Tropylium-Promoted Carbonyl-Olefin Metathesis

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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), Phenylchloride, 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, 1H; 100.6 MHz, 13C, 376.5 MHz, 19F) or an Avance III 300 (300 MHz, 1H; 75 MHz, 13C; 282.5 MHz, 19F). Data is expressed in parts per million (ppm) downfield shift from tetramethylsilane with residual solvent as an internal reference (δ 7.26 ppm for chloroform, 5.27 ppm for dichloromethane) and is reported as position (δ in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (J in Hz) and integration (number of protons). 13C 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 (δ 77.2 ppm for the central peak of deuterated chloroform).

Infrared spectra were obtained on a ThermoNicolet 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.

Microwave reactions were carried out in 10 mL microwave vials on CEM Discover – SP W/ACTIVENT 909155 or 10 mL vials on Anton Paar Monowave 300.
Table S1 - Optimization of the Intramolecular COM Reaction

| entry | mol% cat. | solvent | T (°C) | t (h) | yieldb |
|-------|-----------|---------|--------|-------|--------|
| 1     | 20        | MeCN    | rt     | 48    | traces |
| 2     | 20        | MeCN    | 90     | 24    | 86%    |
| 3     | 20        | DCM     | 45     | 24    | 59%    |
| 4     | 20        | DCE     | 90     | 24    | 60%    |
| 5     | 20        | PhCl    | 90     | 24    | 61%    |
| 6     | 20        | PhMe    | 90     | 24    | 21%    |
| 7     | 20        | neat    | 90     | 24    | 92%    |
| 8     | 15        | neat    | 90     | 24    | 92%    |
| 9     | 10        | neat    | 90     | 24    | 55%    |
| 10    | 15        | neat    | 70     | 24    | 62%    |
| 11    | 15        | neat    | 50     | 24    | 13%    |
| 12c   | 15        | neat (MW) | 120   | 2     | 82%    |
| 13d   | 15        | MeCN    | 120    | 2     | 88%    |
| 14e   | 15        | neat    | 90     | 24    | 94%    |
| 15    | 0         | neat    | 90     | 24    | n.r.   |

a Reaction conditions: Substrate 1a (0.5 mmol) and tropylium tetrafluoroborate 2 (mol%/cat.) and solvent (0.5 mL) were charged to a closed-cap N2-filled reaction vial and heated to indicated temperature for indicated time. b Yield of the isolated product. c Heated in a microwave reactor. d Continuous tubular flow-reactor with 10 mL MeCN as solvent. e Before starting the reaction, the inner pressure was adjusted to 8 mbar.

Our initial reactions using 20 mol% tropylium tetrafluoroborate as catalyst met with very encouraging results, although elevated temperature was required for efficient conversion of the substrate (entries 1-2, Table S1). A quick solvent screening study revealed that acetonitrile or neat conditions afforded the best product yields (entries 2-7, Table S1). On the other hand, although the reaction in dichloromethane (entry 3) was sluggish due to the low boiling point of the solvent, it gave very clean conversion of substrate 1a to product 3a (also see Figure 1). Some other commonly used organic solvents did not efficiently mediate this intramolecular
carbonyl-olefin metathesis reaction (entries 4-6, Table 1), which is due in part to the low solubility of the tropylium salt catalyst in these solvents.

Optimization of catalyst loading and reaction temperature showed that 15 mol% of tropylium tetrafluoroborate at 90 °C in neat conditions are optimal for this reaction on substrate 1a (entry 8, Table 1). We also tried microwave-assisted reaction conditions, which gave comparable outcomes with shorter reaction time (entry 12, Table 1). A simple continuous flow setup also facilitated the reaction smoothly with slightly better product yield than the batch reaction (entry 13). Although the microwave-assisted or flow-chemistry settings need to be further explored, these proof-of-concept experiments showed that they could be attractive options for future development of the carbonyl-olefin metathesis reaction process. Interestingly, a reaction at reduced initial pressure, being carried out in a sealed vial, also afforded better yield of product 3a (entry 14). Presumably, the reduced pressure helps to remove some acetone by-product (4a) out of the reaction mixture and drives the reaction to completion. This phenomenon could potentially be exploited in process design of the intramolecular COM reaction for future synthetic applications.
In Situ $^1$H-NMR Experiment for Intramolecular Carbonyl-Olefin Metathesis.

An NMR tube containing Trop.BF$_4$ (3 mg, 0.017 mmol) was charged with 1b (26.1 mg, 0.11 mmol) and CD$_2$Cl$_2$ (0.5 mL). The reaction mixture was then measured in a 400 MHz NMR at regular time points at 45 °C. An abbreviated series of spectra is shown below, including time points at 2, 4, 8, 12, 24 and 36 h. As indicated in the figure, the disappearance of 1b is accompanied by the emergence of 3b + acetone (4a, singlet for (CH$_3$)$_2$C=O at 2.2 ppm) over time. The reaction was very clean and completed after ca. 48 h at 45 °C.

Figure S1: In situ $^1$H-NMR experiments. From top to bottom: 1) $^1$H-NMR of substrate 1b. 2) Reaction mixture of substrate 1b and 15 mol% Trop.BF$_4$ in CD$_2$Cl$_2$ at 0h. 3-5) Same reaction mixture after 8, 12 and 36 hours. 6) $^1$H-NMR of product 3b.
A dried 4ml vial was charged with tropylium tetraphenylborate and a stirring bar. Starting ketone was added to the vial under Argon condition. Then the vial was sealed tightly and the mixture was stirred for 24 h at 90 °C, unless otherwise specified. Upon completion (as determined by TLC analysis), the crude mixture was directly purified by flash column chromatography, with the indicated eluent to give pure metathesis adducts.
Characterization Data of Intramolecular Products

The cyclization of 1a was performed on 0.525 mmol scale using the general procedure. Purification by flash column chromatography eluting with hexane provided 3a (76 mg, 92%) as a colorless liquid.\(^2\)

\[^{1}\text{H} \text{NMR} \ (300 \text{ MHz; CDCl}_3) \delta \ 7.38-7.29 (m, 4H), 7.25-7.19 (m, 1H), 2.78-2.72 (m, 2H), 2.53-2.48 (m, 2H), 1.95-1.85 (m, 5H);\]

\[^{13}\text{C} \text{NMR} \ (75 \text{ MHz; CDCl}_3) \delta \ 138.8, 135.2, 134.8, 128.0, 127.6, 126.0, 40.1, 37.3, 21.9, 15.5.\]

The cyclization of 1b was performed on 0.73 mmol scale with a total reaction time of 6 h at 70 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (100:1) provided 116 mg of 3b (85%) as a colorless liquid.

