Alkene Cyclopropanation by Metallocarbenes Generated from Monocarbonyl Iodonium Ylides

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General Experimental Details Methods

All reactions were carried out in flame-dried glassware under a dry nitrogen atmosphere, unless otherwise noted. All solvents were obtained pure and dry from a JC Meyer solvent purification system. All reagents were purchased from Sigma-Aldrich and used without further purification. $^1$H NMR spectra were recorded on Bruker instruments at 300 MHz, and were referenced to residual $^1$H shift in CDCl$_3$ (7.24 ppm). All $^{13}$C [$^1$H] NMR were recorded at 75 MHz, and CDCl$_3$ (77.0 ppm) was used as the internal reference. $^{31}$P NMR spectra were recorded at 121 MHz, and referenced to the H$_3$PO$_4$ signal at 0 ppm. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br s = broad singlet. Reactions were monitored by thin-layer chromatography (TLC) on commercial silica pre-coated plates with a particle size of 60 Å and viewed by UV lamp (254 nm), by gas chromatography (HP5890A Series II) with a J&W Scientific 30m x 0.53mm DB624 column with 3 micron film thickness (run settings: 2.5 min at 75
°C, 7.5 °C/min to 250 °C), and by \(^{31}\)P NMR. Flash chromatography was performed using 60Å (230-400 mesh) silica gel. Melting points were performed using a MeltTemp apparatus. InfraRed (IR) data was recorded using an ATR-FTIR (Attenuated Total Reflection Fourier Transform InfraRed) instrument. The following abbreviations were used to explain the IR peak intensities: (s) = strong, (m) = medium, (w) = weak. Positive ion electrospray ionization (ESI) was performed with a Thermo Scientific Q-Exactive hybrid mass spectrometer. Accurate mass determinations were performed at a mass resolution of 70,000. For ESI, samples were infused at 10 µL/min in 1:1 CH\(_3\)OH/H\(_2\)O + 0.1% formic acid.

**General Procedure for Synthesis of Iodosoarenes (GP1)**

Iodosoarenes 2a-2g are all known compounds, and prepared over two steps from the corresponding aryliodides.\(^1\)

**Table SI-1: Optimization of the Cyclopropanation Reaction**

In a dry 10 mL round bottom flask containing CHCl\(_3\) (3 mL) was added iodosoarene 2, the catalyst and additive (if used) and this was stirred at room temperature. Wittig reagent 1 (1 equiv) in CHCl\(_3\) (1 mL) was then added dropwise to the reaction mixture by syringe pump over 1 hour, and the reaction stirred for an additional until the indicated length of time at room temperature.

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<th>2 (Equiv)</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Catalyst (mol %)</th>
<th>Yield (%)</th>
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General Procedure for Synthesis of Cyclopropanes 4 (GP2)

In a dry 10 mL round bottom flask, iodosoarene 2 (0.28 mmol, 2 equiv), Cu(tfacac)2 (0.014 mmol, 0.1 equiv), alkene 3 (0.70 mmol, 5 equiv), then CHCl3 (3 mL) was stirred at room temperature. Wittig reagent 1 (0.14 mmol, 1 equiv) in CHCl3 (1 mL) was then added to the solution by syringe pump addition over 1 hour, and the reaction stirred for an additional 0.5 hour (1.5 hours total time) at room temperature. The reaction was quenched with 10 % K2CO3 (2 mL) and transferred to a separatory funnel. Extraction of product using CH2Cl2 (3 x 10 mL), followed by washing the
combined organic extracts with brine (2 x 10 mL). The organic extracts were dried over MgSO₄, filtered, concentrated on a rotary evaporator and then placed under high vacuum. The crude reaction mixture was loaded onto a column of silica gel using a minimal amount of CH₂Cl₂. Elution was accomplished using mixtures of EtOAc/hexanes.

**Ethyl 2-phenylcyclopropanecarboxylate (4a)**

![Ethyl 2-phenylcyclopropanecarboxylate](PhCO₂Et)

Synthesized according to **GP2** using iodosoarene **2e** (0.201 g, 0.86 mmol, 2 equiv), Cu(tfacac)₂ (0.016 g, 0.043 mmol, 0.1 equiv), styrene (0.247 mL, 2.15 mmol, 5 equiv), CHCl₃ (4.3 mL), and Wittig reagent **1a** (0.150 g, 0.43 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 8:1) led to the title compound isolated as a pale yellow oil (0.042 g, 53% yield) with a 2.3:1 *trans:*cis ratio. Rᵣ = 0.64 (hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.²

