

# Supplementary Materials: Thermodynamics of Hydrogen Storage: Equilibrium Study of Liquid Organic Hydrogen Carrier System 1-methylindole/octahydro-1-methylindole

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**Table S1.** The composition of the initial mixtures for the study of chemical equilibrium<sup>a</sup>.

Initial mixture/% mol	m substance/g	m solvent /g	
0.98 – [0H-MI]; 0.02 – [2H-MI]; 0.13 – [8H-MI]; 9.82 – [H <sub>2</sub> ]; 88.96 – [n-C <sub>6</sub> ]	2.15	102.7	<b>a</b>
1.10– [0H-MI]; 0.01 – [2H-MI]; 0.01 – [4H-MI]; 0.09– [8H-MI]; 6.23 – [H <sub>2</sub> ]; 92.56 – [n-C <sub>6</sub> ]	2	99.7	<b>b</b>
0.93– [0H-MI]; 0.004 – [2H-MI]; 0.316 – [4H-MI]; 8.42 – [H <sub>2</sub> ]; 90.33 – [n-C <sub>6</sub> ]	2.05	97.6	<b>c</b>
1.11– [0H-MI]; 0.01 – [2H-MI]; 18.09 – [H <sub>2</sub> ]; 80.79 – [n-C <sub>6</sub> ]	2.1	99.9	<b>d</b>
0.53– [0HMI]; 0.12 – [2H-MI]; 0.05 – [4H-MI]; 0.52– [8H-MI]; 7.84 – [H <sub>2</sub> ]; 90.94 – [n-C <sub>6</sub> ]	1.87	91.5	<b>e</b>
1.11 – [0H-MI]; 0.03 – [4H-MI]; 11.89 – [H <sub>2</sub> ]; 86.97 – [n-C <sub>6</sub> ]	1.98	99.5	<b>f</b>

<sup>a</sup> In this table [0H-MI] = 1-Methylindole; [2H-MI] = Dihydro-1-Methylindole, [4H-MI] =Tetrahydro-1-Methylindole, [8H-MI] = Octahydro-Methylindole, [n-C<sub>6</sub>] = n-hexane.

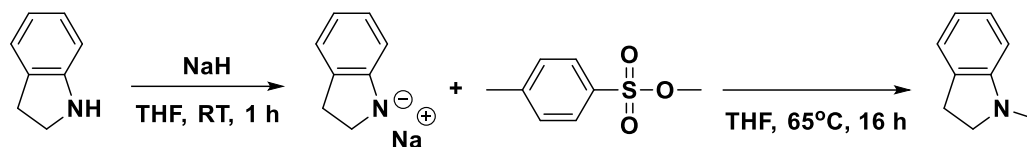
## Synthesis of 1-methylindoline

Indoline and methyl *p*-toulenesulfonate (MeOTs) was purchased from TCI America at 98% purity. Sodium hydride (NaH) was purchased from Alfa Aesar as a 60 wt% dispersion in mineral oil. Anhydrous THF was purchased EMD Millipore. MeOH was purchased from the University of Alabama Chemistry Department stockroom at ACS grade. All chemicals were used as received without further purification.

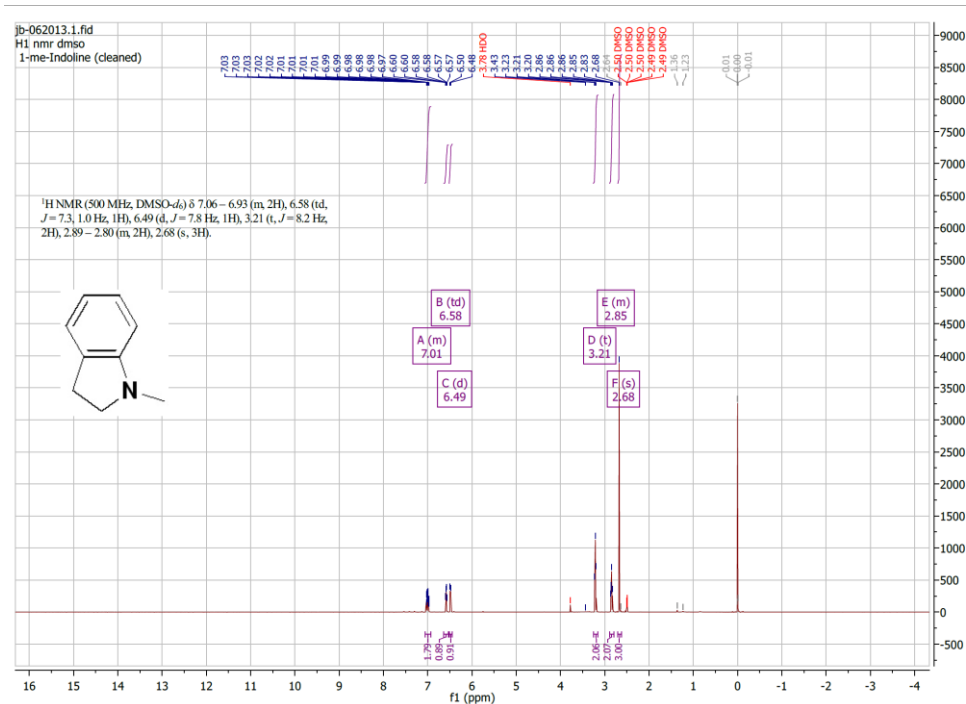
The overall reaction scheme is presented in Figure S1. Indoline (20.00 g, 167.8 mmol) was added to a 500 mL three-neck round bottom flask equipped with a magnetic stirrer, condenser and N<sub>2</sub> purge. 250 mL of anhydrous THF were transferred into the flask under an N<sub>2</sub> atmosphere via a cannula and the solid dissolved. 8.056 g of the NaH dispersion (201.4 mmol active NaH) were added slowly at ambient temperature (~22°C). H<sub>2</sub> bubbles were observed to form immediately and were allowed to vent. The reaction mixture was observed to turn into a bright green/yellow slurry which is presumably associated with the anionic intermediate. After all of the NaH was added and bubbling had ceased, MeOTs (28.13 g, 151.0 mmol) was added to the reaction mixture in several portions. The reaction mixture became more difficult to stir, due to the formation of insoluble sodium *p*-toluenesulfonate (NaOTs) as a by-product. To facilitate stirring, ~150 mL additional anhydrous THF was added. The reaction mixture was then warmed to 65°C and stirred overnight (~16 h). The color of the slurry became white as the reaction progressed.

