Electronic Supplementary Information for:

**A C-to-O atom-swapping reaction sequence enabled by Ni-catalyzed decarbonylation of lactones**

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1. Materials and Methods

Room temperature is defined as 23 °C. All reagents were purchased from commercial suppliers and used without further purification, unless otherwise noted. Acetonitrile, \( N,N \)-dimethylformamide, dichloromethane, tetrahydrofuran, diethyl ether and toluene were obtained from a 800L Solvent Purification System by Pure Process Technology, in which the solvent was dried over alumina and dispensed under an atmosphere of Ar. Where indicated, experiments were carried out in a nitrogen-filled mBraun glovebox. All other solvents were purchased from commercial suppliers and used without further purification, unless otherwise noted. Rotary evaporation was carried out at 40 °C.

Routine \(^1\)H NMR spectra were recorded on Bruker 400 or 600 MHz spectrometers at ambient temperature unless otherwise stated. All NMR solvents were purchased from Cambridge Isotope Laboratories and used without further purification. Methanol-\( d_4 \), Chloroform-\( d_3 \), and dichloromethane-\( d_2 \), were stored at ambient temperature. Spectra were processed using MestReNova 14.0.1 using the automatic phasing and polynomial baseline correction capabilities. Splitting was determined using the automatic multiplet analysis function with manual intervention as necessary. Spectral data are reported as follows: chemical shift (multiplicity [singlet (s), broad singlet (br s), doublet (d), triplet (t), quartet (q), pentet (p), multiplet (m), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplet of doublets (dt), doublet of doublet of doublets (ddddd), doublet of triplets (dt), triplet of doublets (td), etc.], coupling constant, integration). Chemical shifts are reported in ppm (δ), and coupling constants are reported in Hz. \(^1\)H Resonances are referenced to solvent residual peaks for CD\(_3\)OD (3.31 ppm), CDCl\(_3\) (7.26 ppm), C\(_6\)D\(_6\) (7.16 ppm), and CD\(_2\)Cl\(_2\) (5.32 ppm). \(^{13}\)C Resonances are referenced to solvent residual peaks for CD\(_3\)OD (49.00 ppm), CDCl\(_3\) (77.16 ppm), C\(_6\)D\(_6\) (128.06 ppm), and CD\(_2\)Cl\(_2\) (53.84 ppm). Note: Small deviations in chemical shifts may be observed depending on the concentration of NMR samples.

Analytical thin-layer chromatography was performed using 60 Å Silica Gel F\(_{254}\) pre-coated plates (0.25 mm thickness). TLC plates were visualized by irradiation with a UV lamp. Normal-phase column chromatography was performed using 60 Å Silica Gel (32–62 micron) with an appropriate mobile phase composition and gradient. Automated column chromatography was performed using a CombiFlash NextGen 300+ System by Teledyne ISCO on RediSep Rf Gold silica gel columns or RediSep Rf disposable flash columns. Positive (and/or negative) ion mode mass spectra were obtained using the Agilent (Santa Clara, CA) mass spectrometer. Agilent LC 1200 series system, equipped with Agilent autosampler was used. 1 µl of sample (concentration of approximately 10 ppm) was injected into the JetStream ESI ion source. Water/MeOH (0.1% Formic acid) 50/50 was used as effluent solvent. The mass range was kept constant from 100 to 1000 amu. The instrument was operated in the 4GHz HRes mode. Accurate mass measurement was achieved by constantly infusing a calibrant (masses: 121.0508 and 922.0098). In some cases, mass spectrometry was performed using the Agilent 7250 GC Q-TOF MSMS with FID detector. Infrared spectra were recorded on a Bruker Tensor 37 ATR/FT-IR spectrometer, and \( \nu_{\text{max}} \) are reported in cm\(^{-1}\).
2. Abbreviations

BnBr  Benzy1 bromide
BrettPhos  2-Dicyclohexylphosphino-3,6-dimethoxy-2′,4′,6′-triisopropyl-1,1′-biphenyl (CAS # 1070663-78-3)
MOMCl  Chloromethyl methyl ether
cod  Cyclooctadiene
Cy  Cyclohexyl
DCC  Dicyclohexylcarbodiimide
DCM  Dichloromethane
DIC  Diisopropylcarbodiimide
DMAP  4-(Dimethylamino)pyridine
DMF  N,N-Dimethylformamide
DMSO  Dimethylsulfoxide
Et  Ethyl
EtOAc  Ethyl acetate
HRMS  High-resolution mass spectrometry
Hx  Hexanes
iPr  Isopropyl
IR  Infrared
MeCN  Acetonitrile
mCPBA  meta-Chloroperoxybenzoic acid
MTBE  Methyl tert-butyl ether
NMR  Nuclear magnetic resonance
PCg  tetramethylphosphatrioxaadamantyl
Rac  racemic
rt  Room temperature
RuPhos  2-Dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl (CAS # 787618-22-8)
SPhos  2-Dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (CAS # 657408-07-6)
tBu  tert-Butyl
tBuOH  tert-Butyl alcohol
TFA  Trifluoroacetic acid, trifluoroacetate
THF  Tetrahydrofuran
TLC  Thin-layer chromatography
Tosyl/Ts  p-Toluenesulfonyl
Xantphos  4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene (CAS # 161265-03-8)
3. Experimental procedures for additional optimization studies

3.1. Ligand screen (Table S1)

A 2-dram vial was charged with a magnetic stir bar, 1a (0.0110 g, 0.050 mmol), and a ligand (see Figure 4 in the main text). The vial was brought into a glovebox, then Ni(cod)$_2$ (2.8 mg, 0.010 mmol, 20 mol%), CsF (7.6 mg, 0.050 mmol, 1.0 equiv), and toluene (0.50 mL) were added. The vial was sealed and brought outside and placed in an aluminum heating block preheated at 150 °C. The mixture was stirred for 15 h. After cooling to room temperature, the mixture was directly loaded onto a silica gel column (0.5 × 3.0 cm). The column was eluted with hexanes (5.0 mL) and the product containing fractions were collected. The solvent was then removed using rotary evaporator and high-vacuum oil pump to give 2a as a white solid.

Table S1. Ligand screen.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Isolated yield (%)</th>
<th>Entry</th>
<th>Ligand</th>
<th>Isolated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>dcype</td>
<td>0</td>
<td>10</td>
<td>dcyppb</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>dbpe</td>
<td>0</td>
<td>11</td>
<td>dppb</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>dppf</td>
<td>0</td>
<td>12</td>
<td>dcyppb</td>
<td>29</td>
</tr>
<tr>
<td>4</td>
<td>dcppf</td>
<td>0</td>
<td>13</td>
<td>dcyp</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>dippf</td>
<td>0</td>
<td>14</td>
<td>Dalphos</td>
<td>22</td>
</tr>
<tr>
<td>6</td>
<td>dbpf</td>
<td>0</td>
<td>15</td>
<td>rac-L1</td>
<td>21</td>
</tr>
<tr>
<td>7</td>
<td>IAd</td>
<td>0</td>
<td>16</td>
<td>meso-L1</td>
<td>60</td>
</tr>
<tr>
<td>8</td>
<td>IPr·HCl</td>
<td>0</td>
<td>17</td>
<td>rac-L2</td>
<td>28</td>
</tr>
<tr>
<td>9</td>
<td>dcypte</td>
<td>0</td>
<td>18</td>
<td>meso-L2</td>
<td>80</td>
</tr>
</tbody>
</table>

![Diagram of reaction](image-url)
3.2. Solvent screen (Table S2)

A 2-dram vial was charged with a magnetic stir bar, 1a (11.0 mg, 0.050 mmol), meso-L2 (5.7 mg, 0.010 mmol, 20 mol%). The vial was brought into a glovebox, then Ni(cod)₂ (2.8 mg, 0.010 mmol, 20 mol%), CsF (7.6 mg, 0.050 mmol, 1.0 equiv.), and a solvent (0.50 mL) were added. The vial was sealed and brought outside and placed in an aluminum heating block preheated at 150 °C. The mixture was stirred for 15 h. After cooling to room temperature, the mixture was directly loaded onto a silica gel column (0.5 × 3.0 cm). The column was eluted with hexanes (5.0 mL) and the product containing fractions were collected. The solvent was then removed using rotary evaporator and high-vacuum oil pump to give 2a as a white solid.

Table S2. Solvent screen.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>isolated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>toluene</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>dioxane</td>
<td>&lt;5</td>
</tr>
<tr>
<td>3</td>
<td>DMF</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>DMSO</td>
<td>0</td>
</tr>
</tbody>
</table>

3.3. Additive screen (Table S3)

A 2-dram vial was charged with a magnetic stir bar, 1a (11.0 mg, 0.050 mmol), meso-L2 (5.7 mg, 0.010 mmol, 20 mol%). The vial was brought into a glovebox, then Ni(cod)₂ (2.8 mg, 0.010 mmol, 20 mol%), an additive (see Table S3, 0-1.0 equiv.), and toluene (0.50 mL) were added. The vial was sealed and brought outside and placed in an aluminum heating block preheated at 150 °C. The mixture was stirred for 15 h. After cooling to room temperature, the mixture was directly loaded onto a silica gel column (0.5 × 3.0 cm). The column was eluted with hexanes (5.0 mL) and the product containing fractions were collected. The solvent was then removed using rotary evaporator and high-vacuum oil pump to give 2a as a white solid.

Table S3. Additive screen.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive</th>
<th>isolated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CsF</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>KF</td>
<td>54</td>
</tr>
<tr>
<td>3</td>
<td>Cs₅CO₃</td>
<td>34</td>
</tr>
<tr>
<td>4</td>
<td>K₃PO₄</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>No additive</td>
<td>74</td>
</tr>
</tbody>
</table>
3.4. Reaction concentration screen (Table S4)

A 2-dram vial was charged with a magnetic stir bar, 1a (11.0 mg, 0.050 mmol), *meso*-L2 (5.7 mg, 0.010 mmol, 20 mol%). The vial was brought into a glovebox, then Ni(cod)$_2$ (2.8 mg, 0.010 mmol, 20 mol%), CsF (7.6 mg, 0.050 mmol, 1.0 equiv.), and toluene (0.25, 0.50, 0.70, 0.80, or 1.0 mL) were added. The vial was sealed and brought outside and placed in an aluminum heating block preheated at 150 °C. The mixture was stirred for 15 h. After cooling to room temperature, the mixture was directly loaded onto a silica gel column (0.5 × 3.0 cm). The column was eluted with hexanes (5.0 mL) and the product containing fractions were collected. The solvent was then removed using rotary evaporator and high-vacuum oil pump to give 2a as a white solid.

**Table S4.** Concentration screen. The yields shown are averages of two runs.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Toluene (mL)</th>
<th>Concentration (M)</th>
<th>Isolated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.50</td>
<td>0.10</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>0.70</td>
<td>0.071</td>
<td>31</td>
</tr>
<tr>
<td>3</td>
<td>0.80</td>
<td>0.063</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>1.00</td>
<td>0.050</td>
<td>14</td>
</tr>
</tbody>
</table>

3.5. Temperature and reaction time screen (Table S5)

A 2-dram vial was charged with a magnetic stir bar, 1a (0.0110 g, 0.050 mmol), *meso*-L2 (0.0057 g, 0.010 mmol, 20 mol%). The vial was brought into a glovebox, then Ni(cod)$_2$ (2.8 mg, 0.010 mmol, 20 mol%), CsF (7.6 mg, 0.050 mmol, 1.0 equiv.), and toluene (0.50 mL) were added. The vial was sealed and brought outside and placed in an aluminum heating block preheated at 120, 130, 140, or 150 °C as indicated in Table S4. The mixture was stirred for a certain time (4 h, 15 h, 24 h, or 48 h) as indicated in Table S4. After cooling to room temperature, the mixture was directly loaded onto a silica gel column (0.5 × 3.0 cm). The column was eluted with hexanes (5.0 mL) and the product containing fractions were collected. The solvent was then removed using rotary evaporator and high-vacuum oil pump to give 2a as a white solid.

**Table S5.** Temperature and reaction time screen.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Isolated yield (%)</th>
<th>Entry</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Isolated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>150</td>
<td>15</td>
<td>80</td>
<td>4</td>
<td>120</td>
<td>15</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>140</td>
<td>15</td>
<td>40</td>
<td>5</td>
<td>150</td>
<td>5</td>
<td>63</td>
</tr>
<tr>
<td>3</td>
<td>130</td>
<td>15</td>
<td>54</td>
<td>6</td>
<td>150</td>
<td>24</td>
<td>99</td>
</tr>
</tbody>
</table>
4. Synthesis and characterization data for ligands in Figure 4
Ligands rac- and meso-L1 were synthesized according to a literature procedure. Ligands rac- and meso-L2 were synthesized in a similar manner as described below.

4-(tetramethylphosphatrioxaadamantyl)-5-bromo-1,2-dimethoxybenzene (SL2): A 40-mL vial was charged with a magnetic stir-bar, 4,5-dibromo-1,2-dimethoxybenzene (2.23 g, 7.50 mmol, 1.5 equiv), and K2CO3 (1.38 g, 10.0 mmol, 2.0 equiv). The vial was brought inside a glovebox. The phosphine HPCg (32% solution in toluene, 3.38 g, 5.0 mmol, 1.0 equiv), the catalyst Pd(PPh3)4 (0.29 g, 0.25 mmol, 5.0 mol%), and toluene (10 mL) were then added. The vial was sealed with a Teflon-lined cap, brought outside of the glovebox, and placed on an aluminum heating block preheated at 110 °C. The reaction mixture was stirred at 110 °C for 48 h and was cooled to room temperature. Dichloromethane (10 mL) and water (20 mL) were added. The mixture was then transferred to a separatory funnel. The organic layer was collected, and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic fractions were dried with Na2SO4 and concentrated using rotary evaporator. The resulting red oil was chromatographed (silica gel column, 5 × 20 cm, packed in hexanes, eluted with hexanes/ethyl acetate 90/10) to give the product SL2 as a white solid (1.45 g, 3.36 mmol, 67%).

TLC (90/10 hexanes/ethyl acetate): Rf = 0.20 (visualized by UV).

1H NMR (600 MHz, CDCl3) δ 7.89 (br s, 1H), 7.07 (br s, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 2.10 (dd, J = 13.3, 7.4 Hz, 1H), 1.98 – 1.86 (m, 2H), 1.51 (dd, J = 13.5, 4.0 Hz, 1H), 1.47 (d, J = 12.5 Hz, 3H), 1.41 (m, 9H).

13C{1H} NMR (151 MHz, CDCl3) δ 150.6, 148.1, 125.2 (d, J = 27.5 Hz), 124.0 (d, J = 35.2 Hz), 116.6, 116.2 (d, J = 4.4 Hz), 96.8, 95.9, 74.4 (d, J = 9.9 Hz), 73.8 (d, J = 23.7 Hz), 56.1, 56.0, 45.7 (d, J = 18.7 Hz), 36.5, 28.3 (d, J = 19.8 Hz), 28.2, 27.8, 26.8 (d, J = 11.0 Hz).

31P{1H} NMR (243 MHz, CDCl3) δ –30.90.

IR (FT-ATR, cm⁻¹, neat) νmax 3092 (w), 2987 (m), 2931 (m), 2839 (w), 1591 (m), 1562 (w), 1499 (s), 1470 (m), 1440 (m), 1375 (m), 1349 (m), 1316 (w), 1243 (s), 1211 (s), 1198 (s), 1181 (s), 1135 (m), 1082 (m), 1043 (w), 1030 (m), 974 (m), 958 (m), 899 (m), 866 (w), 833 (m), 787 (m), 695 (w), 662 (w).

HRMS: Exact mass calculated for C18H24BrO5P requires m/z = 430.0545, found m/z = 430.0542 (EI).
**Ligand L2**: A 20-mL vial was charged with a magnetic stir-bar, SL2 (0.180 g, 0.42 mmol, 1.0 equiv), and K$_2$CO$_3$ (0.118 g, 0.84 mmol, 2.0 equiv). The vial was brought inside a glovebox. The phosphine HPCg (32% solution in toluene, 0.284 g, 0.42 mmol, 1.0 equiv), the catalyst Pd(PPh$_3$)$_4$ (0.030 g, 0.021 mmol, 5.0 mol%), and toluene (2.0 mL) was then added. The vial was sealed with a Teflon-lined cap, brought outside of the glovebox, and placed on an aluminum heating block preheated at 110 °C. The reaction mixture was stirred at 110 °C for 48 h and was then cooled to room temperature. Dichloromethane (5 mL) and water (10 mL) were added. The mixture was transferred to a separatory funnel. The organic layer was collected, and the aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic fractions were dried with Na$_2$SO$_4$ and concentrated using rotary evaporator. The resulting red oil was chromatograph (silica gel column, 3 × 15 cm, packed in hexanes, eluted with hexanes/ethyl acetate 95/5) to give the products rac-L2 (0.111 g, 0.20 mmol, 48%, $R_f = 0.15$ (90/10 hexanes/ethyl acetate)) and meso-L2 (0.067 g, 0.12 mmol, 29%, $R_f = 0.10$ (90/10 hexanes/ethyl acetate)) as white solids.

The stereochemical configurations of the ligands were assigned based on the order of elution as compared to ligands L1.$^1$ The stereochemical configuration of ligand meso-L2 was further confirmed by an X-ray crystal structure of a nickel complex meso-L2-Ni-2a (see section 5.3).

\[
\text{TLC (90/10 hexanes/ethyl acetate): } R_f = 0.15 \text{ (visualized by UV)}
\]

\[
^1\text{H NMR (600 MHz, CDCl}_3\text{): } \delta 7.99 \text{ (app t, } J = 2.4 \text{ Hz, 2H), 3.89 \text{ (s, 6H), 2.12 \text{ (dt, } J = 13.1, 3.5 \text{ Hz, 2H), 1.99 \text{ (d, } J = 13.4 \text{ Hz, 2H), 1.95 \text{ (d, } J = 13.2 \text{ Hz, 1H), 1.90 \text{ (d, } J = 13.1 \text{ Hz, 1H), 1.46 – 1.34 \text{ (m, 26H).}}}
\]

\[
^{13}\text{C}[^1\text{H}] \text{ NMR (151 MHz, CDCl}_3\text{): } \delta 149.1 \text{ (2C), 135.6 \text{ (d, } J = 2.6 \text{ Hz, 2C), 116.2 \text{ (d, } J = 2.3 \text{ Hz, 2C), 98.6 \text{ (2C), 95.8 \text{ (2C), 74.6 \text{ (2 x d, } J = 6.3 \text{ Hz, 2C), 74.0 \text{ (d, } J = 5.4 \text{ Hz), 73.9 \text{ (d, } J = 5.0 \text{ Hz, 55.7 \text{ (2C), 46.1 \text{ (app t, } J = 9.5 \text{ Hz, 2C), 36.3 \text{ (2C), 28.3 \text{ (2C), 27.70 \text{ (2C), 27.5 \text{ (app t, } J = 11.8 \text{ Hz, 2C), 26.6 \text{ (app t, } J = 5.4 \text{ Hz, 2C).}}}
\]

\[
^{31}\text{P}[^1\text{H}] \text{ NMR (243 MHz, CDCl}_3\text{): } \delta -41.20.
\]

\[
\text{IR (FT-ATR, cm}^{-1}\text{, neat) } \nu_{\text{max}} 3128 \text{ (w), 3112 \text{ (w), 2983 \text{ (m), 2964 \text{ (m), 2931 \text{ (m), 2843 \text{ (w), 1585 \text{ (w), 1562 \text{ (m), 1503 \text{ (m), 1467 \text{ (m), 1441 \text{ (m), 1381 \text{ (m), 1349 \text{ (m), 1316 \text{ (m), 1260 \text{ (m), 1214 \text{ (s), 1188 \text{ (s), 1132 \text{ (s), 1089 \text{ (m), 1043 \text{ (m), 984 \text{ (s), 961 \text{ (m), 945 \text{ (w), 895 \text{ (s), 863 \text{ (m), 820 \text{ (w), 800 \text{ (m), 734 \text{ (w), 692 \text{ (m), 667 \text{ (w), 626 \text{ (w).}}}
\]

\[
\text{HRMS: Exact mass calculated for } [\text{C}_{28}\text{H}_{40}\text{O}_{2}\text{P}_2\text{H}]^+ \text{ requires } m/z = 567.2271, \text{ found } m/z = 567.2283. \text{ (ESI+).}
\]
TLC (90/10 hexanes/ethyl acetate): \( R_f = 0.10 \) (visualized by UV).

