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8. Spectra
1. General Considerations

Ligands, \( \alpha \)-diimine-NiBr\(_2\), \( \alpha \)-diimine-NiMe\(_2\), and most substrates were synthesized following literature procedures. All air- and moisture-sensitive manipulations were carried out in a glove box or using standard Schlenk techniques. Volatiles and liquid chemicals were dried over 4 Å molecular sieves or CaH\(_2\), followed by vacuum transfer. \(^1\)H NMR spectra were recorded on a Bruker 400 or 600 Avance spectrometer (400 MHz or 600 MHz). \(^4\) Chemical shifts were reported in ppm relative to tetramethylsilane, with the residual solvent resonance as the internal reference (CDCl\(_3\), \( \delta = 7.26\)). Spectra are reported as follows: chemical shift (\( \delta \) ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet), coupling constant (Hz), integration and assignment. \(^{13}\)C NMR spectra were recorded on a Bruker 600 Avance spectrometer (151 MHz). Chemical shifts were reported in ppm relative to tetramethylsilane with the solvent resonance used as the internal reference (CDCl\(_3\), \( \delta = 77.2\)). HRMS was recorded on a commercial apparatus (ESI or APCI Source). EPR spectra were recorded on a Bruker EMXplus EPR spectrometer.

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4. The CPTCI-cryoprobe was acquired through the support of the National Institutes of Health S10 grant under award number OD016343.
2. Synthesis of Catalysts and Substrates

1) Synthesis of [((α-diimine)Ni(I)Br]_2 catalysts

\[
\begin{align*}
\text{Ar} & \quad \text{Ni} \quad \text{Br} \\
\text{Ar} & \quad \text{Ni} \quad \text{Br} \\
\end{align*}
\]

\[\begin{align*}
\text{Ar} = 2,6\text{-diisopropylphenyl} \\
\end{align*}\]

A 20-mL scintillation vial was charged with (α-diimine)NiBr₂ (248 mg, 0.4 mmol), ligand (160 mg, 0.4 mmol), and 4 mL THF. After stirring for 5 mins, Ni(COD)₂ (110 mg, 0.4 mmol) was added, which resulted in an immediate color change from brown to purple. The reaction was stopped after 2 mins, filtered through Celite, layered with 10 mL pentane, and stored in a –35 °C freezer overnight. Complex 5 was obtained as a purple crystalline solid in 90% yield, structure confirmed by X-ray crystallographic analysis. $^1$H NMR (400 MHz, Benzene-$_d_6$) δ 13.89 (br, 12H, CH$_3$), 3.97 (br, 24H, CH$_3$ of iPr), 1.80 (br, 24H, CH$_3$ of iPr), -13.67 (br, 8H, CH of iPr). IR (in KBr) 3618, 3412, 3062, 2961, 2927, 2868, 1640, 1585, 1461, 1438, 1382, 1363, 1325, 1254, 1208, 1141, 1119, 1058, 1043, 987, 935, 883, 792, 764, 737.

2) Synthesis of 3-substituted substrates

\[
\begin{align*}
\text{MeO}_2\text{C} & \quad \text{CO}_2\text{Me} \\
\text{MeO}_2\text{C} & \quad \text{CO}_2\text{Me} \\
\end{align*}
\]

Substituted allyl dimethyl malonates were synthesized by Knoevenagel condensation$^{5,6}$ and Michael addition.$^7$ To a THF solution of substituted allyl dimethyl malonate (1.0 equiv) was

added NaH (2.0 equiv) under nitrogen at 0 °C. After stirring for 30 mins, allylbromide (2.2 equiv) was added via syringe. The mixture was stirred at 22 °C for 2 hours, then heated to 40 °C and left to stir overnight. Upon completion, the reaction was washed with saturated aqueous NH₄Cl and extracted with Et₂O three times. The organic layers were combined, dried over MgSO₄, and concentrated under reduced pressure. After purification by column chromatography (hexane : Et₂O = 10 : 1), the diene substrate was obtained as a colorless oil.

Yield: 68%; ¹H NMR (600 MHz, Chloroform-d) δ 5.83 – 5.72 (m, 2H), 5.12 – 5.00 (m, 4H), 3.72 (s, 3H), 3.71 (s, 3H), 2.91 – 2.81 (m, 1H), 2.63 (m, 2H), 1.10 (d, J = 6.9 Hz, 3H). ¹³C NMR (151 MHz, Chloroform-d) δ 170.9, 170.8, 139.0, 133.2, 118.5, 116.3, 61.7, 52.0, 42.1, 38.6, 16.6. HRMS (ESI-TOF) m/z: [M + Na]+ calcd 249.1097, found 249.1093.

Yield: 72%; ¹H NMR (600 MHz, Chloroform-d) δ 5.76 – 5.64 (m, 2H), 5.17 (dd, J = 10.2, 2.3 Hz, 1H), 5.08 – 4.99 (m, 3H), 3.71 (s, 3H), 3.71 (s, 3H), 2.66 (ddt, J = 14.1, 6.8, 1.2 Hz, 1H), 2.60 – 2.53 (m, 2H), 2.03 (hept, J = 6.8, 2.3 Hz, 1H), 0.93 (d, J = 6.8 Hz, 3H), 0.65 (d, J = 6.8 Hz, 3H). ¹³C NMR (151 MHz, Chloroform-d) δ 171.5, 171.1, 134.1, 132.8, 118.9, 118.6, 60.9, 53.3, 52.1, 52.0, 39.4, 28.0, 23.4, 17.9. HRMS (ESI-TOF) m/z: [M + Na]+ calcd 277.1410, found 277.1418.

Yield: 63%; ¹H NMR (600 MHz, Chloroform-d) δ 7.31 – 7.26 (m, 2H), 7.25 – 7.21 (m, 1H), 7.16 – 7.13 (m, 2H), 6.39 (ddd, J = 17.0, 10.2, 8.5 Hz, 1H), 5.75 (dddd, J = 16.7, 10.6, 8.1, 6.3 Hz, 1H), 5.11 (ddd, J = 10.3, 1.7, 0.9 Hz, 1H), 5.07 – 4.97 (m, 3H), 4.01 (d, J = 8.5 Hz, 1H), 3.74 (s, 3H), 3.67 (s, 3H), 2.59 (dt, J = 14.1, 6.3, 1.4 Hz, 1H), 2.42 (ddt, J = 14.2, 8.2, 1.1 Hz, 1H). ¹³C NMR (151 MHz, Chloroform-d) δ 170.6, 170.4, 138.9, 137.6, 133.3, 129.2, 128.3, 127.3, 118.6, 117.3, 63.1, 54.6, 52.1, 52.0, 39.5. HRMS (ESI-TOF) m/z: [M + Na]+ calcd 311.1254, found 311.1253.

3) Synthesis of Radical Clock 40

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276-277.
A solution of 1-ethoxycyclopropan-1-ol in MeOH was prepared from 1-ethoxycyclopropoxy)trimethylsilane (5 mmol, synthesized according to the reported procedure\textsuperscript{8}). It was combined with allylamine (0.57 g, 10 mmol), NaCN (0.49 g, 10 mmol), and AcOH (20 mmol) in a bomb flask. Next, the solution was heated at around 50 °C for 3 days. Finally, the reaction mixture was poured into cold water and extracted with Et\textsubscript{2}O. The combined organic layers were dried over MgSO\textsubscript{4}, filtered, concentrated by rotary evaporation, and purified by column chromatography (hexane : Et\textsubscript{2}O = 6 : 1). 0.27 g (44% total yield) light yellow oil was collected.

\textsuperscript{1}H NMR (600 MHz, Chloroform-\textit{d}) \(\delta\) 5.86 (ddt, \(J = 17.1, 10.2, 6.1\) Hz, 1H), 5.25 (dq, \(J = 17.1, 1.5\) Hz, 1H), 5.13 (dq, \(J = 10.2, 1.5\) Hz, 1H), 3.45 (dt, \(J = 6.1, 1.5\) Hz, 2H), 3.13 – 2.31 (br, 1H), 1.23 – 1.18 (m, 2H), 1.08 – 1.02 (m, 2H). \textsuperscript{13}C NMR (151 MHz, Chloroform-\textit{d}) \(\delta\) 135.2, 121.6, 117.1, 50.3, 27.9, 16.2.

