NEW JOURNAL OF CHEMISTRY

Optically Active and Photoswitchable Tröger's Base Analogs

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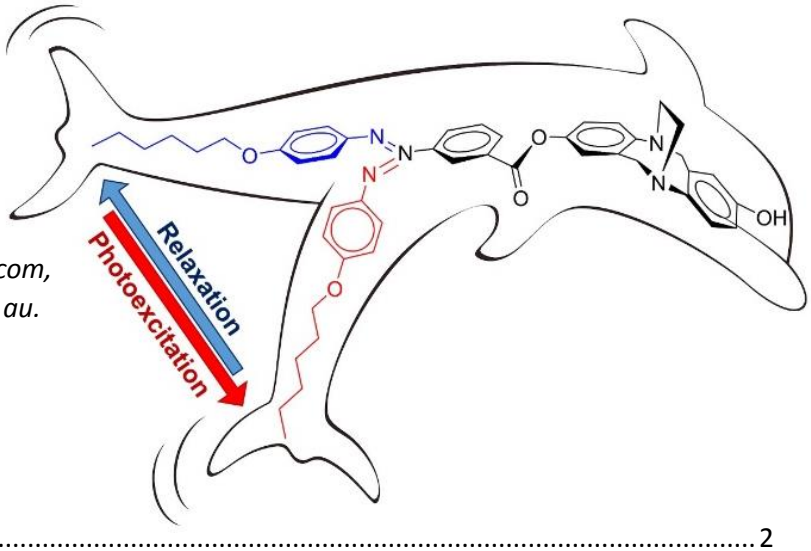

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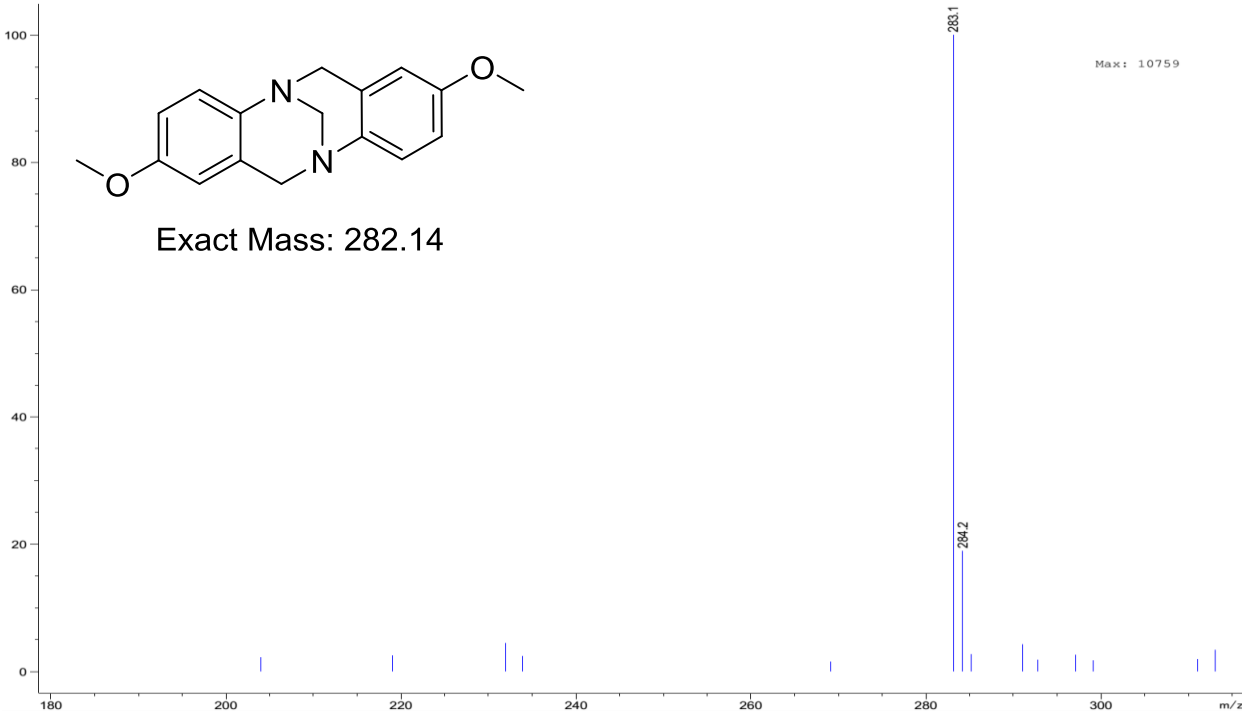
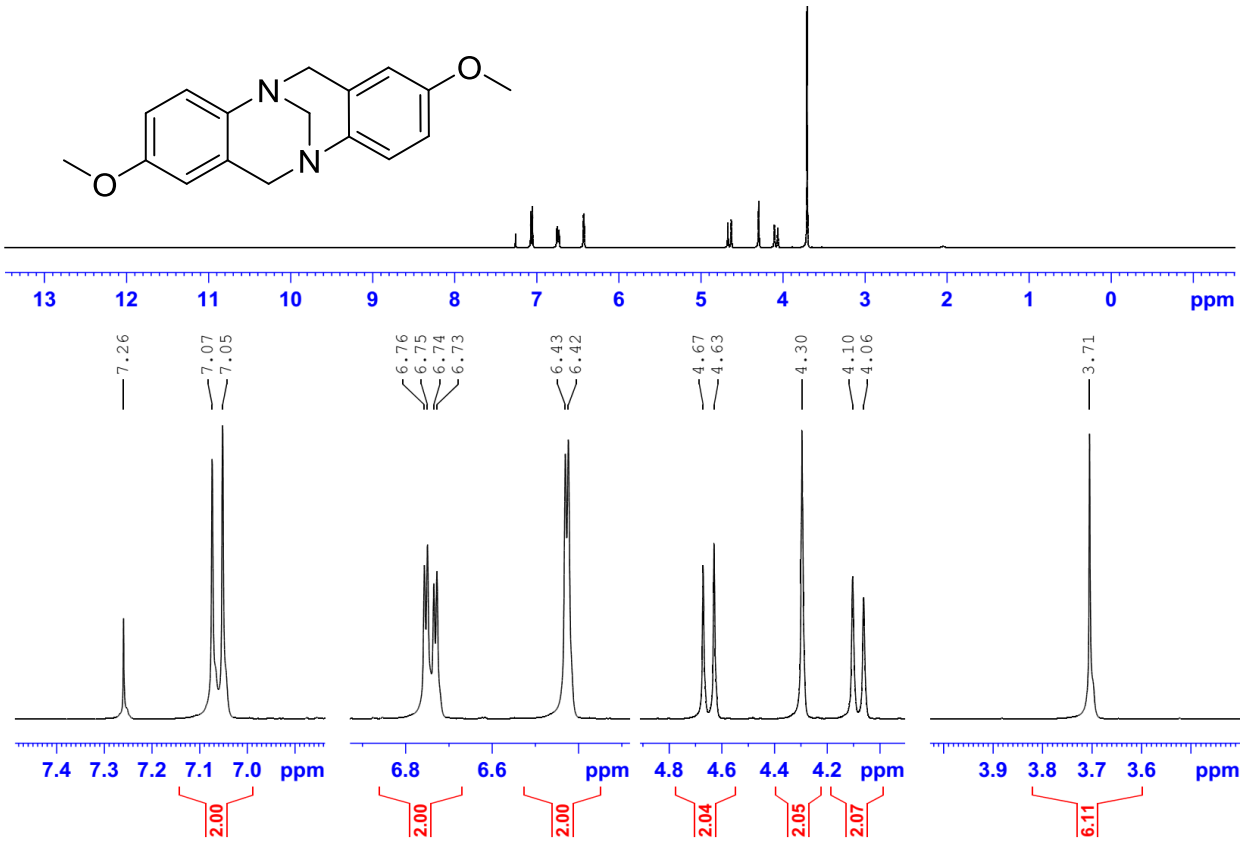
Spectroscopic Characterization

1. Characterization of compound (**1**)

2,8-Dimethoxy-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine



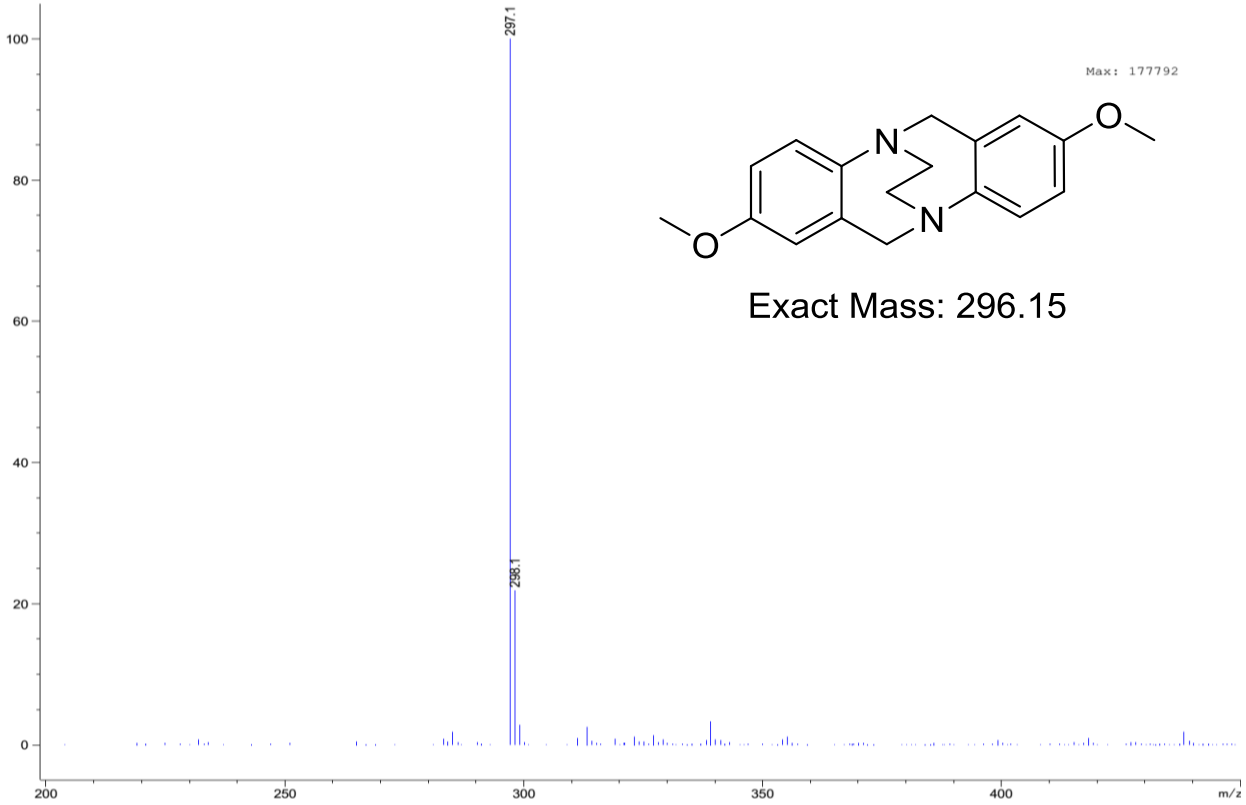
Compound 1, MS (ESI +)



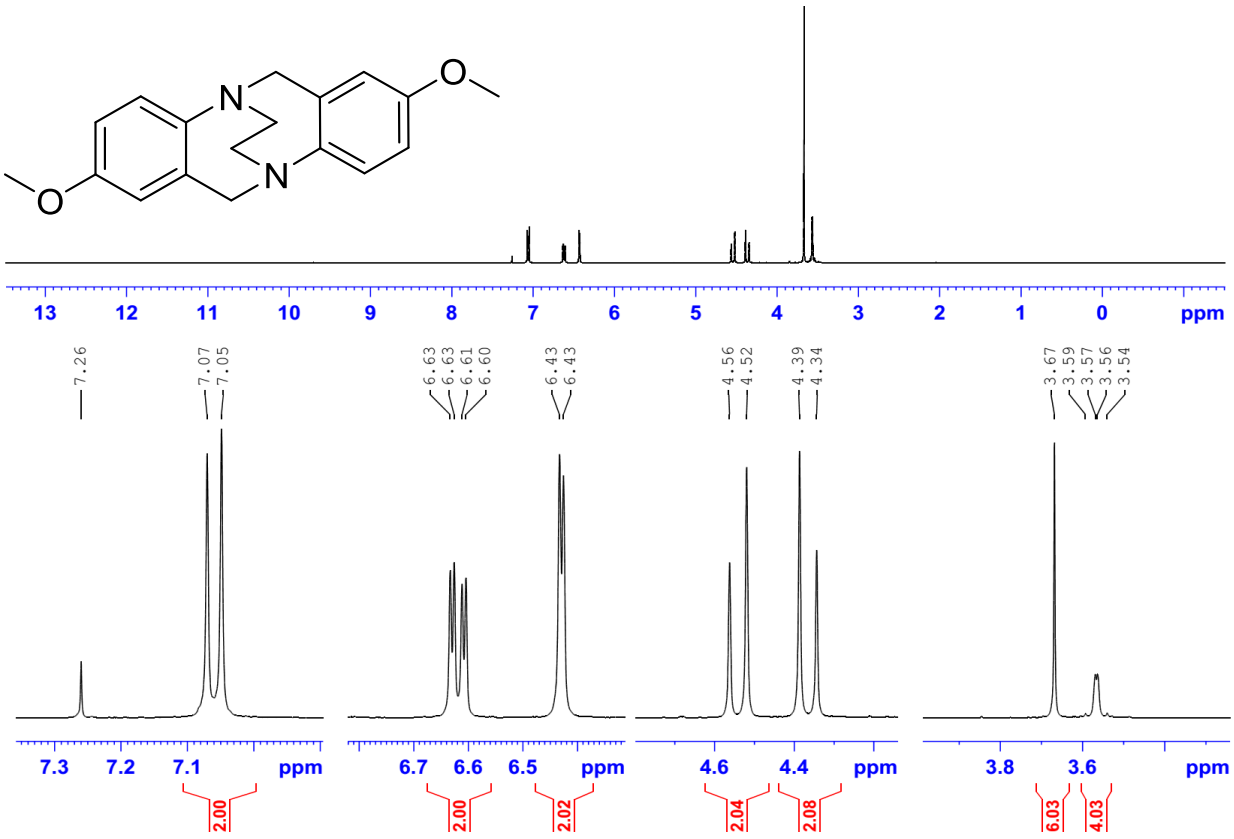
Compound 1, ^{1}H NMR (400MHz, $CDCl_3$)

2. Characterization of compound (**2**)

2,8-Dimethoxy-6*H*,12*H*-5,11-ethanodibenzo[*b*,*f*][1,5]diazocine

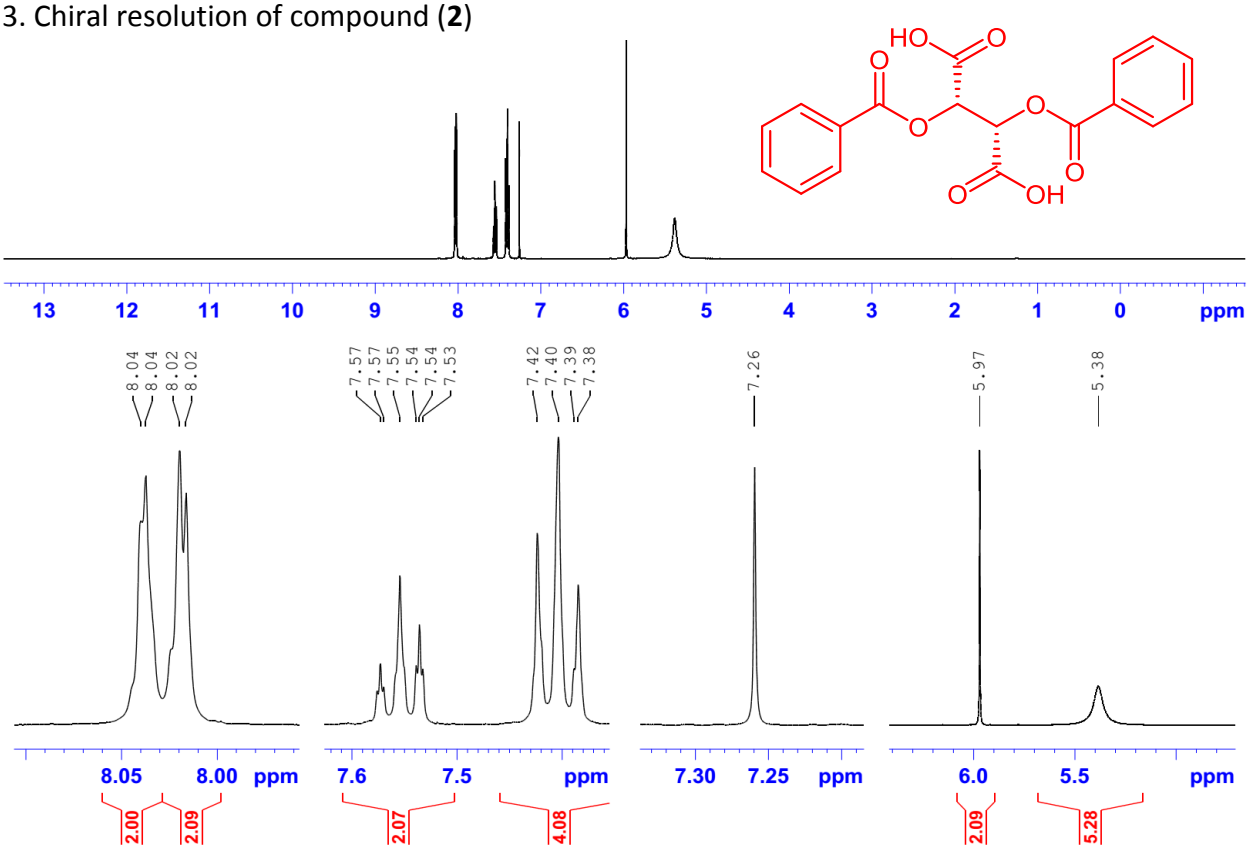


Compound 2, MS (ESI +)

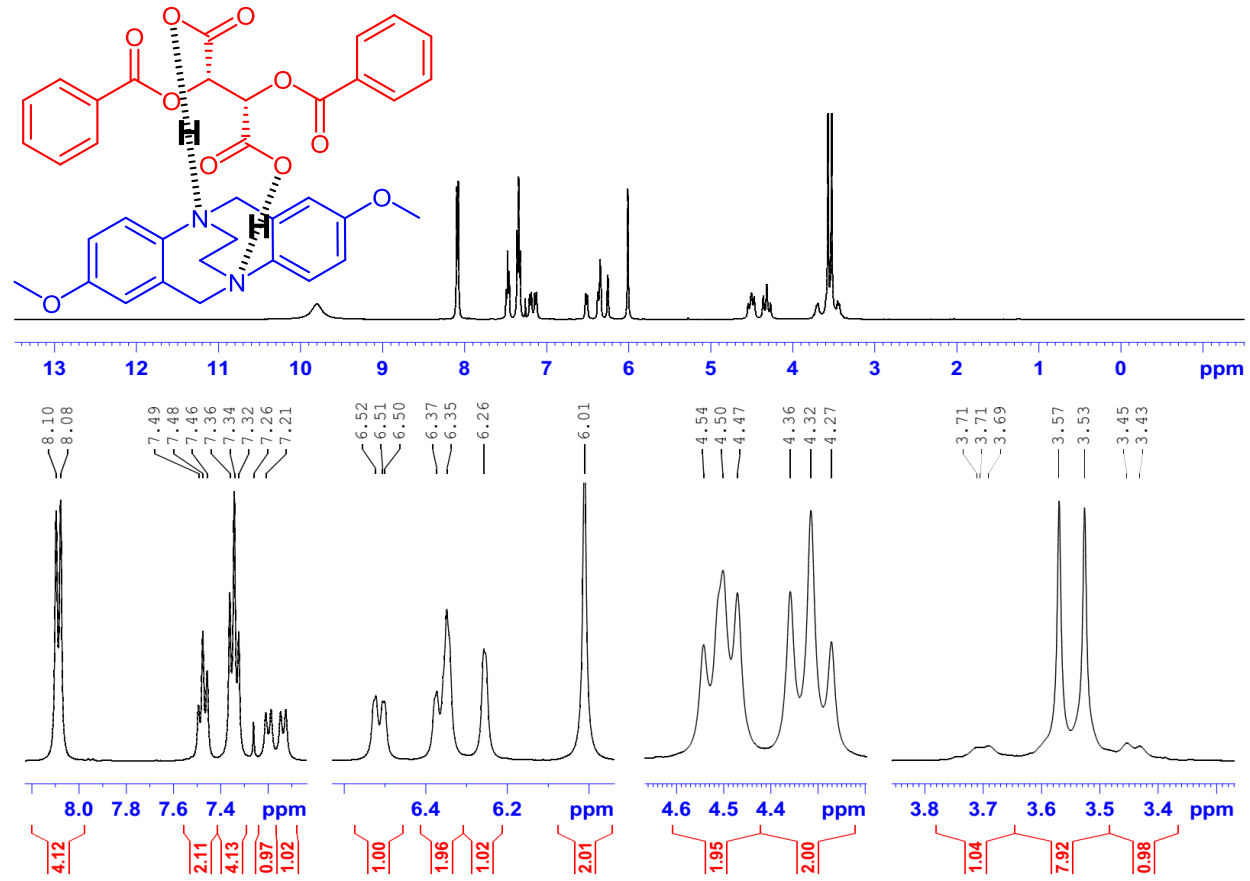


Compound 2, ^{1}H NMR (400MHz, $CDCl_3$)

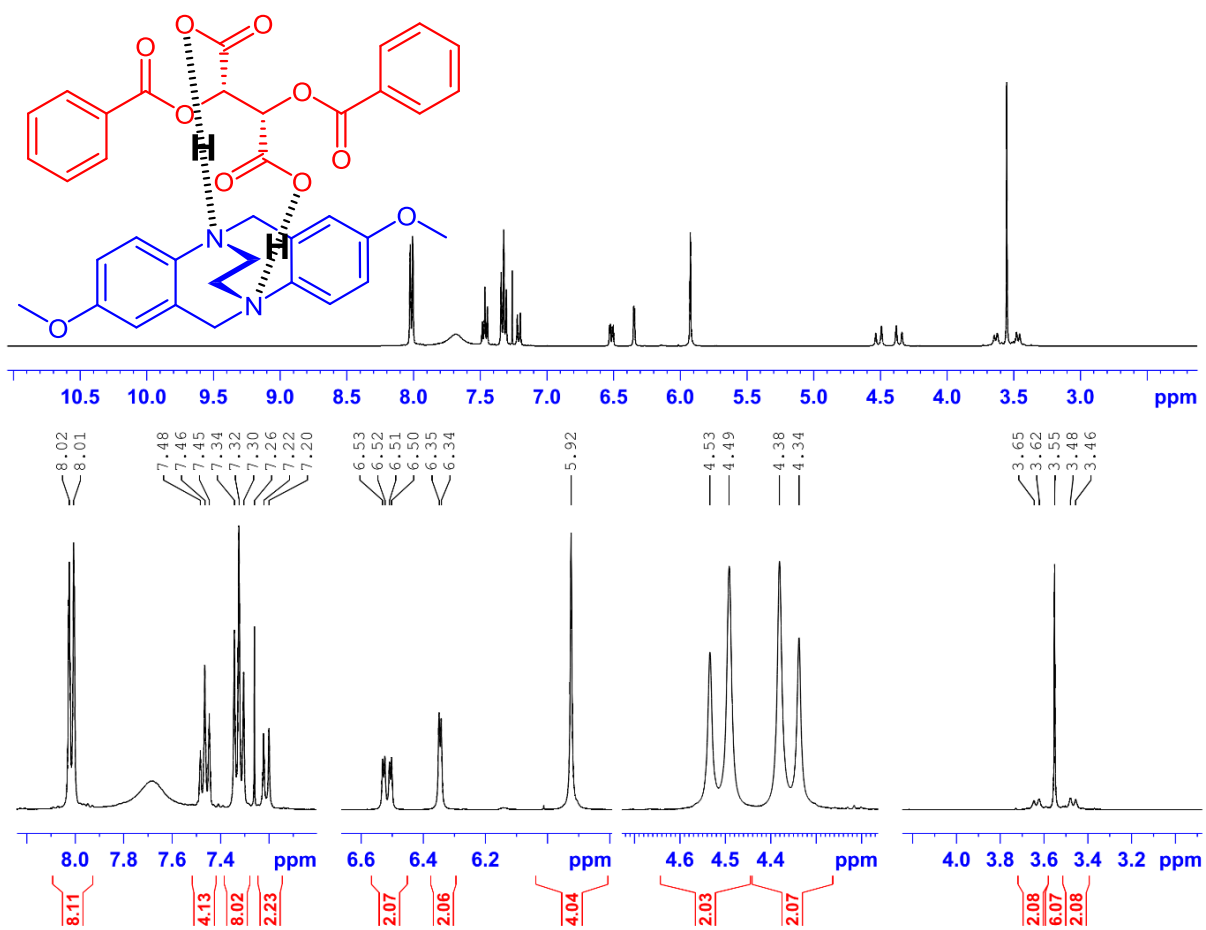
3. Chiral resolution of compound (**2**)



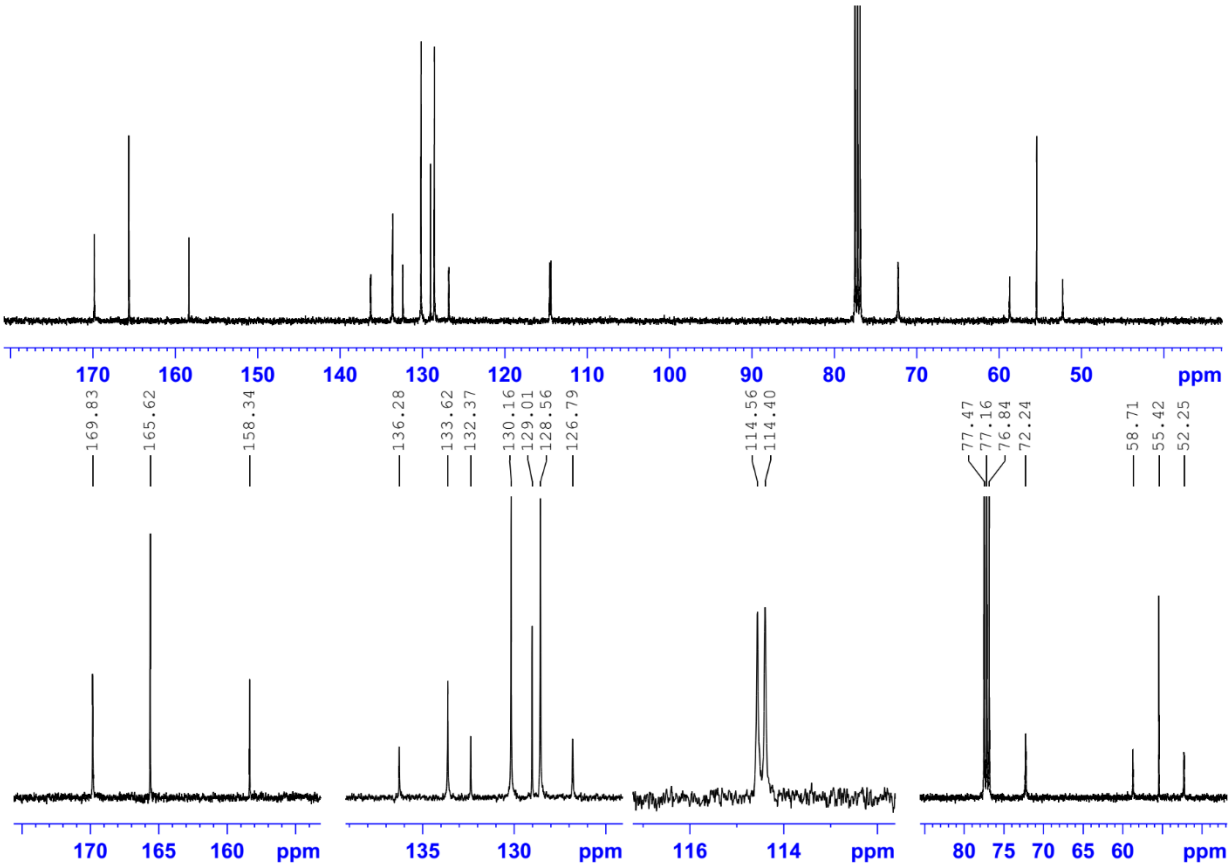
Chiral Discriminator (–)-DBTA, ^{1}H NMR (400MHz, $CDCl_3$)



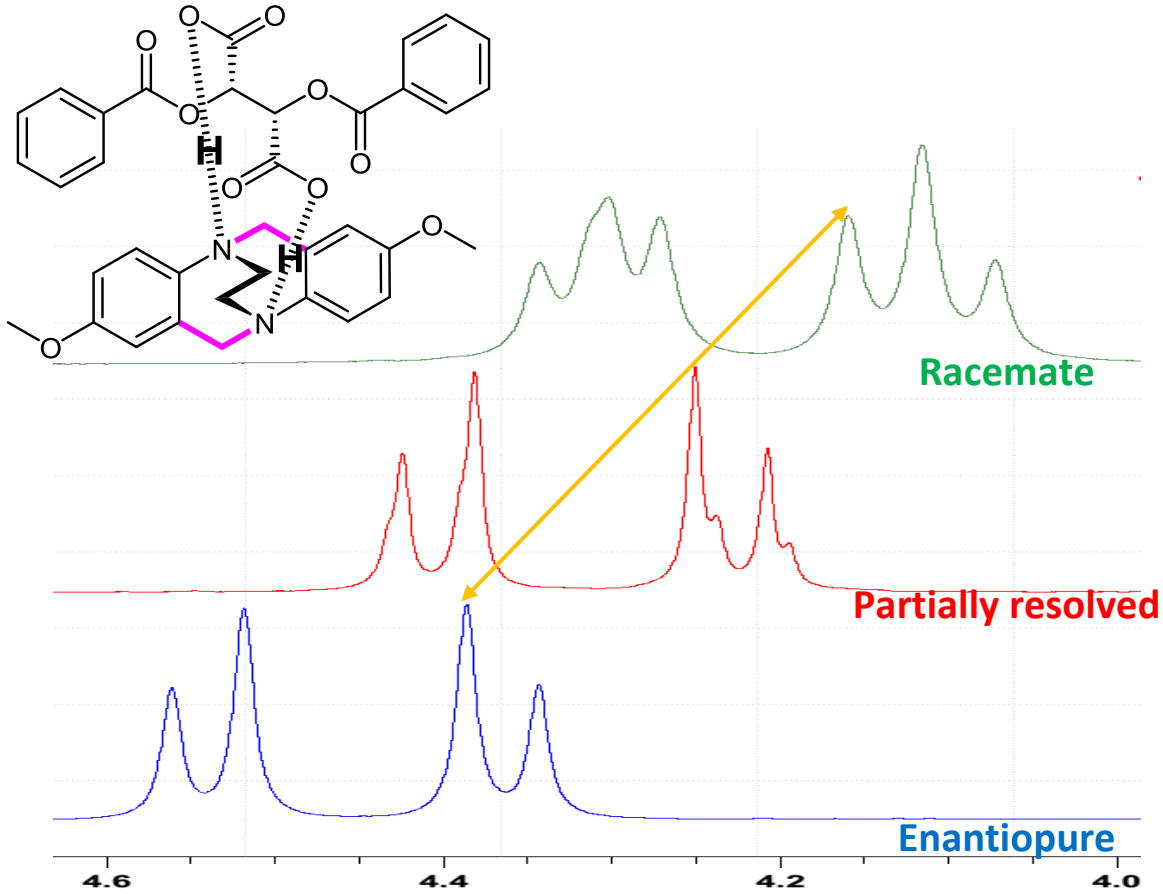
(±)-2 and (–)-DBTA, Mole ratio 1:1, ^{1}H NMR titration (400MHz, $CDCl_3$)



(+)-(*R*,*R*)-2 and (–)-DBTA, Mole ratio 1:2, ^{1}H NMR titration (400MHz, $CDCl_3$)

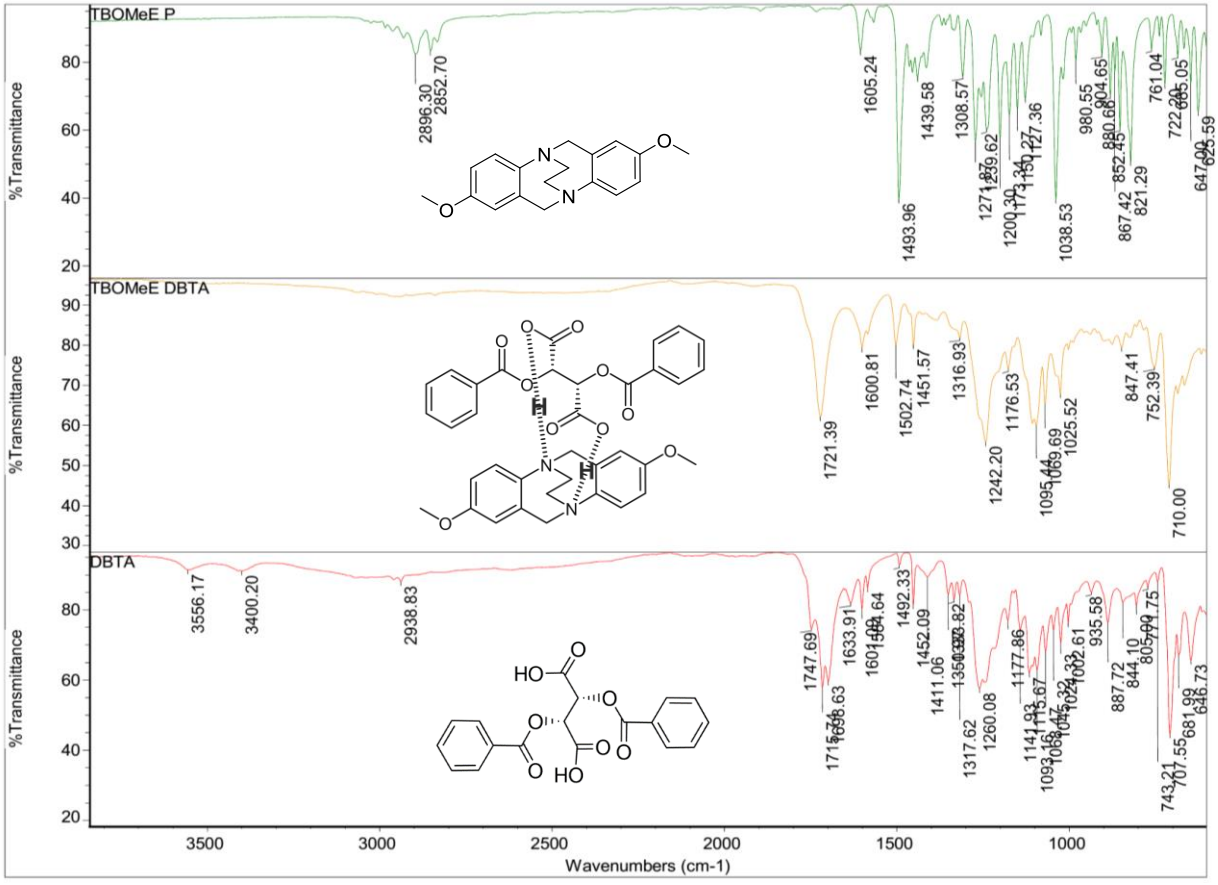


(+)-(*R*,*R*)-2 and (–)-DBTA, Mole ratio 1:2, ^{13}C NMR titration (100MHz, $CDCl_3$)

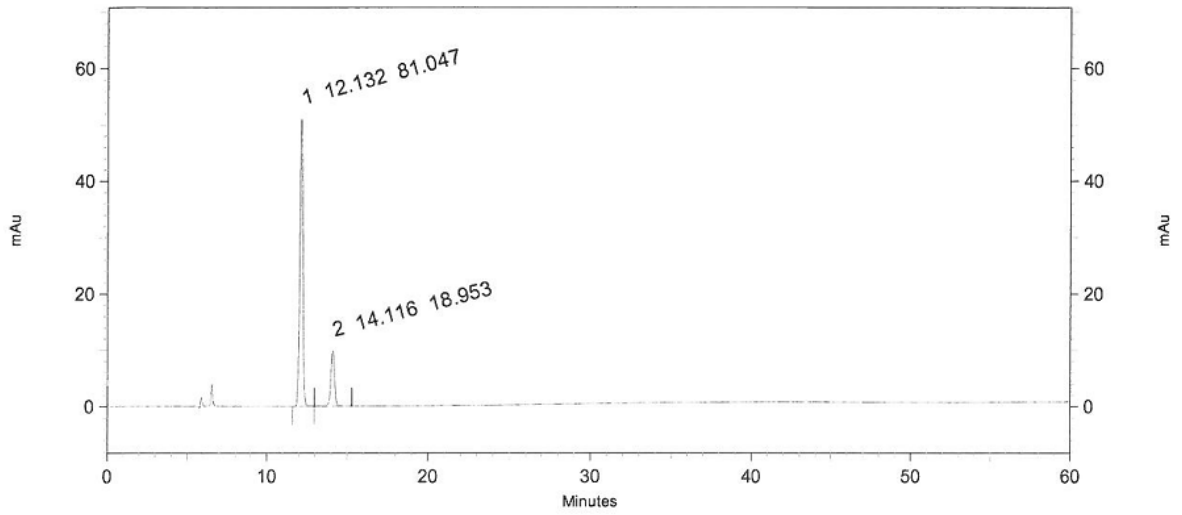


^{1}H NMR titration, Compound 2 in the presence of two mol equivalents of (–)-BDTA

(Stacked view, with a 15% horizontal step, of the peaks corresponding to the indicated CH_2 groups in pink)



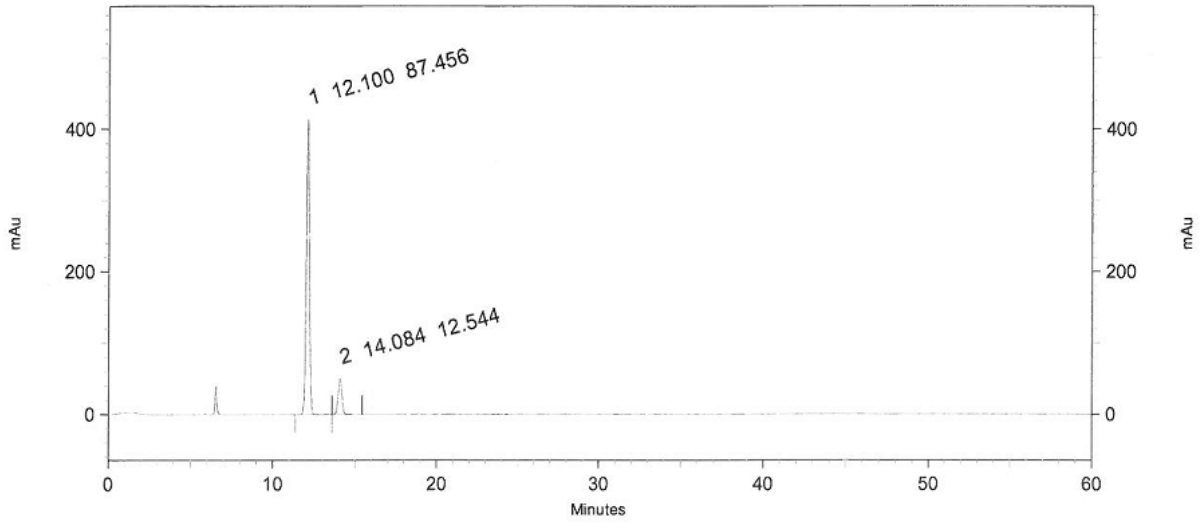
Stacked IR spectra (transmittance)



3: 254 nm, 4 nm Results

Pk #	Retention Time	Area	Area %
1	12.132	676701	81.05
2	14.116	158252	18.95
Totals		834953	100.00

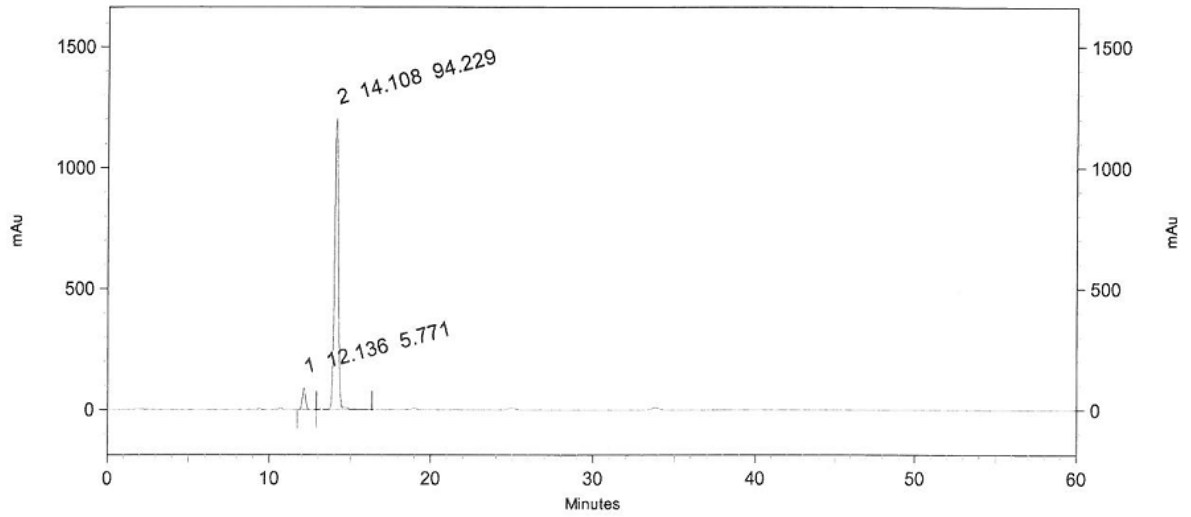
Chiral HPLC chromatogram, partially resolved 2 (The 1st crop of crystals)



3: 254 nm, 4 nm Results

Pk #	Retention Time	Area	Area %
1	12.100	5528689	87.46
2	14.084	793026	12.54
Totals		6321715	100.00

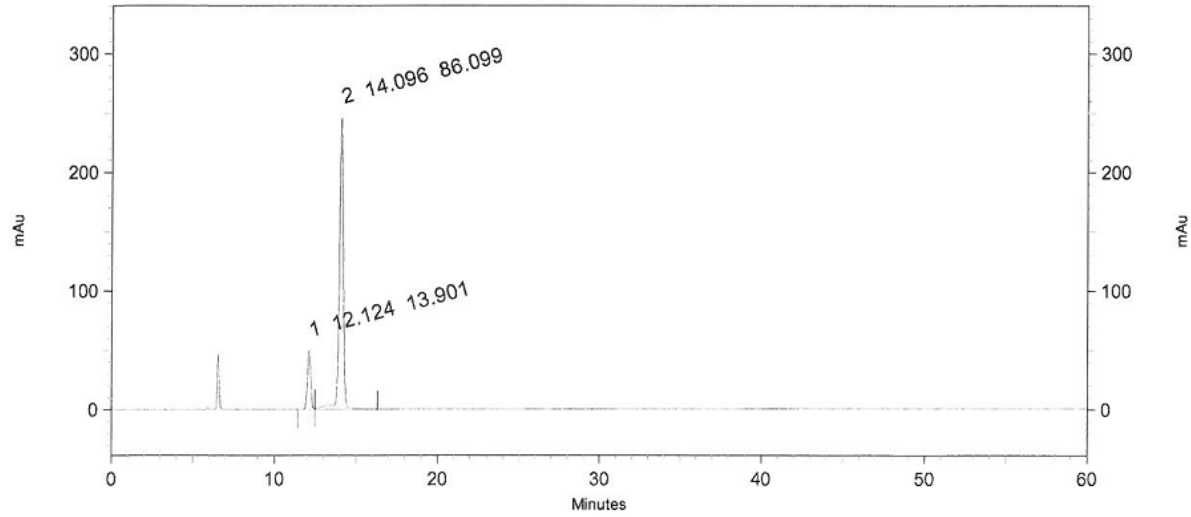
Chiral HPLC chromatogram, partially resolved 2 (The 2nd crop of crystals)



3: 254 nm, 4 nm Results

Pk #	Retention Time	Area	Area %
1	12.136	1207847	5.77
2	14.108	19720336	94.23
Totals		20928183	100.00

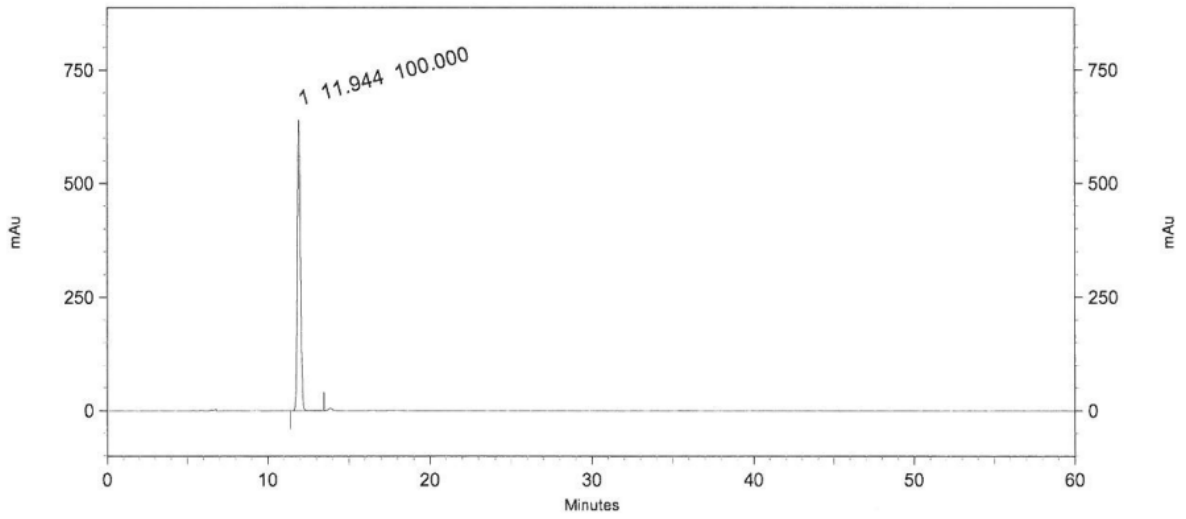
Chiral HPLC chromatogram, partially resolved 2 (The 2nd mother liquor)



3: 254 nm, 4 nm Results

Pk #	Retention Time	Area	Area %
1	12.124	680150	13.90
2	14.096	4212500	86.10
Totals		4892650	100.00

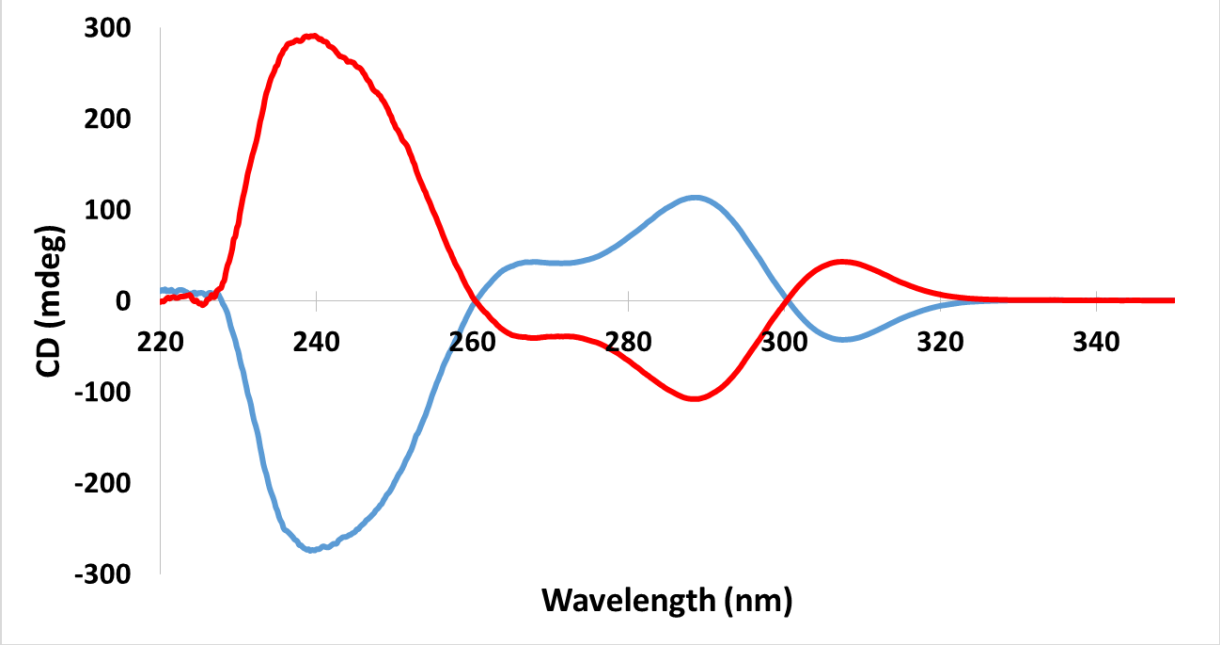
Chiral HPLC chromatogram, partially resolved 2 (The 1st mother liquor)



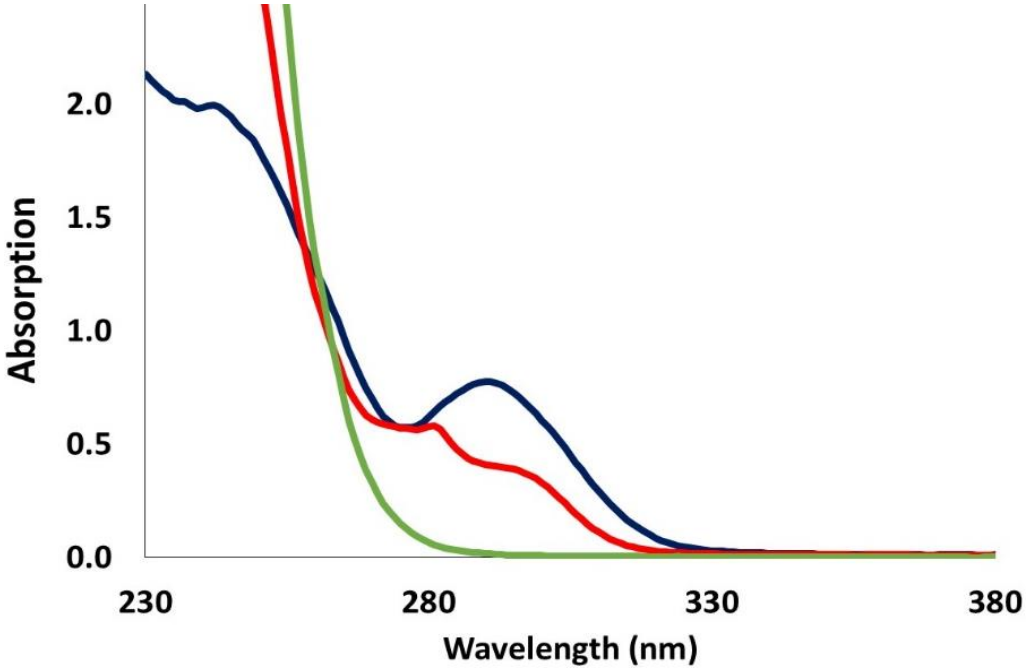
3: 254 nm, 4 nm Results

Pk #	Retention Time	Area	Area %
1	11.944	8423288	100.00
Totals		8423288	100.00

Chiral HPLC chromatogram, (+)-(*R*,*R*)-2 (The 4th recrystallization)



CD spectra, (+)-(*R*,*R*)-2 and (–)-(*S*,*S*)-2 in DCM

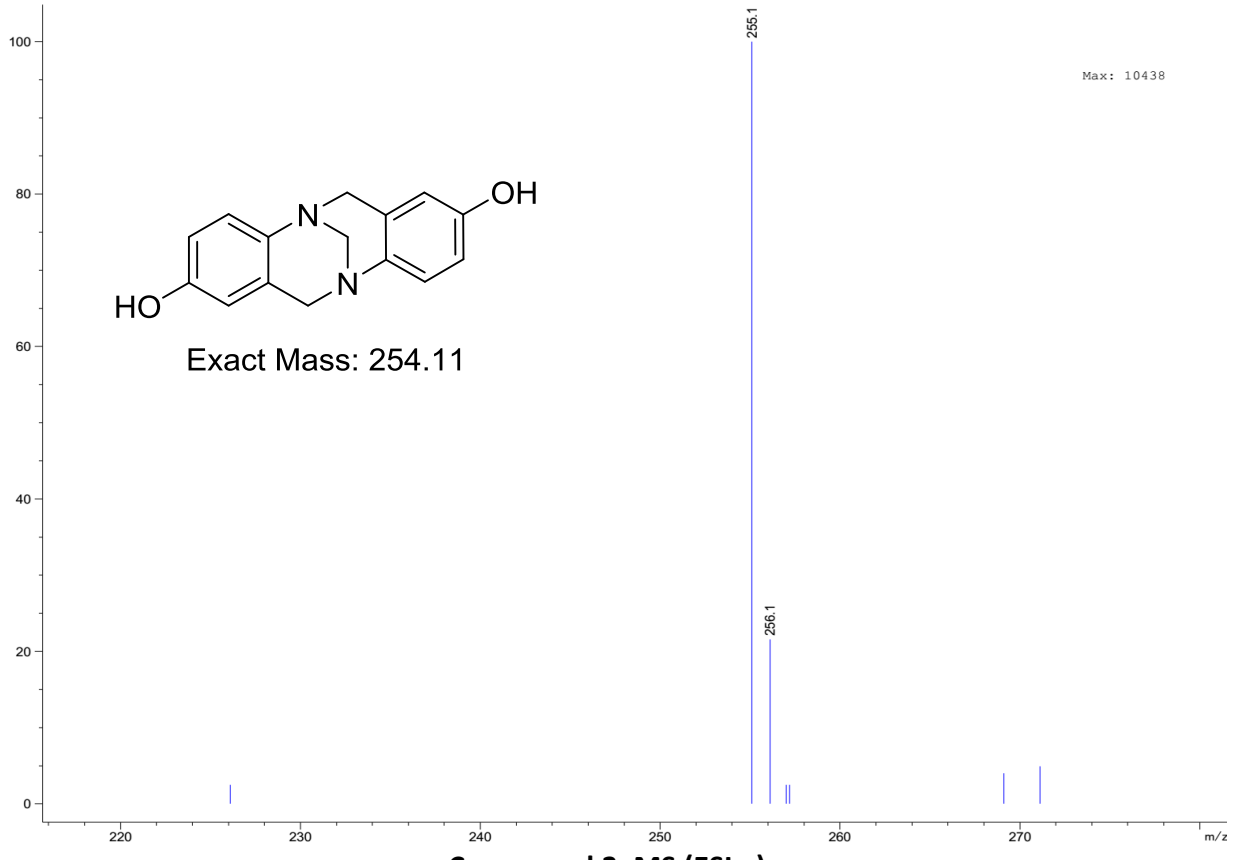


UV-Vis absorption spectra

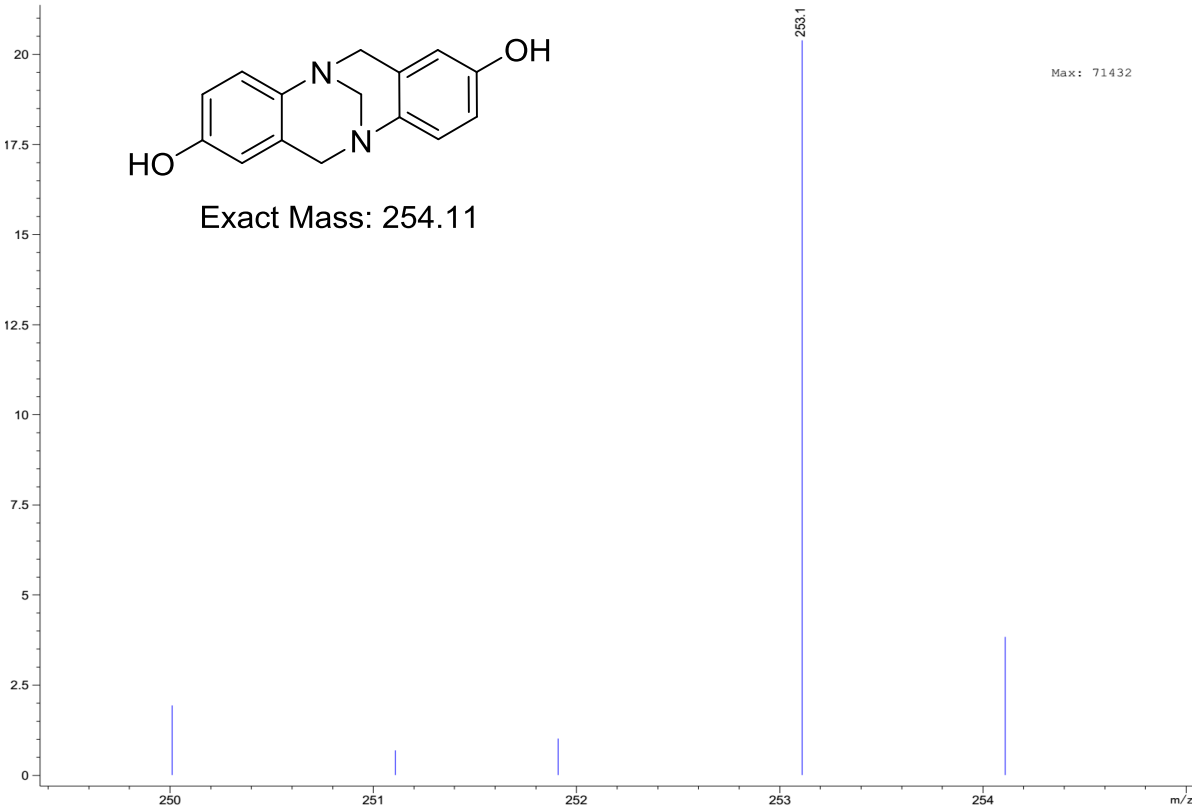
2 in CH_3CN (in blue), TCA in CH_3CN (*C* 0.05%, in green), and 1:1 combination of both (in red)

4. Characterization of compound (**3**)

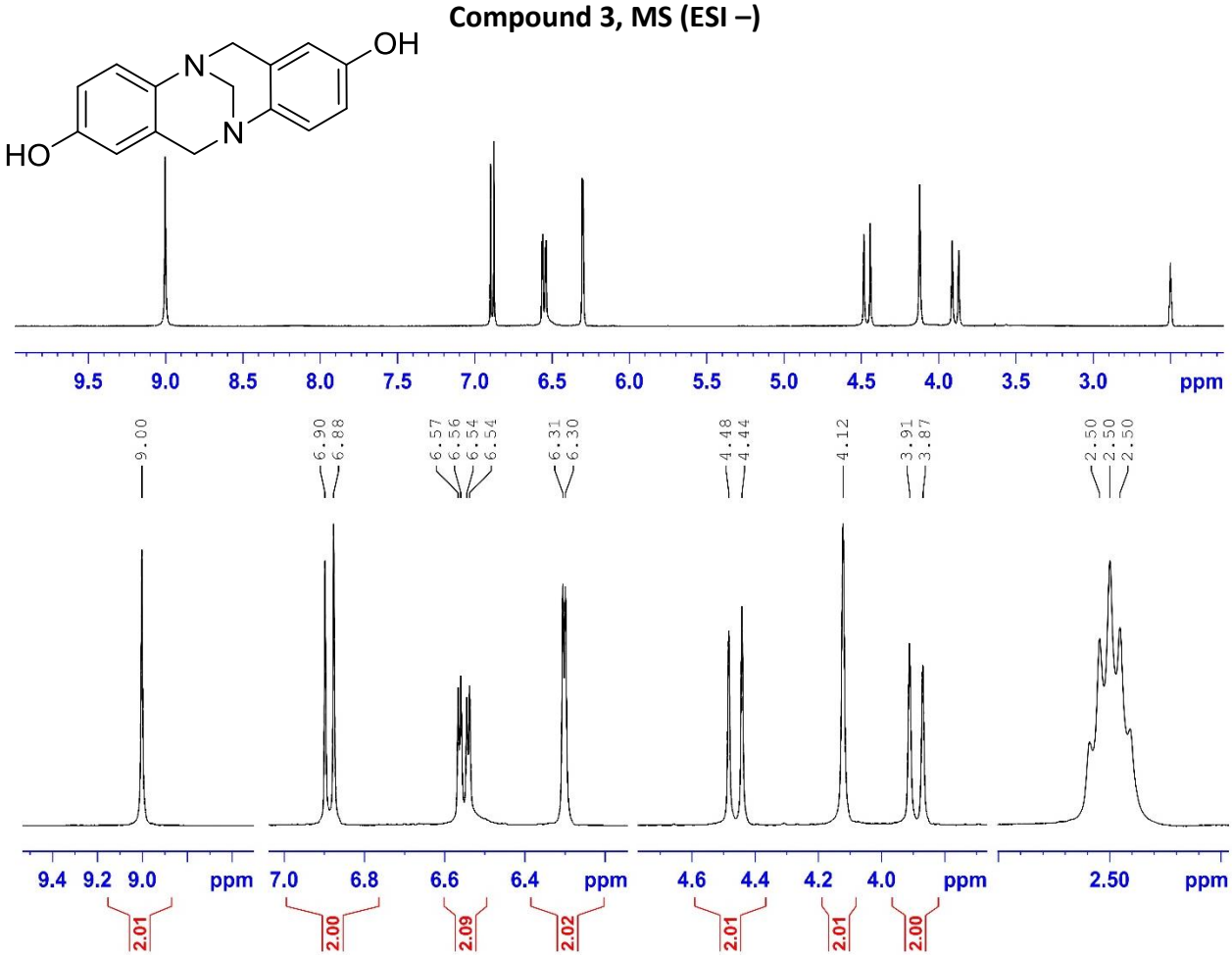
6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine-2,8-diol



Compound 3, MS (ESI +)



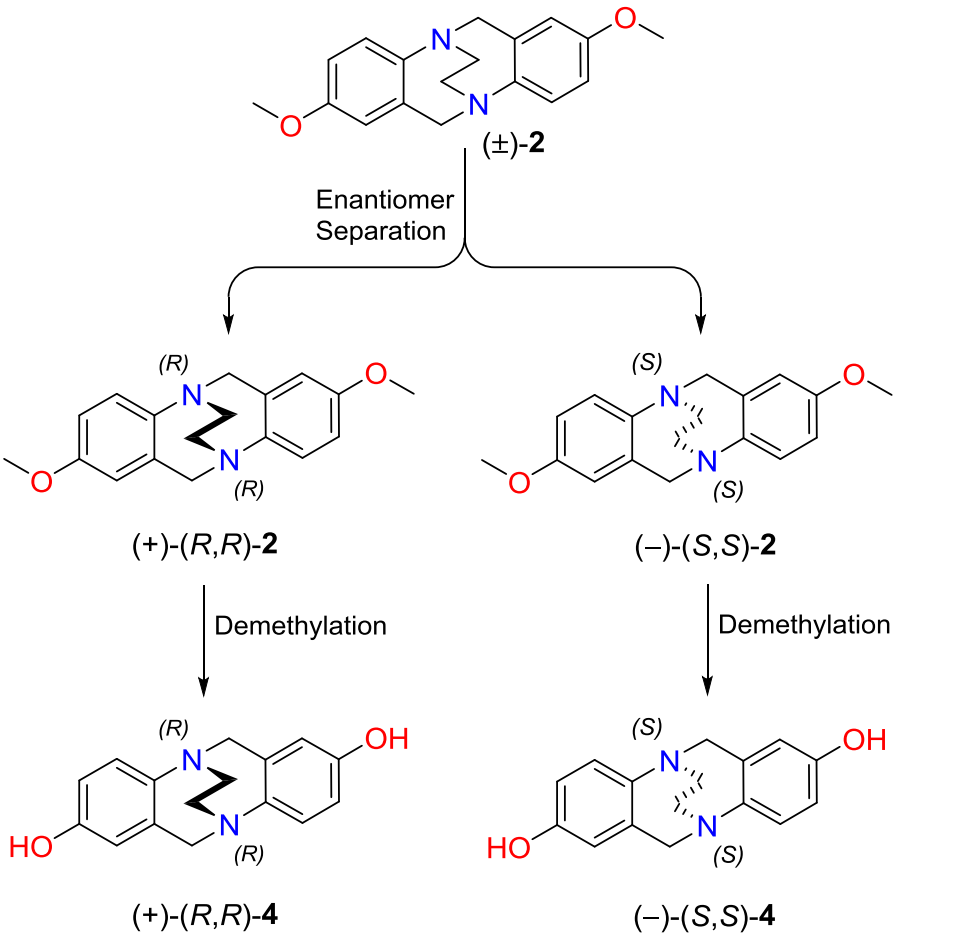
Compound 3, MS (ESI –)