**Ethyl 2-(4-chlorophenyl)cyclopropanecarboxylate (4b)**

![Ethyl 2-(4-chlorophenyl)cyclopropanecarboxylate](ClCO₂Et)

Synthesized according to **GP2** using iodosoarene **2e** (0.200 g, 0.86 mmol, 2 equiv), Cu(tfacac)₂ (0.016 g, 0.043 mmol, 0.1 equiv), 4-chlorostyrene (0.288 mL, 2.15 mmol, 5 equiv), CHCl₃ (4.3 mL), and Wittig reagent **1a** (0.150 g, 0.43 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 10:1) led to the title compound isolated as a pale yellow oil (0.040 g, 42% yield) with a 2.3:1 *trans:*cis ratio. Rᵣ = 0.30 (hexanes:Et₂O 10:1). The characterization data matches what has been previously reported in the literature.³

**Ethyl 2-(4-(tert-butyl)phenyl)cyclopropanecarboxylate (4c)**

![Ethyl 2-(4-(tert-butyl)phenyl)cyclopropanecarboxylate](tBuCO₂Et)

Synthesized according to **GP2** using iodosoarene **2e** (0.066 g, 0.28 mmol, 2 equiv), Cu(tfacac)₂ (0.005 g, 0.014 mmol, 0.1 equiv), 4-tert-butylstyrene (0.128 mL, 0.70 mmol, 5 equiv), CHCl₃ (1.9 mL), and Wittig reagent **1a** (0.050 g, 0.14 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 10:1) led to the title compound isolated as a pale
yellow oil (0.013 g, 38% yield) with a 2.4:1 \textit{trans:cis} ratio. $R_f = 0.63$ (hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.\(^4\)

**Ethyl 2-(4-methoxyphenyl)cyclopropanecarboxylate (4d)**

![Chemical structure of ethyl 2-(4-methoxyphenyl)cyclopropanecarboxylate (4d)](image)

Synthesized according to GP2 using iodosoarene 2e (0.201 g, 0.86 mmol, 2 equiv), Cu(tfacac)\(_2\) (0.016 g, 0.043 mmol, 0.1 equiv), 4-methoxystyrene (0.286 mL, 2.15 mmol, 5 equiv), CHCl\(_3\) (4.3 mL), and Wittig reagent 1a (0.150 g, 0.43 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 9:1) led to the title compound isolated as a pale yellow oil (0.054 g, 57% yield) with a 2.3:1 \textit{trans:cis} ratio. $R_f = 0.59$ (hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.\(^3\)

**Ethyl 2-(3,4-dimethoxyphenyl)cyclopropanecarboxylate (4e)**

![Chemical structure of ethyl 2-(3,4-dimethoxyphenyl)cyclopropanecarboxylate (4e)](image)

Synthesized according to GP2 using iodosoarene 2e (0.065 g, 0.28 mmol, 2 equiv), Cu(tfacac)\(_2\) (0.005 g, 0.014 mmol, 0.1 equiv), 3,4-dimethoxystyrene (0.115 g, 0.70 mmol, 5 equiv), CHCl\(_3\) (3.0 mL), and Wittig reagent 1a (0.050 g, 0.14 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 12:1) led to the title compound isolated as a pale yellow oil (0.024 g, 68% yield) with a 2.3:1 \textit{trans:cis} ratio. $R_f = 0.34$ (hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.\(^5\)

**Ethyl 2-(3,4,5-trimethoxyphenyl)cyclopropanecarboxylate (4f)**

![Chemical structure of ethyl 2-(3,4,5-trimethoxyphenyl)cyclopropanecarboxylate (4f)](image)

Synthesized according to GP2 using iodosoarene 2e (0.065 g, 0.28 mmol, 2 equiv), Cu(tfacac)\(_2\) (0.005 g, 0.014 mmol, 0.1 equiv), 3,4,5-trimethoxystyrene (0.136 g, 0.70 mmol, 5 equiv), CHCl\(_3\) (3.0 mL), and Wittig reagent 1a (0.050 g, 0.14 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 12:1 to 8:1) led to the title compound isolated as a pale yellow oil (0.029 g, 74% yield) with a 1.9:1 \textit{trans:cis} ratio. $R_f = 0.28$
Ethyl 2-methyl-2-phenylcyclopropanecarboxylate (4g)

\[
\begin{align*}
\text{Me} & \quad \text{Ph} \\
& \quad \text{CO}_2\text{Et}
\end{align*}
\]

