Supporting Information for:

Iron-Catalyzed Synthesis of Cyclopropanes by in situ Generation and Decomposition of Electronically Diversified Diazo Compounds

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1. General Information

All cyclopropanation reactions were run under an argon atmosphere with oven-dried glassware using standard techniques for manipulating air-sensitive compound.\(^1\) CH\(_2\)Cl\(_2\) was distilled over calcium hydride under argon prior to use. Flash column chromatography was performed on 230-400 \(\mu\)m mesh silica with the indicated eluent. Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). Melting points were obtained on a Buchi melting point apparatus and are uncorrected. Nuclear magnetic resonance spectra were recorded on either a 400 or 500 MHz spectrometers (Bruker Ultrashield 400 or Bruker Ultrashield 500 plus) at 293 K. The corresponding chemical shifts for \(^1\)H NMR and \(^{13}\)C NMR spectra are reported in parts per million relative to the chemical shift of tetramethylsilane and recorded in (CD\(_3\))\(_2\)SO, using the residual (CH\(_3\))\(_2\)SO as reference (\(^1\)H: 52.50 ppm, \(^{13}\)C: 83.52 ppm); or in CDCl\(_3\), using the residual CHCl\(_3\) as reference (\(^1\)H: 7.26 ppm, \(^{13}\)C: 77.16 ppm). The corresponding chemical shifts of \(^{19}\)F NMR spectra are reported in parts per million and recorded in DMSO-\(d_6\) or CDCl\(_3\), using \(\alpha,\alpha,\alpha\)-trifluorotoluene (\(^{19}\)F: -63.72 ppm) as reference. The data is reported as follows: chemical shift (ppm), multiplicity (s = singlet, br = broad singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, ddd = doublet of doublet of doublets, dttd = doublet of triplet of doublets, t = triplet, app. t = apparent triplet, q = quadruplet, quin = quintet, sext = sextet and m = multiplet), coupling constant in Hz, integration. For new compounds, DEPT 135 experiments were conducted to assign the substitution pattern for each carbon (C\(_q\), CH, CH\(_2\), CH\(_3\)). Infrared spectra were recorded on a Bruker Vertex Series FTIR and are reported in reciprocal centimeters (cm\(^{-1}\)). High resolution mass spectra were performed by the Centre régional de spectroscopie de masse de l’Université de Montréal.

2. Reagents

Commercially available reagents were used as supplied or purified by standard techniques where necessary. Non-commercial starting materials were synthesized according to literature procedures.

3. Optimization

Hydrazones screening

\[
\text{Ar} \quad \text{O=S=O} \quad \text{NH} \\
\text{Ph} \quad \text{H} \quad \text{Ph}
\]

1) NaH (1.5 equiv)
CH\(_2\)Cl\(_2\) [0.1 M], rt, 1 h

2) Styrene (5 equiv)
ClFe(TPP) (10 mol%) 
CH\(_2\)Cl\(_2\) [0.1 M], rt, o/n

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ar</th>
<th>dr</th>
<th>Yield (%)(^{a,b})</th>
<th>Mass balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Tolyl</td>
<td>-</td>
<td>27%</td>
<td>hydrazone recovered</td>
</tr>
<tr>
<td>2</td>
<td>Triisopropylphenyl</td>
<td>92:8</td>
<td>24%</td>
<td>dimerization</td>
</tr>
<tr>
<td>3</td>
<td>Mesityl</td>
<td>-</td>
<td>17%</td>
<td>dimerization</td>
</tr>
<tr>
<td>4</td>
<td>o-nitroaryl</td>
<td>92:8</td>
<td>65%</td>
<td>dimerization</td>
</tr>
</tbody>
</table>

\(^{a}\) Determined by \(^1\)H NMR (Ph\(_3\)CH used as internal standard).
\(^{b}\) Combined \(^1\)H NMR yields of both diastereomers.

Solvents screening

\[
\text{Ns} \quad \text{NH} \\
\text{Ph} \quad \text{H} \quad \text{Ph}
\]

1) NaH (1.5 equiv)
\textbf{Solvent} [0.1 M], rt, 1 h

2) Styrene (5 equiv)
ClFe(TPP) (10 mol%) 
\textbf{Solvent} [0.1 M], rt, o/n

<table>
<thead>
<tr>
<th>Entry</th>
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<th>dr</th>
<th>Yield (%)(^{a,b})</th>
<th>Mass balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH(_2)Cl(_2)</td>
<td>92:8</td>
<td>65%</td>
<td>dimerization</td>
</tr>
<tr>
<td>2</td>
<td>Et(_2)O</td>
<td>-</td>
<td>6%</td>
<td>hydrazone recovered</td>
</tr>
<tr>
<td>3</td>
<td>ACN</td>
<td>93:7</td>
<td>43%</td>
<td>dimerization</td>
</tr>
<tr>
<td>4</td>
<td>THF</td>
<td>94:6</td>
<td>56%</td>
<td>dimerization</td>
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</table>
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<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>dr</th>
<th>Yield (%)&lt;sup&gt;a,b&lt;/sup&gt;</th>
<th>Mass balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaH</td>
<td>92:8</td>
<td>65%</td>
<td>dimerization</td>
</tr>
<tr>
<td>2</td>
<td>NaH (1.01 equiv)</td>
<td>91:9</td>
<td>40%</td>
<td>hydrazone recovered</td>
</tr>
<tr>
<td>3</td>
<td>LiOt·Bu</td>
<td>-</td>
<td>0%</td>
<td>hydrazone recovered</td>
</tr>
<tr>
<td>4</td>
<td>NaOt·Bu</td>
<td>90:10</td>
<td>26%</td>
<td>hydrazone recovered</td>
</tr>
<tr>
<td>5</td>
<td>KOt·Bu</td>
<td>92:8</td>
<td>14%</td>
<td>hydrazone recovered</td>
</tr>
<tr>
<td>6</td>
<td>Cs₂CO₃</td>
<td>-</td>
<td>12%</td>
<td>hydrazone recovered</td>
</tr>
<tr>
<td>7</td>
<td>Cs₂CO₃</td>
<td>(temperature of the reaction = 40 °C)</td>
<td>81:9</td>
<td>67%</td>
</tr>
<tr>
<td>8</td>
<td>Cs₂CO₃</td>
<td>(temperature of the reaction = 40 °C)</td>
<td>90:10</td>
<td>73%</td>
</tr>
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<sup>a</sup> Determined by <sup>1</sup>H NMR (Ph₃CH used as internal standard).

<sup>b</sup> Combined <sup>1</sup>H NMR yields of both diastereomers.
Concentrations screening

1) NaH (1.5 equiv)  
CH$_2$Cl$_2$ [x M], 0 °C, 1 h  

2) Styrene (5 equiv)  
ClFe(TPP) (10 mol%)  
CH$_2$Cl$_2$ [x M], 0 °C to rt, o/n

<table>
<thead>
<tr>
<th>Entry</th>
<th>Concentration [x M]</th>
<th>dr</th>
<th>Yield (%)$^{a,b}$</th>
<th>Mass balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[0.1 M] (deprotonation at rt)</td>
<td>92:8</td>
<td>65%</td>
<td>dimerization</td>
</tr>
<tr>
<td>2</td>
<td>[0.1 M]</td>
<td>91:9</td>
<td>75%</td>
<td>dimerization</td>
</tr>
<tr>
<td>3</td>
<td>[0.2 M]</td>
<td>92:8</td>
<td>74%</td>
<td>dimerization</td>
</tr>
<tr>
<td>4</td>
<td>[0.05 M]</td>
<td>92:8</td>
<td>85%</td>
<td>quench of the diazo</td>
</tr>
<tr>
<td>5</td>
<td>[0.025 M]</td>
<td>91:9</td>
<td>74%</td>
<td>dimerization</td>
</tr>
</tbody>
</table>

$^a$ Determined by $^1$H NMR (1,3,5-trimethoxybenzene used as internal standard).  
$^b$ Combined $^1$H NMR yields of both diastereomers.

Catalyst loading

1) NaH (1.5 equiv)  
CH$_2$Cl$_2$ [0.05 M], 0 °C, 1 h  

2) Styrene (5 equiv)  
ClFe(TPP) (y mol%)  
CH$_2$Cl$_2$ [0.05 M], 0 °C to rt, o/n

<table>
<thead>
<tr>
<th>Entry</th>
<th>Loading (y mol%)</th>
<th>dr</th>
<th>Yield (%)$^{a,b}$</th>
<th>Mass balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 mol%</td>
<td>92:8</td>
<td>85%</td>
<td>quench of the remaining diazo</td>
</tr>
<tr>
<td>2</td>
<td>5 mol%</td>
<td>91:9</td>
<td>53%</td>
<td>hydrazone recovered</td>
</tr>
<tr>
<td>3</td>
<td>2.5 mol%</td>
<td>91:9</td>
<td>64%</td>
<td>hydrazone recovered</td>
</tr>
<tr>
<td>4</td>
<td>2.5 mol% (2 days)</td>
<td>92:8</td>
<td>75%</td>
<td>dimerization</td>
</tr>
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</table>

$^a$ Determined by $^1$H NMR (1,3,5-trimethoxybenzene used as internal standard).  
$^b$ Combined $^1$H NMR yields of both diastereomers.
Attempts using others transition metal catalysts

\[
\begin{align*}
1) & \text{NaH (1.5 equiv)} \\
& \text{CH}_2\text{Cl}_2 [0.05 \text{ M}], 0 ^\circ \text{C}, 1 \text{ h} \\
2) & \text{Styrene (5 equiv)} \\
& \text{catalyst (x mol%)} \\
& \text{CH}_2\text{Cl}_2 [0.05 \text{ M}], 0 ^\circ \text{C to rt, o/n}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (x mol%)</th>
<th>dr</th>
<th>Yield (%)$^{ab}$</th>
<th>Mass balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AgBF$_4$ (20 mol%)</td>
<td>22:78</td>
<td>54%</td>
<td>hydrazone recovered</td>
</tr>
<tr>
<td></td>
<td>(in CH$_2$Cl$_2$ [0.1M])</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Rh$_2$(OPiv)$_4$ (10 mol%)</td>
<td>17:83</td>
<td>72%</td>
<td>hydrazone recovered</td>
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</table>

$^a$ Determined by $^1$H NMR (triphenylmethane used as internal standard).

