

Efficient synthesis of cyclic carbonates by the CoI₂/ligand catalyzed reactions of carbon dioxide and epoxides

Sergey E. Lyubimov, Polina V. Cherkasova and Ramil Z. Arifulin

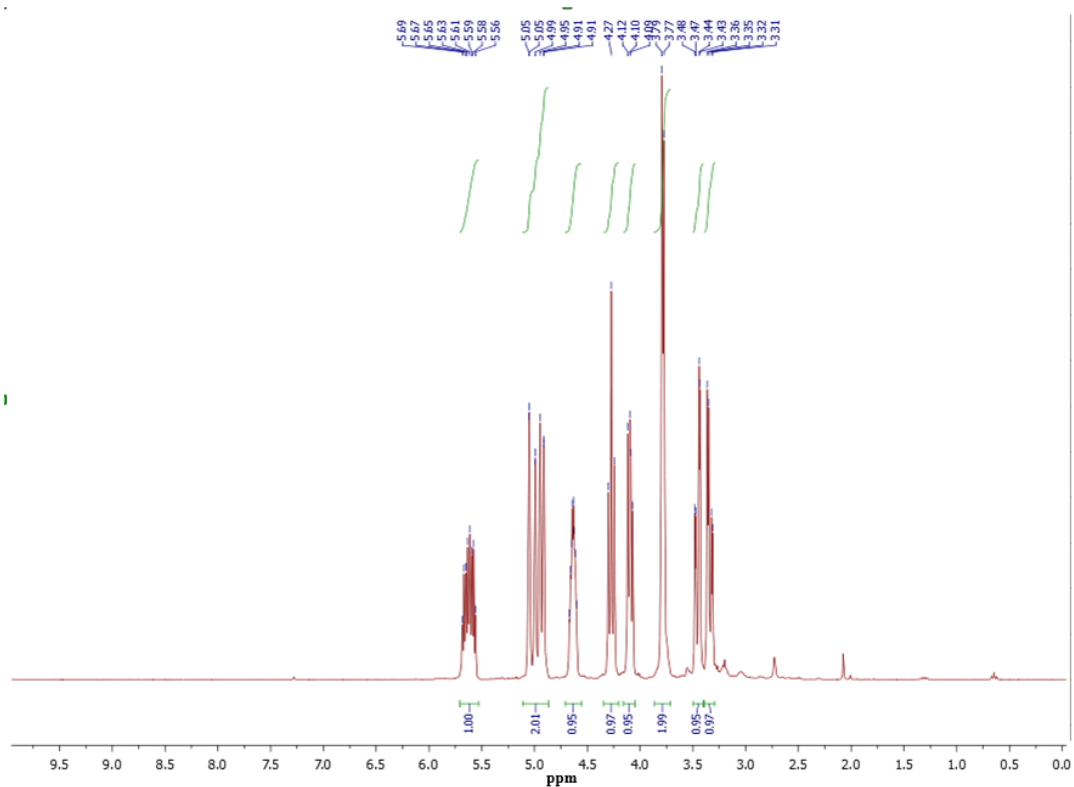
¹H NMR spectra were recorded on a Bruker Avance 300 instrument (300.0 MHz). The chemical shifts were referred to the signals of residual protons of the solvent (CDCl₃). Amines and phosphines **1-5**, oxiranes **6a-f**, **8**, **10** and CoI₂ are commercially available compounds (Aldrich).

Synthesis of carbonates 7a—f, 9 and 11 (general procedure).

Cobalt diiodide (0.06 mmol) and the corresponding ligand (0.12 mmol) were placed in a 10 ml autoclave, and oxirane (6 mmol) was added. Carbon dioxide was supplied to the autoclave at room temperature, and the autoclave was heated to the specified temperature in a thermostat. Once the reaction was completed, the autoclave was cooled to 5 °C, and CO₂ was slowly released. The residue was analyzed by NMR. Spectral characteristics of carbonates 7a—f, 9 and 11 correspond to the published data [W. W. Yu, X. G. Meng, Z. Y. Gan, W. Li, Y. L. Zhang and J. Zhou, *Catal. Sci. Technol.*, 2024, **14**, 6215; <https://doi.org/10.1039/D4CY00639A>]. The yields were determined after dissolving the carbonates in acetonitrile, passing the solutions through a thin pad of silica gel and solvent evaporation.

