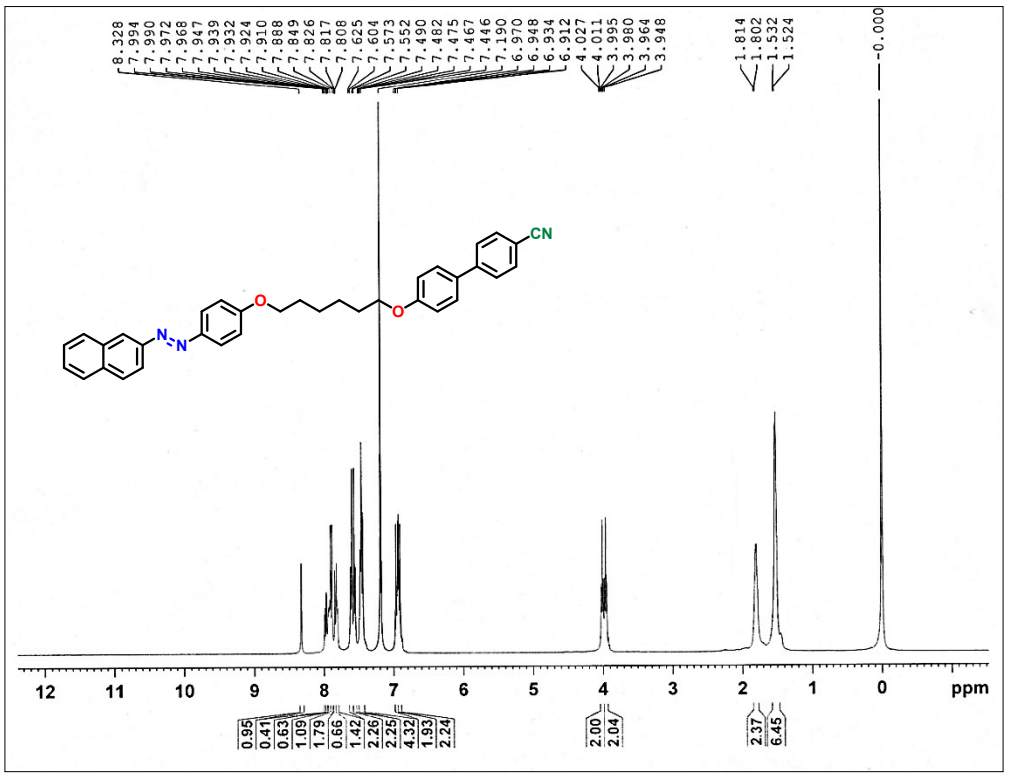


Fig. S14: ^{1}H-NMR spectra of *CB6AZ*

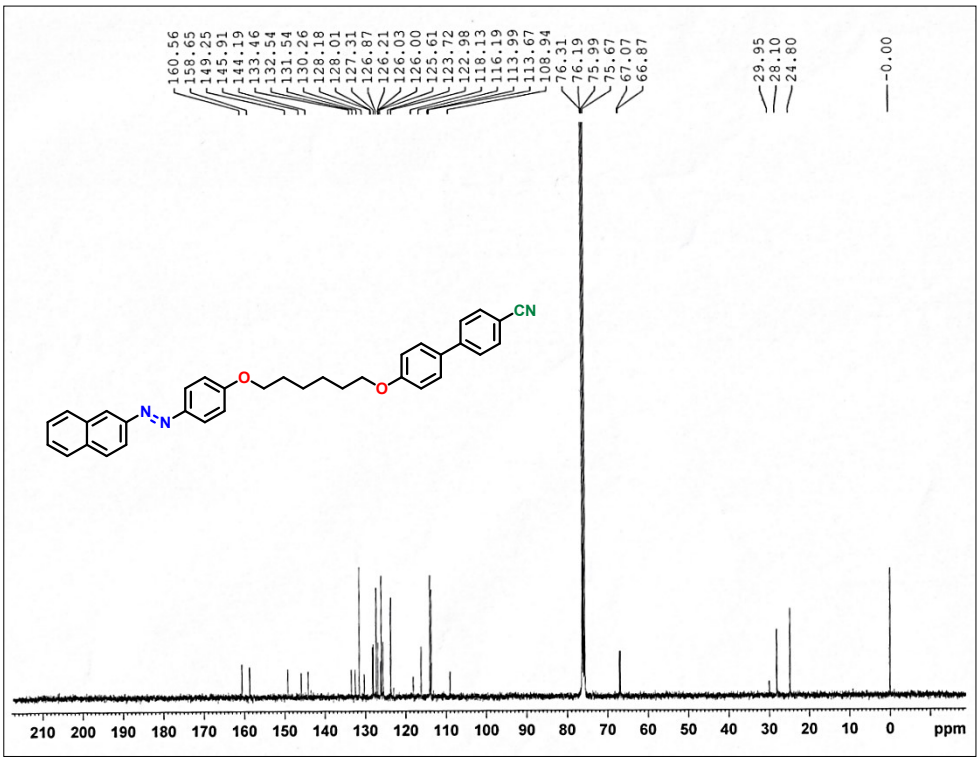
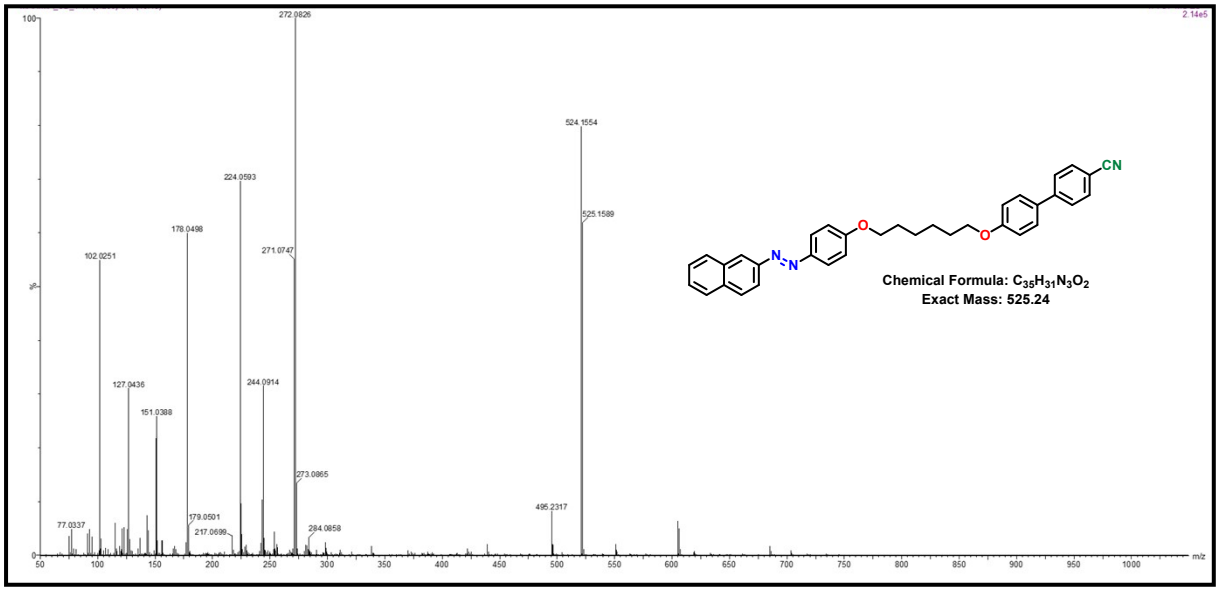


