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Nitrogen Functionalities in Palladium-Catalyzed Reactions on Solid Supports: A Case Study

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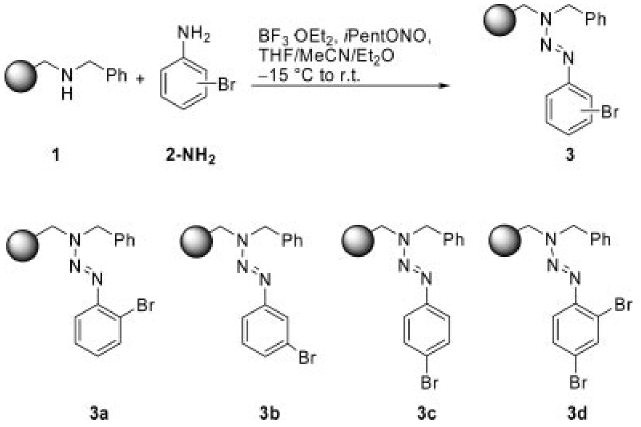
Three different Palladium-catalyzed reactions (Heck, Suzuki, Sonogashira) were carried out on three different types of linkers on solid supports.

Introduction

Modern metal-catalyzed reactions play a pivotal role in the synthesis of complex molecular architectures since they show in general a broad functional group tolerance.[1] In particular, palladium-mediated processes are valuable techniques in combination with solid phase synthesis for achieving molecular diversity.[2] However, although both the palladium-chemistry and solid phase synthesis methodologies seem to be mature and well established, the combination of both is met with varied success. In particular, the variation of reaction types and linkers has to be predictable in order to execute large library syntheses.

In this article, different palladium-mediated reactions on different solid-supported substrates are compared to achieve a better understanding of the influence of reaction types, linker types, and substrates. The main goal is to investigate the interaction of nitrogen functionalities with palladium-catalyzed processes. For this purpose, four different anilines, **2**, were immobilized via a diazotization reaction onto benzylamine resin **1**, which was prepared in a one-step reaction from Merrifield resin (Scheme 1).[3] The triazene resins were originally designed by the Moore group using a propylamine resin,[3f] later optimized by us[3a–3d] and also used by others with success.[3e]

For purposes of comparison, a 3-bromo-4-aminobenzoic ester resin, **7** (Scheme 2), was synthesized starting with Merrifield resin (**4**). In the first step, *p*-aminobenzoic acid (**5**) was immobilized onto the solid support under basic conditions. Then the product underwent bromination via an aromatic substitution with *N*-bromsuccinimide. The efficiency of this reaction was determined by cleavage of the resin **7** with the nucleophilic base sodium methoxide to obtain methyl 3-bromo-4-aminobenzoate (**8**) in high yields (> 90%) and purities (> 95%). The bromination reaction of the corresponding carboxyaniline in solution phase was less selective, and the purification of the product was difficult due to the formation of the of the amino acid zwitterion.



Scheme 1. Synthesis of the triazene resins **3** for comparison of the palladium-mediated reactions.

Efforts to conduct a clean bromination in solution prior to immobilization were difficult, because by-products such as the di- and tribrominated aminobenzoic acids were obtained. These products can not be effectively removed by column chromatography or distillation.

The amine resin **7** was converted into the triazene **11** to prove that the different reactivities depend on the amino or triazene moiety and not on the linker system.

The immobilized product was treated with isoamyl nitrite and borontrifluoride–diethyl ether to yield the diazonium salt **9**. The latter reacted in situ with diethylamine (**10**) to yield the triazene resin **11** with a loading of 0.5 mmol/g (Scheme 3).

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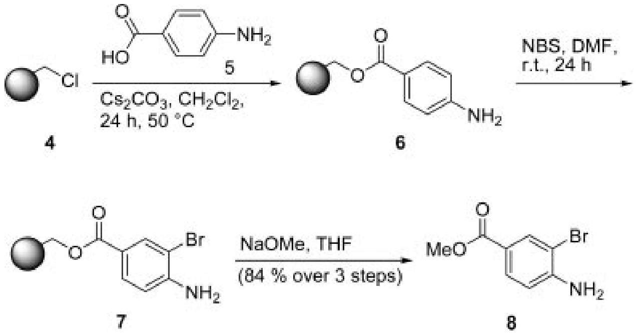
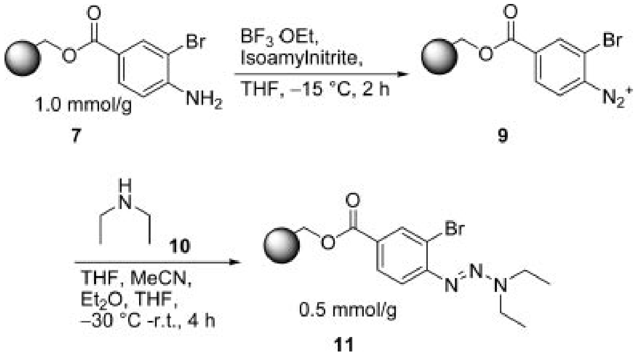


Scheme 2. Synthesis of the 3-bromo-4-aminobenzoic ester resin **7**.



Scheme 3. Synthesis of the ester-bound triazene resin **11**.

Heck Reactions of the (Bromophenyl)triazene Resins

For this work, the differently substituted triazene resins **3a**–**d** were treated with four different alkenes, **12**–**15**, under standard Heck conditions[4] (105 °C, 24 h).[5] During the reaction, the color of the resins changed from orange–light brown to dark brown approaching black (Scheme 4).[6]

The resins were cleaved with trifluoroacetic acid and trimethylsilyl azide[7] to yield the azides **20a**–**23d**. The results are listed in Table 1. To cleave the dibrominated resin **3d**, the amounts of all reagents were doubled. In this case, the mono- and disubstituted products were found. The products were separated by column chromatography and are listed separately in Table 1.

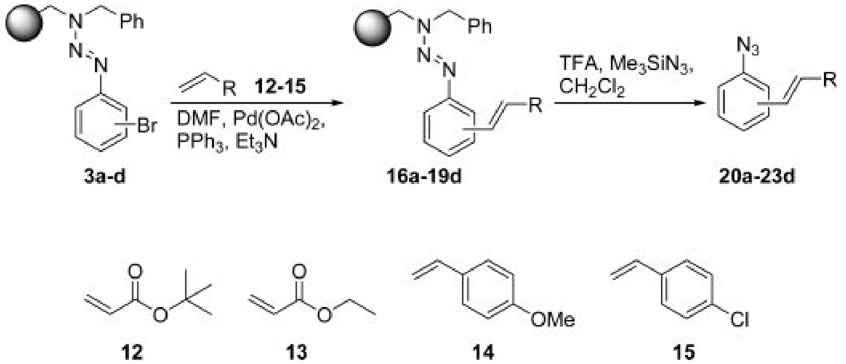
With all the patterns of substitution, the Heck reaction generated the products in moderate to good yields. The purities of all products were higher than 95%. In the case of the dibrominated resin, the *p*-monosubstituted product was always obtained together with the disubstituted product. This could be confirmed in 2D NMR studies. With these results in hand, the conclusion was made that the Heck reaction works for every linker we used therein. However, at this stage it should be pointed out that although the Heck reaction on resin **3** yielded the products in good purities, the yields are still to be improved. An explanation is a premature cleavage of the N–N bond during the Heck reaction leading to a diminished loading, preserving a high conversion to the correct product. This effect has been observed in other cases using triazenes as substrates for cross-coupling reactions, with and without activation,[8] and also with other linkers.[2] However, because the purity of the products remains high after cleavage, this method is still applicable to combinatorial synthesis of compound libraries.

Heck Reaction on the 3-Bromo-4-aminobenzoic Ester Resin

The Heck reaction was performed on the aminobenzoic resin **7** under the same conditions as for the triazene resin [DMF, $Pd(OAc)_2$, PPh_3, Et_3N]. In this case, the starting material was isolated. Even variations of the reaction temperature, reaction time, and the use of different alkenes were not successful. An explanation for these effects could be a coupling of the palladium atom and the amine. However, the reports in relevant literature of successful coupling of *o*-haloanilines show that this might be applicable in all cases.[9]

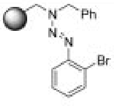
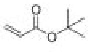
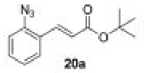
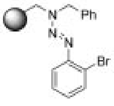
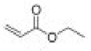
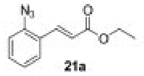
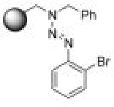
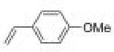
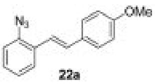
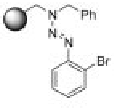
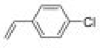
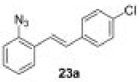
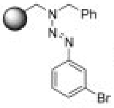
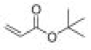
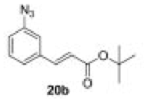
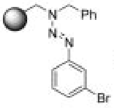
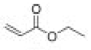
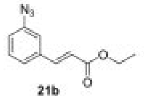
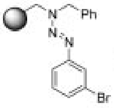
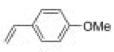
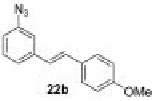
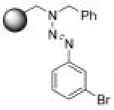
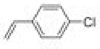
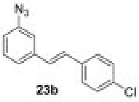
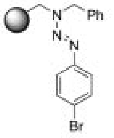
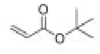
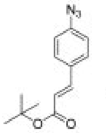
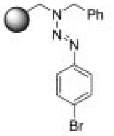
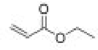
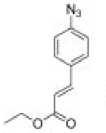
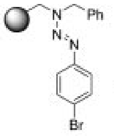
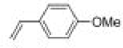
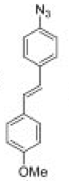
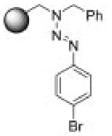
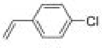
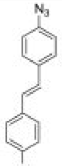
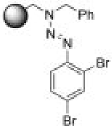
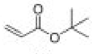
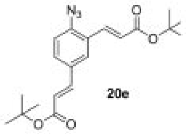
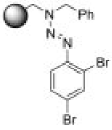
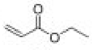
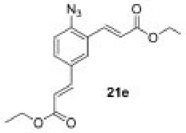
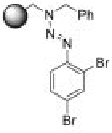
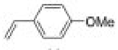
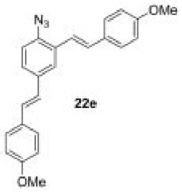
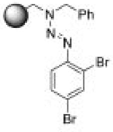
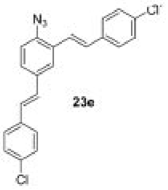
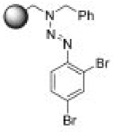
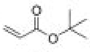
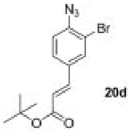
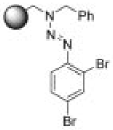
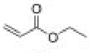
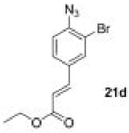
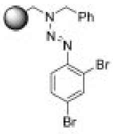
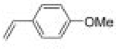
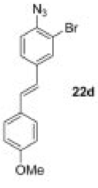
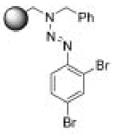
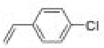
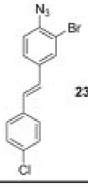
Heck Reaction on the 3-Bromo-4-triazenylbenzoic Ester Resin

The Heck reaction was then carried out on the ester-bound triazene resin using ethyl acrylate (**13**) under the conditions described below. The reaction is shown in

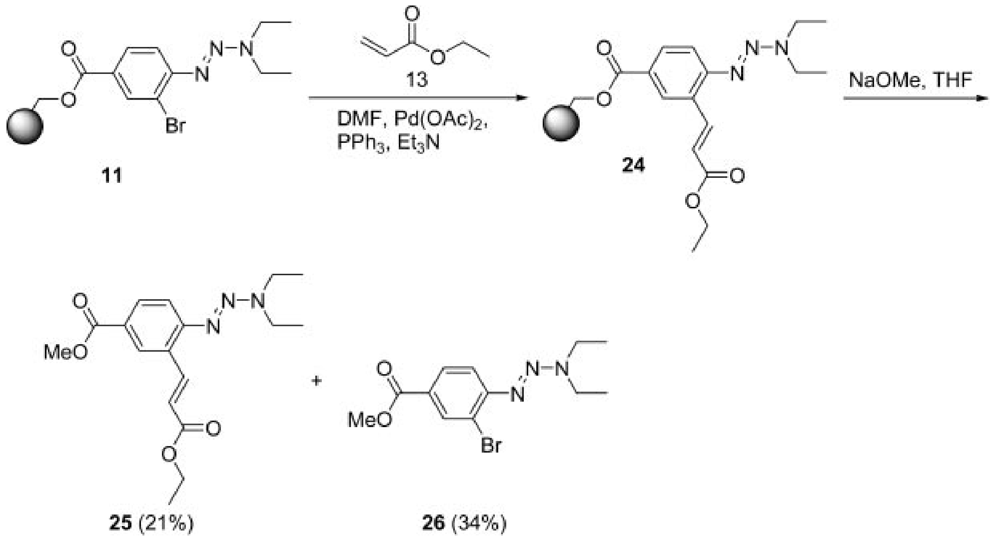


Scheme 4. Heck-reaction on T1 triazene resins **3a**–**d**. For details, see Table 1.