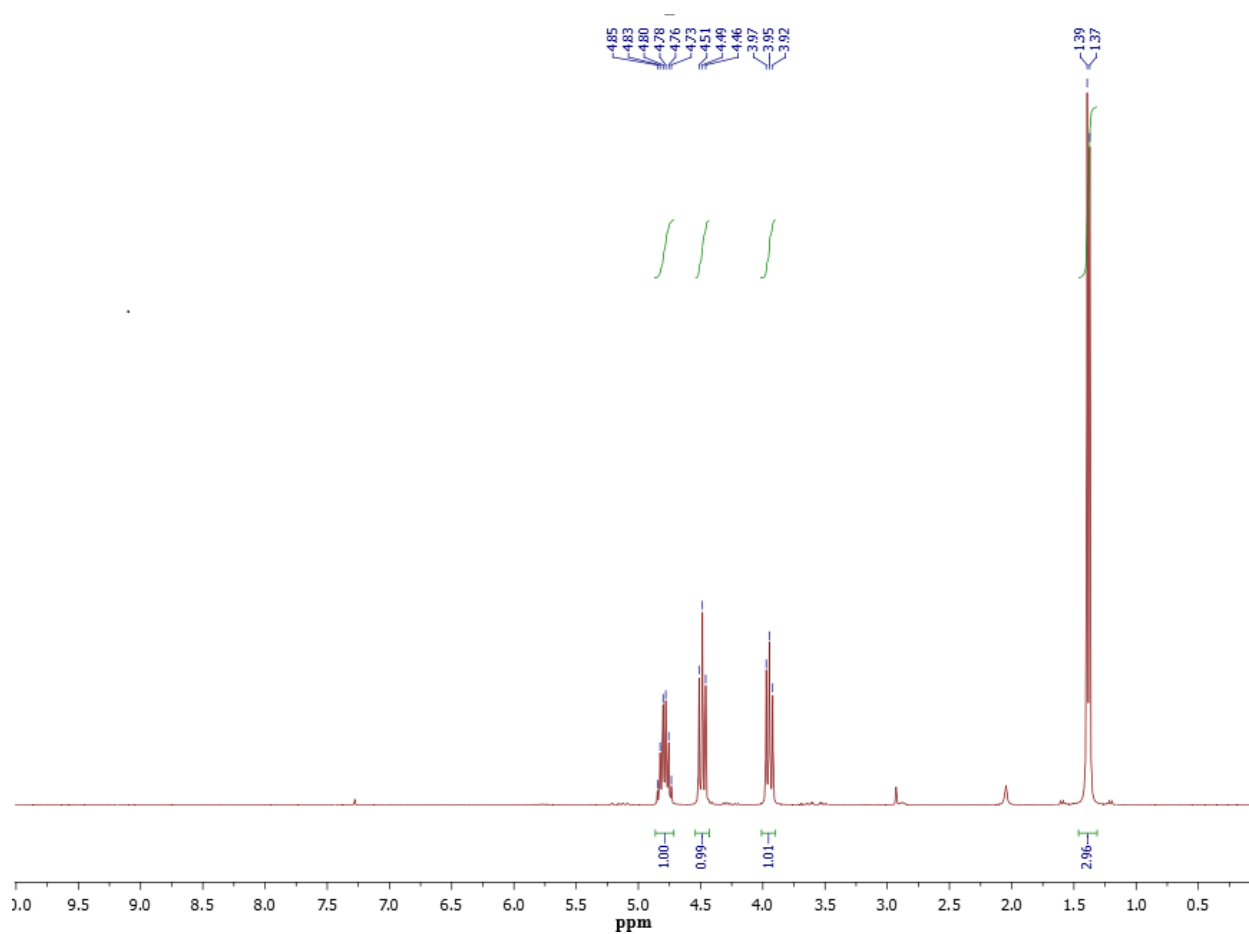
4-[(2-Propen-1-yloxy)methyl]-1,3-dioxolan-2-one (**7a**)