\[^{1}\text{H} \text{NMR} \ (300 \text{ MHz; CDCl}_3) \delta \ 7.36-7.28 (m, 4H), 7.23-7.18 (m, 1H), 3.81 (s, 3H), 2.73-2.67 (m, 2H), 2.51-2.46 (m, 2H), 1.94-1.83 (m, 5H);\]

\[^{13}\text{C} \text{NMR} \ (75 \text{ MHz; CDCl}_3) \delta \ 157.8, 134.1, 133.8, 131.3, 128.7, 113.4, 55.2, 40.1, 37.3, 21.8, 15.5.\]

**IR (Neat):** 2951, 1735, 1605, 1509, 1241;

**HRMS:** calcd for C\(_{13}\)H\(_{16}\)O: 188.1201 found: 188.1195.

\[^2\] A. Soicke, N. Slavov, J. M. Neudörfl, H.G. Schmalz, *Synlett*, 2011, 17, 2487
The cyclization of 1c was performed on 0.57 mmol scale with a total reaction time of 6 h at 70 °C. Purification by flash column chromatography eluting with hexane/EtOAc (100:1) provided 74 mg of 3c (83%) as a colorless liquid.

$^1$H NMR (300 MHz; CDCl$_3$) δ 7.36-7.28 (m, 4H), 7.23-7.18 (m, 1H), 3.81 (s, 3H), 2.73-2.67 (m, 2H), 2.51-2.46 (m, 2H), 1.94-1.83 (m, 5H);

$^{13}$C NMR (75 MHz; CDCl$_3$) δ 159.3, 140.2, 135.6, 134.7, 128.9, 120.2, 113.4, 111.4, 55.2, 40.1, 37.3, 21.9, 15.5.

IR (Neat); 2950, 1734, 1602, 1510, 1243;

HRMS: calcd for C$_{13}$H$_{16}$O: 188.1201, found: 188.1201.

![Image of 3d, 36%](image)

The cyclization of 1d was performed on 0.504 mmol scale with a total reaction time of 20 h at 110 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (50:1) provided 40 mg (36%) of 3d as a white solid.  

$^1$H NMR (400 MHz; CDCl$_3$) δ 7.32-7.09 (m, 8H), 6.47-6.44 (m, 1H), 4.32-4.29 (m, 1H), 2.63-2.52 (m, 3H), 1.94-1.90 (m, 1H);

$^{13}$C NMR (100 MHz; CDCl$_3$) δ 145.4, 144.6, 136.0, 128.8, 128.5, 128.1, 127.4, 126.7, 126.3, 126.0, 51.8, 35.4, 31.6.

![Image of 3e, 82%](image)

The cyclization of 1e was performed on 0.344 mmol scale with a total reaction time of 14h at 90 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (50:1) provided 53 mg (82%) of 3e as a clear oil.  

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2 Jacob R. Ludwig, Paul M. Zimmerman, Joseph B. Gianino, Corinna S. Schindler, *Nature*, 2016, 533, 374.
\(^1\text{H NMR}\) (400 MHz; CDCl\(_3\)) \(\delta\) 7.33-7.23 (m, 5H), 5.84-5.70 (m, 2H), 5.05-4.98 (m, 2H), 2.38-2.29 (m, 3H), 2.19 (dd, \(J = 13.9, 8.1\) Hz, 1H), 2.05 (ddd, \(J = 12.6, 7.9, 6.5\) Hz, 1H), 1.72 (ddd, \(J = 12.5, 8.3, 5.8\) Hz, 1H), 1.22 (s, 3H); 
\(^{13}\text{C NMR}\) (100 MHz; CDCl\(_3\)) \(\delta\) 150.5, 138.1, 136.0, 128.8, 128.0, 127.7, 126.7, 116.7, 50.2, 44.5, 38.2, 39.8, 26.4.

The cyclization of 1f was performed on 1.01 mmol scale with a total reaction time of 20 h at 90 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (50:1) provided 152 mg (61%) of 3f as a white solid.\(^2\)

\(^1\text{H NMR}\) (300 MHz; CDCl\(_3\)) \(\delta\) 8.09-8.06 (m, 2H), 7.62-7.48 (m, 3H), 7.33-7.14 (m, 5H), 6.49-6.48 (m, 1H), 4.98-4.96 (m, 1H), 2.70-2.61 (m, 2H), 2.71-2.49 (m, 1H), 2.15 (ddt, \(J = 11.9, 9.5, 4.8\) Hz, 1H); 
\(^{13}\text{C NMR}\) (75 MHz; CDCl\(_3\)) \(\delta\) 201.3, 141.8, 136.7, 135.8, 133.3, 130.3, 128.89, 128.85, 128.6, 127.3, 126.0, 53.7, 32.6, 30.3.

The cyclization of 1ga was performed on 1.0 mmol scale with a total reaction time of 20 h at 90 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (50:1) provided 194 mg (90%) of 3g as a clear oil.\(^2\)

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\(^2\) Jacob R. Ludwig, Paul M. Zimmerman, Joseph B. Gianino, Corinna S. Schindler, *Nature*, **2016**, 533, 374.
The cyclization of 1gb was performed on 1.0 mmol scale with a total reaction time of 20 h at 90 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (50:1) provided 84 mg (39%) of 3g.  

The cyclization of 1gc was performed on 1.0 mmol scale with a total reaction time of 20 h at 90 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (50:1) provided 39 mg (18%) of 3g.  

\[ \text{1}^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 7.46-7.43 (m, 2H), 7.34-7.28 (m, 2H), 7.25-7.20 (m, 1H), 6.35 (td, } J = 2.6, 1.6 \text{ Hz, 1H), } 4.16-4.04 (m, 2H), 3.98 (m, 1H), 2.73 (m, 1H), 2.56 (m,1H), 2.37 (ddt, } J = 13.0, 9.1, 6.7 \text{ Hz, 1H), } 2.27 (ddt, } J = 13.1, 8.7, 4.4 \text{ Hz, 1H), } 1.15 (t, } J = 7.1 \text{ Hz, 3H);  \\
\text{13C NMR (100 MHz, CDCl}_3\text{): } \delta = 175.2, 141.2, 135.5, 130.1, 128.3, 127.2, 125.9, 60.5, 51.3, 32.5, 29.3, 14.1. \]

The cyclization of 1h was performed on 0.818 mmol scale with a total reaction time of 24 h at 120 °C. Purification by flash column chromatography eluting with hexane/EtOAc (50:1) provided 123 mg (58%) of 3h + 3h’ as a 1:1 mixture of olefin regio-isomers as a colorless oil.  