Table 1. Results of the Heck reaction on the triazene resins.

Entry	Resin	Alkene	Product	Yield (%)[a]
1	 **3a**	 **12**	 **20a**	61
2	 **3a**	 **13**	 **21a**	53
3	 **3a**	 **14**	 **22a**	20
4	 **3a**	 **15**	 **23a**	92
5	 **3b**	 **12**	 **20b**	32
6	 **3b**	 **13**	 **21b**	50
7	 **3b**	 **14**	 **22b**	21
8	 **3b**	 **15**	 **23b**	22
9	 **3c**	 **12**	 **20c**	21
10	 **3c**	 **13**	 **21c**	33
11	 **3c**	 **14**	 **22c**	60
12	 **3c**	 **15**	 **23c**	14
13	 **3d**	 **12**	 **20e**	32
14	 **3d**	 **13**	 **21e**	37
15	 **3d**	 **14**	 **22e**	41
16	 **3d**	 **15**	 **23e**	29
17	 **3d**	 **12**	 **20d**	13
18	 **3d**	 **13**	 **21d**	27
19	 **3d**	 **14**	 **22d**	45
20	 **3d**	 **15**	 **23d**	31

[a] Isolated yield for purified material over three steps based on the loading of the Merrifield resin.



Scheme 5. Heck reaction on the ester-bound triazene resin **11**.

Scheme 5.[10] The ester **24** was cleaved from the resin under basic conditions with sodium methoxide. Product **25** was obtained in an overall yield of 21% and high purity (>95%). The starting material was recovered as the corresponding methyl ester **26** in 34% yield.

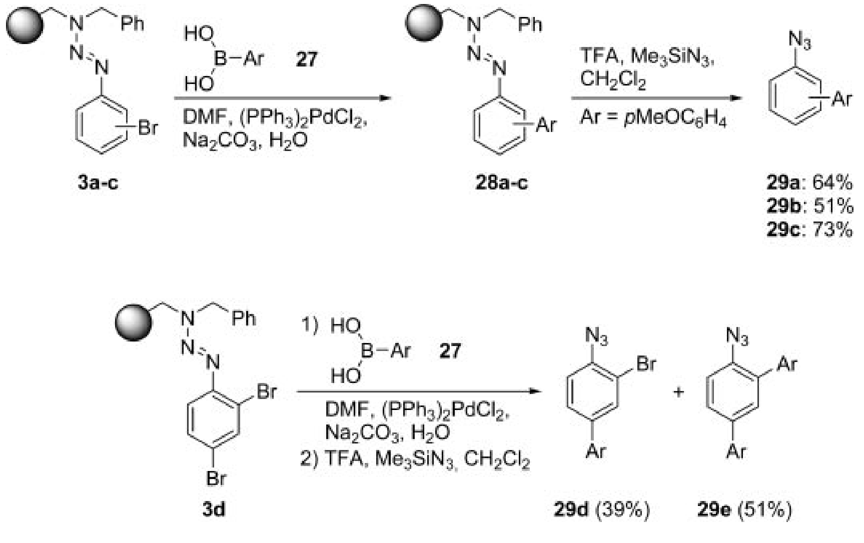
Suzuki Reaction on (Bromophenyl)triazene Resins

To compare this reaction with the other palladium-mediated reactions, the substituted (bromophenyl)triazene resins **3a–d** (Scheme 6) were reacted under standard Suzuki conditions[11] [DMF/H_2O, $(PPh_3)_2PdCl_2$, Na_2CO_3] with *p*-methoxybenzeneboronic acid (**27**). The reaction took place at 85 °C for 12 h in a closed reaction vessel with agitation. During this time, the color of the resin changed from orange to light brown to green.

The resins **28a–c** were cleaved with trifluoroacetic acid and trimethylsilyl azide[7] to yield the azides **29a–c** (Scheme 6, Table 2). For the reaction of the dibrominated resin **3d** the amount of each reagent was doubled. In this case, the mono- (**29d**) and disubstituted (**29e**) products were found. These products were separated by column chromatography.

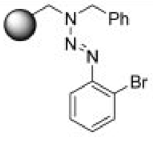
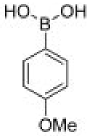
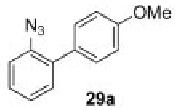
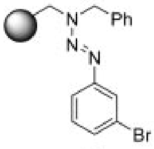
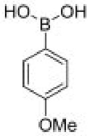
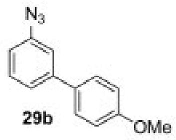
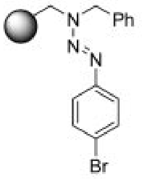
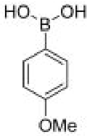
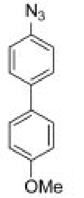
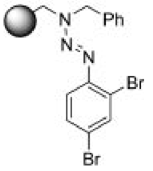
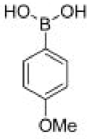
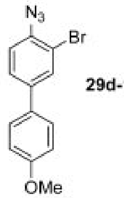
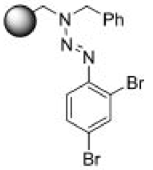
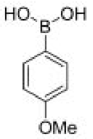
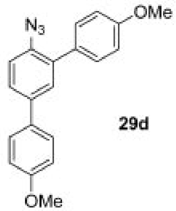
With all monosubstitution patterns, the Suzuki reaction produced very good yields. The purities of the products were higher than 95%. The disubstituted resin **3d** always yielded the disubstituted product and also the *p*-monosubstituted product. Within the bounds of the experiments, it could be seen that the Suzuki reaction took place in every case, with reaction at the *p*-position preferred over the *o*-position.

The Suzuki reactions on the 3-bromo-4-aminobenzoic ester resin **7** were conducted under the same conditions as for the triazene resin **3** [boronic acids **27** or **30**, DMF/H_2O, $(PPh_3)_2PdCl_2$, Na_2CO_3,]. However, only starting material was isolated. Even variations of the reaction temperature



Scheme 6. Suzuki reaction on bromoaryl T1 resins **3a–3d**.

Table 2. Results of the Suzuki reaction on substituted (bromophenyl)triazene resins **3a**–**3d**.

Entry	Resin	Boronic acid	Product	Yield (%)[a]
1	 **3a**	 **27**	 **29a**	64
2	 **3b**	 **27**	 **29b**	51
3	 **3c**	 **27**	 **29c**	73
4	 **3d**	 **27**	 **29d-1**	39
5	 **3d**	 **27**	 **29d**	51

[a] Isolated yield for purified material over three steps based on the loading of the Merrifield resin.

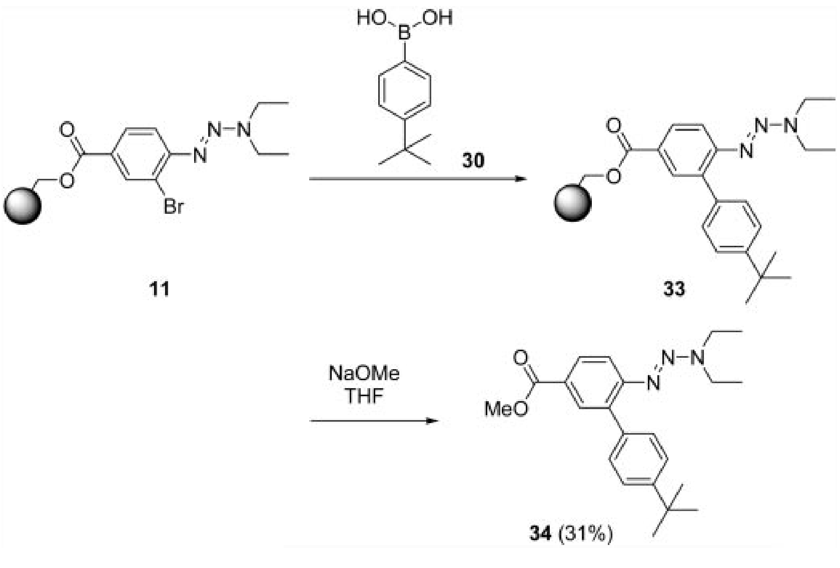
and the reaction time, as well as the use of different boronic acids, were not successful. Similar to the Heck reaction, a coordination of the palladium fragment to the amine could be the reason for this failure.

Suzuki Reaction on (3-Bromo-4-triazenyl)benzoic Ester Resin

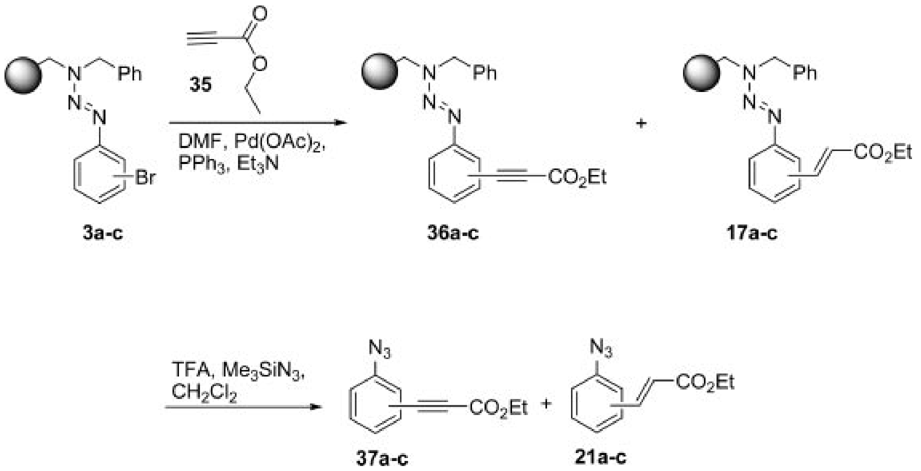
The Suzuki reaction on the ester-bound triazene resin **11** (Scheme 7) was conducted under the aforementioned conditions [DMF/H_2O, $(PPh_3)_2PdCl_2$, Na_2CO_3]. The resulting resin **33** was cleaved with sodium methoxide to obtain methyl ester **34** in mediocre yield (31%) and high purity.

Sonogashira Reaction on (Bromophenyl)triazene Resins

For comparison with the other palladium-mediated reactions, the substituted (bromophenyl)triazene resins **3a**–**d** were reacted under standard Sonogashira reaction conditions[12] [THF, $(PPh_3)_2PdCl_2$ CuI, Et_3N] with ethyl propynoate (**35**). The reaction temperature was varied from room temperature to 100 °C. In all of these cases, no conversion was observed. Only the brominated starting material was found after the reaction. In contrast to the other palladium-mediated reactions described below, the reason for the failure of the reaction could be the complexation of the copper by the triazene. For this reason, in addition to the standard Sonogashira conditions, the reaction was carried out in a copper-free variation under Heck conditions with the alkyne **35**.[13] Two products, which were not separable by column chromatography, were formed. NMR spectroscopic studies of the azide products, cleaved by trifluoroacetic acid and trimethylsilyl azide,[7] showed that the desired products **37a**–**c** were formed, and that the alkenes **17a**–**c** were generated by a Heck-type reaction (Scheme 8). It is not known how the alkene, necessary for the Heck-type reaction, was



Scheme 7. Suzuki reaction on the ester-bound triazene resin.



Scheme 8. Copper-free Sonogashira reactions on the T1 resin.

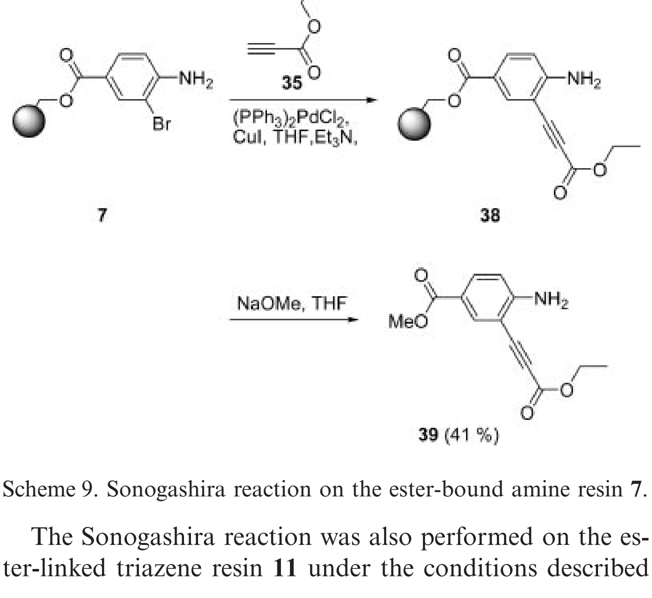
formed. It should be noted that the copper-mediated Sonogashira reaction failed with ethyl propynoate (**35**) in some cases on solid supports.[4]

It was shown that the Sonogashira reaction takes place under copper-free conditions on the solid supported triazenes. An optimization of the reaction conditions should yield the expected products.

Sonogashira Reaction on 3-Bromo-4-aminobenzoic Ester Resins

Sonogashira reactions of *o*-haloanilines were reported to proceed smoothly on solid supports, for example, in the indole synthesis of Collini and Ellingboe.[14]

The Sonogashira reaction was performed on the amine resin **7** with ethyl propynoate (**35**) under the same conditions [THF, $(PPh_3)_2PdCl_2$ CuI, Et_3N] as on the triazene resin. The cleavage of the resin was completed using sodium methoxide to obtain the methyl ester **39** (Scheme 9) in good yield (41 % overall yield) and high purity.



