Supporting information

# Synthesis and characterization of novel phenolic derivatives with the glycerol ketal group as an efficient antioxidant for gasoline stabilization

Zeinab Namazifar [a], Fariba Saadati [a,b1], Ali Akbar Miranbeigi [c]

[a] *Department of Chemistry, Faculty of Science, University of Zanjan, P.O. Box 45371-38791, Zanjan, Iran*

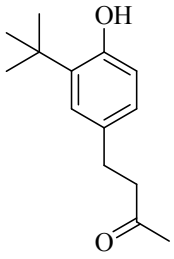
[b] *Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, V6T 1Z1, Canada*

[c] *Oil Refinery Research Division, Research Institute of Petroleum Industry, Tehran, Iran*

[*] Corresponding author. Tel.: +98 24 33052530; fax: +98 24 33283203.
E-mail address: saadati@znu.ac.ir (F. Saadati).

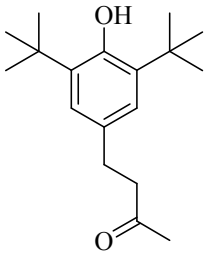
**Characterizations of products**

*4-(3-t-butyl-4-hydroxyphenyl)butan-2-one (**2a**)*



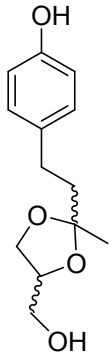

Yellow solid; mp: 77-80 ˚C; $^{1}$H-NMR (250 MHz, $CDCl_3$, $\delta$ /ppm): 7.08 (1H, s ), 6.88 (1H, d, *J*= 7.75 Hz), 6.67 (1H, d, *J*= 7.75 Hz ), 6.26 (1H, s ), 2.85 (2H, t, *J*= 6.75 Hz), 2.79 (2H, t, *J*=7.00 Hz), 2.19 (3H, s), 1.43 (9H, s); $^{13}$C NMR (62.9 MHz, $CDCl_3$, $\delta$ /ppm): 210.18, 153.19, 136.19, 131.92, 128.91, 126.39, 116.58, 45.75, 34.56, 30.11, 29.60, 28.92.
Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.33, H, 9.15 and O, 14.52. Found: C, 77.20, H, 9.20 and O, 13.60.

*4-(3,5-di-t-butyl-4-hydroxyphenyl)butan-2-one (**2b**)*



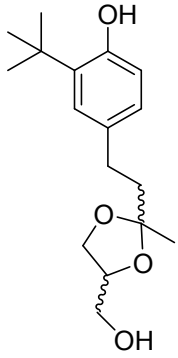

Yellow oil; $^{1}$H NMR (250 MHz, $CDCl_3$, $\delta$ /ppm): 6.97 (2H, s), 5.07 (1H, s), 2.79 (2H, t, *J*= 6.75 Hz), 2.75 (2H, t, *J*=7.00 Hz), 2.16 (3H, s), 1.43 (18H, s); $^{13}$C NMR (62.9 MHz, $CDCl_3$, $\delta$ /ppm): 208.41, 152.05, 135.96, 130.86, 124.76, 45.83, 34.29, 31.43, 30.31, 29.79.
Anal. Calcd. for $C_{18}H_{28}O_2$: C, 78.21, H, 10.21 and O, 11.58. Found: C, 78.2, H, 9.79 and O, 12.01.

*4-(2-(4-(hydroxymethyl)-2-methyl-1,3-dioxolan-2-yl)ethyl)phenol (**3a**)*



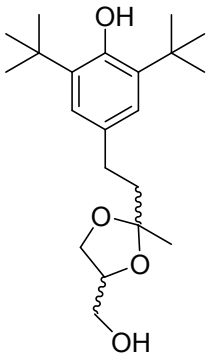

Colorless liquid; mixture of diastereomers, $^{1}$H NMR (250 MHz, $CDCl_3$, $\delta$ /ppm): 7.02 (2H, d, *J*=7.75 Hz), 6.74 (2H, d, *J*=7.75 Hz), 6.11 (1H, s), 4.29-4.23 (1H, m), 4.09-4.03 (1H, m), 3.83-3.79 (2H, m), 3.76-3.64 (1H, m), 2.68-2.58 (2H, m), 2.41 (1H, s), 2.13-1.93 (2H, m) 1.43 (3H, s). $^{13}$C NMR (62.9 MHz, $CDCl_3$, $\delta$ /ppm): 153.72, 134.01, 130.01, 129.31, 115.22, 110.78, 75.91, 65.80, 63.02, 62.86, 41.56, 40.91, 31.40, 29.66, 29.49, 29.15, 24.85, 23.72. Anal. Calcd. for $C_{13}H_{18}O_4$: C, 65.53, H, 7.61 and O, 26.86. Found: C, 65.8, H, 7.80 and O, 26.40.

*2-t-butyl-4-(2-(4-(hydroxymethyl)-2-methyl-1,3-dioxolan-2-yl)ethyl)phenol (**3b**)*




Colorless liquid; $^{1}$H NMR (250 MHz, $CDCl_3$, $\delta$ /ppm): 7.08 (1H, s), 6.86 (1H, d, *J*=7.50 Hz), 6.60 (1H, d, *J*=7.50 Hz), 6.00 (1H, s), 4.38-4.21 (1H, m), 4.14- 4.08 (1H, m), 3.82- 3.67 (3H, m), 2.64 (2H, t, *J*=6.62 Hz), 2.07 (1H,s), 1.98 (2H, t, *J*=6.50 Hz), 1.47 (3H, s), 1.40 (9H, s). $^{13}$C NMR (62.9 MHz, $CDCl_3$, $\delta$ /ppm): 152.77, 136.09, 133.10, 28.85, 126.98, 126.31, 116.38, 111.05, 110.84, 76.58, 75.98, 65.93, 63.06, 62.92, 41.67, 41.00, 34.54, 29.61, 29.50, 24.87, 23.79, 22.97. Anal. Calcd. for $C_{17}H_{26}O_4$: C, 69.36, H, 8.90 and O, 21.74. Found: C, 70.10, H, 9.00 and O, 20.90.

*2,6-di-t-butyl-4-(2-(4-(hydroxymethyl)-2-methyl-1,3-dioxolan-2-yl)ethyl)phenol (**3c**)*




Colorless liquid; $^{1}$H NMR (250 MHz, $CDCl_3$, $\delta$ /ppm): 7.00 (2H, s), 5.05 (1H, s), 4.32-4.21 (1H, m), 4.12-406 (1H, m), 3.87-3.77 (2H, m), 3.66-3.59 (1H, m), 2.65 (2H, t, $J$=9.50 Hz), 2.13 (1H,s), 1.98 (2H, t, $J$=9.00 Hz), 1.41 (18H, s), 1.39 (3H, s). $^{13}$C NMR (62.9 MHz, $CDCl_3$, $\delta$ /ppm): 151.84, 135.88, 132.37, 124.74, 110.87, 110.63, 76.72, 75.97, 65.89, 63.09, 62.88, 41.78, 41.14, 34.31, 31.43, 30.34, 29.91, 29.64, 29.68, 24.79, 23.78.