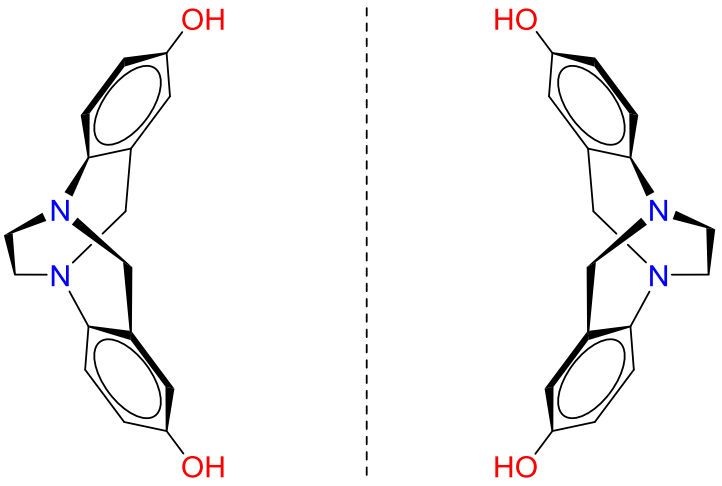


Compound 3, ^{1}H NMR (400 MHz, DMSO-d_6)

5. Characterization of compound (**4**)

6*H*,12*H*-5,11-ethanodibenzo[*b,f*][1,5]diazocine-2,8-diol

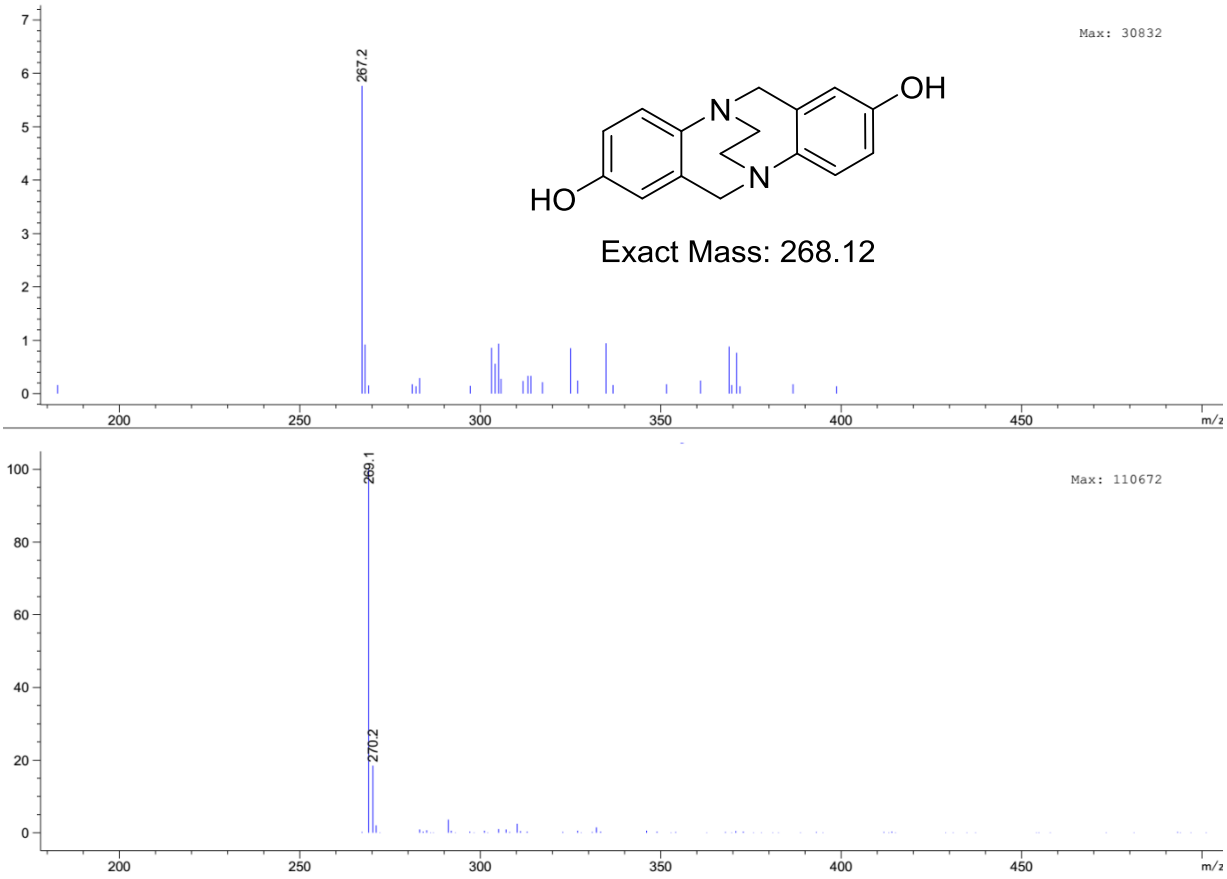




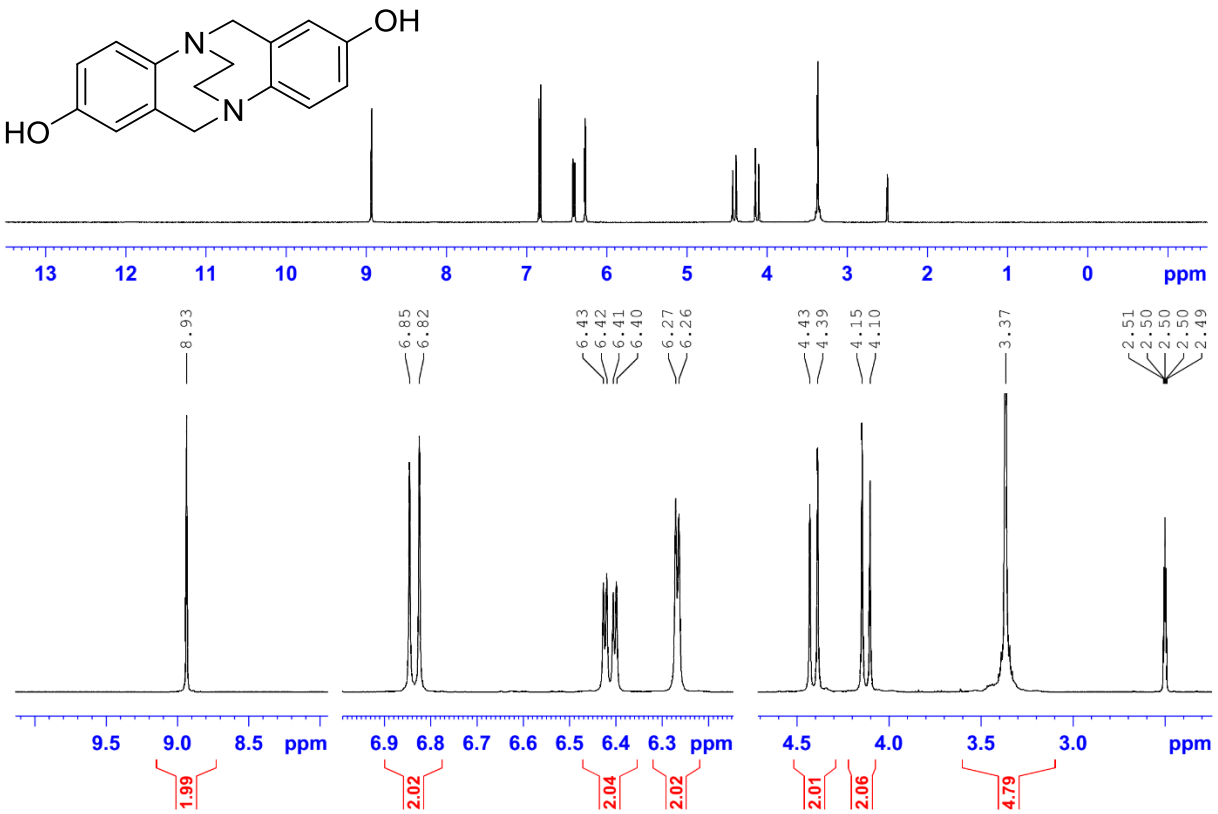
(5*R*,11*R*)-6*H*,12*H*-5,11-ethanodibenzo [*b*,*f*][1,5]diazocine-2,8-diol

(5*S*,11*S*)-6*H*,12*H*-5,11-ethanodibenzo [*b*,*f*][1,5]diazocine-2,8-diol

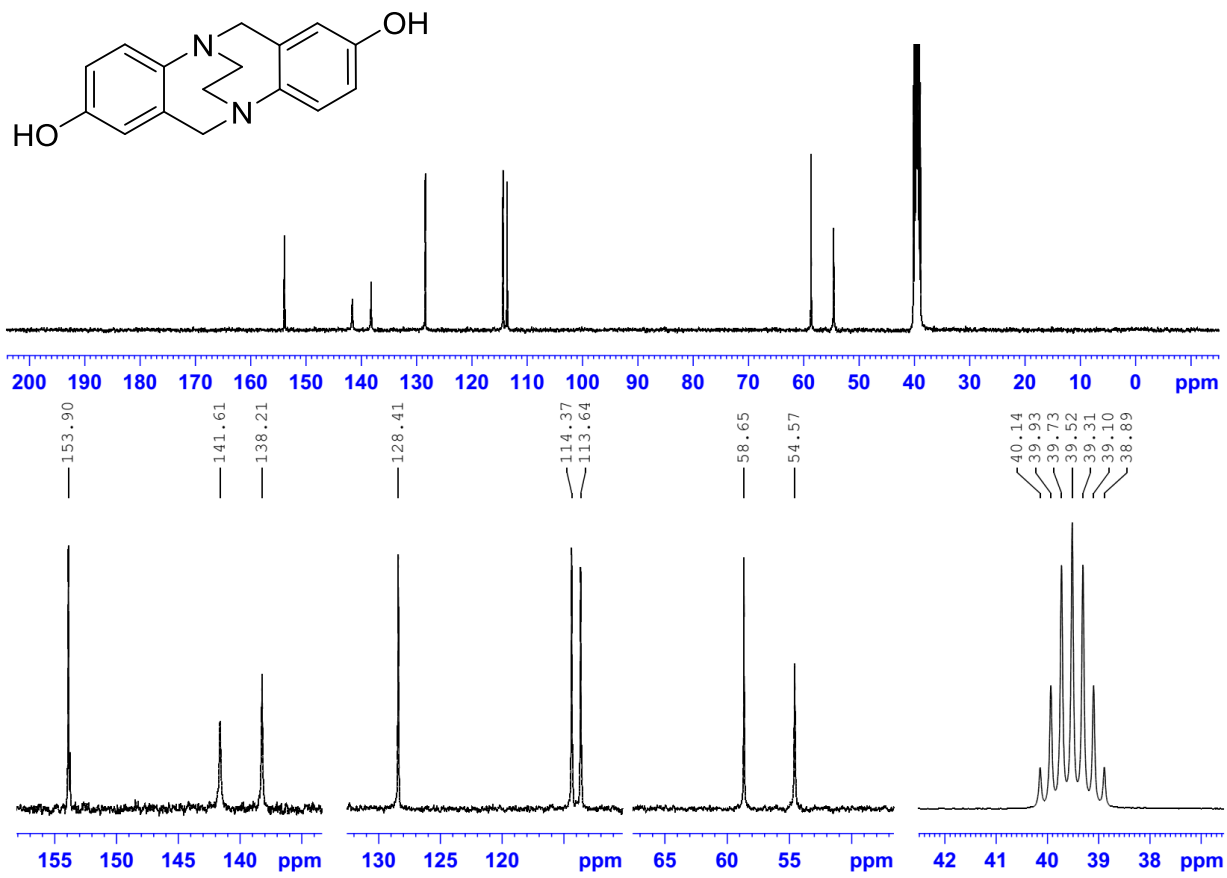
Mirror image presentation of (+)-4 and (–)-4 enantiomers derived from (+)-2 and (–)-2



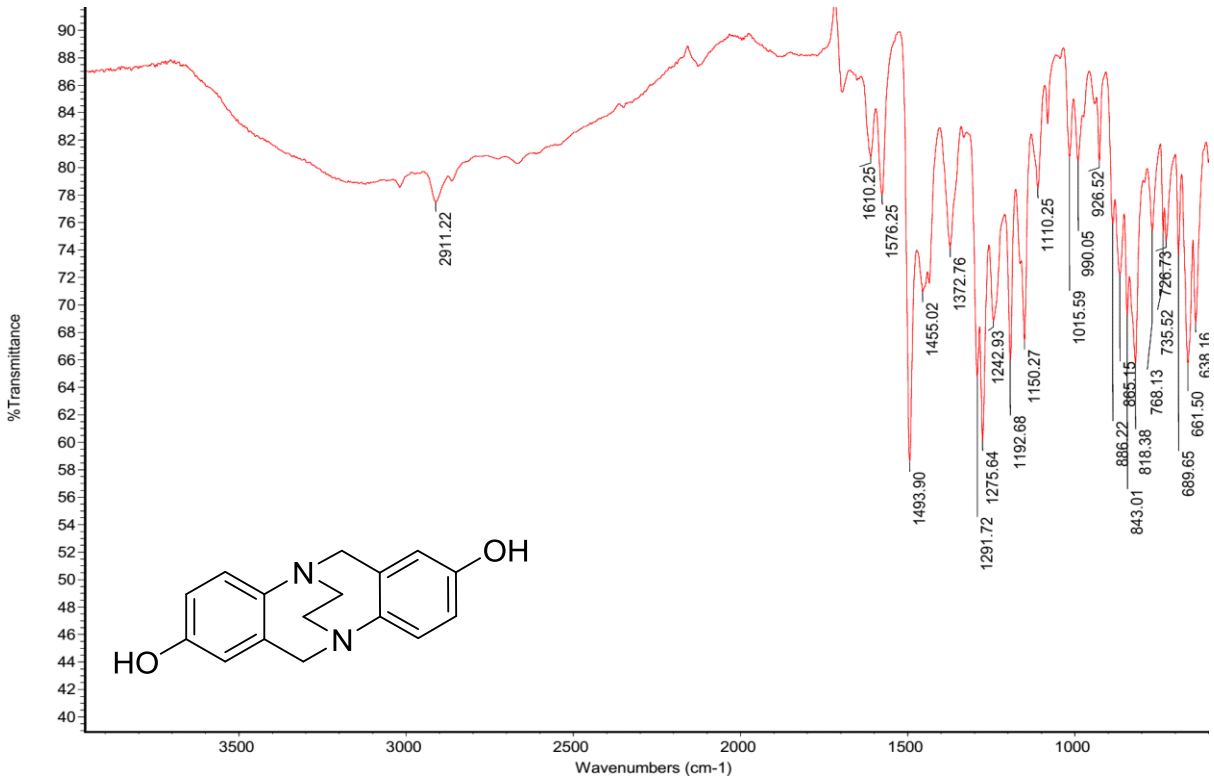
Compound 4, MS (ESI –) top and (ESI +) bottom



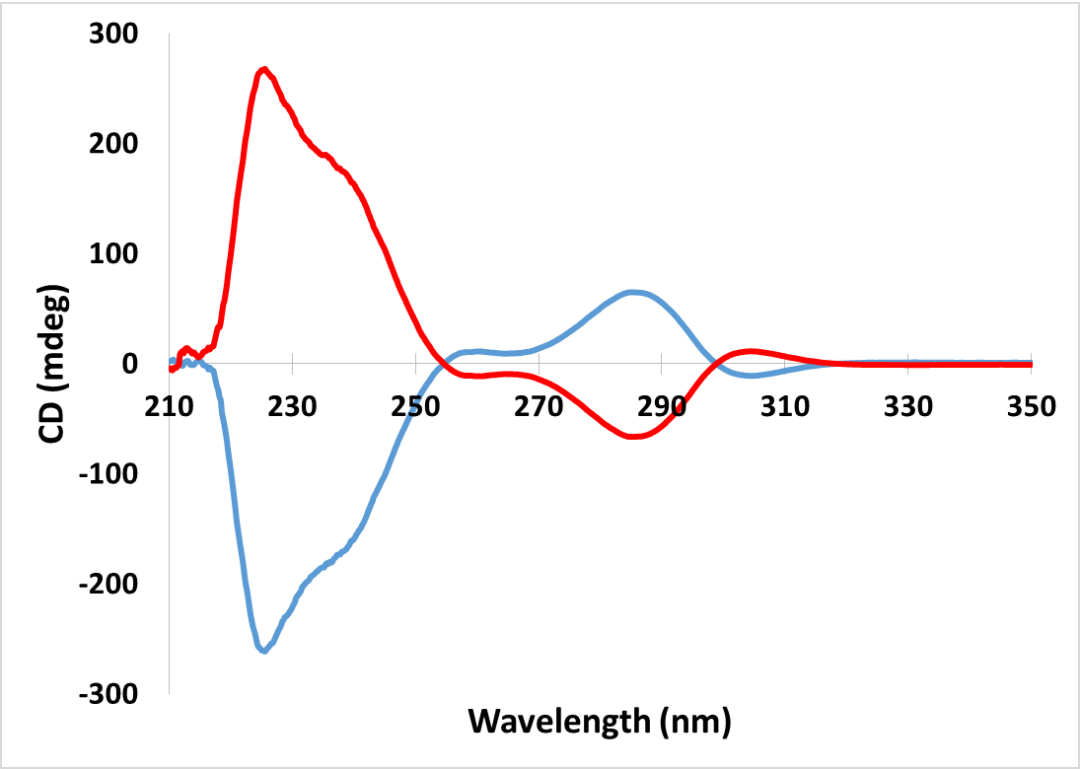
Compound 4, ^{1}H NMR (400 MHz, DMSO-d_6)



Compound 4, ^{13}C NMR (100 MHz, DMSO-d_6)



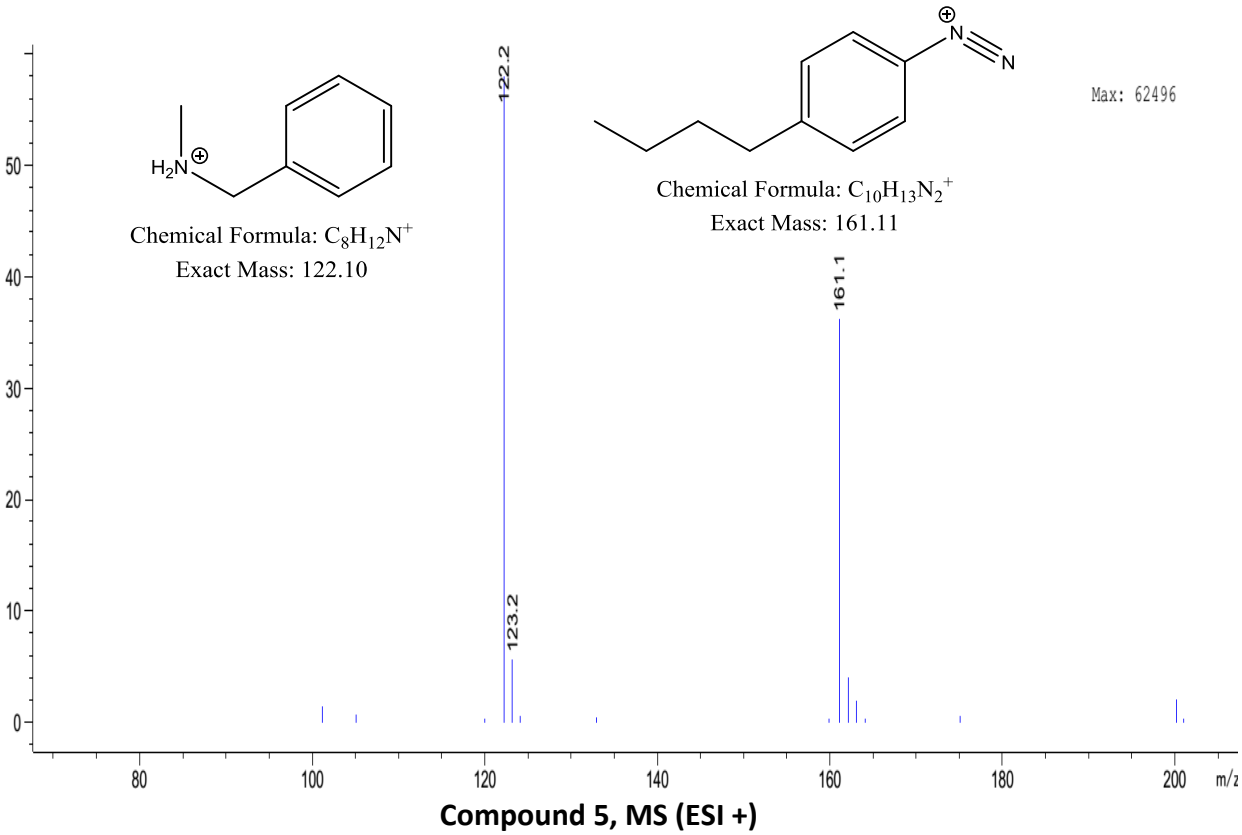
Compound 4, IR transmittance (neat)



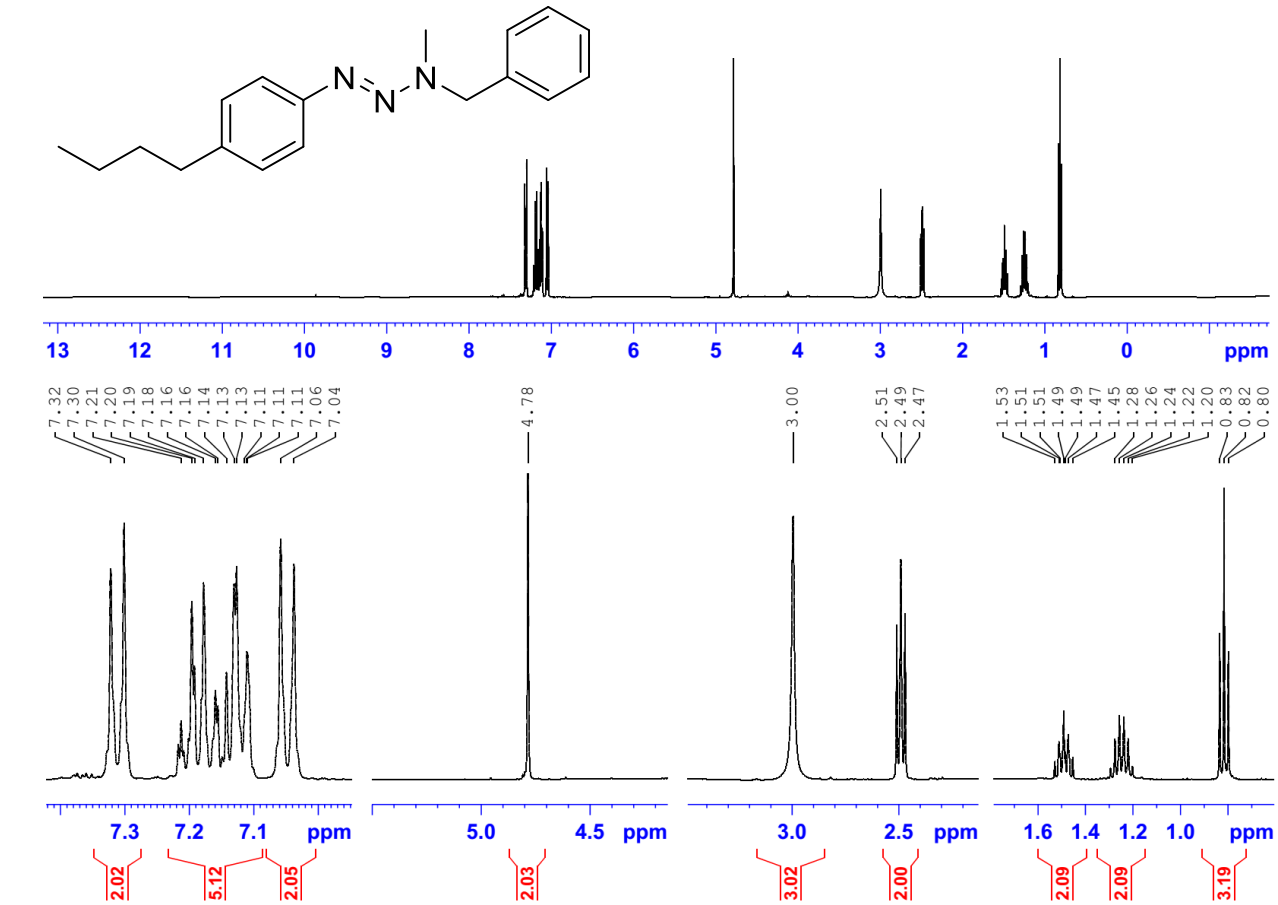
CD spectra, (+)-(*R*,*R*)-4 and (–)-(*S*,*S*)-4 in MeOH

6. Characterization of compound (**5**)

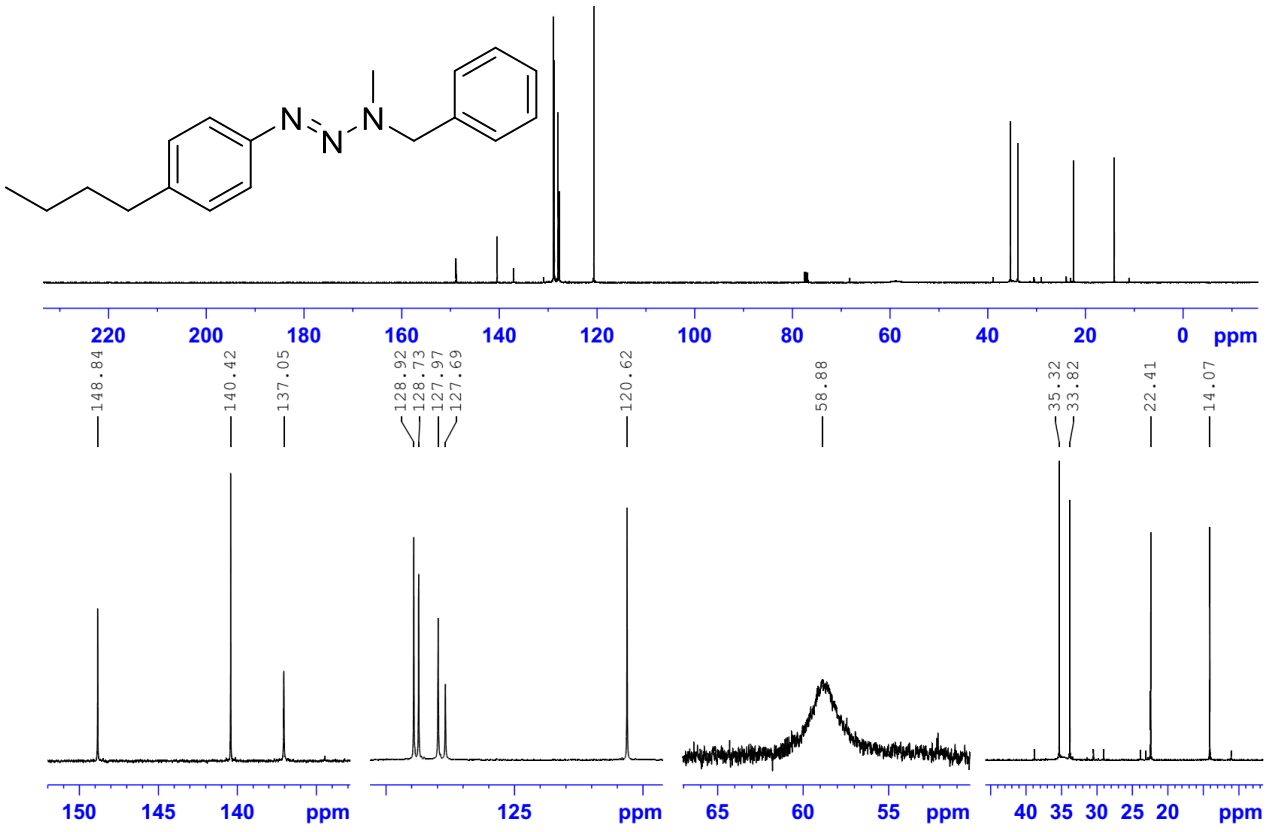
(*E*)-3-benzyl-1-(4-butylphenyl)-3-methyltriaz-1-ene



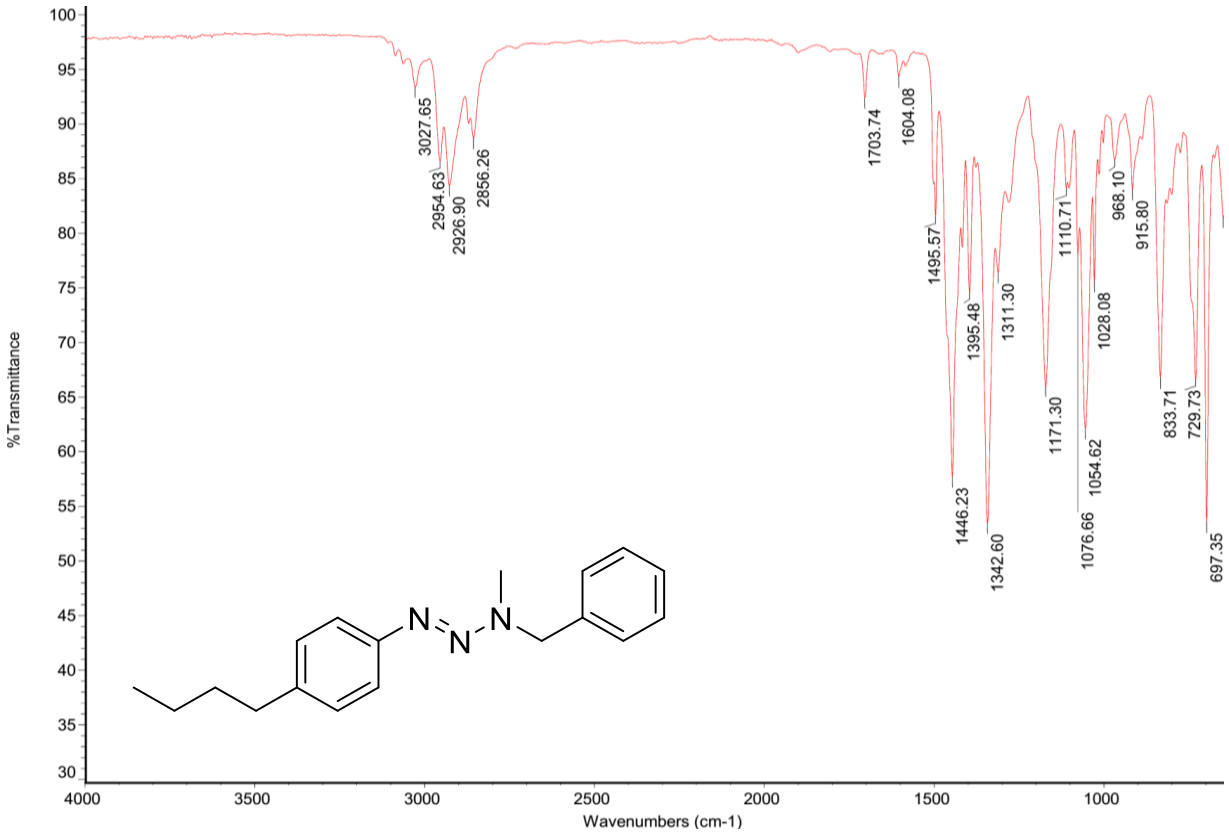
Compound 5, MS (ESI +)



Compound 5, ^{1}H NMR (400 MHz, $CDCl_3$)



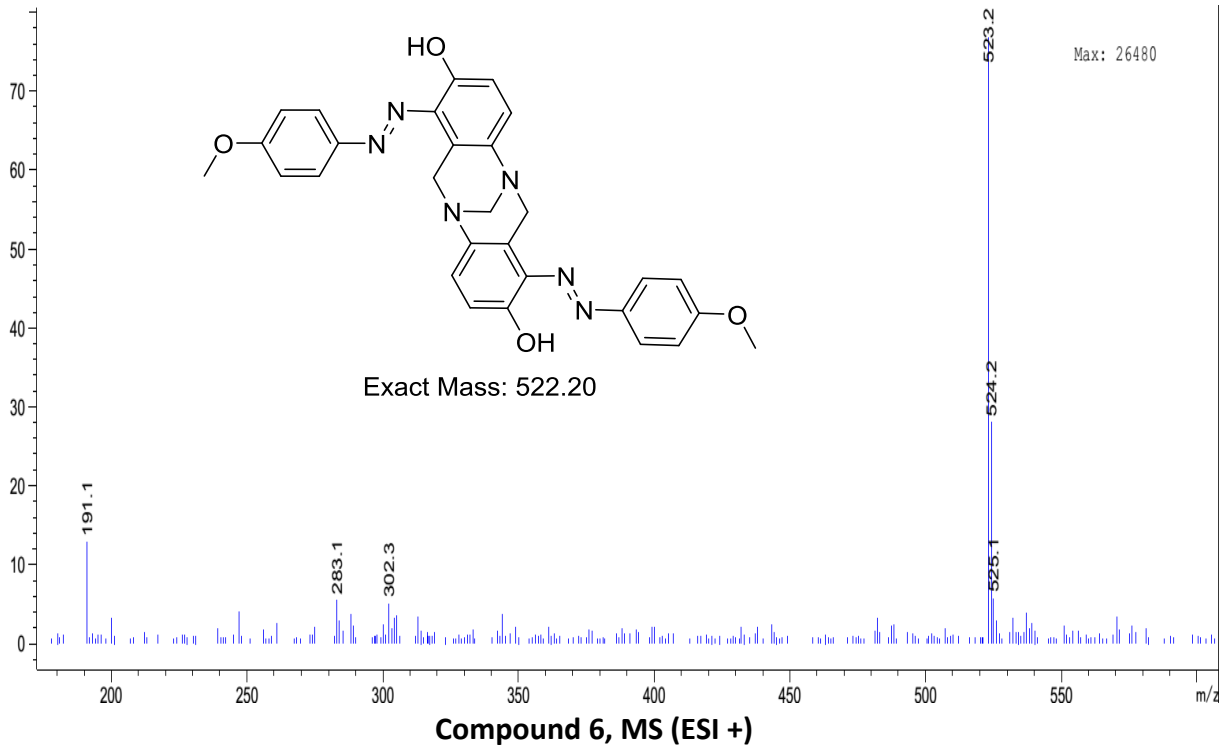
Compound 5, ^{13}C NMR (100 MHz, $CDCl_3$)



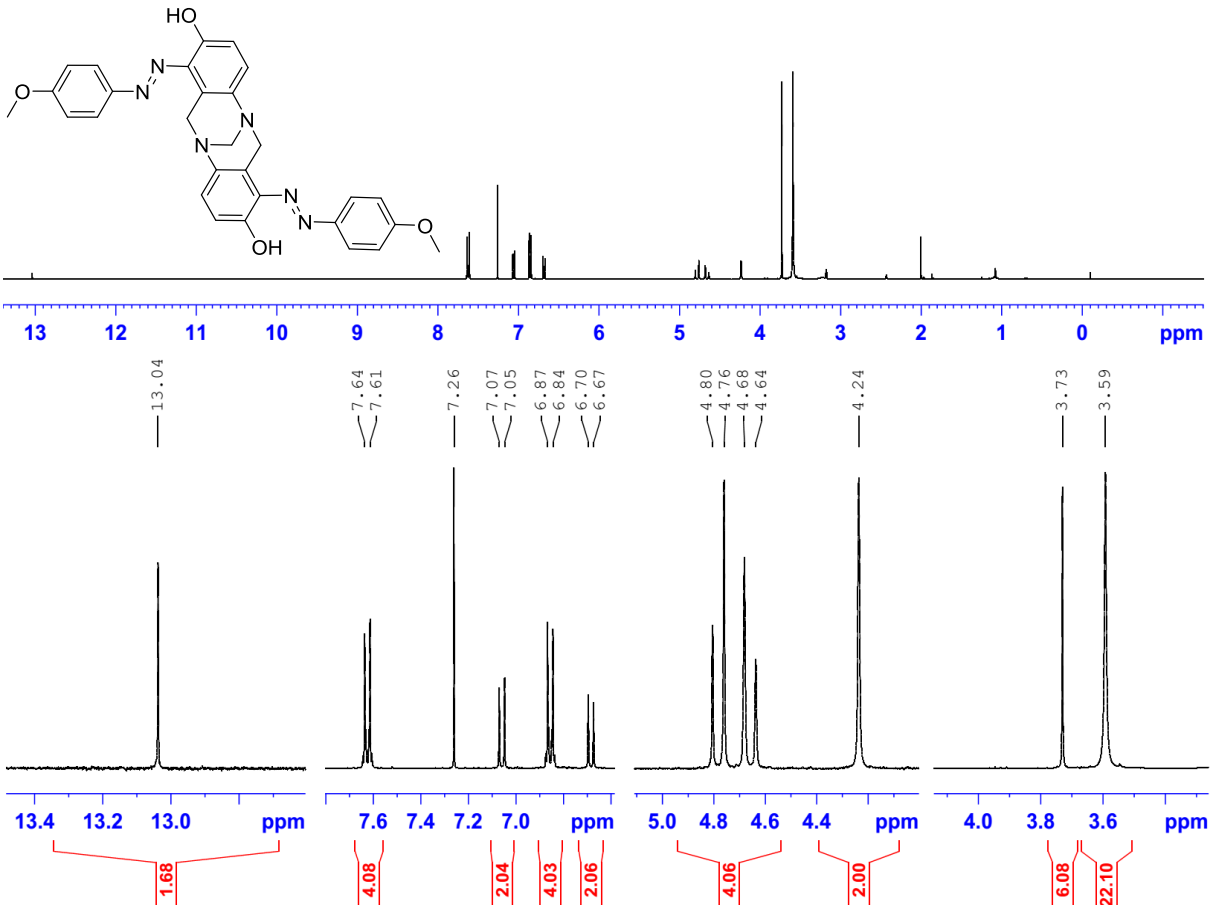
Compound 5, IR transmittance (neat liquid)

7. Characterization of compound (**6**)

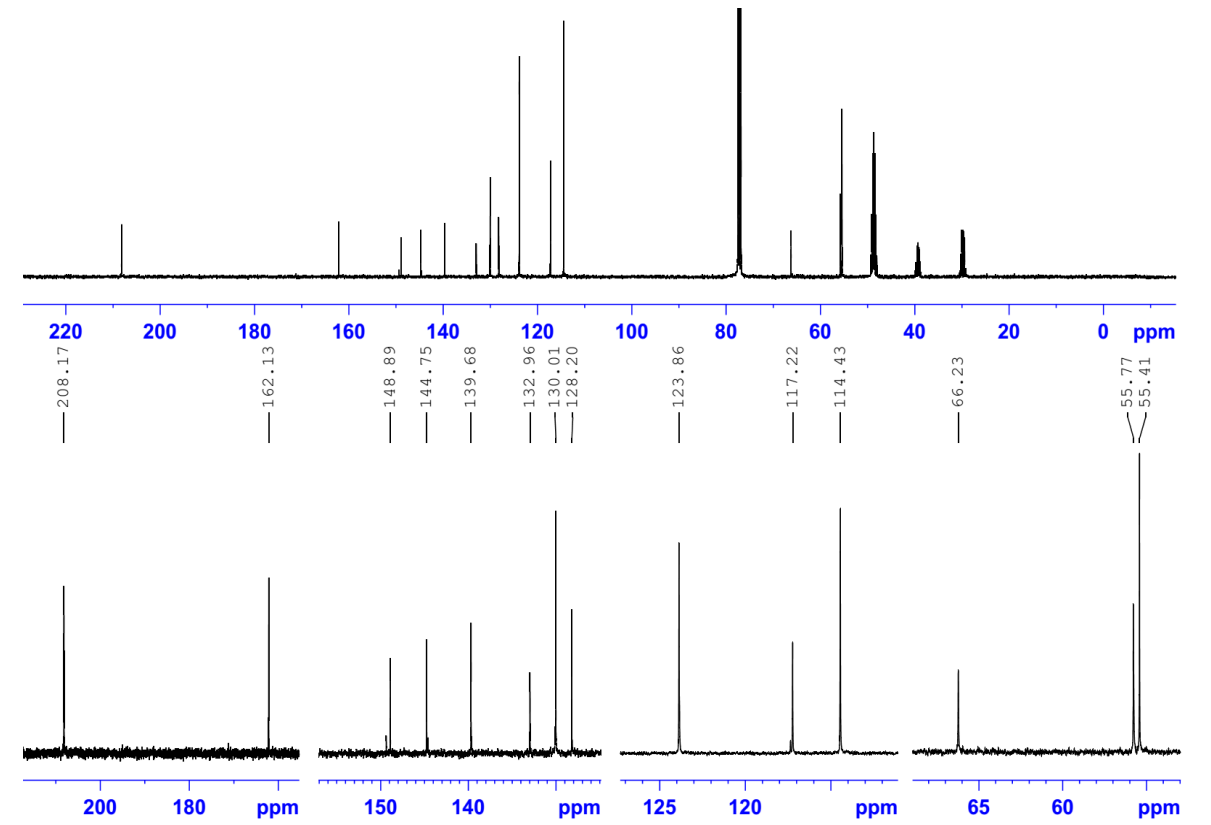
1,7-bis((*E*)-(4-methoxyphenyl)diazenyl)-6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine-2,8-diol



Compound 6, MS (ESI +)

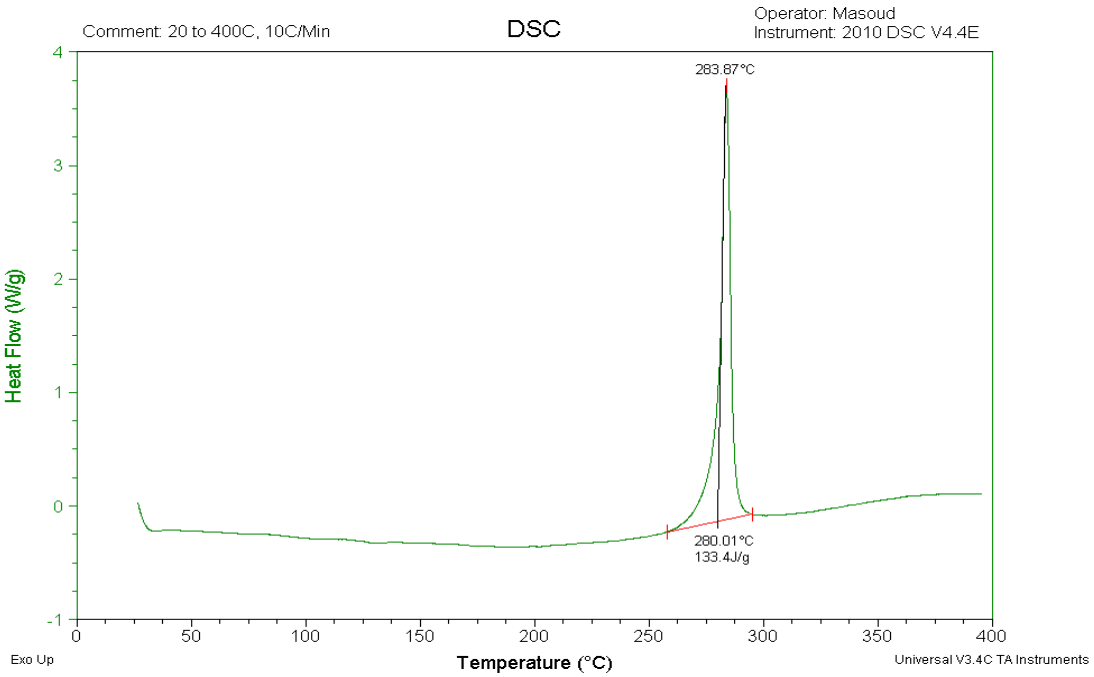


Compound 6, ^{1}H NMR (400 MHz, $CDCl_3$–CD_3OD–$(CD_3)_2CO$–$(CD_3)_2SO$, 7:1:1:1 v/v) ‡



Compound 6, ^{13}C NMR (100 MHz, $CDCl_3$–CD_3OD–$(CD_3)_2CO$–$(CD_3)_2SO$, 7:1:1:1 v/v) ‡

‡ These combined solvents did dissolve **6** without interfering with the locking and shimming.

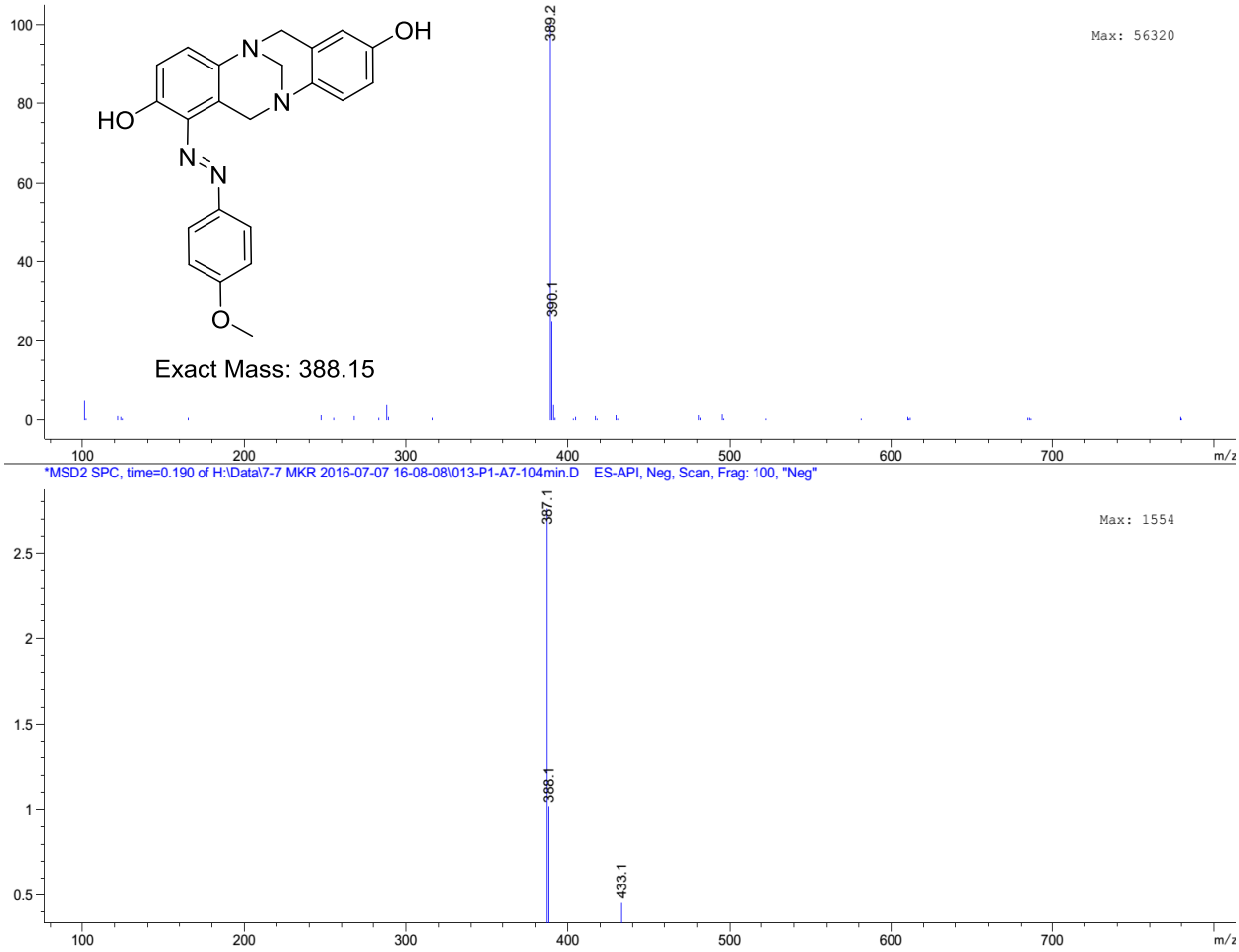


Compound 6, DSC thermogram

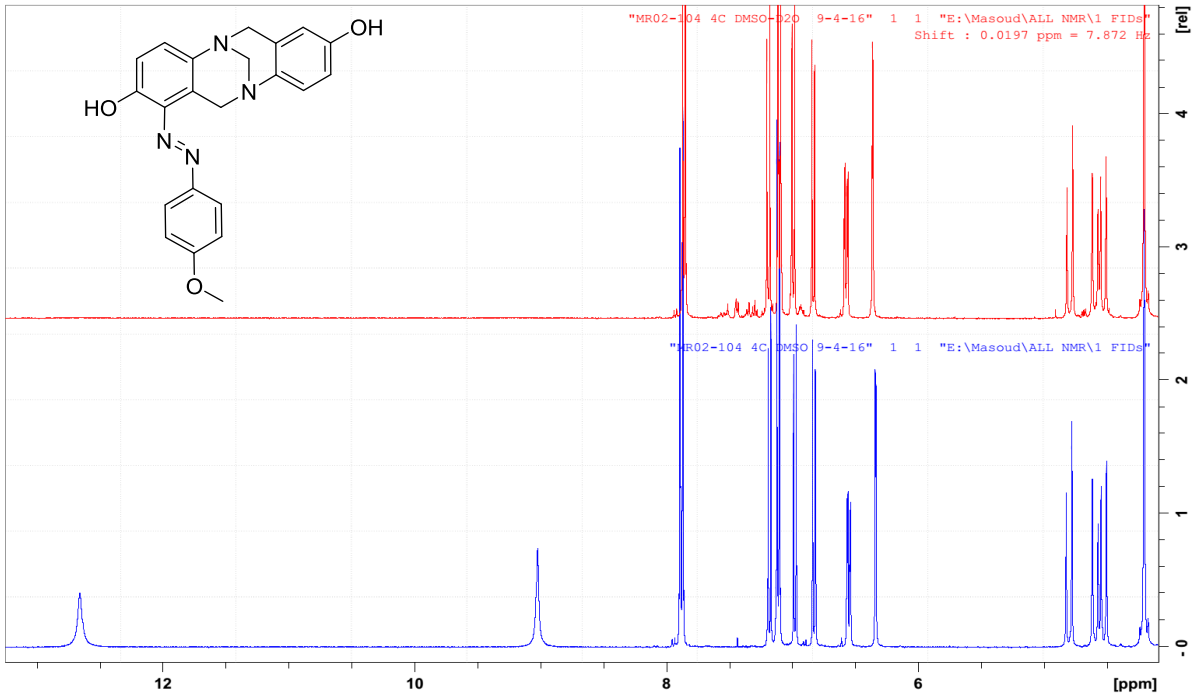
(decomposition without melting at 280–283 °C)

8. Characterization of compound (**7**)

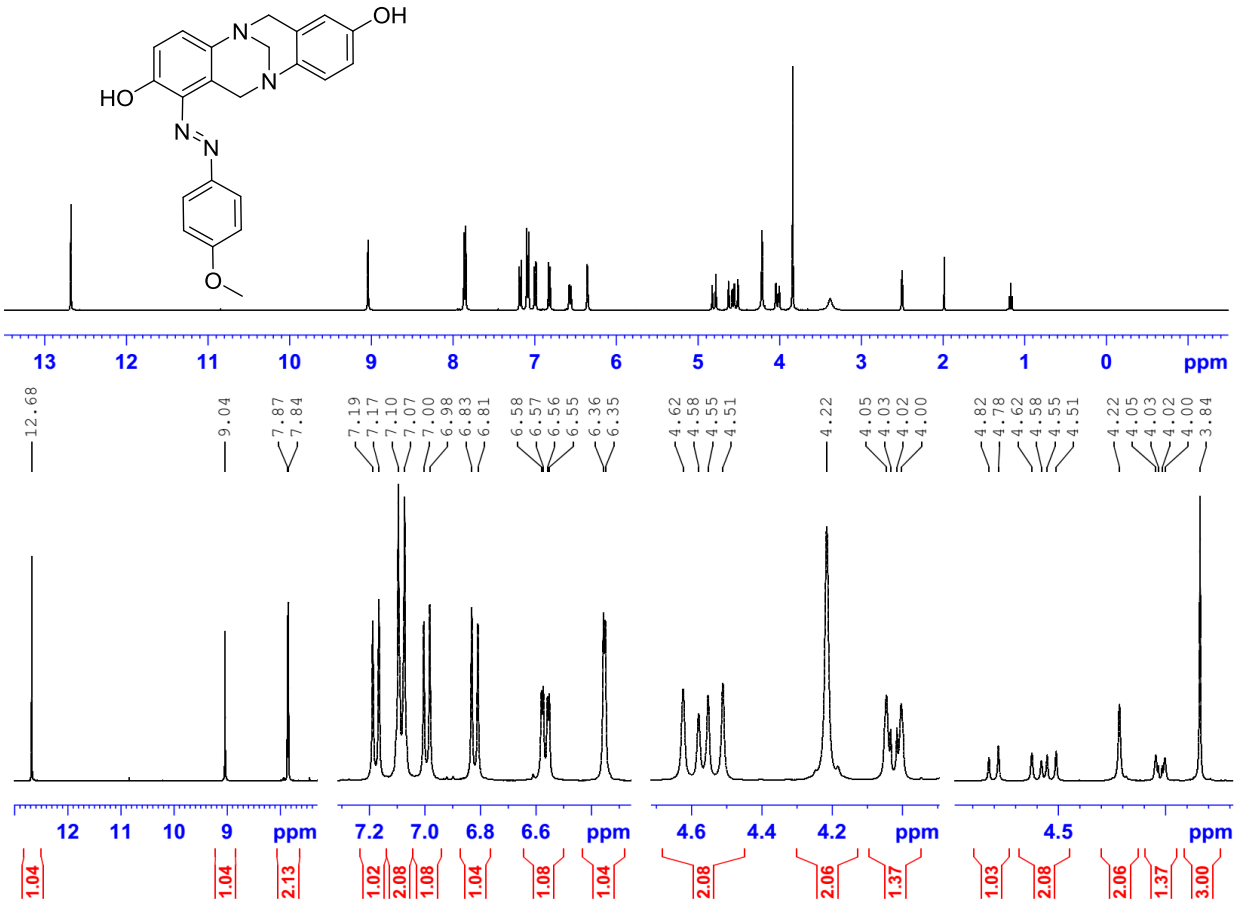
(*E*)-1-((4-methoxyphenyl)diazenyl)-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine-2,8-diol



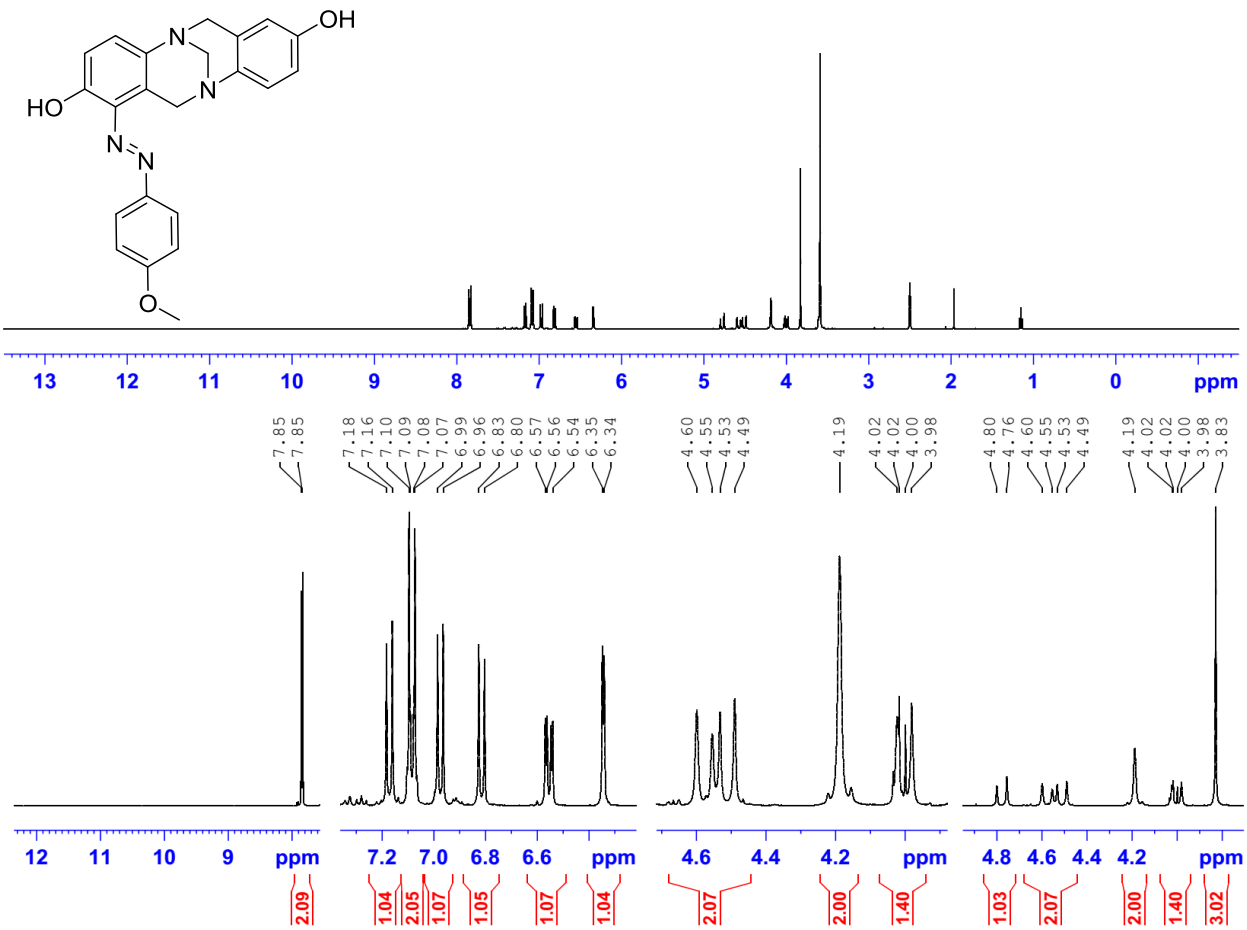
Compound 7, MS (ESI +) top and (ESI –) bottom



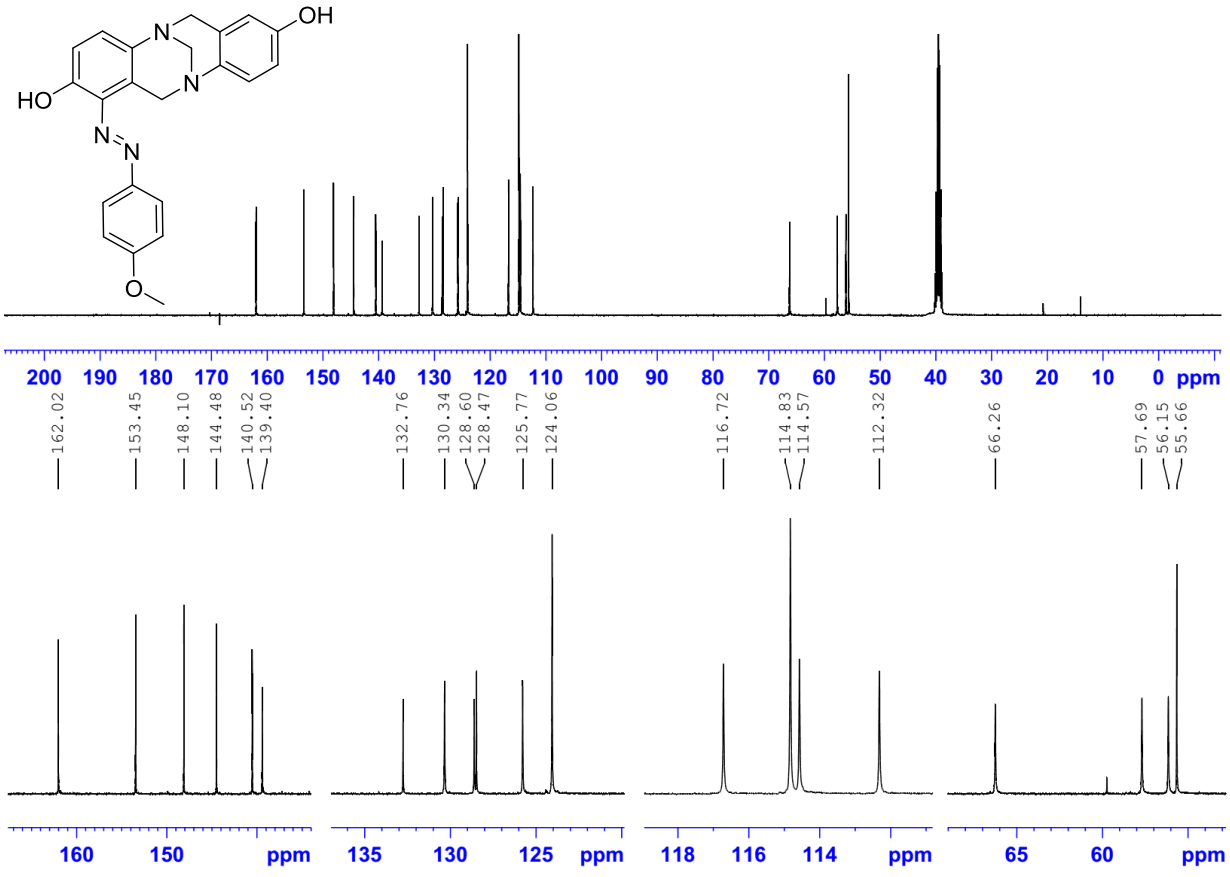
^{1}H NMR 400 MHz of Compound 7 in DMSO-*d*$_6$ (in blue) and in D$_2$O–DMSO-*d*$_6$ (in red)



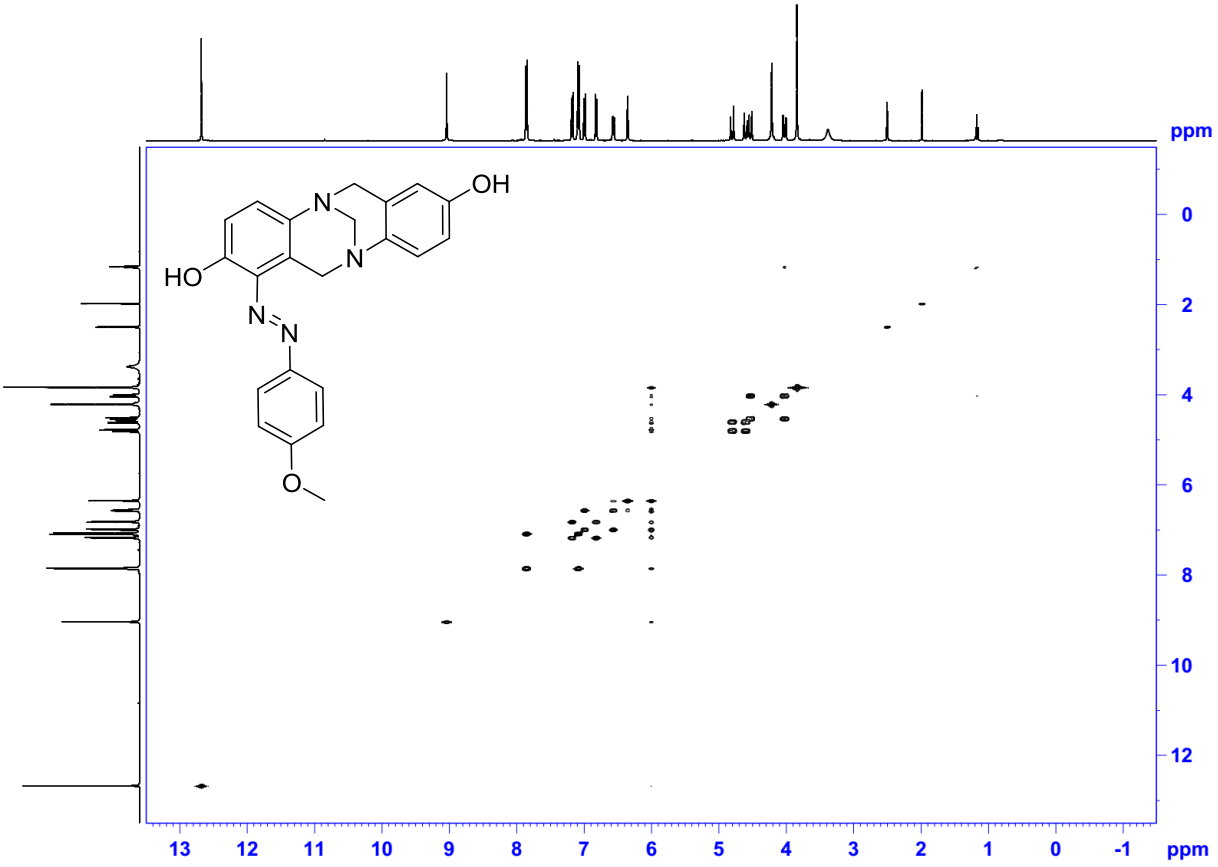
Compound 7, ^{1}H NMR (400 MHz, DMSO-*d*$_6$ – EtOAc)