The starting material (270 mg, 2.21 mmol) was dissolved into 10 mL DCM, and then DMAP (24 mg, 0.221 mmol) was added. Subsequently, TsCl (463 mg, 2.43 mmol) was added. After stirring for 24 hours, the reaction was quenched with saturated aqueous NH\textsubscript{4}Cl. The product was extracted with DCM, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered, and concentrated by rotary evaporation. The product was purified by column chromatography (hexane:EtOAc = 5:1) to give the product 370 mg (61% yield) as a colorless oil. \textsuperscript{1}H NMR (600 MHz, Chloroform-\textit{d}) \(\delta\) 7.82 (d, \(J = 8.3\) Hz, 2H), 7.39 (d, \(J = 8.3\) Hz, 2H), 5.79 (ddt, \(J = 16.8, 10.0, 6.6\) Hz, 1H), 5.32 (dq, \(J = 16.8, 1.2\) Hz, 1H), 5.24 (dq, \(J = 10.0, 1.2\) Hz, 1H), 3.94 (d, \(J = 6.6\) Hz, 2H), 2.46 (s, 3H), 1.76 – 1.64 (m, 2H), 1.45 (m, 2H). \textsuperscript{13}C NMR (151 MHz, Chloroform-\textit{d}) \(\delta\) 144.9, 134.4, 132.4, 130.0, 128.2, 120.3, 118.6, 53.1, 28.1, 21.7, 18.1, 16.2. HRMS (ESI-TOF) \(m/z\): [M + Na]\textsuperscript{+} calcd 299.0825, found 299.0829.

\[\text{N} + \text{TsCl} \rightarrow \text{N}^\text{Ts}\]

The starting material (370 mg, 1.34 mmol) was dissolved in 10 mL THF, and then 1N DIBAL solution (2.68 mL, 2.68 mmol) was added under nitrogen at -78 °C. The reaction was left stirring at room temperature for 6 hours before adding EtOH (0.5 mL) and HCl (10%, 2 mL) at -78 °C. Then, the temperature was slowly increased to about -10 °C before extracting the desired product with Et₂O. The combined organic layers were dried over Na₂SO₄, filtered, and purified by column chromatography on silica gel (hexane:EtOAc = 6:1) to give 270.3 mg (72% yield) colorless oil. ¹H NMR (600 MHz, Chloroform-d) δ 9.27 (s, 1H), 7.77 – 7.70 (m, 2H), 7.35 – 7.27 (m, 2H), 5.87 (ddt, J = 16.9, 10.5, 6.6 Hz, 1H), 5.22 – 5.15 (m, 2H), 3.99 (broad s, 2H), 2.43 (s, 3H), 1.52 – 1.36 (m, 4H). ¹³C NMR (151 MHz, Chloroform-d) δ 200.6, 143.8, 137.8, 133.6, 129.8, 127.3, 119.7, 52.6, 47.8, 21.6. HRMS (ESI-TOF) m/z: [M + Na]⁺ calcd 302.0821, found 302.0820.

nBuLi (1.6 M in hexane, 0.75 mL, 1.2 mmol) was added to a THF solution of PPh₃MeBr (535 mg, 1.5 mmol) at -78 °C. After stirring for 1 hour at 0 °C, a THF solution of the aldehyde (270 mg, 0.98 mmol) was added dropwise to the ylide solution at -78 °C. Then the mixture was warmed to room temperature and stirred for 4 hours before adding saturated aqueous NH₄Cl to quench the reaction. The product was extracted with EtOAc (3 x 10 mL), dried over MgSO₄, filtered and purified by column chromatography on silica gel (hexane:EtOAc = 15:1). ¹H NMR (600 MHz, Chloroform-d) δ 7.71 (m, 2H), 7.28 – 7.26 (m, 2H), 5.84 – 5.74 (ddt, J = 17.1, 10.1, 6.4 Hz, 1H), 5.54 (dd, J = 17.1, 10.7 Hz, 1H), 5.14 (dd, J = 17.1, 1.5 Hz, 1H), 5.07 (dd, J = 10.1, 1.3 Hz, 1H), 4.95 (dd, J = 17.1, 0.7 Hz, 1H), 4.90 (dd, J = 10.7, 0.7 Hz, 1H), 3.96 (dt, J = 6.4, 1.4 Hz, 2H), 2.42 (s, 3H), 1.35 – 1.26 (m, 2H), 0.92 (m, 2H). ¹³C NMR (151 MHz, Chloroform-d) δ 143.2, 139.4, 138.6, 135.0, 129.5, 127.6, 117.7, 112.5, 52.1, 42.4, 21.5, 16.7. HRMS (ESI-TOF) m/z: [M + Na]⁺ calcd 300.1029, found 300.1028.

4) Synthesis of mono-substituted tosylamide substrates
"BuLi (1.6 M in hexane, 1.5 mL, 2.4 mmol) was added to a THF solution of the phosphonium bromide (1.02 g, 2.4 mmol) at -78 °C. After stirring for 1 hour at 0 °C, a THF solution of the aldehyde (506 mg, 2 mmol), prepared according to a reported procedure\(^9\), was added dropwise to the phosphonium ylide solution at -78 °C. The mixture was warmed to room temperature and stirred for 4 hours, then quenched by adding saturated aqueous NH\(_4\)Cl solution. The product was extracted with EtOAc (3 x 10 mL), dried over MgSO\(_4\), filtered, and purified by column chromatography on silica gel to give 360 mg (hexanes:EtOAc = 15:1). \(^1\)H NMR (600 MHz, Chloroform-\(d\)) \(\delta\) 7.77 – 7.66 (m, 2H), 7.32 – 7.28 (m, 2H), 5.65 (ddt, \(J = 17.1, 10.2, 6.2\) Hz, 1H), 5.57 – 5.45 (m, 1H), 5.23 – 5.09 (m, 3H), 3.84 (dd, \(J = 6.9, 0.8\) Hz, 2H), 3.78 (d, \(J = 6.2\) Hz, 2H), 2.42 (s, 3H), 1.96 (qd, \(J = 7.4, 1.2\) Hz, 2H), 1.33 – 1.21 (m, 6H), 0.87 (t, \(J = 7.1\) Hz, 3H). \(^13\)C NMR (151 MHz, Chloroform-\(d\)) \(\delta\) 143.1, 137.6, 134.6, 133.1, 129.6, 127.2, 123.6, 118.6, 49.3, 43.5, 31.4, 29.1, 27.2, 22.5, 21.5, 14.0. HRMS (APCI-TOF) \(m/z\): [M + H]\(^+\) calcd 322.1835, found 322.1834.

**General procedure for Mitsunobu reaction**

\[
\begin{align*}
\text{TsHN} & \quad \longrightarrow \\
\text{+ R} & \quad \longrightarrow \quad \text{THF} \\
\text{DEAD, PPh}_3 & \quad \longrightarrow \\
\text{TsN} & \quad \longrightarrow \\
\end{align*}
\]

Diethyl azodicarboxylate (DEAD, 40 wt% in toluene, 1.74 g, 4.0 mmol) was added to the THF solution of \(N\)-allyl-tosylamide (422 mg, 2.0 mmol), alcohol (2.0 mmol), and PPh\(_3\) (524 mg, 2 mmol) at °C. The mixture was stirred at room temperature for 20 hours, then concentrated, diluted with water, and extracted by Et\(_2\)O. The combined organic layers were dried over MgSO\(_4\), filtered, concentrated, and purified by column chromatography on silica gel (hexanes:EtOAc = 15:1 to 10:1).

Following the Mitsunobu reaction general procedure, 320 mg (55% yield) desired product was collected. \(^1\)H NMR (600 MHz, Chloroform-\(d\)) \(\delta\) 7.75 – 7.63 (m, 2H), 7.31 – 7.27 (m, 2H), 5.61 (ddt, \(J = 17.5, 9.8, 6.3\) Hz, 1H), 5.52 (dtt, \(J = 15.0, 6.8, 1.3\) Hz, 1H), 5.23 – 5.11 (m, 3H), 3.79 (dt, \(J =

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Following the Mitsunobu reaction general procedure, 332 mg (59% yield) desired product was collected. $^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 7.72 – 7.68 (m, 2H), 7.31 – 7.28 (m, 2H), 5.65 (ddt, $J = 17.1$, 10.2, 6.2 Hz, 1H), 5.49 (dtt, $J = 10.8$, 7.4, 1.6 Hz, 1H), 5.17 – 5.12 (m, 2H), 3.84 (ddd, $J = 7.0$, 1.6, 0.8 Hz, 2H), 3.78 (d, $J = 6.3$, 2H), 2.43 (s, 3H), 2.05 – 1.93 (m, 2H), 0.93 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (151 MHz, Chloroform-$d$) $\delta$ 143.1, 137.6, 136.1, 133.1, 129.6, 127.2, 123.9, 118.6, 49.3, 43.3, 21.5, 20.6, 14.0. HRMS (APCI-TOF) m/z: [M + H]$^+$ calcd 280.1366, found 280.1361.

Following the Mitsunobu reaction general procedure, 401 mg (68% yield) desired product was collected. $^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 7.72 – 6.69 (m, 2H), 7.31 – 7.27 (m, 2H), 5.66 (ddt, $J = 17.1$, 10.2, 6.2 Hz, 1H), 5.54 – 5.47 (m, 1H), 5.23 – 5.17 (m, 1H), 5.17 – 5.12 (m, 2H), 3.84 (ddd, $J = 7.0$, 1.6, 0.8 Hz, 2H), 3.80 – 3.77 (m, 2H), 2.43 (s, 3H), 1.98 – 1.92 (m, 2H), 1.34 (m, 2H), 0.87 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (151 MHz, Chloroform-$d$) $\delta$ 143.1, 137.6, 134.3, 133.1, 129.6, 127.2, 123.9, 118.6, 49.3, 43.5, 29.2, 22.6, 21.5, 13.7. HRMS (APCI-TOF) m/z: [M + Na]$^+$ calcd 316.1342, found 316.1339.

3. General Procedure for Reductive Cyclization of Dienes

In a N$_2$-filled glove box, to a 2 mL GC vial was added substrate (0.1 mmol), Et$_2$SiH$_2$ (0.2 mmol, 2.0 equiv), [(α-diamine)NiBr]$_2$ (2.5 mol%), and HFIP (1.0 mL) or Acetone/HOIPr (1.0 mL/0.2 mL). The vial was sealed with crimp™ seal, and the mixture was allowed to react on a thermostaker for 16 h. The reaction was analyzed on a Shimadzu GC 2010 Plus with 2 mg mesitylene as internal standard. In order to obtain isolated products, the solvent was removed, and the product was purified by column chromatography on silica gel.