Fig. S15: ^{13}C-NMR spectra of *CB6AZ*



Mass spectra of CB6AZ

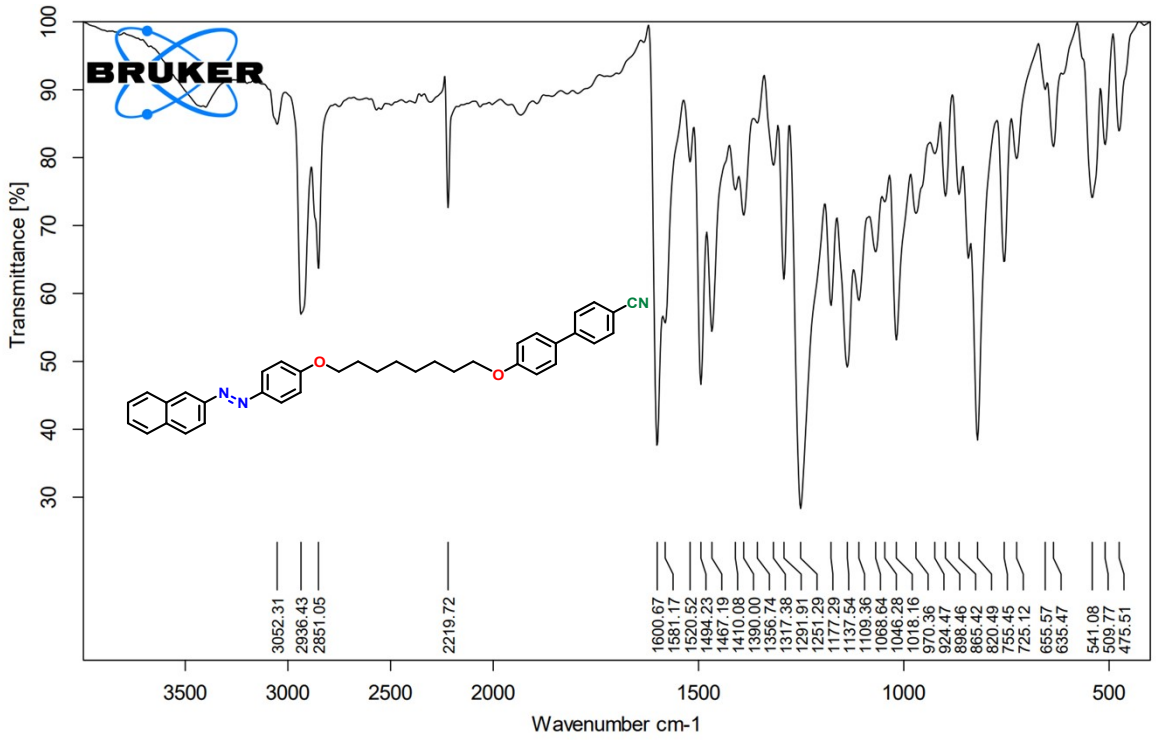


Fig. S16: FT-IR spectra of *CB8AZ*

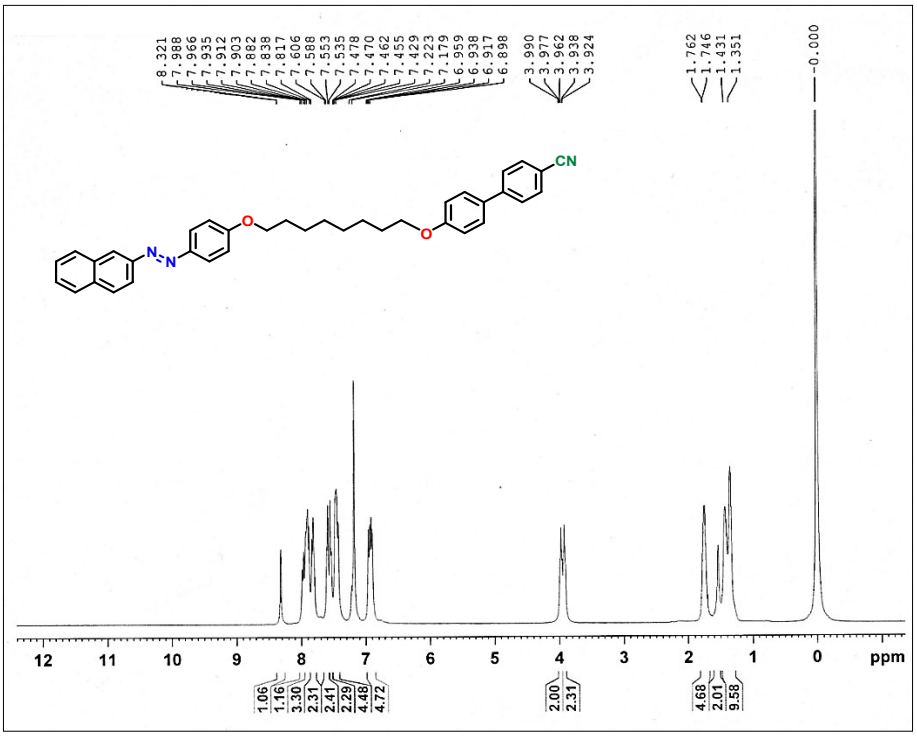


Fig. S17: ^{1}H-NMR spectra of *CB8AZ*

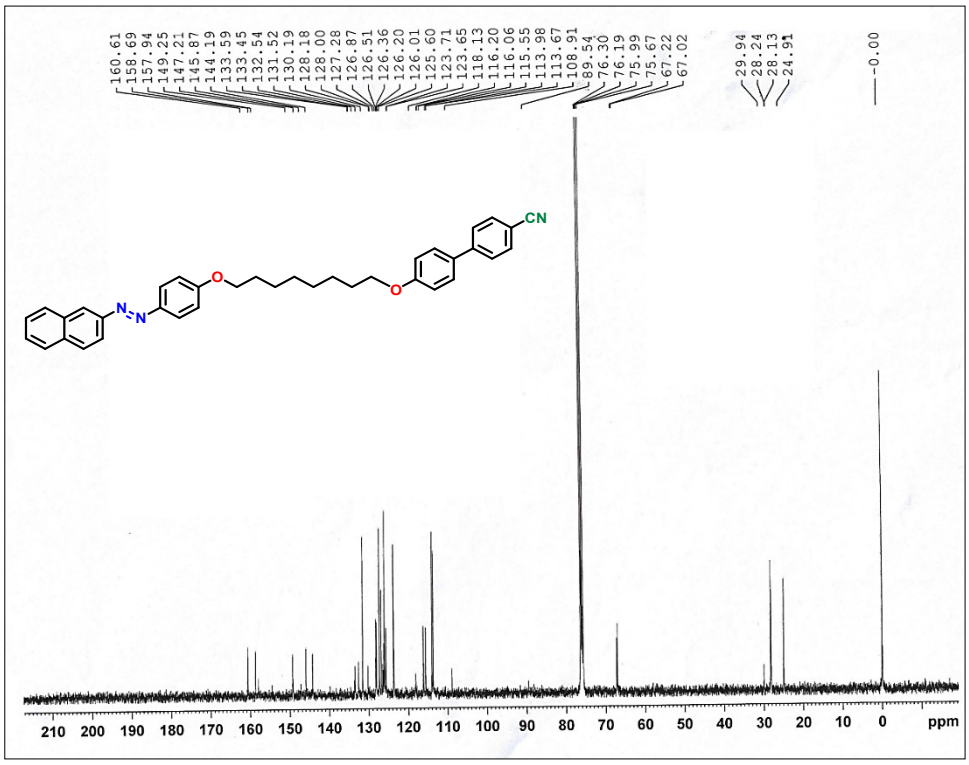


Fig. S18: ^{13}C-NMR spectra of *CB8AZ*

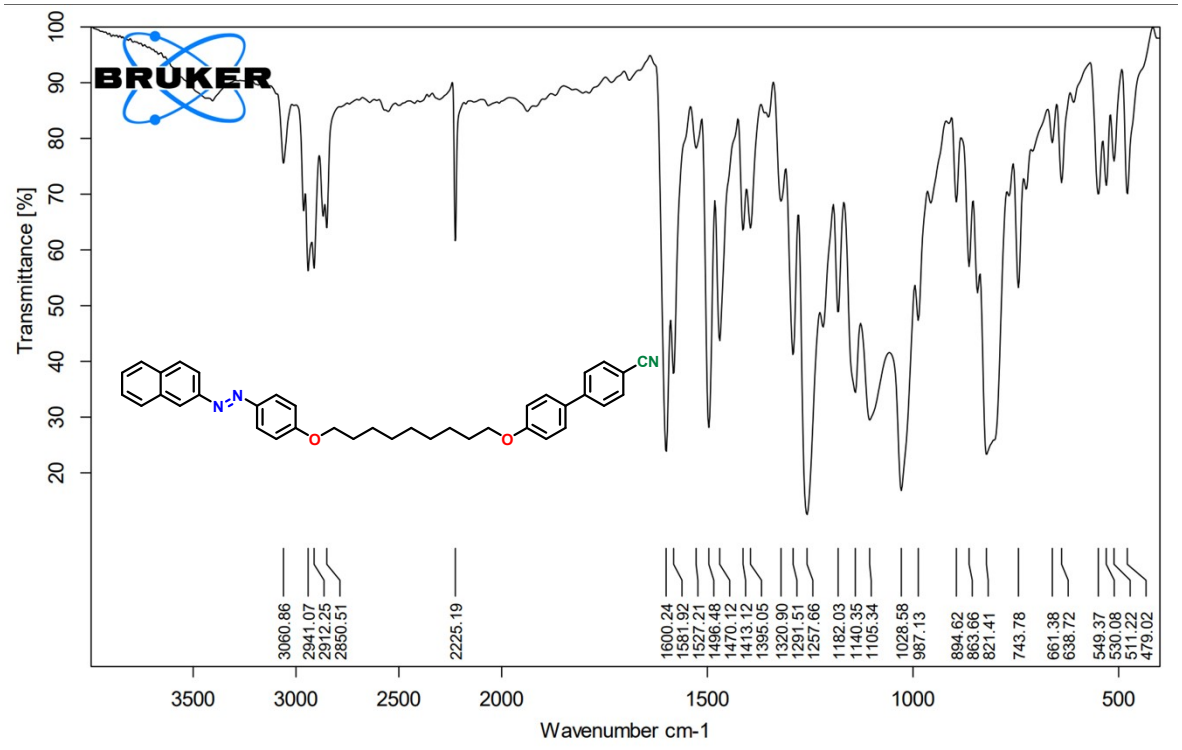


