Supporting Information

for

Superelectrophilic activation of 5-hydroxymethylfurfural and 2,5-diformylfuran:
organic synthesis based on biomass-derived products

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The NMR spectra of compounds solutions in CDCl$_3$ were recorded on a Bruker AM-500 spectrometer at 25 °C (at 500 and 125 MHz for $^1$H and $^{13}$C NMR spectra, respectively). The residual proton solvent peak CDCl$_3$ (δ 7.26 ppm) for $^1$H NMR spectra and the carbon signal of CDCl$_3$ (δ 77.0 ppm) for $^{13}$C NMR spectra were used as references. NMR spectra in TfOH were recorded on a Bruker AVANCE III 400 spectrometer (at 400 and 100 MHz for $^1$H and $^{13}$C NMR spectra, respectively) using CH$_2$Cl$_2$ as internal standard. High resolution mass spectra (HRMS) were measured on a Bruker maXis HRMS-ESI-QTOF mass spectrometer and a Varian 902-MS MALDI one in the positive mode equipped with a 9.4 Tesla superconducting magnet. Chromatography–mass spectrometry data were obtained with a G2570A GC/MSD Agilent Technologies 6850c with a column HP-5MS (3 m × 0.25 mm), a thickness of the stationary phase of 0.25 μm. The preparative reactions were monitored by thin layer chromatography carried out on silica gel plates (Silufol UV-254) using UV light for detection. Column chromatography was performed on silica gel Merck 60 (0.040–0.063 mm) with hexanes/ethyl acetate mixture elution. Zeolite H-USY, CBV-500 and CBV-720 were purchased from Zeolyst Int. (http://www.zeolyst.com).

X-ray crystallography. Single crystal X-ray analysis was performed with a single crystal diffractometer, Agilent Technologies (Oxford Diffraction) «Supernova». A suitable crystal was selected and kept at 100(2) K during data collection. Using Olex2 $^1$, the structure was solved with the ShelXS $^2$ structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization.

CCDC 1483523 5a, CCDC–1483524 5c contains the supplementary crystallographic data, which can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

DFT calculations. All computations were carried out at the DFT/HF hybrid level of theory using Becke’s three-parameter hybrid exchange functional in combination with the gradient-corrected correlation functional of Lee, Yang, and Parr (B3LYP) by using GAUSSIAN 2009 program packages$^3$. The geometry optimizations were performed using the 6-311+G(2d,2p) basis set

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$^1$ O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Cryst., 2009, 42, 339-341.
$^2$ G. M. Sheldrick, Acta Cryst. 2008, A64, 112-126.
$^3$ M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P.
(standard 6-311 basis set added with polarization (d,p) and diffuse functions). Optimizations were performed on all degrees of freedom and solvent-phase optimized structures were verified as true minima with no imaginary frequencies. The Hessian matrix was calculated analytically for the optimized structures in order to prove the location of correct minima and to estimate the thermodynamic parameters. Solvent-phase calculations used the Polarizable Continuum Model (PCM).

5-Chloromethylfurfural (1b) and 5-bromomethylfurfural (1c) were obtained from D-fructose according to the literature procedure.

**General procedure for the reaction of furans 1a–c, 2 with arenes in TfOH (Tables 3–5).** Furan 1a–c or 2 (1 mmol) was added to the mixture of TfOH (2 mL) and arene [benzene (1 mL, see Tables 3 and 5) and other arenes (1.2–10 mmol, see Table 4). The reaction mixture was stirred at room temperature for the time indicated in Tables 3–5. The mixture was poured into water (30 mL), and extracted with chloroform (3 × 30 mL). The combined extracts were washed with water, saturated aqueous solution of NaHCO₃, water again, and dried over Na₂SO₄. The solvent was removed under reduced pressure, and the residue was subjected to chromatographic separation on silica gel using hexanes–ethyl acetate as an eluent.

In the same manner the reactions were carried out in H₂SO₄ for 1a (entry 5, Table 3) and 2 (entry 3, Table 5) and quenched as described above.

Reaction of 2 with benzene was carried out in HSO₃F (2 mL) and SO₂ (1.5 mL) at −45 °C for 2 h (entry 4, Table 5), followed by quenching with concentrated aqueous hydrochloric acid frozen down to −80 °C (30 mL), then diluted with water (50 mL). Extraction and work-up as described above.

Yields of the obtained compounds 3a–o, 4a–e, 5a are given in Tables 3–5.

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Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09, Revision C.01*, Gaussian, Inc., Wallingford CT, 2010.

4 N. Kumari, J.K. Olesen, C.M. Pedersen, M. Bols, *Eur. J. Org. Chem.*, 2011, 1266-1270.
General procedure for the reaction of furans 1a, 2 with arenes under the action of AlX₃ (X = Cl, Br) (Tables 3 and 5). Furan 1a or 2 (1 mmol) was added to the mixture of AlX₃ (X = Cl, Br) (5 mmol) and arene (5 mL). The reaction mixture was stirred at room temperature for 1 h, then poured into water (50 mL) and extracted with chloroform (3 × 30 mL). The combined extracts were washed with water, saturated aqueous solution of NaHCO₃, water again, and dried over Na₂SO₄. The solvent was distilled off under reduced pressure, and the residue was subjected to chromatographic separation on silica gel using hexanes–ethyl acetate as an eluent. Yields of the obtained compounds 5a–g are given in Table 5.

General procedure for the reactions of furans 1a,b and 2 with arenes under the action of H-USY zeolites (CBV-500 and CBV-720) (Tables 3 and 5). H-USY zeolite, CBV-500 or CBV-720, (Si/Al = 5.2 and 13, respectively) was activated at 550 °C for 4 h under air (see estimation of acidity below in Tables S1–S3 and ref.⁵). The activated zeolite (0.45 g), furan 1a,b or 2 (0.37 mmol) and benzene (5 mL), toluene (5 ml) or another arene (in amounts of 2.5–4 equiv in 5 mL CS₂, see Table 4) were loaded in a 15 mL high pressure glass tube. The resulting suspension was magnetically stirred at 130 °C for 1–10 h (see time in Tables 3–5). After cooling, the reaction mixture was filtered to remove the zeolite catalyst. The zeolite was boiled with MeOH (3 × 10 mL) and filtered. The solutions were combined and the solvent distilled off under reduced pressure and the residue was subjected to chromatographic separation on silica gel using hexane–ethyl acetate as an eluent.

Characteristics of zeolites

Table S1: Characteristics of zeolites CBV-500 and CBV-720 from manufacturer Zeolyst Int. (http://www.zeolyst.com).

| Zeolyst Products | SiO₂/Al₂O₃ Mole Ratio | Nominal Cation Form | Na₂O Weight % | Unit Cell Size, Å | Surface Area, m²/g |
|------------------|-----------------------|---------------------|---------------|------------------|-------------------|
| CBV 500          | 5.2                   | Ammonium            | 0.2           | 24.53            | 750               |
| CBV 720          | 30                    | Hydrogen            | 0.03          | 24.28            | 780               |

⁵ N. Fonseca, F. Lemos, S. Laforge, P. Magnoux, F. Ramoa Ribeiro. Reac. Kinet. Mech. Cat. 2010, 100, 249-263.
Table S2: Physicochemical properties of zeolites CBV-500 and CBV-720.\(^5\)

| Catalyst | Unit cell formula | Bulk Si/Al ratio | Crystals size (μm) | Porosity (cm\(^3\)g\(^{-1}\)) |
|----------|------------------|-----------------|-------------------|-------------------------------|
|          |                  |                 |                   | v\(_{\text{micro}}\) | v\(_{\text{meso}}\) |
| CBV-500  | Na\(_{0.4}\)H\(_{29.6}\)Al\(_{30}\)Si\(_{162}\)O\(_{384}\), 22.7 EFAL | 2.6 | 0.5 | 0.239 | 0.117 |
| CBV-720  | Na\(_{0.3}\)H\(_{11.0}\)Al\(_{11.3}\)Si\(_{181}\)O\(_{384}\), 7.3 EFAL | 13 | 0.5 | 0.317 | 0.190 |

Table S3: Zeolite sample acidities measured by pyridine desorption between 150 and 450°C.\(^5\)

| Acidity (μmol g\(^{-1}\)): T (°C) | CBV-500 |            | CBV-720 |            |
|---------------------------------|---------|------------|---------|------------|
|                                 | Brønsted acid sites | Lewis acid sites | Brønsted acid sites | Lewis acid sites |
| 150                             | 672     | 239        | 271     | 101        |
| 250                             | 594     | 160        | 220     | 69         |
| 350                             | 423     | 129        | 75      | 46         |
| 450                             | 195     | 110        | 13      | 26         |

Yields of the obtained compounds 3a–c, f–n, 5a are given in Tables 3–5.

