

Hünlich Base Derivatives as Photo-Responsive Λ -Shaped Hinges

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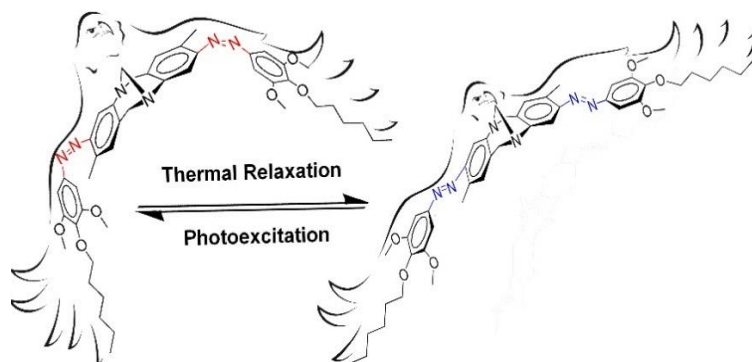


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GENERAL REMARKS

Materials:

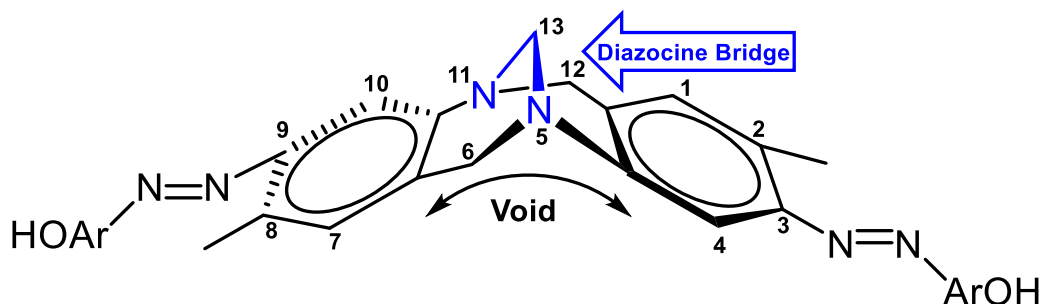
Pursuant to a procedure¹ adopted with minor modifications described in section 17, pure Hünlich's base was prepared. The rest of the starting materials and solvents were purchased from Merck, Fluka and Sigma-Aldrich chemical suppliers and consumed with no extra purification, except acetone and chloroform which were refined by potassium carbonate column just before using.

Instruments:

The direct sample injections (2-5 μ l) to an Agilent-6130 or Shimadzo-2010EV mass spectrometer produced the mass spectra with Electro-Spray-Ionization (ESI). Varian-Cary-1 and Eppendorf-BioSpektrometer-kinetic spectrophotometers recorded the UV-Vis spectra at room temperature. Thermo-Scientific-Nicolet-iS5/ATR10 spectrophotometer produced the IR spectra. The reactions were tracked by Thin Layer Chromatography (TLC) using silica gel-aluminium sheets and 254/365nm UV-light source. Silica gel (40-63 μ m) was used as the stationary phase in the column chromatography and the utilized solvent blends are shown next to a retardation factor (R_f) in each test. Vario-EL-Elementar or PerkinElmer-2400-series-II CHSNO elemental analysers performed the organic elemental analysis. The NMR spectra acquisition performed by a Bruker-AVANCE-DRX400 NMR spectrometer for these nucleons and fields: ^1H : 400.0 MHz, ^{13}C : 100.6 MHz and processing the FID files by Topspin-3.2. The chemical shifts were calibrated relative to the signals of the applied deuterated solvents as shown below:

Deuterated Solvent	$^1\text{H-NMR}$	$^{13}\text{C-NMR}$
CDCl_3	7.26 ppm	77.16 ppm
$\text{DMSO-}d_6$	2.50 ppm	39.52 ppm

The integrals calibration was done by calculating the desired value of the most detectable peak(s). The NMR peak's splitting is indicated by s that stands for *singlet*, d for *doublet*, t for *triplet*, q for *quartet*, m for *multiplet* and b for *broad*. The coupling constants, rounded into one decimal, are indicated by J in Hz which stands for Hertz. The NMR tests were all conducted at 298.15 K unless otherwise mentioned.

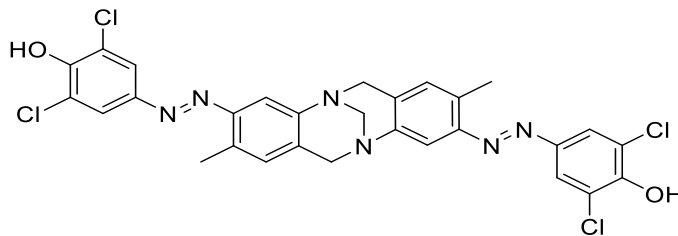


The numbering system used in the NMR interpretation

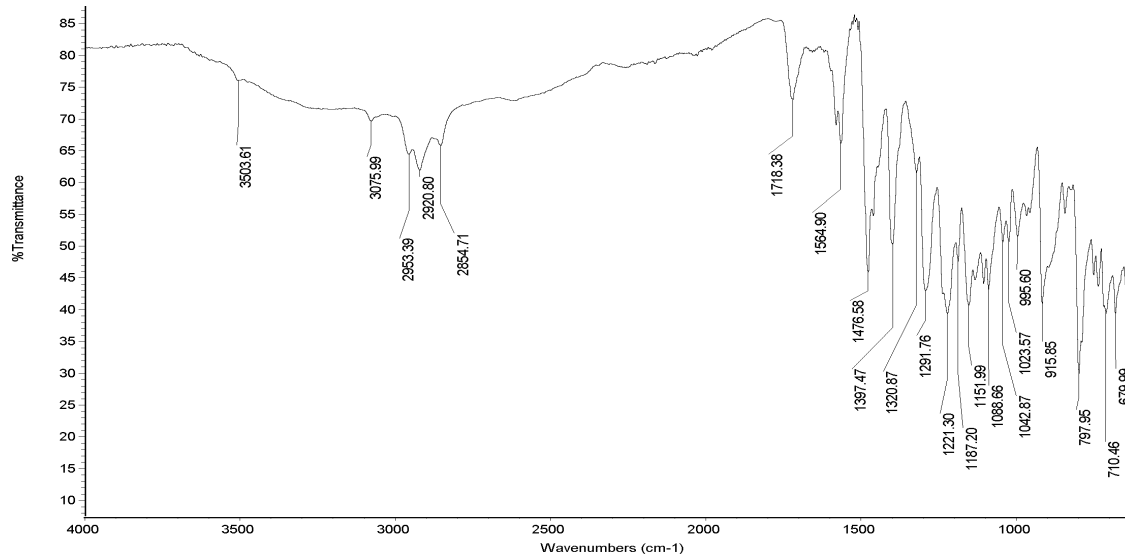
SYNTHESIS AND CHARACTERIZATION

1. Synthesis and Characterization of (±)-1

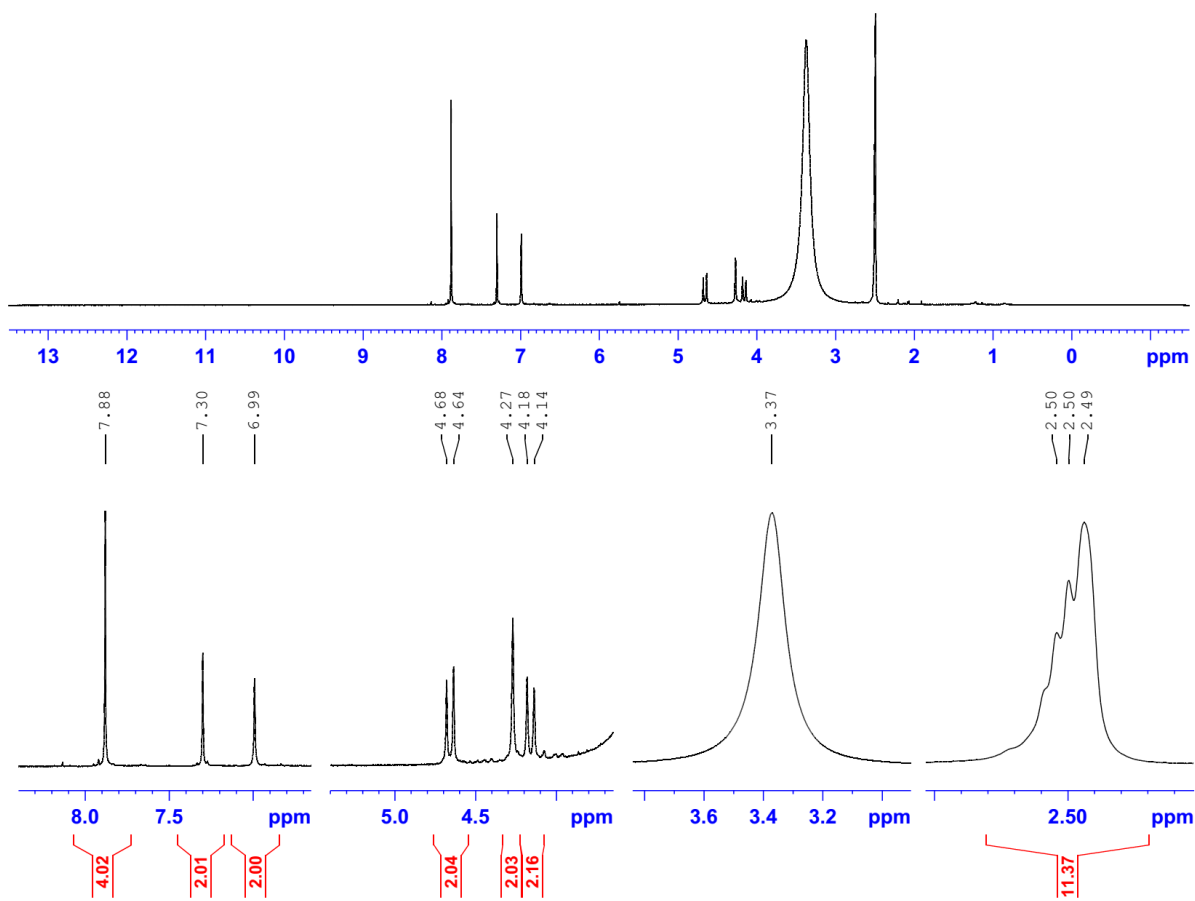
4,4'-((1E,1'E)-(2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-diyl)bis(diazene-2,1-diyl))bis(2,6-dichlorophenol)



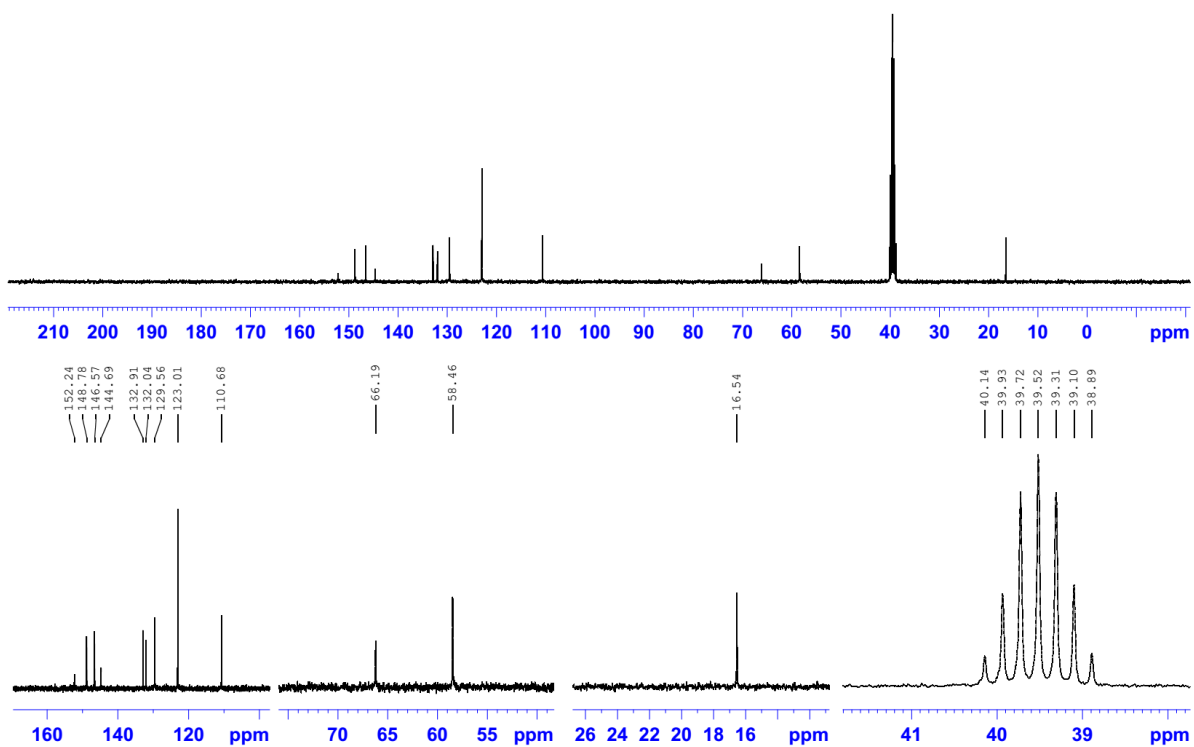
Hünlich's base (0.56 g, 2.0 mmol, 1.0 eq.) was dissolved in H₂SO₄ (6.5% v/v, 30 mL, aq.) at room temperature, then the reaction container was put in an ice/acetone bath to cool it down to -5 °C. An aqueous solution of sodium nitrite (0.30 g, 4.4 mmol, 2.2 eq., 5 mL, 0 °C) was dropped into the reaction mixture by 10 minutes and the stirring continued for 20 more minutes. The resulting yellowish solution was poured into a freshly prepared solution of 2,6-dichloro phenol (0.72 g, 4.4 mmol, 2.2 eq.) and Na₂CO₃ (2.0 g) in 100 mL of ice-cold water. Afterwards, two more grams of Na₂CO₃ gradually added to the mixture and stirred at 0°C for 23 hours. The final pH level of the reaction mixture was about 7 and a dark orange precipitate was filtered from it. The collected precipitate was properly washed with water and desiccated to obtain the crude. The crude was dissolved in 50 ml of 2-butanone, filtered and then shook with brine and NaOH solutions (3N, 100ml x 5). Afterwards, this organic layer was separated, dried up over MgSO₄ and filtered. The purified compound **1** (0.63 g, 1.0 mmol, 50%) was obtained by addition of n-hexane to the 2-butanone solution, filtration and vacuum desiccation respectively. Chemical Formula: C₂₉H₂₂Cl₄N₆O₂, Molecular Weight: 628.34, R_f: 0.32 (DCM/ MeOH = 2% v/v) silica gel. **¹H-NMR**: (400 MHz, DMSO-*d*₆) δ [ppm] 2.49 (s, 6H, 2 × -CH₃), 4.16 (d, *J* = 17.4 Hz, 2H, H-6a, H-12a), 4.27 (s, 2H, -N-CH₂-N-), 4.66 (d, *J* = 17.3 Hz, 2H, H-6b, H-12b), 6.99 (s, 2H, H-1, H-7), 7.30 (s, 2H, H-4, H-10), 7.88 (s, 4H, 4 × CH). **¹³C-NMR**: (100 MHz, DMSO-*d*₆) δ [ppm] 16.53, 58.46, 66.19, 110.68, 123.01, 129.56, 132.04, 132.91, 144.69, 146.57, 148.78, 152.24. **IR**: (Neat) ν_{\max} (cm⁻¹) = 3503, 3076, 2953, 2920, 1718, 1565, 1476, 1397, 1291, 1221, 1151, 915, 797. **MS** (Acetonitrile 90%, EtOAc 5%, H₂O 5%): (ESI negative) calc. for [C₂₉H₂₁Cl₄N₆O₂]⁻: [M-H]⁻ 625.0, found: 625.2 and 627.3. **UV** (EtOAc): λ (lgε) = 353 nm (4.4). Anal. calcd: C, 55.44; H, 3.53; Cl, 22.57; N, 13.38; O, 5.09. found: C, 55.61; H, 3.66; N, 13.14.



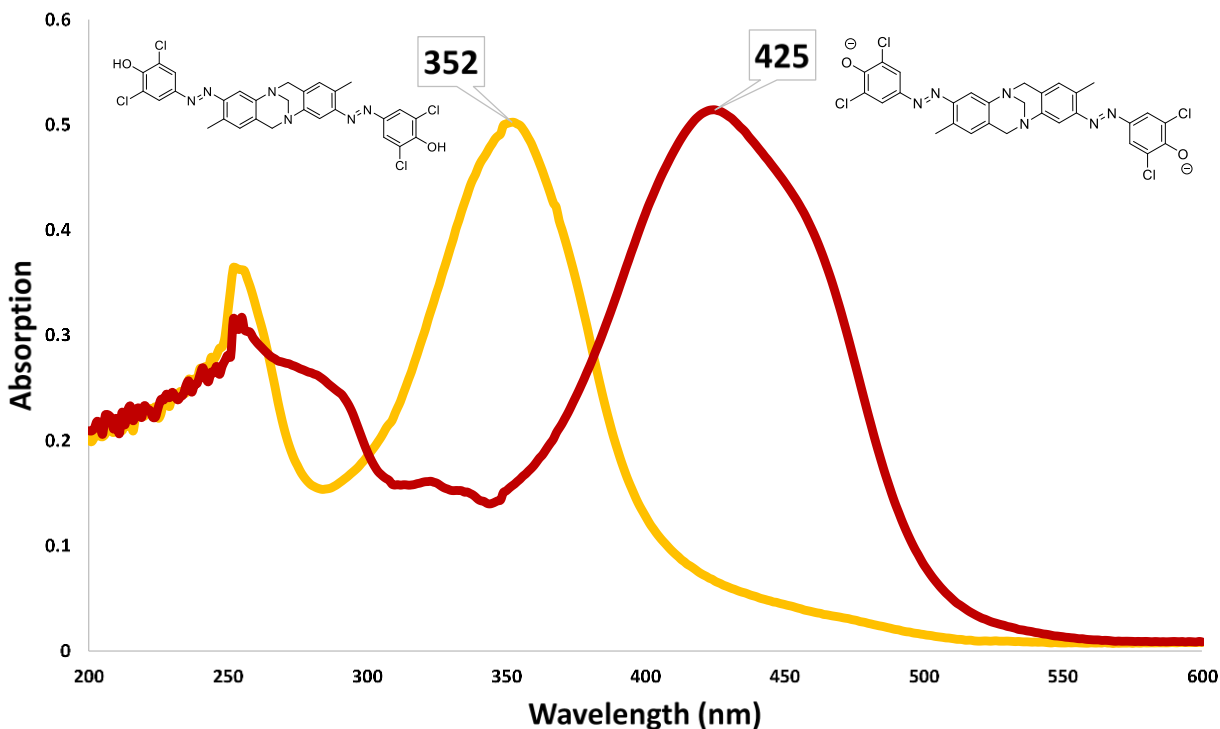
Compound 1, IR transmittance spectra (neat)



Compound 1, $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$)



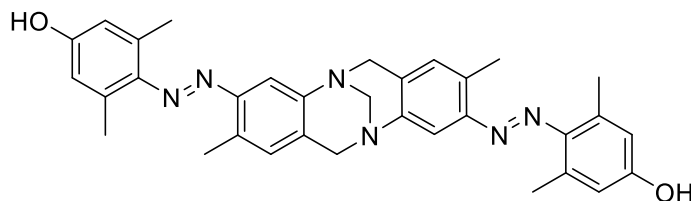
Compound 1, $^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$)



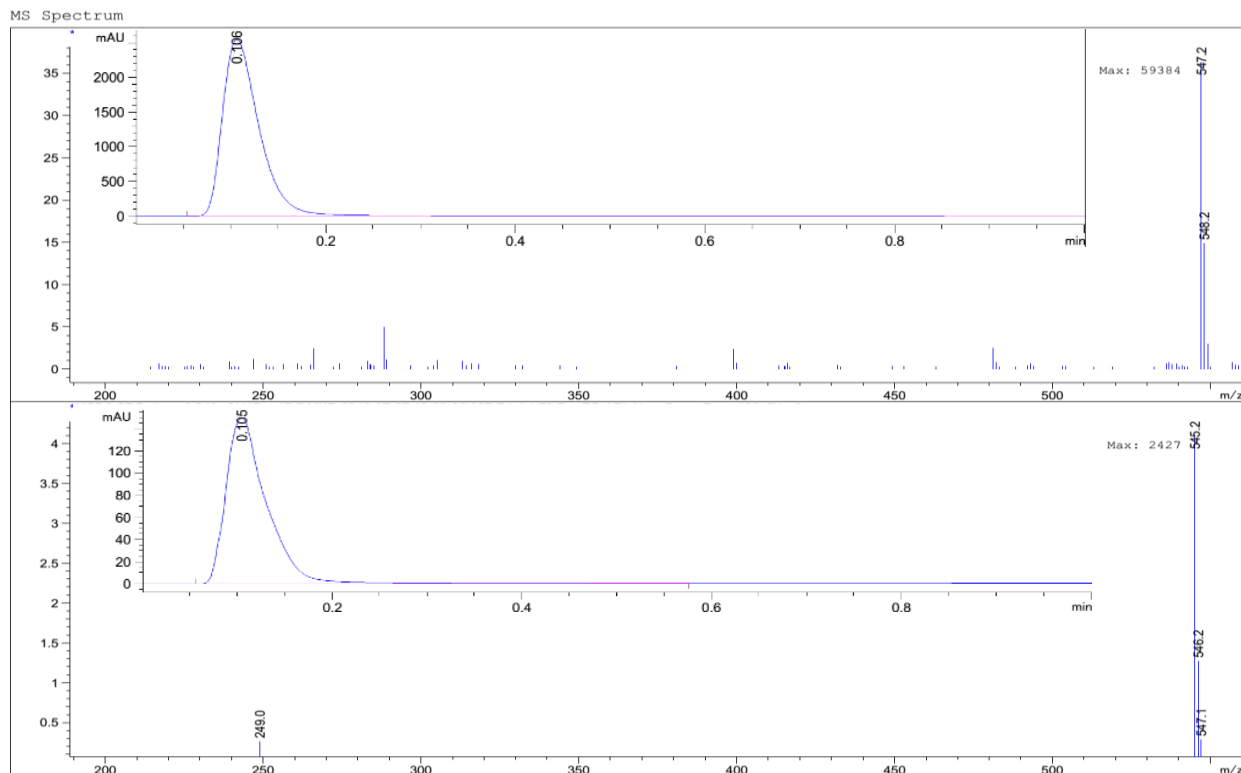
Compound 1 (rt, EtOAc), UV-Vis spectra in the absence (orange) and presence (red) of Et₃N

2. Synthesis and Characterization of (±)-2

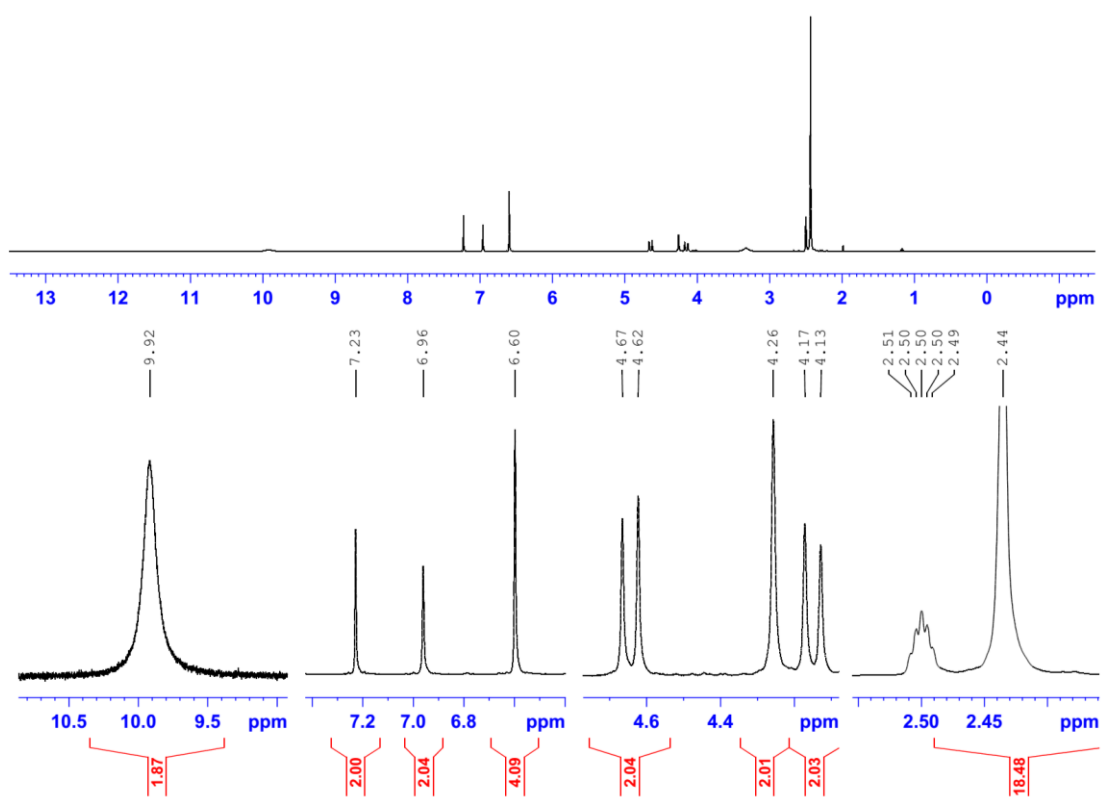
4,4'-((1E,1'E)-(2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-diyl))bis(diazene-2,1-diyl))bis(3,5-dimethylphenol)



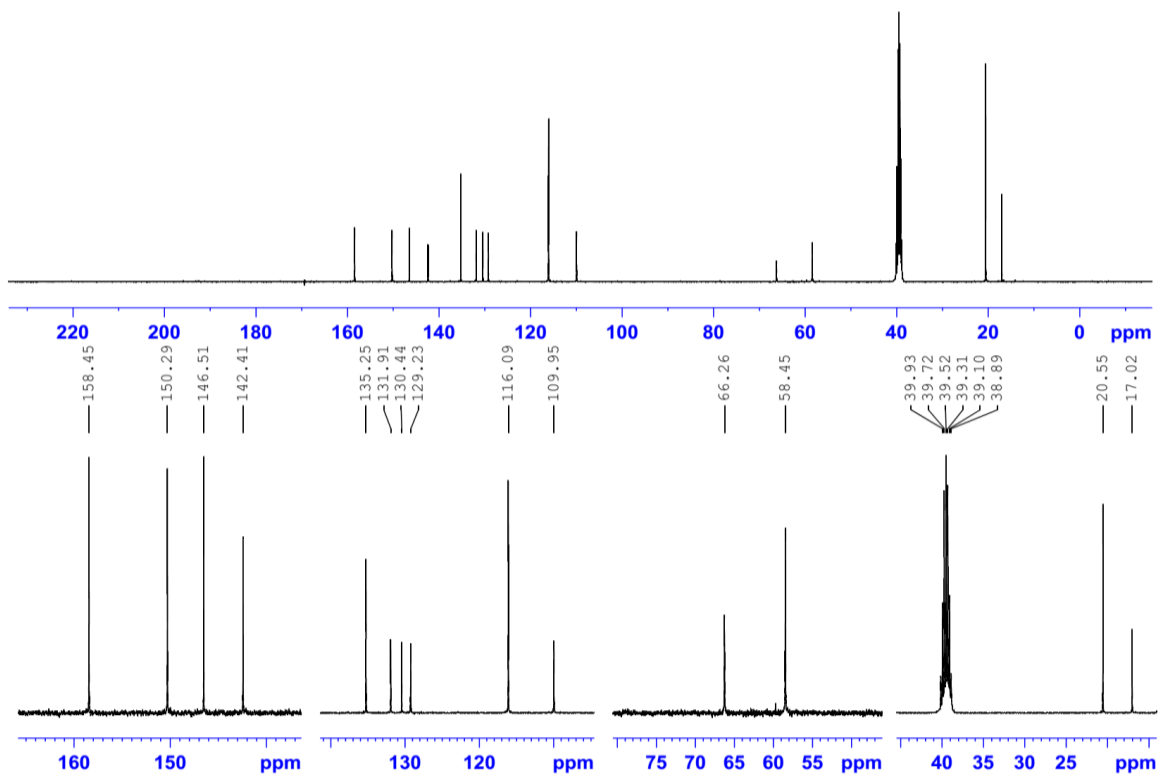
Hünlich's base (0.56 g, 2.0 mmol, 1.0 eq.) was dissolved in H₂SO₄ (6.5%, 30 mL, aq.) at room temperature, then cooled down to -5°C by placing the reaction container in ice/acetone bath. A sodium nitrite solution (0.3 g, 4.4 mmol, 2.2 eq.) in cold water (5 mL) was dropped into the reaction flask over 10 minutes. After continuing the stir for 25 more minutes, the resulting yellowish solution was poured into a prepared solution of 3,5-dimethylphenol (0.51 g, 4.2 mmol, 2.1 eq.) and Na₂CO₃ (2 g) in 100 mL of ice-cold water. The stirring continued for 2 h meanwhile two more grams of Na₂CO₃ was gradually added. After 12 more hours of stirring, an orange precipitate was filtered off from the aqueous mixture (pH=7), washed thoroughly with Milli-Q water and desiccated to obtain the product **2** (0.98 g, 1.8 mmol, 90%). Chemical Formula: C₃₃H₃₄N₆O₂, Molecular Weight: 546.68, **R_f**: 0.25 (EtOAc/ DCM = 5% v/v) silica gel. **¹H-NMR** (400 MHz, DMSO-*d*₆) δ [ppm]: 2.44 (s, 18H, 6 × -CH₃), 4.15 (d, *J* = 17.3 Hz, 2H, H-6a, H-12a), 4.26 (s, 2H, -N-CH₂-N-), 4.65 (d, *J* = 17.2 Hz, 2H, H-6b, H-12b), 6.60 (s, 4H, 4 × CH), 6.96 (s, 2H, H-1, H-7), 7.23 (s, 2H, H-4, H-10), 9.92 (br, 2H, OH). **¹³C-NMR** (100 MHz, DMSO-*d*₆) δ [ppm]: 17.02, 20.55, 58.45, 66.26, 109.95, 116.09, 129.23, 130.44, 131.91, 135.25, 142.41, 146.51, 150.29, 158.45. **IR**: (Neat) ν_{max} [cm⁻¹] = 3533, 3231, 3018, 2957, 2920, 1590, 1483, 1463, 1311, 1153 and 916. **MS** (EtOH 95%, EtOAc 5%): (ESI positive) calc. for [C₃₃H₃₅N₆O₂]⁺: [M+H]⁺ 547.27, found 547.2. (ESI negative) calc. for [C₃₃H₃₃N₆O₂]⁻: [M-H]⁻ 545.27, found 545.2. **UV-Vis**: (EtOAc) λ (lgε) = 361nm (4.5). Anal. calcd: C, 72.50; H, 6.27; N, 15.37; O, 5.85. found: C, 72.21; H, 6.45; N, 15.29.



