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**Supporting Information**

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# Tin-Free Radical Allylation of *B*-Alkylcatecholboranes

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**General Techniques**. $Et_2O$ THF was freshly distilled from sodium-benzophenone; $CH_2Cl_2$ and benzene from $CaH_2$. Catecholborane was obtained from Callery Chemical Compagny (Pittsburgh). The different sulfones were synthesized according to literature procedures.[1,2] Other reagents were obtained from commercial sources and used as received. Flash column chromatography (FC) and filtration: *SDS silica gel* (40-63 μm); AcOEt, $Et_2O$, hexane and pentane as eluents. Thin layer chromatography (TLC): *Merck silica gel 60 $F_{254}$* analytical plates; detection either with UV or dipping in a solution of $KMnO_4$ (3 g), $K_2CO_3$ (20 g), NaOH 5% (5 ml) in $H_2O$ (300 ml) or in a solution of phosphomolibdic acid (25 g), $Ce(SO_4)_2 \cdot 4H_2O$ (10 g), $H_2SO_4$ 96% (60 ml) in $H_2O$ (940 ml) and subsequent heating. NMR spectroscopy: *Bruker AC 300* ($^1H$ = 300 MHz, $^{13}C$ = 75.5 MHz), chemical shift in ppm relative to tetramethylsilane (δ =0 ppm) or $CHCl_3$ for $^1H$ (δ = 7.26 ppm) and $CDCl_3$ for $^{13}C$ (δ = 77.0 ppm). MS: *Micromass AutospecQ* (*Manchester, UK*); EI (70 eV) *m/z* (%). High Resolution Mass Spectra (HRMS) were recorded on a *Micromass AutospecQ* as LSIMS (Liquid Secondary Ion Mass Spectr.) with a $Cs^+$ ion beam at 20KV (polyethyleneglycol as internal standard).

**General procedure GP 1**

Catecholborane (0.8 mL, 7.5 mmol) was added dropwise at 0 °C to a solution of olefin (3.0 mmol) and *N,N*-dimethylacetamide (28.0 μL, 0.3 mmol) in $CH_2Cl_2$ (2.0 mL) under nitrogen. The reaction mixture was heated under reflux for 5 h. MeOH (0.20 mL, 4.8 mmol) was added at 0 °C and the solution was stirred for 15 min at rt. The sulfone (3.6 mmol) was then added and the solution was warmed at reflux and di-*tert*-butylhyponitrite (3 mol%) was added every hour. The reaction was monitored by

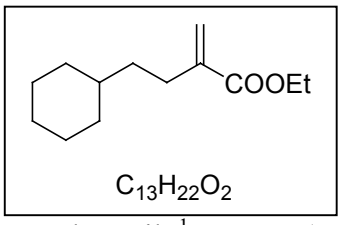
GCMS. At the end of the reaction, the solution turned to black. The crude product was purified by flash chromatography over silicagel.

**General procedure GP 2**

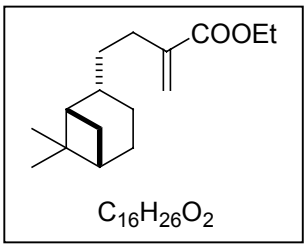
Catecholborane (0.8 mL, 7.5 mmol) was added dropwise at 0 °C and to a solution of olefin (3.0 mmol) and *N,N*-dimethylacetamide (28.0 μL, 0.3 mmol) in $CH_2Cl_2$ (2.0 mL) under nitrogen. The reaction mixture was heated under reflux for 5 h. MeOH (0.20 mL, 4.8 mmol) was added at 0 °C and the solution was stirred for 15 min at rt. The sulfone (9 mmol) was then added and the solution was warmed at reflux and di-*tert*-butylhyponitrite (3 mol%) was added every hour. The reaction was monitored by GCMS. At the end of the reaction, the solution turned to black. The crude product was purified by FC. Analytically pure products were obtained by preparative GC (column: 43 X 1 cm; *20% Carbowax 20M on Chromosorb A 60/80 mesh*).