$^b$ Combined $^1$H NMR yields of both diastereomers.
Timerange of the reaction

\[
\begin{align*}
\text{Ns} & \quad \text{Ph} \\
\text{NH} & \quad \text{H} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

1) NaH (1.5 equiv) 
CH\(_2\)Cl\(_2\) [0.05 M], 0 °C, 1 h

2) Styrene (5 equiv) 
Cl\(\text{Fe(TPP)}\) (10 mol%) 
CH\(_2\)Cl\(_2\) [0.05 M], 0 °C to rt, time

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time</th>
<th>dr</th>
<th>Yield (%)(^{a,b})</th>
<th>Mass balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 h</td>
<td>92:8</td>
<td>26%</td>
<td>hydrazone recovered</td>
</tr>
<tr>
<td>2</td>
<td>3 h</td>
<td>92:8</td>
<td>52%</td>
<td>hydrazone recovered</td>
</tr>
<tr>
<td>3</td>
<td>6 h</td>
<td>91:9</td>
<td>54%</td>
<td>hydrazone recovered</td>
</tr>
<tr>
<td>4</td>
<td>15 h</td>
<td>92:8</td>
<td>80%</td>
<td>hydrazone recovered</td>
</tr>
<tr>
<td>5</td>
<td>19 h</td>
<td>92:8</td>
<td>85%</td>
<td>quench of the remaining diazo</td>
</tr>
<tr>
<td></td>
<td>24 h</td>
<td>91:9</td>
<td>99%</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^{a}\) Determined by \(^{1}\)H NMR (1,3,5-trimethoxybenzene used as internal standard). 

\(^{b}\) Combined \(^{1}\)H NMR yields of both diastereomers

**Yield (%) vs time (h)**
4. Synthetic procedures

**o-nitrobenzenesulfonylhydrazide synthesis**

*N-nitrobenzenesulfonylhydrazide (NsNHN\(_2\)) was prepared according to literature procedure.\(^2\)

**General procedure A - N-nosylhydrazones synthesis**

According to a procedure previously used in our group.\(^3\)

To a 20 mL glass vial containing a suspension of o-nitrobenzenesulfonylhydrazide (1.00 equiv) in EtOH [0.67M] were added the chosen aldehyde (1.01 or 1.05 equiv) in one portion and acetic acid (0.05 equiv). The heterogeneous mixture was vigorously stirred for 2 hours. The reaction mixture was then concentrated under vacuum until about 1/10th of the original volume remains, and excess hexanes was added, causing precipitation. The solid was recovered by filtration on a fritted glass filter then thoroughly washed with hexanes. The resulting solid was dried under reduced pressure overnight to give the pure desired N-nosylhydrazones.

**General procedure B - Cyclopropanation reaction, room temperature**

To an oven-dried 20 mL glass microwave vial equipped with a magnetic stirrer was weighted the chosen nosylhydrazone (0.50 mmol, 1.0 equiv). The flask was then capped with a septum and flushed with argon during few minutes, after which the freshly distilled CH\(_2\)Cl\(_2\) (10 mL, [0.05M]) was added. The reaction mixture was then cooled down to 0 °C with a water/ice bath and the flask was briefly opened to add NaH 50 wt% (36.0 mg, 0.75 mmol, 1.5 equiv) and the reaction mixture was stirred at this temperature for 1 hour. The chosen styrene (2.6 mmol, 5.2 equiv) was then added via syringe and the ClFe(TPP) (35.2 mg, 0.05 mmol, 10 mol%) was added in one portion. The ice-bath was removed and the reaction mixture was allowed to warm up to room temperature and to stir under an argon atmosphere for 24 hours. The reaction mixture was the quenched with an aqueous solution of HCl 2M and diluted with CH\(_2\)Cl\(_2\). The biphasic mixture was then filtered over celite to remove the iron residues, and the cake was washed several times with CH\(_2\)Cl\(_2\). The layers were separated and the aqueous one was extracted three times with CH\(_2\)Cl\(_2\). The combined organic layers were dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated under vacuum. The crude product was then purified by silica gel chromatography.


General procedure B’ - Cyclopropanation reaction, 40 °C

To an oven-dried 20 mL glass microwave vial equipped with a magnetic stirrer was weighted the chosen nosylhydrazone (0.50 mmol, 1.0 equiv). The flask was then capped with a septum and flushed with argon during few minutes, after which the freshly distilled CH₂Cl₂ (10 mL, [0.05M]) was added. The reaction mixture was then cooled down to 0 °C with a water/ice bath and the flask was briefly opened to add NaH 50 wt% (36.0 mg, 0.75 mmol, 1.5 equiv) and the reaction mixture was stirred at this temperature for 1 hour. The chosen styrene (2.6 mmol, 5.2 equiv) was then added via syringe and the ClFe(TPP) (35.2 mg, 0.05 mmol, 10 mol%) was added in one portion. The ice-bath was removed and the reaction mixture was allowed to warm up to room temperature. The flask was then sealed with a pressure cap, put into a 40 °C oil-bath and stirred at this temperature for 24 hours. Then reaction mixture was then cooled down to room temperature, quenched with an aqueous solution of HCl 2M and diluted with CH₂Cl₂. The biphasic mixture was then filtered over celite to remove the iron residues, and the cake was washed several times with CH₂Cl₂. The layers were separated and the aqueous one was extracted three times with CH₂Cl₂. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated under vacuum. The crude product was then purified by silica gel chromatography.
5. Characterization Data

(a) Hydrazones

\[
\text{(E)}-N'\text{-benzylidene-2-nitrobenzenesulfonohydrazide (1a)}
\]

Synthesized from benzaldehyde (440 μL, 4.31 mmol, 1.01 equiv), acetic acid (13 μL, 0.213 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (927 mg, 4.27 mmol, 1.00 equiv) using the general procedure A for N-nosylhydrazones synthesis. Product obtained as a yellow solid (1.28 g, 4.23 mmol, 99%). Product corresponds to literature characterization data.⁴

\[^1\text{H NMR (400 MHz, DMSO)} \delta \text{ 12.12 (s, 1H), 8.07 – 8.05 (m, 2H), 8.02 – 8.00 (m, 1H), 7.91 – 7.86 (m, 2H), 7.58 (dd, J = 6.8, 3.0 Hz, 2H), 7.42 – 7.38 (m, 3H).} \]
\[^{13}\text{C NMR (126 MHz, DMSO)} \delta \text{ 147.87 (Cq), 147.75 (CH), 134.79 (CH), 133.38 (Cq), 132.60 (CH), 130.90 (Cq), 130.50 (CH), 130.36 (CH), 128.83 (CH), 126.93 (CH), 124.52 (CH).} \]

\[
\text{(E)}-N'\text{-}(4\text{-chlorobenzylidene)-2-nitrobenzenesulfonohydrazide (1b)}
\]

Synthesized from 4-chlorobenzaldehyde (630 μL, 4.65 mmol, 1.01 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.60 mmol, 1.00 equiv) using the general procedure A for N-nosylhydrazones synthesis. Product obtained as a white solid (1.30 g, 3.82 mmol, 83%). Product corresponds to literature characterization data.⁴

\[^1\text{H NMR (400 MHz, DMSO)} \delta \text{ 12.24 (s, 1H), 8.07 – 8.00 (m, 3H), 7.92 – 7.87 (m, 2H), 7.61 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H).} \]
\[^{13}\text{C NMR (126 MHz, DMSO)} \delta \text{ 147.85 (Cq), 146.45 (CH), 134.84 (CH), 132.63 (CH), 132.33 (Cq), 130.86 (Cq), 130.47 (CH), 128.93 (CH), 128.58 (CH), 124.56 (CH).} \]

---

(E)-N’-(4-bromobenzylidene)-2-nitrobenzenesulfonohydrazide (1c)

Synthesized from 4-bromobenzaldehyde (860 mg, 4.65 mmol, 1.01 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.60 mmol, 1.00 equiv) using the general procedure A for N-nosylhydrazones synthesis. Product obtained as a yellowish solid (1.62 g, 4.23 mmol, 92%). mp: 154 - 158 °C (degradation).

¹H NMR (400 MHz, DMSO) δ 12.24 (s, 1H), 8.06 – 8.00 (m, 3H), 7.91 – 7.86 (m, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H). ¹³C NMR (126 MHz, DMSO) δ 147.84 (Cq), 146.53 (CH), 134.84 (CH), 132.67 (Cq), 132.64 (CH), 131.84 (CH), 130.87 (Cq), 130.46 (CH), 128.79 (CH), 124.57 (CH), 123.64 (Cq). FTIR (cm⁻¹) (neat): 3237, 1529, 1369, 1181, 936, 819, 583. HRMS (ESI, Pos) calculated for C₁₃H₁₀BrN₃O₄S [M+H]⁺: 383.9648 m/z, found 383.9652 m/z.

(E)-N’-(2-fluorobenzylidene)-2-nitrobenzenesulfonohydrazide (1d)

Synthesized from 2-fluorobenzaldehyde (490 μL, 4.65 mmol, 1.01 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.60 mmol, 1.00 equiv) using the general procedure A for N-nosylhydrazones synthesis. Product obtained as a yellow solid (1.32 g, 4.09 mmol, 89%). mp: 168 - 170 °C.

¹H NMR (400 MHz, DMSO) δ 12.29 (br, 1H), 8.26 (s, 1H), 8.07 – 8.01 (m, 2H), 7.94 – 7.84 (m, 2H), 7.70 (t, J = 6.1 Hz, 1H), 7.47 – 7.45 (m, 1H), 7.28 – 7.21 (m, 2H). ¹³C NMR (101 MHz, DMSO) δ 160.55 (d, J = 250.5 Hz, Cq), 147.79, 140.46 (d, J = 4.6 Hz), 134.87, 132.66, 132.35 (d, J = 8.3 Hz), 130.80, 130.58, 126.16, 124.91, 124.58, 120.90 (d, J = 9.9 Hz), 116.03 (d, J = 20.8 Hz). ¹⁹F NMR (376 MHz, DMSO) δ 4.14 (dd, J = 10.2, 5.7 Hz). FTIR (cm⁻¹) (neat): 3236, 1529, 1175, 1038, 768, 585. HRMS (ESI, Pos) calculated for C₁₃H₁₀FN₃O₄S [M+H]⁺: 324.0449 m/z, found 324.0454 m/z.
(E)-2-nitro-N’-(4-(trifluoromethyl)benzylidene)benzenesulfonohydrazide (1e)

Synthesized from 4-(trifluoromethyl)benzaldehyde (633 µL, 4.64 mmol, 1.01 equiv), acetic acid (13 µL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (997 mg, 4.59 mmol, 1.00 equiv) using the general procedure A for N-nosylhydrazones synthesis. Product obtained as a white solid (1.45 g, 3.90 mmol, 85%). mp: 118 - 120 °C.

$^1$H NMR (400 MHz, DMSO) δ 12.44 (br, 1H), 8.15 (s, 1H), 8.09 – 8.07 (m, 1H), 8.03 – 8.01 (m, 1H), 7.92 – 7.87 (m, 2H), 7.78 (dd, $J = 17.9, 8.1$ Hz, 4H). $^{13}$C NMR (101 MHz, DMSO) δ 147.81, 145.90, 137.32, 134.89, 132.67, 130.84, 130.46, 130.09, 129.78, 127.53, 125.71 (dd, $J = 7.5, 3.7$ Hz, Cq), 124.59. $^{19}$F NMR (376 MHz, DMSO) δ -61.27. FTIR (cm$^{-1}$ (neat): 3206, 1537, 1310, 1066, 941, 833, 577. HRMS (ESI, Pos) calculated for C$_{14}$H$_{11}$F$_3$N$_3$O$_4$S $[M+H]^+$: 374.0417 m/z, found 374.0427 m/z.