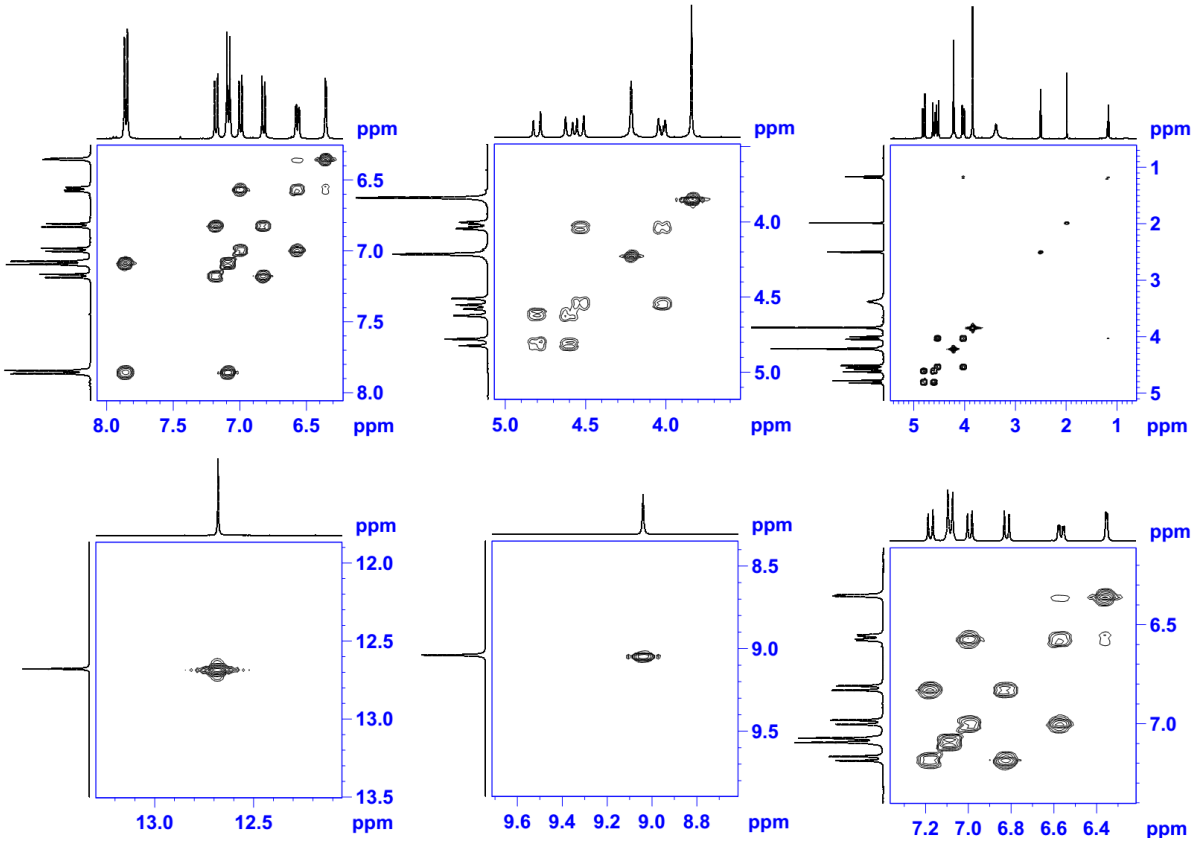
Compound 7, ^{1}H NMR (400 MHz, D_2O – DMSO-d_6 – EtOAc)



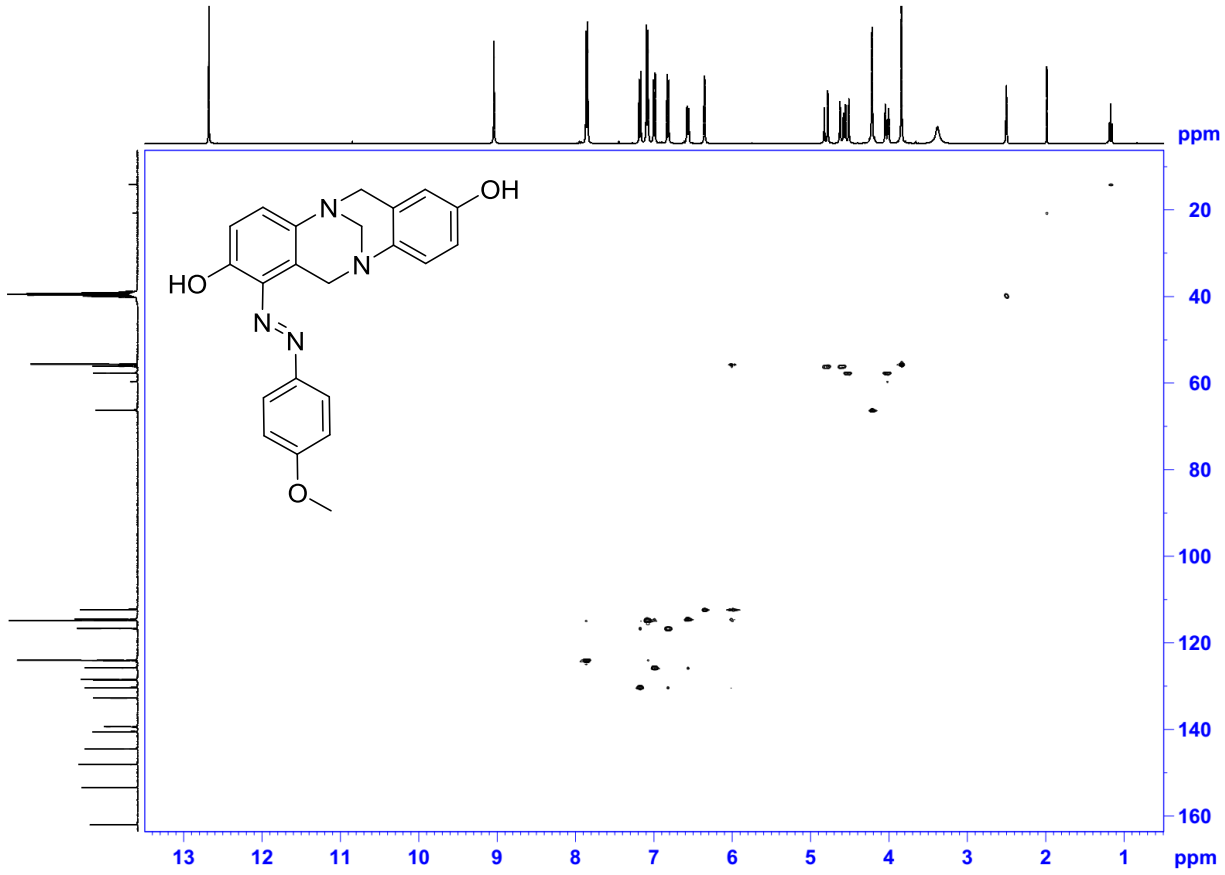
Compound 7, ^{13}C NMR (100 MHz, DMSO-d_6 – EtOAc)



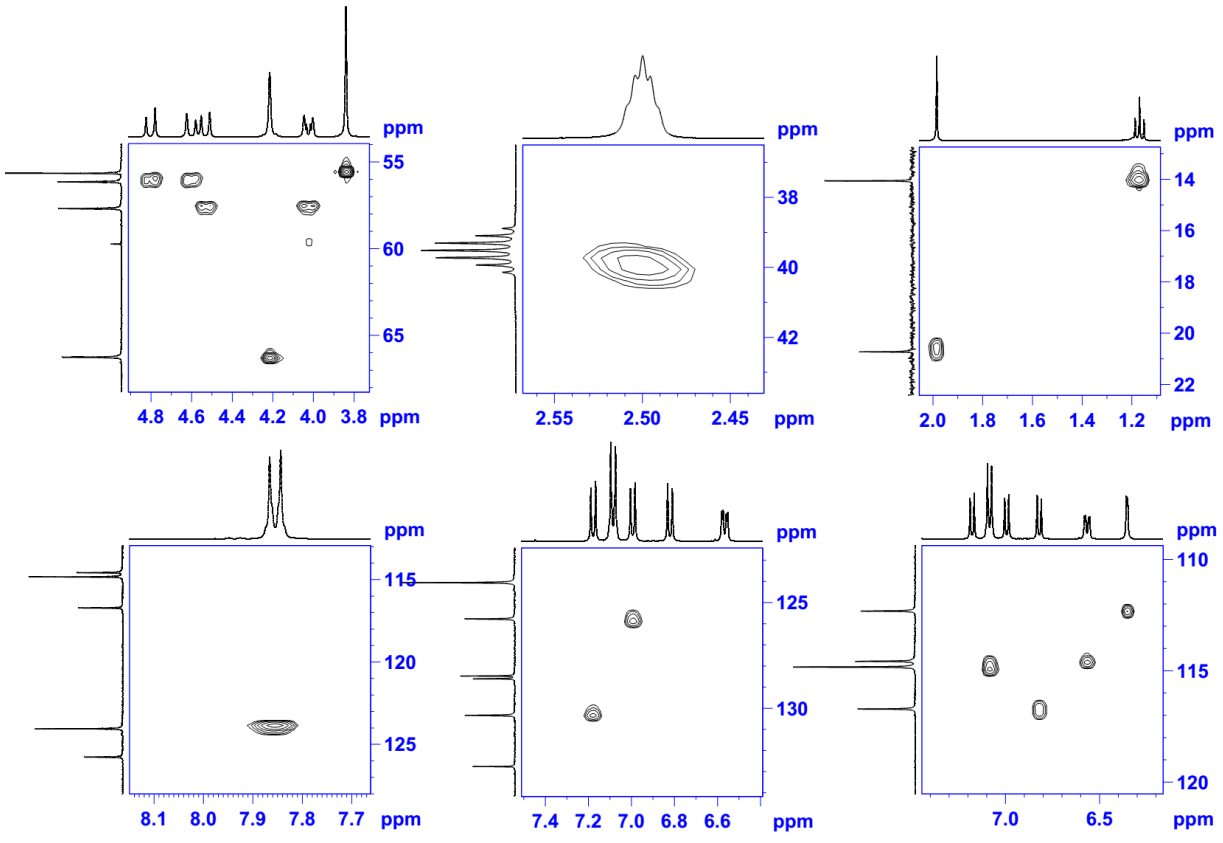
Compound 7, COSY (400 MHz, DMSO-d_6 – EtOAc)



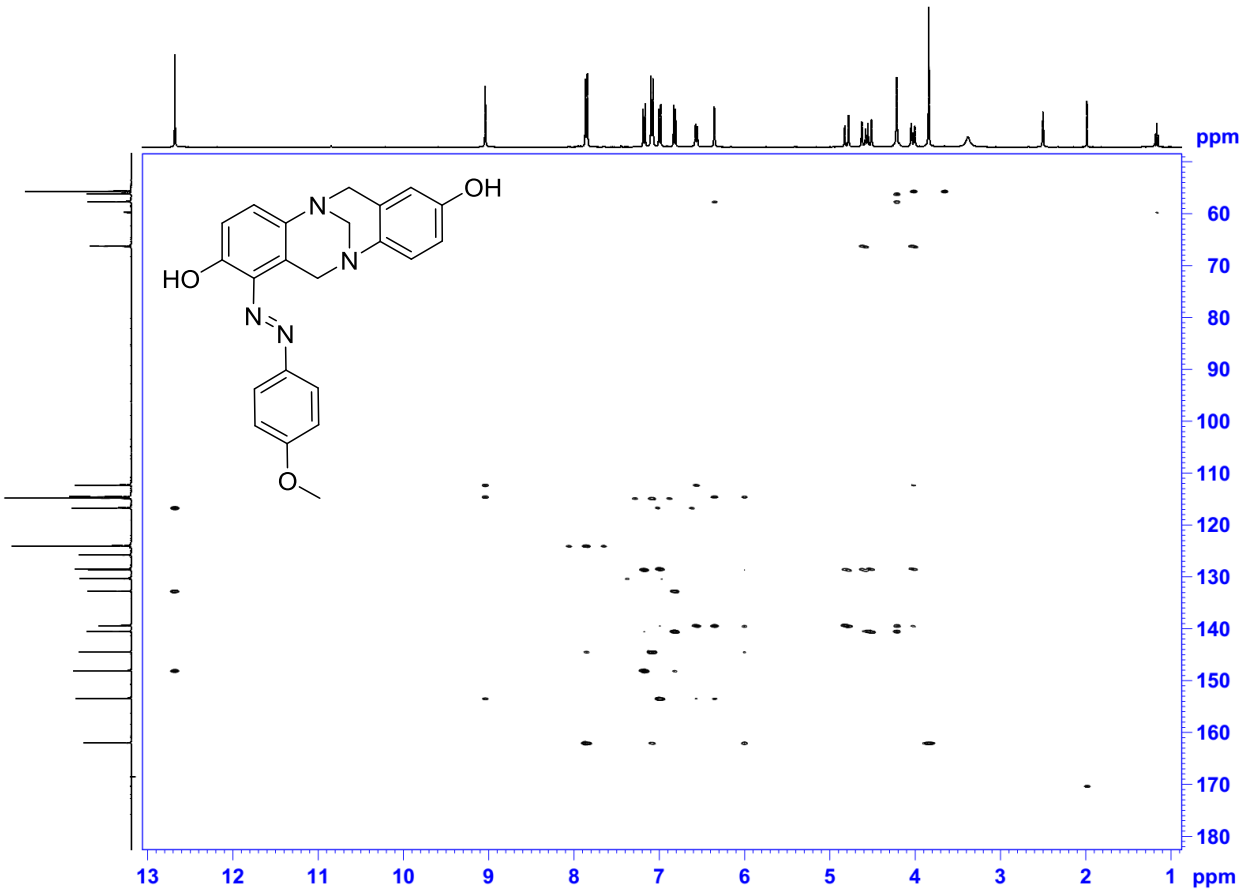
Compound 7, COSY (400 MHz, DMSO-d_6 – EtOAc)



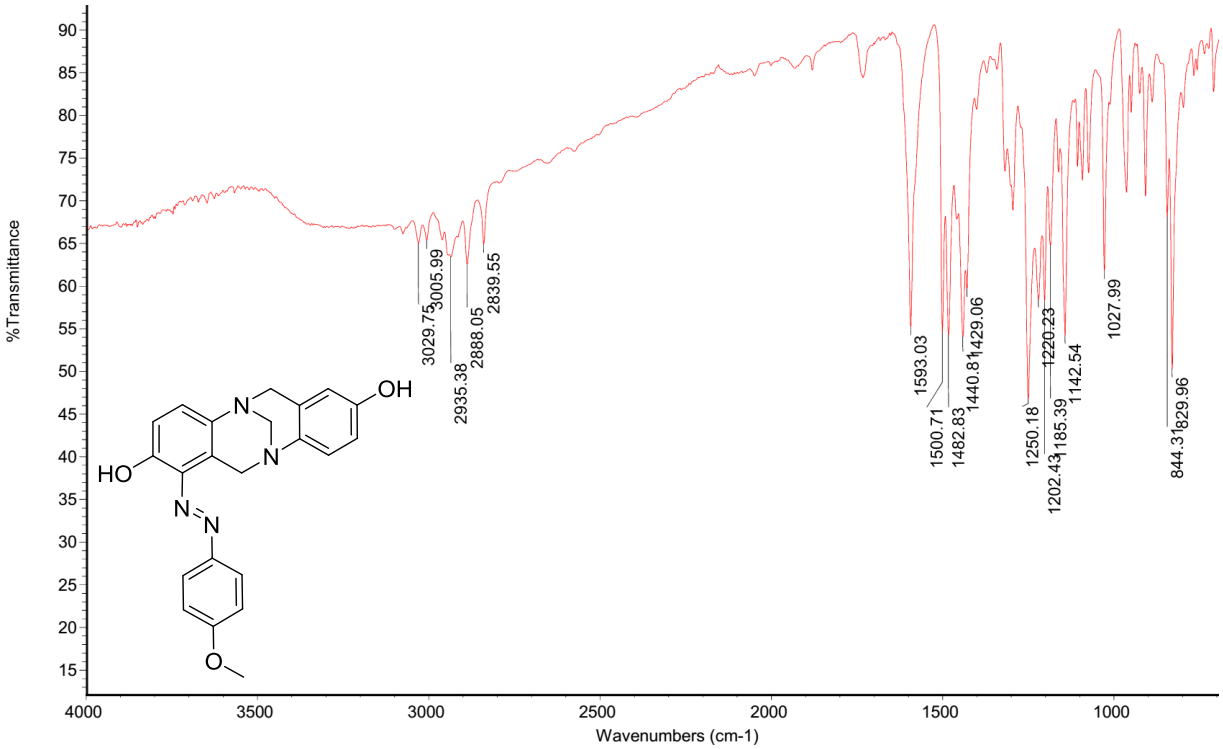
Compound 7, HSQC (400 MHz, DMSO-d_6 – EtOAc)



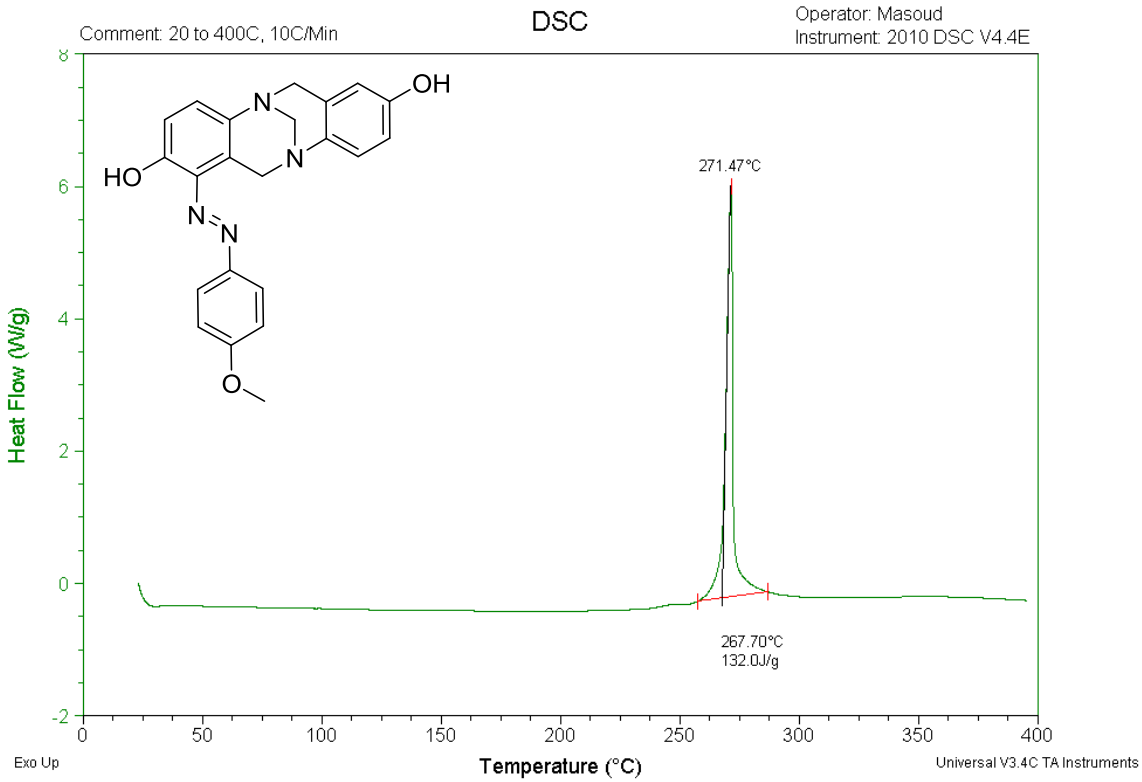
Compound 7, HSQC (400 MHz, DMSO-d_6 – EtOAc)



Compound 7, HMBC (400 MHz, DMSO-d_6 – EtOAc)



Compound 7, IR transmittance (neat)

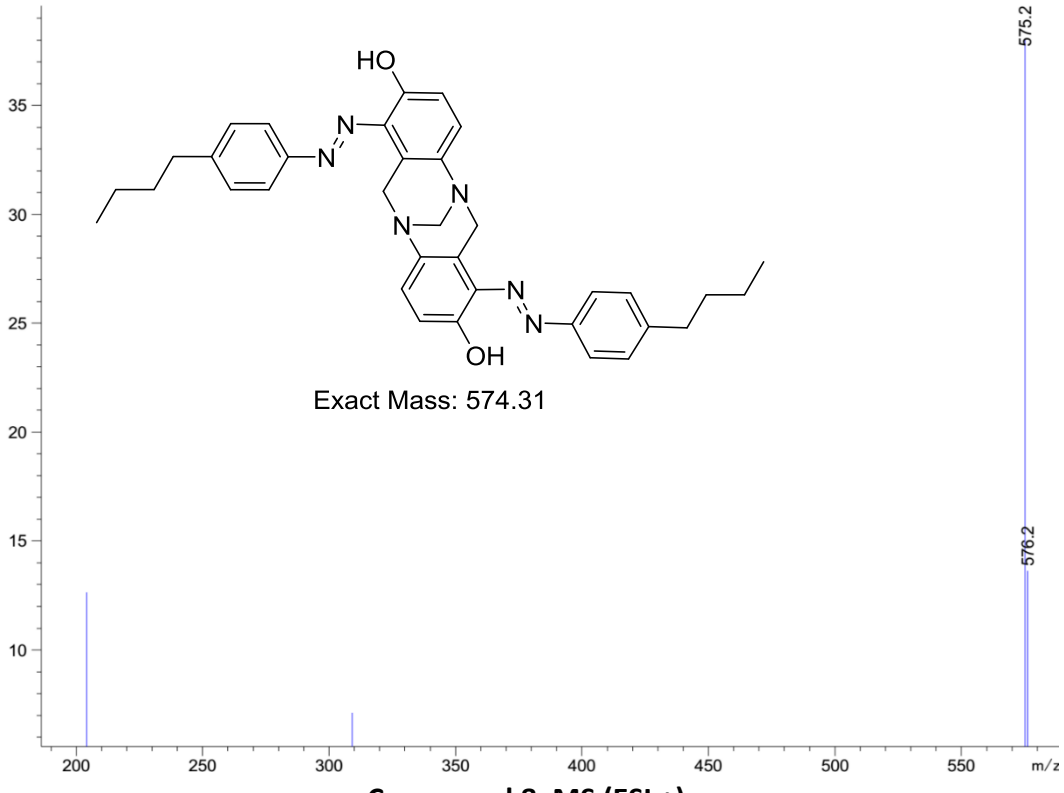


Compound 7, DSC thermogram

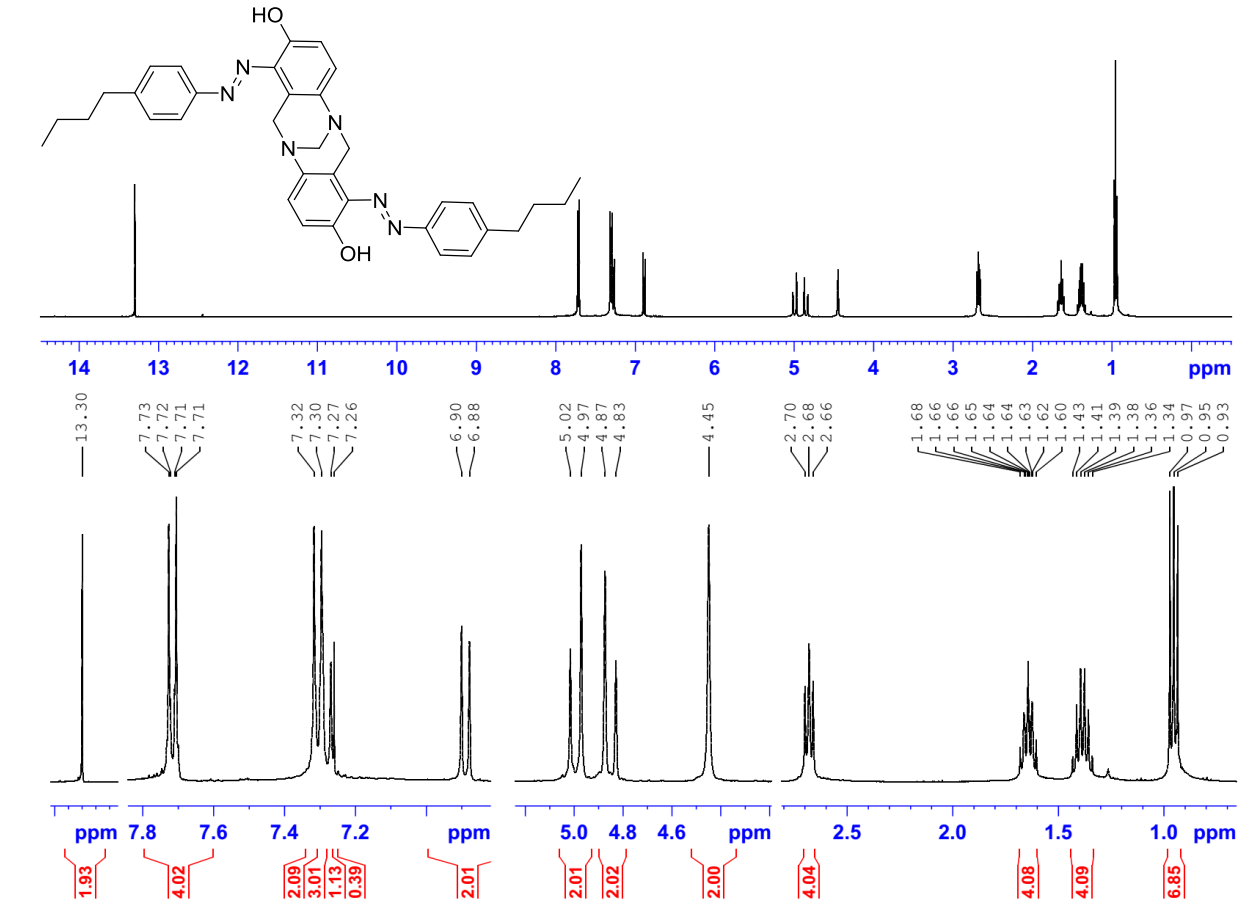
(Decomposition without melting at 267–271 °C)

9. Characterization of compound (**8**)

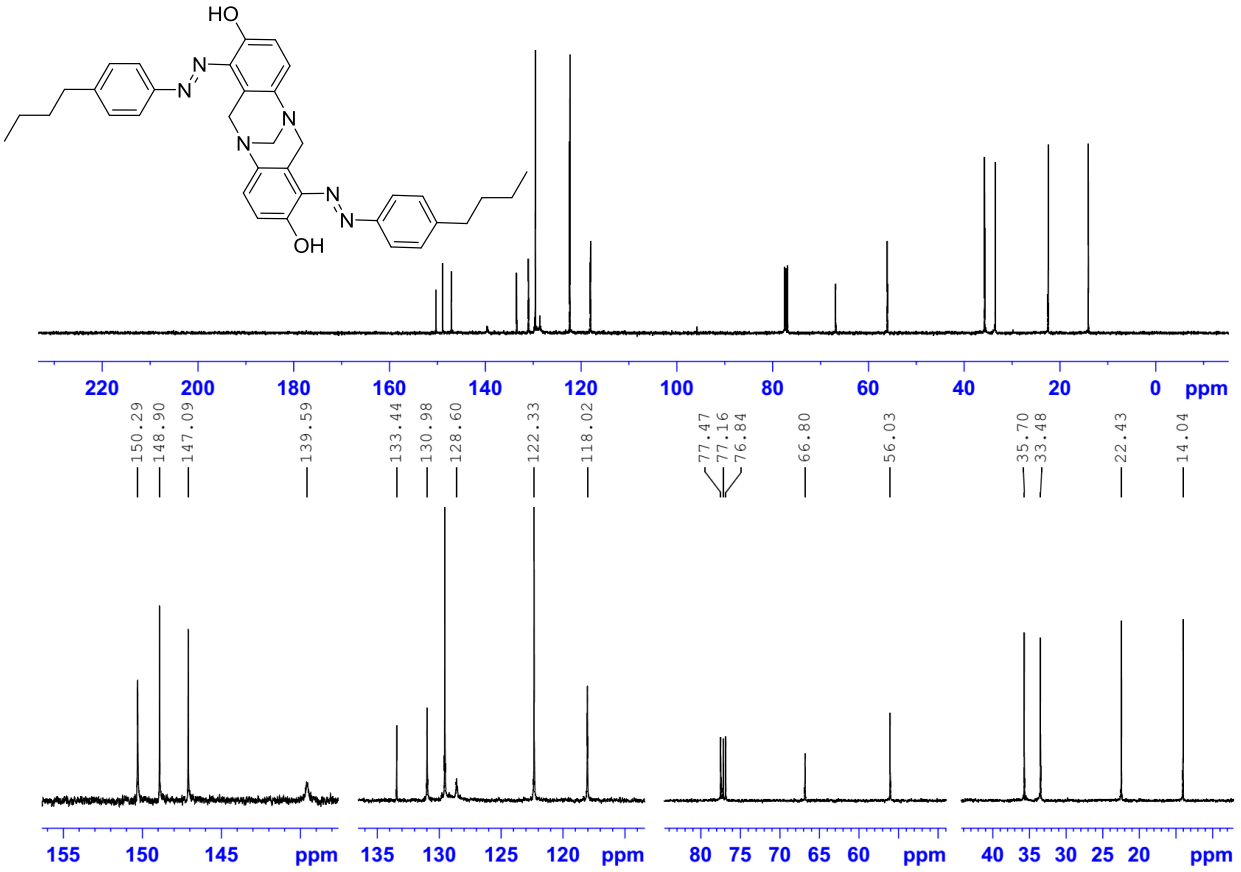
1,7-Bis((*E*)-(4-butylphenyl)diazenyl)-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine-2,8-diol



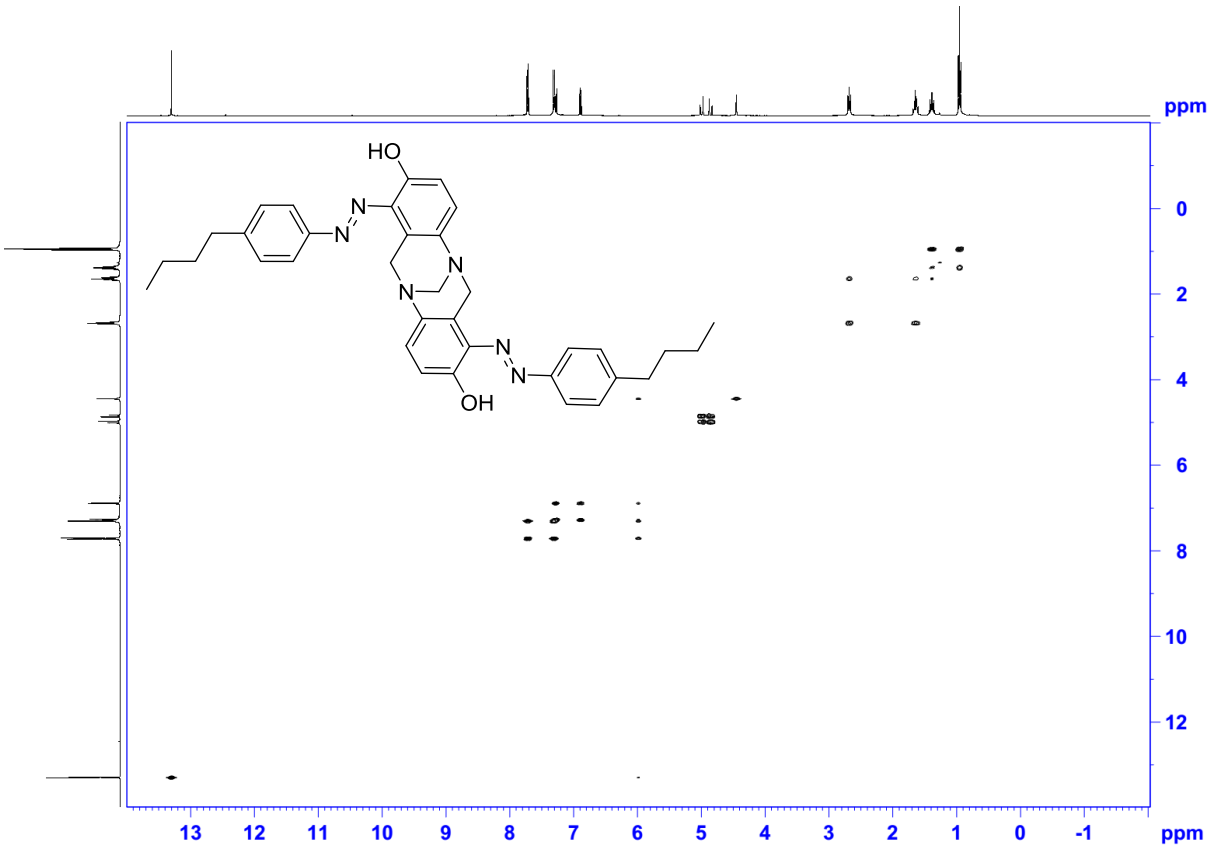
Compound 8, MS (ESI +)



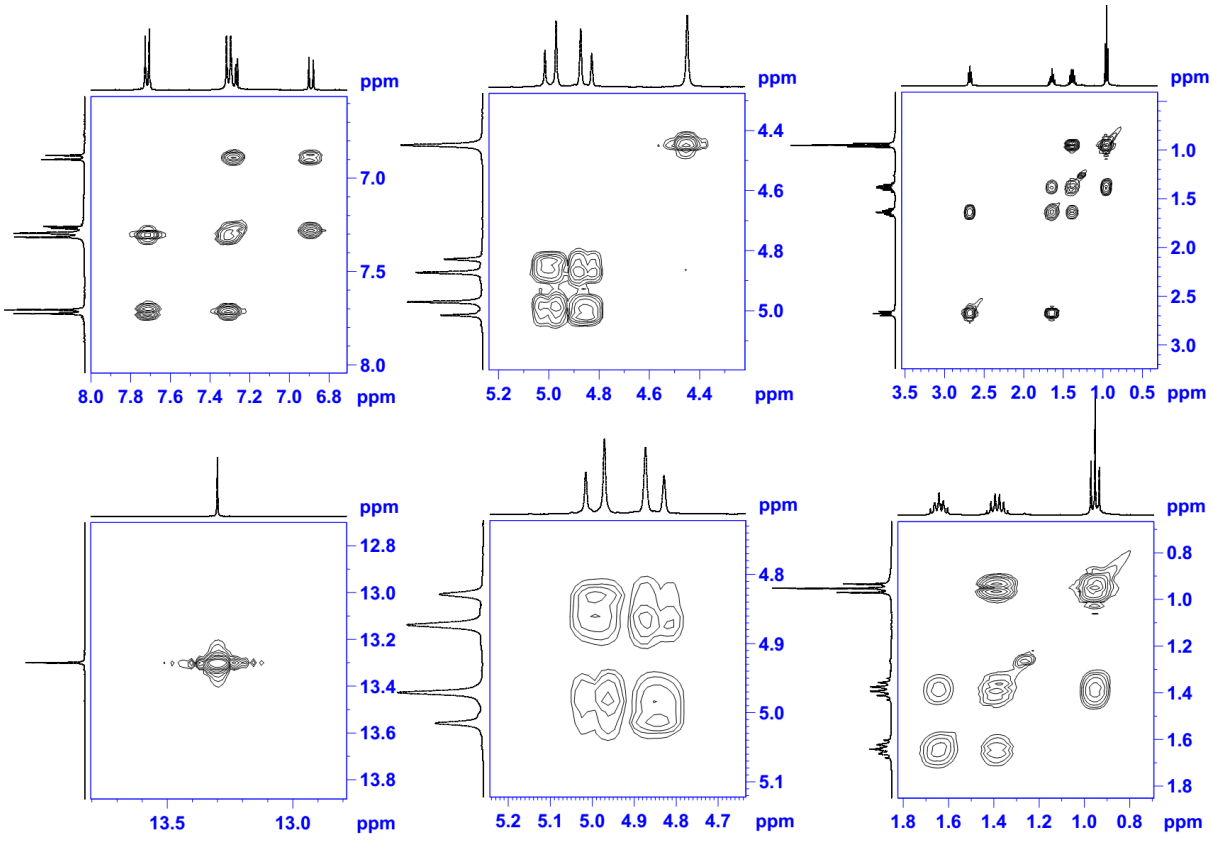
Compound 8,^{1}H NMR (400 MHz, $CDCl_3$)



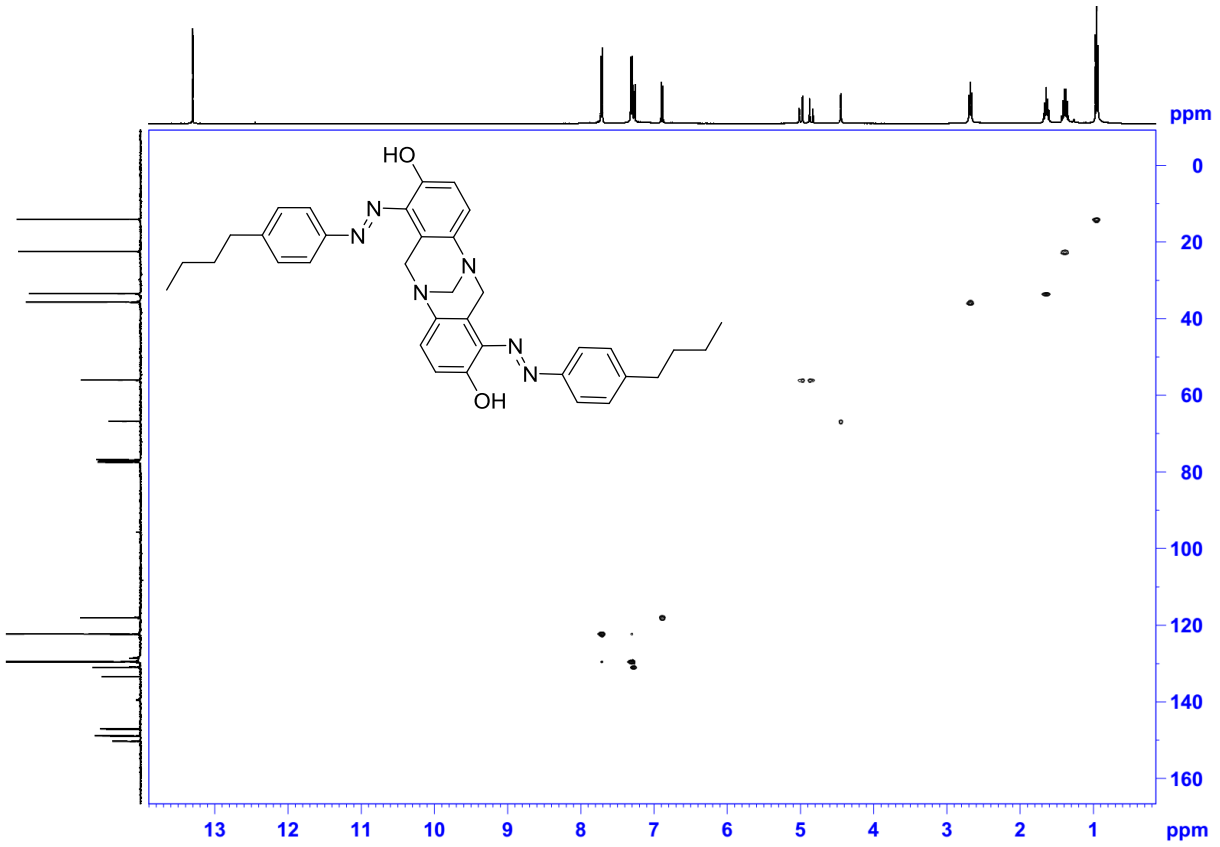
Compound 8,^{13}C NMR (100 MHz, $CDCl_3$)



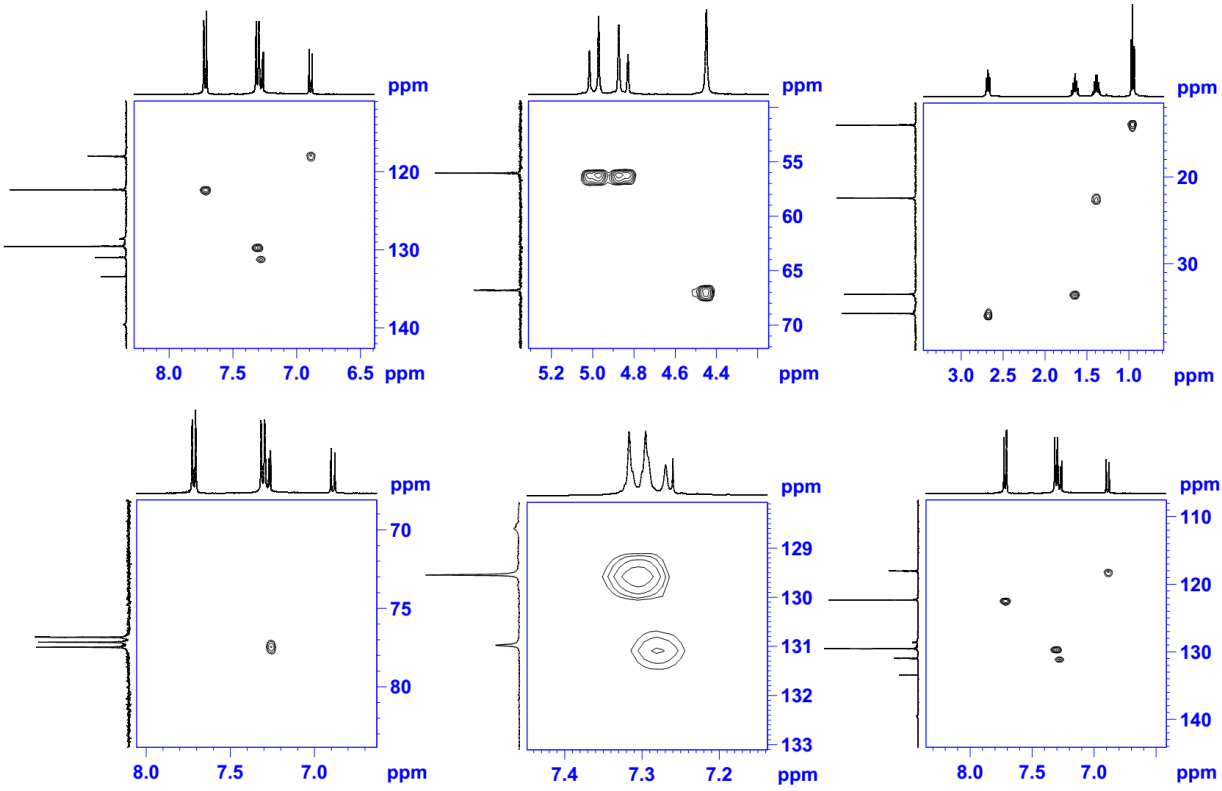
Compound 8, COSY (400 MHz, $CDCl_3$)



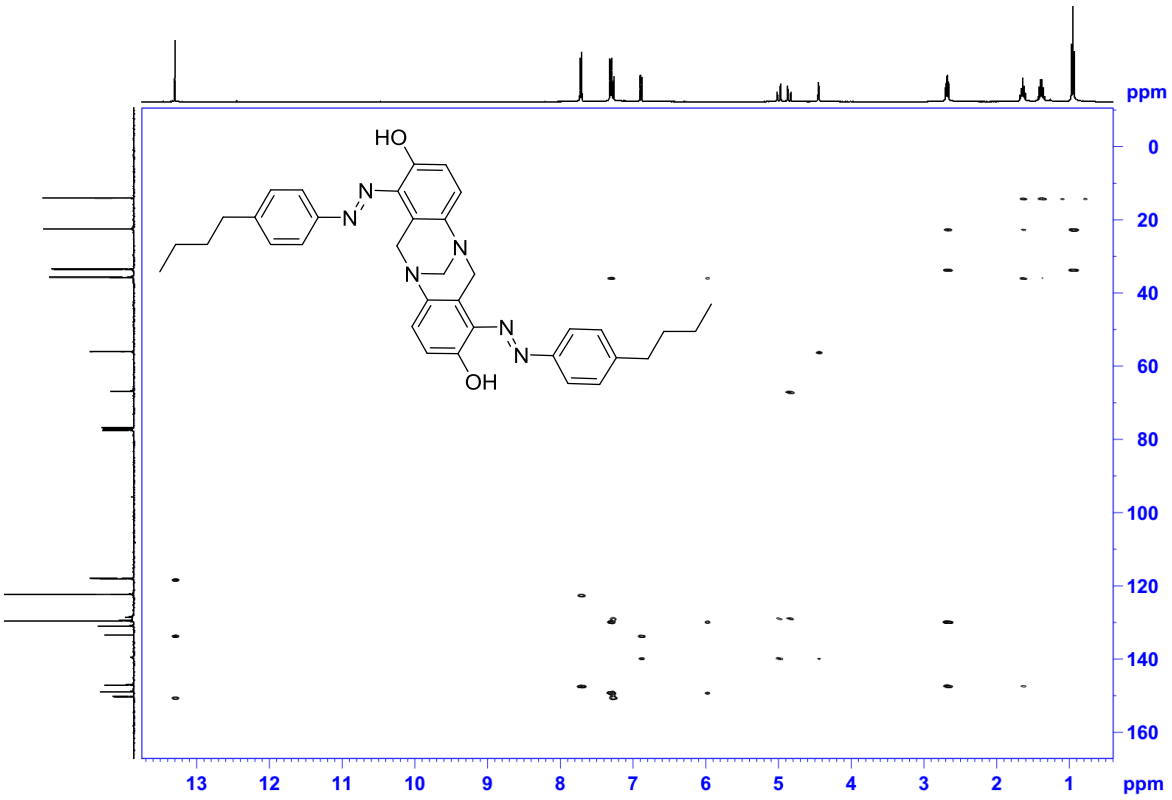
Compound 8, COSY (400 MHz, $CDCl_3$)



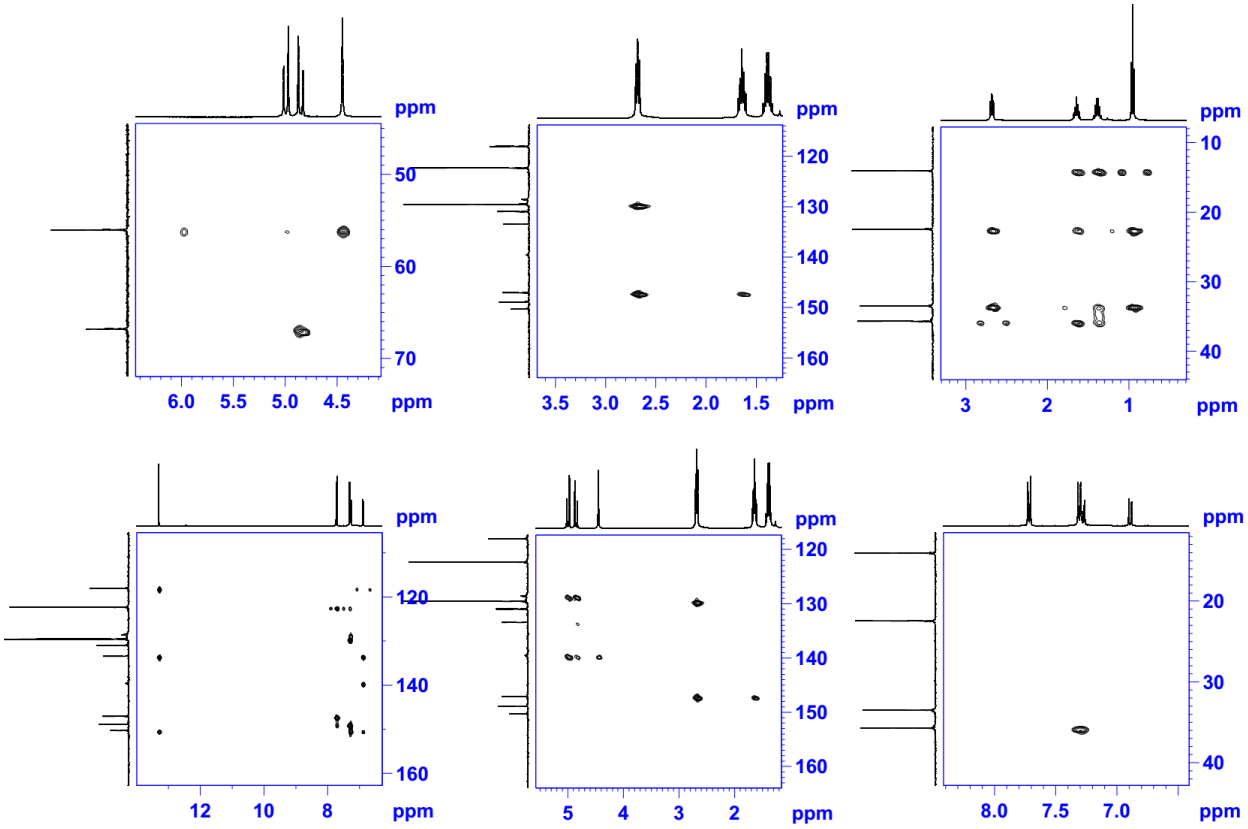
Compound 8, HSQC (400 MHz, $CDCl_3$)



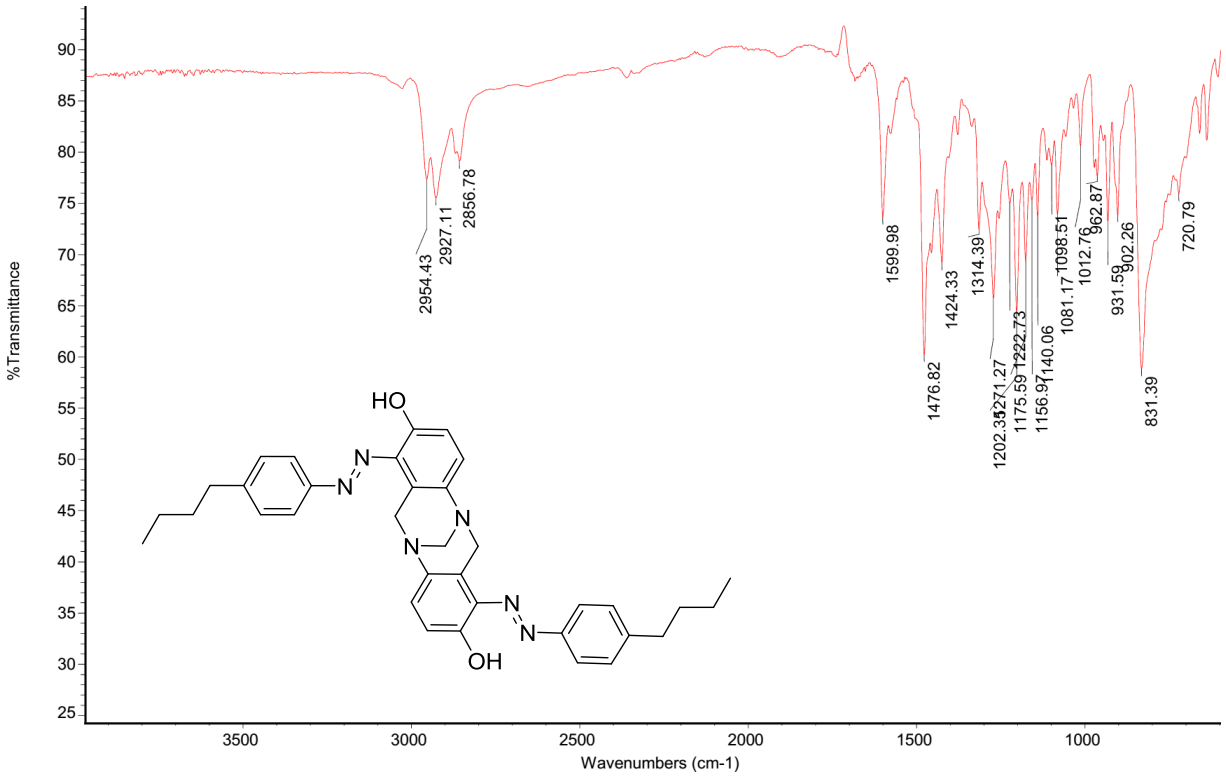
Compound 8, HSQC (400 MHz, $CDCl_3$)



Compound 8, HMBC (400 MHz, $CDCl_3$)



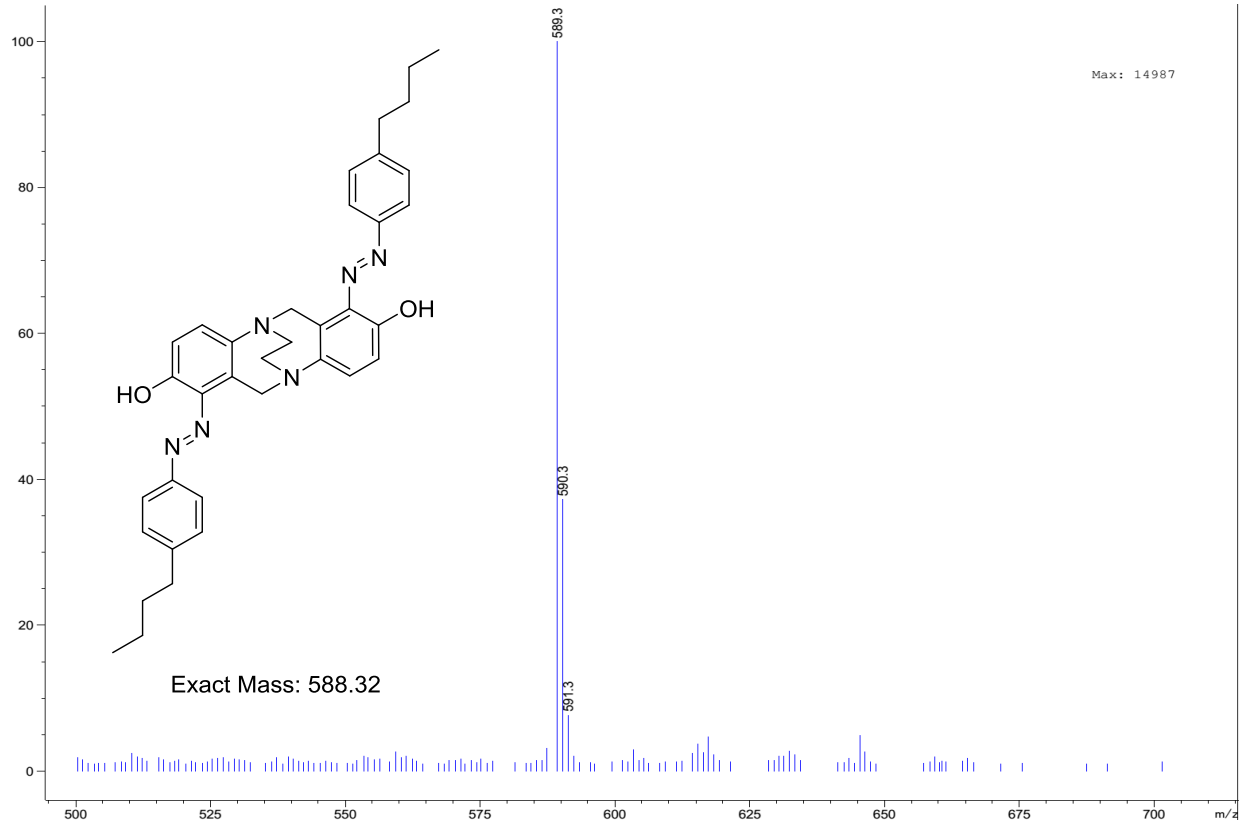
Compound 8, HMBC (400 MHz, $CDCl_3$)



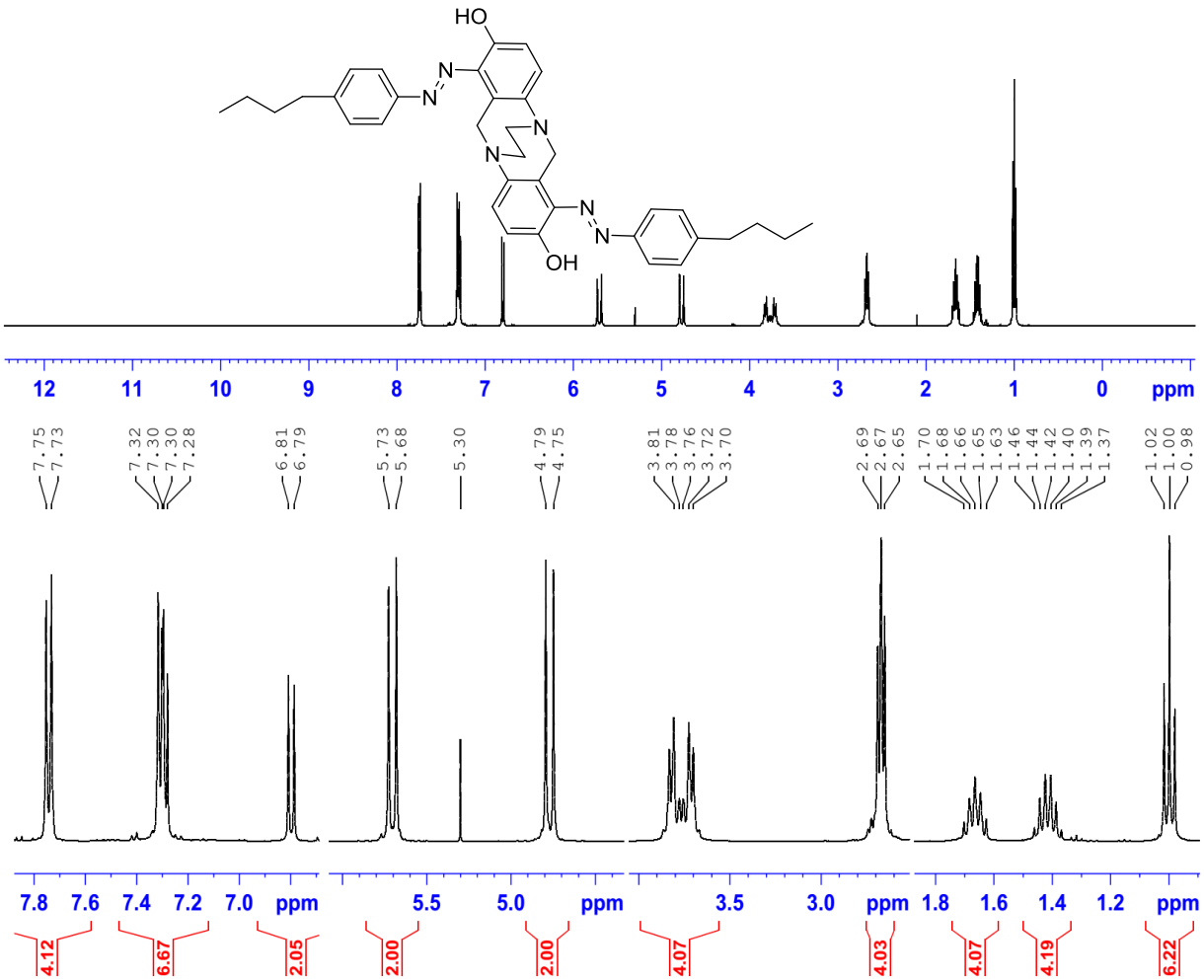
Compound 8, IR transmittance (neat)

10. Characterization of compound (**9**)

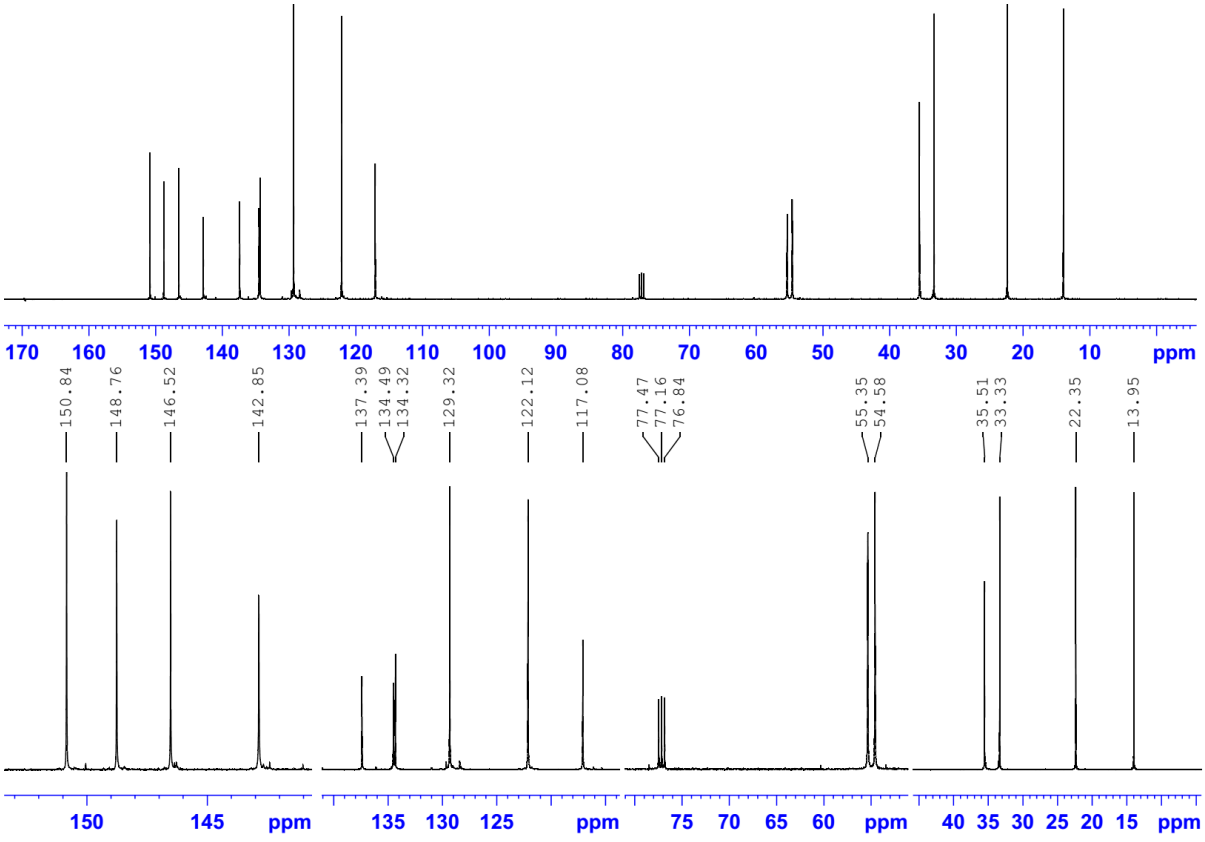
1,7-bis((*E*)-(4-butylphenyl)diazenyl)-6*H*,12*H*-5,11-ethanodibenzo[*b,f*][1,5]diazocine-2,8-diol



