



Article

New Heat Transfer Fluids (HTFs) for Solar Thermal Applications

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Received: 03 August 2013 / Accepted: 29 October 2013 / Published: 01 November 2013

Abstract: Heat transfer fluids (HTFs) are used widely in many industrial processes. They collect and transport thermal energy in process heating, metal working, machine cooling with applications in the aerospace, automotive, and marine industries. Also, these fluids comprise one of the key technological components in electricity generation from concentrating solar power systems (CSPs), where they can store thermal energy as a sensible heat reservoir for later delivery to the power conversion system in absence of solar radiation. In the current work, a new one pot strategy towards biarylated ethers as novel Heat Transfer Fluids, while using minimal amount of reaction solvent, has been developed.

Keywords: Heat Transfer Fluids; biarylated ethers; Solar Thermal Energy Generation.

1. Introduction

The selection of heat transfer fluid and the system design in industrial processes is the main factor for achieving maximum heat transfer with minimum input energy and cost [1]. In general, heat transfer fluids (HTFs) and thermal oils for high temperature applications vary in chemical composition. Many of them are synthetic, and they include ester and diester, polyglycol and water-glycol based fluids, as

well as silicone based greases and oils. They can be formulated from both organic and inorganic compounds. Often, non-synthetic HTFs consist of petroleum or mineral oils, some of which have water included. For high operating temperatures in heat storage and transport, liquid sodium, or molten nitrate salts (sodium nitrate-potassium nitrate) can be used. In the past, most organic heat transfer fluids based on aromatic or aliphatic petrochemicals were used in the temperature range of 0 - 350 °C. However, at higher temperatures, they tend to decompose or oxidize [2]. Nevertheless, synthetic organic HTFs have gained more interest with time, as, though they are more expensive, they provide better thermal properties than the non-synthetic products. HTFs and thermal oils vary in terms of kinematic viscosity, operating temperature, pour point, boiling point, and flash point. Some of the main characteristics of an HTF as an energy storage system are its capacity for storing thermal energy per unit volume, its toxicity and the temperature range over which it operates[3].

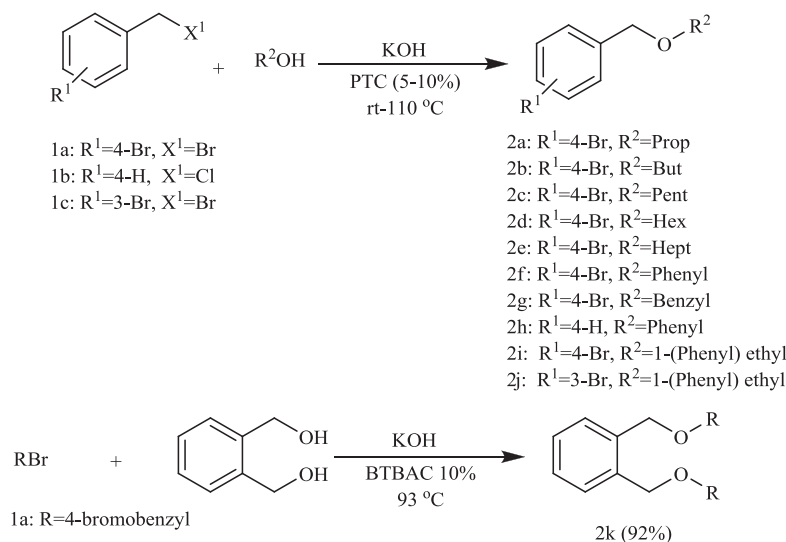
In general, the following characteristics are important for the evaluation of an HTF for CSPs: (high heat capacity, high thermal conductivity, high flash point, large operating range as where temperature is concerned (low melting point and high boiling point), low viscosity and density of the fluid and high vapor pressure) [4].

HTFs can present potential pollution problems [5]. Many of the HTFs used have relatively poor heat transfer characteristics. Additionally, at ambient temperature, many of them are more viscous than water, are less dense than water, and have lower specific heat capacity and thermal conductivity than water. These characteristics force the operators to use higher flow rates, resulting in greater pumping power necessary to obtain the equivalent quantity of energy transported when compared to a system using water.

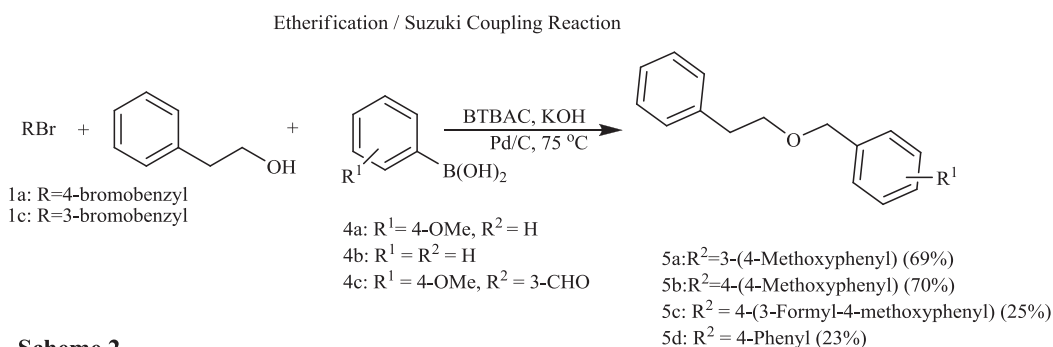
For a new solar thermoelectric generator [6], the authors have been searching for suitable organic HTFs. In the following, the authors discuss the synthesis of a number of new aryl ethers as potential HTFs. 10 years after J. Metzger's seminal article and 20 years after the Rio conference [7], it continues to be crucial to use chemical resources effectively. While it is quite evident that the purification of reaction products consumes more solvents than the reactions themselves, in addition to solid phase material, such as silica gel, it is also true that these can be recycled more easily than the solvents used in the reactions themselves. From this viewpoint, the authors have explored the possibility of solvent minimization for their reactions. Also, the authors have explored one-pot syntheses, combining etherification and Suzuki-Miyaura cross-coupling reactions, partly under solventless conditions.

2. Results and Discussion

Synthesis



Scheme 1

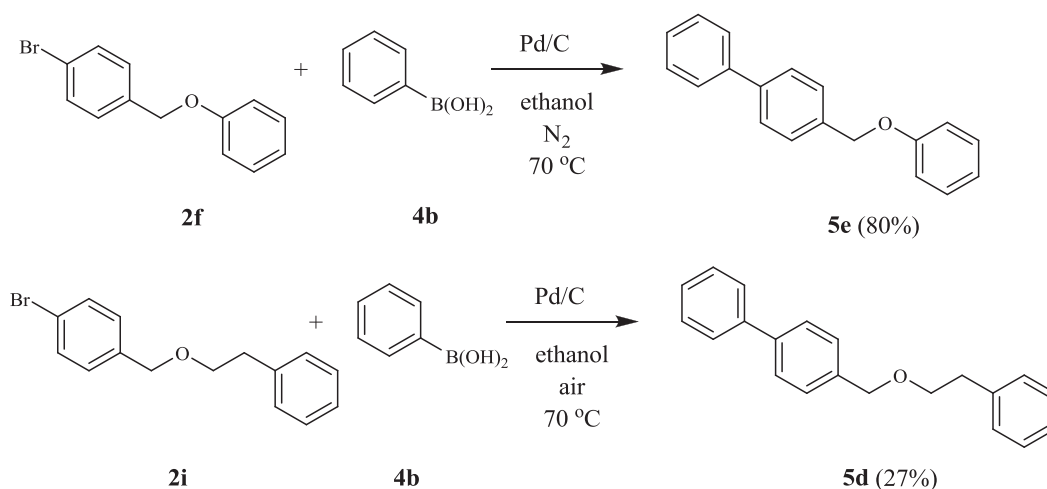


Scheme 2

Benzyl ethers (**2**) were prepared under phase transfer catalysis (PTC) under solventless conditions (Scheme 1). Here, the authors fell back upon a strategy by Rao and Senthilkumar [8] for the etherification of alkyl bromides and alkanols, which uses ground potassium hydroxide as base and tetralkylammonium halides as phase transfer catalysts. However, the authors could show that not only liquid alkyl bromides and alkanols can undergo the reaction under the solventless conditions, but that the reactions go equally well, if one or both of the reaction partners are solids. The reaction mixtures could be heated up to 75 °C without any noticeable decomposition of the ammonium salt phase transfer catalyst, eg., through base catalyzed Hofmann elimination. In the case of **2i**, addition of water after the reaction with subsequent filtration of the solidified reaction product gave **2i** in sufficient purity. Also, in those cases, where 2-phenylpropanol was used as the alcohol component were the products in sufficient purity that they could be used further in a subsequent transformation. These consecutive, but one-pot reactions are described below. For the other ether products, simple chromatography on silica gel provided the compounds with high purity.