After this time, the reaction was stopped and allowed to cool to ambient temperature. Solids were filtered and washed with an additional 100 mL of THF. The liquid phase was reduced via rotary evaporation. 250 mL of MeOH were added which caused the mineral oil to separate as a separate phase, and the vessel stored in a freezer at -10°C for several hours to allow the mineral oil to coalesce at the bottom. The MeOH phase was then carefully decanted from the mineral oil phase. MeOH was removed via rotary evaporation and the product further dried under dynamic vacuum (< 1 mm Hg) for 16 h. The product was obtained as a colorless oil, which was prone to darken upon exposure to light. Yield = 17.18 g (73%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.06 – 6.93 (m, 2H), 6.58 (td, *J* = 7.3, 1.0

Hz, 1H), 6.49 (d,  $J = 7.8$  Hz, 1H), 3.21 (t,  $J = 8.2$  Hz, 2H), 2.89 – 2.80 (m, 2H), 2.68 (s, 3H).  $^1\text{H}$  NMR consistent with published values [1].



**Figure S1.** Reaction scheme employed to produce 1-methylindoline.



**Figure S2.** NMR spectra of 1-methylindoline.

### Combustion calorimetry: liquid state enthalpy of formation determination

The standard molar energies of combustion of 1-methyl-indole and 1-methyl-indoline were measured with a self-made isoperibolic calorimeter with a static bomb and a stirred water bath. The liquid sample was transferred (in the glove box) into the polyethylene bulb (Fa. NeoLab, Heidelberg, Germany) with a syringe. The neck of the bulb was compressed with special tweezers and was sealed by heating the neck in a close proximity to a glowing wire. The bulb with the liquid sample was placed in the crucible and it was burned in oxygen at a pressure of 3.04 MPa. The detailed procedure has been described previously [2,3]. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon but neither was detected. The energy equivalent of the calorimeter  $\epsilon_{\text{calor}}$  was determined with a standard reference sample of benzoic acid (sample SRM 39j, NIST). Correction for nitric acid formation was based on titration with 0.1 mol-dm<sup>-3</sup> NaOH (aq). For the reduction of the data to standard conditions, conventional procedures [4,5] were used. Auxiliary data required for the reduction are collected in Table S2.

**Table S2.** Formula, density  $\rho(T = 293 \text{ K})$ , and massic heat capacity  $c_p(T = 298.15 \text{ K})$  and expansion coefficients  $(\delta V/\delta T)_p$  of the materials used in the present study.<sup>a</sup>

Compounds	Formula	Water content <sup>b</sup> ppm	$\rho$	$c_p$	$(\delta V/\delta T)_p^c$
			$\text{g} \cdot \text{cm}^{-3}$	$\text{J} \cdot \text{K}^{-1} \cdot \text{g}^{-1}$	$10^{-3} \cdot \text{cm}^3 \cdot \text{K}^{-1} \cdot \text{g}^{-1}$
1-methyl-indole (liq)	$\text{C}_8\text{H}_7\text{N}$	216.3	1.05 [6]	1.68 <sup>d</sup>	1.0
1-methyl-indoline (liq)	$\text{C}_8\text{H}_9\text{N}$	303.5	1.027 [6]	1.69 <sup>d</sup>	1.0
polyethylene <sup>c</sup>	$\text{CH}_{1.93}$		0.92	2.53	0.1
cotton <sup>c</sup>	$\text{CH}_{1.774}\text{O}_{0.887}$		1.50	1.67	0.1

<sup>a</sup> Data for density and specific heat capacity of auxiliary materials are from our previous work [7]; specific energy of combustion  $\Delta_c u^\circ(\text{cotton}) = -16945.2 \text{ J} \cdot \text{g}^{-1}$ ;  $u(\Delta_c u^\circ) = 4.2 \text{ J} \cdot \text{g}^{-1}$ . The specific energy of combustion  $\Delta_c u^\circ(\text{polyethylene}) = -46357.3 \text{ J} \cdot \text{g}^{-1}$ ;  $u(\Delta_c u^\circ) = 3.6 \text{ J} \cdot \text{g}^{-1}$  was derived from ten combustion experiments performed in this work. The standard uncertainties are reported for the specific energies of combustion; <sup>b</sup> The results of combustion experiments were corrected for this residual amount of water; <sup>c</sup> Estimated; <sup>d</sup> From Table S5.

**Table S3.** Results for typical combustion experiments at  $T = 298.15 \text{ K}$  ( $p = 0.1 \text{ MPa}$ )<sup>a</sup>.

	1-methyl-indole	1-methyl-indoline
$m$ (substance) /g	0.386223	0.362355
$m'$ (cotton) /g	0.000875	0.001270
$m''$ (polyethylene)/g	0.293972	0.307406
$\Delta T_c$ /K	1.89074	1.90291
$\epsilon_{\text{calor}} \cdot (-\Delta T_c)$ /J	-28143.7	-28324.8
$\epsilon_{\text{cont}} \cdot (-\Delta T_c)$ /J	-31.09	-30.96
$\Delta U_{\text{decomp}} \text{HNO}_3$ /J	60.92	59.43
$\Delta U_{\text{corr}}$ /J	9.62	9.84
$-m' \cdot \Delta_c u'$ /J	14.83	21.52
$-m'' \Delta_c u''$ /J	13627.75	14250.51
$\Delta_c u^\circ$ /(J·g <sup>-1</sup> )	-37443.8	-38676.1

