Diaryl Ether and Diaryl Thioether Syntheses on Solid Supports via Copper (I)-Mediated Coupling

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An efficient method to synthesize diaryl ethers and thioethers on solid supports is described. Starting from immobilized phenols or arylhalides, coupling with an access of aryliodides/arylbromides or phenolic/thiophenolic substrates in solution was successful in the presence of CuCl and Cs_2CO_3 as base. Coupling conditions known from solution-phase syntheses of diaryl ethers have been effectively modified and adapted to solid-phase synthesis. Optimized conditions enabled the coupling of sterically hindered and/or electronically deactivated aryl moieties. After coupling, a newly developed diversity-generating linker based on cinnamic acid allowed the diaryl ethers to be cleaved from the resin either via saponification/transesterification or via ozonolysis. Latter offers the possibility of generating several additional compounds by simple variation of the cleavage conditions. The target substances were generally isolated in good to excellent yields and high purities.

Introduction

Diaryl ethers are important structural motifs that form the central building block in a large number of naturally occurring compounds. Diaryl ether-containing structures have been isolated from lichens (e.g., depsidones),[1] sponges (e.g., bastadines),[2] trees (e.g., combretastatines),[3] mosses (e.g., riccardin B),[4] and several microorganisms (e.g., piperazinomycin).[5] The structural variety of the isolated diaryl ethers is huge; there are important compounds, such as depsidones[1] or aristogines,[6] containing just two aryl components, and there are complex natural products, vancomycin for example,[7] containing several diaryl ether moieties.

Diaryl ether containing structures often show interesting properties that led to the total synthesis of their naturally occurring structures and derivatives thereof.[8] They have been shown to possess antibacterial and antiviral properties. Some act as anticancer agents or have anti-inflammatory, analgesic, and antipyretic activities, just to give a short insight into the great potential of diaryl ether-containing structures.[9]

Here we report the development of new strategies for the syntheses of diaryl ethers and diaryl thioethers on solid supports. These routes were then subsequently used to elaborate molecular libraries of some naturally occurring diaryl ethers and derivatives thereof (unpublished results).

In solution phase, diaryl ether forming reactions are well-known, and since the development of the Ullmann reaction roughly a century ago, many alternative synthetic strategies have been developed to generate even structurally demanding diaryl ethers. Nowadays, one can use diverse copper-catalyzed and copper-mediated coupling reactions, as well as palladium-catalyzed routes.[1,10,11] In all cases, the development of diverse ligands based on phosphorus, nitrogen, or oxygen compounds led to milder reaction conditions and higher yields.[1,11] Even nucleophilic aromatic substitution reactions, being metal free coupling options, still play an important role.[12] In addition to the classic and most commonly used copper- and palladium-mediated or -catalyzed coupling reactions, several slightly modified or alternative procedures to access diaryl ethers have been developed. This constitutes an irrefutable proof of the importance of this class of compounds.[1,11,13]

Although solid-phase techniques have gained much importance regarding the constitution of biologically active and medicinally relevant structure libraries in the last years,[14] the solid-phase synthesis of diaryl ethers has received less attention than its solution-phase counterpart. There are indeed only few examples of diaryl ether syntheses on solid supports. Reactions on bead may be less common because of the limited range of reaction temperatures and the usually poor solubility of the catalysts. Aside, the persistent contamination of the resin by many catalysts is still an unsolved problem. Up to now, most diaryl ether syntheses on solid supports have been reported via nucleophilic aromatic substitution reactions, preferably with aryl fluorides bearing an *ortho*-nitro substituent.[15] In 2001, Nishiyama et al. reported an intramolecular diaryl ether formation on solid phase via a thallium(III) trinitriate phenolic oxidation.[16] Another of the rare metal-assisted diaryl ether syntheses on solid-phase, the Ullmann−Nicolaou reaction, was reported by our group a couple of years ago.[17] This method takes advantage of a triazene linker that allows specific copper-assisted *ortho*-coupling.[18] We have also lately used the triazene linker to synthesize structurally related diaryl amines via an "inverse" Hartwig−Buchwald reaction on solid supports.[19] Recently, Chiang et al. published cross-couplings with aryl boronic acids mediated by a polymer-supported copper complex.[20] To the best of our knowledge, no

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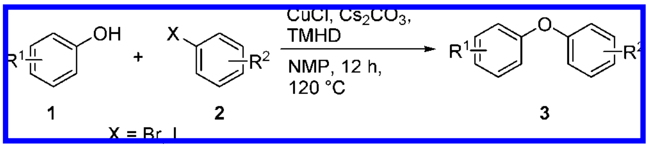
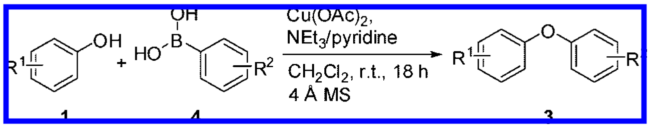
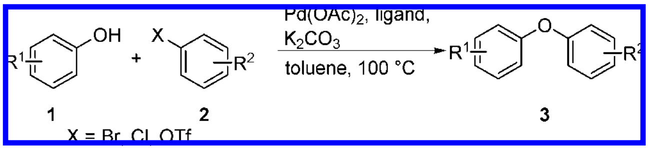
Scheme 1. Cu(I)-Mediated Diaryl Ether Synthesis



Scheme 2. Evans−Chan−Lam Diaryl Ether Synthesis



Scheme 3. Palladium-Catalyzed Diaryl Ether Synthesis



palladium-assisted solid-phase syntheses of diaryl ethers have been reported so far.

Results and Discussion

Our investigations toward a generally applicable method for diaryl ether synthesis on solid supports led us to test two copper-catalyzed, as well as palladium-catalyzed, couplings, all reported in solution phase.

Because of the harsh reaction conditions of the classical Ullmann reaction, several modifications employing milder conditions have been developed. Paine,[21] Meyerstein,[22] and Song[23] use cesium carbonate as base and 2,2,6,6-tetramethylheptane-3,5-dione (TMHD) as the Cu ligand (Scheme 1). This results in faster reaction rates at lower temperatures and enables even deactivated aryl derivatives to react in good yields.

Chan,[24] Evans,[25] and Lam[26] nearly simultaneously reported a Cu-assisted O-arylation of arylboronic acids leading to even milder reaction conditions (Scheme 2).

This procedure allows for diaryl ether formation with a large variety of aryl precursors at room temperature.

In addition to the copper-mediated diaryl ether couplings, Hartwig[27] and Buchwald[28] independently developed a palladium-catalyzed version (Scheme 3). In most cases, aryl bromides or chlorides give better yields than the corresponding iodides.

This is in opposition with the generally observed preference during the copper-mediated reactions. Another intriguing observation is the fact that aryl halides with sterically hindered ortho substituents react faster and give usually better yields at lower temperatures than their nonsubstituted equivalents.

All these reaction conditions have been shown to work in solution phase and should be transferrable, with probably slight modifications, to immobilized structures. This would lead to a generally applicable methodology on solid phase.

We initially investigated the Evans−Chan−Lam and Hartwig−Buchwald procedures and subsequently turned to the Cs$_2$CO$_3$/TMHD-catalyzed model. To do so, we first had to immobilize either the hydroxyl or the halide aryl moiety on solid supports. Both possibilities have been explored.

Linker Immobilization. The presented investigations of potential coupling methods for solid phase syntheses of diaryl ethers are based on sterically nonhindered linker systems that are not affected by basic or oxidative conditions at high temperatures. Initial experiments showed that the immobilization of carboxylic acids directly on Merrifield resin using Cs$_2$CO$_3$ was successful but that these benzyl-benzoyl systems are not stable at temperatures above 100 °C in the presence of an excess of base (data not shown). Therefore, 1,5-pentanediol has been immobilized on Merrifield-resin **5** to provide a non-benzylic linkage, stable to the required conditions and long enough to guarantee minimized sterical hindrance by the resin. 1,5-Pentanediol has been immobilized as linker before by Rodebaugh et al.; the major drawback of their method was the transformation of pentanediol into monoprotected pentanediol prior to attachment to the solid phase.[29] The 1,5-pentanediol-linker was then modified via the Appel reaction using CBr$_4$/PPh$_3$ to give brominated resin **6b** to which different benzoic acids, containing either a halide substituent or a protected hydroxyl function, were attached in the presence of cesium carbonate to give resin **7** (Scheme 4).

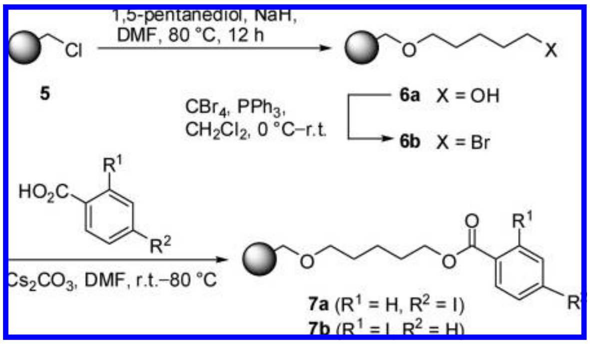
Cinnamic acid-based linkers have also been explored. These systems have the advantage of offering an additional cleavage method (ozonolysis) with the possibility to obtain either the acid, ester, alcohol, or aldehyde derivatives. Whereas 4-bromo cinnamic acid could directly be attached to resin **6b** (to give **12d**, Figure 1), according to the previously described procedure (Scheme 4), the phenol function of hydroxyl cinnamic acid derivatives had to be protected in a prior step (Scheme 5).

This was achieved via protection of **8** in the presence of dihydropyran leading to esters **9**, followed by saponification. The free acid function of **10** was then coupled to resin **6b**, and the phenol function was deprotected on bead to yield cinnamic acid based linkers **12**.

With different aryl halide and phenolic linkers in hand (Figure 1), we started investigating the different diaryl ether coupling methods which have previously been reported in solution phase on solid supports.

Palladium-Catalyzed Diaryl Ether Synthesis. Although different reaction conditions were tested with either the immobilized phenolic moiety or the arylhalide,[28,30] no ether formation could be detected (data not shown). The Hartwig−

Scheme 4. Synthesis of the Linker Unit **6b** and Immobilization of the First Aryl Moiety **7a**, **b**



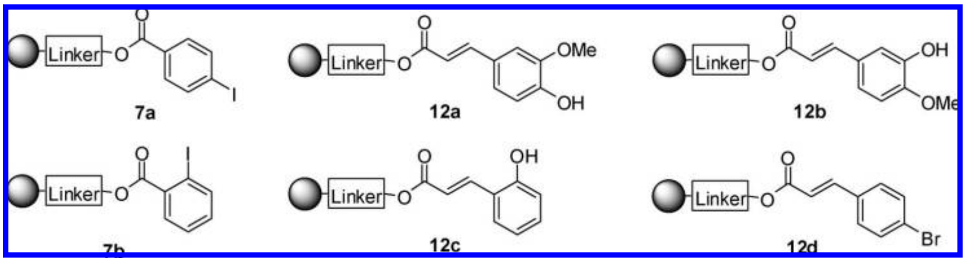
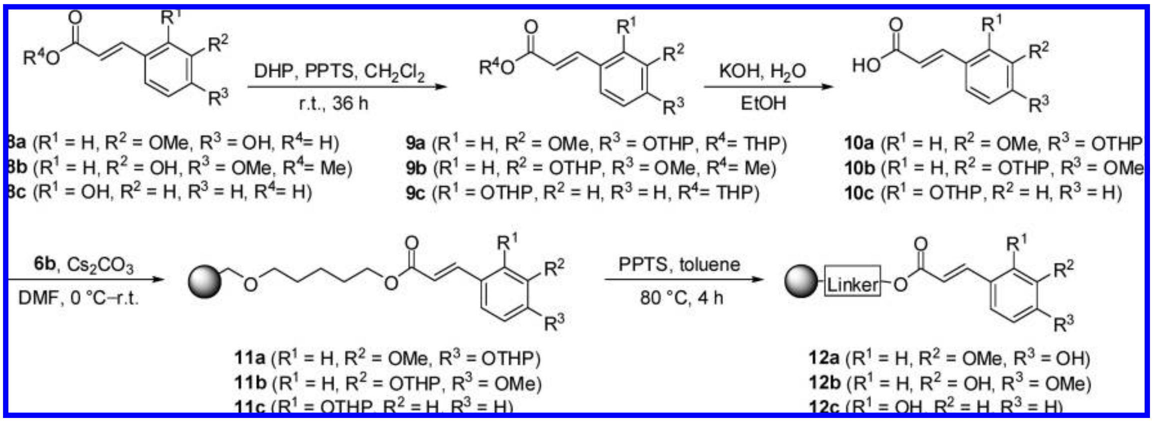
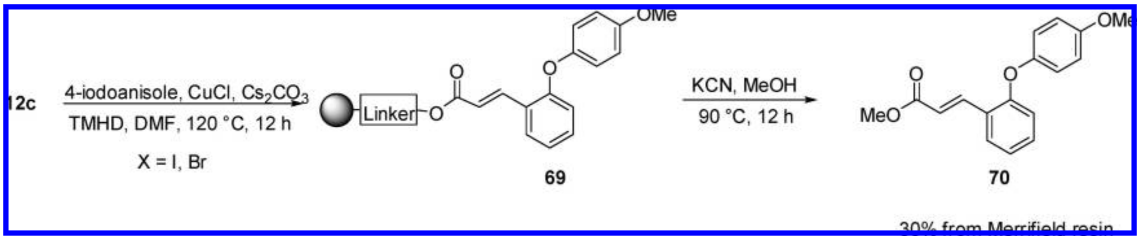


Figure 1. Phenol and aryl-iodide, -bromide moieties immobilized on the linker-resin construct.

Scheme 5. Immobilization of Cinnamic Acid Derivatives on Solid Phase as Phenolic Aryl Moiety **12a−c**



Scheme 6. Cleavage of Methylester **70** from Cinnamic Acid Resin **69**



Buchwald approach was consequently abandoned, and we turned toward the use of boronic acids.

Coupling of Phenols and Boronic Acids. Although the Chan−Evans−Lam route worked very well in solution phase, we were not able to develop an efficient solid-phase procedure. All attempts to couple immobilized phenols with different boronic acids resulted in either no reaction at all or incomplete reactions even after several turnovers (data not shown). After failure of this copper-assisted approach, we started investigating the modified Ullmann reaction using Cs_2CO_3/TMHD.

Synthesis of Diaryl Ethers via Coupling of Phenols and Arylhalides. We first tested iodo benzoate linkers **7a**, **b** in the presence of cesium carbonate as base and 2,2,6,6-tetramethylheptane-3,5-dione (TMHD) as Cu ligand. The use of CuCl as copper source and DMF/MeCN as solvent heating at 120 °C turned out to be the best conditions and delivered the corresponding diarylether in most cases with high conversion, excellent yields, and purities. Cleavage from the solid support could either be achieved by transesterification (Tables 1 and 2) or by saponification (Table 3). In both cases, several methods had to be tested before the optimum conditions, KCN in MeOH and KOH in *i*-PrOH/H_2O 2:1, respectively, were found. Most of the time, quantitative conversions were observed (detected via GC-MS). The only exceptions being substrates bearing nitro, formyl or cyano substituents (entries 2, 8, 15, Table 1). Generally speaking, our conditions allow the coupling of ortho-substituted phenols (entries 8−13, 15−16, Table 1), as well as of ortho-substituted immobilized iodoaryl resins (entries 1−3, Table 2), in good to excellent yields. Various ortho substituents are tolerated, even carbonyl groups (entries 9, 11, Table 1), which to the best of our knowledge have never been reported to undergo diaryl ether formation on solid supports. The developed method also allows for the preparation of 2,2′-di-ortho-substituted diaryl ethers (Table 2, entry 1). One limitation is however excessive steric hindrance.

In addition, Figure 2 shows five phenols that did not react at all under the optimized conditions. We were not surprised to see that catechols **55a**, **b** did not undergo diaryl ether formation. This may be the result of solubility problems of these substrates. Neither did we expect sterically hindered di-ortho-substituted phenol **55c** to react. We were however

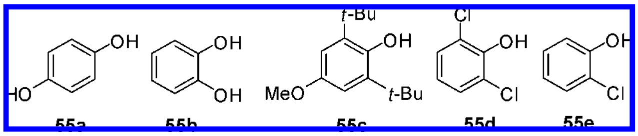
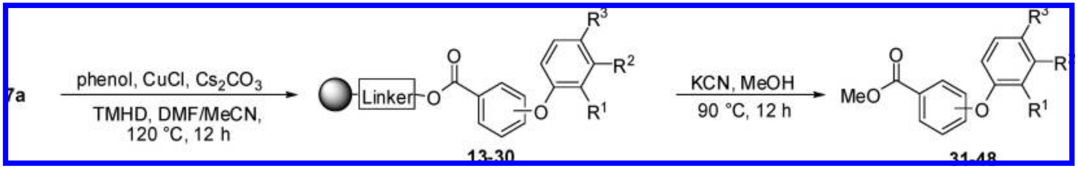


Figure 2. Phenols not reacting with immobilized iodoaryl linkers **7a**, **b**.