Anal. Calcd. for $C_{21}H_{34}O_4$: C, 71.96, H, 9.78 and O, 18.26. Found: C, 72.60, H, 10.10 and O, 17.30.

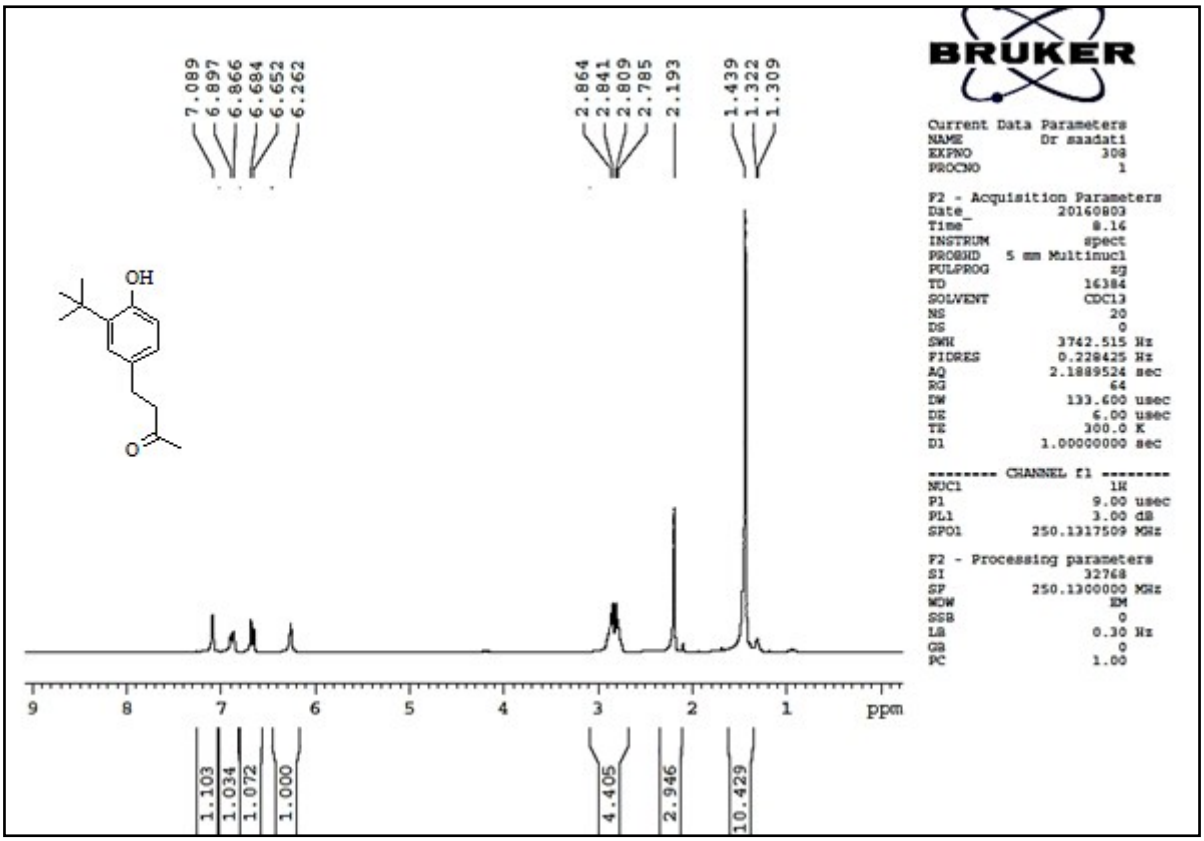



**Fig. S1.** [1]H NMR of 4-(3-*t*-butyl-4-hydroxyphenyl)butan-2-one (**2a**)

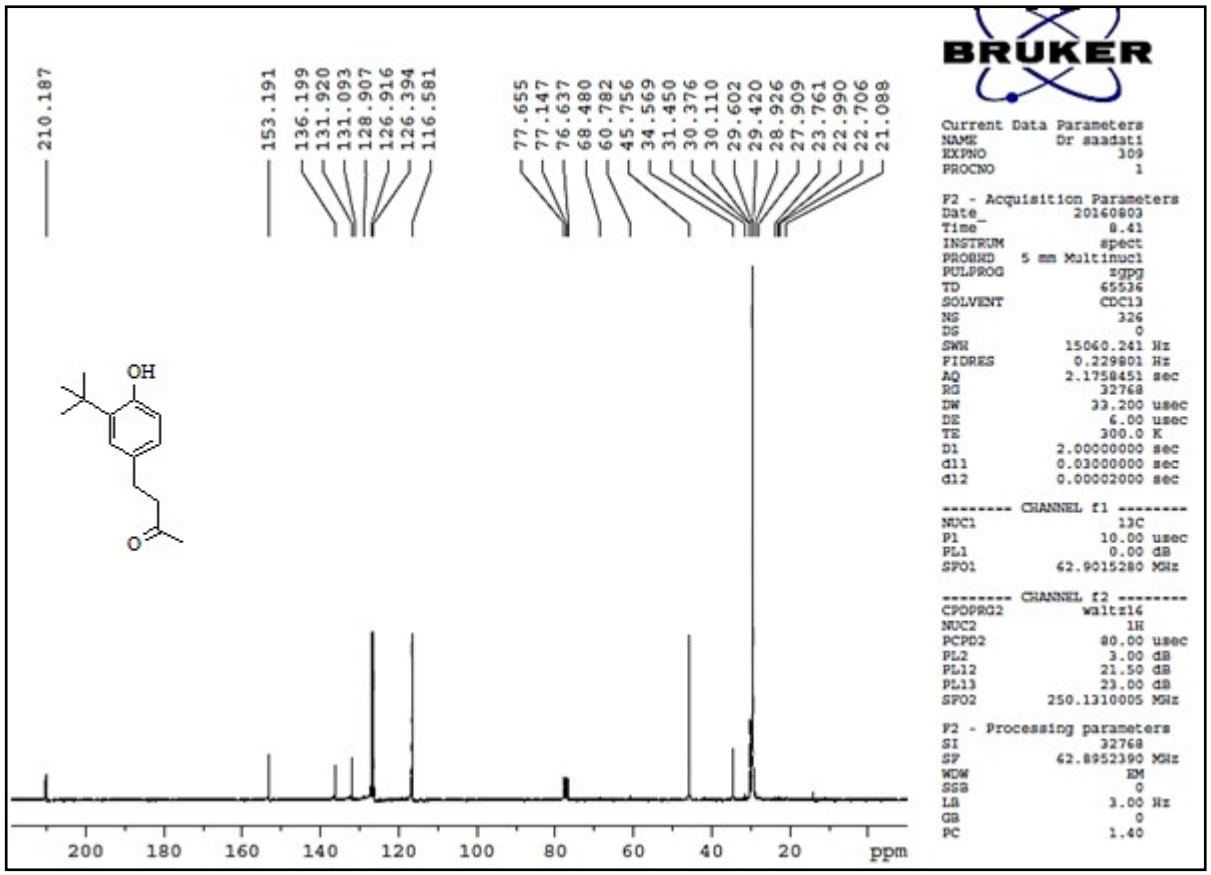



