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Electrochemical oxidation of furans into 2,5-dimethoxy-2,5-dihydrofurans

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Synthesis. All synthetic manipulations were carried out in air. Solvents were purchased from commercial sources and purified by distilling from conventional drying agents under an argon atmosphere prior to use. Sodium methoxide was obtained from dissolving sodium metal in methanol, NH_4Br (Sigma Aldrich) was used without further purification. All reactions were held in electrochemical reactor Electrasyn (IKA) with Pt-Pt electrode pair. The reaction mass was cooled down to -20°C with saturated NaCl aqueous solution and liquid nitrogen.

General procedure. Furan derivative **1a-d** (5 mmol) was dissolved in methanol (10 ml) containing MeONa (3 mmol) and NH_4Br (0.08 mmol), and this was placed in a glass undivided cell. The cell was connected to Electrasyn system and flushed with argon. The cell was cooled down to specified temperature, and the electrolysis was started with current strength of 0.1 A (j = 40 mA cm^{-2}) for 2 hours (Q ~ 1.86 F mol^{-1}). After the reaction was completed, the mixture was transferred into a separation funnel and the product was extracted with hexane for 3-5 times. The hexane phase was separated and concentrated *in vacuo*. The resulting products were isolated as colorless or yellowish oils.

cis/trans-2,5-Dimethoxy-2-methyl-2,5-dihydrofuran ***2a***. Synthesized by general procedure from 2-methylfuran **1a**. Colorless oil. Yield: 360 mg (50%).^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.92 (m, 2H, H-4, H-3), 5.47 (s, 1H, H-5), 3.49 (s, 3H, OMe), 3.19 (s, 3H, OMe), 1.50 (s, 3H, Me); ^{1}H NMR (minor isomer, $CDCl_3$) δ: 6.0 (m, 2H, H-4, H-3), 5.76 (s, 1H, H-5), 3.41 (s, 3H, OMe), 3.10 (s, 3H, OMe), 1.58 (s, 3H, Me). MS (EI, 70 eV), *m/z* (%): 157 (M-H$^-$, 60), 83 (100), 115 (40), 97 (35).

cis/trans-2,5-Dimethoxy-2,5-dimethyl-2,5-dihydrofuran ***2b*****.** Synthesized by general procedure from 2,5-dimethylfuran **1b**. Colorless oil. Yield: 395 mg (50%).^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.88 (s, 2H, H-3, H-4), 3.2 (s, 6H, OMe), 1.57 (s, 6H, Me); ^{1}H NMR (minor isomer, $CDCl_3$) δ: 5.87 (s, 2H, H-3, H-4), 3.30 (s, 6H, OMe), 1.57 (s, 6H, Me). MS (EI, 70 eV), *m/z* (%): 143 (M-H$^-$, 47), 111 (100), 127 (90), 95 (68).

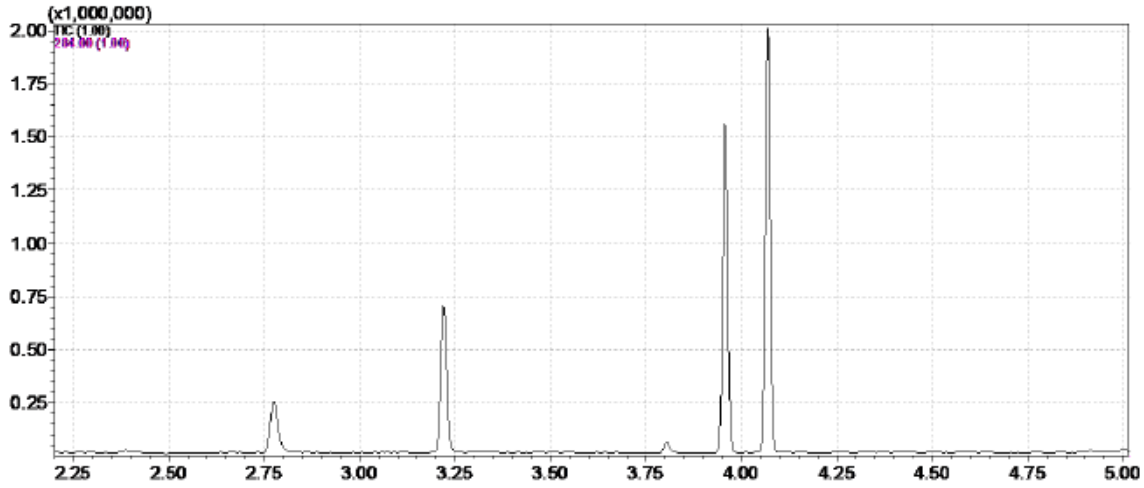
cis/trans-(2,5-Dimethoxy-2,5-dihydrofuran-2-yl)methanol ***2c*****.** Synthesized by general procedure from 2-(hydroxymethyl)furan **1c**. Yellowish oil. Yield: 400 mg (60%).^{1}H NMR (400 MHz, $CDCl_3$) *δ:* 5.83 (m, 1H, H-4), 5.66 (m, 1H, H-3), 5.13 (br.s., 1H, H-5), 4.47 (m, 1H, CH_2OH), 4.05 (m, 1H, CH_2OH), 3.05 (s, 3H, OMe). 2.75 (s, 3H, OMe); ^{1}H NMR (minor isomer, $CDCl_3$) *δ:* 5.86 (m, 1H, H-4), 5.75 (m, 1H, H-3), 5.48 (br.s., 1H, H-5), 4.87 (m, 1H, CH_2OH), 4.44 (m, 1H, CH_2OH), 2.97 (s, 3H, OMe), 2.69 (s, 3H, OMe). MS (EI, 70 eV), *m/z* (%): 159 ($M-H^-$, 10), 45 (100), 113 (73), 81 (29).

cis/trans-2,5-Dimethoxy-2,5-dihydrofuran ***2d.*** Synthesized by general procedure from furan **1d**. Colorless oil. Yield: 293 mg (45%).^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 6.06 (s, 2H, H-4, H-3), 5.89 (s, 1H, H-5), 3.39 (s, 3H, OMe); ^{1}H NMR (minor isomer, $CDCl_3$) *δ*: 6.05 (s, 2H, H-4, H-3), 5.61 (s, 1H, H-5), 3.41 (s, 3H, OMe). MS (EI, 70 eV), *m/z* (%): 129 ($M-H^-$, 35), 113 (100), 101 (60), 43 (70).