Table 1. Solid-Phase Diaryl Ether Synthesis with Immobilized para-Substituted Iodo-Aryls



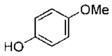
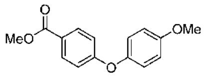
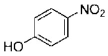
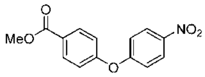
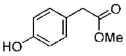
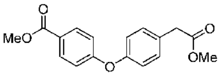
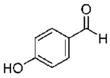
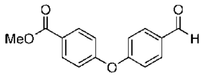
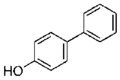
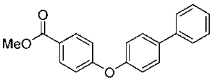
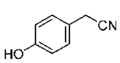
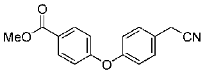
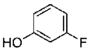
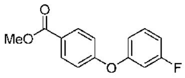
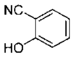
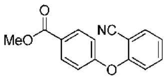
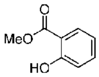
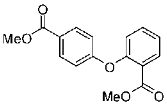
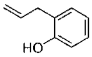
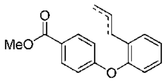
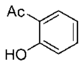
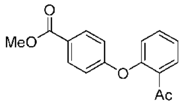
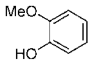
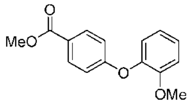
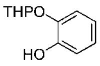
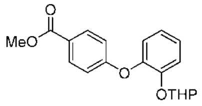
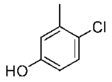
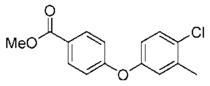
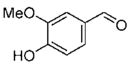
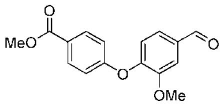
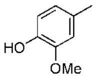
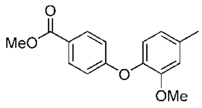
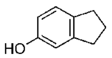
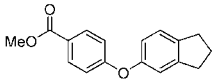
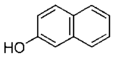
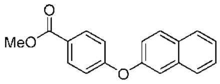
Entry	Phenol	Resin	Diaryl ether	Conversion [%][a]	Purity [%][a]	Yield [%][b]
1		**13**	 **31**	quant	97	quant
2		**14**	 **32**	82	48	66
3		**15**	 **33**	quant	99	83
4		**16**	 **34**	quant	65	65
5		**17**	 **35**	quant	98	99
6		**18**	 **36**	99	81	65
7		**19**	 **37**	quant	95	65
8		**20**	 **38**	81	66	89
9		**21**	 **39**	quant	98	quant
10		**22**	 **40**	quant	99[c]	87

Table 1. Continued

Entry	Phenol	Resin	Diaryl ether	Conversion [%][a]	Purity [%][a]	Yield [%][b]
11		**23**	 **41**	quant	95	75
12		**24**	 **42**	quant	92	66
13		**25**	 **43**	quant	> 99	79
14		**26**	 **44**	quant	99	94
15		**27**	 **45**	49	70	89
16		**28**	 **46**	quant	94	75
17		**29**	 **47**	quant	94	67
18		**30**	 **48**	quant	92	74

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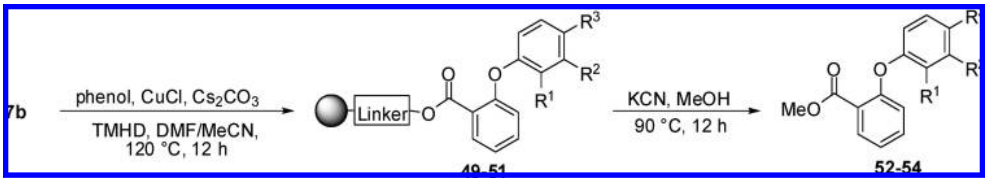
[a] Determined by GC-MS analysis of crude product. [b] Yield over 2 steps (coupling/cleavage). [c] Mixture of isomers (*E*, *Z*, and allyl).

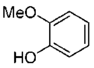
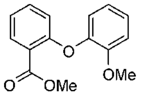
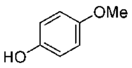
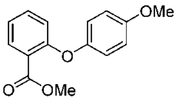
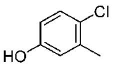
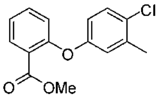
surprised to note that 2,6-dichlorophenol (**55d**) and 2-chlorophenol (**55e**) did not even deliver traces of the desired diaryl ether.

The immobilized diaryl ethers **13**, **24**, and **28** have also been cleaved by saponification and gave benzoic acids **56**−**58** (Table 3). Saponification was performed by heating the resin-bound diaryl ethers (suspended in $H_2O/^iPrOH$) for 14 h at 90 °C in pressure resistant vials in the presence of KOH. Yields refer to isolated compounds (after purification for compound **58**) and show that diaryl ether formation on solid phases can be used for the synthesis of benzoic acids in high yields as well.

After the investigation of immobilized iodo-substituted aryls, resins containing hydroxyl functionality were reacted to give

Table 2. Solid-Phase Diaryl Ether Synthesis with Immobilized ortho-Substituted Iodo-Aryls



Entry	Phenol	Resin	Diaryl ether	Conversion [%][a]	Purity [%][a]	Yield [%][b]
1		**49**	 **52**	quant	88	quant
2		**50**	 **53**	quant	97	81
3		**51**	 **54**	quant	99	quant

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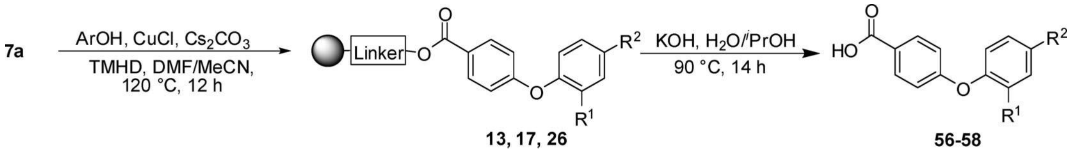
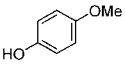
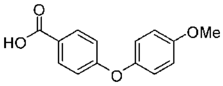
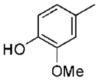
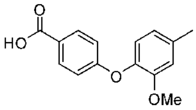
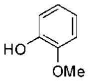
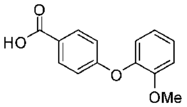
[a] Determined by GC-MS analysis of crude product. [b] Yield over 2 steps (coupling/cleavage).

Table 3. Solid-Phase Diaryl Ether Synthesis and Cleavage by Saponification



Entry	Aryl iodide	Resin	Diaryl ether	Yield [%][a]
1		**13**	 **56**	quant
2		**28**	 **57**	quant
3		**24**	 **58**	58[a]

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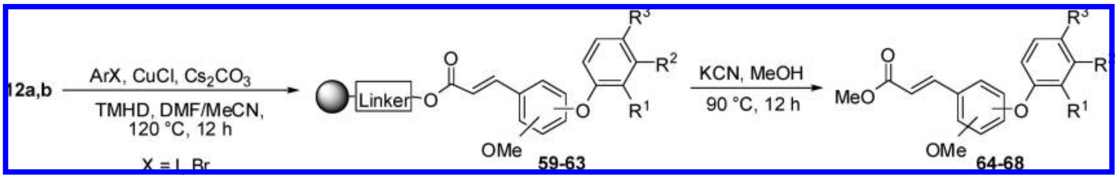
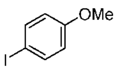
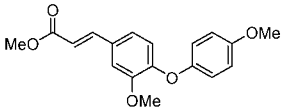
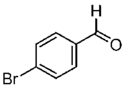
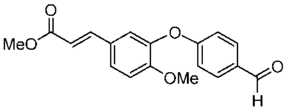
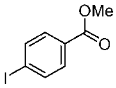
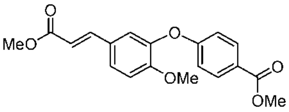
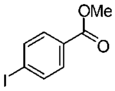
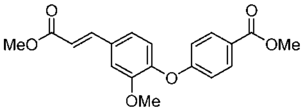
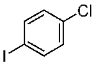
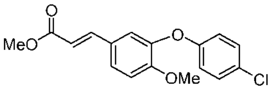
[a] Yield over 2 steps (coupling/cleavage). [b] After purification by preparative TLC.

Table 4. Solid-Phase Diaryl Ether Synthesis with Immobilized (Hydroxyphenyl)Acrylates **12a**, **b**



Entry	Aryl halide	resin	Diaryl ether	Conversion [%][a]	Purity [%][b]	Yield [%][c]
1		**59**	 **64**	quant	81	56
2		**60**	 **65**	quant	70	27
3		**61**	 **66**	quant	82	63
4		**62**	 **67**	quant	82	44
5		**63**	 **68**	quant	85	49

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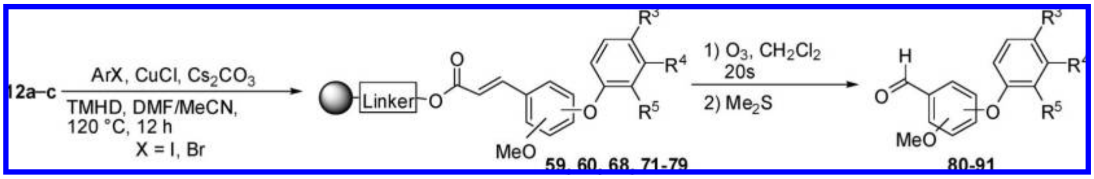
[a] Determined by GC-MS analysis of crude product. [b] Determined by GC-MS analysis of crude product. Cleavage step was performed over a period of 12 h. [c] Over 6 steps from Merrifield resin.

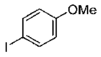
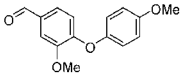
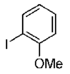
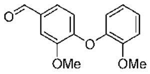
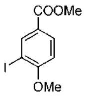
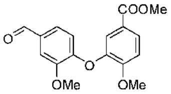
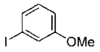
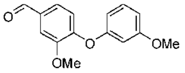
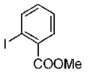
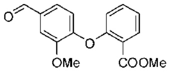
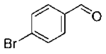
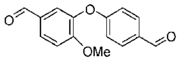
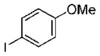
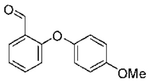
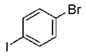
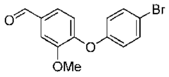
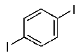
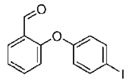
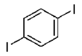
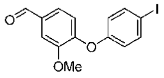
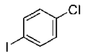
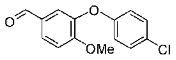
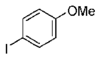
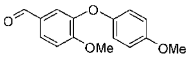
diaryl ethers on solid phases. For the formation of those diaryl ethers, resins **12a**−**c** (Figure 1) were synthesized (Scheme 5). With those (hydroxyphenyl)acrylate systems **12** in hand, the corresponding diaryl ethers could be obtained in good yields purities over six steps starting with Merrifield resin. When the adapted coupling method is used in combination with the transesterification conditions described in Table 1, cleavage times of 14 h must not be exceeded. Otherwise, the obtained purities decrease significantly. As it has already been seen for iodobenzoate linkers **7a**, **b** (Tables 1 and 2), this system allows the formation of ortho-substituted products; purities are however generally lower than the ones reported for the cleavage of benzoates. In contrast to **7a**, **b**, however, (hydroxyphenyl)acrylate system **12c** did not react with *ortho*-methoxy- or -carbonyl-substituted aryl moieties (data not shown).

Table 4 includes just examples for the formation of diaryl ethers with *para*- and *meta*-hydroxyl cinnamic esters, and the formation of those diaryl ethers from *ortho*-hydroxyl cinnamic esters was successful as well (compound **70**, Scheme 6). The purity of the cleaved product (64%) was lower than those of compounds **64**−**68**, but diaryl ether **70** could be isolated in 30% yield after purification.

In a second step, cleavage of selected resins via ozonolysis to generate the corresponding formyl diaryl ethers has been

Table 5. Solid-Phase Formyl (Diaryl Ether) Synthesis with Immobilized (Hydroxyphenyl)Acrylates **12** by Ozonolysis



Entry	Aryl halide	Resin	Diaryl ether	Conversion [%][a]	Purity [%][a]	Yield [%][e]
1		**59**	 **80**	quant	93	36
2		**71**	 **81**	quant	99	44
3		**72**	 **82**	quant	87	32
4		**73**	 **83**	quant	87	47
5		**74**	 **84**	quant	99	28
6		**60**	 **85**	quant	92	44
7		**75**	 **86**	quant	96	43
8		**76**	 **87**	quant	91[b] (6[c])	29
9		**77**	 **88**	quant	87 (3[d])	51
10		**78**	 **89**	quant	91	42
11		**63**	 **90**	quant	91	65
12		**79**	 **91**	quant	93	52

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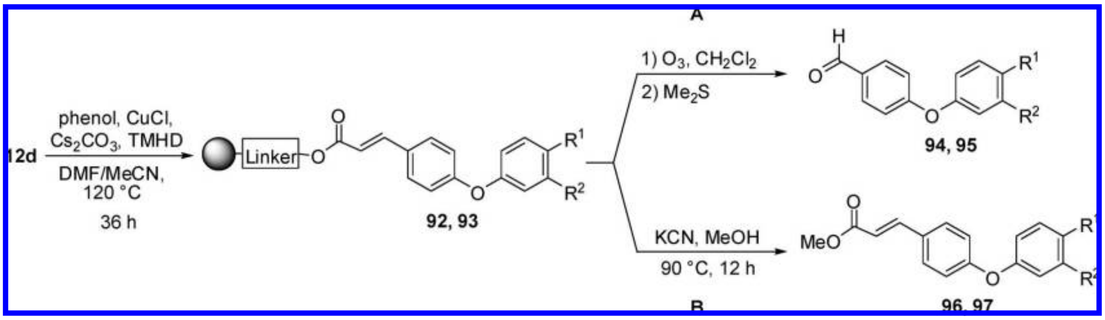
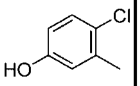
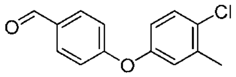
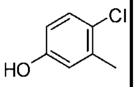
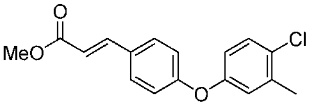
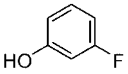
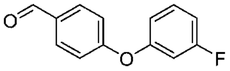
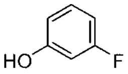
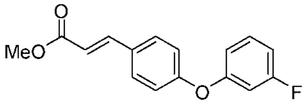
[a] Determined by GC-MS analysis of crude product. [b] Bromo-diaryl ether. [c] Iodo-diaryl ether. [d] Deiodated diaryl ether. [e] Yield over 6 steps starting from Merrifield resin.

Table 6. Solid-Phase Diaryl Ether Synthesis and Cleavage via Ozonolysis and Methanolysis



Entry	Phenol	Method/ resin	Diaryl ether	Reaction time [h]	Conversion [%][a]	Purity [%][a]	Yield [%][b]
1		A/**92**	 **94**	12 36	65 93	85 94	43 43
2		B/**92**	 **96**	36	90	70	70
3		A/**93**	 **95**	12 36	48 98	85 93	55 54
4		B/**93**	 **97**	36	98	67	quant

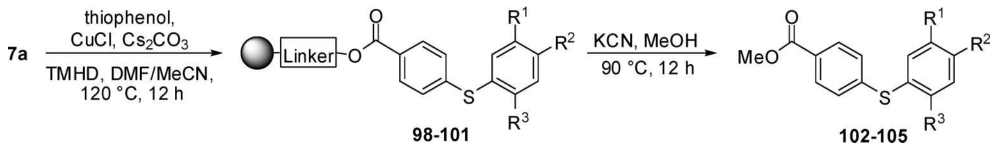
[a] Determined by GC-MS analysis of crude product. [b] Yield over 6 steps starting from Merrifield resin. Method A: cleavage via ozonolysis. Method B: cleavage via transesterification.

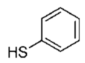
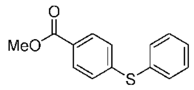
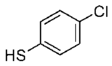
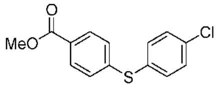
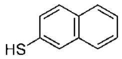
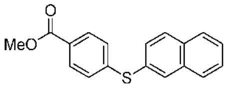
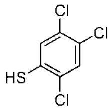
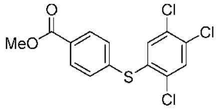
explored. Basically, ozonolysis could deliver several different products, for example, acids, esters, alcohols, or benzaldehydes depending on the reaction conditions. As seen above however, the first two product classes are also accessible via saponification and transesterification respectively. Thus, special emphasis was put on ozonolysis under reductive conditions generating the corresponding aldehydes (Table 5).

The key advantage of ozonolysis in combination with dimethylsulfide is that no subsequent washing procedure is needed because both reactants can simply be eliminated under high vacuum. Despite this key point, ozonolysis on solid supports has mostly been reported with nonvolatile reductants like triphenylphosphine or thioureas.[31]

Our system allows for the preparation of the corresponding formyl diaryl ethers in quantitative conversion and excellent purities (Table 5). The reaction time of the immobilized cinnamic acid in the presence of ozone has however to be rigorously controlled. If left for three minutes (Table 5, entry 1), the purity of the crude product was only about 11%. A reaction time of 20 s led to quantitative conversion along with 93% purity (Table 5, entry 1). The kinetics of the cleavage is obviously very fast and if left too long, the generated diaryl ethers probably decompose. If however a reaction time of 20 s is not exceeded, this method bears a very broad application spectrum and delivers the desired compounds very efficiently in high yields and excellent purities. It offers, as seen before, not only the opportunity to prepare ortho-substituted compounds but also the possibility to readily prepare iodo and bromo diaryl ethers (entries 8−10), which would be more demanding to access by solution-phase synthesis. Most intriguing about these examples is however the fact that during the diaryl ether formation already described above, the generated immobi-

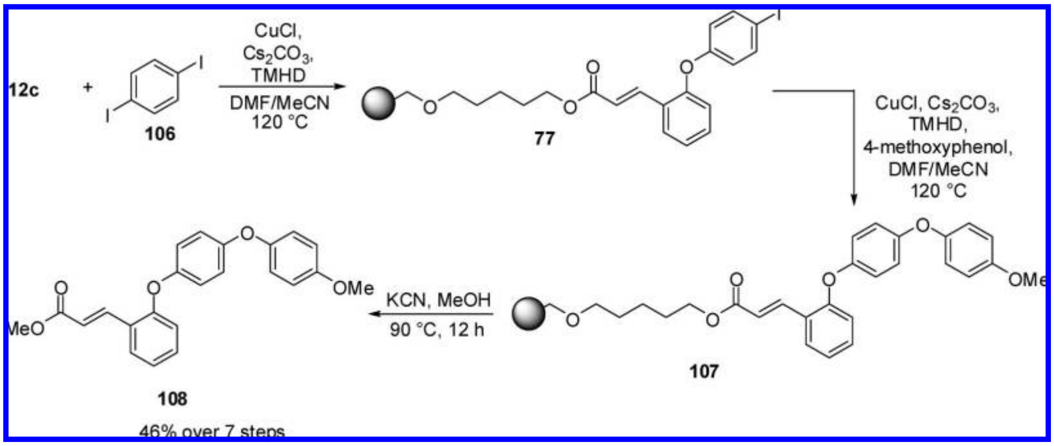
Table 7. Solid-Phase Synthesis of Diaryl Thioethers Using Linker System **7a**



Entry	Thiophenol	Resin	Diaryl thioether	Conversion [%][a]	Purity [%][a]	Yield [%][b]
1		**98**	 **102**	quant	93	quant
2		**99**	 **103**	quant	94	quant
3		**100**	 **104**	91	95	71
4		**101**	 **105**	quant	99	86

[a] Determined by GC-MS analysis of crude product. [b] Yield over two steps (coupling/cleavage).