<sup>a</sup> Results are referenced to  $T = 298.15 \text{ K}$  ( $p^\circ = 0.1 \text{ MPa}$ ). The definition of the symbols assigned according to ref. [4,5]. 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;  $V(\text{bomb}) = 0.33 \text{ dm}^3$  is the internal volume of the calorimetric bomb;  $p_i(\text{gas}) = 3.04 \text{ MPa}$  is the initial oxygen pressure in the bomb;  $m^i(\text{H}_2\text{O}) = 1.00 \text{ g}$  is the mass of water added to the bomb for dissolution of combustion gases;  $\epsilon_{\text{calor}} = (14885.0 \pm 0.9) \text{ J} \cdot \text{K}^{-1}$ , uncertainty for the energy equivalent is expressed as the standard uncertainty;  $\Delta T_c = T^f - T^i - \Delta T_{\text{corr}}$  is the corrected temperature rise from initial temperature  $T^i$  to final temperature  $T^f$ , with the correction  $\Delta T_{\text{corr}}$  for heat exchange during the experiment;  $\epsilon_{\text{cont}}$  is the energy equivalents of the bomb contents in their initial  $\epsilon_{\text{cont}}^i$  and final states  $\epsilon_{\text{cont}}^f$ , the contribution for the bomb content is calculated with  $(\epsilon_{\text{cont}}) \cdot (-\Delta T_c) = (\epsilon_{\text{cont}}^f) \cdot (T^f - 298.15) + (\epsilon_{\text{cont}}^i) \cdot (298.15 - T^i + \Delta T_{\text{corr}})$ ;  $\Delta U_{\text{decomp}} \text{HNO}_3$  is the energy correction for the nitric acid formation.  $\Delta U_{\text{corr}}$  is the correction to standard states. Auxiliary data are given in Table S2.

### Transpiration Method

Absolute vapour pressures were measured using the transpiration method [8,9]. The main idea of this method is to saturate the gas stream flowing over the sample and to determine the amount of compound transferred by the gas within a given time. Approximately 0.5 to 0.8 g of the sample is mixed with glass beads (diameter 1 mm) and placed in the thermostatted U-shaped saturator. The glass beads are needed to enlarge the contact area between gas and sample. A stream of nitrogen at a well-defined flow rate was passed through the saturator at constant temperature ( $\pm 0.1 \text{ K}$ ), and the transported material was collected in a cold trap. The amount of the condensed substance was determined by GC. The saturation vapour pressure  $p_i$  at each temperature  $T_i$  was calculated from the amount of condensate collected within a definite period of time:

$$p_i = m_i \cdot R \cdot T_a / V \cdot M_i ; \quad V = (n_{\text{N}_2} + n_i) \cdot R \cdot T_a / P_a \quad (\text{S1})$$

where  $V$  is the volume of the gas phase consisting of the  $n_{N_2}$  moles of the carrier gas and  $n_i$  mole of gaseous compound under study (with the molar mass  $M_i$ ) at the atmospheric pressure  $P_a$  and the ambient temperature  $T_a$ . The volume of the carrier gas  $V_{N_2}$  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  $V_{N_2}$  was readied from the digital flow rate sensor. The amount of the compound under investigation  $n_i$  in the carrier gas was estimated at each temperature using the ideal gas law.

Before starting the vapour pressure measurements, the sample was first pre-conditioned at 310-320 K (within about 1h) in order to remove possible traces of water. The saturator was then kept at 310-315 K (to remove possible traces of volatile compounds). In order to assure the competition of pre-conditioning at the selected temperature, three samples were taken during the sample flashing and analyzed by the GC. A constant vapour pressure at this temperature indicated that the transpiration experiments could begin. GC analysis of the transported material did not reveal any additional contamination. The absence of impurities and decomposition products was re-checked by GC analysis of the saturator content at the end of the entire series of experiments.

The experimental vapor pressures  $p_i$  measured by the transpiration are fitted with the following equation [8,9]:

$$R \times \ln(p_i / p_{ref}) = a + \frac{b}{T} + \Delta_1^g C_{p,m}^o \times \ln\left(\frac{T}{T_0}\right) \quad (S2)$$

where  $R = 8.31446 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  is the molar gas constant, the reference pressure  $p_{ref} = 1 \text{ Pa}$ ,  $a$  and  $b$  are adjustable parameters, the arbitrary temperature  $T_0$  applied in Eq. (S2) was chosen to be  $T_0 = 298.15 \text{ K}$  and  $\Delta_1^g C_{p,m}^o$  is the difference of the molar heat capacities of the gas and liquid phases respectively (see Table S5). The vapor pressures measured at different temperatures,  $T$ , are used to derive the enthalpies of sublimation/vaporisation using the following equation

$$\Delta_1^g H_m^o(T) = -b + \Delta_1^g C_{p,m}^o \times T \quad (S3)$$

Experimental vapour pressures temperature dependences were also used to derive the vaporization entropies at temperatures  $T$  by using the following equation:

$$\Delta_1^g S_m^o(T) = \Delta_1^g H_m^o(T) / T + R \times \ln(p_i / p^o) \quad (S4)$$

with  $p^o = 0.1 \text{ MPa}$ . Coefficients  $a$  and  $b$  of Eq. (S2),  $\Delta_1^g H_m^o(T)$  and  $\Delta_1^g S_m^o(T)$  values are collected in Table S4. The combined uncertainties of the vaporization enthalpies include uncertainties from the experimental conditions of transpiration, uncertainties in vapour pressure and uncertainties due to the temperature adjustment to  $T = 298.15 \text{ K}$  as described elsewhere [10,11].

### Temperature adjustments of vaporization enthalpies

According to general practice, all thermochemical quantities must be represented at the reference temperature  $T = 298.15 \text{ K}$ . Vaporization enthalpy derived from vapor pressure measurements are usually referenced to the average temperature,  $T_{av}$ , of the experimental range. In any case, they need to be adjusted to  $T = 298.15 \text{ K}$  using a Kirchhoff's Law. The isobaric heat capacity differences  $\Delta_1^g C_{p,m}^o$  are required for temperature adjustment of vaporization enthalpies according to Kirchhoff's rule. A simple and straightforward method was developed by Chickos and Acree [12]. They suggested an empirical way to assess  $\Delta_1^g C_{p,m}^o$ -values by equation:

$$\Delta_1^g C_{p,m}^o(298.15 \text{ K}) = 0.26 \times C_{p,m}^o(\text{liq}, 298.15) + 10.58 \quad (S5)$$

where  $C_{p,m}^o$ (liq, 298.15 K)-data are of experimental origin or they can be also estimated according to the group-additivity procedure [13]. The  $\Delta_1^g C_{p,m}^o$ -values calculated according to Eq. (S4) are given in Table S1.

