Understanding the gelation properties of fluorophenyl glycosides of arabinoside gelators: Experimental and theoretical studies

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1. **Synthesis of the fluorogelators 3a-e**

1.1 General Procedures

All chemicals, solvents and reagents were procured from commercial source and were used as received. Column chromatography was performed by using silica gel (230-400 mesh) under medium pressure. TLC was performed on precoated aluminium plates of silica gel 60-F$_{254}$. TLC spot were visualized by staining with vanillin solution and subsequent heating on a hot plate. ^{1}H and ^{13}C NMR spectra are recorded on Bruker AC-400 NMR spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C) in solution of CDCl$_3$ or d$_6$-DMSO using the peaks of the residual non-deuterated solvent as internal standard. δ Values are reported in parts per million (ppm) and coupling constant (*J*) in Hertz. HRMS spectra are recorded on Waters Xevo G2-XS QT Mass Sectrometer and Optical rotation recorded by Anton Paar MCP 5100 Polarimeter.

1.2 General procedure for synthesis of fully de-protected phenolic glycosides

D-Arabinose (3.0 g, 19.9 mmol) was stirred in a solution of acetic anhydride (9.4 mL, 99.4 mmol) and pyridine (32.0 mL, 396.4 mmol) at room temperature for 12 hours. After completion of the reaction, 20 mL of H$_2$O was added to quench the reaction following which it was extracted with ethyl acetate (60 mL x 3) three times. The combined ethyl acetate extract was then washed with brine solution and dried over anhydrous sodium sulphate (Na$_2$SO$_4$) and evaporated it *in vacuo* to yield a syrupy residue of 1,2,3,4-tetra-*O*-acetyl-D-arabinopyranoside **2** (5.95 g, 94%) which was used further without purification.

Subsequently, the 1,2,3,4-tetra-*O*-acetyl-D-arabinopyranose **2** (5.95 g, 18.69 mmol) was dissolved in acetic acid (104 mL) followed by the dropwise addition of phosphorus tri-bromide (17.75 mL, 186.88 mmol) under nitrogen atmosphere. The solution was stirred at room temperature for 4 hours after which the reaction mixture was poured into ice/water (200 mL), and the aqueous phase was extracted thrice with dichloromethane (DCM, 80 mL each). The combined extract was then washed with brine and then dried over anhydrous Na$_2$SO$_4$. Concentration of the extract *in vacuo* to yield a colourless solid of 2,3,4- tri-*O*-acetyl-1-bromo-β-D-arabinopyranoside (5.42 g, 85%).

Subsequently, the 2,3,4-tri-*O*-acetyl-1-bromo-α-D-arabinopyranoside (5.42 g, 15.98 mmol) was dissolved in anhydrous DMF (30 mL) and fluoro-phenol derivatives (2.10 mL, 23.97 mmol, 1.5 equiv.) followed by Sodium hydride (0.95 g, 39.95 mmol, 2.5 equiv.) was added to the reaction mixture. The progress of the reaction was monitored by TLC. After 2 h, when the reaction was completed, the mixture was quenched with ethyl acetate. Then the reaction mixture was extracted thrice with ethyl acetate (40 mL x 3). The combined organic

extract was then dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to yield the crude product. The crude product was purified by column chromatography (20% EA/PE) to afford 2,3,4-tri-*O*-acetyl-1-fluoro-phenoxy-β-D-arabinopyranoside (3.03 g, 54%, over two steps from **2**).

Further, the 2,3,4-tri-*O*-acetyl-1-fluoro-phenoxy-β-D-arabinopyranoside (3.03 g, 8.60 mmol) was dissolved in methanol (20 mL) followed by Sodium methoxide (NaOMe, 0.139 g, 2.57 mmol, 0.3 equiv.) was added to the reaction mixture. The progress of the reaction was monitored by TLC. After 1 h, when the reaction was completed, the mixture was neutralized with amberlite IR 120 H^+ resin. Then the reaction mixture was filtered and concentrated *in vacuo* to yield the crude product. The crude product was purified by column chromatography (5-10% MeOH/CHCl$_3$) to afford white solid fluoro-phenoxy-β-D-arabinopyranoside **3**.

1.3. Characterization data for compounds

1.3.1. 1-(2-fluorophenoxy)-β-D-arabinopyranosides (3a): It was synthesized following the general procedure and elution of the column with 9% methanol (MeOH) in Chloroform (CHCl$_3$) to afford **3a** (0.252 g, 66%) from compound **2** (over three steps) as a white solid. m.p. 127–129 °C $[\alpha]_D^{25}$ = –9.747 (*c* = 0.266 in MeOH); ^1H NMR (400 MHz, d$_6$-DMSO): δ (ppm) 7.25–7.19 (m, 2H), 7.13–7.09 (m, 1H), 7.03–6.98 (m, 1H), 5.31 (d, *J* = 5.3 Hz, 1H), 4.93 (d, *J* = 6.7 Hz, 1H), 4.89 (d, *J* = 5.6 Hz, 1H), 4.72 (d, *J* = 4.2 Hz, 1H), 3.75–3.69 (m, 2H), 3.67–3.62 (m, 1H), 3.59–3.56 (m, 1H), 3.49–3.45 (m, 1H). $^{13}C\{1H\}$ NMR (100 MHz, d$_6$-DMSO): δ (ppm) 153.5, 151.1, 144.7 (d, *J* = 10.4 Hz), 124.8 (d, *J* = 3.6 Hz), 122.6 (d, *J* = 6.9 Hz), 118.0, 116.3 (d, *J* = 18.2 Hz), 101.2, 72.5, 70.3, 67.4, 65.6. HRMS calcd. for $C_{11}H_{13}FO_5Na^+$ (M + Na)$^+$ 267.0639; found 267.0637.

1.3.2. 1-(3-fluorophenoxy)-β-D-arabinopyranosides (3b): It was synthesized following the general procedure and elution of the column with 9% methanol (MeOH) in Chloroform (CHCl$_3$) to afford **3b** (0.231 g; 60%) from compound **2** (over three steps) as a white solid. m.p. 139–141 °C $[\alpha]_D^{25}$ = –1.80 (*c* = 0.166 in MeOH); ^1H NMR (400 MHz, d$_6$-DMSO): δ (ppm) 7.35–7.29 (m, 1H), 6.87–6.79 (m, 3H), 5.27 (d, *J* = 5.1 Hz, 1H), 4.90 (d, *J* = 5.3 Hz, 1H), 4.88 (d, *J* = 6.8 Hz, 1H), 4.70 (d, *J* = 4 Hz, 1H), 3.74–3.68 (m, 2H), 3.64–3.56 (m, 2H), 3.47–3.43 (m, 1H). $^{13}C\{1H\}$ NMR (100 MHz, d$_6$-DMSO): δ (ppm) 164.0, 161.6, 158.6 (d, *J* = 11.0 Hz), 130.7 (d, *J* = 10.1 Hz), 112.5 (d, *J* = 2.5 Hz), 108.5, 108.3, 103.8, 103.6, 100.6, 72.5, 70.2, 67.6, 65.9. HRMS calcd. for $C_{11}H_{13}FO_5Na^+$ (M + Na)$^+$ 267.0639; found 267.0634.

1.3.3. 1-(4-fluorophenoxy)-β-D-arabinopyranosides (3c): It was synthesized following the general procedure and elution of the column with 9% methanol (MeOH) in Chloroform (CHCl$_3$) to afford **3c** (0.283 g; 74%) from compound **2** (over three steps) as a white solid. m.p. 152–154 °C [α]$_D^{25}$ = –50.555 (c = 0.233 in MeOH); ^{1}H NMR (400 MHz, d$_6$-DMSO): δ (ppm) 7.15–7.09 (m, 2H), 7.04–6.99 (m, 2H), 5.25 (d, J = 5 Hz, 1H), 4.88 (d, J = 5.6 Hz, 1H), 4.77 (d, J = 6.9 Hz, 1H), 4.68 (d, J = 4.1 Hz, 1H), 3.74–3.68 (m, 2H), 3.60–3.55 (m, 2H), 3.46–3.42 (m, 1H). ^{13}C{1H} NMR (100 MHz, d$_6$-DMSO): δ (ppm) 158.4, 156.1, 153.6 (d, J = 1.9 Hz), 118.0 (d, J = 8.1 Hz), 116.0, 115.73, 101.48, 72.52, 70.34, 67.67, 65.79**.** HRMS calcd. for C$_{11}$H$_{13}$FO$_5$H$^+$ (M + H)$^+$ 245.0820; found 245.0848.

61.3.4. 1-(2,3-difluorophenoxy)-β-D-arabinopyranosides (3d): It was synthesized following the general procedure and elution of the column with 9% methanol (MeOH) in Chloroform (CHCl$_3$) to afford **3d** (0.280 g; 71%) from compound **2** (over three steps) as a white solid. m.p. 140–142 °C [α]$_D^{25}$ = +6.666 (c = 0.333 in MeOH); ^{1}H NMR (400 MHz, d$_6$-DMSO): δ (ppm) 7.14–7.01 (m, 3H), 5.36 (d, J = 5.2 Hz, 1H), 4.96 (d, J = 6.4 Hz, 1H), 4.88 (d, J = 5.6 Hz, 1H), 4.73 (d, J = 4.0 Hz, 1H), 3.75–3.71 (m, 2H), 3.67–3.58 (m, 3H). ^{13}C{1H} NMR (100 MHz, d$_6$-DMSO): δ (ppm) 151.9 (d, J = 10.2 Hz), 149.5 (d, J = 10.5 Hz), 146.4 (dd, J_1 = 7.5 Hz, J_2 = 2.5 Hz), 142.2 (d, J = 14.1 Hz), 139.7 (d, J = 14.4 Hz), 124.2 (dd, J_1 = 8.6 Hz, J_2 = 5.0 Hz), 113.4 (d, J = 2.6 Hz), 110.3 (d, J = 17.0 Hz), 101.4, 72.5, 70.3, 67.4, 65.7**.** HRMS calcd. for C$_{11}$H$_{12}$F$_2$O$_5$Na$^+$ (M + Na)$^+$ 285.0545; found 285.0543.

1.3.5. 1-(3,4-difluorophenoxy)-β-D-arabinopyranosides (3e): It was synthesized following the general procedure and elution of the column with 9% methanol (MeOH) in Chloroform (CHCl$_3$) to afford **3e** (0.271 g; 64%) from compound **2** (over three steps) as a white solid. m.p. 135–137 °C [α]$_D^{25}$ = +6.313 (c = 0.333 in MeOH); ^{1}H NMR (400 MHz, d$_6$-DMSO): δ (ppm) 7.33 (dd, J =19.6 and 9.2 Hz, 1H), 7.11-7.05 (m, 1H), 6.84-6.82 (m, 1H), 5.28 (d, J = 4.8 Hz, 1H), 4.86-4.81 (m, 2H), 4.68 (d, J = 3.6 Hz, 1H), 3.73–3.69 (m, 2H), 3.61-3.55 (m, 3H). ^{13}C{1H} NMR (100 MHz, d$_6$-DMSO): δ (ppm) 153.9 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz), 150.8 (d, J = 13.8 Hz) 148.4 (d, J = 13.8 Hz), 146.1 (d, J = 12.6 Hz), 143. (d, J = 12.6 Hz), 117.7 (d, J = 18.3 Hz), 112.9 (dd, J_1 = 5.8 Hz, J_2 = 3.3 Hz), 106.2, 106.0,101.3, 72.6, 70.3, 67.7, 65.9**.** HRMS calcd. for C$_{11}$H$_{12}$F$_2$O$_5$Na$^+$ (M + Na)$^+$ 285.0545; found 285.0543.

2. Gelation studies of 3a-e in various solvents

Table S1 Gelation studies of **3a, 3b, 3c, 3d, and 3e** in various solvents.[a]

Solvent	(MGC,[b] T_g[c])				
	3a	**3b**	**3c**	**3d**	**3e**
Benzene	**G,** (0.5%, 42-43 °C)	**G,** (0.6%, 47-48 °C)	**G,** (0.6%, 40-41 °C)	**G,** (1%, 60-70 °C)	**G**, (0.5%, 60-70 °C)
Toluene	**G,** (0.6%, 51-52 °C)	**G,** (0.7%, 54-55 °C)	**G,** (0.7%, 53-54 °C)	**G,** (1%, 60-70 °C)	**G,** (0.5%, 60-70 °C)
o-xylene	**G,** (0.7%, 56-57 °C)	**G,** (0.7%, 55-56 °C)	**G,** (0.7%, 57-58 °C)	**G,** (1%, 60-70 °C)	**G,** (0.5%, 60-70 °C)
m-xylene	**G,** (0.7%, 58-59 °C)	**G,** (0.7%, 58-59 °C)	**G,** (0.8%, 59-60 °C)	**G,** (1%, 60-70 °C)	**G,** (0.5%, 60-70 °C)
p-xylene	**G,** (0.6%, 57-58 °C)	**G,** (0.8%, 55-56 °C)	**G,** (0.7%, 55-56 °C)	**G,** (1%, 60-70 °C)	**G,** (0.5%, 60-70 °C)
Chlorobenzene	**G,** (0.7%, 53-54 °C)	**G,** (0.7%, 56-57 °C)	**G,** (0.8%, 57-58 °C)	**G,** (1%, 60-70 °C)	**G,** (0.5%, 60-70 °C)
Hexane	PS	PS	PS	PS	PS
DCM	PS	PS	PS	PS	PS
Chloroform	PS	PS	PS	PS	PS
Ethyl acetate	PS	PS	PS	PS	PS
Aceto nitrile	S	S	S	S	S
Ethanol	S	S	S	S	S
Methanol	S	S	S	S	S
n-butyl alcohol	S	S	S	S	S
Amyl alcohol	S	S	S	S	S
Water	S	S	S	S	S
DMF	S	S	S	S	S
DMSO	S	S	S	S	S

[a]**G** = Gel; S = Solution; PS = Partial soluble; [b]MGC = Minumum Gelation Concentration % (w/v). [c]Tg= Gelation temperature.
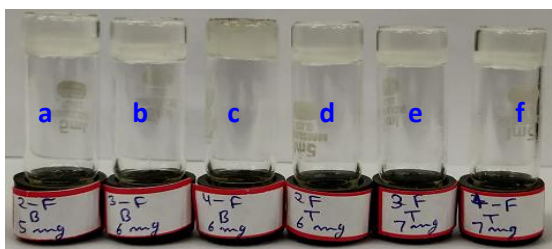
Fig. S1 Gels of **1-3** in Benzene (a) 0.5% w/v (b) 0.6% w/v (c) 0.6% w/v, and **1-3** in toluene (d) 0.6% w/v (e) 0.7% w/v (f) 0.7% w/v respectively.
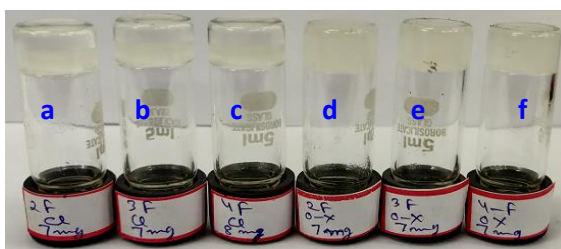
Fig. S2 Gels of **1-3** in Chlorobenzene (a) 0.7% w/v (b) 0.7% w/v (c) 0.8% w/v, and **1-3** in *o*-xylene (d) 0.7% w/v (e) 0.7% w/v (f) 0.7% w/v respectively.
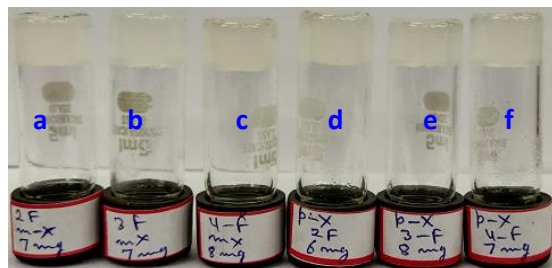
Fig. S3 Gels of **1-3** in *m*-xylene (a) 0.7% w/v (b) 0.7% w/v (c) 0.8% w/v, and **1-3** in *p*-xylene (d) 0.6% w/v (e) 0.8% w/v (f) 0.7% w/v respectively.
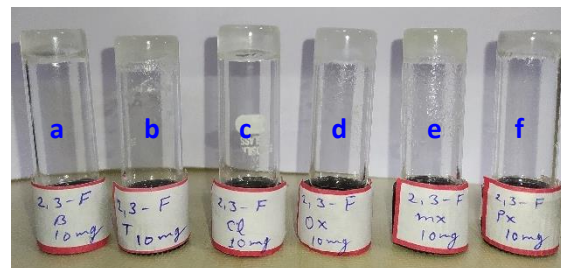
Fig. S4 Gels of **4** in (a) benzene 1% w/v (b) toluene 1% w/v (c) chlorobenzene 1 % w/v, (d) *o*-xylene 1% w/v (e) *m*-xylene 1% w/v and (f) *p*-xylene 1% w/v respectively.
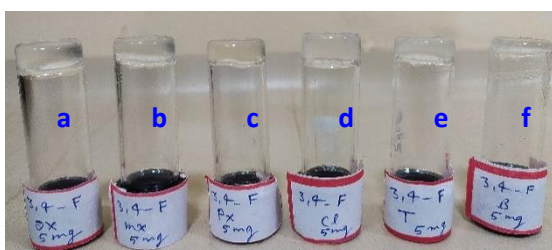
Fig. S5 Gels of **5** in (a) *o*-xylene 0.5% w/v (b) *m*-xylene 0.5% w/v (c) *p*-xylene 0.5 % w/v, (d) chlorobenzene 0.5 % w/v (e) toluene 0.5 % w/v and (f) benzene 0.5 % w/v respectively.

3. WXRD Data
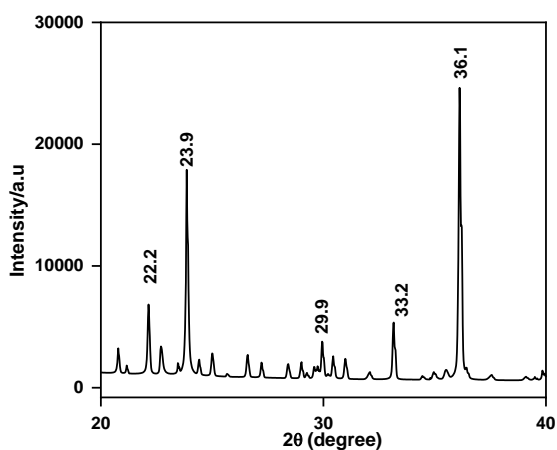
Fig. S6 WXRD diffractogram of **3a**.
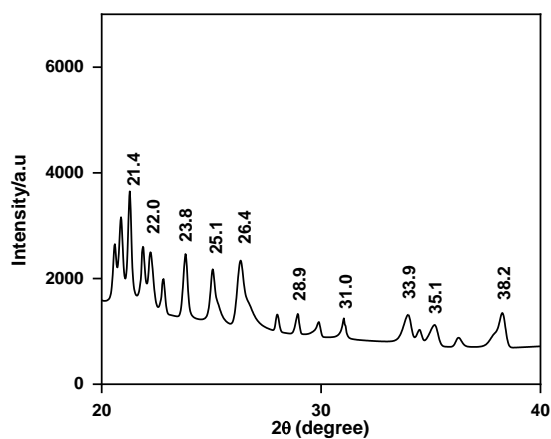
Fig. S7 WXRD diffractogram of **3b**.
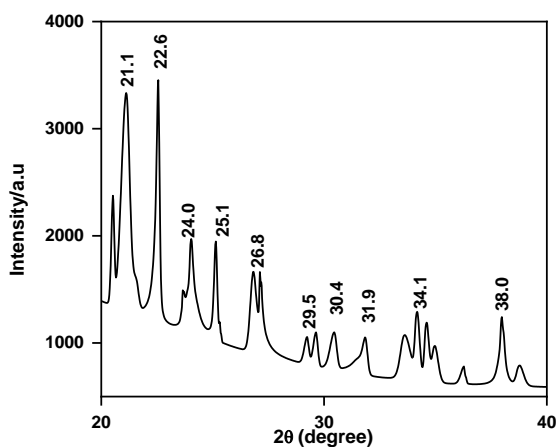
Fig. S8 WXRD diffractogram of **3c**.
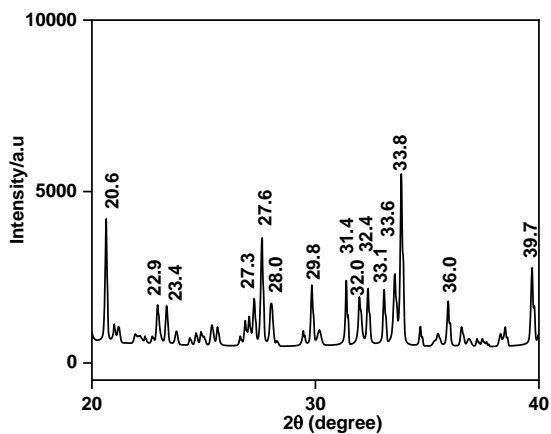
Fig. S9 WXRD diffractogram of **3d**.
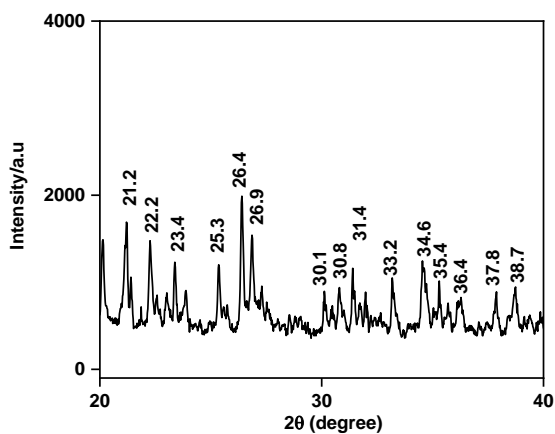
Fig. S10 WXRD diffractogram of **3e**.