(300 MHz, CDCl₃): δ 3.34 (dd, J = 10.2, 3.6 Hz, 1H, O-CH₂), 3.46 (dd, J = 11.3, 2.4 Hz, 1H, O-CH₂), 3.78 (d, J = 5.4 Hz, 2H, O-CH₂ Vinyl), 4.09 (dd, J = 8.4, 6 Hz, 1H, COO-CH₂), 4.27 (t, J = 8.4 Hz, 1H, COO-CH₂), 4.60-4.67 (m, 1H, COO-CH), 4.97 (ddd, J = 27, 17.4, 1.5 Hz, 2H, CH₂-Vinyl), 5.56-5.69 (m, 1H, CH-Vinyl). Yield 97%.



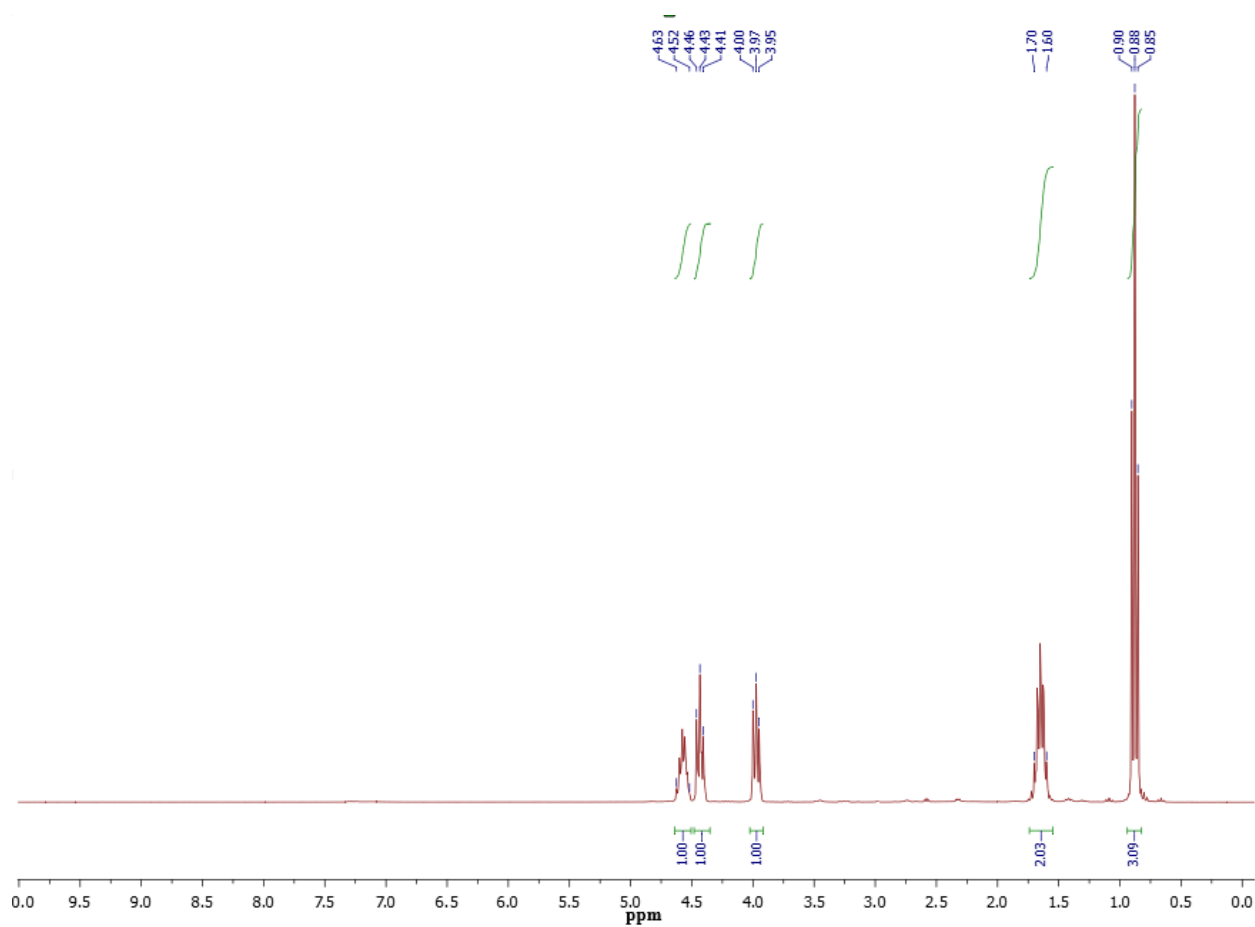
4-Methyl-1,3-dioxolan-2-one (**7b**)