Scheme 9. Sonogashira reaction on the ester-bound amine resin **7**.

The Sonogashira reaction was also performed on the ester-linked triazene resin **11** under the conditions described [THF, $(PPh_3)_2PdCl_2$ CuI, Et_3N]. In this case, no product was obtained.

Conclusion

The results of the different palladium-mediated cross-coupling reactions on different resins (**3a**–**d**, **7** and **11**) are listed in Table 3. The Heck reaction took place without any hindrance in the *o*-position on the triazene unit, while no conversion took place when there was a free amine in the *o*-position. The Suzuki reaction yielded analogous results to the Heck reaction. The regioselectivity pattern was explained by combination of the palladium catalyst with the free amine. The prerequisite for the successful Sonogashira reaction is the absence of copper. When copper is present, the free amine in the *o*-position does not affect the reaction, as the copper is complexed by the triazene unit. In this case, no reaction can take place. The Sonogashira reaction conducted under copper-free conditions takes place.

Table 3. Summary of the results of the palladium-mediated reactions on solid supports.

	Triazene as linker (**3a**–**d**)	Triazene on solid phase (**11**)	Amine on solid phase (**7**)
Heck reaction	successful	successful	not successful
Suzuki reaction	successful	successful	not successful
Sonogashira reaction	not successful	not successful	successful
Copper-free alkyne coupling	successful, but alkyne and alkene were obtained	–	–

However, the Nicolaou–Ullmann reaction[15] of haloaryltriazenes with phenolates only takes place when the leaving group is *ortho* to the triazene group. The strong complexation of the copper ion with the triazene moiety[16] facilitates the displacement of the halide. On the other hand, the same combination might be responsible for the failure of the copper-induced Sonogashira reaction. Hence, copper-free conditions[17] are more suitable in this case.

Experimental Section

General Methods: ^{1}H NMR: Bruker DP 300 (300 MHz), Bruker DP 400 (400 MHz); δ = 2.50 ppm for [D$_5$]dimethyl sulfoxide, 3.31 ppm for [D$_3$]methanol, and 7.26 ppm for CHCl$_3$. The spectra were analyzed according to first order. All coupling constants are absolute values. ^{13}C NMR: Bruker DP 300 (75 MHz), Bruker DP 400 (100 MHz); δ = 39.52 ppm for [D$_6$]dimethyl sulfoxide, 77.16 ppm for CDCl$_3$, and 49.00 for [D$_4$]methanol. The signal structure was analysed by DEPT and described as follows: + = primary or tertiary C-atom (positive signal), – = secondary C-atom (negative signal), q = quaternary C-atom (no signal). IR: Perkin–Elmer FT-IR 1750. The substances were dissolved in distilled dichloromethane. The resins were measured as KBr pellets on a Bruker IFS88 IR; ps = polystyrene. EI-HRMS (electronic ionization–high resolution mass spectroscopy): Kratos MS 50 (70 eV) and Thermo Quest Finnigan MAT 95 XL (70 eV). GC : Hewlett–Packard HP 5890 Serie II 12 m × 0.25 mm capillary column HP I (carrier gas N$_2$). TLC: Silica gel coated aluminium plates (Merck, silica gel 60, F$_{254}$). Detection under UV light at 254 nm, displayed with molybdato phosphate (5% phosphomolybdic acid in ethanol, dipping solution) or potassium permanganate (0.45 g potassium permanganate and 2.35 g of sodium carbonate in 90 mL of water, dipping solution). Elemental analysis: Elementar vario EL at the Mikroanalytisches Labor des Kekulé-Instituts für Organische Chemie und Biochemie der Universität Bonn. Experiments without nominated temperature were completed at room temperature (r.t.). Solid materials (except for resins) were powdered. Chemicals, solvents, and reagents were purchased from Aldrich, Fluka, Janssen, and Merck. Merrifield resin (1–2% cross-linked, 200–400 mesh) was obtained from CalBioChem-NovaBioChem; loading: 1.06 g·mol^{-1}.

Solvents for reactions using organometallic and other sensitive materials (ether, tetrahydrofuran, dichloromethane) were distilled under argon. All resins were washed sequentially by using a vacuum reservoir connected to a sintered glass frit. Cleavage was conducted using Teflon tubes with a frit connected to a vacuum line or with a glass pipette filled with glass wool or simply paper-filtered. Evaporation of the solvent was achieved using a rotary evaporator and/or high vacuum (ca. 0.1 mbar).

General Washing Procedures: Methanol, THF, pentane, dichloromethane − three times. Methanol, DMF, pentane, THF − once. Pentane, dichloromethane, pentane − two times.

General Procedure 1. Attachment of Amines to Merrifield Resin: The amine (2.5 mmol) was placed in a round-bottom flask and stirred in tetrahydrofuran (150 mL) for 15 min at room temperature. Borontrifluoride–diethyl ether (0.037 mol) was added, the mixture was stirred for 15 min at room temperature, and then cooled to –15 °C. Isoamyl nitrite (3.5 mmol) was added, and the mixture was stirred at –15 °C for two hours.

In a round-bottom three-necked flask equipped with an overhead stirrer, the resin (5 g, 1.0 mmol/g) was expanded in diethyl ether (100 mL) and pyridine (13.5 mL), and cooled to –25 °C. The diazonium salt dissolved in acetonitrile (100 mL) was added, and the mixture was slowly warmed to room temperature.

General Procedure 2. Cleavage to Methyl Esters Under Basic Conditions: The resin was expanded in THF (0.1 mmol/ml) in a round-bottom flask. A solution of sodium methoxide in methanol (30%, 1 ml/mmol) was added to the suspension, and the mixture was shaken for three hours. The resin was filtered, the solution was hydrolysed with water, and the organic phase was extracted twice with ethyl acetate. After drying with magnesium sulfate, the solvent was removed under reduced pressure. The products were purified by column chromatography (silica, cyclohexane/ethyl acetate, 3:1).

General Procedure 3. Cleavage Protocol to the Azides: The triazene resin (500 mg, 0.9 mmol/g) was expanded in dichloromethane (10 mL) and mixed with azidotrimethylsilane (0.2 mL) and trifluoroacetic acid (0.15 mL).[7] The mixture was shaken for 30 min, then the residue was filtered off. The solvent was removed under reduced pressure.

General Procedure 4. Heck Reaction on Solid Supports: Resin (1 equiv.), triethylamine (1 equiv.), palladium acetate (0.10 equiv.), triphenylphosphane (0.50 equiv.) and the appropriate alkene (10 equiv.) in dimethylformamide (10 mL/g resin) were placed in an argon-flushed vial. The vial was shaken from time to time during 24 h at 105 °C. After cooling to room temperature, the resin was washed with water, followed by the general washing procedure. The resin was dried under high vacuum. In the case of the dibrominated resin, the amounts of all starting materials except for the resin were doubled.

General Procedure 5. General Procedure for Suzuki Coupling: Pd(PPh$_3$)$_4$ (0.10 equiv.) was added to a suspension of the polymer-bound aryl halide (1 equiv.) under argon in DMF. The slurry was stirred for 5 min, and then benzeneboronic acid (2 equiv.) and a solution of Na$_2$CO$_3$ (2 M, 2.5 equiv.) was added. The mixture was shaken for 12 h at 85 °C, and then cooled to room temperature, diluted with NH$_4$OAc solution (25% in water), and shaken for an additional 5 min before being filtered. The resin was washed following the general washing procedure and dried under high vacuum.

[Benzyl(2-bromophenylazo)amino]methylpolystyrene (3a): Following general procedure 1, Merrifield resin (10.0 g, 1 mmol/g) was reacted with 8.60 g (50.0 mmol) of 2-bromoaniline. Loading: 0.8 mmol/g. Elemental analysis (found, %): C 85.06, H 7.299, N 2.752. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3896 (s), 3811 (s), 3582 (m), 3437 (s), 3082 (m), 3025 (m, ps), 2926 (s, ps), 2850 (m), 2731(m), 2516 (s), 1943 (m, ps), 1872 (m, ps), 1803 (m, ps), 1678 (m), 1602 (m, ps), 1494 (m, ps), 1452 (m, ps), 1376 (vs), 1154 (s, ps), 983 (s), 907 (m, ps), 762 (m, ps), 707 (m, ps), 620 (m).

[Benzyl(3-bromophenylazo)amino]methylpolystyrene (3b): Following general procedure 1, Merrifield resin (10.0 g, 1 mmol/g) was reacted with 3-bromoaniline (8.60 g, 50.0 mmol). Loading: 0.8 mmol/g. Elemental analysis (found, %): C 84.28, H 7.265, N 2.723. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3812 (s), 3579 (m), 3026 (vs, ps), 2914 (vs, ps), 1943 (m, ps), 1872 (m, ps), 1804 (m, ps), 1673 (m), 1451 (m, ps), 1347 (vs), 1158 (s, ps), 992 (m), 843 (m), 758 (s, ps), 703 (m, ps).

[Benzyl(4-bromophenylazo)amino]methylpolystyrene (3c): Following general procedure 1, Merrifield resin (10.0 g, 1 mmol/g) was reacted with 4-bromoaniline (8.60 g, 50.0 mmol). Loading: 0.8 mmol/g. Elemental analysis (found, %): C 84.28, H 7.262, N 2.724. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3895 (s), 3811 (s), 3582 (m), 3437 (s), 3082 (m), 3025 (m, ps), 2926 (s, ps), 2850 (m), 2733(m), 2516 (s), 1943 (m, ps), 1872 (m, ps), 1803 (m, ps), 1678 (m), 1602 (m, ps), 1494 (m, ps), 1452 (m, ps), 1376 (vs), 1154 (s, ps), 983 (s), 907 (m, ps), 762 (m, ps), 706 (m, ps).

[Benzyl(2,4-dibromophenylazo)amino]methylpolystyrene (3d): Following general procedure 1, Merrifield resin (10.0 g, 1 mmol/g) was reacted with 2,4-bromoaniline (12.50 g, 50.0 mmol). Loading: 0.9 mmol/g. Elemental analysis (found, %): C 74.33, H 6.396, N

2.829. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3896 (s), 3811 (s), 3582 (m), 3437 (s), 3082 (m), 3025 (m, ps), 2926 (s, ps), 2850 (m), 2731(m), 2516 (s), 1943 (m, ps), 1872 (m, ps), 1803 (m, ps), 1678 (m), 1602 (m, ps), 1494 (m, ps), 1452 (m, ps), 1376 (vs), 1154 (s, ps), 983 (s), 907 (m, ps), 762 (m, ps), 707 (m, ps), 620 (m).

1-Azido-2-bromobenzene (2a-N$_3$): Following general procedure 3, resin **3a** (500 mg) was cleaved, yielding a light brown solid (92.1 mg, 0.47 mmol, 93%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 7.01 (td, ^3J = 7.83 Hz, ^4J = 1.40 Hz, 1 H, 5-H), 7.17 (d, ^3J = 7.83 Hz, 1 H, 6-H), 7.35 (td, ^3J = 7.83 Hz, ^4J = 1.40 Hz, 1 H, 4-H), 7.55 (d, ^3J = 7.83 Hz, 1 H, 3-H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ = 114.0 (q, C-2), 119.6 (+, C-6), 126.1 (q, C-4), 128.7 (+, C-5), 134.0 (+, C-3), 138.9 (q, C-1). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2132 (N$_3$), 1586 (arene). MS (EI): *m/z* (%) = 199, 197 [M$^+$, 15], 169, 171 (100), 118 (10), 77 (25), 63 (5), 51 (30). HRMS (C$_6$H$_4$BrN$_3$): calcd. 198.9589; found 198.9587.

1-Azido-3-bromobenzene (2b-N$_3$): Following general procedure 3, resin **3b** (500 mg) was cleaved, yielding a light brown solid (87.0 mg, 0.44 mmol, 97%). ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ = 6.54 (t, ^4J = 1.66 Hz, 1 H, 2-H), 7.83 (t, ^3J = 7.94 Hz, 1 H, 5-H), 6.99–7.06 (m, ca. 2 H, 4-H, 6-H). ^{13}C NMR (75 MHz, CDCl$_3$, ppm): δ = 117.8 (+, C-2), 122.2 (+, C-6), 123.3 (q, C-3), 128.0 (+, C-4), 130.9 (+, C-5), 141.6 (q, C-1). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2101 (N$_3$), 1588 (Ar), 855. MS (EI), *m/z* (%) = 199, 197 [M$^+$, 15], 169, 171 (35), 90 (100), 63 (30). HRMS (C$_6$H$_4$BrN$_3$): calcd. 198.9589; found 198.9585.

1-Azido-4-bromobenzene (2c-N$_3$): Following general procedure 3, resin **3c** (500 mg) was cleaved, yielding a light brown solid (92.1 mg, 0.47 mmol, 95%). ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ = 6.81 (d, ^3J = 7.83 Hz, 2 H, 5-H), 7.45 (d, ^3J = 7.83 Hz, 2 H, 6-H). ^{13}C NMR (75 MHz, CDCl$_3$, ppm): δ = 117.8 (q, C-4), 120.7 (+, C-2,6), 132.8 (+, C-3,5), 139.7 (q, C-1). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2132 (N$_3$), 1586 (Ar). MS (EI), *m/z* (%) = 199, 197 [M$^+$, 10], 169, 171 (100), 118 (5), 105 (5), 89 (20), 63 (10).

