Supporting Information

for

Heterogeneous acidic catalysts for the tetrahydropyranylation of alcohols and phenols in green ethereal solvents

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Full experimental details, copies of IR spectra of fresh and recycled $NH_4HSO_4@SiO_2$ and copies of ^1H and ^{13}C NMR spectra

General Information. All reagents and solvents were purchased from commercial suppliers and used without further purification, unless otherwise indicated. $H_2SO_4@SiO_2$ (25 wt %) was prepared as described in ref. [1]. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with a Bruker Ascend 400 spectrometer in $CDCl_3$ solutions with $SiMe_4$ as internal standard. The FTIR spectra were recorded from KBr pellets on a Fourier Transform Infrared Spectrophotometer

on a Jasco FT/IR-480 Plus. Gas chromatographic analyses were recorded on a Agilent 6890N Network GC System. The HRMS spectra were acquired on a Thermo Finnigan Q Exactive instrument with API-HESI source. Samples were introduced as 0.1 mg/L solutions in MS grade methanol with a 5 µL/min flow and the following source parameters: positive polarity; Sheath gas flow rate: 5 a.u.; Aux gas flow rate: 3 a.u.; Sweep gas flow rate: 0 a.u.; Spray voltage: 3.50 kV; Capillary temperature: 250 °C; S-lens RF level: 60,0 V; Aux gas heater temperature: 0 °C.

Preparation of the NH_4HSO_4@SiO_2 catalyst. *Preparation of NH_4HSO_4@SiO_2*

NH_4HSO_4@SiO_2 (25wt %) was prepared by wet impregnation. 17.4 g of SiO_2 (column chromatographic grade, 60 Å, 200–400 mesh) were added to a stirred solution of 5.8 g (50 mmol) of NH_4HSO_4 dissolved in 30 mL of H_2O, and the suspension was stirred at 50 °C during 1 h, followed by solvent evaporation under reduced pressure. The resulting white powder was dried at 120 °C for 48 h, then transferred and stored in a desiccator over $CaCl_2$. IR (cm^{-1}): 3448, 3172, 1641, 1507, 1400, 1190, 1098, 971, 879, 600.

General procedure: Tetrahydropyranylation reactions were carried out in a round bottom flask equipped with a reflux condenser, a $CaCl_2$ tube and a magnetic stirring bar. To a solution of 1.0×10^{-2} mol of compound **1** in 2.5 mL of the solvent (CPME or 2-MeTHF) were added 1.1×10^{-2} mol (0.93 g, 1.0 mL) of 2,3-dihydropyran (**2**) and the required amount of the catalyst (3.3×10^{-4} or 3.3×10^{-5} mol; see Table 1 and Schemes 1 and 2). The resulting mixtures were vigorously stirred for the reported time at the reported temperature (Table 1 and Schemes 1 and 2). The crude mixtures were filtered, the solvent evaporated and the crude product analyzed by ^{1}H-NMR spectroscopy to determine the conversion of compound **1**, then purified and characterized as reported below.

2-(Phenylethoxy)tetrahydro-2*H*-pyran (3a) [2]**.** Pale yellow oil, purified by flash chromatography, (AcOEt/Petroleum Ether/Et_3N = 3/7/0.1, R_f = 0.56); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.46-1.95 (m, 6H), 2.95 (t, *J* = 7.2 Hz, 2H), 3.42-3.48 (m, 1H), 3.63 (q, *J* = 8.0 Hz, 1H), 3.74-3.81 (m, 1H), 3.96 (q, *J* = 8.0 Hz, 1H), 4.63 (bs, 1H), 7.18-7.32 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 25.4, 30.7, 36.4, 62.1, 68.3, 98.7, 126.1, 128.2, 129.0, 139.1.

2-(6-Chlorohexyloxy)tetrahydro-2*H*-pyran (3b) [3,4]**.** Pale yellow oil, purified by fractional distillation, bp 115 °C/ 1Torr, Lit. bp 107 °C/0.25 Torr [4]; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.35-1.90 (14H, m), 3.36-3.42 (1H, m), 3.45-3.56 (3 H, m), 3.70-3.78 (1H, m), 3.84-3.90 (1H, m), 4.57 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.7, 25.5, 25.6, 26.7, 29.6, 30.8, 32.6, 45.0, 62.4, 67.4, 98.9.

2-(11-Bromoundecyloxy)tetrahydro-2*H*-pyran (3c) [5]**.** Colourless oil, purified by flash chromatography, (AcOEt/Petroleum Ether/Et_3N = 0.5/9.5/0.1, R_f= 0.52); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.28-1.46 (m, 14H), 1.47-1.64 (m, 6H), 1.65-1.76 (m, 1H), 1.78-1.90 (m, 3H), 3.34-3.43 (m. 3H), 3.48-3.52 (m, 1H), 3.73 (q, 1H, *J* = 7.6 Hz), 3.83-3.90 (m, 1H), 4.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.7,19.7, 25.5, 26.2, 28.1, 28.7, 29.4, 29.4, 29.5, 29.7, 30.8, 32.8, 34.0, 62.3, 67.7, 98.8.

2-(4-Chlorobenzyloxy)tetrahydro-2*H*-pyran (3d) [2]. Colourless oil, purified by flash chromatography, (AcOEt/Petroleum Ether/Et_3N = 3/7/0.1, R_f = 0.58); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.50-1.67 (4H, m), 1.68-1.77 (1H, m), 1.80-1.93 (1H, m), 3.50-3.58 (1H, m), 3.90 (1H, t, *J* = 9.6 Hz), 4.48 (1H, d, *J* = 12.0 Hz), 4.69 (1H, bs), 4.75 (1H, d, *J* = 12.0 Hz), 7.31 (4H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3, 25.4, 30.5, 62.1, 67.9, 97.7, 128.4, 129.0, 133.1, 136.8.

2-(4-Bromobenzyloxy)tetrahydro-2*H*-pyran (3e) [6]. Colourless oil, purified by flash chromatography, (AcOEt/Petroleum Ether/Et_3N = 3/7/0.1, R_f = 0.61); ^{1}H-NMR (400

MHz, $CDCl_3$) δ 1.51-1.72 (4H, m), 1.72-1.82 (1H, m), 1.83-1.95 (1H, m), 3.53-3.62 (1H, m), 3.88-3.97 (1H, m), 4.49 (1H, d, *J* = 12.4 Hz), 4.69 (1H, t, *J* = 3.2 Hz), 4.75 (1H, d, *J* = 12.4 Hz), 7.26-7.29 (2H, m), 7.50-7.52 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3, 25.4, 30.5, 62.1, 68.0, 97.7, 121.3, 129.4, 131.4, 137.3.

Methyl 4-[(tetrahydro-2*H*-pyran-2-yl)oxymethyl]benzoate (3f) [7]. Colourless oil, purified by flash chromatography, (AcOEt/Petroleum Ether/Et_3N = 2/8/0.1, R_f = 0.48); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.42-2.00 (6H, m), 3.52-3.58 (1H, m), 3.87-3.99 (1H, m), 3.91 (3H, s), 4.56 (1H, d, *J* = 13.2 Hz), 4.72 (1H, bs), 4.84 (1H, d, *J* = 13.2 Hz) 1 H 7.42-7.44 (2 H, m), 8.01-8.03 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 19.4, 25.5, 30.6, 52.2, 62.3, 68.3, 76.8, 77.2, 77.5, 98.1, 127.3, 129.3, 129.8, 143.8, 167.1.

2-(4-Methoxybenzyloxy)tetrahydro-2*H*-pyran (3g) [8]. Colourless oil, purified by flash chromatography, (AcOEt/Petroleum Ether/Et_3N = 2/8/0.1, R_f = 0.53); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.48-1.66 (4H, m), 1.67-1.77 (1H, m), 1.80-1.89 (1H, m), 3.50-3.58 (1H, m), 3.81 (3H, s), 3.88-3.96 (1H, m), 4.44 (1H, d, *J* = 11.6 Hz), 4.69 (1H, t, *J* = 3.6 Hz), 4.73 (1H, d, *J* = 11.6 Hz), 6.86-6.90 (2H, m), 7.27-7.32 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 25.5, 30.6, 55.2, 62.1, 68.4, 97.4, 113.7, 129.4, 130.3, 159.1.

2-(2-Phenylpropoxy)tetrahydro-2*H*-pyran (3h) [9]**.** Colourless oil, 1:1 mixture of diastereoisomers, purified by flash chromatography (AcOEt/Petroleum Ether/Et_3N = 3/7/0.1, R_f = 0.60); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.31 (1.5H, d *J* = 5.2 Hz), 1.33 (1.5 H, d, *J* = 5.2 Hz), 1.42-1.76 (6H, m), 3.04 (1H, sex, *J* = 6.8 Hz), 3.37-3.54 (2H, m), 3.63 (0.5H, m), 3.73-3.89 (1.5H, m), 4.53 (0.5H, t, *J* = 3.6 Hz), 4.59 (0.5H, t, *J* = 3.6 Hz), 7.16-7.32 (5H, m) (fractional integrals due to the presence of two diastereomers); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.3, 18.4, 19.3, 19.4, 25.5, 25.5, 30.6,

40.0, 40.0, 61.9, 62.0, 73.0, 73.2, 98.5, 98.8, 126.2, 126.2, 127.4, 127.4, 128.2, 128.2, 144.5, 144.6.

2-[(1*R*,2*S*,5*R*)-5-Methyl-2-(1-methylethyl)cyclohexyloxy]tetrahydro-2*H*-pyran (3i) [10,11]**.** Colourless oil, 1:1 mixture of diastereoisomers, purified by fractional distillation, bp 132 °C/ 1 Torr, Lit. bp 100 °C/ 5 Torr [11]; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.77 (1.5 H, d, *J* = 6.8 Hz), 0.80 (1,5H, d, *J* = 7.6 Hz), 0.81-1.11 (8,5H, m), 1.18-1.30 (0.5H, m), 1.30-1.90 (9.5H, m), 2.03-2.19 (1.5H, m), 2.35 (0.5H, pentd, *J* = 10.8, 2.4 Hz), 3.31 (0.5H, td, *J* = 10.8, 4.4 Hz), 3.43-3.53 (1.5H, m), 3.84-3.92 (0.5H, m), 3.93-4.00 (0.5H, m), 4.57-4.61 (0.5H, m), 4.77-4.81 (0.5H, m) (fractional integrals due to the presence of two diastereomers); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 16.3, 19.7, 20.3, 21.2, 21.2, 22.2, 22.4, 23.0, 23.3, 25.2, 25.5, 25.6, 25.6, 31.2, 31.3, 31.4, 31.8, 34.4, 34.6, 40.1, 43.6, 48.1, 48.9, 62.4, 63.0, 74.1, 79.9, 94.3, 101.3.

2-[(1-Ethenyl-1,5-dimethyl-4-hexen-1-yl)oxy]tetrahydro-2*H*-pyran (3j) [12,13]. Colourless oil, 1:1 mixture of diastereoisomers, purified by fractional distillation, bp 110-115 °C/ 1Torr, Lit. bp 80-83 °C/0.04 Torr [13]; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.27 (1.5H, s), 1.32 (1.5H, s), 1.46-1.71 (6H, m) 1.78-2.11 (3H, m), 3.39-3.48 (1H, m), 3.91-3.99 (1H, m), 4.62-4.68 (1.5H, m), 5.07-5.19 (2.5H, m), 5.80 (0.5H, dd, *J* = 17.2, 11.6 Hz), 5.95 (0.5H, dd, *J* = 17.6, 10.8 Hz) (fractional integrals due to the presence of two diastereomers); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.5, 20.5, 20.6, 22.5, 22.6, 22.8, 23.5, 25.4, 25.5, 25.6, 32.2, 32.4, 40.2, 41.7, 63.0, 63.2, 78.4, 78.6, 94.1, 94.5, 113.4, 114.3, 124.6, 131.2, 143.2, 143.6.

4-[4-[(Tetrahydro-2*H*-pyran-2-yl)oxy]phenyl]butan-2-one (3k) [14]**.** Colourless oil, purified by aqueous basic work up; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.57-1.66 (3H, m), 1.84-1.88 (2H, m), 1.97-2.02 (1H, m), 2.71 (2H, t, *J* = 7.2 Hz), 2.83 (2H, t, *J* = 7.2 Hz), 3.54-3.64 (1H, m), 3.90 (1H, t, *J* = 10.4 Hz), 5.36 (1H, bs), 6.95-6.97 (2H, m), 7.07-

7.09 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.8, 25.2, 28.9, 30.0, 30.3, 45.3, 62.0, 96.4, 116.5, 129.1, 133.9, 155.4, 208.0.

2-(4-*tert*-Butylphenoxy)tetrahydro-2*H*-pyran (3l) [15,16]**.** Colourless oil, purified by aqueous basic work up; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.30 (9H, s), 1.56-1.74 (3H, m) 1.82-1.88 (2H, m), 1.96-2.08 (1H, m), 3.56-3.64 (1H, m), 3.89-3.98 (1H, m), 5.39 (t, 1 H, *J* = 3.2 Hz), 6.96-7.00 (2H, m), 7.28-7.32 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.9, 25.3, 30.5, 31.5, 34.1, 62.0, 96.5, 115.9, 126.1, 144.2, 154.8.

One-pot two-step synthesis of 3-[4-(tetrahydro-2*H*-pyran-2-yl)oxymethylphenyl]-3-pentanol (4fa). THP ether **3f** was prepared according to the general procedure by reacting 4-carboxymethylbenzyl alcohol **1f** (0.84 g, 5.0 mmol) with DHP (0.5 mL, 0.46 g, 5.5 mmol) under dry Ar in a two-necked flask equipped with reflux condenser and magnetic stirrer in dry 2-MeTHF (1.2 mL, distilled from Na/K alloy under dry Ar) in the presence of 3 mol ‰ of NH_4HSO_4@SiO_2 (1.5×10^{-5} mol of NH_4HSO_4, 25 wt %, 7.0 mg). After 4 h stirring at rt, the reaction mixture was filtered under dry Ar and dropwise added to a 2.5 M solution of EtMgBr in dry 2-MeTHF (5.0 mL, 2.5 equiv). The resulting mixture was stirred at reflux during 2 h, chilled at 0 °C, then quenched by slow dropwise addition of sat. NH_4Cl (37.5 mL). The organic phase was separated, the aqueous phase extracted with 2-MeTHF (2 × 10 mL) and the reunited organic phases were washed with sat. NH_4Cl (3 × 10 mL), H_2O (10 mL), dry (Na_2SO_4), filtered and evaporated to afford a colourless oil which was purified by flash chromatography, (AcOEt/Petroleum Ether/Et_3N = 4/6/0.1, R_f = 0.61); HRMS (ESI) m/z: calc per $C_{17}H_{26}O_3K^+$ = 317.15135 $[M^+K]^+$, found 317.15161; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.76 (6H, t, *J* = 7.4 Hz), 1.50-1.94 (11H, m), 3.52-3.60 (1H, m), 3.89-3.97 (1H, m), 4.49 (1H, d, *J* = 12.0 Hz), 4.72 (1H, t, *J* = 3.2 Hz), 4.79

(1H, d, *J* = 12.0 Hz), 7.31-7.37 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.7, 19.3, 25.4, 30.5, 34.9, 62.0, 68.6, 77.2, 97.7, 125.5, 127.4, 136.1, 145.1.

