Supporting information

General: Unless otherwise noted, all commercially available compounds were used as provided without further purification. Chemicals used in this manuscript were purchased from Sigma Aldrich and Alfa Aesar.

Solvents used in reactions were p.A. grade. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel silica gel aluminium plates with F-254 indicator, visualised by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.063 – 0.2 mm). Solvent mixtures are understood as volume/volume.

$^1$H-NMR, $^{19}$F-NMR and $^{13}$C-NMR were recorded on a Varian AV600 spectrometer in CDCl$_3$. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated br (broadened singlet), s (singlet), d (doublet), t (triplet), q (quartet), p (pentelet) m (multiplet); coupling constants (J) are in Hertz (Hz).

EI MS data were recorded on a Shimadzu GCMS sytem (QP 2010 SE and GC2010plus, CP@Sil@8@MS column, 30m, 0.25μm ID, method: 60°C 5min, 20K/min to 300°C and keep for 20min). HRMS data were recorded on a ThermoFisher Scientific LTQ Orbitrap XL using ESI ionization.

IR spectra were recorded on a Perkin Elmer-100 spectrometer and are reported in terms of frequency of absorption (cm$^{-1}$).

Syringe pump: Chemyx Inc. Model Fusion 710.

Important safety note:

Safety hazards of diazo acetonitrile, described within this manuscript, have not been investigated. However, it should be noted this particular diazo compound was reported to be highly explosive.$^{[1]}$

Handling of diazo acetonitrile should only be done in a well-ventilated fume cupboard using an additional blast shield. No incidents occurred handling all diazoalkanes during the preparation of this manuscript, yet the reader should be aware of carcinogenicity and explosiveness of the herein diazo acetonitrile. General safety precautions when working with diazomethane and its derivatives should be followed. Any reactions described in this manuscript should not be performed without strict risk assessment and proper safety precautions.

General procedure for the synthesis of styrenes

Methyl triphenylphosphonium bromide (1.25 eq) was suspended in THF and n-butyl lithium (1.2 eq) is added slowly at 0 °C. The resulting suspension was stirred at 0 °C for another 60 minutes, then it is cooled to -78 °C and the respective aldehyde was added slowly. The cold bath was removed and the reaction was allowed to warm to rt. Then sat. NH$_4$Cl was added,
and the resulting mixture was extracted three times with diethyl ether. The combined organic layers were dried over Na$_2$SO$_4$, concentrated in vacuo and purified by column chromatography with pentane as eluent to afford the styrene derivative.

**General procedure for the synthesis of α-methyl-styrenes**

Methyl triphenylphosphonium bromide (1.2 eq) was suspended in THF and potassium t-butoxide (1.2 eq) is added slowly at 0 °C. The resulting suspension was stirred at 0 °C for another 60 minutes, then the respective aldehyde was added slowly. The cold bath was removed and the reaction was allowed to warm to rt over night. Then sat. NH$_4$Cl was added, and the resulting mixture was extracted three times with diethyl ether. The combined organic layers were dried over Na$_2$SO$_4$, concentrated in vacuo and purified by column chromatography with pentane as eluent to afford the α-methyl-styrene derivative.

**General procedure for catalyst screening using the slow-release protocol**

Catalyst, additives (0.1 eq, if used) and amino acetonitrile hydrochloride (2 eq) were dissolved in degassed water (1 mL) and styrene (0.2 or 0.4 mmol, 1 eq) was added under argon atmosphere. NaNO$_2$ (3 eq) was dissolved in 0.5 or 1 mL degassed water, the solution was purged with argon for a minute and was then added via syringe pump over 10 h. After complete addition the resulting reaction mixture was stirred for 4 h. The crude mixture was analysed by NMR to determine the diastereoselectivity. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over MgSO$_4$ and concentrated under reduced pressure. The residue was purified on silica gel (hexanes / ethyl acetate 20/1) to afford the cyclopropane.

**General procedure for biphasic reaction to nitrile substituted cyclopropanes using the slow-release protocol**

FeTPPCl (1 or 3 mol%), amino acetonitrile hydrochloride (2 eq) and styrene derivative (0.4 mmol, 1 eq) were dissolved in 0.1 mL degassed dichloromethane and 1 mL degassed water under argon atmosphere. NaNO$_2$ (3 eq) was dissolved in 1 mL degassed water. The solution was purged with argon for a minute and was added via syringe pump over 10 h. After complete addition the resulting reaction mixture was stirred for 4 h. The crude mixture was analysed by NMR to determine the diastereoselectivity. The aqueous phase was extracted three times with dichloromethane; the combined organic layers were dried over MgSO$_4$ and concentrated under reduced pressure. The residue was purified on silica gel (hexanes / ethyl acetate 20:1) to afford the desired cyclopropane.

**Procedure for cyclopropanation reaction in gram-scale using the slow-release protocol**

FeTPPCl (0.1 mol%), amino acetonitrile hydrochloride (2 eq) and styrene derivative (0.4 mmol, 1 eq) were dissolved in 1 mL degassed dichloromethane and 10 mL degassed water under argon atmosphere. NaNO$_2$ (3 eq) was dissolved in 25 mL degassed water. The solution was purged with argon for a minute and was added via syringe pump over 10 h. After complete addition the resulting reaction mixture was stirred for 4 h. The aqueous phase was extracted three times with dichloromethane; the combined organic layers were dried over
MgSO₄ and concentrated under reduced pressure. The residue was purified on silica gel (hexanes / ethyl acetate 20:1) to afford the desired cyclopropane.