5-(Phenylmethyl)furan-2-carbaldehyde (3a).\(^5\) Oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 9.52 (s, 1H, CHO), 7.23-7.33 (m, 5H\(_{\text{arom.}}\)), 7.15 (d, \(J = 3.0\) Hz, 1H), 6.17 (d, \(J = 3.0\) Hz, 1H), 4.04 (s, CH\(_2\), 2H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 177.2, 162.1, 152.2, 136.1, 128.9, 128.8, 127.1, 109.8, 34.9. GC-MS (I\(_{\text{rel.}}\),%): 186 M\(^+\) (100), 157 (85), 128 (70), 115 (15).

5-[(4-Methylphenyl)methyl]furan-2-carbaldehyde (3b).\(^6,7\) and 5-[(2-methylphenyl)methyl]furan-2-carbaldehyde (3c)\(^7\) were obtained as inseparable oily mixture of isomers. \(^1\)H NMR (500 MHz, CDCl\(_3\), data for the mixture of isomers 3b and 3c) \(\delta\) 9.53 (s, CHO, 2H), 7.14-7.20 (m, 10H\(_{\text{arom.}}\)), 6.17 (d, \(J = 3.4\) Hz, 1H), 6.06 (d, \(J = 3.4\) Hz, 1H), 4.05 (s, CH\(_2\), 2H), 4.02 (s, CH\(_2\), 2H), 2.34 (s, Me, 3H), 2.29 (s, Me, 3H). \(^13\)C NMR (125 MHz, CDCl\(_3\), data for the mixture of isomers 3b and 3c) \(\delta\) 177.1, 162.4, 161.8, 152.1, 136.6, 134.3, 134.3, 133.0, 130.5, 129.8, 129.4, 128.7, 127.4, 126.3, 123.2, 109.7, 109.7, 34.4, 32.6, 21.0, 19.3. GC-MS (I\(_{\text{rel.}}\),% for 3b): 200 M\(^+\) (94), 185 (42), 171 (44), 154 (25), 141 (23), 128 (100). GC-MS (I\(_{\text{rel.}}\),% for 3c): 200 M\(^+\) (87), 185 (54), 171 (82), 141 (12), 128 (100).

5-[(3,4-Dimethylphenyl)methyl]furan-2-carbaldehyde (3d) and 5-(2,3-dimethylphenyl)methyl]furan-2-carbaldehyde (3e) were obtained as inseparable oily mixture of

\(^5\) a) J. Cabares, L. Mavoungou-Gomes, *Bull. Soc. Chim. France*, 1986, 401–412; b) A. Skrzyńska, A. Przydacz, L. Albrecht, *Org. Lett.*, 2015, 17, 5682–5685.

\(^6\) A. Onorato, C. Pavlik, M.A. Invernale, I.D. Berghorn, G.A. Sotzing, M.D. Mortona, M.B. Smith. *Carbohydrate Research*, 2011, 346, 1662–1670.
isomers. 5-[(3,4-Dimethylphenyl)methyl]furan-2-carbaldehyde (3d). $^1$H NMR (500 MHz, CDCl$_3$, from the spectrum of the mixture of isomers) $\delta$ 9.54 (s, CHO, 1H), 6.98-7.16 (m, 4H$_{\text{arom}}$), 6.18 (d, $J$ = 3.5 Hz, 1H), 3.99 (s, CH$_2$, 2H), 2.24 (s, 2Me, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) from the spectrum of the mixture of isomers: $\delta$ 177.1, 162.1, 152.0, 136.8, 135.2, 133.4, 130.1, 129.9, 126.2, 122.9, 109.5, 34.3, 19.6, 19.2. GC-MS ($I_{\text{rel}},\%$): 214 $M^+$ (100), 199 (70), 185 (52), 168 (15), 153 (16).

5-[(2,3-Dimethylphenyl)methyl]furan-2-carbaldehyde (3e). $^1$H NMR (500 MHz, CDCl$_3$, from the spectrum of the mixture of isomers) $\delta$ 9.54 (s, CHO, 1H), 6.98-7.16 (m, 4H$_{\text{arom}}$), 6.04 (d, $J$ = 3.5 Hz, 1H), 4.07 (s, CH$_2$, 2H), 2.30 (s, Me, 3H), 2.18 (s, Me, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$, from the spectrum of the mixture for compounds) $\delta$ 177.1, 162.1, 152.1, 137.3, 135.0, 134.2, 129.1, 127.8, 125.7, 123.8, 109.6, 33.2, 20.5, 15.2. MS ($I_{\text{rel}},\%$): 214 $M^+$ (100), 199 (52), 185 (68), 153 (31). HRMS (for the mixture of isomers): calcd. for C$_{14}$H$_{14}$O$_2$Na 237.0886 [M+Na]; found 237.0874.

5-[(2,4-Dimethylphenyl)methyl]furan-2-carbaldehyde (3f). Oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.53 (s, CHO, 1H), 7.14 (d, $J$ = 3.5 Hz, 1H), 7.06 (d, $J$ = 7.6 Hz, 1H$_{\text{arom}}$), 7.02 (br.s, 1H$_{\text{arom}}$), 6.98 (d, $J$ = 7.6 Hz, 1H$_{\text{arom}}$), 6.05 (d, $J$ = 3.5 Hz, 1H), 4.01 (s, CH$_2$, 2H), 2.31 (s, Me, 3H), 2.25 (s, Me, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 177.0, 162.1, 152.1, 137.0, 136.2, 131.3, 129.7, 128.3, 127.1, 127.0, 109.6, 32.2, 20.9, 19.3. MS ($I_{\text{rel}},\%$): 214 $M^+$ (100), 199 (80), 185 (45), 168 (25), 153 (15). HRMS (for the mixture of isomers): calcd. for C$_{14}$H$_{14}$O$_2$Na 237.0886 [M+Na]; found 237.0897.

5-[(2,5-Dimethylphenyl)methyl]furan-2-carbaldehyde (3g). Oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.54 (s, CHO, 1H), 7.15 (d, $J$ = 3.5 Hz, 1H), 7.06-7.09 (m, 1H$_{\text{arom}}$), 6.99-7.02 (m, 2H$_{\text{arom}}$), 6.06 (d, $J$ = 3.5 Hz, 1H), 4.01 (s, CH$_2$, 2H), 2.31 (s, Me, 3H), 2.25 (s, Me, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 177.1, 162.0, 152.0, 135.8, 134.1, 133.2, 130.5, 130.4, 128.0, 123.2, 109.6, 32.6, 20.8, 18.9. MS ($I_{\text{rel}},\%$): 214 $M^+$ (100), 199 (50), 185 (25), 168 (22), 153 (20). HRMS (for the mixture of isomers): calcd. for C$_{14}$H$_{14}$O$_2$Na 237.0886 [M+Na]; found 237.0881.

