# Supplementary Materials: Reaction of Glycerol with Trimethyl Orthoformate: Towards the Synthesis of New Glycerol Derivatives

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# 1. Synthesis/Isolation of reaction products

## *1.1. (2-methoxy-1,3-dioxolan-4-yl)methanol (1).*

The isomer identified as **1a** was isolated by distillation over potassium carbonate, as reported in Materials and Methods. The characterization of the isomer **1b** were derived by both GC-MS and by NMR by subtracting the known peaks of **1a** to the spectra ofthe mixture **1a-1b**. Hereafter, the GC/MS spectra of **1a** (Figure S1) or **1b** (Figure S7) and the $^{1}H$, $^{13}C$, HSQC, HMBC and COSY NMR of both **1a** (Figure S2-S6) and the mixture **1a-1b** (Figure S8-S12) are reported.

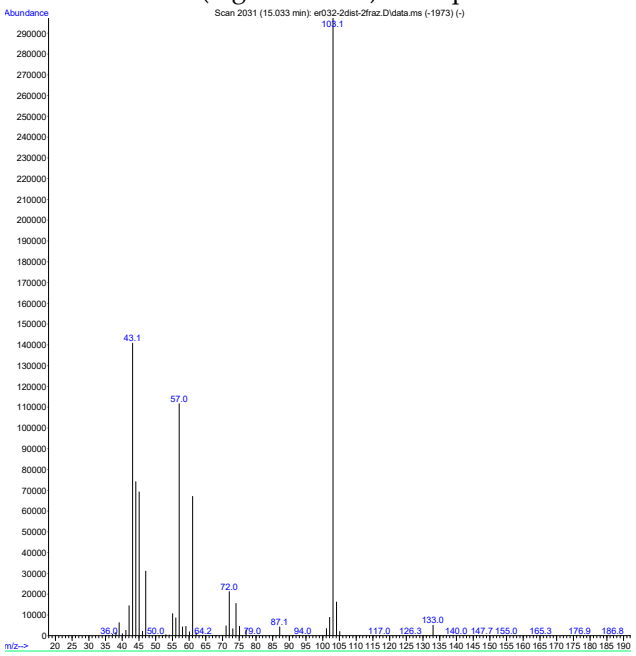


**Figure S1.** MS spectra of **1a:** 134 ($M^{+}$,0);133 (1); 103 (100); 61 (31); 57 (46); 47 (15); 45(32); 44 (31); 43 (65).

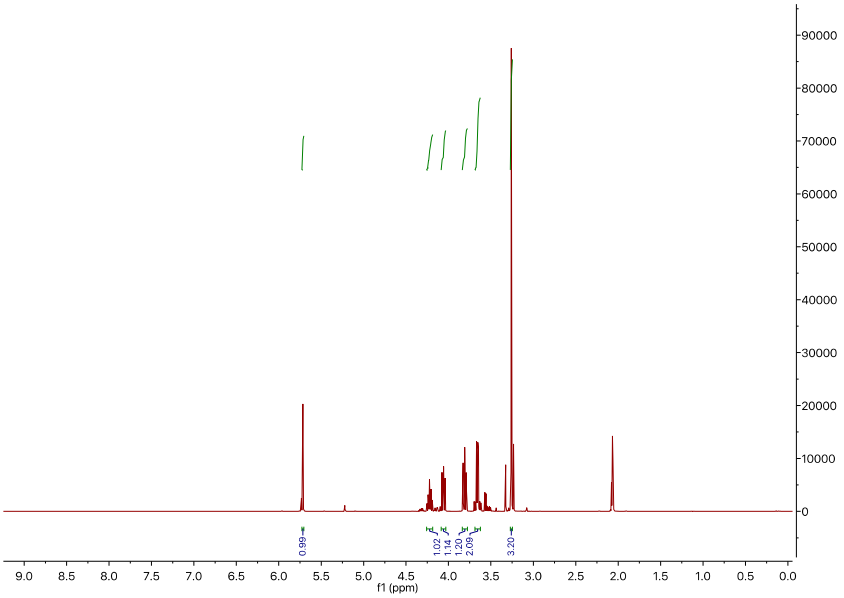


**Figure S2.** $^{1}H$ NMR of **1a** (400 MHz, Acetone-d6): δ = 5.72 (s, 1H), 4.22 (tt, *J*=7.2, 5.2, 1H), 4.09 – 4.03 (m, 1H), 3.84 – 3.78 (m, 1H), 3.69 – 3.62 (m, 2H), 3.26 (s, 3H).