**Table 1.** Survey of different catalysts using the slow-release protocol

<table>
<thead>
<tr>
<th>#</th>
<th>catalyst</th>
<th>mol-%</th>
<th>changes from above</th>
<th>d.r.</th>
<th>%yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ru(TPP)CO</td>
<td>3</td>
<td></td>
<td>2.5:1</td>
<td>23ᵃ</td>
</tr>
<tr>
<td>2</td>
<td>Co(salen)</td>
<td>3</td>
<td></td>
<td>1.3:1</td>
<td>14ᵃ</td>
</tr>
<tr>
<td>3</td>
<td>Rh₂OAc₄</td>
<td>3</td>
<td></td>
<td>1:1</td>
<td>9ᵃ</td>
</tr>
<tr>
<td>4</td>
<td>Fe(TPP)Cl</td>
<td>3</td>
<td></td>
<td>6:1</td>
<td>56</td>
</tr>
</tbody>
</table>

ᵃ 0.2 mmol styrene, 3 mol-% of catalyst, 2 eq aminoacetoneitrile hydrochloride were dissolved in the solvent indicated. NaNO₂ (3 eq) dissolved in 1 mL water was added over a period of 10 h at rt; the resulting mixture was stirred for another 4 h at rt; yields refer to the trans product after column chromatography; the d.r. was determined from the crude reaction mixture by ¹H-NMR; [a] NMR yield using dichloroethane as internal standard.

**Physical data**

**Cyclopropanes**

**trans-2-phenylcyclopropane-1-carbonitrile**

![trans-2-phenylcyclopropane-1-carbonitrile](image)

colorless solid (46 mg, 81%); m.p. = 29°C; ¹H-NMR (600 MHz, CDCl₃): δ = 7.34 – 7.30 (m, 2H), 7.28 – 7.24 (m, 1H), 7.12 – 7.08 (m, 2H), 2.63 (ddd, J = 9.2, 6.7, 4.7 Hz, 1H), 1.62 (dt, J = 9.2, 5.4 Hz, 1H), 1.55 (ddd, J = 8.7, 5.5, 4.8 Hz, 1H), 1.45 (ddd, J = 8.8, 6.7, 5.3 Hz, 1H); ¹³C-NMR (151 MHz, CDCl₃): δ = 137.55, 128.76, 127.41, 126.31, 121.05, 24.90, 15.24, 6.63; HRMS (ESI): m/z calc. for [C₁₀H₉NNa]: 166.06272, found 166.06276; IR (KBr): ν_max/cm⁻¹ = 3044, 2235, 2098, 1761, 1600, 1461, 1220, 1051, 920, 705.

The analytical data is in correspondence with the literature[²]

**trans-2-((p-tolyl)cyclopropane-1-carbonitrile**

![trans-2-((p-tolyl)cyclopropane-1-carbonitrile](image)
colorless solid (52 mg, 84%); m.p. = 84 °C; \(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta = 7.14 - 7.08\) (m, 2H), 7.01 – 6.96 (m, 2H), 2.60 (ddd, \(J = 9.2, 6.7, 4.7\) Hz, 1H), 2.32 (s, 3H), 1.59 (dt, \(J = 9.2, 5.4\) Hz, 1H), 1.50 (ddd, \(J = 8.7, 5.5, 4.7\) Hz, 1H), 1.42 (ddd, \(J = 8.8, 6.7, 5.2\) Hz, 1H); \(^{13}\)C-NMR (151 MHz, CDCl\(_3\)): \(\delta = 137.17, 134.51, 129.40, 126.23, 121.19, 24.67, 21.03, 15.12, 6.48\); HRMS (ESI): m/z calc. for [C\(_{11}\)H\(_{12}\)N]: 158.09643, found 158.09636; IR (KBr): \(\nu_{\text{max}}/\text{cm}^{-1} = 3850, 3028, 2919, 2230, 2087, 1912, 1791, 1516, 1452, 1039, 931, 796, 715\).

trans-2-(4-(tert-butyl)phenyl)cyclopropane-1-carbonitrile

[Diagram]

colorless solid (60 mg, 76%); m.p. = 37 °C; \(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta = 7.35 - 7.32\) (m, 2H), 7.07 – 7.03 (m, 2H), 2.61 (ddd, \(J = 9.2, 6.7, 4.7\) Hz, 1H), 1.60 (dt, \(J = 9.2, 5.4\) Hz, 1H), 1.55 – 1.50 (m, 1H), 1.44 (ddd, \(J = 8.8, 6.7, 5.2\) Hz, 1H), 1.31 – 1.30 (m, 9H); \(^{13}\)C-NMR (151 MHz, CDCl\(_3\)): \(\delta = 50.52, 134.54, 126.04, 125.67, 121.19, 34.51, 31.27, 24.57, 15.14, 6.49\); HRMS (ESI): m/z calc. for [C\(_{14}\)H\(_{17}\)NNa]: 222.12532, found 222.12558; IR (KBr): \(\nu_{\text{max}}/\text{cm}^{-1} = 3032, 2959, 2237, 2106, 1908, 1741, 1516, 1460, 1365, 1269, 1122, 1028, 938, 829, 791\).

trans-2-(4-fluorophenyl)cyclopropane-1-carbonitrile

[Diagram]

colorless solid (49 mg, 76%); m.p. = 66 °C; \(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta = 7.11 - 7.05\) (m, 2H), 7.03 – 6.97 (m, 2H), 2.62 (ddd, \(J = 9.2, 6.6, 4.7\) Hz, 1H), 1.62 (dt, \(J = 9.2, 5.5\) Hz, 1H), 1.51 (ddd, \(J = 8.9, 5.6, 4.7\) Hz, 1H), 1.41 (ddd, \(J = 8.9, 6.7, 5.4\) Hz, 1H); \(^{19}\)F-NMR (564 MHz, CDCl\(_3\)): \(\delta = -114.62 - 114.71\) (m); \(^{13}\)C-NMR (151 MHz, CDCl\(_3\)): \(\delta = 162.84, 161.21, 133.21\) (d, \(J = 3.5\) Hz), 128.10 (d, \(J = 8.5\) Hz), 120.86, 115.68 (d, \(J = 21.3\) Hz), 24.26, 15.07, 6.54; HRMS (ESI): m/z calc. for [C\(_{10}\)H\(_{8}\)NF]: 161.06353, found 161.06383; IR (KBr): \(\nu_{\text{max}}/\text{cm}^{-1} = 3809, 3458, 3036, 2935, 2672, 2326, 2090, 1882, 1751, 1504, 1371, 1215, 1052, 928, 820\).

