Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Exploring Glycosyl Sulphates as Donors for Chemical Glycosylation

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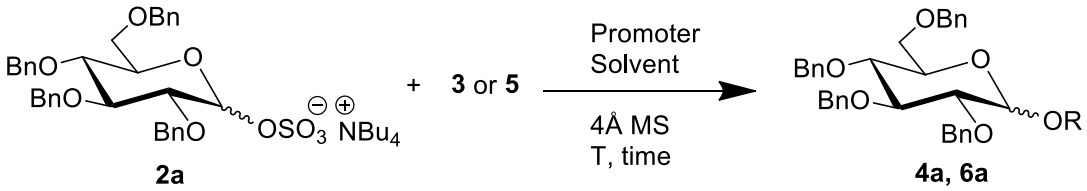
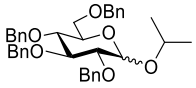
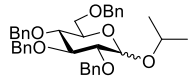
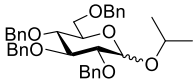
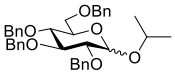
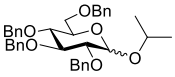
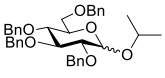
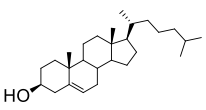
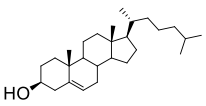
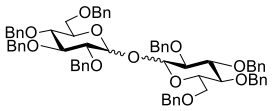
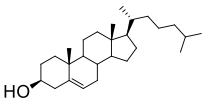
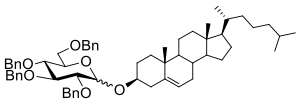
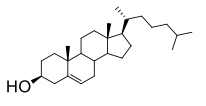
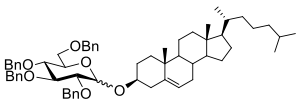
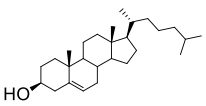
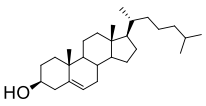
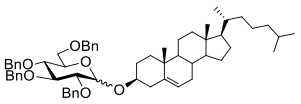
Table S1 Additional glycosylation entries with sulphate donor **2a**

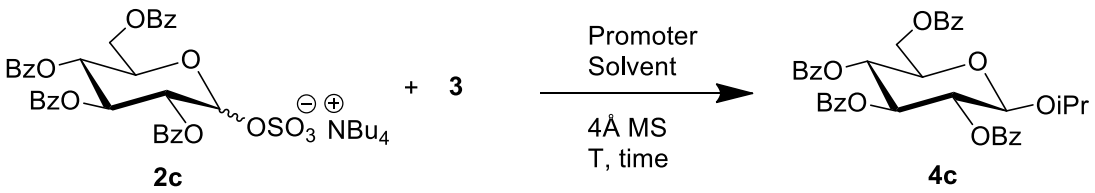


Entry	Acceptor	Promoter (equiv.)	Solvent	T (°C), time	Results(Yield, α/β ratio)
1	2-propanol **3**	$Ca(OTf)_2$ (1.7)	CH_3CN	r.t., 72 h	 **4a** (90% TLC)
2	2-propanol **3**	$Yb(OTf)_3$ (1.1)	CH_2Cl_2:Et_2O 1:2	0°C, 1 h	 **4a** (90% TLC, 3:7)
3	2-propanol **3**	$Ba(OTf)_2$ (1.5)	Et_2O	r.t., 24 h	no reaction
4	2-propanol **3**	BaO (3), TMSOTf (2.5)	CH_2Cl_2:Et_2O 1:2	0°C, 45 min	 **4a** (90% TLC, 7:3)
5	2-propanol **3**	BaO (3), TMSOTf (0.2+0.8 after 24 h)	CH_3CN	0° C to r.t, 48 h	 **4a** (25% TLC)
6	2-propanol **3**	BaO (3), TMSOTf (1+0.5 after 24 h + 0.5 after 28 h)	CH_3CN	0° C to r.t, 48 h	 **4a** (40% TLC)
7	2-propanol **3**	BaO (3), TMSOTf (2+0.5 after 24 h) (Slow reaction until the addition of the second portion of TMSOTf)	CH_3CN	0° C to r.t, 25 h	 **4a** (95% TLC)
8	 **5**	CaO (3)	THF	50°C, 48 h	**no reaction**

9	 **5**	$CaCl_2$ (6)	THF	r. t., 2 h	 **threalose[a] (10%, TLC)**
10	 **5**	$Ca(OTf)_2$ (1.2)	THF:CH_2Cl_2 1:4	r.t., 48 h	 **6a (27% isolated; 50:50)**
11	 **5**	$Ca(OTf)_2$ (2)	CH_3CN	rfx, 4 h	 **6a (65% isolated; 44:56)**
12	 **5**	$Ca(OTf)_2$ (2)	Et_2O	r.t., 24 h	**no reaction**
13	 **5**	$Ca(OTf)_2$ (2)	THF	r.t., 2h then 90°C, 26h	 **6a (30% TLC)**

[a] The formation of trehaloses can be due to the partial hydrolysis of the donor by adventitious water followed by the glycosylation of the anomeric hydroxyl group. In the previous paper the easy formation of trehaloses was already observed, see L. Cipolla, L. Lay, F. Nicotra, L. Panza, G. Russo, *Tetrahedron Lett*. **1994**, *35*, 8669-8670.

Table S2 Glycosylation entries with sulphate donor **2c**



Entry	Acceptor (equiv.)	Promoter (equiv.)	Solvent	T (°C), time	Yield of 4c
1	2-propanol **3** (2)	$Yb(OTf)_3$ (1.2)	CH_3CN	r.t., 24 h	10% (TLC)
2	2-propanol **3** (2)	$Yb(OTf)_3$ (4 additions of 1.5 eq each, every hour)	CH_2Cl_2	r.t., 24 h	53% (isolated)
3	2-propanol **3** (2)	BaO (3), TMSOTf (2.5)	CH_2Cl_2	0°C to r.t. 7 h	traces of a mixture of products
4	2-propanol **3** (2)	BaO (3), TMSOTf (2.5)	CH_3CN	0° C to r.t, 72 h	10% (TLC)
5	2-propanol **3** (2)	TMSOTf (3)	CH_2Cl_2	0°C to r.t. 24 h	10% (TLC)
6	2-propanol **3** (2)	BF_3-OEt_2 (3)	CH_3CN	0° C to r.t, 24 h	no reaction
7	2-propanol 3 (4)	$Yb(OTf)_3$ (1.5)	CH_2Cl_2	reflux, 3 h	50% (TLC)

Isopropyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (4c) was obtained from donor **2c** and acceptor **3** as a white foam in the yield listed in table S2, entry 2. $[\alpha]_D^{20}$ + 12.0 (*c* 0.5, CH_2Cl_2); lit.[1] + 11.4 ($CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.82 (8H, m), 7.62 – 7.26 (12H, m), 5.92 (1H, t, *J* = 9.7 Hz), 5.67 (1H, t, *J* = 9.7 Hz), 5.51 (1H, dd, *J* = 9.8, 7.9 Hz), 4.93 (1H, d, *J* = 7.9 Hz), 4.65 (1H, dd, *J* = 12.0, 3.3 Hz), 4.53 (1H, dd, *J* = 12.0, 5.6 Hz), 4.18 (1H, ddd, *J* = 9.3, 5.5, 3.4 Hz), 4.05 – 3.95 (1H, m), 1.25 (3H, d, *J* = 6.2 Hz), 1.10 (3H, d, *J* = 6.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.17, 165.87, 165.26, 165.05, 133.41, 133.20, 133.13, 133.09, 129.85, 129.79, 129.73, 129.71, 129.66, 129.49, 128.90, 128.41, 128.35, 128.29, 100.13, 73.32, 73.04, 72.12, 70.04, 63.44, 23.24, 22.02. HRMS(ESI) *m*/*z* calcd for $[C_{37}H_{34}O_{10}$ + Na]$^+$: 661.20497, found 661.20312.