One-pot two-steps synthesis of 4-(tetrahydro-2H-pyran-2-yloxymethyl)benzyl alcohol (4fb) [17]**.** THP ether **3f** was prepared as described in the preceding paragraph in dry CMPE (1.2 mL, distilled from Na/K alloy under dry Ar). Once filtered under dry Ar, it was diluted to 8.0 mL with dry CPME and added dropwise to a vigorously stirred suspension of $LiAlH_4$ (0.59 g, 15,5 mmol) in dry CPME (4 mL) at 0 °C. The reaction mixture was stirred during 24 hours at rt, then chilled to 0 °C and slowly quenched by dropwise addition of 20 mL of water (caution!). The resulting mixture was acidified with concentrated HCl (2.0 mL) and extracted with CPME (4 × 20 mL). The organic phases were collected, dried over K_2CO_3 and the solvent removed in vacuo to afford 2.31 g (10.4 mmol, yield 95%) of **4fb** as an oil that solidified upon standing at -18 °C. The compound was sufficiently pure for spectroscopic analysis.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.48-1.79 (6H, m) 1.81-1.93 (1H, m), 3.52-3.59 (1H, m), 3.88-3.97 (1H, m), 4.51 (1H, d, *J* = 12.0 Hz), 4.68-4.72 (3H, m), 4.78 (1H, d, *J* = 12.0 Hz), 7.33-7.39 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) 19.1, 25.2, 30.3, 61.9, 64.5, 64.4, 97.4, 126.8, 127.8, 137.2, 140.3.

Deprotection of 2-[(1*R*,2*S*,5*R*)-5-methyl-2-(1-methylethyl)cyclohexyloxy]tetrahydro-2*H*-pyran (3i). To a stirred solution of **3i** (1.00 g, 4.2 mmol) in CH_3OH (10 mL) was added H_2SO_4@SiO_2 (25 wt %, 49 mg, 1.3 × 10^{-4} mol, 3 mol %), and the resulting mixture was stirred at room temperature. After 4 h, H_2O (15 mL) was added and CH_3OH was removed on a rotary evaporator. The resulting mixture was extracted with AcOEt (3 × 5 mL), and the organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL), H_2O (10 mL), dried (Na_2SO_4), and concentrated on a rotary evaporator to yield crude (−)-menthol (**1j**, 0.620 g, 4.0 ×

10^{-3}, 95%) which, without purification, was characterized as following [18,19]: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.81 (3h, d, *J* = 7.2 Hz), 0-84-1.03 (8H, m), 1.07-1.15 (1H, m), 1.26-1.32 (1H, d, *J* = 8.8 Hz), 1.35-1.49 (1H, m), 1.58-1.70 (2H, m), 1.93-2.00 (1H, m), 2.17 (1H, eptd, *J* = 6.8, 2.8 Hz), 3.41 (1H, td, *J* = 10.4, 4.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 16.0, 21.0, 22.2, 23.1, 25.8, 31.6, 34.5, 45.0, 50.1, 71.4.

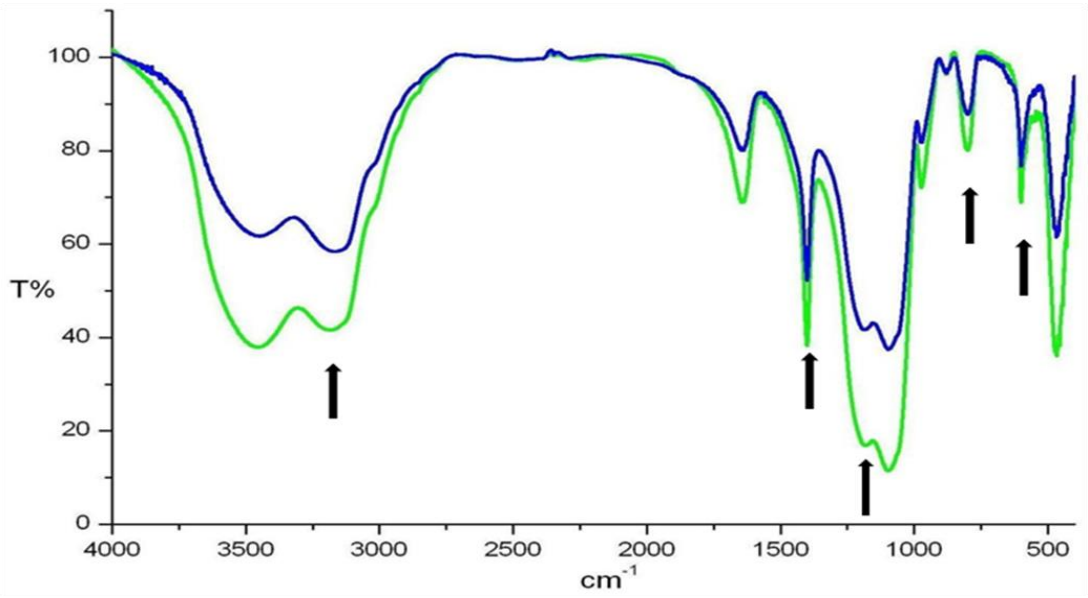
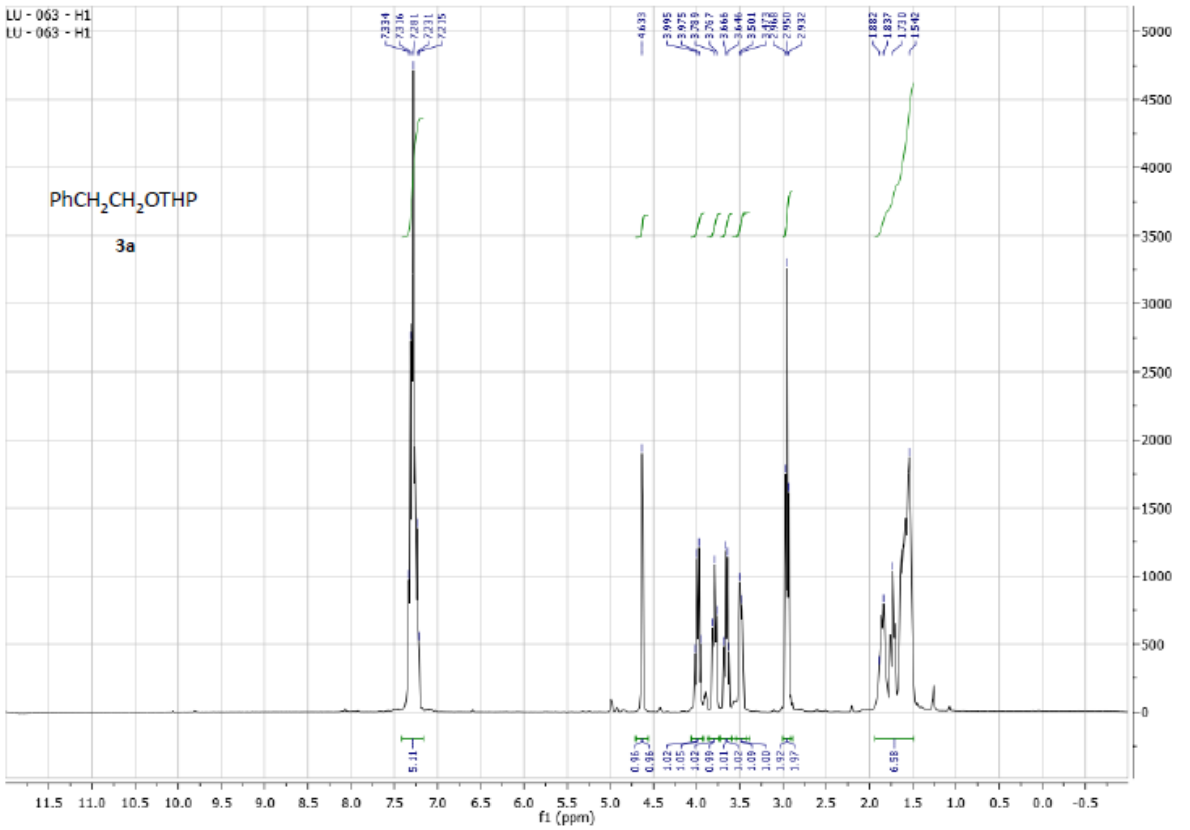