\[ \text{1}^1\text{H NMR (400 MHz; CDCl}_3\text{)} \delta 7.36-7.30 (m, 4H), 6.85-6.81 (m, 4H), 6.23 (q, } J = 2.0 \text{ Hz, 1H), } 4.14-3.99 (m, 8H), 3.92 (m, 1H), 2.82 (m, 4H), 2.74-2.65 (m, 1H), 2.57-2.48 (m, 1H), \]

\[ 3h, 3h + 3h' \text{ (1 : 1), 58\% } R^1 = R^2 = \text{Me} \]

\[ 3h', R^1 = \text{Me, R^2 = Ph} \]

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\[ 2 \text{ Jacob R. Ludwig, Paul M. Zimmerman, Joseph B. Gianino, Corinna S. Schindler, Nature, 2016, 533, 374.} \]
2.35 (dtd, \( J = 13.1, 9.1, 6.9 \) Hz, 1H), 2.25 (tt, \( J = 8.7, 4.3 \) Hz, 1H), 1.96 (quintet, \( J = 7.7 \) Hz, 1H);

\(^{13}\text{C NMR}\) (100 MHz; CDCl3) \( \delta \) 175.4, 166.6, 158.8, 158.2, 152.6, 140.6, 130.3, 129.0, 128.1, 127.9, 127.8, 127.0, 114.3, 113.6, 60.5, 59.9, 51.4, 39.9, 35.3, 32.4, 29.3, 21.9, 14.8, 14.2, 14.1.

\( \text{IR}\) (Neat): 2976, 1719, 1604, 1476, 1391;

\( \text{HRMS}\): calcd for \( \text{C}_{16}\text{H}_{20}\text{O}_{3} \): 260.1412 found: 260.1413.

The cyclization of 1i was performed on 0.71 mmol scale with a total reaction time of 24 h at 110 °C. Purification by flash column chromatography eluting with hexane/EtOAc (50:1) provided 129 mg (74%) of 3i as a colorless oil. This compound might have isomer 3i' but their signal is so small that we cannot provide its full spectra.

\(^{1}\text{H NMR}\) (400 MHz; CDCl3) \( \delta \) 7.36-7.30 (m, 4H), 6.85-6.81 (m, 4H), 6.23 (q, \( J = 2.0 \) Hz, 1H), 4.14-3.99 (m, 8H), 3.92 (m, 1H), 2.82 (m, 4H), 2.74-2.65 (m, 1H), 2.57-2.48 (m, 1H), 2.35 (dtd, \( J = 13.1, 9.1, 6.9 \) Hz, 1H), 2.25 (tt, \( J = 8.7, 4.3 \) Hz, 1H), 1.96 (quintet, \( J = 7.7 \) Hz, 1H);

\(^{13}\text{C NMR}\) (100 MHz; CDCl3) \( \delta \) 175.4, 166.6, 158.8, 158.2, 152.6, 140.6, 130.3, 129.0, 128.1, 127.9, 127.8, 127.0, 114.3, 113.6, 60.5, 59.9, 51.4, 39.9, 35.3, 32.4, 29.3, 21.9, 14.8, 14.15, 14.10.

\( \text{IR}\) (Neat): 2936, 2845, 1723, 1597, 1490, 1460, 1436, 1368, 1329, 1288;

\( \text{HRMS}\): calcd for \( \text{C}_{15}\text{H}_{18}\text{O}_{3} \): 246.1256 found: 246.1253.

The cyclization of 1j was performed on 0.819 mmol scale with a total reaction time of 12h at 130 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (25:1)
provided 161 mg (74%) of mixture of 3j (148 mg, 66%) and 3j' (13 mg, 8%) (8.3:1 ratio by \(^1\)H NMR analysis) as an inseparable mixture as a white solid.\(^2\) We cannot get a full \(^{13}\)C NMR data of 3j' when some of their peaks two small to be detected.

\(^1\)H NMR (400 MHz; CDCl\(_3\)) δ 7.82-7.75 (m, 4.5H), 7.67-7.64 (m, 1.12H), 7.47-7.41 (m, 2.23H), 6.50 (q, J = 2.6 Hz, 1H), 4.17-4.03 (m, 3.3H), 2.99-2.86 (m, 0.5H), 2.62 (m, 1H), 2.42 (ddt, J = 13.1, 9.1, 6.8 Hz, 1H), 2.32 (ddt, J = 13.1, 8.6, 4.3 Hz, 1H), 2.04 (quintet, J = 7.4 Hz, 0.25H), 1.17 (t, J = 7.1 Hz, 3H), 1.08 (t, J = 7.1 Hz, 0.37H);

\(^{13}\)C NMR (100 MHz; CDCl\(_3\)) δ 175.4, 141.1, 133.4, 132.8, 132.7, 130.9, 128.1, 127.9, 127.5, 126.1, 125.8, 124.4, 124.3, 60.6, 51.3, 40.2, 35.3, 32.7, 29.4, 22.0, 14.2.

The cyclization of 1k was performed on 1.0 mmol scale with a total reaction time of 12 h at 90 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (25:1) provided 149 mg 3k (65%) as a colorless oil.\(^2\)

\(^1\)H NMR (300 MHz; CDCl\(_3\)) δ 7.42-7.40 (m, 2H), 7.29-7.24 (m, 2H), 7.21-7.17 (m, 1H), 6.30 (dt, J = 2.6, 1.6 Hz, 1H), 4.95 (sept, J = 6.2 Hz, 1H), 3.94-3.89 (m, 1H), 2.69 (m, 1H), 2.53 (m, 1H), 2.33 (ddt, J = 13.0, 9.1, 6.5 Hz, 1H), 2.22 (ddt, J = 13.1, 8.8, 4.4 Hz, 1H), 1.10 (dd, J = 6.3, 3.3 Hz, 6H);

\(^{13}\)C NMR (75 MHz; CDCl\(_3\)) δ 174.8, 141.4, 135.6, 130.1, 128.3, 127.2, 125.9, 67.7, 51.5, 32.5, 29.2, 21.6;

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\(^2\) Jacob R. Ludwig, Paul M. Zimmerman, Joseph B. Gianino, Corinna S. Schindler, *Nature*, 2016, 533, 374
The cyclization of 1l was performed on 1.0 mmol scale with a total reaction time of 20 h at 110 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (50:1) provided 150 mg 3l (54%) as a colorless oil.²

\(^1\)H NMR (300 MHz; CDCl\(_3\)) δ 7.43-7.41 (m, 2H), 7.31-7.27 (m, 5H), 7.25-7.21 (m, 1H), 7.20-7.17 (m, 2H), 6.35 (q, \(J = 2.1\) Hz, 1H), 5.08 (q, \(J = 11.2\) Hz, 2H), 4.1 (m, 1H), 2.73 (m, 1H), 2.57 (m, 1H), 2.38 (ddt, \(J = 13.1, 8.9, 6.7\) Hz, 1H), 2.29 (ddt, \(J = 13.1, 8.7, 4.4\) Hz, 1H); \(^{13}\)C NMR (75 MHz; CDCl\(_3\)) δ 175.1, 141.0, 136.0, 135.4, 130.3, 128.4, 128.0, 127.9, 127.3, 125.9, 66.5, 51.4, 32.7, 29.5.