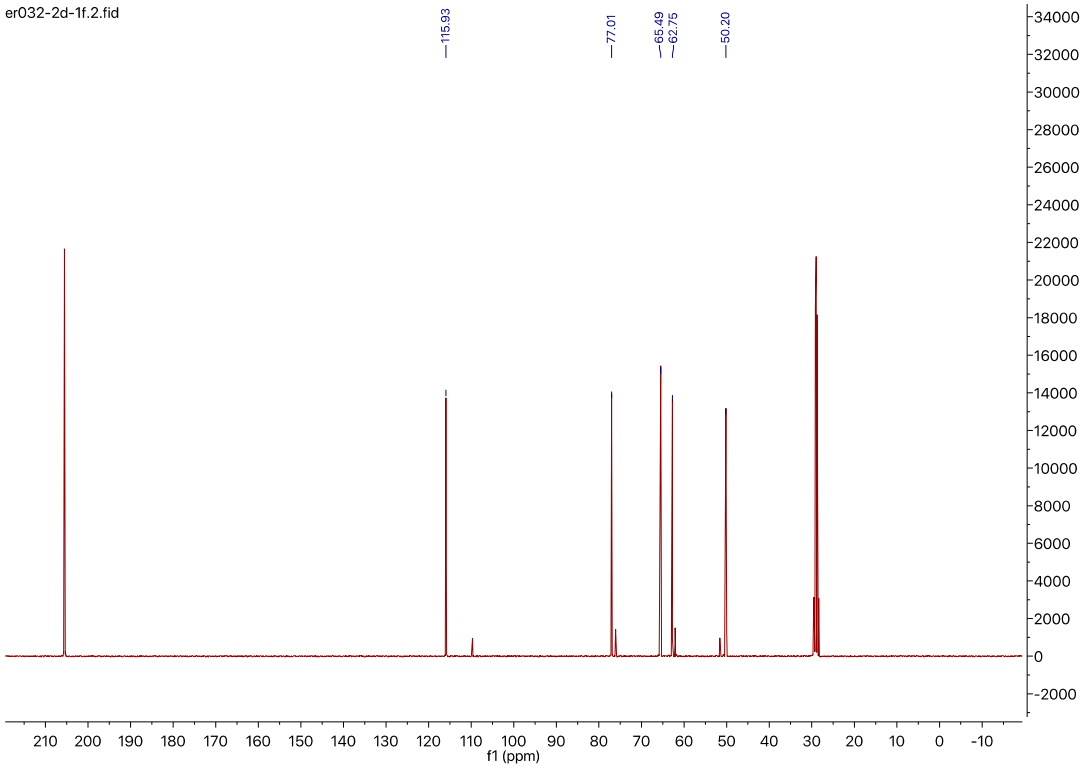


**Figure S3.** $^{13}C$ {$^{1}H$} NMR of **1a** (101 MHz, Acetone-d6) δ = 115.93, 77.01, 65.49, 62.75, 50.20.

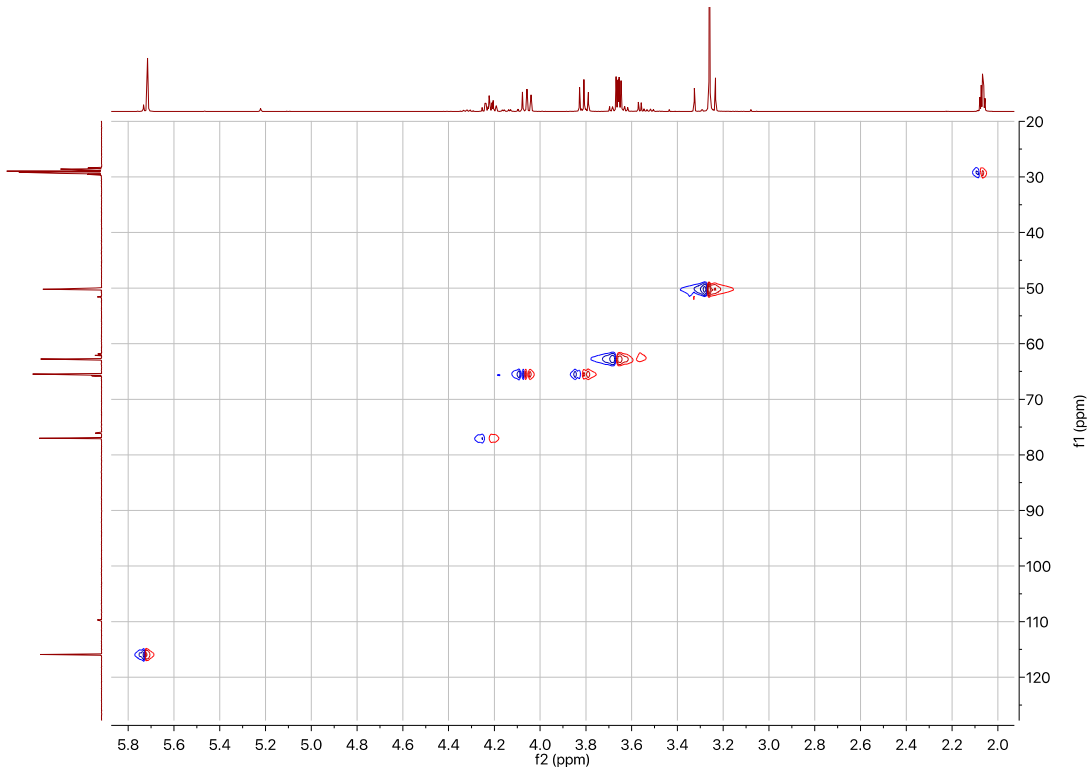


**Figure S4.** HSQC of **1a** (Acetone-d6).

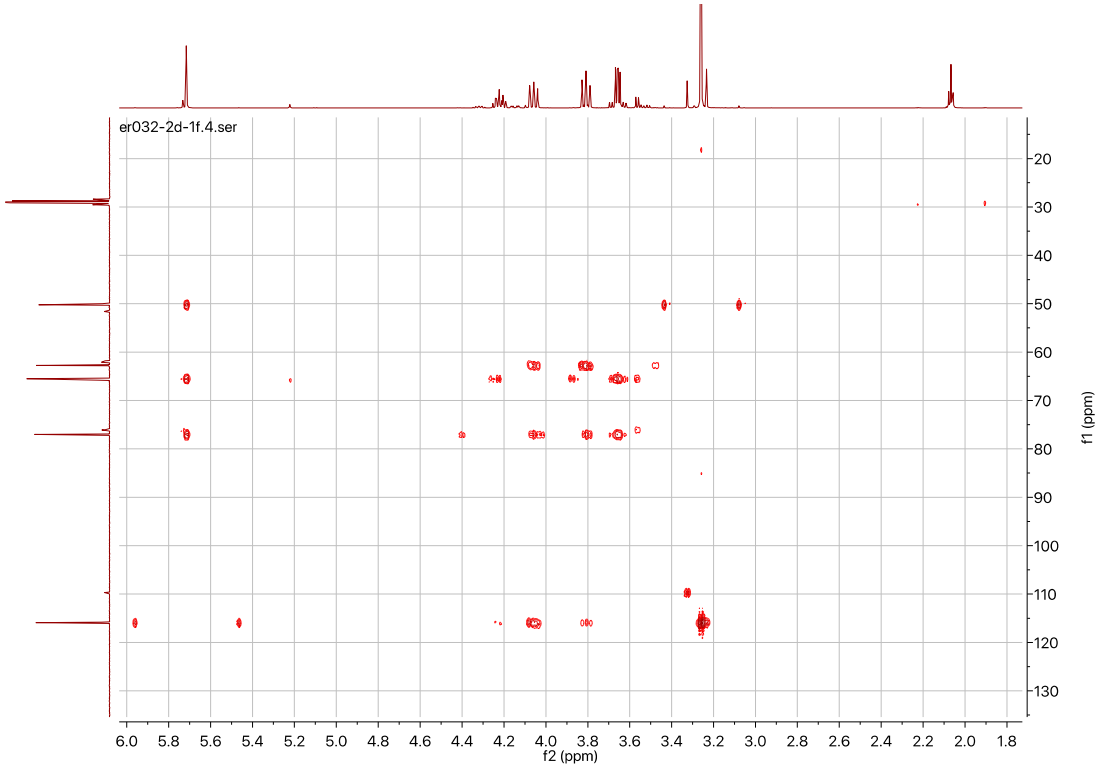


**Figure S5.** HMBC of **1a** (Acetone-d6).

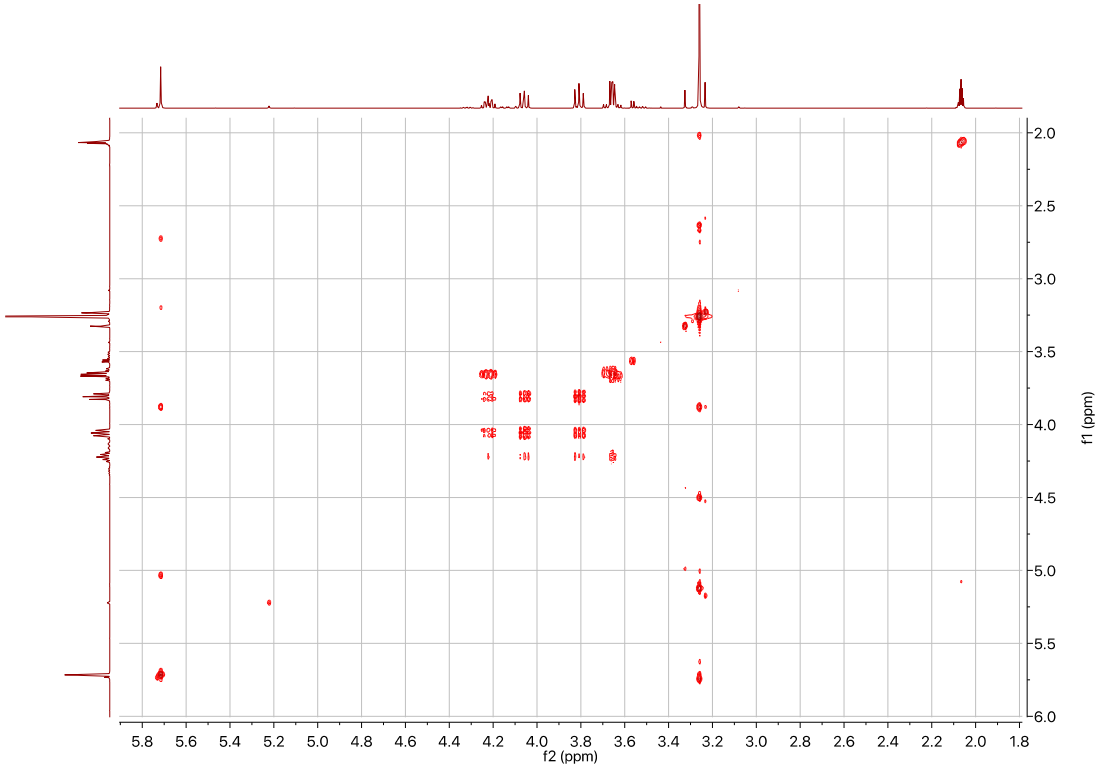


**Figure S6.** COSY of **1a** (Acetone-d6).

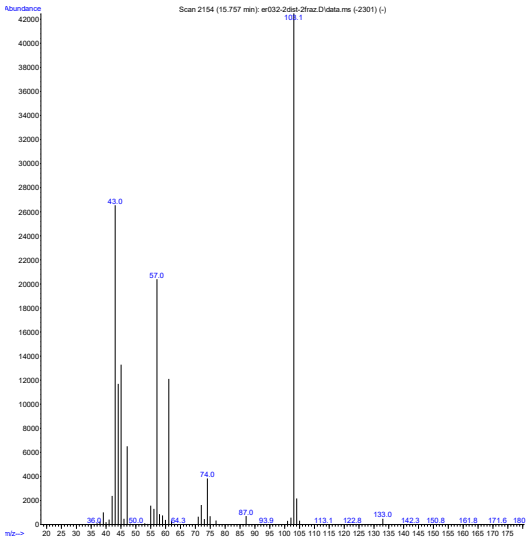


**Figure S7.** MS spectra **1b:** 134 ($M^+$,0);133 (1); 103 (100); 74 (8); 61 (18); 57 (47); 47 (15); 45(28); 44 (14); 43 (46).

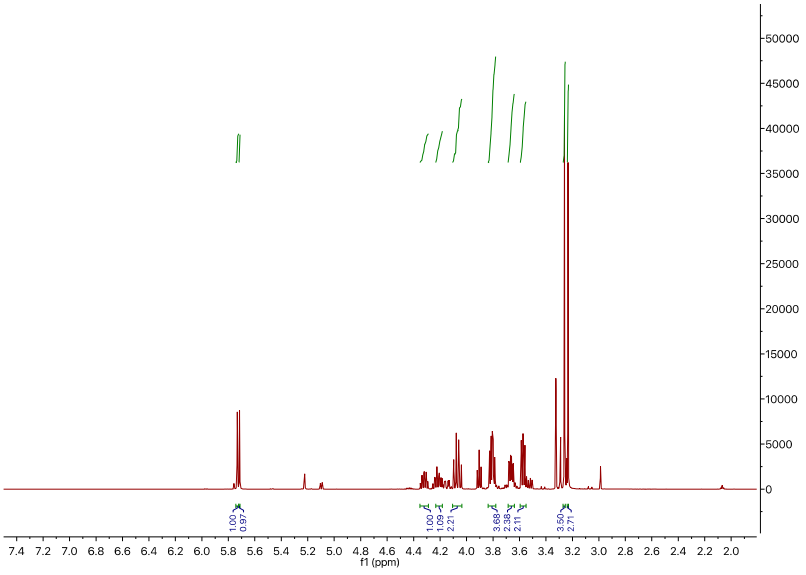


**Figure S8.** $^1$H NMR of **1a,b** (400 MHz, Acetone-d6)**: 1a** δ = 5.72 (s, 1H), 4.23 – 4.18 (m, 1H), 4.11 – 4.04 (m, 1H), 3.84 – 3.78 (m, 1H), 3.66 (ddd, *J*=6.0, 5.2, 2.7, 2H), 3.26 (s, 3H). **1b:** 5.73 (s, 1H), 4.32 (ddt, *J*=6.9, 5.6, 5.0, 1H), 4.11 – 4.04 (m, 1H), 3.84 – 3.78 (m, 1H), 3.57 (dd, *J*=6.0, 5.0, 2H), 3.23 (s, 3H).

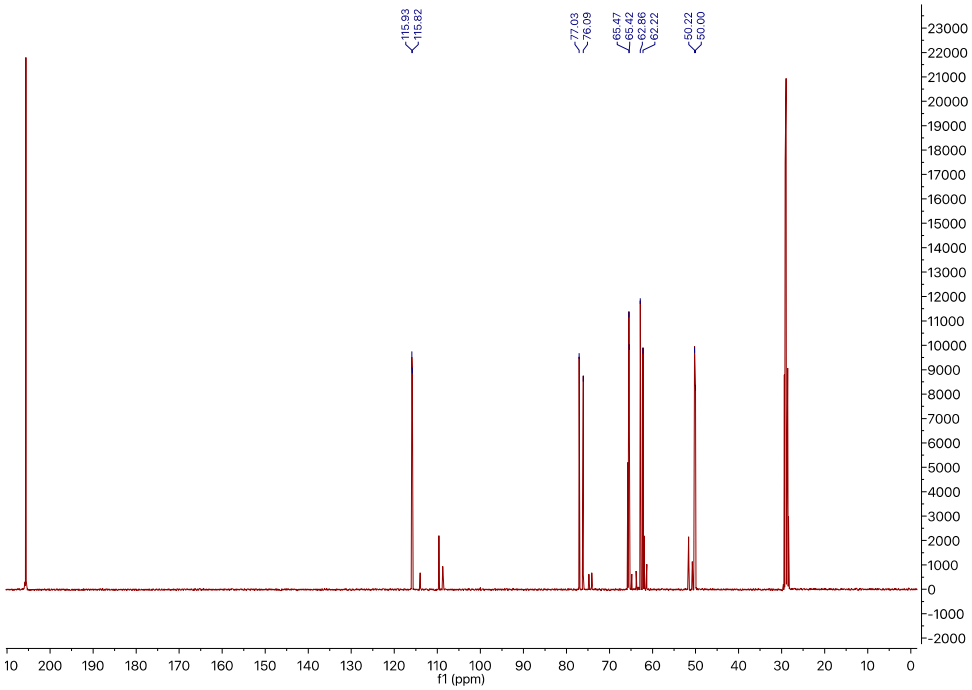


**Figure S9.** $^{13}C$ {$^{1}H$} NMR of **1a,b** (101 MHz, Acetone-d6)**: 1a** δ = 115.93, 77.03, 65.47, 62.86, 50.22, **1b:** δ = 115.82, 76.09, 65.42, 62.22, 50.00.

