Electronic supplementary information for

Cu/*N*-oxyl-catalyzed aerobic oxidative esterification to oxalic acid diesters from ethylene glycol via highly selective intermolecular alcohol oxidation

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Experimental details

Instrumental and reagents

GC analyses were performed on Shimadzu GC-2014 equipped with a flame ionization detector and a Rtx-1 or InertCap-5 capillary column (0.25 mm ID ×30 m length). GC-MS spectra were recorded on Shimadzu GCMS-QP2010 equipped with a InertCap5 capillary column at an ionization voltage of 70 eV. Liquid-state ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on JEOL JNM-ECA 500. ^{1}H and ^{13}C spectra were measured at 500 and 125 MHz, respectively, using tetramethylsilane as an internal reference (δ = 0 ppm), and ^{19}F NMR spectra were measured at 470 Hz using CF_3COOH as an external reference (δ = –76.50 ppm). Cold spray ionization mass spectrometry (CSI-MS) (in CH_3CN) was performed on a JEOL JMS-T100CS spectrometer (using an orifice voltage of 10 V for positive ions, a sample flow of 0.1 mL/min, a spray temperature of −10°C, and an ion source at room temperature). UV-Vis spectra were measured on a Shimadzu UV-3600 plus. Column chromatography on silica gel was performed by using Biotage Isolera. The copper sources, ligands, substrates, aminoxyl radicals (*N*-oxyls), and solvents were obtained from Kanto Chemical, TCI, FUJIFILM Wako Pure Chemical, or Aldrich (reagent grade) and purified before use as required. Molecular sieves 3A (MS-3A) was activated through heating at 400°C *in vacuo* for 3 h and stored under an Ar atmosphere.

General procedures for synthesis of oxalic acid diesters

The reaction was typically performed according to the following procedures. CuCl (0.025 mmol), TMEDA (0.025 mmol), DMN-AZADO (0.015 mmol), MS-3A (200 or 500 mg), benzotrifluoride or *o*-xylene (1.0 mL), and a Teflon-coated magnetic stirring bar were placed sequentially in a Schlenk tube (volume: ~20 mL). The reaction mixture was then purged with O_2, connected to a balloon filled with O_2 gas. The reaction mixture was stirred vigorously for 5 min at room temperature (~23 °C). Subsequently, a benzotrifluoride solution (0.6 mL) containing alcohol (1.1 mmol), ethylene glycol (0.55 mmol), and an internal standard (chlorobenzene, 0.10 mmol) was added to the reaction mixture, which was then vigorously stirred at room temperature. The substrate conversions and product yields were monitored by GC analysis. After the reaction was completed, the crude products were subjected to column chromatography on silica gel using a mixture of hexane/diethyl ether or pentane/diethyl ether (gradient: 1/10–2/8) as the eluent. The gradient programs were performed using Biotage Isolera. The products were identified by GC-MS and/or NMR (^{1}H, ^{13}C, and ^{19}F). The present Cu catalyst was difficult to reuse because the catalyst was a homogeneous one in the reaction solution.

Measurement of CSI-MS spectra

CuCl (0.025 mmol), TMEDA (0.025 mmol), MS-3A (200 mg), acetonitrile (3 mL), and a Teflon-coated magnetic stirring bar were placed sequentially in a Schlenk tube (volume: ~20 mL). The reaction mixture was then purged with O_2, connected to a balloon filled with O_2 gas. The reaction mixture was stirred vigorously for 5 min at room temperature (~23 °C). Subsequently, an acetonitrile solution (0.5 mL) containing *N*-oxyl (0.090 mmol) or alcohol (1.1 mmol) was added to the reaction mixture, which was then vigorously stirred at room temperature. After 1 h, the solution was filtered, diluted to 0.80 mM of Cu species, and characterized by CSI-MS (positive mode).

Discussion on mass balances in 1c synthesis from 1a and 1b (Tables 1, 2, and S2–S6)

The apparently bad mass balances based on ethylene glycol (**1b**) calculated by GC analysis in Tables 1, 2, and S2–S6, *e.g.* conversion of **1b**: >99%, yield of diethyl oxalate (**1c**): 30% (entry 1, Table 1), were probably derived from the presence of intermediates which could not be detected such as glycolaldehyde, α-aldoesters, and hemiacetals. In fact, when the time course was analyzed using the CuCl/TMEDA/DMN-AZADO catalyst, the yield of **1c** increased considerably even after **1b** was completely consumed (Fig. S1). In the case of the bad mass balances based on ethanol (**1a**) in Tables 1, 2, and S2–S6, in addition to the aforementioned intermediates which could not be detected, the volatilization of the corresponding aldehyde, acetaldehyde (**1d**), is also possible to be the reason. However, when using 1-octanol (**1a'**) instead of **1a** as the substrate, while the corresponding aldehyde, 1-octanal (**1d'**), is involatile at room temperature, the same bad mass balance was observed, and the mass balance was improved as the reaction time passes (Table S1). Thus, it can be concluded that the volatilization of **1d** is not the main reason for the apparently bad mass balances based on **1a**.

Optimization of reaction conditions for synthesis of diisopropyl oxalate from 2-propanol and ethylene glycol

To optimize the reaction conditions using secondary alcohols as the substrates, various Cu sources, ligands, and *N*-oxyls were used for the synthesis of diisopropyl oxalate (**16c**) starting from 2-propanol (**16a**) and ethylene glycol (**1b**) under 1 atm of O_2 at room temperature (Table S10). As in the case of primary alcohols, the CuCl/TMEDA/DMN-AZADO catalyst showed the highest catalytic activity, and diisopropyl oxalate was obtained in 93% GC yield by adding 500 mg of MS-3A in *o*-xylene as a solvent (Table S10, entry 1). Furthermore, in the case of the oxidative esterification of secondary alcohols, the effect of *N*-oxyls on the alcohol oxidation selectivity was confirmed, which was not seen for primary alcohols. Sterically encumbered DMN-AZADO hardly induced the oxidation of secondary alcohols, affording the desired oxalic acid diesters selectively, whereas nor-AZADO promoted the secondary alcohol oxidation due to its small steric hindrance, resulting in low selectivity toward the desired reaction (Table S11).

Limitation of substrate scope

Despite the good results obtained for many kinds of oxalic acid diesters, the reaction did not work well with some alcohols (Table S9). First of all, alcohols bearing an amino, an amide, or a sulfide group at the β-position of the hydroxy group gave only low yields of the corresponding oxalic acid diesters (**29c**–**31c**). This may be due to the fact that ethylene glycol was not selectively oxidized when using these alcohols. In addition, the reaction did not proceed well using alcohols having electron-withdrawing functional groups (**32c**–**36c**) probably because the nucleophilicity of the alcohol was low. An alcohol possessing an amine moiety was also unsuitable for this esterification (**37c**). Furthermore, the easy oxidation of benzyl alcohol or 3-pyridinemethanol prevented the synthesis of the corresponding oxalic acid diester (**38c, 39c**). For a tertiary alcohol, the reaction was hampered by steric hindrance (**40c**). Moreover, phenol was not suitable for the reaction (**41c**). This is possibly due to its low nucleophilicity, given the fact that the oxidative esterification of ethyl glycolate (**2b**), of which the corresponding aldehyde is more electrophilic than glycolaldehyde, with phenol (**38a**) can proceed in the presence of the CuCl/TMEDA/DMN-AZADO catalyst (Scheme 1).

Reaction pathway analysis

The following sequential reactions can be envisaged for the present oxalic acid diester synthesis: the oxidation of ethylene glycol to aldehydes, the nucleophilic addition of alcohols to the aldehydes to produce hemiacetals, and the oxidation of the hemiacetals. Since ethylene glycol has two hydroxy groups, there are two possible reaction pathways

(Scheme S7a). One is a reaction path via glyoxal (**3b**), which involves ethylene glycol oxidation followed by oxidation of the other hydroxy group (Scheme S7a, path A). In the second pathway, after ethylene glycol oxidation, alcohols undergo nucleophilic addition to form hemiacetals followed by oxidation to glycolates (Scheme S7a, path B). We conducted several experiments to determine the reaction pathways. First, we performed the oxidative esterification reaction with ethanol (**1a**) using an aqueous solution of glyoxal (**3b**) as the starting substrate; no diethyl oxalate (**1c**) was obtained (Scheme S7b (i)). However, when ethylene glycol was used as the starting substrate under the same conditions in the presence of H_2O, **1c** was obtained in 41% yield (Scheme S7b (ii)). These results suggest that the reaction does not proceed via the glyoxal route (path A). In the presence of **3b**, the oxidation of **1a** hardly occurred either, suggesting that strong coordination of **3b** to the Cu species possibly inhibited the oxidation reactions. By contrast, when ethyl glycolate (**2b**) was used as the starting substrate for the reaction with ethanol, **1c** was obtained in a quantitative yield (Scheme S7b (iii)), and the reaction rate was faster than that of the reaction starting from ethylene glycol (Fig. S11). These results indicate that the present esterification proceeds via path B.

Methods of control reactions in Scheme S6b (i) and (ii)

CuCl (0.025 mmol), TMEDA (0.025 mmol), DMN-AZADO (0.015 mmol), MS-3A (800 mg), benzotrifluoride (3 mL), and a Teflon-coated magnetic stirring bar were placed sequentially in a Schlenk tube (volume: ~20 mL). The reaction mixture was then purged with O_2, connected to a balloon filled with O_2 gas. The reaction mixture was stirred vigorously for 5 min at room temperature (~23 °C). Subsequently, to the reaction mixture, a THF solution (0.5 mL) containing ethanol (1.1 mmol), glyoxal or ethylene glycol (0.55 mmol), water (130 μL), and an internal standard (chlorobenzene, 0.1 mmol) were added at 0.5 mL/h with the resulting mixture vigorously stirred at room temperature. A large amount of glyoxal might inhibit the reaction because we have confirmed that oxalic acid diester products inhibited the oxidative esterification (Scheme S8). Thus, the aforementioned slow addition of substrates was carried out.

DFT calculation

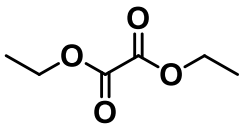
All calculations were performed using the Gaussian 16 Rev B.01 software. Geometry optimizations were conducted using the M06 functional with 6-31G(d,p) basis sets for C, H, N, and O. The Stuttgart/Dresden SDD basis set was used for Cu. The solvent effect was included by using a conductor-like polarizable continuum model for THF. The transition state (TS) structures contained one imaginary frequency exhibiting atom displacements consistent with the anticipated reaction pathway. Intrinsic reaction coordinate (IRC) calculations were utilized to determine the TS structures. All thermodynamic data were calculated at the standard state (25°C and 1 atm). The Cartesian coordinates of the calculated structures for complexes in Fig. 5 are shown in Table S12. The charges and multiplicities of respective molecules are as follows: organic molecules except for *N*-oxyls: charge = 0, multiplicity = 1; *N*-oxyls: charge = 0, multiplicity = 2; Cu complexes without *N*-oxyls: charge = +1, multiplicity = 2; Cu complexes with *N*-oxyls: charge = +1, multiplicity = 1.

The detailed results and discussion on Fig. S8–S10 are as follows. The oxidative esterification described in this study did not proceed when TEMPO or bpy were used as the *N*-oxyl or the ligand (Table 1, entry 7 and Table 2, entry 6). We found that there were almost no differences between the potential energy diagrams for the oxidation reactions using bpy and those using TMEDA (Fig. S8 and S9). This result indicates that the effects of these ligands were irrelevant to the ethylene glycol/hemiacetal oxidation process. In addition, natural population analysis (NPA) of **8** in Fig. S8 revealed that the Cu(I) species with TMEDA is more electron-rich (NPA = 0.573) than that with bpy (NPA =

0.585). These results support the TMEDA-promoted effects on the Cu(I) reoxidation by O_2. Next, the comparison of the potential energy diagrams for ethylene glycol oxidation with TEMPO and DMN-AZADO (Fig. S10) confirmed that the ligand exchange and two-electron/one-proton transfer step using Cu/TEMPO is much more difficult than that using Cu/DMN-AZADO (**5**→**8**). This DFT result is consistent with the assumption that the steric hindrance of TEMPO hinders the oxidation of ethylene glycol.

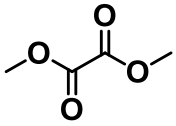
*The details for the Gibbs free energy of the transition state (**7-TS-EtOH**) in Fig. 5 are as follows. The DFT calculations revealed that the electronic energy of **7-TS-EtOH** was higher than that of the initial state (**6-EtOH**). However, the respective addition of their zero-point energy corrections or their thermal free energy corrections to their electronic energies caused the reversal of their resulting energies, that is, the Gibbs free energy of **7-TS-EtOH** was lower than that of **6-EtOH** by only 0.47 kcal/mol. In the case of barrierless reactions, the potential energy surfaces are not suitable for the normal vibration analysis utilizing harmonic oscillator approximation in the present calculations by Gaussian 16. Thus, the accuracy of zero-point energy/thermal free energy corrections based on the unsuitable approximation is not reliable. In addition, in general, the zero-point energy/thermal free energy corrections of transition states tend to be smaller than those of initial states because the contribution of frequencies along the reaction coordinate are not present in the transition state. Therefore, if the Gibbs free energy of activation is quite low, the Gibbs free energy of the initial state can become lower than that of the transition state via the energy corrections. Considering the aforementioned discussion, we conclude that although the accurate value of **7-TS-EtOH**'s Gibbs free energy cannot be determined, the energy barrier of this hydrogen transfer process (**6-EtOH**→**7-TS-EtOH**→**8-EtOH**) is extremely small, i.e., this process is almost barrierless.

Spectral data of synthesized oxalic acid diesters



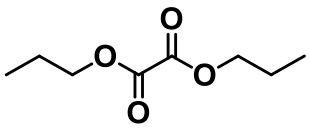
1c (CAS: 95-92-1)

Ethanedioic acid, 1,2-diethyl ester (1c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.39 (t, J = 7.16 Hz, 6H), 4.36 (q, J = 7.16 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 14.02, 63.24, 157.97. MS (EI): *m/z* (%): 74 (8), 73 (3), 45 (11), 43 (4), 31 (13), 30 (6), 29 (100), 28 (10), 27 (15).



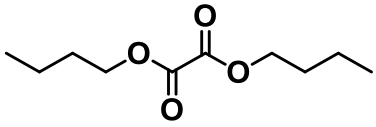
2c (CAS: 553-90-2)

Ethanedioic acid, 1,2-dimethyl ester (2c): MS (EI): *m/z* (%): 59 (100), 45 (39), 31 (8), 30 (7), 29 (28), 28 (7). These mass spectral data accord with those previously reported.[S1]



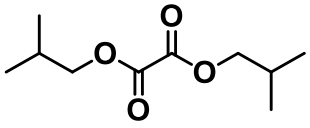
3c (CAS: 615-98-5)

Ethanedioic acid, 1,2-dipropyl ester (3c): MS (EI): *m/z* (%): 133 (2), 89 (2), 71 (1), 59 (2), 44 (4), 43 (100), 42 (8), 41 (30), 39 (5), 31 (2), 30 (2), 29 (5), 28 (4), 27 (20).



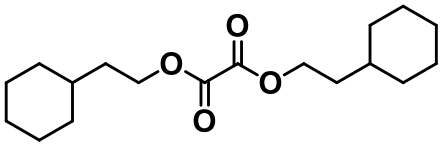
4c (CAS: 2050-60-4)

Ethanedioic acid, 1,2-dibutyl ester (4c): MS (EI): *m/z* (%): 58 (5), 57 (100), 56 (23), 55 (6), 41 (60), 39 (7), 29 (54), 28 (7), 27 (12). These mass spectral data accord with those previously reported.[S2]



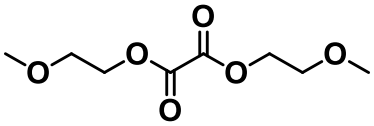
5c (CAS: 2050-61-5)

Ethanedioic acid, 1,2-bis(2-methylpropyl) ester (5c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 0.98 (d, J = 6.59 Hz, 12H), 2.01–2.11 (m, 2H), 4.08 (d, J = 6.59 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 18.91, 27.59, 72.74, 158.12. MS (EI): *m/z* (%): 58 (5), 57 (100), 56 (21), 43 (8), 41 (48), 39 (8), 29 (33), 27 (8).



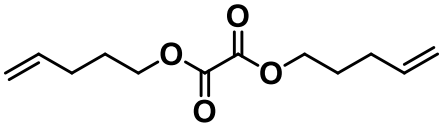
6c

Ethanedioic acid, 1,2-bis(2-cyclohexylethyl) ester (6c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 0.84–0.92 (m, 4H), 1.10–1.22 (m, 6H), 1.29–1.37 (m, 2H), 1.50–1.69 (m, 14H), 4.25 (t, J = 6.87 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 26.19, 26.48, 33.14, 34.46, 35.65, 65.46, 158.15. MS (EI): *m/z* (%): 57 (100), 56 (24), 55 (7), 43 (7), 42 (5), 41 (79), 39 (8), 31 (7), 29 (86), 28 (9), 27 (19). Anal. Calc. for $C_{18}H_{30}O_4$: C, 69.64; H, 9.74. Found: C, 69.45; H, 9.71.



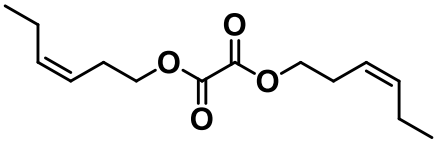
7c (CAS: 36254-34-9)

Ethanedioic acid, 1,2-bis(2-methoxyethyl) ester (7c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 3.40 (s, 6H), 3.68–3.70 (m, 4H), 4.43–4.45 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 58.08, 64.86, 68.69, 156.63. MS (EI): *m/z* (%): 103 (14), 59 (59), 58 (60), 45 (100), 43 (15.52), 31 (36), 29 (50), 28 (11).



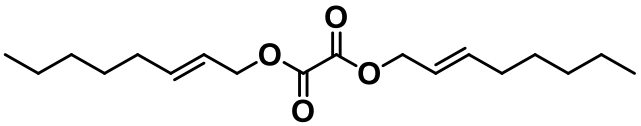
8c

Ethanedioic acid, 1,2-di-4-penten-1-yl ester (8c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.85 (quin, J = 6.87, 4H), 2.15–2.20 (m, 4H), 4.30 (t, J = 6.59 Hz, 4H), 5.00–5.08 (m, 4H), 5.80 (ddt, J = 17.18, 10.31 and 6.59 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 27.39, 29.77, 66.39, 115.75, 136.91, 157.94. MS (EI): *m/z* (%): 69 (33), 68 (77), 67 (31), 53 (7), 41 (100), 39 (17), 29 (8), 27 (9). Anal. Calc. for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.37; H, 7.79.



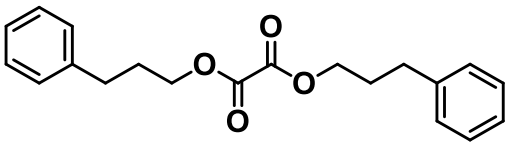
9c (CAS: 1429609-35-7)

Ethanedioic acid, 1,2-di-(3*Z*)-3-hexen-1-yl ester (9c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 0.97 (t, J = 7.45 Hz, 6H), 2.07 (quind, J = 7.45 and 1.43 Hz, 4H), 2.49 (qd, J = 7.16 and 0.86 Hz, 4H), 4.27 (t, J = 7.16 Hz, 4H), 5.32 (tdt, J = 7.45, 10.60 and 1.43 Hz, 2H), 5.55 (tdt, J = 7.45, 10.60 and 1.43 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 14.16, 20.61, 26.40, 66.37, 122.53, 135.43, 157.82. MS (EI): *m/z* (%): 83 (20), 82 (100), 81 (13), 67 (92), 55 (82), 41 (51), 39 (15), 29 (15).



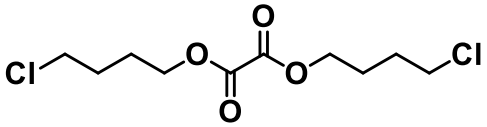
10c (CAS: 2241509-44-2)

Ethanedioic acid, 1,2-di-2-octen-1-yl ester (10c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 0.89 (t, J = 7.16 Hz, 6H), 1.23–1.34 (m, 8H), 1.39 (quin, J = 7.45 Hz, 4H), 2.06 (q, J = 6.87 Hz, 4H), 4.72 (dd, J = 6.87 and 0.86 Hz, 4H), 5.61 (tdt, J = 6.59, 15.46 and 1.43, 2H), 5.87 (tdt, J = 6.59, 15.46 and 1.13, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 14.09, 22.55, 28.45, 31.42, 32.30, 67.91, 122.14, 139.11, 157.76. MS (EI): *m/z* (%): 111 (10), 110 (8), 69 (100), 57 (8), 55 (40), 54 (12), 41 (27), 29 (11).



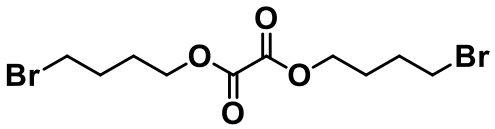
11c

Ethanedioic acid, 1,2-bis-(3-phenylpropyl) ester (11c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.99–2.04 (m, 4H), 2.68 (t, J = 7.73, 4H), 4.24 (t, J = 6.59 Hz, 4H), 7.12–7.15 (m, 6H), 7.21–7.24 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 29.16, 31.26, 66.65, 126.60, 127.79, 127.94, 139.98, 157.29. MS (EI): *m/z* (%): 119 (12), 118 (100), 117 (42), 92 (7), 91 (73), 77 (5), 65 (9), 41 (7). Anal. Calc. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.19; H, 6.81.



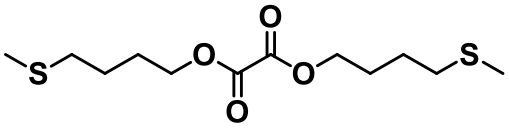
12c (CAS: 857239-10-2)

Ethanedioic acid, 1,2-bis(4-chlorobutyl) ester (12c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.87–1.96 (m, 8H), 3.60 (t, J = 6.30 Hz, 4H), 4.34 (t, J = 6.01 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 25.78, 28.94, 44.32, 66.29, 157.76. MS (EI): *m/z* (%): 93 (10), 91 (31), 56 (7), 55 (100), 54 (6), 41 (13), 39 (9), 29 (19), 27 (9).



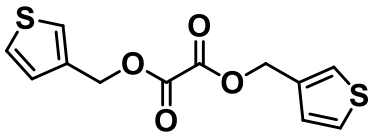
13c

Ethanedioic acid, 1,2-bis(4-bromobutyl) ester (13c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.83–1.89 (m, 4H), 1.89–1.95 (m, 4H), 3.39 (t, J = 6.30, 4H), 4.27 (t, J = 6.30, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 27.02, 29.07, 32.81, 66.19, 157.75. MS (EI): *m/z* (%): 137 (20), 135 (21), 56 (9), 55 (100), 41 (20), 39 (11), 29 (18), 27 (11). Anal. Calc. for $C_{10}H_{16}Br_2O_4$: C, 33.36; H, 4.48. Found: C, 33.20; H, 4.48.



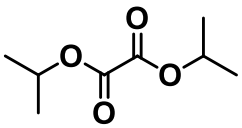
14c

Ethanedioic acid, 1,2-bis(4-(methylthio)butyl) ester (14c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.68–1.74 (m, 4H), 1.84–1.90 (m, 4H), 2.10 (s, 6H), 2.54 (t, J = 7.16 Hz, 4H), 4.32 (t, J = 6.59 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 15.42, 25.22, 27.28, 33.59, 66.57, 157.82. MS (EI): *m/z* (%):294 (15) [M^+], 103 (56), 102 (26), 87 (26), 74 (24), 61 (100), 55 (24), 41 (14). Anal. Calc. for $C_{12}H_{22}O_4S_2$: C, 48.95; H, 7.53. Found: C, 48.83; H, 7.27.



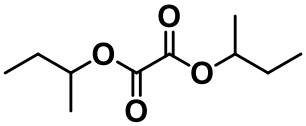
15c

Ethanedioic acid, 1,2-bis(thiophen-3-ylmethyl) ester (15c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 5.31 (s, 4H), 7.12–7.14, (m, 2H), 7.31–7.33, (m, 2H), 7.38–7.40, (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 63.40, 125.98, 126.55, 127.83, 134.81, 157.42. MS (EI): *m/z* (%): 192 (4), 99 (5), 98 (7), 97 (100), 53 (10), 45 (20), 39 (6). Anal. Calc. for $C_{12}H_{10}O_4S_2$: C, 51.05; H, 3.57. Found: C, 51.04; H, 3.79.



16c (CAS: 615-81-6)

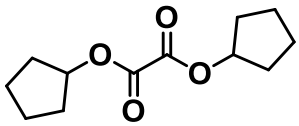
Ethanedioic acid, 1,2-bis(1-methylethyl) ester (16c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.36 (d, J = 6.01 Hz, 12H), 5.16 (sep, J = 6.30 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 21.52, 71.33, 157.85. MS (EI): *m/z* (%): 59 (3), 45 (22), 44 (6), 43 (100), 42 (6), 41 (23), 39 (4), 27 (13).



17c (CAS: 13784-89-9)

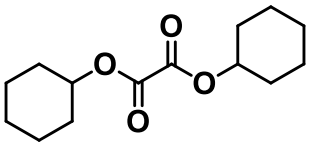
Ethanedioic acid, 1,2-bis(1-methylpropyl) ester (17c):

MS (EI): *m/z* (%): 59 (7), 58 (6), 57 (100), 56 (9), 45 (16), 41 (33), 29 (32), 27 (7). These mass spectral data accord with those previously reported.[S3]



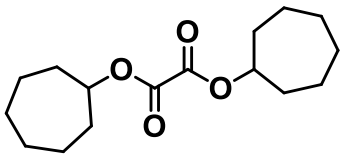
18c (CAS: 33560-68-8)

Ethanedioic acid, 1,2-dicyclopentyl ester (18c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.59–1.66 (m, 4H), 1.75–1.85 (m, 8H), 1.89–1.97 (m, 4H), 5.28–5.31 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 23.70, 32.45, 80.21, 158.21. MS (EI): *m/z* (%): 70 (6), 69 (100), 68 (12), 67 (10), 57 (6), 41 (41), 39 (7).



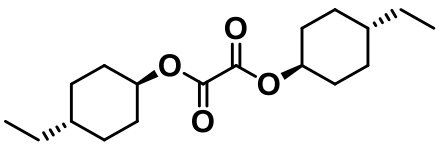
19c (CAS: 620-82-6)

Ethanedioic acid, 1,2-dicyclohexyl ester (19c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.25–1.33 (m, 2H), 1.35–1.43 (m, 4H), 1.53–1.60 (m, 6H), 1.75–1.81 (m, 4H), 1.91–1.95 (m, 4H), 4.89–4.94 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 23.63, 25.18, 31.21, 75.96, 157.88. MS (EI): *m/z* (%): 84 (7), 83 (100), 82 (10), 67 (9), 55 (69), 54 (5), 41 (24), 39 (6), 29 (6).



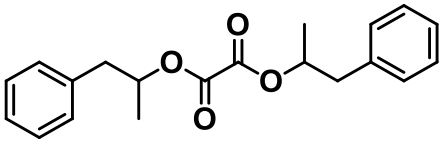
20c (CAS: 33560-69-9)

Ethanedioic acid, 1,2-dicycloheptyl ester (20c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.44–1.51 (m, 4H), 1.57–1.60 (m, 8H), 1.67–1.73 (m, 4H), 1.75–1.82 (m, 4H), 1.95–2.01 (m, 4H), 5.05–5.10 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 21.72, 27.15, 32.39, 77.48, 156.90. MS (EI): *m/z* (%): 98 (8), 97 (100), 96 (8), 81 (8), 69 (10), 67 (8), 56 (5), 55 (95), 54 (6), 43 (6), 41 (17), 39 (6), 29 (8).



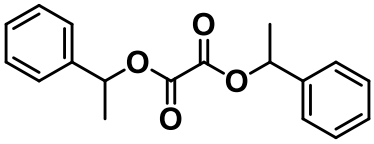
21c

Ethanedioic acid, 1,2-bis((1*r*,4*R*)-4-ethylcyclohexyl) ester (21c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 0.88 (t, J = 7.45 Hz, 6H), 0.97–1.06 (m, 4H), 1.11–1.20 (m, 2H), 1.21–1.26 (m, 4H), 1.44–1.53 (m, 4H), 1.83–1.85 (m, 4H), 2.04–2.07 (m, 4H), 4.79–4.85 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 11.62, 29.09, 30.48, 31.18, 38.16, 157.90. MS (EI): *m/z* (%): 111 (83), 110 (17), 81 (18), 69 (100), 67 (11), 55 (38), 41 (26). Anal. Calc. for $C_{18}H_{30}O_4$: C, 69.64; H, 9.74. Found: C, 69.74; H, 9.64.



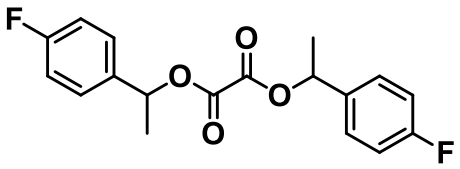
22c

Ethanedioic acid, 1,2-bis(1-phenylpropan-2-yl) ester (22c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.32 (d, J = 6.30 Hz, 6H), 2.85 (ddd, J = 13.75, 6.59 and 2.00 Hz, 2H), 3.03 (dd, J = 13.75 and 6.59 Hz, 2H), 5.21 (sext, J = 6.30 Hz, 2H), 7.20–7.37 (m, 10H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 19.12, 41.93, 74.98, 126.77, 128.47, 129.50, 136.72, 157.42. MS (EI): *m/z* (%): 119 (23), 118 (100), 117 (13), 92 (8), 91 (94), 65 (7), 41 (9). Anal. Calc. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.68; H, 6.63.



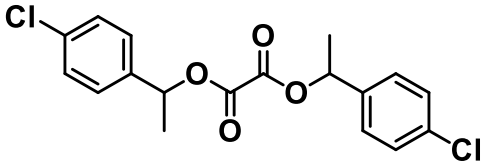
23c (CAS: 24523-30-6)

Ethanedioic acid, 1,2-bis(1-phenylethyl) ester (23c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.64 (dd, J = 6.59 and 2.86 Hz, 6H), 6.00 (qd, J = 6.59 and 1.43 Hz, 2H), 7.29–7.41 (m, 10H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 21.99, 75.56, 126.25, 128.41, 128.63, 140.05, 157.24. MS (EI): *m/z* (%): 106 (11), 105 (100), 104 (7), 103 (7), 79 (8), 78 (5), 77 (12), 51 (4).



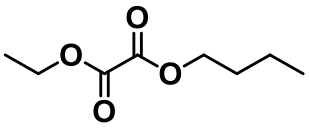
24c

Ethanedioic acid, 1,2-bis(1-(4-fluorophenyl)ethyl) ester (24c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.63 (dd, J = 6.59 and 3.72 Hz, 6H), 5.97 (qd, J = 6.59 and 1.20 Hz, 2H), 7.01–7.07 (m, 4H), 7.35–7.40 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 21.95, 75.05, 115.59, 115.76, 128.30, 128.37, 135,86, 157.17, 161.76, 163.73. ^{19}F NMR (470 MHz, $CDCl_3$, CF_3COOH): δ –111.95, MS (EI): *m/z* (%): 124 (11), 123 (100), 122 (31), 121 (12), 103 (18), 101 (11), 96 (13), 95 (7), 75 (7). Anal. Calc. for $C_{18}H_{16}F_2O_4$: C, 64.67; H, 4.82. Found: C, 64.87; H, 4.79.



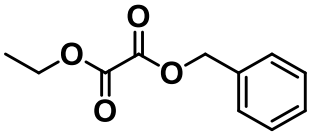
25c

Ethanedioic acid, 1,2-bis(1-(4-chlorophenyl)ethyl) ester (25c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.62 (dd, J = 6.59 and 2.86 Hz, 6H), 5.95 (qd, J = 6.59 and 1.15 Hz, 2H), 7.32 (br, 4H), 7.33 (br, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 21.97, 75.00, 127.81, 128.97, 134.24, 138.52, 157.08. MS (EI): *m/z* (%): 141 (36), 140 (34), 139 (100), 138 (60), 125 (15), 104 (12), 103 (82), 102 (20), 101 (11), 77 (42), 75 (21), 74 (12), 51 (28), 50 (17), 44 (16). Anal. Calc. for $C_{18}H_{16}Cl_2O_4$: C, 58.87; H, 4.39. Found: C, 59.00; H, 4.39.



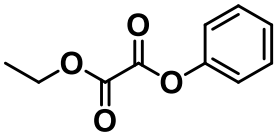
26c (CAS: 26404-27-3)

Ethanedioic acid, 1-butyl 2-ethyl ester (26c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 0.96 (t, J = 7.16 Hz, 3H), 1.37–1.46 (m, 5H), 1.70–1.76 (m, 2H), 4.30 (t, J = 6.87 Hz, 2H), 4.36 (q, J = 7.16 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 13.70, 14.02, 19.04, 30.36, 63.20, 67.02, 158.01, 158.14. MS (EI): *m/z* (%): 57 (100), 56 (24), 55 (7), 43 (7), 42 (5), 41 (79), 39 (8), 31 (7), 29 (86), 28 (9), 27 (19).



27c (CAS: 75406-29-0)

Ethanedioic acid, 1-ethyl 2-(phenylmethyl) ester (27c): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.36 (t, J = 7.16 Hz, 3H), 4.35 (q, J = 7.16 Hz, 2H), 5.31 (s, 2H), 7.34–7.43 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 14.02, 63.34, 68.64, 128.82, 128.87, 128.98, 134.29, 157.76, 157.85. MS (EI): *m/z* (%): 180 (16), 107 (17), 92 (9), 91 (100), 77 (5), 65 (8), 39 (3), 29 (7).



28c (CAS: 15779-81-4)

Ethanedioic acid, 1-ethyl 2-phenyl ester (28c):

MS (EI): *m/z* (%):194 (7) [M^+], 95 (7), 94 (100), 77 (21), 66 (12), 65 (12), 51 (6), 39 (12), 29 (27), 27 (7).

