Synthesis A. N. Baumann et al. Special Topic

One-Pot Preparation of Stable Organoboronate Reagents for the Functionalization of Unsaturated Four- and Five-Membered Carbo- and Heterocycles

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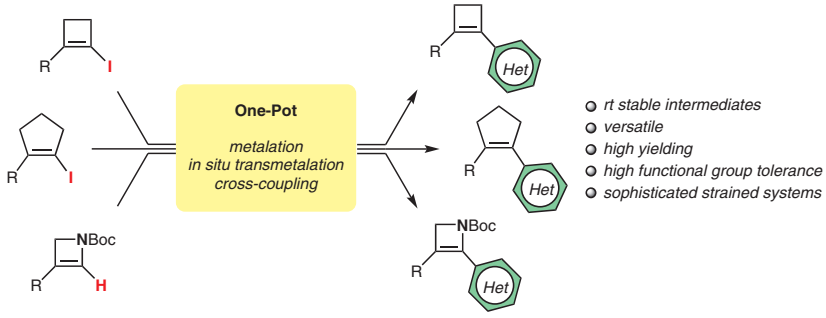

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Abstract Combining a facile preparation of organoboronates with their remarkable stability and functional group tolerance allows for the straightforward synthesis of four- and five-membered carbo- and heterocycles. While most strategies rely on the ex situ preparation of boronic acids as isolated intermediates, we demonstrate that in situ transmetalation of sensitive organometallics with boron alkoxides can lead to great stabilization of such species at room temperature. A considerable extension of the library of unsaturated strained structures is achieved through these sequences, expanding the potential applicability of such unusual building blocks.

Key words cyclobutenes, cyclopentenes, azetines, organoboronates, one-pot sequences

The transition-metal-catalyzed cross-couplings of organoboronic acids with organic halides, a process developed by Suzuki et al.,[1] has become one of the most powerful tools for the creation of C–C bonds.[2] Both simplicity and functional group tolerance have made it a privileged method[3] for assembling complex structures in many fields of chemistry such as drug discovery,[4] materials science,[5] chemosensors[6] and total synthesis.[7] Spurred on by the particular stability of organoboron species, we took on the challenge of generalizing the access to classes of molecules that have been scarcely reported: strained cyclobutenes, cyclopentenes and 2-azetines. Due to their commercial availability, organoboronic acids are employed as stable substrates for numerous cross-coupling reactions. For more elaborated scaffolds however, tailor-made boronic acids must be prepared ex situ in order to be engaged in a subsequent reaction through a two-step process. For the sake of step-economy, we needed to develop a more straightforward access to the targeted compounds, avoiding an extra purification of intermediate boronic acids. Taking into account the recent work of Buchwald and co-workers on direct cross-coupling of lithium organoboronates,[8] Miyaura et al. on base-free coupling of triolborates,[9] Cammidge on coupling of ex situ generated trihydroxyborates,[10] and Knochel's group on the in situ generation of magnesium bis-organoborinates,[11] we designed different strategies in which the cross-coupling reaction would be relayed by the in situ formation of a stable intermediate boron species. Our first objective was to demonstrate the long-term stability of such strained organoboron derivatives over time, opening the strategy to reagent storage; secondly, we aimed to explore the scope and limitations of the method to complete a large library of new building blocks, being hitherto difficult to access.

Cyclobutene and cyclopentene iodides **1a**,**b** were readily prepared from procedures originally described by Negishi et al. involving π-cyclization of *gem*-bismetalated alkenes,[12] which we recently applied to the synthesis of alkylidenecyclobutanes and fused four-membered rings.[13] Halogen–lithium exchanges on **1a** and **1b** were performed employing *n*-BuLi in diethyl ether at –78 °C (as THF led to further alkylation of the newly formed cycloalkenyllithium) and the corresponding cycloalkenyl-boronates **A** and **B** were generated by addition of $B(Oi\text{-}Pr)_3$ in THF (Scheme 1).

Azetinyllithium reagents were generated by α-lithiation of in situ formed azetines **2** using *s*-BuLi in the presence of TMEDA in THF at –78 °C,[14] and subsequently trapped with boron isopropoxide to give **C**.[15]

Organoboronates **A**, **B** and **C** were then stored either in solution or neat at –20 °C or room temperature before being engaged in Suzuki cross-couplings (Scheme 2).

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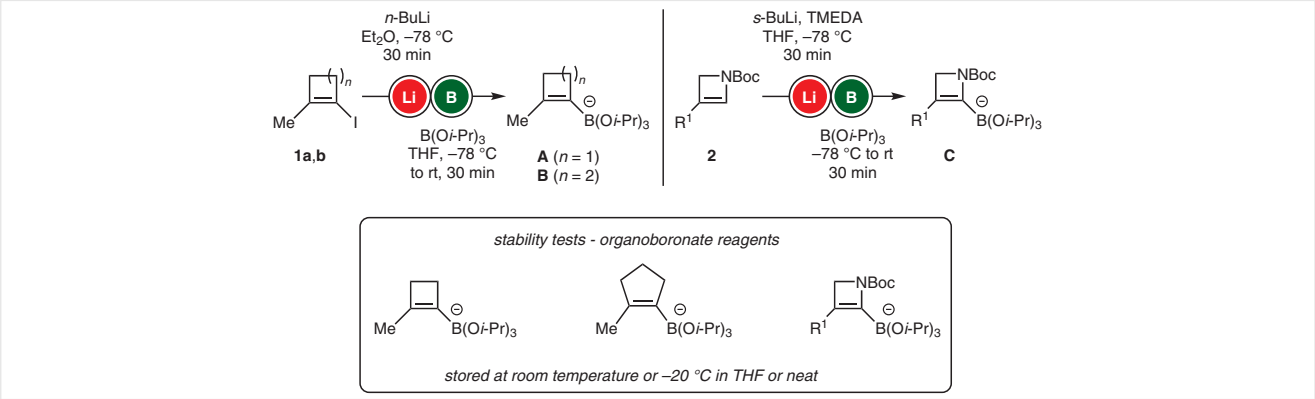
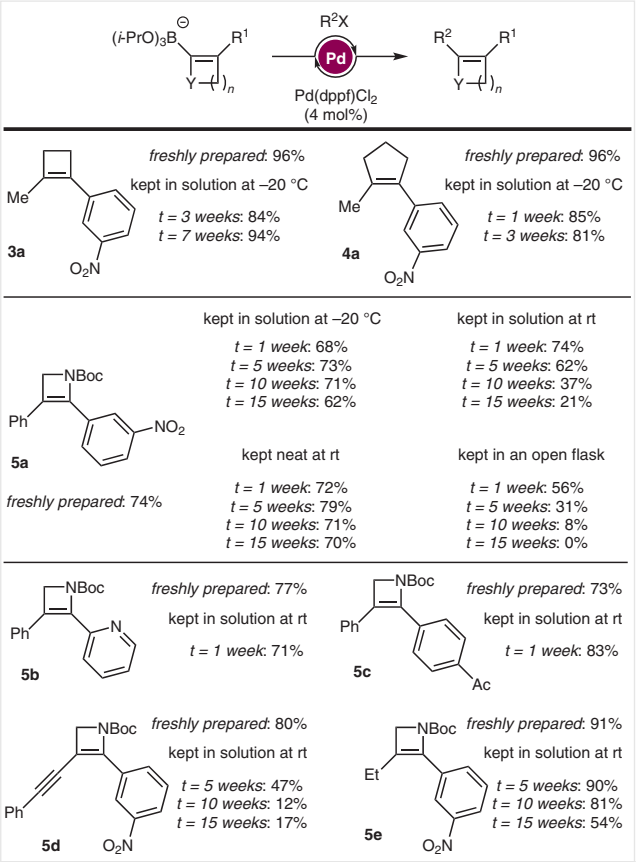


Scheme 1 Organoboronate synthesis through Li/I exchange–transmetalation or α-lithiation–transmetalation

Cyclobutenyl- and cyclopentenylboronates **A** and **B** were coupled with 1-iodo-3-nitrobenzene as a test partner. From freshly prepared solutions, both products **3a**[16] and **4a** were obtained in excellent yields (96%). Keeping solutions at –20 °C showed constancy in reactivity, delivering **3a** in 94% yield after seven weeks and **4a** (81%) after three weeks. Diverse conditions were evaluated for storage of azetinylboronates **C**. When kept in an open flask, the yields decreased drastically after only one week of storage, and a fast decrease in reactivity was also observed on storing **C** in solution at room temperature. However, reproducible results were obtained when the boronate salts were kept either in solution at –20 °C (as for **A** and **B**), or neat at room temperature. Products **5a** were isolated in constant, reasonable yields (up to 70% after fifteen weeks). Stock solutions of azetinylboronate reagents were prepared and further used in cross-coupling reactions after different storage times at room temperature. In some cases (**5b**, **5c** and **5e**), the salts gave reproducible yields after one or ten weeks of storage, showing the great potential of such reagents as building blocks. In some other cases (**5d**), the solution showed a rapid decrease of reactivity, furnishing only a 47% yield of the desired product.