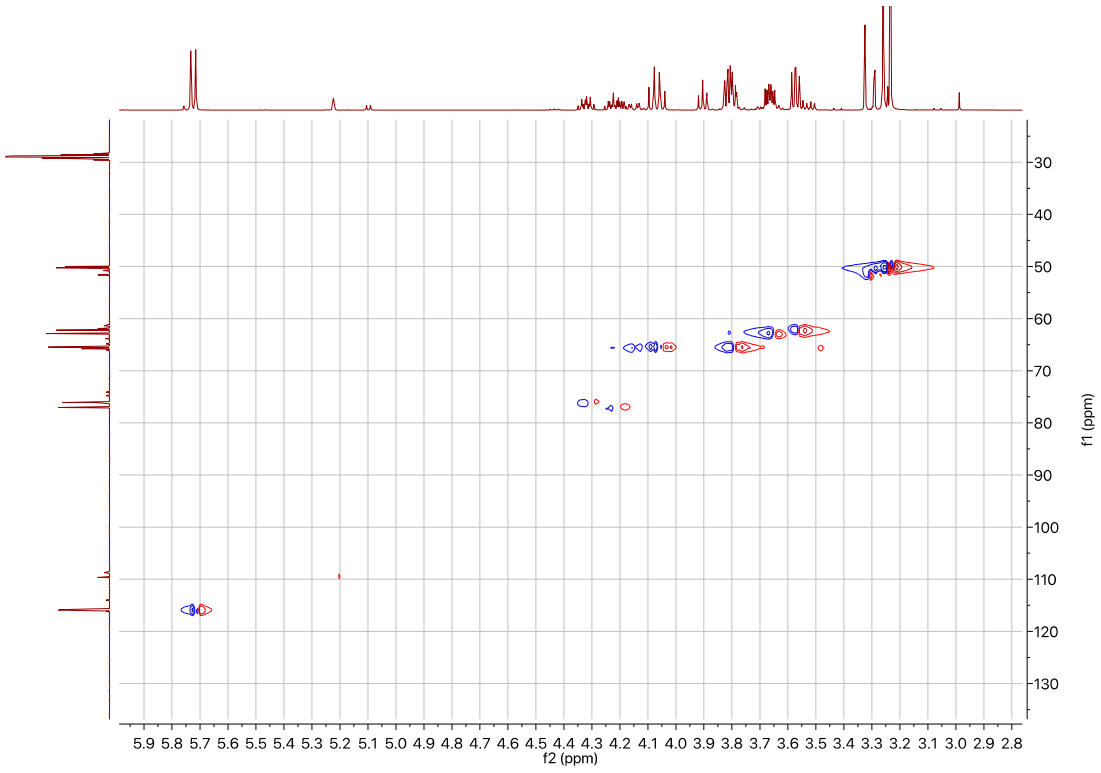


**Figure S10.** HSQC of **1a,b** (Acetone-d6).

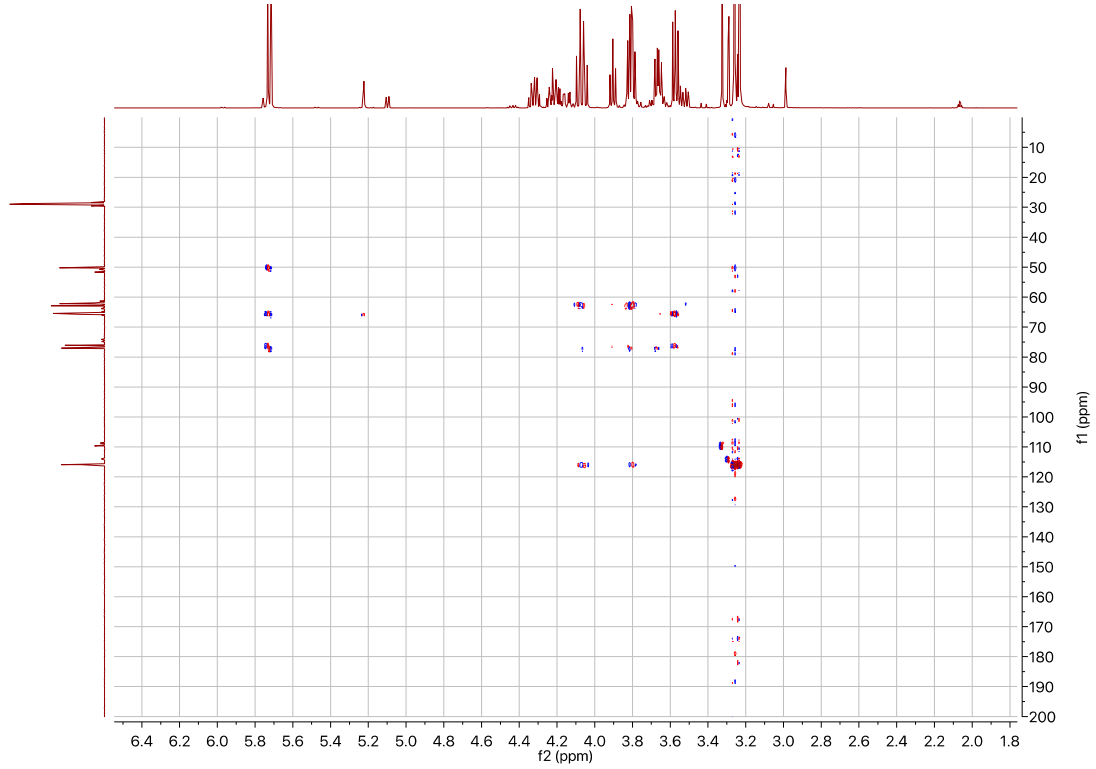


**Figure S11.** HMQC of **1a,b** (Acetone-d6).

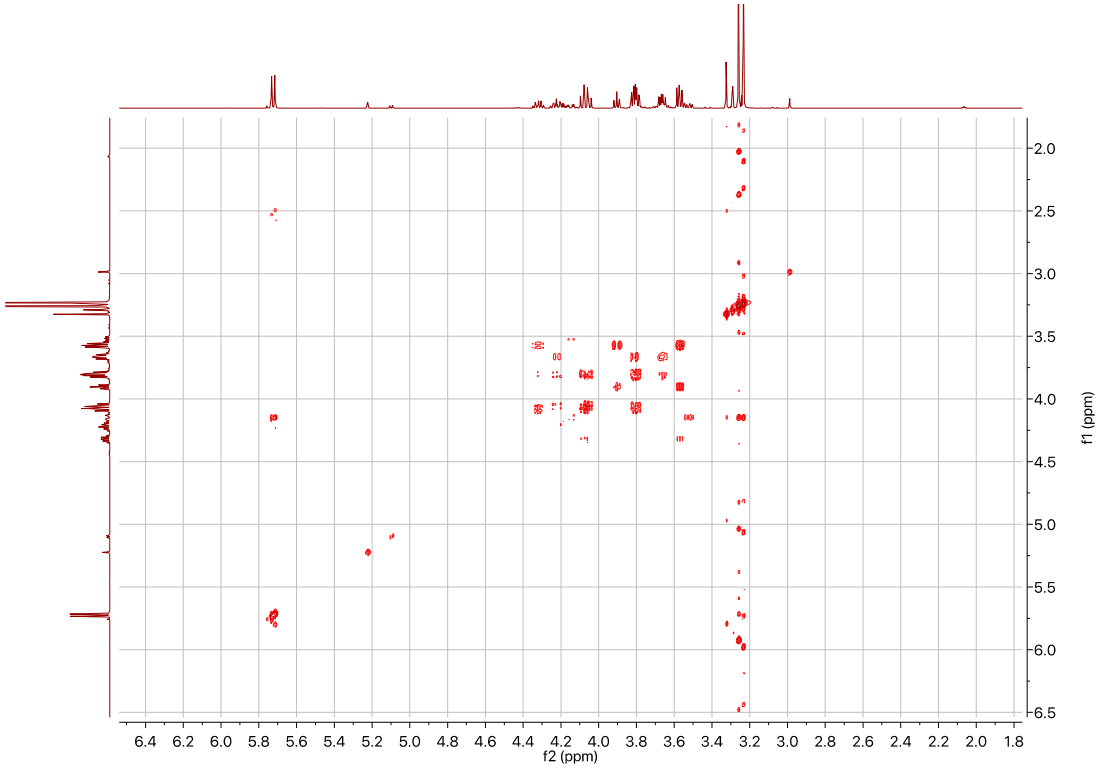


**Figure S12.** COSY of **1a,b** (Acetone-d6).

*1.2. 2,6,7- trioxabyciclo[2.2.1]heptane (2).*

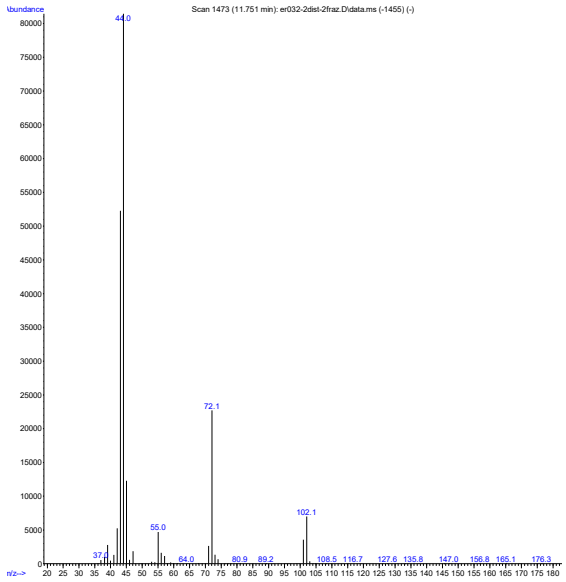


**Figure S13.** GC-MS spectra of **2:** 102 ($M^+$,8);101 (4); 45 (15); 44 (100); 43 (62); 42 (6).

*1.3. 4-(dimethoxymethoxy)methyl)-2-methoxy-1,3-dioxolane (3).*

**3,** as the mixture of the two isomers identified as **3a** and **3b**, was isolated as reported in the Materials and Methods. In Figure S14-S15 the GC/MS spectra of the two isomers (**3a** and **3b**) are reported. The mixture was characterized by $^1$H, $^{13}$C{$^1$H}, DEPT-135, DEPT-90, APT, NOESY, HSQC, HMBC and COSY (Figure S16-S24).

The presence of a mixture of isomers **3a,b** owing a 5-membered ring is supported by the following analytical evidences:

1) The $^1$H NMR spectra (Figure S16) highlights double signals in 1:1 ratio particularly for the protons 2, 4, 8 and 14.

2) The $^{13}$C{$^1$H}, DEPT-135, DEPT-90, APT NMR spectra (Figure S17-S20) show all the peaks relative to **3a,b** as couple of signals in 1:1 ratio clearly separated.

3) COSY (Figure S21) shows the presence of two series of identical coupling patterns for the two isomers **3a** and **3b.** Moreover, any couple of signals in 1:1 ratio do not reveal any crossing interactions. i.e. **6a** at 4.4 ppm does not match with the homologous **6b** at 4.2 ppm.

4) HMBC (Figure S22) shows the correlation spots between H and C in position 6 and 8, while no correlation is present between 2 and 8 thus proving the presence of the 5-membered ring rather than the 6-membered ones.

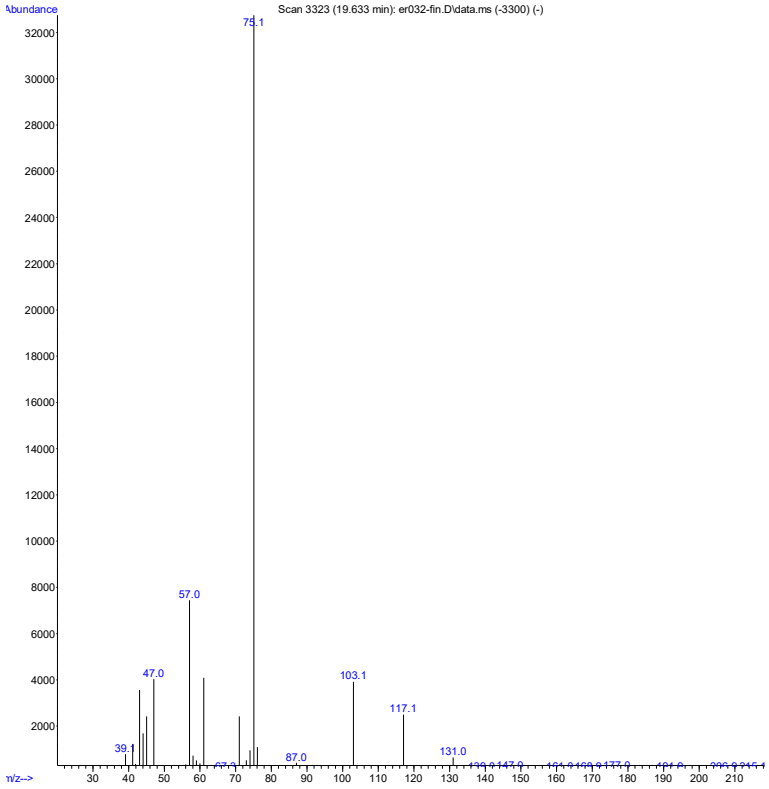


**Figure s14.** MS spectra of **3a:** 208 ($M^+$,0);131 (1); 117 (8); 103 (12); 75 (100); 61 (13); 57 (25); 47 (11); 43(9).

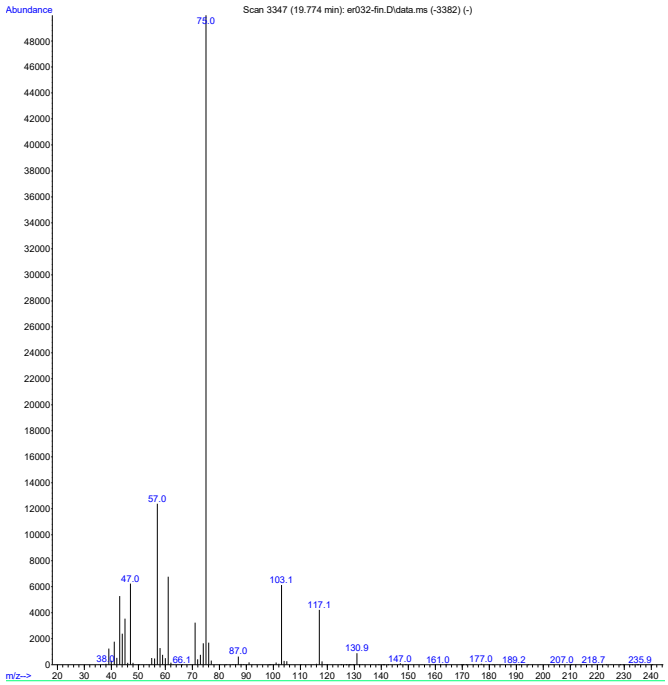


**Figure S15.** MS spectra of **3b:** 208 ($M^+$,0);131 (2); 117 (8); 103 (12); 75 (100); 61 (13); 57 (25); 47 (11); 45(6); 43 (9).

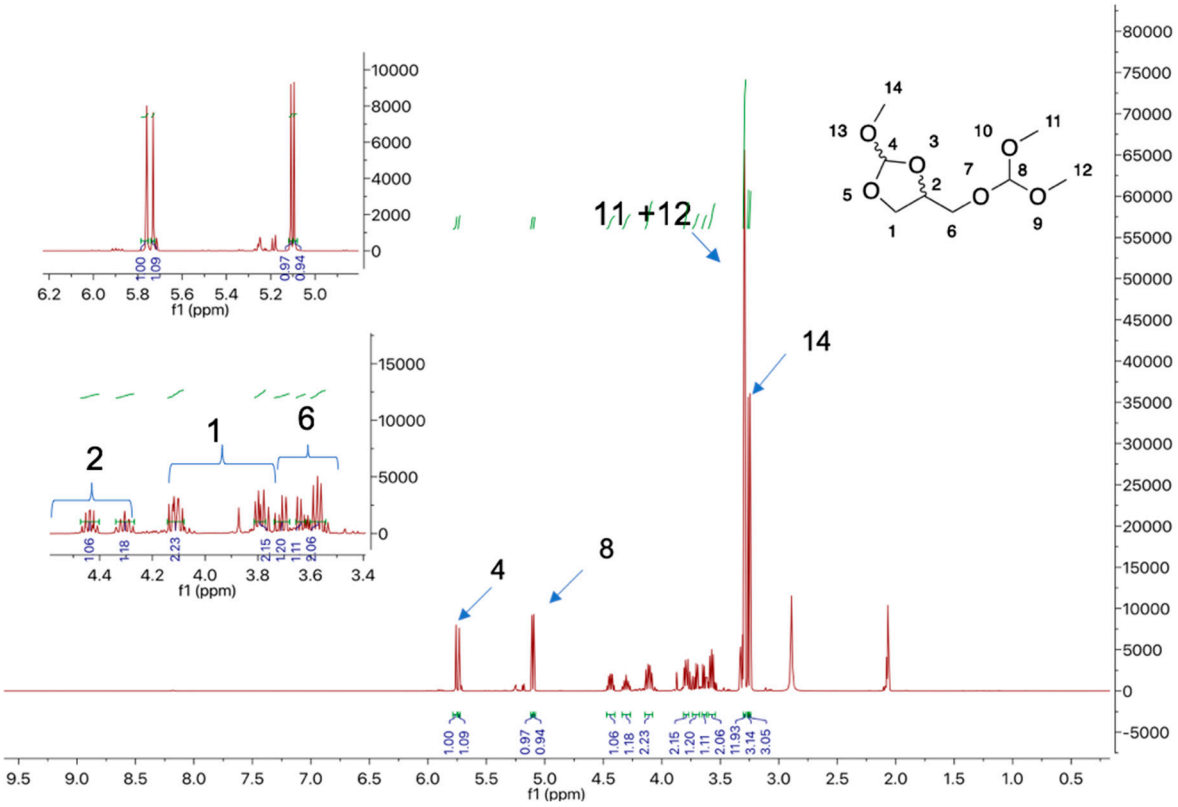


**Figure S16.** [1]H NMR of **3a,b** (400 MHz, Acetone) δ = 5.76 (s, 1H), 5.73 (s, 1H), 5.11 (s, 1H), 5.10 (s, 1H), 4.44 (dq, *J*=6.9, 5.3, 1H), 4.34 – 4.27 (m, 1H), 4.11 (ddd, *J*=7.9, 6.8, 5.6, 2H), 3.81 – 3.77 (m, 2H), 3.71 (dd, *J*=10.6, 6.1, 1H), 3.65 – 3.61 (m, 1H), 3.57 (dd, *J*=6.2, 5.3, 2H), 3.31 – 3.29 (m, 12H), 3.26 (s, 3H), 3.25 (s, 3H).

