# High Regioselectivity in the Ring-Opening Cross-Metathesis of 1-Arylcyclobutene

**Jing Feng,[a] and Günter Szeimies*[a]**

**Keywords:** Metathesis / Ring-opening / Cyclobutenes / Strained molecules

Ring-opening cross-metathesis (ROM/CM) of several 1-arylcyclobutenes with 1-octene and allyltrimethylsilane in the presence of the ruthenium catalyst [$(Cy_3P)_2Cl_2Ru$=CHPh] has been carried out. The isolated products showed a remarkable regioselectivity concerning the cycloaddition of the ruthenium carbene complex to the C-C double bond of the cyclobutene derivatives. The electronic influence of substituents at the aromatic ring of 1-phenylcyclobutene on the rate of the ROM/CM is not very pronounced, but steric effects of substituents in the *ortho*-position of the phenyl ring are substantial.

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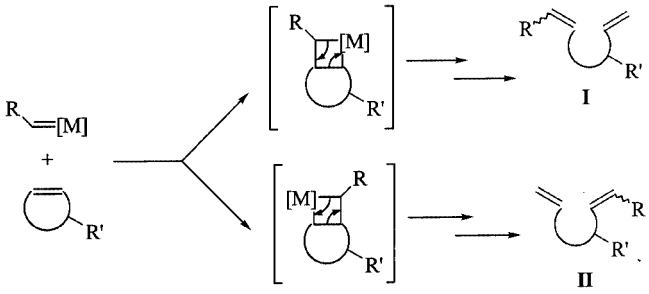
## Introduction

Over the years olefin metathesis has developed to become an important methodology in synthetic organic chemistry.[1] Ring-opening metathesis of cyclic olefins and subsequent coupling with acyclic alkenes (ROM/CM) provides new types of dienes.[2] This reaction is especially effective if relief of strain energy is used as a driving force. Therefore, cyclobutenes, norbornenes and also cyclooctenes have been preferred substrates in ROM/CM investigations.[3] ROM/CM techniques in the solid phase with resin-bound bicyclic alkenes have also been developed.[4]

For ring-opening cross-metathesis, control of the stereo- and regioselectivity of the newly formed double bonds appears to be the most important problem in order to make this reaction an appealing strategy for organic synthesis.[5] In comparison with ring-closing metathesis (RCM), the application of ROM/CM in synthesis has been hampered by the uncertainty of the regioselectivity of this reaction, which has not been investigated sufficiently. For this reason, mostly unsubstituted cyclic olefins, which circumvent the regiochemistry problem, have been used as one component in ROM/CM. The stereoselectivity of ROM/CM could be improved by the development of new metathesis catalysts.[6] Regiochemical problems arise when the starting cyclic olefin is not symmetric (Scheme 1), as two regioisomeric products (**I** and **II**) can be expected from this reaction.[7]

Herein we report the highly regioselective ring-opening cross-metathesis of 1-arylcyclobutenes that possess a trisubstituted double bond. For the metathesis reactions described in this paper the well-defined and commercially available Grubbs' catalyst [$(Cy_3P)_2Cl_2Ru$=CHPh] (**1**) was used.[8]



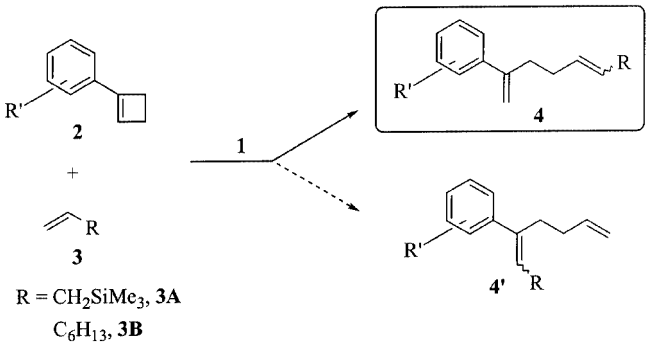

Scheme 1

## Results and Discussion

We have shown recently that 1-arylcyclobutenes **2**[9] are available in good yields starting from 1-(tri-*n*-butyl)stannylcyclobutene with aryl bromides or iodides following the Stille protocol.[10] The ring-opening cross-metathesis of these compounds with a terminal olefin such as allyltrimethylsilane **3A** or 1-octene **3B** has been examined. As indicated in Scheme 2, two possible regioisomers could be expected as the final products; however only diene **4** was formed.