Scheme 2 Stability testing of four- and five-membered carbo- and heterocyclic organoboronates

Having established the stability of strained organoboronates, we next investigated the scope of the transformation toward a new library of cyclobutenes. The protocol of Scheme 1 was used to generate in situ the cyclobutenylboronate **A**, which was then engaged directly in cross-coupling reactions in the presence of $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (Scheme 3). Aromatic and heteroaromatic iodides bearing ketone, ester, nitro or amide moieties led to the expected arylcyclobutenes **3b–g** in moderate to good yields (51 to 82%). Interestingly, an unprotected phenol and a benzoic acid furnished the desired products **3h** and **3i** in excellent yields of 80% and 96%, respectively. Not only iodides, but bromides could be engaged as cross-coupling partners with similar efficacy, furnishing **3j–n** with up to 95% yield and with exceptional functional group tolerance (SF_5, NH_2, OH). Alternatively, an aryl triflate gave a similar result (**3q**, 96%) while aryl chlorides showed decreased efficiency (**3o**,**p**, 23 to 66%).

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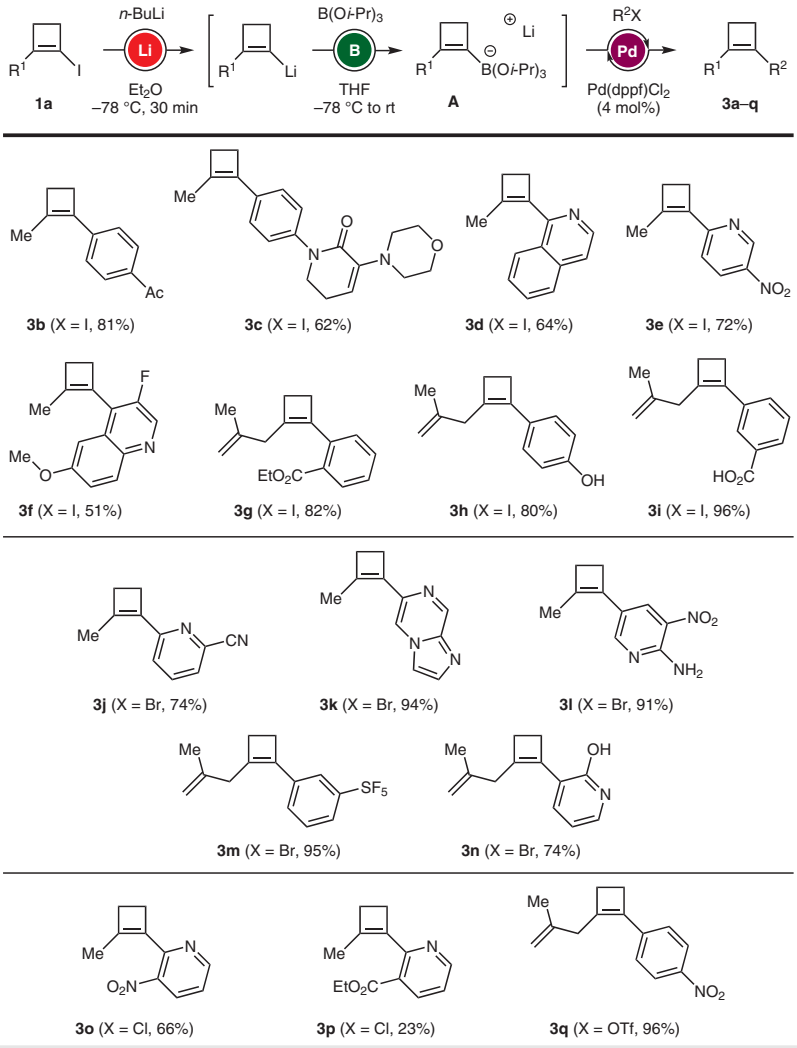

Scheme 3 In situ preparation and further Suzuki cross-coupling of cyclobutenylboronates

The study was then pursued with five-membered rings, utilizing cyclopentenyl iodides as starting materials[17] in a similar one-pot sequence (Scheme 4). Halogen–lithium exchange on **1b** was followed by transmetalation with B(O*i*-Pr)$_3$ and further palladium-catalyzed cross-coupling with diverse aromatic halides. A comparable functional group tolerance was observed for these larger cycloalkenylboronates, as ketone, nitro, amide and aldehyde moieties could be introduced, giving a wide range of unique functionalized cyclopentenes **4a–h** in moderate to excellent yields (52 to 96%).[16] When a β-styryl iodide was used, the reaction resulted in partial double bond isomerization and **4i** was obtained in 95% yield and an 82:18 *E*/*Z* ratio.

Next, we investigated the iodine–lithium exchange in the presence of boron isopropoxide. Given that the exchange reaction should proceed at a higher rate than the nucleophilic addition of *n*-BuLi to the boron atom, the presence of boron species should not perturb the exchange reaction, but rather promote the direct transmetalation of the newly generated lithium species (Scheme 5), as previously exemplified by Li et al.[18] As a result, the undesired alkylation reaction was to be suppressed without having to use Et$_2$O, avoiding the previously required mixture of solvents.

As a proof of concept, the halogen–metal exchange was performed on **1a** and **1b** in the presence of B(O*i*-Pr)$_3$ at –78 °C, and ultimately engaged in the cross-coupling reaction with a representative partner (1-iodo-3-nitrobenzene). Similar results were collected from this simplified procedure (93 to 96% yield).

Toward a more convenient setup, a step further was then taken by developing conditions that would not require low temperatures for the formation of organoboronates. We envisioned that room-temperature metal insertion in the presence of boron alkoxides should lead to the expected intermediate boron species through in situ transmetalation

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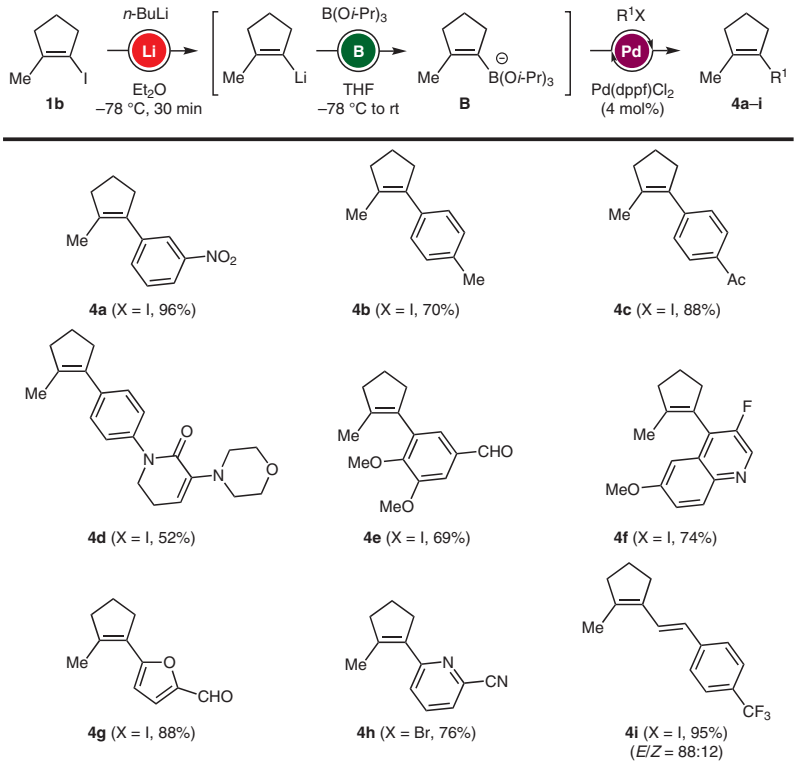
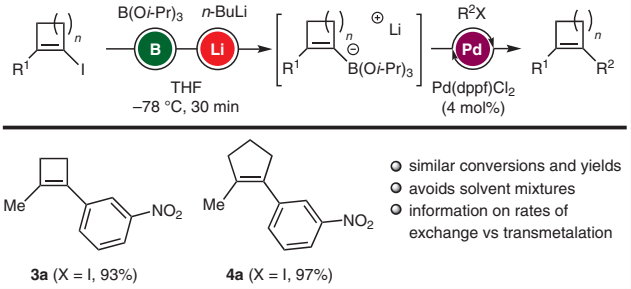


Scheme 4 In situ preparation and further Suzuki cross-coupling of cyclopentenylboronates

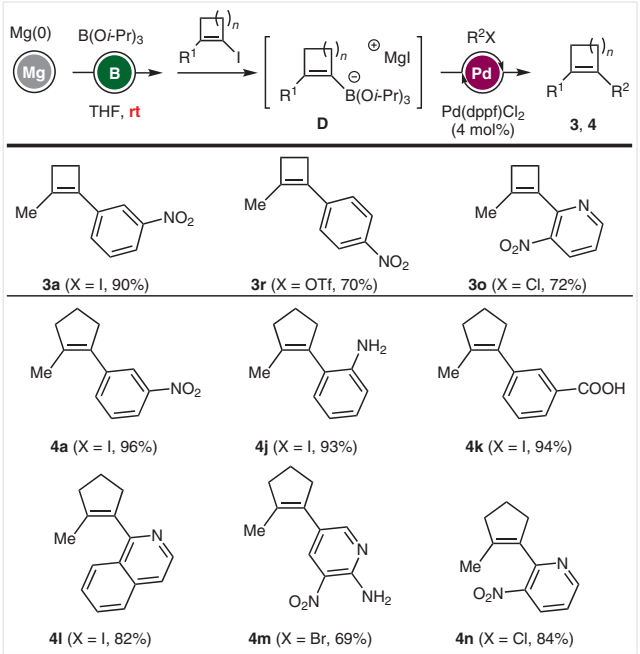
of the transitional cycloalkenylmagnesium species (Scheme 6).