Scheme 7. Synthesis of Diaryl Ether **108** Using Immobilized Linker System **12c**



lized iodo or bromo diaryl ether do not react with a copper ion and can be isolated after cleavage.

As for the benzoate linkers, the inverse coupling method, reacting immobilized (4-bromophenyl)acrylate linker **12d** with free phenols, was also examined (Table 6). The corresponding diaryl ethers were either cleaved via ozonolysis (entries 1 and 3, Table 6) or via transesterification (entries 2 and 4, Table 6). Best conversions and purities were observed if the reaction time for the coupling step was extended to 36 h. In general, the inverse coupling using cinnamic acid based linker works well too and gives the products in excellent conversion along with high purities.

All in all, we have developed solid-phase syntheses of diaryl ethers with good to excellent yields and high to very high purities. We now explore whether the described methodology could be extended to structurally related diaryl thioethers that have been prepared previously in most cases by nucleophilic aromatic substitution on solid phase.[32]

We were successful in preparing some diaryl thioethers by reaction of resin **7a** under standard conditions in the presence of four different thiophenols. These diaryl thioethers could be cleaved from the resin via transesterification; quantitative conversion as well as excellent purity could be detected via GC-MS analysis of the crude product (Table 7). Worthy of note is that *ortho*-chloro-substituted thiophenols react to form thioethers (entry 4, Table 7), whereas the corresponding phenols **55d**, **e** did not react under identical conditions (Figure 2).

Finally, to prove the efficiency of the diaryl ether bond formation, we performed a 2-fold diarylether synthesis on the former mentioned resin **12c** (Scheme 7). In a first coupling step, diiodobenzene was coupled to the solid phase, and the resulting resin was treated with 4-methoxyphenol under the optimized coupling conditions. The success of the transformation could be shown by ^{13}C Gel-NMR, as well as by cleavage of the target substrate from the solid support. The crude product could be isolated with 73% purity and after thin layer chromatography, the target compound could be isolated in 46% yield starting from Merrifield resin.

Conclusion

We have developed an efficient solid-phase synthesis of diaryl ethers and thioethers based on a modified Ullmann reaction using cesium carbonate as base, copper chloride, and 2,2,6,6-tetramethylheptan-3,5-dione (TMHD) as ligand. Two linker systems based on benzoyl and cinnamic acid esters, respectively, bearing either the phenol moiety or the arylhalide component, allow effective ether or thioether formation. In addition, these linkers offer the possibility of several cleavage methods, all giving access to different compounds in high purity.

Although both coupling possibilities have delivered pleasing results, the use of an immobilized aryl halide moiety seems best. In the case of the benzoyl linkers, solid-phase attached halides gave far better yields than the immobilized phenols. For the cinnamic acid based linkers, both alternatives delivered comparable results, the synthesis of the (4-bromophenyl)acrylate linker is however somewhat shorter.

Experimental Section

Instrumentation and Reagents. ^{1}H NMR spectra were recorded on Bruker AM 250 (250 MHz), AM 400 (400 MHz), and AM 500 (500 MHz) spectrometers. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to $CHCl_3$ (7.26 ppm) or acetone[d_6] (2.09 ppm) as internal standard. All couplings constants are absolute values and J values are expressed in Hertz (Hz). The description of signals include s = singlet, d = doublet, bd = broad doublet, t = triplet, dd = doublet of doublets, dt doublet of triplets, m = multiplet. The spectra were analyzed according to first order.^{13}C NMR spectra were recorded on Bruker AM 250 (62.5 MHz), AM 400 (100 MHz), and AM 500 (125 MHz) spectrometers. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to $CHCl_3$ (77.4 ppm) or acetone[d_6] (30.6 ppm) as internal standard. For measurement of ^{13}C NMR-Gel-Spectra, 60−100 mg of the resin were swollen in a NMR-tube with the appropriate amount of $CDCl_3$). The NMR spectrometer was run with pulse program zgpg30 (relaxation delay D1 = 0.2 s, linebroadening LB = 9.0 Hz, 5120 scans). MS (EI) (electron impact mass spectrometry): Finnigan MAT 90 (70 eV). The molecular fragments are quoted as the relation between mass and charge (*m*/*z*); the intensities are presented as a percentage value relative to the intensity of the base signal (100%). The abbreviation [M^+] refers to the molecule ion. IR (infrared spectroscopy): FTIR Bruker IFS 88. IR spectra of solids were recorded in KBr and as thin films on KBr for oils and liquids. The deposit of the absorption band was given in wave numbers in cm^{-1}. The forms and intensities of the bands were characterized as follows: m= weak 70−90% T, vw = very weak 90−100% T. Routine monitoring of reactions were performed using silica gel-coated aluminum plates (Merck, silica gel 60, F_{254}) which were analyzed under UV light at 254 nm or dipped into a solution of molybdato phosphate (5% phosphor molybdic acid in ethanol, dipping solution) and heated with a heat gun. Solvent mixtures are understood as volume/volume. Solid materials were powdered. Solvents, reagents, and chemicals were purchased from Aldrich, Fluka and Acros. Tetrahydrofuran was distilled from sodium/benzophenone under argon prior use. Dichloromethane, ethyl acetate, and diethyl ether were distilled from calcium hydride. All reactions involving moisture sensitive reactants were executed under an argon atmosphere using oven-dried or flame dried glassware; all other solvents, reagents and chemicals were used as purchased unless stated otherwise. Merrifield Resin was purchased from Polymer Laboratories (PL-CMS Resin, 0.97 mmol/g, 75−150 μm, 1% cross-linked, CMS 161 Lot 1). Vials from Macherey-Nagel were used for all reactions beyond room temperature (size 20−20 and 20−10, in combination with N20 oA and N20 TB/oA-M septum) unless stated otherwise. GC-MS spectra were performed on an Agilent chromatograph with high-resolution gas chromatography column from J&W Scientific. Temperature program: initial temp 120 °C for 3 min, heating 15 °C/min up to end temperature of 280 °C (20 min).

General Procedures and Analytical Data for Resins. All compounds that are not mentioned in the Experimental Section were prepared according to literature known procedures. Data for cleaved products are given for selected examples that could be determined via NMR of the crude products after cleavage or via NMR after TLC chromatography. Signals referring to the linker-unit in the ^{13}C-Gel-NMR data were marked (*).

Yields of the cleaved products were determined as follows:

(1) Yields of substrates summed up in Tables 1−3 and 7 are determined over two steps from the aryliodide-resin **7a** or **b** (including two steps, coupling and cleavage). The loading of the starting material **7a** or **b** (0.418 mmol/g) was used to determine the theoretical loading of the diarylether-containing target resin [1000/(2392.3 − 126.9[I] + x[mass of OAr])] in case of quantitative conversion.

The ratio of cleaved product and theoretical yield over two steps was formed.

(2) Yields of substrates summed up in Tables 4−6 are determined over all steps on solid phases from the starting material Merrifield resin (**8**). The loading of the starting material (0.97 mmol/g) was used to determine the theoretical loading of the diarylether-containing target resin in case of quantitative conversion. The ratio of cleaved product and theoretical yield over six steps (five steps for Table 6) was formed.

Removal of THP-Protecting Groups (GP1). The THP-protected phenolic resin (1.00 g) was swollen in toluene and 3.00 mmol pyridinium *para*-toluenesulfonate (PPTS) were added. After 5 h shaking at 80 °C (orbital shaking, 200 rpm), the supernatant was removed via filtration, and the resin was washed three times with acetone, methanol, and dichloromethane (30 mL per washing step). The resin was vacuum dried.

Immobilization of Benzoic Acids/Cinnamic Acids (GP2). Merrifield resin, functionalized with bromoalkyl linker (1.00 g, 0.864 mmol), was swollen in 10.0 mL of DMF, and 5.00 mmol (5.79 eq) Cs_2CO_3 and 5.00 mmol (5.79 eq) benzoic acid were added at rt. The mixture was shaken for 1 h at rt and then for 10 h at 80 °C (orbital shaking, 200 rpm). The resin was isolated by filtration and was washed two times with acetone, methanol, water, and acetone and three times with dichloromethane (30 mL per washing step). The resin was vacuum dried.

Cleavage by Transesterification with KCN (GP3). The resin (100 mg) was swollen in methanol (2.00 mL) and KCN (2 mg, 30.7 mmol) was added. The reaction vessel was heated at 90 °C for 12 or 14 h. The reaction mixture was treated with K_2CO_3 (150 mg, 1.09 mmol), 50 mL of H_2O, and 50 mL of ethyl acetate. This mixture was filtered, and the filtrate was separated in a separating funnel. The organic layer was washed with 50 mL of H_2O again. The aqueous layer was re-extracted with ethyl acetate (100 mL) and washed with 50 mL of H_2O. The combined organic layers were dried over Na_2SO_4 and filterted. The solvent was removed under reduced pressure, and the crude product was analyzed via GC-MS. Yields are given over 2 steps (coupling/cleavage) for immobilized benzoate esters and over 6/7 steps (starting from Merrifield resin) for cinnamic esters.

Cleavage by Saponification (GP4). The resin (100 mg) was swollen in ^{i}PrOH/H_2O (3 mL, 2/1 v/v) and KOH (56 mg, 1 mmol) was added. The reaction vessel (pressure resistant vials) was closed carefully and was heated at 90 °C for 14 h. The reaction mixture was neutralized by addition of 1 N HCl, and the resulting solution was extracted two times with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. Yields are given over two steps (coupling/cleavage).

Coupling of Phenols and Arylhalides to Give Diaryl Ethers (GP5a−d).

(a) To the resin (150 mg) in MeCN (1.50 mL) and DMF (3.00 mL) were added Cs_2CO_3 (600 mg, 1.84 mmol), CuCl (40 mg, 404 μmol), and 2,2,6,6-tetramethyl-3,5-heptanedione (50 mg, 271 μmol). Then, phenol (2.00 mmol) was added, and the reaction mixture was shaken at 120 °C for 12 h.

(b) To the resin (150 mg) in MeCN (1.50 mL) and DMF (3.00 mL) were added Cs_2CO_3 (600 mg, 1.84 mmol), CuCl (40 mg, 404 μmol), and 2,2,6,6-tetramethyl-3,5-heptanedione (50 mg, 271 μmol). Then, aryl halogenide (2.00 mmol) was added, and the reaction mixture was shaken at 120 °C for 12 h.

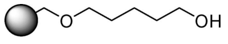
(c) To the resin (150 mg) in MeCN (1.50 mL) and DMF (3.00 mL) were added Cs_2CO_3 (600 mg, 1.84 mmol), CuCl (40 mg, 404 μmol), and 2,2,6,6-tetramethyl-3,5-heptanedione (50 mg, 271 μmol). Then, phenol (2.00 mmol) was added, and the reaction mixture was shaken at 120 °C for 36 h.

(d) To the resin (150 mg) in MeCN (1.50 mL) and DMF (3.00 mL) were added Cs_2CO_3 (600 mg, 1.84 mmol), CuCl (40 mg, 404 μmol), and 2,2,6,6-tetramethyl-3,5-heptanedione (50 mg, 271 μmol). Then, thiophenol (2.00 mmol) was added, and the reaction mixture was shaken at 120 °C for 12 h. The resin was isolated by filtration and washed with 30 mL of water, followed with 30 mL of acetone. The crude resin was washed with 20 mL of a saturated solution of sodium diethyldithiocarbamic acid trihydrate in DMF. Then, the resin was washed with acetone until no further color could be detected in the filtrate (~100 mL). Finally, the resin was washed with 30 mL of methanol and three times with 30 mL of dichloromethane.

Ozonolysis of Immobilized Olefins (GP6). Two hundreed milligrams of immobilized olefin in 5.00 mL of CH_2Cl_2 was treated for 20 s at rt with a stream of O_2/O_3. The reaction mixture was shaken in presence of 0.2 mL of dimethylsulfide for 30 min. The resin was separated by filtration and washed two times with acetone (each washing 30 mL). The solvent of the filtrate was removed under reduced pressure, and the residue was analyzed via GC-MS. Yields are given over 6 steps (starting from Merrifield resin).

Protection of Phenols with THP Protecting Group (GP7). The phenol was dissolved in CH_2Cl_2 (10 mL per mmol phenol) and was treated at rt with 1.20−2.00 equiv of dihydropyran. Then, 0.10 equiv of pyridinium *para*-toluene sulfonate were added, and the mixture was stirred at rt until complete conversion could be detected. The reaction was quenched by addition of saturated $NaHCO_3$ solution, and the layers were separated. The aqueous solution was extracted once with CH_2Cl_2, and the combined organic layers were dried with Na_2SO_4. After removal of the solvent under reduced pressure, the crude product was purified via flash chromatography. For protection of cinnamic acids, the amount of acid was not modified, but the amount of dihydropyran had to be doubled.

5-Hydroxypentyloxymethyl polystyrene (6a). Merrifield resin (**8**, 1.00 g, 0.97 mmol) was suspended in 20 mL of DMF in an 50 mL flask, and 625 mg (6 mmol) of 1,5-pentanediol were added. The reaction mixture was cooled

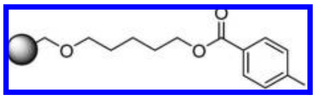


to 0 °C, and within 30 min, 320 mg (8 mmol) of NaH (60% disp) was added portionwise. After gas evolution had finished, the suspension was stirred for 1 h at rt and for 48 h at 80 °C. To the brown-reddish suspension was added very carefully 100 mL of acetone and then 100 mL water. The supernatant was removed by filtration, and the resin was washed successively with acetone (2 × 50 mL), water (2 × 50 mL), and methanol (1 × 20 mL). The residue was washed (4 × 50 mL) with CH_2Cl_2. The target resin could be obtained (1.066 g, 0.91 mmol/g loading) in quantitative yield. ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 22.4*, 29.4*, 32.4*, 62.6*, 70.0*, 72.8*. FTIR: ν = 3602 (w), 3366 (w), 2985 (vw), 2870 (vw), 2786 (w), 1969 (w), 1897 (w), 1820 (w), 1679 (w), 1629 (w), 1564 (w), 1549 (w), 1529 (w) cm^{-1}.

1-Bromopentyl-5-oxymethyl polystyrene (6b). Six grams

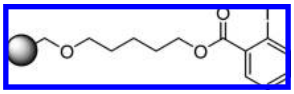
of pentanediol-resin **6a** was suspended in 100 mL of CH_2Cl_2, and 9.44 g (36.0 mmol) of PPh_3 and 11.9 g (36.0 mmol) of CBr_4 were added at 0 °C. The reaction mixture was shaken for 1 h at 0 °C and at rt for 12 h. Then, 100 mL of acetone was added, and the supernatant was removed by filtration. The resulting residue was washed two times with acetone, methanol, and CH_2Cl_2. ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 24.9*, 28.9*, 32.52*, 33.7*, 69.7*, 72.8*. - FTIR: ν = 3589 (w), 3440 (w), 3030 (m), 2846 (m), 2337 (w), 2246 (w), 1944 (m), 1872 (m), 1803 (m), 1726 (m), 1675 (w), 1601 (m) cm^{-1}.

4-Iodobenzoic acid-5-pentyloxymethylpolystyrene (7a).



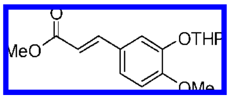
General procedure 2 (GP2) and the reaction of 10.0 g (8.64 mmol) of 5-bromopentyloxymethyl polystyrene (**6b**) gave 10.8 g of target resin with a loading of 0.418 mmol/g. ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 23.1*, 28.8*, 29.6 *, 65.4*, 70.1*, 73.0*, 100.8, 131.2, 137.8, 166.3 (*C*OOR). FTIR: ν = 3802 (vw), 3648 (w), 3620 (vw), 3429 (vw), 3031 (m), 2849 (m), 2603 (w), 2337 (w), 2311 (w), 2246 (w), 1944 (m), 1873 (w), 1804 (m), 1727 (m), 1682 (m), 1602 (m) cm^{-1}.

2-Iodobenzoic acid-5-pentyloxymethylpolystyrene (7b).

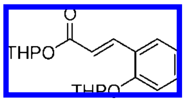


General procedure 2 (GP2) and the reaction of 5.0 g (4.32 mmol) of 5-bromopentyloxymethyl polystyrene (**6b**) gave 5.41 g of target resin with a loading of 0.418 mmol/g. ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.8*, 28.4*, 29.4*, 65.6*, 69.9*, 72.7*, 94.9, 130.8, 132.4, 135.4, 141.2, 166.6. FTIR: ν = 3650 (vw), 3437 (vw), 3037 (w), 2841 (w), 2337 (vw), 2247 (vw), 1944 (w), 1871 (w), 1803 (w), 1736 (w), 1602 (w), 1561 (w) cm^{-1}.

