

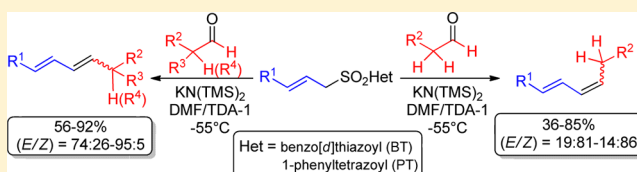
Julia–Kocienski Reaction-Based 1,3-Diene Synthesis: Aldehyde-Dependent (*E,E/Z*)-Selectivity

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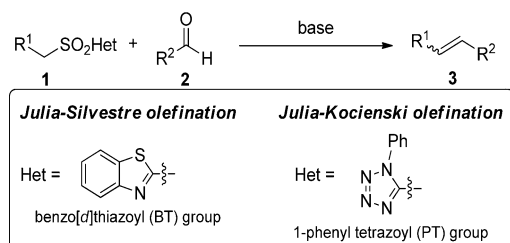
Supporting Information

ABSTRACT: A new modification of Julia–Kocienski olefination reaction based on the use of cation-specific chelating agents that yields 1,3-dienes with predictable (*E/Z*)-selectivity on newly created double bond was developed. The influence of the aldehyde structure on reaction (*E/Z*) selectivity is discussed and rationalized.



Over the past few decades, our synthetic tools were enriched by various novel and fundamentally different approaches to alkene synthesis. Unfortunately, none of the developed methods yet provided a universal solution in terms of yield, selectivity, and functional group tolerance. Since the mid-1990s, the second-generation Julia olefination reaction has become a privileged synthetic method when two complex molecular fragments should be connected (Scheme 1).¹ The

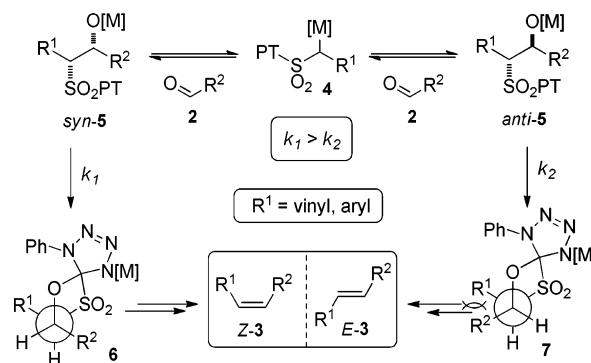
Scheme 1. Second-Generation Julia Olefination Reaction



popularity of this synthetic method is based not only on its versatility, wide functional group tolerance and mild reaction conditions under which the reaction proceeds, but also on its generally high (*E*)-selectivity.

In our group, we are focused on the development of new more selective modifications of Julia–Kocienski olefination reaction.² After our recent success where we were able to increase the (*E*)-selectivity of this reaction,² we decided to focus our attention on the development of (*Z*)-selective modification of this reaction (Scheme 2). Taking into account the mechanism of the Julia–Kocienski reaction,¹ we reasoned that if the addition of sulfonyl anion 4 to aldehyde 2 was reversible,³ reaction selectivity would be determined by the relative rate of Smiles rearrangement of *syn* and *anti* alkoxides 5. It is known that for steric reasons the Smiles rearrangement of *syn*-5 adduct that yields (*Z*)-olefins proceeds faster as compared to the rearrangement of *anti*-5 adduct that yields (*E*)-olefins.⁴

In the literature, the addition of sulfonyl anion 4 to aldehyde 2 (*R*¹, *R*² = alkyl) is reported to be nonreversible.^{1b,4} However,

Scheme 2. Proposed Equilibrium-Based Approach to (*Z*)-Olefins

we assumed that if allylic or benzylic anions 4 (*R*¹ = alkyl or benzyl) would be reacted with aldehyde 2, the addition reaction might be reversible.⁵ To investigate this hypothesis, the reactivity and reaction selectivity of α -sulfonyl anions generated from allylic and benzylic sulfones⁶ were studied in the context of 1,3-diene synthesis.⁷

Our study started with the investigation of the key step of our hypothesis, the reversibility of the addition of allylic and benzylic sulfonyl anions to aldehydes. Thus, hydroxy sulfones 8a and 8b were prepared⁸ and reacted with LiN(TMS)₂ or KN(TMS)₂ in the presence of *p*-nitrobenzaldehyde 12b (Table 1).⁹ The goal of these experiments was to find suitable reaction conditions under which alcoholate 9 would not undergo Smiles rearrangement (transformation of alcoholate 9 to olefin 13a) but rather retroaddition reaction (transformation of alcoholate 9 to benzylic anion 11 and aldehyde 12a) (Scheme 3). The formation of the benzylic anion 11 would then be proved by its trapping with reactive aldehyde 12b and the consecutive olefin 13b formation.

Received: May 22, 2012

Published: July 5, 2012

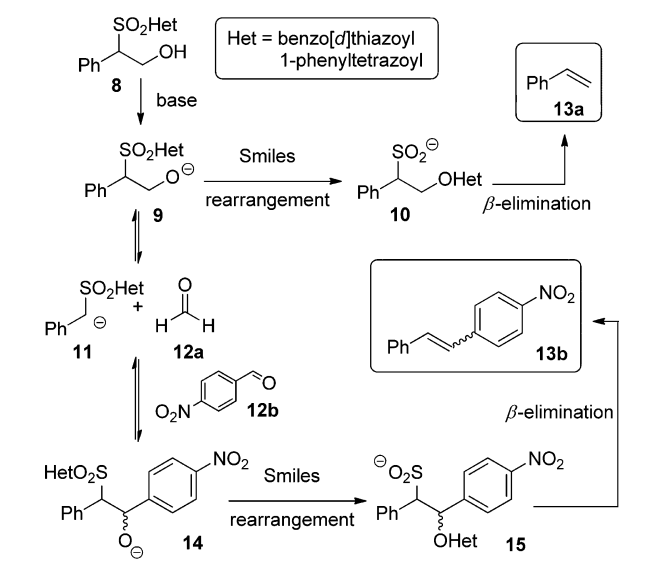
Table 1. Hydroxy Sulfone 8 Retroaddition Reaction Evaluation

8a, Het = BT
8b, Het = PT

entry	sulfone	conditions	13a:13b ratio ^a
1	8a	LiN(TMS) ₂ (2.2 equiv), -60 °C, DMF/HMPA = 3:1	>98:<2
2	8a	KN(TMS) ₂ (1.2 equiv), DMF, -55 °C	>98:<2
3	8a	KN(TMS) ₂ (1.2 equiv), 18-crown-6 (2.5 equiv), DMF, -55 °C	34:66
4	8a	KN(TMS) ₂ (1.2 equiv), DMF/TDA-1 = 3:1, -60 °C	22:78 (72) ^b
5	8b	KN(TMS) ₂ (1.2 equiv), -55 °C, 18-crown-6 (2.5 equiv), DMF	15:85 (65) ^b
6	8b	KN(TMS) ₂ (1.2 equiv), DMF/TDA-1 = 3:1, -60 °C	<2:>98 (93) ^b

^aBased on HPLC analysis. ^bIsolated yield of 13b (in %).

