Supporting Information

Iodonium-Catalyzed Carbonyl-Olefin Metathesis Reactions
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General Methods

Reactions, unless otherwise stated, were conducted under a positive pressure of argon in oven-dried glassware. Toluene, dichloromethane (DCM), dichloroethane (DCE), tetrahydrofuran (THF) and acetonitrile were dried with an SPS apparatus. Commercially available reagents were used as purchased unless otherwise noted. Analytical thin layer chromatography was performed using aluminium plates precoated with silica gel 60 F₂₅₄ (0.2 mm). Flash chromatography employed 230-400 mesh silica gel. Solvents used for chromatography are quoted as volume/volume ratios.

NMR spectroscopy was performed at 298 K using an Avance III HD 400 (400.1 MHz, \(^1\)H; 100.6 MHz, \(^13\)C, 376.5 MHz, \(^19\)F) or an Avance III 300 (300 MHz, \(^1\)H; 75 MHz, \(^13\)C; 282.5 MHz, \(^19\)F). Data is expressed in parts per million (ppm) downfield shift from tetramethylsilane with residual solvent as an internal reference (\(\delta\) 7.26 ppm for chloroform, 5.27 ppm for dichloromethane) and is reported as position (\(\delta\) in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (\(J\) in Hz) and integration (number of protons). \(^13\)C NMR spectra were recorded at 298 K with complete proton decoupling. Data is expressed in parts per million (ppm) downfield shift relative to the internal reference (\(\delta\) 77.2 ppm for the central peak of deuterated chloroform).

Infrared spectra were obtained on a Thermo Nicolet Avatar 370 FT-IR spectrometer and are reported in wavenumbers (cm\(^{-1}\)). HRMS were performed at the Bioanalytical Mass Spectrometry Facility within the Mark Wainwright Analytical Centre at the University of New South Wales on an Orbitrap LTQ XL (Thermo Fisher Scientific, San Jose, CA, USA) ion trap mass spectrometer.
Mechanistic Studies of the Intramolecular COM Reaction

A 4 mL vial was charged with iodine and a stirring bar. Starting material 1a (0.5 mmol) was added to the vial at ambient atmosphere, unless otherwise specified. Then the vial was closed by a cap and the mixture was stirred for 24 h at room temperature, unless otherwise specified. \(^1\)H NMR analysis was performed after 24 h to calculate the conversion to the product. Reactions carried out in the dark means the vial was wrapped with aluminum foil from the beginning.

<table>
<thead>
<tr>
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<th>Catalyst (and additive)</th>
<th>Conditions</th>
<th>Conversion</th>
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<tr>
<td>1</td>
<td>I(_2) (10 mol%)</td>
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<td>100%</td>
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<tr>
<td>9</td>
<td>BHT (100 mol%)</td>
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<tr>
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<tr>
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<td>no reaction</td>
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<tr>
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<td>Catalyst/Additive</td>
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<tr>
<td>14&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>100%</td>
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<td>15</td>
<td>ICl (10 mol%)</td>
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<td>60% (100%)&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>NBS (10 mol%)</td>
<td>air, lab light</td>
<td>messy reaction</td>
</tr>
<tr>
<td>18</td>
<td>Br₂ (10 mol%)</td>
<td>air, lab light</td>
<td>messy reaction</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: substrate 1a (0.5 mmol) and catalyst/additive were stirred for 24 h at rt;

<sup>b</sup>Air = ambient atmosphere (means the reaction was carried out without exclusion of air), lab light = normal fumehood lighting (4 x 13W fluorescent lamps), N₂ = reaction carried out under dried nitrogen, no light = reaction carried out in the dark;  
<sup>c</sup>NXS was recrystallized;  
<sup>d</sup>Conversion in the parentheses were estimated after 48 h.
General Procedures for Intramolecular Carbonyl-Olefin Metathesis

**General procedure A**

A 4 mL vial was charged with NIS (10 mol%) and a stirring bar. Starting material 1 was added to the vial under ambient atmosphere, along with three drops of DCE, added to help with the stirring of reaction mixture. The vial was closed by a cap and the mixture was stirred for 24 h at room temperature, unless otherwise specified. Upon completion (as determined by TLC analysis), the crude mixture was directly purified by flash column chromatography, to give the metathesis products.

