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# A cycloalkane-based thermomorphic system for palladium-catalyzed cross-coupling reactions

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**Abstract**

In this paper, we describe a practical and efficient protocol for Sonogashira, Suzuki–Miyaura, and Mizoroki–Heck cross-coupling using a CBT system. The use of substrates with cycloalkane-soluble tags facilitates separation of the desired products and the homogeneous Pd catalyst via simple liquid–liquid extraction, thereby eliminating the need for a catalyst removal process.


## 1. Introduction

Solution-phase tag-assisted organic synthesis is being developed as a useful alternative to the classical heterogeneous resin-supported and combinatorial methodologies.[1,2] Efforts to design phase tags based on solid-phase extraction (SPE) have led to investigation of the effects of high reactivity of the soluble species and the possibility of using routine analytical methods (NMR, TLC, MS, etc.) to monitor the reaction process and directly determine the structures of products, even when they are attached to liquid-phase tags. In particular, hydrophobic phase-tagging strategies based on SPE using C18 silica have been recognized as useful methods which result in effective generation of target products.[3] While most procedures for recovery of target molecules emphasize SPE, liquid–liquid extraction (LLE) may also have broad potential, because suitably phase-tagged compounds in a biphasic system often show particular affinity for one phase without further supports.

A recent study by Bergbreiter and co-workers opened the door to the use of thermomorphic systems, which can be applied in the form of a recyclable catalytic system in palladium-catalyzed cross-coupling and other reactions.[4] In the course of our investigations of thermomorphic systems, we found that cycloalkanes (especially cyclohexanes) show thermosensitive phase transitions with a wide variety of typical polar organic solvents under moderate conditions (Fig. 1).[5] This system, which utilizes selective separation of tagged products from the reaction mixture into the cycloalkane phase, is expected to be highly useful for parallel synthesis and the construction of combinatorial libraries, and results in high reactivity even when tagged substrates and insoluble catalysts are used. In addition, highly selective formation of separable phase-tagged products confers a significant advantage in terms of monitoring the reaction progress and identification of products.

The scope of Pd-catalyzed reactions in cycloalkane-based thermomorphic (CBT) systems has thus far been mostly

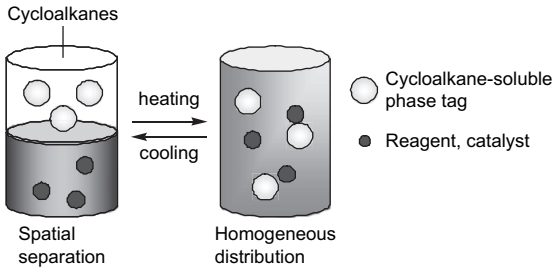


Figure 1. Schematic view of a CBT system.

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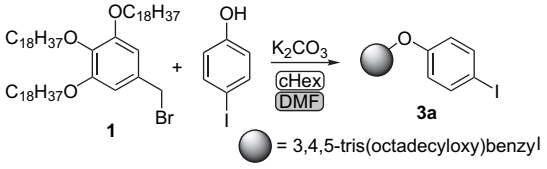
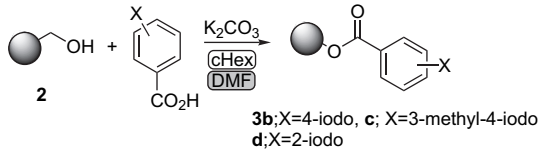
limited to the cycloalkane phase tag-linked aryl halides via esters bond.[5b] In addition, synthetic application of the hydrophobic products has not been reported, although the CBT process can facilitate continuous multi-step synthesis toward further chemical modification. In this paper, we describe the application of the CBT system in Sonogashira, Mizoroki–Heck, and Suzuki–Miyaura reactions as typical examples of Pd-catalyzed cross-coupling reactions. Furthermore, we demonstrate the synthetic application of a phase-tagged product containing an internal alkyne group.

## 2. Results and discussion

Initially, we prepared hydrophobic aryl halides **3a–d** in a cyclohexane/DMF media system. As shown in Scheme 1, 4-iodophenol was successfully attached to 3,4,5-trisoctadecyloxy-benzyl bromide **1** in cHex/DMF in the presence of $K_2CO_3$. Treatment of cycloalkane-soluble alcohol **2** with various benzoic acids using *N*,*N*′-diisopropylcarbodiimide (DIC) as a coupling reagent in the presence of a catalytic amount of *N*,*N*-dimethylaminopyridine (DMAP) gave the corresponding product in excellent yield (Scheme 2).




Scheme 1. Loading of aryl halides to cycloalkane-soluble phase tag **1**.




Scheme 2. Loading of aryl halides to cycloalkane-soluble phase tag **2**.

### *2.1. Sonogashira reaction with hydrophobically tagged alkene and aryl halides in a CBT system*

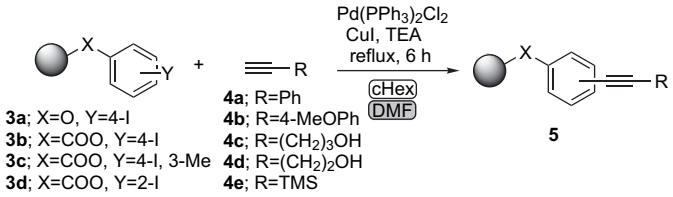
In order to facilitate the construction of hydrophobic product libraries in the cycloalkane phase, we examined Sonogashira cross-coupling in a cHex/DMF system using substrates **3a–d** prepared under conventional heating conditions. The hydrophobic aryl halides were allowed to react with terminal alkynes in the presence of triethylamine (TEA) and 2 mol % $Pd(PPh_3)_2Cl_2$. The results are summarized in Table 1: the cross-coupling reactions proceeded successfully to form the corresponding products in excellent yields. Aromatic (**4a** and **b**) and aliphatic (**4c–e**) alkynes were successfully coupled with electron-rich (Table 1, entries 1 and 2) and electron-deficient (entries 3–5) aryl iodides. The reaction of sterically hindered *ortho*-substituted aryl iodide **3d** also proceeded successfully. The desired products, with cyclohexane-soluble tags, were dissolved almost quantitatively in the cyclohexane layer and obtained in highly-pure-form. In addition, the product was monitored as a single TLC spot and identified using $^1$H NMR and mass spectroscopy without cleavage of the hydrophobic tag. In this CBT system, it was found that palladium complex stayed mainly in the DMF section of the biphase (estimated from ICP-MS: less than 0.04% leaching of Pd into the cyclohexane phase), while almost all of the tagged product remained in the cycloalkane phase.