The cyclization of 1m was performed on 0.184 mmol scale with a total reaction time of 14 h at 110 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (50:1) provided 30 mg of 3m (72%) as a colorless oil.³

\(^1\)H NMR (300 MHz; CDCl\(_3\)) δ 7.31-7.26 (m, 4 H), 7.23-7.20 (m, 1H), 6.17 (t, \(J = 2.6\) Hz, 1H), 4.15 (dt, \(J = 10.7, 7.0, 3.6\) Hz, 2 H), 2.62 (m, 1H), 2.53 (m, 1H), 2.49-2.43 (m, 1H), 1.97 (ddd, \(J = 12.6, 8.5, 5.7\) Hz, 1H), 1.44 (s, 3 H), 1.16 (t, \(J = 7.1\) Hz, 3H); \(^{13}\)C NMR (75 MHz; CDCl\(_3\)) δ 177.5, 146.5, 135.7, 129.9, 128.2, 127.0, 126.3, 60.7, 55.9, 39.8, 30.9, 22.5, 14.1.

The cyclization of 1n was performed on 0.43 mmol scale with a total reaction time of 14 h at 110 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (50:1) provided 55 mg of 3n (51%) as a colorless oil.²

³ Jacob R. Ludwig, Paul M. Zimmerman, Joseph B. Gianino, Corinna S. Schindler, Nature, 2016, 533, 374.
**1H NMR** (300 MHz; CDCl₃) δ 7.30-7.25 (m, 4H), 7.23-7.20 (m, 1H), 6.18 (t, J = 2.6 Hz), 5.70-5.56 (m, 1H), 5.0 (d, J = 5.4 Hz, 1H), 4.97 (s, 1H), 4.20-4.13 (m, 2H), 2.70-2.55 (m, 3H), 2.43 (m, 1H), 2.33 (m, 1H), 2.12 (ddd, J = 13.1, 9.0, 6.6 Hz, 1H) 1.18 (t, J = 7.1 Hz, 3H);

**13C NMR** (75 MHz; CDCl₃) δ 177.0, 144.6, 136.1, 134.6, 132.2, 128.4, 127.3, 126.8, 118.1, 60.9, 59.6, 39.4, 35.4, 31.6, 14.3.

The cyclization of 1o was performed on 0.552 mmol scale with a total reaction time of 6h at 70 °C. Purification by flash column chromatography eluting with hexanes provided 110 mg of 3o (69 mg, 65%) and 3o’ (41 mg, 32%) (2.1:1.0 ratio by NMR analysis), as a white solid.³

**1H NMR** (300 MHz, CDCl₃; as a mixture of 3o and 3o’ as an inseparable mixture) δ 8.75-8.66 (m, 6.25H), 8.14 – 8.00 (m, 4.01H), 7.84 – 7.80 (m, 2.00H), 7.71-7.54 (m, 13.48H), 5.57 (s, 1H), 5.00 (s, 1H), 2.74 (s, 6.35H), 2.69 (s, 3.1H), 2.14 (s, 3.04H);

**13C NMR** (75 MHz, CDCl₃; as a mixture of 3o and 3o’) δ 144.46, 138.48, 132.48, 132.09, 132.02, 131.98, 130.46, 130.38, 129.68, 129.61, 129.53, 128.86, 128.68, 128.56, 128.30, 127.82, 127.58, 126.73, 126.63, 126.57, 126.51, 126.21, 125.90, 125.80, 125.60, 124.89, 124.66, 123.00, 122.77, 122.53, 122.45, 116.71, 24.86, 20.06, 16.52.

The cyclization of 1p was performed on 0.4 mmol scale with a total reaction time of 14 h at 90 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (100:1)

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³ Christopher C. McAtee, Paul S. Riehl, Corinna S. Schindler, JACS, 2017, 139 (8), 2960
provided 37 mg of 3p (19mg, 29%) and 3p’ (18mg, 20%) as an inseparable mixture (1.1:1.0; ratio by NMR analysis), as a white solid.\(^3\)

\(^1\)H NMR (300 MHz, CDCl₃; as a mixture of 3p and 3p’) \(\delta\) 8.74-8.64 (m, 3.81H), 8.15-8.11 (m, 1.85H), 8.09-8.05 (m, 0.85H), 7.82-7.79 (m, 0.81H), 7.68-7.56 (m, 7.48H), 7.13 (dd, \(J = 17.9, 11.3\) Hz, 1H), 5.85 (dd, \(J = 11.4, 2.2\) Hz, 1H), 5.42 (dd, \(J = 17.9, 2.2\) Hz, 1H), 2.75 (s, 3H), 2.74 (s, 2.66H);

\(^13\)C NMR (75 MHz, CDCl₃; as a mixture of 3p and 3p’) \(\delta\) 135.75, 133.93, 132.69, 132.30, 132.23, 131.35, 130.59, 129.93, 129.89, 129.55, 129.36, 129.29, 129.22, 128.04, 126.94, 126.88, 126.79, 126.73, 126.62, 126.46, 126.42, 126.26, 126.01, 125.90, 125.32, 124.87, 123.21, 122.98, 122.77, 122.66, 121.79, 20.25, 17.17.
Table S2 - Optimization of the Intermolecular COM Reaction

![Chemical reaction diagram]

| entry | mol% cat. | 5a:6a ratio | solvent | T (°C) | t (h) | yield (%) |
|-------|-----------|-------------|---------|--------|-------|-----------|
| 1     | 20        | 1:1         | MeCN    | 90     | 24    | 14        |
| 2     | 20        | 1:1         | DCE     | 90     | 24    | 21        |
| 3     | 20        | 1:1         | DCM     | 45     | 24    | 20        |
| 4     | 20        | 1:1         | neat    | 90     | 24    | 18        |
| 5     | 20        | 1:1         | neat    | 45     | 72    | 18        |
| 6     | 20        | 1:5         | neat    | 45     | 72    | 11        |
| 7     | 20        | 2.5:1       | neat    | 45     | 72    | 34        |
| 8     | 20        | 5:1         | neat    | 45     | 72    | 38        |
| 9     | 20        | 5:1         | DCM     | 45     | 24    | 37        |
| 10    | 10        | 5:1         | DCM     | 45     | 24    | 41        |
| 11    | 10        | 5:1         | DCM     | 80     | 0.5   | 52        |
| 12    | 10        | 5:1         | DCM     | 80     | 1     | 50        |