Synthesized according to GP2 using iodosoarene 2e (0.135 g, 0.58 mmol, 2 equiv), Cu(tfacac)$_2$ (0.010 g, 0.029 mmol, 0.1 equiv), α-Methylstyrene (0.189 mL, 1.45 mmol, 5 equiv), CHCl$_3$ (4.0 mL), and Wittig reagent 1a (0.100 g, 0.29 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 12:1 to 10:1) led to the title compound isolated as a pale yellow oil (0.037 g, 63% yield) with a 1.4:1 trans:cis ratio. R$_f$ = 0.62 (hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.\(^6\)

Ethyl 2-phenyl-2-((trimethylsilyl)oxy)cyclopropanecarboxylate (4h)

\[
\begin{align*}
\text{Me}_3\text{SiO} & \quad \text{Ph} \\
& \quad \text{CO}_2\text{Et}
\end{align*}
\]

Synthesized according to GP2 using iodosoarene 2e (0.201 g, 0.86 mmol, 2 equiv), Cu(tfacac)$_2$ (0.016 g, 0.043 mmol, 0.1 equiv), α-(Trimethylsiloxy)styrene (0.410 g, 2.15 mmol, 5 equiv), CHCl$_3$ (5.0 mL), and Wittig reagent 1a (0.150 g, 0.43 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 9:1) led to the title compound isolated as a pale yellow oil (0.067 g, 56% yield) with a 1:1 trans:cis ratio. R$_f$ = 0.36 (hexanes:EtOAc 9:1). The characterization data matches what has been previously reported in the literature.\(^7\)

Ethyl 2-methyl-3-phenylcyclopropanecarboxylate (4i)

\[
\begin{align*}
\text{Me} & \quad \text{Ph} \\
& \quad \text{CO}_2\text{Et}
\end{align*}
\]

Synthesized according to GP2 using iodosoarene 2e (0.065 g, 0.28 mmol, 2 equiv), Cu(tfacac)$_2$ (0.005 g, 0.014 mmol, 0.1 equiv), β-Methylstyrene (0.091 mL, 0.70 mmol, 5 equiv), CHCl$_3$ (4.0 mL), and Wittig reagent 1a (0.050 g, 0.14 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 6:1 to 5:1) led to the title compound isolated as a pale yellow oil (0.017 g, 59% yield) with a 2.5:1 trans:cis ratio. R$_f$ = 0.51 (hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.\(^8\)
Ethyl 2-methoxy-3-(4-methoxyphenyl)cyclopropanecarboxylate (4k)

Synthesized according to GP2 using iodosoarene 2e (0.131 g, 0.56 mmol, 2 equiv), Cu(tfacac)$_2$ (0.010 g, 0.029 mmol, 0.1 equiv), (Z)-1-methoxy-4-(2-methoxyvinyl)benzene (0.230 g, 1.4 mmol, 5 equiv), CHCl$_3$ (4.0 mL), and Wittig reagent 1a (0.100 g, 0.29 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 10:1 to 8:1) led to the title compound isolated as a pale yellow oil (0.042 g, 60% yield). R$_f$ = 0.53 (hexanes:EtOAc 3:1); IR: 2935 (w), 1717 (s), 1515 (s), 1287 (m), 830 (s) cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) 7.18 (d, $J$ = 9.0 Hz, 2H), 6.83 (d, $J$ = 9.0 Hz, 2H), 4.15 (q, $J$ = 7.2 Hz, 2H), 3.77 - 3.80 (m, 4H), 3.30 (s, 3H), 2.65 (dd, $J$ = 6.3, 6.3 Hz, 1H), 2.11 (dd, $J$ = 6.0, 2.7 Hz, 1H), 1.27 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) 175.1, 161.3, 132.2, 129.6, 116.5, 68.8, 63.7, 61.6, 58.1, 34.8, 30.9, 17.1; HRMS: ESI$^+$ [M+H]$^+$ calcd for C$_{14}$H$_{19}$O$_4$ 251.1278, found 251.1278.