4. Mechanistic Studies

1) EPR spectrum of the reaction catalyzed by 7
Figure S1. X-band EPR spectrum of the reaction mixture of 1 catalyzed by 7 at 10 K. Solvent = HFIP. Spectroscopic parameters: $g_x = 2.37$, $g_y = 1.99$, $g_z = 2.00$, $A_{xx} = -8$ MHz, $A_{yy} = 21$ MHz, $A_{zz} = 10$ MHz. Microwave frequency = 9.380 GHz, power = 2.00 mW, modulation amplitude = 1 mT/100 kHz.

2) Deuterium Labeling Studies

Reactions were set up following the general procedure in the indicated solvents. Products were purified by flash column and analyzed by $^1$H NMR (Figure S2), $^{13}$C NMR and $^{13}$C APT (Figure S3) NMR spectroscopy. H/D exchange was observed between Et$_2$SiH$_2$ and the solvent.

<table>
<thead>
<tr>
<th>Silane</th>
<th>Solvent</th>
<th>Yield (%)</th>
<th>$C_{CH_3}$ : $C_{CH_2D}$ ratio of product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et$_2$SiH$_2$</td>
<td>acetone-$d_6$/PrOH-$d_6$</td>
<td>82</td>
<td>$C_{CH_3}$ : $C_{CH_2D} = 1 : 1.16$</td>
</tr>
<tr>
<td>Et$_2$SiD$_2$</td>
<td>acetone/PrOH</td>
<td>79</td>
<td>$C_{CH_3}$ : $C_{CH_2D} = 1 : 0.43$</td>
</tr>
<tr>
<td>Et$_2$SiD$_2$</td>
<td>acetone-$d_6$/PrOH-$d_6$</td>
<td>82</td>
<td>$C_{CH_3}$ : $C_{CH_2D} = 1 : 2.59$</td>
</tr>
</tbody>
</table>
Figure S2. $^1$H NMR spectra of reductive cyclization of 1 with Et$_2$SiD$_2$ in (A) acetone-$d_6$/iPrOH-$d_8$ and (B) acetone/iPrOH.
**Figure S3.** $^{13}$C APT spectra of reductive cyclization of 1 using Et$_2$SiH$_2$ in acetone/iPrOH (top, blue), Et$_2$SiD$_2$ in acetone/iPrOH (middle, green), or Et$_2$SiD$_2$ in acetone-$d_6$/iPrOH-$d_8$ (bottom, red).

3) **Synthesis of ($^{\alpha\alpha}$-diimine)Ni(I)Bn 37**

Into a 20-mL scintillation vial, [(Ar-$\alpha$-diimine)Ni(I)Br]$_2$ (21 mg, 0.018 mmol) was weighed and dissolved in 2 mL of THF. After cooling this mixture to −78 °C in a cold well for 20 mins, a solution of BnMgBr (40 μL, 0.04 mmol, 1 M in Et$_2$O) was added, which resulted in a color change from purple to brown. Subsequently, the solvent was removed under vacuum, and the
residual was extracted with pentane. The solvent was concentrated to 1 mL and stored in a –35 °C freezer overnight to afford 37 (11.0 mg, 48%) as a dark purple solid. The structure was confirmed by X-ray crystallography and EPR spectroscopy.

4) Cyclization of Radical Clock 40

The cyclization reaction was set up according to the standard procedure. After the reaction, the reaction mixture was concentrated and filtered through Celite. After addition of 2.5 mg 1,3,5-trimethyloxylbenzene as an internal standard, the reaction was analyzed by 1H NMR spectroscopy (Figure S4). Subsequently, the mixture was concentrated and purified by column chromatography to isolate the fully-reduced 43, mono-reduced 42, and reductive cycloisomerization product 41 (Figure S5).

\[ N-(1\text{-ethylecyclopropyl})-4\text{-methyl-N-propylbenzenesulfonamide (43)}: \]

This material was obtained from column chromatography (hexane:EtOAc = 15:1) as the first fraction to give 7.1 mg colorless oil. 1H NMR (600 MHz, Chloroform-\(d\)) \(\delta\) 7.71 – 7.67 (m, 2H), 7.26 – 7.23 (m, 2H), 3.28 – 3.08 (m, 2H), 2.39 (s, 3H), 2.00 – 1.94 (m, 2H), 1.51 – 1.49 (m, 2H), 1.23 (m 4H), 0.96 (t, \(J = 7.4\) Hz, 3H), 0.86 (t, \(J = 7.4\) Hz, 3H). 13C NMR (151 MHz, Chloroform-\(d\)) \(\delta\) 138.5, 129.5, 127.4, 125.3, 50.0, 29.7, 26.2, 22.0, 21.5, 13.9, 12.1, 11.3, 11.2. HRMS (APCI-TOF) \(m/z\): [M + H]\(^+\) calcd 282.1522, found 282.1531.

\[ 4\text{-methyl-N-propyl-N-(1-vinylecyclopropyl)benzenesulfonamide (42)}: \]

This material was purified by column chromatography (hexane:EtOAc = 15:1) as the second fraction to give 7.5 mg colorless oil. 1H NMR (600 MHz, Chloroform-\(d\)) \(\delta\) 7.71 – 7.68 (m, 2H), 7.28 – 7.26 (m, 2H), 5.60 (dd, \(J = 17.1, 10.7\) Hz, 1H), 4.95 (dd, \(J = 17.1, 0.7\) Hz, 1H), 4.88 (dd, \(J = 10.7, 0.7\) Hz, 1H), 3.24 – 3.21 (m, 2H), 2.41 (s, 3H), 1.67 – 1.63 (m, 2H), 1.28 – 1.23 (m, 4H), 0.84 (t, \(J = 7.4\) Hz, 3H). 13C NMR (151 MHz, Chloroform-\(d\)) \(\delta\) 143.0, 140.3, 138.8, 129.5, 127.4, 127.4, 112.1, 51.4, 41.9, 23.1, 21.5, 16.9 11.4, 11.4. HRMS (APCI-TOF) \(m/z\): [M + H]\(^+\) calcd 280.1366, found 280.1370.

\[ \text{trans-6,7-dimethyl-4-tosyl-4-azaspiro[2.4]heptane (41)}: \]
This material was purified by column chromatography (hexane:EtOAc = 10:1) as the third fraction to give 8.3 mg colorless oil. \(^1\)H NMR (600 MHz, Chloroform-\(d\)) \(\delta\) 7.75 – 7.73 (m, 2H), 7.31 – 7.28 (m, 2H), 3.72 (dd, \(J = 10.6, 7.9\) Hz, 1H), 3.04 (dd, \(J = 10.6, 8.6\) Hz, 1H), 2.43 (s, 3H), 1.90 (ddd, \(J = 11.8, 6.2, 5.6\) Hz, 1H), 1.78 – 1.70 (m, 1H), 1.29 – 1.15 (m, 2H), 1.14 – 1.07 (m, 2H), 0.93 (d, \(J = 6.7\) Hz, 3H), 0.51 (d, \(J = 6.7\) Hz, 3H). \(^{13}\)C NMR (151 MHz, Chloroform-\(d\)) \(\delta\) 143.0, 136.3, 129.5, 127.5, 55.8, 48.0, 43.8, 38.7, 21.5, 16.7, 12.9, 7.0, 6.9. HRMS (ESI-TOF) \(m/z\): [M + Na]\(^+\) calcd 302.1185, found 302.1187.

**Figure S4.** Crude \(^1\)H NMR spectrum of the reductive cyclization of radical clock 40. Internal standard = 1,3,5-trimethyloxylbenzene.
**Figure S5.** Comparison of the crude $^1$H NMR spectrum of the reductive cyclization of radical clock 40 with isolated 41, 42, and 43.

5) **Control experiment with cycloisomerization product 45**

The redox cycloisomerization product 45 was synthesized according to the literature procedure.$^{10}$ Molecule 45 (21.2 mg) was reacted under reductive conditions, the reaction mixture was purified by column chromatography to remove the catalyst and the ligand. The resulting product mixture was analyzed by $^1$H NMR spectroscopy. When HFIP was used as the solvent, the cyclopentene product from olefin migration was observed as the major product, along with minor reduced product formed as cis:trans mixture in a ratio of 2:1 (Figure S6).$^{11}$


when acetone/HO'Pr was used as the solvent, only the starting material (15.2 mg, 72%) was recovered.

**Figure S6.** Crude $^1$H NMR spectrum of the control experiment shown in Figure 5B in HFIP.

5. **Characterization Data of Products**

**dimethyl trans-3,4-dimethylcyclopentane-1,1-dicarboxylate (2):**

The product was obtained by using the standard procedure in HFIP (0.5 mL) at 50 °C for 3 hours. After concentration, it was purified by column chromatography (hexane : Et$_2$O = 20:1) to give a colorless oil (16.7 mg, 78% yield). $^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 3.70 (s, 6H), 2.51 (dd, $J = 13.6, 6.7$ Hz, 2H), 1.72 (dd, $J = 13.6, 10.8$ Hz, 2H), 1.47 (m, 2H), 0.96 (d, $J = 6.1$ Hz, 6H). $^{13}$C NMR (151 MHz, Chloroform-$d$) $\delta$ 173.5,
The product matches with the literature reports.\textsuperscript{12,13} HRMS (ESI-TOF) \textit{m/z}: [M + Na]\textsuperscript{+} calc 237.1097, found 237.1100.