* Reaction conditions: Substrate 5a (1.0 mmol), substrate 6a (indicated ratio) and tropylium tetrafluoroborate 2 (mol% cat.) and solvent (0.5 mL) were charged to a closed-cap N₂-filled reaction vial and heated to indicated temperature for indicated time. Yield of the isolated product. Heated in a microwave reactor.
Kinetic Studies of the Intermolecular COM Reaction

Below is the chart reflecting the kinetic studies of entries 9 and 10 of Table S2 by $^1$H NMR spectroscopy (298K, CD$_2$Cl$_2$, 400 MHz):

![Chart S1. Kinetic studies of the intermolecular COM reactions](image)

It is clear that the initial reaction rate double when the catalyst loading of 2 increase from 10 mol\% ($k_1 = 0.3$ M/h) to 20 mol\% ($k_2 = 0.6$ M/h), which means the reaction rate is first-order with respect to the concentration of tropylium ion.
General Procedures for Intermolecular Carbonyl-Olefin Metathesis

A mixture of aldehyde 5 (5 equiv.) and alkene 6 (1 equiv.) was taken up in dry dichloromethane (2 mL) in a microwave vessel charged with Trop.BF₄ (10.0 mol%) and a stirrer bar. The reaction mixture was heated to 80 °C in a microwave reactor (ramp-up time 2 min, holding time 30 min) then cooled to room temperature. The reaction mixture was concentrated under reduced pressure, then was purified by silica gel column chromatography to give the product.

The compound 7a was prepared according to the general procedure from 2-naphtaldehyde and 2-methyl-2-butene. Purification by flash column chromatography eluting with n-hexane provide product 7a as a white solid in 52% yield.⁴

¹H NMR (400 MHz; CDCl₃) δ 7.78-7.73 (m, 3H), 7.64 (brs, 1H), 7.55 (dd, J = 8.6, 1.7 Hz, 1H), 7.45-7.35 (m, 2H), 6.55 (dd, J = 15.8, 1.2 Hz, 1H), 6.35 (dq, J = 15.7, 6.5, 1H), 1.92 (dd, J = 6.5, 1.5 Hz, 3H);
¹³C NMR (100 MHz; CDCl₃) δ 135.4, 133.7, 132.6, 131.2, 128.0, 127.8, 127.6, 126.2, 126.1, 125.4, 125.2, 123.5, 18.6.

The compound 7b was prepared from benzaldehyde and 2-methyl-2-butene according to the general procedure. The product was obtained in 56% yield by silica gel column chromatography eluting with n-hexane as a colorless liquid. Spectral data were in accordance with those previously reported.⁴

⁴ V. R. Naidu, J. Bah, J. Franzén, Eur. J. Org. Chem. 2015, 1834.
The compound 7c was prepared from p-tolualdehyde and 2-methyl-2-butene according to the general procedure in 62% yield as a colorless liquid after purification by silica gel column chromatography eluting with n-hexane. Spectral data were in accordance with those previously reported.4

The compound 7d was prepared from 4'-bromobenzaldehyde and 2-methyl-2-butene according to the general procedure. Purification by flash column chromatography eluting with n-hexane provides 7d as a white solid in 48% yield. Spectral data were in accordance with those previously reported.4

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4 V. R. Naidu, J. Bah, J. Franzén, Eur. J. Org. Chem. 2015, 1834.
The compound 7e was prepared from benzaldehyde and methyl 3-methylbut-2-enoate according to the general procedure in 45% yield. The product was obtained by silica gel column chromatography eluting with n-hexane as a colorless liquid. Spectral data were in accordance with those previously reported.4

\[ ^1\text{H NMR} \ (400 \text{ MHz, Chloroform-d}) \delta \ 7.70 \ (d, J = 16.0 \text{ Hz, } 1\text{H}), \ 7.53 \ (dd, J = 6.7, 2.9 \text{ Hz, } 2\text{H}), \ 7.43 – 7.35 \ (m, 3\text{H}), \ 6.45 \ (d, J = 16.0 \text{ Hz, } 1\text{H}), \ 3.81 \ (s, 3\text{H}); \]
\[ ^{13}\text{C NMR} \ (101 \text{ MHz, Chloroform-d}) \delta \ 167.4, \ 144.9, \ 134.4, \ 130.3, \ 128.9, \ 128.1, \ 117.8, \ 51.7. \]

The compound 7f was prepared from p-tolualdehyde and 2-methylhept-2-ene according to the general procedure in 70% yield. The product was obtained by silica gel column chromatography eluting with n-hexane as a colorless liquid. Spectral data were in accordance with those previously reported.4

\[ ^1\text{H NMR} \ (400 \text{ MHz, Chloroform-d}) \delta \ 7.30 \ (d, J = 8.7 \text{ Hz, } 2\text{H}), \ 6.87 \ (d, J = 8.7 \text{ Hz, } 2\text{H}), \ 6.35 \ (dt, J = 15.7, 1.5 \text{ Hz, } 1\text{H}), \ 6.11 \ (dt, J = 15.8, 6.9 \text{ Hz, } 1\text{H}), \ 3.83 \ (s, 3\text{H}), \ 2.22 \ (qd, J = 7.1, 1.4 \text{ Hz, } 2\text{H}), \ 1.56 – 1.24 \ (m, 4\text{H}), \ 0.96 \ (t, J = 7.2 \text{ Hz, } 3\text{H}); \]
\[ ^{13}\text{C NMR} \ (101 \text{ MHz, Chloroform-d}) \delta \ 158.6, \ 130.8, \ 129.1, \ 129.0, \ 127.0, \ 113.9, \ 55.3, \ 32.7, \ 31.7, \ 22.3, \ 14.0. \]

The compound 7g was prepared from benzaldehyde and (2-methylprop-1-en-1-yl)benzene according to the general procedure in 59% yield. The product was obtained by silica gel column chromatography eluting with n-hexane as a colorless liquid. Spectral data were in accordance with those previously reported.4