Ethyl 2-methoxy-3-(4-methoxyphenyl)cyclopropanecarboxylate (4l)

Synthesized according to GP2 using iodosoarene 2e (0.140 g, 0.60 mmol, 2 equiv), Cu(tfacac)$_2$ (0.011 g, 0.030 mmol, 0.1 equiv), (E)-1-methoxy-4-(2-methoxyvinyl)benzene (0.246 g, 1.50 mmol, 5 equiv), CHCl$_3$ (4.0 mL), and Wittig reagent 1a (0.104 g, 0.30 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 20:1 to 8:1) led to the title compound isolated as a pale yellow oil (0.046 g, 61% yield) with a 1:2.9 trans:cis ratio. R$_f$ = 0.40 (hexanes:EtOAc 3:1); IR: 2935 (w), 1732 (s), 1515 (s), 1243 (s) cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) 7.31 (d, $J$ = 8.6 Hz, 2H), 6.81 (d, $J$ = 8.6 Hz, 2H), 4.02 (dq, $J$ = 7.1, 4.1 Hz, 2H), 3.74 - 3.83 (m, 4H), 3.40 (s, 3H), 2.51 (dd, $J$ = 10.1, 7.1 Hz, 1H), 1.97 (dd, $J$ = 10.1, 6.1 Hz, 1H), 1.29 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) 171.1, 161.1, 134.1, 128.4, 116.2, 66.2, 62.9, 62.0, 58.0, 30.6, 26.7, 17.1; HRMS: ESI$^+$ [M+H]$^+$ calcd for C$_{14}$H$_{19}$O$_4$ 251.1278, found 251.1275.

Ethyl 2-methoxy-3-(3,4,5-trimethoxyphenyl)cyclopropanecarboxylate (4m)

Ethyl 2-methoxy-3-(3,4,5-trimethoxyphenyl)cyclopropanecarboxylate (4m)
Synthesized according to GP2 using iodosoarene 2e (0.065 g, 0.28 mmol, 2 equiv), Cu(tfacac)$_2$ (0.005 g, 0.014 mmol, 0.1 equiv), (Z)-1,2,3-trimethoxy-5-(2-methoxyvinyl)benzene (0.157 g, 0.70 mmol, 5 equiv), CHCl$_3$ (4.0 mL), and Wittig reagent 1a (0.050 g, 0.14 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 12:1 to 8:1) led to the title compound isolated as a pale yellow oil (0.035 g, 81% yield). R$_f$ = 0.27 (hexanes:EtOAc 3:1); IR: 2936 (w), 1718 (s), 1587 (m), 1123 (s), 834 (w) cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) 6.49 (s, 2H), 4.16 (q, $J = 7.2$ Hz, 2H), 3.78 - 3.89 (m, 10H), 3.34 (s, 3H), 2.62 (dd, $J = 6.3$, 6.3 Hz, 1H), 2.13 (dd, $J = 6.0$, 2.7 Hz, 1H), 1.27 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) 172.1, 153.1, 137.0, 130.7, 105.6, 66.2, 61.1, 59.0, 56.3, 32.8, 28.7, 14.4; HRMS: ESI$^+$ [M+H]$^+$ calcd for C$_{16}$H$_{23}$O$_6$ 311.1489, found 311.1487.

**Benzyl 2-phenylcyclopropanecarboxylate (4n)**

Synthesized according to GP2 using iodosoarene 2e (0.112 g, 0.48 mmol, 2 equiv), Cu(tfacac)$_2$ (0.009 g, 0.024 mmol, 0.1 equiv), styrene (0.137 mL, 1.20 mmol, 5 equiv), CHCl$_3$ (4.0 mL), and Wittig reagent 1b (0.100 g, 0.24 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 9:1 to 3:1) led to the title compound isolated as a pale yellow oil (0.033 g, 55% yield) with a 3:1 trans:cis ratio. R$_f$ = 0.56 (hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.10

**1-(2-Phenylcyclopropyl)ethanone (4o)**

Synthesized according to GP2 using iodosoarene 2e (0.112 g, 0.48 mmol, 2 equiv), Cu(tfacac)$_2$ (0.009 g, 0.024 mmol, 0.1 equiv), styrene (0.137 mL, 1.20 mmol, 5 equiv), CHCl$_3$ (2.5 mL), and Wittig reagent 1c (0.075 g, 0.24 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 10:1) led to the title compound isolated as a pale yellow oil (0.018 g, 46% yield) with a 2:1 trans:cis ratio. R$_f$ = 0.73 (hexanes:EtOAc 2:1). The characterization data matches what has been previously reported in the literature.11
(2-(4-Methoxyphenyl)cyclopropyl)(phenyl)methanone (4p)