[1] L. R. Schroeder and J. W. Green *J. Chem. Soc. C*, **1966**, 530-531

Fig. S1 ^{1}H NMR spectrum of **2a** in $CDCl_3$ (400 MHz)

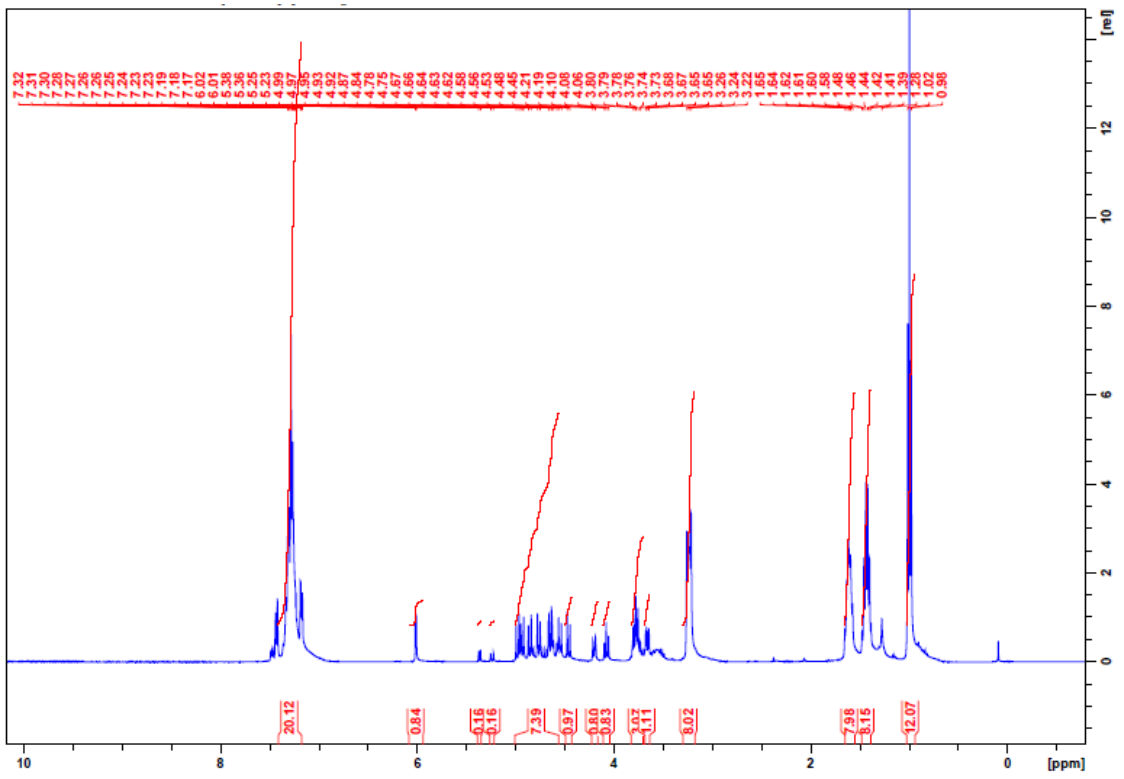


Fig. S2 Apt NMR spectrum of **2a** in $CDCl_3$ (101 MHz)

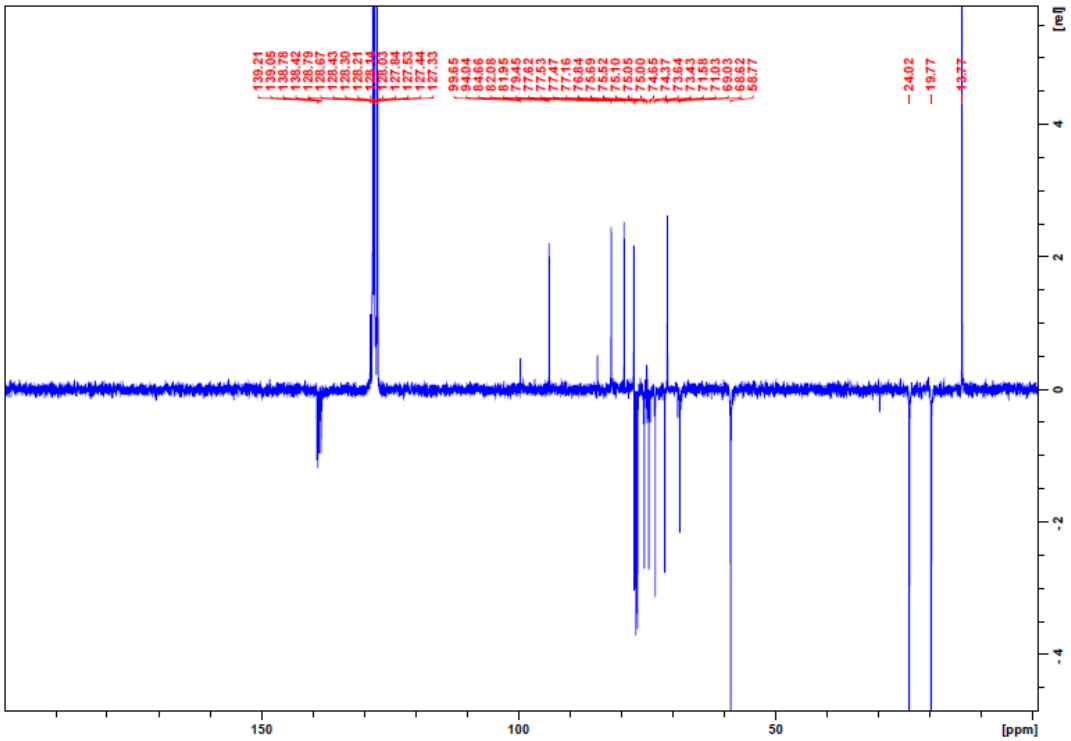


Fig. S3 Cosy NMR spectrum of **2a** in $CDCl_3$ (400 MHz)