1-Azido-2,4-dibromobenzene (2d-N$_3$): Following general procedure 3, resin **3d** (500 mg) was cleaved, yielding a lightly brown solid (128 mg, 0.47 mmol, 93%). ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ = 7.02 (d, ^3J = 8.66 Hz, 1 H, 6-H), 7.44 (dd, ^3J = 8.66 Hz, ^4J = 2.07 Hz,1 H, 5-H), 7.69 (d, ^4J = 2.07 Hz, 1 H, 3-H). ^{13}C NMR (75 MHz, CDCl$_3$, ppm): δ = 114.8 (q, C-2), 117.9 (q, C-4), 120.6 (+, C-6), 131.7 (+, C-5), 136.3 (+, C-3), 138.2 (q, C-1). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2099 (N$_3$), 1574 (arene).

[(4-Aminophenyl)carbonyloxy]methylpolystyrene (6): Merrifield resin (3.00 g, 1.00 mmol/g) was treated with *p*-aminobenzoic acid (0.82 g, 6.00 mmol) and cesium carbonate (1.95 g, 6.00 mmol) at 50 °C for 24 h while stirring. The resin was washed following the general washing procedure and dried under high vacuum. Loading: 1.1 mmol/g. Elemental analysis (found, %): C 87.03, H 7.234, N 1.543. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3646 (vs), 3484 (s), 3383 (s), 3222 (m), 3059 (s), 3025 (m, ps), 2936 (s, ps), 2849 (m), 2667 (s), 2527 (s), 2382 (m), 2255 (m), 2114 (m), 1945 (m, ps), 1873 (m, ps), 1804 (m, ps), 1713 (s), 1606 (s, ps), 1452 (m, ps), 1374 (m), 1311 (s), 1174 (m, ps), 1112 (s), 1028 (m), 965 (m), 907 (m, ps), 773 (s, ps), 709 (m, ps).

[(4-Amino-3-bromophenyl)carbonyloxy]methylpolystyrene (7): In a round-bottom flask, resin **6** (1.00 g, 1.10 mmol/g) was expanded in DMF (100 mL) and reacted with *N*-bromosuccinimide (0.89 g, 5.00 mmol) for 24 h at room temperature while shaking. The resin was washed with water, followed by the general washing procedure, and dried under high vacuum. Loading: 1.0 mmol/g. Elemental analysis (found, %): C 84.27, H 7.82 N 2.154. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3813 (vs), 3486 (s), 3384 (m), 3199 (m), 3059 (s), 3026 (m, ps), 2913 (s, ps), 2849 (m), 2632 (s), 2384 (m), 1944 (m, ps), 1872 (m, ps), 1803 (m, ps), 1718 (s), 1616 (s, ps), 1494 (m, ps), 1452 (m, ps),1374 (m), 1317 (m), 1248 (m), 1175 (m, ps), 1116 (m), 964 (m), 907 (m, ps), 825 (m), 765 (m, ps), 706 (m, ps), 622 (m).

{(3-Bromo-4-[(diethylamino)diazenyl]phenyl)carbonyloxy}methylpolystyrene (11): Resin **7** (4.00 g, 1.00 mmol/g) was reacted with borontrifluoride–diethyl ether (2.40 mL, 15.0 mmol) and isoamyl nitrite (1.50 mL, 15.0 mmol) at –15 °C. To yield the diazonium salt, diethylamine (0.76 mL, 15.0 mmol) was added, and then the mixture was warmed to room temperature. The resin was filtered, washed following the general washing procedure, and dried under high vacuum. Loading: 0.5 mmol/g. Elemental analysis (found, %): C 81.35, H 7.392, N 1.831.

Methyl 4-Amino-3-bromobenzoate (8): Following general procedure 2, resin **7** (500 mg) were cleaved yielding a light brown solid (86.1 mg, 0.38 mmol, 84%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 3.09 (s, 1 H, CH$_3$), 4.50 (br. s, 2 H, NH$_2$), 6.72 (d, ^3J = 8.46 Hz, 1 H, 5-H), 7.78 (dd, ^3J = 8.46 Hz, ^4J = 2.02 Hz, 1 H, 6-H), 8.11 (d, ^4J = 2.02 Hz, 1 H, 2-H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ = 51.9 (+, OCH$_3$), 107.9 (q, C-3), 114.3 (+, C-5), 121.0 (q, C-1), 130.3 (+, C-6), 134.6 (+, C-2), 148.2 (q, C-4), 166.0 (q, CO$_2$). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 3604, 1574, 906. MS (EI): *m/z* (%) = 228, 226 [M$^+$, 60], 197, 195 (100), 169, 167 (10), 142 (5), 98 (5), 89 (35), 62 (10), 51 (5). HRMS (C$_8$H$_8$BrNO$_2$): calcd. 228.9738; found 228.9745.

{Benzyl[2-(*tert*-butoxycarbonylethenyl)phenylazo]amino}methylpolystyrene (16a): Following general procedure 4, resin **3a** (1.00 g, 0.9 mmol/g) was treated with *tert*-butyl acrylate (1.00 mL, 10 mmol). Loading: 0.6 mmol/g. Elemental analysis (found, %): C 84.14, H 7.91, N 2.252. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3646 (s), 3026 (s, ps), 2921 (vs, ps), 2602 (m), 1944 (m, ps), 1875 (m, ps), 1804 (m, ps), 1677 (s), 1604 (m, ps), 1494 (m, ps), 1452 (m, ps), 1346 (s), 1249 (m), 1175 (m, ps), 1108 (s), 1030 (m), 906 (m, ps), 831 (m), 756 (m, ps), 702 (m, ps).

{Benzyl[2-(ethoxycarbonylethenyl)phenylazo]amino}methylpolystyrene (17a): Following general procedure 4, resin **3a** (1.00 g, 0.9 mmol/g) was treated with ethyl acrylate (1.43 mL, 10 mmol). Loading: 0.7 mmol/g. Elemental analysis (found, %): C 85.57, H 7.361, N 2.541. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3547 (m), 3343 (vs), 3027 (s, ps), 2847 (s), 2602 (s), 2311 (s), 1943 (m, ps), 1873 (m, ps), 1804 (m, ps), 1741 (s), 1601 (m, ps), 1452 (m, ps), 1324 (s), 1180 (s, ps), 1105 (m), 1029 (m), 906 (m, ps), 842 (m), 756 (m, ps), 703 (m, ps).

{Benzyl[2-(*p*-methoxystyryl)phenylazo]amino}methylpolystyrene (18a): Following general procedure 4, resin **3a** (1.00 g, 0.9 mmol/g) was treated with *p*-methoxystyrene (0.40 mL, 10 mmol). Loading: 0.7 mmol/g. Elemental analysis (found, %): C 86.84, H 7.403, N 2.538. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3645 (m), 3026 (s, ps), 2921 (vs, ps), 2602 (m), 2057 (m), 1944 (m, ps), 1875 (m, ps), 1804 (m, ps), 1677 (m), 1604 (m, ps), 1452 (m, ps), 1346 (s), 1249 (m), 1175 (s, ps), 1108 (s), 1030 (m), 964 (m), 906 (m, ps), 832 (m), 756 (m, ps), 702 (m, ps).

{Benzyl[2-(*p*-methoxystyryl)phenylazo]amino}methylpolystyrene (19a): Following general procedure 4, resin **3a** (1.00 g, 0.9 mmol/g) was treated with *p*-chlorostyrene (1.25 mL, 10 mmol). Loading: 0.7 mmol/g. Elemental analysis (found, %): C 86.84, H 7.403, N 2.538. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3896 (s), 3811 (s), 3582 (m), 3437 (s), 3082 (m), 3025 (m, ps), 2926 (s, ps), 2850 (m), 2731(m), 2516 (s), 1943 (m, ps), 1872 (m, ps), 1803 (m, ps), 1678 (m), 1602 (m, ps), 1494 (m, ps), 1452 (m, ps), 1376 (vs), 1154 (s, ps), 983 (s), 907 (m, ps), 762 (m, ps), 707 (m, ps), 620 (m).

{Benzyl[3-(*tert*-butoxycarbonylethenyl)phenylazo]amino}methylpolystyrene (16b): Following general procedure 4, resin **3b** (1.00 g, 0.9 mmol/g) was treated with *tert*-butyl acrylate (1.00 mL, 10 mmol). Loading: 0.7 mmol/g. Elemental analysis (found, %): C 85.81, H 7.657, N 2.466. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3646 (s), 3026 (s, ps), 2921 (vs, ps), 2602 (m), 1944 (m, ps), 1875 (m, ps), 1804 (m, ps), 1677 (s), 1604 (m, ps), 1494 (m, ps), 1452 (m, ps), 1346 (s), 1249 (m), 1175 (m, ps), 1108 (s), 1030 (m), 906 (m, ps), 831 (m), 756 (m, ps), 702 (m, ps).

{Benzyl[3-(ethoxycarbonylethenyl)phenylazo]amino}methylpolystyrene (17b): Following general procedure 4, resin **3b** (1.00 g, 0.9 mmol/g) was treated with ethyl acrylate (1.43 mL, 10 mmol). Loading: 0.7 mmol/g. Elemental analysis (found, %): C 85.14, H 7.36, N 2.523. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3811 (s), 3433 (vs), 2924 (s, ps), 2849 (m), 2336 (m), 1944 (m, ps), 1873 (m, ps), 1804 (m, ps), 1739 (s), 1602 (m, ps), 1494 (m, ps), 1452 (m, ps), 1347 (s), 1179 (s, ps), 1108 (m), 991 (m),845 (m), 758 (m, ps), 699 (m, ps).

{Benzyl[3-(*p*-methoxystyryl)phenylazo]amino}methylpolystyrene (18b): Following general procedure 4, resin **3b** (1.00 g, 0.9 mmol/g) was treated with *p*-methoxystyrene (0.40 mL, 10 mmol). Loading: 0.7 mmol/g. Elemental analysis (found, %): C 86.87, H 7.40, N 2.535. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3645 (m), 3026 (s, ps), 2921 (vs, ps), 2602 (m), 2057 (m), 1944 (m, ps), 1875 (m, ps), 1804 (m, ps), 1677 (m), 1604 (m, ps), 1452 (m, ps), 1346 (s), 1249 (m), 1175 (s, ps), 1108 (s), 1030 (m), 964 (m), 906 (m, ps), 832 (m), 756 (m, ps), 702 (m, ps).

{Benzyl[3-(*p*-chlorostyryl)phenylazo]amino}methylpolystyrene (19b): Following general procedure 4, resin **3b** (1.00 g, 0.9 mmol/g) was treated with *p*-chlorostyrene (1.25 mL, 10 mmol). Loading: 0.7 mmol/g. Elemental analysis (found, %): C 85.62, H 7.216, N 2.452. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3896 (s), 3811 (s), 3582 (m), 3437 (s), 3082 (m), 3025 (m, ps), 2926 (s, ps), 2850 (m), 2731(m), 2516 (s), 1943 (m, ps), 1872 (m, ps), 1803 (m, ps), 1678 (m), 1602 (m, ps), 1494 (m, ps), 1452 (m, ps), 1376 (vs), 1154 (s, ps), 983 (s), 907 (m, ps), 762 (m, ps), 707 (m, ps), 620 (m).

{Benzyl[4-(*tert*-butoxycarbonylethenyl)phenylazo]amino}methylpolystyrene (16c): Following general procedure 4, resin **3c** (1.00 g, 0.9 mmol/g) was treated with *tert*-butyl acrylate (1.00 mL, 10 mmol). Loading: 0.7 mmol/g. Elemental analysis (found, %): C 85.47, H 7.563, N 2.495. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3646 (s), 3026 (s, ps), 2921 (vs, ps), 2602 (m), 1944 (m, ps), 1875 (m, ps), 1804 (m, ps), 1677 (s), 1604 (m, ps), 1494 (m, ps), 1452 (m, ps), 1346 (s), 1249 (m), 1175 (m, ps), 1108 (s), 1030 (m), 906 (m, ps), 831 (m), 756 (m, ps), 702 (m, ps).

{Benzyl[4-(ethoxycarbonylethenyl)phenylazo]amino}methylpolystyrene (17c): Following general procedure 4, resin **3c** (1.00 g, 0.9 mmol/g) was treated with ethyl acrylate (1.43 mL, 10 mmol). Loading: 0.7 mmol/g. Elemental analysis (found, %): C 85.57, H 7.361, N 2.541. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3547 (m), 3343 (vs), 3027 (s, ps), 2847 (s), 2602 (s), 2311 (s), 1943 (m, ps), 1873 (m, ps), 1804 (m, ps), 1741 (s), 1601 (m, ps), 1452 (m, ps), 1324 (s), 1180 (s, ps), 1105 (m), 1029 (m), 906 (m, ps), 842 (m), 756 (m, ps), 703 (m, ps).