In most of our ROM/CM experiments, the terminal alkene was used in substantial excess (sixfold). Under these conditions, the self-metathesis of the terminal alkene was unavoidable, although the self-metathesis products [tetradec-7-ene or 1,4-bis(trimethylsilyl)-2-butene] could be easily removed by flash chromatography. A 0.1 M solution of arylcyclobutenes in dichloromethane was allowed to react with the terminal alkene (**3A** or **3B**, 6 equiv.) at room temper-

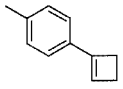
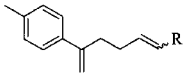
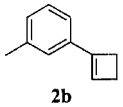
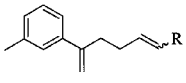
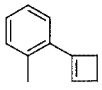
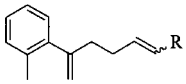
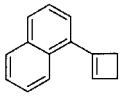
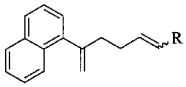
[a] Institut für Chemie der Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, Germany
E-mail: guenter.szeimies@rz.hu-berlin.de




Scheme 2

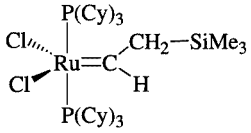
ature in the presence of **1** (5 mol %) for 72 h and produced dienes **4**. The long reaction time was necessary because of the relatively low reactivity of the trisubstituted cyclobutene. Optimal yields were obtained when the terminal olefin and the catalyst were added in three portions at 24 h intervals. The reaction led to a mixture of *Z*/*E* stereoisomers. It has been reported that increasing the steric bulk of the silyl group in the allyltrialkylsilane can significantly enhance the *E* selectivity of the cross-metathesis (CM).[11] An attempt at the ROM/CM reaction with (triisopropyl)allylsilane was unsuccessful. The results of the ROM/CM of several 1-arylcyclobutenes with 1-octene and allyltrimethylsilane are shown in Table 1.

Table 1. ROM/CM products of 1-arylcyclobutenes with allyltrimethylsilane or 1-octene (isolated yields)
[a] NMR yield.

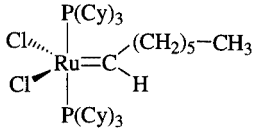
| Starting material | Product | R | Yield (%) | *Z*/*E* |
|---|---|---|---|---|
|  **2a** |  | **4aA** $CH_2SiMe_3$ | 64 | 1:2.5 |
| | | **4aB** $C_6H_{13}$ | 73 | 1:1.3 |
|  **2b** |  | **4bA** $CH_2SiMe_3$ | 78 | 1:2.4 |
| | | **4bB** $C_6H_{13}$ | 84 | 1:2.2 |
|  **2c** |  | **4cA** $CH_2SiMe_3$ | <10[a] | – |
| | | **4cB** $C_6H_{13}$ | 65 | 1:6.4 |
|  **2d** |  | **4dA** $CH_2SiMe_3$ | <10[a] | – |
| | | **4dB** $C_6H_{13}$ | 48 | 1:4.8 |

The structures of **4a**, **4b**, **4c** and **4d** were established by $^1H$ and $^{13}C$ NMR spectroscopy. The *Z*/*E* ratio of the final products **4A** was determined by integration of the signals for the $CH_2SiMe_3$ groups, which were in most cases well separated in the $^1H$ NMR spectrum of the *Z*/*E* mixtures. The *Z*/*E* ratio of products **4B** were determined by analytical GC.

*para*-Tolylcyclobutene (**2a**) is converted into the dienes **4aA** (64% yield) and **4aB** (73% yield), respectively. Varying the substitution pattern from *para*-methyl to *meta*-methyl in the phenyl ring has no significant effect on the reactivity as reflected by the yields of both products **4bA** and **4bB**. However, introduction of an *ortho*-methyl group to **2c** leads to a dramatic lowering of the yields of **4cA** and a substantial change in the *Z*/*E* ratio of **4cB**. If we assume that the active catalyst adding to the C-C double bond of **2c** is **III** in the first case and **IV** in the second, there might be a somewhat greater steric repulsion in the transition state of the first reaction of **III** with **2c** than in the reaction of **IV** with **2c**. As a consequence, unchanged starting material **2c** was recovered on work-up. The increase of the *Z*/*E* ratio of product **4cB** in the second experiment is not well understood.

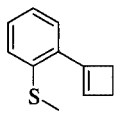



**III**

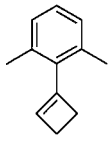



**IV**

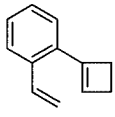
The results with 1-naphthylcyclobutene (**2d**) are similar to those of **2c**, probably because steric interactions in both model compounds are of similar size. Steric hindrance at the cyclobutenyl site is greater in cyclobutenes **2e**, **2f** and **2g**.




**2e**



**2f**

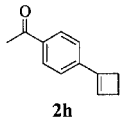
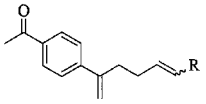
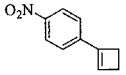
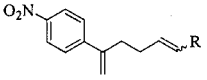
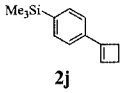
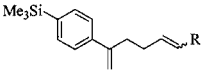
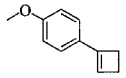
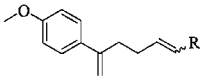
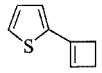
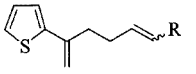
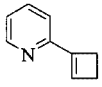
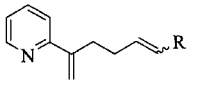


**2g**

As a consequence, these model compounds gave no products in the reaction with either **3A** or **3B**. In addition to steric hindrance, the thioether in **2e** could lead to a blocking of the metathesis catalyst by complexation through the sulfur. However, we observed a substantial amount of self-metathesis product of **3A** and **3B**, indicating that the catalyst remained active. Cyclobutene **2g** could react at the double bond of the four-membered ring or at the double bond of the styrene subunit. The lack of reactivity might be attributed to a mutual steric blocking of the approach of the catalyst by both olefin units.