**Preparation of Di-*tert*-butylhyponitrite**

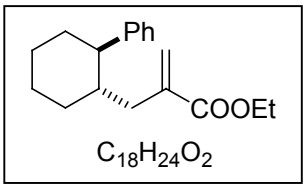
Zinc chloride (1.56 g, 11.4 mmol), dried under vacuum, was added to a mixture of *tert*-butyl bromide (10 mL) in dry ether (10 mL). Sodium hyponitrite (Aldrich, dried at 1 torr to constant weight) (1.2 g, 11.4 mmol) was then added over 5 min by portions by keeping the temperature of the reaction mixture below 45 °C. After 75 min at room temperature, the inorganic salts were removed by filtration and the organic phase was washed with 10 mL of water. The aqueous phase was extracted with 8 mL of ether and the combined organic phases washed with 4 X 10 mL of water and dried over $MgSO_4$. The solvent was removed by evaporation under reduced pressure. The residue was recrystallized from pentane at 4 °C to give white needles (O.812 g, 41%).



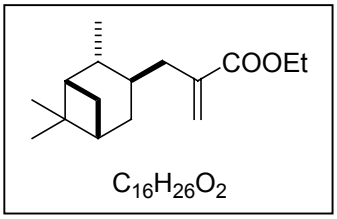

**Ethyl 2-(2-cyclohexylethyl)acrylate (7)**. According to GP1. Starting from methylenecyclohexane **1** (0.288 g, 3 mmol), FC (hexane/AcOEt 4:1) afforded **7** (0.350 g, 55%) as a clear oil. $^1$H NMR (300 MHz, $CDCl_3$): 6.03 (s, 1H), 5.42 (s, 1H), 4.12 (q, $J$ = 5.2 Hz, 2H), 2.22 (m, 2H), 1.60 (m, 5H), 1.20 (m, 9H), 0.82 (m, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$): 167.8, 141.9, 124.2, 60.9, 37.7, 36.6, 33.6, 29.6, 26.8, 26.7, 14.6. MS (EI): m/z (%) 210 [$M^+$], 182, 164, 115, 102, 96, 87, 81.



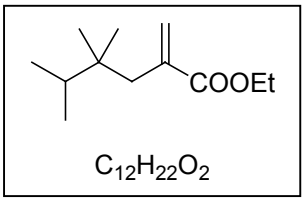

**Ethyl 2-{2-[(1*S*, 2*R*, 5*S*)-6,6-dimethylbicyclo[3.1.1] hept -2-yl]ethyl}acrylate (8)**. According to GP1. Starting from (-)-β-pinene **2** (0.409 g, 3 mmol), FC (hexane/$Et_2O$ 9:1) afforded **8** (0.466 g, 62%) as a colourless oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 6.10 (s, 1H), 5.49 (d, $J$ = 1.5 Hz, 1H), 4.19 (q, $J$ = 7.0 Hz, 2H), 2.28 (m, 3H), 1.93 (m, 6H), 1.55 (m, 3H), 1.30 (t, $J$ = 7.0 Hz, 3H), 1.17 (s, 3H), 0.99 (s, 3H), 0.87 (d, $J$ = 9.5 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): 167.5, 141.3, 124.0, 60.5, 46.4, 41.5, 41.4, 38.7, 36.5, 33.7, 30.4, 28.2, 26.5, 23.3, 22.3, 14.2. MS (EI): m/z (%): 250 [$M^+$], 235, 221, 176, 161, 133, 121, 107, 93. HRMS calcd. for $C_{16}H_{26}O_2$: 250.19328, found: 250.19342.



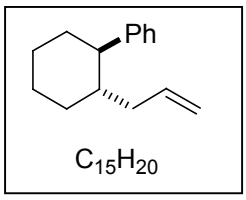

**Ethyl2-{[(1*S*,2*R*)-2-phenylcyclohexyl]methyl}acrylate (9)**. According to GP1. Starting from the sulfone (0.571 g, 2.25 mmol) FC (hexane/AcOEt 9:1) afforded **9** (0.468 g, 76%) as a colourless oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.25 (m, 5H), 6.10 (s, 1H), 5.35 (s, 1H), 4.16 (qd, $J$ = 7.0, 1.83 Hz, 2H), 2.31 (d, $J$ = 11.4 Hz, 1H), 2.19 (m, 1H), 1.78 (m, 6H), 1.37 (m, 6H), 0.94 (m, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): 167.2, 139.5, 128.3, 127.7, 126.0, 125.9, 60.4, 51.5, 41.0, 37.4, 36.3, 31.8, 26.9, 26.3, 14.2.