As the authors have investigated previously one-pot transformations [9-13], where in addition to a metal catalyzed C-C bond forming reactions, another reaction was performed consecutively, such as a Wittig reaction, we were interested to find out whether an etherification could be performed in a one-pot methodology with a metal catalyzed Suzuki-Miyaura coupling reaction, given the fact that the

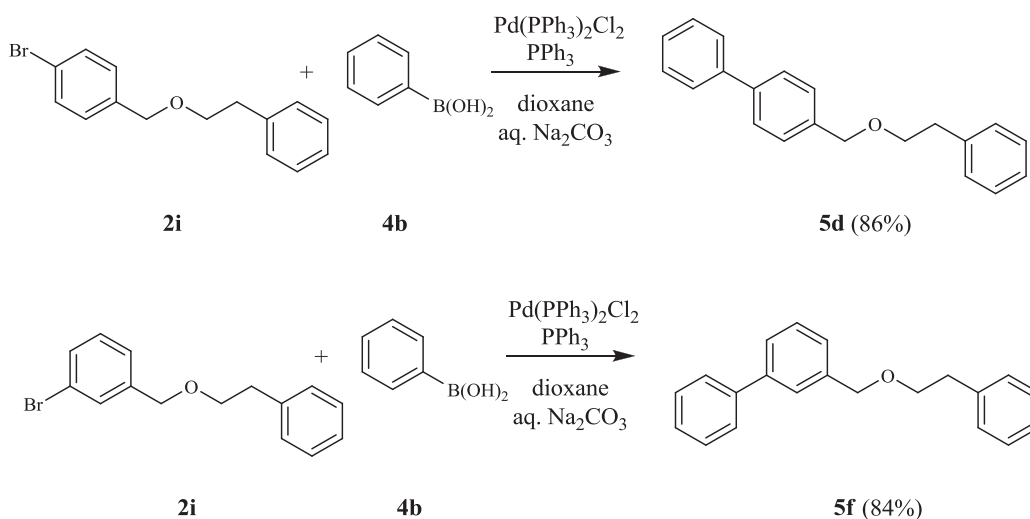
ethers provided in the reactions above were of sufficient purity. In addition, it must be stated that Jeffery had communicated reaction conditions for Pd-catalysed Heck reactions [14,15] that are close to the reaction conditions that we had used for the etherification above, namely the performing of these reactions with Pd on carbon catalyst under solventless conditions, while using an ammonium salt as a phase transfer catalyst. The reaction of 3-bromo- and 4-bromobenzyl bromides **xx** and **xx** with 4-methoxyboronic acid and 2-phenylethanol under Pd/C (5wt% Pd on carbon, Aldrich) catalysis in the presence of benzyltributylammonium bromide (BTBAC) at 75 °C for 24h led to the desired products **5a** and **5b** in 69% and 70% isolated yields (Scheme 2). The reactions were carried out under normal atmosphere, i.e., obviating the use of inert gases.



Scheme 3

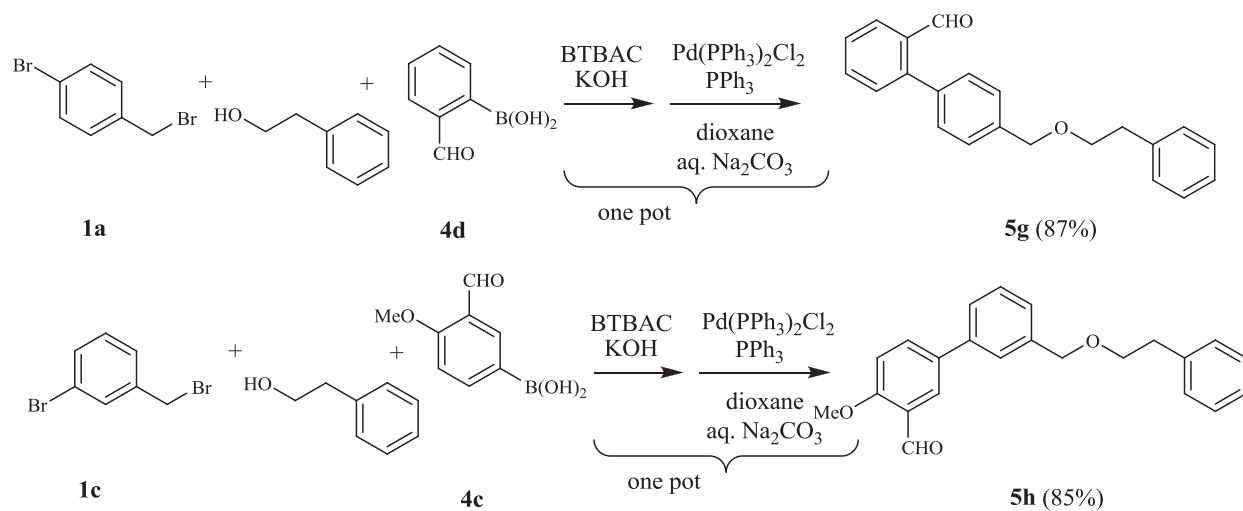
Less stabilized arylboronic acids, i.e., arylboronic acids with electron-withdrawing groups such as 3-formyl-4-methoxyboronic acid, led to much lower yields of product, where the main compounds gained from the reactions were the bromobenzyl ethyl ethers **2**, indicating that the Suzuki reaction proceeded sluggishly (Scheme 2). Also, the employment of phenylboronic acid gave the cross coupling products only in low yield (Scheme 2).

In order to understand whether the low yields were associated with the conditions used, i.e., with the solventless conditions, apart from 2-phenylethanol as an added reagent, or with the BTBAC added as a catalyst, Suzuki-Miyaura cross-coupling reactions were run with the Pd/C catalyst utilized above in ethanol as solvent. Previously, the authors had run Suzuki-Miyaura reactions under similar conditions [16], albeit under inert atmosphere (see for instance the transformation of **2f** to **5e**). In contrast to the results found at that time, the yields of Suzuki coupling products (**2i**, phenylboronic acid, Pd/C, ethanol, air) remained low (Scheme 3). Before, the Thiemann group had noted that newly opened, commercial Pd on activated carbon catalyst loses quickly its activity in Suzuki-Miyaura cross-coupling reactions, when stored under air. So, this may have contributed to the low yields above, when employing Pd/C in Suzuki-Miyaura reactions with non-alkoxy-substituted arylboronic acids under air.