Further reactions were carried out to learn more about the influence of electronic factors on the rate of the ROM/CM. The results are given in Table 2. Again, electron-withdrawing (**2h**, **2i**) or electron-donating groups (**2j**, **2k**) in the *para*-position of the phenyl ring of **2** to avoid steric hindrance, give the expected ROM/CM products, although in better yields for acceptor substituents. Again the ROM/CM reactions are highly regioselective, but lead to *Z*/*E*-mixtures of the final dienes **4hA**, **4hB**, **4iA**, **4iB**, **4jA**, **4jB**, **4kA** and **4kB**.

Table 2. ROM/CM products of substituted 1-aryl- or 1-heteroarylcyclobutenes with allyltrimethylsilane or 1-octene (isolated yields)

| Starting material | Product | R | Yield (%) | *Z*/*E* |
|---|---|---|---|---|
|  **2h** |  | **4hA** $CH_2SiMe_3$ | 62 | 1 : 1.9 |
| | | **4hB** $C_6H_{13}$ | 74 | 1 : 1.8 |
|  **2i** |  | **4iA** $CH_2SiMe_3$ | 81 | 1 : 1.3 |
| | | **4iB** $C_6H_{13}$ | 92 | 1 : 1.7 |
|  **2j** |  | **4jA** $CH_2SiMe_3$ | 45 | 1 : 2.3 |
| | | **4jB** $C_6H_{13}$ | 60 | 1 : 3.8 |
|  **2k** |  | **4kA** $CH_2SiMe_3$ | 54 | 1 : 2.4 |
| | | **4kB** $C_6H_{13}$ | 62 | 1 : 3.1 |
|  **2l** |  | **4lA** $CH_2SiMe_3$ | 36 | 1 : 1.6 |
| | | **4lB** $C_6H_{13}$ | 54 | 1 : 1.9 |
|  **2m** |  | **4mA** $CH_2SiMe_3$ | - | - |
| | | **4mB** $C_6H_{13}$ | - | - |

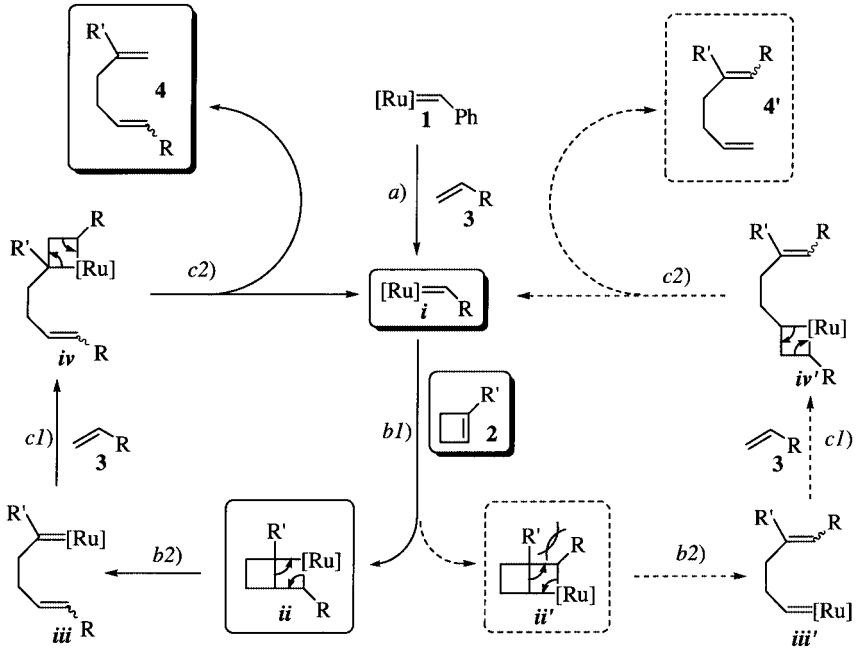
A similar protocol was applied to heteroaromatic cyclobutenes (**2l** and **2m**). Whereas **4lA** and **4lB** were isolated in moderate yields (36% and 54%), 1-pyridylcyclobutene (**2m**) failed to undergo a ROM/CM. In the reaction only a trace amount of the self-metathesis product of **2B** was obtained. This observation can be rationalized by assuming that the N atom of pyridine coordinates to the ruthenium catalyst and inhibits the metathesis reactions.

A simplified reaction path for metal-catalyzed ring-opening cross-metathesis is depicted in Scheme 3.[12] The catalytic cycle is divided into three steps: a) the added ruthenium catalyst is converted into the active catalyst [Ru]=CH-R ***i*** by cycloaddition of **1** to the terminal olefin **3** and cyclo-reversion with formation of ***i*** and styrene; b) the active catalyst ***i*** adds to the cyclobutene **2** to give the bicyclic intermediate ***ii***, which isomerizes to the carbene complex ***iii***; c) carbene complex ***iii*** adds to the C-C double bond of the terminal olefin **3** to give the metallacycle ***iv***, which decomposes to the final product **4** and the regenerated catalyst ***i***.