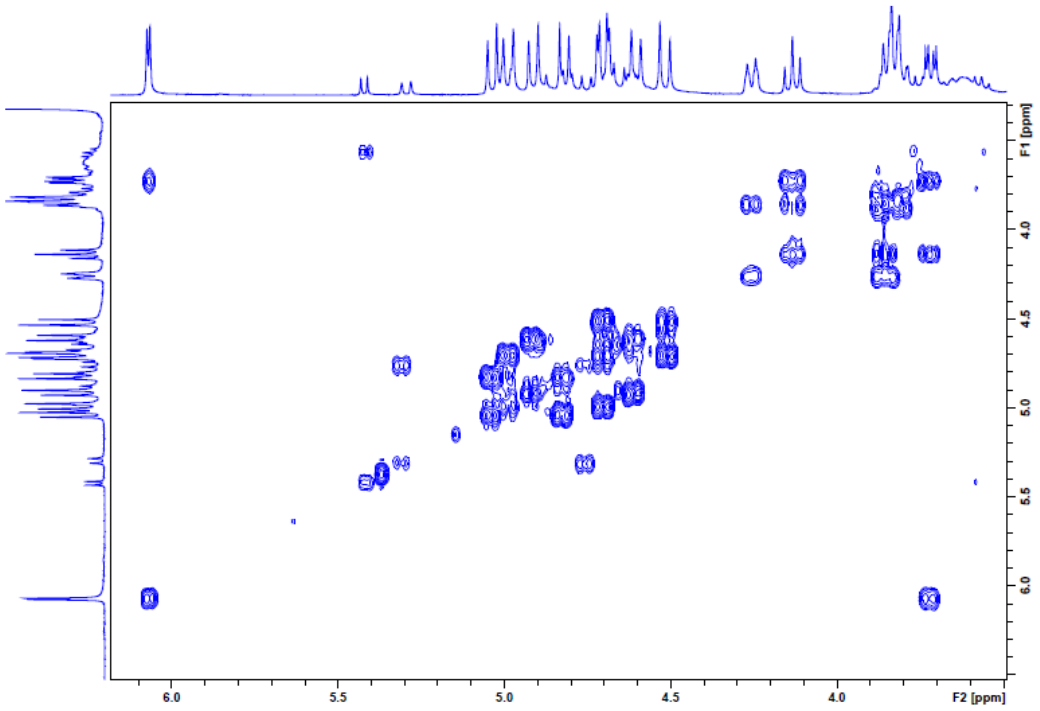


Fig. S4 HSQC NMR spectrum of **2a** in $CDCl_3$

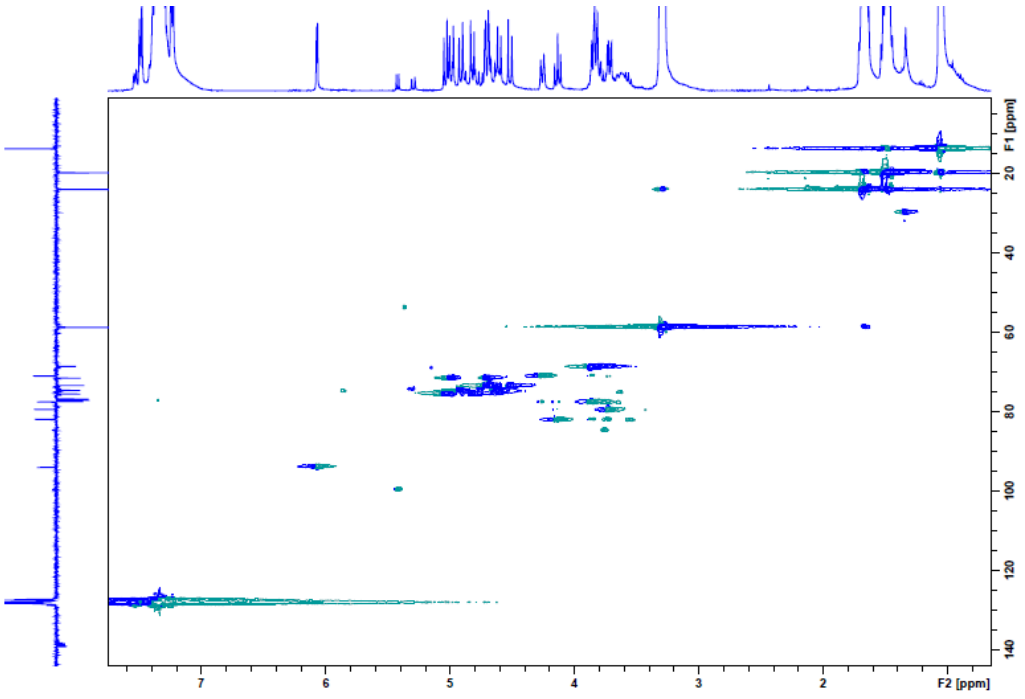


Fig. S5 ^{1}H NMR spectrum of **2b** in $CDCl_3$ (400 MHz)

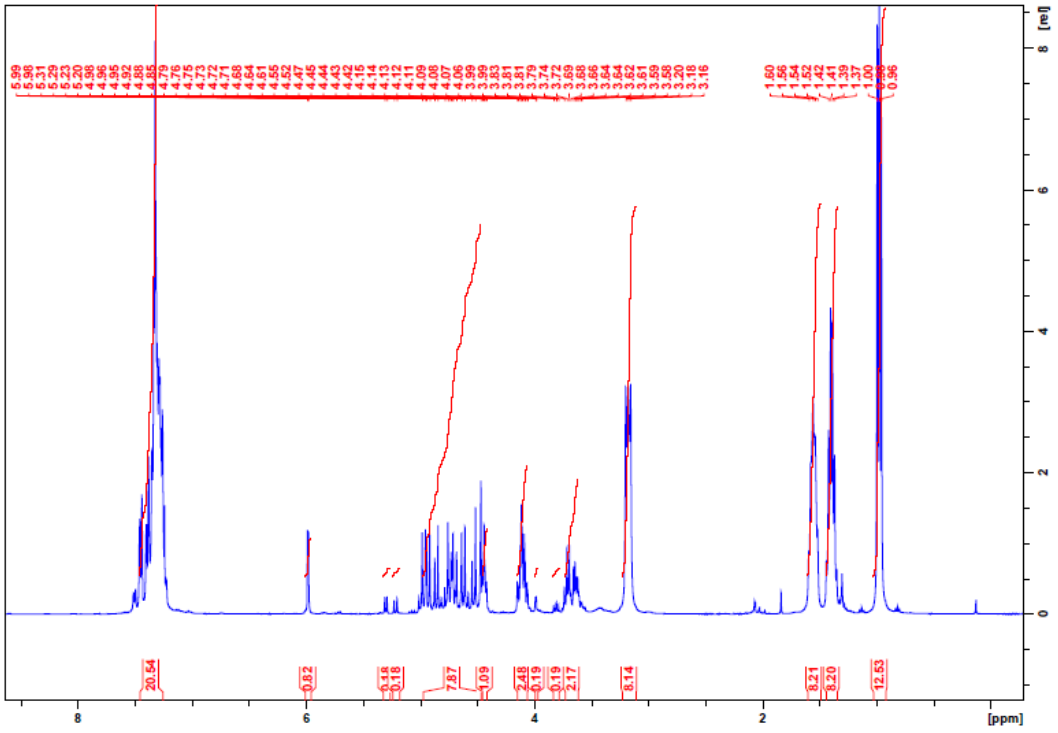


Fig. S6 Apt NMR spectrum of **2b** in $CDCl_3$ (101 MHz)

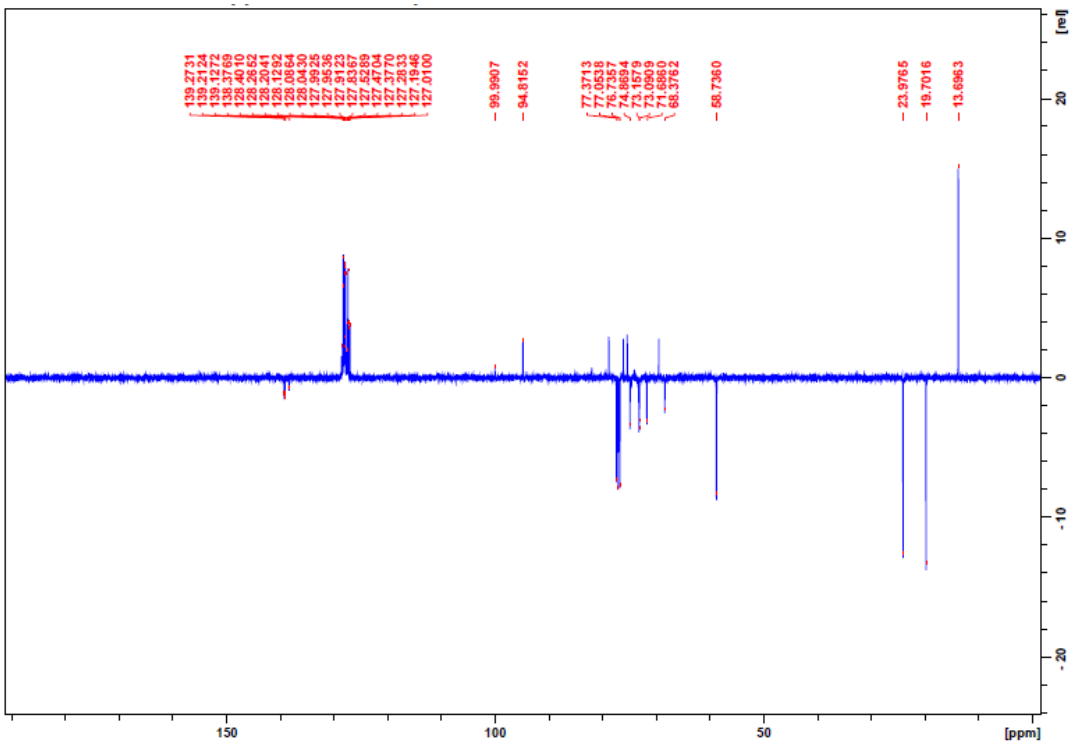


Fig. S7 Cosy NMR spectrum of **2b** in $CDCl_3$ (400 MHz)