Scheme 4

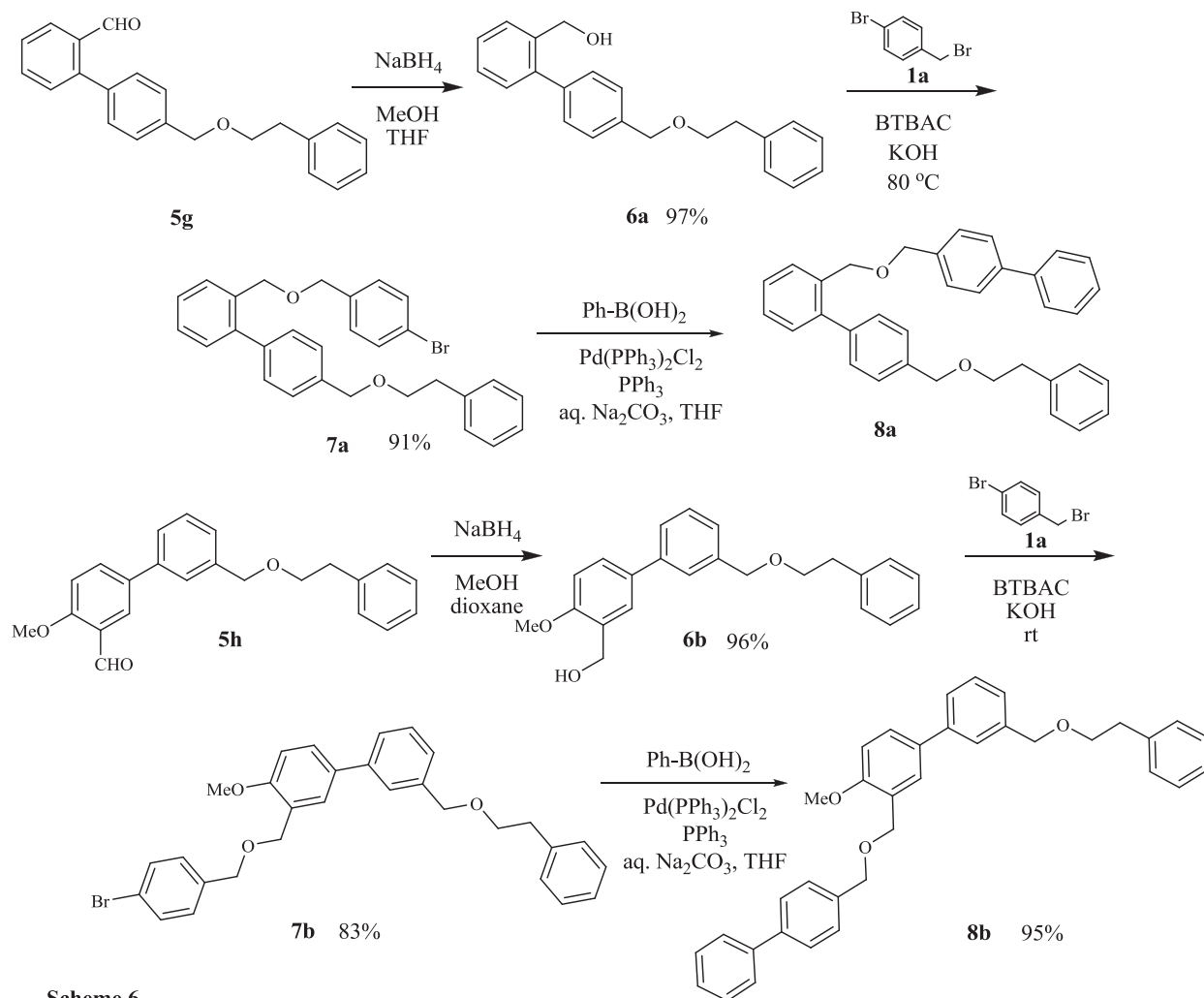
The same reactions carried under biphasic conditions that the authors normally use [Pd(PPh₃)₄, PPh₃, aq. Na₂CO₃ and an ether solvent such as DME, dioxane, or THF] the reaction yield for the biphenylated ethers **5d** and **5f** improved markedly (Scheme 4).



Scheme 5

To improve the yields of the coupling products with electron withdrawing substituents, while maintaining the strategy of a one-pot reaction, the authors decided to add small amounts of water and dioxane or THF as organic solvent, after completion of the solventless etherification. Furthermore, Pd/C catalyst again was changed to Pd(PPh₃)₂Cl₂/PPh₃, based on the good results obtained above (Scheme 4). The difference between this methodology and the previously published procedures remains in the fact that while etherification and Suzuki-Miyaura coupling are carried out consecutively, they are still carried out in a one-pot procedure. With this new set of conditions, reactions could be carried out with both 3-bromobenzyl bromide (**1c**) and 4-bromobenzyl bromide (**1a**), arylboronic acids and 2-phenylethanol to give the biphenylmethyl phenylpropyl ethers **5g** and **5h** in good yield (Scheme 5).

The formyl groups in **5g** and **5h** were reduced with NaBH_4 in a solvent mixture MeOH/dioxane (or THF) to hydroxymethyl functions (Scheme 6). While **6b** was purified by column chromatography on silica gel, it was ultimately seen, eg., in the case of **6a**, that no further purification was needed for employing **6a** in the next step. Thus, after adding water to the reaction mixture, it was extracted with CHCl_3 , and the resulting organic phase to give the alcohol in sufficient purity. The alcohols were reacted subsequently with 4-bromobenzyl bromide to the bisethers **7a** and **7b** (Scheme 6) under the PTC conditions (BTBAC, ground KOH) used previously (see above, Scheme 1). In these cases, the etherification was not carried out concurrently with the Suzuki-Miyaura coupling, due to the fact that the properties of the brominated diether **7a** and **7b** were to be scrutinized. In all fairness, it must be stated that the diether **7b** was produced with small amounts of two not yet identified by-products, which necessitate column chromatographic separation. Whether a concurrent Suzuki cross coupling would lead to a more complex reaction mixture, will still need to be studied. As the alcohol **6b** did not crystallize in our hands, the etherification to **7b** was run at rt. On the other hand, alcohol **6a** was gained as a solid. Thus, its etherification to **7a** was run at 80 °C (Scheme 6).



Scheme 6

Estimation of physical and thermal properties and relation to measured values:

According to the interest in enhancing of the thermal and physical properties of the synthesized HTFs, a pre-study was performed to find some of these properties by group contribution estimation methods. There are different reported methods for estimation of properties of pure compounds such as Joback and Reid [18], Lydersen [19], Ambrose [20], Klincewicz and Reid [21], Lyman et al. [22], Horvath [23], and Marrero and Gani [24]. The chemical structure of pure compound is analyzed into different groups and based on the contribution of each group, the properties are calculated using certain formulas. In this work, the isobaric heat capacity of liquid (C_p) is very important thermal property for calculations of enthalpy in heating and cooling processes. According to a three-level group contribution method reported by Kolsk et al. [25], the heat capacity as a function of temperature ($C_p^l(T)$) was estimated for all synthesized ethers by two approaches (Nonhierarchic (NH) and Hierarchic (H)) using the following formulas:

$$C_p^l(T) = C_{p0}^l(T) + \sum_i N_i C_{p1-i}^l(T) + w \sum_j M_j C_{p2-j}^l(T) + z \sum_k O_k C_{p3-k}^l(T) \quad (1)$$

with

$$C_{p,q}^{l, \text{thlevel}-i,j, \text{or } k}(T) = a_{q-i,j, \text{or } k} + b_{q-i,j, \text{or } k} \left(\frac{T}{100}\right) + d_{q-i,j, \text{or } k} \left(\frac{T}{100}\right)^2 \quad (2)$$

Where in eq. (1): $C_{p1-i}^l(T)$ is the contribution of the first-level group of type i , $C_{p2-j}^l(T)$ is the contribution of the second-level group of type j , and $C_{p3-k}^l(T)$ is the contribution of the third-level group of type k . N_i , M_j , and O_k indicate to the number of occurrences of the individual groups (of type i , j , or k , respectively) in a compound. $C_{p0}^l(T)$ (which could be considered as the contribution of the zero-level group) is an additional adjustable parameter. Variables w and z are weighting factors that are assigned to 0 or 1, depending on whether the second-level and third-level contributions, respectively, are used or not. In eq. (2), $a_{q-i,j, \text{or } k}$, $b_{q-i,j, \text{or } k}$, and $d_{q-i,j, \text{or } k}$ are adjustable parameters for the temperature dependence of $C_{p0}^l(T)$, $C_{p1-i}^l(T)$, $C_{p2-j}^l(T)$, and $C_{p3-k}^l(T)$.