(300 MHz, CDCl₃): δ 1.38 (d, J = 6.3 Hz, 3H, CH₃); 3.95 (t, J = 7.5 Hz, 1H, COO-CH₂), 4.49 (t, J = 8.4 Hz, 1H, COO-CH₂), 4.73–4.85 (m, 1H, CHCH₃). Yield 96%.



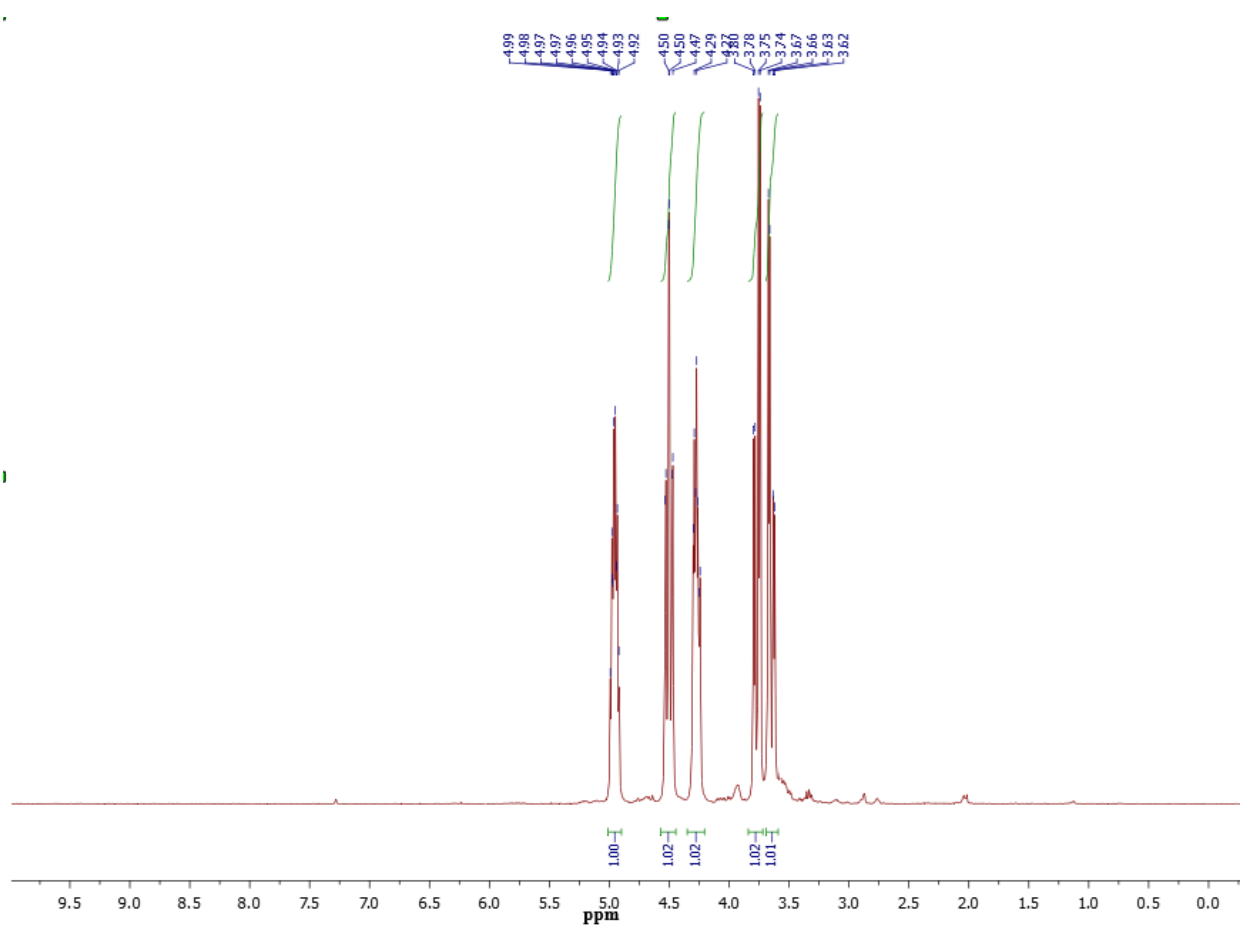
4-Ethyl-1,3-dioxolan-2-one (7c)