5-[(2,4,5-Trimethylphenyl)methyl]furan-2-carbaldehyde (3h) and 5-[(2,3,5-Trimethylphenyl)methyl]furan-2-carbaldehyde (3i) were obtained as inseparable oily mixture of isomers. 5-[(2,4,5-Trimethylphenyl)methyl]furan-2-carbaldehyde (3h). $^1$H NMR (500 MHz, CDCl$_3$, from the spectrum of the mixture of isomers) $\delta$ 9.53 (s, CHO, 1H), 7.15 (d, $J$ = 3.5 Hz, 1H), 6.97 (s, 1H$_{\text{arom}}$), 6.95 (s, 1H$_{\text{arom}}$), 6.07 (dd, $J$ = 3.5, 0.6 Hz, 1H), 3.99 (s, CH$_2$, 2H), 2.28 (s, Me, 3H), 2.23 (s, 2Me, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$, data for the mixture for isomers 3h and 3i) $\delta$ 177.15, 177.1, 162.3, 161.9, 152.1, 135.5, 135.4, 134.7, 134.4, 134.3, 133.5, 132.6, 131.9, 131.8, 131.5, 131.2, 130.0, 128.8, 128.5, 127.7, 109.6, 109.2, 32.2, 29.3, 20.7, 20.1, 19.2, 19.1, 18.7. GC-MS ($I_{\text{rel}},\%$): 228 $M^+$ (100), 213 (80), 199 (25), 182 (22), 167 (18), 156 (43). 5-[(2,3,5-Trimethylphenyl)methyl]furan-2-carbaldehyde (3i). $^1$H NMR (500 MHz, CDCl$_3$, from the spectrum of the mixture of isomers) $\delta$ 9.53 (s, CHO, 1H), 7.12 (d, $J$ = 3.5 Hz, 1H), 6.94-7.04 (m,
2H_{arom.}), 5.91 (d, J = 3.5 Hz, 1H), 4.11 (s, CH₂, 2H), 2.23 (s, Me, 3H), 2.22 (s, Me, 3H). GC-MS (I_{rel, %}): 228 M⁺ (100), 213 (80), 199 (25), 182 (22), 167 (18), 156 (43). HRMS (for mixture of isomers): calcd. for C₁₅H₁₇O₂ 229.1223 [M+H]; found 229.1224.

5-[(3,4-Dichlorophenyl)methyl]furan-2-carbaldehyde (3j). Oil. ¹H NMR (500 MHz, CDCl₃) δ 9.55 (s, CHO, 1H), 7.39 (d, J = 8.2 Hz, 1H_{arom.}), 7.33 (d, J = 2.0 Hz, 1H_{arom.}), 7.17 (d, J = 3.5 Hz, 1H), 7.09 (dd, J = 8.2, 2.0 Hz, 1H_{arom.}), 6.23 (d, J = 3.5 Hz, 1H), 4.01 (s, CH₂, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 177.2, 160.1, 152.5, 136.3, 132.8, 131.3, 130.73, 130.69, 128.2, 122.8, 110.0, 33.9. HRMS: calcd. for C₁₂H₉Cl₂O₂ 254.9974 [M+H]; found 254.9978.

5-[(2,3-Dichlorophenyl)methyl]furan-2-carbaldehyde (3k) was obtained as oily mixture with its isomer (3j). ¹H NMR (500 MHz, CDCl₃, from spectrum of the mixture of isomers) δ 9.54 (s, CHO, 1H), 7.16-7.40 (m, 4H_{arom.}), 6.22-6.23 (m, 1H), 4.22 (s, CH₂, 2H). HRMS: calcd. for C₁₂H₉Cl₂O₂ 254.9974 [M+H]; found 254.9978.

5-[(4-Methoxyphenyl)methyl]furan-2-carbaldehyde (3l). Oil. ¹H NMR (500 MHz, CDCl₃) δ 9.54 (s, CHO, 1H), 7.15-7.18 (m, 3H_{arom.}), 6.86-6.88 (2H_{arom.}), 6.15-6.16 (m, 1H), 4.00 (s, CH₂, 2H), 3.80 (s, 3H, MeO). ¹³C NMR (125 MHz, CDCl₃) δ 177.1, 162.6, 157.7, 147.8,129.9, 128.6, 121.9, 114.2, 109.5, 55.3, 34.0. GC-MS (I_{rel, %}): 216 M⁺ (100), 187 (87), 144 (35), 128 (25), 115 (44).

5-[(2-Methoxyphenyl)methyl]furan-2-carbaldehyde (3m) was obtained as oily mixture with its isomer (3l). ¹H NMR (500 MHz, CDCl₃, from spectrum of the mixture of compounds) δ 9.88 (s, CHO, 1H), 6.84-7.84 (m, 5H_{arom.}), 6.14 (d, J = 3.4 Hz, 1H), 3.88 (s, 3H, MeO), 3.86 (s, CH₂, 2H). GC-MS (I_{rel, %}): 216 M⁺ (100), 187 (87), 144 (35), 128 (25), 115 (44). HRMS: calcd. for C₁₃H₁₂O₃Na 239.0679 [M+Na]; found 239.0682.

5-[(3,4-Dimethoxyphenyl)methyl]furan-2-carbaldehyde (3n). Oil. ¹H NMR (500 MHz, CDCl₃) δ 9.53 (s, CHO, 1H), 7.15 (d, J = 3.4 Hz, 1H), 6.76-6.81 (m, 3H_{arom.}), 6.17 (d, J = 3.4 Hz, 1H), 3.99 (s, CH₂, 2H), 3.86 (s, 3H, MeO), 3.85 (s, 3H, MeO). ¹³C NMR (125 MHz, CDCl₃) δ 177.2, 162.4, 152.1, 149.1, 148.1, 128.5, 123.2, 121.0, 112.1, 111.4, 109.6, 55.9, 55.8, 34.5. MS (I_{rel, %}): 246 M⁺ (100), 231 (15), 215 (60), 203 (8), 115 (12). HRMS: calcd. for C₁₄H₁₄O₄Na 269.0784 [M+Na]; found 269.0775.

5-[(2,4,6-Trimethylphenyl)methyl]furan-2-carbaldehyde (3o). Oil. ¹H NMR (500 MHz, CDCl₃) δ 9.52 (s, CHO, 1H), 7.10 (d, J = 3.5 Hz, 1H), 6.89 (s, 2H_{arom.}), 5.91 (d, J = 3.5 Hz, 1H), 4.04 (s, CH₂, 2H), 2.28 (s, Me, 3H), 2.26 (s, 2Me, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 177.2, 160.1, 152.5, 136.3, 132.8, 131.3, 130.73, 130.69, 128.2, 122.8, 110.0, 33.9. MS (I_{rel, %}): 228 M⁺ (100), 213 (48),

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* A. Skrzyńska, A. Przydacz, L. Albrecht, *Org. Lett.*, 2015, 17, 5682–5685.
Compounds i-4a were obtained as a mixture of isomers with predominance of p-methylphenyl substituted furan.

2-[(4-Methylphenyl)methyl]-5-[bis(4-methylphenyl)methyl]furan (4a). Oil. \(^1\)H NMR (500 MHz, CDCl\(_3\), from the spectrum of the mixture of isomers) \(\delta\) 7.03-7.16 (m, 12H\(_{\text{arom.}}\)), 5.85 (s, 1H), 5.76 (s, CH, 1H), 5.34 (s, 1H), 3.89 (s, CH\(_2\), 2H), 2.33 (s, 3Me, 9H). \(^13\)C NMR (125 MHz, CDCl\(_3\), from the spectrum of the mixture of isomers) \(\delta\) 155.8, 154.2, 139.3, 136.0, 129.1, 129.0, 128.6, 108.8, 106.5, 50.1, 34.1, 21.0. MS (I\(_{\text{rel}},\%)\): 366 \(M^+\) (36), 351 (12), 275 (16), 261 (100). HRMS: calcd. for C\(_{27}\)H\(_{20}\)NaO 389.1876 [M+Na]; found 389.1991.