**diethyl (3R,4R)-3,4-dimethylcyclopentane-1,1-dicarboxylate (9)**

The product was obtained by using the standard procedure in HFIP (1.0 mL) at 50 °C for 16 hours. After concentration, it was purified by column chromatography (hexane : Et\textsubscript{2}O = 15:1) to give a colorless oil (20.4 mg, 84\% yield). \textsuperscript{1}H NMR (600 MHz, Chloroform-\textit{d}) \textit{δ} 4.20 – 4.15 (m, 4H), 2.50 (dd, \textit{J} = 13.5, 6.7 Hz, 2H), 1.72 (dd, \textit{J} = 13.5, 10.8 Hz, 2H), 1.53 – 1.44 (m, 2H), 1.23 (t, \textit{J} = 7.1 Hz, 6H), 0.97 (d, \textit{J} = 6.0 Hz, 6H). \textsuperscript{13}C NMR (151 MHz, Chloroform-\textit{d}) \textit{δ} 173.0, 61.2, 58.2, 42.8, 41.7, 17.4, 14.1. HRMS (APCI-TOF) \textit{m/z}: [M + H]\textsuperscript{+} calc 243.1591, found 243.1597.

**dibenzyl trans-3,4-dimethylcyclopentane-1,1-dicarboxylate (10):**

The product was obtained by using the standard procedure in HFIP (1.0 mL) with 5 mol\% \textit{[((α-diimine)Ni(μ-Br)]\textsubscript{2}} \textit{δ} 4.20 – 4.15 (m, 4H), 2.50 (dd, \textit{J} = 13.5, 6.7 Hz, 2H), 1.72 (dd, \textit{J} = 13.5, 10.8 Hz, 2H), 1.53 – 1.44 (m, 2H), 1.23 (t, \textit{J} = 7.1 Hz, 6H), 0.97 (d, \textit{J} = 6.0 Hz, 6H). \textsuperscript{13}C NMR (151 MHz, Chloroform-\textit{d}) \textit{δ} 172.7, 135.7, 128.5, 128.2, 127.9, 67.0, 58.3, 42.8, 41.7, 17.3. HRMS (ESI-TOF) \textit{m/z}: [M + Na]\textsuperscript{+} calc 389.1723, found 389.1712.

**trans-2,3,8,8-tetramethyl-7,9-dioxaspiro[4.5]decane (11):**

The product was obtained by using the standard procedure with \textit{[(α-diimine)Ni(μ-Br)]\textsubscript{2}} in acetone/HO\textsubscript{2}Pr (1.0 mL/0.2 mL) at 50 °C for 16 hours. After trying a series of methods to do purification, there was still some impurity visible in the \textsuperscript{1}H NMR spectrum of the product. For this reason, the 1.2 mg 1,3,5-trimethyloxybenzene was


used as an internal standard to determine yield of 98% by $^1$H NMR. From the crude NMR, the product could be identified. $^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 3.59 – 3.52 (m, 4H), 1.86 (dd, $J = 12.0, 6.7$ Hz, 2H), 1.43 – 1.41 (m, 2H), 1.40 (s, 6H), 1.00 – 0.96 (m, 2H), 0.94 (d, $J = 6.1$ Hz, 6H). $^{13}$C NMR (151 MHz, Chloroform-$d$) $\delta$ 97.5, 70.4, 42.8, 41.0, 39.6, 23.9, 18.0. HRMS (ESI-TOF) $m/z$: $[M + K – H_2O]^+$ calc 219.1146, found 219.1153.

**trans-3,4-dimethylcyclopentane-1,1-diyl)bis(methylene) bis(4-methylbenzenesulfonate) (12):**

The product was obtained by using the standard procedure with $\left[\left(\alpha\text{-diimine}\right)\text{Ni(\mu-Br)}\right]_2$ 5 in HFIP (0.5 mL) at 50 °C for 16 hours. After concentration, it was purified by column chromatography (hexane : EtOAc = 8:1) to give a colorless oil (43.8 mg, 94% yield). $^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 7.74 – 7.71 (m, 4H), 7.36 – 7.34 (m, 4H), 3.78 (d, $J = 9.3$ Hz, 2H), 3.74 (d, $J = 9.3$ Hz, 2H), 2.46 (s, 6H), 1.67 (dd, $J = 13.7, 6.6$ Hz, 2H), 1.34 – 1.24 (m, 2H), 0.91 (dd, $J = 13.7, 10.9$ Hz, 2H), 0.85 (d, $J = 5.9$ Hz, 6H). $^{13}$C NMR (151 MHz, Chloroform-$d$) $\delta$ 145.0, 132.6, 129.9, 127.9, 72.6, 44.0, 41.0, 40.7, 21.7, 17.4. HRMS (ESI-TOF) $m/z$: $[M + Na]^+$ calc 489.1376, found 489.1373.

**trans-3,4-dimethyl-3'H-spiro[cyclopentane-1,1'-isobenzofuran]-3'-one (13):**

The product was obtained by using the standard procedure with 5 mol% $\left[\left(\alpha\text{-diimine}\right)\text{Ni(\mu-Br)}\right]_2$ 5 in HFIP (1.0 mL) at 50 °C for 16 hours. After concentration, it was purified by column chromatography (hexane : Et$_2$O = 10:1) to give a colorless oil (18.7 mg, 86% yield). $^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 7.82 (td, $J = 7.7, 1.1$ Hz, 1H), 7.66 (td, $J = 7.5, 1.1$ Hz, 1H), 7.48 (td, $J = 7.5, 0.9$ Hz, 1H), 7.39 (td, $J = 7.7, 0.9$ Hz, 1H), 2.43 (dd, $J = 14.7, 9.3$ Hz, 1H), 2.18 (ddd, $J = 13.7, 6.0, 1.8$ Hz, 1H), 2.08 – 1.98 (m, 1H), 1.93 (ddd, $J = 14.7, 8.6, 1.8$ Hz, 1H), 1.82 – 1.73 (m, 2H), 1.13 (d, $J = 6.6$ Hz, 3H), 1.09 (d, $J = 6.6$ Hz, 3H). $^{13}$C NMR (151 MHz, Chloroform-$d$) $\delta$ 170.1, 153.7, 134.2, 128.7, 125.7, 125.3, 120.8, 94.0, 49.5, 47.1, 42.1, 41.9, 18.7, 17.7. HRMS (ESI-TOF) $m/z$: $[M + Na]^+$ calc 239.1043, found 239.1045.

**dimethyl trans-3-ethyl-4-methylcyclopentane-1,1-dicarboxylate (14):**

The product was obtained by using the standard procedure with 2.5 mol% $\left[\left(\alpha\text{-diimine}\right)\text{Ni(\mu-Br)}\right]_2$ 5 in HFIP (0.5 mL) at 50 °C for 16 hours. However, the mono-reduced byproduct was difficult to separate from the desired product. Several methods were attempted to purify this compound, including changing the eluent.
and adding AgNO₃ or an oxidant to interact with the byproduct, but all attempts were unsuccessful. For this reason, 1.0 mg 1,3,5-trimethyloxybenzene was used as an internal standard to determine an NMR yield of 59%. For the assignments of these mixture peaks, the 2D COSY was used. However, overlap of the signals from the product and byproduct make it difficult to identify the $^{13}$C NMR resonances of the product. $^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 3.72 (s, 3H), 3.71 (s, 3H), 2.56 – 2.44 (m, 2H), 1.75 (td, $J = 13.8, 10.8$ Hz, 2H), 1.61 – 1.55 (m, 2H), 1.19 – 1.15 (m, 1H), 1.15 – 1.04 (m, 1H), 0.97 (d, $J = 6.4$ Hz, 3H), 0.90 (t, $J = 7.4$ Hz, 3H). HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ calc 251.1254, found 251.1257.

The product was obtained by using the standard procedure with $[(\alpha$-diimine)Ni($\mu$-Br)$_2$]•5 in Acetone/HO$i$Pr (1.0 mL/0.2) at 50 °C for 16 hours. After concentration, it was purified by column chromatography (hexane : EtOAc = 10:1) to give a colorless oil (24.9 mg, 86% yield). Diastereoselectivity was detected by GC-MS to be 6:1 with a full conversion, the major conformation was also confirmed by 2D COSY and NOESY experiments. $^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 7.30 – 7.23 (m, 5H), 3.75 (s, 3H), 3.69 (d, $J = 11.7$ Hz, 1H), 3.07 (s, 3H), 2.45 (dd, $J = 13.8, 11.8$ Hz, 1H), 2.29 (dd, $J = 13.8, 7.3$ Hz, 1H), 1.93 – 1.84 (m, 1H), 1.59 – 1.51 (m, 1H), 1.12 (d, $J = 6.4$ Hz, 3H), 0.90 (d, $J = 6.5$ Hz, 3H). $^{13}$C NMR (151 MHz, Chloroform-$d$) $\delta$ 173.5, 171.4, 139.7, 129.0, 127.9, 126.8, 64.4, 58.7, 52.6, 51.8, 46.3, 42.6, 39.8, 17.3, 15.9. HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ calc 313.1410, found 313.1413.