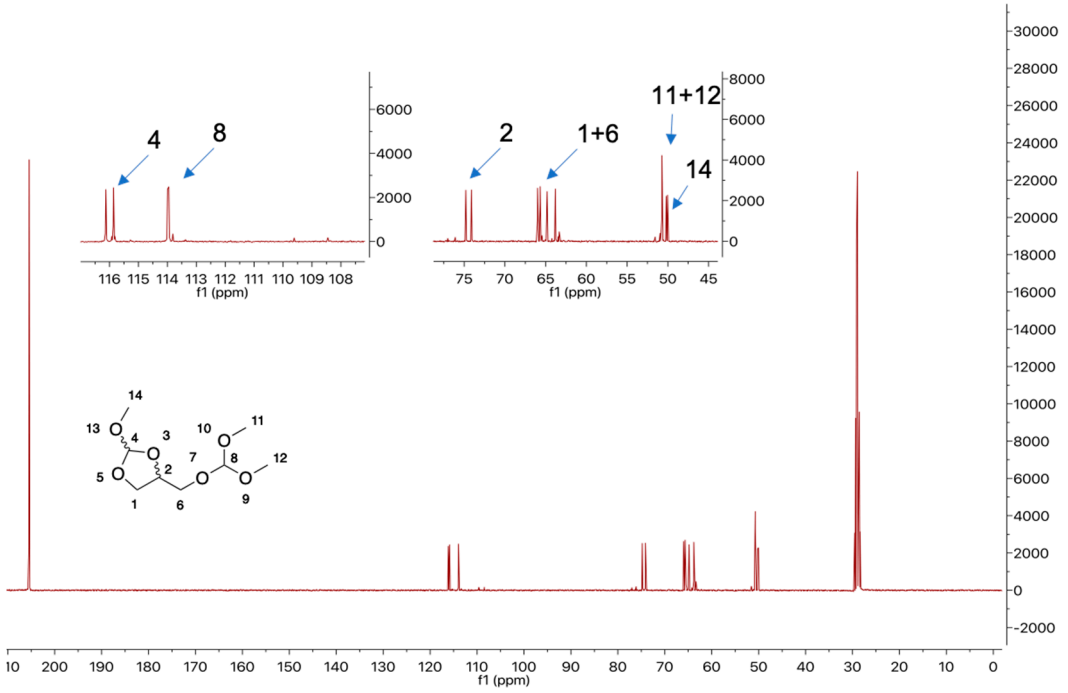


**Figure S17.** $^{13}C$ {$^{1}H$} NMR of **3a,b** (101 MHz, Acetone-d6) δ = 116.13, 115.86, 113.99, 113.95, 74.80, 74.11, 66.00, 65.68, 64.82, 63.80 (d, *J*=2.1), 50.72, 50.71, 50.21, 50.04.

