Supporting information for:

Supramolecular Activation in Triggered Cascade Inversion

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NMR-analyses of cascade reaction and H-bond formation

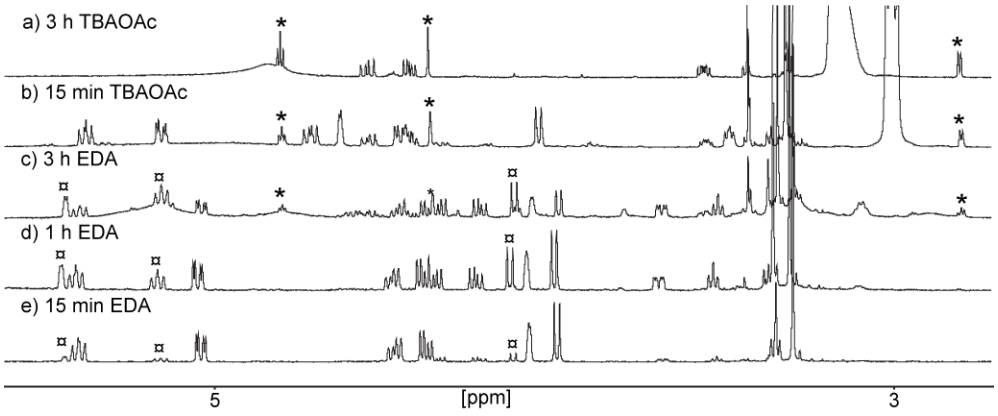


Fig. 1 Cascade reaction with 5 eq. TBAOAc (a-b) or EDA (c-e). ∗ and ¤ indicate resonances from compound **4**, and **5**, respectively.

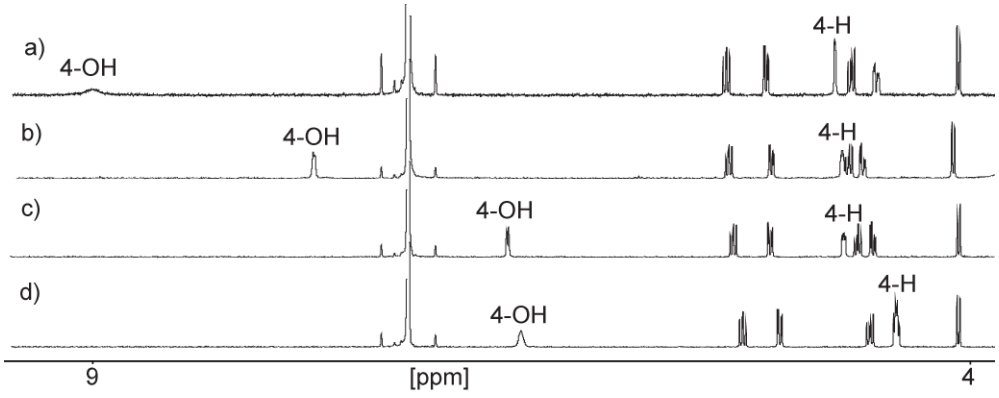


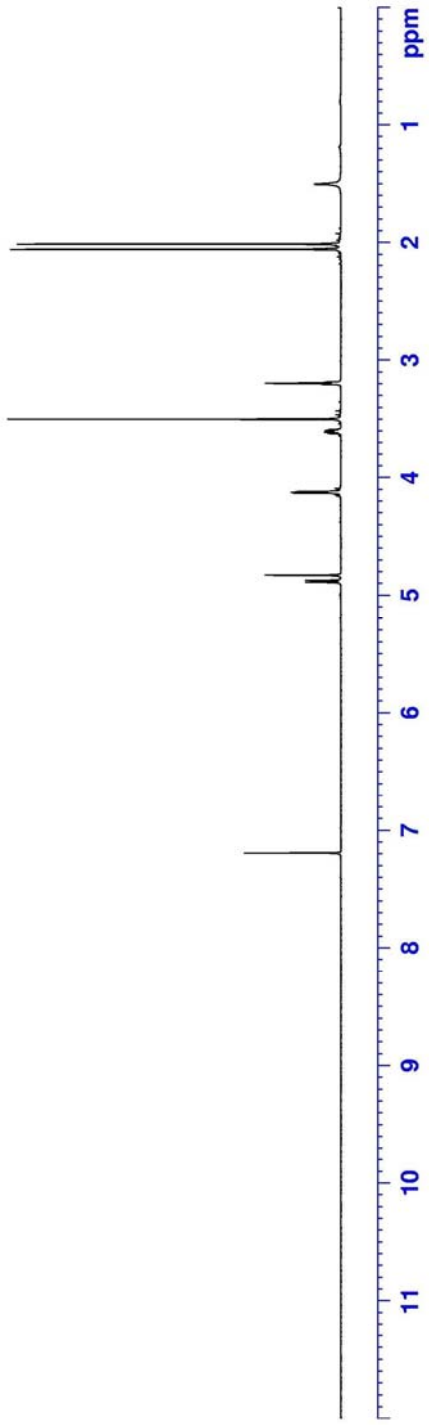
Fig. 2H-bond formation between the 4-OH group of compound **2** and tested anionic reagents (5 eq.); a: $TBANO_2$; b: TBACl; c: TBABr; d: TBASCN. $\delta_{4\text{-OH}}$ for compound **2** alone: 1.8.