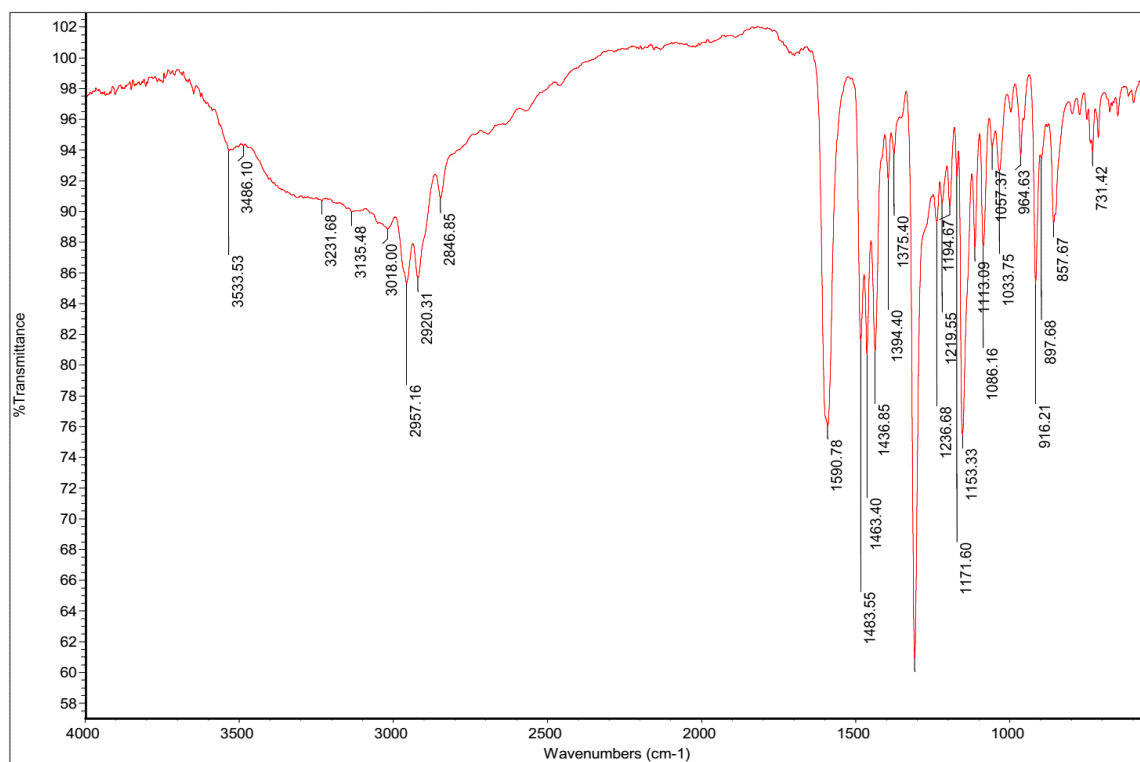
Compound 2, LCMS results ESI+ (top) and ESI- (bottom)



Compound 2, ¹H-NMR (400 MHz, DMSO-*d*₆)



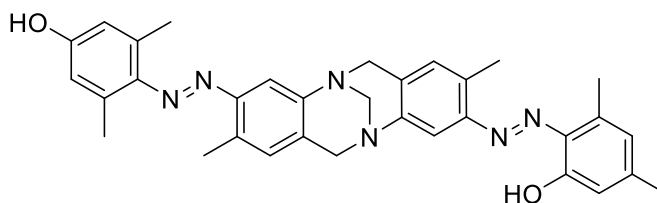
Compound 2, ^{13}C -NMR (100 MHz, $\text{DMSO}-d_6$)



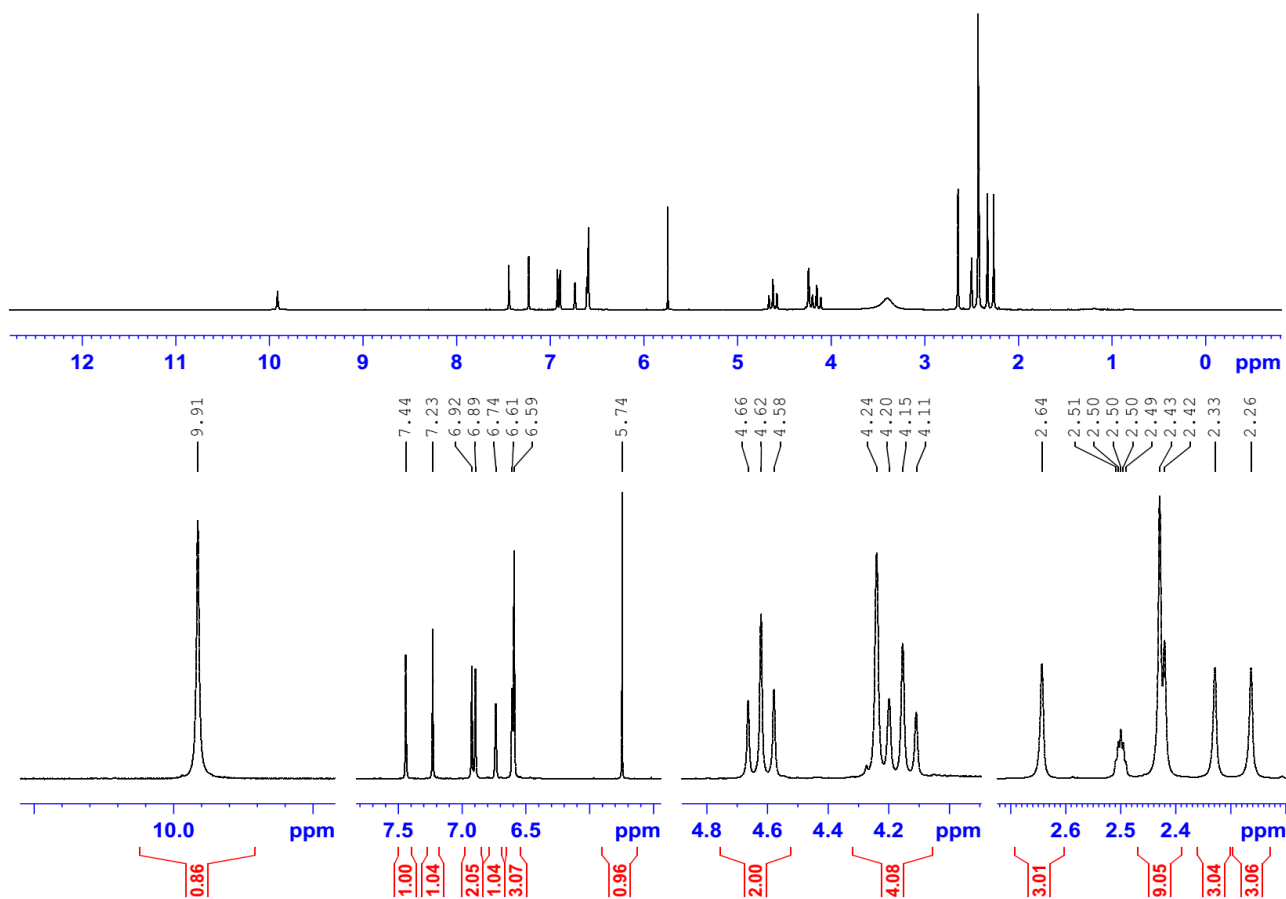
Compound 2, IR transmittance spectra (neat)

3. Synthesis and Characterization of (±)-3

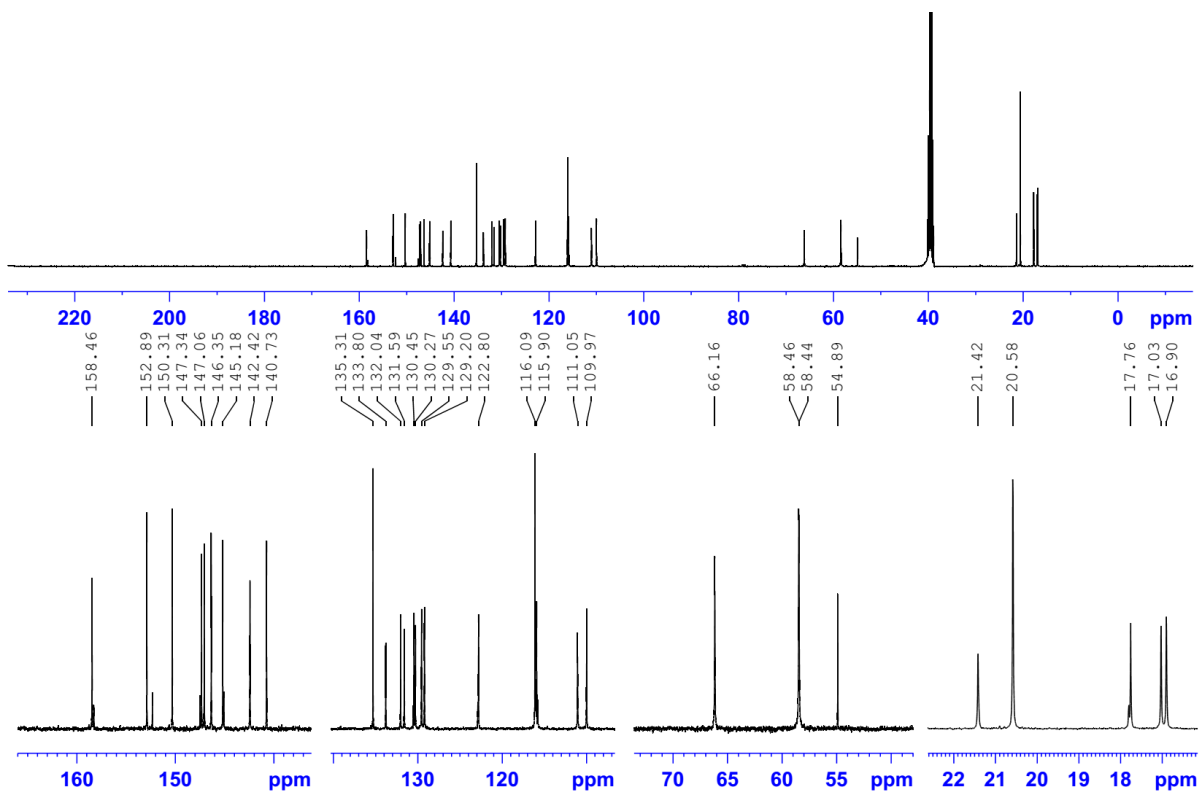
2-((E)-(9-((E)-(4-hydroxy-2,6-dimethylphenyl)diazenyl)-2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocin-3-yl)diazenyl)-3,5-dimethylphenol



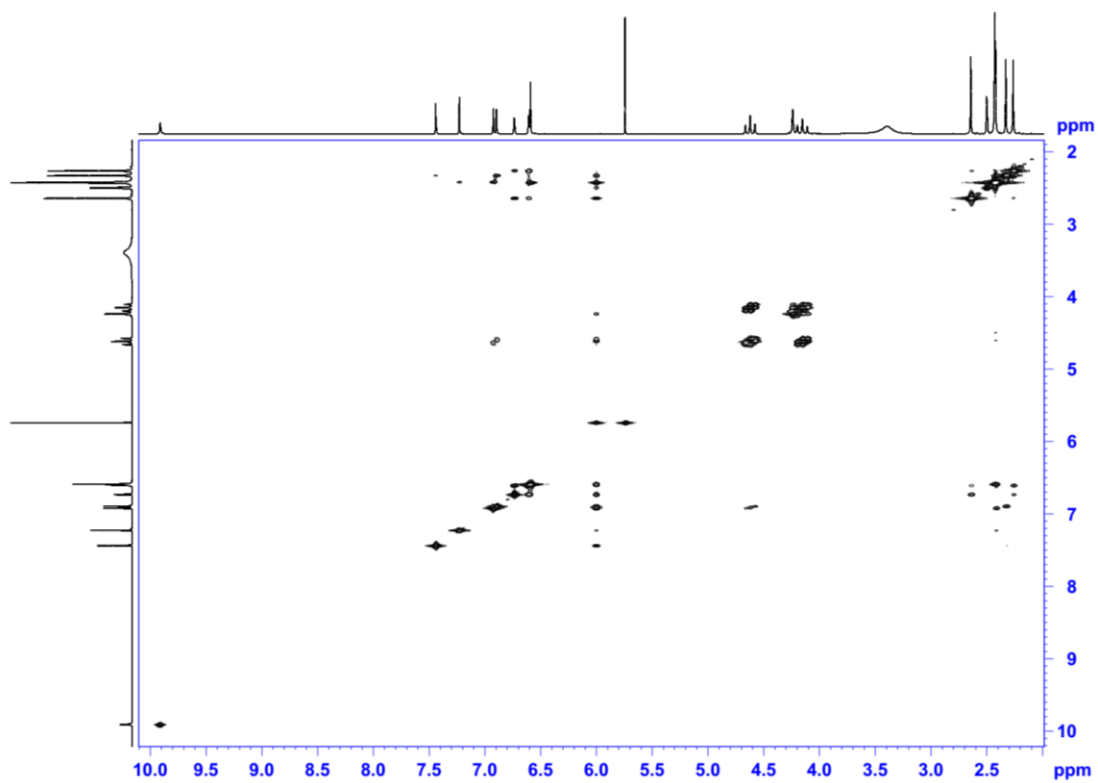
The side-product of the 2nd reaction, obtained during the column chromatography as a light orange solid (0.02 g, 0.03 mmol, 1.8%). Chemical Formula: C₃₃H₃₄N₆O₂, Molecular Weight: 546.68, **R_f**: 0.22 (MeOH/ DCM = 4% v/v) silica gel. **¹H-NMR** (400 MHz, DMSO-*d*₆) δ [ppm]: 2.26 (s, 3H, CH₃), 2.33 (s, 3H, CH₃), 2.42 (s, 3H, CH₃), 2.43 (s, 6H, 2 × -CH₃), 2.64 (s, 3H, CH₃), 4.11-4.24 (m, 2H), 4.24 (s, 2H, -N-CH₂-N-), 4.58-4.66 (m, 2H), 5.74 (s, 1H, OH), 6.59 (s, 2H, 2 × CH), 6.61 (s, 1H, CH), 6.74 (s, 1H, CH), 6.89 (s, 1H, CH), 6.92 (s, 1H, CH), 7.23 (s, 1H, CH), 7.44 (s, 1H, CH), 9.91 (s, 1H, OH). **¹³C-NMR** (100 MHz, DMSO-*d*₆) δ [ppm]: 16.90, 17.03, 17.76, 20.58, 21.42, 54.89, 58.44, 58.46, 66.16, 109.97, 111.05, 115.90, 116.09, 122.80, 129.20, 129.55, 130.27, 130.45, 131.59, 132.04, 133.80, 135.31, 140.73, 142.42, 145.18, 146.35, 147.06, 147.34, 150.31, 152.89, 158.46. **IR**: (Neat) ν_{\max} [cm⁻¹] = 3521, 3236, 3022, 2949, 2932, 1585, 1479, 1458, 1316, 1144 and 928. **MS** (EtOH 95%, EtOAc 5%): (ESI positive) calc. for [C₃₃H₃₅N₆O₂]⁺: [M+H]⁺ 547.27, found 547.3. (ESI negative) calc. for [C₃₃H₃₃N₆O₂]⁻: [M-H]⁻ 545.27, found 545.2. **UV-Vis**: (EtOAc) λ (lge) = 361nm (4.5). Anal. calcd: C, 72.50; H, 6.27; N, 15.37; O, 5.85. found: C, 72.81; H, 6.46; N, 15.51.



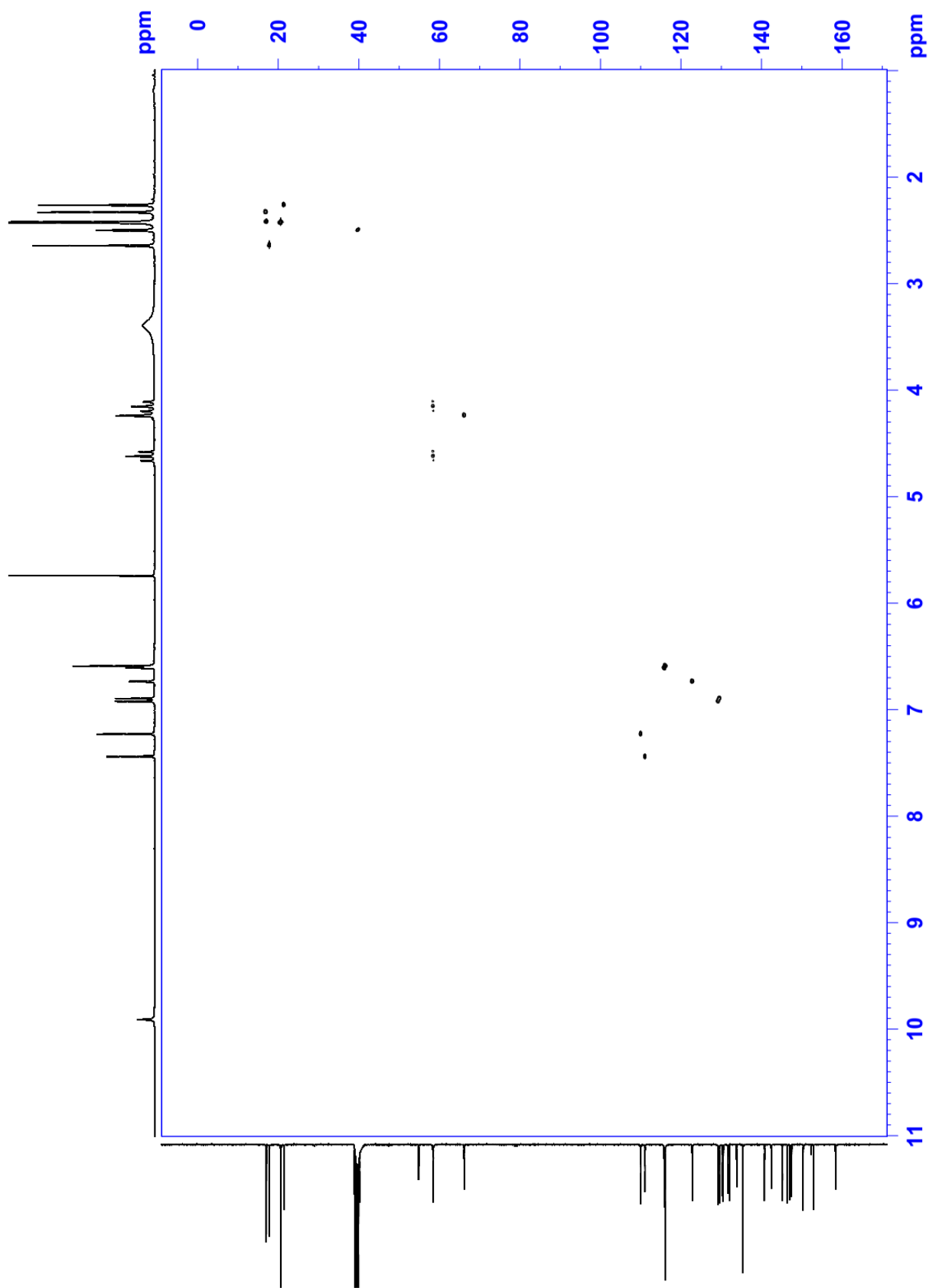
Compound 3, ¹H-NMR (400 MHz, DMSO-*d*₆)



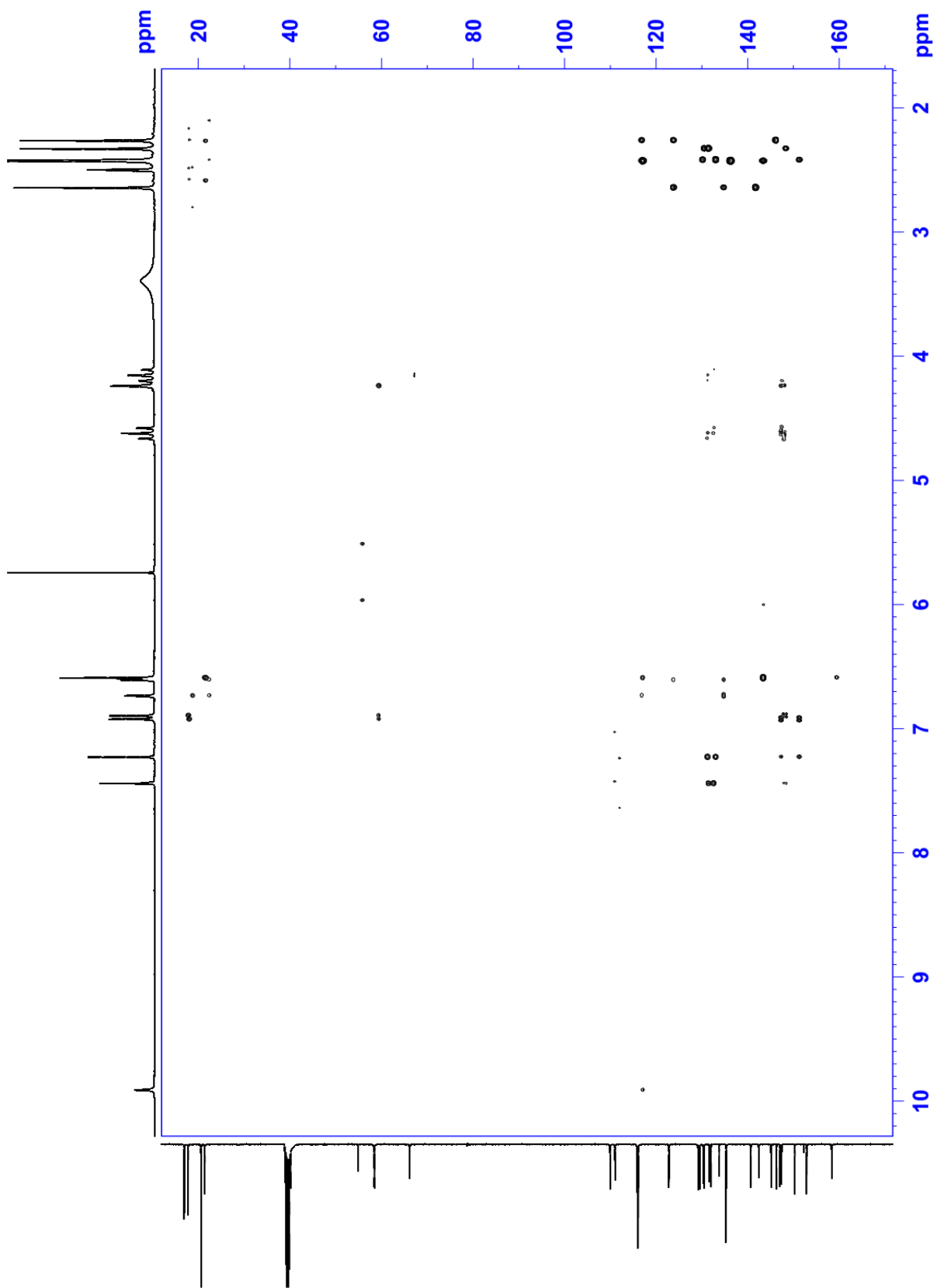
Compound 3, ¹³C-NMR (100 MHz, DMSO-d₆)



Compound 3, COSY (DMSO-d₆)



Compound 3, HSQC (DMSO-*d*₆)

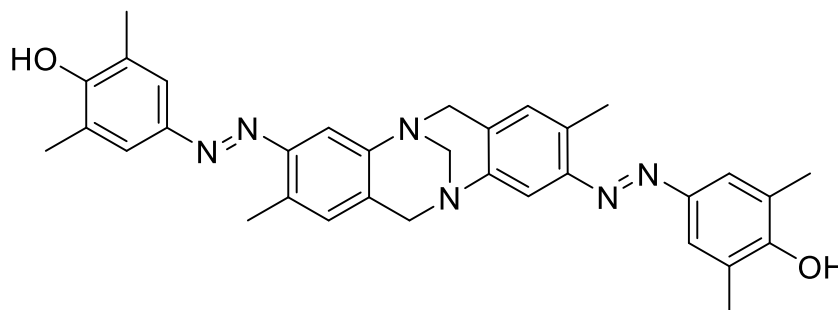


Compound 3, HMBC (DMSO-*d*₆)

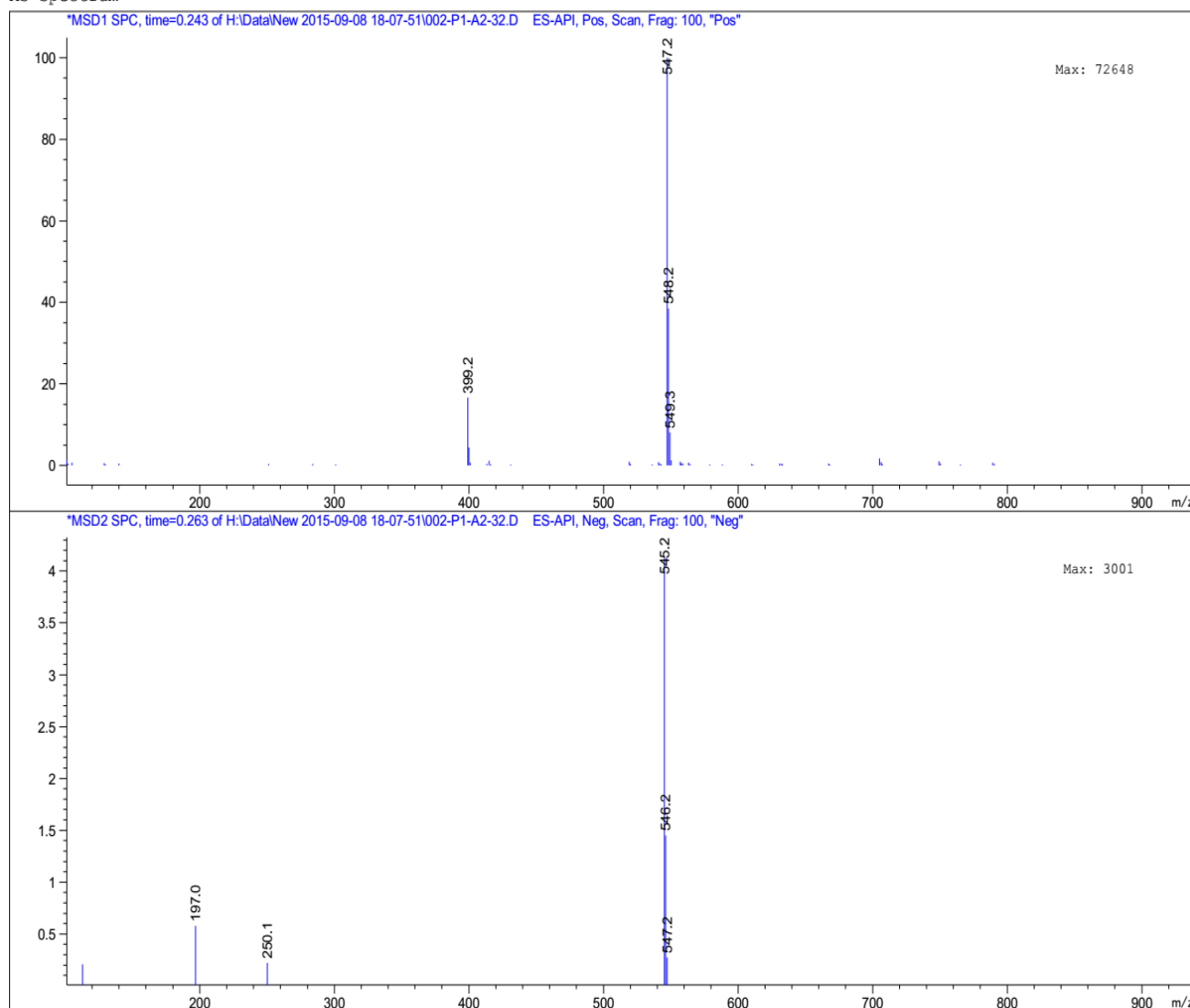
4. Synthesis and Characterization of (\pm)-4

4,4'-((2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-diyl)bis(diazene-2,1-diyl))bis(2,6-dimethylphenol)

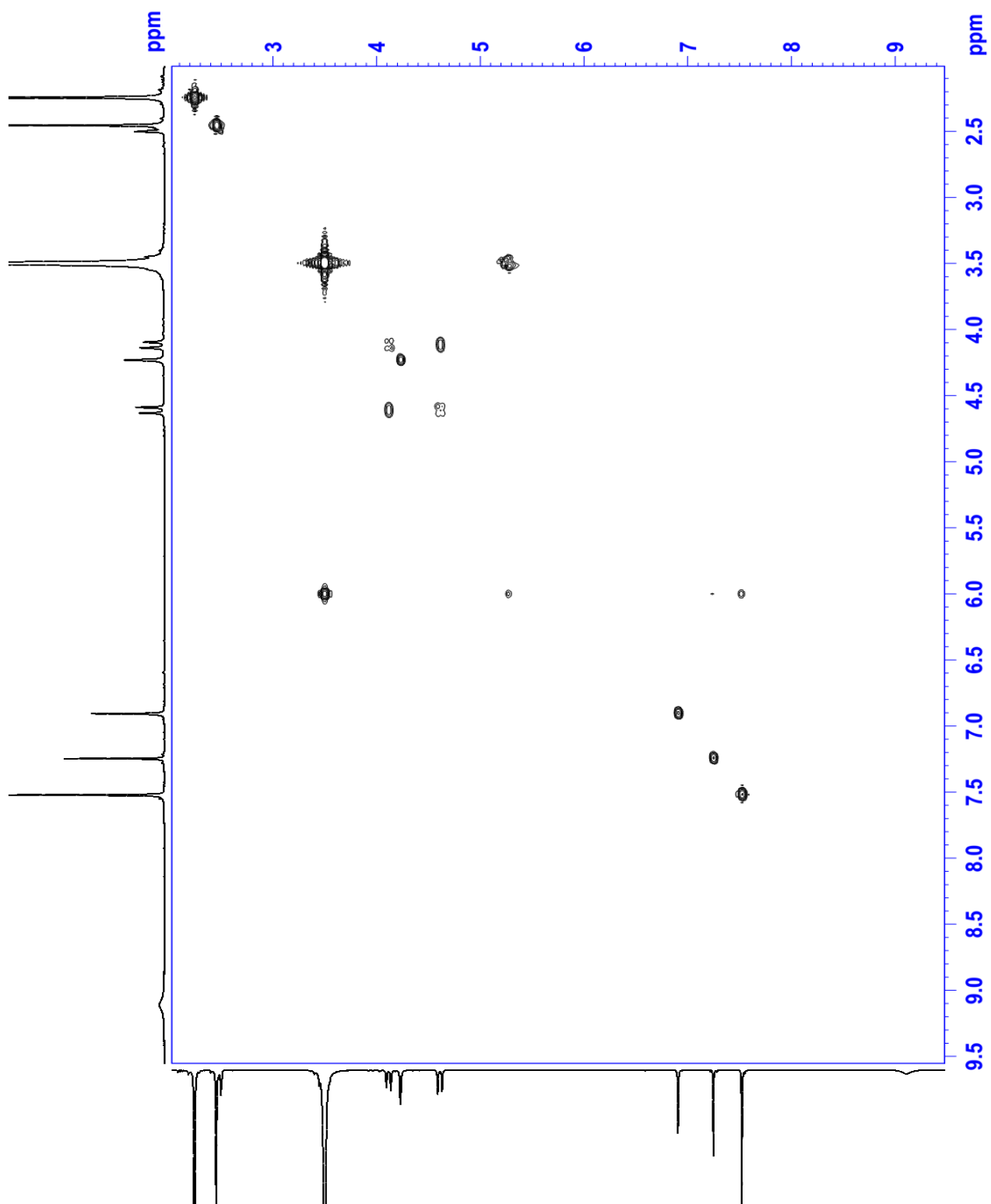
For the detailed preparation and purification procedures please see: M. Kazem-Rostami, *Synthesis*, 2017, **49**, in press, DOI: 10.1055/s-0036-1588913.



