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Webbing a network of reliable thermochemistry around lignin building blocks: tri-methoxy-benzenes

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Table S1

Provenance, Purity, and Methods of Purification of Sample Used in This Work.

Compound	State	Source	Initial purity	Final purity [a]	Final purity [b]
1,2,3-tri-methoxy-benzene	cr	TCI	0.99	0.9999	0.9997
1,2,4-tri-methoxy-benzene	liq	TCI	0.98	0.9997	
1,3,5-tri-methoxy-benzene	cr	Sigma-Aldrich	0.99	0.9999	0.9999
3,4,5-tri-methoxy-toluene	liq	Alfa-Aesar	0.98	0.9997	

[a] Solid samples were purified by using fractional sublimation at reduced pressure. Liquid samples were purified by using vacuum fractional distillation. Mass fraction impurity determined by the gas chromatography. Not significant mass fraction of water at the level of 15-20 ppm (detection level of the KF titration) was detected by the Karl Fisher titration. The final purities are given on the water-free basis.

[b] Mass fraction impurity determined by the differential scanning calorimetry

Table S2.

Compilation of data on molar heat capacities $C_{p,m}^{o}$(cr or liq) and heat capacity differences $\Delta_{cr,l}^{g}C_{p,m}^{o}$ (in J·K^{-1}·mol^{-1}) at $T = 298.15$ K for the methoxy-substituted benzenes

Compounds	$C_{p,m}^{o}(cr)_a$	$-\Delta_{cr}^{g}C_{p,m}^{o}$ [b]	$C_{p,m}^{o}(liq)$ [a]	$-\Delta_{l}^{g}C_{p,m}^{o}$ [b]
1,2,3-tri-methoxy-benzene	243.3 [c]	37.2	335.7	97.9
1,2,4-tri-methoxy-benzene	243.3	37.2	335.7	97.9
1,3,5-tri-methoxy-benzene	243.3	37.2	335.7	97.9
3,4,5-tri-methoxy-toluene	270.9	41.4	364.1	105.2

[a] Calculated by the group-contribution procedure developed by Chickos *et al.*[1,2]. We used the contribution for the methoxy group 39.9 J·K^{-1}·mol^{-1} (liq). The latter contribution was derived from the experimental value $C_{p,m}^{o}(liq) = 199.0$ J·K^{-1}·mol^{-1} of methoxybenzene.[3]

[b] Calculated according to the procedure developed by Chickos and Acree.[2].

[c] For comparison the experimental value $C_{p,m}^{o}(cr, 298.15\ K) = 240.9$ J·K^{-1}·mol^{-1} (see Table S3).

Heat capacity measurements. We used PerkinElmer DSC Pyris 1. The experimental protocol of heat capacity determination included the three equal iterations with an empty pan, a reference sample of sapphire and a sample of each compound being researched. For each iteration there was an equal thermal program of study; for all steps of each measurement the same pan was used. In each iteration the sample was heated with the step of 50 K at heating rate of 10 K·min⁻¹. Before and after each scanning step sample was kept isothermally for two minutes. Inside each iteration the temperature range was divided into intervals of 50 K to heat samples and between them there was a shift of 25 K. Each step for all iterations was repeated 4 times.

The heat capacity was derived with the Perkin Elmer software. The heat capacity determination technique was tested with a reference sample of benzoic acid by Parr Instrument Company. In the chosen temperature range the experimental values agreed with the reference values within ±1 %. The expanded uncertainty (k = 2) for the heat capacity measured by this method was estimated to be $0.02 \times C_{p,m}^{o}$. See for more details ref. [4].

Table S3 Compilation of data on molar heat capacities $C_{p,m}^{o}$(cr or liq) (in J·K⁻¹·mol⁻¹) at $T = 298.15$ K for 1,2,3-trimethoxy-benzene

T, K	$C_{p,m}^{o}$(cr)[a]	T, K	$C_{p,m}^{o}$(liq)
238	201.86	335	343.11
241	203.33	337	343.65
246	206.31	340	344.66
251	209.40	343	345.62
256	212.56	346	346.61
261	216.16	349	347.49
266	219.67	335	343.11
271	222.89	337	343.65
276	226.60		
281	230.43		
286	233.98		
291	235.94		
296	238.98		

[a] The experimental data were fitted with the following equation:
$C_{p,m}^{o}(cr)$/R = 0.0311 + 4.734×10⁻⁴(T/K) from 238 to 296 K (with R = 8.314462 J·K⁻¹·mol⁻¹).
$C_{p,m}^{o}(cr, 298.15\ K)$ = 240.9 J·K⁻¹·mol⁻¹

Transpiration Method. Vapour pressures were measured using the transpiration method. About 0.8 g of the sample was mixed with small glass beads and placed in the thermostatted U-shaped saturator. A stream of N_2 with a well-defined flow rate was passed through the saturator at constant temperature (± 0.1 K), and the transported material was collected in a cold trap. The amount of condensed substance was determined by GC. The saturation vapour pressure p_i at each temperature T_i was calculated from the amount of product collected within a definite period of time:
$$p_i = m_i \cdot R \cdot T_a / V \cdot M_i ; \qquad V = (n_{N2} + n_i) \cdot R \cdot T_a / P_a \qquad (S1),$$
where V is the volume of the gas phase consisting of the n_{N2} moles of the carrier gas and n_i mole of gaseous compound under study at the atmospheric pressure P_a and the ambient temperature T_a. The volume of the carrier gas V_{N2} was determined by the digital flow rate sensor from integration with a microcontroller. We used the Honeywell S&C - HAFBLF0200C2AX5 digital flow rate sensor with uncertainty at the level of 2.5 %. The flow rate of the nitrogen stream was also controlled by using a soap bubble flow meter (HP soap film flowmeter (model 0101-0113)) and

optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The volume of the carrier gas V_{N2} was readied from the digital flow rate sensor. The amount of the compound under study n_i in the carrier gas was estimated applying the ideal gas law at each temperature. Prior to the beginning the vapour pressure measurements, the pre-conditioning of the sample was performed first at (293-300) K (one hour) in order to withdraw possible water traces. Then the saturator was kept at 310-315 K (in order to remove possible traces of volatile compounds). In order to ascertain the completing of pre-conditioning, three samples were taken during the sample flashing at a suitable temperature and analysed by the GC. A constant vapour pressure at this temperature indicated that the transpiration experiments could start. No additional impurities were detected by the GC analysis of the transported material. The absence of impurities and decomposition products was rechecked by GC analysis of the saturator content after completing of the whole series of experiments. The primary experimental data are given in Table S4. See for more details refs. [5,6].

