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Novel Carbazole (Cbz)-Based Carboxylated Functional Monomers: Design, Synthesis, and Characterization

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A series of novel functional carbazole (Cbz)-based carboxylated monomers were synthesized and characterized. A Clauson-Kaas procedure, a deprotection step, amide coupling, and hydrolysis were utilized as key chemical reactions towards the multistep synthesis of monomers in good to excellent isolated yields. The design strategy was further extended to complex carbazole-COOH monomers incorporated arylazo groups as photoreactive moieties. In addition, photoreactive hybrid carbazole (Cbz)-pyrrole (Pyr)-based carboxylated monomers, comprising a pyrrole core linking a carbazole and a photoreactive phenylazide or benzophenone moiety through an amide spacer in the molecular structure, were also synthesized. The latter can be utilized for surface modification of polymeric films in their monomeric form or as polymeric microparticles (MPs).

Introduction

The development of nanomaterials has gained tremendous research interest in recent years due to their potential applications in the various fields, such as biomedical, imaging, sensing, drug delivery, therapy systems, and so forth.[1] In this regard, the design and fabrication of polymeric nanoparticles/microparticles (NPs/MPs) have attracted considerable attention because of the availability of a wide range of polymerization methods, of monomeric source materials, and of tunable NP/MP surface functionalities, which make these particles attractive for numerous applications.[2] Conducting polymer (CP)-based nanomaterials such as polyaniline (PANI), polypyrrole (polypyr), and polythiophene (polyTh) have been already extensively investigated and well documented.[3] In contrast, polycarbazole-based particles are less reported.[4–7] This can be attributed to higher oxidation potentials of carbazole-based materials, making them less prone to oxidation and causing ineffective oxidative electrochemical/chemical polymerizations. Another reason for the lack of research into this class of material is that carbazole-based monomers are not easy to synthesize.

Carbazole-based materials have emerged as new and attractive advanced materials having been used in organic light-emitting diodes (OLEDs),[8] organic solar cells (OSCs),[9] chemical sensors,[10] photoconductive materials,[11] and electrochromic materials.[12] In addition, carbazole derivatives are potential alkaloids.[13] Polycarbazole polymers as conducting materials have several advantageous properties since the carbazole heterocycle is chemically stable and can be easily modified at the C3, C6, and 9 positions that can improve thermal stability and impart good electrooptical properties on the resulting polymers. Furthermore, the moderate oxidation potential of carbazole-containing compounds makes them promising hole transporting materials in optoelectronic applications. Usually, carbazole-based materials are designed through π-conjugation dendrimers, oligomers or polymers. Along this line, carbazole-based small molecules are also emerging as promising materials for use in OSCs,[14] solution processed/thermal evaporation-based OLEDs,[15,16] and thermally activated delay fluorescence (TADF) materials.[17]

Recently, we reported a novel strategy for designing new carbazole-based materials and the formation of the corresponding well-shaped spherical poly-carbazole (polyCbz)-based MPs using an oxidative liquid-phase polymerization method.[18] These earlier studies revealed that various aromatic functionalities can be introduced into polyCbz-based MPs including phenyl bromide and carbazole heterocycle. We specially designed a number of photoreactive molecules by extending our previous protocol and investigated their reactivity towards highly chemically stable poly(2-chloro-paraxylelene) (Parylene C) films.[19] Our efforts continue towards the design and development of new Cbz-based monomers/polymeric nanomaterials with tailored physical, chemical and biological properties.

Herein, we report the design, synthesis, and full characterization of a novel class of Cbz-and Cbz-pyrrole (Pyr)-based hybrid oxidizable monomers following multistep synthetic strategies. By replacing aromatic components at the ω-position of (*S*)-methyl 6-amino-2-carbazol-9-yl-hexanoate, we synthesized various monomers incorporating arylazo- and photoreactive moi-

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eties and systematically characterized them. This versatile molecular design can lead to several advantageous properties: 1) nanostructures having chirality since those starting materials are derived from chiral amino acid lysine, which has been extensively studied as a precursor for self-assembling nanostructures; 2) functionalization of the active sites at C3 and C6 positions of the carbazole unit can provide ready access to new materials with interesting properties. Furthermore, monomers **M7**–**M12** could reveal potential UV-mediated photo-responsive properties upon UV irradiation.

Results and Discussion

The chemical structures of monomers **M1**–**M6** are shown in Figure 1. Schemes 1–4 depict the synthetic routes for monomers **M1**–**6**. The preparation of Cbz-based monomers **M1**–**M6** was carried out according to our previously reported procedure.[20,21] Interestingly, monomers **M1**–**M4** were specially designed to investigate the morphology of the resultant MPs in order to compare with our earlier findings.[18] The key starting material, (*S*)-methyl 6-(benzyloxycarbonylamino)-2-(9*H*-carbazol-9-yl)hexanoate (**3**) was synthesized by treatment of ω-NHZ-lysine methyl ester and 2,5-dimethoxy-tetrahydrofuran (DMT; **2**) in mixtures of 1,4-dioxane/acetic acid/12 M HCl at reflux for 2–4 hours.[18] Then, key amine **4**[18] was obtained by catalytic hydrogenation of **3** with 10% palladium on carbon in a mixed solvent of tetrahydrofuran (THF)/isopropanol at room temperature. Amidation of the acid chloride of 2-carboxythiophene **5** with amine **4** in the presence of triethylamine at room temperature afforded compound **6** in 95% yield. On the other hand, compounds **8** and **10** were obtained by reacting amine building block **4** with pyrrole-2-carboxylic acid **7** and 2-(thiophen-3-yl) acetic acid **9**, respectively, using standard amide coupling reagents *N*,*N*′-dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (HOBt) and triethylamine at room temperature in 83% yield.