**Fig. S2.** $^{13}$C NMR of 4-(3-*t*-butyl-4-hydroxyphenyl)butan-2-one (**2a**)

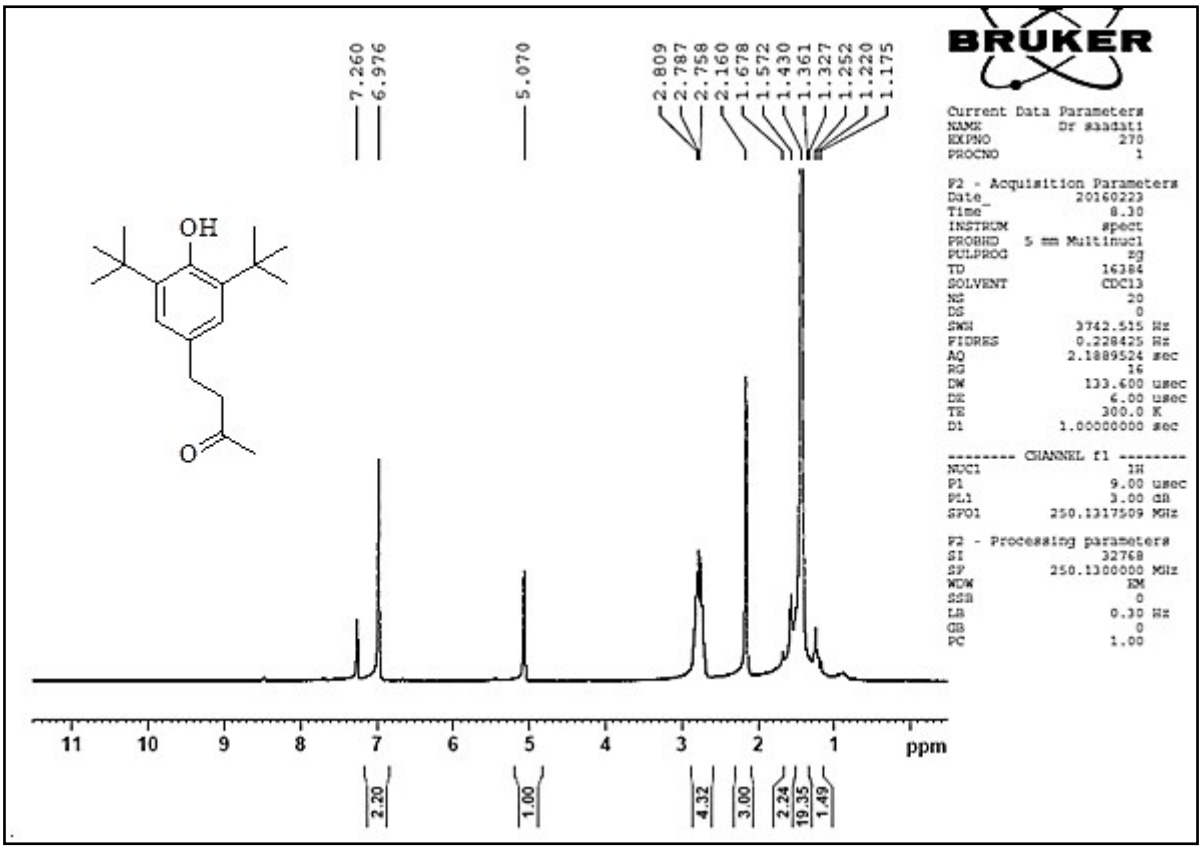



**Fig. S3.** $^{1}$H NMR of 4-(3,5-di-*t*-butyl-4-hydroxyphenyl)butan-2-one (**2b**)

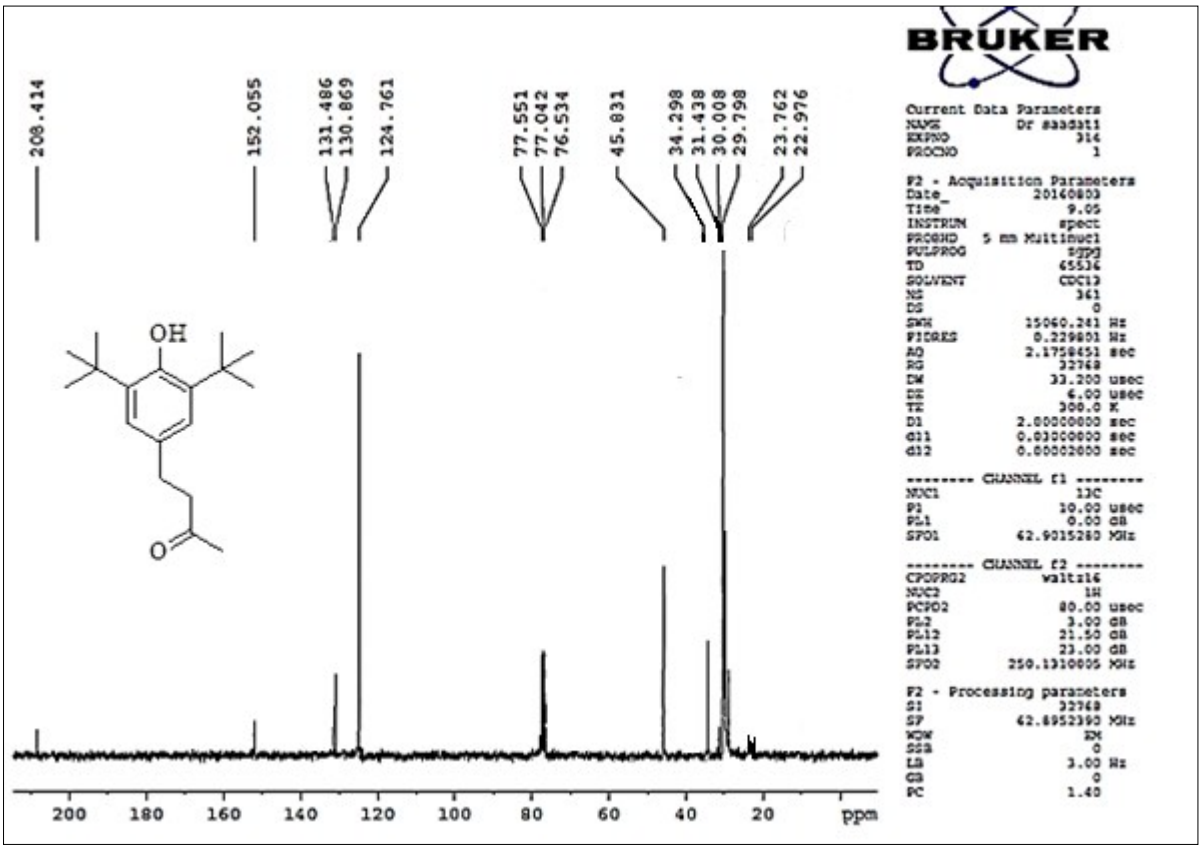



**Fig. S4.