Fig. S19: FT-IR spectra of *CB9AZ*

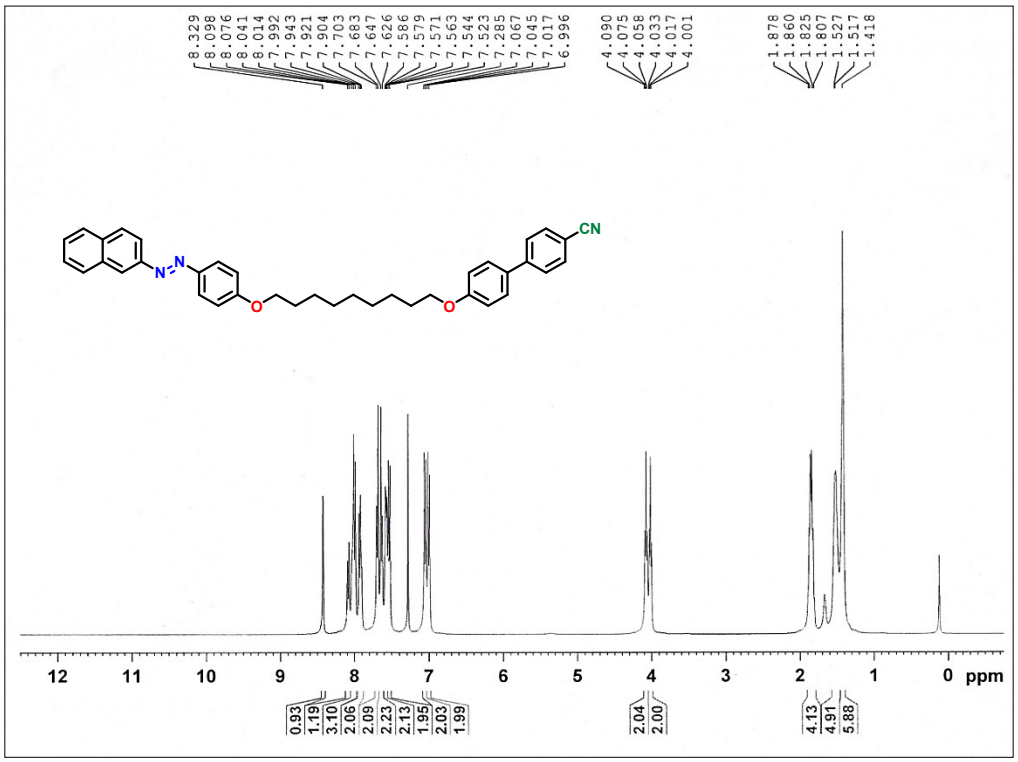


Fig. S20: ^{1}H-NMR spectra of *CB9AZ*

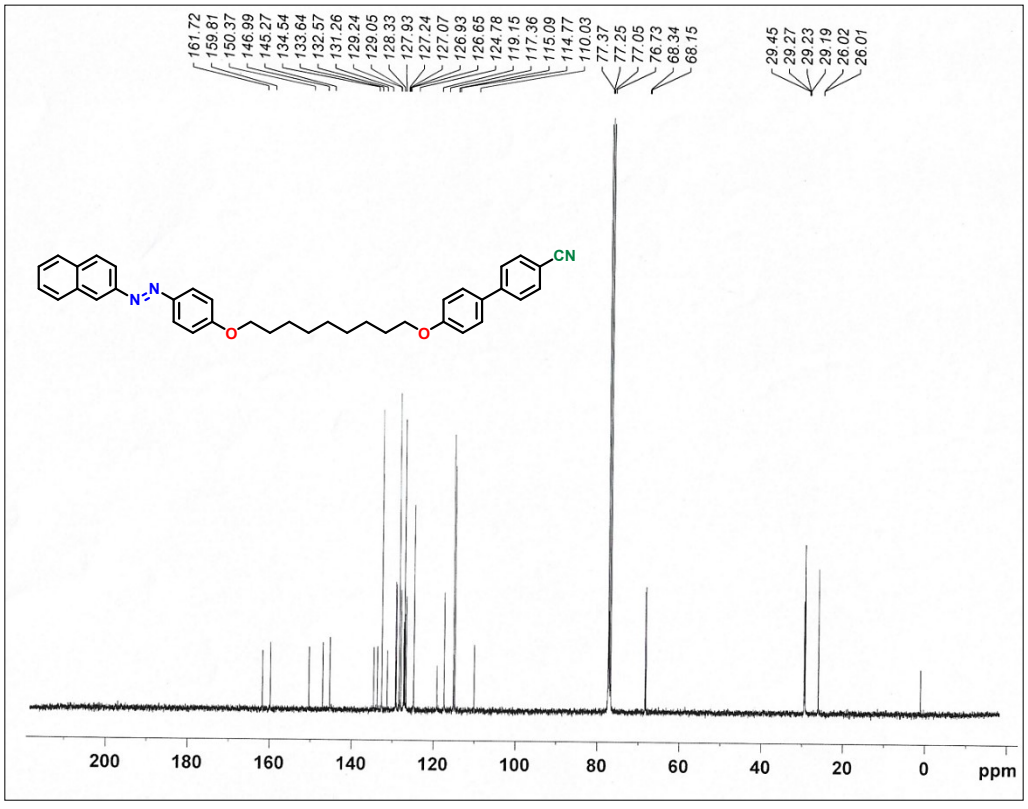


Fig. S21: ^{13}C-NMR spectra of *CB9AZ*

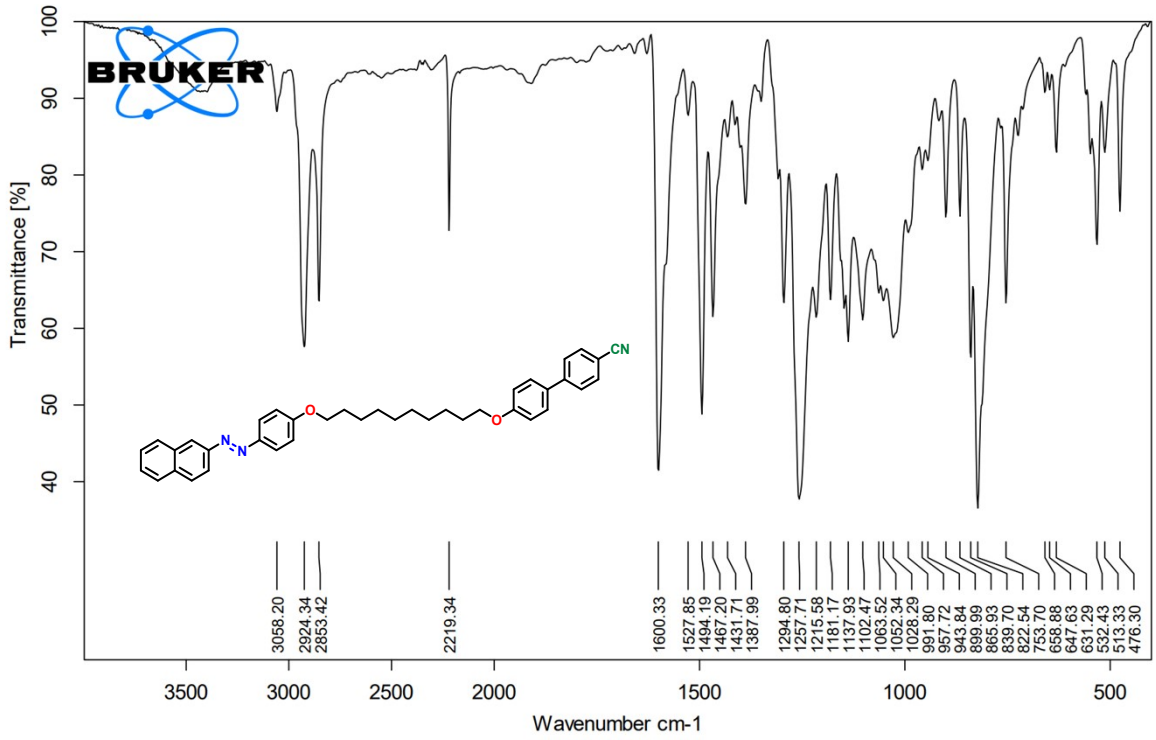


Fig. S22: FT-IR spectra of *CB10AZ*

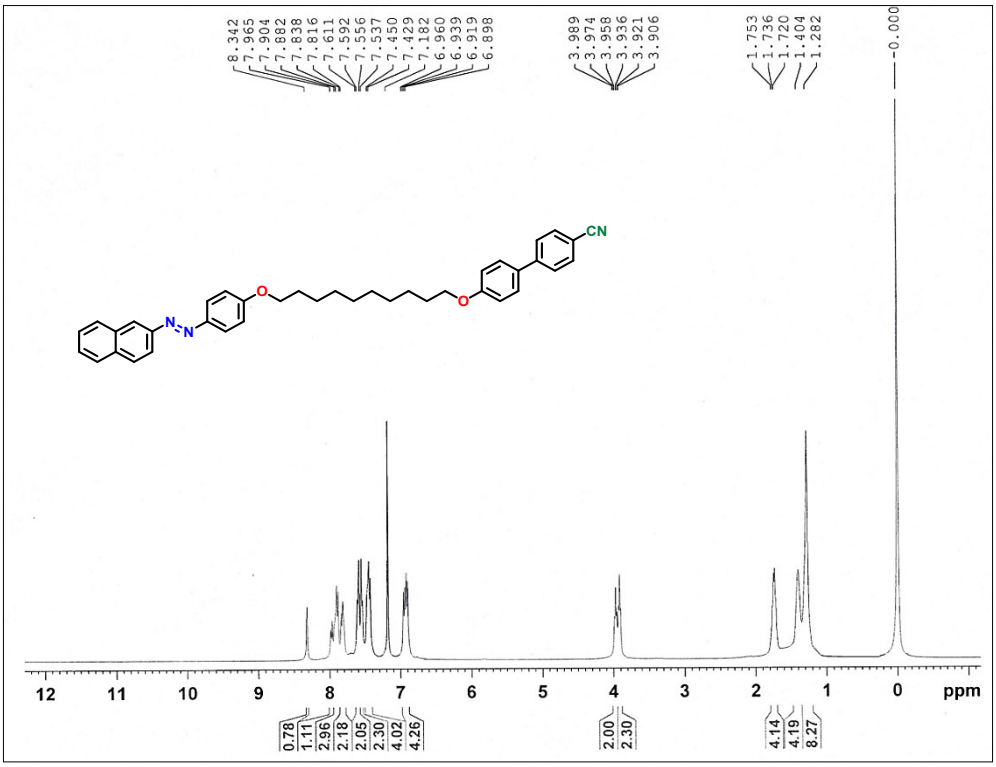
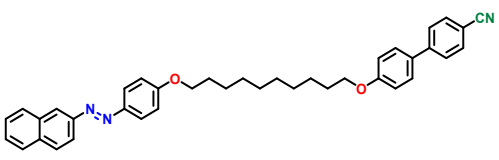


