Electronic Supplementary Material (ESI) for Green Chemistry
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ESI for:

Conversion of Oxiranes and CO_2 to Organic Cyclic Carbonates using a Recyclable, Bifunctional Polystyrene-Supported Organocatalyst

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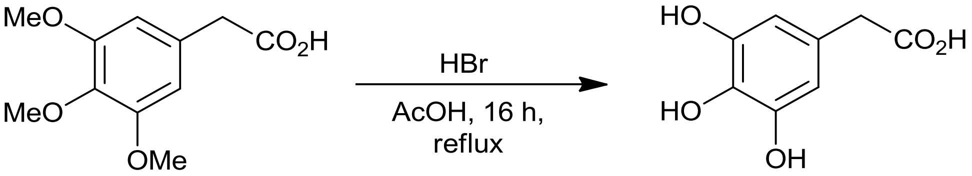
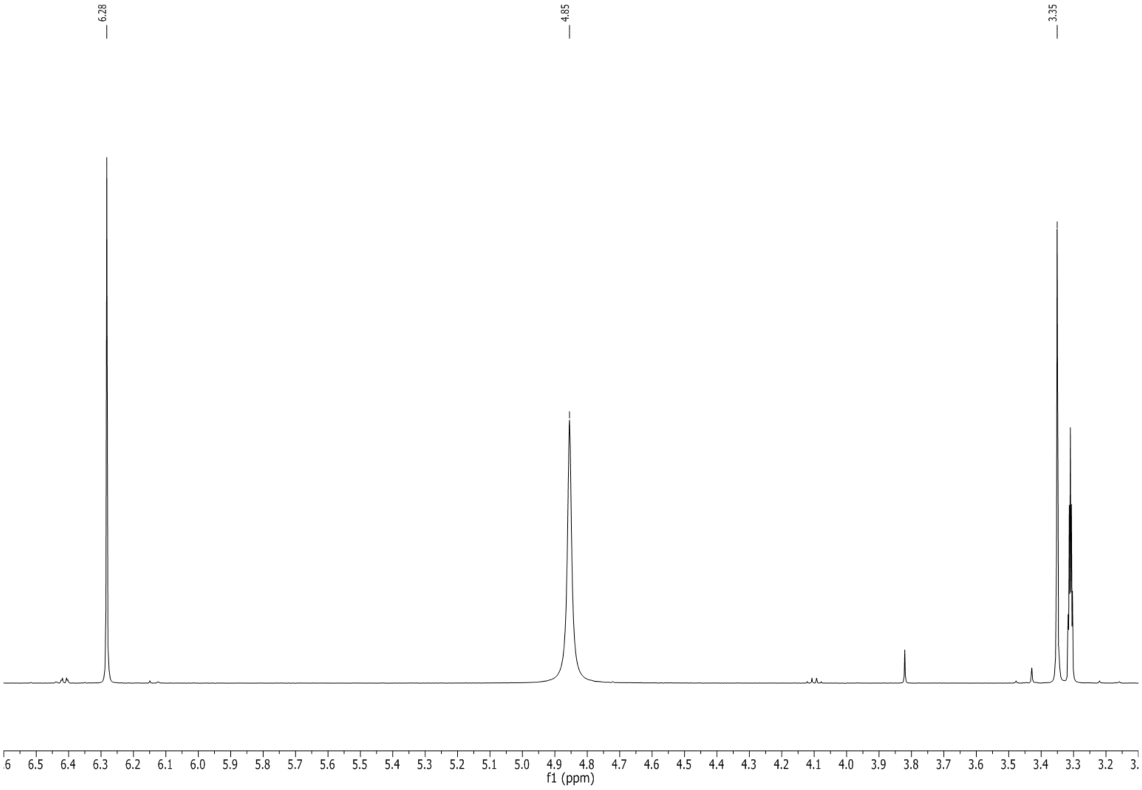
Content:

Synthesis and spectroscopic data for PS-Supported catalysts

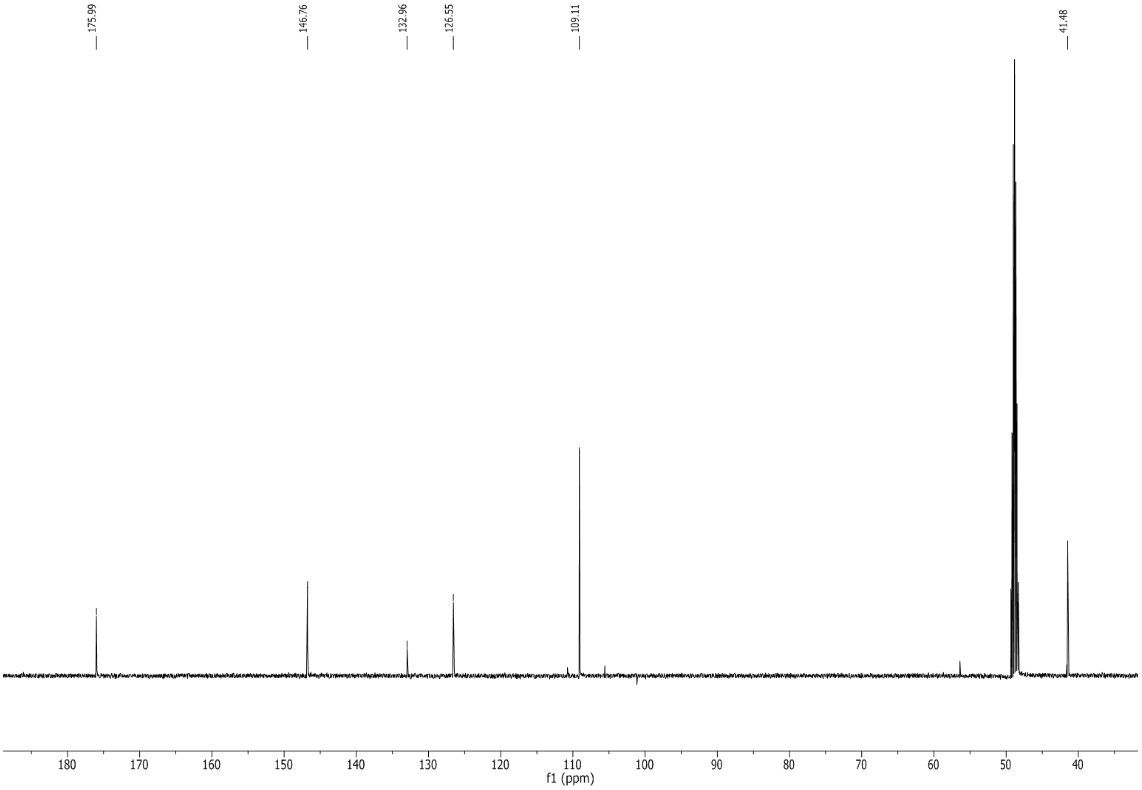
(**1**) 2-(3,4,5-trihydroxyphenyl)acetic acid:



This compound was prepared as previously described.[1] ^{1}H NMR (MeOD, 500 MHz) δ 6.28 (s, 2H; ArH), 4.85 (br s, 3H; ArOH), 3.35 (s, 2H; $ArCH_2$). $^{13}C\{^1H\}$ NMR (MeOD, 125 MHz) δ 176.0 (C=O), 147.0, 133.0, 126.6, 109.1 (all ArC), 41.5 (Ar<u>C</u>H_2).

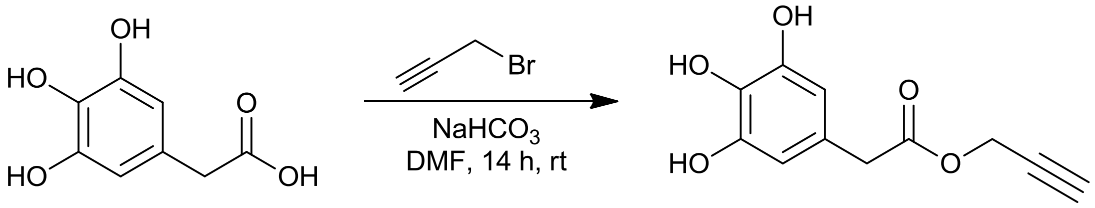


^{1}H NMR spectrum (MeOD)



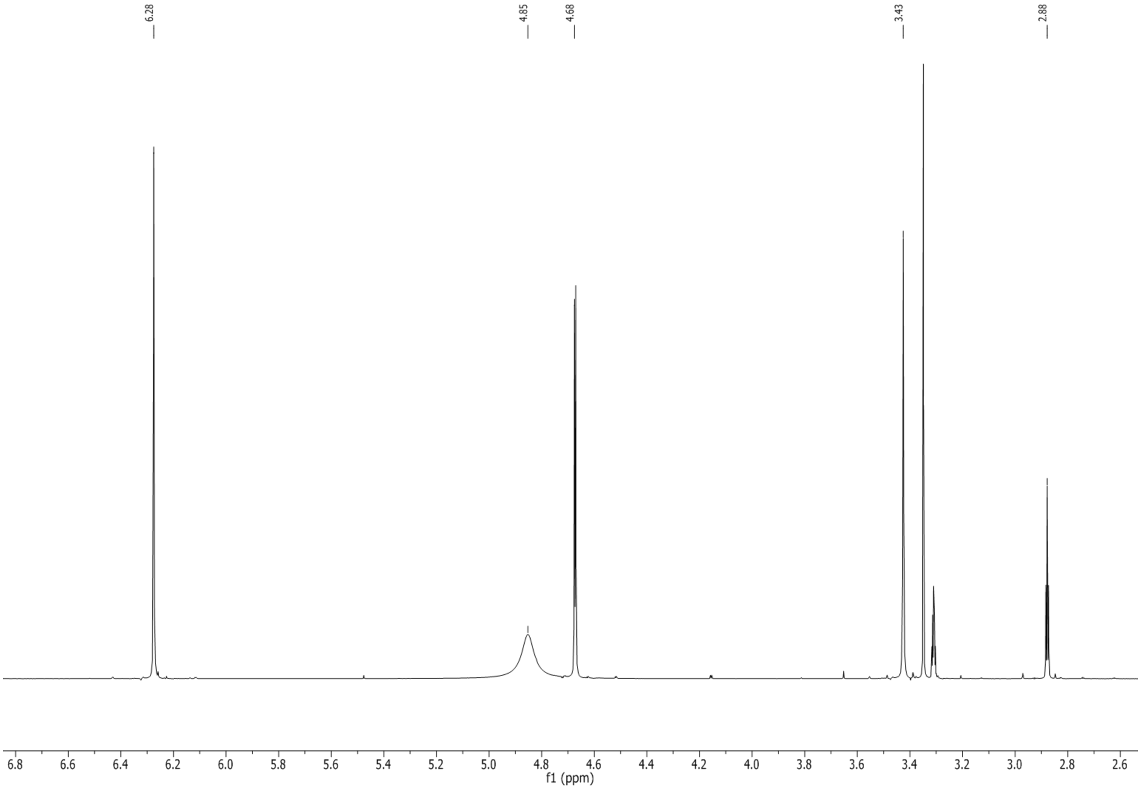
$^{13}C\{^{1}H\}$ NMR spectrum (MeOD)

(**2**) Prop-2-yn-1-yl 2-(3,4,5-trihydroxyphenyl)acetate:

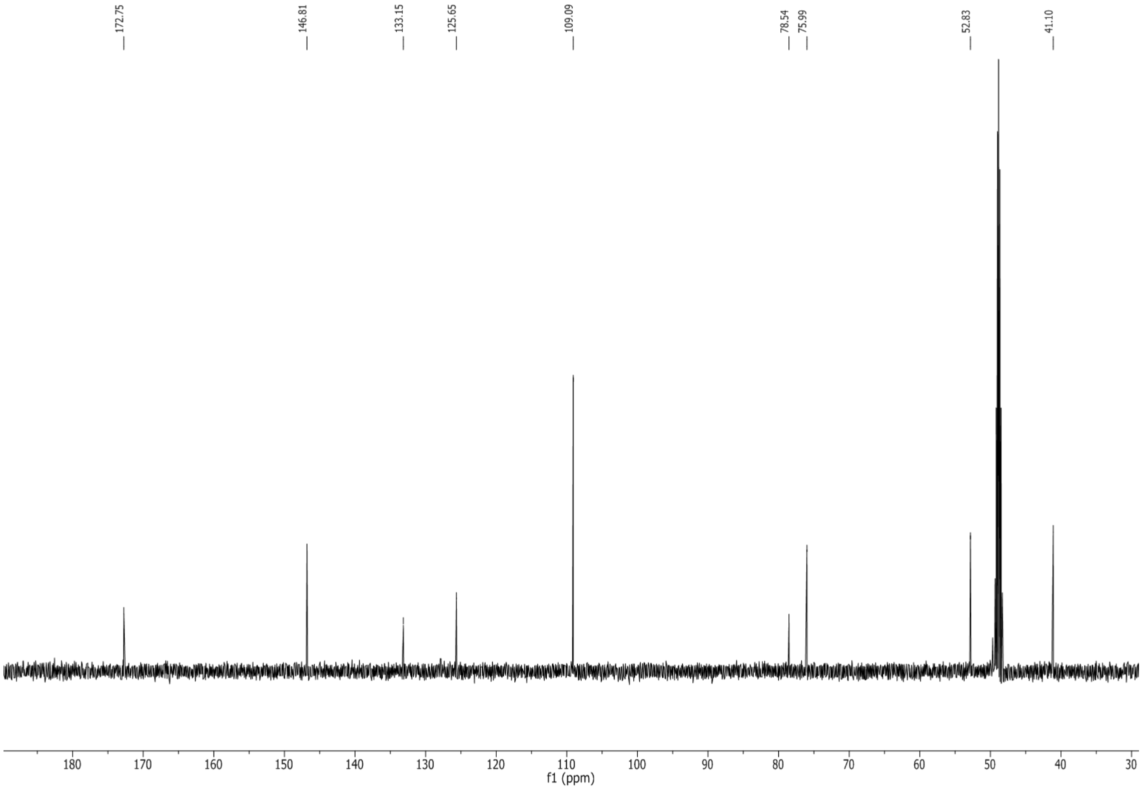


2-(3,4,5-Trihydroxyphenyl)acetic acid (2.20 g, 12.0 mmol, 1.0 eq.) was dissolved in anhydrous DMF (60 mL). The solution was cooled to 0 ˚C and sodium bicarbonate (2.40 g, 28.7 mmol, 2.4 eq.) was added. The resulting mixture was stirred for a further 30 minutes. Following, Propargyl bromide (2.84 g, 2.10 mL, 23.9 mmol, 2.0 eq.) and potassium iodide (1.98 g, 12.0 mmol, 1.0 eq.) were slowly added. The reaction was allowed to warm to room temperature and stirred overnight. The reaction mixture was filtered and the solvent removed under reduced pressure. The crude product was purified by column chromatography (CH_2Cl_2/MeOH 9:1) to obtain prop-2-yn-1-yl 2-(3,4,5-trihydroxyphenyl)acetate as a brown oil (1.70 g, 64 %). ^{1}H NMR (MeOD, 500

MHz) δ 6.28 (s, 2H; ArH), 4.85 (br s, 3H; ArOH), 4.68 (m, 2H; C(O)OCH$_2$), 3.43 (s, 2H; ArCH$_2$), 2.88(t, $^4J_{HH}$ = 2.5 Hz, 1H; C≡CH). ^{13}C{^{1}H} NMR (MeOD, 125 MHz) δ 172.8 (C=O), 146.8 (ArC), 133.2 (ArC), 125.7 (ArC), 109.1 (ArC), 78.5 ($\underline{C}$≡CH), 76.0 (C≡$\underline{C}$H), 52.8 (C(O)O$\underline{C}$H$_2$), 41.1 (Ar$\underline{C}$H$_2$). HRMS (ESI-) [M-H]$^-$ *m/z* calcd.: 221.0459. Found: 221.0455.