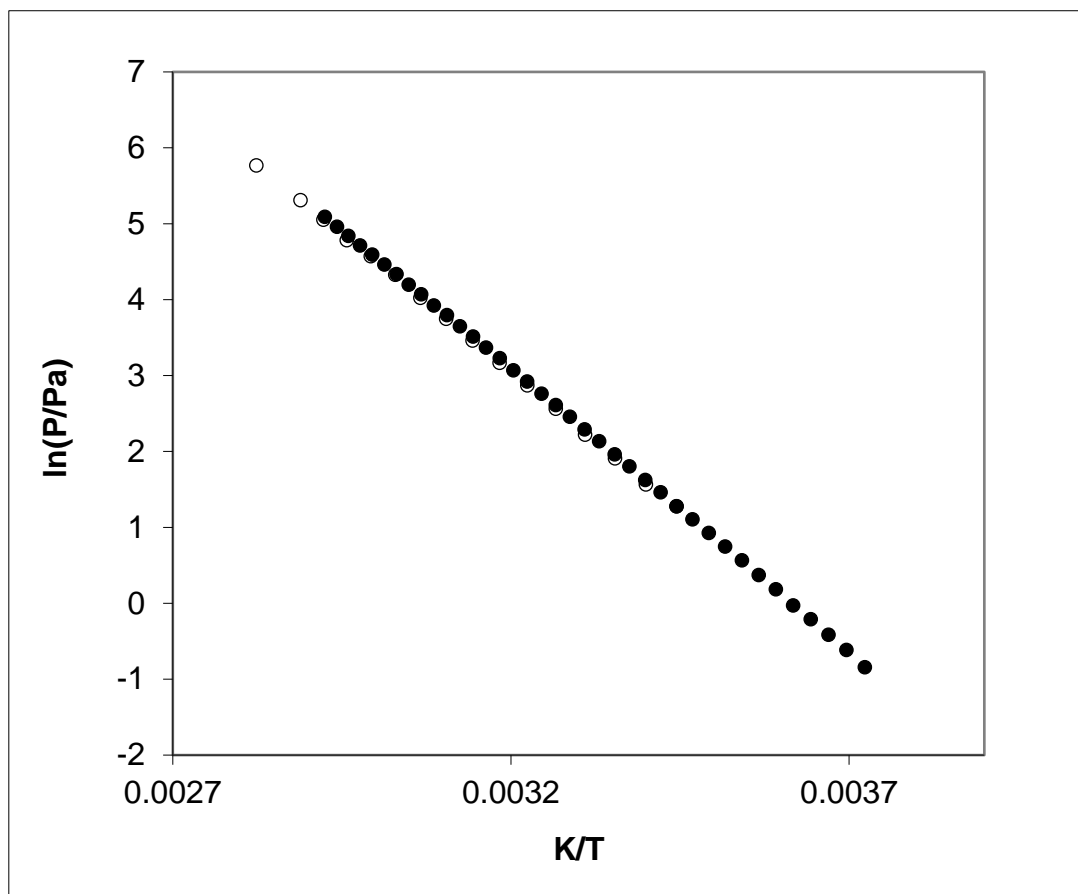
**Table S4.** Results of transpiration method for indole derivatives: absolute vapor pressures  $p$ , standard molar vaporization enthalpies and standard molar vaporization entropies.

$T/$ <b>K<sup>a</sup></b>	$m/$ <b>mg<sup>b</sup></b>	$V(N_2)^c/$ <b>dm<sup>3</sup></b>	$T_a/$ <b>K<sup>d</sup></b>	<b>Flow/</b> <b>dm<sup>3</sup>·h<sup>-1</sup></b>	$p/$ <b>Pa<sup>e</sup></b>	$u(p)/$ <b>Pa<sup>f</sup></b>	$\Delta_1^g H_m^o(T)/$ <b>kJ·mol<sup>-1</sup></b>	$\Delta_1^g S_m^o(T)/$ <b>J·K<sup>-1</sup>·mol<sup>-1</sup></b>
1-methyl-indole: $\Delta_1^g H_m^o(298.15 \text{ K}) = (62.4 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$								
$\ln(p/p_{ref}) = \frac{293.9}{R} - \frac{82921.4}{RT} - \frac{69.1}{R} \ln \frac{T}{298.15}; p_{ref} = 1 \text{ Pa}$								
294.2	1.56	6.152	295.9	4.10	4.78	0.12	62.6	130.1
298.2	1.47	4.101	295.9	4.10	6.74	0.19	62.3	129.2
302.2	1.34	2.734	295.9	4.10	9.21	0.26	62.0	128.1
306.2	1.65	2.392	295.9	4.10	12.96	0.35	61.8	127.3
310.2	1.61	1.709	295.9	4.10	17.64	0.47	61.5	126.4
314.2	1.73	1.367	295.9	4.10	23.75	0.62	61.2	125.5
318.2	1.60	0.946	295.9	2.18	31.83	0.82	60.9	124.6
322.2	1.52	0.670	295.9	2.01	42.40	1.09	60.7	123.7
326.2	1.30	0.435	295.9	1.04	55.91	1.42	60.4	122.9
330.2	1.80	0.445	295.9	1.07	75.73	1.92	60.1	122.3
334.2	1.79	0.348	295.9	1.04	96.59	2.44	59.8	121.3
338.2	1.64	0.258	295.9	1.07	119.32	3.01	59.6	120.2
342.2	2.18	0.261	295.9	1.04	156.25	3.93	59.3	119.5
346.2	8.01	0.741	295.9	2.02	202.20	5.08	59.0	118.9
354.2	4.76	0.278	295.9	1.04	319.56	8.01	58.4	117.3
1-methyl-indoline: $\Delta_1^g H_m^o(298.15 \text{ K}) = (57.4 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1}$								
$\ln(p/p_{ref}) = \frac{293.3}{R} - \frac{78290.2}{RT} - \frac{70.0}{R} \ln \frac{T}{298.15}; p_{ref} = 1 \text{ Pa}$								
278.4	1.36	3.319	293.2	4.74	7.70	0.22	58.8	132.5
281.6	1.23	2.224	293.2	4.77	10.35	0.28	58.6	131.8
283.4	1.40	2.138	293.2	4.75	12.17	0.33	58.5	131.4
289.3	2.17	2.037	294.4	4.79	19.81	0.52	58.0	129.8
296.1	1.66	0.914	293.2	3.05	33.38	0.86	57.6	127.9
298.1	1.09	0.514	294.4	1.54	39.08	1.00	57.4	127.4
300.1	1.31	0.528	294.4	1.44	45.83	1.17	57.3	127.0
302.9	1.27	0.402	293.2	1.05	57.92	1.47	57.1	126.5
307.8	1.18	0.269	294.4	1.08	80.42	2.04	56.7	125.1
311.7	1.58	0.267	294.4	1.07	109.25	2.76	56.5	124.5
312.7	1.59	0.254	293.2	1.05	114.83	2.90	56.4	124.1
316.6	2.36	0.286	294.4	1.07	151.66	3.82	56.1	123.4
318.6	2.51	0.271	293.2	1.05	169.62	4.27	56.0	122.7
322.2	4.76	0.389	294.4	1.46	224.64	5.64	55.7	122.3
322.6	3.25	0.260	294.4	1.04	229.59	5.76	55.7	122.2
328.2	6.61	0.368	294.4	1.47	329.40	8.26	55.3	121.1
333.2	13.53	0.550	294.4	1.50	450.28	11.28	55.0	120.1