The product was obtained by using the standard procedure with 2.5 mol% $[(\alpha$-diimine)Ni($\mu$-Br)$_2$]•5 in HFIP (1.0 mL) at 50 °C for 16 hours. After concentration, it was purified by column chromatography (hexane : EtOAc = 10:1) to give a colorless oil (24.6 mg, 96% yield). Diastereoselectivity was detected by GC-MS to be 4:1 with a full conversion, the major conformation was also confirmed to be the identical one by 2D COSY and NOESY experiments. $^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 3.71 (s, 3H), 3.70 (s, 3H), 2.43 (ddd, $J = 8.6, 3.0, 0.7$ Hz, 1H), 2.17 (dd, $J = 13.3, 7.2$ Hz, 1H), 2.01 (dd, $J = 13.3, 11.7$ Hz, 1H), 1.94 (td, $J = 6.9, 3.0$ Hz, 1H), 1.45 (ddd, $J = 9.7, 8.6, 6.5$ Hz, 1H), 1.36 –
1.30 (m, 1H), 1.05 (d, J = 6.5 Hz, 3H), 1.01 (d, J = 6.4 Hz, 3H), 0.96 (d, J = 7.0 Hz, 3H), 0.78 (d, J = 6.9 Hz, 3H). 

$^{13}$C NMR (151 MHz, Chloroform-$d$) δ 173.6, 172.1, 63.4, 56.7, 52.6, 52.2, 42.4, 41.4, 39.9, 27.8, 23.5, 19.7, 17.7, 17.3. HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ calcld 279.1567, found 279.1571.

**dimethyl (2,3-trans,3,4-trans)-2,3,4-trimethylcyclopentane-1,1-dicarboxylate (17):**

The product was obtained by using the standard procedure with 2.5 mol% $[(\alpha\text{-diimine})\text{Ni}(\mu\text{-Br})]_2$ in HFIP (0.5 mL) at 50 °C for 16 hours. After concentration, it was purified by column chromatography (hexane : EtOAc = 20:1) to give a colorless oil (20.7 mg, 91% yield). Diastereoselectivity was detected by GC-MS to be 2:1 with a full conversion, the major conformation was also confirmed to be the identical one by 2D COSY and NOESY experiments. 

$^1$H NMR (600 MHz, Chloroform-$d$) δ 3.72 (s, 3H), 3.69 (s, 3H), 2.29 – 2.21 (m, 2H), 2.08 (dd, J = 13.8, 10.7 Hz, 1H), 1.40 (dddd, J = 17.1, 8.1, 6.5, 4.1 Hz, 1H), 1.18 – 1.10 (m, 1H), 1.00 (d, J = 6.4 Hz, 3H), 0.96 (d, J = 7.0 Hz, 3H), 0.94 (d, J = 6.5 Hz, 3H). 

$^{13}$C NMR (151 MHz, Chloroform-$d$) δ 173.6, 172.6, 62.6, 52.5, 52.0, 48.0, 47.8, 41.7, 40.2, 17.7, 16.0, 14.6. 

HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ calcld 251.1254, found 251.1258.

**trans-7,8-dimethyl-2-oxaspiro[4.4]nonan-1-one (32):**

The product was obtained by using the standard procedure in HFIP (0.5 mL) with 2.5 mol% $[(\alpha\text{-diimine})\text{Ni}(\mu\text{-Br})]_2$ at 50 °C for 16 hours. After concentration, it was purified by column chromatography (hexane : EtOAc = 10:1) to give a colorless oil (13.1 mg, 78% yield). 

$^1$H NMR (600 MHz, Chloroform-$d$) δ 4.26 – 4.15 (m, 2H), 2.34 (dd, J = 13.2, 8.1 Hz, 1H), 2.21 – 2.09 (m, 2H), 1.84 (dd, J = 12.7, 6.6 Hz, 1H), 1.73 – 1.62 (m, 2H), 1.55 – 1.45 (m, 1H), 1.25 (dd, J = 13.2, 9.9 Hz, 1H), 1.00 (d, J = 6.3 Hz, 3H), 0.96 (d, J = 6.7 Hz, 3H). 

$^{13}$C NMR (151 MHz, Chloroform-$d$) δ 183.3, 65.5, 46.6, 45.5, 45.2, 42.4, 41.6, 38.7, 18.1, 17.3. HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ calcld 191.1043, found 191.1046.

**trans-3,4-dimethyl-1-tosylpyrrolidine (18):**

The product was obtained by using the standard procedure in acetone/HO$i$Pr (1.0 mL/0.2 mL) at 50 °C for 16 hours. After concentration, it was purified by column chromatography (hexane : EtOAc = 10:1) to give a white solid (20.0 mg, 79% yield, dr = 15:1), after recrystallization in DCM/hexane, the pure diastereomer (dr >19:1) product could be easily
obtained. $^1$H NMR (600 MHz, Chloroform-$d$) δ 7.71 (d, $J = 8.2$ Hz, 2H), 7.31 (dt, $J = 8.0$, 0.7 Hz, 2H), 3.50 (dd, $J = 9.8$, 6.9 Hz, 2H), 2.79 (t, $J = 9.5$ Hz, 2H), 2.43 (s, 3H), 1.63 – 1.46 (m, 2H), 0.90 (d, $J = 6.2$ Hz, 6H). $^1$H NMR (400 MHz, C$_6$D$_6$) δ 7.79 (d, $J = 8.2$ Hz, 2H), 6.85 – 6.79 (m, 2H), 3.42 (dd, $J = 9.7$, 6.9 Hz, 2H), 2.66 (t, $J = 9.4$ Hz, 2H), 1.90 (s, 3H), 1.10 – 0.99 (m, 2H), 0.44 (d, $J = 6.2$ Hz, 6H). $^{13}$C NMR (151 MHz, Chloroform-$d$) δ 143.2, 134.2, 129.6, 127.5, 55.0, 40.5, 21.5, 15.6. The product matches with the literature values.

The product was obtained by using the standard procedure with 2.5 mol% [(α-diimine)Ni($μ$-Br)$_2$] in acetonitrile/CH$_2$Cl$_2$ (1.0 mL/0.2 mL) at 50 °C for 16 hours. After concentration, it was purified by column chromatography (hexane : EtOAc = 8:1) to give a colorless oil (21.8 mg, 82% yield). $^1$H NMR (600 MHz, Chloroform-$d$) δ 7.74 – 7.68 (m, 2H), 7.35 – 7.29 (m, 2H), 3.48 (ddd, $J = 18.3$, 9.7, 7.5 Hz, 2H), 2.83 (dd, $J = 9.8$, 8.7 Hz, 1H), 2.76 (dd, $J = 9.7$, 9.0 Hz, 1H), 2.43 (s, 3H), 1.66 (ddt, $J = 9.0$, 7.3, 4.2 Hz, 1H), 1.51 – 1.42 (m, 2H), 1.09 – 1.02 (m, 1H), 0.90 (d, $J = 6.6$ Hz, 3H), 0.84 (d, $J = 6.2$ Hz, 6H). $^{13}$C NMR (151 MHz, Chloroform-$d$) δ 143.2, 134.0, 129.6, 127.5, 55.0, 47.5, 38.7, 24.7, 21.5, 16.3, 12.3. HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ calcd 290.1185, found 290.1189.

**trans-3-ethyl-4-methyl-1-tosylpyrrolidine (19):**

The product was obtained by using the standard procedure with 2.5 mol% [(α-diimine)Ni($μ$-Br)$_2$] in acetone/CH$_2$Cl$_2$ (1.0 mL/0.2 mL) at 50 °C for 16 hours. After concentration, it was purified by column chromatography (hexane : EtOAc = 8:1) to give a colorless oil (21.8 mg, 82% yield). $^1$H NMR (600 MHz, Chloroform-$d$) δ 7.74 – 7.68 (m, 2H), 7.35 – 7.29 (m, 2H), 3.48 (ddd, $J = 18.3$, 9.7, 7.5 Hz, 2H), 2.83 (dd, $J = 9.8$, 8.7 Hz, 1H), 2.76 (dd, $J = 9.7$, 9.0 Hz, 1H), 2.43 (s, 3H), 1.66 (ddt, $J = 9.0$, 7.3, 4.2 Hz, 1H), 1.51 – 1.42 (m, 2H), 1.09 – 1.02 (m, 1H), 0.90 (d, $J = 6.6$ Hz, 3H), 0.84 (d, $J = 6.2$ Hz, 6H). $^{13}$C NMR (151 MHz, Chloroform-$d$) δ 143.2, 134.0, 129.6, 127.5, 55.0, 47.5, 38.7, 24.7, 21.5, 16.3, 12.3. HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ calcd 290.1185, found 290.1189.