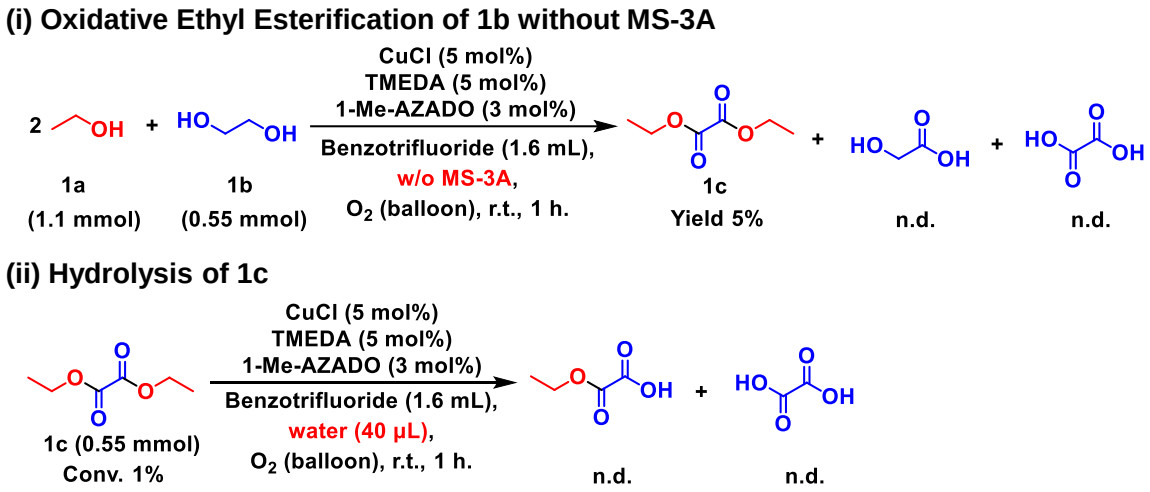
Additional references

(S1) S. R. Liao, Y. Tang, L. Xu, X. F. Zhou, J. F. Wang, B. Yang and Y. H. Liu, *Tetrahedron* 2017, **73**, 98–107.

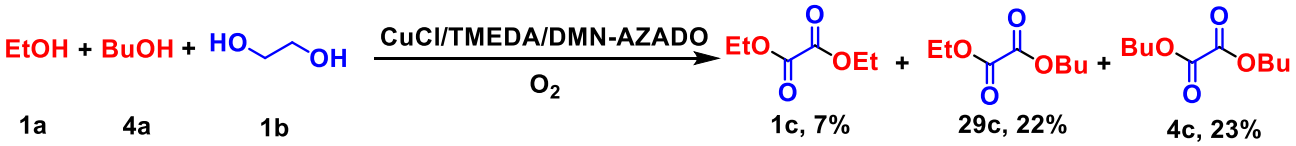
(S2) H. Zhang, F. Xu, X. Zhou, G. Zhang and C. Wang, *Green Chem.* 2007, **9**, 1208–1211.

(S3) Spectral data were obtained from Wiley Subscription Services, Inc. (US).

Supplementary schemes

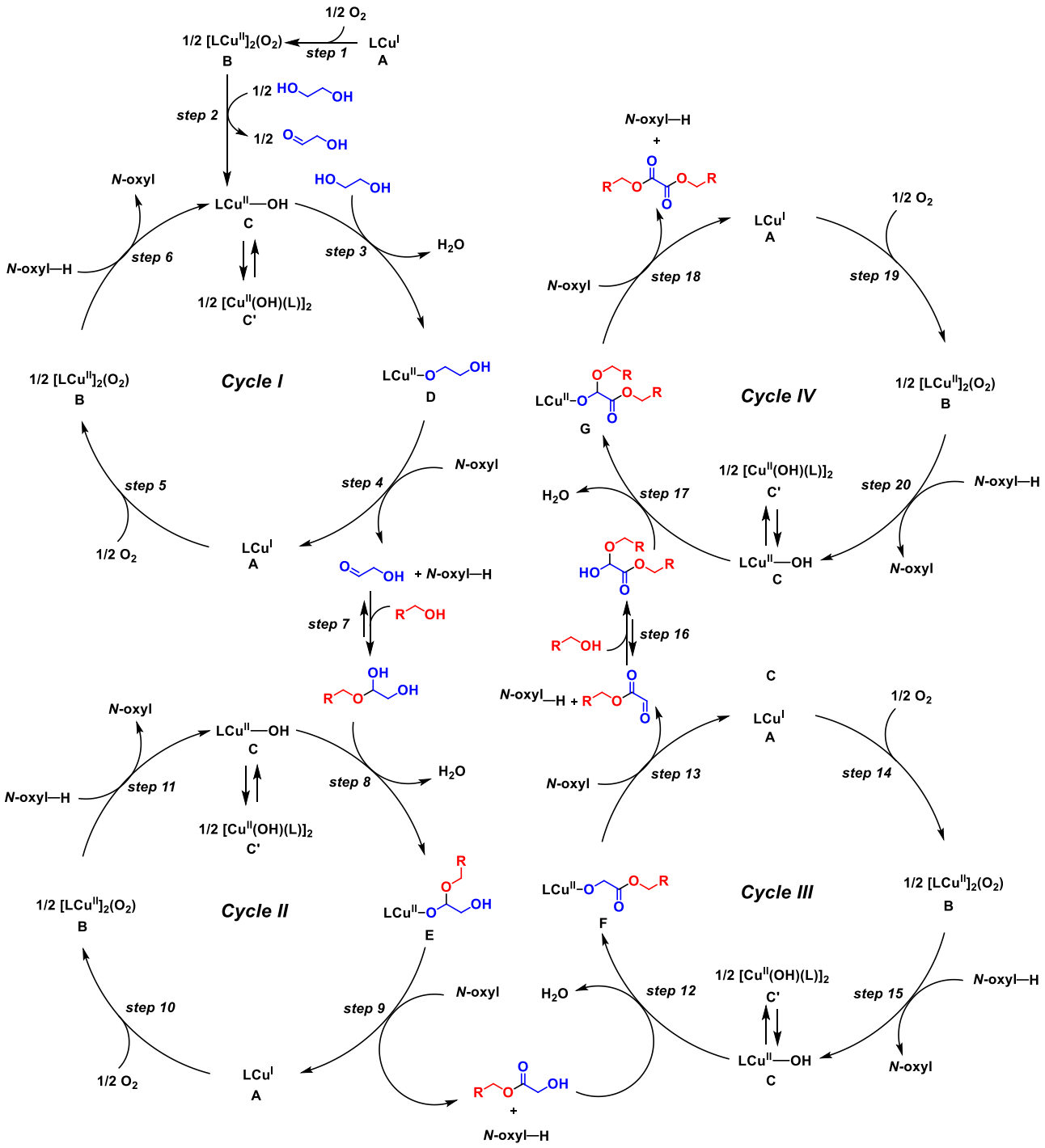


Scheme S1 Investigation of water effect. (i) Oxidative esterification of **1b** with **1a** without MS-3A. (ii) Hydrolysis of **1c** to carboxylic acids with water. The reaction conditions are indicated in this scheme.



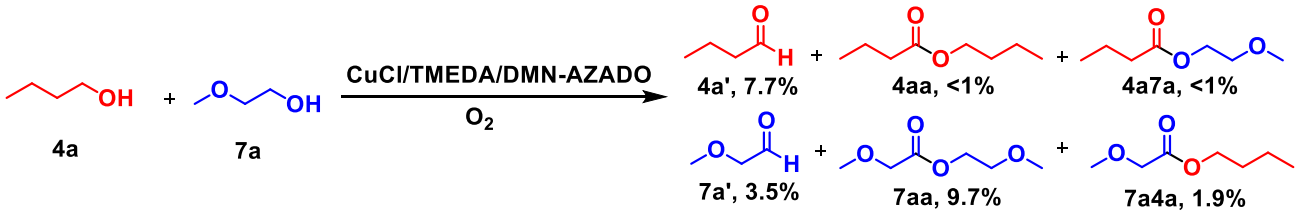
Scheme S2 Synthesis of an unsymmetrical oxalic acid diester starting from ethylene glycol.

Reaction conditions: **1a** (0.55 mmol), **4a** (0.55 mmol), **1b** (0.55 mmol), CuCl (0.025 mmol), TMEDA (0.025 mmol), DMN-AZADO (0.015 mmol), benzotrifluoride (1.6 mL), O_2 (balloon), MS-3A (200 mg), room temperature, 1 h. Yields were determined by GC using PhCl (0.1 mmol) as an internal standard.

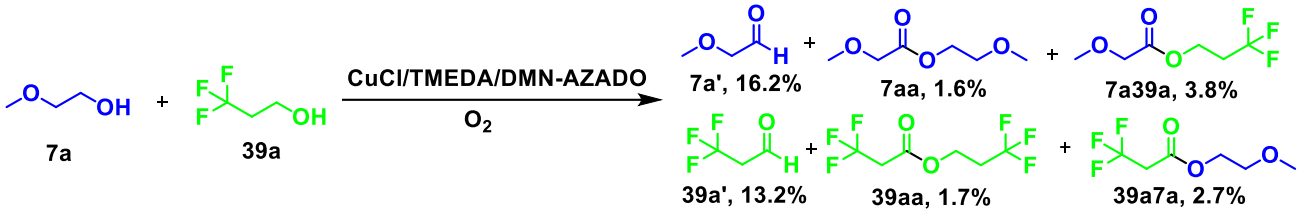


Scheme S3 Plausible reaction mechanism for proposed CuCl/TMEDA/DMN-AZADO-catalyzed oxidative esterification of ethylene glycol with alcohols.

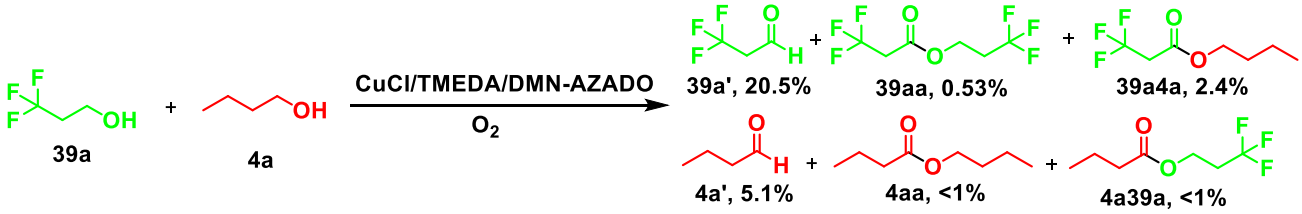
4a vs 7a



7a vs 39a

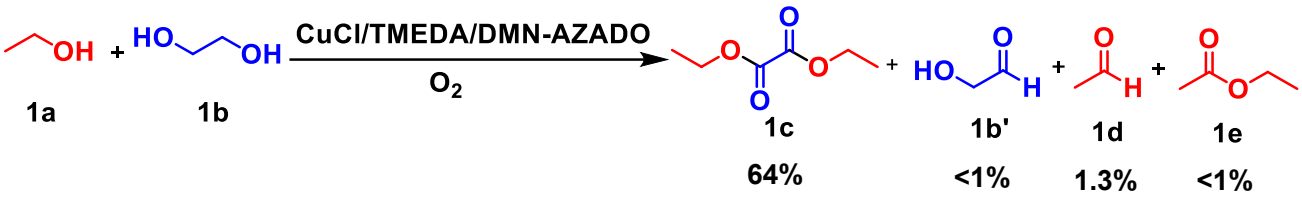


39a vs 4a

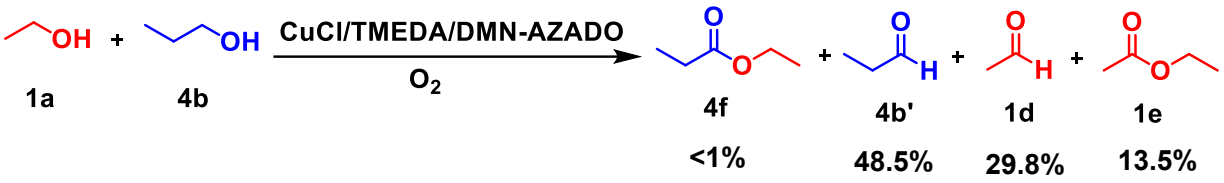


Scheme S4 Yields of products as of 150 second in CuCl/TMEDA/DMN-AZADO-catalyzed competitive oxidation using 1-butanol, 2-methoxyethanol, and 3,3,3-trifluoro-1-propanol.

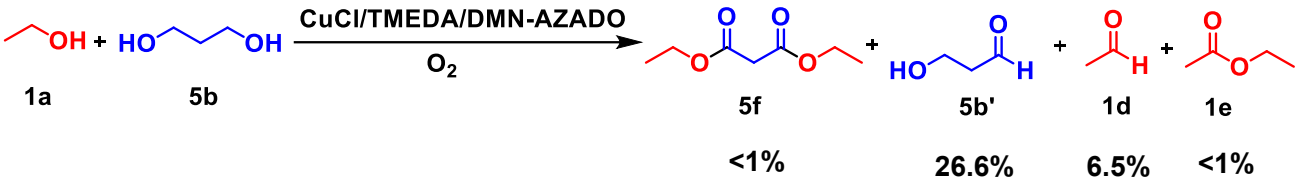
Reaction conditions: Alcohols (1.1 mmol), CuCl (0.025 mmol), TMEDA (0.025 mmol), DMN-AZADO (0.015 mmol), THF (1.6 mL), O_2 (balloon), MS-3A (200 mg), room temperature, PhCl (0.1 mmol) as an internal standard.



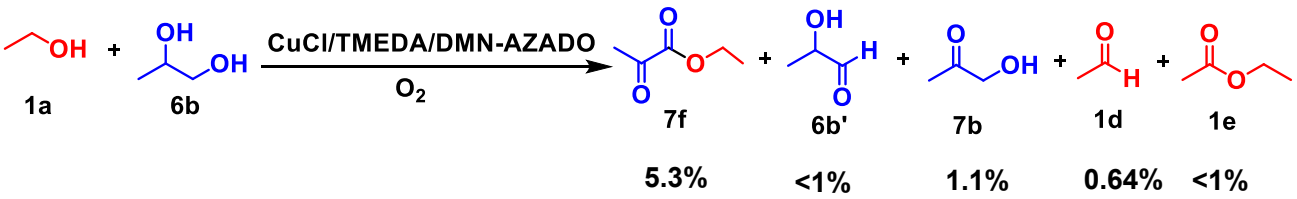
Excess ratio of f = (**1c** + **1b'** − **1d** – **1e**) (mmol)×100/(**1c** + **1b'** + **1d** + **1e**) (mmol) = 92.6%



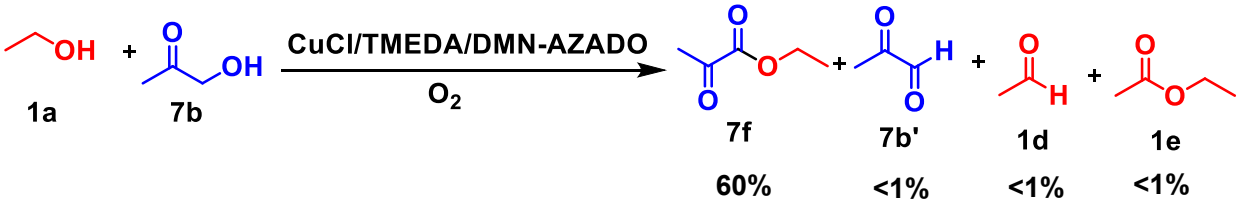
Excess ratio of f = (**4f** + **4b'** – **1d** – **1e**) (mmol)×100/(**4f** + **4b'** + **1d** + **1e**) (mmol) = 8.6%



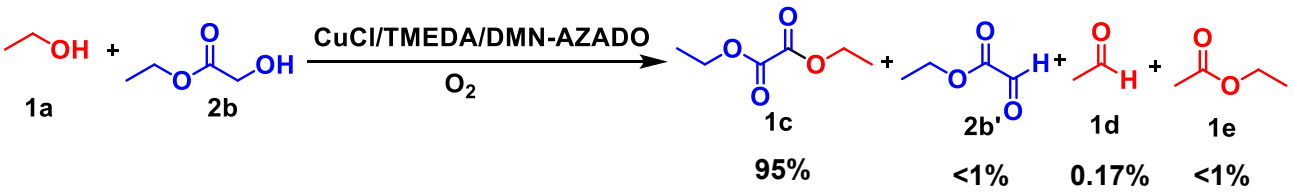
Excess ratio of f = (**5f** + **5b'** − **1d** – **1e**) (mmol)×100/(**5f** + **5b'** + **1d** + **1e**) (mmol) = 34.5%



Excess ratio of f = (**7f** + **6b'** + **7b** − **1d** – **1e**) (mmol)×100/(**7f** + **6b'** + **7b** + **1d** + **1e**) (mmol) = 70.5%



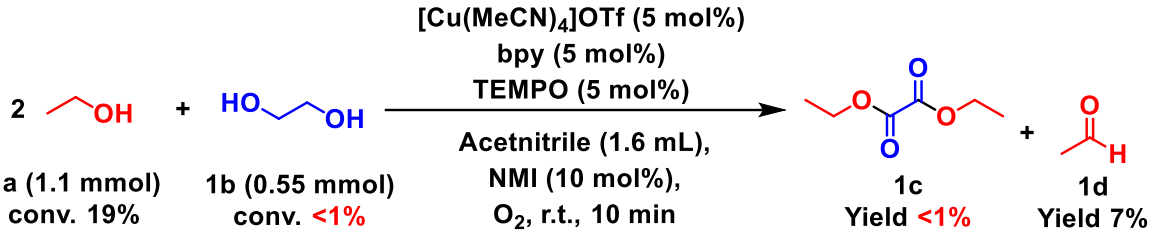
Excess ratio of f = (**7f** + **7b'** − **1d** – **1e**) (mmol)×100/(**7f** + **7b'** + **1d** + **1e**) (mmol) = 100%



Excess ratio of f = (**1c** + **2b'** − **1d** – **1e**) (mmol)×100/(**1c** + **2b'** + **1d** + **1e**) (mmol) = 99.6%

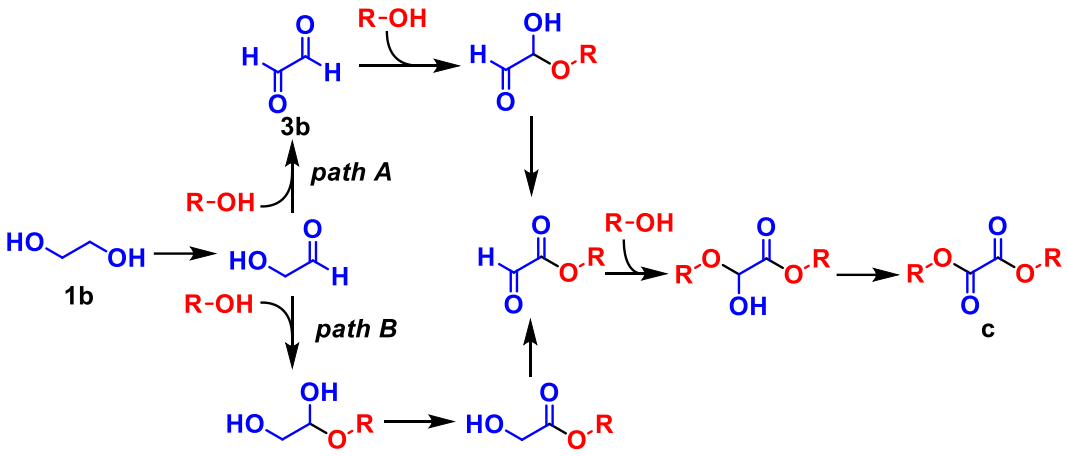
Scheme S5 Selectivity of alcohol (**b**) oxidation to the corresponding aldehyde-derived products in the presence of ethanol (**1a**).

Reaction conditions: **1a** (1.1 mmol), **1b**, **5b, 6b** (0.55 mmol).**2b**, **4b**, **7b** (1.1 mmol), CuCl (0.025 mmol), TMEDA (0.025 mmol), DMN-AZADO (0.015 mmol), THF (1.6 mL), O_2 (balloon), MS-3A (200 mg), room temperature, 1 h, PhCl (0.1 mmol) as an internal standard. Other products were not detected by GC and GC-MS analysis.

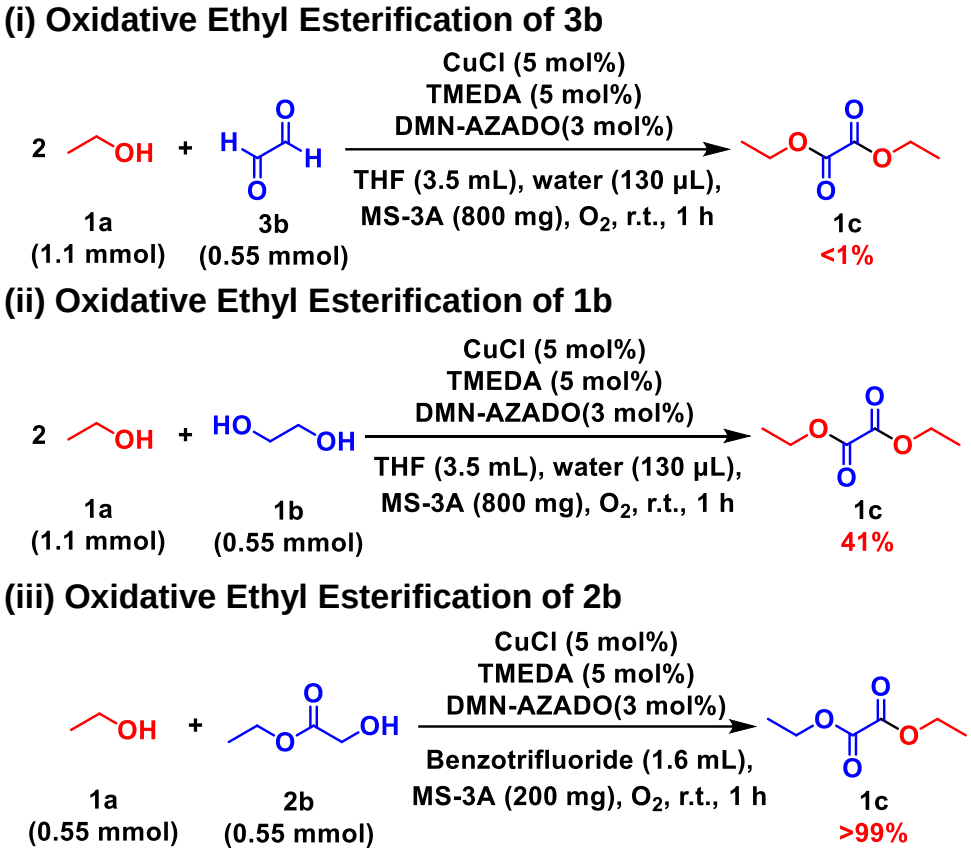


Scheme S6 Oxidative esterification of ethylene glycol with ethanol using Cu(OTf)/bpy/TEMPO catalyst system. Reaction conditions: **1a** (1.1 mmol), **1b** (0.55 mmol), $[Cu(MeCN)_4]OTf$ (0.025 mmol), bpy (0.025 mmol), TEMPO (0.015 mmol), acetonitrile (1.6 mL), NMI (0.05 mmol), O_2 (balloon), room temperature, 10 min. Yields were determined by GC using PhCl (0.1 mmol) as an internal standard. NMI = *N*-methylimidazole.

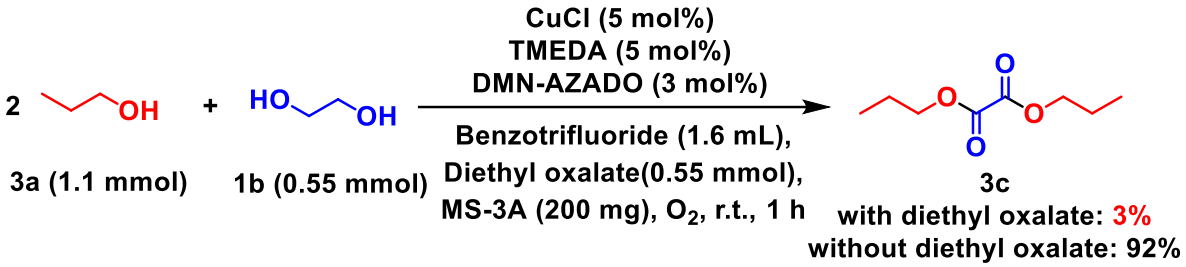
(a)



(b)



Scheme S7 Reaction pathway analysis: (a) Assumed esterification reaction pathway. (b) Control experiments for determining the present reaction pathway.



Scheme S8 Inhibition of **1c** production by the presence of an oxalic acid diester.

Reaction conditions: **3a** (1.1 mmol), **1b** (0.55 mmol), CuCl (0.025 mmol), TMEDA (0.025 mmol), DMN-AZADO (0.015 mmol), benzotrifluoride (1.6 mL), diethyl oxalate (**1c**) (0.55 mmol), O_2 (balloon), room temperature, 1 h. Yields were determined by GC using PhCl (0.1 mmol) as an internal standard.

Supplementary figures

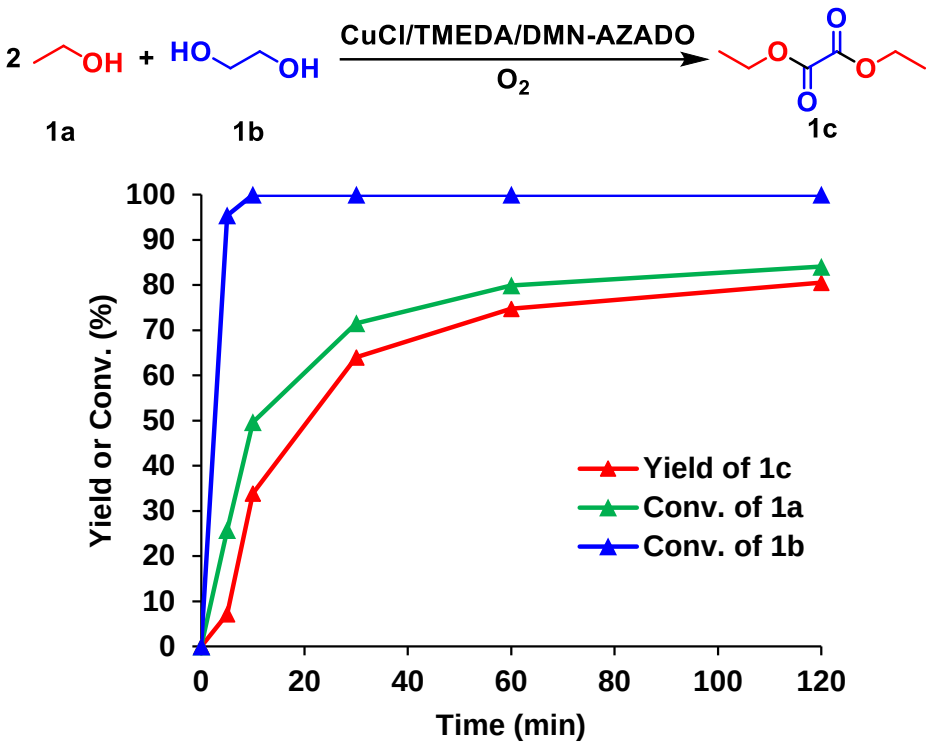


Fig. S1 Time course analysis of the synthesis of **1c** from **1a** and **1b**.

Reaction conditions: **1a** (4.4 mmol), **1b** (2.2 mmol), CuCl (0.025 mmol), TMEDA (0.025 mmol), DMN-AZADO (0.015 mmol), benzotrifluoride (6.4 mL), O_2 (balloon), MS-3A (800 mg), room temperature, PhCl (0.1 mmol) as an internal standard.

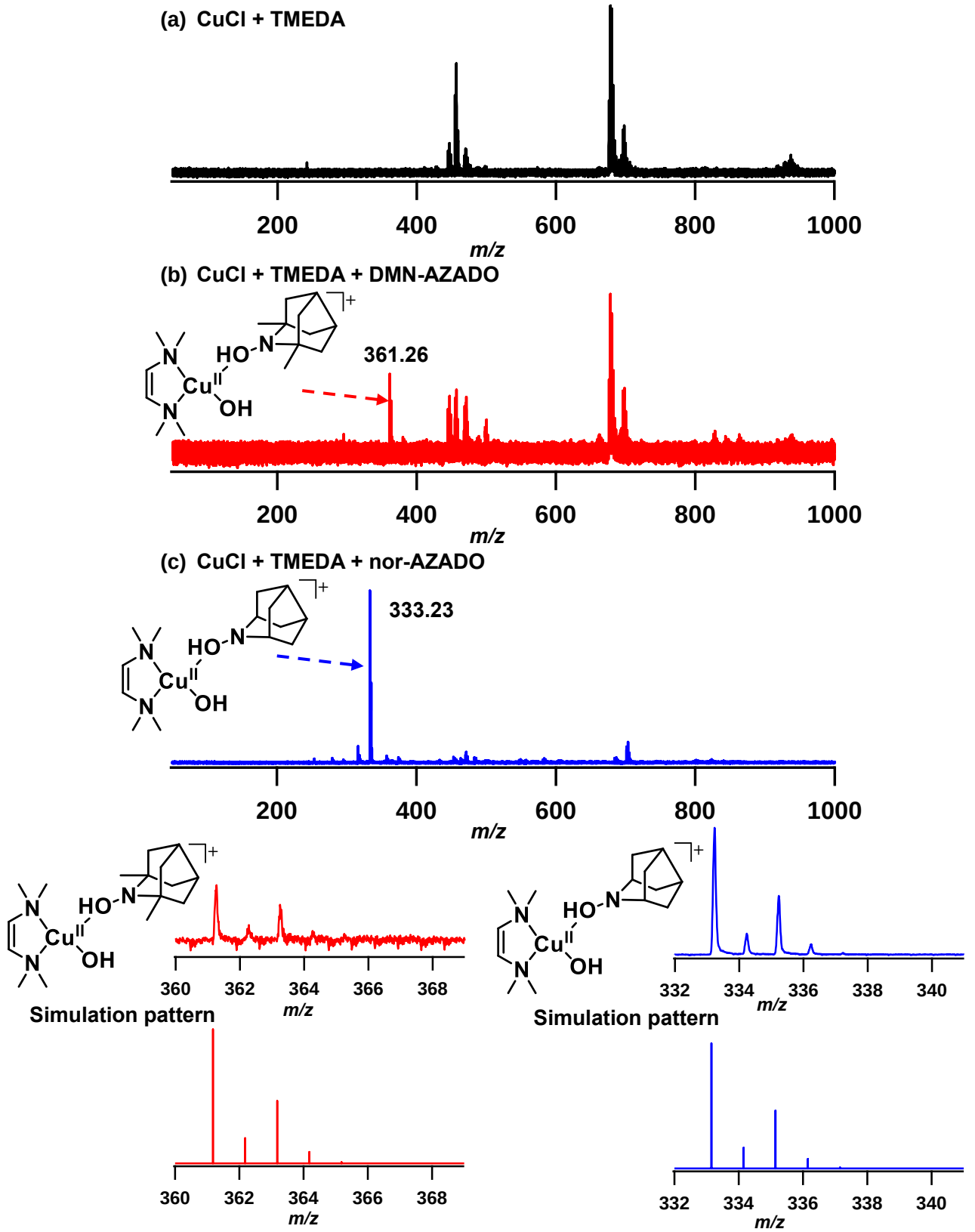


Fig. S2 CSI-MS spectra of CuCl/TMEDA/*N*-oxyl solutions: (a) CuCl and TMEDA; (b) CuCl, TMEDA, and DMN-AZADO; (c) CuCl, TMEDA, and nor-AZADO. Measurement conditions: Positive-ion CSI-MS of acetonitrile solution (1.6 mL) including CuCl (0.025 mmol), TMEDA (0.025 mmol) and *N*-oxyl (0.090 mmol) stirred under reaction conditions. TMEDA/*N*-oxyls were probably oxidized/reduced in the process of ionization because under the reaction conditions no oxidation of TMEDA has been observed by GC and GC-MS.

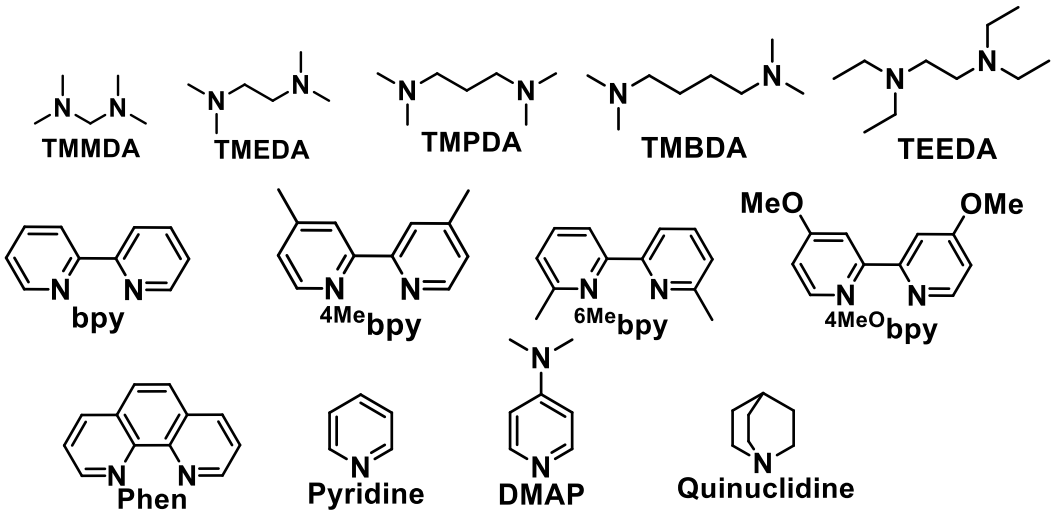


Fig. S3 Ligands used in Table 2.

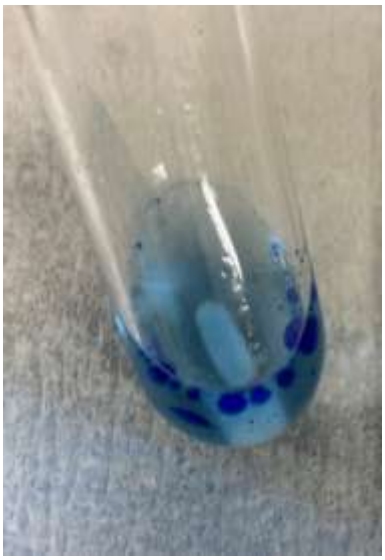


Fig. S4 Image after the reaction without MS-3A under the conditions indicated in Scheme S1(i).