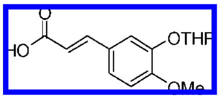
Methyl-(*E*)-3-(4-methoxy-3-(tetrahydro-2*H*-pyran-2-yloxy)phenyl)acrylate (9b). Chromatography: *n*-hexane/ethyl acetate 10:1, yield: 71%. R_f = 0.08 (*n*-hexane/ethyl acetate 10:1). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.43−2.04 (m, 6 H), 3.60−3.45 (m, 1 H), 3.69 (s, 3 H), 3.77 (s, 3 H), 3.82−3.97 (m, 1 H), 5.33 (m, 1 H), 6.22 (d, 1H, ^3J = 16.0 Hz), 6.78 (d, 1 H, ^3J = 8.4 Hz), 7.06 (dd, 1 H, ^3J = 8.4 Hz, ^4J = 1.6 Hz), 7.27 (s, 1 H), 7.53 (d, 1 H, ^3J = 16.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 18.5, 24.9, 30.0, 51.2, 55.7, 61.8, 97.3, 111.6, 115.2, 116.3, 123.4, 127.1, 144.4, 146.2, 152.0, 167.3. FTIR (KBr): ν = 2947 (s), 2873 (w), 2841 (w), 1716 (s), 1634 (s), 1599 (s), 1580 (m), 1512 (s), 1435 (s), 1389 (w), 1262 (s) cm^{-1}. EI-MS (70 eV, 120 °C) *m/z* (%): 292 (8) $[M]^+$, 208 (100), 177 (16), 85 (22).



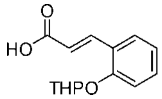
Tetrahydro-2*H*-pyran-2-yl-(E)-3-(2-(tetrahydro-2H-pyran-2-yloxy)phenyl)acrylate (9c). Chromatography: *n*-hexane/ethyl acetate 20:1 → 10:1, yield: 57%. ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 0.82−1.90 (m, 12 H), 3.42−4.10 (m, 4H), 5.50 (m, 1H), 6.10 (m, 1H), 6.49 (d, 1H, ^3J = 16.1 Hz), 6.94 (dd, 1H, ^3J = 7.6 Hz, ^3J = 7.6 Hz), 7.12 (d, 1H, ^3J = 8.2 Hz), 7.27 (ddd, 1H, ^3J = 8.2 Hz, ^3J = 7.6 Hz, ^3J = 1.5 Hz), 7.50 (dd, 1H, ^3J = 7.6 Hz, ^4J = 1.5 Hz), 8.10 (d, 1H, ^3J = 16.1 Hz). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 18.5, 18.6, 25.0, 25.2, 30.9, 31.5, 62.9, 63.3, 92.5, 96.1, 115.1, 118.2, 121.5, 123.8, 128.2, 131.5, 140.6, 155.6, 165.9. FTIR (KBr): ν = 3433 (vw), 2944 (s), 2872 (m), 1716 (s), 1630 (m), 1599 (m), 1577 (m), 1486 (m), 1456 (w), 1119 (s) cm^{-1}. EI-MS (70 eV, 90 °C) *m/z* (%): 332 (0.2) $[M]^+$, 248 (8.4), 85 (100). HRMS ($C_{19}H_{24}O_5$): calcd 332.1624, found 332.1627.



(*E*)-3-(4-Methoxy-3-(tetrahydro-2*H*-pyran-2-yloxy)phenyl)acrylic acid (10b). Yield: 89%. H NMR (250 MHz, $CDCl_3$): δ (ppm) = 1.54−2.05 (m, 6 H), 3.61−3.66 (m, 1 H), 3.89 (s, 3 H), 3.95−4.03 (m, 1 H), 5.37−5.45 (m, 1 H), 6.30 (d, 1 H, ^3J = 15.9 Hz), 6.90 (d, 1 H, ^3J = 8.4 Hz), 7.16−7.20 (m, 1 H), 7.36 (d, 1 H, ^4J = 1.9 Hz), 7.70 (d, 1 H, ^3J = 15.9 Hz). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 18.8, 25.2, 30.3, 56.0, 62.2, 97.6, 112.0, 115.0, 116.8, 124.2, 127.1, 146.5, 146.9 152.6, 172.3. FTIR (KBr): ν = 2937 (m), 2846 (m), 2593 (m), 2038 (m), 1861 (m), 1627 (m), 1598 (m). EI-MS (70 eV, 90 °C) *m/z* (%): 278 (1) $[M]^+$, 194 (100), 133 (14). HRMS ($C_{15}H_{18}O_5$): calcd 278.1154, found 278.1149.

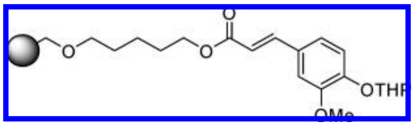


(*E*)-3-(2-(Tetrahydro-2*H*-pyran-2-yloxy)phenyl)acrylic acid (10c). Yield: 93%. ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 1.33−1.94 (m, 6 H), 3.66−4.02 (m, 2 H), 5.41 (m,



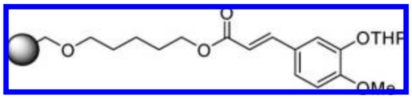
1 H), 6.51 (d, 1 H, $^3J = 16.1$ Hz), 6.86 (dd, 1 H, $^3J = 7.6$ Hz, $^4J = 0.6$ Hz), 7.08 (d, 1 H, $^3J = 8.2$ Hz, $^4J = 0.6$ Hz), 7.22 (ddd, 1 H, $^3J = 8.2$ Hz, $^3J = 7.6$ Hz, $^4J = 1.5$ Hz), 7.43 (dd, 1 H, $^3J = 7.6$ Hz, $^4J = 1.5$ Hz), 7.99 (d, 1 H, $^3J = 16.1$ Hz). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 18.6, 25.1, 30.9, 61.9, 96.3, 115.0, 119.9, 121.5, 124.1, 128.7, 131.2, 140.4, 155.6, 172.6. FTIR (KBr): ν = 3399 (m), 2943 (m), 2872 (m), 1916 (w), 1691 (m), 1632 (m), 1599 (m), 1576 (m), 1537 (w), 1489 (m), 1456 (m) cm^{-1}. EI-MS (70 eV, 120 °C) *m/z* (%): 248 (16) $[M]^+$, 231 (6), 165 (18), 85 (100). HRMS ($C_{14}H_{16}O_4$): calcd 248.1049, found 248.1046.

3-Methoxy-4-(tetrahydropyran-2′-yloxy)cinnamic acid-5-pentyloxymethylpolystyrene (11a). Conversion of resin **6b** was performed according to general procedure (GP2).



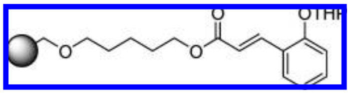
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 18.6 (THP), 22.7*, 25.1 (THP), 28.6*, 29.4*, 30.1 (THP), 56.0 (OCH$_3$), 62.0 (THP), 64.4*, 70.0*, 72.5*, 97.1 (THP), 111.0, 116.2, 122.2, 144.5 (CHCHCOOR), 150.1. FTIR: ν = 3648 (vw), 3579 (w), 3031 (m), 2848 (m), 2603 (w), 2337 (w), 233 (w), 2248 (w), 1944 (m), 1874 (m), 1805 (m), 1738 (m), 1604 (m), 1499 (m) cm^{-1}.

4-Methoxy-3-(tetrahydropyran-2′-yloxy)cinnamic acid-5-pentyloxymethylpolystyrene (11b). Conversion of resin **6b** according to general procedure (GP2).



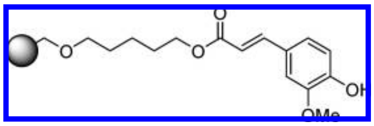
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 18.7 (THP), 22.7*, 25.1 (THP), 28.5*, 29.4*, 30.2 (THP), 55.9 (OCH$_3$), 62.1, 64.3*, 69.8*, 72.6*, 97.5 (THP), 111.8, 115.7, 116.5, 123.6, 125.6, 146.3 (CHCHCOOR), 154.7. FTIR: ν = 3025 (m), 2851 (m), 2337 (vw), 2312 (vw), 2247 (w), 1944 (w), 1874 (w), 1804 (w), 1710 (m), 1679 (m), 1632 (m) cm^{-1}.

2-(Tetrahydropyran-2′-yloxy)cinnamic acid-pentyloxymethylpolystyrene (11c). Conversion of resin **6b** was performed according to general procedure (GP2).



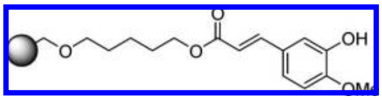
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 18.6 (THP), 22.7*, 25.1 (THP), 28.6*, 29.4*, 30.2 (THP), 61.8 (THP), 64.3*, 70.0*, 72.6*, 96.2 (THP), 115.0, 118.5, 121.5, 124.0, 131.3, 139.9 (CHCHCOOR), 155.5, 167.6 (COOR). FTIR: ν = 3029 (m), 2845 (m), 2337 (w), 2311 (m), 1944 (w), 1874 (w), 1805 (m), 1719 (m), 1631 (m), 1601 (m), 1494 (m), 1452 (m) cm^{-1}.

4-Hydroxy-3-methoxyphenylcinnamic acid-5-pentyloxymethylpolystyrene (12a). Conversion of resin **11a** was performed according to general procedure (GP1).



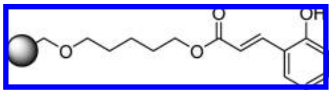
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.7*, 28.6*, 29.4*, 55.8 (OCH$_3$), 64.3*, 69.8*, 72.8*, 109.3, 114.7, 115.4, 123.0, 144.7 (CHCHCOOR), 146.7, 147.9, 168.7 (COOR). FTIR: ν = 3649 (vw), 3034 (vw), 2842 (w), 1605 (w), 2338 (w), 2312 (w), 2248 (w), 1945 (w), 1877 (w), 1806 (w), 1724 (w), 1604 (w) cm^{-1}.

3-Hydroxy-4-methoxycinnamic acid-5-pentyloxymethylpolystyrene (12b). Conversion of resin **11b** was performed according to general procedure (GP1).



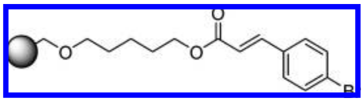
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.9*, 28.8*, 29.6*, 56.0 (OCH$_3$), 64.5*, 70.0*, 73.0*, 108.0, 110.7, 113.2, 116.4, 144.6 (CHCHCOOR), 146.0, 148.6, 167.5 (COOCH$_3$). FTIR: ν = 3649 (vw), 3033 (w), 2844 (w), 2337 (vw), 1943 (w), 1872 (w), 1804 (w), 1746 (w), 1701 (w), 1601 (w), 1494 (w), 1454 (w) cm^{-1}.

2-Hydroxycinnamic acid-5-pentyloxymethylpolystyrene (12c). Conversion of resin **11c** was performed according to general procedure (GP1).



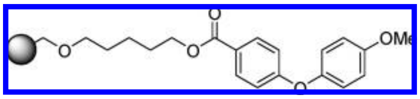
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.7*, 28.6*, 29.4*, 64.6*, 69.9*, 72.7*, 118.1, 120.3, 140.7 (CHCHCOOR), 155.7, 168.2 (COOR). FTIR: ν = 3649 (vw), 3527 (w), 3299 (w), 3028 (w), 2858 (w), 2603 (w), 2340 (w), 2312 (w), 1945 (w), 1874 (w), 1804 (w), 1686 (w), 1630 (w), 1603 (m), 1544 (w), 1496 (m), 1456 (m) cm^{-1}.

4-Bromocinnamic acid-5-pentyloxymethylpolystyrene (12d). Conversion of resin **6b** was performed according to general procedure (GP2).



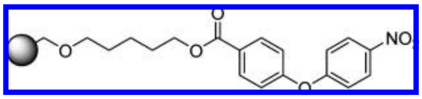
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.7*, 28.5*, 29.4*, 64.6*, 69.8*, 72.7*, 118.9 (CHCHCOOR), 129.4, 133.2, 143.1 (CHCHCOOR), 166.5 (COOR). FTIR: ν = 3649 (vw), 3414 (vw), 3029 (w), 2949 (w), 2632 (vw), 2603 (vw), 2337 (vw), 2312 (vw), 1944 (w), 1872 (w), 1804 (w), 1718 (w), 1638 (w), 1602 (w), 1491 (m), 1454 (m) cm^{-1}.

4-(4′-Methoxyphenoxy)benzoic acid-5-M-oxypentylester (13). Conversion of resin **7a** was performed according to general procedure (GP5a). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.8*, 28.6*, 29.3*, 55.5 (OCH$_3$), 64.8*, 69.8*, 72.7*, 114.9, 116.4, 121.5, 131.5, 148.5, 156.5, 162.6, 166.3

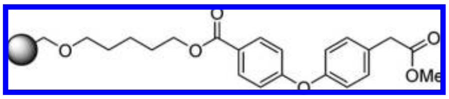


(*C*OOR). FTIR: ν = 3648 (vw), 3420 (vw), 3163 (w), 3030 (m), 2845 (m), 2778 (w), 2632 (w), 2338 (vw), 2312 (w), 2260 (vw), 2033 (vw), 1945 (w), 1874 (w), 1805 (w), 1718 (m), 1674 (m), 1604 (m), 1506 (m) cm^{-1}.

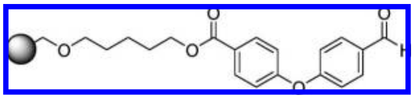
4-(4′-Nitrophenoxy)benzoic acid-5-pentyloxymethylpolystyrene (14). Conversion of resin **7a** was performed according to general procedure (GP5a). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.8*, 28.5*, 29.4*, 65.1*, 69.8*, 72.8*, 118.1, 119.4, 126.0, 132.0, 137.6, 158.7, 161.7, 165.6 (*C*OOR). FTIR: ν = 3432 (vw), 3060 (w), 3030 (w), 2945 (w), 2858 (w), 2382 (vw), 2338 (vw), 2247 (vw), 1944 (vw), 1873 (vw), 1803 (vw), 1723 (w), 1603 (w), 1522 (w), 1494 (w) cm^{-1}.



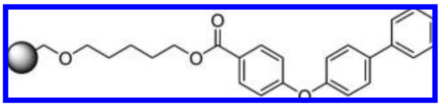
4-(4′-Methoxycarbonylmethylphenoxy)benzoic acid-5-pentyloxymethylpolystyrene (15). Conversion of resin **7a** was performed according to general procedure (GP5a). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.8*, 28.7*, 29.5*, 52.1 ($COOCH_3$), 64.9*, 69.9*, 72.9*, 117.3, 120.0, 130.8, 154.7, 161.4, 164.7 (*C*OOR), 173.4 (*C*OOMe). FTIR: ν = 3649 (vw), 3036 (vw), 2842 (w), 2600 (w), 2340 (w), 1948 (w), 1882 (w), 1757 (w), 1600 (w), 1439 (w) cm^{-1}.



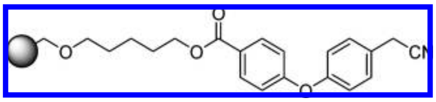
4-(4′-Formylphenoxy)benzoic acid-5-pentyloxymethylpolystyrene (16). Conversion of resin **7a** was performed according to general procedure (GP5a). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.8*, 28.6*, 29.4*, 65.0*, 69.8*, 72.8*, 118.7, 131.9, 190.5 (*C*HO). FTIR: ν = 3650 (vw), 3028 (w), 2909 (w), 2336 (w), 2248 (w), 1944 (w), 1876 (w), 1806 (w), 1699 (w), 1600 (w) cm^{-1}.



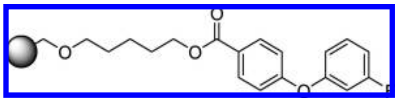
4-(Biphenyl-4′-yloxy)benzoic acid-5-pentyloxymethylpolystyrene (17). Conversion of resin **7a** was performed according to general procedure (GP5a). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.8*, 28.6*, 29.4*, 64.8*, 68.8*, 72.8*, 117.4, 120.4, 126.9, 128.6, 131.7, 137.4, 140.1, 155.0, 161.5, 166.2 (*C*OOR). FTIR: ν = 3419 (vw), 3162 (vw), 3082 (w), 3061 (w), 3026 (w), 2911 (w), 2847 (w), 2631 (vw), 2603 (vw), 2443 (vw), 2399 (vw), 2337 (vw), 2312 (vw), 2031 (vw), 1944 (w), 1873 (w), 1803 (w), 1721 (w), 1599 (w) cm^{-1}.



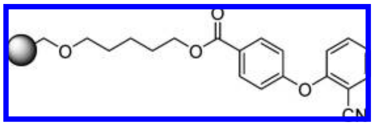
4-(4′-Cyanomethylphenoxy)benzoic acid-5-M-oxypentylester (18). Conversion of resin **7a** was performed according to general procedure (GP5a). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.9*, 28.5*, 29.4*, 64.6*, 69.9*, 72.6*, 117.5, 120.3, 125.7, 129.6, 131.6, 155.6, 161.0, 165.7 (*C*OOR). FTIR: ν = 3462 (vw), 3027 (w), 2918 (w), 2335 (vw), 2250 (vw), 1943 (w), 1869 (w), 1801 (w), 1718 (w), 1600 (w) cm^{-1}.



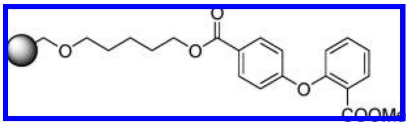
4-(3′-Fluorophenoxy)benzoic acid-5-pentyloxymethylpolystyrene (19). Conversion of resin **7a** was performed according to general procedure (GP5a). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.8*, 28.6 *, 29.4*, 64.9*, 69.8*, 72.7*, 107.3 (d, ^2J = 21.0 Hz), 111.0, 115.1, 117.9, 125.6, 130.7, 131.7, 157.1, 160.6, 164.7, 165.8 (*C*OOR). FTIR: ν = 3164 (vw), 3082 (w), 3060, 3027, 2922, 2849, 2632 (vw), 2603 (vw), 2386 (vw), 2337 (vw), 2077 (w), 1943 (w), 1871 (w), 1802 (w), 1719 (w), 1676 (w), 1599 (w), 1491 (w) cm^{-1}.