Scheme 3. Competitive Experiment Designed To Determine if Hydroxy Sulfone 8 Can Undergo Retroaddition Reaction



Our competitive experiments showed that the hydroxy sulfones **8** undergo retroaddition only when polar solvents and efficient cation-chelating agents (18-crown-6, TDA-1 for K⁺) are used. Moreover, it was shown that BT-containing sulfone **8a** underwent retroaddition less readily as compared to sulfone **8b** (Table 1, entries 3 vs 5 and 4 vs 6). This observation could be

explained by the difference in reactivity of the imine-like electrophilic centers present in BT- and PT-sulfones.^{1,9,10}

Having established the conditions under which the addition of benzylic sulfones to aldehydes is reversible, we focused our attention on the (*E/Z*)-selectivity of the newly created olefin bond evaluation (Table 2).⁹ Our goal was to find reaction conditions under which the transformation of *syn*-5 adduct to spiro **6** (*k*₁, yields olefin (*Z*)-**3**) proceeds faster than the adduct *anti*-5 to spiro **7** (*k*₂, yields olefin (*E*)-**3**) (Scheme 2).

First, the reaction of allyl PT-sulfone **16** and aldehyde **12c** was carried out using the standard Barbier-type¹¹ Julia olefination protocol (Table 1, entries 1 and 2). As expected, if THF was used as solvent, (*E*)-**13c** olefin was formed predominantly (entry 1). The use of “equilibrating” reaction conditions, DMF as a solvent and 18-crown-6 as cation scavenger, flipped the selectivity and yielded (*Z*)-**13c** olefin as the major product (entry 2). To increase further the (*Z*)-selectivity, we decided to premetallate sulfone **16** with KN(TMS)₂ and add aldehyde **12c** 30 min later (entry 3). Gratifyingly, olefin **13c** was formed in an increased 25:75 (*E/Z*) ratio. Addition of K⁺-specific chelating agent, 18-crown-6, increased further the (*Z*)-selectivity of the olefin **3c** formation ((*E/Z*) = 16:84) but substantially diminished the reaction yield (entry 4).

It was found that prolonged premetallation reaction time carried out in the presence of cation scavenger led to rapid sulfone **16** degradation. Gratifyingly, the stirring of sulfone **16** with KN(TMS)₂ and 18-crown-6 for only 2 min prior to aldehyde **12c** addition yielded the targeted olefin **13c** with a 15:85 (*E/Z*) ratio and 74% yield (entry 6). If a shorter

Table 2. Reaction between Allyl Sulfones **16** and **17** and Dihydrocinnamaldehyde **12c**

16, Het = PT
17, Het = BT

entry	conditions ^a	yield ^b (%)	<i>E/Z</i> ^c
1	KN(TMS) ₂ added to a solution of 16 and 12c in THF at -78 °C	nd	68:32
2	KN(TMS) ₂ added to a solution of 16 , 12c and 18-crown-6 in DMF at -55 °C	73	35:65
3	KN(TMS) ₂ added to a solution of 16 in DMF at -55 °C, stirred for 30 min, aldehyde 12c added at -55 °C	64	25:75
4	KN(TMS) ₂ added to a solution of 16 and 18-crown-6 in DMF at -55 °C, stirred for 30 min, aldehyde 12c added at -55 °C	17	16:84
5	KN(TMS) ₂ added to a solution of 16 and 18-crown-6 in DMF at -55 °C, stirred for 1 min, aldehyde 12c added at -55 °C	79	23:77
6	KN(TMS) ₂ added to a solution of 16 in DMF/TDA-1 = 3:1 (v/v) at -60 °C, stirred for 2 min, aldehyde 12c added at -60 °C	78	14:86
7	KN(TMS) ₂ added to a solution of 17 in DMF/TDA-1 = 3:1 (v/v) at -60 °C, stirred for 2 min, aldehyde 12c added at -60 °C	52	16:84

^aThe following quantities of given reagents were used: sulfone **16** or **17** (1.0 equiv), KN(TMS)₂ (1.1 equiv), aldehyde **12c** (1.1 equiv), and 18-crown-6 (2.3 equiv). ^bAverage of two runs. Isolated yield. ^cAverage of two runs. Based on GC analysis.

Table 3. Synthesis of Dienes 13 via Julia–Kocienski and Julia–Silvestre Reactions

entry	sulfone	aldehyde	product ^a	conditions ^b : yield ^c (E:Z) ^d	entry	sulfone	aldehyde	product ^a	conditions ^b : yield ^c (E:Z) ^d	
1				A: 72% (63:37)	53				A: 81% (55:45)	
2				B: 65% (58:42)	54				B: 75% (63:47)	
3				C: 74% (15:85)	55				C: 72% (88:12)	
4				D: 78% (14:86)	56				D: 80% (82:18)	
5				A: 68% (79:21)	57				A: 66% (58:42)	
6				B: 47% (62:38)	58				B: 52% (69:21)	
7				C: 36% (15:85)	59				C: 45% (92:8)	
8				D: 48% (14:86)	60				D: 49% (95:5)	
9				A: 82% (66:34)	61				A: 68% (59:41)	
10				B: 67% (55:45)	62				B: 53% (57:43)	
11				C: 63% (69:31)	63				C: 39% (30:70)	
12				D: 72% (72:28)	64				D: 42% (20:80)	
13				A: 65% (71:29)	65				A: 69% (65:35)	
14				B: 58% (40:60)	66				B: 65% (52:48)	
15				C: 50% (16:84)	67				C: 73% (20:80)	
16				D: 40% (13:87)	68				D: 74% (19:81)	
17				A: 69% (55:45)	69				A: 72% (56:44)	
18				B: 59% (66:34)	70				B: 66% (52:48)	
19				C: 55% (75:25)	71				C: 70% (68:32)	
20				D: 56% (74:26)	72				D: 71% (70:30)	
21				A: 82% (62:38)	73				A: 75% (58:42)	
22				B: 69% (54:46)	74				B: 72% (55:45)	
23				C: 50% (83:17)	75				C: 69% (20:80)	
24				D: 62% (82:18)	76				D: 73% (17:83)	
25				A: 73% (65:35)	77				A: 68% (55:45)	
26				B: 63% (51:49)	78				B: 69% (60:40)	
27				C: 59% (77:23)	79				C: 65% (90:10)	
28				D: 68% (82:18)	80				D: 70% (91:9)	
29				A: 59% (61:39)	81				A: 56% (49:51)	
30				B: 65% (70:30)	82				B: 49% (45:55)	
31				C: 58% (94:6)	83				C: 53% (72:28)	
32				D: 63% (96:4)	84				D: 55% (78:22)	
33				A: 64% (55:45)	85				A: 86% (57:43)	
34				B: 55% (51:49)	86				B: 79% (55:45)	
35				C: 51% (76:24)	87				C: 82% (18:82)	
36				D: 58% (74:26)	88				D: 85% (15:85)	
37				A: 70% (56:44)	89				A: 95% (48:52)	
38				B: 60% (48:52)	90				B: 92% (42:58)	
39				C: 65% (86:14)	91				C: 74% (15:85)	
40				D: 63% (89:11)	92				D: 73% (14:86)	
41				A: 68% (56:44)	93				A: 85% (42:58)	
42				B: 69% (52:48)	94				B: 70% (32:68)	
43				C: 59% (16:84)	95				C: 91% (81:19)	
44				D: 60% (14:86)	96				D: 92% (83:17)	
45				A: 57% (65:35)	^a Overall yields refer to pure, isolated products. ^b Method A: Sulfone (1.0 equiv), aldehyde (1.1 equiv), THF (-78°C) then KN(TMS) ₂ (1.1 equiv). Method B: Sulfone (1.0 equiv), aldehyde (1.1 equiv), DMF (-55°C) then KN(TMS) ₂ (1.1 equiv). Method C: Sulfone (1.0 equiv), 18-crown-6 (2.5 equiv), KN(TMS) ₂ (1.1 equiv), DMF (-55°C), 2 min at -55°C then aldehyde (1.1 equiv). Method D: Sulfone (1.0 equiv), KN(TMS) ₂ (1.1 equiv), DMF/TDA-1 = 3:1 (V/V) (-60°C), 2 min at -60°C then aldehyde (1.1 equiv). ^c (E/Z)-Ratio refers to newly created olefin bond. Based on crude ¹ H-NMR analysis. ^d Color code indicates a substantial increase in (E) or (Z) selectivity in olefin 13 formation observed under our newly developed cation-free conditions.					
46				B: 53% (60:40)						
47				C: 36% (15:85)						
48				D: 48% (14:86)						
49				A: 81% (42:58)						
50				B: 63% (55:45)						
51				C: 55% (60:40)						
52				D: 69% (56:44)						

