Radical chain reactions involving 9-alkyl-9-borafluorenes

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Dedicated to Prof. Pierre Vogel on the occasion of his 70th birthday

Abstract

The preparation of 9-alkyl-9-borafluorenes and their use as radical precursors in chain reactions were investigated. These organoboranes were found to be excellent precursors of primary and secondary alkyl radicals. Reactions were readily initiated by traces of oxygen and efficient processes involving sulfonyl-based radical traps were discovered. Due to the very high reactivity of the intermediate 9-*H* and 9-alkyl-9-borafluorenes, problems of reproducibility were identified.

Keywords: Radical reaction, Lewis acidity, hydroboration, sulfurization, thiosulfonates, sulfones, sulfonyl chloride

Introduction

Nowadays, radical reactions represent a very useful tool in organic synthesis.[1] Efficient and environmentally friendly ways to generate carbon-centered radicals remain a challenging problem faced by organic chemists. Organoboranes are privileged precursors for the generation of alkyl radicals[2,3] via homolytic substitution (S_H) by heteroatom-centered radicals.[4] Radical chain reactions involving organoboranes have been intensively investigated.[2,3,5,6,7] Initiation is usually performed by molecular oxygen, di-*tert*-butylperoxide or di-*tert*-butylhyponitrite. The use of benzenesulfonyl-containing radical trap (PhSO$_2$X) led to efficient chain processes with a variety of alkyboron derivatives such as alkylcatecholboranes.[6,8] The chain is propagated by the transient benzenesulfonyl radical PhSO$_2$• (Scheme 1, eq. 1). Recently, Scaiano reported a theoretical investigation on the substitution reaction involving oxygen-centered radicals and trialkyl-/triarylboranes.[9] The reaction mechanism involves an initial nucleophilic attack of the oxygen lone pair on the empty p orbital at boron and is best described as a nucleohomolytic reaction that shares many characteristics with conventional nucleophilic substitution (Scheme 1,

eq. 2). Based on this report, it is expected that the Lewis acidity of the organoborane may play an important role in the process leading to homolytic substitution.
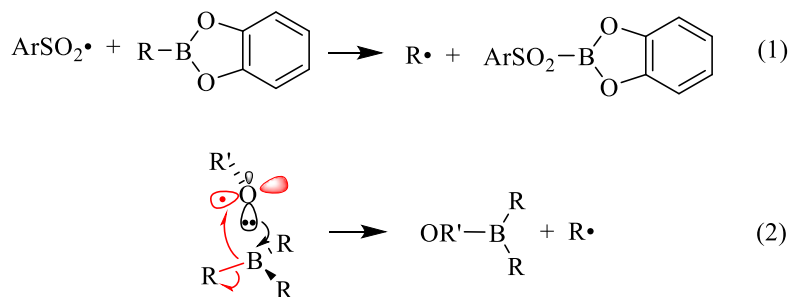

Scheme 1. Nucleohomolytic reaction at boron.

9-Alkyl-9-borafluorenes represent a fascinating class of organoboranes due to the 4π antiaromatic nature of the central borole ring since the vacant p-orbital at boron is conjugated with the π-system. Interactions with a Lewis base breaks the planarity, removing the p-orbital from the conjugation.[10] Therefore, 9-borafluorenes are strong Lewis acids and highly reactive. They were first synthesized by Köster and Benedikt in 1963[11,12] and by Narula and Nöth in 1985,[13] but the most efficient synthesis was developed only recently by Holthausen, Wagner and coworkers (Scheme 2).[14,15,16] 2,2'-Dibromobiphenyl **1** underwent double lithium-bromine exchange, followed by lithium-boron exchange[15] delivering desired 9-chloro-9-borafluorene **2**. Then, 9-*H*-9-borafluorene **3** could be generated by reduction of 9-chloro-9-borafluorene **2** or 9-bromo-9-borafluorene in the presence of triethylsilane in benzene.[16] Borane **3** is particularly unstable due to its antiaromatic character and it tends to reversibly form a dimer and to rapidly degrade, affording isomers and oligomers that exclude boron's empty p-orbital from the π-plane.[14,16,17,18] The mechanisms of isomerization and polymerization have been studied.[16,17,18] Unsymmetrical borafluorenes, synthesized by boron insertion in C–H[19] and C–C[20] bonds, and fluorinated 9-borafluorenes[21] were also studied.
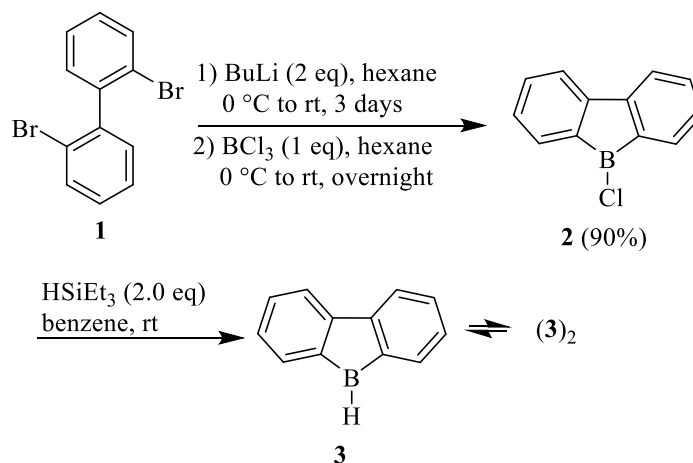
Scheme 2. Reported synthesis of 9-alkyl-9-borafluorenes.