2-[(3,4-Dimethylphenyl)methyl]-5-[bis(3,4-dimethylphenyl)methyl]furan (4b). Oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.05-7.07 (m, 4H\(_{\text{arom.}}\)), 6.98-7.00 (m, 4H\(_{\text{arom.}}\)), 6.91 (dd, \(J = 7.7, 1.7\) Hz, 2H\(_{\text{arom.}}\)), 5.88 (d, \(J = 2.8\) Hz, 1H), 5.79 (d, \(J = 2.8\) Hz, 1H), 5.29 (s, CH, 1H), 3.87 (s, CH\(_2\), 2H), 2.25 s (3H, Me), 2.25 s (6H, 2Me), 2.24 s (3H, Me), 2.22 s (6H, 2Me). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 155.9, 154.2, 139.8, 136.4, 136.3, 135.8, 134.6, 134.3, 130.0, 129.9, 129.6, 129.5, 126.03, 126.0, 108.7, 106.4, 50.2, 34.0, 19.8, 19.6, 19.3, 19.2. MS (I\(_{\text{rel}},\%)\): 408 \(M^+\) (35), 289 (100), 246 (8), 215 (5). HRMS: calcd. for C\(_{30}\)H\(_{22}\)ONa 431.2351 [M+Na]; found 431.2364.

2-[(2,4-Dimethylphenyl)methyl]-5-[bis(2,4-dimethylphenyl)methyl]furan (4c). Oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.06 (d, \(J = 7.8\) Hz, 1H\(_{\text{arom.}}\)), 6.93-7.00 (m, 4H\(_{\text{arom.}}\)), 6.90 (d, \(J = 7.6\) Hz, 2H\(_{\text{arom.}}\)), 6.70 (d, \(J = 7.8\) Hz, 2H\(_{\text{arom.}}\)), 5.70 (d, \(J = 2.5\) Hz, 1H), 5.54 (d, \(J = 2.5\) Hz, 1H), 5.52 (s, CH, 1H), 3.86 (s, CH\(_2\), 2H), 2.30 (s, 4Me, 12H), 2.18 (s, 2Me, 6H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 155.0, 153.7, 137.0, 136.0, 135.9, 133.5, 131.2, 131.1, 131.0, 129.3, 128.4, 127.2, 126.6, 126.5, 126.4, 109.5, 106.6, 48.8, 31.9, 20.9, 19.2, 19.0. MS (I\(_{\text{rel}},\%)\): 408 \(M^+\) (65), 289 (100), 246 (8), 207 (35). HRMS: calcd. for C\(_{30}\)H\(_{22}\)ONa 431.2351 [M+Na]; found 431.2345.

2-[(2,5-Dimethylphenyl)methyl]-5-[bis(2,5-dimethylphenyl)methyl]furan (4d). Oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.05 (d, \(J = 7.6\) Hz, 3H\(_{\text{arom.}}\)), 6.96 (d, \(J = 7.6\) Hz, 3H\(_{\text{arom.}}\)), 6.94 (s, 1H\(_{\text{arom.}}\)), 6.63 (s, 2H\(_{\text{arom.}}\)), 5.77 (d, \(J = 2.8\) Hz, 1H), 5.58 (d, \(J = 2.8\) Hz, 1H), 5.55 (s, CH, 1H), 3.88 (s, CH\(_2\), 2H), 2.29 (s, Me, 3H), 2.24 (s, Me, 3H), 2.23 (s, 2Me, 6H), 2.18 (s, 2Me, 6H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 154.8, 153.5, 139.6, 135.1, 133.1, 130.1, 130.0, 129.1, 127.2, 109.7, 106.8, 44.4, 32.4, 21.2, 20.9, 18.9. MS (I\(_{\text{rel}},\%)\): 408 \(M^+\) (85), 289 (100), 246 (30), 207 (90). HRMS: calcd. for C\(_{30}\)H\(_{32}\)ONa 431.2351 [M+Na]; found 431.2357.

2-[(2,4,5-Trimethylphenyl)methyl]-5-[bis(2,4,5-trimethylphenyl)methyl]furan (4e). Oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 6.96-6.97 (m, 2H\(_{\text{arom.}}\)), 6.93 (s, 2H\(_{\text{arom.}}\)), 6.64 (s, 2H\(_{\text{arom.}}\)), 5.78 (d, \(J = 3.0\) Hz, 1H), 5.62 (d, \(J = 3.0\) Hz, 1H), 5.53 (s, CH, 1H), 3.89 (s, CH\(_2\), 2H), 2.26 (s, 5Me, 15H), 2.20 (s, 2Me, 6H), 2.17 (s, 2Me, 6H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 155.2, 153.7, 137.3, 134.4, 134.3,
134.0, 133.7, 133.5, 133.47, 133.3, 131.62, 131.55, 130.7, 129.8, 109.4, 106.6, 43.7, 32.0, 19.4, 19.2, 19.1, 18.7. MS (I<sub>rel</sub>, %): 450 M<sup>+</sup> (60), 317 (100), 274 (12), 235 (35), 197 (23). HRMS: calcd. for C<sub>33</sub>H<sub>38</sub>Ona 473.2815; found 473.2839.

5-(Diphenylmethyl)furan-2-carbaldehyde (5a). Colorless solid, m.p. 91–93°C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.55 (s, CHO, 1H), 7.30 (t, J = 7.6 Hz, 4H<sub>arom</sub>), 7.24 (t, J = 3.6 Hz, 2H<sub>arom</sub>), 7.17 (d, J = 3.5 Hz, 1H), 7.15 (d, J = 7.6 Hz, 4H<sub>arom</sub>), 6.14 (d, J = 3.5 Hz, 1H), 5.55 (s, CH, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 177.5, 163.7, 152.4, 140.2, 128.9, 128.6, 127.1, 122.1, 111.6, 51.0. MS (I<sub>rel</sub>, %): 262 M<sup>+</sup> (58), 233 (100), 215 (20), 203 (22), 185 (21). HRMS: calcd. for C<sub>18</sub>H<sub>15</sub>O<sub>2</sub> 263.1067 [M+H]; found 263.1071.

5-[Bis(3,4-dimethylphenyl)methyl]furan-2-carbaldehyde (5b). Oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.56 (s, 1H, CHO), 7.18 (d, J = 3.4 Hz, 1H), 7.07 (d, J = 7.6 Hz, 2H<sub>arom</sub>), 6.94 s (2H<sub>arom</sub>), 6.88 (d, J = 7.6 Hz, 2H<sub>arom</sub>), 6.16 (d, J = 3.4 Hz, 1H), 5.40 (s, 1H, CH), 2.23 (s, 6H, 2Me), 2.21 s (6H, 2Me). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 177.6, 164.5, 152.3, 137.9, 136.7, 135.3, 129.8, 129.8, 125.8, 121.8, 111.2, 50.4, 19.7, 19.2. MS, m/z (I<sub>rel</sub>, %): 318 M<sup>+</sup> (52), 303 (28), 289 (100), 274 (11), 259 (9), 246 (11), 231 (7), 213 (13). HRMS: calcd. for C<sub>22</sub>H<sub>22</sub>O<sub>2</sub> 319.1693 [M+H]; found 319.1702.