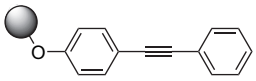
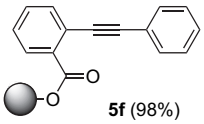
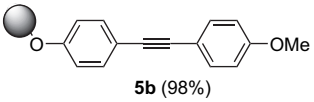
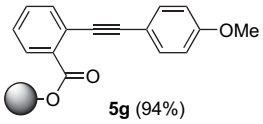
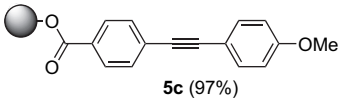
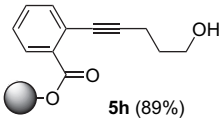
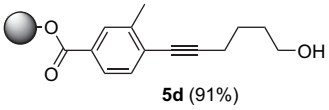
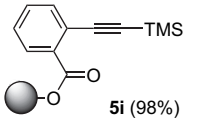
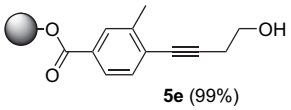
It is noteworthy that the CBT system employing a cycloalkane-soluble carrier may facilitate the construction of chemical libraries upon optimization of the reaction conditions. Because the reaction components are homogeneously distributed in the mono-phase, hydrophobic substrates in cHex are allowed to interact effectively with DMF-soluble alkynes, Pd catalysts, and bases to give hydrophobic products that may be separated into the cHex phase. It was found to be difficult to complete these reactions under conventional monophasic conditions, even in biphasic solutions composed of *n*-alkanes and typical polar solvents. Obviously, effective mutual miscibility of the co-solvents plays a significant role in the reaction of the phase-tagged substrate with the insoluble catalyst. After completion of the reaction, the soluble tag allows spatial separation of the products from the mixture of catalyst and base. It is generally difficult to extract low-molecular-weight compounds quantitatively from DMF solution in a single run of liquid–liquid extraction because of the high solubility of polar and even less polar compounds in DMF. It is expected that the ability to carry out a single LLE manipulation via the CBT process will effectively facilitate sequential reaction and purification steps, which should ensure its usefulness in the realization of continuous flow or multi-step processes.

In an attempt to further accelerate the CBT process, Sonogashira cross-coupling in cHex/DMF was attempted under microwave irradiation; the results are outlined in Table 2.[6] Using microwave heating at 100 W (100 °C), all reactions were completed within 20 min. Combining the CBT system with microwave irradiation had a positive effect in terms of acceleration of the targeted reactions. The reaction of hydrophobic aryl halides with terminal alkynes proceeded smoothly to give the corresponding products in the cyclohexane phase, as occurred under conventional heating conditions. Thus, the microwave-assisted CBT reaction system allows for further acceleration of Sonogashira cross-coupling reactions in monophasic solution followed by product isolation in biphase upon cooling.

Next, we attempted the synthetic application of one of the products obtained from the CBT reaction, 2-(phenylethynyl)-benzoate ester **5f**. Treatment of **5f** with iodide as an electrophilic reagent in dichloromethane afforded the corresponding isocoumarin derivative **6** in good yield, as shown in Scheme 3. Addition of MeOH followed by ODS-filtration allows removal of the hydrophobic phase tag from the reaction mixture, because phase tags within a certain range of molecular weight and hydrophobicity can easily be precipitated with polar solvents. Alternatively, treatment of **3f** with a catalytic amount of NaOMe in cHex/MeOH solution, followed by neutralization with DOWEX, gave the methyl ester **7** in the MeOH

Table 1
A CBT system for palladium-catalyzed Sonogashira cross-coupling reactions[a]



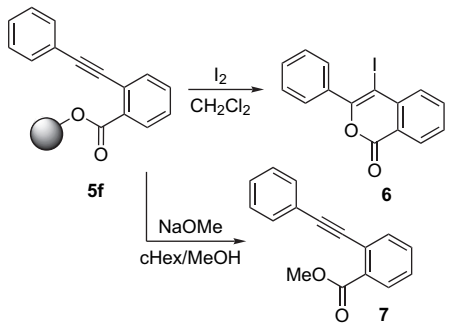

| Entry | Substrates | Product[b] | Entry | Substrates | Product[b] |
|---|---|---|---|---|---|
| 1[c] | **3a/4a** |  **5a** (95%) | 6 | **3d/4a** |  **5f** (98%) |
| 2 | **3a/4b** |  **5b** (98%) | 7 | **3d/4b** |  **5g** (94%) |
| 3 | **3b/4b** |  **5c** (97%) | 8 | **3d/4d** |  **5h** (89%) |
| 4 | **3c/4c** |  **5d** (91%) | 9 | **3d/4e** |  **5i** (98%) |
| 5 | **3c/4d** |  **5e** (99%) | | | |

[a] All reactions were carried out using aryl halides **3a–d**, 1.5 equiv of alkyne, 3 equiv of TEA, CuI (1 mol %), and 2 mol % of $Pd(PPh_3)_2Cl_2$ in cHex/DMF.
[b] Isolated yield.
[c] Reusability of the recovered Pd catalyst was also tested; see Section 4.

Table 2
A CBT system for palladium-catalyzed Sonogashira cross-coupling reactions under the microwave-irradiated condition[a]

| Entry | Product | Reaction time (min) | Yield[b] (%) |
|---|---|---|---|
| 1 | **5a** | 15 | 97 |
| 2 | **5b** | 20 | 95 |
| 3 | **5c** | 10 | 99 |
| 4 | **5d** | 20 | 99 |
| 5 | **5f** | 10 | 94 |

[a] Reaction conditions: $PdCl_2(PPh_3)_2$ (2 mol %), alkyne (1.5 equiv), TEA (3 equiv). Microwave irradiation 100 W, 100 °C.
[b] Isolated yield.

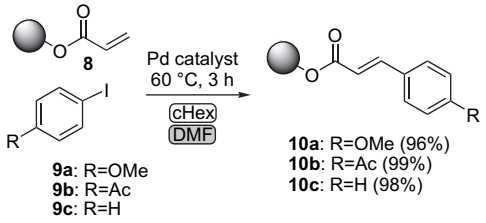



Scheme 3. The synthetic application of the separable phase-tagged product **5f** containing an internal alkyne group.

phase and compound **2** in the cHex layer. In this case, compound **2** was easily removed from reaction media and was recyclable after cleavage via a simple liquid–liquid extraction process.

### *2.2. Mizoroki–Heck reaction with hydrophobically tagged alkene and aryl halides in the CBT system*

Encouraged by the excellent results described above, we were keen to develop this methodology for use with another palladium-mediated C–C bond-formation reaction, the Mizoroki–Heck coupling reaction. We carried out coupling of acrylate with aryl iodides in the same CBT solution. In a typical reaction, 0.5 mmol of acrylate **8** in 3 mL of a cHex/DMF solvent mixture was treated with 1.5 equiv of aryl iodide at 60 °C for 3 h under conventional heating conditions in the presence of 3 equiv of triethylamine and 2 mol % of a palladium catalyst, tris(dibenzylideneacetone)dipalladium [$Pd_2(dba)_3$]. The results are shown in Scheme 4. The use of 4-methoxyiodobenzene **9a**, 4-iodoacetophenone **9b**, and iodobenzene **9c** gave yields of 96, 99, and 98%, respectively. As expected, the coupling reaction also proceeded successfully using a microwave-assisted CBT system, giving the products in excellent yields.