NMR spectroscopy. NMR spectra were collected with Varian Inova 400MHz spectrometer. All NMR data were obtained using $CDCl_3$ solutions. Chemical shifts (*δ*, ppm) are referred to tetramethylsilane (TMS) as internal standard. In all cases an inseparable mixture of isomers was analysed.

GC-MS. The GC-MS analysis of reaction mixtures was carried out by Shimadzu GCMS-QP2020 Gas Chromatograph Mass Spectrometer with SH-RTx-5MS column (30 m × 0.25 mm i.d. × 0.25 µm), electron (EI) ionization method and single quadrupole mass-analyzer (positive ions). 1 µl of compounds solution in acetonitrile (99.9+% HPLC gradient grade, Chem-Lab) were injected. General MS parameters were: source temperature 200 °C, interface temperature 250 °C, scan range 33–650 amu. The operating conditions were as follows: injection temperature 250 °C, helium (He 99.9999%) as the carrier gas, column flow rate of 1.01 mL/min and split ratio of 1:10; from 40 °C (1 min) to 290 °C at 30 °C/min, with a final holding for 5 min at 290 °C.

Supplementary figures.



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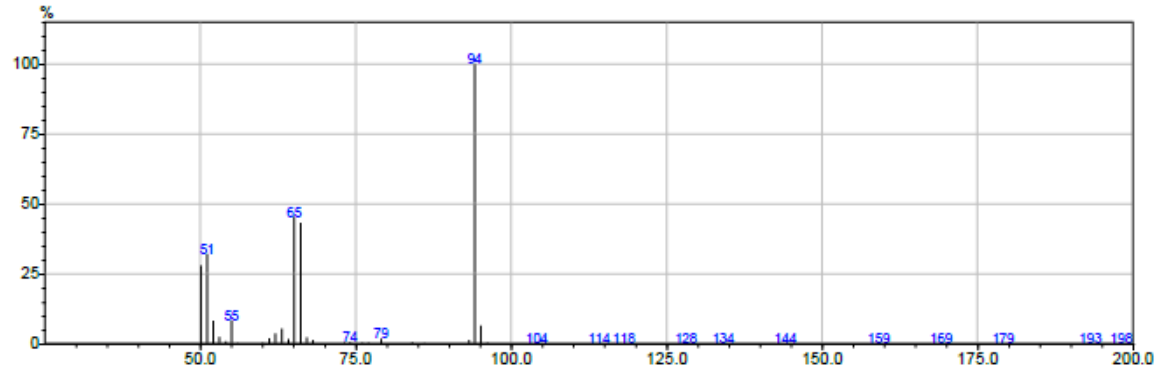

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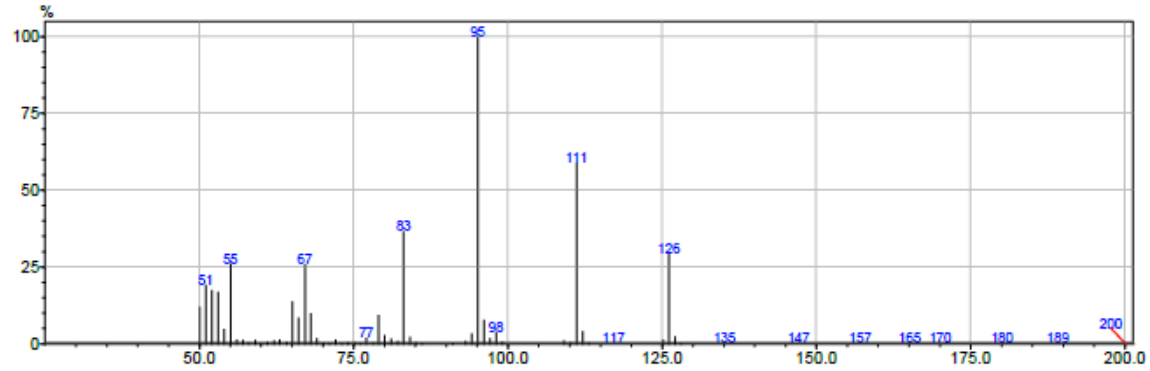

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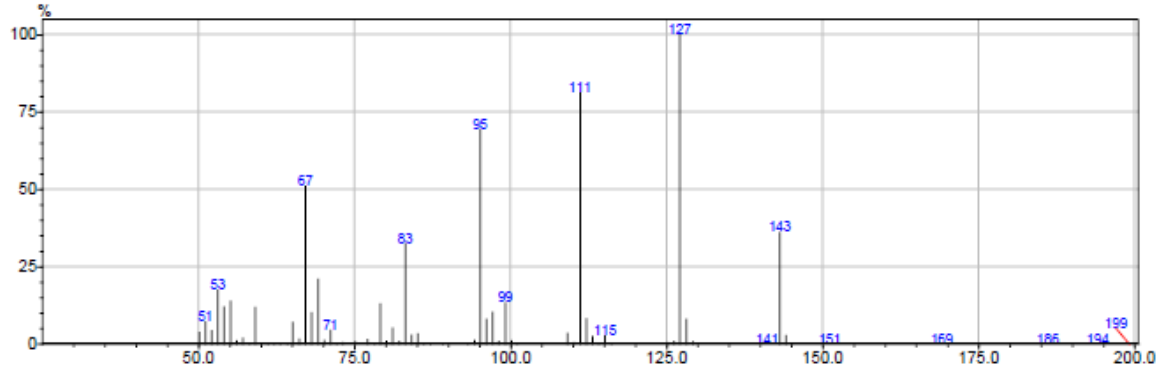