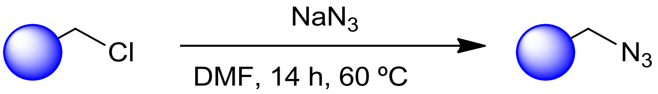


^{1}H NMR spectrum (MeOD)

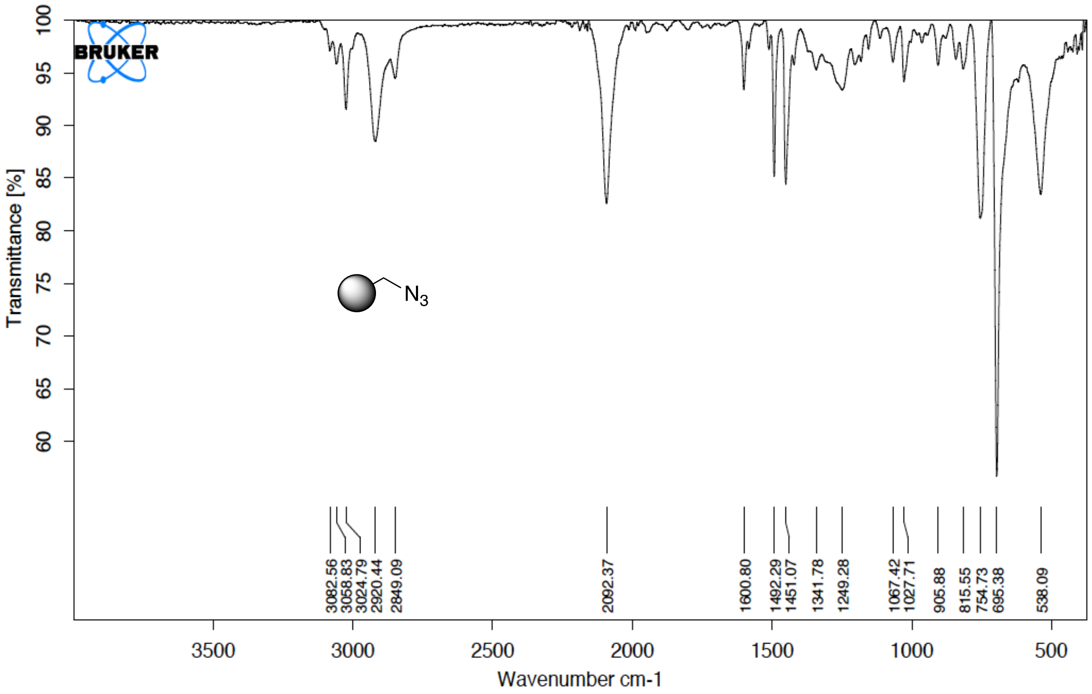


$^{13}C\{^1H\}$ NMR spectrum (MeOD)

Azidomethyl polystyrene:[2,3]

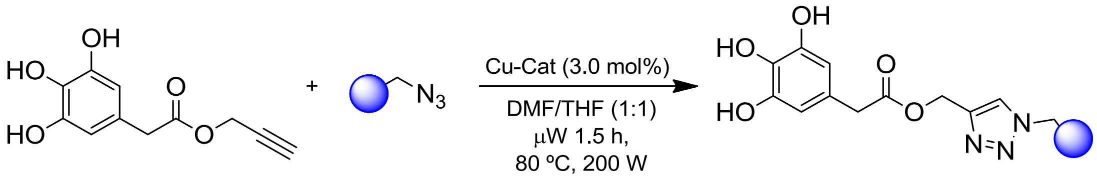


To a suspension of Merrifield resin (100 – 200 mesh, Novabiochem, f = 1.3 mmol·g^{-1}, 500 mg, 0.65 mmol) in DMF (20 mL) was added sodium azide (211 mg, 3.25 mmol, 5.0 eq.) and the reaction was shaken over night at 60 ˚C. The reaction mixture was filtered and the resin was successively washed with H_2O, H_2O/MeOH (1:1), MeOH, MeOH/THF (1:1), THF and DCM. The solid was dried under reduced pressure at 40 ˚C for 24 h. The degree of functionalization was calculated on the basis of nitrogen elemental analysis. Elemental analysis (%): N, 5.43; C, 86.41; H, 7.23; f = 1.3 mmol·g^{-1} (f_{max} = 1.3 mmol·g^{-1}). IR (ATR): 3082, 3058, 3024, 2920 (C-H st), 2849, 2092 (N≡N st), 1600 (C=C st), 1492, 1451, 1341, 1249, 1067, 1027, 905, 815, 754, 695 (C-H δ), 538 cm^{-1}.

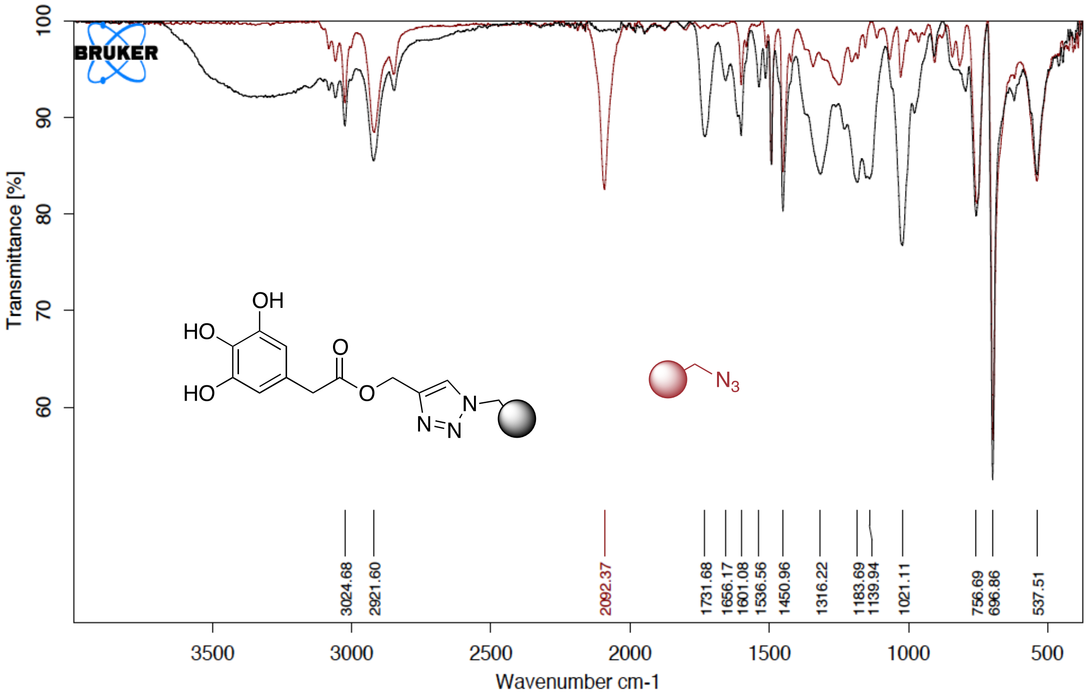


IR Spectrum

PS-Support 1:

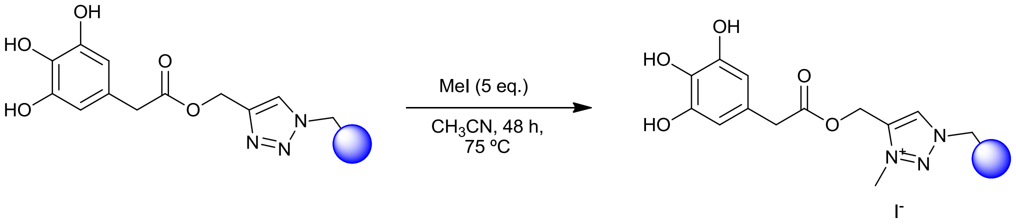


Azidomethyl polystyrene (500 mg, 0.65 mmol, 1.0 eq., f = 1.3 mmol·g^{-1}) and *tris*(1-benzyl-1*H*-1,2,3-triazol-4-yl)methanol·CuCl catalyst[4] (12 mg, 19 µmol, 0.03 eq.) were placed in a microwave tube and swollen in THF/DMF (4.50 mL, 1:1) for 15 minutes. A solution of prop-2-yn-1-yl 2-(3,4,5-trihydroxyphenyl)acetate (**3**) in THF/DMF (0.50 mL, 1:1) was added and the reaction mixture was heated to 80 ˚C for 1.5 h under microwave irradiation at 200 W. The reaction progress was monitored by FT-IR spectroscopy. When the IR band of the azide (2092 cm^{-1}) had completely disappeared, the reaction mixture was filtered and the resin was successively washed with H_2O, H_2O/MeOH (1:1), MeOH, MeOH/THF (1:1), THF and DCM. The solid was dried under reduced pressure at 40 ˚C for 24 h. The degree of functionalization was calculated on the basis of nitrogen elemental analysis. Elemental analysis (%): N, 4.20; C, 80.06; H, 6.77; f = 1.0 mmol·g^{-1} ($f_{\max}$ = 1.0 mmol·g^{-1}). IR (ATR): 3360 (O-H st), 3024, 2921(C-H st), 1731 (C=O st), 1656 (N-C=C st), 1601 (C=C st), 1536, 1450, 1316, 1183, 1139, 1021 (C-O st), 696 (C-H δ), 537 cm^{-1}.



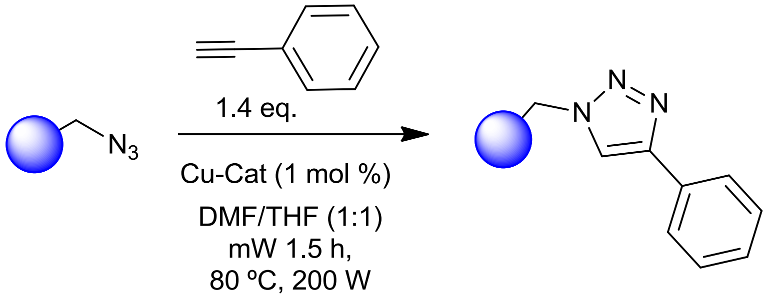
IR Spectra

PS-Support 2:

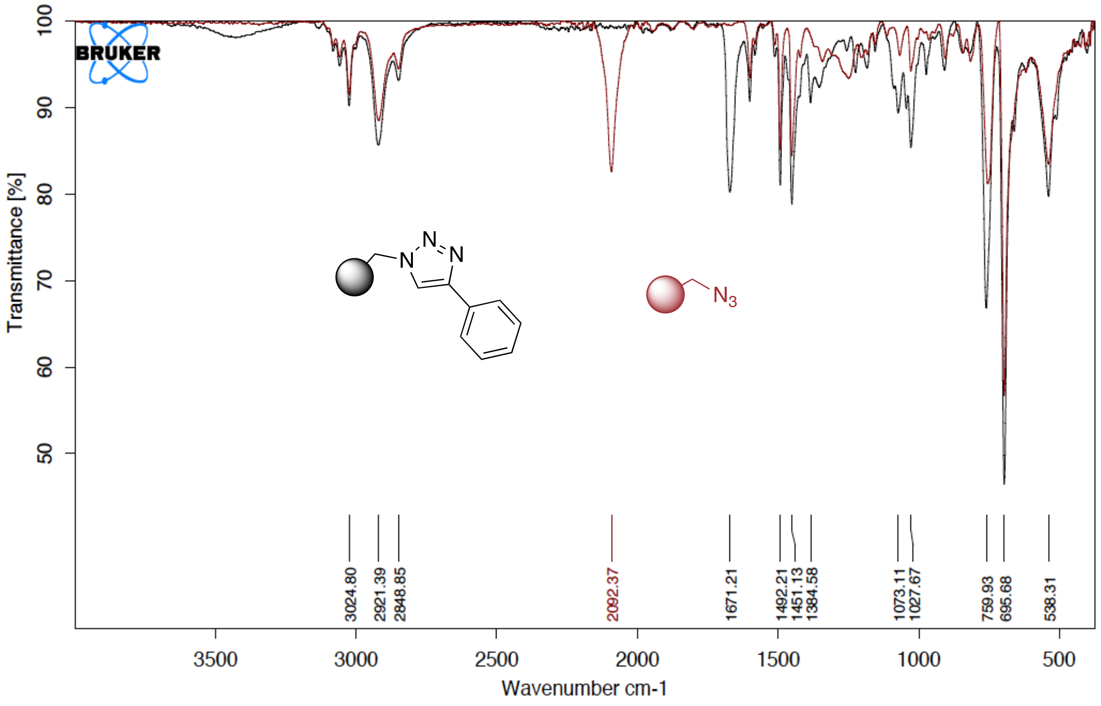


A suspension of **PS-Support 1** (558 mg, 558 mmol, 1.0 eq., *f* = 1.0 mmol·g^{-1}) and methyl iodide (396 mg, 174 µL, 2.79 mmol, 5.0 eq.) in acetonitrile (2.5 mL) was placed in a pressure tube. The reaction mixture was heated to 75 ˚C for 48 hours. The reaction mixture was filtered and the resin was successively washed with H_2O, H_2O/MeOH (1:1), MeOH, MeOH/THF (1:1), THF and DCM. The solid was dried under reduced pressure at 40 ˚C for 24 h. The degree of functionalization was calculated on the basis of nitrogen elemental analysis. Elemental analysis (%): N, 3.36; C, 71.36; H, 6.34. *f* = 0.8 mmol·g^{-1} (f_{max} = 0.9 mmol·g^{-1}).

PS-Support 3:

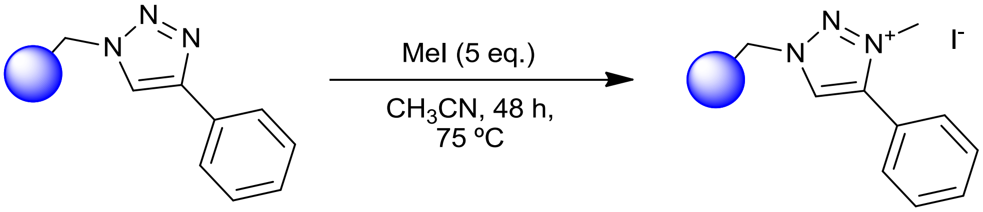


Azidomethyl polystyrene (500 mg, 0.65 mmol, 1.0 eq., *f* = 1.3 mmol·g^{-1}) and *tris*(1-benzyl-1*H*-1,2,3-triazol-4-yl)methanol·CuCl catalyst[4] (12 mg, 20 µmol, 0.03 eq.) were placed in a microwave tube and swollen in THF/DMF (4.50 mL, 1:1) for 15 min. Ethynylbenzene (93 mg, 100 µL, 910 µmol, 1.4 eq.) in DMF/THF (0.50 mL, 1:1) was added and the reaction mixture was heated to 80 ˚C for 1.5 h under microwave irradiation at 200 W. The reaction progress was monitored by FT-IR spectroscopy. When the IR band of the azide (2092 cm^{-1}) had completely disappeared, the reaction mixture was filtered and the resin was successively washed with H_2O, H_2O/MeOH (1:1), MeOH, MeOH/THF (1:1), THF and DCM. The solid was dried under reduced pressure at 40 ˚C for 24 h. The degree of functionalization was calculated on the basis of nitrogen elemental analysis. Elemental analysis (%): N, 4.69; C, 86.37; H, 7.12. *f* = 1.1 mmol·g^{-1} (f_{max} = 1.1 mmol·g^{-1}). IR (ATR): 3024, 2921 (C-H st), 2848, 1671 (N-C=C st), 1600 (C=C st), 1492, 1451, 1384, 1073, 1027, 759, 695 (C-H δ), 538 cm^{-1}.



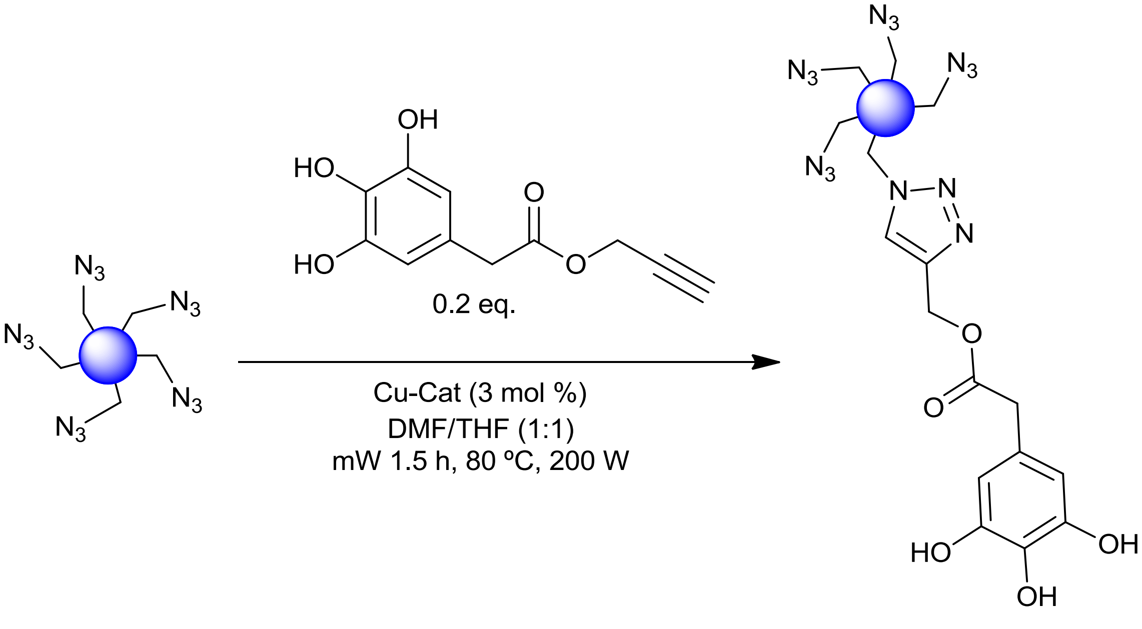
IR Spectra

PS-Support 4:

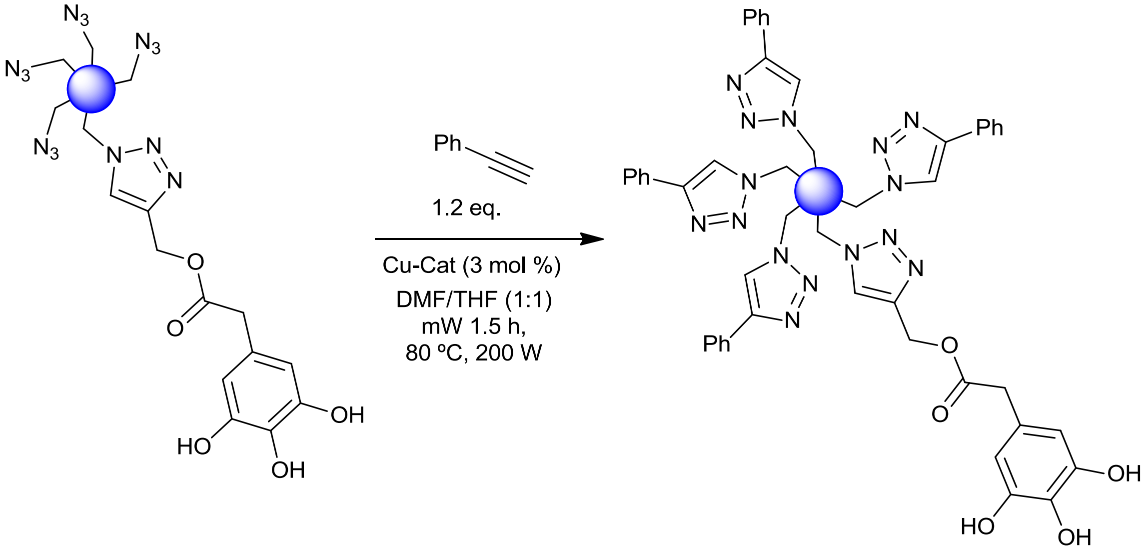


A suspension of **PS-Support 3** (535 mg, 559 mmol, 1.0 eq., *f* = 1.1 mmol·g^{-1}) and methyl iodide (425 mg, 187 µL, 3.00 mmol, 5.0 eq.) was placed in a pressure tube with acetonitrile (2.0 mL). The reaction mixture was heated to 75 ˚C for 48 hours. The reaction mixture was filtered and the resin was successively washed with H_2O, H_2O/MeOH (1:1), MeOH, MeOH/THF (1:1), THF and DCM. The solid was dried under reduced pressure at 40 ˚C for 24 h. The degree of functionalization was calculated on the basis of nitrogen elemental analysis. Elemental analysis (%): N, 4.14; C, 76.32; H, 6.49. *f* = 1.0 mmol·g^{-1} (f_{max} = 1.0 mmol·g^{-1}).