(300 MHz, CDCl_3): δ 0.88 (t, $J = 7.5$ Hz, 3H, CH_3), 1.60–1.70 (m, 2H, CH_2CH_3), 3.97 (t, $J = 8.4$ Hz, 1H, COO-CH_2), 4.43 (t, $J = 8.4$ Hz, 1H, COO-CH_2), 4.52–4.63 (m, 1H, CH). Yield 97%.



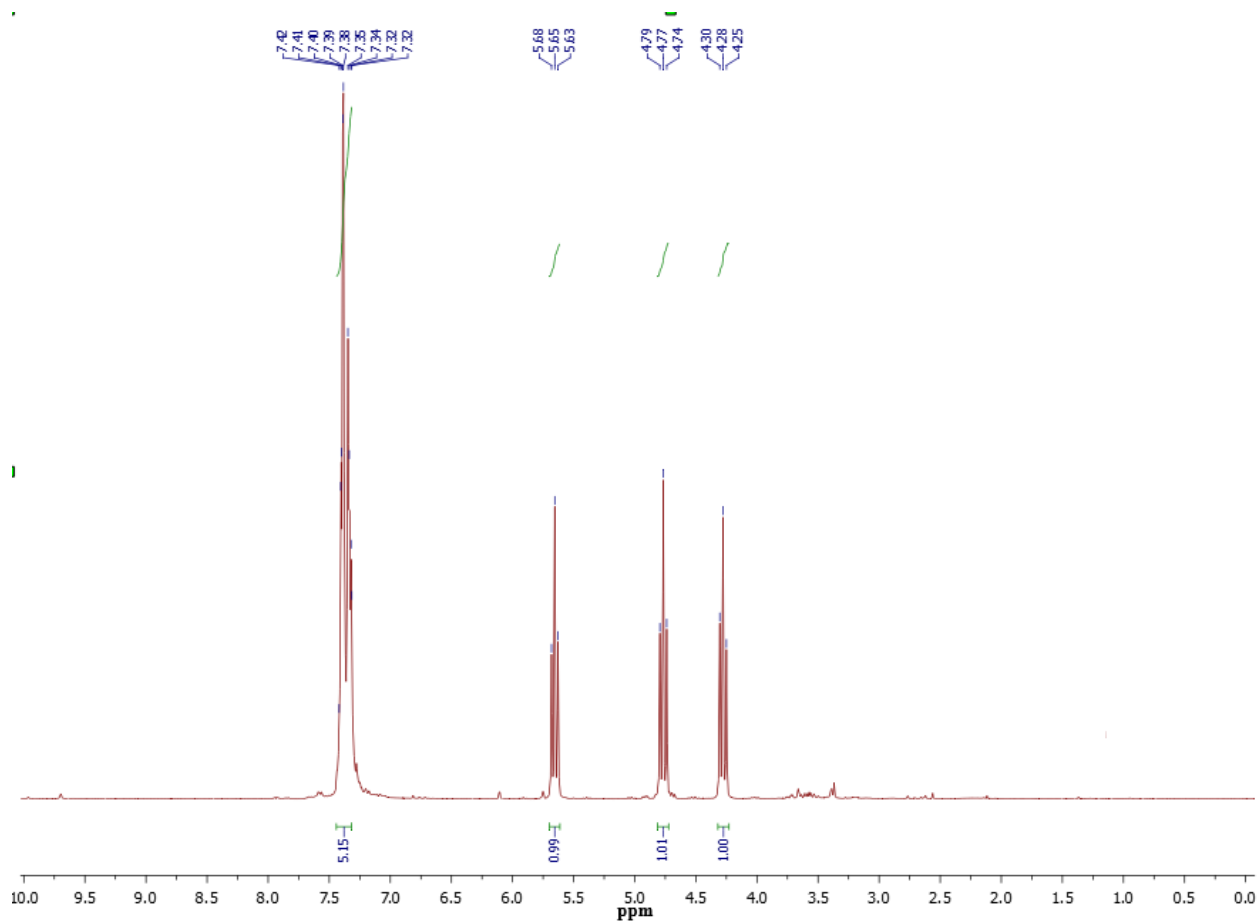
4-Chloromethyl-1,3-dioxolan-2-one (**7d**)