A 4 mL vial was charged with ICl (10 mol%, as a stock solution in DCE) and a stirring bar. Starting material 1 was added to the vial under nitrogen atmosphere. The vial was kept under nitrogen and the mixture was stirred for 24 h at room temperature, unless otherwise specified. Upon completion (as determined by TLC analysis), the crude mixture was directly purified by flash column chromatography, to give the metathesis products.
Characterization Data of Intramolecular Carbonyl-Olefin Metathesis Products

The cyclization of 1a was performed on 0.5 mmol scale using the general procedure. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 146 mg of 2a (89%) when following procedure A, and 121 mg of 2a (74%), when following procedure B, as a white solid.\(^4\)

\[ ^1H \text{ NMR} \ (300 \text{ MHz, CDCl}_3) \ \delta = 7.79 \ (d, J = 8.3 \text{ Hz}, 2\text{H}), \ 7.31 \ (d, J = 8.0 \text{ Hz}, 2\text{H}), \ 7.27 - 7.06 \ (m, 4\text{H}), \ 5.80 \ (q, J = 2.0 \text{ Hz}, 1\text{H}), \ 5.02 \ (dddd, J = 9.0, 6.2, 4.1, 3.1, 1.7 \text{ Hz}, 1\text{H}), \ 4.30 \ (q, J = 2.5 \text{ Hz}, 2\text{H}), \ 2.38 \ (d, J = 16.9 \text{ Hz}, 6\text{H}), \ 1.50 \ (d, J = 6.4 \text{ Hz}, 3\text{H}) \text{ ppm}; \]

\[ ^{13}C \text{ NMR} \ (75 \text{ MHz, CDCl}_3) \ \delta = 143.4, 143.2, 138.1, 135.1, 130.1, 129.8, 129.4, 127.3, 126.3, 117.9, 63.0, 54.8, 22.1, 21.5, 21.2 \text{ ppm}. \]

The cyclization of 1b was performed on 0.5 mmol scale using the general procedure using the general procedure. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 111 mg of 2b (71%) when following procedure A, and 106 mg of 2b (68%), when following procedure B, as a white solid.\(^4\)

\[ ^1H \text{ NMR} \ (400 \text{ MHz, CDCl}_3) \ \delta = 7.76 \ (d, J = 8.2 \text{ Hz}, 2\text{H}), \ 7.35 - 7.26 \ (m, 7\text{H}), \ 5.83 - 5.81 \ (m, 1\text{H}), \ 5.03 - 5.0 \ (m, 1\text{H}), \ 4.30 - 4.28 \ (m, 2\text{H}), \ 2.40 \ (s, 3\text{H}), \ 1.48 \ (d, J = 6.0 \text{ Hz}, 3\text{H}) \text{ ppm}; \]

\[ ^{13}C \text{ NMR} \ (100 \text{ MHz, CDCl}_3) \ \delta = 143.5, 143.4, 135.1, 133.0, 129.8, 128.7, 128.2, 127.3, 126.3, 118.8, 62.9, 54.8, 22.1, 21.5 \text{ ppm}. \]
The cyclization of \( \text{1c} \) was performed on 0.5 mmol scale using the general procedure. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 77 mg of \( \text{2c} \) (49%) when following procedure A (yield based on recovered starting material is 70%). When following procedure B and heating the mixture at 50 °C, the reaction provided 93 mg of \( \text{2c} \) (60%), as a white solid.\(^4\)