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 7.93 (t, \( J = 2.4 \) Hz, 2H), 3.90 (s, 6H), 2.26 (d, \( J = 13.5 \) Hz, 2H), 2.20 (dt, \( J = 13.1, 3.5 \) Hz, 2H), 1.93 (d, \( J = 13.2 \) Hz, 1H), 1.89 (d, \( J = 13.1 \) Hz, 1H), 1.66 (dt, \( J = 13.6, 2.2 \) Hz, 2H), 1.45 (s, 6H), 1.38 (s, 6H), 1.32 (t, \( J = 6.3 \) Hz, 6H), 1.27 – 1.18 (m, 6H).

\(^{31}\)P\(^{1}\)H NMR (243 MHz, CDCl\(_3\)) \( \delta \) -42.06.

\(^{13}\)C\(^{1}\)H NMR (151 MHz, CDCl\(_3\)) \( \delta \) 149.4, 136.5, 116.8, 97.2, 95.9, 75.63 – 74.01 (m, 2C), 55.8, 46.1 (t, \( J = 9.4 \) Hz), 37.2, 29.5 (t, \( J = 10.5 \) Hz), 28.6, 27.8, 26.6 (t, \( J = 5.2 \) Hz).

IR (FT-ATR, cm\(^{-1}\), neat) \( \nu_{\text{max}} \) 3141 (w), 3119 (w), 2997 (m), 2964 (m), 2934 (m), 2915 (m), 2836 (w), 1585 (w), 1562 (w), 1496 (m), 1463 (m), 1440 (m), 1372 (m), 1345 (m), 1312 (m), 1260 (m), 1214 (s), 1191 (s), 1138 (m), 1083 (m), 1066 (w), 1036 (m), 981 (s), 961 (m), 941 (w), 892 (s), 849 (m), 826 (w), 790 (m), 744 (w), 685 (w), 665 (w), 629 (w).

HRMS: Exact mass calculated for [C\(_{28}\)H\(_{40}\)OP\(_2\)+H]\(^+\) requires m/z = 567.2271, found m/z = 567.2286. (ESI+).

5. Experimental procedures and characterization data for compounds in Figure 3, 5, and 6

5.1. Synthesis of compound 3

\[ \text{Br} \quad \text{S3-1} \quad \text{OPMB} \quad \text{Br} \quad \text{S3-1} \quad \text{OH} \]

1-bromo-2-((4-methoxybenzyl)oxy)benzene (S3-1): An oven-dried 100 mL Schlenk flask was charged with a stir bar, evacuated and back-filled with N\(_2\) (x 3). 2-bromophenol (2.00 mL, 18.94 mmol, 1 equiv.) was added by syringe, followed by MeCN (35 mL). K\(_2\)CO\(_3\) (5.44 g, 39.34 mmol, 2.08 equiv.) was added as a solid. Under vigorous stirring, PMB-Cl (3.2 mL, 23.60 mmol, 1.25 equiv.) via syringe. The reaction was heated in a 60 °C oil bath for 14 h. After cooling to RT, the reaction was quenched with 1:1 brine/H\(_2\)O (50 mL) and transferred to a separatory funnel with EtOAc (20 mL). After phase separation, the aqueous layer was extracted with EtOAc (2 × 30 mL). The combined organics were washed with brine, dried over Na\(_2\)SO\(_4\), filtered, and concentrated with a rotary evaporator. The crude product was washed with hexanes (30 mL). The white solids were isolated by vacuum filtration, washed with hexanes (2 × 20 mL), and dried under high vacuum to give the pure product (5.13 g, 89%) as a white solid. This solid was used immediately for the next reaction.
1H NMR (600 MHz, CDCl₃) δ 7.56 (dd, J = 7.9, 1.6 Hz, 1H), 7.44-7.37 (m, 2H), 7.23 (ddd, J = 8.2, 7.4, 1.6 Hz, 1H), 6.97-6.90 (m, 3H), 6.84 (ddd, J = 7.9, 7.4, 1.4 Hz, 1H), 5.09 (s, 2H), 3.82 (s, 3H).

2-(2-bromobenzyl)phenol (3): A 3-neck round bottom flask, equipped with a reflux condenser, was charged with a stir bar, Mg turnings (0.629 g, 26.4 mmol, 1.5 equiv), and compound S3-1 (5.14 g, 17.5 mmol, 1.0 equiv). The flask was evacuated and put under a N₂ atmosphere. THF (40 mL) was added, and the mixture was heated at 40 °C with vigorous stirring for 2 h. The mixture was then cooled to room temperature.

A Schlenk flask was charged with a stir bar, 2-bromobenzaldehyde (1.36 mL, 2.16 g, 11.7 mmol), and THF (40 mL) under a N₂ atmosphere. The solution was cooled to 0 °C in an ice bath. The Grignard reagent was then cannulated in a dropwise manner from the 3-neck round bottom flask to the Schlenk flask at 0 °C with stirring. After finishing addition, the mixture was warmed to room temperature and stirred for 12 h, and then quenched with water (10 mL). The mixture was transferred to a separatory funnel, then ethyl acetate (100 mL) and water (100 mL) were added. The organic layer was collected, and the aqueous layer was extracted with ethyl acetate (2 × 100 mL). The combined organic fractions were dried with Na₂SO₄ and concentrated by rotary evaporator to dryness to give a yellow solid. The yellow solid was dissolved in dichloromethane (14 mL). Triethylsilane (6.16 mL, 4.48 g, 39 mmol, 3.3 equiv) and Et₂O·BF₃ (4.76 mL) were then added at 0 °C. The resulting solution was stirred at 0 °C for 1.5 h and another 2.0 equiv of Et₃SiH (3.74 mL, 2.72 g, 23.4 mmol) was added followed by 1.0 mL of TFA. The solution was stirred for another 1.5 h at 0 °C and was warmed to room temperature. The reaction was quenched with 100 mL of a saturated aqueous NH₄Cl solution. The mixture was transferred to a separatory funnel and the organic layer was collected. The aqueous layer was extracted with dichloromethane (3 × 50 mL). The combined organic fractions were dried with Na₂SO₄, and the solvent was removed by rotary evaporator. The yellow residue was chromatographed (silica gel, 5 × 20 cm column, packed in hexanes, eluted with 95/5 hexanes/ethyl acetate) to give compound 3 as a colorless oil (1.27 g, 4.83 mmol, 41%). NMR data of 3 match with previously reported values.

TLC (90/10 hexanes/ethyl acetate): Rf = 0.50 (visualized by UV)

1H NMR (400 MHz, CDCl₃) δ 7.61-7.59 (m, 1H), 7.24 – 7.20 (m, 1H), 7.19 – 7.14 (m, 1H), 7.12 – 7.05 (m, 3H), 6.91 (dt, J = 7.5, 1.2 Hz, 1H), 6.82 (dd, J = 8.0, 1.2 Hz, 1H), 4.85 (br s, 1H), 4.11 (s, 2H).

13C{1H} NMR (101 MHz, CDCl₃) δ 153.7, 139.4, 132.9, 131.1, 130.8, 128.1 (2 × s), 127.7, 125.6, 125.0, 121.2, 115.7, 36.2.
5.2. Synthesis of dcpye-Ni-2a from 3

A 20-mL vial was charged with a stir bar and 3 (0.066 g, 0.25 mmol). The vial was brought inside a glove box. The ligand dcpye (0.110 g, 0.25 mmol), Ni(cod)₂ (0.070 g, 0.25 mmol), and benzene (5.0 mL) were then added. The vial was sealed, brought outside the glovebox, and placed in an aluminum heating block preheated at 80 °C. After 3 h, the vial was brought back inside the glovebox and NaH (0.0090 g, 0.38 mmol, 1.5 equiv) was added. The vial was sealed and was brought outside to heat again at 80 °C. After 3 h, the vial was brought back inside the glovebox and the mixture was filtered through a syringe filter. Pentane (5.0 mL) was added to the red filtrate and the resulting solution was let sit at room temperature in the glovebox. After 24 h, the orange crystals formed were collected and washed with pentane (5.0 mL). A specimen of the crystals was used for X-ray crystallographic analysis. The remaining were dried under vacuum for 5 h to give dcpye-Ni-2a·C₆H₆ (0.0611 g, 0.0825 mmol, 33%). Crystallographic parameters for dcpye-Ni-2a·C₆H₆ are provided below and are available free of charge from the Cambridge Crystallographic Data Center, CCDC 2116182.

1H NMR (600 MHz, CD₂Cl₂) δ 7.35 (s, 6H, benzene), 7.02 (t, J = 7.2 Hz, 1H), 6.95 (d, J = 7.2 Hz, 1H), 6.83-6.66 (m, 3H), 6.36 (d, J = 7.9 Hz, 1H), 6.23 (t, J = 7.1 Hz, 1H), 5.99 (d, J = 12.2 Hz, 1H), 3.63 (d, J = 12.2 Hz, 1H), 3.19 (br s, 1H), 2.47 (d, J = 10.5 Hz, 2H), 2.26 (d, J = 8.1 Hz, 2H), 2.05 – 0.80 (multiple overlapping signals, 44H). The region 2.05 – 0.80 ppm may contain residual pentane and grease, leading to larger than expected integral values.

13C{1H} NMR (151 MHz, CD₂Cl₂) δ 164.0, 151.0, 150.4, 135.8, 128.7 (benzene), 128.6, 128.1, 127.6, 124.5 (m), 123.6, 121.1 (2 × s), 112.2, 44.8, 36.5-25.0 (multiple overlapping signals for dcpye).

31P{1H} NMR (243 MHz, CD₂Cl₂) δ 62.77 (d, J = 14.3 Hz), 55.77 (d, J = 14.3 Hz).

X-ray crystallographic data

An orange block-like specimen of the crystals, approximate dimensions 0.020 mm × 0.080 mm × 0.120 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 VENTURE diffractometer system equipped with a microfocus sealed tube (Cu Kα, λ = 1.54178 Å) and a multilayer mirror monochromator. The total exposure time was 4.74 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 32358 reflections to a maximum θ angle of 66.65 (0.84 Å resolution), of which 7167 were independent (average redundancy 4.515, completeness = 100.0%, Rint = 5.75%, Rsig = 5.51%) and 6927
(96.65%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 9.0475(15)$ Å, $b = 18.2763(14)$ Å, $c = 12.7484(11)$ Å, $\beta = 105.437(9)$, volume = 2032.0(4) Å$^3$, are based upon the refinement of the XYZ-centric of 9957 reflections above 20 $\sigma(I)$ with $8.672 < 2\theta < 133.1$. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.827. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8250 and 0.9670. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P 1 2 1 1$, with $Z = 2$ for the formula unit, $C_{45}H_{64}NiOP_2$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 437 variables converged at $R1 = 3.50\%$, for the observed data and $wR2 = 8.01\%$ for all data. The goodness-of-fit was 1.130. The largest peak in the final difference electron density synthesis was $0.621 \text{ e/Å}^3$ and the largest hole was $-0.372 \text{ e/Å}^3$ with an RMS deviation of 0.054 e/Å$^3$. On the basis of the final model, the calculated density was 1.212 g/cm$^3$ and $F(000)$, 800 e$^-$. Additional details are provided in Table S6.

**Table S6. Crystal and structural data for dcype-Ni-2a·C₆H₆**

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<td>Crystal habit</td>
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<td>Crystal system</td>
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<td></td>
<td>$c = 12.7484(11)$ Å $\gamma = 90^\circ$</td>
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<tr>
<td>$F(000)$</td>
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<td>Structure solution technique</td>
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5.3. Synthesis of meso-L2-Ni-2a from 3

A 20-mL vial was charged with a stir bar and 3 (0.066 g, 0.25 mmol). The vial was brought inside a glove box. The ligand meso-L2 (0.140 g, 0.25 mmol), Ni(cod)2 (0.070 g, 0.25 mmol), and benzene (5.0 mL) were then added. The vial was sealed and brought outside to place on an aluminum heating block preheated at 80 °C. After 3 h, the vial was brought back inside the glovebox and NaH (0.0090 g, 0.38 mmol, 1.5 equiv) was added. The vial was sealed and was brought outside to heat again at 80 °C. After 3 h, the vial was brought back inside the glovebox and the mixture was filtered through a syringe filter. Pentane (5.0 mL) was added to the red filtrate and the resulting solution was let sit at room temperature in the glovebox. After 24 h, the orange crystals formed were collected and washed with pentane (5.0 mL). A specimen of the crystals was used for X-ray crystallographic analysis and showed two isomers in the unit cell. Crystallographic parameters for meso-L2-Ni-2a·C6H6 are provided below and are available free of charge from the Cambridge Crystallographic Data Center, CCDC 2116181. The remaining were dried under vacuum for 5 h to give meso-L2-Ni-2a·C6H6 (0.0908 g, 0.103 mmol, 41%). $^{31}$P and $^1$H NMR of the crystals gave complex spectra of the two isomers. Therefore, no meaningful analyses were possible. Attempts to separate the isomers by fractional recrystallization in benzene/pentane were not successful. $^{31}$P($^1$H) NMR (243 MHz, CD2Cl2) $\delta$ 25.23 (d, J = 9.5 Hz), 21.97 (d, J = 11.9 Hz), 2.86 (d, J = 14.3 Hz), 2.79 (d, J = 9.5 Hz).
X-ray crystallographic data

An orange block-like specimen of the crystals, approximate dimension 0.100 mm × 0.160 mm × 0.180 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 VENTURE diffractometer system equipped with a microfocus sealed tube (Cu Kα, λ = 1.54178 Å) and a multilayer mirror monochromator. The total exposure time was 3.71 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 57746 reflections to a maximum θ angle of 63.30 (0.86 Å resolution), of which 7735 were independent (average redundancy 7.466, completeness = 99.8%, Rint = 5.99%, Rsig = 3.66%) and 7224 (93.39%) were greater than 2σ(F²). The final cell constants of a = 12.239(4) Å, b = 20.228(3) Å, c = 19.483(2) Å, β = 99.971(10), volume = 4750.6(18) Å³, are based upon the refinement of the XYZ-centroids of 9471 reflections above 20 σ(I) with 6.372 < 2θ < 133.1. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.750. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7540 and 0.8510. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, C₅₀H₅₉NiO₉P₂. The final anisotropic full-matrix least-squares refinement on F² with 557 variables converged at R1 = 6.51%, for the observed data and wR2 = 18.18% for all data. The goodness-of-fit was 1.109. The largest peak in the final difference electron density synthesis was 2.020 e⁻/Å³ and the largest hole was –0.913 e⁻/Å³ with an RMS deviation of 0.078 e⁻/Å³. On the basis of the final model, the calculated density was 1.293 g/cm³ and F(000), 1956 e⁻. Additional details are provided in Table S7.

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Table S7. Crystal and structural data for meso-L2-Ni-2a·C₆H₆
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5.4. Stoichiometric experiments with dcype (Figure 3)

Stoichiometric experiment with dcype and 1a (Figure 3A): In a glove box, a 2-dram vial was charged with a stir bar, the ligand dcype (11.0 mg, 0.025 mmol), Ni(cod)$_2$ (7.0 mg, 0.025 mmol), and C$_6$D$_6$ (0.50 mL). The mixture was stirred at room temperature for 10 min then the lactone 1a (5.5 mg, 0.025 mmol) was added. The vial was sealed and brought outside to place on a heating block preheated at 80 °C. After stirring for 3 h, the vial was brought back inside the glovebox and the solution was transferred to an NMR tube. The NMR tube was sealed then a $^{31}$P NMR spectrum was acquired (Figure S1-B). The main signals matched with dcype-Ni-2a (Figure S1-A), and dcype-Ni(CO)$_2$. The $^{31}$P signal of dcype-Ni(CO)$_2$ at 64.00 ppm was assigned based on previously reported values. The NMR tube was brought back inside the glovebox and the NMR solution was transferred back to the vial and the mixture was heated further at 150 °C for 3 h on a heating block. After cooling to room temperature, the vial was brought back inside the glovebox and the solution was transferred to another NMR tube. A $^{31}$P NMR spectrum was acquired again (Figure S1-C). The signals for the complex dcype-Ni(CO)$_2$ disappeared. A singlet appeared at 82.2 ppm, corresponding to an unknown species.

![Diagram](image.png)

**Figure S1.** $^{31}$P{$^{1}$H} NMR (253 MHz, C$_6$D$_6$) of A) dcype-Ni-2a, B) stoichiometric reaction at 80 °C, and C) stoichiometric reaction at 150 °C (top).

Stoichiometric reductive elimination test with dcype-Ni-2a (Figure 3B): In a glovebox, an oven-dried 2-dram vial was charged with a stir bar, dcype-Ni-2a (0.037 g, 0.050 mmol), and toluene (0.50 mL). The vial was sealed and brought outside to place on an aluminum heating block preheated at 150 °C. The reaction was stirred at 150 °C for 3 h. After cooling to room temperature,
the reaction was analyzed by TLC (100% hexanes). No product spot was observed under UV. The reaction was then concentrated by rotary evaporator and CDCl₃ (0.50 mL) was added. The black solids were removed by syringe filter. A ¹H NMR spectrum was then acquired for the filtrate and showed no signals corresponding to the product 2a or the complex dctype-Ni-2a.

5.5. Stoichiometric experiments with meso-L2 (Figure 5):

Stoichiometric experiment with meso-L2 and 1a: In a glovebox, a 2-dram vial was charged with a stir bar, the ligand meso-L2 (0.014 g, 0.025 mmol), Ni(cod)₂ (0.0070 g, 0.025 mmol), and C₆D₆ (0.50 mL). The mixture was stirred at room temperature for 10 min then the lactone 1a (0.0055 g, 0.025 mmol) was added. The vial was sealed and brought outside to place on a heating block preheated at 110 °C. After stirring for 3 h, the vial was brought back inside the glovebox and the solution was transferred to an NMR tube. The NMR tube was sealed then ¹H and ³¹P NMR spectra were acquired (Figure S2-A and S3-A). The main signals were lactone 1a. In the glovebox, the solution in the NMR tube was transferred back to the vial and the mixture was heated further at 120 °C for 3 h on a heating block. After cooling to room temperature, the vial was brought back inside the glovebox and the solution was transferred to an NMR tube. ¹H and ³¹P NMR spectra were acquired again to show a 40:60 ratio of 2a:1a (Figure S2-B) and meso-L2-Ni(CO)₂. (Figure S3-B). The complex meso-L2-Ni-2a was not detected (Figure S3-A and S3-B vs. S3-E). The mixture was again heated in the manner described above at 150 °C for 3 h to give 2a:1a = 100:0 (Figure S2-C).