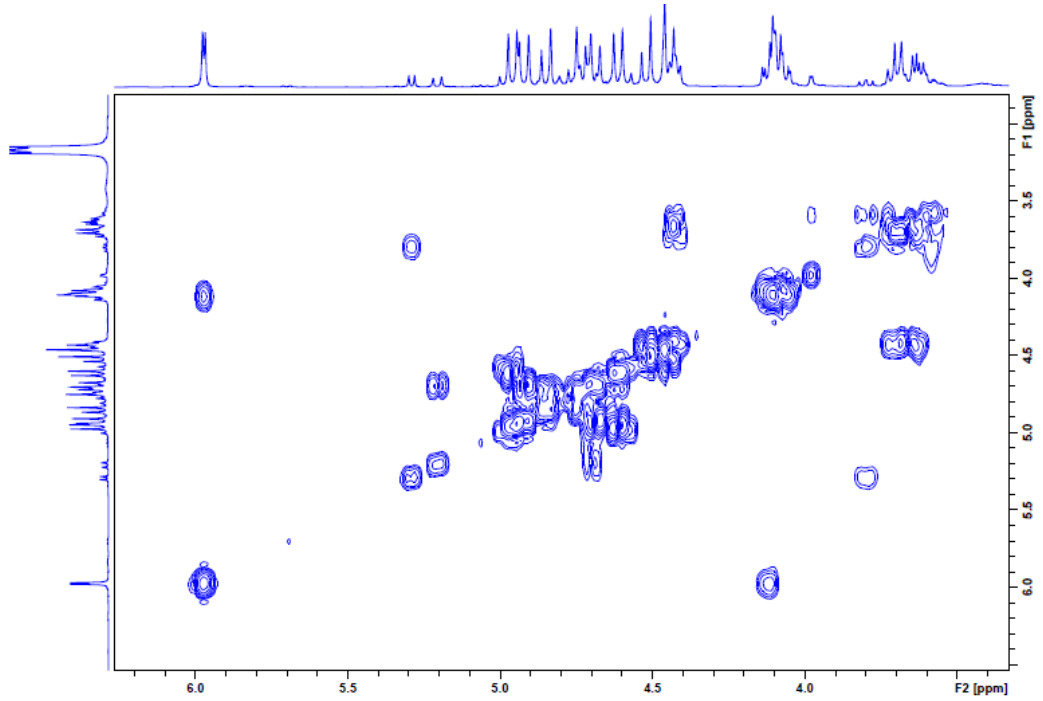


Fig. S8 HSQC NMR spectrum of **2b** in $CDCl_3$

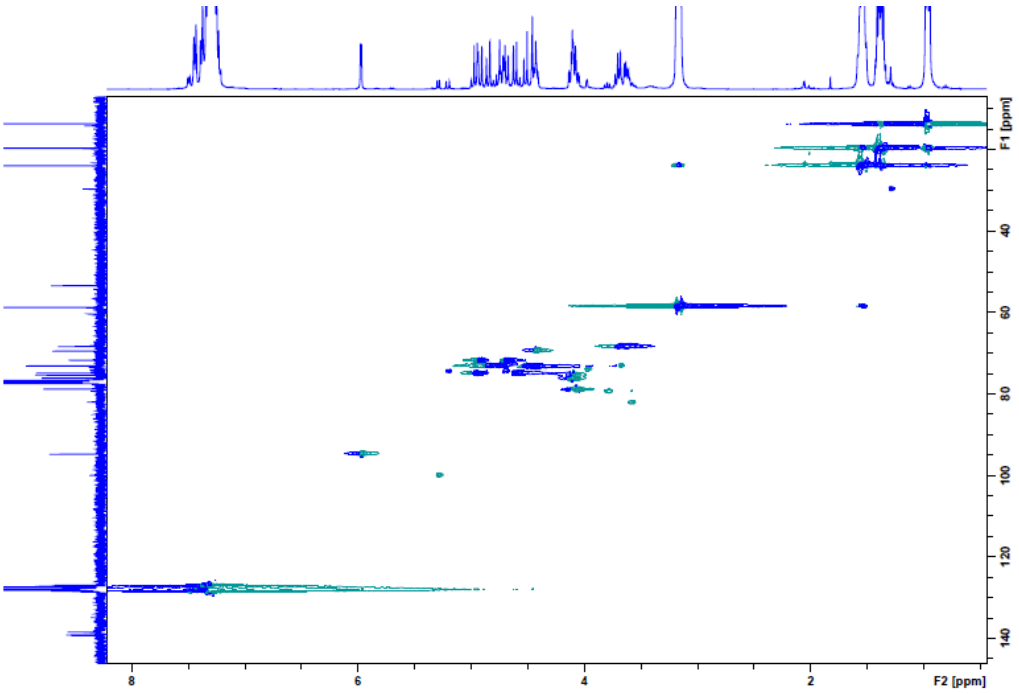


Fig. S9 ^{1}H NMR spectrum of **2c** in $CDCl_3$ (400 MHz)

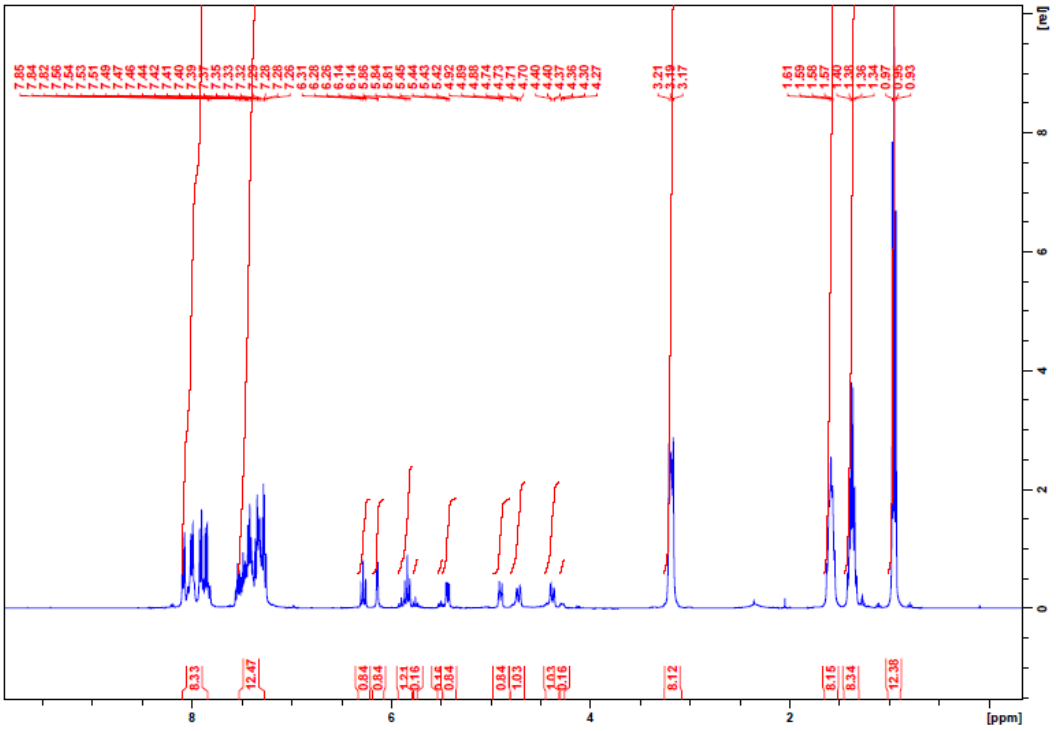


Fig. S10 Apt NMR spectrum of **2c** in $CDCl_3$ (101 MHz)