When 9-*H*-9-borafluorene **3** was placed in the presence of ethylene, hydroboration was observed.[14] In the case of a terminal alkyne, mono or double hydroboration were observed.[16] To circumvent the stability problem of compound **3**, pyridine[16] and dimethylsulfide[18] stabilized complexes of the 9-*H*-9-borafluorene **3** were prepared from 9-chloro-9-borafluorene **2** in nearly quantitative yield. The complex **3**·SMe$_2$ was claimed to be a storable adduct of the reagent **3** (it does not oligomerize) and could be directly used for the hydroboration of alkynes (Scheme 3). These hydroborations led to 9-alkyl and 9-alkenyl-9-borafluorenes **4** and **5**. After hydroboration, Me$_2$S could be removed by storing the compound for several days under dynamic vacuum.
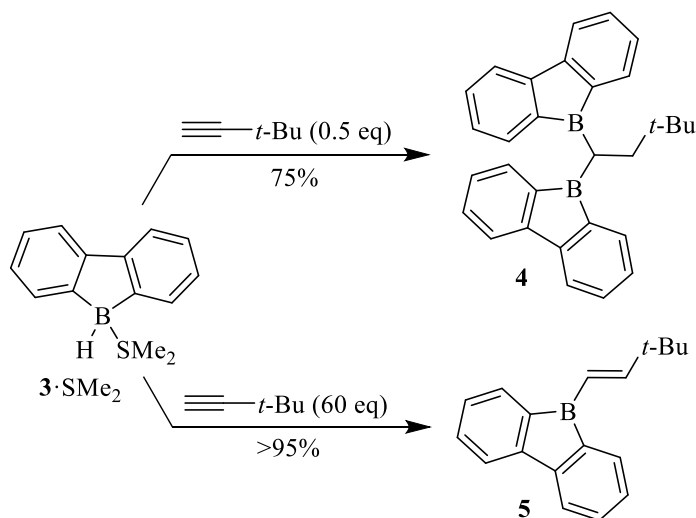

Scheme 3. Hydroboration with 9-*H*-9-borafluorene-dimethylsulfide complex **3**·SMe$_2$.

Due to their exceptional Lewis acidity, 9-alkyl-9-borafluorenes are expected to be highly reactive radical precursors that deliver selectively alkyl radicals due to their greater stability over aryl radicals. This hypothesis is nicely supported by the report of Chung who patented the use of 9-octylperoxy-9-borafluorene, generated by reaction of 9-octyl-9-borafluorene with oxygen, as an initiator for radical living polymerization processes.[22] In connection with our interest in organoboranes and their use as radical precursors,[5,23,24] we decided to synthesize and investigate the use of 9-alkyl-9-borafluorenes in radical reactions. We report herein that these compounds readily afford alkyl radicals that can be trapped successfully. The scope and limitations of this approach are presented.