Table S2 WXRD of compound **3a**

2θ	d spacing	2θ	d spacing
22.2	4.0	33.2	2.7
23.9	3.7	36.1	2.5

2θ	d spacing	2θ	d spacing
29.9	3.0		

Table S3. WXRD of compound **3b**

2θ	d spacing	2θ	d spacing
21.4	4.2	28.9	3.1
22.0	4.0	31.0	2.9
23.8	3.7	33.9	2.6
25.1	3.5	35.1	2.6
26.4	3.4	38.2	2.4

Table S4. WXRD of compound **3c**

2θ	d spacing	2θ	d spacing
21.1	4.2	30.4	2.9
22.6	3.9	31.9	2.8
24.0	3.7	38.0	2.4
25.1	3.5	34.1	2.6
29.5	3.0	38.0	2.4

Table S5. WXRD of compound **3d**

2θ	d spacing	2θ	d spacing
20.6	4.3	32.0	2.8
22.9	3.9	32.4	2.8
23.4	3.8	33.1	2.7
27.3	3.3	33.6	2.7
27.6	3.2	33.8	2.7
28.0	3.2	36.0	2.5
29.8	3.0	39.7	2.3
31.4	2.8		

Table S6 WXRD of compound **3e**

2θ	d spacing	2θ	d spacing
21.2	4.2	31.4	2.8
22.2	4.0	33.2	2.7
23.4	3.8	34.6	2.6
25.3	3.5	35.4	2.5
26.4	3.4	36.4	2.5
26.9	3.3	37.8	2.4
30.1	3.0	38.7	2.3
30.8	2.9		

Table S7 Microstructure of p-xylene xerogels of **3a-e.**

Gelator	Solvent	Microstructure
3a	*p*-xylene	Sheet like
3b	*p*-xylene	Interconnected fiber bundles
3c	*p*-xylene	Interconnected fiber bundles
3d	*p*-xylene	Interconnected fiber bundles
3e	*p*-xylene	Interconnected fiber bundles

4. DFT results
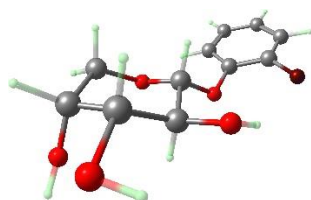
Fig. S11 DFT-optimized geometry of **3a**.
Table S8 DFT-optimized cartesian coordinates of **3a**.

C	9.014385	3.204506	6.545253
H	9.920781	3.494438	7.082162
C	9.110747	2.730689	5.233338
H	10.069361	2.635197	4.721276
C	7.953759	2.357179	4.545264
C	8.410619	2.706569	2.247788
H	8.110004	3.753363	2.475516
C	10.322919	3.409411	1.074191
H	11.405870	3.225015	1.048963
H	10.153138	4.485616	1.283457
C	9.718938	3.068360	−0.287628
H	10.037413	3.854465	−1.005063
C	8.188436	3.082309	−0.203191
H	7.841474	4.122026	−0.030482
C	7.726708	2.232992	0.971339
H	8.058072	1.190903	0.804710
O	7.970513	1.858712	3.270953
O	9.805206	2.614172	2.129704
O	10.168388	1.798971	−0.695250
H	9.559096	1.518285	−1.396939
O	7.682432	2.580787	−1.423096
H	6.750667	2.360782	−1.273536
O	6.324178	2.338385	1.058590
H	6.046636	1.869460	1.860546
C	6.605942	2.928535	6.488019
H	5.618108	2.996848	6.948312
C	6.710058	2.470768	5.179839
C	7.768499	3.298564	7.172402
H	7.695934	3.661780	8.200104
F	5.606151	2.130164	4.494511
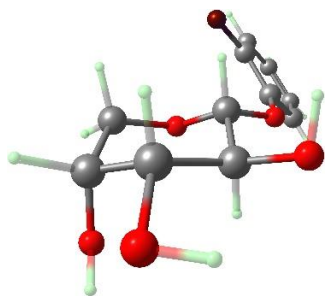
Fig. S12 DFT-optimized geometry of **3a'**.
Table S9 DFT-optimized cartesian coordinates of **3a'**.

C	8.707036	3.842081	6.352755
H	9.358180	4.649994	6.693374
C	8.398526	3.778245	4.998072
C	7.576657	2.764365	4.482164
C	8.049768	3.070836	2.149911
H	8.113052	4.180649	2.151988
C	10.275948	2.936148	1.386509
H	11.217508	2.432173	1.644236
H	10.433618	4.032077	1.446691
C	9.866388	2.558734	-0.034726
H	10.552011	3.074497	-0.740366
C	8.435866	3.039987	-0.301886
H	8.436416	4.152791	-0.322049
C	7.489370	2.588222	0.814530
H	7.474620	1.488856	0.846431
O	7.208139	2.628195	3.173646
O	9.323044	2.522816	2.348407
O	9.935105	1.162260	-0.187305
H	9.412669	0.959582	-0.979853
O	8.016298	2.519523	-1.543769
H	7.046145	2.542471	-1.537032
O	6.167500	3.003929	0.535258
H	6.099598	3.957932	0.687086
C	7.342800	1.891053	6.742281
H	6.920662	1.144837	7.419337
C	7.055310	1.824162	5.379227
C	8.177587	2.898291	7.234709
H	8.416619	2.953563	8.298910
H	6.420375	1.037639	4.966745
F	8.903409	4.727041	4.182140
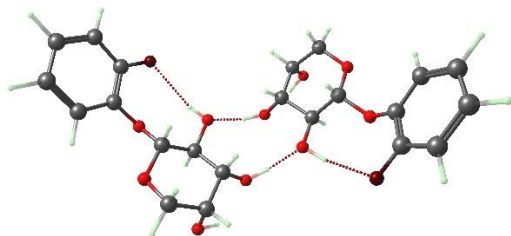
Fig. S13 DFT-optimized geometry of **3a-H**.
Table S10 DFT-optimized cartesian coordinates of **3a-H**.

C	7.511023	-7.158530	-7.282098
H	7.112307	-6.412089	-7.972893
C	6.631408	-7.951140	-6.538476
H	5.548235	-7.852139	-6.625088
C	7.138570	-8.909371	-5.658364
C	5.588075	-9.170542	-3.885068

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H      6.142113    -8.302972    -3.460720
C      3.532363    -8.187466    -3.364068
H      2.574765    -7.935997    -3.840473
H      3.994764    -7.252743    -2.984606
C      3.286879    -9.133296    -2.192126
H      2.825480    -8.540186    -1.372946
C      4.601999    -9.732980    -1.655558
H      5.178495    -8.946470    -1.134258
C      5.439309   -10.250388    -2.820379
H      4.909883   -11.101334    -3.283408
O      6.338877    -9.741523    -4.924084
O      4.346564    -8.760768    -4.376643
O      2.436124   -10.174332    -2.604584
H      2.523887   -10.860078    -1.921448
O      4.286688   -10.784707    -0.776121
H      4.722334   -10.608922     0.083173
O      6.725884   -10.629482    -2.354976
H      7.276598   -10.817378    -3.132473
C      9.408369    -8.278617    -6.267602
H     10.482500    -8.427376    -6.139354
C      8.525309    -9.053182    -5.525629
C      8.893170    -7.324280    -7.151387
H      9.578786    -6.709375    -7.738934
F      8.994995    -9.964252    -4.652974
C      7.645955    -5.812499     5.397168
H      8.500780    -5.354041     5.899679
C      7.749498    -7.120040     4.912443
H      8.662571    -7.707757     5.021429
C      6.656494    -7.709146     4.273582
C      7.524408    -9.272727     2.717541
H      7.670176    -8.352385     2.108603
C      9.655721   -10.063228     2.163375
H     10.558914   -10.456027     2.650495
H      9.930282    -9.151722     1.593016
C      9.102464   -11.107436     1.198064
H      9.781258   -11.142818     0.318442
C      7.695158   -10.732156     0.693609
H      7.767012    -9.869174     0.006555
C      6.821407   -10.332431     1.877425
H      6.671647   -11.218132     2.518831
O      6.670605    -8.988892     3.794406
O      8.749060    -9.733742     3.205657
O      9.044291   -12.355756     1.843381
H      8.462407   -12.901746     1.288469
O      7.141668   -11.846026     0.036215
H      6.902937   -11.576674    -0.874460
O      5.586419    -9.815393     1.405610
H      5.099527    -9.465839     2.169665
C      5.356383    -5.679127     4.607053
H      4.414450    -5.143710     4.471334
C      5.474336    -6.974347     4.119329
C      6.454282    -5.096381     5.249485
H      6.373529    -4.077681     5.635436
F      4.442167    -7.553180     3.477167
```
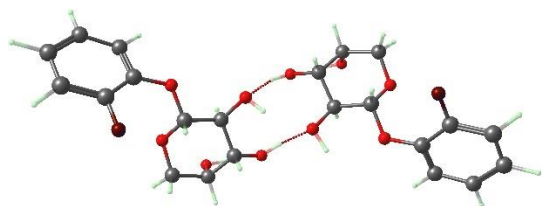
Fig. S14 DFT-optimized geometry of **3a'-H**.

Table S11 DFT-optimized cartesian coordinates of **3a'-H**.

C	7.997639	5.719318	5.196386
H	8.450976	6.706982	5.089256
C	7.893848	4.917262	4.065316
C	7.331389	3.635068	4.131810
C	8.154293	2.760073	2.039443
H	8.086612	3.673319	1.414441
C	10.445842	2.625239	1.626924
H	11.392149	2.499748	2.170181
H	10.472637	3.590632	1.083352
C	10.277020	1.481152	0.630054
H	10.978247	1.654725	-0.212821
C	8.851015	1.441036	0.050320
H	8.702256	2.324384	-0.603456
C	7.849061	1.526237	1.200499
H	7.980440	0.644022	1.849197
O	7.182312	2.796666	3.057691
O	9.419460	2.648779	2.608042
O	10.553283	0.262932	1.278181
H	10.224600	-0.432026	0.685304
O	8.726158	0.244274	-0.672164
H	7.993841	0.354197	-1.317198
O	6.513256	1.579798	0.691841
H	5.942288	1.837000	1.434341
C	6.939242	3.985657	6.503642
H	6.561686	3.611145	7.457768
C	6.858320	3.180749	5.366648
C	7.515394	5.256483	6.422680
H	7.591579	5.889052	7.309647
H	6.432274	2.176275	5.407084
F	8.340712	5.394362	2.887954
C	3.541919	0.902840	-7.669061
H	2.553757	1.301873	-7.908043
C	3.924578	0.860143	-6.332643
C	5.174903	0.352976	-5.945842
C	4.760721	0.106157	-3.595709
H	4.139198	1.012267	-3.444358
C	2.992362	-1.262762	-2.871415
H	2.423853	-2.143929	-3.199701
H	2.292623	-0.408533	-2.767614
C	3.646764	-1.552070	-1.524860
H	2.854918	-1.560016	-0.745940
C	4.647919	-0.445519	-1.165223
H	4.074813	0.487482	-0.964055
C	5.590947	-0.169564	-2.341448
H	6.183462	-1.075206	-2.541897
O	5.642374	0.285023	-4.666219
O	3.947116	-0.998539	-3.879148
O	4.310159	-2.790657	-1.587759

```
H       4.914810      -2.807540      -0.829012
O       5.337257      -0.873680      -0.015103
H       5.922799      -0.151605       0.277227
O       6.494630       0.894727      -2.067490
H       6.162661       1.438927      -1.333659
C       5.673423      -0.037508      -8.296487
H       6.369413      -0.391508      -9.060535
C       6.040311      -0.093434      -6.952240
C       4.417373       0.455826      -8.660711
H       4.117254       0.495546      -9.710047
H       7.008463      -0.489335      -6.639304
F       3.064098       1.329178      -5.405345
```
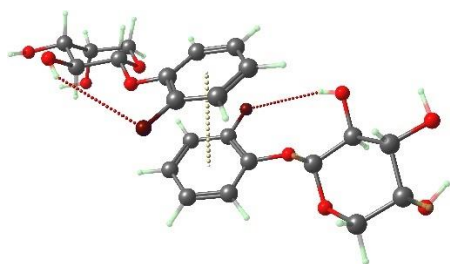

Fig. S15 DFT-optimized geometry of **3a-π**.
Table S12 DFT-optimized cartesian coordinates of **3a-π**.

```
C       2.140912      -9.134582       3.997728
H       1.505376      -8.977298       3.123299
C       1.778425      -8.559045       5.220435
H       0.857434      -7.985566       5.325698
C       2.594603      -8.741480       6.339495
C       1.705658      -6.979672       7.678840
H       2.066882      -6.306677       6.871253
C      -0.392672      -5.920033       7.724577
H      -1.461053      -6.171080       7.673343
H      -0.150079      -5.237216       6.884158
C      -0.104496      -5.202069       9.042380
H      -0.539871      -4.182459       8.973548
C       1.409127      -5.069605       9.250578
H       1.821001      -4.366701       8.496942
C       2.074054      -6.422244       9.050980
H       1.663863      -7.128661       9.795920
O       2.342523      -8.215057       7.576481
O       0.313830      -7.142479       7.585382
O      -0.674322      -5.925398      10.105507
H      -0.237875      -5.598982      10.908665
O       1.624745      -4.582692      10.559172
H       2.553548      -4.753261      10.775795
O       3.466800      -6.252488       9.205285
H       3.881975      -7.103200       8.993899
C       4.109713     -10.107704       5.014471
H       5.044522     -10.666215       4.949103
C       3.756955      -9.514784       6.217299
C       3.296872      -9.909354       3.893850
H       3.585015     -10.350368       2.937831
F       4.553868      -9.639755       7.291817
C       6.040510      -6.832155       6.574350
H       6.505402      -6.870701       7.562125
C       6.499401      -7.690879       5.570084
```

```
H      7.279541    -8.421253    5.779893
C      5.901527    -7.663181    4.308771
C      7.456772    -9.143162    3.261212
H      8.268197    -8.459830    3.596945
C      8.567753   -11.037581    4.124932
H      8.368821   -11.895160    4.781849
H      9.405068   -10.450672    4.553656
C      8.969204   -11.538476    2.739612
H      9.990341   -11.967760    2.817833
C      9.008388   -10.369794    1.748730
H      9.835656    -9.683255    2.023643
C      7.702556    -9.591971    1.824084
H      6.874093   -10.275767    1.562219
O      6.238893    -8.468204    3.259242
O      7.378605   -10.259610    4.113335
O      8.043268   -12.505061    2.306312
H      8.182898   -12.592456    1.349777
O      9.205827   -10.903631    0.457045
H      8.976565   -10.205240   -0.174516
O      7.793768    -8.505046    0.932658
H      6.954198    -8.024269    0.975225
C      4.381339    -5.925957    5.070502
H      3.551288    -5.255104    4.839831
C      4.841335    -6.774766    4.075864
C      4.986839    -5.951158    6.332549
H      4.619008    -5.309010    7.133230
F      4.270431    -6.769582    2.863386
```
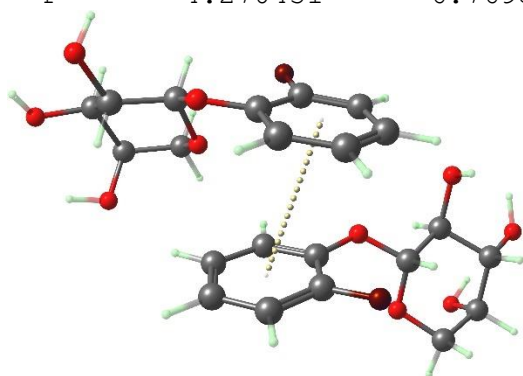

Fig. S16 DFT-optimized geometry of **3a'-π**.
Table S13 DFT-optimized cartesian coordinates of **3a'-π**.

```
C     11.804412    -4.518319    3.723941
H     11.946613    -4.910600    4.733305
C     10.847368    -5.118672    2.915782
C     10.606634    -4.669649    1.610713
C      8.514894    -5.761674    1.159793
H      8.671411    -6.581862    1.890624
C      6.509346    -5.133993    2.241669
H      6.035885    -4.237799    2.666285
H      6.621021    -5.888360    3.047846
C      5.623071    -5.708275    1.139304
H      4.730857    -6.166682    1.617090
C      6.388827    -6.800012    0.386334
H      6.544724    -7.659030    1.076763
C      7.764990    -6.298080   -0.058225
H      7.635525    -5.460552   -0.758902
O      9.729497    -5.237817    0.726910
```

```
O      7.776094     -4.729421      1.760431
O      5.254109     -4.685279      0.247670
H      4.942611     -5.135976     -0.553352
O      5.619386     -7.191228     -0.729786
H      6.231195     -7.615051     -1.351991
O      8.443626     -7.321113     -0.767864
H      8.715369     -8.004058     -0.137696
C     12.363306     -3.013267      1.918203
H     12.967852     -2.208263      1.495867
C     11.378002     -3.609239      1.131874
C     12.572291     -3.462859      3.224322
H     13.335160     -3.001376      3.855565
H     11.197251     -3.285711      0.107450
F     10.168789     -6.182118      3.404993
C     11.779578     -7.238680     -0.646918
H     11.054689     -7.420370     -1.441366
C     12.834935     -6.370249     -0.896466
C     13.756167     -6.033668      0.106986
C     14.820298     -4.165342     -0.988964
H     14.935780     -4.585046     -2.013667
C     13.498430     -2.375950     -1.799397
H     12.507234     -1.933182     -1.627575
H     13.546462     -2.728480     -2.849289
C     14.581621     -1.331426     -1.557624
H     14.537439     -0.580048     -2.373337
C     15.951444     -2.014332     -1.590240
H     16.140140     -2.367567     -2.628691
C     15.984286     -3.229804     -0.659624
H     15.829086     -2.887212      0.373955
O     14.817609     -5.185155     -0.036744
O     13.613580     -3.460903     -0.902578
O     14.372003     -0.726892     -0.302081
H     15.212297     -0.300629     -0.068675
O     16.925714     -1.073450     -1.197220
H     17.703284     -1.582260     -0.917597
O     17.261280     -3.835227     -0.692174
H     17.362023     -4.309750     -1.530319
C     12.572370     -7.523852      1.617170
H     12.468557     -7.964432      2.610623
C     13.607704     -6.625265      1.365692
C     11.651911     -7.826589      0.612040
H     10.828911     -8.516654      0.812810
H     14.320304     -6.341904      2.141586
F     12.964053     -5.850879     -2.135039
```
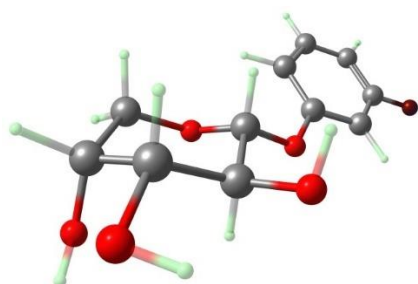

Fig. S17 DFT-optimized geometry of **3b**.
Table S14 DFT-optimized cartesian coordinates of **3b'**.
```
C      8.802433      3.689131      6.348125
```

H	9.585444	4.363340	6.704071
C	8.777164	3.328604	4.997140
H	9.549751	3.681422	4.316372
C	7.774928	2.459284	4.544056
C	8.268479	2.764693	2.231617
H	8.147247	3.861172	2.411355
C	10.371654	3.097446	1.186386
H	11.403271	2.727330	1.263770
H	10.377878	4.193775	1.359046
C	9.831772	2.818954	−0.213169
H	10.338038	3.511081	−0.919447
C	8.326893	3.101393	−0.243615
H	8.169540	4.195722	−0.114052
C	7.617869	2.378277	0.902909
H	7.762966	1.294743	0.780570
O	7.645915	2.051565	3.246480
O	9.635873	2.439654	2.204178
O	10.073593	1.476819	−0.554123
H	9.483596	1.285383	−1.300753
O	7.819312	2.669019	−1.486171
H	6.865671	2.537039	−1.364112
O	6.225083	2.609000	0.843125
H	6.045312	3.521199	1.114010
C	6.888569	2.318371	6.770693
C	6.823330	1.944607	5.434433
C	7.862471	3.193031	7.252205
H	7.874528	3.460071	8.309991
H	6.045727	1.268880	5.077233
F	5.976509	1.826946	7.622242
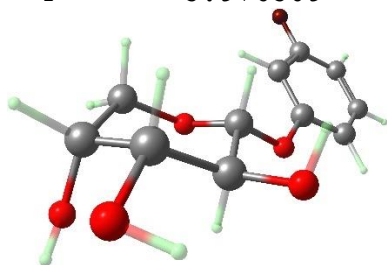
Fig. S18 DFT-optimized geometry of **3b'**.
Table S15 DFT-optimized cartesian coordinates of **3b'**.

C	8.772268	3.711446	6.334209
C	8.752834	3.367128	4.983326
H	9.517236	3.763208	4.317698
C	7.772851	2.467633	4.545232
C	8.266965	2.778314	2.232155
H	8.151653	3.875880	2.409986
C	10.377307	3.083763	1.189664
H	11.403791	2.701069	1.272506
H	10.397603	4.181176	1.353400
C	9.836299	2.801061	−0.208650
H	10.354173	3.479706	−0.919479
C	8.336084	3.105241	−0.244445
H	8.194273	4.202218	−0.119080
C	7.614661	2.396378	0.902991
H	7.743913	1.310507	0.784266
O	7.638280	2.069446	3.246218
O	9.631430	2.443469	2.211493

```
O          10.058764          1.452502          -0.538261
H           9.470205          1.264844          -1.286948
O           7.825226          2.675312          -1.486502
H           6.869306          2.558932          -1.366566
O           6.225272          2.647116           0.840365
H           6.059377          3.564420           1.102946
C           6.915909          2.277248           6.797028
C           6.855392          1.917826           5.452414
C           7.874492          3.186678           7.257532
H           7.939080          3.485132           8.304900
H           6.106605          1.218844           5.076740
H           6.199634          1.847622           7.501698
F           9.707215          4.577838           6.754525
```
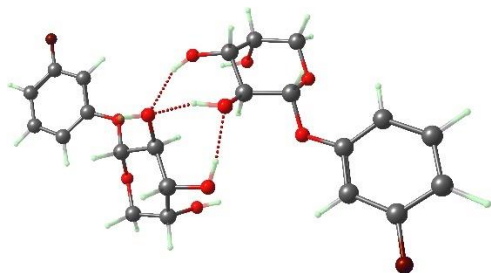

Fig. S19 DFT-optimized geometry of **3b-H**.

Table S16 DFT-optimized cartesian coordinates of **3b-H**.