Alternatives concerning the regioselectivity of the metallacyclobutane formation are conceivable, although these alternatives are more complex than the mechanism depicted in Scheme 3. Here, product formation is determined by the regioselectivity of step b). There are two possible structures (***ii*** and ***ii′***) of the metallacyclobutane. Obviously ***ii*** is the sterically favorable structure, while in ***ii′*** the repulsive interaction of the substituent R and the aryl group make this intermediate energetically inferior.

## Conclusion

Under appropriate experimental conditions, an arylcyclobutene can undergo ROM/CM with a terminal olefin to form 1,5-dienes regioselectively in moderate to good yields. The influence of electronic factors due to different substitution patterns of the aryl group on the reaction rate are shown to be low, while *ortho*-substitution of the aryl group reduces the rate of reaction when allyltrimethylsilane is the




Scheme 3

olefin substantially. Our results based on product structure and on yields suggest a mechanism in which the regioselectivity of the cycloaddition of 1-arylcyclobutene to the metallacarbene complex plays a major role. Although the regiochemistry of the ROM/CM of 1-arylcyclobutene can be explained consistently well, the stereoselectivity of the olefin formation remains an important challenge in the development of ROM/CM as a synthetically useful reaction.

## Experimental Section

**General Methods:** All reactions were carried out under nitrogen. Dichloromethane was distilled from over calcium hydride. Bis(tricyclohexylphosphane)benzylideneruthenium(IV) dichloride was purchased from Strem Chemical Inc. Flash chromatography was performed on silica gel 230−400 mesh. $^1$H NMR spectra were recorded on a Bruker DPX 300 at 300 MHz; $^{13}$C NMR spectra were recorded on the same instrument at 75 MHz, with $CDCl_3$ as solvent.

The experiments were carried out on a small scale; in most cases, besides NMR only HRMS characterization of the pure products was possible.

**General Procedure for the Metathesis Reaction:** The terminal olefin **3A** or **3B** (1.2 mmol) and a solution of bis(tricyclohexylphosphane)benzylideneruthenium(IV) dichloride **1** (8.2 mg, 0.01 mmol) in 3 mL of dichloromethane was added in three portions at 24 h intervals to a stirred solution of 1-arylcyclobutene (0.20 mmol) in 2 mL of dichloromethane at room temperature. The solvent and most of the excess of **3A** or of **3B** were then removed in vacuo. The crude product was purified by silica gel chromatography using mixtures of petroleum ether and ethyl acetate as eluent. The self-metathesis products and traces of allyltrimethylsilane or 1-octene appeared in the first fraction and were in most cases not further investigated. All products were characterized by $^1$H and $^{13}$C NMR spectroscopy (the chemical shifts given in brackets are those of the *Z* component), and by MS and HRMS. For **4dB**, **4iB** and **4lA** elemental analyses were obtained.

**Trimethyl[(2*E*/*Z*)-6-(4-methylphenyl)-2,6-heptadienyl]silane (4aA):** Colorless oil, yield 32 mg (64%). $R_f$ = 0.37 (petroleum ether). $^1$H NMR ($CDCl_3$): δ = 0.00 (s, 9 H), 1.40 (1.43) (d, *J* = 8.0 Hz, 2 H), 2.15 (m, 2 H), 2.36 (s, 3 H), 2.53 (m, 2 H), 5.02 (m, 1 H), 5.25 (m, 1 H), 5.37 (m, 2 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H) ppm. $^{13}$C NMR ($CDCl_3$): δ = −2.0 ($CH_3$), 21.1 ($CH_3$), 22.6 (18.5) ($CH_3$), 31.6 (26.0) ($CH_2$), 35.9 (35.3) ($CH_2$), 111.5 ($CH_2$), 126.0 (CH), 126.6 (CH), 128.0 (CH), 128.9 (CH), 137.0 ($C_q$), 138.4 ($C_q$), 147.9 ($C_q$) ppm. MS (EI): *m*/*z* (%) = 258 (5) [$M^+$], 184 (16), 157 (45), 115 (16), 91(12), 73 (100). HRMS ($C_{17}H_{26}Si$): calcd. 258.1804; found 258.1805.

**(5*E*/*Z*)-2-(4-Methylphenyl)-1,5-dodecadiene (4aB):** Colorless oil, yield 38 mg (73%). $R_f$ = 0.43 (petroleum ether). $^1$H NMR ($CDCl_3$): δ = 0.81 (t, *J* = 7 Hz, 3 H), 1.19 (m, 8 H), 1.88 (m, 2 H), 2.06 (m, 2 H), 2.26 (s, 3 H), 2.43 (m, 2 H), 4.93 (s, 1 H), 5.16 (m, 1 H), 5.32 (m, 2 H), 7.04 (d, *J* = 8.0 Hz, 2 H), 7.22 (d, *J* = 8.0 Hz, 2 H) ppm. $^{13}$C NMR ($CDCl_3$): δ = 14.1 ($CH_3$), 21.1 ($CH_3$), 22.6, 28.8, 29.5, 31.4, 31.7, 32.6, 35.5 ($CH_2$), 111.5 ($CH_2$), 126.0 (CH), 128.4 (CH), 128.9 (CH), 130.9 (CH), 137.0 ($C_q$), 138.4 ($C_q$), 147.9 ($C_q$) ppm. MS (EI): *m*/*z* (%) = 256 (16) [$M^+$], 188 (16), 157 (100), 129 (36), 117 (50), 91 (54), 77 (18). HRMS ($C_{19}H_{28}$): calcd. 256.2191; found 256.2197.