Other physical properties such as melting point (T_m), boiling point (T_b), and critical temperature (T_c) were estimated using Marrero and Gani's model [24] according to the equations:

$$\text{Normal melting point } (T_m): \exp\left(\frac{T_m}{T_{m0}}\right) = \sum_i N_i T_{m1i} + \sum_j M_j T_{m2j} + \sum_k O_k T_{m3k} \quad (3)$$

$$\text{Normal boiling point } (T_b): \exp\left(\frac{T_b}{T_{b0}}\right) = \sum_i N_i T_{b1i} + \sum_j M_j T_{b2j} + \sum_k O_k T_{b3k} \quad (4)$$

$$\text{Critical temperature } (T_c): \exp\left(\frac{T_c}{T_{c0}}\right) = \sum_i N_i T_{c1i} + \sum_j M_j T_{c2j} + \sum_k O_k T_{c3k} \quad (5)$$

The symbols in eq. (3, 4 and 5) T_{m1i} , T_{b1i} and T_{c1i} represent the contributions (i) of the first-order groups for the corresponding properties. Similarly, T_{m2j} , T_{b2j} and T_{c2j} and T_{m3k} , T_{b3k} and T_{c3k} represent the contributions (j) and (k) of the second and third-order groups, respectively. The T_{m0} , T_{b0} and T_{c0} are additional adjustable parameters of the estimation models. N_i , M_j , and O_k indicate to the number of occurrences of the individual groups (of type i , j , or k , respectively) in a compound.

The following table shows some estimated properties according to the methods [24] and [25], noting that the heat capacity is estimated at 300 K:

Table. 1: Computed physical and Thermal properties.

Compound	Cp [J/(mole.K)] (J/(g.K))		T _m (°C)	T _b (°C)	T _c (°C)
	(NH) Appr.	(H) Appr.			
2a	309.2 (1.35)	299.6 (1.31)	44	153	375
2b	338.7 (1.39)	328.8 (1.35)	48	167	386
2c	368.2 (1.43)	358.0 (1.39)	52	181	398
2d	397.7 (1.47)	387.1 (1.43)	56	194	408
2e	427.2 (1.50)	416.3 (1.46)	60	206	419
2f	349.1 (1.33)	332.8 (1.26)	94	221	441
2g	348.9 (1.26)	346.9 (1.25)	37	205	424
2h	327.9 (1.78)	311.5 (1.69)	69	188	391
2i	402.7 (1.38)	378.9 (1.30)	39	229	444
2j	403.1 (1.38)	379.4 (1.30)	7	228	443
5a	682.4 (2.14)	515.9 (1.62)	68	252	500
5b	682.0 (2.14)	515.4 (1.62)	90	253	500
5c	795.4 (2.30)	565.8 (1.63)	104	366	614
5d	568.7 (1.97)	464.8 (1.61)	65	240	492
5f	569.2 (1.97)	465.3 (1.61)	39	238	491
5g	678.9 (2.15)	512.1 (1.62)	91	354	605
5h	795.8 (2.30)	566.3 (1.63)	84	365	614
8a	950.5 (1.96)	764.8 (1.58)	132	440	706
8b	1067.4 (2.07)	819.1 (1.59)	127	447	712

It must be noted that according to the table, the specific heat capacities of the extended ethers **8** are appreciably high. Experimental and measured specific capacities have been found in agreement. Thus, experimentally, the specific heat capacity of **2d** was measured to be 1.35 J/g.K.

For the melting points, it can be said that for simple molecules, there was a good agreement between the calculated and measured values. For the extended ethers, this does not hold true. Most likely, due to their complicated geometric structure molecular packing is frustrated, and so these ethers are liquids at room temperature. Density measurements have shown that up to 90 °C, there is a linear relationship between the density and temperature, with a decrease in density with an increase of temperature.

Importantly, Thermal Gravimetric Analysis (TGA) has shown that especially the extended ethers such as **8b** are stable up to 300 °C, even in air.

3. Experimental Section

General. – Melting points were measured with a Stuart SMP10 melting point apparatus and are uncorrected. ¹H NMR (at 400 MHz) and ¹³C NMR (at 100.5 MHz) spectra were taken on a Varian 400 MHz spectrometer. IR measurements were performed on a Thermo Nicolet FT-IR spectrometer, model Nexus 470. Density measurements were performed on an Anton-Barr DMA 4500M densitometer. TGA measurements were carried out with a Shimadzu TGA-50. Column chromatography was executed on silica gel S (Riedel de Haen) and on silica gel (Merck grade 9385).

Triphenylphosphine (Sigma-Aldrich), 4-bromobenzyl bromide (**1a**) (Fluka), 3-bromobenzyl bromide (**1c**) (Aldrich), propanol (J. T. Baker), 1-butanol, 1-pentanol (Fluka), 1-hexanol (Merck Schuchardt), 1-heptanol (Riedel de Haen), benzyl alcohol (Fluka), 2-phenylethanol (Merck-Schuchardt), benzyltrimethylammonium iodide (BTEAI) (Fluka), benzyltributyl ammonium chloride (BTBAC) (Fluka), potassium hydroxide (KOH) (UNI-Chem), phenylboronic acid (Aldrich), 4-methoxyphenylboronic acid (Aldrich), 3-formyl-4-methoxyboronic acid (Aldrich), bis(triphenylphosphine)palladium(II) dichloride (TCD), palladium on carbon (5 wt% Pd on activated carbon, Aldrich) were acquired commercially and used without further purification.

Selected procedures and spectroscopic data for the compounds prepared. -

General procedure A – solventless etherification under PTC conditions: Synthesis of 4-bromobenzyl *n*-propyl ether (**2a**): A mixture of 4-bromobenzyl bromide (**1a**) (2.0 g, 8.0 mmol), 1-propanol (1.44 g, 24 mmol), finely ground KOH (0.67 g, 12 mmol) and BTEAI (130 mg, 0.4 mmol) of BTEAI was left under stirring at rt. for 16 hrs. Then, CH₂Cl₂ (2 X 30 mL) was added, and the mixture was extracted with water (40 mL). The organic phase was dried over MgSO₄. After concentration *in vacuo*, the organic residue is filtered over a column (benzene/hexane, 1 : 3) to give 4-bromobenzyl *n*-propyl ether (**2a**) (1.59 g, 87%) as a colorless oil; δ_{H} (400 MHz, CDCl₃) 0.93 (3H, t, ³*J* = 7.2 Hz, CH₃), 1.62 (2H, qt, ³*J* = 7.2 Hz, ³*J* = 6.8 Hz), 3.41 (2H, t, ³*J* = 6.8 Hz, OCH₂), 4.44 (2H, s, OCH₂), 7.21 (2H, d, ³*J* = 8.4 Hz), 7.45 (2H, d, ³*J* = 8.4 Hz); δ_{C} (100.5 MHz, CDCl₃) 10.6 (CH₃), 22.9 (CH₂), 72.0 (OCH₂), 72.2 (OCH₂), 121.3 (C_{quat}), 129.2 (2C, CH), 131.4 (2C, CH), 137.8 (C_{quat}).