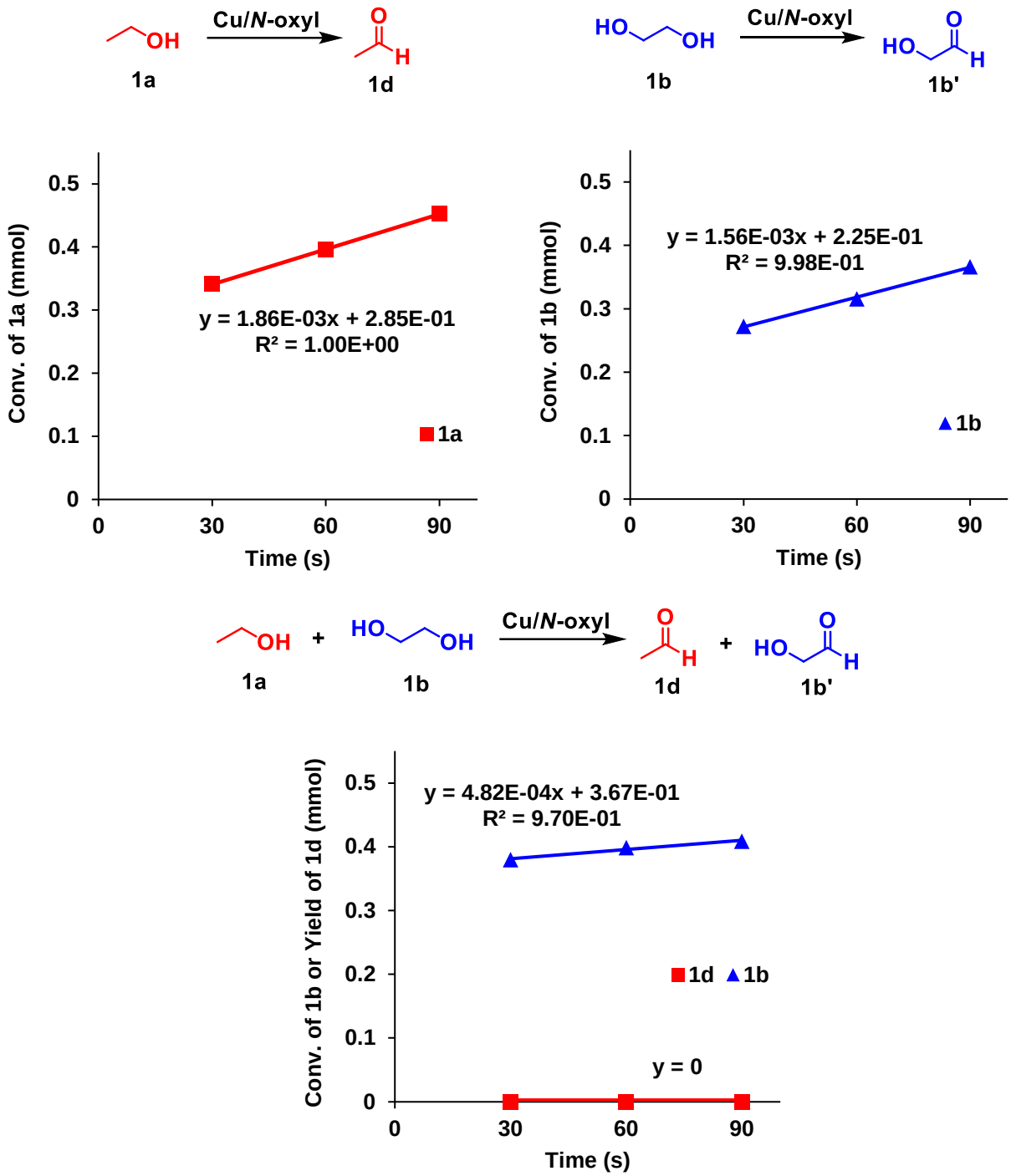


Fig. S5 Independent oxidation and competitive oxidation of **1a** and **1b**.

Reaction conditions: **1a** (1.1 mmol) and/or **1b** (0.55 mmol), CuCl (0.025 mmol), TMEDA (0.025 mmol), DMN-AZADO (0.015 mmol), THF (1.6 mL), O_2 (balloon), MS-3A (200 mg), room temperature, PhCl (0.1 mmol) as an internal standard.

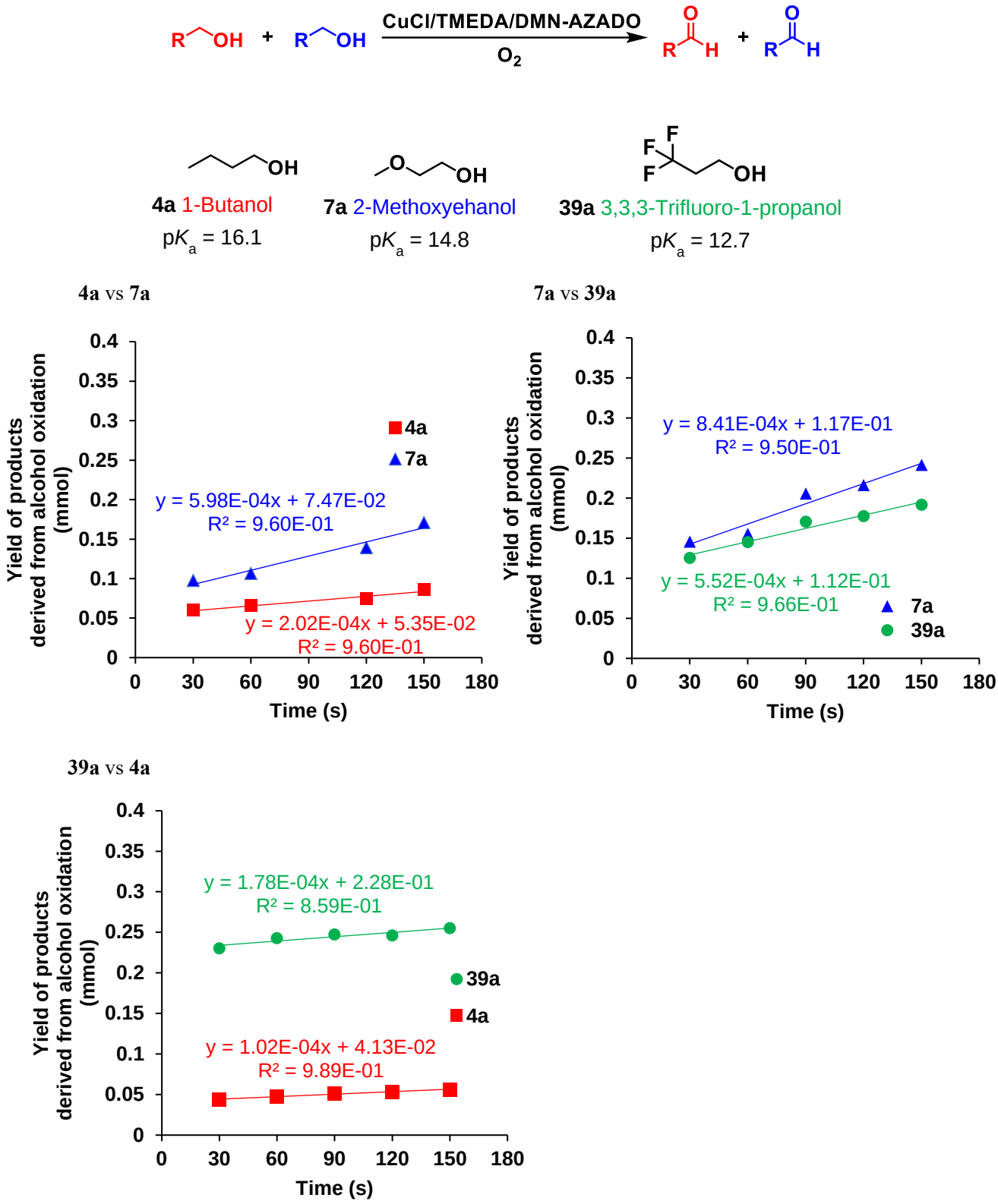


Fig. S6 Reaction rates of CuCl/TMEDA/DMN-AZADO-catalyzed competitive oxidation using 1-butanol (**4a**), 2-methoxyethanol (**7a**), and 3,3,3-trifluoro-1-propanol (**39a**).

Reaction conditions: Alcohols (1.1 mmol), CuCl (0.025 mmol), TMEDA (0.025 mmol), DMN-AZADO (0.015 mmol), THF (1.6 mL), O_2 (balloon), MS-3A (200 mg), room temperature, PhCl (0.1 mmol) as an internal standard.

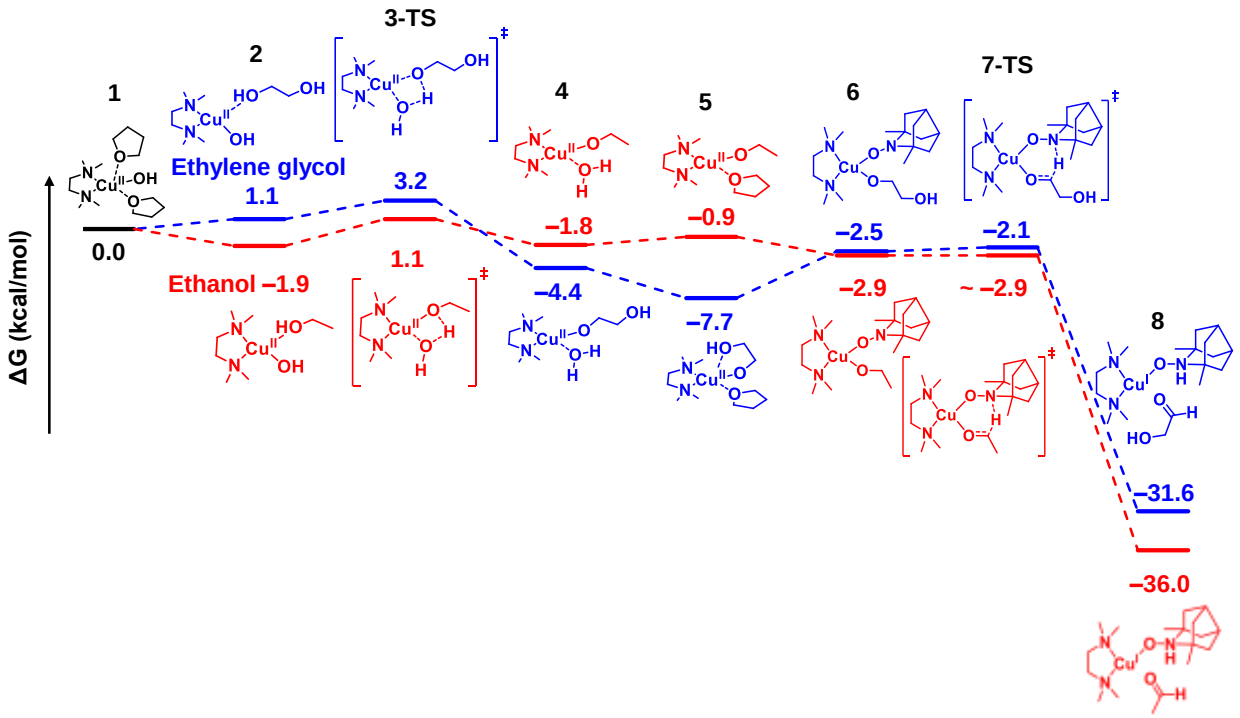


Fig. S7 DFT calculation in ethanol oxidation and ethylene glycol (monodentate coordination) oxidation catalyzed by CuCl/TMEDA/DMN-AZADO.

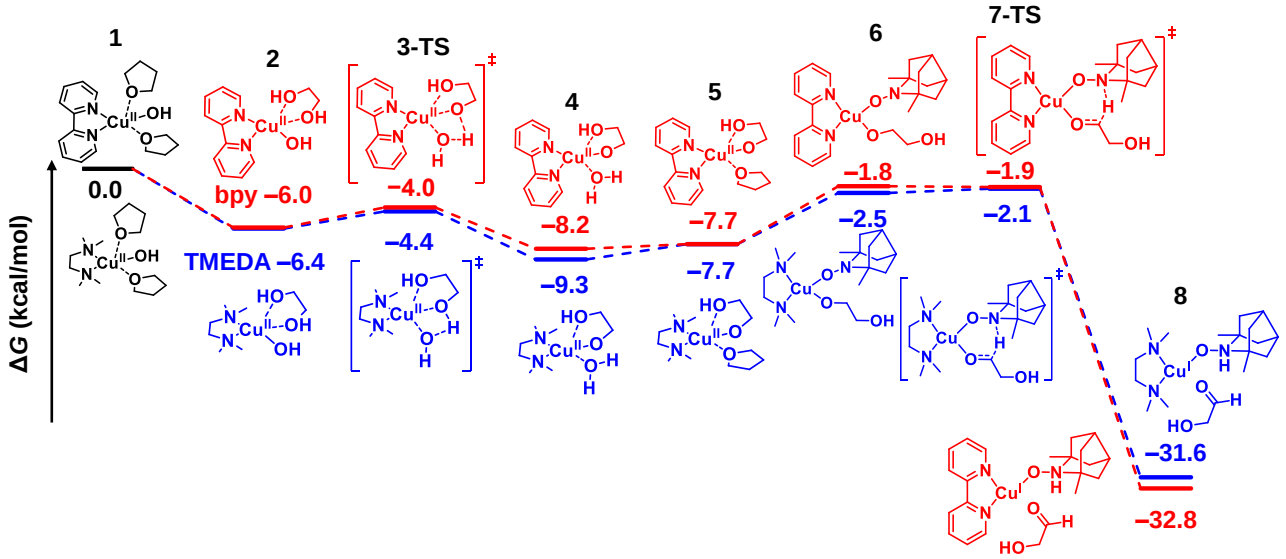


Fig. S8 DFT calculation in ethylene glycol oxidation catalyzed by CuCl/TMEDA/DMN-AZADO or CuCl/bpy/DMN-AZADO.

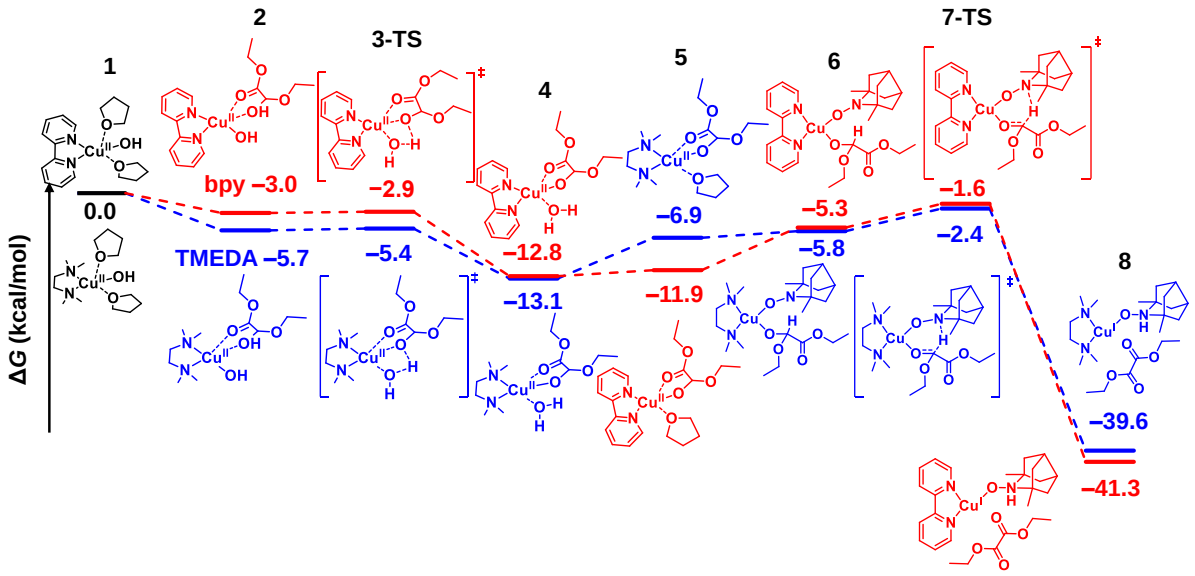


Fig. S9 DFT calculation in hemiacetal oxidation catalyzed by CuCl/TMEDA/DMN-AZADO or CuCl/bpy/DMN-AZADO.

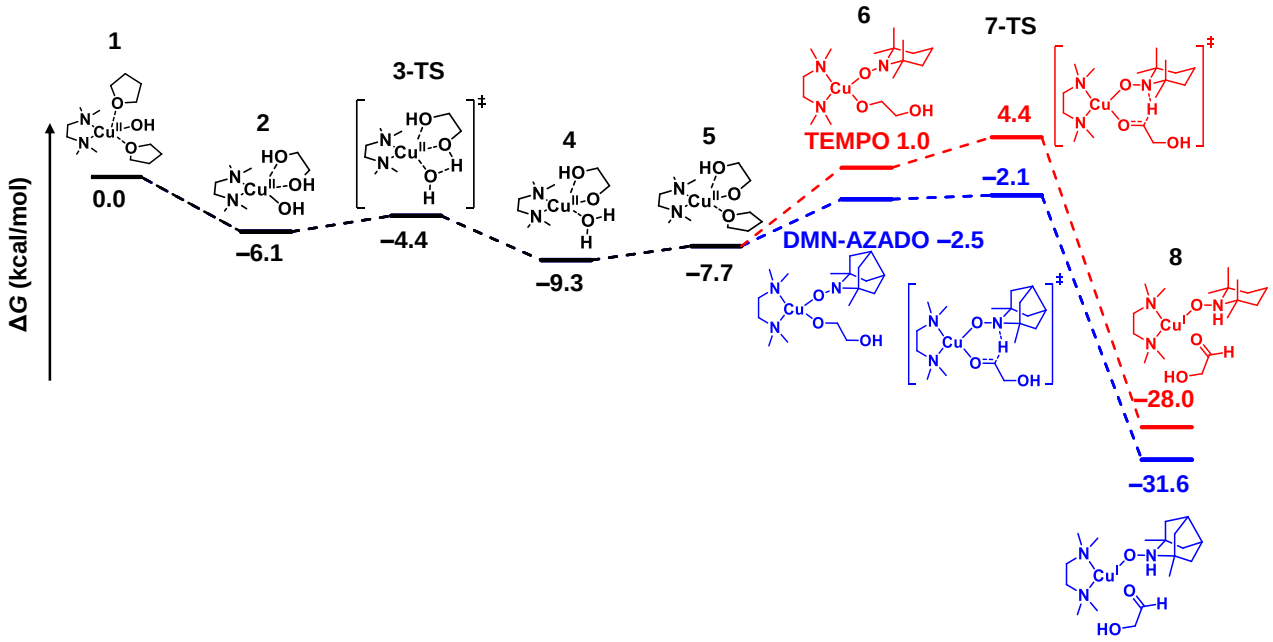


Fig. S10 DFT calculation in ethylene glycol oxidation catalyzed by CuCl/TMEDA/DMN-AZADO or CuCl/TMEDA/TEMPO.

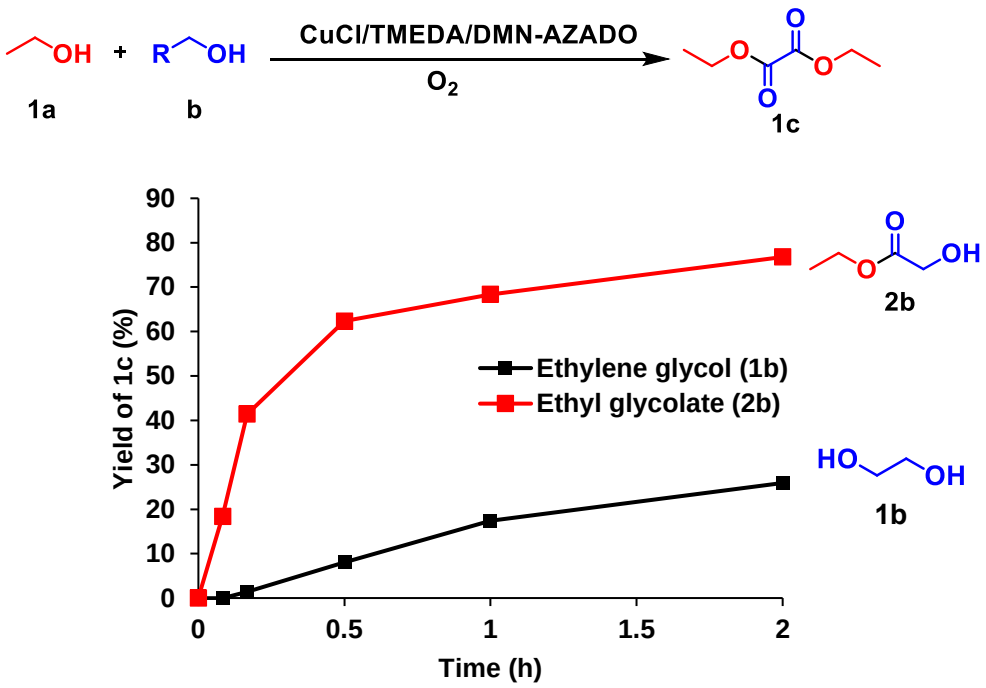
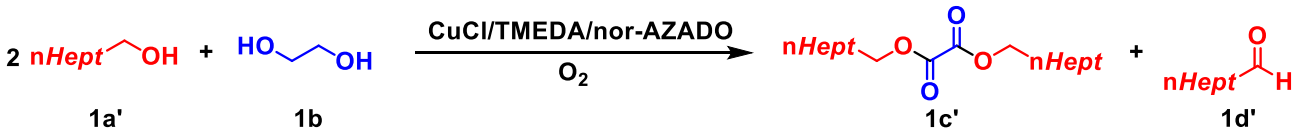


Fig. S11 Synthesis of **1c** starting from **1b** or **2b**.

Reaction conditions: **1a** (6.6 mmol for **1b**, 3.3 mmol for **2b**), **1b** (3.3 mmol), CuCl (0.025 mmol), TMEDA (0.025 mmol), DMN-AZADO (0.015 mmol), benzotrifluoride (9.6 mL), O_2 (balloon), MS-3A (1200 mg), room temperature, PhCl (0.1 mmol) as an internal standard.

Supplementary tables

Table S1 Oxidative esterification of ethylene glycol with 1-octanol (**1a'**) instead of **1a**.

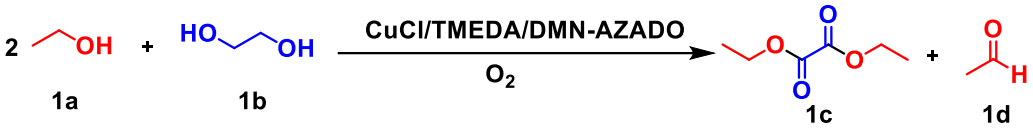


1a' **1b** **1c'** **1d'**

Entry	Time [min]	Conv. [%]		Yield [%]	
		1a'	**1b**	**1c'**	**1d'**
1	10	71	>99	36	7
2	60	70	>99	45	7

Reaction conditions: **1a'** (0.55 mmol), **1b** (1.1 mmol), CuCl (0.025 mmol), TMEDA (0.025 mmol), nor-AZADO (0.015 mmol), benzotrifluoride (1.6 mL), O_2 (balloon), MS-3A (200 mg), room temperature, PhCl (0.1 mmol) as an internal standard. Conversions and yields were determined by GC analysis.

Table S2 Effect of Cu sources.

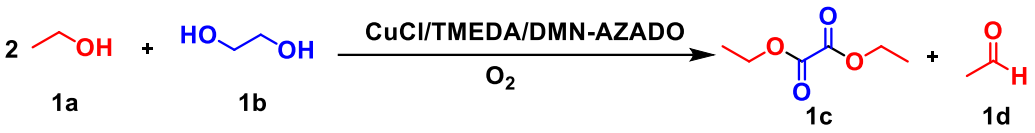


1a **1b** **1c** **1d**

Entry	Cu sources	Conv. [%]		Yield [%]	
		1a	**1b**	**1c**	**1d**
1	CuCl	97	>99	84	5
2	$CuCl_2$	41	>99	17	2
3	CuBr	24	97	6	1
4	CuI	15	44	<1	<1
5	Cu(OAc)	22	68	3	1

Reaction conditions: **1a** (0.55 mmol), **1b** (1.1 mmol), Cu catalyst (0.025 mmol), TMEDA (0.025 mmol), DMN-AZADO (0.015 mmol), benzotrifluoride (1.6 mL), O_2 (balloon), MS-3A (200 mg), 10 min, room temperature, PhCl (0.1 mmol) as an internal standard. Conversions and yields were determined by GC analysis.

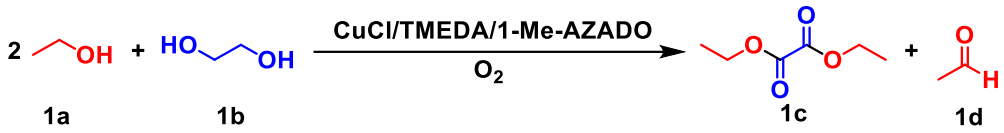
Table S3 Effect of solvents.



Entry	Solvent	Conv. [%]		Yield [%]	
		1a	**1b**	**1c**	**1d**
1	**Benzotrifluoride**	**99**	**>99**	**81**	**4**
2	Toluene	97	>99	73	4
3[a]	*o*-xylene	-	-	73	5
4	Butyl acetate	85	98	69	2
5	Heptane	>99	>99	69	1
6	Methyl *tert*-butyl ether	89	99	68	2
7[a]	CPME	-	99	68	2
8	DCE	90	>99	68	5
9	Ethyl acetate	84	>99	63	2
10	Mesitylene	99	>99	65	3
11	*p*-xylene	>99	>99	61	5
12	THF	77	>99	61	1
13	MeCN	75	>99	58	3
14	1,4-dioxane	71	99	56	4
15	*m*-xylene	99	>99	55	8
16[a]	γ-Butyrolactone	70	-	42	1
17	Nitrobenzene	55	>99	33	<1
18	PC	7	89	7	<1
19	NMP	7	97	2	<1
20	DCM	98	>99	74	5
21	Hexane	97	>99	70	1
22	Cyclohexane	98	>99	62	3

Reaction conditions: **1a** (0.55 mmol), **1b** (1.1 mmol), CuCl (0.025 mmol), TMEDA (0.025 mmol), DMN-AZADO (0.015 mmol), solvent (1.6 mL), propylene carbonate (0.1 mmol), O_2 (balloon), MS-3A (200 mg), 1 h, room temperature, PhCl (0.1 mmol) as an internal standard. Conversions and yields were determined by GC analysis. CPME = cyclopentyl methyl ether, DCE = 1,2-dichloroethane, THF = tetrahydrofuran, PC = propylene carbonate, NMP = *N*-methylpyrrolidone, DCM = dichloromethane. [a]Conversions of **1a** and/or **1b** were not determined by GC analysis because of the overlap of their peaks with solvent peaks.

Table S4 Effect of green solvents.

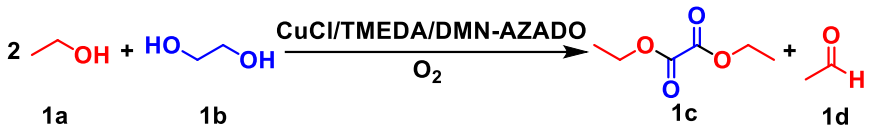


1a 1b 1c 1d

Entry	Solvent	Conv. [%]		Yield [%]	
		1a	**1b**	**1c**	**1d**
1	Benzotrifluoride	80	>99	73	8
2	Anisole	85	>99	68	8
3	Ethyl acetate	67	>99	58	6
4	Butyl acetate	61	>99	54	4
5[a]	Acetone	-	>99	55	2
6	Methyl ethyl ketone	67	>99	57	4
7	Methyl isobutyl ketone	78	>99	62	5
8[b]	Ethanol	-	>99	38	-
9[c]	-	73	>99	36	5

Reaction conditions: **1a** (0.55 mmol), **1b** (1.1 mmol), CuCl (0.025 mmol), TMEDA (0.025 mmol), 1-Me-AZADO (0.015 mmol), solvent (1.6 mL), O_2 (balloon), MS-3A (200 mg), 2 h, room temperature, PhCl (0.1 mmol) as an internal standard. Conversions and yields were determined by GC analysis. [a]Conversion of **1a** was not determined by GC analysis because of the overlap of the peak with solvent peaks. [b]Conversion of **1a** and yield of **1d** were not determined by GC analysis because of the excess amount of **1a**. [c]1 h.

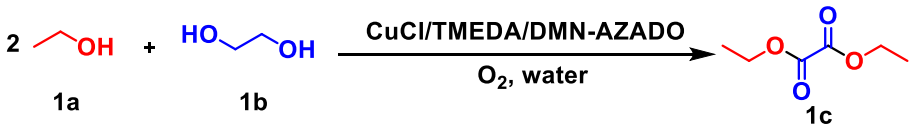
Table S5 Control experiments.



Entry	Conditions	Conv. (%)		Yield (%)	
		1a	**1b**	**1c**	**1d**
1	No change	>99	>99	93	2
2[a]	Oxalic acid instead of **1b**	71	–	<1	<1
3[b]	Glycolic acid instead of **1b**	53	–	<1	6
4	Without CuCl	13	18	<1	<1
5	Without TMEDA	87	>99	10	20
6	Without DMN-AZADO	19	26	<1	<1
7	Without MS-3A	52	68	8	<1
8[c]	Ar atmosphere	30	37	<1	<1

Reaction conditions: **1a** (1.1 mmol), **1b** (0.55 mmol), CuCl (0.025 mmol), TMEDA (0.025 mmol), DMN-AZADO (0.015 mmol), benzotrifluoride (1.6 mL), O_2 (balloon), MS-3A (200 mg), room temperature, 24 h. Conversions and yields were determined by gas chromatography analysis. [a]Oxalic acid (0.55 mmol) instead of **1b**. [b]Glycolic acid (0.55 mmol) instead of **1b**, 1-Me-AZADO (0.015 mmol) was used instead of DMN-AZADO. [c]Ar (1 atm).

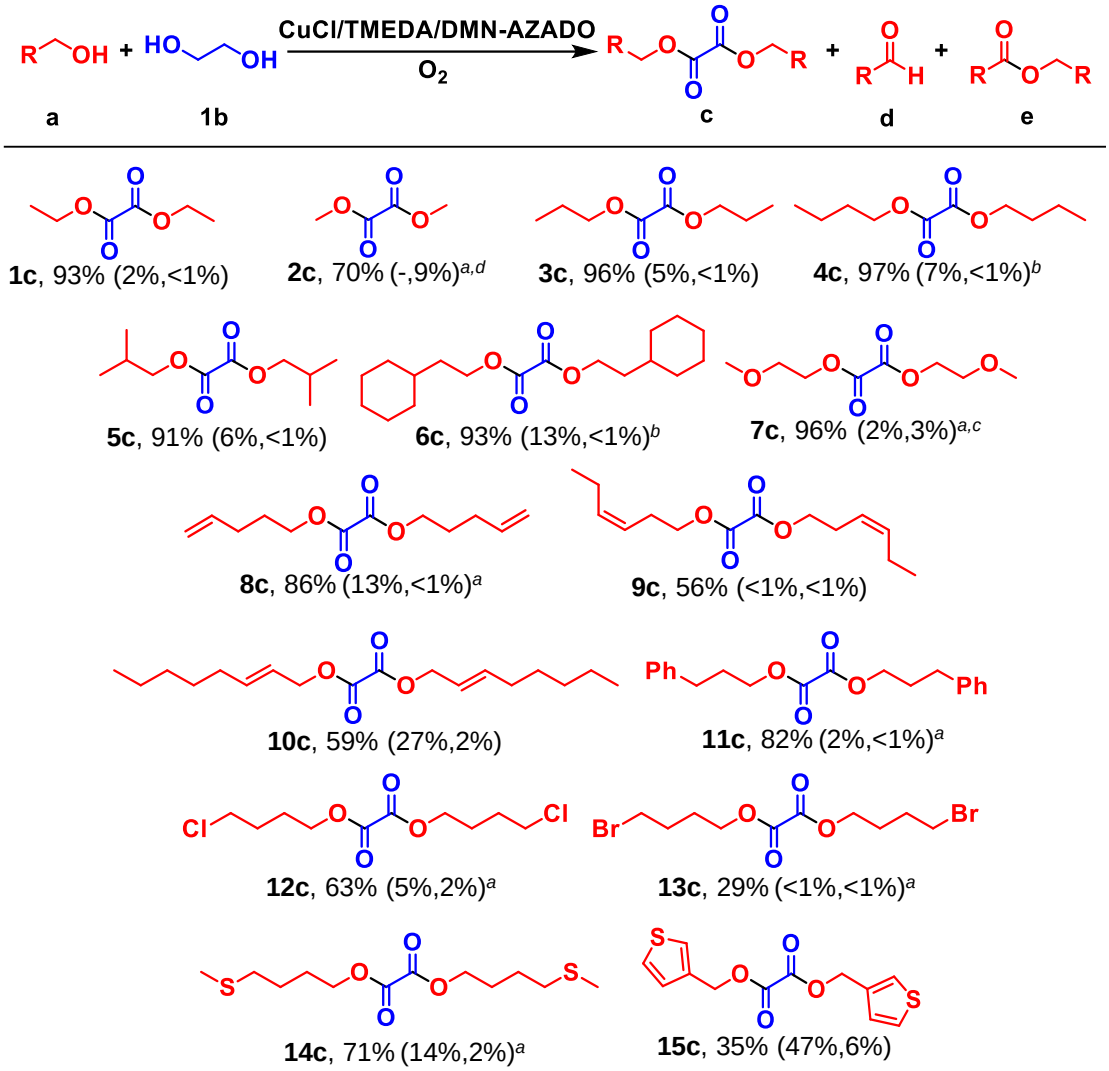
Table S6 Effect of MS-3A.