5-[Bis(3,5-dimethylphenyl)methyl]furan-2-carbaldehyde (5c) and 5-[bis(2,4-dimethylphenyl)methyl]furan-2-carbaldehyde (5d) were obtained as inseparable oily mixture of isomers. 5-[Bis(3,5-dimethylphenyl)methyl]furan-2-carbaldehyde (5c). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, from the spectrum of the mixture of isomers) δ 9.57 (s, 1H, CHO), 7.19 (d, J = 3.6 Hz, 1H), 6.89 s (2H<sub>arom</sub>), 6.77 s (4H<sub>arom</sub>), 6.16 (d, J = 3.6 Hz, 1H), 5.37 (s, 1H, CH), 2.27 (s, 12H, 4 Me). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, from the spectrum of the mixture of isomers) δ 177.8, 164.4, 152.4, 140.3, 138.1, 128.8, 126.4, 121.9, 111.5, 51.1, 21.3. GC-MS, m/z (I<sub>rel</sub>, %): 318 M<sup>+</sup> (87), 303 (21), 289 (100), 246 (26), 213 (21), 141 (19). 5-[Bis(2,4-dimethylphenyl)methyl]furan-2-carbaldehyde (5d). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, from the spectrum of the mixture of isomers) δ 9.56 (s, 1H, CHO), 7.17 (d, J = 3.6Hz, 1H), 7.08-6.91 m (6H<sub>arom</sub>), 6.04 (d, J = 3.6 Hz, 1H), 5.56 (s, 1H, CH), 2.26 (s, 6H, 2Me), 2.30 (s, 6H, 2Me), 2.26 (s, 6H, 2Me). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, from the spectrum of the mixture of isomers) δ 177.7, 164.6, 144.0, 139.7, 138.7, 131.5, 128.8, 128.7, 127.7, 122.4, 111.9, 47.4, 20.9, 19.5. GC-MS, m/z (I<sub>rel</sub>, %): 318 M<sup>+</sup> (77), 308 (21), 289 (100), 246 (16), 213 (20). HRMS (for mixture of isomers): calcd. for C<sub>22</sub>H<sub>22</sub>O<sub>2</sub> 319.1693 [M+H]; found 319.1702.

5-[Bis(2,5-dimethylphenyl)methyl]furan-2-carbaldehyde (5e). Colorless solid, m.p. 110–112°C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.57 (s, 1H, CHO), 7.19 (d, J = 3.6 Hz, 1H), 7.06 (d, J = 7.5 Hz, 2H<sub>arom</sub>), 6.99 (d, J = 7.5 Hz, 4H<sub>arom</sub>), 5.96 (d, J = 3.6 Hz, 1H), 5.68 (s, 1H, CH), 2.23 (s, 6H, 2Me), 2.14 (s, 6H, 2Me). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 177.6, 164.0, 152.4, 137.9, 135.4, 133.0, 130.4, 128.8, 127.8, 126.2, 122.4, 112.3, 44.6, 21.09, 18.8. GC-MS, m/z (I<sub>rel</sub>, %): 318 M<sup>+</sup> (100),
308 (26), 289 (50), 246 (16), 213 (25), 183 (43). HRMS: calcd. for C_{22}H_{23}O_{2} 319.1693 [M+H]; found 319.1685.

5-[Bis(3,4-dichlorophenyl)methyl]furan-2-carbaldehyde (5f) and 5-[Bis(2,3-dichlorophenyl)methyl]furan-2-carbaldehyde (5g) were obtained as inseparable oily mixture of isomers. 5-[Bis(3,4-dichlorophenyl)methyl]furan-2-carbaldehyde (5f). $^1$H NMR (500 MHz, CDCl$_3$, from the spectrum of the mixture of isomers) $\delta$ 9.59 (s, 1H, CHO), 7.42 (d, 2H$_{arom.}$ $J = 8.4$, 3.6 Hz), 7.22-7.17 (m, 2H$_{arom.}$), 7.22-7.17 (m, 1H, CH), 6.98 (d.d, 2H$_{arom.}$ $J = 8.3$, 2.1 Hz), 6.20 (d, 1H, $J = 3.6$ Hz), 5.44 (s, 1H, CH). $^{13}$C NMR (125 MHz, CDCl$_3$, from the spectrum of the mixture of isomers) $\delta$ 177.5, 160.6, 152.9, 139.3, 133.2, 132.1, 130.9, 127.9, 121.9, 111.9, 49.3. GC-MS, m/z (I$_{rel.}$, %): 400 $^+$ (45), 371 (100), 306 (35), 253 (38), 236 (37), 200 (12), 162 (22). 5-[Bis(2,3-dichlorophenyl)methyl]furan-2-carbaldehyde (5g) $^{1}$H NMR (500 MHz, CDCl$_3$, from the spectrum of the mixture of isomers) $\delta$ 9.59 (s, 1H, CHO), 7.42-7.40 (m, 2H$_{arom.}$), 7.22-7.17 (m, 1H, CH), 6.90 (d.d, 2H$_{arom.}$ $J = 7.8$, 3.6 Hz), 6.14 (d, 1H, $J = 3.6$ Hz), 5.96 (s, 1H, CH). $^{13}$C NMR (125 MHz, CDCl$_3$, from the spectrum of the mixture of isomers) $\delta$ 177.5, 139.2, 138.6, 130.8, 129.9, 128.2, 128.0, 127.5, 122.5, 112.4, 47.8. GC-MS, m/z (I$_{rel.}$, %): 400 $^+$ (57), 371 (100), 306 (33), 270 (24), 253 (35), 236 (52), 200 (30), 162 (34), 135 (17), 118 (17), 100 (18). HRMS (for mixture of isomers): calcd. for C$_{18}$H$_{11}$Cl$_4$O$_2$ 398.9508 [M+H]; found 398.9511.
$^1$H and $^{13}$C NMR Spectra of compounds 3a–o, 4a–e, 5a–g

Figure S1. $^1$H NMR spectrum of compound 3a (500 MHz, CDCl$_3$).

Figure S2. $^{13}$C NMR spectrum of compound 3a (125 MHz, CDCl$_3$).
Figure S3. $^1$H NMR spectrum of mixture of compounds 3b and 3c (500 MHz, CDCl$_3$).

Figure S4. $^{13}$C NMR spectrum of mixture of compounds 3b and 3c (125 MHz, CDCl$_3$).
Figure S5. $^1$H NMR spectrum of mixture of compounds 3d and 3e (500 MHz, CDCl$_3$).

Figure S6. $^{13}$C NMR spectrum of mixture of compounds 3d and 3e (125 MHz, CDCl$_3$).
Figure S7. $^1$H NMR spectrum of compound 3f (500 MHz, CDCl$_3$).

Figure S8. $^{13}$C NMR spectrum of compound 3f (125 MHz, CDCl$_3$).
Figure S9. $^1$H NMR spectrum of compound 3g (500 MHz, CDCl$_3$).

Figure S10. $^{13}$C NMR spectrum of compound 3g (125 MHz, CDCl$_3$).
Figure S11. $^1$H NMR spectrum of mixture of compounds 3h and 3i (500 MHz, CDCl$_3$).

Figure S12. $^{13}$C NMR spectrum of mixture of compounds 3h and 3i (125 MHz, CDCl$_3$)
Figure S13. $^1$H NMR spectrum of compound 3j (500 MHz, CDCl$_3$).

Figure S14. $^{13}$C NMR spectrum of compound 3j (125 MHz, CDCl$_3$).
Figure S15. $^1$H NMR spectrum of mixture of compounds 3j and 3k (500 MHz, CDCl$_3$).

Figure S16. $^1$H NMR spectrum of compound 3l (500 MHz, CDCl$_3$).
Figure S17. $^1$H NMR spectrum of mixture of compounds 3l and 3m (500 MHz, CDCl$_3$).

Figure S18. $^1$H NMR spectrum of compound 3n (500 MHz, CDCl$_3$).
Figure S19. $^{13}$C NMR spectrum of compound 3n (125 MHz, CDCl$_3$).

Figure S20. $^1$H NMR spectrum of compound 3o (500 MHz, CDCl$_3$).
Figure S21. $^{13}$C NMR spectrum of compounds 3o (125 MHz, CDCl$_3$).

Figure S22. $^1$H NMR spectrum of compound 4a (500 MHz, CDCl$_3$).
Figure S23. $^{13}$C NMR spectrum of compound 4a (125 MHz, CDCl$_3$).