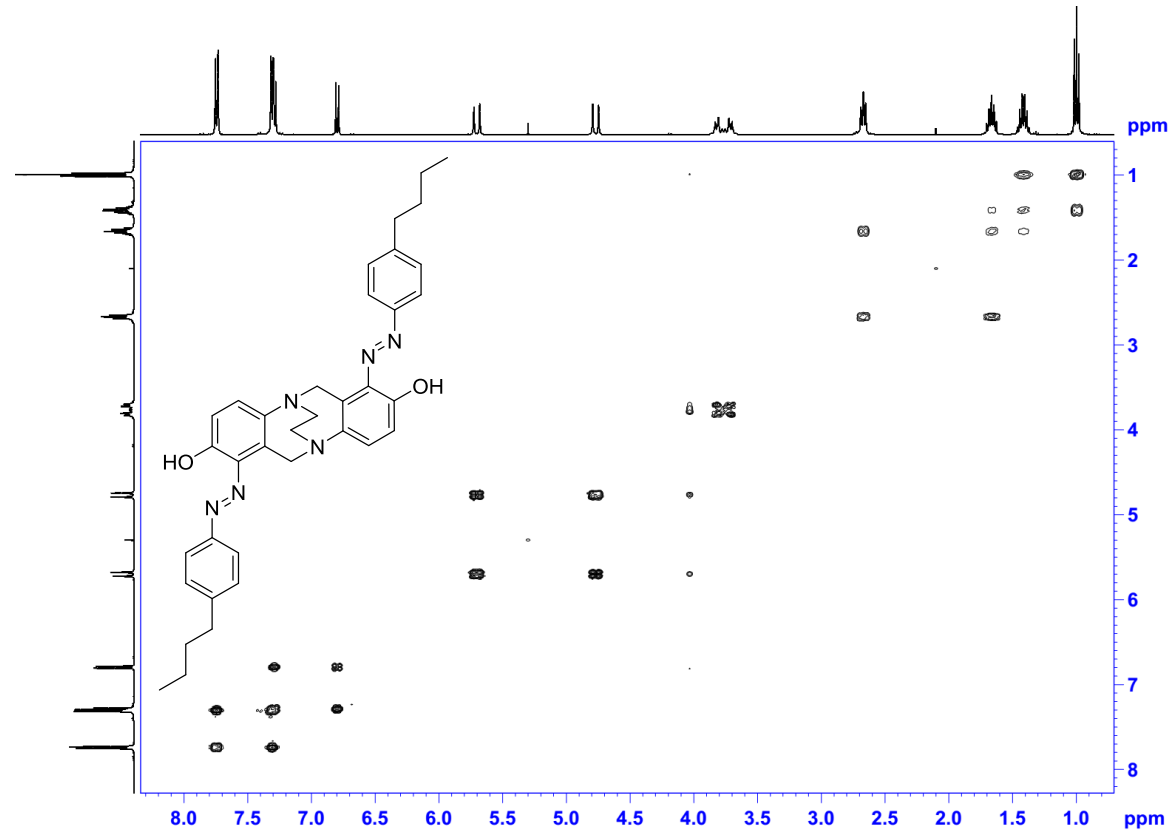
Compound 9, MS (ESI +)



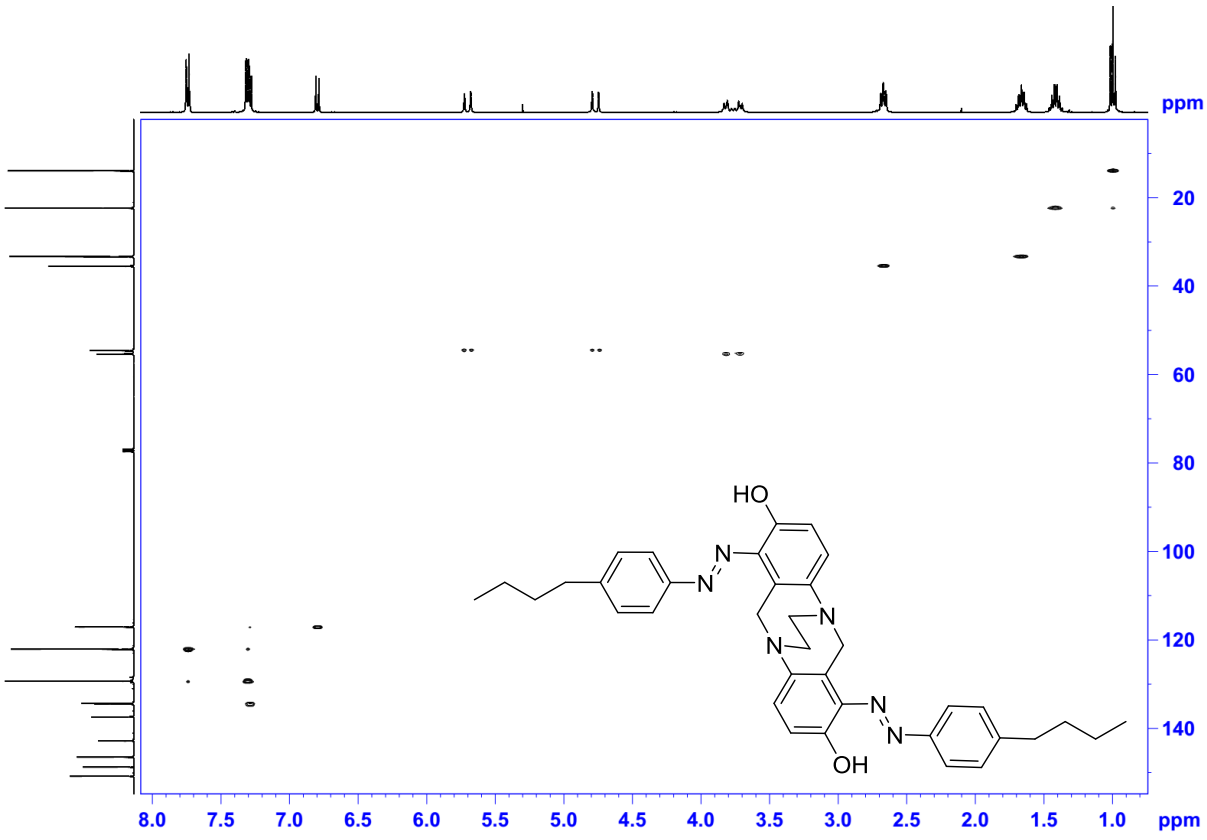
Compound 9, ^{1}H NMR (400 MHz, $CDCl_3$, DCM as an internal standard)



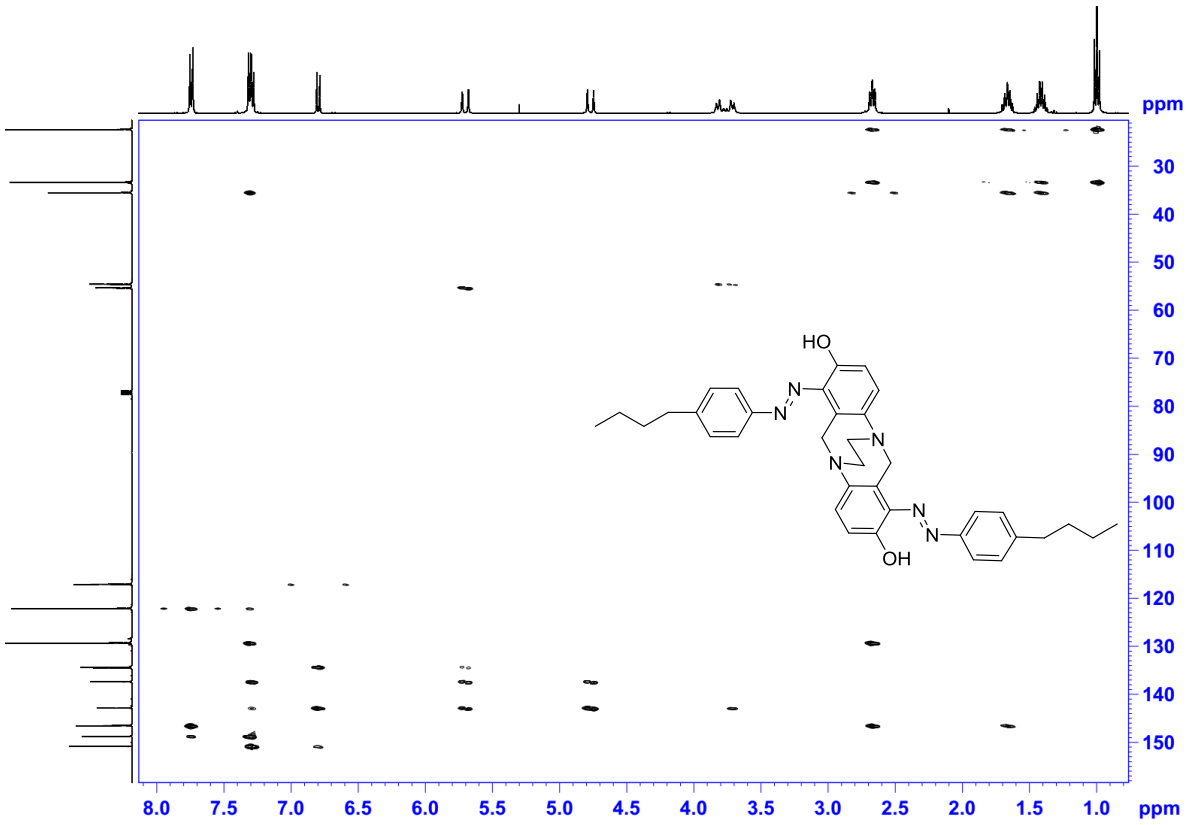
Compound 9, ^{13}C NMR (100 MHz, $CDCl_3$)



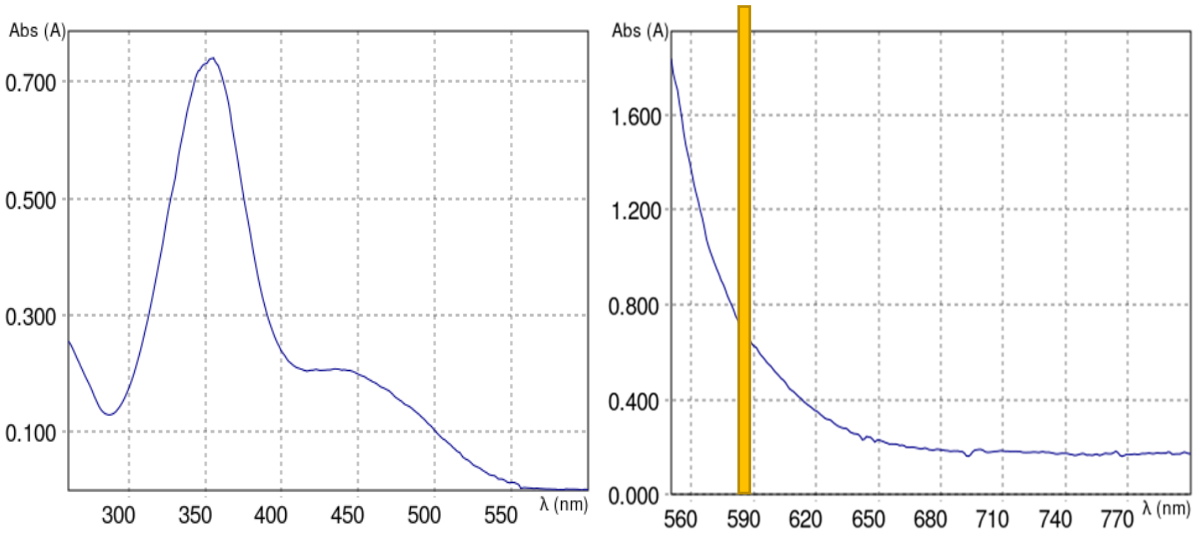
Compound 9, COSY (400 MHz, $CDCl_3$)



Compound 9, HSQC (400 MHz, $CDCl_3$)

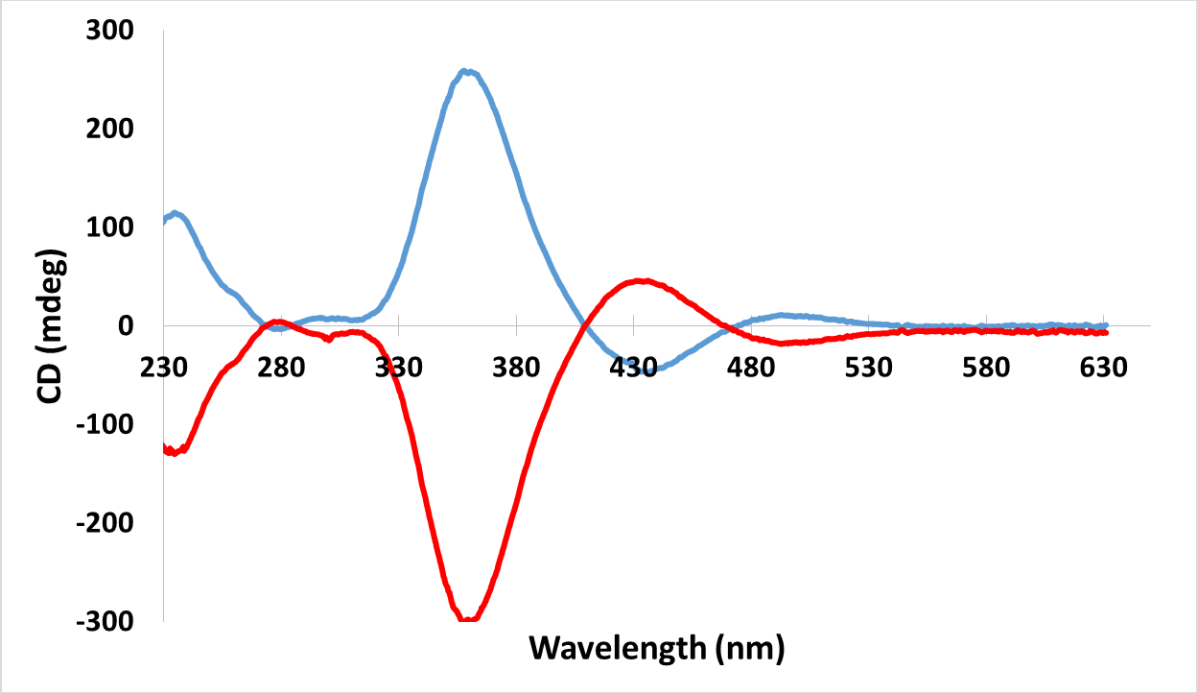


Compound 9, HMBC (400 MHz, $CDCl_3$)

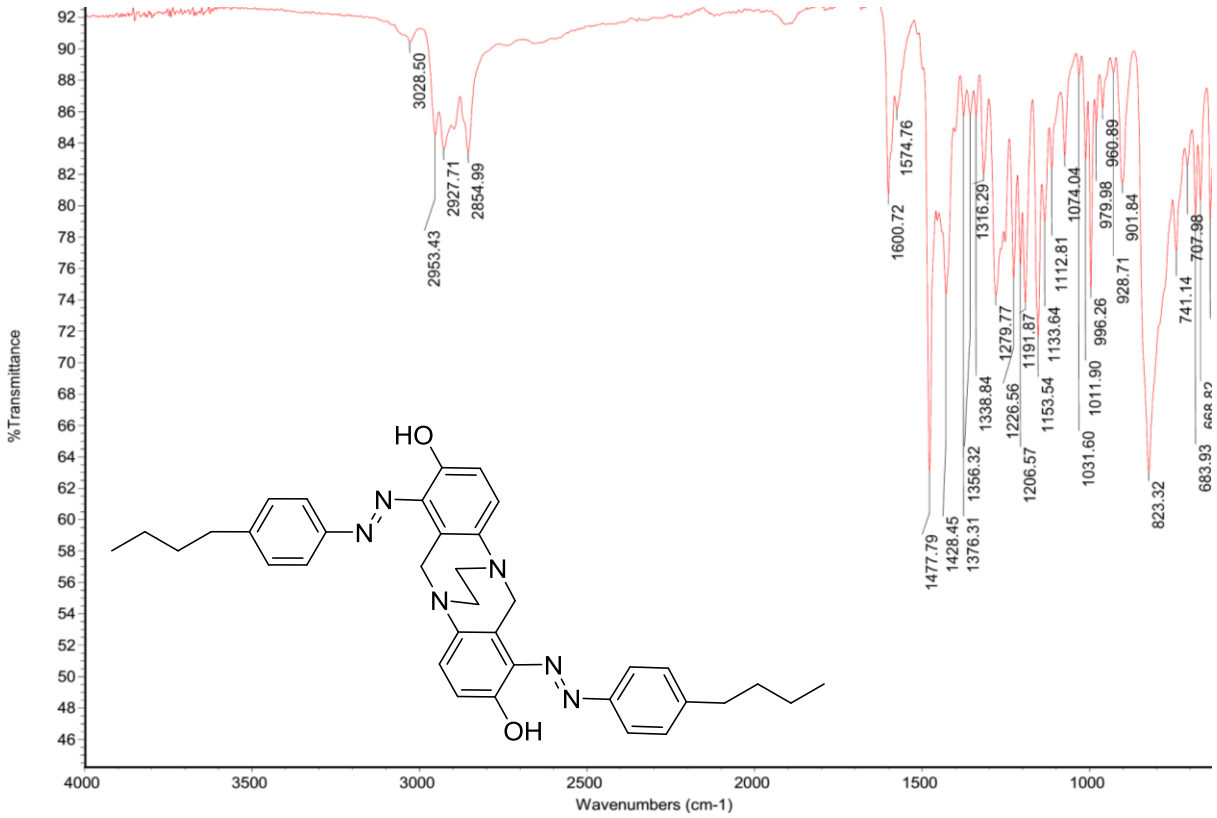


Compound 9, UV-Vis absorption spectra

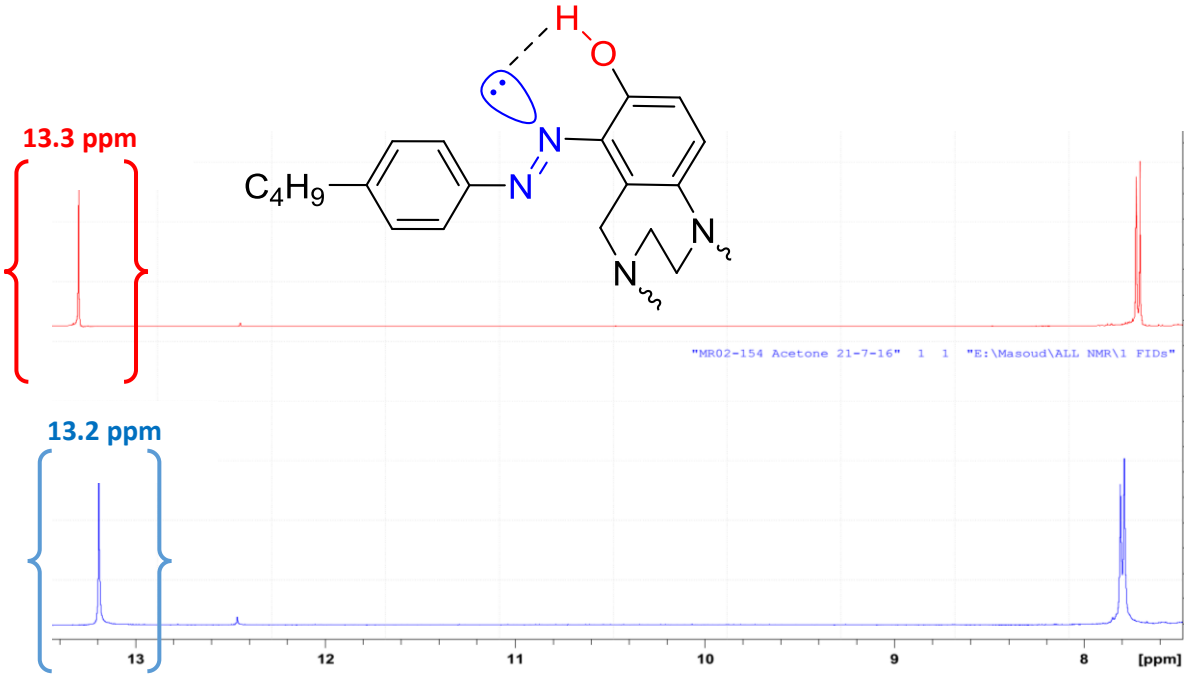
1.6×10^{-5} M in EtOAc (Left), and *c* 0.100 in DCM (Right)



CD spectra, (+)-(*R*,*R*)-9 and (–)-(*S*,*S*)-9 in DCM



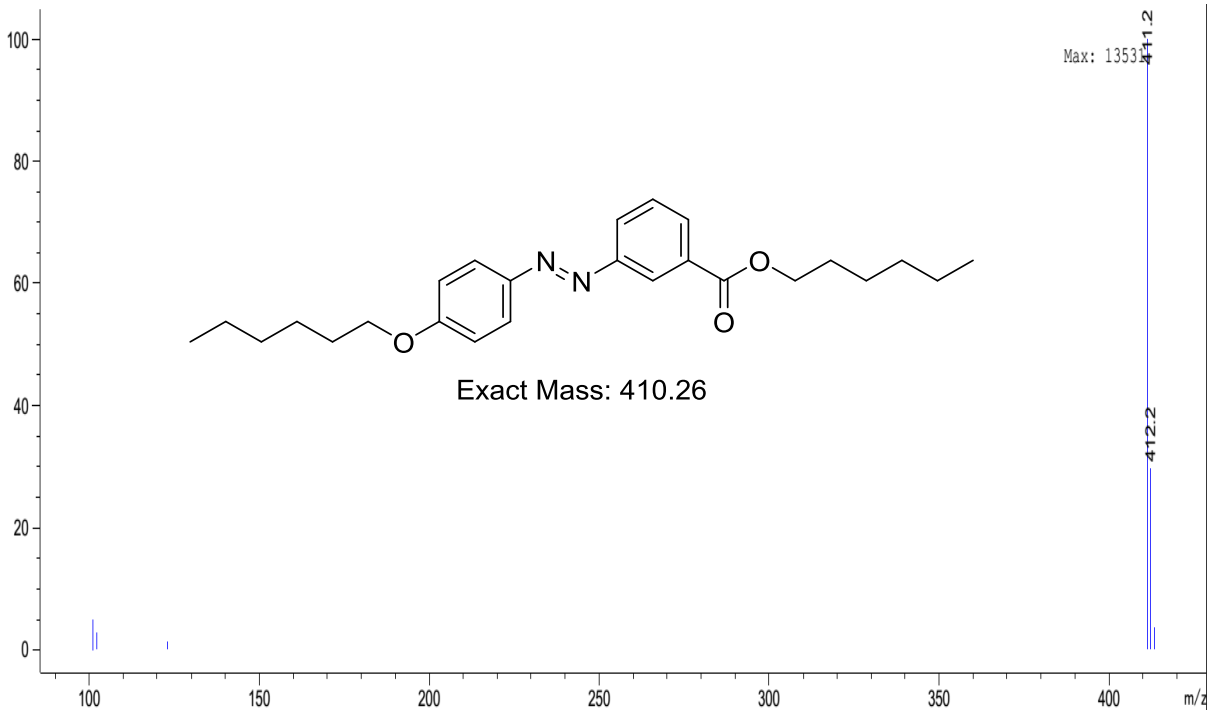
Compound 9, IR transmittance (neat)



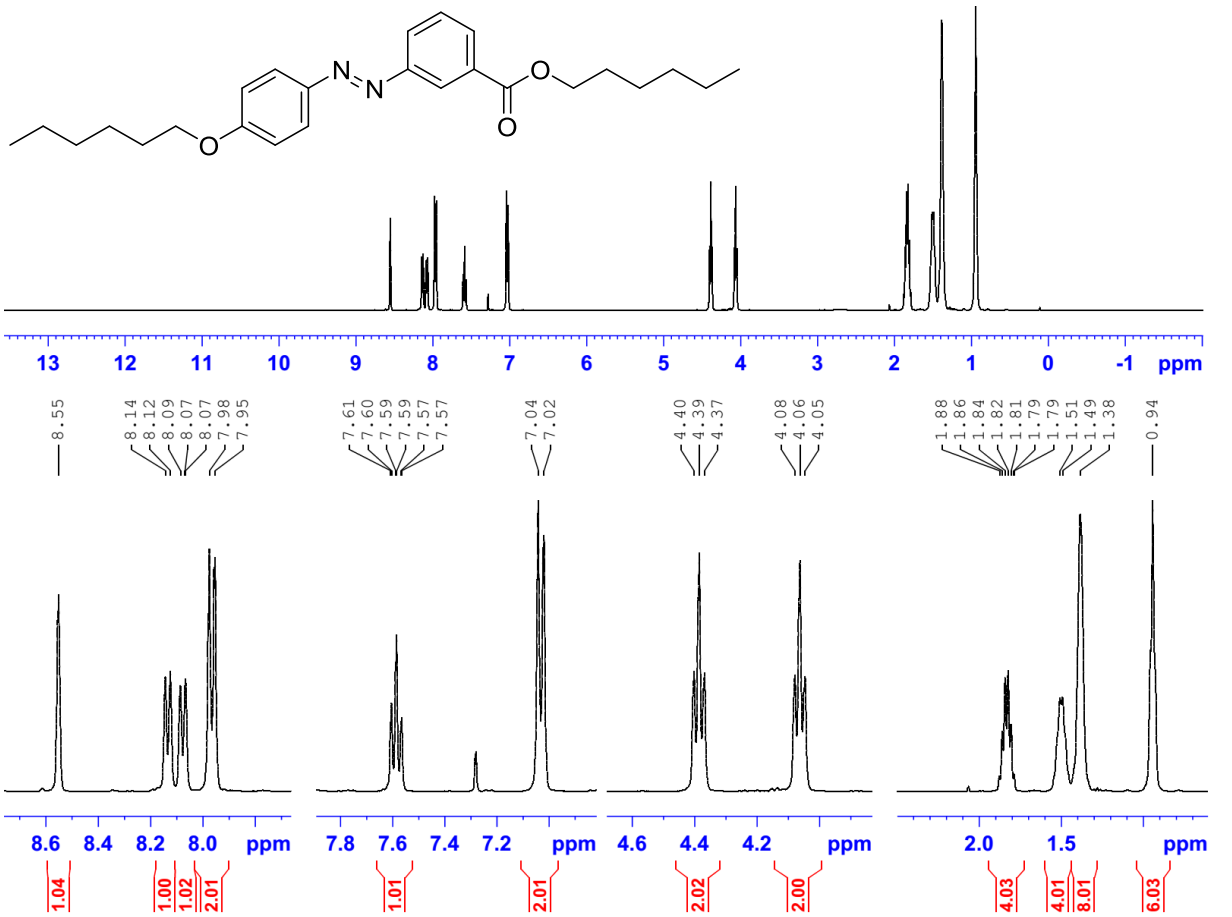
^{1}H NMR spectra of 9's hydroxyl groups in $CDCl_3$ (in red) and in $(CD_3)_2CO$ (in blue)

11. Characterization of compound (**10**)

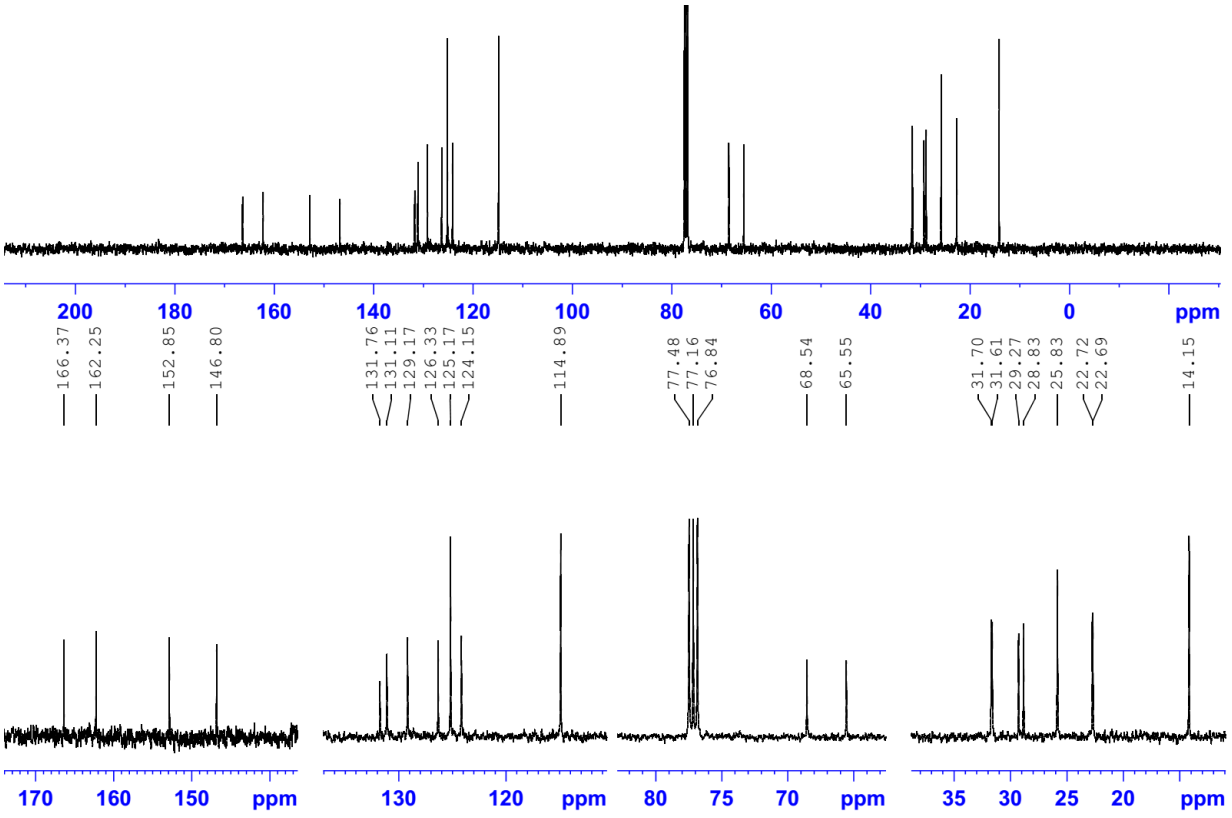
Hexyl (*E*)-3-((4-(hexyloxy)phenyl)diazenyl)benzoate



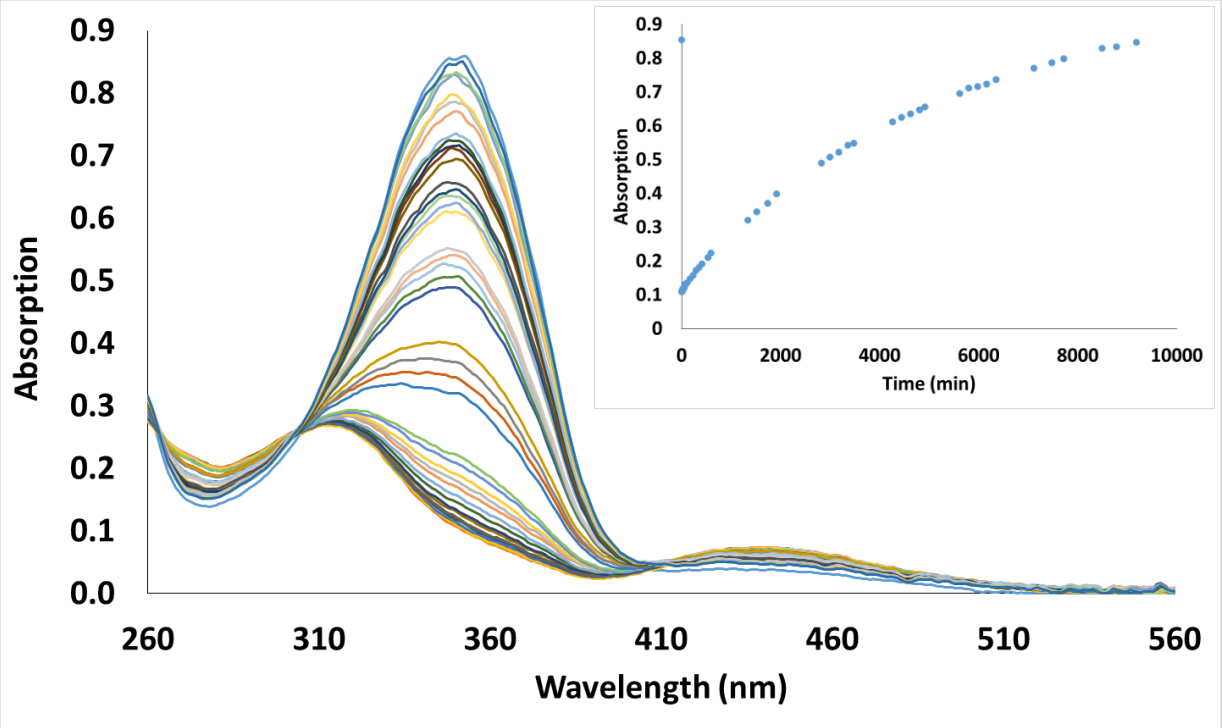
Compound 10, MS (ESI +)



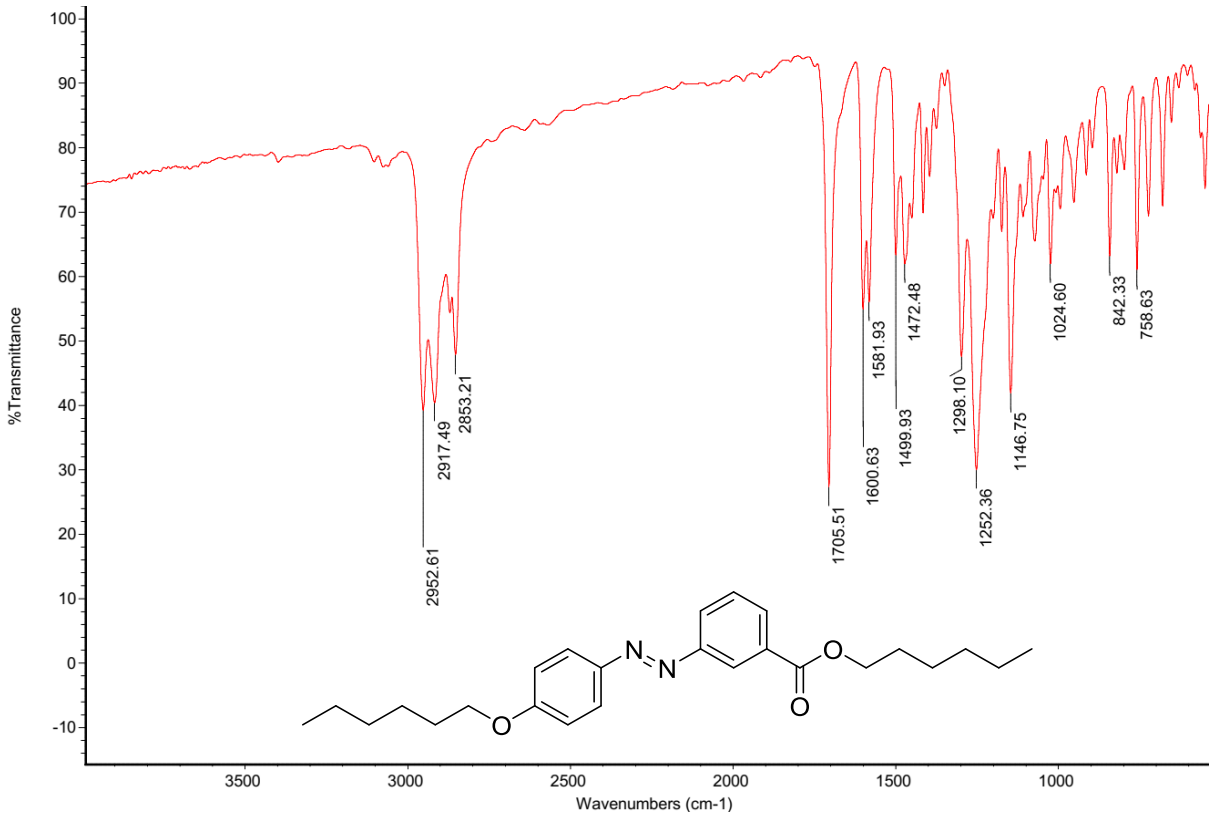
Compound 10, ^{1}H NMR (400 MHz, $CDCl_3$)



Compound 10, ^{13}C NMR (100 MHz, $CDCl_3$)



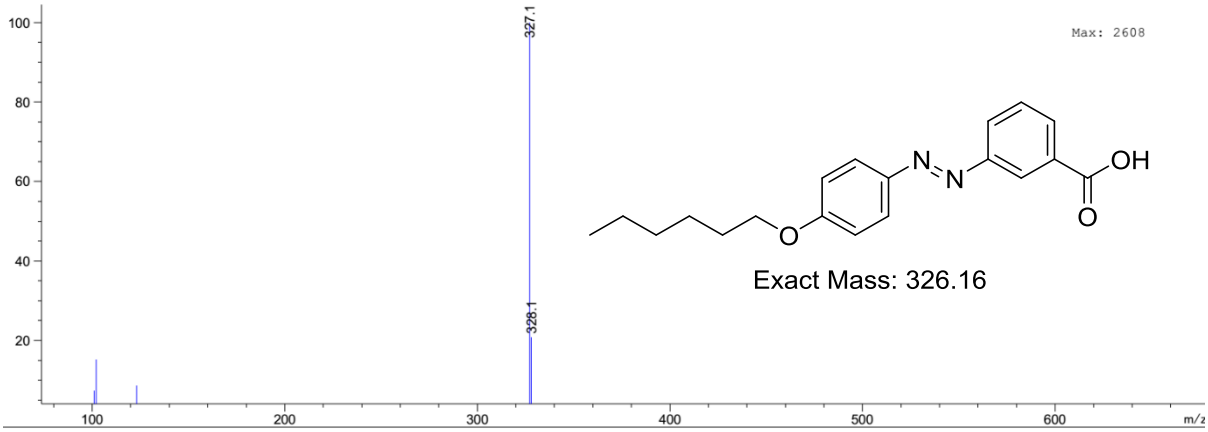
UV-Vis absorption spectra of 10 (260–560nm) and its absorption at 350nm at various stages of the photoisomerization – thermal relaxation

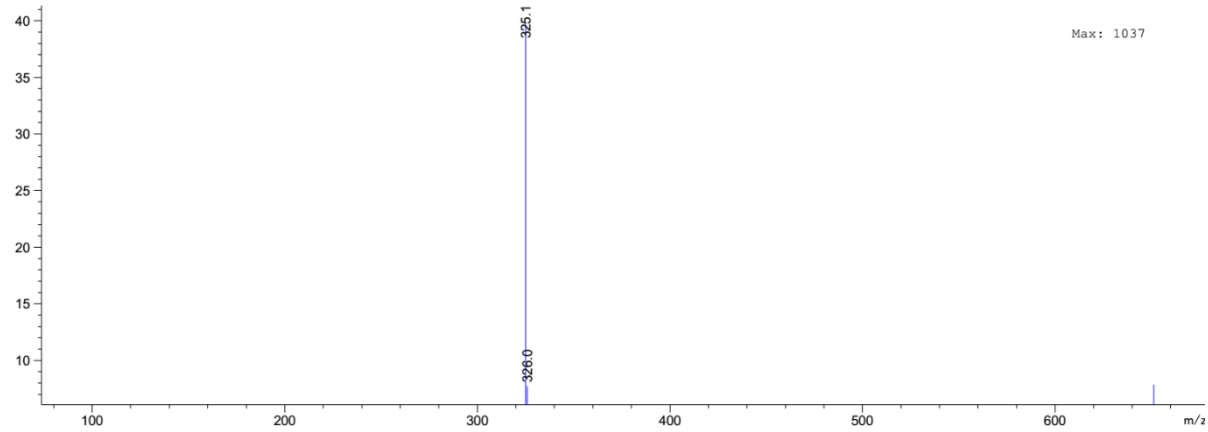


Compound 10, IR transmittance (neat)

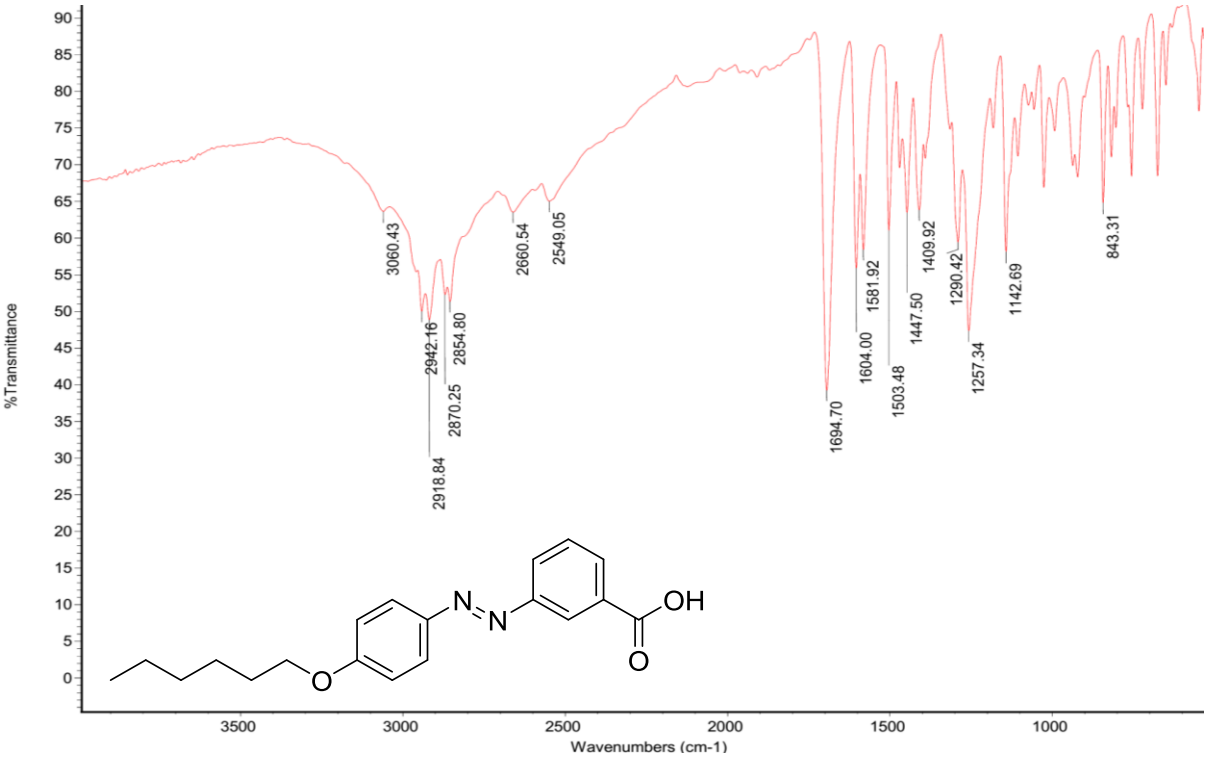
12. Characterization of compound (**11**)

(*E*)-3-((4-(hexyloxy)phenyl)diazenyl)benzoic acid

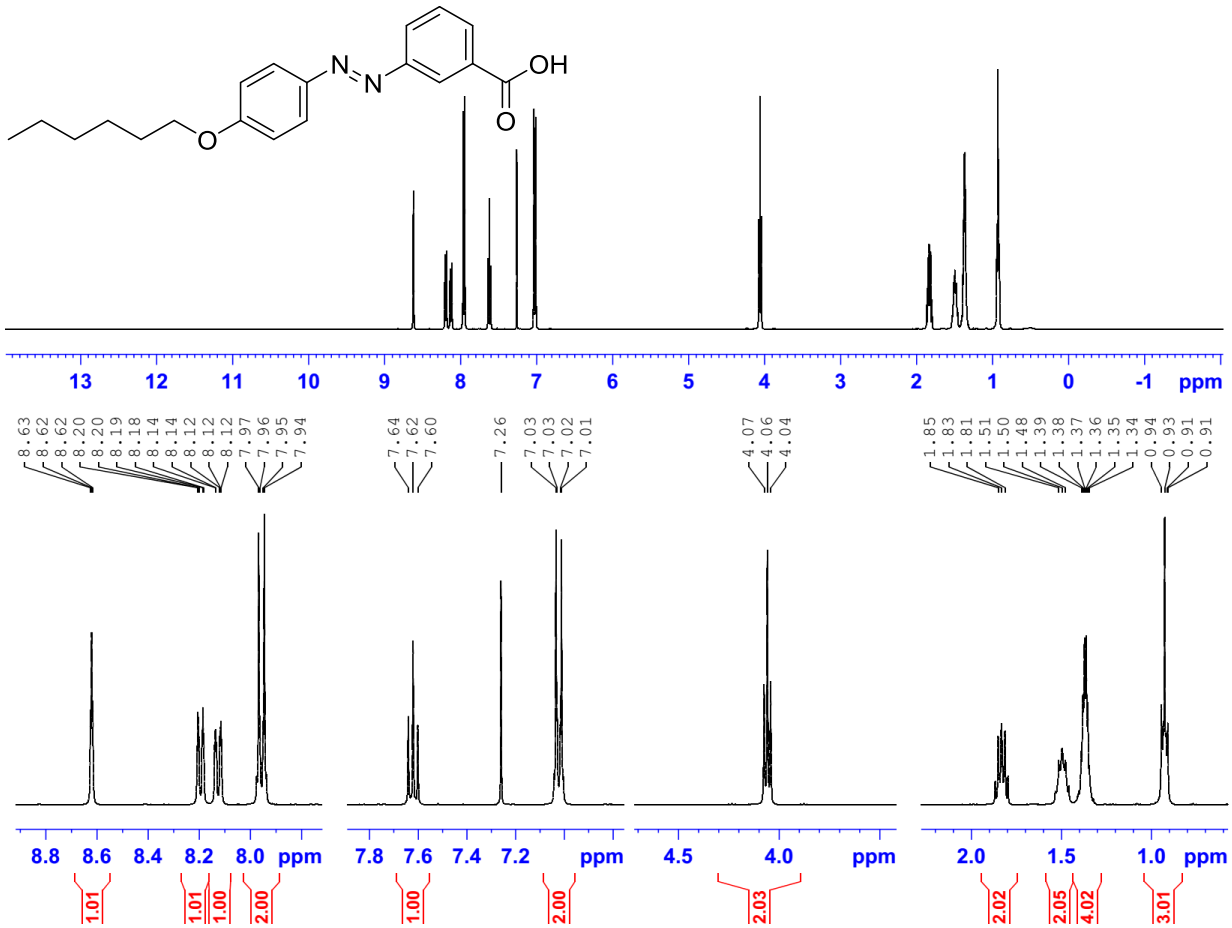




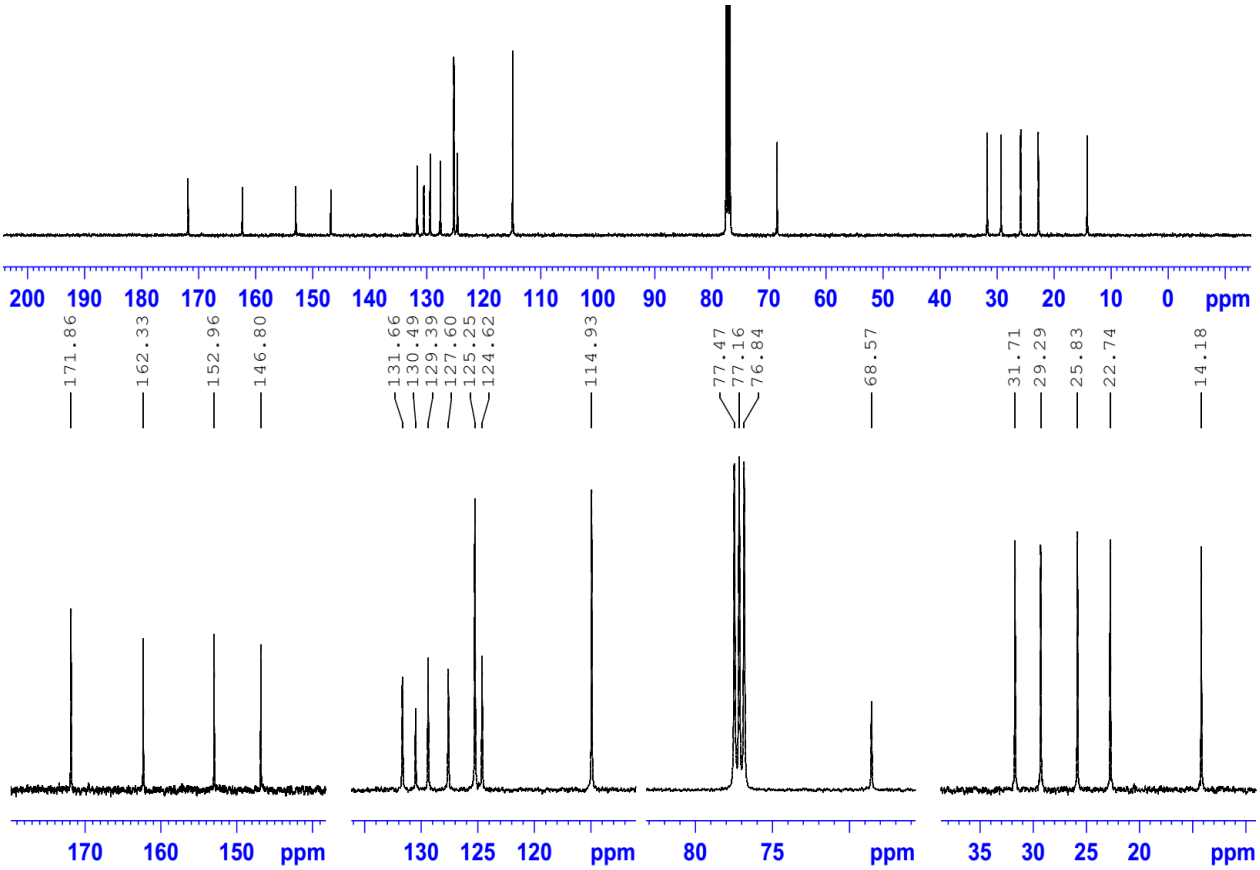
Compound 11, MS (ESI +) top and (ESI –) bottom



Compound 11, IR transmittance



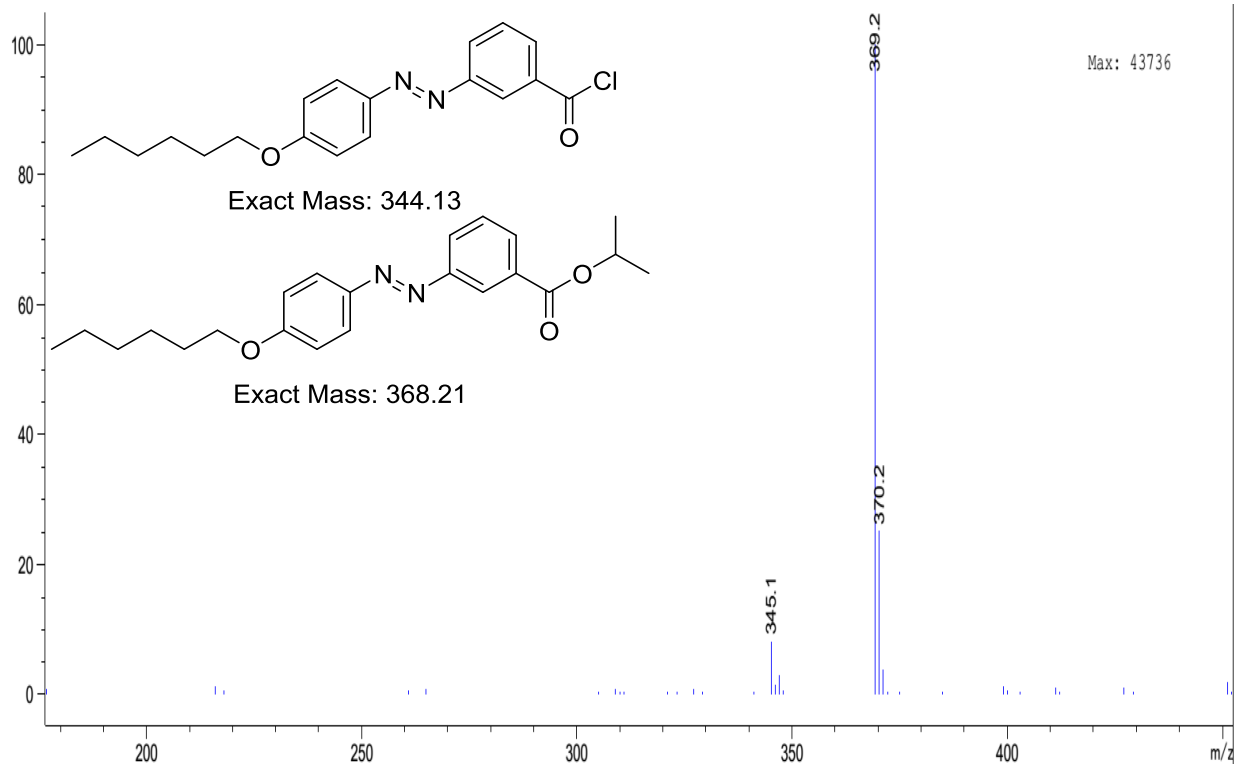
Compound 11, ^{1}H NMR (600 MHz, $CDCl_3$)



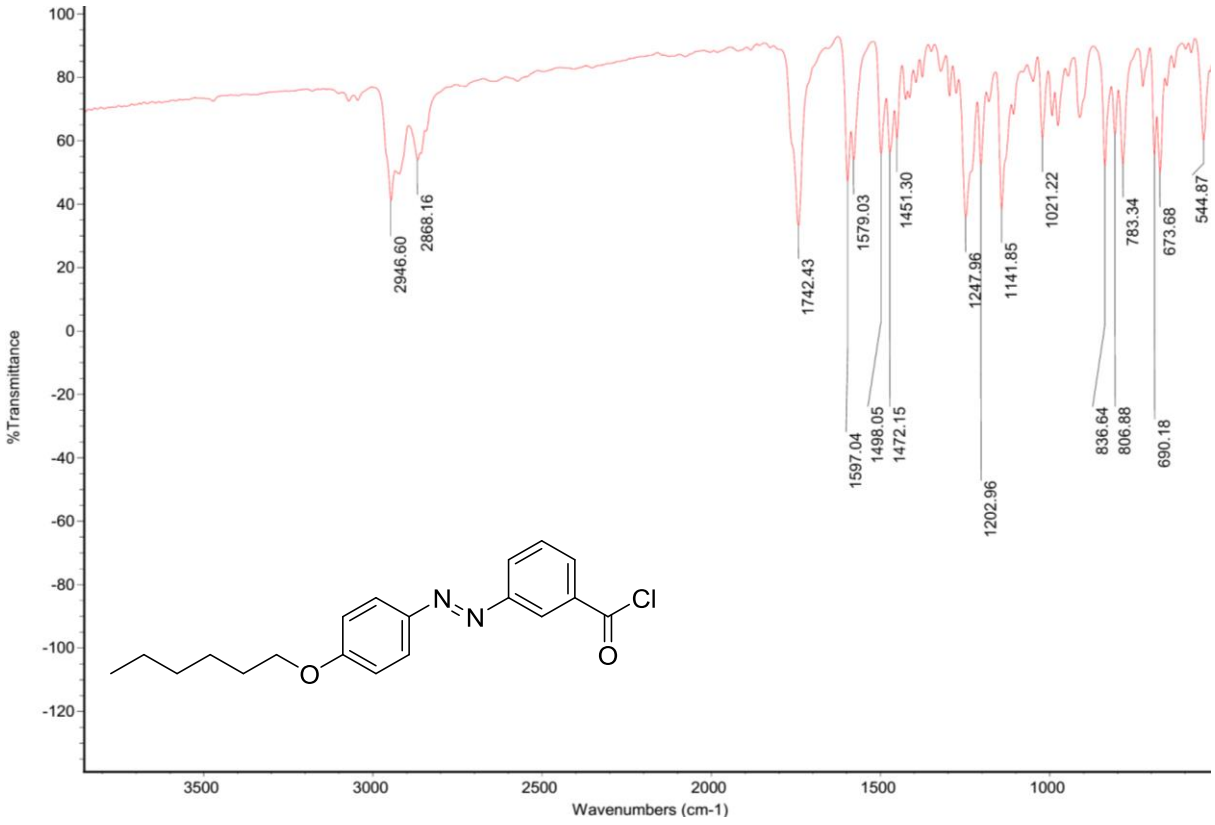
Compound 11, ^{13}C NMR (150 MHz, $CDCl_3$)

13. Characterization of compound (**12**)

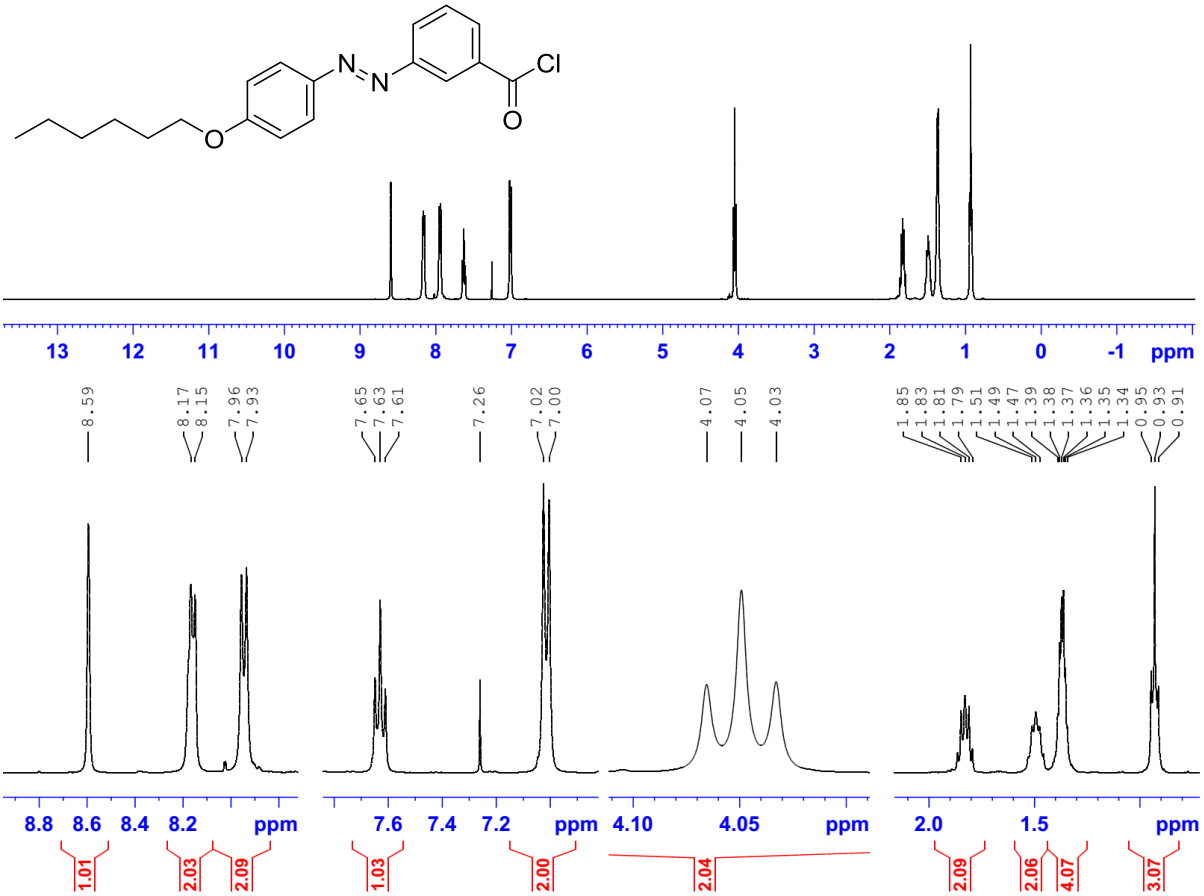
(*E*)-3-((4-(Hexyloxy)phenyl)diazenyl)benzoyl chloride



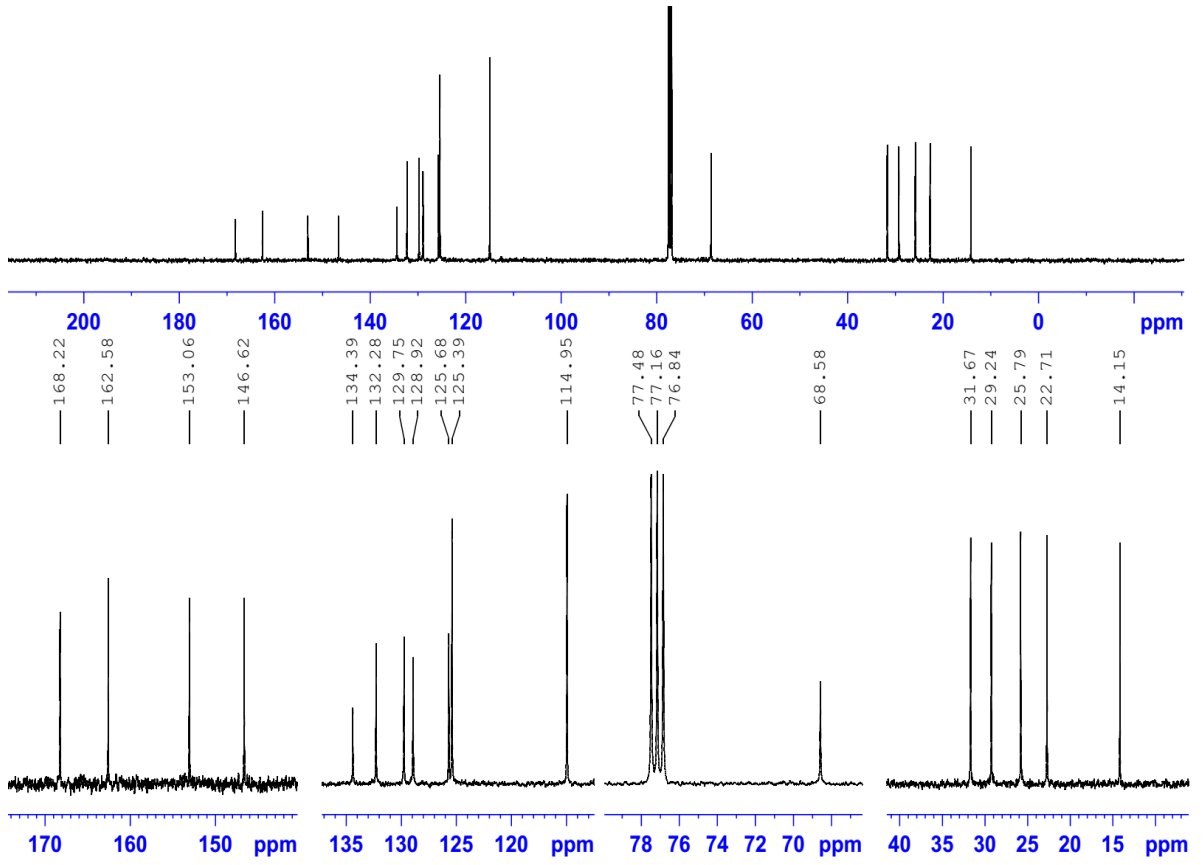
Compound 12, MS (ESI +): $[M + H]^+$ and $[M + i\text{PrOH} - Cl]^+$