Hydrolysis of the methyl ester of compounds **6**, **8** and **10** gave the desired carboxylated monomers, **M1**, **M2** and **M3** with 85–86% isolated yields (Schemes 1 and 2). Next, we synthesized compound **12** using previously reported work in our laboratory.[21] Compound **12** was then coupled with amine **4** using a similar amide coupling strategy to afford **13** in 82% yield. Monomer **M4** was obtained in 95% yield in a two-step procedure as shown in Scheme 3. To generalize the synthetic variant towards more complex monomers design, we synthe-

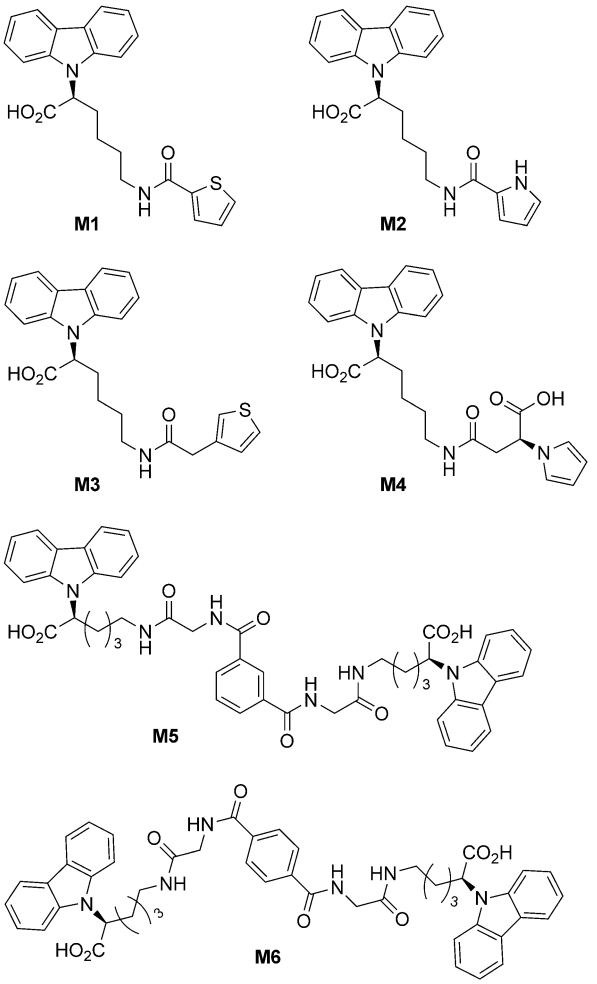
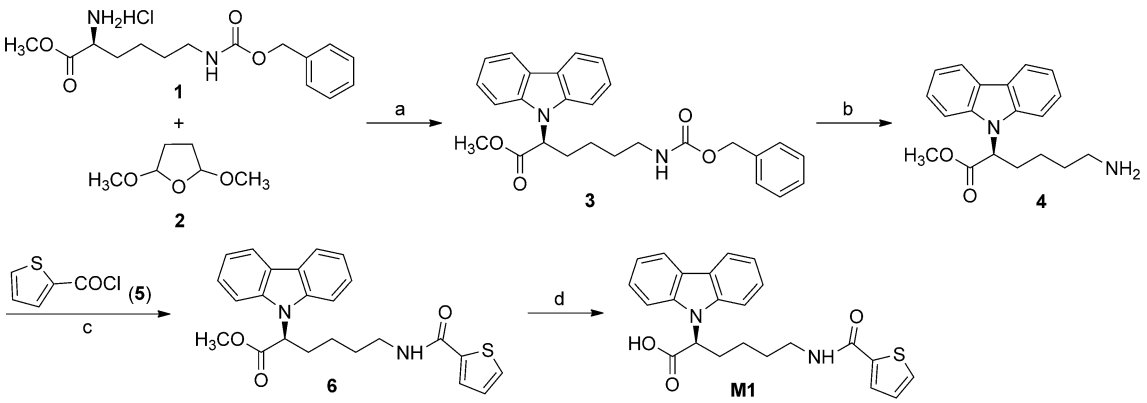
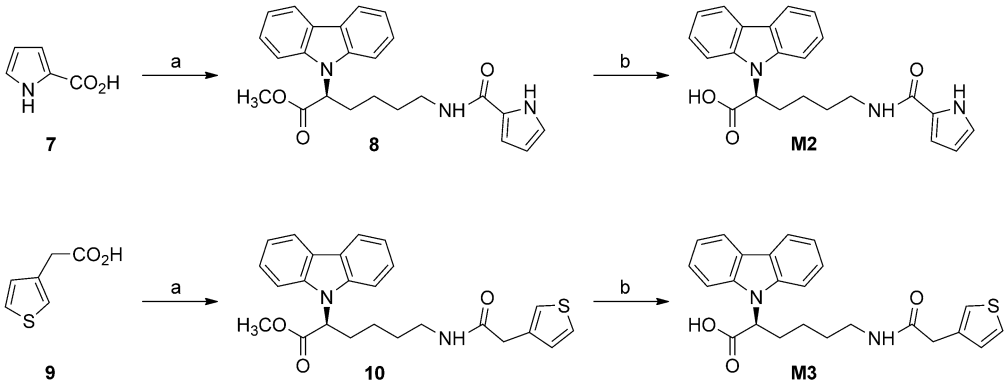


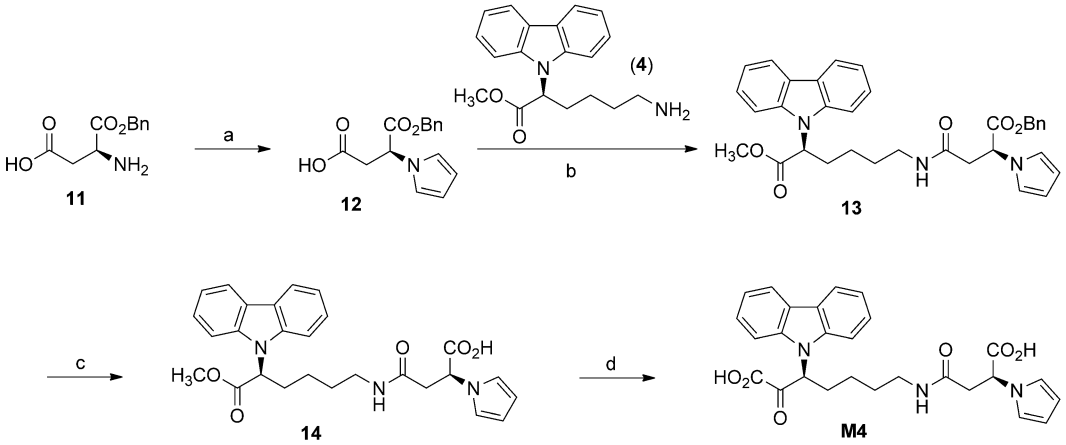
Figure 1. Chemical structures of Cbz-based oxidizable carboxylated monomers **M1**–**6**.