Fig. S23: ^{1}H-NMR spectra of *CB10AZ*



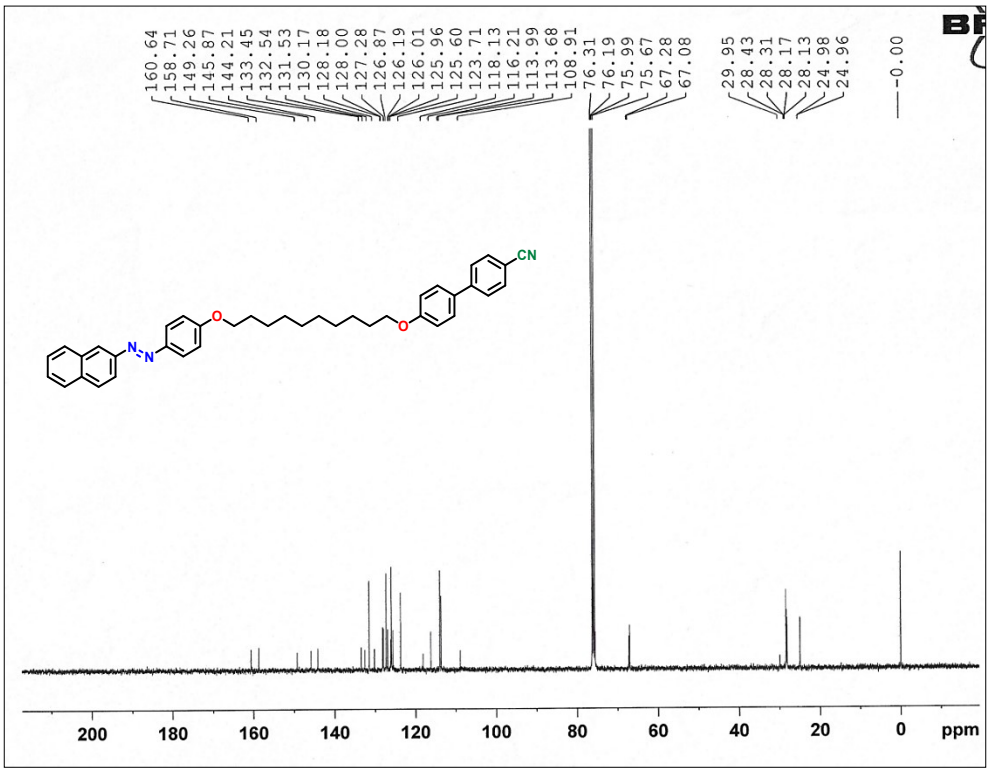


Fig. S24: ^{13}C-NMR spectra of *CB10AZ*

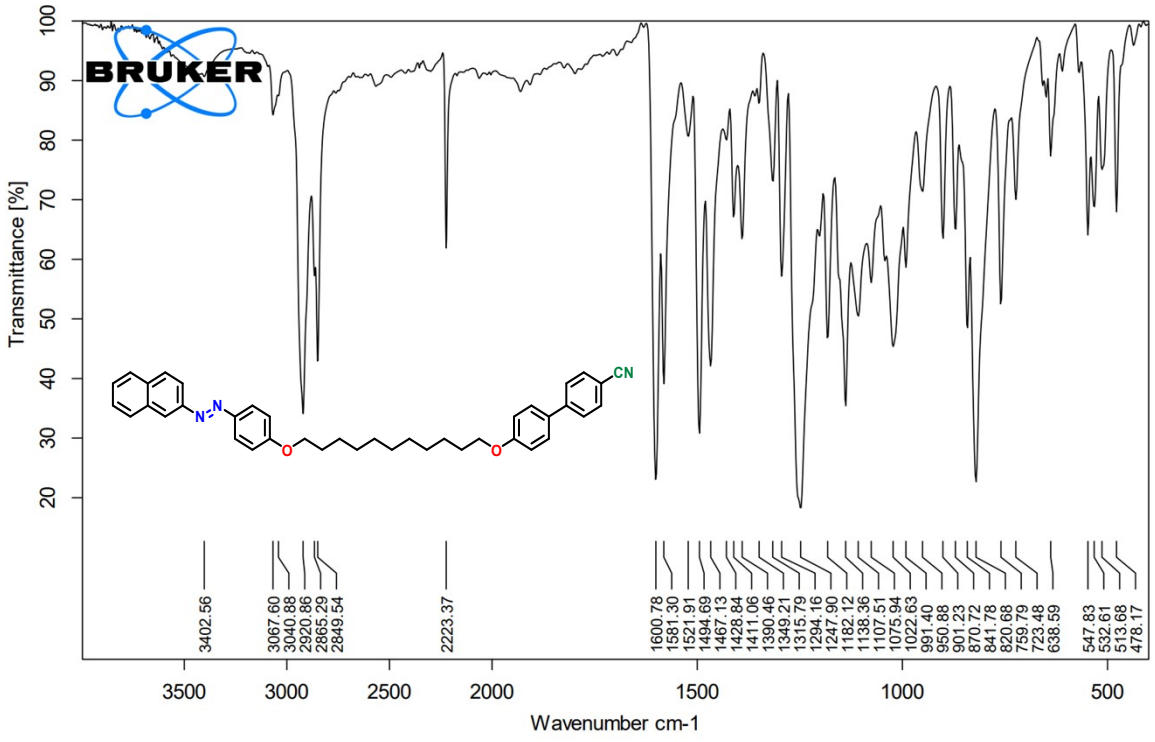


Fig. S25: FT-IR spectra of *CB11AZ*

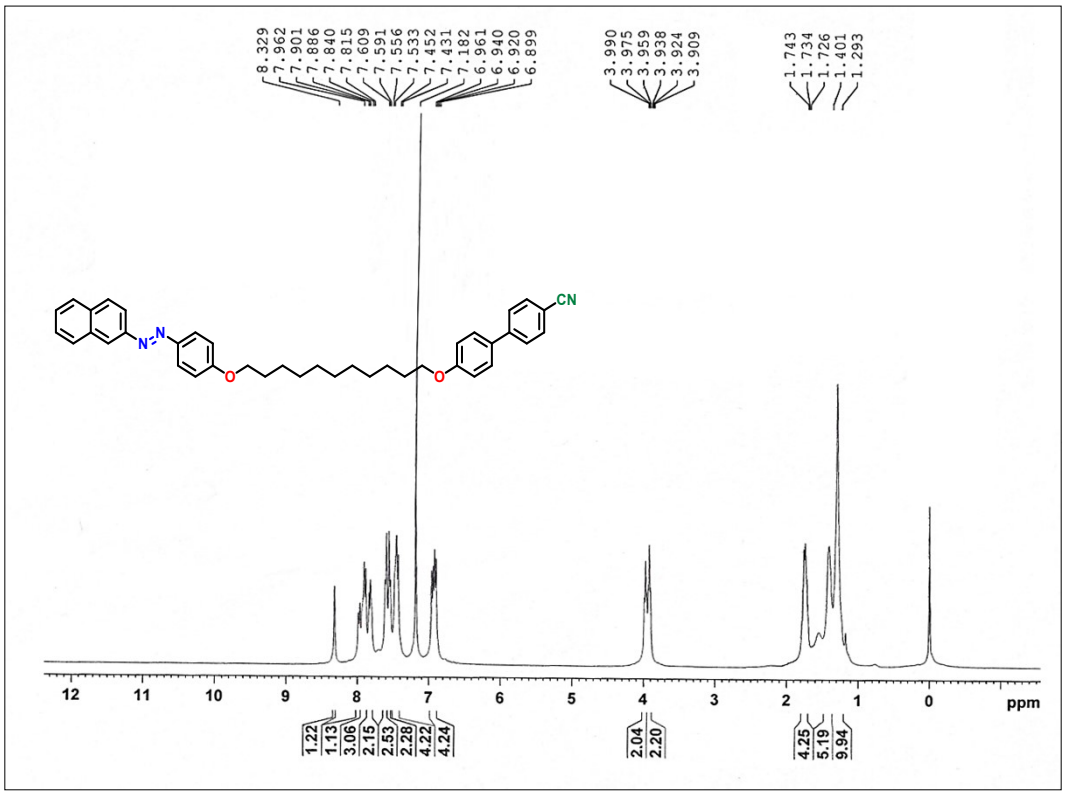


Fig. S26: ^{1}H-NMR spectra of *CB11AZ*