(300 MHz, CDCl₃): δ 3.65 (dd, J = 12.6, 3.6 Hz, 1H, ClCH₂), 3.77 (dd, J = 12.3, 3.9 Hz, 1H, ClCH₂), 4.24-4.30 (m, 1H, COO-CH₂), 4.50 (td, J = 8.7, 1.5 Hz, 1H, COO-CH₂), 4.92-4.99 (m, 1H, CH). Yield 97%.



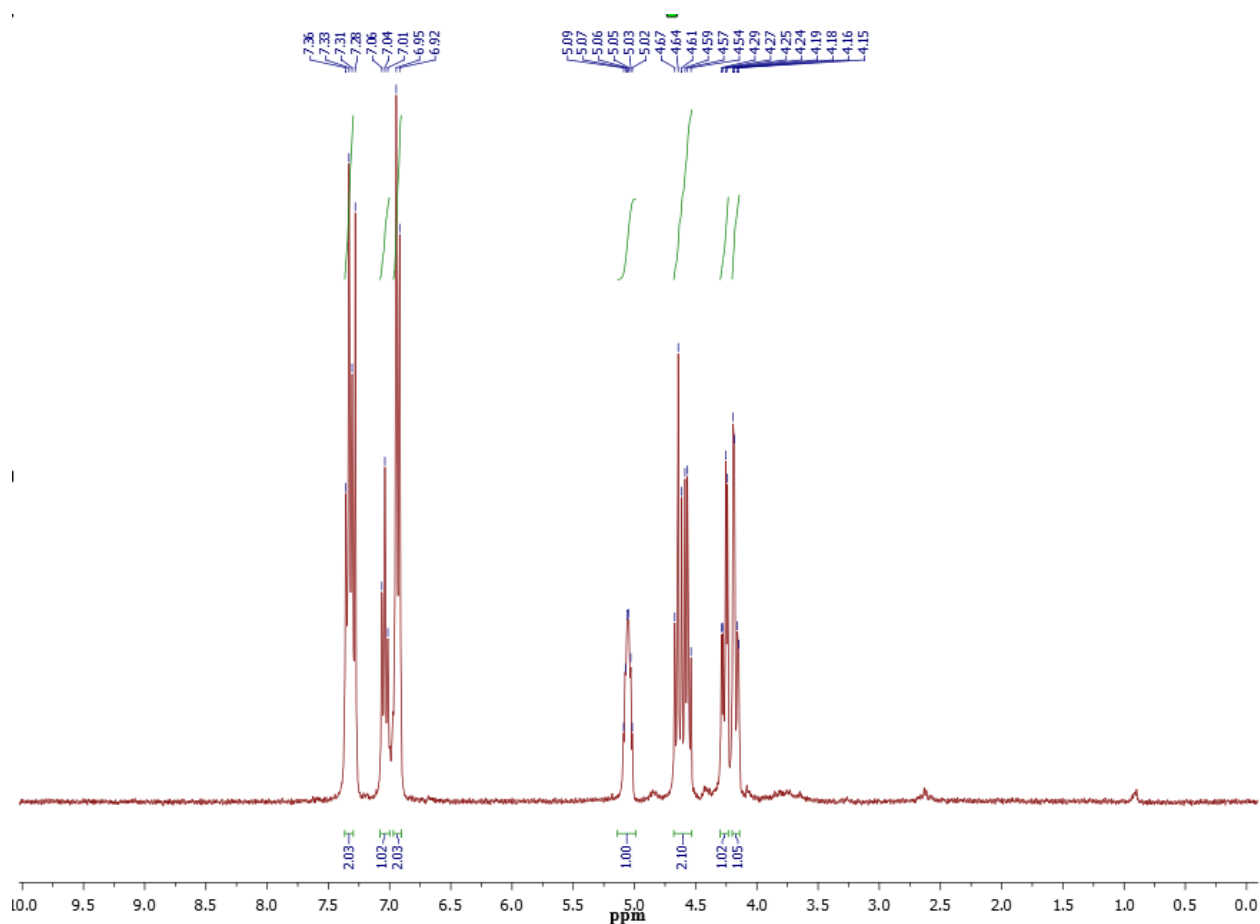
4-Phenyl-1,3-dioxolan-2-one (**7e**)

(300 MHz, CDCl₃): δ 4.28 (t, J = 7.8 Hz, 1H, CH₂), 4.77 (t, J = 8.4 Hz, 1H, CH₂), 5.65 (t, J = 7.8 Hz, 1H, CH), 7.32–7.42 (m, 5H, Ph). Yield 96%.



