New Heat Transfer Fluids (HTFs) for Solar Thermal Applications

T. Thiemann,[1]*, Y. Al Jasem,[2] B. Al Hindawi,[1] H. Butt,[2] M. Barkhad,[2] M. Al Khazali,[3] M. Al-Azani[1]

[1]Department of Chemistry, [2]Department of Chemical Engineering, [3]Department of Petroleum Engineering, United Arab Emirates University, Al Ain, Abu Dhabi, United Arab Emirates.

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Introduction

Heat Transfer Fluids (HTFs):

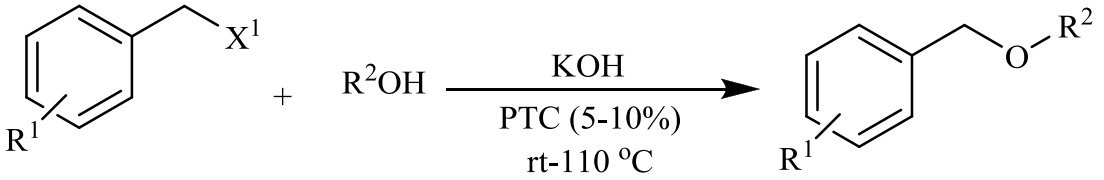
- collect and transport thermal energy in various industrial processes.
- one of the key technological components in electricity generation from concentrating solar power systems (CSPs)
- Synthetic HTFs include ester and diester, polyglycol and water-glycol based fluids, as well as silicone based greases and oils.
- Non-synthetic HTFs include petroleum or mineral oils.
- Synthetic organic HTFs are more expensive, but they provide better thermal properties than the non-synthetic products.

HTFs

- HTFs can present potential pollution problems.
- Many HTFs have relatively poor heat transfer characteristics
- 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.
- So, preparing new HTFs with enhanced thermal and physical properties in environmental benign ways is the aim of 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.

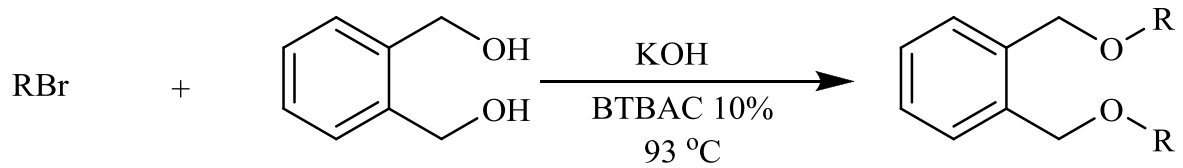
Synthesis

Synthesis of ethers in solvent-less reactions with the use of a Phase Transfer Catalyst (PTC)



1a: R^1=4-Br, X^1=Br
1b: R^1=4-H, X^1=Cl
1c: R^1=3-Br, X^1=Br

2a: R^1=4-Br, R^2=Prop, X^1=Br
2b: R^1=4-Br, R^2=But, X^1=Br
2c: R^1=4-Br, R^2=Pent, X^1=Br
2d: R^1=4-Br, R^2=Hex, X^1=Br
2e: R^1=4-Br, R^2=Hept, X^1=Br
2f: R^1=4-Br, R^2=Phenyl, X^1=Br
2g: R^1=4-Br, R^2=Benzyl, X^1=Br
2h: R^1=4-H, R^2=Phenyl, X^1=Cl
2i: R^1=4-Br, R^2=1-(Phenyl) ethyl, X^1=Br
2j: R^1=3-Br, R^2=1-(Phenyl) ethyl, X^1=Br



1a: R=4-bromobenzyl

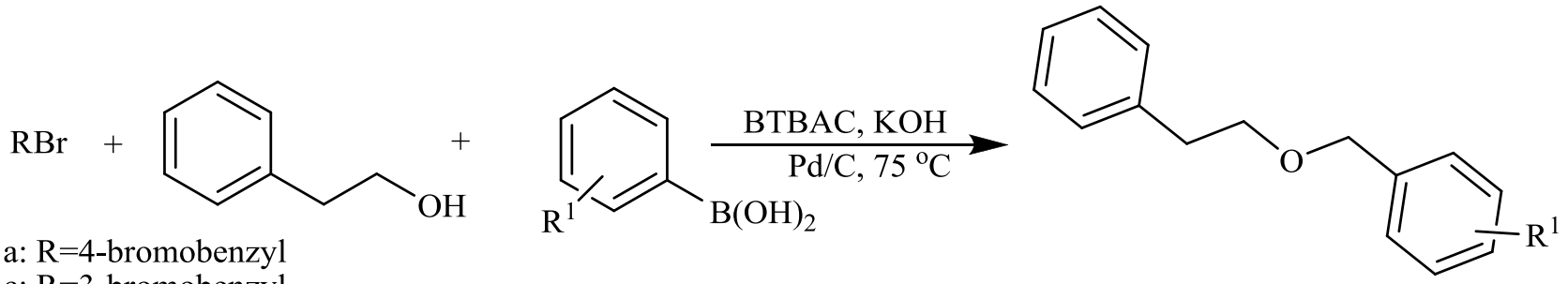
2k (92%)