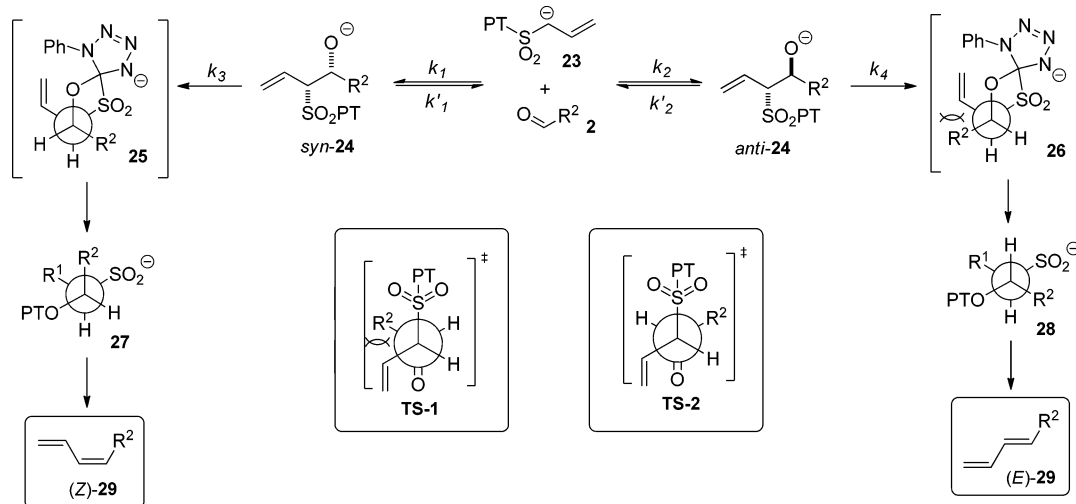
premetalation period (1 min) was employed, erosion of the (Z)-selectivity was observed (entry 5). To further increase the (Z)-13c formation, TDA-1¹² was used as cosolvent (entries 6 and 7). The use of DMF/TDA-1 = 3:1 (V/V) solvent mixture afforded olefin 13c in the same (E/Z) ratio but slightly better yield (entry 6).

The selectivity of BT-containing sulfone 17 under the developed reaction conditions was also evaluated. Because of the results of our preliminary addition/retroaddition study

(Table 1), we expected that the reaction of BT-sulfone 17 with aldehyde 12c might proceed with lower (Z)-selectivity. However, under all tested reaction conditions, olefins 13c were obtained with similar (E/Z)-selectivity, although in lower yield (see Table 2, entry 6 vs entry 7).⁹

Having established the optimal reaction conditions, the scope and limitations of this method (Table 3) were examined and the results were compared with reactions performed without the presence of chelating agents.¹³

Scheme 4. Proposed Mechanism of “Cation-Free” Julia–Kocienski Reaction of Allyl PT-sulfones



In general, reactions of PT-sulfones **16**, **18**, and **19** (Table 3, entries 1–60) were more stereoselective than those performed with BT-sulfones **17** and **20–22** (Table 3, entries 61–96). In both cases, the (*E/Z*)-selectivity of newly formed olefins **13** proved to be aldehyde dependent. When primary α -non-branched aldehydes **12c,d** were used, the newly created olefins formed under “cation-free” conditions (methods C and D) were obtained with higher (*Z*)-selectivity as compared to standard conditions (methods A and B). The only exception was found when nonbranched α -alkoxy aldehyde **12e** was used (entries 9–12, 17–20, 49–52, 69–72, and 93–96). In these cases, the reactions yielded the corresponding olefins **13h–l,n,p,q** with moderate to good (*E*)-selectivity. The same trend was observed when α di- and trisubstituted or aromatic aldehydes **12g–j** and **n** were used (entries 21–40, 45–48, 53–60, and 77–80). In these cases, the (*E*)-olefins **13h–l,n,p,q** were formed as main products of the reaction. Interestingly, in these cases the obtained (*E/Z*) ratio was also superior to that obtained under the standard reaction conditions.

We believe that the stereochemical outcome of the 1,3-dienes **13** prepared by Julia–Kocienski and Julia–Silvestre reactions and presented in Table 3 can be easily rationalized (Scheme 4). If the olefination reactions were carried out under standard reaction conditions (methods A or B, addition step is not reversible ($k'_1, k'_2 \ll k_3, k_4$)), the (*E/Z*) ratio of **13** corresponds to the *syn/anti*-**24** adduct ratio.^{1,2a} Thus, the Smiles rearrangement becomes the rate-determining step, but the addition step is the selectivity-determining step.

However, if chelating agents are employed (methods C and D), the addition step is reversible ($k'_1, k'_2 \ll k_3, k_4$) and the Smiles rearrangement becomes the rate and selectivity determination step. However, the final stereochemical outcome of the reaction ((*E/Z*) ratio) strongly depends on the aldehyde structure. If α -nonbranched aldehydes are employed, we expect that, for steric reasons, the Smiles rearrangement of adduct *syn*-**24** to intermediate **27** proceeds faster than the rearrangement of adduct *anti*-**24** to intermediate **28** ($k_3 > k_4$). (*Z*)-Olefins are thus preferentially formed.

However, the reaction becomes (*E*)-selective if the steric repulsion between R^2 and the vinyl group in TS-1 becomes important (α -branched and aromatic aldehydes). In this case, the relative rate of *syn* and *anti* addition starts to play a role in

determining selectivity; *anti* addition is predicted to be preferred ($k_2 > k_1$).