<sup>a</sup> Saturation temperature measured with the standard uncertainty ( $u(T) = 0.1 \text{ K}$ ); <sup>b</sup> Mass of transferred sample condensed at  $T = 243 \text{ K}$ ; <sup>c</sup> Volume of nitrogen ( $u(V) = 0.005 \text{ dm}^3$ ) used to transfer  $m$  ( $u(m) = 0.0001 \text{ g}$ ) of the sample. Uncertainties are given as standard uncertainties; <sup>d</sup>  $T_a$  is the temperature of the soap bubble meter used for measurement of the gas flow; <sup>e</sup> Vapour pressure at temperature  $T$ , calculated from the  $m$  and the residual vapour pressure at the condensation temperature calculated by an iteration procedure; <sup>f</sup> Expanded uncertainties were calculated with  $u(p_i/\text{Pa}) = 0.025 +$

0.025( $p_i/\text{Pa}$ ). The standard uncertainties for  $T$ ,  $V$ ,  $p$ ,  $m$ , are standard uncertainties with 0.683 confidence level. Uncertainty of the vaporisation/ enthalpy  $U(\Delta_1^g H_m^o)$  is the expanded uncertainty (0.95 level of confidence) calculated according to procedure described elsewhere [10,11]. Uncertainties include uncertainties from the experimental conditions and the fitting equation, vapour pressures, and uncertainties from adjustment of vaporisation enthalpies to the reference temperature  $T = 298.15$  K.

Our vapour pressures for N-methyl-indole are in agreement with those reported by Almeida and Monte [14]



**Figure S3.** Comparison of vapor pressures for 1-methyl-indole: ● - this work; ○ - static method [14].

**Table S5.** Compilation of data on molar heat capacities  $C_{p,m}^o(\text{liq})$  and heat capacity differences  $\Delta_1^g C_{p,m}^o$  (in J.K<sup>-1</sup>.mol<sup>-1</sup>) at  $T = 298.15$  K.

Compounds	$C_{p,m}^o(\text{liq})^a$	$-\Delta_1^g C_{p,m}^o^b$
1-methyl-indole	225.1 [Table S6] 228.7	69.1
1-methyl-indoline	228.9	70.0

<sup>a</sup> Calculated according to the procedure developed by Chickos et al. [13]; <sup>b</sup> Calculated according to the procedure developed by Acree and Chickos [12] by using experimental heat capacities  $C_{p,m}^o(\text{liq})$  from this table.

### Heat capacity measurements [15]

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 under study. 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<sup>-1</sup>. Before and after each scanning step sample was kept isothermally for two minutes. Inside each iteration the temperature

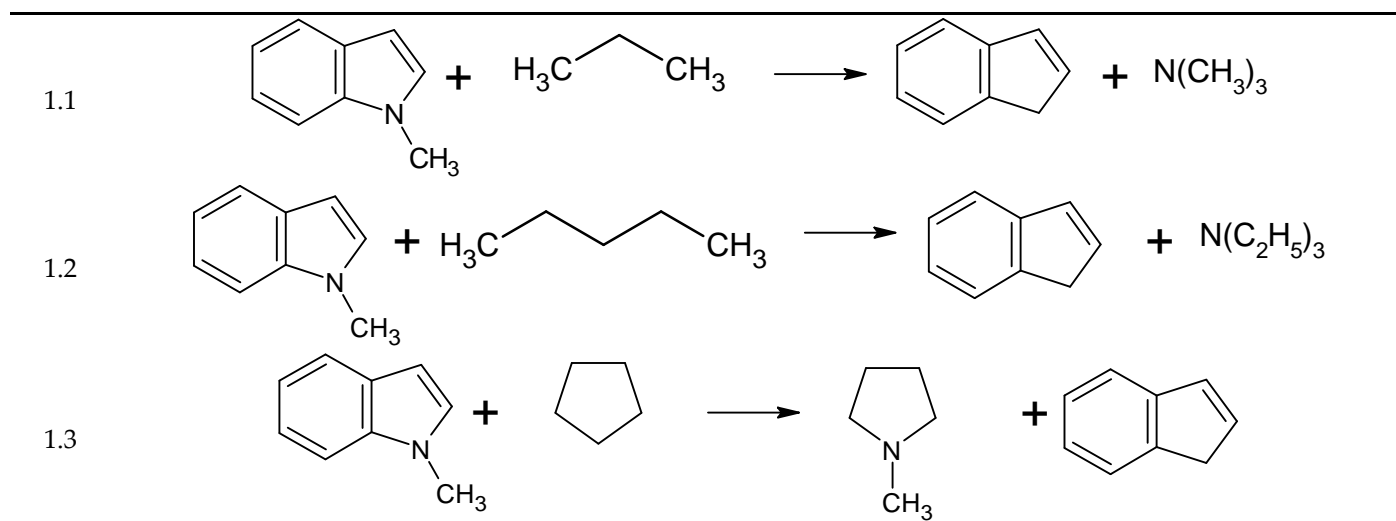
range was divided into intervals of 50 K to heat samples and between them there was a shift of 25 K. Each step for all iterations was repeated 4 times.

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 ranges the experimental values agreed with the reference values within  $\pm 1$  %. The expanded uncertainty ( $k = 2$ ) for the heat capacity measured by this method was estimated to be  $0.02 \times C_{p,m}^o$ .

**Table S6.** Experimental molar heat capacities  $C_{p,m}^o(\text{liq})$  (in  $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) of 1-methylindole.