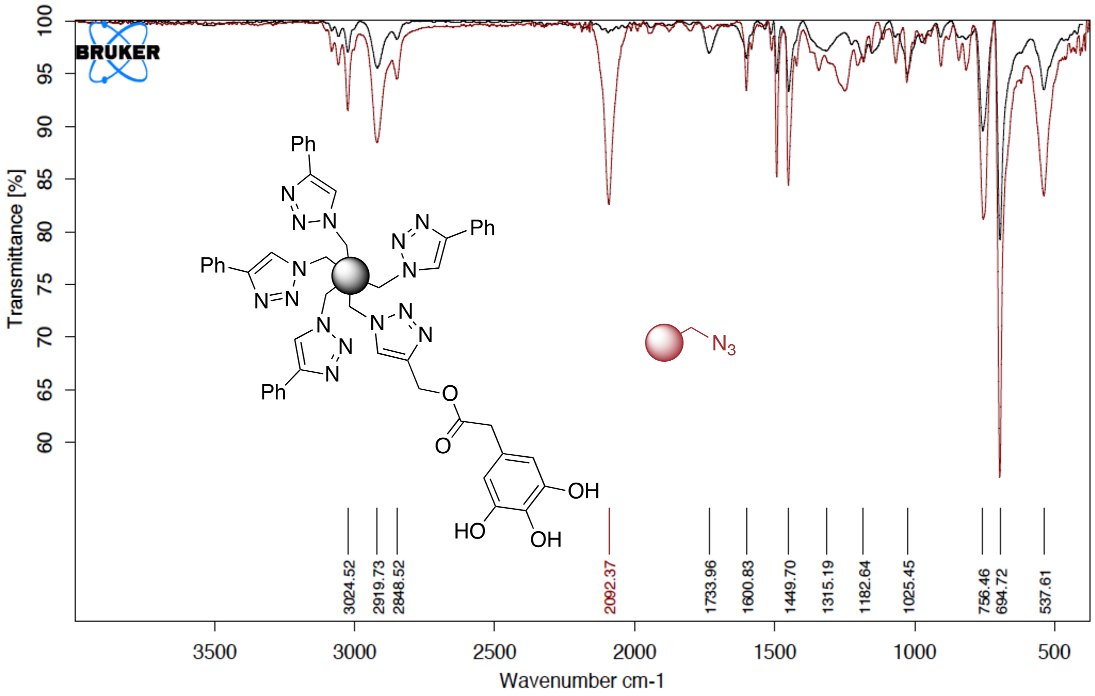
PS-Support 5:



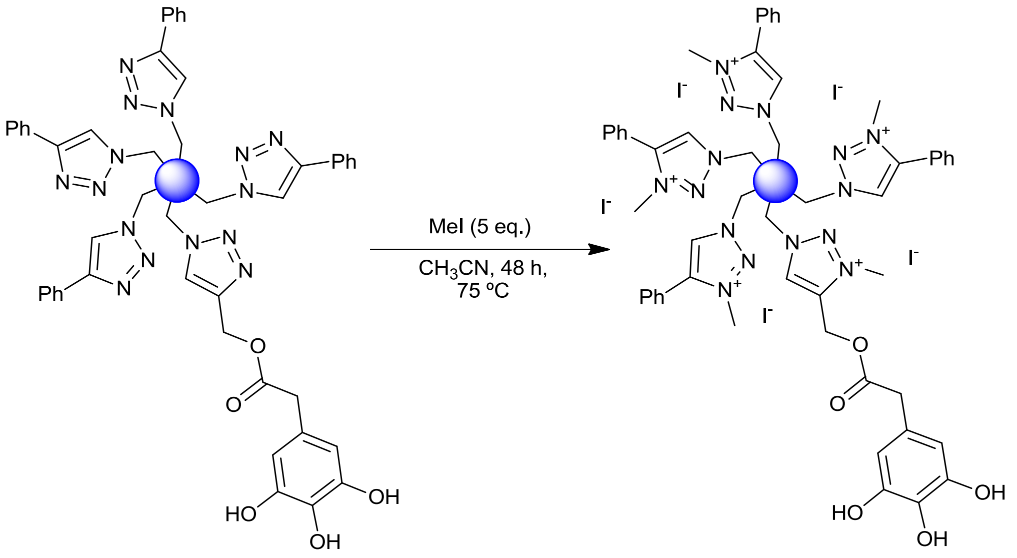
Azidomethyl polystyrene (500 mg, 0.65 mmol, 1.0 eq., *f* = 1.3 mmol·g^{-1}) and *tris*(1-benzyl-1*H*-1,2,3-triazol-4-yl)methanol·CuCl catalyst[4] (12 mg, 19 µmol, 0.03 eq.) were placed in a microwave tube and swollen in THF/DMF (4.50 mL, 1:1) for 15 min. A solution of prop-2-yn-1-yl 2-(3,4,5-trihydroxyphenyl)acetate (**3**) (29 mg, 129 µmol, 0.2 eq.) in DMF/THF (0.50 mL, 1:1) was added and the reaction mixture was heated to 80 ˚C for 1.5 h under microwave irradiation at 200 W. The reaction progress was monitored by TLC. When prop-2-yn-1-yl 2-(3,4,5-trihydroxyphenyl)acetate was completely consumed, the reaction mixture was filtered and the resin was successively washed with H_2O, H_2O/MeOH (1:1), MeOH, MeOH/THF (1:1), THF and DCM. The solid was dried in vacuo at 40 ˚C for 24 h to yield the **intermediate support (a)**.



The **intermediate support (a)** (500 mg, 0.65 mmol, 1.0 eq.) and *tris*(1-benzyl-1*H*-1,2,3-triazol-4-yl)methanol·CuCl catalyst[4] (12 mg, 19 µmol, 0.03 eq.) were placed in a microwave tube and swollen in THF/DMF (4.50 mL, 1:1) for 15 min. A solution of ethynylbenzene (79 mg, 85 µL, 774 µmol, 1.2 eq.) in DMF/THF (0.50 mL, 1:1) was added and the reaction mixture was heated to 80 ˚C for 1.5 h under microwave irradiation at 200 W. The reaction progress was monitored by FT-IR spectroscopy. When the IR band of the azide (2092 cm^{-1}) had completely disappeared, the reaction mixture was filtered and the resin was successively washed with H_2O, H_2O/MeOH (1:1), MeOH, MeOH/THF (1:1), THF and DCM. The solid was dried under reduced pressure at 40 ˚C for 24 h to yield the **intermediate support (b)**. The degree of functionalization was calculated on the basis of nitrogen elemental analysis. Elemental analysis (%): N, 4.62; C, 84.71; H, 7.00; $f = 1.1$ mmol·g^{-1} ($f_{max} = 1.1$ mmol·g^{-1}). IR (ATR): 3024, 2919 (C-H st), 2848, 1733 (C=O st), 1600 (C=C st), 1449, 1315, 1182, 1025 (C-O st), 756, 694 (C-H δ), 537 cm^{-1}.



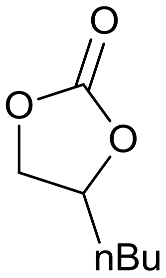
IR Spectra

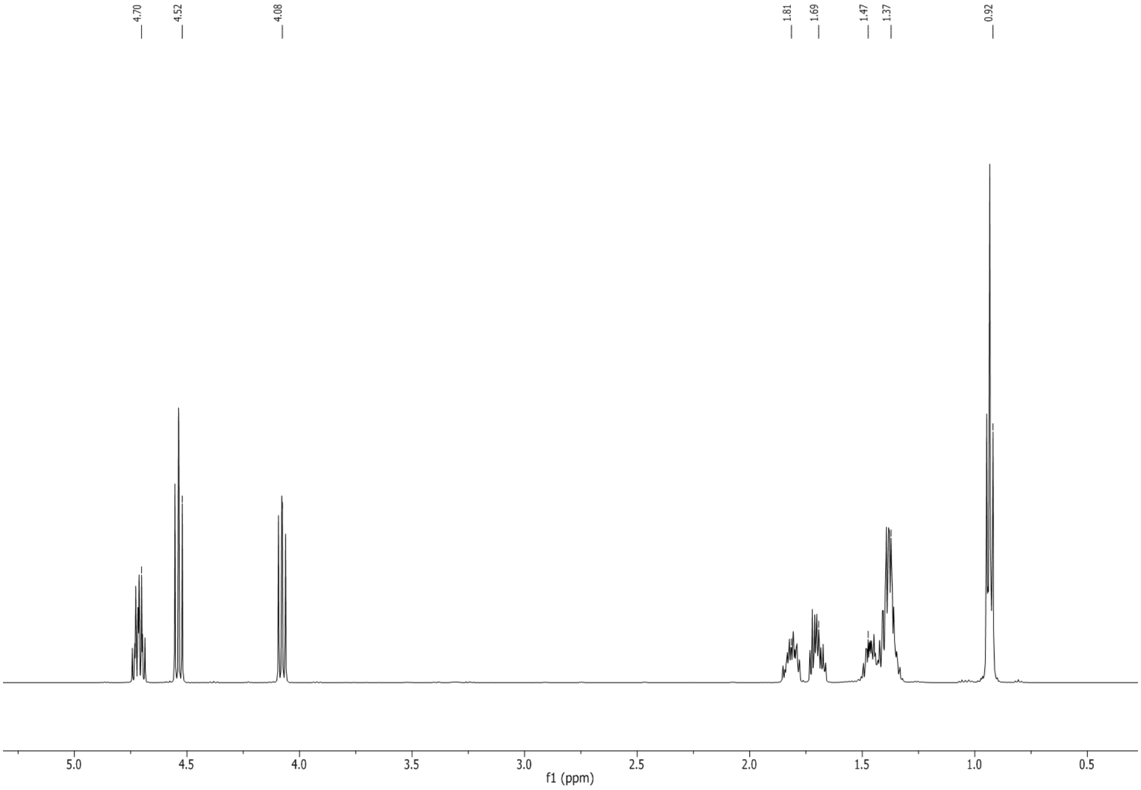


Intermediate support (b) (1.07 g, 1.19 mmol, 1.0 eq., *f* = 1.1 mmol·g^{-1}) and methyl iodide (846 mg, 371 µL, 5.96 mmol, 5.0 eq.) were added to a pressure tube with acetonitrile (4.2 mL). The reaction mixture was heated to 75 ˚C for 48 hours. The reaction mixture was filtered and the resin was successively washed with H_2O, H_2O/MeOH (1:1), MeOH, MeOH/THF (1:1), THF and DCM. The solid was dried under reduced pressure at 40 ˚C for 24 h. The degree of functionalization was calculated on the basis of nitrogen elemental analysis. Elemental analysis (%): N, 3.47; C, 73.71; H, 6.41. *f* = 0.8 mmol·g^{-1} (f_{max} = 1.0 mmol·g^{-1}).

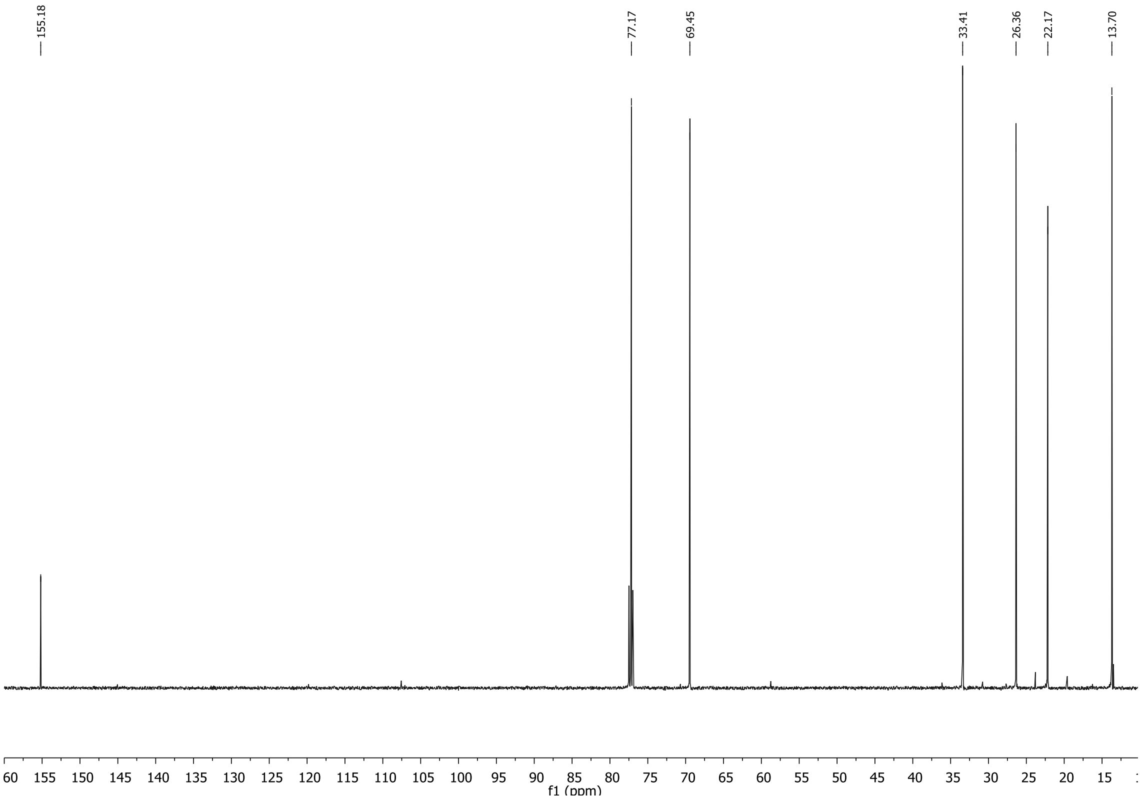
^{1}H, ^{13}C {^{1}H} NMR and IR spectra for cyclic organic carbonate products

(**4a**) 4-butyl-1,3-dioxolan-2-one:[5]

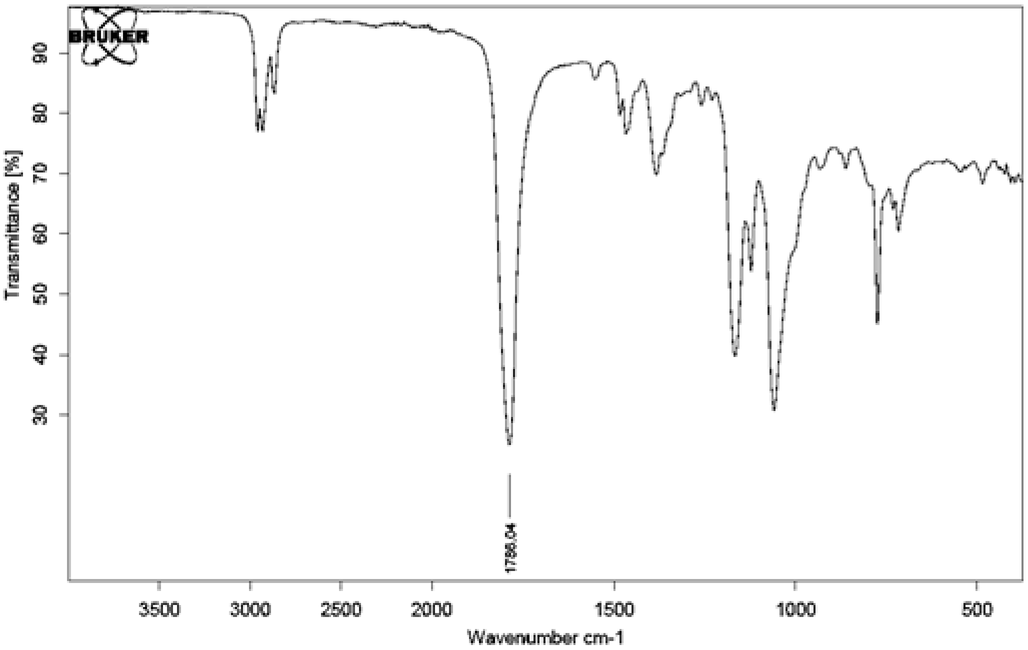




^{1}H NMR ($CDCl_3$)