Figure S24. $^1$H NMR spectrum of compound 4b (500 MHz, CDCl$_3$).
Figure S25. $^{13}$C NMR spectrum of compound 4b (125 MHz, CDCl$_3$).

Figure S26. $^1$H NMR spectrum of compound 4c (500 MHz, CDCl$_3$).
Figure S27. $^{13}$C NMR spectrum of compound 4c (125 MHz, CDCl$_3$).

Figure S28. $^1$H NMR spectrum of compound 4d (500 MHz, CDCl$_3$).
Figure S29. $^{13}$C NMR spectrum of compound 4d (125 MHz, CDCl$_3$).

Figure S30. $^1$H NMR spectrum of compound 4e (500 MHz, CDCl$_3$).
Figure S31. $^1$H NMR spectrum of compound $4e$ (125 MHz, CDCl$_3$).

Figure S32. $^1$H NMR spectrum of compound $5a$ (500 MHz, CDCl$_3$).
Figure S33. $^{13}$C NMR spectrum of compound 5a (125 MHz, CDCl$_3$).

Figure S34. $^1$H NMR spectrum of compound 5b (500 MHz, CDCl$_3$).
Figure S35. $^{13}$C NMR spectrum of compound 5b (125 MHz, CDCl$_3$).

Figure S36. $^1$H NMR spectrum of mixture of compounds 5c and 5d (500 MHz, CDCl$_3$).
Figure S37. $\textsuperscript{13}$C NMR spectrum of mixture of compounds 5c and 5d (125 MHz, CDCl$_3$).

Figure S38. Fragment of $\textsuperscript{13}$C NMR spectrum of mixture of compounds 5c and 5d (125 MHz, CDCl$_3$).
Figure S39. $^1$H NMR spectrum of compound 5e (500 MHz, CDCl$_3$).

Figure S40. $^{13}$C NMR spectrum of compound 5e (125 MHz, CDCl$_3$).
Figure S41. $^1$H NMR spectrum of mixture of compounds 5f and 5g (500 MHz, CDCl$_3$).

Figure S42. Fragment of $^1$H NMR spectrum of mixture of compounds 5f and 5g (500 MHz, CDCl$_3$).
Figure S43. $^{13}$C NMR spectrum of mixture of compounds 5f and 5g (125 MHz, CDCl$_3$).

Figure S44. Fragment of $^{13}$C NMR spectrum of mixture of compounds 5f and 5g (125 MHz, CDCl$_3$).
$^1$H and $^{13}$C NMR Spectra of cations A, D in TfOH and their comparison with the spectra of neutral initial compounds 1a and 2

$^1$H NMR spectrum of cation A (CF$_3$SO$_3$H, 400 MHz, r.t.).

$^1$H NMR spectrum of compound 1 (CDCl$_3$, 500 MHz, r.t.).

$^1$H NMR spectrum of compound 1 (CDCl$_3$, 500 MHz, r.t.).

Figure S45. Comparison of $^1$H NMR spectra of A and 1a (arrows show shifts of the corresponding signals).
\(^{13}\text{C}\) NMR spectrum of cation A (CF\(_3\)SO\(_3\)H, 100 MHz, r.t.).

\(^{13}\text{C}\) NMR spectrum of compound 1 [CDCl\(_3\), 125 MHz, r.t.].

Figure S46. Comparison of \(^{13}\text{C}\) NMR spectra of A (mesomeric structures are shown) and 1a (arrows show shifts of the corresponding signals). At the bottom \(^{13}\text{C}\) NMR spectra of 1a (CDCl\(_3\), 125 MHz).
$^1$H NMR spectrum of cation D [CF$_3$SO$_3$H, 500 MHz, r.t.].

$^1$H NMR spectrum of compound 2 [CDCl$_3$, 500 MHz, r.t.].

Figure S47. Comparison of $^1$H NMR spectra of D and 2 (arrows show shifts of the corresponding signals).
$^{13}$C NMR spectrum of compound 2 [CDCl$_3$, 125 MHz, r.t.].

Figure S48. Comparison of $^{13}$C NMR spectra of D (mesomeric structures are shown) and 2 (arrows show shifts of the corresponding signals).
MALDI-MS data for oligomers obtained under the reaction of 2,5-DFF with o- and m-xylene in TfOH

Figure S49. MALDI-MS spectrum of oligomers obtained at the reaction of 2 with ortho-xylene.
Figure S50. MALDI-MS spectrum of oligomers obtained at the reaction of 2 with meta-xylene.
Details of DFT-calculations of compounds 1, 2 and cations A, B, C, D

**Compound 1a**

Energy $E = -458.041834074 \text{ h}$, $G^{298} = -457.964668 \text{ h}$, $\mu = 6.61 \text{ D}$

Cartesian coordinates, Å

| N | atom | x     | y     | z     |
|---|------|-------|-------|-------|
| 1 | O    | 0.000000 | 0.864407 | 0.000000 |
| 2 | C    | -0.986483 | -0.055234 | 0.000000 |
| 3 | C    | -0.465924 | -1.320824 | 0.000000 |
| 4 | C    | 0.941784 | -1.170256 | 0.000000 |
| 5 | C    | 1.197128 | 0.176033 | 0.000000 |
| 6 | C    | -2.379881 | 0.468972 | 0.000000 |
| 7 | O    | -3.267098 | -0.641692 | 0.000000 |
| 8 | C    | 2.398652 | 0.969177 | 0.000000 |
| 9 | O    | 3.531129 | 0.505984 | 0.000000 |
| 10| H    | -1.029505 | -2.235689 | 0.000000 |
| 11| H    | 1.683763 | -1.949320 | 0.000000 |
| 12| H    | -2.529668 | 1.098175 | 0.883123 |
| 13| H    | -2.529668 | 1.098175 | -0.883123 |
| 14| H    | -4.168596 | -0.306828 | 0.000000 |
| 15| H    | 2.229774 | 2.058686 | 0.000000 |
Summary of Natural Population Analysis:

| Atom | No | Charge  | Core   | Valence | Rydberg | Total   |
|------|----|---------|--------|---------|---------|---------|
| O    | 1  | -0.46421| 1.99969| 6.43866 | 0.02586 | 8.46421 |
| C    | 2  | 0.35201 | 1.99898| 3.62440 | 0.02462 | 5.64799 |
| C    | 3  | -0.30165| 1.99902| 4.28329 | 0.01934 | 6.30165 |
| C    | 4  | -0.19225| 1.99904| 4.17480 | 0.01840 | 6.19225 |
| C    | 5  | 0.15211 | 1.99891| 3.82465 | 0.02434 | 5.84789 |
| C    | 6  | -0.06574| 1.99911| 4.04446 | 0.02218 | 6.06574 |
| O    | 7  | -0.75019| 1.99978| 6.73865 | 0.01176 | 8.75019 |
| C    | 8  | 0.37870 | 1.99931| 3.58987 | 0.03212 | 5.62130 |
| O    | 9  | -0.60820| 1.99977| 6.58343 | 0.02500 | 8.60820 |
| H    | 10 | 0.24446 | 0.00000| 0.75387 | 0.00167 | 0.75554 |
| H    | 11 | 0.24186 | 0.00000| 0.75638 | 0.00176 | 0.75814 |
| H    | 12 | 0.19463 | 0.00000| 0.80291 | 0.00246 | 0.80537 |
| H    | 13 | 0.19463 | 0.00000| 0.80291 | 0.00246 | 0.80537 |
| H    | 14 | 0.48723 | 0.00000| 0.50815 | 0.00463 | 0.51277 |
| H    | 15 | 0.13661 | 0.00000| 0.86030 | 0.00308 | 0.86339 |

* Total * 0.00000 17.99361 47.78673 0.21966 66.00000

Bond lengths, Å
Cation A

Energy $E = -458.83480078 \text{ hartrees}$, $G^{298} = -458.72961 \text{ hartrees}$, $\mu = 8.11 \text{ D}$