**Trimethyl[(2*E*/*Z*)-6-(3-methylphenyl)-2,6-heptadienyl]silane (4bA):** Colorless oil, yield 40 mg (78%). $R_f$ = 0.37 (petroleum ether). $^1$H NMR ($CDCl_3$): δ = 0.00 (s, 9 H), 1.41 (d, *J* = 8.0 Hz, 2 H), 2.17 (m, 2 H), 2.37 (s, 3 H), 2.53 (m, 2 H), 5.05 (m, 1 H), 5.25 (m, 1 H), 5.37 (m, 2 H), 7.10−7.22 (m, 4 H) ppm. $^{13}$C NMR ($CDCl_3$): δ = −1.9 ($CH_3$), 22.6 (18.5) ($CH_2$), 21.5 ($CH_3$), 31.5 (26.0) ($CH_2$), 35.9 ($CH_2$), 112.1 ($CH_2$), 123.2 (CH), 125.9 (CH), 126.6 (CH), 126.9 (CH), 128.0 (CH), 128.1 (CH), 137.7 ($C_q$), 141.4 ($C_q$), 148.3 ($C_q$) ppm. MS (EI): *m*/*z* (%) = 258 (4) [$M^+$], 230 (4), 184 (30), 157 (80), 115 (22), 91 (18), 73 (100). HRMS ($C_{17}H_{26}Si$): calcd. 258.1804; found 258.1810.

**(5*E*/*Z*)-2-(3-Methylphenyl)-1,5-dodecadiene (4bB):** Colorless oil, yield 43 mg (84%). $R_f$ = 0.41 (petroleum ether). $^1$H NMR ($CDCl_3$): δ = 0.81 (t, *J* = 8.0 Hz, 3 H), 1.19 (m, 8 H), 1.88 (m, 2 H), 2.07 (m, 2 H), 2.29 (s, 3 H), 2.46 (m, 2 H), 4.96 (m, 1 H), 5.17 (m, 1 H), 5.33 (m, 2 H), 7.01−7.13 (m, 4 H) ppm. $^{13}$C NMR ($CDCl_3$): δ = 14.1 ($CH_3$), 21.5 ($CH_3$), 22.6, 28.8, 29.5, 31.4, 31.8, 32.6, 35.5 ($CH_2$), 112.1 ($CH_2$), 123.2 (CH), 126.9 (CH), 128.0 (CH), 128.1 (CH), 129.3 (CH), 130.5 ($C_q$), 130.9 (CH), 137.7 ($C_q$), 141.4 ($C_q$) ppm. MS (EI): *m*/*z* (%) = 256 (10) [$M^+$], 171 (20), 157 (90), 142 (45), 128 (45), 115 (64), 105 (100), 91 (60), 65 (80). HRMS ($C_{19}H_{28}$): calcd. 256.2191; found 256.2189.

**(5*E*/*Z*)-2-(2-Methylphenyl)-1,5-dodecadiene (4cB):** Colorless oil, yield 34 mg (65%). $R_f$ = 0.38 (petroleum ether). $^1$H NMR ($CDCl_3$): δ = 0.81 (t, *J* = 7.0 Hz, 3 H), 1.19 (m, 8 H), 1.87 (m, 2 H), 2.01 (m, 2 H), 2.22 (s, 3 H), 2.30 (m, 2 H), 4.79 (m, 1 H), 5.10 (m, 1 H), 5.32 (m, 2 H), 7.08−7.12 (m, 4 H) ppm. $^{13}$C NMR ($CDCl_3$): δ = 14.1 ($CH_3$), 19.8 ($CH_3$), 22.6, 28.8, 29.5, 30.8, 31.7, 32.6, 37.8 ($CH_2$), 113.8 ($CH_2$), 125.3 (CH), 126.7 (CH), 128.4 (CH), 129.4 (CH), 130.0 (CH), 130.9 (CH), 134.8 ($C_q$), 143.0 ($C_q$), 149.6 ($C_q$) ppm. MS (EI): *m*/*z* (%) = 256 (18) [$M^+$], 188 (20), 171 (20), 157 (100), 117 (70), 104 (50), 91 (20). HRMS ($C_{19}H_{28}$): calcd. 256.2191; found 256.2193.

