Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Smart Supramolecular Photoresponsive Gelator with Long-alkyl chain Azobenzene Incorporated Sugar Derivatives for Recycling Aromatic Solvents and Sequestration of Cationic Dyes

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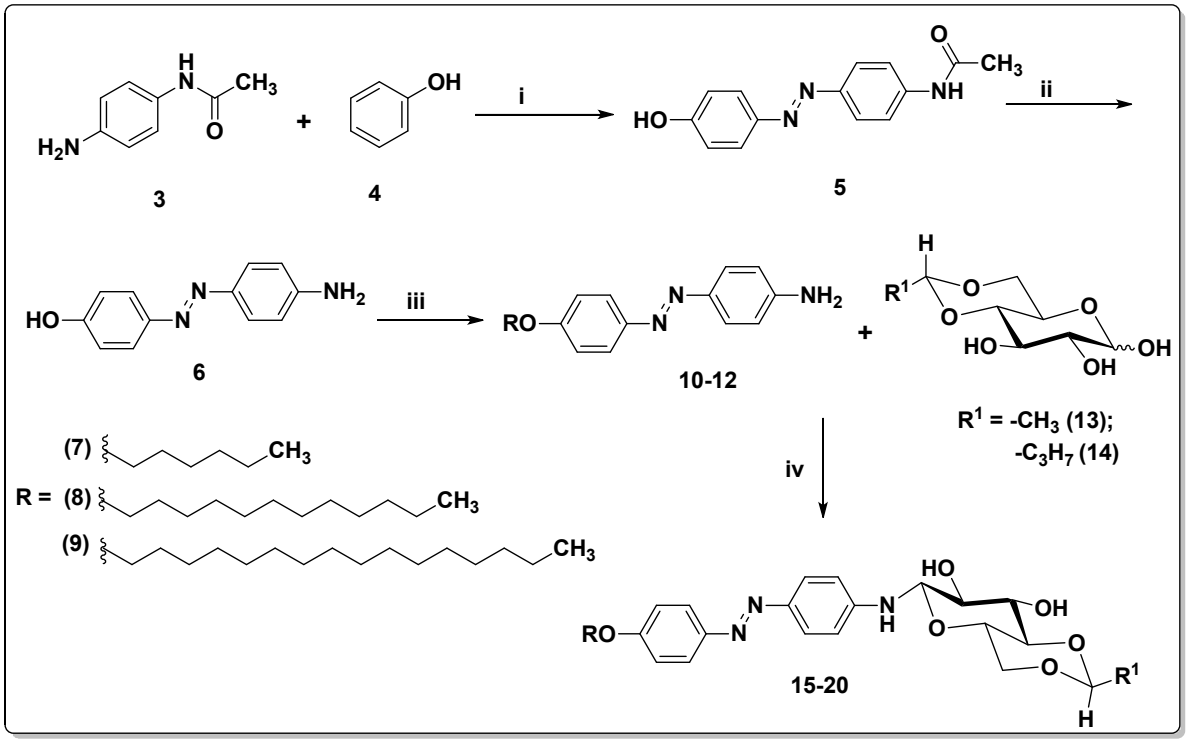


Scheme S1 Synthetic route of long-chain azobenzene based sugar derivatives (**15-20**). Reagents and reaction conditions: i) $NaNO_2$, H_2O:HCl, NaOH, Na_2CO_3, 97%; ii) KOH, 90 ^oC, ethanol, 1h, 75%; iii) R-Br (**7-9**), K_2CO_3, DMF, 90-94%; iv) 4,6-*O*-protected D-glucose (**13** and **14**), ethanol, rt, 78-86%.

Table S1: Gelation test results for the compounds **(15-20)**

Status of compound (CGC%) (mg/mL)						
Solvent	**15**	**16**	**17**	**18**	**19**	**20**
Hexane	I	I	I	I	I	I
H_2O	I	I	I	I	I	I
Cyclohexane	I	I	I	I	I	I
DCM	S	S	S	S	S	S
Ethanol	S	S	S	S	S	S
Methanol	S	S	S	S	S	S
Ethyl acetate	S	S	S	S	S	S

DMF	S	S	S	S	S	S
DMF + Glycerol (1:1)	G (3)	G (3)	G (3)	G (3)	G (3)	G (3)
DMSO	S	S	S	S	S	S
DMSO + Glycerol (1:1)	G (3)	G (3)	G (3)	G (3)	G (3)	G (3)
THF	S	S	S	S	S	S
Diethyl ether	S	S	S	S	S	S
Chloroform	PG	PG	PG	PG	PG	PG
Acetonitrile	G (0.5)	G (0.5)	G (0.4)	G (0.4)	G(0.4)	G(0.4)
Toluene	G(0.6)	G (0.5)	G (0.5)	G (0.4)	G (0.4)	G (0.4)
Benzene	G (0.6)	G (0.6)	G (0.5)	G (0.5)	G (0.5)	G (0.5)
NO_2-benzene	S	S	S	S	S	S
Glycerol	I	I	I	I	I	I
1-Heptanol	G (1.5)	G (1.5)	G (1.5)	G (1.4)	G (1.3)	G (1.3)
t-butyl alcohol	S	S	S	S	S	S
1-butanol	P	P	P	P	P	P
1,2-dichloroethane	S	S	S	S	S	S
1,2-dichlorobenzene	G (1.6)	G (1.6)	G (1.6)	G (1.6)	G (1.5)	G (1.5)
1,2-dichloromethane	S	S	S	S	S	S
2-methoxy ethanol	S	S	S	S	S	S
2-propanol	P	P	P	P	P	P
Petrol	S	S	S	S	S	S
Kerosene	P	P	P	P	P	P
Coconut oil	S	S	S	S	S	S

S- soluble, G- stable gel formed at RT, PG- partial gel formation at RT, P- precipitate, I- insoluble. CGC- critical gelation concentration (mg/mL), which corresponds to the minimum concentration of a gelator necessary to induce gelation of the solvent.

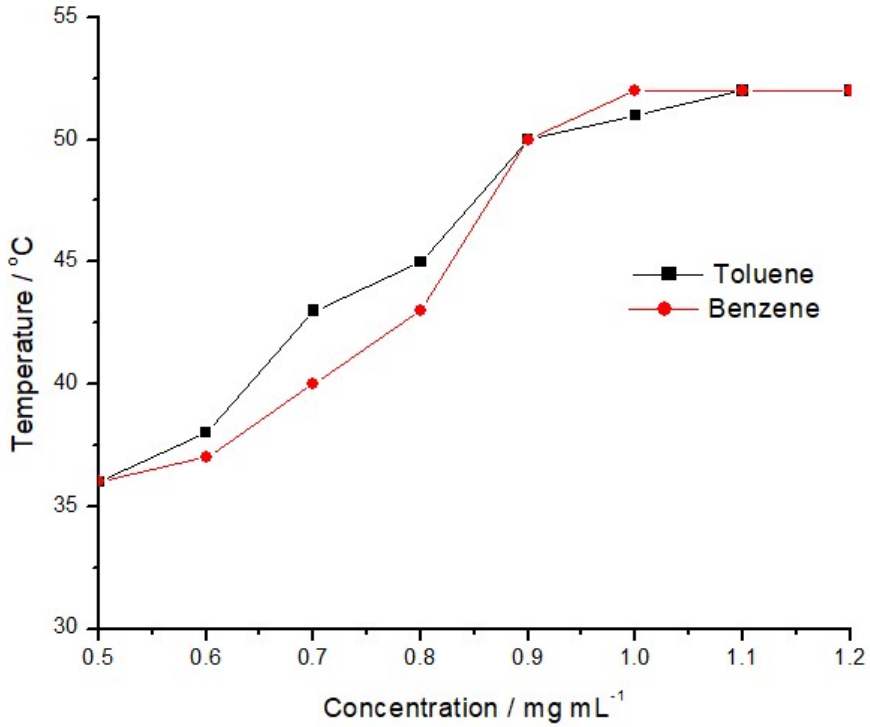
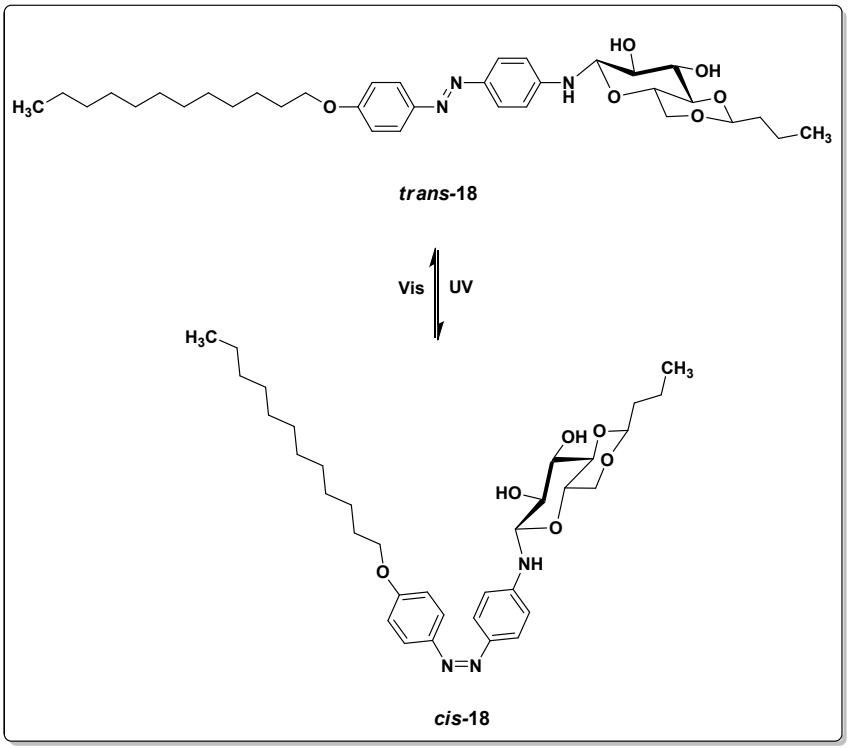


Fig. S1 Concentration-dependent phase-transition temperature (T_{gel}) of compound **18** in toluene and benzene.



Scheme S2 Schematic representation of UV-Vis induced *trans*–*cis* isomerization of gelator **18**.

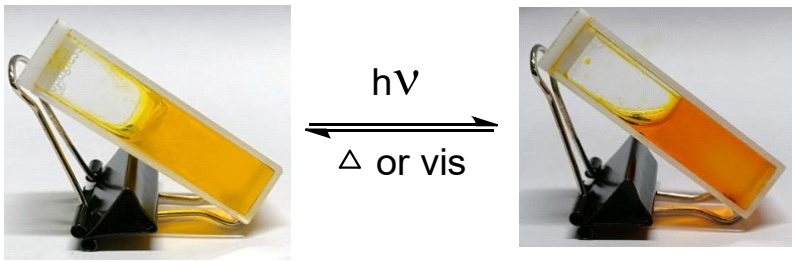


Fig. S2 Gel-sol transition photograph of compound **18** in toluene.

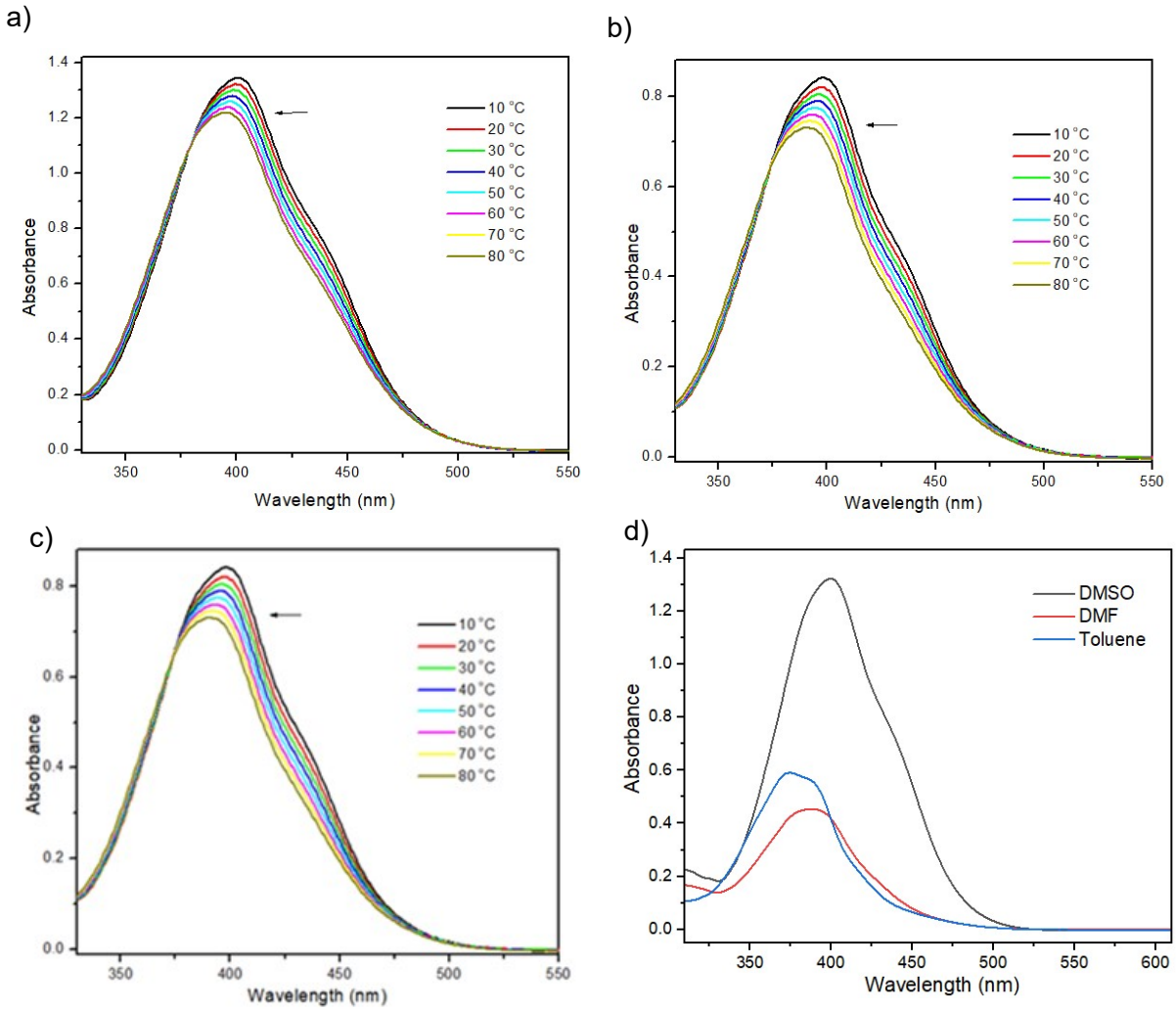
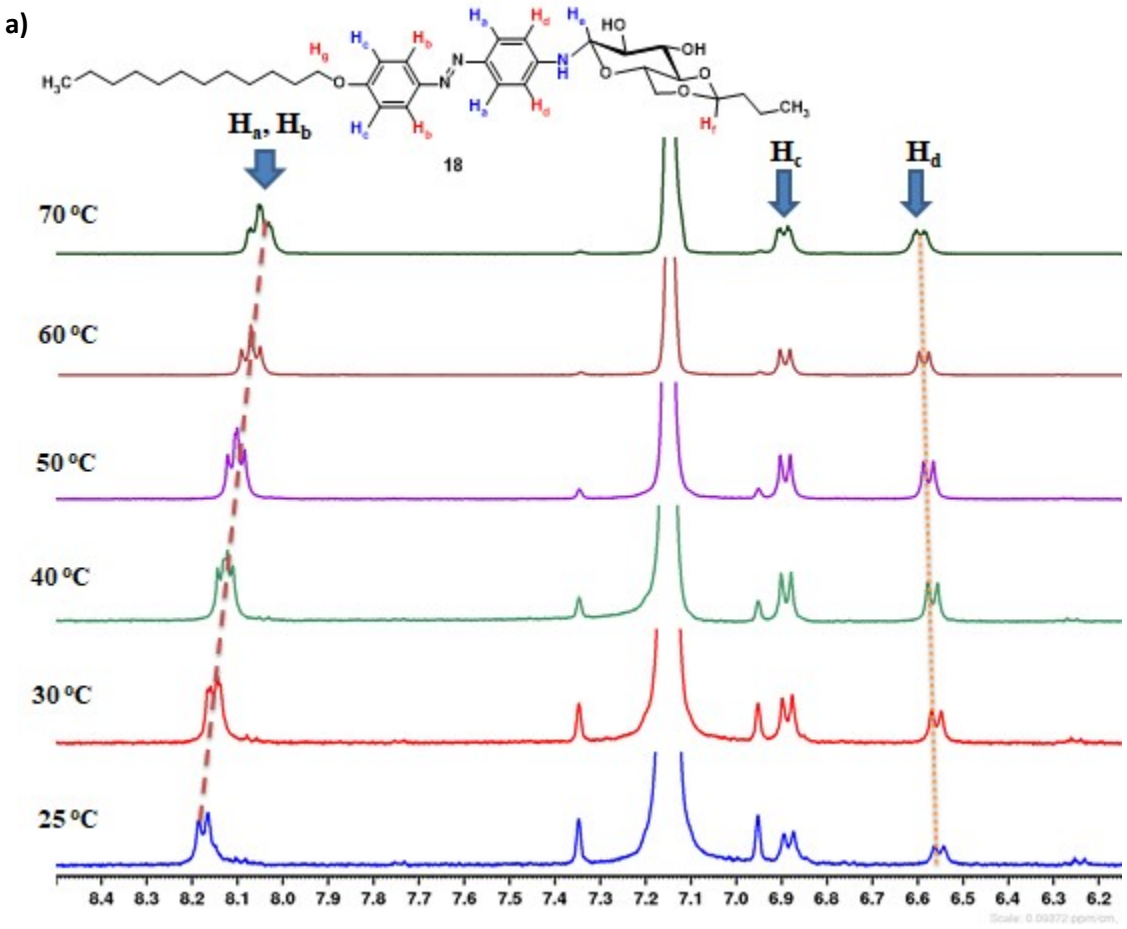


Fig. S3 a) Temperature-dependent absorption studies of compound **18** ($1x10^{-5}$ M) in DMSO (a), toluene (b) and DMF (c); b) Solvatochromism behaviour of compound **18** in different solvents such as DMSO, DMF, Toluene.

a)



b)

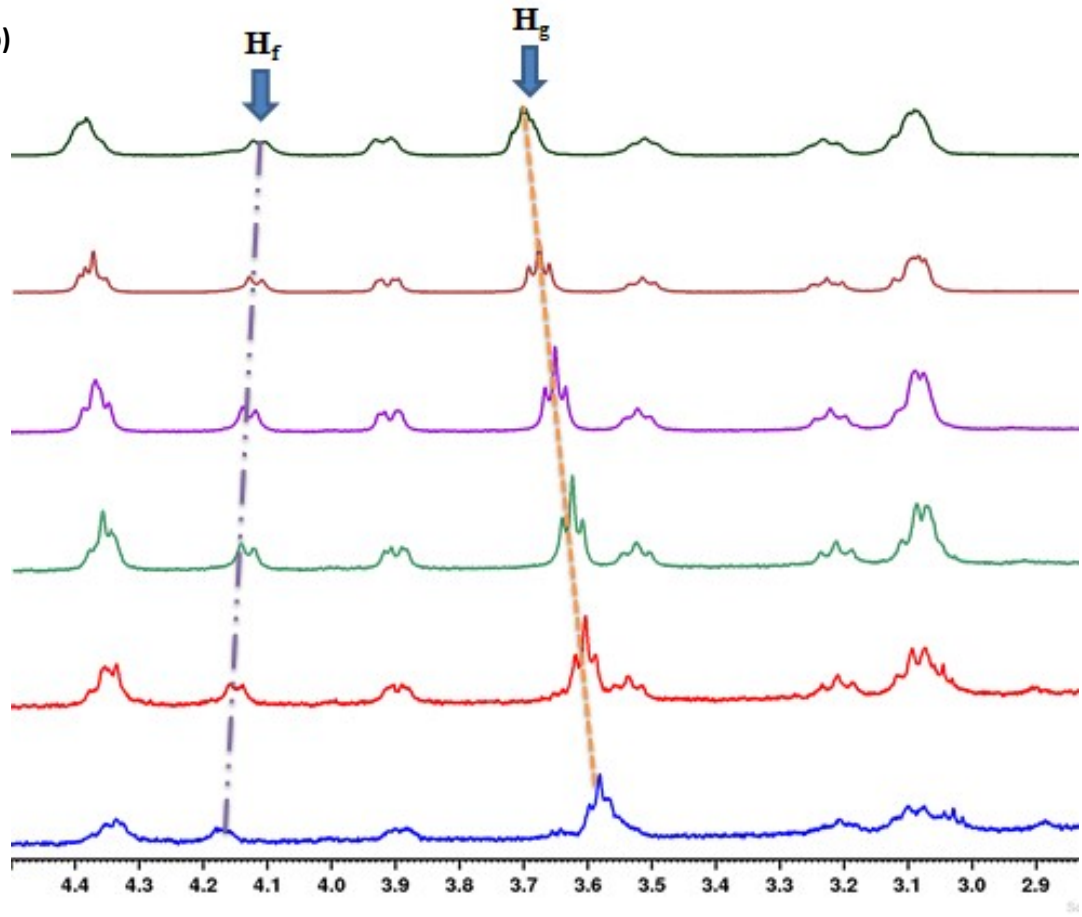


Fig. S4 Partial ^{1}H NMR studies of compound **18** (10 mg/ml) in Benzene-d_6 at temperatures of 25 °C, 30 °C, 40 °C, 50 °C, 60 °C, 70 °C, and 80 °C; a) aromatic region and b) saccharide region.