Scheme 1. Synthesis of monomer **M1**. *Reagents and conditions*: a) AcOH, dioxane, 75–110 °C, 2–3 h, rt, 5–6 h; b) 10% Pd–C, H_2, isopropanol/THF (1:1), rt, 4 h; c) Et_3N, CH_2Cl_2, rt, 2 h, 95%; d) alc. KOH, 60 °C, 5 h, then H_3O^+, 0 °C, 30 min, 85%.



Scheme 2. Synthesis of monomers **M2**–**M3**. *Reagents and conditions*: a) 1. DCC, HOBt, Et_3N, CH_2Cl_2, 15 min, rt; 2. amine **4**, CH_2Cl_2, rt, 30 min, 83%; b) alc. KOH, 60 °C, 5 h, then H_3O^+, 0 °C, 30 min, 86%.

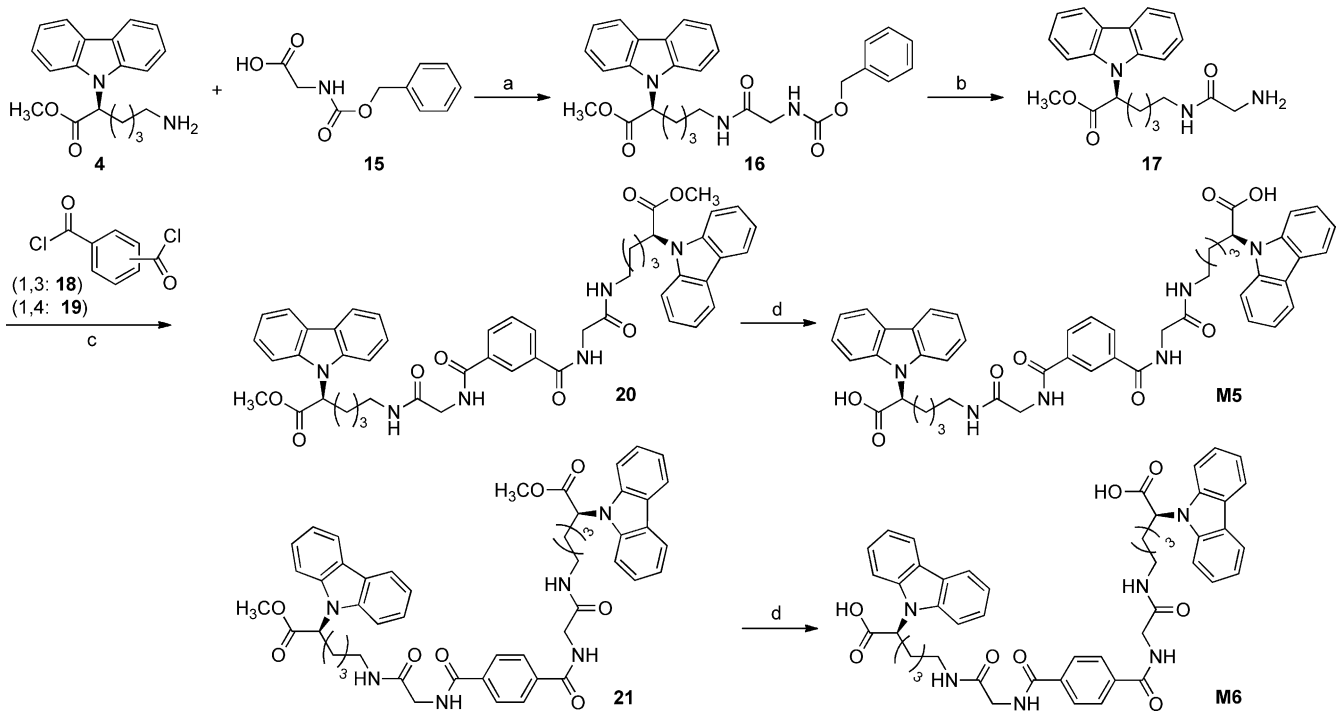


Scheme 3. Synthesis of monomer **M4**. *Reagents and conditions*: a) 1. NaOAc, H_2O, AcOH, rt–75 °C, 30 min, 2. **2**, 75 °C, 2 h, 90%; b) 1. DCC, HOBt, Et_3N, CH_2Cl_2, 30 min, rt; 2. amine **4**, CH_2Cl_2, rt, 30 min, 82%; c) 10% Pd–C, H_2, isopropanol/THF (1:1), rt, 5 h, 88%; d) alc. KOH, 60 °C, 90 min, then H_3O^+, 0 °C, 30 min, 95%.

sized two C2-symmetric monomers **M5** and **M6** by incorporating the peptide bonds in Cbz-COOH monomers based on 1,3 and 1,4 linkers in our earlier report.[18] Compounds containing the 1,3 (**M5**) and 1,4 (**M6**) linkers were synthesized by straightforward coupling of intermediate **4** with *N*-benzoyloxy glycine **15** employing the same amidation procedure as previously described to obtain intermediate **16**, followed by catalytic hydrogenation (10% Pd/C), acid chloride amidation with isophthaloyl dichloride (1,3) or terephthaloyl dichloride (1,4) and finally basic hydrolysis (Scheme 4). All of the monomers (**M1**–**M6**) and intermediates were characterized by NMR (^1H, ^{13}C) and IR spectroscopy, and mass spectrometry. Detailed synthetic procedures and complete characterization data are given in the Experimental Section and Supporting Information.

We believe that well-shaped spherical polyCbz-MPs can be formed from monomers **M1**–**M6** (Figure 1) using an oxidative liquid-phase polymerization, and studies to this end are ongoing.[18] Monomers **M1**–**M6** have some advantages in terms of the shape/morphology of the resultant MPs. First, these monomers contain active sites at C3 and C6 positions on the carbazole moiety offering potential polymerization. In addition, monomers **M1** and **M3** contain reactive sites at position 5 (**M1**) and at positions 2,5 (**M3**) of the thiophene moiety. Furthermore, these monomers can be functionalized post-polymerization at these positions. Interestingly, among the three monomers, **M3** produces MPs with a smooth spherical morphology, thus we assume that the polymerization not only takes place at the 3,6 positions of the carbazole moiety but also at the 2,5 positions of the thiophene unit.