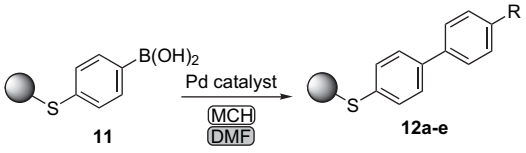

Scheme 4. Mizoroki–Heck reactions of aryl iodides **9a–c** in a CBT system.

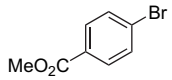
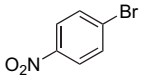
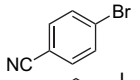
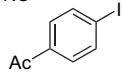
### 2.3. Suzuki–Miyaura cross-coupling reaction with a cycloalkane-soluble phase-tagged boronic acid in the CBT system

In our previous letter, we reported a general method for microwave-promoted Suzuki–Miyaura cross-coupling of aryl halides attached to a cycloalkane-soluble tag with arylboronic acids in a CBT system.[5b] We then turned our attention to designing a hydrophobic tag for boronic acid to allow reaction with aryl halides. Thus, we synthesized the boronic acid derivative **11**, which was found to be an excellent coupling partner in the reaction. The results of coupling reactions between the hydrophobically tagged boronic acid and various aryl halides are shown in Table 3. The target coupling reaction of the hydrophobically tagged boronic acid **11** with aryl halides also proceeded in excellent yield in a microwave-assisted CBT system. These results indicated that selective tagging onto boronic acid derivatives or aryl halides can facilitate the construction of widely ranging cross-coupling product libraries.

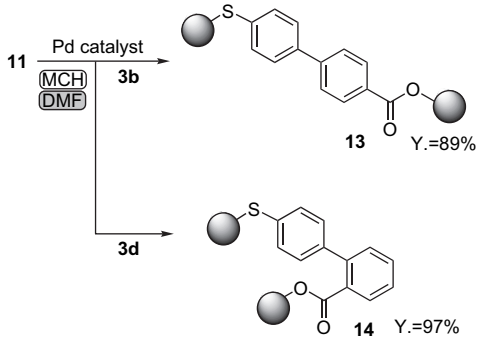
In order to investigate the effects of interaction between two types of cycloalkane-soluble tag in the CBT reaction system, we prepared two hydrophobically tagged substrates and carried out the coupling reaction under the conditions

Table 3
Microwave-promoted Suzuki–Miyaura cross-couplings of aryl halides with cycloalkane-soluble phase-tagged boronic acid **11**[a]




| Entry | Aryl halide | Product | Yield[b] (%) |
|---|---|---|---|
| 1 |  | **12a**: R=$CO_2Me$ | 86 |
| 2 |  | **12b**: R=$NO_2$ | 92 |
| 3 |  | **12c**: R=CN | 97 |
| 4 |  | **12d**: R=Ac | 99 |

[a] Reaction conditions: 0.5 mmol of boronic acid, 1.5 equiv of aryl halide, 3.0 equiv of $K_3PO_4$, and 3 mL of methylcyclohexane (MCH)/DMF (1:1). Microwave power 150 W, 100 °C, 5 min.
[b] Isolated yield.




Scheme 5. Suzuki–Miyaura cross-coupling of both cycloalkane-soluble phase-tagged substrates in a CBT system.

described previously. As shown in Scheme 5, the target reactions between **11** and each of the cycloalkane-soluble tags proceeded to afford double-tagged products in good yield, although reaction with tagged substrates in the solid phase is generally difficult. We attribute these results to the fact that the mutual miscibility of DMF (catalyst phase) and cHex (tag-soluble phase) and the affinity of the tagged substrates in the CBT solution play significant roles in the coupling reaction. In addition, it is expected that this reaction system will provide a facility for constructing various useful cycloalkane-soluble tags.

Finally, we attempted to decrease the quantity of DMF used in the reaction. Decreasing the volume of the lower phase (DMF phase) was found to lead to an increase in productivity. Our objective was to determine the minimum amount of DMF required to give the coupling products in good yield. To find this, we carried out the reaction of aryl halide **3b** and *p*-fluorophenyl boronic acid in DMF/CH solvent mixtures with various ratios.

As shown in Figure 2, we found that it was possible to reduce the amount of DMF to 5% of the solvent medium.

The quantity used can be further reduced to 1% with a significant decrease in product yield. In the absence of DMF, the

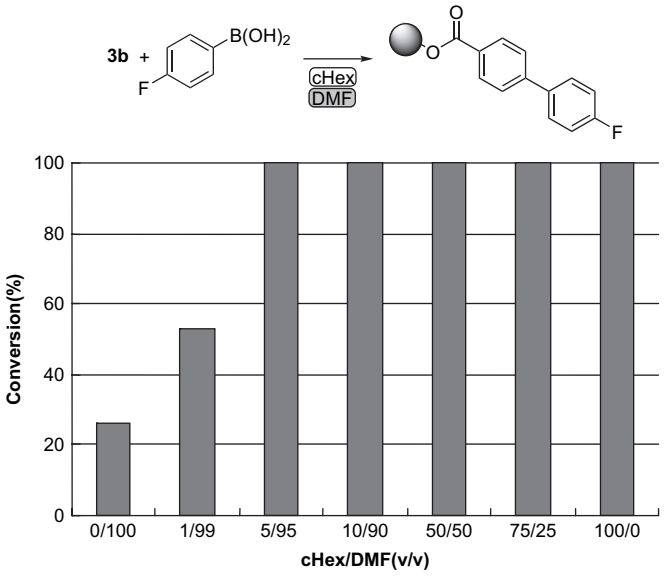



Figure 2. Effects of volume ratio of each phase on microwave-promoted Suzuki–Miyaura coupling of aryl bromide **3b** and *p*-fluorophenyl boronic acid.

biaryl product was obtained in only 26% yield. The use of more than 5% DMF resulted in quantitative yield. Similar observations were made for the reaction as carried out under conventional heating conditions. To find out whether the use of a cycloalkane in the reaction had a deleterious effect on product yield, we monitored the conversion rate for the biaryl product using DMF and 20% cHex/DMF, respectively, under microwave conditions, and found that the conversion rates obtained in both cases were almost the same. This result suggests that the addition of cycloalkane to the reaction medium has no deleterious effect on the coupling reaction. The system is therefore advantageous in terms of productivity (volume efficiency of the tagged products) and also diminishes the requirement for the cumbersome refreshment process of polar organic solvents such as DMF, which contain catalyst, base, and other chemicals.