4-Bromobenzyl *n*-butyl ether (**2b**): Following general procedure A and using *n*-butanol (1.77 g, 24 mmol), **1a** was converted in 15h. to 4-bromobenzyl *n*-butyl ether (**2b**) (1.71 g, 88% yield) as a colorless oil; δ_{H} (400 MHz, CDCl₃) 0.91 (3H, t, ³*J* = 7.4 Hz, CH₃), 1.36 – 1.39 (2H, m), 1.56 – 1.59 (2H, m), 3.45 (2H, t, ³*J* = 6.6 Hz, OCH₂), 4.44 (2H, s, OCH₂), 7.20 (2H, d, ³*J* = 8.4 Hz), 7.45 (2H, d, ³*J* = 8.4 Hz); δ_{C} (100.5 MHz, CDCl₃) 13.9 (CH₃), 19.4 (CH₂), 31.8 (CH₂), 70.3 (OCH₂), 72.1 (OCH₂), 121.3 (C_{quat}), 129.2 (2C, CH), 131.4 (2C, CH), 137.8 (C_{quat}).

4-Bromobenzyl *n*-heptyl ether (**2e**): Following general procedure A and using *n*-heptanol (2.8 g, 24 mmol), **1a** was converted in 19h to 4-bromobenzyl *n*-heptyl ether (**2e**) (1.96 g, 86% yield) as a colorless oil; δ_{H} (400 MHz, CDCl_3) 0.87 (3H, t, $^3J = 6.8$ Hz, CH_3), 1.24 – 1.38 (8H, m), 1.60 (2H, tt, $^3J = 6.6$, $^3J = 6.6$ Hz), 3.44 (2H, t, $^3J = 6.6$ Hz), 4.44 (2H, s, OCH_2), 7.20 (2H, d, $^3J = 8.0$ Hz), 7.45 (2H, d, $^3J = 8.0$ Hz); δ_{C} (100.5 MHz, CDCl_3) 14.1 (CH_3), 22.6 (CH_2), 26.1 (CH_2), 29.1 (CH_2), 29.7 (CH_2), 31.8 (CH_2), 70.6 (OCH_2), 72.1 (OCH_2), 121.3 (C_{quat}), 129.2 (2C, CH), 131.4 (2C, CH), 137.7 (C_{quat}).

4-Bromobenzyl *n*-hexyl ether (**2d**): Modified procedure A' (scaled-up procedure A): To a mixture of 4-bromobenzyl bromide (**1a**) (6.0 g, 24 mmol), *n*-hexanol (7.34 g, 72 mmol), and KOH (2.0 g, 36 mmol) was added BTEAI (490 mg, 1.2 mmol, 5 mol% of **1a**). The resulting reaction mixture was left to stir at rt. for 17 hrs. Then, CH_2Cl_2 (3 X 25 mL) was added, and the mixture was extracted with water (50 mL). The organic phase was dried over anhydrous MgSO_4 . After concentration *in vacuo*, the organic residue was filtered over a column (benzene/hexane, 1:3) to give 4-bromobenzyl *n*-hexyl ether (**2d**) (5.72 g, 88%) as a colorless oil; δ_{H} (400 MHz, CDCl_3) 0.88 (3H, t, $^3J = 6.8$ Hz, CH_3), 1.24 – 1.38 (6H, m), 1.55 – 1.63 (2H, m), 3.44 (2H, t, $^3J = 6.8$ Hz, OCH_2), 4.44 (2H, s, OCH_2), 7.20 (2H, d, $^3J = 8.0$ Hz), 7.45 (2H, d, $^3J = 8.0$ Hz); δ_{C} (100.5 MHz, CDCl_3) 14.0 (CH_3), 22.6 (CH_2), 25.8 (CH_2), 26.7 (CH_2), 31.7 (CH_2), 70.7 (OCH_2), 72.1 (OCH_2), 121.3 (C_{quat}), 129.2 (2C, CH), 131.4 (2C, CH), 137.8 (C_{quat}).

4-Bromobenzyl *n*-pentyl ether (**2c**): Following general procedure A' and using *n*-pentanol (6.34 g, 72 mmol), **1a** was converted in 29h to 4-bromobenzyl *n*-pentyl ether (**2c**) (5.30 g, 86%) as a colorless oil; δ_{H} (400 MHz, CDCl_3) 0.89 (3H, t, $^3J = 7.0$ Hz, CH_3), 1.31 – 1.35 (4H, m), 1.60 (2H, m), 3.44 (2H, t, $^3J = 6.6$ Hz, OCH_2), 4.44 (2H, s, OCH_2), 7.20 (2H, d, $^3J = 7.8$ Hz), 7.45 (2H, d, $^3J = 7.8$ Hz); δ_{C} (100.5 MHz, CDCl_3) 14.0 (CH_3), 22.5 (CH_2), 28.3 (CH_2), 29.4 (CH_2), 70.6 (OCH_2), 72.1 (OCH_2), 121.3 (C_{quat}), 129.2 (2C, CH), 131.4 (2C, CH), 137.7 (C_{quat}).

4-Bromobenzyl benzyl ether (**2g**): Following general procedure A' and using benzyl alcohol (7.8 g, 72 mmol), **1a** was converted in 17h to 4-bromobenzyl benzyl ether (**2g**) (6.05 g, 91%) as a colorless oil; δ_{H} (400 MHz, CDCl_3) 4.42 (2H, s, OCH_2), 4.47 (2H, s, OCH_2), 7.15 (2H, d, $^3J = 9.0$ Hz), 7.19 – 7.24 (3H, m), 7.25 – 7.28 (2H, m), 7.39 (2H, d, $^3J = 9.0$ Hz); δ_{C} (100.5 MHz, CDCl_3) 71.3 (OCH_2), 72.2 (OCH_2), 121.5 (C_{quat}), 127.8 (CH), 127.8 (2C, CH), 128.5 (2C, CH), 129.4 (2C, CH), 131.5 (2C, CH), 137.3 (C_{quat}), 138.0 (C_{quat}).

Benzyl phenyl ether (**2h**): To a mixture of benzyl chloride (**1b**) (2.0 g, 15.0 mmol), phenol (1.8 g, 19 mmol), and KOH (1.8 g, 32 mmol) was added BTEAI (244 mg, 0.75 mmol, 5 mol% of **1b**). The resulting reaction mixture was stirred at 65 °C for 20 hrs. Then, CH_2Cl_2 (2 X 30 mL) was added, and the mixture was extracted with water (40 mL). The organic phase was dried over anhydrous MgSO_4 . After concentration *in vacuo*, the organic residue was filtered over a column (benzene/hexane, 1:3) to give benzyl phenyl ether (**2h**) (2.15 g, 78%) as a slowly crystallizing solid; δ_{H} (400 MHz, CDCl_3) 5.10 (2H, s, OCH_2), 6.94 - 7.00 (3H, m), 7.25 (2H, s, CH), 7.27 – 7.45 (5H, m); δ_{C} (100.5 MHz, CDCl_3)

69.9 (OCH₂), 114.8 (2C, CH), 120.9 (CH), 127.5 (2C, CH), 127.9 (CH), 128.6 (2C, CH), 129.5 (2C, CH), 137.0 (C_{quat}), 158.8 (C_{quat}).