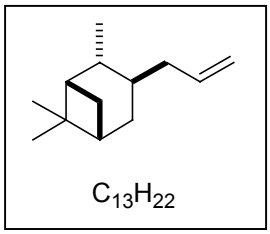

**Ethyl 2-{[(1*S*,2*R*,3*R*,5*S*)-2,6,6-trimethylbicyclo [3.1.1] hept-3-yl]methyl}acrylate (10)**. According to GP1. Starting from (-)-α-pinene **4** (0.409 g, 3 mmol), FC (hexane/AcOEt 5:1) afforded **10** (0.668 g, 89%) as a colourless oil. $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 6.13 (d, $J$ = 1.5 Hz, 1H), 5.51 (d, $J$ = 1.5 Hz, 1H), 4.19 (m, 2H), 2.52 (dd, $J$ = 13.1, 4.4 Hz, 1H), 2.28 (m, 1H), 2.11 (m, 2H), 2.17-1.60 (m, 5H), 1.39 (ddd, $J$ = 13.1, 5.9, 2.6 Hz, 1H), 1.28 (t, $J$ = 7.0 Hz, 3H), 1.16 (s, 3H), 0.99 (m, 5H), 0.75 (d, $J$ = 9.9 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): 167.3, 139.9, 125.3, 60.4, 48.2, 43.5, 43.4, 41.9, 38.7, 34.6, 34.2, 34.1, 28.0, 22.9, 21.4, 14.1. MS (EI): m/z (%): 250 [$M^+$], 207, 176, 137, 121, 107, 81, 55, 41.



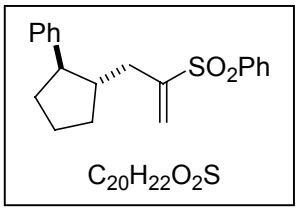

**Ethyl 2-(2,2,3-trimethylbutyl)acrylate (11)**. According to GP1. Starting from 2,3-dimethyl-2-butene **5** (0.168 g, 2 mmol), FC (hexane/AcOEt 5:1) afforded **11** (0.255 g, 64%) as a colourless oil. $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 6.16 (m, 1H), 5.44 (m, 1H), 4.20 (qd, $J$ = 7.0, 0.7 Hz, 2H), 2.31 (s, 2H), 1.48 (sept, $J$ = 7.0 Hz, 1H), 1.30 (td, $J$ = 7.0, 0.7 Hz, 3H), 0.87 (d, $J$ = 7.0 Hz, 6H), 0.75 (s, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): 166.3, 139.4, 126.8, 60.6, 40.0, 36.6, 36.3, 23.4, 17.6, 14.2. MS (EI): m/z (%): 155[($M^+$)-propyl], 127, 109, 85, 69, 55, 41.



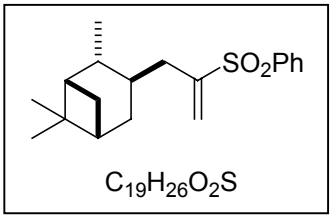

**(1*S*,2*R*)-1-allyl-2-phenylcyclohexane (12)**. According to GP2. Starting from 1-phenylcyclohexene **3** (0.348 g, 2.2 mmol), FC (pentane) afforded **12** (0.246 g, 56%) as a colourless oil according to literature[8b].