Magnesium powder was then employed, furnishing the intermediary magnesium salt **D**, being an analog of **A** and **B**. Performing the full sequence at room temperature afforded the desired cross-coupling products in excellent yields, comparable to those obtained via the lithium path (up to 96%). The reaction also showed similarly high functional group tolerance, with the ability to introduce unprotected amines (**4j**, **4m**: 69 to 93%) and a carboxylic acid (**4k**, 94%).

In addition, we recently demonstrated the potential of in situ generated azetinylboronates to undergo unprecedented cross-coupling, transposing the methodology to



Scheme 5 Iodine–lithium exchange in the presence of $B(Oi\text{-}Pr)_3$ for direct transmetalation



Scheme 6 Formation of organoboronates through magnesium insertion and in situ transmetalation

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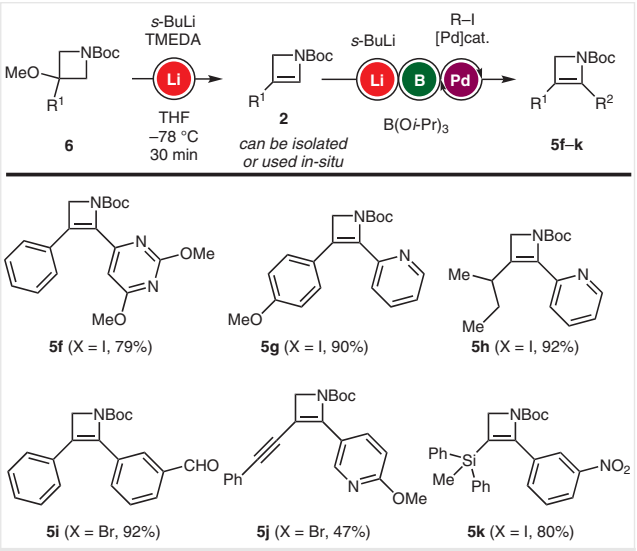
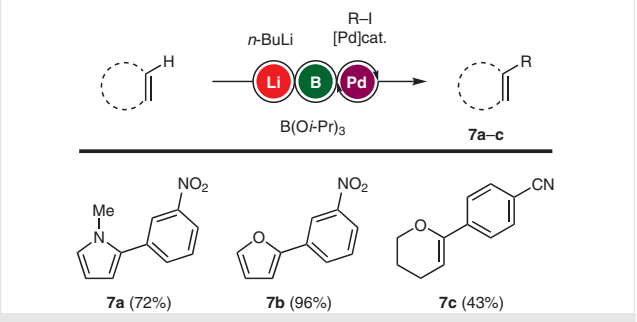
heterocyclic four-membered structures. A one-pot sequence was designed to access the desired boronates through a double α-lithiation of readily available azetidines **6**, followed by trapping with boron isopropoxide and palladium-catalyzed cross-coupling. Representative examples are given in Scheme 7. Alkyl, aryl, alkynyl and silyl groups were introduced at position 3, and the cross-coupling was performed using a large range of functionalized aromatic halides.[15]



Scheme 7 Single-pot access to 3,4-disubstituted azetines through a lithiation/transmetalation/cross-coupling sequence

Furthermore, we showed the applicability of this strategy to pyrroles, furans and hydropyrans to open the scope to a larger array of heterocyclic scaffolds. A simple metalation with *n*-BuLi was performed to access the initial organometallic derivatives, before transmetalation with B(O*i*-Pr)$_3$. Heteroaromatic starting materials furnished the desired cross-coupled compounds **7a**[16] and **7b** in good yields (up to 96%). However, employing hydrofuran resulted in only 43% of the substituted styrene derivative **7c** (Scheme 8).



Scheme 8 Extension to other heterocycles

In conclusion, we have assembled a new efficient one-pot sequence for the synthesis of cyclobutenes, cyclopentenes and azetines by using in situ prepared boron alkoxides possessing a remarkable functional group tolerance. Diverse conditions were successfully developed relying either on halogen/metal exchanges or on an advantageous room temperature insertion/transmetalation procedure. Through the intermediate formation of stable organoboronate building blocks, we have unlocked a wide library of unexplored strained architectures, opening modern organic chemistry to new classes of modules for further applications.

Commercially available starting materials were used without further purification unless otherwise stated. All reactions were carried out under N_2 atmospheres in flame-dried glassware. Syringes, which were used to transfer anhydrous solvents or reagents, were purged with nitrogen prior to use. CH_2Cl_2 was predried over $CaCl_2$ and distilled from CaH_2. THF was refluxed and distilled from sodium benzophenone ketyl under nitrogen. Et_2O was predried over $CaCl_2$ and passed through activated Al_2O_3 (using a solvent purification system SPS-400-2 from Innovative Technologies Inc.). Toluene was predried over $CaCl_2$ and distilled from CaH_2. *n*-BuLi was purchased from Rockwood Lithium GmbH; [*n*-BuLi] = 2.44 M in hexane (titration with isopropanol/1,10-phenanthroline).

Chromatographic purifications were performed using silica gel (SiO_2, 0.040–0.063 mm, 230–400 mesh ASTM) from Merck. The spots were visualized under UV (254 nm) or by staining the TLC plate with $KMnO_4$ solution [K_2CO_3 (10 g), $KMnO_4$ (1.5 g), H_2O (150 mL), NaOH (10% in H_2O, 1.25 mL)] or *p*-anisaldehyde (PAA) solution [concd H_2SO_4 (10 mL), EtOH (200 mL), AcOH (3 mL), *p*-anisaldehyde (4 mL)]. Melting points were determined on a Büchi B-540 apparatus and are uncorrected. Diastereoisomeric ratios were determined by ^{1}H NMR and ^{13}C NMR spectroscopy. ^{1}H and ^{13}C NMR spectra were recorded on VARIAN Mercury 200, BRUKER ARX 300, VARIAN VXR 400 S and BRUKER AMX 600 instruments. Chemical shifts are reported as δ values in ppm relative to the residual solvent peak (^{1}H NMR) or the solvent peak (^{13}C NMR) in deuterated chloroform ($CDCl_3$: δ 7.26 for ^{1}H NMR and δ 77.16 for ^{13}C NMR). Abbreviations for multiplicities are as follows: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), m (multiplet) and br (broad). Reaction endpoints were determined by GC monitoring. Gas chromatography was performed with an Agilent Technologies 7890 instrument, using a column of type HP 5 (Agilent 5% phenylmethylpolysiloxane; length: 15 m; diameter: 0.25 mm; film thickness: 0.25 µm) or Hewlett-Packard 6890 or 5890 series II instruments, using a column of type HP 5 (Hewlett-Packard, 5% phenylmethylpolysiloxane; length: 15 m; diameter: 0.25 mm; film thickness: 0.25 µm). High-resolution mass spectra (HRMS) and low-resolution mass spectra (LRMS) were recorded on Finnigan MAT 95Q, Finnigan MAT 90 or JEOL JMS-700 instruments. Single crystals (for X-ray analysis) were grown in small quench vials with a volume of 5.0 mL from slow evaporation of dichloromethane/hexanes mixtures at room temperature. Suitable single crystals were then introduced into perfluorinated oil and mounted on top of a thin glass wire. Data collection was performed at 100 K with a Bruker D8 Venture TXS equipped with a Spellman generator (50 kV, 40 mA) and a Kappa CCD detector operating with Mo-Kα radiation (l = 0.71071 Å).

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General Procedure A

To a solution of cycloalkenyl iodide (1.00 equiv) in Et_2O (0.5 M) was slowly added a solution of *n*-BuLi (2.44 M in hexane, 1.10 equiv) at –78 °C. After stirring for 30 min at the aforementioned temperature, B(O*i*-Pr)$_3$ (1.15 equiv) and THF (total concn 0.25 M) were added and the resulting mixture stirred for an additional 1 h at room temperature. Pd(dppf)Cl_2·CH_2Cl_2 (4 mol%), the cross-coupling partner (aromatic or vinylic iodide, bromide, tosylate or chloride) (0.90 equiv) and an aqueous solution of NaOH (1.5 equiv 1.00 M) were subsequently added and the reaction mixture was stirred overnight. The crude material was extracted with Et_2O (3 × 20 mL), washed with a saturated aqueous solution of sodium chloride (20 mL), dried over magnesium sulfate, filtered, concentrated and purified via flash column chromatography.