Cartesian coordinates, Å

| N | atom | x       | y       | z       |
|---|------|---------|---------|---------|
| 1 | O    | -0.034647 | -0.664499 | -0.329771 |
| 2 | C    | -0.996473  | 0.260455  | -0.293952  |
| 3 | C    | -0.487065  | 1.509913  | -0.000781  |
| 4 | C    | 0.887770   | 1.340062  | 0.159221   |
| 5 | C    | 1.144682   | -0.013442 | -0.048386  |
| 6 | C    | -2.374739  | -0.186572 | -0.588529  |
| 7 | O    | -3.048099  | -0.572566 | 0.720438   |
| 8 | C    | 2.279331   | -0.812097 | -0.040912  |
| 9 | O    | 3.483550   | -0.435385 | 0.204686   |
|10 | H    | -1.050448  | 2.422100  | 0.080969   |
|11 | H    | 1.609190   | 2.104541  | 0.390482   |
|12 | H    | -2.984046  | 0.624438  | -0.965188  |
|13 | H    | -2.412685  | -1.053176 | -1.237058  |
|14 | H    | -4.018369  | -0.469969 | 0.683095   |
|15 | H    | 2.184463   | -1.868826 | -0.258565  |
|16 | H    | 3.585496   | 0.510239  | 0.407099   |
|17 | H    | -2.841074  | -1.479667 | 1.016374   |
## Summary of Natural Population Analysis:

### Natural Population

| Atom No | Charge | Core      | Valence  | Rydberg   | Total   |
|---------|--------|-----------|----------|-----------|---------|
| 1       | -0.40565 | 1.99968   | 6.38072  | 0.02524   | 8.40565 |
| 2       | 0.37106  | 1.99902   | 3.60605  | 0.02386   | 5.62894 |
| 3       | -0.21975 | 1.99904   | 4.20222  | 0.01849   | 6.21975 |
| 4       | -0.09663 | 1.99908   | 4.08050  | 0.01705   | 6.09663 |
| 5       | 0.15832  | 1.99895   | 3.82204  | 0.02069   | 5.84168 |
| 6       | -0.06003 | 1.99899   | 4.04175  | 0.01929   | 6.06003 |
| 7       | -0.62124 | 1.99973   | 6.61222  | 0.00929   | 8.62124 |
| 8       | 0.42789  | 1.99910   | 3.54737  | 0.02564   | 5.57211 |
| 9       | -0.53880 | 1.99972   | 6.51636  | 0.02273   | 8.53880 |
| 10      | 0.27072  | 0.00000   | 0.72767  | 0.00161   | 0.72928 |
| 11      | 0.26700  | 0.00000   | 0.73150  | 0.00150   | 0.73300 |
| 12      | 0.26228  | 0.00000   | 0.73626  | 0.00145   | 0.73772 |
| 13      | 0.25756  | 0.00000   | 0.74065  | 0.00179   | 0.74244 |
| 14      | 0.57891  | 0.00000   | 0.41813  | 0.00295   | 0.42109 |
| 15      | 0.23780  | 0.00000   | 0.76064  | 0.00156   | 0.76220 |
| 16      | 0.53445  | 0.00000   | 0.46299  | 0.00256   | 0.46555 |
| 17      | 0.57608  | 0.00000   | 0.42097  | 0.00294   | 0.42392 |

*Total* 2.00000 17.99331 47.80805 0.19864 66.00000

Bond lengths, Å
Cation B

Energy $E = -382.322457055 \text{ h}$, $G^{298} = -382.24397 \text{ h}$, $\mu = 1.69 \text{ D}$

Cartesian coordinates, Å

| N | atom | x     | y     | z     |
|---|------|-------|-------|-------|
| 1 | O    | -0.443138 | -0.875729 | 0.000657 |
| 2 | C    | -1.579324 | -0.097073 | 0.000080 |
| 3 | C    | -1.205667 | 1.265717 | -0.000139 |
| 4 | C    | 0.181127 | 1.305297 | 0.000159 |
| 5 | C    | 0.583835 | -0.029310 | 0.000587 |
| 6 | C    | -2.798187 | -0.697398 | -0.000418 |
| 7 | C    | 1.876294 | -0.681916 | -0.000158 |
| 8 | O    | 2.992995 | -0.112648 | -0.000394 |
| 9 | H    | -1.886556 | 2.100022 | -0.000482 |
|10 | H    | 0.803960 | 2.182990 | 0.000156 |
|11 | H    | -3.693034 | -0.091669 | -0.001234 |
|12 | H    | -2.885630 | -1.775051 | -0.000139 |
|13 | H    | 1.909434 | -1.767012 | -0.001161 |
|14 | H    | 3.004495 | 0.865838 | 0.000089 |
### Summary of Natural Population Analysis:

#### Natural Population

| Atom | No | Charge   | Core     | Valence | Rydberg | Total   |
|------|----|----------|----------|---------|---------|---------|
| O    | 1  | -0.37376 | 1.99968  | 6.34862 | 0.02545 | 8.37376 |
| C    | 2  | 0.20914  | 1.99901  | 3.77025 | 0.02160 | 5.79086 |
| C    | 3  | -0.01031 | 1.99909  | 3.99406 | 0.01716 | 6.01031 |
| C    | 4  | -0.16214 | 1.99907  | 4.14528 | 0.01779 | 6.16214 |
| C    | 5  | 0.31326  | 1.99904  | 3.99406 | 0.01716 | 6.01031 |
| C    | 6  | 0.05403  | 1.99915  | 3.93465 | 0.01217 | 5.94597 |
| C    | 7  | 0.52780  | 1.99927  | 3.44718 | 0.02575 | 5.47220 |
| O    | 8  | -0.45322 | 1.99969  | 6.42998 | 0.02356 | 8.45322 |
| H    | 9  | 0.28457  | 0.00000  | 0.71402 | 0.00142 | 0.71543 |
| H    | 10 | 0.28751  | 0.00000  | 0.71080 | 0.00169 | 0.71249 |
| H    | 11 | 0.25309  | 0.00000  | 0.74581 | 0.00110 | 0.74691 |
| H    | 12 | 0.25219  | 0.00000  | 0.74645 | 0.00136 | 0.74781 |
| H    | 13 | 0.25731  | 0.00000  | 0.74120 | 0.00150 | 0.74269 |
| H    | 14 | 0.56054  | 0.00000  | 0.43707 | 0.00239 | 0.43946 |

* Total * 2.00000 15.99401 39.83217 0.17382 56.00000

Bond lengths, Å
Compound 2

Energy $E = -456.829375906 \text{ h}$, $G^{298} = -456.773016 \text{ h}$, $\mu = 0.44 \text{ D}$

Cartesian coordinates, Å

| N | atom | x     | y     | z     |
|---|------|-------|-------|-------|
| 1 | C    | 0.000000 | -1.092442 | 0.024938 |
| 2 | C    | 0.000000 | -0.704168 | -1.293969 |
| 3 | C    | 0.000000 | 0.704168  | -1.293969 |
| 4 | C    | 0.000000 | 1.092442  | 0.024938  |
| 5 | C    | 0.000000 | 0.000000  | 0.835837  |
| 6 | C    | 0.000000 | 2.392438  | 0.678584  |
| 7 | O    | 0.000000 | 3.446190  | 0.070458  |
| 8 | C    | 0.000000 | -2.392438 | 0.678584  |
| 9 | O    | 0.000000 | -3.446190 | 0.070458  |
|10 | H    | 0.000000 | -1.363436 | -2.143574 |
|11 | H    | 0.000000 | 1.363436  | -2.143574 |
|12 | H    | 0.000000 | 2.358377  | 1.779244  |
|13 | H    | 0.000000 | -2.358377 | 1.779244  |
Summary of Natural Population Analysis:

Natural Population

| Atom | No | Charge  | Core     | Valence | Rydberg | Total    |
|------|----|---------|----------|---------|---------|----------|
| C    | 1  | 0.20968 | 1.99895  | 3.76720 | 0.02416 | 5.79032  |
| C    | 2  | -0.20918| 1.99905  | 4.19188 | 0.01825 | 6.20918  |
| C    | 3  | -0.20918| 1.99905  | 4.19188 | 0.01825 | 6.20918  |
| C    | 4  | 0.20968 | 1.99895  | 3.76720 | 0.02416 | 5.79032  |
| O    | 5  | -0.43639| 1.99970  | 6.41236 | 0.02433 | 8.43639  |
| C    | 6  | 0.39144 | 1.99935  | 3.57741 | 0.03181 | 5.60856  |
| O    | 7  | -0.56826| 1.99977  | 6.54363 | 0.02485 | 8.56826  |
| C    | 8  | 0.39144 | 1.99935  | 3.57741 | 0.03181 | 5.60856  |
| O    | 9  | -0.56826| 1.99977  | 6.54363 | 0.02485 | 8.56826  |
| H    | 10 | 0.24957 | 0.00000  | 0.74869 | 0.00174 | 0.75043  |
| H    | 11 | 0.24957 | 0.00000  | 0.74869 | 0.00174 | 0.75043  |
| H    | 12 | 0.14493 | 0.00000  | 0.85216 | 0.00290 | 0.85507  |
| H    | 13 | 0.14493 | 0.00000  | 0.85216 | 0.00290 | 0.85507  |

* Total * 0.00000 17.99394 45.77430 0.23176 64.00000

Bond lengths, Å
Cation C

Energy \( E = -457.230436542 \text{ h}, \quad G^{298} = -457.161104 \text{ h}, \quad \mu = 8.27 \text{ D} \)

Cartesian coordinates, Å

| N | atom | x     | y     | z     |
|---|------|-------|-------|-------|
| 1 | C    | -1.120282 | 0.128944 | 0.000000 |
| 2 | C    | -0.847112 | -1.229886 | 0.000000 |
| 3 | C    | 0.538545 | -1.344397 | 0.000000 |
| 4 | C    | 1.045949 | -0.042077 | 0.000000 |
| 5 | O    | 0.000000 | 0.852180 | 0.000000 |
| 6 | C    | 2.311716 | 0.521564 | 0.000000 |
| 7 | O    | 3.437887 | -0.103273 | 0.000000 |
| 8 | C    | -2.399780 | 0.871803 | 0.000000 |
| 9 | O    | -3.460135 | 0.294496 | 0.000000 |
|10 | H    | -1.574695 | -2.020974 | 0.000000 |
|11 | H    | 1.110430 | -2.256356 | 0.000000 |
|12 | H    | 2.409071 | 1.600222 | 0.000000 |
|13 | H    | -2.311546 | 1.966977 | 0.000000 |
|14 | H    | 3.370513 | -1.072801 | 0.000000 |
Summary of Natural Population Analysis:

| Atom | No | Charge | Core   | Valence | Rydberg | Total   |
|------|----|--------|--------|---------|---------|---------|
| C    | 1  | 0.32980| 1.99902| 3.64685 | 0.02433 | 5.67020 |
| C    | 2  | -0.21737| 1.99906| 4.19928 | 0.01902 | 6.21737 |
| C    | 3  | -0.10552| 1.99908| 4.08938 | 0.01706 | 6.10552 |
| C    | 4  | 0.16148 | 1.99896| 3.81875 | 0.02081 | 5.83852 |
| O    | 5  | -0.40416| 1.99969| 6.37912 | 0.02535 | 8.40416 |
| C    | 6  | 0.41692 | 1.99909| 3.55823 | 0.02576 | 5.58308 |
| O    | 7  | -0.54471| 1.99972| 6.52237 | 0.02262 | 8.54471 |
| C    | 8  | 0.40043 | 1.99939| 3.56892 | 0.03127 | 5.59957 |
| O    | 9  | -0.50246| 1.99977| 6.47805 | 0.02464 | 8.50246 |
| H    | 10 | 0.26824 | 0.00000| 0.72988 | 0.00187 | 0.73176 |
| H    | 11 | 0.26448 | 0.00000| 0.73401 | 0.00151 | 0.73552 |
| H    | 12 | 0.23609 | 0.00000| 0.76234 | 0.00157 | 0.76391 |
| H    | 13 | 0.16363 | 0.00000| 0.83426 | 0.00211 | 0.83637 |
| H    | 14 | 0.53315 | 0.00000| 0.46427 | 0.00258 | 0.46685 |

* Total * 1.00000 17.99377 45.78571 0.22052 64.00000

Bond lengths, Å
Cation D

Energy $E = -457.60669012 \, \text{h}$, $G^{298} = -457.523348 \, \text{h}$, $\mu = 2.80 \, \text{D}$

Cartesian coordinates,Å

| N | atom | x     | y     | z     |
|---|------|-------|-------|-------|
| 1 | C    | -0.015980 | -1.081155 | 0.000000 |
| 2 | C    | 1.319768  | -0.697717 | 0.000000 |
| 3 | C    | 1.319768  | 0.697717  | 0.000000 |
| 4 | C    | -0.015980 | 1.081155  | 0.000000 |
| 5 | O    | -0.828188 | 0.000000  | 0.000000 |
| 6 | C    | -0.703129 | 2.321798  | 0.000000 |
| 7 | O    | -0.184974 | 3.477155  | 0.000000 |
| 8 | C    | -0.703128 | -2.321798 | 0.000000 |
| 9 | O    | -0.184974 | -3.477155 | 0.000000 |
|10 | H    | 2.186249  | -1.335940 | 0.000000 |
|11 | H    | 2.186249  | 1.335941  | 0.000000 |
|12 | H    | -1.787533 | 2.313127  | 0.000000 |
|13 | H    | -1.787533 | -2.313128 | 0.000000 |
|14 | H    | 0.789872  | 3.520973  | 0.000000 |
|15 | H    | 0.789873  | -3.520972 | 0.000000 |
### Summary of Natural Population Analysis:

| Atom | No. | Charge | Core     | Valence | Rydberg | Total   |
|------|-----|--------|----------|---------|---------|---------|
| C    | 1   | 0.22845| 1.99901  | 3.75205 | 0.02050 | 5.77155 |
| C    | 2   | -0.11924| 1.99908  | 4.10252 | 0.01764 | 6.11924 |
| C    | 3   | -0.11924| 1.99908  | 4.10252 | 0.01764 | 6.11924 |
| C    | 4   | 0.22845 | 1.99901  | 3.75205 | 0.02050 | 5.77155 |
| O    | 5   | -0.37561| 1.99969  | 6.35168 | 0.02425 | 8.37561 |
| C    | 6   | 0.48830 | 1.99920  | 3.48679 | 0.02571 | 5.51170 |
| O    | 7   | -0.48915| 1.99970  | 6.46631 | 0.02313 | 8.48915 |
| C    | 8   | 0.48830 | 1.99920  | 3.48679 | 0.02571 | 5.51170 |
| O    | 9   | -0.48915| 1.99970  | 6.46631 | 0.02313 | 8.48915 |
| H    | 10  | 0.28056 | 0.00000  | 0.71777 | 0.00167 | 0.71944 |
| H    | 11  | 0.28056 | 0.00000  | 0.71777 | 0.00167 | 0.71944 |
| H    | 12  | 0.24898 | 0.00000  | 0.74950 | 0.00152 | 0.75102 |
| H    | 13  | 0.24898 | 0.00000  | 0.74950 | 0.00152 | 0.75102 |
| H    | 14  | 0.54990 | 0.00000  | 0.44764 | 0.00246 | 0.45010 |
| H    | 15  | 0.54990 | 0.00000  | 0.44764 | 0.00246 | 0.45010 |

*Total* 2.00000 17.99368 45.79682 0.20950 64.00000

Bond lengths, Å