**(5*E*/*Z*)-2-(1-Naphthyl)-1,5-dodecadiene (4dB):** Colorless oil, yield 28 mg (48%). $R_f$ = 0.43 (petroleum ether). $^1$H NMR ($CDCl_3$): δ = 0.8 (t, *J* = 7.0 Hz, 3 H), 1.19 (m, 8 H), 1.86 (m, 2 H), 2.05 (m, 2 H), 2.48 (m, 2 H), 5.00 (m, 1 H), 5.32 (m, 3 H), 7.18−7.94 (m, 7 H) ppm. $^{13}$C NMR ($CDCl_3$): δ = 14.1 ($CH_3$), 22.6, 28.8, 29.5, 31.1, 31.7, 32.6, 38.6 ($CH_2$), 115.4 ($CH_2$), 125.6, 125.9, 127.1, 128.2, 129.3, 131.1 (CH), 125.2 ($C_q$), 131.3 ($C_q$), 133.7 ($C_q$), 141.3 ($C_q$) ppm. MS (EI): *m*/*z* (%) = 292 (2) [$M^+$], 208 (10), 188 (50), 141 (100), 128 (55), 117 (100), 104 (95), 91 (35). HRMS ($C_{22}H_{28}$): calcd. 292.2191; found 292.2189. $C_{22}H_{28}$ (292.5): calcd. C 90.35, H 9.65; found C 90.30, H 9.70.

**1-{4-[(*E*/*Z*)-1-Methylene-6-trimethylsilyl-4-hexenyl]phenyl}-1-ethanone (4hA):** Colorless oil, yield 35 mg (62%). $R_f$ = 0.28 (petroleum ether/ethyl acetate, 20:1). $^1$H NMR ($CDCl_3$): δ = −0.06 (s, 9 H), 1.34 (d, *J* = 8.0 Hz, 2 H), 2.10 (m, 2 H), 2.51 (m, 2 H), 2.56 (s, 3 H), 5.13−5.33 (m, 4 H), 7.42 (d, *J* = 8.0 Hz, 2 H), 7.88 (d, *J* = 8.0 Hz, 2 H) ppm. $^{13}$C NMR ($CDCl_3$): δ = −2.0 ($CH_3$), 22.6 (18.5)($CH_2$), 25.8 (31.4) ($CH_2$), 26.6 ($CH_3$), 35.6 (35.1) ($CH_2$), 114.4 ($CH_2$), 126.3 (CH), 127.0 (CH), 127.5 (CH), 128.4 (CH), 135.9 ($C_q$), 146.1 ($C_q$), 147.2 ($C_q$), 197.7 ($C_q$) ppm. MS (EI): *m*/*z* (%) = 286 (30) [$M^+$], 258 (80), 232 (75), 185 (20), 114 (20), 73 (100). HRMS ($C_{18}H_{26}OSi$): calcd. 286.1753; found 286.1755.

**1-{4-[(*E*/*Z*)-1-methylene-4-undecenyl]phenyl}-1-ethanone (4hB):** Colorless oil, yield 42 mg (74%). $R_f$ = 0.38 (petroleum ether/ethyl acetate, 15:1). $^1$H NMR ($CDCl_3$): δ = 0.81 (t, *J* = 7.0 Hz, 3 H), 1.20 (m, 8 H), 1.89 (m, 2 H), 2.07 (m, 2 H), 2.48 (m, 2 H), 2.52 (s, 1 H), 5.10 (m, 1 H), 5.30 (m, 3 H), 7.40 (d, *J* = 8.5 Hz, 2 H), 7.85 (d, *J* = 8.5 Hz, 2 H) ppm. $^{13}$C NMR ($CDCl_3$): δ = 14.1 ($CH_3$),

22.6, 28.8, 29.5, 31.2, 31.7, 32.5, 35.2 ($CH_2$), 26.6 ($CH_3$), 114.4 ($CH_2$), 126.2 (CH), 128.4 (CH), 128.9 (CH), 131.3 (CH), 135.9 ($C_q$), 146.1 ($C_q$), 147.3 ($C_q$), 197.7 ($C_q$) ppm. MS (EI): *m/z* (%) = 284 (20) [$M^+$], 241 (8), 199 (60), 185 (100), 147 (30), 115 (30). HRMS ($C_{20}H_{28}O$): calcd. 284.2140; found 284.2138.

**Trimethyl[(2*E*/*Z*)-6-(4-nitrophenyl)-2,6-heptadienyl]silane (4iA):** Yellow oil, yield 46 mg (81%). $R_f$ = 0.38 (petroleum ether/ethyl acetate, 40:1). $^1$H NMR ($CDCl_3$): δ = −0.0002 (s, 9 H), 1.41 (d, *J* = 8.0 Hz, 2 H), 2.16 (m, 2 H), 2.58 (m, 2 H), 5.26−5.43 (m, 4 H), 7.53 (d, *J* = 8.0 Hz, 2 H), 8.20 (d, *J* = 8.0 Hz, 2 H) ppm. $^{13}$C NMR ($CDCl_3$): δ = −2.0 ($CH_3$), 22.6 (18.6) ($CH_2$), 31.2 (25.7) ($CH_2$), 35.5 (35.0) ($CH_2$), 115.9 ($CH_2$), 123.6 (CH), 125.7 (CH), 126.6 (CH), 126.9 (CH), 127.3 (CH), 146.6 ($C_q$), 146.9 ($C_q$), 148.0 ($C_q$) ppm. MS (EI): *m/z* (%) = 289 (2) [$M^+$], 272 (20), 222 (10), 141 (15), 115 (30), 73 (100). HRMS ($C_{16}H_{23}NO_2Si$): calcd. 289.1498; found 289.1502.

