

Cross Olefin Metathesis for the Selective Functionalization, Ferrocenylation, and Solubilization in Water of Olefin-Terminated Dendrimers, Polymers, and Gold Nanoparticles and for a Divergent Dendrimer Construction

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Abstract: Olefin cross metathesis was used to efficiently functionalize polyolefin dendrimers, polymers, and gold nanoparticles using the second-generation Grubbs catalyst. In these structures, the tethers were lengthened to prevent the facile cross metathesis that otherwise predominates in polyolefin dendrimers having short tethers. This synthetic strategy allows the one-step access to polyacid, polyester, and polyferrocenyl structures from polyolefins. Cross metathesis is also used to efficiently achieve an iterative divergent dendritic construction. All the cross metathesis reactions were monitored by ¹H NMR showing the chemo-, regio-, and stereoselectivity. MALDI-TOF mass spectrometry was a very useful technique to confirm the efficiency of this synthetic strategy.

Introduction

Olefin metathesis¹ has recently emerged as a powerful and convenient synthetic technique in organic chemistry and polymer science with the development of well-known catalysts that possess high tolerance toward functional groups.¹ Ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP) are possibly the most popular facets of olefin metathesis, because of their considerable impact on the synthesis of biologically important cyclic compounds and polymers, respectively.¹

Olefin metathesis has also transformed the way chemists design new molecular structures. Remarkable examples can be found in transition-metal architectures such as RCM metathesis of olefin-terminated ligands.^{2,3} RCM was also the synthetic approach chosen by the Gladysz,² van Koten⁴ and Newkome⁴ groups to construct giant ring structures. Zimmerman and his

group applied the RCM to dendrimer chemistry and showed that this reaction successfully allows molecular imprinting inside dendrimers and its application to the fabrication of nanotubes.⁵

Compared with RCM and ROMP, cross metathesis (CM) remains an underrepresented area of olefin metathesis. This has been predominantly the result of several factors: (i) low catalyst activity to effect a reaction without a strong enthalpic driving force (such as ring-strain release in ROMP) or the entropic advantage of intramolecular reactions (such as RCM); (ii) low product selectivity for the CM product; and (iii) poor stereoselectivity in the newly formed olefin.¹ Blechert et al. showed, however, that the use of excess of one olefin together with that of Schrock's Mo catalyst^{1c} favors the formation of the cross product, whereas steric factors favor *E* stereoselectivity.⁶ Grubbs' group categorized four types of olefins by reactivity and rationalized a useful general mode that predicts the product selectivity and stereoselectivity in CM.^{7b} They have shown that, when a terminal olefin is metathesized with catalyst A (second-generation Grubbs catalyst), in the presence of another olefin

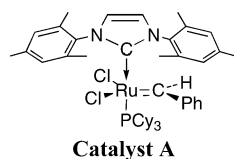
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bearing a strongly electron-withdrawing substituent, the stereoselectivity leads to high yields of the *E* functionalized cross olefin.⁷



Despite the usefulness of this property that has been applied in organic synthesis,⁷ its application to functionalization of nanostructures is still scarce.⁸ Liang and Fréchet used CM to incorporate small guest molecules into the interior of a dendrimer bearing 22 allyl groups throughout the interior.^{8a} Our group recently reported the construction of organic cyclophane capsules by triple RCM followed by CM between allyl termini.⁹ Functionalization of structures such as dendrimers, polymers, or nanoparticles is considerably more challenging than that of mono-olefin molecules, because it requires a clean and quantitative reaction to avoid the formation of mixtures among the branch termini.¹⁰

CM in polyolefin molecules is often condemned by the possibility of intramolecular RCM reaction or by the intermolecular cross-linking. Our challenge now is to show that polyolefin molecules can be efficiently functionalized by CM using catalyst **A**.

We have reported, in a preliminary form, the monofunctionalization of dendrimers with carboxylic acid and ester termini by CM, using catalyst **A** in the presence of acrylic acid and methyl acrylate, respectively.¹¹ The intradendritic RCM was avoided by lengthening the dendrimer tethers, which cancelled the possibility to form five- or six-membered rings by RCM. The use of catalyst **A** in the presence of an electron-deficient olefin favored CM and avoided interdendritic cross-linking.

After the remarkable results obtained using catalyst **A** in terms of selectivity in cross metathesis of polyolefin dendrimers with methyl acrylate, we have now generalized the reaction to other acrylate derivatives that contain ferrocenyl groups or dendronic bricks. We have extended this synthetic approach to efficiently functionalize, by CM, different kinds of structures such as dendrimers, polymers, and gold nanoparticles (AuNPs) with acid, ester, and ferrocenyl termini. In this work, we also show that CM can be an astute strategy to iteratively achieve divergent dendrimer construction.

Results and Discussion

1. Functionalization of Dendrimers by Cross Metathesis.

CM was first applied to the known nonallyl core **1**, $C_6H_5\{C(CH_2CH=CH_2)_3\}_3$, synthesized by the $CpFe^+$ -induced activation of mesitylene under ambient conditions in the presence of KOH and allyl bromide in THF,¹² followed by photochemical decomplexation.¹³ Our group showed that the nonallyl core **1** provides organometallic and organic cyclophane capsules such as **2**, in the presence of catalyst **A**. Two of the three allyl branches of the triallyl tripods readily undergo RCM, and the remaining allyl branch reacts intermolecularly by CM of the allyl termini forming the capsules (Scheme 1).⁹ The same reaction in the presence of an electron-deficient olefin such as acrylic acid or methyl acrylate avoids the formation of the capsules. Even if the RCM is always the most favored reaction, the third allyl branch, in the presence of catalyst **A**, undergoes only stereoselective CM with the acrylate derivative (electron-deficient olefin), affording the bifunctionalized molecules **3a** and **3b** (Scheme 1).

To achieve the monofunctionalization of the dendrimers, we have lengthened the dendritic tethers to avoid the formation of the favored five- or six-membered rings by RCM. This was achieved by hydrosilylation^{14,15} of **1** with $HSi(Me)_2CH_2Cl$ followed by Williamson reaction with $p.OHC_6H_4O(CH_2)_9CH=CH_2$, **4**, giving the nonaolefin **6**.

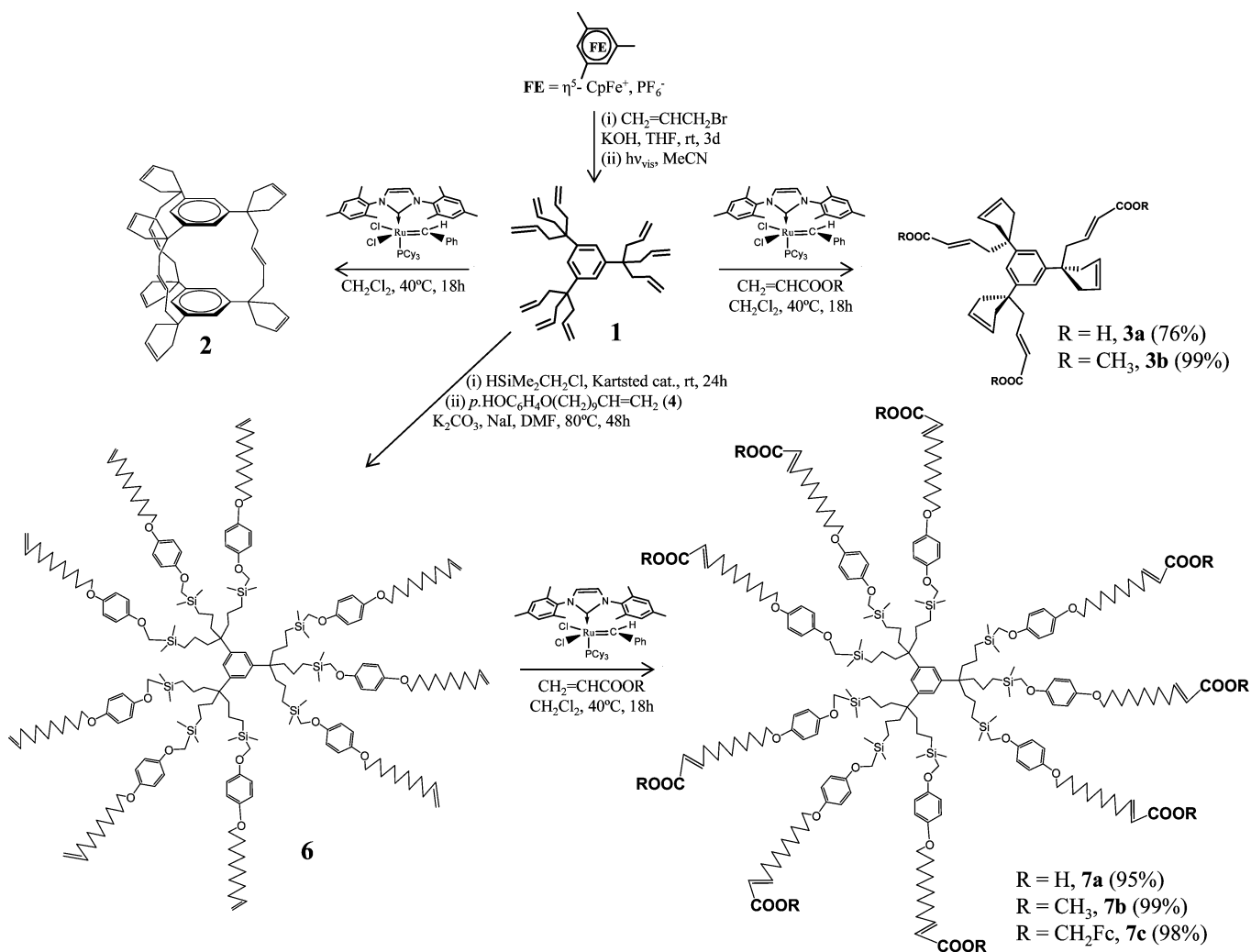
Since polyferrocenyl dendrimers present interesting applications in nanoelectronics because of their redox properties, we have now synthesized an acrylate derivative that contains a ferrocenyl group (ferrocenylmethyl acrylate, **5**) to introduce it in the dendrimer periphery by CM. This synthesis was achieved by reaction of acryloyl chloride with ferrocenemethanol in dichloromethane in the presence of triethylamine.¹⁶

Contrary to that of **1**, the metathesis reaction of **6** with $CH_2=CHCO_2R$ ($R = H, CH_3$, and CH_2Fc , $Fc =$ ferrocenyl) selectively yields the CM products **7a**, **7b**, and **7c**, resulting from stereoselective terminal olefin functionalization (Scheme 1 and Figure 1). Likewise, the tethers of the known 27- and 81-allyl dendrimers¹⁵ (G_1 and G_2), resulting from sequential hydrosilylation of **1** with $HSiMe_2CH_2Cl$ and reaction with the dendron $p.HOC_6H_4C(allyl)_3$,¹⁷ were lengthened using the same synthetic strategy, to give the new 27- and 81-olefin dendrimers **8** and **10**. These dendrimers were also submitted to the metathesis reaction in the presence of catalyst **A** and the acrylate derivatives, efficiently yielding only the CM products (eqs 1 and 2).