** $^{13}$C NMR of 4-(3,5-di-*t*-butyl-4-hydroxyphenyl)butan-2-one (**2b**)

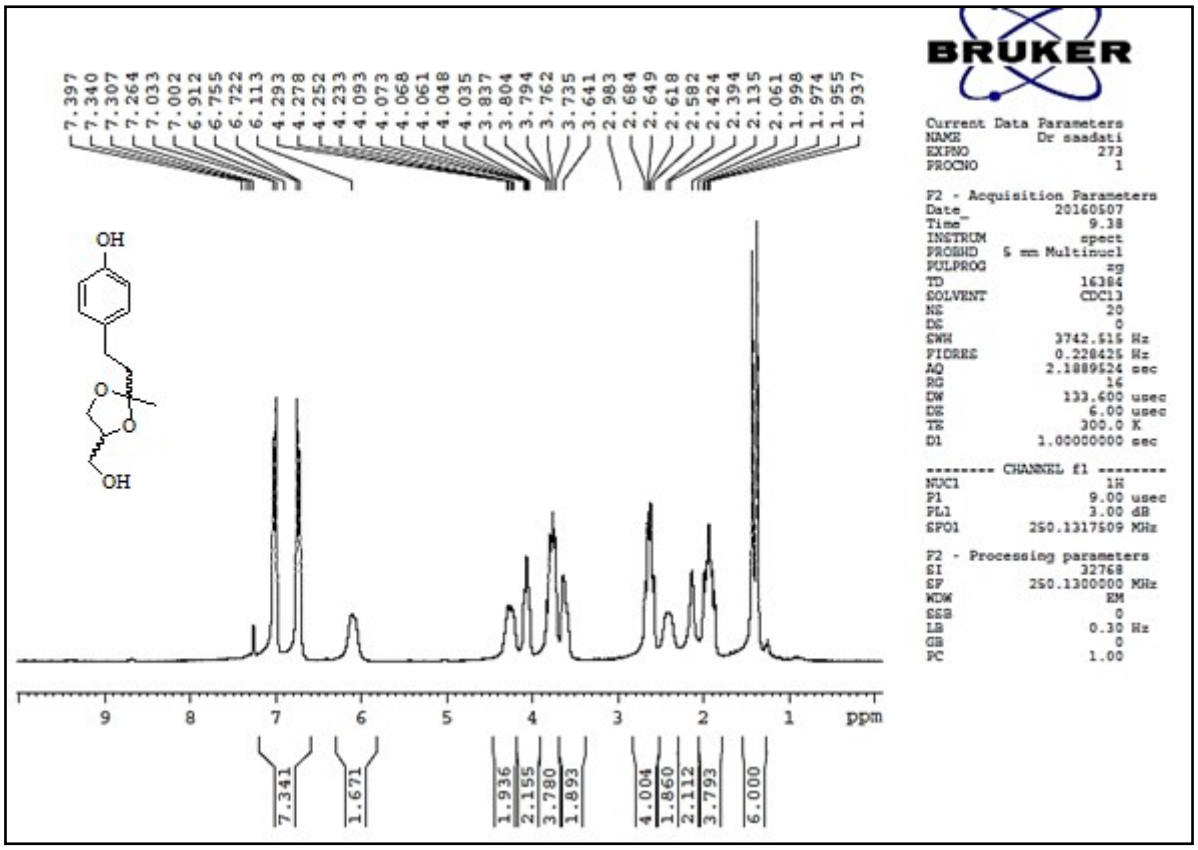



**Fig. S5.** $^{1}$H NMR of 4-(2-(4-(hydroxymethyl)-2-methyl-1,3-dioxolan-2-yl)ethyl)phenol (**3a**)

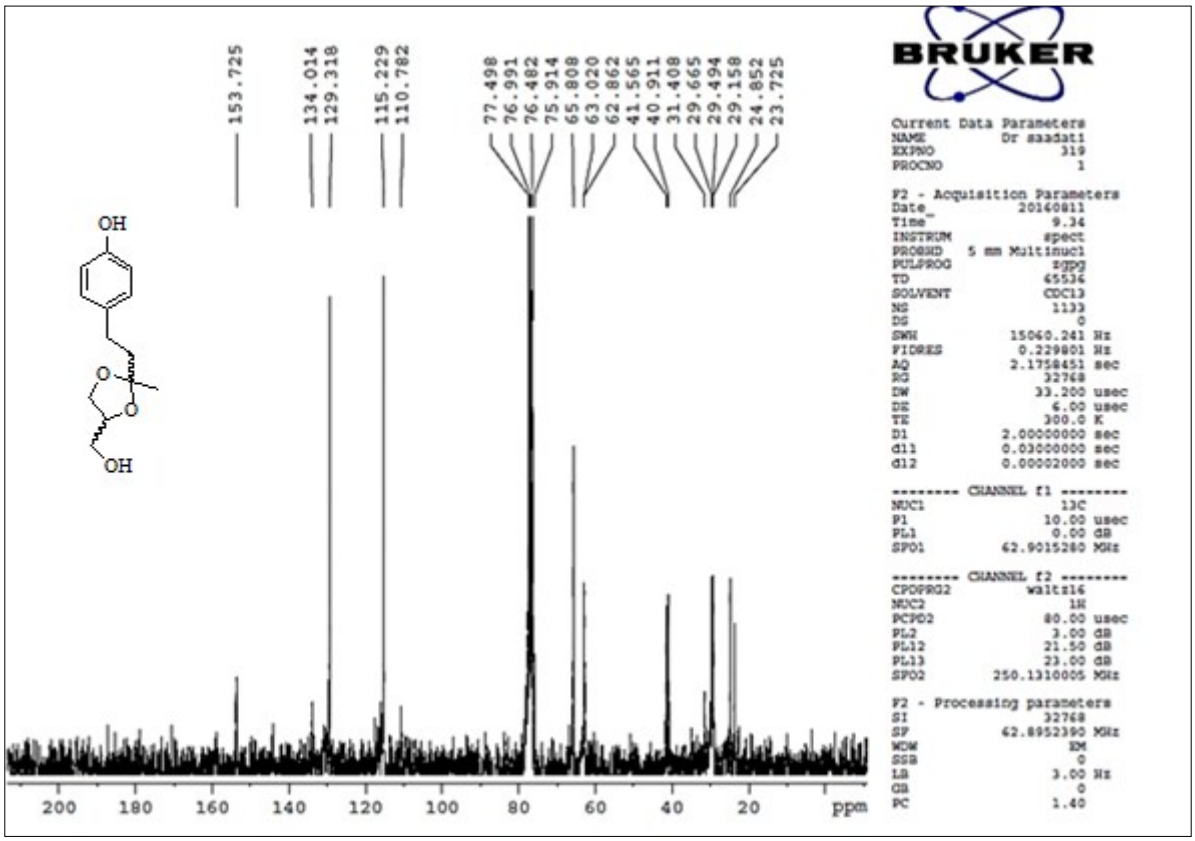



**Fig. S6.** $^{13}$C NMR of 