Entry	Addition of Water [mmol]	MS-3A [mg]	Conv. [%]		Yield [%]
			1a	**1b**	**1c**
1	-	200	>99	98	87
2	2.2		48	84	12
3	-	400	>99	>99	79
4	2.2		>99	>99	75

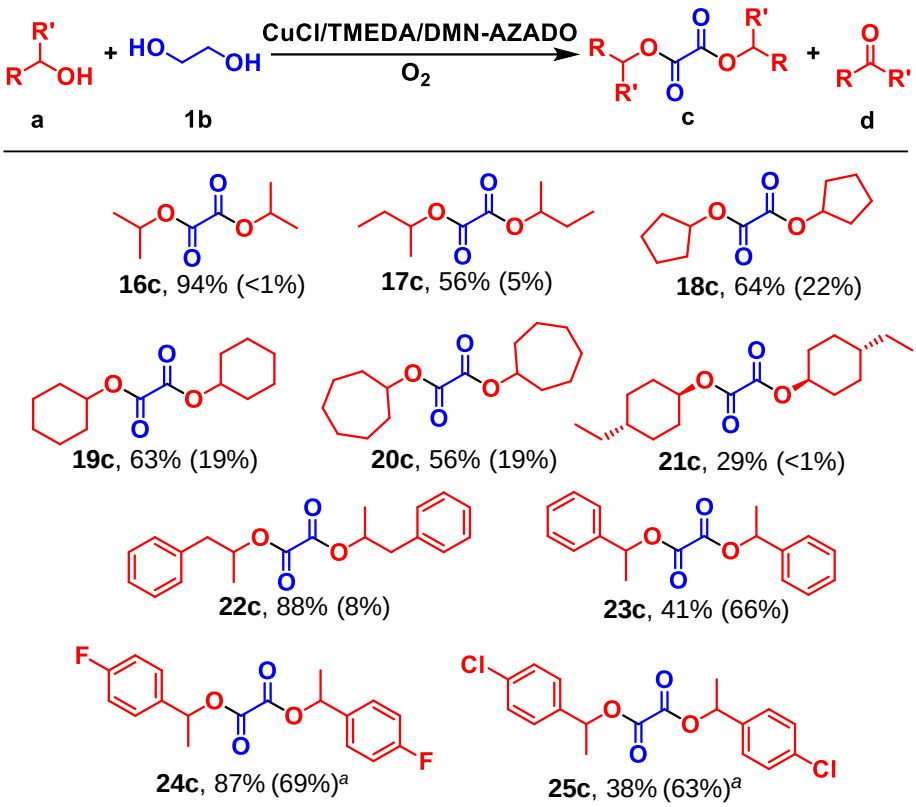
Reaction conditions: **1a** (1.1 mmol), **1b** (0.55 mmol), CuCl (0.025 mmol), TMEDA (0.025 mmol), DMN-AZADO (0.015 mmol), benzotrifluoride (1.6 mL), O_2 (balloon), 1 h, room temperature, PhCl (0.1 mmol) as an internal standard. Conversions and yields were determined by GC analysis.

Table S7 GC yields of oxalic acid diesters and byproducts in substrate scope for primary alcohols.



Reaction conditions: **a** (1.1 mmol), **1b** (0.55 mmol), CuCl (0.025 mmol), TMEDA (0.025 mmol), DMN-AZADO (0.015 mmol), benzotrifluoride (1.6 mL), O_2 (balloon), MS-3A (200 mg), room temperature, 24 h, PhCl (0.1 mmol) as an internal standard. GC yields are shown. Byproduct yields are shown in the parentheses; left: yields of **d** (aldehydes derived from **a**), right: yields of **e** (homo-esterification products derived from **a**). [a]MS-3A (500 mg). [b]1 h. [c]96 h. [d]The corresponding aldehyde (formaldehyde) cannot be detected by GC-FID.

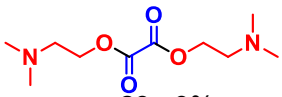
Table S8 GC yields of oxalic acid diesters and byproducts in substrate scope for secondary alcohols.

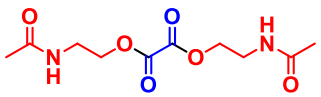


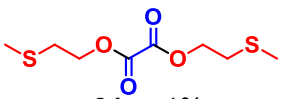
Reaction conditions: **a** (1.1 mmol), **1b** (0.55 mmol), CuCl (0.025 mmol), TMEDA (0.025 mmol), DMN-AZADO (0.015 mmol), *o*-xylene (1.6 mL), O_2 (balloon), MS-3A (500 mg), room temperature, 24 h, PhCl (0.1 mmol) as an internal standard. GC yields are shown. Yields of byproducts (ketones derived from **a**) are shown in the parentheses. [a]**a** (5.5 mmol).

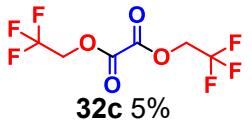
Table S9 Limitation of substrate scope.

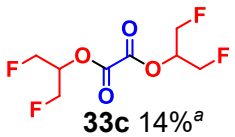
a 1b c

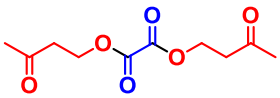

29c 9%

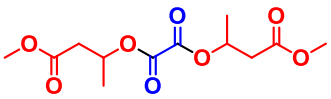

30c <1%

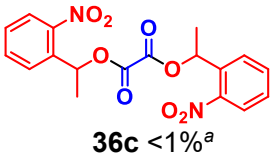

31c <1%

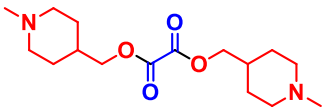

32c 5%

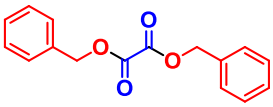

33c 14%[a]

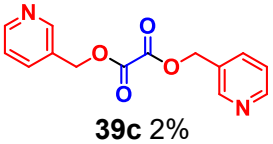

34c 2%

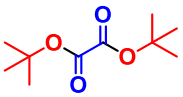

35c 2%[a]

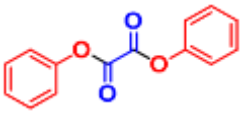

36c <1%[a]


37c 4%


38c <1%

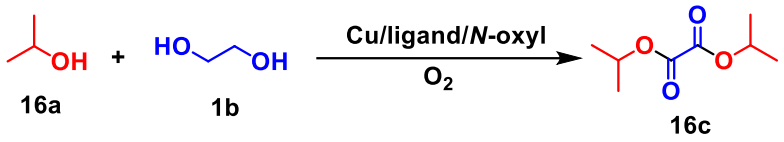

39c 2%


40c <1%


41c 2%

Reaction conditions: **a** (0.55 mmol), **1b** (1.1 mmol), CuCl (0.025 mmol, 5 mol%), TMEDA (0.025 mmol, 5 mol%), DMN-AZADO (0.015 mmol, 3 mol%), benzotrifluoride (1.6 mL), O_2 (balloon), MS-3A (200 mg), room temperature, 24 h, PhCl (0.1 mmol) as an internal standard. GC yields are shown. [a]*o*-xylene (1.6 mL), MS-3A (500 mg).

Table S10 Optimization of the reaction conditions using a secondary alcohol (**16a**) as the substrate.

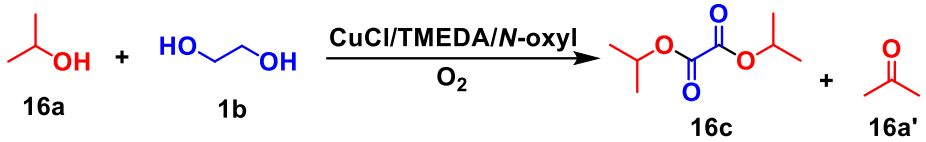


16a + 1b → 16c

Entry	Cu Source	Ligand	*N*-oxyl	Yield [%]
				16c
1[a]	**CuCl**	**TMEDA**	**DMN-AZADO**	**93**
2	CuCl	TMEDA	DMN-AZADO	48
3	CuCl	TMEDA	keto-ABNO	24
4	CuCl	TMEDA	AZADO	21
5	CuCl	TMEDA	1-Me-AZADO	24
6	CuCl	TMEDA	nor-AZADO	16
7	CuCl	TMPDA	DMN-AZADO	29
8	CuCl	bpy	DMN-AZADO	3
9	CuCl	DMAP	DMN-AZADO	48
10	CuCl	Quinuclidine	DMN-AZADO	18
11	$CuCl_2$	TMEDA	DMN-AZADO	20
12	CuBr	TMEDA	DMN-AZADO	28
13	CuI	TMEDA	DMN-AZADO	5
14	Cu(OTf)	TMEDA	DMN-AZADO	5
15	Cu(OAc)	TMEDA	DMN-AZADO	<1

Reaction conditions: **16a** (0.55 mmol), **1b** (1.1 mmol), Cu source (5 mol%), ligand (5 mol%), *N*-oxyl (3 mol%), *o*-xylene (1.6 mL), O_2 (balloon), MS-3A (200 mg), 24 h, room temperature, PhCl (0.1 mmol) as an internal standard. Yields were determined by GC analysis. [a]MS-3A (500 mg).

Table S11 *N*-oxyl effect on the selectivity of **1b** oxidation in the presence of **16a**.



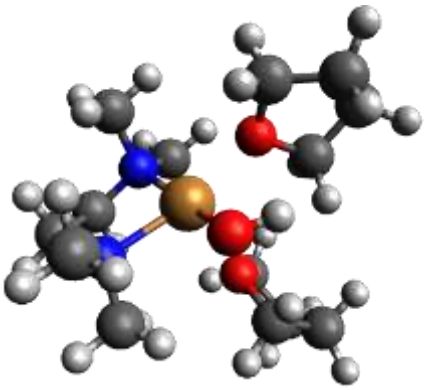
16a + 1b → 16c + 16a'

Entry	*N*-oxyl	Conv. [%]		Yield [%]	
		16a	**1b**	**16c**	**16a'**
1	DMN-AZADO	94	>99	94	<1
2	nor-AZADO	86	>99	22	32

Reaction conditions: **16a** (1.1 mmol), **1b** (0.55 mmol), CuCl (0.025 mmol), TMEDA (0.025 mmol), *N*-oxyl (0.015 mmol), *o*-xylene (1.6 mL), O_2 (balloon), MS-3A (500 mg), room temperature, 24 h. Conversions and yields were determined by GC using PhCl (0.1 mmol) as an internal standard.

Table S12 Cartesian coordinates of the calculated structures.

1



Atom	x (Å)	y (Å)	z (Å)
Cu	-0.47275	-0.42598	-0.36673
N	-1.22967	-0.77292	1.50315
N	-2.41715	0.22112	-0.83726
C	-2.33057	1.65542	-1.15679
H	-1.65675	1.78364	-2.00784
H	-3.32653	2.04677	-1.41321
H	-1.92797	2.21074	-0.30419
C	-2.95062	-0.50526	-1.99951
H	-3.971	-0.16254	-2.22843
H	-2.296	-0.33015	-2.85508
H	-2.97093	-1.5793	-1.78842
C	-1.61028	-2.19907	1.53523
H	-0.70293	-2.80819	1.55732
H	-2.20557	-2.41829	2.43403
H	-2.18866	-2.47607	0.64909
C	-0.31967	-0.50976	2.62812
H	-0.80168	-0.77996	3.57908
H	0.59087	-1.10142	2.50307
H	-0.06198	0.55113	2.65426
C	-2.41579	0.10516	1.60716
H	-2.04885	1.13166	1.7366
H	-3.00554	-0.15244	2.5007
C	-3.25754	-0.00493	0.35807
H	-3.706	-1.00172	0.28238
H	-4.08961	0.71356	0.38684
O	0.01241	-0.36086	-2.14586
H	0.95714	-0.54138	-2.20146
O	0.56748	1.74835	0.18025
C	1.04965	2.42601	1.35202
C	1.8335	3.63724	0.86287
H	1.69461	1.73199	1.91249

H	0.19905	2.70017	1.99154
C	2.24613	3.20564	-0.53958
H	2.67437	3.87828	1.51891
H	1.18304	4.51865	0.80695
C	1.00197	2.47085	-0.98535
H	3.10414	2.52096	-0.49876
H	2.50339	4.04176	-1.19574
H	1.13023	1.7425	-1.79195
H	0.21726	3.1851	-1.28546
O	1.29132	-1.45602	0.18723
C	1.51062	-2.76294	-0.40573
C	2.54381	-0.73615	0.26635
C	3.61061	-1.78559	0.03746
H	2.5892	-0.24621	1.24569
H	2.5556	0.03861	-0.51406
C	2.92214	-2.71797	-0.95358
H	3.83312	-2.31653	0.97107
H	4.53983	-1.35352	-0.34293
H	3.3762	-3.7107	-1.00804
H	2.93352	-2.28272	-1.96145
H	0.73456	-2.92752	-1.16112
H	1.40791	-3.51443	0.38873

Zero-point correction = 0.476394 (Hartree/Particle)

Thermal correction to Energy = 0.501707

Thermal correction to Enthalpy = 0.502651

Thermal correction to Gibbs Free Energy = 0.421552

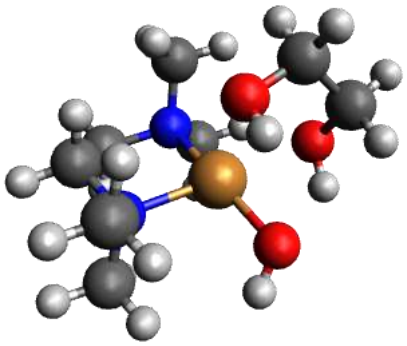
Sum of electronic and zero-point Energies = -1084.713820

Sum of electronic and thermal Energies = -1084.688507

Sum of electronic and thermal Enthalpies = -1084.687563

Sum of electronic and thermal Free Energies = -1084.768662

2-EG



Atom	x (Å)	y (Å)	z (Å)
Cu	0.10329	-0.24441	-0.43923
N	-0.46902	1.65684	-0.01012
N	-1.75115	-0.85279	0.21828
C	-2.63713	-1.13808	-0.9238
H	-2.25985	-2.00998	-1.46412
H	-3.65496	-1.35722	-0.56988
H	-2.67253	-0.29178	-1.61525
C	-1.64016	-2.05299	1.0637
H	-2.6318	-2.35256	1.4329
H	-1.21068	-2.86868	0.47584
H	-0.98883	-1.84364	1.91678
C	0.25964	2.21259	1.14425
H	1.322	2.28045	0.8966
H	-0.11283	3.22005	1.37734
H	0.13774	1.57016	2.02123
C	-0.22485	2.50706	-1.19234
H	-0.60634	3.52345	-1.01888
H	0.84937	2.55228	-1.38802
H	-0.729	2.07944	-2.06514
C	-1.92447	1.58471	0.27986
H	-2.4626	1.62727	-0.67368
H	-2.24035	2.45945	0.86522
C	-2.23598	0.30034	1.00968
H	-1.72302	0.27443	1.97928
H	-3.31471	0.2066	1.2058
O	0.66446	-1.75971	-1.35714
H	-0.02709	-2.09615	-1.93529
O	2.17666	0.29902	-1.00625
C	3.14263	-0.32219	-0.14742
C	2.66702	-0.31155	1.2855
H	4.09573	0.21439	-0.22517
H	3.30535	-1.35582	-0.4795

O	1.36766	-0.88223	1.41261
H	2.58516	0.71221	1.66415
H	3.39332	-0.83944	1.91634
H	1.96377	-0.36929	-1.6893
H	1.41742	-1.81217	1.14289

Zero-point correction = 0.328076 (Hartree/Particle)

Thermal correction to Energy = 0.346939

Thermal correction to Enthalpy = 0.347883

Thermal correction to Gibbs Free Energy = 0.282541

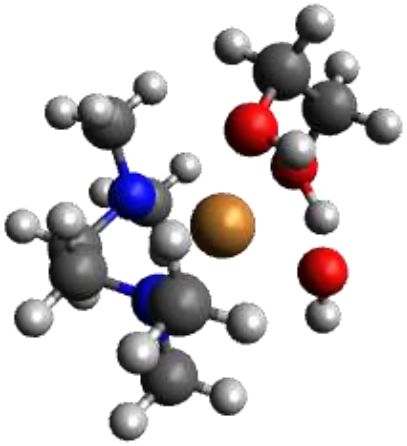
Sum of electronic and zero-point Energies = -850.393520

Sum of electronic and thermal Energies = -850.374657

Sum of electronic and thermal Enthalpies = -850.373713

Sum of electronic and thermal Free Energies = -850.439056

3-TS-EG



Atom	x (Å)	y (Å)	z (Å)
Cu	0.14821	-0.23516	-0.34455
N	-0.58184	1.65596	-0.06406
N	-1.65796	-0.93035	0.24106
C	-2.43955	-1.35444	-0.93582
H	-1.94788	-2.2129	-1.3996
H	-3.45442	-1.64542	-0.62993
H	-2.50433	-0.54994	-1.67359
C	-1.49836	-2.07325	1.1568
H	-2.4823	-2.44475	1.4764
H	-0.96157	-2.87437	0.64018
H	-0.92878	-1.76365	2.03727
C	0.04303	2.32704	1.08889
H	1.1123	2.44794	0.89542
H	-0.40191	3.32168	1.23464
H	-0.0913	1.73675	2.00023
C	-0.32523	2.44512	-1.28379
H	-0.77456	3.44464	-1.19549
H	0.75388	2.53995	-1.42758
H	-0.75352	1.93375	-2.15177
C	-2.04042	1.48404	0.15463
H	-2.52737	1.43865	-0.82587
H	-2.45432	2.35764	0.67742
C	-2.29176	0.21529	0.93516
H	-1.84429	0.2831	1.93465
H	-3.36849	0.03469	1.06773
O	0.82023	-1.76832	-1.40398
H	0.34141	-1.87219	-2.2345
O	2.0273	0.18741	-1.05655
C	3.0771	-0.1626	-0.17099
C	2.65259	-0.05936	1.27724

H	3.94534	0.48862	-0.34044
H	3.39997	-1.19743	-0.37664
O	1.41874	-0.7524	1.49571
H	2.46016	0.98072	1.55897
H	3.4368	-0.44568	1.93956
H	1.64557	-0.8228	-1.48704
H	1.58564	-1.70314	1.41862

Zero-point correction = 0.324642 (Hartree/Particle)

Thermal correction to Energy = 0.342402

Thermal correction to Enthalpy = 0.343346

Thermal correction to Gibbs Free Energy = 0.280089

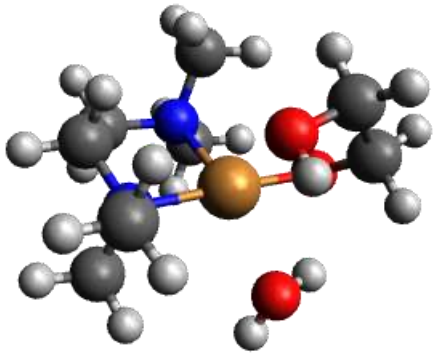
Sum of electronic and zero-point Energies = -850.391683

Sum of electronic and thermal Energies = -850.373923

Sum of electronic and thermal Enthalpies = -850.372979

Sum of electronic and thermal Free Energies = -850.436236

4-EG



Atom	x (Å)	y (Å)	z (Å)
Cu	0.23361	-0.18023	-0.30381
N	-0.71443	1.65377	-0.03319
N	-1.52895	-1.02767	0.24527
C	-2.31826	-1.387	-0.94863
H	-1.86149	-2.25309	-1.43369
H	-3.34618	-1.65081	-0.66128
H	-2.34806	-0.56172	-1.66582
C	-1.34483	-2.23075	1.0759
H	-2.3198	-2.65288	1.35849
H	-0.78476	-2.98111	0.50864
H	-0.78802	-1.97307	1.98024
C	-0.04282	2.34494	1.07934
H	1.01287	2.47365	0.82611
H	-0.50261	3.32999	1.2485
H	-0.12006	1.75558	1.99915
C	-0.60423	2.46687	-1.25356
H	-1.1012	3.43885	-1.1172
H	0.45431	2.62223	-1.47608
H	-1.06997	1.9402	-2.09292
C	-2.12456	1.35333	0.29903
H	-2.69841	1.31383	-0.6335
H	-2.5601	2.16023	0.9058
C	-2.20205	0.03308	1.03206
H	-1.68495	0.09904	1.9982
H	-3.24672	-0.24719	1.23512
O	0.85686	-1.70246	-1.71035
H	0.30925	-1.8643	-2.48873
O	1.86458	0.58855	-0.87291
C	2.96355	0.07541	-0.18451
C	2.65426	-0.13652	1.28136
H	3.82588	0.75912	-0.26718
H	3.30544	-0.89751	-0.60017

O	1.4601	-0.93542	1.40664
H	2.42116	0.81424	1.77344
H	3.48409	-0.61164	1.81799
H	1.51727	-1.03445	-1.98317
H	1.69226	-1.85659	1.22106

Zero-point correction = 0.327130 (Hartree/Particle)

Thermal correction to Energy = 0.346063

Thermal correction to Enthalpy = 0.347007

Thermal correction to Gibbs Free Energy = 0.281398

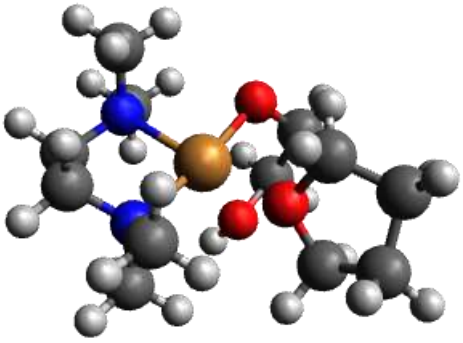
Sum of electronic and zero-point Energies = -850.398378

Sum of electronic and thermal Energies = -850.379444

Sum of electronic and thermal Enthalpies = -850.378500

Sum of electronic and thermal Free Energies = -850.444110

5-EG



Atom	x (Å)	y (Å)	z (Å)
Cu	0.32679	-0.14028	0.13658
N	2.36701	-0.3272	0.50743
N	0.77005	1.81142	-0.3962
C	0.73973	1.91481	-1.866
H	-0.26441	1.67728	-2.22875
H	1.00421	2.93365	-2.18555
H	1.44412	1.20899	-2.31564
C	-0.15317	2.80514	0.17969
H	0.18372	3.82311	-0.06516
H	-1.16013	2.65287	-0.21555
H	-0.18271	2.68866	1.26783
C	2.52196	-0.3712	1.971
H	1.96291	-1.22795	2.3547
H	3.58458	-0.47023	2.23965
H	2.12387	0.53965	2.42863
C	2.91493	-1.55746	-0.07782
H	3.99165	-1.63768	0.13536
H	2.38376	-2.41167	0.34801
H	2.7646	-1.54566	-1.16261
C	3.01587	0.86229	-0.07561
H	3.17984	0.66656	-1.14211
H	4.00631	1.02543	0.37638
C	2.13635	2.07425	0.11563
H	2.0486	2.31983	1.1807
H	2.56668	2.95514	-0.38451
O	0.01535	-1.83405	0.8786
C	-0.79599	-2.59829	0.05767
C	-0.27488	-2.64783	-1.3668
H	-1.84335	-2.22998	0.0332
H	-0.84847	-3.63855	0.42609
O	-0.12764	-1.29232	-1.81155
H	-0.97121	-3.189	-2.02296

H	0.70051	-3.1557	-1.38969
H	0.40507	-1.27592	-2.61419
O	-1.73085	0.32388	0.1906
C	-2.69825	0.36693	-0.8745
C	-3.97912	0.79453	-0.19112
H	-2.78347	-0.63118	-1.32764
H	-2.33749	1.06633	-1.63754
C	-3.86906	0.06564	1.14418
H	-4.86957	0.52506	-0.76519
H	-3.98111	1.88178	-0.03651
C	-2.39405	0.21656	1.47089
H	-4.12863	-0.9933	1.01996
H	-4.51085	0.48375	1.92405
H	-1.9574	-0.635	2.00359
H	-2.18862	1.14003	2.03154

Zero-point correction = 0.419816 (Hartree/Particle)

Thermal correction to Energy = 0.442307

Thermal correction to Enthalpy = 0.443252

Thermal correction to Gibbs Free Energy = 0.368589

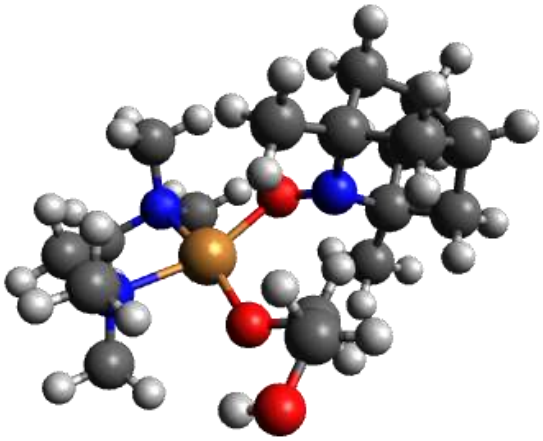
Sum of electronic and zero-point Energies = -1006.207906

Sum of electronic and thermal Energies = -1006.185415

Sum of electronic and thermal Enthalpies = -1006.184471

Sum of electronic and thermal Free Energies = -1006.259134

6-EG



Atom	x (Å)	y (Å)	z (Å)
Cu	1.2763	-0.12947	-0.23676
N	3.26743	0.39842	0.28254
N	1.94266	-2.07189	-0.09519
C	1.51572	-2.66785	1.18044
H	0.42232	-2.67616	1.22169
H	1.88588	-3.7004	1.26402
H	1.89227	-2.08423	2.02631
C	1.40689	-2.87383	-1.20571
H	1.80156	-3.90011	-1.16729
H	0.31547	-2.90938	-1.12973
H	1.68572	-2.41569	-2.16025
C	3.92096	1.02518	-0.87202
H	3.3189	1.8751	-1.20389
H	4.93186	1.36906	-0.60407
H	3.99703	0.31277	-1.69946
C	3.21377	1.34251	1.40413
H	4.22602	1.62163	1.73566
H	2.67688	2.24147	1.08794
H	2.67416	0.88897	2.24375
C	3.93853	-0.85768	0.66507
H	3.73597	-1.04577	1.72579
H	5.03053	-0.7665	0.56199
C	3.41832	-1.99424	-0.18535
H	3.67531	-1.83179	-1.23941
H	3.86958	-2.95213	0.11557
O	0.96461	1.60515	-0.80139
C	-3.64579	0.65007	-1.12092
C	-4.23855	0.37316	0.26427
C	-3.28162	1.00893	1.2776
C	-3.36785	-1.65555	-0.82487

C	-3.00384	-1.29369	1.59006
C	-4.04627	-1.18586	0.46907
C	-1.80385	-0.48179	-2.51323
H	-5.2721	0.711	0.37122
H	-4.97373	-1.72004	0.68933
H	-3.27851	1.67678	-1.24106
H	-4.36041	0.4579	-1.93055
H	-3.72152	1.08933	2.2791
H	-2.93974	2.00991	0.98614
H	-4.08284	-1.86006	-1.63181
H	-2.73915	-2.54563	-0.69187
H	-2.40609	-2.21292	1.54373
H	-3.44514	-1.22385	2.5924
N	-1.5951	-0.19941	-0.05117
O	-0.51765	-0.87679	-0.11799
C	-2.55599	-0.4108	-1.20887
C	-2.16877	-0.02909	1.3455
C	-1.06645	0.24725	2.33569
H	-2.53134	-0.60081	-3.32352
H	-1.11529	-1.33173	-2.54326
H	-1.23506	0.43648	-2.69973
H	-0.49269	1.1412	2.05743
H	-0.3761	-0.5969	2.43196
H	-1.51823	0.43027	3.31656
C	-0.23519	2.24423	-0.76943
C	-0.17444	3.45552	0.14369
H	-1.0539	1.56129	-0.39465
H	-0.57074	2.53958	-1.78474
O	0.83176	4.34613	-0.27632
H	0.00626	3.10918	1.18006
H	-1.12904	3.99814	0.13492
H	1.595	3.7942	-0.49252

Zero-point correction = 0.550416 (Hartree/Particle)

Thermal correction to Energy = 0.577970

Thermal correction to Enthalpy = 0.578914

Thermal correction to Gibbs Free Energy = 0.495397

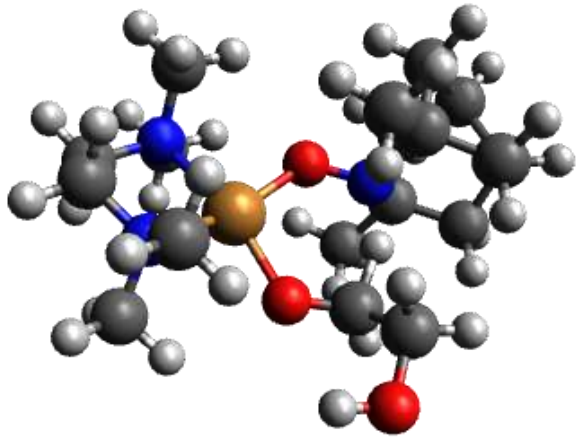
Sum of electronic and zero-point Energies = -1294.031202

Sum of electronic and thermal Energies = -1294.003649

Sum of electronic and thermal Enthalpies = -1294.002705

Sum of electronic and thermal Free Energies = -1294.086221

7-TS-EG



Atom	x (Å)	y (Å)	z (Å)
Cu	1.31747	-0.07649	-0.22882
N	3.25113	0.61391	0.292
N	2.15815	-1.98604	-0.11492
C	1.76551	-2.6175	1.15193
H	0.67539	-2.71259	1.17948
H	2.21982	-3.61619	1.24652
H	2.07679	-2.004	2.00367
C	1.70245	-2.81911	-1.23418
H	2.17454	-3.81381	-1.20412
H	0.61569	-2.93781	-1.1717
H	1.95216	-2.33259	-2.18311
C	3.84432	1.29011	-0.86654
H	3.18548	2.10482	-1.18066
H	4.83595	1.69772	-0.61416
H	3.9518	0.59171	-1.70262
C	3.13781	1.55439	1.41137
H	4.12741	1.92278	1.72552
H	2.52062	2.40406	1.10156
H	2.65383	1.0602	2.2618
C	4.02215	-0.58449	0.671
H	3.82607	-0.79346	1.72943
H	5.10401	-0.39982	0.57984
C	3.61601	-1.76807	-0.18355
H	3.87289	-1.58398	-1.23446
H	4.15958	-2.67437	0.1286
O	0.80644	1.66393	-0.77283
C	-3.6748	0.42142	-1.10627
C	-4.22193	0.11462	0.29258
C	-3.31285	0.84679	1.28561
C	-3.18836	-1.84477	-0.7767

C	-2.82315	-1.41596	1.61698
C	-3.89059	-1.41704	0.51678
C	-1.77268	-0.60328	-2.51671
H	-5.27966	0.36243	0.40894
H	-4.76397	-2.02705	0.75973
H	-3.40077	1.47509	-1.24507
H	-4.38326	0.16196	-1.90246
H	-3.74662	0.90453	2.29134
H	-3.06888	1.8711	0.97778
H	-3.89249	-2.12646	-1.56973
H	-2.48306	-2.67394	-0.64018
H	-2.14658	-2.27802	1.57169
H	-3.25146	-1.37453	2.62646
N	-1.52016	-0.19287	-0.06489
O	-0.44008	-0.90784	-0.10382
C	-2.50345	-0.54662	-1.19902
C	-2.11419	-0.08889	1.35367
C	-1.02802	0.2748	2.33312
H	-2.50177	-0.83423	-3.30118
H	-1.00728	-1.3851	-2.51758
H	-1.29773	0.34986	-2.77277
H	-0.52236	1.20843	2.05754
H	-0.27675	-0.51721	2.41775
H	-1.4838	0.4207	3.31851
C	-0.42993	2.09675	-0.79638
C	-0.69753	3.29671	0.09543
H	-1.16027	1.12556	-0.3718
H	-0.87179	2.209	-1.80807
O	-0.01576	4.42359	-0.40199
H	-0.39135	3.06283	1.13028
H	-1.766	3.54718	0.10152
H	0.92386	4.20161	-0.41347

Zero-point correction = 0.546197 (Hartree/Particle)

Thermal correction to Energy = 0.573559

Thermal correction to Enthalpy = 0.574503

Thermal correction to Gibbs Free Energy = 0.491437

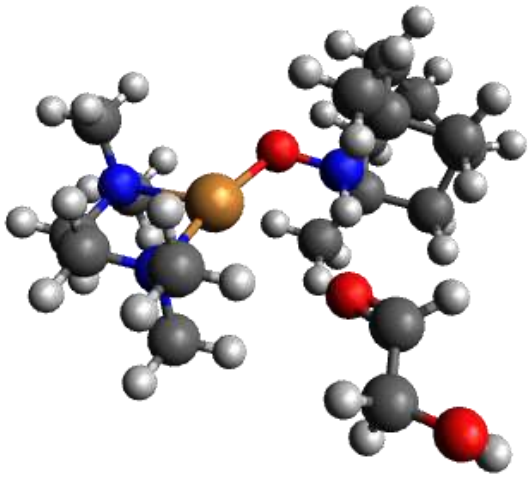
Sum of electronic and zero-point Energies = -1294.030772

Sum of electronic and thermal Energies = -1294.003411

Sum of electronic and thermal Enthalpies = -1294.002467

Sum of electronic and thermal Free Energies = -1294.085532

8-EG



Atom	x (Å)	y (Å)	z (Å)
Cu	1.3566	-0.3181	0.22758
N	2.72978	1.11399	0.25268
N	3.11171	-1.72129	-0.21507
C	3.32107	-2.5476	0.96861
H	2.43286	-3.16583	1.14201
H	4.19814	-3.21003	0.85553
H	3.47158	-1.92142	1.85485
C	2.87787	-2.5559	-1.38611
H	3.75132	-3.18636	-1.63138
H	2.01924	-3.21104	-1.19854
H	2.64497	-1.92441	-2.25204
C	2.68461	1.82999	-1.03536
H	1.70592	2.30859	-1.13948
H	3.47671	2.59503	-1.08111
H	2.81392	1.13151	-1.86794
C	2.48712	2.07343	1.34215
H	3.25921	2.85987	1.35288
H	1.50515	2.53562	1.20273
H	2.49448	1.55015	2.30334
C	4.04303	0.45771	0.45094
H	4.10916	0.17889	1.51037
H	4.85501	1.17703	0.25309
C	4.20548	-0.77169	-0.42498
H	4.20875	-0.48048	-1.48283
H	5.18914	-1.23308	-0.22597
O	-0.70527	2.13992	-0.39823
C	-3.35185	-0.36586	-1.40299
C	-4.13027	-0.83221	-0.17007
C	-3.58893	-0.01228	1.00388

C	-2.56315	-2.53477	-1.01406
C	-2.80421	-2.17916	1.41009
C	-3.59346	-2.29752	0.09877
C	-1.0458	-0.93471	-2.36082
H	-5.215	-0.76845	-0.28598
H	-4.37958	-3.05604	0.13207
H	-3.22723	0.72404	-1.45514
H	-3.81074	-0.68798	-2.34585
H	-4.22971	-0.05963	1.89289
H	-3.44311	1.04981	0.7627
H	-3.02098	-2.88283	-1.9484
H	-1.77805	-3.24551	-0.73565
H	-2.00087	-2.91736	1.50235
H	-3.44334	-2.25938	2.29822
N	-1.39207	-0.65722	0.07715
O	-0.21368	-1.34774	0.29017
C	-2.04121	-1.12628	-1.24361
C	-2.29553	-0.7501	1.32471
C	-1.52965	-0.21801	2.51
H	-1.5356	-1.1733	-3.31172
H	-0.17576	-1.58626	-2.24077
H	-0.70069	0.10741	-2.41047
H	-1.17856	0.80754	2.32728
H	-0.66606	-0.84507	2.74581
H	-2.19712	-0.19491	3.37882
C	-1.28008	3.18156	-0.14504
C	-0.70107	4.53263	-0.4572
H	-1.18747	0.35092	-0.05049
H	-2.27611	3.19732	0.35249
O	-1.57769	5.579	-0.16703
H	-0.33978	4.52275	-1.49789
H	0.1939	4.64946	0.173
H	-2.20167	5.67528	-0.89458