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5 Tan, E. W.; Chan, B.; Blackman, A. G.; J. Am. Chem. Soc. (2002), 124, 2078-2079.
6 Guo, X.; Wang, J.; Li, C; J. Am. Chem. Soc. (2009), 131, 15092-15093.
7 Bandari, R.; Hoeche, T.; Prager, A.; Dirnberger, K.; Buchmeiser, M.I R.; Chem. Eur. J (2010), 16, 4650-4658.
$^1\text{H NMR}$ (400 MHz, Chloroform-d) $\delta$ 7.55 (dd, $J = 8.1$, 1.4 Hz, 4H), 7.39 (t, $J = 7.6$ Hz, 4H), 7.33 – 7.25 (m, 2H), 7.15 (s, 2H);

$^{13}\text{C NMR}$ (101 MHz, Chloroform-d) $\delta$ 137.3, 128.7, 127.6, 126.5.
**General Procedures for Ring-opening Carbonyl-Olefin Metathesis**

A dried 4ml vial was charged with tropylium tetraphenylborate and a stirring bar. Starting aldehyde 5 was added to the vial, followed by cyclic alkene 8 under Argon condition. Then the vial was closed tightly and the mixture was stirred for 24 h at 50 °C (unless otherwise specified). Upon completion (as determined by TLC analysis), the crude mixture was directly purified by flash column chromatography eluting with hexanes/EtOAc (50:1) to give the target product.

The compound 9c was prepared from 4'-tolualdehyde and 1-methylcyclobutene according to the general procedure at 70 °C for 4 h. Purification by flash column chromatography provided product 9c as a colorless liquid in 31% yield.

**1H NMR** (400 MHz, CDCl$_3$): 7.22 (d, $J = 8.0$ Hz, 2H), 7.09 (d, $J = 7.8$ Hz, 2H), 6.38 (d, $J = 15.8$ Hz, 1H), 6.20 (dt, $J = 15.8$, 7.0 Hz, 1H), 2.60 (t, $J = 7.3$ Hz, 2H), 2.47 (q, $J = 7.0$ Hz, 2H), 2.32 (s, 3H), 2.17 (s, 3H);

**13C NMR** (100 MHz, CDCl$_3$): 208.1, 136.8, 134.6, 130.6, 129.2, 127.7, 125.9, 43.3, 30.1, 27.2, 21.1;

**IR** (neat): 3022, 2921, 1714, 1512, 1425, 1359;

**HRMS** calcd for C$_{13}$H$_{16}$ONa$^+$: 211.1093, found: 211.1093.

The compound 9g1 was prepared from Benzaldehyde and 1-methylcyclopentene according to the general procedure. Purification by flash column chromatography provided product 9g1 as a white solid in 56% yield.  

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8 A. J. Musacchio, L. Q. Nguyen, G. H. Beard, R. R. Knowles, *J. Am. Chem. Soc.* 2014, 136, 12217.
The compound 9g2 was prepared from p-tolualdehyde and 1-methylcyclopentene according to the general procedure. Purification by flash column chromatography provided product 9g2 as a white solid in 59% yield.

The compound 9g3 was prepared 2-naphtaldehyde and 1-methylcyclopentene according to the general procedure. Purification by flash column chromatography provided product 9g3 as a white solid in 48% yield.
The compound 9g4 was prepared from 3-bromobenzaldehyde and 1-methylcyclopentene according to the general procedure. Purification by flash column chromatography provide product 9g4 as a white solid in 26% yield.

\[ \text{H NMR (400 MHz; CDCl}_3\text{)} \delta 7.51-7.46 \text{ (m, 1H), 7.31-7.29} \text{ (m, 1H), 7.26-7.11} \text{ (m, 2H), 6.29} \text{ (d, } J = 15.8 \text{ Hz, 1H), 6.15} \text{ (dt, } J = 15.8, 6.8 \text{ Hz, 1H), 2.46} \text{ (t, } J = 7.3 \text{ Hz, 2H), 2.23-2.18} \text{ (m, 2H), 2.12} \text{ (s, 3H), 1.78-1.71} \text{ (m, 2H);} \]

\[ \text{C NMR (100 MHz; CDCl}_3\text{)} \delta 208.7, 139.8, 131.6, 130.0, 129.8, 129.3, 128.9, 124.7, 122.7, 42.8, 32.2, 30.0, 23.1. \]

\[ \text{IR (Neat): 2929, 1710, 1421, 1370;} \]

\[ \text{HRMS: calcd for C}_{13}\text{H}_{15}\text{ClOH}^+: 267.0379 \text{ found: 267.0379.} \]

The compound 9g5 was prepared from 4-bromobenzaldehyde and 1-methylcyclopentene according to the general procedure. Purification by flash column chromatography provided product 9g5 as a white solid in 37% yield.

\[ \text{H NMR (400 MHz; CDCl}_3\text{)} \delta 7.40-7.37 \text{ (m, 2H), 7.17} \text{ (m, 2H), 6.30} \text{ (d, } J = 15.8 \text{ Hz, 1H), 6.14} \text{ (dt, } J = 15.8, 6.9 \text{ Hz, 1H), 2.45} \text{ (t, } J = 7.3 \text{ Hz, 2H), 2.22-2.16} \text{ (m, 2H), 2.12} \text{ (s, 3H), 1.78-1.70} \text{ (m, 2H);} \]

\[ \text{C NMR (100 MHz; CDCl}_3\text{)} \delta 208.7, 136.5, 131.6, 130.8, 129.5, 127.5, 120.6, 42.8, 32.3, 30.0, 23.1. \]

\[ \text{IR (Neat): 2941, 1727, 1486, 1371;} \]

\[ \text{HRMS: calcd for C}_{13}\text{H}_{15}\text{ClOH}^+: 267.0379 \text{ found: 267.0379.} \]
The compound 9g6 was prepared from 4’-chlorobenzaldehdye and 1-methylcyclopentene according to the general procedure. Purification by flash column chromatography provided product 9g6 as a colorless liquid in 45% yield.

$^1$H NMR (400 MHz; CDCl$_3$) $\delta$ 7.27 (bs, 4H), 6.30 (d, $J = 15.8$ Hz, 1H), 6.14 (dt, $J = 15.8$, 6.9 Hz, 1H), 2.45 (t, $J = 7.3$ Hz, 2H), 2.22-2.16 (m, 2H), 2.12 (s, 3H), 1.78-1.70 (m, 2H);

$^{13}$C NMR (100 MHz; CDCl$_3$) $\delta$ 208.7, 136.5, 131.6, 130.8, 129.5, 127.5, 120.6, 42.8, 32.3, 30.0, 23.1.