trans-2-(4-chlorophenyl)cyclopropane-1-carbonitrile

[Diagram]

colorless solid (58 mg, 82%); m.p. = 86 °C; \(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta = 7.32 - 7.24\) (m, 2H), 7.07 – 6.98 (m, 2H), 2.60 (ddd, \(J = 9.2, 6.7, 4.7\) Hz, 1H), 1.63 (dt, \(J = 9.2, 5.5\) Hz, 1H), 1.53 (ddd, \(J = 8.9, 5.6, 4.7\) Hz, 1H), 1.42 (ddd, \(J = 8.8, 6.7, 5.4\) Hz, 1H); \(^{13}\)C-NMR (151 MHz, CDCl\(_3\)): \(\delta = 136.03, 133.25, 128.91, 127.74, 120.71, 24.33, 15.19, 6.73\); HRMS (ESI): m/z calc. for
trans-2-(4-bromophenyl)cyclopropane-1-carbonitrile

yellowish solid (75 mg, 84%); m.p. = 87 °C; $^1$H-NMR (600 MHz, CDCl$_3$): δ = 7.49 – 7.40 (m, 2H), 7.03 – 6.93 (m, 2H), 2.59 (ddd, $J$ = 9.2, 6.7, 4.7 Hz, 1H), 1.63 (dt, $J$ = 9.2, 5.5 Hz, 1H), 1.53 (ddd, $J$ = 8.8, 5.6, 4.7 Hz, 1H), 1.42 (ddd, $J$ = 8.9, 6.7, 5.5 Hz, 1H); $^{13}$C-NMR (151 MHz, CDCl$_3$): δ = 136.57, 131.86, 128.07, 121.25, 120.68, 24.39, 15.18, 6.71; HRMS (ESI): m/z calc. for [C$_{10}$H$_8$NClNa]: 243.97323, found 243.97345; IR (KBr): $\nu$ max/cm$^{-1}$ = 3046, 2927, 2232, 2093, 1909, 1740, 1488, 1221, 1086, 917, 792.

trans-2-(4-methoxyphenyl)cyclopropane-1-carbonitrile

colorless solid (51 mg, 74%); m.p. = 76 °C; $^1$H-NMR (600 MHz, CDCl$_3$): δ = 7.09 – 6.97 (m, 2H), 6.88 – 6.77 (m, 2H), 3.79 (s, 3H), 2.59 (ddd, $J$ = 9.2, 6.7, 4.7 Hz, 1H), 1.57 (dt, $J$ = 9.2, 5.3 Hz, 1H), 1.46 (ddd, $J$ = 8.8, 5.4, 4.7 Hz, 1H), 1.39 (ddd, $J$ = 8.8, 6.7, 5.2 Hz, 1H); $^{13}$C-NMR (151 MHz, CDCl$_3$): δ = 158.90, 129.49, 127.62, 121.26, 114.13, 55.33, 24.40, 14.92, 6.31; HRMS (ESI): m/z calc. for [C$_{11}$H$_{11}$ONa]: 196.07329, found 196.07345; IR (KBr): $\nu$ max/cm$^{-1}$ = 3012, 2949, 2241, 1605, 1506, 1461, 1239, 1179, 1021, 934, 826, 705.

trans-2-(m-tolyl)cyclopropane-1-carbonitrile

yellowish solid (50 mg, 80%); m.p. = 42 °C; $^1$H-NMR (600 MHz, CDCl$_3$): δ = 7.20 (t, $J$ = 7.6 Hz, 1H), 7.09 – 7.04 (m, 1H), 6.94 – 6.87 (m, 2H), 2.59 (ddd, $J$ = 9.2, 6.7, 4.7 Hz, 1H), 1.60 (dt, $J$ = 9.1, 5.4 Hz, 1H), 1.56 – 1.50 (m, 1H), 1.44 (ddd, $J$ = 8.7, 6.7, 5.2 Hz, 1H); $^{13}$C-NMR (151 MHz, CDCl$_3$): δ = 138.50, 137.50, 128.65, 128.15, 127.09, 123.26, 121.12, 24.87, 21.35, 15.20, 6.54; HRMS (ESI): m/z calc. for [C$_{11}$H$_{12}$N]: 158.09634, found 158.09645; IR (KBr): $\nu$ max/cm$^{-1}$ = 3839, 3537, 2922, 2338, 2229, 2100, 1875, 1746, 1598, 1459, 1163, 1040, 955, 891, 778, 697.
**trans-2-(3-fluorophenyl)cyclopropane-1-carbonitrile**

![trans-2-(3-fluorophenyl)cyclopropane-1-carbonitrile](image)

Yellowish oil (52 mg, 81%); $^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 7.30 – 7.24$ (m, 1H), 6.98 – 6.93 (m, 1H), 6.92 – 6.89 (m, 1H), 6.81 – 6.77 (m, 1H), 2.62 (ddd, $J = 9.2$, 6.7, 4.7 Hz, 1H), 1.65 (dt, $J = 9.2$, 5.6 Hz, 1H), 1.59 – 1.54 (m, 2H), 1.44 (ddd, $J = 8.9$, 6.6, 5.5 Hz, 1H); $^{19}$F NMR (564 MHz, CDCl$_3$): $\delta = -112.39 – -112.46$ (m); $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta = 163.77$, 162.14, 140.12 (d, $J = 7.8$ Hz), 130.34 (d, $J = 8.6$ Hz), 120.61, 114.41 (d, $J = 21.2$ Hz), 113.27 (d, $J = 22.1$ Hz), 24.52 (d, $J = 2.4$ Hz), 15.34, 6.89; HRMS (ESI): m/z calc. for [C$_{10}$H$_9$NF]: 162.07114, found 162.07135.