General Procedure B

Magnesium powder (1.30 equiv) and LiCl (1.10 equiv) were placed in a reaction tube and flame-dried in vacuo three times. After cooling to ambient temperature, enough THF was added to cover the solids. The magnesium was activated by addition of a few drops of dibromoethane and heating. After cooling back to ambient temperature, B(O*i*-Pr)$_3$ (1.00 equiv) was added. The cycloalkenyl iodide was added dropwise as a solution in THF (1.00 equiv, 0.5 M) and the resulting solution stirred for 2 h, after which a grey suspension had formed, which was divided into equimolar portions in new reaction tubes. To the portions were then added Pd(dppf)Cl_2·CH_2Cl_2 (4 mol%), the cross-coupling partner (aromatic iodide, bromide, tosylate or chloride) (0.80 equiv) and an aqueous solution of NaOH (1.5 equiv 1.00 M). The reaction mixture was stirred overnight and then extracted with Et_2O (3 × 20 mL), washed with a saturated aqueous solution of sodium chloride (20 mL), dried over magnesium sulfate, filtered, concentrated and purified via flash column chromatography.

1-Iodo-2-methylcyclopent-1-ene (1b)

Commercially available 5-iodopent-1-yne (1.93 g, 10 mmol, 1.0 equiv) was dissolved in dry pentane (30 mL) in a Schlenk tube and cooled to –78 °C. *n*-BuLi (2.39 M, 10 mmol, 1.0 equiv) was then added dropwise and the reaction mixture was stirred for 30 min before being warmed to –50 °C for 5 min. The mixture was then cooled back to –78 °C and dimethylaluminum chloride (1 M in CH_2Cl_2, 10 mmol, 1.0 equiv) was added dropwise and the resulting mixture stirred for a further 30 min. The mixture was then allowed to reach room temperature. In another Schlenk flask, zirconocene dichloride (2.93 g, 10 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (25 mL) and trimethylaluminum (2 M, 20 mmol, 2.0 equiv) was added at room temperature and the mixture stirred for 1 h. The first Schlenk flask was then cooled back to –78 °C before dropwise addition of the solution from the second Schlenk flask. The combined reaction mixture was allowed to reach room temperature and stirred for 1 h. The solvent was then removed in vacuo and a red solid remained, which was dissolved in THF (50 mL). After 30 min, complete conversion into the cyclized pentene was confirmed by GC–MS. The reaction mixture was cooled to –78 °C and iodine (5.58 g, 22 mmol, 2.2 equiv) was added portionwise. The mixture was allowed to reach room temperature and then poured into ice-cold HCl (2 M, 200 mL). The layers were separated and the aqueous layer was extracted with hexane (2 × 100 mL). The combined organics were washed with a saturated sodium thiosulfate solution. The organics were dried over $MgSO_4$, filtered and the solvent evaporated at 20 °C (60 mbar) due to the volatility of the desired product. Column chromatography (hexane) yielded the desired product as a colorless oil, which was stored at –20 °C to avoid decomposition.

Yield: 1.48 g, 7.09 mmol (71%); R_f = 0.79 (hexane; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.74–2.54 (m, 2 H), 2.31 (t, *J* = 8.5 Hz, 2 H), 2.04–1.82 (m, 2 H), 1.80–1.72 (m, 3 H).

Spectroscopic data are in agreement with the previously reported characterization.[15]

1-(2-Methylcyclobut-1-en-1-yl)-3-nitrobenzene (3a)

Using 1-iodo-2-methylcyclobut-1-ene and 1-iodo-3-nitrobenzene according to general procedure A provided **3a** as a yellow solid.

Yield: 49 mg, 0.26 mmol (96%); R_f = 0.32 (hexane/EtOAc, 98:2; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (t, *J* = 2.0 Hz, 1 H), 8.01 (ddd, *J* = 8.1, 2.4, 1.0 Hz, 1 H), 7.60 (dt, *J* = 7.7, 1.4 Hz, 1 H), 7.47 (t, *J* = 7.9 Hz, 1 H), 2.70–2.63 (m, 2 H), 2.52–2.42 (m, 2 H), 2.08–1.99 (m, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.6, 143.0, 137.7, 135.7, 131.2, 129.3, 121.0, 120.0, 30.2, 26.3, 16.5.

MS (EI): *m*/*z* (%) = 189 (11) $[M]^+$, 172 (43), 141 (67), 128 (100), 115 (58).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{11}H_{11}NO_2$: 189.0790; found: 189.0783.

Compound **3a** was also synthesized according to general procedure B.

Yield: 41 mg, 0.22 mmol (90%); mp 115–117 °C.

1-[4-(2-Methylcyclobut-1-en-1-yl)phenyl]ethan-1-one (3b)

Using 1-iodo-2-methylcyclobut-1-ene and 1-(4-iodophenyl)ethan-1-one according to general procedure A provided **3b** as a colorless oil.

Yield: 30 mg, 0.16 mmol (81%); R_f = 0.5 (hexane/EtOAc, 95:5; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.4 Hz, 2 H), 7.37 (d, *J* = 8.4 Hz, 2 H), 2.66–2.63 (m, 2 H), 2.58 (s, 3 H), 2.49–2.44 (m, 2 H), 2.05–2.02 (m, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.7, 143.4, 140.7, 137.1, 134.9, 128.7, 125.4, 30.3, 26.7, 26.2, 16.7.

MS (EI): *m*/*z* (%) = 186 $[M]^+$ (30), 171 (20), 143 (80), 128 (100), 115 (40).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{14}O$: 186.1045; found: 186.1037.

1-[4-(2-Methylcyclobut-1-en-1-yl)phenyl]-3-morpholino-5,6-dihydropyridin-2(1*H*)-one (3c)

Using 1-iodo-2-methylcyclobut-1-ene and 1-(4-iodophenyl)-3-morpholino-5,6-dihydropyridin-2(1*H*)-one according to general procedure A provided **3c** as a colorless oil.

Yield: 40 mg, 0.12 mmol (62%); R_f = 0.2 (hexane/EtOAc, 6:4; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.27 (m, 4 H), 5.63 (t, *J* = 4.7 Hz, 1 H), 3.84–3.80 (m, 4 H), 3.78 (t, *J* = 6.7 Hz, 2 H), 2.93–2.86 (m, 4 H), 2.64–2.55 (m, 2 H), 2.48 (td, *J* = 6.7, 4.6 Hz, 2 H), 2.44–2.39 (m, 2 H), 2.00–1.94 (m, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.3, 143.8, 140.8, 139.0, 137.0, 134.1, 125.6, 124.7, 114.2, 66.7, 50.5, 48.6, 29.8, 26.1, 23.4, 16.2.

1-(2-Methylcyclobut-1-en-1-yl)isoquinoline (3d)

Using 1-iodo-2-methylcyclobut-1-ene and 1-iodoisoquinoline according to general procedure A provided **3d** as a colorless oil.

Yield: 25 mg, 0.13 mmol (64%); R_f = 0.3 (hexane/EtOAc, 9:1; UV, $KMnO_4$, PAA).

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^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 5.6 Hz, 1 H), 8.30 (d, *J* = 8.5 Hz, 1 H), 7.80 (d, *J* = 7.0 Hz, 1 H), 7.67–7.63 (m, 1 H), 7.56 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1 H), 7.50 (d, *J* = 5.6 Hz, 1 H), 3.11–3.06 (m, 2 H), 2.63–2.57 (m, 2 H), 2.02 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.3, 147.5, 142.5, 137.8, 136.8, 129.9, 127.1, 126.9, 126.7, 126.6, 119.2, 31.1, 29.9, 17.2.

MS (EI): *m*/*z* (%) = 194 [M – H]$^+$ (100), 180 (100), 167 (30), 154 (20).

HRMS (EI): *m*/*z* [M – H]$^+$ calcd for $C_{14}H_{12}N$: 194.0970; found: 194.0962.

2-(2-Methylcyclobut-1-en-1-yl)-5-nitropyridine (3e)

Using 1-iodo-2-methylcyclobut-1-ene and 2-iodo-5-nitropyridine according to general procedure A provided **3e** as a yellow oil.

Yield: 27 mg, 0.14 mmol (72%); R_f = 0.5 (hexane/EtOAc, 9:1; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.37 (d, *J* = 2.6 Hz, 1 H), 8.39 (dd, *J* = 8.7, 2.7 Hz, 1 H), 7.26 (d, *J* = 8.7 Hz, 1 H), 2.81–2.70 (m, 2 H), 2.59–2.49 (m, 2 H), 2.21 (t, *J* = 1.9 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.2, 153.3, 145.5, 141.5, 136.8, 131.4, 119.6, 31.1, 26.1, 17.2.

MS (EI): *m*/*z* (%) = 190 [M]$^+$ (40), 175 (100), 143 (60), 129 (70).

HRMS (EI): *m*/*z* [M – H]$^+$ calcd for $C_{10}H_9N_2O_2$: 189.0664; found: 189.0656.

3-Fluoro-6-methoxy-4-(2-methylcyclobut-1-en-1-yl)quinoline (3f)

Using 1-iodo-2-methylcyclobut-1-ene and 3-fluoro-4-iodo-6-methoxyquinoline according to general procedure A provided **3f** as a colorless oil.