Results and Discussion

Preparation of the 9-*H*-9-borafluorene. The first part of our study consisted in optimizing the protocol to prepare the desired reagent 9-chloro-9-borafluorene **2**. The literature procedure (Scheme 2) requires about 4 days[15] and was giving very variable results. We observed that the

second lithium-bromine exchange (conversion of **1** to **2**) is particularly slow in hexane. In ether solvents (THF or Et₂O) both exchanges could take place effectively in 3 hours, but remaining traces of the solvent hampered further reaction with boron trichloride, possibly by forming complexes with boron or organolithium species. To avoid these problems, the lithium-bromine exchange reaction on 2,2'-dibromobiphenyl **1** was performed in refluxing toluene.[25] After one hour, the double exchange reaction was complete. Boron trichloride was directly added to the dilithiated biphenyl and the reaction mixture was stirred overnight at room temperature (Scheme 4). After distillation, the chloroborane **2** was obtained in 77% yield and the physical and spectroscopic properties of **2** are in accordance with literature data.[15] Even if the reduction of **2** to the borane **3** works well on the crude chloride, we found that distillation of **2** enhanced the reproducibility of the whole procedure. By this procedure, **3** was prepared on 500 mg scale within 24 hours when it took about 4 days using the literature procedure.[15]
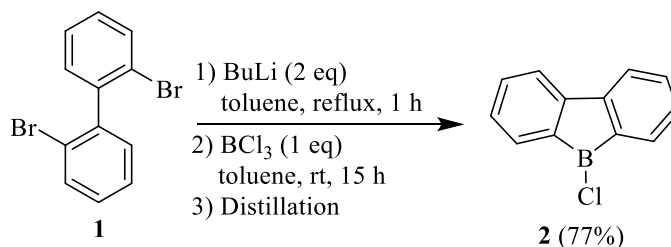

Scheme 4. Optimized synthesis of 9-chloro-9-borafluorene.

Generation of radicals. Reduction of 9-chloro-9-borafluorene **2** to 9-*H*-9-borafluorene **3** was performed in benzene according to literature procedure.[16] As reported, this compound is not stable and polymerizes rapidly.[16] Therefore, **3** was used immediately and was neither isolated nor stored. 9-*H*-9-borafluorene **3** was tested for the hydroboration of cyclohexene **6a**. The reaction was simply performed by adding the alkene to the previous reaction mixture (Scheme 5). After two hours at room temperature, *S*-phenyl benzenethiosulfonate (PhSO₂SPh) was added. The reaction was allowed to react for 20 h at room temperature and afforded the desired cyclohexyl phenyl sulfide **8a**.[24] The reaction was presumably initiated by traces of oxygen present in the solvent. Addition of a radical initiator like di-*tert*-butylhyponitrite did not change significantly the reaction outcome. The whole sequence was performed as a one-pot procedure and provided **8a** in essentially quantitative yield. Attempts to use other solvents such as hexane, dichloromethane, diethyl ether were unsuccessful. In toluene, the yield for the formation of **8a** was noticeably lower (below 20%).
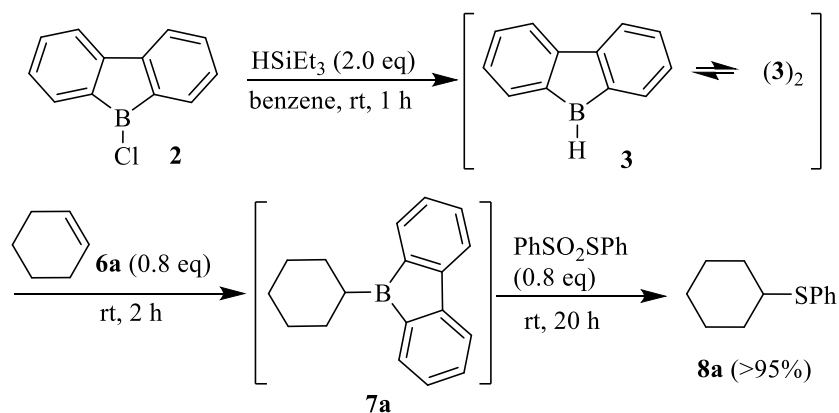
**Scheme 5.** Hydroboration-radical sulfurization of cyclohexene **6a**.