(E)-N’-(4-cyanobenzylidene)-2-nitrobenzenesulfonohydrazide (1f)

Synthesized from 4-cyanobenzaldehyde (609 mg, 4.65 mmol, 1.01 equiv), acetic acid (13 µL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (999 mg, 4.60 mmol, 1.00 equiv) using the general procedure A for N-nosylhydrazones synthesis. Product obtained as a yellow solid (1.39 g, 4.19 mmol, 91%). Product corresponds to literature characterization data.

$^1$H NMR (400 MHz, DMSO) δ 12.51 (br, 1H), 8.12 (s, 1H), 8.10 – 8.05 (m, 1H), 8.05 – 7.99 (m, 1H), 7.90 – 7.85 (m, 4H), 7.77 – 7.76 (m, 2H). $^{13}$C NMR (101 MHz, DMSO) δ 147.78, 145.57, 137.76, 134.93, 132.72, 132.66, 130.75, 130.52, 127.46, 124.56, 118.51, 112.17.
(E)-N'-(4-methylbenzylidene)-2-nitrobenzenesulfonohydrazide (1g)

Synthesized from 4-methylbenzaldehyde (437 µL, 4.69 mmol, 1.01 equiv), acetic acid (13 µL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.64 mmol, 1.00 equiv) using the general procedure A for N-nosylhydrazones synthesis. Product obtained as a yellow solid (1.18 g, 3.71 mmol, 80%). mp: 133 - 140 °C.

$^1$H NMR (400 MHz, DMSO) $\delta$ 12.02 (s, 1H), 8.13 – 7.94 (m, 3H), 7.94 – 7.79 (m, 2H), 7.46 (d, $J$ = 7.2 Hz, 2H), 7.21 (d, $J$ = 7.2 Hz, 2H), 2.30 (s, 3H).

$^{13}$C NMR (126 MHz, DMSO) $\delta$ 147.97 (CH), 147.93 (Cq), 140.31 (Cq), 134.77 (CH), 132.60 (CH), 130.99 (Cq), 130.73 (Cq), 130.53 (CH), 129.45 (CH), 126.96 (CH), 124.54 (CH), 21.03 (CH$_3$).

FTIR (cm$^{-1}$) (neat): 3265, 1533, 1367, 1176, 740, 570.

HRMS (ESI, Pos) calculated for C$_{14}$H$_{14}$N$_3$O$_4$S [M+H]$^+$: 320.0700 m/z, found 320.0706 m/z.

![Image](image1.png)

(E)-N'-(4-methoxybenzylidene)-2-nitrobenzenesulfonohydrazide (1h)

Synthesized from 4-methoxybenzaldehyde (570 µL, 4.67 mmol, 1.01 equiv), acetic acid (13 µL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.63 mmol, 1.00 equiv) using the general procedure A for N-nosylhydrazones synthesis. Product obtained as an orange solid (1.35 g, 4.03 mmol, 87%). mp: 94 - 100 °C.

$^1$H NMR (400 MHz, DMSO) $\delta$ 11.91 (s, 1H), 8.06 – 8.04 (m, 1H), 8.01 – 7.99 (m, 2H), 7.89 – 7.87 (m, 2H), 7.52 (d, $J$ = 8.5 Hz, 2H), 6.95 (d, $J$ = 8.4 Hz, 2H), 3.77 (s, 3H).

$^{13}$C NMR (126 MHz, DMSO) $\delta$ 160.99 (Cq), 147.92 (Cq), 147.81 (CH), 134.68 (CH), 132.52 (CH), 130.98 (Cq), 130.47 (CH), 128.59 (CH), 125.97 (Cq), 124.47 (CH), 114.30 (CH), 55.30 (CH$_3$).

FTIR (cm$^{-1}$) (neat): 3252, 1545, 1464, 1174, 1126, 810, 735, 570.

HRMS (ESI, Pos) calculated for C$_{14}$H$_{14}$N$_3$O$_5$S [M+H]$^+$: 336.0649 m/z, found 336.0643 m/z.

![Image](image2.png)

((E)-N'-(2-methoxybenzylidene)-2-nitrobenzenesulfonohydrazide (1i)
Synthesized from 2-methoxybenzaldehyde (560 μL, 4.64 mmol, 1.01 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.60 mmol, 1.00 equiv) using the general procedure A for N-nosylhyrazones synthesis. Product obtained as a yellow solid (1.39 g, 4.14 mmol, 90%). mp: 159 - 162 °C.

**1H NMR (400 MHz, DMSO)** δ 12.03 (s, 1H), 8.39 (s, 1H), 8.02 (dd, J = 15.5, 3.5 Hz, 2H), 7.94 – 7.80 (m, J = 2.6 Hz, 2H), 7.59 (d, J = 7.5 Hz, 1H), 7.39 (t, J = 7.37 Hz, 1H), 7.07 (d, J = 8.1 Hz, 1H), 6.94 (t, J = 7.35 Hz, 1H), 3.82 (s, 3H).

**13C NMR (126 MHz, DMSO)** δ 157.60 (Cq), 147.86 (Cq), 143.30 (CH), 134.75 (CH), 132.60 (CH), 131.95 (CH), 130.95 (Cq), 130.52 (CH), 125.27 (CH), 124.53 (CH), 121.33 (Cq), 120.70 (CH), 111.87 (CH), 55.71 (CH₃).

**FTIR (cm⁻¹) (neat):** 3252, 1531, 1375, 1177, 766, 574.

**HRMS (ESI, Pos) calculated for C₁₄H₁₄N₃O₅S [M+H⁺]:** 336.0649 m/z, found 336.0652 m/z.

(E)-N’-(3-methoxybenzylidene)-2-nitrobenzenesulfonohydrazide (1j)

Synthesized from 3-methoxybenzaldehyde (570 μL, 4.65 mmol, 1.01 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.60 mmol, 1.00 equiv) using the general procedure A for N-nosylhyrazones synthesis. Product obtained as a white solid (1.31 g, 3.82 mmol, 83%). Product corresponds to literature characterization data.⁴

**1H NMR (400 MHz, DMSO)** δ 12.13 (s, 1H), 8.10 – 8.04 (m, 1H), 8.04 – 7.97 (m, 2H), 7.95 – 7.84 (m, 2H), 7.31 (t, J = 8.1 Hz, 1H), 7.21 – 7.08 (m, 2H), 6.98 (d, J = 7.6 Hz, 1H), 3.76 (s, 3H).

**13C NMR (126 MHz, DMSO)** δ 159.51 (Cq), 147.98 (Cq), 147.64 (CH), 134.91 (CH), 134.85 (Cq), 132.60 (CH), 130.81 (Cq), 130.60 (CH), 130.03 (CH), 124.50 (CH), 119.66 (CH), 116.37 (CH), 111.55 (CH), 55.20 (CH₃).

(E)-2-nitro-N’-(2,4,6-trimethylbenzylidene)benzenesulfonohydrazide (1k)

Synthesized from mesitaldehyde (690 μL, 4.69 mmol, 1.02 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.60 mmol, 1.00 equiv).
using the general procedure A for N-nosylhydrazones synthesis. Product obtained as a yellowish solid (1.51 g, 4.37 mmol, 95%). mp: 128 - 130 °C.

$^1$H NMR (400 MHz, DMSO) δ 11.89 (s, 1H), 8.36 (s, 1H), 8.06 – 8.03 (m, 1H), 8.02 – 7.99 (m, 1H), 7.92 – 7.86 (m, 2H), 6.85 (s, 2H). 2.20 (s, 3H), 2.16 (s, 6H). $^{13}$C NMR (101 MHz, DMSO) δ 148.04, 147.90, 138.58, 137.07, 134.72, 132.46, 130.88, 130.79, 129.34, 127.40, 124.50, 20.63 (CH$_3$), 20.60 (CH$_3$). FTIR (cm$^{-1}$) (neat): 3236, 1533, 1369, 1177, 782, 578. HRMS (ESI, Pos) calculated for C$_{16}$H$_{17}$N$_3$O$_4$S [M+H]$^+$ : 348.1013 m/z, found 348.1021 m/z.

![Diagram](image.png)

(E)-2-nitro-N’-(thiophen-3-ylmethylene)benzenesulfonohydrazide (1l)

Synthesized from 3-thiophenecarboxaldehyde (410 μL, 4.69 mmol, 1.01 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.65 mmol, 1.00 equiv) using the general procedure A for N-nosylhydrazones synthesis. Product obtained as a yellow solid (1.19 g, 3.81 mmol, 82%). Product corresponds to literature characterization data.4

$^1$H NMR (400 MHz, DMSO) δ 11.95 (s, 1H), 8.08 (s, 1H), 8.05 – 8.03 (m, 1H), 8.01 – 7.98 (m, 1H), 7.88 – 7.87 (m, 3H), 7.57 – 7.55 (m, 1H), 7.29 (d, $J$ = 5.0 Hz, 1H). $^{13}$C NMR (126 MHz, DMSO) δ 147.91 (Cq), 143.55 (CH), 136.55 (Cq), 134.76 (CH), 132.57 (CH), 130.90 (Cq), 130.56 (CH), 128.82 (CH), 127.80 (CH), 124.50 (CH), 124.35 (CH).

![Diagram](image.png)

(E)-2-nitro-N’-(thiophen-2-ylmethylene)benzenesulfonohydrazide (1m)

Synthesized from 2-thiophenecarboxaldehyde (435 μL, 4.65 mmol, 1.01 equiv) acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.61 mmol, 1.00 equiv) using the general procedure A for N-nosylhydrazones synthesis. Product obtained as a yellow solid (1.08 g, 3.46 mmol, 75%). mp: 122 - 128 °C.
1H NMR (400 MHz, CDCl3) δ 8.31 (br, 1H), 8.29 – 8.26 (m, 1H), 8.14 (s, 1H), 7.85 – 7.83 (m, 2H), 7.79 – 7.75 (d, J = 4.72 Hz, 1H), 7.02 (t, J = 4.5 Hz, 1H), 1.68 (br, 1H). 13C NMR (126 MHz, DMSO) δ 147.82 (Cq), 142.95 (CH), 137.86 (Cq), 134.77 (CH), 132.57 (CH), 131.34 (CH), 130.91 (Cq), 130.44 (CH), 129.19 (CH), 127.88 (CH), 124.60 (CH).

FTIR (cm⁻¹) (neat): 3245, 1529, 1349, 1173, 718, 570.