Scheme 1

Synthesis

Developing a one pot (etherification / Suzuki Coupling) reaction with the use of PTC, with Pd/C as catalyst, under ambient atmosphere.

Etherification / Suzuki Coupling Reaction



1a: R=4-bromobenzyl
1c: R=3-bromobenzyl

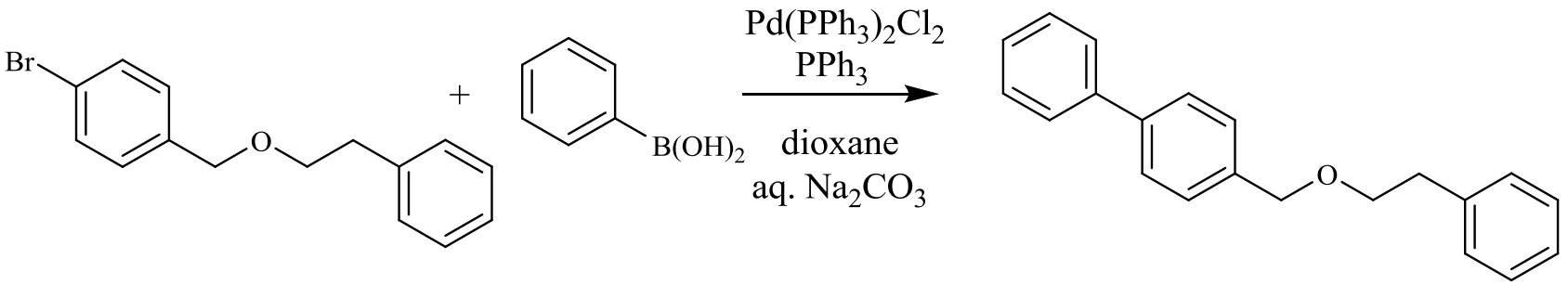
4a: R^1= 4-OMe, R^2 = H
4b: R^1 = R^2 = H

5a:R^2=3-(4-Methoxyphenyl) (69%)
5b:R^2=4-(4-Methoxyphenyl) (70%)

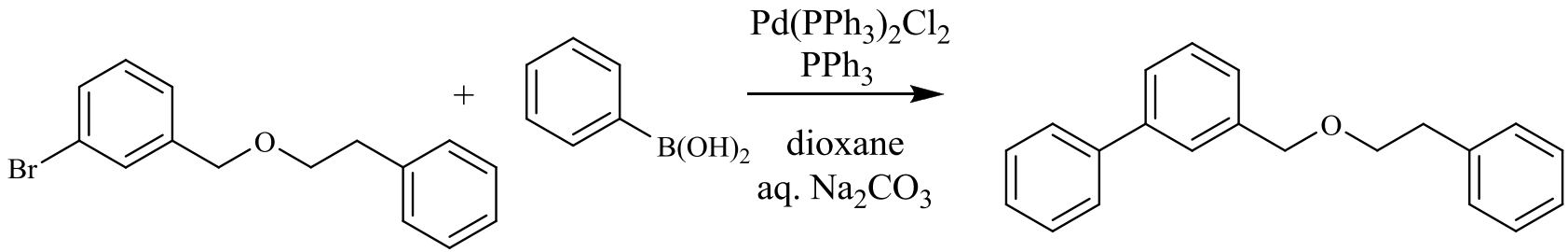
Scheme 2

Synthesis

Suzuki-Miyaura reaction to biarylated ethers under biphasic conditions, using $Pd(PPh_3)_2Cl_2$ as catalyst.