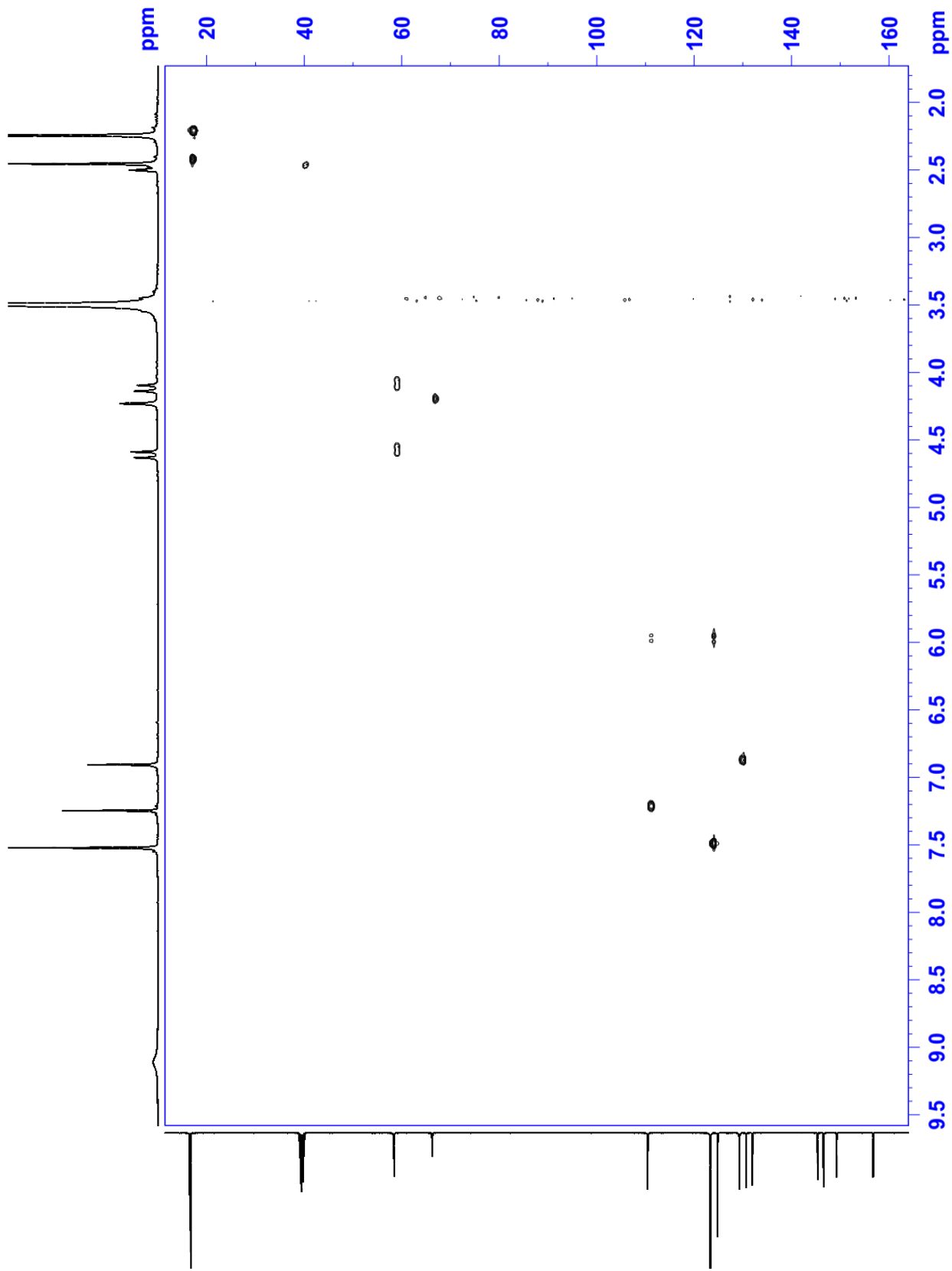
MS Spectrum



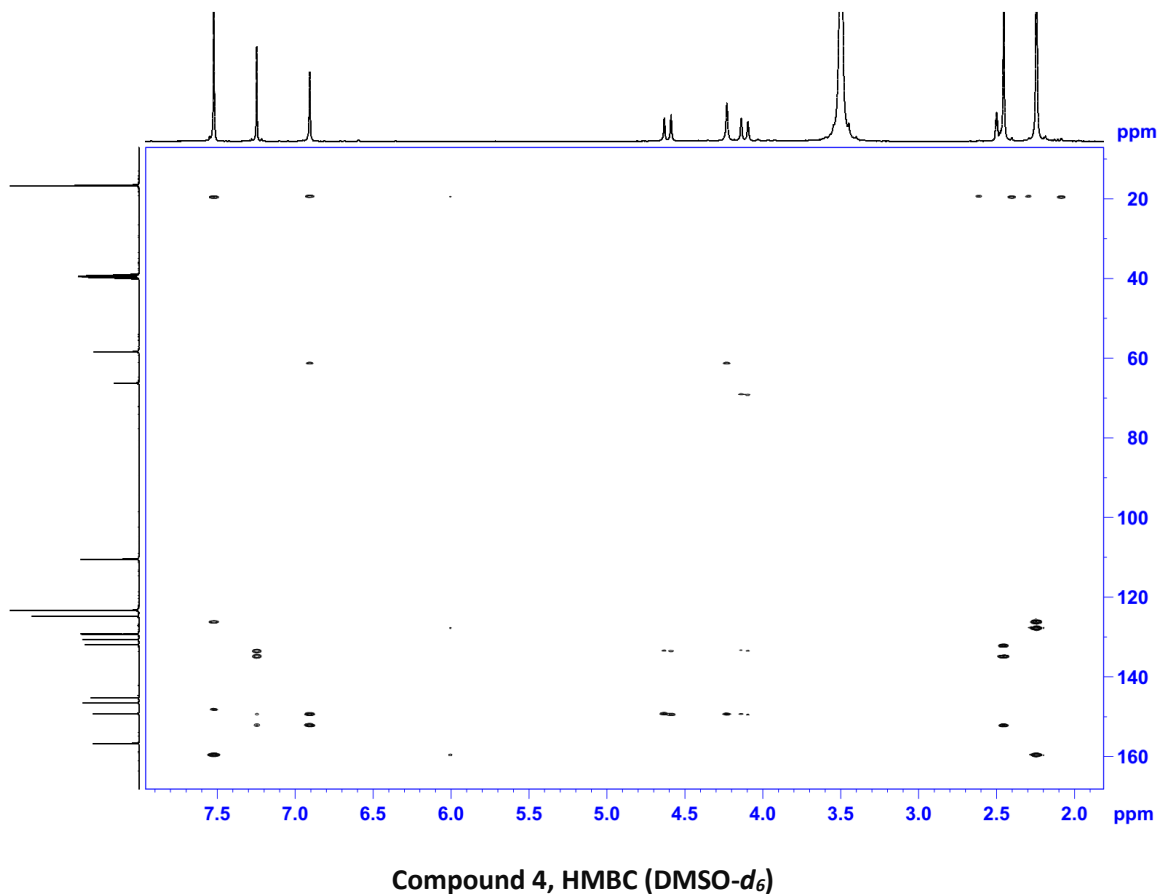
Compound 4, Mass Spectra ESI+ (top) and ESI- (bottom)



Compound 4, COSY (DMSO- d_6)

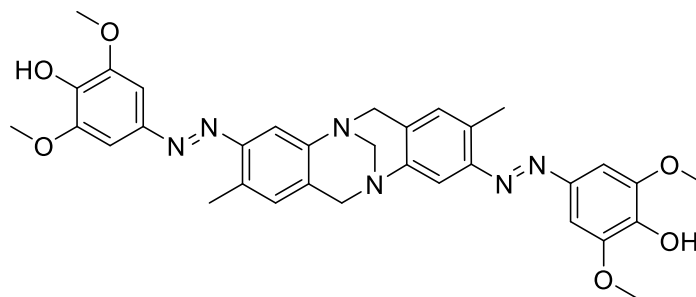


Compound 4, HSQC (DMSO-*d*₆)



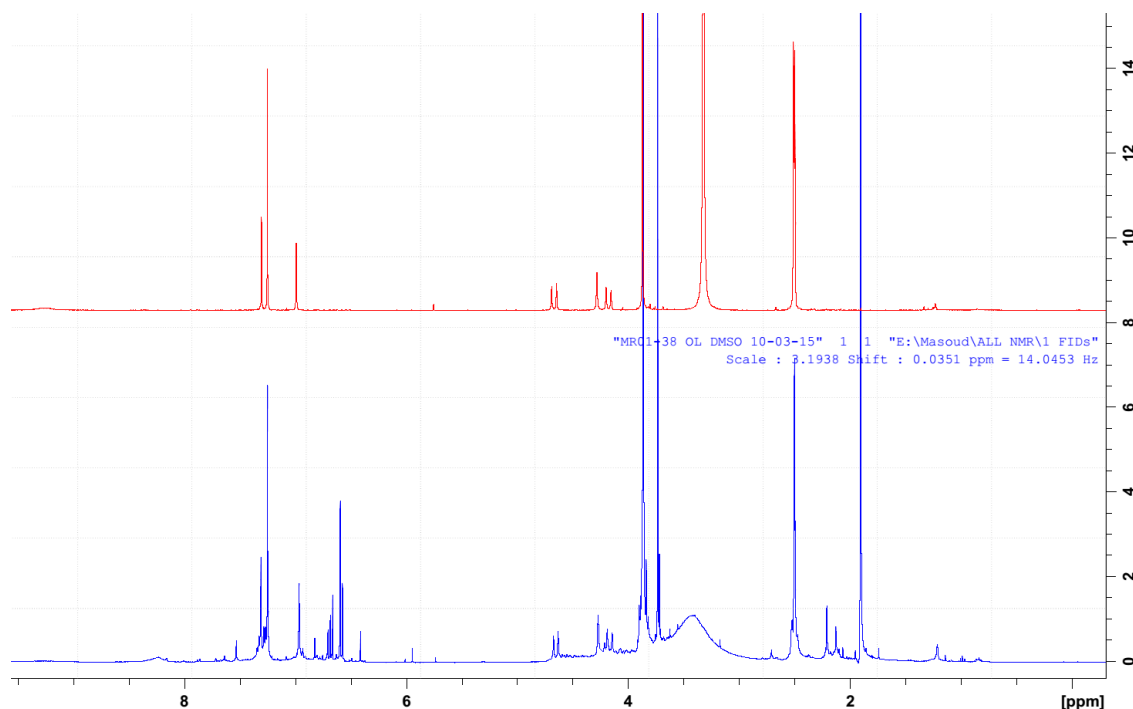
5. Synthesis and Characterization of (±)-5

4,4'-((2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-diyl)bis(diazene-2,1-diyl))bis(2,6-dimethoxyphenol)

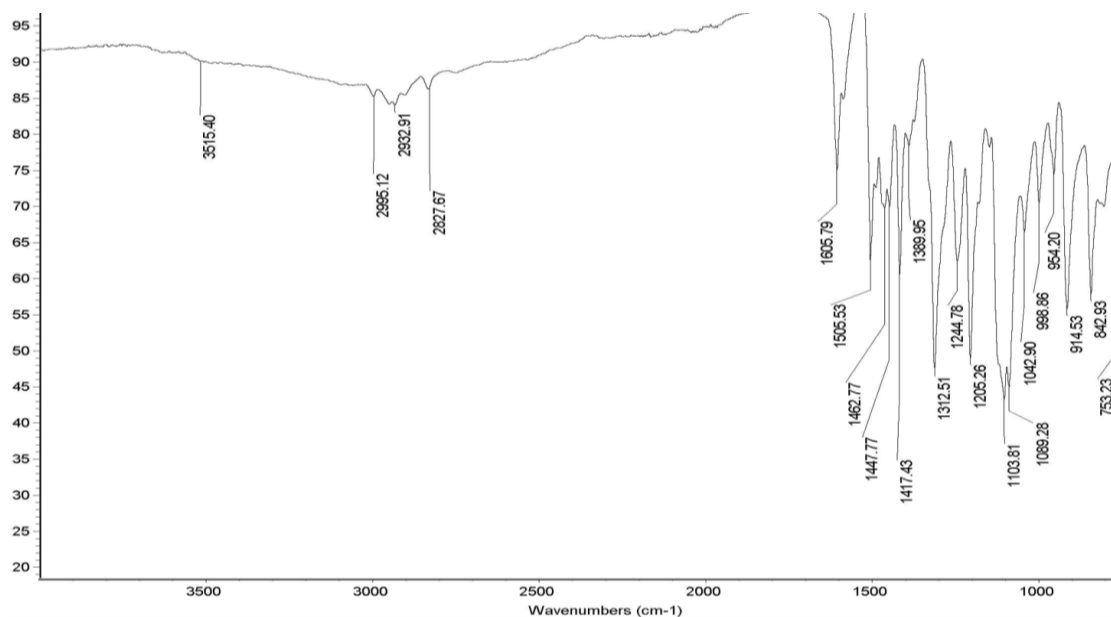


Hünlich's base (0.56 g, 2.0 mmol, 1.0 eq.) was dissolved in H₂SO₄ (6.5%, 30 mL, aq.) at room temperature, then cooled down to -5°C by putting the reaction container in an ice/acetone bath. A solution of sodium nitrite (0.30 g, 4.4 mmol, 2.2 eq.) in cold water (5 mL) was dropped into the reaction flask with continues stirring for 30 minutes. The resulting yellowish solution was poured into a freshly prepared solution of 2,6-dimethoxy phenol (1.0 g, 6.5 mmol, 3.3 eq.) and Na₂CO₃ (2.0 g) in 50 mL of acetonitrile/water 3:7 solution and stirred for 1 hour at -5 °C. Two more grams of Na₂CO₃ was gradually added to neutralize the mixture and mixed two more hours until reached to the room temperature. After acidifying the reaction mixture (acetic acid, pH=5), an orange organic layer was extracted by ethyl acetate, washed with brine properly and evaporated to obtain the crude (0.93 g, contained almost 60% of the expected product based on the crude's NMR). Further purification was done by column chromatography to obtain a highly pure yellow solid however a significant portion of the product stuck

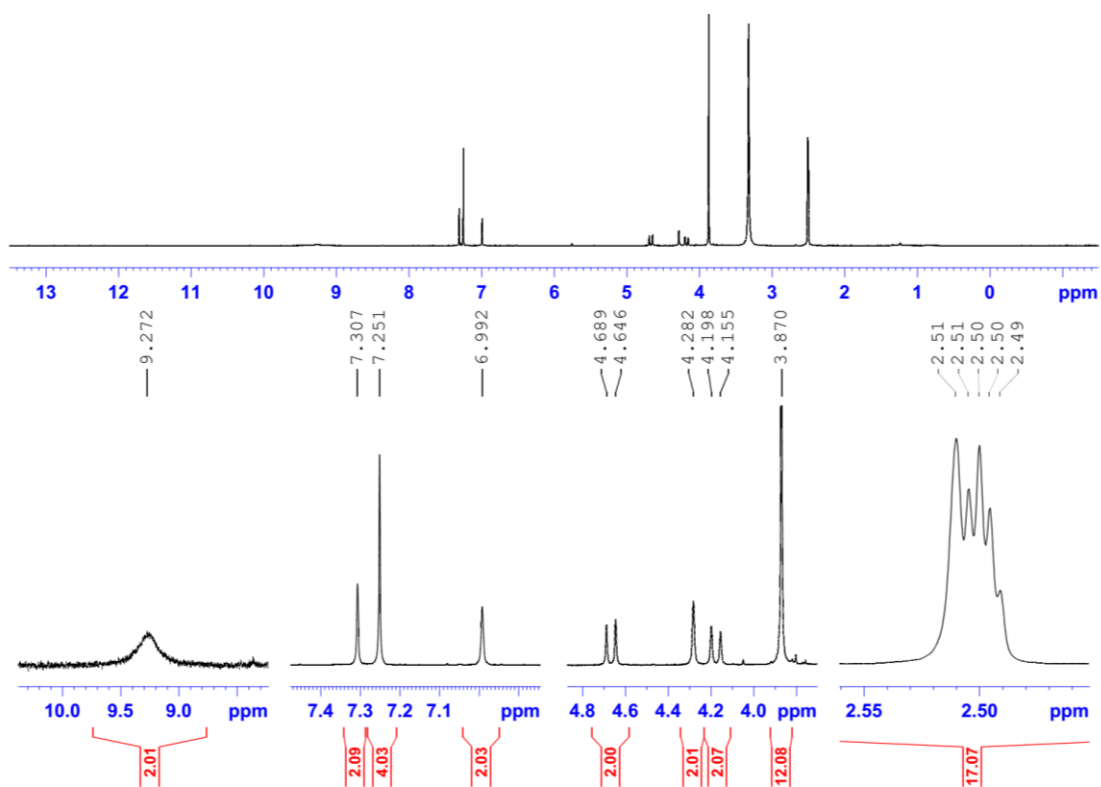
to the silica and the retrieved amount was (0.06 g, 0.1 mmol, 5%). Chemical Formula: $C_{33}H_{34}N_6O_6$, Molecular Weight: 610.67, R_f : 0.38 (MeOH/ DCM = 4% v/v) silica gel. **1H -NMR:** (400 MHz, DMSO- d_6) δ [ppm] 2.51 (s, 6H, 2 \times -CH $_3$), 3.87 (s, 12H, 4 \times -OCH $_3$), 4.17 (d, J = 17.30 Hz, 2H, H-6a, H-12a), 4.28 (s, 2H, -N-CH $_2$ -N-), 4.66 (d, J = 17.22 Hz, 2H, H-6b, H-12b), 6.99 (s, 2H, H-1, H-7), 7.25 (s, 4H, 4 \times CH), 7.30 (s, 2H, H-4, H-10), 9.27 (br, 2H, OH). **^{13}C -NMR:** (100 MHz, DMSO- d_6) δ [ppm] 16.48, 55.99, 58.46, 66.27, 100.78, 110.5, 129.39, 130.94, 132.13, 139.39, 144.41, 146.57, 148.17, 149.01. **IR:** (Neat) ν_{max} (cm $^{-1}$) = 3515, 2995, 2827, 1605, 1505, 1417, 1312, 1205, 1103, 914, 842, 619. **MS:** (Acetonitrile 90%, EtOAc 5%, H $_2$ O 5%): (ESI positive) calc., for $[C_{33}H_{35}N_6O_6]^+$: $[M+H]^+$ 611.25, found 611.5 (ESI negative) calc. for $[C_{33}H_{33}N_6O_6]^-$: $[M-H]^-$ 609.25, found 609.0. **UV:** (EtOAc) λ (lg ϵ) = 384 nm(4.5). Anal. calcd: C, 64.91; H, 5.61; N, 13.76; O, 15.72. found: C, 64.78; H, 5.97; N, 13.99.



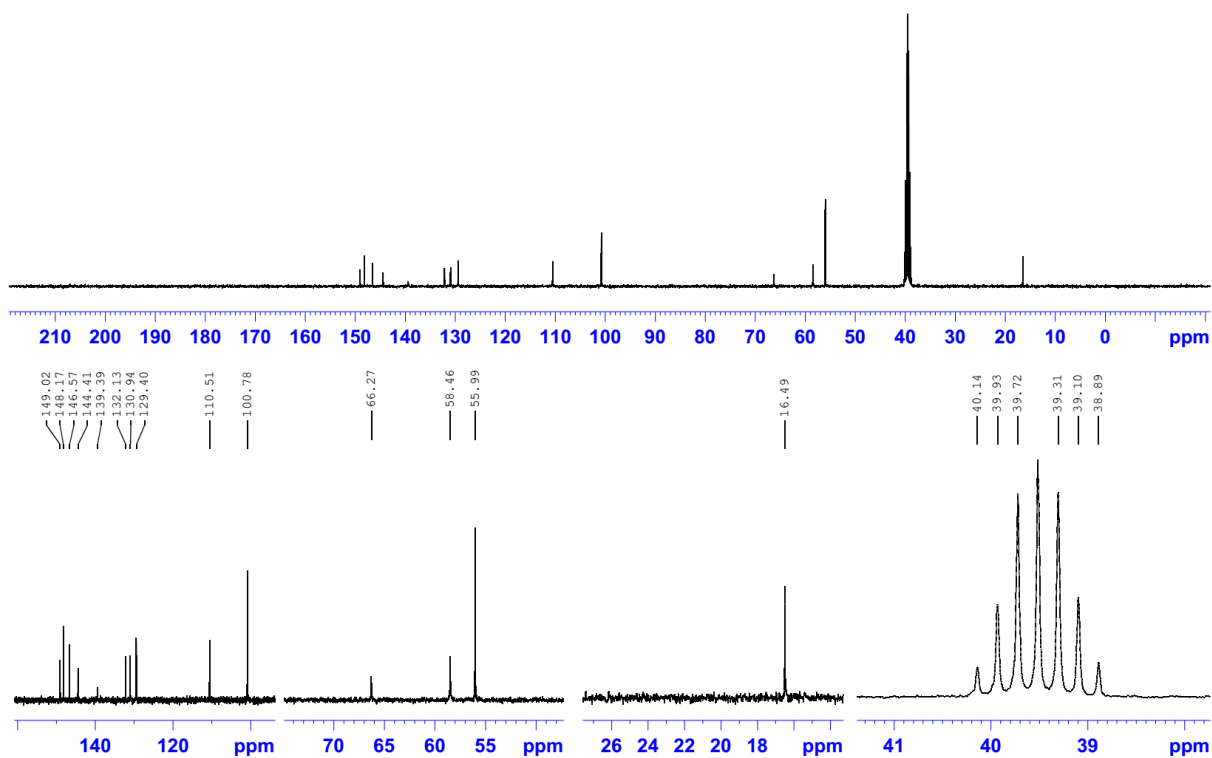
Compound 5 (top) and the Crude (bottom), 1H -NMR (400 MHz, DMSO- d_6)



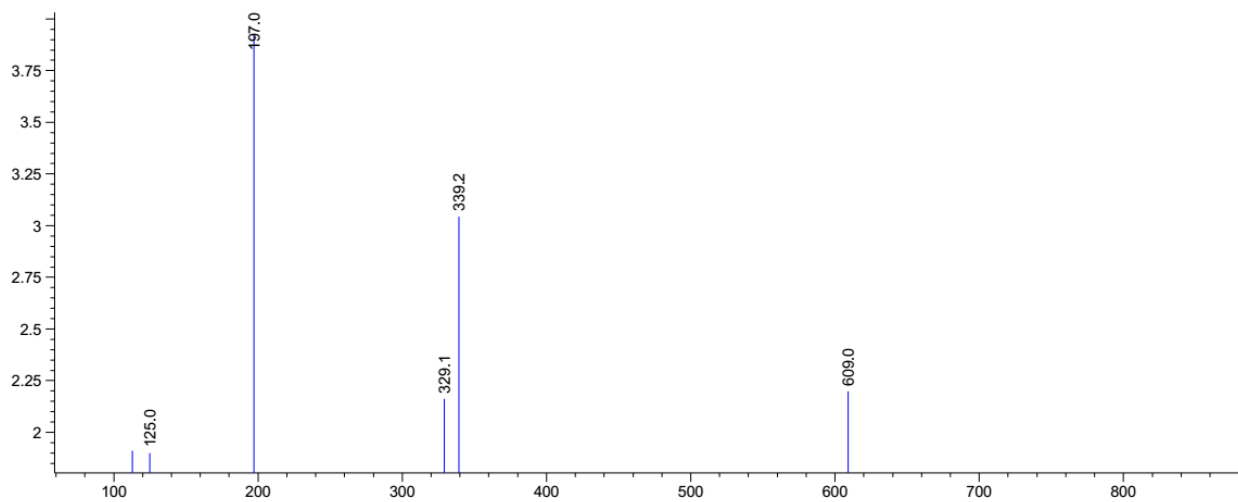
Compound 5, IR transmittance spectra (neat)



Compound 5, $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$)



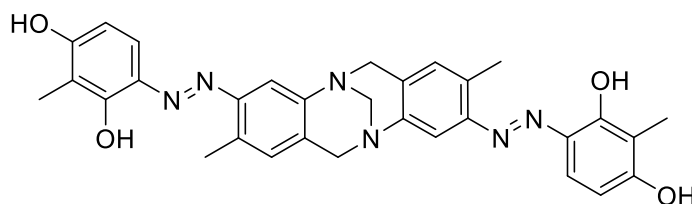
Compound 5, $^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$)



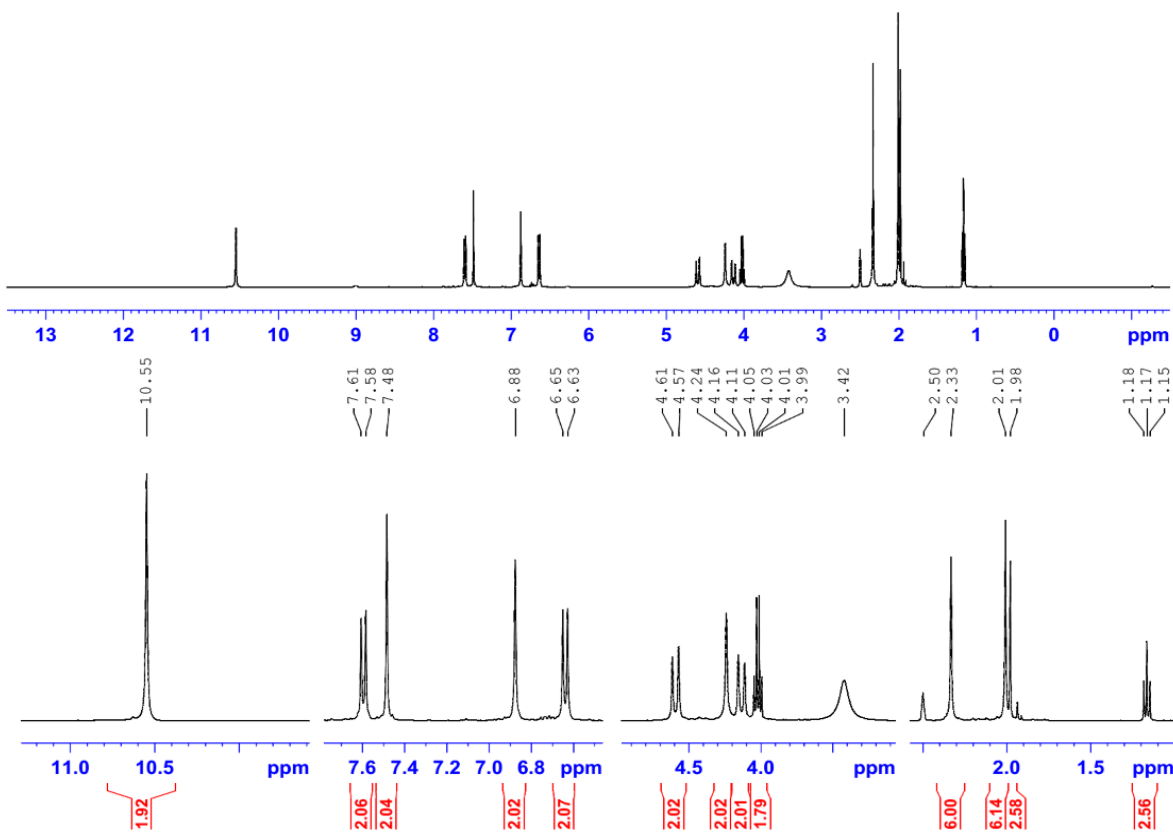
Compound 5, Mass spectra m/z (ESI negative)

6. Synthesis and Characterization of (±)-6

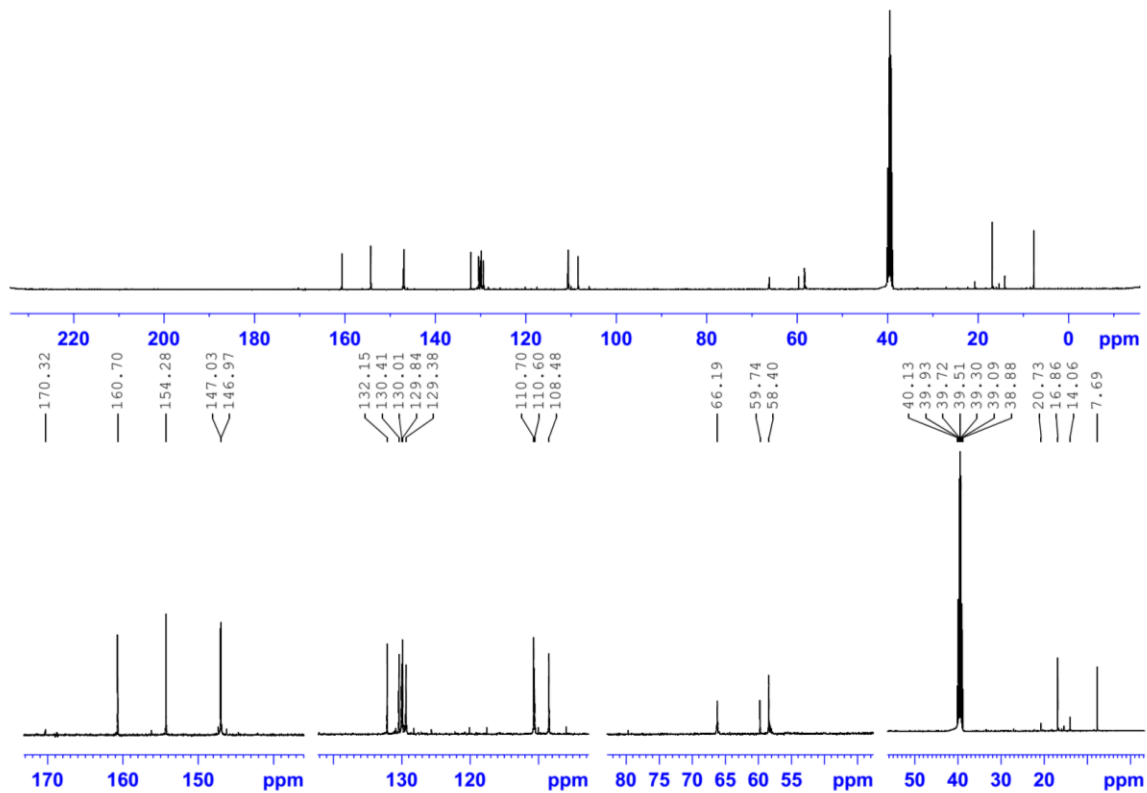
4,4'-((1E,1'E)-(2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-diyl)bis(diazene-2,1-diyl))bis(2-methylbenzene-1,3-diol)



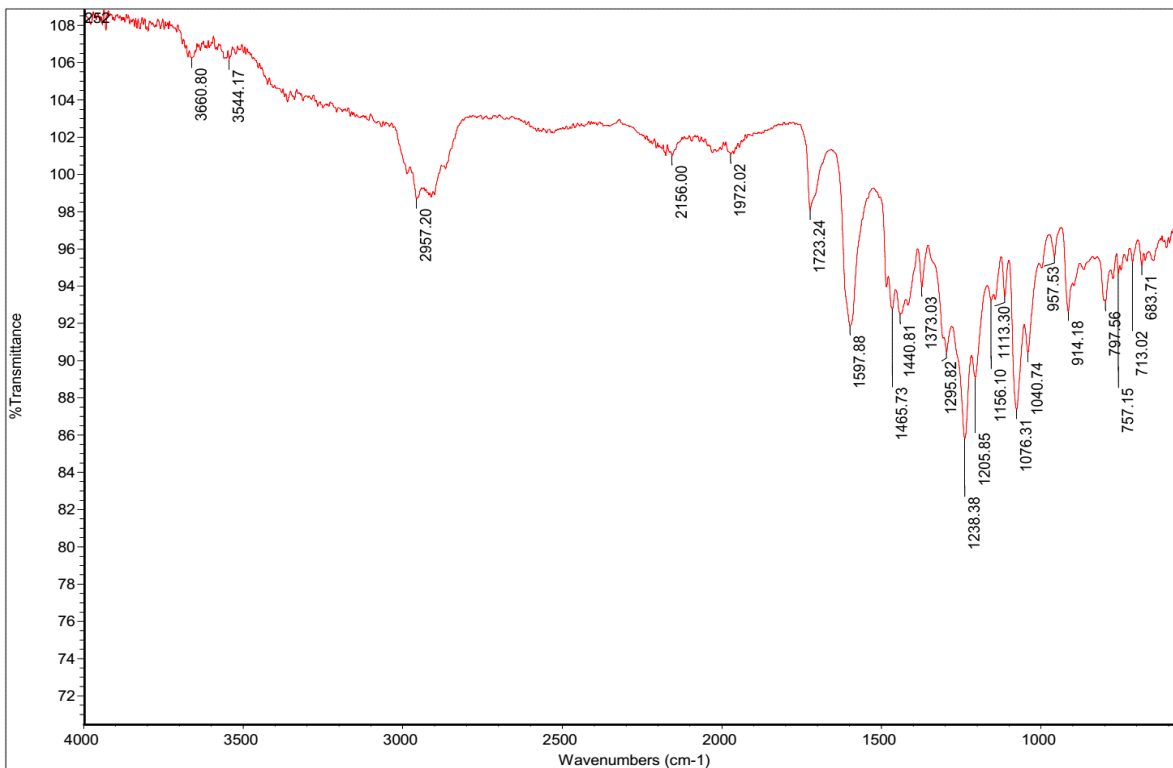
Hünlich's base (0.56 g, 2.0 mmol, 1.0 eq.) was dissolved in H₂SO₄ (6.5%, 30 mL, aq.) at room temperature, then cooled down to -5°C by placing the reaction container in an ice/acetone bath. A sodium nitrite solution (0.30 g, 4.4 mmol, 2.2 eq.) in cold water (5 mL) was dropped into the reaction flask and stirred for 30 minutes. The resulting yellowish solution was poured into a prepared solution of 2-methyl resorcinol (0.52 g, 4.2 mmol, 2.1 eq.) and Na₂CO₃ (2.0 g) in 100 mL of ice-cold water. Stirring was continued for 2 h at 0°C meanwhile two more grams of Na₂CO₃ was gradually added. Afterwards, a dark orange precipitate was extracted from the aqueous mixture (pH=7) by EtOAc (3 x 50 ml). The organic layers were combined, dried over MgSO₄ and evaporated to dryness (0.89 g, 1.62 mmol, 80%). Chemical Formula: C₃₁H₃₀N₆O₄, Molecular Weight: 550.62, R_f: 0.5 (EtOAc/ DCM = 50% v/v) silica gel. ¹H-NMR (400 MHz, DMSO-*d*₆) δ [ppm]: 2.01 (s, 6H, 2 × -CH₃), 2.33 (s, 6H, 2 × -CH₃), 4.13 (d, *J* = 17.3 Hz, 2H, H-6a, H-12a), 4.24 (s, 2H, -N-CH₂-N-), 4.59 (d, *J* = 17.3 Hz, 2H, H-6b, H-12b), 6.64 (d, *J* = 8.85 Hz, 2H, CH), 6.88 (s, 2H, H-1, H-7), 7.48 (s, 2H, H-4, H-10), 7.59 (d, 2H, *J* = 8.80 Hz, CH), 10.55 (s, 2H, OH). ¹³C-NMR (100 MHz, DMSO-*d*₆) δ [ppm]: 7.69, 16.86, 58.40, 66.19, 108.48, 110.60, 110.70, 129.38, 129.84, 130.01, 130.41, 132.15, 146.97, 147.03, 154.28 and 160.70. IR: (Neat) ν_{max} [cm⁻¹] = 3365, 3544, 2981, 1723, 1595, 1484, 1238, 1076 and 914. MS (Acetonitrile 48%, isopropyl alcohol 48%, MeOH 4%): (ESI positive) calc. for [C₃₁H₃₁N₆O₄]⁺: [M+H]⁺ 551.23, found 551.2. (ESI negative) calc. for [C₃₁H₂₉N₆O₄]⁻: [M-H]⁻ 549.23, found 549.2. UV-Vis: (EtOAc) λ (lgε) = 396nm (4.6). Anal. calcd: C, 67.62; H, 5.49; N, 15.26; O, 11.62. found: C, 68.01; H, 5.81; N, 14.98.