**trans-3-methyl-4-propyl-1-tosylpyrrolidine (20):**

The product was obtained by using the standard procedure with 5 mol% [(α-diimine)Ni($μ$-Br)$_2$] in acetone/CH$_2$Cl$_2$ (1.0 mL/0.2 mL) at 50 °C for 16 hours. After concentration, it was purified by column chromatography on silica gel (hexanes:EtOAc = 10:1) to give a white solid (16.3 mg, 58% yield). $^1$H NMR (600 MHz, Chloroform-$d$) δ 7.72 – 7.69 (m, 2H), 7.32 – 7.29 (m, 2H), 3.50 (dd, $J = 9.8$, 7.5 Hz, 1H), 3.46 (dd, $J = 9.7$, 7.5 Hz, 1H), 2.81 (dd, $J = 9.8$, 8.9 Hz, 1H), 2.76 (dd, $J = 9.7$, 8.9 Hz, 1H), 2.43 (s, 3H), 1.65 (tdd, $J = 8.9$, 7.2, 6.4 Hz, 1H), 1.56 – 1.47 (m, 1H), 1.40 (dtt, $J = 13.2$, 10.3, 6.1, 4.3 Hz, 1H), 1.27 – 1.23 (m, 1H), 1.21 – 1.16 (m, 1H), 1.00 (dtt, $J = 13.2$, 9.8, 5.1 Hz, 1H), 0.90 (d, $J = 6.6$ Hz, 3H), 0.85 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (151 MHz, Chloroform-$d$) δ 143.2, 134.0, 143.2, 134.2, 129.6, 127.5, 55.0, 47.5, 38.7, 24.7, 21.5, 16.3, 12.3.

trans-3-butyl-4-methyl-1-tosylpyrrolidine (21):

The product was obtained by using the standard procedure with 10 mol% [(α-diimine)Ni(μ-Br)]_2 5 in acetone/HO^iPr (5/1, 0.2 mL) at 50 °C for 16 hours. After concentration, it was purified by column chromatography on silica gel (hexanes:EtOAc = 10:1) to give a colorless oil (14.5 mg, 49% yield from the cis-alkene; 11.5 mg, 39% from the trans-alkene). ¹H NMR (600 MHz, Chloroform-d) δ 7.71 – 7.68 (m, 2H), 7.32 – 7.29 (m, 2H), 3.49 (dd, J = 9.8, 7.5 Hz, 1H), 3.46 (dd, J = 9.7, 7.5 Hz, 1H), 2.81 (dd, J = 9.8, 8.9 Hz, 1H), 2.76 (dd, J = 9.7, 9.0 Hz, 1H), 2.42 (s, 3H), 1.66 – 1.63 (m, 1H), 1.49 (tdd, J = 9.2, 4.6, 3.0 Hz, 1H), 1.45 – 1.38 (m, 1H), 1.26 – 1.11 (m, 4H), 1.04 – 0.96 (m, 1H), 0.90 (d, J = 6.6 Hz, 3H). ¹³C NMR (151 MHz, Chloroform-d) δ 143.2, 134.0, 129.6, 127.5, 54.9, 53.5, 45.8, 39.0, 31.6, 30.2, 22.8, 21.5, 16.3, 13.9. HRMS (APCI-TOF) m/z: [M + H]^+ calcd 296.1679, found 296.1679.

trans-3-hexyl-4-methyl-1-tosylpyrrolidine (22):

The product was obtained by using the standard procedure with 5 mol% [(α-diimine)Ni(μ-Br)]_2 5 in HFIP (0.2 mL) at 50 °C for 16 hours. After concentration, it was purified by column chromatography on silica gel (hexane : Et₂O = 8:1) to give a colorless oil (14.2 mg, 44% yield). ¹H NMR (600 MHz, Chloroform-d) δ 7.74 – 7.69 (m, 2H), 7.33 – 7.30 (m, 2H), 3.50 (dd, J = 9.8, 7.5 Hz, 1H), 3.47 (dd, J = 9.7, 7.5 Hz, 1H), 2.82 (dd, J = 9.8, 8.8 Hz, 1H), 2.77 (dd, J = 9.7, 8.9 Hz, 1H), 1.69 – 1.61 (m, 1H), 1.52 – 1.47 (m, 1H), 1.46 – 1.39 (m, 1H), 1.25 – 1.17 (m, 8H), 1.04 – 0.98 (m, 1H), 0.91 (d, J = 6.6 Hz, 3H), 0.87 (s, 3H). ¹³C NMR (151 MHz, Chloroform-d) δ 143.2, 134.0, 129.6, 127.5, 54.9, 53.5, 45.9, 39.0, 31.9, 31.7, 29.4, 28.0, 22.6, 21.5, 16.3, 14.1. HRMS (APCI-TOF) m/z: [M + H]^+ calcd 324.1992, found 324.1990.

trans-3,4-diethyl-1-tosylpyrrolidine (23):

The product was obtained by using the standard procedure in acetone/HO^iPr (1.0 mL/0.2 mL) at 50 °C for 16 hours. After concentration, it was purified by column chromatography (hexane : Et₂O = 8:1) to give a colorless oil (8.7 mg, 31% yield). ¹H NMR (600 MHz, Chloroform-d) δ 7.75 – 7.68 (m, 2H), 7.35 – 7.29 (m, 2H), 3.51 –
3.42 (m, 2H), 2.83 (dd, J = 9.8, 8.0 Hz, 2H), 2.44 (s, 3H), 1.57 – 1.53 (m, 2H), 1.48 (ddt, J = 10.2, 7.5, 4.0 Hz, 2H), 1.14 – 1.02 (m, 2H), 0.83 (t, J = 7.4 Hz, 6H). $^{13}$C NMR (151 MHz, Chloroform-d) δ = 143.2, 133.8, 129.6, 127.5, 53.1, 45.7, 25.3, 21.6, 12.3. HRMS (ESI-TOF) m/z: [M + H]$^+$ calc 304.1342, found 304.1341. The major byproduct of the reaction was the direduced starting material.

$^1$H NMR (600 MHz, Chloroform-d) δ = 7.71 (d, J = 6.0 Hz, 2H), 7.32 (d, J = 6.0 Hz, 2H), 3.46 (dd, J = 9.7, 7.0 Hz, 2H), 2.83 (dd, J = 9.8, 7.9 Hz, 2H), 2.44 (s, 3H), 1.58 – 1.52 (m, 2H), 1.48 (ddt, J = 10.1, 7.5, 4.0 Hz, 2H), 1.13 – 1.03 (m, 2H), 0.83 (t, J = 7.4 Hz, 6H). $^{13}$C NMR (151 MHz, Chloroform-d) δ 143.2, 133.8, 129.6, 127.5, 53.1, 45.7, 25.3, 21.6, 12.3.

3,3,4-trimethyl-1-tosylpyrrolidine (24):

The product was obtained by using the standard procedure in acetone/HO$i$Pr (1.0 mL/0.2 mL) at 50 °C for 16 hours. After concentration, it was purified by column chromatography (hexanes:Et$_2$O = 8:1) to give a colorless oil (12.5 mg, 47% yield). $^1$H NMR (600 MHz, Chloroform-d) δ 7.72 – 7.69 (m, 2H), 7.32 – 7.29 (m, 2H), 3.47 (dd, J = 9.8, 7.8 Hz, 1H), 3.16 (d, J = 9.6 Hz, 1H), 3.00 – 2.93 (m, 1H), 2.89 (t, J = 9.7 Hz, 1H), 2.43 (s, 3H), 1.77 – 1.67 (m, 1H), 0.90 (s, 3H), 0.78 (d, J = 6.9 Hz, 3H), 0.66 (s, 3H). $^{13}$C NMR (151 MHz, Chloroform-d) δ 143.1, 134.4, 129.5, 127.4, 61.0, 53.5, 42.4, 40.3, 24.8, 21.5, 20.0, 11.4. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calc 290.1185, found 290.1190.

trans-3-methyl-1-tosylcahydro-1H-indole (25):

The product was obtained by using the standard procedure with 5 mol% [(α-diimine)Ni(μ-Br)$_2$] in acetone/HO$i$Pr (5/1, 0.2 mL) at 50 °C for 16 hours. Purification by column chromatography (hexanes:Et$_2$O = 8:1) gave a mixture of saturated and unsaturated products in a 1:1 ratio. Reduction of the mixture with 1 atm H$_2$ of 25 mL bomb flask in the presence of Pd/C (10 wt%, 5 mg), followed by purification by column chromatography (hexanes:Et$_2$O = 8:1) gave

the single diastereomer 25 as a colorless oil (20.0 mg, 68% yield). $^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 7.72 – 7.70 (m, 2H), 7.31 – 7.28 (m, 2H), 3.65 (dt, $J = 10.5$, 6.4 Hz, 1H), 3.61 (dd, $J = 9.6$, 7.4 Hz, 1H), 2.69 (t, $J = 9.6$ Hz, 1H), 2.42 (s, 3H), 2.24 – 2.16 (m, 1H), 2.01 – 1.96 (m, 1H), 1.67 – 1.59 (m, 2H), 1.48 – 1.37 (m, 3H), 1.24 (ddd, $J = 8.5$, 4.7, 2.2 Hz, 1H), 1.18 (dddd, $J = 11.8$, 10.0, 4.7, 3.3 Hz, 2H), 0.82 (d, $J = 6.5$ Hz, 3H). $^{13}$C NMR (151 MHz, Chloroform-$d$) $\delta$ 143.0, 135.4, 129.5, 127.3, 60.2, 54.7, 44.6, 33.1, 30.9, 24.3, 23.7, 21.5, 20.9, 15.9. HRMS (APCI-TOF) $m/z$: [M + H]$^+$ calcd 294.1522, found 294.1520.