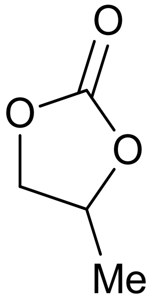


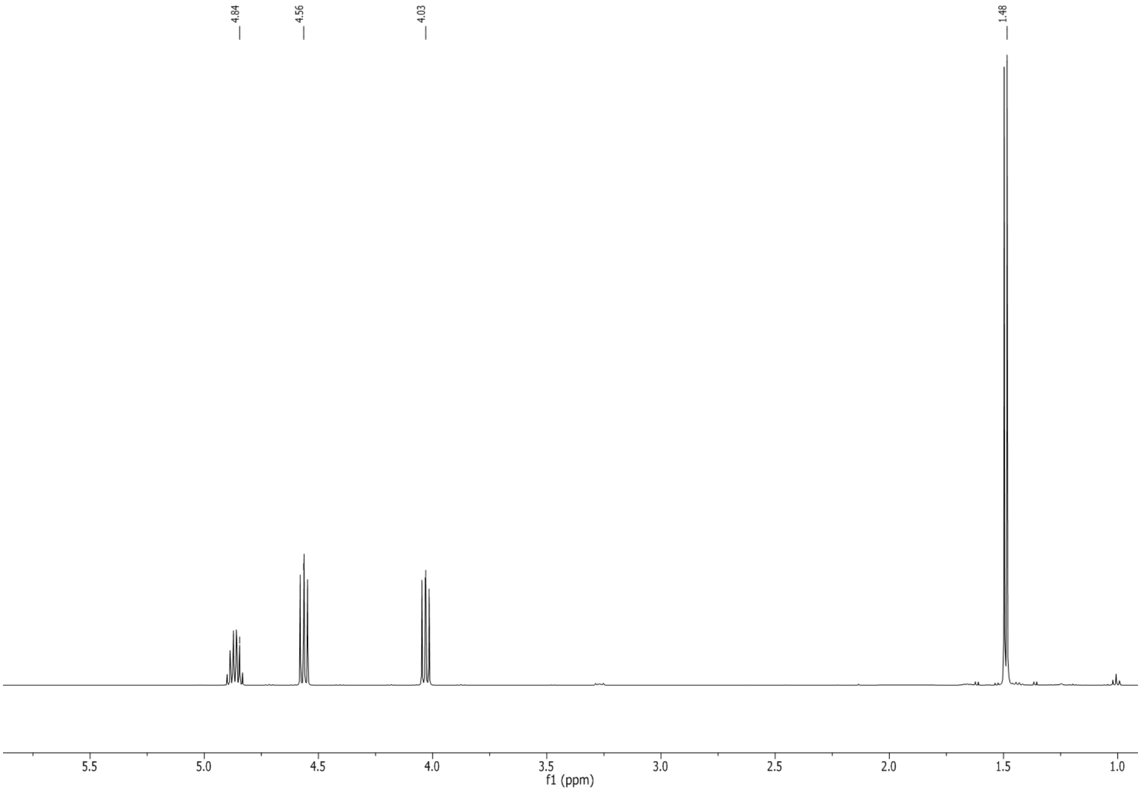
$^{13}C\ \{^{1}H\}$ NMR ($CDCl_3$)



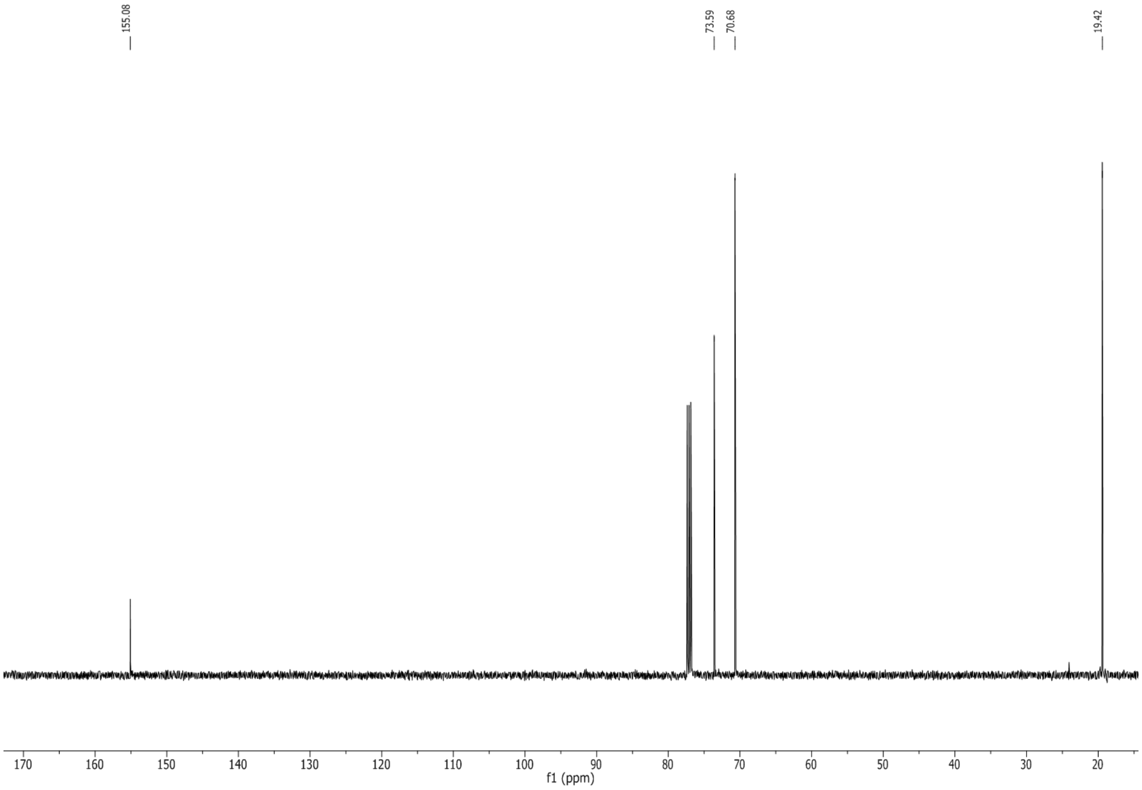
IR (neat)

(**5a**) 4-methyl-1,3-dioxolan-2-one:[5]

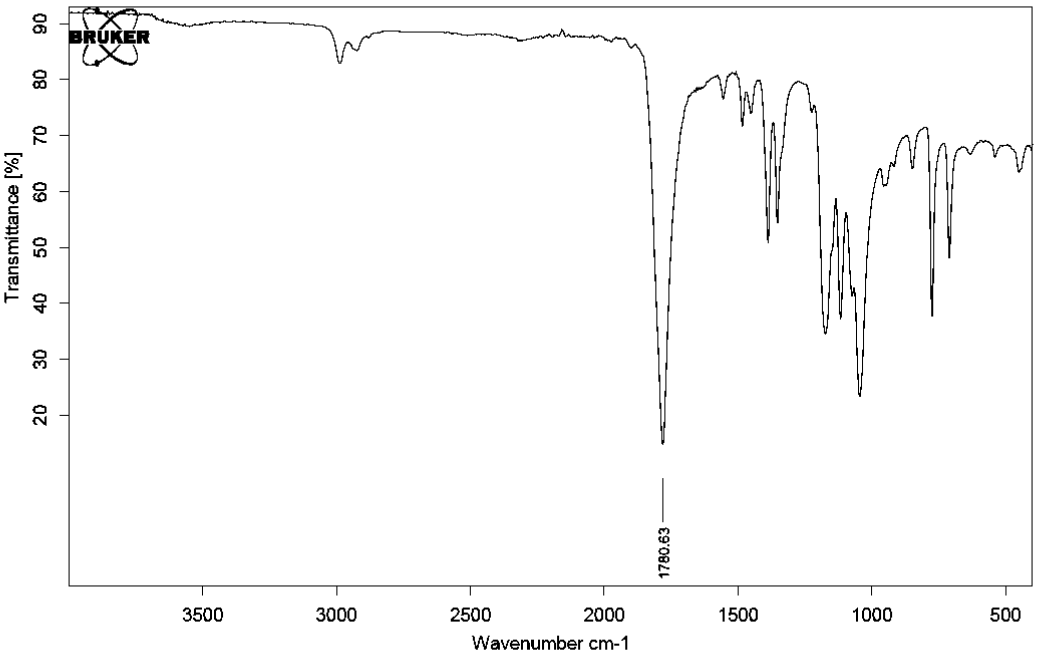




^{1}H NMR ($CDCl_3$)

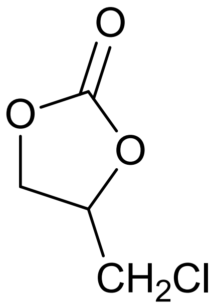


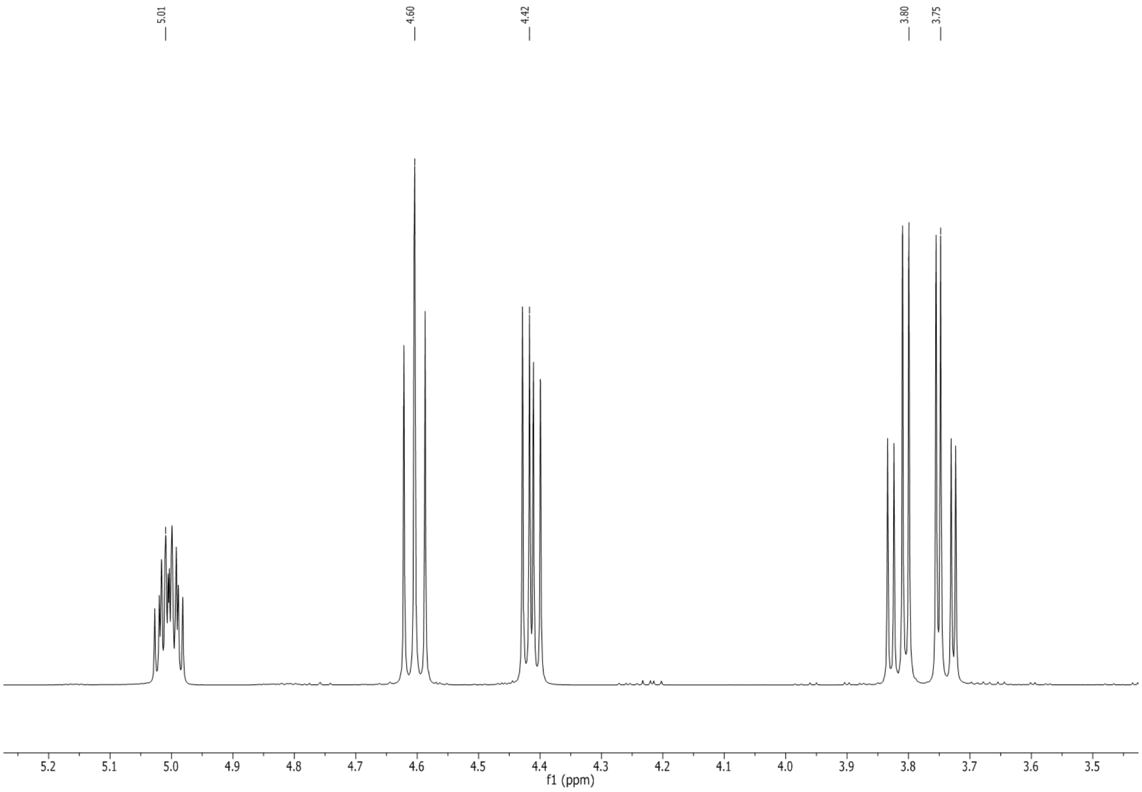
$^{13}C\ \{^1H\}$ NMR ($CDCl_3$)



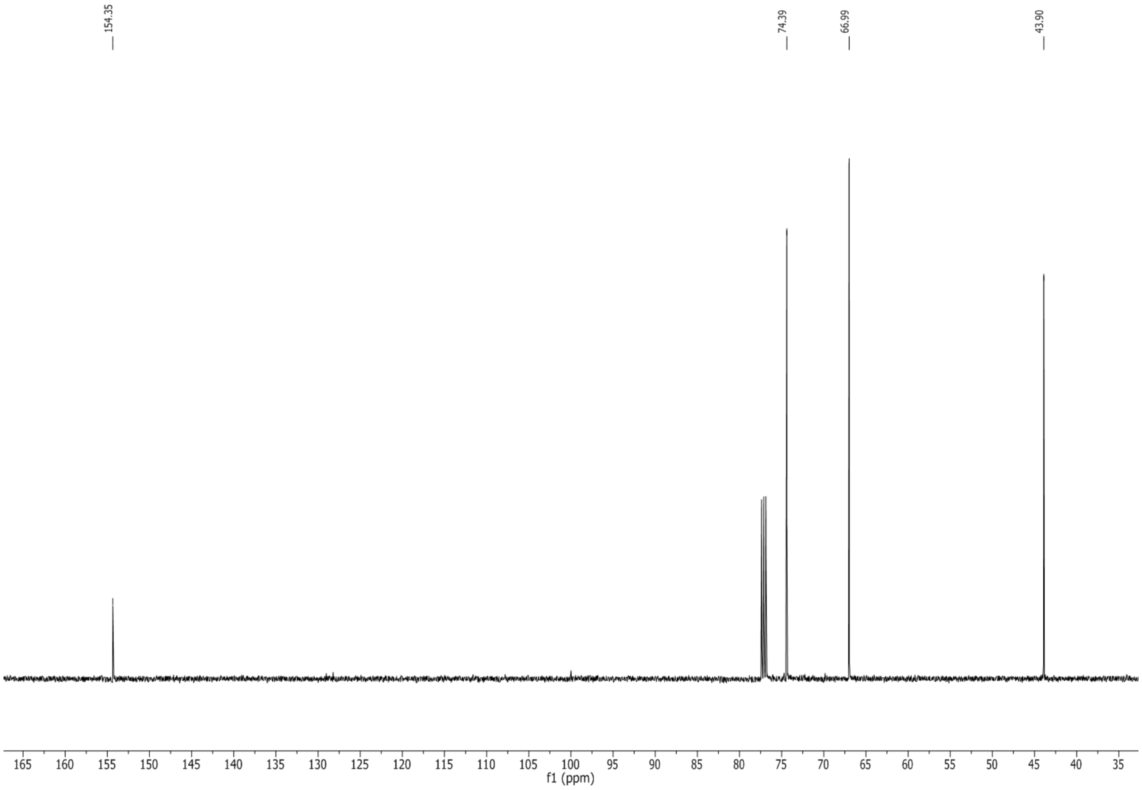
IR (neat)

(**6a**) 4-chloro-1,3-dioxolan-2-one:[6]

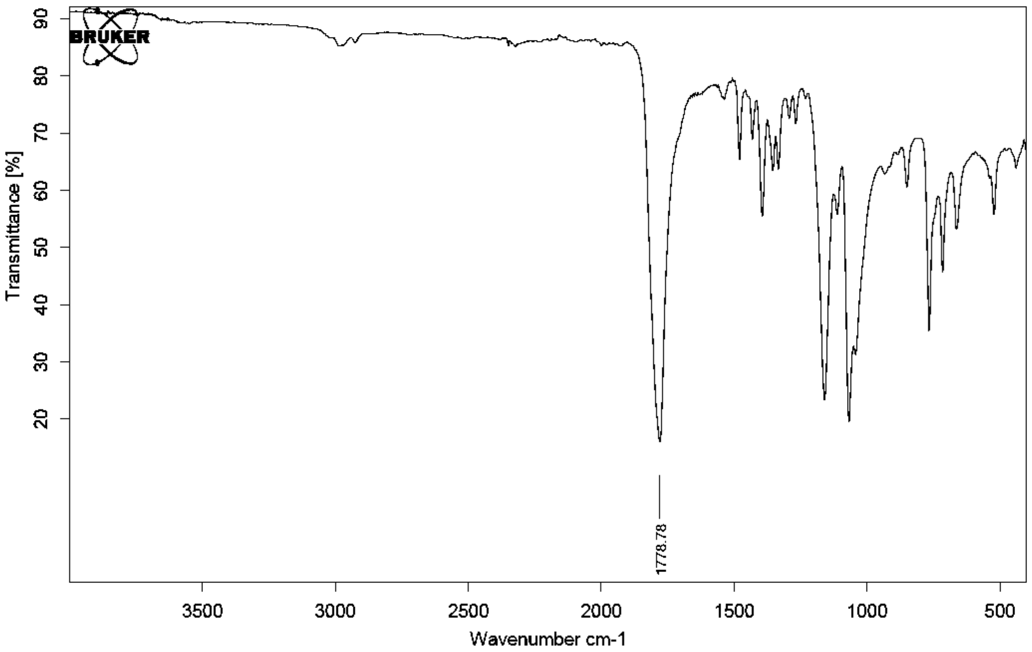




^{1}H NMR ($CDCl_3$)