Figure S2. ¹H NMR (600 MHz, C₆D₆) spectra for the stoichiometric reaction using meso-L2 and 1a at A) 110 °C, B) 120 °C, and C) 150 °C.
**In situ generation and observation of meso-L2-Ni(CO)₂ in ³¹P NMR:** In a glovebox, a 2-dram vial was charged with a stir bar, *meso*-L2 (0.0070 g, 0.0125 mmol), (Ph₃P)₂Ni(CO)₂ (0.0075 g, 0.0125 mmol), and C₆D₆ (0.50 mL). The solution was stirred at room temperature in the glovebox for 1 h and was filtered by syringe filter into an NMR tube. The NMR tube was sealed and brought outside to acquire a ³¹P NMR spectrum. The signal for *meso*-L2-Ni(CO)₂ was seen at 36.76 ppm (Figure S3-D).

**Figure S3.** ³¹P{¹H} NMR (253 MHz, C₆D₆) spectra of A) stoichiometric reaction at 110 °C, B) 120 °C, C) 150 °C, D) *meso*-L2-Ni(CO)₂, and E) *meso*-L2-Ni-2a.

**Stoichiometric reductive elimination test with meso-L2-Ni-2a·C₆H₆:** In a glovebox, an oven-dried 2-dram vial was charged with a stir bar, *meso*-L2-Ni-2a·C₆H₆ (0.088 g, 0.050 mmol), and toluene (0.50 mL). The vial was sealed and brought outside to place on an aluminum heating block preheated at 110 °C. The reaction was stirred at 110 °C for 3 h. After cooling to room temperature, the reaction was analyzed by TLC (100% hexanes). The product 2a was visualized under UV. The reaction was then loaded directly onto a silica gel column (1 × 5 cm). The column was eluted with 50 mL of hexanes. The product containing fractions were combined and concentrated by rotary evaporator. The residue was dried under vacuum using an oil pump to give 2a (0.0091 g, 0.050 mmol, >99%). Characterization data for 2a is provided in section 6.2.

The same reaction carried out at 80 °C for 24 h gave 0% of 2a.
5.6. Carbonylation tests (Figure 6A)

Stoichiometric carbonylation test with dcype-Ni-2a·C₆H₆: In a glovebox, an oven-dried 2-dram vial was charged with a stir bar, dcype-Ni-2a·C₆H₆ (0.037 g, 0.050 mmol), Cr(CO)₆ (0.011 g, 0.050 mmol, 1.0 equiv), and C₆D₆ (0.50 mL). The vial was sealed and brought outside to place on an aluminum heating block preheated at 80 °C. The reaction was stirred at 80 °C for 24 h. After cooling to room temperature, the reaction was analyzed by TLC (100% hexanes). A spot matching with 1a was visualized under UV. The reaction was then loaded directly onto a silica gel column (1 × 10 cm, packed in hexanes). The column was eluted with 100 mL of 90/10 hexanes/ethyl acetate. The fractions containing 1a was collected and concentrated by rotary evaporator. The residue was dried under vacuum using an oil pump to give 1a as a white solid (0.0095 g, 0.045 mmol, 90%). NMR data of 1a matched with previously reported values.⁴

Stoichiometric carbonylation test with meso-L₂-Ni-2a·C₆H₆: In a glovebox, an oven-dried 2-dram vial was charged with a stir bar, meso-L₂-Ni-2a·C₆H₆ (0.088 g, 0.050 mmol), Cr(CO)₆ (0.011 g, 0.050 mmol, 1.0 equiv), and C₆D₆ (0.50 mL). The vial was sealed and brought outside to place on an aluminum heating block preheated at 80 °C. The reaction was stirred at 80 °C for 24 h. After cooling to room temperature, the reaction was analyzed by TLC (100% hexanes). A spot matching with 2a was visualized under UV. The reaction was then loaded directly onto a silica gel column (1 × 10 cm, packed in hexanes). The column was eluted with 100 mL of hexanes. The fractions containing 2a was collected and concentrated by rotary evaporator. The residue was dried under vacuum using an oil pump to give 2a as a white solid (0.0089 g, 0.049 mmol, 98%). Characterization data for 2a are provided in section 6.2.

5.7. Catalytic experiments with meso-L₂-Ni-2a:

An oven-dried 2-dram vial was charged with a stir bar, and 1d (0.030 g, 0.100 mmol). The vial was brought inside a glovebox, then meso-L₂-Ni-2a·C₆H₆ (0.018 g, 0.020 mmol), CsF (0.015 g, 0.100 mmol), and toluene (1.00 mL) were added. The vial was sealed and brought outside to place on an aluminum heating block preheated at 150 °C. The reaction was stirred at 150 °C for 24 h. After cooling to room temperature, the reaction was loaded directly onto a silica gel column (2 × 15 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 80/20 hexanes/ethyl acetate. The products containing fractions were collected and concentrated by rotary evaporator. The residues were dried under vacuum using an oil pump to give 2d as a white solid (0.0175 g, 0.065 mmol, 65% from 1d) and 2a (0.0036 g, 0.020 mmol, >99% from meso-L₂-Ni-2a·C₆H₆). Characterization data for 2a and 2d are provided in section 6.
6. Experimental procedures and characterization data for compounds in Figure 7

6.1. Synthesis of substrates and characterization data for substrates
Substrates 1a, 1f, 1h, and 1n were synthesized according to a literature procedure.4

6.1.1. Synthesis of substrate 1b

2-bromo-4-(trifluoromethyl)benzoic acid (S1b-1): To a solution of KMnO₄ (1.42 g, 9 mmol, 2.25 equiv.) in H₂O (20 mL) was added 2-bromo-4-(trifluoromethyl)benzaldehyde (1.01 g, 4 mmol, 1 equiv.) in tBuOH (4 mL) at RT. The reaction was stirred at 85 °C for 2 h. The reaction was cooled to RT, then the pH was adjusted to 14 with 10% aq. NaOH. The green solution with brown precipitate was filtered through Celite, rinsing with H₂O. The pH of the aqueous filtrate was adjusted to 1 with 4N HCl and extracted with Et₂O (50 mL × 2). The combined organics were dried over Na₂SO₄, filtered, and concentrated on a rotary evaporator to give S1b-1 as a white solid (973 mg, 90% yield).¹H NMR data match reported data.⁵

TLC (50% EtOAc/hexanes): Rf = 0.15 (visualized by UV)
¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, J = 8.1 Hz, 1H), 8.00 – 7.97 (m, 1H), 7.68 (d, J = 8.2 Hz, 1H).
¹³C{¹H} NMR (101 MHz, CDCl₃) δ 170.0, 135.3, (q, J = 33.6 Hz), 133.8, 132.8, 132.0 (q, J = 3.8 Hz), 124.4 (q, J = 3.7 Hz), 123.0, 122.7 (q, J = 273 Hz).
¹⁹F NMR (376 MHz, CDCl₃) δ -63.34.
2-bromo-4-(trifluoromethyl)benzoic acid (S1b-2): To a solution of S1b-1 (958 mg, 3.56 mmol, 1 equiv.) in MeCN (10 mL) in a 25 mL Schlenk flask was added K$_2$CO$_3$ (750 mg, 5.43 mmol, 1.53 equiv.) followed by BnBr (0.52 mL, 4.38 mmol, 1.23 equiv.) at RT. The reaction was stirred at 60 °C for 14 h, then cooled to RT. The reaction was diluted with 1:1 H$_2$O/brine (20 mL) and extracted with EtOAc (20 mL × 3). The combined organic phase was washed with brine, dried over MgSO$_4$, filtered, and concentrated on a rotary evaporator. The crude product was purified by silica gel column chromatography (Combiflash, 0 → 10% EtOAc/hexanes) to give S1b-2 as a colorless oil (941 mg, 72%).

TLC (15% EtOAc/hexanes): $R_f = 0.42$ (visualized by UV)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.92 (s, 1H), 7.88 (d, $J = 8.1$ Hz, 1H), 7.61 (d, $J = 8.1$ Hz, 1H), 7.46 (d, $J = 7.1$ Hz, 2H), 7.40 (dd, $J = 8.1$, 6.4 Hz, 2H), 7.38 – 7.35 (m, 1H), 5.40 (s, 2H).

$^{13}$C$^1$H NMR (151 MHz, CDCl$_3$) δ 165.2, 135.7, 135.2, 134.3 (q, $J = 33.4$ Hz), 131.8, 131.4 (q, $J = 3.8$ Hz), 128.8 (2C), 128.7, 124.2, 122.8 (q, $J = 273$ Hz), 68.0.

$^{19}$F$^1$H NMR (377 MHz, CDCl$_3$) δ -63.20.

IR (FT-ATR, cm$^{-1}$, neat) $\nu_{\text{max}}$ 3089 (w), 3069 (w), 3037 (w), 2961 (w), 1736 (s), 1611 (w), 1572 (w), 1493 (w), 1460 (w), 1388 (m), 1322 (s), 1296 (s), 1250 (s), 1175 (s), 1132 (s), 1083 (s), 1040 (s), 951 (w), 892 9w), 846 (w), 777 (w), 754 (w), 695 (m), 666 (w), 639 (w).

HRMS: Exact mass calculated for C$_{15}$H$_{10}$O$_2$BrF$_3$ requires m/z = 357.9816, found m/z = 357.9807 (EI)

Methyl 4-(benzylxy)-3-(hydroxymethyl)benzoate (S1b-3): Methyl 4-(benzylxy)-3-formylbenzoate$^6$ (600 mg, 2.22 mmol, 1.0 equiv.) was dissolved in 2:1 MeOH/THF (7.5 mL) and cooled to 0 °C. NaBH$_4$ (99.7 mg, 2.44 mmol, 1.2 equiv.) was added portionwise over 5 min. The reaction was stirred at 0 °C for 2 h. Another portion of NaBH$_4$ (16.8 mg, 0.44 mmol, 0.2 equiv.) was added and the reaction stirred for another 2 h, then quenched with brine. The mixture was partially concentrated by rotary evaporation. The aqueous phase was extracted with MTBE (20 mL × 3). Brine was added to aid phase separation. The combined DCM layers were washed with 0.5N HCl (15 mL), brine, dried over Na$_2$SO$_4$, filtered, and concentrated on a rotary evaporator. The crude product was purified by silica gel column chromatography (20%-40% EtOAc/hexanes) to give S1b-3 as a colorless oil (578 mg, 96%).

TLC (30% EtOAc/hexanes): $R_f = 0.21$ (visualized by UV)

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.03 (d, $J = 2.2$ Hz, 1H), 7.98 (dd, $J = 8.6$, 2.2 Hz, 1H), 7.44 – 7.32 (m, 5H), 6.97 (d, $J = 8.6$ Hz, 1H), 5.17 (s, 2H), 4.76 (s, 2H), 3.88 (s, 3H), 2.07 (br s, 1H).

$^{13}$C$^1$H NMR (151 MHz, CDCl$_3$) δ 166.9, 160.2, 136.1, 131.2, 130.2, 129.6, 129.0, 128.5, 127.5, 122.9, 111.2, 70.4, 61.6, 52.1.
IR (FT-ATR, cm\(^{-1}\), neat) \( \nu_{\text{max}} \): 3445 (br s), 3069 (w), 3036 (w), 2951 (w), 2882 (w), 1716 (s), 1608 (m), 1499 (m), 1440 (m), 1387 (w), 1299 (m), 12260 (s), 1194 (m), 1132 (m), 1109 (w), 1147 (w), 1023 (m), 918 (m), 829 (w), 773 (m), 734 (m), 702 (m), 652 (w), 626 (w).

**HRMS**: Exact mass calculated for C\(_{16}\)H\(_{16}\)O\(_{4}\) requires m/z = 272.1049, found m/z = 272.1049 (EI).

**Methyl 4-(benzyloxy)-3-(bromomethyl)benzoate (S1b-4)**: A 50 mL Schlenk flask was charged with S1b-3 (578 mg, 2.12 mmol, 1.0 equiv.), evacuated, and back-filled with N\(_2\) (x3). DCM (16 mL) was added, followed by CBr\(_4\) (1.33 g, 4.03 mmol, 1.9 equiv.). The solution was cooled to 0 °C, then a solution of PPh\(_3\) (834 mg, 3.18 mmol, 1.5 equiv.) in DCM (8 mL) was added. The reaction was stirred for 1 h at 0 °C, then quenched with saturated aqueous NaHCO\(_3\) (20 mL). The aqueous layer was extracted with DCM (20 mL x 2). The combined organic phase was dried over Na\(_2\)SO\(_4\), filtered, and concentrated on a rotary evaporator. The crude product was purified by silica gel column chromatography (100% hexanes-8% EtOAc/hexanes) to give S1b-4 as a white solid (624 mg, 88%).

**TLC (15% EtOAc/hexanes):** \( R_f = 0.21 \) (visualized by UV)

**\(^{1}\)H NMR (400 MHz, CDCl\(_3\))**: \( \delta \): 8.06 (d, \( J = 2.2 \) Hz, 1H), 7.98 (dd, \( J = 8.6, 2.2 \) Hz, 1H), 7.49 (d, \( J = 7.3 \) Hz, 2H), 7.41 (dd, \( J = 8.4, 6.8 \) Hz, 2H), 7.38 – 7.34 (m, 1H), 6.96 (d, \( J = 8.6 \) Hz, 1H), 5.22 (s, 2H), 4.60 (s, 2H), 3.89 (s, 3H).

**\(^{13}\)C\(^{(1}\)H) NMR (151 MHz, CDCl\(_3\))**: \( \delta \): 164.5, 160.2, 136.1, 132.6, 132.3, 128.8, 128.3, 127.3, 126.7, 122.9, 111.8, 70.5, 52.1, 28.3.

**IR (FT-ATR, cm\(^{-1}\), neat)**: \( \nu_{\text{max}} \): 3056 (w), 3026 (w), 2961 (w), 2938 (w), 2924 (w), 2943 (w), 1707 (s), 1611 (m), 1506 (m), 1456 (w), 1231 (m), 1414 (m), 1387 (w), 1325 (m), 1309 (m), 1273 (s), 1266 (s), 1221 (m), 1194 (m), 1152 (m), 1122 (m), 1010 (m), 984 (w), 938 (w), 912 (w), 879 (w), 863 (w), 840 (w), 767 (m), 741 (m), 698 (m), 652 (w), 616 (w).

**HRMS**: Exact mass calculated for C\(_{16}\)H\(_{15}\)BrO\(_3\) requires m/z = 334.0205, found m/z = 334.0204 (EI).

**benzyl 2-(2-(benzyloxy)-5-(methoxycarbonyl)benzyl)-4-(trifluoromethyl)benzoate (S1b-5):**

The formation of the organozinc solution was adapted from a published procedure.\(^{7}\) A 50 mL Schlenk tube was charged with Zn dust (654 mg, 10 mmol, 2.5 equiv.) and a stir bar. The tube was sealed with a rubber septum and evacuated. The Zn dust was heated with a heat gun under vacuum for 5 min, then cooled to RT. THF (5 mL) was added, followed by 1 drop of 1,2-dibromoethane. The mixture was heated to reflux, then 2 drops of trimethylchlorosilane was added. The mixture was stirred vigorously for 15 min, then cooled to 0 °C. A solution of S1b-4 (1.61 g, 4.80 mmol, 1 equiv.) in THF (1.5 mL) was added dropwise over 5 min. After the addition, the ice/water bath
was removed, and the reaction stirred at RT for 2 hours. The concentration of the organozinc solution was calculated to be 0.25 M after titration with I₂ (49.9 mg, 0.20 mmol) in THF (1 mL). A separate Schlenk flask was charged with aryl bromide S₁b-2 (770 mg, 2.14 mmol, 1 equiv.), Pd(OAc)₂ (21.9 mg, 0.0965 mmol, 0.045 equiv. wrt aryl bromide S₁b-2), and SPhos (79.2 mg, 0.193 mmol, 0.09 equiv.). The flask was sealed with a rubber septum under N₂. THF (5 mL) was added. The organozinc solution prepared above (11 mL, 2.75 mmol, 1.29 equiv.) was added dropwise at RT. After the addition, the reaction mixture was stirred at 40 °C for 2 h. After cooling to RT, the reaction was quenched with 0.5N HCl (20 mL) and the aqueous layer extracted with MTBE (20 mL × 3). The grey solid that was poorly soluble in the organic phase was discarded. The combined organic phase was washed with brine, dried over MgSO₄, filtered, and concentrated on a rotary evaporator. The crude product was purified by silica gel column chromatography (100% Hexanes - 10% EtOAc/hexanes - 15% EtOAc/hexanes) to give a yellow oil. Trituration with MeOH and removal of the MeOH gives S₁b-5 a white solid (1.13 g, 95% wrt S₁b-2).

TLC (100% hexanes): Rₜ = 0.35 (visualized by UV).

¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 8.2 Hz, 1H), 7.91 (dd, J = 8.6, 2.2 Hz, 1H), 7.74 (d, J = 2.2 Hz, 1H), 7.51 (d, J = 6.2 Hz, 1H), 7.40 (s, 1H), 7.40 – 7.28 (m, 8H), 7.20 (m, 2H), 6.90 (d, J = 8.7 Hz, 1H), 5.29 (s, 2H), 5.07 (s, 2H), 4.45 (s, 2H), 3.84 (s, 3H).

¹³C{¹H} NMR (151 MHz, CDCl₃) δ 166.9, 166.8, 160.3, 160.4, 154.5, 136.3, 135.5, 133.7, 133.5 (q, J = 32.2 Hz), 132.0, 131.0, 130.5, 128.8, 128.7 (2C), 128.5, 128.4, 128.2, 127.8 (q, J = 3.8 Hz), 127.2, 123.7 (q, J = 272.8 Hz), 123.1 (q, J = 3.1 Hz), 122.8, 111.3, 70.2, 67.3, 52.0, 34.3.

IR (FT-ATR, cm⁻¹, neat) νmax 3069 (w), 3037 (w), 2958 (w), 2905 (w), 2872 (w), 2839 (w), 1716 (s), 1601 (m), 1503 (m), 1456 9w), 1427 (m), 1411 (w), 1385 (w), 1335 (w), 1303 (m), 1260 (s), 1194 (w), 1171 (m), 1122 (s), 1092 (m), 1066 (w), 1027 (w), 977 (w), 954 (w), 941 (w), 905 (w), 853 (w), 793 (w), 771 (w), 754 (m), 721 (w), 695 (w), 649 (w).

HRMS: Exact mass calculated for [C₃₁H₅₅F₃O₅+H]⁺ requires m/z = 535.1732, found m/z = 535.1726 (ESI+).

methyl 6-oxo-9-(trifluoromethyl)-6,11-dihydrodibenzo[b,e]oxepine-2-carboxylate (1b): S₁b-5 (816 mg, 1.53 mmol, 1 equiv.) was dissolved in MeOH/THF 3:1 (40 mL) and 10% Pd/C (245 mg) was added). The flask was evacuated briefly and back-filled with H₂ from a H₂-filled balloon. The reaction was stirred at RT for 4 h, then purged with N₂ for 15 min. The reaction mixture was filtered through Celite, rinsing with EtOAc. The filtrate was concentrated on a rotary evaporator to give a light-yellow solid which was suspended in DCM (60 mL). DMAP (17 mg, 2.30 mmol, 0.1 equiv.) was added, followed by DIC (0.36 mL, 2.32 mmol, 1.52 equiv.) under ambient atmosphere and temperature. The reaction was stirred at RT for 20 h, then Celite was added. The crude product was adsorbed onto Celite by removal of the solvent on a rotary evaporator. Purification by silica gel column chromatography (100% hexanes – 10% – 15% EtOAc/hexanes gave the product 1b was a white solid (428 mg, 83% over 2 steps).
**TLC** (20% hexanes): \( R_f = 0.35 \) (visualized by UV).