2i **4b** **5d** (86%)

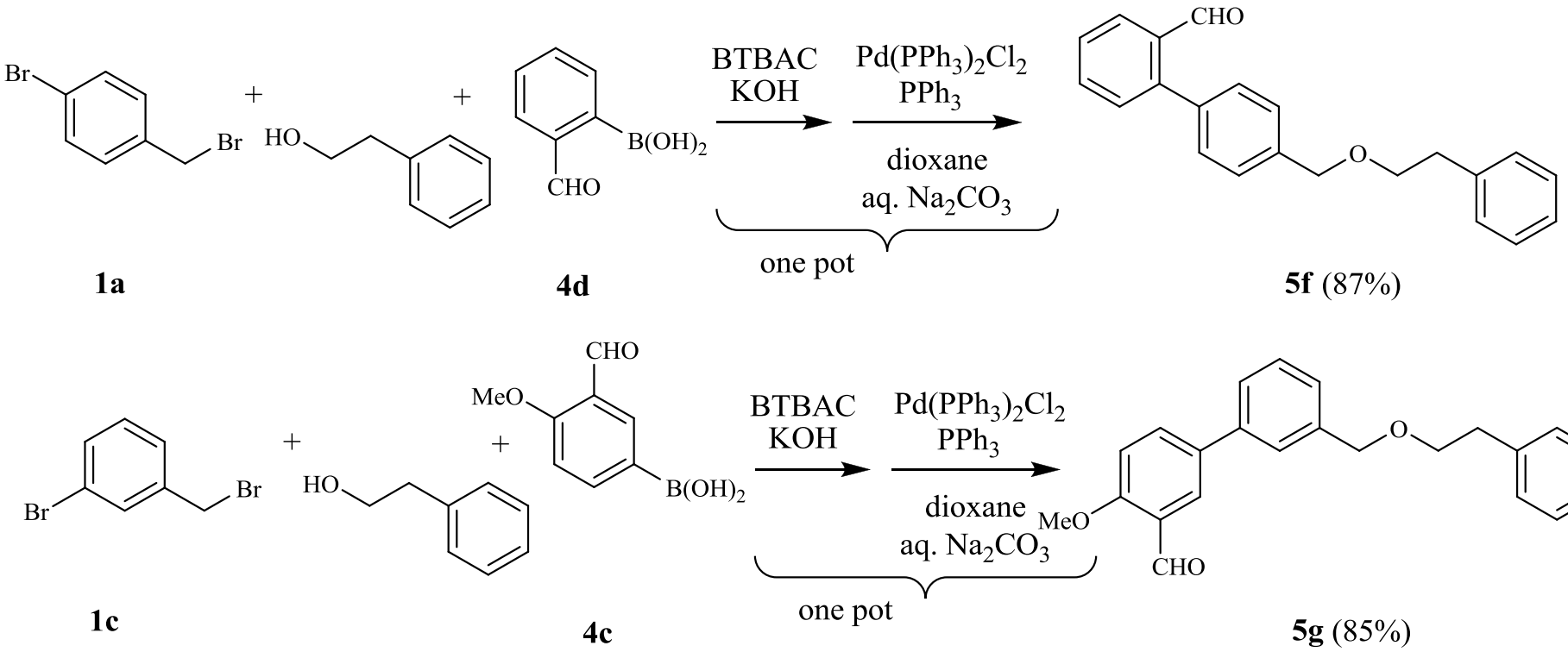


2i **4b** **5e** (84%)