**trans-2-(o-tolyl)cyclopropane-1-carbonitrile**

![trans-2-(o-tolyl)cyclopropane-1-carbonitrile](image)

Yellowish oil (51 mg, 74%); $^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 7.22 – 7.18$ (m, 2H), 7.17 – 7.12 (m, 1H), 6.98 – 6.94 (m, 1H), 2.61 (dt, $J = 9.1$, 6.0 Hz, 1H), 2.46 (s, 3H), 1.66 – 1.59 (m, 1H), 1.48 – 1.42 (m, 2H); $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta = 138.21$, 135.62, 130.16, 127.60, 126.10, 125.91, 121.41, 23.62, 19.58, 13.95, 5.11; HRMS (ESI): m/z calc. for [C$_{11}$H$_{11}$NNa]: 180.07837, found 180.07820; IR (KBr): v$_{max}$/cm$^{-1}$ = 3033, 2236, 1495, 1452, 1241, 1143, 1054, 974, 875, 799, 687.

**trans-2-(2-fluorophenyl)cyclopropane-1-carbonitrile**

![trans-2-(2-fluorophenyl)cyclopropane-1-carbonitrile](image)

Yellowish oil (44 mg, 68%); $^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 7.27 – 7.21$ (m, 1H), 7.11 – 7.02 (m, 2H), 6.97 (td, $J = 7.6$, 1.7 Hz, 1H), 2.76 – 2.64 (m, 1H), 1.67 – 1.61 (m, 2H), 1.52 – 1.46 (m, 1H); $^{19}$F NMR (564 MHz, Chloroform-d) $\delta = -118.01 – -118.18$ (m); $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta = 162.48$, 160.84, 128.99 (d, $J = 8.4$ Hz), 127.24 (d, $J = 3.5$ Hz), 124.71 (d, $J = 14.1$ Hz), 124.27 (d, $J = 3.6$ Hz), 120.85, 115.65 (d, $J = 21.9$ Hz), 19.24 (d, $J = 4.0$ Hz), 14.19 (d, $J = 2.2$ Hz), 5.48 (d, $J = 2.4$ Hz); HRMS (ESI): m/z calc. for [C$_{10}$H$_8$NFNa]: 184.05330, found 184.05356; IR (KBr): v$_{max}$/cm$^{-1}$ = 3049, 2239, 1495, 1452, 1238, 1203, 1096, 1033, 942, 816, 755.
trans-2-(naphthalen-1-yl)cyclopropane-1-carbonitrile

\[
\begin{align*}
\text{NC} & \quad \text{\textbullet} \quad \text{\textbullet} \quad \text{\textbullet} \\
\text{OC} & \quad \text{\textbullet} \quad \text{\textbullet} \quad \text{\textbullet}
\end{align*}
\]

Colorless solid (40 mg, 51%); m.p. = 87 °C; \(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta = 8.25 \text{ (dt, } J = 8.5, 1.0 \text{ Hz, 1H}), 7.89 \text{ (dt, } J = 8.2, 0.9 \text{ Hz, 1H}), 7.80 \text{ (d, } J = 8.1 \text{ Hz, 1H}), 7.64 \text{ (ddd, } J = 8.3, 6.8, 1.4 \text{ Hz, 1H}), 7.56 \text{ (ddd, } J = 8.1, 6.8, 1.2 \text{ Hz, 1H}), 7.39 \text{ (dd, } J = 8.2, 7.1 \text{ Hz, 1H}), 7.24 \text{ (dt, } J = 7.1, 1.2 \text{ Hz, 1H}), 3.09 - 3.02 \text{ (m, 1H)}, 1.78 \text{ (dt, } J = 9.0, 5.0 \text{ Hz, 1H}), 1.64 - 1.53 \text{ (m, 2H)}; \(^{13}\)C-NMR (151 MHz, CDCl\(_3\)): \(\delta = 133.50 \text{ (d, } J = 6.2 \text{ Hz}), 132.70, 128.74, 128.47, 126.84, 126.26, 125.17, 124.40, 123.60, 121.46, 23.33, 13.74, 5.18; \) HRMS (ESI): m/z calc. for [C\(_{14}\)H\(_{11}\)NK]: 232.05231, found 232.05228; IR (KBr): \(\nu_{\text{max}}/\text{cm}^{-1} = 3055, 2924, 2235, 2111, 1816, 1675, 1507, 1259, 1034, 795, 772, 705.

trans-2-(naphthalen-2-yl)cyclopropane-1-carbonitrile

\[
\begin{align*}
\text{CN} & \quad \text{\textbullet} \quad \text{\textbullet} \quad \text{\textbullet}
\end{align*}
\]

Colorless solid (45 mg, 58%); m.p. = 154 °C; \(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta = 7.84 - 7.73 \text{ (m, 3H)}, 7.60 - 7.55 \text{ (m, 1H), } 7.53 - 7.42 \text{ (m, } 2H), 7.21 \text{ (dd, } J = 8.5, 1.9 \text{ Hz, 1H), } 2.80 \text{ (ddd, } J = 9.2, 6.7, 4.7 \text{ Hz, 1H), } 1.70 \text{ (dt, } J = 9.1, 5.3 \text{ Hz, 1H), } 1.65 \text{ (dt, } J = 8.5, 5.1 \text{ Hz, 1H), } 1.58 \text{ (ddd, } J = 8.7, 6.7, 5.1 \text{ Hz, 1H); }^{13}\)C-NMR (151 MHz, CDCl\(_3\)): \(\delta = 134.90, 133.21, 132.58, 128.62, 127.68, 127.48, 126.59, 126.05, 125.18, 124.29, 121.06, 25.19, 15.21, 6.63; \) HRMS (ESI): m/z calc. for [C\(_{14}\)H\(_{11}\)NNa]: 216.07837, found 216.07834; IR (KBr): \(\nu_{\text{max}}/\text{cm}^{-1} = 3741, 3035, 2927, 2662, 2327, 2234, 2092, 1741, 1618, 1506, 1446, 1220, 1035, 955, 798.