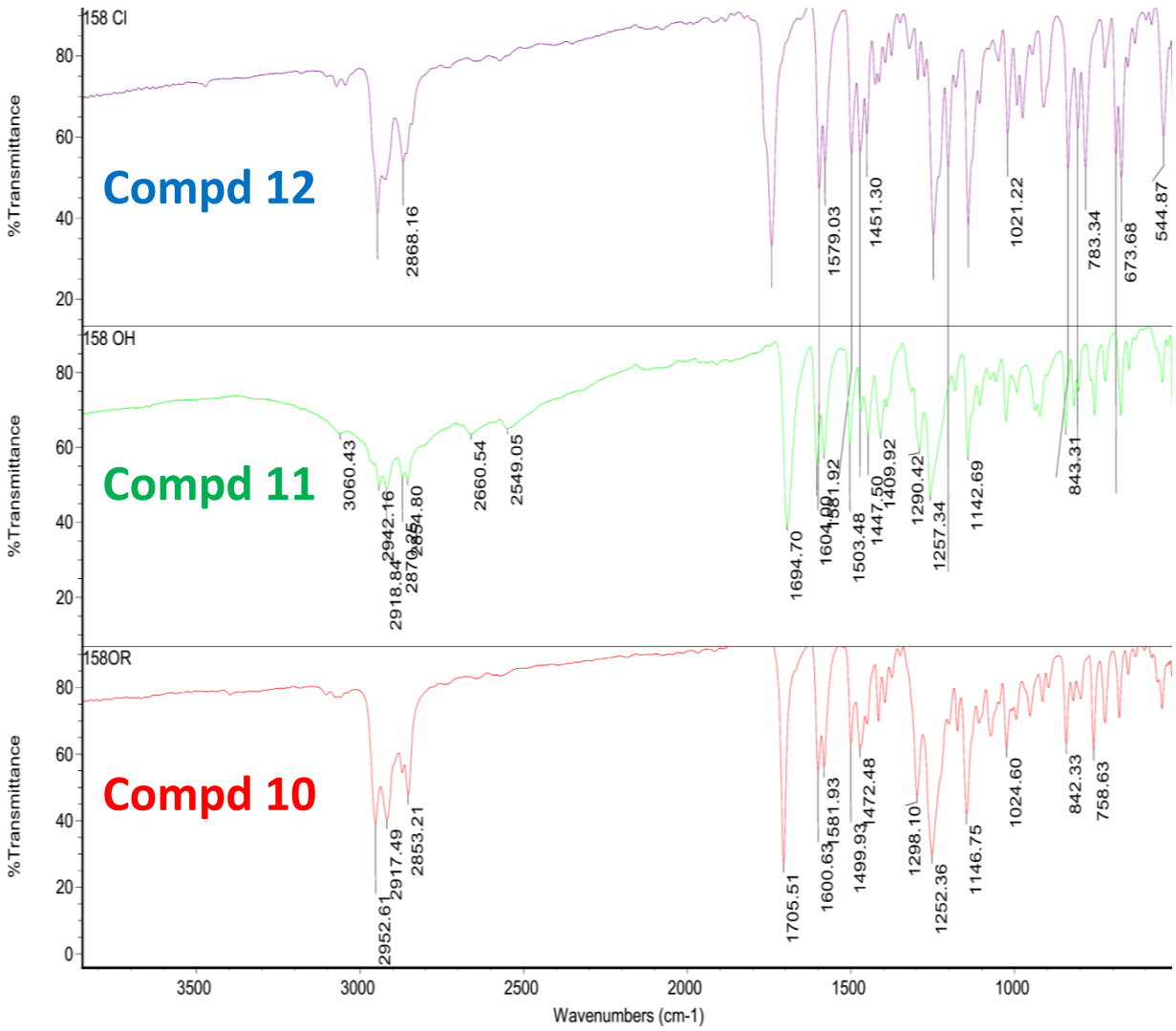
Compound 12, IR transmittance (neat)



Compound 12, ^{1}H NMR (400 MHz, $CDCl_3$)



Compound 12, ^{13}C NMR (100 MHz, $CDCl_3$)



Compounds 10–12, Comparative IR transmittance Spectra (neat)

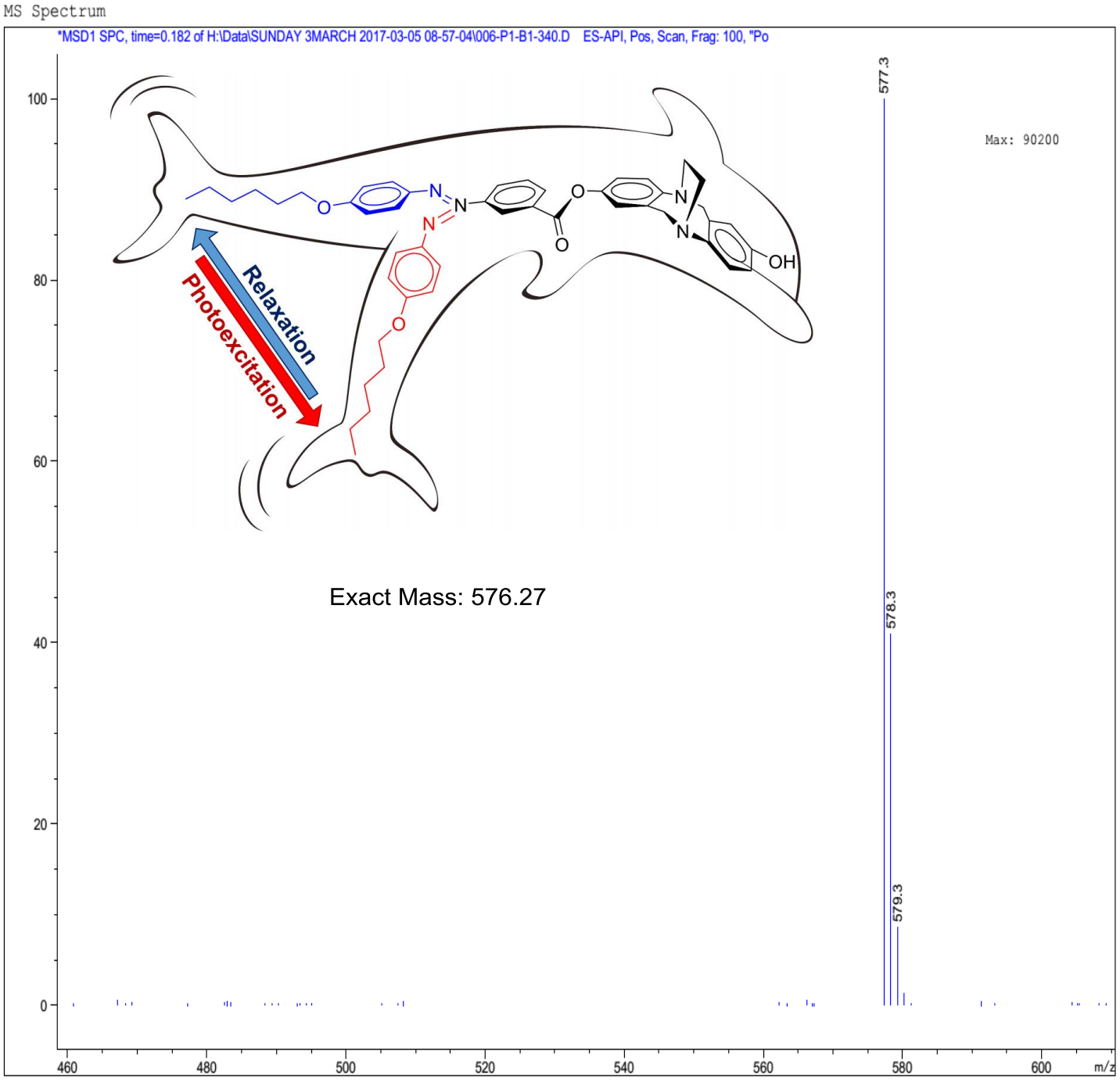
Table 1. IR transmittance summary, Compounds 10–12

Compound	Functional group; IR peak (cm^{-1})‡	Functional group; IR peak (cm^{-1})‡
10	Ester; 1705	Hexyl; 2952
11	Carboxylic acid; 1694	Hydroxyl; 3060–3350
12	Acid chloride; 1742	Chloride; 673

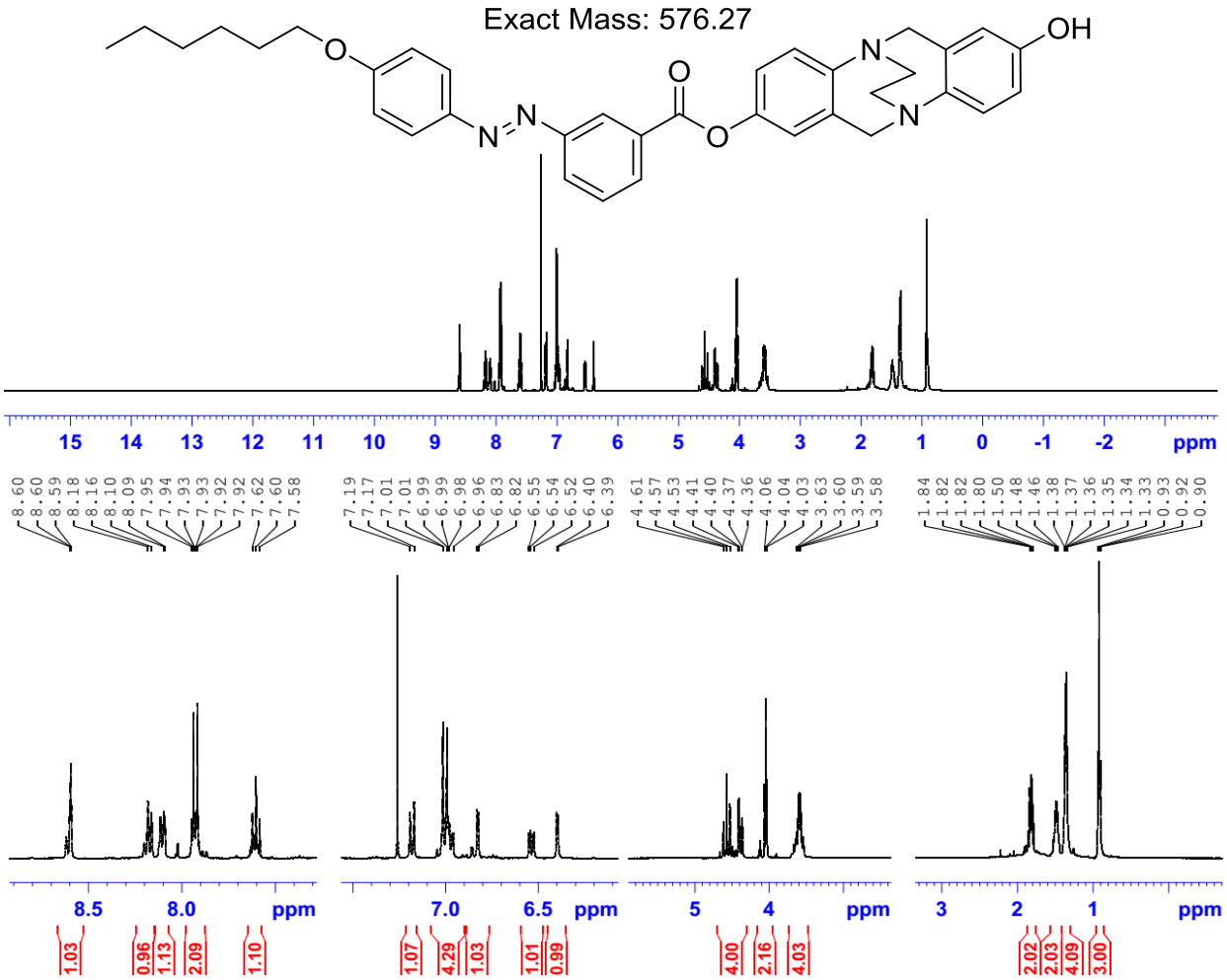
‡The results are in agreement with the literature[1]

14. Characterization of compound (**13**)

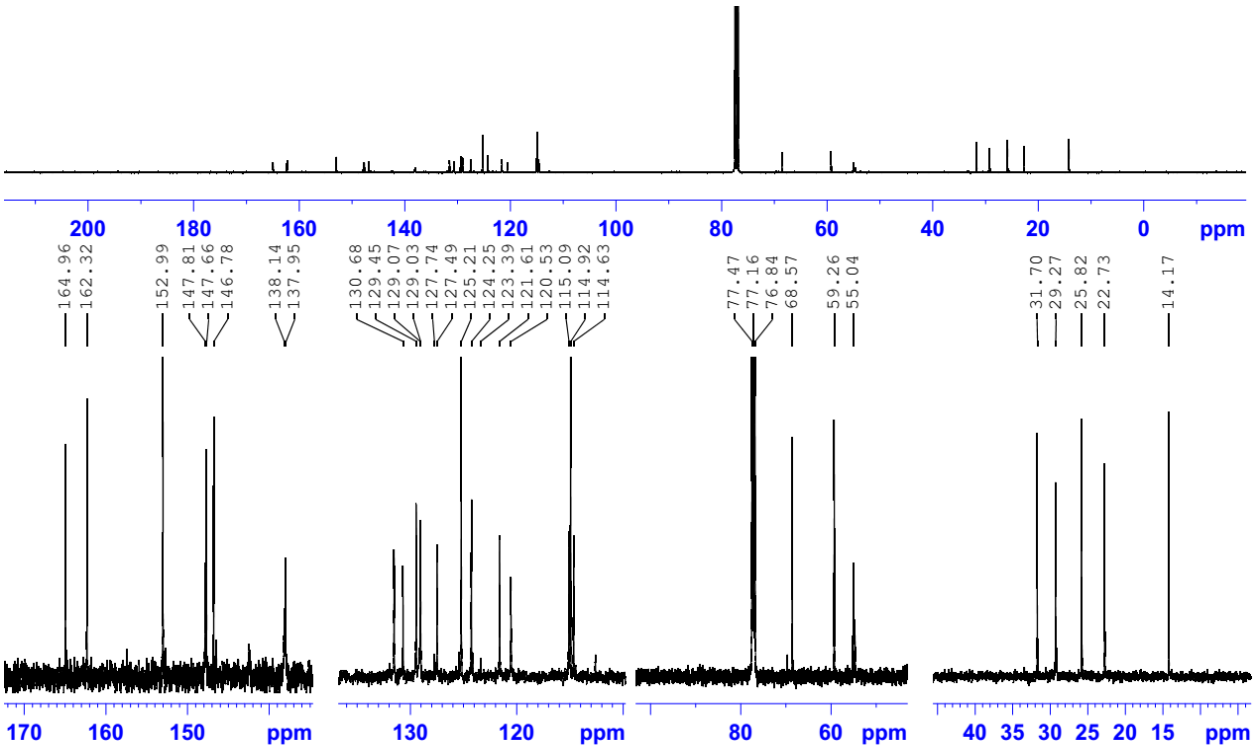
8-hydroxy-6*H*,12*H*-5,11-ethanodibenzo[*b,f*][1,5]diazocin-2-yl(*E*)-3-((4-(hexyloxy)phenyl)diazenyl) benzoate



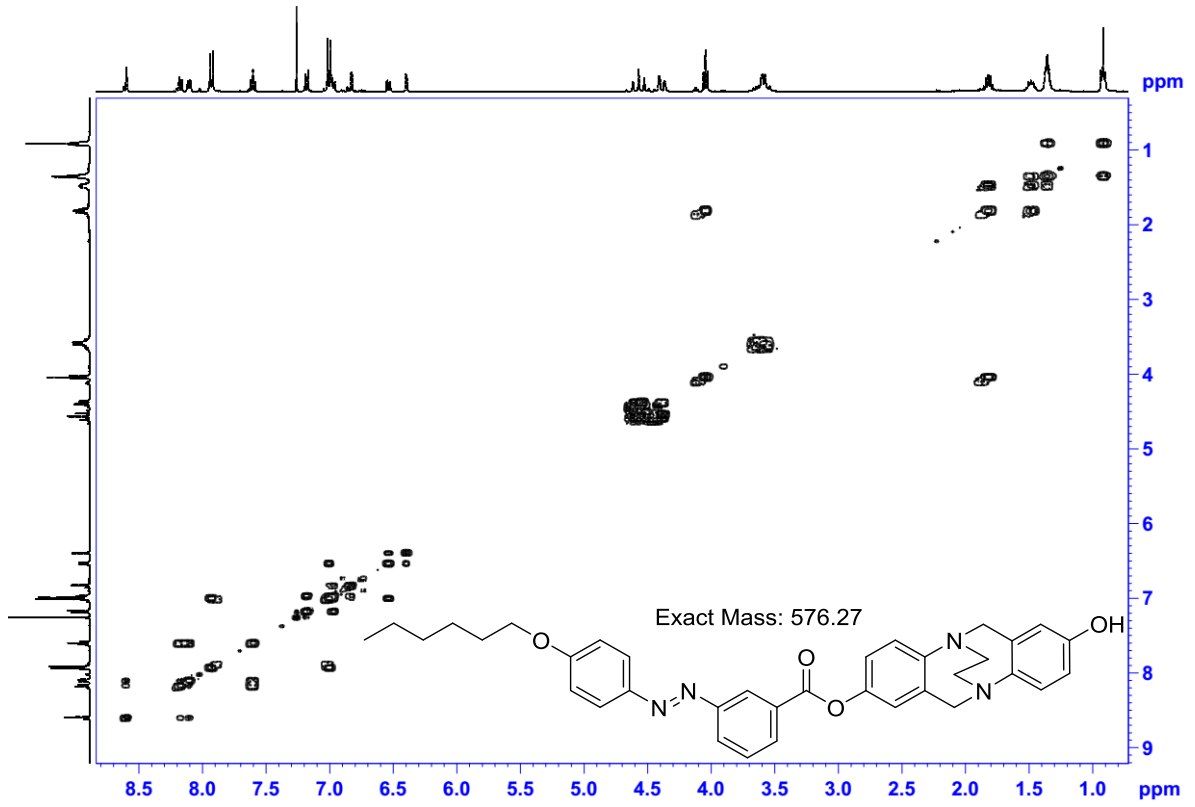
Compound 13, MS (ESI +)



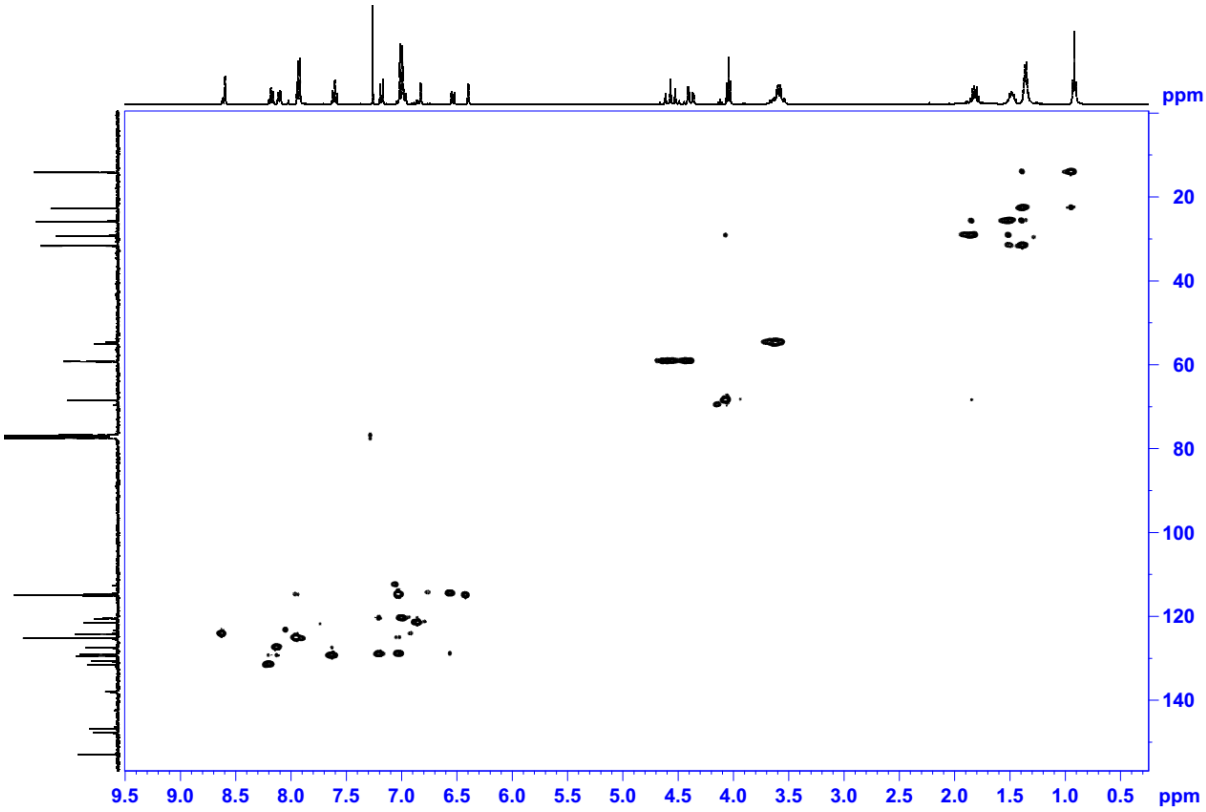
Compound 13, ^{1}H NMR (400 MHz, $CDCl_3$)



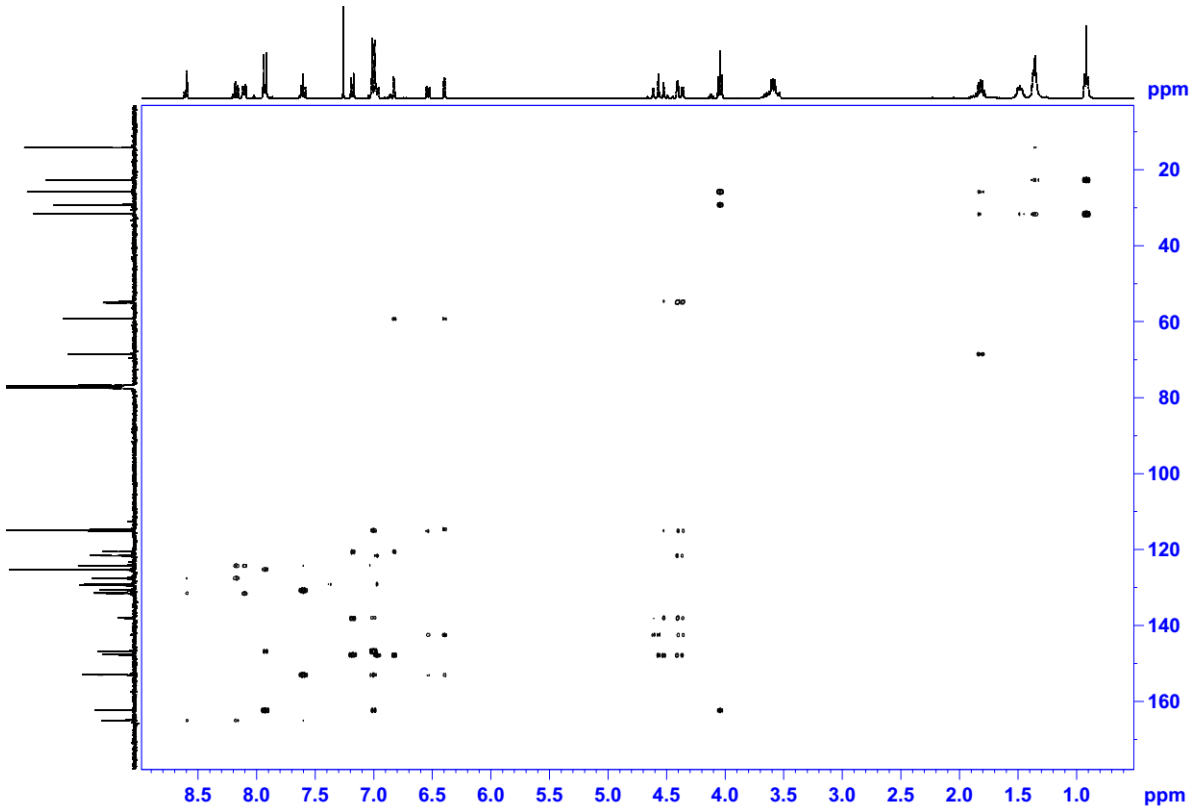
Compound 13, ^{13}C NMR (100 MHz, $CDCl_3$)



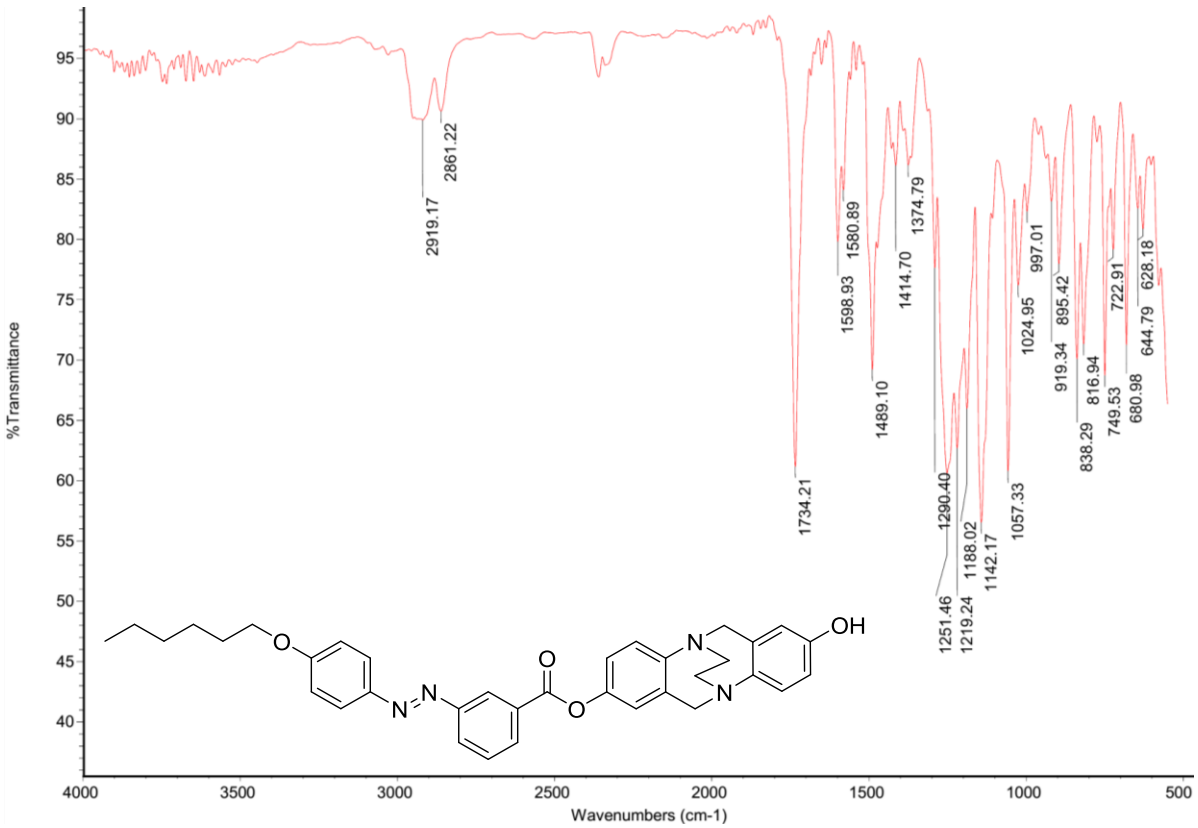
Compound 13, COSY (400 MHz, $CDCl_3$)



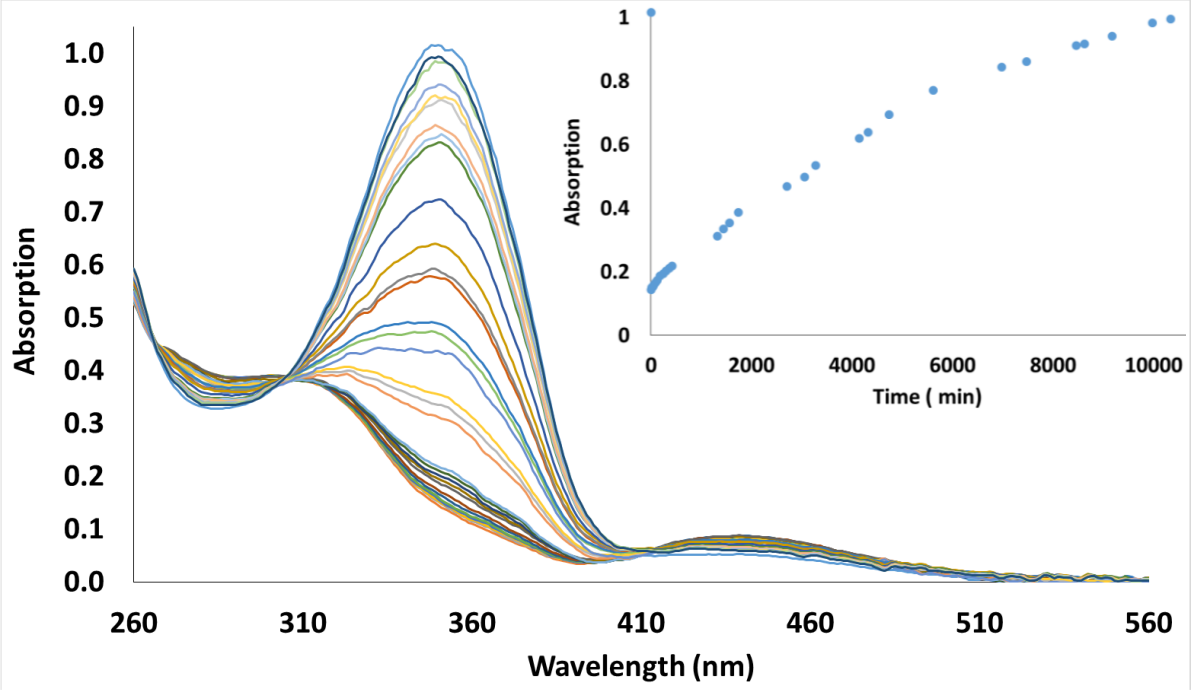
Compound 13, HSQC (400 MHz, $CDCl_3$)



Compound 13, HMBC (400 MHz, $CDCl_3$)



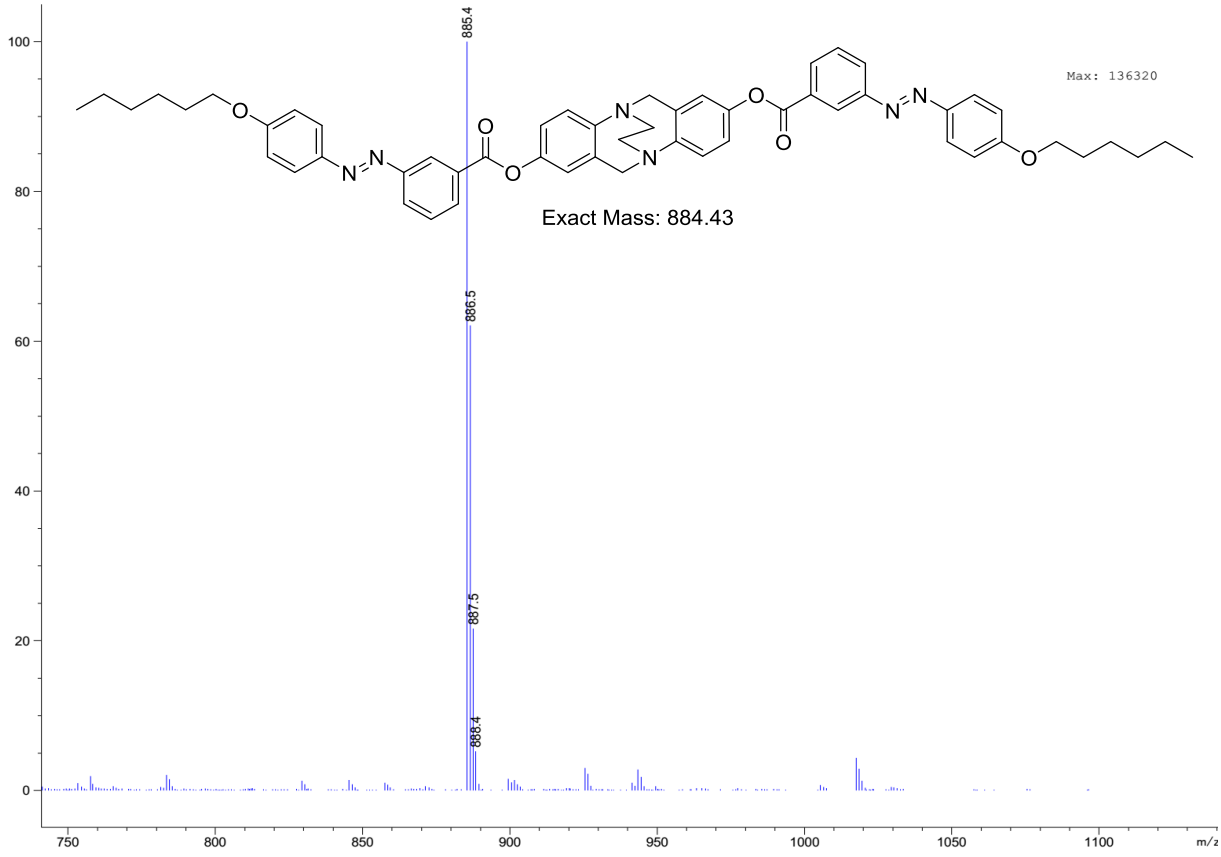
Compound 13, IR transmittance (neat)



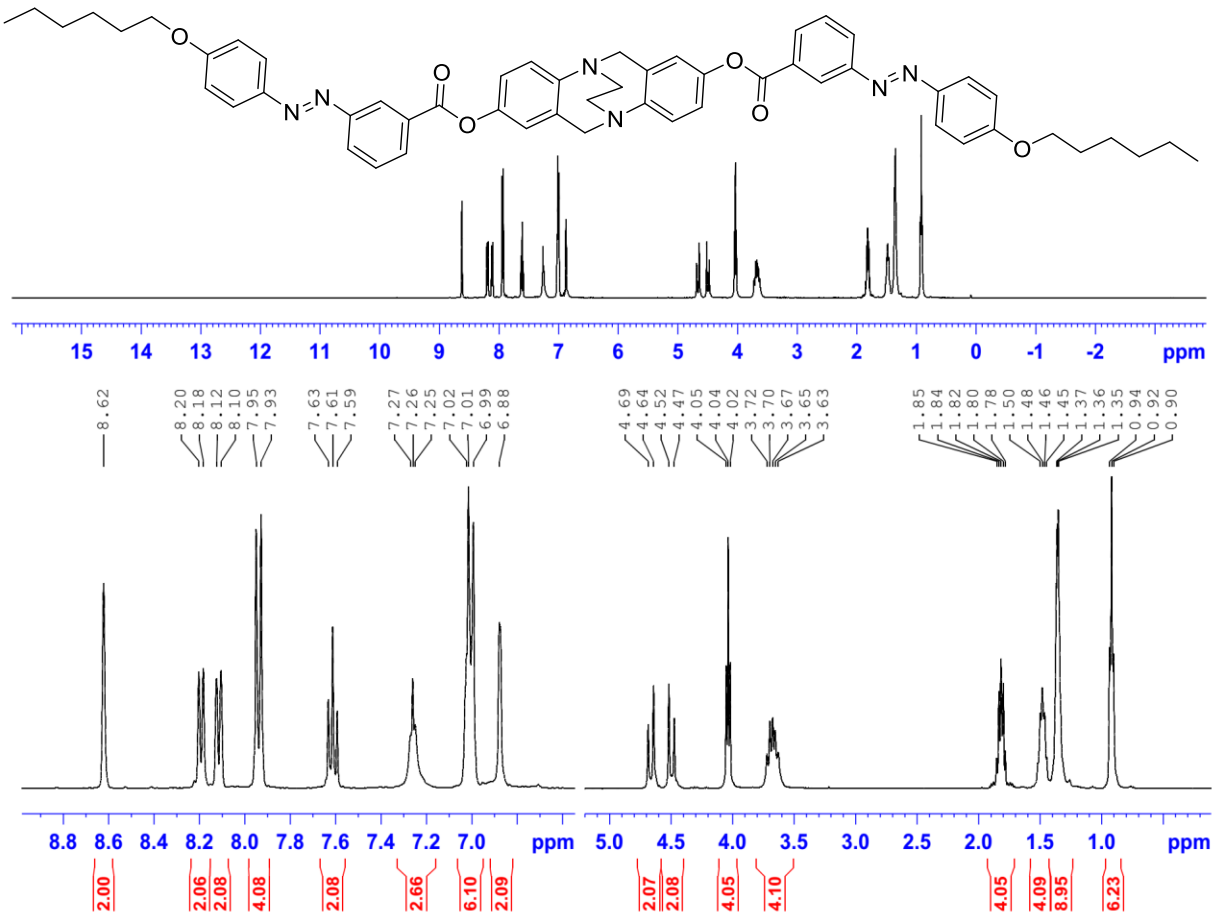
Compound 13, UV-Vis absorption spectra at different stages of photoisomerization

15. Characterization of compound (**14**)

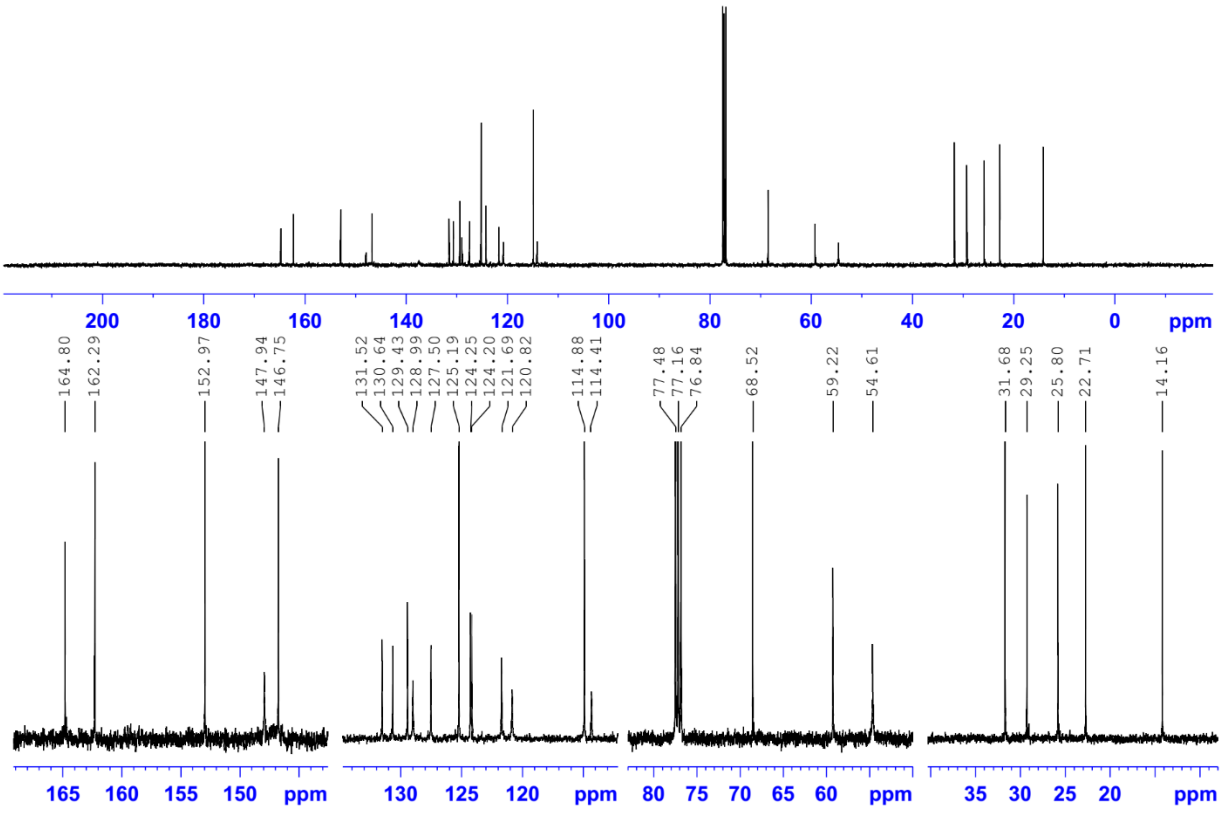
6*H*,12*H*-5,11-ethanodibenzo[*b,f*][1,5]diazocine-2,8-diyl bis 3-((*E*)-(4-(hexyloxy)phenyl) diazenyl)benzoate



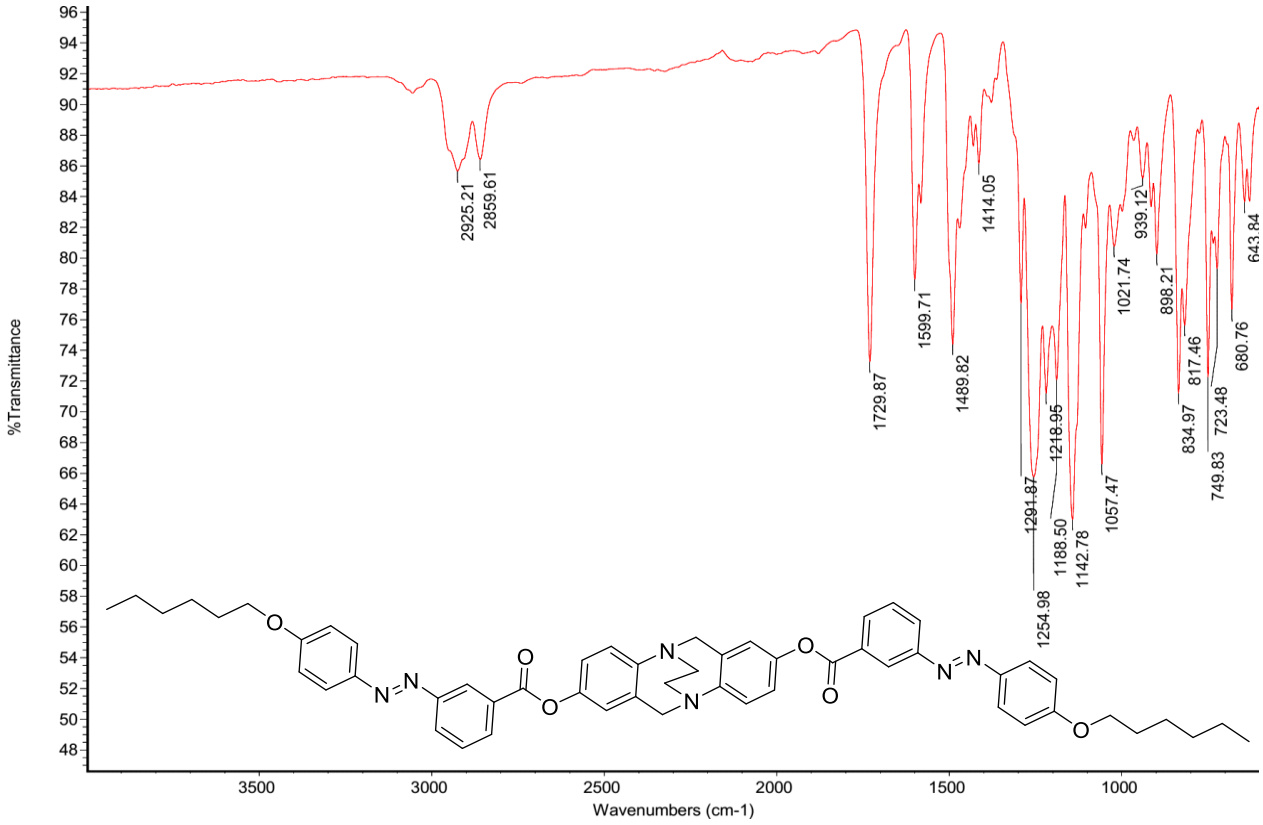
Compound 14, MS (ESI +)



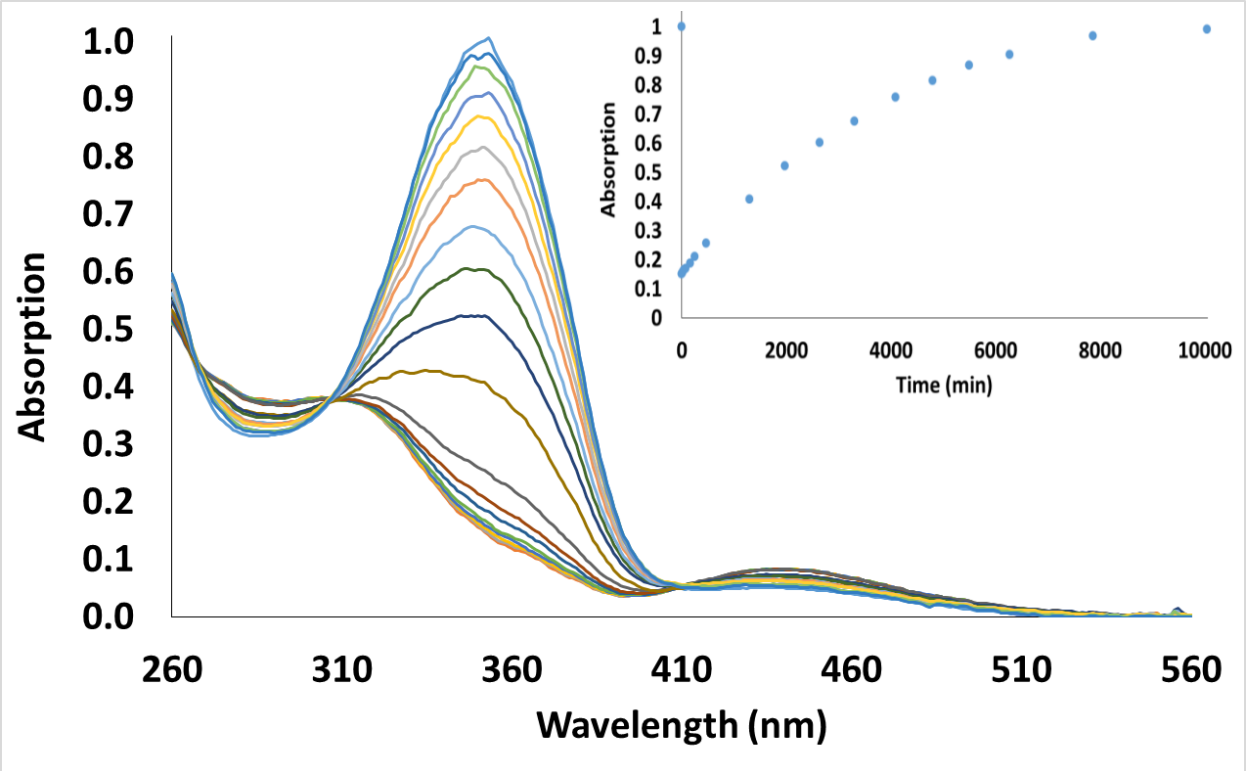
Compound 14, ^{1}H NMR (600 MHz, $CDCl_3$)



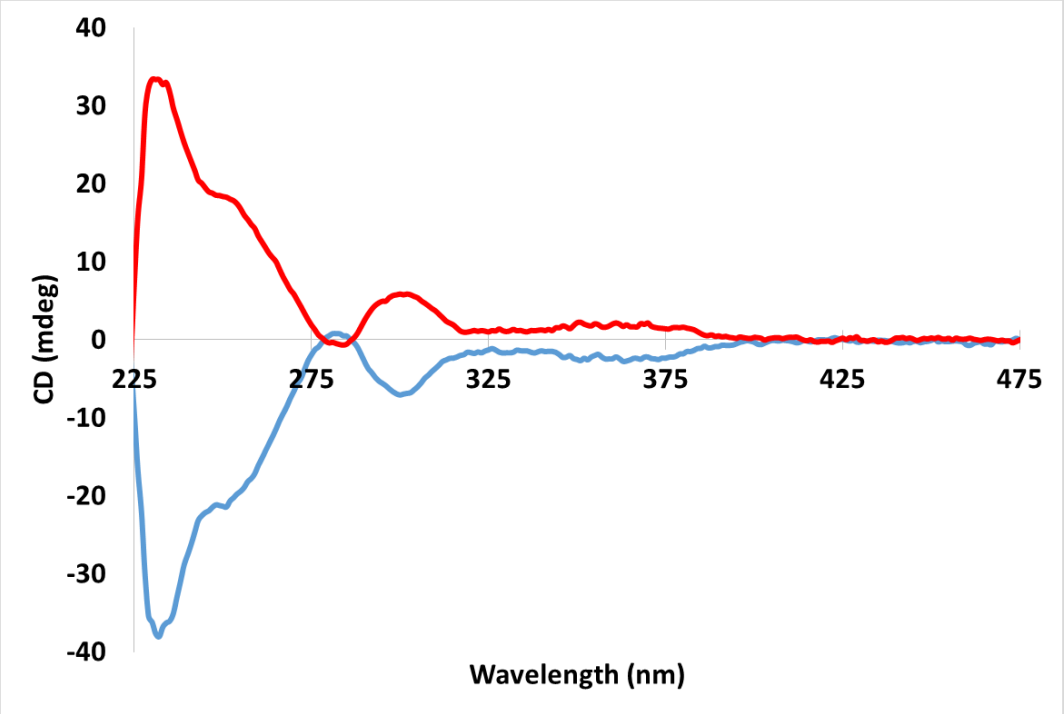
Compound 14, ^{13}C NMR (150 MHz, $CDCl_3$)



Compound 14, IR transmittance (neat)



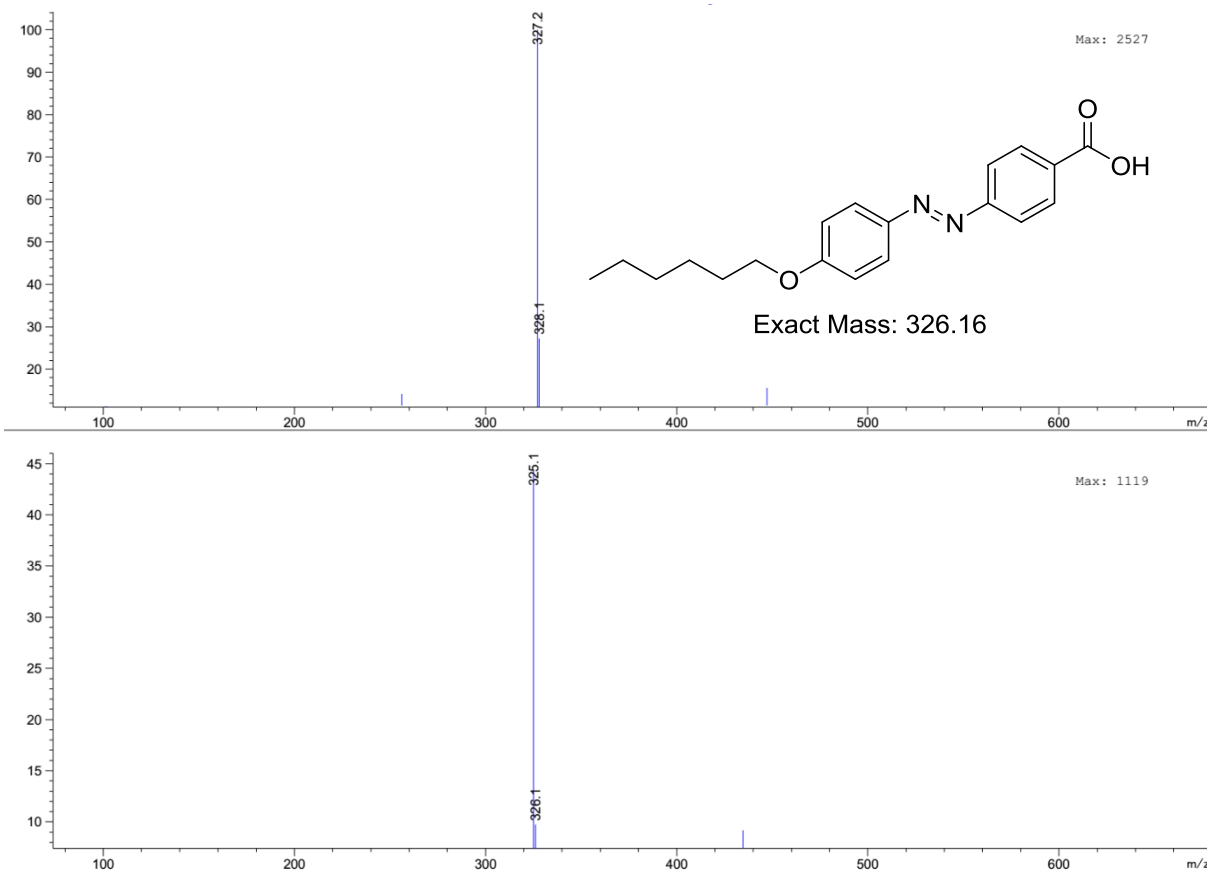
Compound 14, UV-Vis absorption spectra of 14 at different stages of photoisomerization



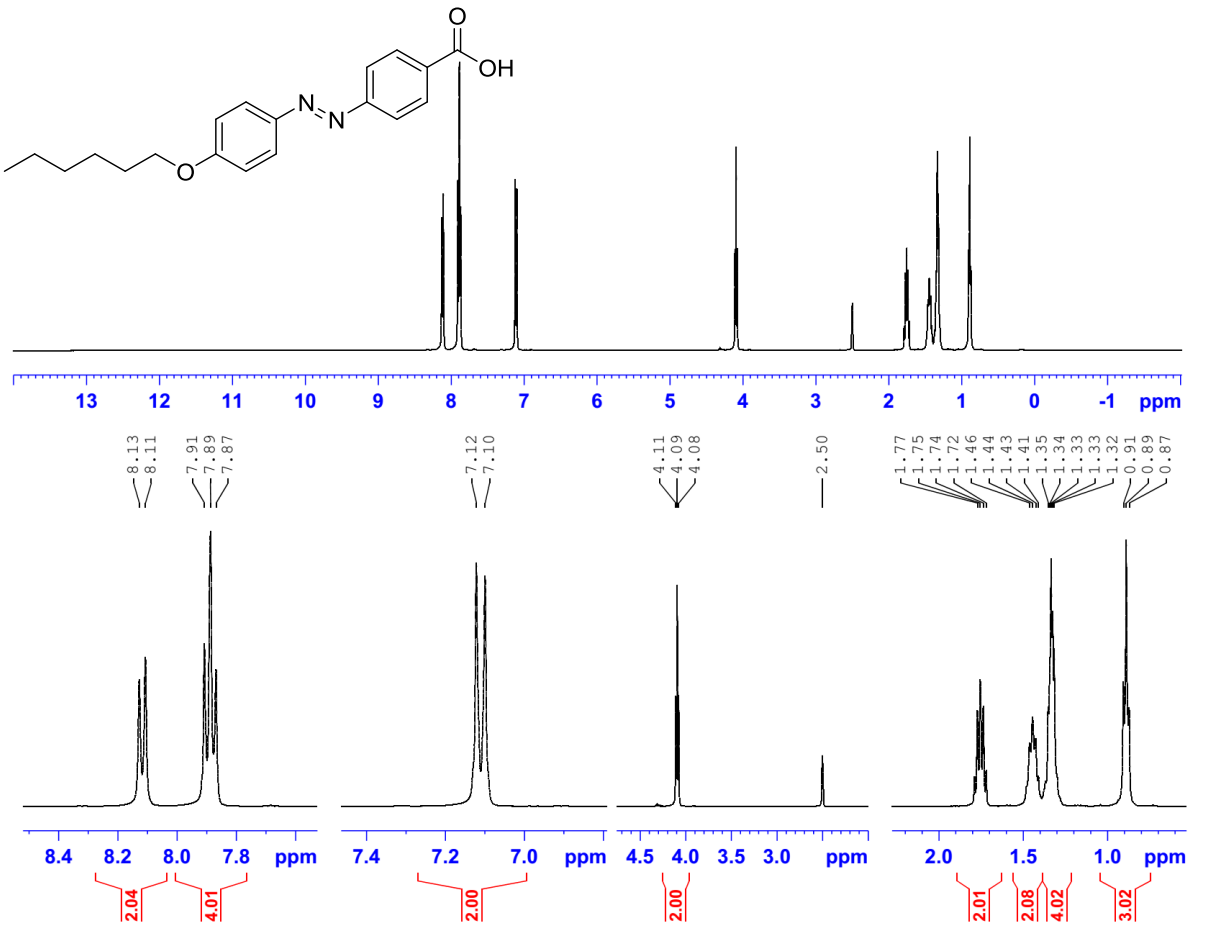
CD spectra, (+)-(*R*,*R*)-14 and (–)-(*S*,*S*)-14 in DCM

16. Characterization of compound (**15**)

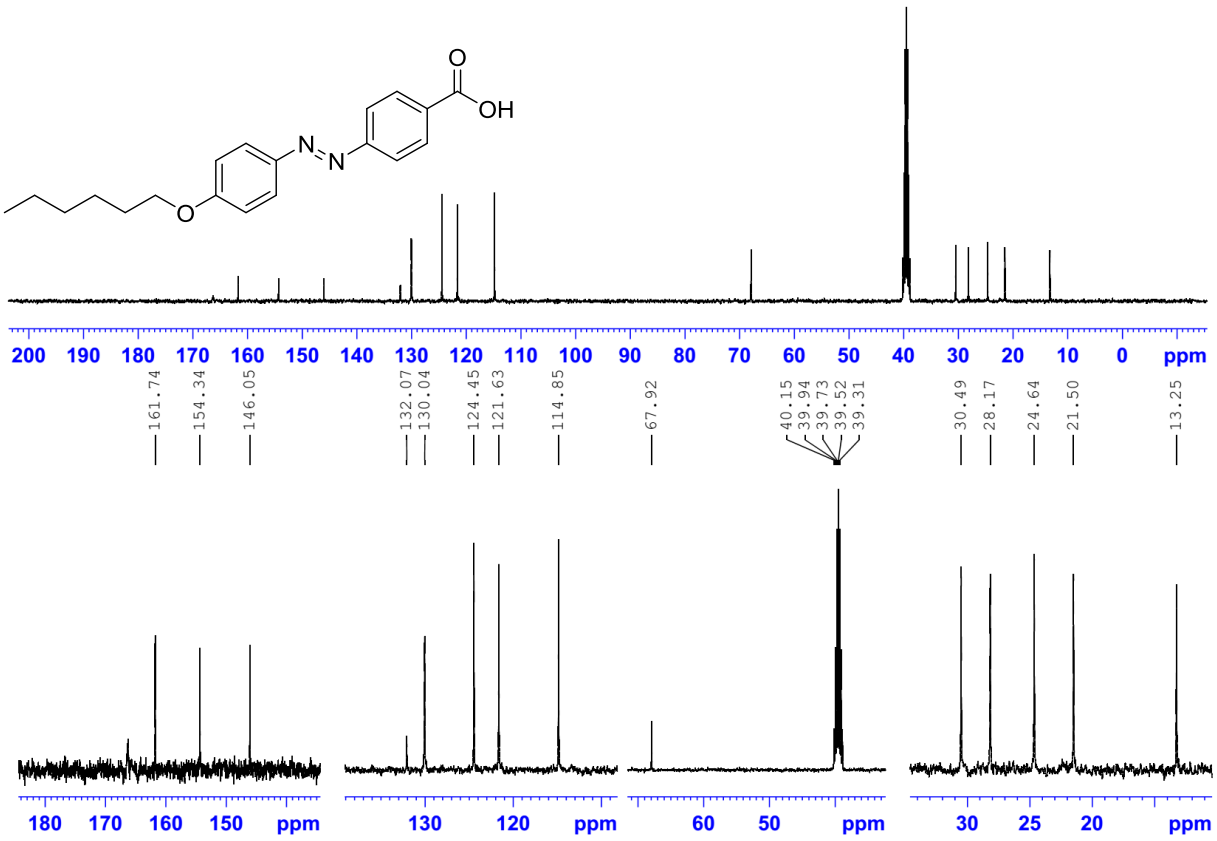
(*E*)-4-((4-(hexyloxy)phenyl)diazenyl)benzoic acid



Compound 15, MS (ESI ±)



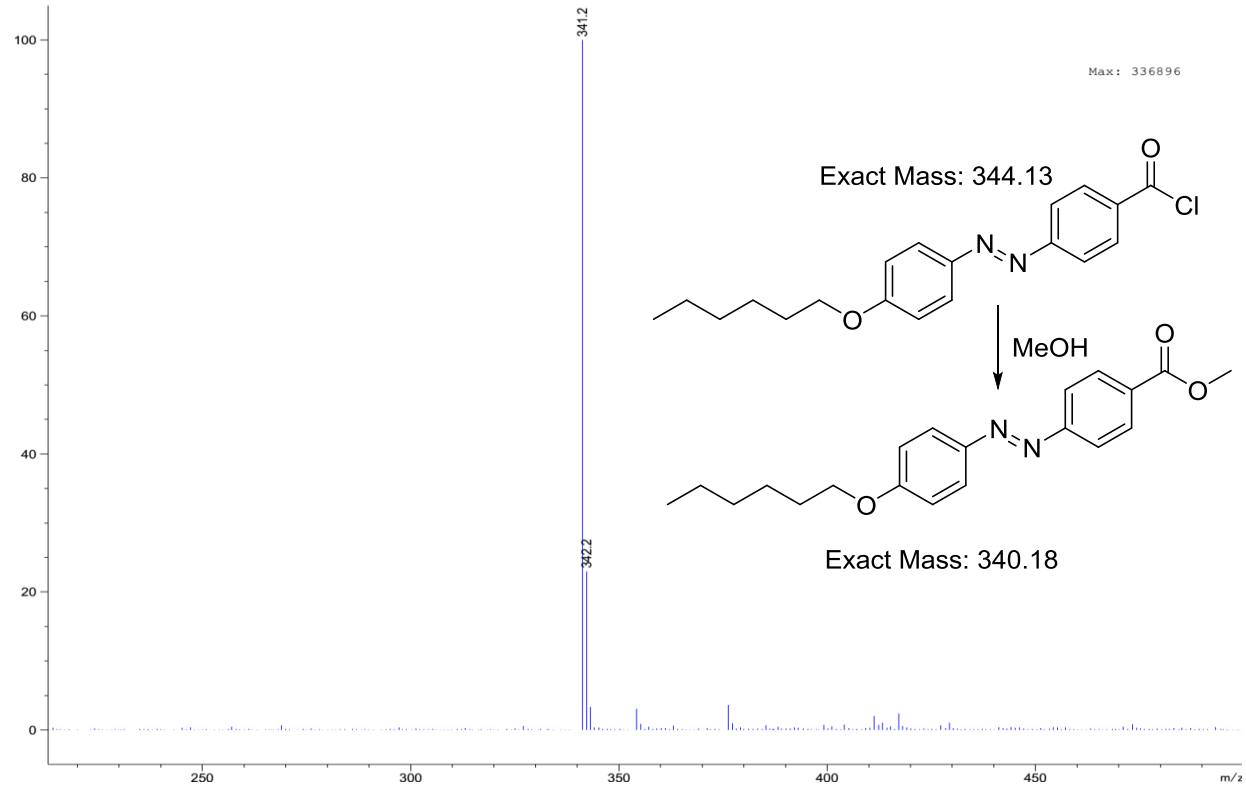
Compound 15, ^{1}H NMR (400 MHz, DMSO-d_6)