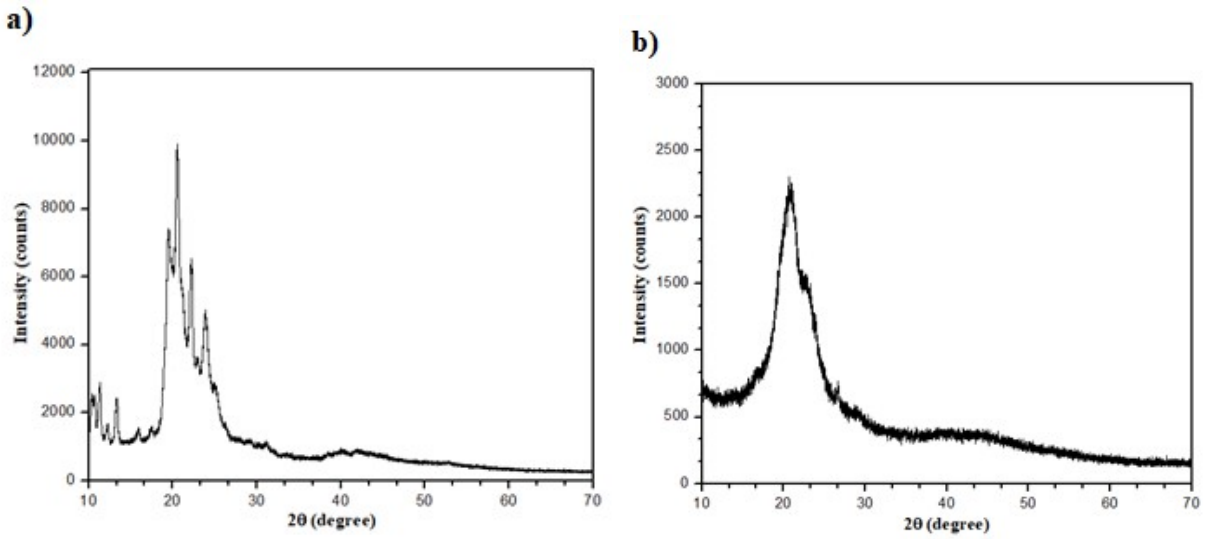


Fig. S5 PXRD patterns of compound **18** a) powder state and b) xerogel state (from its toluene gel) at room temperature.

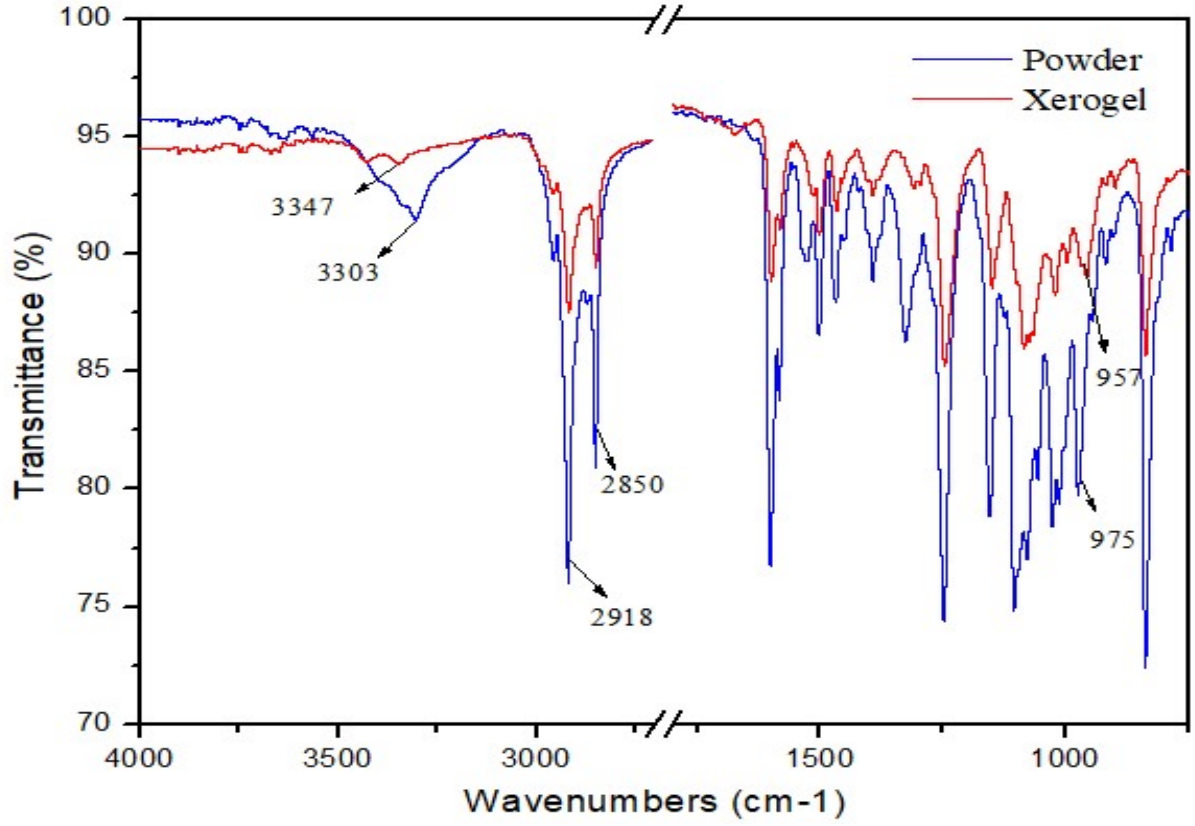


Fig. S6 FT-IR spectra of compound **18** in powder state and xerogel state (from its toluene gel)

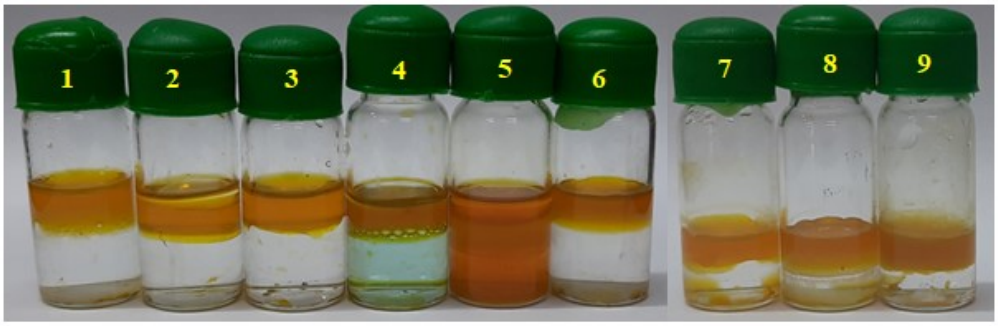


Fig. S7 Photograph showing the phase-selective gelation of compound **18** from a mixture of benzene and aqueous mixture (1:2, v/v) in the presence of 1) tap water, 2) sat. NaCl, 3) sat. $CaCl_2$, 4), $CuSO_4$, 5) $FeCl_3$, 6) $ZnCl_2$, 7) tetrabutyl ammonium sulphate, 8) tetrabutyl ammonium chloride and 9) tetrabutyl ammonium bromide.

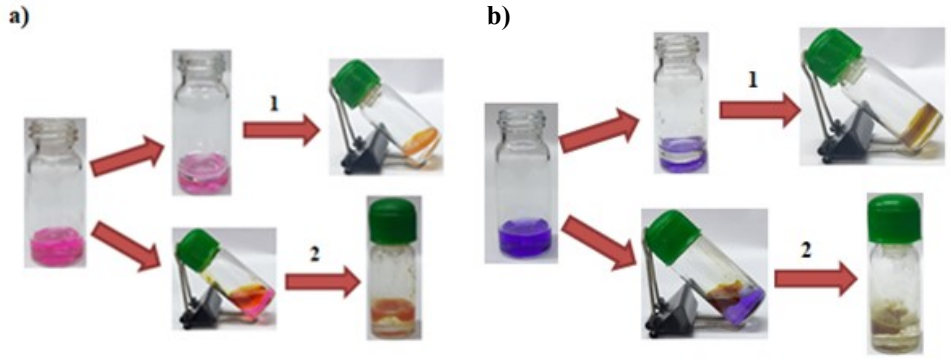


Fig. S8 Photographs of dyes removed from aqueous solution by PSG **18** in different methods. a) RhB and b) CV

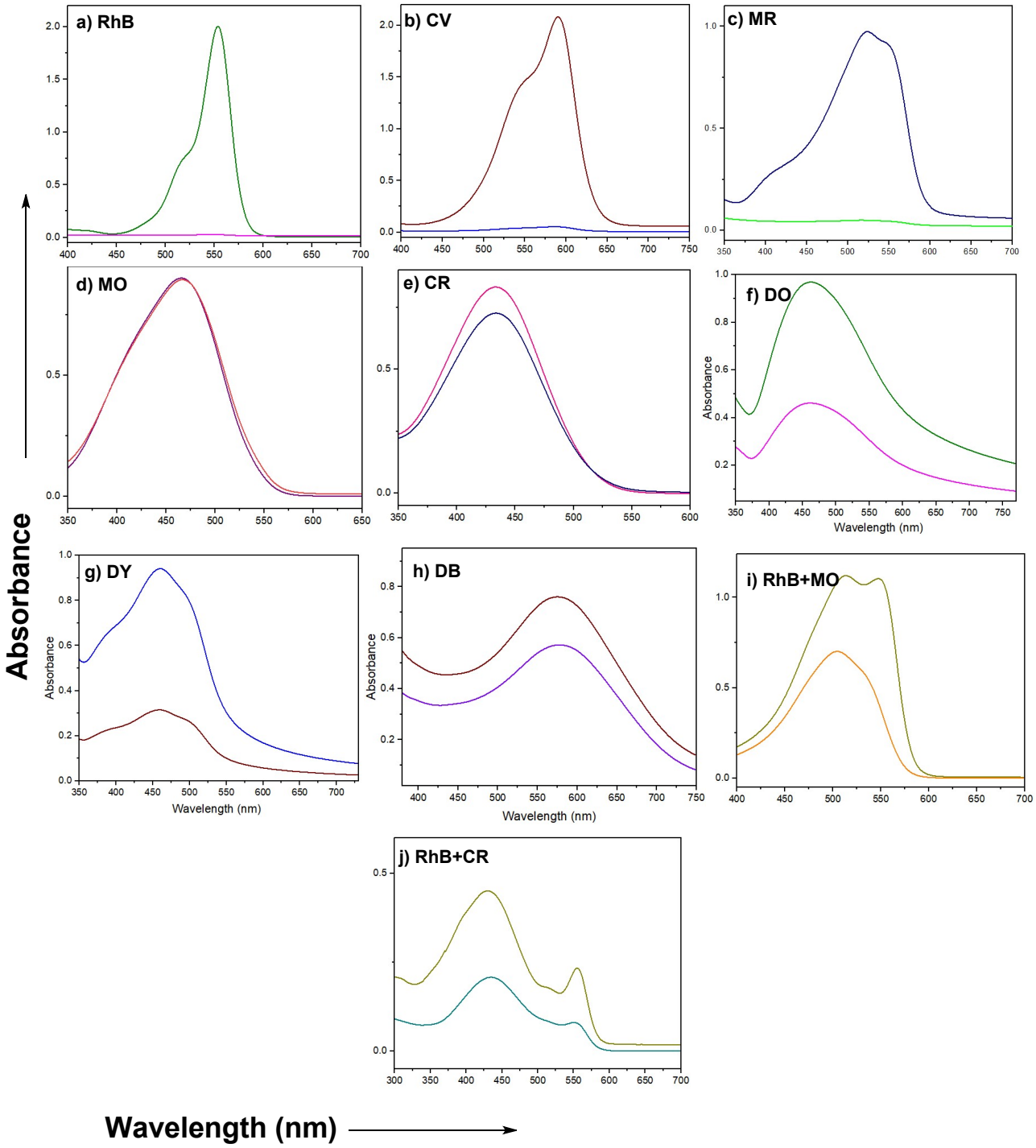


Fig. S9 UV-Vis spectra representing dye adsorption by compound **18**, before and after adsorption (24h) by using benzene gel, a) RhB, b) CV, c) MR, d) MO, e) CR, f) DO, g) DY, h) DB, i) RhB/CR, and j) RhB/MO.

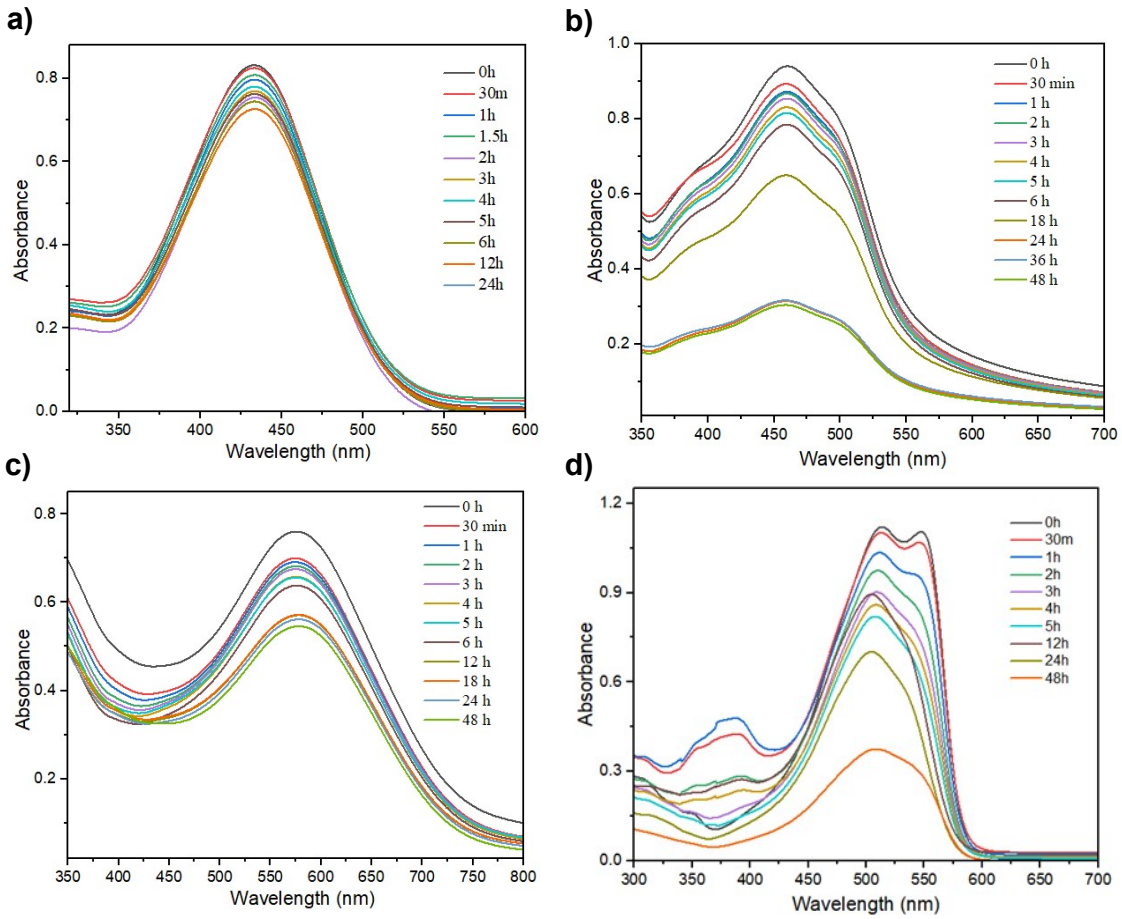
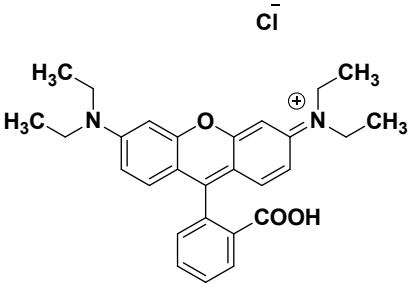
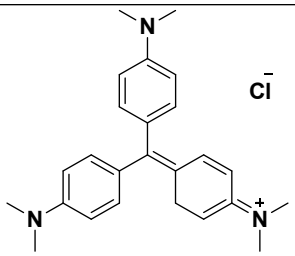
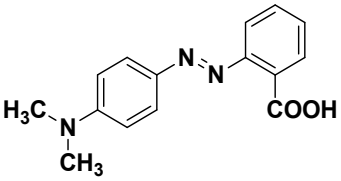
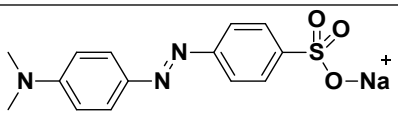
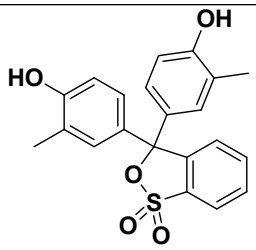
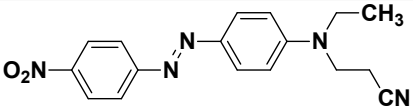
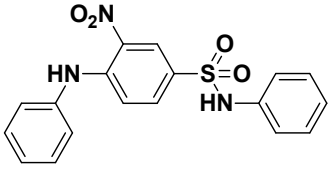
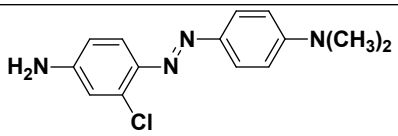


Fig.S10 a) CR, b) DY, c) DB and d) RhB + MO mixture (1:1, v/v).