IR (Neat): 2929, 1710, 1488, 1357;

HRMS: calcd for $\text{C}_{13}\text{H}_{15}\text{Cl}\text{O}$\(^+\): 223.0884, found: 223.0884.
Evidence of the Tropylium-Carbonyl Complexation by $^1$H NMR Spectroscopy

We carried out a series of $^1$H NMR studies to probe the interaction between tropylium ion and carbonyl functionality. 2-Naphthaldehyde (5a, Table S2) was employed as a model substrate for these studies in CD$_3$CN. An up-field shift of the tropylium C$_7$H$_7^+$ signal was observed when it was in the same solution with 2-naphthaldehyde (Figure S2). The up-field movement increased with the aldehyde : tropylium ratio until it stabilized between ~ 5:1 to 10:1, which corresponded to between ~ 20 to 10 mol% of tropylium per one equivalent of the aldehyde substrate, respectively. Since the magnitude of chemical shift probably reflects the relative population of tropylium in the free and complexed form, it might not be a coincidence that 10-20 mol% is the optimal catalyst loading range for most of the carbonyl-olefin metathesis reaction. The odd chemical shift movements and splittings at 3:1 and 4:1 ratios suggested that there might be more than one binding mode between the tropylium ion and the carbonyl group at these ratios. Such a multiple [C$_7$H$_7^+$] C-H···O=C [carbonyl] bonding interaction had been previously observed in host-guest chemistry of tropylium ions. Nonetheless, the relatively small chemical shift < 0.2 ppm suggests that the interaction between tropylium ion and 2-naphthaldehyde is likely to be weak.

Figure S2. Tropylium-Carbonyl Complexation by $^1$H NMR Spectroscopy

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5 Chen, L.; Peng, Z.; Liu, S.; Li, X.; Chen, R.; Ren, Y.; Feng, W.; Yuan, L. Org. Lett. 2015, 17, 5950.
Computational Method

All electronic structure calculations were carried in the Gaussian16\textsuperscript{6} and NWChem\textsuperscript{7} programs. The geometries and thermal corrections of all molecules were optimized at the M06-2X/6-31G(d) level of theory in conjunction with the SMD\textsuperscript{8} implicit solvation model to simulate the solvent (acetonitrile). High level \textit{ab initio} single point calculations, G3(MP2)-RAD,\textsuperscript{9} were performed on the DFT optimized geometries in the presence of the solvent reaction field, and combined with thermal corrections to obtain free energies in the solution phase.\textsuperscript{10} All reported free energies correspond to a standard state of 1 mol L\textsuperscript{-1} and 298 K. All stationary points were verified to be a minima or transition state by frequency calculation. Intrinsic reaction coordinate (IRC) simulations were also carried out to ascertain that the first order saddle point connects the correct reactants and products.

\textsuperscript{6} Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparrini, F.; Egidi, F.; Gogings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

\textsuperscript{7} Valiev, M.; Bylaska, E. J.; Govind, M.; Kowalski, K.; Straatsma, T. P.; van Dam, H. J. J.; Wang, D.; Nieplocha, J.; Apra, E.; Windus, T. L.; de Jong, W. A. Comput. Phys. Commun. \textbf{2010}, \textit{181}, 1477.

\textsuperscript{8} Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. \textit{J. Phys. Chem. B} \textbf{2009}, \textit{113}, 6378-6396.

\textsuperscript{9} Henry, D. J.; Sullivan, M. B.; Radom, L. \textit{J. Chem. Phys.} \textbf{2003}, \textit{118}, 4849-4860.

\textsuperscript{10} Ho, J.; Ertem, M. Z. \textit{J. Phys. Chem. B} \textbf{2016}, \textit{120}, 1319-1329.
NMR Calculations Support \( \pi \)-Stacked Complex as Thermodynamically Most Favourable

To help understand the NMR spectral shifts observed in Figure S2, we have also computed the NMR chemical shifts for the three tropylium:2-Naphthaldehyde complex configurations. These were carried out at the M06-2X/6-311+G(d,p) level of theory in conjunction with the SMD (acetonitrile) model and the GIAO method\(^1\) as implemented in Gaussian16.

![Images of three configurations A, B, and C with energies and shifts](image)

Table S3. Computed proton NMR chemical shifts for free and complexed tropylium ion.

| Proton | Tropylium ion | Config A | Config B | Config C |
|--------|---------------|----------|----------|----------|
| H1     | 21.69         | 21.49    | 21.62    | 23.42    |
| H2     | 21.79         | 21.66    | 20.30    | 22.62    |
| H3     | 21.67         | 21.23    | 21.45    | 22.63    |
| H4     | 21.76         | 21.13    | 21.65    | 22.84    |
| H5     | 21.70         | 21.57    | 21.59    | 23.39    |
| H6     | 21.69         | 21.57    | 19.90    | 22.95    |
| H7     | 21.75         | 21.37    | 21.72    | 22.95    |

|               | 21.721 | 21.43  | 21.18  | 22.97  |
|---------------|--------|--------|--------|--------|
| \( \delta \) (rel to \( \text{C}_6\text{H}_6 \)) /ppm\(^1\) | 9.10   | 9.39   | 9.64   | 7.85   |
| Relative \( \delta \) / ppm | 0.00   | 0.29   | 0.55   | -1.25  |

\(^1\) \( \delta = \sigma_{\text{ref}} - \sigma_i \). \( \sigma_{\text{ref}} \) (benzene) = 23.45 ppm.

As shown, the \( \pi \)-stacked configuration C is the only configuration that results in an upfield shift relative to free tropylium ion. This is consistent with the computed complexation free energies where C is the thermodynamically favoured configuration, and NMR titration experiments (Figure S2) which shows a monotonic upfield shift as the tropylium:aldehyde ratio increases from 8:1 to 1:2.

\(^1\) Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. J. Chem. Phys. 1996, 104, 5497-5509.
**Tropylium mediated COM is likely to occur via a stepwise mechanism:** To better understand the catalytic role of tropylium, we have carried out high-level *ab initio* calculations to compare the energetics of three COM pathways: (1) in the absence of tropylium ion, (2) aldehyde hydrogen bonded to tropylium ion, and (3) coordination of aldehyde to tropylium ion. For pathways (1) and (2), the reactants and products are connected by two concerted cycloaddition transition states and a cycloaddition intermediate (Figure S3), whilst pathway (3) involves four stepwise transition states and additionally two zwitterionic intermediates (Figure S4). Consistent with orbital symmetry rules, both pathways (1) and (2) are accompanied by very high barriers (TS₁ and TS₂) exceeding 200 kJ mol⁻¹, and are unlikely to occur under thermal activation. As shown in Figure S3, it is also interesting to note that hydrogen bonding to tropylium ion does not provide any stabilization of the transition states. Presumably, the concerted nature of these transition states (no charged intermediates) also means that any electrostatic stabilization from tropylium is likely to be minimal.