4-Bromobenzyl phenylethyl ether (**2i**): General Procedure C: To a mixture of 4-bromobenzyl bromide (**1a**) (2.25 g, 9 mmol), 2-phenylethanol (1.0 g, 8.2 mmol), and KOH (1.0 g, 17.8 mmol) was added BTBAC (280 mg, 0.9 mmol, 10 mol% of **1a**). The resulting reaction mixture was left to stir at rt. for 17.5 hrs. Then, water (60 mL) was added to the reaction mixture. The product (**2i**), as a colorless precipitate, was filtered and washed with methanol (10 mL), yielding **2i** (1.7 g, 71%) as a colorless solid, m.p. 47-49 °C. ν_{max} (KBr/cm⁻¹) 3466, 3084, 2942, 2852, 1591, 1488, 1453, 1391, 1357, 1120, 1011, 834, 750, 495; δ_H (400 MHz, CDCl₃) 2.92 (2H, t, ³J = 7.0 Hz), 3.67 (2H, t, ³J = 7.2 Hz), 4.46 (2H, s, OCH₂), 7.15 (2H, d, ³J = 8.0 Hz), 7.20-7.23 (2H, m), 7.26 (H, d, ³J = 8.0 Hz), 7.29-7.31 (2H, m), 7.44 (2H, d, ³J = 8.0 Hz); δ_C (100.5 MHz, CDCl₃) 36.3 (CH₂), 71.3 (OCH₂), 72.2 (OCH₂), 121.3 (C_{quat}), 126.3 (CH), 128.4 (2C, CH), 128.9 (2C, CH), 129.2 (2C, CH), 131.4 (2C, CH), 137.4 (C_{quat}), 138.8 (C_{quat}).

1,2-Bis((4-bromobenzoyloxy)methyl)benzene (**2k**): To a mixture of 4-bromobenzyl bromide (**1a**) (4.0 g, 16 mmol), 1,2-phenylenedimethanol (1.0 g, 7.5 mmol), and KOH (1.68 g, 30 mmol) was added BTBAC (0.5 g, 1.6 mmol, 10 mol% of **1a**). The resulting reaction mixture was left to stir at 93 °C for 18.5 hrs. Then, CH₂Cl₂ (2 X 30 mL) was added, and the mixture was extracted with water (40 mL). The organic phase was dried over anhydrous MgSO₄. The solvent was evaporated *in vacuo*. Thereafter, the product (**2k**) crystallized after addition of hexane (10 mL) to the organic residue, yielding **2k** (3.29 g, 92%) as a colorless solid, m.p. 48 °C; δ_H (400 MHz, CDCl₃) 4.45 (4H, s, OCH₂), 4.58 (4H, s, OCH₂), 7.19 (2H, d, ³J = 8.0 Hz), 7.24 (2H, d, ³J = 8.0 Hz), 7.30-7.32 (2H, m), 7.39-7.42 (2H, m), 7.45 (4H, d, ³J = 8.0 Hz); δ_C (100.5 MHz, CDCl₃) 69.9 (2C, OCH₂), 71.5 (2C, OCH₂), 121.5 (2C, C_{quat}), 128.0 (2C, CH), 129.0 (2C, CH), 129.4 (4C, CH), 131.5 (4C, CH), 136.2 (2C, C_{quat}), 137.2 (2C, C_{quat}).

3-Bromobenzyl phenylethyl ether (**2j**) – General procedure C: Column chromatography on silica gel (CH₂Cl₂-hexane 2 : 1) gives **2j** (73%) as a colorless oil; ν_{max} (neat, cm⁻¹) 3062, 3027, 2919, 2860, 1598, 1571, 1356, 1200, 1109, 777, 749, 698, 671; δ_H (400 MHz, CDCl₃) 2.94 (2H, t, ³J = 7.2 Hz), 3.69 (2H, t, ³J = 7.2 Hz, OCH₂), 4.48 (2H, s, OCH₂), 7.17 – 7.32 (7H, m), 7.38 – 7.41 (1H, m), 7.44 – 7.45 (1H, m); δ_C (100.5 MHz, CDCl₃) 36.3 (CH₂), 71.4 (OCH₂), 72.1 (OCH₂), 122.5 (C_{quat}), 125.9 (CH), 126.3 (CH), 129.9 (CH), 130.5 (CH), 130.6 (CH), 128.4 (2C, CH), 128.9 (2C, CH), 138.8 (C_{quat}), 140.8 (C_{quat}).

4-Phenylbenzyl phenylethyl ether (**5d**) – General procedure D: A mixture of 4-bromobenzyl phenylethyl ether (2.22 g, 7.6 mmol), phenylboronic acid (1.4 g, 11.4 mmol), solid Na₂CO₃ (750 mg, 7.14 mmol) and Pd/C (150 mg, 5 w% Pd) in EtOH (15 mL) was stirred at 70 °C for 14h. Thereafter, the ethanol is evaporated *in vacuo*, and the residue subjected to column chromatography on silica gel (hexane-CH₂Cl₂ 3 : 1) to give **5d** (590 mg, 27%) as a colorless solid; mp. 68 °C; ν_{max} (neat, cm⁻¹) 3033, 2913, 2858, 1486, 1450, 1401, 1369, 1118, 1104, 822, 759, 739, 698; δ_H (400 MHz, CDCl₃)

2.96 (2H, t, $^3J = 7.2$ Hz), 3.73 (2H, d, $^3J = 7.2$ Hz, OCH₂), 4.57 (2H, s, OCH₂), 7.22 – 7.46 (10H, m), 7.56 (2H, d, $^3J = 8.0$ Hz), 7.59 (2H, d, $^3J = 8.0$ Hz); δ_C (100.5 MHz, CDCl₃) 36.4 (CH₂), 71.3 (OCH₂), 72.7 (OCH₂), 126.2 (CH), 127.0 (2C, CH), 127.1 (CH), 127.2 (2C, CH), 128.1 (2C, CH), 128.4 (2C, CH), 128.7 (2C, CH), 129.0 (2C, CH), 137.4 (C_{quat}), 138.9 (C_{quat}), 140.5 (C_{quat}), 140.9 (C_{quat}).

3-Phenylbenzyl phenylethyl ether (**5f**) as a colorless oil; ν_{\max} (neat, cm⁻¹) 3060, 3029, 2920, 2857, 1601, 1480, 1453, 1357, 1088, 1029, 755, 699; δ_H (400 MHz, CDCl₃) 2.96 (2H, t, $^3J = 7.2$ Hz), 3.73 (2H, t, $^3J = 7.2$ Hz, OCH₂), 4.59 (2H, s, OCH₂), 7.19 – 7.58 (14H, m); δ_C (100.5 MHz, CDCl₃) 36.4 (CH₂), 71.3 (OCH₂), 72.9 (OCH₂), 126.2 (CH), 126.3 (CH), 126.4 (CH), 126.5 (CH), 127.2 (2C, CH), 127.3 (CH), 128.3 (2C, CH), 128.7 (2C, CH), 128.8 (CH), 128.9 (2C, CH), 138.9 (C_{quat}), 139.0 (C_{quat}), 141.0 (C_{quat}), 141.3 (C_{quat}).