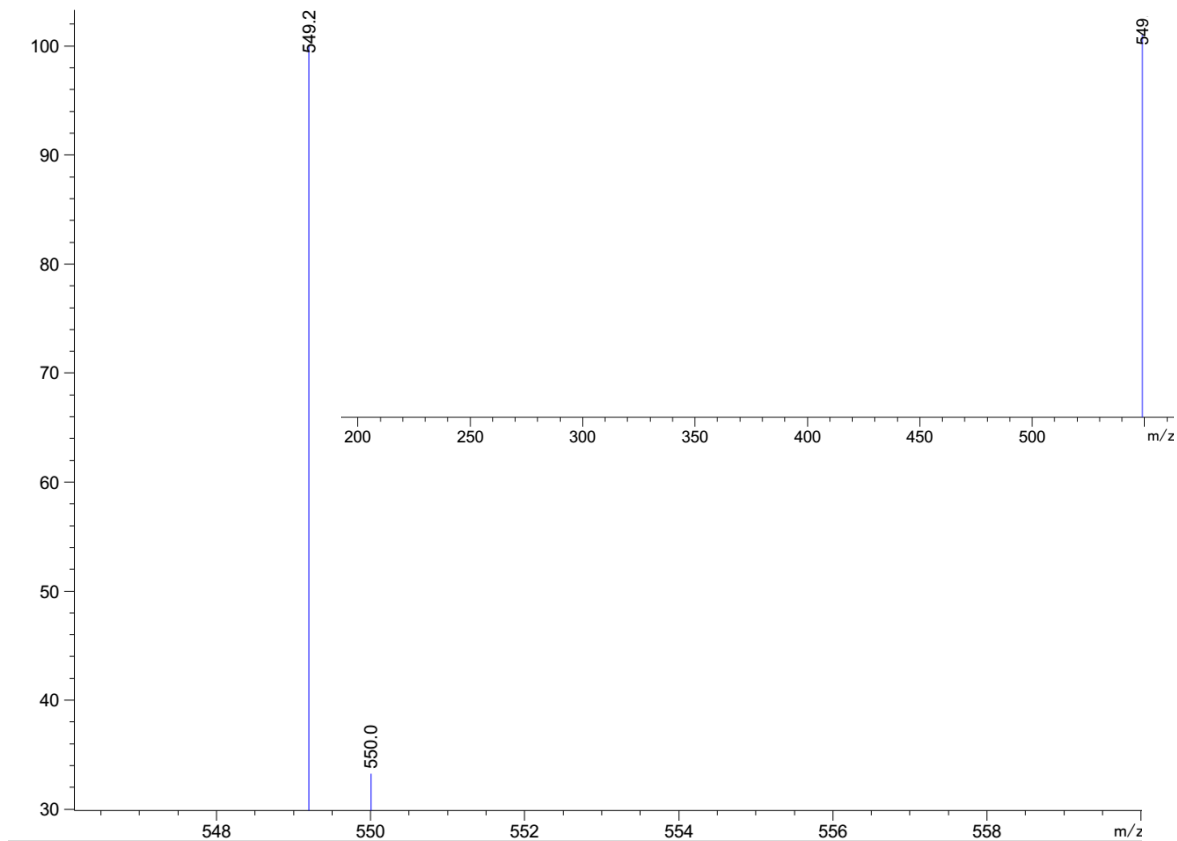
Compound 6, $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$)



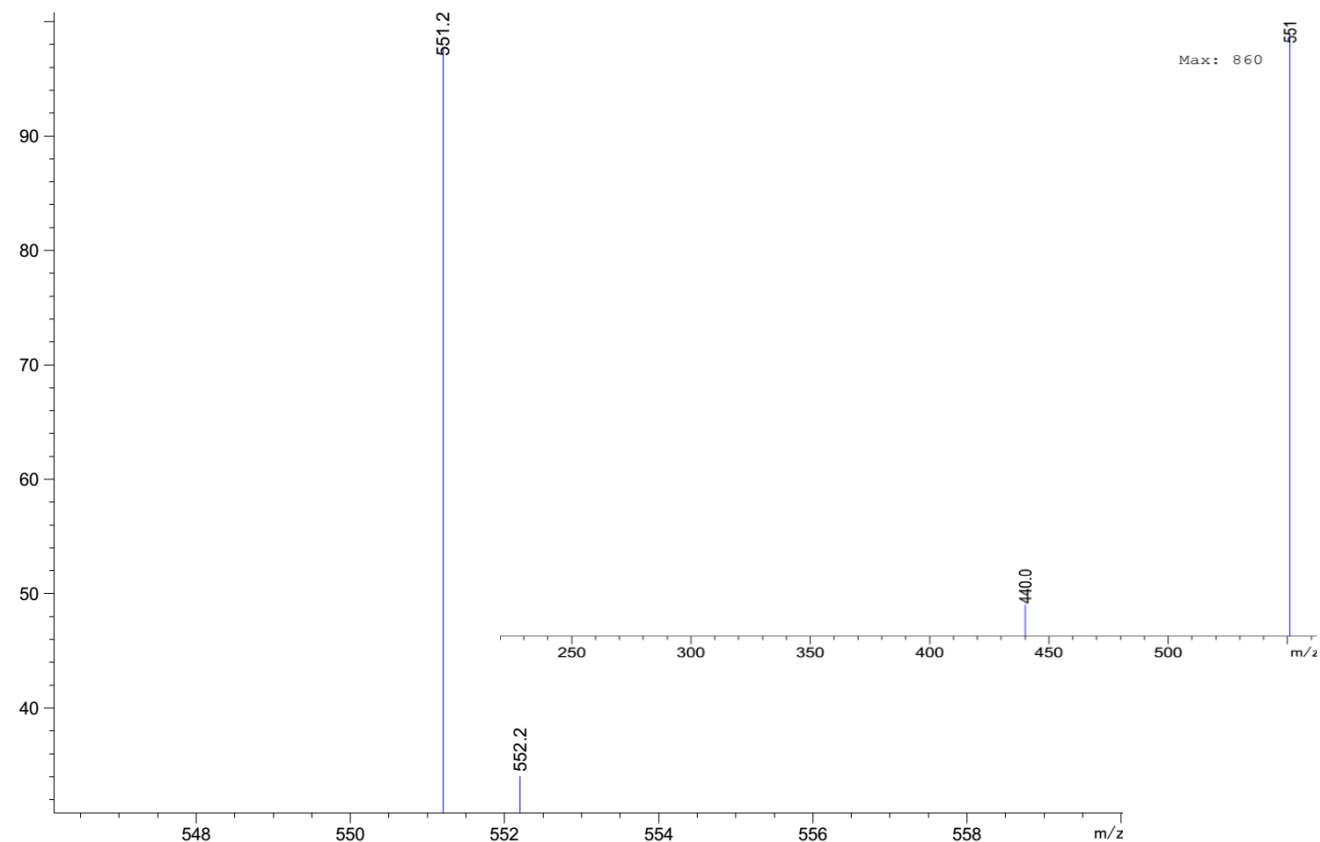
Compound 6, $^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$)



Compound 6, IR transmittance spectra (neat)



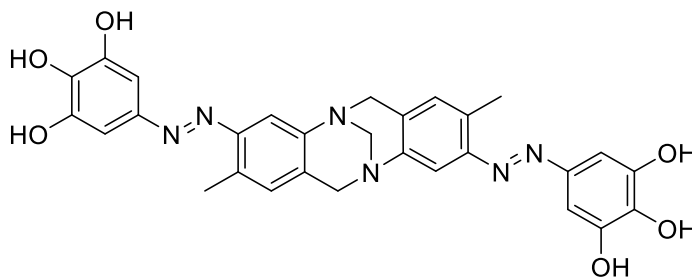
Compound 6, Mass spectra ESI (negative)



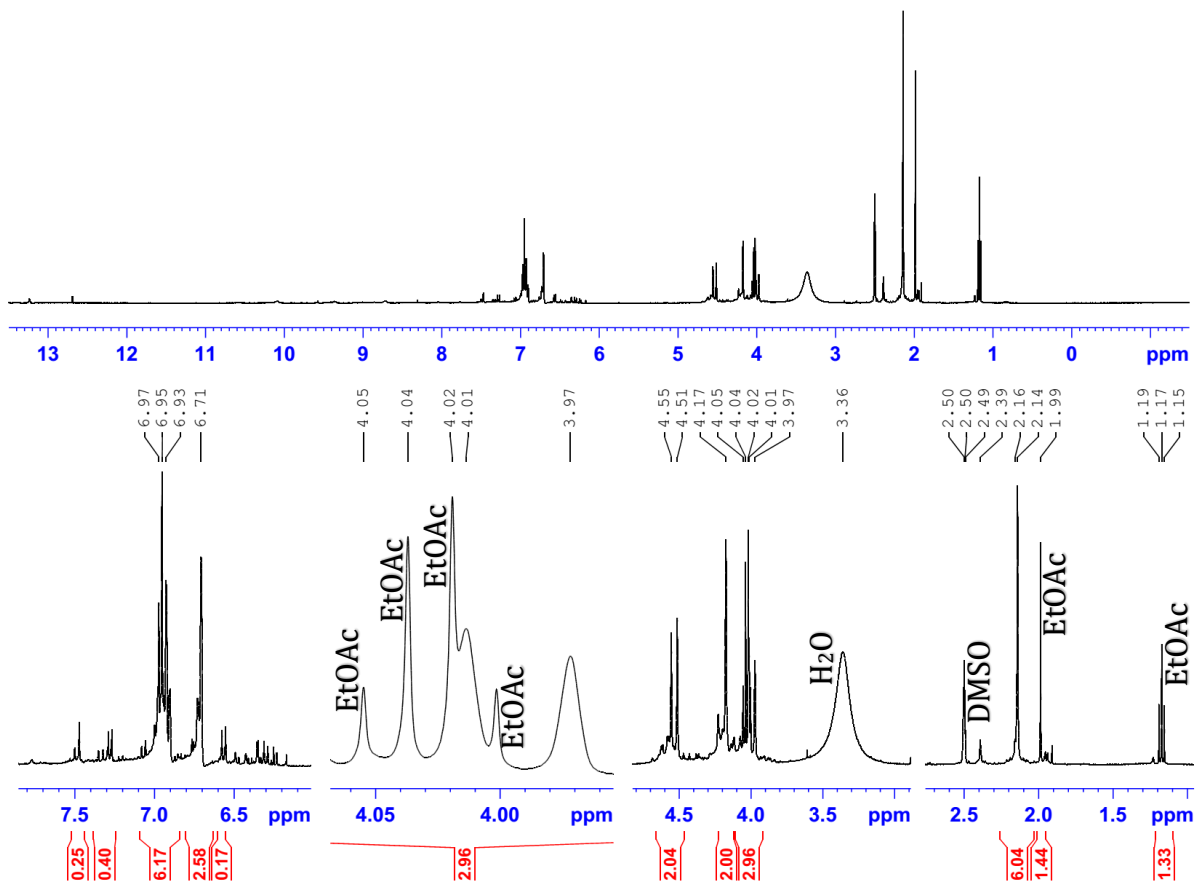
Compound 6, Mass spectra ESI (positive)

7. Synthesis and Characterization of (±)-7

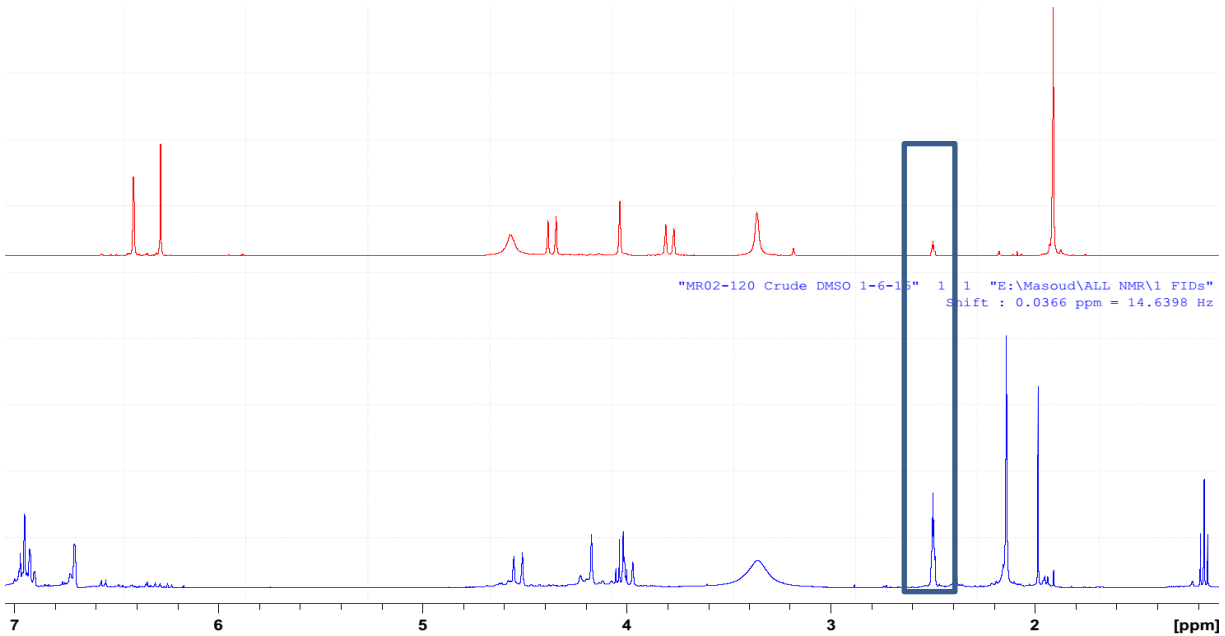
5,5'-((1E,1'E)-(2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-diyl)bis(diazene-2,1-diyl))bis(benzene-1,2,3-triol)



Hünlich's base (0.56 g, 2.0 mmol, 1.0 eq.) was dissolved in H₂SO₄ (6.5%, 30 mL) at room temperature, then cooled down to -5°C by placing the reaction container in ice/acetone bath. A sodium nitrite solution (0.30 g, 4.4 mmol, 2.2 eq.) in cold water (5 mL) was dropped into the reaction flask and stirred for 30 minutes. The resulting yellowish solution was poured into a freshly prepared solution of pyrogallol (1.0 g, excess) and Na₂CO₃ (2.0 g) in 100 mL of ice-cold water. The stirring continued for 4 h at 0°C meanwhile two more grams of Na₂CO₃ was gradually added. Afterwards, the reaction mixture pH was set between 4-5 by adding HCl. Then 3 grams of NaCl were added, and the crude was extracted by EtOAc (5x30 ml). The organic layers were combined, dried over MgSO₄ and evaporated under vacuum to obtain a brown solid (1.1 g). Chemical Formula: C₂₉H₂₆N₆O₆, Molecular Weight: 554.56, R_f: N/A. ¹H-NMR (400 MHz, CDCl₃) δ [ppm] : 2.14 (s, 6H, 2 × -CH₃), 4.00 (d, J = 16.8 Hz, 2H, H-6a, H-12a), 4.17 (s, 2H, -N-CH₂-N-), 4.53 (d, J = 16.6 Hz, 2H, H-6b, H-12b), 6.7 (s, 2H, CH), 6.90-7.00 (m, 6H, CH). Anal. calcd: C, 62.81; H, 4.73; N, 15.15; O, 17.31. found: C, 69.60; H, 6.53; N, 7.98.



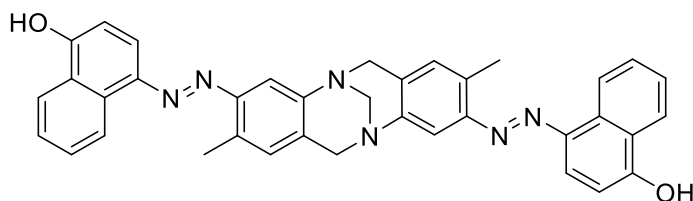
7th Reaction's Crude, ¹H-NMR (400 MHz, DMSO-*d*₆)



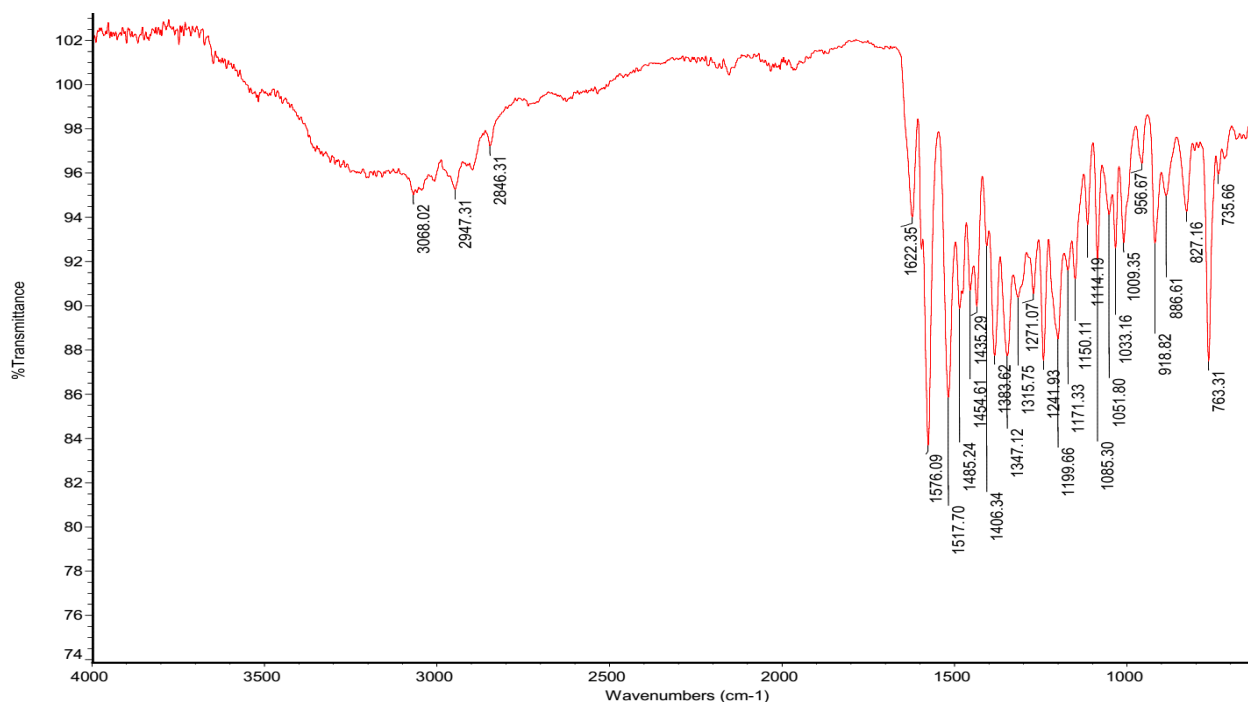
Comparative ¹H-NMR (400 MHz, DMSO-*d*₆, matched at the DMSO peak)
Starting material (top) and the 7's crude (bottom)

8. Synthesis and Characterization of (\pm)-**8**

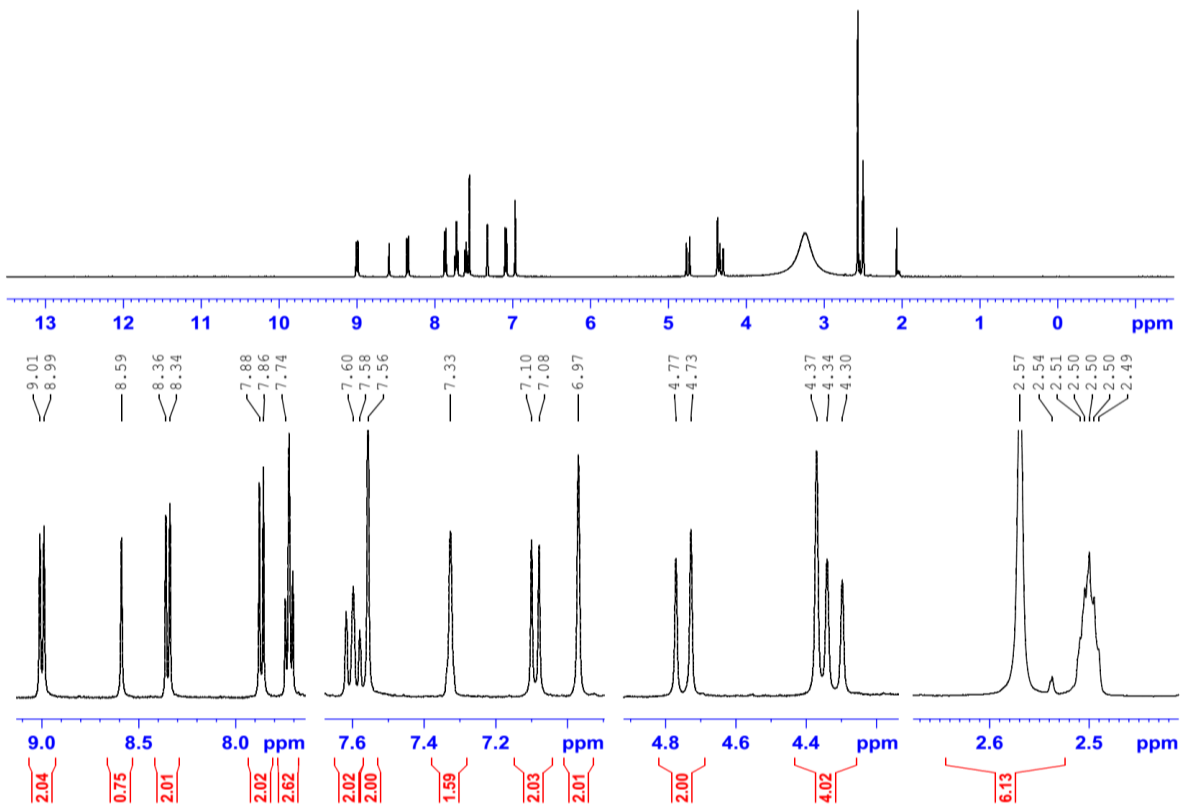
4,4'-((1E,1'E)-(2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-diyl)bis(diazene-2,1-diyl))bis(naphthalen-1-ol)



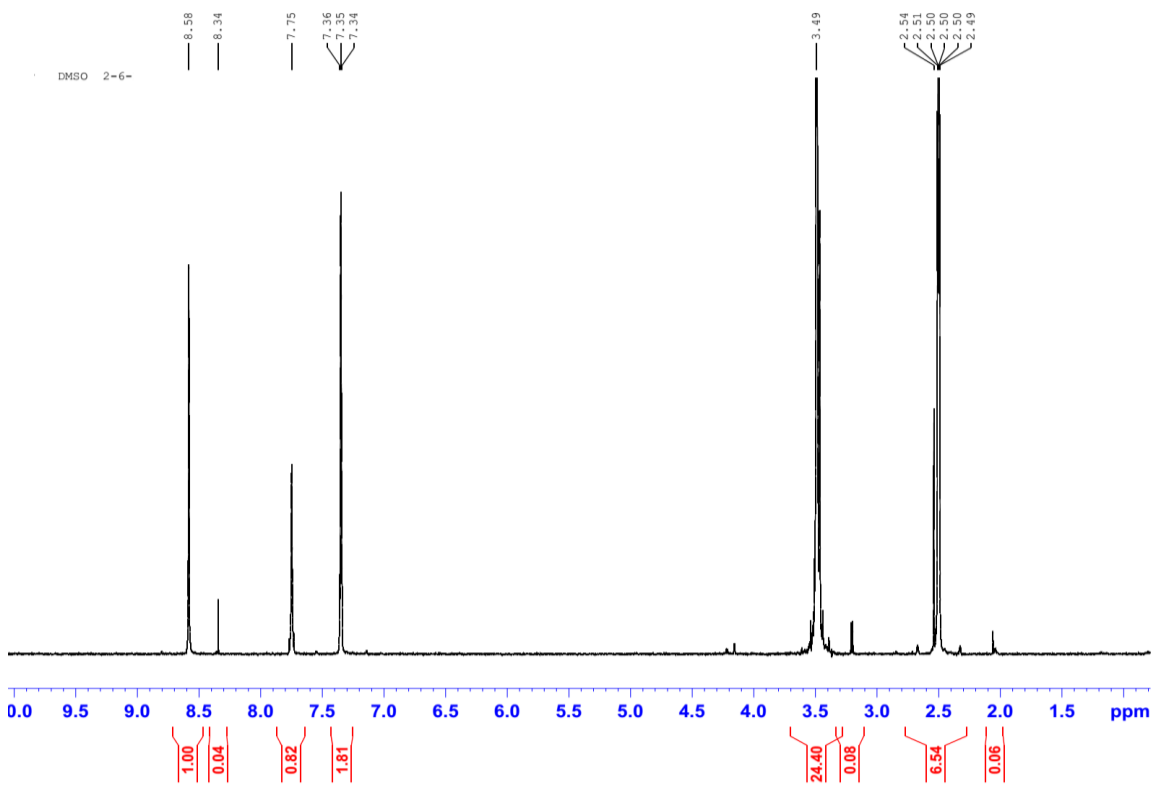
Hünlich's base (0.56 g, 2.0 mmol, 1.0 eq.) was dissolved in H₂SO₄ (6.5%, 30 mL, aq.) at room temperature, then cooled down to -5°C by placing the reaction container in an ice/acetone bath. A sodium nitrite solution (0.30 g, 4.4 mmol, 2.2 eq., in 5 mL of cold water) was dropped into the reaction flask over 10 minutes. After continuing the stirring for 25 more minutes the resulting yellowish solution was poured into a freshly prepared solution of 1-naphthol (0.61 g, 4.2 mmol, 2.1 eq.) and Na₂CO₃ (2.0 g) in 100 mL of ice-cold water. The reaction mixture was stirred for 4 h at 0°C and two more grams of Na₂CO₃ was gradually added into it. Afterwards, NaCl (3.0 g) was added and a brown precipitate was extracted by EtOAc (3 x 80 mL) from the aqueous mixture. The organic layers were combined, dried over MgSO₄ and evaporated to the dryness to obtain **8** (0.82 g, 1.4 mmol, 70%). Chemical Formula: C₃₇H₃₀N₆O₂, Molecular Weight: 590.69, R_f: 0.30 (EtOAc/ n-hexane = 40% v/v) silica gel. ¹H-NMR (80 °C, 400 MHz, DMSO-*d*₆) δ [ppm]: 2.57 (s, 6H, 2 x -CH₃), 4.32 (d, *J* = 17.5 Hz, 2H, H-6a, H-12a), 4.37 (s, 2H, -N-CH₂-N-), 4.75 (d, *J* = 17.4 Hz, 2H, H-6b, H-12b), 6.97 (s, 2H, CH), 7.08 (d, *J* = 8.5 Hz, 2H, CH), 7.56 (s, 2H, CH), 7.60 (t, *J* = 7.8 Hz, 2H, CH), 7.72 (t, *J* = 7.9 Hz, 2H, CH), 7.86 (d, *J* = 8.4 Hz, 2H, CH), 8.35 (d, 2H, *J* = 8.5 Hz, CH), 8.99 (d, 2H, *J* = 8.5 Hz, CH). ¹³C-NMR (80 °C, 100 MHz, DMSO-*d*₆) δ [ppm]: 16.09, 58.27, 66.27, 108.29, 110.99, 114.29, 122.04, 122.37, 124.40, 124.81, 127.16, 128.88, 130.19, 132.10, 146.47, 149.87 and 205.43. IR: (Neat) ν_{max} [cm⁻¹] = 3412, 3068, 2947, 2846, 1622, 1576, 1383, 1199, 1033, 912 and 763. MS (EtOH 60%, EtOAc 40%): (ESI positive) calc. for [C₃₇H₃₁N₆O₂]⁺: [M+H]⁺ 591.24, found 591.2. (ESI negative) calc. for [C₃₇H₂₉N₆O₂]⁻: [M-H]⁻ 589.24, found 589.2. UV-Vis: (EtOAc) λ (lgε) = 408nm (4.6). Anal.: calc. C, 75.24; H, 5.12; N, 14.23; found: C, 75.39; H, 5.23; N, 14.49.