In summary, we have developed a new modification of the Julia reaction that allows us to prepare 1,3-dienes, starting from PT- and BT-allyl sulfones, with high (*Z*) or (*E*) selectivity. It was shown that the olefin stereoselectivity is substrate (aldehyde) dependent. A rational explanation for observed (*E,Z*) selectivity is also proposed.

EXPERIMENTAL SECTION

General Procedures for Olefination Reactions. Method A. A solution of aldehyde **12c** (131 μ L, 1.1 mmol) and allyl sulfone **16** (250 mg, 1.0 mmol) in THF (10 mL, 0.1 M) was cooled to -78°C , and $\text{KN}(\text{TMS})_2$ (0.6 M solution in toluene) (1.83 mL, 1.1 mmol) was added over 2 min. The resulting mixture was stirred at -78°C for 1 h before it was allowed to warm to rt. After being stirred at rt for 6 h, a saturated aqueous solution of NH_4Cl (10 mL) was added. The whole mixture was extracted with EtOAc (3×10 mL); the combined organic layers were washed with brine (10 mL), dried over MgSO_4 , and filtered; the solvents were removed under reduced pressure. The residue was purified by flash column chromatography on SiO_2 (petroleum ether/EtOAc = 50:1), and the reaction yielded 114 mg (72%, *E/Z* = 63:37) of **13c** as a yellowish oil.

Method B. A solution of aldehyde **12c** (131 μ L, 1.1 mmol) and allyl sulfone **16** (250 mg, 1.0 mmol) in DMF (10 mL, 0.1 M) was cooled to -55°C , and $\text{KN}(\text{TMS})_2$ (0.6 M solution in toluene) (1.83 mL, 1.1 mmol) was added over 2 min. The resulting mixture was stirred at -55°C for 1 h before it was allowed to warm to rt. After 6 h at rt, the reaction was terminated and purified using the same protocol as mentioned in method A. The reaction yielded 103 mg (65%, *E:Z* = 58:42) of **13c** as a yellowish oil.

Method C. A solution of allyl sulfone **16** (250 mg, 1.0 mmol) and 18-crown-6 (661 mg, 2.5 mmol) in DMF (10 mL, 0.1 M) was cooled to -55°C , and $\text{KN}(\text{TMS})_2$ (0.6 M solution in toluene) (1.83 mL, 1.1 mmol) was added dropwise within 10 s. The resulting mixture was stirred at -55°C for 2 min, and aldehyde **12c** (131 μ L, 1.1 mmol) in DMF (0.2 mL) was added dropwise. The resulting mixture was stirred at -55°C for 1 h before it was allowed to warm to rt. After 6 h at rt, the reaction was terminated and purified using the same protocol as mentioned in method A. The reaction yielded 117 mg (74%, *E/Z* = 15:85) of **13c** as a yellowish oil.

Method D. A solution of allyl sulfone **16** (250 mg, 1.0 mmol) in DMF/TDA-1 = 3:1 (v/v) (10 mL, 0.1 M) was cooled to -60°C , and $\text{KN}(\text{TMS})_2$ (0.6 M solution in toluene) (1.83 mL, 1.1 mmol) was added dropwise within 10 s. The resulting mixture was stirred at -60°C for 2 min, and aldehyde **12c** (131 μ L, 1.1 mmol) in DMF (0.2 mL)

was added dropwise. The resulting mixture was stirred at -60°C for 1 h before it was allowed to warm to rt. After 6 h at rt, the reaction was terminated and purified using the same protocol as mentioned in method A. The reaction yielded 123 mg (78%, $E/Z = 14:86$) of **13c**¹⁴ as a yellowish oil: ^1H NMR¹⁵ (300 MHz, CDCl_3) δ 2.45 (dd, $J = 15.1$, 7.2 Hz, 2H*), 2.55 (dd, $J = 15.3$, 7.6 Hz, 2H), 2.67–2.80 (m, 2H), 5.01 (d, $J = 9.7$ Hz, 1H*), 5.12 (d, $J = 10.0$ Hz, 1H), 5.22 (dd, $J = 16.9$, 1.7 Hz, 1H), 5.53 (dt, $J = 10.5$, 7.7 Hz, 1H), 5.79 (dt, $J = 15.1$, 7.1 Hz, 1H*), 6.06 (t, $J = 10.9$ Hz, 1H), 6.15 (dd, $J = 15.1$, 10.4 Hz, 1H*), 6.35 (dt, $J = 16.9$, 10.2 Hz, 1H*), 6.65 (dtd, $J = 16.9$, 10.6, 1.0 Hz, 1H), 7.15–7.26 (m, 3H), 7.28–7.37 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 29.8, 34.6*, 35.8*, 36.0, 115.4*, 117.5, 126.1, 128.5, 128.6, 129.9, 131.6 (E), 131.8, 132.3, 134.5, 137.4, 141.9, 142.0*; IR (film) ν^{-1} 3031, 2956, 2887, 1524, 1487, 1334, 1001, 906, 800, 746, 702; MS (EI) m/z 158 (14) $[\text{M}^+]$, 143 (6), 117 (32), 91 (100), 65 (12); HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{14}$ 158.1090, found 158.1094.

Olefin 13d:^{15,16} yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 2.43 (q, $J = 6.7$ Hz, 2H*), 2.54 (dd, $J = 14.2$, 7.2 Hz, 2H), 3.54 (td, $J = 6.8$, 4.6 Hz, 2H), 4.53 (s, 2H*), 4.55 (s, 2H), 5.01 (d, $J = 9.8$ Hz, 1H*), 5.12 (d, $J = 9.8$ Hz, 1H), 5.15 (s, 1H*), 5.23 (d, $J = 15.6$ Hz, 1H), 5.51 (dt, $J = 10.4$, 7.7 Hz, 1H), 5.74 (dt, $J = 15.3$, 7.0 Hz), 6.06–6.19 (m, 1H), 6.33 (dt, $J = 16.9$, 10.3 Hz, 1H), 6.66 (dt, $J = 17.2$, 10.9 Hz, 1H), 7.47–7.16 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ 28.7*, 33.2, 69.85, 69.88*, 73.1, 115.7, 117.8, 127.8, 127.86, 127.89*, 128.6, 131.1, 131.4*, 132.3, 132.9*, 137.3, 138.6*; IR (film) ν^{-1} 3031, 3024, 2986, 1604, 1582, 1463, 1132, 1041, 952, 863, 704; MS (CI) m/z 188 (100) $[\text{M}^+]$, 189 (35) $[\text{M} + \text{H}]^+$; HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{16}\text{O}$ 188.1201, found 188.1203.

Olefin 13e:^{15,16} yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 4.09 (d, $J = 6.3$ Hz, 2H), 4.22 (dd, $J = 6.7$, 1.3 Hz, 2H*), 4.54 (s, 2H and 2H*), 5.08–5.44 (m, 2H and 2H*), 5.66 (dt, $J = 11.8$, 6.8 Hz, 1H*), 5.84 (dt, $J = 14.4$, 6.0 Hz, 1H), 6.19 (t, $J = 11.1$ Hz, 1H*), 6.26–6.45 (m, 2H), 6.60 (dt, $J = 16.8$, 10.6 Hz, 1H*), 7.27–7.42 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 66.0, 70.4, 72.3, 117.8, 119.4, 121.4, 122.5, 124.8, 125.1, 126.6, 128.0, 128.6, 130.3, 131.9, 132.3, 133.5, 136.5, 138.4; IR (film) ν^{-1} 3086, 3028, 2930, 2851, 1456, 1427, 1238, 1095, 1074, 1003, 910, 756, 727; MS (CI) m/z 174 (84) $[\text{M}^+]$, 175 (20) $[\text{M}^+ + 1]$, 149 (100), 145 (54), 133 (49), 118 (56), 117 (81), 115 (62), 105 (94); HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{14}\text{O}$ 174.1039, found 174.1038.