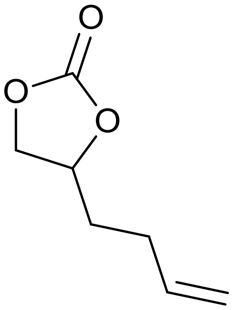


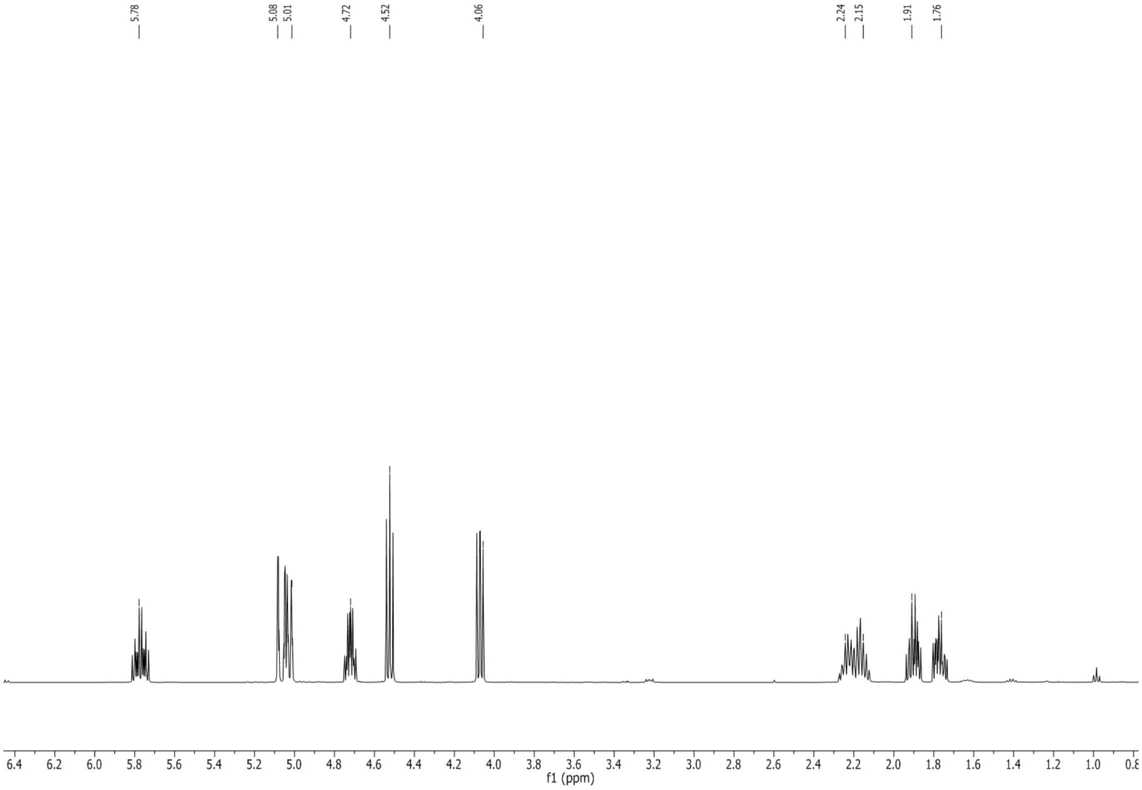
^{13}C {^{1}H} NMR ($CDCl_3$)



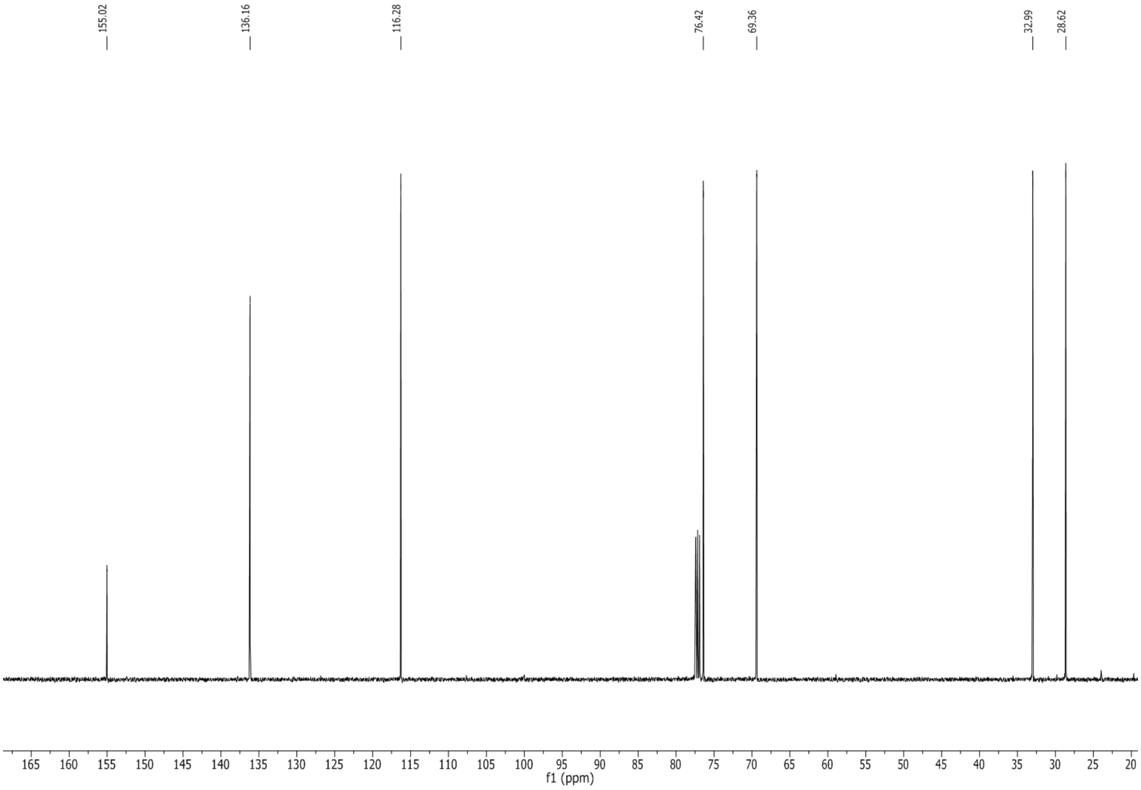
IR (neat)

(**7a**) 4-(but-3-en-1-yl)-1,3-dioxolan-2-one:[7]

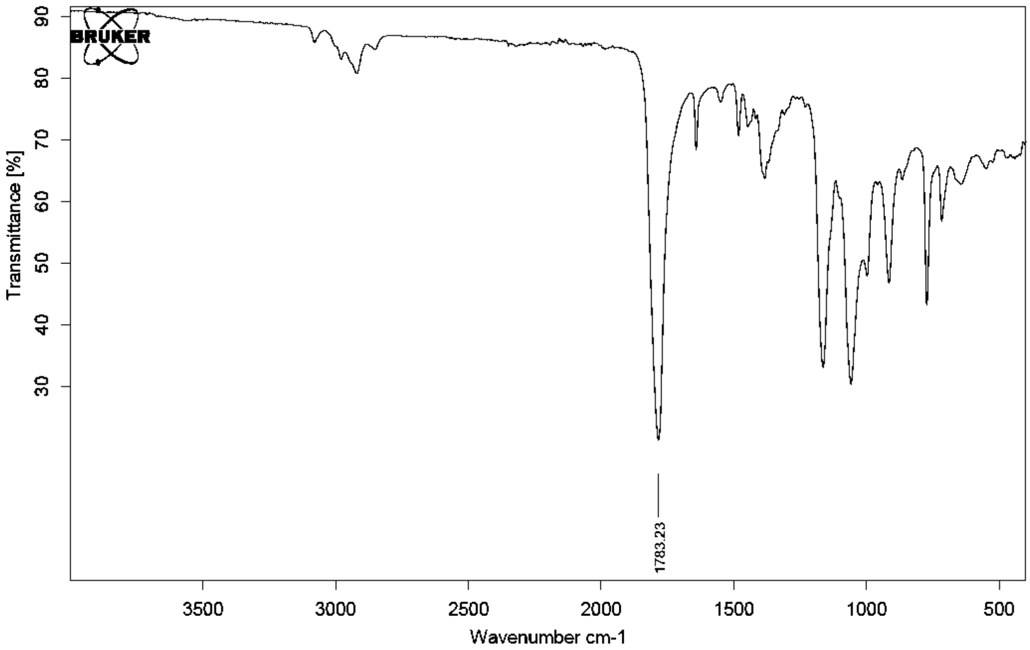




^{1}H NMR ($CDCl_3$)

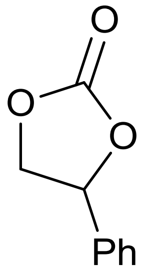


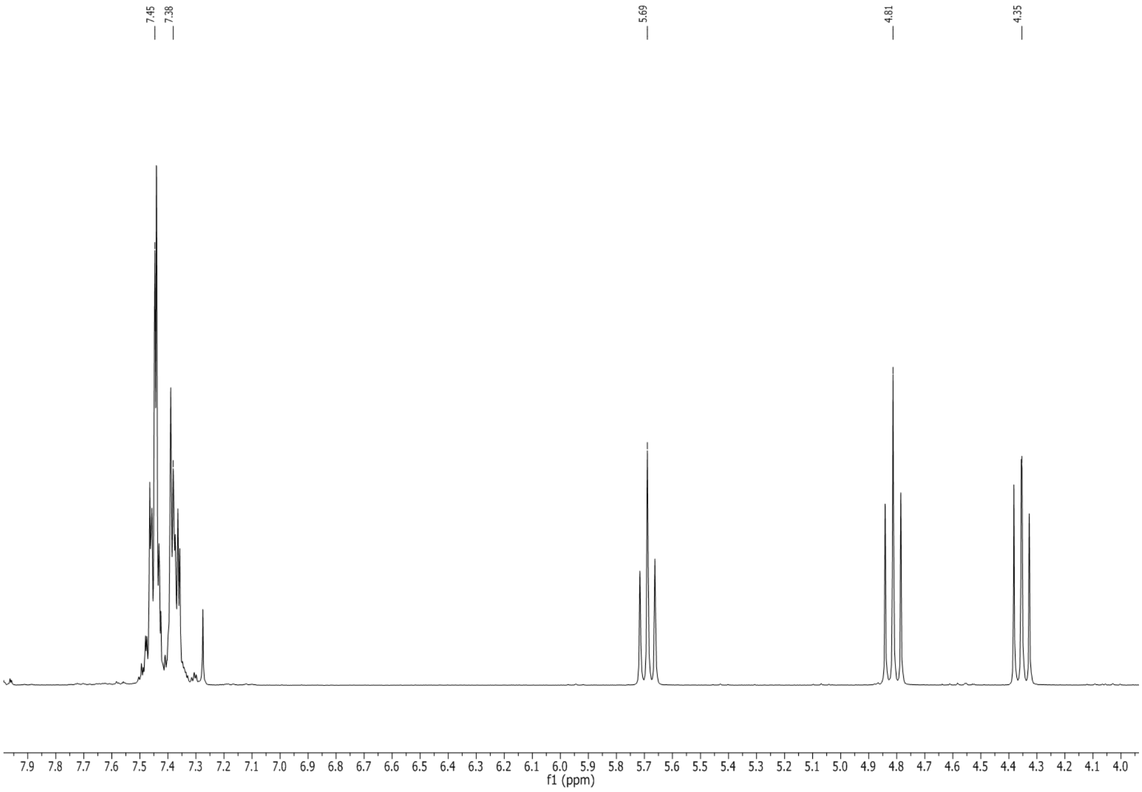
^{13}C {^{1}H} NMR (CDCl$_3$)



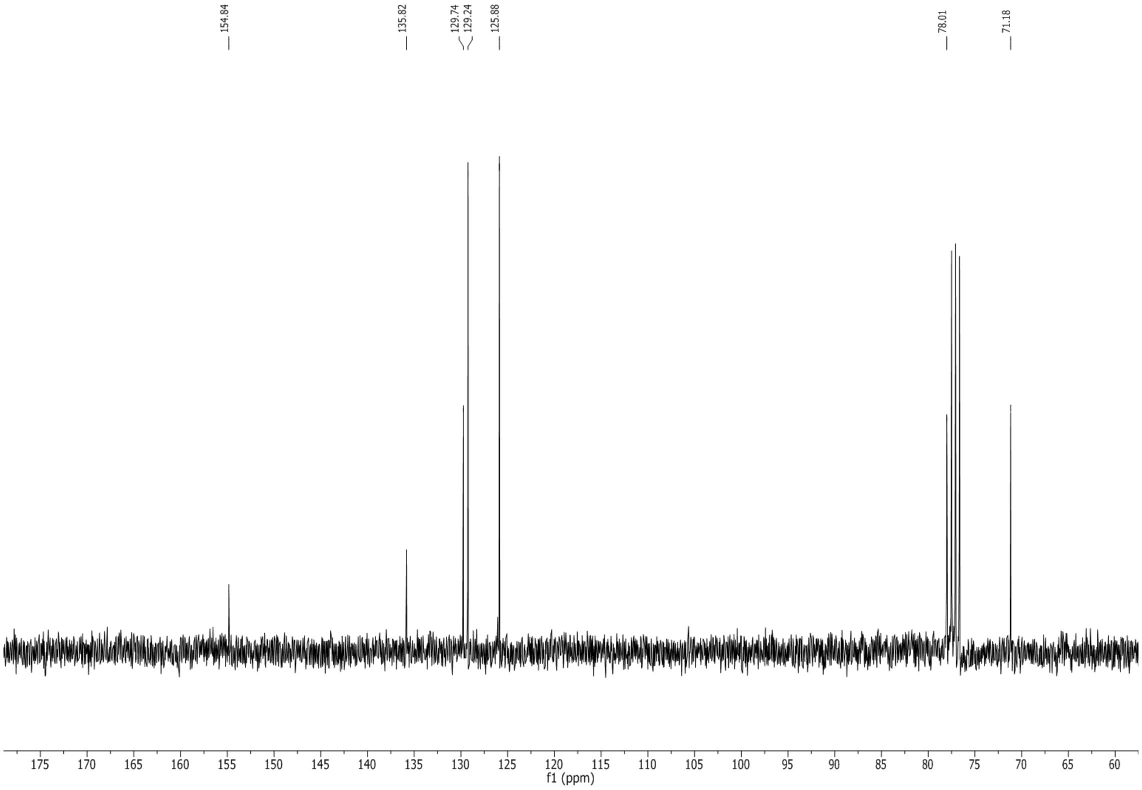
IR (neat)

(**8a**) 4-phenyl-1,3-dioxolan-2-one:[5]

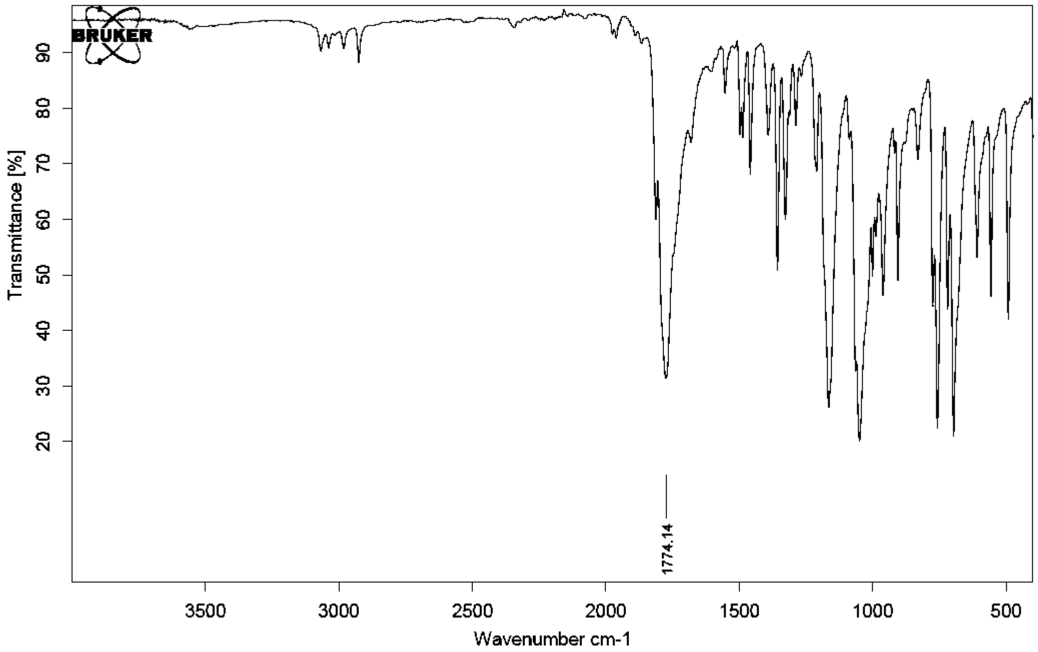




^{1}H NMR ($CDCl_3$)