**\(^1H\) NMR** (400 MHz, CDCl\(_3\) \( \delta \) 8.02 – 7.97 (m, 2H), 7.94 (dd, \( J = 8.4, 2.1 \) Hz, 1H), 7.61 (d, \( J = 8.0 \) Hz, 1H), 7.56 (s, 1H), 7.29 (d, \( J = 8.4 \) Hz, 1H), 4.12 (s, 2H), 3.91 (s, 3H).

**\(^{13}C\)\(^1H\) NMR** (151 MHz, CDCl\(_3\) \( \delta \) 165.9, 164.1, 153.9, 142.8, 135.2 (q, \( J = 33.0 \) Hz), 133.5, 131.3, 130.5, 130.2, 128.2, 124.7 (q, \( J = 3.7 \) Hz), 123.3 (q, \( J = 274 \) Hz), 121.2, 52.5, 36.4.

**\(^{19}F\)\(^1H\) NMR** (376 MHz, CDCl\(_3\) \( \delta \) -63.3.

**IR** (FT-ATR, cm\(^{-1}\), neat) \( \nu_{\text{max}} \) 3052 (w), 3010 (w), 2964 (w), 1723 (s), 1615 (w), 1588 (w), 1496 (w), 1447 (m), 1424 (m), 1339 (m), 1322 (m), 1266 (m), 1234 (m), 1198 (m), 1178 (m) 1132 (m), 1112 (m), 1056 (m), 997 (w), 951 (w), 932 (w), 692 (w), 863 (w), 803 (w), 774 (w), 757 (w), 708 (w), 664 (w), 626 (w).

**HRMS**: Exact mass calculated for \([\text{C}_{17}\text{H}_{11}\text{F}_{3}\text{O}_{4}]^+\) requires \( m/z = 337.0682 \), found \( m/z = 337.0685 \) (ESI+).

### 6.1.2. Synthesis of substrate 1c

**2,9-Dimethoxydibenzo[b,e]oxepin-6(11H)-one** (1c): The synthesis of compound 1c was adapted from a reported procedure for 1a.\(^4\)

**Step 1**: A 40-mL vial was charged with a stir bar, \( N \)-Tosyl hydrazide (3.7246 g, 20 mmol, 1.0 equiv), and MeOH (10 mL). The suspension was stirred vigorously, and 5-methoxy salicylaldehyde (2.50 mL, 3.04 g, 20 mmol, 1.0 equiv) was added. The vial was sealed with a Teflon lined cap and was placed on an aluminum heating block preheated at 70 °C. The mixture was stirred at 70 °C for 2 h and was cooled to room temperature. Hexanes (10 mL) was added, and the vial was placed in a freezer (−36 °C). After 12 h, the white crystals were collected by filtration and washed with hexanes (10 mL). The crystal was dried under vacuum using an oil pump to give S1c and was used directly in the next step without further purification.

**Step 2**: A 40-mL vial was charged with a stir bar, S1c (1.60 g, 5.00 mmol, 2.0 equiv), 2-bromo-4-methoxy benzaldehyde (0.538 g, 2.5 mmol, 1.0 equiv), and \( \text{K}_2\text{CO}_3 \) (1.04 g, 7.5 mmol). The vial was brought inside a glovebox, then [(allyl)PdCl\(_2\)] (23 mg, 0.063 mmol, 2.5 mol%), Xantphos (0.108 g, 0.19 mmol, 7.5 mol%), and dioxane (5.0 mL) were added. The vial was sealed and brought outside and placed on an aluminum heating block preheated at 80 °C. The mixture was vigorously stirred at 80 °C for 16 h and was cooled to room temperature. Ethyl acetate (50 mL) was added and the solid was filtered off using a pad of Celite. The filtrate was concentrated by rotary evaporator and the residue was loaded onto a silica gel column (5 × 20 cm, packed in hexanes). The column was eluted with 90/10 hexanes/ethyl acetate and the product-containing fractions were collected. The solvents were removed by rotary evaporator and the residue was dried under vacuum using an oil pump to give 1c as a yellow solid (0.230 g, 0.83 mmol, 33%).

**TLC** (90/10 hexanes/ethyl acetate): \( R_f = 0.20 \) (visualized by UV).

**\(^1H\) NMR** (400 MHz, CDCl\(_3\) \( \delta \) 7.88 (d, \( J = 8.7 \) Hz, 1H), 7.14 (d, \( J = 8.8 \) Hz, 1H), 6.85 – 6.65 (m, 4H), 3.92 (s, 2H), 3.84 (s, 3H), 3.77 (s, 3H).

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$^{13}$C$^{[1]}$H NMR (151 MHz, CDCl₃) δ 166.4, 163.5, 157.2, 144.9, 144.6, 135.5, 133.7, 121.7, 120.4, 113.6, 112.9, 112.7, 112.6, 55.8, 55.6, 38.2.

IR (FT-ATR, cm⁻¹, neat) $\nu_{\text{max}}$ 2990 (w), 2954 (w), 2918 (w), 2843 (w), 1716 (s), 1605 (m), 1496 (m), 1450 (w), 1424 (w), 1322 (w), 1257 (m), 1204 (m), 1122 (m), 1099 (m), 1066 (m), 1026 (m), 954 (w), 865 (w), 826 (w), 804 (w).

HRMS: Exact mass calculated for [C₁₆H₁₄O₄+H]$^+$ requires m/z = 271.0965, found m/z = 271.0969. (ESI+).

6.1.3. Synthesis of substrate 1d

![Diagram of synthesis process]

1-(benzylxo)-2-(bromomethyl)-4-methoxybenzene (S1d-1): S1d-1 was synthesized according to literature procedure.⁸

TLC (15% EtOAc/hexanes): $R_f = 0.33$ (visualized by UV)

$^1$H NMR (600 MHz, CDCl₃) δ 7.49 (d, $J = 6.9$ Hz, 2H), 7.40 (t, $J = 7.2$ Hz, 3H), 7.37 – 7.31 (m, 2H), 6.93 (d, $J = 3.0$ Hz, 1H), 6.87 (d, $J = 8.9$ Hz, 1H), 6.81 (dd, $J = 9.0$, 3.1 Hz, 1H), 5.12 (s, 2H), 4.59 (s, 2H), 3.78 (s, 3H).

$^{13}$C$^{[1]}$H NMR (151 MHz, CDCl₃) δ 153.8, 150.8, 137.2, 128.7, 128.0, 127.6, 127.4, 116.5, 115.2, 113.9, 70.4, 55.9, 28.6.

Dimethyl 2-(2-(benzylxo)-5-methoxybenzyl)terephthalate (S1d-2): A 10 mL Schlenk tube was charged with LiCl (267 mg, 6.3 mmol, 2.57 equiv.) and a stir bar. The flask was sealed and evacuated. The flask was heated with a heat gun for 5 min, then back-filled with N₂ and cooled to RT. Zn dust (330 mg, 5.04 mmol, 2.07 equiv.) was then added. The flask was re-sealed and evacuated. The flask was heated with a heat gun for 5 min, then back-filled with N₂ and cooled to RT. THF (1 mL) was added. A solution of S1d-1 (753 mg, 2.45 mmol, 1 equiv.) in THF (2 mL mL) was added dropwise over 5 min. The reaction stirred at RT for 2 hours. The concentration of the organozinc solution was calculated to be 0.63 M after titration with I₂ (25.4 mg, 0.10 mmol) in THF (0.5 mL). A separate Schlenk flask was charged with dimethyl 2-bromoterephthalate⁹ (286 mg, 1.05 mmol, 1 equiv.), Pd(OAc)$_2$ (11.9 mg, 0.0525 mmol, 0.05 equiv. wrt aryl bromide), and RuPhos (49.0 mg, 0.105 mmol, 0.1 equiv.). The flask was sealed with a rubber septum under N₂. THF (6 mL) was added. The organozinc solution prepared above (2.5 mL, 1.58 mmol, 1.5 equiv.)
was added dropwise at RT. After the addition, the reaction mixture was stirred at 60 °C for 5 h. After cooling to RT, the reaction was quenched with 0.5N HCl (20 mL) and the aqueous layer extracted with diethyl ether (10 mL × 3). The combined organic phase was washed with brine, dried over MgSO₄, filtered, and concentrated on a rotary evaporator. The crude product was purified by silica gel column chromatography (100% Hexanes - 10% EtOAc/hexanes - 15% EtOAc/hexanes) to give S1d-2 a yellow oil (453 mg, quantitative).

**TLC (15% EtOAc/hexanes):** Rₑ = 0.16 (visualized by UV)

1H NMR (600 MHz, CDCl₃) δ 7.94 – 7.88 (m, 3H), 7.34 – 7.28 (m, 5H), 6.83 (d, J = 8.9 Hz, 1H), 6.68 (dd, J = 8.8, 3.1 Hz, 1H), 6.56 (d, J = 3.1 Hz, 1H), 5.01 (s, 2H), 4.40 (s, 2H), 3.87 (s, 3H), 3.82 (s, 3H), 3.70 (s, 3H).

13C{1H} NMR (151 MHz, CDCl₃) δ 167.8, 166.5, 153.8, 150.8, 142.1, 137.6, 134.5, 132.9, 132.5, 130.7, 130.4, 128.6, 127.8, 127.2 (2C), 117.0, 113.0, 111.5, 70.7, 54.8, 52.4, 52.3, 34.2.

IR (FT-ATR, cm⁻¹, neat) ν max 3064 (w), 3024 (w), 2965 (w), 2916 (w), 2844 9w), 1740 (w), 1714 (s), 1616 (w), 1497 (m), 1455 (w), 1434 (m), 1415 (m), 1278 (m), 1241 (m), 1198 (s), 1152 (w), 1120 (m), 1053 (m), 1038 (w), 978 (m), 942 (w), 916 (w), 896 (w), 857 (m), 811 (m), 788 (w), 771 (w), 742 (m), 706 (w), 630 (w), 611 (w).

**HRMS:** Exact mass calculated for [C_{25}H_{24}O_{6}+H]^+ requires m/z = 421.1646, found m/z = 421.1656. (ESI+).

Methyl 2-methoxy-6-oxo-6,11-dihydrodibenzo[b,e]oxepine-9-carboxylate (1d): A suspension of S1d-2 (435 mg, 1.03 mmol, 1.0 equiv) and 10% Pd/C (43.5 mg) was stirred overnight at RT under an atmosphere of H₂ (H₂ balloon). TLC showed incomplete conversion. The reaction was purged with N₂, then another portion of 10% Pd/C (21.5 mg) was added. The reaction was evacuated briefly and back-filled with H₂ from a balloon. After stirring for another 3 h at RT, TLC showed complete conversion. The reaction was purged with N₂ and filtered through Celite and silica gel. The filtrate was concentrated on a rotary evaporator and suspended in PhMe (30 mL). pTsOH·H₂O (39.2 mg, 0.206 mmol, 0.2 equiv.) was added, and the reaction refluxed for 6 h. The reaction was quenched with saturated aqueous NaHCO₃ (30 mL). After phase separation, the aqueous layer was extracted with EtOAc (15 mL × 2). The combined organic phase was washed with brine, dried over Na₂SO₄, filtered, and concentrated on a rotary evaporator. The crude product was purified by silica gel column chromatography (50% – 80% DCM/hexanes) to give 1d as a white solid (223 mg, 73% over 2 steps).

**TLC (30% EtOAc/hexanes):** Rₑ = 0.29 (visualized by UV)

1H NMR (600 MHz, CDCl₃) δ 7.98 – 7.91 (m, 3H), 7.14 (d, J = 8.8 Hz, 1H), 6.78 (d, J = 3.0 Hz, 1H), 6.72 (dd, J = 8.8, 3.0 Hz, 1H), 4.00 (br s, 2H), 3.93 (s, 3H), 3.77 (s, 3H).

13C{1H} NMR (151 MHz, CDCl₃) δ 166.0, 165.8, 157.4, 144.3, 142.7, 134.2, 133.4, 133.0, 132.2, 128.5, 128.4, 121.7, 113.6, 113.0, 56.3, 52.7, 37.0.

IR (FT-ATR, cm⁻¹, neat) ν max 3064 (w), 3024 (w), 2965 (w), 2916 (w), 2844 9w), 1740 (s), 1714 (s), 1616 (w), 1497 (m), 1455 (w), 1434 (m), 1415 (m), 1278 (m), 1241 (m), 1198 (s), 1152 (w), 1120 (m), 1053 (m), 1038 (w), 978 (m), 942 (w), 916 (w), 896 (w), 857 (m), 811 (m), 788 (w), 771 (w), 742 (m), 706 (w), 630 (w), 611 (w).

**HRMS:** Exact mass calculated for [C_{17}H_{14}O_{5}+H]^+ requires m/z = 299.0914, found m/z = 299.0916. (ESI+).
6.1.4. Synthesis of substrate 1e

2-chloro-9-methoxydibenzo[b,e]oxepin-6(11H)-one (S1e-2): The synthesis of compound S1e-2 was adapted from a reported procedure for 1a.4

**Step 1:** A 40-mL vial was charged with a stir bar, N-tosyl hydrazide (3.72 g, 20 mmol, 1.0 equiv), and MeOH (10 mL). The suspension was stirred vigorously, and 5-chloro salicylaldehyde (3.13 g, 20 mmol, 1.0 equiv) was added. The vial was sealed with a Teflon lined cap and was placed on an aluminum heating block preheated at 70 °C. The mixture was stirred at 70 °C for 2 h and was cooled to room temperature. Hexanes (10 mL) was added, and the vial was placed in a freezer (−36 °C). After 12 h, the white crystals were collected by filtration and washed with hexanes (10 mL). The crystal was dried under vacuum using an oil pump to give S1e-1 and was used directly in the next step without further purification.

**Step 2:** A 40-mL vial was charged with as stir bar, S1e-1 (1.62 g, 5.00 mmol, 2.0 equiv), 2-bromo-4-methoxy benzaldehyde (0.538 g, 2.5 mmol, 1.0 equiv), and K₂CO₃ (1.04 g, 7.5 mmol). The vial was brought inside a glovebox, then [(allyl)PdCl₂] (23 mg, 0.063 mmol, 2.5 mol%), Xantphos (0.108 g, 0.19 mmol, 7.5 mol%), and dioxane (5.0 mL) were added. The vial was sealed and brought outside and placed on an aluminum heating block preheated at 80 °C. The mixture was vigorously stirred at 80 °C for 16 h and was cooled to room temperature. Ethyl acetate (50 mL) was added and the solid was filtered off using a pad of Celite. The filtrate was concentrated by rotary evaporator and the residue was loaded onto a silica gel column (5 × 25 cm, packed in hexanes). The column was eluted with 90/10 hexanes/ethyl acetate and the product-containing fractions were collected. The solvents were removed by rotary evaporator and the residue was dried under vacuum using an oil pump to give S1e-2 as a yellow solid with ca. 1% impurities seen in NMR (0.303 g, 1.10 mmol, ca. 44%).

**TLC** (80/20 hexanes/ethyl acetate): Rₛ = 0.30 (visualized by UV)

**¹H NMR** (400 MHz, CDCl₃) δ 7.88 (d, J = 8.7 Hz, 1H), 7.25 (d, J = 2.2 Hz, 1H), 7.23 – 7.12 (m, 2H), 6.84 (dd, J = 8.7, 2.6 Hz, 1H), 6.74 (d, J = 2.5 Hz, 1H), 3.93 (s, 2H), 3.85 (s, 3H).

**¹³C{¹H} NMR** (101 MHz, CDCl₃) δ 165.4, 163.8, 149.7, 144.1, 136.0, 134.2, 131.0, 128.2 (2 × s), 122.3, 120.0, 113.1, 112.9, 55.7, 37.9.
IR (FT-ATR, cm⁻¹, neat) $\nu_{\text{max}}$ 3096 (w), 2977 (w) 2846 (w), 1726 (s), 1601 (s), 1476 (m), 1431 (w), 1414 (w), 1319 (m), 1263 (s), 1230 (m), 1115 (m), 1056 (w), 1023 (m), 905 (w), 872 (w), 820 (m), 757 (w), 702 (w), 639 (w), 612 (w).

HRMS: Exact mass calculated for [C₁₅H₁₁ClO₃+H]$^+$ requires m/z = 275.0469, found m/z = 275.0466. (ESI+).

9-Methoxy-2-(trifluoromethyl)dibenzo[b,e]oxepin-6(11H)-one (1e): The synthesis of compound 1e was adapted from a reported trifluoromethylation method.¹⁰ In a glovebox, a vial (vial A) was charged with a stir bar, KF (0.058 g, 1.0 mmol, 2.0 equiv), and S1e-2 (0.137 g, 0.50 mmol). Another vial (vial B) was charged with a stir bar, Pd₂dba₃ (0.018 g, 0.015 mmol, 3.0 mol%), BrettPhos (0.024 g, 0.045 mmol, 9.0 mol%), Et₃SiCF₃ (0.19 mL, 0.184 g, 1.0 mmol, 2.0 equiv), and dioxane (1.5 mL). The solution in vial B was stirred at room temperature in the glovebox for 10 min and was then transferred to vial A. Vial A was sealed and brought outside the glovebox to place on the heating block preheated at 130 °C. The reaction was stirred at 130 °C for 16 h and was cooled to room temperature. The reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a plug of Celite. The filtrate was concentrated by rotary evaporator. The residue was loaded on a silica gel column (1 × 20 cm, packed in hexanes). The column was eluted with 99/1 hexanes/ethyl acetate. The product containing fractions were concentrated using rotary evaporator and the residue was dried under vacuum using an oil pump to give 1e as a white solid with ca. 5% impurities seen in NMR (0.0695 g, 0.23 mmol, ca. 45%).

TLC (80/20 hexanes/ethyl acetate): $R_f = 0.20$ (visualized by UV).

¹H NMR (400 MHz, CDCl₃) $\delta$ 7.89 (d, $J = 8.7$ Hz, 1H), 7.54 (s, 1H), 7.50 (d, $J = 8.5$ Hz, 1H), 7.33 (d, $J = 8.4$ Hz, 1H), 6.86 (dd, $J = 8.7$, 2.5 Hz, 1H), 6.77 (d, $J = 2.5$ Hz, 1H), 4.03 (s, 2H), 3.86 (s, 3H).

¹³C{¹H} NMR (101 MHz, CDCl₃) $\delta$ 164.8, 164.0, 153.5, 143.9, 135.8, 133.3, 128.2 (q, $J = 33.1$ Hz), 125.7-125.6 (m, 2C), 123.8 (q, $J = 272.6$ Hz), 121.6, 119.8, 113.2, 113.0, 55.7, 37.9.

¹⁹F{¹H} NMR (377 MHz, CDCl₃) $\delta$ -62.09.