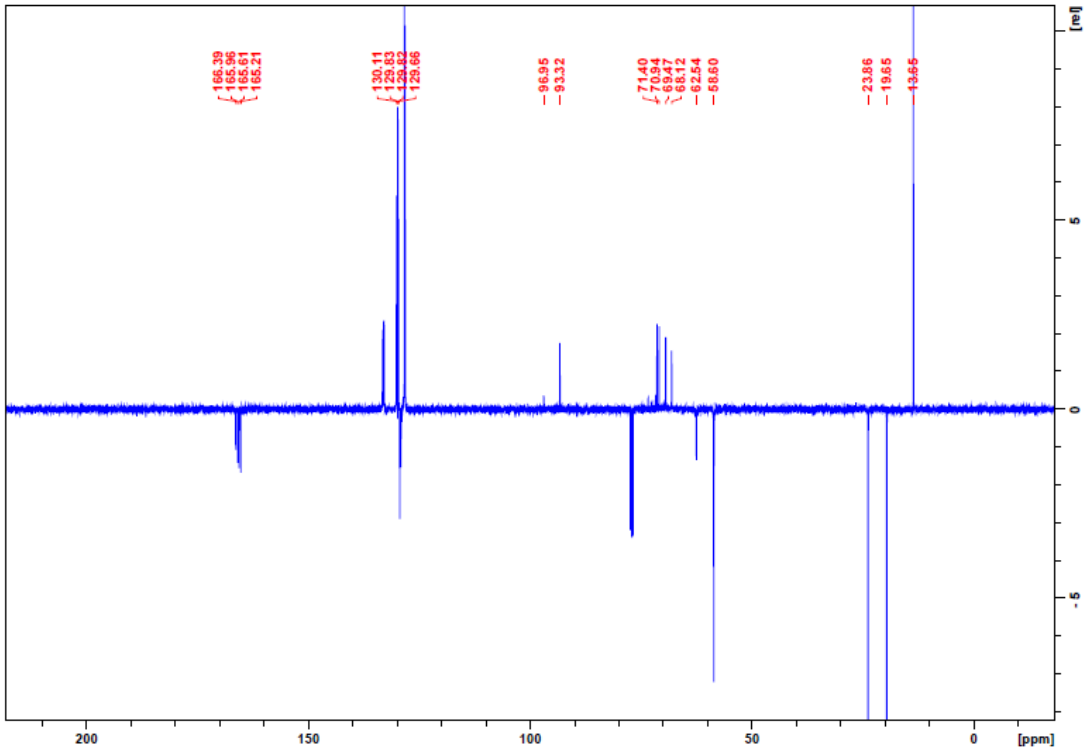


Fig. S11 Cosy NMR spectrum of **2c** in $CDCl_3$ (400 MHz)