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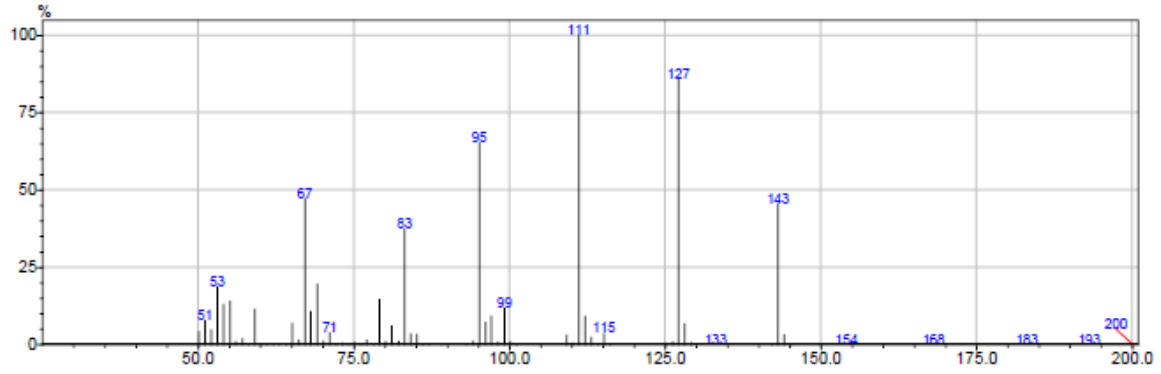
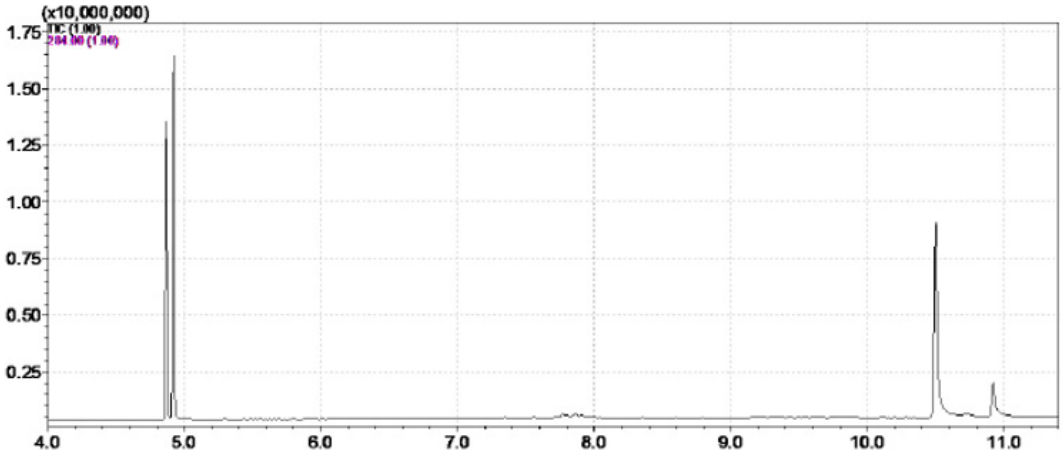


Figure S1. Gas chromatogram and mass spectra of selected peaks of reaction mixture of **2a**.



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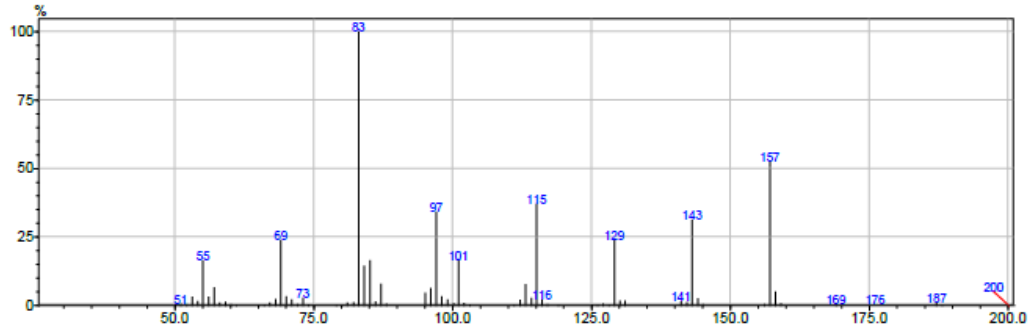

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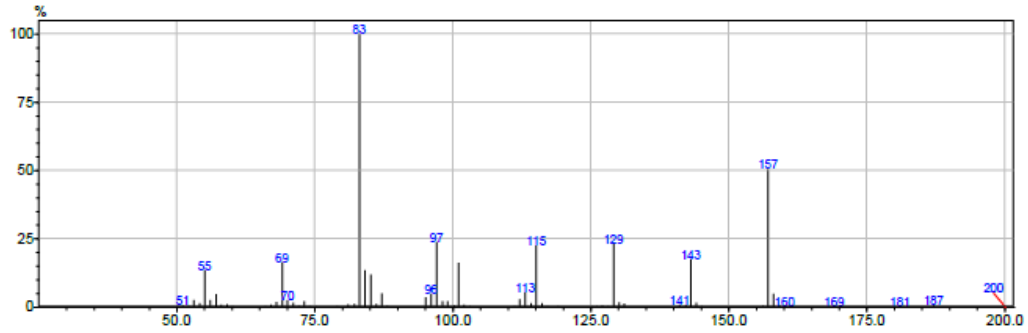