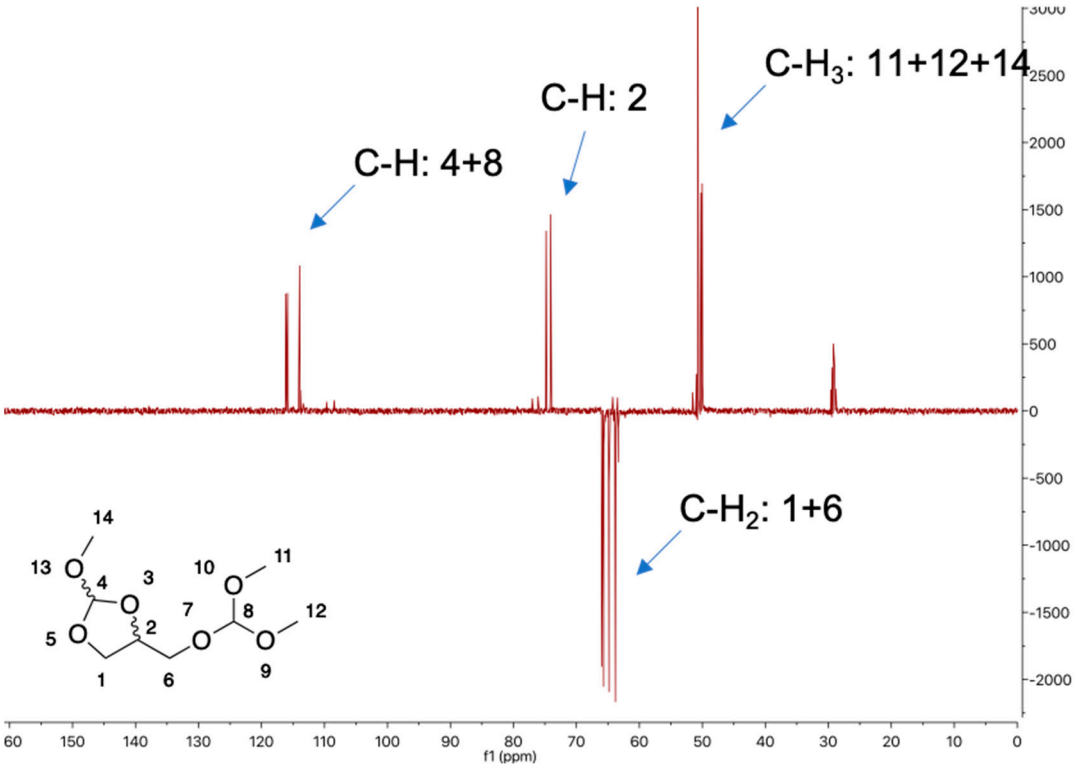


**Figure S18.** DEPT135 of **3a,b** (Acetone-d6).

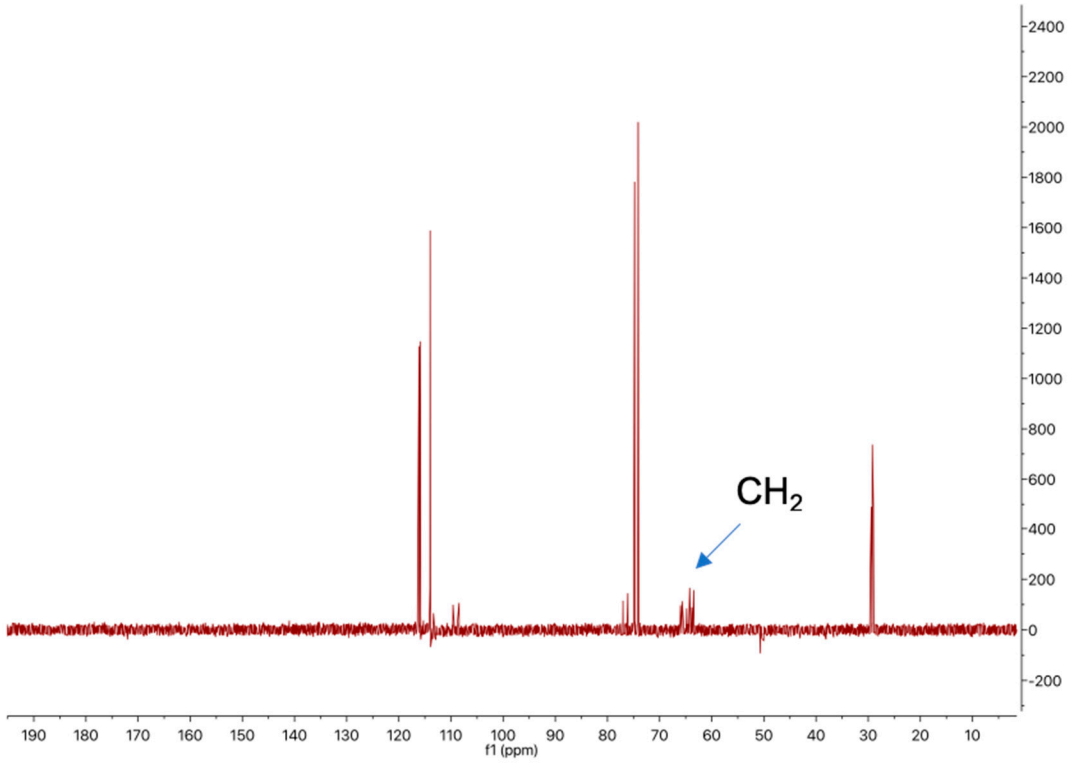


**Figure S19.** DEPT-90 of **3a,b** (Acetone-d6).

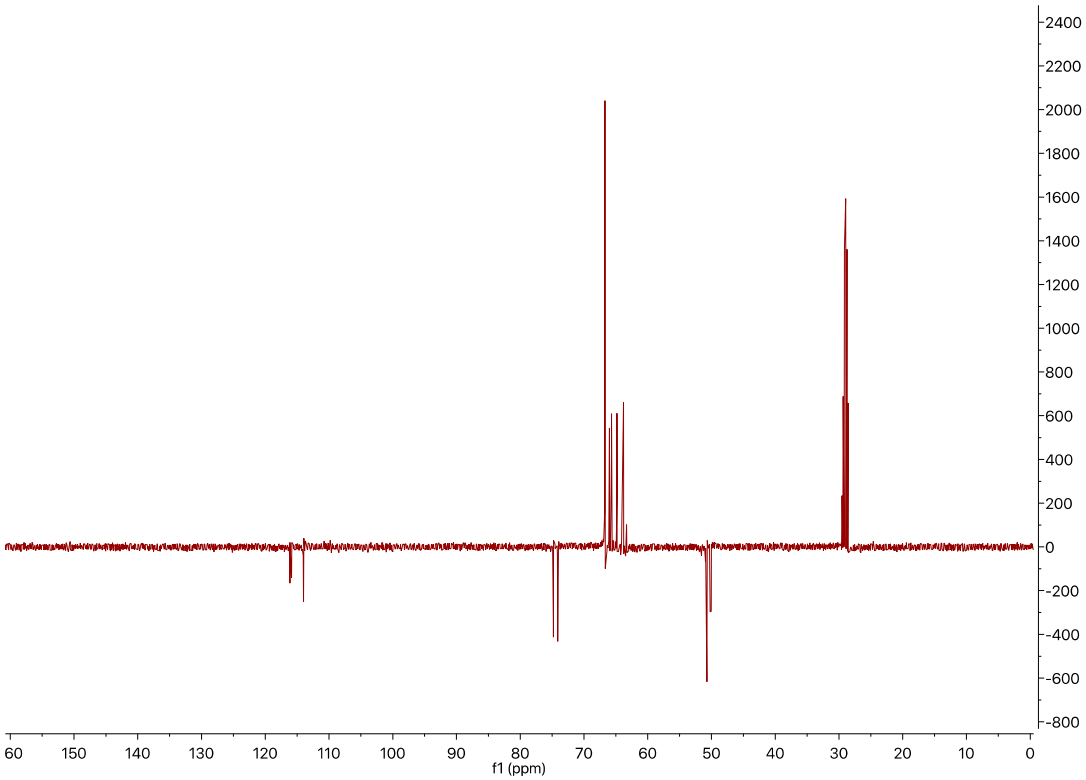


**Figure S20.** ATP of **3a,b** (Acetone-d6).

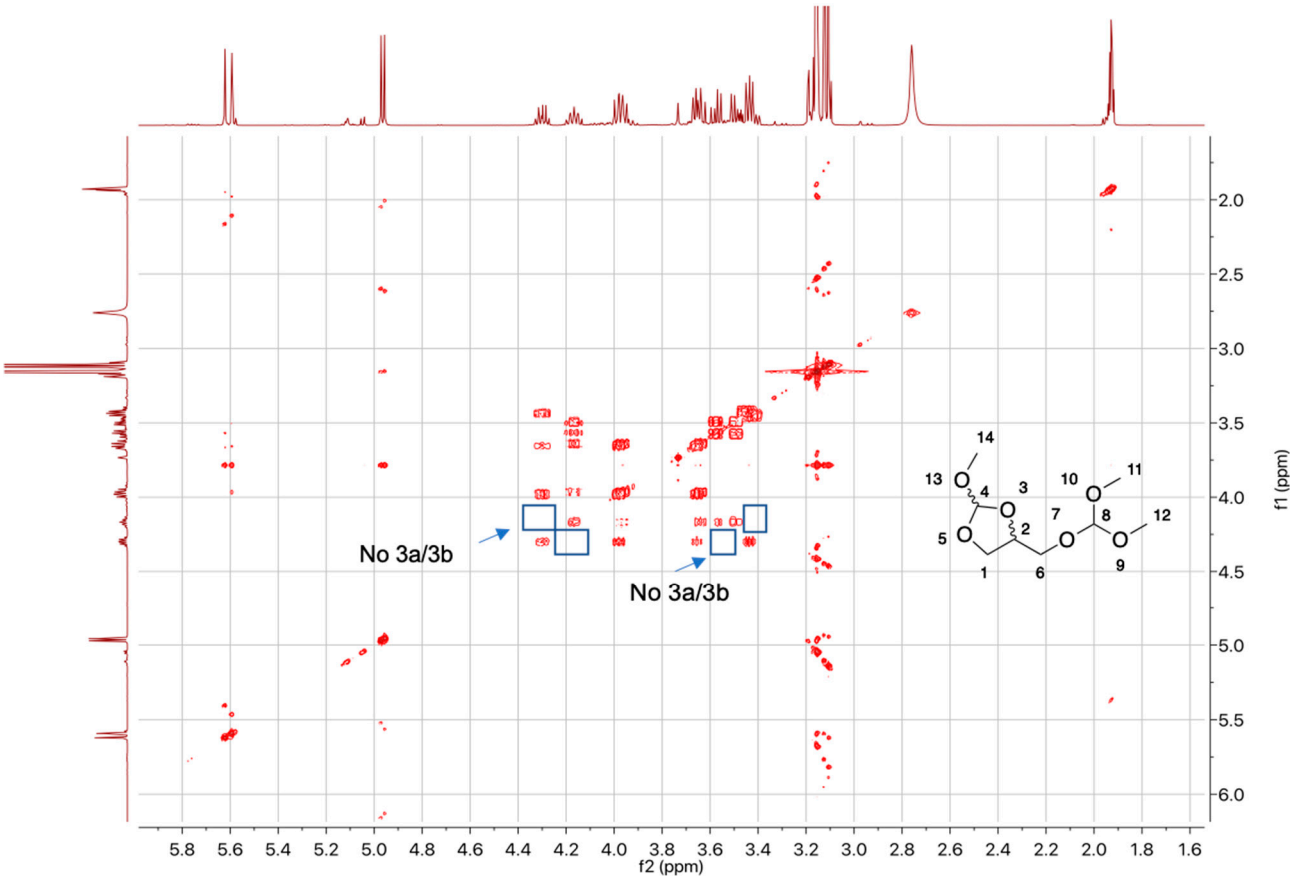


**Figure S21.** COSY of **3a,b** (Acetone-d6).

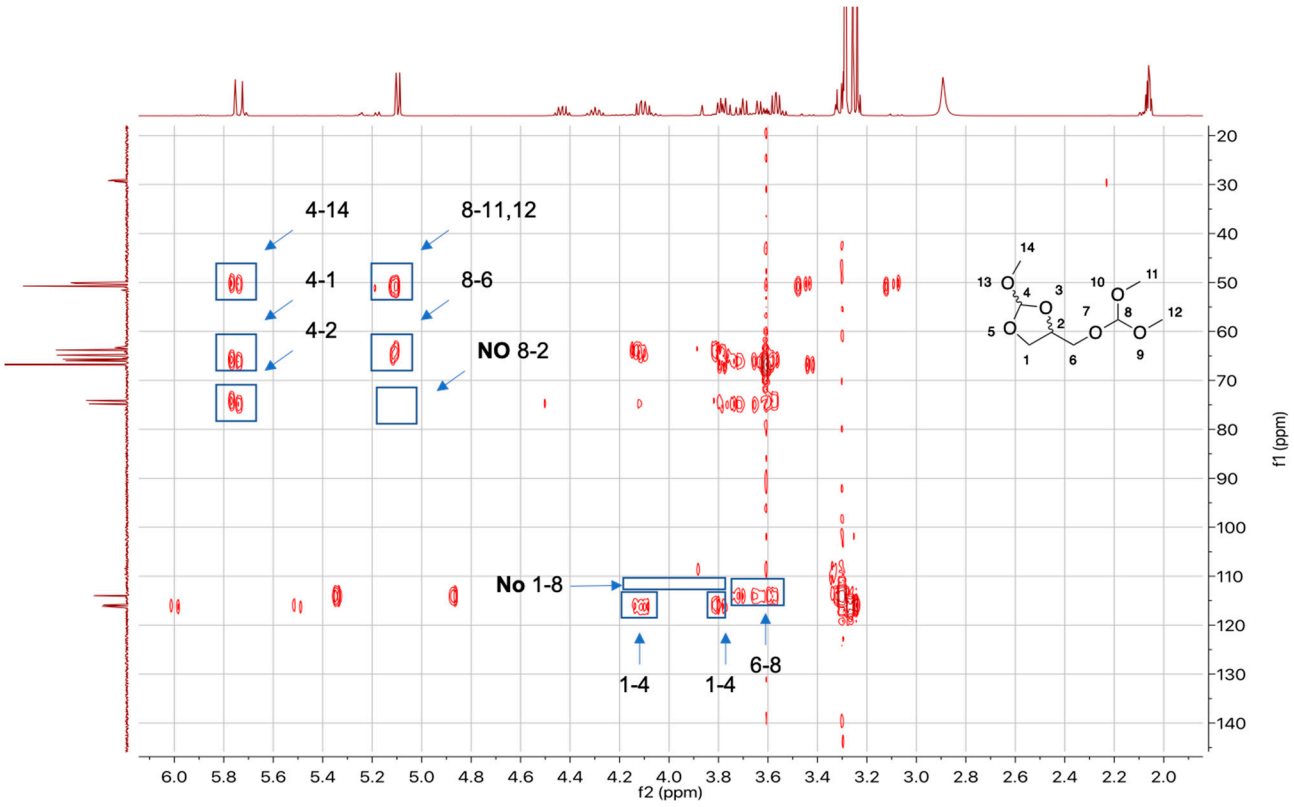


**Figure S22.** HMBC of **3a,b** (Acetone-d6).

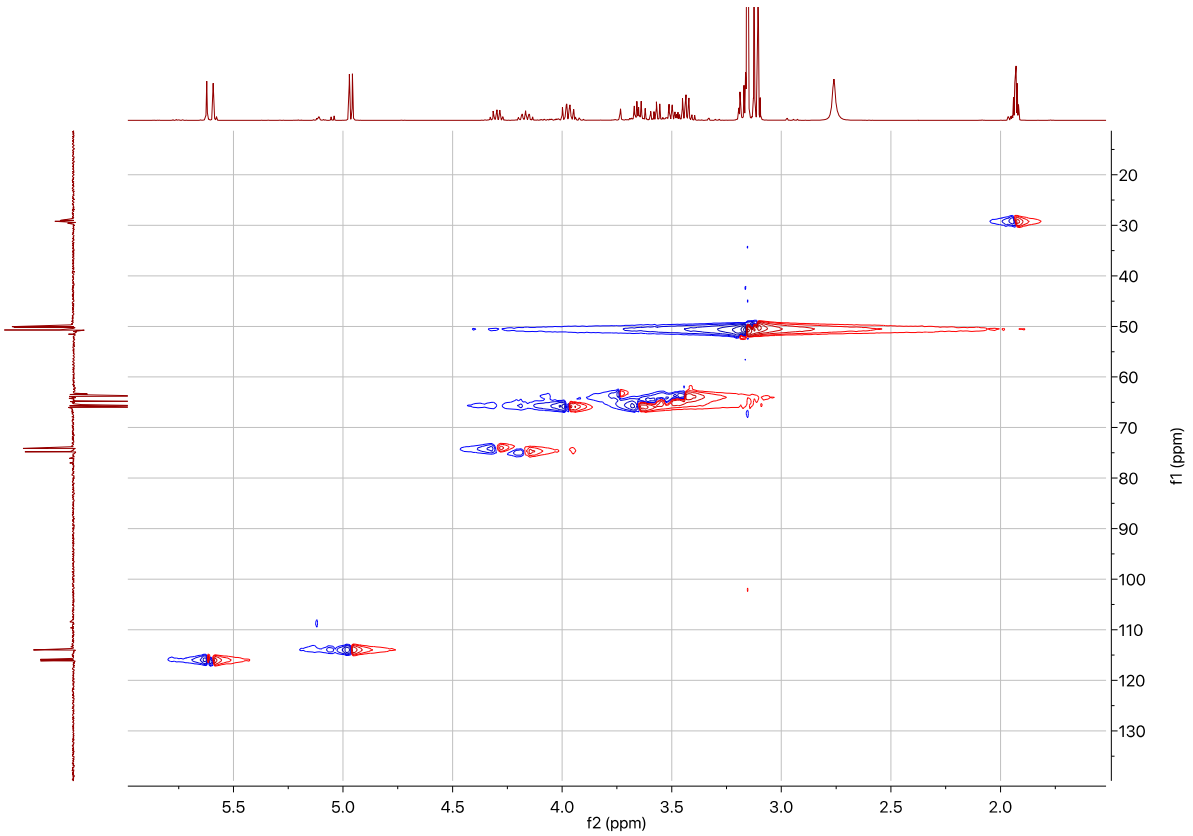


**Figure S23.** HSQC of **3a,b** (Acetone-d6).

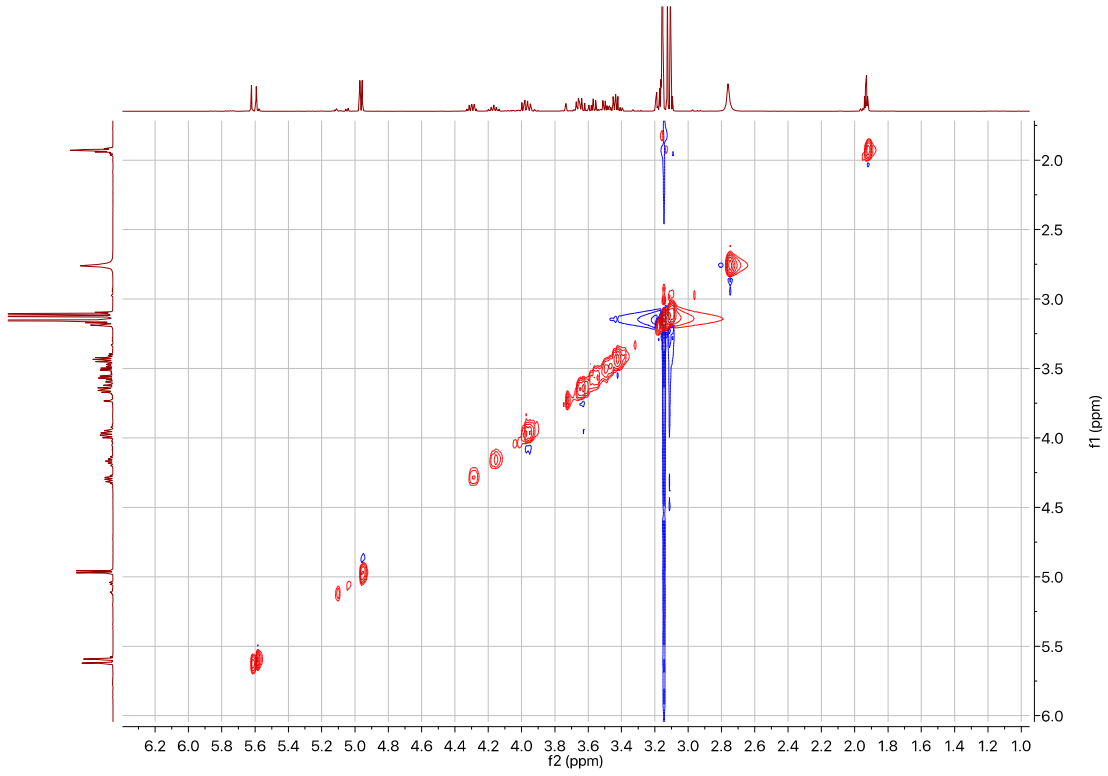


**Figure S24.** NOESY of **3a,b** (Acetone-d6).

## 2. Characterization of Bronsted acidic ionic liquids (BAILs)

### *2.1. Pirydinium paratoluensolfonate (PPTS)*

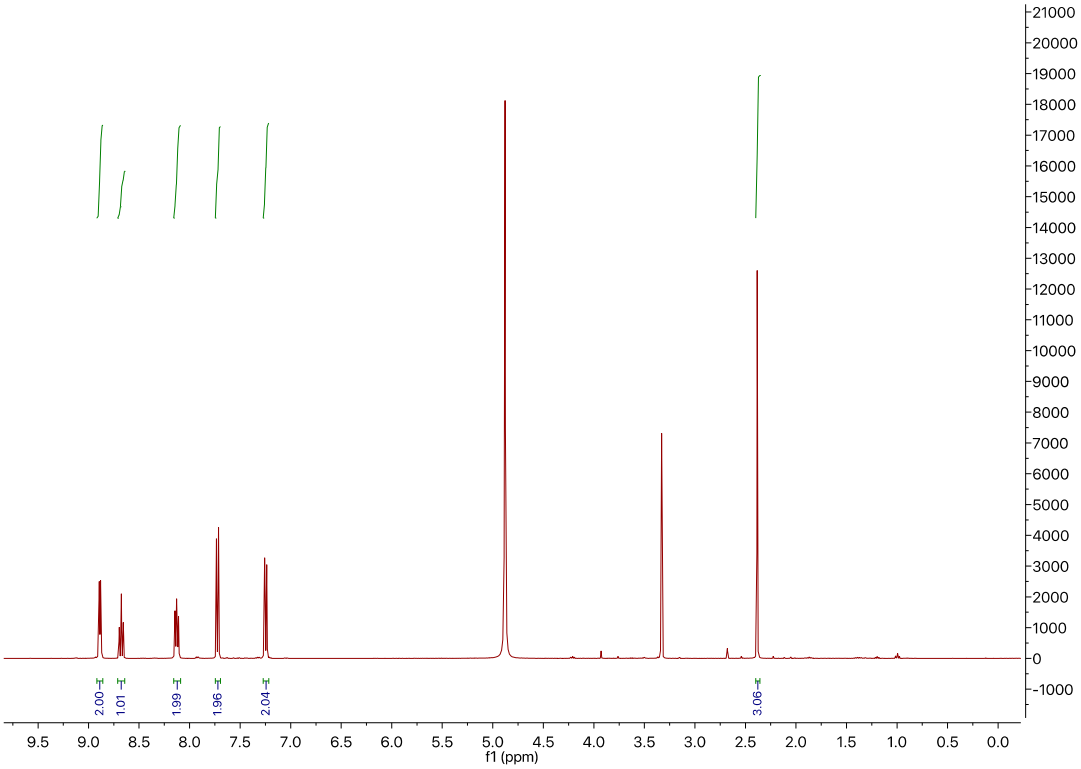


**Figure S25.** $^1$H NMR of PPTS (400 MHz, MeOD) δ = 8.89 (dt, *J*=5.2, 1.6, 2H), 8.68 (tt, *J*=7.9, 1.6, 1H), 8.16 – 8.09 (m, 2H), 7.75 – 7.69 (m, 2H), 7.27 – 7.22 (m, 2H), 2.38 (s, 3H).

*2.2. Diazobicycloundecene bromide (DBUHBr).*