Yield: 25 mg, 0.10 mmol (51%); R_f = 0.3 (hexane/EtOAc, 9:1; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (d, *J* = 1.7 Hz, 1 H), 7.97 (d, *J* = 9.1 Hz, 1 H), 7.30 (dd, *J* = 9.1, 2.8 Hz, 1 H), 7.26 (d, *J* = 4.1 Hz, 1 H), 3.92 (s, 3 H), 2.98–2.89 (m, 2 H), 2.72–2.58 (m, 2 H), 1.84 (d, *J* = 1.3 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.6, 154.0 (d, *J* = 254.5 Hz), 148.4, 141.8 (d, *J* = 2.3 Hz), 138.6 (d, *J* = 29.3 Hz), 131.4, 130.2, 128.3 (d, *J* = 3.4 Hz), 124.8 (d, *J* = 12.7 Hz), 120.8 (d, *J* = 2.7 Hz), 103.9 (d, *J* = 5.4 Hz), 55.6, 32.0, 30.5 (d, *J* = 2.8 Hz), 17.4 (d, *J* = 2.1 Hz).

MS (EI): *m*/*z* (%) = 243 [M]$^+$ (90), 228 (70), 212 (100), 200 (30).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{15}H_{14}FNO$: 243.1059; found: 243.1053.

Ethyl 2-[2-(2-Methylallyl)cyclobut-1-en-1-yl]benzoate (3g)

Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene and ethyl 2-iodobenzoate according to general procedure A provided **3g** as a yellowish oil.

Yield: 42 mg, 0.16 mmol (82%*), *with minor impurities due to the starting material (aryl-I); R_f = 0.6 (hexane/EtOAc, 9:1; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 7.6 Hz, 1 H), 7.39 (t, *J* = 8.1 Hz, 1 H), 7.31–7.19 (m, 2 H), 4.74 (d, *J* = 6.8 Hz, 2 H), 4.31 (q, *J* = 7.1 Hz, 2 H), 2.85 (s, 2 H), 2.68–2.61 (m, 2 H), 2.46–2.36 (m, 2 H), 1.68 (s, 3 H), 1.34 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.6, 142.9, 141.9, 140.2, 136.1, 131.1, 130.3, 129.6, 129.4, 126.7, 111.6, 61.3, 38.2, 29.2, 28.7, 23.0, 14.4.

MS (EI): *m*/*z* (%) = 256 [M]$^+$ (10), 241 (5), 227 (5), 209 (30), 195 (100), 181 (20).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{17}H_{20}O_2$: 256.1463; found: 256.1458.

4-[2-(2-Methylallyl)cyclobut-1-en-1-yl]phenol (3h)

Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene and 4-iodophenol according to general procedure A provided **3h** as a colorless oil.

Yield: 32 mg, 0.16 mmol (80%); R_f = 0.3 (hexane/EtOAc, 8:2; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.21 (m, 2 H), 6.83–6.76 (m, 2 H), 4.81 (d, *J* = 5.6 Hz, 3 H), 3.04 (s, 2 H), 2.64–2.59 (m, 2 H), 2.47–2.40 (m, 2 H), 1.78 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.4, 142.9, 138.6, 137.7, 129.4, 127.2, 115.3, 111.5, 39.0, 28.3, 26.2, 23.1.

MS (EI): *m*/*z* (%) = 200 [M]$^+$ (30), 185 (80), 171 (20), 158 (100), 144 (30).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{14}H_{16}O$: 200.1201; found: 200.1195.

3-[2-(2-Methylallyl)cyclobut-1-en-1-yl]benzoic Acid (3i)

Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene and 3-iodobenzoic acid according to general procedure A provided **3i** as a colorless oil.

Yield: 44 mg, 0.19 mmol (96%); R_f = 0.3 (hexane/EtOAc, 95:5; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (s, 1 H), 7.95 (d, *J* = 7.7 Hz, 1 H), 7.57 (d, *J* = 7.7 Hz, 1 H), 7.43 (t, *J* = 7.7 Hz, 1 H), 4.84 (s, 2 H), 3.13 (s, 2 H), 2.73–2.67 (m, 2 H), 2.53–2.46 (m, 2 H), 1.80 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.3, 142.4, 142.2, 138.2, 136.4, 129.5, 128.7, 128.3, 127.4, 111.9, 39.1, 28.6, 26.2, 23.1.

MS (EI): *m*/*z* (%) = 228 [M]$^+$ (5), 212 (10), 183 (100), 167 (20), 155 (50).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{15}H_{16}O_2$: 228.1150; found: 228.1143.

6-(2-Methylcyclobut-1-en-1-yl)picolinonitrile (3j)

Using 1-iodo-2-methylcyclobut-1-ene and 6-bromopicolinonitrile according to general procedure A provided **3j** as a colorless oil.

Yield: 25 mg, 0.15 mmol (74%); R_f = 0.5 (hexane/EtOAc, 8:2; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (t, *J* = 7.8 Hz, 1 H), 7.44 (d, *J* = 7.6 Hz, 1 H), 7.31 (d, *J* = 8.1 Hz, 1 H), 2.73–2.63 (m, 2 H), 2.53–2.44 (m, 2 H), 2.16 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.9, 149.6, 137.0, 136.2, 133.6, 125.4, 123.0, 117.8, 30.6, 26.0, 16.8.

MS (EI): *m*/*z* (%) = 170 [M]$^+$ (20), 155 (100), 142 (10), 129 (10), 115 (10).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{11}H_{10}N_2$: 170.0844; found: 170.0843.

6-(2-Methylcyclobut-1-en-1-yl)imidazo[1,2-*a*]pyrazine (3k)

Using 1-iodo-2-methylcyclobut-1-ene and 6-bromoimidazo[1,2-*a*]pyrazine according to general procedure A provided **3k** as a yellowish oil.

Yield: 35 mg, 0.19 mmol (94%); R_f = 0.1 (hexane/EtOAc, 5:5; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.06 (s, 1 H), 7.85 (s, 1 H), 7.75 (s, 1 H), 7.63 (s, 1 H), 2.72–2.61 (m, 2 H), 2.55–2.43 (m, 2 H), 2.15 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.5, 143.3, 139.8, 137.5, 135.7, 133.7, 114.1, 113.7, 30.5, 25.7, 16.5.

MS (EI): *m*/*z* (%) = 185 [M]$^+$ (70), 184 (100), 170 (100), 157 (5), 144 (5).

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HRMS (EI): *m*/*z* [M – H]$^+$ calcd for $C_{11}H_{10}N_3$: 184.0875; found: 184.0869.

5-(2-Methylcyclobut-1-en-1-yl)-3-nitropyridin-2-amine (3l)

Using 1-iodo-2-methylcyclobut-1-ene and 5-bromo-3-nitropyridin-2-amine according to general procedure A provided **3l** as a yellow oil.

Yield: 37 mg, 0.18 mmol (91%); R_f = 0.1 (hexane/EtOAc, 8:2; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 2.2 Hz, 1 H), 8.25 (d, *J* = 2.1 Hz, 1 H), 6.69 (s, 2 H), 2.66–2.56 (m, 2 H), 2.50–2.40 (m, 2 H), 1.99 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.3, 151.7, 140.2, 132.8, 130.5, 128.0, 123.7, 30.4, 26.1, 16.5.

MS (EI): *m*/*z* (%) = 205 [M]$^+$ (100), 190 (90), 176 (40), 157 (60), 144 (60).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{10}H_{11}N_3O_2$: 205.0851; found: 205.0840.

Pentafluoro{3-[2-(2-methylallyl)cyclobut-1-en-1-yl]phenyl}-λ^6-sulfane (3m)

Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene and (3-bromophenyl)pentafluoro-λ^6-sulfane according to general procedure A provided **3m** as a colorless oil.

Yield: 59 mg, 0.19 mmol (95%); R_f = 0.6 (hexane; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (s, 1 H), 7.59–7.53 (m, 1 H), 7.45–7.36 (m, 2 H), 4.83 (d, *J* = 9.7 Hz, 2 H), 3.08 (s, 2 H), 2.73–2.63 (m, 2 H), 2.52–2.44 (m, 2 H), 1.78 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.3, 143.4, 142.0, 137.7, 136.8, 128.8, 128.5, 123.9, 123.3, 112.1, 39.1, 28.9, 26.2, 23.0.

MS (EI): *m*/*z* (%) = 310 [M]$^+$ (60), 295 (60), 282 (10), 269 (5), 253 (5).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{14}H_{15}F_5S$: 310.0815; found: 310.0807.

3-[2-(2-Methylallyl)cyclobut-1-en-1-yl]pyridin-2-ol (3n)

Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene and 3-bromopyridin-2-ol according to general procedure A provided **3n** as a colorless oil.

Yield: 30 mg, 0.15 mmol (74%); R_f = 0.1 (hexane/EtOAc, 7:3; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (dd, *J* = 7.0, 2.0 Hz, 1 H), 7.21 (dd, *J* = 6.5, 2.0 Hz, 1 H), 6.25 (t, *J* = 6.7 Hz, 1 H), 4.79–4.74 (m, 2 H), 3.29 (s, 2 H), 2.68–2.63 (m, 2 H), 2.45–2.39 (m, 2 H), 1.75 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.8, 144.5, 143.9, 137.0, 135.0, 132.4, 127.7, 111.2, 106.8, 40.3, 28.5, 26.9, 23.1.