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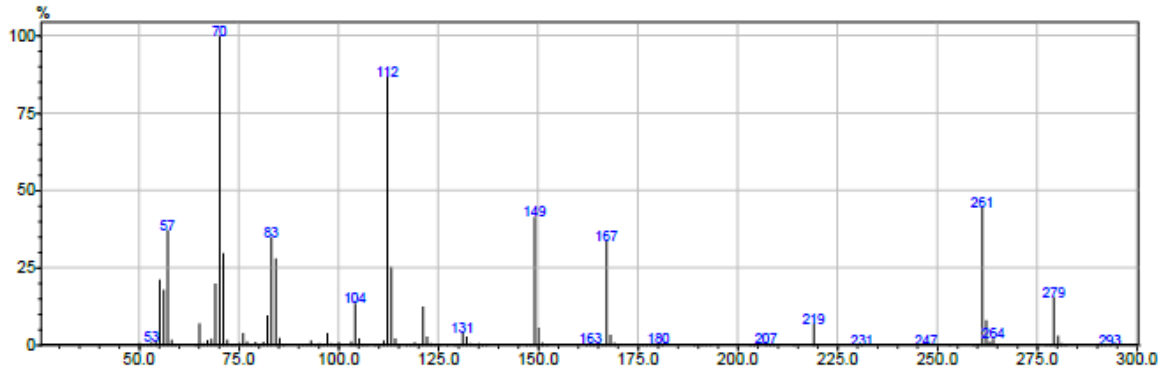

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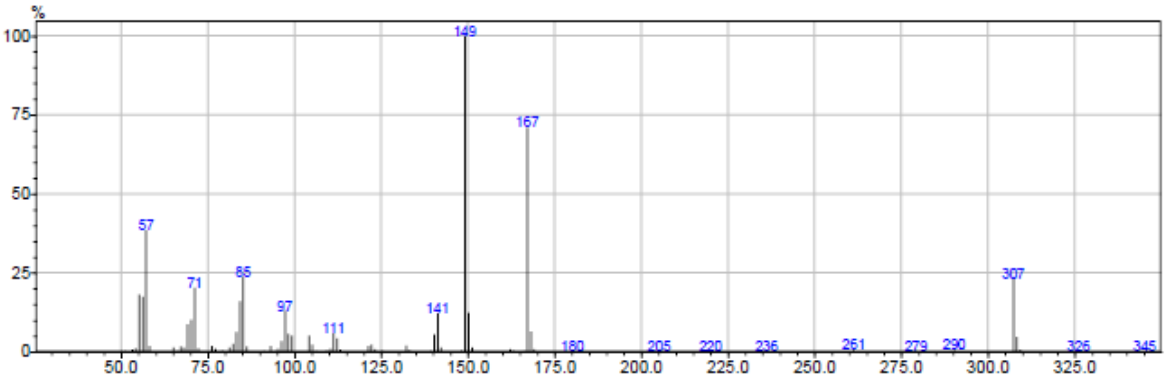
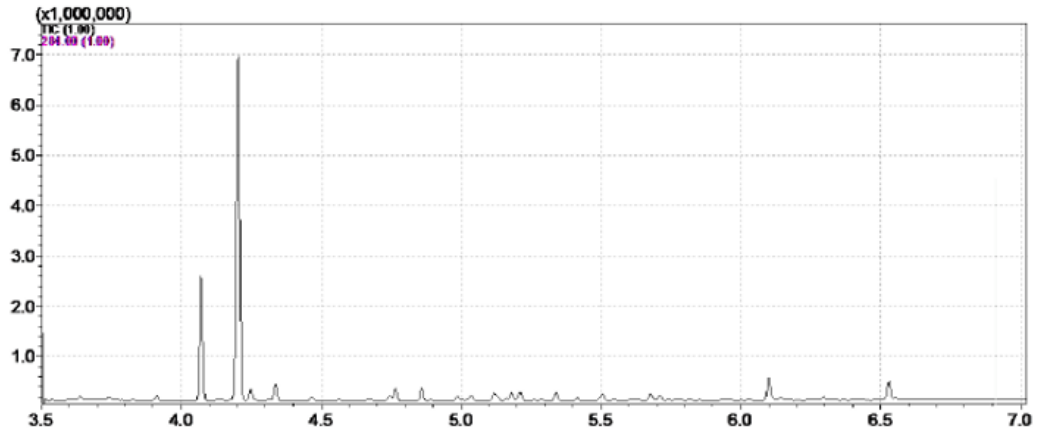


Figure S2. Gas chromatogram and mass spectra of selected peaks of reaction mixture of **2b**.