6. Synthetic Applications

1) Synthesis of the pyrrolidine derivatives 26

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N-Ts
18
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A solution of sodium naphthalenide in DME was prepared by adding DME to a mixture of sodium (50 mg, 2.17 mmol) and naphthalene (350 mg, 2.74 mmol) under nitrogen and stirring the resulting mixture for 2 hours to give a blue solution. Then this solution was added to a solution of starting material (63.3 mg, 0.25 mmol) in 1.0 mL DME dropwise at -78 °C under nitrogen until a green color persisted. Finally, the mixture was left stirring with the reaction allowed to warm to rt overnight. 2 drops saturated aqueous NaHCO$_3$ and 500 mg K$_2$CO$_3$ were added to the mixture. After stirring for 1 hour, the mixture was filtered, washed with Et$_2$O, and treated with 2 equiv. TsOH-H$_2$O (95 mg, 0.5 mmol) for 2 hours. After removing the solvent, hexane was added to wash the concentrated mixture, and the remaining light red oil was purified by recrystallization from DCM and Et$_2$O to afford the product as light red, needle-shaped crystals (48 mg, 71% yield). $^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 8.99 (s, 2H), 7.74 (d, $J = 8.2$ Hz, 2H), 7.24 – 7.18 (m, 2H), 3.53 (ddd, $J = 11.5$, 5.0, 2.1 Hz, 2H), 2.82 (ddd, $J = 10.9$, 7.0, 4.0 Hz, 2H), 2.38 (s, 3H), 1.84 – 1.69 (m, 2H), 1.02 (d, $J = 6.1$ Hz, 6H). $^{13}$C NMR (151 MHz, Chloroform-$d$) $\delta$ 141.4, 140.6, 129.0, 125.8, 51.8, 39.9, 21.4, 14.8. HRMS (ESI-TOF) $m/z$: [M – TsOH + H]$^+$ calcd 100.1126, found 100.1124.

2) Synthesis of the anti-3,4-dimethyl Gababutin 36
According to the reported procedure, a 5 mL THF solution of \(\gamma\)-butyrolactone (166 mg, 2.0 mmol) was dropwise added to a solution of NaHMDS (4.2 mmol) in 4.2 mL THF at -78 °C under nitrogen. Then the mixture was stirred at -20 °C for 30 mins. After cooling back to -78 °C, allylbromide (504 mg, 4.2 mmol) in 5 mL THF was added dropwise to the mixture over 10 mins. The reaction was left stirring overnight while allowing the reaction to warm to rt. Saturated aqueous NH\(_4\)Cl solution was added to quench the reaction and the product was extracted with EtOAc. The combined organic layers were dried over Na\(_2\)SO\(_4\), filtered, concentrated, and purified by column chromatography (hexane:EtOAc = 10:1). 330 mg (99% yield) colorless oil was obtained, which showed a \(^1\)H NMR spectrum matching the reported one. Then, this new synthesized starting material was used to run the next step by using \([Ar\alpha\text{-diimine}Ni(I)Br]_2\) (54 mg, 2.5 mol%), Et\(_2\)SiH\(_2\) (352 mg, 2.0 equiv) and HFIP (5 mL) following the general procedure. After workup, 262 mg (78% yield) colorless oil was obtained.

Substrate (380 mg (2.26 mmol)) was transferred into a 25 mL sealed bomb flask with 2 mL MeOH. Then 2 mL (80 mmol, 35 equiv) liquid ammonia was condensed into the bomb flask through ammonia flow under -78 °C. Then the reaction was stirred for 3 days at room temperature. After the reaction, the solvent was removed to give a white solid. To recover the unreacted starting material, it was washed with Et\(_2\)O, combined, and purified by column chromatography (hexane:Et\(_2\)O = 10:1) to give 84 mg starting material. The product 285 mg (68% yield, 88% brsm yield.) was obtained as a white solid. \(^1\)H NMR (600 MHz, DMSO-\(d_6\)) \(\delta\) 7.02 (s, 1H), 6.69 (s, 1H), 4.30 (t, \(J = 5.0\) Hz, 1H), 3.30 – 3.22 (m, 2H), 2.31 (dd, \(J = 12.8, 6.9\) Hz, 1H), 1.79 – 1.68 (m, 3H), 1.66 – 1.60 (m, 1H), 1.36 (tt, \(J = 10.0, 6.8\) Hz, 1H), 1.24 (tt, \(J = 10.0, 6.8\) Hz, 1H), 1.02 – 0.95 (m, 1H), 0.90 (d, \(J = 2.4\) Hz, 3H), 0.88 (d, \(J = 2.4\) Hz, 3H). \(^{13}\)C NMR (151
MHz, DMSO-\textit{d}_6) \delta 179.4, 58.6, 50.1, 48.0, 45.4, 44.3, 41.8, 40.0, 18.5, 18.4. HRMS (APCI-TOF) \textit{m/z}: [M – H\textsubscript{2}O + H]\textsuperscript{+} calcd 168.1383, found 168.1382.

220 mg (1.19 mmol) starting material and 20 mL anhydrous THF were added to a 50 mL bomb flask. Next, LiAlH\textsubscript{4} (440 mg, 11.9 mmol) was added to the mixture in portions. The mixture was heated at 60 °C for overnight, then quenched by adding aqueous potassium sodium tartrate. The product was extracted with EtOAc (3 x 20 mL). Combined organic layers were extracted with 2 x 20 mL 2 N aqueous HCl. Then, 20% aqueous NaOH was added to the combined aqueous layers to adjust the pH to around 11. The pure product was extracted again from the combined aqueous layers with EtOAc (3 x 20 mL). After drying over Na\textsubscript{2}SO\textsubscript{4}, filtering, and concentrating, 205 mg product (99% yield) was obtained as a colorless oil. \textsuperscript{1}H NMR (600 MHz, Chloroform-\textit{d}) \delta 3.63 – 3.53 (m, 2H), 3.50 – 2.83 (m, 3H), 2.67 (d, \textit{J} = 12.2 Hz, 1H), 2.59 (d, \textit{J} = 12.2 Hz, 1H), 1.72 (m, 2H), 1.65 (m, 2H), 1.39 (m, 2H), 1.06 – 0.94 (m, 2H), 0.93 (dd, \textit{J} = 2.1 Hz, 3H), 0.92 (d, \textit{J} = 2.1 Hz, 3H). \textsuperscript{13}C NMR (151 MHz, Chloroform-\textit{d}) \delta 58.9, 51.3, 46.1, 46.0, 45.0, 41.2, 40.9, 35.3, 18.1, 18.1. HRMS (ESI-TOF) \textit{m/z}: [M + H]\textsuperscript{+} calcd 172.1701, found 172.1698.

Starting material (17.1 mg, 0.1 mmol) and 0.5 mL THF were added into 20-mL vial. Then NEt\textsubscript{3} (111 mg, 0.11 mmol) and Boc\textsubscript{2}O (20.8 mg, 0.1 mmol) were added. After stirring overnight at rt, the solvent was removed and the product was purified by column chromatography (hexane : EtOAc = 2:1) to give 25.3 mg (93% yield) colorless oil. \textsuperscript{1}H NMR (600 MHz, Chloroform-\textit{d}) \delta 4.92 (s, 1H), 3.71 (dtd, \textit{J} = 6.4, 4.0, 2.1 Hz, 2H), 3.22 – 3.09 (m, 1H), 2.95 (d, \textit{J} = 13.7 Hz, 1H), 1.81 (s, 1H), 1.74 – 1.66 (m, 2H), 1.61 (td, \textit{J} = 6.6, 3.2 Hz, 2H), 1.44 (s, 9H), 1.43 – 1.37 (m, 2H), 1.02 (ddd, \textit{J} = 13.0, 10.5, 7.5 Hz, 2H), 0.93 (d, \textit{J} = 3.6 Hz, 3H), 0.92 (d, \textit{J} = 3.6 Hz, 3H). \textsuperscript{13}C
NMR (151 MHz, Chloroform-\(d\)) \(\delta\) 156.7, 60.0, 45.5, 43.7, 43.3, 41.6, 41.4, 41.3, 28.4, 18.1, 18.0, 16.0, 15.8. HRMS (APCI-TOF) \(m/z\): [M – H\(_2\)O + H]\(^+\) calcd 254.2115, found 254.2142.

Substrate (17.4 mg, 0.064 mmol) and prepared PDC reagent (75 mg, 3.5 equiv) were added together in a 50-mL round bottom flask. The flask atmosphere was removed and replaced with nitrogen three times, and 0.1 mL DMF was added and the reaction was stirred for 6 hours. Then, 1 mL water was added and the product was extracted with Et\(_2\)O (3 x 2 mL). The combined organic layers were dried over Na\(_2\)SO\(_4\), filtered, and concentrated, and the product was purified by column chromatography (hexane : EtOAc = 3:1) to give a white solid (15.9 mg, 93% yield). ¹H NMR (600 MHz, Chloroform-\(d\)) \(\delta\) 3.58 (d, \(J\) = 10.5 Hz, 1H), 3.52 (d, \(J\) = 10.5 Hz, 1H), 2.48 (d, \(J\) = 16.8 Hz, 1H), 2.41 (d, \(J\) = 16.8 Hz, 1H), 1.93 (ddd, \(J\) = 20.4, 13.1, 6.9 Hz, 2H), 1.52 (s, 9H), 1.52 – 1.48 (m, 2H), 1.33 – 1.24 (m, 2H), 1.01 – 0.95 (m, 6H). ¹³C NMR (151 MHz, Chloroform-\(d\)) \(\delta\) 173.7, 150.2, 82.8, 59.7, 48.3, 47.6, 47.2, 41.7, 41.6, 40.5, 28.1, 18.4, 18.4. HRMS (APCI-TOF) \(m/z\): [M + H]\(^+\) calcd 268.1907, found 268.1925.