<i>T. K</i>	$C_{p,m}^o(\text{liq})$	<i>T. K</i>	$C_{p,m}^o(\text{liq})$	<i>T. K</i>	$C_{p,m}^o(\text{liq})$
228	205.75	271	217.00	316	230.35
231	207.78	276	218.04	321	231.71
236	209.77	281	219.30	326	232.68
241	211.37	286	220.82	331	234.05
246	212.80	291	222.29	336	234.94
251	214.13	296	223.66	341	236.10
256	213.99	301	226.19	346	237.74
261	215.33	306	227.86	350	238.65
266	216.43	311	228.93		

**Table S7.** Reactions and reaction enthalpies calculated by using quantum-chemical methods for 1-methyl-indole.



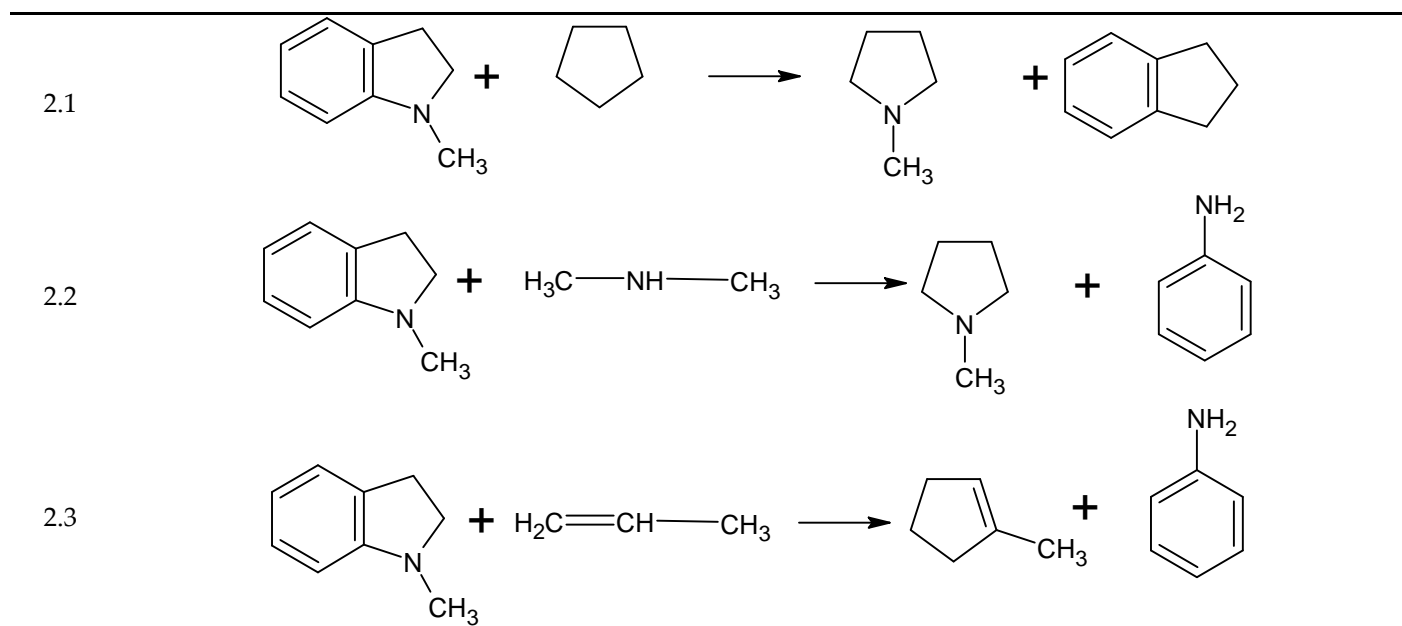
**The enthalpy of formation of 1-methyl-indole  $\Delta_f H_m^o(\text{g}, 298.15 \text{ K})$ , kJ/mol**

method	(AT)	Reaction 1.1	Reaction 1.2	Reaction 1.3
G4	149.9	154.5	157.2	141.5
G4MP2	146.7	156.3	158.7	143.0
G3MP2	148.9	155.2	158.2	142.7
CBS-APNO	138.7	152.1	155.9	139.3

**The enthalpies of reactions involving 1-methyl-indole  $\Delta_r H_m^o(\text{g}, 298.15 \text{ K})$ , kJ/mol**

$\Delta_r H_m^o(\text{g}, 298.15 \text{ K})$	Reaction 1.1	Reaction 1.2	Reaction 1.3
G4	87.2	57.5	78.6
G4MP2	85.4	56.0	77.1
G3MP2	86.5	56.5	77.4
CBS-APNO	89.6	58.8	80.8

**Table S8.** Reactions and reaction enthalpies calculated by using quantum-chemical methods for 1-methyl-indoline.



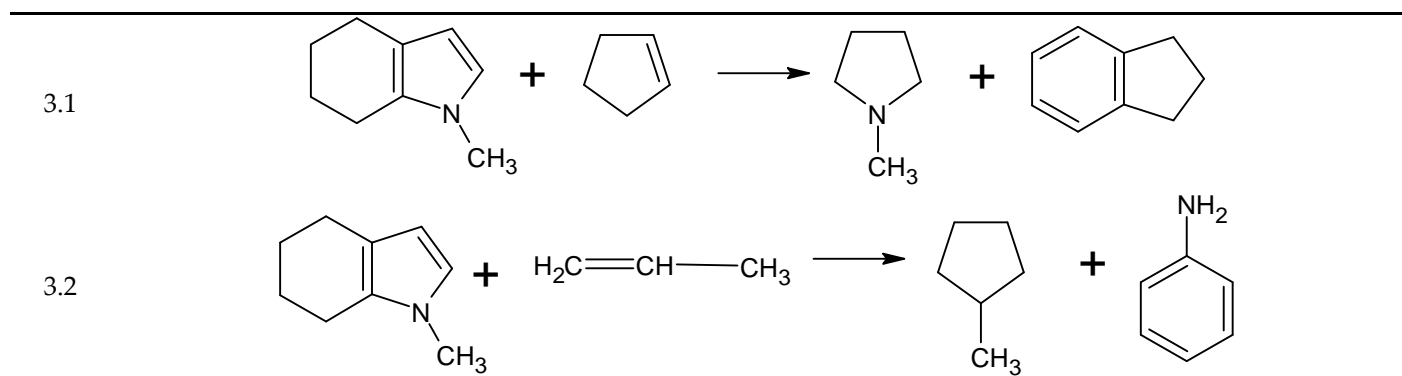
**The enthalpy of formation of 1-methyl-indoline  $\Delta_f H_m^\circ$  (g, 298.15 K), kJ/mol**

method	(AT)	Reaction 2.1	Reaction 2.2	Reaction 2.3
G4	106.1	98.1	94.0	103.7
G4MP2	104.3	99.0	95.7	105.7
G3MP2	104.3	97.5	95.9	104.1
CBS-APNO	92.9	97.5	95.3	104.8