{Benzyl[4-(*p*-methoxystyryl)phenylazo]amino}methylpolystyrene (18c): Following general procedure 4, resin **3c** (1.00 g, 0.9 mmol/g) was treated with *p*-methoxystyrene (0.40 mL, 10 mmol). Loading: 0.8 mmol/g. Elemental analysis (found, %): C 85.90, H 7.251, N 2.574. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3803 (m), 3649 (m), 3025 (m, ps), 2925 (s, ps), 2848 (m), 2602 (m), 2336 (m), 1943 (m, ps), 1872 (m, ps), 1803 (m, ps), 1677 (m), 1602 (m, ps), 1452 (m, ps), 1348 (s), 1174 (s, ps), 1104 (m), 985 (m), 906 (m, ps), 836 (m), 758 (m, ps), 703 (m, ps).

{Benzyl[4-(*p*-chlorostyryl)phenylazo]amino}methylpolystyrene (19c): Following general procedure 4, resin **3c** (1.00 g, 0.9 mmol/g) was treated with *p*-chlorostyrene (1.25 mL, 10 mmol). Loading: 0.7 mmol/g. Elemental analysis (found, %): C 85.27, H 7.185, N 2.504. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3896 (s), 3811 (s), 3582 (m), 3437 (s), 3082 (m), 3025 (m, ps), 2926 (s, ps), 2850 (m), 2731(m), 2516 (s), 1943 (m, ps), 1872 (m, ps), 1803 (m, ps), 1678 (m), 1602 (m, ps), 1494 (m, ps), 1452 (m, ps), 1376 (vs), 1154 (s, ps), 983 (s), 907 (m, ps), 762 (m, ps), 707 (m, ps), 620 (m).

{Benzyl[2,5-bis(*tert*-butoxycarbonylethenyl)phenylazo]amino}-methylpolystyrene (16d): Following general procedure 4, resin **3d** (1.00 g, 0.9 mmol/g) was treated with *tert*-butyl acrylate (2.00 mL, 10 mmol). Loading: 0.6 mmol/g. Elemental analysis (found %): N 2.319, C: 84.09, H 7.109. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3398 (s), 3060 (m), 2923 (vs, ps), 2604 (m), 1943 (m, ps), 1871 (m, ps), 1803 (m, ps), 1706 (s), 1632 (m), 1601 (m, ps), 1452 (m, ps), 1150 (s, ps), 982 (m), 907 (m, ps), 847 (m), 760 (m, ps), 703 (m, ps).

{Benzyl[2,4-bis(ethoxycarbonylethenyl)phenylazo]amino}methylpolystyrene (17d): Following general procedure 4, resin **3d** (1.00 g, 0.9 mmol/g) was treated with ethyl acrylate (2.86 mL, 20 mmol). Loading: 0.6 mmol/g. Elemental analysis (found, %): C 84.14, H 7.113, N 2.252. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3436 (vs), 2923 (s, ps), 2336 (m), 1944 (m, ps), 1872 (m, ps), 1803 (m, ps), 1733 (s), 1602 (m, ps), 1452 (m, ps), 1248 (vs), 1179 (s, ps), 1029 (m), 907 (m, ps), 757 (m, ps), 700 (m, ps).

{Benzyl[2,4-bis(*p*-methoxystyryl)phenylazo]amino}methylpolystyrene (18d): Following general procedure 4, resin **3d** (1.00 g, 0.9 mmol/g) was treated with *p*-methoxystyrene (0.80 mL, 20 mmol). Loading: 0.8 mmol/g. Elemental analysis (found, %): C 83.47, H 7.256 N 2.579. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3645 (m), 3026 (s, ps), 2921 (vs, ps), 2602 (m), 2057 (m), 1944 (m, ps), 1875 (m, ps), 1804 (m, ps), 1677 (m), 1604 (m, ps), 1452 (m, ps), 1346 (s), 1249 (m), 1175 (s, ps), 1108 (s), 1030 (m), 964 (m), 906 (m, ps), 832 (m), 756 (m, ps), 702 (m, ps).

{Benzyl[2,3-bis(*p*-chlorostyryl)phenylazo]amino}methylpolystyrene (19d): Following general procedure 4, resin **3d** (1.00 g, 0.9 mmol/g) was treated with *p*-chlorostyrene (2.50 mL, 20 mmol). Loading: 0.8 mmol/g. Elemental analysis (found, %): C 85.90, H 7.251, N 2.574. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3647 (m), 3026 (vs, ps), 2911 (vs, ps), 2603 (m), 1944 (m, ps), 1873 (m, ps), 1804 (m, ps), 1602 (m, ps), 1547 (m), 1493 (m), 1452 (m, ps), 1347 (vs), 1162 (s, ps), 1093 (s), 1029 (m), 907 (m, ps), 825 (m), 762 (m, ps), 707 (m, ps), 620 (m).

[3-(Ethoxycarbonylethenyl)-4-(*N*,*N*-diethyltriazenyl)phenyl]carbonyloxymethylpolystyrene (24): Following general procedure 4, resin **11** (1.00 g, 0.9 mmol/g) was treated with ethyl acrylate (1.43 mL, 10 mmol). Loading: 0.4 mmol/g. Elemental analysis (found, %): C 83.16, H 7.286, N 1.388.

***tert*-Butyl 2-Azidocinnamate (20a):** Following general procedure 2, resin **15a** (500 mg) was cleaved, yielding a slightly brown liquid (134 mg, 0.55 mmol, 61 %). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 1.54 (s, 9 H, CH$_3$), 6.39 (d, ^3J = 16.16 Hz, 1 H, CHCO$_2$), 7.10–7.19 (m, ca. 2 H, 5,6-H), 7.36 (ddd, ^3J = 7.57 Hz, ^3J = 7.57 Hz, ^4J = 1.51 Hz, 1 H, 4-H), 7.55 (dd, ^3J = 7.83 Hz, ^4J = 1.38 Hz, 1 H, 3-H), 7.80 (d, ^3J = 16.16 Hz, 1 H, C$_{Ar}$CH). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ = 28.3 (+, CH$_3$), 80.7 (q, CCH$_3$), 118.9 (+, *C*HCO$_2$), 122.1 (+, C-4), 125.0 (+, C-6), 126.5 (q, C-2), 128.3 (+, C-3), 131.0 (+, C-5), 137.9 (+, C$_{Ar}$CH), 139.1 (q, C-1), 166.2 (q, CO$_2$). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2140 (N$_3$), 1694 (ester), 1635 (alkene), 1596 (Ar). MS (EI): *m*/*z* (%) = 245 [M$^+$, 15], 172 (25), 147 (5), 143 (15), 133 (5), 115 (30), 104 (5), 89 (30), 63 (10), 57 (100). HRMS (C$_{13}$H$_{15}$N$_3$O$_2$): calcd 245.1164; found 245.1173.

Ethyl 2-Azidocinnamate (21a): Following general procedure 3, resin **17a** (500 mg) was cleaved yielding a slightly brown liquid (51.8 mg, 0.23 mmol, 53%). ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ = 1.34 (t, ^{3}J = 7.06 Hz, 3 H, CH$_3$), 4.26 (q, ^{3}J = 7.06 Hz, 1 H, CH$_2$), 6.47 (d, ^{3}J = 16.10 Hz, 1 H, CHCO$_2$), 7.11–7.19 (m, ca. 2 H, 5,6-H), 7.42 (ddd, ^{3}J = 8.48 Hz, ^{3}J = 8.48 Hz, ^{4}J = 1.32 Hz, 1 H, 4-H), 7.55 (dd, ^{3}J = 6.78 Hz, ^{4}J = 0.94 Hz, 1 H, 3-H), 7.90 (d, ^{3}J = 16.10 Hz, 1 H, C$_{\text{Ar}}$CH). ^{13}C NMR (75 MHz, CDCl$_3$, ppm): δ = 14.4 (+, CH$_3$), 60.7 (–, CH$_2$), 118.9 (+, *C*HCO$_2$), 120.2 (+, C-4), 125.0 (+, C-6), 126.3 (q, C-2), 128.3 (+, C-3), 131.3 (+, C-5), 138.9 (+, C_{Ar}CH), 139.3 (q, C-1), 166.9 (q, CO$_2$). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2095 (N$_3$), 1702 (ester), 1638 (Ar). MS (EI): *m*/*z* (%) = 217 [M$^+$, 40], 189 (5), 172 (30), 161 (5), 143 (25), 130 (90), 117 (100), 105 (5), 89 (60), 77 (5), 63 (25), 58 (5). HRMS (C$_{11}$H$_{11}$N$_3$O$_2$): calcd. 217.0851; found 217.0843.

2-Azido-4′-methoxystilbene (22a): Following general procedure 3, resin **18a** (500 mg) was cleaved, yielding a slightly brown liquid (22.1 mg, 0.09 mmol, 20%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 3.83 (s, 3 H, OCH$_3$), 6.90 (d, ^{3}J = 6.82 Hz, 1 H, 3′,5′-H), 7.05 (d, ^{3}J = 16.42 Hz, 1 H, CH), 7.11–7.30 (m, ca. 4 H, H$_{\text{Ar}}$), 7.45 (d, ^{3}J = 6.82 Hz, 2 H, 2′,6′-H), 7.63 (d, ^{3}J = 16.42 Hz, 1 H, CH). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ = 55.5 (+, OCH$_3$), 114.3 (+, C-3′, C-5′), 118.7 (+, C-4), 121.0 (+, C-6), 125.0 (+, C-3), 126.3 (+, CH), 128.1 (+, C-2′, C-6′), 128.4 (+, CH), 129.7 (q, C-2), 130.0 (+, C-5), 130.3 (q, C-1′), 137.4 (q, C-1), 159.7 (q, C-4′). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2122 (N$_3$), 1606 (Ar), 1512 (OMe). MS (EI): *m*/*z* (%) = 251 [M$^+$, 55], 223 (70), 208 (100), 190 (10), 180 (35), 165 (15), 152 (20), 149 (10), 127 (5), 111 (5), 89 (5), 77 (5), 57 (5). HRMS (C$_{15}$H$_{13}$N$_3$O): calcd. 251.1059; found 251.1058.

2-Azido-4′-chlorostilbene (23a): Following general procedure 3, resin **19a** (500 mg) was cleaved, yielding a slightly brown liquid (103 mg, 0.41 mmol, 92%). ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ = 6.91–7.54 (m, ca. 10 H, CH). ^{13}C NMR (75 MHz, CDCl$_3$, ppm): δ = 118.8 (+, C-4), 123.8 (+, C-6), 125.1 (+, C-3), 126.6 (+, CH=*C*H), 128.0 (+, C-2′, C-6′), 126.3 (+, CH), 128.9 (q, C-2), 129.0 (+, C-3′, C-5′), 129.0 (+, *C*H=CH), 129.1 (+, C-5), 133.6 (q, C-4′), 136.0 (q, C-1), 137.6 (q, C-1′). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2122 (N$_3$), 1606 (arene). MS (EI): *m*/*z* (%) = 257, 255 (M$^+$, 5, 15), 229, 227 (35, 100), 216, 214 (15, 5), 199 (5), 192 (30), 177 (5), 165 (40), 139 (5), 113 (5), 90 (10), 82 (5), 63 (5). HRMS (C$_{14}$H$_{10}$ClN$_3$): calcd. 255.0563; found 255.0568.

***tert*-Butyl 3-Azidocinnamate (20b):** Following general procedure 3, resin **16b** (500 mg) was cleaved, yielding a slightly brown liquid (35.3 mg, 0.14 mmol, 32%). ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ = 1.47 (s, 9 H, CH$_3$), 6.30 (d, ^{3}J = 15.92 Hz, 1 H, CHCO$_2$), 6.79 (m, 1 H, 2-H), 6.95 (ddd, ^{3}J = 7.91 Hz, ^{4}J = 2.26 Hz, ^{4}J = 1.13 Hz, 1 H, 6-H), 7.07 (t, ^{4}J = 2.07 Hz, 1 H, 5-H), 7.20 (m, 1 H, 4-H), 7.46 (d, ^{3}J = 15.92 Hz, 1 H, C$_{\text{Ar}}$CH). ^{13}C NMR (75 MHz, CDCl$_3$, ppm): δ = 28.3 (+, CH$_3$), 80.9 (q, CCH$_3$), 118.1 (+, C-1), 120.5 (+, CHCO$_2$), 121.7 (+, C-6), 124.7 (+, C-4), 130.3 (+, C-5), 136.6 (q, C-3), 140.9 (q, C-1), 142.4 (+, C_{Ar}CH), 166.0 (q, CO$_2$). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2095 (N$_3$), 1695 (ester), 1581 (Ar) (cm^{-1}). MS (EI): *m*/*z* (%) = 245 [M$^+$, 25], 217 (100), 172 (60), 161 (50), 143 (45), 132 (5), 116 (45), 105 (10), 89 (30), 78 (5), 63 (10), 57 (50). HRMS (C$_{13}$H$_{15}$N$_3$O$_2$): calcd. 245.1164; found 245.1166.