Table S4

Results from the Transpiration Method: Absolute Vapour Pressures p_i, Standard Molar Sublimation/Vaporization Enthalpies $\Delta_{cr/l}^{g}H_m^{o}$ and Standard Molar Sublimation/Vaporization Entropies $\Delta_{cr/l}^{g}S_m^{o}$

$T/$ K[a]	$m/$ mg[b]	$V(N_2)^c /$ dm³	$T_a/$ K[d]	Flow/ dm³·h⁻¹	$p_i/$ Pa[e]	$u(p_i)/$ Pa[f]	$\Delta_{cr/l}^{g}H_m^{o}(T)/$ kJ·mol⁻¹	$\Delta_{cr/l}^{g}S_m^{o}(T)/$ J·K⁻¹·mol⁻¹
			1,2,3-trimethoxy-benzene, $\Delta_{cr}^{g}H_m^{o}$(298.15 K) = (92.4 ± 0.7) kJ·mol⁻¹					
			$\ln (p_i/p_{ref}) = \dfrac{348.4}{R} - \dfrac{103491.0}{RT} - \dfrac{37.2}{R}\ln\dfrac{T}{298.15}$					
288.2	2.25	102.929	295.6	2.57	0.32	0.01	92.8	216.7
291.2	1.67	51.023	295.6	2.59	0.48	0.02	92.7	216.4
294.3	1.51	31.166	295.6	2.59	0.71	0.02	92.5	215.9
297.2	1.19	16.662	295.6	2.59	1.05	0.03	92.4	215.7
300.3	0.69	6.734	295.6	2.59	1.49	0.04	92.3	215.1
303.2	0.97	6.561	295.6	2.59	2.17	0.06	92.2	214.9
306.3	1.22	5.784	295.6	2.59	3.08	0.08	92.1	214.3
308.3	1.50	5.525	295.6	2.59	3.95	0.10	92.0	214.2
310.3	1.45	4.144	295.6	2.59	5.11	0.15	91.9	214.2
312.3	1.35	3.151	295.6	2.59	6.24	0.18	91.9	213.7
314.3	1.19	2.245	295.6	2.59	7.78	0.22	91.8	213.5
			1,2,3-trimethoxy-benzene, $\Delta_{l}^{g}H_m^{o}$(298.15 K) = (73.0 ± 0.5) kJ·mol⁻¹					
			$\ln (p_i/p_{ref}) = \dfrac{348.3}{R} - \dfrac{102212.3}{RT} - \dfrac{97.9}{R}\ln\dfrac{T}{298.15}$					
318.1	1.09	1.360	295.5	2.59	11.75	0.32	71.1	148.2
321.2	1.50	1.425	295.5	2.59	15.33	0.41	70.8	147.3
324.3	1.45	1.079	295.5	2.59	19.61	0.52	70.5	146.3
327.2	1.70	0.993	295.5	2.59	25.06	0.65	70.2	145.6
331.2	2.25	0.950	295.5	2.59	34.56	0.89	69.8	144.5
334.3	2.58	0.863	295.5	2.59	43.68	1.12	69.5	143.6
337.3	2.51	0.691	295.5	2.59	53.13	1.35	69.2	142.5
340.2	3.09	0.691	295.5	2.59	65.35	1.66	68.9	141.6
343.1	2.88	0.518	295.5	2.59	81.25	2.06	68.6	140.9
346.3	2.25	0.324	295.5	2.59	101.3	2.56	68.3	140.0

1,2,4-trimethoxy-benzene, $\Delta_l^g H_m^o$(298.15 K) = (75.7 ± 0.5) kJ·mol⁻¹

$$\ln (p_i/p_{ref}) = \frac{350.8}{R} - \frac{104844.6}{RT} - \frac{97.9}{R}ln\frac{T}{298.15}$$

309.7	0.73	3.788	293.8	3.99	2.81	0.08	74.5	153.5
314.1	0.77	2.649	294.4	3.97	4.22	0.11	74.1	152.1
319.2	0.69	1.527	294.9	3.98	6.56	0.19	73.6	150.5
324.2	0.64	0.945	294.9	2.98	9.89	0.27	73.1	148.9
329.1	0.73	0.704	294.7	2.01	15.16	0.40	72.6	147.6
329.2	1.04	1.000	301.2	3.00	15.48	0.41	72.6	147.7
329.2	0.79	0.751	300.8	3.01	15.66	0.42	72.6	147.8
332.1	0.74	0.560	297.0	1.98	19.33	0.51	72.3	146.7
332.1	0.77	0.616	301.8	1.48	18.53	0.49	72.3	146.3
334.2	0.76	0.503	295.0	2.01	21.91	0.57	72.1	145.8
335.2	0.82	0.497	301.4	1.99	24.52	0.64	72.0	145.8
338.2	0.77	0.381	300.9	1.00	29.91	0.77	71.7	144.7
339.2	0.70	0.314	294.7	0.99	32.47	0.84	71.6	144.5
341.2	0.75	0.296	300.3	0.99	37.54	0.96	71.4	143.8
342.1	1.37	0.496	298.2	0.99	40.83	1.05	71.4	143.7
344.1	0.80	0.248	294.7	0.99	46.72	1.19	71.2	143.0
344.1	0.81	0.254	300.6	0.98	47.66	1.22	71.2	143.2
345.2	1.03	0.298	298.1	0.99	51.15	1.30	71.1	142.8
347.1	0.99	0.248	295.0	0.99	58.21	1.48	70.9	142.2
348.2	1.08	0.247	297.0	0.99	64.30	1.63	70.8	142.1
350.1	1.19	0.231	294.8	0.99	75.17	1.90	70.6	141.8