All the dendrimers were characterized by 1H , ^{13}C , and ^{29}Si NMR spectroscopy and elemental analysis. In the 1H NMR spectra, we can clearly see the complete disappearance of the terminal olefinic protons at 5.8 (multiplet) and 4.9 ppm (triplet) and the appearance of the new internal olefinic protons at 7.0

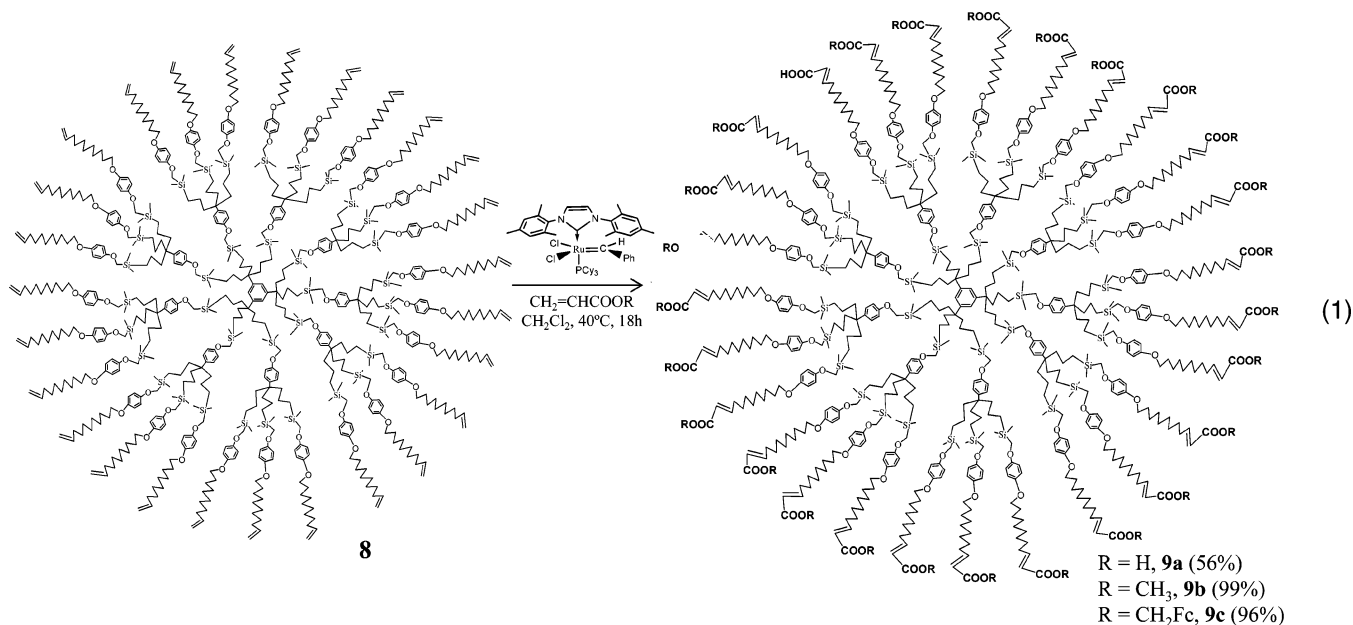
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Scheme 1. Bifunctionalization of the Nonallyl Core, Lengthening of the Dendrimer Tethers, and Efficient Monofunctionalization by Cross Metathesis

(multiplet) and 5.8 ppm (doublet) (Figure 1). No other olefinic protons are present in the ^1H NMR spectra of the functionalized

dendrimers showing the absence (at the NMR accuracy) of the intra- and interdendritic metathesis between the allyl termini



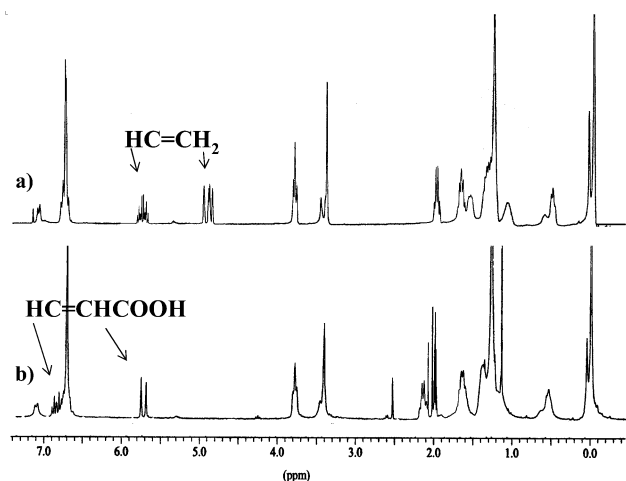


Figure 1. (a) ^1H NMR spectrum of dendrimer **10**. (b) ^1H NMR spectrum of **11a**. By comparing these two ^1H NMR spectra, it is possible to see that the CM reaction is complete (at the NMR accuracy) at the dendrimer periphery (disappearance of the allyl protons in (a) and appearance of the olefin protons in (b)) and that only the trans isomer is obtained (complete absence of cis protons around 6.4 ppm in (b)).

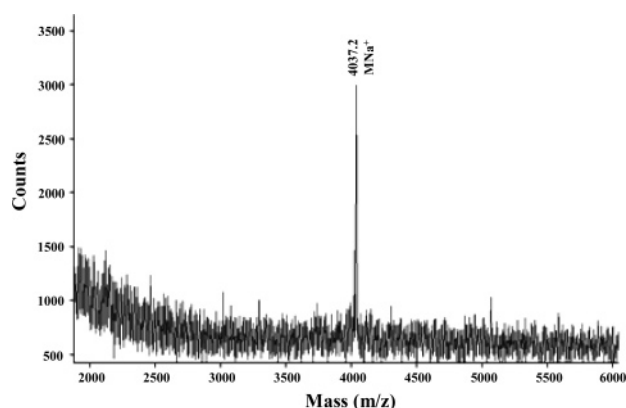


Figure 2. MALDI-TOF mass spectra of **7b**.

(otherwise, a singlet would appear at 5.5 ppm). The new functionalized dendrimers only contain the trans isomers, because otherwise the cis conformation would present the olefinic protons at 6.4 and 6.0 ppm. These NMR data (for NMR spectra, see the Supporting Information, SI, pp 36–37) show that the functionalization of the dendrimers by CM is chemio-, regio-, and stereoselective.

In addition, the MALDI-TOF mass spectra of **7a**, **7b**, **7c**, **9a**, and **9b** show the corresponding molecular peaks (Figure 2 and SI, pp 44–48), which confirms the efficiency of the functionalization strategy. In particular, in Figure 2, the MALDI-TOF mass spectrum of **7b** shows the corresponding molecular peak at 4037.2 (calcd for $\text{C}_{234}\text{H}_{372}\text{Si}_9\text{O}_{36}\text{Na}$: 4037.3), and in SI Figure 4 (SI, p 44), the mass spectrum of **9b** shows the molecular peak 13 813.1 (calcd for $\text{C}_{801}\text{H}_{1272}\text{Si}_{36}\text{O}_{117}\text{Na}$: 13 808.9). Overall, the mass and NMR spectra of the cross metathesis products show that the conversions are larger than 95%.

The dendrimers were also characterized by size exclusion chromatography (SEC). The size exclusion chromatograms shown in Figure 3 with Gaussian-type distributions indicate monodispersities (polydispersity indices between 1.00 and 1.02)

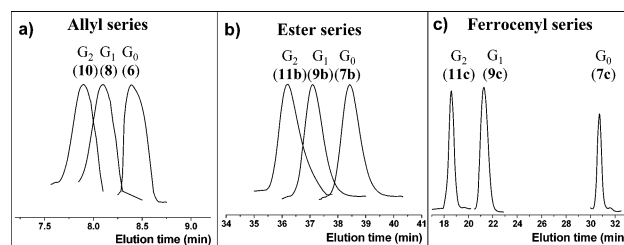


Figure 3. SEC of the three generations of dendrimers (respectively, 9, 27, and 81 tethers): (a) allyl dendrimers (before functionalization by cross metathesis), (b) ester dendrimers functionalized by CM, and (c) ferrocenyl dendrimers functionalized by CM. (Polydispersity indices between 1.00 and 1.02.)

of the three generations of polyallyl, polyester, and polyferrocenyl dendrimers, confirming the size progression from a generation to the next one and including the inexistence of cross-linking between the dendrimers in the metathesis reaction.

Cross metathesis thus proved to be an efficient strategy to cleanly synthesize polyacid, polyester, and polyferrocenyl dendrimers in one step from polyolefin dendrimers with high chemio-, regio-, and stereoselectivity. The polyferrocenyl dendrimers **7c**, **9c**, and **11c** present a single, fully reversible redox wave in cyclic voltammetry at 610 mV vs FcCp^* ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$), for all the equivalent (but distant) ferrocenyl groups whose potentials are similar, the electrostatic factor being apparently very weak (Chart 1).¹⁸ These dendrimers present potential applications in molecular electronics because of their nanosize and high redox stability.¹⁸

The polycarboxylic acid dendrimers give water- or methanol-soluble sodium carboxylate salts upon contact with aqueous NaOH or NaOH in methanol. Water-soluble dendrimers are used for applications such as molecular micelles, cation binding, and vector to drug delivery.¹⁹ The polycarboxylic acid dendrimers are also very useful for their reactions with various amines, a further functionalization procedure. For instance, reaction of the new amine dendron $\text{N}[(\text{CH}_2)_4\text{Fc}]_3$ (Fc = ferrocenyl), **12**, with **11a** gives the supramolecular 243-ferrocenyl dendrimer **13** (eq 3) showing a single wave in cyclic voltammetry (SI).¹⁸

Up to 81 ammonium carboxylate linkages might form, which is shown by the change of solubility from **11a** that is insoluble in methylene chloride (but soluble in acetone) to **13** that becomes soluble in methylene chloride. Moreover, the ^1H and ^{13}C NMR signals of the methylene groups attached to the carboxylate and amine groups, respectively, are strongly shifted in **13** compared to the precursors **11a** and **12** (the NCH_2 signal of **12** at