4-(2-(4-(hydroxymethyl)-2-methyl-1,3-dioxolan-2-yl)ethyl)phenol (**3a**)

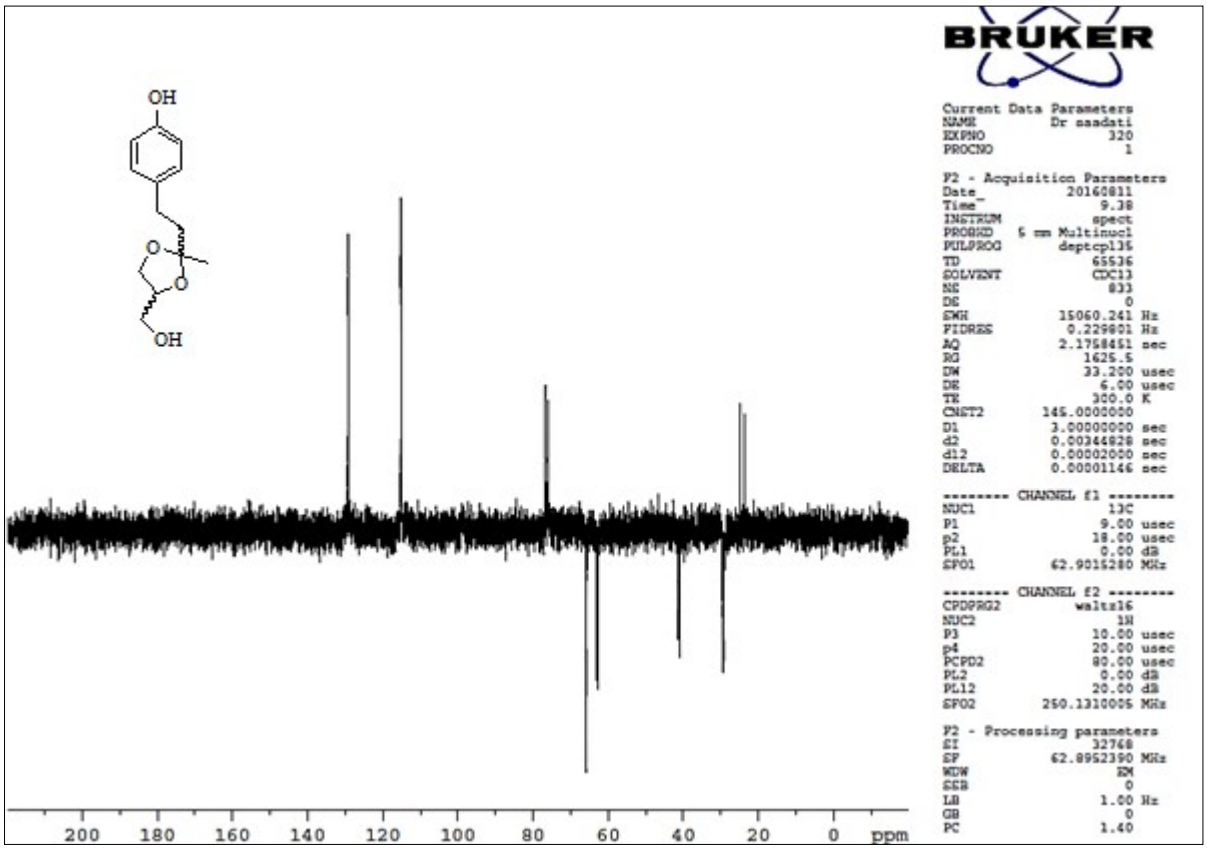



**Fig. S7.** DEPT 135 of 4-(2-(4-(hydroxymethyl)-2-methyl-1,3-dioxolan-2-yl)ethyl)phenol (**3a**)

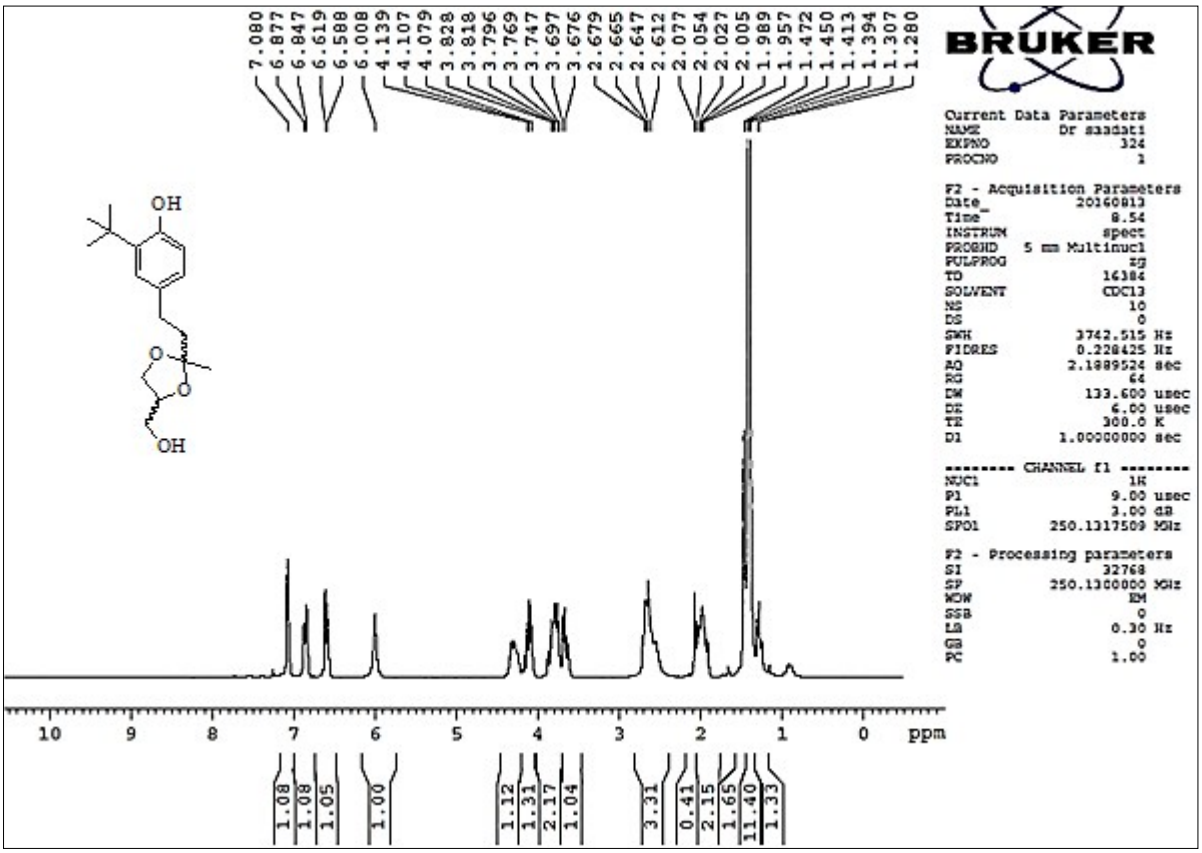



**Fig. S8.