IR (FT-ATR, cm⁻¹, neat) $\nu_{\text{max}}$ 2954 (w), 2921 (m), 2854 (w), 1714 (s), 1608 (m), 1575 (w), 1502 (w), 1484 (w), 1466 (w), 1442 (w), 1339 (m), 1327 (m), 1293 (w), 1260 (s), 1239 (w), 1184 (w), 1160 (s), 1117 (s), 1105 (s), 1081 (w), 1060 (m), 1033 (m), 957 (w), 936 (w), 908 (w), 890 (w), 842 (w), 820 (m), 760 (m), 745 (w), 705 (m), 675 (w), 620 (w).

HRMS: Exact mass calculated for C₁₆H₁₁F₃O₃ requires m/z = 308.0660, found m/z = 308.0655 (EI)
6.1.5. Synthesis of substrate 1g

Step 1: A 40-mL vial was charged with a stir bar, N-tosyl hydrazide (3.7246 g, 20 mmol, 1.0 equiv), and MeOH (10 mL). The suspension was stirred vigorously, and salicylaldehyde (2.50 mL, 3.04 g, 22 mmol, 1.1 equiv) was added. The vial was sealed with a Teflon-lined cap and was placed on an aluminum heating block preheated at 70 °C. The mixture was stirred at 70 °C for 2 h and was cooled to room temperature. Hexanes (10 mL) was added, and the vial was placed in a freezer (–36 °C). After 12 h, the white crystals were collected by filtration and washed with hexanes (10 mL). The crystal was dried under vacuum using an oil pump to give S1g and was used directly in the next step without further purification.

Step 2: A 40-mL vial was charged with as stir bar, S-1g (1.60 g, 5.00 mmol, 2.0 equiv), 2-bromo-5-(trifluoromethyl) benzaldehyde (0.538 g, 2.5 mmol, 1.0 equiv), and K₂CO₃ (1.04 g, 7.5 mmol). The vial was brought inside a glovebox, then [(allyl)PdCl₂]₂ (23 mg, 0.063 mmol, 2.5 mol%), Xantphos (0.108 g, 0.19 mmol, 7.5 mol%), and dioxane (5.0 mL) were added. The vial was sealed and brought outside and placed on an aluminum heating block preheated at 80 °C. The mixture was vigorously stirred at 80 °C for 16 h and was cooled to room temperature. Ethyl acetate (50 mL) was added and the solid was filtered off using a pad of Celite. The filtrate was concentrated by rotary evaporator and the residue was loaded onto a silica gel column (5 × 20 cm, packed in hexanes). The column was eluted with 90/10 hexanes/ethyl acetate and the product-containing fractions were collected. The solvents were removed by rotary evaporator and the residue was dried under vacuum using an oil pump to give 1g as an off-white solid (0.318 g, 1.18 mmol, 47%).

TLC (80/20 hexanes/ethyl acetate): Rₜ = 0.40 (visualized by UV).

¹H NMR (400 MHz, CDCl₃) δ 8.13 (s, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.25 – 7.20 (m, 3H), 7.13 (m, 1H), 4.05 (s, 2H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 164.8, 150.4, 146.2, 131.6, 130.3 (q, J = 33.4 Hz), 130.1-129.8 (m, 2C), 128.9, 128.7, 128.4, 127.9, 126.3, 123.4 (q, J = 27.1 Hz), 120.9, 37.3.

¹⁹F{¹H} NMR (377 MHz, CDCl₃) δ -62.81.

IR (FT-ATR, cm⁻¹, neat) νmax 3079 (w), 3043 (w), 2924 (w), 2856 (w), 1716 (s), 117 (w), 1585 (w), 1493 (w), 1476 (w), 1457 (w), 1427 (w), 1414 (w), 1332 (m), 1312 (m), 1283 (w), 1243 (m), 1171 (m), 1129 (s), 1079 (m), 1033 (w), 997 (w), 954 (w), 918 (w), 865 (w), 842 (w), 787 (w), 757 (m), 728 (w), 667 (w), 646 (w), 613 (w).

HRMS: Exact mass calculated for C₁₅H₉F₃O₂ requires m/z = 278.0555, found m/z = 278.0554 (EI).
6.1.6. Synthesis of substrate 1i and 1j

8-hydroxydibenzo[b,e]oxepin-6(11H)-one (S1i): A three-neck round bottom flask was charged with a stir bar, 1h (0.566 g, 1.79 mmol), and Pd/C (100 mg). The round bottom flask was placed under a H₂ atmosphere and MeOH (10 mL) was added. The mixture was stirred at room temperature for 48 h and the black solid was filtered off using a pad silica gel and Celite (2 cm silica gel on top of 10 cm Celite). The solid was washed with dichloromethane (10 mL) and the filtrate was concentrated to give S1i as a white solid (0.398 g, 1.76 mmol). Compound S1i was used directly in the next step without further purification.

**1H NMR** (400 MHz, CDCl₃/CD₃OD) δ 7.27 (s, 1H), 7.23 – 7.14 (m, 3H), 7.13 – 7.04 (m, 2H), 6.92 (dd, J = 8.3, 2.7 Hz, 1H), 3.88 (s, 2H), 2.57 (br s, 1H).

**13C{1H} NMR** (101 MHz, CDCl₃/CD₃OD) δ 166.9, 156.4, 150.7, 134.2, 133.4, 128.7, 128.4, 128.1, 126.0, 121.2, 120.6, 118.6, 36.6.

**IR** (FT-ATR, cm⁻¹, neat) νmax 3414 (broad s), 3069 (w), 2974 (w), 2915 (w), 2853 (w), 1733 (s), 1697 (s), 1614 (m), 1578 (m), 1490 (m), 1447 (s), 1299 (s), 1260 (m), 1230 (s), 1181 (s), 1119 (m), 1066 (m), 944 (m), 899 (w), 885 (m), 862 (w), 838 (m), 793 (m), 764 (m), 734 (w), 698 (w), 655 (w), 626 (w), 606 (m).

**HRMS**: Exact mass calculated for [C₁₄H₁₀O₃+H]⁺ requires m/z = 227.0703, found m/z = 227.0701. (ESI+).

8-(Methoxymethoxy)dibenzo[b,e]oxepin-6(11H)-one (1i):

A round bottom flask was charged with a stir bar, S1i (0.398 g, 1.76 mmol), and DMF (2.0 mL). The resulting solution was cooled to 0 °C in an ice bath. Diisopropylethylamine (0.46 mL, 0.341 g, 2.64 mmol, 1.5 equiv) was then added followed by chloromethyl methyl ether (0.20 mL, 0.212 g, 2.64 mmol). The mixture was warmed to room temperature. After stirring for 12 h, water (20 mL) was added followed by dichloromethane (10 mL). The mixture was transferred to a separatory funnel and the organic layer was collected. The aqueous layer was extracted with dichloromethane (2 × 10 mL). The combined organic fractions were washed with water (3 × 10 mL), dried with Na₂SO₄ and concentrated using rotary evaporator. The residue was loaded onto a silica gel column (1 × 15 cm, packed in hexanes). The column was eluted with 90/10 hexanes/ethyl acetate and the product containing fractions were combined and concentrated by rotary evaporator. The residue was dried under vacuum using an oil pump to give 1i as a white solid (0.454 g, 1.68 mmol, 95%).
TLC (80/20 hexanes/ethyl acetate): Rf = 0.50 (visualized by UV).

**1H NMR** (400 MHz, CDCl₃) δ 7.55 (d, J = 2.6 Hz, 1H), 7.25 – 7.07 (m, 7H), 5.14 (s, 2H), 3.94 (s, 2H), 3.43 (s, 3H).

**13C{1H} NMR** (101 MHz, CDCl₃) δ 165.9, 156.5, 150.8, 136.3, 133.2, 129.1, 128.5, 128.2 (2C), 126.0, 121.7, 120.8, 119.9, 94.6, 56.2, 36.7.

**IR** (FT-ATR, cm⁻¹, neat) νmax 3059 (w), 3000 (w), 2964 (w), 2908 (w), 2852 (w), 2830 (w), 1720 (s), 1615 (w), 1675 (w), 1493 (m), 1454 (m), 1427 (w), 1286 (m), 1259 (m), 1227 (m), 1177 (m), 1128 (m), 1085 (m), 1063 (m), 1004 (s), 922 (9m), 899 (w), 859 (w), 823 (w), 784 (w), 757 (w), 731 (w), 708 (w), 662 (w), 639 (w).

**HRMS:** Exact mass calculated for [C₁₆H₁₄O₄+H]⁺ requires m/z = 271.0965, found m/z = 271.0959 (ESI⁺).

**tert-butyl (6-oxo-6,11-dihydrodibenzo[b,e]oxepin-8-yl) carbonate (1j):** A round bottom flask was charged with a stir bar, S1i (0.398 g, 1.00 mmol), DMAP (0.012 g, 0.1 mmol, 10 mol%), and THF (5.0 mL). The mixture was stirred at room temperature and ditert-butyl decarbonate (Boc₂O, 0.327 g, 1.50 mmol, 1.5 equiv) was added. The reaction was stirred at room temperature for another 12 h and water (10 mL) was added followed by ethyl acetate (10 mL). The mixture was transferred to a separatory funnel and the organic layer was collected. The aqueous layer was extracted with ethyl acetate (2 × 10 mL). The combined organic fractions were washed with brine (10 mL), dried with Na₂SO₄ and concentrated using rotary evaporator. The residue was loaded onto a silica gel column (1 × 15 cm, packed in hexanes). The column was eluted with 90/10 hexanes/ethyl acetate and the product containing fractions were combined and concentrated by rotary evaporator. The residue was dried under vacuum using an oil pump to give 1j as a white solid (0.326 g, 1.00 mmol, >99%).

TLC (90/10 hexanes/ethyl acetate): Rf = 0.10 (visualized by UV).

**1H NMR** (400 MHz, CDCl₃) δ 7.73 (t, J = 1.5 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.25 – 7.21 (m, 3H), 7.13 (m, 1H), 4.00 (s, 2H), 1.55 (s, 9H).

**13C{1H} NMR** (101 MHz, CDCl₃) δ 165.2, 151.6, 150.7, 150.3, 140.2, 132.5, 129.3, 128.5, 128.4, 128.3, 126.5, 126.2, 125.6, 121.0, 84.3, 36.9, 27.8.

**IR** (FT-ATR, cm⁻¹, neat) νmax 3000 (w), 2981 (w), 2938 (w), 2872 (w), 1756 (s), 1730 (s), 1612 (w), 1582 (w), 1493 (w), 1457 (w), 1428 (w), 1391 (w), 1365 (w), 1282 (m), 1243 (s), 1207 (w), 1175 (m), 1155 (s), 1122 (m), 1096 (w), 1066 (w), 1050 (w), 1023 (w), 938 (w), 902 (w), 872 (w), 838 (w), 810 (w), 780 (w), 754 (w), 702 (w), 662 (w), 623 (w).

**HRMS:** Exact mass calculated for [C₁₀H₁₄O₅+H]⁺ requires m/z = 327.1227, found m/z = 327.1227 (ESI⁺).
6.1.7. Synthesis of substrate 1k

Step 1: S1g was synthesized according to the procedure described in section 6.1.5.

Step 2: A 40-mL vial was charged with a stir bar, S1g (1.18 g, 4.06 mmol, 2.0 equiv), 3-methoxy-2-bromo benzaldehyde (0.437 g, 2.03 mmol, 1.0 equiv), and K₂CO₃ (0.842 g, 6.09 mmol, 3.0 equiv). The vial was brought inside a glovebox, then [(allyl)PdCl₂] (19 mg, 0.051 mmol, 2.5 mol%), Xantphos (0.087 g, 0.15 mmol, 7.5 mol%), and dioxane (5.0 mL) were added. The vial was sealed and brought outside and placed on an aluminum heating block preheated at 80 °C. The mixture was vigorously stirred at 80 °C for 16 h and was cooled to room temperature. Ethyl acetate (50 mL) was added and the solid was filtered off using a pad of Celite. The filtrate was concentrated by rotary evaporator and the residue was loaded onto a silica gel column (5 × 20 cm, packed in hexanes). The column was eluted with 90/10 hexanes/ethyl acetate and the product-containing fractions were collected. The solvents were removed by rotary evaporator and the residue was dried under vacuum using an oil pump to give 1k as a yellow solid (0.250 g, 1.04 mmol, 51%).

TLC (90/10 hexanes/ethyl acetate): Rf = 0.25 (visualized by UV).

1H NMR (600 MHz, CDCl₃) δ 7.44 (dd, J = 7.9, 1.1 Hz, 1H), 7.29 (d, J = 7.5 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.13 – 7.06 (m, 1H), 7.02 (dd, J = 8.2, 1.1 Hz, 1H), 4.09 (s, 2H), 3.89 (s, 3H).

13C{¹H} NMR (151 MHz, CDCl₃) δ 166.3, 154.8, 151.4, 133.0, 131.6, 129.7, 128.6, 128.0, 127.9, 125.8, 124.1, 120.55, 115.0, 56.3, 56.3, 27.6.

IR (FT-ATR, cm⁻¹, neat) νmax 3069 (w), 3016 (w), 2974 (w), 2948 (w), 2921 (w), 2846 (w), 1739 (s), 1565 (m), 1476 (m), 1457 (m), 1434 (m), 1335 (w), 1309 (w), 1269 (s), 1230 (m), 1204 (m), 1174 (w), 1161 (w), 1108 (m), 1065 (w), 1049 (m), 1033 (w), 915 (w), 833 (w), 796 (w), 761 (w), 741 (m), 737 (w), 715 (w), 679 (w), 639 (w), 610 (w).

HRMS: Exact mass calculated for [C₁₅H₁₂O₅+H]+ requires m/z = 241.0859, found m/z = 241.0855. (ESI+).

6.1.8. Synthesis of substrates 1l and 1m
2,2-dimethyl-4-oxo-4H-benzo[d][1,3]dioxin-5-yl trifluoromethanesulfonate (S11-1):
A 100 mL Schlenk flask was charged with 2,2-dimethyl-5-hydroxy-4-oxo-benzo-1,4-dioxin\(^{11}\) (1.94 g, 10 mmol, 1.0 equiv.), DMAP (122 mg, 1 mmol, 0.1 equiv.), and a stir bar. The flask was sealed, evacuated, and back-filled with N\(_2\) (3×). DCM (50 mL) and NEt\(_3\) (7 mL, 50 mmol, 5.0 equiv.) were added sequentially. N-Phenyl-bis(trifluoromethanesulfonimide) (3.57 g, 10 mmol, 1.0 equiv.) was then added portionwise under a flow of N\(_2\) at RT. The reaction was stirred at RT for 18 h, then quenched with the slow addition of 0.5N HCl (40 mL). The mixture was transferred to a separatory funnel. After phase separation, the organic phase was washed with 0.5N HCl (40 mL). The combined aqueous phase was extracted with DCM (40 mL). The DCM layers were washed with saturated NaHCO\(_3\) (aq.), dried over Na\(_2\)SO\(_4\), filtered, and concentrated on a rotary evaporator. The crude product was purified partially by silica gel chromatography (40%–50% DCM/hexanes). The fractions containing the product were concentrated and further purified by recrystallization from EtOAc/hexanes (~1:10 v/v) to afford S11-1 as a white crystalline solid (2.89 g, 89%). \(^{1}\)H NMR and \(^{13}\)C NMR match reported data in the literature.\(^{12}\) \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.60 (t, \(J=8.3\) Hz, 1H), 7.06 (dd, \(J=8.5, 1.0\) Hz, 1H), 7.00 (dq, \(J=8.3, 0.7\) Hz, 1H), 1.76 (s, 6H) \(^{13}\)C\(^{1}\)H NMR (151 MHz, CDCl\(_3\)) \(\delta\) 157.6, 157.3, 148.8, 136.4, 118.9 (q, \(J=321\) Hz), 118.0, 116.7 (q, \(J=1\) Hz), 108.5, 107.0, 25.7. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -73.15.

5-(2-(benzyloxy)benzyl)-2,2-dimethyl-4H-benzo[d][1,3]dioxin-4-one:
A 10 mL Schlenk tube was charged with LiCl (106 mg, 2.5 mmol, 2.5 equiv.) and a stir bar. The flask was sealed and evacuated. The flask was heated with a heat gun for 5 min, then back-filled with N\(_2\) and cooled to RT. Zn dust (131 mg, 2.00 mmol, 2.0 equiv.) was then added. The flask was re-sealed and evacuated. The flask was heated with a heat gun for 5 min, then back-filled with N\(_2\) and cooled to RT. THF (1 mL) was added. A solution of S11-1 (277 mg, 1.00 mmol, 1 equiv.) in THF (1 mL) was added dropwise over 5 min. The reaction was stirred at RT for 2 hours. The concentration of the organozinc solution was calculated to be 0.40 M after titration with I\(_2\) (30.7 mg, 0.121 mmol) in THF (2 mL). A separate Schlenk flask was charged with 1-(benzyloxy)-2-(bromomethyl)benzene\(^{13}\) (150 mg, 0.46 mmol, 1 equiv.), Pd(OAc)\(_2\) (5.2 mg, 0.023 mmol, 0.05 equiv. wrt aryl bromide), and SPhos (18.9 mg, 0.046 mmol, 0.1 equiv.). The flask was sealed with a rubber septum under N\(_2\). THF (3 mL) was added. The organozinc solution prepared above (1.2 mL, 0.48 mmol, 1.04 equiv.) was added dropwise at RT. After the addition, the reaction mixture was stirred at 60 °C for 3 h. After cooling to RT, the reaction was quenched with 0.5N HCl (20 mL) and the aqueous layer extracted with diethyl ether (10 mL × 3). The combined organic phase was washed with brine, dried over MgSO\(_4\), filtered, and concentrated on a rotary evaporator. The
crude product was purified by silica gel column chromatography (100% Hexanes - 10% EtOAc/hexanes - 15% EtOAc/hexanes) to give S1l-2 a yellow oil (162 mg, 94%).

**TLC** (15% EtOAc/hexanes): \( R_f = 0.28 \) (visualized by UV)

**1H NMR** (400 MHz, CDCl₃) 1H NMR (400 MHz, CDCl₃) \( \delta 7.35 - 7.24 \) (m, 5H), 7.24 - 7.18 (m, 2H), 7.10 (d, \( J = 7.4 \) Hz, 1H), 6.99 - 6.87 (m, 2H), 6.82 (d, \( J = 8.2 \) Hz, 1H), 6.76 (d, \( J = 7.7 \) Hz, 1H), 5.05 (s, 2H), 4.59 (s, 2H), 1.66 (s, 6H).

**13C{1H} NMR** (151 MHz, CDCl₃) \( \delta 160.6, 157.1, 156.8, 146.4, 137.4, 135.1, 130.9, 129.2, 128.5, 127.8, 127.3, 124.9, 120.9, 115.2, 112.6, 111.9, 105.2, 70.0, 34.3, 25.7.

**IR** (FT-ATR, cm⁻¹, neat) \( \nu_{\text{max}} \) 3063 (m), 3027 (m), 3004 (m), 2954 (m), 2921 (w), 1736 (s), 1608 (m), 1585 (m), 1576 (m), 1496 (m), 1476 (m), 1453 (m), 1385 (m), 1316 (m), 1270 (m), 1273 (m), 1237 (m), 1211 (m), 1161 (w), 1142 (w), 1109 (m), 1179 (m), 1043 (m), 1023 (m), 970 (w), 928 (m), 849 (w), 823 (w), 777 (w), 751 (m), 702 (m), 642 (w), 620 (w).

**HRMS**: Exact mass calculated for \([C_{24}H_{22}O_{4}+H]^+\) requires \( m/z = 375.1591 \), found \( m/z = 375.1602 \) (ESI+).