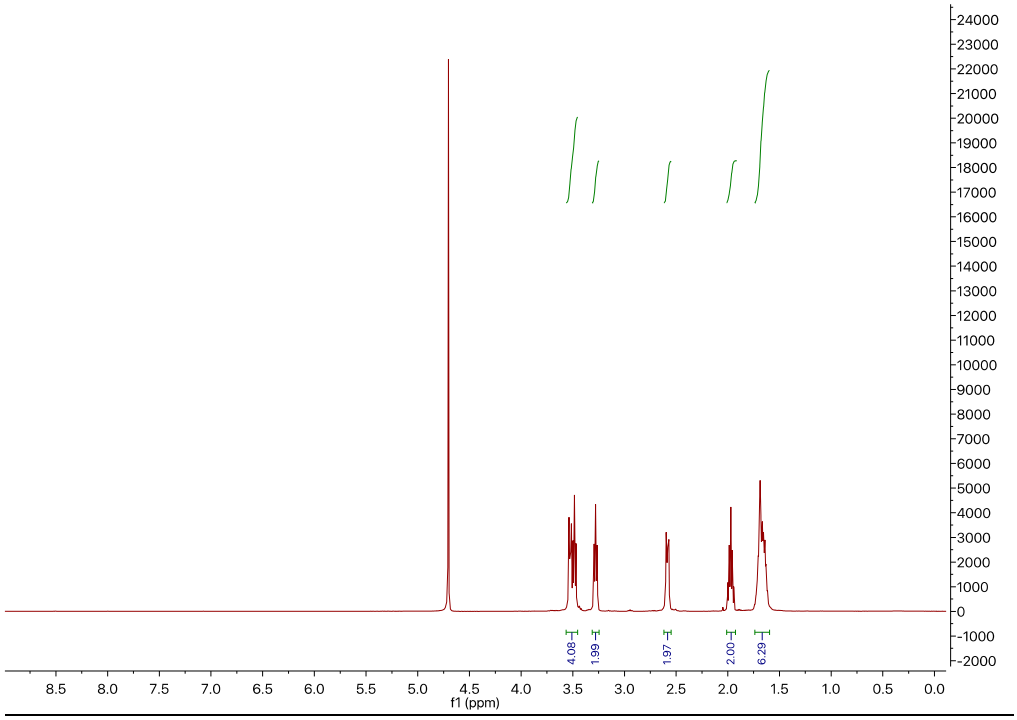


**Figure S26.** $^{1}$H NMR of DBUHBr (400 MHz, $D_2O$) δ = 3.50 (dt, *J*=18.0, 5.6, 4H), 3.28 (t, *J*=5.9, 2H), 2.62 – 2.55 (m, 2H), 1.97 (tt, *J*=7.2, 5.2, 2H), 1.74 – 1.60 (m, 6H).

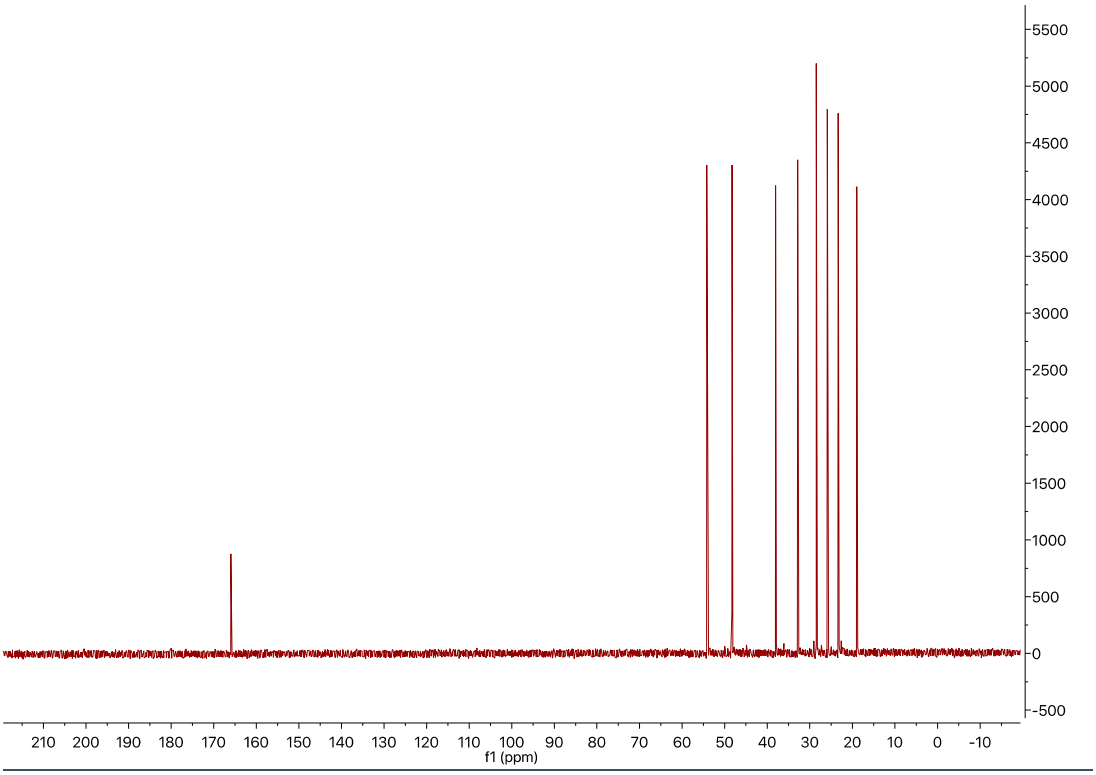


**Figure S27.** $^{13}$C {$^{1}$H} NMR of DBUHBr (101 MHz, $D_2O$) δ = 165.95, 54.19, 48.26, 38.01, 32.87, 28.47, 25.90, 23.34, 18.96.

## *2.3. Butylsolfonylmethylimidazolium hydrogen sulfate (BSMImHSO4)*

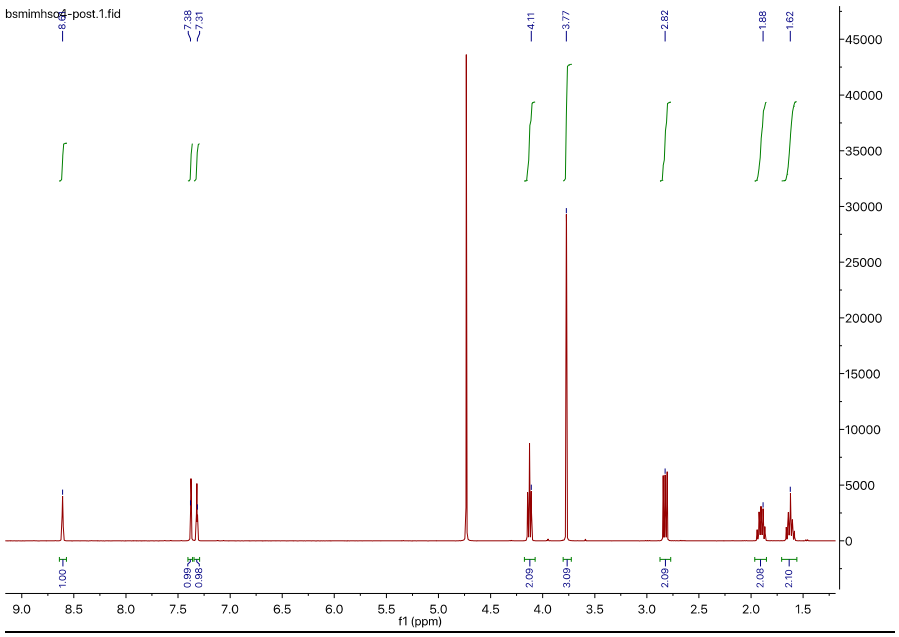


**Figure S28.** $^{1}$H NMR of BSMImHSO$_4$ (400 MHz, D$_2$O) δ = 8.61 (s, 1H), 7.38 (s, 1H), 7.31 (s, 1H), 4.11 (s, 2H), 3.77 (s, 3H), 2.82 (s, 2H), 1.88 (s, 2H), 1.62 (s, 2H).

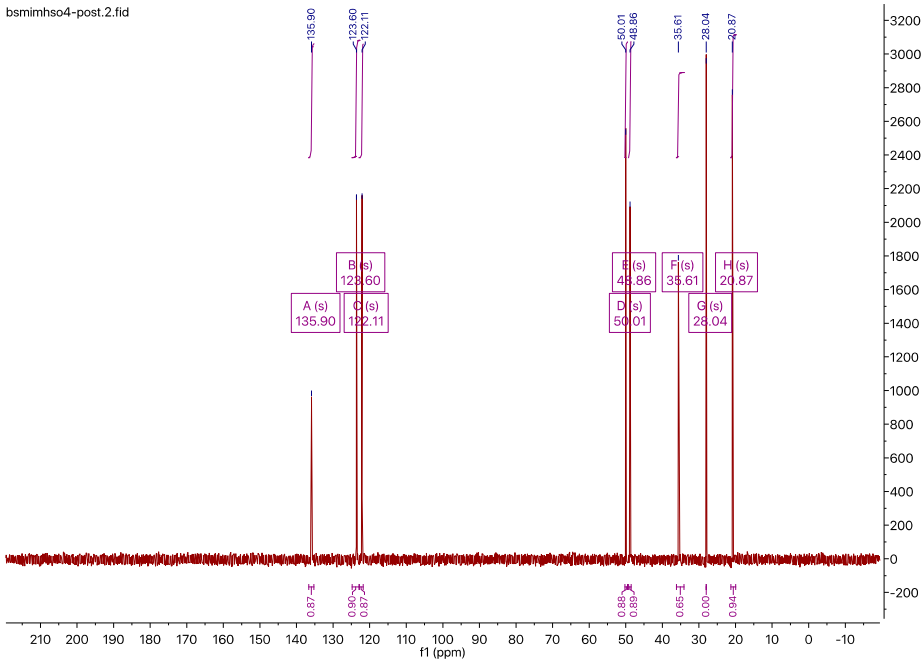


**Figure S29.** $^{13}$C{$^{1}$H} NMR of BSMImHSO$_4$ (101 MHz, D$_2$O) δ = 135.90, 123.60, 122.11, 50.01, 48.86, 35.61, 28.04, 20.87.