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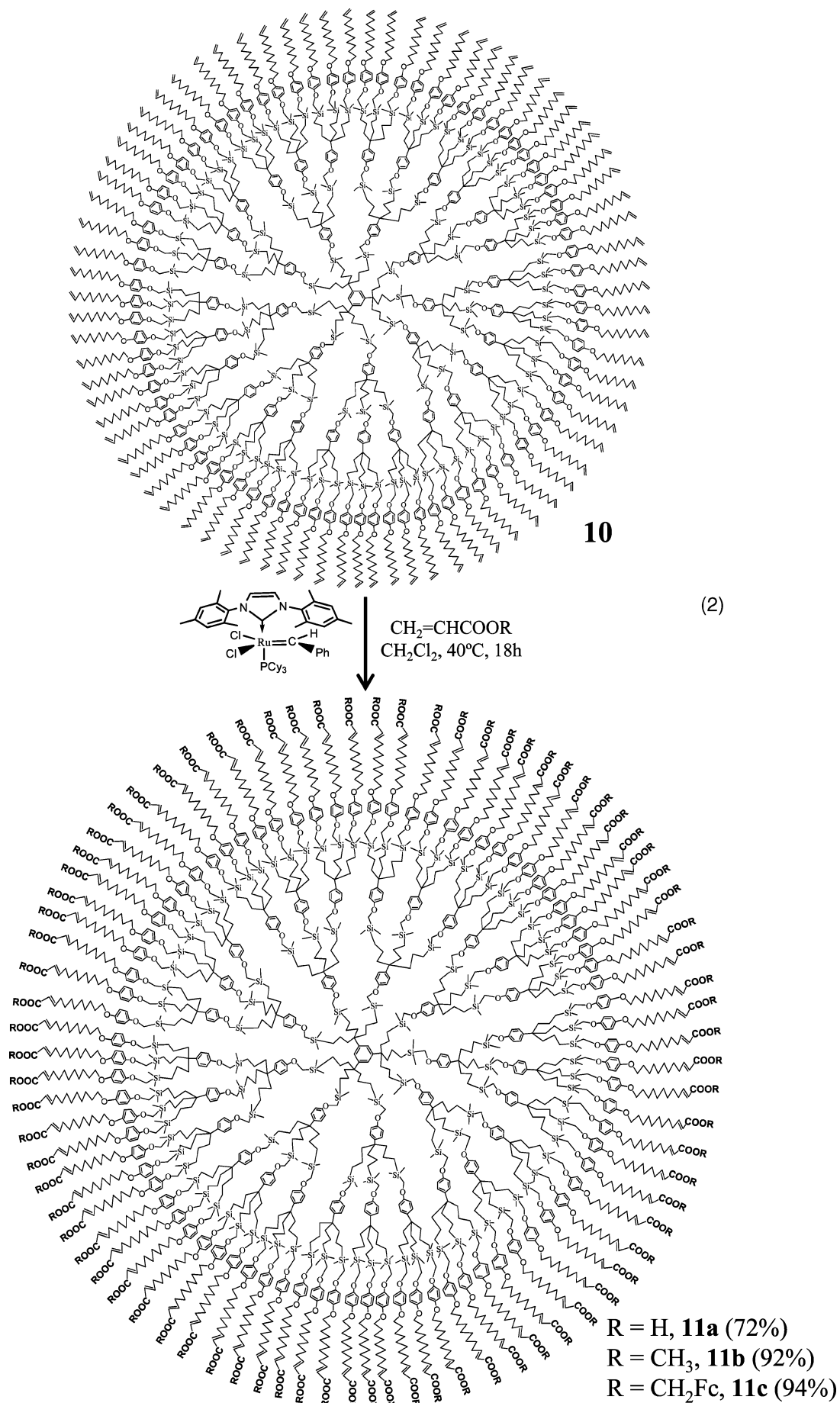
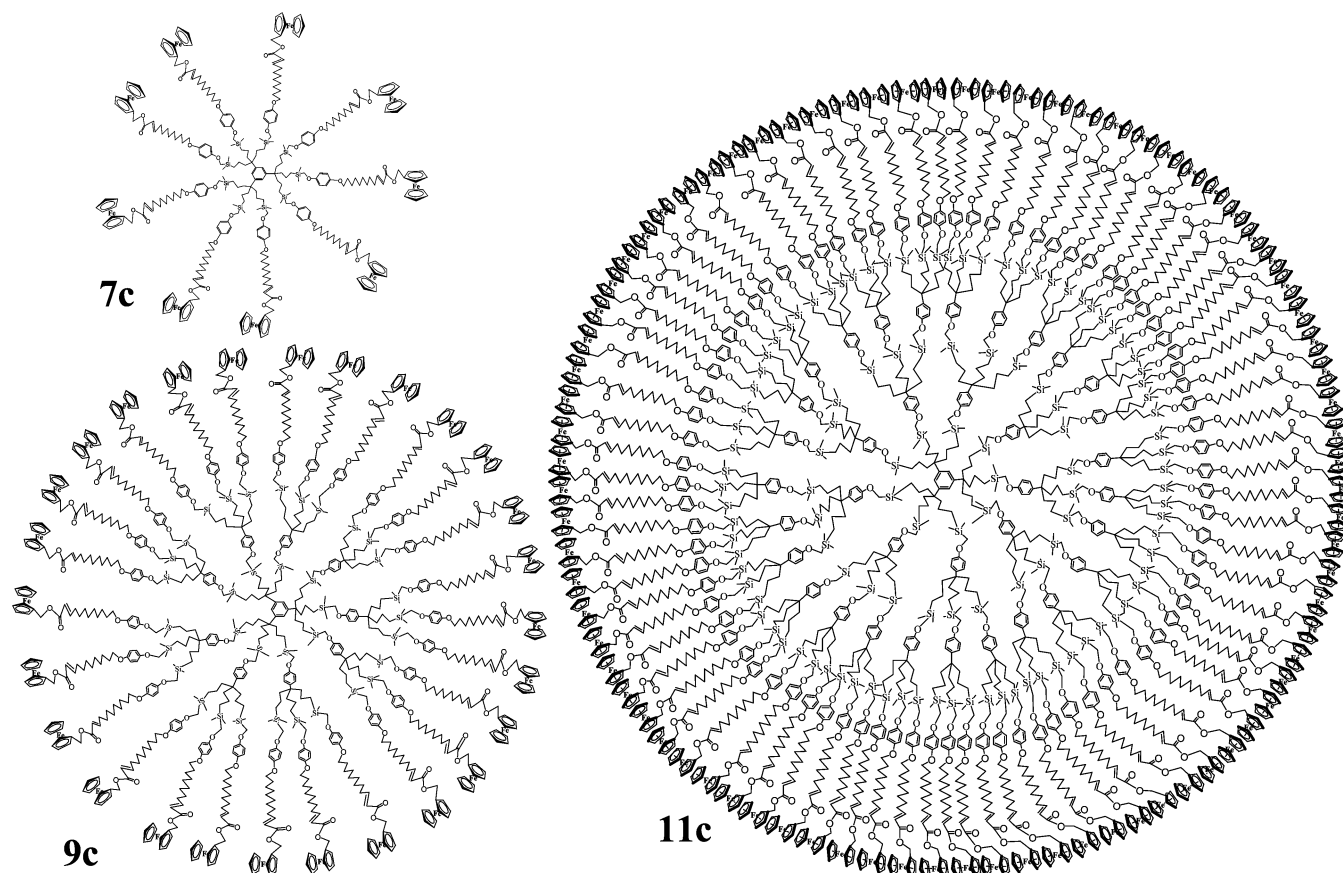
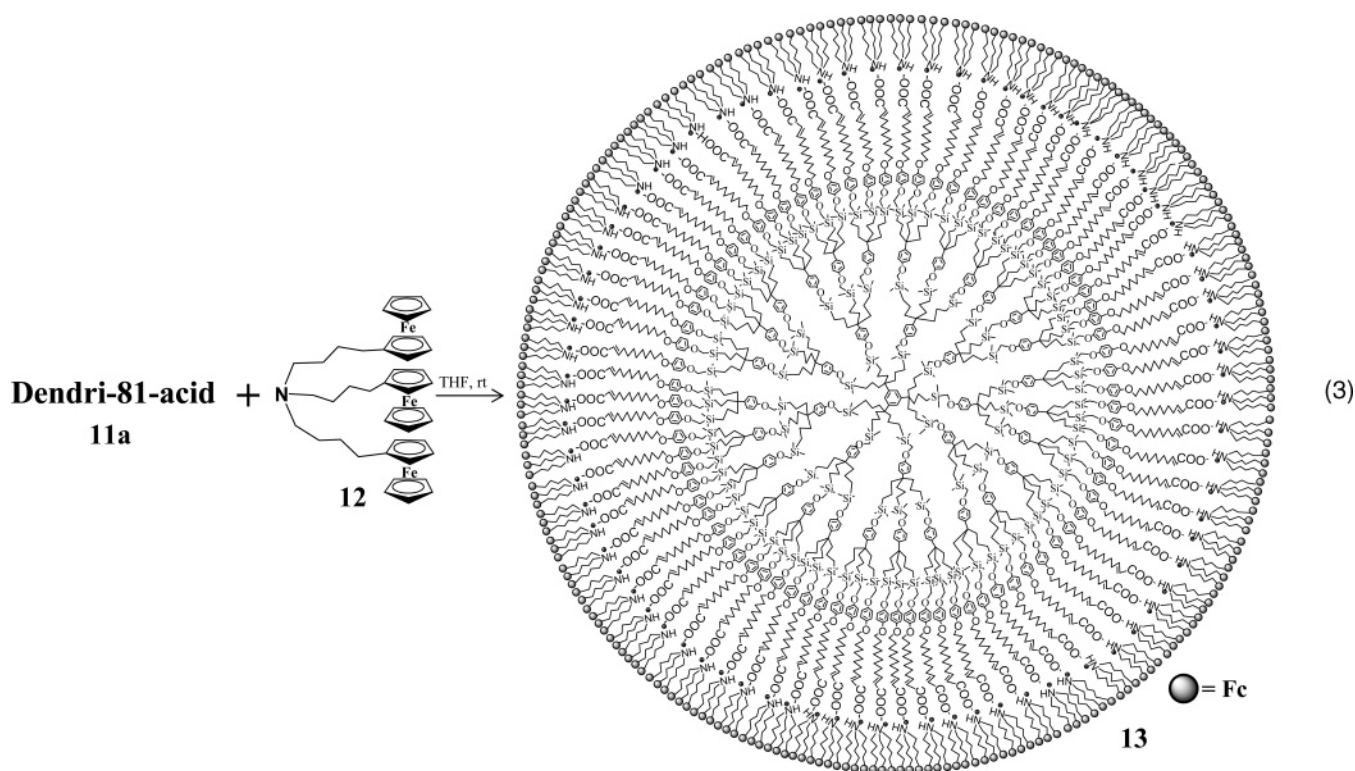


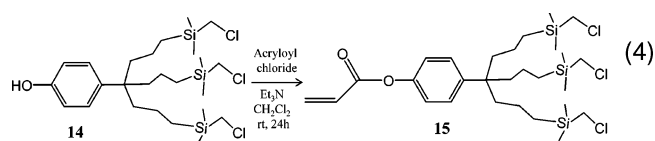
Chart 1. Ferrocenyl Dendrimers **7c**, **9c**, and **11c**, Obtained Directly by Cross Metathesis from the Polyolefin Dendrimers **6**, **8**, and **10**

2.4 ppm is shifted downfield to 2.7 ppm, and the olefin proton of **11a** at 7.0 ppm is shifted upfield at 6.8 ppm in **c**) (SI, p 34).

2. Dendritic Construction by Cross Metathesis. CM can now be used as an efficient synthetic strategy for

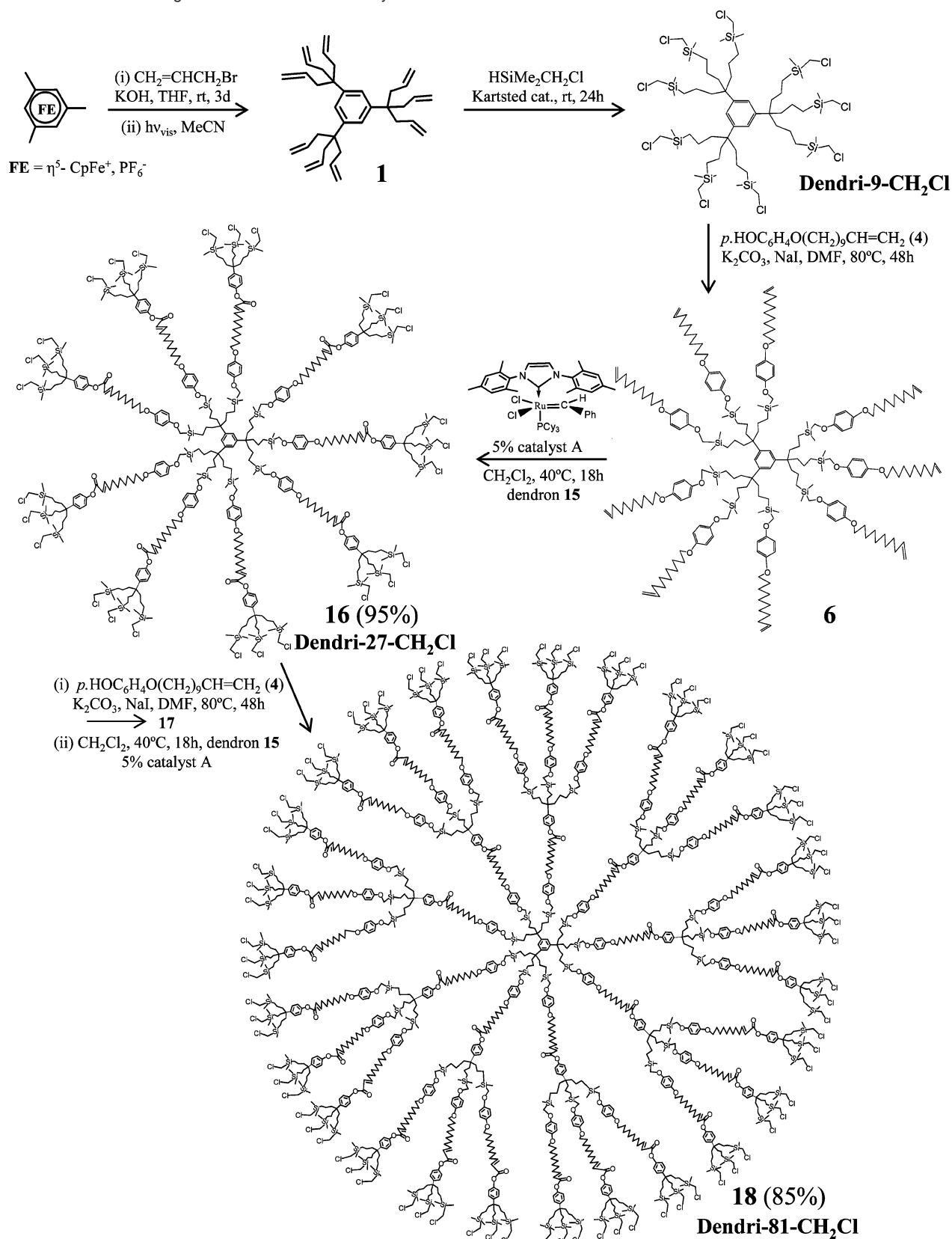
iterative divergent dendritic construction. This could indeed be achieved by functionalizing the focal point of the phenolic dendron (**14**) with the acrylate function (**15**) (eq 4).