1,3,5-trimethoxy-benzene, $\Delta_{cr}^g H_m^o$(298.15 K) = (90.3 ± 0.5) kJ·mol⁻¹

$$\ln (p_i/p_{ref}) = \frac{333.9}{R} - \frac{101366.0}{RT} - \frac{37.2}{R}ln\frac{T}{298.15}$$

288.0	0.67	72.497	296.3	4.78	0.13	0.01	90.7	202.4
296.3	0.56	21.351	296.3	4.78	0.39	0.01	90.3	201.3
298.7	0.63	18.288	296.3	5.08	0.51	0.02	90.3	200.9
303.2	0.83	13.801	296.3	5.08	0.88	0.03	90.1	200.4
304.2	1.03	15.750	296.3	6.30	0.96	0.03	90.1	200.0
307.2	0.90	9.450	296.3	6.30	1.40	0.04	89.9	199.9
308.2	0.49	4.741	296.3	5.08	1.52	0.04	89.9	199.5
311.4	1.23	7.770	296.3	6.30	2.31	0.06	89.8	199.6
314.4	1.10	5.145	296.3	6.30	3.12	0.08	89.7	199.0
316.5	0.90	3.330	296.3	3.77	3.96	0.10	89.6	198.8
317.4	1.19	4.148	296.3	6.30	4.21	0.11	89.6	198.4
319.5	1.11	2.953	296.3	3.77	5.50	0.16	89.5	198.6
320.2	1.24	3.150	296.3	6.30	5.79	0.17	89.5	198.3
323.2	1.24	2.310	296.3	6.30	7.89	0.22	89.3	197.9
325.5	1.75	2.513	296.3	3.77	10.18	0.28	89.3	197.8
326.2	1.10	1.470	296.3	6.30	10.93	0.30	89.2	197.8

1,3,5-trimethoxy-benzene, $\Delta_l^g H_m^o$(298.15 K) = (68.7 ± 0.4) kJ·mol⁻¹

$$\ln (p_i/p_{ref}) = \frac{329.3}{R} - \frac{97850.6}{RT} - \frac{97.9}{R}ln\frac{T}{298.15}$$

330.5	0.57	0.512	296.2	1.06	16.36	0.43	65.5	125.7
331.2	0.62	0.539	296.2	1.06	16.92	0.45	65.4	125.4
333.5	0.69	0.504	296.2	1.06	20.11	0.53	65.2	124.8
336.3	0.81	0.477	296.2	1.06	24.78	0.64	64.9	124.1
337.3	1.13	0.636	296.2	1.06	25.96	0.67	64.8	123.6
339.4	0.83	0.406	296.2	1.06	30.02	0.78	64.6	123.0

341.4	0.98	0.415	296.2	1.06	34.42	0.89	64.4	122.5
342.3	1.12	0.451	296.2	1.06	36.26	0.93	64.3	122.1
345.3	0.79	0.265	296.2	1.06	43.89	1.12	64.1	121.2
346.3	1.09	0.336	296.2	1.06	47.52	1.21	64.0	121.1
348.3	0.84	0.230	296.2	1.06	53.37	1.36	63.8	120.4
350.3	1.23	0.292	296.2	1.06	61.68	1.57	63.6	120.0
351.4	1.01	0.230	296.2	1.06	64.54	1.64	63.5	119.5
354.4	0.93	0.173	296.2	1.06	78.50	1.99	63.2	118.8
355.4	1.44	0.247	296.2	1.06	85.01	2.15	63.1	118.7
357.5	1.13	0.177	296.2	1.06	93.91	2.37	62.9	117.9
359.4	1.52	0.212	296.2	1.06	104.8	2.65	62.7	117.4
360.6	1.38	0.177	296.2	1.06	113.9	2.87	62.6	117.1
363.6	1.59	0.177	296.2	1.06	131.7	3.32	62.3	116.1
364.3	1.70	0.177	296.2	1.06	140.9	3.55	62.2	116.2
366.6	1.82	0.168	296.2	1.06	158.1	3.98	62.0	115.4
368.5	1.90	0.159	296.2	1.06	174.5	4.39	61.8	114.9
369.3	1.87	0.150	296.2	1.06	182.1	4.58	61.7	114.6
371.4	2.17	0.150	296.2	1.06	211.1	5.30	61.5	114.4
372.4	2.11	0.141	296.2	1.06	218.5	5.49	61.4	114.0
374.3	2.15	0.129	296.2	1.06	243.6	6.11	61.2	113.5
375.3	2.34	0.133	296.2	1.06	257.6	6.47	61.1	113.3

3,4,5-trimethoxy-toluene, $\Delta_l^g H_m^o$(298.15 K) = (77.7 ± 0.5) kJ·mol^{-1}

$$\ln (p_i/p_{ref}) = \frac{366.9}{R} - \frac{109273.7}{RT} - \frac{105.8}{R}\ln\frac{T}{298.15}$$