**The enthalpies of reactions involving 1-methyl-indoline  $\Delta_r H_m^\circ$  (g, 298.15 K), kJ/mol**

$\Delta_r H_m^\circ$ (g, 298.15 K)	Reaction 1.1	Reaction 1.2	Reaction 1.3
G4	22.0	-5.3	-40.4
G4MP2	21.1	-7.0	-42.4
G3MP2	22.6	-7.2	-40.8
CBS-APNO	22.6	-6.6	-41.5

**Table S9.** Reactions and reaction enthalpies calculated by using quantum-chemical methods for H4-1-methyl-indole.





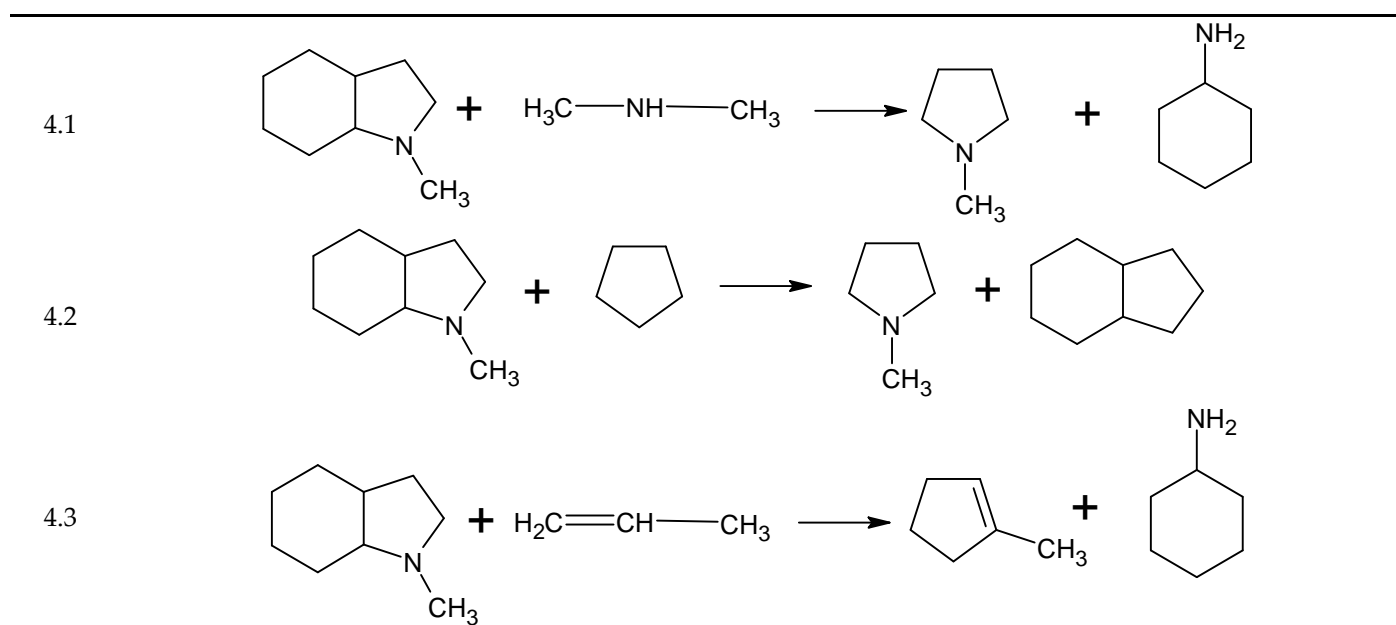
The enthalpy of formation of H4-1-methyl-indole  $\Delta_f H_m^\circ(\text{g}, 298.15 \text{ K})$ , kJ/mol

method	(AT)	Reaction 3.1	Reaction 3.2
G4	41.9	33.6	39.5
G4MP2	41.4	33.9	41.4
G3MP2	43.9	35.7	43.0
CBS-APNO	27.2	37.6	44.3

The enthalpies of reactions involving H4-1-methyl-indole  $\Delta_r H_m^\circ(\text{g}, 298.15 \text{ K})$ , kJ/mol

$\Delta_r H_m^\circ(\text{g}, 298.15 \text{ K})$	Reaction 3.1	Reaction 3.2
G4	-23.8	-78.4
G4MP2	-24.1	-80.3
G3MP2	-25.9	-81.9
CBS-APNO	-27.8	-83.2

**Table S10.** Reactions and reaction enthalpies calculated by using quantum-chemical methods for cis-H8-1-methyl-indole.



The enthalpy of formation of cis-H8-1-methyl-indole  $\Delta_f H_m^\circ(\text{g}, 298.15 \text{ K})$ , kJ/mol

method	(AT)	Reaction 4.1	Reaction 4.2 <sup>a</sup>	Reaction 4.2 <sup>b</sup>	Reaction 4.3
G4	-77.2	-89.7	-87.6	-86.1	-80.0
G4MP2	-75.9	-87.9	-87.0	-85.5	-77.9
G3MP2	-73.7	-86.3	-86.8	-85.1	-78.1
CBS-APNO	-91.4	-84.5	-85.0	-83.7	-75.0

<sup>a</sup> Calculated with trans-octahydro-1-indole; <sup>b</sup> Calculated with cis-octahydro-1-indole.

The enthalpies of reactions involving cis-H8-1-methyl-indole  $\Delta_r H_m^\circ(\text{g}, 298.15 \text{ K})$ , kJ/mol

$\Delta_r H_m^\circ(\text{g}, 298.15 \text{ K})$	Reaction 4.1	Reaction 4.2a	Reaction 4.2b	Reaction 4.3
G4	-12.5	15.5	18.4	-47.6
G4MP2	-14.3	14.9	17.8	-49.7
G3MP2	-15.9	14.7	17.4	-49.5
CBS-APNO	-17.7	12.9	16.0	-52.6

<sup>a</sup> Calculated with trans-octahydro-1-indole; <sup>b</sup> Calculated with cis-octahydro-1-indole.