Table S2 Dye absorption efficiencies towards by benzene gel of compound **18** with various cationic and anionic dyes

Dye	**Dye structure**	**Nature of the dye molecules**	**Efficiency (%)**
Rhodamine B		Cationic	98

Crystal Violet		Cationic	97
Methyl red		Cationic	92
Methyl orange		Anionic	8
Cresol red		Anionic	12
Rhodamine B + Cresol red	-	Cationic + Anionic	58
Rhodamine B + Methyl orange	-	Cationic + Anionic	65
Disperse Orange 25		Non-ionic	54
Disperse Yellow 42		Non-ionic	68
Disperse Black 7		Non-ionic	28

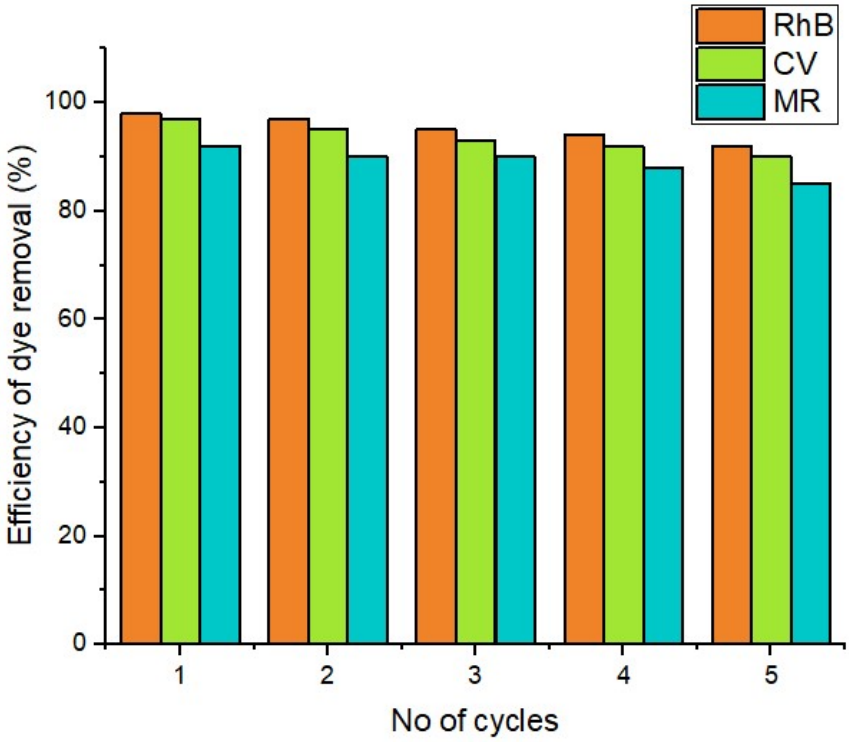


Fig. S11 Bar diagram showing the reusability of gelator molecule **18** after absorption of dyes (Rhodamine B, Crystal Violet and Methyl red).

Materials and Characterization

Octyl bromide, dodecyl bromide, hexadecyl bromide, and potassium carbonate were purchased from Sigma Aldrich Pvt Ltd, USA with high purity. The materials purchased from SRL, Merck India are **D**-glucose, sodiumnitrite, sodiumcarbonate, sodiumhydroxide, and sodiumsulphate. The reagents such as ethanol, dimethylformamide (DMF), ethylacetate, concentrated hydrochloricacid, and other solvents were purchased from Merck, India in high purity and were used without any further purification. The reactions were monitored under thin layer chromatography (TLC) and were purified using columnchromatography which was performed on silica gel (100-200 mesh). The structures of the synthesized compounds were determined by using BRUKER 400 MHz Nuclear Magnetic Resonance (NMR) technique through the observed chemical shift of nuclei. The absorption spectra of the sample were recorded by JascoV-670 UV-NIR spectrophotometer and the corresponding excitation wavelength was noted for the sample. High-resolution mass spectroscopy was measured on Thermo Scientific Exactive™ Plus

Orbitrap Mass Spectrometer. Powder X-ray Diffraction was obtained on a PANalytical Empyrean-3. FE-SEM analysis was measured on FESEM: Quattro S, FEI Company of USA (S.E.A) PTE LTD, Singapore.

Synthesis of compound 5:

To a 4-aminoacetanilide **3** (3 g, 20 mmol), a mixture of 50 mL of water and 9 mL of hydrochloric acid (5:1) was added and kept in an ice-cold condition. Meanwhile, sodiumnitrite (2 g, 29 mmol) dissolved in 50 mL of water was also kept in ice-cold condition. Simultaneously, the sodium nitrite solution was slowly added to the mixture containing 4-aminoacetanilide dropwise. This led to the formation of a diazonium ion. In a separate round bottom flask containing a mixture of sodiumcarbonate (8 g, 75 mmol), sodiumhydroxide (1.04 g, 25 mmol), and phenol **4** (2.7 g, 21 mmol) was dissolved in 50 mL of water and kept in the ice bath. In the meantime, the diazonium mixture was added to the reaction mixture dropwise under stirring. The reaction was monitored through TLC. The resultant orange color precipitate thus obtained was acidified with conc. hydrochloric acid until the pH becomes neutral. Then, the precipitate was washed with water and dried for one day to give an orange solid. The crude was purified by column chromatography (SiO_2, hexane/EtOAc, 1 : 1), and it was obtained as orange solid in 97% yield; ^{1}H NMR (400 MHz, DMSO-d_6+$CDCl_3$): δ 10.15 (s, 2H, Ar-H), 7.75 (s, 5H, Ar-H, -NH), 6.90 (d, J = 8.0 Hz, 2H, Ar-H), 3.47 (s, 1H, -OH), 2.08 (s, 3H, -CH_3); ^{13}C NMR (100 MHz, DMSO-d_6+$CDCl_3$): δ 168.5, 160.4, 147.6, 145.3, 141.3, 124.3, 122.9, 119.1, 115.7, 24.1. HR-MS cald. for $C_{14}H_{13}N_3O_2$ $[M]^+$ 256.10805, Found 256.10872 $(M + H)^+$.

Synthesis of compound 6: To an absolute ethanolic solution of compound **5** (1 g, 1 eq.), potassiumhydroxide (6.26 g, 7 eq.) dissolved in 7:3 of ethanol/water was added and reflux for 1hr at 90 ^{o}C. The product formation was monitored by TLC. Once the reaction gets completed it was allowed to cool at room temperature, then extracted three times with ethyl acetate and dried over anhydrous sodium sulfate. The desired product thus obtained is a dark brown color precipitate and it was purified by column chromatography (SiO_2, hexane/EtOAc, 2 : 1), and it was obtained as dark orange solid in 75% yield; ^{1}H NMR (400 MHz, DMSO-d_6+$CDCl_3$): δ 7.66-7.59 (dd, J = 8.4 Hz, 8.6 Hz, 4H, Ar-H), 6.87 (d, J = 8.4 Hz, 2H, Ar-H), 6.65 (d, J = 8.4 Hz, 2H, Ar-H),

5.85 (s, 2H, -NH), 3.43 (s, 1H, -OH); ^{13}C NMR (100 MHz, DMSO-d_6+$CDCl_3$): δ 159.1, 151.8, 145.5, 142.9, 124.4, 123.6, 115.6, 113.7, 113.4. HR-MS cald. for $C_{12}H_{11}N_3O$ $[M]^+$ 214.09749, Found 214.09781 $(M + H)^+$.

General procedure for the synthesis of compounds (10-12)

A mixture of 4-((4-aminophenyl)diazenyl)phenol **6** (4.7 mmol) and excess anhydrous potassium carbonate (6.1 mmol) were dissolved in DMF and alkylbromide, **5-7** (7 mmol) was added to the reaction mixture and reflux for 1 hr at 80 ^{o}C. The reaction was monitored through TLC, the product was transferred to ice and extracted three times with ethylacetate and dried over anhydrous sodiumsulfate. Then, the product was purified by column chromatography on silica gel with hexane/ethylacetate (8:2, v/v) as eluent to give desired pure product as a yellow color powder.

Physicochemical and spectral data for compound, 10**:** Yield= 94 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 9.2 Hz, 2H, Ar-H), 7.76 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.97 (d, *J* = 9.2 Hz, 2H, Ar-H), 6.73 (d, *J* = 8.8 Hz, 2H, Ar-H), 4.032-3.99 (m, 4H, Ali-OCH_2, -NH_2), 1.84-1.77 (m, 2H, Ali-H), 1.60 (s, 1H, Ali-H), 1.47 (m, 2H, Ali-H), 1.29 (m, 7H, Ali-H), 0.89 (t, *J* = 6.9Hz, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9, 149.1, 147.1, 145.8, 124.7, 124.2, 114.9, 114.7, 68.4, 31.9, 29.5, 29.4, 29.4, 26.2, 22.8, 14.3.

Physicochemical and spectral data for compound, 11**:** Yield= 90 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 10.4 Hz, 2H, Ar-H), 7.77 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.97 (d, *J* = 8.9 Hz, 2H, Ar-H), 6.73 (d, *J* = 8.8 Hz, 2H, Ar-H), 4.032-3.99 (m, 4H, Ali-OCH_2, -NH_2), 1.84-1.77 (m, 2H, Ali-H), 1.64 (s, 1H, Ali-H), 1.50-1.43 (m, 2H, Ali-H), 1.37-1.31 (m, 15H, Ali-H), 0.89 (t, *J* = 6.8 Hz, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 149.1, 147.2, 145.9, 124.8, 124.2, 114.9, 114.8, 68.5, 32.1, 29.9, 29.8, 29.6, 29.5, 29.4, 26.2, 22.9, 14.3. HR-MS cald. for $C_{24}H_{36}N_3O$ $[M]^+$ 382.28458, Found 38228529 $(M + H)^+$.

Physicochemical and spectral data for compound, 12**:** Yield= 90 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.76 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.97 (d, *J* = 9 Hz, 2H, Ar-H), 6.73 (d, *J* = 8.8 Hz, 2H, Ar-H), 4.032-3.98 (m, 4H, Ali-OCH_2, -NH_2), 1.84-1.77 (m, 2H, Ali-H), 1.61 (s, 1H, Ali-H), 1.49-1.45 (m, 2H, Ali-H), 1.37-1.26 (m, 23H, Ali-H), 0.88 (t, *J* = 6.8 Hz, 3H, Ali-CH_3); ^{13}C NMR (100

MHz, $CDCl_3$): δ 160.8, 148.9, 147.0, 145.6, 124.9, 124.6, 124.3, 124.0, 115.0, 114.7, 114.6, 68.3, 32.8, 31.9, 29.7, 29.6, 29.4, 29.2, 26.0, 25.7, 22.7, 14.1. HR-MS cald. for $C_{28}H_{44}N_3O$ $[M]^+$, 438.34789, Found 438.34832 $(M + H)^+$.

General procedure for the synthesis of N-glycosyl amines (15-20)

To a solution of 1.0 mmol of the 4,6-*O*-protected-*β*-**D**-glucopyranose (**13/14**) in 10 ml of absolute ethanol, was added 1.2 mmol of azobenzene based amines (**10-12**). The reaction was then stirred at room temperature, the reactants dissolved within 5-10 minutes. The completion of the reaction was confirmed through the TLC. The solid which separates was filtered off, washed several times with ethanol and diethyl ether to get desired pure product as bright yellow powder.

Physicochemical and spectral data for compound, 15**:** Yield= 86%; ^{1}H NMR (400 MHz, $CDCl_3$+DMSO-d_6): δ 7.76 (dd, *J* = 8.4 Hz, *J* = 6.3 Hz, 4H, Ar-H), 6.89 (dd, *J* = 8.7 Hz, 2H, Ar-H), 6.40 (m, 2H, Ar-H), 5.23-5.12 (m, 2H, Sac-H), 4.78-4.64 (m, 2H, -NH, Sac-H), 4.29-4.01 (m, 3H, Sac-H, Ano-H), 4.02 (t, *J* = 6.4 Hz, 2H, O-CH_2), 3.69-3.46 (m, 6H, Sac-H), 2.16 (m, 1H, Ali-H), 1.82-1.78 (m, 2H, Ali-H), 1.48-1.29 (m, 10H, Ali-H), 0.89 (t, *J* = 6.74 Hz, 3H, Ali-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$+DMSO- d_6): δ 160.4, 148.9, 146.5, 145.0, 124.1, 123.6, 114.3, 113.2, 99.1, 99.0, 92.9, 85.6, 82.8, 80.9, 80.2, 73.7, 73.6, 73.1, 71.5, 70.2, 68.3, 67.9, 66.8, 61.8, 31.4, 29.0, 28.8, 25.6, 22.3, 20.2, 13.9; HR-MS cald. for $C_{28}H_{39}N_3O_6$ $[M]^+$ 514.29116, Found 514.29180 $(M + H)^+$.

Physicochemical and spectral data for compound, 16**:** Yield= 84%; -^{1}H NMR (400 MHz, $CDCl_3$+DMSO-d_6): δ 7.75-7.67 (m, 4H, Ar-H), 6.90-6.86 (m, 2H, Ar-H), 6.74-6.70 (m, 2H, Ar-H), 5.54 (t, *J* = 5.9 Hz, 1H, Sac-H), 4.81 (t, *J* = 4.5 Hz, 1H, Sac-H), 4.61-4.56 (m, 1H, Sac-H), 4.50-4.48 (m, 1H, Sac-H), 4.14-4.11 (m, 1H, Sac-H), 3.95-3.91 (m, 2H, Sac-H), 3.72-3.70 (m, 1H, Sac-H), 3.45-3.38 (m, 3H, Sac-H), 3.29-3.27 (m, 1H, Sac-H), 2.37 (d, 3H, Sac-H, -NH), 1.74-1.69 (m, 2H, Ali-H), 1.61- 1.58 (m, 2H, Ali-H), 1.38-1.20 (m, 10H, Ali-H, Sac-H), 0.86-0.78 (m, 6H, Sac-H, Ali-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6); δ 160.8, 148.3, 146.9, 145.9, 124.4, 124.0, 114.6, 113.7, 102.4, 86.0, 80.2, 74.2, 74.0, 68.2, 67.4, 40.2, 40.0, 39.8, 36.2, 31.7, 29.3, 29.2, 26.0, 22.6, 17.4, 14.1, 13.9; HR-MS cald. for $C_{30}H_{43}N_3O_6$ $[M]^+$ 542.32246, Found 542.32395 $(M + H)^+$.

Physicochemical and spectral data for compound, 17**:** Yield= 88%; ^{1}H NMR (400 MHz, $CDCl_3$+DMSO-d_6): δ 7.80 (t, *J* = 15.3 Hz, 4H, Ar-H), 6.95 (d, *J* = 8.9 Hz, 2H, Ar-H), 6.82 (d, *J* = 8.6 Hz, 2H, Ar-H), 4.79-4.64 (m, 3H, Sac-H), 4.18 (d, *J* = 6.0 Hz, 1H, -NH), 3.99 (t, *J* = 6.4 Hz, 2H, O-CH_2), 3.84 (t, *J* = 8.8 Hz, 1H, Ano-H), 3.72-3.67 (q, *J* = 7 Hz, 4H, Sac-H), 3.54-3.46 (m, 2H, Sac-H), 3.34 (t, *J* = 8.7 Hz, 1H, Sac-H), 2.82 (s, 1H, Sac-H), 2.69 (s, 1H, Sac-H), 2.15 (s, 1H, Sac-H), 1.80-1.76 (m, 2H, Ali-H), 1.57 (s, 7H, Ali-H), 1.44-1.20 (m, 10H, Ali-H), 0.85 (t, *J* = 6.74 Hz, 3H, Ali-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6): δ 160.3, 150.0, 146.4, 146.1, 124.3, 124.0, 123.7, 114.9, 113.2, 98.7, 84.7, 80.5, 73.9, 73.8, 67.9, 67.7, 66.6, 31.4, 29.1, 28.8, 28.7, 25.6, 22.2, 20.5, 14.1; HR-MS cald. for $C_{30}H_{43}N_3O_6$ $[M]^+$ 570.35376, Found 570.35388 $(M + H)^+$.

Physicochemical and spectral data for compound, 18**:** Yield= 87%; ^{1}H NMR (400 MHz, $CDCl_3$+DMSO- d_6): δ 7.85-7.80 (m, 4H, Ar-H), 6.97 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.84 (d, *J* = 8.8 Hz, 2H, Ar-H), 4.79 (t, *J* = 8.5 Hz, 1H, Sac-H), 4.70 (d, *J* = 8.6 Hz, 1H, Sac-H), 4.57 (t, *J* = 5.1 Hz, 1H, Sac-H), 4.22-4.19 (dd, *J* = 3.2 Hz, *J* = 3.7 Hz, 1H, Sac-H), 4.01 (t, *J* = 6.6 Hz, 2H, Sac-H), 3.88-3.83 (m, 1H, Sac-H), 3.73-3.70 (m, 1H, Sac-H), 3.56-3.46 (m, 3H, Sac-H), 3.34 (t, *J* = 9.1 Hz, 1H, Sac-H), 2.84 (s, 1H, Sac-H), 2.75 (s, 1H, Sac-H), 2.17 (s, 1H, -NH), 1.84-1.77 (quint, *J* = 7.0 Hz, 2H, Ali-CH_2), 1.67-1.60 (m, 6H, Ali-H), 1.48-1.22 (m, 14H, Ali-H & Sac-H), 0.93 (t, *J* = 7.3 Hz, 3H, Sac-H), 0.87 (t, *J* = 6.6 Hz, 3H, Ali-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6): δ 160.4, 150.0, 146.5, 144.2, 124.3, 114.9, 113.2, 101.5, 84.9, 80.6, 74.0, 73.9, 68.0, 67.9, 67.0, 36.2, 31.5, 29.3, 29.2, 29.0, 28.9, 28.8, 25.7, 22.3, 18.7, 17.3, 14.1, 14.0; HR-MS cald. for $C_{34}H_{51}N_3O_6$ $[M]^+$ 598.38506, Found 598.38559 $(M + H)^+$.

Physicochemical and spectral data for compound, 19**:** Yield= 84%; ^{1}H NMR (400 MHz, $CDCl_3$+DMSO-d_6): δ 7.82 (t, *J* = 10.2 Hz, 4H, Ar-H), 6.96 (d, *J* = 8.9 Hz, 2H, Ar-H), 6.83 (d, *J* = 8.8 Hz, 2H, Ar-H), 4.78-4.74 (m, 3H, Sac-H), 4.21 (d, *J* = 5.7 Hz, 1H, -NH), 4.01 (t, *J* = 6.6 Hz, 2H, O-CH_2), 3.86 (t, *J* = 9.4 Hz, 1H, Ano-H), 3.74-3.69 (q, *J* = 6.8 Hz, 3H, Sac-H), 3.56-3.47 (m, 3H, Sac-H), 3.36 (t, *J* = 8.9 Hz, 1H, Sac-H), 2.90 (d, *J* = 8.0 Hz, 2H, Sac-H), 2.21-2.11 (m, 2H, Sac-H), 2.00 (s, 1H, Sac-H), 1.82-1.78 (m, 2H, Ali-H), 1.63 (s, 7H, Ali-H), 1.39-1.22 (m, 16H, Ali-H), 0.87 (t, *J* = 6.8 Hz, 3H, Ali-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6): δ 161.4, 146.8, 124.4, 124.2, 114.6,

114.5, 99.7, 80.0, 74.4, 68.2, 67.6, 58.5, 31.9, 30.9, 29.7, 29.6, 29.6, 29.3, 26.2, 26.0, 22.7, 20.30, 18.4, 14.1; HR-MS cald. for $C_{36}H_{55}N_3O_6$ $[M]^+$ 626.41632, Found 626.41632 $(M + H)^+$.