Olefin 13f:¹⁵ yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 0.93 (t, $J = 7.3$ Hz, 3H), 0.94 (t, $J = 7.3$ Hz, 3H*), 1.39–1.47 (m, 2H), 2.02–2.19 (m, 2H), 2.37–2.57 (m, 2H), 2.72 (dd, $J = 8.9$, 6.7 Hz, 2H), 5.37 (dt, $J = 10.8$, 7.5 Hz, 1H), 5.50 (td, $J = 15.8$, 7.6 Hz, 1H), 5.59–5.78 (m, 2H), 5.98–6.14 (m, 2H), 6.30 (dd, $J = 15.2$, 10.9 Hz, 1H), 6.39 (dd, $J = 15.1$, 11.1 Hz, 1H), 7.19–7.34 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.95, 13.99*, 22.72, 22.76*, 29.8, 34.7*, 34.9*, 35.2, 36.11*, 36.16; 123.8, 124.4, 125.8, 126.0, 126.5, 128.5, 129.4, 130.5, 131.1, 132.6, 133.5, 135.2, 142.2; IR (film) ν^{-1} 3086, 3028, 2930, 2851, 1456, 1427, 1238, 1095, 1074, 1003, 910, 756, 727; MS (EI) m/z 200 (13) $[\text{M}^+]$, 201 (2) $[\text{M}^+ + 1]$, 143 (12), 129 (13), 117 (15), 109 (68), 91 (100); HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_{20}$ 200.1560, found 200.1560.

Olefin 13g:¹⁵ yellowish oil; ^1H NMR (300 MHz, CDCl_3) δ 0.93 (t, $J = 6.1$ Hz, 3H), 0.96 (t, $J = 5.2$ Hz, 3H*), 1.39–1.51 (m, 2H), 2.10 (q, $J = 7.1$ Hz, 2H), 2.20 (q, $J = 7.5$ Hz, 2H*), 4.08 (d, $J = 6.3$ Hz, 2H), 4.12 (d, $J = 6.2$ Hz, 1H*), 4.21 (d, $J = 6.8$ Hz, 1H*), 4.54 (s, 2H), 4.56 (s, 2H*), 5.50 (dt, $J = 15.1$, 7.6 Hz, 1H), 5.64–5.78 (m, 2H and 1H*), 6.09 (dd, $J = 14.7$, 10.5 Hz, 1H), 6.27 (dd, $J = 15.2$, 10.3 Hz, 1H), 6.59 (ddd, $J = 15.2$, 11.0, 1.1 Hz, 1H*), 7.27–7.47 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.88, 22.6, 23.0*, 30.0*, 34.9, 35.0*, 66.0*, 70.8, 72.1, 72.3*, 125.0, 125.5, 127.5, 127.7, 127.8, 128.3, 130.2, 130.4, 132.3, 133.1, 135.4, 138.4; IR (film) ν^{-1} 3063, 3026, 2957, 2927, 2858, 1659, 1497, 1454, 1362, 1099, 1070, 989, 734, 696; MS (CI) m/z 216 (64) $[\text{M}^+]$, 217 (12) $[\text{M} + \text{H}]^+$, 159 (100), 134 (78), 125 (52), 91 (82); HRMS (CI) m/z calcd for $\text{C}_{15}\text{H}_{20}\text{O}$ 216.1514, found 216.1521.

Olefin 13h:¹⁵ yellowish oil; ^1H NMR (300 MHz, CDCl_3) δ 0.93 (t, $J = 7.4$ Hz, 3H, H-1), 1.06 (s, $J = 9.8$ Hz, 9H), 1.44 (dq, $J = 14.6$, 7.3 Hz, 2H), 2.02–2.17 (m, 2H), 2.13–2.24 (m, 2H*), 3.65 (dd, $J = 10.5$, 4.8 Hz, 1H), 3.81 (dd, $J = 10.5$, 6.6 Hz, 1H), 4.01 (dt, $J = 12.1$, 6.9 Hz, 2H*), 4.45 (d, $J = 10.0$ Hz, 1H*), 4.46 (d, $J = 12.1$ Hz, 1H), 4.49 (d, $J = 9.9$ Hz, 1H*), 4.65 (d, $J = 12.1$ Hz, 1H), 5.18 (dd, $J = 10.0$, 9.6 Hz,

1H*), 5.46 (dd, $J = 15.2$, 7.6 Hz, 1H), 5.54 (dd, $J = 15.4$, 7.4 Hz, 1H*), 5.71 (dt, $J = 15.0$, 7.2 Hz, 1H), 6.05 (dd, $J = 14.9$, 10.5 Hz, 1H), 6.21 (dd, $J = 15.3$, 10.4 Hz, 1H), 6.52 (dd, $J = 11.1$, 9.3 Hz, 1H*), 7.28–7.48 (m, 11H), 7.61–7.74 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.7, 15.0*, 19.3, 22.4, 22.8*, 24.4*, 26.8, 34.7, 34.9, 66.7*, 67.0, 70.4, 70.5*, 80.6*, 80.7, 127.3, 127.58, 127.64, 127.9*, 128.3, 128.4*, 129.6, 129.7*, 133.4*, 133.9, 135.5*, 135.7, 137.2, 138.8*, 138.9; IR (film) ν^{-1} 3069, 3031, 2986, 2928, 2852, 1470, 1431, 1103, 1089, 989, 702; MS (FAB) m/z 507 (65) $[\text{M} + \text{Na}]^+$, 271 (56), 249 (42), 198 (100); HRMS (FAB) m/z calcd for $\text{C}_{32}\text{H}_{40}\text{O}_2\text{SiNa}$ 507.2695, found 507.2698.

Olefin 13i:^{15,17} yellowish oil; ^1H NMR (300 MHz, CDCl_3) δ 0.91 (t, $J = 5.9$ Hz, 3H), 0.99–1.50 (m, 10H), 1.50–1.88 (m, 3H), 1.90–2.11 (m, 2H), 2.15 (dd, $J = 13.9$, 6.4 Hz, 2H*), 5.16 (t, $J = 10.1$ Hz, 1H*), 5.32 (dt, $J = 15.5$, 6.2 Hz, 1H*), 5.49–5.73 (m, 2H), 5.91–6.09 (m, 2H), 6.23–6.37 (m, 2H*); ^{13}C NMR (75 MHz, CDCl_3) δ 14.0, 22.8, 23.1*, 26.1*, 26.3, 26.4, 30.0*, 33.2, 33.5*, 35.0, 35.2*, 37.0*, 40.9, 41.2*, 127.0*, 128.0, 131.0, 132.6, 134.7*, 136.3*, 138.5, 140.7*; IR (film) ν^{-1} 3016, 2957, 2921, 2851, 1448, 1377, 986; MS (EI) m/z 178 (56) $[\text{M}^+]$, 170 (11), 135 (28), 121 (28), 112 (33), 96 (54), 93 (42), 86 (100); HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{22}$ 178.1716, found 178.1715.