327.2	2.90	3.413	294.8	4.45	15.99	0.42	74.7	155.5
329.2	2.69	2.691	296.4	4.25	18.92	0.50	74.4	154.9
331.1	2.68	2.277	295.0	4.27	22.15	0.58	74.2	154.3
334.1	2.81	1.851	294.6	4.44	28.60	0.74	73.9	153.4
336.5	2.70	1.545	294.2	4.64	32.78	0.84	73.7	152.2
339.1	2.74	1.257	295.2	4.71	41.12	1.05	73.4	151.7
342.0	1.96	0.711	293.4	2.13	51.58	1.31	73.1	150.8
343.9	2.72	0.865	295.0	2.08	59.30	1.51	72.9	150.2
346.4	2.61	0.671	295.4	2.01	73.23	1.86	72.6	149.7
348.9	3.30	0.719	297.6	2.16	87.32	2.21	72.4	148.9
352.1	2.72	0.474	294.6	1.24	107.7	2.72	72.0	147.7
355.0	2.88	0.420	298.4	1.68	130.4	3.29	71.7	146.8
358.1	2.60	0.308	295.4	1.23	158.9	4.00	71.4	145.8
360.9	2.62	0.254	296.4	1.02	194.9	4.90	71.1	145.1
364.2	3.12	0.241	295.2	1.00	243.6	6.12	70.7	144.2
366.2	3.51	0.239	295.6	0.99	276.3	6.93	70.5	143.7

[a] Saturation temperature ($u(T)$ = 0.1 K).
[b] Mass of transferred sample condensed at T = 243 K.
[c] Volume of nitrogen ($u(V)$ = 0.005 dm^3) used to transfer m ($u(m)$ = 0.0001 g) of the sample.
[d] T_a is the temperature of the soap bubble meter used for measurement of the gas flow.
[e] Vapour pressure at temperature T, calculated from the m and the residual vapour pressure at the condensation temperature calculated by an iteration procedure.
[f] Uncertainties were calculated with $u(p_i/\text{Pa})$ = 0.005 +0.025(p_i/Pa) for pressures below 5 Pa and with $u(p_i/\text{Pa})$ = 0.025 + 0.025(p_i/Pa) for pressures from 5 to 3000 Pa. The uncertainties for T, V, p, m, and $\Delta_l^g H_m^o$ are standard uncertainties with 0.683 confidence level, calculated according to procedure described elsewhere.[6-7] The standard uncertainty of vaporization enthalpy $u(\Delta_l^g H_m^o)$ includes uncertainties from transpiration experimental conditions, uncertainties of vapour

pressure, uncertainties from fitting equation, and uncertainties from temperature adjustment to T = 298.15 K.

Correlations of vaporization enthalpies with gas-chromatographic indices. The Kovats´s retention index, J_x, is calculated with help of retention times of n-alkanes used as standards:[8]

$$J_x = \frac{\lg\left(t_x\right) - lg(t_N)}{\lg\left(t_{N+1}\right) - lg(t_N)} \times 100 + 100N$$

(S1),

where x refers to the adjusted retention time t, N is the number of carbon atoms of the n-alkane eluting before, and ($N + 1$) is the number of carbon atoms of the n-alkane eluting after the peak of interest. Thus, the retention time t_x of the compound of interest x is encompassed by retention times of the two n-alkanes. According to the established GC procedure, all retention times are corrected for the "dead" retention time (the retention time of a non-retained component: dichloromethane or methane).[9]

Combustion calorimetry. The liquid samples were encapsulated in small polyethylene ampoules. The solid samples were pressed in pellets. All weightings were performed by using a microbalance with 10^{-6} g resolution. The bomb was not pre-purged with O_2. Test experiments with and without purging with O_2 showed results consistent within the experimental uncertainty. Samples were ignited at 3.04 MPa initial oxygen pressure adjusted to 298.15 K. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but neither was detected. The energy equivalent of the calorimeter ε_{calor} was determined with a standard reference sample of benzoic acid (sample SRM 39j, NIST). Correction for nitric acid (HNO_3) formation was based on titration with 0.1 mol·dm^{-3} NaOH(aq). Auxiliary data required for the reduction are presented in Table S5. See for more details in refs. [10,11].

Table S5.
Formula, density ρ ($T = 293$ K), massic heat capacity c_p ($T = 298.15$ K), of the materials used in the present study.

Compounds	Formula	ρ	$c_p{}^a$
		g·cm^{-3}	J·K^{-1} g^{-1}
1,2,3-tri-methoxy-benzene (cr)	$C_9H_{12}O_3$	1.11 [12]	1.45
1,2,4-tri-methoxy-benzene (liq)	$C_9H_{12}O_3$	1.13 [13]	1.99
3,4,5-tri-methoxy-toluene (liq)	$C_{10}H_{14}O_3$	1.08[14]	2.00
polyethylene [b]	$CH_{1.93}$	0.92	2.53
cotton [b]	$CH_{1.774}O_{0.887}$	1.50	1.67

[a] Estimated by group-contribution method (see Table S2)
[b] Data for density, specific heat capacity, and expansion coefficients of auxiliary materials are from our previous work:[15] specific energy of combustion $\Delta_c u°$(cotton) = -16945.2 J·g^{-1}; $u(\Delta_c u°)$ = 4.2 J·g^{-1}. The specific energy of combustion $\Delta_c u°$(polyethylene) = -46354.6 J·g^{-1}; $u(\Delta_c u°)$ = 3.1 J·g^{-1} was derived from ten combustion experiments performed in this work. The standard uncertainties are reported for the specific energies of combustion.