General procedure E – one-pot etherification – Suzuki-Miyaura cross coupling with Pd/C as catalyst: 4-(4-Methoxyphenyl)benzyl phenylethyl ether (**5b**). - To a mixture of 4-bromobenzyl bromide (**1a**) (2.25 g, 9.0 mmol), 2-phenylethanol (1.0 g, 8.2 mmol), and KOH (1.0 g, 17.8 mmol) was added BTBAC (280 mg, 0.9 mmol, 10 mol% of **1a**). The resulting reaction mixture was left under stirring at rt. for 20 hrs. Then 4-methoxyphenylboronic acid (2.0 g, 13.2 mmol) was added to the reaction mixture, followed by Pd/C (50 mg, 5 wt%, 0.3 atom% Pd [based on phenylethanol]). The reaction mixture was stirred at 75 °C for a further 24 hr. Then, further Pd/C (50 mg, 5wt%, 0.3 atom% Pd [based on phenylethanol]) was added to the reaction mixture, and the reaction was left for another 24 hr under the same conditions. The mixture was cooled, and CH₂Cl₂ (2 X 30 mL) was added, and the mixture was extracted with water (40 mL). The organic phase was dried over anhydrous MgSO₄. After concentration *in vacuo*, the organic residue was filtered over silica gel (hexane/CH₂Cl₂, 1:3) to give 4-(4-methoxyphenyl)benzyl phenylethyl ether (**5b**) (1.83 g, 70%) as a white solid, mp 71 °C; ν_{\max} (KBr/cm⁻¹) 2854, 1607, 1501, 1110, 1037, 816, 697; δ_H (400 MHz, CDCl₃) 2.96 (2H, t, $^3J = 8.0$ Hz), 372 (2H, t, $^3J = 8$ Hz), 3.85 (3H, s, OCH₃), 4.56 (2H, s, OCH₂), 6.98 (2H, d, $^3J = 8.0$ Hz), 7.22-7.36 (9H, m), 7.52 (2H, d, $^3J = 8.0$ Hz); δ_C (100.5 MHz, CDCl₃) 36.4 (CH₂), 55.3 (OCH₃), 71.3 (OCH₂), 72.7 (OCH₂), 114.2 (2C, CH), 126.2 (CH), 126.7 (2C, CH), 128.1 (4C, CH), 128.4 (2C, CH), 129.0 (2C, CH), 133.5 (C_{quat}), 136.8 (C_{quat}), 138.9 (C_{quat}), 140.1 (C_{quat}), 159.1 (C_{quat}).

3-(4-Methoxyphenyl)benzyl phenylethyl ether (**5a**) as a colorless solid; mp. 70 °C; ν_{\max} (neat, cm⁻¹) 1606, 1518, 1484, 1292, 1252, 1184, 1116, 1028, 836, 790, 744, 699, 571, 498; δ_H (400 MHz, CDCl₃) 2.99 (2H, t, $^3J = 7.2$ Hz), 3.75 (2H, t, $^3J = 7.2$ Hz), 3.86 (3H, s, OCH₃), 4.59 (2H, s, OCH₂), 6.99 (2H, d, $^3J = 8.8$ Hz), 7.22 – 7.53 (11H, m); δ_C (100.5 MHz, CDCl₃) 36.4 (CH₂), 55.4 (OCH₃), 71.3 (OCH₂), 73.0 (OCH₂), 114.2 (2C, CH), 125.9 (2C, CH), 126.0 (CH), 126.1 (CH), 126.2 (CH), 128.2 (2C, CH), 128.4 (CH), 128.8 (CH), 129.0 (2C, CH), 133.6 (C_{quat}), 138.9 (C_{quat}), 139.0 (C_{quat}), 140.9 (C_{quat}), 159.2 (C_{quat}).

3-(3-Formyl-4-methoxyphenyl)benzyl phenylethyl ether (**5h**) – General procedure F – one-pot etherification – Suzuki coupling with Pd(PPh₃)₂Cl₂ as catalyst: A mixture of 3-bromobenzyl bromide

(**1c**) (1.54 g, 6.2 mmol), 2-phenylethanol (690 mg, 5.66 mmol), KOH (690 mg, 12.3 mmol) and BTBAC (190 mg, 0.62 mmol) was stirred at rt for 18h. Then, water (10 mL) and dioxane (10 mL) were added. To this, were entered 3-formyl-4-methoxyphenylboronic acid (1.15 g, 6.39 mmol), Pd(PPh₃)₂Cl₂ (30 mg, 4.27·10⁻⁵ mol), triphenylphosphine (PPh₃, 30 mg, 0.11 mmol). The resulting biphasic solution was heated to 75 °C and stirred for 14h. Thereafter, the reaction mixture was given into water (20 mL) and extracted with CH₂Cl₂ (2 X 15 mL) and CHCl₃ (15 mL). The organic phase was dried over anhydrous MgSO₄ and evaporated *in vacuo*. The residue was subjected to column chromatography on silica gel (hexane/ether/CHCl₃ 3:1:1) to give **5h** (1.66 g, 85%) as a colorless oil; ν_{\max} (neat, cm⁻¹) 3028, 2858, 1680, 1608, 1503, 1481, 1454, 1391, 1272, 1181, 1023, 789, 750, 700, 648; δ_{H} (400 MHz, CDCl₃) 2.95 (2H, t, ³J = 7.2 Hz, CH₂), 3.74 (2H, t, ³J = 7.2 Hz, OCH₂), 3.98 (3H, s, 4.57 (2H, s, OCH₂), 7.06 (1H, d, ³J = 8.4 Hz), 7.39 (1H, m), 7.19 – 7.51 (9H, m), 7.75 (1H, m), 8.07 (1H, s), 10.52 (1H, s, CHO); δ_{C} (100.5 MHz, CDCl₃) 36.4 (CH₂), 55.8 (OCH₃), 71.4 (OCH₂), 72.9 (OCH₂), 112.1 (CH), 124.9 (C_{quat}), 125.8 (CH), 125.9 (CH), 126.2 (CH), 126.5 (CH), 126.8 (CH), 128.3 (2C, CH), 128.8 (CH), 128.9 (2C, CH), 133.6 (C_{quat}), 134.4 (CH), 138.6 (C_{quat}), 139.1 (C_{quat}), 139.6 (C_{quat}), 161.3 (C_{quat}), 189.8 (CHO).

4-(2-Formylphenyl)benzyl phenylethyl ether (**5g**) as a colorless oil, prepared according general procedure F; ν_{\max} (neat, cm⁻¹) 3061, 3027, 2919, 2855, 2752, 1692, 1597, 1476, 1452, 1393, 1359, 1254, 1196, 1099, 1006, 828, 766, 700; δ_{H} (400 MHz, CDCl₃) 2.97 (2H, t, ³J = 6.8 Hz, CH₂), 3.75 (2H, t, ³J = 6.8 Hz, CH₂), 4.59 (2H, s, OCH₂), 7.23 – 7.49 (6H, m), 7.34 (2H, d, ³J = 8.0 Hz), 7.40 (2H, d, ³J = 8.0 Hz), 7.61 – 7.64 (2H, m), 8.01 (1H, dd, ³J = 8.4 Hz, ⁴J = 1.2 Hz), 9.97 (1H, d, ⁴J = 1.2 Hz, CHO); δ_{C} (100.5 MHz, CDCl₃) 36.4 (CH₂), 71.6 (OCH₂), 72.5 (OCH₂), 126.3 (CH), 127.6 (3C, CH), 127.7 (CH), 128.4 (2C, CH), 128.9 (2C, CH), 130.1 (2C, CH), 130.8 (CH), 133.6 (CH), 133.7 (C_{quat}), 136.9 (C_{quat}), 138.5 (C_{quat}), 138.9 (C_{quat}), 145.7 (C_{quat}), 192.5 (CHO).

