Electronic Supplementary Material (ESI) for RSC Advances.

The tribological behaviour and tribochemical study of B-N type borate esters in rapeseed oil—compound versus salt

J. C. Yan, [a,b,c] X. Q. Zeng, [c] E. van der Heide, [c] and T. H. Ren, [a,b*] Y. D. Zhao [d]

[a] School of Chemistry and Chemical Engineering, Key Laboratory for Thin Film and Microfabrication, Shanghai Jiao Tong University, China.

[b] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Science, China.

[c] Laboratory for Surface Technology and Tribology, University of Twente, The Netherlands.

[d] Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, China.

*Corresponding author. Tel.: +86 21 5474 7118

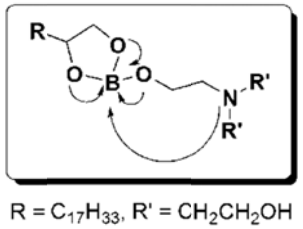
E-mail address: thren@sjtu.edu.cn (TH. Ren).

Supplementary Information

1. Preparation of the additives

The chemicals and solvents were purchased from Shanghai Chemical Reagents, Shanghai, China and were used without purification. A commercial rapeseed oil (referred to rapeseed oil), provided by Grease Factory of China, Lanzhou, China was used as the lubricating oil without any further treatment. The main chemical constituents of the rapeseed oil are as follows: 7.46 wt. % of saturated fatty acids, 64.06 wt. % of monounsaturated fatty acid and 28.48 wt. % of total polyunsaturated fatty acid.

For the design of the additives, vicinal diol group in GMO and nitrogen were introduced to the borate esters, see Fig. S1, with the aim to improve the oil-solubility and hydrolytic stability of borate esters in rapeseed oil. The oxygen and nitrogen elements can be helpful for stabilizing the molecules and the long chain which is symbolised by R group in the image was designed to increase the oil-solubility.



$R = C_{17}H_{33}$, $R' = CH_2CH_2OH$

Fig. S1 The design of the novel borate ester

Specifically, tris(2-hydroxyethyl)amine (TEA) salt of (2-hydroxy-1,3,2-dioxaborolan-4-yl) methyl oleate (OBS) and (2-(2-(bis(2-hydroxyethyl)amino)ethoxy)

-1,3,2-dioxaborolan-4-yl)methyl oleate (OBN) were prepared according to Ref [11]. The preparation as well as the codes of the borate esters is schematically depicted in Fig. S2 and the procedure was described as follow. The commercial GMO is a mixture of 60 wt. % 2,3-dihydroxypropyl oleate, 20 wt. % 3-hydroxypropane-1,2-diyl dioleate and 20 wt. % propane-1,2,3-triyl trioleate, therefore GMO used in the preparation is calculated based on the hydroxyl groups. In a 500 mL of round bottomed flask, 54.2 g (0.1 mol) of GMO, 6.2 g (0.1 mol) of boric acid and some catalyst were added to a solvent then the solution was heated to 110 °C. As the reaction proceeded, water were generated and removed. The solution reflux for 2 hr till the reaction terminated and then 10.1 g (0.1 mol) of tris(2-hydroxyethyl)amine was added. The solution was washed with water and the solvent was evaporated, and at last produced 61.2 g of OBS. When the solution was treated with similar dehydration procedure as described before 59.8 g of OBN was obtained. All of the compounds were characterized by Infra-Red spectroscopy, NMR and elemental analysis. Then boron content of OBS and OBN is 1.97 wt. % and 1.52 wt. %, respectively. The nitrogen content of OBS and OBN is 2.62 wt. % and 2.07 wt. %, respectively. The additives are both mixture, therefore OBS and OBN are only schematically shown as the main content.