Next, we extend our synthetic strategies for the synthesis of a novel class of UV-photoreactive monomers. We designed two types of monomers: azo-based Cbz-COOH monomers (**M7**–**M9**) and phenylazide and benzophenone-based hybrid Cbz-Pyr monomers (**M10**–**M12**) containing a pyrrole core linker between carbazole and phenylazide units or a benzophenone moiety as shown in Figures 2 and 3. Scheme 5 illustrates the route for the synthesis of monomers **M7** and **M8**. Our strategy for designing monomers **M7**–**M9** was to study properties due to *cis*–*trans* isomerization in monomers as well as in their particle state upon photo-irradiation. Monomers **M7** and **M8** were synthesized starting from (*E*)-4,4′-(diazene-1,2-diyl)dibenzoic acid, accessed from 4-nitrobenzoic acid by conversion to acid chloride **22** upon treatment with phosphorus pentachloride at 50 °C for 45 minutes with an isolated yield of 90%.[22] Interest-



Scheme 4. Synthesis of monomer **M5**–**M6**. *Reagents and conditions*: a) 1. DCC, HOBt, *N*-methylmorpholine (NMM), CH_2Cl_2, rt, 30 min; 2. amine **4**, CH_2Cl_2, rt, 1 h, 82%; b) 10% Pd/C, H_2, isopropanol/THF (1:1), rt, 5 h, 97%; c) isophthaloyl dichloride (1,3; to give **M5**) or terephthaloyl dichloride (1,4; to give **M6**) Et_3N, CH_2Cl_2, rt, 2 h, 68–70%; d) alc. KOH, 60 °C, 5 h, then H_3O^+, 0 °C, 30 min, 88–95%.

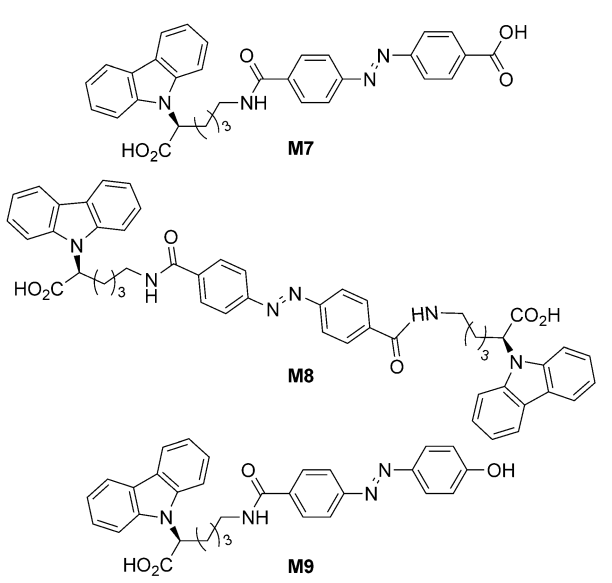


Figure 2. New oxidizable carbazole azo-based carboxylated monomers **M7**–**9**.

ingly, (*E*)-4,4′-(diazene-1,2-diyl)dibenzoic acid is poorly soluble in almost polar solvents but acid chloride derivative **22** is highly soluble in chloroform. Finally, acid chloride **22** was treated with amine **4** in the presence of triethylamine to afford methyl ester derivatives **23** and **24**, precursors of monomers **M7** and **M8**, respectively, depending upon the amount of amine **4** used at room temperature or under ice-cold conditions.

On the other hand, the synthetic route for monomer **M9** was started from 4-aminobenzoic acid. Compounds **25 d** and **25 e** were synthesized following a literature procedure.[23,24] The complete synthetic route for **M9** is provided in Scheme 6. Monomers **M7**–**M9** were obtained in 90–93% yield after basic hydrolysis, as used for previous monomers syntheses, of the methyl ester precursors (**23**, **24**, and **25**).

To study the liquid-phase chemical polymerization of hybrid Cbz-Pyr-based carboxylated monomers, we designed and synthesized new photoreactive monomers **M10**–**M12** (Figure 3). Monomers **M10**–**M12** are new synthetic variants of our previously reported Cbz-based photoreactive monomers.[19] We assumed that the addition of a pyrrole core connecting the carbazole and photoreactive moieties would improve the shape and size of MPs for better reactivity and improved conductivity on the polymeric surfaces as compared with our previously reported materials during UV irradiation. First, we synthesized mono-*tert*-butyloxycarbonyl (BOC)-protected diamines **28** and **29**, which were then coupling with the appropriate acid (**30** and **33**) employing our standard amidation protocol (for details, see the Experimental Section), and finally ω-NH_2 free building blocks **35**–**37** using trifluoroacetic acid (TFA) at room temperature with 68–97% isolated yields. Amidation coupling reaction employing 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC)/HOBt was used to obtain compounds **38**, **39** and **40** in 65–70 isolated yields (for experimental procedures, see the Supporting Information). The Cbz-Pyr hybrids **38**, **39** and **40** were hydrolyzed employing a previous protocol to obtain the final Cbz-Pyr hybrid photoreactive monomers **M10**–**M12** (Schemes 7 and 8).