MS (EI): *m*/*z* (%) = 201 [M]$^+$ (100), 186 (50), 167 (30), 134 (30).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{13}H_{15}NO$: 201.1154; found: 201.1149.

2-(2-Methylcyclobut-1-en-1-yl)-3-nitropyridine (3o)

Using 1-iodo-2-methylcyclobut-1-ene and 2-chloro-3-nitropyridine according to general procedure A provided **3o** as a yellowish oil.

Yield: 25 mg, 0.13 mmol (66%).

Compound **3o** was also synthesized according to general procedure B.

Yield: 32 mg, 0.17 mmol (72%); R_f = 0.6 (hexane/EtOAc, 8:2; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (dd, *J* = 4.7, 1.6 Hz, 1 H), 7.92 (dd, *J* = 8.1, 1.6 Hz, 1 H), 7.21 (dd, *J* = 8.2, 4.7 Hz, 1 H), 2.72–2.61 (m, 2 H), 2.55–2.46 (m, 2 H), 2.10 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.6, 151.9, 147.2, 144.4, 133.6, 131.4, 120.8, 31.6, 27.5, 17.2.

MS (EI): *m*/*z* (%) = 172 (5), 160 (950), 145 (30), 130 (90), 117 (100).

HRMS (EI): *m*/*z* [M – H]$^+$ calcd for $C_{10}H_9N_2O_2$: 189.0664; found: 189.0657.

Ethyl 2-(2-Methylcyclobut-1-en-1-yl)nicotinate (3p)

Using 1-iodo-2-methylcyclobut-1-ene and ethyl 2-chloronicotinate according to general procedure A provided **3p** as a yellowish oil.

Yield: 10 mg, 0.05 mmol (23%); R_f = 0.6 (hexane/EtOAc, 8:2; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (dd, *J* = 4.8, 1.8 Hz, 1 H), 7.87 (dd, *J* = 7.8, 1.8 Hz, 1 H), 7.13 (dd, *J* = 7.8, 4.8 Hz, 1 H), 4.36 (q, *J* = 7.2 Hz, 2 H), 2.76–2.71 (m, 2 H), 2.48–2.42 (m, 2 H), 2.01 (s, 3 H), 1.38 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.0, 152.9, 151.1, 148.6, 137.0, 136.9, 126.0, 120.4, 61.8, 30.8, 28.3, 16.7, 14.4.

MS (EI): *m*/*z* (%) = 217 [M]$^+$ (10), 187 (100), 174 (15).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{13}H_{15}NO_2$: 217.1103; found: 217.1099.

1-[2-(2-Methylallyl)cyclobut-1-en-1-yl]-4-nitrobenzene (3q)

Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene and 4-nitrophenyl trifluoromethanesulfonate according to general procedure A provided **3q** as a colorless oil.

Yield: 44 mg, 0.19 mmol (96%); R_f = 0.7 (hexane/EtOAc, 9:1; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.8 Hz, 2 H), 7.42 (d, *J* = 8.8 Hz, 2 H), 4.83 (d, *J* = 16.7 Hz, 2 H), 3.12 (s, 2 H), 2.84–2.61 (m, 2 H), 2.58–2.41 (m, 2 H), 1.79 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.9, 146.0, 141.9, 141.6, 137.8, 126.1, 124.0, 112.2, 39.3, 29.1, 26.1, 23.1.

MS (EI): *m*/*z* (%) = 229 [M]$^+$ (2), 212 (90), 182 (100), 168 (50), 153 (50).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{14}H_{15}NO_2$: 229.1103; found: 229.1102.

1-(2-Methylcyclobut-1-en-1-yl)-4-nitrobenzene (3r)

Using 1-iodo-2-methylcyclobut-1-ene and 4-nitrophenyl trifluoromethanesulfonate according to general procedure B provided **3r** as a yellow oil.

Yield: 32 mg, 0.17 mmol (70%); R_f = 0.29 (hexane/EtOAc, 98:2; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19–8.09 (m, 2 H), 7.46–7.28 (m, 2 H), 2.76–2.57 (m, 2 H), 2.57–2.40 (m, 2 H), 2.15–1.96 (m, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.9, 145.8, 142.3, 136.3, 125.7, 124.0, 30.6, 26.2, 16.7.

MS (EI): *m*/*z* (%) = 189 [M]$^+$ (23), 172 (34), 143 (63), 128 (100), 115 (50), 102 (14).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{11}H_{11}NO_2$: 189.0790; found: 189.0783.

1-(2-Methylcyclopent-1-en-1-yl)-3-nitrobenzene (4a)

Using 1-iodo-2-methylcyclopent-1-ene and 1-iodo-3-nitrobenzene according to general procedure A provided **4a** as a light-yellow oil.

Yield: 39 mg, 0.19 mmol (96%); R_f = 0.2 (hexane/EtOAc, 99:1; UV, $KMnO_4$, PAA).

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^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (t, *J* = 1.9 Hz, 1 H), 8.04 (dd, *J* = 9.1, 2.1 Hz, 1 H), 7.59 (d, *J* = 7.8 Hz, 1 H), 7.48 (t, *J* = 7.9 Hz, 1 H), 2.80–2.72 (m, 2 H), 2.54 (t, *J* = 7.9 Hz, 2 H), 1.94 (quin, *J* = 7.5 Hz, 2 H), 1.88 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.3, 140.5, 138.7, 133.7, 132.4, 129.0, 122.4, 120.9, 40.4, 37.2, 21.9, 15.6.

MS (EI): *m*/*z* (%) = 203 $[M]^+$ (80), 188 (100), 156 (20), 141 (78), 128 (58), 115 (81).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{12}H_{13}NO_2$: 203.0946; found: 203.0939.

Compound **4a** was also synthesized according to general procedure B.

Yield: 39 mg, 0.19 mmol (96%).

1-Methyl-4-(2-methylcyclopent-1-en-1-yl)benzene (4b)

Using 1-iodo-2-methylcyclopent-1-ene and 1-iodo-4-methylbenzene according to general procedure A provided **4b** as a colorless oil.

Yield: 24 mg, 0.14 mmol (70%); R_f = 0.7 (hexane; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.29 (m, 4 H), 2.95–2.86 (m, 2 H), 2.73–2.60 (m, 2 H), 2.52 (s, 3 H), 2.07 (t, *J* = 7.5 Hz, 2 H), 2.05–1.99 (m, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 135.9, 135.7, 134.7, 134.6, 128.8, 127.6, 40.2, 37.4, 22.0, 21.3, 15.6.

MS (EI): *m*/*z* (%) = 172 $[M]^+$ (70), 157 (100), 142 (40), 129 (40), 115 (30).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{16}$: 172.1252; found: 172.1245.

1-[4-(2-Methylcyclopent-1-en-1-yl)phenyl]ethan-1-one (4c)

Using 1-iodo-2-methylcyclopent-1-ene and 1-(4-iodophenyl)ethan-1-one according to general procedure A provided **4c** as a colorless oil.

Yield: 35 mg, 0.18 mmol (88%); R_f = 0.3 (hexane/EtOAc, 95:5; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.4 Hz, 2 H), 7.37 (d, *J* = 8.4 Hz, 2 H), 2.80–2.71 (m, 2 H), 2.60 (s, 3 H), 2.53 (t, *J* = 7.1 Hz, 2 H), 1.97–1.90 (m, 2 H), 1.88 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.9, 143.9, 138.5, 134.8, 134.2, 128.3, 127.7, 40.5, 37.1, 26.7, 22.0, 15.9.

MS (EI): *m*/*z* (%) = 200 $[M]^+$ (57), 185 (100), 157 (22), 142 (25), 128 (32).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{16}O$: 200.1201; found: 200.1195.

1-[4-(2-Methylcyclopent-1-en-1-yl)phenyl]-3-morpholino-5,6-dihydropyridin-2(1*H*)-one (4d)

Using 1-iodo-2-methylcyclopent-1-ene and 1-(4-iodophenyl)-3-morpholino-5,6-dihydropyridin-2-(1*H*)-one according to general procedure A provided **4d** as a light yellow sticky oil.

Yield: 35 mg, 0.10 mmol (52%); R_f = 0.3 (hexane/EtOAc, 1:1; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.25 (m, 4 H), 5.63 (t, *J* = 4.7 Hz, 1 H), 3.84–3.76 (m, 6 H), 2.91 (t, *J* = 4.4 Hz, 4 H), 2.75–2.66 (m, 2 H), 2.53–2.43 (m, 4 H), 1.95–1.84 (m, 2 H), 1.84 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.5, 143.9, 140.6, 136.6, 135.6, 134.3, 128.0, 124.5, 114.2, 66.9, 50.6, 48.7, 40.2, 37.3, 23.5, 21.9, 15.6.

MS (EI): *m*/*z* (%) = 338 $[M]^+$ (14), 320 (100), 307 (20), 281 (35), 253 (34), 239 (31), 207 (55).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{26}N_2O_2$: 338.1994; found: 338.1988.

3,4-Dimethoxy-5-(2-methylcyclopent-1-en-1-yl)benzaldehyde (4e)

Using 1-iodo-2-methylcyclopent-1-ene and 3-iodo-4,5-dimethoxybenzaldehyde according to general procedure A provided **4e** as a colorless oil.