trans-2-(benzo[d][1,3]dioxol-5-yl)cyclopropane-1-carbonitrile

\[
\begin{align*}
\text{OC} & \quad \text{\textbullet} \quad \text{\textbullet} \quad \text{\textbullet} \\
\text{OC} & \quad \text{\textbullet} \quad \text{\textbullet} \quad \text{\textbullet}
\end{align*}
\]

Yellowish solid (51%, 68%); m.p. = 90 °C; \(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta = 6.73 \text{ (d, } J = 8.0 \text{ Hz, 1H}), 6.61 \text{ (dd, } J = 8.0, 1.8 \text{ Hz, 1H}), 6.56 \text{ (d, } J = 1.8 \text{ Hz, 1H}), 5.94 \text{ (s, } 2H), 2.57 \text{ (ddd, } J = 9.2, 6.7, 4.7 \text{ Hz, 1H), } 1.56 \text{ (dt, } J = 9.2, 5.4 \text{ Hz, 1H), } 1.46 \text{ (ddd, } J = 8.8, 5.5, 4.7 \text{ Hz, 1H), } 1.37 \text{ (ddd, } J = 8.8, 6.7, 5.3 \text{ Hz, 1H); }^{13}\)C-NMR (151 MHz, CDCl\(_3\)): \(\delta = 48.00, 146.93, 131.29, 121.08, 120.01, 108.38, 106.79, 101.21, 24.84, 15.00, 6.42; \) HRMS (ESI): m/z calc. for [C\(_{11}\)H\(_{9}\)NO\(_2\)Na]: 210.05255, found 210.05211; IR (KBr): \(\nu_{\text{max}}/\text{cm}^{-1} = 3020, 2896, 2324, 2236, 2102, 1852, 1495, 1449, 1242, 1109, 1035, 930, 803.

**trans-2-(thiophen-2-yl)cyclopropane-1-carbonitrile**

![Formula](https://example.com/formula.png)

Yellowish oil (53 mg, 88%); $^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 7.16$ (dt, $J = 5.1$, 1.3 Hz, 1H), 6.92 (ddd, $J = 5.0$, 3.5, 1.3 Hz, 1H), 6.86 (dq, $J = 3.5$, 1.2 Hz, 1H), 2.79 (dddt, $J = 9.0$, 6.6, 4.6, 1.1 Hz, 1H), 1.66 (ddtd, $J = 9.1$, 5.5, 1.3 Hz, 1H), 1.60 (dddd, $J = 8.8$, 5.7, 4.5, 1.3 Hz, 1H), 1.46 (dddd, $J = 8.8$, 6.5, 5.3, 1.3 Hz, 1H); $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta = 141.32$, 127.07, 124.98, 124.27, 120.49, 20.29, 16.18, 7.63; HRMS (ESI): m/z calc. for [C$_8$H$_7$NNaS]: 172.01914, found 172.01872; IR (KBr): $\nu$_max/cm$^{-1}$ = 3105, 3044, 2329, 2238, 2114, 1441, 1385, 1239, 1043, 914, 846, 790, 702.

**Alpha methylated Cyclopropanes**

**trans-2-phenyl-2-methyl-cyclopropane-1-carbonitrile**

![Formula](https://example.com/formula.png)

Colorless oil (44 mg, 71%); $^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 7.35 – 7.30$ (m, 2H), 7.29 – 7.24 (m, 3H), 1.70 – 1.64 (m, 4H), 1.57 (dd, $J = 9.1$, 5.0 Hz, 1H), 1.31 (t, $J = 5.3$ Hz, 1H); $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta = 142.67$, 128.74, 127.37, 127.32, 120.27, 28.71, 23.48, 21.27, 11.25; HRMS (ESI): m/z calc. for [C$_{11}$H$_{11}$NNa]: 180.07837, found 180.07832; IR (KBr): $\nu$_max/cm$^{-1}$ = 3846, 3517, 2947, 2677, 2253, 2093, 1865, 1447, 1254, 1075, 912, 727.

The analytical data is in correspondence with the literature.$^3$

**trans-2-(p-tolyl)-2-methylcyclopropane-1-carbonitrile**

![Formula](https://example.com/formula.png)

Colorless solid (61 mg, 89%); m.p. = 35 °C; $^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 7.19 – 7.08$ (m, 4H), 2.33 (s, 3H), 1.66 – 1.61 (m, 4H), 1.54 (dd, $J = 9.1$, 5.0 Hz, 1H), 1.29 (t, $J = 5.2$ Hz, 1H); $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta = $139.74, 137.07, 129.37, 127.24, 120.38, 28.40, 23.53, 21.29, 21.00, 11.23; HRMS (ESI): m/z calc. for [C$_{12}$H$_{13}$NNa]: 194.09402, found 194.09398; IR (KBr): $\nu$_max/cm$^{-1}$ = 3025, 2966, 2234, 2102, 1902, 1746, 1516, 1445, 1369, 1259, 1075, 901, 817, 721.
**trans-2-(4-chlorophenyl)-2-methylcyclopropane-1-carbonitrile**

![trans-2-(4-chlorophenyl)-2-methylcyclopropane-1-carbonitrile](image)

colorless oil (65 mg, 85%); $^1$H-NMR (600 MHz, CDCl$_3$): $\delta$ = 7.30 – 7.27 (m, 2H), 7.22 – 7.18 (m, 2H), 1.67 – 1.60 (m, 4H), 1.53 (dd, $J$ = 9.3, 5.2 Hz, 1H), 1.32 (td, $J$ = 5.3, 1.3 Hz, 1H); $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta$ = 141.15, 133.18, 128.86 (d, $J$ = 13.0 Hz), 119.91, 28.17, 23.38, 21.22, 11.35; HRMS (ESI): m/z calc. for [C$_{11}$H$_{10}$ClNa]: 214.03940, found 214.03879, IR (KBr): $\nu_{\text{max}}$/cm$^{-1}$ = 2971, 2237, 2112, 1494, 1443, 1399, 1090, 1012, 949, 897, 830, 778, 728.