\[ ^1\text{H NMR} \ (300 \text{ MHz, CDCl}_3) \delta = 7.79 \ (d, J = 8.3 \text{ Hz, 2H}), 7.39 - 7.31 \ (m, 2H), 7.17 \ (q, J = 8.2 \text{ Hz, 4H}), 5.96 \ (t, J = 2.1 \text{ Hz, 1H}), 4.49 \ (td, J = 4.5, 2.0 \text{ Hz, 2H}), 4.31 \ (td, J = 4.5, 2.2 \text{ Hz, 2H}), 2.43 \ (s, 3H), 2.35 \ (s, 3H) \text{ ppm}; \]

\[ ^{13}\text{C NMR} \ (75 \text{ MHz, CDCl}_3) \delta = 143.5, 138.4, 137.2, 134.1, 129.4, 127.5, 125.3, 117.8, 55.7, 55.0, 21.5, 21.2 \text{ ppm}. \]

The cyclization of \( \text{1d} \) was performed on 0.5 mmol scale using the general procedure. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 76 mg of \( \text{2d} \) (51%), when following procedure A, and 45 mg of \( \text{2d} \) (30%), when following procedure B, as a white solid.\(^3\)

\[ ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \delta = 7.77 \ (d, J = 8.3 \text{ Hz, 2H}), 7.37 - 7.26 \ (m, 7H), 6.01 \ (\text{quint, } J = 2.0 \text{ Hz, 1H}), 4.48 \ (\text{td, } J = 4.6, 1.9 \text{ Hz, 2H}), 4.30 \ (\text{td, } J = 4.6, 1.9 \text{ Hz, 2H}), 2.41 \ (s, 3H) \text{ ppm}; \]

\[ ^{13}\text{C NMR} \ (100 \text{ MHz, CDCl}_3) \delta = 143.5, 137.3, 134.1, 132.5, 129.8, 128.7, 128.4, 127.4, 125.4, 118.8, 55.6, 54.9, 21.5 \text{ ppm}. \]
The cyclization of 1e was performed on 0.5 mmol scale using the general procedure. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 81 mg of 2e (43%) when following procedure A, (yield based on recovered starting material is 49%). When following procedure B on a 0.27 mmol scale and heating the mixture at 50 °C, the reaction yielded 50 mg of 2e (50%), as a light yellow solid (yield based on recovered starting material is 66%).

\[ \text{1H NMR} \ (400 \text{ MHz}, \text{CDCl}_3) \delta = 7.78 \ (d, J = 8.3 \text{ Hz}, 2H), \ 7.46 \ (d, J = 8.5 \text{ Hz}, 2H), \ 7.35 \ (d, J = 8.0 \text{ Hz}, 2H), \ 7.16 \ (d, J = 8.5 \text{ Hz}, 2H), \ 6.04 \ (p, J = 2.1 \text{ Hz}, 1H), \ 4.46 \ (td, J = 4.5, 1.9 \text{ Hz}, 2H), \ 4.30 \ (td, J = 4.5, 2.2 \text{ Hz}, 2H), \ 2.44 \ (s, 3H) \text{ ppm;} \]

\[ \text{13C NMR} \ (100 \text{ MHz}, \text{CDCl}_3) \delta = 143.7, \ 136.4, \ 134.1, \ 131.9, \ 131.4, \ 129.9, \ 127.5, \ 126.9, \ 122.4, \ 119.8, \ 55.7, \ 54.7, \ 21.5 \text{ ppm.} \]

The cyclization of 1f was performed on 0.5 mmol scale using the general procedure A. Purification by flash column chromatography eluting with hexanes/EtOAc (50:1) provided 71 mg (66%) of 2f as a colorless oil.