Figure S1. IR spectra of fresh (▬) and recycled (▬) NH_4HSO_4@SiO_2. Arrows indicate characteristic absorptions of NH_4HSO_4 at 3172, 1400, 1190, 879, and 600 cm^{-1}.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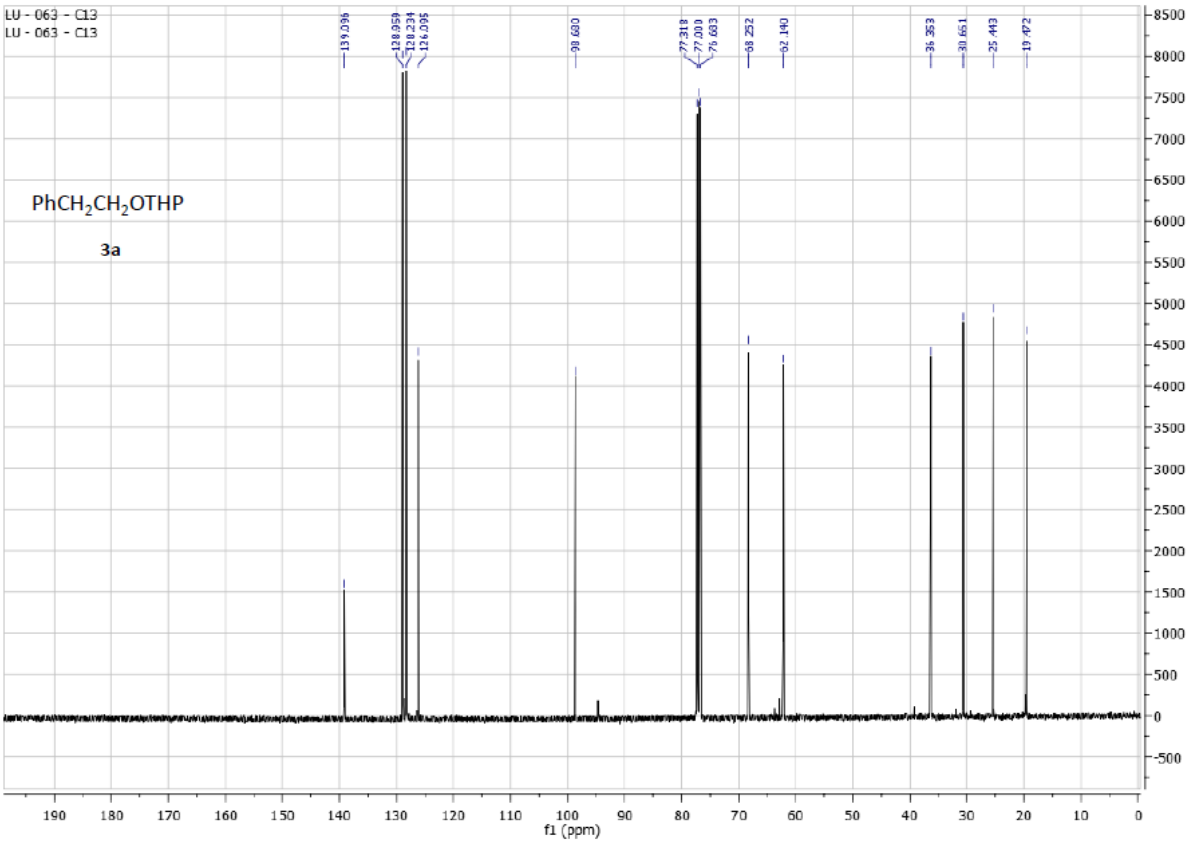
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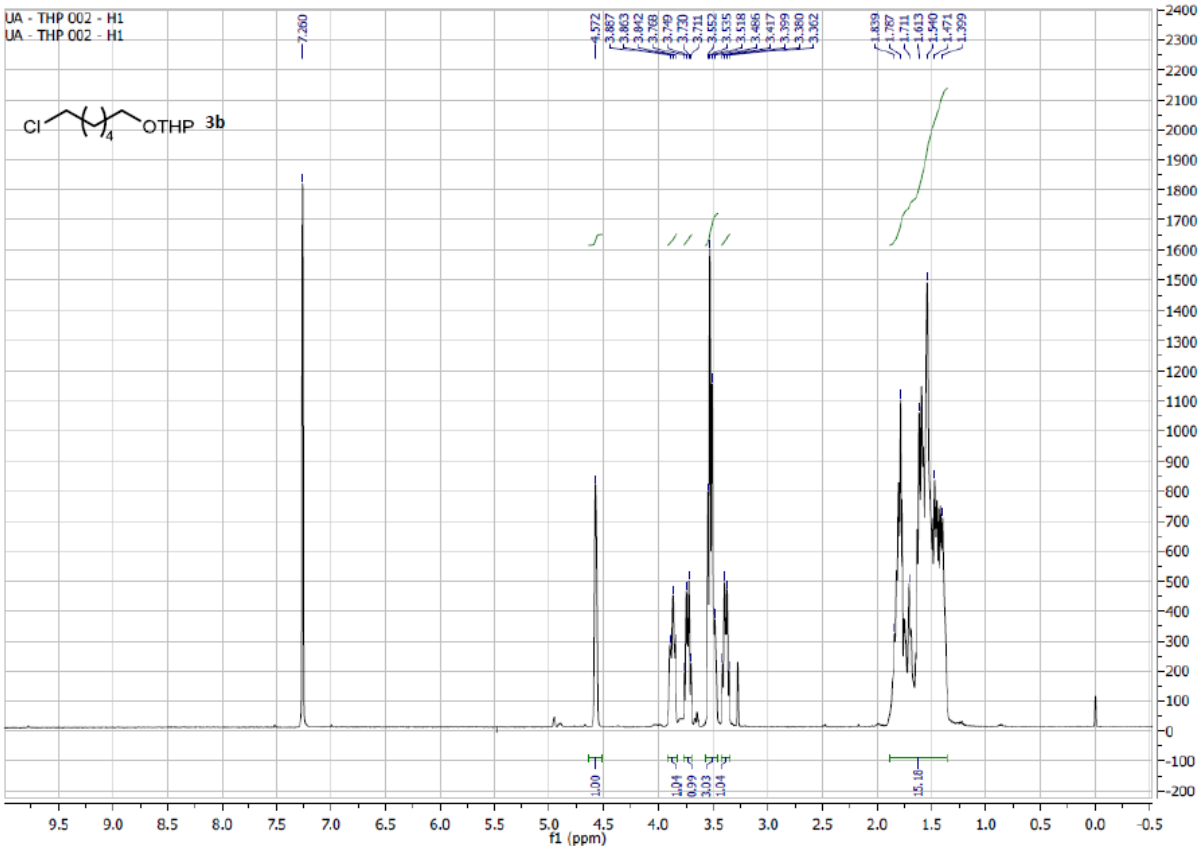
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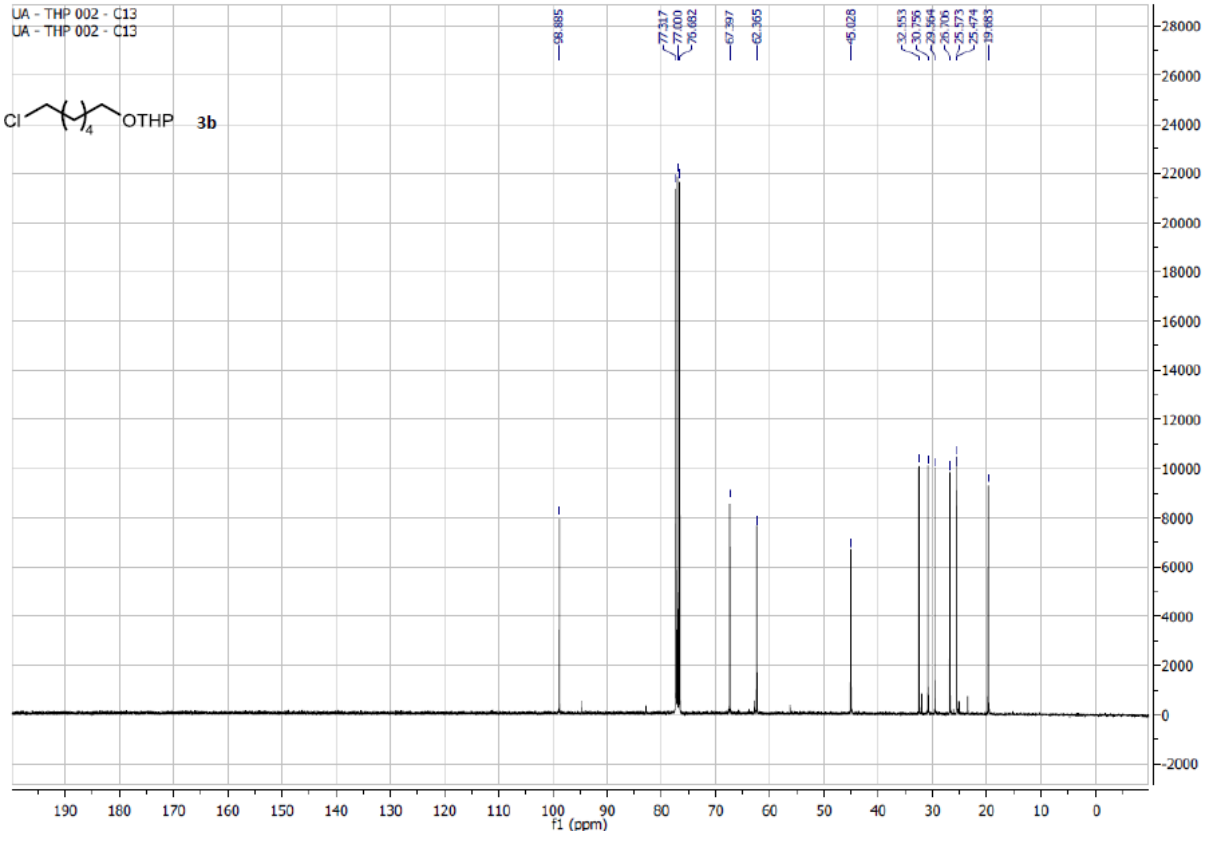
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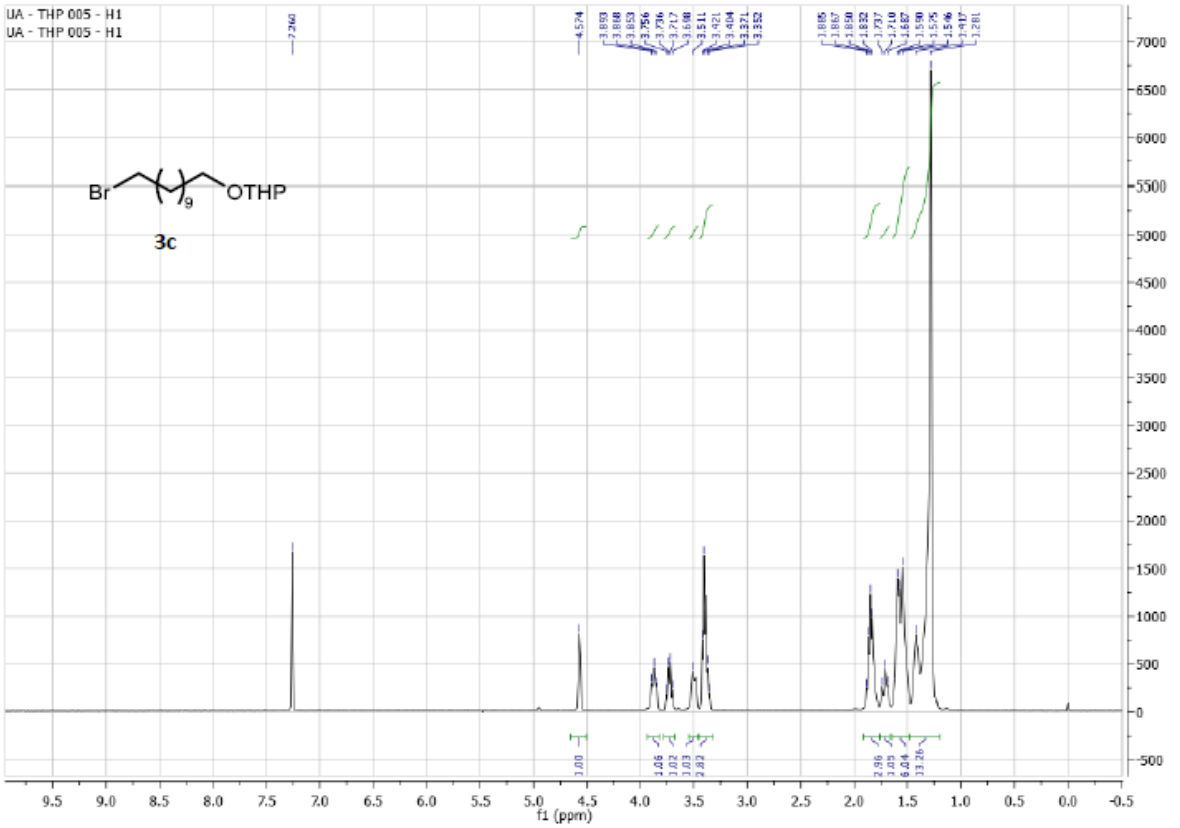
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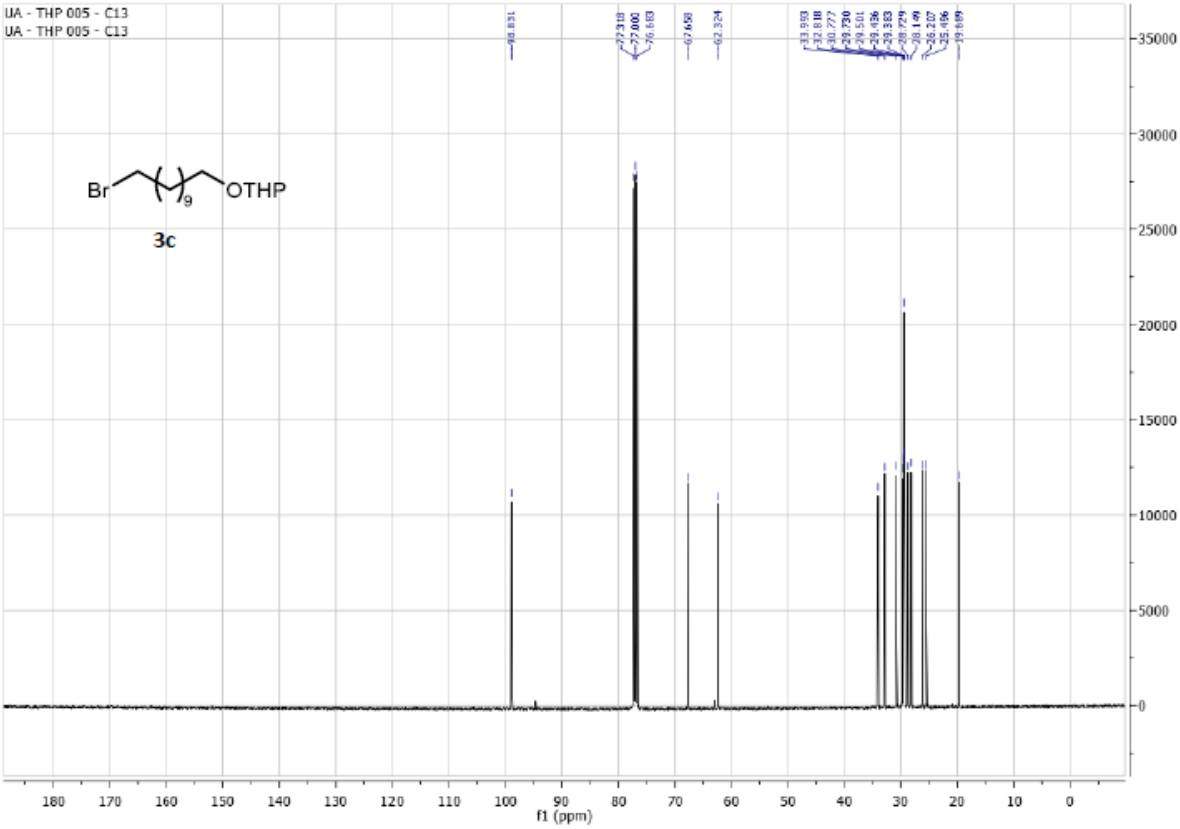
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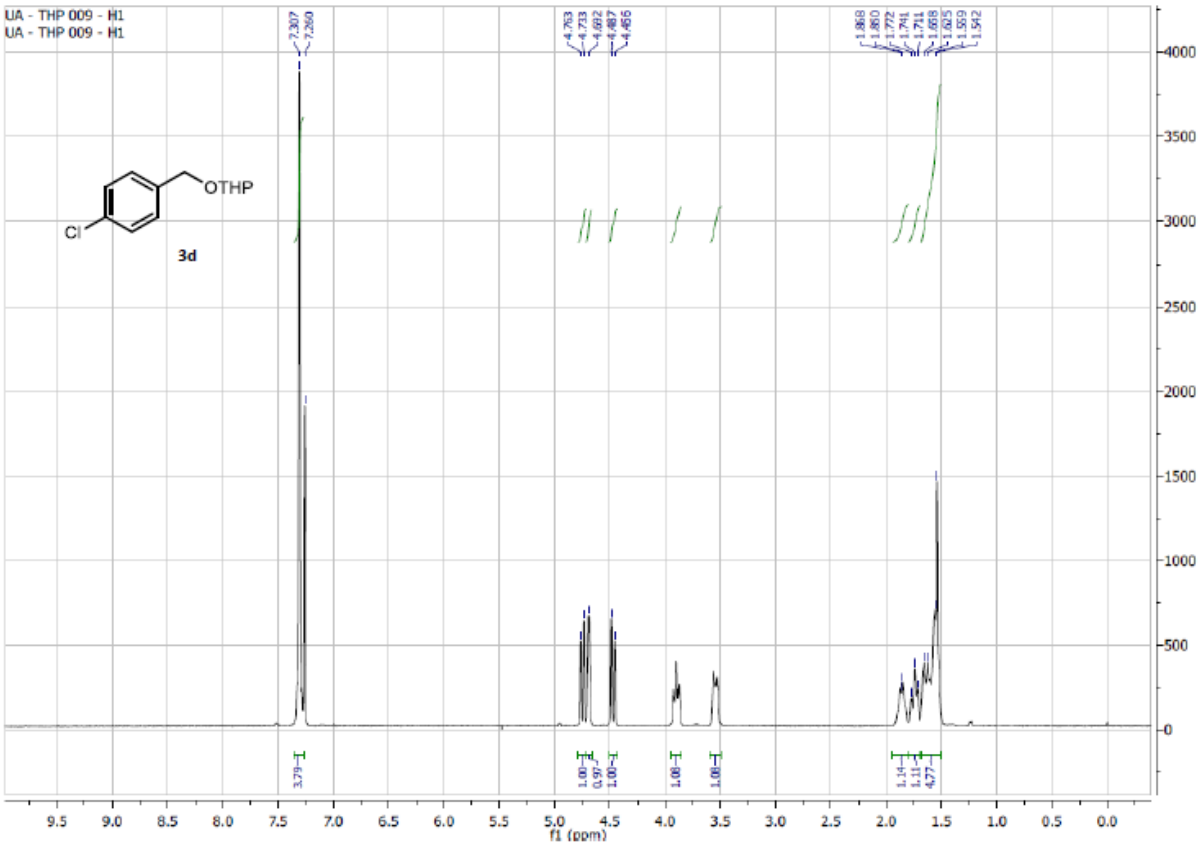
