Supporting Information

**Metal-Free Direct C–H Cyanation of Alkenes**

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anie_201807303_sm_misellaneous_information.pdf
# Supporting information

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1. General

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in pre-heated glassware under an argon atmosphere using standard Schlenk techniques. THF was freshly distilled from K under argon. All other solvents and reagents were purified according to standard procedures or were used as received from Alfa Aesar, TCI, Aldrich, Fluka, Acros or ABCR. The alkenes were synthesized according to literature procedures. IR spectra were recorded on a Digilab FTS 4000 with a Specac MKII Golden Gate Single Reflection ART System. $^1$H NMR and $^{13}$C NMR spectra were recorded on a DPX 300, AV 400 or DD2 600 at 300 K. Spectra were calibrated relative to solvent’s residual proton and carbon chemical shift: CHCl$_3$ ($\delta = 7.26$ for $^1$H NMR and $\delta = 77.0$ for 13C NMR). TLC was performed using Merck silica gel 60 F-254 plates, detection of compounds with UV light or dipping into a solution of KMnO$_4$ (1.5 g in 400 mL H$_2$O, 5 g NaHCO$_3$), followed by heating. Flash column chromatography (FC) was performed using Merck or Fluka silica gel 60 (40-63 µm) applying a pressure of about 0.2 bar. Mass spectra were recorded on a Finnigan MAT 4200S, a Bruker Daltonics Micro Tof, a Waters-Micromass Quatro LCZ (ESI); peaks are given in m/z (% of basis peak).

2. Preparation of starting materials

Cyanation reagents 2a, 2c, 2d, 2i, 2j, 2k, 2l, 2m, 2n and iodine(III) compounds 3f are commercially available from Sigma-Aldrich and were used as received. Cyanation reagents 2b,$^{[1]}$ 2e,$^{[2]}$ 2f,$^{[3]}$ and iodine(III) compounds 2g,$^{[3]}$ 2h,$^{[3]}$ 3d,$^{[4]}$ 3e$^{[1]}$ were prepared according to the previously reported literature procedures.
Alkenes 1a, 1b, 1e, 1h, 1i, 1s, 1u, 1y are commercially available from Alfa Aesar. All commercially available alkynes were used as received. Alkenes 1c, 1d, 1f, 1g, 1j, 1k, 1l, 1n, 1p, 1q, 1t, 1v, 1w, 1x, 1z, 1aa, 1ab were prepared according to a previously reported literature procedure. Alkenes 1m, 1r were prepared according to the following procedure.
Procedure for preparation of 3-(prop-1-en-2-yl)phenyl benzoate 1m

A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with methyltriphenylphosphonium bromide (4.29 g, 12.0 mmol, 2.0 eq.) sealed with a
septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before dry THF (20 mL) was added. Potassium tert-butoxide (1.34 g, 12.0 mmol, 2.0 eq.) was added to the suspension under a flow of argon at 0 °C (ice bath) and a bright yellow color was observed. The mixture was stirred at 0 °C for 30 min. 3-Acetylphenyl benzoate (1.44 g, 6.00 mmol, 1.0 eq.) was added subsequently. The reaction mixture was stirred at 0 °C for 3 h then allowed to warm up to room temperature. The stirring was continued for additional 15 h. After the reaction was complete, the reaction mixture was diluted with Et₂O (30 mL) and filtrated through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by silica gel column chromatography (pentane:EtOAc = 100:1) to give the corresponding pure product 3-(prop-1-en-2-yl) phenyl benzoate 1m as a colorless oil in 63% yield (0.898 g). **TLC** *R*₂ = 0.5 (pentane:EtOAc = 20:1); **¹H NMR** (300 MHz, CDCl₃, 300 K): δ (ppm) = 8.13 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.28 (m, 2H), 7.22 – 7.21 (m, 1H), 7.07 – 7.02 (m, 1H), 5.32 (s, 1H), 5.04 – 5.03 (m, 1H), 2.07 (s, 3H); **¹³C NMR** (75 MHz, CDCl₃, 300 K): δ (ppm) = 165.16, 150.99, 142.98, 142.35, 133.53, 130.14, 129.61, 129.13, 128.53, 123.02, 120.59, 118.84, 113.29, 21.70; **HRMS** (ESI) *m/z* = 261.0886 calcd. for C₁₆H₁₄O₂Na [M+Na]⁺, found: 261.0886; **IR** (neat, cm⁻¹): 3067, 2974, 1733, 1630, 1602, 1577, 1491, 1451, 1434, 1375, 1314, 1247, 1191, 1177, 1112, 1080, 1062, 1025, 1001, 944, 888, 786, 704, 685, 600, 579.

Procedure for the preparation of 1-(tert-butyl)-4-(4-methyl-3-methylenepent-1-yn-1-yl)benzene 1r

\[
\begin{align*}
&\text{Cl} & \text{Pd}((\text{Ph}_3\text{P})_2\text{Cl})_2 & \text{CuI} \quad (\text{1 mol\%}) \quad (\text{3 mol\%}) \\
&\text{i-Pr} & \text{Et}_3\text{N/THF} = 1.2, \text{rt.} & \text{Pd}((\text{Ph}_3\text{P})_2\text{Cl})_2 & \text{CuI} \quad (\text{3 mol\%}) \\
&\text{t-Bu} & \text{THF} = 1.2, \text{rt.} & \text{Pd}((\text{Ph}_3\text{P})_2\text{Cl})_2 & \text{CuI} \quad (\text{3 mol\%}) \\
&\text{H} & \text{KoF-Bu (2.0 eq.)} & \text{MePPPh}_3 \quad \text{THF, 0 °C then rt.} & \text{KoF-Bu (2.0 eq.)} & \text{THF, 0 °C then rt.} \\
&\text{Bu} & \text{Bu} \quad \text{Bu} & \text{Bu} & \text{Bu} & \text{Bu}
\end{align*}
\]
A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with bis(triphenylphosphine)palladium(II) dichloride (70.2 mg, 0.100 mmol, 1 mol%), copper(I) iodide (56.9 mg, 0.300 mmol, 3 mol%), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before triethylamine (10 mL) and THF (20 mL) was added. 4-tert-Butylphenylacetylene (1.58 g, 10.0 mmol, 1.0 eq.) and isobutyryl chloride (1.06 g, 15.0 mmol, 1.5 eq.) were added to the resulting suspension subsequently. The reaction mixture was then stirred at room temperature for 24 hours. After the reaction was complete, the reaction mixture was filtrated through a small pad of silica gel (pentane:EtOAc = 20:1). The solvent was removed under reduced pressure with the aid of a rotary evaporator to give the crude product ketone, which was used without any further purification for the next step.

A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with methyltriphenylphosphonium bromide (3.73 g, 10.4 mmol, 2.0 eq.) sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before dry THF (20 mL) was added. Potassium tert-butoxide (1.17 g, 10.4 mmol, 2.0 eq.) was added to the suspension at 0 °C (ice bath) and a bright yellow color was observed. The mixture was stirred at 0 °C for 30 min. The crude product ketone (1.19 g, 1.0 eq.) in THF (10 mL) was added subsequently. The reaction mixture was stirred at 0 °C for 3 h then allowed to warm up to room temperature. The stirring was continued for additional 15 h. After the reaction was complete, the reaction mixture was diluted with Et₂O (30 mL) and filtrated through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporation and the crude residue was purified by silica gel column chromatography (pentane) to give the corresponding pure product 1-(tert-butyl)-4-(4-methyl-3-methylenepent-1-yn-1-yl)benzene 1r as a colorless oil in 45% yield. TLC Rᵢ = 0.70 (pentane); ¹H NMR (300 MHz, CDCl₃, 300 K): δ (ppm) = 7.37 – 7.30 (m, 2H), 7.29 – 7.23 (m, 2H), 5.28 (d, J = 1.7 Hz, 1H), 5.21 (dd, J₁ = 1.8 Hz, J₂ = 1.1 Hz, 1H), 2.43 (hept, J = 6.7 Hz, 1H), 1.24 (s, 9H), 1.09 (d, J = 6.8 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃, 300 K): δ (ppm) = 151.29, 138.45, 131.30, 125.24,
HRMS (ESI) m/z = 333.07670 calcd. for C17H22Ag [M+Ag]+, found: 333.07738; IR (neat, cm⁻¹): 2962m, 2934w, 2905w, 2871w, 1602w, 1502w, 1465w, 1394w, 1363w, 1268w, 1203w, 1149w, 1107w, 1063w, 1018w, 895m, 833s, 734m.

3. Metal-free direct C-H cyanation of alkenes

General procedure for C-H cyanation of alkenes (GP)

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl)benzene 3d (170 mg, 0.300 mmol, 1.5 eq.), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (2 mL) was added. Trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.) was added under a flow of argon. The trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.) was added under a flow of argon subsequently after a slight yellow solution was formed (appr. 1 min) and a white suspension resulted. Then the corresponding alkene 1 (0.200 mmol, 1.0 eq.) was added under a flow of argon and the reaction mixture was stirred at 40 °C or 70 °C for 15 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography or PTCL (preparative TLC) to afford pure cyanated product 4.