HRMS (ESI, Pos) calculated for C11H9N3O5S2 [M+H]+ : 312.0107 m/z, found 312.0111 m/z.

(E)-N’-(furan-2-ylmethylene)-2-nitrobenzenesulfonohydrazide (1n)

Synthesized from 2-furaldehyde (310 µL, 3.75 mmol, 1.01 equiv), acetic acid (13 µL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (806 mg, 3.71 mmol, 1.00 equiv) using the general procedure A for N-nosylhydrazones synthesis. Product obtained as a yellow solid (905 mg, 3.08 mmol, 83%). mp: 82 – 89 °C.

1H NMR (300 MHz, DMSO) δ 12.10 (br, 1H), 8.04 – 7.99 (m, 2H), 7.95 (s, 1H), 7.95 – 7.86 (m, 2H), 7.77 (d, J = 1.2 Hz, 1H), 6.87 (d, J = 3.4 Hz, 1H), 6.58 (dd, J = 3.4, 1.8 Hz, 1H). 13C NMR (75 MHz, DMSO) δ 148.30 (Cq), 147.82 (Cq), 145.38 (CH), 137.60 (CH), 134.73 (CH), 132.74 (CH), 131.09 (Cq), 130.44 (CH), 124.73 (CH), 114.65 (CH), 112.12 (CH).

FTIR (cm⁻¹) (neat): 3229, 1530, 1362, 1172, 736, 583, 519. HRMS (ESI, Pos) calculated for C11H9N3O5S [M+H]+ : 296.0336 m/z, found 296.0338 m/z.

N’-((1E,2E)-2-methylpent-2-en-1-ylidene)-2-nitrobenzenesulfonohydrazide (1o)

Synthesized from 2-methyl-2-pentenal (530 µL, 4.65 mmol, 1.01 equiv), acetic acid (13 µL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.60 mmol, 1.00 equiv) using the general procedure A for N-nosylhydrazones synthesis. Product obtained as a white solid (1.13 g, 3.77 mmol, 82%). mp: 108 - 110 °C.

1H NMR (500 MHz, CDCl3) δ 8.26 – 8.23 (m, 1H), 8.09 (br, 1H), 7.84 – 7.81 (m, 1H), 7.78 – 7.74 (m, 2H), 7.52 (s, 1H), 5.80 (t, J = 7.1 Hz, 1H), 2.19 (quin, J = 7.5 Hz, 2H), 1.70 (s, 3H), 1.00 (t, J = 7.5 Hz, 3H). 13C NMR (126 MHz, CDCl3) δ 155.94 (CH), 148.41 (Cq),
144.39 (CH), 134.28 (CH), 133.23 (CH), 132.64 (CH), 132.11 (Cq), 131.75 (Cq), 125.21 (CH), 21.91 (CH₂), 13.45 (CH₃), 11.14 (CH₃). **FTIR (cm⁻¹) (neat):** 3203, 1541, 1440, 1174, 604.

**HRMS (ESI, Pos) calculated for C₁₂H₁₆N₃O₄S [M+H]^+:** 298.0856 m/z, found 298.08546 m/z.

N’-(1E,2E)-2-methyl-3-phenylallylidene)-2-nitrobenzenesulfonohydrazide (1p)

Synthesized from α-methyl-trans-cinnamaldehyde (650 μL, 4.65 mmol, 1.01 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.60 mmol, 1.00 equiv) using the general procedure A for N-nosylhydrazones synthesis. Product obtained as a white solid (1.23 g, 3.54 mmol, 77%). mp: 148 – 150 °C.

**¹H NMR (500 MHz, CDCl₃) δ:** 8.30 – 8.28 (m, 1H), 8.26 (br, 1H), 7.87 – 7.83 (m, 1H), 7.79 – 7.75 (m, 2H), 7.70 (s, 1H), 7.38 – 7.33 (m, 4H), 7.31 – 7.27 (m, 1H), 6.72 (s, 1H), 2.01 (d, J = 1.2 Hz, 3H). **¹³C NMR (126 MHz, CDCl₃) δ:** 155.63 (CH), 148.46 (Cq), 139.31 (CH), 136.10 (Cq), 134.41 (CH), 133.66 (Cq), 133.21 (CH), 132.74 (CH), 131.78 (Cq), 129.53 (CH), 128.57 (CH), 128.24 (CH), 125.31 (CH), 13.00 (CH₃). **FTIR (cm⁻¹) (neat):** 3200, 1542, 1365, 1171, 1021, 854, 579, 556. **HRMS (ESI, Pos) calculated for C₁₆H₁₅N₃O₄S [M+H]^+:** 346.0856 m/z, found 346.0859 m/z.

N’-((E)-2-(cinnamyloxy)benzylidene)-2-nitrobenzenesulfonohydrazide (1q)

Synthesized from 2-(cinnamyloxy)benzaldehyde (436 mg, 1.83 mmol, 1.02 equiv), acetic acid (5 μL, 0.90 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (390 mg, 1.80 mmol, 1.00 equiv) using the general procedure A for N-nosylhydrazones synthesis. Product obtained as a yellow solid (684 mg, 1.57 mmol, 87%). mp: 158 – 162 °C.

**¹H NMR (400 MHz, CDCl₃) δ:** 8.41 (s, 1H), 8.36 (br, 1H), 8.32 – 8.30 (m, 1H), 7.83 – 7.78 (m, 2H), 7.77 – 7.72 (m, 2H), 7.42 (d, J = 7.4 Hz, 2H), 7.36 – 7.27 (m, 4H), 6.94 – 6.91 (m, 2H), 6.70 (d, J = 16.1 Hz, 1H), 6.39 (dt, J = 16.1, 5.9 Hz, 1H), 4.72 (dd, J = 5.89, 1.14
Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 157.37 (Cq), 146.45 (CH), 136.20 (Cq), 134.33 (CH), 133.85 (CH), 133.14 (CH), 132.87 (CH), 132.36 (CH), 132.10 (Cq), 128.85 (CH), 128.35 (CH), 126.92 (CH), 126.78 (CH), 125.32 (CH), 123.76 (CH), 121.67 (Cq), 121.13 (CH), 112.53 (CH), 69.37 (CH$_2$). FTIR (cm$^{-1}$) (neat): 3276, 2868, 1528, 1379, 1254, 1179, 749, 596, 581. HRMS (ESI, Pos) calculated for C$_{22}$H$_{19}$N$_3$O$_5$S [M+K]$^+$: 476.0677 m/z, found 476.0682 m/z.
(b) Cyclopropanes

![1,2-diphenylcyclopropane (2a)]

1,2-diphenylcyclopropane (2a)

Synthesized from 1a (153 mg, 0.500 mmol, 1.0 equiv) and styrene (300 µL, 2.61 mmol, 5.22 equiv) using general procedure B. The product was observed in 99% yield (determined by $^1$H NMR) and isolated by flash chromatography (100% petroleum ether) yielded a clear oil (89.5 mg, 0.460 mmol, 92%) (volatile compound) as a mixture of diastereomers trans/cis: 91/9. Rf (100% petroleum ether) = 0.39. The characterization data match the literature.\(^5\)

Characterization data for the major diastereomer:

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 – 7.29 (m, 4H), 7.22 – 7.15 (m, 6H), 2.21 – 2.17 (m, 2H), 1.47 (td, $J$ = 7.4, 1.1 Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 142.67 (Cq), 128.53 (CH), 125.91 (CH), 28.16 (CH), 18.35 (CH$_2$).

![1-chloro-4-(2-phenylcyclopropyl)benzene (2b)]

1-chloro-4-(2-phenylcyclopropyl)benzene (2b)

Synthesized from 1b (170 mg, 0.500 mmol, 1.0 equiv) and styrene (300 µL, 2.61 mmol, 5.22 equiv) using general procedure B. Flash chromatography (100% petroleum ether) yielded a clear oil (99.7 mg, 0.435 mmol, 87%) as a mixture of diastereomers trans/cis: 89/11. Rf (100% petroleum ether) = 0.54.

Characterization data for the major diastereomer:

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.30 (t, $J$ = 7.6 Hz, 2H), 7.25 (d, $J$ = 8.4 Hz, 2H), 7.21 – 7.18 (m, 1H), 7.13 (d, $J$ = 7.5 Hz, 2H), 7.08 – 7.05 (m, 2H), 2.16 – 2.11 (m, 2H), 1.48 – 1.44 (m, 1H), 1.43 – 1.39 (m, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 142.25 (Cq), 141.17 (Cq), 131.50 (Cq), 128.60 (CH), 127.27 (CH), 126.05 (CH), 125.89 (CH), 128.26 (CH), 27.54 (CH), 18.35 (CH$_2$). FTIR (cm$^{-1}$) (neat): 3027, 2923, 2853, 1582, 1493, 1091, 1013, 816, 745, 695, 520. HRMS (APPI, Pos) calculated for C$_{15}$H$_{13}$Cl [M]$^+$: 228.0706 m/z, found 228.0721 m/z.

Synthesized from 1c (192 mg, 0.499 mmol, 1.0 equiv) and styrene (300 µL, 2.61 mmol, 5.22 equiv) using general procedure B. Flash chromatography (100% petroleum ether) yielded a clear oil (115.2 mg, 0.424 mmol, 85%) as a mixture of diastereomers trans/cis: 91/9. Rf = 0.39 (100% petroleum ether).

Characterization data for the major diastereomer:

\(^{1}H\) NMR (500 MHz, CDCl\(_3\)) δ 7.42 – 7.40 (m, 2H), 7.32 – 7.29 (m, 2H), 7.22 – 7.19 (m, 1H), 7.15 – 7.13 (m, 2H), 7.03 – 7.01 (m, 2H), 2.16 – 2.11 (m, 2H), 1.50 – 1.45 (m, 1H), 1.44 – 1.40 (m, 1H). \(^{13}C\) NMR (126 MHz, CDCl\(_3\)) δ 142.20 (Cq), 141.72 (Cq), 131.53 (CH), 128.59 (CH), 127.66 (CH), 126.06 (CH), 126.20 (CH), 124.14 (d, J = 3.5 Hz, CH), 115.26 (d, J = 22.1 Hz, CH), 26.69 (CH), 20.89 (d, J = 4.7 Hz, CH), 17.00 (CH\(_2\)).

FTIR (cm\(^{-1}\)) (neat): 3025, 2923, 2852, 1603, 1488, 1073, 1008, 812, 742, 695, 516. HRMS (APPI, Pos) calculated for C\(_{15}\)H\(_{13}\)Br [M]\(^{+}\) : 272.0201 m/z, found 272.0232 m/z.