Zero-point correction = 0.550070 (Hartree/Particle)

Thermal correction to Energy = 0.579463

Thermal correction to Enthalpy = 0.580407

Thermal correction to Gibbs Free Energy = 0.489644

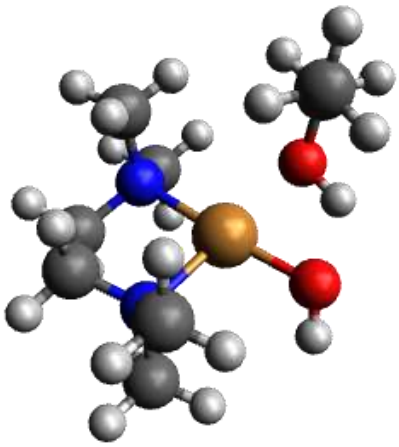
Sum of electronic and zero-point Energies = -1294.072237

Sum of electronic and thermal Energies = -1294.042844

Sum of electronic and thermal Enthalpies = -1294.041900

Sum of electronic and thermal Free Energies = -1294.132663

2-EtOH



Atom	x (Å)	y (Å)	z (Å)
Cu	0.11592	-0.36215	-0.39359
N	-0.17011	1.60655	-0.04775
N	-1.80199	-0.65689	0.27313
C	-2.66905	-1.05108	-0.85187
H	-2.3039	-1.98425	-1.28711
H	-3.69821	-1.2044	-0.4975
H	-2.66936	-0.27969	-1.62703
C	-1.79838	-1.71405	1.30006
H	-2.80615	-1.83936	1.72123
H	-1.46673	-2.6508	0.84736
H	-1.1018	-1.44612	2.10171
C	0.47436	2.02221	1.21343
H	1.55593	1.88655	1.13179
H	0.2658	3.0825	1.41388
H	0.11077	1.42333	2.05337
C	0.36648	2.41369	-1.16075
H	0.12366	3.4752	-1.0114
H	1.45142	2.29346	-1.20789
H	-0.06886	2.07333	-2.10505
C	-1.64256	1.77085	0.03746
H	-2.0366	1.76485	-0.98582
H	-1.89173	2.74726	0.4774
C	-2.23514	0.64043	0.84486
H	-1.89258	0.68311	1.88465
H	-3.33228	0.70225	0.86524
O	0.51969	-2.10387	-0.88023
H	-0.12763	-2.46926	-1.49137
O	2.16546	-0.19894	-0.86089
C	3.18554	-0.12862	0.14925
C	2.83659	-0.9347	1.3765

H	3.30974	0.93557	0.38144
H	4.12814	-0.47001	-0.29549
H	1.90334	-0.58005	1.83686
H	3.62947	-0.84925	2.12636
H	2.71386	-1.99486	1.12918
H	2.05833	-1.13445	-1.15016

Zero-point correction = 0.321738 (Hartree/Particle)

Thermal correction to Energy = 0.339997

Thermal correction to Enthalpy = 0.340941

Thermal correction to Gibbs Free Energy = 0.276440

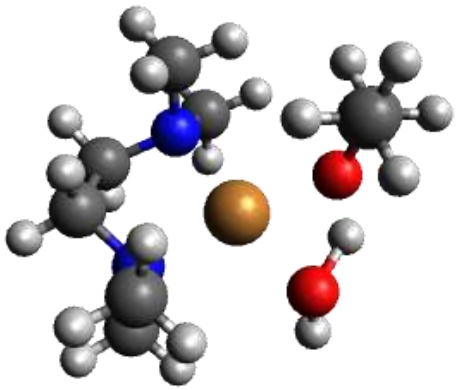
Sum of electronic and zero-point Energies = -775.204272

Sum of electronic and thermal Energies = -775.186013

Sum of electronic and thermal Enthalpies = -775.185069

Sum of electronic and thermal Free Energies = -775.249570

3-TS-EtOH



Atom	x (Å)	y (Å)	z (Å)
Cu	0.15327	-0.32676	-0.33302
N	-0.26947	1.62677	-0.05778
N	-1.73828	-0.73786	0.25088
C	-2.50992	-1.21981	-0.91085
H	-2.04287	-2.12536	-1.30619
H	-3.5404	-1.45267	-0.608
H	-2.53192	-0.46159	-1.69884
C	-1.71113	-1.77511	1.29914
H	-2.727	-1.96542	1.67298
H	-1.29513	-2.69508	0.88211
H	-1.07736	-1.44423	2.12901
C	0.31211	2.10725	1.21102
H	1.40212	2.03881	1.15921
H	0.03026	3.15578	1.38102
H	-0.03533	1.50351	2.05434
C	0.26263	2.4248	-1.1783
H	-0.02483	3.47917	-1.06237
H	1.35204	2.34195	-1.19518
H	-0.13508	2.04306	-2.12323
C	-1.75203	1.69375	-0.02588
H	-2.10784	1.65163	-1.06213
H	-2.0803	2.65568	0.39314
C	-2.29748	0.53347	0.77424
H	-2.01151	0.61843	1.82849
H	-3.39547	0.51089	0.73937
O	0.77608	-2.14979	-0.74818
H	0.43507	-2.48604	-1.58616
O	2.05666	-0.24105	-0.8836
C	3.06763	0.02258	0.0734
C	2.86796	-0.73224	1.3711
H	3.10774	1.10806	0.25733

H	4.03691	-0.24639	-0.372
H	1.90886	-0.47163	1.84495
H	3.66263	-0.49494	2.08614
H	2.87491	-1.81478	1.20084
H	1.70314	-1.39678	-0.93792

Zero-point correction = 0.318325 (Hartree/Particle)

Thermal correction to Energy = 0.335412

Thermal correction to Enthalpy = 0.336357

Thermal correction to Gibbs Free Energy = 0.274814

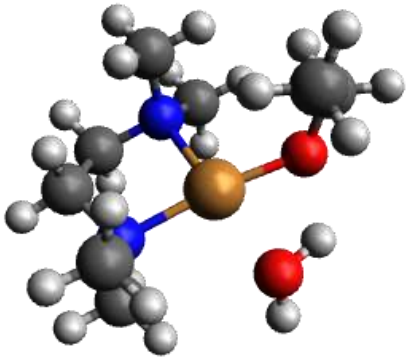
Sum of electronic and zero-point Energies = -775.201273

Sum of electronic and thermal Energies = -775.184185

Sum of electronic and thermal Enthalpies = -775.183241

Sum of electronic and thermal Free Energies = -775.244784

4-EtOH



Atom	x (Å)	y (Å)	z (Å)
Cu	0.17142	-0.35979	-0.31388
N	-0.12465	1.65156	-0.08887
N	-1.76153	-0.61054	0.26032
C	-2.57554	-1.07498	-0.88011
H	-2.20207	-2.03951	-1.23205
H	-3.62349	-1.19531	-0.57137
H	-2.52718	-0.35809	-1.70466
C	-1.83765	-1.59434	1.35769
H	-2.86666	-1.66269	1.73806
H	-1.52178	-2.57395	0.99196
H	-1.17213	-1.28904	2.17261
C	0.43773	2.12597	1.18953
H	1.52398	2.00833	1.17504
H	0.19682	3.18889	1.33359
H	0.03787	1.5528	2.03088
C	0.4888	2.39072	-1.20593
H	0.26868	3.46395	-1.11446
H	1.56941	2.23258	-1.19297
H	0.09124	2.01872	-2.1546
C	-1.59878	1.80421	-0.10891
H	-1.92584	1.73431	-1.15327
H	-1.88247	2.80205	0.25649
C	-2.23392	0.71785	0.72567
H	-1.95489	0.82574	1.7796
H	-3.33033	0.77103	0.67705
O	0.48958	-2.41383	-0.67583
H	0.09775	-2.80273	-1.46877
O	1.96176	-0.36643	-0.87426
C	2.97627	-0.05768	0.03395
C	2.84969	-0.79861	1.35328
H	3.03341	1.03342	0.2241
H	3.94269	-0.31535	-0.43261

H	1.90403	-0.54919	1.86075
H	3.66686	-0.54597	2.03863
H	2.86449	-1.88337	1.18948
H	1.3915	-2.10673	-0.93146

Zero-point correction = 0.321380 (Hartree/Particle)

Thermal correction to Energy = 0.339473

Thermal correction to Enthalpy = 0.340417

Thermal correction to Gibbs Free Energy = 0.276427

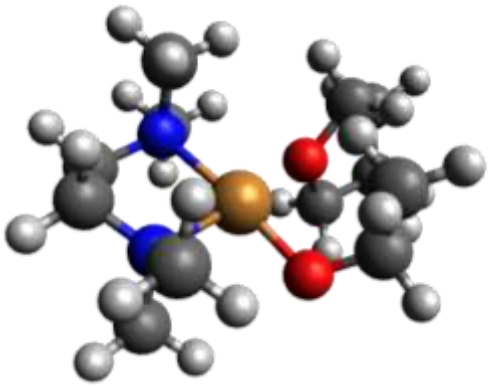
Sum of electronic and zero-point Energies = -775.204441

Sum of electronic and thermal Energies = -775.186348

Sum of electronic and thermal Enthalpies = -775.185404

Sum of electronic and thermal Free Energies = -775.249395

5-EtOH



Atom	x (Å)	y (Å)	z (Å)
Cu	0.33366	0.16819	-0.14422
N	2.38207	0.47324	-0.26689
N	0.81238	-1.77653	0.30062
C	0.71375	-1.9095	1.76696
H	-0.33131	-1.80396	2.07075
H	1.07826	-2.8954	2.09068
H	1.29512	-1.13101	2.27095
C	-0.04729	-2.78578	-0.34165
H	0.29348	-3.79812	-0.08077
H	-1.0806	-2.65517	-0.00994
H	-0.00532	-2.66323	-1.42855
C	2.65546	0.72234	-1.69337
H	2.07244	1.58893	-2.01397
H	3.72732	0.91813	-1.84444
H	2.36487	-0.14346	-2.29673
C	2.80259	1.6367	0.52781
H	3.88814	1.78841	0.43527
H	2.26458	2.51549	0.16656
H	2.54945	1.4724	1.58084
C	3.04554	-0.75888	0.20691
H	3.16876	-0.68232	1.29303
H	4.05436	-0.84265	-0.22308
C	2.2098	-1.9636	-0.1546
H	2.18342	-2.10387	-1.24207
H	2.63319	-2.88022	0.28337
O	0.03279	1.92304	-0.65061
C	-0.91376	2.63444	0.07931
C	-0.6093	2.67933	1.56866
H	-1.94004	2.23923	-0.06707
H	-0.94125	3.66906	-0.30739
O	-1.69848	-0.2932	-0.09312

C	-2.6485	-0.30491	0.99277
C	-3.93134	-0.77869	0.34697
H	-2.74657	0.71185	1.40105
H	-2.26284	-0.96699	1.77567
C	-3.86226	-0.08817	-1.0116
H	-4.8157	-0.50714	0.92902
H	-3.91433	-1.86993	0.22824
C	-2.39031	-0.20713	-1.36555
H	-4.15088	0.96581	-0.91606
H	-4.5044	-0.54923	-1.76629
H	-1.98787	0.65157	-1.91371
H	-2.16924	-1.12837	-1.92191
H	-1.38247	3.22433	2.12411
H	0.35563	3.16548	1.75492
H	-0.55429	1.66036	1.98818

Zero-point correction = 0.413687 (Hartree/Particle)

Thermal correction to Energy = 0.435577

Thermal correction to Enthalpy = 0.436521

Thermal correction to Gibbs Free Energy = 0.362614

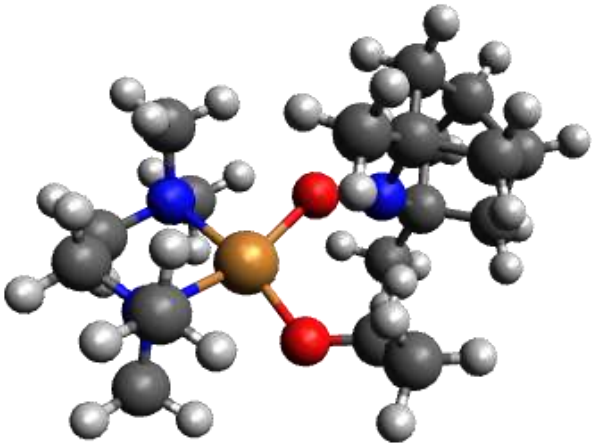
Sum of electronic and zero-point Energies = -931.014344

Sum of electronic and thermal Energies = -930.992455

Sum of electronic and thermal Enthalpies = -930.991510

Sum of electronic and thermal Free Energies = -931.065418

6-EtOH



Atom	x (Å)	y (Å)	z (Å)
Cu	1.30729	0.07096	-0.25485
N	3.27608	0.71468	0.21796
N	2.06742	-1.83323	-0.00641
C	1.66695	-2.36999	1.30302
H	0.57486	-2.42141	1.34781
H	2.08118	-3.37899	1.44816
H	2.01809	-1.72087	2.11113
C	1.56989	-2.72332	-1.06554
H	2.01376	-3.72579	-0.97038
H	0.48165	-2.80683	-0.98293
H	1.82418	-2.30852	-2.04642
C	3.89058	1.29561	-0.98077
H	3.2489	2.09922	-1.35085
H	4.8899	1.69514	-0.74775
H	3.98703	0.53817	-1.76523
C	3.18391	1.72901	1.27339
H	4.18379	2.07909	1.57469
H	2.59906	2.57409	0.89805
H	2.67425	1.3068	2.14759
C	4.00421	-0.48241	0.67408
H	3.81066	-0.61453	1.74505
H	5.09122	-0.34818	0.56262
C	3.53721	-1.69269	-0.10342
H	3.78725	-1.58304	-1.16606
H	4.03336	-2.60782	0.25509
O	0.92356	1.76406	-0.89611
C	-3.63859	0.60138	-1.16172
C	-4.21628	0.37217	0.23875
C	-3.28658	1.10272	1.21256
C	-3.25834	-1.67073	-0.74495

C	-2.90318	-1.16439	1.64461
C	-3.95355	-1.1636	0.52555
C	-1.75316	-0.52382	-2.50005
H	-5.264	0.66826	0.33192
H	-4.8556	-1.72591	0.77925
H	-3.31487	1.63534	-1.33551
H	-4.34579	0.3373	-1.95762
H	-3.72709	1.2155	2.21081
H	-2.99009	2.10063	0.86669
H	-3.96605	-1.94988	-1.5359
H	-2.59031	-2.52372	-0.56781
H	-2.26488	-2.05717	1.64289
H	-3.34439	-1.06254	2.64431
N	-1.54836	-0.09128	-0.06082
O	-0.44848	-0.74281	-0.09022
C	-2.50387	-0.41417	-1.19738
C	-2.12796	0.12084	1.32795
C	-1.03743	0.50164	2.29655
H	-2.47614	-0.71887	-3.29964
H	-1.028	-1.34331	-2.48517
H	-1.22451	0.40617	-2.7386
H	-0.50806	1.40502	1.96687
H	-0.30725	-0.30258	2.43298
H	-1.4941	0.71497	3.2691
C	-0.29875	2.3441	-0.89638
C	-0.37278	3.59733	-0.04054
H	-1.07247	1.60681	-0.50125
H	-0.66258	2.54461	-1.92573
H	-0.10327	3.37343	0.99969
H	-1.38095	4.02923	-0.05364
H	0.32932	4.35287	-0.41225

Zero-point correction = 0.544662 (Hartree/Particle)

Thermal correction to Energy = 0.571247

Thermal correction to Enthalpy = 0.572191

Thermal correction to Gibbs Free Energy = 0.490955

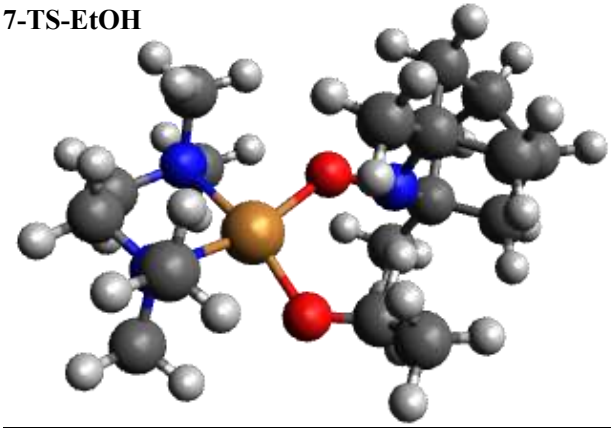
Sum of electronic and zero-point Energies = -1218.850505

Sum of electronic and thermal Energies = -1218.823920

Sum of electronic and thermal Enthalpies = -1218.822975

Sum of electronic and thermal Free Energies = -1218.904212

7-TS-EtOH



Atom	x (Å)	y (Å)	z (Å)
Cu	1.31833	0.08275	-0.25418
N	3.25837	0.80388	0.21546
N	2.15907	-1.81197	0.00154
C	1.76929	-2.34334	1.31431
H	0.67855	-2.42562	1.35536
H	2.21535	-3.33635	1.4809
H	2.09234	-1.67032	2.11504
C	1.6975	-2.72681	-1.04932
H	2.16688	-3.71767	-0.94443
H	0.61056	-2.83695	-0.97501
H	1.94602	-2.31493	-2.03323
C	3.84838	1.39472	-0.98999
H	3.18381	2.17823	-1.36458
H	4.83721	1.82668	-0.76846
H	3.96189	0.63556	-1.77059
C	3.14364	1.82257	1.26386
H	4.13272	2.21557	1.549
H	2.52199	2.64405	0.89382
H	2.66338	1.3887	2.14875
C	4.0299	-0.3639	0.67701
H	3.83983	-0.49588	1.74877
H	5.11167	-0.18859	0.56729
C	3.61743	-1.60495	-0.08806
H	3.87007	-1.49816	-1.15067
H	4.15899	-2.48848	0.28663
O	0.81214	1.77325	-0.92403
C	-3.66554	0.49985	-1.16026
C	-4.21544	0.28762	0.25506
C	-3.30842	1.08567	1.19757
C	-3.17982	-1.73885	-0.67847
C	-2.81731	-1.1487	1.68214
C	-3.88341	-1.22534	0.58279

C	-1.75903	-0.61321	-2.49388
H	-5.27376	0.54152	0.3524
H	-4.75686	-1.81802	0.86546
H	-3.39106	1.54191	-1.3684
H	-4.37216	0.18644	-1.93857
H	-3.74343	1.20814	2.1971
H	-3.0631	2.08657	0.8226
H	-3.88299	-2.07312	-1.45183
H	-2.47423	-2.55666	-0.48548
H	-2.14071	-2.01196	1.69589
H	-3.24723	-1.03923	2.68584
N	-1.51584	-0.04506	-0.076
O	-0.43235	-0.75063	-0.06718
C	-2.49273	-0.47087	-1.18412
C	-2.10832	0.15809	1.32791
C	-1.02334	0.59153	2.28071
H	-2.4871	-0.88421	-3.26643
H	-0.99994	-1.39977	-2.44549
H	-1.27425	0.31939	-2.80204
H	-0.52022	1.50447	1.93993
H	-0.27014	-0.1909	2.42055
H	-1.48018	0.80388	3.25355
C	-0.42459	2.21916	-0.95984
C	-0.70811	3.46394	-0.14435
H	-1.13751	1.29918	-0.49298
H	-0.8703	2.25957	-1.97568
H	-0.38494	3.34238	0.89618
H	-1.7727	3.72424	-0.15871
H	-0.14993	4.30867	-0.56697

Zero-point correction = 0.540955 (Hartree/Particle)

Thermal correction to Energy = 0.567177

Thermal correction to Enthalpy = 0.568121

Thermal correction to Gibbs Free Energy = 0.487922

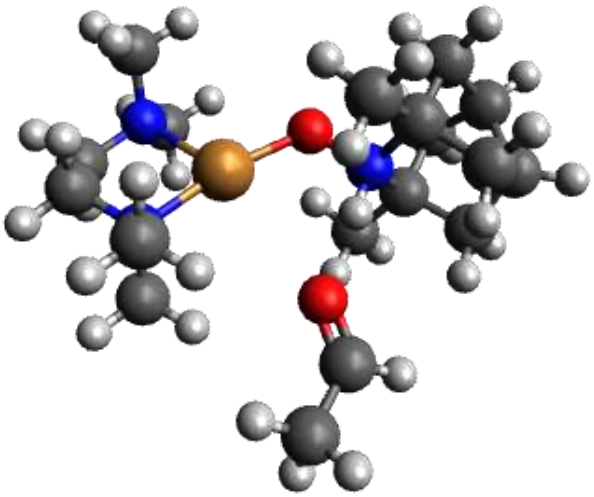
Sum of electronic and zero-point Energies = -1218.852045

Sum of electronic and thermal Energies = -1218.825824

Sum of electronic and thermal Enthalpies = -1218.824880

Sum of electronic and thermal Free Energies = -1218.905079

8-EtOH



Atom	x (Å)	y (Å)	z (Å)
Cu	1.26767	-0.27848	0.17348
N	2.77644	1.00745	0.32323
N	2.87822	-1.82336	-0.2928
C	2.96425	-2.73281	0.84461
H	2.01116	-3.26138	0.96056
H	3.76961	-3.47764	0.7129
H	3.15382	-2.17692	1.7694
C	2.59134	-2.56049	-1.5167
H	3.39705	-3.27026	-1.77625
H	1.65939	-3.12358	-1.39
H	2.45699	-1.85966	-2.34942
C	2.85126	1.79708	-0.91849
H	1.93126	2.38071	-1.02466
H	3.7146	2.48194	-0.89201
H	2.94316	1.14034	-1.78897
C	2.58923	1.92442	1.46079
H	3.44129	2.61844	1.54744
H	1.66684	2.49453	1.31104
H	2.50251	1.34697	2.3869
C	4.00733	0.20784	0.51984
H	4.00875	-0.13254	1.56324
H	4.89627	0.84662	0.38621
C	4.07117	-0.98426	-0.41917
H	4.13968	-0.63991	-1.4587
H	4.99429	-1.55688	-0.21963
O	-0.48108	2.45187	0.00868
C	-3.47874	0.39539	-1.26073
C	-4.25213	-0.10773	-0.03946
C	-3.56392	0.51386	1.17885

C	-2.94018	-1.87774	-1.14149
C	-3.02942	-1.76096	1.31624
C	-3.88428	-1.64542	0.04663
C	-1.30034	-0.32376	-2.39849
H	-5.32529	0.09281	-0.08703
H	-4.75374	-2.30767	0.04635
H	-3.22876	1.4636	-1.20627
H	-4.01345	0.23337	-2.20469
H	-4.16575	0.44327	2.09327
H	-3.30074	1.57117	1.03981
H	-3.4774	-2.06716	-2.07916
H	-2.23494	-2.69995	-0.98201
H	-2.31851	-2.59329	1.28766
H	-3.63413	-1.86135	2.22619
N	-1.50418	-0.27717	0.06753
O	-0.41126	-1.121	0.13921
C	-2.26271	-0.52213	-1.25384
C	-2.35637	-0.39909	1.3487
C	-1.48069	-0.09075	2.53725
H	-1.85444	-0.39284	-3.34139
H	-0.51114	-1.08071	-2.39676
H	-0.83156	0.66968	-2.35334
H	-1.02132	0.90302	2.44346
H	-0.68718	-0.83335	2.6559
H	-2.10193	-0.09143	3.44009
C	-0.8682	3.46514	-0.54852
C	-0.14942	4.76169	-0.51412
H	-1.18204	0.70828	0.0309
H	-1.81369	3.45078	-1.13227
H	0.75194	4.70109	0.10075
H	-0.81847	5.54173	-0.13232
H	0.10961	5.05693	-1.53843

Zero-point correction = 0.544406 (Hartree/Particle)

Thermal correction to Energy = 0.572058

Thermal correction to Enthalpy = 0.573002

Thermal correction to Gibbs Free Energy = 0.486816

Sum of electronic and zero-point Energies = -1218.899191

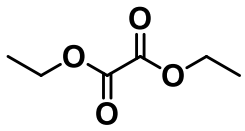
Sum of electronic and thermal Energies = -1218.871539

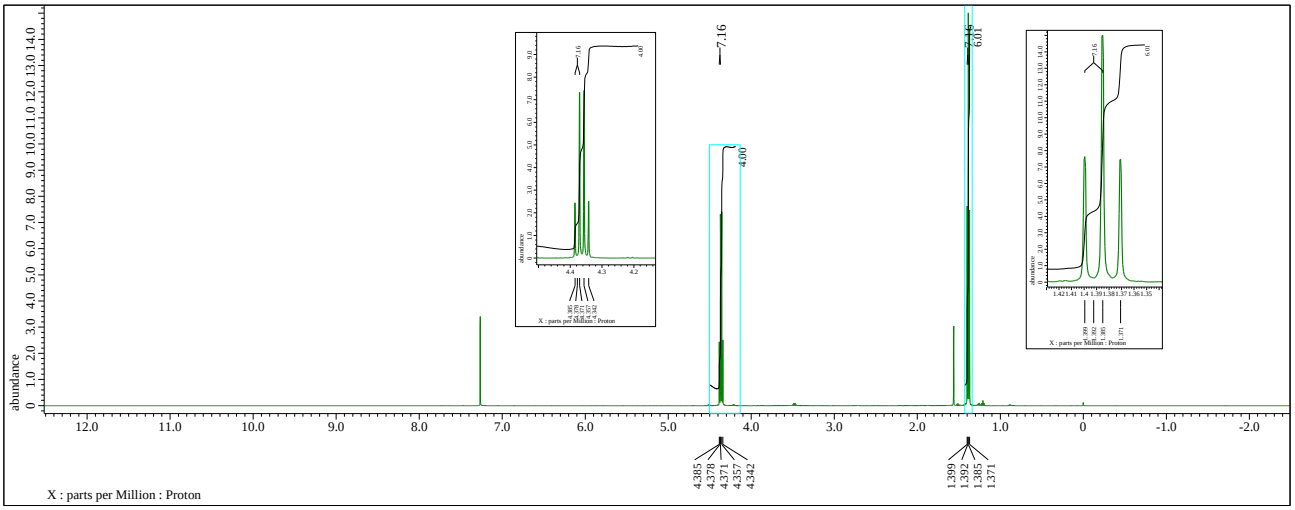
Sum of electronic and thermal Enthalpies = -1218.870595

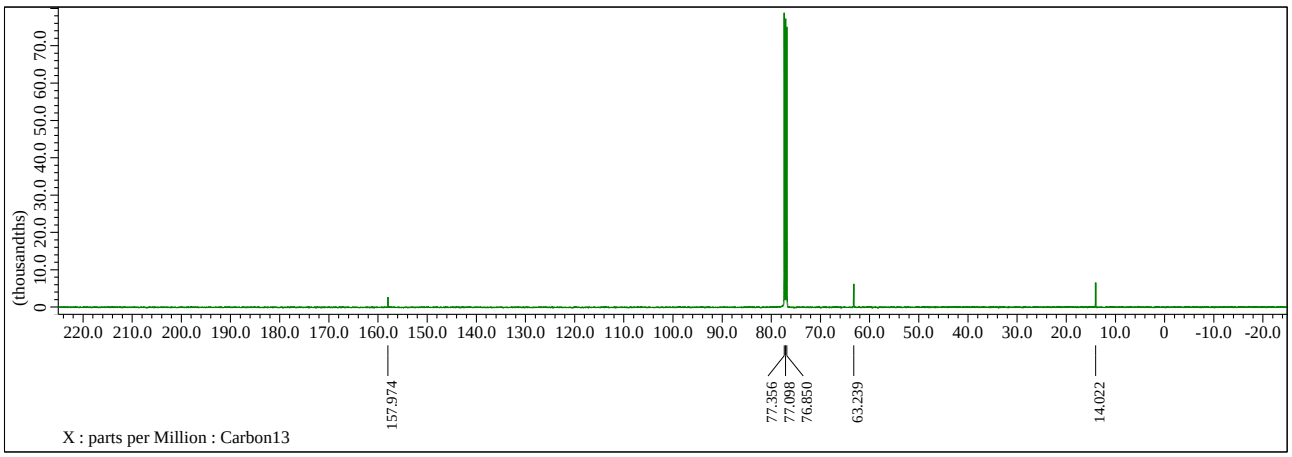
Sum of electronic and thermal Free Energies = -1218.956781

NMR spectra

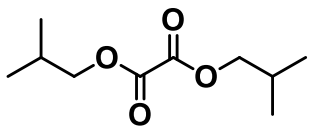
1c

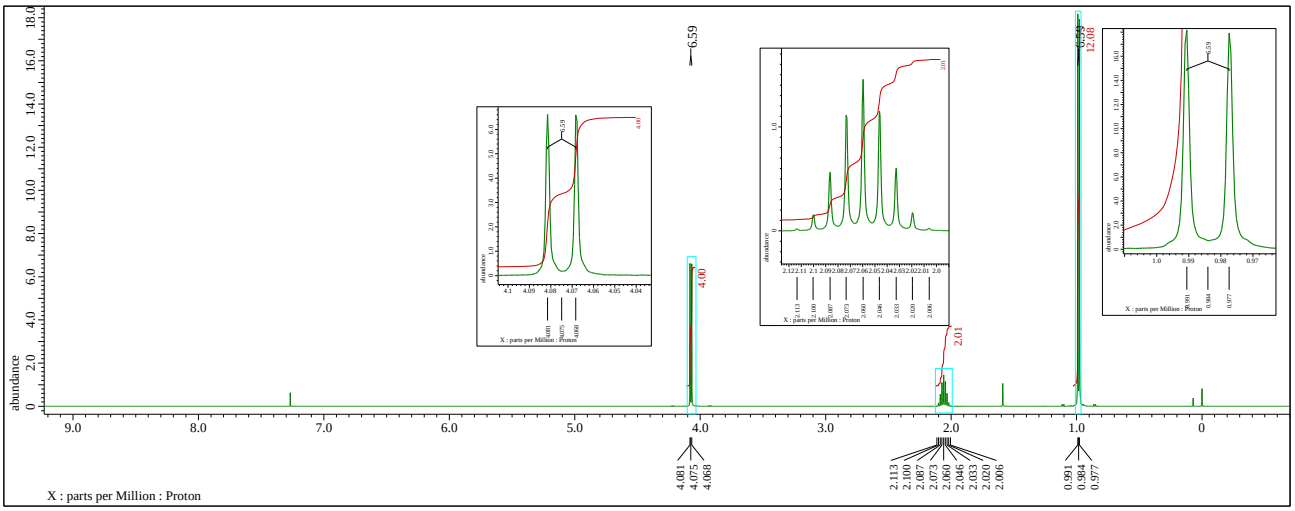


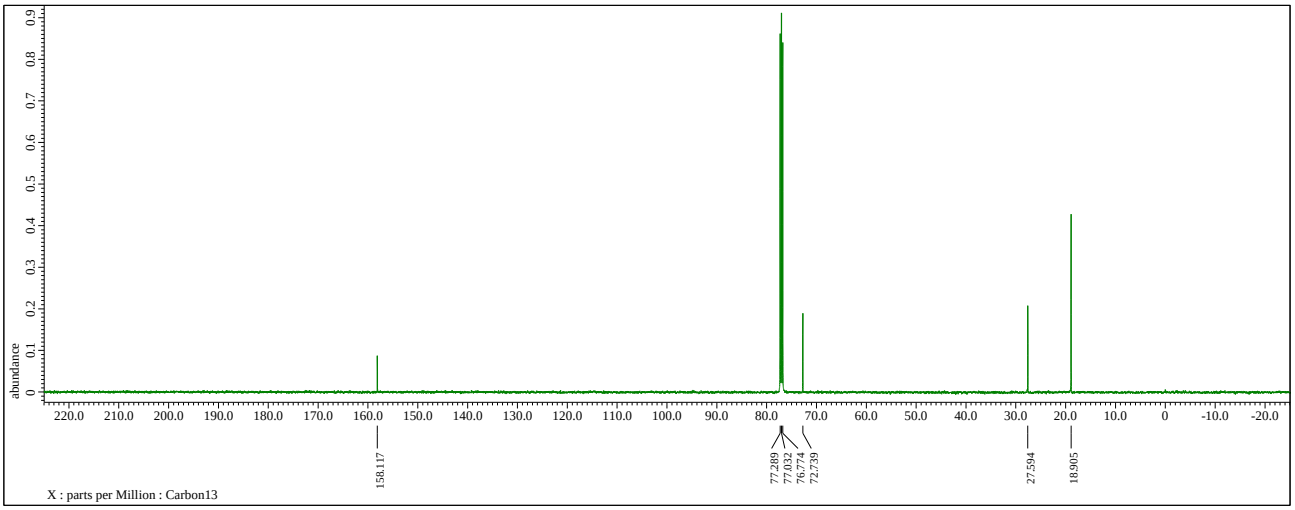




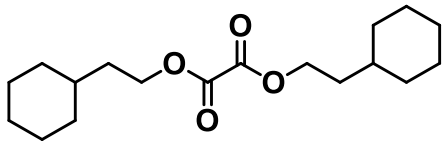
5c

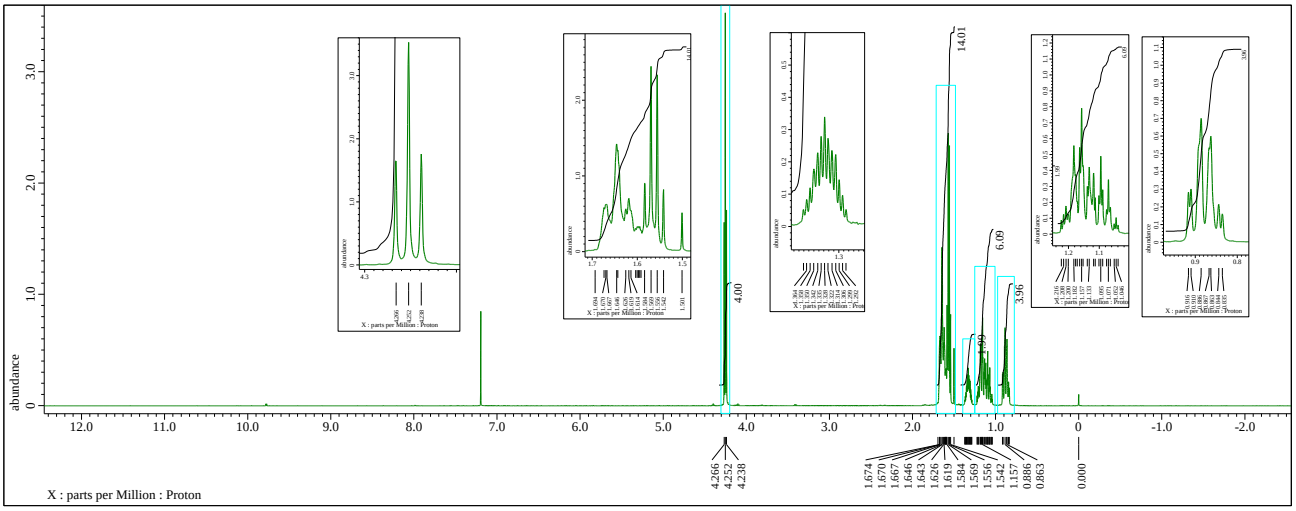


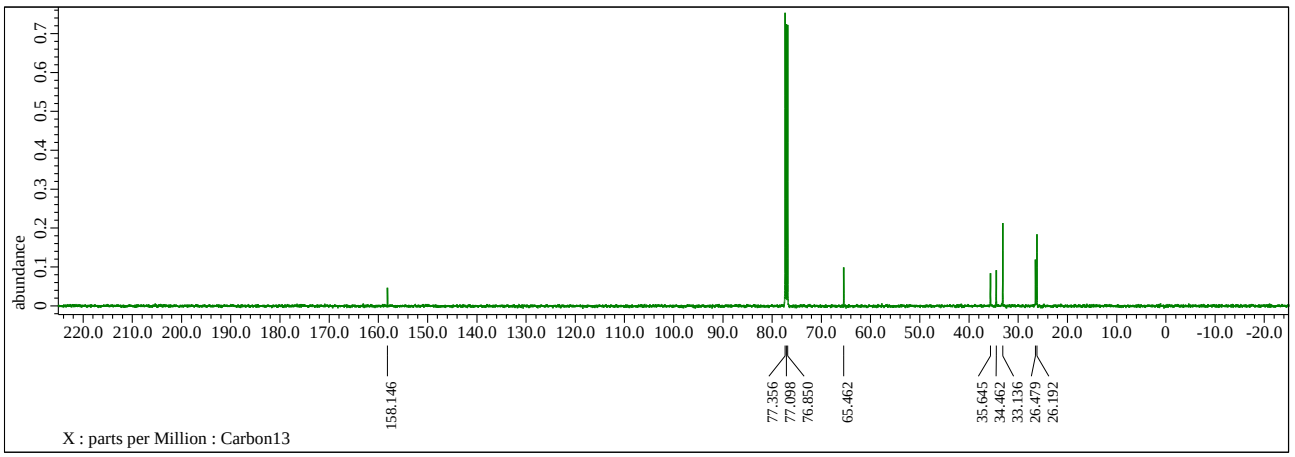

6.59
4.00
2.01
12.08
abundance
X : parts per Million : Proton
4.081
4.075
4.068
2.113
2.100
2.073
2.060
2.046
2.033
2.020
2.006
0.991
0.984
0.977


abundance
X : parts per Million : Carbon13
158.117
77.289
77.032
76.774
72.739
27.594
18.905