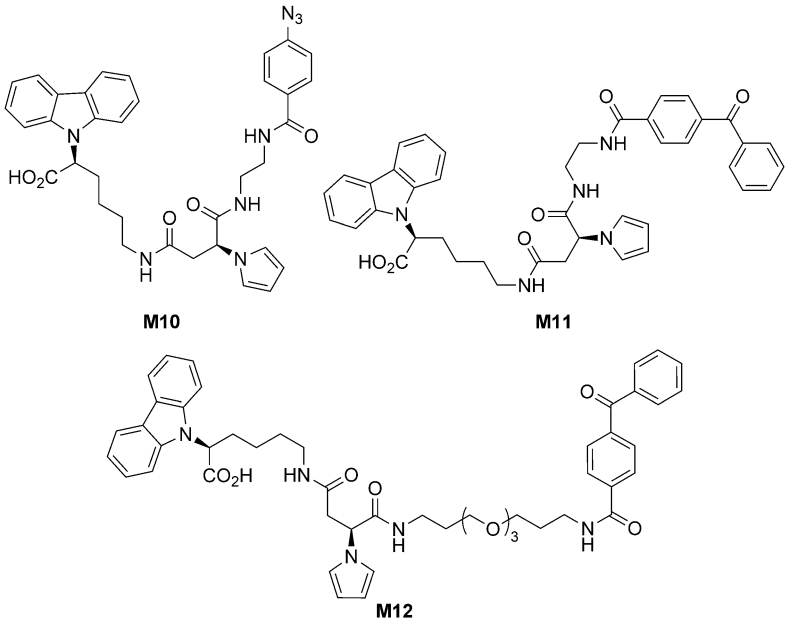


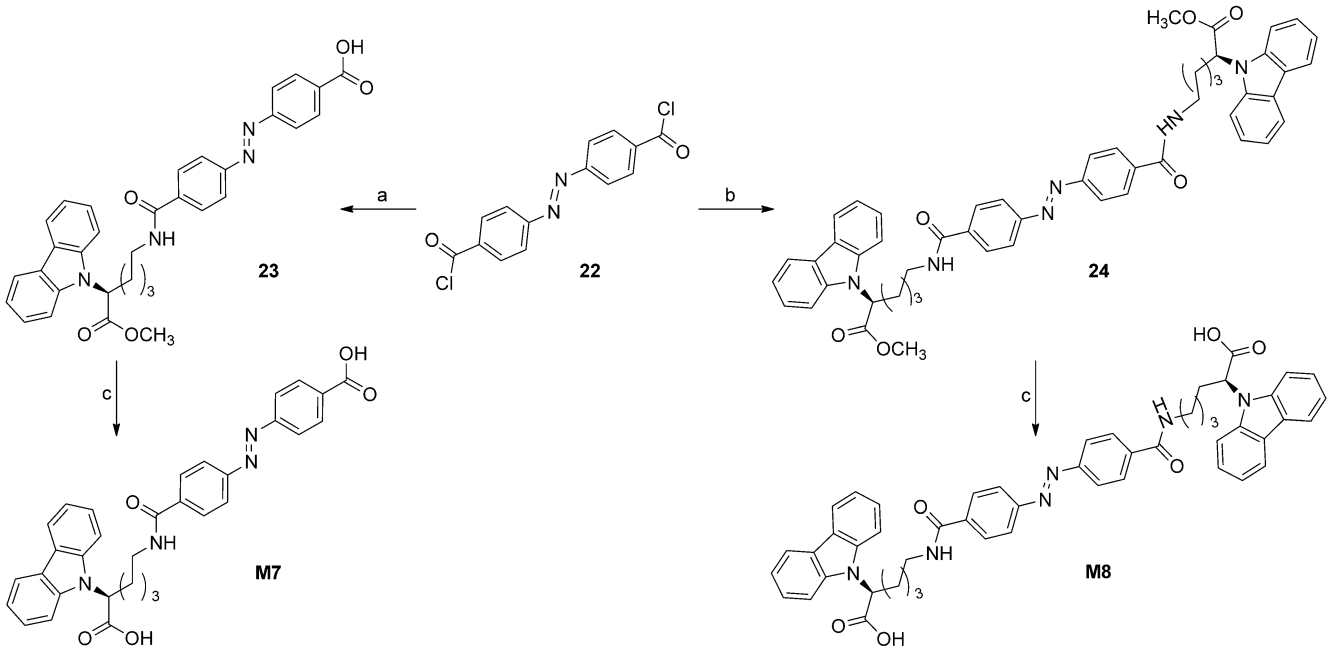
Figure 3. New oxidizable hybrid photoreactive carbazole-pyrrole-based carboxylate monomers **M10**–**12**.

Conclusions

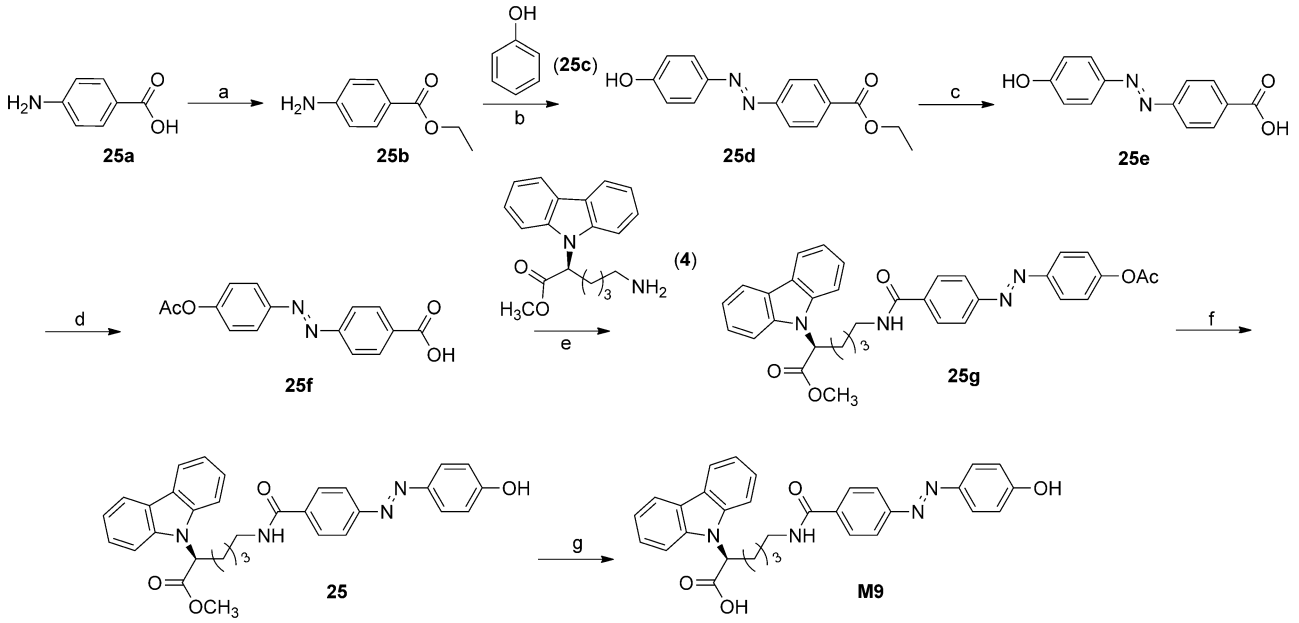
A series of novel Cbz-based monomers **M1**–**M12** were designed, synthesized and characterized. Monomers **M1**–**M4** contain additional reactive sites for potential oxidative polymerization, which can produce good morphology of the resultant MPs after polymerization. Monomers **M5**–**M12** were synthesized following multistep synthetic routes in good to high isolated yields. Due to their dual conducting carbazole or carbazole/thiophene/pyrrole and COOH functionalities, these novel monomers can give interesting opportunities for the functionalization/decoration of various polymeric and non-polymeric surfaces, matrices, and nonfunctional nanomaterials in their monomeric states or as polymeric MPs. The oxidative fabrication of corresponding MPs arising from these monomers is in progress.