7-hydroxydibenzo[b,e]oxepin-6(11H)-one (S1l-3): S1l-2 (1.29 g, 3.44 mmol, 1.0 equiv.) was dissolved in MeOH/EtOAc 5:3 (80 mL) and 10% Pd/C (206 mg) was added. The flask was evacuated briefly and back-filled with H₂ from a H₂-filled balloon. The reaction was stirred at RT for 16 h, then purged with N₂ for 15 min. The reaction mixture was filtered through Celite, rinsing with EtOAc. The filtrate was concentrated on a rotary evaporator. The white solid obtained was suspended in PhMe (50 mL) and pTsOH·H₂O (129 mg, 0.68 mmol, 0.2 equiv.) was added. The reaction was refluxed for 22 h, then cooled to RT. After filtration through Celite and rinsing with EtOAc, the filtrate was concentrated on a rotary evaporator. The crude product was purified by silica gel column chromatography (100% hexanes – 10% EtOAc/hexanes) to give S1l-3 as a white solid (740 mg, 95% over 2 steps).

**TLC** (30% EtOAc/hexanes): \( R_f = 0.56 \) (visualized by UV)

**1H NMR** (600 MHz, CDCl₃) \( \delta 10.25 \) (s, 1H), 7.36 (dd, \( J = 8.4, 7.4 \) Hz, 1H), 7.30 - 7.27 (m, 1H), 7.26 - 7.22 (m, 2H), 7.17 (ddd, \( J = 7.4, 5.5, 3.2 \) Hz, 1H), 6.92 (dd, \( J = 8.4, 1.2 \) Hz, 1H), 6.78 (dd, \( J = 7.4, 1.1 \) Hz, 1H), 3.99 (s, 2H).

**13C{1H} NMR** (151 MHz, CDCl₃) \( \delta 168.9, 162.5, 150.2, 144.3, 135.9, 132.2, 128.3 (2C), 126.7, 120.6, 119.0, 116.8, 111.3, 38.1.

**IR** (FT-ATR, cm⁻¹, neat) \( \nu_{\text{max}} \) 3352 (br s), 3089 (w), 3053 (w), 2971 (w), 2922 (w), 1684 (s), 1608 (m), 1582 (m), 1490 (m), 1454 (s), 1355 (m), 1299 (m), 1250 (m), 1231 (m), 1185 (m), 1159 (m), 1103 (m), 1080 (m), 1053 (w), 1011 (w), 952 (w), 912 (w), 893 (w), 840 (w), 791 (m), 761 (m), 732 (w), 698 (w), 679 (w), 650 (w), 610 (w).

**HRMS**: Exact mass calculated for \([C_{14}H_{10}O_{3}+H]^+\) requires \( m/z = 227.0703 \), found \( m/z = 227.0703 \) (ESI+).
7-(benzyloxy)dibenzo[b,e]oxepin-6(11H)-one (1l):
A 50 mL Schlenk tube was charged with S1l-3 (226 mg, 1.0 mmol, 1.0 equiv.), sealed with a rubber septum, evacuated, and back-filled with N₂ (x2). MeCN (5 mL) was added, followed by K₂CO₃ (276 mg, 2.0 mmol, 2.0 equiv.) under a flow of N₂. BnBr (140 μL, 1.18 mmol, 1.2 equiv.) was added neat at RT. The reaction was stirred in a 60 °C oil bath for 13 h, then cooled to RT. 1:1 brine/H₂O (20 mL) was added, and the mixture was transferred to a separatory funnel. The aqueous layer was extracted with EtOAc (15 mL × 3). The combined organic phase was extracted with brine, dried over Na₂SO₄, filtered, and concentrated on a rotary evaporator. The crude product was purified by silica gel column chromatography (100% hexanes – 20% EtOAc/hexanes) to give the product II as a white solid (314 mg, 99%).

TLC (30% EtOAc/hexanes): Rf = 0.41 (visualized by UV)

¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, J = 7.3 Hz, 2H), 7.41 (dd, J = 8.1, 6.7 Hz, 2H), 7.37 – 7.28 (m, 3H), 7.25 – 7.20 (m, 3H), 7.11 (ddd, J = 7.3, 6.2, 2.4 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H), 6.86 (d, J = 7.6 Hz, 1H), 5.18 (s, 2H), 3.93 (s, 2H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 162.8, 158.8, 151.6, 144.7, 137.9, 133.2, 132.6, 130.3, 128.7, 128.2 (2C), 128.0, 127.0, 125.5, 121.1, 119.0, 117.7, 111.1, 70.9, 37.4.

IR (FT-ATR, cm⁻¹, neat) νmax 3092 (w), 3069 (w), 3033 (w), 2924 (w), 2902 (w), 2878 (w), 2846 (w), 1742 (s), 1598 (m), 1581 (m), 1482 (m), 1450 (m), 1388 (w), 1289 (m), 1263 (m), 1227 (s), 1181 (m), 1154 (w), 1105 (m), 1085 (m), 1069 (m), 1043 (m), 1019 (m), 964 (w), 908 (w), 872 (w), 826 (w), 767 (m), 737 (m), 724 (m), 691 (m), 652 (w), 639 (w), 616 (w).

HRMS: Exact mass calculated for C₂₁H₁₆O₃ requires m/z = 316.1099, found m/z = 316.1100 (EI).

7-methoxydibenzo[b,e]oxepin-6(11H)-one (1m):
A 50 mL Schlenk tube was charged with S1l-3 (226 mg, 1.0 mmol, 1.0 equiv.), sealed with a rubber septum, evacuated, and back-filled with N₂ (x2). MeCN (5 mL) was added, followed by K₂CO₃ (276 mg, 2.0 mmol, 2.0 equiv.) under a flow of N₂. MeI (80 μL, 1.3 mmol, 1.3 equiv.) was added neat at RT. The reaction was stirred in a 60 °C oil bath for 13 h, then cooled to RT. 1:1 brine/H₂O (20 mL) was added, and the mixture was transferred to a separatory funnel. The aqueous layer was extracted with EtOAc (15 mL × 3). The combined organic phase was extracted with brine, dried over Na₂SO₄, filtered, and concentrated on a rotary evaporator. The crude product was purified by silica gel column chromatography (100% hexanes – 20% – 25% EtOAc/hexanes) to give the product 1m as a white solid (220 mg, 92% yield).
**TLC (30% EtOAc/hexanes):** R<sub>f</sub> = 0.32 (visualized by UV)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.32 (t, J = 8.0 Hz, 1H), 7.19 (qd, J = 6.6, 2.8 Hz, 3H), 7.07 (td, J = 7.0, 2.1 Hz, 1H), 6.83 (t, J = 8.7 Hz, 2H), 3.88 (s, 2H), 3.85 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)** δ 163.0, 159.7, 150.7, 144.6, 133.3, 133.0, 128.2 (2C), 125.6, 120.4, 118.7, 116.9, 110.6, 56.3, 36.8.

**IR (FT-ATR, cm<sup>-1</sup>, neat) ν<sub>max</sub>** 3092 (w), 3024 (w), 2981 (w), 2948 (w), 2846 (w), 1745 (s), 1594 (m), 1471 (m), 1454 (m), 1441 (m), 1270 (m), 1224 (s), 1178 (m), 1155 (w), 1102 (m), 1069 (m), 1040 (m), 1020 (m), 961 (w), 905 (w), 872 (w), 820 (w), 777 (m), 738 (w), 705 (w), 675 (w), 639 (w).

**HRMS:** Exact mass calculated for [C<sub>15</sub>H<sub>12</sub>O<sub>3</sub>]+ requires m/z = 241.0859, found m/z = 241.0860. (ESI+).

### 6.1.9. Synthesis of substrate 1o

![Chemical Structure](image)

The starting material **S1o-1** was synthesized according to a reported procedure.<sup>14</sup>

A three-neck round bottom flask was charged with a stir bar, 10% Pd/C (100 mg), **S1o-1** (1.14 g, 4.52 mmol), THF (5.0 mL), and dichloromethane (5.0 mL). The flask was put under a H<sub>2</sub> atmosphere (H<sub>2</sub>-filled balloon). The reaction mixture was stirred at rt for 48 h. The black solids were filtered off using a pad of Celite and the filtrate was concentrated by rotary evaporator. The residue was loaded directly onto a silica gel column (3 × 30 cm, packed in hexanes). The column was eluted with 90/10 hexanes/ethyl acetate followed by 80/20 hexanes/ethyl acetate. The product-containing fractions were combined, and the solvents were removed by rotary evaporator. The residue was dried under vacuum using an oil pump to give **S1o-2** as a white solid (0.521 g, 2.15 mmol, 48%).

**TLC (80/20 hexanes/ethyl acetate):** R<sub>f</sub> = 0.60 (visualized by UV)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.21 (d, J = 7.8 Hz, 1H), 7.99 (br s, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.42-7.33 (m, 2H), 7.23-7.15 (m, 2H), 6.98 (d, J = 7.6 Hz, 1H), 6.90 (t, J = 7.4 Hz, 1H), 3.23 – 3.14 (m, 2H), 2.96 – 2.87 (m, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)** δ 170.9, 154.0, 145.1, 133.8, 132.6, 131.8, 130.6, 128.2, 127.3, 126.9 (2 s), 121.0, 116.3, 36.8, 34.2.

**IR (FT-ATR, cm<sup>-1</sup>, neat) ν<sub>max</sub>** 3332 (s), 3158 (m), 3079 (m), 2960 (w), 2862 (w), 2658 (w), 1699 (s), 1585 (m), 1489 (m), 1460 (w), 1407 (w), 1338 (w), 1299 (m), 1270 (m), 1243 (m), 1217 (m), 1165 (w), 1165 (w), 1138 (w), 1105 (w), 1076 (w), 1043 (w), 1003 (w), 931 (w), 836 (m), 793 (m), 751 (s), 702 (w), 649 (w), 620 (w).

**HRMS:** Exact mass calculated for C<sub>15</sub>H<sub>14</sub>O<sub>3</sub> requires m/z = 242.0943, found m/z = 242.0939 (EI).
**11,12-Dihydro-6H-dibenzo[b,f]oxocin-6-one (1o):**

A round bottom flask was charged with a stir bar, **S1o-2** (0.521 g, 2.15 mmol), DMAP (0.026 g, 0.215 mmol, 10 mol%), and dichloromethane (21.5 mL). DIC (0.35 mL, 0.285 g, 2.25 mmol, 1.05 equiv) was then added with stirring. The solution was stirred at room temperature for 24 h and was then concentrated using rotary evaporator to 10 mL. The residue was then loaded directly onto a silica gel column (3 × 25 cm, packed in hexanes). The column was eluted with dichloromethane. The product-containing fractions were combined. The solvents were removed by rotary evaporator and the residue was dried under vacuum using an oil pump to give 1o as a white solid (0.173 g, 0.77 mmol, 36%). NMR data match with previously reported values.\textsuperscript{15}

**TLC** (80/20 hexanes/ethyl acetate): \( R_f = 0.50 \) (visualized by UV)

**\(^1\)H NMR** (600 MHz, CDCl\(_3\)) \( \delta \) 7.33 (dd, \( J = 7.6, 1.4 \) Hz, 1H), 7.25 (td, \( J = 7.8, 1.6 \) Hz, 1H), 7.16 – 7.12 (m, 2H), 7.10 – 7.04 (m, 2H), 7.04 – 6.98 (m, 2H), 3.25 (t, \( J = 7.4 \) Hz, 2H), 3.17 (t, \( J = 7.4 \) Hz, 2H).

**\(^{13}\)C\{\(^1\)H\} NMR** (151 MHz, CDCl\(_3\)) \( \delta \) 171.0, 151.9, 137.1, 132.3, 132.1, 131.3, 132.1, 129.3, 127.9, 127.8, 126.9, 126.6, 122.1, 32.8, 30.6.

6.2. General procedure and characterization data for decarbonylation products

**General procedure:** An oven-dried 2-dram vial was charged with a magnetic stir bar, a lactone 1 (0.200 mmol), and the ligand **meso-L2** (0.023 g, 0.040 mmol, 20 mol%). The vial was brought into a glovebox, then Ni(cod)\(_2\) (0.011 g, 0.040 mmol, 20 mol%), CsF (0.030 g, 0.200 mmol, 1.0 equiv.), and toluene (2.00 mL) were added. The vial was sealed and brought outside and placed in an aluminum heating block preheated at 150 °C. The mixture was stirred (700 rpm) for 24 h at 150 °C. After cooling to room temperature, the mixture was directly loaded onto a silica gel column and chromatographed as described below for each compound. The product-containing fractions were collected. The solvent was evaporated by rotary evaporator and the residue was dried under vacuum using an oil pump to give the product.

**9H-Xanthene (2a):** Compound 2a was isolated as a white solid (0.0306 g, 0.17 mmol, 85%) from the reaction of 1a (0.0440 g, 0.20 mmol). A 1.00 mmol scale reaction of 1a (0.220 g, 1.00 mmol) gave 2a in 58% yield (0.106 g, 0.58 mmol). Chromatography conditions: silica gel column (1 × 20 cm), packed in hexanes, eluted with 200 mL of hexanes. NMR data match with previously reported values.\textsuperscript{16}

**TLC** (100% hexanes): \( R_f = 0.50 \) (visualized by UV)

**\(^1\)H NMR** (600 MHz, CDCl\(_3\)) \( \delta \) 7.21-7.16 (m, 4H), 7.05-7.01 (m, 4H), 4.06 (s, 2H).

**\(^{13}\)C\{\(^1\)H\} NMR** (151 MHz, CDCl\(_3\)) \( \delta \) 152.1, 129.1, 127.8, 123.1, 120.7, 116.6.
Methyl 7-(trifluoromethyl)-9H-xanthene-2-carboxylate (2b): Compound 2b was isolated as a white solid (0.0331 g, 0.11 mmol, 54%) from the reaction of 1b (0.067 g, 0.200 mmol). Chromatography conditions: silica gel column (1 × 20 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 90/10 hexanes/ethyl acetate.

TLC (90/10 hexanes/ethyl acetate): R_f = 0.30 (visualized by UV).

1H NMR (600 MHz, CDCl_3) δ 7.90 – 7.88 (m, 2H), 7.48 – 7.43 (m, 2H), 7.12 (d, J = 8.4 Hz, 1H), 7.07 (d, J = 9.1 Hz, 1H), 4.10 (s, 2H), 3.91 (s, 3H).

13C{1H} NMR (151 MHz, CDCl_3) δ 166.5, 154.8, 153.8, 131.1, 129.9, 126.6 (q, J = 3.9 Hz), 125.9 (q, J = 33.0 Hz), 125.7, 125.3 (q, J = 3.9 Hz), 124.1 (q, J = 271.2 Hz), 120.6, 119.7, 117.2, 116.8, 52.2, 27.5.

19F{1H} NMR (565 MHz, CDCl_3) δ –61.89.

IR (FT-ATR, cm⁻¹, neat) ν_max 3003 (w), 2960 (w), 2928 (w), 2855 (w), 1716 (s), 1614 (m), 1585 (w), 1496 (m), 1440 (m), 1421 (m), 1332 (s), 1270 (s), 1204 (m), 1181 (m), 1161 (s), 1122 (s), 1073 (s), 990 (w), 961 (w), 954 (w), 896 (w), 846 (w), 830 (m), 810 (w) 767 (m), 731 (w), 708 (w), 656 (w), 616 (w).

HRMS: Exact mass calculated for C_{16}H_{11}F_{3}O_{3} requires m/z = 308.0660, found m/z = 308.0655. (ESI+).

2,7-dimethoxy-9H-xanthene (2c):

Compound 2c was isolated as a white solid (0.0157 g, 0.065 mmol, 32%) from the reaction of 1c (0.054 g, 0.200 mmol). Chromatography conditions: silica gel column (1 × 20 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 90/10 hexanes/ethyl acetate. NMR data match with previously reported values.¹⁷

TLC (90/10 hexanes/ethyl acetate): R_f = 0.25 (visualized by UV).

1H NMR (600 MHz, CDCl_3) δ 6.96 (d, J = 8.9 Hz, 1H), 6.75 (dd, J = 8.9, 3.1 Hz, 1H), 6.69 (d, J = 3.0 Hz, 1H), 3.79 (s, 3H).

13C{1H} NMR (151 MHz, CDCl_3) δ 155.2, 146.4, 120.9, 117.2, 113.5, 113.4, 55.8, 28.9.

Methyl 7-methoxy-9H-xanthene-2-carboxylate (2d):

Compound 2d was isolated as a white solid (0.0362 g, 0.13 mmol, 67%) from the reaction of 1d (0.060 g, 0.200 mmol). Chromatography conditions: silica gel column (2 × 25 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 80/20 hexanes/ethyl acetate. TLC (80/20 hexanes/ethyl acetate): R_f = 0.50 (bright blue spot visualized by UV).

1H NMR (600 MHz, CDCl_3) δ 7.86 (m, 2H), 7.02 (d, J = 8.4 Hz, 1H), 6.97 (d, J = 8.9 Hz, 1H), 6.75 (d, J = 9.1 Hz, 1H), 6.68 (s, 1H), 4.04 (s, 2H), 3.89 (s, 3H), 3.78 (s, 3H).

13C{1H} NMR (151 MHz, CDCl_3) δ 166.8, 155.8, 145.4, 131.1, 129.6, 124.6, 120.7, 119.9, 117.4, 116.5, 113.8, 113.4, 55.8, 52.1, 28.0.
IR (FT-ATR, cm\(^{-1}\), neat) \(\nu_{\text{max}}\) 3016 (w), 2960 (m), 2928 (m), 2855 (m), 1713 (s), 1621 (m), 1581 (m), 1493 (s), 1460 (m), 1427 (m), 1312 (m), 1292 (s), 1266 (s), 1247 (m), 1211 (m), 1194 (m), 1178 (m), 1158 (w), 1122 (m), 1046 (m), 977 (w), 957 (w), 905 (w), 839 (m), 823 (m), 770 (m), 743 (w), 708 (w), 681 (w), 626 (w), 606 (w).

HRMS: Exact mass calculated for \(\text{C}_{16}\text{H}_{14}\text{O}_{4}\) requires \(m/z = 270.0887\), found \(m/z = 270.0889\) (EI).

Methyl 9\(H\)-xanthene-3-carboxylate (2f): Compound 2f was isolated as an off-white solid (0.0151 g, 0.063 mmol, 63%) from the reaction of 1f (0.0270 g, 0.10 mmol). Chromatography conditions: silica gel column (1 × 20 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 90/10 hexanes/ethyl acetate.

TLC (90:10 hexanes/ethyl acetate): \(R_f = 0.60\) (visualized by UV)

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.72 (s, 1H), 7.70 (d, \(J = 7.9\) Hz, 1H), 7.24-7.19 (m, 2H), 7.17 (d, \(J = 7.5\) Hz, 1H), 7.08-7.02 (m, 2H), 4.09 (s, 2H), 3.92 (s, 3H).

\(^{13}\)C\(^{\text{\text{\textsuperscript{1}\text{H}}}\}) NMR (151 MHz, CDCl\(_3\)) \(\delta\) 166.7, 152.0, 151.8, 130.0, 129.1, 129.0, 128.1, 126.1, 124.1, 123.5, 119.9, 117.9, 116.7, 52.3, 28.2.