```
C          13.365715          4.683732          -2.618749
H          13.915888          5.507070          -3.080945
C          12.253316          4.970195          -1.820409
H          11.911936          5.995988          -1.689891
C          11.549210          3.909537          -1.235957
C          10.246547          5.283858           0.221322
H          11.220639          5.683776           0.601873
C           9.366073          7.447694          -0.057269
H           8.925893          8.071039          -0.847112
H          10.288342          7.942681           0.311189
C           8.377910          7.296529           1.088711
H           8.289073          8.277685           1.601558
C           8.877995          6.272296           2.126076
H           9.766954          6.696483           2.645391
C           9.324503          4.990357           1.409616
H           8.444001          4.462657           1.019377
O          10.455955          4.074873          -0.429427
O           9.677857          6.202011          -0.660933
O           7.144198          6.868759           0.575276
H           6.641057          6.552294           1.344569
O           7.804257          6.083329           3.009763
H           7.890483          5.271393           3.557543
O           9.980190          4.069600           2.297367
H          10.882789          4.369377           2.483173
C          13.041178          2.339029          -2.265215
C          11.936209          2.582337          -1.458837
C          13.775015          3.370176          -2.851803
H          14.635991          3.131886          -3.478166
H          11.380595          1.761930          -1.003268
F          13.416674          1.070142          -2.475269
C           3.023530          3.768330           7.161850
H           2.453033          3.026393           7.726292
C           3.827872          3.345798           6.099037
```

S18

```
H        3.859227        2.297015        5.807431
C        4.554876        4.301640        5.376729
C        5.881903        2.712819        4.183522
H        6.163467        2.299501        5.177595
C        5.374548        0.592800        3.295429
H        4.534141        0.061009        2.828521
H        5.648526        0.065441        4.232846
C        6.568536        0.589459        2.349755
H        6.957090       -0.449498        2.286810
C        7.691156        1.482956        2.898611
H        8.133236        1.001799        3.795277
C        7.136581        2.845749        3.322693
H        6.833330        3.394668        2.413179
O        5.370783        3.999924        4.326407
O        4.915855        1.902658        3.573603
O        6.157320        1.058748        1.090717
H        6.973991        1.294474        0.621756
O        8.643299        1.588545        1.854301
H        9.287677        2.296216        2.021708
O        8.071494        3.588701        4.093900
H        8.919502        3.617471        3.612882
C        3.646534        6.042403        6.754098
C        4.467192        5.661897        5.700242
C        2.920409        5.117559        7.504380
H        2.291035        5.462789        8.326024
H        5.041421        6.397303        5.135462
F        3.558235        7.344739        7.064226
```
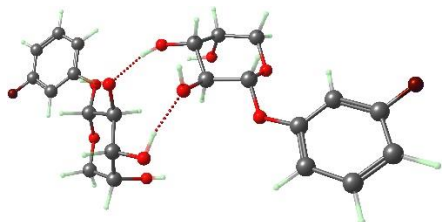

Fig. S20 DFT-optimized geometry of **3b'-H**.
Table S17 DFT-optimized cartesian coordinates of **3b'-H**.

```
C       14.802797        5.127223        2.046419
C       13.425526        5.266466        2.212686
H       12.847690        5.835700        1.486772
C       12.822931        4.607179        3.290728
C       10.718526        5.714139        3.045321
H       11.283987        6.677183        3.119125
C        9.580367        6.426114        1.107783
H        9.411041        6.093999        0.074535
H       10.092383        7.410249        1.082384
C        8.246295        6.570132        1.826593
H        7.722273        7.453244        1.402285
C        8.458033        6.816950        3.331289
H        8.894715        7.831481        3.469861
C        9.450077        5.800035        3.895615
H        8.989848        4.802253        3.881251
O       11.486355        4.678532        3.564795
O       10.416628        5.448316        1.706943
O        7.495507        5.396485        1.653473
H        6.808692        5.437042        2.340728
O        7.195359        6.721003        3.937580
```

```
H          7.267729        6.406133        4.862321
O          9.761768        6.082568        5.257652
H         10.443591        6.767896        5.301644
C         14.957141        3.693453        3.955687
C         13.584514        3.815904        4.162314
C         15.587807        4.353460        2.894986
H         16.660965        4.273395        2.715387
H         13.076522        3.316046        4.988727
H         15.551373        3.077532        4.635195
F         15.384395        5.759157        1.015596
C          1.731830        3.334180        8.144774
C          3.042811        3.211060        7.688102
H          3.671357        2.402493        8.055923
C          3.487490        4.107426        6.708244
C          5.787705        3.503379        6.897937
H          5.721761        3.807789        7.970433
C          6.748747        1.432059        7.479951
H          6.580182        0.357909        7.322718
H          6.698873        1.641141        8.568962
C          8.125910        1.814577        6.956977
H          8.888368        1.386408        7.642214
C          8.305343        3.342152        6.950971
H          8.347463        3.692542        8.009196
C          7.098433        4.016521        6.289361
H          7.075364        3.753194        5.221940
O          4.747056        4.079009        6.181224
O          5.707637        2.106491        6.796473
O          8.277880        1.322249        5.650622
H          9.038334        1.799430        5.279591
O          9.516103        3.586234        6.285269
H          9.641304        4.535998        6.082056
O          7.172666        5.432031        6.358047
H          7.450591        5.709786        7.241631
C          1.322472        5.179476        6.679266
C          2.628239        5.092139        6.200172
C          0.855752        4.301734        7.663939
H         -0.162059        4.351515        8.053705
H          3.009885        5.774480        5.439008
H          0.654302        5.948626        6.284048
F          1.300334        2.468933        9.075859
```
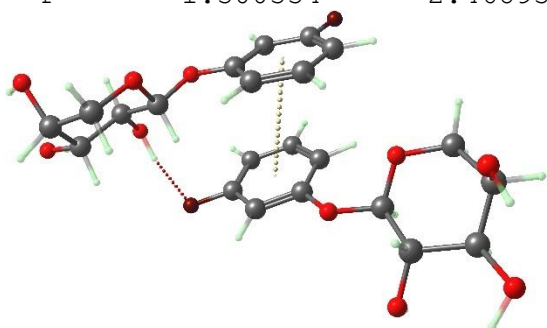

Fig. S21 DFT-optimized geometry of **3b-π**.
Table S18 DFT-optimized cartesian coordinates of **3b-π**.

```
C          7.677611        6.459966        1.835566
H          7.242902        7.289898        1.275085
C          7.158845        6.145928        3.093852
H          6.309633        6.698864        3.488713
```

```
C       7.685521        5.055639        3.797207
C       6.451953        5.469109        5.800757
H       6.877508        6.501916        5.793511
C       4.232231        6.282104        6.041536
H       3.258882        6.186333        5.541007
H       4.533107        7.349549        6.022080
C       4.114554        5.819090        7.488947
H       3.521485        6.574319        8.046800
C       5.512505        5.736930        8.107939
H       5.926597        6.767646        8.183072
C       6.447188        4.908954        7.224118
H       6.051693        3.884589        7.159006
O       7.232120        4.632906        5.012639
O       5.142080        5.494927        5.291908
O       3.498089        4.555779        7.524890
H       3.679305        4.198029        8.408651
O       5.397234        5.150660        9.384487
H       6.275554        4.808634        9.614662
O       7.726446        4.809598        7.815338
H       8.164292        5.672023        7.765159
C       9.214207        4.652412        2.004787
C       8.731486        4.298323        3.254215
C       8.711561        5.715121        1.264892
H       9.097161        5.924067        0.266778
H       9.144341        3.453477        3.805524
F      10.216094        3.898855        1.472328
C       4.560413        3.982623        2.568046
H       4.308720        3.568349        3.545545
C       5.467880        3.307456        1.748257
H       5.879211        2.349765        2.059956
C       5.814574        3.864329        0.509557
C       7.513174        2.256055        0.043458
H       7.939365        2.461848        1.050486
C       7.453573       -0.066088        0.497446
H       6.739352       -0.901147        0.480242
H       7.829384        0.052814        1.535375
C       8.629413       -0.380532       -0.422617
H       9.244129       -1.168703        0.062870
C       9.489476        0.874143       -0.598687
H       9.985959        1.105143        0.369490
C       8.630712        2.079975       -0.987398
H       8.136636        1.868872       -1.947761
O       6.712151        3.316566       -0.359313
O       6.734060        1.084572        0.094131
O       8.148948       -0.809627       -1.672451
H       8.893588       -0.704791       -2.286481
O      10.449367        0.614950       -1.600929
H      10.724784        1.480355       -1.943397
O       9.447254        3.213976       -1.186646
H       9.866376        3.442730       -0.342237
C       4.339292        5.708901        0.929770
C       5.240246        5.070585        0.089086
C       3.983633        5.189917        2.172003
H       3.279875        5.730333        2.806015
H       5.516415        5.502135       -0.873110
F       3.817607        6.884795        0.536619
```
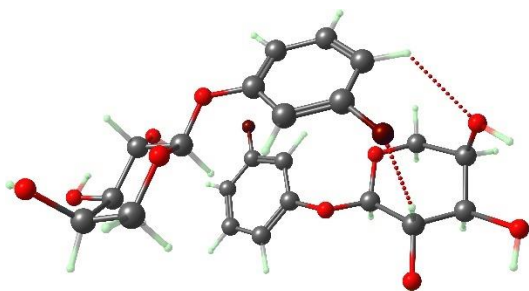
Fig. S22 DFT-optimized geometry of **3b'-π**.

Table S19 DFT-optimized cartesian coordinates of **3b'-π**.

C	11.544681	5.180269	4.824575
C	10.498383	4.586400	5.523073
H	9.543714	4.390846	5.041506
C	10.721462	4.218507	6.855670
C	8.526058	4.193544	7.786881
H	8.675208	5.249250	8.122765
C	6.514740	4.746529	6.652349
H	6.089358	4.672459	5.642249
H	6.569162	5.818568	6.932330
C	5.624925	4.011390	7.648383
H	4.692341	4.599993	7.780154
C	6.343245	3.930558	8.998871
H	6.404429	4.960011	9.419342
C	7.767611	3.393309	8.846179
H	7.722111	2.358835	8.480123
O	9.766258	3.584078	7.601597
O	7.812812	4.186626	6.577027
O	5.343665	2.721008	7.167581
H	5.098511	2.189418	7.942012
O	5.592988	3.089372	9.846335
H	6.196905	2.781150	10.540306
O	8.408557	3.346815	10.106351
H	8.544165	4.253000	10.420390
C	13.001137	5.012332	6.725717
C	11.971477	4.420780	7.457637
C	12.798159	5.403682	5.396738
H	13.578748	5.895309	4.812602
H	12.107885	4.109042	8.494343
H	13.973799	5.180612	7.194085
F	11.348773	5.524874	3.546491
C	8.237045	1.121461	5.741984
C	9.603768	1.016621	5.508194
H	10.252991	0.580269	6.263473
C	10.094301	1.452569	4.271905
C	12.387374	1.399142	4.920181
H	12.125356	2.141976	5.705683
C	13.426227	0.023010	6.541704
H	13.399867	-1.017070	6.895571
H	13.146664	0.689085	7.384488
C	14.839635	0.370982	6.082858
H	15.481240	0.459010	6.986071
C	14.820489	1.719676	5.358658
H	14.589521	2.517379	6.097004
C	13.734061	1.741018	4.280702
H	13.944567	0.944717	3.550861

O	11.416427	1.402451	3.927867
O	12.470812	0.115870	5.499920
O	15.317229	-0.629035	5.217293
H	16.055569	-0.223273	4.734791
O	16.088865	1.931301	4.775397
H	15.948352	2.560815	4.049733
O	13.773455	2.961033	3.572872
H	13.424928	3.665345	4.141215
C	7.856136	2.046367	3.578552
C	9.221300	1.965839	3.302984
C	7.341090	1.626685	4.809276
H	6.287904	1.715743	5.073108
H	9.639125	2.303875	2.353378
H	7.179180	2.453831	2.823108
F	7.772031	0.709274	6.940445
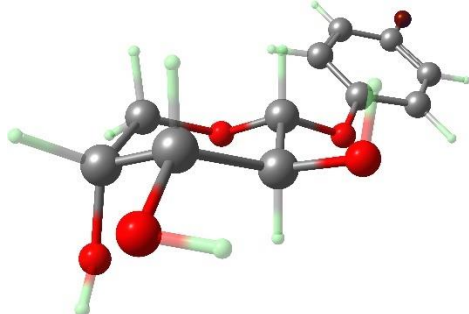
Fig. S23 DFT-optimized geometry of **3c**.

Table S20 DFT-optimized cartesian coordinates of **3c**.

C	8.842698	3.673601	6.349460
C	8.805242	3.298007	5.003076
H	9.588974	3.629363	4.323379
C	7.784865	2.453064	4.548082
C	8.268545	2.757483	2.234818
H	8.137442	3.853445	2.415379
C	10.367253	3.119460	1.187657
H	11.404009	2.763410	1.262997
H	10.358746	4.215505	1.363125
C	9.829699	2.837687	-0.212131
H	10.326308	3.538228	-0.917035
C	8.321287	3.100242	-0.240321
H	8.149616	4.192188	-0.107998
C	7.622609	2.365983	0.905373
H	7.781207	1.284511	0.781096
O	7.656808	2.038276	3.248543
O	9.641391	2.448762	2.203609
O	10.089060	1.499669	-0.556808
H	9.500080	1.301724	-1.302558
O	7.817831	2.663753	-1.483182
H	6.866156	2.519311	-1.359414
O	6.226675	2.578939	0.846598
H	6.036370	3.488891	1.118090
C	6.864883	2.336646	6.787105
C	6.819946	1.971802	5.443237
C	7.875887	3.191283	7.224693
H	6.037994	1.312495	5.061812
H	6.122706	1.972858	7.500526
H	9.629831	4.327909	6.729529

F	7.920171	3.549618	8.518285
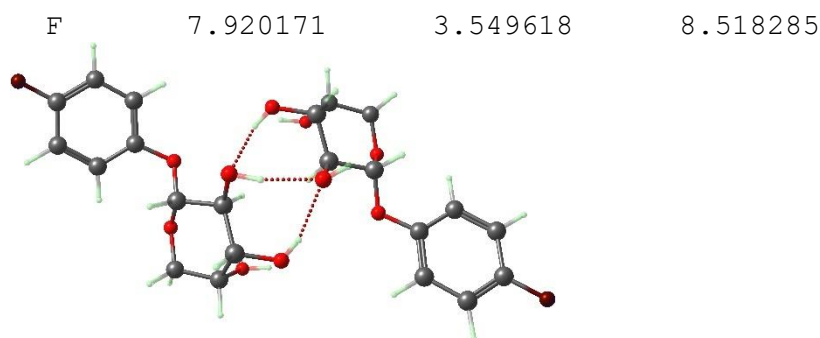
Fig. S24 DFT-optimized geometry of **3c-H**.
Table S21 DFT-optimized cartesian coordinates of **3c-H**.

C	13.300324	5.996161	1.098936
C	12.027617	5.595255	1.515220
H	11.159823	5.776975	0.882263
C	11.879265	4.915670	2.730732
C	9.508693	5.147124	2.834569
H	9.687802	6.244688	2.780546
C	7.879739	5.214400	1.133956
H	7.672581	4.760496	0.155027
H	7.972300	6.312644	1.001421
C	6.729474	4.919185	2.086387
H	5.843285	5.498620	1.749833
C	7.078561	5.376913	3.510256
H	7.105510	6.485849	3.538626
C	8.466191	4.865561	3.916284
H	8.415536	3.767312	4.025523
O	10.672554	4.491456	3.218424
O	9.100328	4.659598	1.584185
O	6.470352	3.538029	2.079190
H	5.938832	3.366940	2.873279
O	6.042782	4.869894	4.333074
H	6.242010	4.971682	5.278582
O	8.941672	5.486869	5.103500
H	8.230402	5.486734	5.770210
C	14.272387	5.007746	3.092361
C	13.002051	4.619714	3.514629
C	14.405586	5.700036	1.889494
H	12.854120	4.088437	4.456926
H	15.161325	4.789002	3.687459
H	13.444442	6.525713	0.155017
F	15.627160	6.085312	1.482877
C	2.522122	1.716938	9.293221
C	3.801955	1.790471	8.734499
H	4.622112	1.212876	9.160189
C	4.011253	2.573714	7.593531
C	6.398500	2.538226	7.708126
H	6.280278	2.976775	8.731097
C	7.921830	0.909482	8.465038
H	8.030384	-0.183332	8.482403
H	7.897845	1.278551	9.511268
C	9.102198	1.530037	7.733064
H	10.007574	1.399047	8.363239
C	8.894128	3.042414	7.519221
H	8.955360	3.552180	8.507590
C	7.494473	3.294340	6.951121

```
H        7.454387        2.951237        5.909111
O        5.230547        2.713057        6.980576
O        6.689761        1.176442        7.814347
O        9.246324        0.905684        6.485560
H        9.823943        1.495017        5.971075
O        9.930606        3.454664        6.665931
H        9.702963        4.252380        6.138064
O        7.165972        4.692846        6.920404
H        7.027151        5.024638        7.820168
C        1.667850        3.176538        7.549485
C        2.945211        3.260795        6.999167
C        1.472610        2.408594        8.697085
H        3.141017        3.855833        6.104744
H        0.820579        3.702482        7.105066
H        2.328175        1.111561       10.180873
F        0.244353        2.330779        9.232839
```
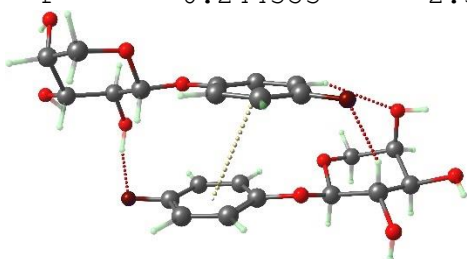

Fig. S25 DFT-optimized geometry of **3c-π**.

Table. S22 DFT-optimized cartesian coordinates of **3c-π**.

```
C        0.982593        0.633011       -5.225089
C        2.367405        0.454547       -5.199918
H        2.854200        0.076557       -4.305210
C        3.119228        0.697838       -6.356490
C        5.344827        0.467533       -5.414622
H        5.328194        1.468251       -4.915355
C        5.906829       -0.696814       -3.409103
H        5.486769       -1.487988       -2.772414
H        5.991867        0.229922       -2.805369
C        7.286911       -1.103136       -3.905920
H        7.984285       -1.113161       -3.042175
C        7.770050       -0.062438       -4.917128
H        7.930396        0.897837       -4.376568
C        6.725863        0.165274       -6.010105
H        6.607233       -0.764083       -6.584906
O        4.457362        0.450759       -6.480908
O        4.993892       -0.522163       -4.475941
O        7.205565       -2.373103       -4.507136
H        7.991333       -2.457946       -5.070809
O        8.974880       -0.523312       -5.486458
H        9.082331       -0.054500       -6.329126
O        7.182663        1.139474       -6.927538
H        7.200273        2.000963       -6.485349
C        1.106871        1.318520       -7.556361
C        2.488058        1.141883       -7.526382
C        0.380127        1.052914       -6.401596
H        3.100678        1.317584       -8.411891
H        0.591789        1.649558       -8.460046
H        0.373023        0.394451       -4.352703
F       -0.979086        1.174972       -6.441086
```