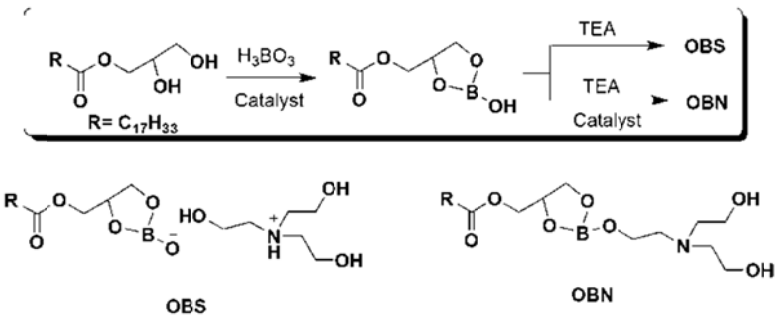


Fig. S2 The preparation, structure and scheme of the additives

2. Characterization of the additives

The additives were characterized by elemental analysis and the results are shwon in Table S1. The Infra-Red spectroscopy and NMR results are shown in Fig. S3 to Fig. S6.

Table 1 The elemental analysis of the borate esters [a]

Items	C (wt. %)	H (wt. %)	B (wt. %)	N (wt. %)
OBN	64.21 (63.15)	11.20 (10.21)	1.52 (2.11)	2.07 (2.73)
OBS	64.03 (63.15)	10.52 (10.21)	1.97 (2.11)	2.62 (2.73)

[a] Calculated value (balanced by oxygen)