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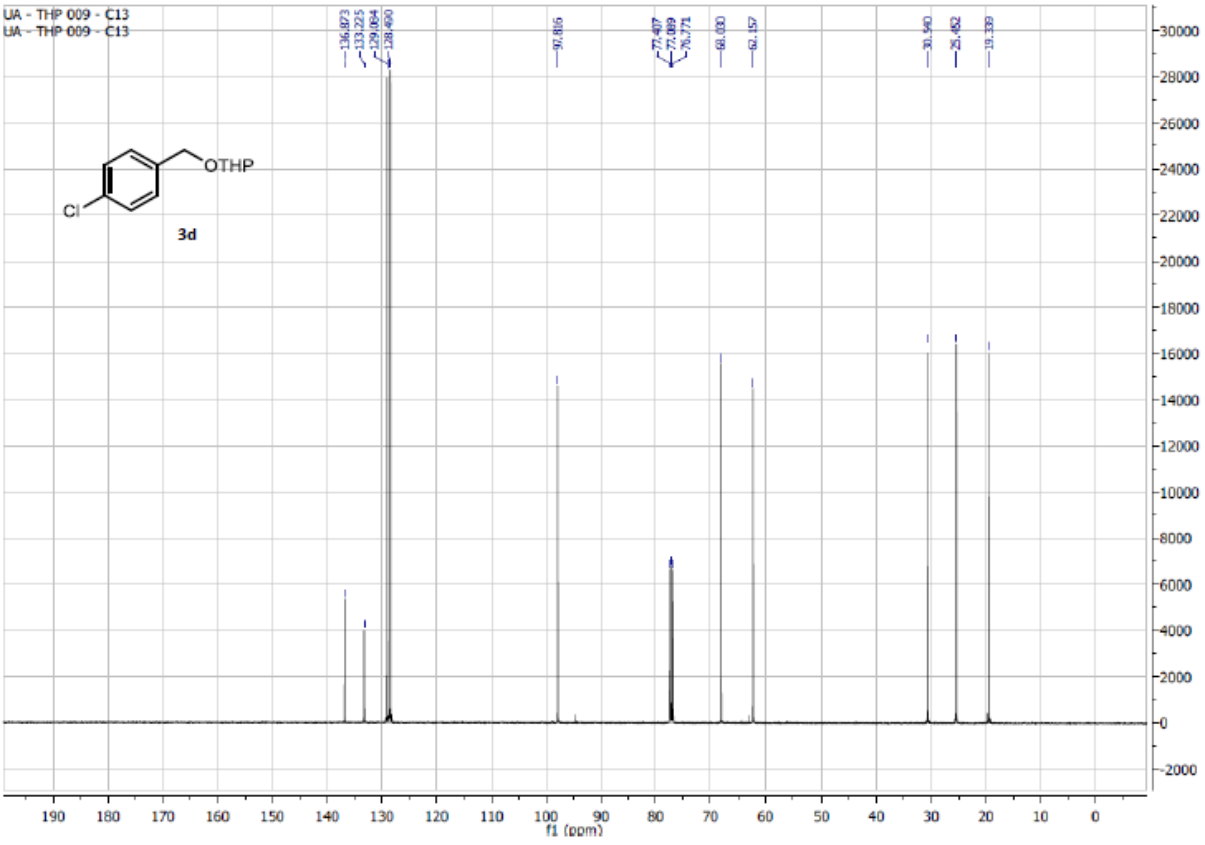
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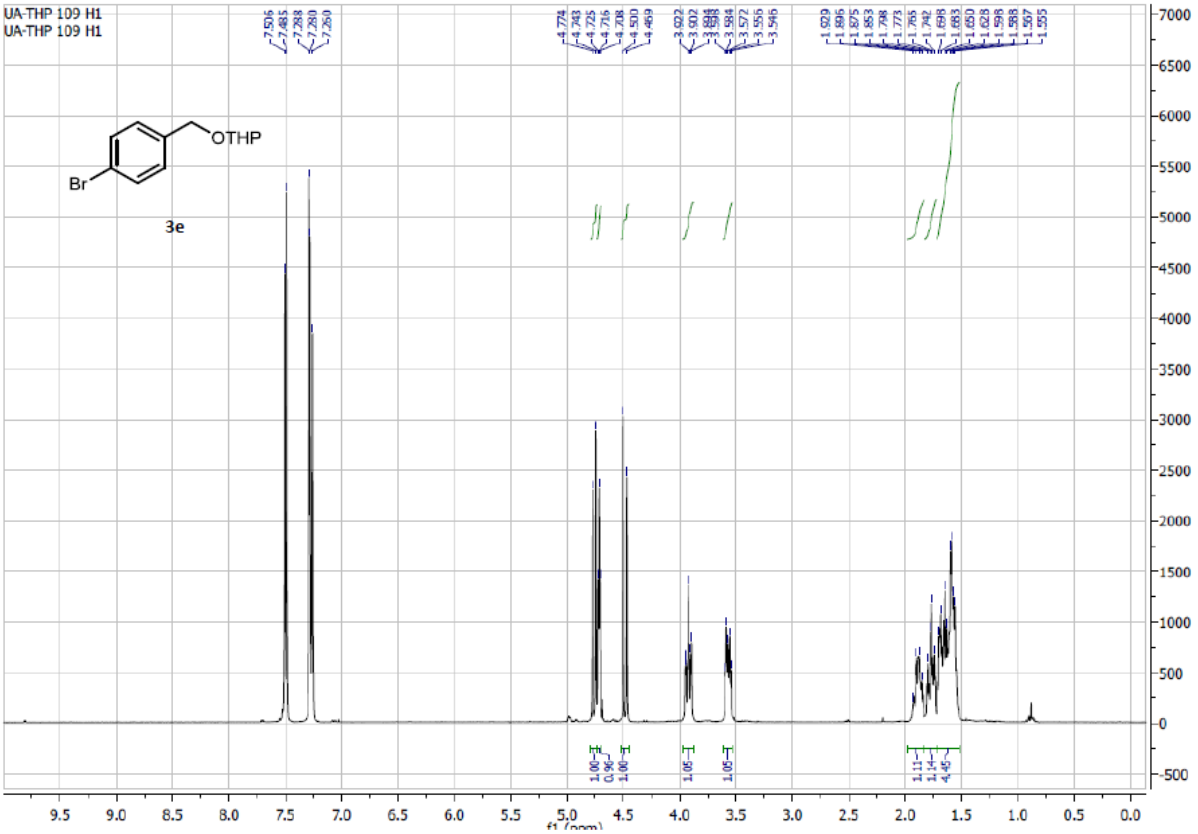
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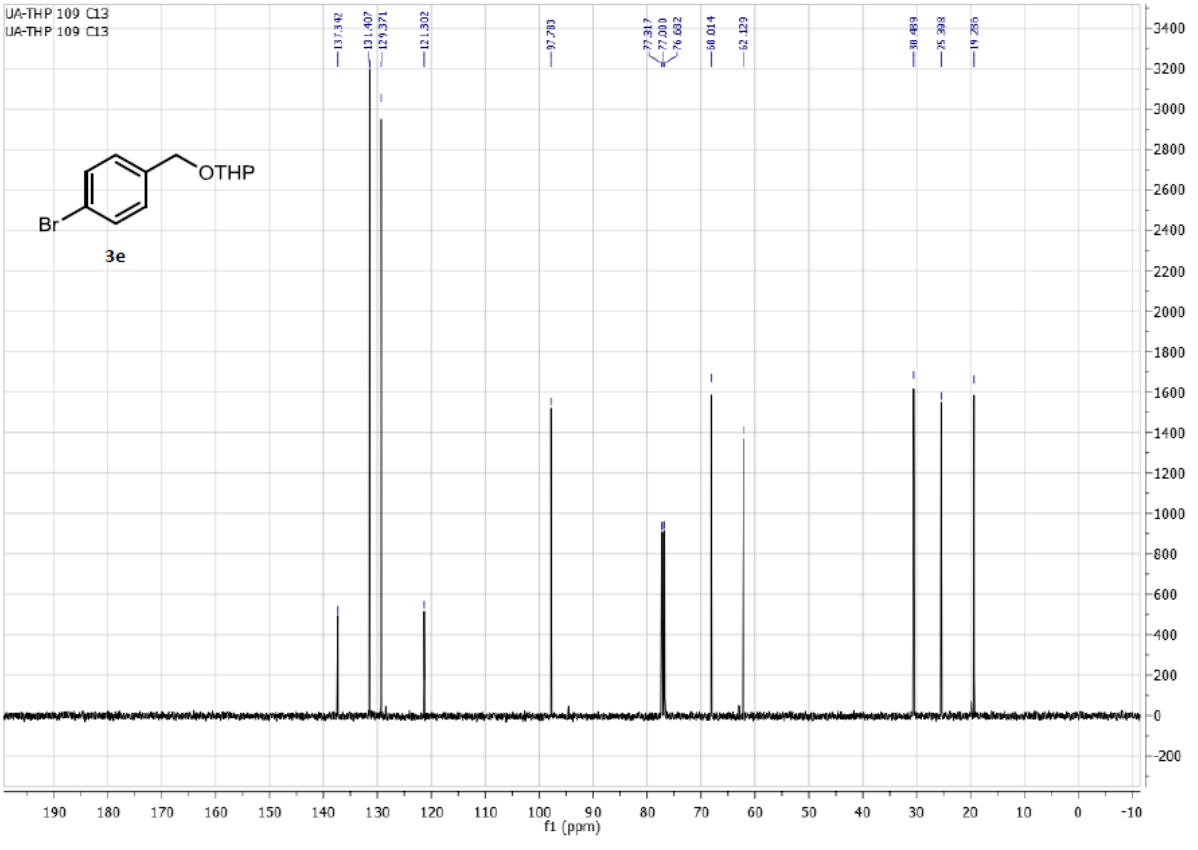
3e
f1 (ppm)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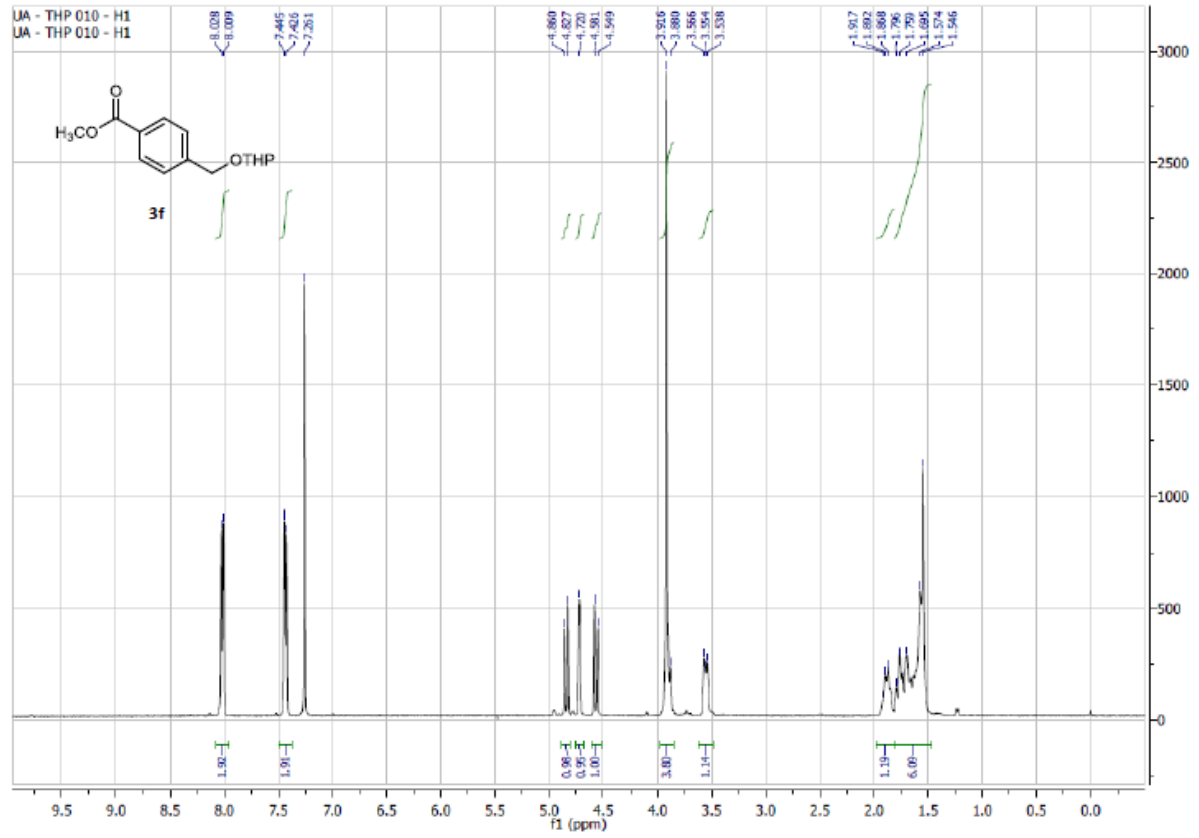
Br
3e
f1 (ppm)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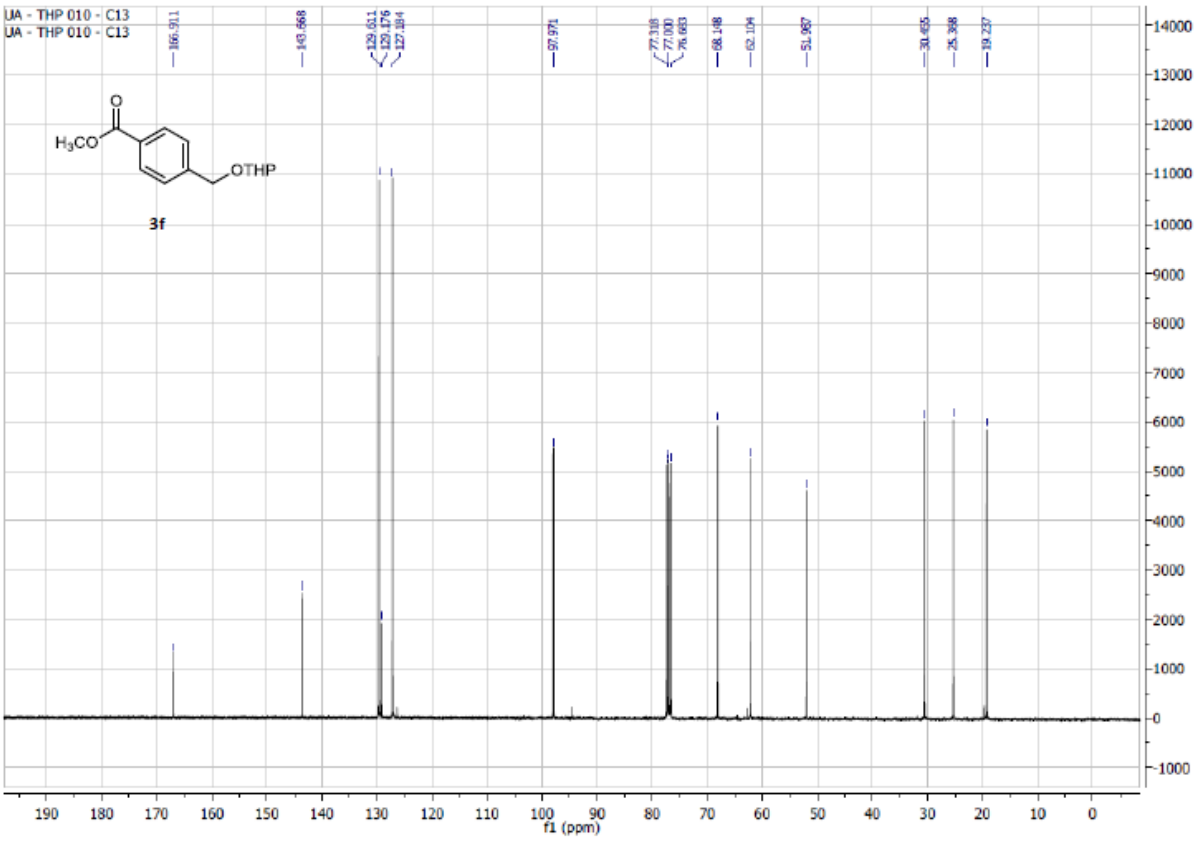
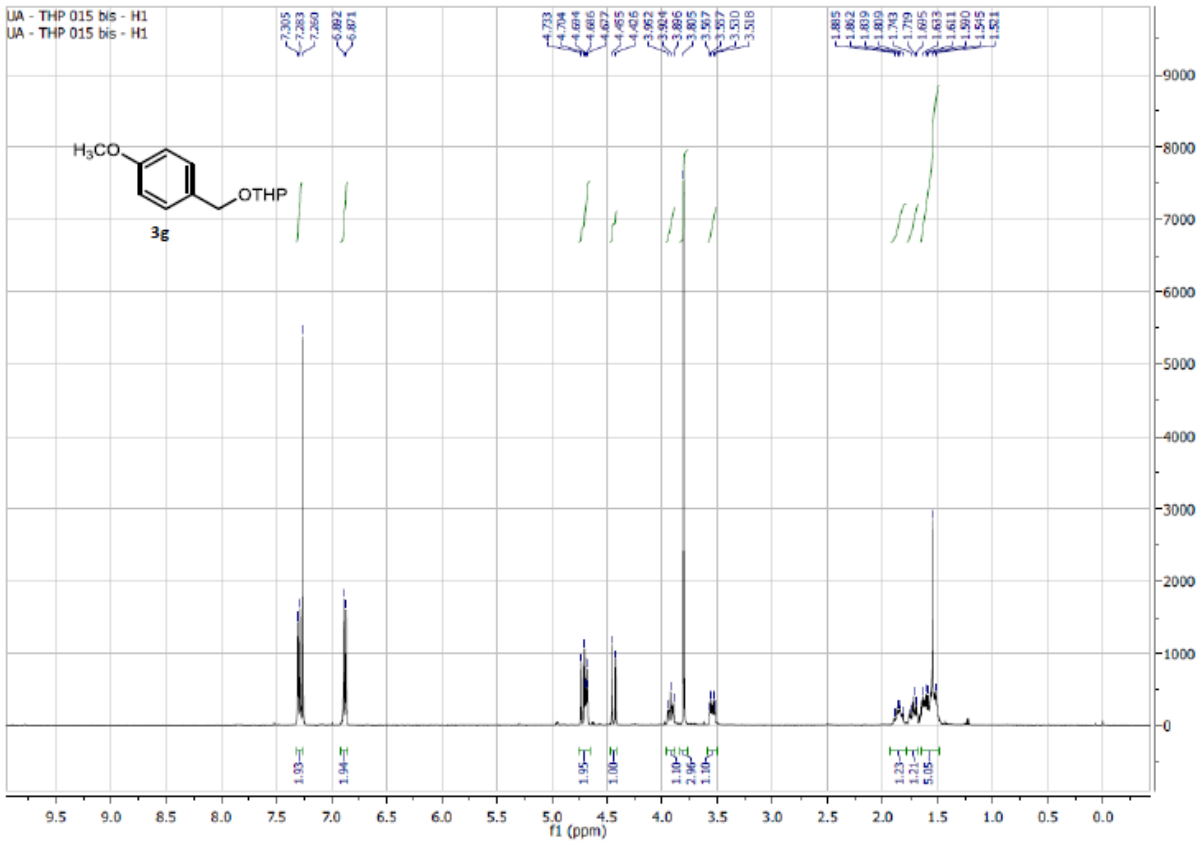
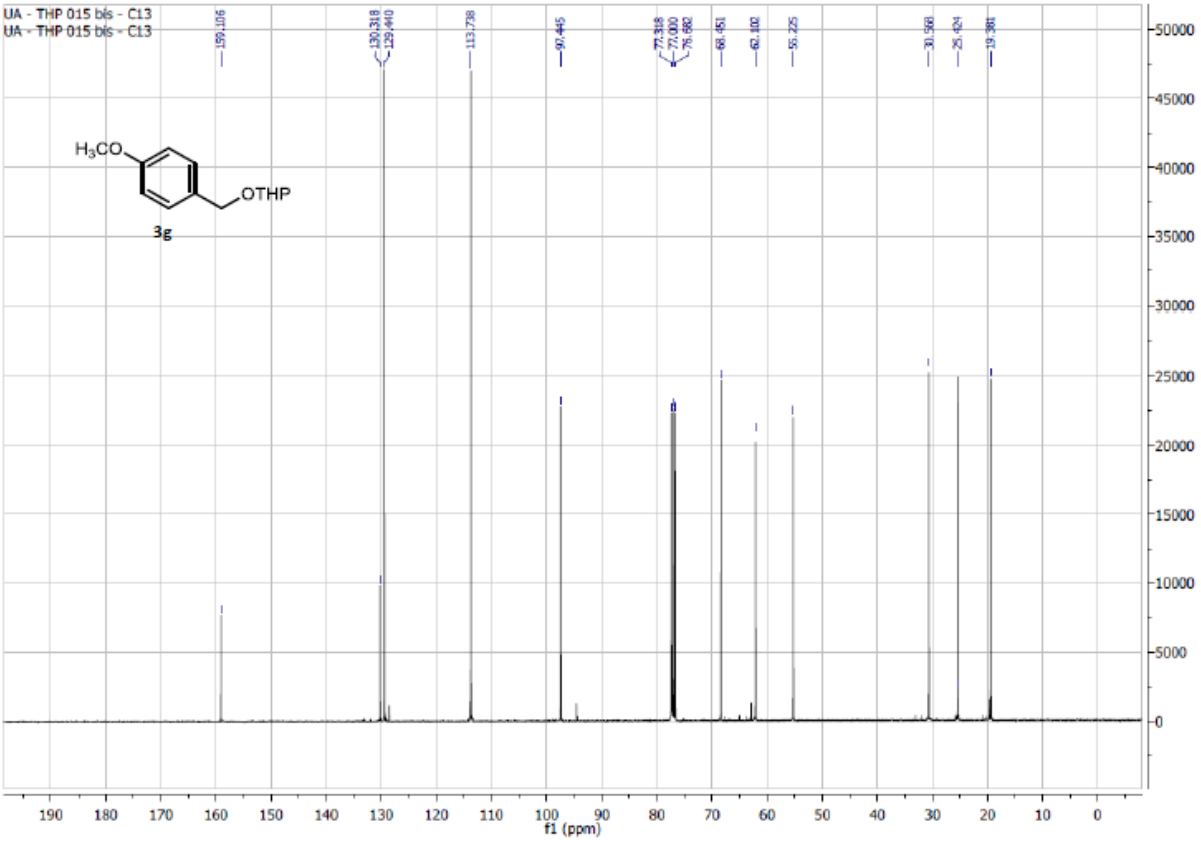
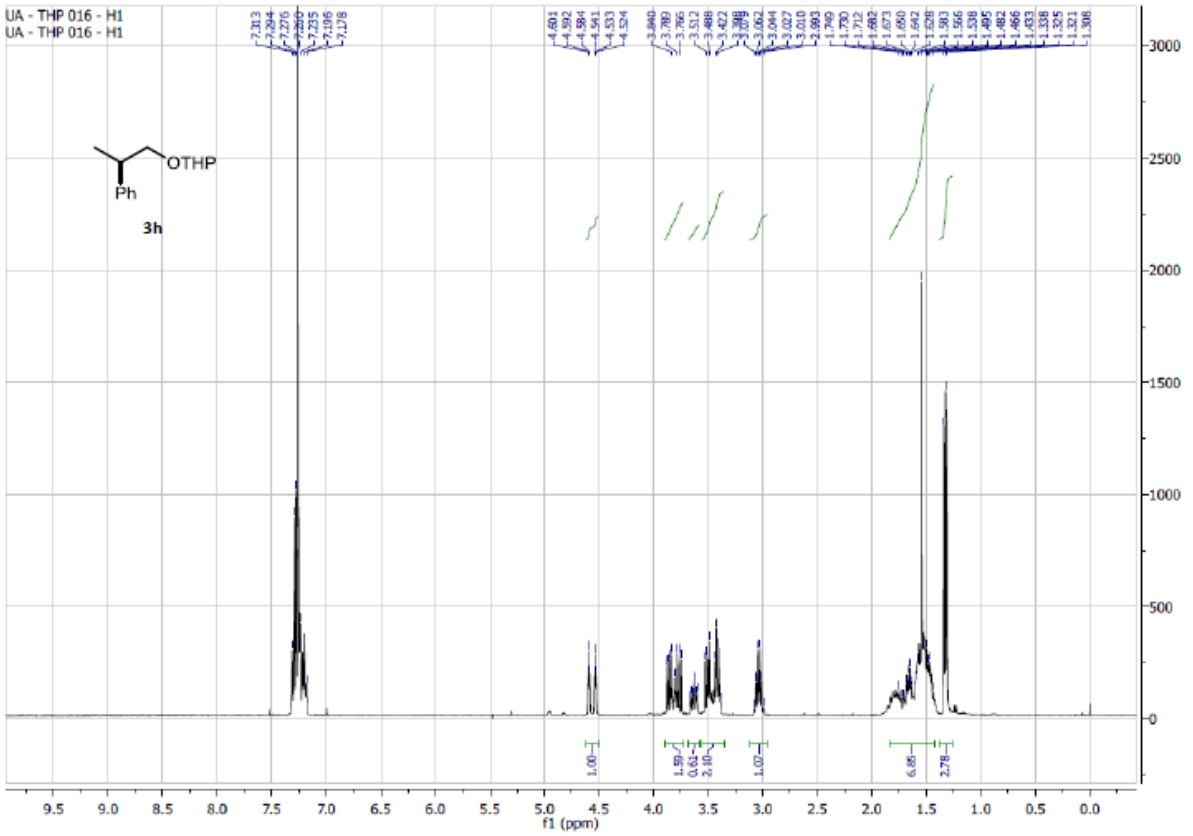
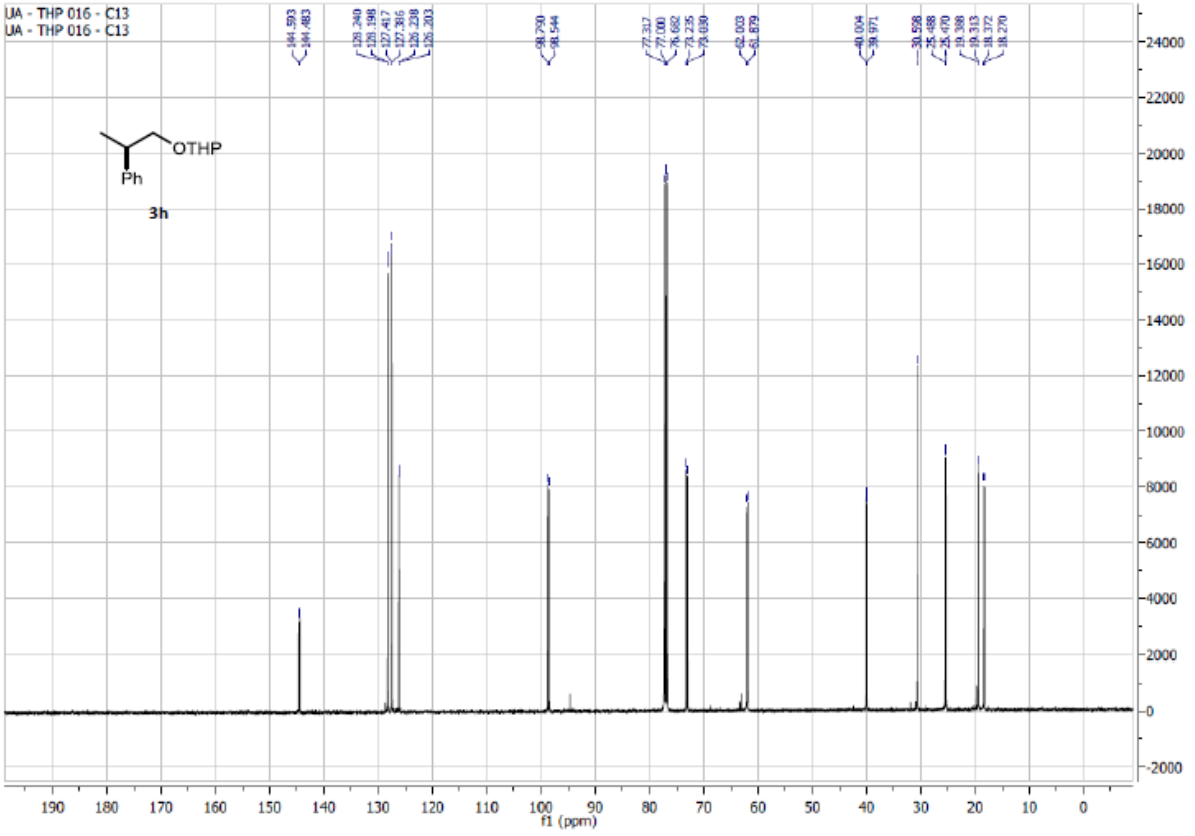
3f
f1 (ppm)