IR (FT-ATR, cm\(^{-1}\), neat) \(\nu_{\text{max}}\) 3072 (w), 3036 (w), 2997 (w), 2954 (m), 2924 (m), 2856 (m), 1710 (s), 1670 (w), 1601 (w), 1572 (m), 1508 (w), 1487 (m), 1457 (m), 1434 (m), 1296 (s), 1243 (m), 1213 (9m), 1191 (m), 1189 (m), 1149 (w), 1129 (m), 1092 (m), 1033 (w), 987 (m), 958 (m), 895 (w), 869 (w), 849 (w), 813 (w), 809 (w), 770 (s), 715 (w), 688 (w).

HRMS: Exact mass calculated for \(\text{C}_{15}\text{H}_{12}\text{O}_{3}\) requires \(m/z = 240.0786\), found \(m/z = 240.0773\) (EI).

3-(Trifluoromethyl)-9\(H\)-xanthene (2g): Compound 2g was isolated as a white solid (0.0168 g, 0.068 mmol, 67%) from the reaction of 1g (0.014 g, 0.10 mmol). Chromatography conditions: silica gel column (1 × 20 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 90/10 hexanes/ethyl acetate. \(^1\)H NMR data match with previously reported values.\(^{18}\)

TLC (100% hexanes): \(R_f = 0.50\) (visualized by UV)

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.31 (s, 1H), 7.27 (m, 2H), 7.22 (t, \(J = 7.8\) Hz, 1H), 7.18 (d, \(J = 7.5\) Hz, 1H), 7.07 (dd, \(J = 8.1, 5.2\) Hz, 2H), 4.09 (s, 2H).

\(^{19}\)F\(^{\text{\text{\textsuperscript{1}\text{H}}}\}) NMR (565 MHz, CDCl\(_3\)) \(\delta\) 62.6.

\(^{13}\)C\(^{\text{\text{\textsuperscript{1}\text{H}}}\}) NMR (151 MHz, CDCl\(_3\)) \(\delta\) 152.2, 151.6, 130.4 (q, \(J = 32.9\) Hz), 129.6, 129.0, 128.2, 124.7, 124.0 (q, \(J = 272.2\) Hz), 123.7, 119.8, 119.6 (q, \(J = 3.7\) Hz), 116.7, 114.0 (q, \(J = 4.0\) Hz), 28.0

3-(benzyloxy)-9\(H\)-xanthene (2h): Compound 2h was isolated as a white solid (0.023 g, 0.080 mmol, 67%) from the reaction of 1h (0.032 g, 0.100 mmol). Chromatography conditions: silica
gel column (1 × 20 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 90/10 hexanes/ethyl acetate.

**TLC** (100% hexanes): R$_f$ = 0.40 (visualized by UV)

**$^1$H NMR** (600 MHz, CDCl$_3$) δ 7.46 (d, J = 7.3 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.37 – 7.33 (m, 1H), 7.23 – 7.16 (m, 2H), 7.09 – 7.00 (m, 3H), 6.71 (m, 2H), 5.08 (s, 2H), 4.00 (s, 2H).

**$^{13}$C{[H] NMR** (151 MHz, CDCl$_3$) δ 156.9, 152.6, 151.6, 129.5, 127.7, 127.6, 123.1, 120.9, 116.6, 109.5, 109.1, 104.2, 55.8, 22.8.

**IR** (FT-ATR, cm$^{-1}$, neat) ν$_{max}$ 3079 (w), 3000 (w), 2974 (m), 1650 (m), 1611 (s), 1506 (w), 1483 (w), 1470 (m), 1450 (m), 1361 (w), 1322 (m), 1277 (m), 1177 (w), 1161 (s), 1099 (w), 1076 (s), 997 (s), 958 (m), 921 (m), 875 (w), 855 (w), 838 (w), 787 (w), 761 (m), 708 (w), 668 (w), 633 (w).

**HRMS**: Exact mass calculated for C$_{20}$H$_{16}$O$_2$ requires m/z = 288.1145, found m/z = 288.1150 (EI).

**3-(methoxymethoxy)-9H-xanthe (2i):** Compound 2i was isolated as a white solid (0.020 g, 0.083 mmol, 41%) from the reaction of 1i (0.054 g, 0.200 mmol). Chromatography conditions: silica gel column (1 × 20 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 90/10 hexanes/ethyl acetate.

**TLC** (90/10 hexanes/ethyl acetate): R$_f$ = 0.30 (visualized by UV)

**$^1$H NMR** (600 MHz, CDCl$_3$) δ 7.21 – 7.14 (m, 2H), 7.07 (d, J = 8.4 Hz, 1H), 7.05 – 7.01 (m, 2H), 6.79 (d, J = 2.5 Hz, 1H), 6.74 (dd, J = 8.3, 2.5 Hz, 1H), 5.17 (s, 2H), 4.00 (s, 2H), 3.50 (s, 3H).

**$^{13}$C{[H] NMR** (151 MHz, CDCl$_3$) δ 156.9, 152.6, 151.9, 129.5, 127.7, 123.1, 120.8, 116.6, 114.0, 111.6, 104.5, 94.7, 56.1, 27.4.

**IR** (FT-ATR, cm$^{-1}$, neat) ν$_{max}$ 3079 (w), 3000 (w), 2974 (w), 2928 (w), 2852 (w), 2829 (w), 1650 (m), 1611 (s), 1506 (w), 1483 (w), 1470 (m), 1450 (m), 1361 (w), 1322 (m), 1277 (m), 1177 (w), 1161 (s), 1099 (w), 1076 (s), 997 (s), 958 (m), 921 (m), 875 (w), 855 (w), 838 (w), 787 (w), 761 (m), 708 (w), 668 (w), 633 (w).

**HRMS**: Exact mass calculated for C$_{15}$H$_{14}$O$_3$ requires m/z = 242.0943, found m/z = 242.0945 (EI).

**1-(methoxy)-9H-xanthene (2k):** Compound 2k was isolated as a white solid (0.023 g, 0.11 mmol, 55%) from the reaction of 1k (0.048 g, 0.200 mmol). Chromatography conditions: silica gel column (1 × 20 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 90/10 hexanes/ethyl acetate. NMR data match with previously reported values.$^{19}$

**TLC** (90/10 hexanes/ethyl acetate): R$_f$ = 0.40 (visualized by UV)

**$^1$H NMR** (600 MHz, CDCl$_3$) δ 7.72 – 7.11 (m, 3H), 7.05 – 6.99 (m, 2H), 6.69 (d, J = 8.2 Hz, 1H), 6.56 (d, J = 8.2, 1H), 3.96 (s, 2H), 3.87 (s, 3H).

**$^{13}$C{[H] NMR** (151 MHz, CDCl$_3$) δ 157.7, 152.5, 151.6, 129.5, 127.7, 127.5, 123.0, 120.2, 116.5, 109.5, 109.1, 104.2, 55.8, 22.8.
4-Benzylxoy-9H-xanthene (2l): Compound 2l was isolated as a white solid (0.026 g, 0.090 mmol, 45%) from the reaction of 1l (0.063 g, 0.200 mmol). Chromatography conditions: silica gel column (1 × 20 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 90/10 hexanes/ethyl acetate.

TLC (90/10 hexanes/ethyl acetate): Rf = 0.30 (visualized by UV).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.50 (d, J = 7.1 Hz, 2H), 7.39 (t, J = 7.3 Hz, 2H), 7.32 – 7.15 (m, 3H), 7.09 – 7.00 (m, 1H), 6.91 (t, J = 7.8 Hz, 2H), 6.82 (dd, J = 16.7, 6.2 Hz, 2H), 5.22 (2, 4H), 4.06 (s, 2H).

$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) δ 152.0, 147.3, 142.6, 137.4, 128.9, 128.7, 128.0, 127.7, 127.4, 123.2, 122.6, 122.0, 121.5, 120.7, 117.0, 113.5, 71.7, 28.1.

IR (FT-ATR, cm$^{-1}$, neat) v$_{\text{max}}$ 3065 (w), 3032 (w), 2954 (w), 2924 (w), 2879 (w), 2852 (w), 2826 (w), 1582 (m), 1483 (m), 1463 (m), 1391 (w), 1335 (w), 1302 (w), 1273 (m), 1237 (s), 1204 (m), 1112 (m), 1085 (w), 1062 (m), 1032 (w), 967 (w), 883 (w), 840 (w), 747 (s), 728 (w), 695 (w), 623 (w).

HRMS: Exact mass calculated for C$_{20}$H$_{16}$O$_2$ requires m/z = 288.1145, found m/z = 288.1151 (EI).

4-Methoxy-9H-xanthene (2m): Compound 2m was isolated as a white solid (0.021 g, 0.097 mmol, 48%) from the reaction of 1m (0.048 g, 0.200 mmol). Chromatography conditions: silica gel column (1 × 20 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 200 mL of 90/10 hexanes/ethyl acetate. NMR data match with previously reported values.$^{20}$

TLC (90/10 hexanes/ethyl acetate): Rf = 0.25 (visualized by UV).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.23 – 7.14 (m, 3H), 7.03 (ddd, J = 7.6, 5.9, 2.6 Hz, 1H), 7.00 – 6.94 (m, 1H), 6.82 (dd, J = 8.2, 1.5 Hz, 1H), 6.78 (ddt, J = 7.7, 1.6, 0.9 Hz, 1H), 4.06 (t, J = 0.9 Hz, 2H), 3.94 (s, 3H).

$^{13}$C{$^1$H} NMR (151 MHz, CDCl$_3$) δ 151.9, 148.2, 141.7, 128.9, 127.7, 123.3, 122.7, 121.7, 120.8, 120.5, 117.0, 110.3, 56.3, 28.0.

10H-[1,3]Dioxolo[4,5-b]xanthene (2n): Compound 2n was isolated as an off-white solid (0.016 g, 0.071 mmol, 36%) from the reaction of 1n (0.052 g, 0.20 mmol). Chromatography conditions: silica gel column (1 × 20 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 90/10 hexanes/ethyl acetate. NMR data match with previously reported values.$^{21}$

TLC (90/10 hexanes/ethyl acetate): Rf = 0.40 (visualized by UV).

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.18 (t, J = 7.2 Hz, 1H), 7.14 (d, J = 8.1 Hz, 1H), 7.01 (t, J = 7.4 Hz, 2H), 6.60 (d, J = 0.9 Hz, 2H), 5.93 (s, 2H), 5.39 (s, 2H), 3.96 (s, 2H).
\[ ^{13}C\{^1H\}\text{NMR (151 MHz, CDCl}_3\} \delta 152.1, 146.9, 146.6, 143.4, 128.9, 127.7, 123.0, 120.3, 116.4, 112.2, 107.6, 101.3, 98.7, 28.2. \]

**10,11-Dihydrodibenzo[b,f]oxepine (2o):** Compound 2o was isolated as a colorless oil (0.0166 g, 0.085 mmol, 42%) from the reaction of 1o (0.0440 g, 0.20 mmol). Chromatography conditions: silica gel column (1 × 15 cm), packed in hexanes, eluted with 200 mL of hexanes. \(^1\)H NMR data match with previously reported values.\(^{22}\)

TLC (100% hexanes): \(R_f = 0.50\) (visualized by UV)

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta 7.21\)–7.16 (m, 4H), 7.14 (d, \(J = 7.8\) Hz, 2H), 7.04–6.99 (apparent t, \(J = 7.0\) Hz, 2H), 3.16 (s, 4H).

\(^{13}C\{^1H\}\text{NMR (101 MHz, CDCl}_3\) \(\delta 157.2, 132.0, 130.5, 127.4, 124.0, 121.2, 31.3. \)

### 6.3. Unsuccessful substrates
Substrates 1p, 1q, and 1r were synthesized according to literature methods.\(^{23-25}\) Applying the general procedure for decarbonylation (section 6.2) to 1p, 1q, and 1r did not lead to the corresponding ether products.

#### Decarbonylation of 1s
Substrate 1s was synthesized according to a literature procedure.\(^{26}\)

An oven dried 2-dram vial was charged with a magnetic stir bar, 1s (8.1 mg, 0.050 mmol), \textit{meso-L2} (5.7 mg, 0.010 mmol, 20 mol%). The vial was brought into a glovebox, then Ni(cod)$_2$ (2.8 mg, 0.010 mmol, 20 mol%), CsF (7.6 mg, 0.050 mmol, 1.0 equiv.), and toluene (0.50 mL) were added. The vial was sealed and brought outside and placed in an aluminum heating block preheated at 150 °C. The mixture was stirred for 24 h. After cooling to room temperature, the reaction mixture was transferred to a 40-mL vial using CH\(_2\)Cl\(_2\) and ethyl acetate. The solvents were then removed by rotary evaporator. The residue was dissolved in CDCl\(_3\). \(^1\)H NMR spectrum of the sample was obtained and showed full conversion of 1s along with signals for \(E\)-2s and \(Z\)-2s in 82:18 ratio. The NMR spectrum is provided on page S88 and matches with a previously reported spectrum of a 88:12 mixture of \(E\)-2s and \(Z\)-2s.\(^{27}\)
7. Experimental procedures for Figure 8

7.1. Synthesis of xanthone 7 from Quinizarin

Dimethylquinizarin 4 was synthesized from quinizarin following a reported procedure.\textsuperscript{28}

\textbf{1,4-Dimethoxydibenzob[e]oxepine-6,11-dione (5):} Compound 5 (0.623 g, 2.19 mmol, 75\%) was obtained as a yellow solid from dimethylquinizarin 4 (0.784 g, 2.92 mmol) following a literature procedure.\textsuperscript{28} NMR data match with previously reported values.\textsuperscript{28}

\textbf{TLC (100\% hexanes):} R\textsubscript{f} = 0.50 (visualized by UV)

\textbf{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})} \(\delta\) 8.15 (d, \(J = 7.9\) Hz, 1H), 7.76 - 7.62 (m, 3H), 7.00 (d, \(J = 8.9\) Hz, 1H), 6.75 (d, \(J = 8.9\) Hz, 1H), 3.89 (s, 3H), 3.81 (s, 3H).

\textbf{\textsuperscript{13}C\textsuperscript{1}H NMR (151 MHz, CDCl\textsubscript{3})} \(\delta\) 191.2, 163.2, 150.1, 145.0, 142.6, 139.3, 134.5, 133.3, 132.6, 127.4, 124.8, 124.1, 116.1, 109.6, 57.0, 56.9.

\textbf{1,4-dimethoxydibenzob[e]oxepin-6(11H)-one (6):} A Schlenk flask was charged with a stir bar and the lactone 5 (0.142 g, 0.500 mmol). The flask was put under an N\textsubscript{2} atmosphere and TFA (0.50 mL) was added. The solution was cooled to 0 °C in an ice bath and Et\textsubscript{3}SiH (0.18 mL, 0.128 g, 1.10 mmol, 2.2 equiv) was added dropwise. The solution was then warmed to room temperature and stirred for 12 h. The reaction was quenched with a saturated solution of NaHCO\textsubscript{3} (10 mL) and diluted with dichloromethane (10 mL). The mixture was transferred to a separatory funnel and the organic layer was collected. The aqueous layer was extracted with dichloromethane (2 × 10 mL). The combined organic fractions were dried with
Na$_2$SO$_4$ and concentrated using a rotary evaporator. The residue was loaded directly onto a silica gel column (1 × 20 cm, packed in 50/50 hexanes/ethyl acetate). The column was eluted with 50/50 hexanes/ethyl acetate and the product-containing fractions were collected. The solvents were removed by rotary evaporation and the residue was dried under vacuum using an oil pump to give 6 as a white solid (0.124 g, 0.46 mmol, 91%).

**TLC** (85/15 hexanes/ethyl acetate): $R_f = 0.50$ (visualized by UV)

**$^1$H NMR** (600 MHz, CDCl$_3$) δ 7.94 – 7.85 (d, $J = 7.9$ Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 1H), 7.35 – 7.26 (m, 2H), 6.72 (d, $J = 9.0$ Hz, 1H), 6.63 (d, $J = 9.0$ Hz, 1H), 4.07 (s, 2H), 3.83 (s, 3H), 3.81 (s, 3H).

**$^{13}$C($^1$H) NMR** (151 MHz, CDCl$_3$) δ 165.6, 149.5, 145.1, 143.1, 140.6, 133.3, 132.7, 128.3, 127.5, 127.3, 123.8, 110.5, 107.8, 56.5, 56.4, 28.8.

**IR** (FT-ATR, cm$^{-1}$, neat) $v_{max}$ 3020 (w), 2997 (w), 2957 (w), 2937 (w), 2836 (w), 1733 (s), 1673 (w), 1608 (w), 1499 (s), 1453 (m), 1319 (w), 1273 (m), 1243 (m), 1213 (m), 1181 (m), 1119 (m), 1089 (m), 1066 (m), 1036 (w), 981 (w), 954 (w), 793 (m), 777 (w), 754 (w), 741 (w), 718 (m), 646 (w), 620 (w).

**HRMS**: Exact mass calculated for [C$_{16}$H$_{14}$O$_4$+H]$^+$ requires m/z = 271.0965, found m/z = 271.0965 (ES$I^+$).

**1,4-dimethoxy-9H-xanthene (S4-1)**:

An oven-dried 2 dram vial was charged with a magnetic stir bar, 6 (0.054 g, 0.200 mmol), and the ligand meso-L2 (0.023 g, 0.040 mmol, 20 mol%). The vial was brought into a glovebox, then Ni(cod)$_2$ (0.011 g, 0.040 mmol, 20 mol%), CsF (0.030 g, 0.200 mmol, 1.0 equiv.), and toluene (2.00 mL) were added. The vial was sealed and brought outside and placed in an aluminum heating block preheated at 150 °C. The mixture was stirred (700 rpm) for 24 h at 150 °C. After cooling to room temperature, the mixture was directly loaded onto a silica gel column (1 × 20 cm, packed in hexanes). The column was eluted with 100 mL of hexanes, 50 mL of 90/10 hexanes/ethyl acetate followed by 50 mL 80/20 hexanes/ethyl acetate. The product containing fractions were collected. The solvent was evaporated by rotary evaporator and the residue was dried under vacuum using an oil pump to give the product S4-1 as a white solid (0.0251 g, 0.104 mmol, 52%).

**TLC** (80/20 hexanes/ethyl acetate): $R_f = 0.50$ (visualized by UV)

**$^1$H NMR** (400 MHz, CDCl$_3$) δ 7.21 – 7.15 (m, 3H), 7.03 (t, $J = 7.2$ Hz, 1H), 6.76 (d, $J = 8.8$ Hz, 1H), 6.47 (d, $J = 8.8$ Hz, 1H), 3.96 (s, 2H), 3.90 (s, 3H), 3.83 (s, 3H).

**$^{13}$C($^1$H) NMR** (101 MHz, CDCl$_3$) δ 151.4, 151.3, 142.4, 142.1, 129.3, 127.7, 123.3, 119.9, 117.2, 110.9, 110.3, 102.9, 56.9, 55.8, 23.0.

**IR** (FT-ATR, cm$^{-1}$, neat) $v_{max}$ 3066 (w), 3020 (w), 2934 (m), 2852 (w), 2839 (w), 1608 (w), 1586 (m), 1499 (s), 1463 (m), 1312 (w), 1258 (s), 1240 (s), 1197 (w), 1115 (m), 1095 (s), 947 (w), 879 (w), 793 (w), 777 (m), 751 (m), 728 (w), 718 (w), 679 (w), 623 (w).