**(5*E*/*Z*)-2-(4-Nitrophenyl)-1,5-dodecadiene (4iB):** Yellow oil, yield 53 mg (92%). $R_f$ = 0.42 (petroleum ether/ethyl acetate = 20 :1). $^1$H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 8.0 Hz), 3 H), 1.27 (m, 8 H), 1.96 (m, 2 H), 2.14 (m, 2 H), 2.56 (m, 2 H), 5.25−5.41 (m, 4 H), 7.52 (d, *J* = 8.0 Hz, 2 H), 8.17 (d, *J* = 8.0 Hz, 2 H) ppm. $^{13}$C NMR ($CDCl_3$): δ = 14.1 ($CH_3$), 22.6, 28.8, 29.5, 31.1, 31.7, 32.5, 35.1 ($CH_2$), 115.9 ($CH_2$), 123.6 (CH), 126.9 (CH), 128.5 (CH), 131.6 (CH), 146.5 ($C_q$), 146.9 ($C_q$) 148.0 ($C_q$) ppm. MS (EI): *m/z* (%) = 287 (8) [$M^+$], 241 (2), 202 (50), 188 (100), 142 (20), 115 (30), 69 (25). HRMS ($C_{18}H_{25}NO_2$): calcd. 287.1885; found 287.1892. $C_{18}H_{25}NO_2$ (287.4): calcd. C 75.22, H 8.77, N 4.87; found C 75.24, H 8.75, N 4.67.

**Trimethyl{(2*E*/*Z*)-6-[4-(trimethylsilyl)phenyl]-2,6-heptadienyl}silane (4jA):** Colorless oil, yield 29 mg (45%). $R_f$ = 0.48 (petroleum ether). $^1$H NMR ($CDCl_3$): δ = 0.00 (s, 9 H), 0.29 (s, 9 H), 1.43 (d, *J* = 8.0 Hz, 2 H), 2.17 (m, 2 H), 2.53 (m, 2 H), 5.07 (m, 1 H), 5.30−5.38 (m, 3 H), 7.42 (d, *J* = 8.0 Hz, 2 H), 7.49 (d, *J* = 8.0 Hz, 2 H) ppm. $^{13}$C NMR ($CDCl_3$): δ = −2.0 ($CH_3$), −1.1 ($CH_3$), 22.6 (18.5) ($CH_2$), 31.6 (25.9) ($CH_2$), 35.7(35.2) ($CH_2$), 112.4 ($CH_2$), 125.4 (CH), 126.6 (CH), 128.0 (CH), 133.3 (CH), 139.3 ($C_q$), 141.8 ($C_q$), 148.2 ($C_q$) ppm. MS (EI): *m/z* (%) = 301 (5) [$M^+ - CH_3$], 227 (6), 199 (8), 159 (5), 73 (100), 59 (20). HRMS ($C_{18}H_{29}Si_2$): calcd. 301.1808; found 301.1810.

**Trimethyl{4-[(*E*/*Z*)-1-methylene-4-undecenyl]phenyl}silane (4jB):** Colorless oil, yield 37 mg (60%). $R_f$ = 0.36 (petroleum ether). $^1$H NMR ($CDCl_3$): δ = 0.20 (s, 9 H), 0.81 (t, *J* = 7.0 Hz, 3 H), 1.20 (m, 8 H), 1.88 (m, 2 H), 2.08 (m, 2 H), 2.48 (m, 2 H), 4.98 (s, 1 H), 5.21 (s, 1 H), 5.34 (m, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.40 (d, *J* = 8.0 Hz, 2 H) ppm. $^{13}$C NMR ($CDCl_3$): δ = −1.12 ($CH_3$), 14.1 ($CH_3$), 22.6, 28.8, 29.5, 31.4, 31.7, 32.6, 35.3 ($CH_2$), 112.4 ($CH_2$), 125.4 (CH), 129.3 (CH), 131.0 (CH), 133.3 (CH), 139.3 ($C_q$), 141.7 ($C_q$), 148.1 ($C_q$) ppm. MS (EI): *m/z* (%) = 314 (3) [$M^+$], 299 (10), 230 (40), 215 (100), 174 (30), 143 (16), 117 (20), 73 (60). HRMS ($C_{21}H_{34}Si$): calcd. 314.2430; found 314.2430.