The scope of the sulfurization reaction was examined with different alkenes (Scheme 6). Primary radicals generated from 4-(phenyl)methylenecyclohexane **6b** and β-(–)-pinene **6c** provided the desired sulfides **8b** and **8c** in 89% and 21% yield, respectively. The secondary radical generated from α-(–)-pinene **6d** afforded **8d** in 63% yield. As anticipated, for the two pinenes **6c** and **6d**, hydroboration occurred preferentially from the least hindered face. The sulfides **8c** and **8d** were obtained as single diastereomers demonstrating that the hydroboration and the radical reaction (for **8d**) are fully diastereoselective. For compound **8b**, a 4:5 diastereomeric ratio was obtained. When a mixture of the two pinenes **6c** and **6d** (2 equivalents of each relative to borane **3**) was used, only the compound **8c** coming from the hydroboration of the terminal alkene β-(–)-pinene **6c** was observed demonstrating that despite its high reactivity, borane **3** reacts with the same chemoselectivity as classical hydroborating agents such as BH$_3$ and dialkyboranes.
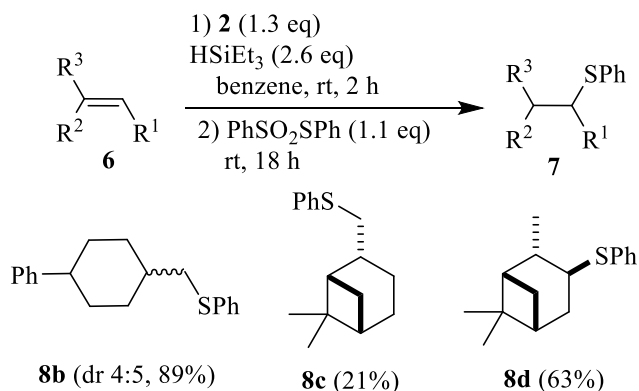
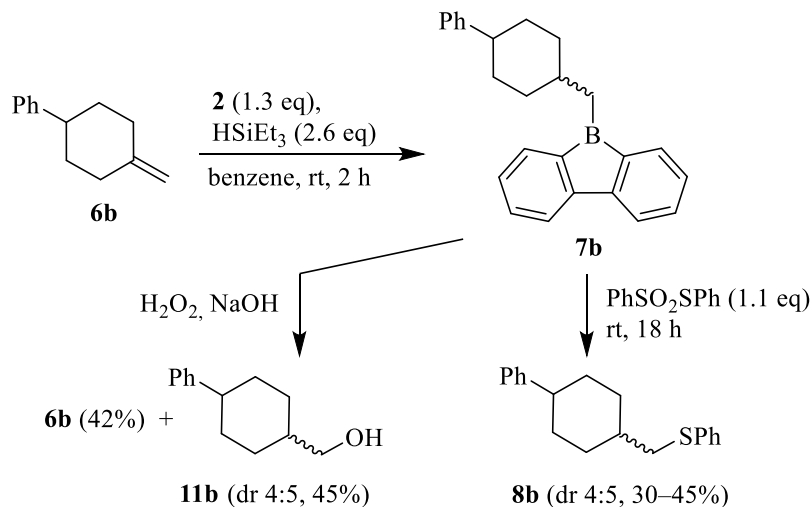**Scheme 6.** Hydroboration-radical sulfurization of alkenes.

The use of radical traps was tested next starting from 4-(phenyl)methylenecyclohexane **6b**. The chlorination reaction with benzenesulfonyl chloride[24] afforded **9b** in 94% yield (Scheme 7,

eq. 3). Allylation with ethyl 2-((phenylsulfonyl)methyl)acrylate[8] was also investigated. Despite the use of 1.6 equivalents of the trap and initiation by di-tert-butyl hyponitrite at 45 °C, the yield for the formation of allylated compound **10b** remained modest (Scheme 7, eq. 4). Other radical traps such as phenyl phenylethynyl sulfone[23] and cyclohexenenone[26] were also tested but did not provide the desired products.
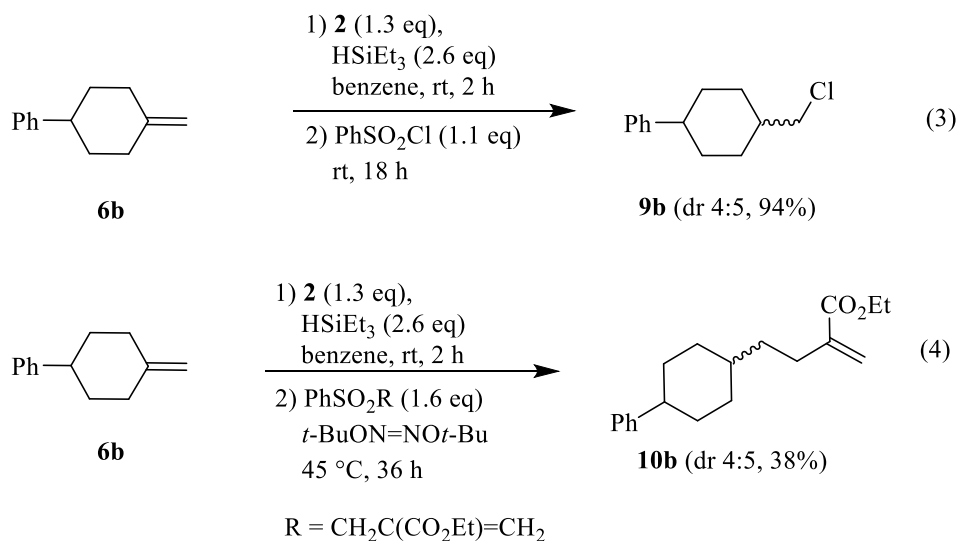
Scheme 7. Hydroboration-radical chlorination and allylation of alkenes.