Scheme 3

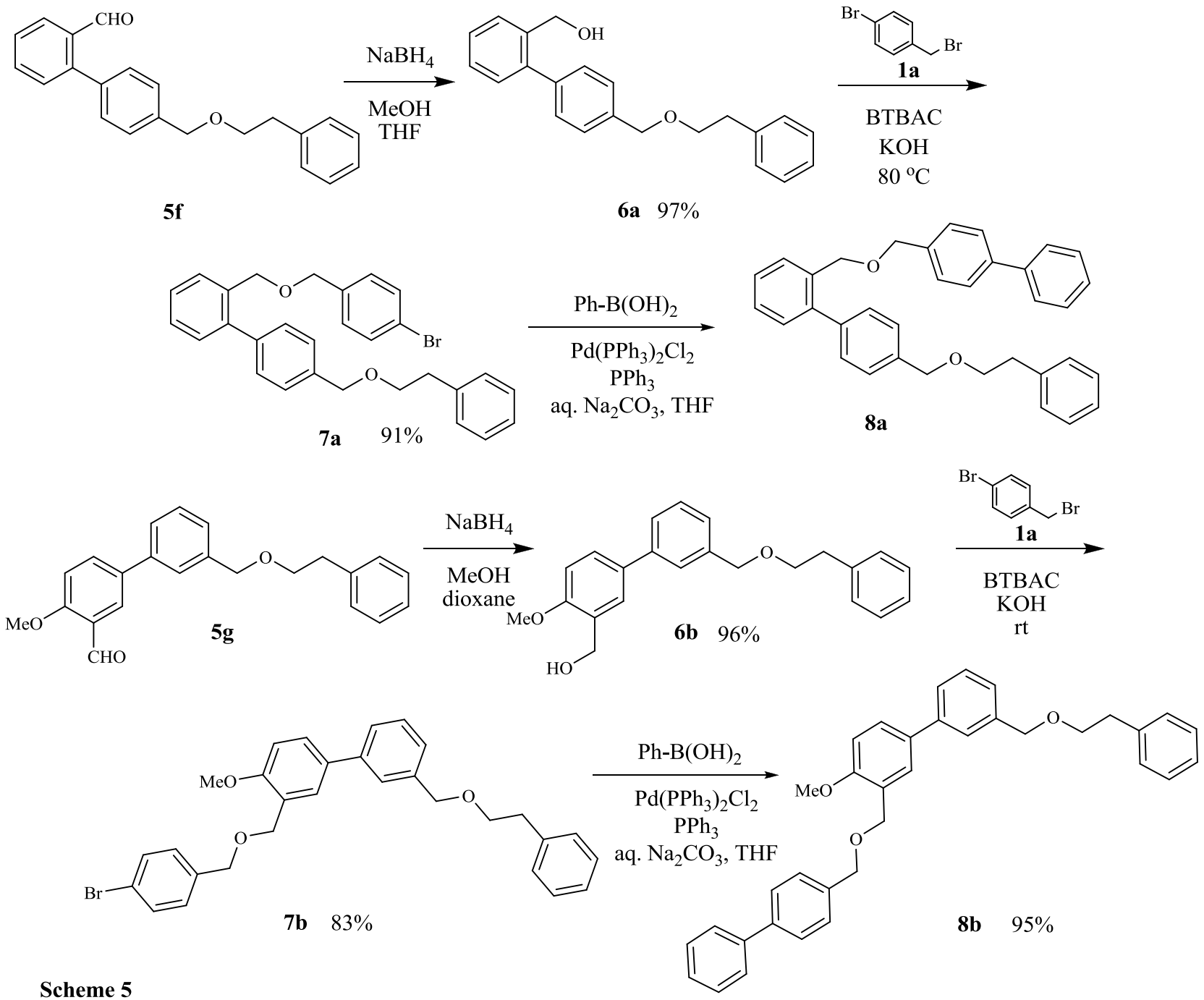
Synthesis

Further improvement with maintaining the strategy of a one-pot etherification / Suzuki coupling reaction.



Scheme 4

Further reactions to extended ethers



Scheme 5

Estimation of physical and thermal properties

- There are different reported methods for the estimation of properties of pure compounds, such as developed by Joback and Reid, Lydersen, Ambrose, Klincewicz and Reid, Lyman et al., Horvath, and Marrero and Gani.
- Properties of interest for HTFs in general: Heat Capacity, Melting point, Boiling Point, Critical Temperature.
- The heat capacity as a function of temperature ($C_p^l\ (T)$) for products was estimated according to Kolsk et al.'s three-level group contribution method.
- Melting point, Boiling Point, Critical Temperature were estimated by Marrero and Gani's model.

Estimation of physical and thermal properties

- Heat Capacity equations:

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

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

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), $a_{q\text{-}i,\,j,\text{ or }k}$, $b_{q\text{-}i,\,j,\text{ or }k}$, and $d_{q\text{-}i,\,j,\text{ or }k}$ are adjustable parameters for the temperature dependence of $C_{p0}^l(T)$, $C_{p1-i}^l(T)$, $C_{p2-j}^l(T)$, and $C_{p3-k}^l(T)$.

Estimation of physical and thermal properties

- According to Marrero and Gani's model:
- Normal melting point (T_m):

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

- Normal boiling point (T_b):

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

- 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) $T_{\mathrm{m1}i}$, $T_{\mathrm{b1}i}$ and $T_{\mathrm{c1}i}$ 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.