\[ \text{1H NMR} \ (400 \text{ MHz}, \text{CDCl}_3) \delta = 7.53 – 7.41 \ (m, 2H), \ 7.37 – 7.28 \ (m, 2H), \ 7.28 – 7.20 \ (m, 1H), \ 6.36 \ (td, J = 2.6, 1.6 \text{ Hz}, 1H), \ 4.12 \ (qd, J = 7.1, 3.7 \text{ Hz}, 2H), \ 4.00 \ (dtd, J = 9.0, 2.7, 1.3 \text{ Hz}, 1H), \ 2.75 \ (dddt, J = 17.8, 9.1, 6.7, 2.6 \text{ Hz}, 1H), \ 2.67 – 2.51 \ (m, 1H), \ 2.46 – 2.34 \ (m, 1H), \ 2.34 – 2.21 \ (m, 1H), \ 1.17 \ (t, J = 7.1 \text{ Hz}, 3H) \text{ ppm;} \]

\[ \text{13C NMR} \ (100 \text{ MHz}, \text{CDCl}_3) \delta = 175.2, \ 141.2, \ 135.5, \ 130.1, \ 128.3, \ 127.2, \ 127.7, \ 125.9, \ 60.5, \ 51.3, \ 35.1, \ 32.5, \ 29.3, \ 22.5, \ 22.0, \ 14.1 \text{ ppm.} \]
The cyclization of 1g was performed on 0.5 mmol scale using the general procedure. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 61 mg of 2g (50%) when following procedure A (yield based on recovered starting material is 57%). When following procedure B, the reaction yielded 45 mg of 2g (37%), as a yellow oil (yield based on recovered starting material is 48%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.56 – 7.41$ (m, 2H), 7.41 – 7.11 (m, 3H), 6.35 (td, J = 2.6, 1.6 Hz, 1H), 4.13 – 3.90 (m, 3H), 2.75 (ddddd, J = 17.3, 8.9, 4.6, 2.6 Hz, 1H), 2.68 – 2.53 (m, 1H), 2.48 – 2.14 (m, 1H), 1.63 – 1.42 (m, 2H), 1.37 – 1.19 (m, 2H), 0.87 (t, J = 7.3 Hz, 3H) ppm;

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 175.3, 141.2, 135.5, 130.0, 128.3, 127.2, 125.8, 64.4, 51.3, 32.5, 30.6, 29.3, 19.0, 13.6$ ppm.

IR (neat): 3055, 2960, 1726, 1457, 1383, 1330 cm$^{-1}$;

HRMS: calcd for [C$_{16}$H$_{20}$O$_2$Na]+: m/z = 267.1361, found: m/z = 267.1356.

The cyclization of 1h was performed on 0.5 mmol scale using the general procedure. Purification by flash column chromatography eluting with hexane/EtOAc (50:1) provided 45.5 mg (37%) of 2h as a clear oil (yield based on recovered starting material is 81%).

$^1$H NMR (400 MHz; CDCl$_3$) $\delta = 7.32 – 7.18$ (m, 1H), 7.10 – 6.94 (m, 2H), 6.80 (ddd, J = 8.2, 2.6, 0.9 Hz, 1H), 6.36 (td, J = 2.6, 1.6 Hz, 1H), 4.12 (qq, J = 7.1, 3.7 Hz, 2H), 3.97 (ddddd, J = 8.8, 4.2, 2.7, 1.4 Hz, 1H), 3.82 (s, 3H), 2.74 (dddt, J = 17.7, 9.0, 6.6, 2.6 Hz, 1H), 2.64 – 2.48 (m, 1H), 2.43 – 2.33 (m, 1H), 2.33 – 2.19 (m, 1H), 1.18 (t, J = 7.1 Hz, 3H) ppm;
\( ^{13}\text{C NMR} \) (100 MHz; CDCl\(_3\)) \( \delta = 175.3, 159.6, 141.1, 136.9, 130.5, 129.3, 118.4, 112.8, 111.4, 60.5, 55.2, 51.3, 32.5, 29.3, 14.1 \) ppm.