Ethyl 3-Azidocinnamate (21b): Following general procedure 3, resin **17b** (500 mg) was cleaved, yielding a slightly brown liquid (48.8 mg, 0.23 mmol, 50%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 1.26 (t, ^{3}J = 7.07 Hz, 3 H, CH$_3$), 4.19 (q, ^{3}J = 7.07 Hz, 2 H, CH$_2$), 6.35 (d, ^{3}J = 16.04 Hz, 1 H, CHCO$_2$), 6.96 (ddd, ^{3}J = 8.96 Hz, ^{4}J = 1.26 Hz, ^{4}J = 0.99 Hz, 1 H, 4-H), 7.18 (ddd, ^{4}J = 2.15 Hz, ^{4}J = 1.77 Hz, ^{4}J = 0.38 Hz, 1 H, 2-H), 7.20 (dd, ^{3}J = 6.31 Hz, ^{3}J = 6.31 Hz, 1 H, 5-H), 7.28 (d, ^{3}J = 7.84 Hz, 1 H, 6-H), 7.54 (d, ^{3}J = 16.04 Hz, 1 H, CH). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ = 14.7 (+, CH$_3$), 61.0 (–, CH$_2$), 118.5 (+, C-2), 120.1 (+, *C*HCO$_2$), 121.0 (+, C-6), 125.0 (+, C-4), 130.6 (+, C-5), 136.7 (q, C-3), 141.2 (q, C-1), 143.3 (q, CH), 167.0 (q, CO$_2$). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2096 (N$_3$), 1702 (ester), 1580 (Ar). MS (EI): *m*/*z* (%) = 217 [M$^+$, 40], 189 (100), 172 (35), 160 (5), 143 (45), 132 (10), 116 (50), 104 (10), 89 (40), 78 (5), 72 (5), 63 (15), 51 (5). HRMS (C$_{11}$H$_{11}$N$_3$O$_2$): calcd. 217.0851; found 217.0846.

3-Azido-4′-methoxystilbene (22b): Following general procedure 3, resin **18b** (500 mg) was cleaved, yielding a slightly brown liquid (23.7 mg, 0.09 mmol, 21%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 3.75 (s, 3 H, CH$_3$), 6.80–7.40 (m, ca. 10 H, 8×H$_{\text{Ar}}$, 2×CH). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ = 55.36 (+, OCH$_3$), 114.3 (+, C-3′,5′), 116.5 (+, C-2), 117.7 (+, C-6), 123.0 (+, C-4), 125.5 (+, C-5), 127.9 (+, C-3′,5′), 129.5, 129.7 (+, CH=CH), 130.0 (q, C-1′), 139.6 (q, C-3), 140.4 (q, C-1), 160.0 (q, C-4′). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2108 (N$_3$), 1596 (Ar), 1512 (OMe). MS (EI): *m*/*z* (%) = 251 (100) [M$^+$], 222 (15), 192 (10), 180 (35), 165 (10), 152 (15), 127 (5), 105 (5), 89 (5), 77 (5). HRMS (C$_{15}$H$_{13}$N$_3$O): calcd. 251.1059; found 251.1060.

3-Azido-4′-chlorostilbene (23b): Following general procedure 3, resin **19b** (500 mg) was cleaved, yielding a slightly brown liquid (25.2 mg, 0.10 mmol, 22%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 6.85 (ddd, ^{3}J = 7.83 Hz, ^{4}J = 1.26 Hz, ^{4}J = 1.01 Hz, 1 H, 4-H), 6.87–7.20 (m, ca. 5 H, 3×H$_{\text{Ar}}$, 2×CH), 7.23 (d, ^{3}J = 8.59 Hz, 2 H, 3′,5′-H), 7.33 (d, ^{3}J = 8.59 Hz, 2 H, 2′,6′-H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ = 116.9 (+, C-2), 118.4 (+, C-6), 123.4 (+, C-4), 127.9 (+, C-2′,6′), 128.3 (+, C-5), 128.8 (+, CH=*C*H), 129.1 (+, C-3′,5′), 130.2 (+, *C*H=CH), 133.8 (q, C-3), 135.54 (q, C-1′), 139.0 (q, C-4′), 140.7 (q, C-1). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2103 (N$_3$), 1581 (Ar). MS (EI): *m*/*z* (%) = 257, 255 (M$^+$, 35, 100), 229, 227 (20, 70), 199 (10), 192 (80), 190 (40), 177 (10), 165 (90), 152 (10), 139 (5), 115 (5), 95 (10), 82 (10), 63 (5). HRMS (C$_{14}$H$_{10}$ClN$_3$): calcd. 255.0563; found 255.0564.

***tert*-Butyl 4-Azidocinnamate (20c):** Following general procedure 3, resin **16c** (500 mg) was cleaved, yielding a slightly brown liquid (23.1 mg, 0.09 mmol, 21%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 1.52 (s, 9 H, CH$_3$), 6.29 (d, ^{3}J = 15.98 Hz, 1 H, CHCO$_2$), 7.00 (d, ^{3}J = 6.82 Hz, 2 H, 2,6-H), 7.47 (d, ^{3}J = 6.82 Hz, 2 H, 3,5-H), 7.52 (d, ^{3}J = 15.98 Hz, 1 H, C$_{\text{Ar}}$CH). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ = 28.3 (+, CH$_3$), 80.6 (q, *C*CH$_3$), 119.5 (+, C-2,6), 120.0 (+, *C*HCO$_2$), 129.5 (+, C-3,5), 131.7 (q, C-4), 141.7 (q, C-1), 142.4 (q, C_{Ar}CH), 166.3 (q, CO$_2$). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2086 (N$_3$), 1695 (ester), 1636 (Ar). MS (EI): *m*/*z* (%) = 245 [M$^+$, 30], 217 (30), 202 (5), 189 (5), 172 (30), 161 (100), 143 (90), 134 (10), 116 (20), 104 (5), 89 (20), 78 (5), 63 (10), 57 (30). HRMS (C$_{13}$H$_{15}$N$_3$O$_2$): calcd. 245.1164; found 245.1162.

Ethyl 4-Azidocinnamate (21c): Following general procedure 3, resin **17c** (500 mg) was cleaved, yielding a slightly brown liquid (32.2 mg, 0.15 mmol, 33%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 1.33 (t, ^{3}J = 7.14 Hz, 3 H, CH$_3$), 4.25 (q, ^{3}J = 7.14 Hz, 2 H, CH$_2$), 6.36 (d, ^{3}J = 16.04 Hz, 1 H, CHCO$_2$), 7.01 (d, ^{3}J = 6.69 Hz, 2 H, 2,6-H), 7.49 (d, ^{3}J = 6.69 Hz, 2 H, 3,5-H), 7.62 (d, ^{3}J = 16.04 Hz, 1 H, C$_{\text{Ar}}$CH). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ = 14.4 (+, CH$_3$), 60.6 (–, CH$_2$), 118.0 (+, *C*HCO$_2$), 119.6 (+, C-2,6), 129.7 (+, C-3,5), 131.4 (q, C-4), 142.0 (q, C-1), 143.4 (q, C_{Ar}CH), 167.0 (q, CO$_2$). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2087 (N$_3$), 1695 (ester), 1641 (Ar). MS (EI): *m*/*z* (%) = 217 [M$^+$, 45], 189 (65), 176 (5), 172 (15), 161 (15), 143 (100), 134 (10), 115 (20), 104 (5), 89 (25), 78 (5), 63 (10). HRMS (C$_{11}$H$_{11}$N$_3$O): calcd. 217.0851; found 217.0844.

4-Azido-4′-methoxystilbene (22c): Following general procedure 3, resin **18c** (500 mg) was cleaved, yielding a slightly brown liquid (67.8 mg, 0.27 mmol, 60%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 3.83 (s, 3 H, OCH$_3$), 6.93 (d, ^3J = 8.50 Hz, 2 H, 3′,5′-H), 6.98 (d, ^3J = 16.38 Hz, 1 H, C*H*=CH), 7.07 (d, ^3J = 7.85 Hz, 2 H, 2,6-H), 7.22 (d, ^3J = 16.38 Hz, 1 H, CH=C*H*), 7.46 (m, ca. 4 H, 3,5,2′,6′-H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ = 55.4 (+, OCH$_3$), 114.3 (+, C-3′,5′), 119.3 (+, C-2,6), 125.5 (+, C-3, C-5), 127.6 (+, *C*H=CH), 127.7 (+, C-2′,6′), 128.1 (+, CH=*C*H), 130.0 (q, C-4), 134.7 (q, C-1′), 138.6 (q, C-1), 159.4 (q, C-4′). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2113 (N$_3$), 1608 (Ar), 1513 (C=C). MS (EI): *m*/*z* (%) = 251 [M$^+$, 45], 223 (100), 208 (20), 190 (10), 180 (15), 165 (10), 152 (15), 127 (5), 111 (5). HRMS (C$_{15}$H$_{13}$N$_3$O): calcd. 251.0159; found 251.1057.

4-Azido-4′-chlorostilbene (23c): Following general procedure 3, resin **19c** (500 mg) was cleaved, yielding a slightly brown liquid (16.1 mg, 0.06 mmol, 14%). ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ = 7.00–7.03 (m, ca. 4 H, 2×CH, 2,6-H), 7.32 (dt, ^3J = 6.78 Hz, ^4J = 2.08 Hz, 2 H, 3′,5′-H), 7.41 (dt, ^3J = 8.48 Hz, ^4J = 2.26 Hz, 2 H, 3,5-H), 7.49 (dt, ^3J = 6.78 Hz, ^4J = 2.08 Hz, 2 H, 2′,6′-H). ^{13}C NMR (75 MHz, CDCl$_3$, ppm): δ = 119.5 (+, C-2,6), 127.3 (+, *C*H=CH), 127.7 (+, C-3,5), 128.0 (+, C-2′,6′), 128.3 (+, CH=*C*H), 129.0 (+, C-3′,5′), 133.4 (q, C-4), 134.1 (q, C-4′), 135.8 (q, C-1′), 139.5 (q, C-1). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2105 (N$_3$), 1603 (Ar), 1507 (C=C). MS (EI): *m*/*z* (%) = 257, 255 [M$^+$, 10, 40], 229, 227 (30, 100), 201 (5), 192 (45), 165 (60), 152 (10), 139 (10), 105 (5), 82 (5), 75 (5). HRMS (C$_{14}$H$_{10}$ClN$_3$): calcd. 255.0563; found 255.0571.

***tert*-Butyl 4-Azido-3-bromocinnamate (20d) and *tert*-Butyl 2-Azido-4-*tert*-butoxycarbonyl(vinyl)cinnamate (20e):** Following general procedure 3, resin **16d** (500 mg) was cleaved, yielding **20d** (53.4 mg, 0.14 mmol, 32%) as a light brown solid and **20e** (18.9 mg, 0.06 mmol, 13%) as a slightly brown liquid. **20e**: ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 1.48 (s, 18 H, CH$_3$), 6.06 (d, ^3J = 13.90 Hz, 1 H, CH=C*H*), 6.30 (d, ^3J = 15.81 Hz, 1 H, CH=C*H*), 6.91 (d, ^3J = 7.85 Hz, 1 H, 6-H), 7.53 (d, ^3J = 15.81 Hz, 1 H, C*H*=CH), 7.56 (d, ^3J = 13.90 Hz, 1 H, C*H*=CH), 6.85 (d, ^3J = 7.85 Hz, 1 H, 5-H), 7.72 (m, 1 H, 3-H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ = 28.2 (+, CH$_3$), 77.8 [q, C(CH$_3$)$_3$], 113.6 (+, C-3), 116.9 (+, CH=*C*H), 118.3 (+, CH=*C*H), 124.3 (+, C-6), 126.7 (+, C-5), 128.6 (q, C-4), 134.9 (q, C-2), 139.1 (q, C-1), 144.6 (+, *C*H=CH), 146.6 (+, *C*H=CH), 164.9 (q, CO$_2$). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2100 (N$_3$), 1695 (ester), 1641 (alkene), 1600 (Ar). MS (EI): *m*/*z* (%) = 373, 371, 369 (M$^+$, 10, 30, 20), 345, 343, 341 (3, 5, 1), 300, 298, 296 (10, 45, 30), 270 (5), 231 (50), 213 (45), 187 (70), 170 (15), 159 (5), 140 (15), 115 (10). HRMS (C$_{20}$H$_{25}$N$_3$O$_4$): calcd. 371.1845; found 371.1849. **20d**: ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 1.55 (s, 9 H, CH$_3$), 6.25 (d, ^3J = 15.81 Hz, 1 H, CH=C*H*), 7.16 (d, ^3J = 7.85 Hz, 1 H, 6-H), 7.39 (dd, ^3J = 7.85 Hz, ^4J = 1.66 Hz, 1 H, 5-H), 7.41 (m, 1 H, 3-H), 7.82 (d, ^3J = 15.81 Hz, 1 H, C*H*=CH). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ = 28.2 (+, CH$_3$), 80.9 [q, C(CH$_3$)$_3$], 114.3 (q, C-2), 119.6 (+, C-6), 121.2 (+, CH=*C*H), 128.1 (+, C-5), 139.2 (q, C-4), 133.0 (+, C-3), 139.9 (q, C-1), 140.8 (+, *C*H=CH), 165.7 (q, CO$_2$). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2100, 1695, 1641, 1600.