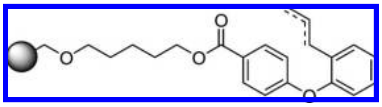
4-(2′-Cyanophenoxy)benzoic acid-5-pentyloxymethylpolystyrene (20). Conversion of resin **7a** according to general procedure (GP5a). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.8*, 28.6*, 29.4*, 65.1*, 69.8*, 72.8*, 104.8, 115.5, 118.6, 124.0, 130.9, 131.8, 134.3, 158.0, 159.3, 165.7 (*C*OOR). FTIR: ν = 3649 (vw), 3421 (vw), 3111 (vw), 2981 (vw), 2790 (w), 2364 (vw), 2233 (w), 1734 (w), 1696 (w), 1636 (w), 1570 (w) cm^{-1}.



4-(2′-Methylcarboxyphenoxy)benzoic acid-5-M-oxypentylester (21). Conversion of resin **7a** was performed according to general procedure (GP5a). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.8*, 28.6*, 29.4*, 52.1 ($COOCH_3$), 64.8*, 69.8*, 72.9*, 116.5, 122.5, 124.8, 131.9, 133.9, 154.5, 162.1 (*C*OOR), 165.5 (*C*$OOCH_3$). FTIR: ν = 3649 (w), 3419 (w), 3162 (w), 3031 (m), 2944 (m), 2632 (w), 2603 (w), 2337 (vw), 2312 (vw), 2255 (vw), 2038 (vw), 1944 (w), 1872 (w), 1803 (w), 1737 (m), 1604 (m), 1456 (m) cm^{-1}.

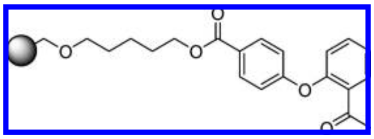


4-(2′-Allylphenoxy)benzoic acid-5-pentyloxymethylpolystyrene (22). Conversion of resin **7a** was performed accord-

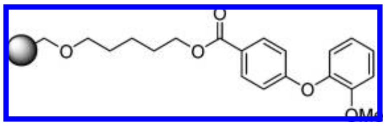


ing to general procedure (GP5a). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 22.8*, 28.6*, 29.4*, 34.2, 64.8*, 69.8*, 72.8*, 116.2, 120.8, 125.1, 130.8, 131.6, 135.9, 152.8, 162.1, 166.2 (*C*OOR). FTIR: ν = 3649 (vw), 3451 (m), 3028 (m), 2949 (m), 2468 (w), 2337 (w), 2247 (w), 1943 (w), 1871 (w), 1802 (w), 1717 (m), 1638 (m), 1603 (m), 1457 (s) cm^{-1}.

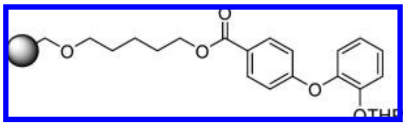
4-(2′-Acetylphenoxy)benzoic acid-5-pentyloxymethylpolystyrene (23). Conversion of resin **7a** was performed according to general procedure (GP5a). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 22.6*, 28.3*, 29.1*, 31.0 (CO*C*H$_3$), 64.6*, 69.7*, 72.7*, 117.1, 120.5, 124.5, 125.4, 130.4, 131.7, 133.6, 154.4, 160.8, 165.7 (*C*OOR), 197.9 (*C*OCH$_3$). FTIR: ν = 3648 (vw), 3567 (w), 3348 (w), 3062 (w), 3031 (w), 2632 (vw), 2603 (vw), 2337 (vw), 2312 (vw), 2033 (vw), 1944 (w), 1872 (w), 1803 (w), 1717 (w), 1684 (w), 1601 (w), 1541 (w), 1456 (m) cm^{-1}.



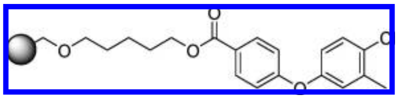
4-(2′-Methoxyphenoxy)benzoic acid-5-pentyloxymethylpolystyrene (24). Conversion of resin **7a** was performed according to general procedure (GP5a). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 22.7*, 28.9*, 29.4*, 55.8 (O*C*H$_3$), 64.8*, 69.8*, 73.0*, 112.9, 115.7, 121.2, 122.2, 125.9, 131.4, 143.2, 151.6, 162.2, 166.1 (*C*OOR). FTIR: ν = 3649 (vw), 3466 (w), 3163 (w), 3061 (m), 3030 (m), 2946 (m), 2632 (w), 2337 (w), 2312 (vw), 2026 (vw), 1944 (w), 1872 (w), 1802 (w), 1718 (m), 1683 (m), 1605 (m), 1458 (m) cm^{-1}.



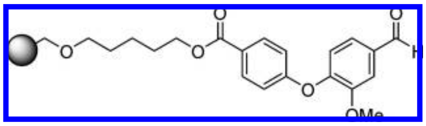
4-[2′-(Tetrahydropyran-2″-yloxy)phenoxy]benzoic acid-5-pentyloxymethylpolystyrene (25). Conversion of resin **7a** was performed according to general procedure (GP5a). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 18.1 (THP), 23.0*, 25.2 (THP), 28.8*, 30.1*, 30.2 (THP), 61.7 (THP), 64.9*, 70.1*, 72.7*, 96.9 (THP), 109.1, 115.7, 117.7, 122.9, 126.3, 131.5, 144.2, 149.2, 163.9, 168.8 (*C*OOR). FTIR: ν = 3648 (w), 3031 (m), 2847 (m), 2337 (w), 2312 (w), 2246 (w), 1943 (m), 1873 (w), 1804 (w), 1717 (m), 1604 (m), 1497 (m) cm^{-1}.



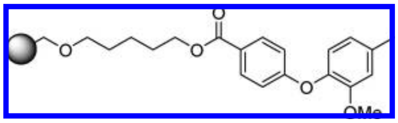
4-(4′-Chloro-3′-methylphenoxy)benzoic acid-5-pentyloxymethylpolystyrene (26). Conversion of resin **7a** was performed according to general procedure (GP5a). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 20.2 (*C*H$_3$), 22.8*, 28.5*, 29.2*, 65.0*, 69.9*, 72.6*, 117.3 (C-3), 118.5, 122.3, 130.17, 131.7, 137.9, 154.0, 161.2 (*C*OOR). FTIR: ν = 3446 (w), 2958 (m), 2927 (m), 2845 (m), 2312 (w), 1945 (w), 1868 (w), 1732 (m), 1608 (m), 1580 (w), 1512 (m) cm^{-1}.



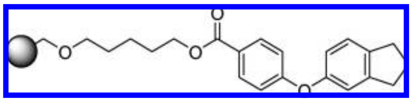
4-(4′-Formyl-2′-methoxyphenoxy)benzoic acid-5-pentyloxymethylpolystyrene (27). Conversion of resin **7a** was performed according to general procedure (GP5a). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 22.8*, 28.6*, 29.3*, 56.0 (O*C*H$_3$), 64.9*, 69.8*, 72.9*, 111.0, 117.2, 120.4, 125.4, 129.5, 131.7, 165.9 (*C*OOR), 190.7 (*C*HO). FTIR: ν = 3376 (vw), 2968 (w), 2870 (vw), 2825 (w), 2246 (w), 1695 (w), 1617 (vw), 1572 (vw) cm^{-1}.



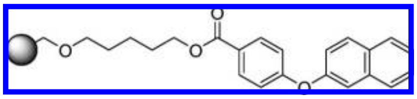
4-(2′-Methoxy-4′-methylphenoxy)benzoic acid-5-pentyloxymethylpolystyrene (28). Conversion of resin **7a** according to general procedure (GP5a). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 21.4 (*C*H$_3$), 22.8*, 29.4*, 30.9*, 55.7 (O*C*H$_3$), 64.7*, 69.9*, 72.8*, 113.7, 115.5, 121.7, 122.7, 123.9, 131.4, 136.0, 140.9, 151.3, 162.3, 166.3 (*C*OOR). FTIR: ν = 3649 (vw), 3413 (vw), 3115 (vw), 2981 (vw), 2785 (vw), 2491 (vw), 2247 (w), 2022 (vw), 1774 (vw), 1695 (vw), 1625 (vw) cm^{-1}.



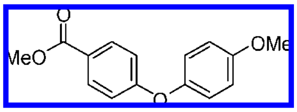
4-(Indan-5-yloxy)benzoic acid-5-pentyloxymethylpolystyrene (29). Conversion of resin **7a** was performed according to general procedure (GP5a). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 22.8*, 25.7, 28.6*, 29.4*, 32.2, 33.0, 64.8*, 68.8*, 72.8*, 116.3, 116.8, 118.0, 125.2, 131.5, 140.3, 146.3, 154.0, 166.2, 166.2 (*C*OOR). FTIR: ν = 3411 (w), 3163 (vw), 3083 (w), 3059 (w), 3026 (w), 2913 (w), 2849 (w), 2632 (vw), 2603 (vw), 2385 (vw), 2337 (vw), 2311 (vw), 2258 (vw), 1943 (w), 1872 (w), 1803 (w), 1719 (w), 1672 (w), 1602 (w), 1481 (w), 1452 (m) cm^{-1}.



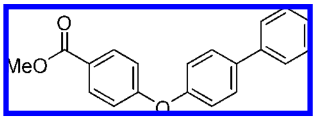
4-(Naphthalen-2′-yloxy)benzoic acid-5-pentyloxymethylpolystyrene (30). Conversion of resin **7a** was performed according to general procedure (GP5a). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 22.8*, 28.6*, 29.4*, 64.8*, 69.8*, 72.8*, 115.9, 117.5, 120.2, 125.7, 126.7, 127.2, 130.1, 131.7, 134.1, 153.3, 161.5, 166.2 (*C*OOR). FTIR: ν = 3413 (vw), 3162 (vw), 3058 (w), 3027 (w), 2905 (w), 2847 (w), 2630 (vw),



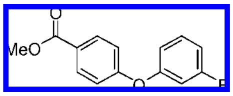
2603 (vw), 2388 (vw), 2337 (vw), 2311 (vw), 1944 (w), 1872 (w), 1802 (w), 1720 (w), 1631 (w), 1600 (w), 1541 (w), 1492 (w) cm^{-1}.



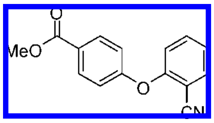
Methyl 4-(4-Methoxyphenoxy)benzoate (31). Resin **13** (305 mg) was treated according to the general procedure (GP3) to give compound **31** (33 mg, quant.). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 3.83 (s, 3 H), 3.89 (s, 3 H), 6.92−7.05 (m, 4 H), 7.01 (bd, 2 H, ^3J = 9.0 Hz), 7.97 (bd, 2 H, ^3J = 8.9 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 52.0, 55.7, 115.1, 116.3, 121.7, 131.7, 148.6, 162.1, 166.7. FTIR (KBr): ν = 3358 (vw), 2921 (vw), 2851 (vw), 2348 (vw), 2283 (vw), 1881 (vw), 1721 (vw), 1689 (vw), 1679 (vw), 1606 (vw), 1511 (vw) cm^{-1}. EI-MS (70 eV, 80 °C) *m*/*z* (%): 258 (100) [M]$^+$, 243 (13), 227 (25). HRMS ($C_{15}H_{14}O_4$): calcd 258.0892, found 258.0890.



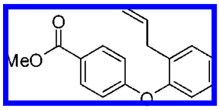
Methyl 4-(biphenyl-4-yloxy)benzoate (35). Resin **17** (317 mg) was treated according to the general procedure (GP3) to give compound **35** (48 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.91 (s, 3 H), 7.05 (bd, 2 H, ^{3}J = 8.8 Hz), 7.14 (bd, 2 H, ^{3}J = 8.6 Hz), 7.36 (m, 1H), 7.46 (m, 2H), 7.60 (m, 4 H), 8.04 (d, 2 H, ^{3}J = 8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 51.9, 117.4, 120.2, 124.6, 126.9, 127.2, 128.7, 128.8, 131.7, 137.4, 140.3, 155.1, 161.7, 166.6. EI-MS (GC-MS, 120 °C) *m*/*z* (%): 304 (100) [M]$^+$, 273 (55), 152 (13).



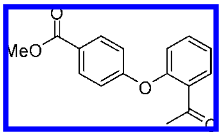
Methyl 4-(3-fluorophenoxy)benzoate (37). Resin **19** (326 mg) was treated according to the general procedure (GP3) to give compound **37** (22 mg, 65%). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 3.90 (s, 3 H), 6.71−6.93 (m, 3 H), 7.02 (d, 2 H, ^3J = 8.9 Hz), 7.20−7.39 (m, 1 H), 8.03 (d, 2 H, ^3J = 8.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 52.1, 107.4 (d, ^2J = 24.2 Hz), 111.2 (d, ^2J = 21.2 Hz), 115.2 (d, ^4J = 3.3 Hz), 117.9, 125.2, 130.8 (d, ^3J = 9.8 Hz), 131.7, 157.1 (d, ^3J = 10.4 Hz), 160.8, 163.5 (d, ^1J = 247.6 Hz), 166.4 (*C*OOCH$_3$). FTIR (KBr): ν = 3425 (vw), 3073 (vw), 2953 (w), 2854 (w), 1924 (vw), 1723 (m), 1600 (m), 1505 (m), 1485 (m), 1436 (m), 1273 (m) cm^{-1}. EI-MS (70 eV, 60 °C) *m*/*z* (%): 246 (98) [M]$^+$, 215 (100), 159 (6), 133 (16). HRMS ($C_{14}H_{11}FO_3$): calcd 246.0692, found 246.0690.



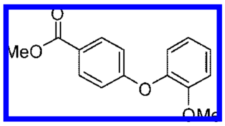
Methyl 4-(2-cyanophenoxy)benzoate (38). Resin **20** (340 mg) was treated according to the general procedure (GP3) to give compound **38** (32 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.92 (s, 3 H), 6.99 (bd, 1 H, ^3J = 8.5 Hz), 7.09 (d, 2 H, ^3J = 8.9 Hz), 7.23 (ddd, 1H, ^3J = 7.7 Hz, ^3J = 7.6 Hz, ^4J = 1.0 Hz), 7.55 (ddd, 1H, ^3J = 8.5 Hz, ^3J = 7.6 Hz, ^4J = 1.7 Hz), 7.70 (dd, 1H, ^3J = 7.7 Hz, ^4J = 1.7 Hz), 8.08 (d, 2 H, ^3J = 8.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 52.2, 105.0, 115.5, 118.6, 118.7, 124.1, 126.4, 131.9, 134.1, 134.4, 158.1, 159.4, 166.2. FTIR (KBr): ν = 3073 (vw), 2952 (vw), 2848 (vw), 2232 (w), 1720 (s), 1601 (m), 1578 (w), 1504 (m), 1485 (m), 1449 (m), 1436 (m), 1416 (m), 1281 (s), 1247 (s) cm^{-1}. EI-MS (70 eV, 100 °C) *m*/*z* (%): 253 (16) [M]$^+$, 222 (39), 98 (100). HRMS ($C_{15}H_{11}NO_3$): calcd 253.0739, found 253.0737.



Methyl 4-(2-allylphenoxy)benzoate (40). Resin **22** (350 mg) was treated according to the general procedure (GP3) to give compound **40** (34 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.33 (d, 2 H, *J* = 6.7 Hz), 3.89 (s, 3 H), 4.98−5.01 (m, 1 H), 5.03 (t, 1H, *J* = 1.4 Hz), 5.96−5.84 (m, 1 H), 6.90 (d, 2 H, ^3J = 8.9 Hz), 6.98 (dd, 1 H, *J* = 8.0, *J* = 1.3 Hz), 7.27−7.15 (m, 2 H), 7.30 (dd, 1 H, ^3J = 7.4, ^4J = 1.7 Hz), 7.98 (d, 2 H, ^3J = 8.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 34.2, 52.0, 116.2, 116.3, 120.9, 125.2, 126.8, 127.9, 130.9, 132.4, 136.0, 152.8, 162.1, 166.6. FTIR (KBr): ν = 2951 (vw), 1720 (s), 1638 (w), 1605 (w), 1583 (w), 1504 (w), 1486 (w), 1452 (w), 1435 (w), 1279 (s), 1241 (s) cm^{-1}. EI-MS (70 eV, 80 °C) *m*/*z* (%): 268 (100) [M]$^+$, 253 (32), 239 (11), 237 (35), 209 (52), 181 (26). HRMS ($C_{17}H_{16}O_3$): calcd 268.1099, found 268.1096.



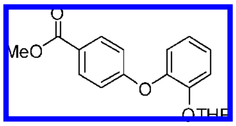
Methyl 4-(2-acetylphenoxy)benzoate (41). Resin **23** (210 mg) was treated according to the general procedure (GP3) to give compound **41** (18 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.57 (s, 3 H), 3.91 (s, 3 H), 6.94−7.06 (m, 3 H), 7.27 (dd, 1 H, ^3J = 7.5 Hz, ^3J = 7.5 Hz), 7.47−7.57 (m, 1 H), 7.87 (dd, 1 H, ^3J = 7.8 Hz, ^4J = 1.7 Hz), 8.04 (d, 2 H, ^3J = 8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 31.3, 52.1, 117.3, 120.9, 124.8, 125.2, 130.7, 131.3, 131.9, 133.8, 154.6, 160.9, 166.4, 198.3. FTIR (KBr): ν = 3073 (w), 3031 (w), 2953 (w), 2851 (vw), 2073 (vw), 1931 (vw), 1723 (m), 1680 (m), 1604 (m), 1504 (w), 1478 (m), 1448 (m), 1359 (w), 1283 (m), 1237 (m) cm^{-1}. EI-MS (70 eV, 80 °C) *m*/*z* (%): 270 (100) [M]$^+$, 239 (31), 211 (57), 119 (1). HRMS ($C_{16}H_{14}O_4$): calcd 270.0892, found 270.0894.