## 3. Conclusions

We have developed a practical and efficient protocol for Sonogashira, Suzuki–Miyaura, and Mizoroki–Heck cross-coupling reactions using a CBT system. The use of substrates with cycloalkane-soluble tags facilitates separation of the desired products and the Pd catalyst via simple liquid–liquid extraction, thereby eliminating the need for a cumbersome process to remove the homogeneous catalyst. In this reaction system, there was no observable phosphorus or palladium in the cycloalkane phase after the separation process. In addition, the catalyst phase (DMF) can be recycled at least three times without any significant loss of activity. It may be possible to apply this CBT system in various Pd-catalyzed reactions, allowing for their use in a parallel or combinatorial format.

## 4. Experimental section

### *4.1. Loading of aryl halides onto compound **1**: 5-((4-iodophenoxy)methyl)-1,2,3-tris(octadecyloxy)benzene (**3a**)*

A mixture of $K_2CO_3$ (97 mg, 0.7 mmol) and 4-iodophenol (110 mg, 0.55 mmol) in 3 mL of DMF was treated with aryl halides attached to the cycloalkane-soluble platform 1 (488 mg, 0.5 mmol) dissolved in 3 mL of cyclohexane. The solution was refluxed for 5 h. After cooling, the cyclohexane layer was separated and evaporated under vacuum. Methanol was added to the residue followed by filtration to afford the product **3a** (529 mg, 95%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.56 (d, 2H, $J$=8.5 Hz), 6.75 (d, 2H, $J$=8.5 Hz), 6.58 (s, 2H), 4.91 (s, 2H), 3.95 (m, 6H), 1.84–1.01 (m, 96H), 0.88 (t, 9H, $J$=6.6 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 158.7, 153.4, 138.8, 138.1, 131.3, 117.3, 106.1, 92.5, 73.4, 70.4, 69.2, 31.9, 30.3, 29.7, 29.7, 29.6, 29.4, 29.4, 26.9, 26.1, 22.7, 14.1. TOF-MS (pos) calcd for $C_{67}H_{119}IO_4$ [M+$Na^+$] 1137.8051, found 1137.8012.

### *4.2. Loading of aryl halides onto compound **2***

The appropriate benzoic acid (1.5 mmol), *N*,*N*′-diisopropylcarbodiimide (1.5 mmol), and a catalytic amount of 4-dimethylaminopyridine (0.2 mmol) in 3 mL of DMF were added to the cycloalkane-soluble platform (914 mg, 1.0 mmol) dissolved in 3 mL of cyclohexane, and the reaction mixture was stirred at 55 °C for 1 h. After cooling, the cyclohexane layer was separated and evaporated under vacuum. Methanol was added to the residue, followed by filtration to afford the compounds **3b** (98%), **3c** (99%), and **3d** (99%).

#### *4.2.1. 3,4,5-Tris(octadecyloxy)benzyl 4-iodobenzoate (**3b**)*

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.80 (d, 2H, $J$=8.63 Hz), 7.76 (d, 2H, $J$=8.63 Hz), 6.60 (s, 2H), 5.23 (s, 2H), 3.99–3.92 (m, 6H), 1.84–1.71 (m, 6H), 1.48–1.25 (m, 90H), 0.88 (t, 9H, $J$=6.79 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 165.8, 153.2, 138.2, 137.6, 131.1, 130.5, 129.5, 107.0, 73.4, 69.2, 67.4, 31.9, 30.4, 29.8, 29.7, 29.5, 29.4, 26.2, 22.8, 14.1. TOF-MS (pos) calcd for $C_{68}H_{119}IO_5$ [M+$Na^+$] 1165.8000, found 1165.7965.

#### *4.2.2. 3,4,5-Tris(octadecyloxy)benzyl 4-iodo-3-methylbenzoate (**3c**)*

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.48 (d, 1H, $J$=1.4 Hz), 7.93 (dd, 1H, $J$=8.0, 1.4 Hz), 7.29 (d, 1H, $J$=8.0 Hz), 6.61 (s, 2H), 5.23 (s, 2H), 3.97 (m, 6H), 2.48 (s, 3H), 1.85–1.20 (m, 96H), 0.88 (t, 9H, $J$=7.0 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 165.0, 153.2, 146.9, 140.1, 138.4, 130.1, 129.5, 129.4, 129.4, 100.5, 73.5, 69.2, 68.0, 31.9, 30.3, 29.7, 29.7, 29.4, 29.4, 29.4, 29.3, 28.4, 26.1, 25.6, 22.7, 14.1. TOF-MS (pos) calcd for $C_{69}H_{121}IO_5$ [M+$Na^+$] 1179.8156, found 1179.8139.

#### *4.2.3. 3,4,5-Tris(octadecyloxy)benzyl 2-iodobenzoate (**3d**)*

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.96 (dd, 1H, $J$=8.0, 1.0 Hz), 7.77 (dd, 1H, $J$=8.0, 1.0 Hz), 7.37 (ddd, 1H, $J$=8.0, 1.0 Hz), 7.13 (ddd, 1H, $J$=8.0, 1.0 Hz), 6.63 (s, 2H), 5.25 (s, 2H), 3.93 (m, 6H), 1.88–1.07 (m, 96H), 0.88 (t, 9H, $J$=7.0 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 166.6, 153.2, 142.2, 138.3, 135.2, 132.6, 131.0, 130.4, 127.9, 107.3, 94.0, 73.4, 69.2, 67.8, 31.9, 30.3, 29.7, 29.6, 29.6, 29.6, 29.4, 29.4, 29.3, 26.1, 26.1, 23.4, 22.7, 14.1. TOF-MS (pos) calcd for $C_{68}H_{119}IO_5$ [M+$Na^+$] 1165.8000, found 1165.7993.

### *4.3. General procedure for Sonogashira coupling reaction*

A mixture of $PdCl_2(PPh_3)_2$ (7.0 mg, 2 mol %), CuI (1 mg, 1 mol %), triethylamine (206 μL, 1.5 mmol), and alkynes **4a–e** (0.75 mmol) in 3 mL of DMF was treated with compounds **3a–d** (0.5 mmol) dissolved in 3 mL of cyclohexane, and the solution was refluxed for 6 h under Ar. After cooling, the cyclohexane layer was separated and evaporated under vacuum. Methanol was added to the residue, followed by filtration to afford the products **5a–i**.

### *4.4. Microwave irradiation experiments*

All microwave irradiation experiments were carried out in a CEM-Discover mono-mode microwave apparatus, operating at a frequency of 2.45 GHz with continuous irradiation power

from 0 to 300 W. The reactions were carried out in glass tubes sealed with a pressure lock. The pressure was controlled by a load cell connected directly to the vessel. The reaction temperature was measured using an IR sensor on the outer surface of the process vial. Microwave irradiation of 100 W was used, with the temperature ramped from room temperature to 100 °C in 5 min. On reaching 100 °C, the reaction mixture was held at that temperature.