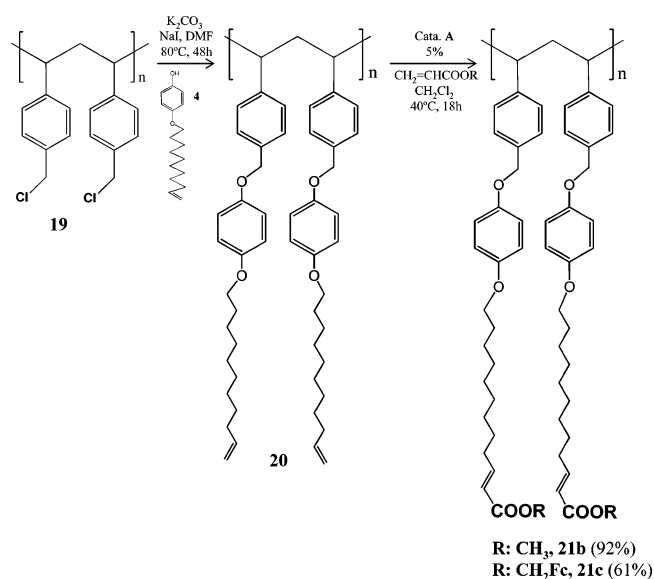




This dendron was used as an electron-deficient olefin in CM reaction with dendrimer **6**, using catalyst **A**. This reaction quantitatively yielded a 27-chloromethyl dendrimer, **16**, that is suitable to continue the dendritic construction. Reaction of

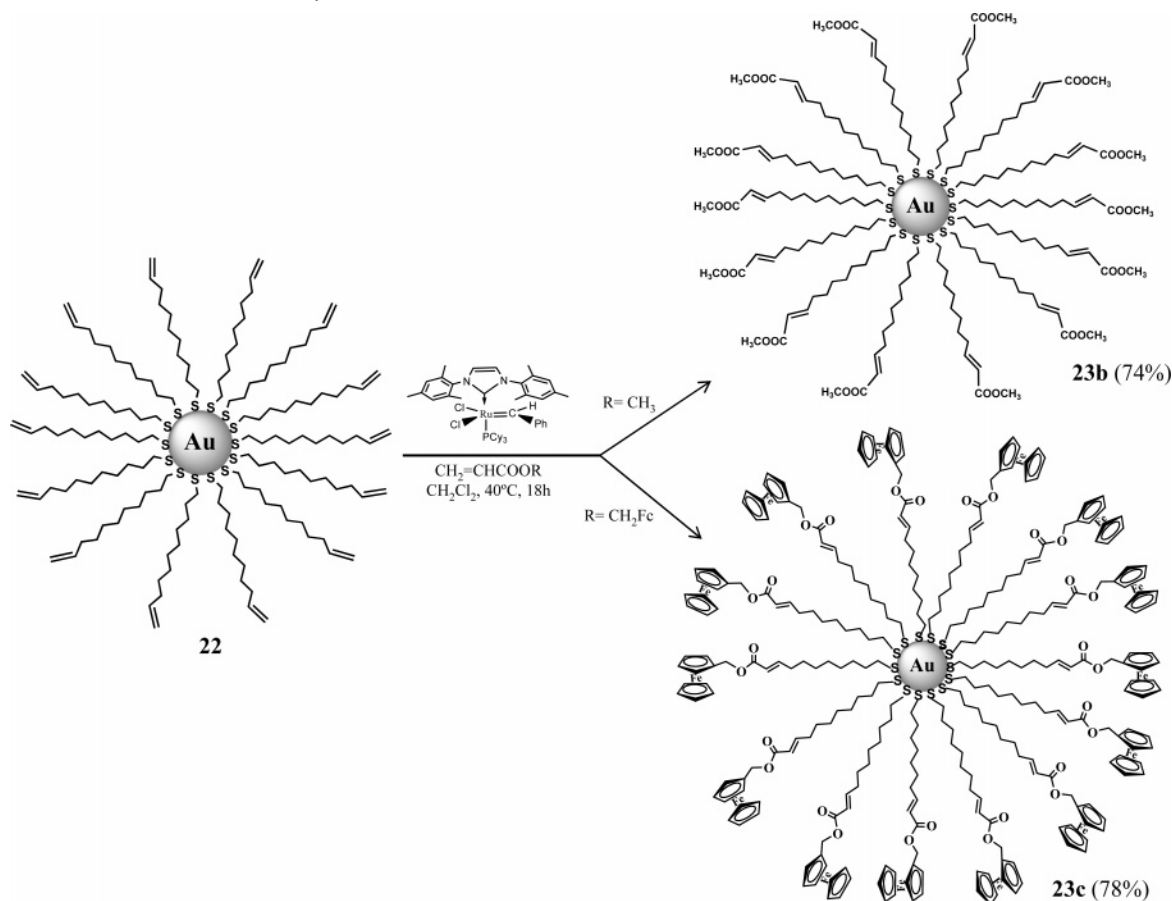
Scheme 2. Interactive Divergent Dendritic Construction by Selective Cross Metathesis



Scheme 3. Functionalization of Polymers by Olefin Cross Metathesis

dendrimer **16** with *p*.HOC₆H₄O(CH₂)₉CH=CH₂ (**4**) yielded the dendrimer **17** that contains 27 long allyl tethers. CM of the dendrimer **17** with dendron **15** successfully afforded the dendrimer **18** that contains 81 chloromethyl termini (Scheme 2).

We show here two complete iterations (lengthening of dendrimer tethers and CM) in the synthesis of a new dendrimer series. The success of this strategy is evidenced by the

Scheme 4. Functionalization of AuNPs by Olefin Cross Metathesis

characterization of dendrimer **16** by mass spectrometry, showing its molecular peak at 8729.77 (calcd for C₄₅₀H₇₅₉O₃₆Si₃₆Cl₂₇-Na: 8736.90) in the MALDI-TOF spectrum (SI, p 50). The ¹H NMR of the series clearly shows the signals of the protons corresponding to the expected double bonds (see the NMR spectra in the SI, pp 38–40). Correct elemental analysis obtained for the new series of dendrimers confirms the efficiency and purity of the products obtained. In conclusion, the functionalization of dendrons with the acrylate function opens a wide range of possibilities to achieve convergent or divergent dendritic construction by selective cross metathesis.

3. Functionalization of Polymers by Cross Metathesis. The functionalization of polymers is often limited by steric problems, and polymer chemists resort to dramatic reaction conditions or high stoichiometries to achieve functionalization. We now show that cross metathesis can be a useful strategy to easily achieve the functionalization of polyolefin polymers. Classic radical polymerization of chloromethyl styrene using AIBN as an initiator yielded the chloromethyl styrene polymer (**19**). Further reaction with *p*.hydroxyphenyl undecene-1-yl ether **4**, in the presence of K₂CO₃ and NaI in DMF at 80 °C for 48 h, yielded a styrenic polymer with long olefinic tethers (**20**). This polymer was submitted to cross metathesis, using catalyst **A**, with methyl acrylate and ferrocenylmethyl acrylate (**5**), affording the corresponding ester and ferrocenyl polymers (**21b** and **21c**, respectively) (Scheme 3).

The functionalization of polymer **20** by CM was achieved using only 2 equiv per branch of reactant and 5% of catalyst, which is a remarkable feature in polymer chemistry. The

polydispersity of the polymers (1.33, obtained by SEC) did not change after CM, indicating the absence of cross-linking between the olefinic termini during the metathesis reaction (for the NMR spectra, see the SI, pp 41–42). The ferrocenyl polymer **21c** presents a single, fully reversible redox wave at 610 mV in cyclic voltammetry, for all the equivalent (but distant) ferrocenyl groups whose potentials are almost identical.¹⁸

4. Functionalization of AuNPs by Cross Metathesis. AuNPs are finding a rapidly increasing number of important applications in nanoscience, such as catalysts and optoelectronic sensors including biosensors and vectors.²⁰ Thus, cross metathesis can be a useful strategy to efficiently functionalize AuNPs.

Alkene-terminated AuNPs (**22**) were synthesized from 11-undecenethiol using the Brust method.²¹ These polyolefin AuNPs were submitted to cross metathesis, using catalyst **A**, with methyl acrylate and ferrocenylmethyl acrylate (**5**), affording the corresponding ester and ferrocenyl AuNPs (Scheme 4). The success of the metathesis reaction was confirmed by ¹H NMR that clearly shows the disappearance of the olefinic protons of **22** at 5.78 and 4.98 ppm and the appearance of the protons of the new internal double bond at 6.97 and 5.80 ppm (for the NMR spectra, see the SI, p 43).

The AuNPs were characterized by TEM before and after metathesis reaction to study the influence of the CM in the size of the AuNPs. It was found that the AuNPs **22** (before CM) have a diameter of 2.1 ± 0.3 nm, and the AuNPs **23b** (after CM) have a diameter of 2.2 ± 0.3 nm (SI, pp 50–51). There is no significant difference between the AuNPs before and after CM, thus the Grubbs catalyst only acts at the AuNPs periphery and does not change the metallic core of the AuNPs.

Characterization of the purple product **23c** by cyclic voltammetry confirmed the presence of the ferrocenyl groups in the molecule presenting a reversible redox wave at 610 mV vs. FeCp₂* (Cp* = η⁵-C₅Me₅).

Conclusion

The disclosure of this remarkable quantitative chemio-, regio-, and stereoselective cross olefin metathesis between different nanostructures and acrylate derivatives, using the catalyst **A**, provides a unique way to functionalize polyolefin dendrimers, polymers, and AuNPs. This synthetic approach allows an easy access to useful polycarboxylic acid and polyferrocenyl dendrimers in large scales from simple polymethyl benzenes in a few steps.¹⁴ Finally, CM is a new astute and efficient strategy to iteratively achieve divergent dendritic construction.

Experimental Section

General Data. Products **1**,¹² **2**,⁹ and **14**^{18c} were prepared according to the literature. Ferrocenylmethyl acrylate was synthesized by improving the reported method¹⁶ (see the synthesis of **5**, SI, p 6). Acryloyl chloride was obtained from acrylic acid and lauroyl chloride at 100 °C for 18 h and recovered with a trap-to-trap vacuum system. Methylene chloride (CH₂Cl₂) was distilled from calcium hydride just before use. All other chemicals were used as received. All manipulations were carried out using Schlenk techniques or in a nitrogen-filled Vacuum Atmosphere drylab. NMR spectra were recorded at 25 °C with a Bruker AC 300 spectrometer. All chemical shifts are reported in parts per

million (δ, ppm) with reference to Me₄Si (TMS). Elemental analyses were performed by the Center of Microanalyses of the CNRS at Lyon-Villeurbanne, France. MALDI mass spectra were recorded with a PerSeptive Biosystems Voyager Elite time-of-flight mass spectrometer.