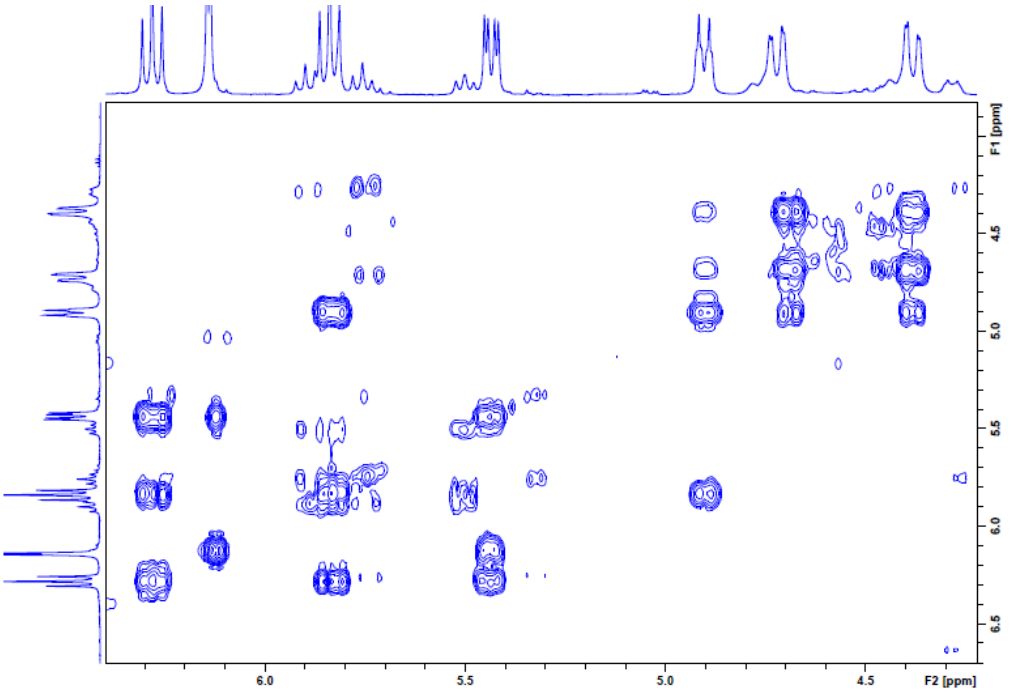


Fig. S12 HSQC NMR spectrum of **2c** in $CDCl_3$

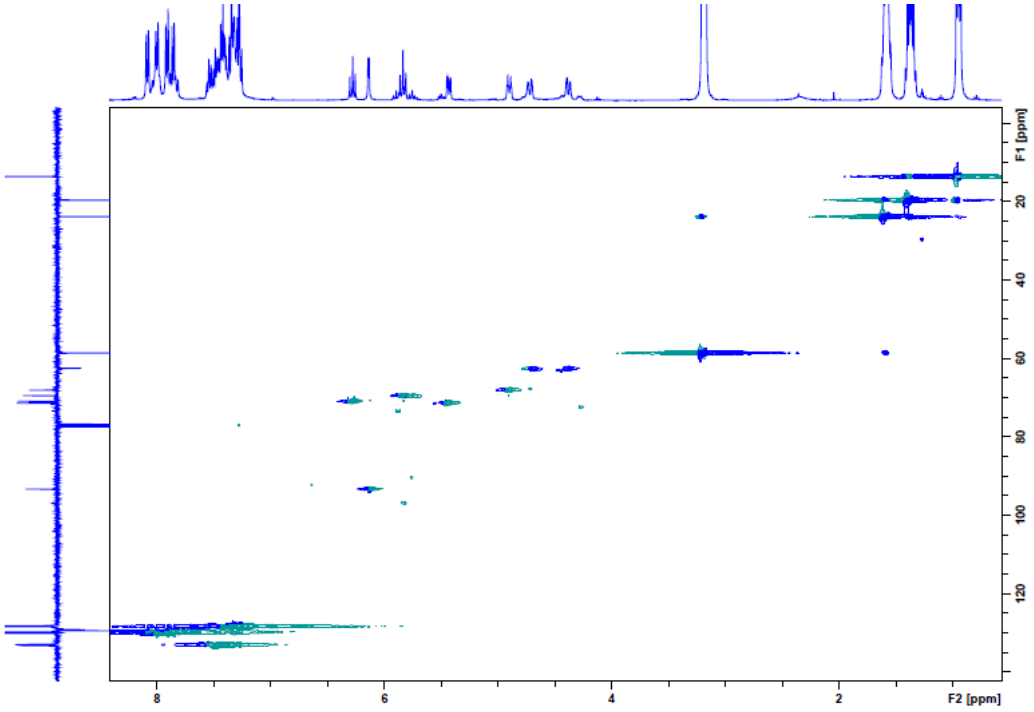


Fig. S13 ^{1}H NMR spectrum of **4c** in $CDCl_3$

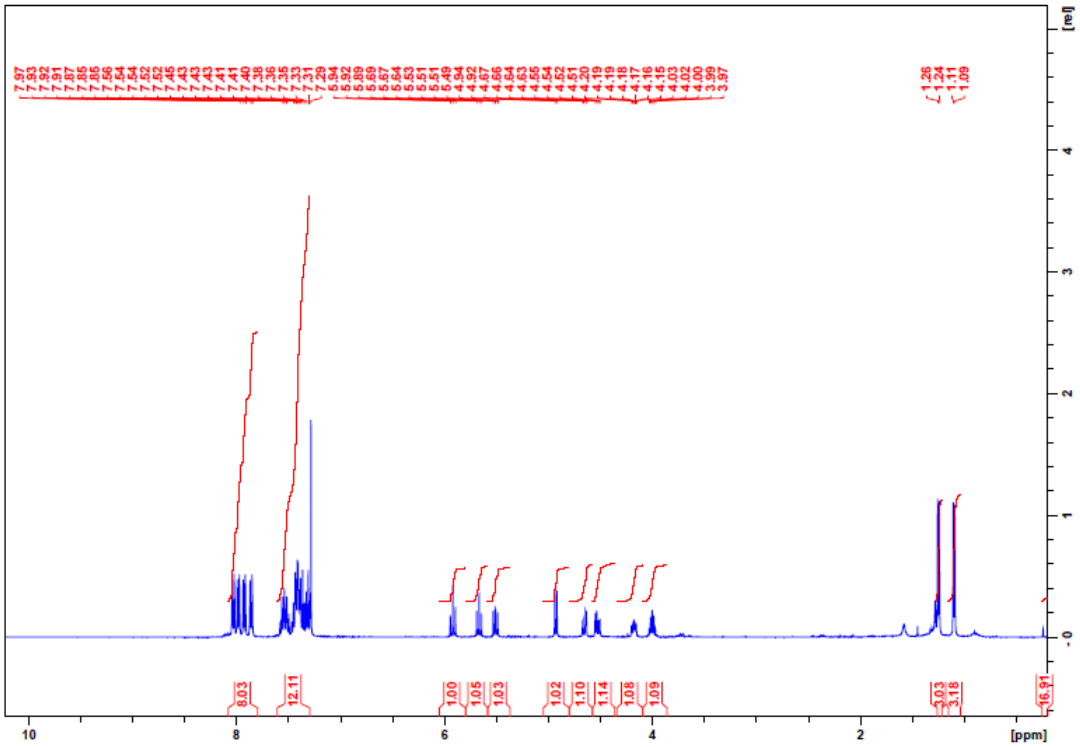


Fig. S14 ^{13}C NMR spectrum of **4c** in $CDCl_3$

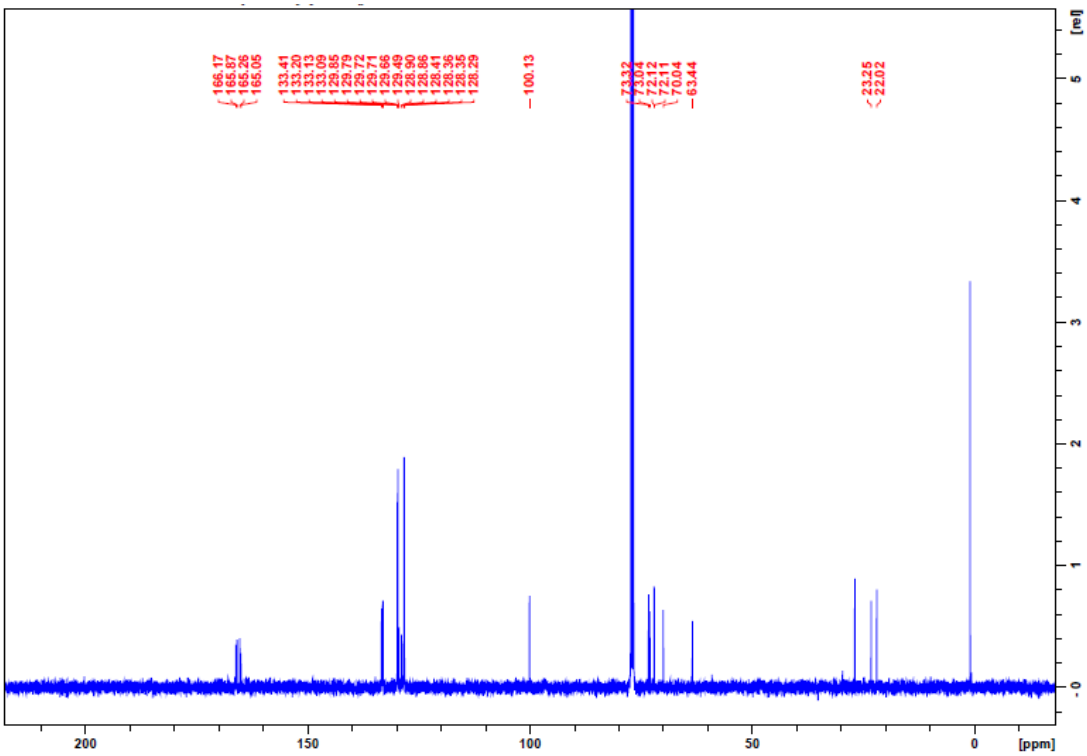


Fig. S15 ^{1}H NMR spectrum of **4a** in $CDCl_3$ (400 MHz)

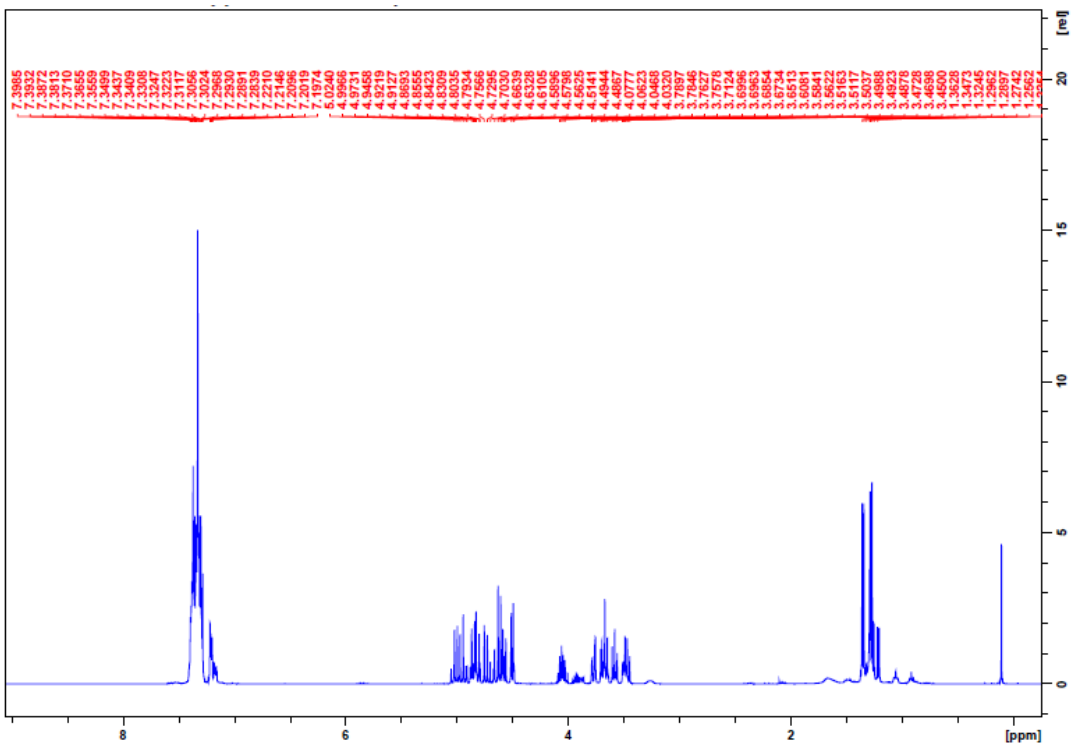


Fig. S16 ^{1}H NMR spectrum of **6a** in $CDCl_3$ (400 MHz)

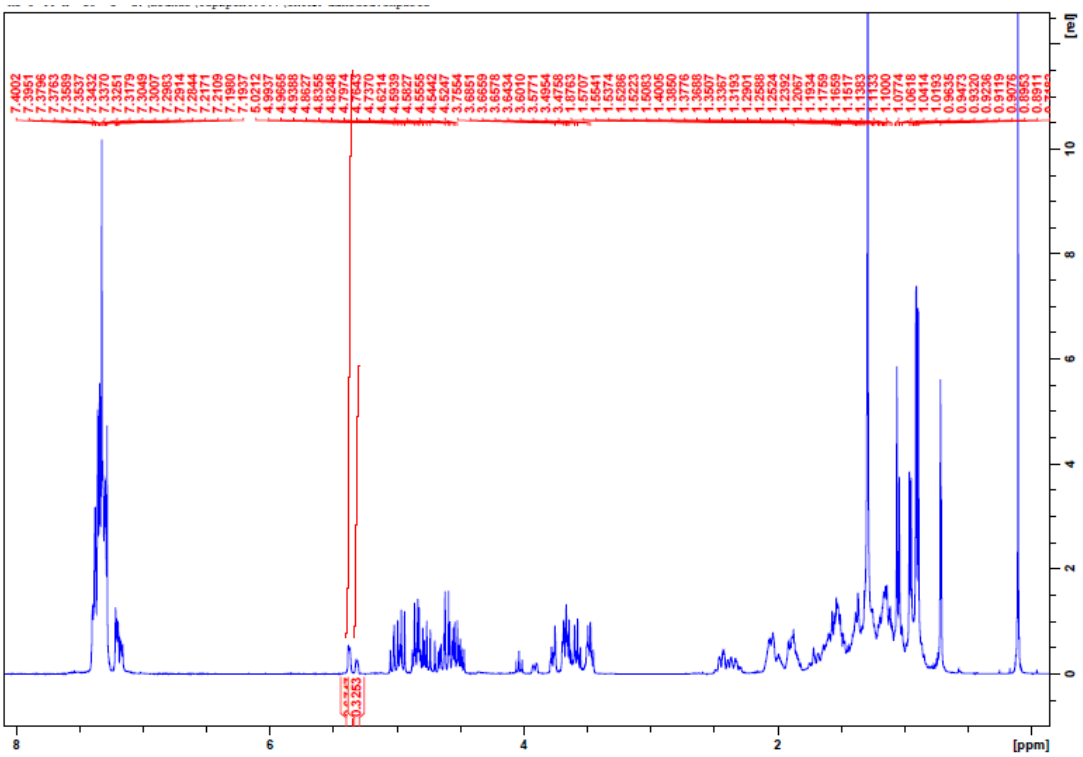


Fig. S17 ^{1}H NMR spectrum of **8a** in $CDCl_3$ (400 MHz)

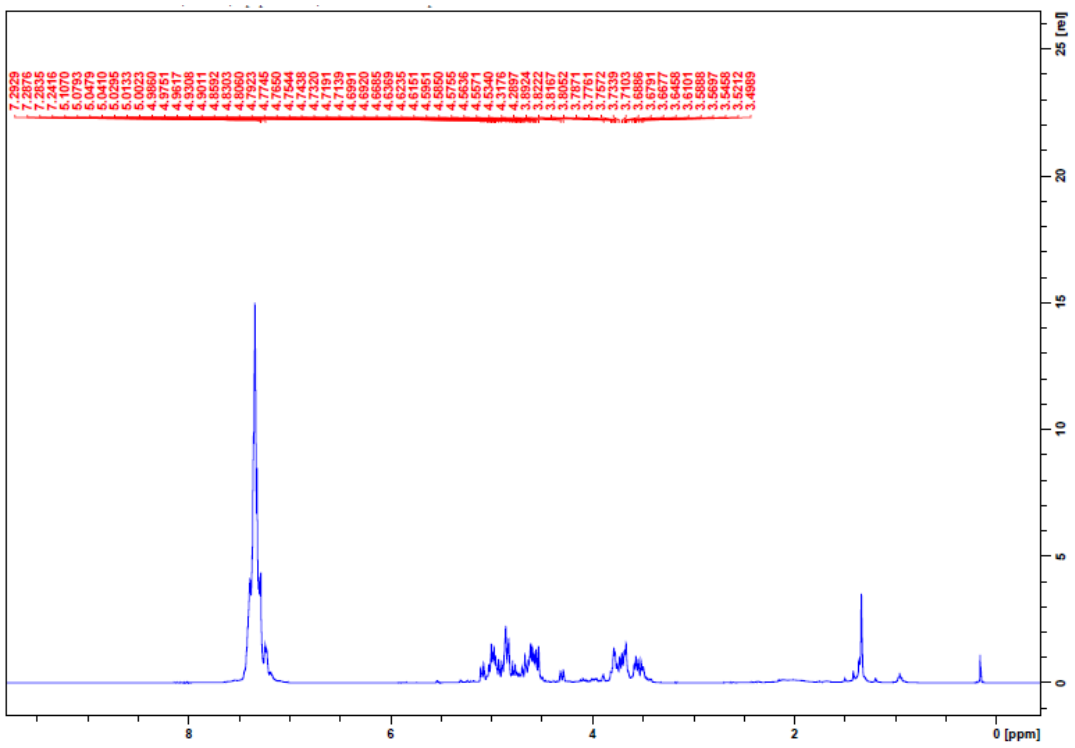


Fig. S18 ^{1}H NMR spectrum of **10a** in $CDCl_3$ (400 MHz)

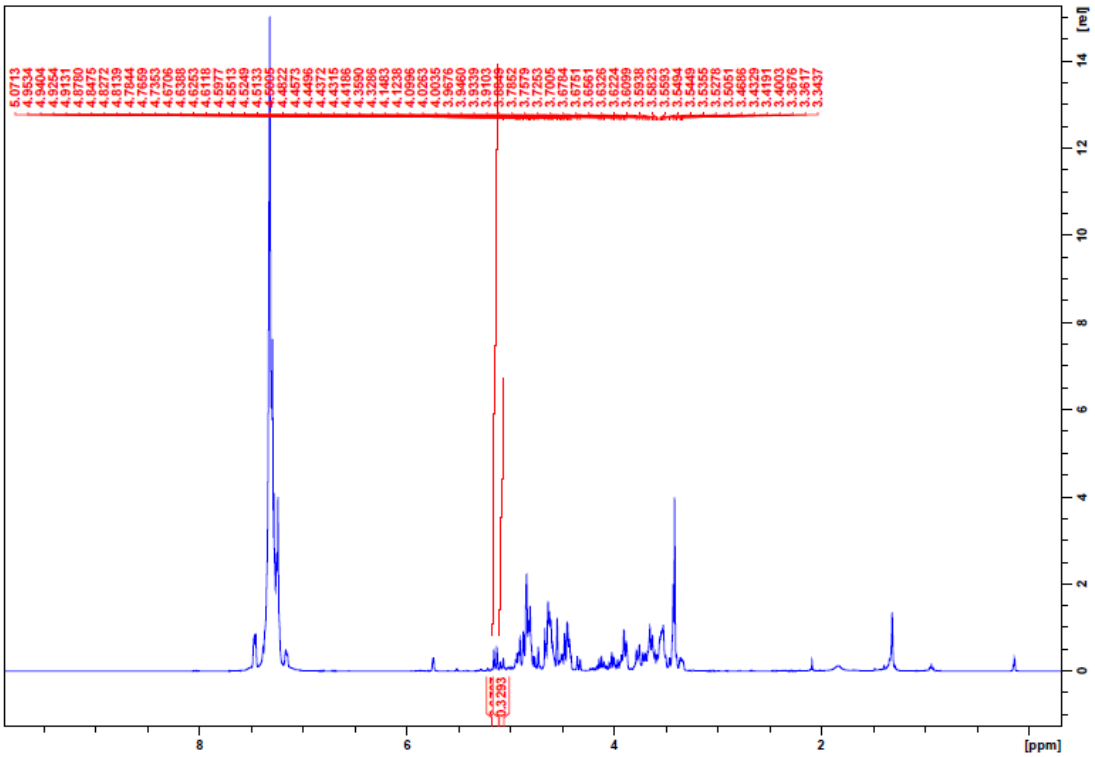


Fig. S19 ^{1}H NMR spectrum of **4b** in $CDCl_3$ (400 MHz)

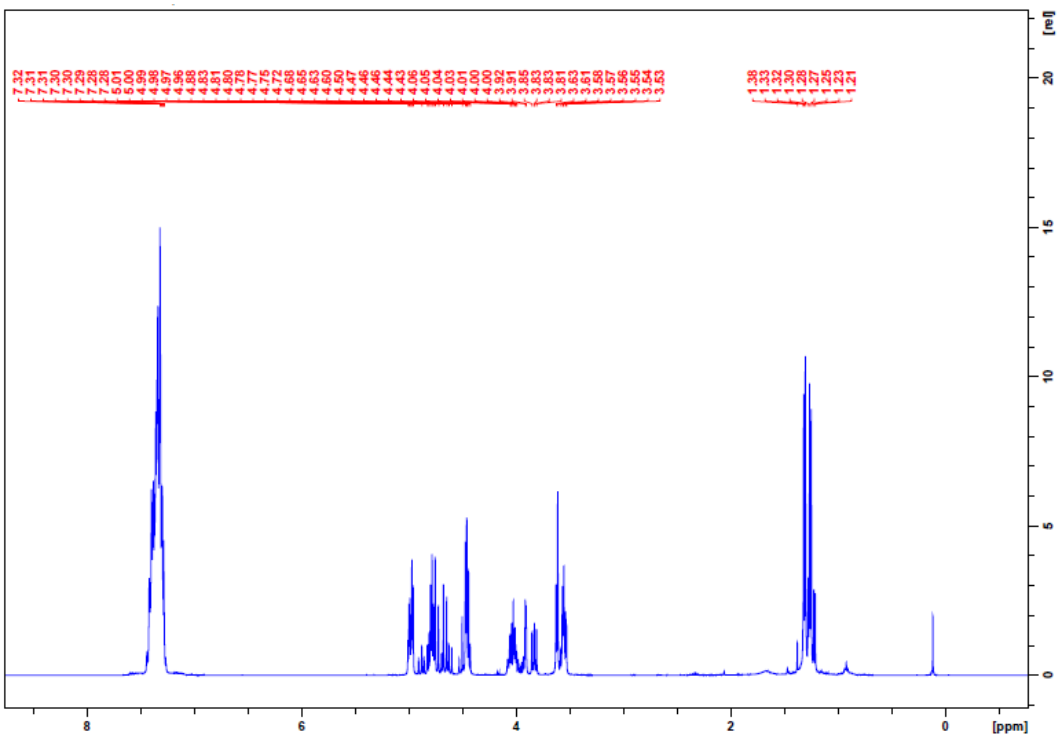


Fig. S20 ^{1}H NMR spectrum of **6b** in $CDCl_3$ (400 MHz)

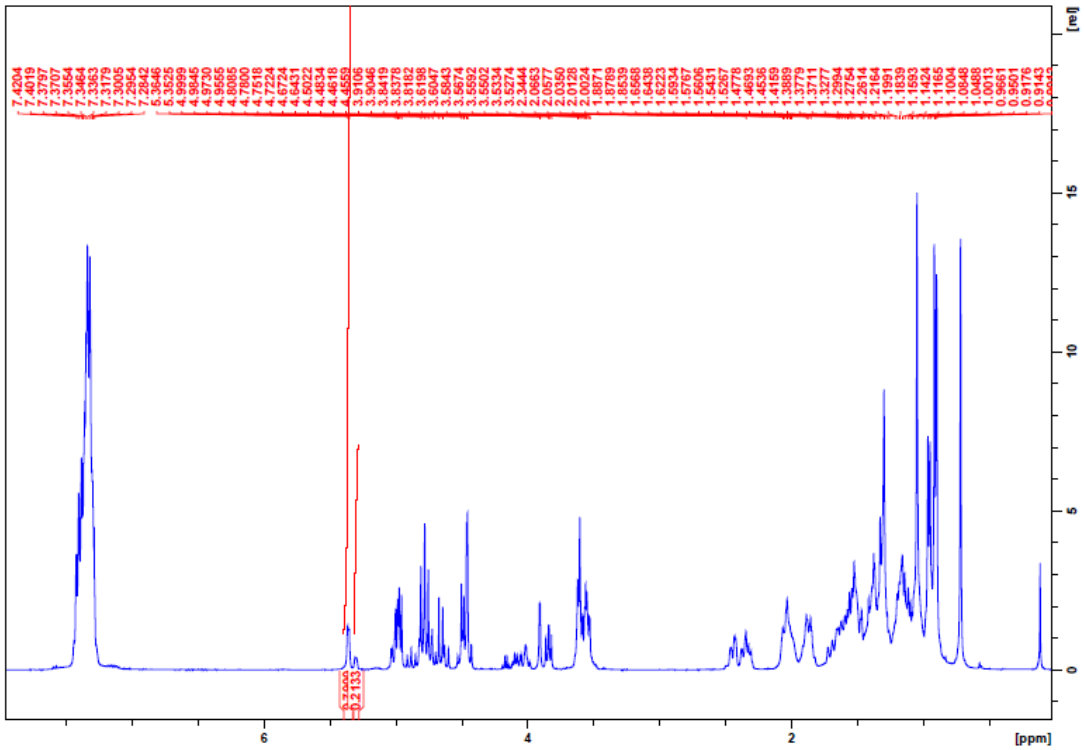


Fig. S21 ^{1}H NMR spectrum of **8b** in $CDCl_3$ (400 MHz)

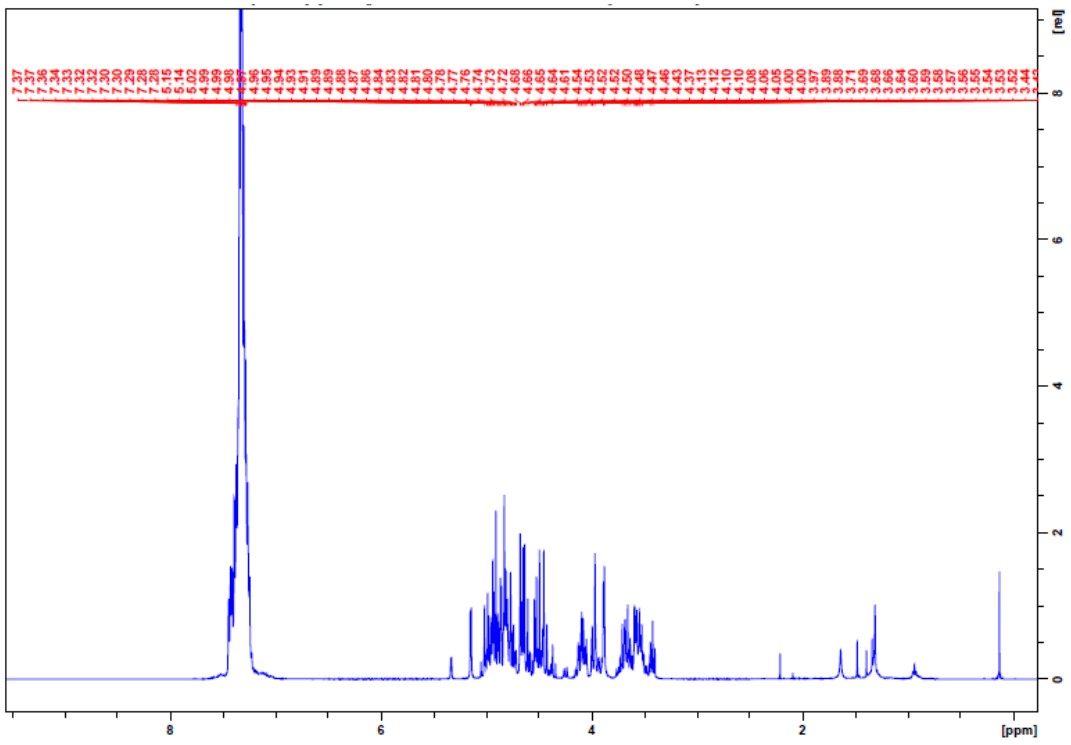


Fig. S22 ^{1}H NMR spectrum of **10b** in $CDCl_3$ (400 MHz)