Olefin 13j:^{15,18} colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 0.062 (s, 3H), 0.067 (s, 3H), 0.88–0.95 (s, 12H), 1.22 (d, $J = 6.3$ Hz, 3H), 1.31–1.58 (m, 2H), 2.06 (dd, $J = 14.4$, 7.1 Hz, 2H), 4.33 (p, $J = 6.2$ Hz, 1H), 5.57 (dd, $J = 14.6$, 5.7 Hz, 1H), 5.66 (dd, $J = 14.5$, 7.0 Hz, 1H), 5.94–6.17 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ -4.61, -4.42, 14.0, 18.51, 22.7, 25.9*, 26.1, 35.0, 65.5*, 69.3, 128.7, 130.1, 134.4, 135.6; IR (film) ν^{-1} 2957, 2927, 2891, 2858, 1550, 1504, 1462, 1252, 1089, 987, 832; MS (CI) m/z 254 (100) $[\text{M}^+]$, 255 (35) $[\text{M} + \text{H}]^+$, 139 (43), 115 (65); HRMS (CI) m/z calcd for $\text{C}_{15}\text{H}_{30}\text{OSi}$ 254.2066, found 254.2068.

Olefin 13k:¹⁵ yellowish oil; ^1H NMR (300 MHz, CDCl_3) δ 0.94 (t, $J = 7.3$ Hz, 3H*), 0.96 (t, $J = 7.4$ Hz, 3H), 1.32–1.61 (m, 2H), 2.14 (p, $J = 6.9$ Hz, 2H), 2.28 (dt, $J = 14.9$, 7.4 Hz, 2H*), 5.47–5.73 (m, 1H*), 5.76–6.02 (m, 2H), 6.40 (d, $J = 15.7$ Hz, 1H), 6.51 (d, $J = 10.1$ Hz, 1H*), 6.75 (dd, $J = 15.6$, 10.4 Hz, 1H), 7.06 (dt, $J = 11.1$, 9.2 Hz, 1H*), 7.22–7.45 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.94, 14.01*, 22.6, 23.1*, 30.3*, 35.2, 124.6*, 125.3*, 126.4, 127.5, 127.7*, 128.6, 128.8*, 128.9, 130.6, 130.8*, 131.4, 132.7*, 136.4*, 136.5*, 136.7, 138.9; IR (film) ν^{-1} 3012, 2959, 2928, 2872, 1641, 1489, 1456, 1091, 1012, 986, 845, 820, 798, 735; MS (EI) m/z 206 (68) $[\text{M}^+]$, 207 (18) $[\text{M} + 1]^+$, 208 (33) $[\text{M} + 2]^+$, 209 (6) $[\text{M} + 3]^+$, 205 (11), 179 (37), 177 (100), 167 (37), 165 (87), 163 (46), 141 (49); HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{Cl}$ 206.0857, found 206.0857.

Olefin 13l:¹⁵ yellowish solid; mp = 32–33 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 0.95 (t, $J = 7.8$ Hz, 3H), 1.42–1.53 (m, 2H), 2.16 (dt, $J = 14.2$, 6.8 Hz, 2H), 2.31 (dt, $J = 13.1$, 6.6 Hz, 2H*), 5.68 (dt, $J = 15.6$, 8.6 Hz, 1H*), 5.76–6.02 (m, 2H), 6.19 (dt, $J = 15.4$, 9.4 Hz, 1H*), 6.47 (d, $J = 15.5$ Hz, 1H), 6.53 (d, $J = 10.6$ Hz, 1H*), 6.88 (dd, $J = 15.7$, 10.4 Hz, 1H), 7.19 (dt, $J = 11.2$, 9.3 Hz, 1H*), 7.46 (t, $J = 8.1$ Hz, 2H), 7.51 (t, $J = 7.8$ Hz, 2H*), 8.03 (d, $J = 8.7$ Hz, 2H), 8.09 (d, $J = 8.2$ Hz, 2H*); ^{13}C NMR (75 MHz, CDCl_3) δ 13.9, 22.5, 35.2, 124.9, 125.6, 127.4, 129.3, 129.6, 130.1, 132.0, 132.7, 133.3, 135.0, 138.7, 139.8, 140.7, 141.6, 148.9; IR (film) ν^{-1} 3062, 2983, 2945, 2875, 1523, 1346, 995, 825, 864, 723; MS (EI) m/z 217 (75) $[\text{M}^+]$, 218 (11) $[\text{M} + 1]^+$, 188 (67), 158 (34), 142 (81), 141 (100), 128 (58), 115 (46); HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{O}_2\text{N}$ 217.1097, found 217.1093.

Olefin 13m:¹⁵ yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 2.49 (dd, $J = 14.9$, 7.1 Hz, 2H*), 2.64 (dd, $J = 14.6$, 7.3 Hz, 2H), 2.75–2.86 (m, 2H), 5.59 (dt, $J = 10.7$, 7.6 Hz, 1H), 5.88 (dt, $J = 15.2$, 7.1 Hz, 1H*), 6.20 (t, $J = 10.9$ Hz, 1H), 6.27 (dd, $J = 15.0$, 10.0 Hz, 1H*), 6.47 (d, $J = 15.8$ Hz, 1H*), 6.54 (d, $J = 15.5$ Hz, 1H), 6.77 (dd, $J = 15.6$, 10.4 Hz, 1H*), 7.03 (ddd, $J = 15.4$, 11.3 Hz, 1H), 7.19–7.42 (m, 10H); ^{13}C NMR (125 MHz, CDCl_3) δ 30.1, 34.9*, 36.0*, 36.1, 124.5, 126.2, 126.4*, 126.6, 127.4*, 127.6, 128.6, 128.7, 128.8, 129.5, 130.7*, 131.3*, 132.0, 132.6, 134.8*, 137.8, 141.9; IR (film) ν^{-1} 3071, 3024, 2924, 2870, 1495, 1452, 1074, 986, 945, 748, 729; MS (EI) m/z 234 (18) $[\text{M}^+]$, 235 (3) $[\text{M} + \text{H}]^+$, 143 (100), 128 (47), 91 (54), 84 (41); HRMS (EI) m/z calcd for $\text{C}_{18}\text{H}_{18}$ 234.1403, found 234.1400.