***Physicochemical and spectral data for compound, 20*:** Yield= 82%; ^{1}H NMR (400 MHz, $CDCl_3$+DMSO-d_6): δ 7.84-7.79 (m, 4H, Ar-H), 6.97 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.84 (d, *J* = 8.8 Hz, 2H, Ar-H), 4.78 (t, *J* = 8.3 Hz, 1H, Sac-H), 4.70 (d, *J* = 8.5 Hz, 1H, Sac-H), 4.57 (t, *J* = 5.04 Hz, 1H, Sac-H), 4.22-4.19 (dd, *J* = 3.4Hz, *J* = 3.72 Hz, 1H, Sac-H), 4.01 (t, *J* = 6.6 Hz, 2H, Sac-H), 3.85 (t, J = 8.8 Hz, 1H, Sac-H), 3.56-3.45 (m, 3H, Sac-H), 3.34 (t, *J* = 8.9 Hz, 1H, Sac-H), 2.87 (s, 1H, Sac-H), 2.79 (s, 1H, Sac-H), 2.17 (s, 1H, -NH), 1.84-1.77 (quint, *J* = 7.0 Hz, 2H, Ali-CH_2), 1.66 - 1.60 (m, 5H, Ali-H), 1.48 - 1.25 (m, 24H, Ali-H, Sac-H), 0.93 (t, *J* = 7.4 Hz, 3H, Sac-H), 0.87 (t, *J* = 6.8 Hz, 3H, Ali-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$+DMSO- d_6): δ 161.3, 147.5, 147.2, 147.0, 124.7, 124.5, 114.9, 114.8, 102.8, 85.6, 80.3, 74.7, 74.5, 68.6, 67.9, 36.5, 32.2, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 26.3, 22.9, 17.7, 14.4, 14.2; HR-MS cald. for $C_{38}H_{59}N_3O_6$ $[M]^+$ 654.44766, Found 654.44803 $(M + H)^+$.

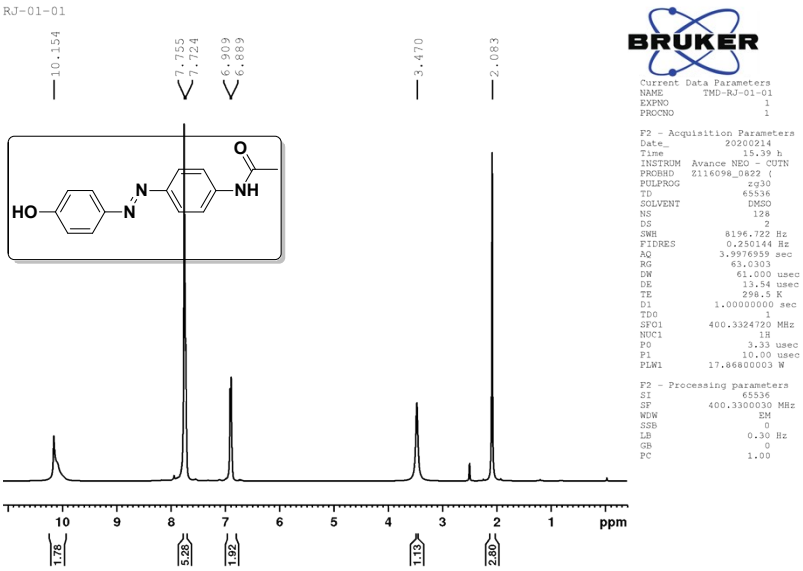


Fig. S12 ^{1}H NMR Spectrum of compound, 5 ($CDCl_3$+DMSO- d_6, 400 MHz)

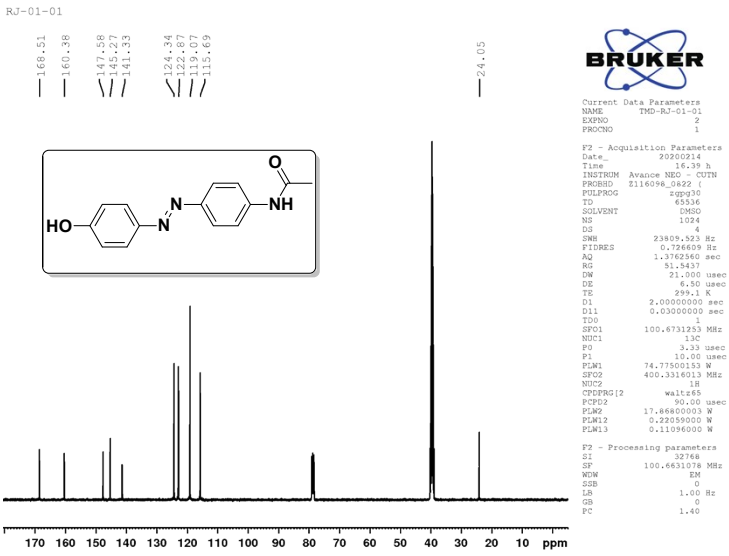


Fig. S13 ^{13}C NMR Spectrum of compound, 5 ($CDCl_3$+DMSO-d_6, 100 MHz)

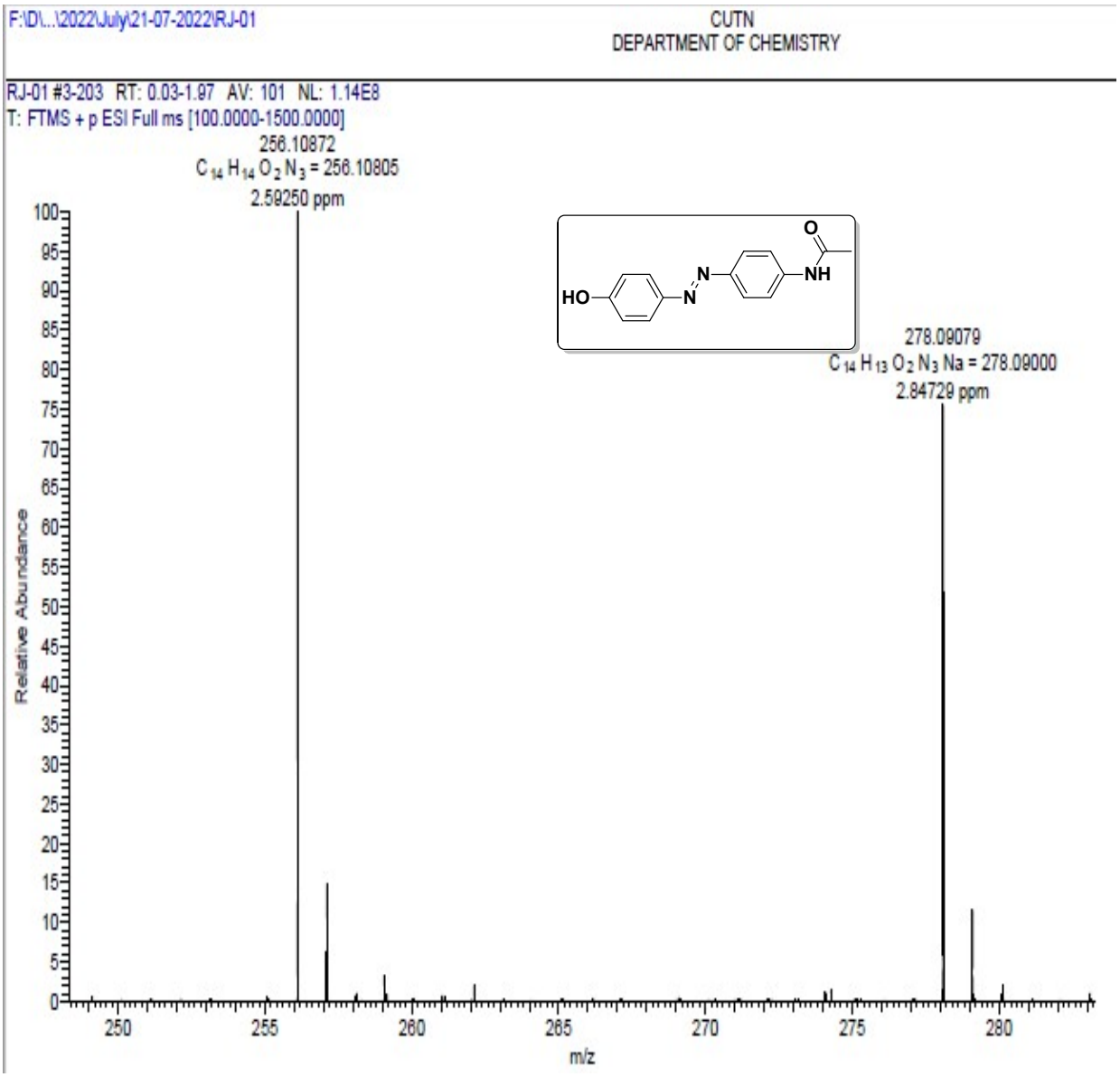


Fig. S14 HR-MS Spectrum of compound, 5

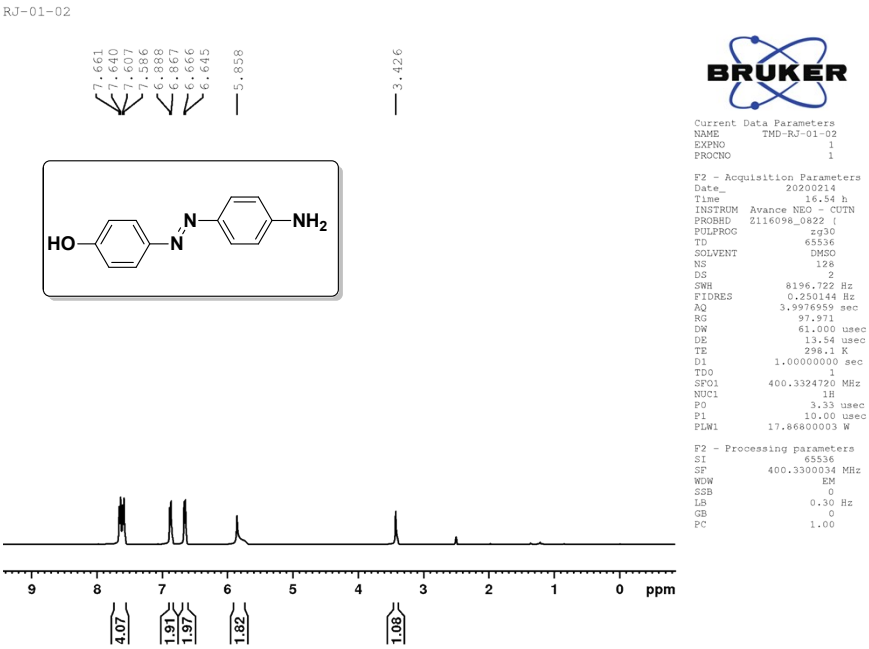


Fig. S15 ^{1}H NMR Spectrum of compound, 6 (CDCl3+DMSO- d_6, 400 MHz)

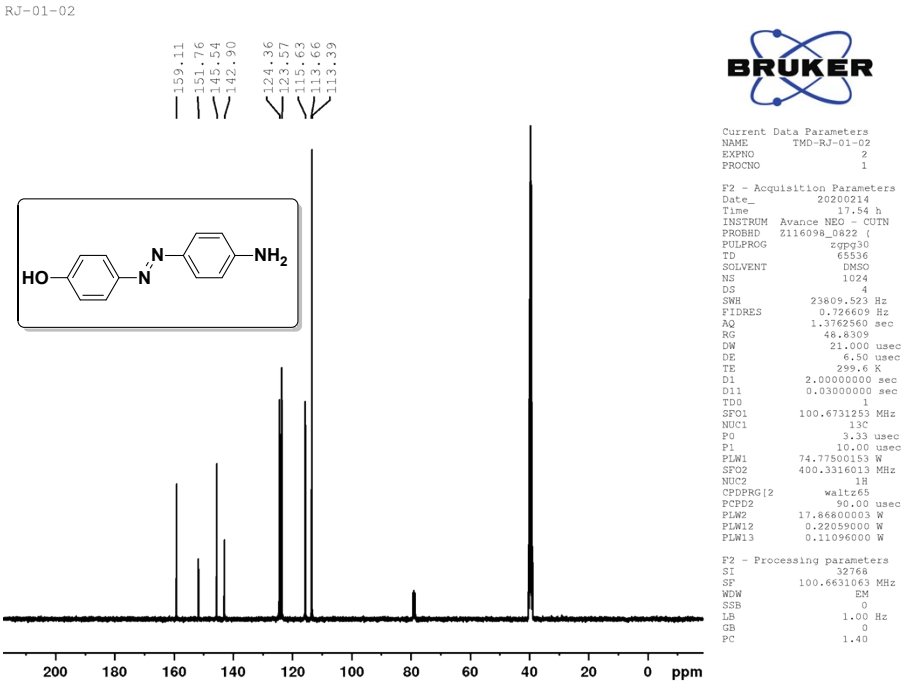


Fig. S16 ^{13}C NMR Spectrum of compound, 6 ($CDCl_3$+DMSO- d_6, 100 MHz)

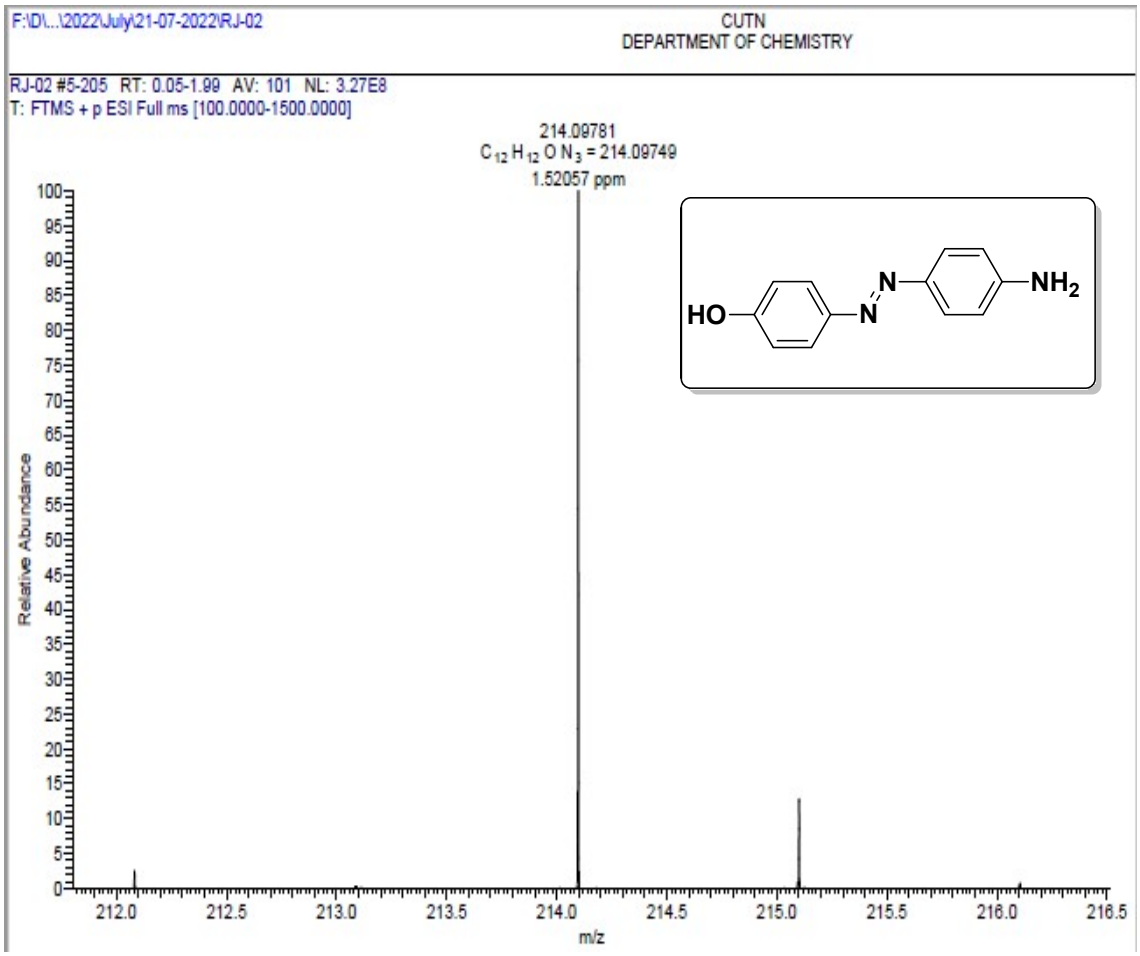


Fig. S17 HR-MS Spectrum of compound, 6

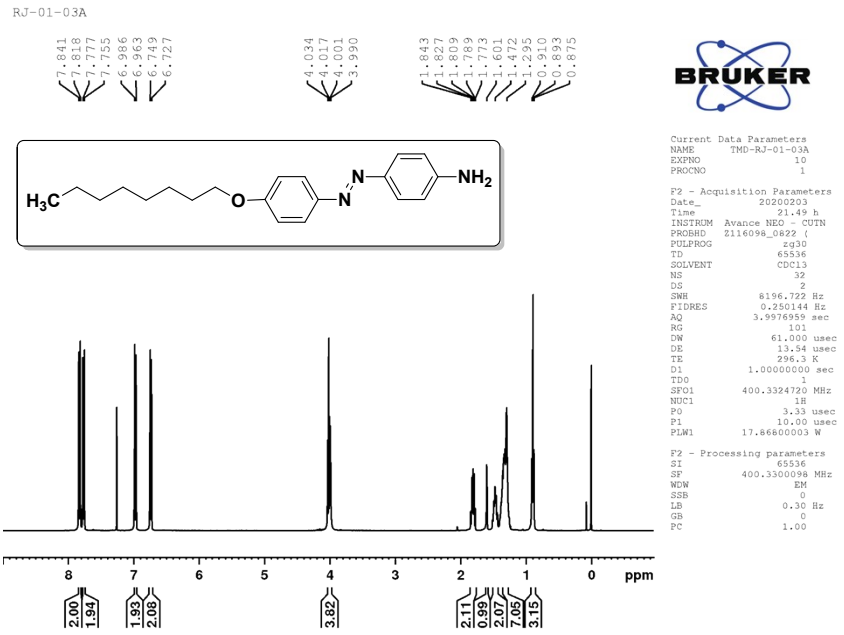


Fig. S18 ^{1}H NMR Spectrum of compound, 10 (CDCl3, 400 MHz)

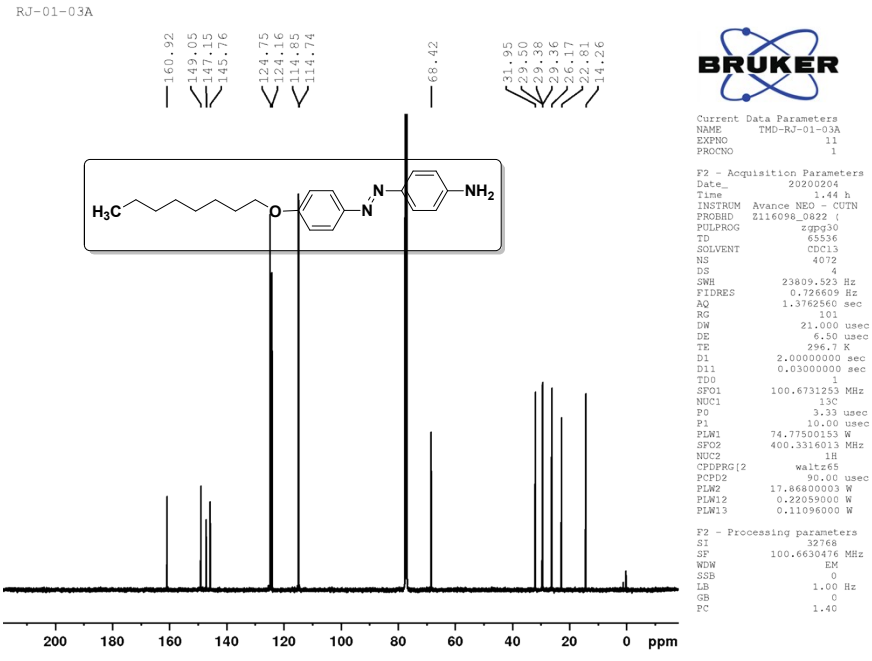


Fig. S19 ^{13}C NMR Spectrum of compound, 10 ($CDCl_3$, 100 MHz)