Reproducibility of the results. The reactions reported here were shown to be difficult to reproduce. All reactions were repeated several times and significant variations of conversion and yield were observed. All our efforts to identify the factors responsible for these variations were inconclusive. However, experimental observations indicate that the problem is related to the formation of the 9-alkyl-9-borafluorene and not to the radical reaction. Indeed, oxidative treatment of the organoborane **7b** obtained by hydroboration of **6b** with freshly distilled 9-chloro-9-borafluorene **3** was investigated (Scheme 8). The alcohol **11b** was obtained in only 45% yield together with 42% of starting alkene **6b**. The possibility of a reversible hydroboration step was investigated but could not be clearly demonstrated. The same batch of **7b** afforded the sulfide **8b** in 30–45% yield upon reaction with PhSO$_2$SPh (the reaction was repeated 3–4 times)**.**

Scheme 8. Hydroboration-oxidation/sulfurization of 4-(phenyl)methylenecyclohexane **6b**.

Conclusions

9-Alkyl-9-borafluorenes have been shown to be extremely valuable radical precursors. The reactivity of these compounds is such that residual traces of oxygen in the solvent are sufficient to initiate efficient radical chain reactions involving phenylsulfonyl radicals. Primary and secondary alkyl radicals could be generated and trapped using benzenesulfonyl based radical traps. Despite this proof of concept, the high instability of 9-*H*- and 9-alkyl-9-borafluorenes limits the reproducibility of the method. A more reliable procedure involving stabilization of the borane **3** and the alkylborane intermediate **7** by complexation with Lewis base such as dimethyl sulfide is currently under investigation.

Experimental Section

General. All reactions were performed in heat-gun dried or oven dried glassware, under nitrogen or argon atmosphere, using schlenk technique. Solvents were filtered over anhydrous alumina columns under a positive pressure of argon. Extraction and purification solvents were technical grade, and were distilled prior to use. Commercial reagents were used without prior purification. 2,2'-dibromobiphenyl was synthesized using a known procedure[27]. Flash column chromatography was performed using Silicycle silica 60 (230-400 mesh). Filtration was performed using aluminium oxide (AlOx), 507-C-I Neutral. Thin layer chromatography (TLC) was performed using Silicycle glass backed silica gel 60 F_{254} plates, and vizualisation was achieved with UV irradiation (254 nm) or using $KMnO_4$ stain. Gas chromatography (GC) was performed on a Thermo Electron instrument Trace GC Ultra fitted with a Macherey-Nagel