```
C         3.239766      -2.265759      -8.399426
C         1.910956      -2.313902      -7.964963
H         1.108360      -2.147877      -8.680798
C         1.632696      -2.591350      -6.622278
C        -0.719742      -2.298301      -6.871930
H        -0.536334      -1.357105      -7.439148
C        -2.025877      -3.168010      -8.649353
H        -2.076021      -4.062141      -9.286427
H        -1.859189      -2.282620      -9.298620
C        -3.345533      -2.992902      -7.905099
H        -4.115404      -2.669322      -8.638205
C        -3.187331      -1.898530      -6.847161
H        -3.052802      -0.922813      -7.364381
C        -1.951316      -2.139192      -5.975132
H        -2.073752      -3.092229      -5.439132
O         0.374429      -2.603718      -6.078190
O        -0.930320      -3.358575      -7.775784
O        -3.707099      -4.205317      -7.291428
H        -4.359531      -3.967951      -6.612966
O        -4.352735      -1.883804      -6.050220
H        -4.104991      -1.459083      -5.213482
O        -1.855875      -1.124687      -4.996478
H        -1.726369      -0.275511      -5.448378
C         4.004359      -2.834896      -6.166909
C         2.681854      -2.863635      -5.733105
C         4.263186      -2.519638      -7.496970
H         2.436367      -3.081154      -4.692136
H         4.840184      -3.009194      -5.488523
H         3.483768      -2.035802      -9.438389
F         5.546499      -2.442243      -7.913911
```
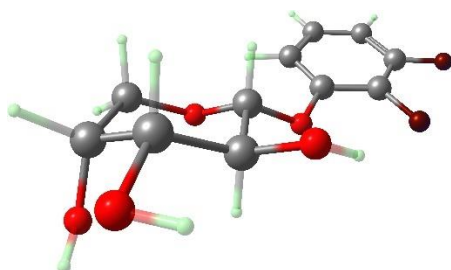

Fig. S26 DFT-optimized geometry of **3d**.
Table S23 DFT-optimized cartesian coordinates of **3d**.
```
C         8.925425       3.502409       6.439579
C         8.984599       3.094811       5.103966
C         7.886611       2.440283       4.535452
C         8.397391       2.769205       2.231185
H         8.212284       3.845844       2.443825
C        10.404261       3.222000       1.085371
H        11.455054       2.901509       1.084073
H        10.368093       4.313748       1.277400
C         9.788163       2.938993      -0.283669
H        10.211329       3.673739      -1.000990
C         8.268731       3.134502      -0.228630
H         8.041828       4.209184      -0.071514
C         7.693592       2.353497       0.943556
H         7.920175       1.281465       0.794967
O         7.838055       1.990787       3.250384
```

O	9.773550	2.515094	2.144009
O	10.090153	1.621275	-0.671932
H	9.463553	1.407415	-1.381928
O	7.728964	2.681701	-1.452444
H	6.776306	2.568375	-1.315497
O	6.307376	2.601108	0.991935
H	5.949065	2.103405	1.741970
C	6.708441	2.596044	6.644197
C	6.742381	2.197918	5.308125
C	7.793328	3.254027	7.218848
H	7.730584	3.554839	8.266057
H	9.875834	3.249624	4.496321
H	9.783648	4.010851	6.884336
F	5.686485	1.593341	4.756150
F	5.608420	2.346191	7.359357
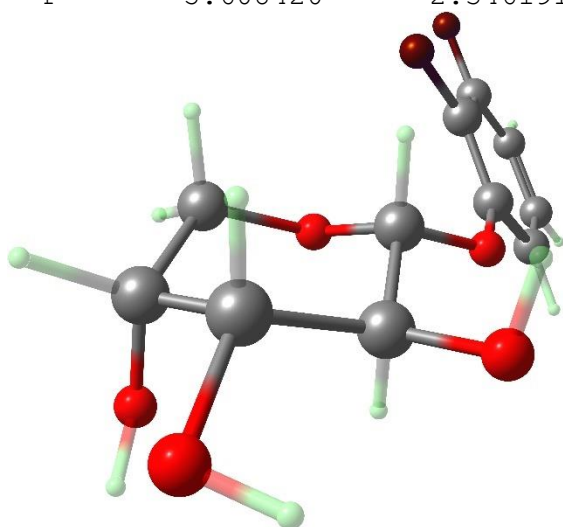
Fig. S27 DFT-optimized geometry of **3d'**.
Table S24 DFT-optimized cartesian coordinates of **3d'**.

C	8.745447	3.799521	6.347485
C	8.430154	3.769861	4.985830
C	7.581045	2.772615	4.484992
C	8.044973	3.089858	2.150673
H	8.094953	4.200732	2.145179
C	10.271448	2.971546	1.387715
H	11.218889	2.482821	1.652545
H	10.414495	4.069896	1.435642
C	9.866273	2.570961	-0.028116
H	10.546354	3.084377	-0.740647
C	8.430459	3.032782	-0.302283
H	8.418988	4.145174	-0.339067
C	7.488255	2.587316	0.820576
H	7.484956	1.488347	0.866991
O	7.207087	2.646326	3.180054
O	9.322376	2.556650	2.354005
O	9.950381	1.173395	-0.160174
H	9.435826	0.952792	-0.953049
O	8.017342	2.489316	-1.536210
H	7.046951	2.498577	-1.530248
O	6.162375	2.985441	0.537448
H	6.089559	3.943853	0.656116
C	7.339108	1.901568	6.741585

C	7.038051	1.842695	5.382791
C	8.204857	2.880554	7.238056
H	8.470340	2.947573	8.294243
H	6.381111	1.073826	4.973420
H	6.903653	1.168271	7.423731
F	8.956701	4.715546	4.191243
F	9.576028	4.753954	6.779009
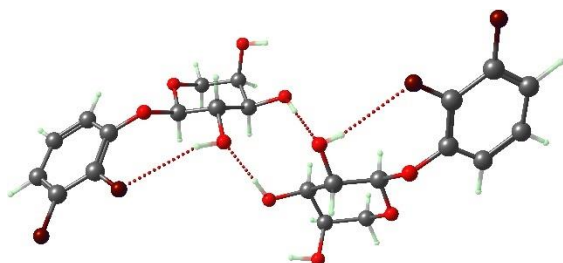
Fig. S28 DFT-optimized geometry of **3d-H**.

Table S25 DFT-optimized cartesian coordinates of **3d-H**.

C	12.737758	5.478622	2.420956
C	11.415751	5.125685	2.140890
C	11.008256	3.800082	2.314947
C	8.707146	3.829199	2.868654
H	9.088899	3.936548	3.908531
C	7.171603	5.560074	3.186934
H	6.853439	6.501083	2.718099
H	7.528941	5.777144	4.214423
C	5.987870	4.601723	3.259669
H	5.289835	4.982672	4.035500
C	6.432863	3.191028	3.683583
H	6.767918	3.216493	4.740906
C	7.624220	2.755430	2.833254
H	7.296362	2.649808	1.784350
O	9.740774	3.369173	2.037064
O	8.235997	5.054588	2.393994
O	5.364509	4.540185	2.001046
H	4.821295	3.734877	2.026688
O	5.308718	2.360676	3.524105
H	5.553192	1.411957	3.591313
O	8.146370	1.536025	3.333275
H	8.982931	1.356299	2.875472
C	13.238172	3.206737	3.043875
C	11.917929	2.841322	2.775338
C	13.654878	4.523628	2.869562
H	14.693945	4.776394	3.088310
H	10.683503	5.850368	1.784061
H	13.062868	6.511918	2.282095
F	11.516243	1.577589	2.960184
F	14.089288	2.276423	3.482438
C	0.743256	-3.287264	5.129889
C	2.048788	-3.024396	5.551831
C	2.993471	-2.582995	4.621623
C	4.563030	-1.220921	5.759108
H	3.780882	-0.446570	5.593865
C	4.879464	-0.545135	7.974264
H	4.910957	-0.970018	8.986816
H	4.075015	0.217592	7.934454

```
C       6.215595       0.120677       7.660339
H       6.279342       1.051662       8.262969
C       6.308209       0.515501       6.176979
H       5.583727       1.329915       5.971009
C       5.917372      -0.679701       5.311935
H       6.659780      -1.484356       5.453310
O       4.296799      -2.333541       4.943873
O       4.580373      -1.620932       7.096095
O       7.261060      -0.763652       7.978848
H       8.039876      -0.412751       7.515891
O       7.631476       0.941262       5.961757
H       7.815492       1.056543       5.004916
O       5.847464      -0.280318       3.953136
H       5.464923      -1.010400       3.440663
C       1.321833      -2.673165       2.873625
C       2.625794      -2.394027       3.284774
C       0.374604      -3.119185       3.791539
H      -0.637516      -3.327652       3.439854
H       2.363584      -3.158062       6.587521
H       0.001224      -3.636220       5.851219
F       3.528642      -1.939280       2.404825
F       0.998591      -2.494193       1.591243
```
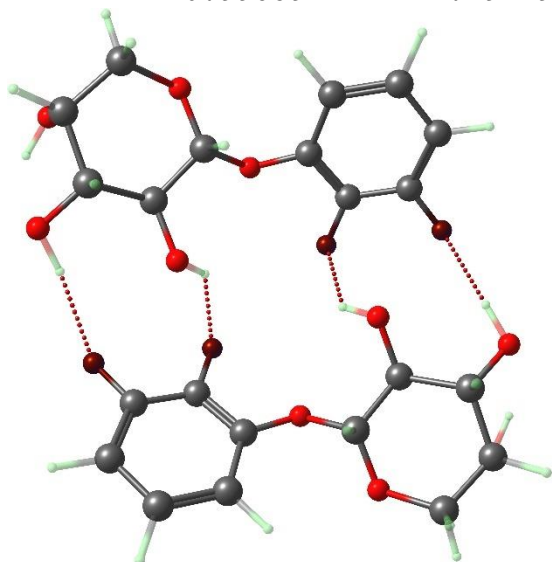

Fig. S29 DFT-optimized geometry of **3d-H_a**.
Table S26 DFT-optimized cartesian coordinates of **3d-H_a**.

```
C       6.890122       7.588356       3.722183
  C       6.197776       6.635124       2.971017
  C       5.160708       5.907509       3.566164
  C       4.014741       5.230446       1.595123
  H       3.933208       6.327259       1.430668
  C       4.606991       4.769262      -0.636114
  H       5.395869       4.250309      -1.197593
  H       4.590146       5.832494      -0.952079
  C       3.254071       4.137394      -0.957145
  H       2.993622       4.414888      -2.000848
  C       2.176035       4.695344      -0.021313
  H       2.011637       5.768891      -0.249804
  C       2.641607       4.588731       1.422493
  H       2.751530       3.518449       1.673560
  O       4.398541       4.986971       2.923903
```

```
O          4.964499         4.668062          0.735297
O          3.339735         2.741574         -0.809259
H          2.421470         2.433118         -0.740636
O          0.995435         3.949166         -0.223845
H          0.429381         4.074369          0.554877
O          1.684451         5.230402          2.229441
H          1.803420         4.929397          3.140594
C          5.547348         7.084856          5.646681
C          4.858334         6.121454          4.916538
C          6.570294         7.824399          5.062005
H          7.096050         8.568473          5.662418
H          6.453791         6.429970          1.931107
H          7.699711         8.154665          3.256637
F          3.851674         5.432838          5.481995
F          5.192235         7.305182          6.923199
C         -2.832842         6.654056          3.507515
C         -2.070118         7.014673          4.621635
C         -0.931200         6.269667          4.949662
C          0.120156         7.896281          6.335636
H         -0.015516         8.547412          5.444642
C         -0.585431         9.536478          7.869893
H         -1.315867         9.655605          8.681830
H         -0.792103        10.303814          7.095535
C          0.823266         9.753418          8.417694
H          0.930090        10.834840          8.648904
C          1.866868         9.377329          7.359692
H          1.814250        10.099633          6.518765
C          1.568296         7.992099          6.807240
H          1.694609         7.257475          7.622642
O         -0.084610         6.555796          5.969730
O         -0.789102         8.233590          7.342238
O          1.005614         8.966859          9.568847
H          1.967049         8.918848          9.697871
O          3.136625         9.411779          7.975823
H          3.742463         8.870786          7.445079
O          2.450426         7.756568          5.736019
H          2.451154         6.806294          5.557584
C         -1.359855         4.812838          3.063213
C         -0.605024         5.142189          4.184549
C         -2.482185         5.558261          2.715175
H         -3.058850         5.267947          1.835473
H         -2.352784         7.856584          5.253983
H         -3.721450         7.236498          3.254711
F          0.480640         4.420019          4.510496
F         -0.975750         3.771852          2.306869
```


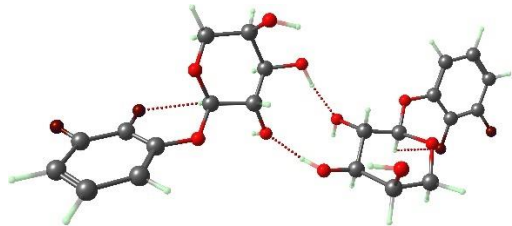**Fig. S30** DFT-optimized geometry of **3d'-H**.

Table S27 DFT-optimized cartesian coordinates of **3d'-H**.

```
C         14.562080         6.396760          4.152388
C         13.204800         6.116797          3.971078
```

```
C      12.789704      4.807271      3.690395
C      10.553784      5.319525      2.990746
H      10.354602      6.131537      3.722988
C      10.193792      6.824667      1.230932
H      10.683284      7.174418      0.311821
H      10.069003      7.686843      1.916932
C       8.830128      6.235715      0.891627
H       8.147307      7.069502      0.623044
C       8.226635      5.505712      2.104294
H       7.970410      6.268043      2.876163
C       9.258377      4.552957      2.722834
H       9.479813      3.745396      2.011668
O      11.496129      4.420932      3.504669
O      11.056880      5.861045      1.806343
O       8.971886      5.329149     -0.173672
H       8.156305      4.802163     -0.176619
O       7.081578      4.845501      1.638107
H       6.660834      4.321255      2.349396
O       8.765073      3.924532      3.897048
H       8.487845      4.591467      4.540064
C      15.106986      4.086866      3.833375
C      13.760086      3.797265      3.627271
C      15.523686      5.395959      4.093464
H      16.571390      5.657743      4.249338
H      13.417681      2.785338      3.405679
H      15.846055      3.284554      3.780710
F      12.329312      7.129846      4.079167
F      14.911747      7.662276      4.403250
C       0.436894      0.360512      1.896410
C       1.718845      0.707354      2.331230
C       2.522322      1.549224      1.550179
C       4.628904      1.117284      2.611354
H       4.244026      0.950046      3.640707
C       5.536039     -1.046875      2.587154
H       5.531918     -1.949080      1.960481
H       5.115037     -1.303406      3.580422
C       6.964513     -0.542621      2.751439
H       7.504710     -1.243024      3.423335
C       6.983574      0.848971      3.406220
H       6.643582      0.742870      4.462111
C       6.000389      1.785589      2.693540
H       6.354266      1.971558      1.670206
O       3.772081      1.967854      1.901171
O       4.708947     -0.100028      1.933649
O       7.578742     -0.470617      1.488814
H       8.360063      0.092449      1.615058
O       8.307278      1.303159      3.337928
H       8.380914      2.223693      3.664581
O       5.931472      3.056373      3.327201
H       5.526304      2.971879      4.201305
C       0.718793      1.701034     -0.069758
C       2.004904      2.041310      0.344618
C      -0.078705      0.851748      0.703149
H      -1.086938      0.562032      0.402870
H       2.648016      2.690779     -0.251199
H       0.333003      2.094847     -1.012489
```
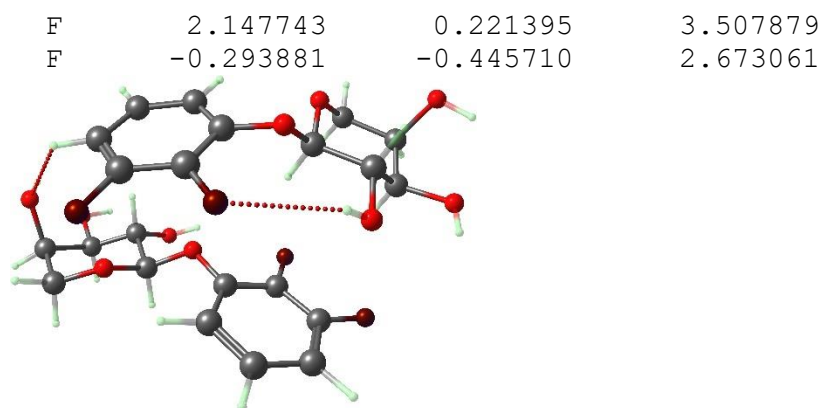
F	2.147743	0.221395	3.507879
F	-0.293881	-0.445710	2.673061

Fig. S31 DFT-optimized geometry of **3d-π**.

Table S28 DFT-optimized cartesian coordinates of **3d-π**.

C	11.011405	7.045358	2.951022
C	10.027662	6.122898	3.314074
C	9.478387	6.179918	4.599103
C	7.402029	5.044268	4.318843
H	7.025741	5.998516	3.888290
C	6.584374	3.752854	2.516449
H	6.953306	3.010377	1.795698
H	6.190996	4.624757	1.955854
C	5.453433	3.150578	3.346460
H	4.559776	3.070767	2.693489
C	5.113813	4.075105	4.521403
H	4.657259	5.006844	4.128521
C	6.378281	4.452198	5.279660
H	6.830295	3.533094	5.694226
O	8.552613	5.294648	5.076312
O	7.704593	4.133658	3.297088
O	5.833394	1.880398	3.825418
H	5.223526	1.682341	4.554818
O	4.209237	3.387897	5.360878
H	4.185452	3.866384	6.203195
O	6.015849	5.363489	6.292833
H	6.825198	5.608102	6.765322
C	10.923127	8.047293	5.132021
C	9.917308	7.156889	5.497793
C	11.467870	8.009118	3.853997
H	12.256967	8.717412	3.596446
H	9.700821	5.336180	2.636017
H	11.446539	6.998623	1.950484
F	9.403640	7.197118	6.739070
F	11.358532	8.930692	6.035333
C	8.943768	1.677495	6.172112
C	9.939478	2.352899	6.883051
C	10.935252	3.038450	6.183088
C	11.575540	4.740299	7.694103
H	10.618493	5.193086	7.366192
C	11.081958	5.188411	9.943626
H	11.048677	4.676581	10.915325
H	10.073955	5.594215	9.721416
C	12.073907	6.349164	10.016777
H	11.612623	7.146824	10.637017
C	12.331903	6.916118	8.616252
H	11.413109	7.403272	8.241116

```
C        12.692822        5.777168        7.671501
H        13.601528        5.275982        8.052546
O        11.943337        3.730370        6.795385
O        11.437191        4.203651        8.983654
O        13.280812        5.901323       10.585985
H        13.944621        6.568396       10.348209
O        13.387334        7.850405        8.720361
H        13.658350        8.071403        7.817265
O        12.891262        6.309624        6.381337
H        12.987558        5.564173        5.768730
C         9.934099        2.350547        4.092651
C        10.928163        3.038806        4.784136
C         8.935443        1.666370        4.775704
H         8.134737        1.191309        4.209380
H         9.971017        2.362409        7.972796
H         8.159422        1.145382        6.715455
F        11.852959        3.738354        4.112566
F         9.936204        2.397764        2.755835
```
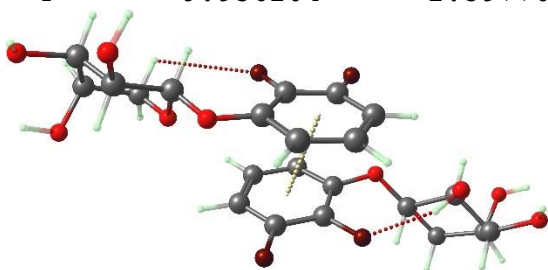

Fig. S32 DFT-optimized geometry of **3d'-π**.

Table S29 DFT-optimized cartesian coordinates of **3d'-π**.

```
C         7.889677        2.049193        1.828755
C         6.707315        1.794975        1.126380
C         5.696931        1.023022        1.716557
C         4.062264        1.237033       -0.050809
H         4.311849        2.319669       -0.078752
C         4.285480        1.092343       -2.398135
H         4.818084        0.493038       -3.149686
H         4.607961        2.148385       -2.497264
C         2.782201        0.990766       -2.636103
H         2.534939        1.564536       -3.554362
C         2.036405        1.615056       -1.452677
H         2.227718        2.711846       -1.456360
C         2.546654        1.052185       -0.122974
H         2.350422       -0.029923       -0.094907
O         4.520436        0.661727        1.132101
O         4.662625        0.577700       -1.134242
O         2.423982       -0.362998       -2.768180
H         1.461955       -0.394722       -2.643852
O         0.660562        1.348805       -1.606803
H         0.258152        1.449175       -0.729649
O         1.833048        1.619401        0.956817
H         2.092730        2.547591        1.052195
C         7.082042        0.810828        3.703336
C         5.901844        0.539028        3.017591
C         8.095727        1.573602        3.115233
H         9.052150        1.752404        3.606486
H         5.109061       -0.068443        3.455881
H         7.222453        0.412319        4.710393
```

F	6.607060	2.279610	-0.122328
F	8.839512	2.742539	1.197181
C	7.334952	-1.732647	0.954555
C	8.544610	-1.266309	1.465292
C	9.370199	-0.435830	0.699107
C	11.487038	-0.644687	1.798492
H	11.119461	-1.680060	1.962518
C	13.660025	-1.443206	1.355578
H	14.445290	-1.342976	0.593572
H	13.369864	-2.512420	1.423066
C	14.204491	-0.993144	2.709865
H	14.911020	-1.771976	3.068235
C	13.053418	-0.875176	3.714058
H	12.652119	-1.890554	3.922950
C	11.925248	-0.027352	3.125252
H	12.322156	0.973658	2.895420
O	10.478362	0.146048	1.235498
O	12.565007	-0.662826	0.905380
O	14.847889	0.250039	2.571827
H	14.912818	0.612119	3.470130
O	13.555439	-0.284648	4.892923
H	12.786537	0.043006	5.385279
O	10.885950	0.130684	4.074666
H	10.201554	-0.536346	3.916161
C	7.753056	-0.558893	-1.094056
C	8.967580	-0.090437	-0.593869
C	6.928130	-1.385188	-0.327059
H	5.954382	-1.717196	-0.685710
H	9.611850	0.577994	-1.165882
H	7.427272	-0.260249	-2.091494
F	8.883953	-1.582553	2.736198
F	6.558518	-2.482559	1.742610
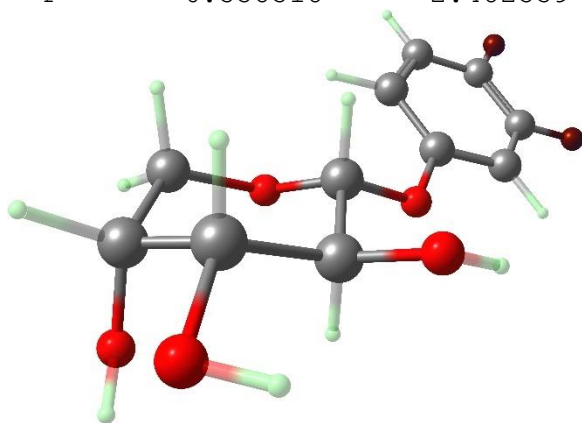
Fig. S33 DFT-optimized geometry of **3e**.
Table S30 DFT-optimized cartesian coordinates of **3e**.

C	8.849385	3.679106	6.347586
C	8.790410	3.356515	4.987493
C	7.754841	2.538165	4.520860
C	8.283417	2.856288	2.207173
H	8.189903	3.953455	2.373206
C	10.396302	3.086478	1.183417
H	11.412113	2.676519	1.266900
H	10.444933	4.183484	1.341595
C	9.850168	2.811863	-0.215776