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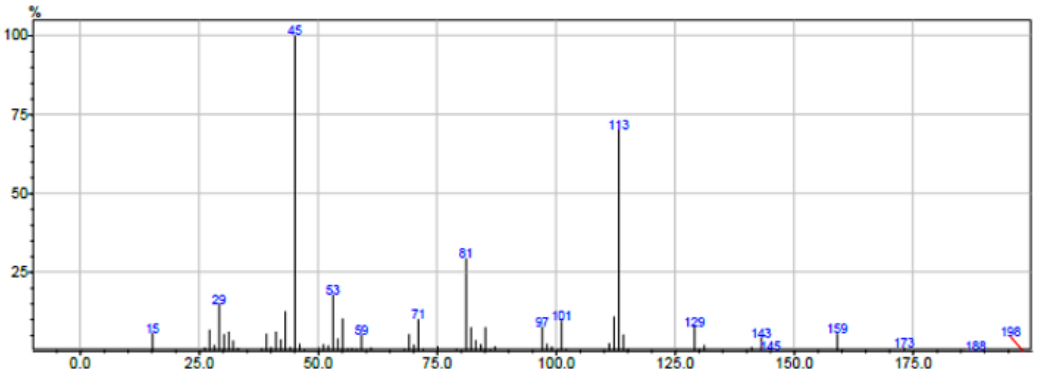

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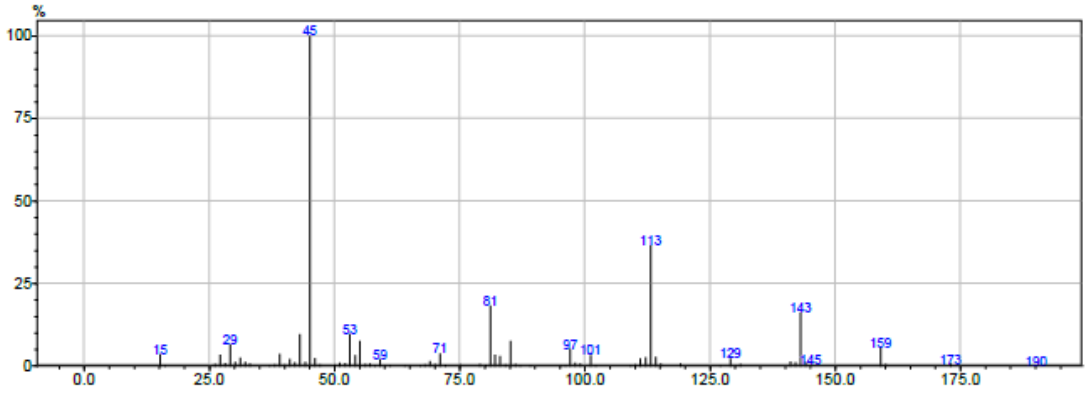
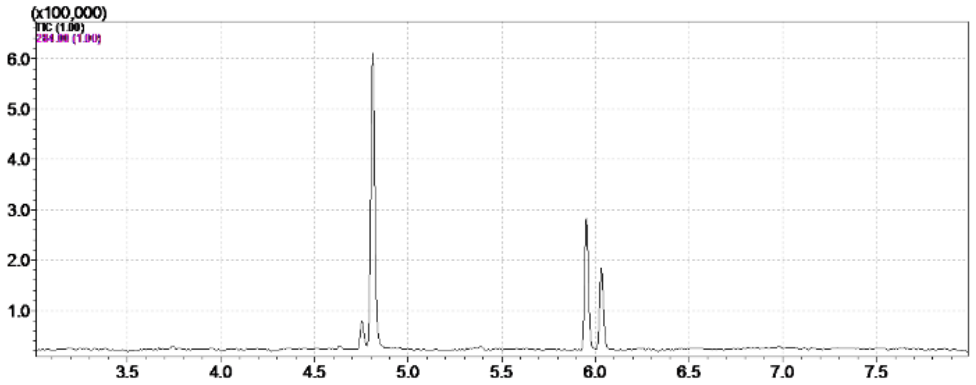


Figure S3. Gas chromatogram and mass spectra of selected peaks of reaction mixture of **2c**.



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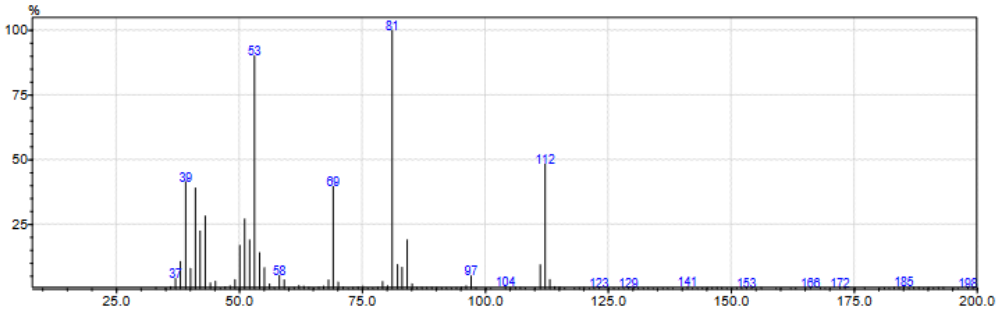

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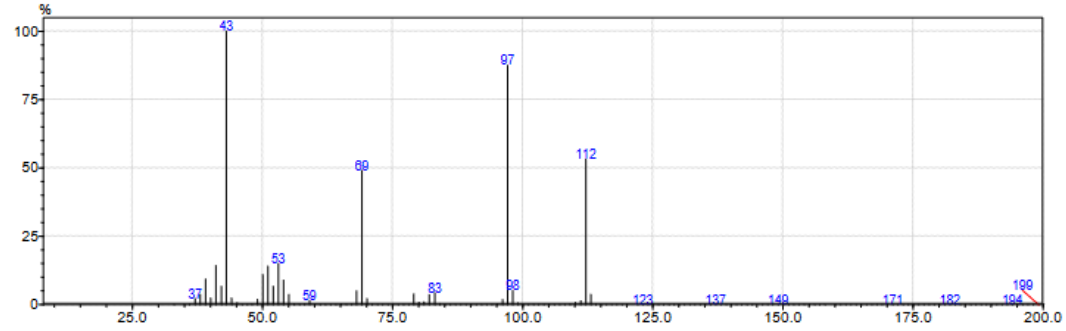