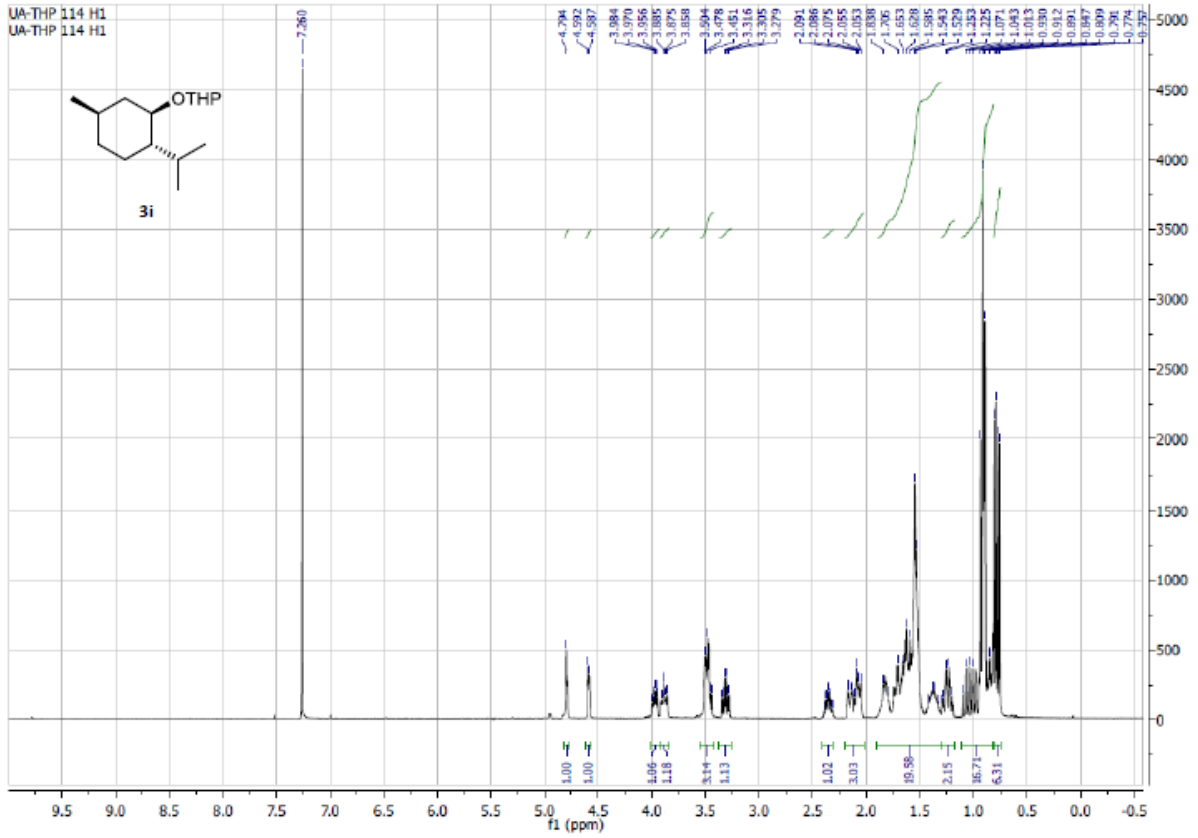

UA - THP 010 - C13
UA - THP 010 - C13
H3CO
OTHP
3f
f1 (ppm)