** $^{1}$H NMR of 2-*t*-butyl-4-(2-(4-(hydroxymethyl)-2-methyl-1,3-dioxolan-2-yl)ethyl)phenol (**3b**)

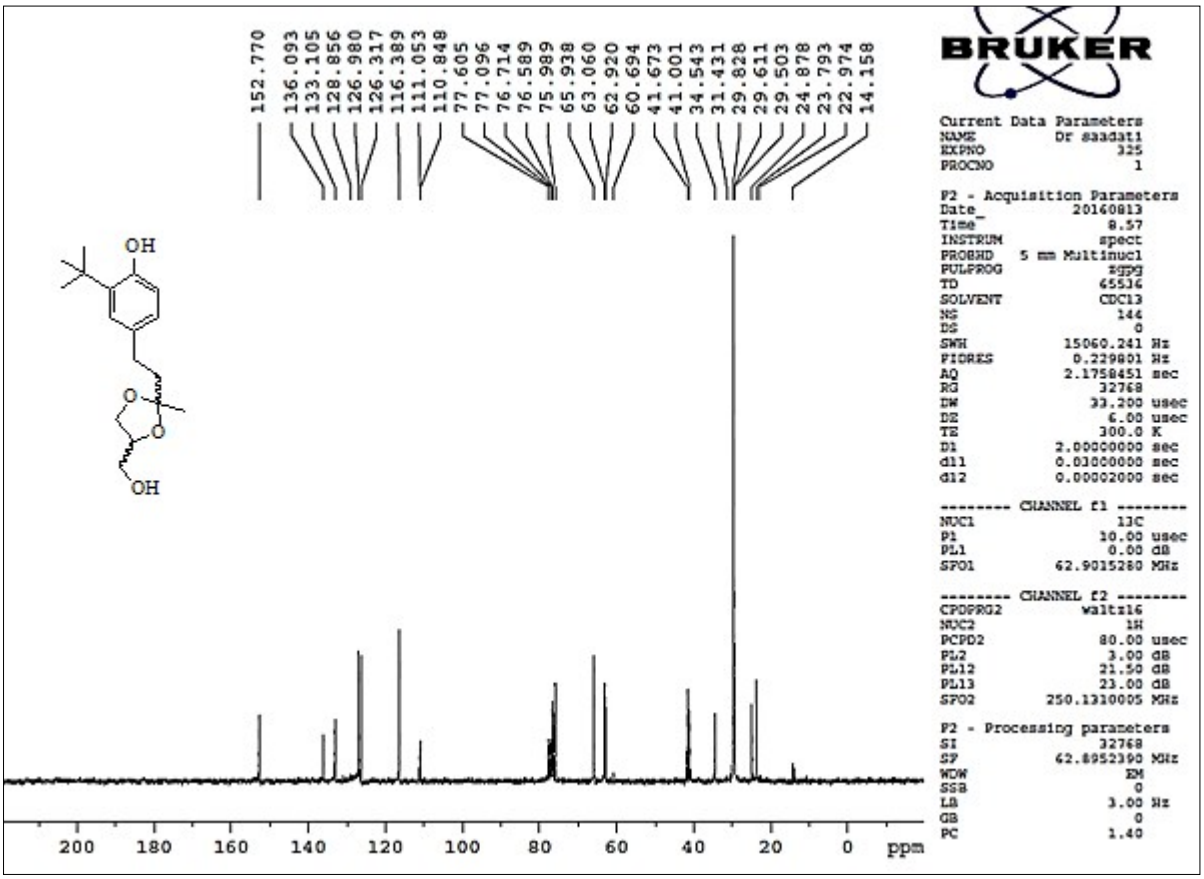



**Fig. S9.** $^{13}$C NMR of 2-*t*-butyl-4-(2-(4-(hydroxymethyl)-2-methyl-1,3-dioxolan-2-yl)ethyl)phenol (**3b**)

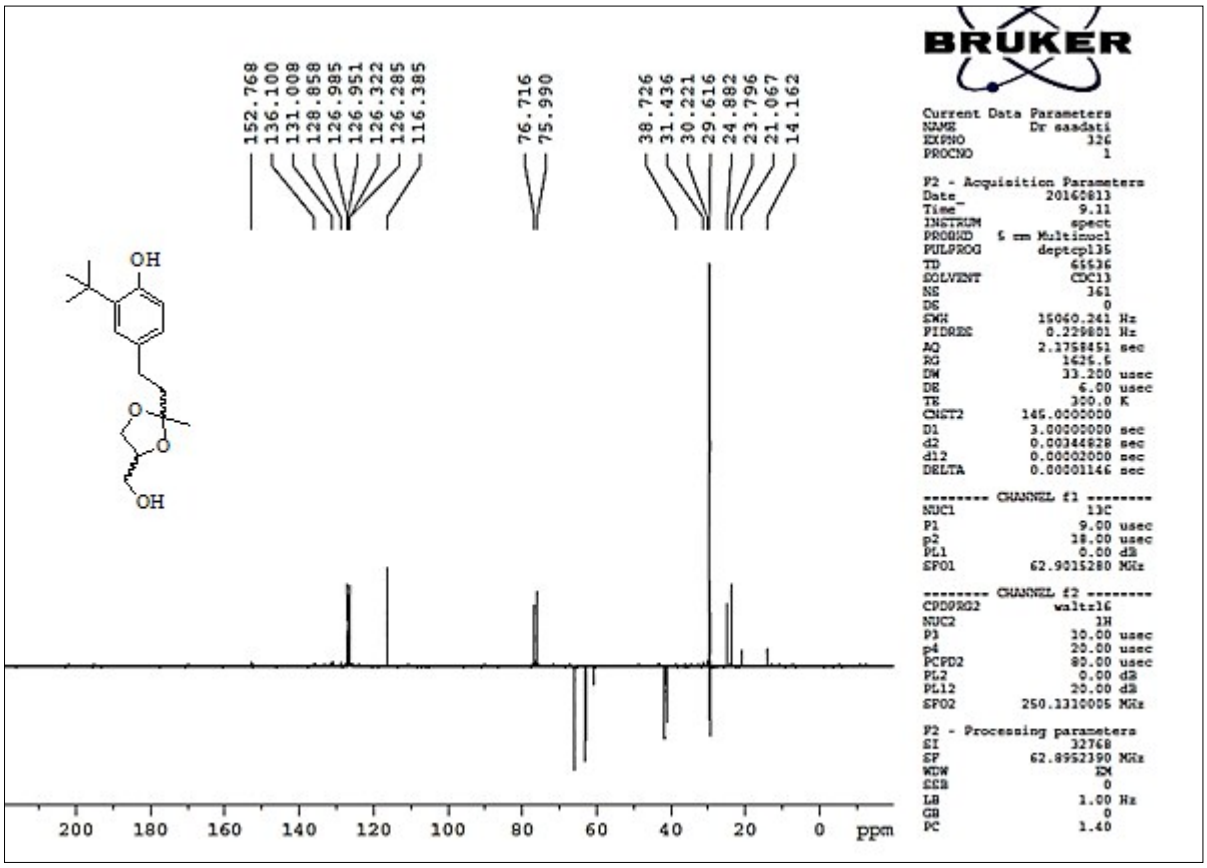