```
H        10.385493        3.477628       -0.925461
C         8.356577        3.149186       -0.267607
H         8.224561        4.245230       -0.156416
C         7.629279        2.467692        0.883739
H         7.754799        1.374384        0.779322
O         7.600157        2.168100        3.212324
O         9.633054        2.472433        2.210756
O        10.050203        1.458015       -0.540812
H         9.459492        1.278154       -1.289648
O         7.855292        2.706891       -1.511145
H         6.889098        2.696621       -1.437179
O         6.275081        2.855081        0.813062
H         5.800358        2.393940        1.518536
C         6.879403        2.354510        6.759286
C         6.797006        2.033485        5.411660
C         7.901915        3.184087        7.233438
H         5.991706        1.390951        5.053816
H         9.567106        3.705930        4.310396
H         9.648532        4.311732        6.739437
F         5.975881        1.877504        7.618939
F         7.957426        3.479934        8.536583
```
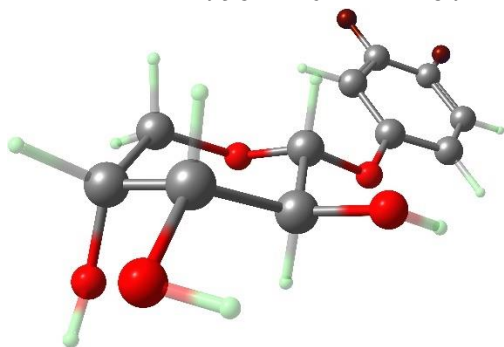

Fig. S34 DFT-optimized geometry of **3e'**.

Table S31 DFT-optimized cartesian coordinates of **3e'**.
```
C         8.857181        3.659638        6.329248
C         8.799849        3.330338        4.978466
C         7.746409        2.528234        4.520700
C         8.278893        2.848101        2.208460
H         8.176988        3.944323        2.376686
C        10.392048        3.100748        1.191098
H        11.410861        2.698523        1.274991
H        10.431314        4.197098        1.355437
C         9.850975        2.828505       -0.210759
H        10.380916        3.504319       -0.914870
C         8.353860        3.150267       -0.263537
H         8.210264        4.244386       -0.147293
C         7.632175        2.455493        0.883276
H         7.772746        1.364328        0.775454
O         7.598514        2.154908        3.212441
O         9.631558        2.475120        2.213959
O        10.065631        1.478859       -0.543275
H         9.476968        1.296302       -1.293034
O         7.859169        2.708315       -1.509842
H         6.892997        2.688122       -1.436739
O         6.272888        2.824493        0.810551
H         5.804988        2.357859        1.517006
C         6.860334        2.385726        6.768700
```

```
C       6.779550        2.054522        5.416213
C       7.896779        3.192408        7.228443
H       5.970770        1.427364        5.038284
H       9.598295        3.665212        4.319387
H       6.118136        2.028206        7.485339
F       9.854809        4.423760        6.781474
F       7.988692        3.521309        8.521650
```
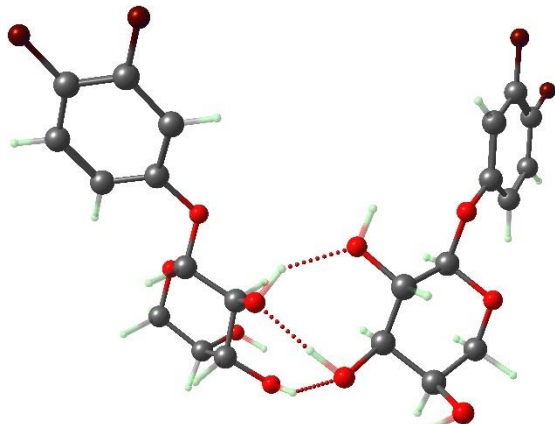

Fig. S35 DFT-optimized geometry of **3e-H**.

Table S32 DFT-optimized cartesian coordinates of **3e-H**.

```
C       10.686752       8.196200        4.424429
  C     10.167617       7.779303        3.194304
  C     10.706527       6.648192        2.571106
  C      8.990381       6.513824        0.908684
  H      8.255398       6.445693        1.743120
  C      7.758683       8.237387       -0.086906
  H      7.901741       9.248767       -0.490554
  H      7.026734       8.286168        0.745037
  C      7.218479       7.326213       -1.181883
  H      6.160283       7.606918       -1.368261
  C      7.240993       5.854125       -0.739741
  H      6.493459       5.700262        0.063594
  C      8.620068       5.503982       -0.180869
  H      9.367271       5.598667       -0.988061
  O     10.256740       6.150752        1.373225
  O      9.024302       7.812581        0.394819
  O      8.001852       7.489012       -2.337322
  H      7.782113       6.741296       -2.915512
  O      6.897406       5.095123       -1.885726
  H      6.993311       4.131262       -1.674430
  O      8.610947       4.192776        0.368592
  H      9.462307       4.066256        0.814327
  C     12.280298       6.388900        4.376370
  C     11.771044       5.952994        3.160478
  C     11.735432       7.507233        5.018071
  H     12.200999       5.076073        2.674718
  H      9.380192       8.354115        2.711443
  H     10.287909       9.076414        4.932734
  F     13.292745       5.738391        4.952434
  F     12.238294       7.901468        6.191813
  C      6.819013      -3.025780        1.127315
  C      6.299368      -1.732830        1.004781
  C      7.156250      -0.632840        1.133701
  C      5.614983       0.962311        0.260723
```

```
H          5.612355        0.340496       -0.662793
C          3.266269        1.014600        0.329712
H          2.441897        0.795062        1.022082
H          3.157191        0.368307       -0.565667
C          3.197375        2.475142       -0.095567
H          2.320540        2.597087       -0.765894
C          4.453094        2.880222       -0.882182
H          4.449231        2.364271       -1.864149
C          5.709273        2.440142       -0.125461
H          5.775900        3.019205        0.810452
O          6.745836        0.666665        1.021821
O          4.464537        0.707213        1.021015
O          3.077164        3.282472        1.050741
H          3.282189        4.183545        0.754392
O          4.374758        4.280710       -1.040277
H          5.138367        4.616094       -1.549878
O          6.855752        2.640179       -0.939162
H          7.616259        2.838916       -0.357229
C          9.013330       -2.115083        1.532782
C          8.518267       -0.825238        1.401956
C          8.168659       -3.221513        1.389382
H          9.188734        0.028731        1.502317
H          5.232924       -1.579064        0.849500
H          6.173874       -3.901870        1.034075
F         10.309567       -2.313195        1.785057
F          8.674033       -4.453674        1.514386
```
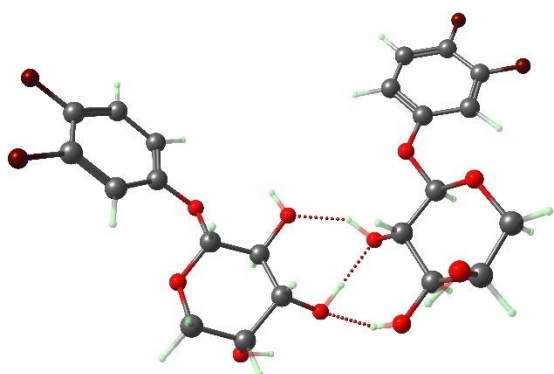

Fig. S36 DFT-optimized geometry of **3e'-H**.
Table S33 DFT-optimized cartesian coordinates of **3e'-H**.

```
C          7.311303        4.616971        8.530706
C          6.997819        5.409607        7.430362
C          7.921754        5.510700        6.381913
C          6.425084        6.705881        4.948783
H          5.690589        5.879712        5.084044
C          4.835765        8.344225        5.502958
H          4.701358        9.177538        6.206104
H          4.033624        7.598581        5.681589
C          4.733037        8.861722        4.074641
H          3.673921        9.135037        3.882937
C          5.129201        7.774219        3.063351
H          4.350053        6.984479        3.055160
C          6.449877        7.120643        3.476574
H          7.258325        7.862670        3.362607
O          7.709060        6.253508        5.255694
O          6.107089        7.784062        5.783167
```

```
O        5.580625        9.974586        3.927665
H        5.673579       10.100583        2.969651
O        5.213695        8.425622        1.813836
H        5.521577        7.815441        1.115599
O        6.679767        5.973217        2.672518
H        7.644179        5.813019        2.623022
C        9.448449        4.055922        7.571652
C        9.147234        4.836063        6.455842
C        8.529932        3.940397        8.610670
H        9.852649        4.935034        5.629584
H        6.062445        5.965754        7.434119
H       10.397498        3.521843        7.651435
F        6.439928        4.510085        9.537566
F        8.803598        3.195153        9.687601
C       14.495945        8.173731       -0.207476
C       13.147880        7.851034       -0.335618
C       12.702812        6.610549        0.137568
C       10.375796        7.136073       -0.127870
H       10.532390        8.006304        0.549596
C        9.315326        8.478953       -1.728325
H        9.376915        8.715054       -2.799078
H        9.469258        9.412176       -1.149351
C        7.937155        7.910549       -1.411560
H        7.202193        8.740216       -1.479881
C        7.885842        7.352770        0.019797
H        7.954275        8.190445        0.742295
C        9.075573        6.420970        0.247794
H        8.974136        5.551208       -0.424179
O       11.396328        6.201011        0.064543
O       10.357654        7.553061       -1.460742
O        7.643552        6.889201       -2.331455
H        6.885830        6.407908       -1.963051
O        6.641673        6.687299        0.143544
H        6.605660        6.243051        1.029268
O        9.135661        6.021066        1.610966
H        9.951993        5.510715        1.721760
C       14.952252        6.042773        0.821869
C       13.603674        5.705190        0.710430
C       15.400975        7.279390        0.368652
H       13.234540        4.740825        1.062839
H       12.482988        8.550084       -0.839375
H       15.674613        5.354842        1.265748
F       14.939524        9.350578       -0.654603
F       16.689058        7.620062        0.473622
```
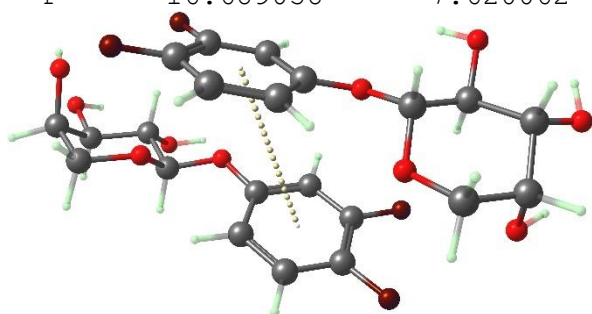

Fig. S37 DFT-optimized geometry of **3e-π**.
Table S34 DFT-optimized cartesian coordinates of **3e-π**.

```
C        9.626825        4.540707        3.378797
```

```
C         8.915565        4.984326        2.258419
C         7.549024        4.705027        2.164624
C         7.198979        6.013731        0.180537
H         7.577605        6.916466        0.711114
C         8.677951        6.308059       -1.647145
H         9.417854        5.725676       -2.211124
H         9.174226        7.200402       -1.214370
C         7.565376        6.760518       -2.589122
H         7.975975        7.565674       -3.235340
C         6.402088        7.340185       -1.778016
H         6.728774        8.283735       -1.293514
C         5.992131        6.364043       -0.685046
H         5.666993        5.421867       -1.160122
O         6.755566        5.070448        1.108467
O         8.214401        5.453906       -0.611678
O         7.128513        5.666771       -3.353956
H         6.256647        5.914311       -3.699945
O         5.327169        7.576656       -2.662568
H         4.535660        7.690070       -2.114969
O         4.953319        6.971321        0.053377
H         4.660296        6.335192        0.720483
C         7.628956        3.542278        4.271857
C         6.903781        3.985522        3.178159
C         8.993300        3.821545        4.381288
H         5.842154        3.750993        3.100071
H         9.433287        5.497779        1.451442
H        10.697455        4.733410        3.473537
F         7.023648        2.823900        5.223136
F         9.681648        3.366093        5.433023
C         9.512263        2.131278       -0.592462
C         9.175353        1.552354        0.635829
C         7.829914        1.479000        1.007871
C         8.227952        0.171098        2.982572
H         8.708363       -0.615942        2.358335
C        10.067409        0.297626        4.469708
H        10.733515        1.059748        4.894073
H        10.675775       -0.448213        3.918551
C         9.316246       -0.403375        5.598238
H        10.037276       -1.063842        6.125853
C         8.199717       -1.276172        5.016051
H         8.650412       -2.115924        4.447299
C         7.346527       -0.459133        4.056986
H         6.890708        0.376737        4.616432
O         7.384104        0.952600        2.192021
O         9.206008        0.985605        3.574823
O         8.777395        0.559626        6.467165
H         8.083489        0.105906        6.970944
O         7.419749       -1.758985        6.089649
H         6.590982       -2.085387        5.707932
O         6.372795       -1.326287        3.515258
H         5.804702       -0.799755        2.935925
C         7.190584        2.570420       -1.041150
C         6.834493        1.986211        0.163341
C         8.530622        2.639646       -1.429879
H         5.786062        1.948423        0.459216
H         9.956239        1.211127        1.311538
```

```
H        10.555726       2.215713      -0.902990
F         6.246015       3.094109      -1.829514
F         8.857383       3.226166      -2.585809
```
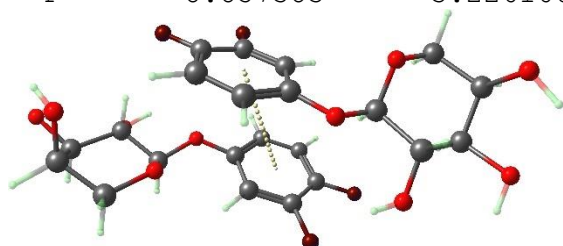

Fig. S38 DFT-optimized geometry of **3e'-π**.
Table S35 DFT-optimized cartesian coordinates of **3e'-π**.

```
C         6.518750       5.183416       3.510897
C         7.628661       4.535937       4.040973
C         8.254073       3.540857       3.281770
C         9.938437       3.150276       4.934837
H        10.071436       4.244859       5.076291
C         9.562022       2.828653       7.238254
H         8.833912       2.349076       7.906850
H         9.602011       3.911223       7.479250
C        10.943592       2.220118       7.468653
H        11.318675       2.587874       8.447418
C        11.907162       2.686644       6.374108
H        12.090920       3.775309       6.479404
C        11.295416       2.456282       4.997005
H        11.104580       1.374620       4.868076
O         9.393712       2.891607       3.676113
O         9.082970       2.632877       5.918333
O        10.846769       0.816324       7.458620
H        11.751226       0.494294       7.315243
O        13.108938       1.958816       6.516505
H        13.608059       2.085117       5.695195
O        12.220158       2.950071       4.058385
H        11.854855       2.859180       3.167853
C         6.607539       3.821564       1.526461
C         7.736413       3.178930       2.032063
C         5.999841       4.823917       2.270363
H         8.243829       2.401443       1.459459
H         7.977562       4.831641       5.027207
H         6.206781       3.594758       0.537170
F         5.946700       6.183726       4.195698
F         4.934514       5.489650       1.785857
C        11.207678       5.618787       2.316300
C        10.133183       5.873789       1.473769
C         9.120977       6.737877       1.905500
C         7.914389       6.808711      -0.193757
H         8.692687       7.425917      -0.697249
C         7.919332       5.144451      -1.881292
H         8.084650       4.062422      -1.978398
H         8.673358       5.672043      -2.499741
C         6.524226       5.504291      -2.375032
H         6.497866       5.365543      -3.475695
C         6.240330       6.975624      -2.062289
H         6.915459       7.611668      -2.671677
C         6.509402       7.260099      -0.591578
H         5.812412       6.654590       0.010491
```

```
O      7.985087       6.993633       1.190476
O      8.096511       5.450396      -0.508631
O      5.579996       4.673746      -1.739235
H      4.723317       5.121941      -1.828531
O      4.887638       7.230451      -2.374319
H      4.653007       8.065892      -1.942371
O      6.306480       8.641534      -0.385506
H      6.336081       8.801871       0.567889
C     10.287134       7.071000       3.998096
C      9.202408       7.342054       3.165905
C     11.295062       6.206631       3.578288
H      8.391167       7.993733       3.492677
H     10.069567       5.354852       0.521384
H     10.368146       7.524418       4.988218
F     12.159822       4.766133       1.910934
F     12.327638       5.928112       4.381122
```
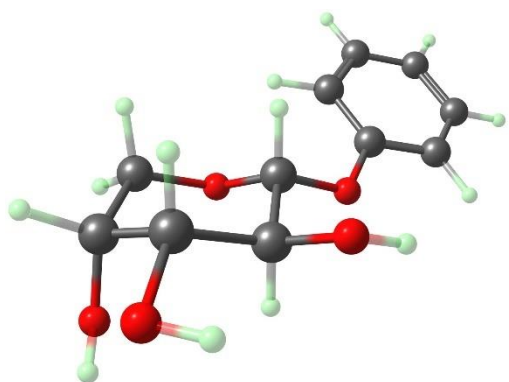

Fig. S39 DFT-optimized geometry of **1**.
Table S36 DFT-optimized cartesian coordinates of **1**.

```
C     8.82286064363239       3.69516407043760       6.34664324945710
  H   9.62704433241044       4.34322674156055       6.70505723919857
  C   8.78270842926563       3.34980211761223       4.99197876915165
  H   9.56229891955277       3.69119037285011       4.31261799080474
  C   7.75533741421816       2.51808739198682       4.52962160788761
  C   8.29280746440836       2.82336465100850       2.21554963277092
  H   8.19747359285814       3.92014317113167       2.38367247101691
  C  10.39576743000992       3.07914598041685       1.18249795852992
  H  11.41608220398323       2.67780355072104       1.25343068964738
  H  10.43594233492818       4.17480248798697       1.35357608767179
  C   9.84337133098491       2.81833787377403      -0.21753567534855
  H  10.36641256719795       3.50080878752391      -0.92064826547952
  C   8.34532658192521       3.13786944173895      -0.25542563147957
  H   8.20032190376878       4.23091487382743      -0.13172020987526
  C   7.63527986695681       2.43617081115922       0.89376762635598
  H   7.77630321803796       1.34547160504096       0.77982336128531
  O   7.61802843230288       2.13185194191058       3.22044523766617
  O   9.64539367430726       2.44644918616580       2.20635748756197
  O  10.05695235761311       1.47193345363568      -0.56509454866551
  H   9.45582308377729       1.29533162089945      -1.30643870819110
  O   7.84019436384976       2.70297266134293      -1.50080210086180
  H   6.87534223240975       2.67155951112072      -1.41579374180012
  O   6.27469447335175       2.80264728095606       0.83586184240162
  H   5.82116477004144       2.34867146835587       1.56005023978867
  C   6.85303310227553       2.36807003992265       6.76894817001329
  H   6.09880727092988       1.97766170952007       7.45725090977345
```

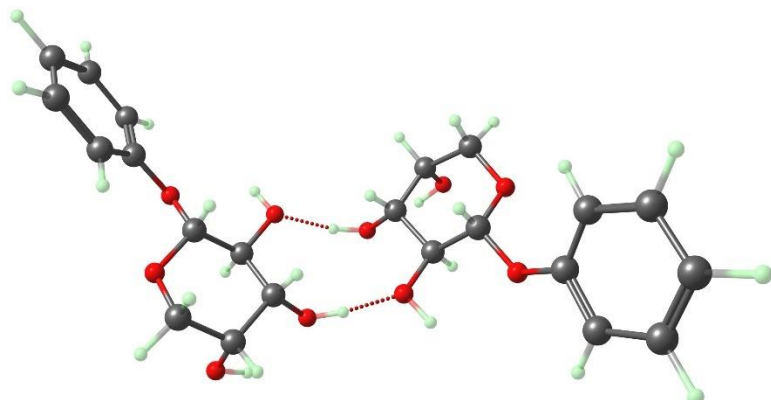| C | 6.79387226451746 | 2.02264267397620 | 5.41978653763591 |
C	7.86484451157389	3.21227122581203	7.24016332452094
H	7.90871310901522	3.48469210933719	8.29718096804282
H	6.00877437989580	1.36978167826786	5.03260485051868

Fig. S40 DFT-optimized geometry of **1-H**.
Table S37 DFT-optimized cartesian coordinates of **1-H**.

C	7.75033507230870	−6.91934606985017	−6.98908287998348
H	7.48492942015779	−5.87679781612991	−7.18350150898734
C	6.98537649992919	−7.65648845521636	−6.07912277492695
H	6.11563902434091	−7.21057729205914	−5.59850249360033
C	7.32266972810762	−8.99227211636235	−5.83027173567059
C	5.84392710954291	−9.22184419375734	−3.95724735801833
H	6.37313256094630	−8.35222346971174	−3.50389492511904
C	3.76271494176555	−8.22612158536689	−3.54607180945431
H	2.83440233325952	−7.97032040074606	−4.07522719907855
H	4.21091773739795	−7.29224109251053	−3.14735919311970
C	3.44802779753121	−9.16192187251279	−2.38404697588711
H	2.94946295073407	−8.56132229611005	−1.59251174290746
C	4.73002509468870	−9.76793206041022	−1.77984344022177
H	5.28360608260714	−8.98381805312465	−1.23086797162766
C	5.62272306787424	−10.29813288554426	−2.89713239096898
H	5.10565888266927	−11.14184764852549	−3.38609823726142
O	6.64641326222528	−9.79516536349854	−4.94547532788203
O	4.62439368089036	−8.81302805305014	−4.50845368476445
O	2.61326127862682	−10.19994139060627	−2.83399224436125
H	2.66374192881759	−10.88339041669301	−2.14482953682694
O	4.36507501817269	−10.81859546484218	−0.91732093061856
H	4.71114160366230	−10.62233649514408	−0.02316849204754
O	6.86932792322490	−10.70222774124318	−2.34994849184481
H	7.42585568556643	−10.99569201952388	−3.08687222096977
C	9.14483279920635	−8.84259191375031	−7.41314410746114
H	9.98323318167415	−9.31285768855911	−7.93358302099058
C	8.39798404658978	−9.58773732317078	−6.50205700106017
C	8.82914793544632	−7.50122793485467	−7.65752236220955
H	9.41641048073441	−6.91725737001579	−8.36989213912376
C	7.59453926585635	−5.59143110837420	5.14272016600410
H	8.48946489039291	−4.96356295591656	5.14120343696702
C	7.61178504055504	−6.80030511228741	4.43910174896252
H	8.51552371288347	−7.12972054965544	3.92828348677384
C	6.46683820399241	−7.60603360360088	4.44055508486151
C	7.28226246154600	−9.09668987221754	2.74934759477718
H	7.43485036454389	−8.19749483674235	2.10935599689884
C	9.46280838991399	−9.83632616782107	2.31066510780241
H	10.35794574253707	−10.17771904853301	2.84860001712127

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H    9.72783066519403      -8.93291586678801       1.72280203128281
C    8.99130929107550     -10.92943020600678       1.35763873261233
H    9.70597460946932     -10.96600008978571       0.50687651735403
C    7.59322688464176     -10.62154516945232       0.78731356076660
H    7.66310706627327      -9.78046163743402       0.07345283114741
C    6.65610226537367     -10.21478914122873       1.91962957515731
H    6.51470059113038     -11.08285363754613       2.58629681069786
O    6.37485773320816      -8.79873659298251       3.76729544227736
O    8.49943123725497      -9.51213373757682       3.30072190264243
O    8.95162311213061     -12.15876972348932       2.03914434812686
H    8.41005187976269     -12.74200209730058       1.48141393172562
O    7.10171121342485     -11.77623415529848       0.14968552720184
H    6.92984684867844     -11.56129577689886      -0.78943152039278
O    5.42222553398885      -9.77696442163429       1.37020968252722
H    4.86165589602052      -9.49251761373143       2.10743098238755
C    5.33050489461410      -6.01424359990453       5.86306859104483
H    4.43893288084673      -5.71578483624412       6.42071861280079
C    5.32860965010930      -7.21716784430638       5.15865699659562
C    6.46184238448704      -5.19037517598589       5.85366798013881
H    6.46129959411908      -4.24631682770750       6.40332962252808
H    8.63169937005386     -10.63446955960898      -6.29542990422227
H    4.45387588722302      -7.87114792104976       5.15051781242464
```

Table S38 Enthalpy and Gibbs free energy of **3a-e** and their H-bonded and π-π stacked assemblies.