General Procedure for the Metathesis Reactions. The polyolefin, dry CH₂Cl₂, the acrylate derivative (2 equiv per branch), and catalyst **A** (5% equivalent per branch) were successively introduced into a Schlenk flask under an inert atmosphere. The solution was stirred at 40 °C for 18 h. After the solvent was removed under vacuum, the product was washed with methanol and precipitated with dichloromethane/methanol in the case of polyester or polyferrocenyl or with THF/methanol in the case of the polycarboxylic acid dendrimers.

Synthesis of 3a. The product **3a** was synthesized from the nonallyl derivative **1** (0.050 g, 0.10 mmol), acrylic acid (0.130 g, 1.80 mmol), and catalyst **A** (0.040 g, 0.047 mmol), following the general procedure for the metathesis reactions, and it was obtained as a white solid in 76% yield (0.042 g).

¹H NMR (CD₃COCD₃, 300 MHz), δ_{ppm}: 7.19 (m, 3H, CH=CHCOOH), 7.16 (s, 3H, CH_{Ar}), 5.87 (d, 3H, CH=CHCOOH), 5.80 (m, 6H, CH=CH), 2.86 (m, 12H, CH₂CH=CH), 2.33 (m, 6H, CH₂-CH=CH). ¹³C NMR (CH₃COCH₃, 75 MHz), δ_{ppm}: 168.1 (C=O), 149.1 (CH=CHCOOH), 129.9 (CH₂CH=CHCH₂), 119.2 (CHCOOH), 39.9 and 37.1 (CH₂CH). IR (KBr), ν_{C=O}: 1711 cm⁻¹. Anal. Calcd for C₃₃H₃₆O₆: C, 74.98; H, 6.86. Found: C, 74.59; H, 6.61.

Synthesis of 3b. The product **3b** was synthesized from **1** (0.050 g, 0.10 mmol), methyl acrylate (0.155 g, 1.80 mmol), and catalyst **A** (0.040 g, 0.047 mmol), following the general procedure for the metathesis reactions, and it was obtained as a white solid in 99% yield (0.059 g).

¹H NMR (CDCl₃, 300 MHz), δ_{ppm}: 7.25 (m, 3H, CH=CHCOOCH₃), 7.08 (s, 3H, CH_{Ar}), 5.79 (d, 3H, CHCOOCH₃), 5.68 (m, 6H, CH=CH), 3.76 (s, 9H, COOCH₃), 2.71 (m, 12H, CH₂CH=CH), 2.46 (m, 6H, CH₂CH=CH). ¹³C NMR (CDCl₃, 75.00 MHz), δ_{ppm}: 167.2 (C=O), 148.8 (CH=CHCOOH), 130.2 (CH₂CH=CHCH₂), 119.1 (CHCOOH), 50.98 (COOCH₃), 39.7 and 36.7 (CH₂CH). IR (KBr), ν_{C=O}: 1732 cm⁻¹. Anal. Calcd for C₃₆H₄₂O₆: C, 75.76; H, 7.42. Found: C, 75.71; H, 7.39.

Synthesis of 7a. The nonacarboxylic acid dendrimer **7a** was synthesized from **6** (0.100 g, 0.029 mmol), acrylic acid (0.037 g, 0.52 mmol), and catalyst **A** (0.011 g, 0.013 mmol), following the general procedure for the metathesis reactions, and it was obtained as a white waxy product in 95% yield (0.107 g).

¹H NMR (CD₃COCD₃, 300 MHz), δ_{ppm}: 7.01 (s, 3H, CH arom. core), 6.95 (m, 9H, HC=CHCOOH), 6.81 (d, 36H, CH arom.), 5.82 (d, 9H, HC=CHCOOH), 3.82 (t, 18H, OCH₂), 3.41 (s, 18H, Si(CH₃)₂O), 2.18 (m, 36H, CH₂CH=CH), 1.69 (m, 36H, OCH₂CH₂ and CH₂CH₂-CH₂Si), 1.27 (m, 108H, (CH₂)₆), 1.14 (s, 18H, CH₂CH₂CH₂Si), 0.54 (s, 18H, CH₂CH₂CH₂Si), 0.051 (s, 54H, Si(CH₃)₂). ¹³C NMR (CD₃-COCD₃, 75 MHz), δ_{ppm}: 168.0 (C=O), 154.7 and 151.9 (arom. OC_q), 149.8 (CH=CHCOOH), 145.6 (arom. C_q, core), 122.0 (CH=CHCOOH), 121.1 (arom. CH, core), 114.3 and 113.8 (arom. CH), 67.6 (OCH₂-(CH₂)₈), 59.9 (SiCH₂O), 43.2 (CH₂CH₂CH₂Si), 42.0 (benzylic C_q), 33.8 (CH₂HC=CH), 29.4 and 26.0 ((CH₂)₆), 17.8 (CH₂CH₂CH₂Si), 14.6 (CH₂CH₂CH₂Si), -4.5 (SiMe₂). ²⁹Si NMR (CD₃COCD₃, 59.62 MHz), δ_{ppm}: 0.30 (SiCH₂O). IR (KBr), ν_{C=O}: 1711 cm⁻¹. MS (MALDI-TOF, *m/z*): Calcd for C₂₂₅H₃₅₄Si₉O₃₆: 3 888.03; found: 3 886.97 (M-H). Anal. Calcd for C₂₂₅H₃₅₄Si₉O₃₆: C, 69.51; H, 9.18. Found: C, 69.39; H, 8.97.

Synthesis of 7b. The nonaester dendrimer **7b** was synthesized from **6** (0.100 g, 0.029 mmol), methyl acrylate (0.045 g, 0.52 mmol), and catalyst **A** (0.011 g, 0.013 mmol), following the general procedure for the metathesis reactions, and it was obtained as a white waxy product in 99% yield (0.116 g).

¹H NMR (CDCl₃, 300 MHz), δ_{ppm}: 7.03 (s, 3H, CH arom. core), 6.94 (m, 9H, HC=CHCOOCH₃), 6.80 (d, 36H, CH arom.), 5.81 (m, 9H, HC=CHCOOCH₃), 3.81 (t, 18H, OCH₂), 3.71 (s, 18H, COOCH₃), 3.39 (s, 18H, SiCH₂O), 2.01 (m, 36H, CH₂CH=CH), 1.71 (m, 36H,

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OCH₂CH₂ and CH₂CH₂CH₂Si), 1.29 (m, 108H, (CH₂)₆), 1.14 (s, 18H, CH₂CH₂CH₂Si), 0.60 (s, 18H, CH₂CH₂CH₂Si), 0.061 (s, 54H, Si(CH₃)₂). ¹³C NMR (CDCl₃, 75 MHz), δ_{ppm}: 167.1 (C=O), 154.5 and 151.6 (arom. OC_q), 148.7 (CH=CHCOOCH₃), 145.6 (arom. C_q, core), 122.1 (CH=CHCOOCH₃), 121.1 (arom. CH, core), 114.3 and 113.8 (arom. CH), 67.6 (OCH₂(CH₂)₈), 59.9 (SiCH₂O), 50.3 (COOCH₃), 43.2 (CH₂CH₂CH₂Si), 42.0 (benzylic C_q), 33.5 (CH₂HC=CH), 29.4 and 26.0 ((CH₂)₆), 17.8 (CH₂CH₂CH₂Si), 14.6 (CH₂CH₂CH₂Si), -4.5 (SiMe₂). ²⁹Si NMR (CDCl₃, 59.62 MHz), δ_{ppm}: 0.30 (SiCH₂O). IR (KBr), ν_{C=O}: 1732 cm⁻¹. MS (MALDI-TOF, *m/z*): Calcd for C₂₃₄H₃₇₂Si₉O₃₆Na: 4037.27; found: 4037.20 (MNa). Anal. Calcd for C₂₃₄H₃₇₂Si₉O₃₆: C, 70.01; H, 9.34. Found: C, 69.78; H, 9.24.

Synthesis of 7c. The nonaferrocenyl dendrimer **7c** was synthesized from **6** (0.100 g, 0.029 mmol), **5** (0.140 g, 0.52 mmol), and catalyst **A** (0.011 g, 0.013 mmol), following the general procedure for the metathesis reactions, and it was obtained as a yellow waxy product in 98% yield (0.161 g).

¹H NMR (CDCl₃, 300 MHz), δ_{ppm}: 7.03 (s, 3H, CH arom. core), 6.96 (m, 9H, HC=CHCOOCH₂Fc), 6.80 (d, 36H, CH arom.), 5.81 (d, 9H, HC=CHCOOCH₂Fc), 4.96 (s, 18H, CH₂Fc), 4.29 and 4.17 (d, 81H, CH of Fc), 3.85 (t, 18H, OCH₂), 3.46 (s, 18H, SiCH₂O), 2.20 (m, 36H, CH₂CH=CH), 1.71 (m, 36H, OCH₂CH₂ and CH₂CH₂CH₂Si), 1.29 (m, 108H, (CH₂)₆), 1.15 (s, 18H, CH₂CH₂CH₂Si), 0.59 (s, 18H, CH₂CH₂CH₂Si), 0.09 (s, 54H, Si(CH₃)₂). ¹³C NMR (CDCl₃, 75 MHz), δ_{ppm}: 166.4 (C=O), 155.7 and 153.0 (arom. OC_q), 149.7 (CH=CHCOOCH₂Fc), 145.8 (arom. C_q, core), 121.2 (arom. CH, core), 121.1 (CH=CHCOOCH₂Fc), 115.3 and 114.7 (arom. CH), 81.7 (C_q of Fc), 69.6 (OCH₂(CH₂)₈), 68.5 (CH of Fc), 62.5 (CH₂Fc), 60.9 (SiCH₂O), 43.9 (CH₂CH₂CH₂Si), 42.0 (benzylic C_q), 32.1 (CH₂HC=CH), 29.4 and 26.0 ((CH₂)₆), 17.8 (CH₂CH₂CH₂Si), 14.6 (CH₂CH₂CH₂Si), -4.5 (SiMe₂). ²⁹Si NMR (CDCl₃, 59.62 MHz), δ_{ppm}: 0.30 (SiCH₂O). IR (KBr), ν_{C=O}: 1732 cm⁻¹. MS (MALDI-TOF, *m/z*): Calcd for C₃₂₄H₄₄₄Si₉O₃₆Fe₉: 5670.48; found: 5670.85. Anal. Calcd for C₃₂₄H₄₄₄Si₉O₃₆Fe₉: C, 68.63; H, 7.89. Found: C, 68.30; H, 8.41.

Synthesis of 9a. The 27-carboxylic acid dendrimer **9a** was synthesized from **8** (0.086 g, 0.00701 mmol), acrylic acid (0.027 g, 0.379 mmol), and catalyst **A** (0.008 g, 0.0095 mmol), following the general procedure for the metathesis reactions, and it was obtained as a colorless waxy product in 56% yield (0.0525 g).