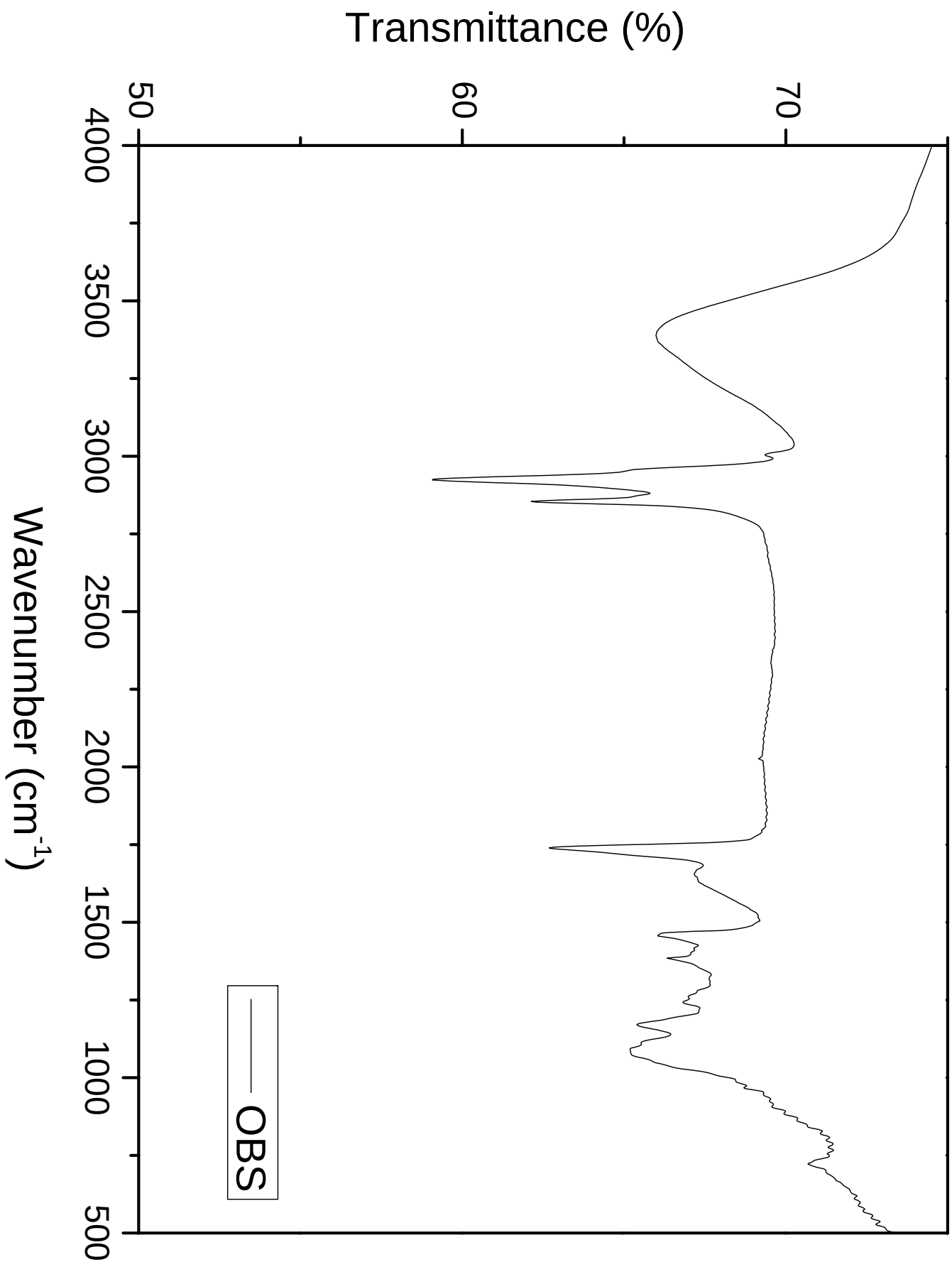


Fig. S3 IR spectrum of OBS

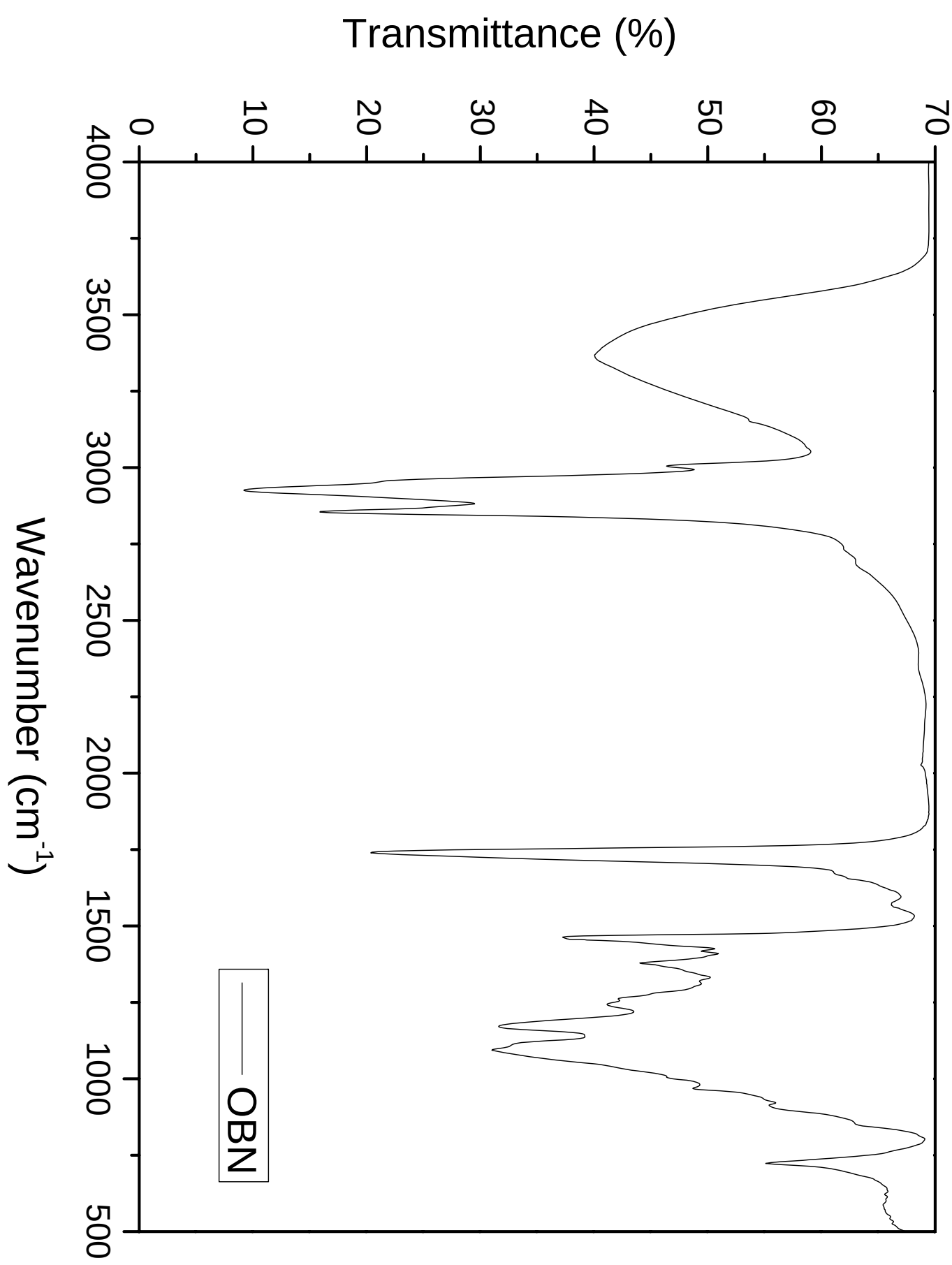