Experimental Section

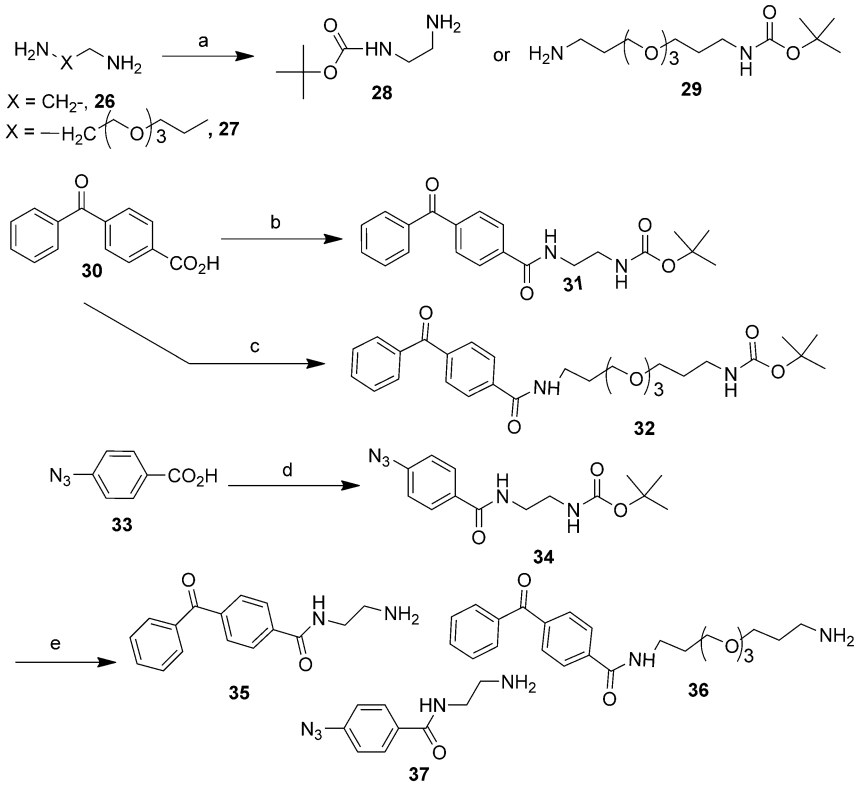
General remarks: Reactions were performed under nitrogen and were magnetically stirred. Solvents were distilled from appropriate dying agent prior to use. All reagents were obtained commercially from Sigma–Aldrich and used as received without any further purification unless otherwise noted. Chromatographic purification of products were accomplished using flash chromatography on Merck silica gel 60 (0.040–0.063) 230–400 mesh ASTM. Room temperature (RT) refers to 20–22 °C. All reactions were monitored by TLC with Macherey–Nagel pre-coated aluminum foil sheets (0.20 mm with fluorescent indicator UV_{254}). Compounds were visualized with UV light at 254 nm and 365 nm. Melting points were measured on a Fargo MP-1D and are uncorrected. Fourier transformed infrared (FTIR) spectra were recorded on a Bruker TENSOR 27 spectrometer at a resolution better than 1.0 cm^{-1} for the indicated wavelength spectral window (400–4000 cm^{-1}).



Scheme 5. Synthesis of monomer **M7**–**M8**. *Reagents and conditions*: a) 1. amine **4** (1.0 mmol), acid chloride (2.0 mmol), Et_3N, CH_2Cl_2, 0 °C, 2 h, 61 %; 2) amine **4** (2.0 mmol), acid chloride (1.0 mmol), Et_3N, CH_2Cl_2, 0 °C→rt, 30 min, 85 %; c) alc. KOH, CH_3OH/toluene (2:1), 60–70 °C, 2–3 h, then H_3O^+, 0 °C, 30 min, 90–93 %.



Scheme 6. Synthesis of monomer **M9**. *Reagents and conditions*: a) EtOH, H_2SO_4, reflux, 4 h; b) 1. $NANO_2$, 1 M aq HCl, 0 °C, 30 min; 2. **25c**, $NaHCO_3$, 0 °C, 1 h, 81 %; c) alc. KOH, EtOH, reflux, 4 h, then H_3O^+, 93 %; d) pyridine, Ac_2O, rt, 2 h, 92 %; e) 1. PCl_5, $CHCl_3$, rt, 2 h; 2. amine **4**, Et_3N, CH_2Cl_2, rt, 12 h, 65 %, two steps; f) K_2CO_3, CH_3OH, rt, 30 min, 99 %; g) alc. KOH, CH_3OH/toluene (2:1), 60 °C, 4 h, then H_3O^+, 0 °C, 30 min, 93 %.