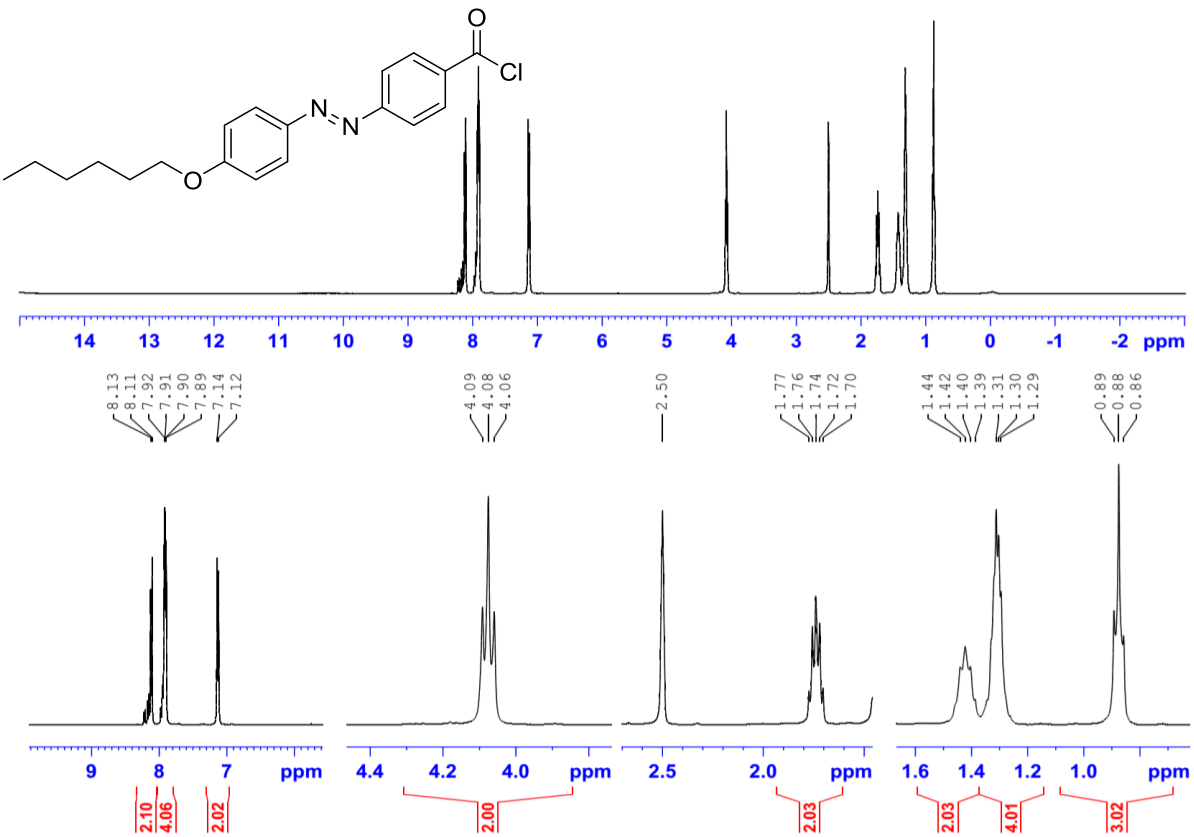
Compound 15, ^{13}C NMR (100 MHz, DMSO-d_6)

17. Characterization of compound (**16**)

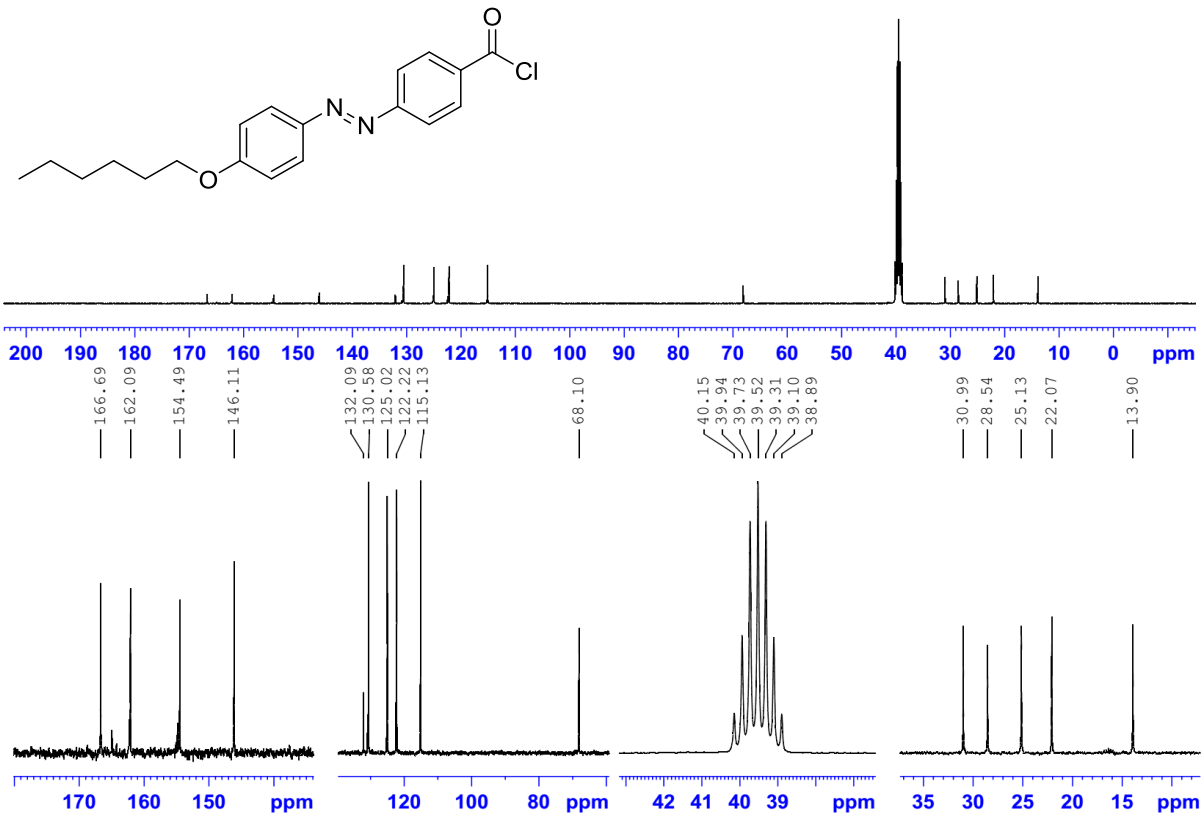
(*E*)-4-((4-(hexyloxy)phenyl)diazenyl)benzoyl chloride



Compound 16, MS (ESI +) in MeOH



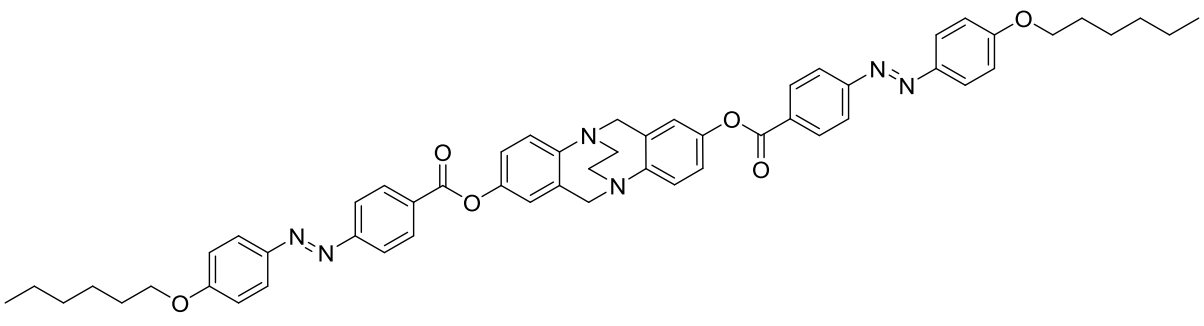
Compound 16, ^{1}H NMR (400 MHz, DMSO-d_6)



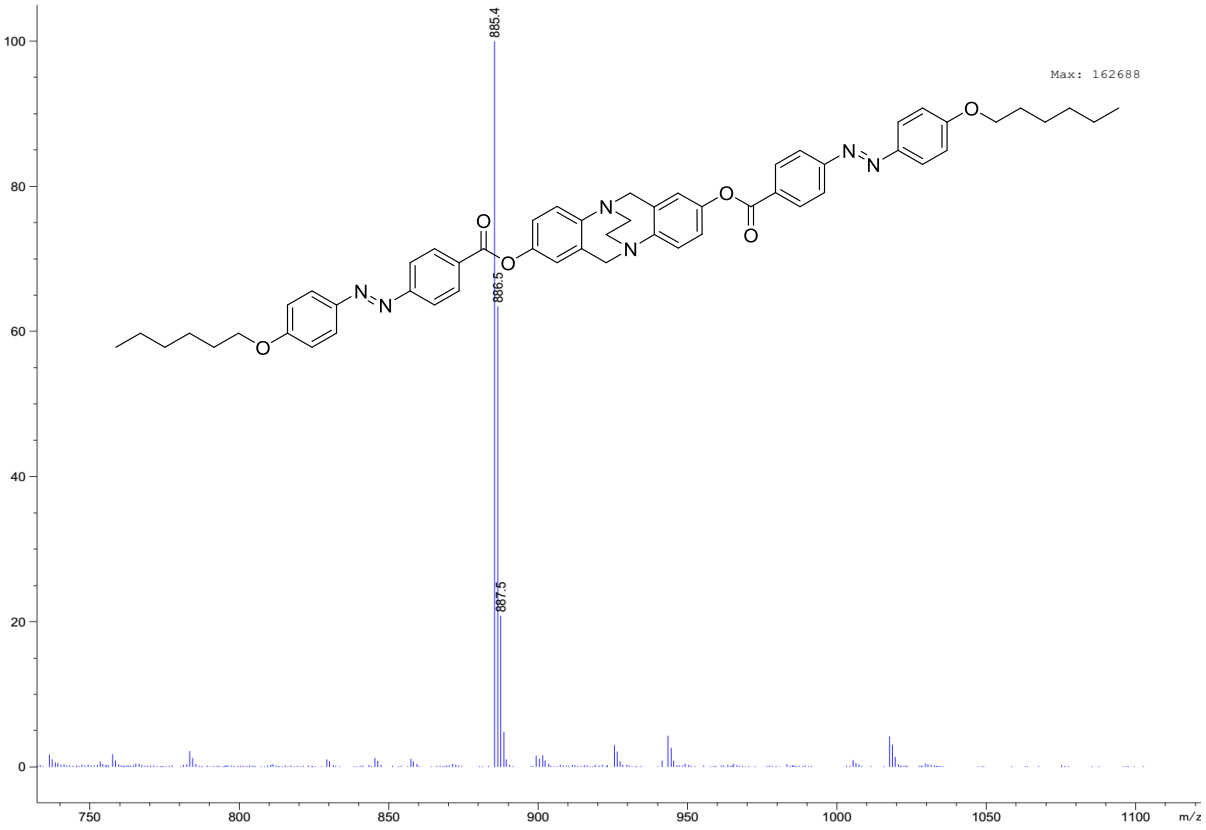
Compound 16, ^{13}C NMR (100 MHz, DMSO-d_6)

18. Characterization of compound (**17**)

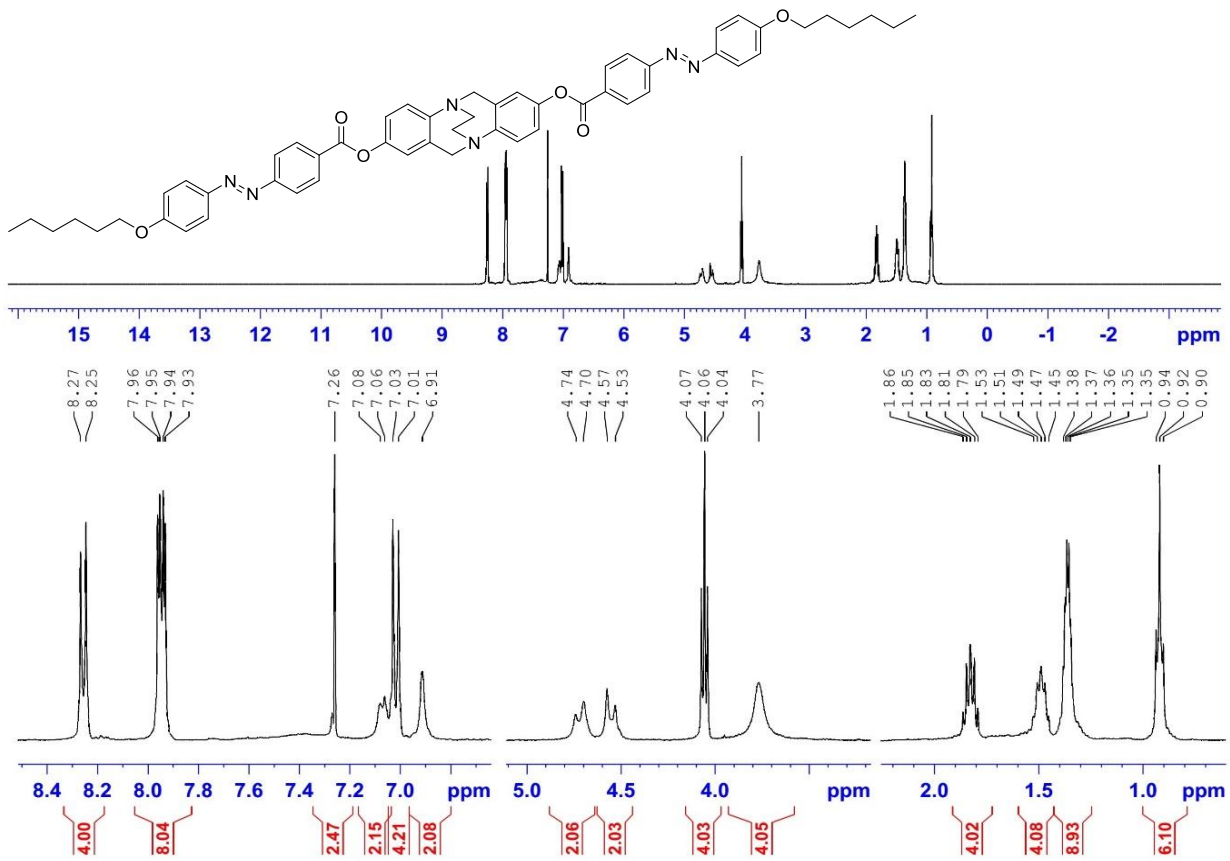
6*H*,12*H*-5,11-ethanodibenzo[*b*,*f*][1,5]diazocine-2,8-diyl bis(4-((*E*)-4-(hexyloxy)phenyl)diazenyl) benzoate



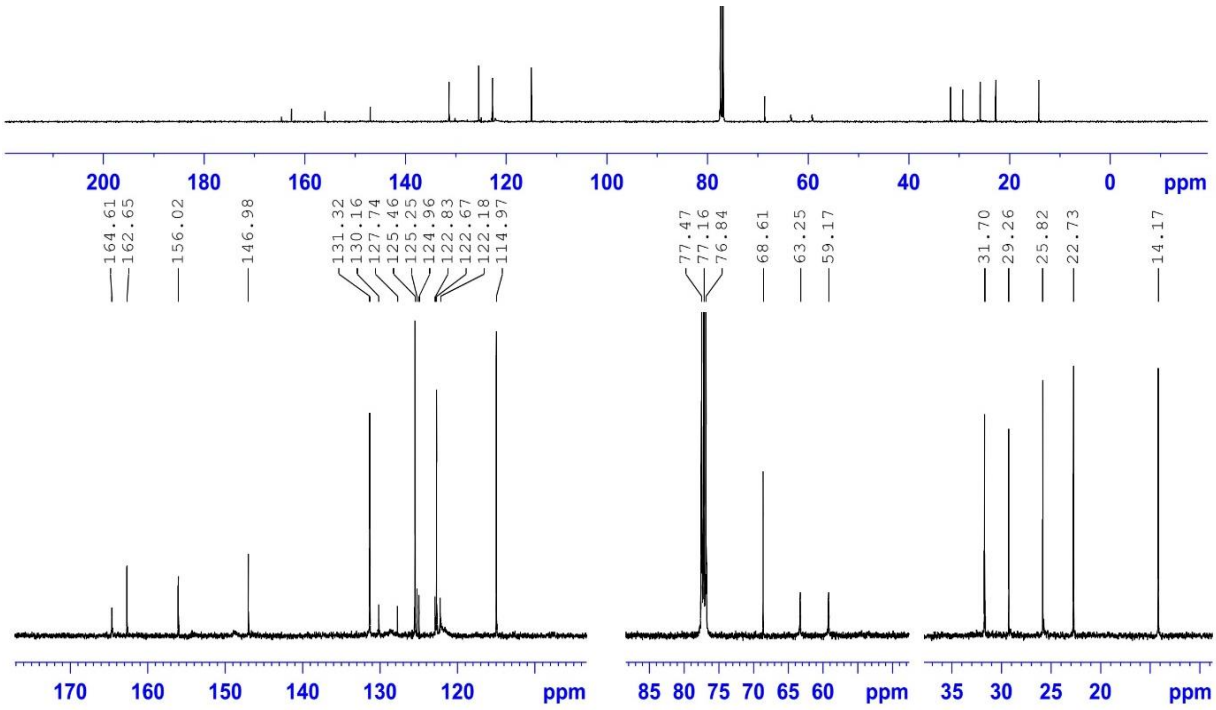
Exact Mass: 884.43



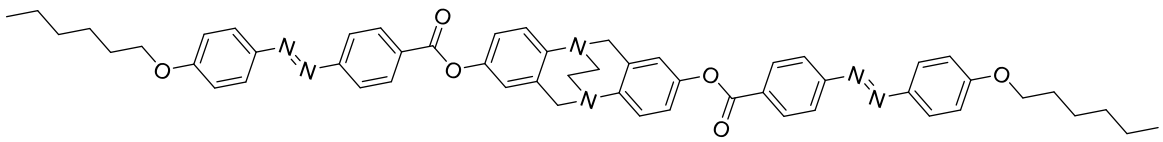
Compound 17, MS (ESI +)

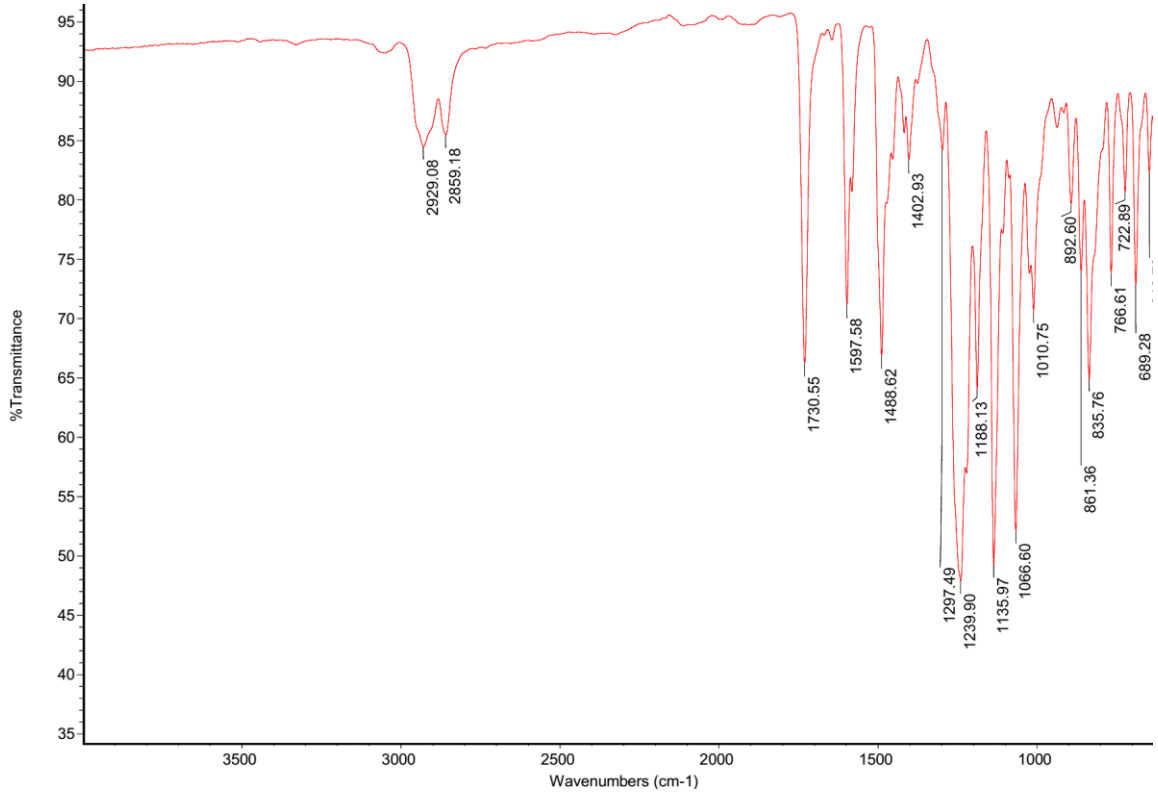


Compound 17, ^{1}H NMR (400 MHz, $CDCl_3$)

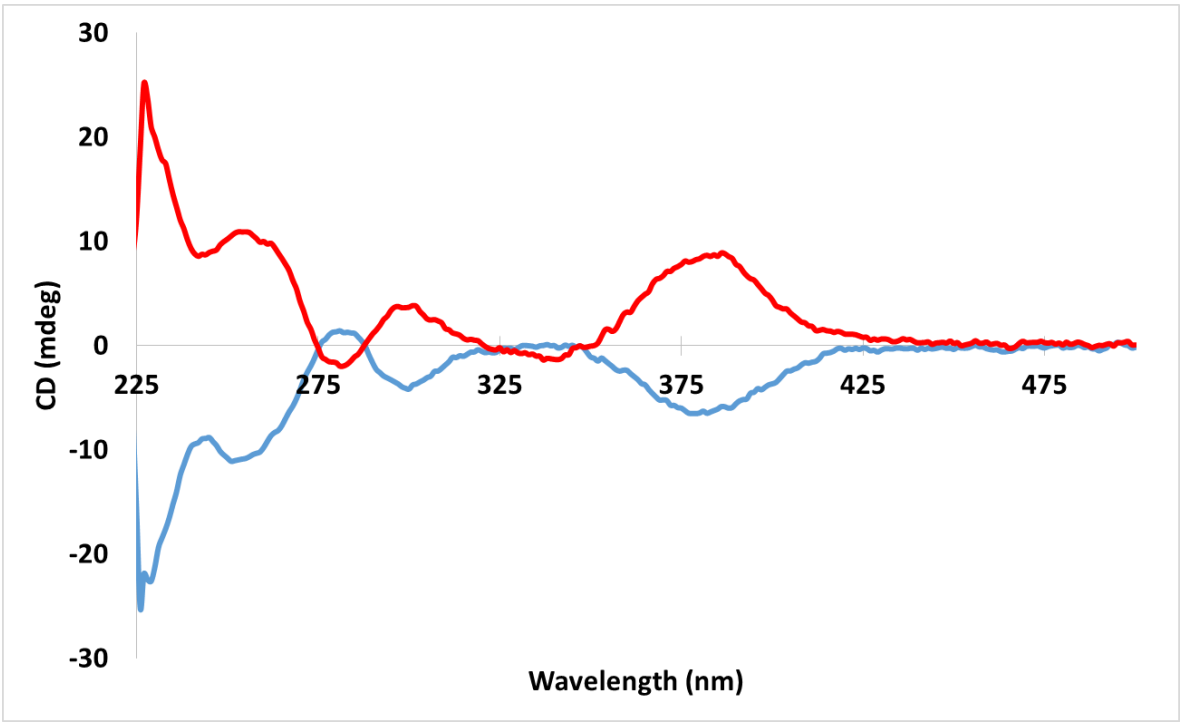


Compound 17, ^{13}C NMR (100 MHz, $CDCl_3$)

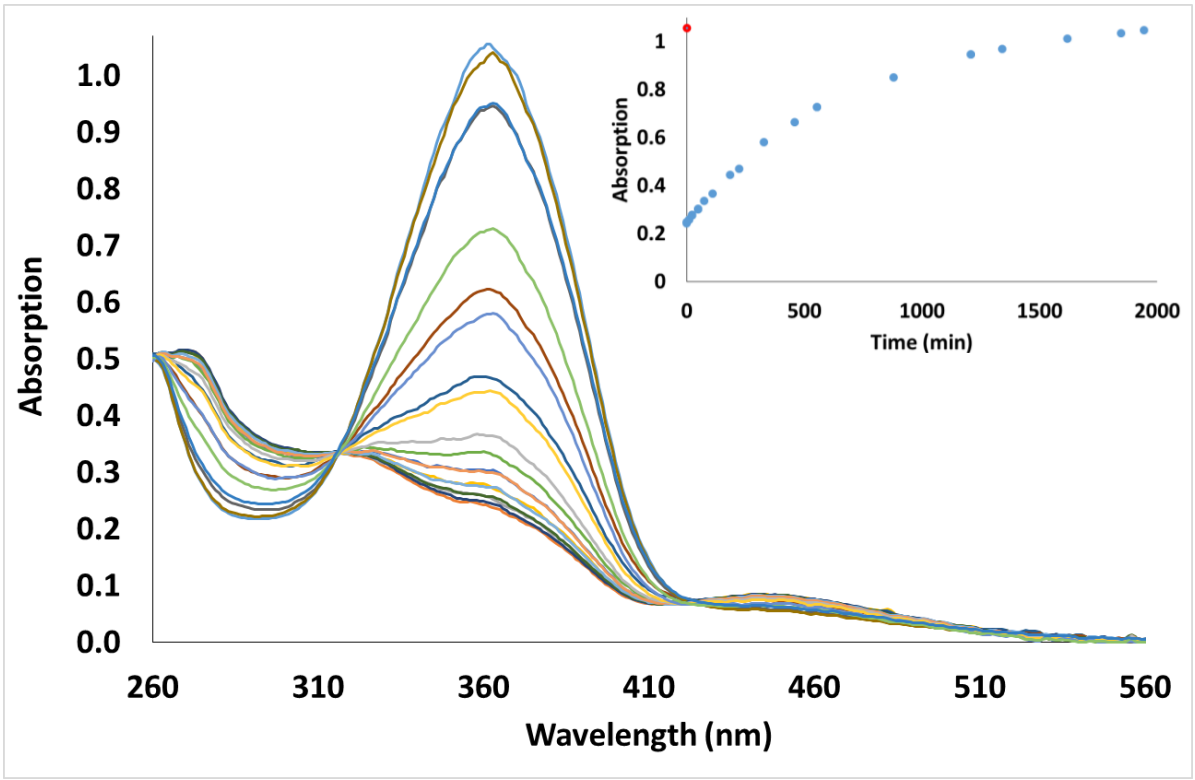




Compound 17, IR transmittance (neat)



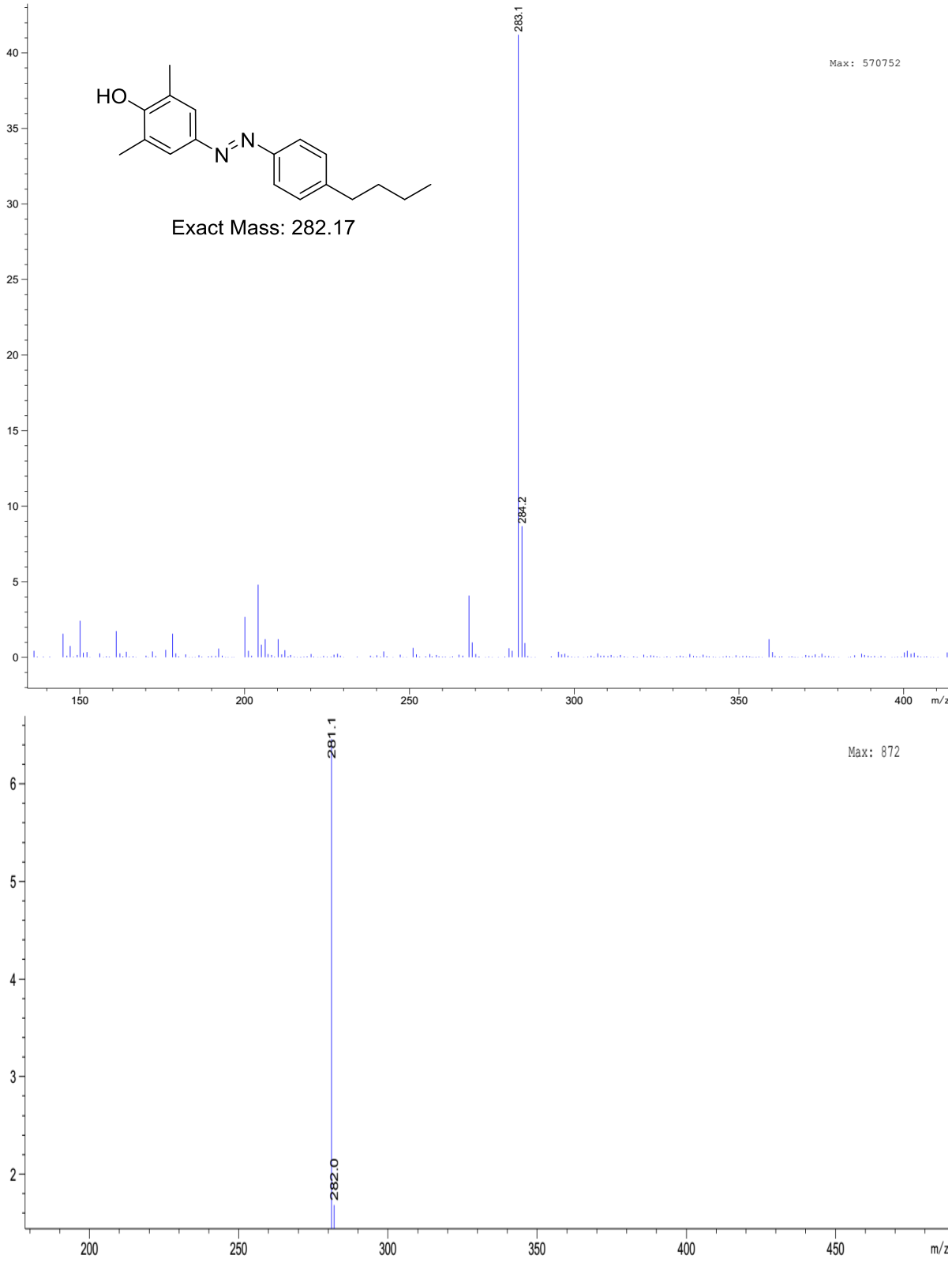
CD spectra, (+)-(*R*,*R*)-17 and (–)-(*S*,*S*)-17 in DCM



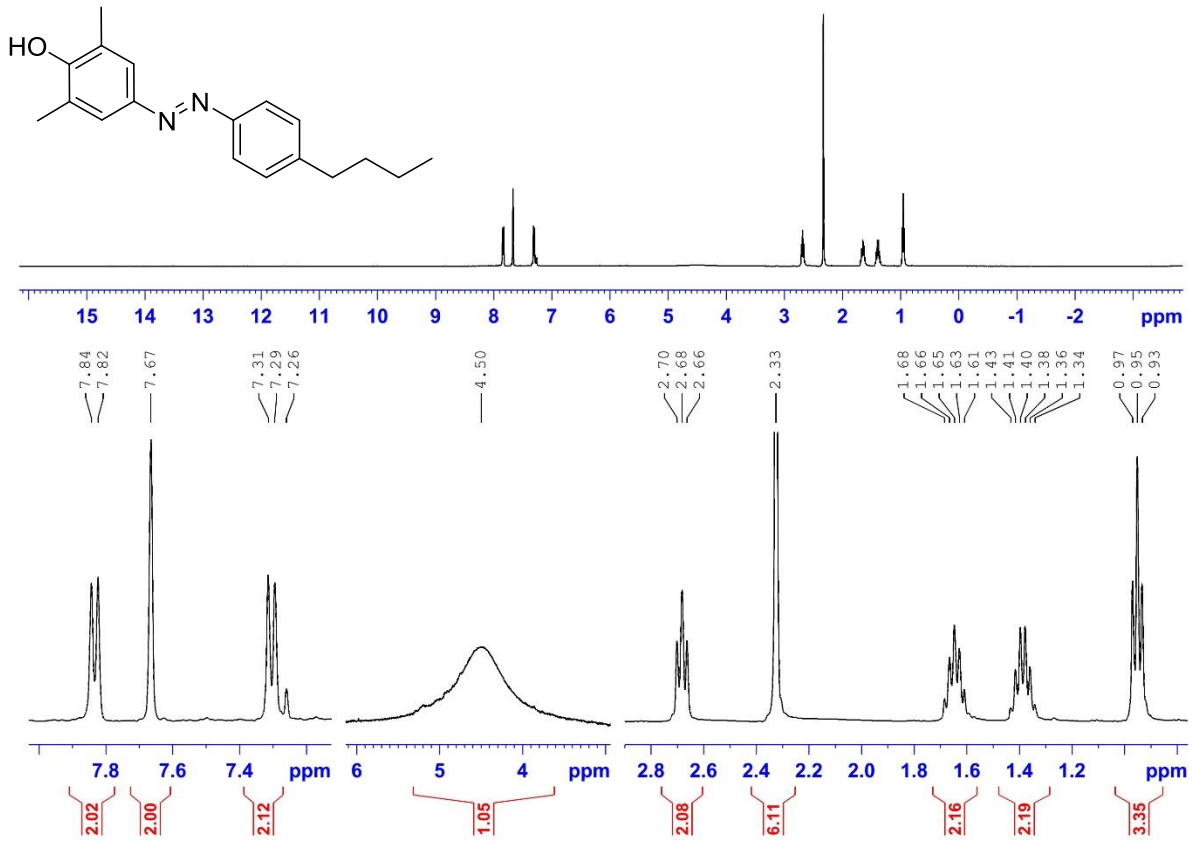
Compound 17, UV-Vis absorption spectra at different stages of the photoisomerization

19. Characterization of compound (**18**)

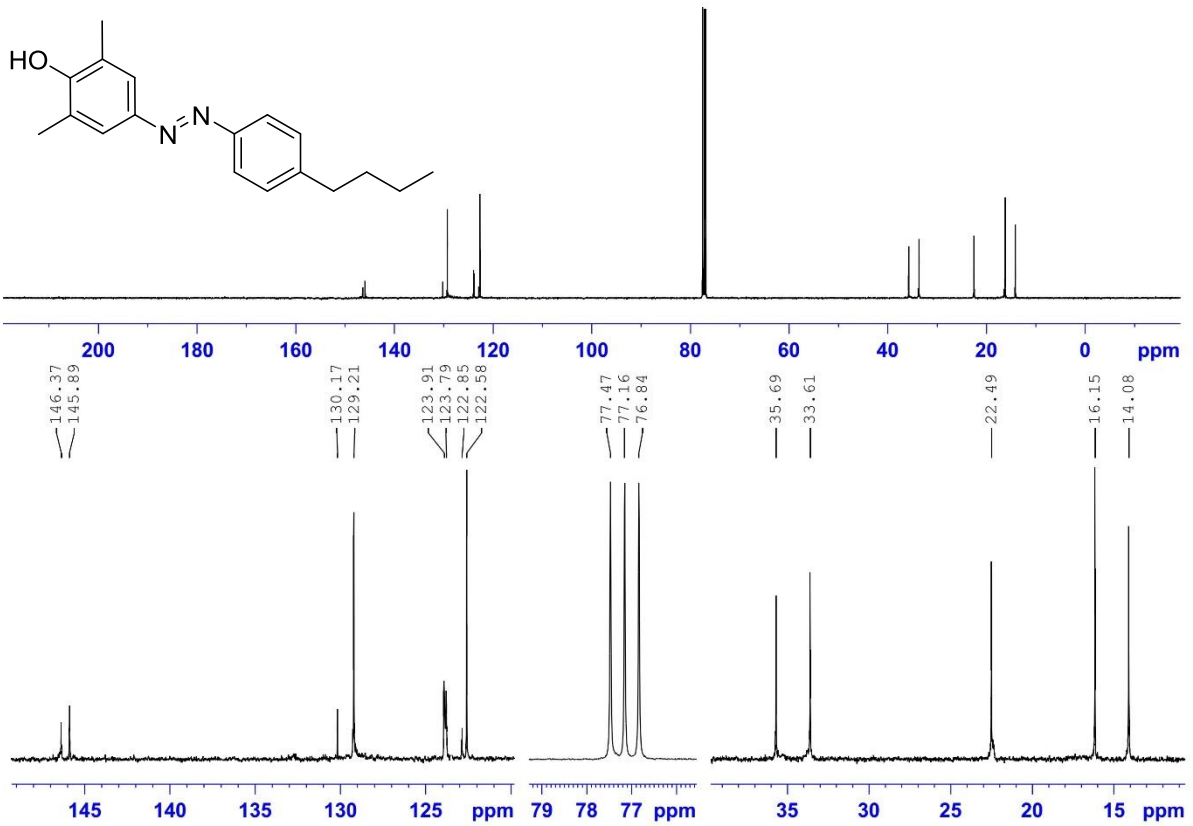
(*E*)-4-((4-butylphenyl)diazenyl)-2,6-dimethylphenol



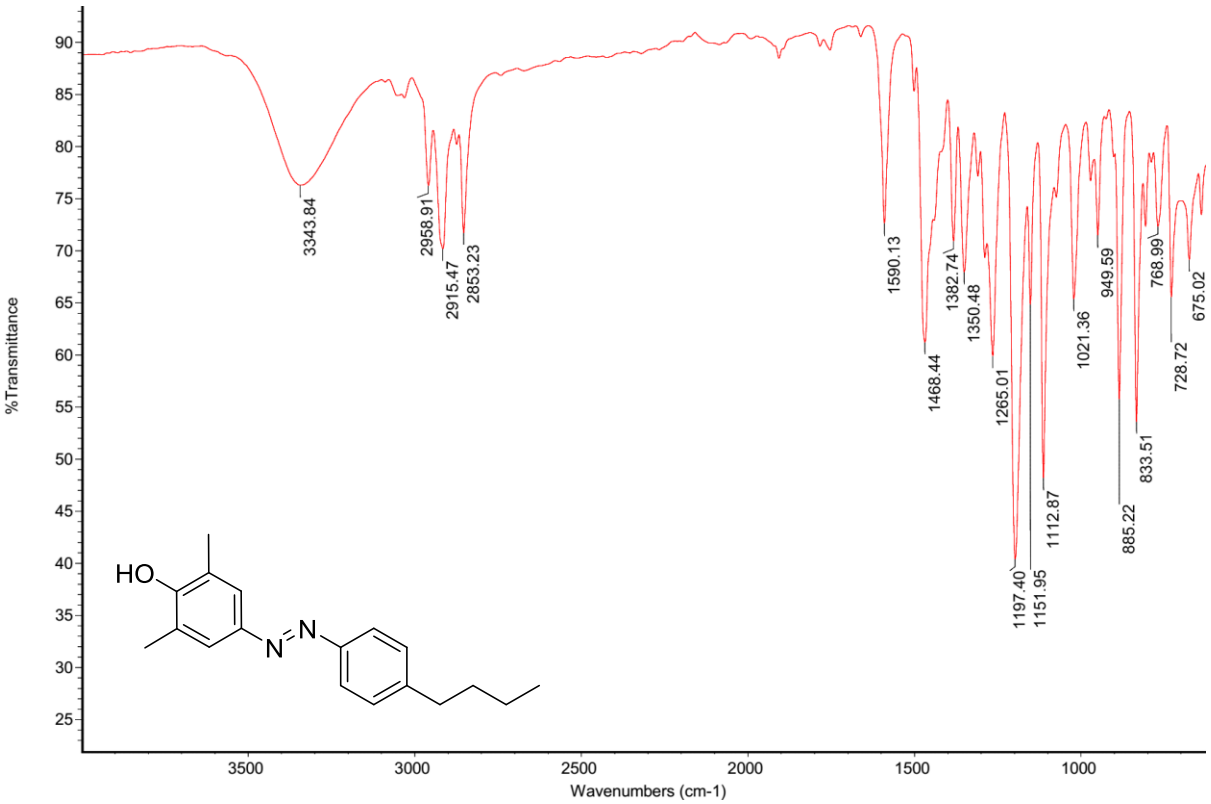
Compound 18, MS (ESI ±)



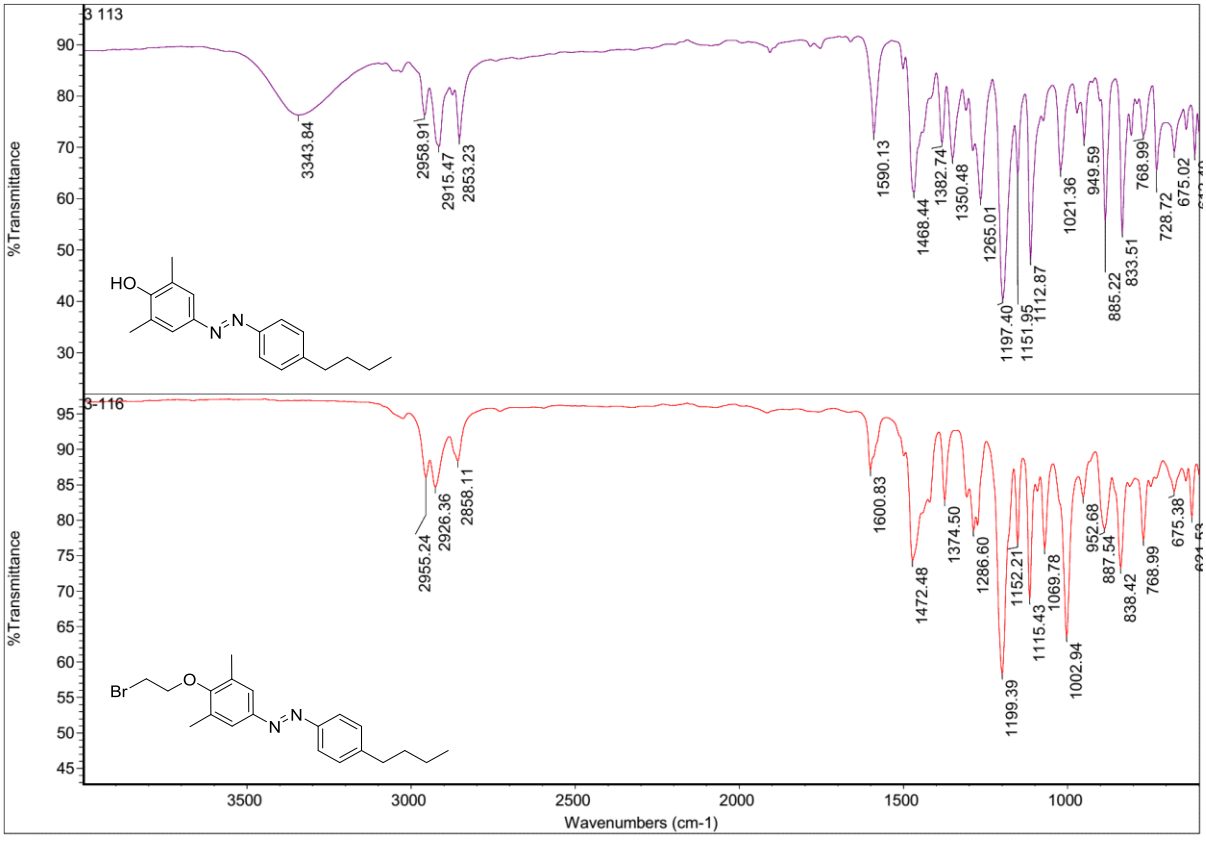
Compound 18, ^{1}H NMR (400 MHz, $CDCl_3$)



Compound 18, ^{13}C NMR (100 MHz, $CDCl_3$)



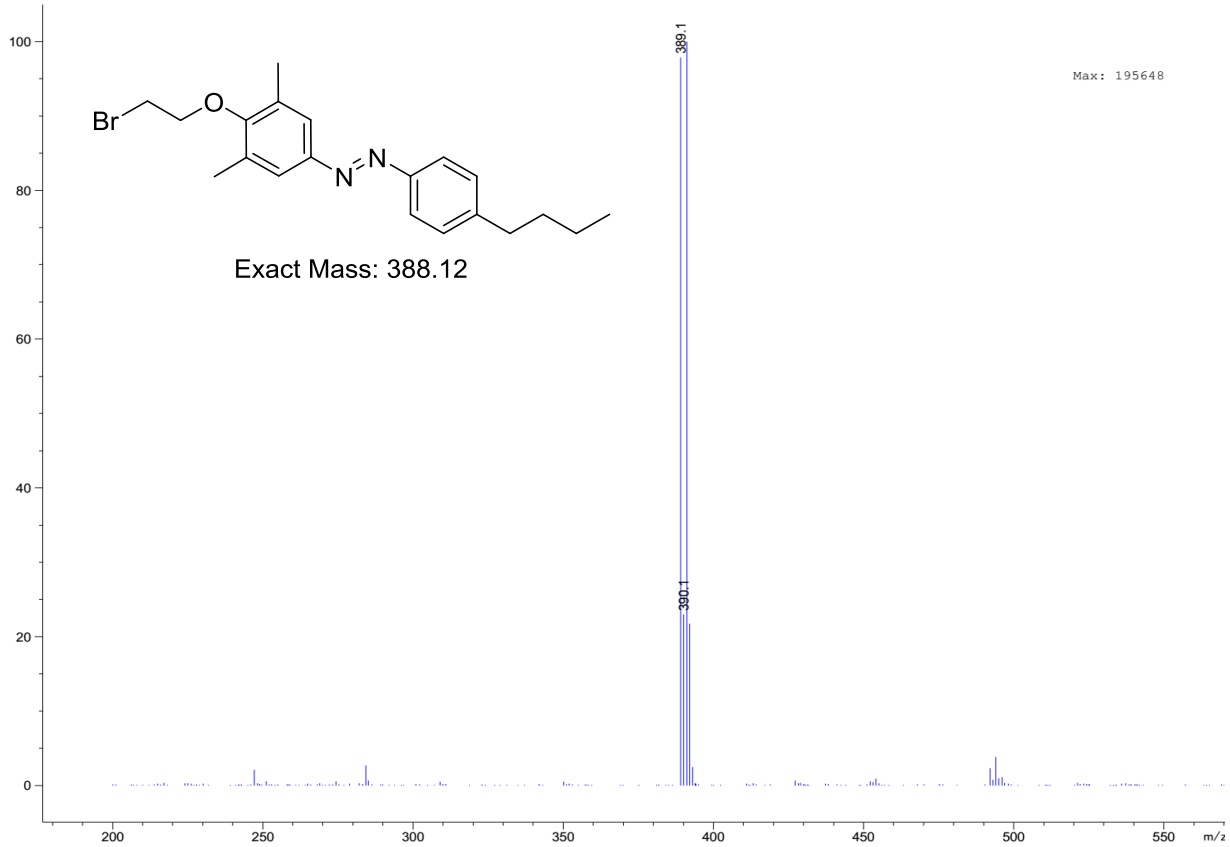
Compound 18, IR transmittance (neat)



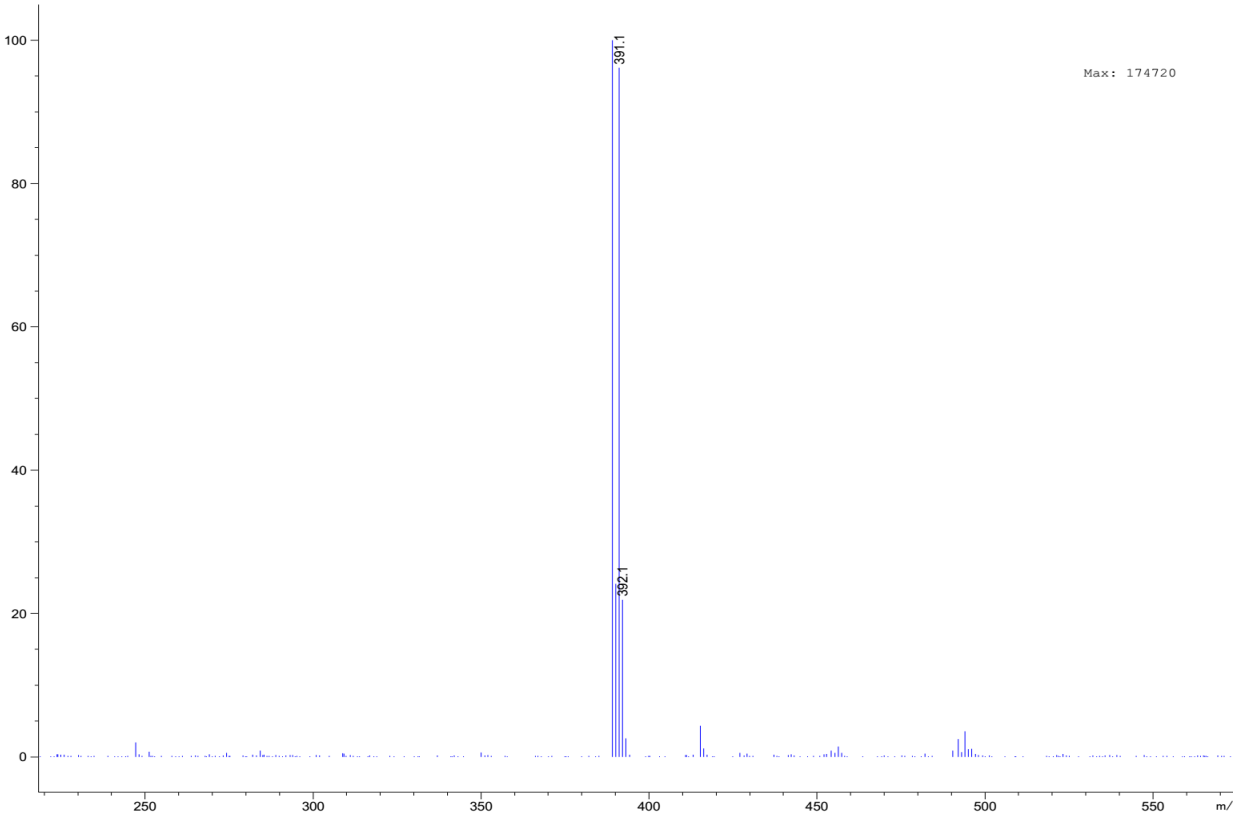
Compound 18, IR transmittance before (in blue) and after alkylation (in red)

20. Characterization of compound (**19**)

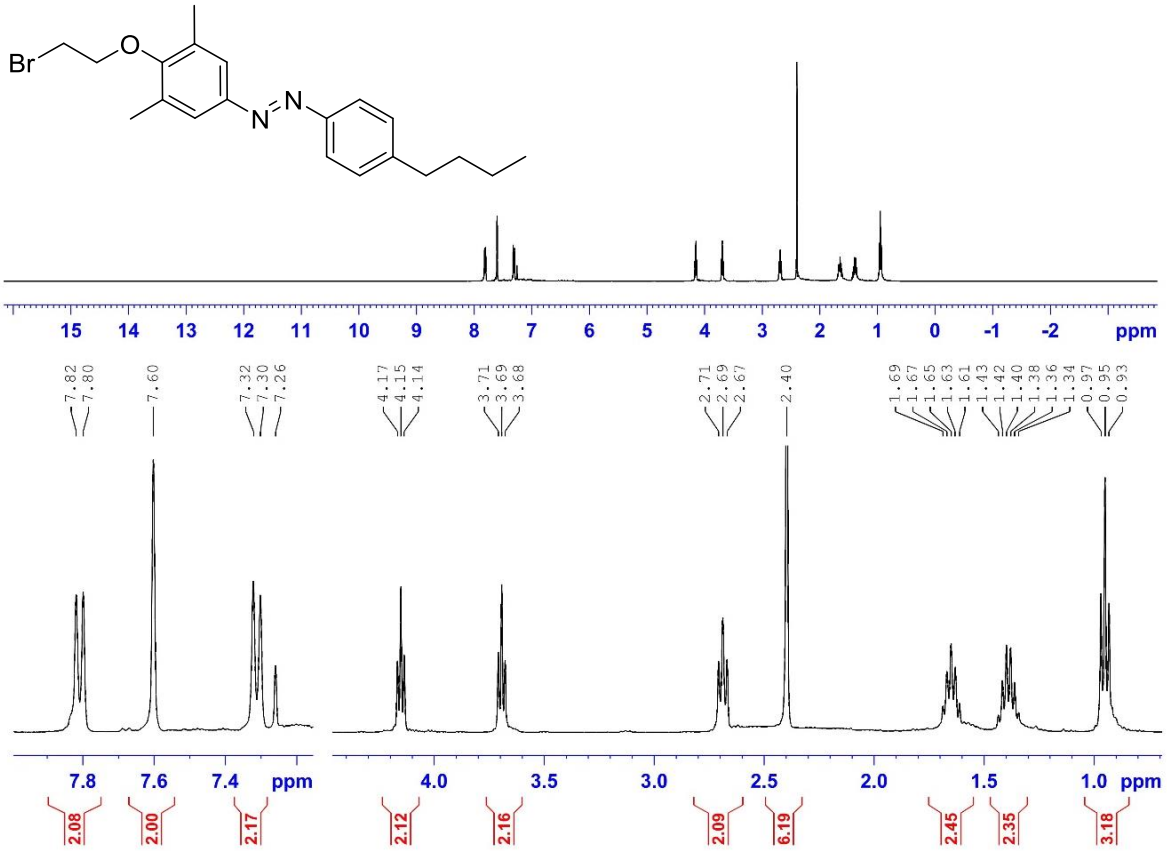
(*E*)-1-(4-(2-bromoethoxy)-3,5-dimethylphenyl)-2-(4-butylphenyl)diazene



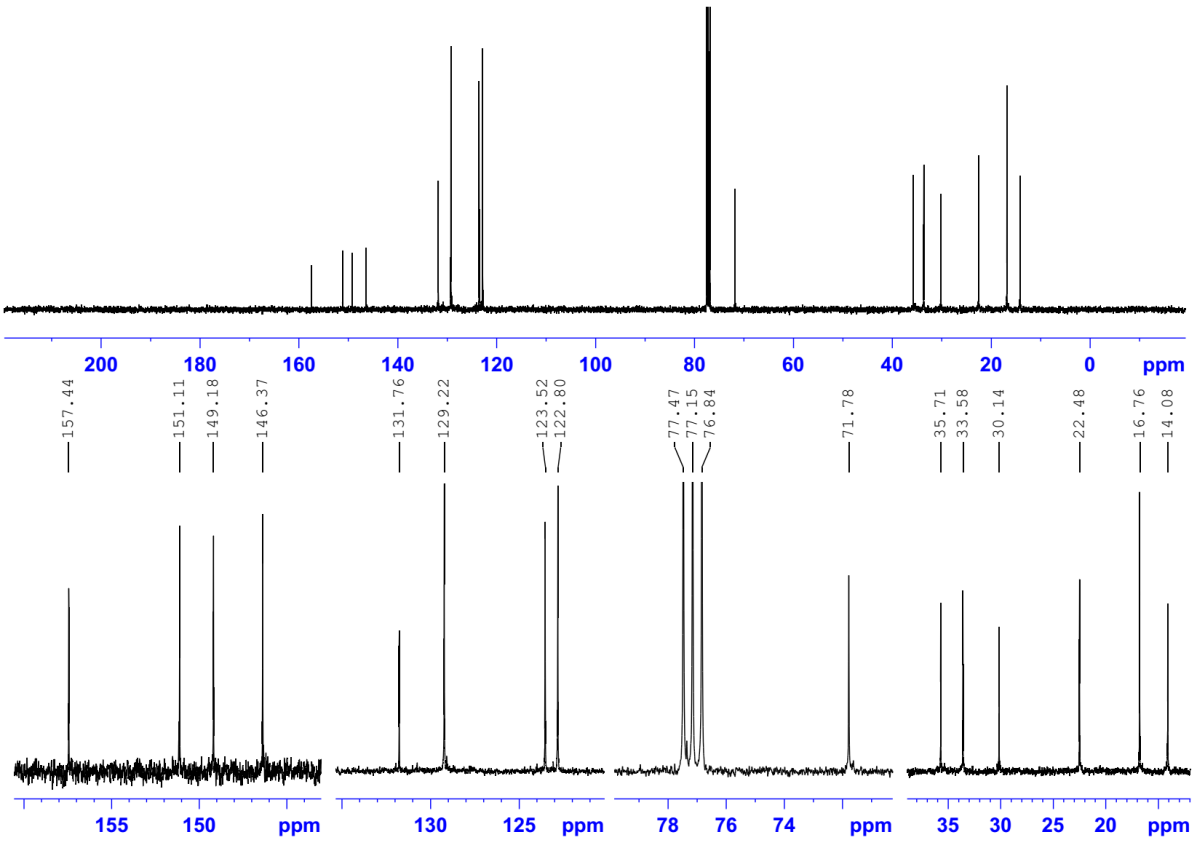
Compound 19, MS (ESI +)



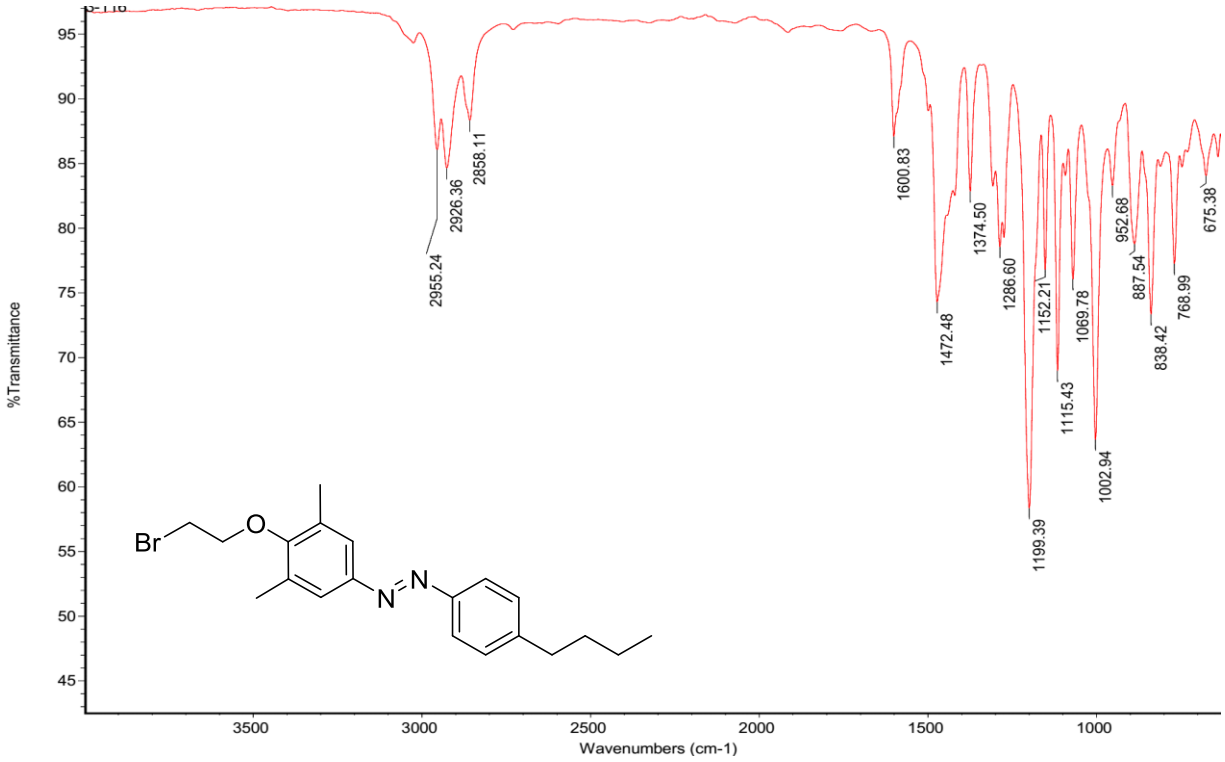
Compound 19, MS (ESI +)



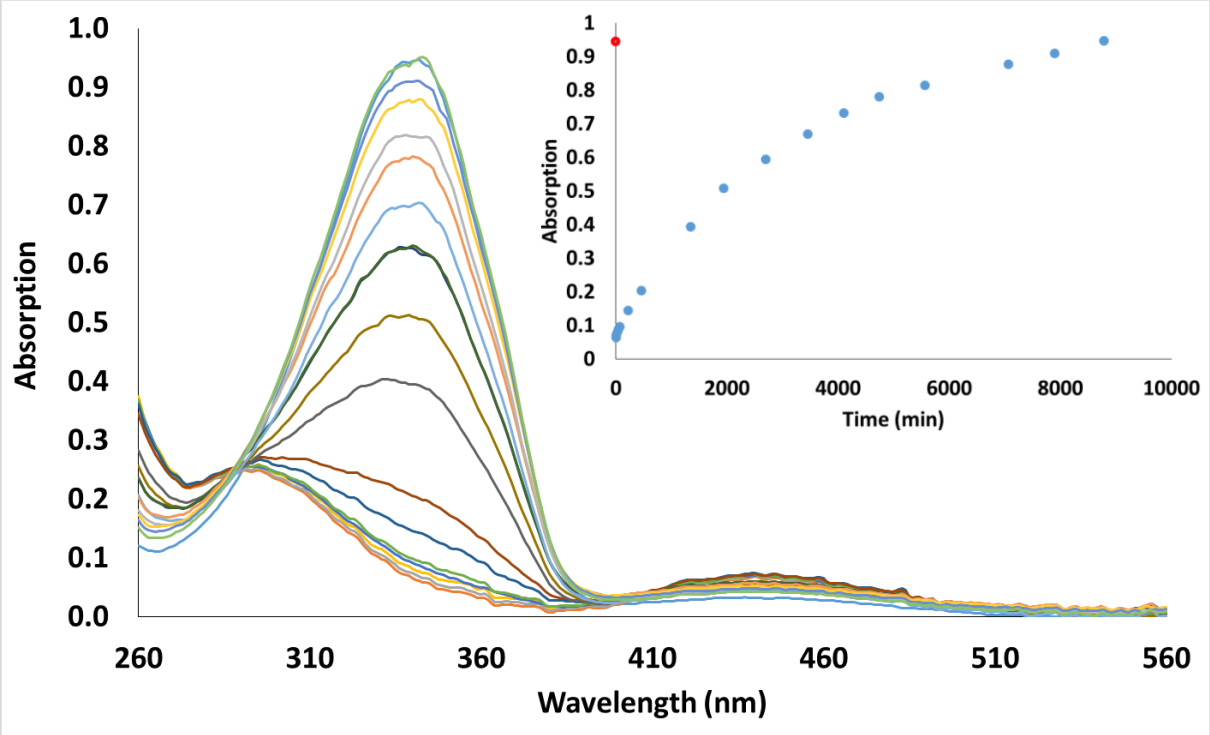
Compound 19, ^{1}H NMR (400 MHz, $CDCl_3$)



Compound 19, ^{13}C NMR (100 MHz, $CDCl_3$)



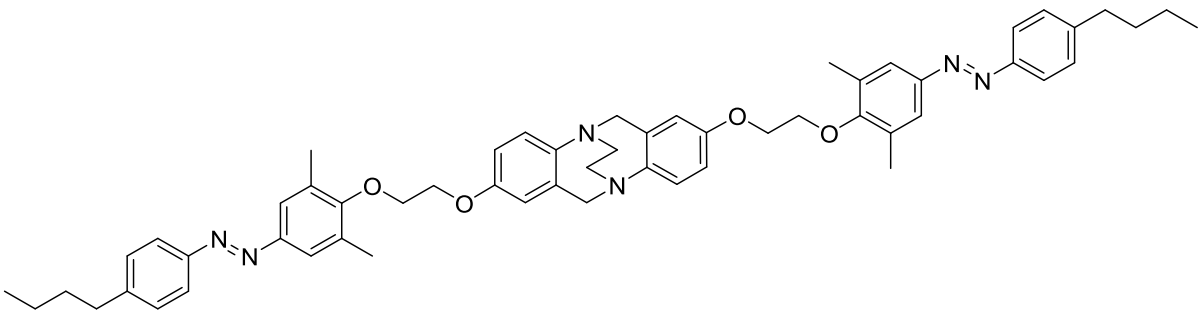
Compound 19, IR transmittance (neat)