**Table S11.** Reactions and reaction enthalpies calculated by using quantum-chemical methods for trans-H8-1-methyl-indole.

**The enthalpy of formation of trans-H8-1-methyl-indole  $\Delta_f H_m^0$  (g, 298.15 K), kJ/mol**

method	(AT)	Reaction 4.1	Reaction 4.2a	Reaction 4.2b	Reaction 4.3
G4	-74.8	-87.3	-85.2	-83.7	-77.6
G4MP2	-73.6	-85.6	-84.7	-83.2	-75.6
G3MP2	-72.2	-84.8	-85.3	-83.6	-76.6
CBS-APNO	-93.6	-86.6	-87.1	-85.9	-77.2

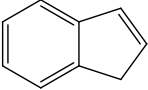
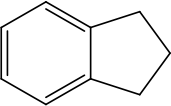
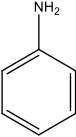

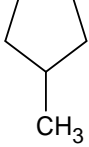
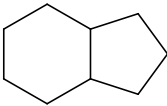
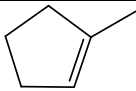
<sup>a</sup> Calculated with trans-octahydro-1-indole; <sup>b</sup> Calculated with cis-octahydro-1-indole

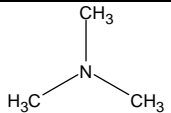
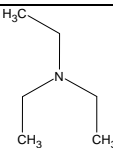
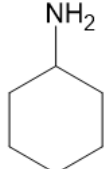
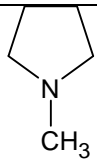
**The enthalpies of reactions involving trans-H8-1-methyl-indole  $\Delta_r H_m^0$  (g, 298.15 K), kJ/mol**

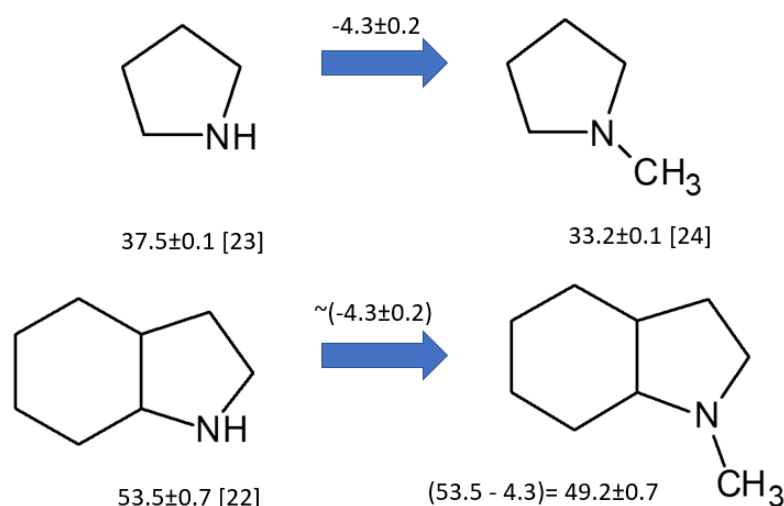
$\Delta_f H_m^0$ (g, 298.15 K)	Reaction 4.1	Reaction 4.2a	Reaction 4.2b	Reaction 4.3
G4	-14.9	13.1	16.0	-50.0
G4MP2	-16.6	12.6	15.5	-52.0
G3MP2	-17.4	13.2	15.9	-51.0
CBS-APNO	-15.6	15.0	18.2	-50.4

<sup>a</sup> Calculated with trans-octahydro-1-indole; <sup>b</sup> Calculated with cis-octahydro-1-indole

**Table S12.** Reference values for  $\Delta_f H_m^0$  (g, 298.15 K) used for calculation reaction enthalpies in Tables S7-S11 with help of quantum-chemical methods.

structure	CAS	compound	Formula	$\Delta_f H_m^0$ (g, 298.15 K)	Ref
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>3</sub>	74-98-6	propane	C <sub>3</sub> H <sub>6</sub>	-104.7 ± 0.5	[16]
	95-13-6	indene	C <sub>9</sub> H <sub>8</sub>	160.7 ± 1.3	[17]
CH <sub>3</sub> -NH-CH <sub>3</sub>	124-40-4	dimethylamine	C <sub>2</sub> H <sub>7</sub> N	-18.6 ± 0.8	[16]
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>	109-66-0	pentane	C <sub>5</sub> H <sub>12</sub>	-146.8±0.6	[16]
H <sub>2</sub> C=CH-CH <sub>3</sub>	115-07-1	propene	C <sub>3</sub> H <sub>6</sub>	20.0 ± 0.8	[16]
	496-11-7	indane	C <sub>9</sub> H <sub>10</sub>	60.7 ± 1.8	[18]
	62-53-3	aniline	C <sub>6</sub> H <sub>7</sub> N	87.1 ± 1.0	[19]
	287-92-3	cyclopentane	C <sub>5</sub> H <sub>10</sub>	-76.4 ± 0.8	[16]
	96-37-7	methyl-cyclopentane	C <sub>6</sub> H <sub>12</sub>	-106.0±0.8	[16]
	4551-51-3	cis-octahydro-1H-indene	C <sub>9</sub> H <sub>16</sub>	-127.1 ± 2.0	[16]
	3296-50-2	trans-octahydro-1H-indene	C <sub>9</sub> H <sub>16</sub>	-131.5 ± 2.2	[16]
	693-89-0	1-methyl-cyclopentene	C <sub>6</sub> H <sub>10</sub>	-3.8 ± 0.7	[16]

	75-50-3	trimethylamine	C <sub>3</sub> H <sub>9</sub> N	-23.7±0.7	[16]
	121-44-8	triethylamine	C <sub>6</sub> H <sub>15</sub> N	-92.8±0.6	[16]
	108-91-8	cyclo-hexylamine	C <sub>6</sub> H <sub>13</sub> N	-92.8±0.6	[20]
	120-94-5	1-methyl-pyrrolidine	C <sub>5</sub> H <sub>11</sub> N	-17.0±1.6	[21]



**Figure S4.** Calculation enthalpy of vaporization,  $\Delta_1^g H_m^0(298.15 \text{ K})$ , of H8-1-methyl-indole based on the vaporization enthalpy of H8-indole [22–24].

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