Optima delta-3-0.25μm capillary column (20 m, 0.25 mm); gas carrier: He 1.4 mL/min; injector: 220°C split mode; detector: FID 280°C, H_2 35 mL/min, air 350 mL/min. Method : Starting from 50°C for 1 minute, the temperature was increased to 180°C at 8 °C/min, then to 280°C at 40 °C/min. Gas chromatography – mass spectroscopy (GCMS) were performed on a Finnigan Trace GC/MS (quadrupole mass analyzer using electron impact 70 eV), fitted with a Macherey-Nagel Optima delta-3-0.25μm capillary column (20 m, 0.25 mm); gas carrier: He 1.2 mL/min; injector: 220°C split mode, using the same method. Proton NMR (^{1}H NMR) and carbon NMR (^{13}C NMR) spectra were recorded on a Brüker Avance 300 or Brüker Avance II 400 spectrometers (^{1}H frequency at 300.18 or 400.13 MHz, ^{13}C frequency at 75.48 or 100.62 MHz) at room temperature (rt). Boron NMR (^{11}B NMR) was recorded on a Bruker Avance II 400 spectrometer ([11]B frequency at 128.38 MHz) at room temperature. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual proton signals in $CDCl_3$ (δ 7.26, 77.16 ppm) or C_6D_6 (δ 7.16, 128.06 ppm) for ^{1}H and ^{13}C, and to Et_2OBF_3 as an external standard (δ 0 ppm) for ^{11}B NMR. Coupling constants (J) are reported in Hertz (Hz) and refer to apparent multiplicities. The following abbreviations are used for the multiplicities: s: singlet, brs: broad singlet, d: doublet, t: triplet, q: quartet and m: multiplet). Infrared spectra (IR) were recorded on a Jasco FT-IR-460 Plus spectrometer equipped with a Specac MKII Golden Gate Single Reflection Diamond ATR System. The characteristic IR absorption frequencies are reported in wave numbers (cm^{-1}). Low resolution mass spectroscopy (MS) was obtained from the GCMS. High-resolution mass spectra (HRMS) were performed on a Thermo Scientific LTQ Orbitrap XL mass S-3 spectrometer using ESI mode at the University of Bern or on a Thermo DFS double-focusing magnetic sector mass spectrometer using EI mode at 45 eV at the University of Zürich.

9-Chloro-9-borafluorene (2).[15] To a solution of 2,2'-dibromobiphenyl (900 mg, 2.9 mmol) in toluene (20 mL) was added at room temperature a 2.5M solution of *n*BuLi in hexane (2.3 mL, 5.8 mmol). The reaction mixture was refluxed for 1h, and was followed by performing GCMS on hydrolyzed aliquots of the reaction to monitor the disappearance of 2,2'-dibromobiphenl and 2-bromobiphenyl and the appearance of biphenyl. The progressive appearance of a white precipitate was observed. The reaction mixture was then cooled to 0 °C, and a 1M solution of BCl_3 in heptane (2.9 mL, 2.9 mmol) was added. The suspension turned yellow, and was stirred at room temperature for 15h. The suspension was decanted, and salts were separated from the liquid, rinced twice with dry toluene (5 mL) and discarded. Toluene was removed from the filtrate by distillation at 45°C and 65 mbar. A bright yellow oil was obtained. It could be distilled to afford a bright yellow oil[15] (439 mg, 77%), or could be used without prior purification. ^{1}H NMR analyses differs slightly from the literature, as we used C_6D_6 instead of chlorinated solvents, the other analyses matched literature data.[15] ^{1}H NMR (C_6D_6, 300 MHz): δ 7.60 (d, J 7.0 Hz, 2H), 7.36-7.33 (m, 2H), 7.17-7.11 (m, 2H), 7.01-6.94 (m, 2H). ^{13}C NMR (C_6D_6, 75 MHz): δ 153.5, 135.3, 133.0, 128.8, 120.0. The carbon directly attached to boron was not detected. ^{11}B NMR (C_6D_6, 128 MHz): δ 63.6 (s).

General Procedure. 9-Chloro-9-borafluorene (100 mg, 0.48 mmol) was dissolved in benzene (1 mL) and triethylsilane (0.15 mL, 0.96 mmol) was added. The reaction mixture was stirred at room temperature for 1h. The alkene was then added (0.37 mmol) in benzene (1 mL), and the reaction mixture was further stirred for 2h. The trap (0.4 mmol) was then added, the reaction mixture was stirred at room temperature for 18-20h and filtered through aluminium oxide. The pad of aluminium oxide was rinsed with diethylether, and the solvents were removed under reduced pressure. The crude material was purified by silica gel column chromatography using pure pentane as the eluent and afforded the desired compound.

Cyclohexyl(phenyl)sulfane (8a).[28] Prepared according to general procedure. The title compound was obtained as a colorless oil (71 mg, **quantitative yield**). Analyses matched literature data[28]. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.52-7.42 (m, 2H), 7.40-7.22 (m, 3H), 3.23-3.11 (m, 1H), 2.12-2.00 (m, 2H), 1.90-1.79 (m, 2H), 1.73-1.63 (m, 1H), 1.52-1.24 (m, 5H). MS (EI): *m/z* 192.2.