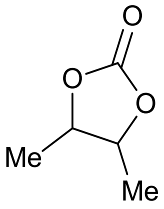


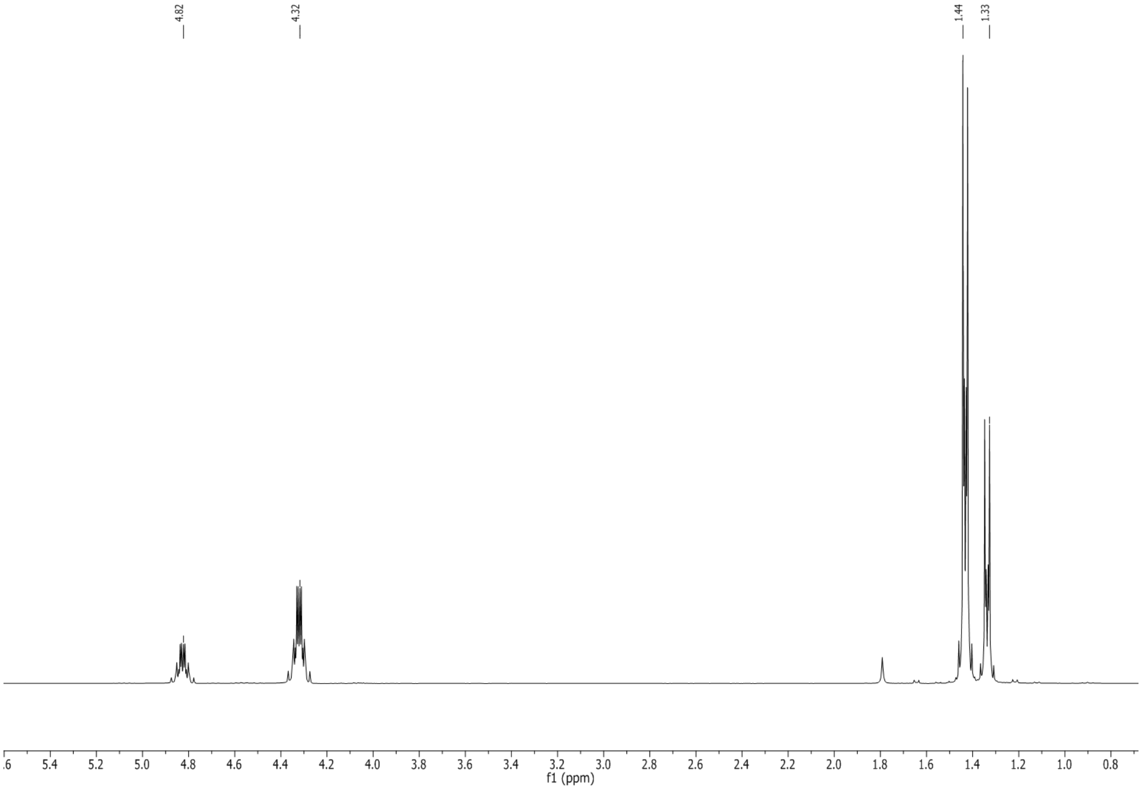
^{13}C {^1H} NMR ($CDCl_3$)



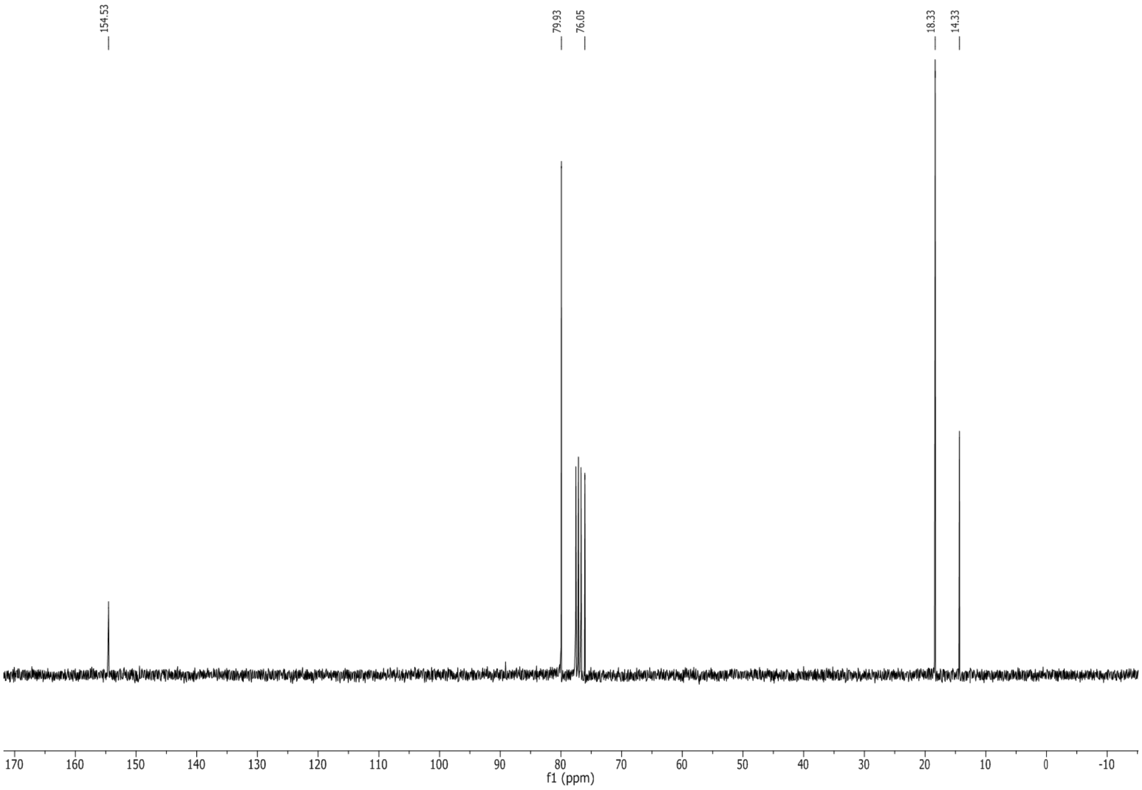
IR (neat)

(**9a**) 4,5-dimethyl-1,3-dioxolan-2-one:[8]

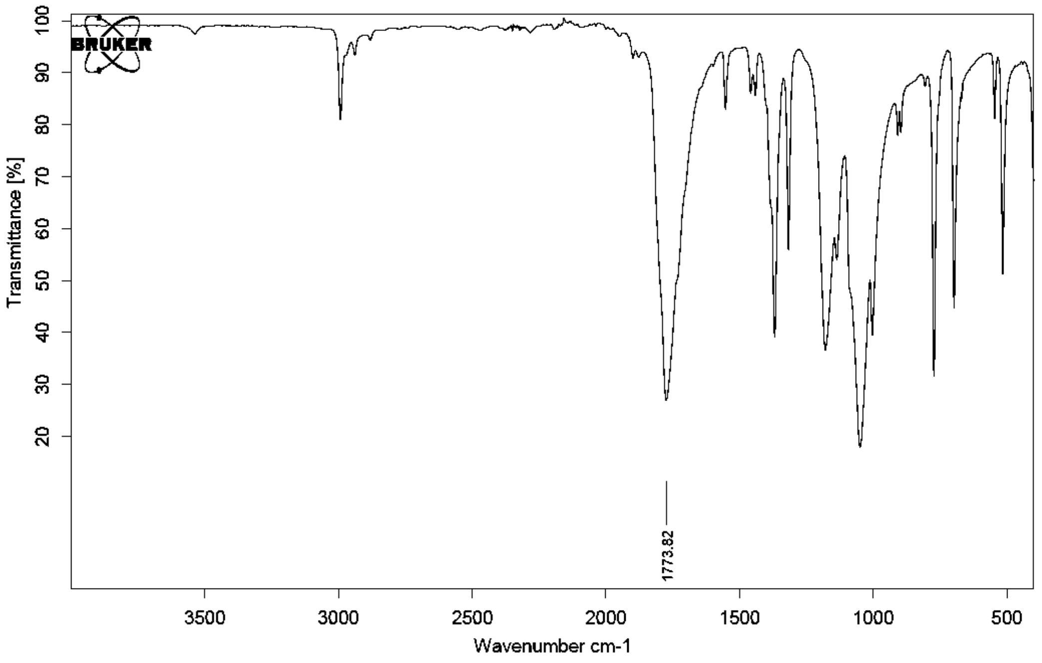




^{1}H NMR ($CDCl_3$): product is a mixture of *cis*- and *trans*-carbonate.

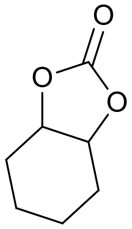


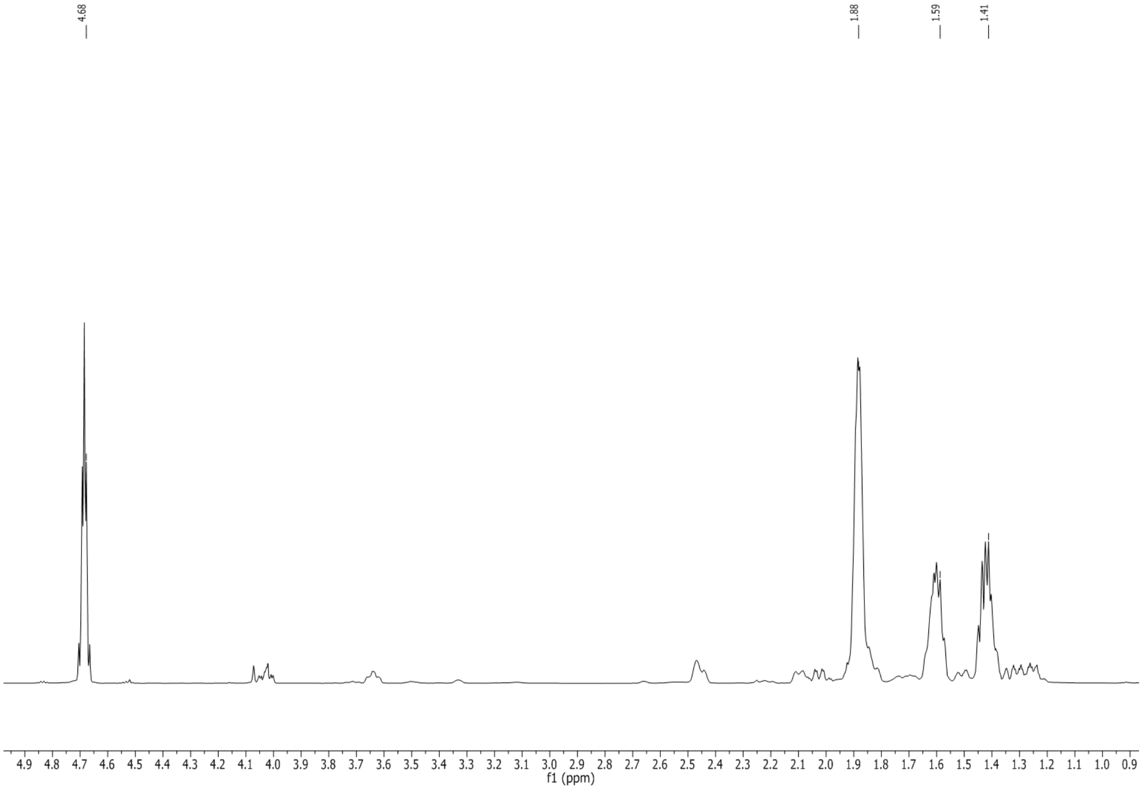
$^{13}C\ \{^1H\}$ NMR ($CDCl_3$): product is a mixture of *cis*- and *trans*-carbonate



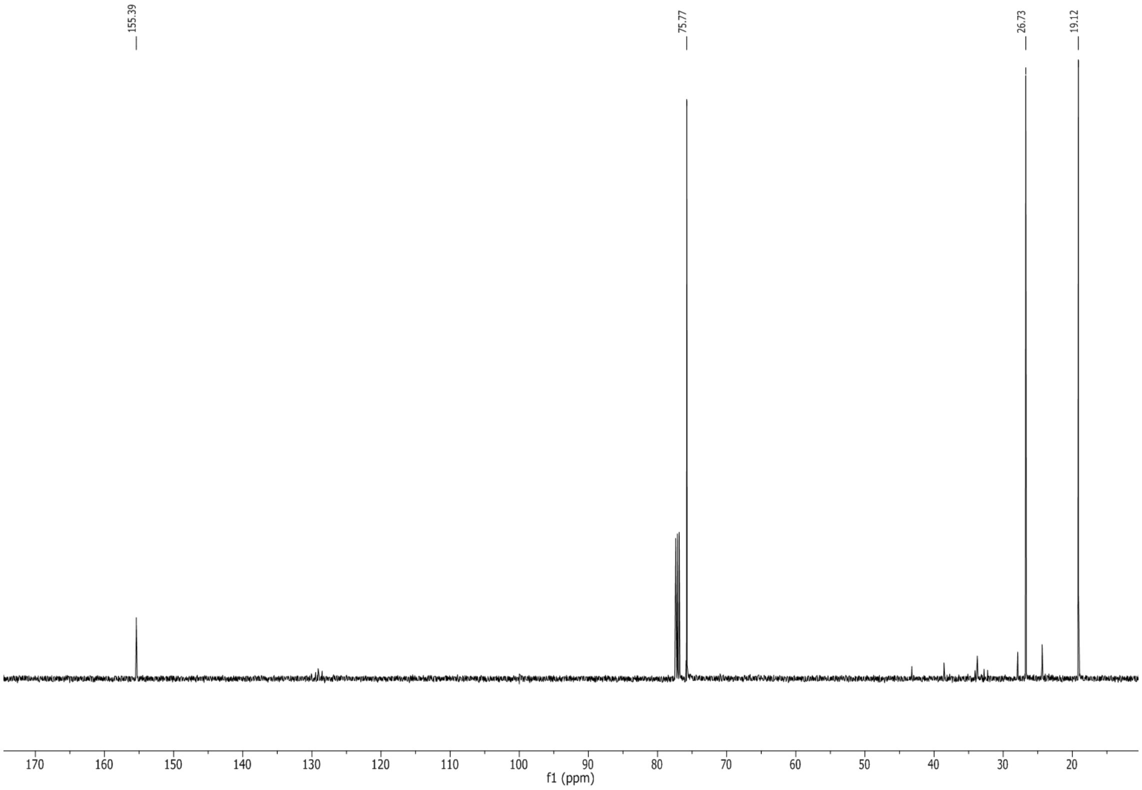
IR (neat)

(**10a**) hexahydrobenzo[*d*][1,3]dioxol-2-one[9]

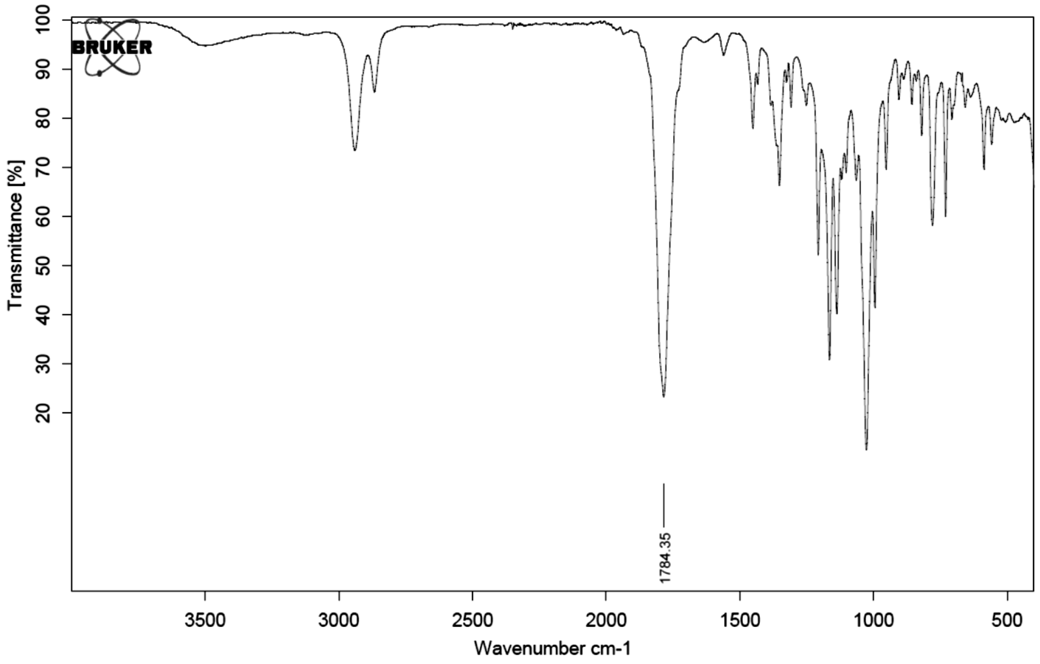




^{1}H NMR ($CDCl_3$)

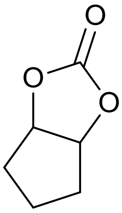


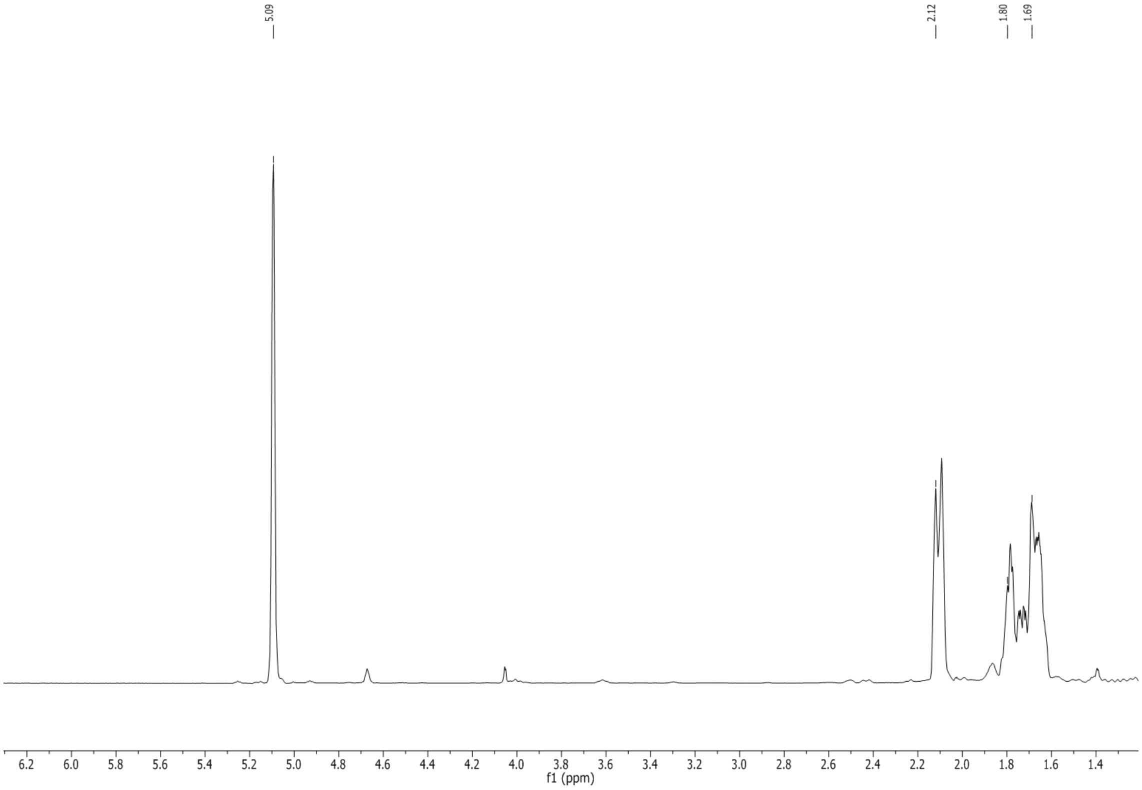
$^{13}C\ \{^{1}H\}$ NMR ($CDCl_3$)