**Fig. S10.** DEPT 135 of 2-*t*-butyl-4-(2-(4-(hydroxymethyl)-2-methyl-1,3-dioxolan-2-yl)ethyl)phenol (**3b**)

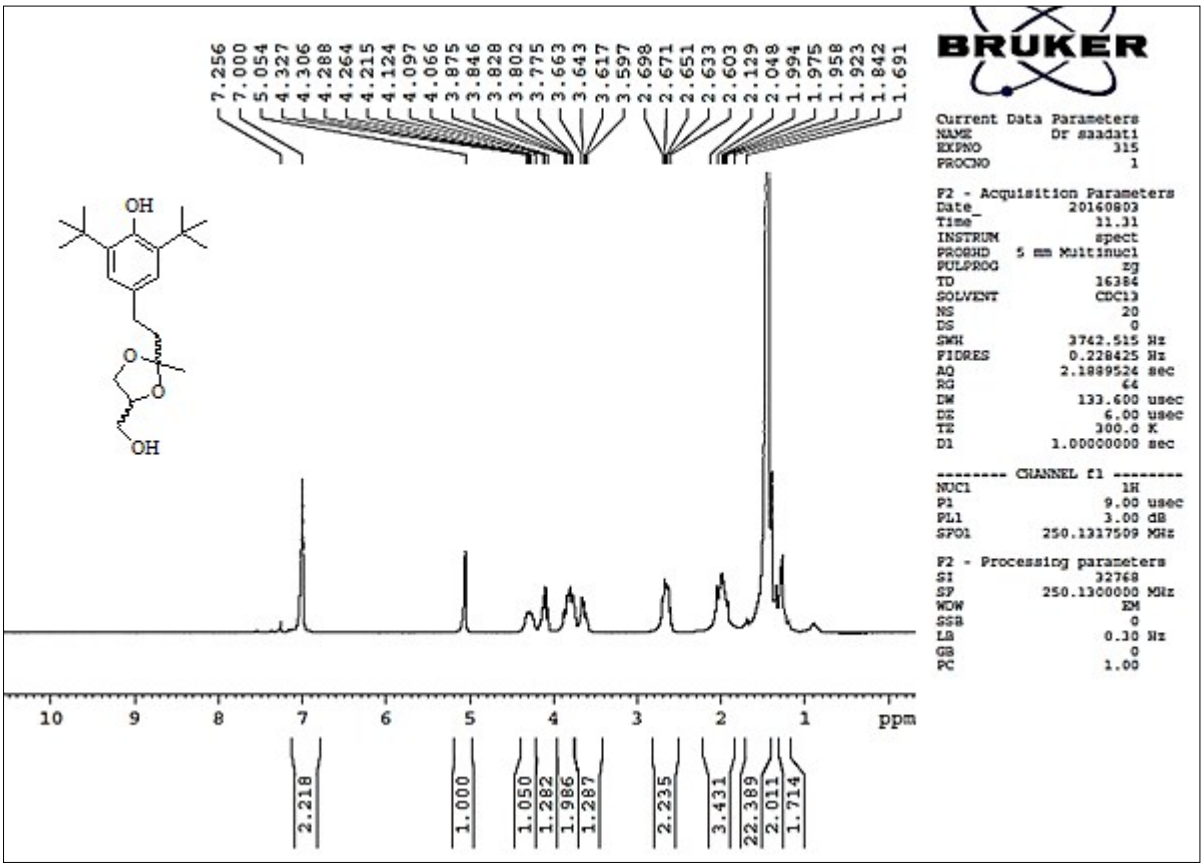



**Fig. S11.** [1]H NMR of 2,6-di-*t*-butyl-4-(2-(4-(hydroxymethyl)-2-methyl-1,3-dioxolan-2-yl)ethyl)phenol (**3c**)

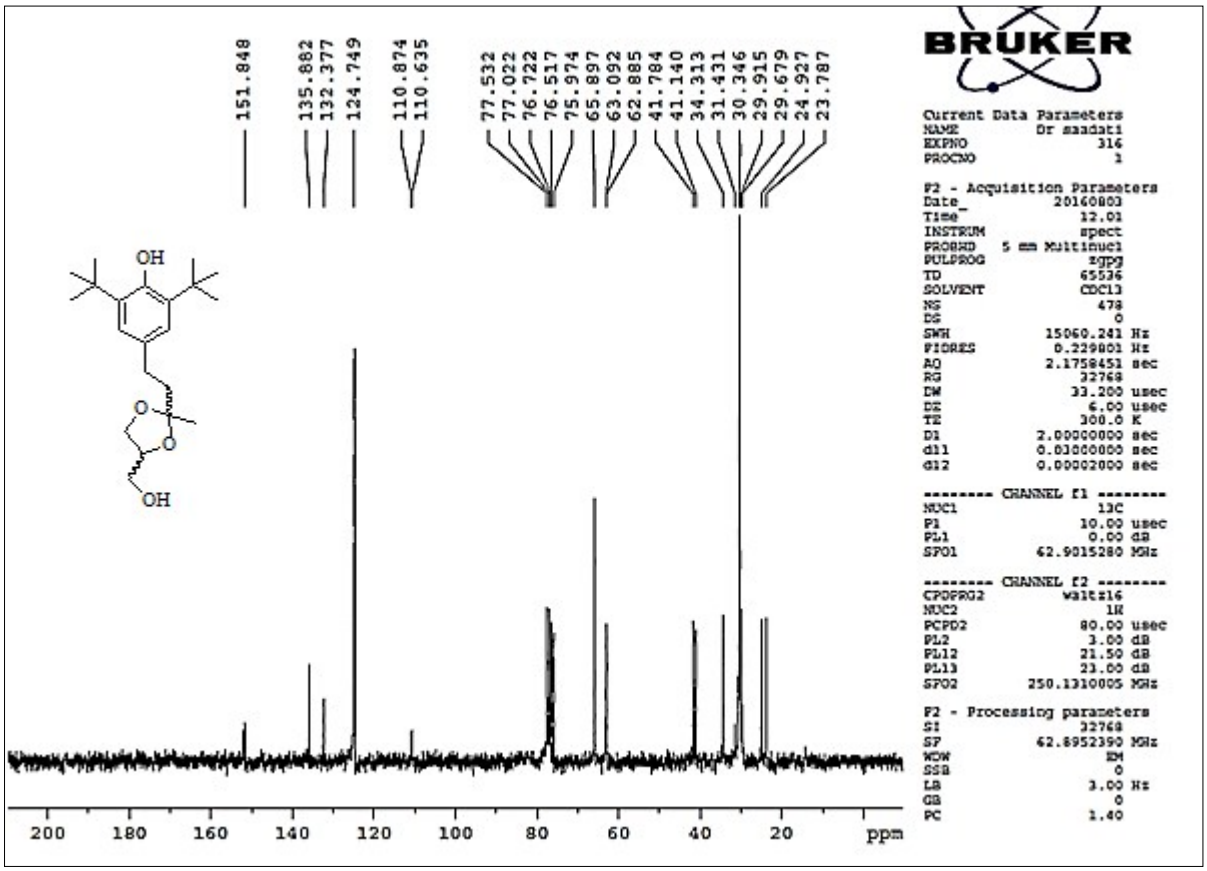