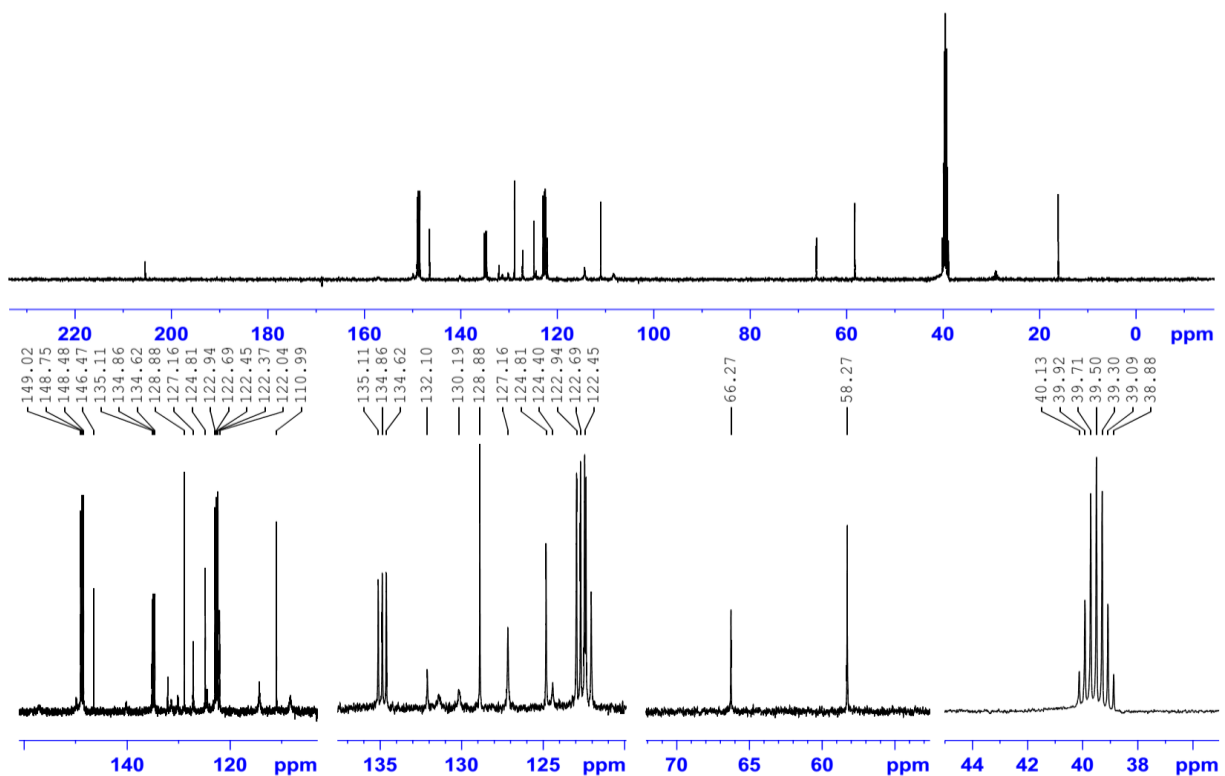
Compound **8**, IR transmittance spectra (neat)



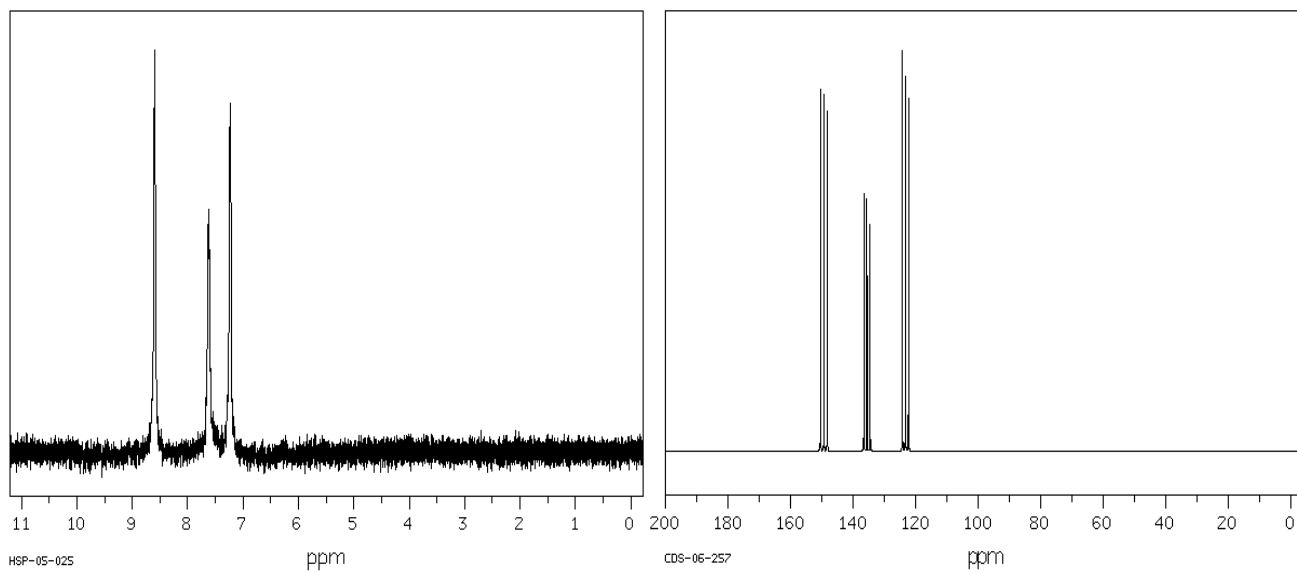
Compound 8, $^1\text{H-NMR}$ (353°K, 400 MHz, $\text{DMSO-}d_6$ and $\text{Pyridine-}d_5$)



$^1\text{H NMR}$ 400MHz, $\text{Pyridine-}d_5$ in $\text{DMSO-}d_6$

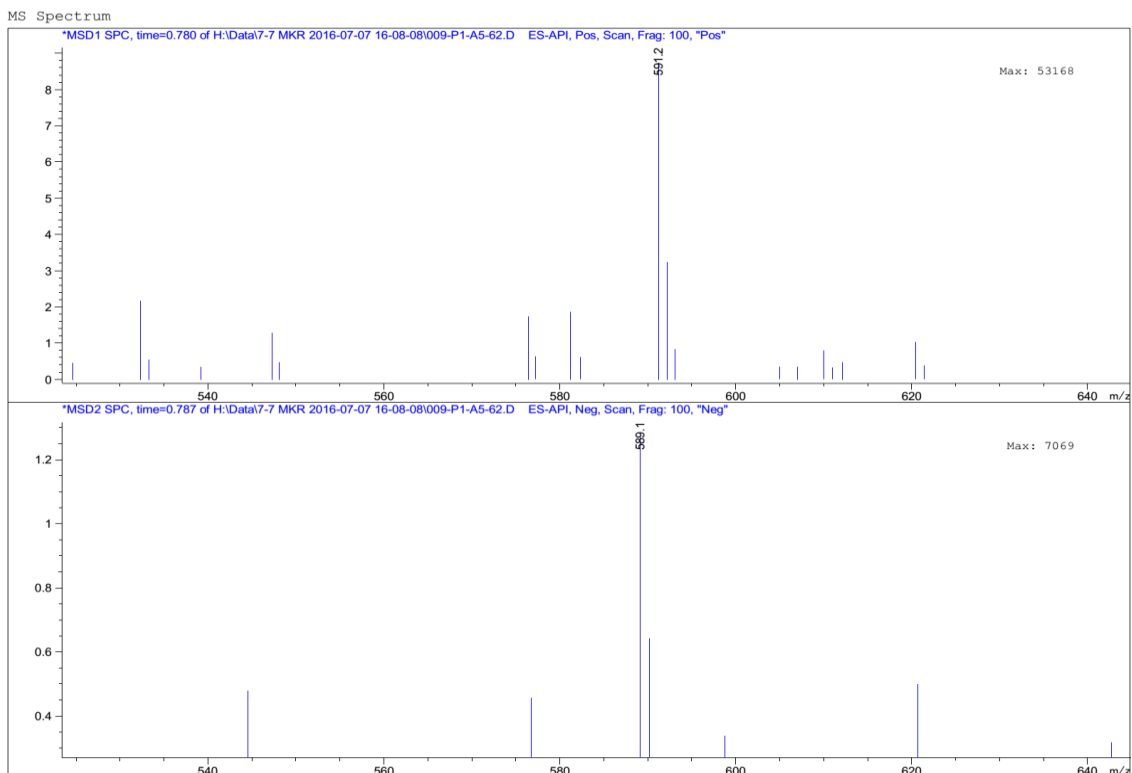


Compound 8, ^{13}C -NMR (353°K, 100 MHz, $\text{DMSO-}d_6$ and $\text{Pyridine-}d_5$)



^1H - (Left, 89.56 MHz) and ^{13}C -NMR (Right, 25.16 MHz) spectra*, Neat $\text{pyridine-}d_5$

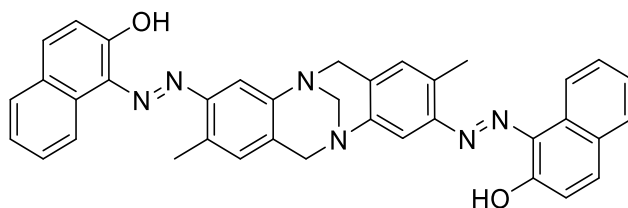
*The spectral data adopted from: <http://sdb.sdb.aist.go.jp> (National Institute of Advanced Industrial Science and Technology, 10/23/2016)



Compound 8, Mass Spectra ESI+ (top) and ESI- (bottom)

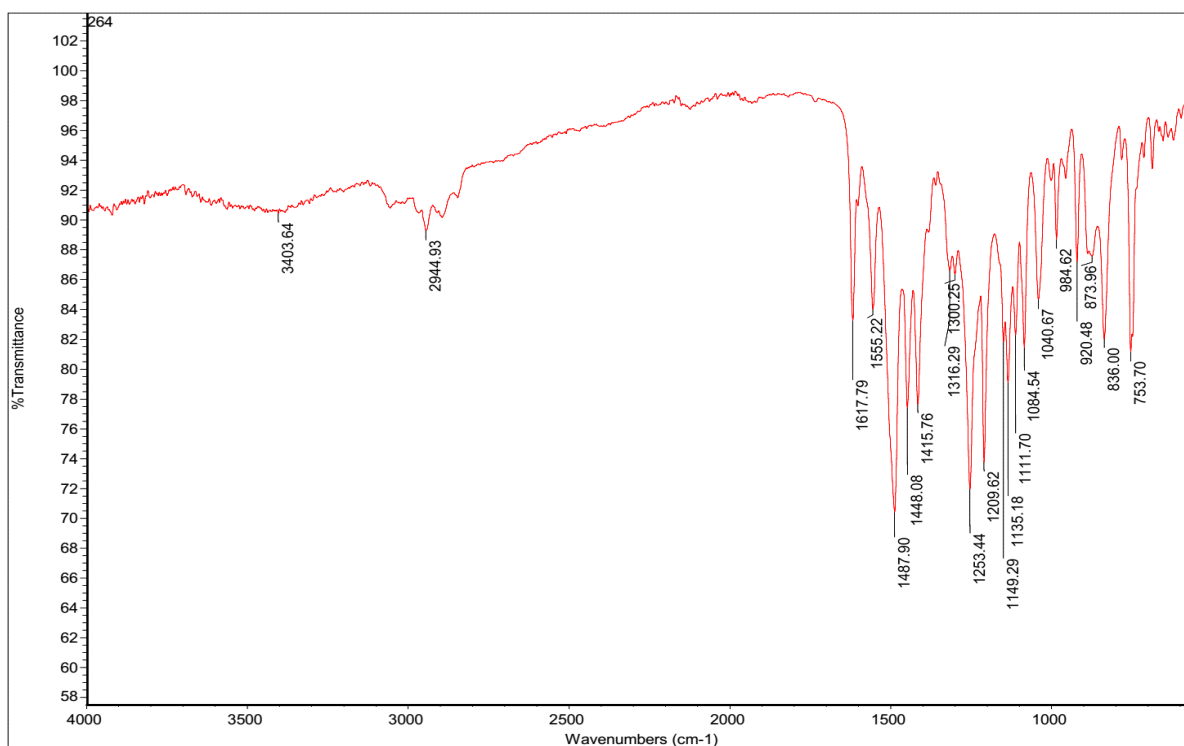
9. Synthesis and Characterization of (\pm)-9

1,1'-((1E,1'E)-(2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-diyl)bis(diazene-2,1-diyl))bis(naphthalen-2-ol)

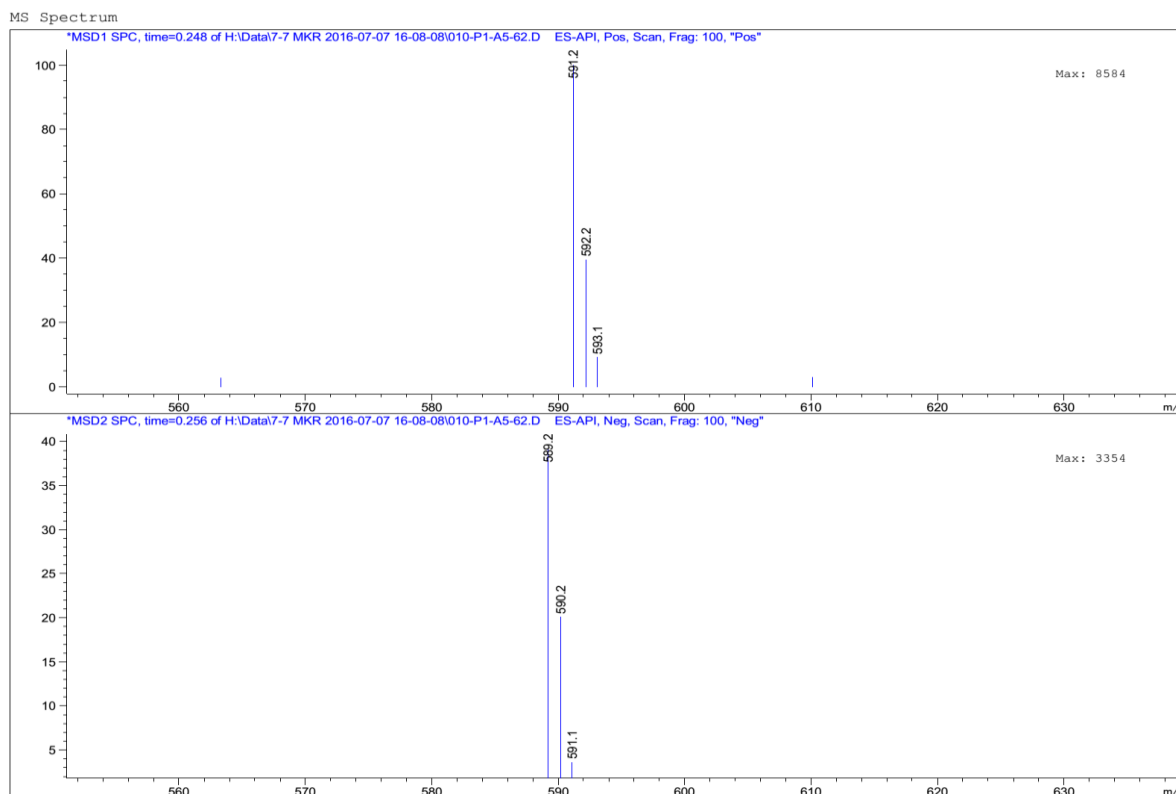


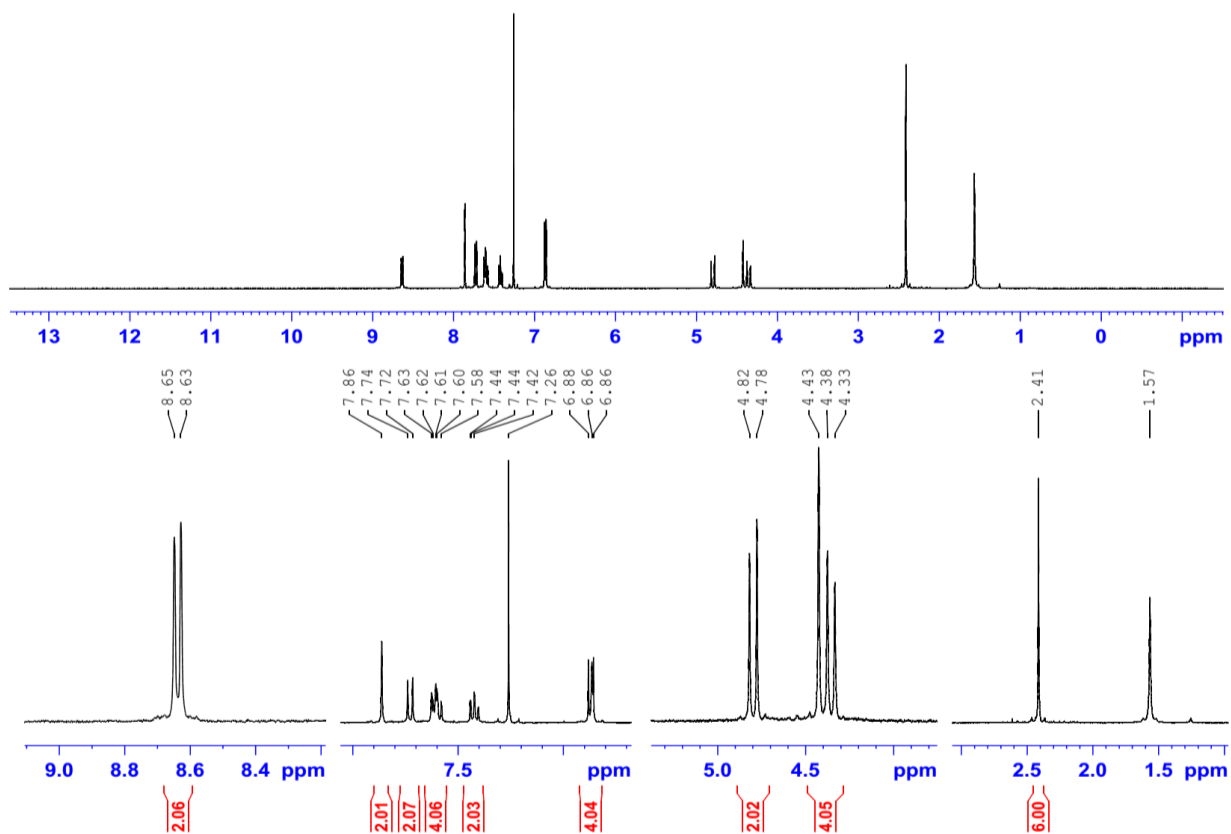
Hünlich's base (0.56 g, 2.0 mmol, 1.0 eq.) was dissolved in H₂SO₄ (6.5%, 30 mL, aq.) at room temperature, then cooled down to -5°C by placing the reaction container in an ice/acetone bath. A sodium nitrite solution (0.30 g, 4.4 mmol, 2.2 eq., in cold water 5 mL) was dropped into the reaction flask over 10 minutes. The stirring continued for 25 more minutes and then the resulting yellowish solution was poured into a fresh solution of 2-naphthol (0.61 g, 4.2 mmol, 2.1 eq.) and Na₂CO₃ (2.0 g) in 100 mL of ice-cold water. The stirring continued for 4 h at 0°C meanwhile two more grams of Na₂CO₃ were gradually added. Afterwards, NaCl (3.0 g) was added and the aqueous mixture was acidified by addition of 5% H₂SO₄ (pH=3) to form a hot-pink precipitate which finally was collected by vacuum filtration. The precipitate was rinsed with distilled water and then desiccated under high-vacuum to obtain **9** (0.88 g, 1.49 mmol, 75%). Chemical Formula: C₃₇H₃₀N₆O₂, Molecular Weight: 590.69, **R_f**: 0.50 (EtOAc/ n-hexane = 40% v/v) silica gel. **¹H-NMR** (400 MHz, CDCl₃) δ [ppm] : 2.41 (s, 6H, 2 \times -CH₃), 4.35 (d, J = 17.0 Hz, 2H, H-6a, H-12a), 4.42 (s, 2H, -N-CH₂-N-), 4.79 (d, J = 17.3 Hz, 2H, H-6b, H-12b), 6.85-6.88 (m, 4H, CH), 7.40-7.44 (m, 2H, CH), 7.57-7.62 (m, 4H, CH), 7.72 (d, 2H, J = 9.5 Hz, CH), 7.86 (s, 2H, CH), 8.63 (d, 2H, J = 8 Hz, CH). **¹³C-NMR** (100 MHz, CDCl₃) δ [ppm]: 17.18, 59.11, 67.18, 109.75, 111.87, 121.93, 125.14, 125.20, 125.99, 127.08, 128.18, 128.84, 129.07, 129.59, 130.87, 133.68, 140.42, 142.15, 147.55 and 173.14. **IR**: (Neat) ν_{\max} [cm⁻¹] = 3403, 2944, 2925, 1617, 1555, 1487, 1448, 1415, 1253, 1209, 1135, 1084, 836 and 753. **MS** (EtOH 80%, EtOAc 20%): (ESI positive)

calc. for $[C_{37}H_{31}N_6O_2]^+$: $[M+H]^+$ 591.24, found 591.2. (ESI negative) calc. for $[C_{37}H_{29}N_6O_2]^-$: $[M-H]^-$ 589.24, found 589.2. **UV-Vis:** (EtOAc) λ ($\lg\epsilon$) = 493nm (4.4). Anal. calcd: C, 75.24; H, 5.12; N, 14.23; O, 5.42. found: C, 75.02; H, 5.03; N, 14.51.

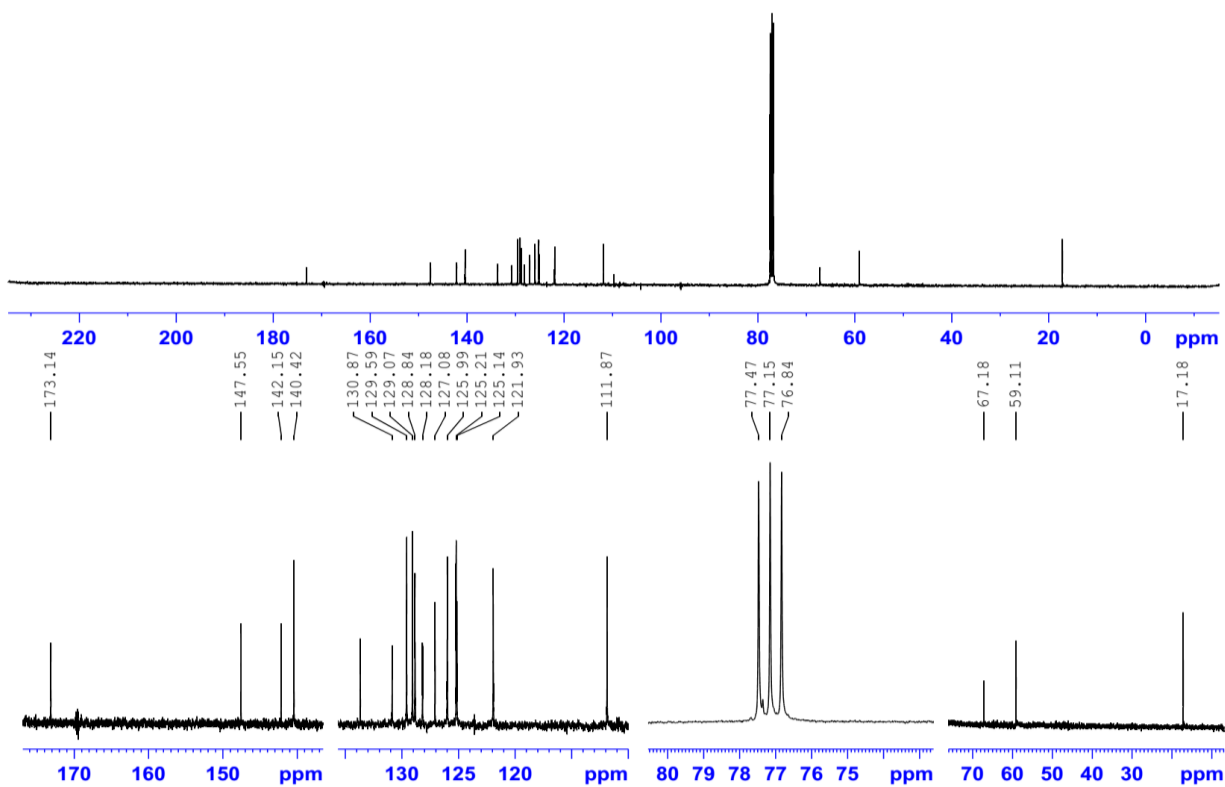


Compound 9, IR transmittance spectra (neat)





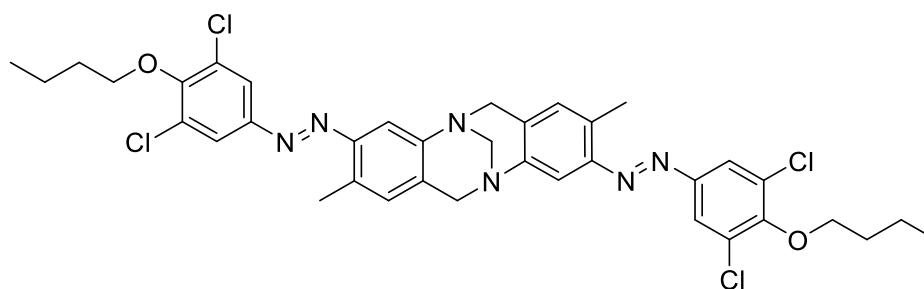
Compound 9, ¹H-NMR (400 MHz, CDCl₃)



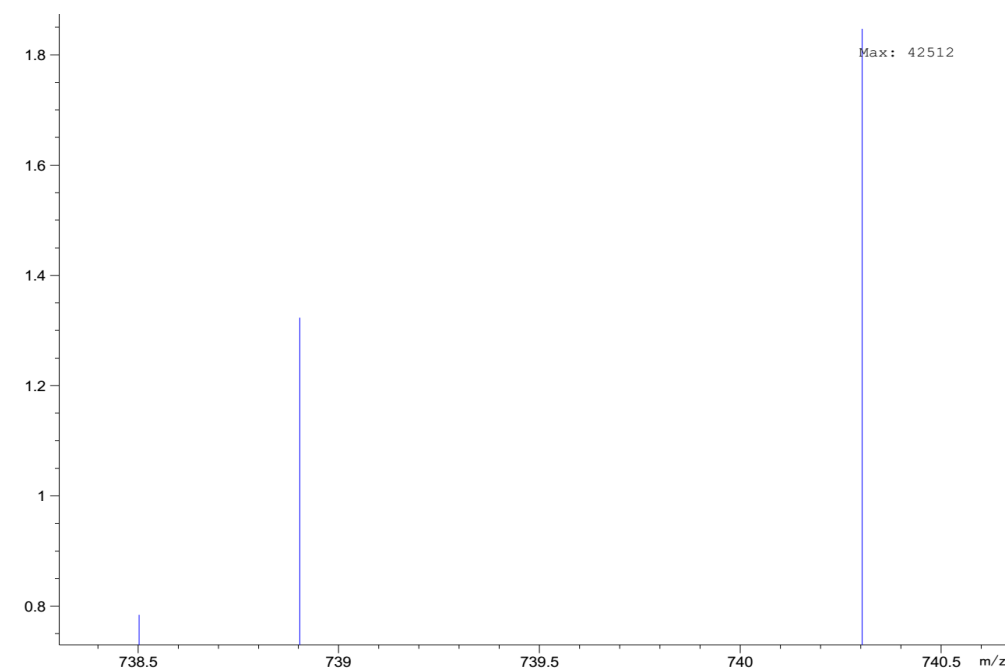
Compound 9, ¹³C-NMR (100 MHz, CDCl₃)

10. Synthesis and Characterization of (±)-1A

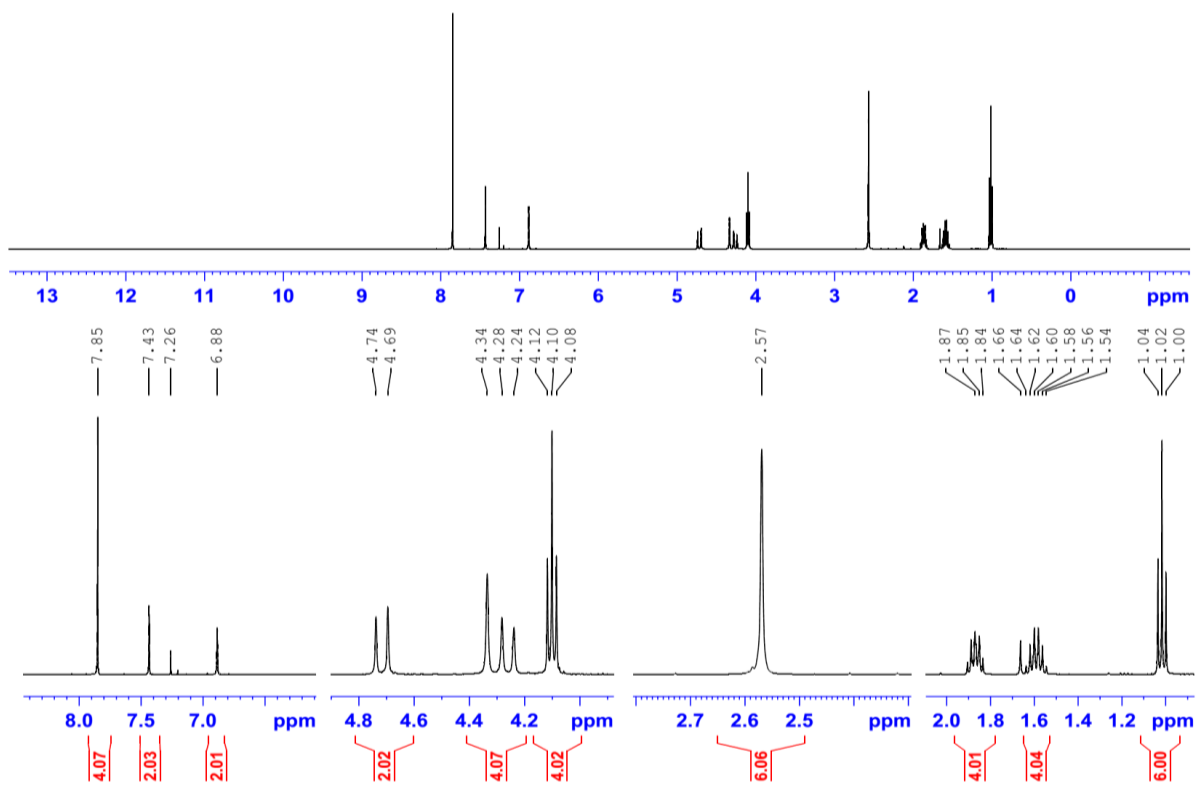
3,9-bis((E)-(4-butoxy-3,5-dichlorophenyl)diazenyl)-2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine



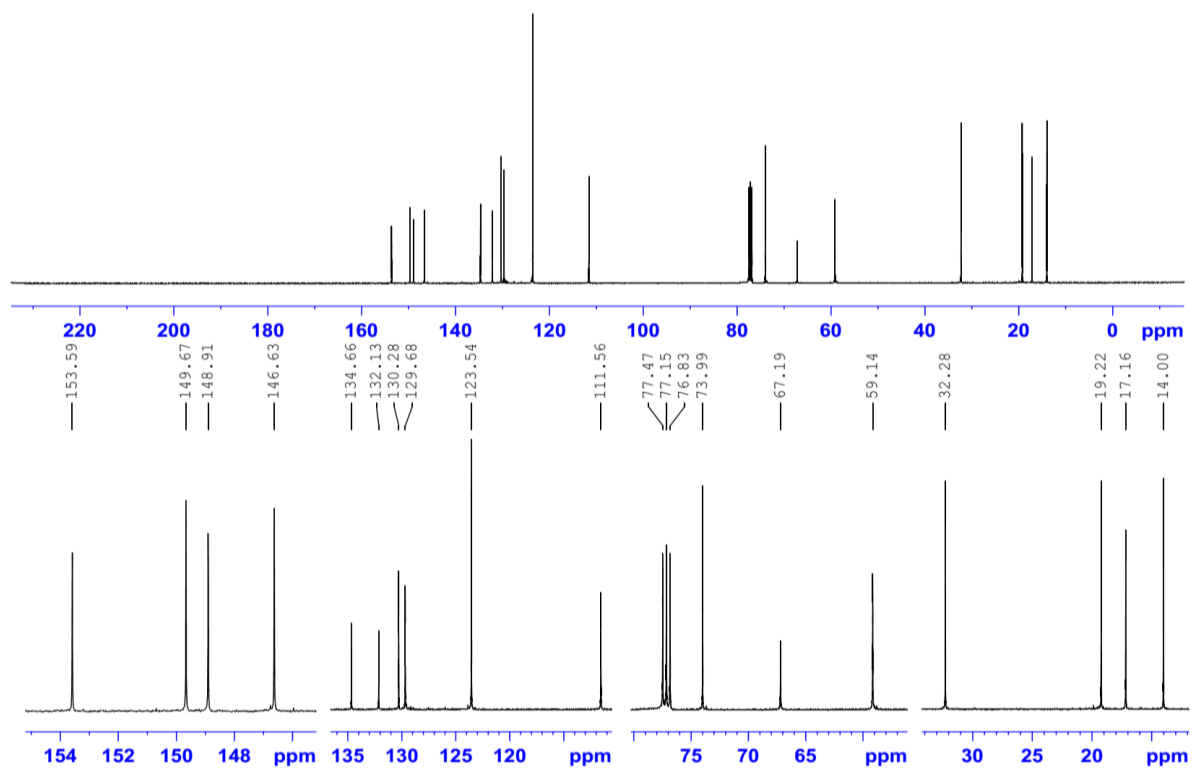
Compound **1** (0.31 g, 0.50 mmol, 1.0 eq.) and K₂CO₃ (0.55 g, 4 mmol) were mixed in dried acetone (5 mL) at room temperature for 15 minutes in a sealed round-bottom flask. Then, 1-iodobutane (0.24 g, 1.2 mmol, 2.4 eq.) was injected into the mixture and refluxed for 6 hours at 55°C in darkness. The reaction profile was monitored by TLC, which showed a single spot at the conclusion of the reaction. Then the resulting mixture was added to 50 ml of distilled water and the crude was extracted by EtOAc (3 x 30 ml). The organic layers were combined, dried over MgSO₄ and filtered. After solvent removal under reduced pressure, the solid residue was chromatographed to obtain a shiny orange solid **1A** (0.29 g, 0.39 mmol, 77%). Chemical Formula: C₃₇H₃₈Cl₄N₆O₂, Molecular Weight: 740.55, **R_f**: 0.5 (EtOAc/ n-hexane = 20% v/v) silica gel. **¹H-NMR** (400 MHz, CDCl₃) δ [ppm]: 1.02 (t, *J* = 7.6 Hz, 6H, CH₃), 1.59 (m, 4H, CH₂), 1.85 (m, 4H, CH₂), 2.57 (s, 6H, CH₃), 4.10 (t, *J* = 7.9 Hz, 4H, CH₂), 4.26 (d, *J* = 17.1 Hz, 2H, H-6a, H-12a), 4.34 (s, 2H, -N-CH₂-N-), 4.72 (d, *J* = 17.1 Hz, 2H, H-6b, H-12b), 6.88 (s, 2H, H-1, H-7), 7.43 (s, 2H, H-4, H-10), 7.85 (s, 4H, CH). **¹³C-NMR** (100 MHz, CDCl₃) δ [ppm]: 14.00, 17.16, 19.22, 32.28, 59.14, 67.19, 73.99, 111.56, 123.54, 129.68, 130.28, 132.13, 134.66, 146.63, 148.91, 149.67 and 153.59. **IR**: (Neat) ν_{max} [cm⁻¹] = 2929, 2858, 1561, 1482, 1447, 1381, 1254, 1233, 1081, 984, 930, 899, 802, 729. **MS** (Acetonitrile 45%, isopropyl alcohol 45%, EtOAc 5%, MeOH 5%): (ESI positive) calc. for [C₃₇H₃₉Cl₄N₆O₂]⁺: [M+H]⁺ 739.18, found 738.9 and 740.3. **UV-Vis**: (EtOAc) λ (lgε) = 347 nm (4.5). Anal. calcd: C, 60.01; H, 5.17; Cl, 19.15; N, 11.35; O, 4.32. found: C, 59.71; H, 5.36; N, 11.51.