**trans-2-(4-bromophenyl)-2-methylcyclopropane-1-carbonitrile**

![trans-2-(4-bromophenyl)-2-methylcyclopropane-1-carbonitrile](image)

eyellowish solid (62 mg, 65%); m.p. = 53 °C; $^1$H-NMR (600 MHz, CDCl$_3$): $\delta$ = 7.49 – 7.37 (m, 2H), 7.18 – 7.09 (m, 2H), 1.66 – 1.61 (m, 4H), 1.53 (dd, $J$ = 9.2, 5.2 Hz, 1H), 1.32 (t, $J$ = 5.3 Hz, 1H); $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta$ = 141.67, 131.87, 129.16, 119.25, 119.88, 28.24, 23.33, 21.17, 11.31; HRMS (ESI): m/z calc. for [C$_{11}$H$_{10}$BrNa]: 257.98888, found 257.98871, IR (KBr): $\nu_{\text{max}}$/cm$^{-1}$ = 3042, 2968, 2236, 2106, 1488, 1448, 1388, 1076, 1007, 825, 713.

**trans-2-(4-cyanophenyl)-2-methylcyclopropyl-1-carbonitrile**

![trans-2-(4-cyanophenyl)-2-methylcyclopropyl-1-carbonitrile](image)

colorless solid (62 mg, 85%); m.p. = 59 °C; $^1$H-NMR (600 MHz, CDCl$_3$): $\delta$ = 7.66 – 7.59 (m, 2H), 7.41 – 7.34 (m, 2H), 1.71 (dd, $J$ = 9.2, 5.6 Hz, 1H), 1.67 (s, 3H), 1.59 (dd, $J$ = 9.2, 5.4 Hz, 1H) 1.40 (t, $J$ = 5.5 Hz, 1H); $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta$ = 147.73, 132.64, 128.14, 119.33, 118.35, 111.38, 28.40, 22.88, 21.31, 11.75; HRMS (ESI): m/z calc. for [C$_{12}$H$_{10}$N$_2$Na]: 205.07429, found 205.07321; IR (KBr): $\nu_{\text{max}}$/cm$^{-1}$ = 3046, 2974, 2231, 2097, 1811, 1692, 1608, 1508, 1445, 1403, 1284, 1109, 1079, 842, 774.

**trans-2-(3-fluorophenyl)-2-methylcyclopropane-1-carbonitrile**

![trans-2-(3-fluorophenyl)-2-methylcyclopropane-1-carbonitrile](image)
yellowish oil (39 mg, 56%) $^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 7.31 - 7.26$ (m, 1H), 7.07 - 7.02 (m, 1H), 6.99 - 6.91 (m, 2H), 1.68 (dd, $J = 9.2$, 5.6 Hz, 1H), 1.65 (s, 3H), 1.56 (dd, $J = 9.2$, 5.2 Hz, 1H), 1.33 (t, $J = 5.4$ Hz, 1H); $^{13}$F NMR (564 MHz, Chloroform-d) $\delta = 112.23 - 112.32$ (m); $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta = 163.62$, 161.98, 145.09 (d, $J = 7.3$ Hz), 130.35 (d, $J = 8.4$ Hz), 122.85 (d, $J = 3.0$ Hz), 119.82, 114.41 (dd, $J = 21.0$, 16.4 Hz), 28.24, 23.13, 21.36, 11.57; $^{19}$F NMR (564 MHz,CDCl$_3$) $\delta = -112.28$ (ddd, $J = 10.0$, 8.5, 6.0 Hz); HRMS (ESI): m/z calc. for [C$_{11}$H$_{13}$NFN]: 198.06895, found 198.06897; IR (KBr): $\nu_{\text{max}}$/cm$^{-1}$ = 3048, 2972, 2237, 2115, 1613, 1587, 1490, 1440, 1267, 1201, 1074, 959, 922, 870, 785, 694.

**trans-2-(5,6,7,8-tetrahydronaphthalen-2-yl)-2-methylcyclopropane-1-carbonitrile**

![trans-2-(5,6,7,8-tetrahydronaphthalen-2-yl)-2-methylcyclopropane-1-carbonitrile](image1)

colorless solid (64mg, 76%); m.p. = 86 °C; $^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 7.03 - 6.95$ (m, 3H), 2.77 - 2.68 (m, 4H), 1.78 (p, $J = 3.4$ Hz, 4H), 1.66 - 1.61 (m, 4H), 1.53 (dd, $J = 9.1$, 5.0 Hz, 1H), 1.27 (t, $J = 5.3$ Hz, 1H); $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta = 139.81$, 137.52, 136.39, 129.49, 128.07, 124.45, 120.46, 29.39, 29.01, 28.47, 23.58, 23.08 (d, $J = 3.0$ Hz), 21.26, 11.14; HRMS (ESI): m/z calc. for [C$_{15}$H$_{17}$NNa]: 234.12532, found 234.12526; IR (KBr): $\nu_{\text{max}}$/cm$^{-1}$ = 3038, 2929, 2858, 2231, 1802, 1698, 1501, 1435, 1248, 1183, 1081, 917, 807, 712.

**trans-2-(benzo[d][1,3]dioxol-5-yl)-2-methylcyclopropane-1-carbonitrile**

![trans-2-(benzo[d][1,3]dioxol-5-yl)-2-methylcyclopropane-1-carbonitrile](image2)

yellowish solid (53 mg, 66%); m.p. = 72 °C; $^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 6.77 - 6.71$ (m, 3H), 5.94 (s, 2H), 1.63 - 1.59 (m, 4H), 1.50 (dd, $J = 9.1$, 5.0 Hz, 1H), 1.26 (t, $J = 5.3$ Hz, 1H); $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta = 147.80$, 146.73, 136.69, 120.64, 120.23, 108.28, 108.17, 101.19, 28.75, 23.86, 21.40, 11.30; HRMS (ESI): m/z calc. for [C$_{12}$H$_{12}$O$_3$NK]: 240.0414, found 240.04204; IR (KBr): $\nu_{\text{max}}$/cm$^{-1}$ = 2972, 2897, 2231, 1490, 1457, 1434, 1349, 1226, 1080, 1033, 924, 869, 808, 728.