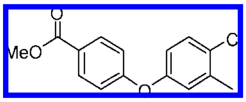
Methyl 4-(2-methoxyphenoxy)benzoate (42). Resin **24** (210 mg) was treated according to the general procedure (GP3) to give compound **42** (15 mg, 66%). ^{1}H NMR (500

MHz, CDCl$_3$): δ (ppm) = 3.79 (s, 3 H), 3.88 (s, 3 H), 6.91 (d, 2 H, J = 8.9 Hz), 6.98 (ddd, 1 H, ^3J = 8.0 Hz, ^3J = 7.8 Hz, ^4J = 1.3 Hz), 7.03 (dd, 1 H, ^3J = 8.2 Hz, ^4J = 1.3 Hz), 7.07 (dd, 1 H, ^3J = 7.8 Hz, ^4J = 1.6 Hz), 7.21 (ddd, ^3J = 8.2, Hz, ^3J = 8.0 Hz, ^4J = 1.6 Hz), 7.97 (d, 2 H, ^3J = 8.9 Hz). ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) = 51.9, 55.9, 113.0, 115.8, 121.3, 122.3, 123.9 126.0, 131.5, 143.4, 151.7, 162.2, 166.7. FTIR (KBr): ν = 3440 (vw), 3069 (vw), 3002 (vw), 2952 (w), 2841 (vw), 2293 (vw), 1925 (vw), 1720 (w), 1609 (w), 1586 (w), 1501 (w), 1458 (w), 1436 (w) cm^{-1}. EI-MS (70 eV, 80 °C) m/z (%): 258 (100) [M]$^+$, 227 (56), 184 (11). HRMS ($C_{15}H_{14}O_4$): calcd 258.0892, found 258.0895.

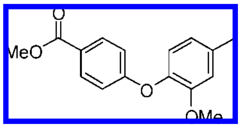
Methyl 4-(2-(tetrahydro-2*H*-pyran-2-yloxy)phenoxy)benzoate (43). Resin **25** (200 mg) was treated according to the general procedure (GP3) to give compound **43** (21 mg, 79%). ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) = 1.23−1.29 (m), 1.68−1.38 (m), 3.51−3.55 (m, 3 H), 3.71−3.75 (m, 1 H), 5.38 (m, 1 H), 6.92 (d, 2 H, ^3J = 8.9 Hz), 7.03 (ddd, ^3J = 7.8 Hz, ^3J = 7.8 Hz, ^4J = 1.4 Hz), 7.14 (dd, 1 H, ^3J = 8.0 Hz, ^4J = 1.6 Hz), 7.21−7.16 (m, 1 H), 7.25 (dd, ^4J = 1.4 Hz), 7.96 (d, 2 H, ^3J = 8.9 Hz). ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) = 17.9, 25.0, 30.0, 51.9, 61.6, 96.7, 115.5, 117.5, 122.4, 122.8, 123.6, 126.2, 131.4, 143.9, 149.0, 162.7, 166.8. FTIR (KBr): ν = 3442 (vw), 2949 (w), 2851 (vw), 1720 (w), 1609 (w), 1586 (w), 1496 (w), 1455 (w), 1435 (w), 1357 (vw), 1262 (w) cm^{-1}. EI-MS (70 eV, 120 °C) m/z (%): 328 (0.3) [M]$^+$, 244 (100), 213 (23), 85 (54). HRMS ($C_{19}H_{20}O_5$): calcd 328.1311, found 328.1313.



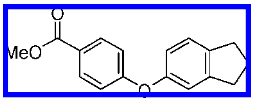
Methyl 4-(4-chloro-3-methylphenoxy)benzoate (44). Resin **26** (398 mg) was treated according to the general procedure (GP3) to give compound **44** (43 mg, 94%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 2.36 (s, 3 H), 3.90 (s, 3 H), 6.84 (dd, 1 H, ^3J = 8.6 Hz, ^4J = 2.7 Hz), 6.94 (d, 1 H, ^4J = 2.7 Hz), 6.97 (d, 2 H, ^3J = 8.9 Hz), 7.33 (d, 1 H, ^3J = 8.6 Hz), 8.00 (d, 2 H, ^3J = 8.9 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 20.2, 52.0, 117.3, 118.3, 122.4, 124.7, 129.8, 130.3, 131.7, 138.0, 154.0, 161.5, 166.5. FTIR (KBr) ν = 3434 (vw), 3071 (vw), 2952 (w), 2925 (w), 2851 (vw), 2348 (vw), 2281 (vw), 1721 (m), 1600 (w), 1504 (w), 1476 (m), 1435 (w), 1277 (m), 1242 (m) cm^{-1}. EI-MS (70 eV, 80 °C) m/z (%): 276/278 [M]$^+$, 245/247. HRMS ($C_{15}H_{13}ClO_3$) calcd 276.0553, found 276.0550.



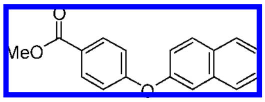
Methyl 4-(2-methoxy-4-methylphenoxy)benzoate (46). Resin **28** (235 mg) was treated according to the general procedure (GP3) to give compound **46** (20 mg, 75%). ^{1}H NMR (250 MHz, CDCl$_3$): δ (ppm) = 2.38 (s, 3 H), 3.77 (s, 3 H), 3.88 (s, 3 H), 6.77 (dd, 1 H, ^3J = 8.0 Hz, ^4J = 1.3 Hz), 6.83 (d, 1 H, ^4J = 1.3 Hz), 6.89 (d, 2 H, ^3J = 9.0 Hz), 6.95 (d, ^3J = 8.0 Hz), 7.95 (d, 2 H, ^3J = 9.0 Hz). ^{13}C NMR (62.5 MHz, CDCl$_3$): δ (ppm) = 21.4, 51.9, 55.8, 113.8, 115.5, 121.6, 122.1, 123.6, 131.5, 136.1, 140.9, 151.3, 162.5, 166.8. EI-MS (GC-MS, 120 °C) m/z (%): 272 (100) [M]$^+$, 241 (50), 198 (24).



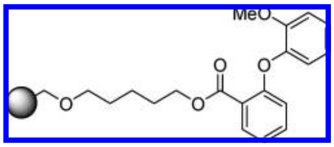
Methyl 4-(2,3-dihydro-1H-inden-5-yloxy)benzoate (47). Resin **29** (253 mg) was treated according to the general procedure (GP3) to give compound **47** (19 mg, 67%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 2.07−2.17 (m, 1 H), 2.90 (t, 2 H, ^3J = 7.4 Hz), 3.89 (s, 3 H), 6.83 (dd, 1 H, ^3J = 8.0 Hz, ^4J = 2.1 Hz), 6.92 (d, 1 H, ^4J = 2.1 Hz), 6.96 (d, 2 H, ^3J = 8.9 Hz), 7.21 (d, 1H, ^3J = 8.0 Hz), 7.98 (d, 2 H, ^3J = 8.9 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 25.8, 32.2, 33.0, 52.0, 116.5, 116.8, 118.1, 123.9, 125.3, 131.6, 140.5, 146.4, 153.9, 162.5, 166.7. EI-MS (GC-MS, 120 °C) m/z (%): 268 (100) [M]$^+$, 237 (39), 117 (44).



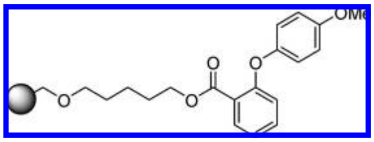
Methyl 4-(naphthalen-2-yloxy)benzoate (48). Resin **30** (339 mg) was treated according to the general procedure (GP3) to give compound **48** (29 mg, 74%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 3.91 (s, 3 H), 7.05 (bd, 2 H, ^3J = 8.8 Hz), 7.26 (dd, 1 H, ^3J = 8.9 Hz, ^4J = 2.4 Hz), 7.49 (m, 3H), 7.76 (d, 1 H, ^3J = 7.9 Hz), 7.87 (t, 2 H, ^3J = 8.8 Hz), 8.03 (bd, 2 H, ^3J = 8.8 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 52.0, 116.0, 117.5, 120.3, 124.6, 125.3, 126.7, 127.3, 127.8, 130.2, 130.7, 131.7, 134.2, 153.3, 161.7, 166.6.



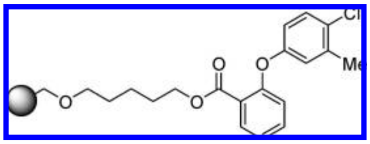
2-(2′-Methoxyphenoxy)benzoic acid-5-pentyloxymethylpolystyrene (49). Conversion of resin **7b** was performed according to general procedure (GP5a). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 22.8*, 28.6*, 29.4*, 56.0 (O*C*H$_3$), 64.9*, 69.9*, 72.7*, 129.5, 132.7, 166.5 (*C*OOR). FTIR: ν = 3649 (vw), 3061 (w), 2851 (w), 2602 (w), 2337 (w), 1944 (w), 1874 (w), 1803 (w), 1731 (w), 1602 (w), 1454 (m) cm^{-1}.



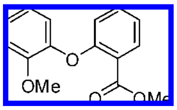
2-(4′-Methoxyphenoxy)benzoic acid-5-pentyloxymethylpolystyrene (50). Conversion of resin **7b** was performed according to general procedure (GP5a). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 22.7*, 28.4*, 29.3*, 55.5 (O*C*H$_3$), 64.9*,



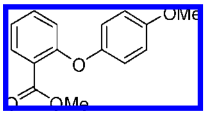
69.4*, 72.7*, 114.7, 119.3, 119.9, 122.6, 131.6, 133.2, 150.6, 155.6, 157.1, 167.1 (*C*OOR). FTIR: ν = 3059 (m), 3027 (m), 2849 (m), 2337 (vw), 2247 (vw), 1944 (w), 1873 (w), 1804 (w), 1740 (w), 1711 (w), 1659 (w), 1632 (m) cm^{-1}.



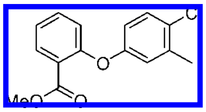
2-(4′-Chloro-3′-methylphenoxy)benzoic acid-5-pentyloxymethylpolystyrene (51). Conversion of resin **7b** was performed according to general procedure (GP5a). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 20.3 (*C*H$_3$), 22.8*, 28.5*, 29.4*, 65.0*, 70.0*, 72.8*, 116.3, 120.0, 121.3, 124.0, 124.0, 132.9, 137.4, 156.3, 166.6. FTIR: ν = 3649 (vw), 3621 (vw), 3438 (w), 3163 (w), 3030 (w), 2850 (w), 2623 (w), 2604 (w), 2338 (w), 2312 (w), 2257 (w), 1945 (w), 1874 (w), 1806 (w), 1728 (w), 1603 (w), 1495 (w) cm^{-1}.



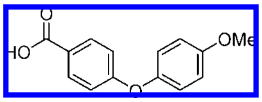
Methyl 2-(2-Methoxyphenoxy)benzoate (52). Resin **49** (336 mg) was treated according to the general procedure (GP3) treated to give compound **52** (37 mg, quant.). ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) = 3.84 (s, 6 H), 6.83 (d, 1 H, ^{3}J = 8.2 Hz), 6.92−6.88 (m, 2 H), 7.00 (d, 1 H, ^{3}J = 8.1 Hz), 7.09−7.13 (m, 2 H), 7.36−7.43 (m, 1 H), 7.90 (dd, 1 H, ^{3}J = 7.8 Hz, ^{4}J = 1.5 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 52.1, 56.1, 113.0, 118.6, 120.2, 121.1, 121.8, 122.5, 124.6, 131.8, 133.4, 137.0, 145.6, 151.0. FTIR (KBr): ν = 3448 (vw), 3069 (vw), 2924 (w), 2853 (w), 1734 (w), 1603 (w), 1579 (vw), 1500 (w), 1485 (w), 1452 (w), 1384 (vw), 1302 (w), 1263 (w) cm^{-1}. EI-MS (70 eV, 80 °C) *m/z* (%): 258 (100) [M]$^{+}$, 227 (16), 212 (7). HRMS (C$_{15}$H$_{14}$O$_4$): calcd 258.0892, found 258.0891.



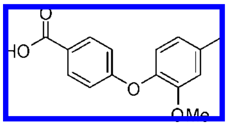
Methyl 2-(4-Methoxyphenoxy)benzoate (53). Resin **50** (333 mg) was treated according to the general procedure (GP3) to give compound **53** (29 mg, 81%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 3.80 (s, 3 H), 3.86 (s, 3 H), 6.80 (bd, 2 H, ^{3}J = 9.1 Hz), 6.89 (bd, 2 H, ^{3}J = 9.1 Hz), 7.11 (m, 1 H), 7.19 (bs, 1 H), 7.38−7.42 (m, 1 H), 7.87 (dd, 1 H, ^{3}J = 7.8 Hz, ^{4}J = 1.9 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 52.2, 55.7, 114.9, 119.1, 120.3, 122.2, 122.5, 131.7, 133.4, 148.0, 150.5, 155.9, 156.5. FTIR (KBr): ν = 3458 (vw), 2927 (vw), 2855 (vw), 1721 (vw), 1609 (vw), 1501 (vw), 1438 (vw), 1265 (w), 1230 (vw) cm^{-1}. EI-MS (70 eV, 80 °C) *m/z* (%): 258 (100) [M]$^{+}$, 227 (63), 184 (19). HRMS (C$_{15}$H$_{14}$O$_4$): calcd 258.0892, found 258.0894.



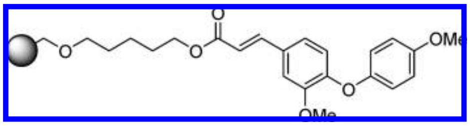
Methyl 2-(4-Chloro-3-methylphenoxy)benzoate (54). Resin **51** (345 mg) was treated according to the general procedure (GP3) to give compound **54** (40 mg, quant.). ^{1}H NMR (100 MHz, CDCl$_3$): δ (ppm) = 2.32 (s, 3 H), 3.82 (s, 3 H), 6.72 (dd, 1 H, ^{3}J = 8.7 Hz, ^{4}J = 2.7 Hz), 6.84 (d, 1 H, ^{4}J = 2.7 Hz), 6.97 (dd, 1 H, ^{3}J = 8.3 Hz, ^{4}J = 0.9 Hz), 7.17−7.27 (m, 2 H), 7.48 (ddd, 1 H, ^{3}J = 8.3 Hz, ^{3}J = 7.4 Hz, ^{4}J = 1.8 Hz), 7.92 (dd, 1 H, ^{3}J = 7.8 Hz, ^{4}J = 1.8 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 20.2, 52.2, 116.6, 120.4, 120.9, 123.2, 123.8, 128.3, 129.9, 131.9, 133.7, 137.5, 155.9, 156.1, 166.0. FTIR (KBr) ν = 3446 (vw), 2951 (w), 2850 (vw), 1733 (m), 1602 (w), 1574 (w), 1476 (m), 1451 (m), 1434 (w), 1408 (vw), 1241 (m) cm^{-1}. EI-MS (70 eV, 60 °C) *m/z* (%): 276/278 (77/26) [M]$^{+}$, 245/247 (100/35), 209 (12), 181 (17), 156 (30). HRMS (C$_{15}$H$_{13}$ClO$_3$): calcd 276.0553, found 276.0550.



4-(4-Methoxyphenoxy)benzoic acid (56). Resin **13** (231 mg) was treated according to the general procedure (GP4) to give compound **56** (24 mg, quant.). ^{1}H NMR (250 MHz, acetone-[d$_6$]): δ (ppm) = 3.82 (s, 3 H), 8.36−8.20 (m, 6 H), 8.01 (d, 2 H, ^{3}J = 8.8 Hz). ^{13}C NMR (62.5 MHz, acetone-[d$_6$]): δ (ppm) = 56.9, 117.0, 118.1, 123.5, 133.6, 150.4, 158.8, 164.7, 168.2.

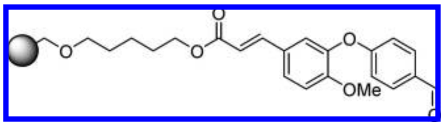


4-(4-Methoxyphenoxy)benzoic acid (57). Resin **26** (453 mg) was treated according to the general procedure (GP4) to give compound **57** (49 mg, quant.). ^{1}H NMR (250 MHz, methanol-[d$_4$]): δ (ppm) = 2.32 (s, 3 H), 3.67 (s, 3 H), 6.73−6.78 (m, 3 H), 6.90−6.89 (m, 2 H), 7.86 (d, 2 H, ^{3}J = 8.9 Hz). ^{13}C NMR (62.5 MHz, methanol-[d$_4$]): δ (ppm) = 21.4, 56.3, 115.2, 116.2, 122.7, 123.4, 126.2, 132.6, 137.7, 142.2, 153.0, 164.0, 170.5. FAB (3NBA) *m/z* (%): 258.3 (67) [M]$^{+}$, 154.4 (100).

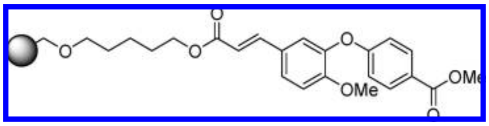


3-Methoxy-4-(4′-methoxyphenoxy)cinnamic acid 5-pentyloxymethylpolystyrene (59). Conversion of resin **12a** was performed according to general procedure (GP5b). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 22.7*, 28.6*, 29.4*, 55.5 (O*C*H$_3$), 55.9 (O*C*H$_3$), 64.3*, 69.9*, 72.7*, 110.9, 114.8, 116.9, 117.7, 120.3, 121.9, 144.2 (*C*HCHCOOR), 149.7, 150.3, 156.0, 166.7 (1 C, *C*OOR). FTIR: ν = 3648 (vw), 3619 (vw), 3510 (w), 3029 (w), 2849 (m), 2338 (m), 2311 (w), 2246 (w), 1944 (w), 1871 (w), 1803 (w), 1717 (w), 1635 (w), 1602 (w), 1506 (w), 1456 (w) cm^{-1}.