Fig. S4 IR spectrum of OBN

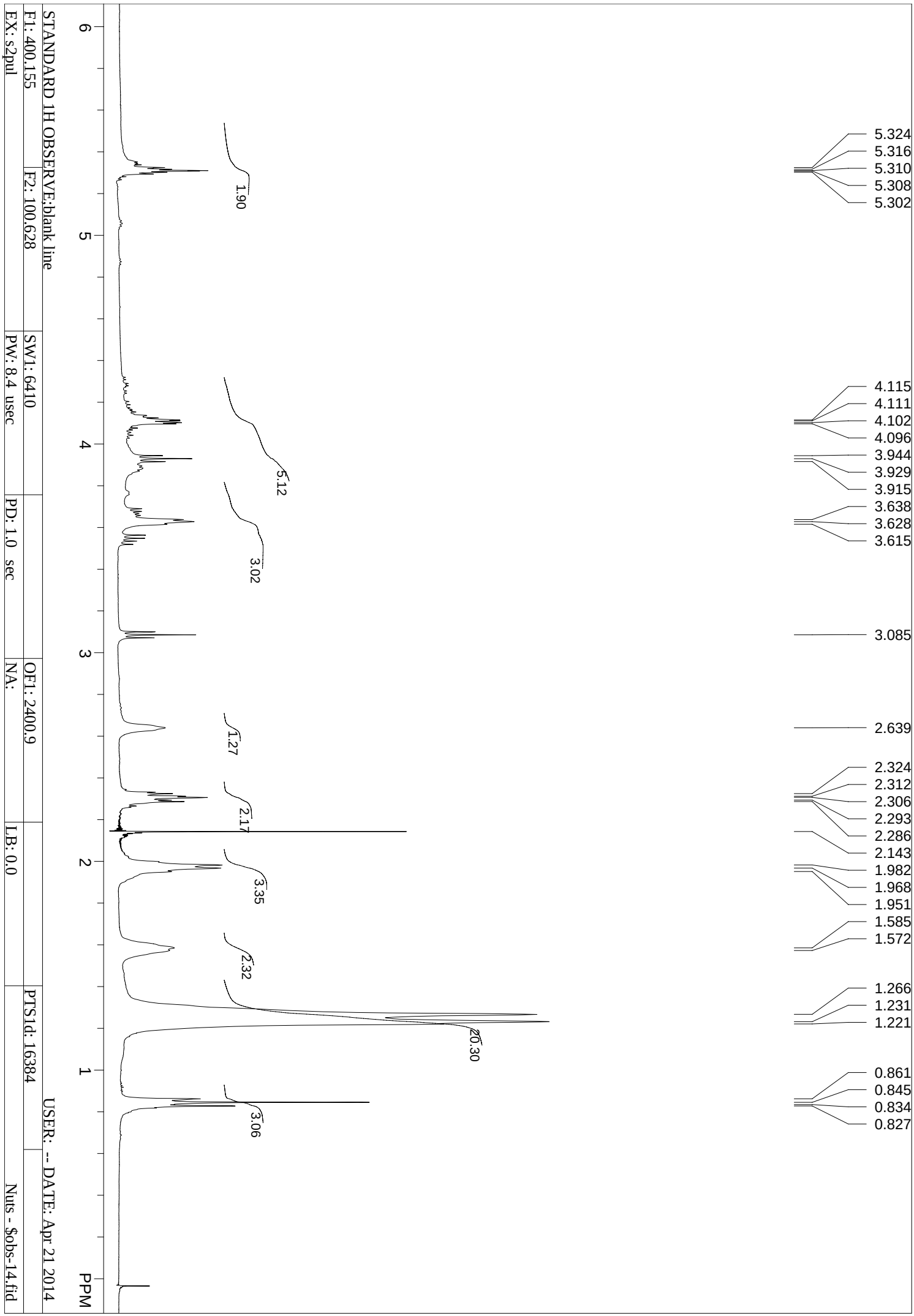