Synthesized from 1d (161 mg, 0.499 mmol, 1.0 equiv) and styrene (300 µL, 2.61 mmol, 5.22 equiv) using general procedure B. Flash chromatography (100% petroleum ether) yielded a clear oil (85.9 mg, 0.404 mmol, 81%) as a mixture of diastereomers trans/cis: 90/10. Rf = 0.51 (100% petroleum ether). The characterization data match the literature.\(^6\)

Characterization data for the major diastereomer:

\(^{1}H\) NMR (500 MHz, CDCl\(_3\)) δ 7.33 – 7.30 (m, 2H), 7.22 – 7.19 (m, 3H), 7.17 – 7.14 (m, 1H), 7.11 – 7.08 (m, 1H), 7.05 – 7.01 (m, 2H), 2.40 – 2.36 (m, 1H), 2.24 – 2.20 (m, 1H), 1.48 – 1.45 (m, 2H). \(^{13}C\) NMR (126 MHz, CDCl\(_3\)) δ 161.84 (d, J = 245.3 Hz, Cq), 142.26 (Cq), 129.55 (d, J = 14.4 Hz, Cq). 128.55 (CH), 127.76 (CH), 127.15 (d, J = 8.1 Hz, CH), 126.34 (d, J = 4.2 Hz, CH), 126.20 (CH), 126.06 (CH), 124.14 (d, J = 3.5 Hz, CH), 115.26 (d, J = 22.1 Hz, CH), 26.69 (CH), 20.89 (d, J = 4.7 Hz, CH), 17.00 (CH\(_2\)).

1-(2-phenylcyclopropyl)-4-(trifluoromethyl)benzene (2e)

Synthesized from 1e (186 mg, 0.499 mmol, 1.0 equiv) and styrene (300 µL, 2.61 mmol, 5.22 equiv) using general procedure B. Flash chromatography (100% petroleum ether) yielded a clear oil (127 mg, 0.484 mmol, 97%) as a mixture of diastereomers trans/cis: 91/9. Rf = 0.64 (100% petroleum ether).

Characterization data for the major diastereomer:

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.54 (d, J = 8.1 Hz, 2H), 7.33 – 7.30 (m, 2H), 7.24 – 7.21 (m, 3H), 7.16 – 7.14 (m, 2H), 2.22 (t, 2H), 1.57 – 1.47 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 146.93 (Cq), 141.89 (Cq), 128.65 (CH), 126.22 (CH), 126.03 (CH), 125.94 (CH), 125.47 (q, J = 7.4, 3.7 Hz, Cq), 28.84 (CH), 27.91 (CH), 18.73 (CH$_2$). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -63.24. FTIR (cm$^{-1}$) (neat): 3028, 2926, 2855, 1619, 1322, 1162, 1114, 1066, 1015, 823, 695, 517. HRMS (APPI, Pos) calculated for C$_{16}$H$_{13}$F$_3$ [M]$^+$: 262.0969 m/z, found 298.0989 m/z.

4-(2-phenylcyclopropyl)benzonitrile (2f)

Synthesized from 1f (163 mg, 0.495 mmol, 1.0 equiv) and styrene (300 µL, 2.61 mmol, 5.22 equiv) using general procedure B'. Flash chromatography (100% petroleum ether) yielded a clear oil (103 mg, 0.470 mmol, 95%) as a mixture of diastereomers trans/cis: 85/15. Rf = 0.42 (10% ethyl acetate in hexanes).

Characterization data for the major diastereomer:

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.58 – 7.56 (m, 2H), 7.33 – 7.29 (m, 2H), 7.24 – 7.19 (m, 3H), 7.15 – 7.13 (m, 2H), 2.25 – 2.17 (m, 2H), 1.62 – 1.56 (m, 1H), 1.53 – 1.48 (m, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 148.60 (Cq), 141.84 (Cq), 132.36 (CH), 128.68 (CH), 126.39 (CH), 125.93 (CH), 119.25 (Cq), 109.41 (Cq), 29.40 (CH), 28.23 (CH), 19.09 (CH$_2$). FTIR (cm$^{-1}$) (neat): 3027, 2924, 2224, 1604, 1497, 1179, 821, 750, 696, 549. HRMS (APPI, Pos) calculated for C$_{16}$H$_{13}$N [M]$^+$: 220.1121 m/z, found 220.1149 m/z.
1-methyl-4-(2-phenylcyclopropyl)benzene (2g)

Synthesized from 1g (159 mg, 0.499 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using general procedure B. Flash chromatography (100% hexanes) yielded a clear oil (23 mg, 0.110 mmol, 22%) as a mixture of diastereomers trans/cis: 92/8.

Synthesized from 1g (160 mg, 0.502 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using general procedure B'. Flash chromatography (100% petroleum ether) yielded a clear oil (95.3 mg, 0.457 mmol, 91%) as a mixture of diastereomers trans/cis: 90/10. \( R_f = 0.67 \) (100% petroleum ether).

Characterization data for the major diastereomer:

\[^{1}H\text{ NMR (500 MHz, CDCl}_3\] \( \delta \) 7.30 (t, \( J = 7.7 \text{ Hz, 2H} \), 7.20 – 7.11 (m, 5H), 7.05 (d, \( J = 8.1 \text{ Hz, 2H} \), 2.34 (s, 3H), 2.17 – 2.12 (m, 2H), 1.43 (t, \( J = 7.4 \text{ Hz, 2H} \)). \[^{13}C\text{ NMR (126 MHz, CDCl}_3\] \( \delta \) 142.83 (Cq), 139.59 (Cq), 135.42 (Cq), 129.21 (CH), 128.51 (CH), 125.87 (CH), 125.84 (CH), 125.80 (CH), 27.98 (CH), 27.88 (CH), 21.12 (CH\(_3\)), 18.16 (CH\(_2\)). \[\text{FTIR (cm}^{-1}\text{ (neat)})\] 3025, 2922, 2854, 1603, 1498, 809, 750, 695, 512. \[\text{HRMS (APPI, Pos)}\] calculated for C\(_{16}\)H\(_{16}\)[M]\(^{+}\) : 208.1252 m/z, found 208.1259 m/z.

1-methoxy-4-(2-phenylcyclopropyl)benzene (2h)

Synthesized from 1h (169 mg, 0.504 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using general procedure B'. Flash chromatography (using a gradient from 100% hexanes to 98:2 hexanes/ethyl acetate) yielded a red oil (95.4 mg, 0.423 mmol, 84%) as a mixture of diastereomers trans/cis: 89/11. \( R_f = 0.52 \) (2% ethyl acetate in hexanes). The characterization data match the literature.\(^6\)

Characterization data for the major diastereomer:

\[^{1}H\text{ NMR (400 MHz, CDCl}_3\] \( \delta \) 7.32 – 7.28 (m, 2H), 7.22 – 7.13 (m, 3H), 7.11 – 7.07 (m, 2H), 6.87 – 6.83 (m, 2H), 3.80 (s, 3H), 2.17 – 2.07 (m, 2H), 1.42 – 1.38 (m, 2H). \[^{13}C\text{ NMR (126 MHz, CDCl}_3\] \( \delta \) 158.00 (Cq), 142.88 (Cq), 134.66 (Cq), 128.51 (CH), 127.06 (CH), 125.84 (CH), 125.78 (CH), 114.00 (CH), 55.48 (CH\(_3\)), 27.65 (CH), 27.47 (CH), 17.95 (CH\(_2\)).
1-methoxy-2-(2-phenylcyclopropyl)benzene (2i)

Synthesized from 1i (169 mg, 0.504 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using general procedure B. Flash chromatography (using a gradient from 100% hexanes to 98:2 hexanes/ethyl acetate) yielded an orange oil (68.0 mg, 0.302 mmol, 60%) as a mixture of diastereomers trans/cis: 89/11.

Synthesized from 1i (168 mg, 0.501 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using general procedure B'. Flash chromatography (using a gradient from 100% hexanes to 98:2 hexanes/ethyl acetate) yielded a redish oil (108.0 mg, 0.481 mmol, 96%) as a mixture of diastereomers trans/cis: 86/14. \( R_f = 0.59 \) (2% ethyl acetate in hexanes). The characterization data match the literature.6

Characterization data for the major diastereomer:

\[ ^1H \text{NMR (500 MHz, CDCl}_3 \delta 7.30 \ (t, J = 7.6 \text{ Hz, 2H}), \ 7.22 - 7.16 \ (m, 4H), \ 6.99 \ (dd, J = 7.6, 1.6 \text{ Hz, 1H}), \ 6.93 \ (t, J = 7.6 \text{ Hz, 1H}), \ 6.87 \ (d, J = 8.1 \text{ Hz, 1H}), \ 3.84 \ (s, 3H), \ 2.53 - 2.47 \ (m, 1H), \ 2.17 - 2.13 \ (m, 1H), \ 1.43 - 1.37 \ (m, 2H). \]

\[ ^{13}C \text{NMR (126 MHz, CDCl}_3 \delta 158.30 \ (Cq), \ 143.14 \ (Cq), \ 130.99 \ (Cq), \ 128.42 \ (CH), \ 126.77 \ (CH), \ 126.27 \ (CH), \ 125.72 \ (CH), \ 125.22 \ (CH), \ 120.64 \ (CH), \ 110.44 \ (CH), \ 55.65 \ (CH_3), \ 26.67 \ (CH), \ 21.77 \ (CH), \ 17.18 \ (CH_2). \]

1-methoxy-3-(2-phenylcyclopropyl)benzene (2j)

Synthesized from 1j (168 mg, 0.502 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using general procedure B’. Flash chromatography (using a gradient from 100% hexanes to 98:2 hexanes/ethyl acetate) yielded a red oil (94.0 mg, 0.417 mmol, 83%) as a mixture of diastereomers trans/cis: 90/10. \( R_f = 0.43 \) (2% ethyl acetate in hexanes). The characterization data match the literature.6

Characterization data for the major diastereomer:

\[ ^1H \text{NMR (500 MHz, CDCl}_3 \delta 7.30 \ (dt, J = 9.5, 1.7 \text{ Hz, 2H}), \ 7.24 - 7.19 \ (m, 2H), \ 7.16 - 7.14 \ (m, 2H), \ 6.76 - 6.73 \ (m, 2H), \ 6.71 - 6.70 \ (m, 1H), \ 3.81 \ (s, 3H), \ 2.21 - 2.13 \ (m, 2H), \ 1.46 \ (t, 2H). \]

\[ ^{13}C \text{NMR (126 MHz, CDCl}_3 \delta 159.89 \ (Cq), \ 144.41 \ (Cq), \ 142.59 \ (Cq), \ 129.51 \ (Cq). \]

\[ ^1H \text{NMR (500 MHz, CDCl}_3 \delta 7.30 \ (t, J = 7.6 \text{ Hz, 2H}), \ 7.22 - 7.16 \ (m, 4H), \ 6.99 \ (dd, J = 7.6, 1.6 \text{ Hz, 1H}), \ 6.93 \ (t, J = 7.6 \text{ Hz, 1H}), \ 6.87 \ (d, J = 8.1 \text{ Hz, 1H}), \ 3.84 \ (s, 3H), \ 2.53 - 2.47 \ (m, 1H), \ 2.17 - 2.13 \ (m, 1H), \ 1.43 - 1.37 \ (m, 2H). \]

\[ ^{13}C \text{NMR (126 MHz, CDCl}_3 \delta 158.30 \ (Cq), \ 143.14 \ (Cq), \ 130.99 \ (Cq), \ 128.42 \ (CH), \ 126.77 \ (CH), \ 126.27 \ (CH), \ 125.72 \ (CH), \ 125.22 \ (CH), \ 120.64 \ (CH), \ 110.44 \ (CH), \ 55.65 \ (CH_3), \ 26.67 \ (CH), \ 21.77 \ (CH), \ 17.18 \ (CH_2). \]
Synthesized from 1k (173 mg, 0.499 mmol, 1.0 equiv) and styrene (300 µL, 2.61 mmol, 5.22 equiv) using general procedure B'. Flash chromatography (100% petroleum ether) yielded a clear oil (70.0 mg, 0.294 mmol, 59%) as a mixture of diastereomers trans/cis: 71/29. $R_f = 0.28$ (100% petroleum ether).