General triggered cascade carbohydrate epimerization procedure. To a solution of compound **1** or **2** (140 mg, 0.5 mmol), in CH_2Cl_2 (5 mL) was added pyridine (0.53 mL) at -20 °C. Trifluoromethanesulfonic anhydride (420 mg, 1.5 mmol) in CH_2Cl_2 (2 mL) was added dropwise, and the mixture was stirred while allowing to warm from -20 °C to 10 °C over 2 h. The resulting mixture was subsequently diluted with CH_2Cl_2 and washed with 1 M HCl, aqueous $NaHCO_3$, water, and brine. The organic phase was dried over Na_2SO_4 and concentrated in vacuo at low temperature. The residue was used directly in the next step without further purification. $TBANO_2$ (720 mg, 2.5 mmol) and ethylenediamine (0.167 mL, 2.5 mmol) were added to a solution of the protected triflate residue in dry toluene or acetonitrile (5.0 mL), and then allowed to react at room temperature for 4 h. The resulting mixture was directly purified by flash column chromatography (2:1 hexane–ethyl acetate), yielding **7** or **8** as a colorless syrup.

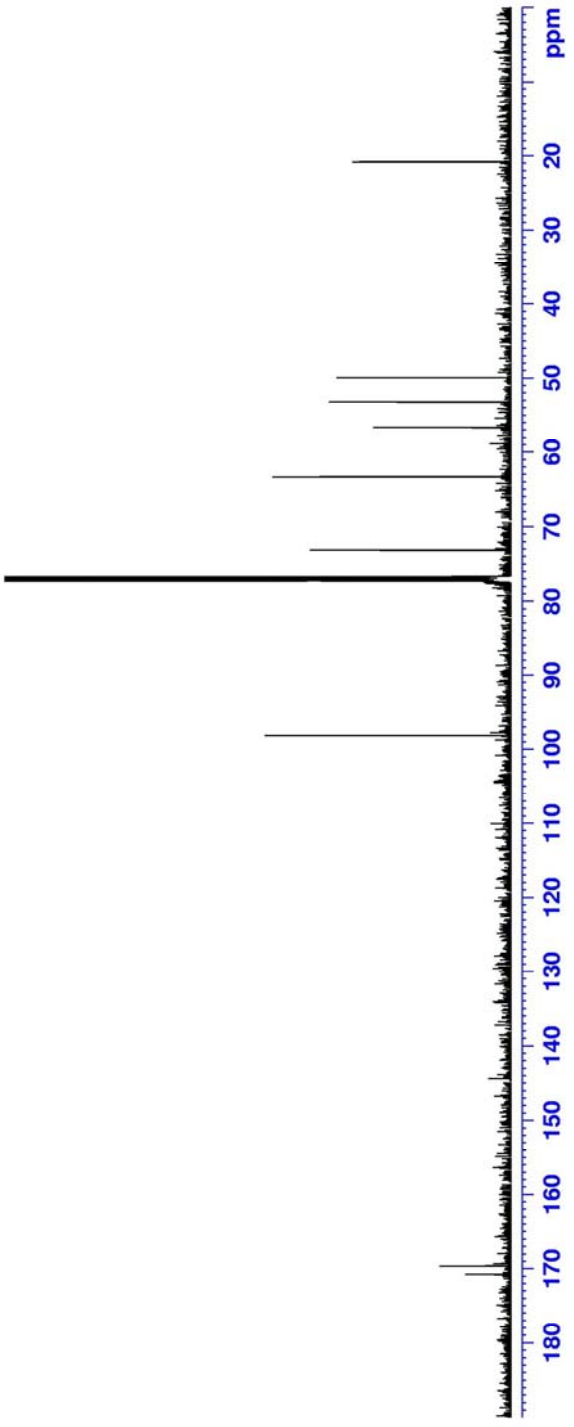
Compound 7: Yield: 117 mg, 0.45 mmol, 90%; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 4.94 (d, 1 H, $J_{4,5}$ = 8.1 Hz, H_4), 4.89 (s, 1 H, H_1), 4.1-4.2 (m, 2 H, H_6), 3.6-3.7 (m, 1 H, H_5), 3.56 (s, 3 H, OMe), 3.2-3.3 (m, 2 H, H_2, H_3), 2.11 (d, 3 H, OAc), 2.07 (d, 3 H, OAc); ^{13}C NMR ($CDCl_3$ 125 MHz): δ = 170.93, 169.80, 98.32, 73.35, 63.54, 63.49, 56.9, 53.42, 50.15, 21.01, 20.97; MS (M+Na): 283.0794. Observed: 283.0791.

Compound 8: Yield: 109 mg, 0.42 mmol, 84%; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 4.99 (d, 1 H, $J_{4,3}$ = 4.1 Hz, H_4), 4.78 (s, 1 H, H_1), 4.28 (dd, 1 H, $J_{6a,5}$ = 6.9 Hz, $J_{6a,6b}$ = 11.6 Hz, H_{6a}), 4.22 (dd, 1 H, $J_{6b,5}$ = 5.6Hz, H_{6b}), 3.75-3.85 (m, 1 H, H_5), 3.65 (dd, 1 H, $J_{3,2}$ = 3.8 Hz, H_3), 3.6 (s, 3 H, OMe), 3.3 (d, 1H, H_2), 2.15 (d, 3 H, OAc), 2.05 (d, 3 H, OAc); ^{13}C NMR ($CDCl_3$ 125 MHz): δ = 170.81, 170.78, 98.67, 72.66, 64.59, 62.19, 56.99, 51.38, 51.21, 20.94, 20.85; MS (M+Na): 283.0794. Observed: 283.0786.