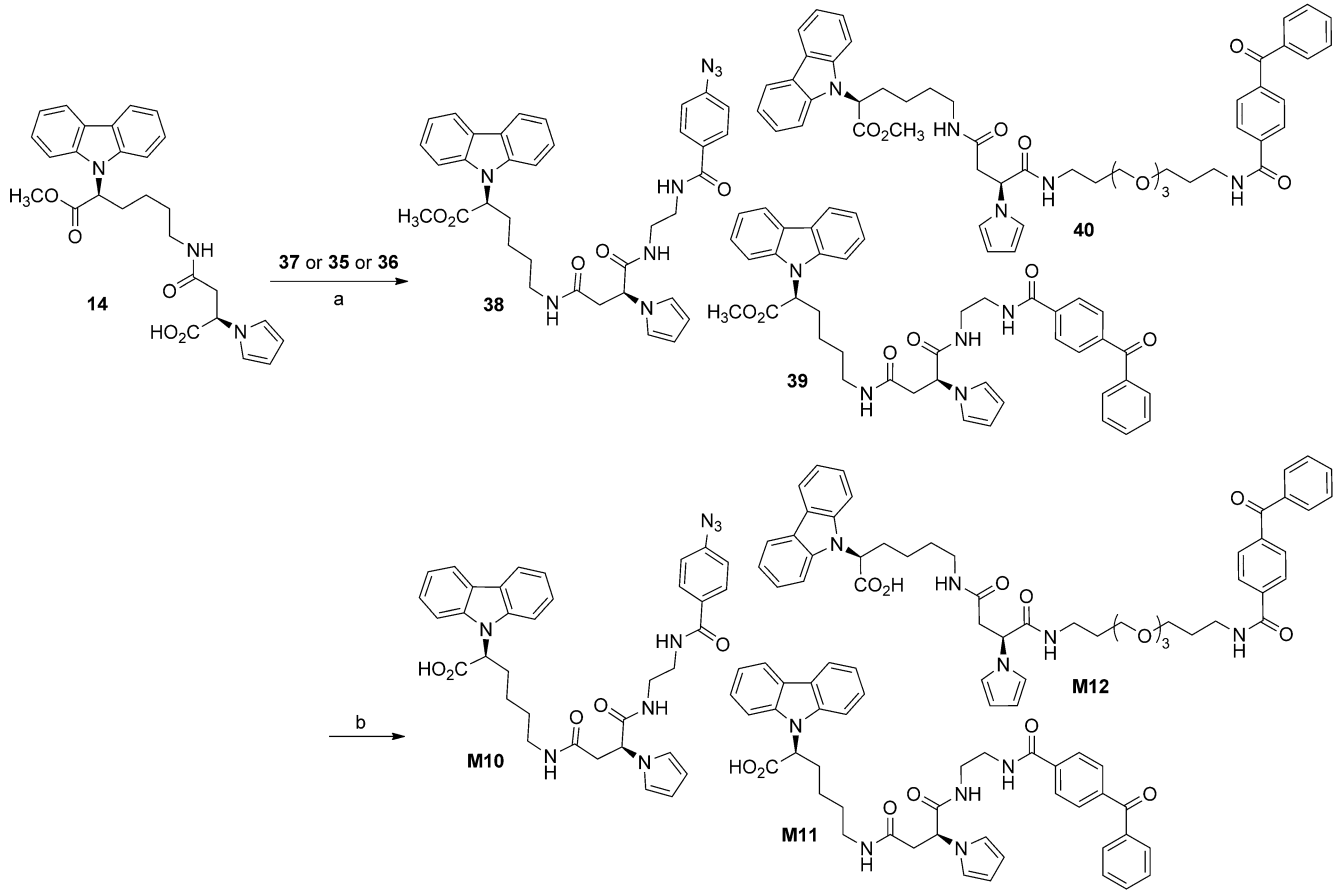


Scheme 7. Synthesis of amine **35**, **36** and **37**. *Reagents and conditions*: a) BOC_2O, $CHCl_3$, 0 °C→rt, 12 h; b) 1. PCl_5, $CHCl_3$, 0 °C, 45 min; 2. amine **28**, Et_3N, $CHCl_3$, rt, 30 min, 94 %; c) 1. EDC, Et_3N, CH_2Cl_2, 15 min, rt; 2. amine **29**, Et_3N, CH_2Cl_2, rt, 6 h, 85 %; d) 1. PCl_5, $CHCl_3$, 0 °C, 45 min; 2. amine **28**, Et_3N, $CHCl_3$, rt, 30 min, 78 %, two steps; e) TFA, $CHCl_3$, rt, 12–20 h, 95–97 %.

^1H and ^{13}C NMR spectra were recorded on a Bruker DRX spectrometer (300 MHz and 75.5 MHz for ^1H and ^{13}C, respectively). Nuclear displacements are referenced internally (TMS or solvent references). Data for ^1H NMR are reported as follows: chemical shift (δ in ppm), multiplicity (s, singlet; br, broad signal; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ in ppm). Mass spectra (MS) analyses were performed on a Waters VG-Fison AutoSpec Premier high resolution spectrometer. MALDI-TOF analyses were performed on a Bruker Autoflex mass spectrometer.

Abbreviations: carbazole (Cbz); *N,N′*-dicyclohexylcarbodiimide (DCC); 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC); *N*-hydroxybenzotriazole (HOBt); *N*-methylmorpholine (NMM); pyrrole (Pyr).

General procedure 1. Amide coupling of acid chloride and amine in the presence of base: To a stirred solution of amine, (S)-



Scheme 8. Synthesis of monomer **M10**–**M12**. *Reagents and conditions*: a) 1. EDC, HOBt, Et_3N, CH_2Cl_2, 30 min, rt, 5–12 h; 2. amine **37** (for **38**/**M10**) or **35** (for **39**/**M11**) or **36** (for **40**/**M12**), CH_2Cl_2, rt, 6–12 h, 65–70%; b) 1. alc. KOH, 50–60 °C, 3–7 h; 2. H_3O^+, 0 °C, 30 min, 72–91%.

methyl 6-amino-2-carbazol-9-yl-hexanoate **4** (1.0 mmol) in dry CH_2Cl_2 (10 mL) was added dry Et_3N (0.5 mL) at 0 °C under nitrogen atmosphere. Acid chloride (1.0 mmol) in dry CH_2Cl_2 was then added dropwise to the reaction mixture. The reaction mixture was brought to RT and stirred for 2–3 h. Evaporation of the volatiles under reduced pressure gave a thick oily residue, which was purified by flash chromatography on silica gel (230–400 mesh) using CH_2Cl_2/MeOH (98:2) as eluent to obtain a solid.