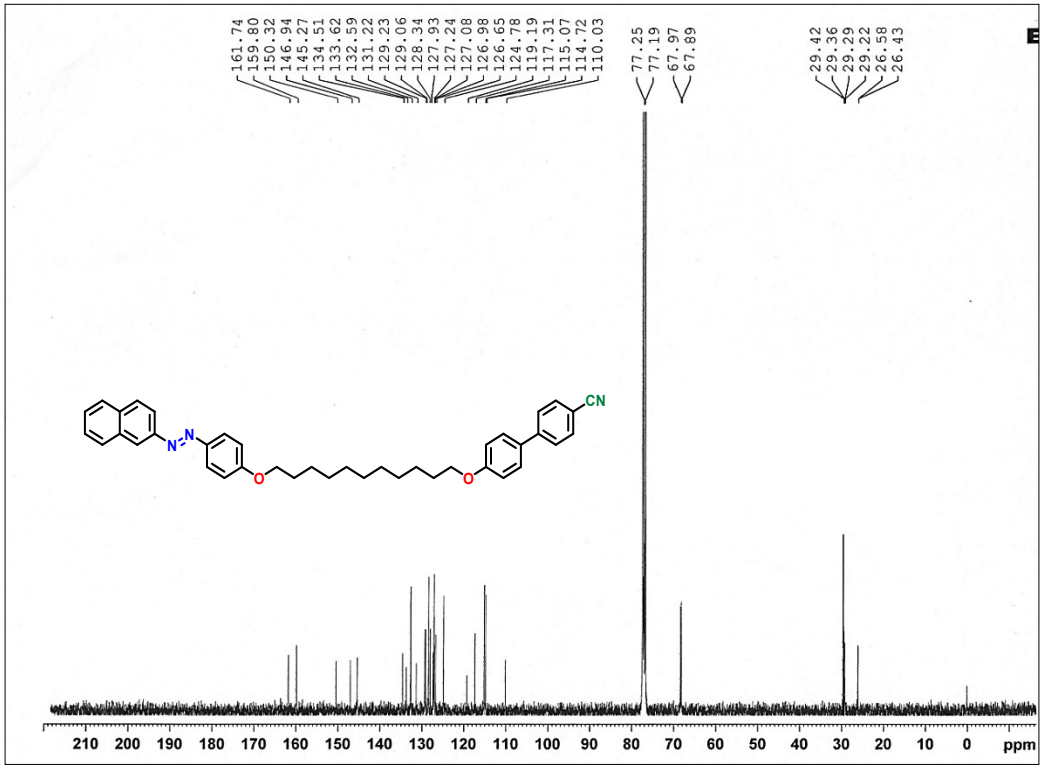


Fig. S27: ^{13}C-NMR spectra of *CB11AZ*

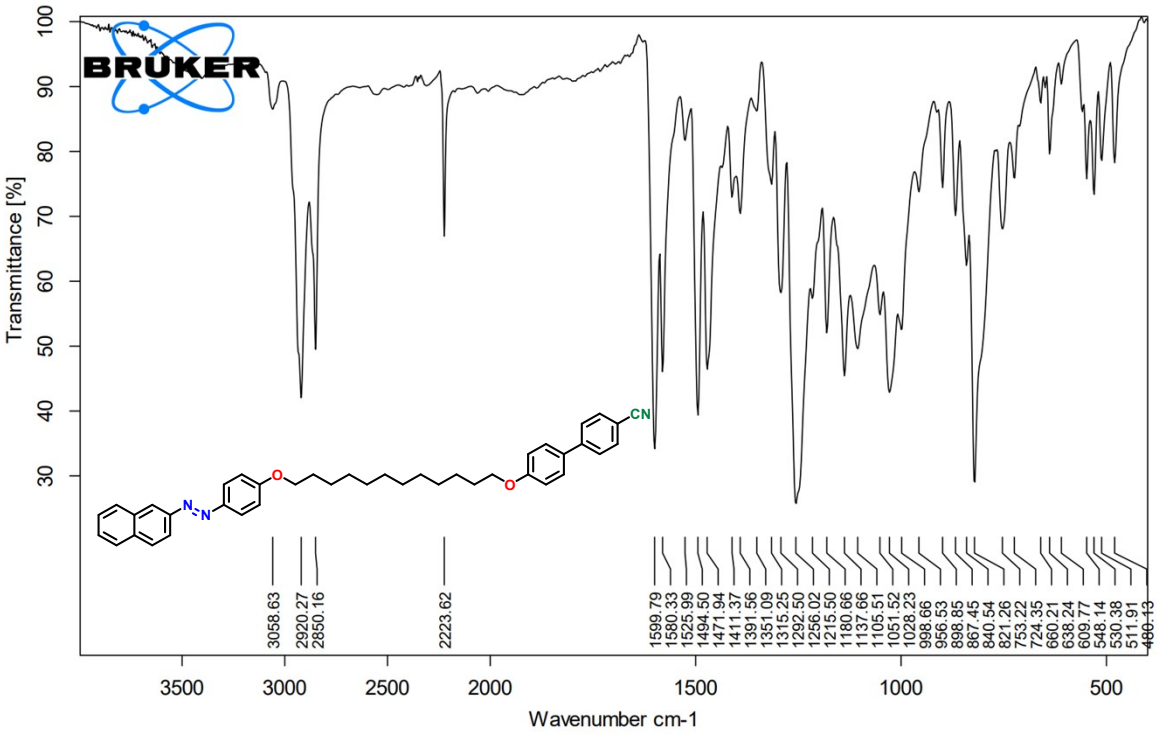


Fig. S28: FT-IR spectra of *CB12AZ*

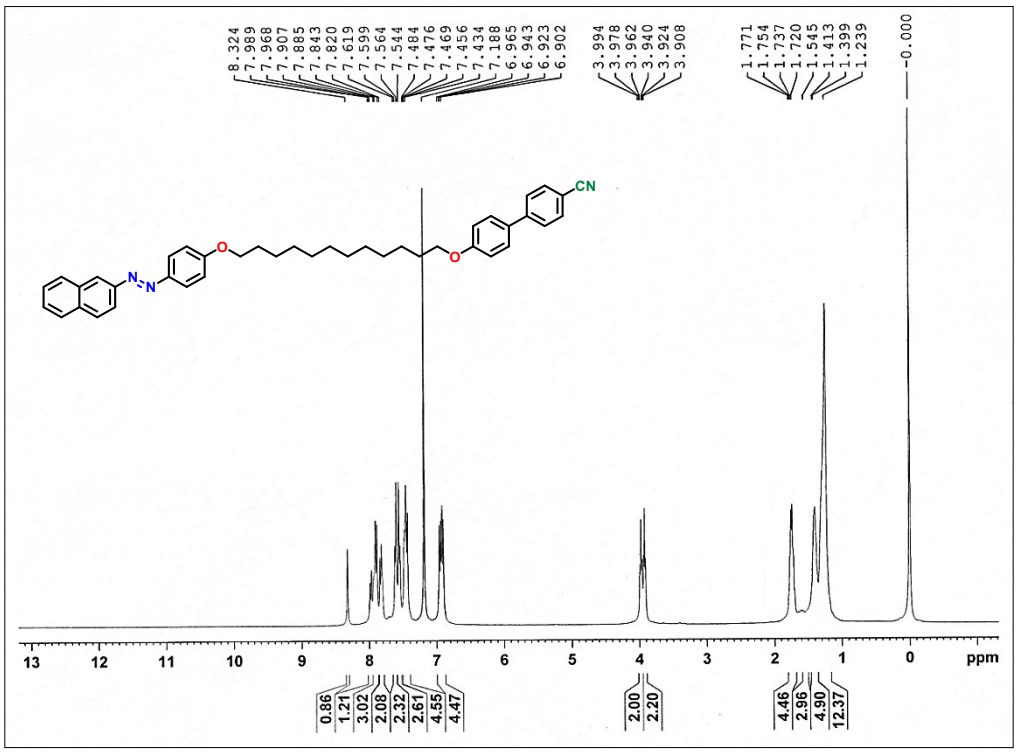


Fig. S29: ^{1}H-NMR spectra of *CB12AZ*

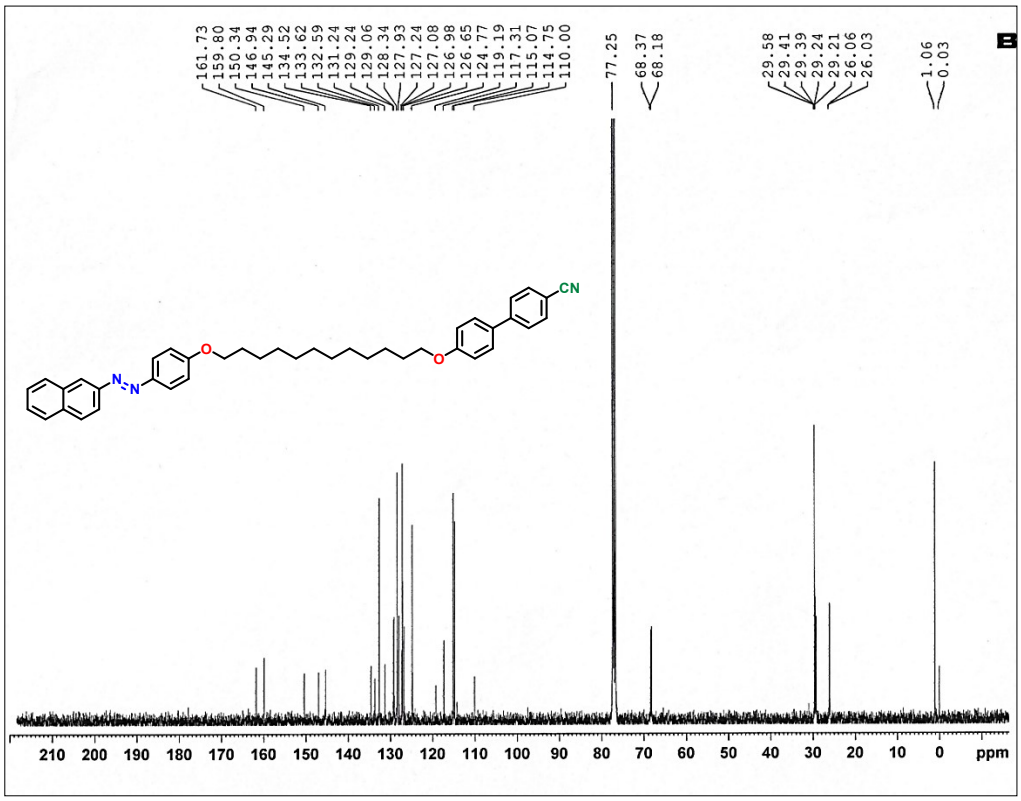