Yield: 34 mg, 0.14 mmol (69%); R_f = 0.35 (hexane/EtOAc, 9:1; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.87 (s, 1 H), 7.34 (d, *J* = 1.9 Hz, 1 H), 7.24 (d, *J* = 1.9 Hz, 1 H), 3.92 (s, 3 H), 3.79 (s, 3 H), 2.76–2.61 (m, 2 H), 2.47 (t, *J* = 7.0 Hz, 2 H), 1.95 (quin, *J* = 7.5 Hz, 2 H), 1.65 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 191.6, 153.6, 152.7, 138.0, 133.6, 132.10, 132.08, 127.6, 108.7, 60.8, 56.1, 38.9, 37.8, 22.7, 15.4.

MS (EI): *m*/*z* (%) = 246 $[M]^+$ (100), 231 (27), 217 (18), 203 (18), 189 (24), 161 (26), 115 (35).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{18}O_3$: 246.1256; found: 246.1250.

3-Fluoro-6-methoxy-4-(2-methylcyclopent-1-en-1-yl)quinoline (4f)

Using 1-iodo-2-methylcyclopent-1-ene and 3-fluoro-4-iodo-6-methoxyquinoline according to general procedure A provided **4f** as colorless oil.

Yield: 38 mg, 0.15 mmol (74%); R_f = 0.3 (hexane/EtOAc, 9:1; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62 (d, *J* = 9.2 Hz, 1 H), 8.00 (d, *J* = 9.2 Hz, 1 H), 7.31 (dd, *J* = 9.2, 2.8 Hz, 1 H), 6.99 (d, *J* = 2.8 Hz, 1 H), 3.89 (s, 3 H), 2.86–2.74 (m, 1 H), 2.71–2.66 (m, 1 H), 2.62 (t, *J* = 7.3 Hz, 2 H), 2.20–1.99 (m, 2 H), 1.56 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.9, 154.3 (d, *J* = 252.4 Hz), 142.0, 141.9, 138.9 (d, *J* = 29.3 Hz), 131.7, 129.4 (d, *J* = 3.6 Hz), 128.8 (d, *J* = 14.4 Hz), 126.7, 120.8 (d, *J* = 3.2 Hz), 104.1 (d, *J* = 5.9 Hz), 55.9, 39.2, 37.8 (d, *J* = 2.1 Hz), 23.5, 15.9.

MS (EI): *m*/*z* (%) = 257 $[M]^+$ (100), 242 (25), 226 (20), 214 (40), 198 (22), 184 (36), 172 (20).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{16}FNO$: 257.1216; found: 257.1210.

5-(2-Methylcyclopent-1-en-1-yl)furan-2-carbaldehyde (4g)

Using 1-iodo-2-methylcyclopent-1-ene and 5-iodofuran-2-carbaldehyde according to general procedure A provided **4g** as a crystalline solid.

Yield: 31 mg, 0.18 mmol (88%); mp 93–97 °C; R_f = 0.2 (hexane/EtOAc, 98:2; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.56 (s, 1 H), 7.23 (d, *J* = 3.7 Hz, 1 H), 6.34 (d, *J* = 3.7 Hz, 1 H), 2.80–2.65 (m, 2 H), 2.60–2.48 (m, 2 H), 2.12 (quin, *J* = 1.6 Hz, 3 H), 1.93 (quin, *J* = 7.6 Hz, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.0, 159.1, 151.2, 144.1, 124.1, 123.4, 109.4, 40.9, 34.4, 22.1, 16.4.

MS (EI): *m*/*z* (%) = 176 $[M]^+$ (100), 161 (50), 147 (78), 129 (21), 119 (46), 105 (22).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{11}H_{12}O_2$: 176.0837; found: 176.0831.

6-(2-Methylcyclopent-1-en-1-yl)picolinonitrile (4h)

Using 1-iodo-2-methylcyclopent-1-ene and 6-bromopicolinonitrile according to general procedure A provided **4h** as a colorless oil.

Yield: 28 mg, 0.15 mmol (76%); R_f = 0.3 (hexane/EtOAc, 95:5; UV, $KMnO_4$, PAA).

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^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 = (t, *J* = 7.9 Hz, 1 H), 7.46 (d, *J* = 7.6 Hz, 1 H), 7.41 (d, *J* = 8.1 Hz, 1 H), 2.85–2.76 (m, 2 H), 2.58 (t, *J* = 7.4 Hz, 2 H), 2.10 (s, 3 H), 1.92 (quin, *J* = 7.6 Hz, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.8, 145.2, 136.9, 133.1, 132.4, 125.2, 125.1, 117.8, 41.3, 35.8, 21.7, 16.4.

MS (EI): *m*/*z* (%) = 184 [M]$^+$ (70), 169 (100), 155 (46), 142 (36), 129 (13), 118 (12), 103 (17).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{12}H_{12}N_2$: 184.1000; found: 184.0994.

(*E*)-1-[2-(2-Methylcyclopent-1-en-1-yl)vinyl]-4-(trifluoromethyl)benzene (4i)

Using 1-iodo-2-methylcyclopent-1-ene and (*Z*)-1-(2-iodovinyl)-4-(trifluoromethyl)benzene according to general procedure A provided **4i** (*E*/*Z* = 88:12 by crude GC, isolated *E*/*Z* = 56:44) as a colorless oil.

Yield: 48 mg, 0.19 mmol (95%); R_f = 0.56/0,68 (hexane; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59–7.46 (m, 3 H), 7.37–7.30 (m, 1 H), 6.46–6.33 (m, 2 H), 2.36–2.28 (m, 2 H), 2.22–2.11 (m, 2 H), 1.75 (quin, *J* = 7.4 Hz, 2 H), 1.67 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.6 (d, *J* = 1.6 Hz), 142.3, 133.8, 129.2, 128.7 (d, *J* = 5.0 Hz), 128.0, 125.9, 124.7 (q, *J* = 3.8 Hz), 123.1 (d, *J* = 1.5 Hz), 38.6, 35.8, 22.8, 15.1.

MS (EI): *m*/*z* (%) = 252 [M]$^+$ (91), 237 (100), 209 (75), 183 (53), 159 (35), 141 (34), 115 (22).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{15}H_{15}F_3$: 252.1126; found: 252.1119.

2-(2-Methylcyclopent-1-en-1-yl)aniline (4j)

Using 1-iodo-2-methylcyclopent-1-ene and 2-iodoaniline according to general procedure B provided **4j** as a light yellow oil.

Yield: 32 mg, 0.19 mmol (93%); R_f = 0.2 (hexane/EtOAc, 95:5; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07 (td, *J* = 7.8, 1.5 Hz, 1 H), 6.98 (dd, *J* = 7.5, 1.4 Hz, 1 H), 6.79–6.69 (m, 2 H), 3.66 (s, 2 H), 2.68–2.57 (m, 2 H), 2.48 (t, *J* = 7.3 Hz, 2 H), 1.96 (quin, *J* = 7.5 Hz, 2 H), 1.61 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.6, 136.9, 133.4, 129.3, 127.7, 124.9, 118.2, 115.2, 38.8, 37.9, 22.6, 15.2.

MS (EI): *m*/*z* (%) = 173 [M]$^+$ (67), 158 (22), 144 (100), 130 (53), 117 (22), 77 (20).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{12}H_{15}N$: 173.1204; found: 173.1198.

3-(2-Methylcyclopent-1-en-1yl)benzoic Acid (4k)

Using 1-iodo-2-methylcyclopent-1-ene and 3-iodobenzoic acid according to general procedure B provided **4k** as a light brown solid.

Yield: 38 mg, 0.19 mmol (94%); mp 116–120 °C; R_f = 0.4 (hexane/1% MeOH; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.39 (s, 1 H), 8.01 (s, 1 H), 7.91 (d, *J* = 7.6 Hz, 1 H), 7.47 (d, *J* = 7.4 Hz, 1 H), 7.36 (t, *J* = 7.3 Hz, 1 H), 2.72 (s, 2 H), 2.49 (s, 2 H), 1.90 (quin, *J* = 7.2 Hz, 2 H), 1.83 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.8, 139.1, 136.7, 134.1, 132.7, 129.9, 129.4, 128.2, 127.9, 40.3, 37.3, 22.0, 15.6.

MS (EI): *m*/*z* (%) = 202 [M]$^+$ (100), 187 (81), 157 (52), 128 (77), 115 (67), 77 (28).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{13}H_{14}O_2$: 202.0994; found: 202.0989.

1-(2-Methylcyclopent-1-en-1-yl)isoquinoline (4l)

Using 1-iodo-2-methylcyclopent-1-ene and 1-iodoisoquinoline according to general procedure B provided **4l** as a light yellow oil.