**Figure S3.** G3(MP2)-RAD+SMD(DCM) free energies for reactions in the absence of tropylium, and with hydrogen bonding to tropylium. The barriers for the latter are shown in parenthesis.
Figure S4. G3(MP2)-RAD+SMD(DCM) free energies (at 298 K) for reactions catalyzed by coordination of CO oxygen to tropylium.

Figure S4 shows the free energy profile for the stepwise pathway and it is evident that coordination of the anionic oxygen to tropylium ion lowers the barriers significantly. Specifically, the rate-limiting step for this pathway is about 90 kJ mol\(^{-1}\) lower compared to the reaction in the absence of tropylium ion (153 c.f. 245 kJ mol\(^{-1}\)). This result is somewhat surprising because coordination to oxygen to form the heptatriene adduct inevitably disrupts the aromaticity of the tropylium ring. Presumably, this enthalpic cost is more than compensated when the anionic oxygen is neutralized through coordination to tropylium.

The structures of the stepwise transition states hint at a termolecular mechanism, although intrinsic reaction coordinate (IRC) simulations of these transition states show that they relax to reactants and products where the tropylium ion remains coordinated. On the other hand, potential energy scans indicate that addition of CO oxygen to tropylium (while the remaining atoms are constrained to positions at the transition state geometry) is approximately barrierless. A plausible mechanistic picture is that tropylium exists as a p-stacked complex with aldehyde 5b (c.f. Table S3 configuration C), which spontaneously coordinates to the C-O oxygen as the anionic charge develops upon nucleophilic addition. Indeed, our kinetic experiments (c.f. page S17) show that the rate of metathesis is first-order with respect to the concentration of tropylium ion. It is also worth pointing out that the computed barriers in Figure S4 are likely to represent upper bound estimates of the actual values. This is because these reactions involve the consumption of an aromatic cation (tropylium) and the generation of a localized carbocation, so the solvation contribution is likely to be under-estimated by quantum chemical implicit solvation models. Regardless, it is clear from the calculations that
the reaction is significantly enhanced only when tropylium acts as a Lewis acid to stabilize the zwitterionic intermediate formed in the stepwise pathway.

**CO Addition to Tropylium Ion Is Spontaneous upon C-C Bond Formation**

We have also carried out constrained potential energy surface (PES) scans to investigate the energy profile for CO addition to tropylium. Figure S5 depicts the PES scan for transition state TS\(_C\) (in Figure S4) where the O-C(tropylium) bond is incremented at 0.1 Å. All atoms shown in black are constrained to their coordinates at the transition state geometry. As shown, the CO addition to tropylium cation is approximately barrier-less (about 5 kJ mol\(^{-1}\)) and downhill, which supports our mechanistic hypothesis that the p-stacked tropylium ion spontaneously coordinates with the anionic C-O oxygen, thereby providing a significant stabilization to the transition state.

![Figure S5](image)

*Figure S5.* M06-2X/6-31G(d) + SMD (acetonitrile) constrained potential energy surface scan.
Gaussian Archives

2

\[\text{HB Config A}\]

\[\text{HB Config B}\]

\[\text{HB Config C}\]
**TS2**

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 1\ GIN-CR3817/FTS/RM062X/Gen/C12H1601/ROOT-12-Aug-2017/0/\#m062X/gen
 6D OPT=(CalcFC,Ts,Noeigen) freq=norman INT(grid=ultrafine) SCRF=(SMD,
Solvent=acetonitrile) \cis-concerted-ts.a2.freq 1,10v=0.234370
7963,-0.1438210580,-0.1616893299,C,0.2026965872,0.566109572,0.6309525
894,C,0.1616711649,1.7305154123,0.6492996821,C,1.4147166976,0.43971662
08,-0.4126631402,-0.1491617362,1.6275911505,1.7417714446,0.343344
3659,2.0908168360,-0.4376924858,H,1.9066033357,1.3002214759,1.61168681
52,C,6.2142055822,2.7594568997,1.3600422244,C,6.235355517,0.457443300
98,-0.310547999,H,1.4819339044,1.0001238493,-1.3742259632,H,-0.30152168
50,0.6695537595,2.1330137792,H,-1.705544611,1.5891966058,1.4681135969
H,F,6.2358327015,H,1.6218097234,2.5432970189,2.7540476207,0.19090909,
-1.3942617831,0.125275353,0.3499437181,-0.1501893569,-1.424455457
22,2.7978890691,0.5363600744,H,2.3822444068,3.0701750378,-0.86882024
20,2.3106362583,2.3180570873,0.1369150597,H,2.6327835913,3.6464252675
H,0.7725674805,H,-1.6968238436,0.3175609311,-1.0714902171,-2.63742810
20,0.1182658309,-0.7403934449,-3.821217613,0.4068688718,-1.2857488
25,C,-0.5334230095,0.0306696027,-0.9728410846,-5.5823904077,-3.538
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709064,-1.0959503688,0.8261952985,-2.4704603848,-1.141949315,0.1915
536027,H,-3.7092030637,0.12134803076,-1.9783691422,H,-5.9086326352,0.58
29537016,-1.4968192695,-5.4062221993,-2.5289401417,1.2925482508,H,0.
0387787315,2.9156519670,1.51620687326,-1.4294089427,-1.3468682181,0
.4338488193,H,-6.660935187,0.8226675654,-0.0422134444,C,0.3797391634
-0.2216893288,-0.5072186326,C,0.8980719277,-0.6422895377,-0.397333434
1,C,0.8514276207,-2.1514495923,-0.0607663344,C,0.6953755707,-0.295353
625,0.6835964712,2.5956511469,-1.5512022629,0.5576909792,H,0.82813171
147,-0.0338491947,-4.710473436,0.7917897625,-0.8796510154,-1.5213288
59,0.7090567619,-2.8101048272,0.0345082687,H,0.6554447321,-3.2457778
23,1.3586824515,H,1.6808090935,-1.7272618908,1.1173233884,0\ Version=E6
4L-G09Rev01. State=1-A\HF=-812.473502, RMSD=7.584e-09, RMSF=2.340e-06\ dipole=-6.934644,1.5852822,0.5799413\ Quadrupole=3.9077288,-11.3247486,-25.6825374,0.106269,0.104967,-6.7256308\ PG=C01 [X(C12H1601)]
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NMR Spectra of Carbonyl-Olefin Metathesis Product
3j, 65.9 %
R¹ = R² = Me

3j, 8.1 %
R¹ = R² = Me