¹H NMR (CD₃COCD₃, 300 MHz), δ_{ppm}: 7.21 (d, 18H, arom.), 6.95 (m, 27H, HC=CHCOOH), 6.82 (s, 126H, arom.), 5.82 (d, 27H, HC=CHCOOH), 3.86 (t, 54H, OCH₂CH₂), 3.50 (s, 18H, inner SiCH₂O), 3.44 (s, 54H, outer SiCH₂O), 2.19 (t, 54H, CH₂HC=CH₂), 1.72 (d, 126H, OCH₂CH₂ and CH₂CH₂CH₂Si), 1.33 (m, 324H, (CH₂)₆), 1.20 (s, 72H, CH₂CH₂CH₂Si), 0.60 (s, 72H, CH₂CH₂CH₂Si), 0.044 (s, 216H, Si(CH₃)₂). ¹³C NMR (CD₃COCD₃, 75.0 MHz), δ_{ppm}: 168.0 (C=O), 159.0 (inner arom. OC_q), 156.6 and 154.1 (outer arom. C_q), 150.4 (CH=CHCOOH), 128.1 and 113.4 (arom. CH of the dendron), 122.2 (CH=CHCOOH), 116.0 and 115.6 (arom. CH), 69.0 (OCH₂(CH₂)₈), 61.4 (outer SiCH₂O), 60.2 (inner SiCH₂O), 43.5 (CH₂CH₂CH₂Si), 42.4 (benzylic C_q), 32.8 (CH₂HC=CH), 30.2 and 26.5 ((CH₂)₆), 17.8 (CH₂CH₂CH₂Si), 14.6 (CH₂CH₂CH₂Si), -4.5 (SiMe₂). ²⁹Si NMR (CD₃COCD₃, 59.62 MHz), δ_{ppm}: 0.48 and 0.29 (inner and outer SiCH₂O). IR (KBr), ν_{C=O}: 1711 cm⁻¹. MS (MALDI-TOF, *m/z*): calcd for C₇₇₄H₁₂₁₈O₁₁₇Si₃₆Na: 13 430.2; found: 13 434.2. Anal. Calcd for C₇₇₄H₁₂₁₈O₁₁₇Si₃₆: C, 69.34; H, 9.16. Found: C, 69.07; H, 8.90.

Synthesis of 9b. The 27-ester dendrimer **9b** was synthesized from **8** (0.051 g, 0.00418 mmol), methyl acrylate (0.019 g, 0.221 mmol), and catalyst **A** (0.005 g, 0.0056 mmol), following the general procedure for the metathesis reactions, and it was obtained as a colorless waxy product in 99% yield (0.0575 g).

¹H NMR (CDCl₃, 300 MHz), δ_{ppm}: 7.19 (d, 18H, arom.), 6.95 (m, 27H, HC=CHCOOCH₃), 6.79 (d, 126H, arom.), 5.80 (d, 27H, HC=CHCOOCH₃), 3.84 (t, 54H, OCH₂CH₂), 3.71 (s, 81H, COOCH₃), 3.50 (s, 18H, inner SiCH₂O), 3.44 (s, 54H, outer SiCH₂O), 2.19 (t, 54H, CH₂HC=CH), 1.71 (d, 126H, OCH₂CH₂ and CH₂CH₂CH₂Si), 1.30 (d,

324H, (CH₂)₆), 1.19 (s, 72H, CH₂CH₂CH₂Si), 0.56 (s, 72H, CH₂CH₂CH₂Si), 0.030 (s, 216H, Si(CH₃)₂). ¹³C NMR (CDCl₃, 75 MHz), δ_{ppm}: 167.1 (C=O), 159.0 (inner arom. OC_q), 155.7 and 153.0 (outer arom. C_q), 149.7 (CH=CHCOOCH₃), 127.2 and 113.4 (arom. CH of the dendron), 120.8 (CH=CHCOOCH₃), 115.5 and 114.8 (arom. CH), 68.6 (OCH₂(CH₂)₈), 60.9 (outer SiCH₂O), 60.2 (inner SiCH₂O), 51.3 (COOCH₃), 43.0 (CH₂CH₂CH₂Si), 42.0 (benzylic C_q), 32.2 (CH₂HC=CH), 29.4 and 26.0 ((CH₂)₆), 17.6 (CH₂CH₂CH₂Si), 14.6 (CH₂CH₂CH₂Si), -4.5 (SiMe₂). ²⁹Si NMR (CDCl₃, 59.62 MHz), δ_{ppm}: 0.46 and 0.29 (inner and outer SiCH₂O). IR (KBr), ν_{C=O}: 1732 cm⁻¹. MS (MALDI-TOF, *m/z*): Calcd for C₈₀₁H₁₂₇₂O₁₁₇Si₃₆Na: 13 808.9; found: 13 813.1 (MNa). Anal. Calcd for C₈₀₁H₁₂₇₂O₁₁₇Si₃₆: C, 68.73; H, 9.16. Found: C, 68.72; H, 9.23.

Synthesis of 9c. The 27-ferrocenyl dendrimer **9c** was synthesized from **8** (0.050 g, 0.0041 mmol), **5** (0.060 g, 0.221 mmol), and catalyst **A** (0.005 g, 0.0055 mmol), following the general procedure for the metathesis reactions, and it was obtained as a yellow waxy product in 96% yield (0.074 g).

¹H NMR (CDCl₃, 300 MHz), δ_{ppm}: 7.12 (d, 18H, arom.), 6.96 (m, 27H, HC=CHCOOCH₂Fc), 6.79 (d, 126H, arom.), 5.81 (d, 27H, HC=CHCOOCH₂Fc), 4.94 (s, 54H, CH₂Fc), 4.28 and 4.16 (d, 243H, CH of Fc), 3.84 (t, 54H, OCH₂CH₂), 3.46 (s, 72H, SiCH₂O), 2.17 (m, 54H, CH₂CH=CH), 1.69 (d, 126H, OCH₂CH₂ and CH₂CH₂CH₂Si), 1.28 (d, 324H, (CH₂)₆), 1.18 (s, 72H, CH₂CH₂CH₂Si), 0.55 (s, 72H, CH₂CH₂CH₂Si), 0.078 and 0.018 (s, 216H, Si(CH₃)₂). ¹³C NMR (CDCl₃, 75 MHz), δ_{ppm}: 166.4 (C=O), 158.9 (inner arom. OC_q), 155.6 and 153.0 (outer arom. OC_q), 149.7 (CH=CHCOOCH₂Fc), 127.2 and 113.4 (arom. CH of the dendron), 121.0 (CH=CHCOOCH₂Fc), 115.2 and 114.7 (arom. CH), 81.5 (C_q of Fc), 69.6 (OCH₂(CH₂)₈), 68.6 (CH of Fc), 62.5 (CH₂Fc), 60.8 (outer SiCH₂O), 60.2 (inner SiCH₂O), 43.9 (CH₂CH₂CH₂Si), 42.0 (benzylic C_q), 32.2 (CH₂HC=CH), 29.4 and 26.0 ((CH₂)₆), 17.6 (CH₂CH₂CH₂Si), 14.6 (CH₂CH₂CH₂Si), -4.6 (SiMe₂). ²⁹Si NMR (CDCl₃, 59.62 MHz), δ_{ppm}: 0.46 and 0.29 (inner and outer SiCH₂O). IR (KBr), ν_{C=O}: 1732 cm⁻¹. Anal. Calcd for C₁₀₇₁H₁₄₈₈Si₃₆O₁₁₇Fe₂₇: C, 68.59; H, 8.00. Found: C, 68.21; H, 7.97.

Synthesis of 11a. The 81-carboxylic acid dendrimer **11a** was synthesized from **10** (0.080 g, 0.00209 mmol), acrylic acid (0.024 g, 0.340 mmol), and catalyst **A** (0.014 g, 0.0169 mmol), following the general procedure for the metathesis reactions, and it was obtained as a colorless waxy product in 72% yield (0.063 g).

¹H NMR (CD₃COCD₃, 300 MHz), δ_{ppm}: 7.21 (d, 72H, arom.), 6.95 (m, 81H, HC=CHCOOH), 6.82 (s, 396H, arom.), 5.87 (d, 81H, HC=CHCOOH), 3.86 (t, 162H, OCH₂CH₂), 3.49 (s, 234H, SiCH₂O), 2.22 (m, 162H, CH₂HC=CH₂), 1.70 (d, 396H, OCH₂CH₂ and CH₂CH₂CH₂Si), 1.33 (m, 972H, (CH₂)₆), 1.20 (s, 234H, CH₂CH₂CH₂Si), 0.59 (s, 234H, CH₂CH₂CH₂Si), 0.13 and 0.070 (s, 702H, Si(CH₃)₂). ¹³C NMR (CD₃COCD₃, 75.0 MHz), δ_{ppm}: 168.0 (C=O), 159.0 (inner arom. OC_q), 156.6 and 154.1 (outer arom. C_q), 150.4 (CH=CHCOOH), 128.1 and 113.1 (arom. CH of the dendron), 122.2 (CH=CHCOOH), 116.0 and 115.6 (arom. CH), 69.0 (OCH₂(CH₂)₈), 61.4 (outer SiCH₂O), 43.5 (CH₂CH₂CH₂Si), 42.4 (benzylic C_q), 32.8 (CH₂HC=CH), 30.2 and 26.5 ((CH₂)₆), 17.8 (CH₂CH₂CH₂Si), 14.6 (CH₂CH₂CH₂Si), -4.3 (SiMe₂). ²⁹Si NMR (CD₃COCD₃, 59.62 MHz), δ_{ppm}: 0.49 (inner SiCH₂O), 0.29 (outer SiCH₂O). IR (KBr), ν_{C=O}: 1711 cm⁻¹. Anal. Calcd for C₂₄₂₁H₃₈₁₀O₃₆₀Si₁₁₇: C, 69.29; H, 9.15. Found: C, 69.47; H, 9.11.

Synthesis of 11b. The 81-ester dendrimer **11b** was synthesized from **10** (0.052 g, 0.00130 mmol), methyl acrylate (0.018 g, 0.211 mmol), and catalyst **A** (0.009 g, 0.0105 mmol), following the general procedure for the metathesis reactions, and it was obtained as a colorless waxy product in 92% yield (0.052 g).

¹H NMR (CDCl₃, 300 MHz), δ_{ppm}: 7.19 (d, 72H, arom.), 6.95 (m, 81H, HC=CHCOOCH₃), 6.79 (d, 396H, arom.), 5.80 (d, 81H, HC=CHCOOCH₃), 3.84 (t, 162H, OCH₂CH₂), 3.71 (s, 243H, COOCH₃), 3.50 (s, 54H, inner SiCH₂O), 3.44 (s, 162H, outer SiCH₂O), 2.19 (t, 162H, CH₂HC=CH), 1.71 (d, 396H, OCH₂CH₂ and CH₂CH₂CH₂Si), 1.30 (d, 972H, (CH₂)₆), 1.19 (s, 234H, CH₂CH₂CH₂Si), 0.56 (s, 234H,

$\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 0.030 (s, 702H, $\text{Si}(\text{CH}_3)_2$). ^{13}C NMR (CDCl_3 , 75 MHz), δ_{ppm} : 166.5 ($\text{C}=\text{O}$), 159.0 (inner arom. OC_q), 155.7 and 153.0 (outer arom. C_q), 149.9 ($\text{CH}=\text{CHCOOCH}_3$), 129.0 and 112.4 (arom. CH of the dendron), 120.8 ($\text{CH}=\text{CHCOOCH}_3$), 115.2 and 114.8 (arom. CH), 68.6 ($\text{OCH}_2(\text{CH}_2)_8$), 60.9 (outer SiCH_2O), 60.2 (inner SiCH_2O), 51.3 (COOCH_3), 44.0 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 43.0 (benzylic C_q), 32.5 ($\text{CH}_2\text{HC}=\text{CH}$), 29.5 and 26.0 ($(\text{CH}_2)_6$), 17.1 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 14.9 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), -4.8 (SiMe_2). ^{29}Si NMR (CDCl_3 , 59.62 MHz), δ_{ppm} : 0.50 (inner SiCH_2O), 0.29 (outer SiCH_2O). IR (KBr), $\nu_{\text{C}=\text{O}}$: 1732 cm^{-1} . Anal. Calcd for $\text{C}_{3002}\text{H}_{3972}\text{O}_{360}\text{Si}_{117}$: C, 69.72; H, 9.29. Found: C, 69.73; H, 9.94.