Table S6. Results for Typical Combustion Experiments at T = 298.15 K ($p°$ = 0.1 MPa) of the Substituted Benzenes [a]

	1,2,3-trimethoxybenzene	1,2,4-trimethoxybenzene	3,4,5-trimethoxytoluene
m (substance) /g	0.395761	0.310990	0.282183
m'(cotton) /g	0.002210	0.001256	0.001238
m''(polyethene) /g	-	0.239774	0.236263
T_i /K	298.13267	298.15260	298.14147
T_f /K	298.97204	299.56601	299.51592
ΔT_c /K	0.76814	1.35641	1.31562
$(\varepsilon_{calor})\cdot(-\Delta T_c)$ /J	-11367.26	-20072.66	-19469.03
$(\varepsilon_{cont})\cdot(-\Delta T_c)$ /J	-12.04	-30.76	-27.64
ΔU_{decomp} HNO_3 /J	3.58	50.17	44.2
ΔU_{corr} /J	6.37	10.32	8.95
$-m'\cdot\Delta_c u'$ /J	37.45	21.28	20.98
$-m''\cdot\Delta_c u''$ /J	-	11114.63	10951.88
$\Delta_c u°$ (liq) /(J·g^{-1})	-28633.2	-28640.8	-30018.3

[a] Results are referenced to T = 298.15 K ($p°$ = 0.1 MPa). The definition of the symbols assigned according to ref.[16,17] as follows: m(substance), m'(cotton) and m''(polyethylene) are, respectively, the mass of compound burnt, the mass of fuse (cotton) and auxiliary polyethylene used in each experiment, masses were corrected for buoyancy; V(bomb) = 0.32 dm^3 is the internal volume of the calorimetric bomb; p^i(gas) = 3.04 MPa is the initial oxygen pressure in the bomb; $m^i(H_2O)$ = 1.00 g is the mass of water added to the bomb for dissolution of combustion gases; ε_{calor} = (14798.37 ± 0.83) J·K^{-1}, uncertainty for the energy equivalent is expressed as the standard uncertainty; $\Delta T_c = T^f - T^i + \Delta T_{corr}$ is the corrected temperature rise from initial temperature T^i to final temperature T^f, with the correction ΔT_{corr} for heat exchange during the experiment; ε_{cont} is the energy equivalents of the bomb contents in their initial ε^i_{cont} and final states ε^f_{cont}, the contribution for the bomb content is calculated with $(\varepsilon_{cont})\cdot(-\Delta T_c)$ = $(\varepsilon^i_{cont})\cdot(T^i - 298.15)$ + $(\varepsilon^f_{cont})\cdot(298.15 - T^f + \Delta T_{corr}.)$. ΔU_{decomp} HNO_3 is the energy correction for the nitric acid formation. ΔU_{corr} is the correction to standard states. Auxiliary data are given in Table S5.

Enthalpy of fusion measurements. Thermal behavior of crystalline samples including melting temperatures and enthalpies of fusion was studied with a commercial Perkin-Elmer DSC Pyris-1. A sample was placed in the standard non-pinned aluminium pan of 40 μl volume. Pan and sample were weighted with a microbalance with the standard uncertainty of 5·10^{-6} g. In the first DSC run the sample was heated with a rate 10 K·min^{-1} to 398 K (~ 30 K above melting temperature provided by supplier) and then cooled down to 298 K, also with the rate 10 K·min^{-1}. Such procedure provided sufficient contact between the sample and the bottom of pan. The DSC experiments were repeated three times. The calibration of the DSC was checked with melting behaviour of reference indium sample. The twice standard deviation of the enthalpy of fusion in the test measurements for reference compound was ± 0.3 kJ·mol^{-1} and ± 0.3 K for the melting temperature. Uncertainties of the enthalpy of fusion values are expressed as expanded uncertainties (at a level of confidence of 0.95, k=2). They include uncertainties from fusion experiment and calibration. Details are reported elsewhere [4].

As a rule, thermochemical calculations are commonly performed at the reference temperature T = 298.15 K. The adjustment of $\Delta_{cr}^{l} H_{m}^{o}(T_{fus})$ was performed with help of the equation [2]:

$$\Delta_{cr}^{l}H_m^o(298.15 \text{ K})/(\text{J·mol}^{-1}) = \Delta_{cr}^{l}H_m^o(T_{\text{fus}}/\text{K}) - (\Delta_{cr}^{g}C_{p,m}^o - \Delta_{l}^{g}C_{p,m}^o) \times [(T_{\text{fus}}/\text{K}) - 298.15 \text{ K}] \quad (S2)$$

where $\Delta_{cr}^{g}C_{p,m}^o$ and $\Delta_{l}^{g}C_{p,m}^o$ were taken from Table S2. With this adjustment, the molar enthalpies of fusion, $\Delta_{cr}^{l}H_m^o(298.15 \text{ K})$ were calculated. Uncertainties in the temperature adjustment of fusion enthalpy from T_{fus} to the reference temperature were estimated to account with 30 % to the total adjustment [2].

Table S7
Thermochemical Data at $T = 298.15$ K ($p° = 0.1$ MPa) for Reference Compounds (in kJ·mol⁻¹).

	$\Delta_f H_m^o(\text{liq})$	$\Delta_l^g H_m^o$	$\Delta_f H_m^o(\text{g})$
benzene	49.0±0.9 [18]	33.9±0.1 [18]	82.9±0.9 [18]
toluene	12.0±1.1 [18]	38.1±0.1 [18]	50.1±1.1 [18]
methoxy-benzene	-117.1±1.4 [19]	46.4±0.3[19]	-70.7±1.4[19]

Table S8
Experimental and Theoretical Gas-Phase Enthalpies of Formation $\Delta_f H_m^o(\text{g})$ at $T = 298.15$ K ($p° = 0.1$ MPa) for Substituted Benzenes as Calculated by G4 Method (in kJ·mol⁻¹).

compound	Exp.[a]	G4		G4	
		AT	calc-exp	AT(corr) [b]	calc-exp
1,2,3-tri-methoxy-benzene	-346.0±2.0	-355.1	9.1	-351.8	5.8
1,2,4-tri-methoxy-benzene	-360.6±2.3	-364.0	3.4	-360.7	0.1
1,3,5-tri-methoxy-benzene	-381.6±3.2	-385.2	3.6	-382.0	0.4
3,4,5-tri-methoxy-toluene	-383.2±2.5	-386.6	3.4	-383.4	0.2