Phenyl((4-phenylcyclohexyl)methyl)sulfane (8b). Prepared according to general procedure. The title compound was obtained as a yellow oil. Obtained as a 4:5 mixture of diastereoisomers with traces of inseparable side product PhSSPh (92 mg, **89%**). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.40-7.16 (m, 20H), 3.07 (d, *J* 7.5 Hz, 2H) and 2.90 (d, *J* 6.8 Hz, 2H), 2.67-2.56 (m, 1H) and 2.50 (tt, *J* 3.3, 12.1 Hz, 1H), 2.15-1.56 (m, 14H), 1.48 (dq, *J* 3.3, 12.8 Hz, 2H) and 1.20 (dq, *J* 3.3, 12.8 Hz, 2H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 147.4, 147.1, 137.6, 137.2, 129.1 (2), 129.0 (4), 128.8 (2), 128.4 (4), 127.0 (2), 126.9 (2), 126.1, 126.0, 125.8, 125.7, 44.4, 43.4, 41.0, 37.4, 36.6, 34.0 (2), 33.2 (2), 32.7, 29.6 (2), 28.8 (2). IR: ν$_{max}$ 3023, 2920, 2849, 1584, 1479, 1447, 1437, 1024, 734, 697, 688. HRMS (ESI): *m/z* calcd. for [M]$^+$ C$_{19}$H$_{22}$S: 282.1437, found: 282.1442.[29]

((6,6-Dimethylbicyclo[3.1.1]heptan-2-yl)methyl)(phenyl)sulfane (8c).[30] 9-Chloro-9-borafluorene, (obtained from 2,2'-dibromobiphenyl (150 mg, 0.48 mmol) and used without prior purification) was dissolved in benzene (1 mL) and triethylsilane (0.15 mL, 0.96 mmol) was added. The reaction mixture was stirred at room temperature for 1h. α-pinene (154 µL, 0.96 mmol) and β-pinene (154 µL, 0.96 mmol) were then added, and the reaction mixture was further stirred for 2h. The trap (0.48 mmol) was then added, the reaction mixture was stirred at room temperature for 24h and filtered through aluminium oxide. The pad of aluminium oxide was rinsed with diethylether, and the solvents were removed under reduced pressure. The crude was purified by silica gel column chromatography using pentane as the eluent and afforded the desired compound as a colorless oil, with traces of inseparable side product (25 mg, **21%**). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.35-7.24 (m, 4H), 7.21-7.13 (m, 1H), 3.06-2.91 (m, 2H), 2.39-2.19 (m, 2H), 2.11-1.81 (m, 5H), 1.65-1.56 (m, 1H), 1.20 (s, 3H), 1.04 (s, 3H), 0.89 (d, *J* 9.6 Hz, 1H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 137.3, 129.0 (2), 128.9 (2), 125.7, 45.8, 41.4, 41.0, 40.7, 38.8, 33.5, 28.1, 26.3, 23.4, 22.2. IR: ν$_{max}$ 3000-2700, 1580, 1477, 1437, 1024, 735, 687. HRMS (ESI): *m/z* calcd. for [M]$^+$ C$_{16}$H$_{22}$S: 246.1437, found: 246.1440.[29]

Phenyl(2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)sulfane (8d).[31] Prepared according to general procedure. The title compound was obtained as a colorless oil (57 mg, **63%**). Analyses matched literature data[31]. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.47-7.39 (m, 2H), 7.34-7.14 (m, 3H), 3.45-3.34 (m, 1H), 2.59-2.44 (m, 1H), 2.38-2.27 (m, 1H), 2.15-2.02 (m, 2H), 1.99-1.88 (m, 1H), 1.88-1.78 (m, 1H), 1.20 (s, 3H), 1.11 (d, *J* 7.1 Hz, 3H), 1.02 (s, 3H), 0.98 (d, *J* 9.5 Hz, 1H). MS (EI): *m/z* 246.3.

(4-(Chloromethyl)cyclohexyl)benzene (9b). Prepared according to general procedure. The title compound was obtained as a colorless oil, in a 4:5 mixture of diastereoisomers (72 mg, **94%**). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.34-7.28 (m, 4H), 7.25-7.19 (m, 6H), 3.64 (d, *J* 7.7 Hz, 2H) and 3.46 (d, *J* 6.3 Hz, 2H), 2.70-2.60 (m, 1H) and 2.50 (tt, *J* 3.5, 12.0 Hz, 1H), 2.11-1.93 (m, 6H), 1.91-1.82 (m, 2H), 1.80-1.66 (m, 6H), 1.51 (dq, *J* 3.4, 12.7 Hz, 2H) and 1.22 (dq, *J* 3.6, 12.7 Hz, 2H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 147.2, 146.8, 128.5 (4), 127.0 (2), 126.9 (2), 126.1, 126.1, 51.0, 47.5, 44.3, 43.1, 40.0, 36.2, 33.7 (2), 31.1 (2), 28.8 (2), 28.0 (2). IR: ν$_{max}$ 2923, 2853, 1491, 1449, 729, 697. HRMS (EI): *m/z* calcd. for [M]$^+$ C$_{13}$H$_{17}$^{35}Cl: 208.10133, found: 208.10130.