4-Azido-3-bromo-4′-chlorostilbene (23d) and 2-Azido-4-(4′′-chlorostyryl)-4′-chlorostilbene (23e): Following general procedure 3, resin **19d** (500 mg) was cleaved, yielding **23d** (46.3 mg, 0.14 mmol, 31%) as a slightly brown liquid and **23e** (51.0 mg, 0.13 mmol, 29%) as a slightly brown liquid. **23d**: ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ = 6.62 (d, ^3J = 7.87 Hz, 1 H, 6-H), 6.82–7.55 (m, ca. 8 H, CH). ^{13}C NMR (75 MHz, CDCl$_3$, ppm): δ = 111.0 (q, C-2), 116.4 (+, C-6), 122.8 (+, C-5), 127.1 (CH=*C*H), 127.6 (+, C-3), 128.7 (+, C-2′, C-6′), 129.8 (q, C-4), 131.5 (q, C-1), 133.1 (+, *C*H=CH), 133.9 (q, C-4′), 135.3 (q, C-1′). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2089, 1596. MS (EI): *m*/*z* (%) = 332 [M$^+$, 5], 306 (40), 293 (100), 269 (10), 225 (10), 211 (10), 191 (30), 178 (90), 151 (5), 95 (5), 87 (15), 74 (10), 62 (5). HRMS (C$_{14}$H$_9$BrClN$_3$): calcd. 332.9668; found 332.9667. **23e**: ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ = 6.79–7.61 (m, ca. 15 H). ^{13}C NMR (75 MHz, CDCl$_3$, ppm): δ = 114.3 (+, C-3), 2×127.0 (+, 2×CH), 127.1 (+, C-2′,6′), 127.6 (+, CH), 128.7 (+, C-2′′,6′′), 129.2 (+, C-3′,3′′,5′,5′′), 129.8 (q, C-4), 130.9 (+, CH), 133.9 (q, C-4′,4′′), 134.7 (+, CH), 135.7 (q, C-2), 137.9 (q, C-1′), 139.5 (q, C-1′′). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2089 (N$_3$), 1596 (Ar). MS (EI): *m*/*z* (%) = 391 [M$^+$, 10], 363 (100), 255 (40), 227 (10), 201 (5), 192 (45), 165 (60), 152 (10), 139 (10), 105 (5), 82 (5), 75 (5). HRMS (C$_{22}$H$_{15}$Cl$_2$N$_3$): calcd. 391.0643; found 391.0641.

Ethyl 4-Azido-3-bromocinnamate (21d) and Ethyl 2-Azido-4-ethoxycarbonyl(vinyl)cinnamate (21e): Following general procedure 3, 500 mg of resin **17d** were cleaved yielding 35.8 mg (0.12 mmol, 27%) of **21d** as a slightly brown liquid and 52.4 mg (0.16 mmol, 37%) of **21e** as a slightly brown liquid. **21d**: ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 1.23 (s, 3 H, CH$_3$), 4.06 (m, 2 H, CH$_2$), 6.23 (d, ^3J = 15.87 Hz, 1 H, CH=C*H*), 7.21 (d, ^3J = 7.82 Hz, 1 H, 6-H), 7.39 (dd, ^3J = 7.82 Hz, ^4J = 1.66 Hz, 1 H, 5-H), 7.45 (m, 1 H, 3-H), 7.82 (d, ^3J = 15.87 Hz, 1 H, C*H*=CH). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ = 14.4 (+, CH$_3$), 60.1 (+, CH$_2$), 114.1 (q, C-2), 118.6 (+, C-6), 122.0 (+, CH=*C*H), 128.2 (+, C-5), 139.2 (q, C-4), 133.3 (+, C-3), 139.7 (q, C-1), 140.5 (+, *C*H=CH), 166.2 (q, CO$_2$). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2127, 1709, 1637. **21e**: ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ = 1.31 (td ^3J = 7.16 Hz, ^4J = 1.50 Hz, 6 H,, CH$_3$), 4.25 (qd ^3J = 7.16 Hz, ^4J = 1.88 Hz, 4 H,, CH$_2$), 6.37 (d, ^3J = 16.01 Hz, 1 H, CO$_2$CH), 6.48 (d, ^3J = 16.20 Hz, CO$_2$CH), 7.16 (d, ^3J = 8.29 Hz, 1 H, 6-H), 7.49–7.64 (ca. 3 H, 3-H, 2×CH), 7.81 (d, ^3J = 16.01 Hz, 1 H, 5-H). ^{13}C NMR (75 MHz, CDCl$_3$, ppm): δ = 14.3 (+, 2×CH$_3$), 60.6 (+, 2×CH$_2$), 118.8 (+, C-3), 119.3 (+, CH), 120.9 (+, CH), 126.5 (q, C-4), 127.9 (+, C-6), 130.2 (+, C-5), 131.4 (q, C-2), 138.0 (+, CH), 140.5 (q, C-1), 142.6 (+, CH), 166.5 (+, 2×CO$_2$). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2087 (N$_3$), 1695 (ester), 1643 (alkene), 1599 (Ar). MS (EI), *m*/*z* (%) = 317, 315 (M$^+$, 35, 35), 287, 285 (100, 100), 270, 268 (45, 45), 259 (10), 241 (65), 228 (15), 215 (25), 196 (35), 186 (25), 170 (90), 156 (15), 140 (45), 130 (25), 115 (30), 97 (5), 83 (5), 57 (10). HRMS (C$_{16}$H$_{17}$N$_3$O$_4$): calcd. 315.1219; found 315.1219.

4-Azido-3-bromo-4′-methoxystilbene (22d) and 2-Azido-4-(4′′-methoxystyryl)-4′-methoxystilbene (22e): Following general procedure 3, 500 mg of resin **18d** were cleaved yielding 66.6 mg (0.20 mmol, 45%) of **22d** as a slightly brown liquid and 70.7 mg (0.18 mmol, 41%) of **22e** as a slightly brown liquid. **22d**: ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 3.91 (s, 3 H, CH$_3$), 6.74 (d, ^3J = 7.85 Hz, 1 H, 6-H), 6.82–7.55 (ca. 8 H, CH). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ = 55.4 (+, OCH$_3$), 111.0 (q, C-2), 114.3 (+, C-3′,5′), 119.5 (+, C-6), 124.1 (+, C-5), 126.4 (CH=*C*H), 127.9 (+, C-3), 129.5 (+, C-2′,6′), 131.2 (+, *C*H=CH), 136.2 (q, C-4), 136.9 (q, C-1), 159.7 (q, C-4′). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2126 (N$_3$), 1606 (Ar), 1511 (C=C). MS (EI), *m*/*z* (%) = 329, 327 [M$^+$, 15], 302, 300 (40), 287, 285 (10), 222 (100), 207 (15), 190 (20), 165 (10), 152 (15), 126 (5), 97 (5), 71 (5), 57 (10). HRMS (C$_{15}$H$_{12}$BrN$_3$O): calcd. 329.0164; found 329.0160. **22e**: ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 3.76 (s, 6 H, CH$_3$), 6.82–7.63 (ca. 15 H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ = 55.4 (+, 2×OCH$_3$), 114.3 (+, C-3), 114.7 (+, C-3′,3′′,5′,5′′), 124.1 (+, C-6), 126.6 (+, C-2′,6′), 127.0 (+, CH), 127.1 (+, C-5), 128.3 (+, C-2′′,6′′), 128.7 (q, C-1′′), 129.8 (q, C-4), 130.9 (+, CH), 132.8 (q, C1′), 134.7 (+, CH), 135.7 (q, C-2), 139.7 (q, C-1), 160.1 (q, C-4′, C-4′′). IR (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2126 (N$_3$), 1606 (Ar), 1512 (C=C). MS (EI), *m*/*z* (%) = 385, 383 (M$^+$, 5, 5), 344, 342 (100, 100), 322 (5), 302 (25), 279 (5), 251 (40), 238 (5), 222 (20), 208 (5), 181 (20), 165 (20), 137 (10), 125 (15), 11 (25), 97 (30), 57 (25). HRMS ($C_{24}H_{21}N_3O_2$): calcd. 383.1634; found 383.1636.

Methyl 3-Bromo-4-[(diethylamino)diazenyl]benzoate (26): Following general procedure 2, resin **11** (500 mg) was cleaved, yielding a light brown solid (52.1 mg, 0.15 mmol, 34%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.09 (t, ^3J = 7.00 Hz, 6 H, CH_2CH_3), 3.29 (q, ^3J = 7.00 Hz, 2 H, CH_2), 3.92 (s, 3 H, OCH_3), 7.72 (d, ^3J = 7.21 Hz, 1 H, 5-H), 8.08 (dd, ^3J = 7.21 Hz, ^4J = 1.67 Hz, 1 H, 6-H), 8.23 (d, ^4J = 1.67 Hz, 1 H, 2-H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 11.8 (+, CH_2CH_3), 46.4 (–, CH_2), 52.1 (+, OCH_3), 110.4 (q, C-3), 113.7 (+, C-5), 125.1 (q, C-1), 132.3 (+, C-6), 134.9 (+, C-2), 147.1 (q, C-4), 165.7 (q, CO_2).

Methyl 3-(Ethoxycarbonylethenyl)-4-[(diethylamino)diazenyl]benzoate (25): Following general procedure 2, resin **24** (500 mg) was cleaved, yielding a light brown solid (31.5 mg, 0.09 mmol, 21%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.11 (t, ^3J = 7.00 Hz, 6 H, CH_2CH_3), 1.24 (t, ^3J = 7.18 Hz, 3 H, CH_2CH_3), 3.19 (q, ^3J = 7.00 Hz, 2 H, CH_2), 3.87 (s, 3 H, OCH_3), 4.14 (q, ^3J = 7.18 Hz, 2 H, CH_2), 6.07 (d, ^3J = 13.96 Hz, 1 H, CH=*CH*), 7.58 (d, ^3J = 13.96 Hz, 1 H, *CH*=CH), 7.92 (d, ^3J = 7.21 Hz, 1 H, 5-H), 8.06 (dd, ^3J = 7.21 Hz, ^4J = 1.67 Hz, 1 H, 6-H), 8.13 (d, ^4J = 1.67 Hz, 1 H, 2-H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 11.8 (+, CH_3), 14.4 (+, CH_3), 46.3 (–, CH_2), 51.3 (+, OCH_3), 60.0 (–, OCH_2), 115.7 (+, CH=*C*H), 120.3 (q, C-1), 123.6 (+, C-5), 128.8 (q, C-3), 129.5 (+, C-2), 132.0 (+, C-6), 141.9 (+, *C*H=CH), 152.2 (q, C-4), 161.6 (q, CO_2), 167.3 (q, CO_2).

{Benzyl[2-(*p*-methoxyphenyl)phenylazo]amino}methylpolystyrene (28a): Following general procedure 5, resin **3a** (1.00 g, 0.9 mmol/g) was treated with 4-methoxybenzeneboronic acid (304 mg, 5.00 mmol). Loading: 0.8 mmol/g. Elemental analysis (found, %): C 85.90, H 7.251, N 2.574. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3618 (s), 3027 (vs, ps), 2913 (vs, ps), 1943 (m, ps), 1873 (m, ps), 1804 (m, ps), 1672 (m), 1602 (m, ps), 1493 (m, ps), 1452 (m, ps), 1349 (vs), 1178 (s, ps), 1109 (m), 1004 (m), 907 (m, ps), 830 (m), 757 (m, ps), 704 (m, ps).

{Benzyl[3-(*p*-methoxyphenyl)phenylazo]amino}methylpolystyrene (28b): Following general procedure 5, resin **3b** (1.00 g, 0.9 mmol/g) was treated with 304 mg (5.00 mmol) of 4-methoxybenzeneboronic acid. Loading: 0.8 mmol/g. Elemental analysis (found) (%): N 2.574, C: 85.90, H 7.251. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3809 (m), 3589 (m), 3447 (m), 3027 (m, ps), 2914 (s, ps), 2850 (m), 1943 (m, ps), 1871 (m, ps), 1804 (m, ps), 1673 (m), 1451 (m, ps), 1348 (vs), 1148 (s, ps), 1075 (m), 993 (m), 843 (m), 762 (s, ps), 704 (m, ps).

{Benzyl[4-(*p*-methoxyphenyl)phenylazo]amino}methylpolystyrene (28c): Following general procedure 5, resin **3c** (1.00 g, 0.9 mmol/g) was treated with 4-methoxybenzeneboronic acid (304 mg, 5.00 mmol). Loading: 0.8 mmol/g. Elemental analysis (found, %): C 85.90, H 7.251, N 2.574. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3618 (s), 3027 (vs, ps), 2913 (vs, ps), 1943 (m, ps), 1873 (m, ps), 1804 (m, ps), 1672 (m), 1602 (m, ps), 1493 (m, ps), 1452 (m, ps), 1349 (vs), 1178 (s, ps), 1109 (m), 1004 (m), 907 (m, ps), 830 (m), 757 (m, ps), 704 (m, ps).

{Benzyl[2,4-bis(*p*-methoxyphenyl)phenylazo]amino}methylpolystyrene (28d): Following general procedure 5, resin **3d** (1.00 g, 0.9 mmol/g) was treated with 4-methoxybenzeneboronic acid (608 mg, 10.00 mmol). Loading: 0.8 mmol/g. Elemental analysis (found, %): C 86.11, H 7.352 N 2.321. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3811 (s), 3582 (m), 3441 (vs), 3060 (m), 3026 (m, ps), 2920 (s, ps), 2849 (m), 1943 (m, ps), 1873 (m, ps), 1804 (m, ps), 1602 (m, ps), 1452 (s, ps), 1348 (s), 1175 (s, ps), 1026 (m), 983 (m), 906 (m, ps), 759 (m, ps), 702 (m, ps), 622.