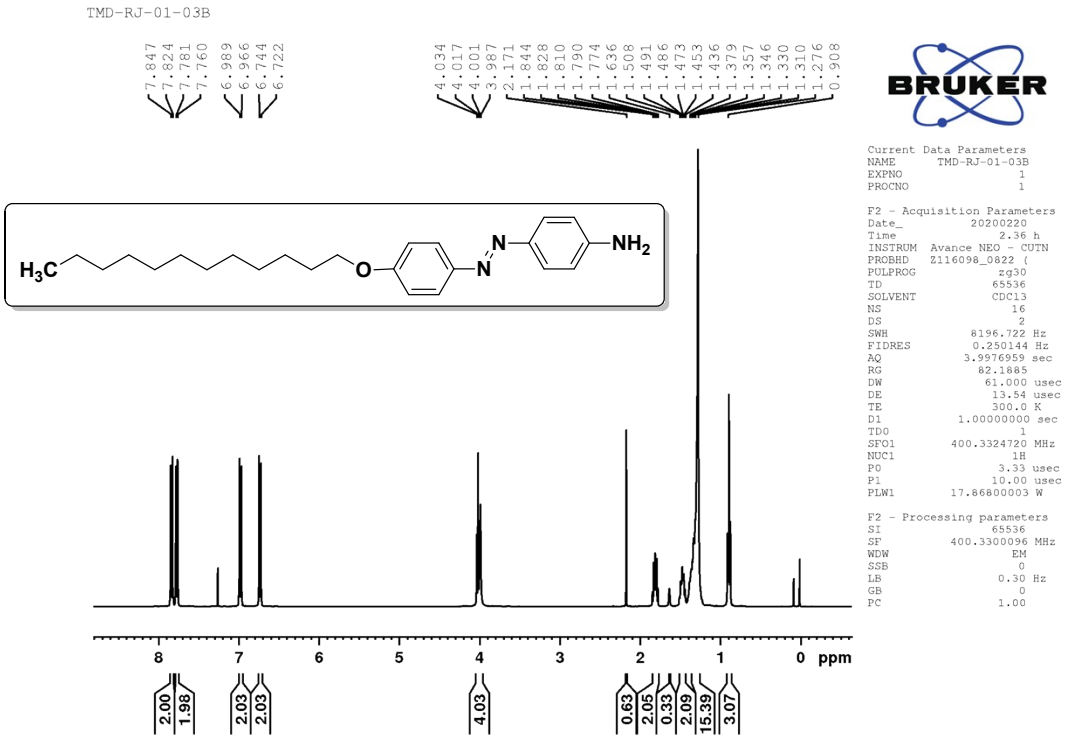


Fig. S20 ^{1}H NMR Spectrum of compound, 11 ($CDCl_3$, 400 MHz)

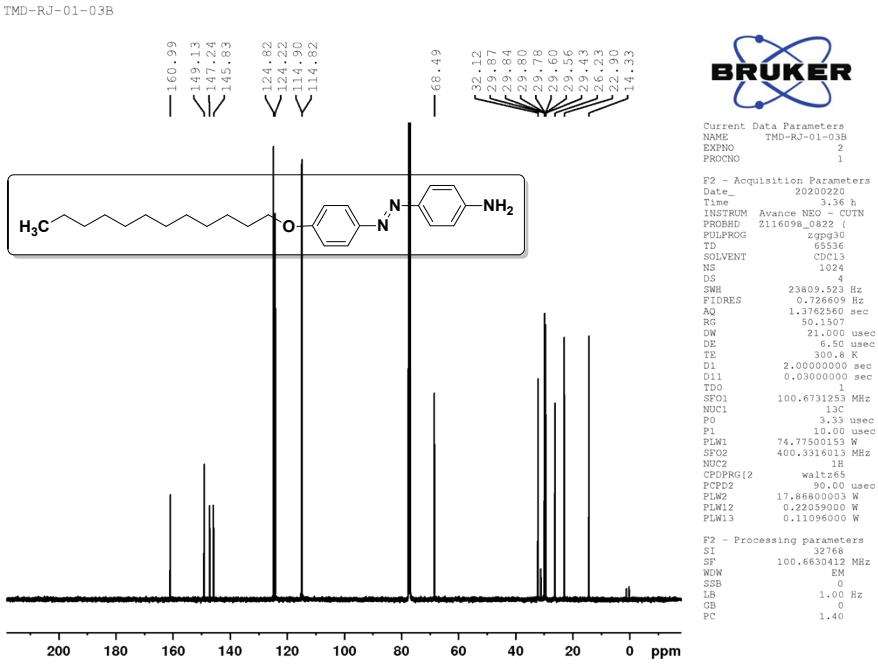


Fig. S21 ^{13}C NMR Spectrum of compound, 11 ($CDCl_3$, 100 MHz)

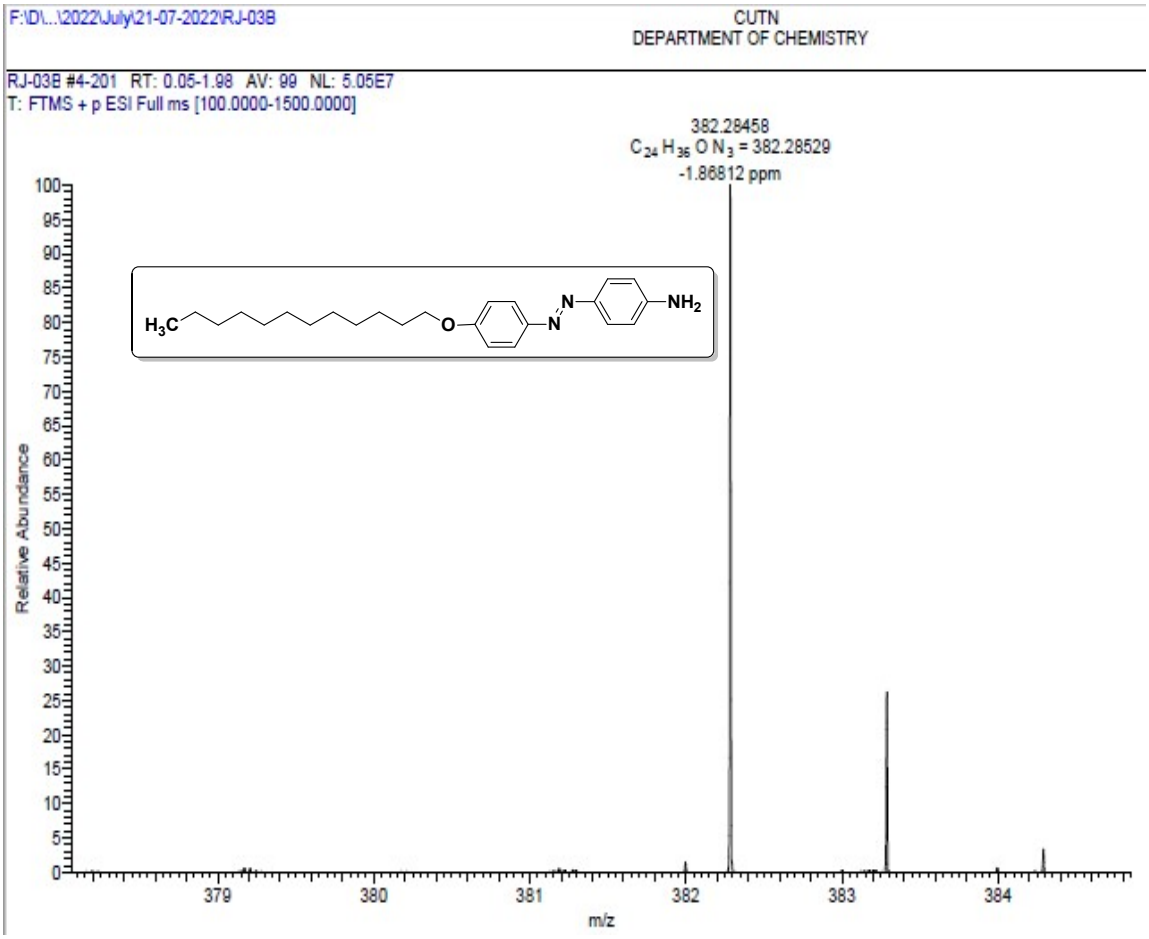


Fig. S22 HR-MS Spectrum of compound, 11

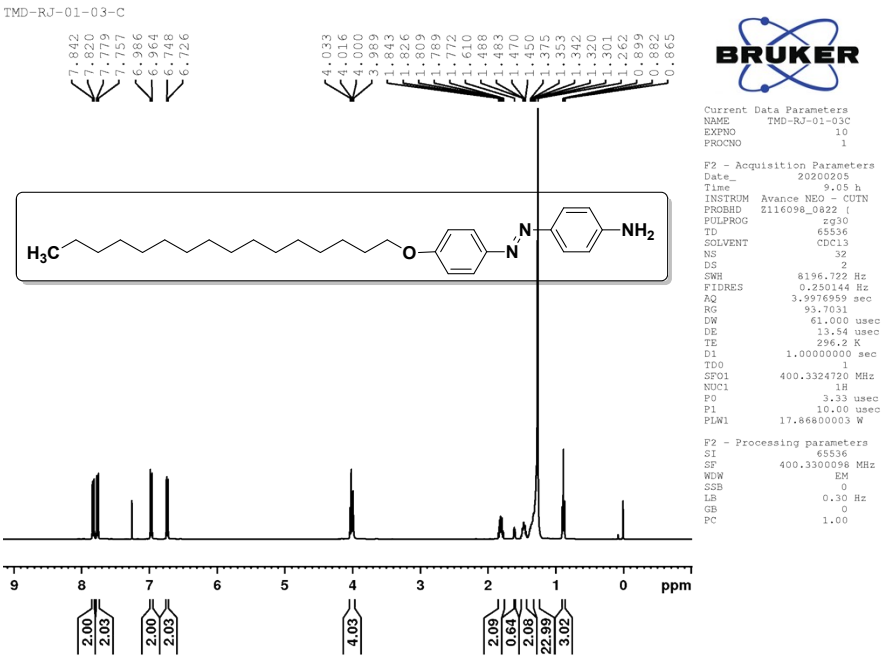


Fig. S23 ^{1}H NMR Spectrum of compound, 12 ($CDCl_3$, 400 MHz)

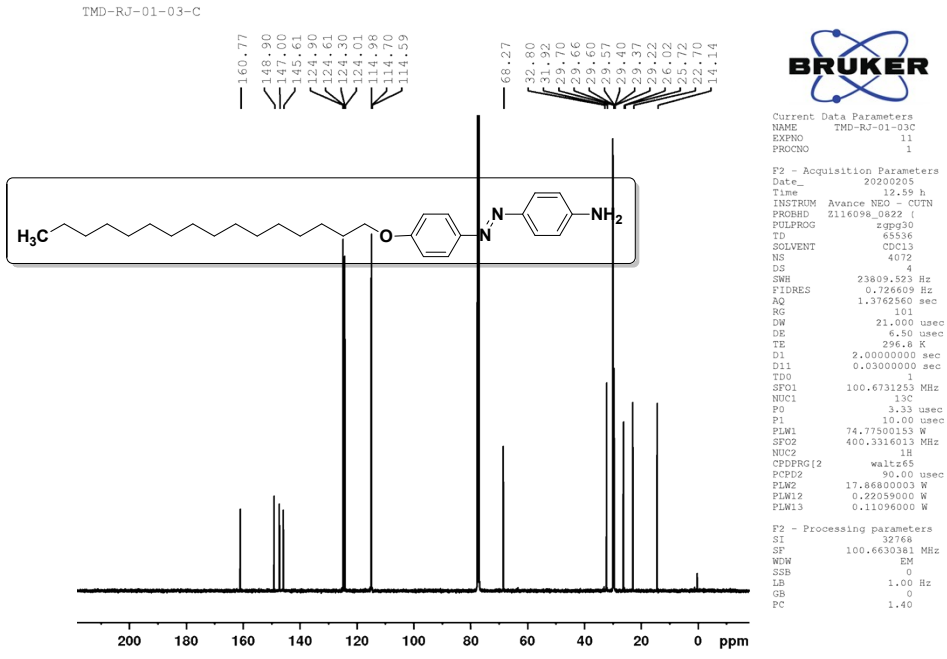


Fig. S24 ^{13}C NMR Spectrum of compound, 12 ($CDCl_3$, 100 MHz)

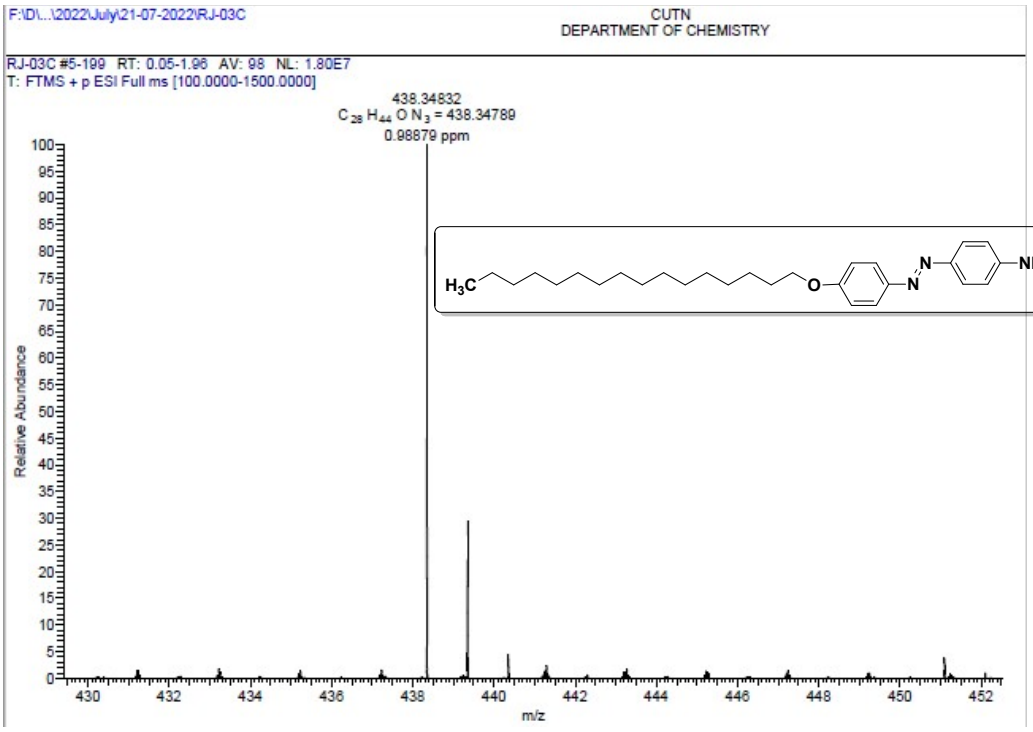


Fig. S25 HR-MS Spectrum of compound, 12

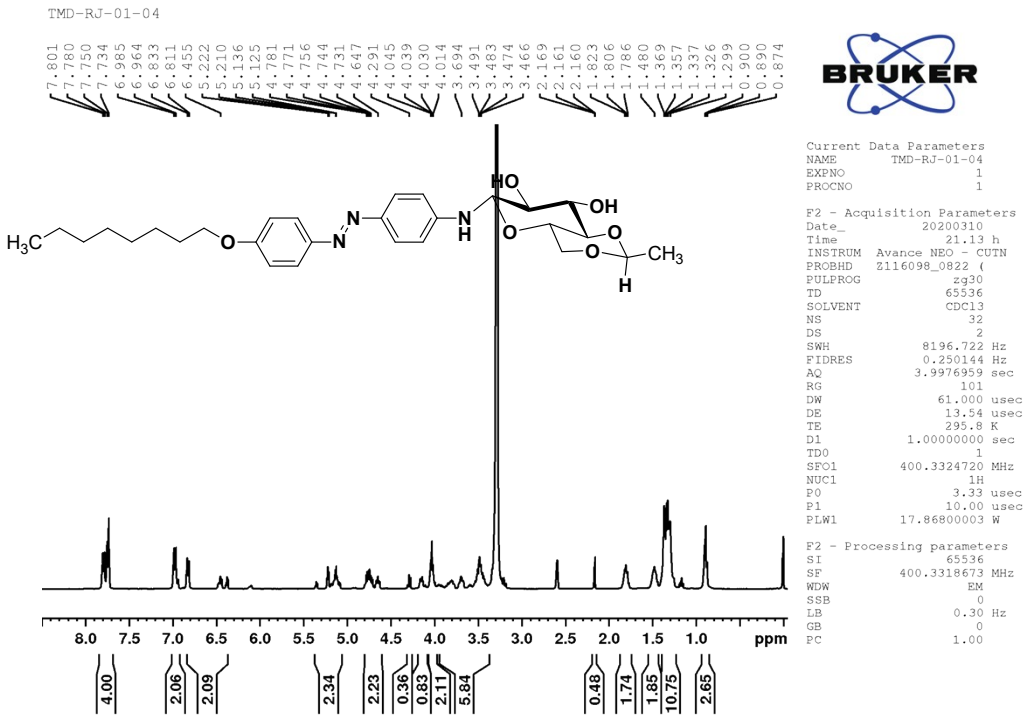


Fig. S26 ^{1}H NMR Spectrum of compound, 15 ($CDCl_3$+DMSO-d_6, 400 MHz)

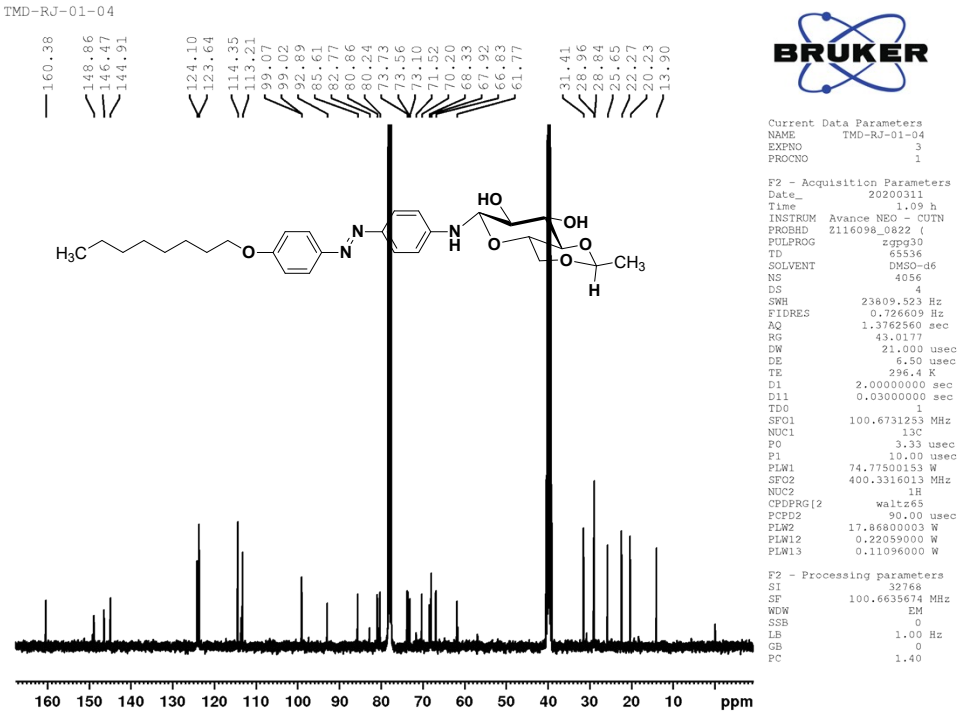


Fig. S27 ^{13}C NMR Spectrum of compound, 15 ($CDCl_3$+DMSO-d_6, 100 MHz)