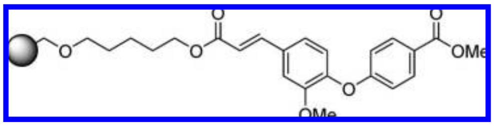
3-(4′-Formylphenoxy)-4-methoxycinnamic acid 5-pentyloxymethylpolystyrene (60). Conversion of resin **12b** was performed according to general procedure (GP5b). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 22.7*, 28.5*, 29.4*, 55.9 (O*C*H$_3$), 64.4*, 69.8*, 72.8*, 112.9, 116.2, 117.1, 121.3, 131.8, 143.1 (*C*HCHCOOR), 145.2, 151.4, 153.1, 162.9 (*C*OOR), 190.6 (*C*HO). FTIR: ν = 3815 (vw), 3648 (w), 3380 (w), 3161 (w), 3031 (s), 2943 (s), 2732 (m), 2632 (w), 2337 (w), 2311 (w), 2215 (w), 1945 (m), 1873 (m), 1803 (m), 1699 (m), 1636 (m), 1605 (m), 1506 (m), 1455 (m) cm^{-1}.



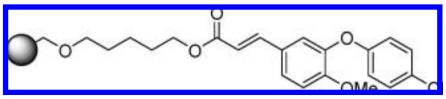
4-Methoxy-3-(4′-methoxycarbonylphenoxy)cinnamic acid 5-pentyloxymethylpolystyrene (61). Conversion of resin **12b** was performed according to general procedure (GP5b). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 22.7*, 28.5*, 29.4*, 51.9 (COO*C*H$_3$), 55.9 (O*C*H$_3$), 64.4*, 69.8*, 72.5*, 112.8, 115.8, 116.9, 121.0, 124.2, 131.5, 143.4 (*C*HCHCOOR), 153.2, 161.5, 166.5. FTIR: ν = 3649 (vw), 3025 (w), 2840 (w), 2602 (w), 2337 (w), 2312 (w), 1945 (w), 1876 (w), 1806 (w), 1732 (w), 1600 (w), 1506 (w), 1455 (w) cm^{-1}.



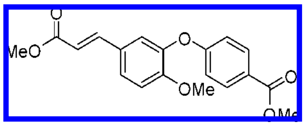
3-Methoxy-4-(4′-methoxycarbonylphenoxy)cinnamic acid 5-pentyloxymethylpolystyrene (62). Conversion of resin **12a** was performed according to general procedure (GP5b). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 22.7*, 28.6*, 29.5*, 51.9 (COO*C*H$_3$), 55.8 (O*C*H$_3$), 64.6*, 69.8*, 72.6*, 111.6, 116.2, 118.1, 121.8, 131.5, 143.7 (*C*HCHCOOR), 151.6, 161.4, 166.4 (*C*OOR). FTIR: ν = 3053 (w), 2839 (w), 2247 (w), 1947 (w), 1807 (w), 1451 (w) cm^{-1}.



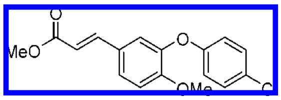
3-(4-Chlorophenoxy)-4-methoxycinnamic acid-5-M-oxypentylester (63). Conversion of resin **12b** was performed according to general procedure (GP5b). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 22.7*, 28.7*, 29.4*, 56.1 (O*C*H$_3$), 64.4*, 69.9*, 72.7*, 112.7, 116.9, 118.4, 119.8, 129.6, 143.5 (*C*HCHCOOR), 152.9, 156.1, 169.8 (*C*OOR). FTIR: ν = 3648 (vw), 3061 (w), 2603 (w), 2337 (vw), 2311 (vw), 2046 (vw), 1945 (w), 1874 (w), 1805 (w), 1701 (w), 1636 (w), 1600 (w), 1513 (w), 1367 (w) cm^{-1}.



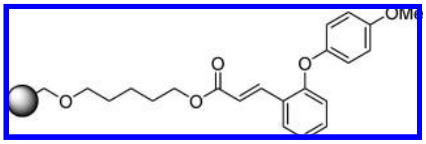
(*E*)-Methyl 4-(2-methoxy-5-(3-methoxy-3-oxoprop-1-enyl)phenoxy)benzoate (66). Resin **61** (315 mg) was treated according to the general procedure (GP3) to give compound **66** (48 mg, 63%). ^{1}H NMR (250 MHz, CDCl$_3$): δ (ppm) = 3.78 (s, 3 H), 3.83 (s, 3 H), 3.89 (s, 3 H), 6.27 (d, 1 H, ^{3}J = 16.0 Hz), 6.92 (d, 1 H, ^{3}J = 9.0 Hz), 7.02 (d, 1 H, ^{3}J = 8.5 Hz), 7.27 (bs, 1 H), 7.33 (dd, 1 H, ^{3}J = 8.5 Hz, ^{4}J = 2.1 Hz), 7.56 (d, 1 H, ^{3}J = 16.0 Hz), 7.95 (d, 1 H, ^{3}J = 9.0 Hz). ^{13}C NMR (63.5 MHz, CDCl$_3$): δ (ppm) = 51.7, 52.0, 56.0, 112.9, 115.9, 116.5, 121.0, 124.3, 126.7, 128.0, 131.6, 143.6, 143.8, 153.4, 161.7, 166.6, 167.4. EI-MS (GC-MS, 120 °C) *m*/*z* (%): 342 (100) [M]$^{+}$, 311 (25), 268 (9), 160 (17).



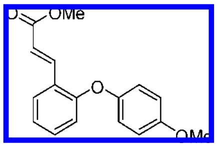
(*E*)-Methyl 3-(3-(4-chlorophenoxy)-4-methoxyphenyl)-acrylate (68). Resin **63** (330 mg) was treated according to the general procedure (GP3) to give compound **68** (37 mg, 49%). ^{1}H NMR (250 MHz, CDCl$_3$): δ (ppm) = 3.74 (s, 3 H), 3.82 (s, 3 H), 6.20 (d, 1 H, ^{3}J = 16.0 Hz), 6.84 (d, 2 H, ^{3}J = 9.0 Hz), 6.95 (d, 1 H, ^{3}J = 8.5 Hz), 7.11 (d, 1 H, ^{4}J = 2.1), 7.19−7.30 (m, 3 H), 7.54 (d, 1 H, ^{3}J = 16.0 Hz). ^{13}C NMR (63.5 MHz, CDCl$_3$): δ (ppm) = 51.6, 56.1, 112.7, 116.4, 118.5, 119.7, 125.9, 127.8, 129.6, 143.7, 145.0, 153.1, 156.1, 167.4.



2-(4-Methoxy-phenoxy)cinnamic acid-5-pentyloxymethylpolystyrene (69). Conversion of resin **12c** was performed according to general procedure (GP5b). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 22.6*, 28.5*, 29.3*, 55.5 (O*C*H$_3$), 64.4*, 69.8*, 72.7*, 114.9 (C-3′), 117.2, 119.3, 120.7 (C-2′), 122.6, 131.2, 139.3 (*C*HCHCOOR), 149.5, 156.0, 157.1, 167.3 (*C*OOR). - FTIR: ν = 3648 (vw), 3035 (w), 2338 (w), 2312 (w), 1947 (w), 1874 (w), 1803 (w), 1633 (w), 1454 (w) cm^{-1}.

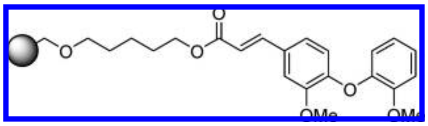


(*E*)-Methyl 3-(2-(4-methoxyphenoxy)phenyl)acrylate (70). Resin **69** (220 mg) was treated according to the general procedure (GP3) to give compound **70** (14 mg, 30%) starting from Merrifield resin. ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) = 3.79 (s, 3 H), 3.81 (s, 3 H), 6.58 (d, 1 H, ^{3}J = 16.2 Hz), 6.76 (d, 1 H, ^{3}J = 8.2 Hz), 6.89 (d, 2 H, ^{3}J = 9.1 Hz), 6.97 (d, 2 H, ^{3}J = 9.1 Hz), 7.06 (t, 1 H, ^{3}J = 7.5 Hz), 7.60 (dd,

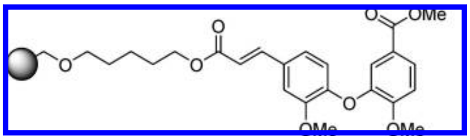


1 H, $^3J = 7.8$ Hz, $^4J = 1.4$ Hz), 8.07 (d, 1 H, $^3J = 16.2$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 51.6, 55.7, 115.0, 117.25, 119.0, 120.9, 122.7, 125.0, 128.6, 131.3, 139.6, 149.66, 156.2, 157.3, 167.7. FTIR (KBr): ν = 3450 (vw), 2922 (w), 2852 (w), 2388 (vw), 2348 (vw), 2285 (vw), 1723 (w), 1711 (w), 1690 (w), 1658 (w), 1641 (w), 1630 (w) cm^{-1}. EI-MS (GC-MS, 80 °C) *m/z* (%): 284 (51) [M]$^+$, 252 (100).

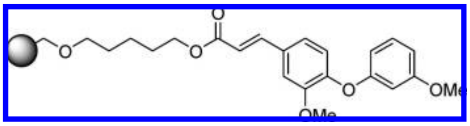
3-Methoxy-4-(2-methoxyphenoxy)cinnamic acid-5-pentyloxymethylpolystyrene (71). Conversion of resin **12a** was performed according to general procedure (GP5b). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.7*, 28.6*, 29.4*, 55.8 (OCH_3), 64.5*, 69.9*, 72.6*, 110.9, 112.7, 116.8, 120.5, 121.8, 144.5 (*C*HCHCOOR).



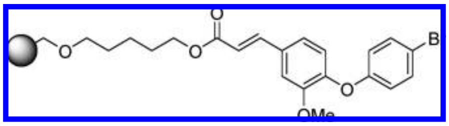
3-Methoxy-4-(2′-methoxy-5′-methoxycarbonylphenoxy)-cinnamic acid-5-pentyloxymethylpoly styrene (72). Conversion of resin **12a** was performed according to general procedure (GP5b). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.6*, 28.7*, 29.5*, 51.9 (COOCH_3), 55.9 (OCH_3), 64.3*, 69.9*, 72.7*, 111.6, 117.1, 166.2 (*C*OOCH_3). FTIR: ν = 3647 (vw), 3515 (w), 3056 (m), 2848 (m), 2600 (w), 2336 (w), 1943 (w), 1872 (w), 1802 (w), 1693 (w), 1602 (w), 1503 (w) cm^{-1}.



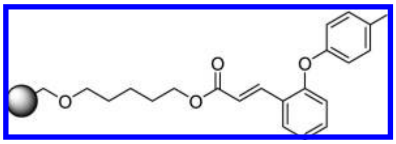
3-Methoxy-4-(3′-methoxyphenoxy)cinnamic acid-5-pentyloxymethylpolystyrene (73). Conversion of resin **12a** was performed according to general procedure (GP5b). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 2.7*, 28.6*, 29.4*, 55.9 (OCH_3), 64.4*, 69.8*, 72.6*, 104.1, 108.9, 110.1, 111.3, 117.4, 120.1, 121.8, 130.0, 144.1 (*C*HCHCOOR), 151.2, 158.1, 160.9, 167.1 (*C*OOR). FTIR: ν = 3649 (vw), 3620 (vw), 3028 (w), 2863 (w), 2632 (w), 2338 (w), 2247 (w), 1945 (w), 1873 (w), 1804 (w), 1698 (w), 1637 (w), 1506 (w) cm^{-1}.



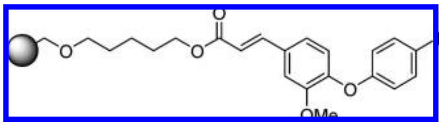
4-(4′-Bromophenoxy)-3-methoxycinnamic acid-5-pentyloxymethylpolystyrene (76). Conversion of resin **12a** was performed according to general procedure (GP5b). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.7*, 28.6*, 29.4*, 55.9 (OCH_3), 64.5*, 69.8*, 72.8*, 111.4, 115.5, 117.7, 119.3, 120.4, 121.7, 132.5, 143.8 (*C*HCHCOOR), 151.2, 156.31, 167.1 (*C*OOR). FTIR: ν = 3649 (vw), 3620 (vw), 3163 (vw), 3057 (w), 2843 (w), 2631 (w), 2337 (vw), 2311 (vw), 2061 (vw), 1944 (w), 1875 (w), 1804 (w), 1717 (w), 1637 (w), 1601 (w), 1505 (w) cm^{-1}.



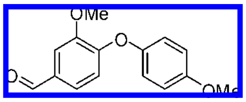
2-(4′-Iodphenoxy)cinnamic acid-5-pentyloxymethylpolystyrene (77). Conversion of resin **12c** was performed according to general procedure (GP5b). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.7*, 28.5*, 29.4*, 64.5*, 69.9*, 72.8*, 119.2, 119.2, 119.8, 124.0, 126.1, 131.3, 138.7, 155.1, 156.9, 166.9 (*C*OOR). FTIR: ν = 3649 (vw), 3032 (w), 2843 (w), 2337 (w), 1945 (w), 1877 (w), 1802 (w), 1717 (w), 1635 (w), 1601 (w), 1456 (w), 1354 (w) cm^{-1}.



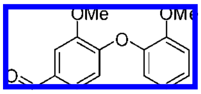
4-(4′-Iodphenoxy)-3-methoxycinnamic acid-5-pentyloxymethylpolystyrene (78). Conversion of resin **12a** was performed according to general procedure (GP5b). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.7*, 28.5*, 29.4*, 55.9 (OCH_3), 64.5*, 69.8*, 72.8*, 85.7, 111.4, 117.7, 119.7, 120.6, 121.7, 138.7, 143.8 (*C*HCHCOOR), 151.2, 157.2, 167.0 (*C*OOR). FTIR: ν = 3648 (w), 3620 (vw), 3033 (m), 2941 (m), 2631 (w), 2337 (w), 2312 (w), 2061 (vw), 1944 (m), 1874 (m), 1803 (m), 1719 (m), 1682 (m), 1638 (m), 1601 (m), 1507 (m) cm^{-1}.



3-Methoxy-4-(4-methoxyphenoxy)benzaldehyde (80). Resin **59** (355 mg) was treated according to the general procedure (GP6) to give compound **80** (24 mg, 36%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.82 (s, 3 H), 3.99 (s, 3 H), 6.80 (d, 1 H, $^3J = 8.2$ Hz), 6.92 (d, 2 H, $^3J = 9.1$ Hz), 7.03 (d, 2 H, $^3J = 9.1$ Hz), 7.35 (dd, 1 H, $^3J = 8.2$ Hz, $^3J = 1.5$ Hz), 7.51 (d, 1 H, $^4J = 1.5$ Hz), 9.88 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 55.6, 56.1, 110.3, 115.0, 115.8, 121.3, 125.9, 131.5, 148.6, 150.3, 153.6, 156.7, 190.9. EI-MS (GC-MS, 120 °C) *m/z* (%): 258 (100) [M]$^+$, 243 (21).

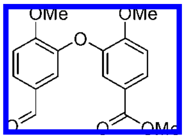


3-Methoxy-4-(2-methoxyphenoxy)benzaldehyde (81). Resin **71** (368 mg) was treated according to the general procedure (GP6) to give compound **81** (30 mg, 44%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.79 (s, 3H), 3.99 (s, 3H), 6.69 (d, 1 H, $^3J = 8.2$ Hz), 6.88−6.96 (m, 2 H), 7.00 (dd, 1H, $^3J = 7.9$ Hz), 7.14 (m, 1H), 7.26 (dd, 1 H, $^3J = 8.2$

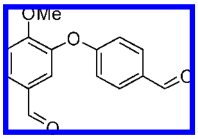


Hz, ^4J =1.8 Hz), 7.44 (d, 1 H, ^4J = 1.9 Hz), 9.86 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 55.8, 56.1, 110.3, 112.8, 115.0, 121.2, 121.9, 125.9, 126.1, 131.4, 143.2, 149.9, 151.3, 153.0, 190.9. - EI-MS (GC-MS, 120 °C) *m/z* (%): 258 (100) $[M]^+$, 212 (28), 184 (11).

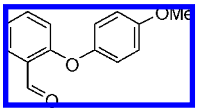
3-(5-Formyl-2-methoxy-phenoxy)-4-methoxy-benzoic acid methyl ester (82). Resin **72** (336 mg) was treated according to the general procedure (GP6) to give compound **82** (24 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.87 (s, 3 H), 3.93 (s, 3 H), 3.99 (s, 3 H), 6.75 (d, 1H, ^3J = 8.2 Hz), 7.04 (d, 1H, ^3J = 8.7 Hz), 7.35 (dd, 1H, ^3J = 8.2, ^4J = 1.5 Hz), 7.44 (d, 1H, ^3J = 1.5 Hz), 7.71 (d, 1H, ^4J = 1.9 Hz), 7.93 (dd, 1H, ^3J = 8.7, ^4J = 1.9 Hz), 9.89 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 52.3, 56.2, 56.3, 110.4, 111.9, 115.7, 122.5, 128.0, 132.0, 166.3, 190.9. FTIR (KBr): ν = 2924 (m), 2851 (m), 1718 (m), 1687 (m), 1593 (m), 1510 (m), 1464 (m), 1438 (m), 1423 (m), 1393 (m), 1267 (m) cm^{-1}. EI-MS (70 eV, 130 °C) *m/z* (%): 316 (100) $[M]^+$, 285 (26), 165 (28). HRMS ($C_{17}H_{16}O_6$): calcd 316.0949, found 316.0947.



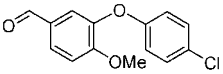
3-(4-Formylphenoxy)-4-methoxybenzaldehyde (85). Resin **60** (370 mg) was treated according to the general procedure (GP6) to give compound **85** (30 mg, 44%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.90 (s, 3 H), 7.01 (d, 2 H, ^3J = 8.7 Hz), 7.16 (d, 1 H, ^3J = 8.4 Hz), 7.63 (d, 1H, ^4J = 2.0 Hz), 7.79 (dd, 1H, ^3J = 8.4, ^4J = 2.0 Hz), 7.85 (d, 2 H, ^3J = 8.7 Hz), 9.88 (s, 1 H), 9.92 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 56.3, 112.5, 116.6, 122.3, 129.5, 130.4, 131.5, 132.0, 143.8, 156.8, 162.6, 190.0, 190.7. EI-MS (GC-MS, 120 °C) *m/z* (%): 256 (100) $[M]^+$, 127 (14).