**trans-2-(benzofuran-2-yl)-2-methylcyclopropane-1-carbonitrile**

![trans-2-(benzofuran-2-yl)-2-methylcyclopropane-1-carbonitrile](image3)

yellowish solid (65 mg, 82%); m.p. = 54°C; $^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 7.52 - 7.46$ (m, 1H), 7.36 - 7.34 (m, 1H), 7.26 - 7.19 (m, 2H), 6.58 - 6.55 (m, 1H), 2.11 (dd, $J = 9.3$, 6.0 Hz, 1H), 1.90 (dd, $J = 9.4$, 5.2 Hz, 1H), 1.77 (s, 3H), 1.39 (dd, $J = 6.0$, 5.2 Hz, 1H); $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta = 157.05$, 154.18, 128.40, 124.16, 123.01, 120.57, 119.23, 110.84, 102.85, 22.35, 21.21, 18.36, 11.77; HRMS (ESI): m/z calc. for [C$_{13}$H$_{13}$ONa]: 220.07329, found 220.07317; IR (KBr): $\nu_{\text{max}}$/cm$^{-1}$ = 2976, 2238, 2112, 1597, 1454, 1253, 1169, 1090, 960, 938, 807, 747, 673.
**trans-2-{(thiophen-2-yl)}-2-methylcyclopropane-1-carbonitrile**

![Structure](image1)

colorless oil (44 mg, 67%); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.28\ (dd, J = 5.1, 3.0\ Hz, 1H), 7.04\ (dd, J = 3.0, 1.4\ Hz, 1H), 6.87\ (dd, J = 5.1, 1.4\ Hz, 1H), 1.69\ (s, 3H), 1.66\ (dd, J = 9.1, 5.7\ Hz, 1H), 1.57\ (dd, J = 9.1, 5.2\ Hz, 1H), 1.33\ (t, J = 5.4\ Hz, 1H); \(^1\)C-NMR (101 MHz, CDCl\(_3\)): \(\delta = 143.70, 126.67, 125.41, 120.70, 119.87, 24.15, 22.34, 21.78, 12.49\); HRMS (ESI): m/z calc. for \([C_9H_9NKS]\): 202.00873, found 202.00871; IR (KBr): \(\nu_{max}/\text{cm}\(^{-1}\) = 3102, 2971, 2237, 1442, 1263, 1070, 841, 780, 701.

**trans-2-{(5-bromothiophen-2-yl)}-2-methylcyclopropane-1-carbonitrile**

![Structure](image2)

yellow oil (62 mg, 64%); \(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta = 6.85\ (d, J = 3.8\ Hz, 1H), 6.59\ (d, J = 3.8\ Hz, 1H), 1.75 – 1.68\ (m, 4H), 1.60\ (dd, J = 9.2, 5.4\ Hz, 1H), 1.38\ (t, J = 5.6\ Hz, 1H); \(^1\)C-NMR (151 MHz, CDCl\(_3\)): \(\delta = 148.51, 129.63, 124.33, 119.08, 110.42, 24.39, 22.95, 22.60, 13.78\); HRMS (ESI): m/z calc. for \([C_9H_8NBrNaS]\) 263.94530, found 263.94537; IR (KBr): \(\nu = 3093, 2969, 2969, 2325, 2238, 1903, 1741 1442, 1044, 960, 790, 666.

**trans-2-{(thiophen-3-yl)}-2-methylcyclopropane-1-carbonitrile**

![Structure](image3)

off-white solid (45 mg, 69%); m.p. = 99\ °C; \(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta = .28\ (dd, J = 5.0, 3.0\ Hz, 1H), 7.03\ (dd, J = 3.0, 1.4\ Hz, 1H), 6.87\ (dd, J = 5.1, 1.4\ Hz, 1H), 1.69\ (s, 3H), 1.66\ (dd, J = 9.1, 5.7\ Hz, 1H), 1.57\ (dd, J = 9.1, 5.2\ Hz, 1H), 1.33\ (t, J = 5.4\ Hz, 1H); \(^1\)C-NMR (151 MHz, CDCl\(_3\)): \(\delta = 143.70, 126.67, 125.41, 120.71, 119.87, 24.15, 22.35, 21.78, 12.49\); HRMS (ESI): m/z calc. for \([C_9H_9NNaS]\) 186.0379, found 186.03477; IR (KBr): \(\nu_{max}/\text{cm}\(^{-1}\) = 3103, 2966, 2236, 1445, 1381, 1261, 1205, 1076, 935, 862, 771, 676.

**Other Cyclopropanes and Cyclopropene**

**trans-phenyl-2-ethylcyclopropane-1-carbonitrile**

![Structure](image4)
yellow oil (47 mg, 69%); \(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta = 7.34 - 7.30\) (m, 2H), 7.28 - 7.23 (m, 3H), 1.93 (ddq, \(J = 14.7, 7.3, 1.2\) Hz, 1H), 1.82 (dq, \(J = 14.6, 7.4\) Hz, 1H), 1.68 (dd, \(J = 9.0, 5.4\) Hz, 1H), 1.48 (dd, \(J = 9.0, 4.9, 1.2\) Hz, 1H), 1.28 (t, \(J = 5.2\) Hz, 1H), 0.93 (t, \(J = 7.4\) Hz, 3H); \(^{13}\)C-NMR (151 MHz, CDCl\(_3\)): \(\delta = 140.78, 129.03, 128.52, 127.43, 120.44, 34.83, 30.55, 20.19, 10.82, 10.25\); HRMS (ESI): \(m/z\) calc. for [C\(_{12}\)H\(_{13}\)NK]: 210.06796, found 210.06786; IR (KBr): \(\nu_{\text{max}}/\text{cm}^{-1} = 3035, 2965, 2876, 2234, 2102, 1896, 1751, 1600, 1449, 1377, 1075, 910, 761, 698\).