Synthesis of 11c. The 81-ferrocenyl dendrimer **11c** was synthesized from **10** (0.050 g, 0.00130 mmol), **5** (0.057 g, 0.212 mmol), and catalyst **A** (0.004 g, 0.00527 mmol), following the general procedure for the metathesis reactions, and it was obtained as a yellow waxy product in 94% yield (0.071 g).

^1H NMR (CDCl_3 , 300 MHz), δ_{ppm} : 7.11 (d, 72H, arom.), 6.96 (m, 81H, $\text{HC}=\text{CHCOOCH}_2\text{Fc}$), 6.79 (d, 396H, arom.), 5.80 (d, 81H, $\text{HC}=\text{CHCOOCH}_2\text{Fc}$), 4.94 (s, 162H, CH_2Fc), 4.27 and 4.15 (d, 729H, CH of Fc), 3.84 (t, 162H, OCH_2CH_2), 3.48 (s, 72H, SiCH_2O), 2.16 (m, 162H, $\text{CH}_2\text{CH}=\text{CH}$), 1.70 (d, 396H, OCH_2CH_2 and $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 1.25 (m, 972H, $(\text{CH}_2)_6$), 1.18 (s, 234H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 0.54 (s, 72H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 0.067 (s, 702H, $\text{Si}(\text{CH}_3)_2$). ^{13}C NMR (CDCl_3 , 75 MHz), δ_{ppm} : 166.5 ($\text{C}=\text{O}$), 159.0 (inner arom. OC_q), 155.6 and 152.9 (outer arom. OC_q), 149.8 ($\text{CH}=\text{CHCOOCH}_2\text{Fc}$), 127.1 and 113.3 (arom. CH of the dendron), 121.0 ($\text{CH}=\text{CHCOOCH}_2\text{Fc}$), 115.1 and 114.7 (arom. CH), 81.5 (C_q of Fc), 69.6 ($\text{OCH}_2(\text{CH}_2)_8$), 68.6 (CH of Fc), 62.5 (CH_2Fc), 60.8 (outer SiCH_2O), 60.2 (inner SiCH_2O), 42.9 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 42.0 (benzylic C_q), 32.2 ($\text{CH}_2\text{HC}=\text{CH}$), 29.4 and 26.0 ($(\text{CH}_2)_6$), 17.6 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 14.5 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), -4.6 (SiMe_2). ^{29}Si NMR (CDCl_3 , 59.62 MHz), δ_{ppm} : 0.46 and 0.29 (inner and outer SiCH_2O). IR (KBr), $\nu_{\text{C}=\text{O}}$: 1732 cm^{-1} . Anal. Calcd for $\text{C}_{3312}\text{H}_{4620}\text{Si}_{117}\text{O}_{360}\text{Fe}_{81}$: C, 68.58; H, 8.03; found: C, 68.03; H, 7.81.

Synthesis of 13. An acetone solution of **11a** (0.038 g, 0.052 mmol) was added to another acetone solution of **12** (0.027 g, 6.43×10^{-4} mmol), formation of a precipitate was observed, and the solvent was removed under vacuum.

^1H NMR (CDCl_3 , 300 MHz), δ_{ppm} : 7.12 (d, 72H, arom.), 6.78 (m, 477H, arom. and $\text{HC}=\text{CHCOO}$), 5.87 (d, 81H, $\text{HC}=\text{CHCOO}^-$), 4.08 and 4.04 (d, 2 187H, Cp), 3.83 (t, 162H, OCH_2CH_2), 3.52 and 3.49 (s, 234H, inner and outer SiCH_2O), 2.63 (t, 486H, NH_2CH_2), 2.34 (t, 486H, FcCH_2), 2.17 (m, 162H, $\text{CH}_2\text{HC}=\text{CH}_2$), 1.71 (d, 396H, OCH_2CH_2 and $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 1.52 (m, 972H, $\text{NH}_2\text{CH}_2(\text{CH}_2)_2$), 1.28 (d, 972H, $(\text{CH}_2)_6$), 1.11 (s, 234H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 0.54 (s, 234H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 0.073 and 0.0093 (s, 702H, $\text{Si}(\text{CH}_3)_2$). ^{13}C NMR (CDCl_3 , 75 MHz), δ_{ppm} : 169.7 ($\text{C}=\text{O}$), 158.0 (inner arom. OC_q), 155.7 and 153.0 (outer arom. C_q), 151.2 ($\text{CH}=\text{CHCOO}^-$), 128.1 and 113.0 (unsubstituted arene C of the dendron), 122.0 ($\text{CH}=\text{CHCOO}^-$), 115.2 and 114.7 (arom. CH), 88.8 (C_q of Cp), 69.0 ($\text{OCH}_2(\text{CH}_2)_8$), 68.3 and 67.1 (Cp), 60.9 (outer SiCH_2O), 52.8 (NH_2CH_2), 43.5 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 42.4 (benzylic C_q), 32.1 ($\text{CH}_2\text{HC}=\text{CH}$), 30.9 ($\text{CH}_2\text{CH}_2\text{NH}_2$), 29.4 and 28.1 ($(\text{CH}_2)_6$), 28.9 (FcCH_2CH_2), 26.1 (FcCH_2), 15.4 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 12.1 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), -4.14 (SiMe_2). ^{29}Si NMR (CDCl_3 , 59.62 MHz), δ_{ppm} : 0.23 (SiCH_2O). Anal. Calcd for $\text{C}_{5823}\text{H}_{7941}\text{O}_{360}\text{Si}_{117}\text{Fe}_{243}\text{N}_{81}$: C, 68.75; H, 7.87. Found: C, 67.98; H, 7.27.

Synthesis of 15. Freshly prepared acryloyl chloride (0.095 g, 1.05 mmol, dissolved in 20 mL of dichloromethane) was added to a dichloromethane (20 mL) solution of dendron **14** (0.300 g, 0.52 mmol) and dry triethylamine (3 mL) at 0 °C. The reaction mixture was stirred at room temperature for 24 h under a nitrogen atmosphere. The mixture was washed twice with an aqueous solution of K_2CO_3 , dried with sodium sulfate, and filtered, and the solvent was removed under vacuum. The crude product was submitted to silica gel flash chromatography using CH_2Cl_2 as eluent, which provided 0.304 g (96%) of dendron **15** as a colorless oil.

^1H NMR (CDCl_3 , 300 MHz), δ_{ppm} : 7.30 and 7.07 (2d, 4H, arom. CH), 6.61, 6.31 and 5.96 (m, 3H, $\text{CH}_2=\text{CH}$), 2.72 (s, 6H, CH_2Cl),

1.62 (s, 6H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 1.09 (s, 6H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 0.58 (s, 6H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 0.051 (s, 18H, $\text{Si}(\text{CH}_3)_2$). ^{13}C NMR (CDCl_3 , 75 MHz), δ_{ppm} : 164.4 ($\text{C}=\text{O}$), 148.1 (OC_{Ar}), 144.9 (arom. C_q), 132.2 ($\text{CH}_2=\text{CH}$), 128.0 ($\text{CH}_2=\text{CH}$), 127.2 and 120.7 (unsubstituted arene C of the dendron), 43.4 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 41.7 (benzylic C_q), 30.3 (CH_2Cl), 17.4 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 14.3 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), -4.55 (SiMe_2). IR (KBr), $\nu_{\text{C}=\text{O}}$: 1732 cm^{-1} . Anal. Calcd for $\text{C}_{28}\text{H}_{49}\text{O}_2\text{Si}_3\text{Cl}_3$: C, 55.29; H, 8.12. Found: C, 55.68; H, 8.03.

Synthesis of 16. The 27-Cl dendrimer **16** was synthesized from **6** (0.050 g, 0.0145 mmol), dendron **15** (0.159 g, 0.261 mmol), and catalyst **A** (0.006 g, 0.0065 mmol), following the general procedure for the metathesis reactions, and it was obtained as a colorless waxy product in 95% yield (0.120 g).

^1H NMR (CDCl_3 , 300 MHz), δ_{ppm} : 7.29 and 7.06 (2d, 36H, arom. CH), 7.14 (m, 9H, $\text{HC}=\text{CHCOO}$), 6.80 (d, 36H, arom.), 6.01 (d, 9H, $\text{HC}=\text{CHCOO}$), 3.86 (t, 18H, OCH_2CH_2), 3.45 (s, 9H, SiCH_2O), 2.73 (s, 54H, CH_2Cl), 2.28 (t, 18H, $\text{CH}_2\text{HC}=\text{CH}$), 1.87 (d, 72H, OCH_2CH_2 and $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 1.33 (d, 108H, $(\text{CH}_2)_6$), 1.10 (s, 54H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 0.59 (s, 54H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 0.078 and 0.034 (s, 216H, $\text{Si}(\text{CH}_3)_2$). ^{13}C NMR (CDCl_3 , 75 MHz), δ_{ppm} : 165.0 ($\text{C}=\text{O}$), 155.7 and 152.9 (arom. C_q), 151.7 ($\text{CH}=\text{CHCOO}$), 148.3 (OC_{Ar}), 145.8 and 144.6 (arom. C_q), 127.2 and 120.8 (unsubstituted arene C of the dendron), 119.8 ($\text{CH}=\text{CHCOO}$), 115.1 and 114.7 (arom. CH), 68.6 ($\text{OCH}_2(\text{CH}_2)_8$), 60.8 (SiCH_2O), 43.4 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 41.8 (benzylic C_q), 32.4 ($\text{CH}_2\text{HC}=\text{CH}$), 30.4 (CH_2Cl), 29.4 and 26.0 ($(\text{CH}_2)_6$), 17.4 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 14.4 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), -4.54 (SiMe_2). ^{29}Si NMR (CDCl_3 , 59.62 MHz), δ_{ppm} : 0.46 and 0.29 (inner and outer SiCH_2O). IR (KBr), $\nu_{\text{C}=\text{O}}$: 1732 cm^{-1} . MS (MALDI-TOF, m/z): Calcd for $\text{C}_{450}\text{H}_{759}\text{O}_{36}\text{Si}_{36}\text{Cl}_{27}$: Na: 8736.90; found: 8729.77. Anal. Calcd for $\text{C}_{450}\text{H}_{759}\text{O}_{36}\text{Si}_{36}\text{Cl}_{27}$: C, 62.02; H, 8.78. Found: C, 61.89; H, 8.65.

Synthesis of 17. The 27-Cl dendrimer **16** (0.100 g, 0.0115 mmol), *p*-hydroxyphenyl undecene-1-yl ether **4** (0.162 g, 0.620 mmol), and K_2CO_3 (0.435 g, 3.11 mmol) were introduced into a Schlenk flask, and 30 mL of dry DMF was added. The reaction mixture was stirred at 80 °C for 48 h. DMF was removed under vacuum, the residue was dissolved in dichloromethane and filtered to remove K_2CO_3 , and the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 and precipitated with methanol. Dendrimer **17** was obtained as a colorless waxy product in 82% yield (0.145 g).