Yield: 34 mg, 0.16 mmol (82%); R_f = 0.2 (hexane/EtOAc, 9:1; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 5.7 Hz, 1 H), 7.97 (d, *J* = 8.4 Hz, 1 H), 7.82 (d, *J* = 8.2 Hz, 1 H), 7.70–7.62 (m, 1 H), 7.57–7.51 (m, 2 H), 2.97–2.82 (m, 2 H), 2.62 (t, *J* = 7.1 Hz, 2 H), 2.09 (quin, *J* = 7.5 Hz, 2 H), 1.55 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.2, 142.5, 139.9, 136.5, 134.5, 130.1, 127.5, 127.1, 127.0, 126.9, 119.3, 39.4, 38.6, 22.9, 15.6.

MS (EI): *m*/*z* (%) = 208 [M – H]$^+$ (100), 191 (11), 180 (40), 167 (15).

HRMS (EI): *m*/*z* [M – H]$^+$ calcd for $C_{15}H_{14}N$: 208.1126; found: 208.1120.

5-(2-Methylcyclopent-1-en-1-yl)-3-nitropyridin-2-amine (4m)

Using 1-iodo-2-methylcyclopent-1-ene and 5-bromo-3-nitropyridin-2-amine according to general procedure B provided **4m** as a yellow solid.

Yield: 30 mg, 0.14 mmol (69%); mp 177–180 °C; R_f = 0.2 (hexane/EtOAc, 9:1; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 2.1 Hz, 1 H), 8.31 (d, *J* = 2.0 Hz, 1 H), 6.70 (s, 2 H), 2.76–2.64 (m, 2 H), 2.51 (t, *J* = 7.1 Hz, 2 H), 1.93 (quin, *J* = 7.5 Hz, 2 H), 1.86 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.1, 151.7, 137.6, 133.0, 129.7, 127.9, 125.4, 40.2, 36.9, 21.8, 15.7.

MS (EI): *m*/*z* (%) = 219 [M]$^+$ (100), 204 (67), 173 (22), 158 (30).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{11}H_{13}N_3O_2$: 219.1008; found: 219.0992.

2-(2-Methylcyclopent-1-en-1-yl)-3-nitropyridine (4n)

Using 1-iodo-2-methylcyclopent-1-ene and 2-chloro-3-nitropyridine according to general procedure B provided **4n** as a yellow oil.

Yield: 26 mg, 0.17 mmol (84%); R_f = 0.3 (hexane/EtOAc, 8:2; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (dd, *J* = 4.7, 1.6 Hz, 1 H), 8.15 (dd, *J* = 8.2, 1.6 Hz, 1 H), 7.34 (dd, *J* = 8.2, 4.7 Hz, 1 H), 2.84–2.70 (m, 2 H), 2.50 (t, *J* = 8.0 Hz, 2 H), 2.01 (quin, *J* = 7.5 Hz, 2 H), 1.61 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.9, 152.6, 146.5, 142.1, 132.2, 132.0, 121.8, 39.4, 36.7, 22.8, 15.0.

MS (EI): *m*/*z* (%) = 187 (70), 174 (35), 156 (95), 147 (100), 130 (75), 117 (65), 103 (23).

HRMS (EI): *m*/*z* [M – H]$^+$ calcd for $C_{11}H_{11}N_2O_2$: 203.0821; found: 203.0814.

1-Methyl-2-(3-nitrophenyl)-1*H*-pyrrole (7a)

To a solution of 1-methyl-1*H*-pyrrole (90 µL, 1.014 mmol) and TMEDA (200 µL, 1.33 mmol, 1.33 equiv) in Et_2O (2 mL, 0.5 M) was slowly added a solution of *n*-BuLi (410 µL, 2.44 M in hexane, 1.00 equiv) at 0 °C. After stirring for 2 h at ambient temperature, B(O*i*-Pr)$_3$ (230 µL, 1.00 mmol, 1.00 equiv) and THF (2 mL) were added and the resulting mixture stirred for another 1 h at room temperature. Pd(dppf)Cl_2 dichloromethane adduct (16 mg, 4 mol%), 1-iodo-3-nitrobenzene (125 mg, 0.5 mmol, 0.5 equiv) and an aqueous solution of sodium hydroxide (1.5 mL, 1.5 equiv 1.00 M) were subsequently added and the mixture stirred overnight. The mixture was extracted with Et_2O (3 × 20 mL), washed with a saturated aqueous solution of sodium chloride

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(20 mL), dried over magnesium sulfate, filtered, concentrated and purified via flash column chromatography. Compound **7a** was obtained as a yellow solid.

Yield: 73 mg, 0.36 mmol (72%); mp 73–75 °C; R_f = 0.09 (hexane/EtOAc, 98:2; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (t, *J* = 2.0 Hz, 1 H), 8.13 (ddd, *J* = 8.3, 2.3, 1.1 Hz, 1 H), 7.74 (ddd, *J* = 7.7, 1.7, 1.1 Hz, 1 H), 7.57 (t, *J* = 8.0 Hz, 1 H), 6.79 (t, *J* = 2.3 Hz, 1 H), 6.36 (dd, *J* = 3.7, 1.8 Hz, 1 H), 6.24 (dd, *J* = 3.7, 2.7 Hz, 1 H), 3.73 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.5, 135.0, 134.1, 132.1, 129.5, 125.4, 122.8, 121.4, 110.4, 108.5, 35.4.

MS (EI): *m*/*z* (%) = 202 $[M]^+$ (100), 156 (45), 141 (11), 128 (35), 115 (25).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{11}H_{10}N_2O_2$: 202.0742; found: 204.0736.

2-(3-Nitrophenyl)furan (7b)

To a solution of furan (75 µL, 1.014 mmol) in Et_2O (2 mL, 0.5 M) was slowly added a solution of *n*-BuLi (410 µL, 2.44 M in hexane, 1.00 equiv) at 0 °C. After stirring for 1 h at ambient temperature, B(O*i*-Pr)$_3$ (230 µL, 1.00 mmol, 1.00 equiv) and THF (2 mL) were added and the resulting mixture stirred for another 1 h at room temperature. Pd(dppf)Cl_2 dichloromethane adduct (16 mg, 4 mol%), 1-iodo-3-nitrobenzene (125 mg, 0.5 mmol, 0.5 equiv) and an aqueous solution of sodium hydroxide (1.5 mL, 1.5 equiv 1.00 M) were subsequently added and the mixture stirred overnight. The mixture was extracted with Et_2O (3 × 20 mL), washed with a saturated aqueous solution of sodium chloride (20 mL), dried over magnesium sulfate, filtered, concentrated and purified via flash column chromatography. Compound **7b** was obtained as a colorless oil.

Yield: 91 mg, 0.48 mmol (96%); R_f = 0.14 (hexane/EtOAc, 98:2; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (t, *J* = 1.9 Hz, 1 H), 8.06 (dd, *J* = 8.2, 1.7 Hz, 1 H), 7.93 (d, *J* = 7.8 Hz, 1 H), 7.57–7.42 (m, 2 H), 6.79 (d, *J* = 3.5 Hz, 1 H), 6.52 (dd, *J* = 3.4, 1.8 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.6, 148.8, 143.4, 132.4, 129.8, 129.3, 121.7, 118.5, 112.2, 107.4.

MS (EI): *m*/*z* (%) = 189 $[M]^+$ (100), 143 (23), 131 (10), 115 (100), 102 (7).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{10}H_7NO_3$: 189.0426; found: 189.0420.

4-(3,4-Dihydro-2*H*-pyran-6-yl)benzonitrile (7c)

To a solution of 3,4-dihydro-2*H*-pyran (90 µL, 1.014 mmol) and TMEDA (50 µL, 0.33 mmol, 0.33 equiv) in Et_2O (2 mL, 0.5 M) was slowly added a solution of *n*-BuLi (550 µL, 2.44 M in hexane, 1.34 equiv) at ambient temperature. After stirring for 30 min, B(O*i*-Pr)$_3$ (230 µL, 1.00 mmol, 1.00 equiv) and THF (2 mL) were added and the resulting mixture stirred for 1 h at room temperature. Pd(dppf)Cl_2 dichloromethane adduct (16 mg, 4 mol%), 4-bromobenzonitrile (91 mg, 0.5 mmol, 0.5 equiv) and an aqueous solution of sodium hydroxide (1.5 mL, 1.5 equiv 1.00 M) were subsequently added and the mixture stirred overnight. The mixture was extracted with Et_2O (3 × 20 mL), washed with a saturated aqueous solution of sodium chloride (20 mL), dried over magnesium sulfate, filtered, concentrated and purified via flash column chromatography. Compound **7c** was obtained as a yellow oil.

Yield: 40 mg, 0.22 mmol (43%); R_f = 0.17 (hexane/EtOAc, 98:2; UV, $KMnO_4$, PAA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65–7.59 (m, 2 H), 7.59–7.54 (m, 2 H), 5.50 (t, *J* = 4.2 Hz, 1 H), 4.17 (t, *J* = 5.3 Hz, 2 H), 2.24 (td, *J* = 6.4, 4.1 Hz, 2 H), 1.96–1.85 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.2, 140.5, 132.0, 124.7, 119.2, 110.9, 101.0, 66.7, 22.2, 21.0.

MS (EI): *m*/*z* (%) = 185 $[M]^+$ (56), 170 (9), 156 (6), 140 (7), 130 (100), 116 (5), 102 (44).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{12}H_{11}NO$: 185.0841; found: 185.0834.

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Supporting Information

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