General procedure 2. Amide coupling of acid and amine in the presence of DCC, HOBt and *N*-methyl morpholine/Et_3N: A mixture of acid (1.0 mmol), HOBt (1.10 mmol), DCC (1.10 mmol) and *N*-methyl morpholine/Et_3N (2.4 mmol) in dry CH_2Cl_2 (10 mL) was stirred at RT under nitrogen atmosphere for 15–30 min. Then a solution of amine **4** (1.0 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise into the reaction mixture. A thick gelatinous precipitate was observed once the addition was completed. The reaction mixture was allowed to stir under same condition for 30 min. After completion of the reaction (TLC), the precipitated solid was filtered, and the filtrate was washed successively with ice-cold dil. HCl (5.0 mL), saturated aq $NaHCO_3$ (5 mL), and brine (2×10 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure provided gummy residue, which was purified by flash column chromatography on silica gel (230–400 mesh) using CH_2Cl_2/MeOH (99:1→98:2) to furnish a solid.

General procedure 3. Amide coupling of acid and amine in the presence of EDC, HOBt and *N*-methyl morpholine/Et_3N: To a stirred solution of acid (1.0 mmol) in CH_2Cl_2 (10 mL) was added EDC (1.0 mmol), HOBt (1.0 mmol) and Et_3N (1.5–2.0 mmol, excess) successively at RT under nitrogen atmosphere to give a clear solution. Amine (1.0 mmol) in CH_2Cl_2 (5 mL) was added to this solution, which turned from clear to turbid. The reaction was kept stirring overnight at RT. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with brine (2×20 mL). After drying and evaporation, the crude residue was purified by flash column chromatography (CH_2Cl_2/CH_3OH, 9.9:0.1→9.8:0.2) to afford a solid.

General procedure 4. Hydrolysis of ester to the corresponding acid: To a solution of methyl ester (1.0 mmol) in CH_3OH (10 mL)/toluene (5 mL) was added methanolic KOH (2–3 mmol) at RT. The reaction mixture was heated at 60–80 °C for 5 h. After cooling to 0 °C, 1 M aq HCl was added dropwise for acidification to pH 3–4, and the mixture was extracted with EtOAc (2×30 mL). The combined organic extracts were washed with water (2×20 mL), dried over anhydrous Na_2SO_4, and filtered. Removal of solvent under reduced pressure provided.

(*S*)-2-(9*H*-Carbazol-9-yl)-6-(thiophene-2-carboxamido)hexanoic acid (M1): To a solution of (*S*)-2-carbazol-9-yl-6-[(thiophene-2-carbonyl)-amino]-hexanoic acid methyl ester (**5**) (0.370 g, 0.880 mmol) in CH_3OH (10 mL)/toluene (5 mL) was added methanolic KOH (0.099 g, 1.77 mmol) at RT. The reaction mixture was heated at

60 °C for 5 h. After cooling to 0 °C, 1 M aq HCl was added dropwise for acidification to pH 3–4, and the mixture was extracted with EtOAc (2×30 mL). The combined organic extracts were washed with water (2×20 mL), dried over anhydrous Na_2SO_4, and filtered. Removal of solvent under reduced pressure provided **M1** as a white solid (0.305 g, 85%).

(*S*)-2-(9*H*-Carbazol-9-yl)-6-(1*H*-pyrrole-2-carboxamido)hexanoic acid (M2): white solid (0.310 g, 86%) was obtained following general procedure 4.

(*S*)-2-(9*H*-Carbazol-9-yl)-6-(2-(thiophen-3-yl)acetamido)hexanoic acid (M3): White solid (0.270 g, 86%).

(*S*)-2-(9*H*-Carbazol-9-yl)-6-{(*S*)-3-carboxy-3-(1*H*-pyrrol-1-yl)propanamido)hexanoic acid (M4): White solid (0.230 g, 95%).

2-Carbazol-9-yl-6-[2-(3-{[(5-carbazol-9-yl-5-carboxy-pentylcarbamoyl)-methyl]-carbamoyl}-benzoylamino)-acetylamino]-hexanoic acid (M5): White solid (0.260 g, 88%).

2-Carbazol-9-yl-6-[2-(4-{[(5-carbazol-9-yl-5-carboxy-pentylcarbamoyl)-methyl]-carbamoyl}-benzoylamino)-acetylamino]-hexanoic acid (M6): White solid (0.290 g, 92%).

(*S,E*)-4-((4-(5-(9*H*-Carbazol-9-yl)-5-carboxypentylcarbamoyl) phenyl)diazenyl)benzoic acid (M7): Red solid (0.065 g, 90%).

(*S*)-6-(4-((*E*)-(4-((*S*)-5-(9*H*-Carbazol-9-yl)-6-methoxy-6-oxohexylcarbamoyl)phenyl)diazenyl)benzamido)-2-(9*H*-carbazol-9-yl)hexanoic acid (M8): Red solid (0.063 g, 93%).

(*S,E*)-2-(9*H*-Carbazol-9-yl)-6-(4-(4-hydroxyphenyl)diazenyl)benzamido)hexanoic acid (M9): Red solid (0.045 g, 93%).

(*S*)-6-{(*S*)-4-(2-(4-Azidobenzamido)ethylamino)-4-oxo-3-(1*H*-pyrrol-1-yl)butanamido)-2-(9*H*-carbazol-9-yl)hexanoic acid (M10): White solid (0.190 g, 91%).

(*S*)-6-{(*S*)-4-(2-(4-Benzoylbenzamido)ethylamino)-4-oxo-3-(1*H*-pyrrol-1-yl)butanamido)-2-(9H-carbazol-9-yl)hexanoic acid (M11): White solid (0.180 g, 72%).

(18*S*,26*S*)-1-(4-Benzoylphenyl)-26-(9*H*-carbazol-9-yl)-1,17,20-trioxo-18-(1*H*-pyrrol-1-yl)-6,9,12-trioxa-2,16,21-triazaheptacosan-27-oic acid (M12): White solid (0.395 g, 86%).

Supporting Information: Complete details of all synthetic procedures together with characterization data (IR, ^1H, ^{13}C NMR, and HRMS/MS) for all intermediate and final compounds is available as Supporting Information under http://dx.doi.org/10.1002/open.201500059.

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