6c




abundance
X : parts per Million : Proton
14.01
6.09
4.00
3.96
4.266
4.252
4.238
1.674
1.670
1.667
1.646
1.643
1.626
1.614
1.584
1.569
1.556
1.542
1.157
0.886
0.863
0.000


abundance
X : parts per Million : Carbon13
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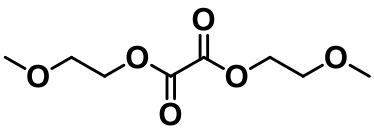
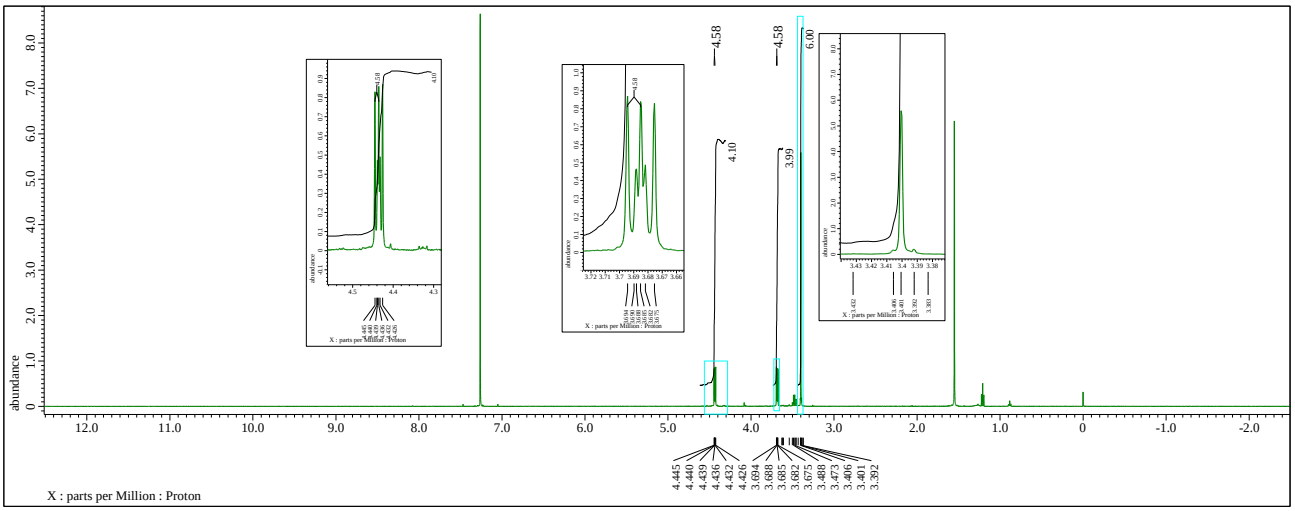
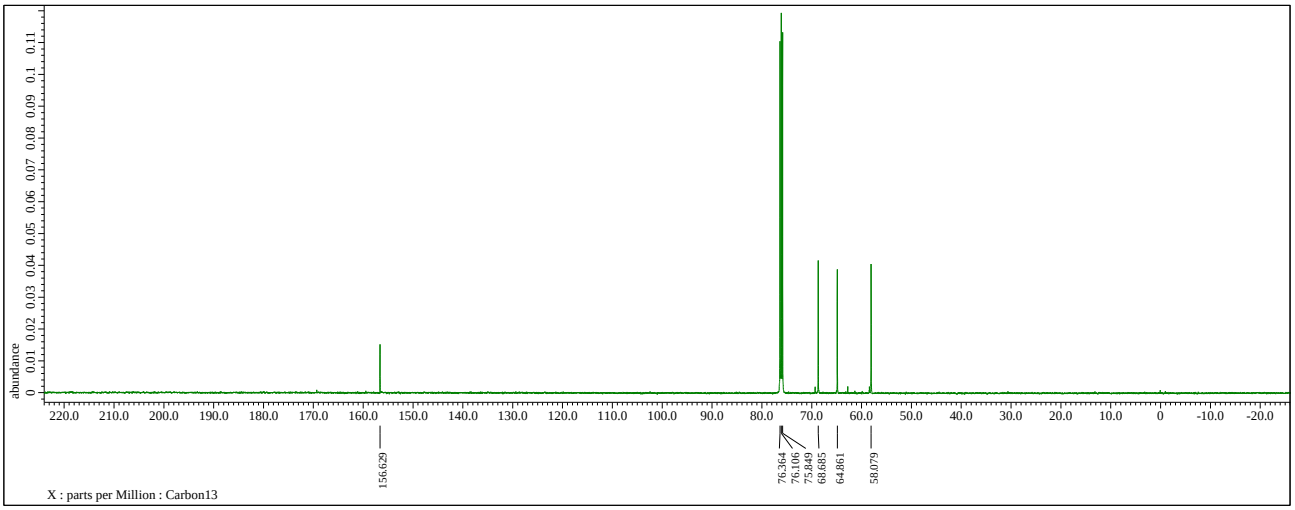
77.356
77.098
76.850
65.462
35.645
34.462
33.136
26.479
26.192

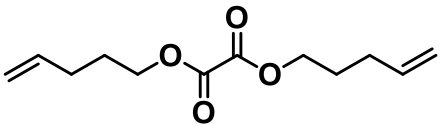
7c

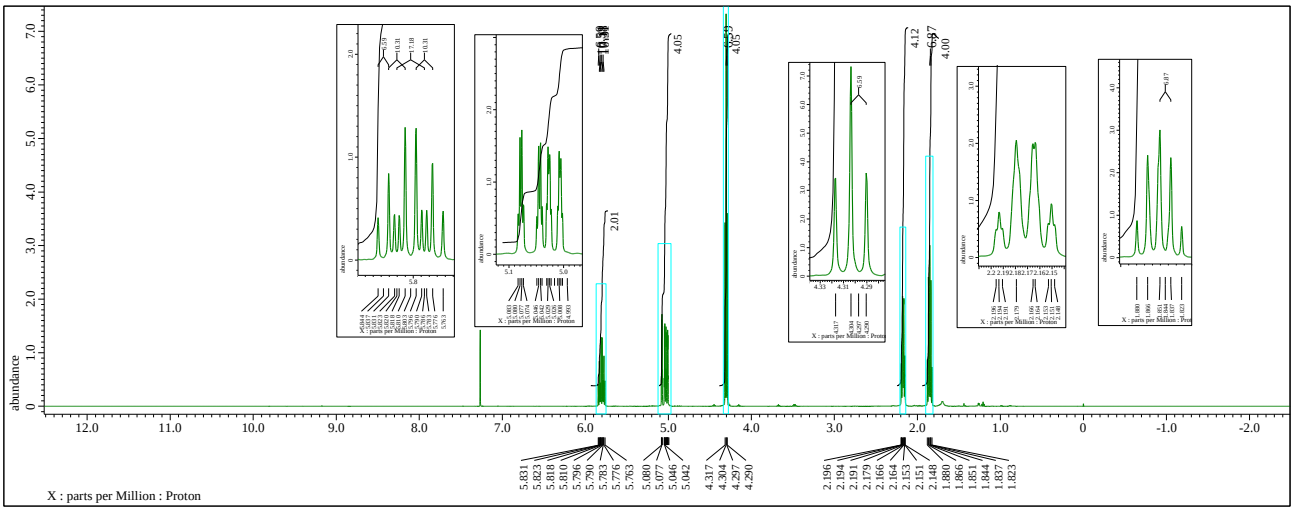


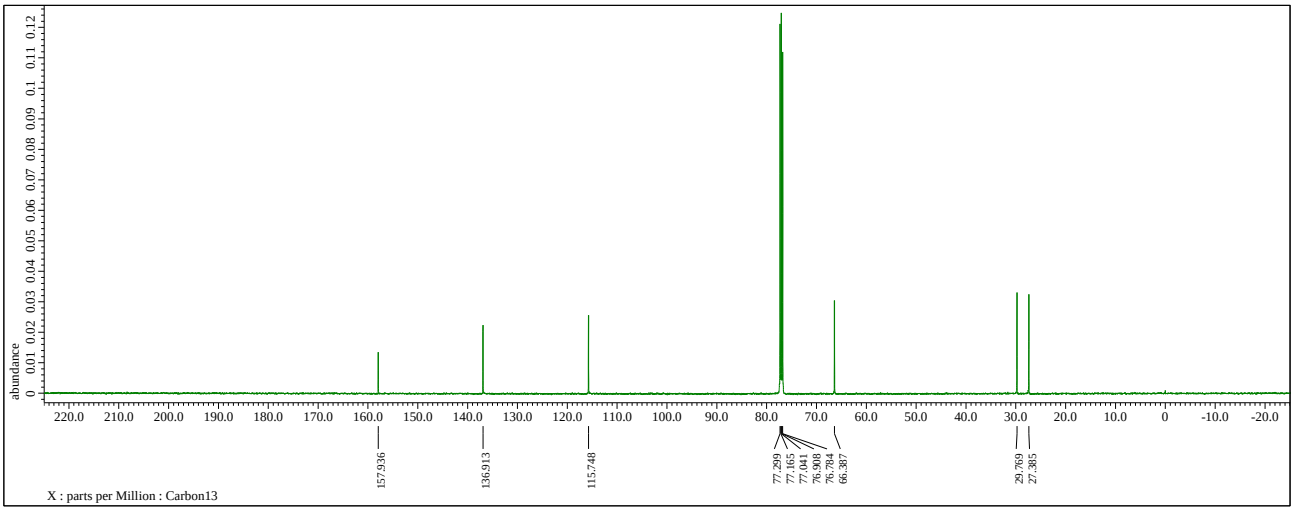

abundance
X : parts per Million : Proton
4.58
4.58
6.00
4.10
3.99
4.445
4.440
4.439
4.436
4.432
4.426
3.694
3.688
3.685
3.682
3.675
3.473
3.406
3.401
3.392


abundance
X : parts per Million : Carbon13
156.629
76.364
76.106
75.849
66.605
64.861
58.079

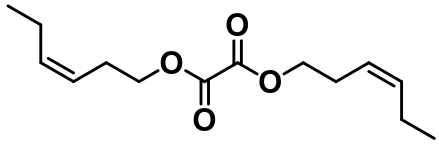
8c

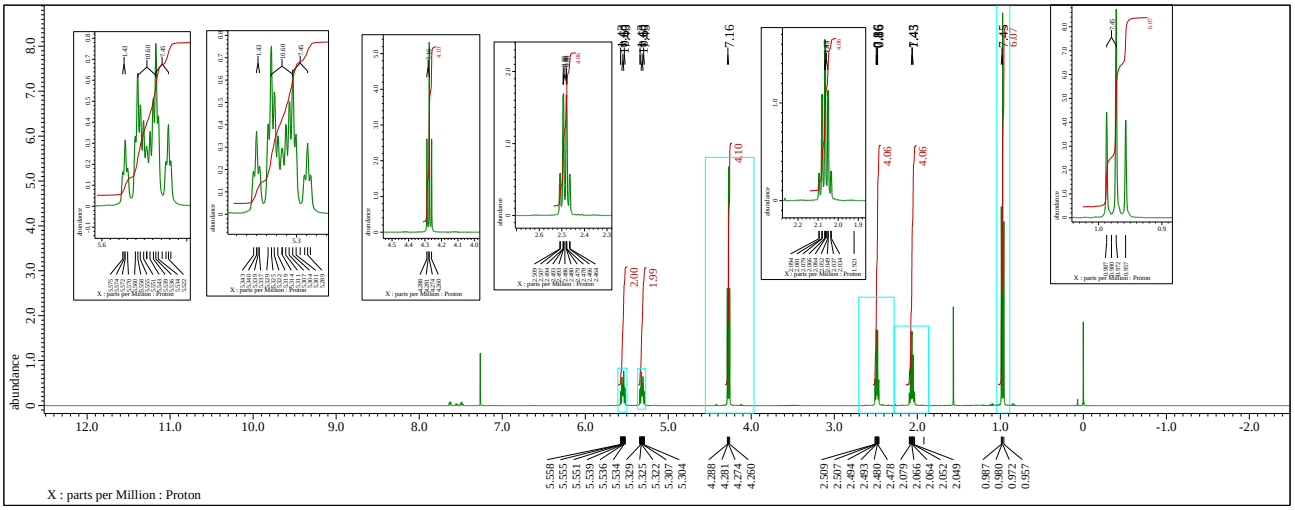


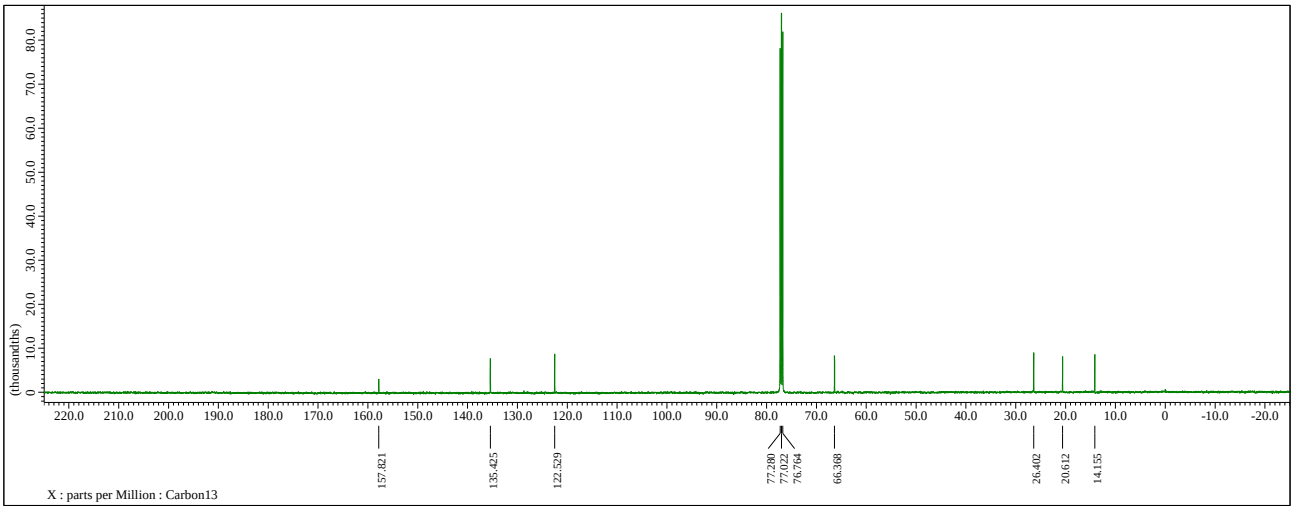

abundance
X : parts per Million : Proton


abundance
X : parts per Million : Carbon13

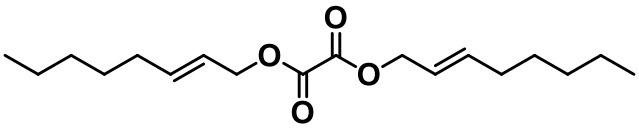
9c

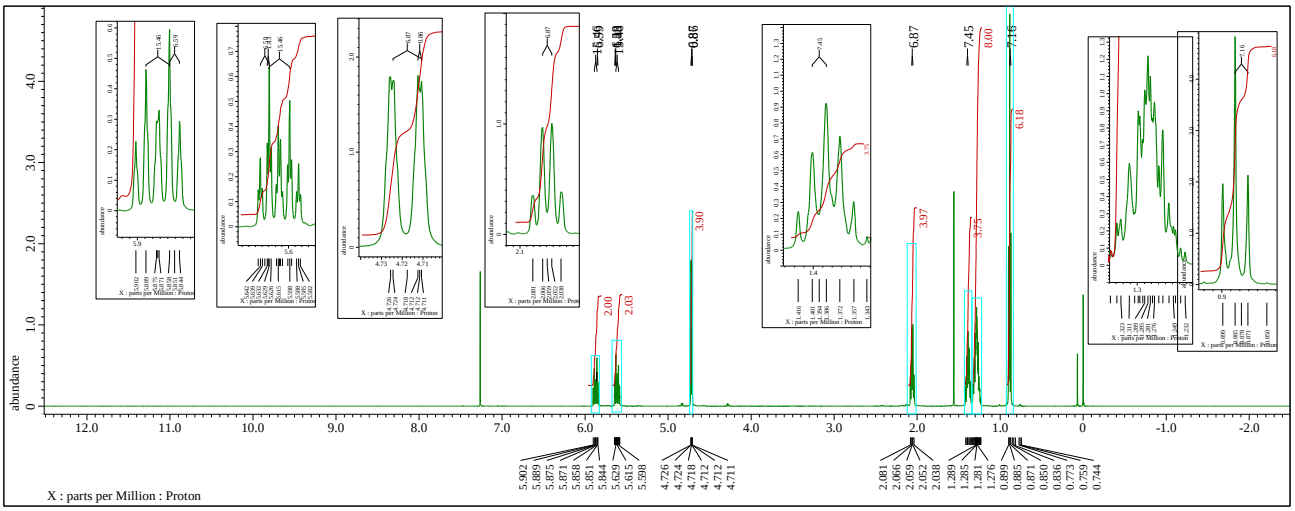


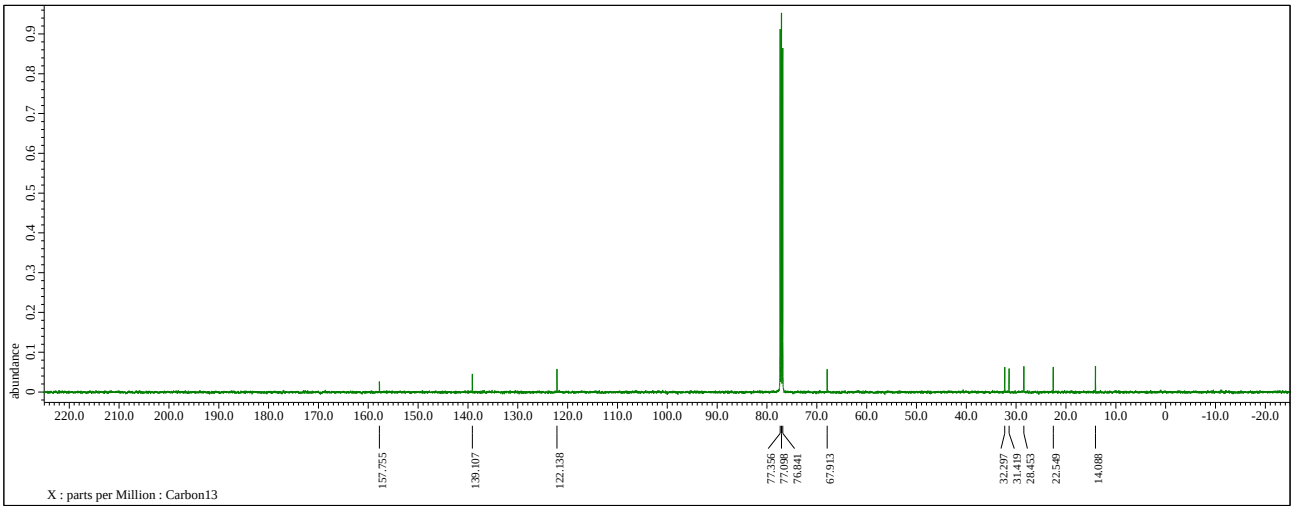

abundance
X : parts per Million : Proton
7.16
4.10
2.00
1.99
4.06
4.06
7.43
7.45
6.07
0.86


(thousandths)
X : parts per Million : Carbon13
157.821
135.425
122.529
77.230
77.022
76.764
66.368
26.402
20.612
14.155

10c




abundance
X : parts per Million : Proton
0.86
2.00
2.03
3.90
3.97
3.75
6.87
7.45
8.00
7.16
6.16


abundance
X : parts per Million : Carbon13
157.755
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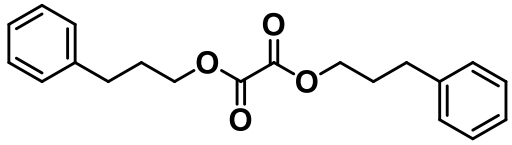
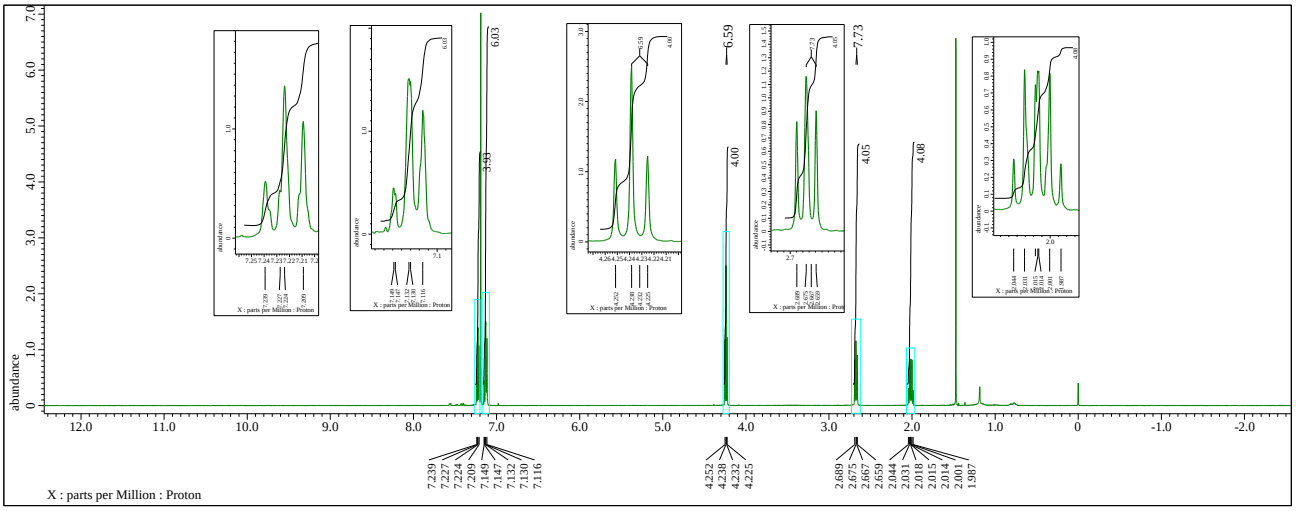
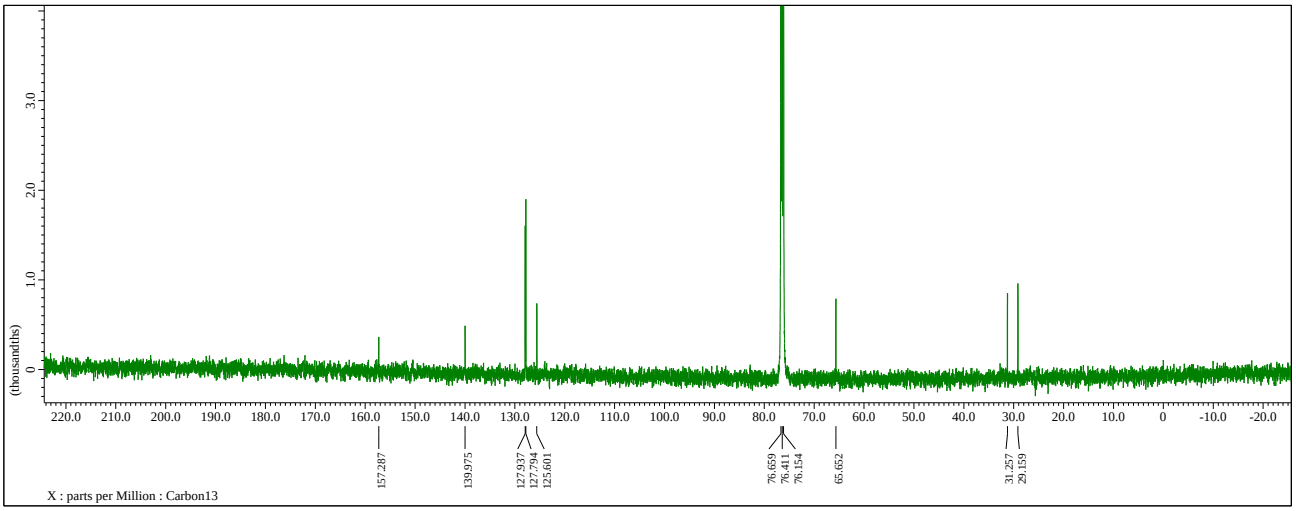
122.138
77.356
77.098
76.841
67.913
32.297
31.419
28.453
22.549
14.088

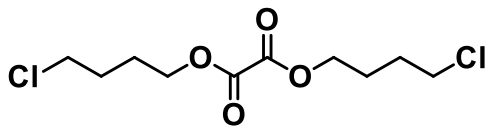
11c

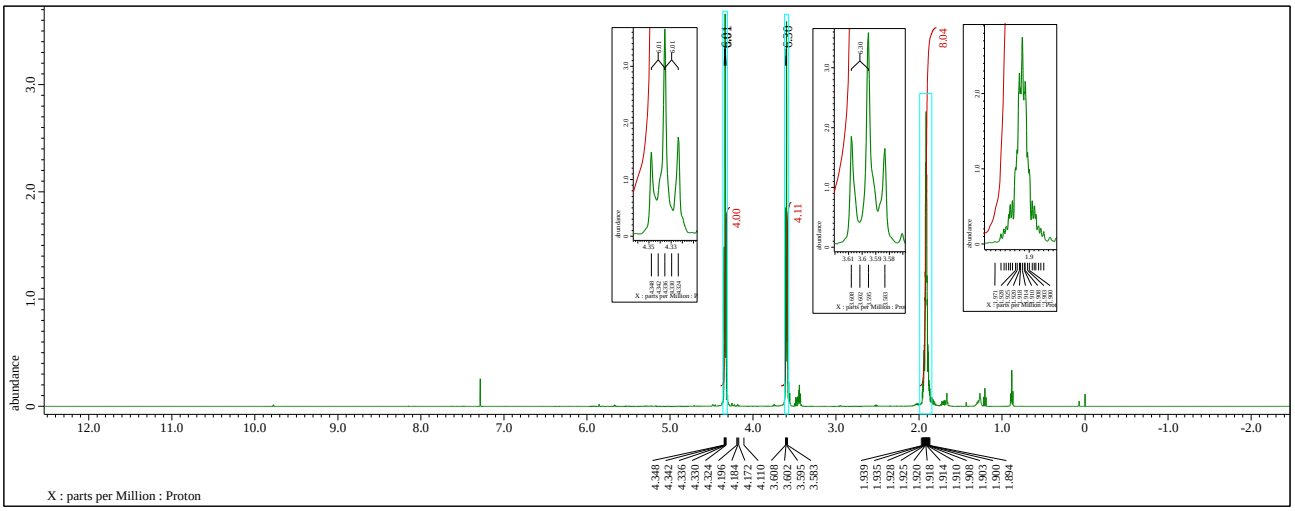


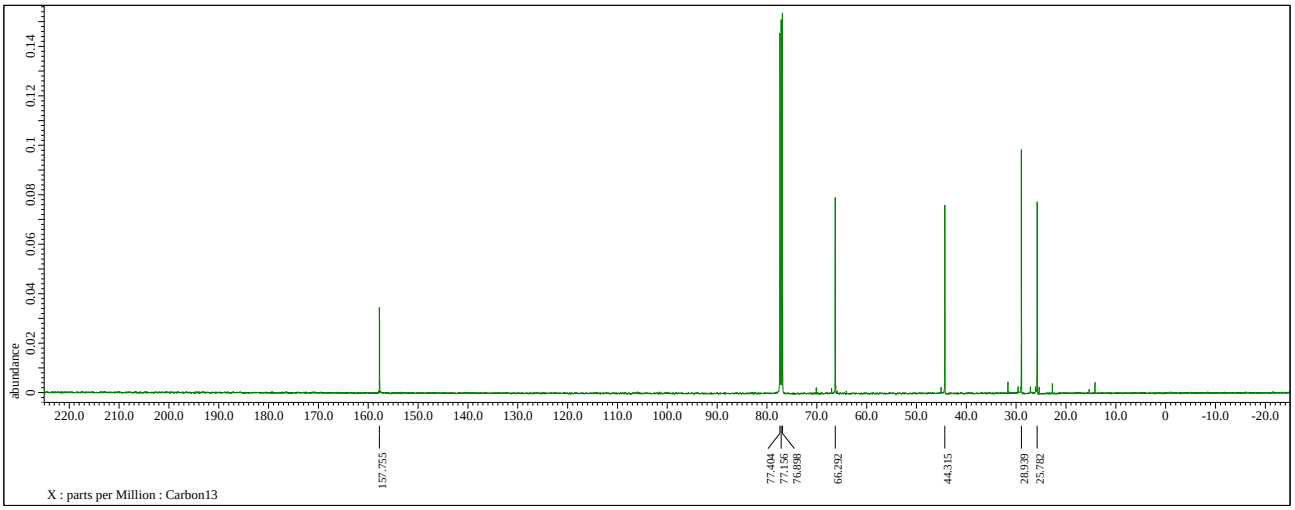

abundance
X : parts per Million : Proton
6.03
3.93
6.59
4.00
7.73
4.05
4.08


(thousandths)
X : parts per Million : Carbon13
157.287
139.975
127.937
127.794
125.601
76.659
76.411
76.154
65.652
31.257
29.159

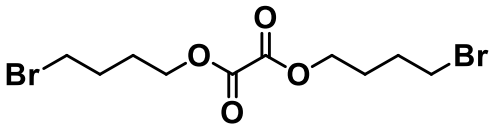
12c

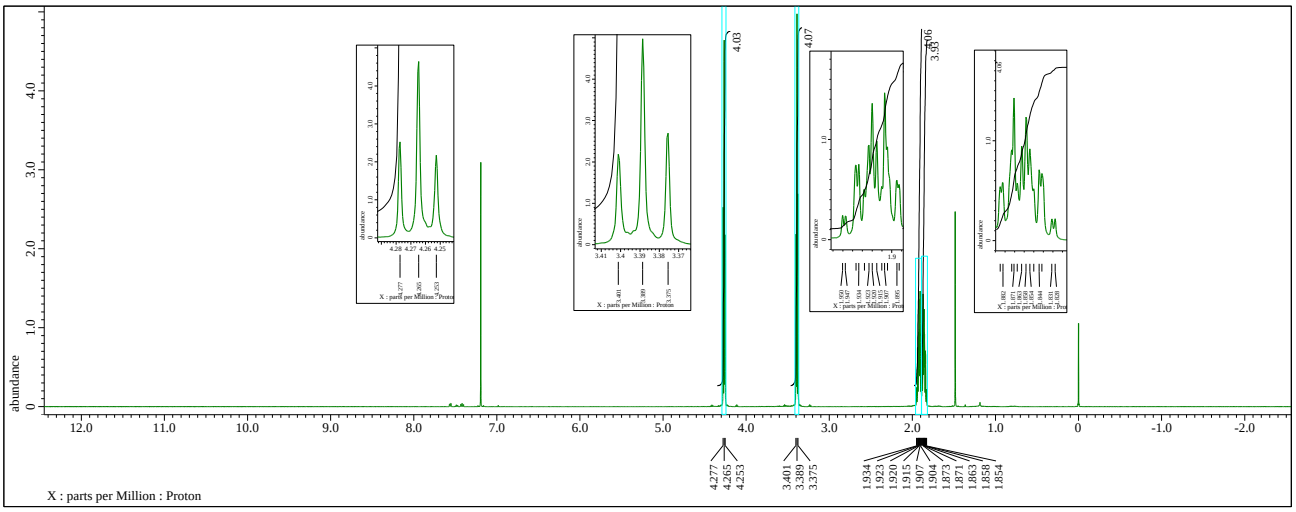

Cl
O
O
O
O
Cl

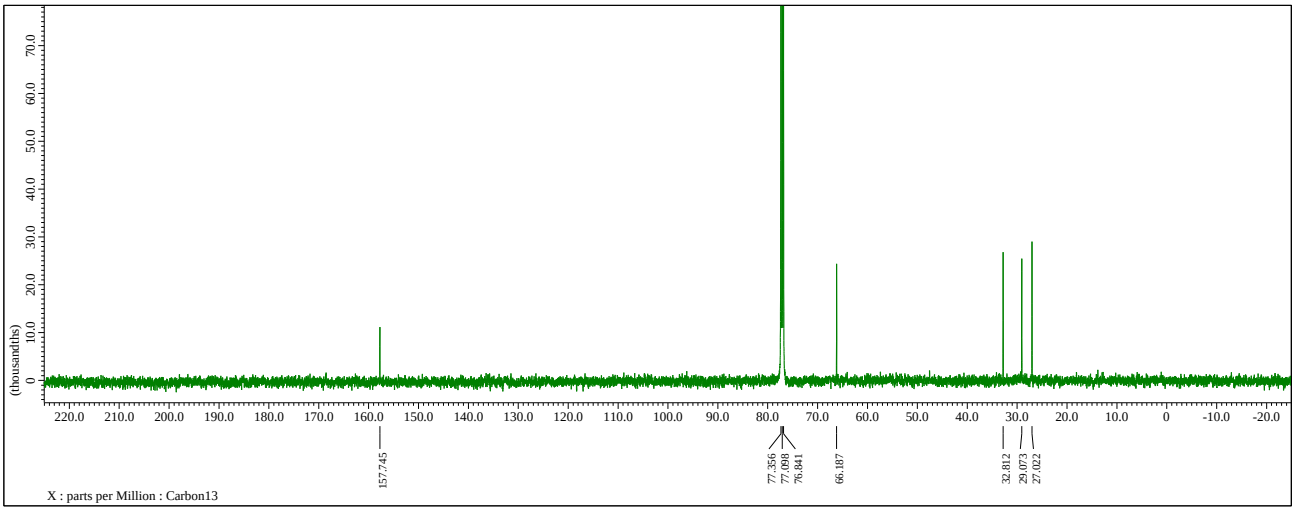

abundance
6.01
6.30
8.04
4.00
4.11
4.348
4.342
4.336
4.330
4.324
4.196
4.184
4.172
4.110
3.608
3.602
3.595
3.583
1.939
1.935
1.928
1.925
1.920
1.918
1.914
1.910
1.908
1.903
1.900
1.894
X : parts per Million : Proton


abundance
157.755
77.404
77.156
76.898
66.292
44.315
28.939
25.782
X : parts per Million : Carbon13