![Compound 2i](image)

The cyclization of \( \text{2i} \) was performed on 0.5 mmol scale using the general procedure A. Purification by flash column chromatography eluting with hexanes/EtOAc (25:1) provided 98.5 mg (70\%) \( \text{2i} \) as a white solid.\(^1\)

\( ^{1}\text{H NMR} \) (400 MHz; CDCl\(_3\)) \( \delta = 7.88 – 7.77 \) (m, 4H), 7.70 (dd, \( J = 8.6, 1.8 \) Hz, 1H), 7.55 – 7.41 (m, 2H), 6.52 (td, \( J = 2.6, 1.5 \) Hz, 1H), 4.23 – 4.02 (m, 3H), 2.90 – 2.74 (m, 1H), 2.73 – 2.57 (m, 1H), 2.54 – 2.25 (m, 2H), 1.20 (t, \( J = 7.1 \) Hz, 3H) ppm;

\( ^{13}\text{C NMR} \) (100 MHz; CDCl\(_3\)) \( \delta = 175.4, 141.1, 133.5, 132.8, 132.7, 130.9, 128.2, 127.9, 127.6, 126.2, 125.8, 124.5, 124.3, 60.6, 51.3, 32.7, 29.4, 14.2 \) ppm.

![Compound 2j](image)

The cyclization of \( \text{1j} \) was performed on 0.5 mmol scale using the general procedure and 20\% catalyst. Purification by flash column chromatography eluting with hexanes/EtOAc (50:1) provided 70 mg of \( \text{2j} \) (56\%) as white solids.\(^1\)\(^2\)

\( ^{1}\text{H NMR} \) (300 MHz; CDCl\(_3\)) \( \delta = 8.16 – 7.97 \) (m, 2H), 7.68 – 7.43 (m, 3H), 7.39 – 7.08 (m, 5H), 6.50 (dt, \( J = 2.6, 1.2 \) Hz, 1H), 4.97 (d, \( J = 1.8 \) Hz, 1H), 2.75 – 2.41 (m, 2H), 2.25 – 2.06 (m, 2H) ppm;

\( ^{13}\text{C NMR} \) (75 MHz; CDCl\(_3\)) \( \delta = 201.2, 141.7, 136.5, 135.6, 133.1, 130.1, 128.7, 128.7, 128.4, 127.1, 125.8, 53.5, 32.4, 30.1 \) ppm.
References


NMR Spectra of Carbonyl-Olefin Metathesis Products

2-methyl-3-(p-toly1)-1-tosyl-2,5-dihydro-1H-pyrrole (2a); $^1$H NMR (400 MHz, CDCl3), $^{13}$C NMR (100 MHz, CDCl3).
3-(p-tolyl)-1-tosyl-2,5-dihydro-1H-pyrrole (2b); $^1$H NMR (400 MHz, CDCl3), $^{13}$C NMR (100 MHz, CDCl3).
2-methyl-3-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole (2c); $^1$H NMR (400 MHz, CDCl3), $^{13}$C NMR (100 MHz, CDCl3).
3-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole (2d); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
3-(4-bromophenyl)-1-tosyl-2,5-dihydro-1H-pyrrole (2e); $^1$H NMR (400 MHz, CDCl3), $^{13}$C NMR (100 MHz, CDCl3).
Ethyl 2-phenylcyclopent-2-ene-1-carboxylate (2f), $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
butyl 2-phenyleclopent-2-ene-1-carboxylate (2g); \(^1\)H NMR (400 MHz, CDCl\(_3\)), \(^{13}\)C NMR (100 MHz, CDCl\(_3\)).
Ethyl 2-(3-methoxyphenyl)cyclopent-2-ene-1-carboxylate (2h); $^1$H NMR (400 MHz, CDCl3), $^{13}$C NMR (100 MHz, CDCl3).
Ethyl 2-(naphthalen-2-yl)cyclopent-2-ene-1-carboxylate (2i); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
Phenyl(2-phenylcyclopent-2-en-1-yl)methanone (2j); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).