Fig. S30: ^{13}C-NMR spectra of *CB12AZ*

➢ ***DSC thermograms of the prepared dimers***

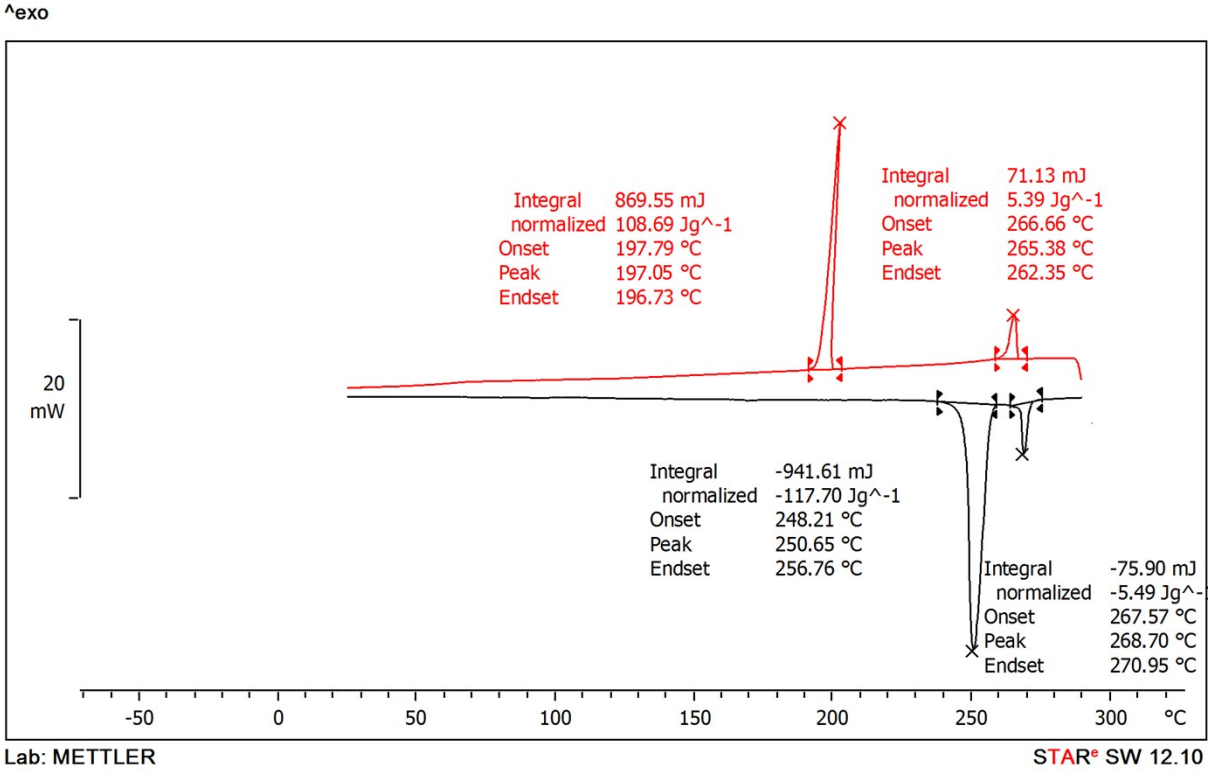


Fig. S31: DSC thermogram of *CB2AZ*

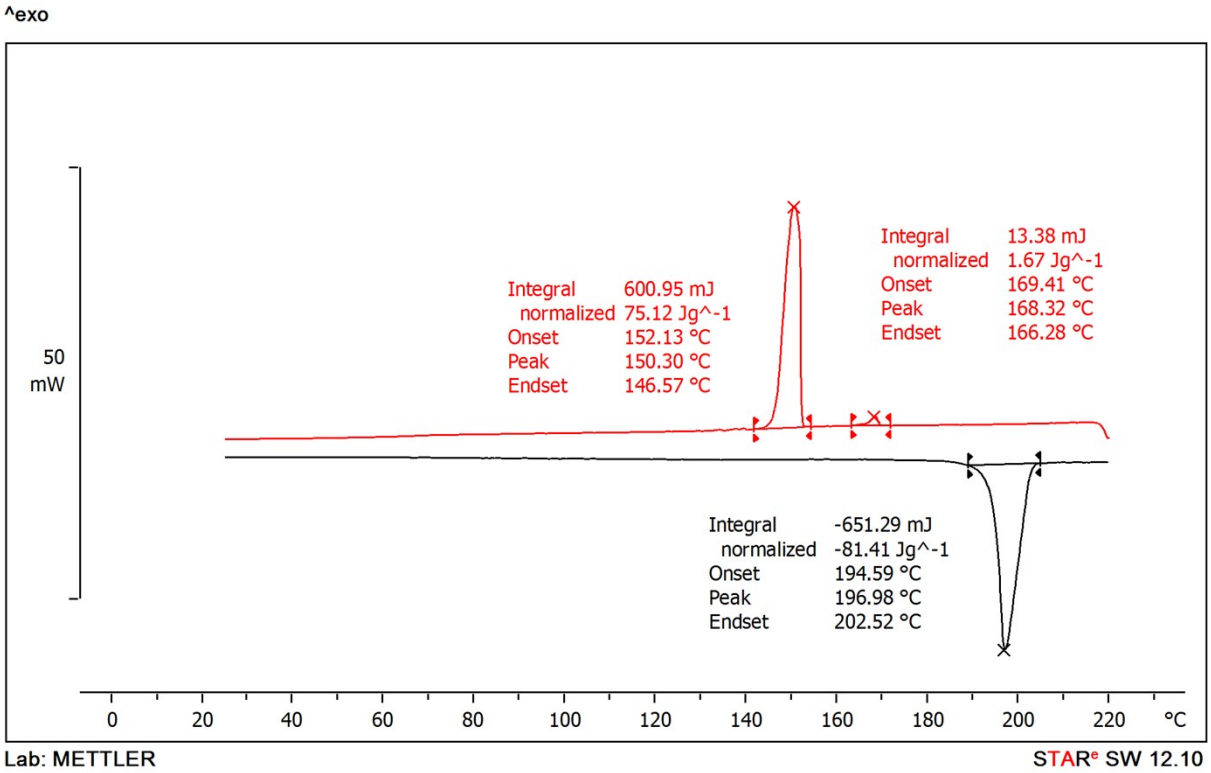


Fig. S32: DSC thermogram of *CB3AZ*

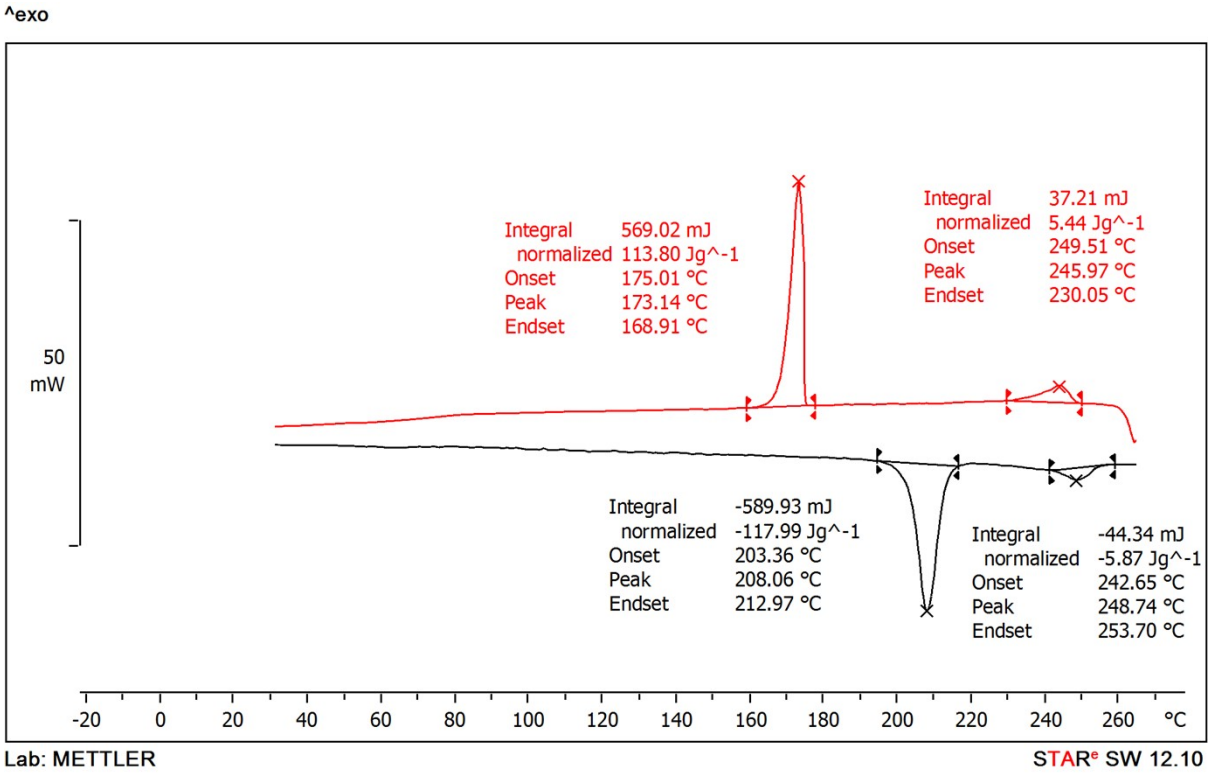