Olefin 13n:¹⁵ slightly yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 0.96 (d, J = 6.6 Hz, 3H), 1.11–1.34 (m, 1H), 1.34–1.52 (m, 1H), 1.52–1.62 (m, 1H), 1.64 (s, 3H), 1.72 (s, 3H), 2.04 (dq, J = 14.3, 7.3 Hz, 2H), 2.11–2.26 (m, 1H), 2.32 (dt, J = 13.5, 6.7 Hz, 1H), 5.14 (t, J = 7.0 Hz, 1H), 5.57 (dt, J = 10.5, 8.0 Hz, 1H), 5.84 (dt, J = 15.0, 7.4 Hz, 1H*), 6.24 (t, J = 10.9, 1H), 6.47 (d, J = 15.7 Hz, 1H*), 6.55 (d, J = 15.6 Hz, 1H), 6.80 (dd, J = 15.6, 10.3 Hz, 1H*), 7.09 (dd, J = 15.5, 11.1 Hz, 1H), 7.18–7.48 (m, 5H); ¹³C NMR (125 MHz, CDCl₃) δ 17.9, 19.8, 25.9, 26.0, 29.9, 33.1*, 33.4, 35.4, 37.0, 40.6*, 124.8, 125.0, 126.3*, 126.5, 127.3*, 127.5, 128.8, 129.7, 130.1*, 131.4, 131.9*, 132.2, 132.2, 134.7*, 137.9; IR (film) ν⁻¹ 3078, 3058, 2926, 2908, 2870, 1595, 1493, 1448, 1377, 984, 945, 908; MS (CI) m/z 254 (100) [M]⁺, 255 (31) [M + 1]⁺, 211 (23), 163 (11), 143 (16); HRMS (CI) m/z calcd for C₁₉H₂₆ 254.2035, found 254.2027.

Olefin 13o:¹⁵ yellow viscous oil; ¹H NMR (300 MHz, CDCl₃) δ 4.19 (d, J = 6.1 Hz, 2H), 4.36 (d, J = 6.8 Hz, 2H*), 4.63 (d, J = 6.0 Hz, 2H), 5.77 (dt, J = 11.1, 6.8 Hz, 1H*), 6.00 (dt, J = 15.1, 6.1 Hz, 1H), 6.41 (t, J = 11.0 Hz, 1H*), 6.51 (dd, J = 15.2, 10.5 Hz, 1H), 6.62 (d, J = 15.7 Hz, 1H), 6.65 (d, J = 15.5 Hz, 1H*), 6.87 (dd, J = 15.6, 10.5 Hz, 1H), 7.07 (dd, J = 15.5, 11.2 Hz, 1H*), 7.24–7.54 (m, 10H); ¹³C NMR (75 MHz, CDCl₃) δ 65.9*, 70.5, 72.1*, 72.2, 123.8, 126.5, 126.6*, 127.66, 127.70, 127.74, 127.8, 128.0, 128.3*, 128.48, 128.50, 128.7, 130.2, 132.0, 132.8, 133.0, 134.3, 137.1*, 137.2, 138.3*, 138.4; IR (film) ν⁻¹ 3080, 3059, 3026, 2920, 2850, 1597, 1494, 1450, 1360, 1097, 1070, 989, 732, 692; MS (EI) m/z 250 (8) [M]⁺, 159 (22), 131 (53), 117 (56), 115 (75); HRMS (CI) m/z calcd for C₁₈H₁₈O 250.1352, found 250.1346.

Olefin 13p:¹⁵ yellowish syrup; ¹H NMR (300 MHz, CDCl₃) δ 1.06 (s, 9H*), 1.07 (s, 9H), 3.70 (dd, J = 10.6, 5.0 Hz, 1H and 1H*), 3.86 (dd, J = 10.7, 6.4 Hz, 1H and 1H*), 3.89 (dd, J = 11.4, 6.8 Hz, 1H*), 4.06 (dd, J = 11.9, 6.7 Hz, 1H), 4.49 (dd, J = 12.1, 6.3 Hz, 1H and 1H*), 4.68 (dd, J = 12.2, 3.8 Hz, 1H and 1H*), 5.41 (dd, J = 10.1, 9.8 Hz, 1H*), 5.71 (dd, J = 15.4, 7.5 Hz, 1H), 6.39 (dd, J = 15.5, 10.5 Hz, 1H, H-1), 6.45 (dd, J = 10.8, 6.2 Hz, 1H*), 6.56 (d, J = 15.7 Hz, 1H, H-1), 6.57 (d, J = 15.4 Hz, 1H*), 6.78 (dd, J = 15.5, 10.2 Hz, 1H), 6.87 (dd, J = 14.9, 10.5 Hz, 1H*), 7.28–7.52 (m, 15), 7.58–7.80 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 19.5, 26.9*, 27.1, 66.9*, 67.1, 70.4*, 70.9, 75.4, 80.6, 124.3, 126.6, 126.8, 127.7, 128.1, 128.5, 128.76, 128.85, 129.5, 129.8, 132.0, 132.8, 135.1, 135.9, 137.4, 138.8, 138.9; IR (film) ν⁻¹ 3068, 3028, 2957, 2929, 2856, 1471, 1427, 1110, 1083, 991, 700; MS (FAB) m/z 541 (85) [M + Na]⁺, 411 (24), 271 (68), 249 (32), 197 (100); HRMS (FAB) m/z calcd for C₃₃H₃₈O₂SiNa 541.2539, found 541.2543.

Olefin 13q:^{15,18} yellowish oil; ¹H NMR (300 MHz, CDCl₃) δ 1.25 (s, 9H*), 1.27 (s, 9H), 5.51 (d, J = 11.9 Hz, 1H*), 5.88 (d, J = 15.5 Hz, 1H), 6.02 (t, J = 11.8 Hz, 1H*), 6.17 (dd, J = 15.5, 10.2 Hz, 1H), 6.46 (d, J = 15.4 Hz, 1H*), 6.49 (d, J = 15.7 Hz, 1H), 6.77 (dd, J = 15.6, 10.2 Hz, 1H), 7.18–7.40 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 22.9, 29.6*, 29.8, 124.1*, 125.6, 126.3, 126.6*, 127.2, 127.6*, 128.8, 130.1, 130.4, 131.9*, 137.9, 147.0; IR (film) ν⁻¹ 3024, 2958, 2916, 2849, 1595, 1488, 1462, 1361, 1232, 987, 910, 744; MS (EI) m/z 186 (27) [M]⁺, 187 (2) [M + H]⁺, 171 (26), 86 (66), 84 (100), 57 (14); HRMS (EI) m/z calcd for C₁₄H₁₈ 186.1403, found 186.1399.

Olefin 13r:^{15,19} yellowish oil; ¹H NMR (500 MHz, CDCl₃) δ 2.62 (dd, J = 15.0, 7.0 Hz, 2H*), 2.69–2.80 (m, 2H), 2.80–3.01 (m, 2H and 2H*), 5.79 (dt, J = 11.6, 6.9 Hz, 1H), 6.35 (dt, J = 15.8, 6.7 Hz, 1H*), 6.51 (d, J = 15.9 Hz, 1H*), 6.54 (d, J = 11.6 Hz, 1H), 7.21–7.49 (m, 10H); ¹³C NMR (125 MHz, CDCl₃) δ 30.6, 35.1*, 36.1*, 36.3, 126.1*, 126.2, 126.8, 127.1*, 128.3, 128.5, 128.7, 128.9, 129.6, 130.1*, 130.5*, 132.0, 137.7, 137.9*, 141.8, 141.9*; IR (film) ν⁻¹ 3061, 3024, 2922, 2854, 1601, 1495, 1452, 1074, 1030, 964, 908, 735, 696; MS (EI) m/z 208 (7) [M]⁺, 209 (2) [M + 1]⁺, 129 (12), 117 (100), 115 (66), 91 (86); HRMS (EI) m/z calcd for C₁₆H₁₆ 208.1247, found 208.1248.