**(1*S*,2*R*,3*S*,5*S*)-3-allyl-2,6,6-trimethylbicyclo[3.1.1]heptane (13)**. According to GP2. Starting from (-)-α-pinene **4** (0.409 g, 3 mmol), FC (pentane) afforded **13** (0.278 g, 52%) as a colourless oil. $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 5.84 (m, 1H), 5.02 (m, 2H), 2.29 (m, 2H), 2.15-1.91 (m, 3H), 1.75 (m, 3H), 1.51 (m, 1H), 1.21 (s, 3H), 1.03 (m, 6H), 0.78 (d, $J$ = 9.5 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): 138.1, 115.3, 48.2, 44.9, 43.0, 41.9, 38.9, 36.2, 34.2, 33.9, 28.1, 23.0, 21.6. MS (EI): m/z (%): 178 [$M^+$], 137, 121, 107, 93, 81, 69, 55, 41.

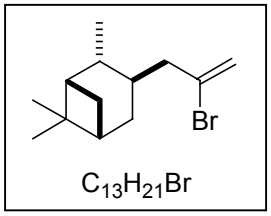



**Phenyl 1-{[(1*S*,2*R*)-2-phenylcyclopentyl]methyl} vinyl sulfone (14)**. According to GP1. Starting from phenyl-1-cyclopentene **6** (0.216 g, 1.5 mmol), FC (hexane/AcOEt 5:1) afforded **14** (0.364 g, 74%) $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.81 (m, 2H), 7.68 (m, 1H), 7.45 (m, 2H), 7.20 (m, 5H), 6.34 (s, 1H), 5.67 (s, 1H), 2.44 (m, 1H), 2.31 (m, 1H), 2.05 (m, 4H), 1.72 (m, 4H). $^{13}$C NMR (75 MHz, $CDCl_3$): 149.6, 138.5, 133.3, 129.0, 128.5, 128.3, 128.2, 127.5, 126.2, 124.0, 53.0, 46.0, 35.2, 34.4, 31.7, 23.7. MS (EI): m/z (%): 326 [$M^+$], 250, 184, 145, 104, 91, 77, 51. HRMS calcd. for $C_{20}H_{22}0_2S$: 326.13405, found: 326.13409.

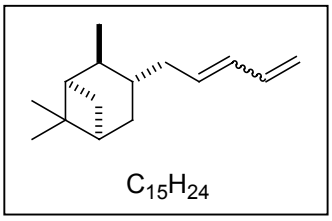



**Phenyl 1-{[(1*S*,2*R*,3*R*,5*S*)-2,6,6-trimethylbicyclo [3.1.1] hept-3yl]methyl}vinyl sulfone (15)**. According to GP1. Starting from (-)-α-pinene **4** (0.409 g, 3 mmol), FC (hexane/AcOEt 4:1) afforded **15** (0.848 g, 89%) as a colourless oil. $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.93-7.83 (m, 2H), 7.64-7.45 (m, 3H), 6.41 (s, 1H), 5.80 (s, 1H), 2.52 (dd, $J$ = 15.1, 3.7 Hz, 1H), 2.24 (m, 1H), 2.06 (m, 1H), 1.95-1.69 (m, 3H), 1.54 (m, 1H), 1.23 (m, 2H), 1.13 (s, 3H), 0.93 (m, 3H), 0.86 (s, 3H), 0.61 (d, $J$ = 9.6 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): 149.3, 139.2, 133.4, 129.1, 128.2, 124.6, 47.9, 43.7,

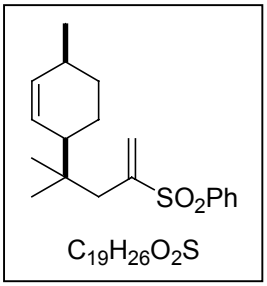
41.6, 38.6, 34.1, 34.2, 33.9, 27.9, 22.8, 21.2. MS (EI): m/z (%): 319[$M^+$+1], 246, 218, 177, 137, 81, 55, 41. HRMS (ESI-MS) calcd. for $C_{19}H_{27}O_2S$ ([M+1]$^+$) : 319.1731, found: 319.1729.