		Enthalpy (H) in a.u.	*Gibbs free energy (G) in a.u.*
	3a	-901.58653993	-901.64305816
	3a'	-901.57927334	-901.63565126
ortho-	**3a-H**	-1803.20091045	-1803.29136008
	3a'-H	-1803.19036891	1803.28096781
	3a-π	-1803.19186609	-1803.28275213
	3a'-π	-1803.17835901	-1803.26717376
	3b	-901.58452214	-901.64096528
	3b'	-901.58480227	-901.64123325
	3b-H	-1803.19934994	-1803.28705385
meta-	**3b'-H**	-1803.19653424	-1803.28326435
	3b-π	-1803.19259370	-1803.28276822
	3b'-π	-1803.19370741	-1803.28349267
	3c	-901.58315667	-901.63961724
para-	**3c-H**	-1803.19578777	-1803.28604414
	3c-π	-1803.19356766	-1803.28273182
	3d	-1000.71519480	-1000.77363184
	3d'	-1000.70833470	-1000.76658582
	3d-H	-2001.45789663	-2001.55207092
ortho-meta	**3d-H_a**	-2001.45242476	-2001.54355446
	3d'-H	-2001.44182342	-2001.53583063
	3d-π	-2001.46124946	-2001.55412606
	3d'-π	-2001.44046567	-2001.53417341
	3e	-1000.71763640	-1000.77595401
	3e'	-1000.71784118	-1000.77613028
	3e-H	-2001.46551465	-2001.55849306
meta-para	**3e'-H**	-2001.46592756	-2001.55930662
	3e-π	-2001.46199979	-2001.55520075
	3e'-π	-2001.46304869	-2001.55423219
Without F	**1**	-802.45392068	-802.50832573
	1-H	-1604.93444588	-1605.02108363

Table S39 DFT-calculated chemical properties of **3a-e**.

Compound	HOMO (eV) (*-I*)	LUMO (eV) (*-A*)	Energy gap (eV)	Electronegativity [(I+A)/2] (eV)	Dipole moment (Debye)	Hardness (η) (eV) [(I-A)/2]	Softness ($S = 1/\eta$) (eV)
3a	-6.76	-0.55	6.21	3.65	2.46	3.10	0.32
3a'	-6.34	-0.28	6.06	3.31	2.26	3.03	0.33
3b	-6.46	-0.37	6.09	3.41	3.98	3.05	0.33
3b'	-6.40	-0.33	6.07	3.36	3.08	3.04	0.33
3c	-6.33	-0.54	5.79	3.43	3.46	2.89	0.34
3d	-6.79	-0.48	6.31	3.63	2.50	3.15	0.31
3d'	-6.54	-0.28	6.26	3.41	1.97	3.13	0.32
3e	-6.45	-0.65	5.80	3.55	2.79	2.90	0.34
3e'	-6.43	-0.63	5.80	3.54	2.88	2.90	0.34

5. NMR Spectra
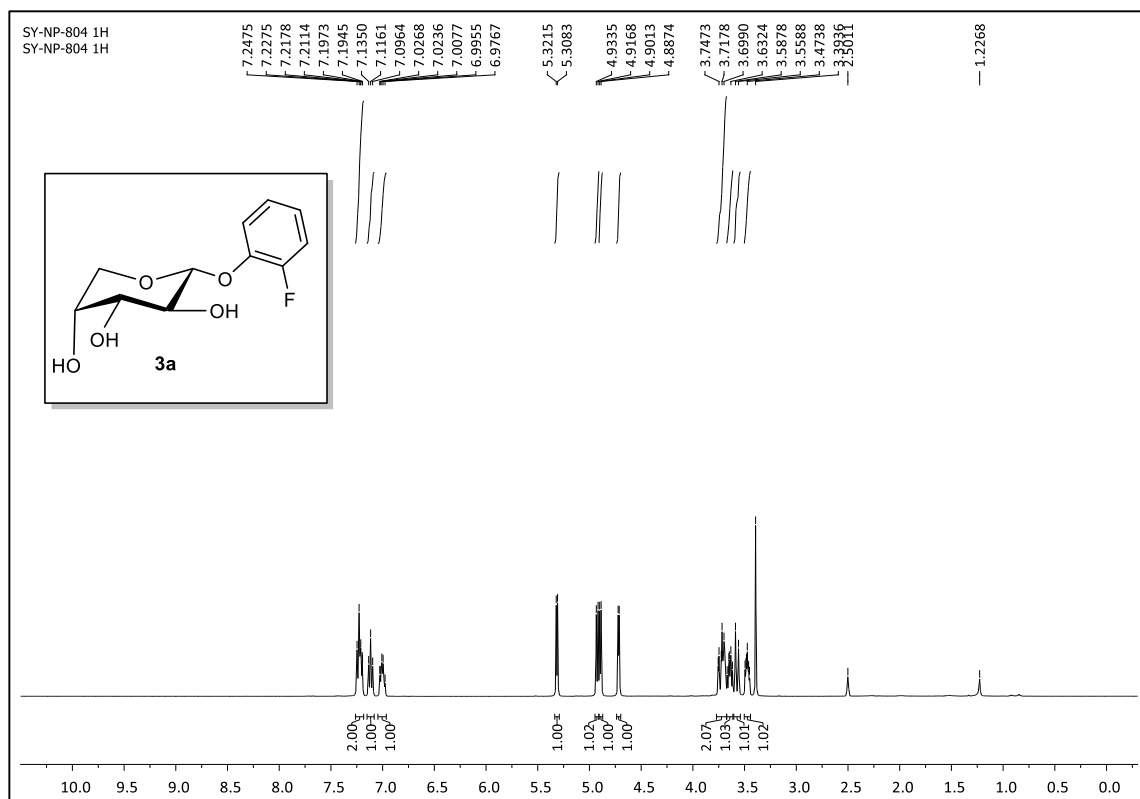
Fig. S41 ¹H-NMR (400 MHz, DMSO-d6) spectrum of **3a**.
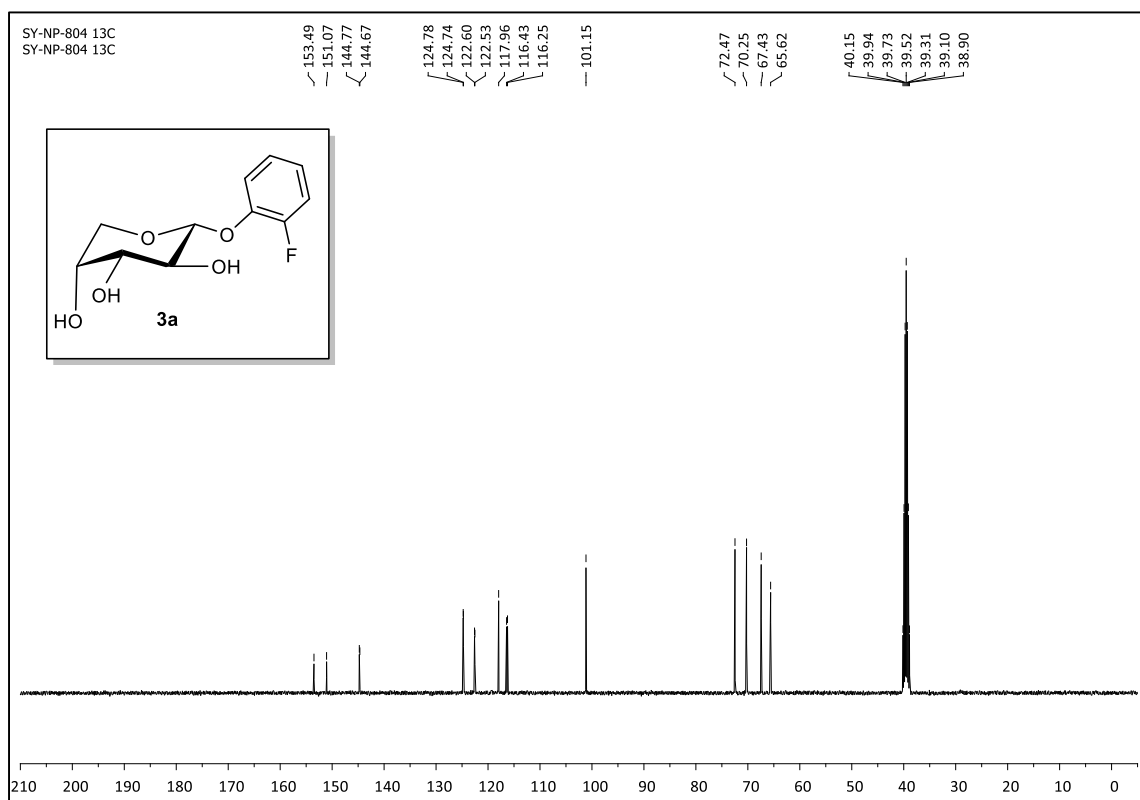
Fig. S42 ¹³C{1H} NMR (100 MHz, DMSO-d6) spectrum of **3a**.

-133.35
-133.37
-133.38
-133.39
-133.40
-133.41
-133.42

3a

10   0   -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -120   -140   -160   -180   -200
f1 (ppm)
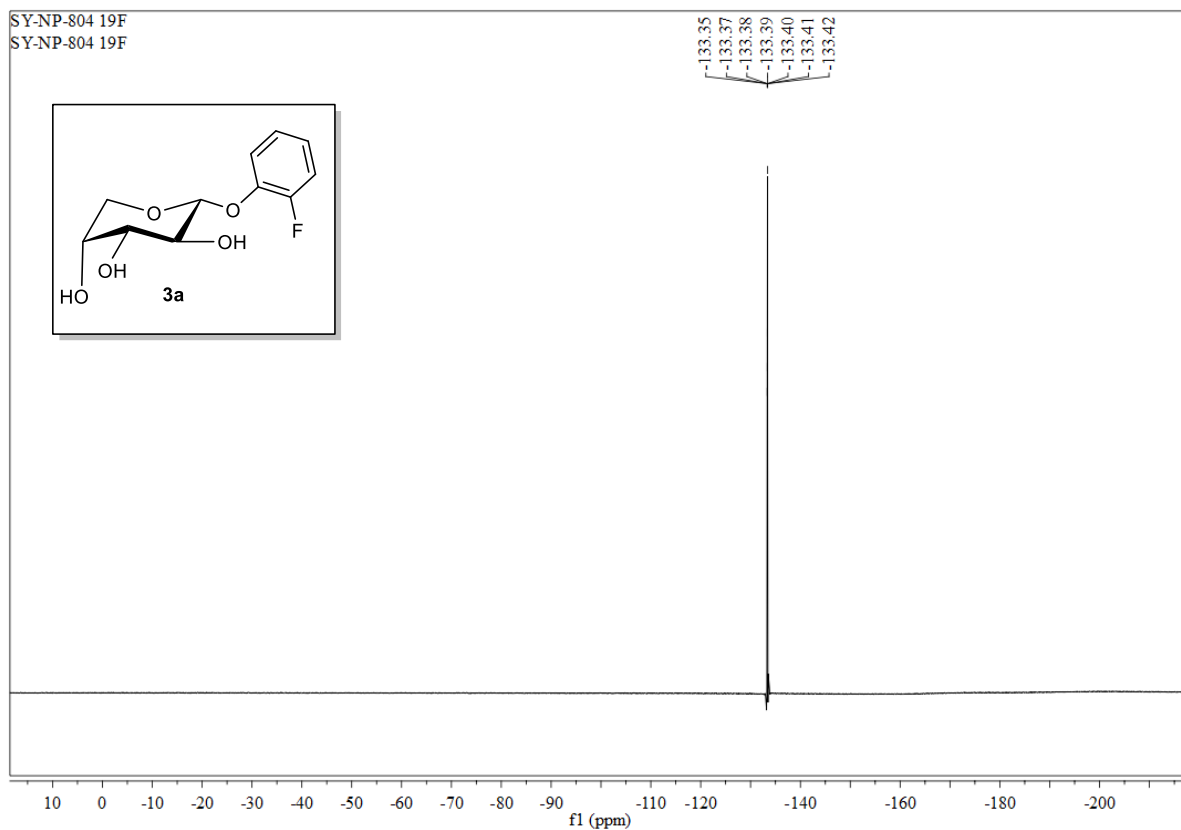
Fig. S43 ^{19}F NMR (377 MHz, DMSO-d6) spectrum of **3a**

7.3497
7.3325
7.3291
7.3152
7.3096
7.2931
7.2903
6.8659
6.8597
6.8571
6.8433
6.8383
6.8347
5.2644
4.9055
4.8922
4.8751
4.7032
4.6933
3.7062
3.6931
3.6854
3.6425
3.6135
3.4512
2.5056
2.5011
2.4967
2.4925
1.2262

3b

1.01
3.00
1.00
0.92
1.09
1.00
2.02
2.01
1.02

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
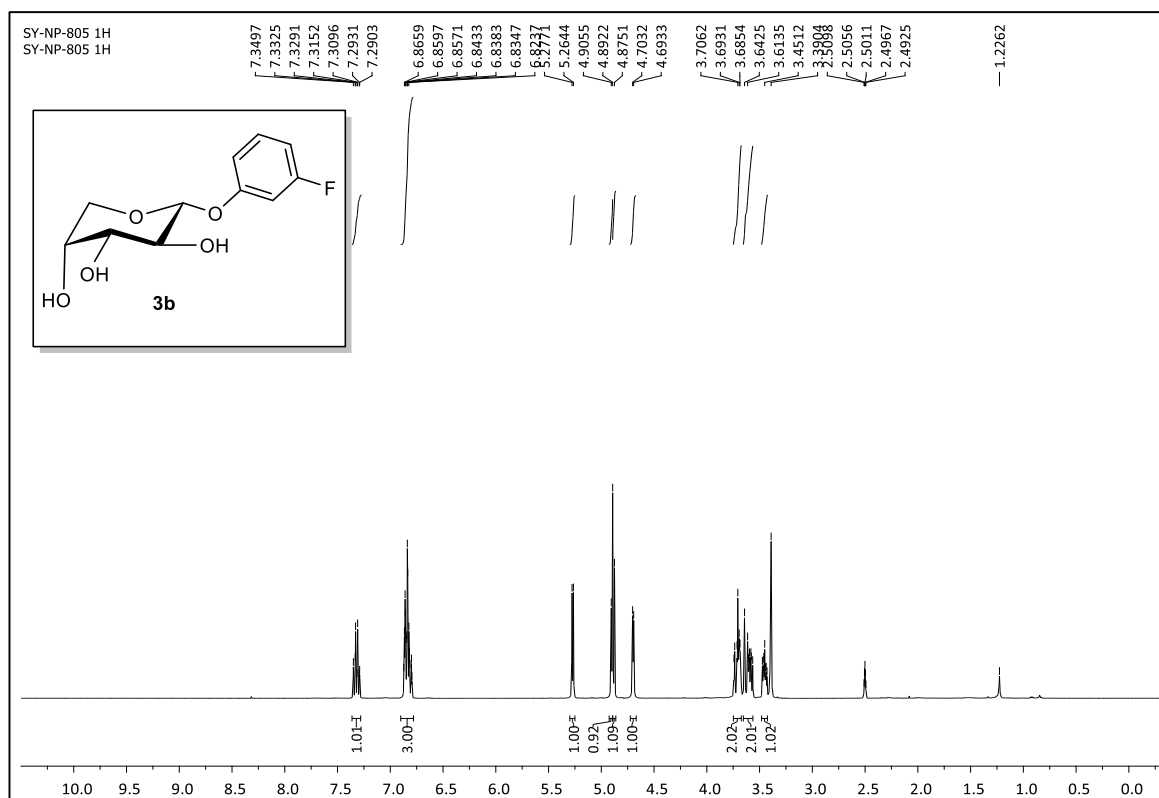
Fig. S44 ^{1}H-NMR (400 MHz, DMSO-d6) spectrum of **3b**.