Scale-up experiment
A flame-dried 250 mL Schlenk-flask equipped with a magnetic stir bar was charged with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl)benzene 3d (8.49 g, 15.0 mmol, 1.5 eq.), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (100 mL) was added. Trimethylsilyl trifluoromethanesulfonate (3.33 g, 15.0 mmol, 1.5 eq.) was slowly added at 0 °C (ice bath). The trimethylsilyl cyanide 2k (5.46 g, 55.0 mmol, 5.5 eq.) was added subsequently at room temperature after a slight yellow solution was formed (appr. 3 min) and a white suspension resulted. Then 1,1-diphenylethylene 1a (1.80 g, 10.0 mmol, 1.0 eq.) was added and the reaction mixture was stirred at 40 °C for 30 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography to afford 3,3-diphenylacrylonitrile 4a as a slight yellow oil in 91% yield (1.87 g).

**Screening of reaction conditions**
| entry<sup>a</sup> | 2 “CN” source | oxidant (eq.) | promoter (eq.) | temp(°C) | yield(%)<sup>b</sup> |
|-----------------|----------------|---------------|---------------|----------|------------------|
| 1               | 2a (2.0)      | none          | none          | 70       | NP.              |
| 2               | 2b (2.0)      | none          | AuCl₃ (0.05)  | 70       | NP.              |
| 3               | 2c (2.0)      | none          | CuCl (0.1)    | 70       | NP.              |
| 4               | 2d (2.0)      | none          | BF₃ Et₂O (2.0)| 70       | NP.              |
| 5               | 2e (2.0)      | none          | none          | 70       | NP.              |
| 6               | 2f (2.0)      | none          | none          | 70       | NP.              |
| 7               | 2g (2.0)      | none          | CuCl (0.1)    | 70       | trace            |
| 8               | 2h (2.0)      | none          | Fe(OAc)₂ (0.1)| 70       | trace            |
| 9               | 2i (2.0)      | none          | Fe(OAc)₂ (0.1)| 70       | trace            |
| 10              | 2j (2.0)      | none          | none          | 70       | trace            |
| 11              | 2k (2.0)      | 3a (2.0)      | none          | 70       | NP.              |
| 12              | 2k (2.0)      | 3b (2.0)      | none          | 70       | NP.              |
| 13              | 2k (2.0)      | 3c (2.0)      | none          | 70       | NP.              |
| 14              | 2k (4.0)      | 2e (1.5)      | none          | 70       | 7                |
| 15              | 2k (4.0)      | 2f (1.5)      | none          | 70       | 32               |
| 16              | 2k (4.0)      | 2g (1.5)      | none          | 70       | 44               |
| 17              | 2k (4.0)      | 2h (1.5)      | none          | 70       | 87               |
| 18              | 2k (5.5)      | 3d (1.5)      | TMSOTf (1.5)  | 70       | 88               |
| 19              | 2k (5.5)      | 3d (1.5)      | TMSOTf (1.5)  | 40       | 90<sup>c</sup>   |
| 20              | 2k (5.5)      | 3d (1.5)      | TMSOTf (1.5)  | rt.      | 14               |
| 21              | 2k (5.5)      | 3e (1.5)      | TMSOTf (1.5)  | 40       | 34               |
| 22              | 2k (2.0)      | 3d (1.5)      | TMSOTf (1.5)  | 40       | 27               |
| 23              | 2k (3.0)      | 3d (1.5)      | TMSOTf (1.5)  | 40       | 81               |
| 24              | 2k (4.0)      | 3d (1.5)      | TMSOTf (1.5)  | 40       | 85               |
| 25              | NaCN (5.5)    | 3d (1.5)      | TMSOTf (1.5)  | 40       | NP.              |
| 26              | KCN (5.5)     | 3d (1.5)      | TMSOTf (1.5)  | 40       | NP.              |
| 27              | Bu₄NCN (5.5)  | 3d (1.5)      | TMSOTf (1.5)  | 40       | NP.              |

<sup>a</sup>Reaction condition: 1a (0.20 mmol, 1.0 equiv), 2, 3, 4, DCM (2 mL), 15 h. <sup>b</sup>Yield determined by ¹H NMR analysis using MeNO₂ as an internal standard. <sup>c</sup>Isolated in 87% yield.

“CN” sources and oxidants tested

![CN sources and oxidants tested](image)

General procedure for entries 1-10
A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with “CN” source 2 (0.40 mmol, 2.0 eq.), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (2 mL) was added. The promoter (if mentioned in the reaction conditions screening table) was added under a flow of argon. After 1 min, 1,1-diphenylethylene 1a (36.1 mg, 0.200 mmol, 1.0 eq.) was added under a flow of argon and the reaction mixture was then stirred at 70 °C for 15 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The yield of desired product 3,3-diphenylacrylonitrile 4a was determined by GC-MS and \(^1\)H NMR analysis using MeNO$_2$ as internal standard.

**General procedure for entries 11, 12, 14-17**

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with oxidant 3a-b, 2e-f, 2g-h, sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (2 mL) was added. The trimethylsilyl cyanide 2k was added subsequently at room temperature under a flow of argon. After 1 min, 1,1-diphenylethylene 1a (36.1 mg, 0.200 mmol, 1.0 eq.) was added under a flow of argon and the reaction mixture was then stirred at 70 °C for 15 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The yield of desired product 3,3-diphenylacrylonitrile 4a was determined by \(^1\)H NMR analysis using MeNO$_2$ as internal standard.

**Procedure for entry 13**

A flame-dried Schlenk-tube equipped with a magnetic stir bar was sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (2 mL) was added. The tert-butyl hydroperoxide 3e (51.4 mg, 0.400 mmol, 2.0 eq., 70% in H$_2$O) and trimethylsilyl cyanide 2k (39.6 mg, 0.400 mmol, 2.0 eq.) were added under a flow of argon successively. Then 1,1-diphenylethylene 1a (36.1 mg, 0.200 mmol, 1.0 eq.) was added under a flow of argon and the reaction mixture was then stirred at the indicated temperature for 15 h.
After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The yield of the desired product 3,3-diphenylacrylonitrile 4a was determined by $^1$H NMR analysis using MeNO$_2$ as internal standard.

**General procedure for entries 18-21**

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with 3f-g (0.300 mmol, 1.5 eq.), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (2 mL) was added. Trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.) was added under a flow of argon. The trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.) was added under a flow of argon subsequently. Then 1,1-diphenylethylene 1a (36.1 mg, 0.200 mmol, 1.0 eq.) was added under a flow of argon and the reaction mixture was then stirred at the indicated temperature for 15 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The yield of the desired product 3,3-diphenylacrylonitrile 4a was determined by $^1$H NMR analysis using MeNO$_2$ as internal standard.

**General procedure for entries 22-24**

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with 3d (0.300 mmol, 1.5 eq.), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (2 mL) was added. Trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.) was added under a flow of argon. The indicated amount of trimethylsilyl cyanide 2k was added under a flow of argon subsequently. Then 1,1-diphenylethylene 1a (36.1 mg, 0.200 mmol, 1.0 eq.) was added under a flow of argon and the reaction mixture was then stirred at 40 °C for 15 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The yield of the desired product 3,3-diphenylacrylonitrile 4a was determined by $^1$H NMR analysis using MeNO$_2$ as internal standard.

**General procedure for entries 25-27**
A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with 3d (0.300 mmol, 1.5 eq.), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (2 mL) was added. Trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.) was added under a flow of argon. The CN source (sodium cyanide, or potassium cyanide, or tetrabutylammonium cyanide) was added under a flow of argon subsequently. Then 1,1-diphenylethylene 1a (36.1 mg, 0.200 mmol, 1.0 eq.) was added under a flow of argon and the reaction mixture was then stirred at 40 °C for 15 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. No desired product 3,3-diphenylacrylonitrile 4a was detected by TLC and GC-MS analysis.

4. \( E \rightarrow Z \) isomerization

According to a modified literature procedure\(^{[22]}\), a flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with the \( \alpha,\beta \)-unsaturated nitrile 4p (\( Z:E = 1.2:1 \), 36.2 mg 0.17 mmol, 1.0 eq.), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before MeCN (3 mL) was added. (−)-Riboflavin (3.3 mg, 8.5 \( \mu \)mol, 5 mol%) was added under a flow of argon. The reaction mixture was stirred for 60 h under 402 nm UV light irradiation. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The \( Z/E \)-isomer ratio (17:1) was determined by analysis of the \(^1\)H NMR spectra of crude residue. The crude residue was purified by PTLC (pentane:EtOAc = 20:1) to afford the desired product 2-(6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ylidene)acetonitrile 4p as a colorless oil in 70% yield (25.3 mg, \( Z:E = 17:1 \)).
According to a modified literature procedure[22], a flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with the α,β-unsaturated nitrile 4q (E:Z > 20:1, 18.3 mg 0.10 mmol, 1.0 eq.), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before MeCN (3 mL) was added. (−)-Riboflavin (1.9 mg, 5.0 μmol, 5 mol%) was added under a flow of argon. The reaction mixture was stirred for 18 h under 402 nm UV light irradiation. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The Z/E-isomer ratio (20:1) was determined by analysis of the \(^1\)H NMR spectra of crude residue. The crude residue was purified by PTLC (pentane:EtOAc = 20:1) to afford the desired product (Z)-2-(6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ylidene)acetonitrile \(Z\-4q\) as a colorless oil in quantitative yield (18.3 mg, Z:E = 20:1).

5. Mechanistic studies

5.1 Radical clock probe experiment

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl)benzene \(3d\) (170 mg, 0.300 mmol, 1.5 eq.), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (2 mL) was added. Trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.) was added under a flow of argon. The trimethylsilyl cyanide \(2k\) (109 mg, 1.10 mmol, 5.5 eq.) was added under a
flow of argon subsequently after a slight yellow solution was formed (appr. 1 min) and a white suspension resulted. Then (1-cyclopropylvinyl)benzene 1ab (28.8 mg, 0.200 mmol, 1.0 eq.) was added under a flow of argon and the reaction mixture was then stirred at 70 °C for 15 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The normal cyanated product 4ab\textsuperscript{[22, 23]} was formed in 36% \((E:Z = 2:1)\) by \(^1\)H NMR analysis of the crude residue using MeNO\(_2\) as internal standard, whereas the ring-opening product 5 was not detected in the \(^1\)H NMR spectrum of the crude residue.

5.2 Control experiment

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl)benzene 3d (170 mg, 0.300 mmol, 1.5 eq.), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (2 mL) was added. The trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.) was added under a flow of argon subsequently. Then 1,1-diphenylethylene 1a (36.1 mg, 0.200 mmol, 1.0 eq.) was added successively under a flow of argon and the reaction mixture was stirred at 40 °C for 15 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. No desired product 3,3-diphenylacrylonitrile 4a was detected by TLC, GC-MS and \(^1\)H NMR analysis.
A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate 2h (154 mg, 0.300 mmol, 1.5 eq.), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (2 mL) was added. The trimethylsilyl cyanide 2k (79.2 mg, 0.800 mmol, 4.0 eq.) was added under a flow of argon subsequently. Then 1,1-diphenylethylene 1a (36.1 mg, 0.200 mmol, 1.0 eq.) was added successively under a flow of argon and the reaction mixture was stirred at 40 °C for 15 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography to afford 3,3-diphenylacrylonitrile 4a as a slight yellow oil in 87% yield.

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate 2h (154 mg, 0.300 mmol, 1.5 eq.), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (2 mL) was added. 1,1-Diphenylethylene 1a (36.1 mg, 0.200 mmol, 1.0 eq.) was added successively under a flow of argon and the reaction mixture was then stirred at 40 °C for 15 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. No desired product 3,3-diphenylacrylonitrile 4a was detected and the starting material 1,1-diphenylethylene 1a was fully decomposed based on TLC, GC-MS and ¹H NMR analysis.
A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate 2h (154 mg, 0.300 mmol, 1.5 eq.), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (2 mL) was added. Sodium cyanide 2l (19.6 mg, 0.800 mmol, 4.0 eq.), or potassium cyanide 2m (26.0 mg, 0.800 mmol, 4.0 eq) or tetrabutylammonium cyanide 2n (215 mg, 0.800 mmol, 4.0 eq.) was added subsequently at room temperature. Then 1,1-diphenylethylene 1a (1.80 g, 10.0 mmol, 1.0 eq.) was added and the reaction mixture was stirred at 40 °C for 15 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. No desired product 3,3-diphenylacrylonitrile 4a was detected by TLC and GC-MS analysis.

A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate 2h (154 mg, 0.300 mmol, 1.5 eq.), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (2 mL) was added. Chlorotrimethylsilane (86.4 mg, 0.800 mmol, 4.0 eq.) was added subsequently at room temperature. Then 1,1-diphenylethylene 1a (1.80 g, 10.0 mmol, 1.0 eq.) was added and the reaction mixture was stirred at 40 °C for 15 h. After the reaction was complete, the solvent
was removed under reduced pressure with the aid of a rotary evaporator. No desired product 3,3-diphenylacrylonitrile 4a was detected by TLC, GC-MS, and $^1$H NMR analysis. The crude residue was purified by silica gel column chromatography to afford (2-Chloroethene-1,1-diyl)dibenzene 6 in 34% yield as a slight yellow solid (14.6 mg). TLC $R_f = 0.75$ (pentane); $^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta$ (ppm) = 7.41 – 7.18 (m, 8H), 7.17 – 7.09 (m, 2H), 6.51 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta$ (ppm) = 143.88, 140.13, 137.58, 129.84, 128.41, 128.19, 128.05, 127.94, 127.70, 115.87.

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with diphenyliodonium triflate 3f (129 mg, 0.300 mmol, 1.5 eq.), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (2 mL) was added. The trimethylsilyl cyanide 2k (79.2 mg, 0.800 mmol, 4.0 eq.) was added under a flow of argon subsequently. After 1 min, 1,1-diphenylethylene 1a (36.1 mg, 0.200 mmol, 1.0 eq.) was added successively under a flow of argon and the reaction mixture was stirred at 40 °C for 15 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. No desired product 3,3-diphenylacrylonitrile 4a and ethene-1,1,2-triyltribenzene 7 was detected by TLC and GC-MS analysis of the crude residue.

5.3 Cyanation with isotopically labeled alkenes
A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl)benzene 3d (170 mg, 0.300 mmol, 1.5 eq.), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (2 mL) was added. Trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.) was added under a flow of argon. The trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.) was added under a flow of argon subsequently after a slight yellow solution was formed (appr. 1 min) and a white suspension resulted. Then 1,1-diphenylethylene 1a (1.80 g, 10.0 mmol, 1.0 eq.) and (ethene-1,1-diyl-2,2-d2)dibenzene 1a-D2 (36.4 mg, 0.200 mmol, 1.0 eq.) was added under a flow of argon simultaneously and the reaction mixture was stirred at 40 °C for 1 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The resulting ESI-MS of the crude reaction mixture indicated $k_{H}/k_{D} = 1.1$.

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl)benzene 3d (170 mg, 0.300 mmol, 1.5 eq.), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (2 mL) was added. Trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.) was added under a flow of argon. The trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.) was added under a flow of argon subsequently after a slight yellow solution was formed (appr. 1 min) and a white suspension resulted. Then (ethene-1,1-diyl-2-d) dibenzene 1a-D1 (36.2 mg, 0.200 mmol, 1.0 eq.) was added under a flow of argon successively and the reaction mixture was stirred at 40 °C for 15 h. After the reaction was complete, the
solvent was removed under reduced pressure with the aid of a rotary evaporator. The resulting ESI-MS of the crude reaction mixture indicated $k_H/k_D = 3.3$.

6. Spectral data

Spectral data of C-H cyanation products 4

3,3-Diphenylacrylonitrile (4a)[26]: The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl)benzene 3d (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), and trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), 1,1-diphenylethylene 1a (36.1 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 40 °C for 15 h. Purification via silica gel chromatography (pentane:EtOAc = 120:1) gave the desired product 3,3-diphenylacrylonitrile 4a as a slight yellow oil in 87% yield (35.7 mg). **TLC $R_f = 0.4$** (pentane:EtOAc = 20:1); $^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta$ (ppm) = 7.42 – 7.25 (m, 9H), 7.25 – 7.19 (m, 2H), 5.65 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta$ (ppm) = 163.08, 138.92, 137.04, 130.35, 129.97, 129.50, 128.61, 128.50, 128.41, 117.81, 94.88.

(E)-3-Phenylbut-2-enenitrile (4b)[27]: The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl)benzene 3d (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and prop-1-en-2-ylbenzene 1b (23.6 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 40 °C for 15 h. The reaction gave desired product (E)-3-phenylbut-2-enenitrile 4b in 78% NMR yield. $E/Z = 20:1$; (Because the desired product (E)-3-phenylbut-2-enenitrile 4b was volatile on a high vacuum line, the corresponding yield and $E/Z$ ratio of the alkene was based on $^1$H NMR analysis of the crude residue remaining after rotary evaporation with MeNO$_2$ as internal standard.). **TLC $R_f = 0.55$** (pentane:acetone =
$(E)$-3-[(1,1'-Biphenyl)-4-yl]but-2-enenitrile (4c): The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl)benzene 3d (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and 4-(prop-1-en-2-yl)-1,1'-biphenyl 1c (38.8 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 40 °C for 15 h. Purification via PTLC (pentane:acetone = 13:1) gave the desired product $(E)$-3-[(1,1'-biphenyl)-4-yl]but-2-enenitrile 4c as a white solid in 55% yield (24.4 mg). $E/Z > 20:1$; TLC $R_f$ = 0.25 (pentane:acetone = 20:1); MP: 110 °C; $^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta$ (ppm) = $\delta$ 7.58 – 7.51 (m, 4H), 7.49 – 7.46 (m, 2H), 7.42 – 7.37 (m, 2H), 7.34 – 7.28 (m, 1H), 5.61 (s, 1H), 2.44 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta$ (ppm) = 159.11, 143.14, 139.88, 136.98, 128.94, 127.97, 127.43, 127.04, 126.34, 117.65, 95.31, 20.10; HRMS (ESI) $m/z$ = 242.0940 calcd. for C$_{16}$H$_{13}$NNa [M+Na]$^+$, found: 242.0935; IR (neat, cm$^{-1}$): 2919 w, 2215 m, 1600 w, 1488 w, 1409 w, 1381 s, 1279 w, 1141 w, 1077 w, 1005 w, 919 w, 847 w, 813 m, 767 s, 722 w, 692 m.

$(E)$-3-4-((Triisopropylsilyl)ethynyl)phenyl)but-2-enenitrile (4d): The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl)benzene 3c (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and triisopropyl((4-(prop-1-en-2-yl)phenyl)ethynyl)silane 1d (59.6 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 70 °C for 15 h. Purification via silica gel chromatography (pentane:acetone = 200:1) gave the desired product $(E)$-3-4-((triisopropylsilyl)ethynyl)phenyl)but-2-enenitrile 4d as a slight yellow oil in
70% yield (45.1 mg). \(E/Z = 13:1\); **TLC** \(R_f = 0.6\) (pentane:acetone = 20:1); \(^1\)H NMR (300 MHz, CDCl\(_3\), 300 K): \(\delta\) (ppm) = 7.42 (d, \(J = 8.4\) Hz, 2H), 7.32 (d, \(J = 8.4\) Hz, 2H), 5.55 (q, \(J = 1.1\) Hz, 1H), 2.38 (d, \(J = 1.0\) Hz, 3H), 1.06 (br, 21H); \(^1\)C NMR (75 MHz, CDCl\(_3\), 300 K): \(\delta\) (ppm) = 158.69, 137.76, 132.34, 125.66, 125.57, 117.37, 106.07, 96.04, 93.57, 20.00, 18.63, 11.29; **HRMS** (ESI) \(m/z = 324.21420\) calcd. for \(C_{21}H_{30}NSi\) [M+H]+, found: 324.21406; **IR** (neat, cm\(^{-1}\)) : 2942 m, 2891 w, 2865 m, 2215 m, 2157 w, 1601 m, 1549 w, 1530 m, 1462 m, 1443 w, 1410 w, 1382 w, 1332 w, 1232 w, 1187 w, 1072 w, 1015 w, 996 w, 920 w, 882 s, 836 s, 813 s, 716 m, 676 s, 662 m, 647 m.

\[\text{(E)-3-(p-Tolyl)but-2-enenitrile (4e)}^{[28]}: \] The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxoy)iodo]-3,5-bis(trifluoromethyl)benzene 3d (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and 1-methyl-4-(prop-1-en-2-yl)benzene 1e (26.4 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 40 °C for 15 h. The reaction gave the desired product (E)-3-(p-tolyl)but-2-enenitrile 4e in 63% NMR yield. \(E/Z > 20:1\); (Because the desired product (E)-3-(p-tolyl)but-2-enenitrile 4e was volatile on a high vacuum line, the corresponding yield and \(E/Z\) ratio of the alkene was based on \(^1\)H NMR analysis of the crude residue remaining after rotary evaporation with MeNO\(_2\) as internal standard.) **TLC** \(R_f = 0.55\) (pentane:acetone = 10:1); \(^1\)H NMR (300 MHz, CDCl\(_3\), 300 K): \(\delta\) (ppm) = 7.28 (d, \(J = 8.3\) Hz, 2H), 7.12 (d, \(J = 8.0\) Hz, 2H), 5.50 (s, 1H), 2.36 (d, \(J = 1.0\) Hz, 3H), 2.29 (s, 3H); \(^1\)C NMR (75 MHz, CDCl\(_3\), 300 K): \(\delta\) (ppm) = 159.41, 140.58, 135.27, 129.43, 125.70, 117.74, 94.44, 21.17, 19.97.

\[\text{(E)-3-(4-(tert-Butyl)phenyl)but-2-enenitrile (4f)}^{[22]}: \] The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxoy)iodo]-3,5-bis(trifluoromethyl)benzene 3c (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5
eq.), and 1-(tert-butyl)-4-(prop-1-en-2-yl)benzene If (34.8 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 40 °C for 15 h. Purification via silica gel chromatography (pentane:acetone = 120:1) gave the desired product (E)-3-(4-(tert-butyl)phenyl)but-2-enenitrile 4f as a slight yellow solid in 71% yield (28.1 mg). E/Z = 17:1; TLC Rf = 0.45 (pentane:acetone = 20:1); MP: 97 °C; 1H NMR (300 MHz, CDCl3, 300 K): δ (ppm) = 7.34 (br, 4H), 5.53 (q, J = 1.1 Hz, 1H), 2.38 (d, J = 1.0 Hz, 3H), 1.25 (s, 9H); 13C NMR (75 MHz, CDCl3, 300 K): δ (ppm) = 159.41, 153.79, 135.25, 125.73, 125.61, 117.80, 94.57, 34.76, 31.11, 20.00.

(E)-4-(1-Cyanoprop-1-en-2-yl)phenyl benzoate (4g): The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl)benzene 3c (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and 4-(prop-1-en-2-yl)phenyl benzoate 1g (47.6 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 70 °C for 15 h. Purification via PTLC (pentane:acetone = 7:1) gave the desired product (E)-4-(1-cyanoprop-1-en-2-yl)phenyl benzoate 4g as a slight yellow solid in 69% yield (36.5 mg). E/Z = 12:1; TLC Rf = 0.6 (pentane:acetone = 7:1); MP: 97 °C; 1H NMR (300 MHz, CDCl3, 300 K): δ (ppm) = 8.13 (dd, J1 = 8.3 Hz, J2 = 1.4 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.47 (d, J = 8.4 Hz, 3H), 7.43 (s, 1H), 7.21 (d, J = 8.8 Hz, 2H), 5.56 (s, 1H), 2.42 (s, 3H); 13C NMR (75 MHz, CDCl3, 300 K): δ (ppm) = 164.84, 158.71, 152.47, 135.90, 133.86, 130.22, 129.13, 128.65, 127.17, 122.19, 117.42, 95.79, 20.25; HRMS (ESI) m/z = 286.0838 calcd. for C17H13NO2Na [M+Na]+, found: 286.0834; IR (neat, cm⁻¹): 3068w, 2927w, 2215w, 1728s, 1598w, 1512w, 1414w, 1313w, 1274s, 1222m, 1174m, 1087w, 1066m, 1025w, 879w, 807w, 707s, 681w.

(E)-3-(4-Fluorophenyl)but-2-enenitrile (4h): The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl)benzene 3d (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg,
0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and 1-fluoro-4-(prop-1-en-2-yl)benzene 1h (27.2 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 70 °C for 15 h. The reaction gave the desired product (E)-3-(4-fluorophenyl)but-2-enenitrile 4h in 60% NMR yield. E/Z = 13:1; (Because the desired product (E)-3-(4-fluorophenyl)but-2-enenitrile 4h was volatile on a high vacuum line, the corresponding yield and E/Z ratio of the alkene was based on 1H NMR analysis of the crude residue remaining after rotary evaporation with MeNO2 as internal standard.)

**TLC Rf** = 0.55 (pentane:acetone = 10:1). **1H NMR** (300 MHz, CDCl3, 300 K): δ (ppm) = 7.50 – 7.25 (m, 2H), 7.19 – 6.72 (m, 2H), 5.49 (q, J = 1.2 Hz, 1H), 2.37 (d, J = 1.0 Hz, 3H); **13C NMR** (75 MHz, CDCl3, 300 K): δ (ppm) = 163.79 (d, J = 251.2 Hz, 1C), 158.30, 134.25 (d, J = 3.5 Hz, 1C), 127.77 (d, J = 8.5 Hz), 117.30, 115.76 (d, J = 21.8 Hz, 1C), 95.40, 20.12.

![Structure of (E)-3-(4-Chlorophenyl)but-2-enenitrile](image)

**(E)-3-(4-Chlorophenyl)but-2-enenitrile (4i)**[21]: The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl) benzene 3c (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and 1-chloro-4-(prop-1-en-2-yl)benzene 1i (30.4 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 40 °C for 15 h. Purification via silica gel chromatography (pentane:acetone = 100:1) gave the desired product 1-chloro-4-(prop-1-en-2-yl)benzene 4i as a slight yellow oil in 55% yield (19.3 mg). E/Z = 13:1; **TLC Rf** = 0.55 (pentane:acetone = 10:1); **1H NMR** (300 MHz, CDCl3, 300 K): δ (ppm) = 7.35 – 7.28 (m, 4H), 5.53 (s, 1H), 2.38 (d, J = 1.0 Hz, 3H); **13C NMR** (75 MHz, CDCl3, 300 K): δ (ppm) = 158.34, 136.64, 136.41, 129.07, 127.15, 117.23, 96.10, 20.13.

![Structure of (E)-3-(4-Bromophenyl)but-2-enenitrile](image)

**(E)-3-(4-Bromophenyl)but-2-enenitrile (4j)**[28]: The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl) benzene 3c (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and
(E)-3-(4-bromophenyl)but-2-enenitrile 1j (39.2 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 70 °C for 15 h. Purification via PTLC (pentane:acetone = 13:1) gave the desired product (E)-3-(4-bromophenyl)but-2-enenitrile 4j as a slight yellow oil in 66% yield (29.3 mg). E/Z = 10:1; TLC Rf = 0.30 (pentane:acetone = 20:1); 1H NMR (300 MHz, CDCl3, 300 K): δ (ppm) = δ 7.46 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.6 Hz, 2H), 5.54 (s, 1H), 2.37 (s, 3H); 13C NMR (75 MHz, CDCl3, 300 K): δ (ppm) = 158.41, 137.10, 132.04, 127.35, 80.9, 124.67, 117.20, 96.15, 20.07.

(E)-3-(4-Iodophenyl)but-2-enenitrile (4k): The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl) benzene 3c (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and 1-iodo-4-(prop-1-en-2-yl)benzene 1k (48.8 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 70 °C for 15 h. Purification via silica gel chromatography (pentane:acetone = 100:1) gave the desired product (E)-3-(4-iodophenyl)but-2-enenitrile 4k as a slight yellow solid in 45% yield (24.4 mg). E/Z = 10:1; TLC Rf = 0.60 (pentane:acetone = 10:1); MP: 75 °C; 1H NMR (300 MHz, CDCl3, 300 K): δ (ppm) = 7.67 (d, J = 8.6 Hz, 2H), 7.11 (d, J = 8.5 Hz, 2H), 5.54 (s, 1H), 2.37 (s, 3H); 13C NMR (75 MHz, CDCl3, 300 K): δ (ppm) = 158.58, 138.03, 137.70, 127.45, 117.20, 96.53, 96.15, 19.99. HRMS (ESI) m/z = 291.9594 calcd. for C10H8INa [M+Na]+, found: 291.9591; IR (neat, cm⁻¹): 3056w, 2216m, 1604m, 1584w, 1484w, 1484w, 1441w, 1398w, 1228s, 1188w, 1084w, 1028s, 1004s, 920w, 846w, 809s, 641w.

Methyl (E)-4-(1-cyanoprop-1-en-2-yl)benzoate (4l)[29]: The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl) benzene 3c (340 mg, 0.600 mmol, 3.0 eq.), trimethylsilyl trifluoromethanesulfonate (133 mg, 0.600 mmol, 3.0 eq.), trimethylsilyl cyanide 2k (139 mg, 1.40 mmol, 7.0 eq.), and methyl 4-(prop-1-en-2-yl)benzoate 1l (35.2 mg, 0.200 mmol, 1.0 eq.) in DCE (4 mL) at 70 °C for 15 h. Purification via silica gel chromatography
(pentane:acetone = 100:1) gave the desired product methyl (E)-4-(1-cyanoprop-1-en-2-yl)benzoate 4l as a white solid in 40% yield (16.2 mg).  
$E/Z = 8:1$; 45% overall yield. **TLC** $R_f = 0.30$ (pentane:acetone = 10:1); **MP:** 103 °C; 
$^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta$ (ppm) = 7.99 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.3$ Hz, 2H), 5.62 – 5.61 (m, 1H), 3.87 (s, 3H), 2.42 (d, $J = 1.1$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta$ (ppm) = 166.20, 158.61, 142.38, 131.56, 130.01, 125.88, 117.00, 97.49, 52.31, 20.18.

**(E)-3-(1-Cyanoprop-1-en-2-yl)phenyl benzoate (4m):** The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl) benzene 3c (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and 3-(prop-1-en-2-yl)phenyl benzoate 1m (47.6 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 70 °C for 15 h. Purification via silica gel chromatography (pentane:acetone = 20:1) gave the desired product (E)-3-(1-cyanoprop-1-en-2-yl)phenyl benzoate 4m as a white solid in 44% yield (22.9 mg). $E/Z = 17:1$; **TLC** $R_f = 0.55$ (pentane:acetone = 5:1); **MP:** 89 °C; $^1$H NMR (300 MHz, CDCl$_3$, 300 K): $\delta$ (ppm) = 8.14 – 8.11 (m, 2H), 7.62 – 7.56 (m, 1H), 7.48 – 7.43 (m, 2H), 7.39 (d, $J = 7.9$ Hz, 1H), 7.30 (dt, $J^1 = 7.8$ Hz, $J^2 = 1.3$ Hz, 1H), 7.25 – 7.19 (m, 2H), 5.58 (q, $J = 1.0$ Hz, 1H), 2.40 (d, $J = 1.0$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): $\delta$ (ppm) = 164.97, 158.64, 151.27, 139.81, 133.84, 130.18, 129.90, 129.12, 128.65, 123.54, 123.31, 119.42, 117.21, 96.53, 20.18; **HRMS** (ESI) $m/z = 286.0838$ calcd. for C$_{17}$H$_{13}$NO$_2$Na [M+Na]$^+$, found: 286.0854; **IR** (neat, cm$^{-1}$): 3073w, 2923w, 2214m, 1734s, 1608w, 1580w, 1485w, 1450w, 1439w, 1318w, 1315w, 1247s, 1177s, 1080m, 1062s, 1025m, 1000w, 892w, 825w, 783w, 707s, 707s, 692w, 605w, 579w.

**(E)-3-(Naphthalen-2-yl)but-2-enenitrile (4n)$^{[28]}$:** The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl) benzene 3e
(170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and 2-(prop-1-en-2-yl)naphthalene 1n (33.6 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 40 °C for 15 h. Purification via silica gel chromatography (pentane:EtOAc = 20:1) gave the desired product (E)-3-(naphthalen-2-yl)but-2-enenitrile 4n as a slight yellow oil in 57% yield (22.1 mg). E/Z = 13:1; TLC Rf = 0.40 (pentane:EtOAc = 20:1); 1H NMR (300 MHz, CDCl3, 300 K): δ (ppm) = 7.87 (d, J = 1.9 Hz, 1H), 7.82 – 7.76 (m, 3H), 7.50 – 7.43 (m, 3H), 5.69 (s, 1H), 2.51 (d, J = 1.0 Hz, 3H).

(E)-3-Phenylhex-2-enenitrile (4o)[22]: The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl) benzene 3c (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and pent-1-en-2-ylbenzene 1o (29.2 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 40 °C for 15 h. Purification via silica gel chromatography (pentane:EtOAc = 120:1) gave the desired product (E)-3-phenylhex-2-enenitrile 4o as a slight yellow oil in 67% yield (21.0 mg). E/Z = 13:1; TLC Rf = 0.45 (pentane:EtOAc = 20:1); 1H NMR (300 MHz, CDCl3, 300 K): δ (ppm) = 7.33 (br, 5H), 5.44 (s, 1H), 2.96 – 2.62 (m, 2H), 1.44 (tq, J1 = 7.5 Hz, J2 = 7.5 Hz, 2H), 0.88 (t, J = 7.4 Hz, 1H); 13C NMR (75 MHz, CDCl3, 300 K): δ (ppm) = 164.92, 137.73, 129.96, 128.84, 126.28, 117.42, 95.88, 35.77, 21.73, 13.55.

3-Cyclohexyl-3-phenylacrylonitrile (4p, 4p’): The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl) benzene 3c (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and (1-cyclohexylvinyl)benzene 1p (37.2 mg, 0.200 mmol, 1.0 eq.) in DCE (2
mL) at 70 °C for 15 h. Purification via PTLC (pentane:EtOAc = 20:1) gave the desired product \((E)-2-(6,7,8,9$-tetrahydro-5H-benzo[7]annulen-5-ylidene)acetonitrile 4p\) as a colorless oil in 38% yield (16.2 mg). **TLC** \(R_f = 0.65\) (pentane:acetone = 20:1); **\(^1\)H NMR** (300 MHz, CDCl\(_3\), 300 K): \(\delta\) 7.33 – 7.25 (m, 3H), 7.16 – 7.12 (m, 2H), 5.17 (s, 1H), 2.86 (t, \(J^1 = 12.1\) Hz, \(J^2 = 3.0\) Hz, 1H), 1.77 – 1.03 (m, 10H; **\(^13\)C NMR** (75 MHz, CDCl\(_3\), 300 K): \(\delta\) (ppm) = 171.40, 139.55, 128.75, 128.23, 126.98, 116.85, 96.64, 45.32, 31.19, 26.27, 25.58; **HRMS** (ESI) \(m/z = 234.1253\) calcd. for \(C_{13}H_{17}\)NNa \([M+Na]^+\), found: 234.1248; **IR** (neat, cm\(^{-1}\)): 2929s, 2854m, 2216m, 1597w, 1574w, 1491w, 1450w, 1285w, 1138w, 1031w, 1000w, 921w, 892w, 847m, 760s, 700s, 644w. Purification via PTLC (pentane:EtOAc = 20:1) gave the desired product \((Z)-2-(6,7,8,9$-tetrahydro-5H-benzo[7]annulen-5-ylidene)acetonitrile 4p′\) as a colorless oil in 47% yield (20.0 mg). **TLC** \(R_f = 0.50\) (pentane:acetone = 20:1); **\(^1\)H NMR** (300 MHz, CDCl\(_3\), 300 K): \(\delta\) (ppm) = 7.38 – 7.31 (m, 3H), 7.28 – 7.22 (m, 3H), 5.24 (d, \(J = 1.3\) Hz, 1H), 2.37 (t, \(J = 11.1\) Hz, 1H), 1.76 – 1.61 (m, 5H), 1.29 – 1.00 (m, 5H); **\(^13\)C NMR** (75 MHz, CDCl\(_3\), 300 K): \(\delta\) (ppm) = 171.49, 138.38, 129.07, 128.51, 127.26, 117.69, 94.40, 45.66, 31.77, 26.28, 25.90; **HRMS** (ESI) \(m/z = 234.1253\) calcd. for \(C_{13}H_{17}\)NNa \([M+Na]^+\), found: 234.1248; **IR** (neat, cm\(^{-1}\)): 3062w, 2929s, 2854m, 2218m, 2186w, 2158w, 1613w, 1573w, 1496w, 1443m, 1345w, 976w, 918w, 895w, 817w, 773w, 701s. \(Z/E = 1.2:1\).
40:1); ¹H NMR (300 MHz, CDCl₃, 300 K): δ (ppm) = 7.23 – 7.25 (m, 4H), 5.26 (s, 1H), 2.71 (dt, $J^1 = 6.0$ Hz, $J^2 = 6.0$ Hz, 4H), 1.85 – 1.68 (m, 4H); ¹³C NMR (75 MHz, CDCl₃, 300 K): δ (ppm) = 168.94, 140.23, 139.74, 129.57, 129.36, 127.17, 126.56, 116.89, 96.73, 34.59, 33.62, 27.62, 26.55.

1-[(tert-Butyl)-4-(4-methyl-3-methylenepent-1-yn-1-yl)benzene (4r, 4r')]: The title compound was prepared according to general procedure (GP) with 1-[(bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl) benzene 3c (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and 1-[(tert-butyl)-4-(4-methyl-3-methylenepent-1-yn-1-yl)benzene 1r (45.2 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 70 °C for 15 h. Purification via PTLC (pentane:EtOAc = 20:1) gave the desired product (Z)-5-(4-(tert-butyl)phenyl)-3-isopropylpent-2-en-4-ynenitrile 4r as a slight yellow oil in 46% yield (23.2 mg). TLC Rᵣ = 0.40 (pentane:EtOAc = 20:1); ¹H NMR (300 MHz, CDCl₃, 300 K): δ (ppm) = δ 7.42 (d, $J = 8.6$ Hz, 2H), 7.31 (d, $J = 8.6$ Hz, 2H), 5.38 (d, $J = 1.0$ Hz, 1H), 2.54 (m, 1H), 1.25 (s, 9H), 1.13 (d, $J = 6.7$ Hz, 6H); ¹³C NMR (75 MHz, CDCl₃, 300 K): δ (ppm) = 153.32, 153.18, 132.04, 125.48, 118.69, 117.05, 102.03, 100.12, 84.54, 36.05, 34.92, 31.09, 21.28; HRMS (ESI/FTMS) $m/z = 274.1566$ calcd. for C₁₈H₂₁NaNa [M+Na]+, found: 274.1568; IR (neat, cm⁻¹): 2968s, 2908w, 2871w, 2218m, 2193m, 1581m, 1505m, 1464m, 1365m, 1279m, 1177w, 1139w, 1108w, 1074w, 1037w, 894w, 836s, 805w, 563m. Purification via PTLC (pentane:EtOAc = 20:1) gave the desired product (E)-5-(4-(tert-butyl)phenyl)-3-isopropylpent-2-en-4-ynenitrile 4r' as a slight yellow solid in 25% yield (12.5 mg). TLC Rᵣ = 0.70 (pentane:EtOAc = 20:1), MP: 58 °C; ¹H NMR (300 MHz, CDCl₃, 300 K): δ (ppm) = δ 7.37 – 7.28 (m, 4H), 5.41 (s, 1H), 3.12 (m, 1H), 1.25 (s, 9H), 1.15 (d, $J = 6.7$ Hz, 6H); ¹³C NMR (75 MHz, CDCl₃, 300 K): δ (ppm) = 153.92, 153.21, 131.79, 125.57, 118.64, 116.24, 100.41, 84.89, 34.95, 34.21, 31.09, 21.29; HRMS (ESI/FTMS) $m/z = 274.15662$ calcd. for C₁₈H₂₁NaNa [M+Na]+, found: 274.15641; IR (neat, cm⁻¹): 2967s, 2932w, 2907w,
1H-Indene-2-carbonitrile (4s): The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl) benzene 3c (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and 1H-indene 1s (25.8 mg, 0.200 mmol, 1.0 eq. purity = 90%) in DCE (2 mL) at 40 °C for 15 h. Purification via PTLC (pentane:acetone = 10:1) gave the desired product 1H-Indene-2-carbonitrile 4s as a slight yellow oil in 60% yield (17.0 mg). TLC Rf = 0.50 (pentane:acetone = 10:1); 1H NMR (300 MHz, CDCl3, 300 K): δ (ppm) = 7.53 (d, J = 2.1 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.35 – 7.27 (m, 2H), 3.61 (d, J = 2.0 Hz, 2H); 13C NMR (75 MHz, CDCl3, 300 K): δ (ppm) = 146.14, 143.09, 141.41, 128.35, 127.46, 124.08, 123.24, 117.00, 114.24, 40.91.

(Z)-3-(4-(tert-Butyl)phenyl)-2-methylacrylonitrile (4t): The title compound was prepared according to general procedure (GP) with (3,5-bis(trifluoromethyl)phenyl)(cyano)-13-iodanyl trifluoromethanesulfonate 3e (154 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (29.7 mg, 0.30 mmol, 1.5 eq.), and (E)-1-(tert-butyl)-4-(prop-1-en-1-yl)benzene 1t (34.8 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 70 °C for 15 h. Purification via silica gel chromatography (pentane:acetone = 150:1) gave the desired product (Z)-3-(4-(tert-butyl)phenyl)-2-methylacrylonitrile 4t as a slight yellow oil in 53% yield (21.0 mg). Z/E = 8:1, 60% overall yield; TLC Rf = 0.50 (pentane:acetone = 20:1); 1H NMR (300 MHz, CDCl3, 300 K): δ (ppm) = 7.58 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 6.83 (s, 1H), 2.07 (d, J = 1.6 Hz, 3H), 1.25 (s, 9H); 13C NMR (75 MHz, CDCl3, 300 K): δ (ppm) = 153.25, 143.89, 131.09, 128.23, 125.71, 119.46, 104.97, 34.84, 31.13, 22.10; HRMS (ESI/FTMS) m/z = 222.1253 calcd. for C14H17NNa [M+Na]+, found: 222.1254; IR (neat, cm⁻¹): 2965s, 2928m, 2866w, 2210m, 1624w, 1607w, 1515w, 1459w, 1414w,
(Z)-2,3-diphenylacrylonitrile (4u): The title compound was prepared according to general procedure (GP) with (3,5-bis(trifluoromethyl)phenyl)(cyano)-13-iodanyl trifluoromethane sulfonate 3e (154 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (29.7 mg, 0.30 mmol, 1.5 eq.), and (E)-1,2-diphenylethene 1u (36.0 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 70 °C for 15 h. Purification via silica gel chromatography (pentane:EtOAc = 150:1) gave the desired product (Z)-2,3-diphenylacrylonitrile 4u as a slight yellow solid in 40% yield. Z/E = 4.3:1 (based on GC-MS analysis); 49% overall yield (20.0 mg); TLC Rf = 0.35 (pentane:EtOAc = 20:1); $^1$H NMR (300 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.81 (dd, $^J_1$ = 7.7 Hz, $^J_2$ = 1.9 Hz, 2H), 7.69 – 7.53 (m, 2H), 7.46 (s, 1H), 7.44 – 7.28 (m, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$, 300 K): δ (ppm) = 142.21, 134.41, 133.66, 130.49, 129.22, 129.16, 128.91, 125.95, 117.95, 111.64.

2-Methyl-3,3-diphenylacrylonitrile (4v): The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl) benzene 3e (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and prop-1-ene-1,1-diyl dibenzene 1v (38.8 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 40 °C for 15 h. Purification via silica gel chromatography (pentane:acetone = 100:1) gave the desired product 2-methyl-3,3-diphenylacrylonitrile 4v as a colorless oil in 79% yield (34.5 mg). TLC Rf = 0.45 (pentane:acetone = 10:1); $^1$H NMR (300 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.33 – 7.24 (m, 8H), 7.07 – 7.04 (m, 2H), 2.00 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$, 300 K): δ (ppm) = 157.15, 139.77, 138.63, 129.27, 129.12, 128.68, 128.36, 128.26, 120.49, 106.10, 19.42.
9-Methyl-6,7-dihydro-5H-benzo[7]annulene-8-carbonitrile (4w):
The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoracetoxyl)iodo]-3,5-bis(trifluoromethyl) benzene 3c (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and 9-methyl-6,7-dihydro-5H-benzo[7]annulene 1w (31.6 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 40 °C for 15 h. Purification via silica gel chromatography (pentane:acetone = 100:1) gave the desired product 9-methyl-6,7-dihydro-5H-benzo[7]annulene-8-carbonitrile 4w as a colorless oil in 33% yield (12.2 mg). TLC Rf = 0.60 (pentane:acetone = 20:1); 1H NMR (300 MHz, CDCl3, 300 K): δ (ppm) = 7.24 – 7.13 (m, 4H), 2.51 (t, J = 7.0 Hz, 2H), 2.35 (s, 3H), 2.14 (p, J = 6.7 Hz, 2H), 2.01 (t, J = 7.0 Hz, 2H); 13C NMR (75 MHz, CDCl3, 300 K): δ (ppm) = 154.55, 140.11, 139.23, 129.16, 128.97, 126.56, 126.49, 119.83, 109.02, 34.02, 31.53, 28.22, 22.17; HRMS (ESI/FTMS) m/z = 206.0940 calcd. for C13H13NNa [M+Na]+, found: 206.0946; IR (neat, cm⁻¹): 3069w, 2934s, 2859m, 2207s, 1735w, 1613w, 1458w, 1448m, 1380w, 1045w, 759w.