Olefin 13s:^{15,20} yellowish oil; ¹H NMR (300 MHz, CDCl₃) δ 4.25 (d, J = 6.0 Hz, 2H), 4.36 (dd, J = 6.4, 1.1 Hz, 2H*), 4.58 (s, 2H*), 4.63 (s, 2H), 5.97 (dt, J = 12.4, 6.3 Hz, 1H*), 6.39 (dt, J = 15.9, 6.0 Hz, 1H), 6.67 (d, J = 11.2 Hz, 1H*), 6.69 (d, J = 16.0 Hz, 1H), 7.21–7.53 (m, 10H); ¹³C NMR (75 MHz, CDCl₃) δ 67.1*, 70.9, 72.3, 72.6*, 126.2, 126.7, 127.3*, 127.8, 127.98, 128.04*, 128.4*, 128.6,

128.7, 129.0, 129.1*, 132.0*, 132.7, 136.7*, 136.9, 138.3*, 138.4; IR (film) ν⁻¹ 3061, 3026, 2922, 2848, 1494, 1452, 1360, 1112, 1072, 966, 732, 692; MS (FAB) m/z 295 (15) [M + Na]⁺, 281 (61), 263 (20), 247 (100), 237 (35), 221 (56), 199 (42), 180 (65); HRMS (FAB) m/z calcd for C₁₆H₁₆ONa 247.1099, found 247.1097.

Hydroxysulfone 8 Synthesis. Epoxide Opening.⁸ A solution of styrene oxide (690 μL, 6.07 mmol) and BT-SH (1.12 g, 6.68 mmol) in CH₂Cl₂ (66.8 mL, 0.1 M) was cooled to 0 °C, and Sm(OTf)₃ (36 mg, 0.06 mmol) was added in one portion. The resulting mixture was allowed to warm to rt and stirred for 8 h. After the mixture was stirred at rt for 8 h, a saturated aqueous solution of NaHCO₃ (50 mL) was added. The resulting layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 70 mL); the combined organic layers were washed with brine (50 mL), dried over MgSO₄, and filtered; and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography on SiO₂ (petroleum ether/EtOAc = 4:1 → 2:1), and the reaction yielded 1.70 g (98%) of **hydroxy BT-sulfide** as a colorless viscous oil: ¹H NMR (300 MHz, CDCl₃) δ 3.97 (broad s, 1H), 4.17–4.35 (m, 2H), 5.16 (dd, J = 7.2, 5.6 Hz, 1H), 7.29–7.48 (m, 7H), 7.75 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 55.4, 67.5, 121.3, 121.8, 124.9, 126.5, 128.1, 128.6, 129.3, 135.7, 137.7, 152.8, 166.7; MS (CI) m/z 288 (100) [M + 1]⁺, 289 (19) [M + 2]⁺, 290 (11) [M + 2]⁺, 151 (8), 149 (25); HRMS (CI) m/z calcd for C₁₅H₁₄ONS₂ 288.0517, found 288.0515. **Hydroxy PT-sulfide:** colorless viscous oil; ¹H NMR (300 MHz, CDCl₃) δ 3.06 (broad s, 1H), 4.24 (d, J = 6.1 Hz, 2H), 5.19 (t, J = 6.3 Hz, 1H), 7.28–7.44 (m, 5H), 7.53 (broad s, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 55.5, 67.5, 121.3, 121.8, 124.9, 126.5, 128.1, 128.6, 129.3, 135.7, 137.7, 152.8, 166.7; MS (ESI) m/z 299 (100) [M + 1]⁺, 300 (21) [M + 2]⁺, 301 (8) [M + 3]⁺, 239 (30), 151 (20); HRMS (ESI) m/z calcd for C₁₅H₁₅ON₂S 299.0961, found 299.0964.

Sulfide Oxidation. A solution of hydroxy BT-sulfide (500 mg, 1.74 mmol) in EtOH (17.4 mL, 0.2 M) was cooled to 0 °C, and a cold (0 °C) yellow solution of molybdate (108 mg, 87 μmol) in 35% aqueous H₂O₂ (2 mL, 17.5 mmol) was added dropwise. The resulting mixture was allowed to warm to rt and stirred for an additional 18 h. The resulting slightly yellow milky solution was cooled to 0 °C, and aqueous saturated Na₂S₂O₃ (10 mL) was added dropwise. Water (10 mL) was added, and the whole mixture was extracted with EtOAc (3 × 25 mL). The combined organic layers were washed with brine (10 mL), dried over MgSO₄, and filtered, and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography on SiO₂ (petroleum ether/EtOAc = 2:1 → 1:1 → 0:100), and the reaction yielded 410 mg (74%) of **8a** as a colorless solid: mp = 161–162 °C; ¹H NMR (500 MHz, CDCl₃) δ 2.60 (broad s, 2H), 4.30 (dd, J = 12.4, 4.9 Hz, 1H), 4.78 (dd, J = 12.4, 7.5 Hz, 1H), 4.93 (dd, J = 7.4, 4.9 Hz, 1H), 7.21–7.35 (m, 5H), 7.58 (dd, J = 11.2, 4.1 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 4.64 (dt, J = 7.7, 1.0 Hz, 1H), 8.24 (d, J = 8.3 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 61.5, 72.6, 111.6, 122.4, 125.7, 127.9, 128.3, 129.2, 129.8, 130.1, 137.3, 152.7, 165.3; MS (ESI) m/z 342 (100) [M + Na]⁺, 301 (64), 214 (17), 121 (8); HRMS (ESI) m/z calcd for C₁₅H₁₄O₃NS₂ 320.0410, found 320.0412.

Sulfone 8b: colorless viscous syrup; ¹H NMR (300 MHz, CDCl₃) δ ¹H NMR (300 MHz, CDCl₃) δ 3.09 (broad s, 1H), 4.20 (dd, J = 12.3, 4.8 Hz, 1H), 4.64 (dd, J = 12.3, 8.5 Hz, 1H), 5.02 (dd, J = 8.4, 4.8 Hz, 1H), 7.21–7.43 (m, 7H), 7.45–7.63 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 61.4, 73.8, 126.2, 127.6, 129.4, 130.3, 130.5, 131.6, 132.9, 153.7; MS (ESI) m/z 353 (100) [M + Na]⁺, 331 (15) [M + 1]⁺, 267 (8), 119 (10); HRMS (ESI) m/z calcd for C₁₅H₁₅O₃N₂S 331.0859, found 331.0863.

■ ASSOCIATED CONTENT

Supporting Information

Optimization tables, additional information, and ¹H and ¹³C NMR spectra for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Fabio Lucaccioni (U.C.L.) is gratefully acknowledged for his help with GC and HPLC separation method development. J.P. is grateful to Prof. István E. Markó (U.C.L.) for his continuous support. The Université Catholique de Louvain and the Fond de la Recherche Scientifique (Chargé de Recherche F.R.S.-FNRS to J.P., Chercheur Qualifié F.R.S.-FNRS to R.R.) are gratefully acknowledged for financial support.

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