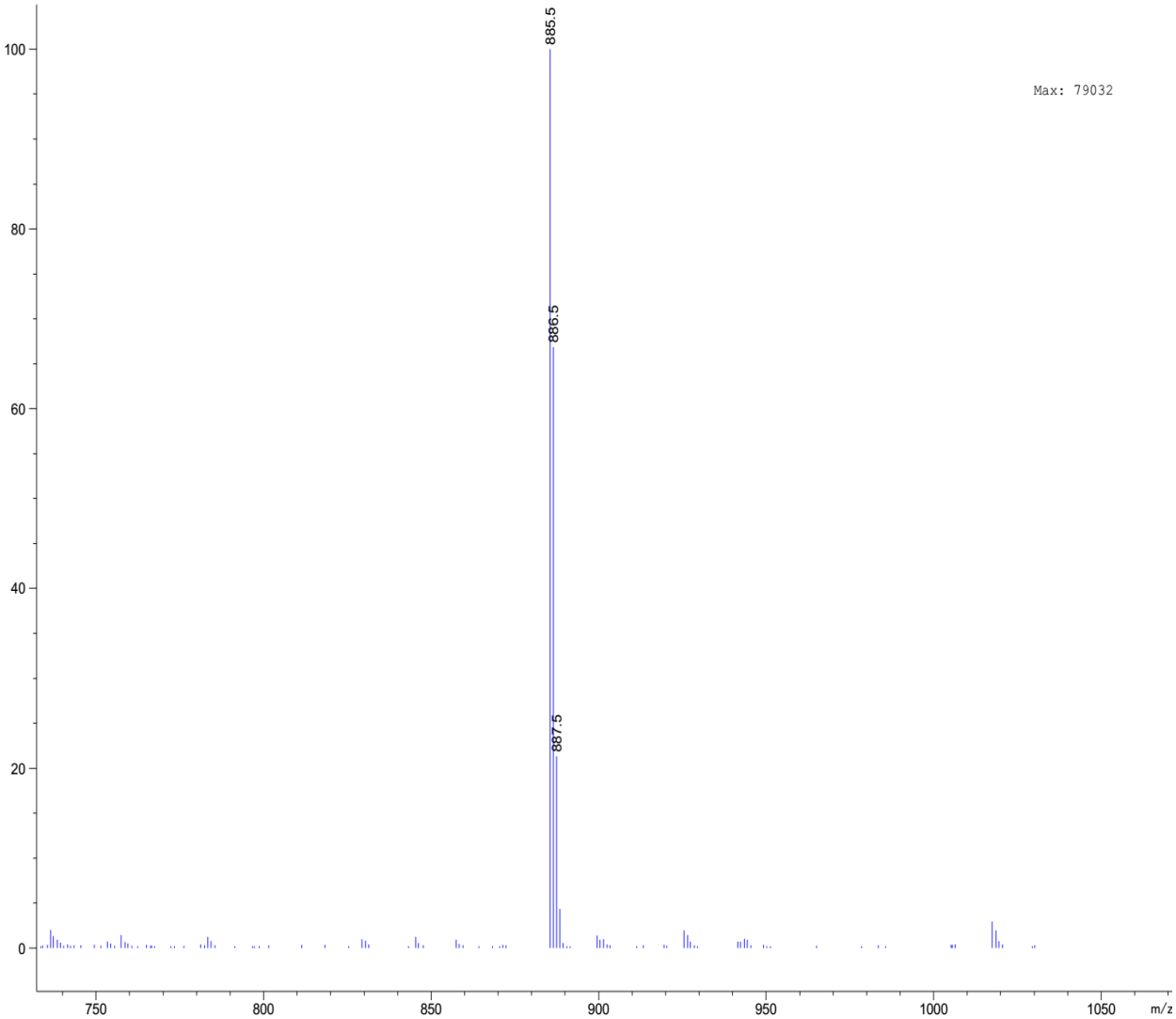
Compound 19, UV-Vis absorption spectra at different stages of photoisomerization

21. Characterization of compound (**20**)

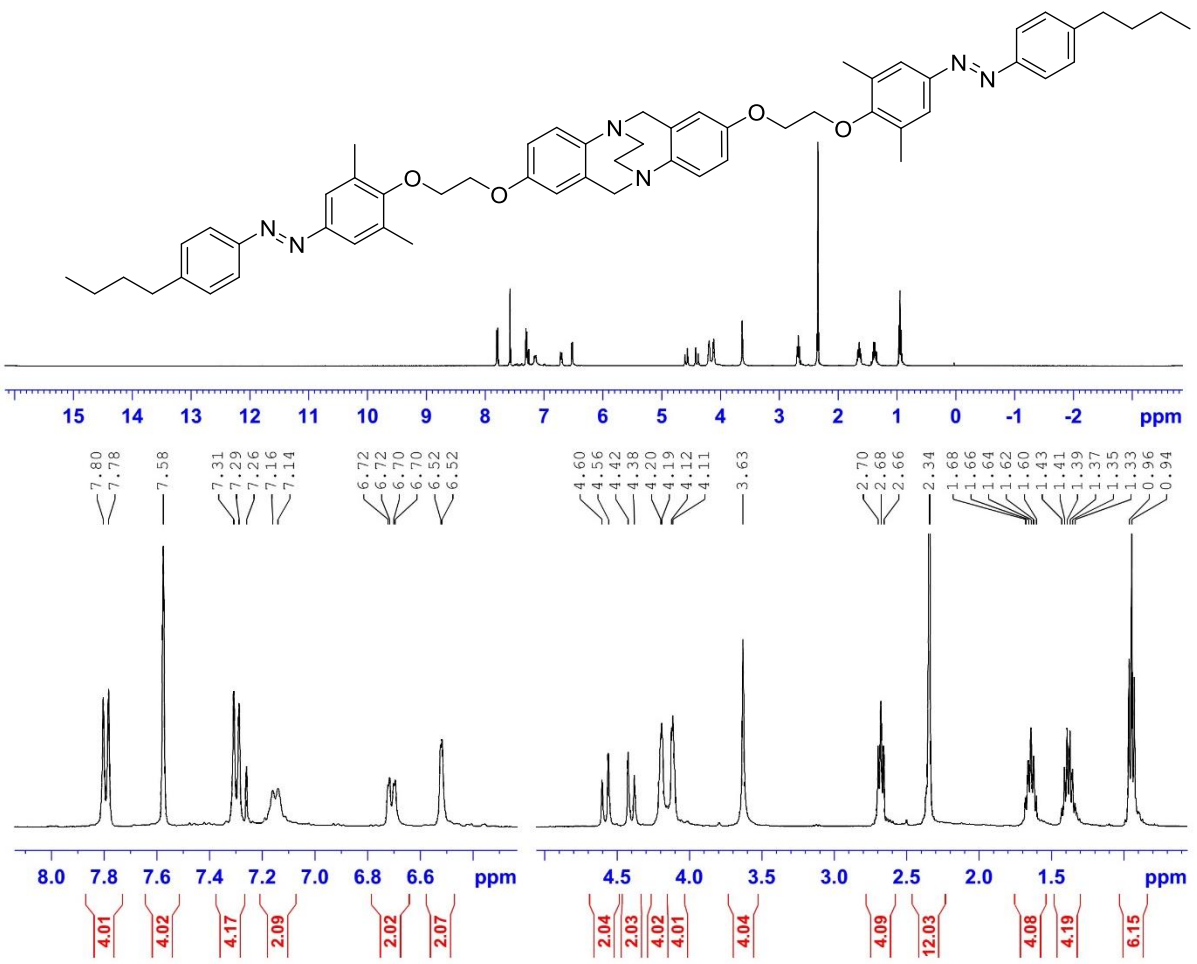
2,8-bis(2-(4-((*E*)-(4-butylphenyl)diazenyl)-2,6-dimethylphenoxy)ethoxy)-6*H*,12*H*-5,11-ethanodibenzo[*b,f*][1,5]diazocine



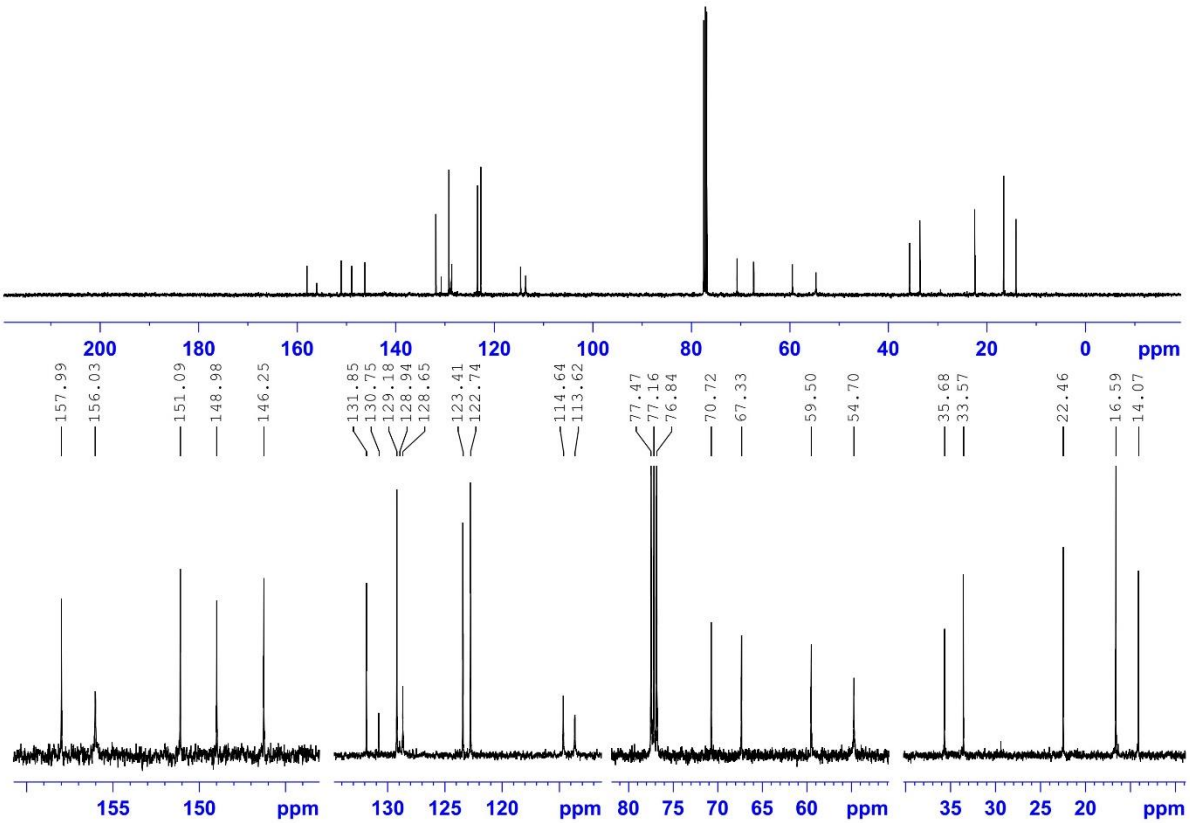
Exact Mass: 884.50



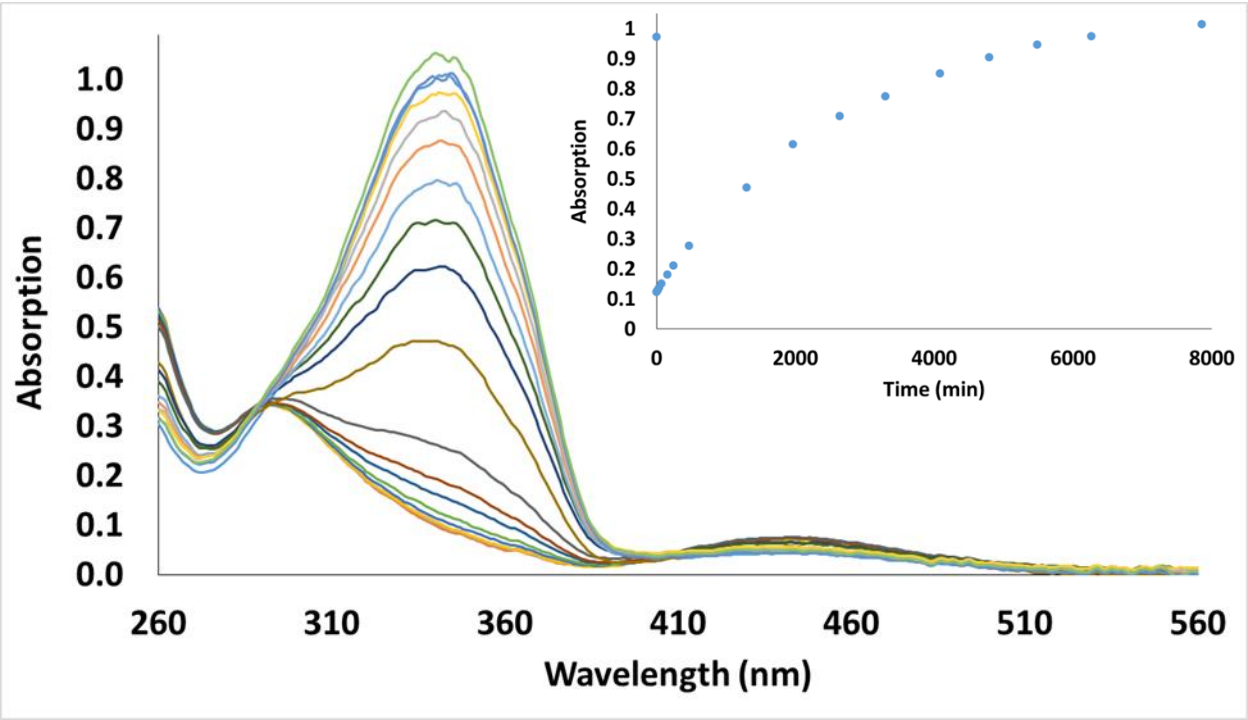
Compound 20, MS (ESI +)



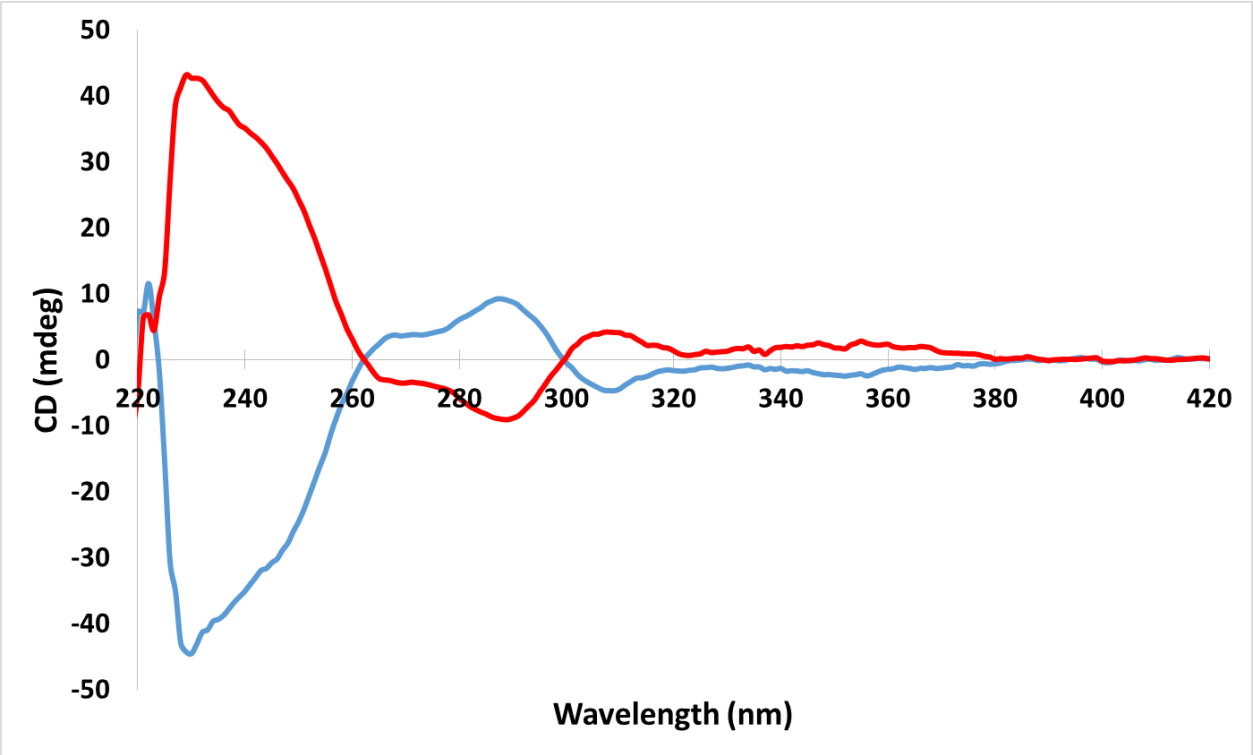
Compound 20, ^{1}H NMR (400 MHz, $CDCl_3$)



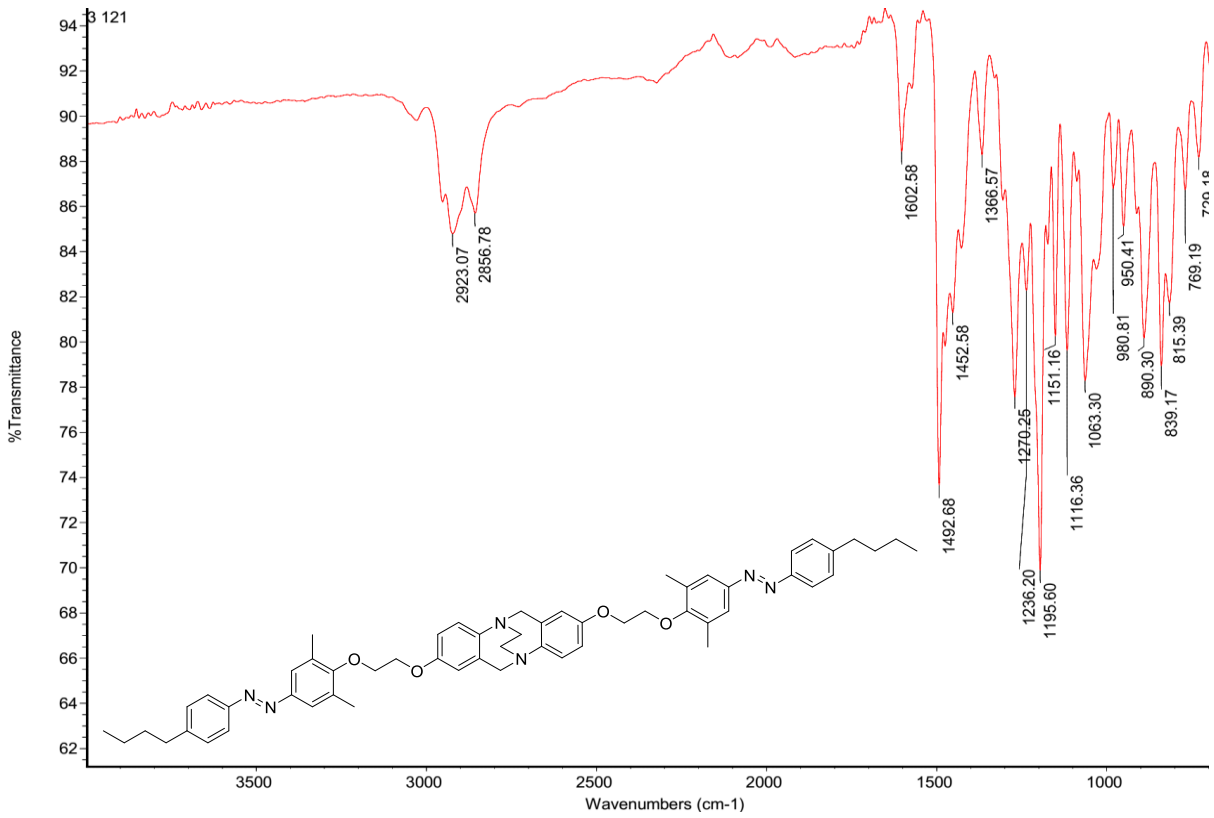
Compound 20, ^{13}C NMR (100 MHz, $CDCl_3$)



Compound 20, UV-Vis absorption spectra at different stages of photoisomerization



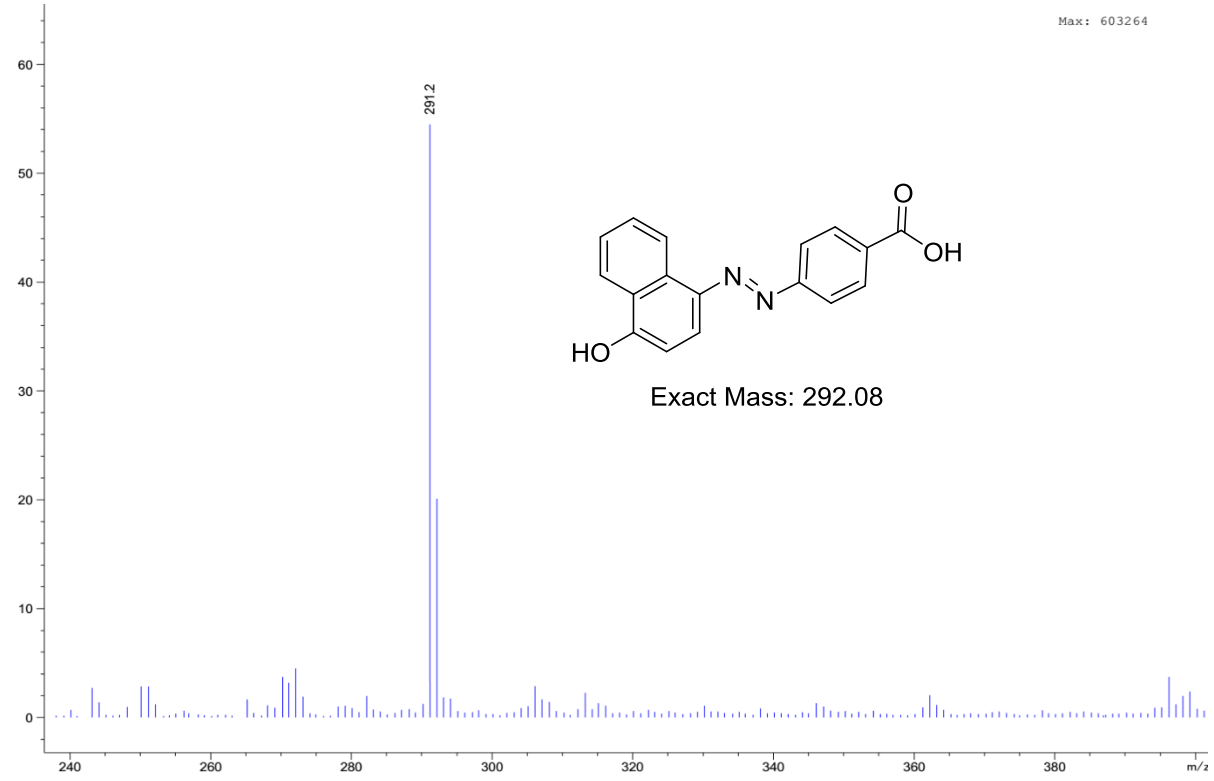
CD spectra, (+)-(*R*,*R*)-20 and (–)-(*S*,*S*)-20 in DCM



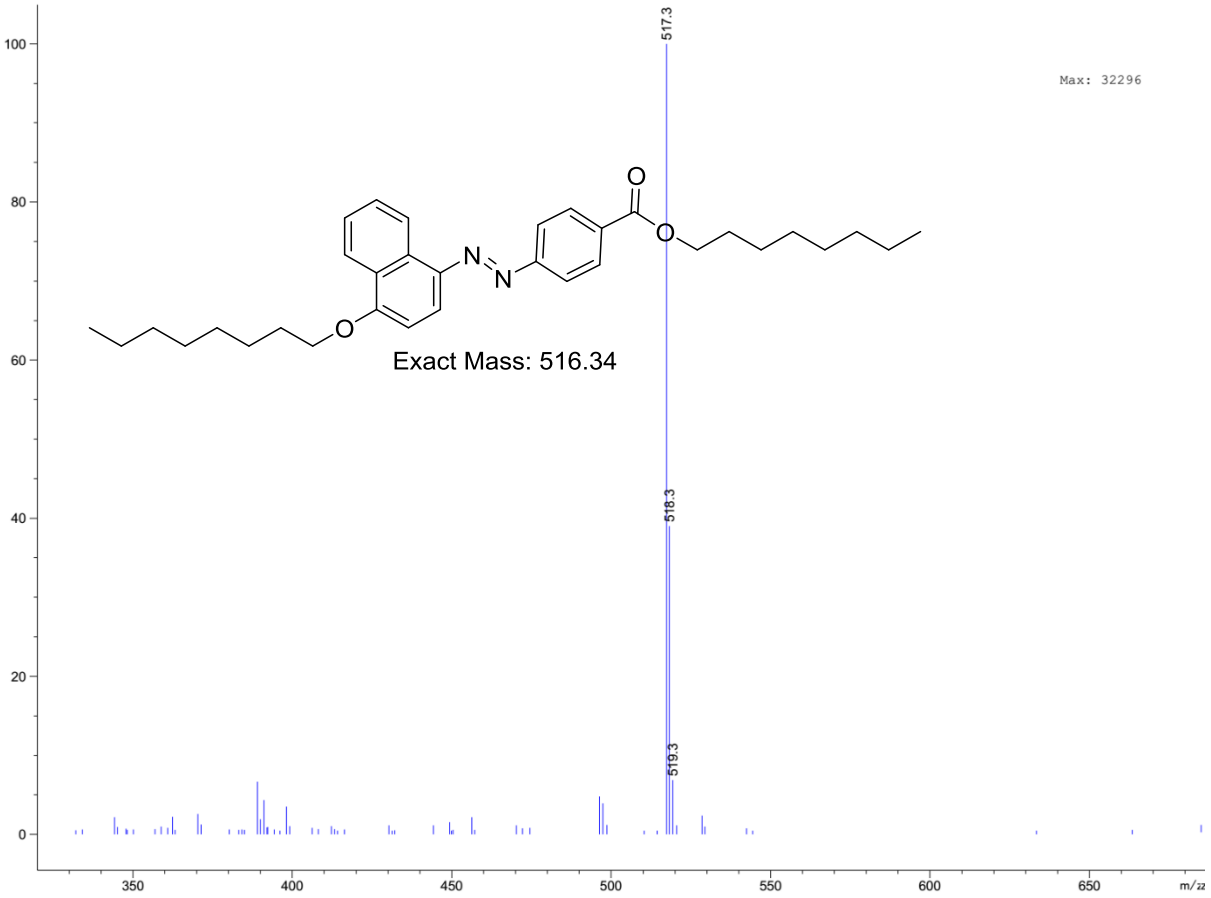
Compound 20, IR transmittance (neat)

22. Characterization of compound (**21**)

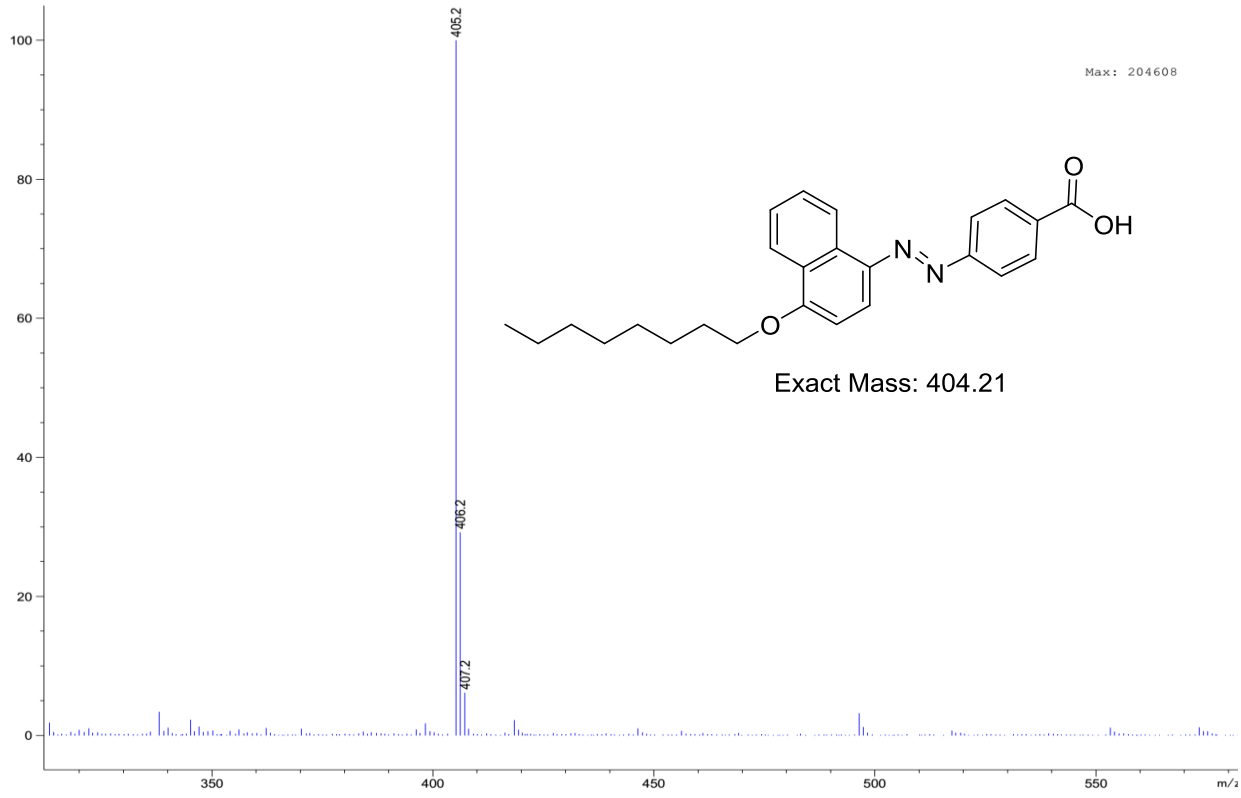
(*E*)-4-((4-(octyloxy)naphthalen-1-yl)diazenyl)benzoic acid



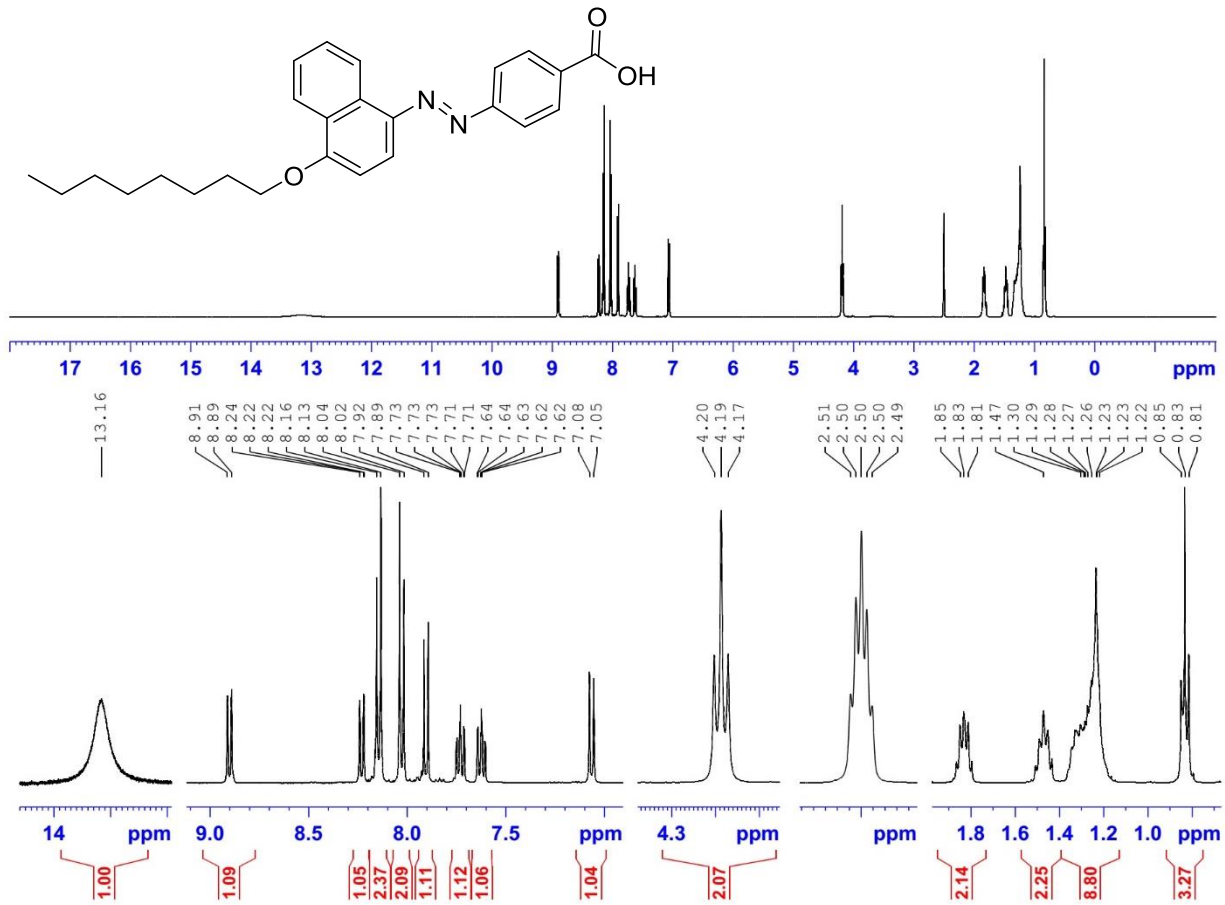
Crude 21 (before octylation), MS (ESI –)



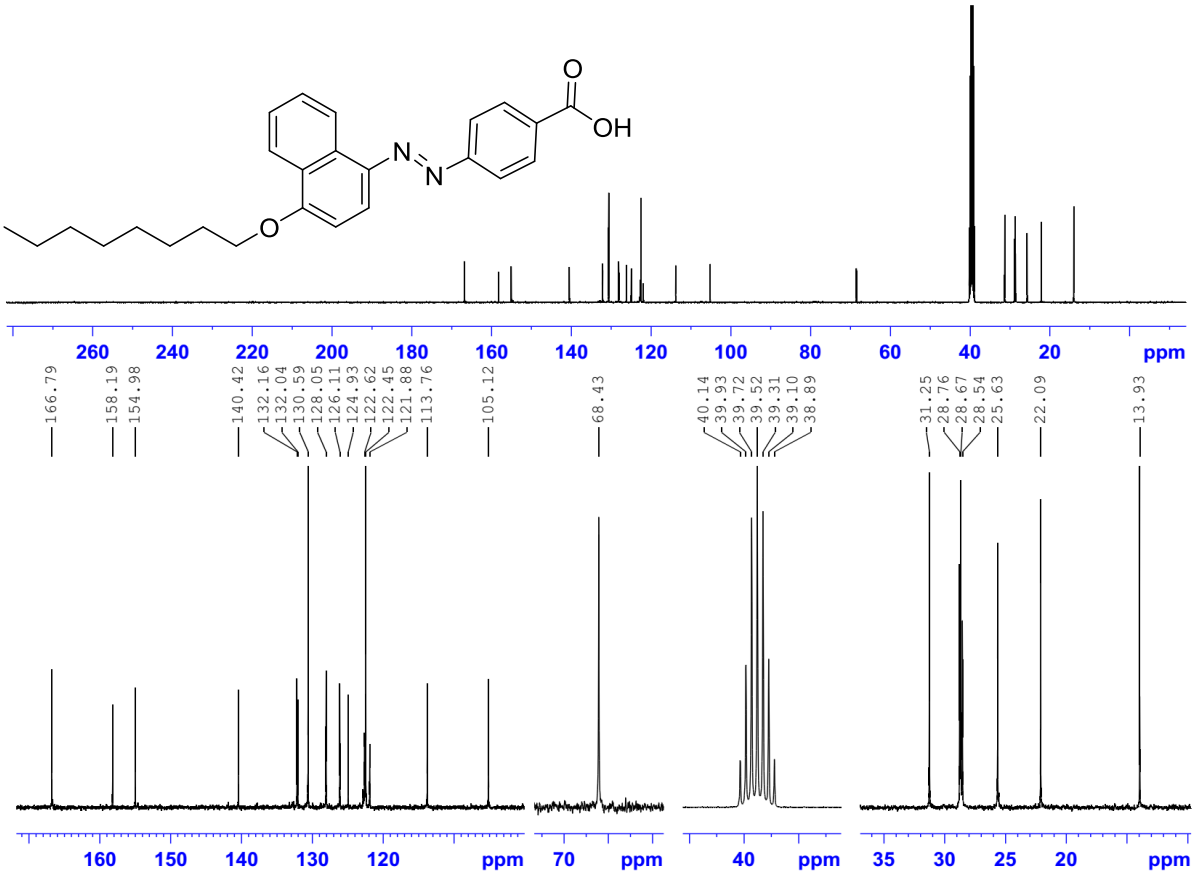
Crude 21 (after octylation), MS (ESI +)



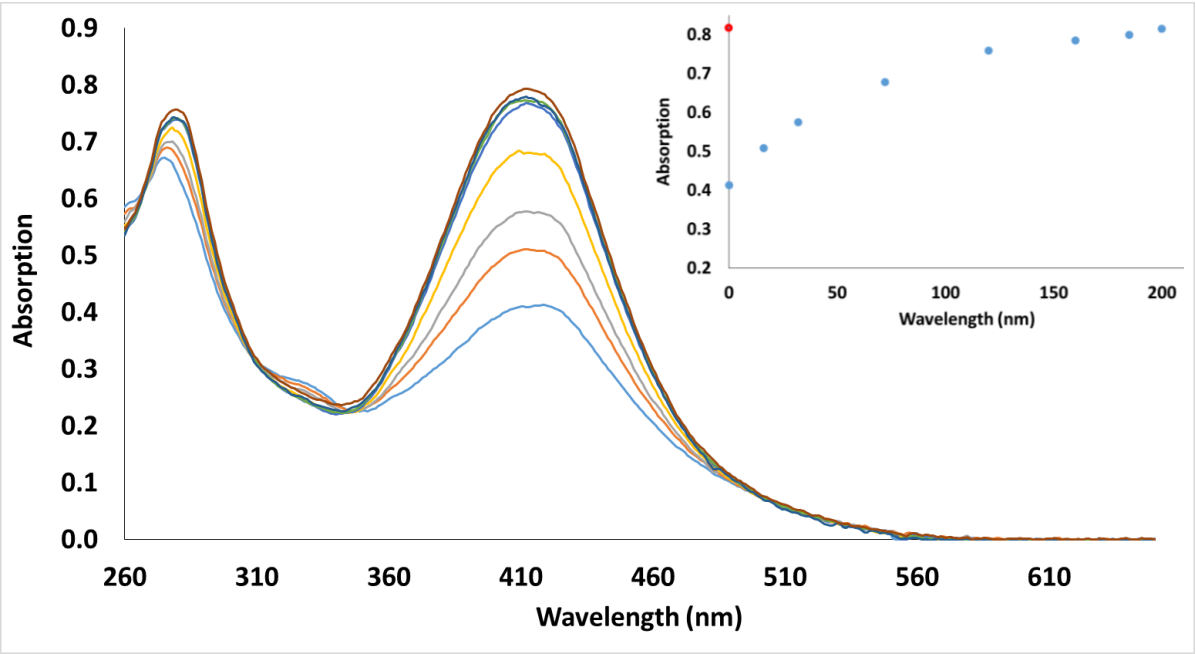
Compound 21 (after hydrolysis), MS (ESI +)



Compound 21, ^{1}H NMR (600 MHz, DMSO-d_6)



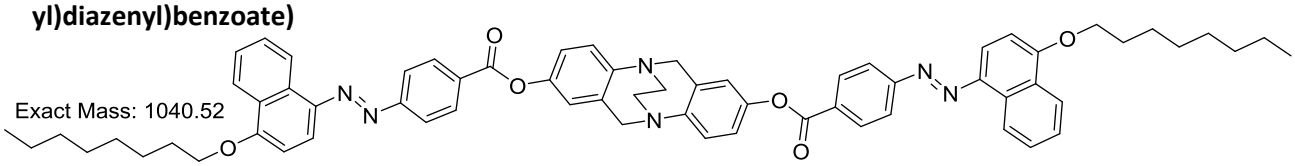
Compound 21, ^{13}C NMR (150 MHz, DMSO-d_6)

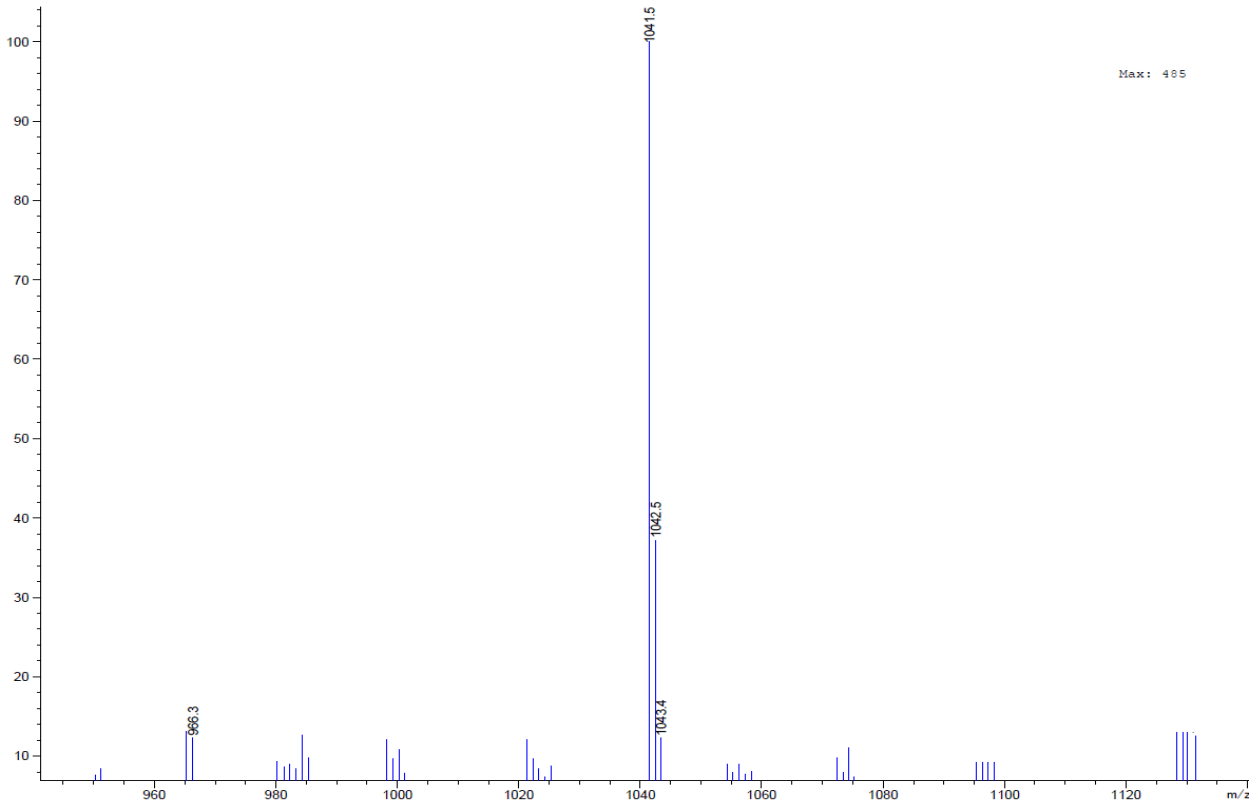


Compound 21, UV-Vis absorption spectra at different stages of photoisomerization

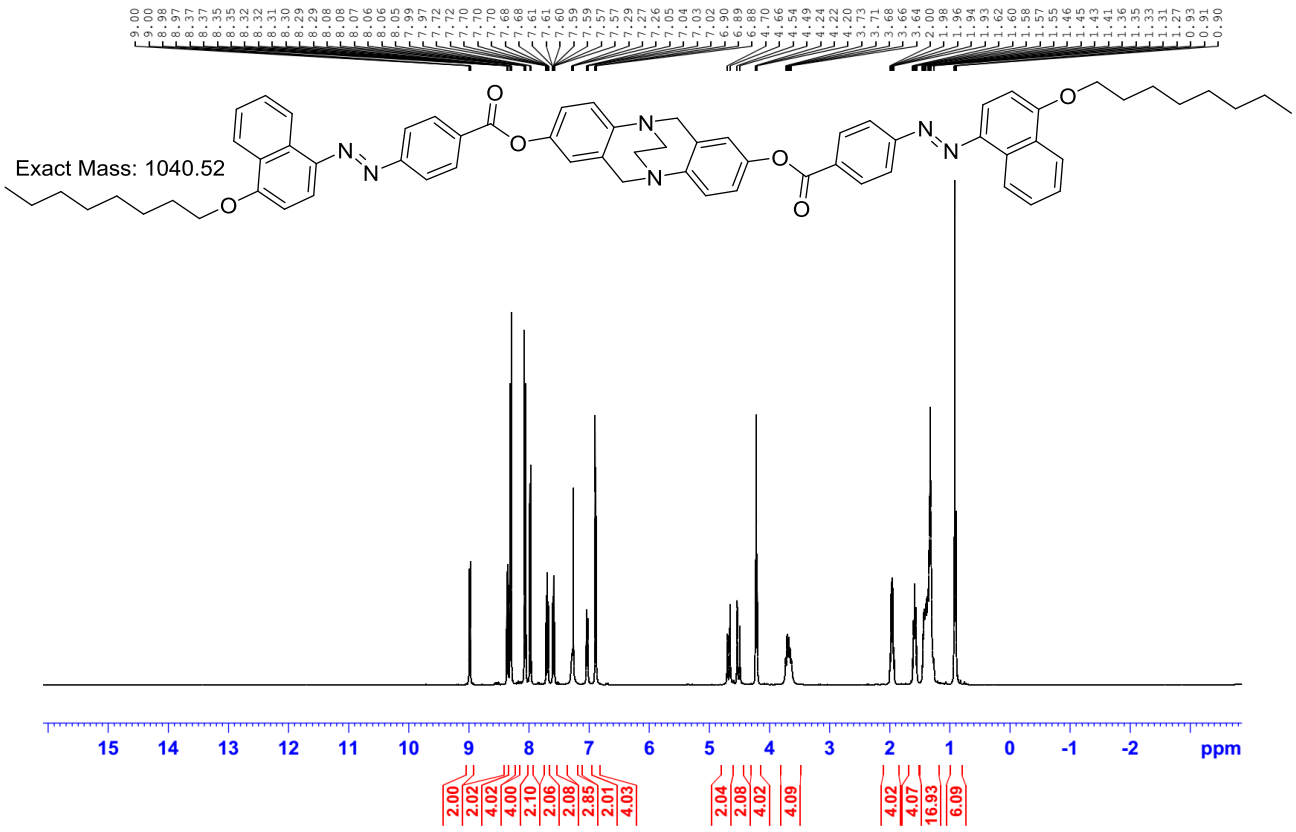
23. Characterization of compound (**22**)

6*H*,12*H*-5,11-ethanodibenzo[*b*,*f*][1,5]diazocine-2,8-diyl bis(4-((*E*)-(4-(octyloxy)naphthalen-1-yl)diazenyl)benzoate)

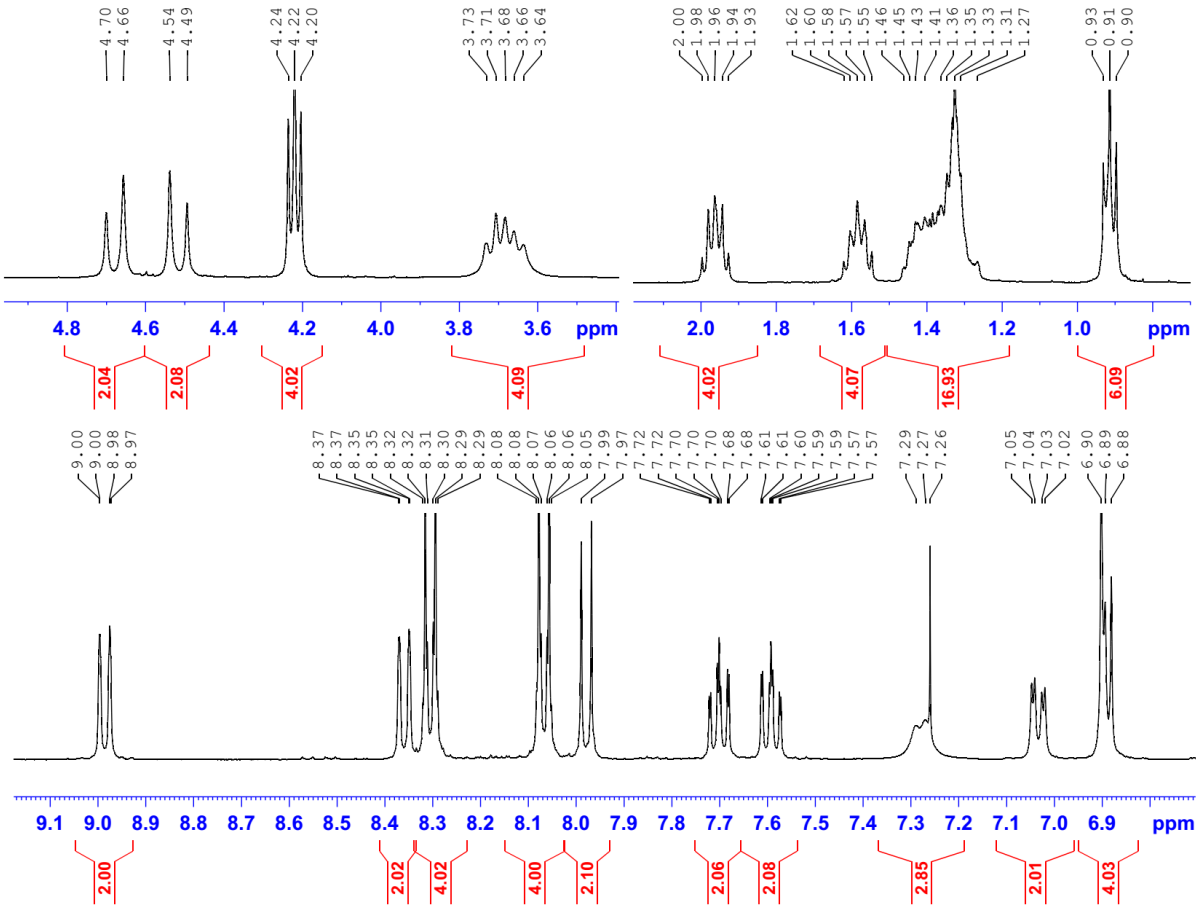




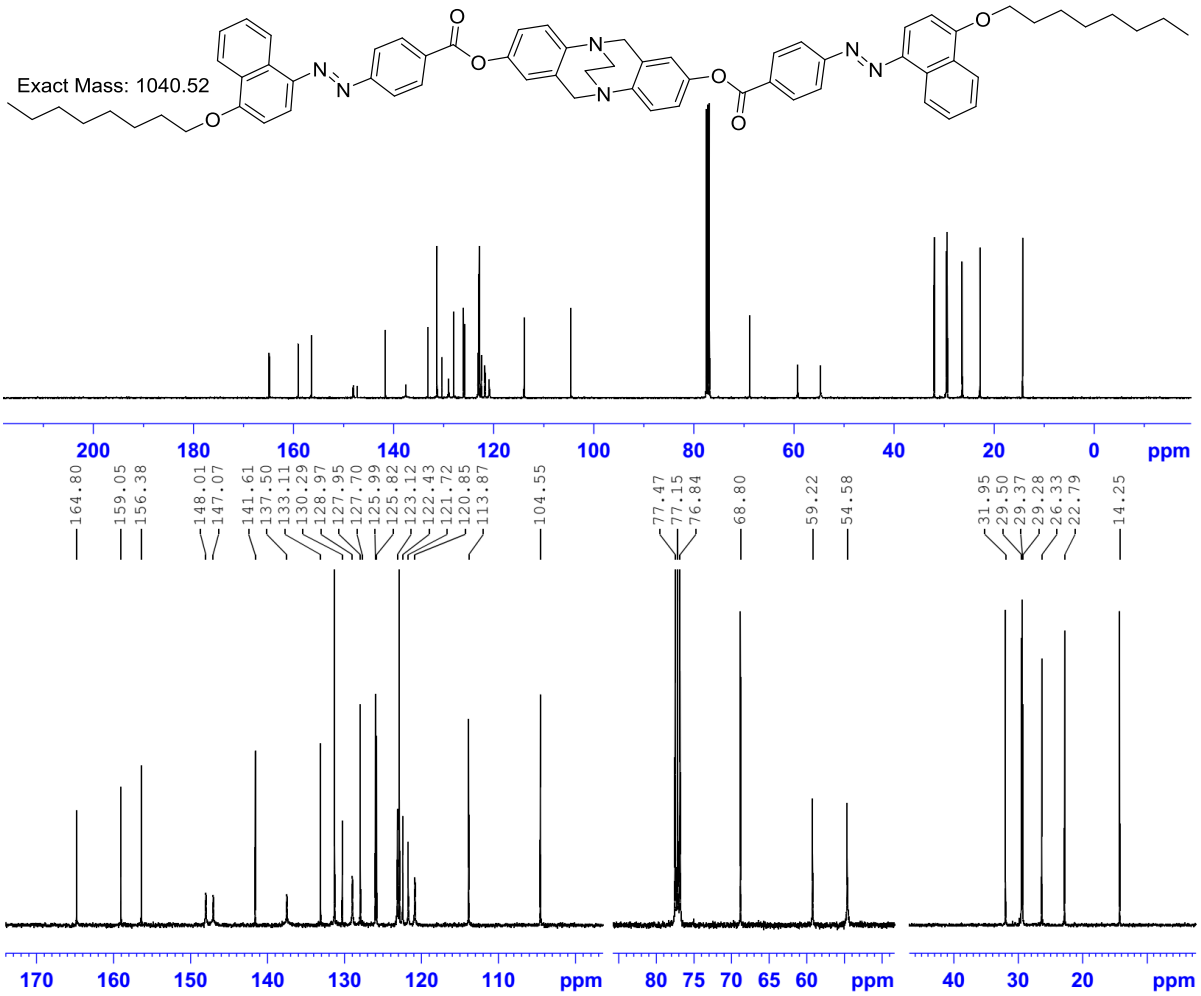
Compound 22, MS (ESI +)



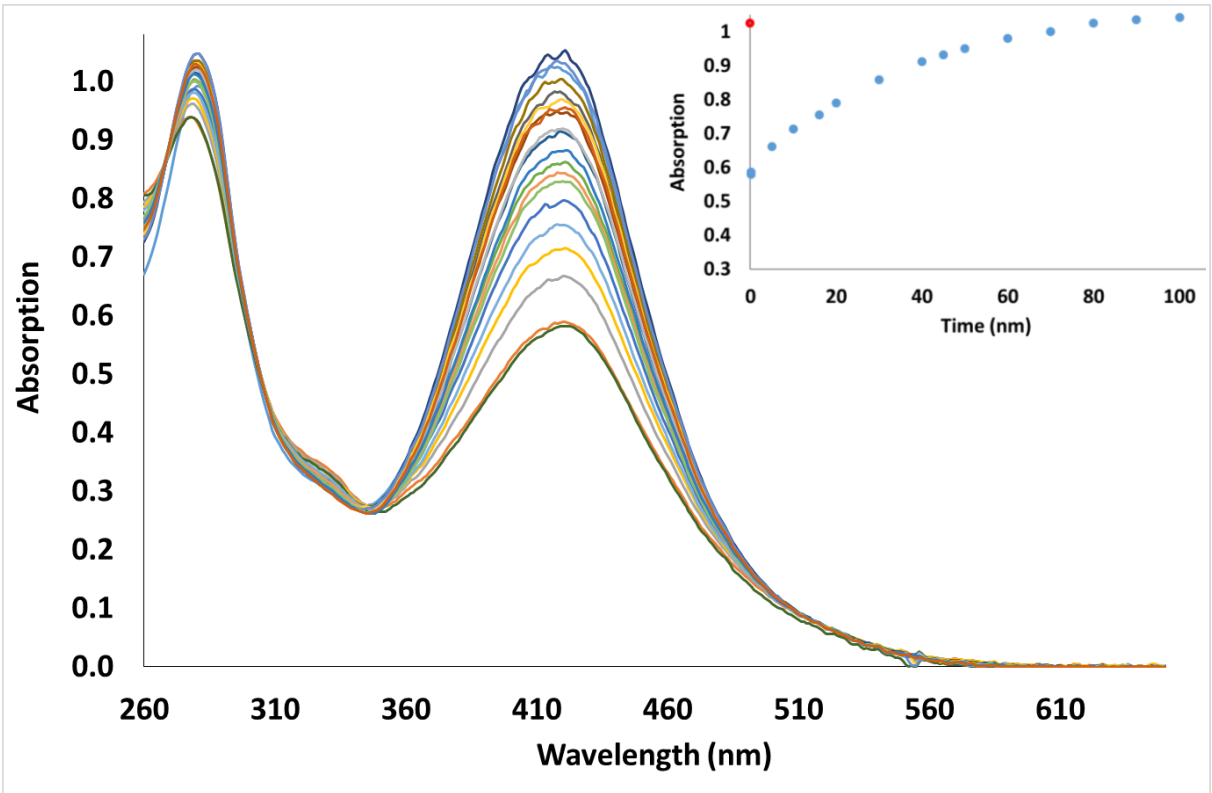
Compound 22, ^{1}H NMR (600 MHz, $CDCl_3$)



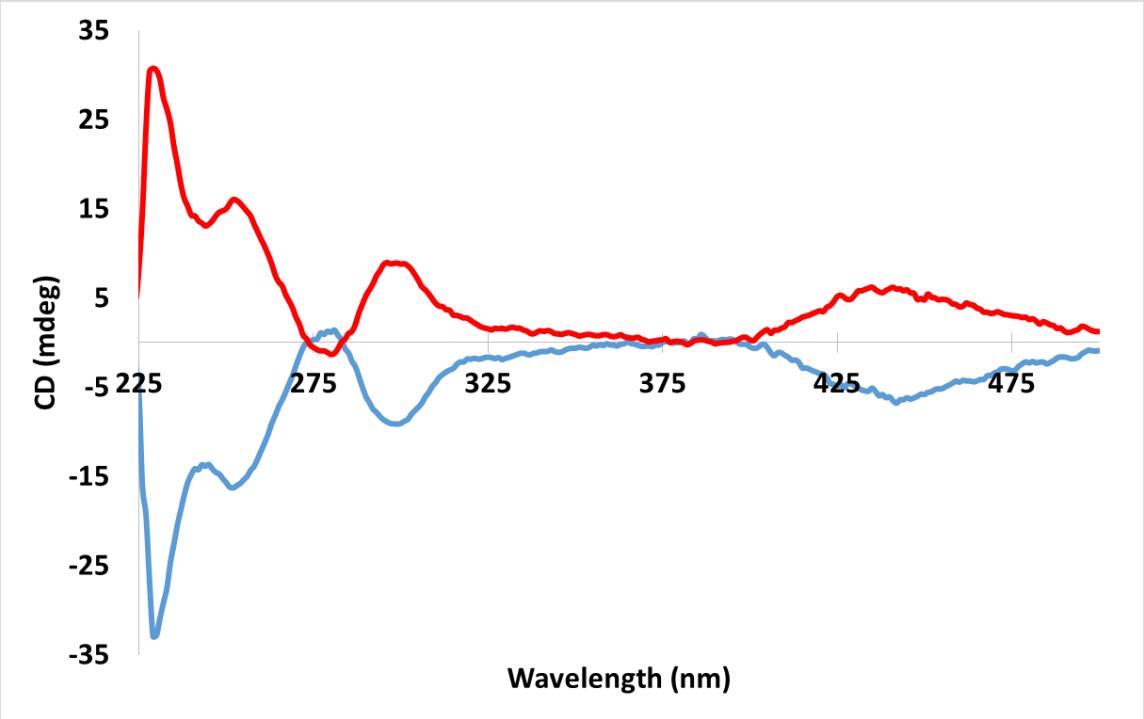
Compound 22, ^{1}H NMR (600 MHz, $CDCl_3$)



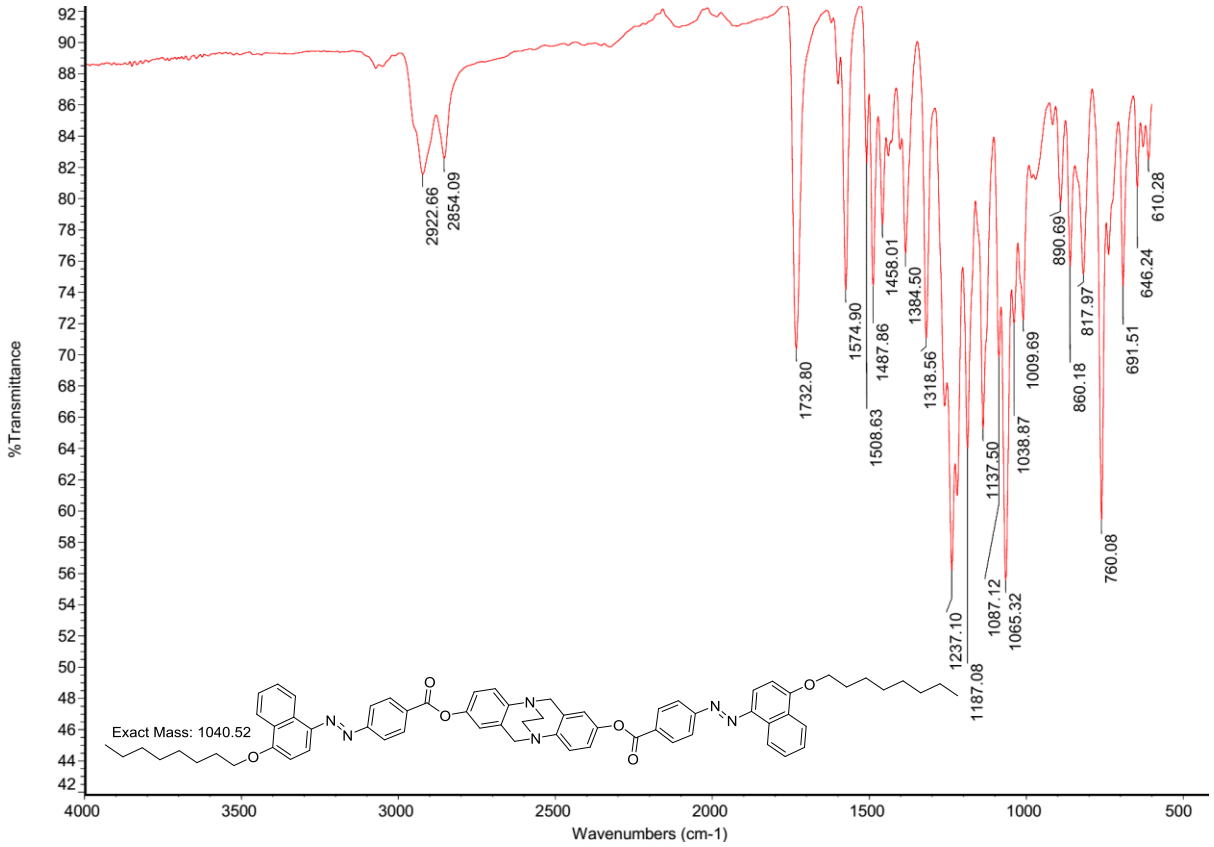
Compound 22, ^{13}C NMR (150 MHz, $CDCl_3$)



Compound 22, UV-Vis absorption spectra at different stages of photoisomerization



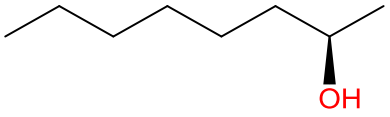
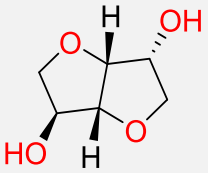
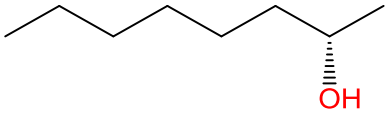
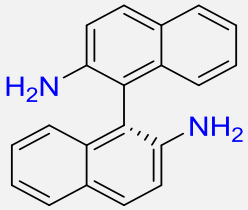
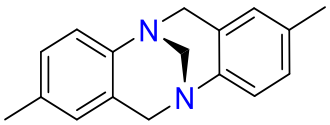
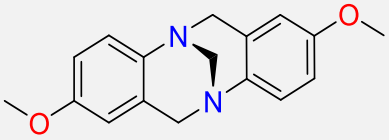
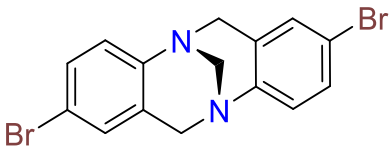
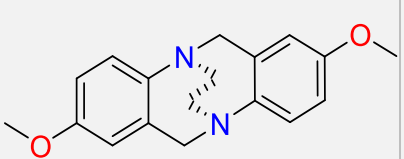
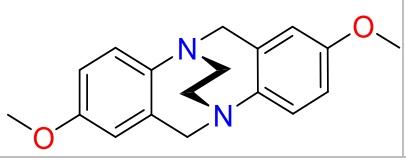
CD spectra, (+)-(*R*,*R*)-22 and (–)-(*S*,*S*)-22 in DCM

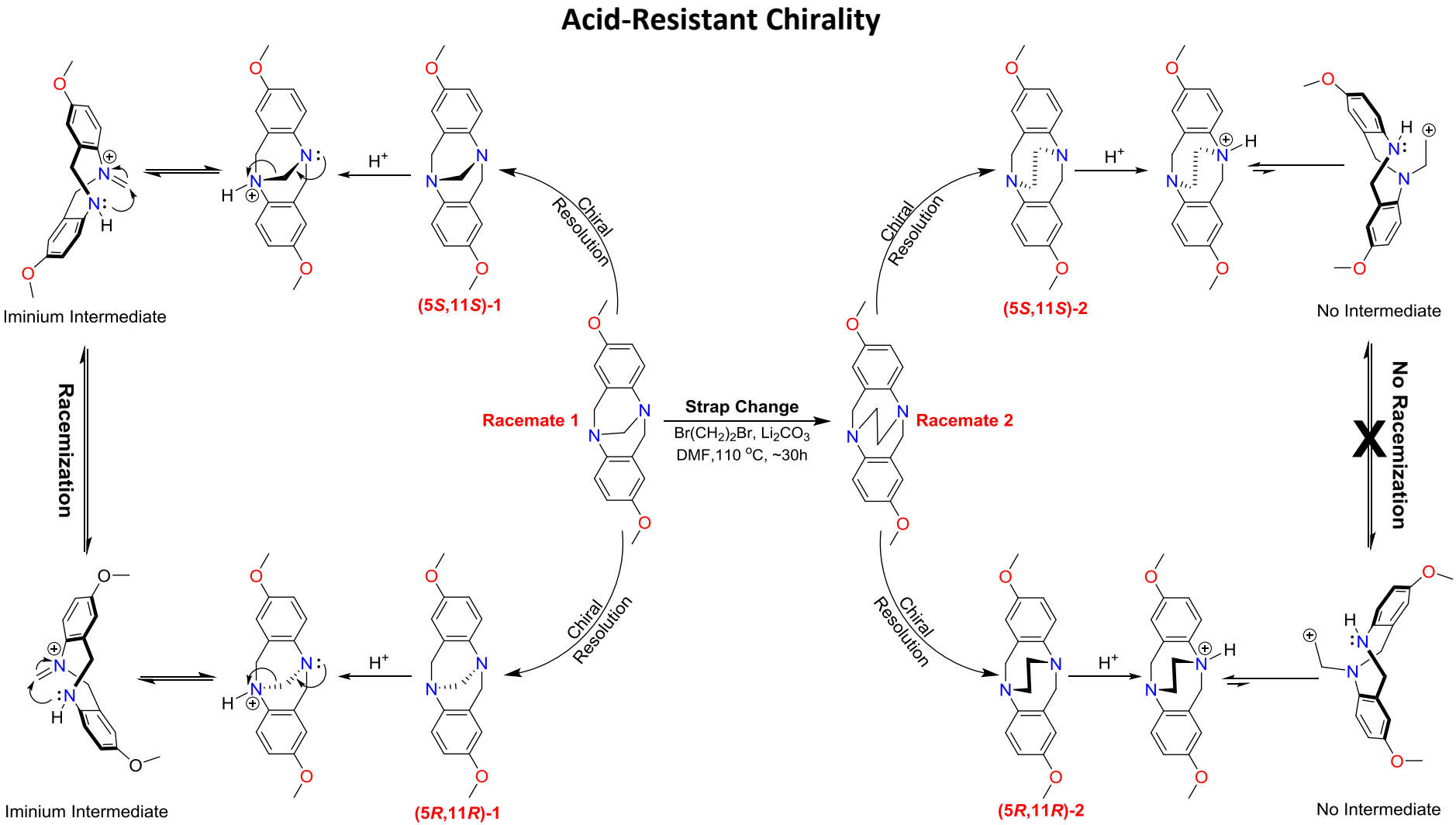


Compound 22, IR transmittance (neat)

Chiral Cores

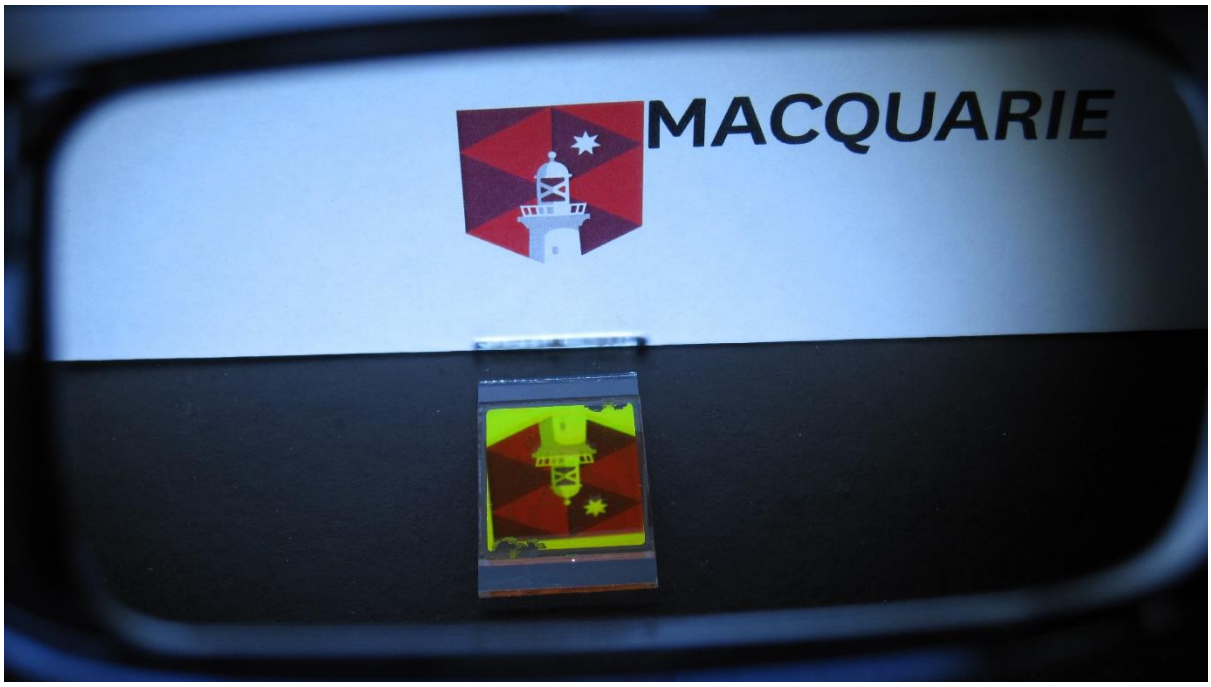
Table 2. Comparing the optical activity of TBAs to other types of chiral centers employed in the design of photoresponsive chiral compounds

Compound name	Chemical structure	$[\alpha]_D^{21\pm4^\circ C}$ ± 1°	Ref.
(*R*)-(–)-2-Octanol		**– 9.5 °** (*neat*)	2
Dianhydro-D-glucitol		**+ 45 °** (*C* = 3, H_2O)	2a, 3
(*S*)-(+)-2-Octanol		**+ 9.5 °** (*neat*)	2
(*R*)-(+)-1,1'-Binaphthyl-2,2'-diamine		**+ 157 °** (*C*=1, Py)	2a, 4
(5*S*,11*S*)-2,8-Dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5] diazocine		**+ 282 °** (*C*=0.11, $CHCl_3$)	5
(5*S*,11*S*)-2,8-Dimethoxy-6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5] diazocine		**+ 236 °** (*C*=0.11, $CHCl_3$)	5
(5*S*,11*S*)-2,8-Dibromo-6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine		**+ 379 °** (*C*=0.11, $CHCl_3$)	5
(–)-(5*S*,11*S*)-2,8-dimethoxy-6*H*,12*H*-5,11-ethanodibenzo[*b,f*][1,5]diazocine		**– 332 °** (*C*=0.10, DCM)	This work
(+)-(5*R*,11*R*)-2,8-dimethoxy-6*H*,12*H*-5,11-ethanodibenzo[*b,f*][1,5]diazocine[10]		**+ 337 °** (*C*=0.10, DCM)	This work



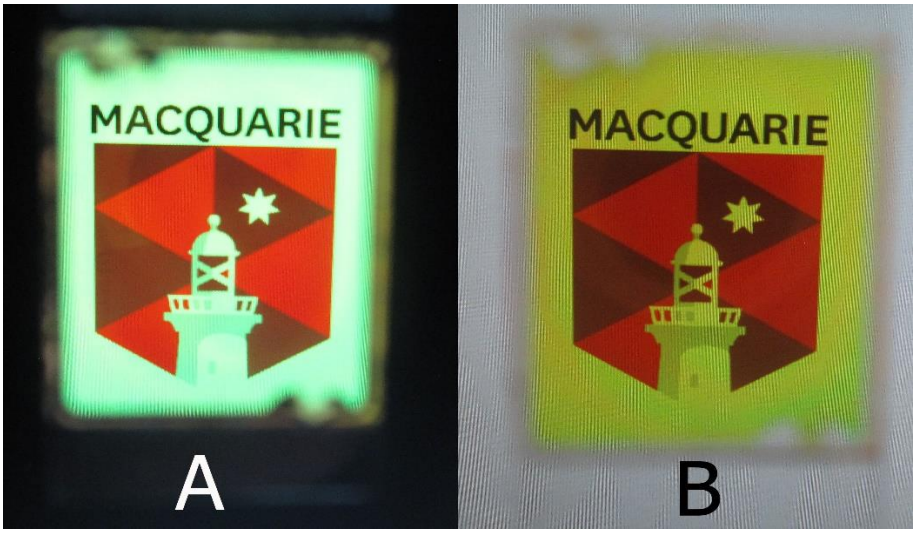
Elaboration on the acid-resistant chirality of the modified Tröger's base analogues

Photographs of Planar Cell



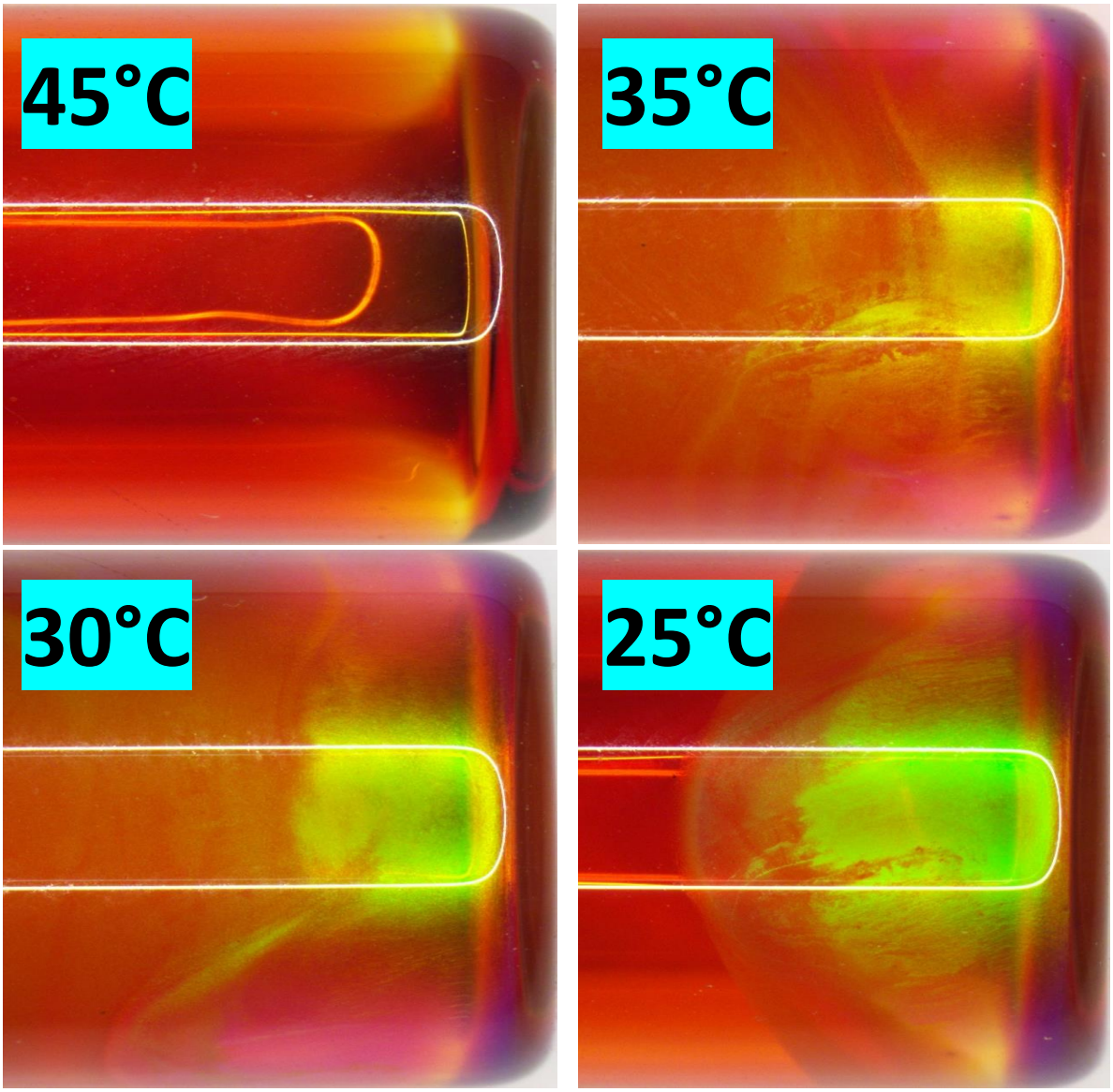
Observing an image reflected off a planar cell filled with (+)-(*R*,*R*)-9 doped 7CB (3.2 mol%) through the left filter of a passive 3D glasses

Observing an image reflected off a planar cell filled with (+)-(*R*,*R*)-9 doped 7CB (3.2 mol%) through the right filter of a passive 3D glasses



The planar cell placed between a pair of crossed (A) and parallel (B) linear polarizers

Phase Transition Observation



Phase transition and thermochromism of (+)-(*R*,*R*)-9 doped 7CB (3.2 mol%)

Experimental

General Experimental Methods. NMR spectra were recorded at 298 K using Bruker DRX400 and Cryoplatform600 MHz instruments, and Topspin V. 3.2 software. IR transmittance spectra were recorded at rt using Thermo Scientific Nicolet iS5/ATR10. HPLC chromatograms were recorded at 254 nm (optical detection) using Shimadzu CTO-20A instrument equipped with Phenomenex chiral analytical column (Lux-amylose-1, 250x4.6mm, 5 µm). Gravity-column chromatography was performed at rt using Davisil silica gel (LC60Å, 40–63µm) or Sigma-Aldrich alumina (neutral, 60–325 mesh) as stationary phases. Merck DC-Kieselgel60-F_{254} aluminium plates were used for analytical TLC. Solvent systems reported with R_f values were used for both TLC and column chromatography. Fluorescence analysis cabinet (CM-10) fitted with Spectroline UV lamps ENF-260C/FE [230V, 0.17 A, 50Hz]-256/365 nm was employed for TLC screening and illumination experiments. LC/ESI-MS was performed by Agilent-6130 Quadrupole using CH_3CN as mobile phase modified with formic acid (0.05 %) or ammonium formate (0.10 %) for positive and negative scans, respectively. Elemental analysis performed by Vario EL-Elementar and Perkin-Elmer-2400-SII analyzers. UV-Vis spectra were recorded at rt using Varian (Cary-1) or Eppendorf (Kinetic-Bio) spectrophotometers. Perkin-Elmer P-1010 polarimeter recorded optical rotations; *c* and [α] are reported in g/100mL and (deg.mL)/(g.dm), respectively. Jasco J-810 spectropolari meter recorded CD spectra.

Synthesis Procedures and Analytical Data

COMPOUND 1

*2,8-Dimethoxy-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine (**1**).*

Synthesized and purified according to the literature. [6] R_f 0.22 (silica gel; *i*PrOH – *n*Hex, 10% v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (d, *J* = 8.8 Hz, 2H), 6.75 (dd, *J* = 8.8, 2.8 Hz, 2H), 6.43 (d, *J* = 2.8 Hz, 2H), 4.65 (d, *J* = 16.5 Hz, 2H), 4.30 (s, 2H), 4.08 (d, *J* = 16.5 Hz, 2H), 3.71 (s, 6H). MS (ESI +, Quadrupole): *m/z* $[M + H]^+$ calcd for $[C_{17}H_{19}N_2O_2]^+$: 283.14; found: 283.1. Mp: 164–165°C (lit.[7] 163–165°C).

COMPOUND 2

*2,8-Dimethoxy-6H,12H-5,11-ethanodibenzo[b,f][1,5]diazocine (**2**).*

Synthesized and purified according to the literature.[8] Jameson's procedure [5] with slight changes, enabled the chiral resolution of **2** through its co-precipitation with enantiopure *O, O'*-dibenzoyl-tartaric acid (Mole ratio of 1:3 respectively), using dry CH_3CN instead of DCE, and recrystallizing the precipitated complex in fresh CH_3CN for four times before the final work-up. R_f 0.30 (silica gel; *i*PrOH – *n*Hex, 10% v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (d, *J* = 8.6 Hz, 2H), 6.62 (dd, *J* = 8.6, 2.8 Hz, 2H), 6.43 (d, *J* = 2.8 Hz, 2H), 4.54 (d, *J* = 17.3 Hz, 2H), 4.37 (d, *J* = 17.3 Hz, 2H), 3.67 (s, 6H), 3.54–3.59 (m, 4H). MS (ESI +, Quadrupole): *m/z* $[M + H]^+$ calcd for $[C_{18}H_{21}N_2O_2]^+$: 297.15; found: 297.1. Enantiomer (+)-(*R*,*R*)-**2**: $[\alpha]_D^{22}$ +337 (*c* 0.100, DCM), Chiral HPLC ^{t}R 12.1 ± 0.2 min (major >99.8%, er >99.5:0.5); Enantiomer (–)-(*S*,*S*)-**2**: $[\alpha]_D^{23}$ –332 (*c* 0.100, DCM), Chiral HPLC ^{t}R 14.1 ± 0.2 min (major >99.8%, er >99.5:0.5). Mp: 186–187°C (lit.[8] 186–189°C). **[10]**

COMPOUND 3

*6H,12H-5,11-Methanodibenzo[b,f][1,5]diazocine-2,8-diol (**3**).*

Compound **1** converted to **3** according to the literature.[9] R_f 0.4 (silica gel; EtOAc). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.00 (s, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.55 (dd, *J* = 8.7, 2.7 Hz, 2H), 6.31 (d, *J* = 2.7 Hz, 2H), 4.46 (d, *J* = 16.7 Hz, 2H), 4.12 (s, 2H), 3.89 (d, *J* = 16.6 Hz, 2H). MS (ESI +, Quadrupole): *m/z* $[M + H]^+$ calcd for $[C_{15}H_{15}N_2O_2]^+$: 255.11; found: 255.1; MS (ESI –, Quadrupole): *m/z* $[M – H]^–$ calcd for $[C_{15}H_{13}N_2O_2]^–$: 253.11; found: 253.1. Mp: 128–130°C.

COMPOUND 4

*6H,12H-5,11-Ethanodibenzo[b,f][1,5]diazocine-2,8-diol (**4**).*

An enantiomer of **2** (1.0 g, 3.3 mmol) in dry DCM (20mL) cooled down to –78°C under argon atmosphere, then neat BBr_3 (8.2 g, 33 mmol, excess) was cautiously added by addition funnel. The suspension was stirred (48 h, rt), poured into crushed ice (200 g), thoroughly mixed, and its pH was adjusted to 5 by adding NaOH (4.0 g) and AcOH (2 mL). The resulting solution was extracted with EtOAc (5 × 50mL) and discarded. The collected organic layers were combined, dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure to obtain product **4** as a white powder. Yield: 0.86 g (3.2 mmol, 97%); R_f 0.5 (silica gel; EtOAc). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.93 (s, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.40 (dd, *J* = 8.4, 2.7 Hz, 2H), 6.26 (d, *J* = 2.7 Hz, 2H), 4.41 (d, *J* = 17.2 Hz, 2H), 4.13 (d, *J* = 17.2 Hz, 2H), 3.37 (s, 4H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 153.9, 141.6, 138.2, 128.4, 114.3, 113.6, 58.6, 54.6. MS (ESI +, Quadrupole): *m/z* $[M + H]^+$ calcd for $[C_{16}H_{17}N_2O_2]^+$: 269.12; found: 269.1. MS (ESI –, Quadrupole): *m/z* $[M – H]^–$ calcd for $[C_{16}H_{15}N_2O_2]^–$: 267.12; found: 267.2. IR (neat): 3200, 2911, 1610, 1576, 1493, 1372, 1291, 1275, 1192, 1150, 1110, 1015, 843, 818, 661 cm^{-1}. UV-Vis: (EtOAc) λ (lgε) = 289 nm (3.868). Mp: 282–283° C. Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.51; H, 6.28; N, 10.35. Enantiomer (+)-(*R*,*R*)-**4**: $[\alpha]_D^{22}$ +261 (*c* 0.100, EtOAc) obtained from (+)-(*R*,*R*)-**2**; Enantiomer (–)-(*S*,*S*)-**4**: $[\alpha]_D^{24}$ –232 (*c* 0.100, EtOAc) obtained from (–)-(*S*,*S*)-**2**.

COMPOUND 5

*(E)-3-Benzyl-1-(4-butylphenyl)-3-methyltriaz-1-ene (**5**).*

Water (50 mL), H_2SO_4 (98%, 4 mL), 4-*n*-butylaniline (1.2 g, 8.0 mmol), and CH_3CN (30 mL) respectively poured into a round bottom flask and mixed together until homogeneous. The solution was cooled to –5°C, added $NaNO_2$ (0.69 g, 10 mmol, excess, in cold water 5 mL), and stirred (40 min, –5°C). The resulting clear solution was added to a cooled mixture of *n*-benzylmethylamine (3.0 mL, excess), Na_2CO_3 (9.0 g), water (50 mL), and CH_3CN (30 mL) and stirred (3 h, –5°C). The reaction mixture was diluted with cold water (200 mL) to precipitate out a beige waxy lump that was then extracted with DCM (2 × 50mL). The DCM layers were combined, dried over Na_2SO_4, filtered, and evaporated to dryness. The crude was chromatographed to obtain **5** as a slightly yellow oil that was then stored at –20°C. Yield: 2.12g (7.54 mmol, 94%); R_f 0.6 (silica gel; EtOAc–*n*Hex, 10% v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.11–7.21 (m, 5H), 7.05 (d, *J* = 8.3 Hz, 2H), 4.78 (s, 2H), 3.00 (s, 3H), 2.49 (t, 2H, *J* = 7.8 Hz), 1.45–1.53 (m, 2H), 1.20–1.29 (m, 2H), 0.82 (t, *J* = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.8, 140.4, 137.0, 128.9, 128.7, 127.9, 127.7, 120.6, 68.5, 58.8, 35.3, 33.8, 22.4, 14.1. MS (ESI +, Quadrupole): *m/z* calcd for $[C_{10}H_{13}N_2]^+$: 161.11; found: 161.1; *m/z* calcd for $[C_8H_{12}N]^+$: 122.10; found: 122.2. Anal. NA (unstable oil). IR (neat): 3027, 2954, 2926, 2856, 1495, 1446, 1342, 1171, 1054, 833, 729 cm^{-1}. UV-Vis: (EtOAc) λ (lgε) = 313 nm (3.462).

COMPOUND 6

*1,7-Bis((E)-(4-methoxyphenyl)diazenyl)-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine-2,8-diol (**6**).* 4-Anisidine (0.54 g, 4.4 mmol) in dilute H_2SO_4 (6.5%, 30 mL) cooled down to –5°C. $NaNO_2$ (0.30 g, 4.4 mmol, in cold water 5 mL) was dropped into the solution and stirred (30 min, –5°C). The resulting yellowish solution was added to a fresh solution of **3** (0.51 g, 2.0 mmol) and Na_2CO_3 (4.0 g) in ice-cold water (100 mL) and stirred for 18 h. A brown precipitate was filtered off, washed thoroughly with distilled water, and desiccated to obtain the crude that was then chromatographed to obtain **6** as the minor product. Yield: 0.13 g (0.25 mmol, 12%); R_f 0.55 (silica gel; MeOH–DCM, 4% v/v). ^{1}H NMR (400 MHz, $CDCl_3$–CD_3OD–$(CD_3)_2CO$–DMSO-d_6, 7:1:1:1 v/v): δ 13.04 (s, 2H Exchangeable, OH), 7.63 (d, *J* = 9.1 Hz, 4H, CH), 7.06 (d, *J* = 8.9 Hz, 2H, CH), 6.85 (d, *J* = 9.1 Hz, 4H, CH), 6.68 (d, *J* = 8.9 Hz, 2H, CH), 4.78 (d, *J* = 17.7 Hz, 2H, CH_2), 4.66(d, *J* = 17.7 Hz, 2H, CH_2), 4.24 (s, 2H, NCH_2N), 3.73 (s, 6H, OCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$–CD_3OD–$(CD_3)_2CO$–DMSO-d_6, 7:1:1:1 v/v): δ 162.1, 148.9, 144.7, 139.7, 132.9, 130.0, 128.2, 123.8, 117.3, 114.4, 66.2, 55.7, 55.4. MS (ESI +, Quadrupole): *m/z* $[M + H]^+$ calcd for $[C_{29}H_{27}N_6O_4]^+$: 523.21, found 523.2; (ESI –, Quadrupole) calc. for $[C_{29}H_{25}N_6O_4]^-$: $[M – H]^-$ 521.19, found 521.1. IR (neat): 3452, 3018, 2942, 2898, 2844, 1587, 1515, 1473, 1433, 1242, 1151, 1037 and 869 cm^{-1}. Dec. range: 280–283 °C (determined by DSC). UV-Vis: (EtOAc) λ (lgε) = 368nm (4.482). Anal. Calcd for $C_{29}H_{26}N_6O_4$: C, 66.66; H, 5.02; N, 16.08. Found: C, 66.42; H, 5.21; N, 15.95.

COMPOUND 7

*(E)-1-((4-Methoxyphenyl)diazenyl)-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine-2,8-diol (**7**).* Obtained as the major product of the previous reaction that described the synthesis of **6**. This asymmetrical product precipitated out of the reaction mixture due to its poor solubility, and hence was not well exposed to the diazonium salt and became the major product. Yield: 0.48 g (1.23 mmol, 62%); R_f 0.45 (silica gel; EtOAc–DCM, 50% v/v). ^{1}H NMR (400 MHz, DMSO-d_6 – EtOAc): δ 12.68 (s, 1H, OH), 9.04 (s, 1H, OH), 7.85 (d, *J* = 8.8 Hz, 2H, CH), 7.18 (d, *J* = 8.8 Hz, 1H, CH), 7.08 (d, *J* = 9.2 Hz, 2H, CH), 6.99 (d, *J* = 8.7 Hz, 1H, CH), 6.82 (d, *J* = 8.9 Hz, 1H, CH), 6.56 (dd, *J* = 8.6, 2.6 Hz, 1H, CH), 6.35 (d, *J* = 2.5 Hz, 1H, CH), 4.51–4.82 (m, 3H, CH_2), 4.22 (s, 2H, NCH_2N), 4.03 (m, 1H, CH_2), 3.84 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6 – EtOAc): δ 162.0, 153.4, 148.1, 144.5, 140.5, 139.4, 132.7, 130.3, 128.6, 128.5, 125.7, 124.1, 116.7, 114.8, 114.5, 112.3, 66.2, 57.7, 56.1, 55.6. MS (ESI +, Quadrupole): *m/z* $[M + H]^+$ calcd for $[C_{22}H_{21}N_4O_3]^+$: 389.15, found 389.2; (ESI –, Quadrupole) calc. for $[C_{22}H_{19}N_4O_3]^-$: $[M – H]^-$ 387.15, found 387.1. IR (neat): 3433, 3029, 2935, 2888, 2839, 1593, 1500, 1482, 1440, 1250, 1142, 1027 and 829 cm^{-1}. Dec. range: 267–271 °C (determined by DSC). UV-Vis: (EtOAc) λ (lgε) = 367 nm (4.256). Anal. Calcd for $C_{22}H_{20}N_4O_3$: C, 68.03; H, 5.19; N, 14.42. Found: C, 68.27; H, 5.38; N, 14.19.

COMPOUND 8

*1,7-Bis((E)-(4-butylphenyl)diazenyl)-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine-2,8-diol (**8**)*. Distilled water (25 mL) was poured into a 100mL round-bottom flask, then added H_2SO_4 (98%, 2 mL). A solution of 4-*n*-butylaniline (1.2 g, 8.0 mmol) in CH_3CN (20 mL) was added to the flask while the acid solution was still warm (50–60 °C). The solution cooled down to –5°C, $NaNO_2$ solution (0.69 g, 10 mmol in cold water 5 mL) was added dropwise, and stirred for 35 min. The resulting clear solution was slowly added to a mixture consisting of **3** (0.51 g, 2.0 mmol), Na_2CO_3 (4.0 g), water (20 mL), and CH_3CN (20 mL), and stirred (2h, –5°C). Cold water (50 mL) was added and stirred again (12 h, rt). A few drops of HCl solution (0.1 N) was added to form a brown organic precipitate that was then extracted from the aqueous mixture with DCM (2 × 50 mL). The DCM layers were combined, dried over $MgSO_4$, filtered, and evaporated to dryness. The crude was

chromatographed to obtain **8** as a maroon solid. Yield: 1.1 g (1.9 mmol, 95%); R_f 0.3 (silica gel; EtOAc – *n*Hex, 20% v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.30 (s, 2H, OH), 7.72 (d, *J* = 8.5 Hz, 4H, CH), 7.31 (d, *J* = 8.5 Hz, 4H, CH), 7.29 (d, *J* = 9.0 Hz, 2H, CH), 6.89 (d, *J* = 9.0 Hz, 2H, CH), 5.00 (d, *J* = 17.8 Hz, 2H, CH_2), 4.85 (d, *J* = 17.8 Hz, 2H, CH_2), 4.45 (s, 2H, NCH_2N), 2.68 (t, *J* = 7.7 Hz, 4H, CH_2), 1.60–1.68 (m, 4H, CH_2), 1.34–1.43 (m, 4H, CH_2), 0.93–0.97 (t, *J* = 7.4 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.3, 148.9, 147.1, 139.6, 133.4, 130.9, 129.5, 128.6, 122.3, 118.0, 66.8, 56.0, 35.7, 33.4, 22.4, 14.0. MS (ESI +, Quadrupole): *m/z* $[M + H]^+$ calcd for $[C_{35}H_{39}N_6O_2]^+$: 575.30, found 575.29. IR (neat): 3062, 2954, 2927, 2856, 1599, 1476, 1424, 1314, 1175, 1081, 902, 831 cm^{-1}. Mp: 160–162°C. UV-Vis: (EtOAc) λ (lgε) = 353nm (4.658). Anal. Calcd for $C_{35}H_{38}N_6O_2$: C, 73.14; H, 6.66; N, 14.62. Found: C, 73.26; H, 6.75; N, 14.83.

COMPOUND 9

*1,7-bis((E)-(4-butylphenyl)diazenyl)-6H,12H-5,11-ethanodibenzo[b,f][1,5]diazocine-2,8-diol (**9**)*. The synthesis procedure of **8** was started with one enantiomer of **4** (0.54 g, 2 mmol) instead of using **3**. This resulted in **9** as a maroon solid. Yield: 0.98 g (1.6 mmol, 83%); R_f 0.3 (silica gel; EtOAc – *n*Hex, 15% v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.30 (s, 2H, OH), 7.74 (d, *J* = 8.5 Hz, 4H, CH), 7.31 (d, *J* = 8.5 Hz, 4H, CH), 7.29 (d, *J* = 8.8 Hz, 2H, CH), 6.80 (d, *J* = 8.8 Hz, 2H, CH), 5.70 (d, *J* = 18.5 Hz, 2H, NCH_2), 4.77 (d, *J* = 18.5 Hz, 2H, NCH_2), 3.70–3.81 (m, 4H, NCH_2), 2.67 (t, *J* = 7.5 Hz, 4H, CH_2), 1.63–1.70 (m, 4H, CH_2), 1.37–1.46 (m, 4H, CH_2), 1.00 (t, *J* = 7.3 Hz, 6H, CH_3). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 150.8, 148.7, 146.5, 142.8, 137.4, 134.5, 134.3, 129.3, 122.1, 117.1, 55.3, 54.6, 35.5, 33.3, 22.3, 13.9. MS (ESI +, Quadrupole): *m/z* $[M + H]^+$ calcd for $[C_{36}H_{41}N_6O_2]^+$: 589.32, found 589.3. IR (neat): 3028, 2953, 2927, 2855, 1600, 1477, 1316, 1279, 1153, 996, 823 cm^{-1}. Mp: 116–118°C. UV-Vis: (DCM) λ (lgε) = 355 nm (4.663). Anal. Calcd for $C_{36}H_{40}N_6O_2$: C, 73.44; H, 6.85; N, 14.27. Found: C, 73.61; H, 6.94; N, 14.09. Enantiomer (+)-(*R*,*R*)-**9**: $[\alpha]_D^{29}$ +1826 (*c* 0.100, DCM) obtained from (+)-(*R*,*R*)-**4**; Enantiomer (–)-(*S*,*S*)-**9**: $[\alpha]_D^{29}$ –1754 (*c* 0.100, DCM) obtained from (–)-(*S*,*S*)-**4**.

COMPOUND 10

*Hexyl (E)-3-((4-(hexyloxy)phenyl)diazenyl)benzoate (**10**).* 3-Aminobenzoic acid (2.0 g, 15 mmol) in HCl solution (7.4%, 100 mL) cooled down to –5°C, then $NaNO_2$ (1.1 g, 16 mmol, in ice-cold water 10 mL) was gradually added and the solution stirred for 30 min. The obtained solution was added to a fresh solution of phenol (1.5 g, 16 mmol) and Na_2CO_3 (2.1 g) in 40 mL of cold water and stirred for 4 h. The solution was acidified with HCl until precipitate out a yellow colour solid. The yellow solid was collected by filtration, rinsed with distilled water and dried under high-vacuum. The crude was added to a mixture of K_2CO_3 (6.2 g, 45 mmol), 1-hexylbromide (7.4 g, 45 mmol), and KI (0.17 g, 1.0 mmol) in 80 mL of dry acetone, and refluxed for 18 h. The reaction mixture cooled, filtered and reduced under high-vacuum to obtain an orange residue that was then chromatographed to obtain **10** as a shiny orange solid. Yield: 4.5 g (11 mmol, 73%); R_f 0.75 (silica gel; EtOAc – *n*Hex, 10% v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (s, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.59 (t, *J* = 8.2 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 4.39 (t, *J* = 7.0 Hz, 2H), 4.06 (t, *J* = 6.6 Hz, 2H), 1.79–1.88 (m, 4H), 1.45–1.55 (m, 4H) , 1.32–1.46 (m, 8H), 0.94 (t, *J* = 7.3 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.3, 162.2, 152.8, 146.8, 131.7, 131.1, 129.1, 126.3, 125.1, 124.1, 114.8, 68.5, 65.5, 31.7, 31.6, 29.2, 28.8, 25.8, 22.7, 22.6, 14.1. MS (ESI +, Quadrupole): *m/z* $[M + H]^+$ calcd for $[C_{25}H_{35}N_2O_3]^+$: 411.26, found 411.2. IR (neat): 2952, 2917, 2853, 1705, 1600, 1499, 1252, 1146, 1024, 842, 758 cm^{-1}. UV-Vis: (EtOAc) λ (lgε)=350nm(4.376).[10]

COMPOUND 11

*(E)-3-((4-(hexyloxy)phenyl)diazenyl)benzoic acid (**11**).* To a solution of **10** (4.5 g, 11 mmol) in boiling EtOH (50 mL) was gradually added an aqueous solution of KOH (3N, 30mL), and refluxed for 24 h. The solution was cooled to rt and acidified (HCl 37%, 2 mL) to precipitate a yellow solid that was collected by filtration, rinsed, and dried under high-vacuum. Yield: 3.44 g (10.5 mmol, 96%); R_f 0.2 (silica gel; EtOAc–*n*Hex, 20% v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.62 (s, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 8.7 Hz, 2H), 7.62 (t, *J* = 8.2 Hz, 1H), 7.02 (d, *J* = 8.5 Hz, 2H), 4.06 (t, *J* = 6.8 Hz, 2H), 1.79–1.88 (m, 2H, CH_2), 1.45–1.53 (m, 2H, CH_2) , 1.32–1.46 (m, 4H, CH_2), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 171.8, 162.3, 152.9, 146.8, 131.6, 130.4, 129.3, 127.6, 125.2, 124.6, 114.9, 68.5, 31.7, 29.3, 25.8, 22.7, 14.1. MS (ESI +, Quadrupole): *m/z* $[M + H]^+$ calcd for $[C_{19}H_{23}N_2O_3]^+$: 327.16, found 327.1; (ESI –, Quadrupole): *m/z* $[M - H]^-$ calcd for $[C_{19}H_{21}N_2O_3]^-$: 325.16, found 325.1. IR (neat): 3060, 2942, 2918, 2854, 1694, 1604, 1503, 1447, 1409, 1257, 1142, 843 cm^{-1}. UV-Vis: (EtOAc) λ = 351 nm. Mp: 141–143°C.

COMPOUND 12

*(E)-3-((4-(Hexyloxy)phenyl)diazenyl)benzoyl chloride (**12**).* A solution of **11** (3.44 g, 10.5 mmol) in $SOCl_2$ (40 mL) refluxed for 6 h. The excess of $SOCl_2$ was removed by distillation and the residue was diluted by dry *n*Hex (50 mL) and cooled down to –20°C to obtain **12** as shiny orange crystals. Yield: 3.3 g, (9.6 mmol, 92%); R_f (too reactive). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (s, 1H), 8.16 (d, *J* = 7.2 Hz, 2H), 7.94 (d, *J* = 8.7 Hz, 2H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 2H), 4.05 (t, *J* = 6.7 Hz, 2H), 1.79–1.88 (m, 2H, CH_2), 1.45–1.53 (m, 2H, CH_2), 1.32–1.56 (m, 4H, CH_2), 0.93 (t, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 168.2, 162.5, 153.0, 146.6, 134.3, 132.2, 129.7, 128.9, 125.6, 125.3, 114.9, 68.5, 31.6, 29.2, 25.7, 22.7, 14.1. MS (ESI +; *i*PrOH, Quadrupole): *m/z* $[M + H]^+$ calcd for $[C_{19}H_{22}ClN_2O_2]^+$: 345.13, found 345.1; *m/z* $[M - Cl + i\text{PrOH}]^+$ calcd for $[C_{22}H_{29}N_2O_3]^+$: 369.21, found 369.2. UV-Vis: (EtOAc) λ = 355 nm. IR (neat): 2946, 2868, 1742, 1597, 1498, 1472, 1451, 1247, 1141, 836, 783, 673 cm^{-1}.

COMPOUND 13

*8-hydroxy-6H,12H-5,11-ethanodibenzo[b,f][1,5]diazocin-2-yl(E)-3-((4-(hexyloxy)phenyl)diazenyl) benzoate (**13**).* Solutions of **4** (0.27 g, 1.0 mmol) in dry DMF (3 mL) and **12** (0.76 g, 2.2 mmol) in dry pyridine (3 mL) were combined and stirred overnight under argon atmosphere. The solution was diluted with DCM (50 mL) and rinsed with $NaHCO_3$ (3 M, 3 × 50 mL). The DCM layer dried over $MgSO_4$, filtered, and evaporated to dryness. The crude was chromatographed to obtain **13** as an orange solid. Yield: 0.48 g (0.83 mmol, 83%); R_f 0.3 (Silica gel; MeOH – DCM = 4% v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (t, *J* = 1.7 Hz, 1H, CH), 8.16–8.20 (m, 1H, CH), 8.08–8.12 (m, 1H, CH), 7.91–7.94 (m, 2H, CH), 7.58–7.63 (m, 1H, CH), 7.16–7.20 (m, 1H, CH), 6.95–7.04 (m, 4H, CH), 6.83 (d, *J* = 2.8 Hz, 1H, CH), 6.52 (dd, *J* = 8.6 Hz, *J* = 2.8 Hz, 1H, CH), 6.39 (d, *J* = 2.8 Hz, 1H, CH), 4.36–4.66 (m, 4H, CH_2), 4.04 (t, *J* = 6.8 Hz, 2H, CH_2), 3.53–3.66 (m, 4H, CH_2), 1.78–1.85 (m, 2H, CH_2), 1.44–1.52 (m, 2H, CH_2), 1.33–1.38 (m, 4H, CH_2), 0.92 (t, *J* = 7.0 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.9, 162.3, 152.9, 147.81, 147.6, 146.7, 138.1, 137.9, 131.5, 130.6, 129.4, 129.1, 129.0, 127.7, 127.4, 125.2, 124.2, 123.3, 121.6, 120.5, 115.0, 114.9, 114.6, 68.5, 59.2, 55.0, 31.7, 29.2, 25.8, 22.7, 14.1. MS (ESI +, Quadrupole): *m/z* $[M + H]^+$ calcd for $[C_{35}H_{37}N_4O_4]^+$: 577.28, found: 577.3. IR (neat): 2919, 2861, 1734, 1598, 1489, 1290, 1142, 838, 816, 749, 680 cm^{-1}. UV-Vis: (EtOAc) λ (lgε) = 350nm (4.421). Anal. Calcd for $C_{35}H_{36}N_4O_4$: C, 72.90; H, 6.29; N, 9.72. Found: C, 73.12; H, 6.48; N, 9.53. Enantiomer (+)-(*R*,*R*)-**13**: $[\alpha]_D^{20}$ +351 (*c* 0.100, EtOAc) obtained from (+)-(*R*,*R*)-**4**; Enantiomer (–)-(*S*,*S*)-**13**: $[\alpha]_D^{22}$ –345 (*c* 0.100, EtOAc) obtained from (–)-(*S*,*S*)-**4**.

COMPOUND 14

*6H,12H-5,11-ethanodibenzo[b,f][1,5]diazocine-2,8-diyl bis 3-((E)-(4-(hexyloxy)phenyl)diazenyl) benzoate (**14**).* Obtained from compounds **4** (0.27 g, 1.0 mmol) and **12** (1.14 g, 3.3 mmol, excess) using the procedure described for **13**. Yield: 0.65 g (0.73 mmol, 73%); R_f 0.4 (Silica gel; MeOH–DCM= 2% v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.62 (s, 2H), 8.19 (d, *J* = 7.8 Hz, 2H), 8.11 (d, *J* = 7.8 Hz, 2H), 7.94 (d, *J* = 8.9 Hz, 4H), 7.61 (t, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.9 Hz, 4H), 6.88 (s, 2H), 4.66 (d, *J* = 17.5 Hz, 2H), 4.49 (d, *J* = 17.5 Hz, 2H), 4.04 (t, *J* = 6.5 Hz, 4H), 3.63–3.72 (m, 4H), 1.78–1.85 (m, 4H), 1.45–1.51 (m, 4H), 1.34–1.38 (m, 8H), 0.92 (t, *J* = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 164.8, 162.3, 152.9, 147.9, 146.7, 131.5, 130.6, 129.4, 128.9, 127.5, 125.2, 124.2, 124.2, 121.7, 120.8, 114.9, 114.4, 68.5, 59.2, 54.6, 31.7, 29.2, 25.8, 22.7, 14.1. MS (ESI +, Quadrupole): *m/z* $[M + H]^+$ calcd for $[C_{54}H_{57}N_6O_6]^+$: 885.43, found: 885.4. IR (neat): 2925, 2859, 1729, 1599, 1489, 1291, 1142, 834, 817, 749, 680 cm^{-1}. Mp: 80–82 °C. UV-Vis: (DCM) λ (lgε) = 353 nm (4.725). Anal. Calcd for $C_{54}H_{56}N_6O_6$: C, 73.28; H, 6.38; N, 9.50. Found: C, 73.13; H, 6.47; N, 9.82. Enantiomer (+)-(*R*,*R*)-**14**: $[\alpha]_D^{29}$ +319 (*c* 0.100, DCM) obtained from (+)-(*R*,*R*)-**4**; Enantiomer (–)-(*S*,*S*)- **14**: $[\alpha]_D^{29}$ –319 (*c* 0.100, DCM) obtained from (–)-(*S*,*S*)-**4**.

COMPOUND 15

*(E)-4-((4-(hexyloxy)phenyl)diazenyl)benzoic acid (**15**).* The procedures described the synthesis of **10** and **11** were started with 4-aminobenzoic acid to obtain **15** as an orange solid. Yield: 2.39 g (10.4 mmol, 95%); R_f 0.3 (silica gel; EtOAc–*n*Hex, 30% v/v). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 4.09 (t, *J* = 6.5 Hz, 2H), 1.72–1.78 (m, 2H), 1.40–1.48 (m, 2H) , 1.28-1.38 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 167.3, 161.7, 154.3, 146.0, 132.0, 130.0, 124.4, 121.6, 114.8, 67.9, 30.4, 28.1, 24.6, 21.5, 13.2. IR (neat): 3068, 2940, 2928, 1688, 1523, 1445, 1408, 1261, 1143, 867 cm^{-1}. MS (ESI +, Quadrupole): *m/z* $[M + H]^+$ calcd for $[C_{19}H_{23}N_2O_3]^+$: 327.17, found 327.2; (ESI –, Quadrupole): *m/z* $[M – H]^–$ calcd for $[C_{19}H_{21}N_2O_3]^–$: 325.15, found 325.1. Mp: 219–221 °C. UV-Vis: (EtOAc) λ (lgε) = 360nm (4.384).

COMPOUND 16

*(E)-4-((4-(Hexyloxy)phenyl)diazenyl)benzoyl chloride (**16**).* Obtained from **15** (2.39 g, 10.4 mmol) applying the preparation procedure of **12**. Yield: 2.93 g (8.53 mmol, 82%); R_f (reacts). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 2H), 4.08 (t, *J* = 6.5 Hz, 2H), 1.70–1.77 (m, 2H), 1.38–1.45 (m, 2H) , 1.20–1.35 (m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 166.7, 162.1, 154.5, 146.1, 132.1, 130.6, 125.0, 122.2, 115.1, 68.1, 40.0, 28.5, 25.1, 22.1, 13.9. MS (ESI +, MeOH, Quadrupole): *m/z* $[M – Cl + MeOH]^+$ calcd for $[C_{20}H_{25}N_2O_3]^+$: 341.18, found 341.2. Anal. (Unstable), IR (neat): 2950, 2871, 1738, 1601, 1487, 1453, 1142, 856, 773, 608 cm^{-1}. UV-Vis: (EtOAc) λ = 355 nm.

COMPOUND 17

*6H,12H-5,11-ethanodibenzo[b,f][1,5]diazocine-2,8-diyl bis(4-((E)-4-(hexyloxy)phenyl)diazenyl) benzoate (**17**).* Obtained from compounds **4** (0.27 g, 1.0 mmol) and **16** (1.14 g, 3.3 mmol, excess) applying the preparation procedure of **14**. Yield: 0.71 g (0.81 mmol, 81%); R_f 0.4 (Silica gel; MeOH – DCM= 2% v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.6 Hz, 4H), 7.95 (d, *J* = 8.9 Hz, 4H), 7.94 (d, *J* = 8.6 Hz, 4H), 7.25 (s, 2H), 7.07 (d, *J* = 6.7 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 4H), 6.91 (d, *J* = 6.7 Hz, 2H), 4.72 (d, *J* = 16.9 Hz, 2H), 4.55 (d, *J* = 16.9 Hz, 2H), 4.06 (t, *J* = 6.6 Hz, 4H), 3.77 (b, 4H), 1.79–1.86 (m, 4H), 1.45–1.53 (m, 4H), 1.34–1.38 (m, 8H), 0.92 (t, *J* = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.6, 162.6, 156.0, 146.9, 131.3, 130.1, 127.7, 125.4, 125.2, 124.9, 124.8, 122.8, 122.6, 122.2, 114.9, 68.6, 63.2, 59.1, 31.7, 29.2, 25.8, 22.7, 14.1. MS (ESI +, Quadrupole): *m/z* $[M + H]^+$ calcd for $[C_{54}H_{57}N_6O_6]^+$: 885.43, found: 885.4. IR (neat): 2929, 2859, 1730, 1597, 1488, 1297, 1135, 1066, 861, 835, 689 cm^{-1}. UV-Vis: (DCM) λ (lgε) = 364nm (4.709). Anal. Calcd for $C_{54}H_{56}N_6O_6$: C, 73.28; H, 6.38; N, 9.50. Found: C, 72.96; H, 6.35; N, 9.42. Enantiomer (+)-(*R*,*R*)-**17**: $[\alpha]_D^{29}$ +468 (*c* 0.100, DCM) obtained from (+)-(*R*,*R*)-**4**; Enantiomer (–)-(*S*,*S*)-**17**: $[\alpha]_D^{28}$ –473 (*c* 0.100, DCM) obtained from (–)-(*S*,*S*)-**4**.

COMPOUND 18

*(E)-4-((4-butylphenyl)diazenyl)-2,6-dimethylphenol (**18**).* Synthesized similarly to compound **5** except using 2,6-dimethylphenol (1.2 g, 10 mmol) instead of *n*-benzylmethylamine. Yield: 2.03g (7.2 mmol, 89%); R_f 0.2 (silica gel; EtOAc–*n*Hex, 5% v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.9, 2H), 7.67 (s, 2H), 7.30 (d, *J* = 7.9, 2H), 4.50 (b, 1H, OH), 2.68 (t, *J* = 7.7, 2H), 2.32 (s, 6H), 1.60–1.68 (m, 2H), 1.33–1.44 (m, 2H), 0.95 (t, *J* = 7.5, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.3, 145.9, 130.2, 129.2, 123.9, 123.8, 122.8, 122.5, 35.7, 33.6, 22.5, 16.1, 14.1. MS (ESI +, Quadrupole): *m/z* calcd for $[C_{18}H_{23}N_2O]^+$: 283.18; found: 283.1(ESI –, Quadrupole): *m/z* calcd for $[C_{18}H_{21}N_2O]^-$: 281.16; found: 281.1. IR (neat): 3343, 2958, 2915, 2853, 1590, 1468, 1197, 1112, 885, 833, 728 cm^{-1}. Mp: 50–51 °C. UV-Vis: (DCM) λ = 354nm. Anal. Calcd for $C_{18}H_{22}N_2O$: C, 76.56; H, 7.85; N, 9.92. Found: C, 76.42; H, 7.96; N, 9.73.

COMPOUND 19

*(E)-1-(4-(2-bromoethoxy)-3,5-dimethylphenyl)-2-(4-butylphenyl)diazene (**19**).* Compound **18** (1.13 g, 4.0 mmol) was added to a mixture of K_2CO_3 (1.2 g, 9.0 mmol), freshly prepared [9a] 1,2-dibromoethane (5 mL, excess), KI (0.17 g, 1.0 mmol), and acetone (25 mL), and refluxed for 24 h. The reaction mixture was cooled, filtered and reduced under high-vacuum to obtain a dark red residue that was then chromatographed to obtain **19** as a red oil. Yield: 1.42 g (3.68 mmol, 92%); R_f 0.6 (silica gel; EtOAc–*n*Hex, 5% v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 7.9, 2H), 7.60 (s, 2H), 7.31 (d, *J* = 7.9, 2H), 4.15 (t, *J* = 6.1, 2H), 3.69 (t, *J* = 6.1, 2H), 2.69 (t, *J* = 7.5, 2H), 2.40 (s, 6H), 1.60–1.70 (m, 2H), 1.34–1.44 (m, 2H), 0.95 (t, *J* = 7.2, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.4, 151.1, 149.2, 146.3, 131.7, 129.2, 123.5, 122.8, 71.8, 35.7, 33.6, 30.1, 22.5, 16.7, 14.1. MS (ESI +, Quadrupole): *m/z* calcd for $[C_{20}H_{26}BrN_2O]^+$: 389.12 and 391.12; found: 389.1 and 391.1. IR (neat): 2955, 2926, 2858, 1600, 1472, 1286, 1199, 1115, 1002, 838, 768 cm^{-1}. UV-Vis: (DCM) λ (lgε) = 343nm (4.342). Anal. Calcd for $C_{20}H_{25}BrN_2O$: C, 61.70; H, 6.47; N, 7.20. Found: C, 61.82; H, 6.33; N, 7.04.

COMPOUND 20

*2,8-bis(2-(4-((E)-(4-butylphenyl)diazenyl)-2,6-dimethylphenoxy) ethoxy)-6H,12H-5,11-ethanodi benzo [b,f] [1,5] diazocine (**20**).* Compounds **4** (0.27 g, 1.0 mmol), **19** (0.97 g, 2.5 mmol), K_2CO_3 (0.62 g, 4.5 mmol), dry DMF (10 mL), and KI (0.17 g, 1.0 mmol) were mixed, and stirred at 65 °C overnight. The reaction mixture was cooled to rt, mixed with $NaHCO_3$ solution (3N, 50 mL), and extracted with DCM (3 × 30 mL). The collected DCM layers were combined, dried over $MgSO_4$, and filtered. The solvent was removed, and the residue was purified by column chromatography to obtain **20** as a light-orange solid. Yield: 0.74 g (0.84 mmol, 84%); R_f 0.5 (silica gel; MeOH–DCM, 2% v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.1 Hz, 4H), 7.58 (s, 4H), 7.30 (d, *J* = 8.1 Hz, 4H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.70 (dd, *J* = 8.3, 2.6 Hz, 2H), 6.51 (d, *J* = 2.6 Hz, 2H), 4.58 (d, *J* = 17.2 Hz, 2H), 4.40 (d, *J* = 17.2 Hz, 2H), 4.24–4.15 (b, 4H), 4.14–4.07 (b, 4H), 3.57–3.67 (b, 4H), 2.67 (t, *J* = 2.6 Hz, 4H), 2.34 (s, 12H), 1.60–1.68 (m, 4H), 1.33–1.42 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.9, 156.0, 151.1, 148.9, 146.2, 131.8, 130.7, 129.1, 128.9, 128.6, 123.4, 122.7, 114.6, 113.6, 70.7, 67.3, 59.5, 54.7, 35.6, 33.5, 22.4, 16.5, 14.0. MS (ESI +, Quadrupole): *m/z* calcd for $[C_{56}H_{65}N_6O_4]^+$: 885.50; found: 885.5. IR (neat): 2923, 2856, 1602, 1492, 1270, 1195, 1116, 1063, 890, 839 cm^{-1}. Mp: 70–71 °C. UV-Vis: (DCM) λ (lgε) = 344nm (4.687). Anal. Calcd for $C_{56}H_{64}N_6O_4$: C, 75.99; H, 7.29; N, 9.49. Found: C, 76.12; H, 7.08; N, 9.63. Enantiomer (+)-(*R*,*R*)-**20**: $[\alpha]_D^{25}$ +236 (*c* 0.100, DCM) obtained from (+)-(*R*,*R*)-**4**; Enantiomer (–)-(*S*,*S*)-**20**: $[\alpha]_D^{26}$ –241 (*c* 0.100, DCM) obtained from (–)-(*S*,*S*)-**4**.

COMPOUND 21

*(E)-4-((4-(octyloxy)naphthalen-1-yl)diazenyl)benzoic acid (**21**).* 4-Aminobenzoic acid (2.0 g, 15 mmol) in HCl solution (7.4%, 100 mL) cooled down to –5°C. $NaNO_2$ (1.1 g, 16 mmol, in ice-cold water 10 mL) was gradually added and the reaction mixture stirred for 30 min. The obtained solution was added to a fresh solution of 1-naphthol (2.2 g, 15 mmol) and Na_2CO_3 (2.1 g, 20 mmol) in 40 mL of cold water, and stirred for 4 h. Added HCl (37%, 2mL) to precipitate out a red solid that was then collected by filtration, rinsed with water, and dried under high-vacuum. R_f 0.1 (silica gel; MeOH – DCM, 4% v/v). MS (ESI –, Quadrupole): *m/z* calcd for $[C_{17}H_{11}N_2O_3]^-$: 291.07; found: 291.2. The crude was added to a mixture of K_2CO_3 (6.2 g, 45 mmol), 1-octylbromide (7.7 g, 40 mmol), and KI (0.17 g, 1.0 mmol, cat) in dry DMF (80 mL), and stirred for 18 h at 70 °C. The reaction mixture cooled to rt, filtered and reduced under high-vacuum at 60°C to obtain a dark red residue which was then chromatographed to obtain a red waxy solid. R_f 0.7 (silica gel; EtOAc – *n*Hex, 10% v/v). MS (ESI +, Quadrupole): *m/z* calcd for $[C_{33}H_{45}N_2O_3]^+$: 517.34; found: 517.3. This product was then dissolved in boiling *i*PrOH (50 mL) and an aqueous solution of KOH (6N, 20mL) was gradually added to its solution, and refluxed for 48 h. Afterward, the solution was acidified by the addition of concd HCl to precipitate **21** as a deep red solid that was collected by filtration, rinsed with water, dried under high-vacuum, and then recrystallized from DCM – *n*Hex 30% v/v. Yield: 3.7 g (9.3 mmol, 62%); R_f 0.4 (silica gel; EtOAc – *n*Hex, 40% v/v). ^{1}H NMR (600 MHz, DMSO-d_6): δ 13.16 (b, 1H), 8.90 (d, *J* = 8.4 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 2H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 4.18 (t, *J* = 6.3 Hz, 2H), 1.78–1.88 (m, 2H), 1.42–1.51 (m, 2H), 1.18–1.35 (m, 8H), 0.83 (t, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6): δ 166.8, 158.2, 154.9, 140.4, 132.1, 132.0, 130.6, 128.0, 126.1, 124.9, 122.6, 122.4, 121.8, 113.7, 105.1, 68.4, 31.2, 28.7, 28.6, 28.5, 25.6, 22.1, 13.9. MS (ESI +, Quadrupole): *m/z* $[M + H]^+$ calcd for $[C_{25}H_{29}N_2O_3]^+$: 405.21, found 405.2. IR (neat): 3073, 2963, 2917, 2844, 1692, 1603, 1488, 1249, 1148, 840 cm^{-1}. Mp: 207–209 °C. UV-Vis: (DCM) λ (lg ε) = 420nm (4.471) and 283nm (4.436).

COMPOUND 22

*6H,12H-5,11-ethanodibenzo[b,f][1,5]diazocine-2,8-diyl bis(4-((E)-4-(octyloxy)naphthalen-1-yl) diazenyl)benzoate (**22**).* Compounds **4** (0.27 g, 1.0 mmol), **21** (0.89 g, 2.2 mmol), *N*-(3-dimethyl aminopropyl)-*N'*-ethylcarbodiimide hydrochloride (0.42 g, 2.2 mmol), 4-(dimethylamino)pyridine (0.12 g, 1.0 mmol) stirred in dry DCM (50 mL, 0–5 °C, 2 d). The solvent was removed under reduced pressure, $NaHCO_3$ solution (3N, 50 mL) was added, and then extracted with DCM (3 × 30 mL). The collected organic layers were combined, dried over $MgSO_4$, and filtered. The solvent was removed, and the residue was chromatographed to obtain **22** as a red solid. Yield: 0.81 g (0.78 mmol, 78%); R_f 0.7 (silica gel; EtOAc – *n*Hex, 40% v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.98 (d, *J* = 8.4 Hz, 2H), 8.36 (d, *J* = 8.4 Hz, 2H), 8.30 (d, *J* = 8.8 Hz, 4H), 8.06 (d, *J* = 8.8 Hz, 4H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.70 (t, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.90 (s, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 4.67 (d, *J* = 17.5 Hz, 2H), 4.51 (d, *J* = 17.5 Hz, 2H), 4.22 (t, *J* = 6.4 Hz, 4H), 3.61–3.74 (m, 4H), 1.91–1.99 (m, 4H), 1.53–1.63 (m, 4H), 1.25–1.47 (m, 16H), 0.91 (t, *J* = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 164.8, 159.0, 156.3, 148.0, 147.0, 141.6, 137.5, 133.1, 130.3, 128.9, 127.9, 127.7, 125.9, 125.8, 123.3, 123.1, 122.4, 121.7, 120.8, 113.8, 104.5, 68.8, 59.2, 54.5, 31.9, 29.5, 29.3, 29.2, 26.3, 22.7, 14.2. MS (ESI +, Quadrupole): *m/z* $[M + H]^+$ calcd for $[C_{66}H_{69}N_6O_6]^+$: 1041.52, found 1041.5. IR (neat): 2922, 2854, 1732, 1574, 1508, 1318, 1237, 1137, 1065, 760 cm^{-1}. Mp: 230–231 °C. UV-Vis: (DCM) λ (lgε) = 423nm (4.802) and 284nm (4.693). Enantiomer (+)-(*R*,*R*)-**22**: $[\alpha]_D^{28}$ +564 (*c* 0.100, DCM) obtained from (+)-(*R*,*R*)-**4**; Enantiomer (–)-(*S*,*S*)-**22**: $[\alpha]_D^{29}$ –571 (*c* 0.100, DCM) obtained from (–)-(*S*,*S*)-**4**.

References and Notes

1 D. L. Pavia, G. M. Lampman and G. S. Kriz, *Introduction to Spectroscopy*, Brooks/Cole Pub. Co., University of Bellingham, Washington, 4th edn., 2008.

2 a Sigma Aldrich Inc., *www.sigmaaldrich.com*, 2018; b M. Mathews, R. S. Zola, D.-k. Yang and Q. Li, *J. Mater. Chem.*, 2011, **21**, 2098-2103.

3 a T. Yoshioka, T. Ogata, T. Nonaka, M. Moritsugu, S.-N. Kim and S. Kurihara, *Adv. Mater. (Weinheim, Ger.)*, 2005, **17**, 1226-1229; b M. Z. Alam, T. Yoshioka, T. Ogata, T. Nonaka and S. Kurihara, *Liq. Cryst.*, 2007, **34**, 1215-1219.

4 a S. M. Morris, M. M. Qasim, K. T. Cheng, F. Castles, D. H. Ko, D. J. Gardiner, S. Nosheen, T. D. Wilkinson, H. J. Coles, C. Burgess and L. Hill, *Appl. Phys. Lett.*, 2013, **103**, 101105; b H. K. Kwon, K. T. Lee, K. Hur, S. H. Moon, M. M. Quasim, T. D. Wilkinson, J. Y. Han, H. Ko, I. K. Han, B. Park, B. K. Min, B. K. Ju, S. M. Morris, R. H. Friend and D. H. Ko, *Adv. Energy Mater.*, 2015, **5**, 1401347; c O. Jin, D. Fu, Y. Ge, J. Wei and J. Guo, *New J. Chem.*, 2015, **39**, 254-261.

5 D. L. Jameson, T. Field, M. R. Schmidt, A. K. DeStefano, C. J. Stiteler, V. J. Venditto, B. Krovic, C. M. Hoffman, M. T. Ondisco and M. E. Belowich, *J. Org. Chem.*, 2013, **78**, 11590-11596.

6 D. Didier, B. Tylleman, N. Lambert, C. M. L. Vande Velde, F. Blockhuys, A. Collas and S. Sergeyev, *Tetrahedron*, 2008, **64**, 6252-6262.

7 B. G. Bag and U. Maitra, *Synth. Commun.*, 1995, **25**, 1849-1856.

8 Y. Hamada and S. Mukai, *Tetrahedron Asymmetry*, 1996, **7**, 2671-2674.

9 a M. Kazem-Rostami, *Synlett*, 2017, **28**, 1641-1645; b A. Tatar, M. Valík, J. Novotná, M. Havlík, B. Dolenský, V. Král and M. Urbanová, *Chirality*, 2014, **26**, 361-367; c Q. M. Malik, S. Ijaz, D. C. Craig and A. C. Try, *Tetrahedron*, 2011, **67**, 5798-5805.

10 CCDC **1902224** and **1902226** contain crystallographic data for this work; These data can be obtained free of charge via www.ccdc.cam.ac.uk (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +441223 336033).