[a] From Table 8.
[b] Calculated by the G4 method according to the standard atomization procedure. (The expanded uncertainty assessed to be ±3.5 kJ·mol⁻¹).[20]
[c] Results from atomization reactions were corrected with help of following equation:
$$\Delta_f H_m^o(\text{g})_{\text{theor}}/ \text{kJ·mol}^{-1} = 1.0023 \times \Delta_f H_m^o(\text{g, AT}) + 4.1 \quad \text{with } R^2 = 0.9992$$

Table S9
Experimental and Theoretical Gas-Phase Enthalpies of Formation $\Delta_f H_m^o(\text{g})$ at $T = 298.15$ K ($p° = 0.1$ MPa) for Substituted Benzenes as Calculated by G3MP2 Method (in kJ·mol⁻¹).

compound	Exp.[a]	G3MP2		G3MP2	
		AT	calc-exp	AT(corr) [b]	calc-exp
1,2,3-tri-methoxy-benzene	-346.0±2.0	-356.6	10.6	-350.2	4.2
1,2,4-tri-methoxy-benzene	-360.6±2.3	-366.2	5.6	-359.8	-0.8
1,3,5-tri-methoxy-benzene	-381.6±3.2	-387.3	5.7	-381.1	-0.5
3,4,5-tri-methoxy-toluene	-383.2±2.5	-388.5	5.3	-382.3	-0.9

[a] From Table 8.
[b] Calculated by the G3MP2 method according to the standard atomization procedure. (The expanded uncertainty assessed to be ±4.1 kJ·mol⁻¹).[21]

Table S10

Experimental and Theoretical Gas-Phase Enthalpies of Formation $\Delta_f H^o_m(\text{g})$ at T = 298.15 K ($p°$ = 0.1 MPa) for Substituted Benzenes as Calculated by G4MP2 Method (in kJ·mol^{-1}).

compound	Exp.[a]	M06/QZ4P		M06/QZ4P	
		AT	calc-exp	AT(corr)[b]	calc-exp
1,2,3-tri-methoxy-benzene	-346.0±2.0	-359.8	13.8	-348.3	2.3
1,2,4-tri-methoxy-benzene	-360.6±2.3	-370.3	9.7	-358.5	-2.1
1,3,5-tri-methoxy-benzene	-381.6±3.2	-393.9	12.3	-381.5	-0.1

[a] From Table 8.

[b] Calculated by the M06/QZ4P method according to the standard atomization procedure. (The expanded uncertainty assessed to be ±3.5 kJ·mol^{-1}).[22].

[c] Results from atomization reactions were corrected with help of following equation:

$\Delta_f H^o_m(\text{g})_{\text{theor}}$/ kJ·mol^{-1} = 0.9739 × $\Delta_f H^o_m(\text{g, AT})$ +2.1 with R^2 = 0.9992

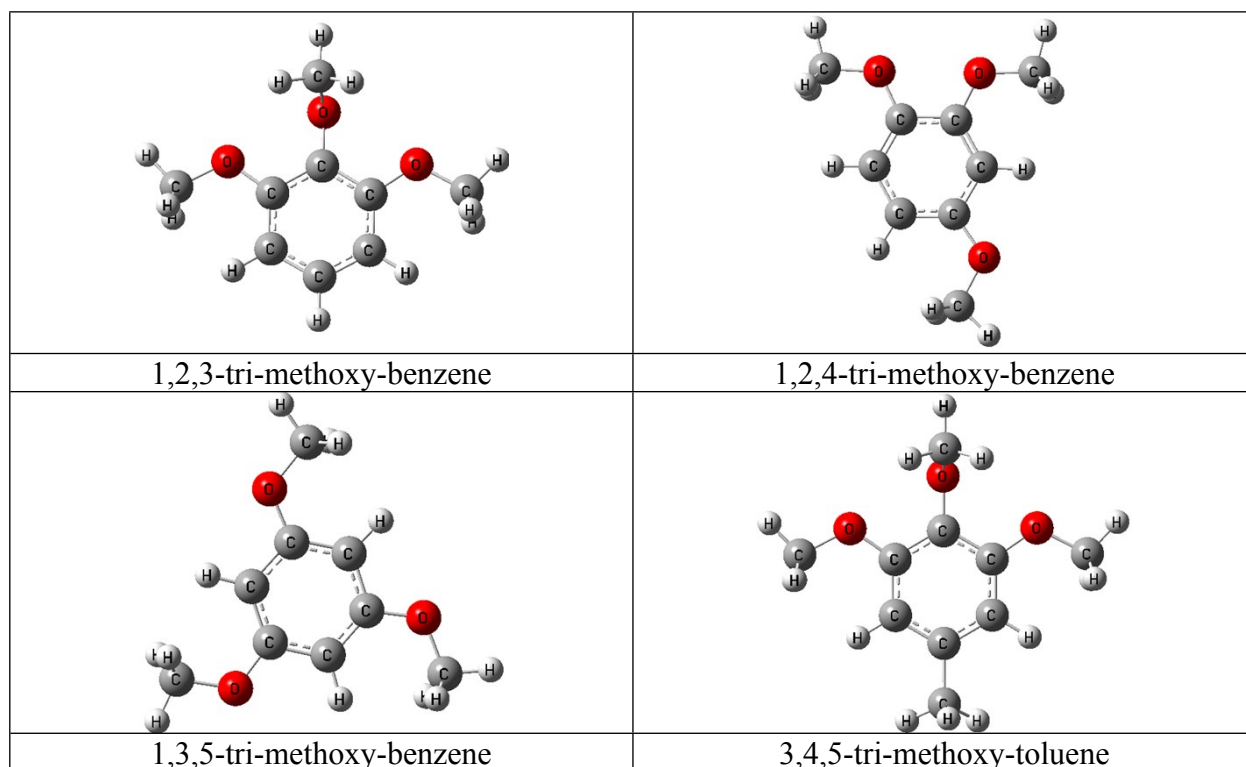|	
1,2,3-tri-methoxy-benzene	1,2,4-tri-methoxy-benzene
1,3,5-tri-methoxy-benzene	3,4,5-tri-methoxy-toluene