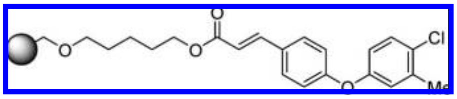
2-(4-Methoxyphenoxy)benzaldehyde (86). Resin **75** (382 mg) was treated according to the general procedure (GP6) to give compound **86** (28 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.83 (s, 3 H), 6.80 (d, 1 H, ^3J = 8.7 Hz), 6.93 (d, 2 H, ^3J = 9.1 Hz), 7.03 (d, 2 H, ^3J = 9.1 Hz), 7.12 (dd, 1 H, ^3J = 7.6 Hz, ^3J = 7.4 Hz), 7.46 (ddd, 1 H, ^3J = 8.7 Hz, ^3J = 7.4, ^4J = 1.8 Hz), 7.91 (dd, 1 H, ^3J = 7.6 Hz, ^4J = 1.8 Hz), 10.57 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 55.7, 115.1, 116.9, 121.2, 122.5, 126.1, 128.3, 135.7, 149.1, 156.6, 161.1, 189.6. FTIR (KBr): ν = 3449 (vw), 3076 (vw), 2922 (vw), 2852 (vw), 1742 (vw), 1688 (vw), 1655 (vw), 1599 (vw), 1505 (vw), 1475 (vw), 1456 (vw) cm^{-1}. EI-MS (70 eV, 80 °C) *m/z* (%): 228 (11) $[M]^+$, 108 (100). HRMS ($C_{14}H_{12}O_3$): calcd 228.0786, found 228.0784.



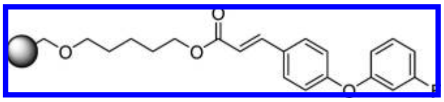
3-(4-Chlorophenoxy)-4-methoxybenzaldehyde (90). Resin **68** (308 mg) was treated according to the general procedure (GP6) to give compound **90** (38 mg, 65%). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 3.94 (s, 3 H), 6.90 (d, 2 H, ^3J = 9.0 Hz), 7.11 (d, 1 H, ^3J = 8.4 Hz), 7.29 (d, 2 H, ^3J = 9.0 Hz), 7.46 (d, 1 H, ^4J = 2.0 Hz), 7.68 (dd, 1 H, ^3J = 8.4 Hz, ^4J = 2.0 Hz), 9.83 (s, 1 H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 56.3, 112.1, 119.1, 119.8, 128.5, 128.5, 129.8, 130.2, 145.8, 155.5, 156.3, 190.2. EI-MS (GC-MS, 120 °C) *m/z* (%): 262/264 (100/35) $[M]^+$, 212 (30), 184 (10).



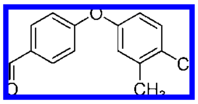
4-(4-Chlor-3-methylphenoxy)cinnamic acid-5-pentyloxymethylpolystyrene (92). Conversion of resin **12d** was performed according to general procedure (GP5c). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.2 (CH_3), 22.7*, 28.6*, 29.4*, 64.5*, 69.8*, 72.7*, 117.0, 118.9, 121.9, 129.7, 130.1, 137.8, 143.1 (*C*HCHCOOR), 154.5, 159.2, 166.8 (*C*OOR). FTIR: ν = 3647 (vw), 3054 (w), 2338 (w), 2247 (w), 1946 (w), 1877 (w), 1806 (w), 1745 (w), 1452 (m) cm^{-1}.



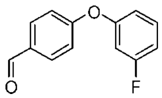
4-(3-Fluorophenoxy)cinnamic acid-5-pentyloxymethylpolystyrene (93). Conversion of resin **12d** was performed according to general procedure (GP5c). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.8*, 28.6*, 29.4*, 64.4*, 69.9*, 72.7*, 106.9 (d, ^2J = 24.1 Hz), 110.7 (d, ^2J = 17.9 Hz), 114.7 (CH*C*HCOOR), 117.3, 119.0, 129.8, 130.6, 145.6 (*C*HCHCOOR), 157.4, 163.6 (d, ^1J = 253.4 Hz), 167.1 (*C*OOR). FTIR: ν = 3039 (w), 2338 (w), 2249 (w), 1947 (w), 1876 (w), 1746 (w), 1455 (m) cm^{-1}.



4-(4-Chloro-3-methylphenoxy)benzaldehyde (94). Resin **92** (321 mg) was treated according to the general procedure (GP6) to give compound **94** (25 mg, 43%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 2.37 (s, 3 H), 6.86 (dd, 1 H, ^3J = 8.6 Hz, ^4J = 2.8 Hz), 6.96 (d, 1 H, ^4J = 2.8 Hz), 7.04 (d, 1 H, ^3J = 8.6 Hz), 7.35 (d, 2 H, ^3J = 8.6 Hz), 7.85 (d, 2 H, ^3J = 8.6 Hz), 9.92 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 14.2, 117.5, 119.0, 122.7, 130.3, 130.4, 131.4, 132.0, 138.2, 153.5, 162.9, 190.7. EI-MS (GC-MS, 120 °C) *m/z* (%): 246 (100) $[M]^+$, 182 (18), 153 (10).

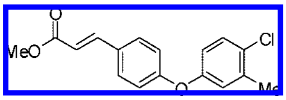


4-(3-Fluorophenoxy)benzaldehyde (95). Resin **93** (322 mg) was treated according to the general procedure (GP6)

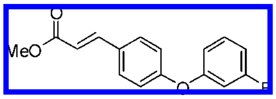


to give compound **95** (28 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.97−6.76 (m, 3 H), 7.09 (d, 2 H, ^3J = 8.6 Hz), 7.39−7.33 (m, 1 H), 7.87 (d, 2 H, ^3J = 8.6 Hz), 9.94 (s, 1 H, C*H*O). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 107.9 (d, ^2J = 24.1 Hz), 111.7 (d, ^2J = 21.2 Hz), 115.6 (d, ^4J = 3.3 Hz), 118.1 130.9 (d, ^3J = 9.8 Hz), 132.0, 156.5 (d, ^3J = 10.6 Hz), 162.2, 163.5 (d, ^1J = 248.2 Hz), 190.7. EI-MS (GC-MS, 120 °C) *m*/*z* (%): 215 (100) [M]$^+$, 159 (26), 133 (14). HRMS ($C_{13}H_9FO_2$): calcd 216.0587, found 216.0586.

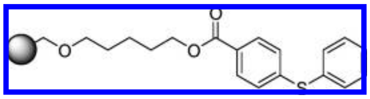
(*E*)-Methyl 3-(4-(4-chloro-3-methylphenoxy)phenyl)acrylate (96). Resin **92** (315 mg) was treated according to the general procedure (GP3) to give compound **96** (49 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.35 (s, 3 H), 3.80 (s, 3 H), 6.35 (d, 1 H, ^3J = 16.0 Hz), 6.82 (dd, 1 H, ^3J = 8.6 Hz, d, 2H, ^4J = 2.9 Hz), 6.92 (d, 1 H, ^4J = 2.9 Hz), 6.96 (d, 2 H, ^3J = 8.7 Hz), 7.31 (d, 1 H, ^3J = 8.6 Hz), 7.49 (d, 2 H, ^3J = 8.7 Hz), 7.66 (d, 1 H, ^3J = 16.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 20.2, 51.7, 116.6, 118.3, 118.4, 122.0, 129.4, 129.4, 129.8, 130.2, 137.9, 144.0, 154.5, 159.2, 167.5. EI-MS (GC-MS, 120 °C) *m*/*z* (%): 302/304 (100/36) [M]$^+$, 271/273 (58/19), 244 (13).



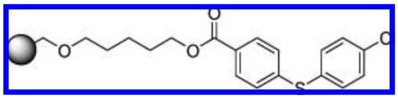
(*E*)-Methyl 3-(4-(3-fluorophenoxy)phenyl)acrylate (97). Resin **93** (321 mg) was treated according to the general procedure (GP3) to give compound **97** (65 mg, quant.). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.80 (s, 3 H), 6.37 (d, 1 H, ^3J = 16.0 Hz), 6.65−6.66 (m, 1 H), 6.73−6.80 (m, 1 H), 7.01 (d, 2 H, ^3J = 8.6 Hz), 7.30 (m, 1 H), 7.51 (d, 2 H, ^3J = 8.6 Hz), 7.64 (d, 1 H, ^3J = 16.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 51.7, 106.9 (^2J = 24.2 Hz), 110.7 (^2J = 21.2 Hz), 114.7 (^4J = 3.0 Hz), 116.9, 119.1, 130.6, 130.7 (^3J = 9.7 Hz), 143.9, 157.7 (^3J = 10.9 Hz), 158.4, 163.5 (^1J = 247.5 Hz), 167.4. EI-MS (GC-MS, 120 °C) *m*/*z* (%): 272 (100) [M]$^+$, 241 (87), 213 (16).



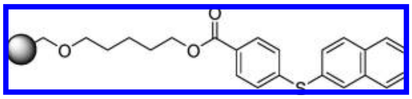
4-Phenylsulfanylbenzoic acid-5-pentyloxymethylpolystyrene (98). Conversion of resin **7a** was performed according to general procedure (GP5d). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.8*, 28.5*, 29.4*, 64.9*, 69.9*, 72.8*, 128.5, 129.6, 130.0, 132.4, 133.5, 144.1, 166.0 (1 C, *C*OOR). FTIR: ν = 3413 (vw), 3163 (vw), 3062 (w), 3031 (w), 2947 (w), 2849 (w), 2632 (vw), 2603 (vw), 2337 (vw), 2312 (vw), 2253 (vw), 1944 (w), 1875 (w), 1805 (w), 1724 (w), 1601 (w), 1544 (vw), 1494 (vw) cm^{-1}.



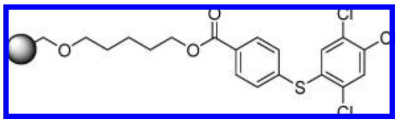
4-(4′-Chlorophenylsulfanyl)benzoic acid-5-pentyloxymethylpolystyrene (99). Conversion of resin **7a** was performed according to general procedure (GP5d). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.8*, 28.5*, 29.4*, 64.9*, 69.8*, 72.8*, 129.7, 130.1, 131.2, 133.52, 134.5, 143.4, 165.7 (*C*OOR).



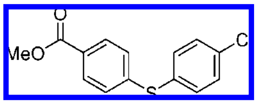
4-(Naphthalen-2′-ylsulfanyl)benzoic acid-5-M-oxypentylester (100). Conversion of resin **7a** was performed according to general procedure (GP5d). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.8*, 28.5*, 29.4*, 64.9*, 69.8*, 72.7*, 126.8, 129.3, 130.1 (C-2), 132.9, 133.7, 144.0, 166.2 (*C*OOR). FTIR: ν = 3419 (w), 3057 (w), 3027 (w), 2909 (w), 2849 (w), 2602 (vw), 2337 (vw), 2310 (vw), 1943 (w), 1873 (w), 1803 (w), 1722 (w), 1679 (w), 1601 (w), 1491 (w) cm^{-1}.



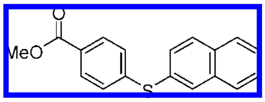
4-Phenylsulfanylbenzoic acid-5-pentyloxymethylpolystyrene (101). Conversion of resin **7a** was performed according to general procedure (GP5d). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.8*, 28.5*, 29.4*, 65.2*, 69.85*, 72.8*, 125.5, 130.6, 131.1, 131.7, 132.3, 132.9, 133.9, 138.7, 165.8 (*C*OOR). FTIR: ν = 3437 (w), 3057 (m), 3028 (m), 2939 (m), 2603 (w), 2338 (w), 2310 (w), 1943 (m), 1871 (m), 1802 (m), 1711 (m), 1679 (m), 1600 (m), 1452 (s) cm^{-1}.



Methyl 4-(4-chlorophenylthio)benzoate (103). Resin **99** (336 mg) was treated according to the general procedure (GP3) to give compound **103** (39 mg, quant.). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.21 (d, *J* = 8.6 Hz), 3.90 (s, 1 H) 7.34−7.42 (m, 4 H), 7.91 (d, 2 H, *J* = 8.6 Hz). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 52.1, 127.9, 129.8, 130.2, 131.2, 134.7, 134.8, 143.5, 166.6. FTIR (KBr) ν = 3420 (w), 3083 (w), 3007 (w), 2957 (w), 2926 (w), 2854 (w), 2566 (w), 2396 (vw), 1944 (w), 1908 (w), 1723 (m), 1595 (m), 1563 (m), 1475 (m), 1288 (m) cm^{-1}. EI-MS (70 eV, 80 °C) *m*/*z* (%): 278/230 (100/39) [M]$^+$, 247/249 (76/29), 184 (32). HRMS ($C_{14}H_{11}S^{35}ClO_2$): calcd 278.0168, found 278.0171.

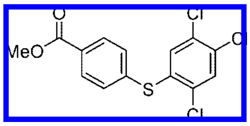


Methyl 4-(naphthalen-2-ylthio)benzoate (104). Resin **100** (210 mg) was treated according to the general procedure (GP3) to give compound **104** (18 mg, 71%). ^{1}H NMR (400

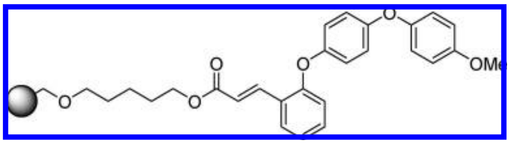


MHz, CDCl$_3$): δ (ppm) = 3.81 (s, 3 H), 7.16 (bd, 2 H, ^3J = 8.6 Hz), 7.39−7.46 (m, 3 H), 7.71−7.83 (m, 3 H), 7.82 (bd, 2 H, ^3J = 8.6 Hz), 7.95 (bs, 1 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 52.1, 126.8, 126.9, 127.5, 127.7, 127.8, 129.4, 129.6, 130.1, 130.3, 132.9, 133.1, 133.8, 144.2, 166.7.

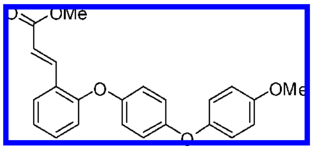
Methyl 4-(2,4,5-trichlorophenylthio)benzoate (105). Resin **101** (310 mg) was treated according to the general procedure (GP3) to give compound **105** (37 mg, 86%). ^{1}H NMR (250 MHz, CDCl$_3$): δ (ppm) = 3.92 (s, 3 H), 7.28 (s, 1 H), 7.35 (bd, 2 H, ^3J = 8.3 Hz), 7.56 (s, 1 H), 8.01 (bd, 2 H, ^3J = 8.3 Hz). ^{13}C NMR (62.5 MHz, CDCl$_3$): δ (ppm) = 52.3, 129.5, 130.6, 130.7, 131.2, 131.8, 132.5, 133.1, 134.0, 134.1, 139.0, 166.4. EI-MS (GC-MS, 120 °C) *m*/*z* (%): 346/348/350 (100/100/36) [M]$^+$, 315/317/319 (95/95/34), 252/254 (69/48).



2-[4-(4′-Methoxyphenoxy)phenoxy]cinnamic acid-5-pentyloxymethylpolystyrene (107). Conversion of resin **77**was performed according to general procedure (GP5a). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 22.7*, 28.5*, 29.4*, 55.5 (OCH$_3$), 64.4*, 69.8*, 72.6*, 114.8, 119.0, 119.5, 120.5, 123.1, 125.4, 131.1, 139.2 (1 C, CHCHCOOR), 150.4, 151.5, 155.5, 155.7, 156.7, 167.7 (1 C, COOR). FTIR: ν = 3648 (vw), 3412 (vw), 3162 (vw), 3058 (w), 3027 (w), 2849 (w), 2632 (w), 2602 (vw), 2337 (vw), 2311 (vw), 2256 (vw), 1944 (w), 1873 (w), 1803 (w), 1718 (w), 1634 (w), 1602 (w), 1456 (m) cm^{-1}.



(*E*)-Methyl 3-(2-(4-(4-methoxyphenoxy)phenoxy)phenyl)acrylate (108). Resin **107** (100 mg) was treated according to the general procedure (GP3) to give compound **97** (12 mg, 46%) starting from Merrifield resin after purification by thin layer chromatography (hexane/ethyl acetate; 5:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 3.73 (s, 3 H), 3.74 (s, 3 H), 6.50 (d, 1 H, ^3J = 16.2 Hz), 6.76 (dd, 1H, ^3J = 8.3 Hz, ^4J = 1.0 Hz), 6.82 (d, 2 H, ^3J = 9.1 Hz), 6.87−6.90 (m, 4 H), 6.92 (d, 2 H, ^3J = 9.1 Hz), 7.00−7.04 (m, 1 H), 7.20−7.24 (m, 1 H), 7.54 (dd, 1 H, ^3J = 7.8, ^4J = 1.6 Hz), 7.98 (d, 1H, ^3J = 16.2 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 51.7, 55.7, 114.9, 117.8, 119.1, 120.4, 120.6, 123.1, 125.3, 128.6, 131.4, 139.5, 150.5, 151.4, 154.5, 155.8, 156.7, 167.6. FTIR (KBr): ν = 3044 (vw), 3000 (vw), 2950 (w), 2863 (w), 1718 (m), 1634 (w), 1600 (w), 1578 (w), 1495 (m), 1454 (m), 1322 (w), 1219 (m) cm^{-1}. EI-MS (70 eV, 140 °C) *m*/*z* (%): 376 (29) [M]$^+$, 344 (14), 303 (14), 215 (17), 165 (31), 161 (100), 123 (27). HRMS (C$_{23}$H$_{20}$O$_5$): calcd 376.1311, found 376.1314.



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Supporting Information Available. ^{1}H NMR and ^{13}C NMR spectra of synthesized compounds, those library members that were characterized additionally by NMR techniques, and ^{13}C-Gel-NMR spectra of all resins. This material is available free of charge via the Internet at http://pubs.acs.org.

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