### *4.5. The reusability of the recovered Pd catalyst in the DMF phase*

Based on a coupling reaction (Table 1, entry 1), the reusability of the recovered Pd catalyst in the DMF phase was tested according to the experiment described in Ref. 4b. The product was obtained in 99 (cycle 1), 97 (cycle 2), and 78% (cycle 3) yields, respectively.

#### *4.5.1. 1,2,3-Tris(octadecyloxy)-5-((4-(phenylethynyl)-phenoxy)methyl)benzene (**5a**)*

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.50 (d, 2H, $J$=7.8 Hz), 7.47 (d, 2H, $J$=8.5 Hz), 7.33 (m, 3H), 6.95 (d, 2H, $J$=8.8 Hz), 6.61 (s, 2H), 4.96 (s, 2H), 3.96 (m, 6H), 1.96–1.10 (m, 96H), 0.87 (t, 9H, $J$=6.6 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 158.5, 153.3, 133.0, 132.1, 131.4, 128.4, 128.3, 127.9, 118.0, 115.7, 114.9, 106.2, 89.3, 86.4, 73.4, 69.1, 69.1, 31.9, 30.9, 30.3, 29.7, 29.6, 29.4, 29.3, 26.1, 26.1, 22.7, 14.1. IR (KBr): 2920, 2850, 1598, 1506, 756 cm$^{-1}$. TOF-MS (pos) calcd for $C_{75}H_{124}O_4$ [M+Na$^+$] 1111.9397, found 1111.9401.

#### *4.5.2. 5-((4-((4-Methoxyphenyl)ethynyl)phenoxy)methyl)-1,2,3-tris(octadecyloxy)benzene (**5b**)*

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.44 (d, 4H, $J$=8.8 Hz), 6.93 (d, 2H, $J$=8.4 Hz), 6.86 (d, 2H, $J$=8.4 Hz), 6.62 (s, 2H), 4.95 (s, 2H), 3.96 (t, 4H, $J$=6.2 Hz), 3.94 (t, 2H, $J$=7.3 Hz), 3.82 (s, 3H), 1.83–1.10 (m, 96H), 0.87 (t, 9H, $J$=6.6 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 159.3, 158.4, 153.2, 132.8, 131.4, 125.8, 121.7, 115.9, 115.6, 114.7, 113.8, 88.0, 87.8, 73.3, 69.1, 65.6, 55.2, 31.8, 31.8, 30.2, 29.6, 29.6, 29.3, 29.3, 26.0, 26.0, 22.6, 14.0. IR (KBr): 2919, 2850, 1597, 1508, 1463, 1244, 1176, 1115 cm$^{-1}$. TOF-MS (pos) calcd for $C_{76}H_{126}O_5$ [M+Na$^+$] 1141.9503, found 1141.9523.

#### *4.5.3. 3,4,5-Tris(octadecyloxy)benzyl 4-((4-methoxyphenyl)-ethynyl)benzoate (**5c**)*

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.98 (d, 2H, $J$=7.8 Hz), 7.62 (d, 2H, $J$=7.8 Hz), 7.42 (d, 2H, $J$=7.7 Hz), 6.93 (dd, 2H, $J$=7.7 Hz), 6.65 (s, 2H), 5.36 (s, 2H), 4.00–3.86 (m, 6H), 3.97 (s, 3H), 1.84–1.73 (m, 6H), 1.47–1.25 (m, 90H), 0.88 (t, 9H, $J$=6.6 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 165.8, 159.9, 153.0, 140.1, 138.0, 133.7, 133.0, 131.6, 127.6, 124.0, 115.2, 113.9, 107.0, 94.7, 92.3, 73.4, 69.2, 67.4, 55.3, 32.0, 29.9, 29.9, 29.9, 29.9, 29.8, 29.8, 29.6, 29.5, 29.5, 26.2, 22.8, 14.3. IR (KBr): 2917, 2848, 2217, 1720, 1594, 1508, 1465, 1438, 1290, 1145 cm$^{-1}$. TOF-MS (pos) calcd for $C_{77}H_{126}O_6$ [M+Na$^+$] 1169.9452, found 1169.9458.

#### *4.5.4. 3,4,5-Tris(octadecyloxy)benzyl 4-(5-hydroxypent-1-ynyl)-3-methylbenzoate (**5d**)*

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.05 (dd, 1H, $J$=1.7, 0.4 Hz), 7.86 (dd, 1H, $J$=8.0, 1.7 Hz), 7.29 (dd, 1H, $J$=1.7, 0.4 Hz), 6.62 (s, 2H), 5.23 (s, 1H), 3.98 (t, 4H, $J$=7.0 Hz), 3.95 (t, 2H, $J$=6.8 Hz), 3.84 (q, 2H, $J$=6.3 Hz), 2.60 (t, 2H, $J$=7.1 Hz), 2.46 (s, 3H), 1.89–1.10 (m, 98H), 0.89 (t, 9H, $J$=7.1 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 165.8, 153.1, 145.3, 138.2, 133.1, 130.7, 129.3, 128.5, 127.6, 124.1, 107.1, 94.3, 79.0, 73.7, 69.2, 67.1, 61.9, 32.0, 29.7, 26.4, 22.7, 21.2, 26.3, 14.1. IR (KBr): 3400, 2912, 2850, 1716, 1587, 1468, 1376, 1226, 1118, 825 cm$^{-1}$. TOF-MS (pos) calcd for $C_{74}H_{128}O_6$ [M+Na$^+$] 1135.9609, found 1135.9638.

#### *4.5.5. 3,4,5-Tris(octadecyloxy)benzyl 4-(4-hydroxybut-1-ynyl)-3-methylbenzoate (**5e**)*

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.07 (d, 1H, $J$=1.7 Hz), 7.87 (dd, 1H, $J$=7.8, 1.7 Hz), 7.26 (dd, 1H, $J$=1.7, 0.4 Hz), 6.62 (s, 2H), 5.22 (s, 1H), 3.97 (t, 4H, $J$=6.1 Hz), 3.95 (t, 2H, $J$=6.5 Hz), 3.84 (q, 2H, $J$=6.3 Hz), 2.74 (t, 2H, $J$=6.1 Hz), 2.46 (s, 3H), 1.89–1.14 (m, 96H), 0.88 (t, 9H, $J$=7.1 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 165.9, 153.1, 145.3, 133.2, 130.9, 130.8, 129.4, 129.0, 128.0, 123.5, 107.1, 91.2, 80.4, 73.4, 69.1, 67.0, 61.1, 31.8, 30.3, 29.6, 29.6, 29.3, 29.3, 26.0, 26.0, 23.8, 22.6, 20.9, 14.0. IR (KBr): 3407, 2919, 2850, 2224, 1714, 1226, 1111 cm$^{-1}$. TOF-MS (pos) calcd for $C_{73}H_{126}O_6$ [M+Na$^+$] 1121.9452, found 1121.9450.