1-Methyl-3,4-dihyronaphthalene-2-carbonitrile (4x): The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoracetoxyl)iodo]-3,5-bis(trifluoromethyl) benzene 3c (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and 4-methyl-1,2-dihyronaphthalene 1x (28.8 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 40 °C for 15 h. Purification via silica gel chromatography (pentane:acetone = 100:1) gave the desired product 1-methyl-3,4-dihyronaphthalene-2-carbonitrile 4x as a brown oil in 90% yield (30.5 mg). TLC Rf = 0.60 (pentane:acetone = 20:1); 1H NMR (300 MHz, CDCl3, 300 K): δ (ppm) = 7.37 – 7.25 (m, 1H), 7.25 – 7.16 (m, 2H), 7.14 – 7.06 (m, 1H), 2.81 – 2.71 (m, 2H), 2.42 (tq, J1 = 8.3 Hz, J2 = 1.5 Hz, 2H), 2.32 (t, J = 1.8 Hz, 3H); 13C NMR (75 MHz, CDCl3, 300 K): δ (ppm) = 147.93, 136.26, 133.16, 129.65, 127.81, 126.95, 124.71, 119.46, 106.69, 27.32, 25.15, 18.24; HRMS
(ESI/FTMS) m/z = 170.09643 calcd. for C_{12}H_{12}N [M+H]^+; IR (neat, cm⁻¹): 3025w, 2984w, 2949w, 2897w, 2840w, 2203s, 1617w, 1567w, 1487w, 1445m, 1382w, 1303m, 1280w, 1234w, 1177w, 1129w, 1060w, 1020w, 761s, 728m, 636w.

(2Z,4E)-2,5-diphenylpenta-2,4-dienenitrile (4y): The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl)benzene 3c (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and (1E,3E)-1,4-diphenylbuta-1,3-diene 1y (41.3 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 70 ºC for 15 h. Purification via PTLC (pentane:EtOAc = 20:1) gave the desired product (2Z,4E)-2,5-diphenylpenta-2,4-dienenitrile 4y as a slight yellow solid in 40% yield (18.3 mg). TLC Rf = 0.35 (pentane:EtOAc = 20:1); major product/other isomers = 4:1; ¹H NMR (300 MHz, CDCl₃, 300 K): δ (ppm) = δ 7.59 – 7.52 (m, 2H), 7.47 (dd, J¹ = 8.0 Hz, J² = 1.7 Hz, 2H), 7.41 – 7.24 (m, 8H), 7.07 – 6.89 (m, 1H); ¹³C NMR (75 MHz, CDCl₃, 300 K): δ (ppm) = 141.55, 141.21, 135.77, 133.26, 129.53, 129.08, 129.04, 128.91, 127.51, 125.60, 125.16, 116.92, 113.20.

3-Vinyl-1H-indene-2-carbonitrile (4z): The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl)benzene 3c (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and 3-vinyl-1H-indene 1z (28.4 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 40 ºC for 15 h. Purification via silica gel chromatography (pentane:EtOAc = 100:1) gave the desired product 3-vinyl-1H-indene-2-carbonitrile 4z as a white solid in 51% yield (17.1 mg). TLC Rf = 0.40 (pentane:EtOAc = 20:1); MP: 67 ºC; ¹H NMR (300 MHz, CDCl₃, 300 K): δ (ppm) = 7.67 – 7.61 (m, 1H), 7.47 – 7.41 (m, 1H), 7.38 – 7.31 (m, 2H), 6.88 (dd, J¹ = 17.9 Hz, J² = 11.6 Hz, 1H), 6.22 (d, J = 17.9 Hz, 1H), 5.72 (d, J = 11.6 Hz, 1H), 3.63 (s, 2H); ¹³C NMR (75 MHz, CDCl₃, 300 K): δ (ppm) = 153.74, 143.18,
2-Phenylcyclohepta-1,3-diene-1-carbonitrile (4aa): The title compound was prepared according to general procedure (GP) with 1-[bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl) benzene 3c (170 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl trifluoromethanesulfonate (66.7 mg, 0.300 mmol, 1.5 eq.), trimethylsilyl cyanide 2k (109 mg, 1.10 mmol, 5.5 eq.), and 2-phenylcyclohepta-1,3-diene 1aa (34.0 mg, 0.200 mmol, 1.0 eq.) in DCE (2 mL) at 40 °C for 15 h. Purification via silica gel chromatography (pentane:EtOAc = 100:1) gave the desired product 2-phenylcyclohepta-1,3-diene-1-carbonitrile 4aa as a colorless oil in 32% yield (12.5 mg). TLC Rf = 0.35 (pentane:EtOAc = 20:1); \(^1\)H NMR (300 MHz, CDCl\(_3\), 300 K): \(\delta\) (ppm) = 7.50 – 7.23 (m, 5H), 6.30 (dt, \(J^1 = 11.3\) Hz, \(J^2 = 5.5\) Hz, 1H), 5.99 (dt, \(J^1 = 11.7\) Hz, \(J^2 = 1.7\) Hz, 1H), 2.51 – 2.47 (m, 2H), 2.35 – 2.29 (m, 2H), 2.13 – 2.05 (m, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\), 300 K): \(\delta\) (ppm) = 153.40, 140.86, 139.81, 129.23, 128.88, 128.43, 128.04, 120.90, 111.66, 32.68, 30.99, 30.42; HRMS (ESI) \(m/z\) = 218.0940 calcd. for C\(_{14}\)H\(_{13}\)NNa [M+Na]\(^+\), found: 218.0955; IR (neat, cm\(^{-1}\)): 3026w, 2931m, 2855w, 2200w, 1603w, 1583w, 1571w, 1493w, 1445m, 1420w, 1278w, 1179w, 1075w, 925w, 780s, 764s, 746s, 699s.
7. Spectra

Spectra of alkenes 1

$^1$H NMR Spectra of 3-(prop-1-en-2-yl)phenyl benzoate 1m

![3-(prop-1-en-2-yl)phenyl benzoate 1m H NMR Spectra](image1)

$^{13}$C NMR Spectra of 3-(prop-1-en-2-yl)phenyl benzoate 1m

![3-(prop-1-en-2-yl)phenyl benzoate 1m C NMR Spectra](image2)
\(^1\)H NMR Spectra of 1-(tert-butyl)-4-(4-methyl-3-methylenepent-1-yn-1-yl) benzene 1r

\(^{13}\)C NMR Spectra of 1-(tert-butyl)-4-(4-methyl-3-methylenepent-1-yn-1-yl) benzene 1r
$^1$H NMR Spectrum of 3,3-diphenylacrylonitrile 4a

$^{13}$C NMR Spectrum of 3,3-diphenylacrylonitrile 4a
$^1$H NMR Spectrum of the crude (E)-3-phenylbut-2-enenitrile 4b
$^1$H NMR Spectrum of (E)-3-phenylbut-2-enenitrile 4b

$^{13}$C NMR Spectrum of (E)-3-phenylbut-2-enenitrile 4b
$^1$H NMR Spectrum of (E)-3-([1,1'-biphenyl]-4-yl)but-2-enenitrile 4c

$^{13}$C NMR Spectrum of (E)-3-([1,1'-biphenyl]-4-yl)but-2-enenitrile 4c
$^1$H NMR Spectrum of the crude (E)-3-[[1,1'-biphenyl]-4-yl]but-2-enenitrile 4c
$^1$H NMR Spectrum of (E)-3-(4-((triisopropylsilyl)ethynyl)phenyl)but-2-enenitrile 4d

$^{13}$C NMR Spectrum of (E)-3-(4-((triisopropylsilyl)ethynyl)phenyl)but-2-enenitrile 4d
$^1$H NMR Spectra of the crude (E)-3-(4-((triisopropylsilyl)ethynyl)phenyl)but-2-enenitrile 4d
$^1$H NMR Spectrum of the crude ($E$)-3-($p$-tolyl)but-2-enenitrile 4e
$^1$H NMR Spectrum of (E)-3-(p-tolyl)but-2-enenitrile 4e

$^{13}$C NMR Spectrum of (E)-3-(p-tolyl)but-2-enenitrile 4e
$^1$H NMR Spectrum of (E)-3-(4-((tert-butyl)phenyl)but-2-enenitrile 4f