S46
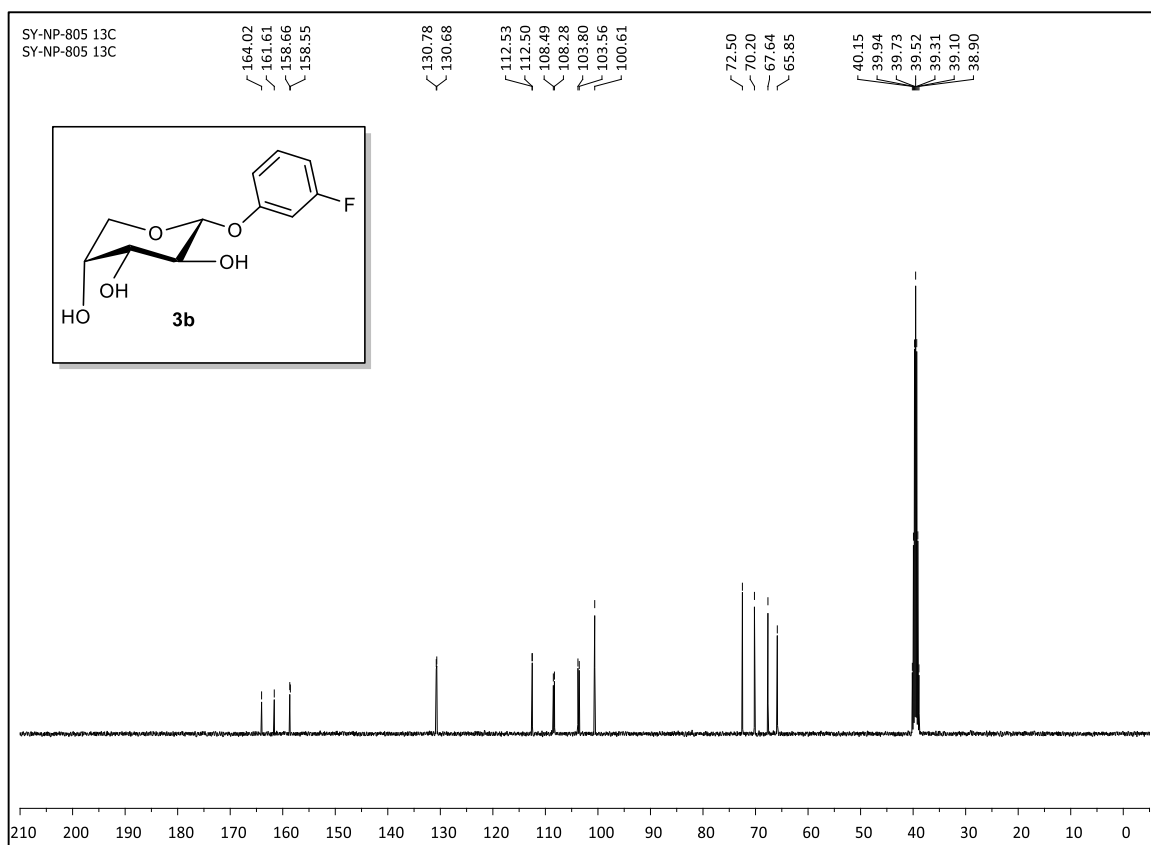
Fig. S45 ¹³C{1H} NMR (100 MHz, DMSO-d6) spectrum of **3b**.
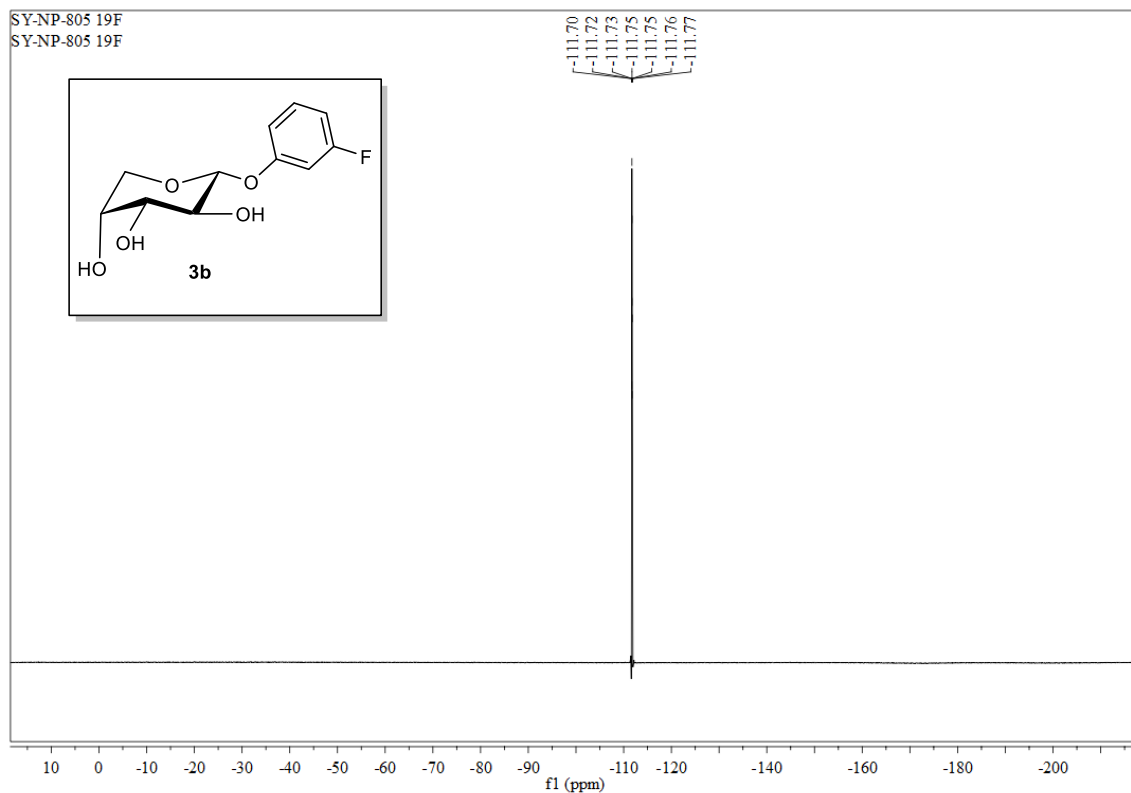
Fig. S46 ¹⁹F NMR (377MHz, DMSO-d6) spectrum of **3b**
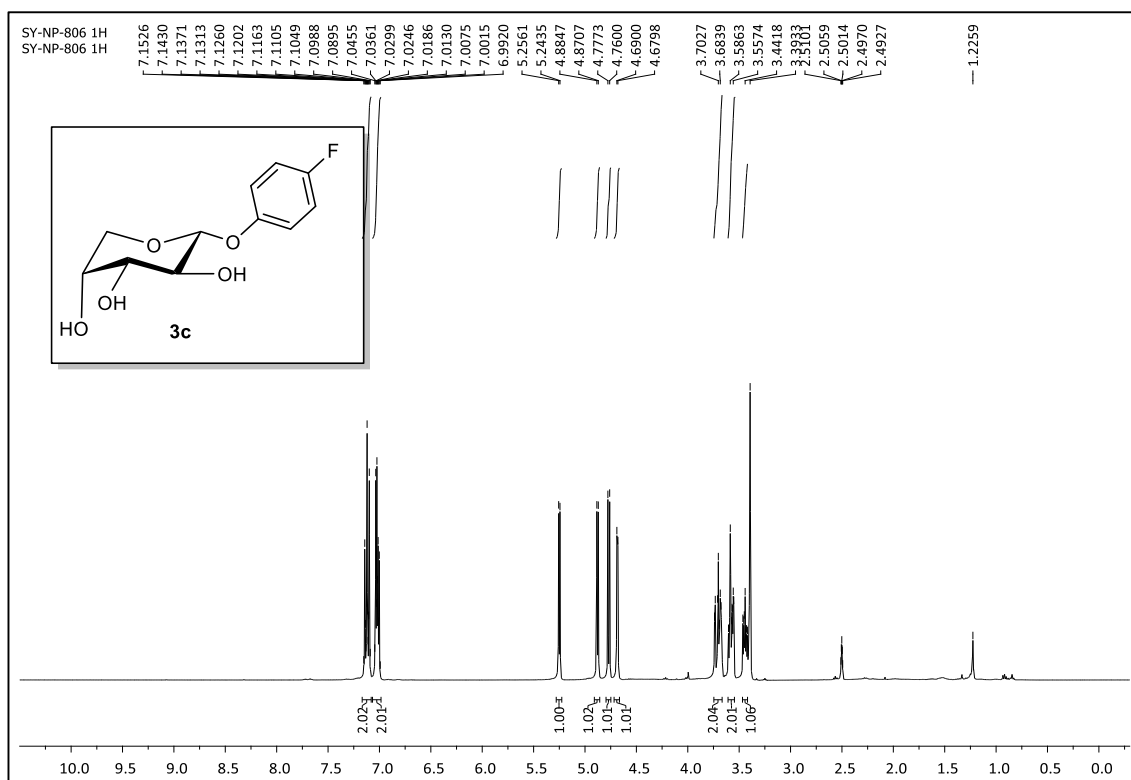
Fig. S47 ^{1}H-NMR (400 MHz, DMSO-d6) spectrum of **3c**
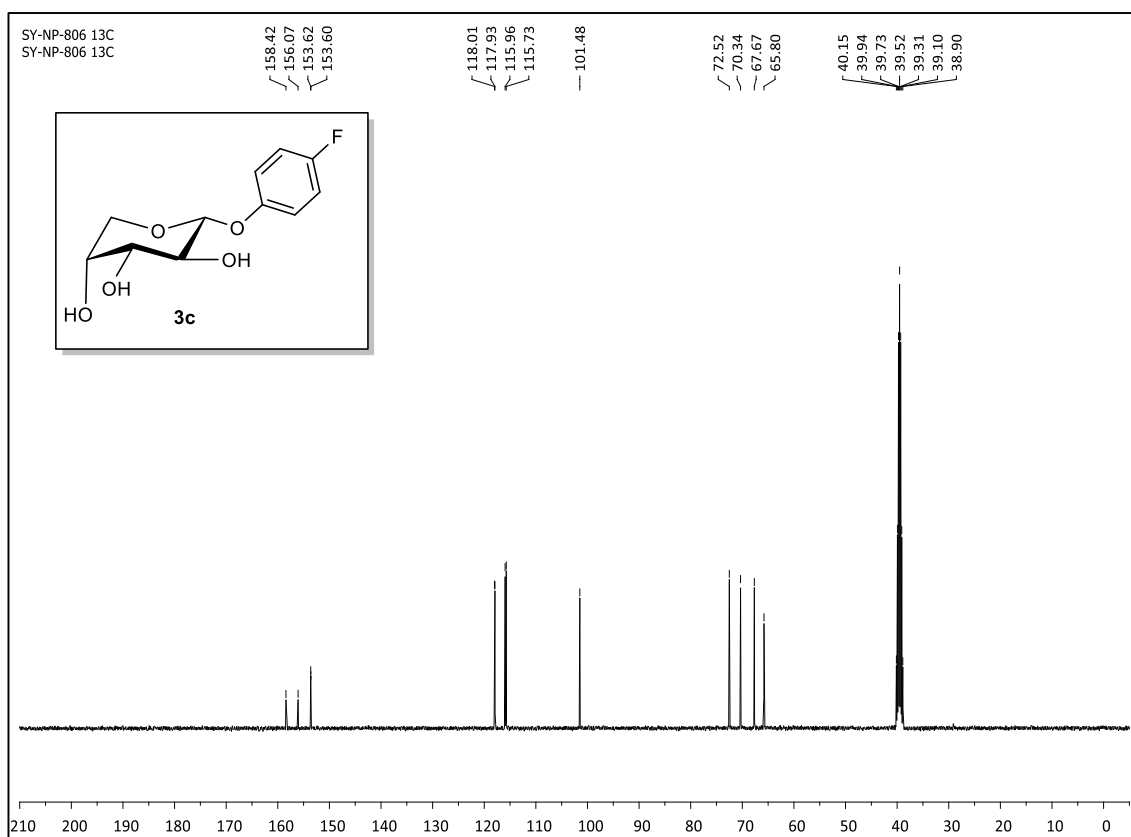
Fig. S48 ^{13}C{1H} NMR (100 MHz, DMSO-d6) spectrum of **3c**.

-122.36
-122.37
-122.38
-122.39
-122.40
-122.41

3c

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -120 -140 -160 -180 -200
f1 (ppm)

Fig. S49 ^{19}F NMR (377 MHz, DMSO-d6) spectrum of **3c**

7.136
7.116
7.098
7.091
7.073
7.054
7.040
7.029
7.009

5.362
5.349

4.963
4.947
4.737
4.727

3.749
3.727
3.719
3.705
3.653
3.639
3.595
2.560

3d

3.09

1.02
1.03
1.00
1.00

2.09
3.01

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
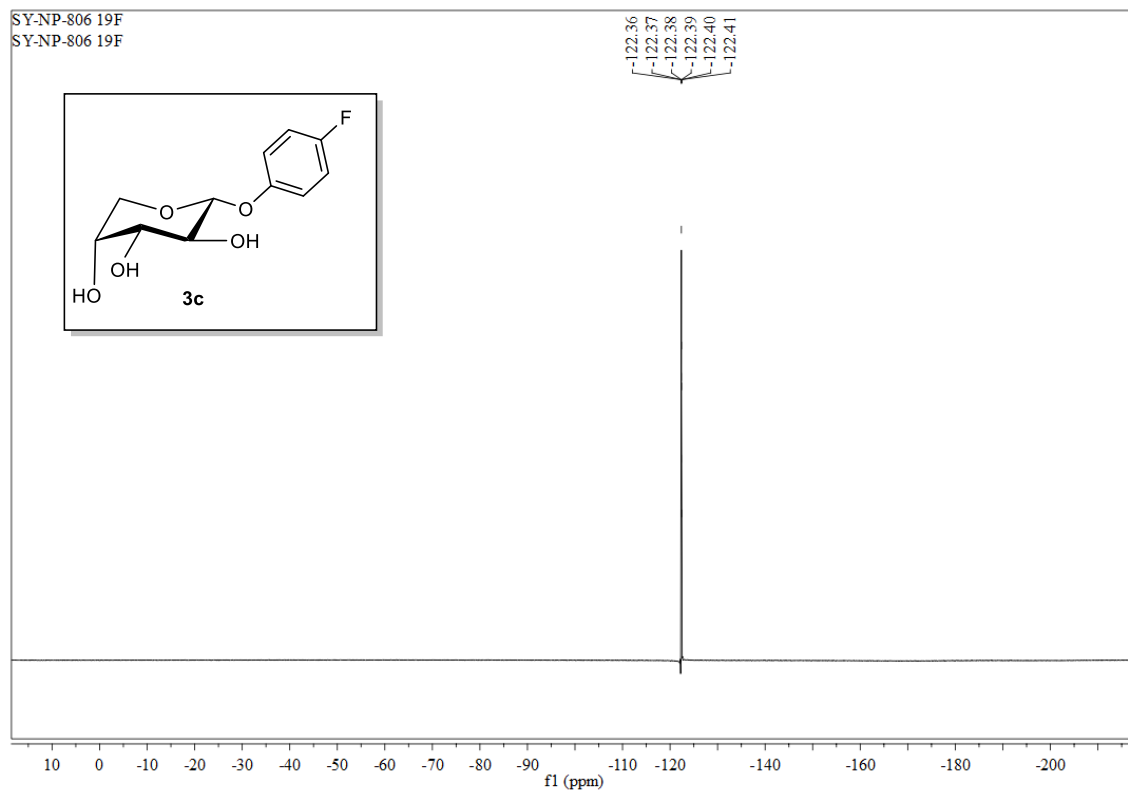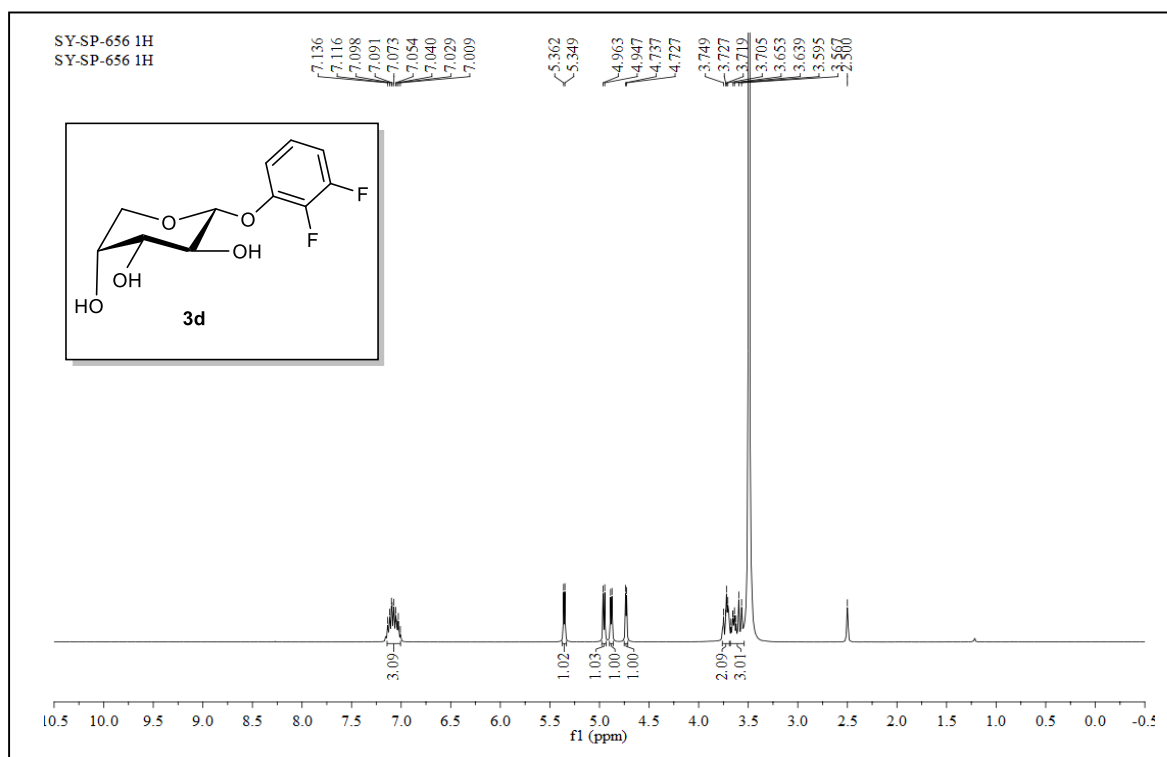
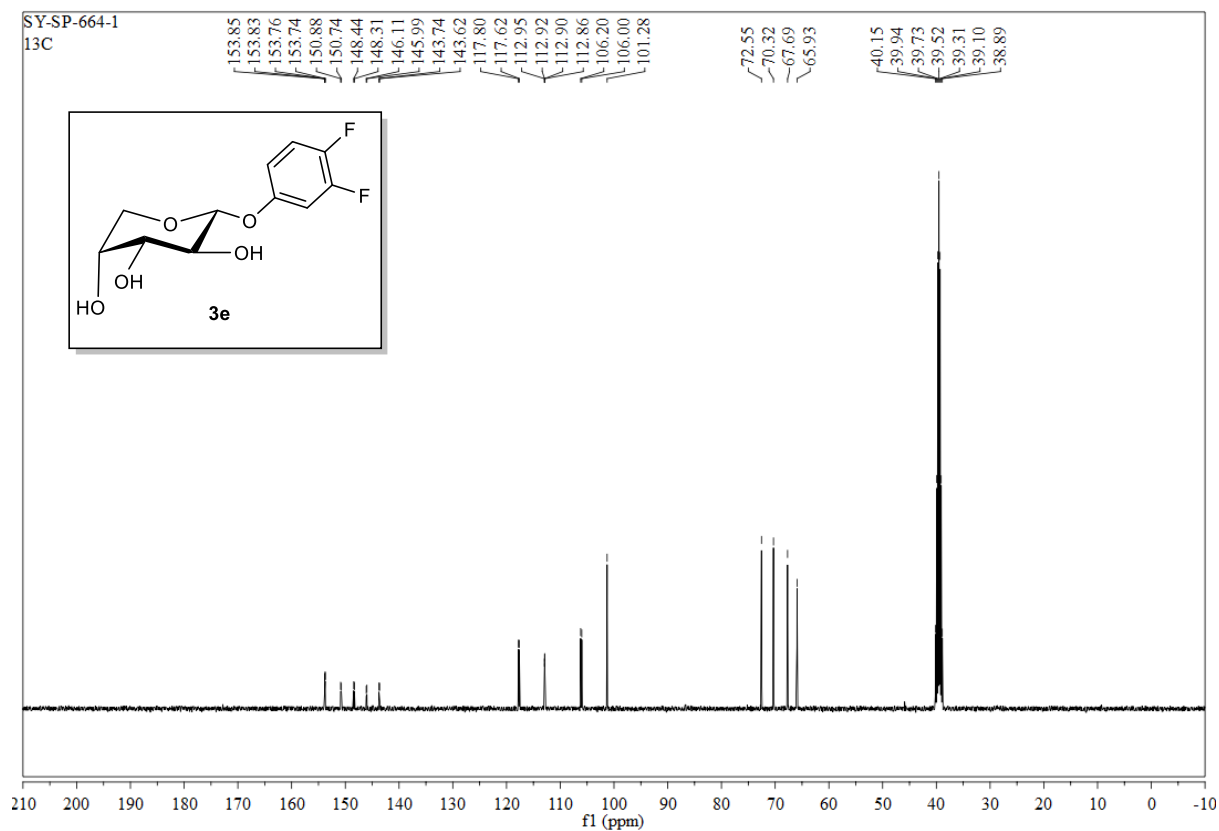**Fig. S50** ^{1}H-NMR (400 MHz, DMSO-d6) spectrum of **3d**