3-(3-Hydroxymethyl-4-methoxyphenyl)benzyl phenylethyl ether (**6b**) as a colorless oil, prepared according to general procedure G (see below); ν_{\max} (neat, cm⁻¹) 3432 (bs, OH), 3016, 2924, 1610, 1482, 1246, 1215 (s), 1086, 1030, 755, 701, 667; δ_{H} (400 MHz, CDCl₃) 2.95 (2H, t, ³J = 7.2 Hz, CH₂), 3.73 (2H, t, ³J = 7.2 Hz, OCH₂), 3.91 (3H, s, OCH₃), 4.58 (2H, s, OCH₂), 4.75 (2H, s, OCH₂), 6.95 (1H, d, ³J = 8.4 Hz), 7.23 – 7.51 (10H, m), 7.37 (1H, dd, ³J = 8.2 Hz, ³J = 8.2 Hz); δ_{C} (100.5 MHz, CDCl₃) 36.4 (CH₂), 55.5 (OCH₃), 62.4 (OCH₂), 71.3 (OCH₂), 73.0 (OCH₂), 110.5 (CH), 125.9 (CH), 126.0 (CH), 126.1 (CH), 126.2 (CH), 127.5 (CH), 127.6 (CH), 128.3 (2C, CH), 128.8 (CH), 129.0 (2C, CH), 129.3 (C_{quat}), 133.6 (C_{quat}), 138.9 (C_{quat}), 139.0 (C_{quat}), 140.7 (C_{quat}), 157.0 (C_{quat})

4-(2-Hydroxymethylphenyl)benzyl phenylethyl ether (**6a**) – General procedure G: To a solution of **5g** (1.0 g, 3.2 mmol) in a solvent mixture of MeOH (10 mL) and THF (10 mL) was given portionwise at rt NaBH₄ (145 mg, 3.8 mmol). The reaction mixture was stirred for 1h at rt. Then, it was given into water (25 mL) and extracted with CH₂Cl₂ (3 X 15 mL). The organic phase, which showed only one product by TLC, was dried over anhydrous MgSO₄ and evaporated *in vacuo* to obtain **6a** (975 mg, 97%) as a colorless solid; mp. 87 – 89 °C; ν_{\max} (neat, cm⁻¹) 3405 (bs, OH), 3061, 3026, 2862, 1603, 1482, 1452, 1196, 1096, 1007, 827, 759, 700; δ_{H} (400 MHz, CDCl₃) 2.97 (2H, t, ³J = 7.2 Hz, CH₂), 3.75 (2H, t, ³J = 7.2 Hz, OCH₂), 4.57 (2H, s, OCH₂), 4.61 (2H, s, OCH₂), 7.22 – 7.39 (12H, m), 7.54 (1H, dd, ³J = 7.2

Hz, $^4J = 1.6$ Hz); δ_C (100.5 MHz, CDCl₃) 36.4 (CH₂), 63.2 (OCH₂), 71.5 (OCH₂), 72.7 (OCH₂), 126.2 (CH), 127.5 (CH), 127.6 (CH), 127.7 (2C, CH), 128.3 (2C, CH), 128.4 (CH), 128.9 (2C, CH), 129.2 (2C, CH), 130.1 (CH), 137.4 (C_{quat}), 138.0 (C_{quat}), 138.9 (C_{quat}), 139.8 (C_{quat}), 141.1 (C_{quat}).

3-(3-[4-Bromobenzyloxymethyl]-4-methoxyphenyl)benzyl phenylethyl ether (**7b**), obtained through general procedure C from **6b** and **1a**, as a colorless oil; ν_{\max} (neat, cm⁻¹) 3027, 2856, 1608, 1248, 1086, 1029, 1011, 791, 700; δ_H (400 MHz, CDCl₃) 2.95 (2H, t, $^3J = 7.2$ Hz, CH₂), 3.73 (2H, t, $^3J = 7.2$ Hz, OCH₂), 3.86 (3H, s, OCH₃), 4.57 (2H, s, OCH₂), 4.58 (2H, s, OCH₂), 4.62 (2H, s, OCH₂), 6.93 (1H, d, $^3J = 8.4$ Hz), 7.19 – 7.50 (11H, m), 7.37 (1H, dd, $^3J = 7.6$ Hz, $^3J = 7.6$ Hz), 7.46 (2H, d, $^3J = 8.4$ Hz), 7.62 (1H, d, $^4J = 2.4$ Hz); δ_C (100.5 MHz, CDCl₃) 36.4 (CH₂), 55.5 (OCH₃), 67.2 (OCH₂), 71.3 (OCH₂), 71.7 (OCH₂), 73.0 (OCH₂), 110.5 (CH), 121.3 (C_{quat}), 126.0 (2C, CH), 126.1 (2C, CH), 126.2 (C_{quat}), 127.4 (CH), 127.9 (C_{quat}), 128.3 (2C, CH), 128.8 (CH), 128.9 (2C, CH), 129.4 (2C, CH), 131.4 (2C, CH), 133.4 (C_{quat}), 137.6 (C_{quat}), 138.8 (CH), 138.9 (C_{quat}), 140.9 (C_{quat}), 156.8 (C_{quat}).

3-(3-[4-Phenylbenzyloxymethyl]-4-methoxyphenyl)benzyl phenylethyl ether (**8b**) as a colorless oil; δ_H (400 MHz, CDCl₃) 2.95 (2H, t, $^3J = 6.8$ Hz, CH₂), 3.72 (2H, t, $^3J = 6.8$ Hz, OCH₂), 3.88 (3H, s, OCH₃), 4.58 (2H, s, OCH₂), 4.69 (4H, 2s, 2 OCH₂), 6.95 (1H, d, $^3J = 8.4$ Hz), 7.18 – 7.60 (19H, m), 7.68 (1H, d, $^4J = 2.0$ Hz); δ_C (100.5 MHz, CDCl₃) 36.4 (CH₂), 55.5 (OCH₃), 67.2 (OCH₂), 71.3 (OCH₂), 72.2 (OCH₂), 73.0 (OCH₂), 110.5 (CH), 125.9 (CH), 126.0 (CH), 126.1 (CH), 126.2 (CH), 126.9 (C_{quat}), 127.0 (2C, CH), 127.1 (2C, CH), 127.2 (CH), 127.3 (CH), 127.9 (CH), 128.2 (2C, CH), 128.3 (2C, CH), 128.7 (3C, 3 CH), 128.9 (2C, CH), 133.4 (C_{quat}), 137.6 (C_{quat}), 138.8 (C_{quat}), 138.9 (C_{quat}), 140.5 (C_{quat}), 141.0 (2C, C_{quat}), 156.8 (C_{quat}).

4-[2-(4-Bromobenzyloxy)methylphenyl]benzyl phenylethyl ether (**7a**) as a colorless oil; δ_H (400 MHz, CDCl₃) 2.98 (2H, t, $^3J = 7.2$ Hz, CH₂), 3.76 (2H, t, $^3J = 7.2$ Hz, OCH₂), 4.41 (2H, s, OCH₂), 4.43 (2H, s, OCH₂), 4.58 (2H, s, OCH₂), 7.14 (2H, d, $^3J = 8.4$ Hz), 7.20 – 7.56 (13H, m), 7.42 (2H, d, $^3J = 8.0$ Hz); δ_C (100.5 MHz, CDCl₃) 36.4 (CH₂), 70.2 (OCH₂), 71.5 (OCH₂), 71.6 (OCH₂), 72.8 (OCH₂), 121.4 (C_{quat}), 126.2 (CH), 127.4 (2C, CH), 127.5 (CH), 127.8 (CH), 128.4 (2C, CH), 128.9 (2C, CH), 129.2 (2C, CH), 129.3 (2C, CH), 129.4 (CH), 130.0 (CH), 131.4 (2C, CH), 135.1 (C_{quat}), 137.2 (C_{quat}), 137.3 (C_{quat}), 138.9 (C_{quat}), 140.0 (C_{quat}), 141.8 (C_{quat}).

4. Conclusion

New benzyl ethers have been synthesized as potential heat transfer fluids (HTFs). Within the synthetic route, a one pot etherification – Suzuki cross coupling protocol has been developed, which in some cases can be run solventless with Pd/C as catalyst under ambient atmosphere. This protocol is more resource-efficient than conventional reaction processes of this type.

The ethers prepared have been calculated to have a relatively high specific heat capacity, which in some cases has been validated experimentally. It has been shown by thermal gravimetric analysis that the extended ethers (such as **8b**) are stable up to 300 °C, even in air, ie., at temperatures that are interesting for the operation of HTFs.

Acknowledgment

This work was supported by SURE project fund 31S097.

Conflict of Interest

The authors see no conflict of interest.

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