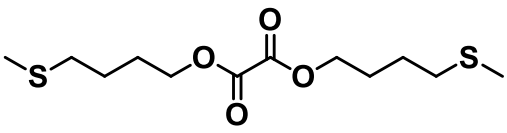
13c

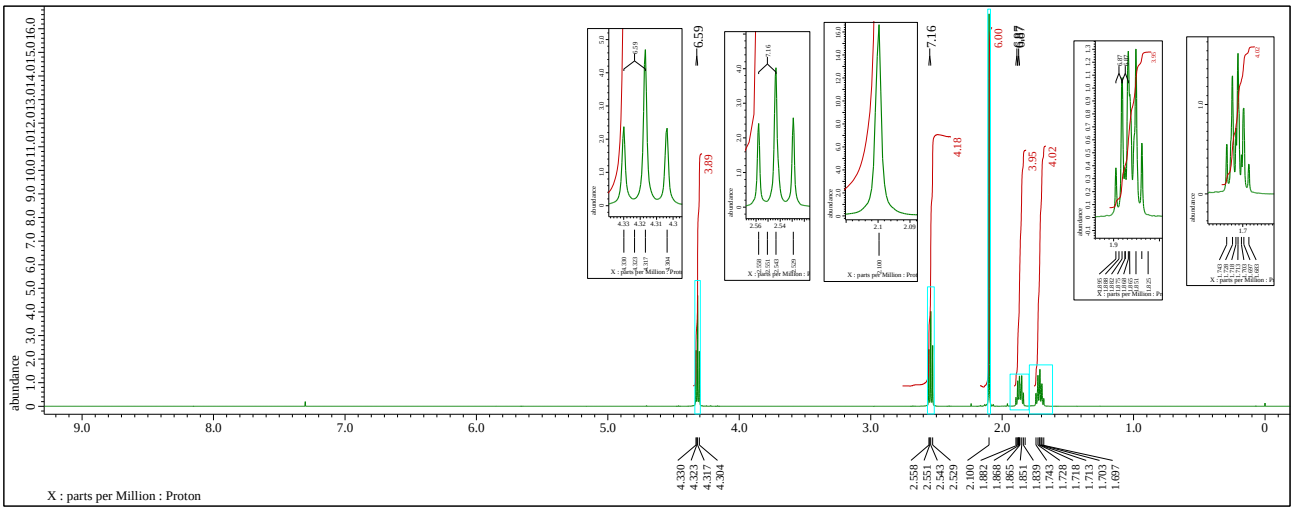

Br
O
O
O
O
Br

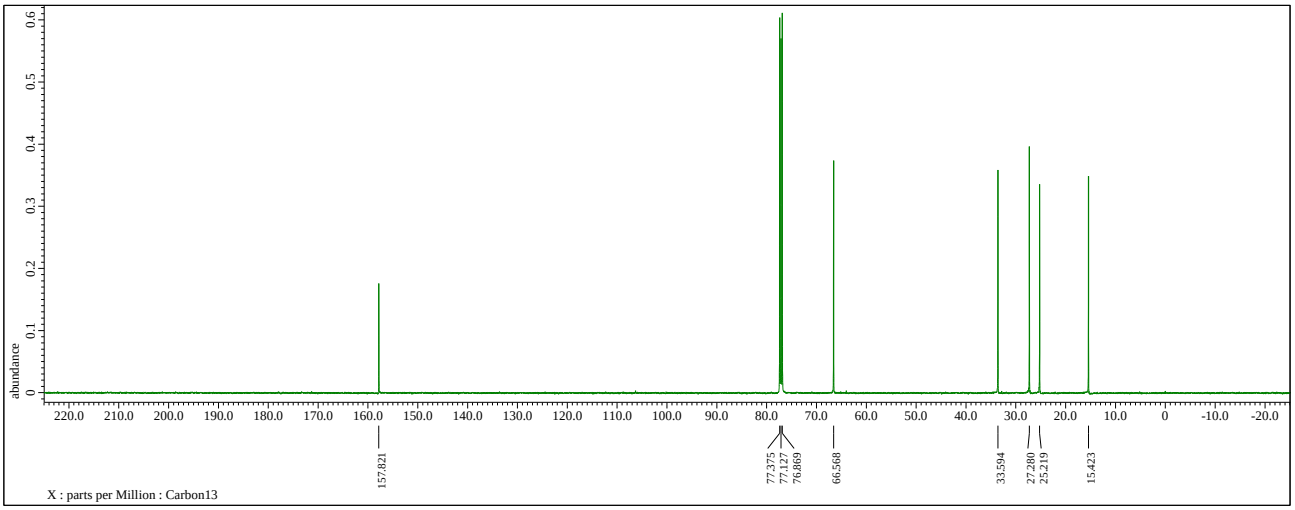

abundance
4.03
4.07
3.406
3.395
4.277
4.265
4.253
3.401
3.389
3.375
1.934
1.923
1.920
1.915
1.907
1.904
1.873
1.871
1.863
1.858
1.854
X : parts per Million : Proton


(thousandths)
157.745
77.356
77.098
76.841
66.187
32.812
29.073
27.022
X : parts per Million : Carbon13

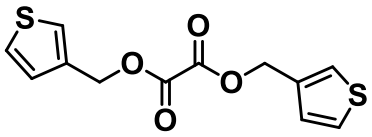
14c

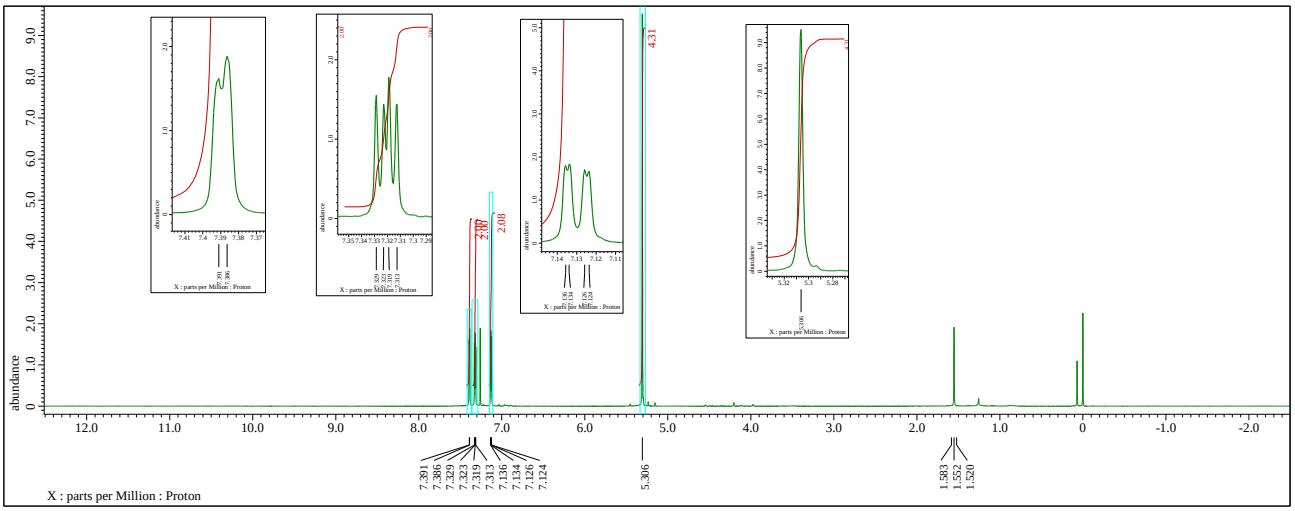


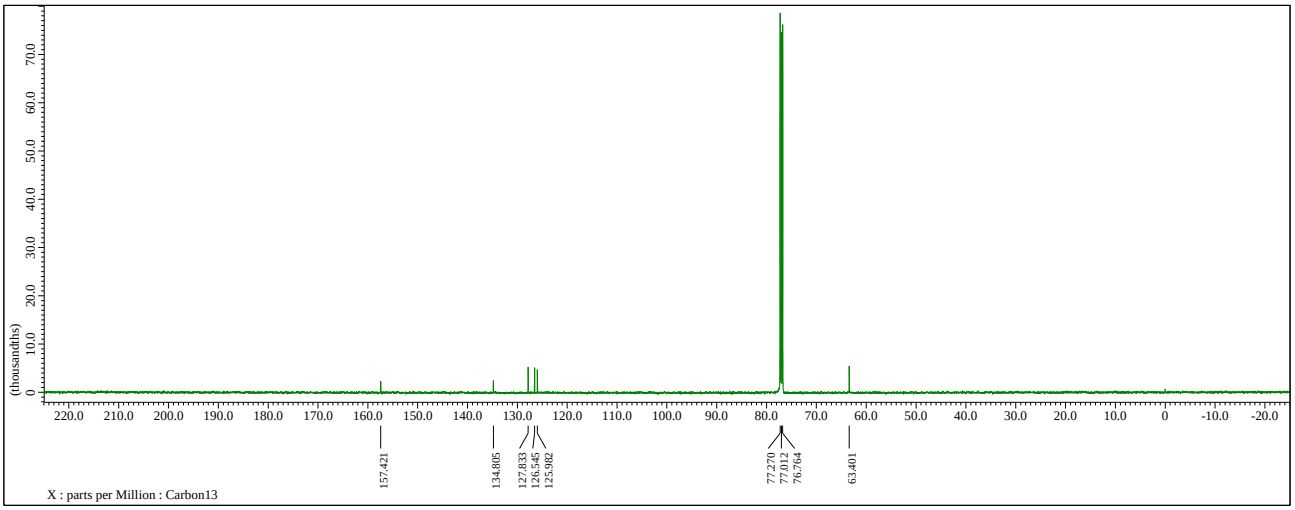

abundance
6.59
3.89
7.16
4.18
6.00
6.07
3.95
4.02
4.330
4.323
4.317
4.304
2.558
2.551
2.543
2.529
2.100
1.882
1.868
1.865
1.851
1.839
1.743
1.728
1.718
1.713
1.703
1.697
X : parts per Million : Proton


abundance
157.821
77.375
77.127
76.869
66.568
33.594
27.280
25.219
15.423
X : parts per Million : Carbon13

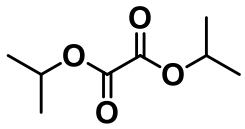
15c

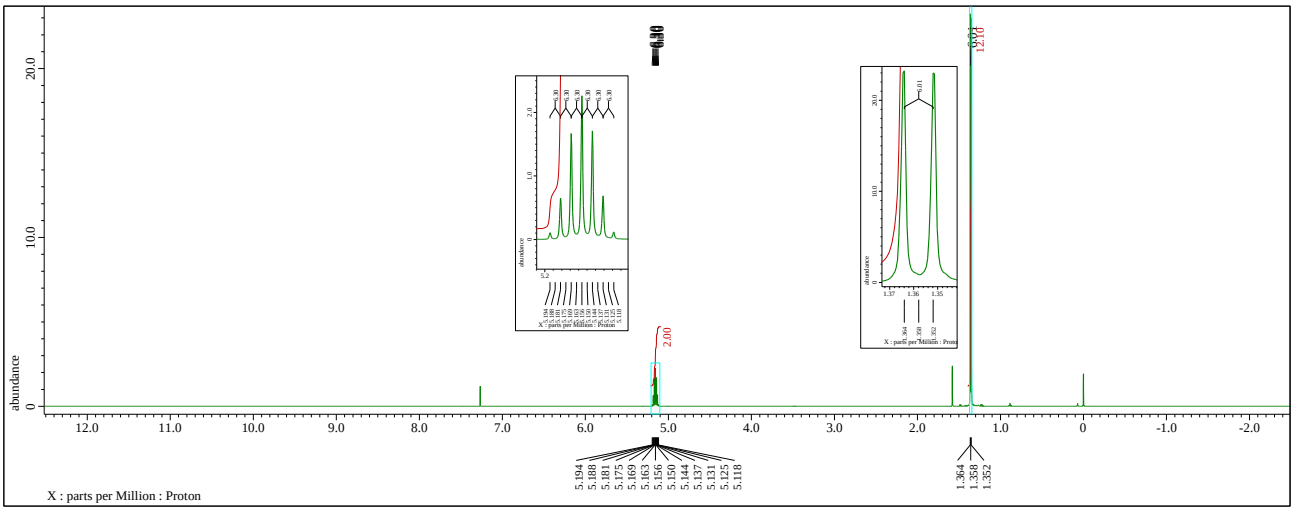

S
O
O
O
O
S

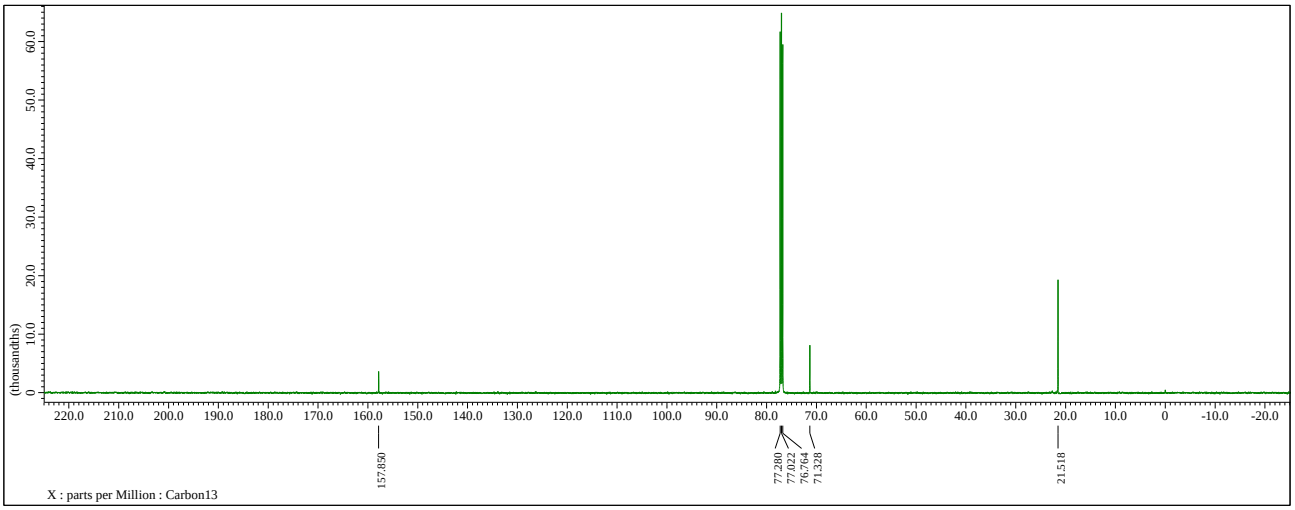

abundance
X : parts per Million : Proton
7.391
7.386
7.329
7.323
7.319
7.313
7.136
7.134
7.126
7.124
5.306
1.583
1.552
1.520
4.31
2.08


(thousandths)
X : parts per Million : Carbon13
157.421
134.805
127.833
126.545
125.982
77.270
77.012
76.764
63.401

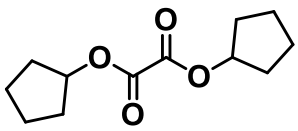
16c

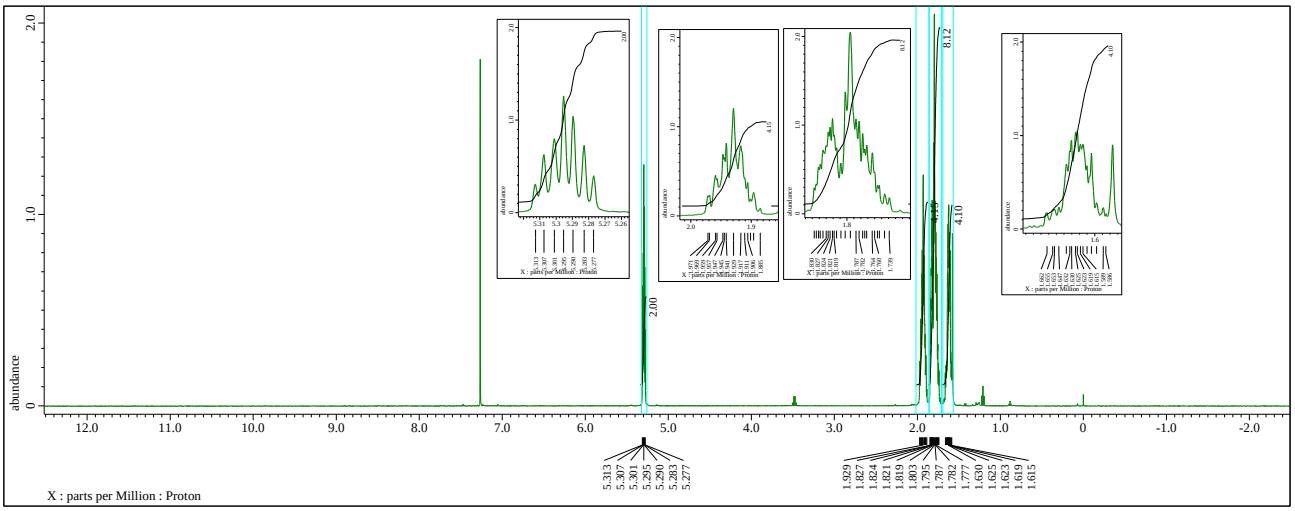


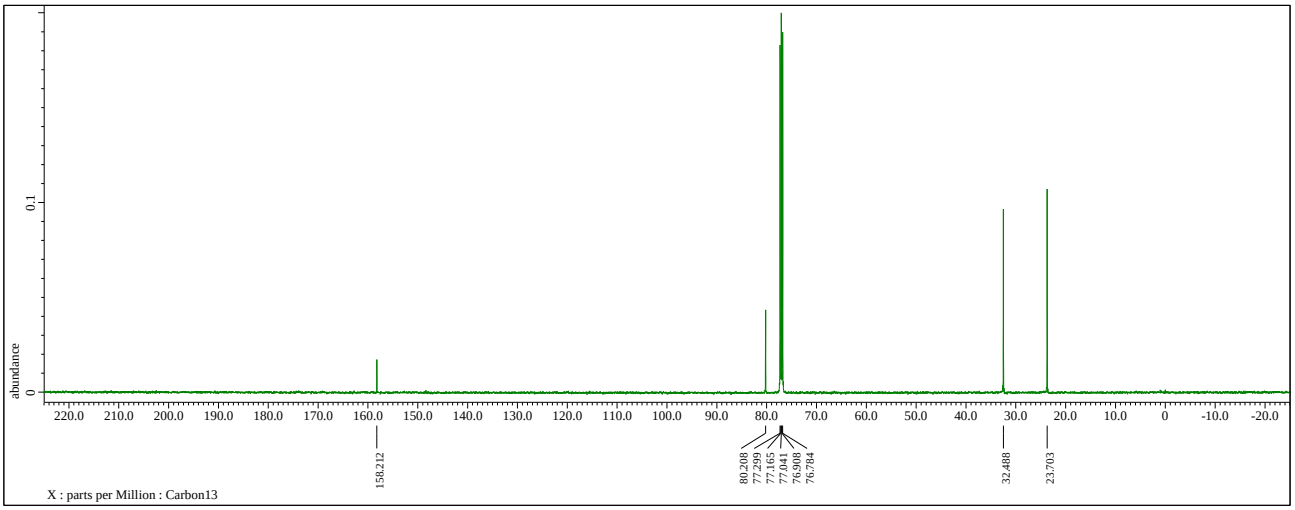

abundance
20.0
10.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
2.00
12.10
5.194
5.188
5.181
5.175
5.169
5.163
5.156
5.150
5.144
5.137
5.131
5.125
5.110
1.364
1.358
1.352
X : parts per Million : Proton


(thousandths)
60.0
50.0
40.0
30.0
20.0
10.0
0
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
157.850
77.280
77.022
76.764
71.328
21.518
X : parts per Million : Carbon13

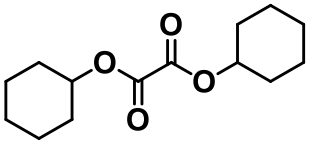
18c

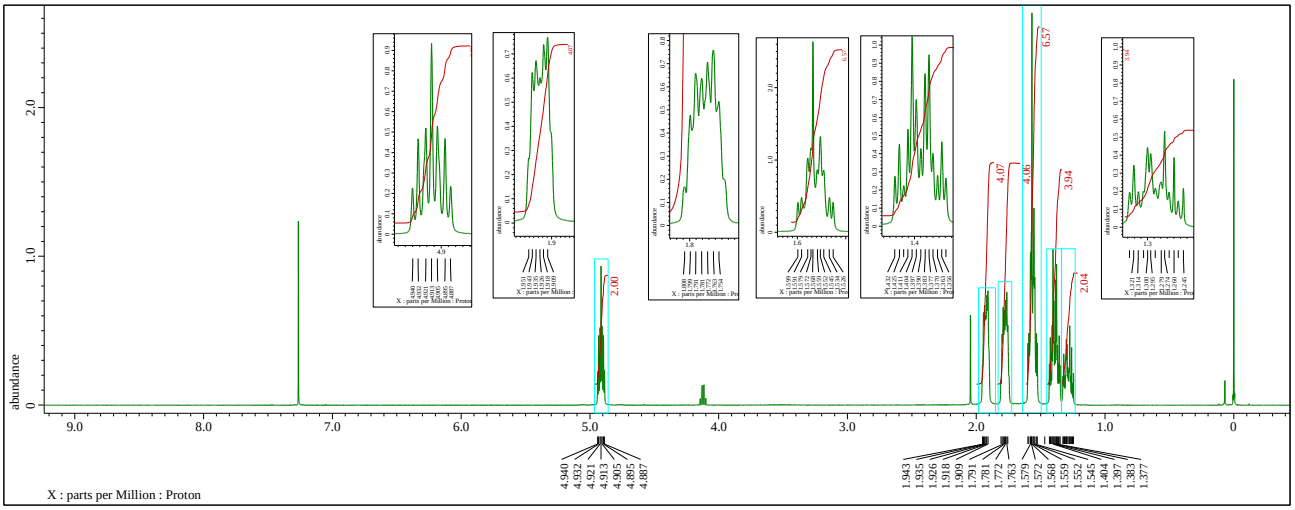


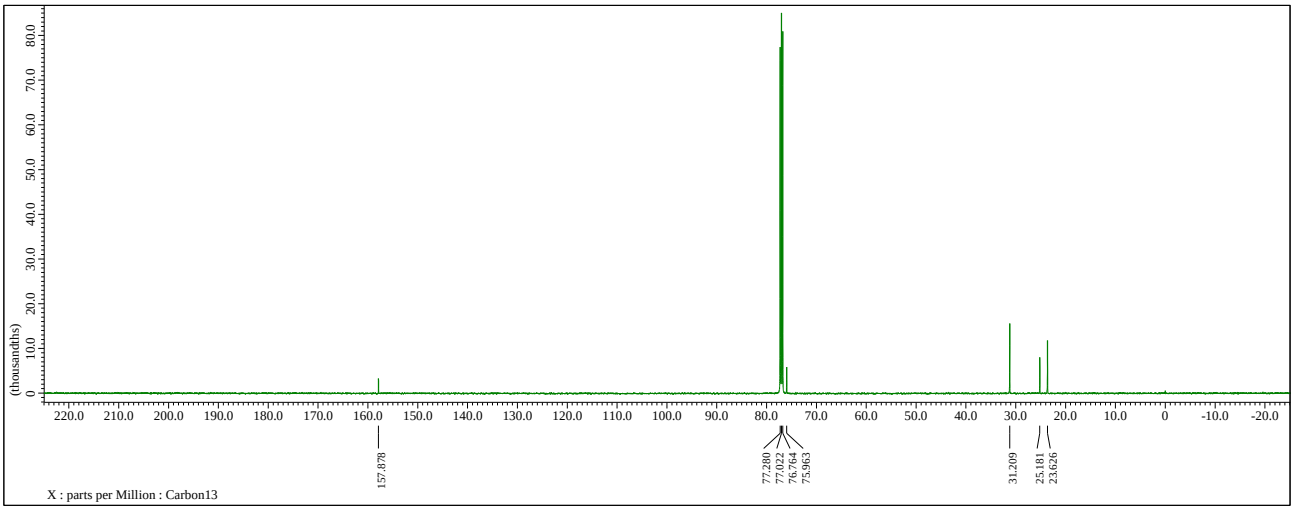

abundance
2.00
8.12
4.19
4.10
5.313
5.307
5.301
5.295
5.290
5.283
5.277
1.929
1.827
1.824
1.821
1.819
1.803
1.795
1.787
1.782
1.777
1.630
1.625
1.623
1.619
1.615
X : parts per Million : Proton


abundance
158.212
80.208
77.299
77.165
77.041
76.908
76.784
32.488
23.703
X : parts per Million : Carbon13

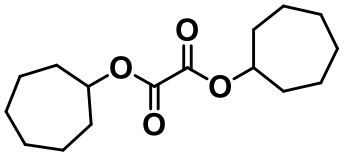
19c

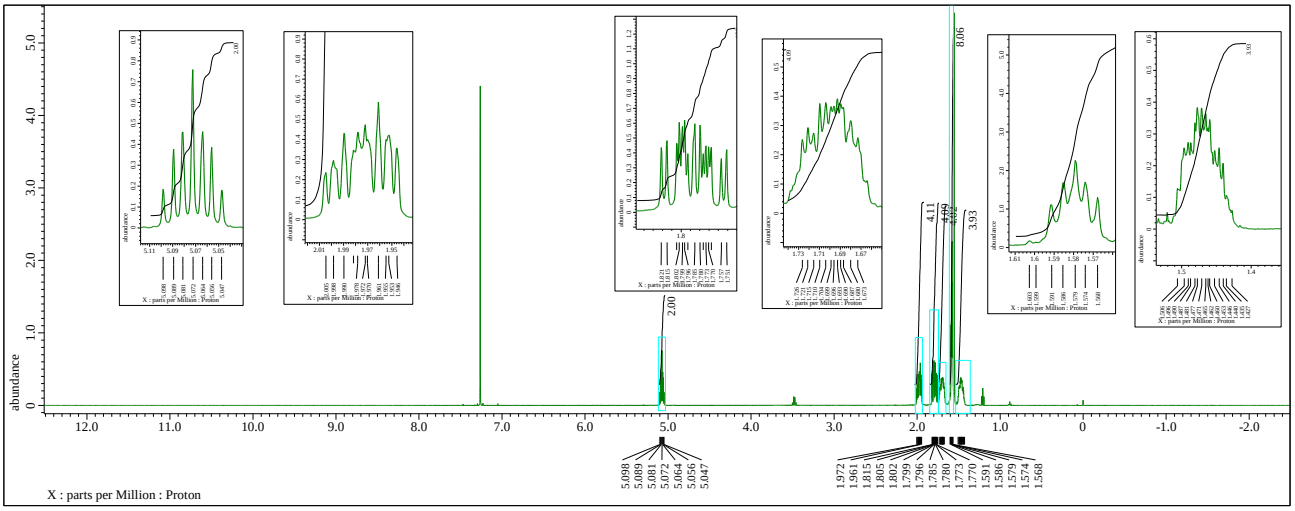


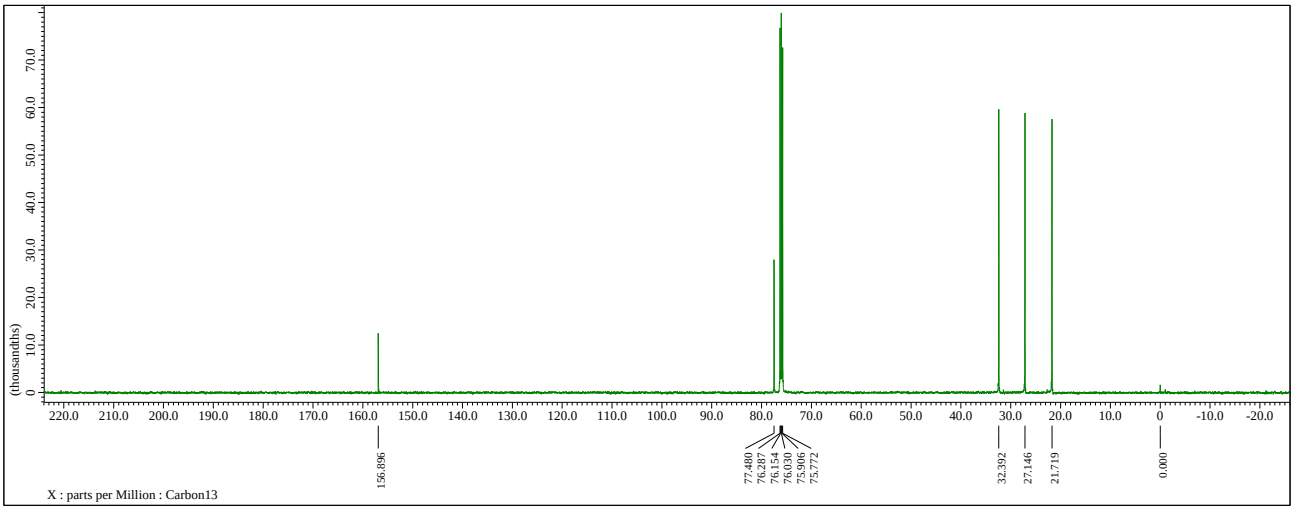

abundance
X : parts per Million : Proton
2.00
6.57
4.07
4.06
3.94
2.04
4.940
4.932
4.921
4.913
4.905
4.895
4.887
1.943
1.935
1.926
1.918
1.909
1.791
1.781
1.772
1.763
1.579
1.572
1.568
1.559
1.552
1.545
1.404
1.397
1.383
1.377


(thousandths)
X : parts per Million : Carbon13
157.878
77.380
77.022
76.764
75.963
31.209
25.181
23.626

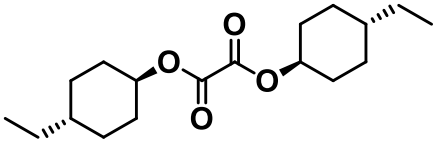
20c

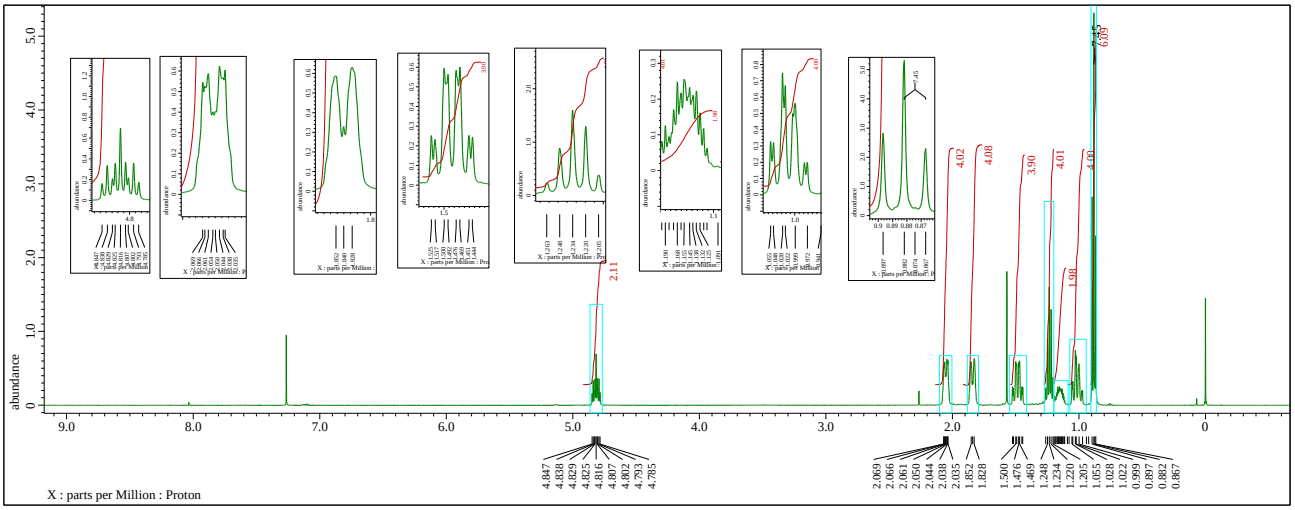


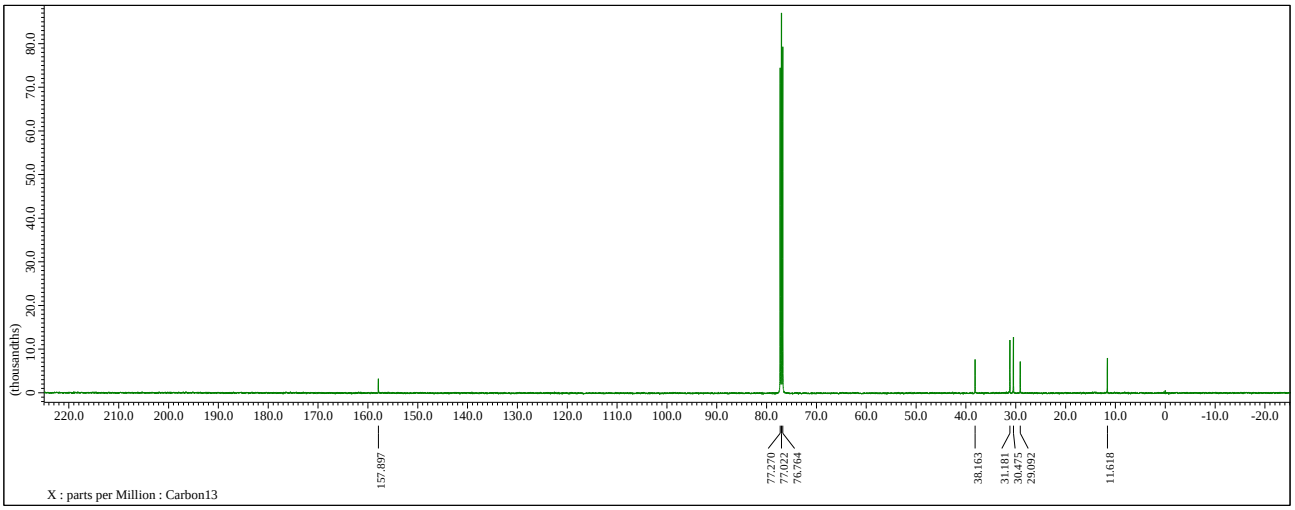

abundance
X : parts per Million : Proton
8.06
4.11
4.09
4.02
3.93
2.00
5.098
5.089
5.081
5.072
5.064
5.056
5.047
1.972
1.961
1.815
1.805
1.802
1.798
1.795
1.785
1.780
1.773
1.770
1.591
1.586
1.579
1.574
1.568