S49
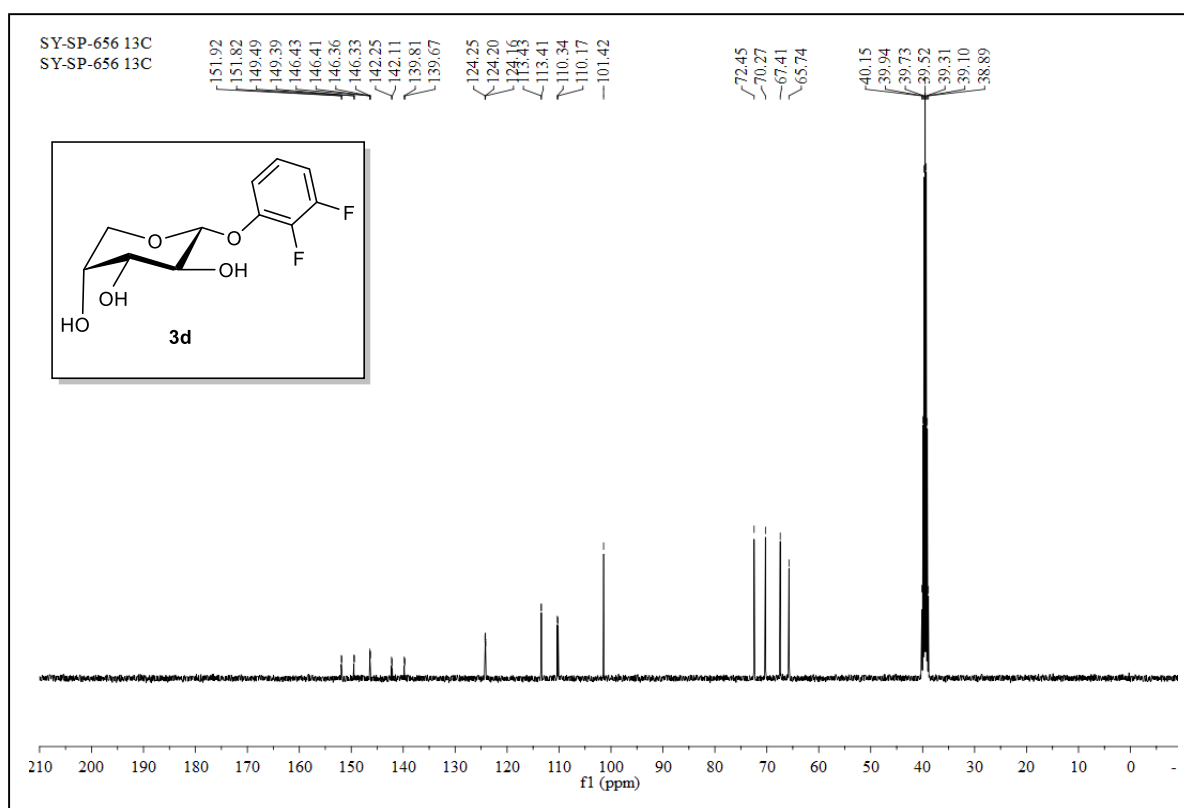
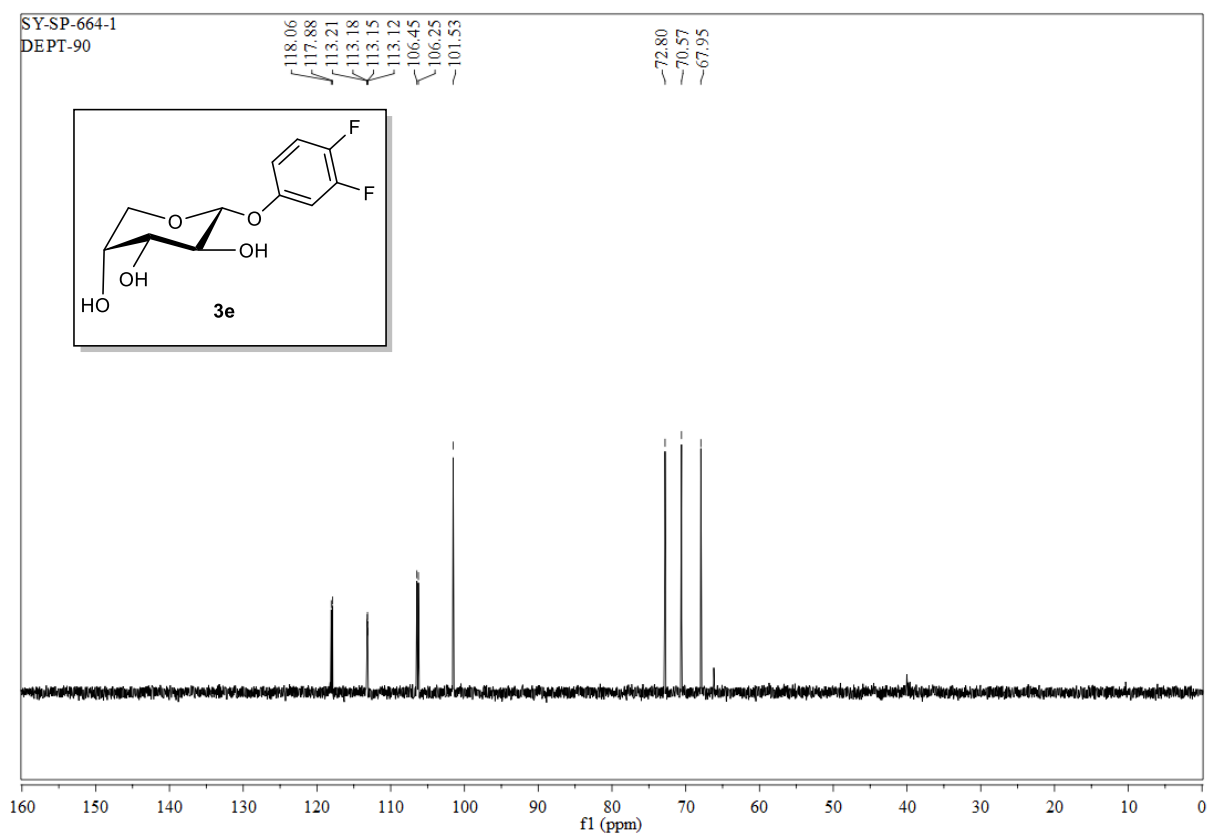**Fig. S51** $^{13}\text{C}\{1\text{H}\}$ NMR (100 MHz, DMSO-d6) spectrum of **3d**
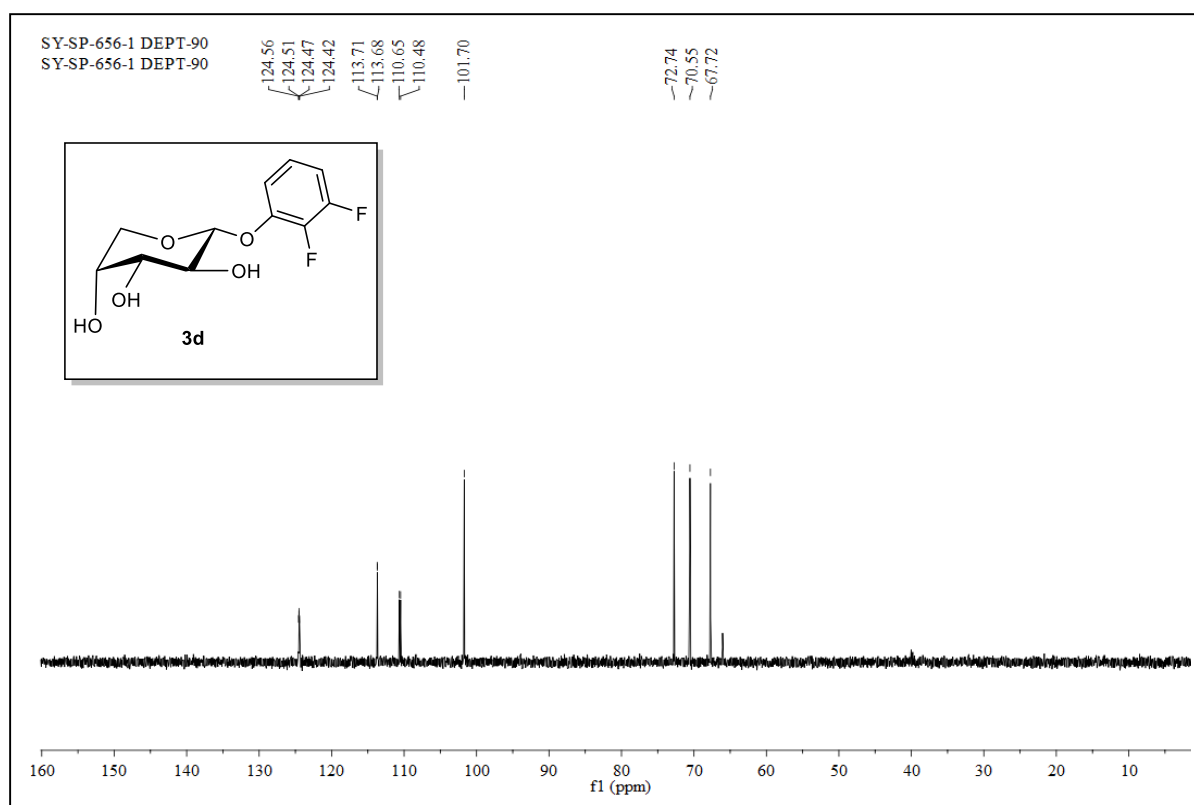
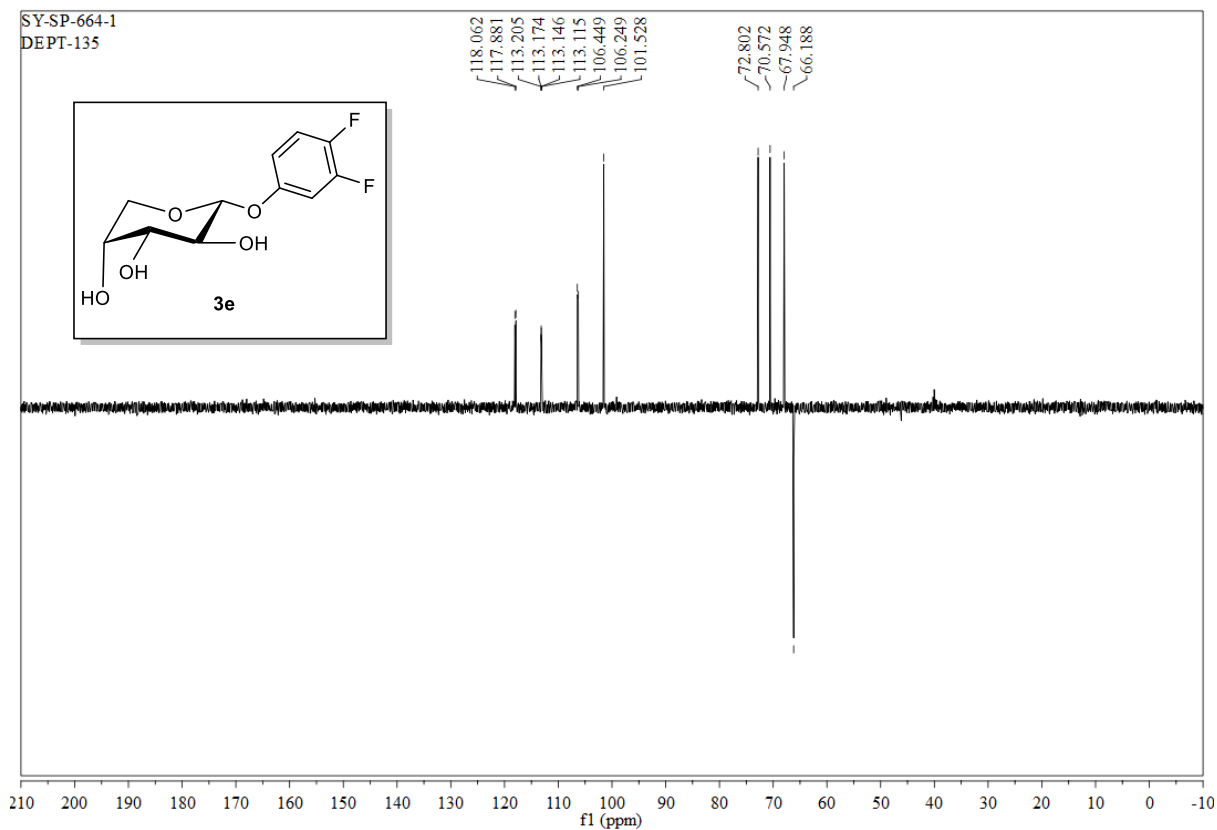**Fig. S52** DEPT 90 NMR (100 MHz, DMSO-d6) spectrum of **3d**

S50
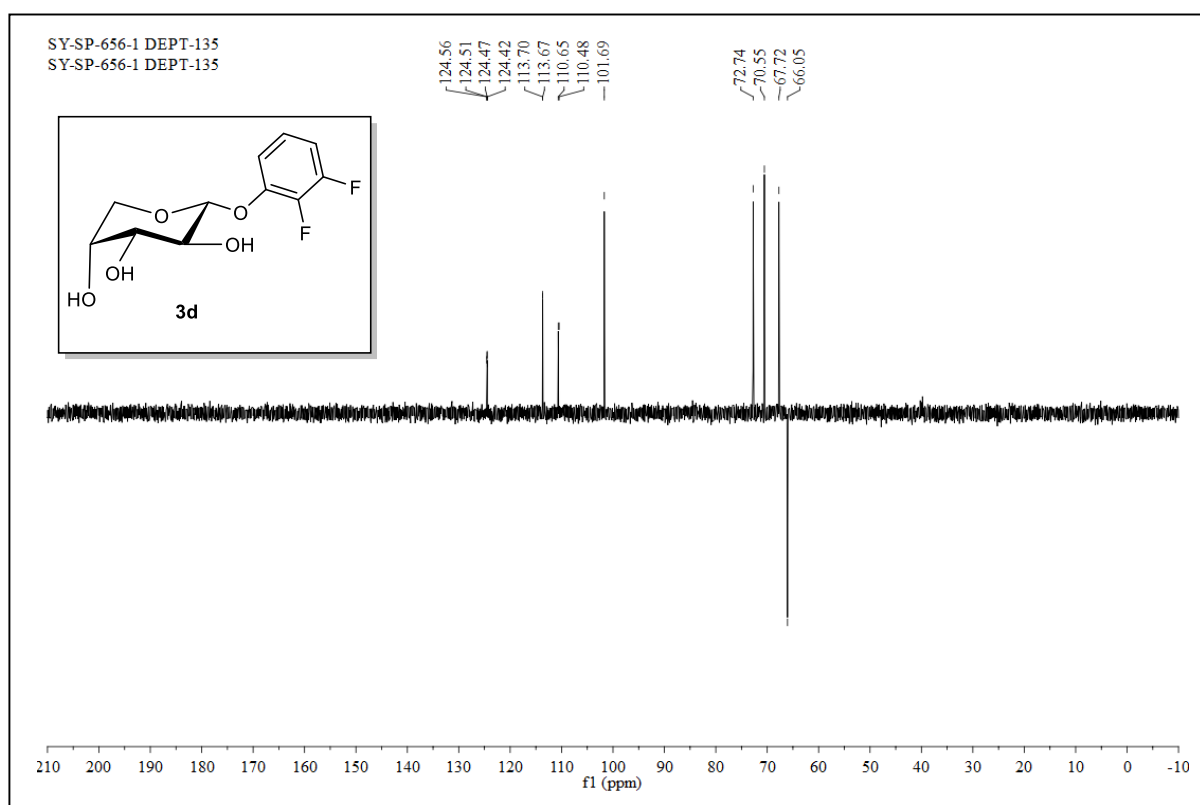
Fig. S53 DEPT 135 NMR (100 MHz, DMSO-d6) spectrum of **3d**
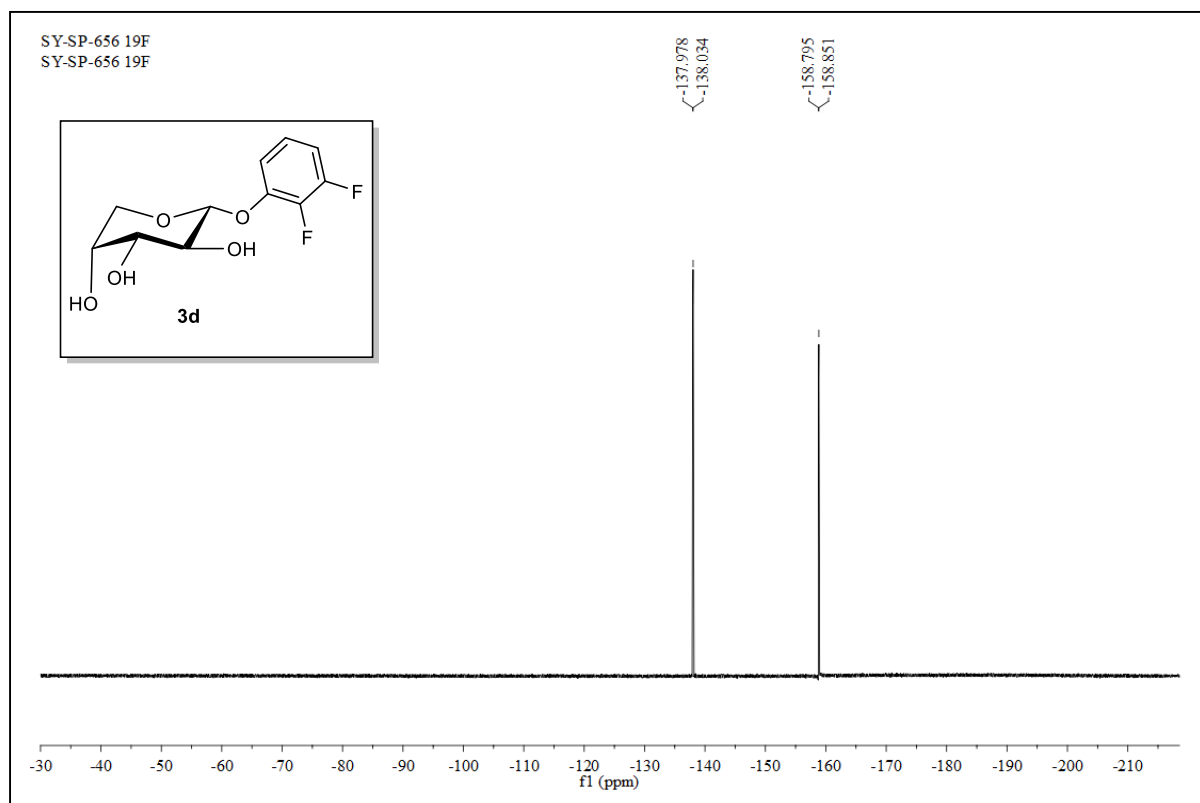
Fig. S54 ¹⁹F NMR (377 MHz, DMSO-d6) spectrum of **3d**

S51
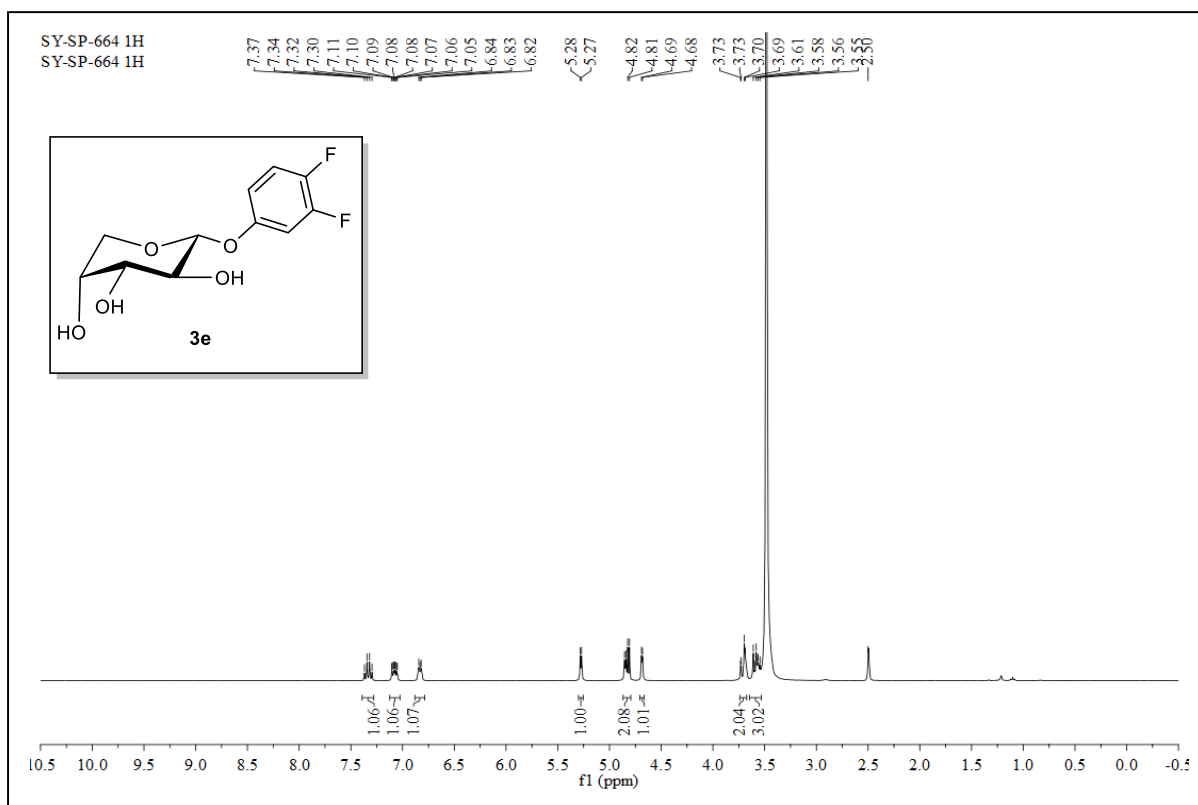
Fig. S55 ^{1}H-NMR (400 MHz, DMSO-d6) spectrum of **3e**

Fig. S56 ^{13}C{1H} NMR (100 MHz, DMSO-d6) spectrum of **3e**

Fig. S57 DEPT 90 NMR (100 MHz, DMSO-d6) spectrum of **3e**

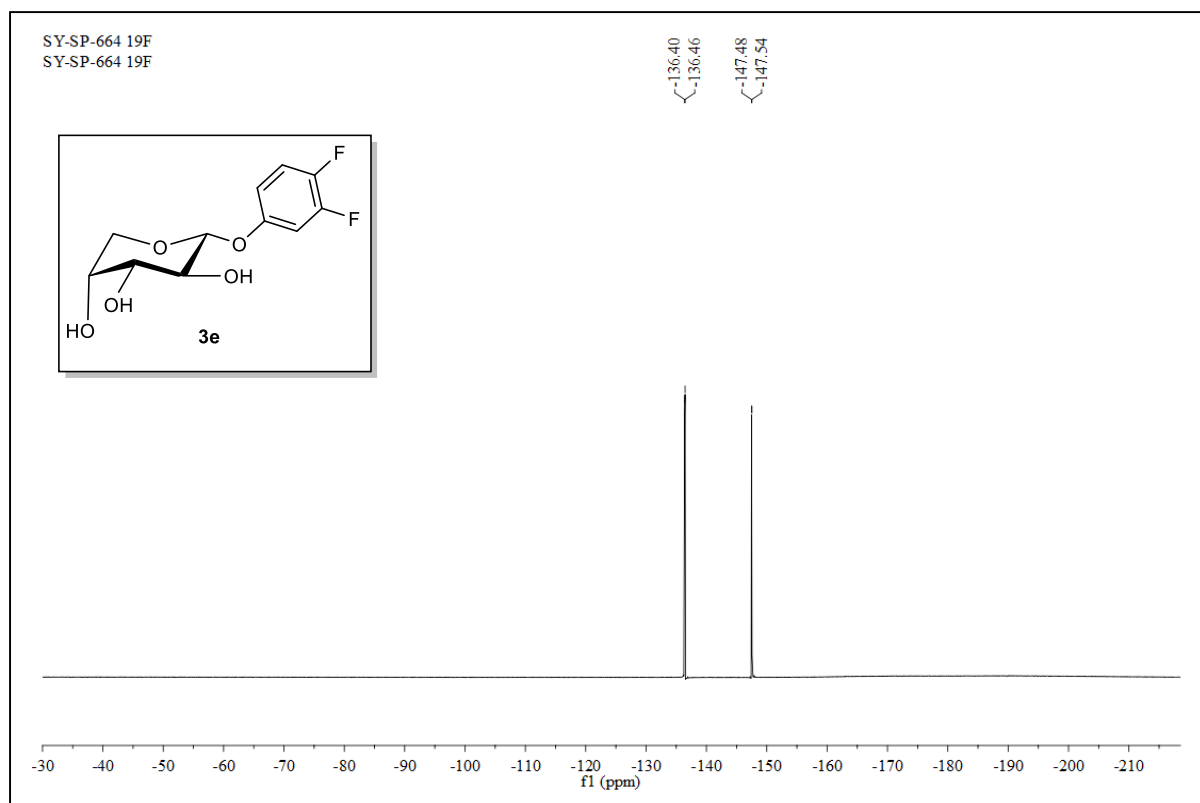**Fig. S58** DEPT 135 NMR (100 MHz, DMSO-d6) spectrum of **3e**

Fig. S59 ^{19}F-NMR (377 MHz, DMSO-d6) spectrum of **3e**

Table S40 Summary of NMR data for compounds **3a-3e.**

Sl. No.	Compound	Anomeric proton (H1) δ (ppm)	Aromatic protons	Anomeric carbon (C1) δ (ppm)
1	**3a**	4.93 (d, J = 6.7 Hz, 1H)	7.25–6.98 (m, 4H)	101.2
2	**3b**	4.88 (d, J = 6.8 Hz, 1H)	7.35–6.79 (m, 4H)	100.6
3	**3c**	4.77 (d, J = 6.9 Hz, 1H)	7.15–6.99 (m, 4H)	101.5
4	**3d**	4.96 (d, J = 6.4 Hz, 1H)	7.14–7.01 (m, 3H)	101.4
5	**3e**	4.86-4.81(m, 2H)	7.33 (dd, J =19.6 and 9.2 Hz, 1H), 7.11-7.05 (m, 1H), 6.84-6.82 (m, 1H)	101.3