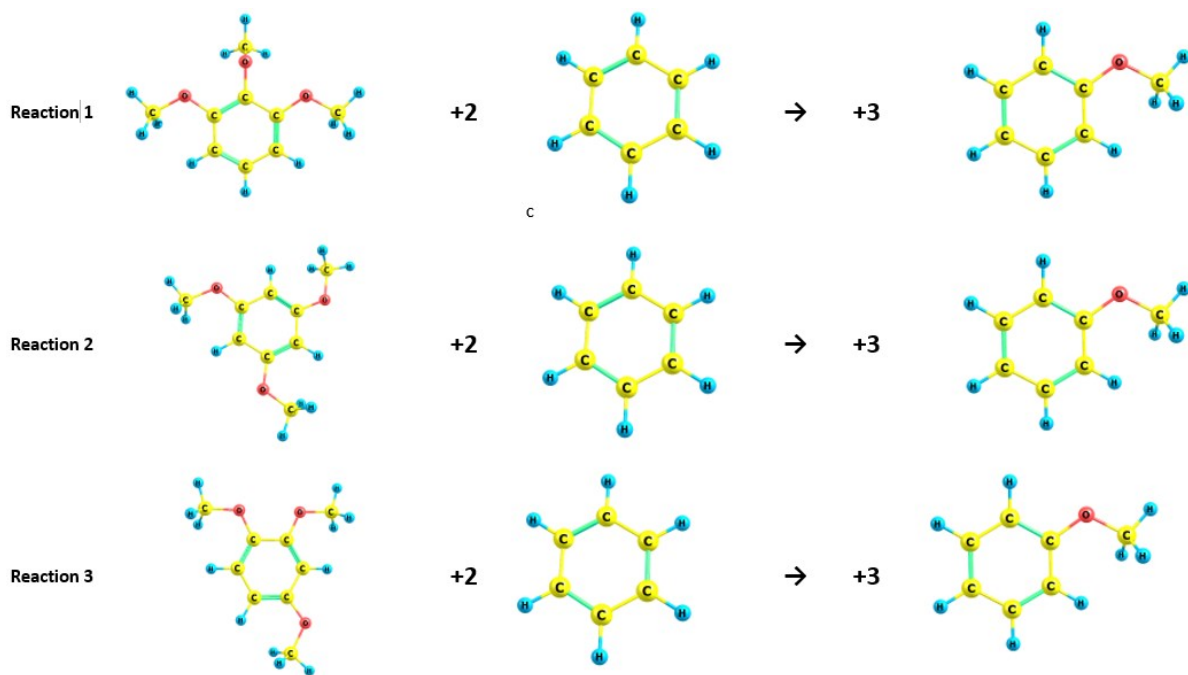**Figure S1**. The most stable conformers of substituted benzenes

Figure S2. Well-balanced reactions for trimethoxy-benzenes.
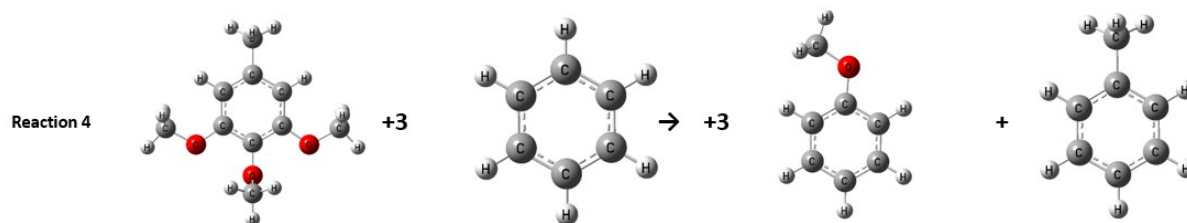

Figure S3. Well-balanced reaction for 3,4,5-trimethoxy-toluene.

Table S11. Standard molar enthalpy of formation 1,2,3-trimethoxy-benzene, $\Delta_f H^o_m(g)$, kJ·mol^{-1} (Reaction R1)

Method	$\Delta_f H^o_m(g)$ (AT)	$\Delta_f H^o_m(g)$ Reaction R1	$\Delta_r H^o_m(g)$ Reaction enthalpy R1
G4	-355.1	-352.2	-25.7
G3MP2	-356.6	-351.5	-26.4
M06/QZ4P	-359.8	-349.3	-28.6

Table S12. Standard molar enthalpy of formation 1,2,4-trimethoxy-benzene, $\Delta_f H^o_m(g)$, kJ·mol^{-1} (Reaction R2)

Method	$\Delta_f H^o_m(g)$ (AT)	$\Delta_f H^o_m(g)$ Reaction R2	$\Delta_r H^o_m(g)$ Reaction enthalpy R2
G4	-364.0	-361.0	-16.9
G3MP2	-366.2	-361.1	-16.8
M06/QZ4P	-371.3	-360.8	-17.1

Table S13. Standard molar enthalpy of formation 1,3,5-trimethoxy-benzene, $\Delta_f H^o_m(g)$, kJ·mol^{-1} (Reaction R3)

Method	$\Delta_f H^o_m(g)$ (AT)	$\Delta_f H^o_m(g)$ Reaction R3	$\Delta_r H^o_m(g)$ Reaction enthalpy R3
G4	-385.2	-382.3	4.4
G3MP2	-387.3	-382.2	4.3
M06/QZ4P	-393.9	-383.4	5.5

Table S14. Standard molar enthalpy of formation 3,4,5-trimethoxy-toluene, $\Delta_f H^o_m(g)$, kJ·mol^{-1} (Reaction R4)

Method	$\Delta_f H^o_m(g)$ (AT)	$\Delta_f H^o_m(g)$ Reaction R4	$\Delta_r H^o_m(g)$ Reaction enthalpy R4
G4	-386.6	-381.8	-27.7
G3MP2	-388.5	-381.2	-27.4
G4MP2	-381.6	-382.1	-28.3

Table S15
Parameters for the Development of "Theoretical Framework" Substituents on the "Centerpieces" for Calculation of $\Delta_f H^o_m$(g) of Substituted Benzene Derivatives at 298.15 K (in kJ·mol^{-1}).