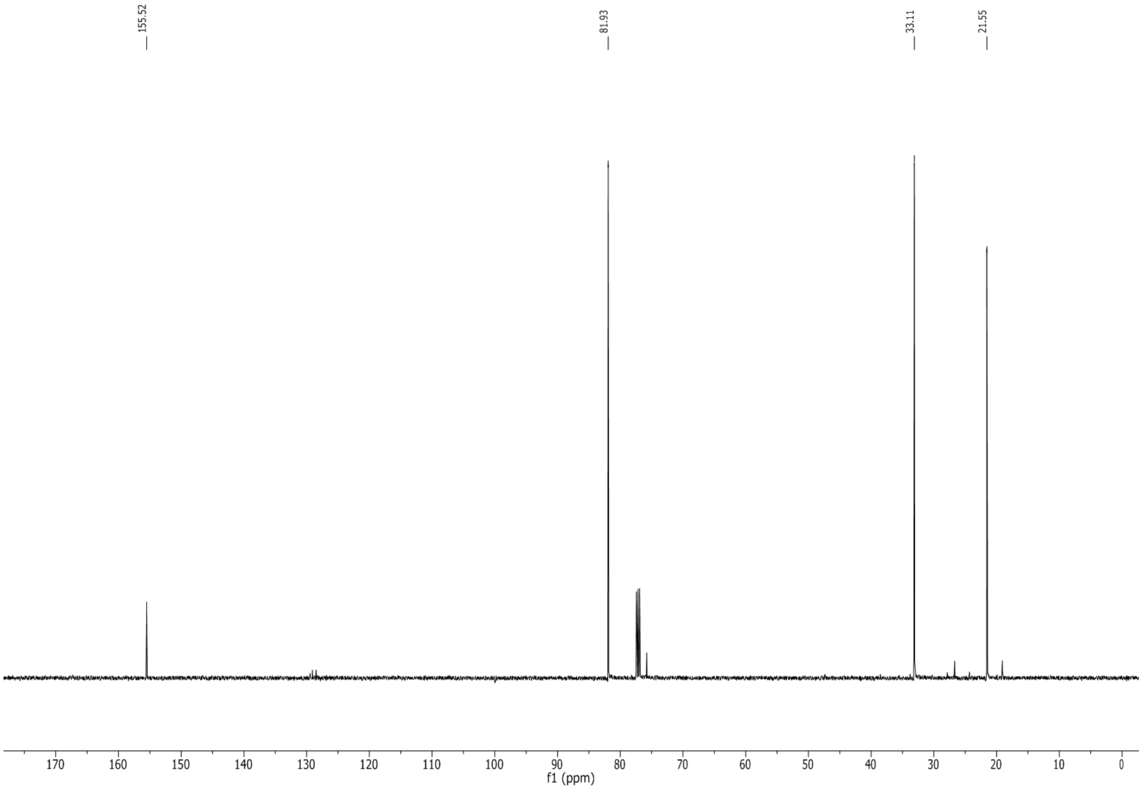
IR (neat)

(**11a**) tetrahydro-3a*H*-cyclopenta[*d*][1,3]dioxol-2-one[10]

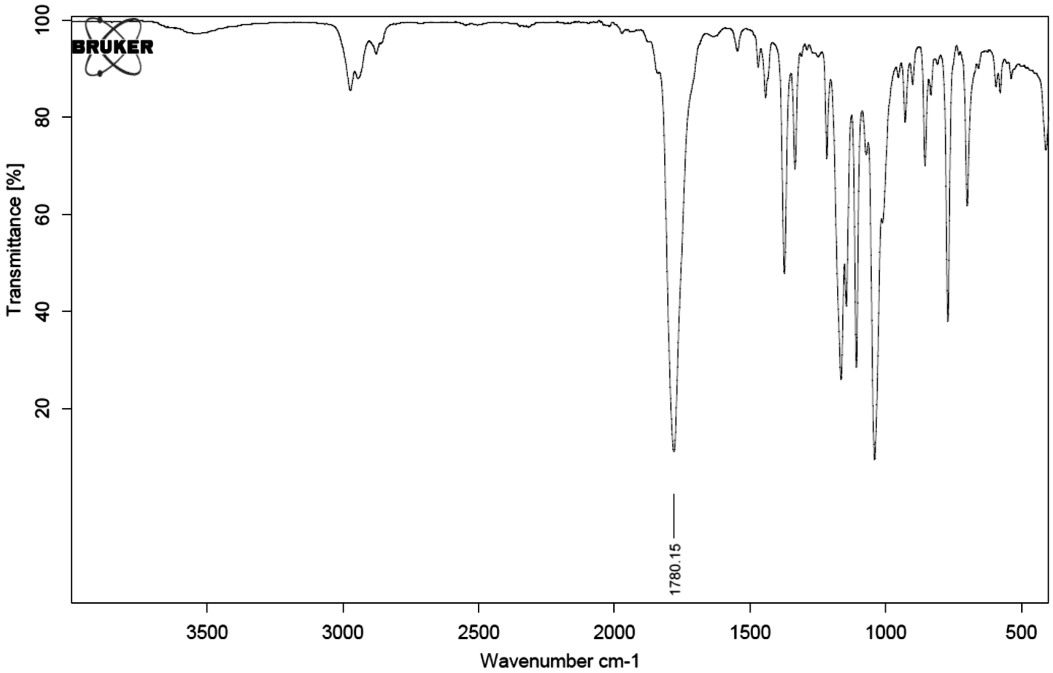




^{1}H NMR ($CDCl_3$)

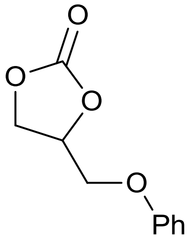


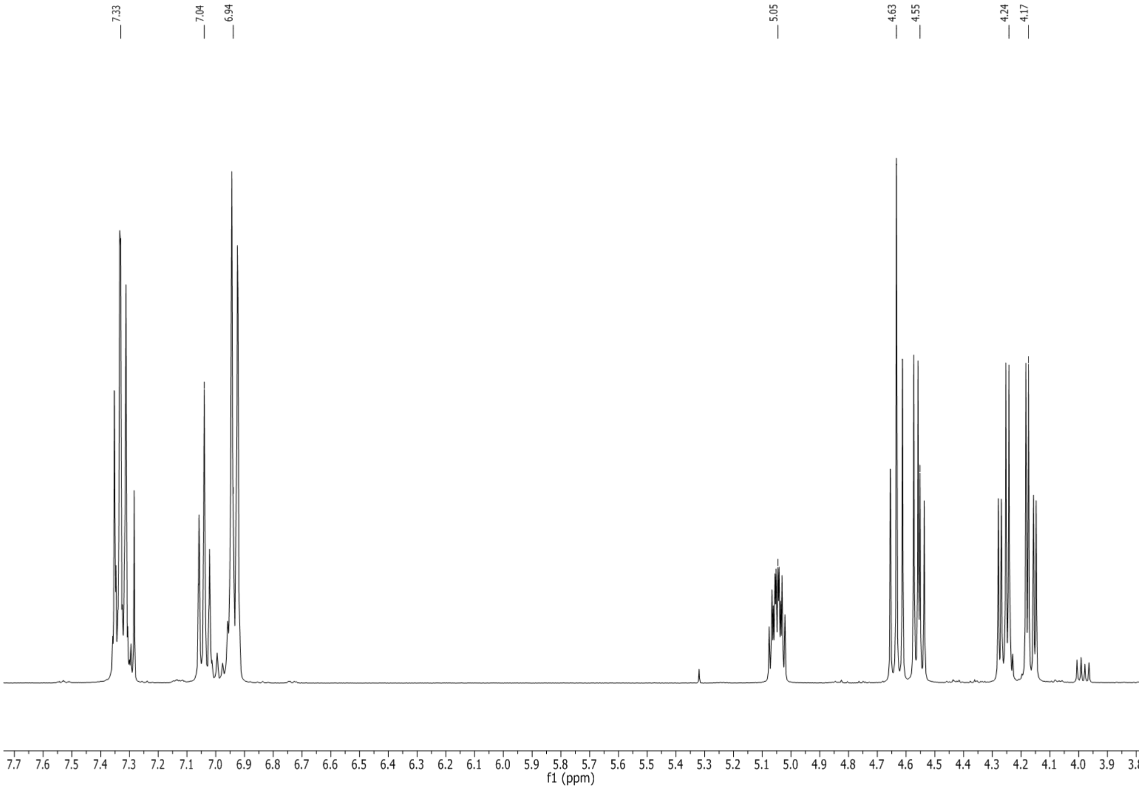
^{13}C {^{1}H} NMR ($CDCl_3$)



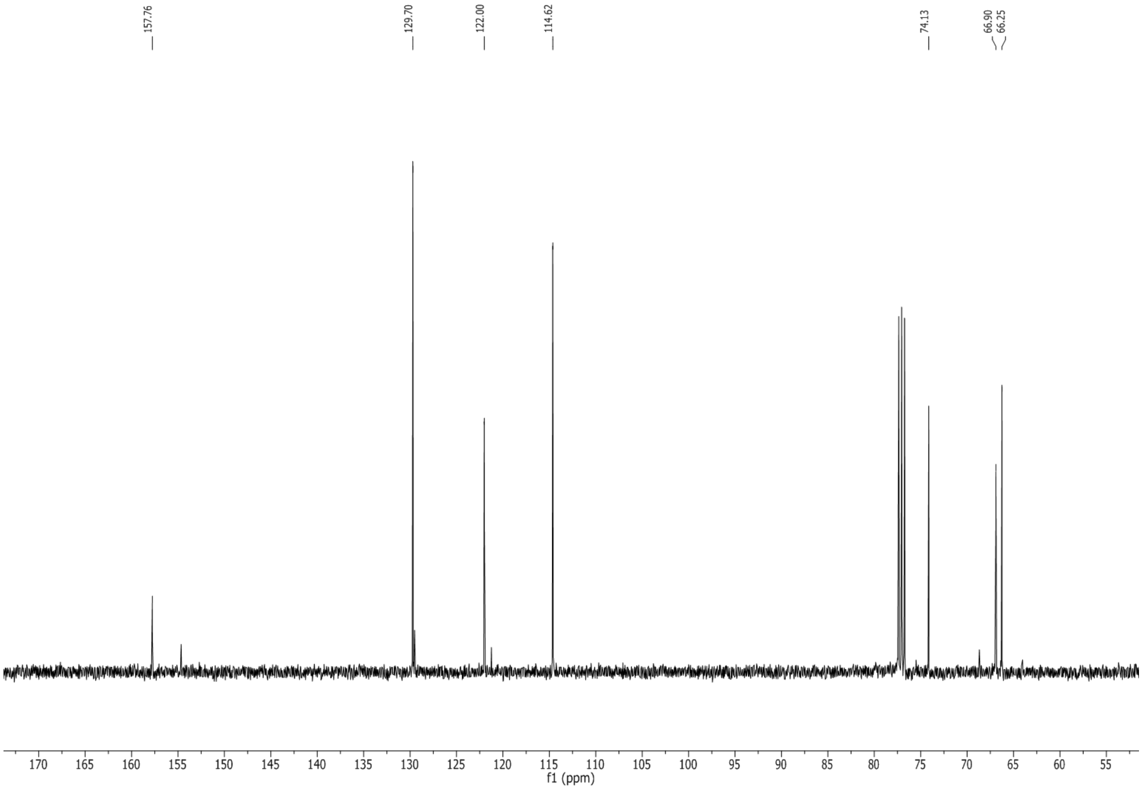
IR (neat)

(**12a**) 4-(phenoxymethyl)-1,3-dioxolan-2-one[11]

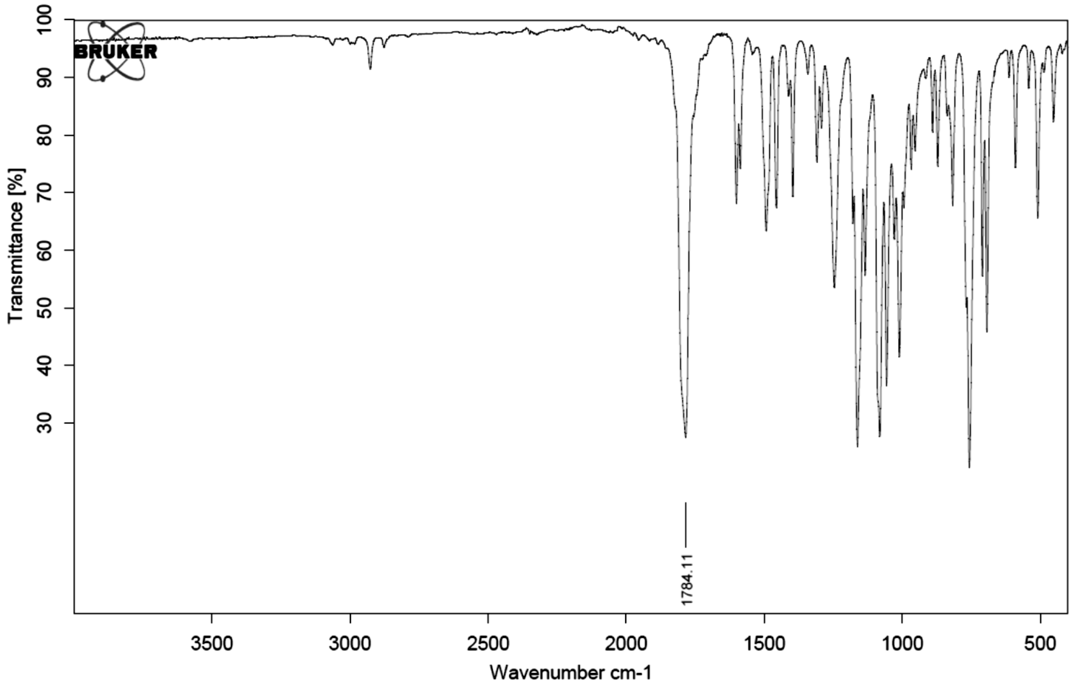




^{1}H NMR (CDCl$_3$)

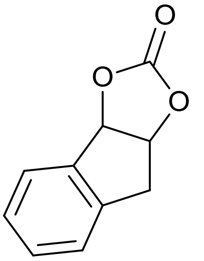


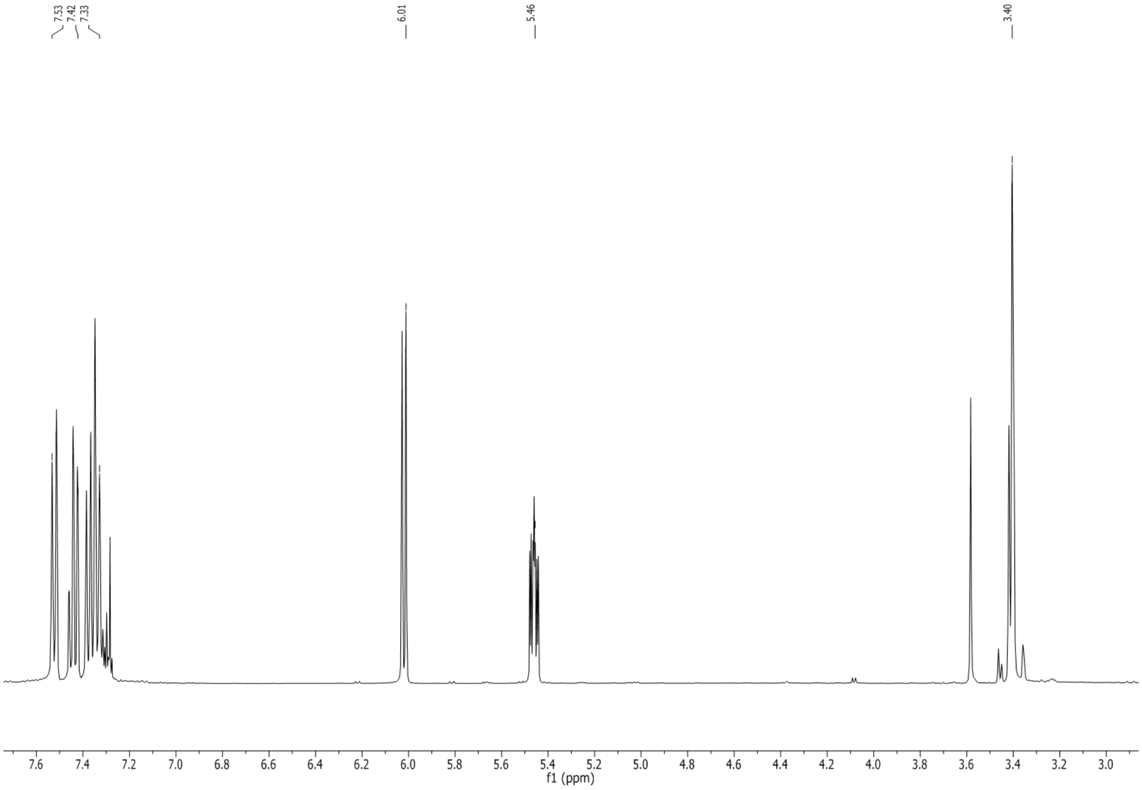
$^{13}C\ \{^{1}H\}$ NMR ($CDCl_3$)