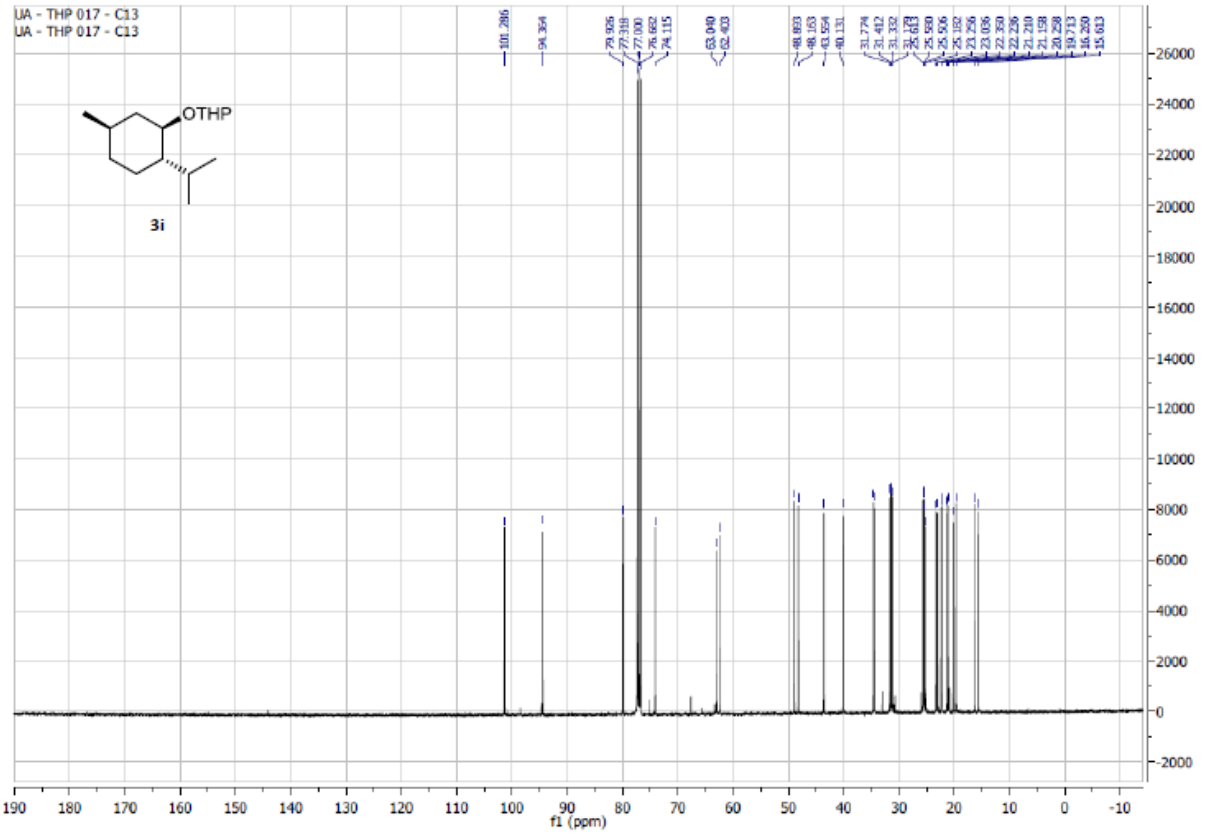

UA - THP 015 bis - H1
UA - THP 015 bis - H1
7.305
7.283
7.269
6.892
6.871
4.733
4.704
4.694
4.686
4.677
4.455
4.426
3.962
3.924
3.896
3.805
3.567
3.510
3.518
1.885
1.862
1.839
1.809
1.743
1.719
1.695
1.673
1.611
1.590
1.545
1.521
H3CO
OTHP
3g
1.93
1.94
1.95
1.00
1.10
2.96
1.10
1.23
1.21
5.05
f1 (ppm)

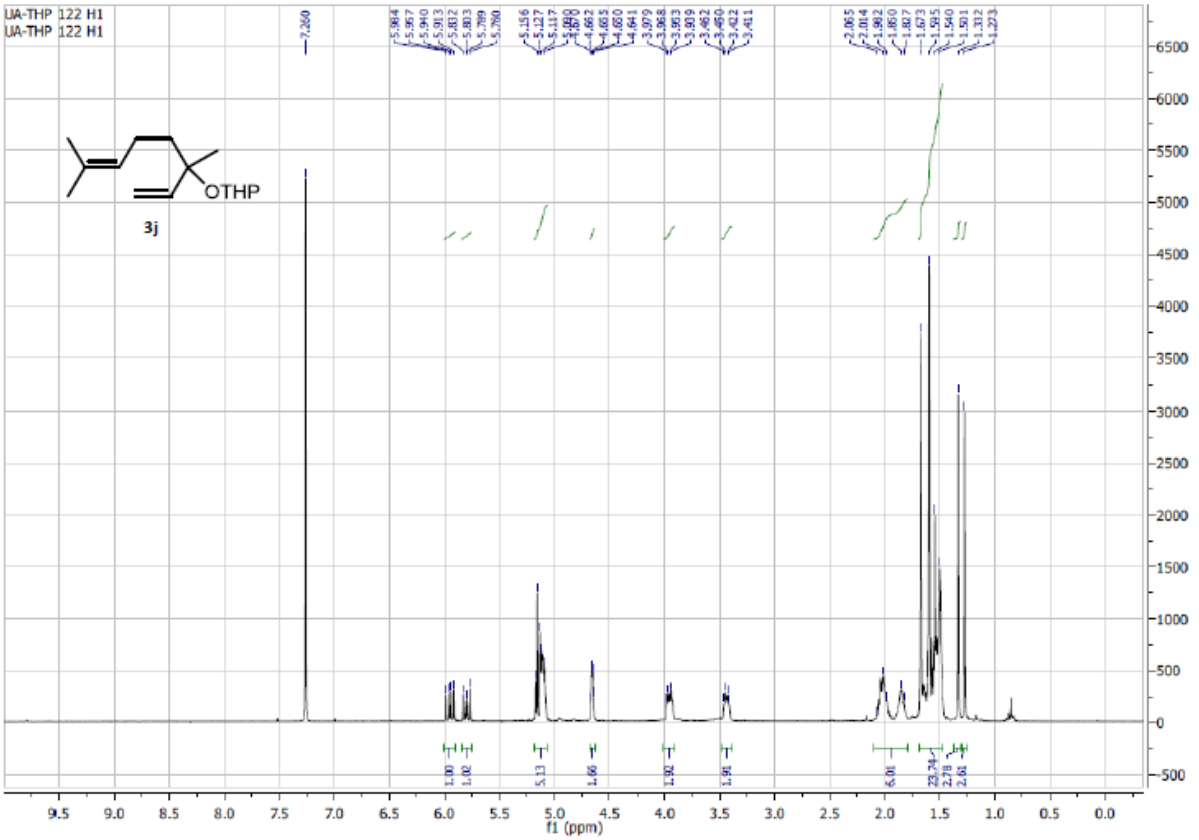

UA - THP 015 bis - C13
UA - THP 015 bis - C13
159.106
130.318
129.940
113.738
97.445
77.318
77.000
76.682
68.451
62.102
55.225
30.568
25.424
19.381
H3CO
OTHP
3g
f1 (ppm)

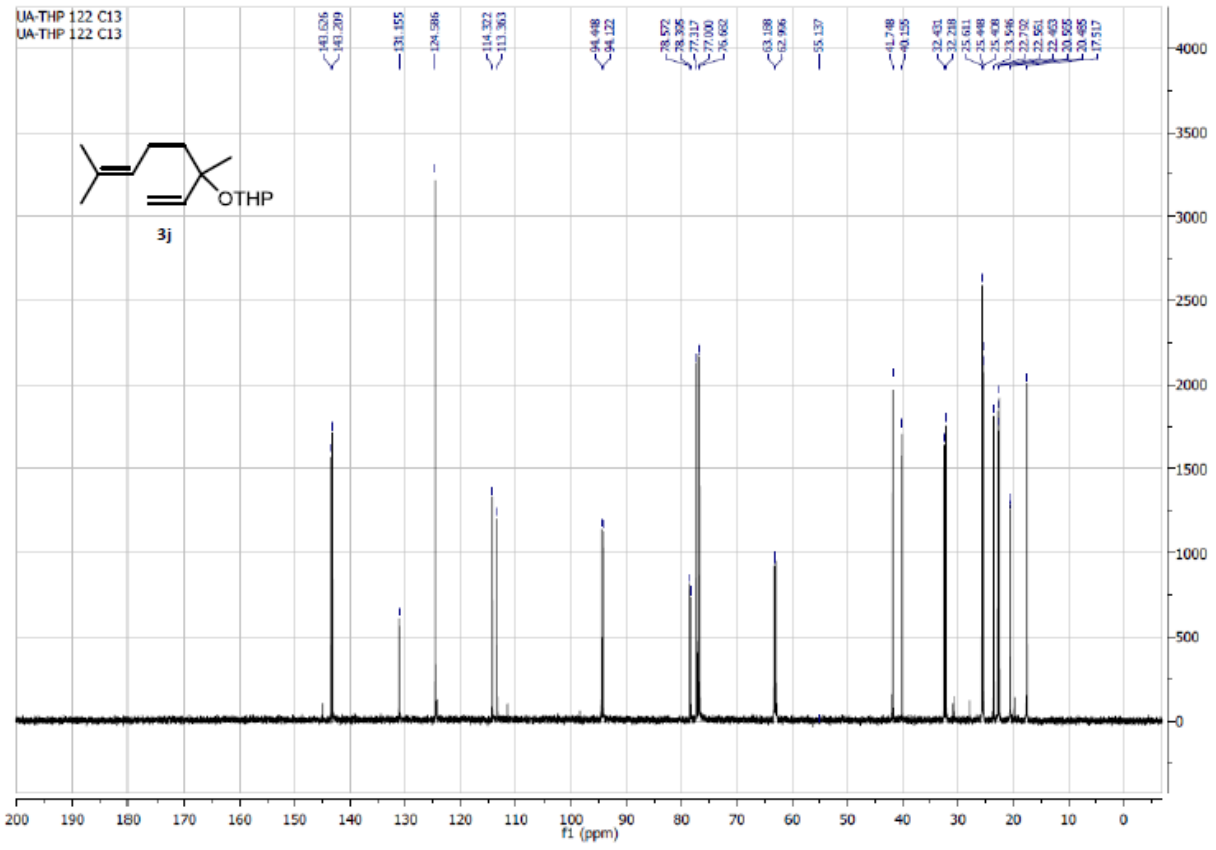

UA - THP 016 - H1
UA - THP 016 - H1
OTHP
Ph
3h
f1 (ppm)

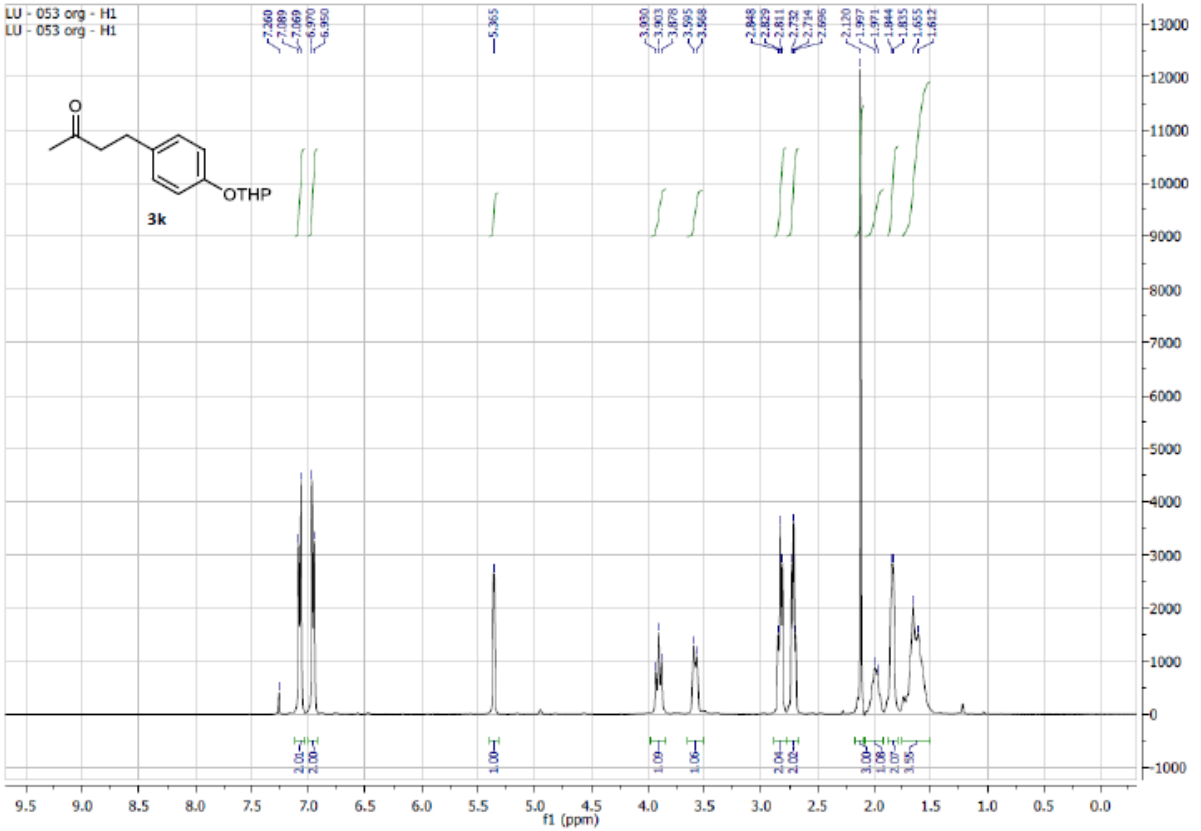

UA - THP 016 - C13
UA - THP 016 - C13
OTHP
Ph
3h
f1 (ppm)