#### *4.5.6. 3,4,5-Tris(octadecyloxy)benzyl 2-(phenylethynyl)-benzoate (**5f**)*

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.97 (dd, 1H, $J$=8.1, 1.2 Hz), 7.63 (d, 1H, $J$=7.6, 0.7 Hz), 7.48 (d, 1H, $J$=7.6, 1.5 Hz), 7.41 (m, 2H), 7.36 (d, 1H, $J$=7.3, 0.7 Hz), 7.30 (m, 3H), 6.62 (s, 2H), 5.29 (s, 2H), 3.90 (t, 4H, $J$=6.4 Hz), 3.85 (t, 2H, $J$=6.6 Hz), 1.76–1.15 (m, 96H), 0.86 (t, 9H, $J$=6.6 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 166.3, 153.2, 134.0, 131.9, 131.7, 130.7, 130.6, 128.5, 128.4, 128.3, 128.2, 127.9, 123.8, 123.2, 107.0, 94.3, 88.3, 73.5, 69.0, 67.5, 31.9, 30.3, 29.7, 29.7, 29.4, 29.4, 29.3, 26.1, 26.1, 22.7, 14.1. TOF-MS (pos) calcd for $C_{76}H_{124}O_5$ [M+Na$^+$] 1139.9346, found 1139.9351.

#### *4.5.7. 3,4,5-Tris(octadecyloxy)benzyl 2-((4-methoxyphenyl)-ethynyl)benzoate (**5g**)*

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.98 (d, 1H, $J$=7.8 Hz), 7.62 (d, 1H, $J$=7.8 Hz), 7.48 (ddd, 1H, $J$=7.5, 1.2 Hz), 7.32 (ddd, 1H, $J$=7.8, 1.2 Hz), 7.35 (ddd, 1H, $J$=7.5, 1.2 Hz), 7.34 (d, 2H, $J$=8.5 Hz), 6.83 (d, 2H, $J$=8.5 Hz), 6.64 (s, 2H), 5.31 (s, 2H), 3.92 (t, 2H, $J$=6.5 Hz), 3.87 (t, 4H, $J$=6.5 Hz), 3.82 (s, 3H), 1.73 (m, 6H), 1.47–1.25 (m, 90H), 0.88 (t, 9H, $J$=6.6 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 165.1, 159.6, 153.0, 140.1, 138.0, 133.7, 133.0, 131.6, 130.6, 130.5, 127.6, 124.0, 115.2, 113.9, 107.0, 94.7, 92.3,

73.4, 69.2, 67.4, 55.3, 32.0, 29.9, 29.9, 29.9, 29.9, 29.8, 29.8, 29.6, 29.5, 29.5, 26.2, 22.8, 14.3. IR (KBr): 2917, 2848, 2217, 1720, 1594, 1508, 1465, 1438, 1290 $cm^{-1}$. TOF-MS (pos) calcd for $C_{77}H_{126}O_6$ [M+$Na^+$] 1169.9452, found 1169.9429.

#### 4.5.8. 3,4,5-Tris(octadecyloxy)benzyl 2-(5-hydroxypent-1-ynyl)benzoate (**5h**)

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.95 (dd, 1H, $J$=8.1, 1.5 Hz), 7.49 (dd, 1H, $J$=8.1, 0.7 Hz), 7.41 (ddd, 1H, $J$=8.1, 1.0 Hz), 7.29 (ddd, 1H, $J$=8.1, 1.0 Hz), 6.62 (s, 2H), 5.22 (s, 2H), 3.95 (t, 4H, $J$=6.6 Hz), 3.92 (t, 2H, $J$=7.0 Hz), 3.77 (q, 2H, $J$=5.6 Hz), 3.47 (d, 1H, $J$=5.6 Hz), 2.49 (t, 2H, $J$=7.1 Hz), 2.15 (m, 2H), 1.85–1.10 (m, 96H), 0.86 (t, 9H, $J$=6.1 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 166.2, 153.3, 138.2, 134.5, 131.6, 130.8, 130.4, 127.3, 125.9, 124.5, 107.7, 95.3, 79.9, 73.5, 69.3, 67.3, 61.8, 31.9, 31.0, 30.3, 29.4, 29.3, 26.1, 22.7, 16.6, 14.1. IR (KBr): 3426, 2917, 2850, 1720 $cm^{-1}$. TOF-MS (pos) calcd for $C_{73}H_{126}O_6$ [M+$Na^+$] 1121.9452, found 1121.9498.

#### 4.5.9. 3,4,5-Tris(octadecyloxy)benzyl 2-((trimethylsilyl)-ethynyl)benzoate (**5i**)

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.91 (dd, 1H, $J$=7.8, 1.2 Hz), 7.59 (dd, 1H, $J$=7.8, 1.2 Hz), 7.4 (ddd, 1H, $J$=7.8, 1.2 Hz), 7.35 (ddd, 1H, $J$=7.8, 1.2 Hz), 6.62 (s, 2H), 5.27 (s, 2H), 3.95 (m, 6H), 1.96–1.20 (m, 96H), 0.88 (t, 9H, $J$=6.6 Hz), 0.22 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 166.2, 153.3, 138.3, 134.9, 132.5, 131.7, 131.0, 130.5, 128.2, 123.7, 117.1, 103.4, 100.2, 73.5, 69.3, 67.2, 32.1, 30.5, 30.0, 29.9, 29.8, 29.8, 29.8, 29.6, 29.6, 29.5, 26.3, 26.3, 22.8, 14.3, 0.137. IR (KBr): 3421, 2917, 2850, 2154, 1727, 1591, 1470, 1240 $cm^{-1}$. TOF-MS (pos) calcd for $C_{73}H_{128}O_5Si$ [M+$Na^+$] 1135.9429, found 1135.9427.

### 4.6. 4-Iodo-3-phenylnaphthalen-1(2H)-one (**6**)

Compound **5f** (447 mg, 0.4 mmol) was dissolved in dichloromethane and then $I_2$ (0.45 mmol) was added. The mixture was stirred at room temperature for 1 h. After the solution was concentrated under vacuum, methanol was added. The suspension was filtrated and the residue was purified by silica gel chromatography (EtOAc/hexane) to give the compound **6** (99 mg, 71%).

### 4.7. Methyl 2-(phenylethynyl)benzoate (**7**)

Compound **5f** (447 mg, 0.4 mmol) was suspended in cHex/MeOH (10 mL, 1:1, v/v), and sodium methoxide (11 mg, 0.2 mmol) was added. The mixture was stirred at 55 °C for 3 h. After cooling and neutralized with DOWEX, cHex layer was separated. The lower layer (MeOH) was filtrated with ODS-filtration (methanol as eluent) followed by evaporation to give methyl 2-(phenylethynyl)benzoate **7** (92 mg, 98%).