Synthesized according to GP2 using iodosoarene 2e (0.182 g, 0.78 mmol, 2 equiv), Cu(tfacac)₂ (0.014 g, 0.039 mmol, 0.1 equiv), 4-methoxystyrene (0.250 mL, 1.95 mmol, 5 equiv), CHCl₃ (3.5 mL), and Wittig reagent 1d (0.150 g, 0.39 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 10:1) led to the title compound isolated as a pale yellow oil (0.029 g, 30% yield) with a 2:1 trans: cis ratio. Rf = 0.58 (hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.¹²

2-Methoxy-3-(4-methoxyphenyl)cyclopropyl)(phenyl)methanone (4q)

Synthesized according to GP2 using iodosoarene 2e (0.031 g, 0.13 mmol, 2 equiv), Cu(tfacac)₂ (0.002 g, 0.007 mmol, 0.1 equiv), (Z)-1-methoxy-4-(2-methoxyvinyl)benzene (0.054 g, 0.33 mmol, 5 equiv), CHCl₃ (3.0 mL), and Wittig reagent 1d (0.025 g, 0.07 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 10:1 to 8:1) led to the title compound isolated as a pale yellow oil (0.010 g, 54% yield). Rf = 0.51 (hexanes:EtOAc 3:1); IR: 2934 (w), 1658 (m), 1245 (s), 1178 (m), 832 (m), 690 (s) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) 8.02 (d, J = 7.5 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.48 (app. t, J = 7.5 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.1 Hz, 2H), 3.98 (dd, J = 6.6, 3.0 Hz, 1H), 3.79 (s, 3H), 3.36 (s, 3H), 3.14 (dd, J = 6.0, 2.4 Hz, 1H), 2.98 (dd, J = 6.0, 6.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) 200.4, 161.4, 140.3, 135.9, 132.3, 131.5, 130.9, 130.2, 116.6, 72.5, 61.8, 58.2, 38.0, 36.6; HRMS: ESI⁺ [M+H]⁺ calcd for C₁₈H₁₉O₃ 283.1329, found 283.1332.

2-Methoxy-3-(3,4,5-trimethoxyphenyl)cyclopropyl)(phenyl)methanone (4r)
Synthesized according to GP2 using iodosoarene 2e (0.164 g, 0.70 mmol, 2 equiv), Cu(tfacac)$_2$ (0.013 g, 0.035 mmol, 0.1 equiv), (Z)-1,2,3-trimethoxy-5-(2-methoxyvinyl)benzene (0.392 g, 1.75 mmol, 5 equiv), CHCl$_3$ (4.0 mL), and Wittig reagent 1d (0.133 g, 0.35 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 20:1 to 8:1) led to the title compound isolated as a pale yellow oil (0.093 g, 78% yield). R$_f$ = 0.19 (hexanes:EtOAc 3:1); IR: 2932 (w), 1669 (m), 1587 (m), 1448(m), 1217 (m), 1008 (s), 689 (m) cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) 8.09 (d, $J$ = 7.3 Hz, 2H), 7.56 (t, $J$ = 7.1 Hz, 1H), 7.49 (t, $J$ = 7.8 Hz, 2H), 6.40 (s, 2H), 3.98 (dd, $J$ = 6.4, 4.4 Hz, 1H), 3.90 (s, 6H), 3.85 (s, 3H), 3.46 (dd, $J$ = 5.0, 4.4 Hz, 1H), 3.30 (s, 3H), 3.05 (dd, $J$ = 6.5, 6.5 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) 195.7, 156.2, 141.1, 139.9, 136.8, 135.8, 131.5, 131.0, 107.0, 72.4, 63.8, 62.0, 59.1, 38.4, 34.2; HRMS: ESI$^+$ [M+H]$^+$ calcd for C$_{20}$H$_{23}$O$_5$ 343.1540, found 343.1538.

(E)-Ethyl 2-styrylcyclopropanecarboxylate (4s)

![Diagram of (E)-Ethyl 2-styrylcyclopropanecarboxylate](image)

Synthesized according to GP2 using iodosoarene 2e (0.066 g, 0.28 mmol, 2 equiv), Cu(tfacac)$_2$ (0.005 g, 0.014 mmol, 0.1 equiv), (E)-1-phenyl-1,3-butadiene (0.091 g, 0.70 mmol, 5 equiv), CHCl$_3$ (3.0 mL), and Wittig reagent 1a (0.050 g, 0.14 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 8:1) led to the title compound isolated as a pale yellow oil (0.018 g, 61% yield) with a 1.6:1 $trans$:cis ratio. R$_f$ = 0.45 (hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.$^{13}$

Ethyl 2-benzylcyclopropanecarboxylate (4t)