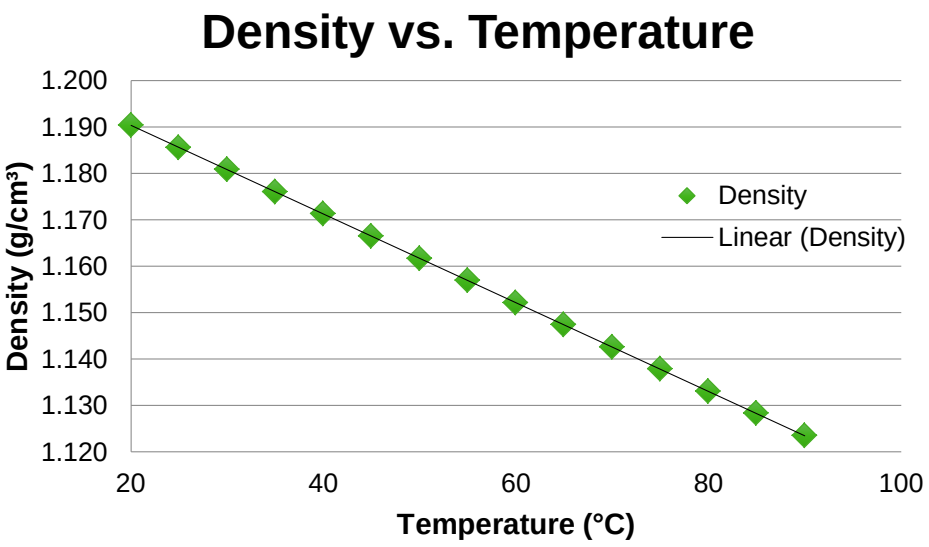
Estimation of physical and thermal properties

- Table of the estimated properties:

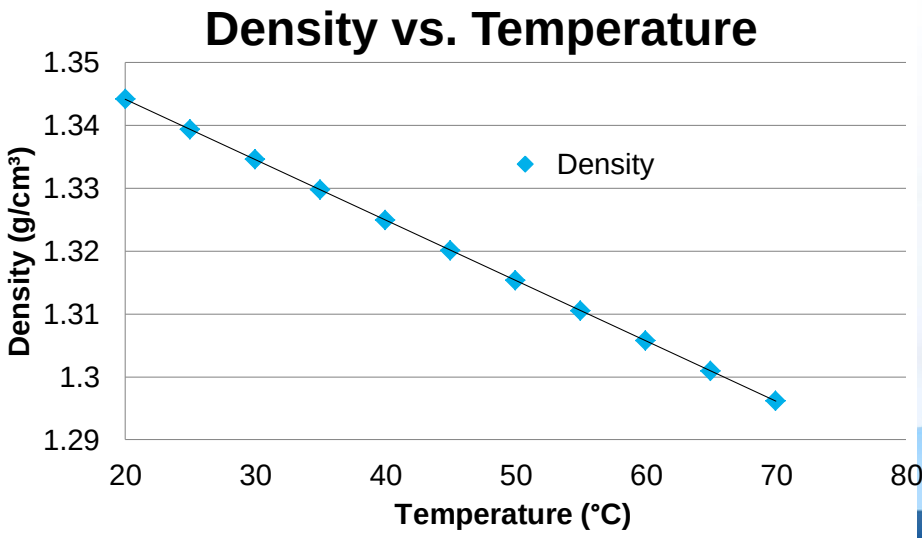
Compound	Cp [J/(mole.K)] (J/(g.K)		T_m (^{0}C)	T_b (^{0}C)	T_c (^{0}C)
	(NH) Appr.	(H) Appr.			
2a	309.2 (1.35)	299.6 (1.31)	44	153	375
2b	338.7 (1.39)	328.8 (1.35)	48	167	386
2c	368.2 (1.43)	358.0 (1.39)	52	181	398
2d	397.7 (1.47)	387.1 (1.43)	56	194	408
2e	427.2 (1.50)	416.3 (1.46)	60	206	419
2f	349.1 (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

Density vs. Temperature

- It is shown that the density of the compounds below decreases linearly with the temperature in the range of 20 - 90 ºC.