Characterization data for the major diastereomer:

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.32 (dd, $J = 10.8, 4.4$ Hz, 2H), 7.22 – 7.18 (m, 3H), 6.86 (s, 2H), 2.37 (s, $J = 10.9$ Hz, 6H), 2.27 (s, 3H), 2.05 – 1.98 (m, 2H), 1.47 – 1.43 (m, 1H), 1.28 – 1.24 (m, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 143.40 (Cq), 138.79 (Cq), 136.01 (Cq), 135.46 (Cq), 128.89 (CH), 128.51 (CH), 125.69 (CH), 125.59 (CH), 26.03 (CH), 25.02 (CH), 20.98 (CH$_3$), 20.95 (CH$_3$), 19.67 (CH$_2$). FTIR (cm$^{-1}$) (neat): 3026, 2918, 2859, 1604, 1496, 1458, 1445, 1376, 1029, 849, 741, 695, 530. HRMS (APCI, Pos) calculated for C$_{18}$H$_{21}$ [M+H]$^+$ : 237.16378 m/z, found 237.16459 m/z.

Synthesized from 1l (157 mg, 0.504 mmol, 1.0 equiv) and styrene (300 µL, 2.62 mmol, 5.22 equiv) using general procedure B. Flash chromatography (using a gradient from 100% hexanes to 98:2 hexanes/ethyl acetate) yielded a redish oil (41 mg, 0.207 mmol, 41%) as a mixture of diastereomers trans/cis: 92/8.

Characterization data for the major diastereomer:

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.32 (dd, $J = 10.8, 4.4$ Hz, 2H), 7.22 – 7.18 (m, 3H), 6.86 (s, 2H), 2.37 (s, $J = 10.9$ Hz, 6H), 2.27 (s, 3H), 2.05 – 1.98 (m, 2H), 1.47 – 1.43 (m, 1H), 1.28 – 1.24 (m, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 143.40 (Cq), 138.79 (Cq), 136.01 (Cq), 135.46 (Cq), 128.89 (CH), 128.51 (CH), 125.69 (CH), 125.59 (CH), 26.03 (CH), 25.02 (CH), 20.98 (CH$_3$), 20.95 (CH$_3$), 19.67 (CH$_2$). FTIR (cm$^{-1}$) (neat): 3026, 2918, 2859, 1604, 1496, 1458, 1445, 1376, 1029, 849, 741, 695, 530. HRMS (APCI, Pos) calculated for C$_{18}$H$_{21}$ [M+H]$^+$ : 237.16378 m/z, found 237.16459 m/z.

3-(2-phenylcyclopropyl)thiophene (2l)

Synthesized from 1l (156 mg, 0.500 mmol, 1.0 equiv) and styrene (300 µL, 2.61 mmol, 5.22 equiv) using general procedure B. Flash chromatography (using a gradient from 100% hexanes to 98:2 hexanes/ethyl acetate) yielded a redish oil (68.5 mg, 0.340 mmol, 68%) as a mixture of diastereomers trans/cis: 89/11. $R_f = 0.72$ (2% ethyl acetate in hexanes).

Characterization data for the major diastereomer:
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.27 (m, 3H), 7.22 – 7.17 (tt, $J = 7.3, 1.3, 1$H), 7.14 (dd, $J = 5.3, 3.4$ Hz, 2H), 6.95 (ddd, $J = 3.0, 1.3, 0.5$ Hz, 1H), 6.92 (dd, $J = 5.0, 1.3$ Hz, 1H), 2.26 – 2.21 (ddd, $J = 8.5, 6.1, 4.6$ Hz, 1H), 2.17 – 2.13 (m, 1H), 1.45 – 1.37 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 143.83 (Cq), 142.52 (Cq), 128.53 (CH), 126.28 (CH), 125.88 (CH), 125.84 (CH), 125.70 (CH), 118.49 (CH), 27.38 (CH), 23.86 (CH), 18.25 (CH$_2$). FTIR (cm$^{-1}$) (neat): 3025, 2924, 2853, 1604, 1499, 775, 746, 695, 635, 506. HRMS (APCI, Pos) calculated for C$_{13}$H$_{13}$S [M+H]$^+$: 201.0732 m/z, found 201.0735 m/z.

2-(2-phenylcyclopropyl)thiophene (2m)

Synthesized from 1m (155 mg, 0.498 mmol, 1.0 equiv) and styrene (300 µL, 2.60 mmol, 5.22 equiv) using general procedure B'. Flash chromatography (using a gradient from 100% hexanes to 99:1 hexanes/ethyl acetate) yielded a redish oil (57.4 mg, 0.289 mmol, 58%) as a mixture of diastereomers trans/cis: 89/11. $R_f = 0.54$ (4% ethyl acetate in hexanes).

Characterization data for the major diastereomer:

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.31 (t, $J = 7.6$ Hz, 2H), 7.22 – 7.19 (m, 1H), 7.16 – 7.14 (m, 2H), 7.09 (dd, $J = 5.1, 1.2$ Hz, 1H), 6.93 (dd, $J = 5.1, 3.5$ Hz, 1H), 6.84 (d, $J = 3.5$ Hz, 1H), 2.39 – 2.36 (m, 1H), 2.25 – 2.21 (m, 1H), 1.52 – 1.44 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 147.13 (Cq), 141.96 (Cq), 128.58 (CH), 127.00 (CH), 126.08 (CH), 125.94 (CH), 122.89 (CH), 122.40 (CH), 28.79 (CH), 23.27 (CH), 19.27 (CH$_2$). FTIR (cm$^{-1}$) (neat): 3026, 2924, 2852, 1604, 1499, 750, 510. HRMS (APCI, Pos) calculated for C$_{13}$H$_{13}$S [M+H]$^+$: 201.0732 m/z, found 201.0728 m/z.

2-(2-phenylcyclopropyl)furan (2n)

Synthesized from 1n (59.3 mg, 201 mmol, 1.0 equiv) and styrene (120 µL, 1.05 mmol, 5.22 equiv) using general procedure B'. The product was observed in 44% yield (determined by $^1$H NMR). This compound is unstable on silica gel.
Synthesized from **1o** (149 mg, 0.502 mmol, 1.0 equiv) and styrene (300 µL, 2.62 mmol, 5.22 equiv) using **general procedure B**. Flash chromatography (100% petroleum ether) yielded a clear oil (28.3 mg, 0.151 mmol, 30%) as a mixture of diastereomers trans/cis: 94/6.

Synthesized from **1o** (149 mg, 0.502 mmol, 1.0 equiv) and styrene (300 µL, 2.61 mmol, 5.22 equiv) using **general procedure B’ (with a reaction time of 48 hours)**. Flash chromatography (100% petroleum ether) yielded a clear oil (51.5 mg, 0.276 mmol, 55%) as a mixture of diastereomers trans/cis: 91/9. **Rf = 0.86** (100% petroleum ether).

Characterization data for the major diastereomer:

**1H NMR (500 MHz, CDCl3)** δ 7.28 – 7.24 (m, 2H), 7.20 – 7.13 (m, 1H), 7.13 – 7.07 (m, 2H), 5.25 (td, J = 7.0, 1.1 Hz, 1H), 2.09 – 2.00 (m, 2H), 1.90 (dt, J = 8.7, 4.3 Hz, 1H), 1.67 – 1.62 (m, 1H), 1.60 (s, 3H), 1.22 – 1.17 (m, 1H), 1.02 (dtd, J = 6.4, 5.4, 1.4 Hz, 1H), 0.96 (t, J = 7.5 Hz, 3H). **13C NMR (126 MHz, CDCl3)** δ 143.55 (Cq), 133.89 (Cq), 128.40 (CH), 126.02 (CH), 125.86 (CH), 125.49 (CH), 31.64, 29.86, 23.28, 21.32, 14.60, 14.47. **FTIR (cm⁻¹) (neat):** 3064, 2961, 2928, 1655, 1499, 1458, 750, 695, 515. **HRMS (APCI, Pos)** calculated for C$_{14}$H$_{19}$[M+H]$^+$: 187.1481 m/z, found 187.1480 m/z.

Synthesized from **1p** (173 mg, 0.501 mmol, 1.0 equiv) and styrene (300 µL, 2.61 mmol, 5.22 equiv) using **general procedure B’ (with a reaction time of 48 hours)**. Flash chromatography (100% petroleum ether) yielded a clear oil (86.0 mg, 0.366 mmol, 73%) as a mixture of diastereomers trans/cis: 86/14. **Rf = 0.65** (100% petroleum ether).

Characterization data for the major diastereomer:

**1H NMR (500 MHz, CDCl3)** δ 7.38 – 7.33 (m, 3H), 7.32 – 7.28 (m, 3H), 7.25 – 7.22 (m, 2H), 7.18 (d, J = 7.88 Hz, 2H), 6.42 (s, 1H), 2.10 – 2.15 (m, 1H), 1.89 (s, 3H), 1.44 – 1.38 (m, 1H), 1.25 – 1.20 (m, 1H). **13C NMR (126 MHz, CDCl3)** δ 143.03 (Cq), 138.42 (Cq), 138.31 (Cq), 128.98 (CH), 128.50 (CH), 128.20 (CH), 126.05 (CH), 125.96 (CH), 125.74 (CH), 124.25 (CH), 32.62 (CH), 23.90 (CH), 16.07 (CH$_3$), 15.05 (CH$_2$). **FTIR (cm⁻¹) (neat):**
3023, 2924, 2854, 1600, 1494, 1441, 733, 694, 516. HRMS (APCI, Pos) calculated for C_{18}H_{19} [M+H]^+: 235.14813 m/z, found 235.1472 m/z.

\[
\text{1-(tert-butyl)-4-(2-phenylcyclopropyl)benzene (3a)}
\]

Synthesized from \(1a\) (153 mg, 0.501 mmol, 1.0 equiv) and 4-tert-butylstyrene (480 \(\mu\)L, 2.61 mmol, 5.22 equiv) using general procedure B. Flash chromatography (100% petroleum ether) yielded a clear oil (124 mg, 0.496 mmol, 99%) as a mixture of diastereomers trans/cis: 92/8. \(R_f = 0.70\) (100% petroleum ether).