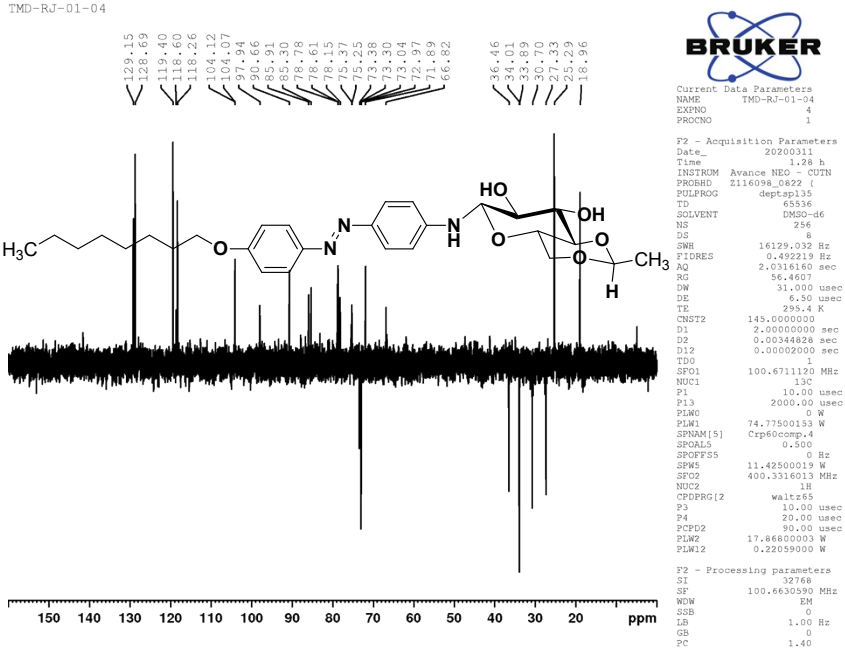


Fig. S28 DEPT-135 Spectrum of compound, 15

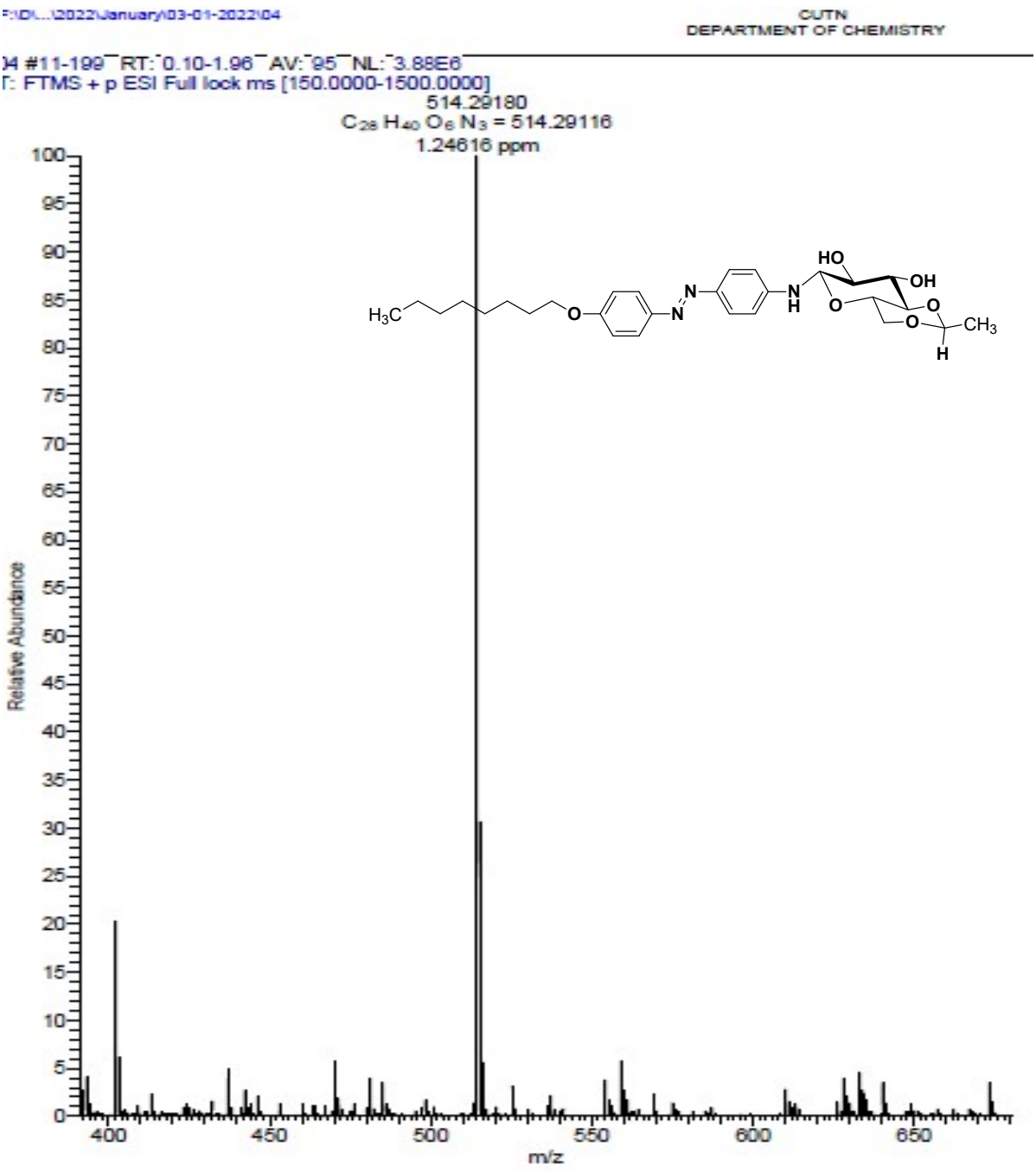


Fig. S29 HR-MS Spectrum of compound, 15

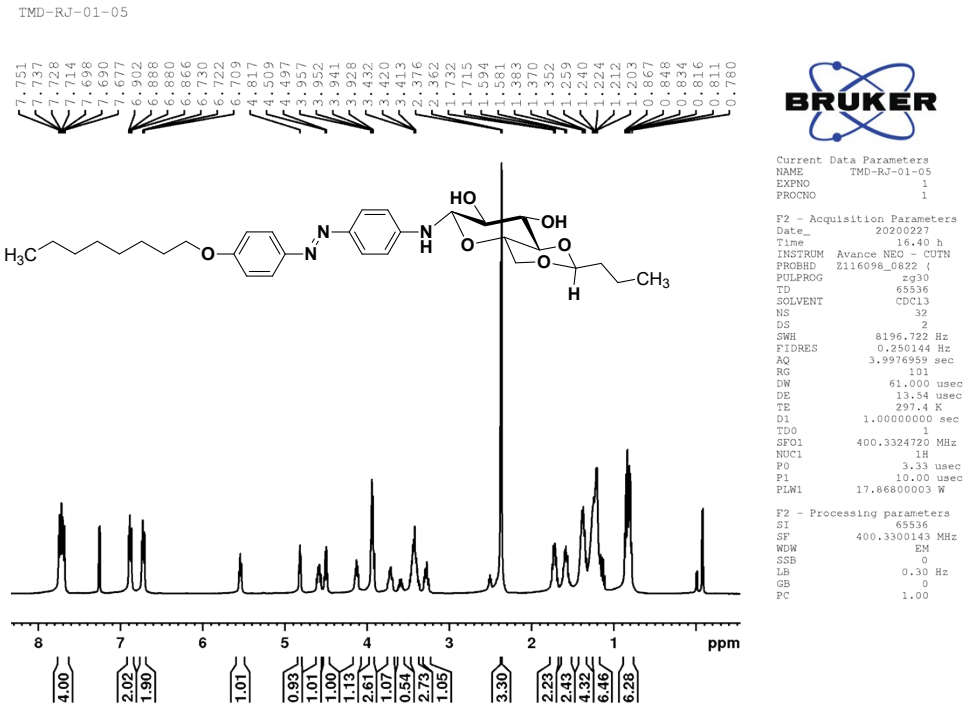


Fig. S30 ^{1}H NMR Spectrum of compound, 16 ($CDCl_3$+DMSO-d_6, 400 MHz)

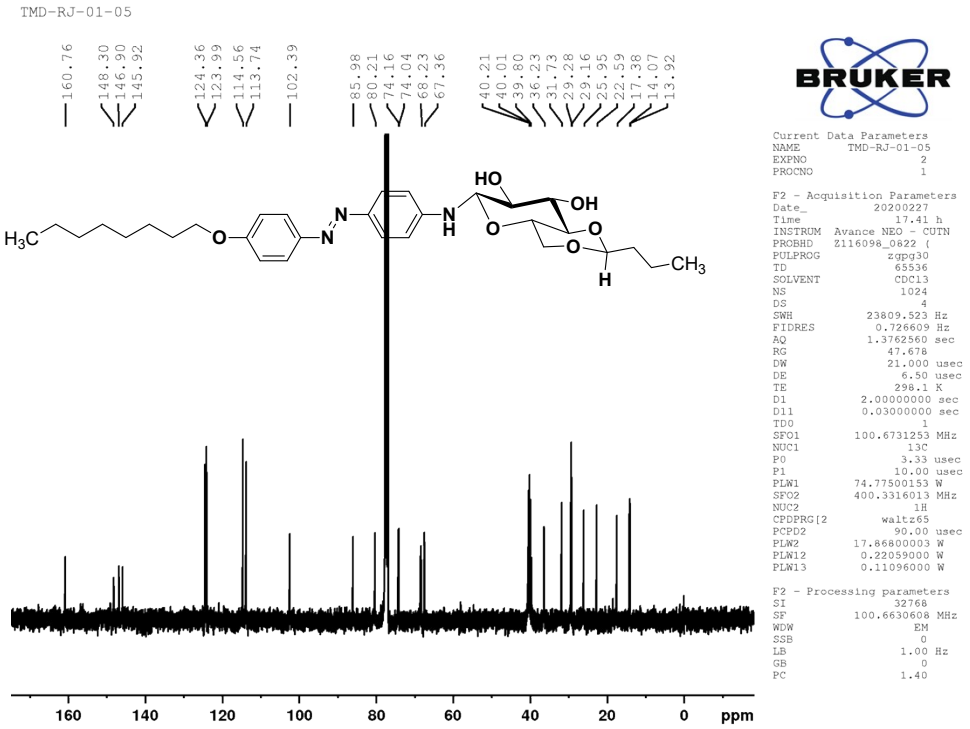


Fig. S31 ^{13}C NMR Spectrum of compound, 16 ($CDCl_3$+DMSO-d_6, 100 MHz)

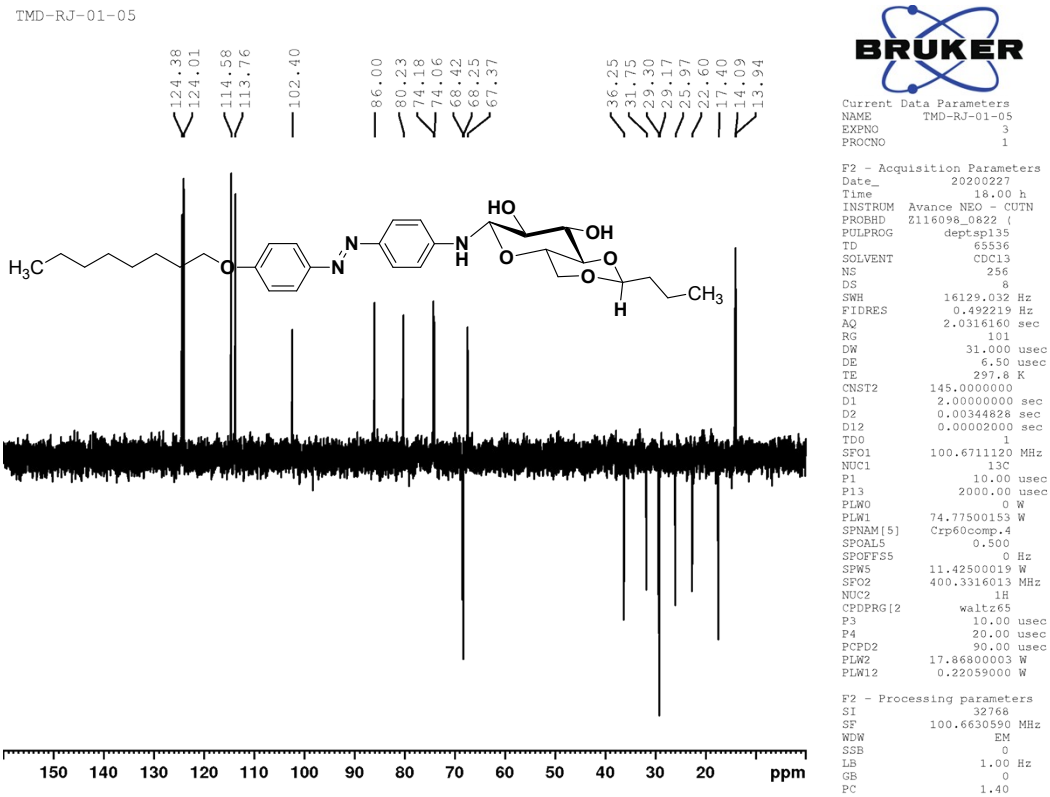


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Fig. S32 DEPT-135 Spectrum of compound, 16

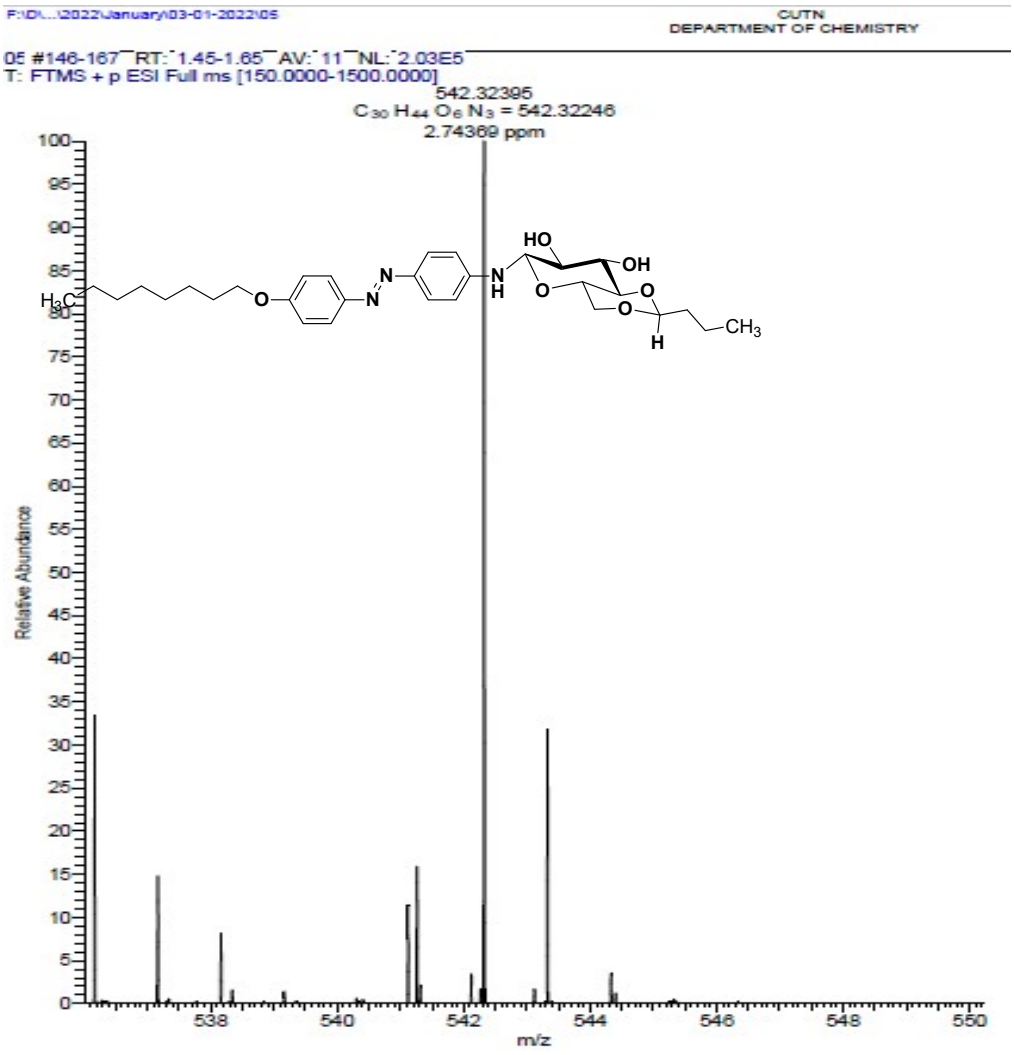
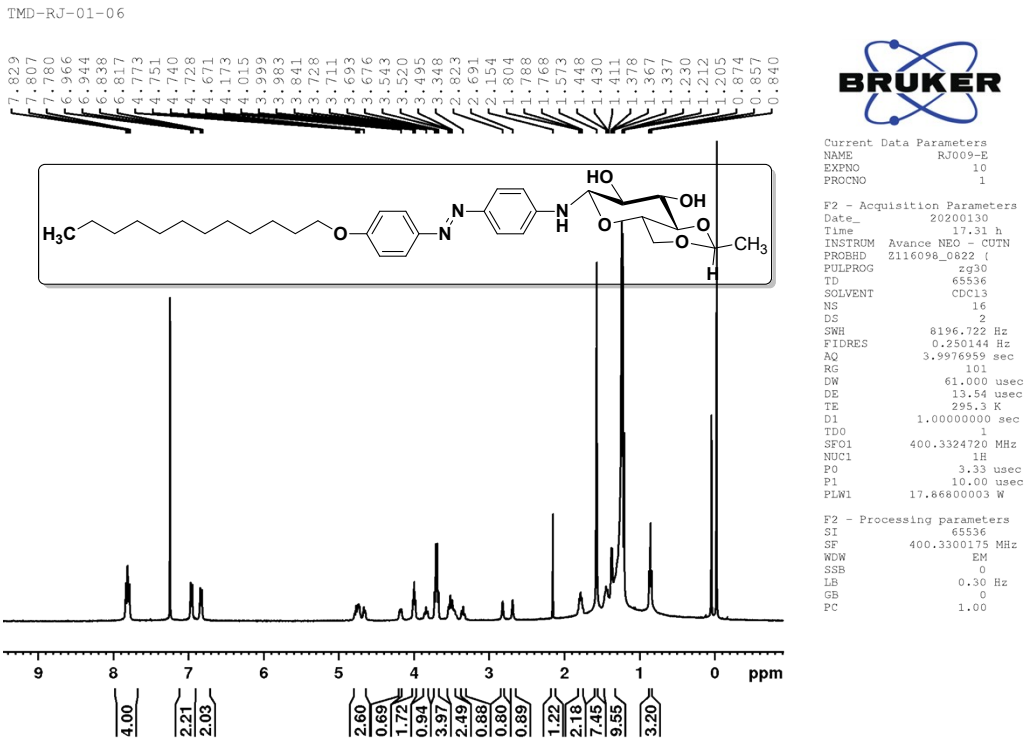