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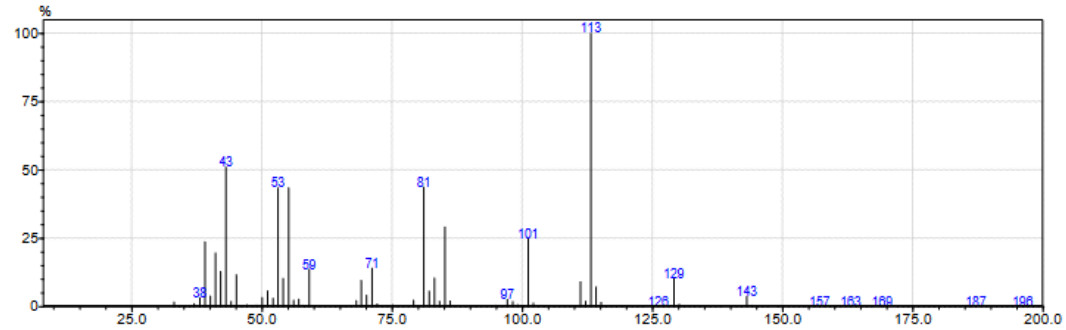

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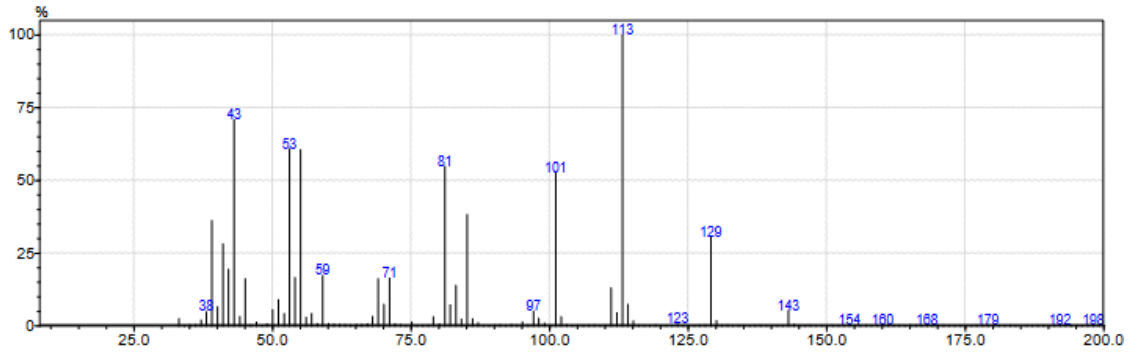

Figure S4. Gas chromatogram and mass spectra of selected peaks of reaction mixture of **2d**.

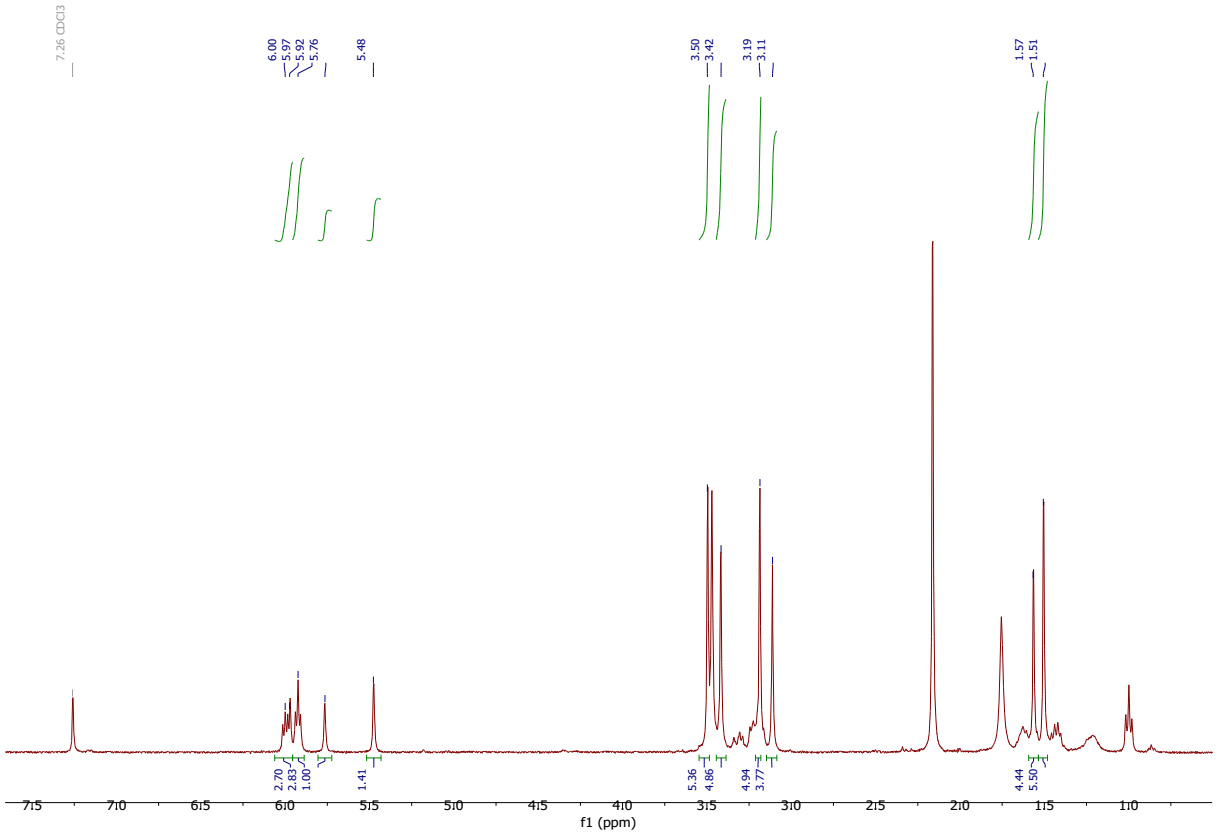

Figure S5. NMR spectrum of a mixture of *cis*- and *trans*-**2a**. Varian INOVA 400 MHz, $CDCl_3$.