Ethyl 2-((4-phenylcyclohexyl)methyl)acrylate (10b). Prepared according to general procedure using ethyl 2-((phenylsulfonyl)methyl)acrylate (150 mg, 0.6 mmol) as a trap and di-*tert*-butylhyponitrite (7 mg, 0.04 mmol) as an initiator. The reaction was then stirred at 45 °C for 36 h. The title compound was obtained as a colorless oil in a 4:5 mixture of diastereoisomers (40 mg, **38%**). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.33-7.14 (m, 10H), 6.15 (brs, 2H), 5.56-5.53 (m, 2H), 4.22 (q, *J* 7.0 Hz, 4H), 2.65-2.41 (m, 2H), 2.40-2.29 (m, 4H), 1.96-1.86 (m, 4H), 1.76-1.37 (m, 16H), 1.32 (t, *J* 7.0 Hz, 6H), 1.17-1.02 (m, 2H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 167.8, 167.6, 147.8, 147.6, 141.6, 141.5, 128.4 (2), 128.4 (2), 127.1 (2), 127.0 (2), 126.0, 125.9, 124.3, 124.2, 60.7 (2), 44.7, 43.7, 37.2, 36.2, 34.4 (2), 33.6 (2), 32.9, 30.9, 30.4, 30.2 (2), 29.5, 29.0 (2) 14.4 (2). IR: 2921, 2852, 1715, 1631, 1492, 1450, 1189, 1150, 1028, 939, 752, 698. HRMS (ESI): *m/z* calcd. for [M+H]$^+$ C$_{19}$H$_{27}$O$_2$: 287.2006 , found: 287.2011.

(4-Phenylcyclohexyl)methanol (11b). 9-chloro-9-borafluorene (100 mg, 0.48 mmol) was dissolved in benzene (1 mL) and triethylsilane (0.15 mL, 0.96 mmol) was added. The reaction mixture was stirred at room temperature for 1h. (4-methylenecyclohexyl)benzene was then added (0.37 mmol), and the reaction mixture was further stirred for 2h. Then, ethanol (0.4 mL) was added and the reaction mixture was stirred at room temperature for 15 minutes. A sodium hydroxide solution (3M, 0.4 mL) and hydrogen peroxide solution (30 wt%, 0.4 mL) were added and the reaction mixture was stirred at room temperature for 18h. Water and ethyl acetate were added and the layers were separated. The aqueous layer was extracted with ethyl acetate twice. The organic layers were combined, dried on Na$_2$SO$_4$, filtered and evaporated. The crude was purified by silica gel column chromatography using pentane to pentane /ethyl acetate 7/3 as the eluent and afforded the desired compound as an off-white paste (30 mg, **45%**), along with starting alkene (25 mg, **42%**). The desired compound was obtained as a 4:5 mixture of

diastereoisomers. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.34-7.16 (m, 10H), 3.72 (d, *J* 7.5 Hz, 2H) and 3.52 (d, *J* 6.3 Hz, 2H), 2,66-2.56 (m, 1H) and 2.50 (dt, *J* 3.0, 12.0 Hz, 1H), 2.01-1.86 (m, 5H), 1.79-1.42 (m, 13H), 1.13 (dq, *J* 4.1, 12.6 Hz, 2H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 147.5, 147.2, 128.4 (4), 127.0 (2), 126.9 (2), 126.0, 125.9, 68.8, 64.5, 44.6, 43.4, 40.2, 36.0, 33.8 (2), 29.9 (2), 29.2 (2), 26.9 (2). IR: ν$_{max}$ 3500-3000, 2919, 2853, 1724, 1492, 1448, 1274, 1031, 754, 697. HRMS (EI): *m/z* calcd. for [M]$^+$ C$_{13}$H$_{18}$O: 190.13522, found: 190.13542.

Acknowledgements

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