**Fig. S12.** $^{13}$C NMR of 2,6-di-*t*-butyl-4-(2-(4-(hydroxymethyl)-2-methyl-1,3-dioxolan-2-yl)ethyl)phenol (**3c**)

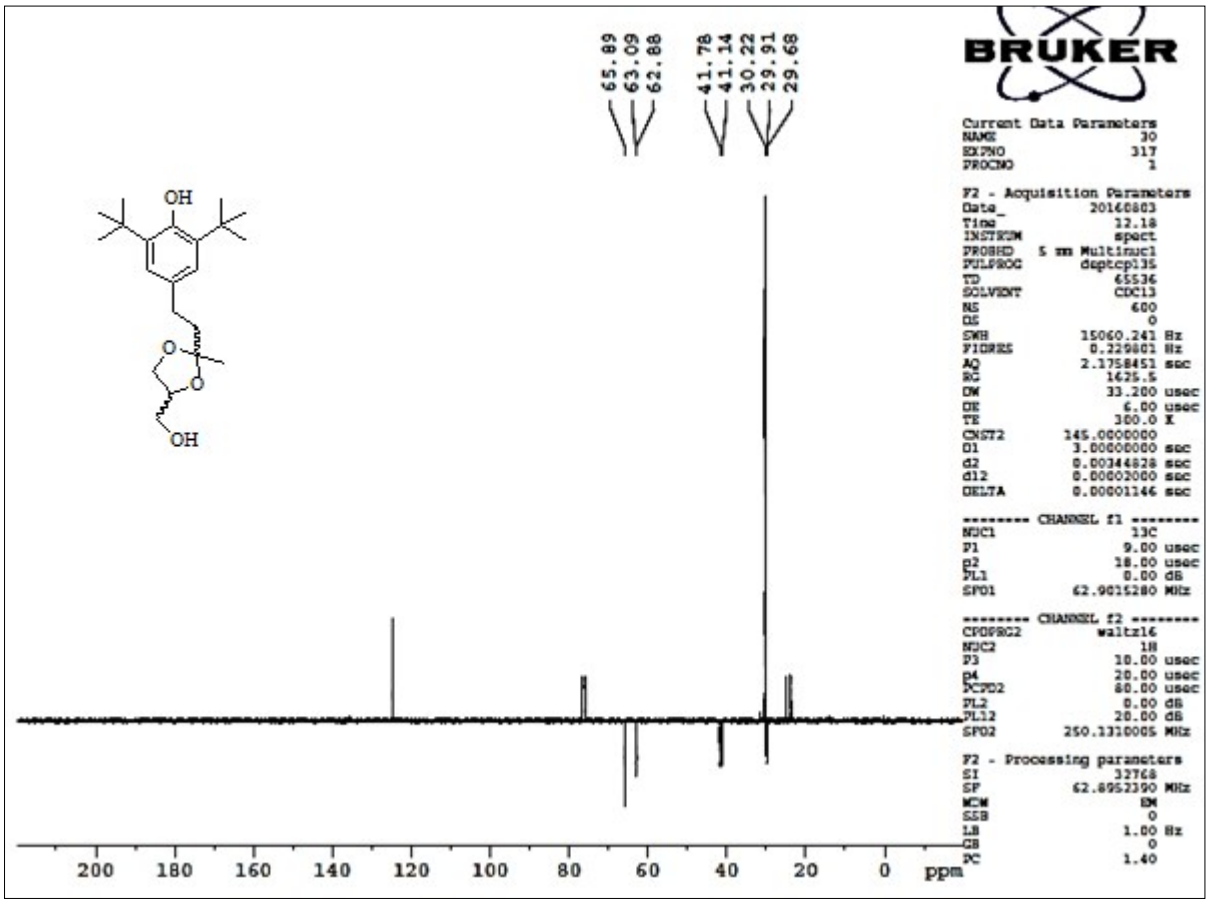



**Fig. S13.** DEPT135 of 2,6-di-*t*-butyl-4-(2-(4-(hydroxymethyl)-2-methyl-1,3-dioxolan-2-yl)ethyl)phenol (**3c**)