### 4.8. General procedure for the Heck reaction in a CBT system

In a 20-mL glass tube were placed acrylate **8** (350 mg, 0.50 mmol), aryl halides **9a–c** (0.75 mmol), triethylamine (1.50 mmol), $Pd_2(dba)_3$ (9.1 mg, 2 mol %), cHex/DMF (each 3 mL), and a magnetic stirring bar. After degassing under argon, the vessel was placed into an oil bath preheated to 60 °C. The reaction mixture was kept in the oil for 3 h before being removed, and the vessel and contents were allowed to cool. The MCH layer was separated and evaporated under vacuum. Methanol was added to the residue, followed by filtration to afford the biaryl products **9a–c**.

#### 4.8.1. 3,4,5-Tris(octadecyloxy)benzyl acrylate (**8**)

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.56 (s, 2H), 6.45 (dd, 1H, $J$=17.3, 1.5 Hz), 6.17 (dd, 1H, $J$=17.3, 10.3 Hz), 5.85 (dd, 1H, $J$=10.3, 1.5 Hz), 5.09 (s, 2H), 4.00–3.89 (m, 6H), 1.85–1.68 (m, 6H), 1.51–1.19 (m, 96H), 0.88 (t, 9H, $J$=6.6 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 169.6, 166.1, 153.3, 153.2, 138.5, 138.3, 131.1, 130.7, 129.8, 128.4, 107.5, 107.0, 77.3, 73.5, 69.3, 69.2, 66.8, 53.8, 32.0, 30.4, 29.8, 29.7, 29.6, 29.5, 29.4, 27.8, 26.2, 26.1, 22.7, 14.1, 8.0. IR (KBr): 2918, 2848, 1728 $cm^{-1}$. TOF-MS (pos) calcd for $C_{64}H_{118}O_5$ [M+$Na^+$] 989.8877, found 989.8921.

#### 4.8.2. 3-(4-Methoxyphenyl)-acrylic acid 3,4,5-tris-octadecyloxy-benzyl ester (**10a**)

$^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.68 (d, 1H, $J$=16.6 Hz), 7.47 (d, 2H, $J$=8.7 Hz), 6.90 (d, 2H, $J$=8.7 Hz), 6.59 (s, 2H), 6.35 (d, 1H, $J$=16.6 Hz), 5.12 (s, 2H), 3.99–3.93 (m, 6H), 3.84 (s, 3H), 1.82–1.71 (m, 6H), 1.49–1.44 (m, 6H), 1.33–1.25 (m, 78H), 0.88 (t, 9H, $J$=6.5 Hz). $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ 167.2, 161.4, 153.2, 144.8, 138.2, 131.0, 129.8, 127.1, 115.4, 114.3, 107.0, 73.4, 69.1, 66.6, 55.4, 31.9, 30.3, 29.7, 29.6, 29.4, 26.1, 22.7, 14.1. TOF-MS (pos) calcd for $C_{71}H_{124}O_6$ [M+Na]$^+$ 1095.9296, found 1095.9288.

#### 4.8.3. 3-(4-Acetyl-phenyl)-acrylic acid 3,4,5-tris-octadecyloxy-benzyl ester (**10b**)

$^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.97 (d, 2H, $J$=8.7 Hz), 7.74 (d, 1H, $J$=16.6 Hz), 7.60 (d, 2H, $J$=8.7 Hz), 6.60 (s, 2H), 6.57 (d, 1H, $J$=16.6 Hz), 5.15 (s, 2H), 3.99–3.93 (m, 6H), 2.61 (s, 3H), 1.82–1.71 (m, 6H), 1.49–1.44 (m, 6H), 1.34–1.25 (m, 78H), 0.88 (t, 9H, $J$=6.5 Hz). $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ 197.2, 166.3, 153.3, 143.5, 138.7, 138.4, 138.1, 130.6, 128.8, 128.2, 120.5, 107.2, 73.4, 69.2, 67.0, 31.9, 30.3, 29.8, 29.7, 29.6, 29.4, 26.6, 26.1, 22.7, 14.1. TOF-MS (pos) calcd for $C_{72}H_{124}O_6$ [M+Na]$^+$ 1107.9296, found 1107.9291.

#### 4.8.4. 3-Phenyl-acrylic acid 3,4,5-tris-octadecyloxy-benzyl ester (**10c**)

$^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.72 (d, 1H, $J$=16.1 Hz), 7.56–7.52 (m, 2H), 7.39–7.38 (m, 3H), 6.60 (s, 2H), 6.49 (d, 1H, $J$=16.1 Hz), 5.14 (s, 2H), 3.99–3.93 (m, 6H), 1.82–1.71 (m, 6H), 1.54–1.44 (m, 6H), 1.30–1.25 (m, 78H), 0.88 (t, 9H, $J$=6.5 Hz). $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ 166.8, 153.2, 145.1, 138.2, 134.4, 130.9, 128.9, 128.1, 107.1, 73.4, 69.2, 66.8, 31.9, 30.3, 29.8, 29.7, 29.6, 29.4, 26.1, 22.7,

14.1. TOF-MS (pos) calcd for $C_{70}H_{122}O_5$ $[M+Na]^+$ 1065.9190, found 1065.9213.

*4.8.5. 4-Tris-octadecyloxy-benzylthiophenyl boronic acid (**11**)*

$^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.08 (d, 2H, $J$=8.05 Hz), 7.39 (d, 2H, $J$=8.05 Hz), 6.56 (s, 2H), 4.15 (s, 2H), 3.95–3.89 (m, 6H), 1.80–1.71 (m, 6H), 1.46–1.25 (m, 90H), 0.88 (t, 9H, $J$=7.32 Hz). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 153.0, 151.4, 143.2, 137.3, 135.6, 131.3, 128.2, 107.2, 73.4, 69.1, 34.3, 31.9, 30.4, 29.8, 29.7, 29.5, 29.4, 26.2, 22.8, 14.2. TOF-MS (pos) calcd for $C_{67}H_{121}BO_5S$ $[M+Na]^+$ 1071.8925, found 1071.8961.