**(1*S*, 2*R*, 3*S*, 5*S*)-3-(2-bromo-2propenyl)-2,6,6-trimethyl bicyclo[3.1.1]heptane (16)**. According to GP1. Starting from (-)-α-pinene **4** (0.409 g, 3 mmol), FC (hexane/AcOEt 4:1) afforded **16** (0.445 g, 58%) as a colourless oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 5.61 (s, 1H), 5.41 (s, 1H), 2.55 (dd, $J$ = 13.9, 4.4 Hz, 1H), 2.35-2.21 (m, 2H), 2.18-2.02 (m, 2H), 1.91 (m, 1H), 1.78 (m, 1H), 1.66 (dquint, $J$ = 7.0, 2.2 Hz, 1H), 1.42 (m, 1H), 1.20 (s, 3H), 1.04 (m, 6H), 0.73 (d, $J$ = 9.5 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): 132.1, 115.2, 50.4, 46.0, 40.9, 39.6, 36.6, 31.9, 31.5, 25.8, 20.8, 19.2. MS (EI): m/z (%): 256 [$M^+$], 215, 177, 159, 137, 121, 93, 83, 55, 42. HRMS calcd. for $C_{13}H_{21}Br$: 256.08266, found: 256.08243.




**(1*R*,2*S*,3*S*,5*R*)-2,6,6-trimethyl-3-[2,4-pentadienyl] bicyclo[3.1.1]heptane (17)**. According to GP1. Starting from (+)-α-pinene **4** (0.136 g, 1 mmol), FC (pentane) afforded **17** (0.102 g, 50%) as a colourless oil. (cis/trans isomers 1:8). $^1$H NMR (300 MHz, $CDCl_3$): (major isomer) $\delta$ 6.33 (td, $J$ = 16.9, 10.3 Hz, 1H), 6.10 (m, 1H), 5.72 (td, $J$ = 16.9, 7.0 Hz, 1H), 5.10 (dd, $J$ = 16.9, 0.7 Hz, 1H), 4.96 (dd, $J$ = 10.3, 0.7 Hz, 1H), 2.28 (m, 2H), 2.05 (m, 2H), 1.89 (m, 1H), 1.72 (m, 3H), 1.51 (m, 1H), 1.19 (s, 3H), 1.00 (m, 6H), 0.75 (d, $J$ = 9.5 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): 137.3, 134.5, 131.9, 114.7, 48.2, 43.5, 43.0, 41.9, 38.9, 36.5, 34.3, 34.0, 28.1, 23.0, 21.7. MS (EI): m/z (%): 204 [$M^+$], 161, 148, 137, 121, 105, 93, 81, 55, 41. HRMS calcd. for $C_{15}H_{24}$: 204.18780, found: 204.18735.




**1-{2-methyl-2-[(1*R*,4*S*)-4-methyl-2-cyclohexen-1-yl]propyl} vinyl phenyl sulfone (19)**. According to GP1. Starting from (+)-2-carene (0.136 g, 1 mmol), FC (hexane/AcOEt 5:1) afforded **19** (0.186 g, 58%) as a colourless oil. $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.87 (m, 2H), 7.54 (m, 3H), 6.49 (s, 1H), 5.87 (m, 1H), 5.68 (m, 1H), 5.53 (m, 1H), 2.26 (s, 2H), 2.17 (m, 1H), 1.95 (m, 1H), 1.68 (m, 1H), 1.41 (m, 3H), 0.94 (d, $J$ = 7.0 Hz, 3H), 0.88 (s, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): 148.9, 139.3, 134.9, 129.1, 128.5, 126.9, 126.5, 44.9, 37.1, 29.1, 28.5, 24.9, 24.7, 20.8, 19.4. MS (EI): m/z (%): 318 [$M^+$], 288, 223, 177, 137, 95, 81, 55, 41. HRMS calcd. for $C_{19}H_{26}O_2S$: 318.16535, found: 318.16534.

**References**

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[2] For the synthesis of the 5-benzenesulfonyl-1,3-pentadiene see: (a) (procedure) Kauffmann, T.; Gaydoul, K.-R. *Tetrahedron Lett.* **1985**, *26*, 4067. (b) (characterization) Epifani, E.; Florio, S.; Ingrosso, G.; Ronzini, L.; Sgarra, R.; Troisi, L. *Tetrahedron*, **1991**, *47*, 7489.