Fig. S33: DSC thermogram of *CB4AZ*

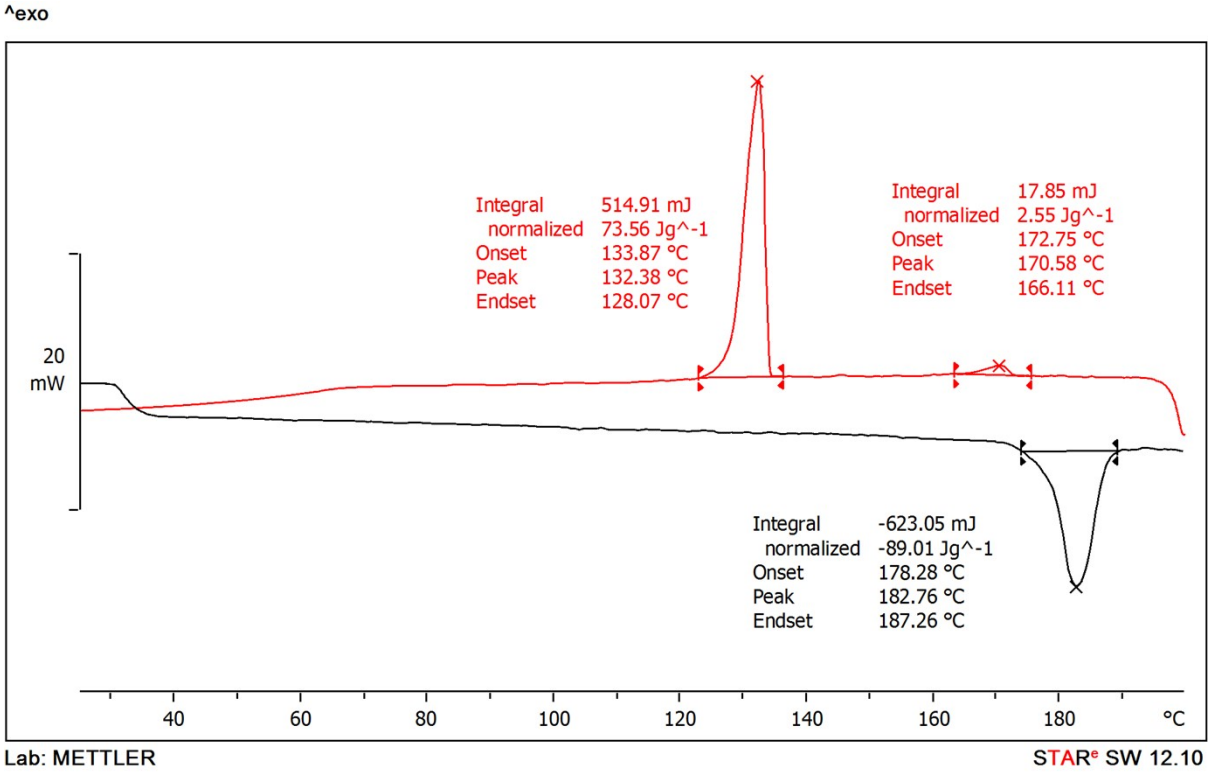


Fig. S34: DSC thermogram of *CB5AZ*

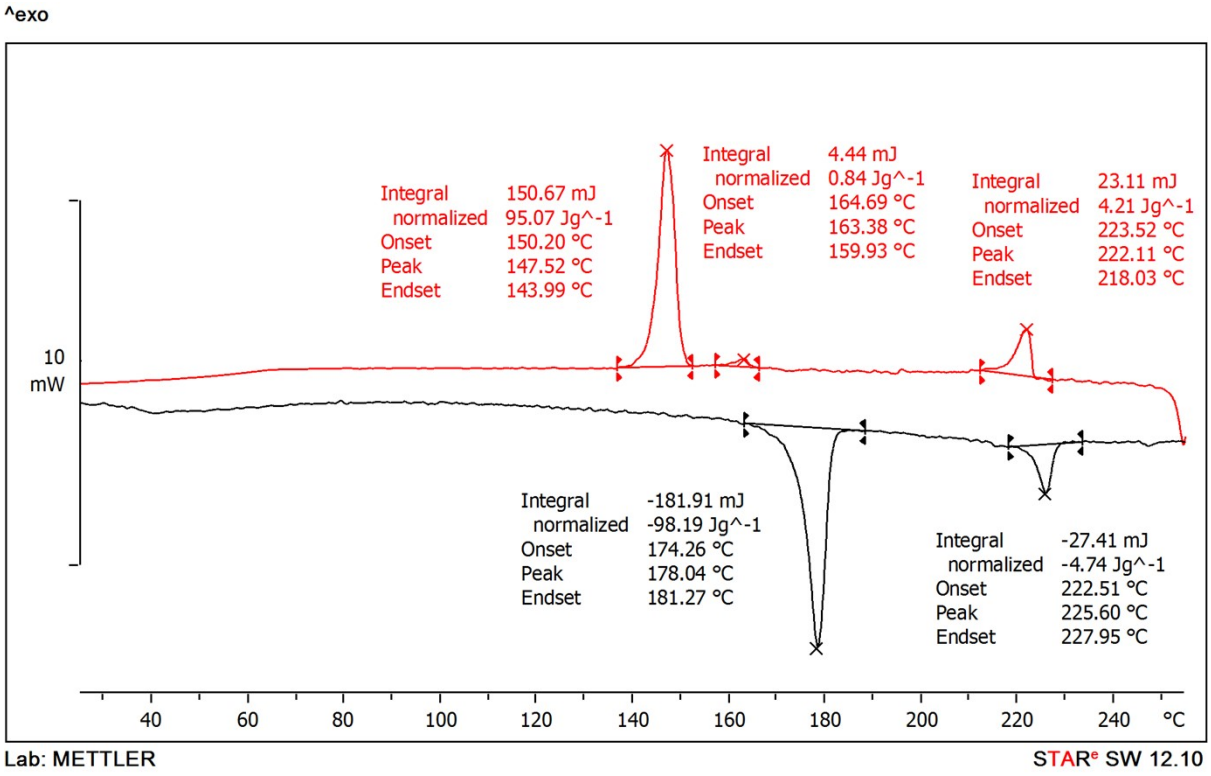


Fig. S35: DSC thermogram of *CB6AZ*

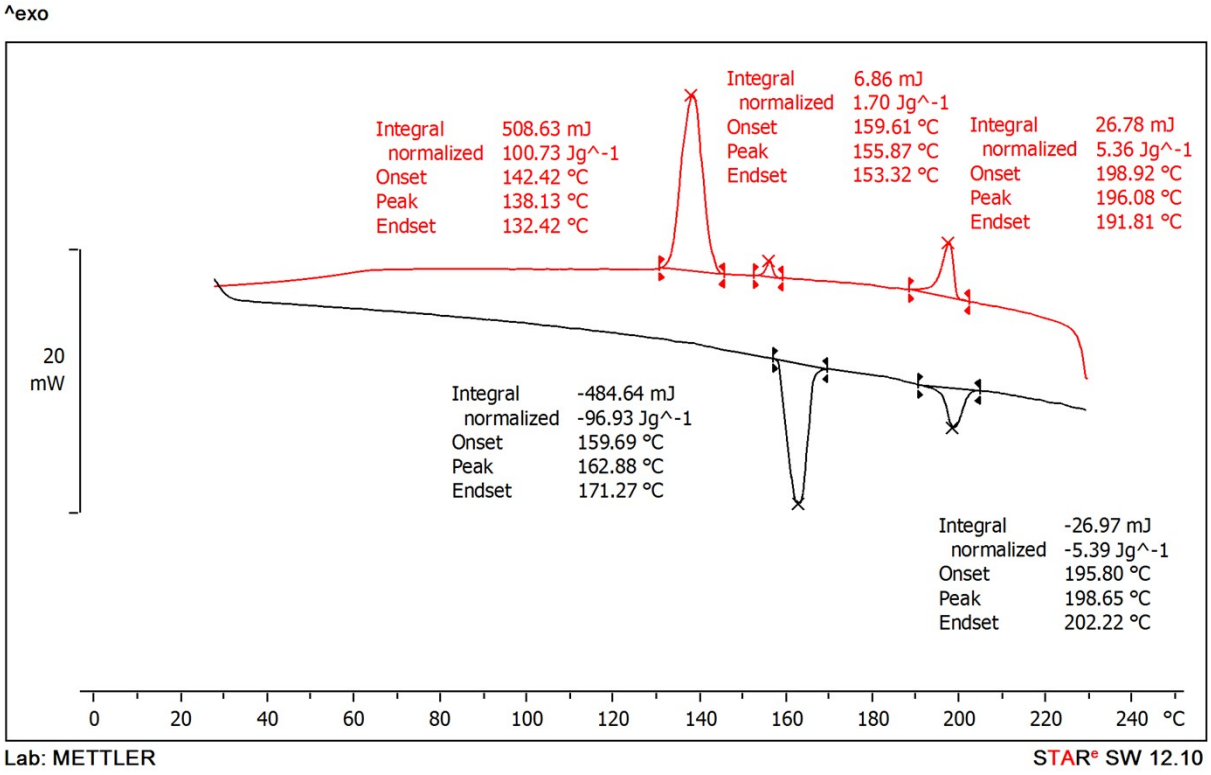


Fig. S36: DSC thermogram of *CB8AZ*

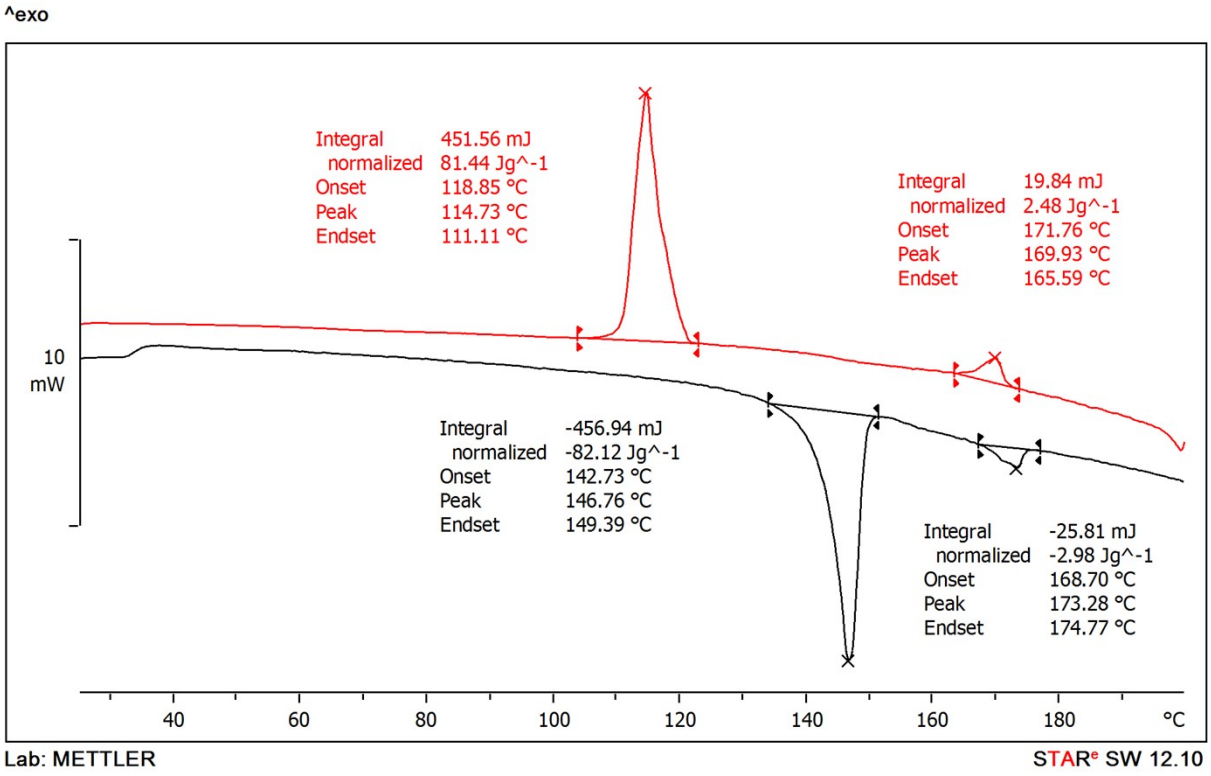