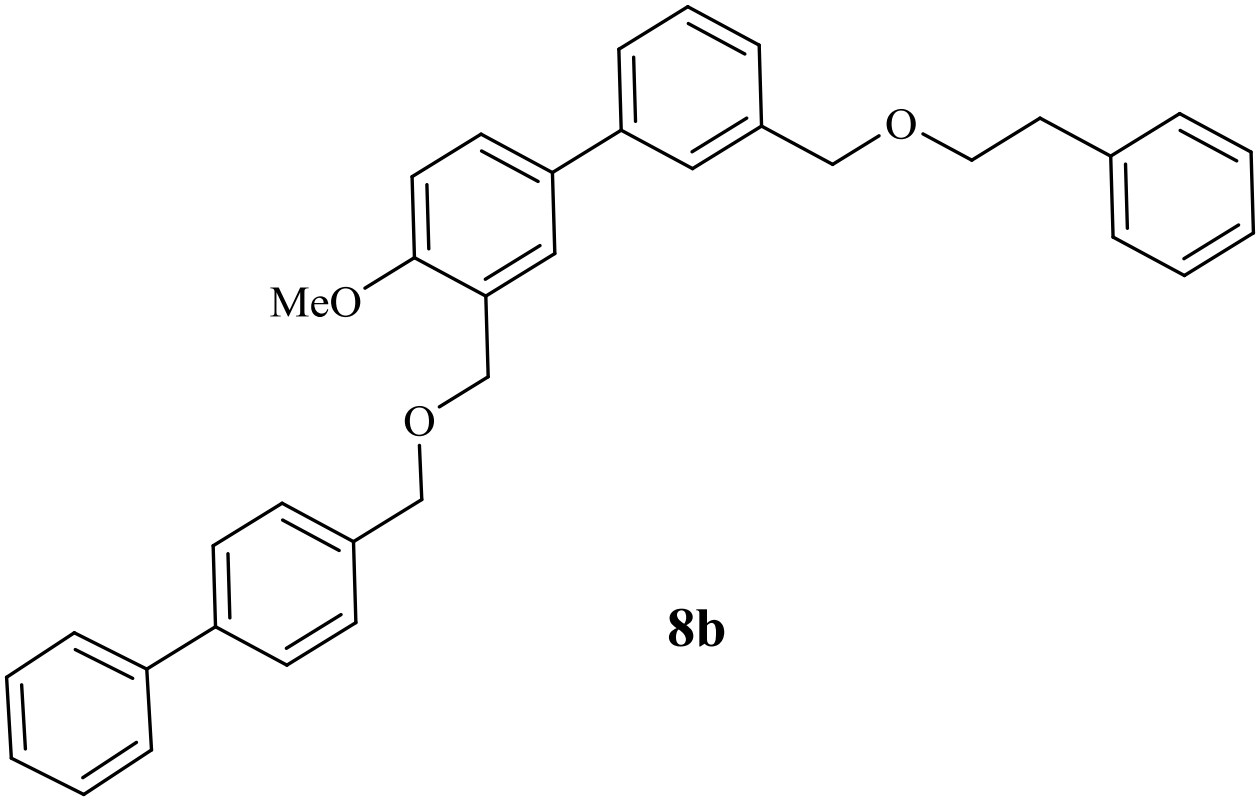


*(4-bromobenzyl hexyl ether (**2d**))*



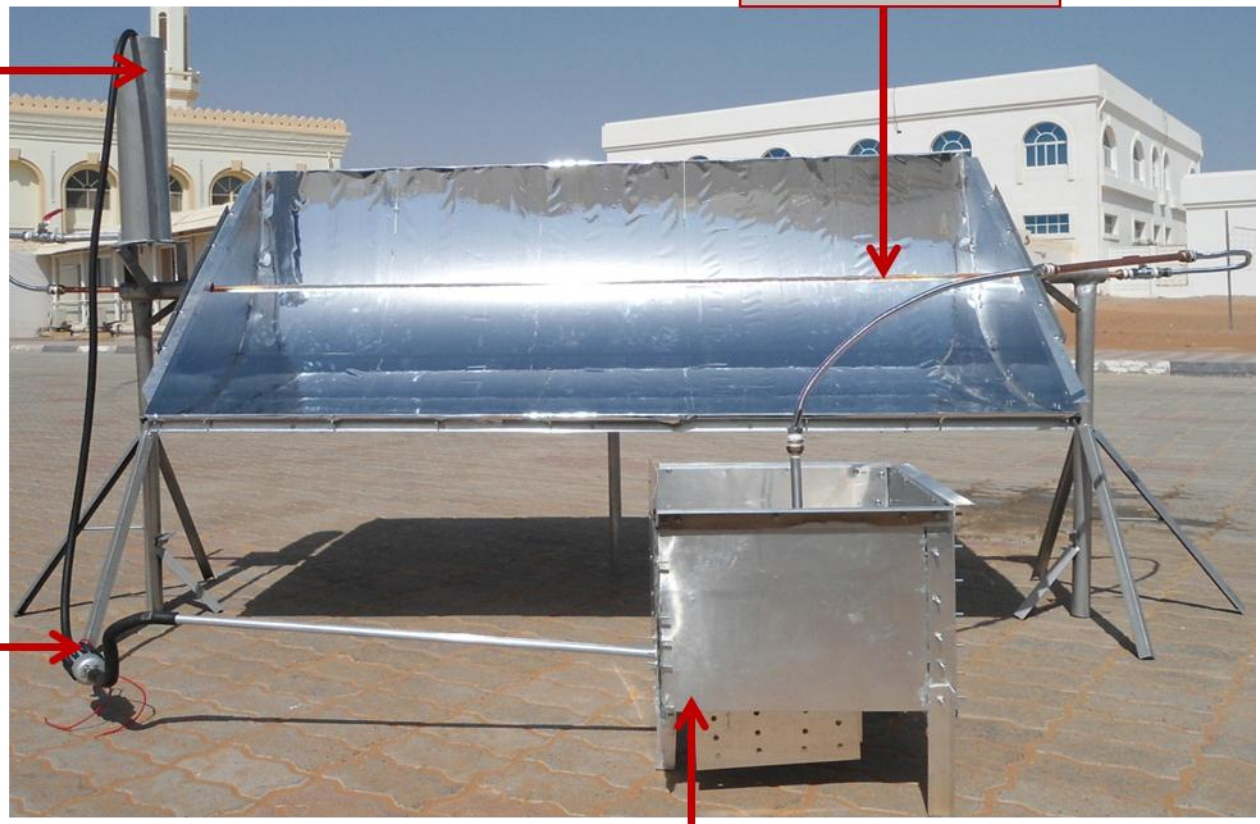
*(4-bromobenzyl benzyl ether (**2g**))*

- TGA measurements show that ethers such as **8b** are stable up to 300 ^{o}C, even in air.



8b

Solar Thermoelectric Generator prototype



Solar Thermoelectric Generator prototype has been built by Y. Al Jasem at UAEU for HTF studies

Conclusion

- A simple strategy has been developed for the synthesis of bisarylethers by a one-pot etherification – Suzuki coupling reaction, partly under solventless conditions.
- The ethers have been calculated to have high specific heat capacities, which has been experimentally verified for some of them.
- Good matches between calculated and measured melting points have been found. However, the extended ethers show to be liquid at room temperature, in contrast to the predicted model, most likely due to the fact that they do not pack well because of their complicated molecular geometry.
- The bisaryl ethers show high thermal stability, even in air.

References

Joback, K.G.; Reid, R.C. Estimation of Pure-Component Properties from Group-Contributions. *Chem. Eng. Comm.* **1987**, 57, 233–243.

Lydersen, A.L. Estimation of critical properties of organic compounds, College Engineering University Wisconsin, Engineering Experimental Station Report 3, Madison, WI, April, **1955**.

Ambrose, D. Correlation and estimation of vapor–liquid critical properties. I. Critical temperatures of organic compounds, National Physical Laboratory, Teddington, UK, NPL Report Chem., 92, September **1978**.

Klincewicz, K.M.; Reid, R.C. Estimation of critical properties with group contribution methods. *AIChE J.* **1984**, 30, 137–142.

Lyman, W.J.; Reehl, W.F.; Rosenblatt, D.H. Handbook of Chemical Property Estimation Methods, American Chemical Society, Washington, DC, **1990**.

Horvath, A.L. Molecular Design, Elsevier, Amsterdam, 1992.

Marrero, J.; Gani, R. Group-contribution based estimation of pure component properties. *Fluid Phase Equilibria*, **2001**, 183–208

Kolská, Z.; Kukal, J.; Zábranský, M.; Růžička, V. Estimation of the Heat Capacity of Organic Liquids as a Function of Temperature by a Three-Level Group Contribution Method. *Ind. Eng. Chem. Res*. **2008**, 47, 2075-2085.

Thank you for your attention