Substrate (17.4 mg, 0.064 mmol) and prepared PDC reagent (75 mg, 3.5 equiv) were added together in a 50-mL round bottom flask. The flask atmosphere was removed and replaced with nitrogen three times, and 0.1 mL DMF was added and the reaction was stirred for 6 hours. Then, 1 mL water was added and the product was extracted with Et\(_2\)O (3 x 2 mL). The combined organic layers were dried over Na\(_2\)SO\(_4\), filtered, and concentrated, and the product was purified by column chromatography (hexane : EtOAc = 3:1) to give a white solid (15.9 mg, 93% yield). ¹H NMR (600 MHz, Chloroform-\(d\)) \(\delta\) 6.03 (s, 1H), 3.22 (d, \(J\) = 9.3 Hz, 1H), 3.20 (d, \(J\) = 9.3 Hz, 1H), 2.28 (d, \(J\) = 16.5 Hz, 1H), 2.22 (d, \(J\) = 16.5 Hz, 1H), 1.95 (dt, \(J\) = 13.0, 7.1 Hz, 2H), 1.55 – 1.42 (m, 2H), 1.35 – 1.26 (m, 2H), 0.97 (d, \(J\) = 3.9 Hz, 3H), 0.96 (d, \(J\) = 3.9 Hz, 3H). ¹³C NMR (151 MHz, Chloroform-\(d\)) \(\delta\) 178.2, 56.2, 48.4, 48.0, 45.8, 45.1, 41.7, 41.6, 40.5, 28.1, 18.4, 18.5. HRMS (APCI-TOF) \(m/z\): [M + H]\(^+\) calcd 168.1383, found 168.1380.
Synthesis of the desired Gababutin derivative can also be achieved through a more direct dehydrogenative pathway\textsuperscript{16}. [Ru(COD)Cl\textsubscript{2}]	extsubscript{n} (2.8 mg, 0.01 mmol, 10 mol%), ICy$\cdot$HBF\textsubscript{4} (3.2 mg, 0.01 mmol, 10 mol%), PCy\textsubscript{3} (2.8 mg, 0.01 mmol, 10 mol%), KOtBu (3.4 mg, 0.03 mmol, 30 mol%) and 0.1 mL toluene were added to a 5 mL bomb flask in a nitrogen-filled glove box. Outside of the glove box, the sealed mixture was heated at 130 °C for 20 mins, then brought back into the box again. Finally, the substrate (18.1 mg, 0.106 mmol) in 0.4 mL toluene was added into the bomb flask, and the reaction was let stir at rt. After 18 hours, the reaction was concentrated and purified by column chromatography on a silica gel (EtOAc : MeOH = 25:1) to give 16.3 mg (93% yield) white solid, which showed an identical $^1$H NMR spectrum as the product obtained from the previous method.

### 7. Details of DFT Calculations

All geometry optimizations were performed using the B3LYP hybrid functional as implemented in Gaussian. The 6-31G* split-valence double zeta basis set was used for the hydrogen, carbon, and nitrogen atoms while the 6-31G** was used for the second-row silicon atom. For the nickel metal center, the LANL2DZ effective core potential and basis was used. Solvation effects were accounted for using the implicit SMD solvation model with Acetone as the solvent. The EPR parameters were calculated with the B3LYP functional using the ORCA package. The polarized split-valence double zeta def2-SV(P) was used as the basis set for the carbon and hydrogens while the polarized triple-zeta def2-TZVP was used for the nickel, silicon, and nitrogen. The spin-orbit coupling was also calculated as a correction to the hyperfine coupling tensor. Solvation was also included in the electronic structure calculation using the COSMO implicit solvation model with Acetone as the solvent.

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8. Spectra

Figure S7. $^1$H NMR spectrum of 5.

Figure S8. FTIR spectrum of 5.
Figure S9. $^1$H NMR spectrum of S17.

Figure S10. $^{13}$C NMR spectrum of S17.
**Figure S11.** $^1$H NMR spectrum of S16.

**Figure S12.** $^{13}$C NMR spectrum of S16.
Figure S13. $^1$H NMR spectrum of S15.

Figure S14. $^{13}$C NMR spectrum of S15.
Figure S15. $^1$H NMR spectrum of S22.

Figure S16. $^{13}$C NMR spectrum of S22.
Figure S17. $^1$H NMR spectrum of S20.

Figure S18. $^{13}$C NMR spectrum of S20.
Figure S19. $^1$H NMR spectrum of S21.

Figure S20. $^{13}$C NMR spectrum of S21.
Figure S21. $^1$H NMR spectrum of 2.

Figure S22. $^{13}$C NMR spectrum of 2.
Figure S23. $^1$H NMR spectrum of 9.

Figure S24. $^{13}$C NMR spectrum of 9.
Figure S25. $^1$H NMR spectrum of 10.

Figure S26. $^{13}$C NMR spectrum of 10.
Figure S27. Crude $^1$H NMR spectrum of 11 with 1,3,5-trimethoxybenzene as internal standard.

Figure S28. $^1$H NMR spectrum of 11.
Figure S29. $^{13}$C NMR spectrum of 11.

Figure S30. $^1$H NMR spectrum of 12.
Figure S31. $^{13}$C NMR spectrum of 12.

Figure S32. $^1$H NMR spectrum of 13.
Figure S33. $^{13}$C NMR spectrum of 13.
**Figure S34.** Crude $^1$H NMR spectrum of 14 with 1,3,5-trimethoxybenzene as an internal standard.

**Figure S35.** $^1$H NMR spectrum of mixture of 14 and monoreduced byproduct S14red.
Figure S36. $^1$H-$^1$H COSY spectra of 14 and S14red.

Figure S37. $^{13}$C NMR spectrum of mixture of 14 and S14red.
Figure S38. $^1$H NMR spectrum of 15.

Figure S39. $^{13}$C NMR spectrum of 15.
Figure S40. $^1$H-$^1$H COSY NMR spectrum of 15.

Figure S41. $^1$H-$^1$H NOESY NMR spectrum of 15.
Figure S42. $^1$H NMR spectrum of 16.

Figure S43. $^{13}$C NMR spectrum of 16.
Figure S44. $^1$H-$^1$H COSY NMR spectrum of 16.

Figure S45. $^1$H-$^1$H NOESY NMR spectrum of 16.
Figure S46. $^1$H NMR spectrum of 12.

Figure S47. $^{13}$C NMR spectrum of 17.
Figure S48. $^1$H-$^1$H COSY NMR spectrum of 17.

Figure S49. $^1$H-$^1$H NOESY NMR spectrum of 17.
Figure S50. $^1$H NMR spectrum of 18.

Figure S51. $^{13}$C NMR spectrum of 18.
Figure S52. ^1^H NMR spectrum of 19.

Figure S53. ^1^3^C NMR spectrum of 19.
Figure S54. $^1$H NMR spectrum of 20.

Figure S55. $^{13}$C NMR spectrum of 20.
Figure S56. $^1$H NMR spectrum of 21.

Figure S57. $^{13}$C NMR spectrum of 21.
Figure S58. $^1$H NMR spectrum of 22.

Figure S59. $^{13}$C NMR spectrum of 22.
Figure S60. $^1$H NMR spectrum of 23.

Figure S61. $^{13}$C NMR spectrum of 23.
Figure S62. $^1$H NMR spectrum of 24.

Figure S63. $^{13}$C NMR spectrum of 24.
Figure S64. $^1$H NMR spectrum of 25.

Figure S65. $^{13}$C NMR spectrum of 25.
Figure S66. \(^1\)H NMR spectrum of 26·TsOH.

Figure S67. \(^{13}\)C NMR spectrum of 26·TsOH.
Figure S68. $^1$H NMR spectrum of 32.

Figure S69. $^{13}$C NMR spectrum of 32.
Figure S70. $^1$H NMR spectrum of 33.

Figure S71. $^{13}$C NMR spectrum of 33.
Figure S72. $^1$H NMR spectrum of 34.

Figure S73. $^{13}$C NMR spectrum of 34.
Figure S74. $^1$H NMR spectrum of S34.

Figure S75. $^{13}$C NMR spectrum of S34.
Figure S76. $^1$H NMR spectrum of S35.

Figure S77. $^{13}$C NMR spectrum of S35.
Figure S78. $^1$H NMR spectrum of 35.

Figure S79. $^{13}$C NMR spectrum of 35.
Figure S80. $^1$H NMR spectrum of S1.

Figure S81. $^{13}$C NMR spectrum of S1.
Figure S82. $^1$H NMR spectrum of S2.

Figure S83. $^{13}$C NMR spectrum of S2.
Figure S84. $^1$H NMR spectrum of S3.

Figure S85. $^{13}$C NMR spectrum of S3.
Figure S86. $^1$H NMR spectrum of 40.

Figure S87. $^{13}$C NMR spectrum of 40.
Figure S88. $^1$H NMR spectrum of 43.

Figure S89. $^{13}$C NMR spectrum of 43.
Figure S90. $^1$H NMR spectrum of 42.

Figure S91. $^{13}$C NMR spectrum of 42.
Figure S92. $^1$H NMR spectrum of 41.

Figure S93. $^{13}$C NMR spectrum of 41.