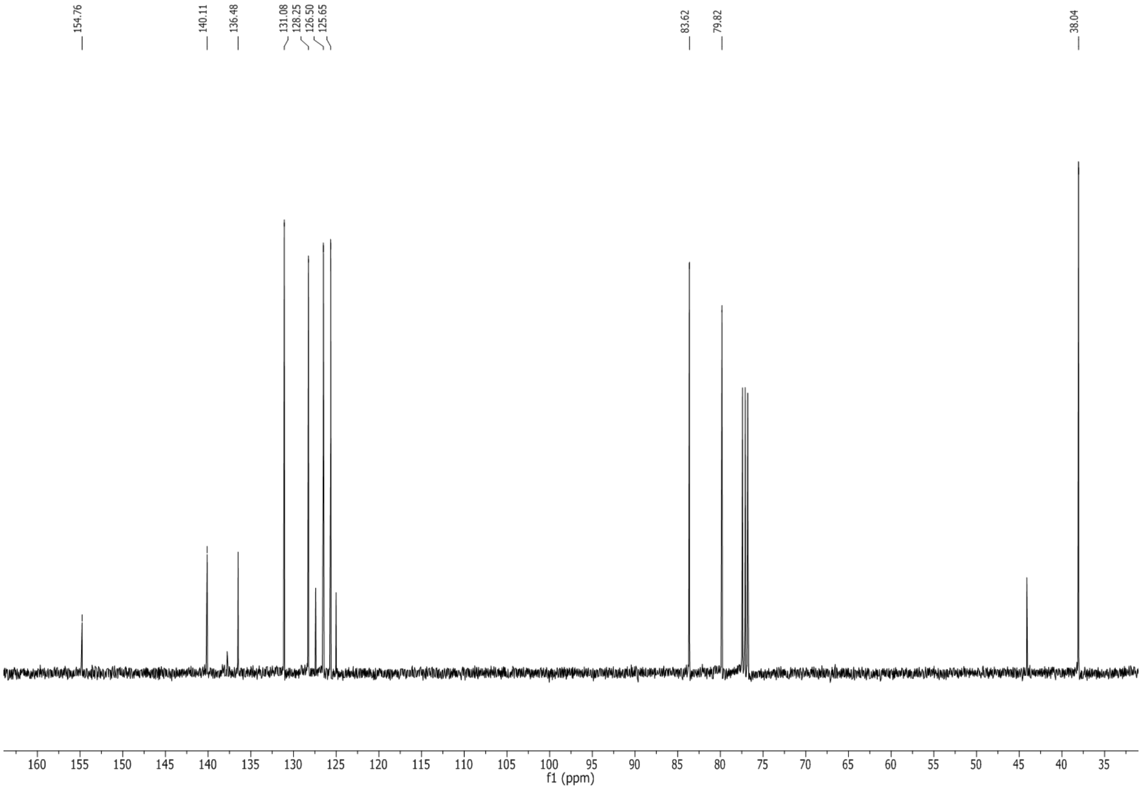
IR (neat)

(13a) 8,8a-dihydro-3a*H*-indeno[1,2-*d*][1,3]dioxol-2-one[9]

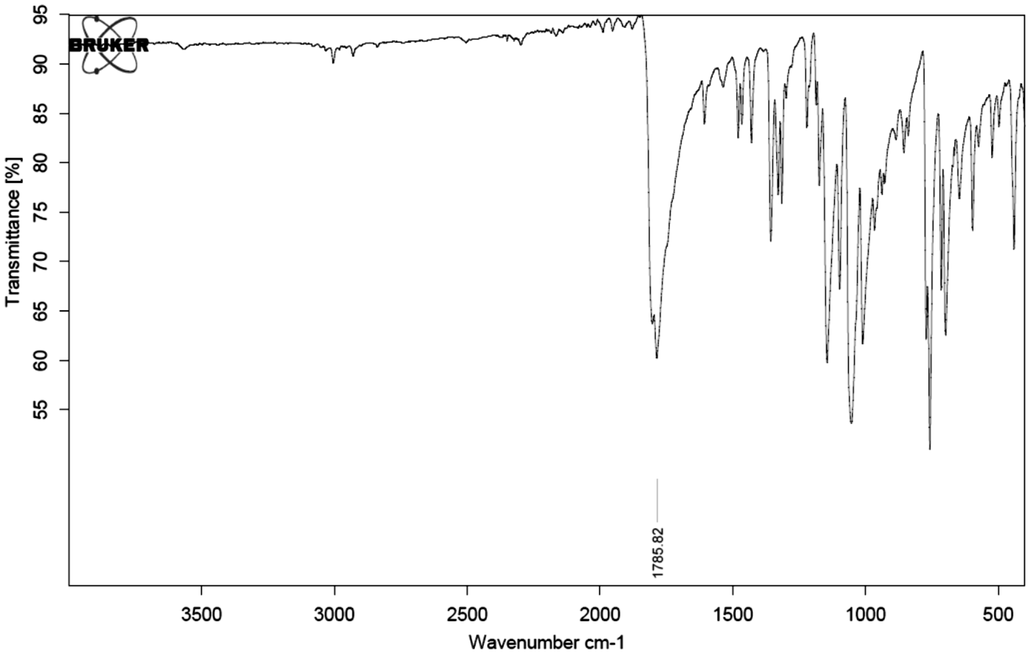




^{1}H NMR ($CDCl_3$) – contains small ketone impurity from starting material.



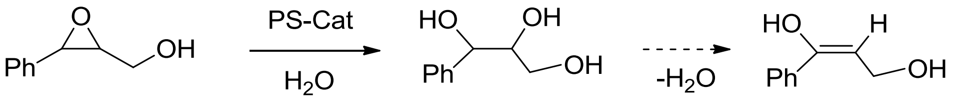
^{13}C {^{1}H} NMR ($CDCl_3$) - contains ketone impurity from starting material

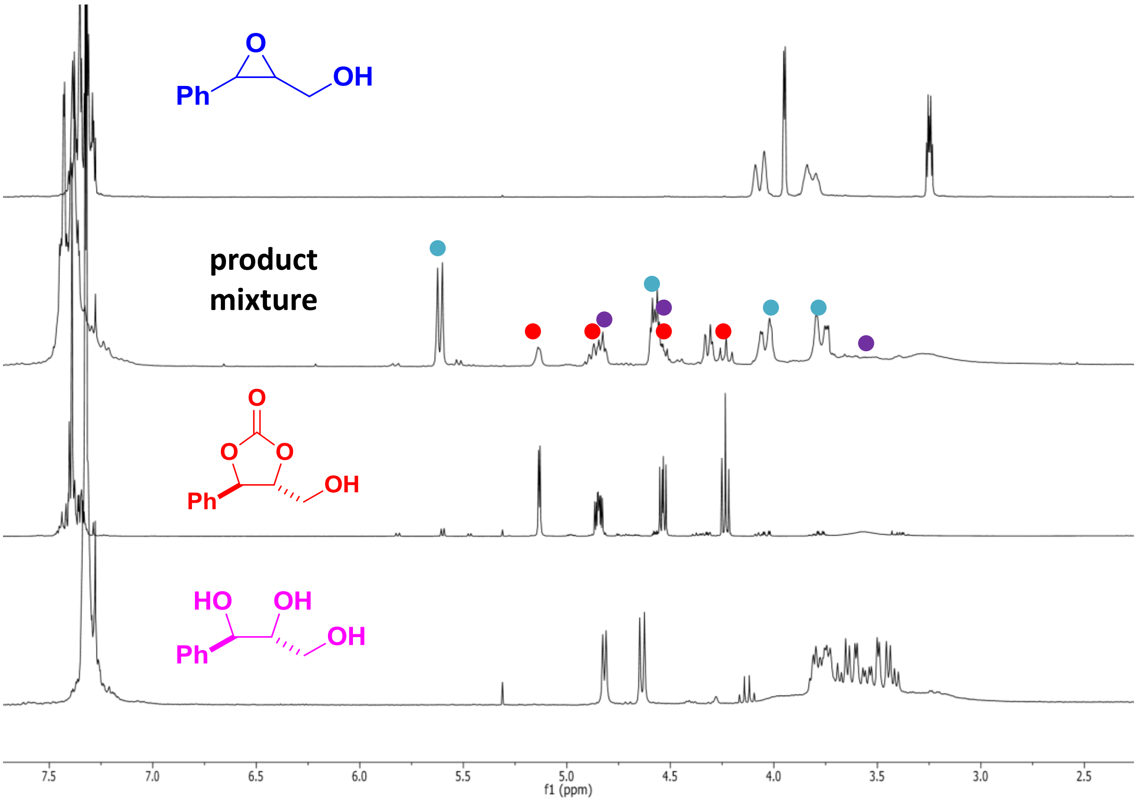


IR (neat)

Attempted synthesis of 14a (Table 3, entry 14):

Reaction of phenyl glycidol substrate:





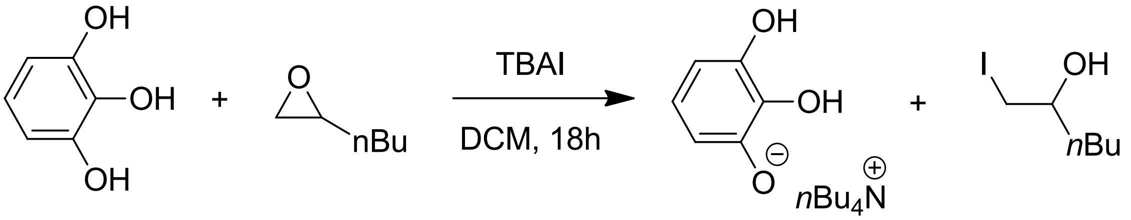
Note that in the product mixture (2nd NMR trace from above in the Figure) small amounts of carbonate product and polyol (triol) were identified. We tentatively assign the peaks of a third component to a dehydrated product arising from the triol derivative as proposed in the scheme above the figure.

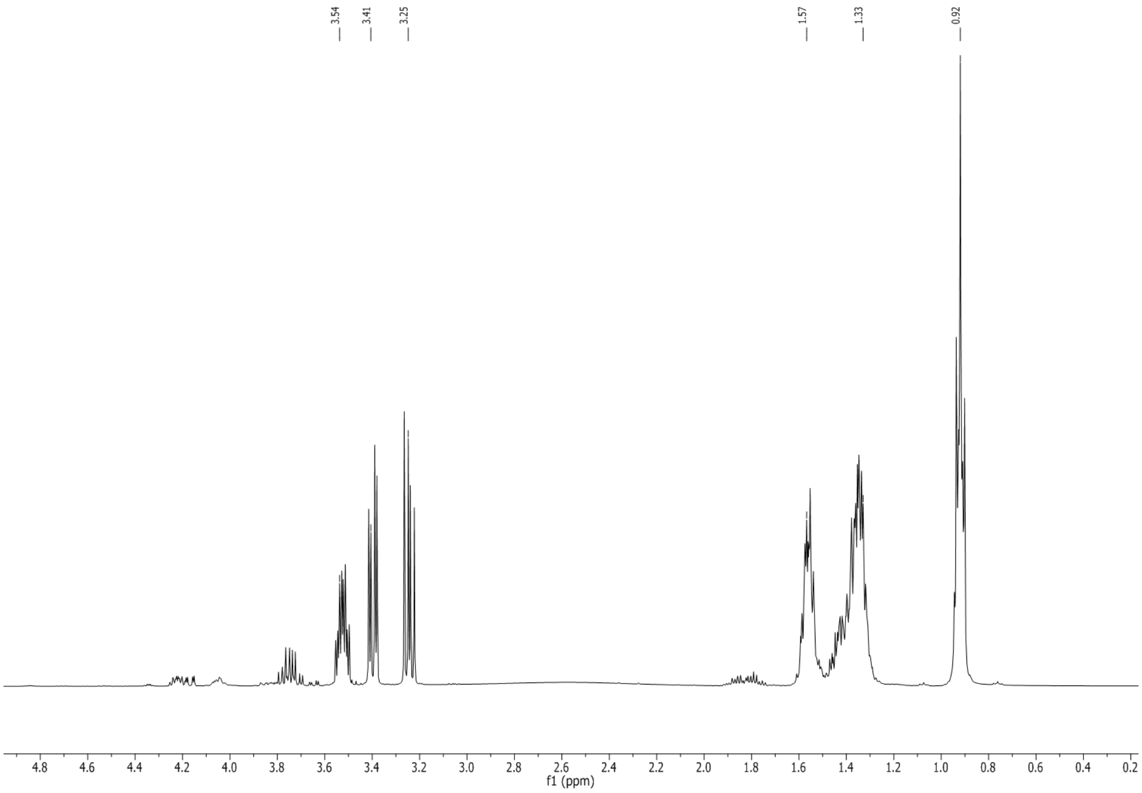
For original data concerning the cyclic carbonate derived from the benzyl glycidol substrate see reference 12:

An authentic sample of the triol was separately made using a previously reported procedure, see reference 13.

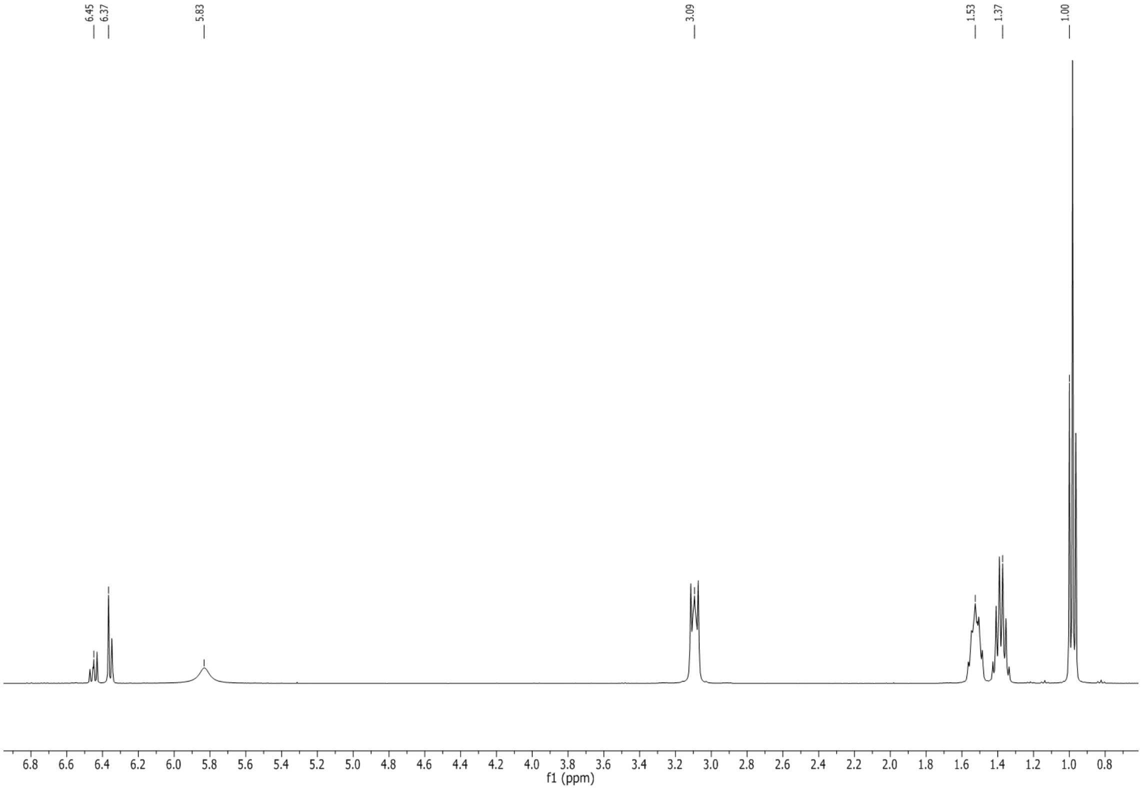
Reaction of pyrogallol, tetrabutylammonium iodide and 1,2-epoxyhexane

The equimolar mixture of pyrogallol, 1,2-epoxyhexane and tetrabutylammonium iodide was stirred for 18 h in sufficient DCM as to dissolve the reaction mixture. Following this, the solvent was removed under vacuum. The residue was suspended in Et_2O and filtered. The products were analysed as the phenolate ammonium salt (solid precipitated from ethereal solution) and the halohydrin (oil after removal of solvent from the filtrate). ^1H NMR ($CDCl_3$) of both products are shown below;





^1H NMR ($CDCl_3$) of halohydrin species obtained.



^{1}H NMR ($CDCl_3$) of phenolate ammonium salt obtained

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