Characterization data for the major diastereomer:

\(^1H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.33 – 7.29 (m, 2H), 7.29 (t, \(J = 7.6\) Hz, 2H), 7.18 (t, \(J = 7.4\) Hz, 1H), 7.14 (d, \(J = 7.8\) Hz, 2H), 7.10 (d, \(J = 8.3\) Hz, 2H), 2.19 – 2.13 (m, 2H), 1.44 (t, \(J = 7.3\) Hz, 2H), 1.33 (s, 9H). \(^{13}C\) NMR (126 MHz, CDCl\(_3\)) \(\delta\) 148.80 (Cq), 142.84 (Cq), 139.65 (Cq), 128.50 (CH), 125.89 (CH), 125.79 (CH), 125.59 (CH), 125.44 (CH), 34.52 (Cq), 31.54 (CH\(_3\)), 27.99 (CH), 27.80 (CH), 18.26 (CH\(_2\)). FTIR (cm\(^{-1}\)) (neat): 3027, 2959, 2925, 1604, 1499, 820, 746, 695, 552. HRMS (APCI, Pos) calculated for C\(_{19}\)H\(_{23}\) [M+H]^+: 251.17943 m/z, found 251.18066 m/z.

\[
\text{1-fluoro-4-(2-phenylcyclopropyl)benzene (3b)}
\]

Synthesized from \(1a\) (154 mg, 0.503 mmol, 1.0 equiv) and 4-fluorostyrene (310 \(\mu\)L, 2.62 mmol, 5.20 equiv) using general procedure B. Flash chromatography (100% petroleum ether) yielded a clear oil (85.0 mg, 0.402 mmol, 80%) as a mixture of diastereomers trans/cis: 91/9. \(R_f = 0.17\) (100% petroleum ether).

Characterization data for the major diastereomer:

\(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33 – 7.29 (m, 2H), 7.20 (tt, \(J = 7.34, 1.95\) or 1.34 Hz, 1H), 7.16 – 7.09 (m, 4H), 7.02 – 6.96 (m, 2H), 2.19 – 2.10 (m, 2H), 1.47 – 1.38 (m, 2H). \(^{13}C\) NMR (126 MHz, CDCl\(_3\)) \(\delta\) 161.38 (d, \(J = 243.6\) Hz, Cq), 142.45 (Cq), 138.20 (d, \(J = 3.0\) Hz, Cq), 128.57 (CH), 127.39 (d, \(J = 7.8\) Hz, CH), 125.96 (CH), 125.86 (CH), 115.28 (d, \(J = 21.3\) Hz, CH), 27.92 (CH), 27.36 (CH), 18.18 (CH\(_2\)). \(^{19}F\) NMR (376 MHz, CDCl\(_3\)) \(\delta\) -
117.55 – 117.65 (m). **FTIR (cm⁻¹) (neat):** 3027, 1603, 1510, 1227, 1208, 1158, 820, 763, 751, 695, 518. **HRMS (APCI, Pos) calculated for C₁₅H₁₃F [M⁺]:** 212.1001 m/z, found 212.0993 m/z.

1-bromo-4-(2-phenylcyclopropyl)benzene (3c = 2c)

Synthesized from **1a** (153 mg, 0.501 mmol, 1.0 equiv) and 4-bromostyrene (340 μL, 2.61 mmol, 5.22 equiv) using **general procedure B.** Flash chromatography (100% petroleum ether) yielded a clear oil (119.4 mg, 0.436 mmol, 87%) as a mixture of diastereomers *trans/cis:* 91/9. **Rf** = 0.39 (100% petroleum ether).

**Characterization data for the major diastereomer:**

**¹H NMR (400 MHz, CDCl₃)** δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 – 7.18 (m, 1H), 7.14 (d, *J* = 7.58 Hz, 2H), 7.01 (d, *J* = 8.41 Hz, 2H), 2.16 – 2.10 (m, 2H), 1.51 – 1.39 (m, 2H). **¹³C NMR (126 MHz, CDCl₃)** δ 142.20 (Cq), 141.71 (Cq), 131.52 (CH), 128.59 (CH), 127.65 (CH), 126.05 (CH), 125.88 (CH), 119.42 (Cq), 28.27 (CH), 27.59 (CH), 18.33 (CH₂). **FTIR (cm⁻¹) (neat):** 3025, 2923, 2852, 1603, 1488, 1073, 1008, 811, 742, 695, 516. **HRMS (APPI, Pos) calculated for C₁₅H₁₃Br [M⁺]:** 272.01951 m/z, found 272.01923 m/z.

1-bromo-2-(2-phenylcyclopropyl)benzene (3d)

Synthesized from **1a** (154 mg, 0.505 mmol, 1.0 equiv) and 2-bromostyrene (320 μL, 2.56 mmol, 5.07 equiv) using **general procedure B.** Flash chromatography (100% petroleum ether) yielded a clear oil (105 mg, 0.384 mmol, 76%) as a mixture of diastereomers *trans/cis:* 91/9. **Rf** (100% petroleum ether) = 0.29.

**Characterization data for the major diastereomer:**

**¹H NMR (400 MHz, CDCl₃)** δ 7.61 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.30 – 7.23 (m, 4H), 7.14 – 7.09 (m, 2H), 2.54 – 2.49 (m, 1H), 2.19 – 2.15 (m, 1H), 1.49 (t, *J* = 7.39 Hz, 2H). **¹³C NMR (126 MHz, CDCl₃)** δ 142.31 (Cq), 141.71 (Cq), 132.66 (CH), 128.49 (CH), 127.57 (CH), 127.50 (CH), 127.04 (CH), 126.25 (Cq), 126.21 (CH), 126.01 (CH), 28.06 (CH), 27.01 (CH), 17.25 (CH₂). **FTIR (cm⁻¹) (neat):** 3026, 2924, 1603, 1475, 1022,
740, 694. HRMS (APCI, Pos) calculated for C_{15}H_{14}Br [M+H]^+ : 273.0273 m/z, found 273.025 m/z.

![tert-butyl 2-phenylcyclopropane-1-carboxylate (3e)]

Synthesized from 1a (153 mg, 0.502 mmol, 1.0 equiv) and tert-butyl acrylate (370 µL, 2.55 mmol, 5.07 equiv) using general procedure B. Flash chromatography (using a gradient from 100% hexanes to 98:2 hexanes/ethyl acetate) yielded a red oil (52.3 mg, 0.241 mmol, 48%) as a mixture of diastereomers trans/cis: 72/28. Rf = 0.30 (2% ethyl acetate in hexanes).

Characterization data for the major diastereomer:

**1H NMR (400 MHz, CDCl$_3$)** $\delta$ 7.32 – 7.30 (m, 2H), 7.22 (tt, $J = 7.37, 2.07$ or $1.29$ Hz, 1H), 7.13 – 7.11 (m, 2H), 2.49 – 2.45 (m, 1H), 1.58 – 1.54 (m, 1H), 1.50 (s, 9H), 1.28 – 1.24 (m, 1H). **13C NMR (126 MHz, CDCl$_3$)** $\delta$ 172.72 (Cq), 140.67 (Cq), 128.56 (CH), 126.46 (CH), 126.21 (CH), 80.70 (Cq), 28.31 (CH$_3$), 25.88 (CH), 25.43 (CH), 17.20 (CH$_2$). **FTIR (cm$^{-1}$) (neat):** 2977, 1716, 1146, 843, 695. HRMS (ESI, Pos) calculated for C$_{14}$H$_{18}$O$_2$Na [M+Na]$^+$ : 241.1199 m/z, found 241.1194 m/z.

![cyclopropane-1,1,2-triyltribenzene (3f)]

Synthesized from 1a (154 mg, 0.503 mmol, 1.0 equiv) and 1,1-diphenylethylene (460 µL, 2.61 mmol, 5.18 equiv) using general procedure B. Flash chromatography (100% petroleum ether) yielded a clear oil (128.2 mg, 0.473 mmol, 94%). Rf = 0.23 (2% ethyl acetate in hexanes). The characterization data match the literature.$^7$

**1H NMR (500 MHz, CDCl$_3$)** $\delta$ 7.33 – 7.26 (m, 4H), 7.20 – 7.16 (m, 1H), 7.15 – 7.03 (m, 8H), 6.89 – 6.87 (m, 2H), 2.87 (dd, $J = 9.0, 6.6$ Hz, 1H), 2.00 (dd, $J = 6.6, 5.4$ Hz, 1H), 1.82 (dd, $J = 9.0, 5.4$ Hz, 1H). **13C NMR (126 MHz, CDCl$_3$)** $\delta$ 147.14 (Cq), 140.33 (Cq), 138.83 (Cq), 131.32 (CH), 128.48 (CH), 128.06 (CH), 127.77 (CH), 127.55 (CH), 126.37 (CH), 126.04 (CH), 125.72 (CH), 39.46 (Cq), 32.53 (CH), 21.03 (CH$_2$).

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$^7$ Nakano, T.; Endo, K.; Ukaji, Y. Synlett 2015, 26, 671.
Synthesized from 1a (152 mg, 0.498 mmol, 1.0 equiv) and α-methylstyrene (520 μL, 2.60 mmol, 5.22 equiv) using general procedure B’. Flash chromatography (100% petroleum ether) yielded a clear oil (89.9 mg, 0.433 mmol, 87%) as a mixture of diastereomers trans/cis: 90/10. Rf (100% petroleum ether) = 0.35. The characterization data match the literature.8

Characterization data for the major diastereomer:

\[
\text{\textit{H NMR (500 MHz, CDCl}_3) \delta 7.40 – 7.29 (m, 8H), 7.26 – 7.20 (m, 2H), 2.44 – 2.41 (m, 1H), 1.47 (dd, J = 8.7, 5.1 Hz, 1H), 1.26 (t, J = 5.77 Hz, 1H), 1.13 (s, 3H).}
\]

\[
\text{\textit{C NMR (126 MHz, CDCl}_3) \delta 147.98 (Cq), 139.24 (Cq), 129.30 (CH), 128.50 (CH), 128.22 (CH), 127.04 (CH), 126.14 (CH), 125.86 (CH), 31.53 (CH), 27.06 (Cq), 21.12 (CH}_3, 18.78 (CH}_2).}
\]

Synthesized from 1a (154 mg, 0.503 mmol, 1.0 equiv) and α-bromostyrene (341 μL, 2.63 mmol, 5.22 equiv) using general procedure B’. Flash chromatography (using a gradient from 100% hexanes to 99.5:0.5 hexanes/ethyl acetate) yielded a yellowish oil (112 mg, 0.412 mmol, 82%) as a mixture of diastereomers trans/cis: 72/28. Rf = 0.51 (2% ethyl acetate in hexanes).