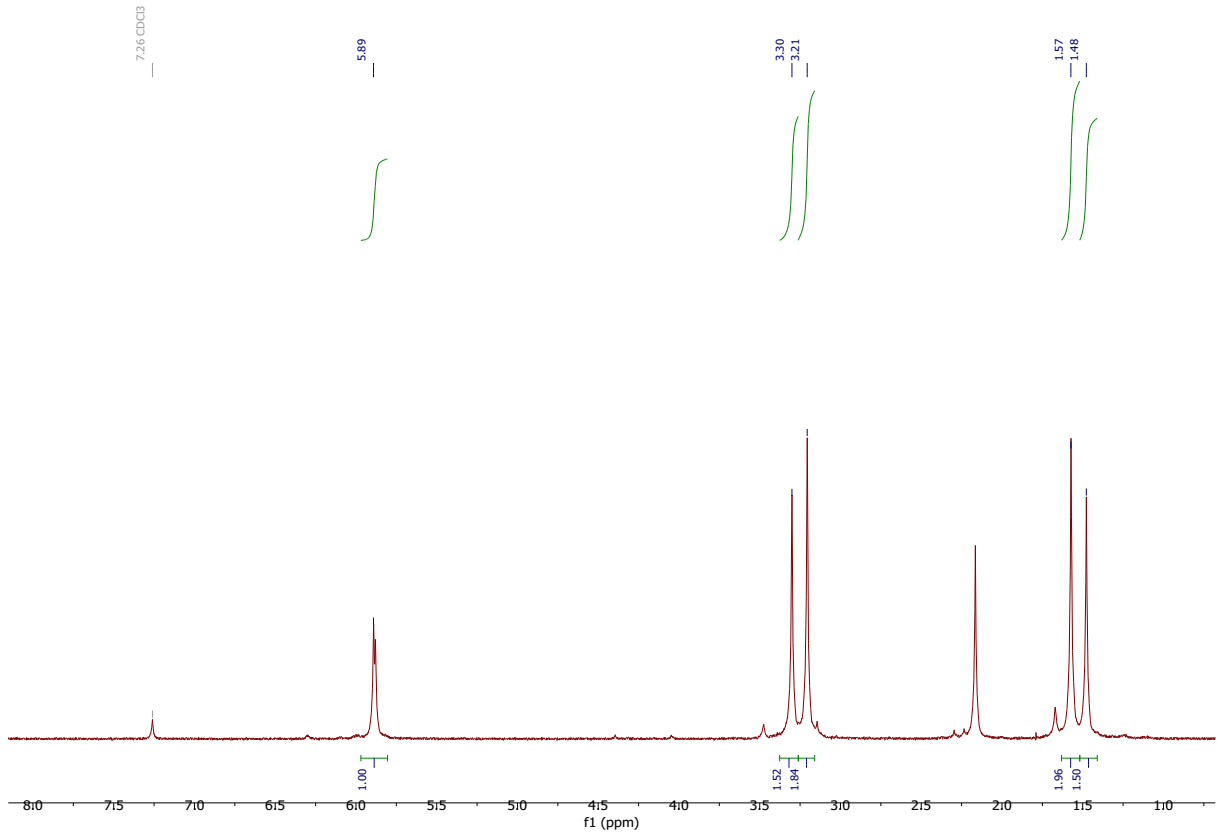

Figure S6. NMR spectrum of a mixture of *cis*- and *trans*-**2b**. Varian INOVA 400 MHz, $CDCl_3$.