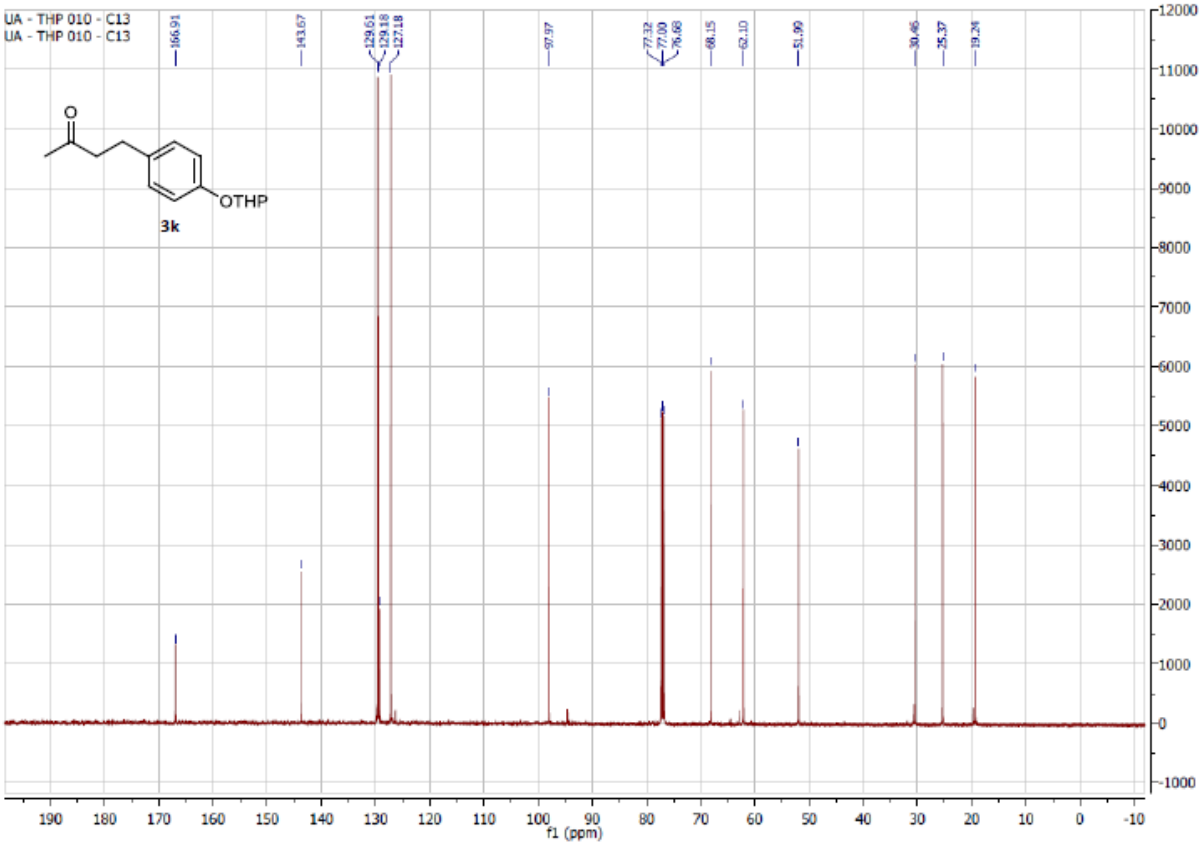

UA-THP 114 H1
UA-THP 114 H1
OTHP
3i
f1 (ppm)

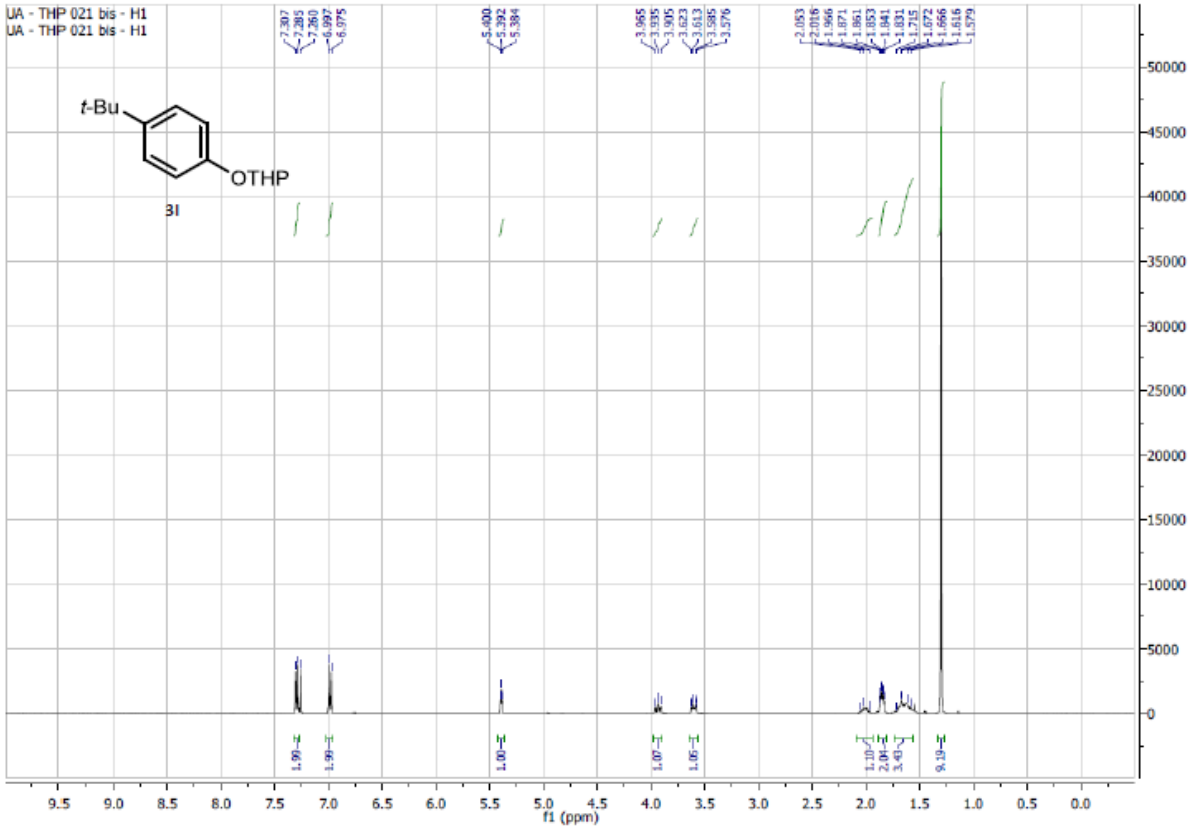

UA - THP 017 - C13
UA - THP 017 - C13
OTHP
3i
f1 (ppm)

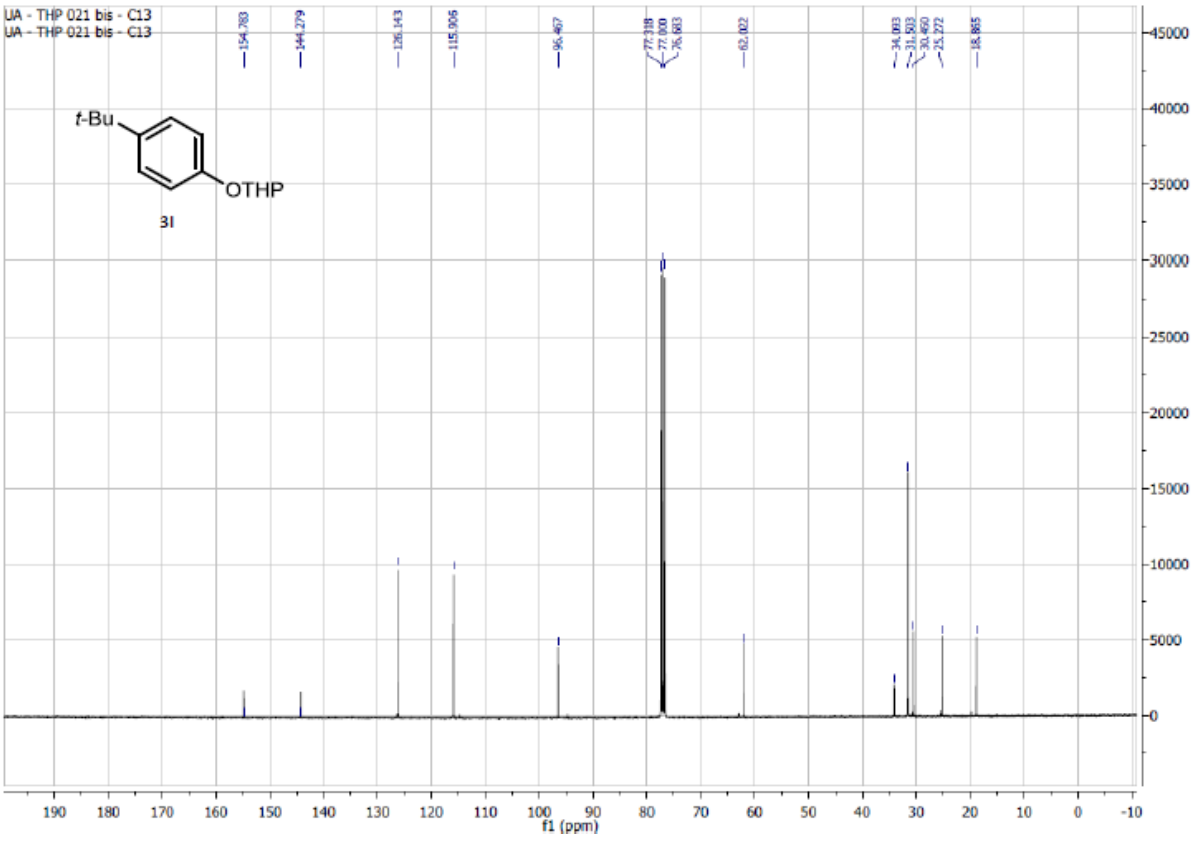

UA-THP 122 H1
UA-THP 122 H1
OTHP
3j
f1 (ppm)

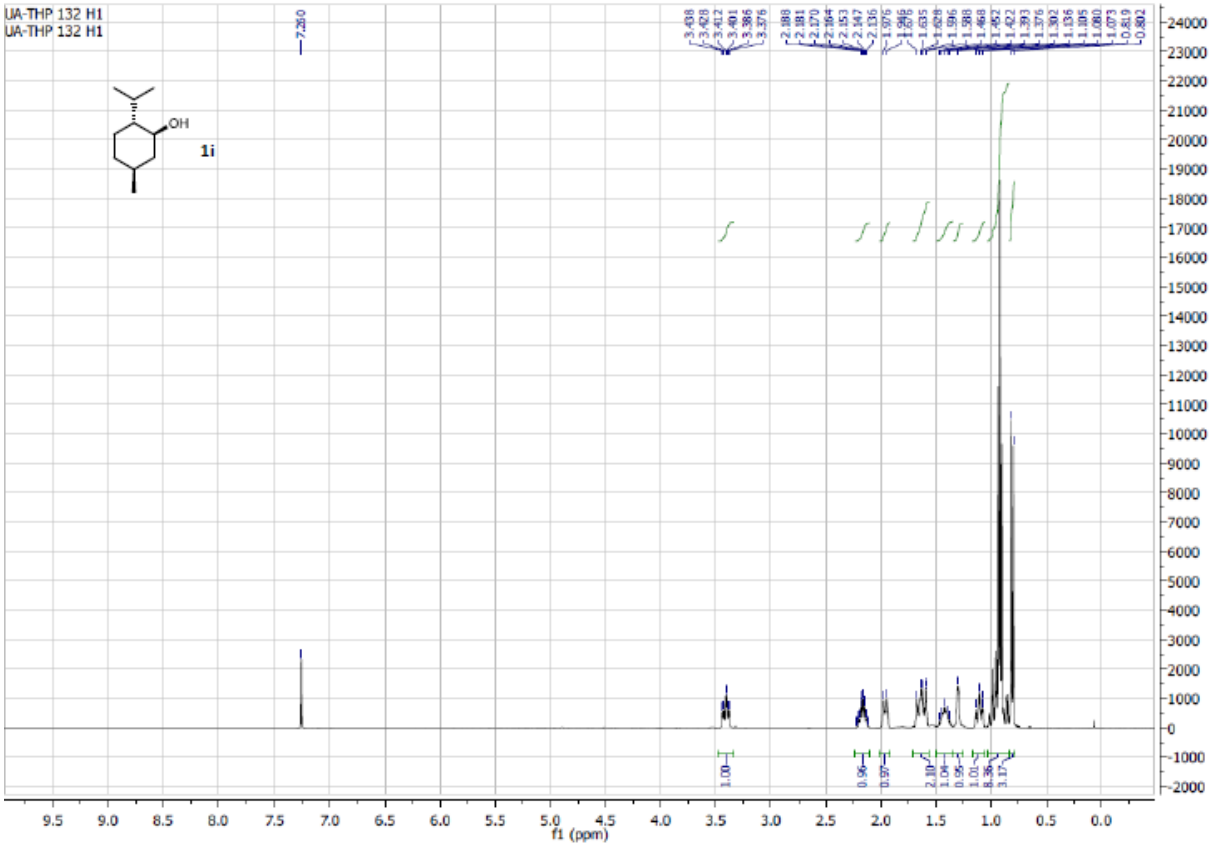

UA-THP 122 C13
UA-THP 122 C13
OTHP
3j
f1 (ppm)

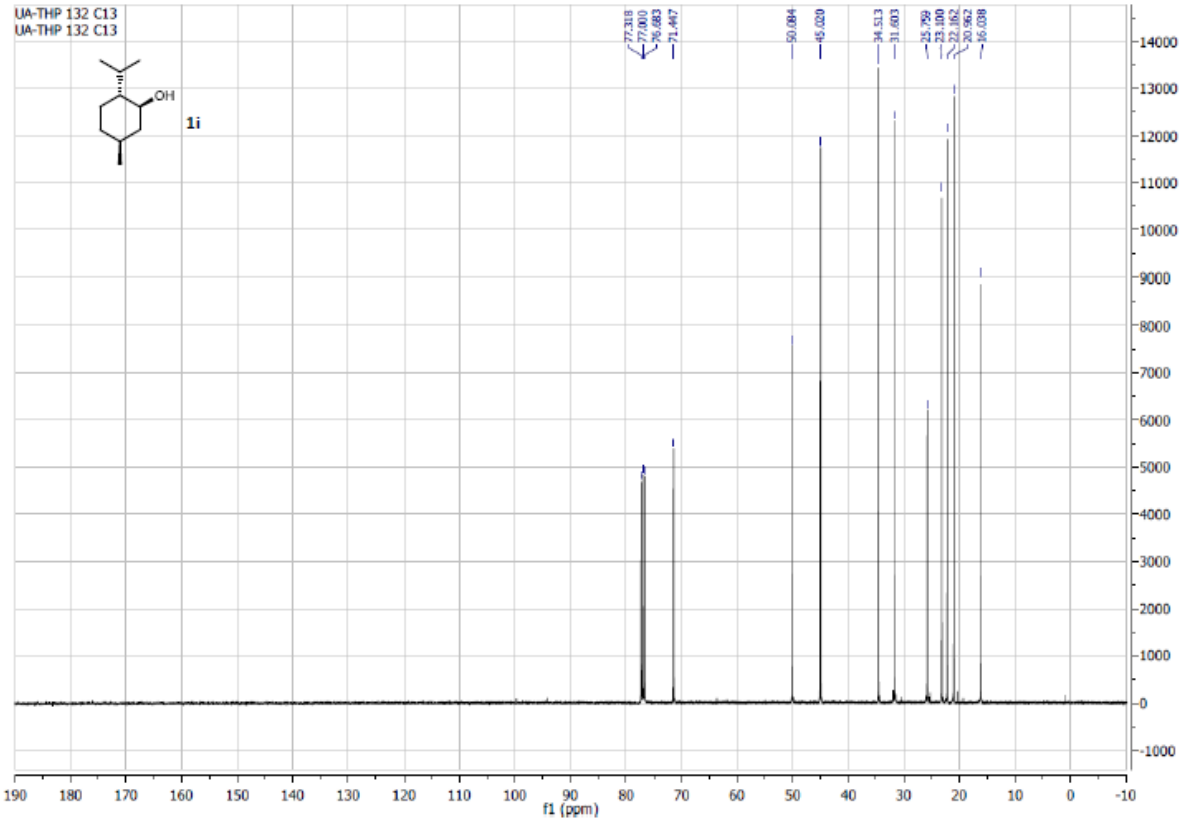

LU - 053 org - H1
LU - 053 org - H1
OTHP
3k
f1 (ppm)