Compound 1A, Mass spectra (ESI positive)



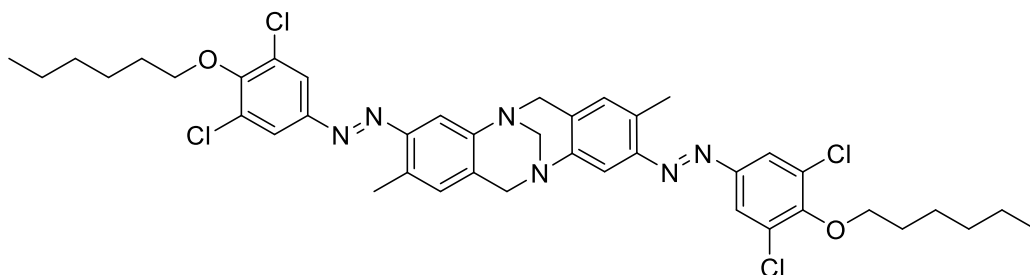
Compound 1A, ¹H-NMR (400 MHz, CDCl₃)



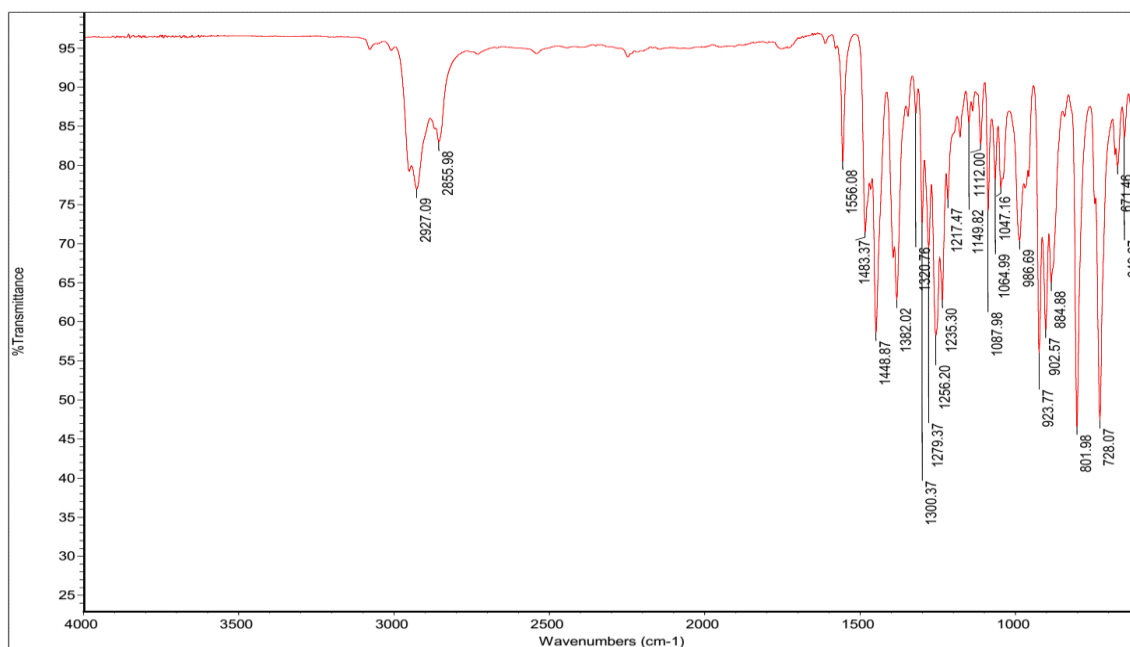
Compound 1A, ¹³C-NMR (100 MHz, CDCl₃)

11. Synthesis and Characterization of (±)-1B

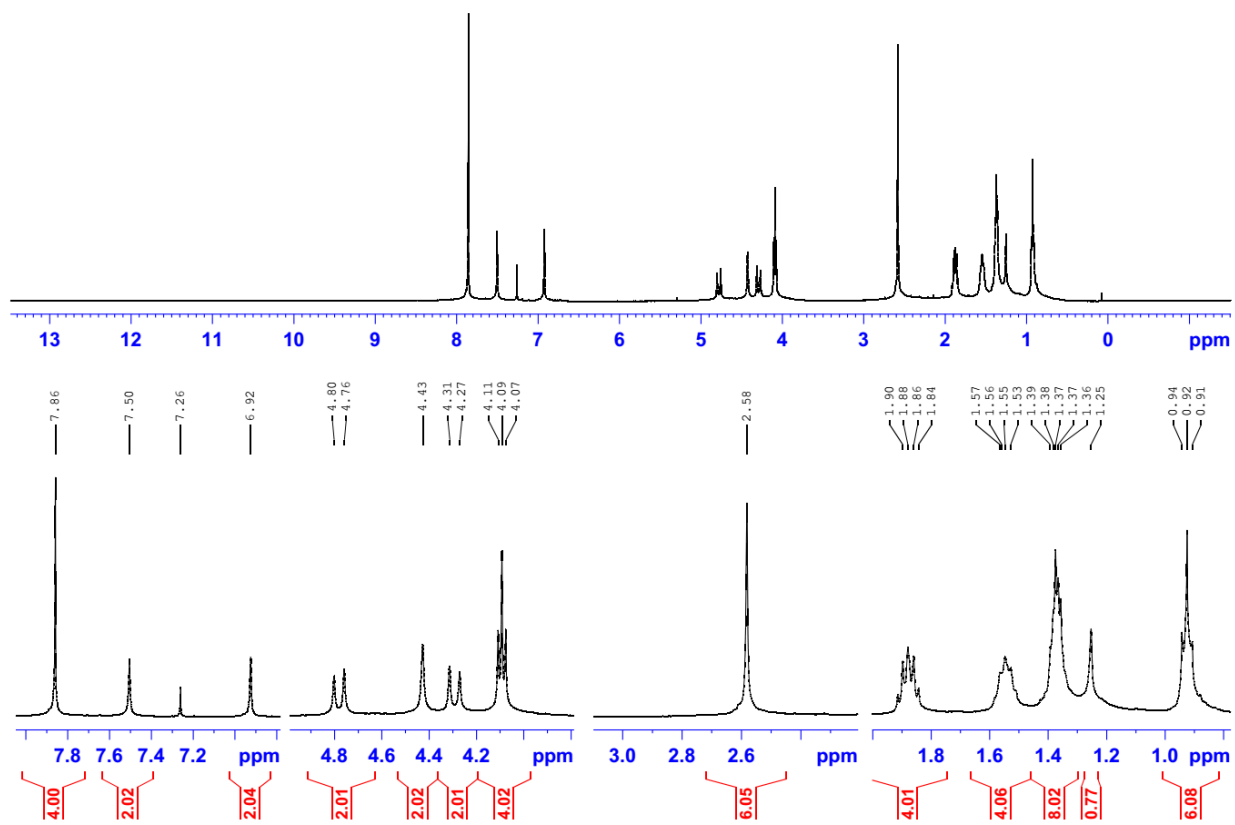
3,9-bis((E)-(3,5-dichloro-4-(hexyloxy)phenyl)diazenyl)-2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine



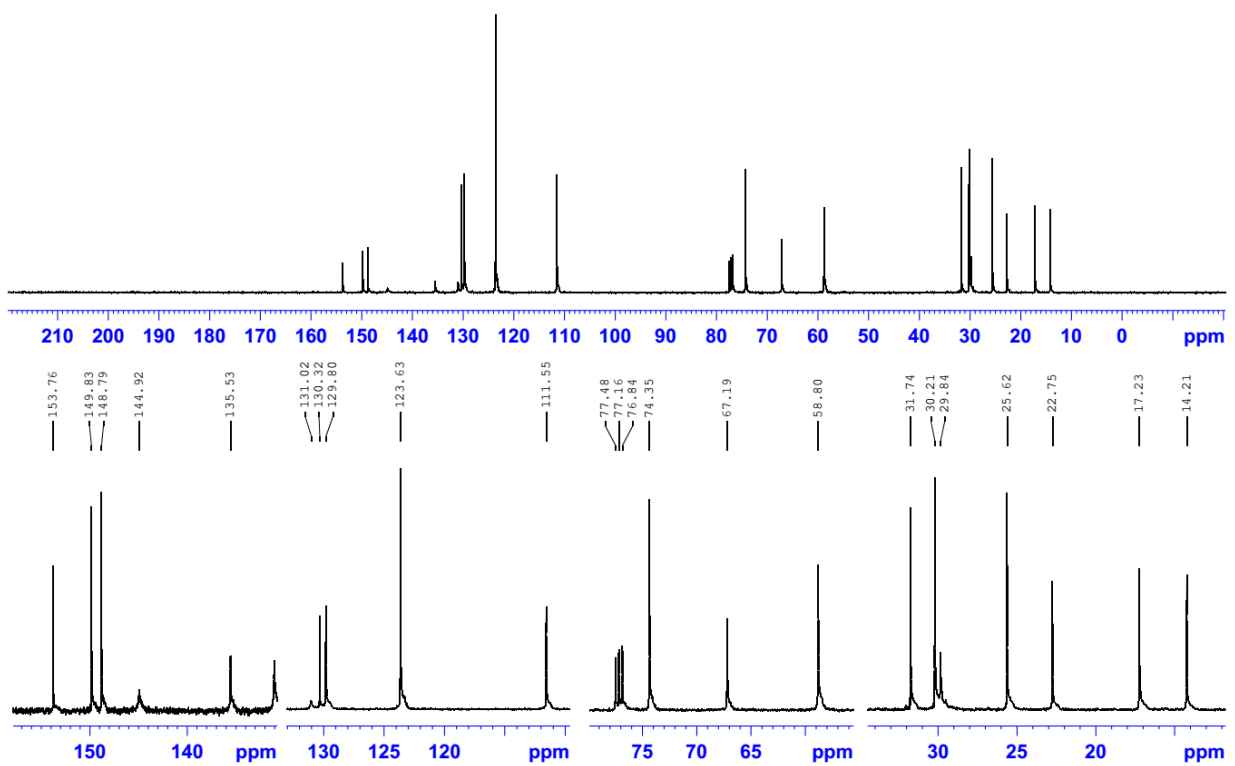
1 (0.31 g, 0.5 mmol, 1eq.), K₂CO₃ (0.55 g, 4 mmol) and a catalytic amount of KI (~0.01 g) were mixed in dried acetone (10 mL) at room temperature for 15 minutes in a sealed round bottom flask, then 1-bromohexane (0.22 g, 1.3 mmol, 2.6 eq.) was injected into the mixture and refluxed for 12 hours at 55°C in darkness. After monitoring the TLC profile which showed a single spot, the resulting orange mixture was poured into 50 ml of cold water, and extracted by ethyl acetate (3 x 30 ml). The organic layers were combined, dried up over MgSO₄ and kept under the reduced pressure to the dryness. Afterwards, the purification was done by column chromatography on silica gel in dark to obtain a shiny orange solid **1B** (0.29 g, 0.36 mmol, 72%). Chemical Formula: C₄₁H₄₆Cl₄N₆O₂, Molecular Weight: 796.66, R_f: 0.62 (MeOH/ DCM = 4% v/v) silica gel. ¹H-NMR(400 MHz, CDCl₃) δ [ppm] : 0.92 (t, J = 7.8 Hz, 6H, CH₃), 1.37 (m, 8H, CH₂), 1.55 (m, 4H, CH₂), 1.88(m, 4H, CH₂), 2.58 (s, 6H, CH₃), 4.10 (t, J = 8.1 Hz, 4H, CH₂), 4.29 (d, J = 17.2 Hz, 2H, H-6a, H-12a), 4.42 (s, 2H, -N-CH₂-N-), 4.77 (d, J = 17.2 Hz, 2H, H-6b, H-12b), 6.92 (s, 2H, H-1, H-7), 7.50 (s, 2H, CH), 7.85 (s, 4H, H-4, H-10). ¹³C-NMR (100 MHz, CDCl₃) δ [ppm]: 14.21, 17.23, 22.75, 25.62, 29.83, 30.20, 31.74, 58.80, 67.18, 74.34, 111.54, 123.62, 129.79, 130.32, 131.02, 135.52, 144.91, 148.79, 149.83, 153.75. IR: (Neat) ν_{max} (cm⁻¹) = 2927, 2855, 1556, 1483, 1448, 1382, 1256, 1235, 1087, 986, 923, 902, 801, 728. MS (Acetonitrile 90%, EtOAc 10%): (ESI positive) calc. for [C₄₁H₄₇Cl₄N₆O₂]⁺: [M+H]⁺ 795.24, found 795.6. UV: (ethyl acetate) λ (lgε) = 346 nm. Anal. calcd: C, 61.81; H, 5.82; Cl, 17.80; N, 10.55; O, 4.02. found: C, 61.93; H, 5.51; N, 10.33.



Compound 1B, IR transmittance spectra (neat)



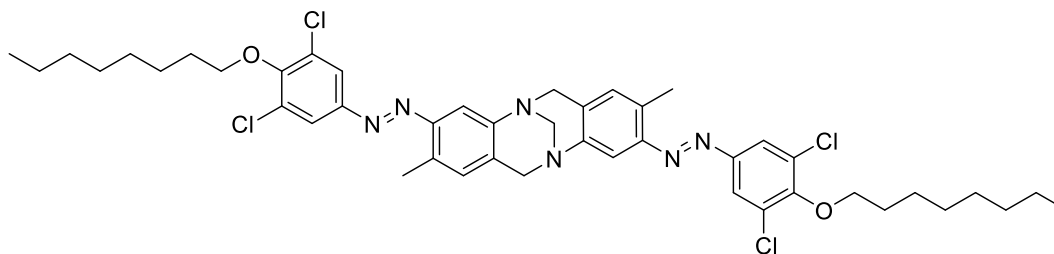
Compound 1B, $^1\text{H-NMR}$ (400 MHz, CDCl_3)



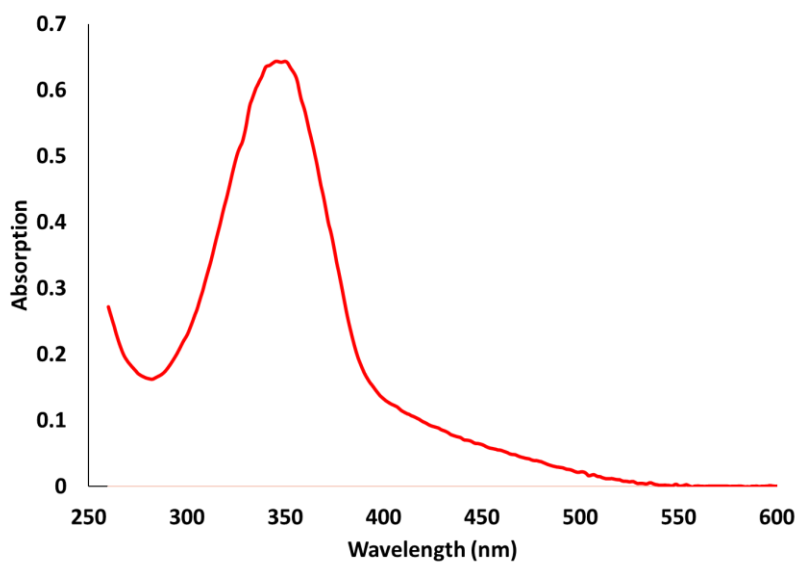
Compound 1B, $^{13}\text{C-NMR}$ (100 MHz, CDCl_3)

12. Synthesis and Characterization of (±)-1C

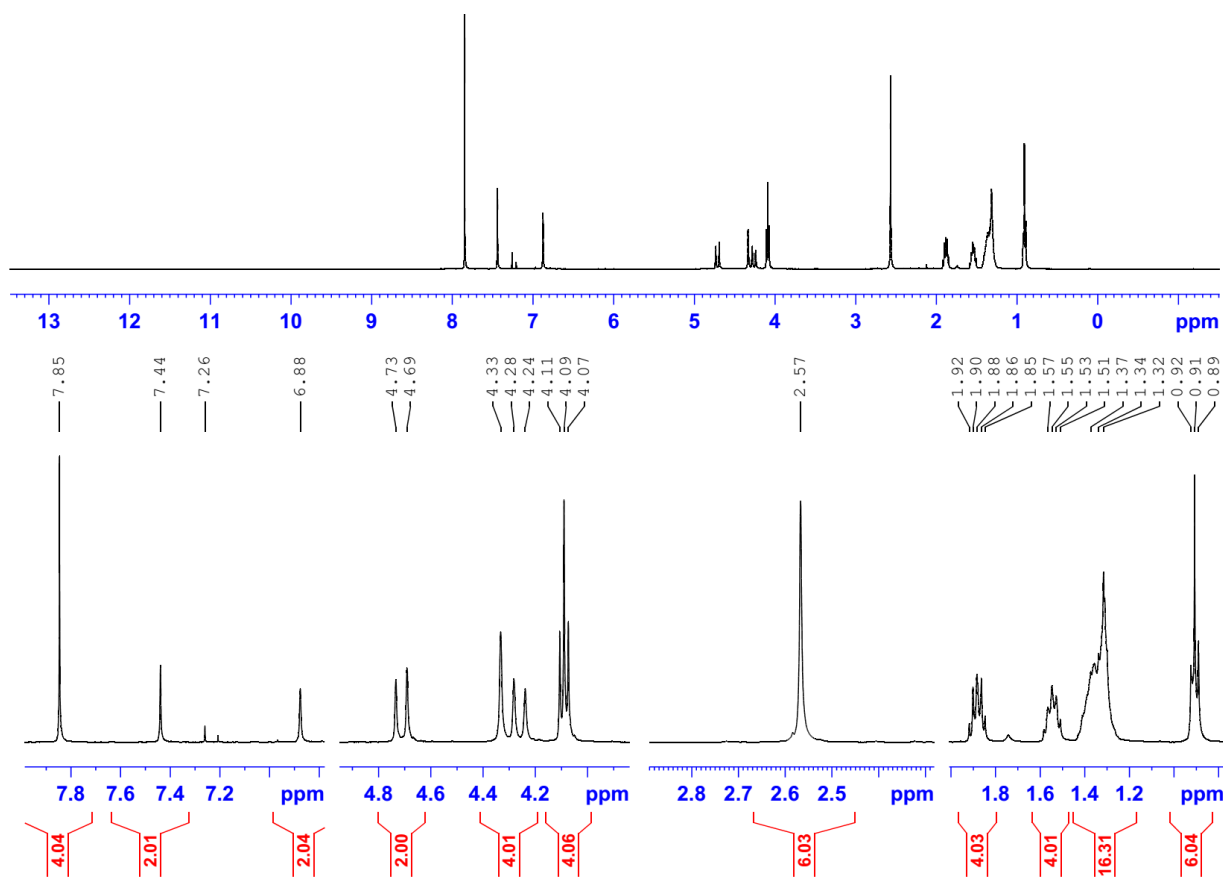
3,9-bis((E)-(3,5-dichloro-4-(octyloxy)phenyl)diazenyl)-2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine



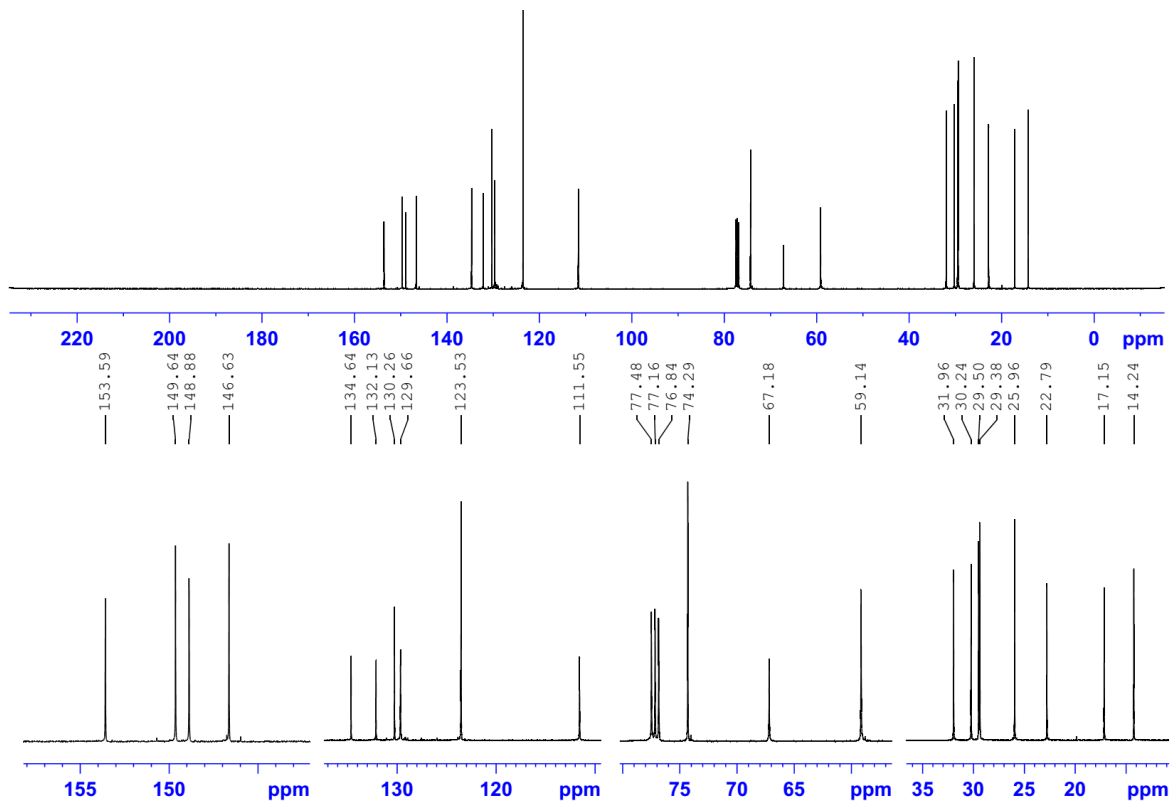
Compound **1** (0.31 g, 0.50 mmol, 1.0 eq.) and K₂CO₃ (0.55 g, 4.0 mmol) were mixed in dried acetone (10 mL) at room temperature for 15 minutes in a sealed round-bottom flask. Then, 1-bromo octane (0.23 g, 1.2 mmol, 2.4 eq.) was injected into the mixture and refluxed for 12 hours at 55°C in darkness. The reaction profile was monitored by TLC which showed a single spot at the conclusion. Afterwards, the reaction mixture was added to 50 ml of distilled water and the crude was extracted by DCM (3 x 50 ml). The organic layers were combined, dried over MgSO₄ and filtered. After solvent removal under reduced pressure, the solid residue was chromatographed to obtain a shiny orange solid **1C** (0.32 g, 0.38 mmol, 75%). Chemical Formula: C₄₅H₅₄Cl₄N₆O₂, Molecular Weight: 852.77, **R_f**: 0.50 (EtOAc/ n-Hex = 20% v/v) silica gel. **¹H-NMR** (400 MHz, CDCl₃) δ [ppm] : 0.91 (t, *J* = 7.8 Hz, 6H, CH₃), 1.34 (m, 16H, CH₂), 1.54 (m, 4H, CH₂), 1.88 (m, 4H, CH₂), 2.57 (s, 6H, CH₃), 4.09 (t, *J* = 8.1 Hz, 4H, CH₂), 4.26 (d, *J* = 17.2 Hz, 2H, H-6a, H-12a), 4.33 (s, 2H, -N-CH₂-N-), 4.71 (d, *J* = 17.1 Hz, 2H, H-6b, H-12b), 6.88 (s, 2H, H-1, H-7), 7.44 (s, 2H, H-4, H-10), 7.85 (s, 4H, CH). **¹³C-NMR** (100 MHz, CDCl₃) δ [ppm]: 14.24, 17.15, 22.79, 25.96, 29.38, 29.50, 30.24, 31.96, 59.14, 67.18, 74.29, 111.55, 123.53, 129.66, 130.26, 132.13, 134.64, 146.63, 148.88, 149.64 and 153.59. **IR**: (Neat) ν_{max} [cm⁻¹] = 2926, 2856, 1555, 1481, 1452, 1379, 1253, 1229, 1088, 989, 921, 801, 725. **MS** (Acetonitrile 45%, isopropyl alcohol 45%, EtOAc 5%, MeOH 5%): (ESI positive) calc. for [C₄₅H₅₅Cl₄N₆O₂]⁺: [M+H]⁺ 851.31, found 851.2, 851.9 and 853.0. **UV-Vis**: (EtOAc) λ (lgε) = 346 nm (4.5). Anal. calcd: C, 63.38; H, 6.38; Cl, 16.63; N, 9.86; O, 3.75. found: C, 63.57; H, 6.54; N, 9.62.



Compound **1C**, UV-Vis spectra (EtOAc, r.t.)



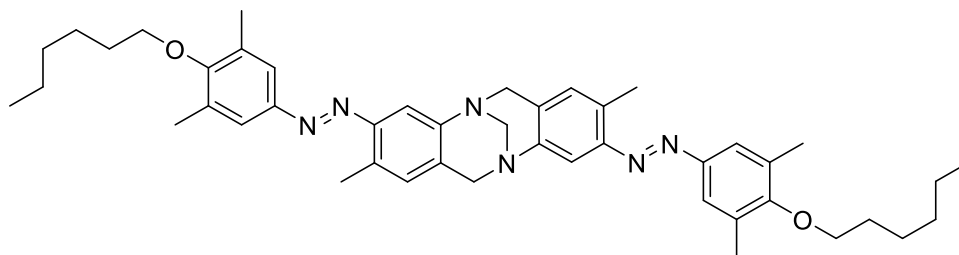
Compound 1C, $^1\text{H-NMR}$ (400 MHz, CDCl_3)



Compound 1C, $^{13}\text{C-NMR}$ (100 MHz, CDCl_3)

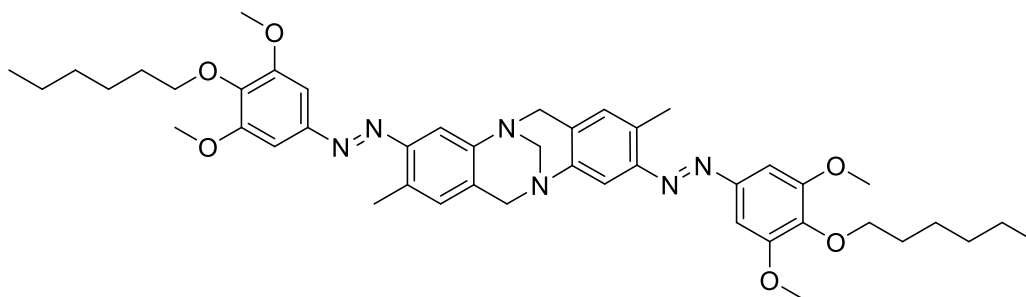
12. Synthesis and Characterization of (\pm)-4A

3,9-bis((E)-4-(hexyloxy)-3,5-dimethylphenyl)diazenyl)-2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine: For the detailed preparation and purification procedures please see: M. Kazem-Rostami, *Synthesis*, 2017, 49, in press, DOI: 10.1055/s-0036-1588913.

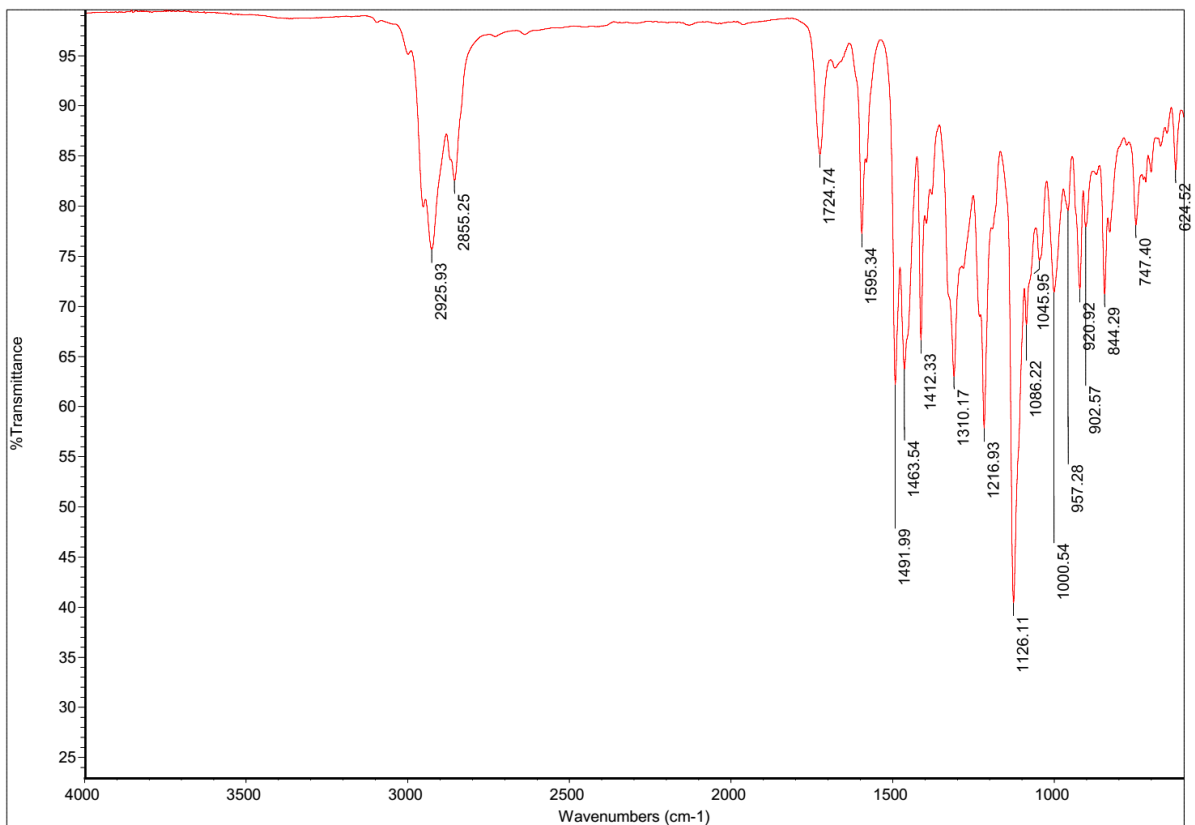


13. Synthesis and Characterization of (\pm)-5A

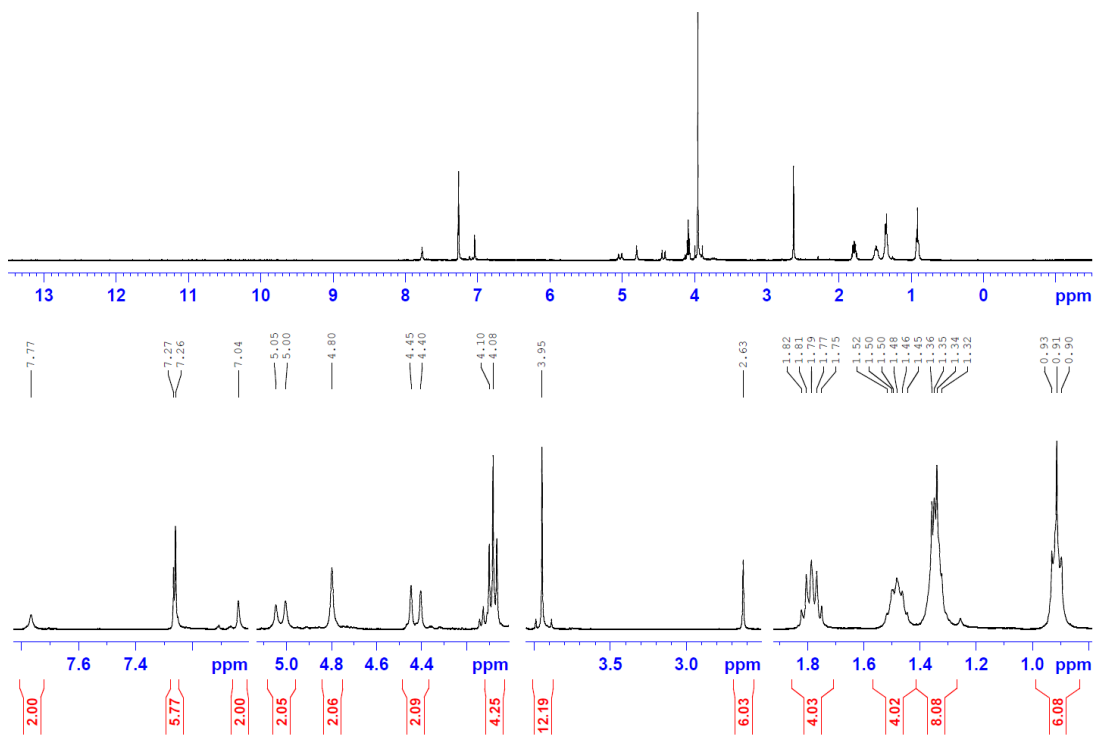
3,9-bis((E)-4-(hexyloxy)-3,5-dimethoxyphenyl)diazenyl)-2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine



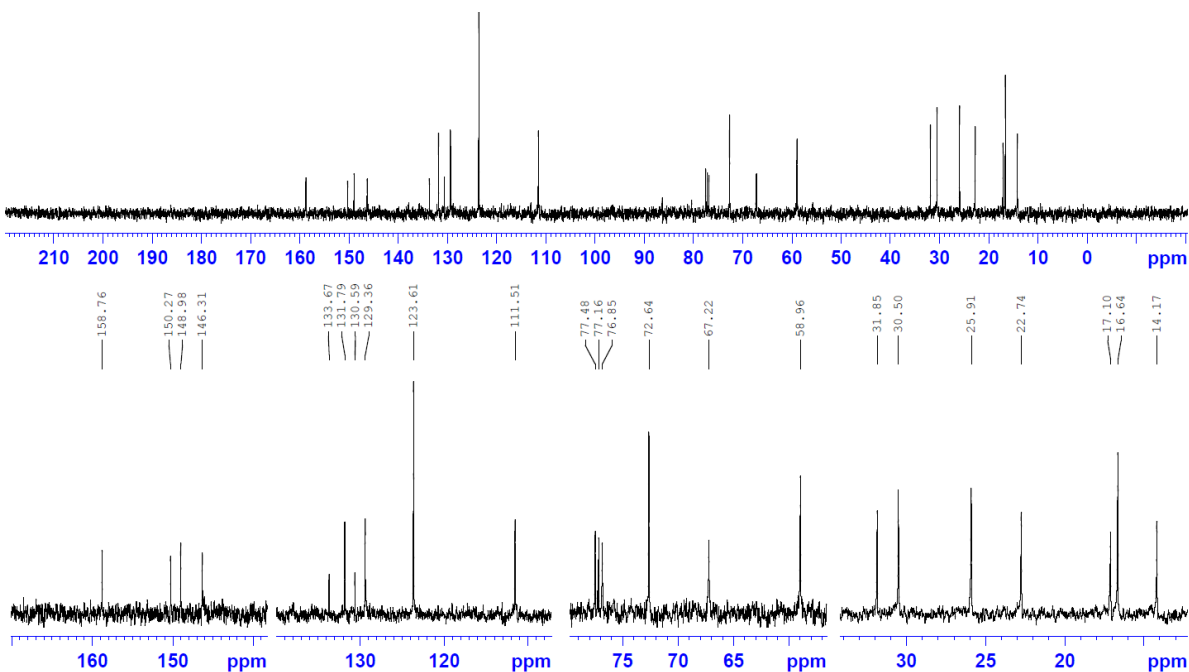
5 (0.31 g, 0.50 mmol, 1.0 eq.), K_2CO_3 (0.55 g, 4.0 mmol) and a catalytic amount of KI (~0.01 g) were mixed in dried acetone (10 mL) at room temperature for 15 minutes in a sealed round bottom flask. Then, 1-bromohexane (0.22 g, 1.3 mmol, 2.6 eq.) was injected into the mixture and refluxed for 18 hours at 58°C in darkness. After monitoring the TLC profile which showed a single spot, the resulting orange mixture was poured into cold water. The crude was extracted by ethyl acetate (3 x 30 ml). The organic layers were combined and dried over $MgSO_4$ and the solvent was removed under reduced pressure. Afterwards, the purification was done by column chromatography in dark to obtain a sticky orange substance **5A** (0.30 g, 0.39 mmol, 76%). Chemical Formula: $C_{45}H_{58}N_6O_6$, Molecular Weight: 779.00, R_f : 0.73 (MeOH/ DCM = 4% v/v) silica gel. ^1H-NMR (400 MHz, $CDCl_3$) δ [ppm] : 0.91 (t, 6H, CH_3), 1.34 (m, 8H, CH_2), 1.48 (m, 4H, CH_2), 1.78(m, 4H, CH_2), 2.62 (s, 6H, CH_3), 3.95 (s, 12H, OCH_3), 4.08 (t, 4H, CH_2), 4.42 (d, $^2J_{H,H} = 17.0$ Hz, 2H, H-6a, H-12a), 4.79 (s, 2H, -N- CH_2 -N-), 5.02 (d, $^2J_{H,H} = 17.0$ Hz, 2H, H-6b, H-12b), 7.04 (s, 2H, H-1, H-7), 7.25 (s, 4H, CH), 7.76 (s, 2H, H-4, H-10). $^{13}C-NMR$ (100 MHz, $CDCl_3$) δ [ppm] : 14.23, 17.30, 22.80, 25.65, 30.24, 31.78, 56.31, 58.06, 67.31, 73.94, 100.92, 111.60, 129.79, 140.63, 148.56, 150.70, 153.92. **IR:** (Neat) ν_{max} (cm^{-1}) = 2925, 2855, 1724, 1595, 1491, 1463, 1412, 1310, 1216, 1126, 1000, 920, 844, 747. **MS** (Acetonitrile 90%, EtOAc 5% (ESI positive) calc. for $[C_{45}H_{59}N_6O_6]^+$: $[M+H]^+$ 779.44, found 779.1. **UV:** (DCM) λ (lge) = 368 nm. Anal. calcd: C, 69.38; H, 7.51; N, 10.79; O, 12.32. found: C, 69.57; H, 7.70; N, 10.98.