![Diagram of Ethyl 2-benzylcyclopropanecarboxylate](image)

Synthesized according to GP2 using iodosoarene 2e (0.065 g, 0.28 mmol, 2 equiv), Cu(tfacac)$_2$ (0.005 g, 0.014 mmol, 0.1 equiv), allylbenzene (0.082 g, 0.70 mmol, 5 equiv), CHCl$_3$ (3.0 mL), and Wittig reagent 1a (0.050 g, 0.14 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 20:1 to 10:1) led to the title compound isolated as a pale yellow oil (0.014 g, 49% yield) with a 1.9:1 $trans$:cis ratio. R$_f$ = 0.68 (hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.$^{14}$

Ethyl 2-oxabicyclo[4.1.0]heptane-7-carboxylate (4u)
Synthesized according to GP2 using iodosoarene 2e (0.066 g, 0.28 mmol, 2 equiv), Cu(tfacac)$_2$ (0.005 g, 0.014 mmol, 0.1 equiv), dihydropyran (0.064 mL, 0.70 mmol, 5 equiv), CHCl$_3$ (2.5 mL), and Wittig reagent 1a (0.050 g, 0.14 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 8:1 to 3:1) led to the title compound isolated as a pale yellow oil (0.014 g, 60% yield) as a 3:1 trans:cis ratio. $R_f = 0.80$ (EtOAc:Petroleum ether 1:4). The characterization data matches what has been previously reported in the literature.$^{15}$

**Ethyl 1-((trimethylsilyl)oxy)bicyclo[4.1.0]heptane-7-carboxylate (4v)**

![Chemical structure]

Synthesized according to GP2 using iodosoarene 2e (0.135 g, 0.58 mmol, 2 equiv), Cu(tfacac)$_2$ (0.010 g, 0.029 mmol, 0.1 equiv), 1-(Trimethylsiloxy)cyclohexene (0.286 mL, 1.45 mmol, 5 equiv), CHCl$_3$ (4.0 mL), and Wittig reagent 1a (0.100 g, 0.29 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 20:1 to 10:1) led to the title compound isolated as a pale yellow oil (0.047 g, 63% yield) as a 1:1.7 trans:cis ratio. $R_f = 0.53$ (hexanes:EtOAc 9:1). The characterization data matches what has been previously reported in the literature.$^8$

**Bicyclo[3.1.0]hexan-2-one (4w)**

![Chemical structure]

To a dry 10 mL round bottom flask was added iodosoarene 2e (0.102 g, 0.44 mmol, 2 equiv), Cu(tfacac)$_2$ (0.008 g, 0.022 mmol, 0.1 equiv), Wittig reagent 1e (0.080 g, 0.22 mmol, 1 equiv), then CHCl$_3$ (4 mL), and the resulting mixture stirred at room temperature for 3.5 hours. The reaction was quenched with 10 % K$_2$CO$_3$ (2 mL), transferred to a seperatory funnel and extracted using CH$_2$Cl$_2$ (3 x 10 mL). The combined organic extracts were washed with brine (2 x 10 mL), dried over MgSO$_4$, filtered, and concentrated by rotary evaporation (keeping the bath temperature below 30 °C). The crude reaction mixture was loaded onto a column of silica gel using a minimal amount of CH$_2$Cl$_2$ and elution was accomplished using (hexanes:EtOAc 10:1 to 5:1), which gave 0.013 g of 4w as a pale yellow oil in 63% yield. The characterization data matches what has been previously reported in the literature.$^{16}$
NMR Spectra of New Compounds
proton, 16 scans
13C observe with 1H decoupling

172.36 158.55 129.50 126.82 113.80

-274.31 14.39 28.17 32.03 66.05 60.92 58.80 53.38 32.03 28.17 14.39

4k
proton, 16 scans

\[
\text{ppm} \begin{array}{cccccccc}
0 & 0 & 1 & 1 & 2 & 2 & 3 & 3 \\
-13.35 & 1.14 & 1.99 & 2.52 & 3.41 & 3.78 & 4.04 & 6.84 & 7.31
\end{array}
\]

\[
\text{SI-16}
\]
$^{13}$C observe with $^1$H decoupling

![Chemical Structure](image)
proton, 16 scans

![Chemical structure](image_url)

ppm

6.49 4.15 3.84 3.81 3.34 3.84 4.15 6.49
13C observe with 1H decoupling
proton, 16 scans

SI-20
13C observe with 1H decoupling

![Chemical structure](image)
$^{13}$C observe with $^1$H decoupling

4r 78%