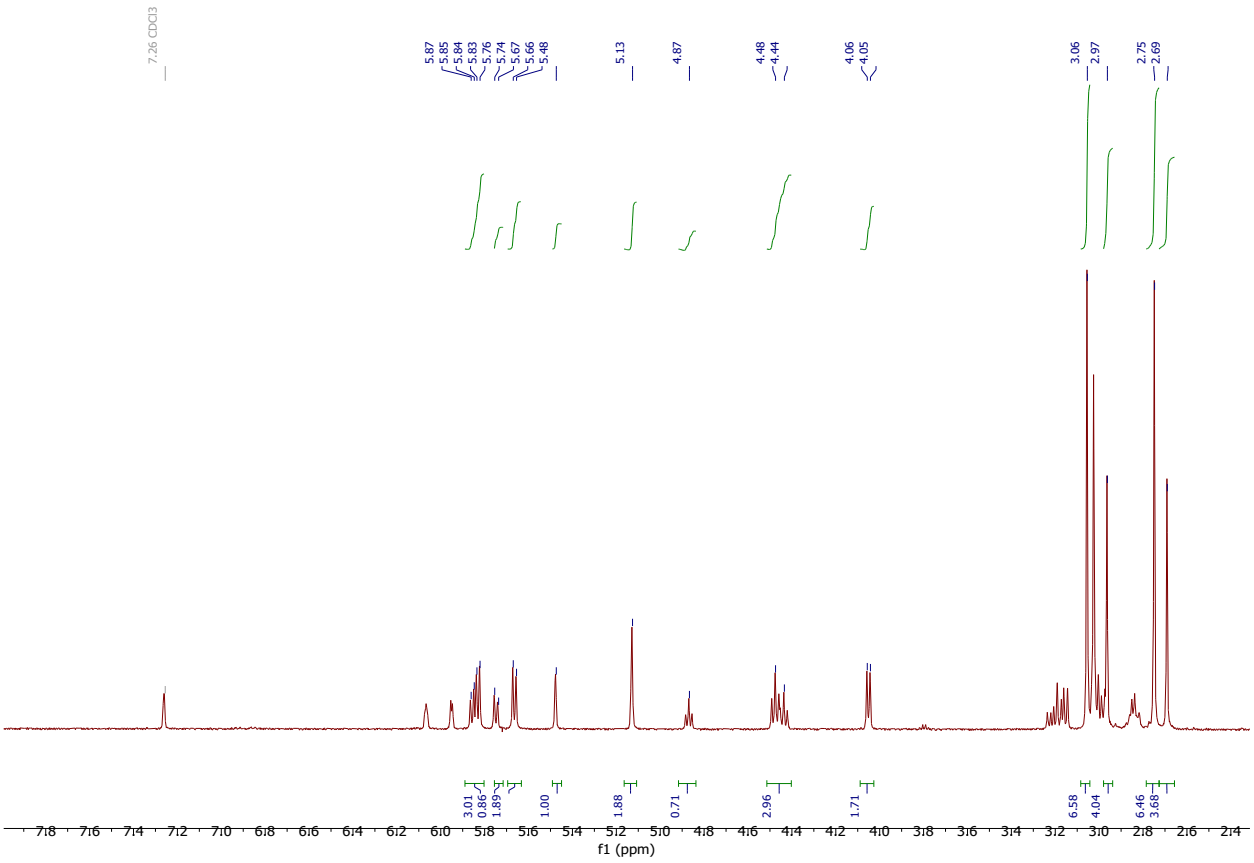

Figure S7. NMR spectrum of a mixture of *cis*- and *trans*-**2c**. Varian INOVA 400 MHz, $CDCl_3$.

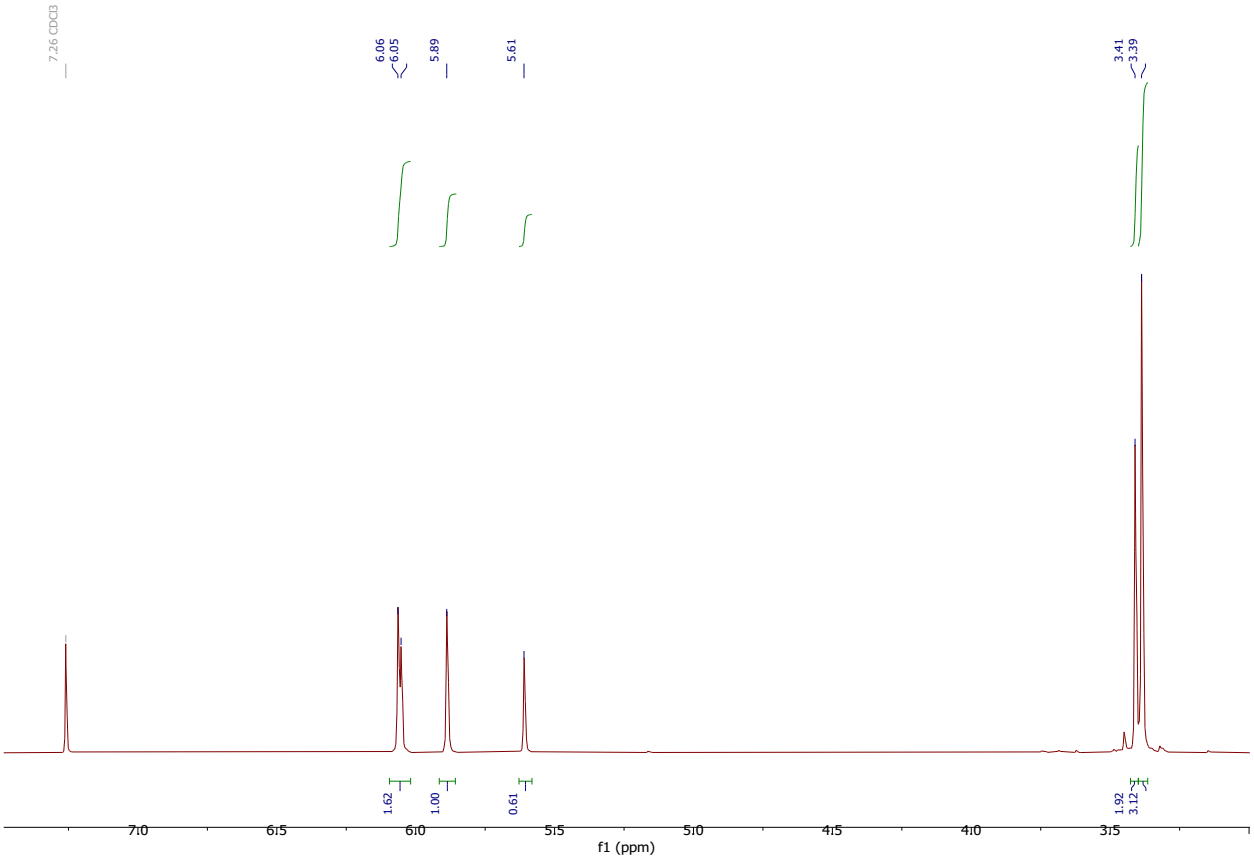

Figure S8. NMR spectrum of a mixture of *cis*- and *trans*-**2d**. Varian INOVA 400 MHz, $CDCl_3$.