Characterization data for the major diastereomer:

\[
\text{\textit{H NMR (500 MHz, CDCl}_3) \delta 7.60 – 7.57 (m, 2H), 7.43 – 7.36 (m, 6H), 7.35 – 7.28 (m, 2H), 2.53 (dd, J = 9.8, 7.9 Hz, 1H), 1.96 – 1.87 (m, 2H).}
\]

\[
\text{\textit{C NMR (126 MHz, CDCl}_3) \delta 144.47 (Cq), 138.00 (Cq), 129.44 (CH), 128.80 (CH), 128.68 (CH), 128.24 (CH), 128.15 (CH), 127.14 (CH), 41.88 (Cq), 31.16 (CH), 21.21 (CH}_3).}
\]

\[
\text{FTIR (cm}^{-1}\text{) (neat):} 3059, 3027, 1601, 1496, 1446, 1029, 765, 692, 571, 550.\text{ Methods available to us did not allow correct product ionization.}
\]

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8 Müller, D. S.; Marek, I. J. Am. Chem. Soc. 2015, 137, 15414.
(2-methyl-2-(prop-1-en-2-yl)cyclopropyl)benzene (3i)

Synthesized from 1a (153 mg, 0.502 mmol, 1.0 equiv) and 2,3-dimethyl-1,3-butadiene (300 µL, 2.66 mmol, 5.30 equiv) using general procedure B’. Flash chromatography (100% petroleum ether) yielded a clear oil (24.1 mg, 0.141 mmol, 28%) as a mixture of diastereomers trans/cis: 73/27. Rf = 0.68 (100% petroleum ether). The characterization data match the literature.5

Characterization data for the major diastereomer:

^1H NMR (500 MHz, CDCl3) δ 7.30 – 7.27 (m, 2H), 7.21 (d, J = 7.6 Hz, 3H), 4.86 – 4.85 (m, 1H), 4.79 – 4.78 (m, 1H), 2.17 (dd, J = 8.7, 6.4 Hz, 1H), 1.83 – 1.81 (m, 3H), 1.23 (dd, J = 8.8, 4.9 Hz, 1H), 0.95 (dd, J = 6.2, 5.1 Hz, 1H), 0.88 (s, 3H). ^13C NMR (126 MHz, CDCl3) δ 150.40 (Cq), 139.52 (Cq), 129.28 (CH), 128.11 (CH), 125.93 (CH), 109.43 (Cq), 29.32 (CH3), 28.66 (Cq), 20.48 (CH), 18.63 (CH3), 17.24 (CH2).

1-phenyl-1,1a,6,6a-tetrahydrocyclopropa[a]indene (3j)

Synthesized from 1a (153 mg, 0.502 mmol, 1.0 equiv) and indene (300 µL, 2.58 mmol, 5.14 equiv) using general procedure B’. Flash chromatography (100% petroleum ether) yielded a yellow solid (with a very low melting point) (38.6 mg, 0.186 mmol, 37%) as a mixture of diastereomers trans/cis: 84/16. Rf (100% petroleum ether) = 0.21.

Characterization data for the major diastereomer:

^1H NMR (500 MHz, CDCl3) δ 7.55 – 7.52 (m, 1H), 7.38 (t, J = 7.7 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.16 – 7.13 (m, 2H), 7.08 – 7.05 (m, 2H), 3.36 (dd, J = 17.3, 6.6 Hz, 1H), 3.16 (d, J = 17.3 Hz, 1H), 2.71 – 2.68 (m, 1H), 2.23 – 2.19 (m, 1H), 1.52 (t, J = 3.1 Hz, 1H). ^13C NMR (126 MHz, CDCl3) δ 142.56 (Cq), 142.47 (Cq), 137.47 (Cq), 128.83 (CH), 128.49 (CH), 127.77 (CH), 126.65 (CH), 125.43 (CH), 123.68 (CH), 36.44 (CH2), 34.54 (CH), 27.87 (CH). FTIR (cm⁻¹) (neat): 3025, 2954, 2921, 2852, 1601, 1477, 961, 748, 694, 522, 429. HRMS (APCI, Pos) calculated for C_{16}H_{15} [M+H]^+: 207.1168 m/z, found 207.1176 m/z.
1,2-bis(4-bromophenyl)cyclopropane (5)

Synthesized from 1c (192 mg, 0.501 mmol, 1.0 equiv) and 4-bromostyrene (340 µL, 2.61 mmol, 5.22 equiv) using general procedure B. Flash chromatography (100% petroleum ether) yielded a clear oil (153 mg, 0.436 mmol, 87%) as a mixture of diastereomers trans/cis: 92/8. Rf = 0.67 (100% petroleum ether). The characterization data match the literature.9

Characterization data for the major diastereomer:

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.42 – 7.39 (m, 4H), 7.01 – 6.98 (m, 4H), 2.08 (t, $J$ = 7.49 or 7.28 Hz, 2H), 1.43 (t, $J$ = 7.49 or 7.28 Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 141.25 (Cq), 131.59 (CH), 127.64 (CH), 119.62 (Cq), 27.71 (CH), 18.30 (CH$_2$).

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6. Procedure for the intramolecular cyclopropanation reaction

![Image of chemical structure](attachment:image.png)

1-phenyl-1,1a,2,7b-tetrahydrocyclopropa[c]chromene (4)

To an oven-dried 20 mL glass microwave vial equipped with a magnetic stirrer was weighted the N’-((E)-2-(cinnamylxy)benzylidene)-2-nitrobenzenesulfonohydrazide (1q) (220 mg, 0.503 mmol, 1.0 equiv). The flask was then flushed with argon during few minutes and freshly distilled CH₂Cl₂ (10 mL, [0.05M]) was added. The reaction mixture was then cooled down to 0 °C with a water/ice bath and the flask was briefly opened to add NaH 50 wt% (36.0 mg, 0.75 mmol, 1.5 equiv) and the reaction mixture was stirred at this temperature for 1 hour. The ClFe(TPP) (35.2 mg, 0.05 mmol, 10 mol%) was added in one portion. The ice-bath was removed and the reaction mixture was allowed to warm up to room temperature. The flask was then screw-capped, put into a 40 °C oil-bath and stirred for 24 hours. The reaction mixture was then cooled down to room temperature, quenched with an aqueous solution of HCl 2M and diluted with CH₂Cl₂ and then filtered over celite with copious CH₂Cl₂ washing. The layers were separated and the aqueous one extracted three times with CH₂Cl₂. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated under vacuum. The crude desired product was the purified by flash chromatography (using a gradient from 100% hexanes to 98:2 hexanes/ethyl acetate) yielded a brown oil (99.5 mg, 0.448 mmol, 89%) as a single diastereomer. Rf = 0.52 (2% ethyl acetate in hexanes). The characterization data match the literature.¹⁰,¹¹

The diastereomeric ratio (96:4) was determined by ¹H NMR on the crude mixture.

Characterization data for the major diastereomer:

**¹H NMR (500 MHz, CDCl₃)** δ 7.31 (t, J = 7.6 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.13 – 7.09 (m, 3H), 6.94 – 6.91 (m, 1H), 6.87 (d, J = 8.1 Hz, 1H), 4.47 (d, J = 10.6 Hz, 1H), 3.98 – 3.95 (m, 1H), 2.56 (t, J = 4.3 Hz, 1H), 2.28 (dd, J = 8.8, 3.8 Hz, 1H), 2.17 – 2.14 (m, 1H). **¹³C NMR (126 MHz, CDCl₃)** δ 152.57 (Cq), 141.12 (Cq), 128.67 (CH), 128.54 (CH), 126.65 (CH), 126.38 (Cq), 126.08 (CH), 125.82 (CH), 121.81 (CH), 117.43 (CH), 62.30 (CH₂), 28.11 (CH), 27.41 (CH), 24.90 (CH).

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7. NMR spectra

1a ($^1$H, 400 MHz, DMSO)

1a ($^{13}$C, 126 MHz, DMSO)
$1c$ ($^1H$, 400 MHz, DMSO)

$1c$ ($^{13}C$, 126 MHz, DMSO)
1f (1H, 400 MHz, DMSO)

1f (13C, 101 MHz, DMSO)
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1i (1H, 400 MHz, DMSO)

1i (13C, 126 MHz, DMSO)
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1k ($^1$H, 400 MHz, DMSO)

1k ($^{13}$C, 101 MHz, DMSO)
$^{1}H$, 400 MHz, CDCl$_3$

$^{13}C$, 126 MHz, DMSO

1m
2a ($^1$H, 400 MHz, CDCl$_3$)

2a ($^{13}$C, 126 MHz, CDCl$_3$)
2b (\textsuperscript{1}H, 500 MHz, CDCl\textsubscript{3})

2b (\textsuperscript{13}C, 126 MHz, CDCl\textsubscript{3})
\[
\text{Br} \quad 2c (\text{H}, 500 \text{ MHz}, \text{CDCl}_3)
\]
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2d (¹H, 500 MHz, CDCl₃)

2d (¹³C, 126 MHz, CDCl₃)
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Emmanuelle M. D. Allouche, Afnan Al-Saleh and André B. Charette*
2i ($^1$H, 500 MHz, CDCl$_3$)

2i ($^{13}$C, 126 MHz, CDCl$_3$)
$Z_1$ ($\text{H, 500 MHz, CDCl}_3$)

$Z_2$ ($\text{13C, 126 MHz, CDCl}_3$)
$2o$ ($^1H$, 500 MHz, CDCl$_3$)

$2o$ ($^{13}C$, 126 MHz, CDCl$_3$)
$^{1}H$, 400 MHz, CDCl$_3$

$^{13}C$, 126 MHz, CDCl$_3$
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3c (¹H, 400 MHz, CDCl₃)

3c (¹³C, 126 MHz, CDCl₃)
$3e$ ($^1$H, 400 MHz, CDCl$_3$)

$3e$ ($^{13}$C, 126 MHz, CDCl$_3$)
3g (¹H, 500 MHz, CDCl₃)

3g (¹³C, 126 MHz, CDCl₃)
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3i (1H, 500 MHz, CDCl3)

3i (13C, 126 MHz, CDCl3)
3j ($^1$H, 500 MHz, CDCl$_3$)

3j ($^{13}$C, 126 MHz, CDCl$_3$)
$5 \left( ^1H, 500 \text{ MHz, CDCl}_3 \right)$

$5 \left( ^{13}C, 126 \text{ MHz, CDCl}_3 \right)$