Compound 5A, IR transmittance spectra (neat)



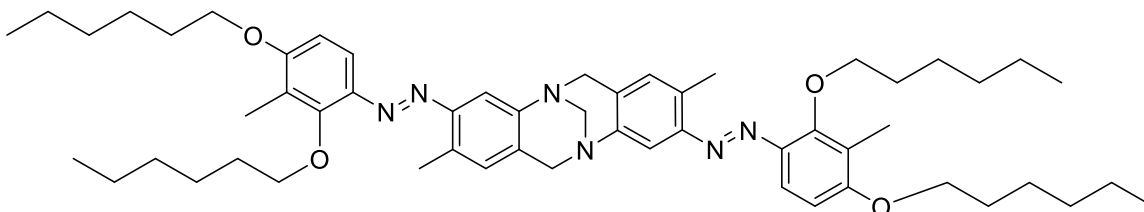
Compound 5A, ¹H-NMR (400 MHz, CDCl₃)



Compound 5A, $^{13}\text{C-NMR}$ (100 MHz, CDCl_3)

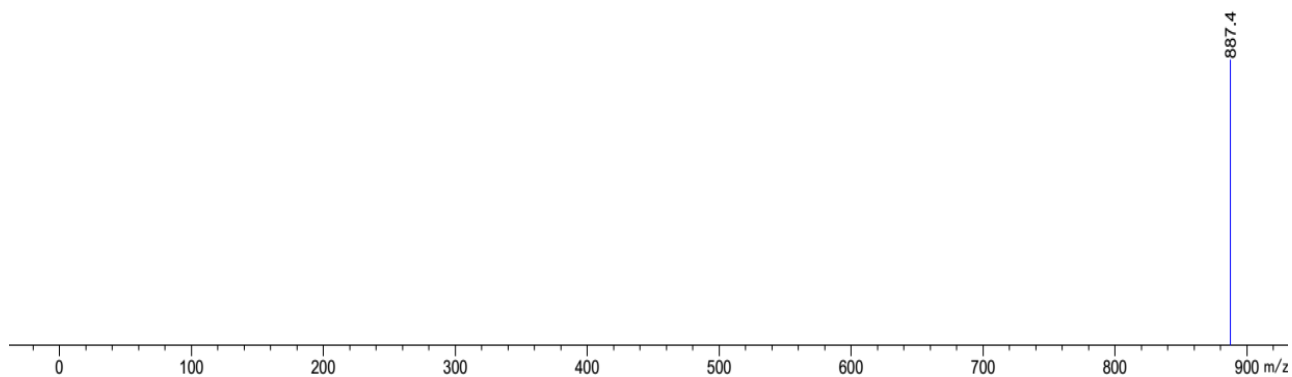
14. Synthesis and Characterization of (\pm)-6A

3,9-bis((E)-(2,4-bis(hexyloxy)-3-methylphenyl)diazenyl) -2,8-dimethyl-6H,12H-5,11-methano dibenzo [b,f][1,5] diazocine

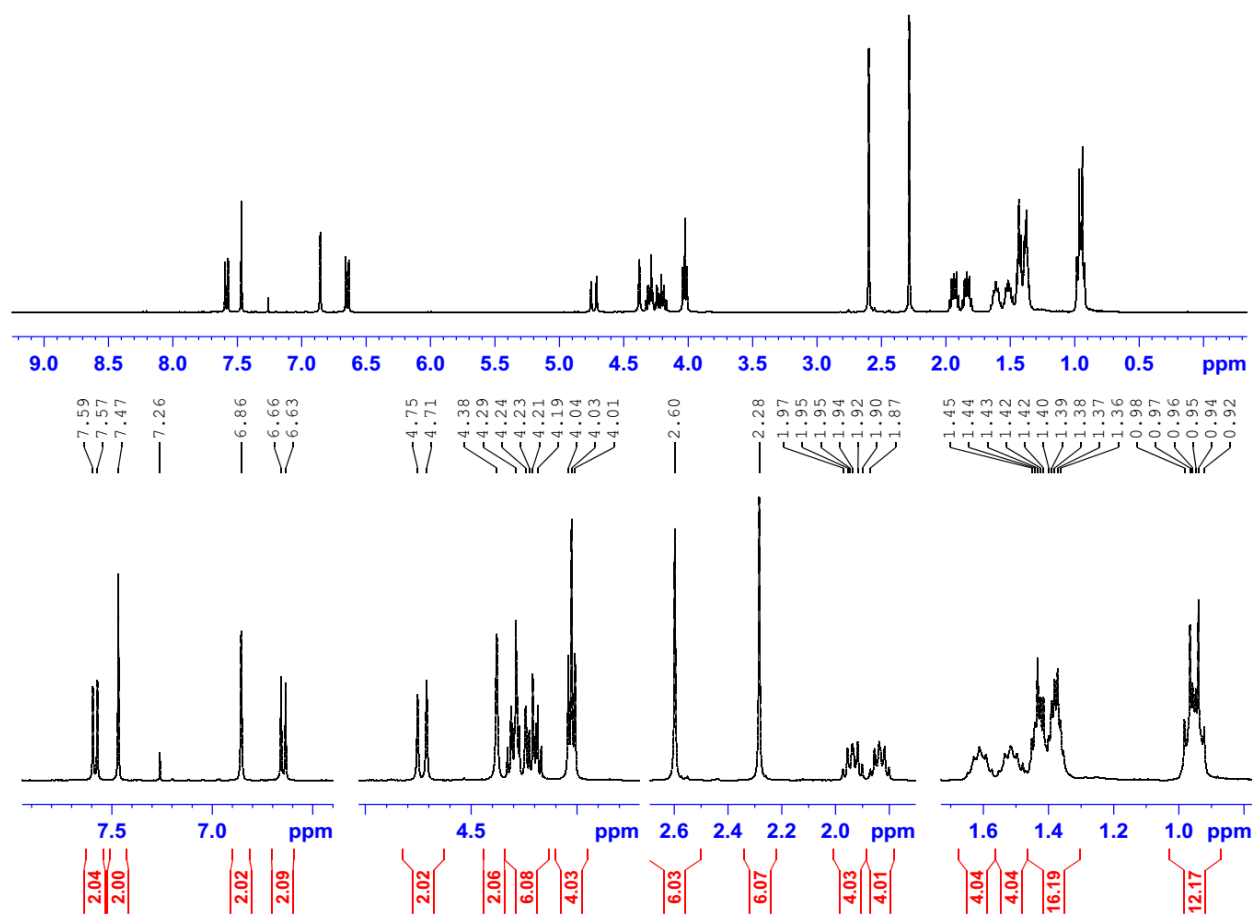


6 (0.28 g, 0.5 mmol, 1.0 eq.), K_2CO_3 (0.55 g, 4.0 mmol, excess) and a catalytic amount of KI (~0.02 g) were mixed in dried acetone (6 mL) at room temperature for 15 minutes in a sealed round bottom flask. Then, 1-bromohexane (0.36 g, 2.2 mmol, 4.4 eq.) was injected into the mixture and refluxed for 48 hours at 60°C in darkness. After monitoring the TLC profile, the final red mixture was poured into 50 ml of cold water. The crude was extracted by DCM (2 x 50ml) and the DCM layers were combined, dried over MgSO_4 and filtered. Afterwards, the volatiles were removed under reduced pressure to obtain a red residue which then purified by column chromatography to obtain a red-orange semisolid substance **6B** (0.26 g, 0.29 mmol, 58%). Chemical Formula: $\text{C}_{55}\text{H}_{78}\text{N}_6\text{O}_4$, Molecular Weight: 887.27, R_f : 0.75 (EtOAc/ n-Hex = 5% v/v) silica gel. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ [ppm] : 0.92-0.98 (m, 12H, CH_3), 1.36-1.45 (m, 16H, CH_2), 1.47-1.58 (m, 4H, CH_2), 1.57-1.65 (m, 4H, CH_2), 1.87-1.94 (m, 4H, CH_2), 1.96-1.98 (m, 4H, CH_2), 2.28 (s, 6H, CH_3), 2.60 (s, 6H, CH_3), 4.01-4.04 (t, $J = 7.8$ Hz, 4H, CH_2), 4.19-4.29 (m, 6H), 4.38 (s, 2H, - $\text{N-CH}_2\text{-N-}$), 4.71-4.75 (d, $J = 17.2$ Hz, 2H, H-6b, H-12b), 6.63-6.66 (d, $J = 8.9$ Hz, 2H), 6.86 (s, 2H, CH), 7.47 (s, 2H, CH), 7.57-7.59 (d, $J = 8.7$ Hz, 2H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ [ppm]: 9.15, 14.12, 14.24, 17.17, 22.71, 22.82, 25.88, 26.08, 29.36, 30.69, 31.66, 31.98, 59.05, 67.29, 68.56, 76.67, 106.62, 111.61, 114.68, 120.45, 129.30, 130.16, 133.66, 140.51, 146.30, 150.60, 157.50, 160.66. IR: (Neat) ν_{max} (cm^{-1}) = 2929, 2853, 1550, 1479, 1452, 1379, 1254,

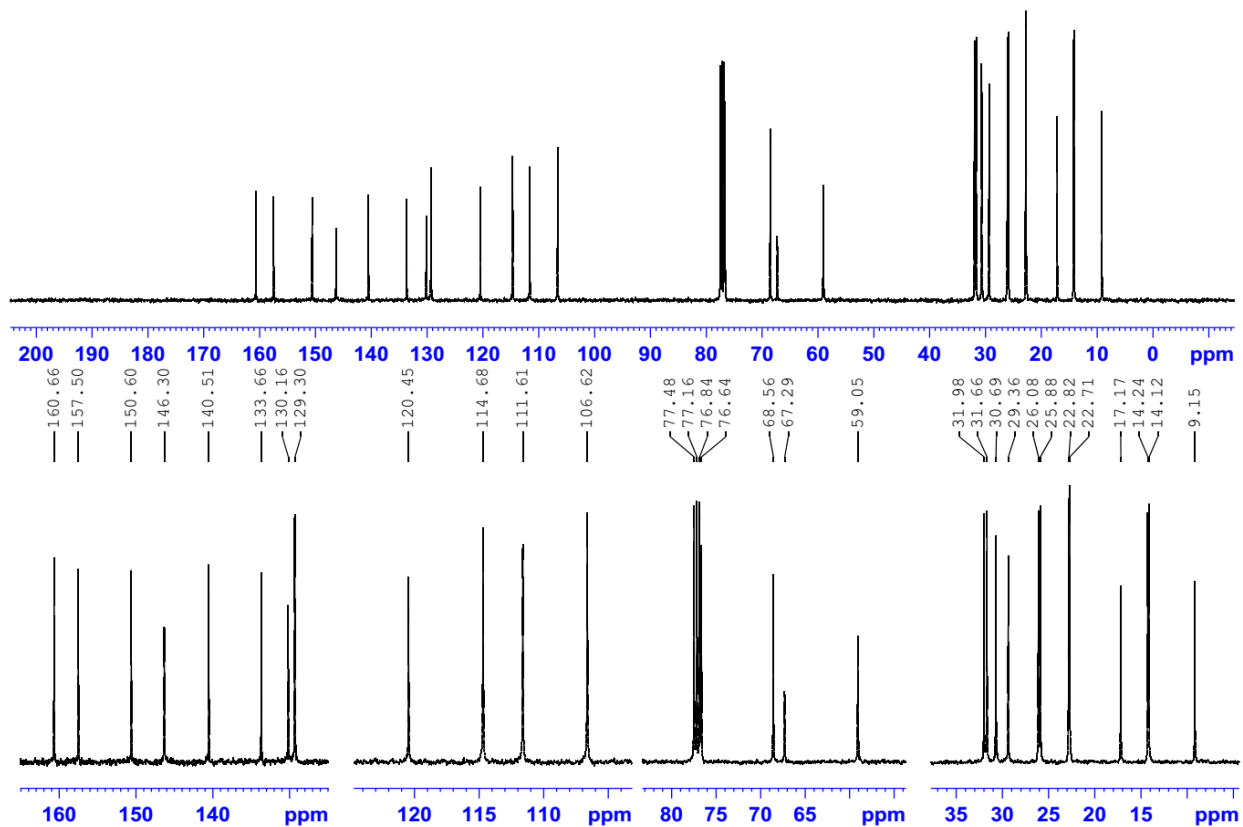
1077, 976, 943, 907, 851. **MS** (Isopropyl alcohol, formic acid 0.05 %): (ESI positive) calc. for $[C_{55}H_{79}N_6O_4]^+$: $[M+H]^+$ 887.61, found 887.4. UV: (ethyl acetate) λ (lg ϵ) = 370 nm (4.6).



Compound 6A, Mass spectra ESI (positive)



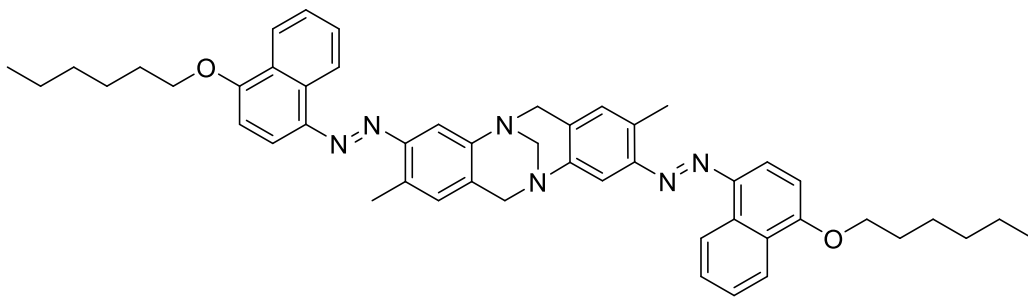
Compound 6A, 1H -NMR (400 MHz, $CDCl_3$)



Compound 6A, $^{13}\text{C-NMR}$ (100 MHz, CDCl_3)

15. Synthesis and Characterization of (\pm)-8A

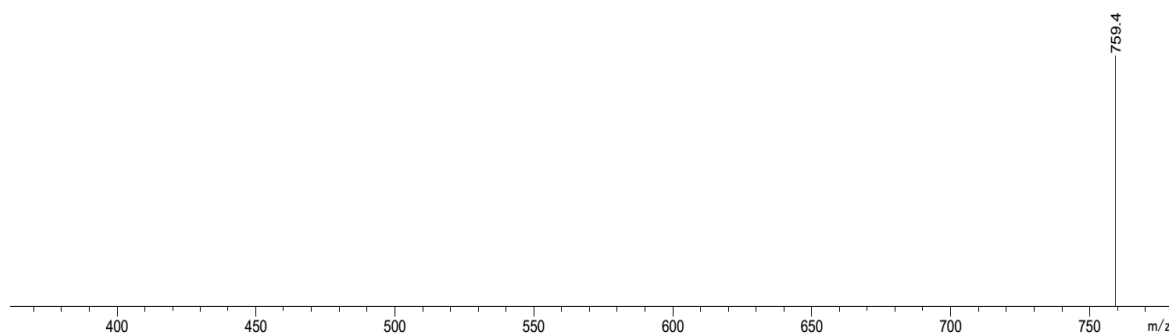
3,9-bis((E)-(4-(hexyloxy)naphthalen-1-yl)diazenyl)-2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine



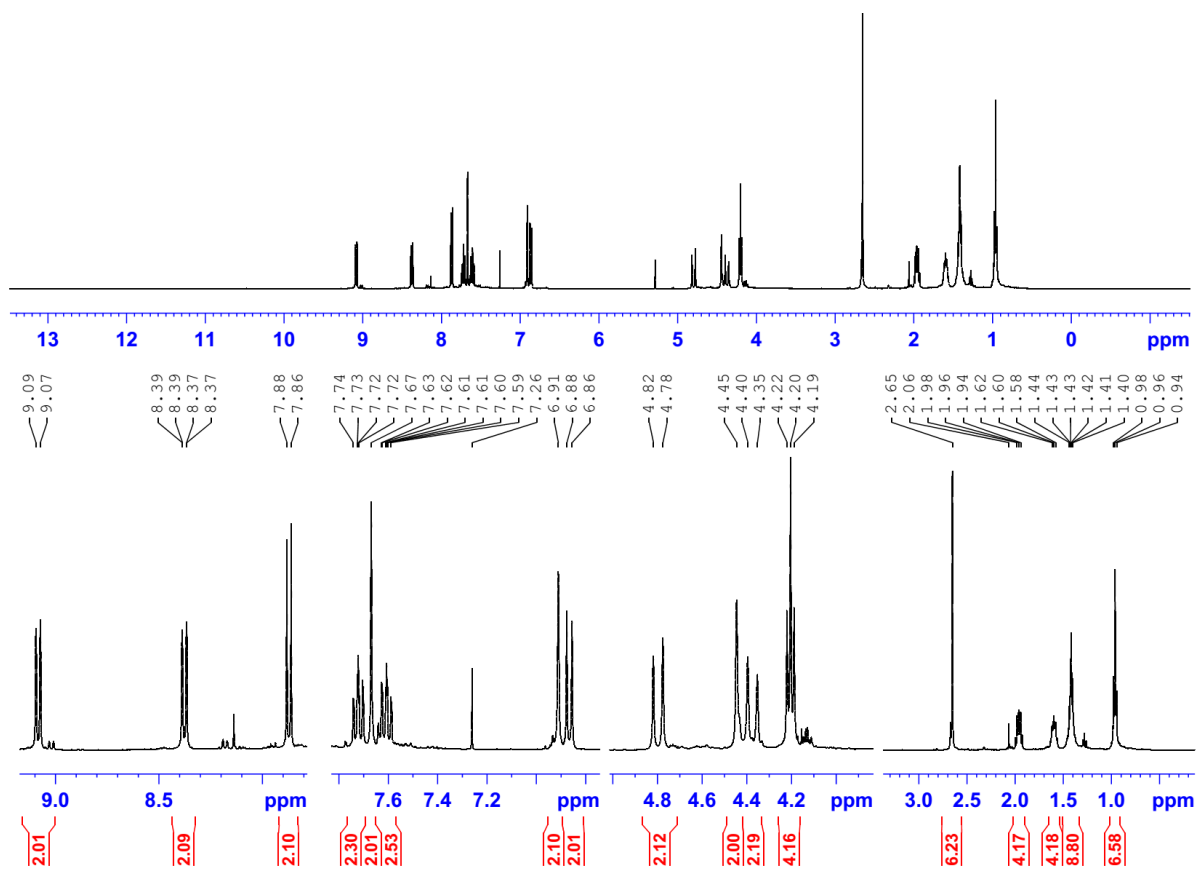
8 (0.59 g, 1.0 mmol, 1.0 eq.), K_2CO_3 (0.55 g, 4.0 mmol) and a catalytic amount of KI (~0.01 g) were sonicated in dried DMF (8 mL) at 40°C for 15 minutes in a sealed round bottom flask; then, 1-bromohexane (0.36 g, 2.2 mmol, 1.1 eq.) was injected into the mixture and stirred for 24 hours at 110°C in darkness. Then, the resulting solution was poured into cold water, and the crude was extracted by DCM (3 x 50 ml). The DCM layers were combined, washed with brine, dried over MgSO_4 , filtered and then evaporated under reduced pressure. Afterwards, further purification was done by column chromatography on silica gel in dark to obtain a sticky maroon substance **8A** (0.34 g, 0.45 mmol, 45%). Chemical Formula: $\text{C}_{49}\text{H}_{54}\text{N}_6\text{O}_2$, Molecular Weight: 759.01, R_f : 0.8 (EtOAc/n-Hex = 40% v/v) silica gel. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ [ppm] : 0.96 (t, J = 7.8 Hz, 6H, CH_3), 1.41 (m, 8H, CH_2), 1.59 (m, 4H, CH_2), 1.96 (m, 4H, CH_2), 2.65 (s, 6H, CH_3), 4.20 (t, J = 7.6 Hz, 4H, CH_2), 4.37 (d, J = 17.2 Hz, 2H, H-6a, H-12a), 4.44 (s, 2H, -N- CH_2 -N-), 4.79 (d, J = 17.1 Hz, 2H, H-6b, H-12b), 6.86 (d, J = 8.6 Hz, 2H, CH), 6.91 (s, 2H, CH), 7.60 (t, J = 7.6 Hz, 2H, CH), 7.66 (s, 2H, CH), 7.72 (t, J = 7.6 Hz, 2H, CH), 7.87 (d, J = 8.5 Hz, 2H, CH), 8.37 (d, J = 8.5 Hz, 4H, CH), 9.08 (d, J = 8.5 Hz, 4H, CH). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ [ppm] : 14.16, 17.28, 22.77, 26.02, 29.29, 31.72, 59.13, 67.28,

68.64, 104.53, 111.87, 113.49, 122.29, 123.45, 125.77, 125.84, 127.52, 129.49, 130.30, 132.80, 133.83, 142.00, 146.29, 150.90, 157.90. **IR:** (Neat) ν_{max} (cm^{-1}) = 2927, 2856, 1576, 1507, 1459, 1385, 1319, 1237, 1087, 920, 764, 728. **MS** (Acetonitrile 20%, EtOAc 80%) (ESI positive) calc. for $[\text{C}_{49}\text{H}_{55}\text{N}_6\text{O}_2]^+$: $[\text{M}+\text{H}]^+$ 759.43, found 759.4. **UV:** (DCM) λ ($\text{lg}\epsilon$) = 407(4.6) nm. Anal. calcd: C, 77.54; H, 7.17; N, 11.07; O, 4.22. found: C, 77.46; H, 7.47; N, 11.35.

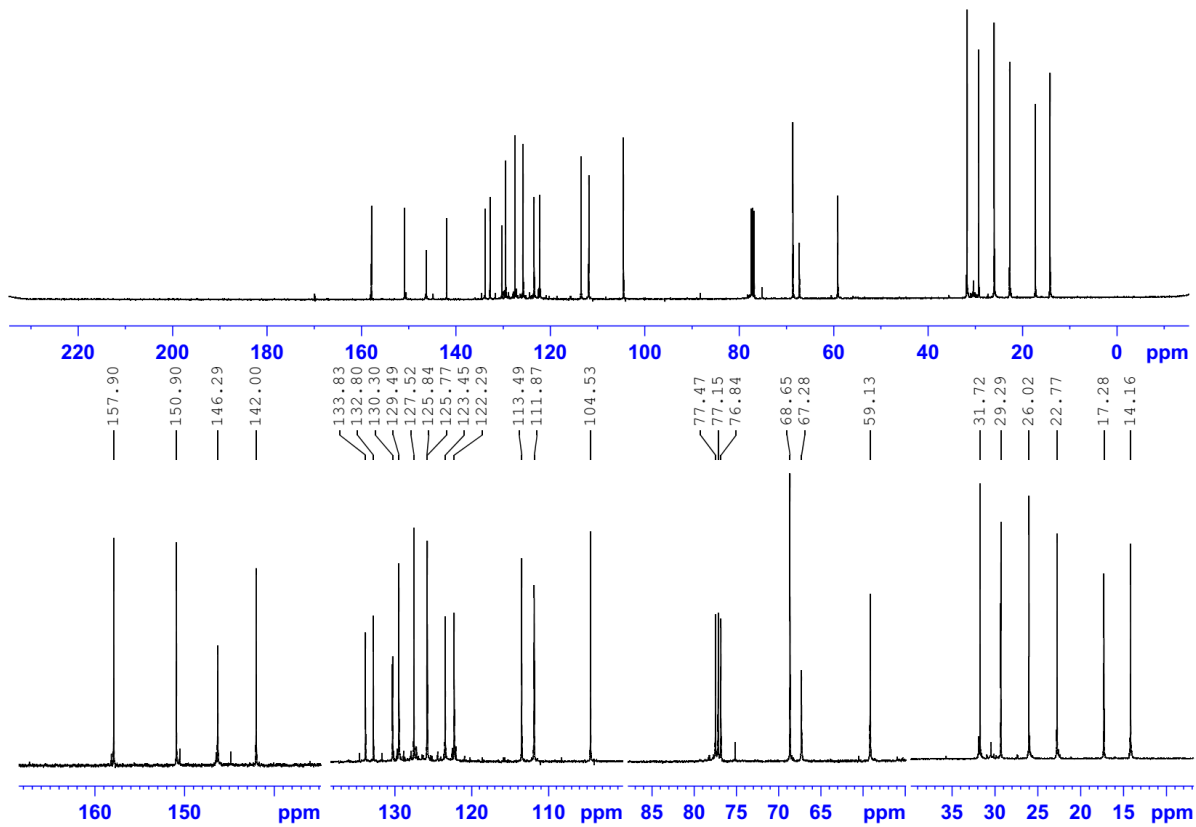
Max: 2335



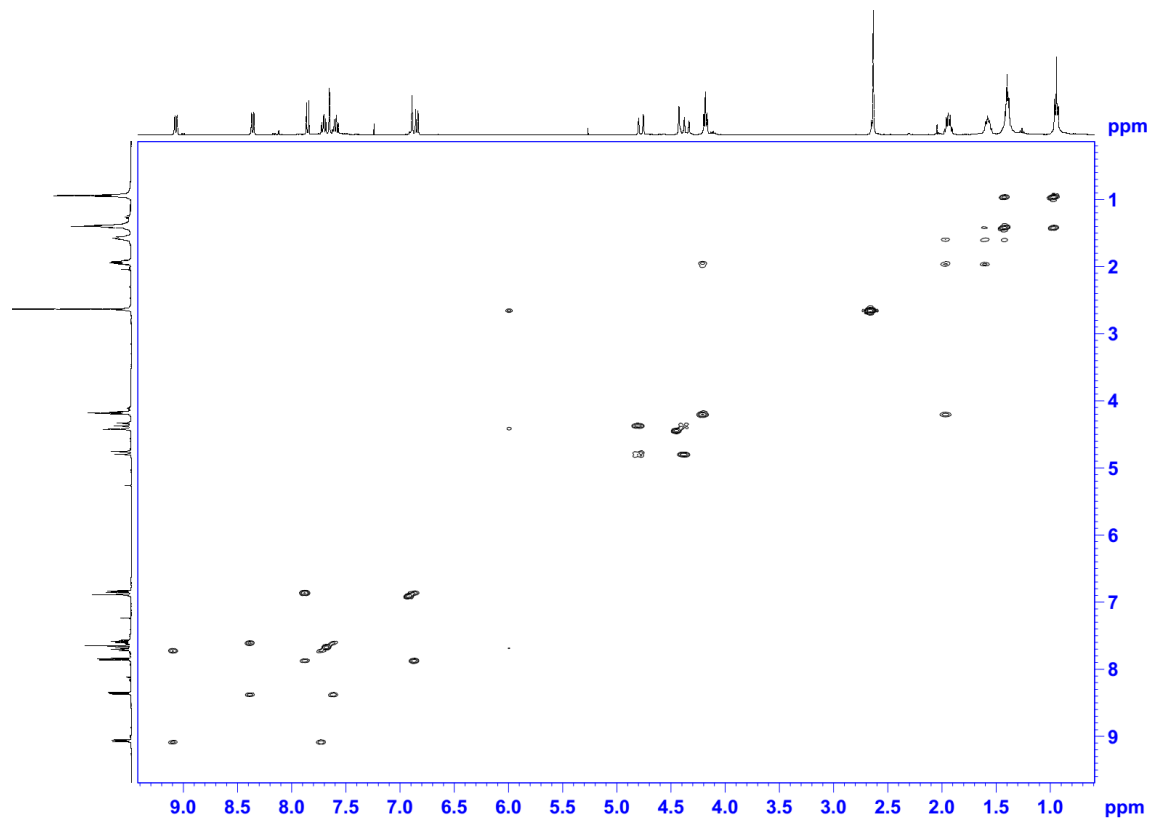
Compound 8A, Mass Spectra ESI +



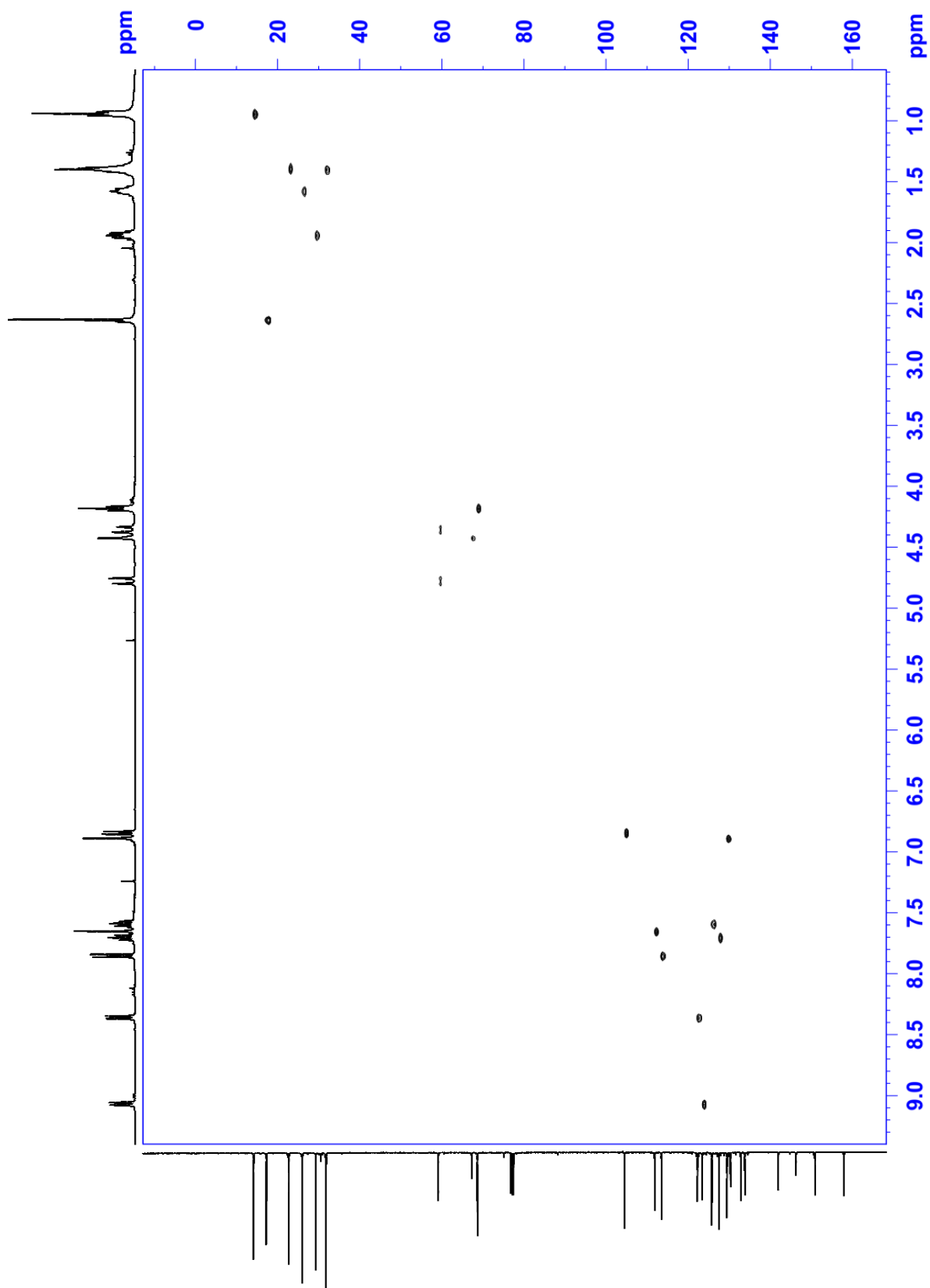
Compound 8A, $^1\text{H-NMR}$ (400 MHz, CDCl_3)