Fig. S33 HR-MS Spectrum of compound, 16



BRUKER

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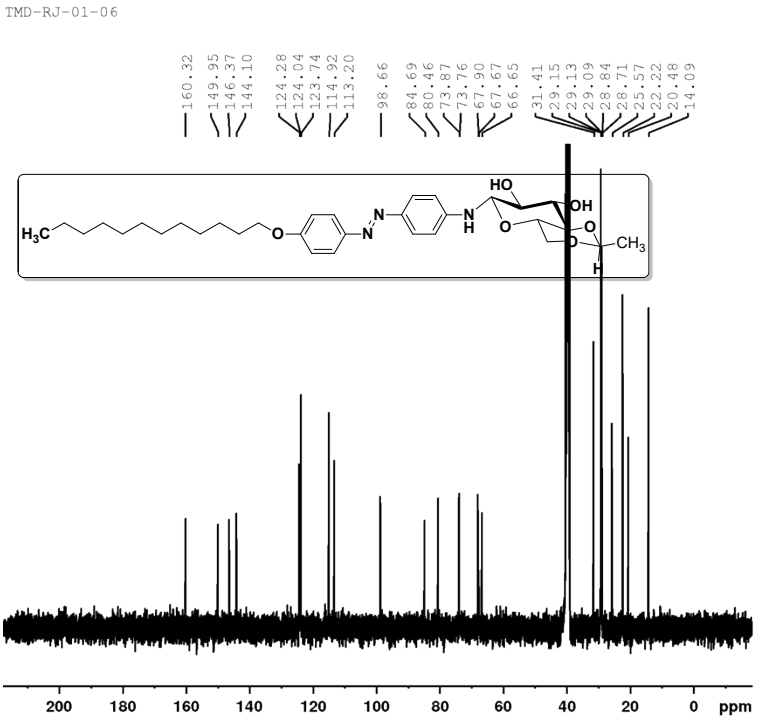
Fig. S34 ^{1}H NMR Spectrum of compound, 17 ($CDCl_3$+DMSO-d_6, 400 MHz)



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P1                 10.00 usec
PLW1           74.77500153 W
SFO2           400.3316013 MHz
NUC2                   1H
CPDPRG[2          waltz65
PCPD2              90.00 usec
PLW2           17.86800003 W
PLW12           0.22059000 W
PLW13           0.11096000 W

F2 - Processing parameters
SI                  32768
SF             100.6630951 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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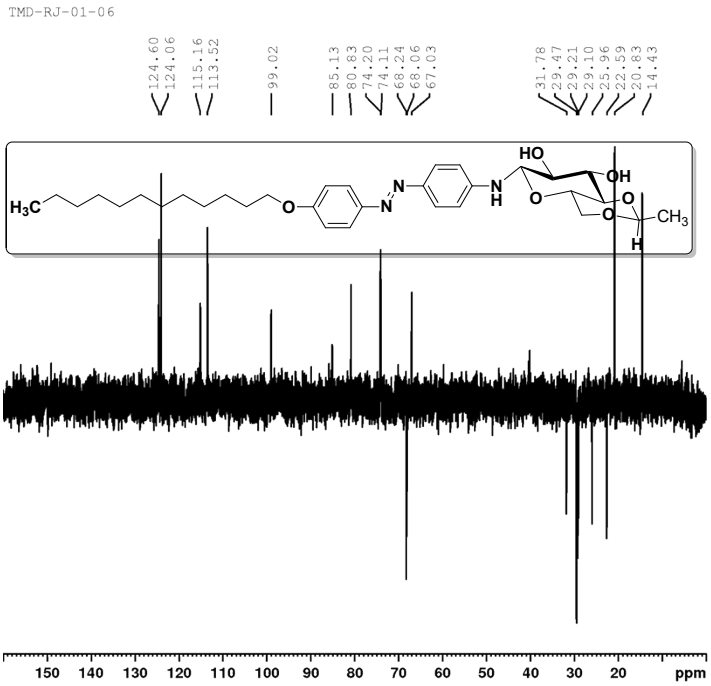
Fig. S35 ^{13}C NMR Spectrum of compound, 17 ($CDCl_3$+DMSO-d_6, 100 MHz)



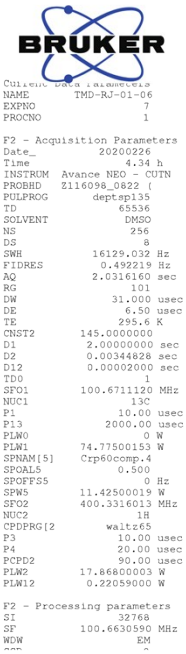


Fig. S36 DEPT-135 Spectrum of compound, 17

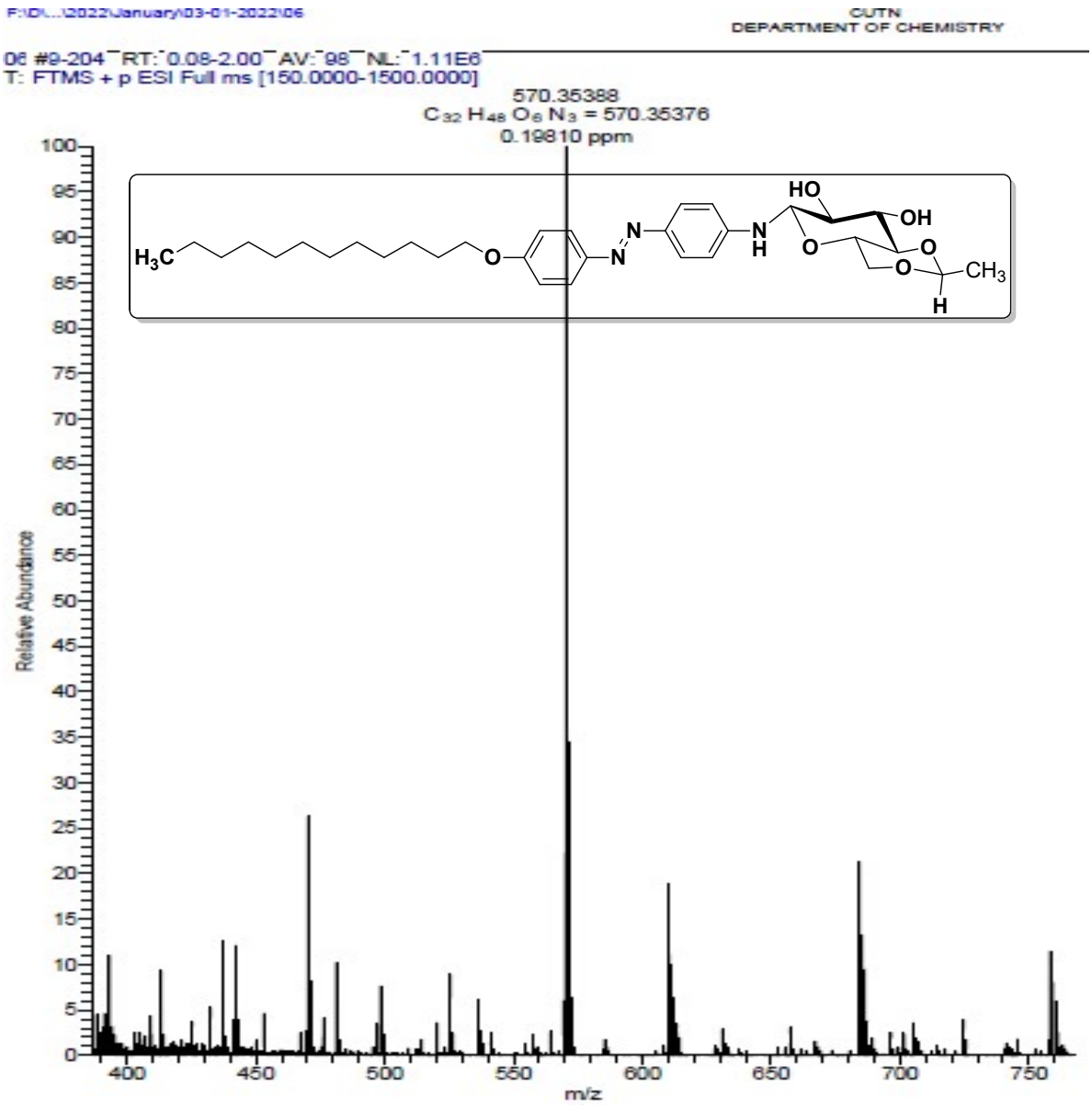


Fig. S37 HR-MS Spectrum of compound, 17

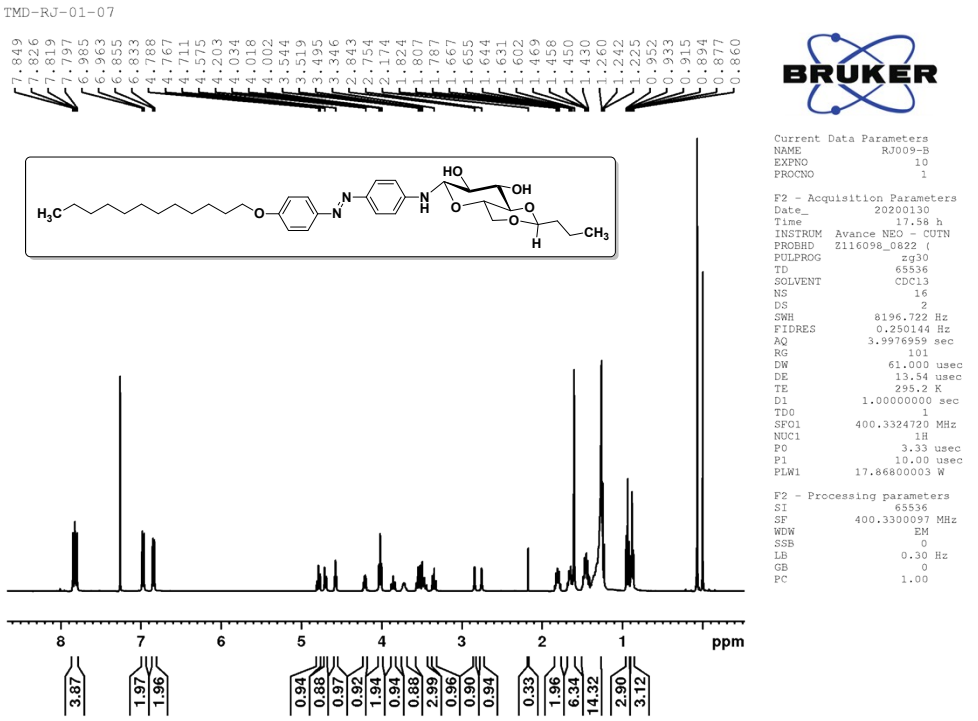


Fig. S38 ^{1}H NMR Spectrum of compound, 18 ($CDCl_3$+DMSO- d_6, 400 MHz)

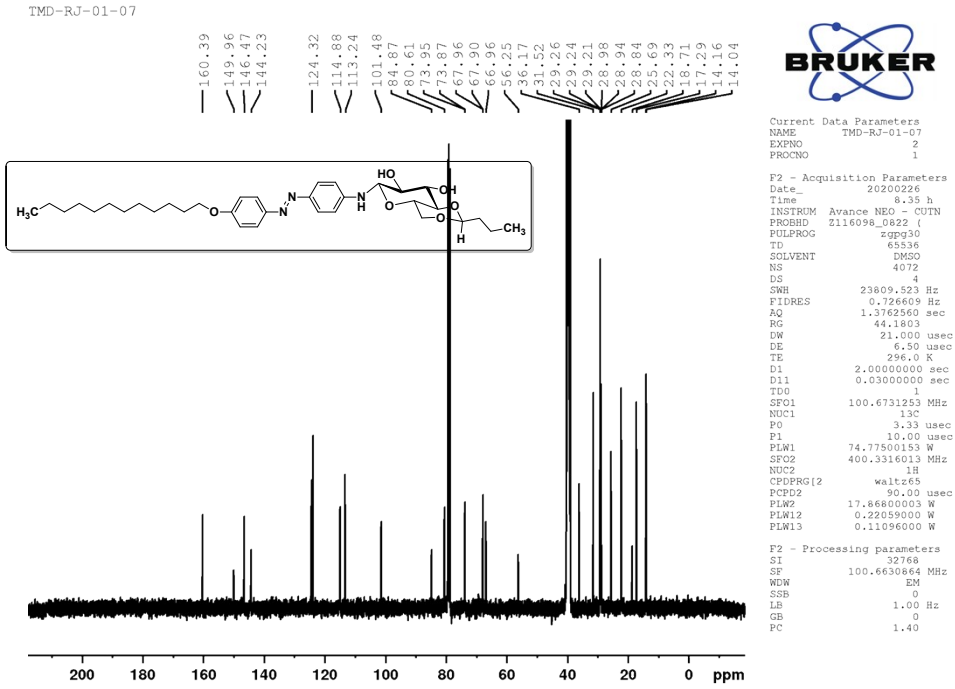
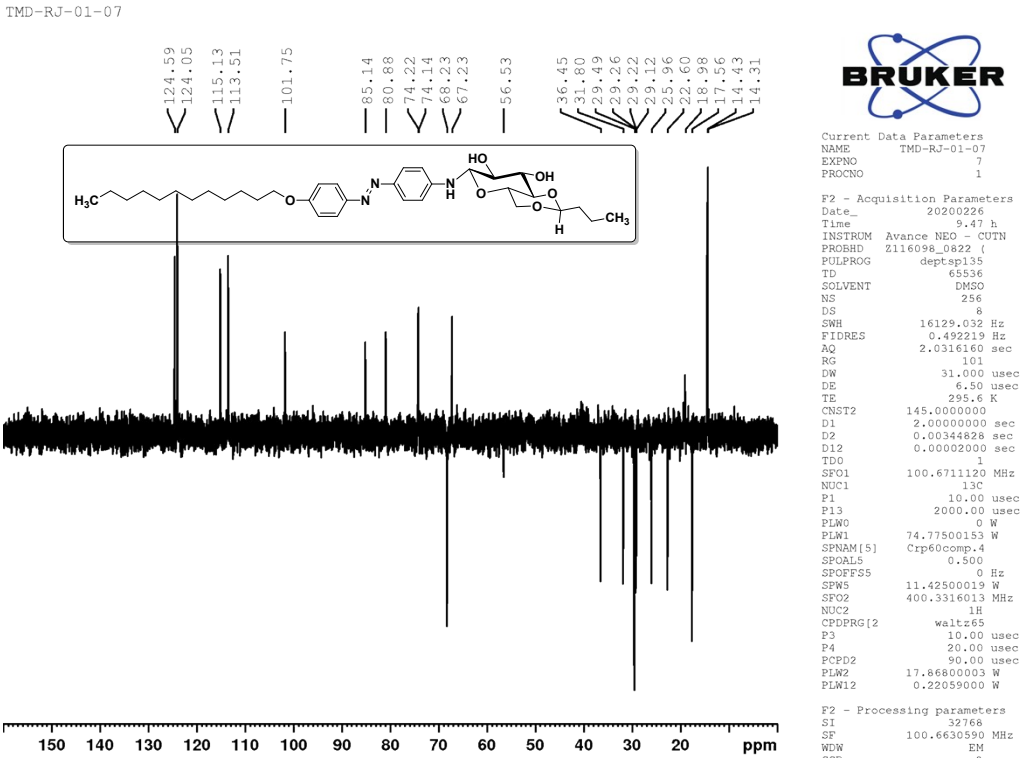


Fig. S39 ^{13}C NMR Spectrum of compound, 18 ($CDCl_3$+DMSO- d_6, 100 MHz)

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Current Data Parameters
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EXPNO                  7
PROCNO                 1

F2 - Acquisition Parameters
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Time                9.47 h
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PULPROG        deptsp135
TD                 65536
SOLVENT             DMSO
NS                   256
DS                     8
SWH            16129.032 Hz
FIDRES          0.492219 Hz
AQ             2.0316160 sec
RG                   101
DW                31.000 usec
DE                 6.50 usec
TE                295.6 K
CNST2         145.0000000
D1             2.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
TD0                    1
SFO1         100.6711120 MHz
NUC1                13C
P1                10.00 usec
P13             2000.00 usec
PLW0                 0 W
PLW1         74.77500153 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5                0 Hz
SPW5         11.42500019 W
SFO2         400.3316013 MHz
NUC2                1H
CPDPRG[2         waltz65
P3                10.00 usec
P4                20.00 usec
PCPD2             90.00 usec
PLW2         17.86800003 W
PLW12         0.22059000 W

F2 - Processing parameters
SI                 32768
SF           100.6630590 MHz
WDW                   EM
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Fig. S40 DEPT-135 Spectrum of compound, 18

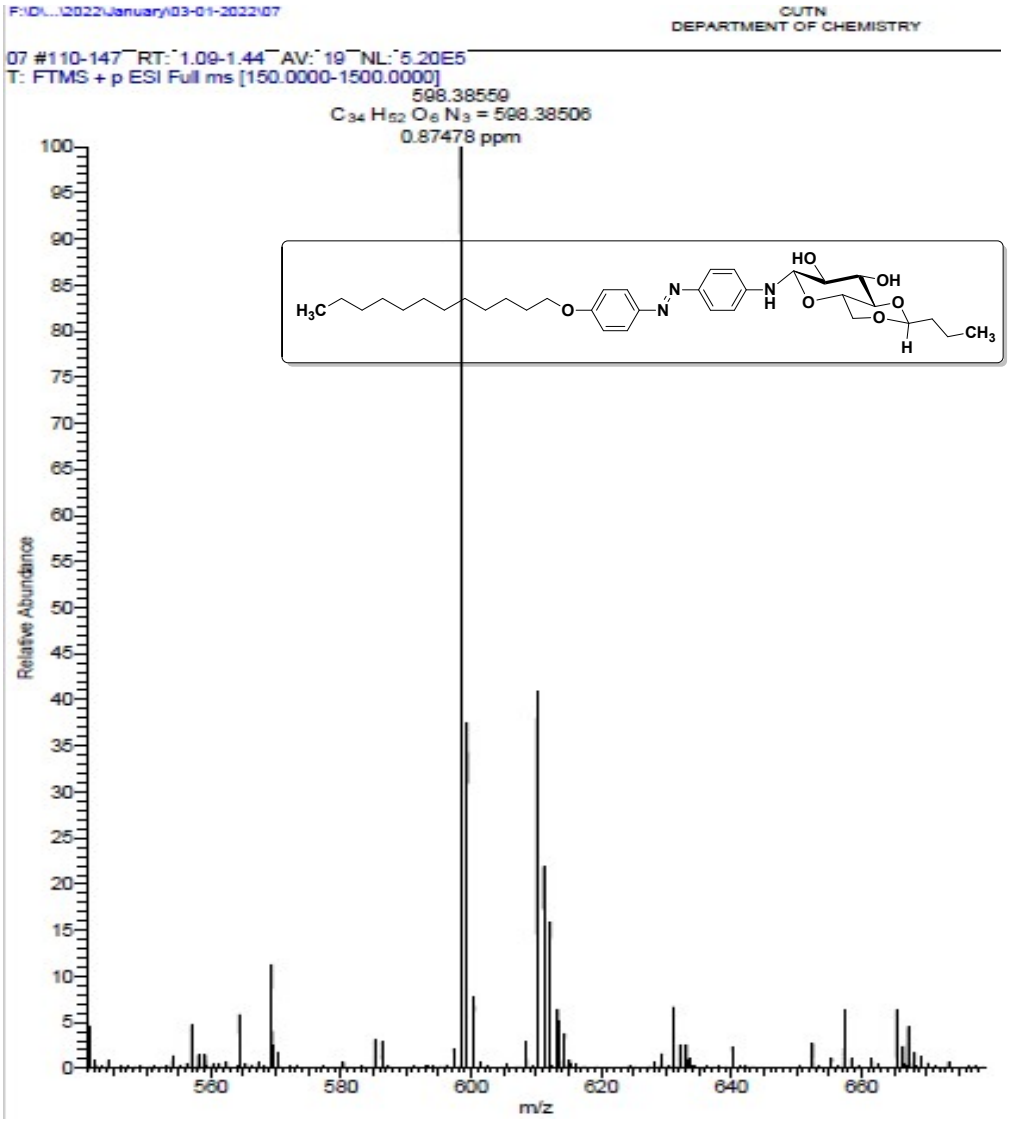

Fig. S41 HR-MS Spectrum of compound, 18

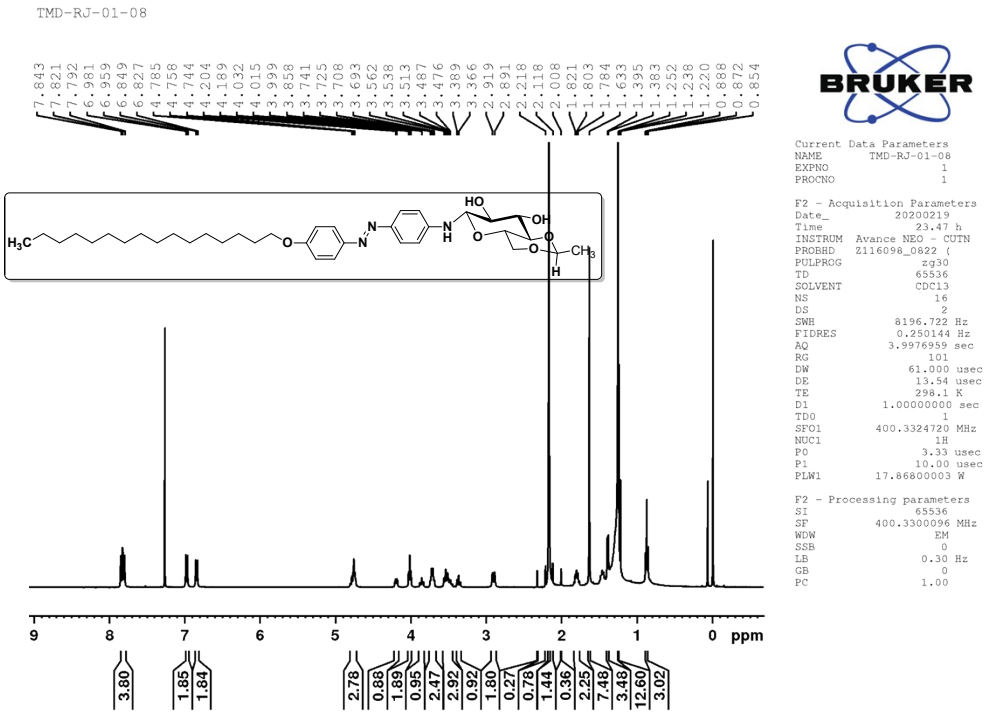

Fig. S42 ^{1}H NMR Spectrum of compound, 19 ($CDCl_3$+DMSO-d_6, 400 MHz)