## *2.4. Butylsolfonylmethylimidazolium bromide (BSMImBr)*

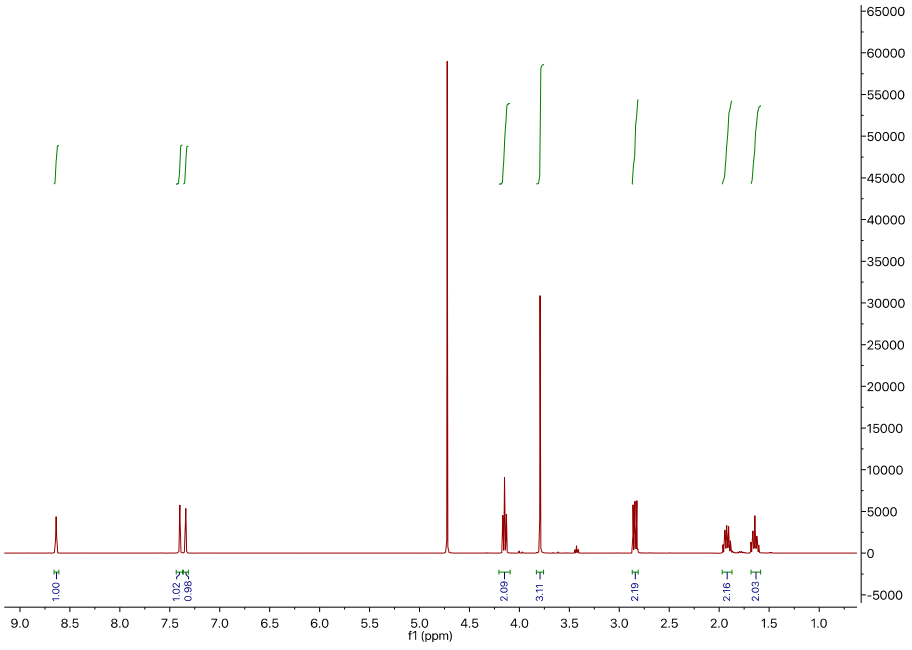


**Figure S30.** $^{1}$H NMR of BSMImBr (400 MHz, $D_2O$) δ = 8.66 – 8.61 (m, 1H), 7.40 (t, *J*=1.8, 1H), 7.34 (t, *J*=1.8, 1H), 4.15 (t, *J*=7.0, 2H), 3.79 (d, *J*=0.6, 3H), 2.87 – 2.81 (m, 2H), 1.97 – 1.87 (m, 2H), 1.68 – 1.58 (m, 2H).

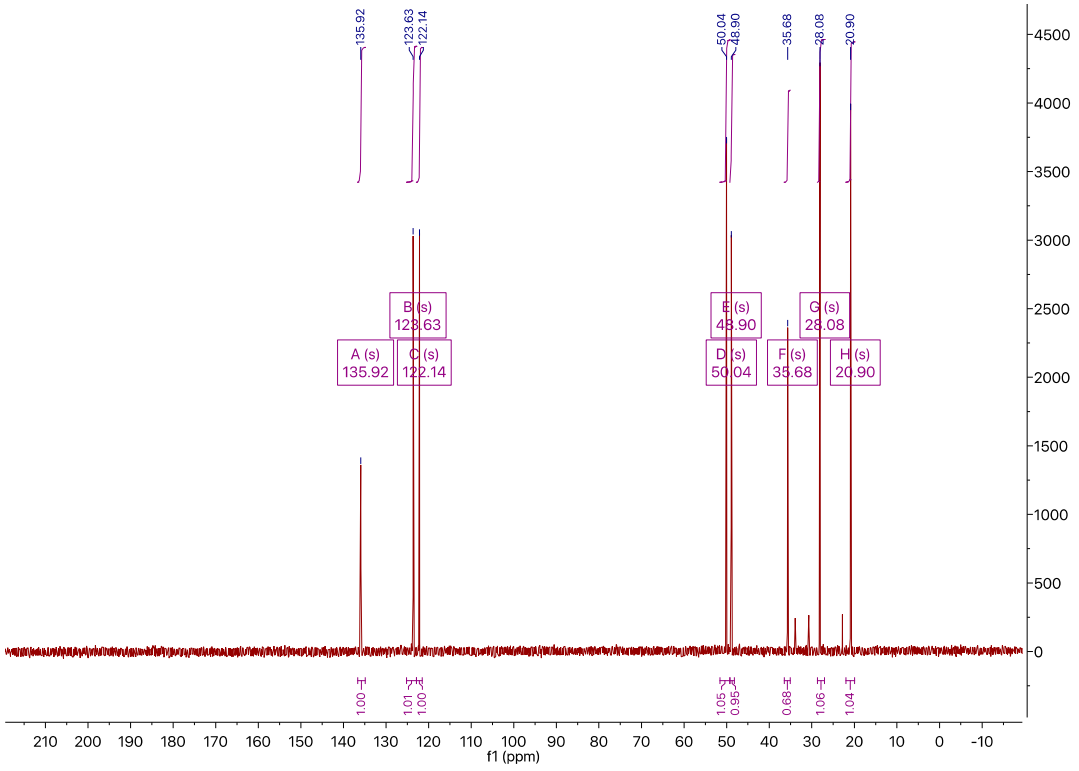


**Figure S31.** $^{13}C\{^{1}H\}$ NMR of BSMImBr (101 MHz, $D_2O$) δ = 135.92, 123.63, 122.14, 50.04, 48.90, 35.68, 28.08, 20.90.

## 3. Reaction profiles

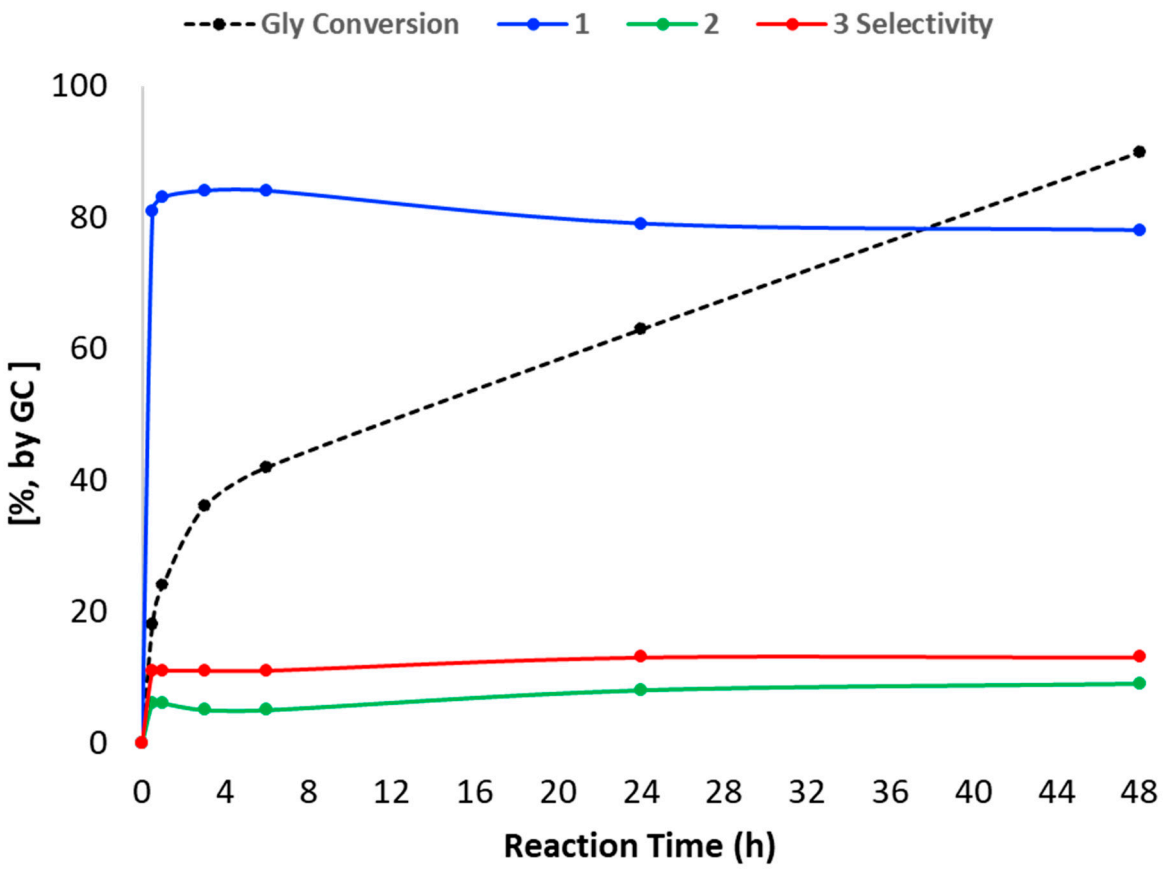


**Figure S32.** Conversion of Gly and products selectivity for the catalyst-free reaction between Gly and $HC(OCH_3)_3$ in function of the reaction time at room temperature and Q=1.

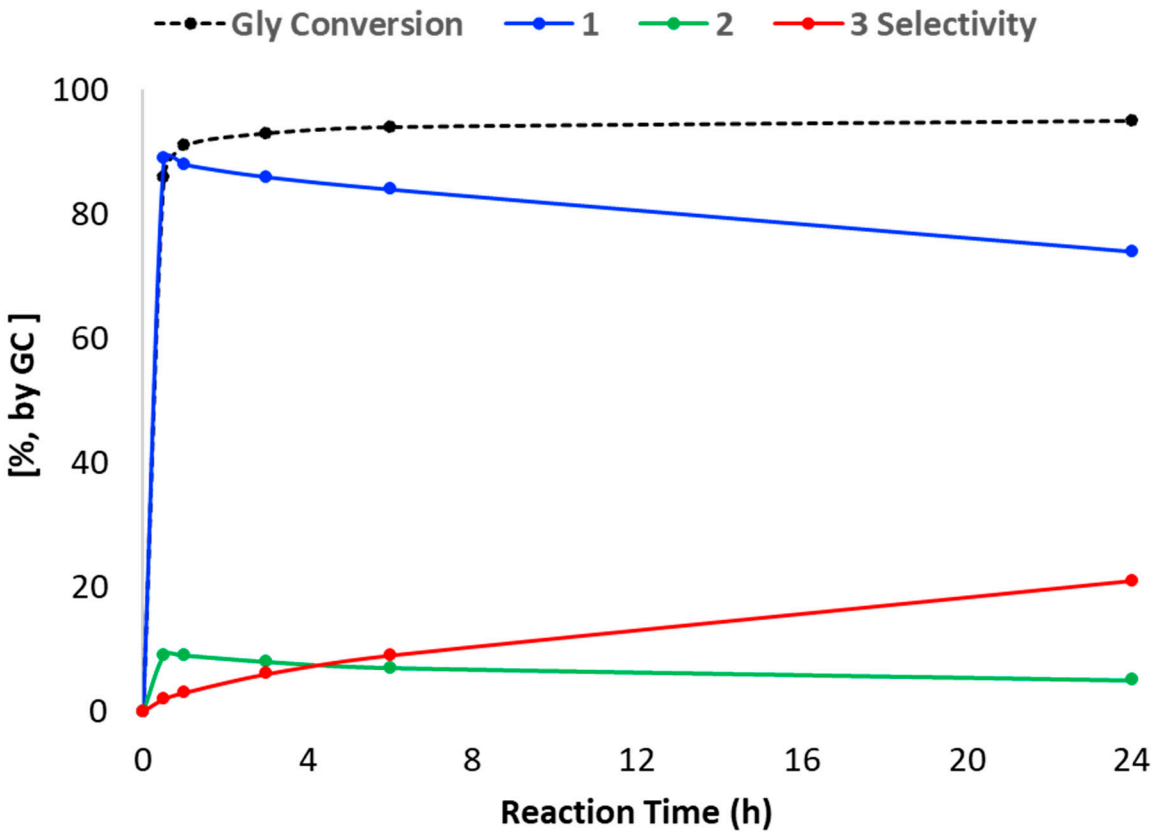


**Figure S33.** Conversion of Gly and products selectivity for the catalyst-free reaction between Gly and $HC(OCH_3)_3$ in function of the reaction time at room temperature and Q=10.