**Trimethyl[(2*E*/*Z*)-6-(4-methoxyphenyl)-2,6-heptadienyl]silane (4kA):** Colorless oil, yield 29 mg (54%). $R_f$ = 0.22 (petroleum ether/ethyl acetate = 50:1). $^1$H NMR ($CDCl_3$): δ = 0.0001 (s, 9 H), 1.40 (d, *J* = 8.5 Hz, 2 H), 2.17 (m, 2 H), 2.52 (m, 2 H), 3.83 (s, 3 H), 4.98 (m, 1 H), 5.21 (m, 1 H), 5.30−5.38 (m, 2 H), 6.86 (d, *J* = 9.0 Hz, 2 H), 7.35 (d, *J* = 9.0 Hz, 2 H) ppm. $^{13}$C NMR ($CDCl_3$): δ = −2.0 ($CH_3$), 22.6 (18.5) ($CH_2$), 31.6 (26.0) ($CH_2$), 35.9 (35.4) ($CH_2$), 55.2 ($CH_3$), 110.8 ($CH_2$), 113.6 (CH), 125.5 (124.5) (CH), 127.1 (CH), 128.0 (126.5) (CH), 133.5 ($C_q$), 147.4 ($C_q$), 158.9 ($C_q$) ppm. MS (EI): *m/z* (%) = 274 (10) [$M^+$], 259 (10), 173 (55), 135 (10), 73 (100). HRMS ($C_{17}H_{26}OSi$): calcd. 274.1753; found 274.1751.

**(5*E*/*Z*)-2-(4-Methoxyphenyl)-1,5-dodecadiene (4kB):** Colorless oil, yield 34 mg (62%). $R_f$ = 0.35 (petroleum ether). $^1$H NMR ($CDCl_3$): δ = 0.81(t, *J* = 7.0 Hz, 3 H), 1.20 (m, 8 H), 1.89 (m, 2 H), 2.07 (m, 2 H), 2.43 (m, 2 H), 3.74 (s, 3 H), 4.90 (s, 1 H), 5.13 (m, 1 H), 5.33 (m, 2 H), 6.78 (d, *J* = 8.0 Hz, 2 H), 7.26 (d, *J* = 8.0 Hz, 2 H) ppm. $^{13}$C NMR ($CDCl_3$): δ = 14.1 ($CH_3$), 22.6, 28.8, 29.5, 31.4, 31.7, 32.6, 35.5 ($CH_2$), 55.2 ($CH_3$), 110.8 ($CH_2$), 113.5 (CH), 127.2 (CH), 129.3 (CH), 130.9 (CH), 133.7 ($C_q$), 147.4 ($C_q$), 158.9 ($C_q$) ppm. MS (EI): *m/z* (%) = 272 (12) [$M^+$], 187 (30), 173 (100), 148 (60), 121 (20), 91 (15). HRMS ($C_{19}H_{28}O$): calcd. 272.2140; found 272.2147.

**Trimethyl[(2*E*/*Z*)-6-(2-thienyl)-2,6-heptadienyl]silane (4lA):** Colorless oil, yield 18 mg (36%). $R_f$ = 0.41 (petroleum ether). $^1$H NMR ($CDCl_3$): δ = 0.00 (s, 9 H), 1.42 (d, *J* = 8.0 Hz, 2 H), 2.29 (m, 2 H), 2.52 (m, 2 H), 4.97 (m, 1 H), 5.33−5.40 (m, 3 H), 6.99−7.18 (m, 3 H) ppm. $^{13}$C NMR ($CDCl_3$): δ = −2.0 ($CH_3$), 22.6 (18.6) ($CH_2$), 31.7 (26.1) ($CH_2$), 36.0 (35.5) ($CH_2$), 110.9 ($CH_2$), 123.2 (CH), 124.0 (CH), 126.9 (CH), 127.3 (CH), 127.7 (CH), 141.3 ($C_q$), 145.4 ($C_q$) ppm. MS (EI): *m/z* (%) = 250 (10) [$M^+$], 222 (5), 181 (10), 149 (20), 73 (100). HRMS ($C_{14}H_{22}SSi$): calcd. 250.1211; found 250.1212. $C_{14}H_{22}SSi$ (250.5): calcd. C 67.13, H 8.85; found C 66.98, H 8.94.

**2-[(*E*/*Z*)-1-Methylene-4-undecenyl]thiophene (4lB):** Colorless oil, yield 26 mg (54%). $R_f$ = 0.38 (petroleum ether). $^1$H NMR ($CDCl_3$): δ = 0.89 (t, *J* = 7.0 Hz, 3 H), 1.27 (m, 8 H), 1.98 (m, 2 H), 2.27 (m, 2 H), 2.50 (m, 2 H), 4.95 (m, 1 H), 5.39−5.44 (m, 3 H), 6.97−7.15 (m, 3 H) ppm. $^{13}$C NMR ($CDCl_3$): δ = 14.1 ($CH_3$), 22.6, 28.8, 29.5, 31.5, 31.7, 32.6, 35.6 ($CH_2$), 110.9 ($CH_2$), 124.0 (123.2) (CH), 125.9 (CH), 127.3 (CH), 129.6 (CH), 131.3 (128.4) (CH), 141.3 ($C_q$), 145.4 ($C_q$) ppm. MS (EI): *m/z* (%) = 248 (15) [$M^+$], 188 (8), 163 (45), 149 (70), 135 (100), 115 (65), 97 (30). HRMS ($C_{16}H_{24}S$): calcd. 248.1599; found 248.1601.

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