^1H NMR (CDCl_3 , 300 MHz), δ_{ppm} : 7.29 and 6.99 (2d, arom. CH), 7.11 (m, $\text{HC}=\text{CHCOO}$), 6.79 (d, arom.), 6.01 (d, $\text{HC}=\text{CHCOO}$), 5.80 (m, $\text{HC}=\text{CH}_2$), 4.95 (m, $\text{HC}=\text{CH}_2$), 3.84 (t, OCH_2CH_2), 3.44 (s, SiCH_2O), 2.04 (m, $\text{CH}_2\text{HC}=\text{CH}$), 1.71 (d, OCH_2CH_2 and $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 1.30 (d, $(\text{CH}_2)_6$), 1.11 (s, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 0.57 (s, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 0.070 and 0.024 (s, $\text{Si}(\text{CH}_3)_2$). ^{13}C NMR (CDCl_3 , 75 MHz), δ_{ppm} : 165.1 ($\text{C}=\text{O}$), 155.6 and 152.9 (arom. C_q), 151.7 ($\text{CH}=\text{CHCOO}$), 148.3 (OC_{Ar}), 145.7 and 144.5 (arom. C_q), 139.1 ($\text{HC}=\text{CH}_2$), 127.2 and 120.8 (unsubstituted arene C of the dendron), 119.8 ($\text{CH}=\text{CHCOO}$), 115.2 and 114.6 (arom. CH), 114.4 ($\text{HC}=\text{CH}_2$), 68.4 ($\text{OCH}_2(\text{CH}_2)_8$), 60.8 (SiCH_2O), 43.3 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 41.8 (benzylic C_q), 33.8 ($\text{CH}_2\text{HC}=\text{CH}_2$), 29.4 and 26.0 ($(\text{CH}_2)_6$), 17.4 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 14.3 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), -4.54 (SiMe_2). ^{29}Si NMR (CDCl_3 , 59.62 MHz), δ_{ppm} : 0.46 and 0.29 (inner and outer SiCH_2O). IR (KBr), $\nu_{\text{C}=\text{O}}$: 1732 cm^{-1} . Anal. Calcd for $\text{C}_{909}\text{H}_{1434}\text{O}_{96}\text{Si}_{36}$: C, 73.70; H, 9.76. Found: C, 73.24; H, 9.57.

Synthesis of 18. The 81-Cl dendrimer **18** was synthesized from **17** (0.070 g, 0.00473 mmol), dendron **15** (0.155 g, 0.255 mmol), and catalyst **A** (0.006 g, 0.0065 mmol), following the general procedure for the metathesis reactions, and it was obtained as a colorless waxy product in 85% yield (0.126 g).

^1H NMR (CDCl_3 , 300 MHz), δ_{ppm} : 7.26 and 7.05 (2d, arom. CH), 7.15 (m, $\text{HC}=\text{CHCOO}$), 6.79 (d, arom.), 6.01 (d, $\text{HC}=\text{CHCOO}$), 3.83 (t, OCH_2CH_2), 3.44 (s, SiCH_2O), 2.72 (s, CH_2Cl), 2.27 (t, $\text{CH}_2\text{HC}=\text{CH}$), 1.96 (d, OCH_2CH_2), 1.67 (t, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 1.32 (d, $(\text{CH}_2)_6$), 1.09 (s, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 0.59 (s, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 0.069 and 0.052 (s, $\text{Si}(\text{CH}_3)_2$). ^{13}C NMR (CDCl_3 , 75 MHz), δ_{ppm} : 165.0 ($\text{C}=\text{O}$), 155.6 and 152.9 (arom. C_q), 151.6 ($\text{CH}=\text{CHCOO}$), 148.3 (OC_{Ar}), 144.6 (arom.

C_q), 127.1 and 122.2 (unsubstituted arene C of the dendron), 120.7 ($CH=CHCOO$), 115.1 and 114.6 (arom. CH), 68.5 ($OCH_2(CH_2)_8$), 60.8 ($SiCH_2O$), 43.8 ($CH_2CH_2CH_2Si$), 41.7 (benzylic C_q), 32.4 ($CH_2HC=CH$), 30.3 (CH_2Cl), 29.6 and 27.9 ($(CH_2)_6$), 17.4 ($CH_2CH_2CH_2Si$), 14.4 ($CH_2CH_2CH_2Si$), -4.54 ($SiMe_2$). ^{29}Si NMR ($CDCl_3$, 59.62 MHz), δ_{ppm} : 0.46 and 0.29 (inner and outer $SiCH_2O$). IR (KBr), $\nu_{C=O}$: 1732 cm^{-1} . Anal. Calcd for $C_{1611}H_{2949}O_{144}Si_{117}Cl_{81}$: C, 62.86; H, 9.66. Found: C, 62.34; H, 9.52.

Synthesis of 21b. The polyester polymer **21b** was synthesized from **20** (0.100 g, 0.263 mmol of monomer), methyl acrylate (0.045 g, 0.527 mmol), and catalyst **A** (0.011 g, 0.0132 mmol), following the general procedure for the metathesis reactions, and it was obtained as a white waxy product in 92% yield (0.107 g).

1H NMR ($CDCl_3$, 300 MHz), δ_{ppm} : 7.12–6.65 (m, arom. and $HC=CHCOOCH_3$), 5.80 (d, $HC=CHCOOCH_3$), 3.85 (s, OCH_2CH_2), 3.70 (s, $COOCH_3$), 2.17 (s, $CH_2HC=CH$), 1.71 (s, OCH_2CH_2 and CH_2 of polymer chain), 1.28 (m, $(CH_2)_7$). ^{13}C NMR ($CDCl_3$, 75 MHz), δ_{ppm} : 166.5 ($C=O$), 154.2 and 152.3 (arom. OC_q), 150.1 ($CH=CHCOOCH_3$), 141.0 and 140.8 (arom. C_q), 127.7 and 127.2 (arom. CH of styrenic ring), 121.2 ($CH=CHCOOCH_3$), 115.7 and 115.0 (arom. CH), 69.3 (benzylic CH_2), 68.8 ($OCH_2(CH_2)_8$), 51.7 ($COOCH_3$), 43.2 and 41.0 (CH and CH_2 of polymer chain), 32.6 ($CH_2HC=CH$), 29.7 and 26.0 (CH_2), 6. IR (KBr), $\nu_{C=O}$: 1732 cm^{-1} . Anal. Calcd for $C_{28}H_{36}O_4$: C, 77.03; H, 8.31. Found: C, 76.15; H, 8.12. Polydispersity obtained by SEC: 1.33.

Synthesis of 21c. The polyferrocenyl polymer **21c** was synthesized from **20** (0.100 g, 0.263 mmol of monomer), **5** (0.142 g, 0.527 mmol), and catalyst **A** (0.011 g, 0.0132 mmol), following the general procedure for the metathesis reactions, and it was obtained as a white waxy product in 61% yield (0.106 g).

1H NMR ($CDCl_3$, 300 MHz), δ_{ppm} : 7.12–6.65 (m, arom. and $HC=CHCOOCH_2Fc$), 5.80 (d, $HC=CHCOOCH_2Fc$), 4.94 (s, CH_2Fc), 4.28 and 4.16 (d, CH of Fc), 3.87 (s, OCH_2CH_2), 2.17 (m, $CH_2HC=CH$), 1.74 (s, OCH_2CH_2 and CH_2 of polymer chain), 1.30 (m, $(CH_2)_7$). ^{13}C NMR ($CDCl_3$, 75 MHz), δ_{ppm} : 166.4 ($C=O$), 154.2 and 152.3 (arom. OC_q), 149.9 ($CH=CHCOOCH_2Fc$), 141.2 and 140.9 (arom. C_q), 127.8 and 127.5 (arom. CH of styrenic ring), 121.0 ($CH=CHCOOCH_2Fc$), 115.6 and 115.1 (arom. CH), 81.4 (C_q of Fc), 69.2 (benzylic CH_2), 68.7 ($OCH_2(CH_2)_8$), 68.7 (CH of Fc), 62.5 (CH_2Fc), 32.2 ($CH_2HC=CH$), 29.7 and 26.0 (CH_2), 6. IR (KBr), $\nu_{C=O}$: 1732 cm^{-1} . Anal. Calcd for $C_{40}H_{46}O_6Fe$: C, 76.94; H, 8.19. Found: C, 76.25; H, 8.02. Polydispersity obtained by SEC: 1.33.

Synthesis of 22. A colorless solution of $N(n-C_8H_{17})_4Br$ (0.262 g, 0.480 mmol) in 10 mL of toluene was added to a yellow water solution (10 mL) of $HAuCl_4$ (0.046 g, 0.137 mmol). The mixture was stirred under positive nitrogen pressure, and separation between the red organic phase (top) and colorless aqueous phase (bottom) resulted. A toluene (10 mL) solution of thiol $HS(CH_2)_9HC=CH_2$ (0.026 g, 0.137 mmol) was added to the organic phase. Then, $NaBH_4$ (0.057 g, 1.52 mmol) in 10 mL of water was slowly added to the stirred reaction mixture. The

red color turned to purple, and the reaction mixture was vigorously stirred for 3 h. The organic phase was separated from the aqueous phase, its volume was reduced to 3 mL, and 100 mL of ethanol was added. The resulting purple precipitate was dissolved in dichloromethane and precipitated again with methanol. The polyolefin AuNP was obtained as dark purple powder.

1H NMR ($CDCl_3$, 300 MHz), δ_{ppm} : 5.78 (m, $HC=CH_2$), 4.98 (m, $HC=CH_2$), 2.50 (m, SCH_2), 2.03 (m, $CH_2HC=CH_2$), 1.29 (m, $(CH_2)_7$). ^{13}C NMR ($CDCl_3$, 75 MHz), δ_{ppm} : 140.2 ($HC=CH_2$), 114.1 ($HC=CH_2$), 33.8 ($CH_2HC=CH_2$), 29.4 and 26.0 (CH_2), 6. Elemental analysis: Au, 74.00; S, 4.40. Nanoparticle size obtained by TEM: 2.1 ± 0.3 nm (~ 285 Au atoms and 103 ligands per nanoparticle; MW of polyolefin AuNP $\approx 75\,389$).

Synthesis of 23b. The polyester AuNP was synthesized from **22** (0.036 g, 0.00048 mmol AuNP, 0.049 mmol olefin termini), methyl acrylate (0.008 g, 0.099 mmol), and catalyst **A** (0.003 g, 0.0025 mmol), following the general procedure for the metathesis reactions, and it was obtained as a dark violet powder in 74% yield (0.029 g).

1H NMR ($CDCl_3$, 300 MHz), δ_{ppm} : 6.97 (m, $HC=CHCOOCH_3$), 5.80 (d, $HC=CHCOOCH_3$), 3.72 (s, $COOCH_3$), 2.47 (m, SCH_2), 2.18 (s, $CH_2HC=CH$), 1.28 (m, $(CH_2)_7$). ^{13}C NMR ($CDCl_3$, 75 MHz), δ_{ppm} : 166.2 ($C=O$), 150.1 ($CH=CHCOOCH_3$), 121.1 ($CH=CHCOOCH_3$), 51.8 ($COOCH_3$), 32.4 ($CH_2HC=CH$), 29.8 and 26.0 (CH_2), 6. IR (KBr), $\nu_{C=O}$: 1732 cm^{-1} . Nanoparticle size obtained by TEM: 2.2 ± 0.3 nm.

Synthesis of 23c. The polyferrocenyl AuNP was synthesized from **22** (0.036 g, 0.00048 mmol AuNP, 0.049 mmol olefin termini), **5** (0.028 g, 0.099 mmol), and catalyst **A** (0.003 g, 0.0025 mmol), following the general procedure for the metathesis reactions, and it was obtained as a dark violet powder in 78% yield (0.038 g).

1H NMR ($CDCl_3$, 300 MHz), δ_{ppm} : 6.97 (m, $HC=CHCOO$), 5.80 (d, $HC=CHCOO$), 4.94 (s, CH_2Fc), 4.28 and 4.16 (d, CH of Fc), 2.47 (m, SCH_2), 2.18 (s, $CH_2HC=CH$), 1.28 (m, $(CH_2)_7$). ^{13}C NMR ($CDCl_3$, 75 MHz), δ_{ppm} : 166.2 ($C=O$), 150.1 ($CH=CHCOO$), 121.1 ($CH=CHCOO$), 81.3 (C_q of Fc), 68.9 (CH of Fc), 62.3 (CH_2Fc), 32.4 ($CH_2HC=CH$), 29.8 and 26.0 (CH_2), 6. IR (KBr), $\nu_{C=O}$: 1732 cm^{-1} .

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Supporting Information Available: Detailed synthetic procedures including those for **4**, **5**, **6**, **8**, **10**, **19**, and **20**, NMR and MALDI-TOF spectra, and TEM images and data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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