2-Azido-4′-methoxybiphenyl (29a): Following general procedure 3, resin **28a** (500 mg) was cleaved, yielding a slightly brown liquid (64.8 mg, 0.29 mmol, 64%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 3.76 (s, 3 H, OCH_3), 6.28 (d, ^3J = 7.78 Hz, 1 H, 6-H), 6.65–7.10 (m, ca. 7 H, CH). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 55.4 (+, OCH_3), 107.9 (+, C-6), 119.3 (+, C-3′, C-5′), 120.4 (+, C-4), 121.7 (+, C-2′,6′), 125.3 (q, C-2), 126.8 (+, C-3), 131.2 (+, C-5), 139.6 (q, C-1), 143.2 (q, C-1′), 157.6 (q, C-4′). IR (CH_2Cl_2, cm^{-1}): $\tilde{\nu}$ = 2127, 1612. MS (EI): *m*/*z* (%) = 225 [M$^+$, 30], 197 (55), 182 (65), 167 (10), 154 (100), 139 (10), 127 (35), 98 (10), 76 (10), 62 (10), 50 (5). HRMS ($C_{13}H_{11}N_3O_4$): calcd. 225.0902; found 225.0904.

3-Azido-4′-methoxybiphenyl (29b): Following general procedure 3, resin **28b** (500 mg) was cleaved, yielding a slightly brown liquid (51.0 mg, 0.13 mmol, 51%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 3.86 (s, 3 H, OCH_3), 6.82 (d, ^3J = 8.46 Hz, 2 H, 5′,6′-H), 7.02 (dd, ^3J = 7.83 Hz, ^3J = 7.70 Hz, 1 H, 5-H), 7.08–7.14 (m, ca. 4 H, 2,6,2′,6′-H), 7.34 (m, 1 H, 4-H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 55.4 (+, OCH_3), 113.3 (+, C-3′, C-5′), 115,1 (+, C-4), 115.7 (+, C-2), 121.7 (+, C-6), 127.3 (+, C-5), 131.8 (+, C-2′, C-6′), 133.4 (q, C-1′), 139.6 (q, C-1), 145.0 (q, C-3), 159.6 (q, C-4′). IR (CH_2Cl_2, cm^{-1}): $\tilde{\nu}$ = 2127, 1612.

4-Azido-4′-methoxybiphenyl (29c): Following general procedure 3, 500 mg of resin **28c** were cleaved yielding 73.9 mg (0.33 mmol) of a slightly brown liquid. 73%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 3.85 (s, 3 H, OCH_3), 6.98 (d, ^3J = 8.86 Hz, 2 H, 2,6-H), 7.07 (d, ^3J = 8.85 Hz, 2 H, 3′,5′-H), 7.49 (d, ^3J = 8.86 Hz, 2 H, 3,5-H), 7.53 (d, ^3J = 8.85 Hz, 2 H, 2′,6′-H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 55.5 (+, OCH_3), 114.5 (+, C-2,6), 119.5 (+, C-3′,5′), 128.0 (+, C-3,5), 128.1 (+, C-2′,6′), 132.9 (q, C-1′), 137.9 (q, C-4), 138.7 (q, C-1), 159.4 (q, C-4′). IR (CH_2Cl_2, cm^{-1}): $\tilde{\nu}$ = 2106, 1696, 1606, 1597. MS (EI), *m*/*z* (%) = 225 [M$^+$, 35], 197 (100), 182 (45), 167 (5), 154 (30), 139 (10), 127 (25), 98 (10), 76 (5), 62 (5). HRMS ($C_{13}H_{11}N_3O_4$): calcd. 225.0902; found 225.0903.

1-Azido-2,4-bis(4′-methoxyphenyl)benzene (29e) and 2-Azido-3-bromo-1-(4′-methoxy)biphenyl (29d): Following general procedure 3, resin **28d** (500 mg) was cleaved, and the mixture separated by column chromatography, yielding **29d** (53.2 mg, 0.18 mmol, 39%) and **31e** (76.0 mg, 0.23 mmol, 51%)as slightly brown liquids. **29d**: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.91 (s, 3 H, OCH_3), 6.84 (d, ^3J = 7.23 Hz, 1 H, 6-H), 6.95 (d, ^3J = 7.23 Hz, 1 H, 5-H), 7.35 (m, ca. 5 H, CH). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 55.6 (+, OCH_3), 102.1 (q, C-2), 108.3 (+, C-6), 114.7 (+, C-3′, C-5′), 123.9 (+, C-5), 128.7 (+, C-2′, C-6′), 130.2 (+, C-3), 133.1 (q, C-1), 134.7 (q, C-1′), 139.7 (q, C-4), 159.2 (q, C-4′). IR (CH_2Cl_2, cm^{-1}): $\tilde{\nu}$ = 2108, 1704, 1603, 904. MS (EI): *m*/*z* (%) = 305/303 [M$^+$, 15], 276/274 (20), 263/261 (40), 246 (10), 225 (50), 199/197 (100), 182 (40), 167 (5), 156/154 (20), 138 (5), 126 (20), 98 (5), 76 (5), 63 (5). **29e**: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.85 [s, 3 H, $(OCH_3)'$], 3.91 [s, 3 H, $(OCH_3)''$], 6.85 (m, ca. 11 H, CH). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 55.3 [+, $(OCH_3)'$], 55.4 [+, $(OCH_3)''$], 109.6 (+, C-6), 114.3 (+, C-3′′, C-5′′), 118.3 (+, C-3′, C-5′), 121.9 (+, C-2′, C-6′), 124. 2 (+, C-3), 126.8 (+, C-2′′, C-6′′), 128.8 (+, C-5), 136.4 (q, C-4), 140.2 (q, C-1′′), 142.6 (q, C-1′), 146.1 (q, C-1), 157.8 (q, C-4′), 158.1 (q, C-4′′). IR (CH_2Cl_2, cm^{-1}): $\tilde{\nu}$ = 2107, 1701, 1603. MS (EI): *m*/*z* (%) = 331 [M$^+$, 5], 286 (10), 246 (5), 225 (50), 197 (100), 182 (40), 167 (5), 154 (20), 138 (5), 126 (20), 98 (5), 76 (5), 63 (5).

{4-[(Diethylamino)azo]-3-(4-*tert*-butylphenyl)phenyl}carbonyloxymethylpolystyrene (33): Following general procedure 5, resin **11** (1.00 g, 0.9 mmol/g) was reacted with 4-methoxybenzeneboronic acid (608 mg, 10.00 mmol). Loading: 0.7 mmol/g. Elemental analysis (found, %): C 85.62, H 7.216, N 2.452. IR (KBr, cm^{-1}): $\tilde{\nu}$ =

3896 (s), 3811 (s), 3582 (vs), 3437 (s), 3082 (m), 3025 (m, ps), 2926 (s, ps), 2850 (m), 2731(m), 2516 (s), 1943 (m, ps), 1872 (m, ps), 1803 (m, ps), 1678 (m), 1602 (m, ps), 1494 (m, ps), 1452 (m, ps), 1376 (vs), 1154 (s, ps), 983 (s), 907 (m, ps), 762 (m, ps), 707 (m, ps), 620 (m).

Methyl 4-[(Diethylamino)azo]-3-(4-*tert*-butylphenyl)benzoate (34): Following general procedure 2, resin **33** (500 mg) was cleaved, yielding a light yellow solid (51.2 mg, 0.14 mmol, 31%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 1.12$ (t, $^3J = 7.00$ Hz, 6 H, CH_2CH_3), 1.22 [s, 9 H, $CH(CH_3)_3$], 3.19 (q, $^3J = 7.00$ Hz, 4 H, CH_2), 3.88 (s, 3 H, OCH_3), 7.46 (d, $^3J = 8.05$ Hz, 2 H, 2′,6′-H), 7.55 (d, $^3J = 8.05$ Hz, 2 H, 3′,5′-H), 8.06–8.23 (m, ca. 3 H, CH). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta = 11.8$ (+, CH_2CH_3), 30.18 [+, $C(CH_3)_3$], 33.7 [q, $C(CH_3)_3$], 46.4 (–, CH_2), 54.2 (+, OCH_3), 108.4 (+, C-5), 122.1 (q, C-1), 124.1 (q, C-3), 124.7 (+, C-2′, C-6′), 125.2 (q, C-3′, C-5′), 130.4 (+, C-2), 132.5 (+, C-6), 146.1 (q, C-1′), 150.2 (q, C-4), 151.2 (q, C-4′), 166.3 (q, CO_2).

Ethyl (2-Azidophenyl)propynoate (37a) and Ethyl 2-Azidocinnamate (21a): Following general procedure 3, resin **36a/17a** (500 mg) was cleaved. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 1.34$ (t, $^3J = 7.06$ Hz, 3 H, CH_3), 1.35 (t, $^3J = 7.10$ Hz, 3 H, CH_3), 4.19 (q, $^3J = 7.10$ Hz, 1 H, CH_2), 4.26 (q, $^3J = 7.06$ Hz, 1 H, CH_2), 6.47 (d, $^3J = 16.10$ Hz, 1 H, $CHCO_2$), 7.11–7.55 (m, ca. 8 H, H_{Ar}), 7.90 (d, $^3J = 16.10$ Hz, 1 H, $C_{Ar}CH$).

Ethyl (3-Azidophenyl)propynoate (37b) and Ethyl 3-Azidocinnamate (21b): Following general procedure 3, resin **37b/17b** (500 mg) was cleaved. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): $\delta = 1.26$ (t, $^3J = 7.07$ Hz, 3 H, CH_3), 1.36 (t, $^3J = 7.09$ Hz, 3 H, CH_3), 4.19 (m, ca. 4 H, CH_2), 6.35 (d, $^3J = 16.04$ Hz, 1 H, $CHCO_2$), 6.85–7.28 (m, ca. 8 H, H_{Ar}), 7.54 (d, $^3J = 16.04$ Hz, 1 H, CH).

Ethyl (4-Azidophenyl)propynoate (37c) and Ethyl 4-Azidocinnamate (21c): Following general procedure 3, resin **37c/17c** (500 mg) was cleaved. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): $\delta = 1.33$ (m, ca. 6 H, CH_3), 4.18 (q, $^3J = 7.10$ Hz, 2 H, CH_2), 4.25 (q, $^3J = 7.14$ Hz, 2 H, CH_2), 6.36 (d, $^3J = 16.04$ Hz, 1 H, $CHCO_2$), 7.01–7.15 (m, ca. 6 H, H_{Ar}), 7.49 (d, $^3J = 6.69$ Hz, 2 H, H_{Ar}), 7.62 (d, $^3J = 16.04$ Hz, 1 H, $C_{Ar}CH$).

4-Amino-3-(ethoxycarbonylethynyl)phenylcarbonyloxymethylpolystyrene (38): Resin **7** (1.00 g, 0.9 mmol/g) was treated with tetrakis(triphenylphosphane)palladium(0) (83.2 g, 0.01 mmol), triethylamine (0.2 mL, 1.00 mmol), copper iodide (95 mg, 0.50 mmol) and ethyl propynoate (1.00 mL, 5.00 mmol) in DMF (10 mL) under argon at 80 °C for two days while shaking. The resin was hydrolysed with saturated ammonium chloride solution, washed following the general washing procedure, and then dried under high vacuum. Loading: 0.6 mmol/g. Elemental analysis (found, %): C 83.12, H 7.123 N 1.615. IR (KBr, cm^{-1}): $\tilde{\nu} = 3484$ (m), 3382 (s), 3059 (m), 3026 (m, ps), 2925 (vs, ps), 2632 (s), 2337 (m), 1943 (m, ps), 1873 (m, ps), 1803 (m, ps), 1738 (s), 1613 (s, ps), 1452 (m, ps), 1246 (s), 1029 (m, ps), 964 (m), 824 (m), 762 (m, ps).

Methyl 4-Amino-3-(ethoxycarbonylethynyl)benzoate (39): Following general procedure 2, resin **38** (500 mg) was cleaved, yielding a light brown solid (40.0 mg, 0.18 mmol, 41%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 1.35$ (t, $^3J = 7.11$ Hz, 3 H, CH_2CH_3), 3.34 (br. s, 2 H, NH_2), 3.83 (s, 3 H, OCH_3), 4.25 (q, $^3J = 7.11$ Hz, 2 H, CH_2), 6.52 (d, $^3J = 8.72$ Hz, 1 H, 5-H), 7.65 (dd, $^3J = 8.72$ Hz, $^4J = 1.82$ Hz, 1 H, 6-H), 7.94 (d, $^4J = 1.82$ Hz, 1 H, 2-H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta = 14.2$ (+, CH_2CH_3), 54.2 (+, OCH_3), 62.7 (–, CH_2), 79.3 (q, $C\equiv C$), 83.0 (q, $C\equiv C$), 109.2 (q, C-3), 115.8 (q, C-5), 125.2 (q, C-1), 131.2 (+, C-6), 134.5 (+, C-2), 153.6 (q, CO_2Et), 158.7 (q, C-4), 166.4 (q, CO_2Me).

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