Fig. S5 NMR spectrum of OBS

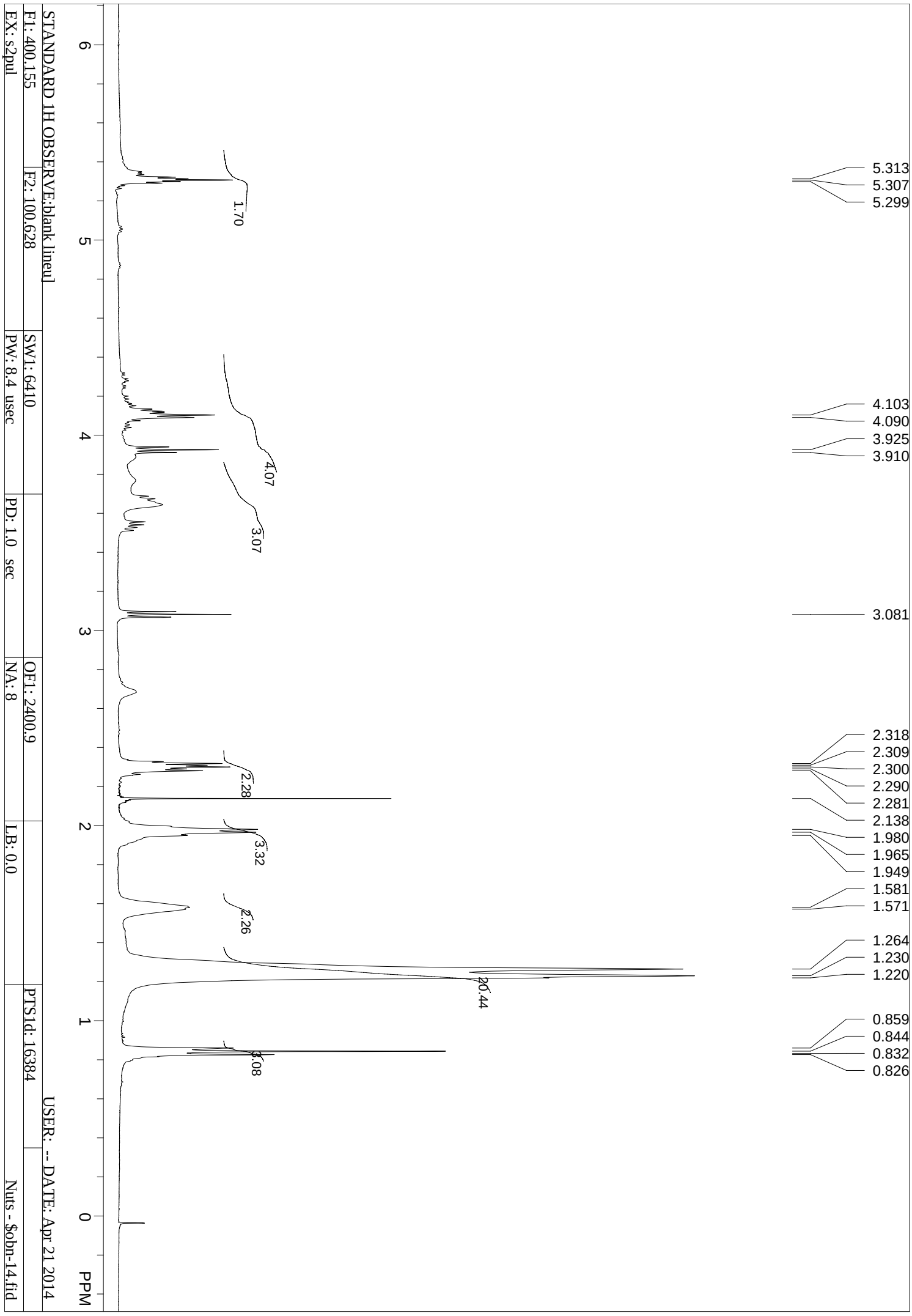


Fig. S6 NMR spectrum of OBN