Centerpiece molecules	$\Delta_f H^o_m$(g)	$\Delta H(H \rightarrow R)$
benzene	82.9±0.9	
toluene	50.1±1.1	**-32.8**
methoxybenzene	-70.7±1.4	**-153.6**
"theoretical framework"	$\Delta_f H^o_m$(g)	Summation:
dimethoxy-benzene	***-224.3***	82.9 + (-153.6)×2
trimethoxybenzene	***-377.9***	82.9 + (-153.6)×3
trimethoxy-toluene	***-410.7***	82.9 + (-153.6)×+(-32.8)
methoxy toluene	***-103.5***	82.9 + (-153.6) + (-32.8)

Table S16
Parameters for Pairwise Nearest and Non-nearest Neighbour Interactions of Substituents on the "Centerpieces" for Calculation of $\Delta_f H^o_m$(g) of Substituted Benzenes at 298.15 K (in kJ·mol^{-1}).

Compounds	$\Delta_f H^o_m$(g)		Pairwise interactions
			CH$_3$O - CH$_3$O
1,2-dimethoxybenzene	-210.0±2.4	(-210.0+***224.3***)	14.3
1,3-dimethoxybenzene	-224.8±2.6	(-224.8+***224.3***)	-0.5
1,4-dimethoxybenzene	-216.9±2.4	(-216.8+***224.3***)	7.4
			CH$_3$O - CH$_3$
2-methoxytoluene	-106.6±1.6	(-106.6+***103.5***)	-3.1
3-methoxytoluene	-102.6±5.0	(-102.6+***103.5***)	0.9
4-methoxytoluene	-99.0±2.0	(-99.0+***103.5***)	4.5

Table S17
Analysis of the Total Amount of Pairwise Nearest and Non-nearest Neighbour Interactions of Substituents on the "Centerpieces" in Terms of $\Delta_f H^o_m$(g) for Trimethoxy Substituted Benzenes at 298.15 K (in kJ·mol^{-1}).

Compound	$\Delta_f H^o_m$(g)[a]	Actual amount of interactions[b]	Theoretical amount of interactions[b]	Δ[c]
1	2	3	4	5
1,2,3-trimethoxybenzene	-350.6±2.4	(-350.6+377.9)= 27.3	28.1	-0.8
1,2,4-trimethoxybenzene	-360.3±1.6	(-360.3+377.9)= 17.6	21.2	-3.6
1,3,5-trimethoxybenzene	-382.1±1.2	(-382.1+377.9) = -4.2	-1.5	-2.7
3,4,5-trimethoxytoluene	-382.1±1.2	(-382.1+377.9) = 28.6	34.4	-5.8

Table S18.

Parameters for the Development of "Theoretical Framework" Substituents on the "Centerpieces" for calculation of $\Delta_l^g H_m^o$ of Substituted Benzenes at 298.15 K (in kJ·mol^{-1}).

Centerpiece molecules	$\Delta_l^g H_m^o$	$\Delta H(H{\to}R)$
benzene	33.9±0.1	
toluene	38.1±0.1	**4.2**
methoxybenzene	46.4±0.3	**12.5**
"theoretical framework"	$\Delta_l^g H_m^o$	Summation:
dimethoxy-benzene	*58.9*	33.9 + (12.5)×2
trimethoxybenzene	*71.4*	33.9 + (12.5)×3
trimethoxy-toluene	*75.6*	33.9 + (12.5)×3 + (4.2)
methoxy toluene	*50.6*	33.9 + (12.5) + (4.2)

Table S19

Parameters of Pairwise Nearest and Non-nearest Neighbour Interactions of Substituents on the "Centerpieces" for Calculation of $\Delta_l^g H_m^o$ of Substituted Benzenes at 298.15 K (in kJ·mol^{-1}).

	$\Delta_l^g H_m^o$		Pairwise interactions
			$CH_3O - CH_3O$
1,2-dimethoxybenzene	64.5±0.3	(64.5 - *58.9*)	5.6
1,3-dimethoxybenzene	59.7±0.2	(59.7 - *58.9*)	0.8
1,4-dimethoxybenzene	61.6±0.2	(61.6 - *58.9*)	2.7
			$CH_3O - CH_3$
2-methoxytoluene	50.2±0.4	(50.2 - *50.6*)	-0.4
3-methoxytoluene	52.8±0.5	(52.8 - *50.6*)	2.2
4-methoxytoluene	53.3±0.4	(53.3 - *50.6*)	2.7

Table S20

Analysis of the Total Amount of Pairwise Nearest and Non-nearest Neighbour Interactions of Substituents on the "Centerpieces" in Terms of $\Delta_l^g H_m^o$ for Trimethoxy Substituted Benzenes at 298.15 K (in kJ·mol^{-1}).

Compound	$\Delta_l^g H_m^o$	Actual amount of interactions	Theoretical amount of interactions	Δ
1	2	3	4	5
1,2,3-trimethoxybenzene	73.0±0.5	(73.0 - *71.4*) = 1.6	12.0	-10.4
1,2,4-trimethoxybenzene	75.7±0.5	(75.7 - *71.4*) = 4.5	9.1	-4.6
1,3,5-trimethoxybenzene	68.7±0.4	(68.7 - *71.4*) = -2.7	2.4	-5.1
3,4,5-trimethoxytoluene	77.7±0.5	(77.7 - *75.6*) = 2.1	19.1	-17.0

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