Fig. S37: DSC thermogram of *CB9AZ*

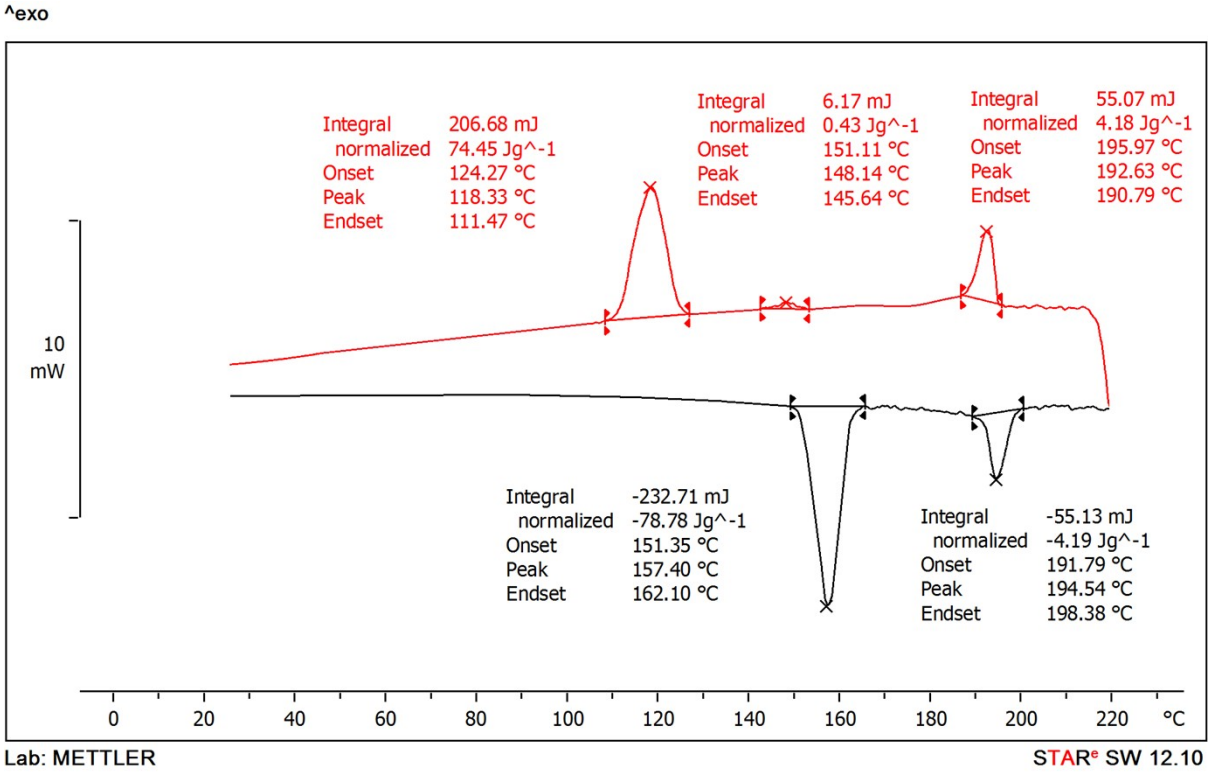


Fig. S38: DSC thermogram of *CB10AZ*

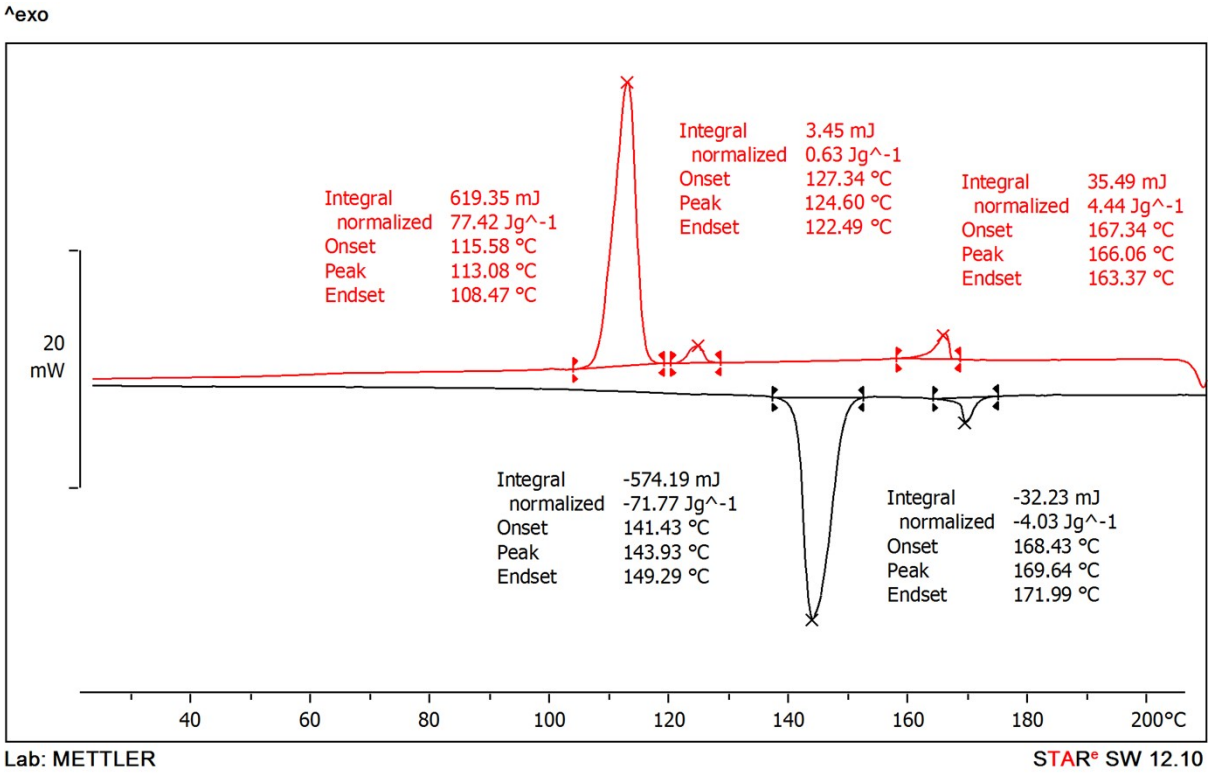


Fig. S39: DSC thermogram of *CB11AZ*

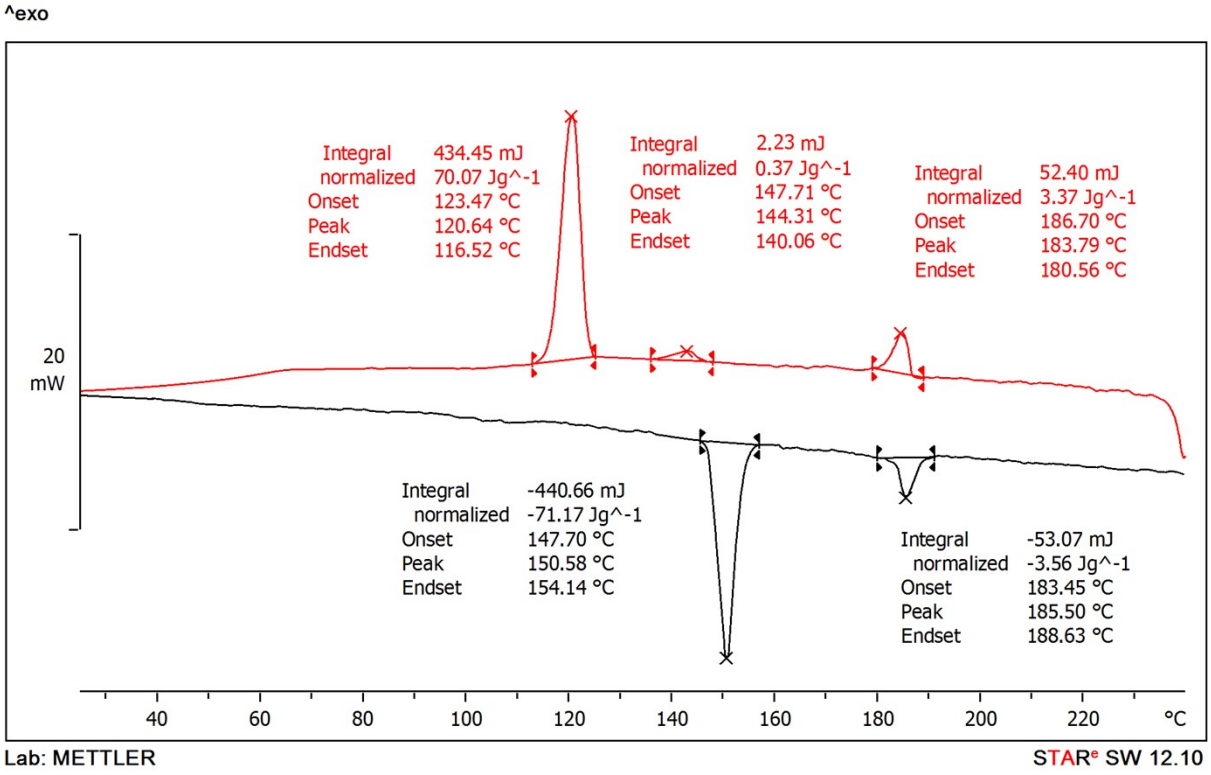


Fig. S40: DSC thermogram of *CB12AZ*