**HRMS**: Exact mass calculated for C$_{15}$H$_{14}$O$_3$ requires m/z = 242.0943, found m/z = 242.0941 (EI).
1,4-dimethoxy xanthone (7):
A round bottom flask was charged with a stir bar, **S4-1** (0.0251 g, 0.104 mmol), and acetone (3.0 mL). The resulting solution was stirred vigorously and KMnO₄ (0.082 g, 0.52 mmol, 5.0 equiv) was added at once. After stirring at room temperature for 1 h, the brown solid was filtered off using a pad of Celite. The solid was washed with 10 mL of acetone and the pink filtrate was concentrated by rotary evaporator to give a brown solid. Dichloromethane (10 mL) was added, and the mixture was filtered through a pad of Celite. The filtrate was concentrated by rotary evaporator and the residue was dried under vacuum using an oil pump to give 7 as an orange solid (0.0226 g, 0.0881 mmol, 85%).

**TLC** (80/20 hexanes/ethyl acetate): \( R_f = 0.35 \) (visualized by UV)

**¹H NMR** (600 MHz, CDCl₃) \( \delta \) 8.31 (dd, \( J = 8.0, 1.7 \) Hz, 1H), 7.68 (ddd, \( J = 8.7, 7.1, 1.8 \) Hz, 1H), 7.54 (d, \( J = 8.4 \) Hz, 1H), 7.35 (ddd, \( J = 8.1, 7.1, 1.2 \) Hz, 1H), 7.19 (d, \( J = 9.0 \) Hz, 1H), 6.71 (d, \( J = 9.0 \) Hz, 1H), 3.98 (s, 3H), 3.97 (s, 3H).

**¹³C{¹H} NMR** (151 MHz, CDCl₃) \( \delta \) 176.7, 155.0, 154.0, 148.1, 142.4, 134.4, 126.9, 124.2, 123.0, 117.7, 116.7, 104.5, 57.1, 56.7.

**IR** (FT-ATR, cm⁻¹, neat) \( \nu_{max} \) 3010 (w), 2961 (m), 2931 (m), 2889 (m), 1663 (s), 1598 (s), 1578 (m), 1489 (s), 1466 (s), 1440 (m), 1355 (w), 1316 (s), 1260 (s), 1287 (m), 1187 (w), 1145 (w), 1089 (m), 1072 (m), 974 (m), 934 (w), 892 (w), 865 (w), 800 (m), 754 (m), 728 (w), 682 (w), 633 (w).

**HRMS**: Exact mass calculated for [C₁₅H₁₂O₄+H]⁺ requires m/z = 257.0808, found m/z = 257.0809. (ESI+).

7.2. Synthesis of dibenzofuran 10 from fluorene

**Fluorenone (S8-1)**: Fluorenone (0.178 g, 0.98 mmol, 98%) was obtained as a yellow solid from fluorene (0.166 g, 1.00 mmol) following a literature procedure²⁹ with the reaction time increased to 24 h. NMR data match with previously reported values.²⁹

**TLC** (80/20 hexanes/ethyl acetate): \( R_f = 0.45 \) (visualized by UV)

**¹H NMR** (400 MHz, CDCl₃) \( \delta \) 7.61 (d, \( J = 7.3 \) Hz, 2H), 7.43 (d, \( J = 5.1 \) Hz, 4H), 7.25 (dq, \( J = 8.6, 4.4 \) Hz, 2H).

**¹³C{¹H} NMR** (151 MHz, CDCl₃) \( \delta \) 193.8, 144.3, 134.7, 134.1, 129.0, 124.2, 120.3.
Benzocoumarin (9): Lactone 9 (0.118 g, 0.60 mmol, 60%) was obtained as a white solid from s8-1 (0.180 g, 1.00 mmol) following a literature procedure.\textsuperscript{30} NMR data match with previously reported values.\textsuperscript{30}

TLC (80/20 hexanes/ethyl acetate): $R_f = 0.30$ (visualized by UV)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.35 (d, $J = 7.9$ Hz, 1H), 8.05 (d, $J = 8.1$ Hz, 1H), 7.99 (d, $J = 8.2$ Hz, 1H), 7.78 (t, $J = 7.7$ Hz, 1H), 7.54 (t, $J = 7.6$ Hz, 1H), 7.48 – 7.39 (m, 1H), 7.34 – 7.24 (m, 2H).

$^{13}$C($^1$H) NMR (151 MHz, CDCl$_3$) $\delta$ 161.2, 151.3, 134.9, 134.8, 130.6, 130.5, 128.9, 124.6, 122.8, 121.7, 121.3, 118.0, 117.8.

Dibenzo[\textit{b,d}]furan (10): An oven-dried 2-dram vial was charged with a stir bar, 9 (19.6 mg, 0.10 mmol), and meso-L2 (12.0 mg, 0.020 mmol, 20 mol%). The vial was brought into a glovebox, then Ni(cod)$_2$ (6.5 mg, 0.020 mmol, 20 mol%), CsF (15.0 mg, 0.100 mmol, 1.0 equiv.), and toluene (1.00 mL) were added. The vial was sealed and brought outside and placed in an aluminum heating block preheated at 150 °C. The mixture was stirred (700 rpm) for 48 h at 150 °C. After cooling to room temperature, the mixture was directly loaded onto a silica gel column (1 × 15 cm, packed in hexanes). The column was eluted with 200 mL of hexanes. The product containing fractions were collected. The solvent was evaporated by rotary evaporation and the residue was dried under vacuum using an oil pump to give the product 10 as a white solid (0.0142 g, 0.084 mmol, 84%). NMR data match with previously reported values.\textsuperscript{31}

TLC (100% hexanes): $R_f = 0.50$ (visualized by UV).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.97 (d, $J = 7.7$ Hz, 2H), 7.58 (t, $J = 8.2$ Hz, 2H), 7.46 (d, $J = 8.3$ Hz, 2H), 7.35 (t, $J = 7.5$ Hz, 2H).

$^{13}$C($^1$H) NMR (151 MHz, CDCl$_3$) $\delta$ 156.3, 127.3, 124.4, 122.8, 120.8, 111.8.

7.3. Synthesis of dibenzoxazepinone 13 from dibenzazepinone

Compound S11-1 was synthesized following a previously reported procedure.\textsuperscript{32}
5-methyl-5H-dibenzo[b,e]azepine-6(11H)-one (11): A 20-mL vial was charged with a stir bar, S11-1 (0.245 g, 1.00 mmol), and NaH (0.036 g, 1.50 mmol, 1.5 equiv). The vial was then placed under a N₂ atmosphere and DMF (5.0 mL) was added via syringe. The vial was placed in heating block preheated at 60 °C and the reaction was stirred at 60 °C for 1 h. The solution turned orange after 1 h and iodomethane (0.12 mL, 0.284 g, 2.0 mmol, 2.0 equiv) was added dropwise. After finishing addition, the reaction was again stirred at 60 °C for 12 h. After cooling to room temperature, water (10 mL) was added followed by dichloromethane (10 mL) and the mixture was transferred to a separatory funnel. The organic layer was collected and the aqueous layer was extracted with dichloromethane (3 × 50 mL). The combined organic fractions were washed with water (200 mL), dried with Na₂SO₄ and concentrated using rotary evaporator. The residue was loaded onto a silica gel column (3 × 15 cm), packed in dichloromethane. The column was eluted with dichloromethane. The product containing fractions were collected and concentrated using rotary evaporator. The residue was dried under vacuum using an oil pump to give 11 as an off-white solid (0.194 g, 0.87 mmol, 87%). NMR data match with previously reported values.

TLC (100% dichloromethane): Rₚ = 0.40 (visualized by UV).

¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, J = 7.7 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.26 – 7.14 (m, 5H), 7.08 (m, 1H), 4.18 (d, J = 13.2 Hz, 1H), 3.63 (s, 3H), 3.55 (d, J = 13.3 Hz, 1H).

¹³C(¹H) NMR (151 MHz, CDCl₃) δ 168.9, 142.5, 141.4, 137.1, 132.6, 131.7, 131.1, 127.6, 127.3, 127.0, 126.1, 125.8, 122.5, 39.0, 37.9

5-methyl-5H-dibenzo[b,e]azepine-6,11-dione (S11-2): Compound S11-2 (0.201 g, 0.85 mmol, 85%) was obtained as a white solid from 11 (0.220 g, 1.00 mmol) using a literature procedure. NMR data match with previously reported values.

TLC (100% dichloromethane): Rₚ = 0.20 (visualized by UV).

¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, J = 8.1 Hz 1H), 7.64 (m, 4H), 7.53 (t, J = 7.8 Hz, 1H), 7.33 (d, J = 8.2 Hz, 1H), 7.26 (t, J = 7.7 Hz, 1H), 3.64 (s, 3H).

¹³C(¹H) NMR (151 MHz, CDCl₃) δ 195.3, 166.6, 140.4, 140.3, 136.5, 132.6, 132.5, 132.4, 132.2, 131.0, 128.2, 126.5, 125.6, 122.4, 38.9.

12-methyl-6H-dibenzo[b,f][1,4]oxazocine-6,11(12H)-dione (12a and 12b): A Schlenk flask was charged with a stir bar and S11-2 (0.0685 g, 0.25 mmol). The flask was placed under a N₂ atmosphere and dichloromethane (5.0 mL) was added followed by urea-hydrogen
peroxide complex (UHP, 0.84 g, 10 mmol, 40 equiv). The resulting mixture was vigorously stirred and TFAA (0.38 mL, 2.5 mmol, 10 equiv) was added dropwise at room temperature. The reaction was stirred for 12 h and turned light pink with white precipitates. Dichloromethane (10 mL) was added followed by water (10 mL). The mixture was transferred to a separatory funnel and the organic layer was collected. The aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic fractions were dried with Na₂SO₄ and concentrated by rotary evaporator to give an off-white solid. The solid was chromatographed (silica gel column (1 × 20 cm, packed in hexanes), eluted with 200 mL 80/20 hexanes/ethyl acetate) to give a mixture of 12a and 12b as a white solid (0.057 g, 0.23 mmol, 90%). The product ratio was determined to be 3:1 by ¹H NMR. Attempts to isolate the two regioisomers to determine the major product were not successful.

TLC (80/20 hexanes/ethyl acetate): Rf = 0.33 (visualized by UV as one spot)

¹H NMR (600 MHz, CDCl₃) δ 7.45 – 7.36 (m, major + minor isomer integral value = 15), 7.31 – 7.27 (m, 2H from minor isomer), 7.25 – 7.13 (m, major + minor isomer integral value = 14), 7.03 (dd, J = 8.2, 1.1 Hz, 1H from minor isomer), 3.46 (s, 3H from major isomer, integral value = 9), 3.44 (s, 3H from minor isomer, integral value = 3).

¹³C{¹H} NMR (151 MHz, CDCl₃) δ 168.9 (major), 167.2 (major), 166.6 (2C, minor), 149.1 (major), 148.7 (minor), 140.7 (minor), 136.5 (major), 133.4, 132.5, 132.0 (major), 131.7, 130.6 (major, 129.4 (major), 129.2 (minor), 129.1 (minor), 128.7 (2C), 128.3, 127.5 (2C, major), 127.4 (major), 127.2 (2C), 127.0, 125.7, 122.3 (major), 121.0, 36.8 (minor), 36.5 (major).

IR (FT-ATR, cm⁻¹, neat) νmax 3385 (w), 3319 (w), 3217 (w), 3069 (w), 2931 (w), 2859 (w), 1756 (s), 1706 (w), 1663 (s), 1601 (w), 1499 (m), 1459 (w), 1417 (w), 1374 (m), 1315 (w), 1283 (m), 1244 (m), 1201 (m), 1188 (w), 1105 (m), 1092 (m), 1056 (m), 1030 (m), 1007 (w), 981 (w), 905 (w), 885 (w), 865 (w), 780 (m), 728 (m), 669 (w), 639 (w).

HRMS: Exact mass calculated for [C₁₅H₁₁NO₃+H]^+ requires m/z = 254.0812, found m/z = 254.0814. (ESI+).

10-methyldibenzo[b,f][1,4]oxazepin-11(10H)-one (13):

An oven-dried 2-dram vial was charged with a magnetic stir bar, the mixture of 12a and 12b (0.057 g, 0.200 mmol), and the ligand meso-L₂ (0.046 g, 0.080 mmol, 40 mol%). The vial was brought into a glovebox, then Ni(cod)₂ (0.022 g, 0.080 mmol, 40 mol%), CsF (0.030 g, 0.200 mmol, 1.0 equiv.), and toluene (2.00 mL) were added. The vial was sealed and brought outside and placed in an aluminum heating block preheated at 150 °C. The mixture was stirred (700 rpm) for 24 h at 150 °C. After cooling to room temperature, the mixture was directly loaded onto a silica gel column (1 × 20 cm, packed in hexanes). The column was eluted with 100 mL of hexanes, 200 mL of 90/10 hexanes/ethyl acetate. The product containing fractions were collected. The solvent was evaporated by rotary evaporator and the residue was dried under vacuum using an oil pump to give the product 13 as a white solid (0.0432 g, 0.192 mmol, 96%). A reaction using 20 mol% Ni(cod)₂ and 20 mol% meso-L₂ gave 13 in 51% yield (0.0230 g, 0.102 mmol). NMR data match with previously reported values.²⁴
TLC (80/20 hexanes/ethyl acetate): $R_f = 0.40$ (visualized by UV)

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.89 (d, $J = 7.7$ Hz, 1H), 7.45 (t, $J = 7.7$ Hz, 1H), 7.28 – 7.17 (m, 5H), 7.14 (dt, $J = 7.6$, 1.7 Hz, 1H), 3.59 (s, 3H).

$^{13}$C($^1$H) NMR (151 MHz, CDCl$_3$) $\delta$ 166.6, 160.8, 153.8, 136.2, 133.7, 132.4, 126.4 (2 × s), 125.9, 125.4, 122.7, 121.6, 120.0, 37.0.
8. References

27. R. Gonzalez-Fernandez, P. Crochet, and V. Cadierno, *Organometallics* 2019, **38**, 3696-3706.
9. NMR spectra of new compounds

\begin{align*}
9. \text{NMR spectra of new compounds} \\
\text{SL2} \\
\left( ^1H \text{NMR, 600 MHz, CDCl}_3 \right) \\
\end{align*}

\begin{align*}
\text{SL2} \\
\left( ^{13}C \left( ^1H \right) \text{NMR, 151 MHz, CDCl}_3 \right) \\
\end{align*}
$^{31}$P($^1$H) NMR, 243 MHz, CDCl$_3$

$^{1}$H NMR, 600 MHz, CDCl$_3$
\[ \text{meso-L2} \]

\[(^{1}H \text{ NMR, 600 MHz, CDCl}_{3})\]

\[\text{(^{13}C\{^1\text{H}\} NMR, 151 MHz, CDCl}_{3})\]
$^{31}\text{P}^{1}\text{H} \text{ NMR, 243 MHz, CDCl}_3$

S3-1

$^1\text{H} \text{ NMR, 400 MHz, CDCl}_3$
dcype-Ni-2a

($^1$H NMR, 600 MHz, CDCl$_3$)

dcype-Ni-2a

($^{13}$C($^1$H) NMR, 151 MHz, CDCl$_3$)
$^{31}P\{^1H\}$ NMR, 243 MHz, CDCl$_3$
$^{13}C\{^1H\}$ NMR, 151 MHz, CDCl$_3$

$^{19}F\{^1H\}$ NMR, 377 MHz, CDCl$_3$
S1b-3

($^1$H NMR, 400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR, 151 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR, 151 MHz, CDCl$_3$)
$^1$H NMR, 400 MHz, CDCl$_3$)

$^{13}$C$^1$H NMR, 151 MHz, CDCl$_3$)
S1b-5
($^{19}$F($^1$H) NMR, 377 MHz, CDCl$_3$)

1b
($^1$H NMR, 400 MHz, CDCl$_3$)
$^{13}$C($^1$H) NMR, 151 MHz, CDCl$_3$}

$^{19}$F($^1$H) NMR, 377 MHz, CDCl$_3$}
$^{1}$H NMR, 400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR, 151 MHz, CDCl$_3$)
$^{19}\text{F}$-$^{1}\text{H}$ NMR, 377 MHz, CDCl$_3$
\[ \text{\textsuperscript{13}C\textsuperscript{1}H} \text{NMR, 101 MHz, CDCl}_3 \]

\[ \text{\textsuperscript{19}F\textsuperscript{1}H} \text{NMR, 377 MHz, CDCl}_3 \]

\( F_3C \)

2g

1g
\[^1\text{H} \text{NMR, 400 MHz, CDCl}_3/\text{CD}_3\text{OD}\]

\[^3\text{C}[^1\text{H}] \text{NMR, 101 MHz, CDCl}_3/\text{CD}_3\text{OD}\]
$\text{MeO} \quad 1k$

$^{13}\text{C}^{1}\text{H} \text{NMR, 151 MHz, CDCl}_3$

$\text{MeO} \quad 1k$

$^1\text{H} \text{NMR, 600 MHz, CDCl}_3$
S11-2

($^1$H NMR, 400 MHz, CDCl$_3$)

S11-2

($^{13}$C($^1$H) NMR, 151 MHz, CDCl$_3$)
$^{1}H$ NMR, 600 MHz, CDCl$_3$
$^{1}$H NMR, 400 MHz, CDCl$_3$}

$^{13}$C($^1$H) NMR, 151 MHz, CDCl$_3$
(1\textsuperscript{H} NMR, 400 MHz, CDCl\textsubscript{3})

(13\textsuperscript{C}(1\textsuperscript{H}) NMR, 151 MHz, CDCl\textsubscript{3})
$^{1}$H NMR, 600 MHz, CDCl$_3$

$^{13}$C($^{1}$H) NMR, 151 MHz, CDCl$_3$
\( ^{19}F(\text{H}) \text{NMR, 151 MHz, CDCl}_3 \)

\( ^1H \text{NMR, 600 MHz, CDCl}_3 \)
\[ \text{MeO}_2C \quad \begin{array}{c} \text{O} \\ \text{O} \end{array} \quad \text{OMe} \]

**2d**

\((^{13}\text{C}^{1}\text{H}) \text{ NMR, 151 MHz, CDCl}_3\)
2f

$\text{MeO}_2\text{C}$

$\left(^{13}\text{C}^{\text{1H}}\right) \text{NMR, 151 MHz, CDCl}_3$

---

2g

$\text{F}_3\text{C}$

$\left(^{19}\text{F}^{\text{1H}}\right) \text{NMR, 565 MHz, CDCl}_3$
$^{13}$C-$^1$H NMR, 151 MHz, CDCl$_3$)

$^1$H NMR, 600 MHz, CDCl$_3$)
BnO

2h

$^{13}$C$^1$H NMR, 151 MHz, CDCl$_3$

MOMO

2i

$^1$H NMR, 600 MHz, CDCl$_3$
MOMO

\( \text{2i} \)

\( (^{13}\text{C}(^{1}\text{H}) \text{ NMR, 151 MHz, CDCl}_3) \)

BnO

\( \text{2I} \)

\( (^1\text{H} \text{ NMR, 400 MHz, CDCl}_3) \)
$E/Z = 82:18$

($^1$H NMR, 600 MHz, CDCl$_3$)
\((^{13}C\{1H\} NMR, 101 \text{ MHz, CDCl}_3)\)

\((^1H \text{ NMR, } 600 \text{ MHz, CDCl}_3)\)
\( ^{13}\text{C}\{^1\text{H}\} \text{ NMR, 151 MHz, CDCl}_3 \)
$^{13}$C-$^1$H NMR, 151 MHz, CDCl$_3$
(\textsuperscript{13}C\textsuperscript{1}H) NMR, 151 MHz, CDCl\textsubscript{3})