*4.8.6. 4′-(3,4,5-Tris-octadecyloxy-benzylsulfanyl)-biphenyl-4-carboxylic acid methyl ester (**12a**)*

$^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.09 (d, 2H, $J$=8.29 Hz), 7.62 (d, 2H, $J$=8.29 Hz), 7.52 (d, 2H, $J$=8.29 Hz), 7.38 (d, 2H, $J$=8.29 Hz), 6.48 (s, 2H), 4.07 (s, 2H), 3.94 (s, 3H), 3.91–3.88 (m, 6H), 1.78–1.70 (m, 6H), 1.47–1.25 (m, 90H), 0.88 (t, 9H, $J$=6.83 Hz). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 166.8, 152.9, 144.6, 137.8, 137.3, 136.8, 131.9, 130.1, 130.0, 128.8, 127.4, 126.6, 107.2, 73.4, 69.1, 52.2, 39.4, 31.9, 30.4, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 26.1, 22.7, 14.2. TOF-MS (pos) calcd for $C_{75}H_{126}O_5S$ $[M+Na]^+$ 1161.9224, found 1161.9253.

*4.8.7. 4′-Nitro-4-(3,4,5-tris-octadecyloxy-benzylsulfanyl)-biphenyl (**12b**)*

$^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.28 (d, 2H, $J$=7.69 Hz), 7.69 (d, 2H, $J$=7.69 Hz), 7.51 (d, 2H, $J$=7.69 Hz), 7.39 (d, 2H, $J$=7.69 Hz), 6.51 (s, 2H), 4.09 (s, 2H), 3.94–3.89 (m, 6H), 1.79–1.71 (m, 6H), 1.48–1.25 (m, 90H), 0.88 (t, 9H, $J$=6.96 Hz). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 153.1, 146.8, 138.4, 136.4, 134.4, 131.8, 130.7, 128.8, 127.6, 124.2, 115.8, 107.4, 73.4, 69.2, 39.4, 31.9, 30.3, 29.8, 29.7, 29.6, 29.4, 26.2, 22.7, 14.1. TOF-MS (pos) calcd for $C_{73}H_{123}NO_5S$ $[M+Na]^+$ 1148.9020, found 1148.9001.

*4.8.8. 4′-(3,4,5-Tris-octadecyloxy-benzylsulfanyl)-biphenyl-4-carbonitrile (**12c**)*

$^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.69 (dd, 2H, $J$=8.54, 1.95 Hz), 7.62 (dd, 2H, $J$=8.54, 1.95 Hz), 7.46 (dt, 2H, $J$=8.54, 1.95 Hz), 7.36 (dt, 2H, $J$=8.54, 1.95 Hz), 6.48 (s, 2H), 4.06 (s, 2H), 3.92–3.85 (m, 6H), 1.77–1.67 (m, 6H), 1.47–1.25 (m, 90H), 0.86 (t, 9H, $J$=6.59 Hz). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 153.2, 144.8, 137.9, 136.9, 132.6, 131.9, 129.9, 128.8, 127.5, 123.3, 118.8, 110.9, 107.4, 73.4, 69.2, 39.2, 31.9, 30.4, 29.7, 29.6, 29.5, 29.4, 29.3, 26.1, 22.7, 14.1. TOF-MS (pos) calcd for $C_{74}H_{123}NO_3S$ $[M+Na]^+$ 1128.9121, found 1128.9125.

*4.8.9. 1-[4′-(3,4,5-Tris-octadecyloxy-benzylsulfanyl)-biphenyl-4-yl]-ethanone (**12d**)*

$^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.02 (d, 2H, $J$=8.54 Hz), 7.64 (d, 2H, $J$=8.54 Hz), 7.52 (d, 2H, $J$=8.54 Hz), 7.38 (d, 2H, $J$=8.54 Hz), 6.49 (s, 2H), 4.07 (s, 2H), 3.94–3.88 (m, 6H), 2.63 (s, 3H), 1.77–1.73 (m, 6H), 1.47–1.25 (m, 90H), 0.88 (t, 9H, $J$=6.83 Hz). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 197.6, 153.1, 144.9, 137.7, 137.1, 135.9, 132.0, 131.7, 130.2, 128.9, 127.5, 126.8, 107.4, 73.5, 69.1, 39.4, 31.9, 30.3, 29.8, 29.7, 29.6, 29.5, 29.4, 26.6, 26.1, 22.7, 14.1. TOF-MS (pos) calcd for $C_{75}H_{126}O_4S$ $[M+Na]^+$ 1145.9274, found 1145.9302.

*4.8.10. 4′-(3,4,5-Tris-octadecyloxy-benzylsulfanyl)-biphenyl-4-carboxylic acid 3,4,5-tris-octadecyloxy ester (**13**)*

$^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ 8.11 (d, 2H, $J$=8.63 Hz), 7.61 (d, 2H, $J$=8.63 Hz), 7.51 (d, 2H, $J$=8.63 Hz), 7.37 (dt, 2H, $J$=8.54, 1.95 Hz), 6.64 (s, 2H), 6.49 (s, 2H), 5.27 (s, 2H), 4.07 (s, 2H), 3.97–3.89 (m, 12H), 1.83–1.71 (m, 12H), 1.46–1.42 (m, 12H), 1.25 (s, 168H), 0.88 (t, 18H, $J$=6.79 Hz). $^{13}C$ NMR (150 MHz, $CDCl_3$): $\delta$ 165.8, 153.2, 138.2, 137.6, 131.1, 130.5, 129.5, 107.0, 73.4, 69.2, 67.4, 31.9, 30.4, 29.8, 29.7, 29.5, 29.4, 26.2, 22.8, 14.1. TOF-MS (pos) calcd for $C_{136}H_{237}O_8S$ $[M+Na]^+$ 2042.7835, found 2042.7849.

*4.8.11. 4′-(3,4,5-Tris-octadecyloxy-benzylsulfanyl)-biphenyl-2-carboxylic acid 3,4,5-tris-octadecyloxy ester (**14**)*

$^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ 7.80 (d, 1H, $J$=7.69 Hz), 7.450 (dd, 1H, $J$=8.30, 7.69 Hz), 7.39 (dd, 1H, $J$=8.30, 7.69 Hz), 7.32 (d, 1H, $J$=7.69 Hz), 7.26 (d, 2H, $J$=8.06 Hz), 7.19 (d, 2H, $J$=8.06 Hz), 6.49 (s, 2H), 6.36 (s, 2H), 4.99 (s, 2H), 4.04 (s, 2H), 3.93–3.87 (m, 12H), 1.80–1.70 (m, 12H), 1.31–1.25 (m, 180H), 0.88 (t, 18H, $J$=6.96 Hz). $^{13}C$ NMR (150 MHz, $CDCl_3$): $\delta$ 168.4, 153.1, 141.7, 139.1, 138.3, 137.5, 136.0, 134.5, 132.1, 131.3, 130.9, 130.6, 130.3, 129.8, 129.1, 128.8, 128.3, 127.2, 107.4, 73.4, 69.2, 67.3, 39.4, 31.9, 30.3, 29.8, 29.7, 29.6, 29.4, 22.6, 14.1. TOF-MS (pos) calcd for $C_{136}H_{237}O_8S$ $[M+Na]^+$ 2042.7835, found 2042.7811.

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