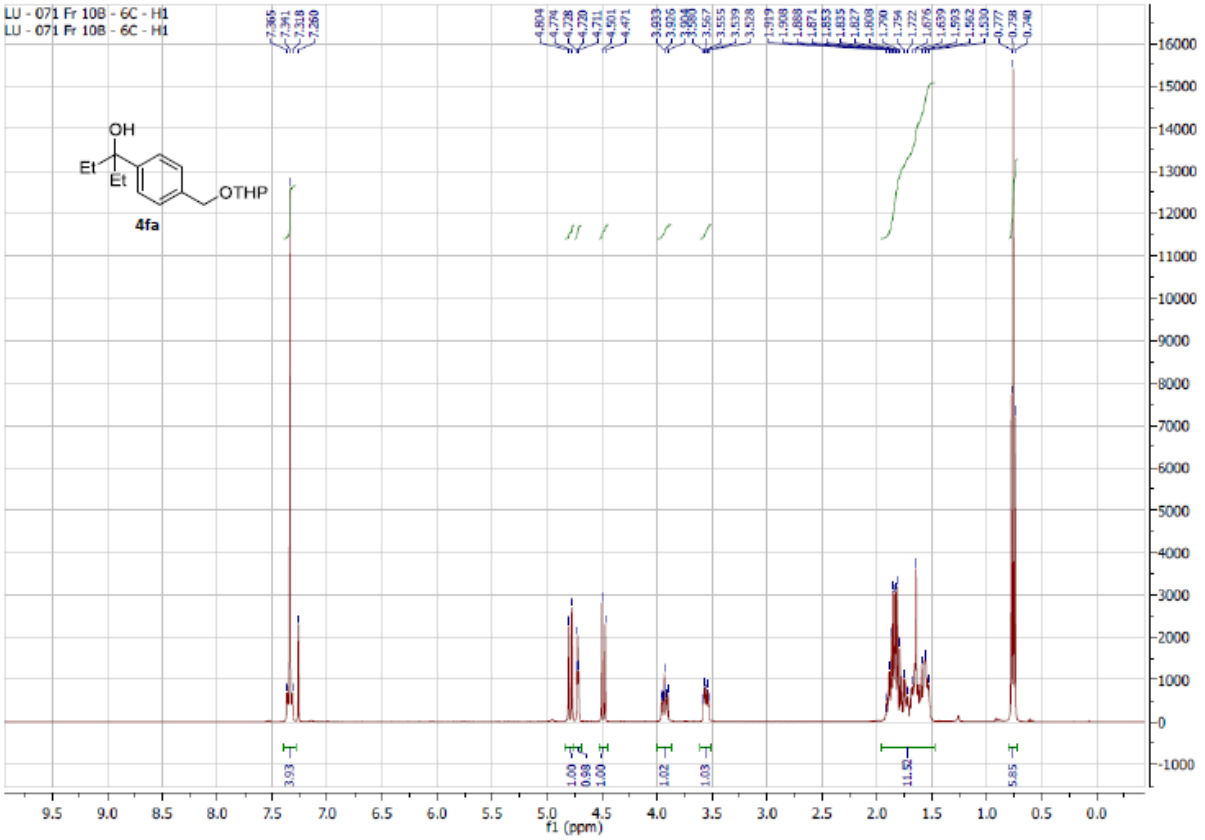

UA - THP 010 - C13
UA - THP 010 - C13
OTHP
3k
f1 (ppm)

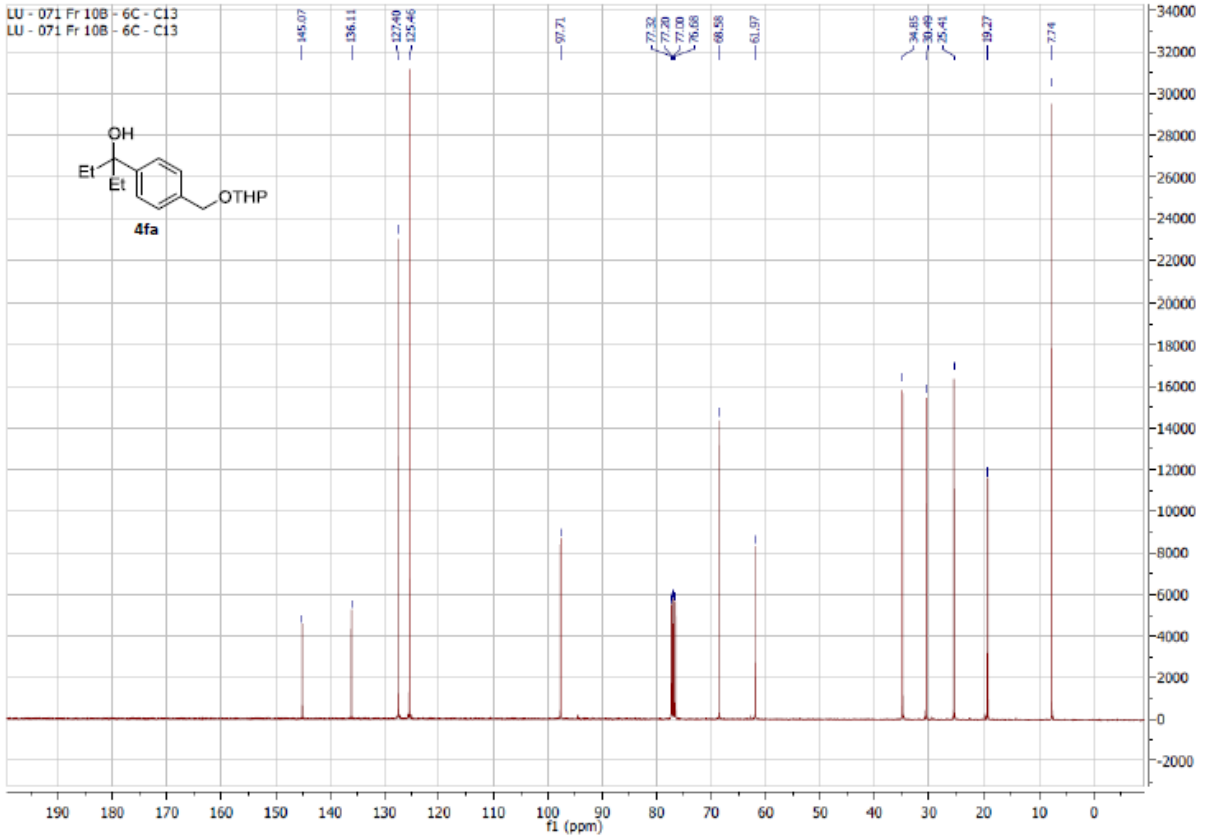

UA - THP 021 bis - H1
UA - THP 021 bis - H1
t-Bu
OTHP
3l
f1 (ppm)

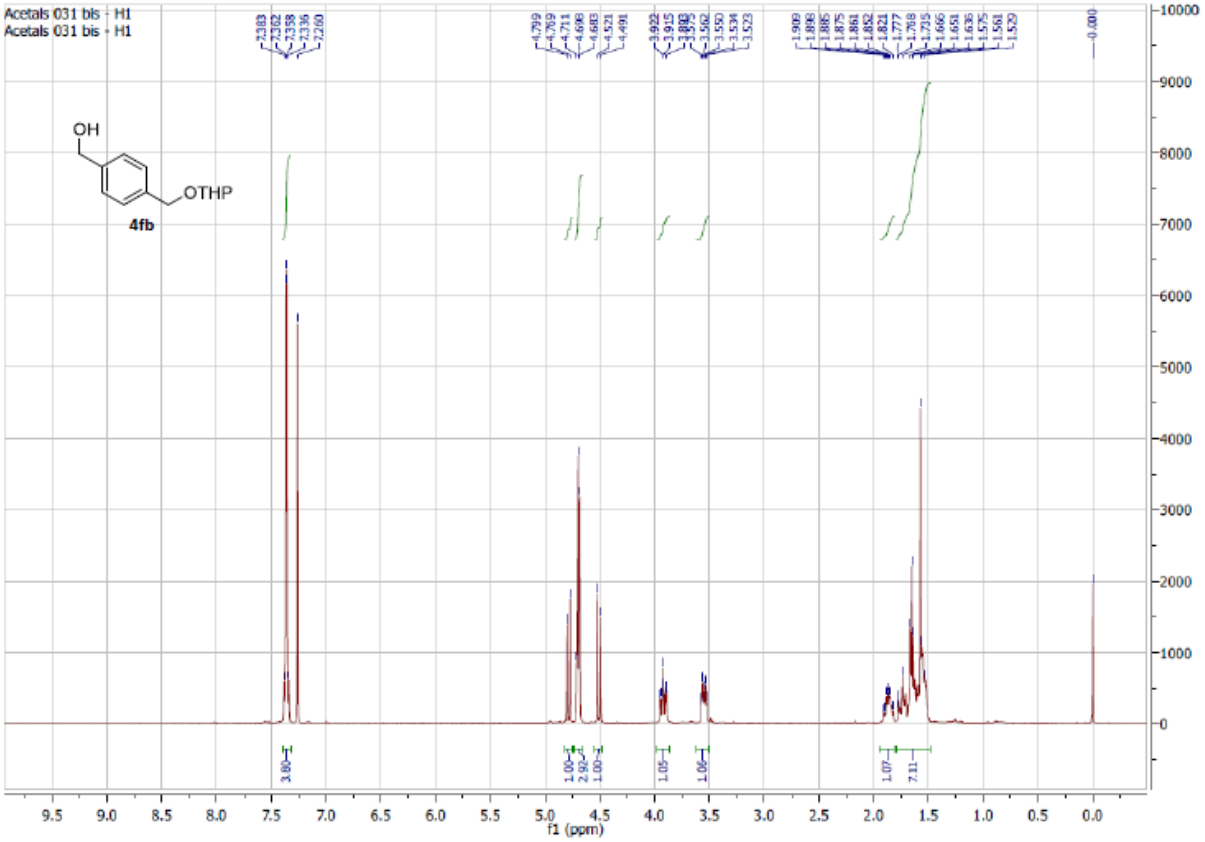

UA - THP 021 bis - C13
UA - THP 021 bis - C13
t-Bu
OTHP
3l
f1 (ppm)

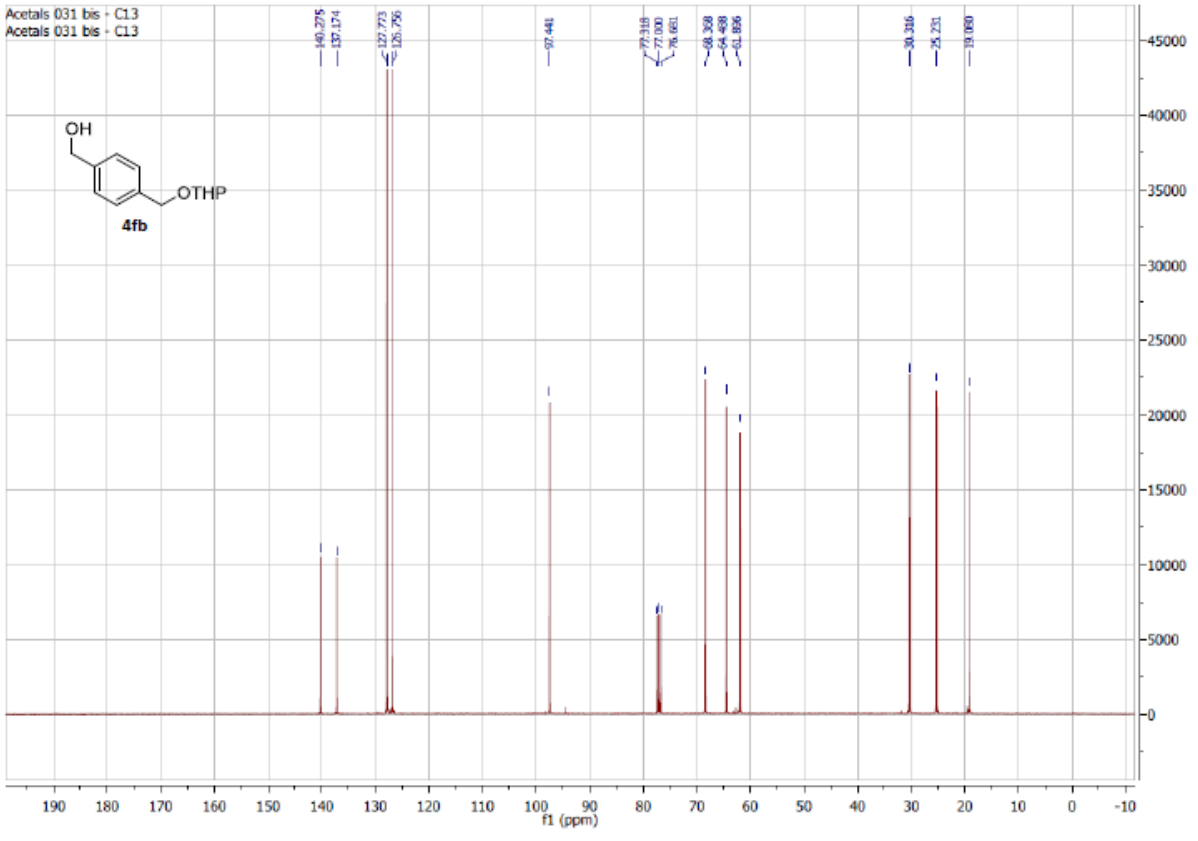

UA-THP 132 H1
UA-THP 132 H1
OH
1i
f1 (ppm)


UA-THP 132 C13
UA-THP 132 C13
OH
1i
f1 (ppm)


LU - 071 Fr 10B - 6C - H1
LU - 071 Fr 10B - 6C - H1
OH
Et
Et
OTHP
4fa
f1 (ppm)


LU - 071 Fr 10B - 6C - C13
LU - 071 Fr 10B - 6C - C13
OH
Et
Et
OTHP
4fa
f1 (ppm)


Acetals 031 bis - H1
Acetals 031 bis - H1
OH
OTHP
4fb
f1 (ppm)


Acetals 031 bis - C13
Acetals 031 bis - C13
OH
OTHP
4fb
f1 (ppm)

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