$^{13}$C NMR Spectrum of (E)-3-(4-((tert-butyl)phenyl)but-2-enenitrile 4f
$^1$H NMR Spectrum of the crude (E)-3-(4-(tert-butyl)phenyl)but-2-enenitrile 4f
$^1$H NMR Spectrum of (E)-4-(1-cyanoprop-1-en-2-yl)phenyl benzoate 4g

$^{13}$C NMR Spectrum of (E)-4-(1-cyanoprop-1-en-2-yl)phenyl benzoate 4g
$^1$H NMR Spectrum of the crude (E)-4-(1-cyanoprop-1-en-2-yl)phenyl benzoate 4g
$^1$H NMR Spectrum of the crude (E)-3-(4-fluorophenyl)but-2-enenitrile 4h
$^1$H NMR Spectrum of (E)-3-(4-fluorophenyl)but-2-enenitrile 4h

$^{13}$C NMR Spectrum of (E)-3-(4-fluorophenyl)but-2-enenitrile 4h
$^1$H NMR Spectrum of $(E)$-3-(4-chlorophenyl)but-2-enenitrile 4i

$^{13}$C NMR Spectrum of $(E)$-3-(4-chlorophenyl)but-2-enenitrile 4i
$^1$H NMR Spectrum of the crude (E)-3-(4-chlorophenyl)but-2-enenitrile 4i
$^1$H NMR Spectrum of (E)-3-(4-bromophenyl)but-2-enenitrile 4j

$^{13}$C NMR Spectrum of (E)-3-(4-bromophenyl)but-2-enenitrile 4j
$^1$H NMR Spectrum of the crude (E)-3-(4-bromophenyl)but-2-enenitrile 4j
$^1$H NMR Spectrum of (E)-3-(4-iodophenyl)but-2-enenitrile 4k

$^{13}$C NMR Spectrum of (E)-3-(4-iodophenyl)but-2-enenitrile 4k
$^1$H NMR Spectrum of the crude (E)-3-(4-iodophenyl)but-2-enenitrile 4k
\(^1\text{H NMR Spectrum of methyl (E)-4-(1-cyanoprop-1-en-2-yl)benzoate 4l}\)

\(^{13}\text{C NMR Spectrum of methyl (E)-4-(1-cyanoprop-1-en-2-yl)benzoate 4l}\)
$^1$H NMR Spectrum of the crude of methyl ($E$)-4-(1-cyanoprop-1-en-2-yl)benzoate
$^1$H NMR Spectrum of (E)-3-(1-cyanoprop-1-en-2-yl)phenyl benzoate 4m

$^{13}$C NMR Spectrum of (E)-3-(1-cyanoprop-1-en-2-yl)phenyl benzoate 4m
$^1$H NMR Spectrum of the crude (E)-3-(1-cyanoprop-1-en-2-yl)phenyl benzoate
4m
$^1$H NMR Spectrum of (E)-3-(naphthalen-2-yl)but-2-enenitrile 4n

$^{13}$C NMR Spectrum of (E)-3-(naphthalen-2-yl)but-2-enenitrile 4n
1D-NOESY Spectrum of (E)-3-(naphthalen-2-yl)but-2-enenitrile 4n

\[ \text{^1H NMR Spectrum of the crude (E)-3-(naphthalen-2-yl)but-2-enenitrile 4n} \]
$^1$H NMR Spectrum of the crude ($E$)-3-phenylhex-2-enenitrile 4o
$^1$H NMR Spectrum of (E)-3-phenylhex-2-enenitrile 4o

$^{13}$C NMR Spectrum of (E)-3-phenylhex-2-enenitrile 4o
^1H NMR Spectrum of (E)-2-(6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ylidene) acetonitrile 4p

^13C NMR Spectrum of (E)-2-(6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ylidene) acetonitrile 4p
1D-NOESY Spectrum of the crude \((E)-2-(6,7,8,9\text{-tetrahydro-5H-benzo}[7] \text{-annulen-5-ylidene})\) acetonitrile 4p

\[\text{1H NMR Spectrum of (Z)-2-(6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ylidene) acetonitrile 4p'}\]
$^{13}$C NMR Spectrum of (Z)-2-(6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ylidene) acetonitrile 4p'

1D-NOESY Spectrum of (Z)-2-(6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ylidene) acetonitrile 4p’
$^1$H NMR Spectrum of (E)-2-(6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ylidene) acetonitrile 4q

$^{13}$C NMR Spectrum of (E)-2-(6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ylidene) acetonitrile 4q
$^1$H NMR Spectrum of the crude (E)-2-(6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ylidene) acetonitrile 4q

1D-NOESY Spectrum of the crude (E)-2-(6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ylidene) acetonitrile 4q
\(^1\)H NMR Spectrum of (Z)-5-(4-(tert-butyl)phenyl)-3-isopropylpent-2-en-4-ynenitrile 4r

\(^{13}\)C NMR Spectrum of (Z)-5-(4-(tert-butyl)phenyl)-3-isopropylpent-2-en-4-ynenitrile 4r
$^1$H NMR Spectrum of (E)-5-(4-(tert-butyl)phenyl)-3-isopropylpent-2-en-4-ynenitrile 4r'

$^{13}$C NMR Spectrum of (E)-5-(4-(tert-butyl)phenyl)-3-isopropylpent-2-en-4-ynenitrile 4r'
\(^1\text{H NMR Spectrum of the crude 5-}(4\text{-}(\text{tert-butyl})\text{phenyl})\text{-}3\text{-isopropylpent-2-en-4-ynenitrile 4r, 4r'}\)
1D-NOESY Spectrum of \((Z)-5-(4-(\text{tert}-\text{butyl})\text{phenyl})-3\text{-isopropylpent-2-en-4-ynenitrile 4r}\)
$^1$H NMR Spectrum of 1H-Indene-2-carbonitrile 4s

$^{13}$C NMR Spectrum of 1H-Indene-2-carbonitrile 4s
$^1$H NMR Spectrum of (Z)-3-(4-(tert-butyl)phenyl)-2-methylacrylonitrile 4t

$^{13}$C NMR Spectrum of (Z)-3-(4-(tert-butyl)phenyl)-2-methylacrylonitrile 4t
$^1$H NMR Spectrum of the crude (Z)-3-(4-(tert-butyl)phenyl)-2-methylacrylonitrile 4t
1D-NOESY Spectrum of the crude (Z)-3-(4-((tert-butyl)phenyl)-2-methyl acrylonitrile 4t
$^{1}$H-NMR Spectrum of the crude (Z)-2,3-diphenylacrylonitrile 4u

$^{13}$C NMR Spectrum of the crude (Z)-2,3-diphenylacrylonitrile 4u
GC-MS Spectrum of the crude (Z)-2,3-diphenylacrylonitrile 4u
$^1$H NMR Spectrum of 2-methyl-3,3-diphenylacrylonitrile 4v

$^{13}$C NMR Spectrum of 2-methyl-3,3-diphenylacrylonitrile 4v
$^1$H NMR Spectrum of 1-methyl-3,4-dihydronaphthalene-2-carbonitrile 4w

$^{13}$C NMR Spectrum of 1-methyl-3,4-dihydronaphthalene-2-carbonitrile 4w
$^1$H NMR Spectrum of 9-methyl-6,7-dihydro-5H-benzo[7]annulene-8-carbonitrile 4x

$^{13}$C NMR Spectrum of 9-methyl-6,7-dihydro-5H-benzo[7]annulene-8-carbonitrile 4x
$^{1}H$ NMR Spectrum of (2Z,4E)-2,5-diphenylpenta-2,4-dienenitrile 4y

$^{13}$C NMR Spectrum of (2Z,4E)-2,5-diphenylpenta-2,4-dienenitrile 4y
$^1$H NMR Spectrum of 3-vinyl-1H-indene-2-carbonitrile 4z

$^{13}$C NMR Spectrum of 3-vinyl-1H-indene-2-carbonitrile 4z
$^1$H NMR Spectrum of 2-phenylcyclohepta-1,3-diene-1-carbonitrile 4aa

$^{13}$C NMR Spectrum of 2-phenylcyclohepta-1,3-diene-1-carbonitrile 4aa
$^1$H NMR Spectrum of the crude (Z)-2-(6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ylidene)acetonitrile 4p’ prepared by photocatalytic $E \rightarrow Z$ isomerization
$^1$H NMR Spectrum of the crude 3-cyclopropyl-3-phenylacrylonitrile 4y
$^1$H NMR Spectrum of (2-Chloroethene-1,1-diyl)dibenzene 6

$^{13}$C NMR Spectrum of (2-Chloroethene-1,1-diyl)dibenzene 6
The mass spectrum of KIE measurement experiment

The mass spectrum of the crude residue in intermolecular kinetic isotope effects measurement experiment

LabelChecker Results

Formula: C15 H12 N
Mass (monoisotopic): 206.10

Difference Value: 0.000070
Error Sum: 0.008
Error (%): 0.240
$^{1}H$ NMR Spectrum of the crude residue in intermolecular kinetic isotope effects measurement experiment

The mass spectrum of the crude residue in intramolecular kinetic isotope effects measurement experiment
LabelChecker Results

Formula: C15 H12 N
Mass (monoisotopic): 206.10

Difference Value: 0.000287
Error Sum: 0.17
Error (%): 0.512
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