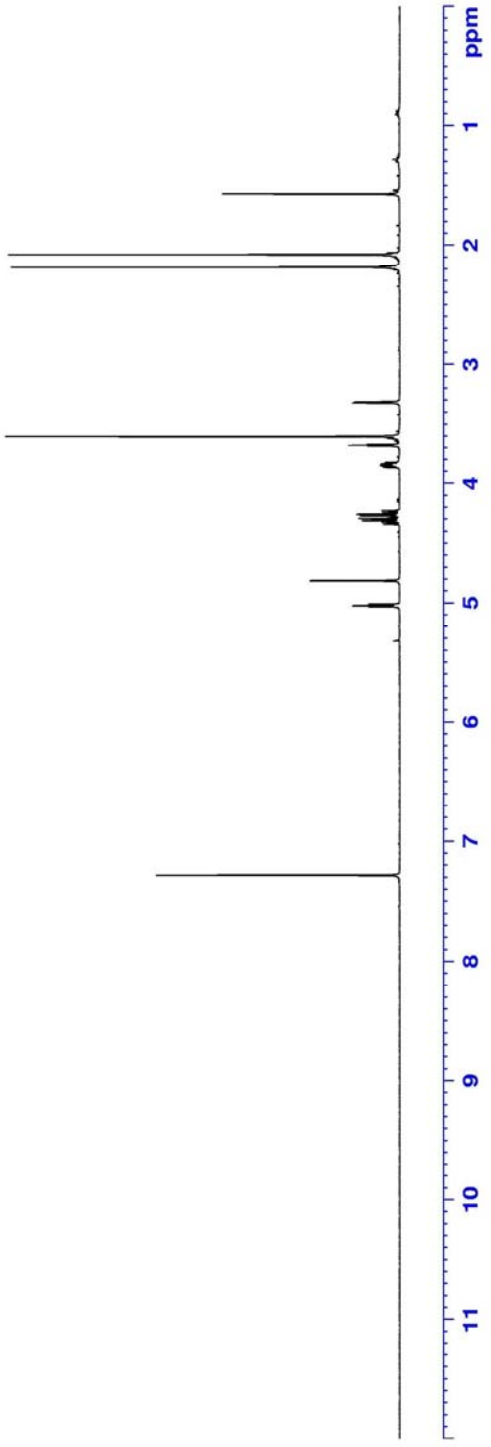
^{1}H-NMR of **7** ($CDCl_3$)



^{13}C-NMR of **7** ($CDCl_3$)



^{1}H-NMR of **8** ($CDCl_3$)



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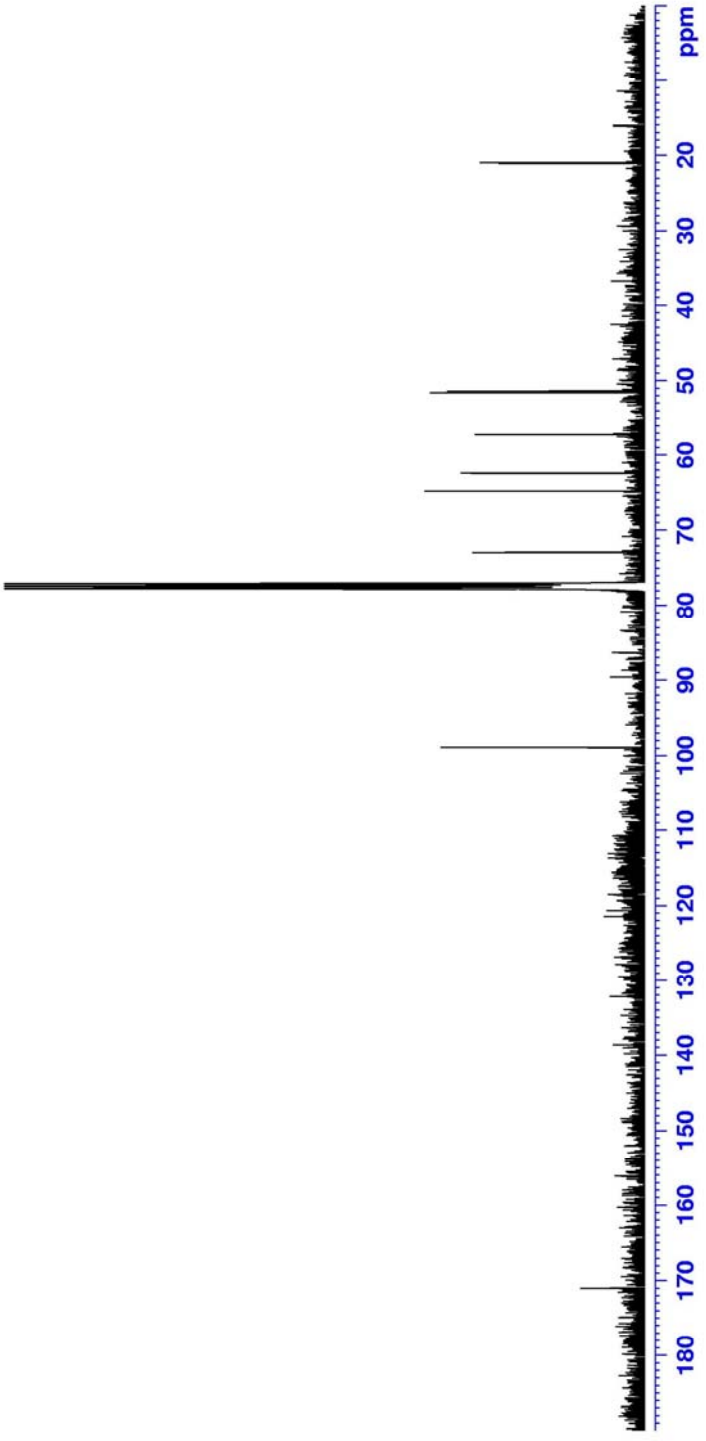
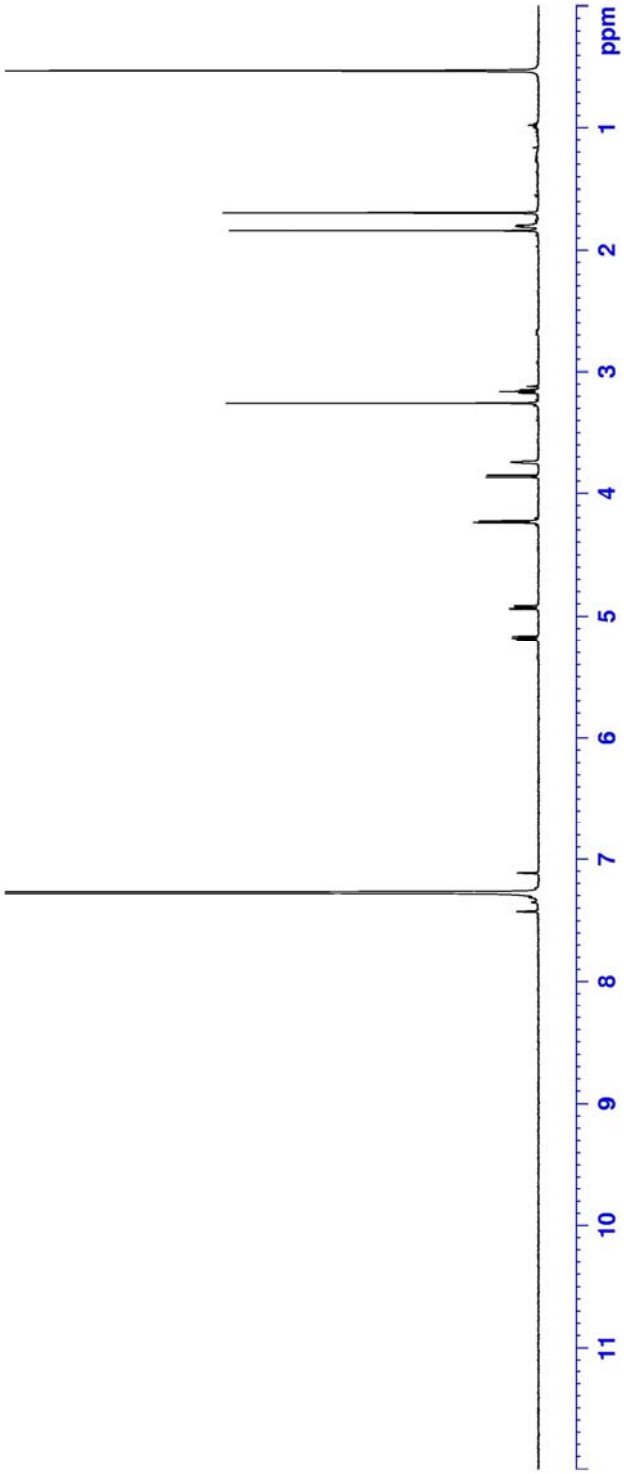
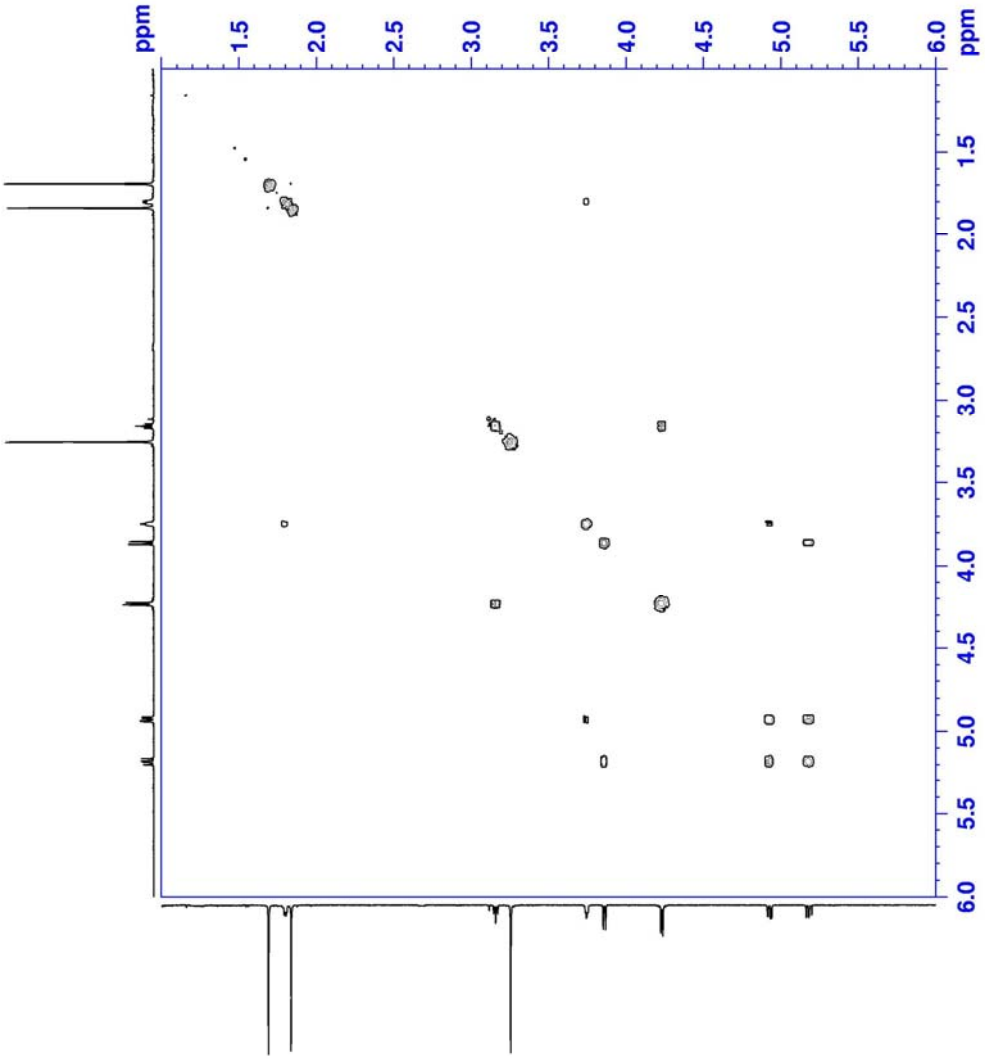


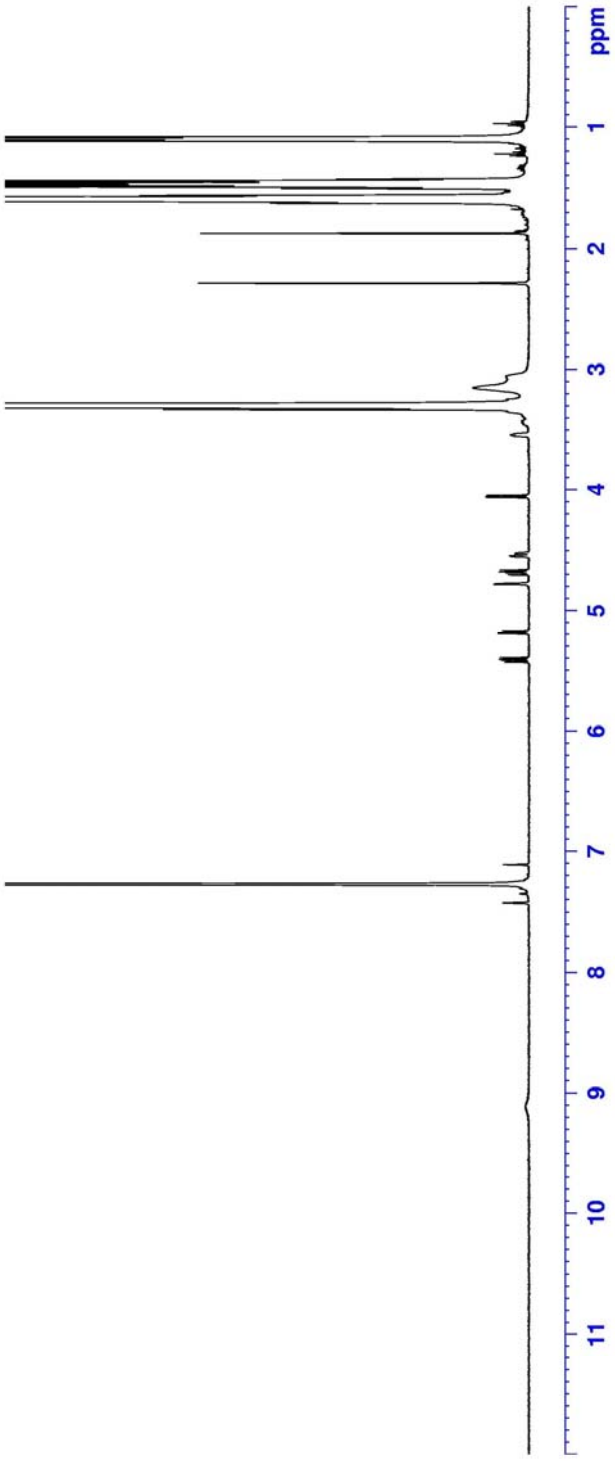
^{1}H-NMR of **6** (C_6D_6)



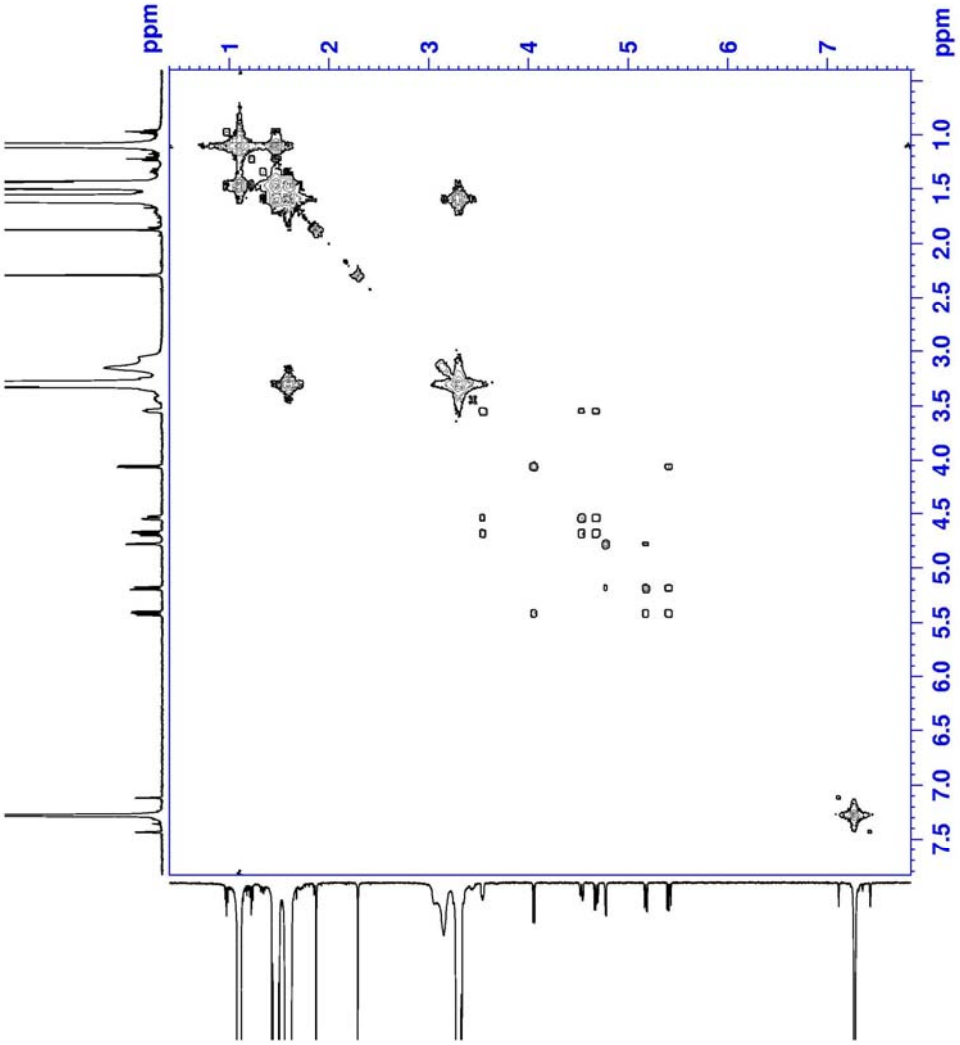
^{1}H-H COSY of **6**



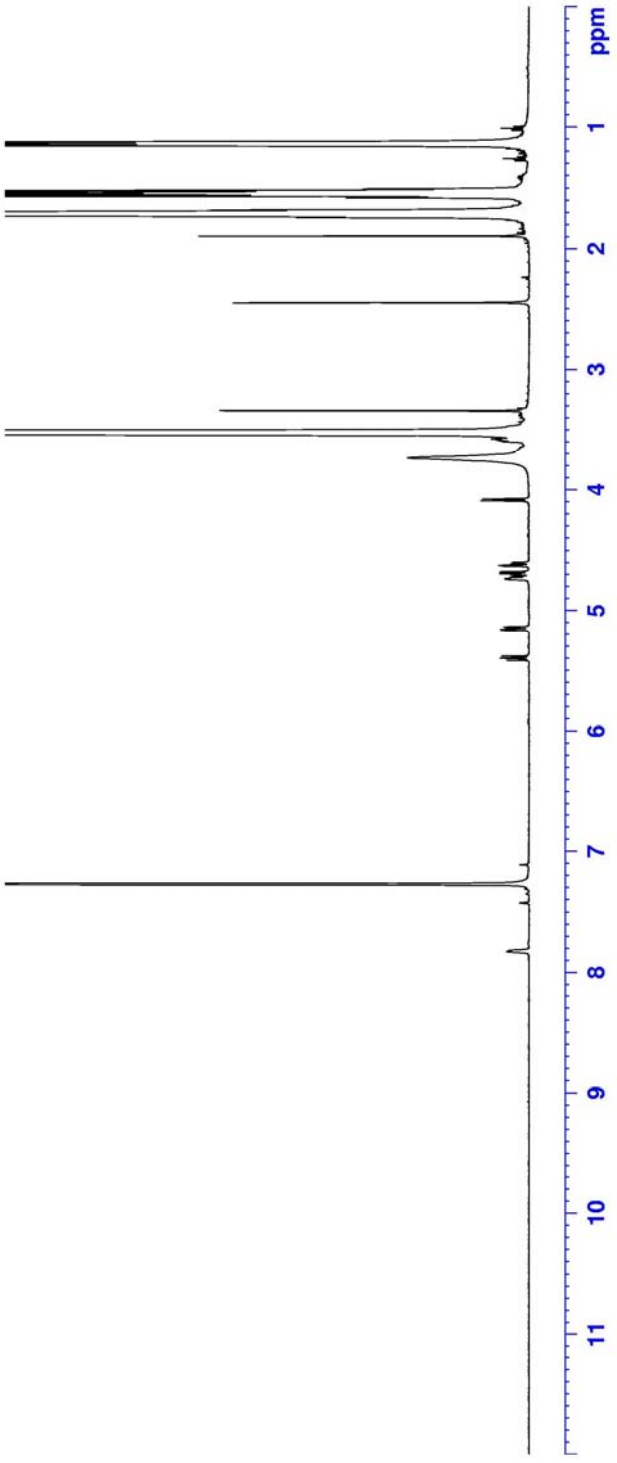
^{1}H-NMR of **6** with $TBANO_2$



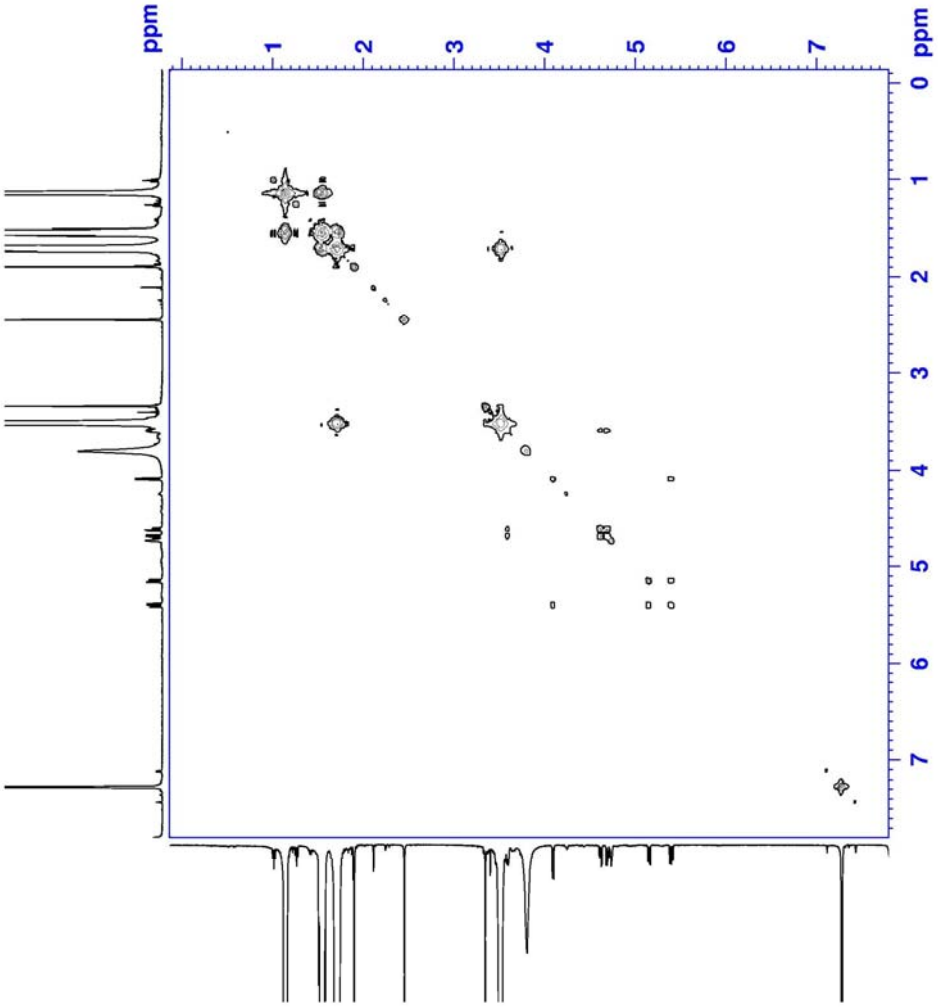
^{1}H-H COSY of **6** with $TBANO_2$



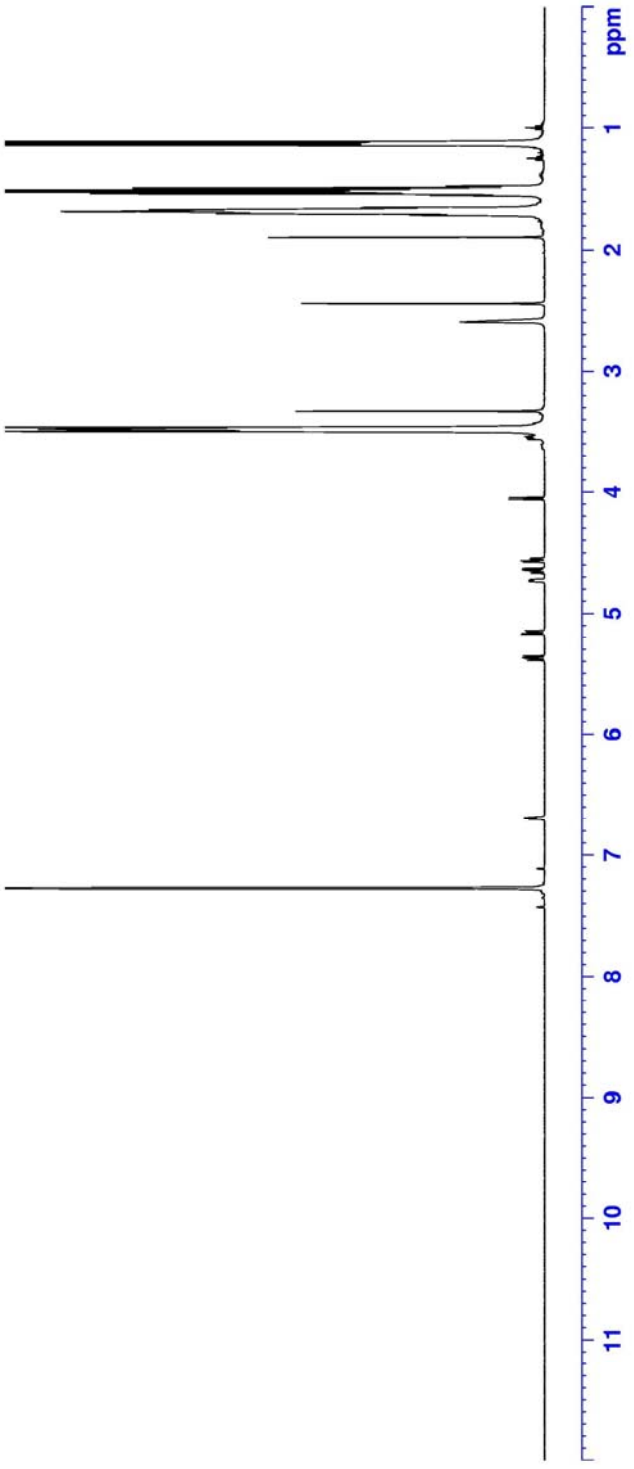
^{1}H-NMR of **6** with $TBANO_2$



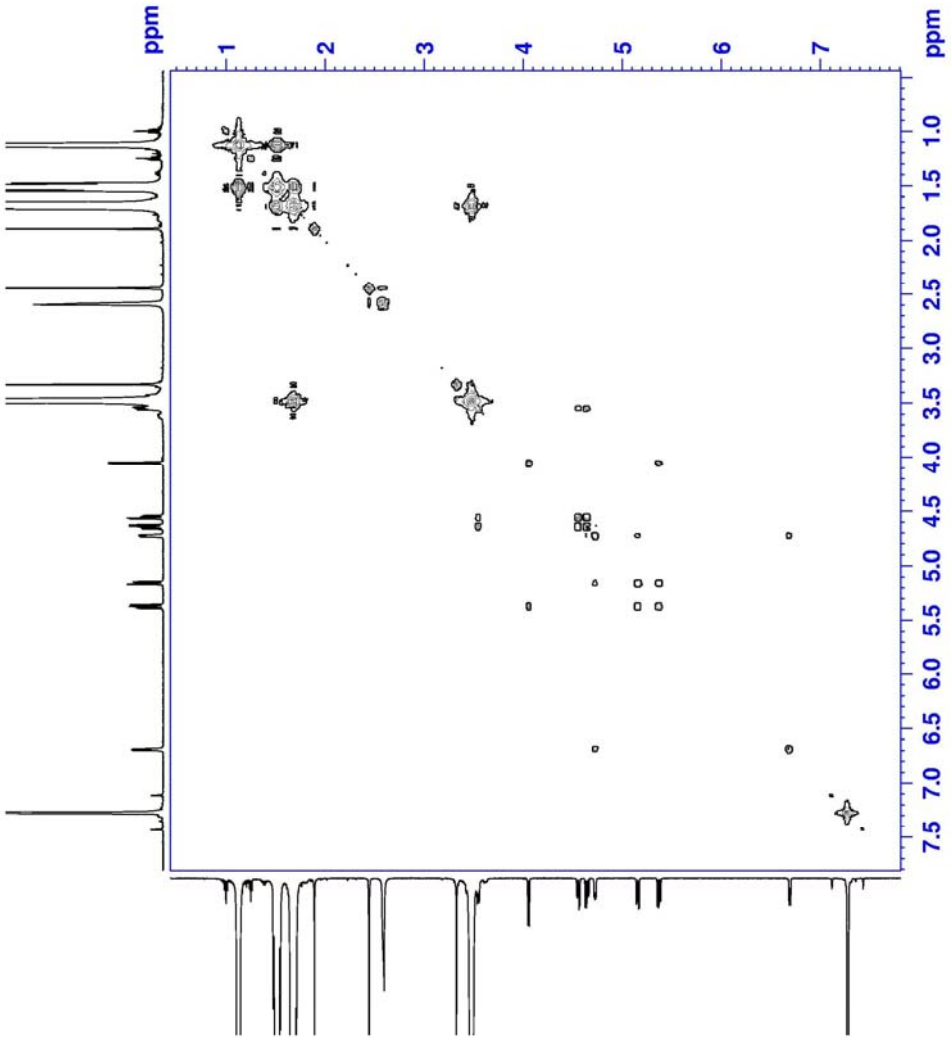
^{1}H-H COSY of **6** with TBACl



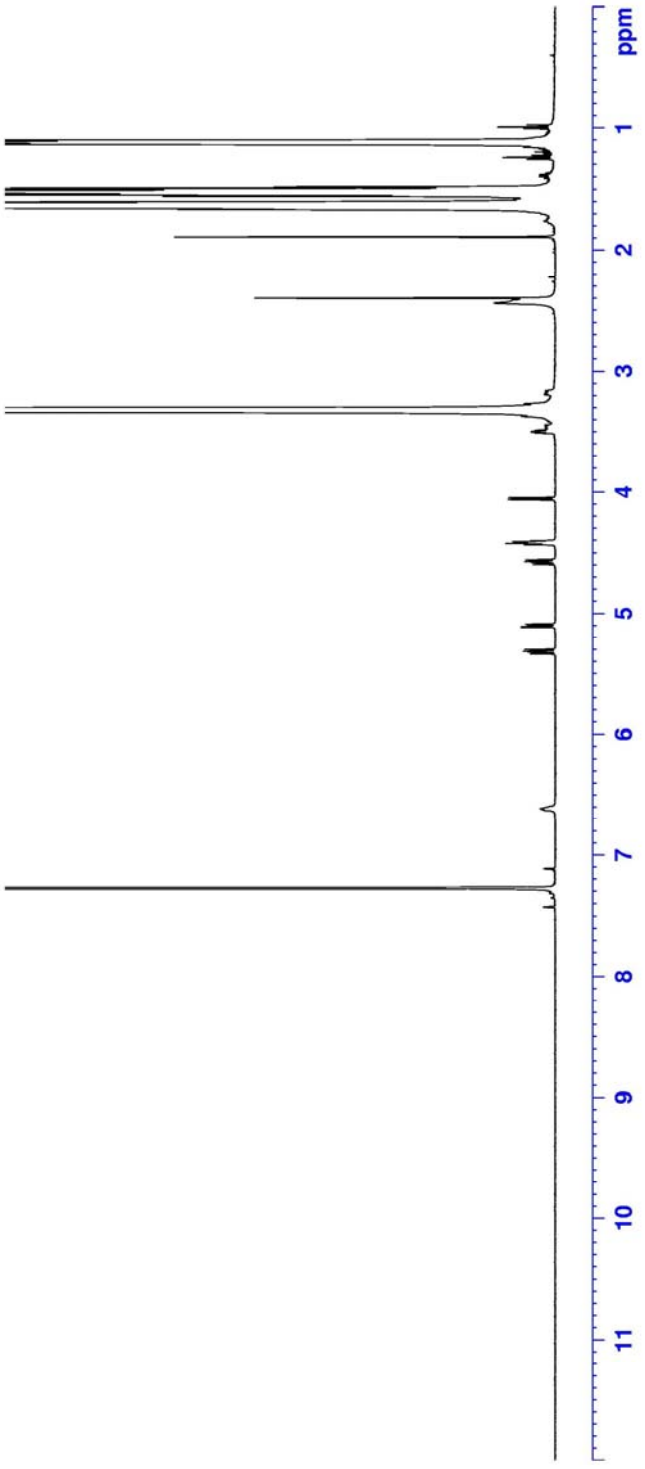
^{1}H-NMR of **6** with TBABr



^{1}H-H COSY of **6** with TBABr



^{1}H-NMR of **6** with TBASCN



^{1}H-H COSY of **6** with TBASCN