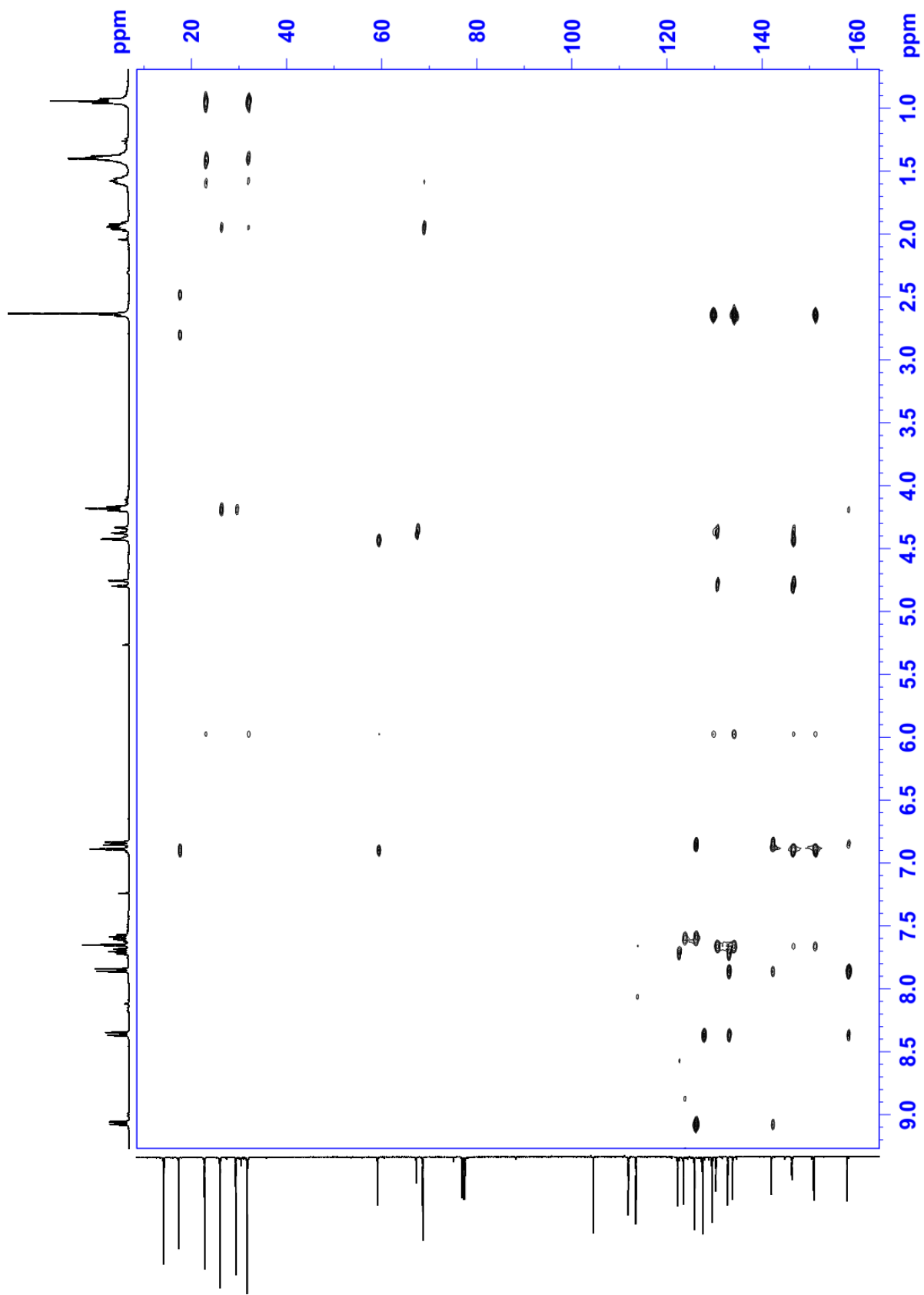
Compound 8A, ¹³C-NMR (100 MHz, CDCl₃)



Compound 8A, COSY



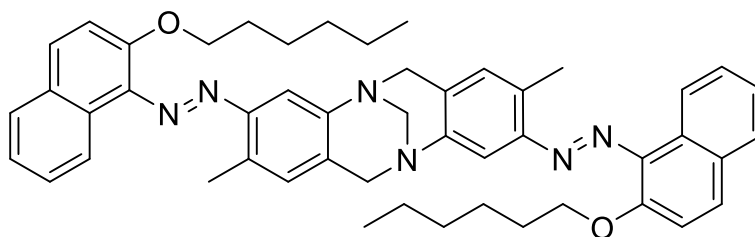
Compound 8A, HSQC



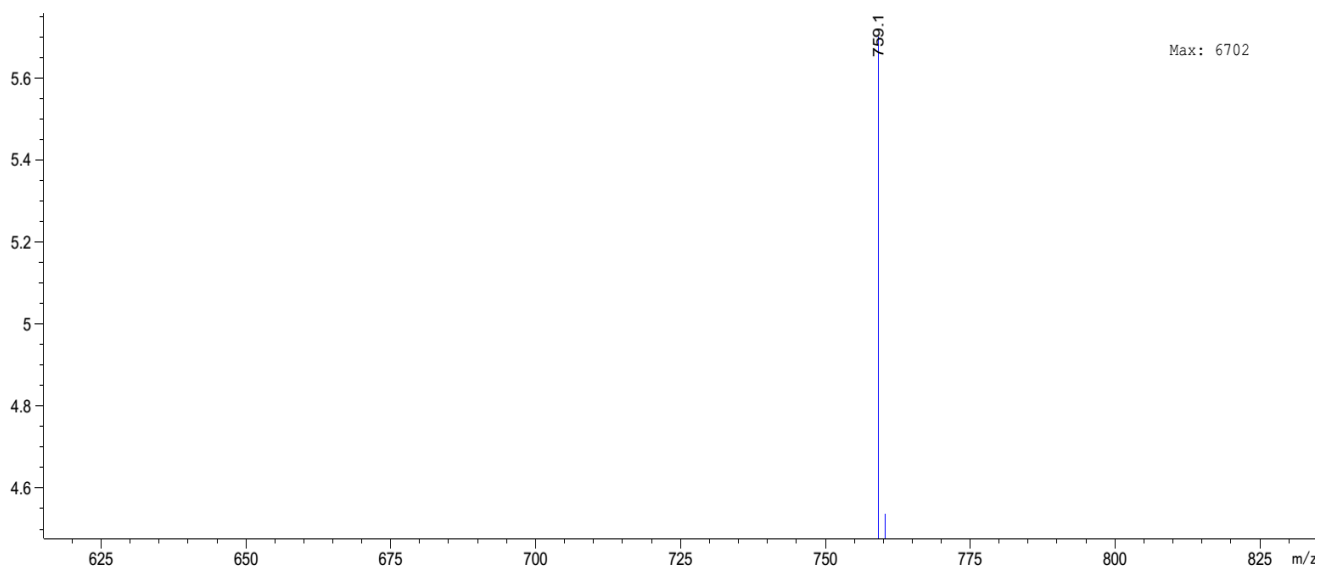
Compound 8A, HMBC

16. Synthesis and Characterization of (±)-9A

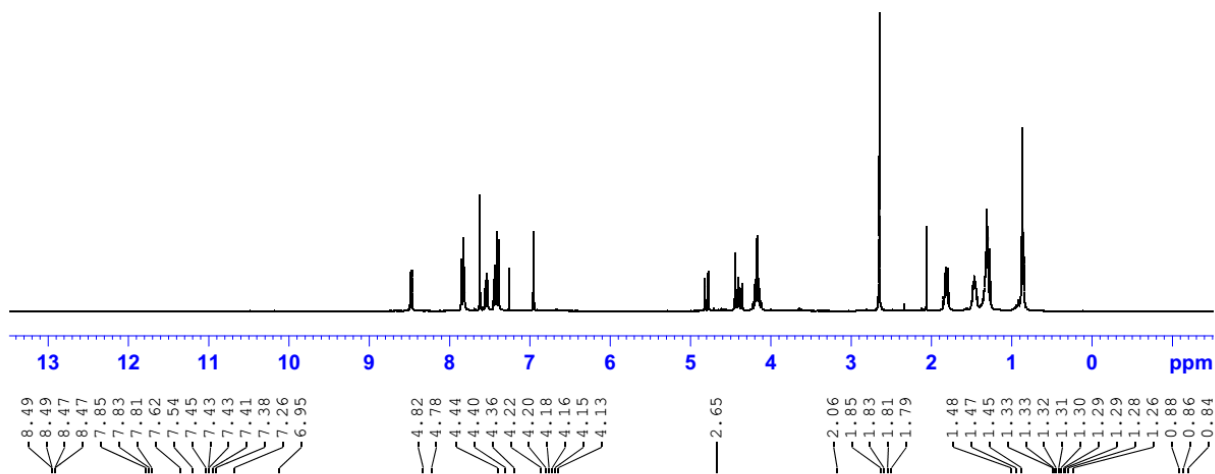
3,9-bis((E)-2-(hexyloxy)naphthalen-1-yl)diazenyl)-2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine



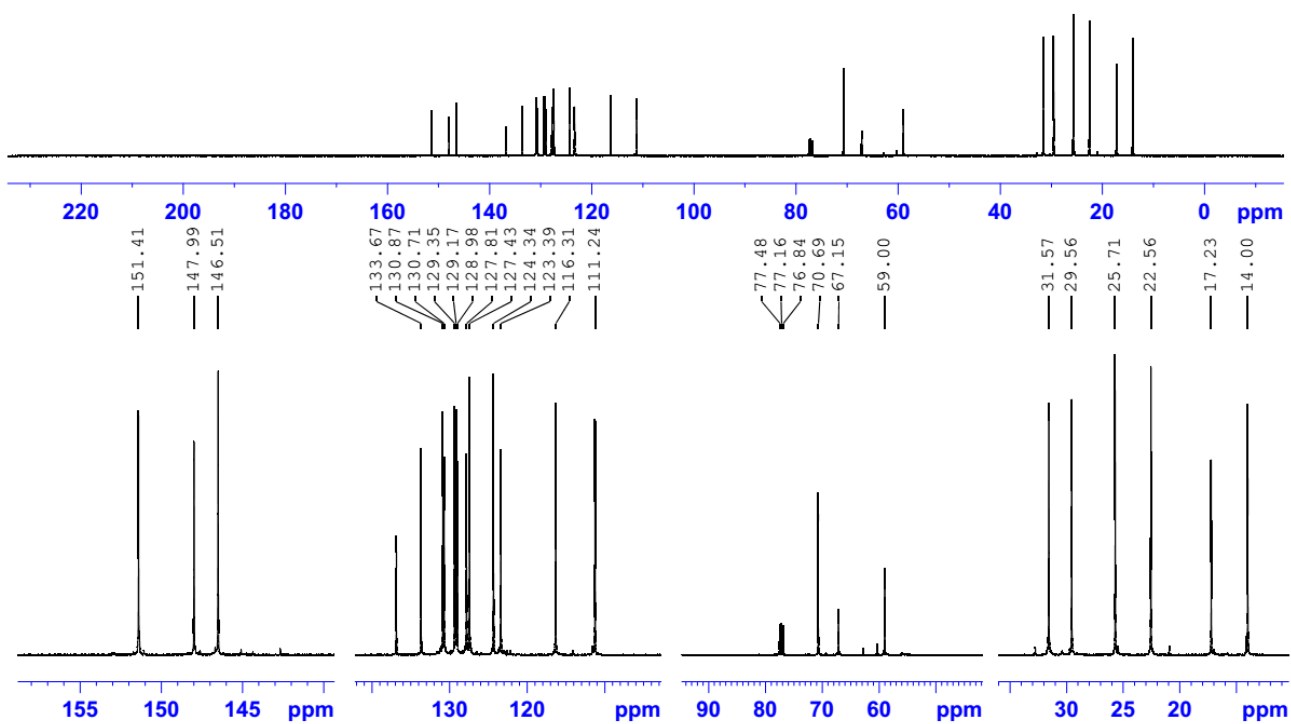
9 (0.59 g, 1.0 mmol, 1.0 eq.), K₂CO₃ (0.55 g, 4.0 mmol) and a catalytic amount of KI (~0.01 g) were sonicated in dried DMF (8 mL) at 40°C for 15 minutes in a sealed round bottom flask, then 1-bromohexane (0.36 g, 2.2 mmol, 1.1 eq.) was injected into the mixture and stirred for 24 hours at 110°C in darkness. Then, the resulting mixture was poured into 100 ml of cold water and the crude was extracted by DCM (3 x 20 ml). The DCM layers were combined, dried over MgSO₄, filtered and evaporated under reduced pressure respectively. Afterwards, the purification was done by column chromatography to obtain a sticky dark red substance **9A** (0.39 g, 0.52 mmol, 52%). Chemical Formula: C₄₉H₅₄N₆O₂, Molecular Weight: 759.01, R_f: 0.6 (EtOAc/n-Hex = 40% v/v) silica gel. **¹H-NMR** (400 MHz, CDCl₃) δ [ppm] : 0.86 (t, J = 7.8 Hz, 6H, CH₃), 1.30 (m, 8H, CH₂), 1.46 (m, 4H, CH₂), 1.81(m, 4H, CH₂), 2.64 (s, 6H, CH₃), 4.17 (m, 4H, CH₂), 4.38 (d, J = 17.0 Hz, 2H, H-6a, H-12a), 4.44 (s, 2H, -N-CH₂-N-), 4.79 (d, J = 17.1 Hz, 2H, H-6b, H-12b), 6.95 (s, 2H), 7.39 (d, 2H, CH), 7.43 (t, 2H), 7.54 (t, 2H), 7.62 (s, 2H), 7.83 (t, 4H), 8.47 (d, 2H). **¹³C-NMR** (100 MHz, CDCl₃) δ [ppm] : 14.00, 17.23, 22.56, 25.71, 29.56, 31.57, 59.00, 67.15, 70.69, 111.24, 116.31, 123.39, 124.34, 127.43, 127.81, 128.98, 129.17, 129.35, 130.71, 130.87, 133.67, 136.85, 146.51, 147.99, 151.41. **IR:** (Neat) ν_{max} (cm⁻¹) = 2924, 2854, 1591, 1463, 1271, 1241, 1086, 1016, 919, 805, 746. **MS** (Acetonitrile 20%, EtOAc 80%) (ESI positive) calc. for [C₄₉H₅₅N₆O₂]⁺: [M+H]⁺ 759.43, found 759.1. **UV:** (DCM) λ (lgε) = 393(4.7) nm. Anal. calcd: C, 77.54; H, 7.17; N, 11.07; O, 4.22. found: C, 77.63; H, 7.33; N, 10.89.



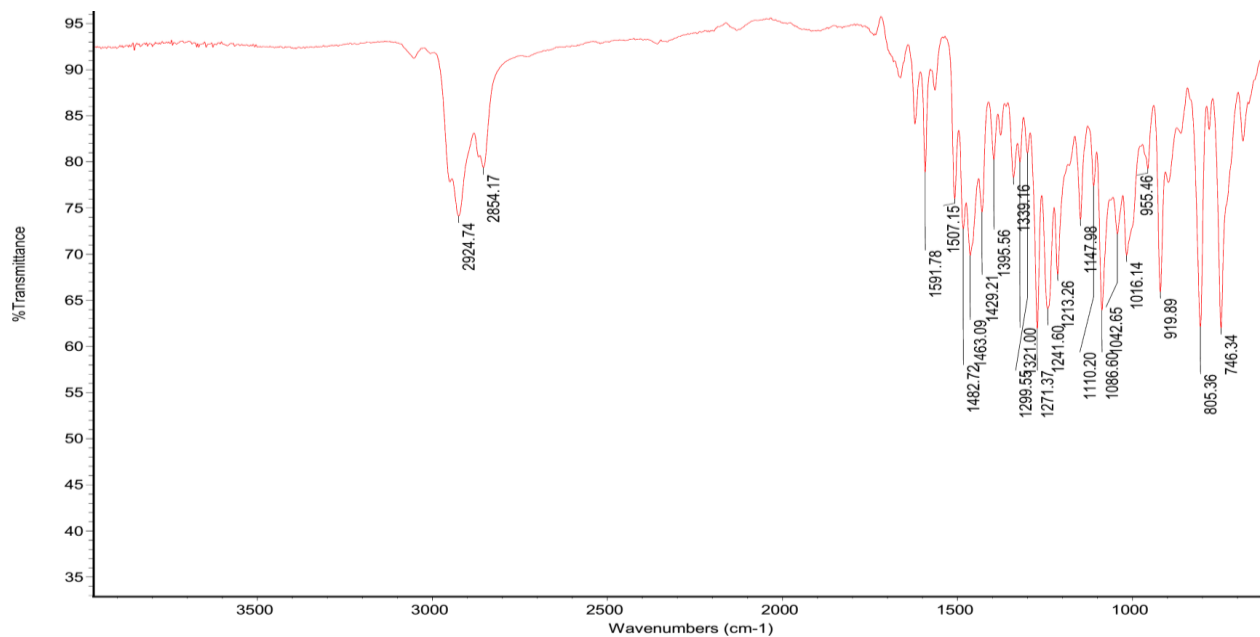
Compound 9A, Mass Spectra ESI +



Compound 9A, ¹H-NMR (400 MHz, CDCl₃)

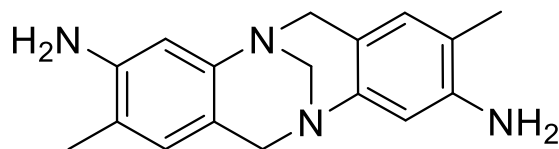


Compound 9A, ¹³C-NMR (100 MHz, CDCl₃)

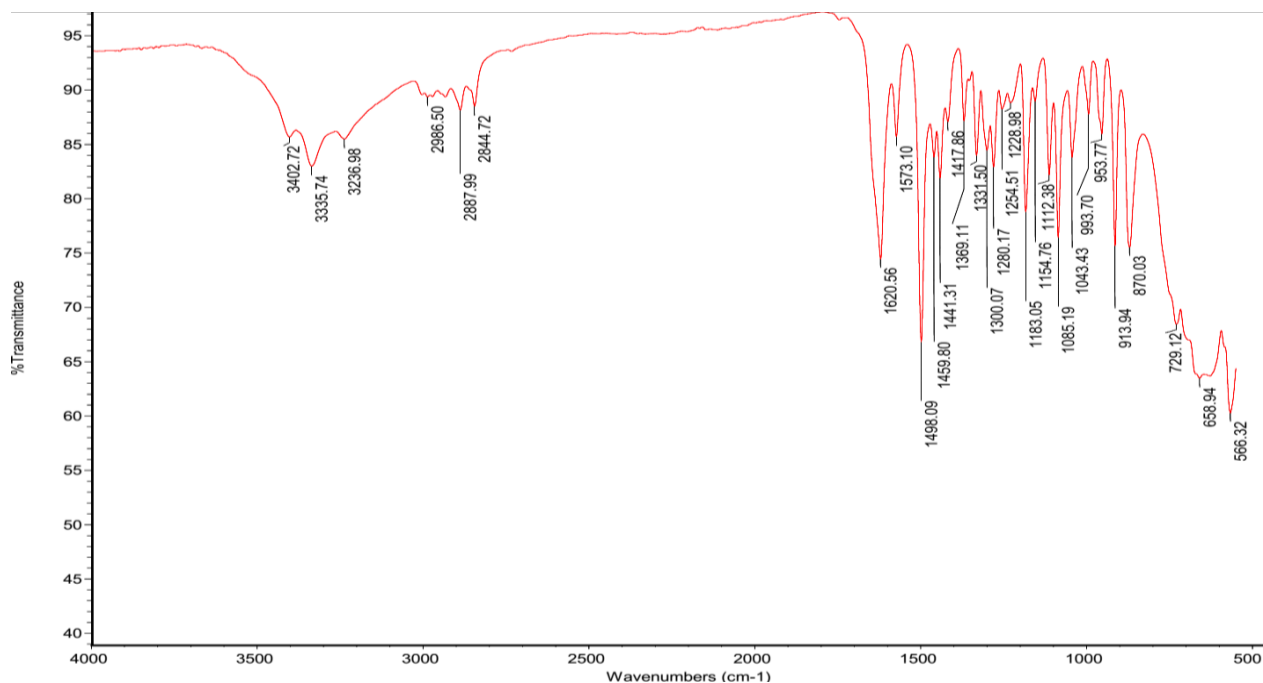


Compound 9A, Infrared Transmittance Spectra (neat)

17. Preparation of the building block (*Hünlich's base*)



For the detailed preparation and purification procedures please see: M. Kazem-Rostami, *Synthesis*, 2017, **49**, in press, DOI: 10.1055/s-0036-1588913. Or alternatively see: S. Rigol, L. Beyer, L. Hennig, J. Sieler and A. Giannis, *Org. Lett.*, 2013, **15**, 1418-1420.



Hünlich's base, IR spectra (neat)

17. Partial resolution of 4A

(-)-O,O'-dibenzoyl-L-tartaric acid (0.36 g, 1.0 mmol, 1.0 eq.) was carefully boiled in 1,2-dichloroethane (6 ml) under a flow of nitrogen gas (to reduce the solution volume up to 4ml) for making sure that the solution is moisture free.² Then, compound **4A** (0.72 g, 1.0 mmol, 1.0 eq.) was added to the solution and refluxed for 2h at 85°C. Afterwards, the container was sealed, kept at 55°C for three days and then gradually cooled down to the rt in darkness over three more days. Then, the reaction flask was put in a heat-insulator container and slowly refrigerated and kept at -20°C for two days. Afterwards, the remaining 1,2-dichloroethane was removed by vacuum, the solid residue was sonicated with NaOH (aq, 6N, 10ml) and then DCM (10 ml) was added. The DCM layer quickly turned orange and was separated and was rigorously worked up with NaOH (aq, 1N, 30ml X 5) for ensuring a total hydrolysis and elimination of the tartaric acid residues. The organic layer was finally separated, dried over Na₂SO₄ and filtered. The solvent was removed under reduced pressure to obtain a partially-resolved product (0.68 g, 0.95 mmol, 0.95 eq., [α]_D^{15.5} = -43 in DCM).

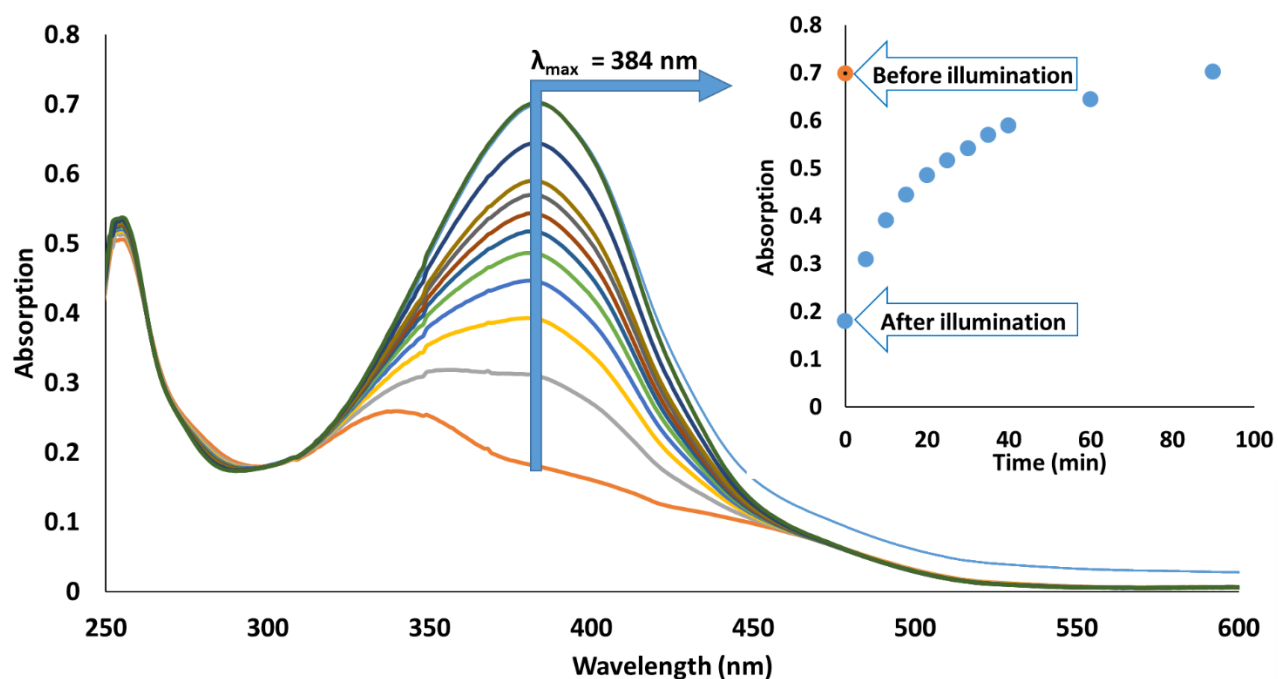
Similarly, this test was performed with (+)-O,O'-dibenzoyl-R-tartaric acid which gave another partially-resolved product (0.66 g, 0.93 mmol, 0.93 eq. [α]_D^{16.2} = +39 in DCM).

To the DCM solutions of these products were added an excess amount of trichloroacetic acid (2.0 mmol, 0.33 g) and stirred at rt for 48 hours. Afterwards, the mixture was neutralized and worked up by NaOH (aq, 1N, 30ml X 3) and the optical rotation was finally recalculated which was almost zero.

PHOTO-EXCITATION AND THERMAL RELAXATION

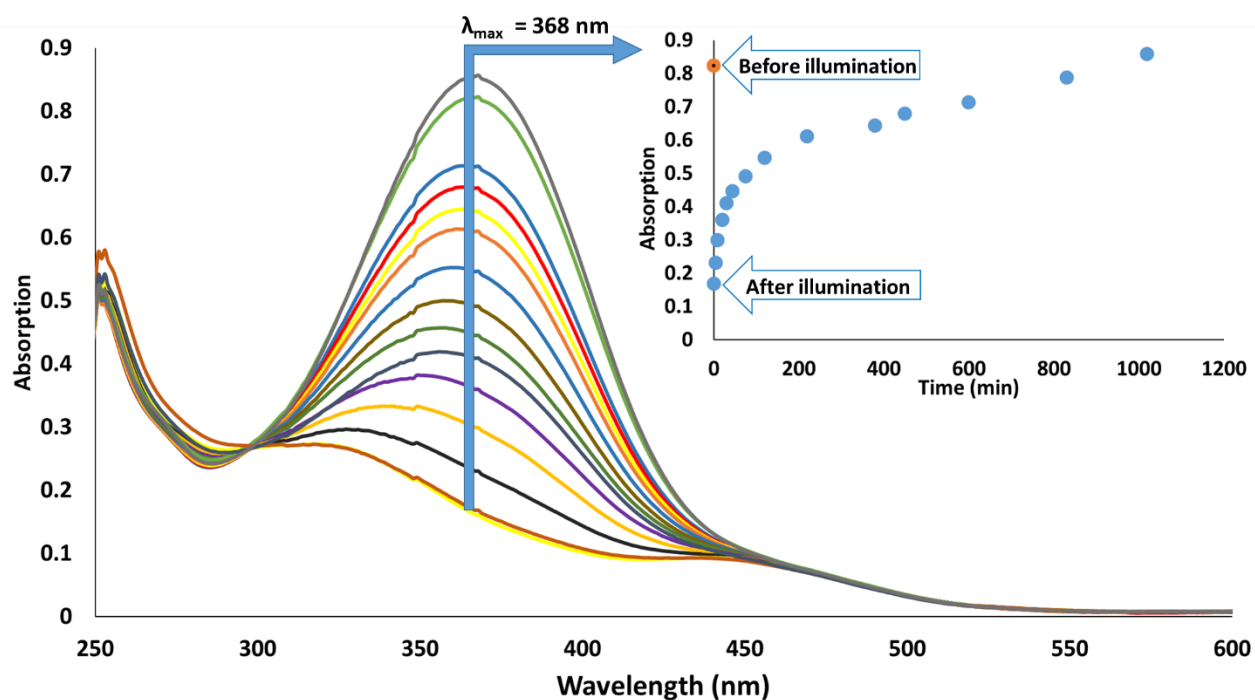
A solution of the selected compound in EtOAc at r.t. (2×10^{-5} mol.L⁻¹) was prepared in darkness and loaded into a tightly sealed quartz cuvette. The UV-Vis absorption spectra of this solution was obtained indicating a dominant population of the *trans* isomer. Afterwards, the cuvette was illuminated by a 365 nm UV light-source (Spectroline® ENF-260C/FE [230V, 50Hz, 0.17A], Spectronics Corporation, Westbury, New York, USA) installed on a standard fluorescence cabinet (Spectroline® CM10) for 5 minutes and instantly rescanned to obtain the UV-Vis spectra when the *cis* isomer reaches to its maximum possible population. Then, rescanning process of the sample, (incubated in darkness at the room temperature), continued to track its thermal back-isomerization until when the spectra reached to its initial shape. Tracking the photo-isomerisation proved a totally repeatable and reversible process in agreement with the NMR results showing no sign of photo-degradation. To simplify the photo-isomerisation results, only one cycle of photo-excitation /thermal relaxation is shown. (The procedure adopted from M. Kazem-Rostami, *Synthesis*, 2017, **49**, in press, DOI: 10.1055/s-0036-1588913).

1. Photo-isomerisation studies of (\pm)-6



Monitoring the changes in UV-vis spectra of 6 in EtOAc at r.t.

2. Photo-isomerisation studies of (\pm)-6A



Monitoring the changes in UV-vis spectra of 6A in EtOAc at r.t.

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