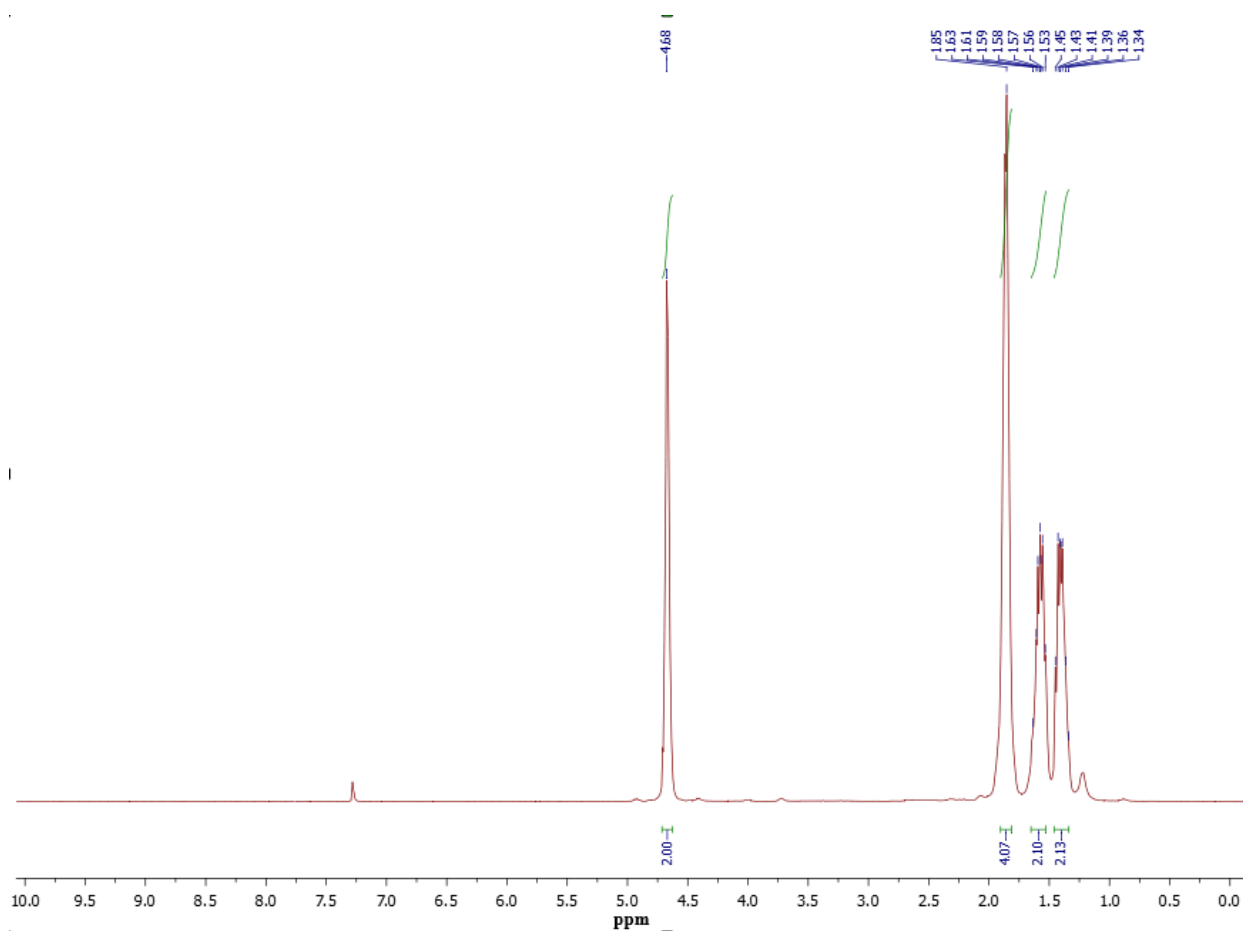
4-Phenoxymethyl-1,3-dioxolan-2-one (**7f**)

(300 MHz, CDCl₃): δ 4.17 (dd, J = 10.5, 3.3 Hz, 1H, CH₂), 4.26 (dd, J = 10.5, 4.2 Hz, 1H, CH₂), 4.54-4.67 (m, 2H, PhOCH₂), 5.02-5.09 (m, 1H, CH), 6.94 (d, J = 8.4 Hz, 2H, Ph), 7.04 (t, J = 7.5 Hz, 1H, Ph), 7.33 (t, J = 7.8 Hz, 2H, Ph). Yield 96%.



Hexahydrobenzo[d][1,3]dioxolan-2-one (9)

(300 MHz, CDCl₃): δ 1.34–1.45 (m, 2H, CH₂), 1.53–1.63 (m, 2H, CH₂), 1.85 (s, 4H, 2CH₂), 4.68 (s, 2H, 2CH). Yield 97%.



4,4'-([Propane-2,2-diylbis(4,1-phenylene)]bis(oxy))bis(methylene))bis(1,3-dioxolan-2-one)
(11)

(300 MHz, CDCl₃): δ 1.64 (s, 6H, 2CH₃), 4.09 (dd, J = 10.8, 3.6 Hz, 2H, 2CH₂), 4.22 (dd, J = 10.8, 3.3 Hz, 2H, 2CH₂), 4.49 (t, J = 6.0 Hz, 2H, 2CH₂), 4.58 (t, J = 8.4 Hz, 2H, 2CH₂), 4.99-5.04 (m, 2H, 2CH), 6.82 (d, J = 8.4 Hz, 4H, Ph), 7.15 (d, J = 8.7 Hz, 4H, Ph). Yield 96%.