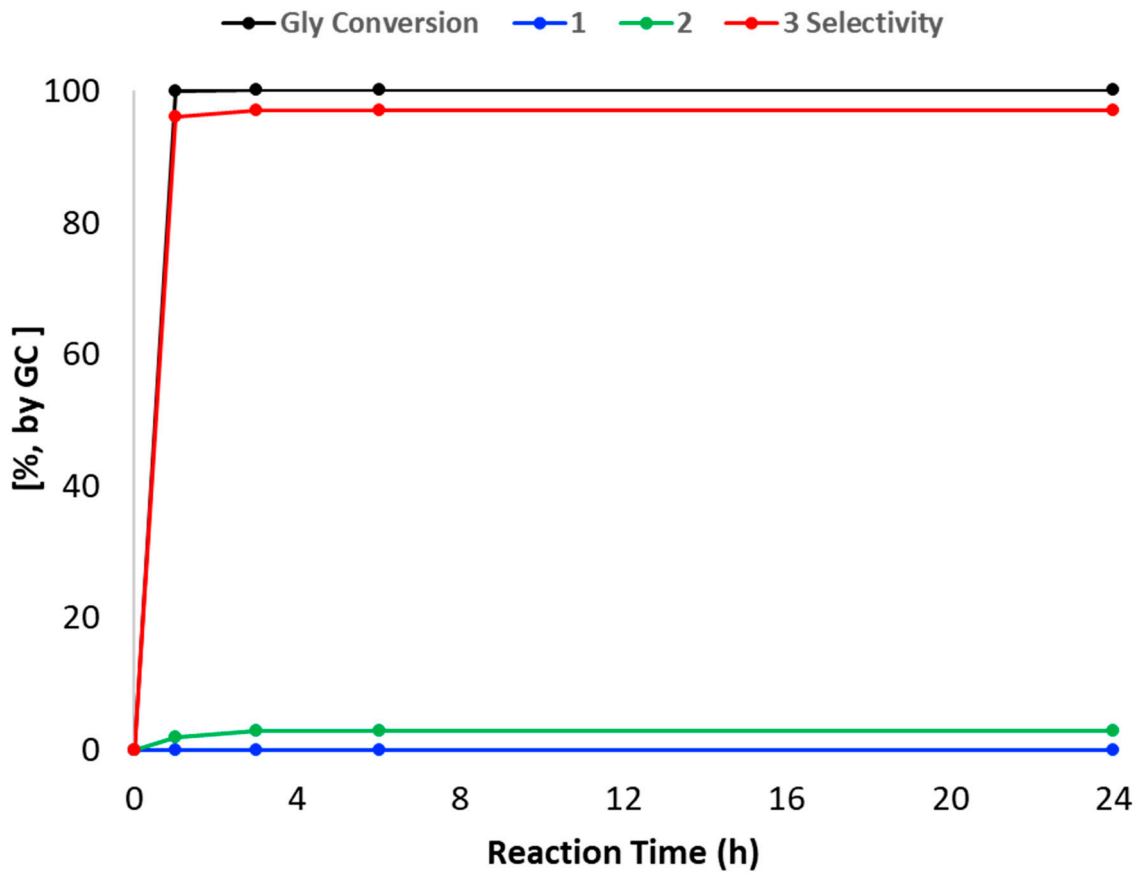


**Figure S34.** Conversion of Gly and and products selectivity for the reaction between $HC(OMe)_3$ and Gly in presence of Pyr-PTSA (10% $w/w_{Gly}$) in function of the reaction time at room temperature and Q=10.

## 4. Reaction of glycerol with $HC(OMe)_3$ in presence of sulfuric acid as catalyst

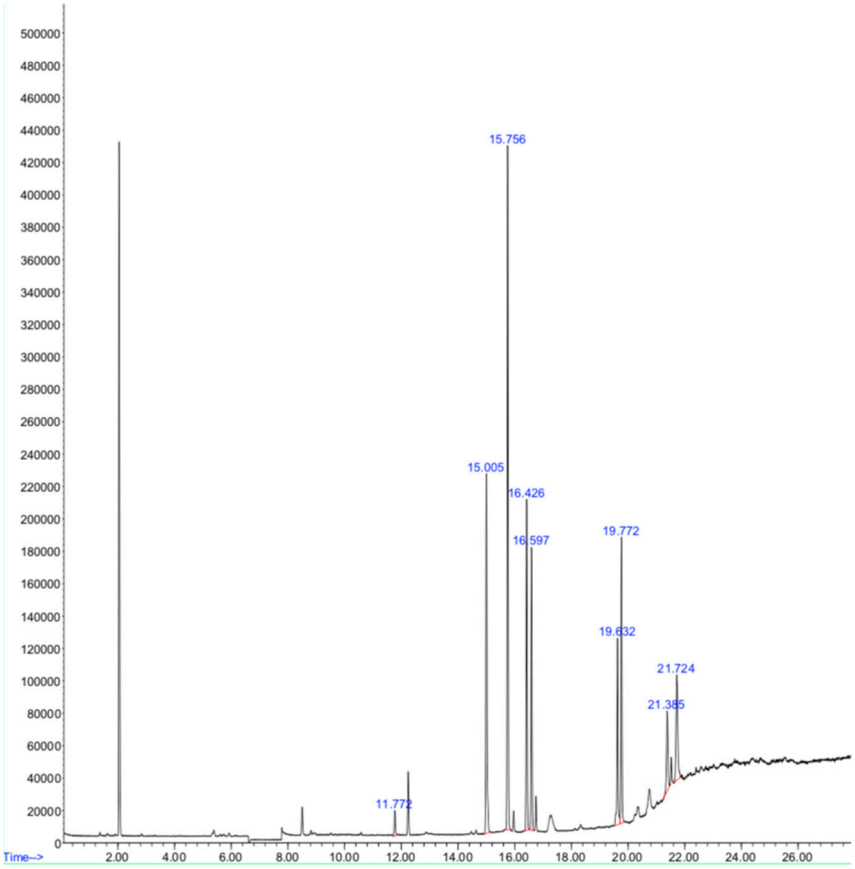


**Figure S35.** GC-MS chromatograph of the reaction between $HC(OMe)_3$ and Gly (Q=10, 90°C, 24h) in presence of sulfuric acid.

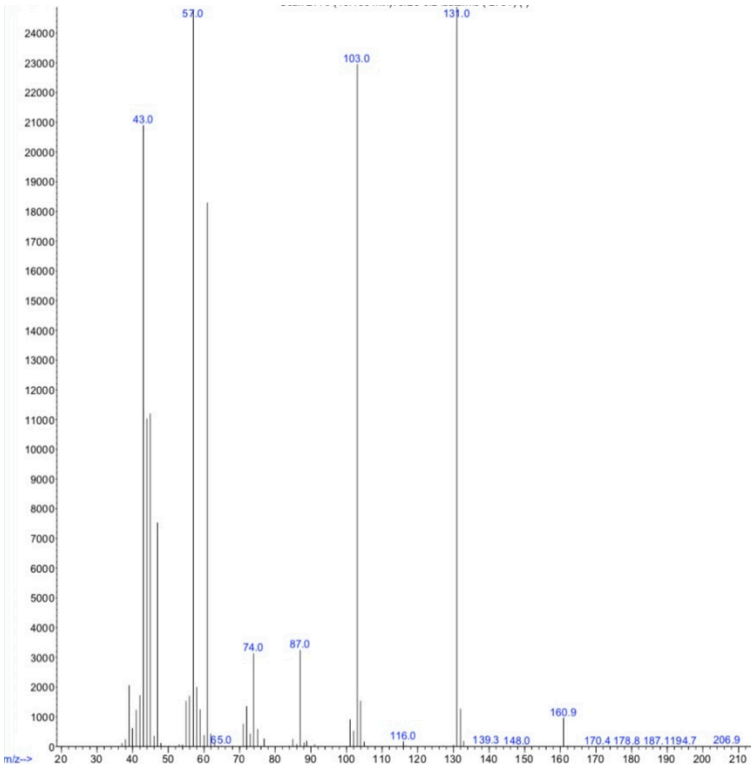


**Figure S36.** MS spectra of the undefined compounds with retention time: 16.43 min. 161 (4);131 (95); 103 (84); 87 (13); 74 (12); 61 (84); 57 (100); 47 (32); 45(44); 44 (49); 43 (85).

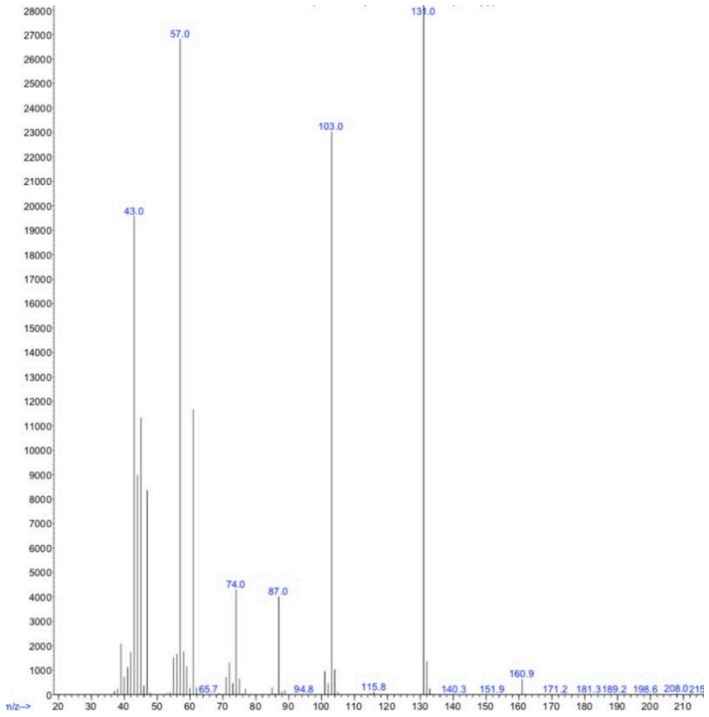


**Figure S37.** MS spectra of the undefined compounds with retention time: 16.59 min. 161 (2);131 (100); 103 (82); 87 (13); 74 (15); 61 (41); 57 (95); 47 (30); 45(40); 44 (32); 43 (69).

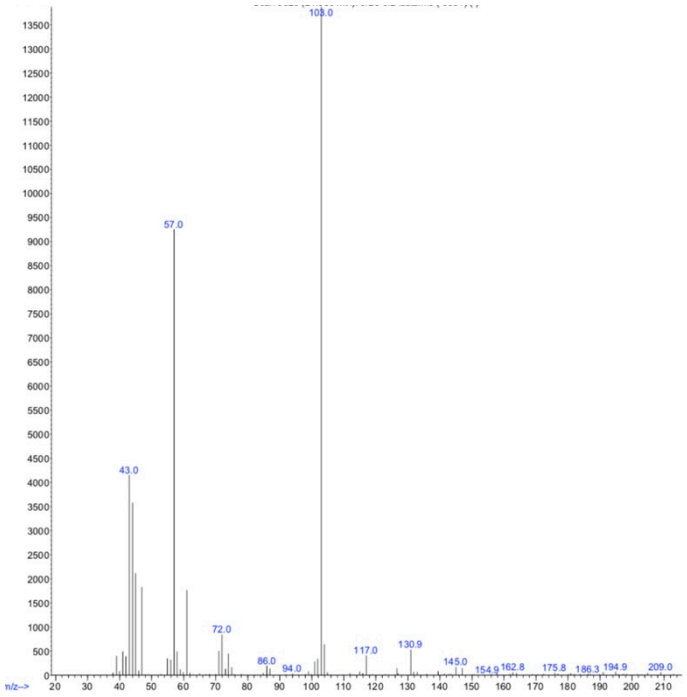


**Figure S38.** MS spectra of the undefined compounds with retention time: 16.43 min. 209 (1); 195 (1); 163 (1); 145 (1); 103 (100); 61 (12); 57 (67); 47 (13); 45(15); 44 (26); 43 (30).

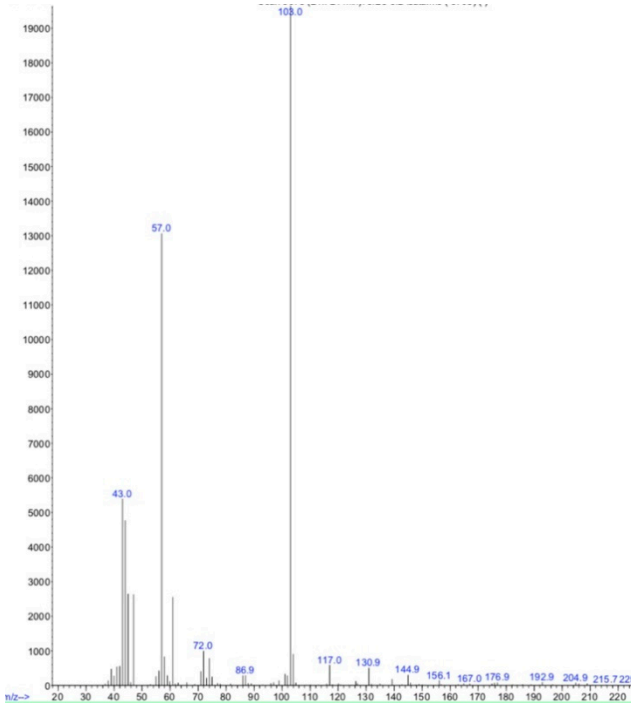


**Figure S39.** MS spectra of the undefined compounds with retention time: 21.72 min. 205 (1); 193 (1); 177 (1); 145 (2); 103 (100); 61 (12); 57 (67); 47 (12); 45(14); 44 (24); 43 (28).