(thousandths)
X : parts per Million : Carbon13
156.896
77.480
76.287
76.154
76.030
75.906
75.772
32.392
27.146
21.719
0.000

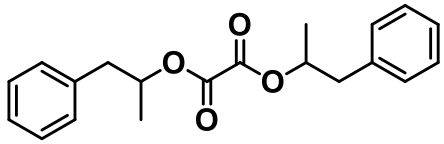
21c

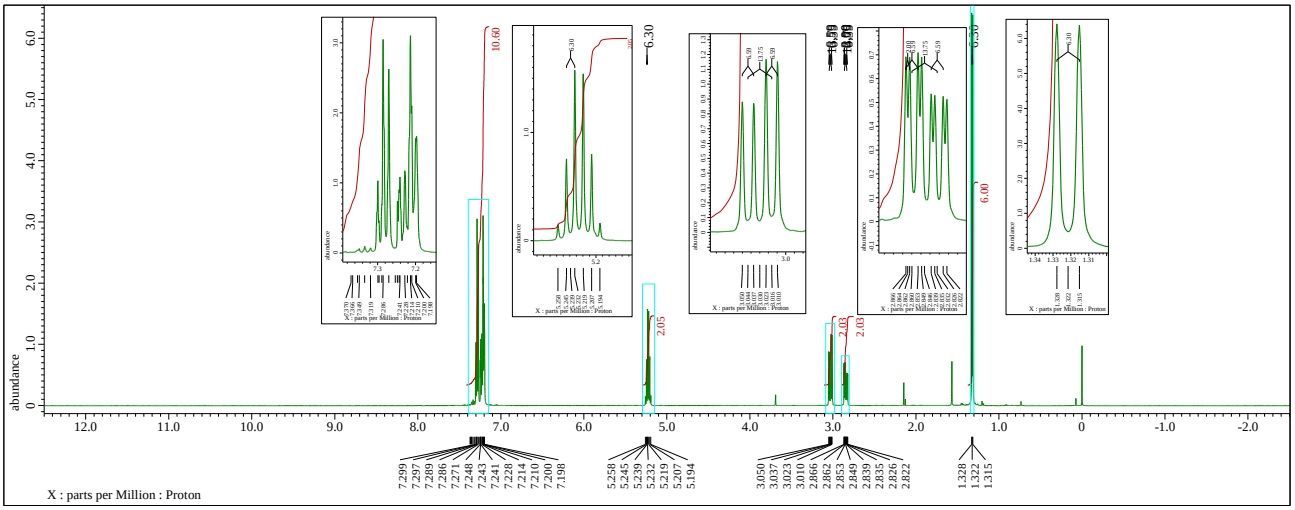


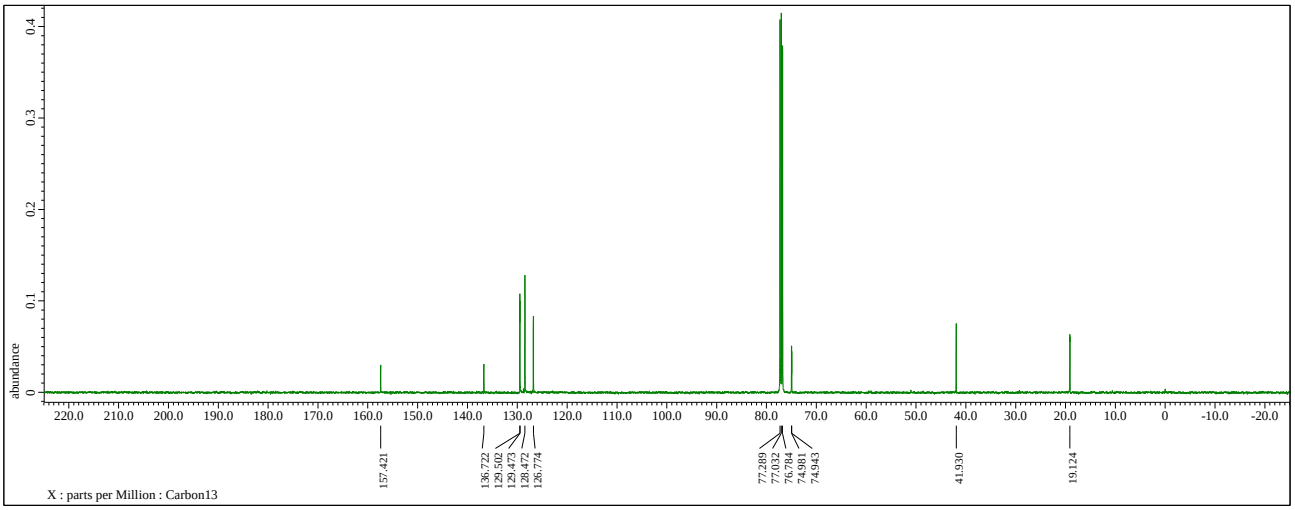

abundance
X : parts per Million : Proton
4.847
4.838
4.829
4.825
4.816
4.807
4.802
4.793
4.785
2.069
2.066
2.061
2.050
2.044
2.038
2.035
1.852
1.828
1.500
1.476
1.469
1.248
1.234
1.220
1.205
1.055
1.028
1.022
0.999
0.897
0.882
0.867
2.11
4.02
4.08
3.90
4.01
4.00
1.98
6.09


(thousandths)
X : parts per Million : Carbon13
157.897
77.270
77.022
76.764
38.163
31.181
30.475
29.092
11.618

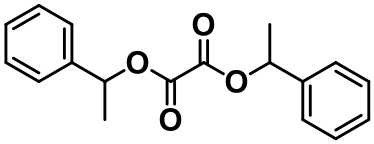
22c

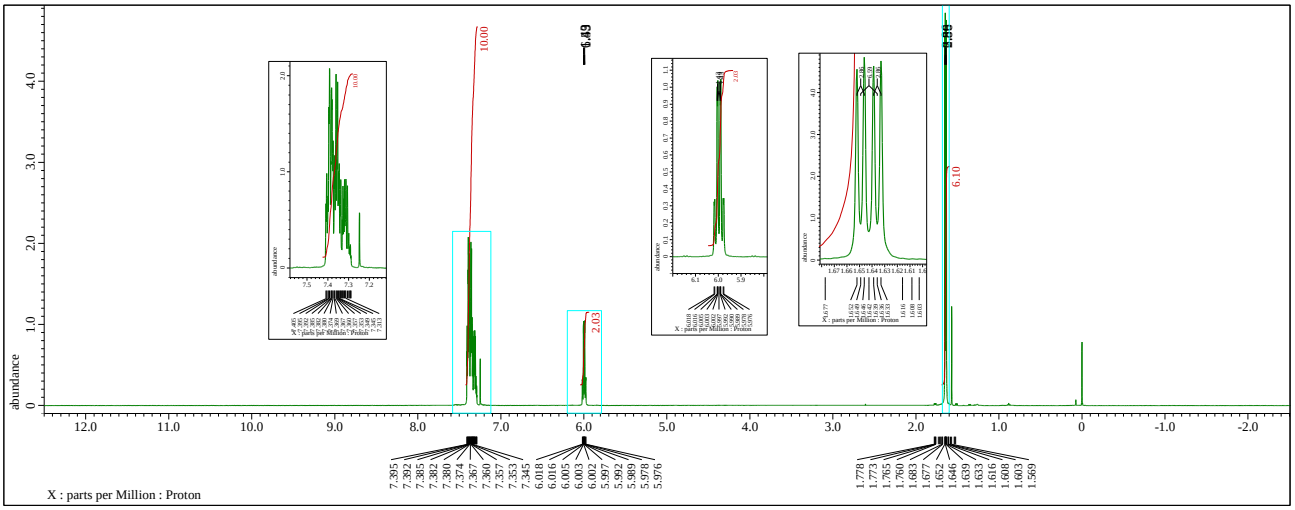


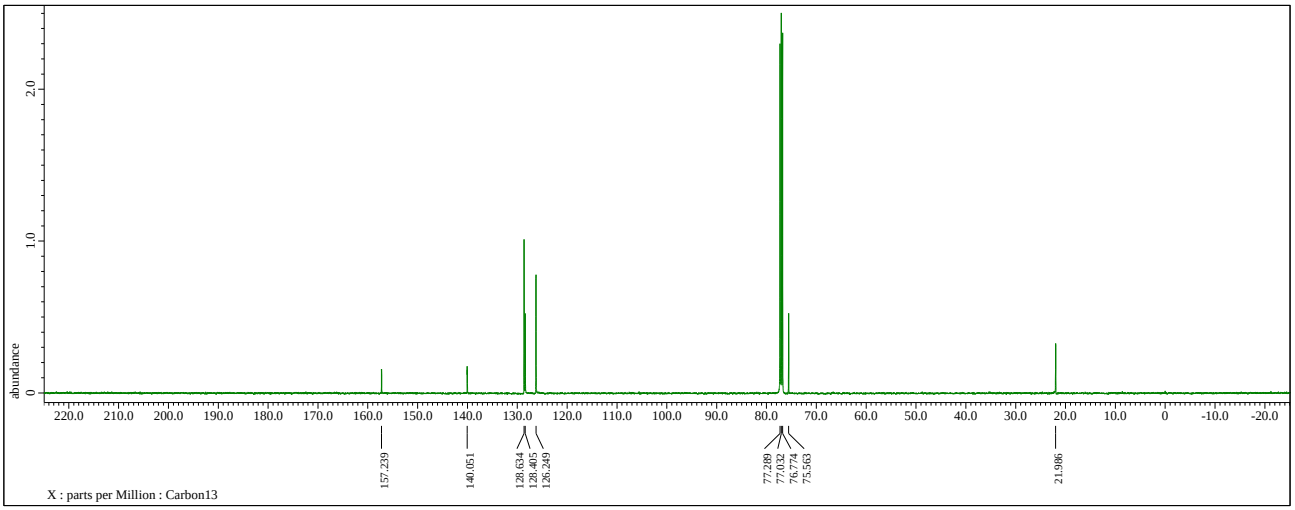

abundance
X : parts per Million : Proton
10.60
6.30
2.05
2.03
2.03
6.00
6.00


abundance
X : parts per Million : Carbon13
157.421
136.722
129.502
129.475
128.472
126.774
77.289
77.032
76.784
74.981
74.943
41.930
19.124

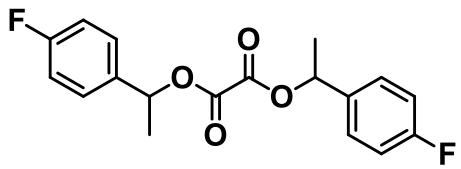
23c

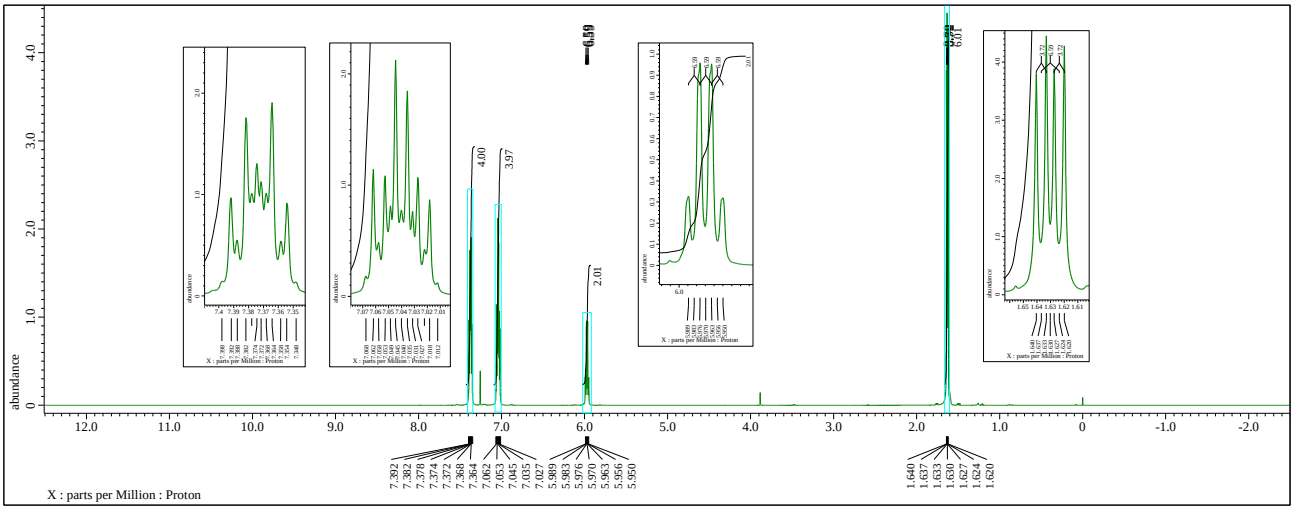


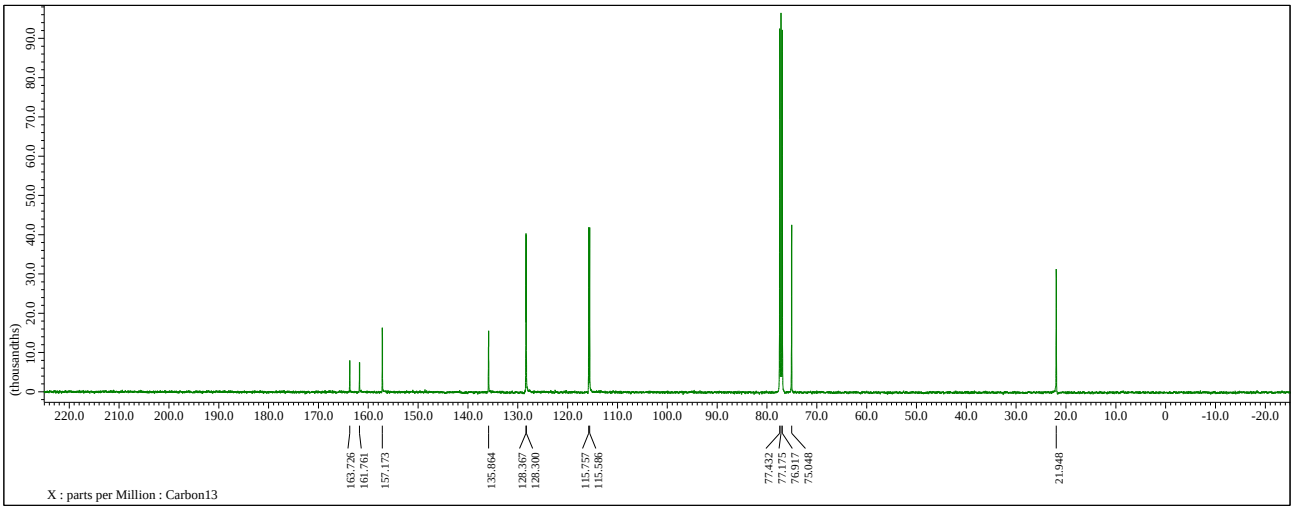

10.00
6.49
2.03
6.10
abundance
X : parts per Million : Proton

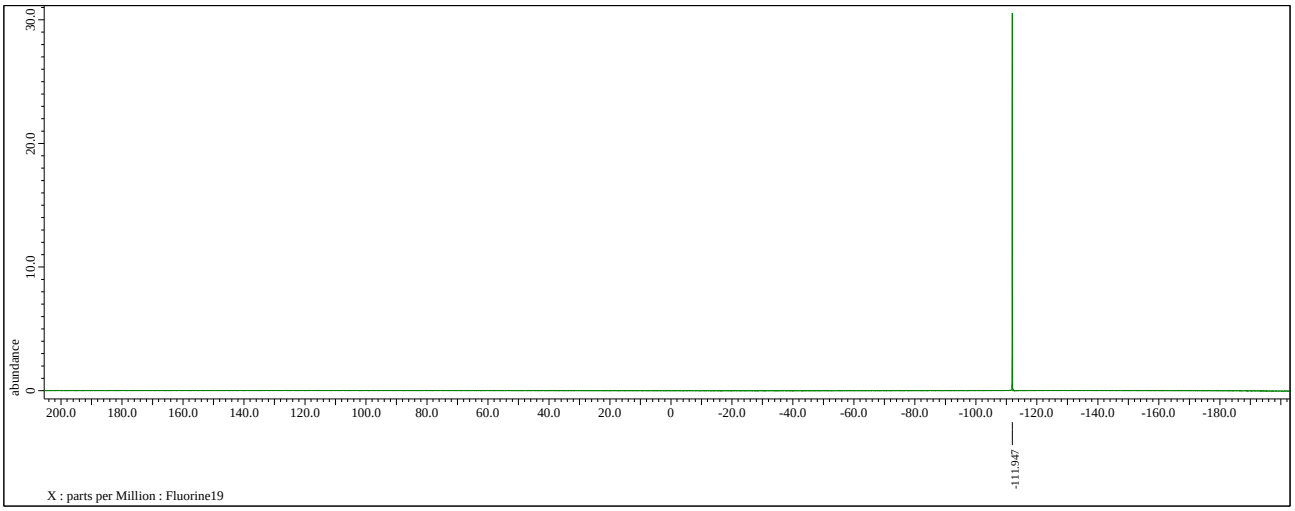

157.239
140.051
128.634
128.405
126.249
77.289
77.072
76.574
75.543
21.986
abundance
X : parts per Million : Carbon13

24c

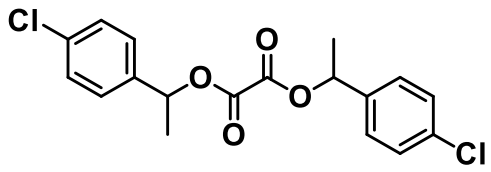

F
O
O
O
O
F

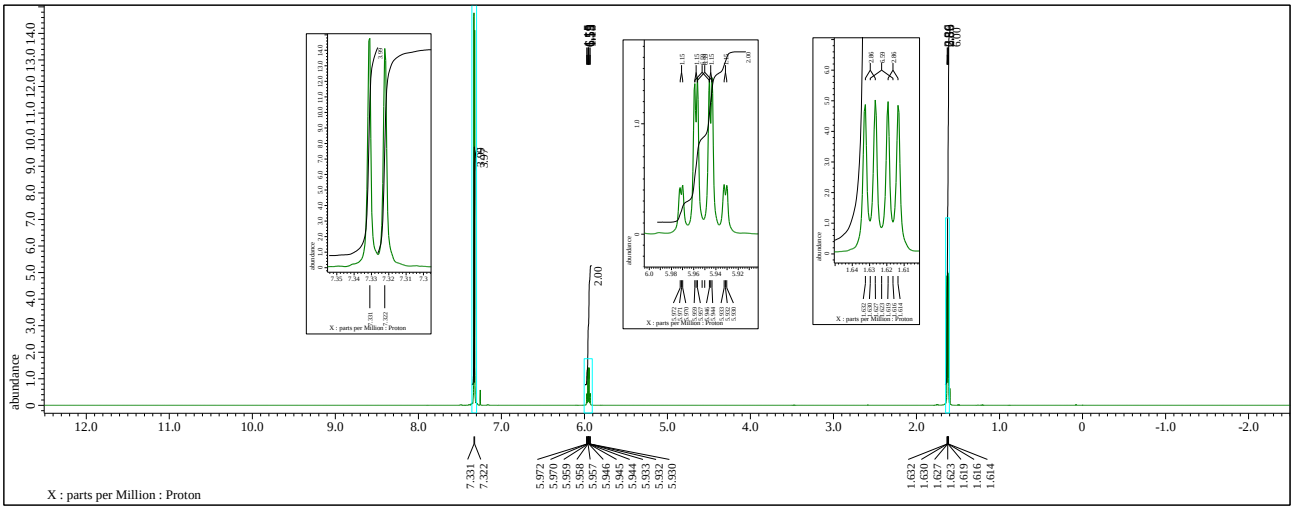

abundance
4.00
3.97
2.01
7.392
7.382
7.378
7.374
7.372
7.368
7.364
7.062
7.055
7.045
7.035
7.027
5.989
5.983
5.976
5.970
5.963
5.956
5.950
1.640
1.637
1.633
1.630
1.627
1.624
1.620
X : parts per Million : Proton

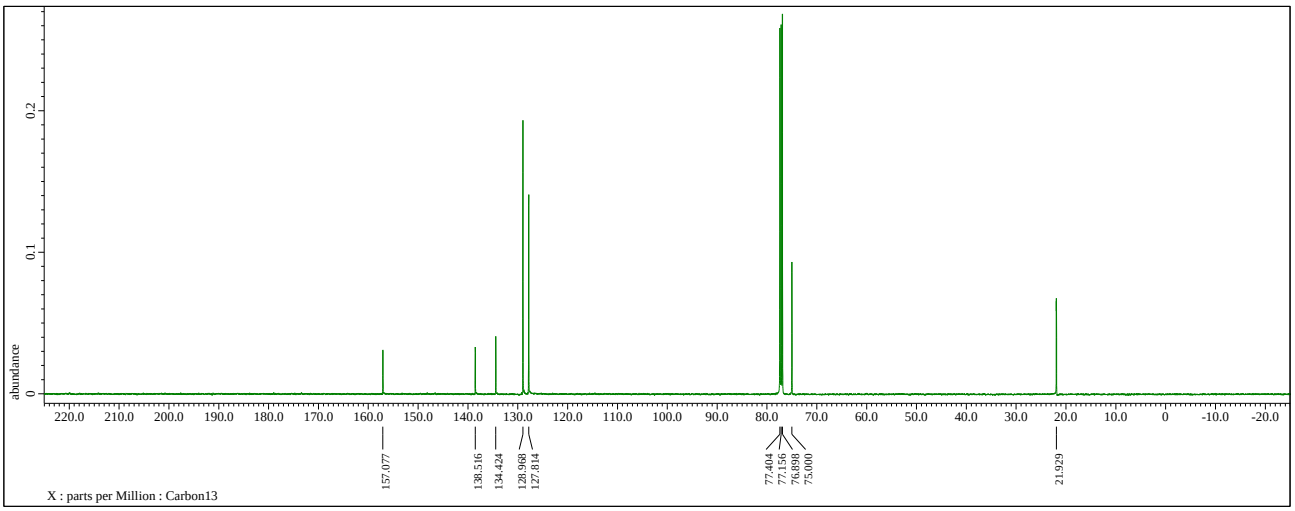

(thousandths)
163.726
161.761
157.173
135.864
128.367
128.300
115.757
115.586
77.432
77.175
76.917
75.048
21.948
X : parts per Million : Carbon13


abundance
-111.947
X : parts per Million : Fluorine19

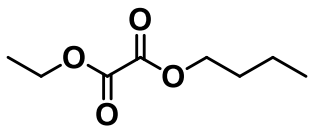
25c

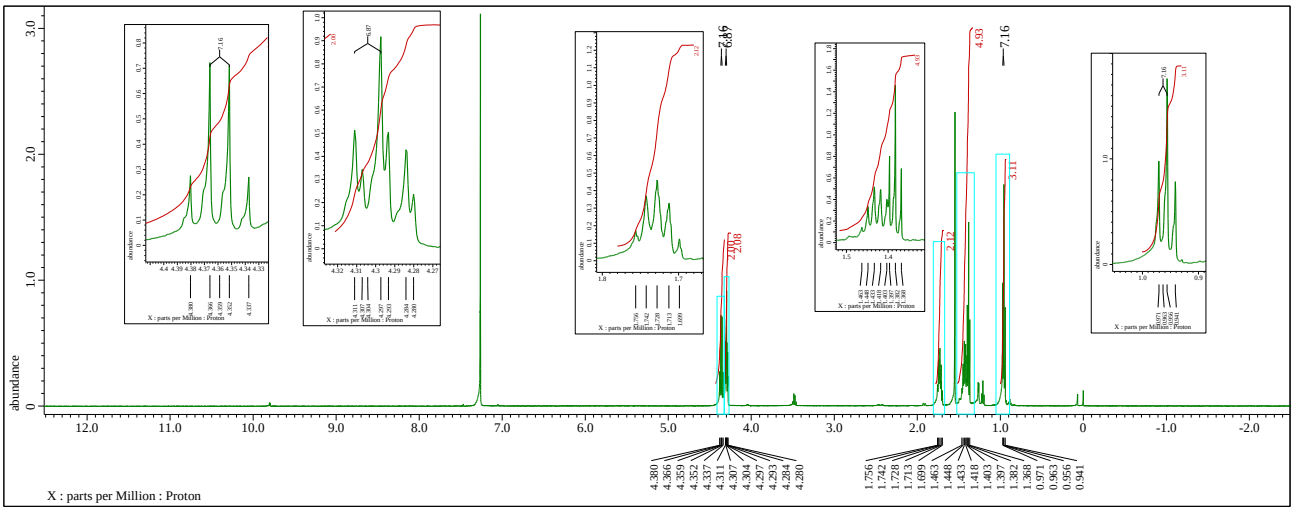

Cl
O
O
O
O
Cl

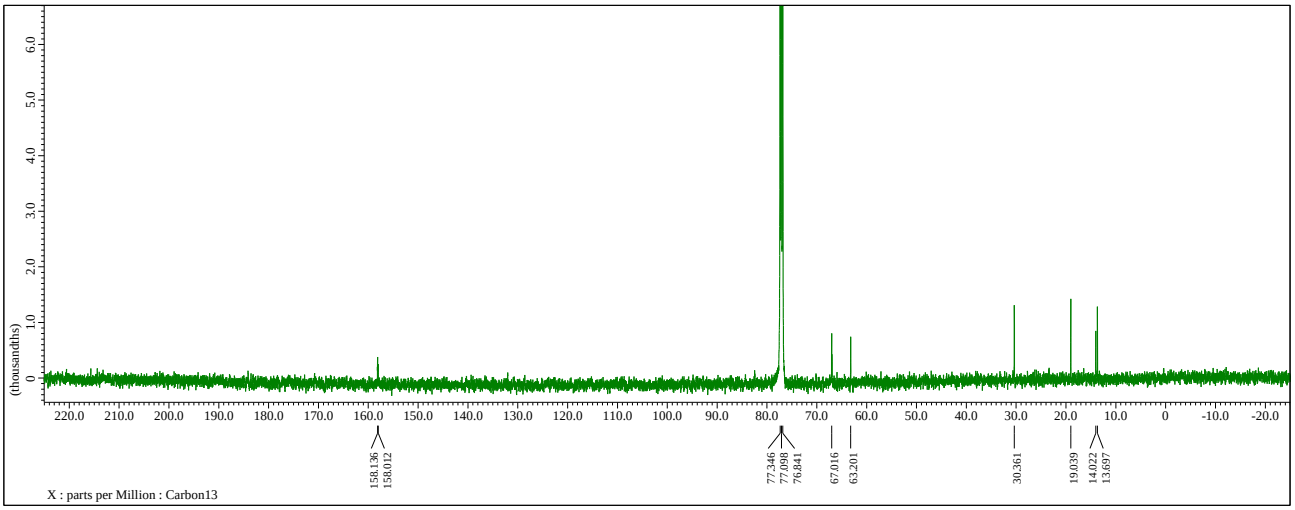

abundance
X : parts per Million : Proton
7.331
7.322
5.972
5.970
5.959
5.958
5.957
5.946
5.945
5.944
5.933
5.932
5.930
1.632
1.630
1.627
1.623
1.619
1.616
1.614


abundance
X : parts per Million : Carbon13
157.077
138.516
134.424
128.968
127.814
77.404
77.156
76.690
75.000
21.929

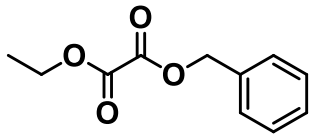
26c

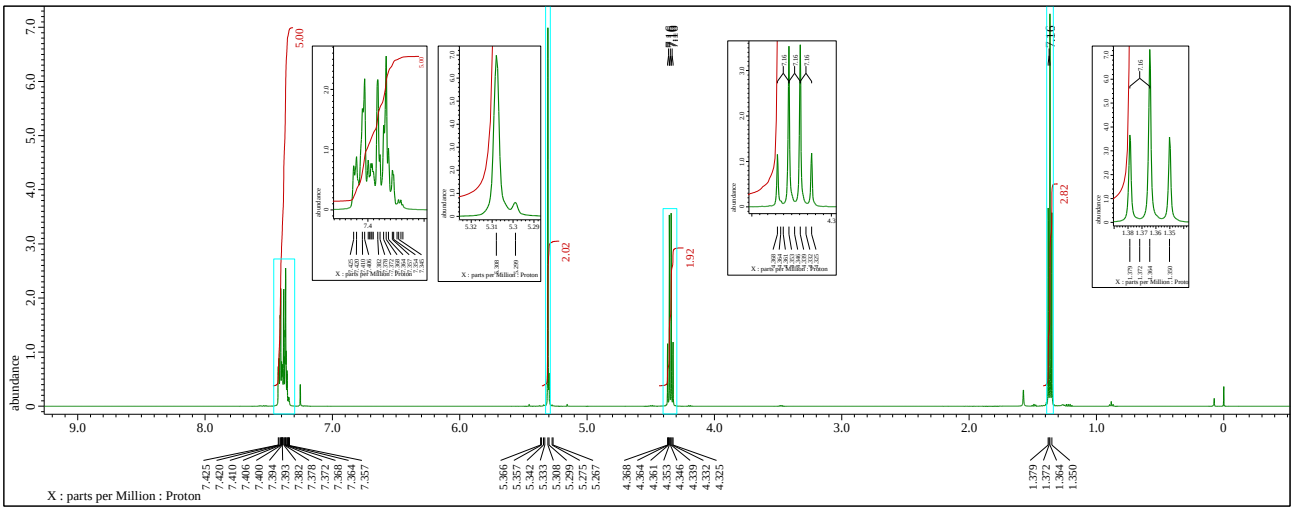


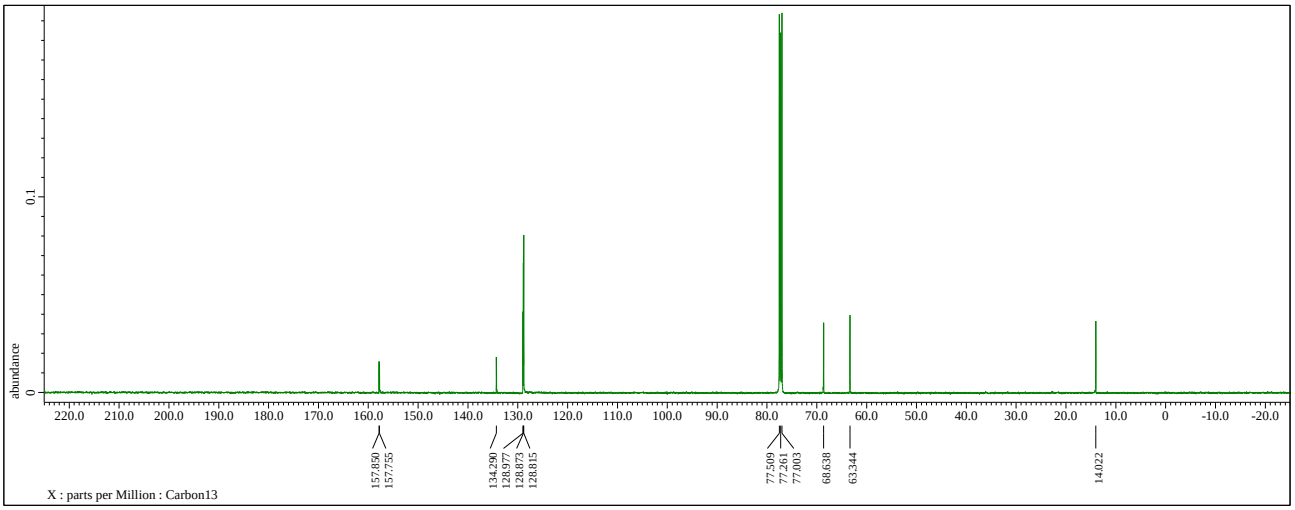

abundance
X : parts per Million : Proton


(thousandths)
X : parts per Million : Carbon13

27c




abundance
X : parts per Million : Proton
5.00
2.02
1.92
2.82
7.425
7.420
7.410
7.406
7.400
7.394
7.393
7.382
7.378
7.372
7.368
7.364
7.357
5.366
5.357
5.342
5.333
5.308
5.290
5.275
5.267
4.368
4.364
4.361
4.353
4.346
4.339
4.332
4.325
1.379
1.372
1.364
1.350


abundance
X : parts per Million : Carbon13
157.850
157.755
134.290
128.977
128.873
128.815
77.509
77.261
77.003
68.638
63.344
14.022