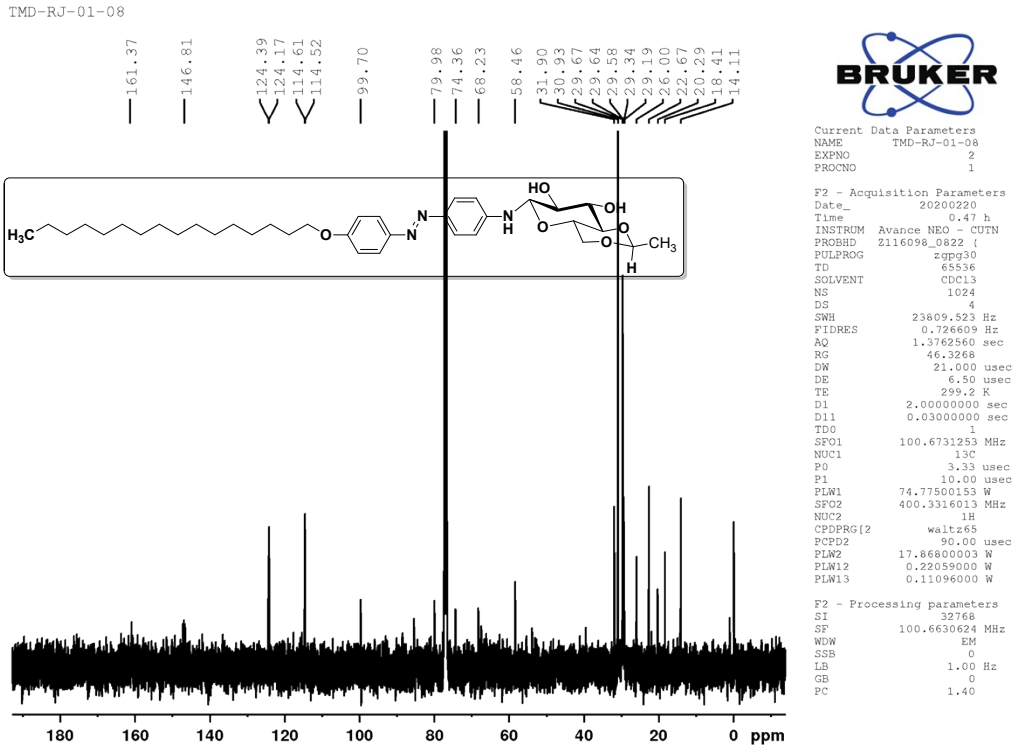

Fig. S43 ^{13}C NMR Spectrum of compound, 19 ($CDCl_3$+DMSO-d_6, 100 MHz)

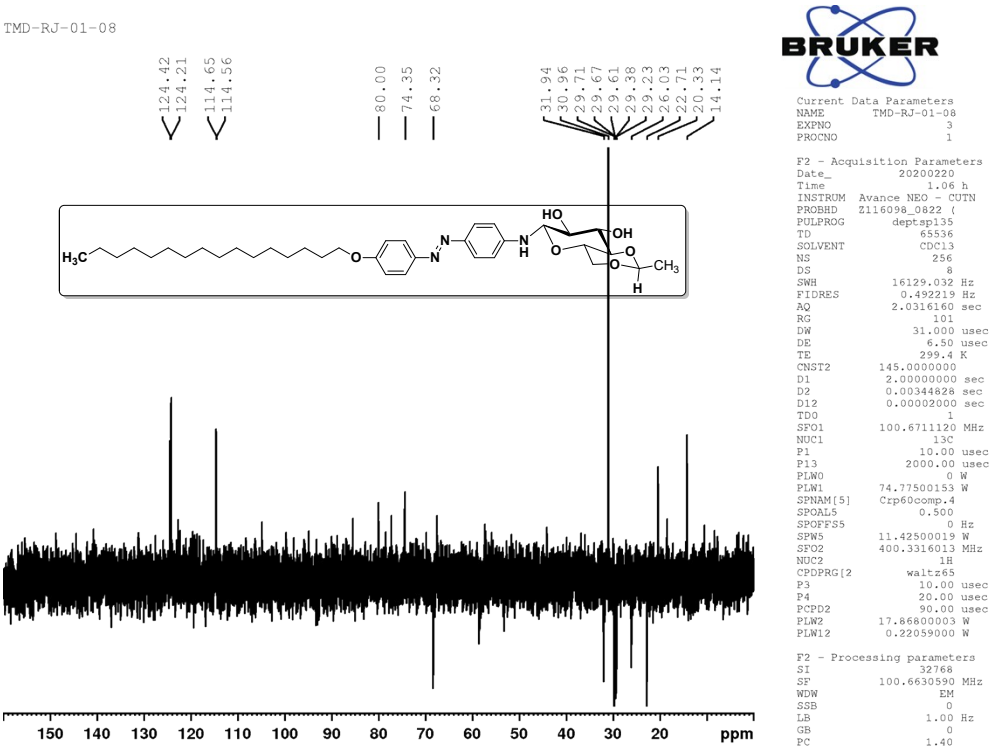

Fig. S44 DEPT-135 Spectrum of compound, 19

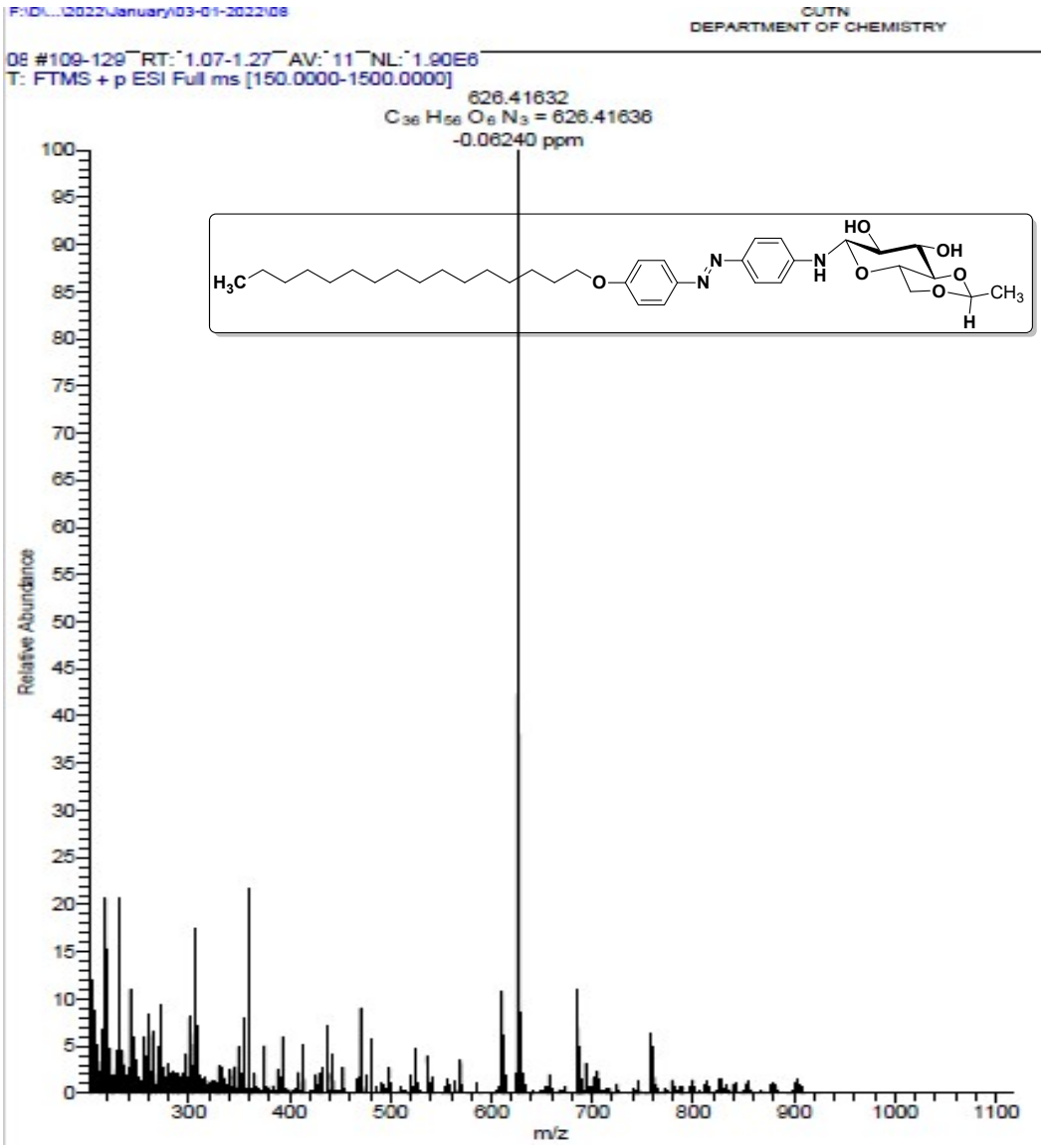

Fig. S45 HR-MS Spectrum of compound, 19

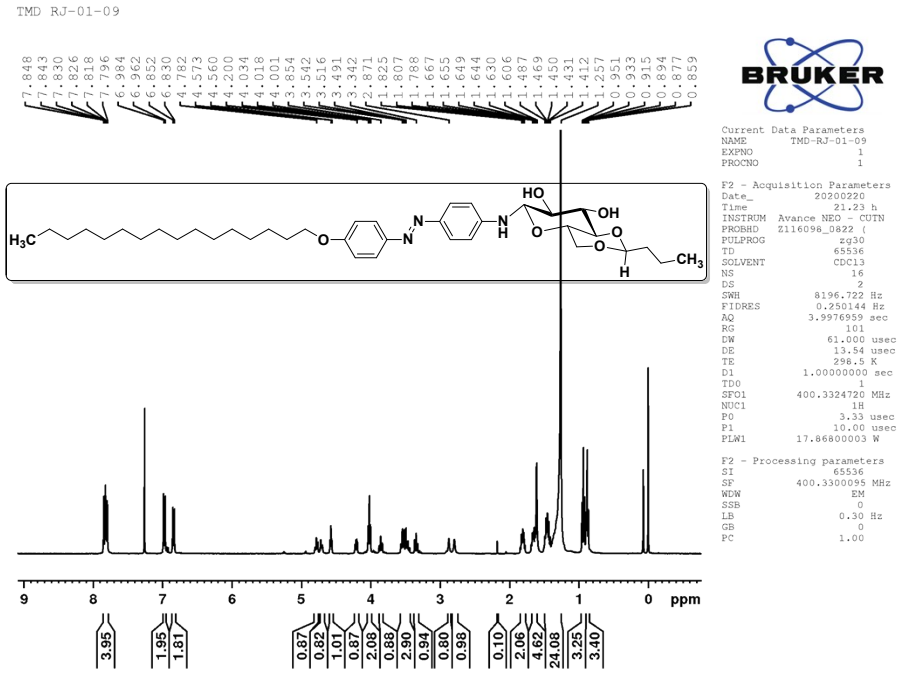

Fig.S46 ^{1}H NMR Spectrum of compound, 20 ($CDCl_3$+DMSO- d_6, 400 MHz)

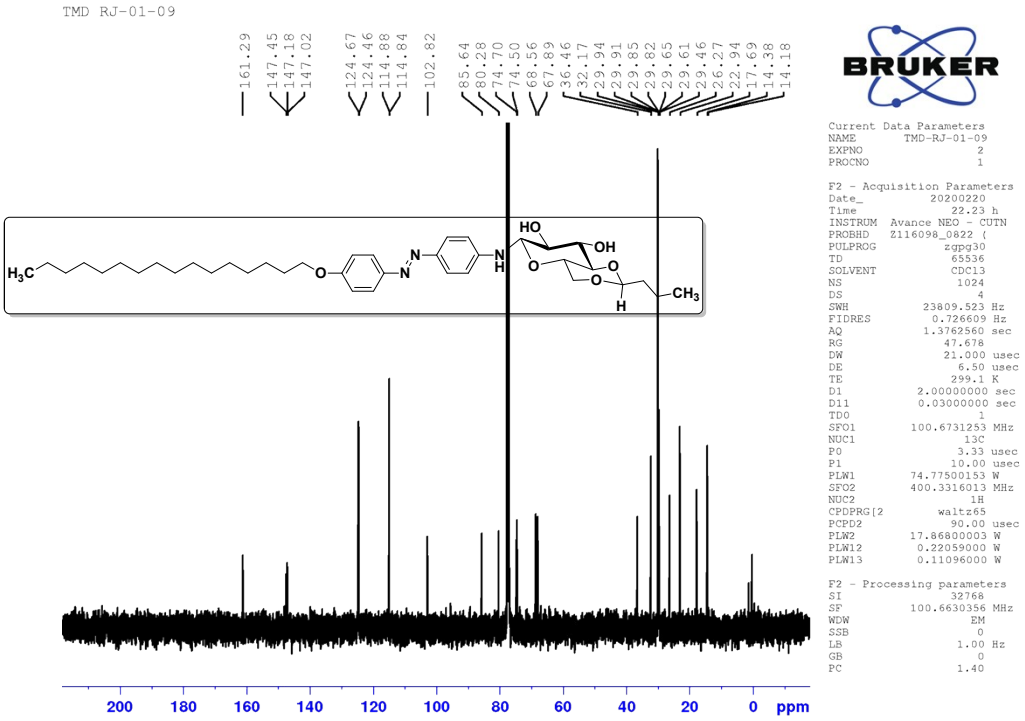

Fig. S47 ^{13}C NMR Spectrum of compound, 20 ($CDCl_3$+DMSO- d_6, 100 MHz)

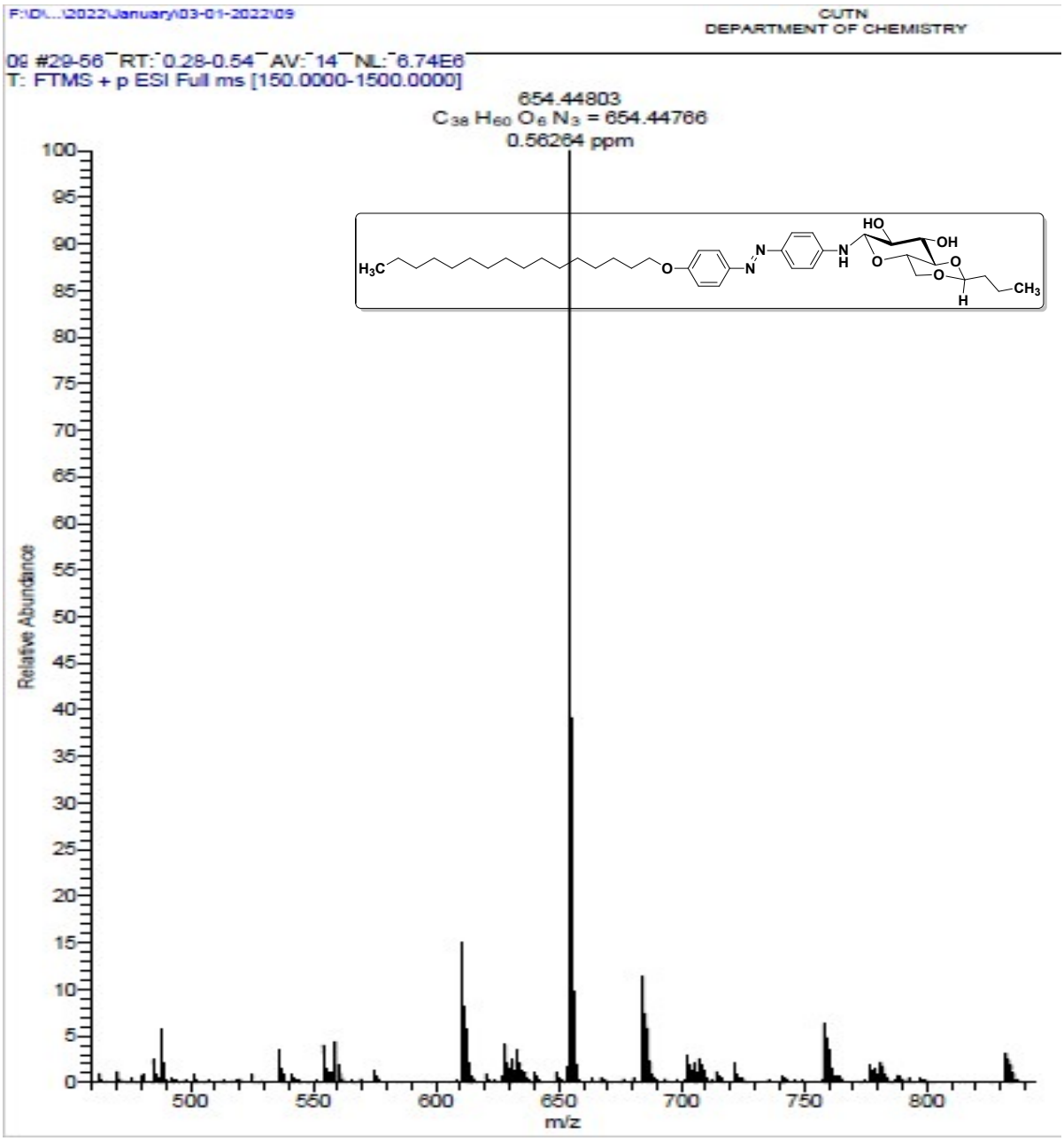

Fig. S48 HR-MS Spectrum of compound, 20