2,2-diphenylcyclopropane-1-carbonitrile

![2,2-diphenylcyclopropane-1-carbonitrile](image)

off-white solid (44 mg, 50%); m.p. = 91 °C; \(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta = 7.47 - 7.40\) (m, 2H), 7.39 - 7.32 (m, 2H), 7.32 - 7.19 (m, 6H), 2.23 (dd, \(J = 9.1, 5.7\) Hz, 1H), 2.03 (t, \(J = 5.5\) Hz, 1H), 1.81 (dd, \(J = 9.2, 5.2\) Hz, 1H). \(^{13}\)C-NMR (151 MHz, CDCl\(_3\)): \(\delta = 142.29, 138.89, 129.36, 128.84, 128.78, 127.92, 127.77, 127.39, 119.48, 38.28, 21.02, 12.22\); HRMS (ESI): \(m/z\) calc. for [C\(_{16}\)H\(_{13}\)NNa]: 242.09402, found 242.09387; IR (KBr): \(\nu_{\text{max}}/\text{cm}^{-1} = 3028, 2926, 2293, 2099, 1882, 1735, 1592, 1492, 1444, 756, 697\).

2-phenyl-2-(trifluoromethyl)cyclopropane-1-carbonitrile

![2-phenyl-2-(trifluoromethyl)cyclopropane-1-carbonitrile](image)

**trans-Isomer**

yellowish solid (48 mg, 57%); m.p. = 58 °C; \(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta = 7.53 - 7.48\) (m, 2H), 7.47 - 7.42 (m, 3H), 7.41 - 7.32 (m, 2H), 2.22 (dd, \(J = 9.6, 6.1\) Hz, 1H), 1.94 (dd, \(J = 9.6, 5.8\) Hz, 1H), 1.74 (tt, \(J = 6.0, 1.6\) Hz, 1H); \(^{13}\)C-NMR (151 MHz, CDCl\(_3\)): \(\delta = 131.38, 129.97, 129.67, 128.97, 125.05\) (q, \(J = 275.6\) Hz), 116.96, 34.75 (q, \(J = 34.2\) Hz), 16.21 (q, \(J = 2.4\) Hz), 8.26 (d, \(J = 3.7\) Hz). \(^{19}\)F NMR (564 MHz, CDCl\(_3\)) \(\delta = -71.19\) (d, \(J = 1.5\) Hz); HRMS (ESI): \(m/z\) calc. for [C\(_{11}\)H\(_{8}\)NF\(_3\)Na]: 234.0511, found 234.04968; IR (KBr): \(\nu_{\text{max}}/\text{cm}^{-1} = 3049, 2250, 1380, 1341, 1288, 1076, 761, 670\).

**Cis-Isomer**

yellowish solid; m.p. = 58 °C; \(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta = 7.46 - 7.36\) (m, 5H), 2.07 - 1.99 (m, 2H), 1.73 (ddq, \(J = 9.1, 5.4, 2.0\) Hz, 1H); \(^{13}\)C-NMR (151 MHz, CDCl\(_3\)): \(\delta = 132.75, 130.57, 129.69, 128.94, 123.99\) (q, \(J = 275.6\) Hz), 116.59, 35.68 (q, \(J = 34.3\) Hz), 16.47 (q, \(J = 3.1\) Hz), 8.84; \(^{19}\)F NMR (564 MHz, CDCl\(_3\)) \(\delta = -67.49\) (d, \(J = 1.9\) Hz); HRMS (ESI): \(m/z\) calc. for [C\(_{11}\)H\(_{8}\)NF\(_3\)Na]: 234.05011, found 234.05008; IR (KBr): \(\nu_{\text{max}}/\text{cm}^{-1} = 3038, 2247, 1452, 1352, 1286, 1150, 1076, 761, 696\).
2-methyl-3-phenylcycloprop-2-ene-1-carbonitrile

![Chemical Structure]

yellow oil (44 mg, 71%); $^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 7.57 - 7.51$ (m, 2H), 7.48 - 7.43 (m, 2H), 7.43 - 7.38 (m, 1H), 2.39 (s, 3H), 2.14 (s, 1H); $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta = 129.57$, 129.26, 128.89, 125.61, 122.58, 104.71 (d, $J = 5.6$ Hz), 10.54, 5.33; HRMS (ESI): m/z calc. for [C$_{11}$H$_9$NNa]: 178.06272, found 178.06293; IR (KBr): $\nu_{\text{max}}$/cm$^{-1}$ = 3054, 2959, 2328, 2220, 2097, 1706, 1594, 1436, 1365, 1165, 1005, 760, 695.

trans-2-phenylcyclopropylmethanamine

![Chemical Structure]

red oil (234 mg, 91%); $^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 7.27 - 7.21$ (m, 2H), 7.17 - 7.12 (m, 1H), 7.08 - 7.02 (m, 2H), 1.72 (dt, $J = 9.2$, 4.8 Hz, 1H), 1.41 (brs, 2H), 1.31 - 1.25 (m, 1H), 0.91 (dt, $J = 8.4$, 5.0 Hz, 1H), 0.85 (dt, $J = 8.7$, 5.3 Hz, 1H); $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta = 143.10$, 128.27, 125.67, 125.42, 46.61, 26.83, 21.82, 14.61; MS (EI): m/z (%) = 147.1 ([M], 5%), 106.1 ([M-C$_2$H$_3$N], 100%), 115.0 ([M-CH$_3$N], 36%), 129.0 ([M-H$_2$N] 12%), 78.0 ([M-C$_6$H$_6$] 9%); IR (KBr): $\nu_{\text{max}}$/cm$^{-1}$ = 3026, 3001, 2875, 2109, 1805, 1601, 1495, 1456, 1086, 1031, 876, 744, 696.

References:


