Single-Pot Access to Bis-Organoborinates: Applications in Zweifel Olefination

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1. General considerations

Commerically available starting materials were used without further purification unless otherwise stated. All reactions were carried out under N\textsubscript{2} atmosphere in flame-dried glassware. Syringes, which were used to transfer anhydrous solvents or reagents, were purged with nitrogen prior to use. THF was refluxed and distilled from sodium benzophenone ketyl under nitrogen. Et\textsubscript{2}O was predried over CaCl\textsubscript{2} and passed through activated Al\textsubscript{2}O\textsubscript{3} (the solvent purification system SPS-400-2 from Innovative Technologies Inc.). Chromatography purifications were performed using silica gel (SiO\textsubscript{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 with KMnO\textsubscript{4} solution (K\textsubscript{2}CO\textsubscript{3}, 10 g – KMnO\textsubscript{4}, 1.5 g – H\textsubscript{2}O, 150 mL – NaOH 10% in H\textsubscript{2}O, 1.25 mL), PAA: p-anisaldehyde solution (conc. H\textsubscript{2}SO\textsubscript{4}, 10 mL – EtOH, 200 mL – AcOH, 3 mL – p-anisaldehyde, 4 mL). 13C and 1H 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 residual solvent peak (1H-NMR) or solvent peak (13C-NMR) in deuterated chloroform (CDCl\textsubscript{3}: δ 7.26 ppm for 1H-NMR and δ 77.16 ppm for 13C-NMR) or deuterated benzene (C\textsubscript{6}D\textsubscript{6}: δ 7.16 ppm for 1H-NMR and δ 128.06 ppm for 13C-NMR). Abbreviations for signal coupling are as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet) and br (broad). Reaction endpoints were determined by GC monitoring of the reactions. Gas chromatography was performed with machines of Agilent Technologies 7890, 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, using a column of type HP 5 (HewlettPackard, 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 or Finnigan MAT 90 instrument or JEOL JMS-700. Infrared spectra were recorded on a Perkin 281 IR spectrometer and samples were measured neat (ATR, Smiths Detection DuraSample IR II Diamond ATR). The absorption bands were reported in wave numbers (cm\textsuperscript{-1}) and abbreviations for intensity are as follows: vs (very strong; maximum intensity), s (strong; above 75% of max. intensity), m (medium; from 50% to 75% of max. intensity), w (weak; below 50% of max. intensity) and br (broad). Melting points were determined on a Büchi B-540 apparatus and uncorrected. n-BuLi, s-BuLi and t-BuLi were purchased as solutions in cyclohexane/hexanes mixtures from Rockwood Lithium GmbH. The concentration of organometallic reagent from commercially purchased and synthesized reagents was determined either by titration of isopropyl alcohol using the indicator 4-(phenylazo)diphenylamine in THF for Grignard reagents or using the indicator 1,10-phenanthroline in THF for organolithium reagents.
2.$^{11}$B NMR Analyses

A) Reference NMR of B(On-Bu)$_3$.

B) Magnesium insertion of the aryl bromide in the presence of equimolar amounts of B(On-Bu)$_3$ in pure THF shows incomplete consumption of the B(On-Bu)$_3$. Two closely related peaks were detected, which were attributed to the monoorganoborinate and bis-organoborinate (2.02 and 1.91 ppm).

C) In the presence of 1,4-dioxane (1:9 v/v), full conversion of the B(On-Bu)$_3$ into the monoorganoborinate is observed.

D) 1.0 equivalents of alkenyl magnesium reagent A1 result in no significant change of the measured boron species.

E) 3.0 equivalents of alkenyl magnesium reagent A1 result in full conversion of the monoorganoborinate. Four new signals are detected (-8.12, -8.21, -8.26, -8.63 ppm), which were all attributed to boron species with up to three consecutive ligand exchanges.
**F)** Reference NMR of B(On-Bu)$_3$.

**G)** Lithium exchange of the aryl bromide, followed by addition of equimolar amounts of B(On-Bu)$_3$ in pure THF. Complete consumption of the B(On-Bu)$_3$ was observed. Again, two closely related peaks were detected, which were attributed to the monoorganoboronate and bis-organoborinate (4.38 and 2.39 ppm, 9:1 ratio by integration). Unfortunately, addition of 1,4-dioxane did not improve the selectivity towards the formation of the monoorganoboronate.

**H)** 1.0 equivalents of alkenyl lithium reagent (A5) result in nearly full consumption of the monoorganoboronate and the desired bis-organoborinate is detected (2.23 ppm).

**I)** 2.0 equivalents of alkenyl lithium reagent (A5) result in full consumption of the monoorganoboronate and the desired bis-organoborinate is detected (2.23 ppm).
3. Experimental Procedures

All chemicals were purchased from commercial sources and were used without further purification unless otherwise stated.

- Prop-1-en-2-ylmagnesium bromide \((\text{A1})\) was prepared following general procedure \(A\) according to literature procedure.¹
- Vinylmagnesium bromide \((\text{A2})\) was prepared following general procedure \(A\) according to literature procedure.¹
- \((1\text{-Phenylvinyl})\text{magnesium bromide (A3)}\) was prepared following general procedure \(A\) according to literature procedure.¹
- \((3,4\text{-Dihydro-2H-pyran-6-yl})\text{lithium (A4)}\) was prepared according to literature.²
- \((1\text{-ethoxyvinyl})\text{lithium (A5)}\) was prepared according to literature.²

3.1 General Procedures

3.1.1 General procedure A: Synthesis of different alkenylmagnesium reagents

\[
\begin{align*}
\text{Br} & \quad \text{LiCl (1.1 eq.)} & \quad \text{THF, r.t., 1 h} & \quad \text{MgBrLiCl} \\
A-\text{Br} & \quad \text{Mg (1.6 eq.)} & & A1-A5
\end{align*}
\]

A Schlenk flask was charged with lithium chloride (1.17 g, 27.5 mmol, 1.1 equiv.) and magnesium turnings (972 mg, 40 mmol, 1.6 equiv.). Lithium chloride was dried in vacuo using a heat gun (600 °C, 2 x 5 min). After addition of THF (5.0 mL) and 1,2-dibromoethane (2 drops), the mixture was heated to boil with a heat gun to activate the magnesium. The bromoalkene \(A-\text{Br}\) (25 mmol, 1.0 equiv.) was dissolved in THF (20.0 mL) and added to the activated magnesium suspension dropwise. After completion of the addition, the mixture was stirred for one hour at room temperature to yield a THF solution of the alkenylmagnesium reagents \(A1-A5\).

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¹ F. M. Piller, P. Appukkuttan, A. Gavryushin, M. Helm, P. Knochel, Angew. Chem. 2008, 120, 6907-6911.
² V. Hornillos, M. Giannerini, C. Vila, M. Fananas-Mastral, B. L. Feringa, Chem Sci 2015, 6, 1394-1398.
3.1.2 General procedure B: Mg-insertion / Ligand exchange with alkenyllithium reagents / Zweifel olefination sequence

A reaction tube was charged with lithium chloride (47 mg, 1.1 mmol, 1.1 equiv.) and magnesium turnings (39 mg, 1.6 mmol, 1.6 equiv.). Lithium chloride was dried in vacuo using a heat gun (600 °C, 5 min). After addition of THF (0.8 mL) / Dioxane (0.2 mL) and 1,2-dibromoethane (1 drop), the mixture was heated to boil with a heat gun to activate the magnesium, before tributylborate (270 µL, 1.0 mmol, 1.0 equiv.) was added at once. Heteroaryl/Aryl bromide (1.0 mmol, 1.0 equiv.) was dissolved in THF (1.0 mL) and added to the activated magnesium suspension at room temperature dropwise (to hold ~23 °C a water bath was used). The mixture was then stirred for one hour at ~23 °C to yield a THF-solution of the magnesium organobororate. The solution was cooled to -78 °C, before the solution of alkenyllithium reagent A4/A5 (1.0 - 2.0 mmol, 1.0 - 2.0 equiv.) was added dropwise. After half an hour, the reaction was warmed to 0 °C and let stir for 1 h. Then, cooled back to -78 °C, iodine (761 mg, 3.0 mmol, 3.0 equiv.), dissolved in THF (2.0 mL), was added dropwise to the solution. After 20 min a suspension of sodium methoxide (270 mg, 5.0 mmol, 5.0 equiv.) in methanol (2.0 mL) was added at once. The reaction was allowed to reach room temperature. After reaching room temperature the reaction is completed. The reaction was then quenched by the addition of saturated solution of Na₂S₂O₃ and extracted with diethyl ether (3 x 20 mL). The combined organic phases were dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel.

Counter-cations have been omitted for more clarity
3.1.3 General procedure C: Mg-insertion / Ligand exchange with alkenylmagnesium reagents / Zweifel olefination sequence

![Chemical diagram]

Counter-cations have been omitted for more clarity

A reaction tube was charged with lithium chloride (47 mg, 1.1 mmol, 1.1 equiv.) and magnesium turnings (39 mg, 1.6 mmol, 1.6 equiv.). Lithium chloride was dried in vacuo using a heat gun (600 °C, 5 min). After addition of THF (0.8 mL) / Dioxane (0.2 mL) and 1,2-dibromoethane (1 drop), the mixture was heated to boil with a heat gun to activate the magnesium, before tributylborate (270 µL, 1.0 mmol, 1.0 equiv.) was added at once. Heteroaryl/Aryl bromide (1.0 mmol, 1.0 equiv.) was dissolved in THF (1.0 mL) and added to the activated magnesium suspension at room temperature dropwise (to hold ~23 °C a water bath was used). The mixture was then stirred for one hour at ~23 °C to yield a THF-solution of the magnesium organoboronate. After that a solution of alkenylmagnesium reagent A1-A3 (3.0 mmol, 3.0 equiv.) was added dropwise at 0 °C and stirred for another 1 h at 0 °C. Then, cooled back to -78 °C, iodine (1.142 g, 4.5 mmol, 4.5 equiv.), dissolved in THF (2.0 mL), was added dropwise to the solution. After 20 min a suspension of sodium methoxide (348 mg, 6.0 mmol, 6.0 equiv.) in methanol (2.0 mL) was added at once. The reaction was allowed to reach room temperature. After reaching room temperature the reaction is completed. The reaction was then quenched by the addition of saturated solution of Na₂S₂O₃ and extracted with diethyl ether (3 x 20 mL). The combined organic phases were dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel.

3.1.4 General procedure D: Br/Li exchange / Ligand exchange with alkenylmagnesium reagents / Zweifel olefination sequence

![Chemical diagram]

Counter-cations have been omitted for more clarity

Under inert atmosphere, heteroaryl/aryl bromide (1 mmol, 1.0 eq.) was dissolved in a reaction tube in THF (1.0 mL) and the solution was cooled down to -78 °C before adding n-BuLi (1.0 mmol, 2.45 M,
The mixture was stirred for 30 min before tributylborate (270 µL, 1.0 mmol, 1.0 equiv.) was added dropwise at -78 °C. The mixture was stirred for 30 min at -78 °C before warming to 0 °C and stirred for another 1 h. After that a solution of alkenylmagnesium reagent A1/A2 (3.0 mmol, 3.0 equiv.) was added dropwise at 0 °C and stirred for another 1 h at 0 °C. Then, cooled back to -78 °C, iodine (1.142 g, 4.5 mmol, 4.5 equiv.), dissolved in THF (2.0 mL), was added dropwise to the solution. After 20 min a suspension of sodium methoxide (348 mg, 6.0 mmol, 6.0 equiv.) in methanol (2.0 mL) was added at once. The reaction was allowed to reach room temperature. After reaching room temperature the reaction is completed. The reaction was then quenched by the addition of saturated solution of Na2S2O3 and extracted with diethyl ether (3 x 20 mL). The combined organic phases were dried over MgSO4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel.

3.1.5 General procedure E: Double Br/Li exchange / Ligand exchange with alkenylmagnesium reagents / Zweifel olefination sequence

Counter-cations have been omitted for more clarity

Under inert atmosphere, heteroaryl/aryl bromide (2 mmol, 1.0 eq.) was dissolved in a reaction tube in THF (2.0 mL) and the solution was cooled down to -78 °C before adding n-BuLi (2.0 mmol, 2.45 M, 1 eq.) dropwise. The mixture was stirred for 30 min before tributylborate (540 µL, 2.0 mmol, 1.0 equiv.) was added dropwise at -78 °C. The mixture was stirred for 30 min at -78 °C before warming to 0 °C and stirred for another 1 h. After that a solution of alkenylmagnesium reagent A1/A2 (6.0 mmol, 3.0 equiv.) was added dropwise at 0 °C and stirred for another 1 h at 0 °C. Then, cooled back to -78 °C, iodine (2.284 g, 9.0 mmol, 9 equiv.), dissolved in THF (2.0 mL), was added dropwise to the solution. After 20 min a suspension of sodium methoxide (648 mg, 12.0 mmol, 12.0 equiv.) in methanol (2.0 mL) was added at once. The reaction was allowed to reach room temperature. After reaching room temperature the reaction is completed. The reaction was then quenched by the addition of saturated solution of Na2S2O3 and extracted with diethyl ether (3 x 20 mL). The combined organic phases were dried over MgSO4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel.
3.1.6 General procedure F: Br/Li-exchange / Ligand exchange with alkenyllithium reagents / Zweifel olefination sequence

Counter-cations have been omitted for more clarity

Under inert atmosphere, heteroarly/aryl bromide (2 mmol, 1.0 equiv.) was dissolved in a reaction tube in THF (2.0 mL) and the solution was cooled down to -78 °C before adding n-BuLi (2 mmol, 2.45 M, 1 eq.) dropwise. The mixture was stirred for 30 min before tributylborate (540 µL, 2.0 mmol, 1.0 equiv.) was added dropwise at -78 °C. The mixture was stirred for 30 min at -78 °C before warming to 0 °C and stirred for another 1 h. The solution was cooled to -78 °C, before the solution of alkenyllithium reagent A6/A7 (1.5 mmol, 1.5 equiv.) was added dropwise. After half an hour, the reaction was warmed to 0 °C and let stir for 1 h. Then, cooled back to -78 °C, iodine (761 mg, 3.0 mmol, 3 equiv.), dissolved in THF (2.0 mL), was added dropwise to the solution. After 20 min a suspension of sodium methoxide (270 mg, 5.0 mmol, 5.0 equiv.) in methanol (2.0 mL) was added at once. The reaction was allowed to reach room temperature. After reaching room temperature the reaction is completed. The reaction was then quenched by the addition of saturated solution of Na₂S₂O₅ and extracted with diethyl ether (3 x 20 mL). The combined organic phases were dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel.
3.1.7 General procedure G: Mg-insertion / Ligand exchange with Heteroaryl/aryl-lithium or -magnesium reagents / Zweifel olefination sequence

Counter-cations have been omitted for more clarity

A reaction tube was charged with lithium chloride (47 mg, 1.1 mmol, 1.1 equiv.) and magnesium turnings (39 mg, 1.6 mmol, 1.6 equiv.). Lithium chloride was dried in vacuo using a heat gun (600 °C, 5 min). After addition of THF (0.8 mL) / Dioxane (0.2 mL) and 1,2-dibromoethane (1 drop), the mixture was heated to boil with a heat gun to activate the magnesium, before tributylborate (270 µL, 1.0 mmol, 1.0 equiv.) was added at once. Alkenylbromide (1.0 mmol, 1.0 equiv.) was dissolved in THF (1.0 mL) and added to the activated magnesium suspension at 0 °C. The mixture was then stirred for 1 h at 0 °C to yield a THF-solution of the magnesium organoborionate.

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a) Use of Heteroaryl/aryl lithium reagent

During that, a solution of heteroaryl/aryl lithium was prepared by using the corresponding bromide (1.5 mmol, 1.5 equiv.) in THF (2.0 mL) followed by the dropwise addition of n-BuLi (1.5 mmol, 1.5 equiv.) at -78 °C. This solution was stirred for 30 min. The prior formed organobororate was then slowly added to the heteroaryl/aryl lithium species at -78 °C. The combined mixture was stirred for 30 min at -78 °C before warming to 0 °C and stirred for another 1 h.

b) Use of Heteroaryl/aryl magnesium reagent

A prior synthesized and titrated heteroaryl/aryl magnesium reagent was prepared by charging a schlenck flask with lithium chloride (448 mg, 11 mmol, 1.1 equiv.) and magnesium turnings (389 mg, 16 mmol, 1.6 equiv.). Lithium chloride was dried in vacuo using a heat gun (600 °C, 2 x 5 min). After addition of THF (5.0 mL) and 1,2-dibromoethane (2 drops), the mixture was heated to boil with a heat gun to activate the magnesium. The corresponding heteroaryl/aryl bromide (10 mmol, 1.0 equiv.) was dissolved in THF (5.0 mL) and added to the activated magnesium suspension dropwisely. After completion of the addition, the mixture was stirred for one hour at room temperature to yield a THF-solution of the organomagnesium reagent.

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Then, cooled back to -78 °C, iodine (761 mg, 3.0 mmol, 3.0 equiv.), dissolved in THF (2.0 mL), was added dropwise to the solution. After 20 min a suspension of sodium methoxide (270 mg, 5.0 mmol, 5.0 equiv.) in methanol (2.0 mL) was added at once. The reaction was allowed to reach room temperature. After reaching room temperature the reaction is completed. The reaction was then quenched by the addition of saturated solution of Na₂S₂O₃ and extracted with diethyl ether (3 x 20 mL). The combined organic phases were dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel.

3.1.8 Optimizations of General Procedure G (b):

\[
\begin{align*}
\text{OMe} & \quad \text{MeO} \\
\text{OMe} & \quad \text{MeO} \\
\end{align*}
\]

\[
\begin{align*}
1. & \quad \text{MeO} \quad \text{MgBr} \quad \text{A8} \\
& \quad \text{I₂ (3 eq.)} \quad \text{THF} \\
2. & \quad \text{NaOMe (5 eq.)} \quad \text{MeOH} \\
& \quad \text{-78 °C, then r.t.} \\
\end{align*}
\]

| entry | A8 (eq.) | GC-ratio 9h:SD. (%) |
|-------|---------|---------------------|
| 1     | 1       | 37 : 63             |
| 2     | 2       | 36 : 64             |
| 3     | 3       | 39 : 61             |

GC-ratios were determined by comparing to n-undecan as internal standard (SD). As shown above, no significant increase in product formation of 9h was observed with increasing amount of aryl magnesium reagent A8.
3.2 Experimental Data

6-Chloro-3-(3,4-dihydro-2H-pyran-6-yl)-2-methylpyridine (8a)

Using 3-bromo-6-chloro-2-methylpyridine and (3,4-dihydro-2H-pyran-6-yl)lithium (A4) according to general procedure B, provided 8a (0.54 mmol, 114 mg, 54%) as orange oil. Rf = 0.4 (hexane/EtOAc 95:5 and 1% NEt3, UV, PAA, KMnO4). 1H NMR (400 MHz, CDCl3) δ 7.53 – 7.51 (d, J = 8.1 Hz, 1H), 7.12 – 7.10 (d, J = 8.0 Hz, 1H), 4.89 – 4.87 (t, J = 3.9 Hz, 1H), 4.15 – 4.13 (t, J = 5.1 Hz, 3H), 2.55 (s, 3H), 2.21 – 2.17 (td, J = 6.4, 3.9 Hz, 2H), 1.96 – 1.90 ppm (dt, J = 12.2, 6.3 Hz, 2H). 13C NMR (101 MHz, CDCl3) δ 157.8, 150.9, 149.3, 139.0, 131.3, 120.9, 96.9, 66.3, 23.2, 22.5, 22.1 ppm. LRMS (DEP/EI-Orbitrap): m/z [%]: 209.1 (100), 194.1 (19), 180.1 (45), 166.1 (24), 154.0 (95). HRMS (EI-Orbitrap): m/z: [M+]+ Calcd for C11H12ClNO+: 209.0607; found: 209.0596. IR (Diamond-ATR, neat) νmax: 2977 (w), 2932 (w), 2886 (w), 1724 (w), 1693 (m), 1584 (w), 1557 (w), 1469 (s), 1378 (m), 1268 (s), 1240 (s), 1122 (s), 1050 (s).

1,2-Dichloro-4-(1-ethoxyvinyl)benzene (8b)

Using 4-bromo-1,2-dichlorobenzene and (1-ethoxyvinyl)lithium (A5) according to general procedure B, provided 8b (0.58 mmol, 125 mg, 58%) as colorless liquid. Rf = 0.50 (hexane and 1% NEt3, UV, PAA, KMnO4). 1H NMR (400 MHz, Benzene-d6) δ 7.71 (d, J = 2.0 Hz, 1H), 7.45 (dd, J = 8.4, 2.0 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 4.64 (d, J = 3.0 Hz, 1H), 4.24 (d, J = 3.0 Hz, 1H), 3.91 (q, J = 7.0 Hz, 2H), 1.42 ppm (t, J = 7.0 Hz, 3H). 13C NMR (101 MHz, Benzene-d6) δ 157.90, 137.07, 132.81, 132.55, 130.29, 127.64, 124.90, 83.46, 63.47, 14.30 ppm. LRMS (DEP/EI-Orbitrap): m/z [%]: 216.0 (8), 188.0 (23), 175.0 (64), 173.0 (100), 146.0 (19), 109.0 (6). HRMS (EI-Orbitrap): m/z: [M+] Calcd for C10H10Cl2O+: 216.0109; found: 216.0104. IR (Diamond-ATR, neat) νmax: 2977 (w), 2932 (w), 2886 (w), 1724 (w), 1693 (m), 1584 (w), 1557 (w), 1469 (s), 1378 (m), 1268 (s), 1240 (s), 1122 (s), 1050 (s).

2-Chloro-4-(1-ethoxyvinyl)-1-fluorobenzene (8c)

Using 4-bromo-2-chloro-1-fluorobenzene and (1-ethoxyvinyl)lithium (A5) according to general procedure B, provided 8c (0.58 mmol, 116 mg, 58%) as colorless oil. Rf = 0.41 (hexane, UV, PAA, KMnO4). 1H NMR (400 MHz, Benzene-d6) δ 7.72 (dd, J = 7.2, 2.2 Hz, 1H), 7.19 (dq, J = 6.4, 2.3 Hz, 2H), 6.61 (t, J = 8.7 Hz, 1H), 4.38 (d, J = 2.9 Hz, 1H), 3.95 (d, J = 2.9 Hz, 1H), 3.43 (q, J = 7.0 Hz, 2H), 2.54 (s, 3H), 2.21 – 2.17 (td, J = 6.4, 3.9 Hz, 2H), 1.96 – 1.90 ppm (dt, J = 12.2, 6.3 Hz, 2H). 13C NMR (101 MHz, Benzene-d6) δ 157.90, 137.07, 132.81, 132.55, 130.29, 127.64, 124.90, 83.46, 63.47, 14.30 ppm. LRMS (DEP/EI-Orbitrap): m/z [%]: 216.0 (8), 188.0 (23), 175.0 (64), 173.0 (100), 146.0 (19), 109.0 (6). HRMS (EI-Orbitrap): m/z: [M+] Calcd for C10H10Cl2O+: 216.0109; found: 216.0104. IR (Diamond-ATR, neat) νmax: 2977 (w), 2932 (w), 2886 (w), 1724 (w), 1693 (m), 1584 (w), 1557 (w), 1469 (s), 1378 (m), 1268 (s), 1240 (s), 1122 (s), 1050 (s).
1.03 ppm (t, J = 7.0 Hz, 3H).\(^{13}\)C NMR (101 MHz, Benzene-\(d_6\)) δ 158.46 (d, J = 249.8 Hz), 158.05 (d), 134.31 (d, J = 3.9 Hz), 125.5, 125.4, 121.2 (d, J = 18.0 Hz), 116.3 (d, J = 21.2 Hz), 82.9 (d, J = 1.4 Hz), 63.5, 14.3 ppm. LRMS (DEP/EI-Orbitrap): m/z [%]: 200.0 (7), 174.0 (14), 172.0 (19), 159.0 (33), 158.0 (7), 157.0 (100), 156 (11), 130.0 (11), 129.0 (35). \(^{13}\)C NMR (101 MHz, Benzene-\(d_6\)) δ 158.46 (d, J = 249.8 Hz), 158.05 (d), 134.31 (d, J = 3.9 Hz), 125.5, 125.4, 121.2 (d, J = 18.0 Hz), 116.3 (d, J = 21.2 Hz), 82.9 (d, J = 1.4 Hz), 63.5, 14.3 ppm. LRMS (DEP/EI-Orbitrap): m/z [%]: 200.0 (7), 174.0 (14), 172.0 (19), 159.0 (33), 158.0 (7), 157.0 (100), 156 (11), 130.0 (11), 129.0 (35). HRMS (EI-Orbitrap): m/z: [M+H]\(^+\) Calcd for C\(\text{H}_{16}\)ClFO: 200.0404; found: 200.0396.

IR (Diamond-ATR, neat) \(\tilde{\nu}_{\text{max}}\): 2976 (w), 2279 (w), 1692 (w), 1593 cm\(^{-1}\) (w).

Using bromobenzene and (3,4-dihydro-2H-pyran-6-yl)lithium (A4) according to general procedure B, provided 8d (0.41 mmol, 66 mg, 41%) as colorless oil. \(R_t = 0.65\) (hexane/EtOAc 95:5, UV, KMnO\(_4\)). \(^1\)H NMR (400 MHz, Benzene-\(d_6\)) δ 7.72 – 7.64 (m, 2H), 7.21 – 7.12 (m, 2H), 7.10 – 7.00 (m, 1H), 5.22 (t, J = 4.0 Hz, 1H), 3.83 (t, J = 6.2, 4.7 Hz, 2H), 1.86 (td, J = 6.4, 4.0 Hz, 2H), 1.51 – 1.39 ppm (m, 2H).

Analytical data was in agreement with the literature.

Using 5-bromo-2,4-dimethoxypyrimidine and (3,4-dihydro-2H-pyran-6-yl)lithium (A4) according to general procedure B, provided 8e (0.45 mmol, 101 mg, 45%) as yellowish oil.

Repeated in 10 mmol gram scale provided 8e (4.20 mmol, 933 mg, 42%) as yellowish oil. \(R_t = 0.3\) (hexane/EtOAc 95:5 and 1% NEt\(_3\), UV, PAA, KMnO\(_4\)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 8.42 (s, 1H), 5.50 – 5.48 (t, J = 4.0 Hz, 1H), 4.15 – 4.13 (t, J = 5.2 Hz, 2H), 4.02 (s, 3H), 3.99 (s, 3H), 2.23 – 2.19 (td, J = 6.4, 4.1 Hz, 2H), 1.93 – 1.87 ppm (dt, J = 11.7, 6.3 Hz, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 167.8, 164.0, 156.5, 145.7, 111.7, 102.5, 66.6, 54.9, 54.3, 22.4, 20.9 ppm. LRMS (DEP/EI-Orbitrap): m/z [%]: 222.2 (98), 207.1 (14), 193.0 (19), 167.1 (100). HRMS (El-Orbitrap): m/z: [M+H]\(^+\) Calcd for C\(\text{H}_{14}\)N\(_2\)O\(_3\): 222.1004; found: 222.0997. IR (Diamond-ATR, neat) \(\tilde{\nu}_{\text{max}}\): 2928 (m), 2870 (w), 1733 (vw), 1717 (w), 1691 cm\(^{-1}\) (w). Fast decomposition in chloroform was observed.

\(^3\) U. Lehmann, S. Awasthi, T. Minehan Org. Lett, 2003, 5, 2405-2408.
Using 4-bromo-3,5-dimethylisoxazole and (3,4-dihydro-2H-pyran-6-yl)lithium (A4) according to general procedure B, provided 8f (0.41 mmol, 74 mg, 41%) as orange oil. $R_f = 0.4$ (hexane/EtOAc 95:5 and 1 % NEt$_3$, UV, PAA, KMnO$_4$). $^3$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.80 – 4.78 (t, $J = 3.9$ Hz, 1H), 4.11 – 4.09 (t, $J = 5.1$ Hz, 2H), 2.41 (s, 3H), 2.26 (s, 3H), 2.19 – 2.15 (td, $J = 6.4, 3.9$ Hz, 2H), 1.92 – 1.87 ppm (m, 2H) $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 179.1 (100), 149.8 (21), 135.9 (90), 123.9 (38), 108.9 (22) ppm. LRMS (DEP/El-Orbitrap): m/z [%]: 152.1 (100), 137.1 (45), 117.1 (70), 102.1 (30), 91.1 (10), 75.1 (20), 63.1 (10), 51.1 (10). HRMS (El-Orbitrap): m/z: [M$^+$] Calcd for C$_{10}$H$_{13}$NO$_2$: 179.0946; found: 179.0938. IR (Diamond-ATR, neat) $\tilde{\nu}_{\text{max}}$: 2929 (w), 2848 (w), 1672 (m), 1653 (w), 1646 cm$^{-1}$ (w). Fast decomposition in chloroform was observed.

1,3-Dimethoxy-2-vinylbenzene (9a)

Using 2-bromo-1,3-dimethoxybenzene and vinylmagnesium bromide (A2) according to general procedure C, provided 9a (0.70 mmol, 115 mg, 70%) as yellow oil. $R_f = 0.67$ (hexane/EtOAc 98:2, UV, PAA, KMnO$_4$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.04 (t, $J = 8.3$ Hz, 1H), 6.88 (dd, $J = 18.0, 12.1$ Hz, 1H), 6.44 (d, $J = 8.4$ Hz, 2H), 5.98 (dd, $J = 18.0, 2.8$ Hz, 1H), 5.35 (dd, $J = 12.2, 2.8$ Hz, 1H), 3.72 ppm (s, 6H). LRMS (DEP/El-Orbitrap): m/z [%]: 164.1 (75), 149.1 (100), 121.1 (30), 105.1 (10), 91.1 (95), 78.1 (25), 63.1 (12), 51.1 (10). Analytical data was in agreement with the literature.

2,2-Difluoro-5-vinylbenzo[d][1,3]dioxole (9b)

Using 5-bromo-2,2-difluorobenzo[d][1,3]dioxole and vinylmagnesium bromide (A2) according to general procedure C, provided 9b (0.64 mmol, 118 mg, 64% yield determined by $^{19}$F NMR vs internal standard hexafluorobenzene) as colorless oil. $R_f = 0.68$ (pentane, UV, PAA, KMnO$_4$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.16 (d, $J = 1.6$ Hz, 1H), 7.07 (dd, $J = 8.2, 1.7$ Hz, 1H), 7.00 (d, $J = 8.3$ Hz, 1H), 6.66 (dd, $J = 17.5, 10.8$ Hz, 1H), 5.66 (d, $J = 17.5$ Hz, 1H), 5.25 ppm (d, $J = 10.8$ Hz, 1H). LRMS (DEP/El-Orbitrap): m/z [%]: 184.1 (95), 118.1 (10), 89.1 (100), 63.1 (30), 51.1 (10). Analytical data was in agreement with the literature.

4-(4-Vinylbenzyl)morpholine (9c)

Using 4-(4-bromobenzyl)morpholine and vinylmagnesium bromide (A2) according to general procedure C, provided 9c (0.502 mmol, 102 mg, 50%) as colorless oil. $R_f = 0.26$ (hexane/EtOAc 7:3, UV, PAA, KMnO$_4$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 (d, $J = 8.1$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 2H), 6.64 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.67 (d, $J = 17.6$ Hz, 1H), 5.16 (d, $J = 10.8$ Hz, 1H), 3.64 (t, $J = 4.6$ Hz, 4H), 3.41 (s, 4B. Bieszczad, M. Barbasiewicz Chem. Eur. J. 2015, 21, 10322-10325.
5 G. Wang, R. Shang, Y. Fu Org. Lett. 2018, 20, 888-891.
Using 1-bromo-4-fluoronaphthalene and vinylmagnesium bromide (A2) according to general procedure C, provided 9d (0.63 mmol, 109 mg, 63%) as colorless oil. **Rf** = 0.79 (pentane, UV, PAA, KMnO₄). **¹H NMR** (400 MHz, CDCl₃) δ 8.17 – 8.08 (m, 2H), 7.63 – 7.52 (m, 3H), 7.41 (dd, J = 17.3, 10.9 Hz, 1H), 7.14 (dd, J = 10.4, 8.0 Hz, 1H), 5.76 (dd, J = 17.2, 1.5 Hz, 1H), 5.47 ppm (dd, J = 10.9, 1.4 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 158.70 (d, J = 252.3 Hz), 133.8, 132.13 (dd, J = 45.3, 4.6 Hz), 127.1, 126.18 (d, J = 2.0 Hz), 123.91 (d, J = 2.9 Hz), 123.8, 123.6, 123.5, 121.08 (d, J = 5.6 Hz), 117.06 (d, J = 1.8 Hz), 109.41 (d, J = 20.1 Hz) ppm. **LRMS** (DEP/EI-Orbitrap): m/z [%]: 171.1 (100), 151.1 (5), 85.1 (10), 75.1 (4). Analytical data was in agreement with the literature.

Using 5-bromo-1-methyl-1H-indole and vinylmagnesium bromide (A2) according to general procedure C, provided 9e (0.52 mmol, 82 mg, 52%) as colorless oil. **Rf** = 0.32 (hexane, UV, PAA, KMnO₄). **¹H NMR** (400 MHz, CDCl₃) δ 7.65 (s, 1H), 7.39 (dd, J = 8.5, 1.5 Hz, 1H), 7.28 (d, J = 8.5 Hz, 1H), 7.04 (d, J = 3.1 Hz, 1H), 6.86 (dd, J = 17.6, 10.9 Hz, 1H), 6.49 – 6.48 (m, 1H), 5.72 (dd, J = 17.6, 1.0 Hz, 1H), 5.15 (dd, J = 10.9, 0.9 Hz, 1H), 3.79 ppm (s, 3H). **LRMS** (DEP/EI-Orbitrap): m/z [%]: 158.1 (11), 157.1 (100), 156.1 (33), 154 (12), 130.1 (8), 115.1 (13). Analytical data was in agreement with the literature.

Using 3-bromo-6-chloro-2-methylpyridine and vinylmagnesium bromide (A2) according to general procedure C, provided 9f (0.45 mmol, 69 mg, 45%) as colorless oil. **Rf** = 0.25 (hexane/EtOAc 95:5, UV, KMnO₄). **¹H NMR** (400 MHz, CDCl₃) δ 7.68 (d, J = 8.1 Hz, 1H), 7.15 (d, J = 8.2 Hz, 1H), 6.83 (dd, J = 17.4, 11.0 Hz, 1H), 5.66 (dd, J = 17.5, 0.9 Hz, 1H), 5.42 (dd, J = 11.0, 0.8 Hz, 1H), 2.55 ppm (s, 3H).

6. C. Yang, J. Han, Y. Zhang, H. Yu, S. Hu, X. Wang Chem. Eur. J. 2018, 24, 10324-10328.
7. J.J. Molloy; C. P. Seath, M. J. West; C. McLaughlin, N. J. Fazakerley, A. R. Kennedy, D. J. Nelson, A. J. B. Watson, J. Am. Chem. Soc. 2018, 140, 126-130.
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 156.5, 149.2, 135.7, 132.3, 131.0, 122.0, 117.9, 22.4 ppm. LRMS (DEP/El-Orbitrap): m/z [%]: 153.1 (100), 116.1 (50), 91.1 (25), 77.1 (25), 63.1 (20), 51.1 (25). HRMS (El-Orbitrap): m/z: [M$^+$] Calcd for C$_8$H$_8$ClN$^+$: 153.0345; found: 153.0340.

IR (Diamond-ATR, neat) $\tilde{\nu}_{\text{max}}$: 2924 (vw), 1692 (vw), 1625 (w), 1575 (m), 1441 (vs), 1252 (w), 1146 (s), 986 (m), 893 (vs), 829 (s), 738 (w) 664 cm$^{-1}$ (vw).

1-Methoxy-4-(prop-1-en-2-yl)benzene (9g)

Using 1-bromo-4-methoxybenzene and prop-1-en-2-ylmagnesium bromide (A1) C provided 9g (0.89 mmol, 187 mg, 89%) as white solid. R$_f$ = 0.2 (pentane/Et$_2$O 9:1, UV, PAA, KMnO$_4$). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43 – 7.41 (d, J = 8.8 Hz, 2H), 6.88 – 6.86 (d, J = 8.8 Hz, 2H), 5.29 (s, 1H), 4.99 (s, 1H), 3.82 (s, 3H), 2.13 ppm (s, 3H). LRMS (DEP/El-Orbitrap): m/z [%]: 148.1 (100), 133.1 (82), 115.0 (11), 105.1 (24).

Analytical data was in agreement with the literature.

1,2-Dimethoxy-4-(prop-1-en-2-yl)benzene (9h)

Using 4-bromo-1,2-dimethoxybenzene and prop-1-en-2-ylmagnesium bromide (A1) according to general procedure C provided 9h (0.72 mmol, 128 mg, 72%) as colorless oil.

General procedure C without base (NaOMe) provided 9h in 61%

General procedure G (a) provided 9h in 45%

General procedure G (b) provided 9h in 40%

R$_f$ = 0.79 (hexane/EtOAc 96:4, UV, PAA, KMnO$_4$). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.04 – 7.00 (m, 2H), 6.83 (d, J = 8.8 Hz, 1H), 5.30 (s, 1H), 5.02 (s, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 2.14 ppm (s, 3H). LRMS (DEP/El-Orbitrap): m/z [%]: 178.2 (100), 163.1 (35), 135.1 (14), 115.1 (11), 107.1 (18), 91.1 (36), 77.1 (16). Analytical data was in agreement with the literature.

$N,N$-Dimethyl-4-(prop-1-en-2-yl)aniline (9i)

Using 4-bromo-$N,N$-dimethylaniline and prop-1-en-2-ylmagnesium bromide (A2) according to general procedure C provided 9i (0.63 mmol, 101 mg, 63%) as colorless oil.

General procedure G (a) provided 9i in 31%.

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8 W. J. Kerr, A. J. Morrison, M. Pazicky, T. Weber, Org. Lett 2012, 9, 2250-2253.
9 A. Flores-Gaspar, R. Martin, Adv. Synth. Catal. 2011, 353, 1223–1228.
$R_f = 0.11$ (hexane/EtOAc 99:1, UV, PAA, KMnO₄). $^1$H NMR (400 MHz, CDCl₃) $\delta$ 7.41 (d, $J = 9.0$ Hz, 2H), 6.71 (d, $J = 9.0$ Hz, 2H), 5.28 (s, 1H), 4.93 (s, 1H), 2.97 (s, 6H), 2.14 ppm (s, 3H). LRMS (DEP/EI-Orbitrap): $m/z$ [%]: 161.1 (100), 146.1 (42), 129.9 (10), 114.9 (13), 102.9 (9), 77.1 (11). Analytical data was in agreement with the literature.¹⁰

Using 2-(3-bromophenyl)-1,3-dioxolane and prop-1-en-2-ylmagnesium bromide (A1) according to general procedure C, provided 9j (0.49 mmol, 93 mg, 49%) as colorless oil. $R_f = 0.2$ (hexane, UV, PAA, KMnO₄). $^1$H NMR (400 MHz, CDCl₃) $\delta$ 7.57 (s, 1H), 7.47 (dt, $J = 7.4$, 1.7 Hz, 1H), 7.41 – 7.32 (m, 2H), 5.83 (s, 1H), 5.39 (s, 1H), 5.10 (t, $J = 1.5$ Hz, 1H), 4.18 – 4.01 (m, 4H), 2.16 ppm (s, 3H). $^{13}$C NMR (101 MHz, CDCl₃) $\delta$ 143.1, 141.6, 137.9, 128.4, 126.5, 125.6, 123.7, 113.0, 103.9, 65.5, 22.0 ppm. LRMS (DEP/El-Orbitrap): $m/z$ [%]: 189.2 (100), 175.1 (25), 162.1 (25), 145.1 (65), 134.1 (20), 118.1 (75), 103.1 (15), 91.1 (35), 77.1 (15), 73.1 (60), 63.1 (10), 51.1 (10).

$^1$Phenyl-4-(prop-1-en-2-yl)naphthalene (9k)

Using 1-Bromo-4-phenylnapthalene and prop-1-en-2-ylmagnesium bromide (A1) according to general procedure C provided 9k (0.59 mmol, 133 mg, 59%) as colorless oil. $R_f = 0.75$ (hexane, UV, PAA, KMnO₄). $^1$H NMR (400 MHz, CDCl₃) $\delta$ 8.25 (dd, $J = 8.5$, 1.3 Hz, 1H), 8.08 – 8.01 (m, 1H), 7.63 – 7.55

¹⁰ E. Peyroux, F. Berthiol, H. Doucet, M. Santelli, Eur. J. Org. Chem. 2004, 1075-1082.
Using 1,3-dibromo-5-(prop-1-en-2-yl)benzene and prop-1-en-2-ylmagnesium bromide (A1) according to general procedure D provided 9f (0.34 mmol, 154 mg, 34%) as colorless oil. \( R_f = 0.59 \) (hexane/EtOAc 98:2, UV, PAA, K\textsubscript{2}MnO\textsubscript{4}). \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.17 (t, \( J = 1.6 \) Hz, 1H), 6.94 (t, \( J = 2.0 \) Hz, 1H), 6.89 (t, \( J = 1.9 \) Hz, 1H), 5.34 (s, 1H), 5.09 (s, 1H), 3.79 (s, 3H), 2.09 ppm (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 160.3, 144.4, 142.1, 122.8, 121.4, 115.7, 114.0, 111.0, 55.6, 21.9 ppm. LRMS (DEP/EI-Orbitrap): m/z [%]: 229.0 (11), 228.0 (98), 227.0 (11), 226 (100), 188.0 (15), 186.0 (15). HRMS (EI-Orbitrap): m/z: [M\textsuperscript{+}] Calcd for C\textsubscript{13}H\textsubscript{12}ClF\textsubscript{3}O: 244.2 (70), 244.1250; found: 244.1252. IR (Diamond-ATR, neat) \( \tilde{\nu}_{\text{max}} \): 2938 (br/w), 1599 (m), 1557 (vs), 1560 (s), 1443 (w), 1370 (vw), 1157 (vw), 1031 (w), 902 (m), 842 (m), 767 (vs), 701 cm\textsuperscript{-1} (vs).

Using 3-bromo-6-chloro-2-methylpyridine and prop-1-en-2-ylmagnesium bromide (A1) according to general procedure C provided 9m (0.71 mmol, 119 mg, 71%) as yellow oil. \( R_f = 0.5 \) (hexane,EtOAc 9:1 UV, PAA, K\textsubscript{2}MnO\textsubscript{4}). \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.37 – 7.35 (d, \( J = 8.0 \) Hz, 1H), 7.12 – 7.10 (d, \( J = 8.0 \) Hz, 1H), 5.34 (m, 1H), 4.93 (s, 1H), 2.51 (s, 3H), 1.39 ppm (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 156.2, 148.7, 142.8, 138.5, 137.6, 121.3, 116.9, 24.0, 22.8 ppm. LRMS (DEP/EI-Orbitrap): m/z [%]: 167.0 (100), 151.9 (35), 132.0 (18), 117.0 (68). HRMS (EI-Orbitrap): m/z: [M\textsuperscript{+}] Calcd for C\textsubscript{9}H\textsubscript{7}ClN\textsuperscript{+}: 167.0502; found: 167.0493. IR (Diamond-ATR, neat) \( \tilde{\nu}_{\text{max}} \): 3508 (m), 3484 (m), 3468 (m), 3444 (m), 3416 (m), 3411 (m), 3397 (m), 3275 (w), 1703 (vs), 1675 (m), 1668 (m), 1662 cm\textsuperscript{-1} (m).

Using 5-bromo-2,4-dimethoxypyrimidine and prop-1-en-2-ylmagnesium bromide (A1) according to general procedure C provided 9n (0.74 mmol, 134 mg, 74%) as yellowish oil.

General procedure G (a) provided 9n in 44%.
5-(Prop-1-en-2-yl)benzofuran (9o)

Using 5-bromobenzofuran and prop-1-en-2-ylmagnesium bromide (A1) according to general procedure C provided 9o (0.66 mmol, 104 mg, 66%) as colorless oil. \( R_f = 0.8 \) (hexane, UV, PAA, KMnO₄). \(^1\)H NMR (400 MHz, CDCl₃) \( \delta 7.62 - 7.61 \) (d, \( J = 2.2 \) Hz, 1H), 7.45 - 7.45 (m, 2H), 6.77 - 6.76 (d, \( J = 2.1 \) Hz, 1H), 5.36 (s, 1H), 5.08 (s, 1H), 2.22 ppm (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl₃) \( \delta 140.8, 139.1, 139.0, 137.7, 124.4, 124.3, 123.6, 123.0, 122.7, 114.9, 24.1 \) ppm. LRMS (DEP/El-Orbitrap): \( m/z \) [\%]: 174.1 (100), 159.1 (26), 148.0 (14), 141.1 (60), 134.0 (25). HRMS (El-Orbitrap): \( m/z \) [\%] Calcd for C₉H₉O⁺: 174.0503; found: 174.0496. IR (Diamond-ATR, neat) \( \tilde{\nu}_{\text{max}} \): 3065 (vw), 2969 (w), 2914 (v), 2851 (v), 1941 (v), 1937 (vw), 1910 (vw), 1791 (vw), 1733 (vw), 1700 (vw), 1695 (vw), 1669 cm⁻¹ (w).

3-(Prop-1-en-2-yl)benzo[b]thiophene (9p)

Using 3-bromobenzo[b]thiophene and prop-1-en-2-ylmagnesium bromide (A1) according to general procedure C provided 9p (0.62 mmol, 108 mg, 62%) as yellow oil. \( R_f = 0.7 \) (hexane, UV, PAA, KMnO₄). \(^1\)H NMR (400 MHz, CDCl₃) \( \delta 7.99 - 7.96 \) (d, \( J = 7.5 \) Hz, 1H), 7.86 - 7.86 (d, \( J = 7.5 \) Hz, 1H), 7.40 - 7.33 (m, 2H), 7.30 (s, 1H), 5.36 (s, 1H), 5.33 (s, 1H), 2.22 ppm (s,3H). \(^{13}\)C NMR (101 MHz, CDCl₃) \( \delta 145.4, 143.5, 136.5, 127.4, 122.3, 118.1, 111.9, 110.9, 106.8, 22.4 \) ppm. LRMS (DEP/El-Orbitrap): \( m/z \) [\%]: 179.0732; found: 158.0725. IR (Diamond-ATR, neat) \( \tilde{\nu}_{\text{max}} \): 3083 (vw), 2971 (w), 2858 (vw), 1772 (vw), 1705 (vw), 1652 (vw), 1628 (w),1610 cm⁻¹ (w).

1,3,5-Trimethyl-4-(prop-1-en-2-yl)-1H-pyrazole (9q)

Using 4-bromo-1,3,5-trimethyl-1H-pyrazole and prop-1-en-2-ylmagnesium bromide (A1) according to general procedure C provided 9q (0.48 mmol, 72 mg, 48%) as yellowish oil. General procedure G (a) provided 9q in 55%.

\( R_f = 0.2 \) (pentane/Et₂O 7:3, UV, PAA, KMnO₄). \(^1\)H NMR (400 MHz, CDCl₃) \( \delta 5.13 \) (s, 1H), 4.76 (s, 1H), 3.71 (s, 3H), 2.21 (s, 3H), 2.20 (s, 3H), 1.99 ppm (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl₃) \( \delta 144.6, 137.8, 134.0, 133.0, 132.4, 131.9, 131.0, 130.7, 129.7, 129.2, 128.9, 128.5, 127.3, 126.6, 125.5, 124.4, 123.9, 122.2, 114.9, 24.1 \) ppm. LRMS (DEP/El-Orbitrap): \( m/z \) [\%]: 179.0732; found: 179.0814. IR (Diamond-ATR, neat) \( \tilde{\nu}_{\text{max}} \): 3082 (vw), 2956 (w), 2910 (vw), 1684 (vw), 1662 (vw), 1587 (s), 1552 cm⁻¹ (s).
Using 3-bromo-6-chloro-2-methylpyridine and (1-phenylvinyl)magnesium bromide (A3) according to general procedure C provided 9r (0.70 mmol, 161 mg, 70%) as yellow oil. \( R_f = 0.2 \) (hexane/EtOAc 98:2, UV, PAA, KMnO₄). \(^1\text{H} \text{NMR} \) (400 MHz, CDCl₃) \( \delta 7.48 - 7.46 \) (d, \( J = 8.0 \) Hz, 1H), 7.33 – 7.30 (m, 3H), 7.24 – 7.20 (m, 3H), 5.84 (s, 1H), 5.23 (s, 1H), 2.28 ppm (s, 3H). \(^{13}\text{C} \text{NMR} \) (101 MHz, CDCl₃) \( \delta 157.8 \), 149.5, 146.6, 140.4, 139.4, 135.6, 128.8, 128.4, 128.3, 127.3, 126.5, 24.9 ppm. \( \text{LRMS} \) (DEP/El-Orbitrap): \( m/z \) [%]: 229.0 (24), 214.0 (100), 178.0 (35), 165.0 (13). \( \text{HRMS} \) (El-Orbitrap): \( m/z \) [%]: [M\(^+\)] Calcd for C\(_{14}\)H\(_{12}\)ClN: 229.0658; found: 229.0654. \( \text{IR} \) (Diamond-ATR, neat) \( \bar{\nu}_{\text{max}} \): 3081 (vw), 3056 (vw), 2977 (vw), 2925 (vw), 1809 (vw), 1700 (vw), 1684 (w), 1669 cm\(^{-1}\) (vw).

### 2,4-Dimethoxy-5-(1-phenylvinyl)pyrimidine (9s)

Using 5-bromo-2,4-dimethoxy pyrimidine and (1-phenylvinyl)magnesium bromide (A3) according to general procedure C provided 9s (0.48 mmol, 116 mg, 48%) as yellow solid.

General procedure G (a) provided 9s in 41%. \( R_f = 0.2 \) (hexane/EtOAc 95:5, UV, PAA, KMnO₄). \(^1\text{H} \text{NMR} \) (400 MHz, CDCl₃) \( \delta 8.14 \) (s, 1H), 7.32 – 7.27 (m, 5H), 5.69 (s, 1H), 5.39 (s, 1H), 4.03 (s, 3H), 3.85 ppm (s, 3H). \(^{13}\text{C} \text{NMR} \) (101 MHz, CDCl₃) \( \delta 168.7 \), 164.9, 158.3, 141.9, 139.9, 128.3, 127.9, 126.5, 116.9, 116.3, 54.9, 54.0 ppm. \( \text{LRMS} \) (DEP/El-Orbitrap): \( m/z \) [%]: 242.1 (100), 227.0 (93), 212.1 (18), 170.0 (13). \( \text{HRMS} \) (El-Orbitrap): \( m/z \) [%]: [M\(^+\)] Calcd for C\(_{15}\)H\(_{14}\)N\(_2\)O\(_2\): 242.1055; found: 242.1053. \( \text{IR} \) (Diamond-ATR, neat) \( \bar{\nu}_{\text{max}} \): 3370 (w), 2989 (w), 2956 (w), 2933 (w), 1591 (vs), 1574 (m), 1554 cm\(^{-1}\) (vs). **Melting Point**: 53-56 °C.

### 1,2-Dichloro-4-(1-phenylvinyl)benzene (9t)

Using 4-bromo-1,2-dichlorobenzene and (1-phenylvinyl)magnesium bromide (A3) according to general procedure C provided 9t (0.76 mmol, 189 mg, 76%) as colorless oil. \( R_f = 0.50 \) (hexane, UV, PAA, KMnO₄). \(^1\text{H} \text{NMR} \) (400 MHz, CDCl₃) \( \delta 7.44 \) (d, \( J = 2.1 \) Hz, 1H), 7.40 (d, \( J = 8.3 \) Hz, 1H), 7.38 – 7.33 (m, 3H), 7.33 – 7.28 (m, 2H), 7.17 (dd, \( J = 8.3, 2.1 \) Hz, 1H), 5.50 (d, \( J = 0.9 \) Hz, 1H), 5.47 ppm (d, \( J = 0.9 \) Hz, 1H).
Hz, 1H). **LRMS (DEP/EI-Orbitrap):** m/z [%]: 248.1 (71), 213.1 (49), 178.1 (100), 152.1 (12), 88.1 (24). Analytical data was in agreement with the literature.  

![1-(1-Phenylvinyl)-4-(trifluoromethyl)benzene (9u)](image)

Using 1-bromo-4-(trifluoromethyl)benzene and (1-phenylvinyl)magnesium bromide (A3) according to general procedure C provided 9u (0.53 mmol, 132 mg, 53%) as colorless oil. \( R_f = 0.74 \) (hexane, UV, PAA, KMnO₄). **\(^1\text{H NMR}\)** (400 MHz, CDCl₃) \( \delta \): 7.60 (d, \( J = 8.2 \) Hz, 2H), 7.46 (d, \( J = 8.1 \) Hz, 2H), 7.39 – 7.30 (m, 5H), 5.57 (s, 1H), 5.53 ppm (s, 1H). **LRMS (DEP/EI-Orbitrap):** m/z [%]: 248.1 (99), 233.0 (32), 178.1 (100), 151.1 (16), 89.0 (19), 77.0 (20), 51.0 (17). Analytical data was in agreement with the literature.

![2,4-Dimethoxy-5-(1-(4-methoxyphenyl)vinyl)pyrimidine (9v)](image)

Using 5-bromo-2,4-dimethoxypyrimidine and (1-(4-methoxyphenyl)vinyl)magnesium bromide according to general procedure C provided 9v (0.67 mmol, 183 mg, 67%) as white solid. \( R_f = 0.3 \) (hexane/ETOAc 8:2, UV, PAA, KMnO₄). **\(^1\text{H NMR}\)** (400 MHz, CDCl₃) \( \delta \): 8.14 (s, 1H), 7.21 – 7.19 (d, \( J = 8.8 \) Hz, 2H), 6.85 – 6.82 (d, \( J = 8.8 \) Hz, 2H), 5.61 (s, 1H), 5.27 (s, 1H), 4.02 (s, 3H), 3.86 (s, 3H), 3.81 ppm (s, 3H).

**\(^{13}\text{C NMR}\)** (101 MHz, CDCl₃) \( \delta \): 168.9, 165.0, 159.5, 158.3, 141.4, 132.6, 127.8, 116.7, 115.4, 113.8, 55.4, 55.0, 54.2 ppm. **LRMS (DEP/EI-Orbitrap):** m/z [%]: 272.1 (69), 257.1 (100), 200.1 (10), 173.1 (11). **HRMS (EI-Orbitrap):** m/z: [M⁺] Calcd for \text{C}_{15}\text{H}_{16}\text{N}_{2}\text{O}_{3}⁺: 272.1161; found: 272.1156. IR (Diamond-ATR, neat) \( \tilde{\nu}_{\text{max}} \): 3091 (vw) 3033 (vw), 3006 (w), 2995 (w), 2958 (w), 2937 (w), 2837 (w), 1604 (m), 1591 cm⁻¹ (s). **Melting Point:** 52-55 °C.

![9-Vinylphenanthrene (10a)](image)

Using 9-bromophenanthrene and vinylmagnesium bromide (A2) according to general procedure D provided 10a (0.55 mmol, 112 mg, 55%) as colorless oil. \( R_f = 0.56 \) (hexane, UV, PAA, KMnO₄). **\(^1\text{H NMR}\)** (400 MHz, CDCl₃) \( \delta \): 8.75 (dd, \( J = 7.8, 1.7 \) Hz, 1H), 8.68 (d, \( J = 8.0 \) Hz, 1H), 8.19 (dd, \( J = 7.7, 1.7 \) Hz, 1H), 7.92 (dd, \( J = 7.5, 1.7 \) Hz, 1H), 7.88 (s, 1H), 7.73 – 7.58 (m, 4H), 7.50 (dd, \( J = 17.1, 10.8 \) Hz, 1H), 7.45 (dd, \( J = 10.8, 7.8 \) Hz, 1H), 7.32 (dd, \( J = 17.1, 10.8 \) Hz, 1H).  

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11 P. K. Tiwari, B. Sivaraman, I. S. Aidhen, Eur. J. Org. Chem., 2017, 3594-3605.  
12 D. S. Choi, J. H. Kim, U. S. Shin, R. R. Deshmukh, C. E. Song, Chem. Commun. 2007, 3482–3484.
Using 1-bromo-4-phenylphenanthren and vinylmagnesium bromide (A2) according to general procedure D provided 10b (0.70 mmol, 161 mg, 70%) as colorless oil. \( R_t = 0.31 \) (hexane, UV, PAA, K\text{MnO}_4). \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 8.22 (d, \( J = 8.5 \) Hz, 1H), 7.96 (dd, \( J = 8.5, 1.6 \) Hz, 1H), 7.74 – 7.65 (m, 1H), 7.58 – 7.42 (m, 9H), 5.86 (dd, \( J = 17.3, 1.6 \) Hz, 1H), 5.54 ppm (dd, \( J = 10.9, 1.6 \) Hz, 1H). \(^{13}\)C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 140.9, 140.4, 135.3, 134.6, 131.8, 131.5, 130.2, 128.4, 127.4, 126.9, 126.8, 126.1, 126.0, 124.2, 123.4, 117.3 ppm. LRMS (DEP/El-Orbitrap): m/z [%]: 230.2 (100), 215.2 (15), 202.1 (20), 153.1 (20), 113.1 (10), 101.1 (10). HRMS (El-Orbitrap): m/z: [M\textsuperscript{+}] Calcd for C\textsubscript{18}H\textsubscript{14}N\textsuperscript{+}: 230.1096; found: 230.1092.

IR (Diamond-ATR, neat) \( \bar{\nu}_{\text{max}} \): 1492 (vw), 1443 (vw), 1377 (w), 984 (w), 912 (m), 843 (m), 766 (vs), 700 cm\textsuperscript{-1} (s).

Using 3,6-dibromo-9-phenyl-9H-carbazole and prop-1-en-2-ylmagnesium bromide (A1) according to general procedure D provided 10c (1.20 mmol, 433 mg, 80%) as colorless oil. \( R_t = 0.60 \) (hexane/EtOAc 98:2, UV, PAA, K\text{MnO}_4). \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 8.17 (d, \( J = 1.8 \) Hz, 1H), 8.06 (d, \( J = 1.5 \) Hz, 1H), 7.53 – 7.46 (m, 3H), 7.43 – 7.33 (m, 4H), 7.22 (d, \( J = 8.6 \) Hz, 1H), 7.15 (d, \( J = 8.9 \) Hz, 1H), 5.34 (s, 1H), 5.04 – 5.00 (m, 1H), 2.19 ppm (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 143.49, 140.75, 139.99, 137.31, 133.98, 130.11, 128.74, 127.87, 127.00, 125.38, 124.74, 123.15, 122.30, 117.45, 112.89, 111.46, 109.76, 22.50 ppm. LRMS (DEP/El-Orbitrap): m/z [%]: 361.1 (100), 348.0 (25), 267.1 (35), 241.1 (12), 133.6 (10). HRMS (El-Orbitrap): m/z: [M\textsuperscript{+}] Calcd for C\textsubscript{21}H\textsubscript{16}BrN\textsuperscript{+}: 361.0466; found: 361.0459. IR (Diamond-ATR, neat) \( \bar{\nu}_{\text{max}} \): 3068 (w), 2966 (w), 2359 (m), 2341 (m), 2334 (m), 1624 (m), 1597 (m), 1500 cm\textsuperscript{-1} (vs).
Using 3,6-dibromo-9-phenyl-9H-carbazole and vinylmagnesium bromide (A2) according to general procedure E provided 10d (0.63 mmol, 186 mg, 63%) as yellowish oil. $R_f = 0.5$ (hexane, UV, PAA, KMnO₄). $^1$H NMR (400 MHz, CDCl₃) δ 8.21 (s, 2H), 7.65 – 7.47 (m, 7H), 7.37 (d, $J = 8.5$ Hz, 2H), 6.96 (dd, $J = 17.6$, 10.9 Hz, 2H), 5.85 (d, $J = 17.5$ Hz, 2H), 5.28 ppm (d, $J = 10.9$ Hz, 2H). $^{13}$C NMR (101 MHz, CDCl₃) δ 141.1, 137.5, 137.4, 130.2, 130.0, 127.6, 127.0, 124.5, 123.7, 118.4, 111.7, 110.0 ppm. LRMS (DEP/EI-Orbitrap): m/z [%]: 295.3 (100), 279.1 (5), 267.1 (10), 254.2 (2). HRMS (EI-Orbitrap): m/z: [M⁺] Calcd for $C_{22}H_{17}N$: 295.1361; found: 295.1353.

IR (Diamond-ATR, neat) $\tilde{\nu}_{\text{max}}$: 3040 (vw), 2959 (w), 2926 (w), 2869 (w), 2246 (v), 1684 (w), 1626 (w), 1596 (m), 1569 (w), 1501 cm⁻¹ (s).

Using 2,8-dibromodibenzo[b,d]thiophene and prop-1-en-2-ylmagnesium bromide (A1) according to general procedure provided 10e (0.61 mmol, 161 mg, 61%) as colorless oil. $R_f = 0.5$ (hexane, UV, PAA, KMnO₄). $^1$H NMR (400 MHz, CDCl₃) δ 8.24 (d, $J = 1.7$ Hz, 2H), 7.79 (d, $J = 8.4$ Hz, 2H), 7.62 (dd, $J = 8.4$, 1.8 Hz, 2H), 5.54 (dd, $J = 1.5$, 0.8 Hz, 2H), 5.24 – 5.20 (m, 2H), 2.33 ppm (s, 6H). $^{13}$C NMR (101 MHz, CDCl₃) δ 143.3, 139.0, 138.0, 135.7, 124.7, 122.6, 118.4, 112.7, 22.3 ppm. LRMS (DEP/EI-Orbitrap): m/z [%]: 264.1 (100), 249.2 (30), 234.1 (10), 221.1 (15), 208.1 (35). HRMS (EI-Orbitrap): m/z: [M⁺] Calcd for $C_{18}H_{16}S$: 264.0973; found: 264.0969.

Using 4,4'-oxybis(bromobenzene) and prop-1-en-2-ylmagnesium bromide (A1) prop-1-en-2-ylmagnesium bromide E provided 10f (0.63 mmol, 158 mg, 63%) as colorless solid. $R_f = 0.15$ (hexane, UV, PAA, KMnO₄). $^1$H NMR (400 MHz, CDCl₃) δ 7.44 (d, $J = 8.7$ Hz, 4H), 6.97 (d, $J = 8.7$ Hz, 4H), 5.33 (s, 2H), 5.05 (s, 2H), 2.14 ppm (s, 6H). $^{13}$C NMR (101 MHz, CDCl₃) δ 156.7, 142.5, 136.4, 127.0, 118.6, 111.9, 22.1 ppm. LRMS (DEP/EI-Orbitrap): m/z [%]: 251.1 (20), 250.1 (100), 235.1 (28), 165.1 (9), 115.1 (13). HRMS (EI-Orbitrap): m/z: [M⁺] Calcd for $C_{18}H_{18}O$: 250.1358; found: 250.1353. IR (Diamond-ATR, neat) $\tilde{\nu}_{\text{max}}$: 2971 (w), 2251 (w), 1624 (w), 1596 cm⁻¹ (w). Melting Point: 99-101 °C
Using (4-bromophenyl)(methyl)sulfane and (cyclohexylidenemethyl)lithium\(^ {14} \) (A6) according to general procedure F provided 11a (0.47 mmol, 103 mg, 47%) as colorless oil. \( R_1 = 0.30 \) (hexane, UV, PAA, KMnO\(_4\)). \(^{1} \)H NMR (400 MHz, CDCl\(_3\)) \( \delta 7.23 – 7.18 \) (m, 2H), 7.15 – 7.10 (m, 2H), 6.17 (s, 1H), 2.48 (s, 3H), 2.39 – 2.33 (m, 2H), 2.27 – 2.21 (m, 2H), 1.67 – 1.51 ppm (m, 6H). \(^{13} \)C NMR (101 MHz, CDCl\(_3\)) \( \delta 143.7, 135.6, 135.5, 129.5, 126.7, 121.5, 37.8, 29.6, 28.7, 28.0, 26.8, 16.3 \) ppm. LRMS (DEP/EI-Orbitrap): \( m/z \) [%]: 218.1 (100), 203.1 (2), 189.1 (5), 171.1 (5). HRMS (El-Orbitrap): \( m/z \): [M\(^+\)] Calcd for C\(_{16}\)H\(_{18}\)S\(^+\): 218.1129; found: 218.1119.

![Trimethyl(3-(1-phenylvinyl)phenyl)silane (11b)](image)

Using (3-bromophenyl)trimethylsilane and (1-phenylvinyl)lithium (A7) according to general procedure F provided 11b (0.26 mmol, 65 mg, 51%) as colorless oil. (1-phenylvinyl)lithium was prepared by treating (1-bromovinyl)benzene (1.5 eq.) with n-BuLi (1.5 eq.) in Et\(_2\)O at -78 °C for 30 minutes. \( R_1 = 0.40 \) (hexane, UV, PAA, KMnO\(_4\)). \(^{1} \)H NMR (400 MHz, CDCl\(_3\)) \( \delta 7.53 – 7.51 \) (m, 1H), 7.48 (dt, \( J = 7.0, 1.4 \) Hz, 1H), 7.38 – 7.28 (m, 7H), 5.49 (d, \( J = 1.2 \) Hz, 1H), 5.46 (d, \( J = 1.2 \) Hz, 1H), 0.26 ppm (s, 9H). \(^{13} \)C NMR (101 MHz, CDCl\(_3\)) \( \delta 150.40, 141.56, 140.82, 140.53, 133.20, 132.85, 129.05, 128.34, 128.27, 127.84, 127.60, 114.37, -0.97 ppm. LRMS (DEP/EI-Orbitrap): \( m/z \) [%]: 252.1 (30), 237.1 (100), 178.1 (12), 75.1 (8).

HRMS (El-Orbitrap): \( m/z \): [M\(^+\)] Calcd for C\(_{17}\)H\(_{20}\)Si\(^+\): 252.1334; found: 252.1328. IR (Diamond-ATR, neat) \( \bar{\nu}_{\text{max}} \): 3081 (vw), 3053 (vw), 3023 (vw), 2955 (w), 2896 (vw), 1610 cm\(^{-1}\) (vw).

![3,3',6,6'-Tetrahydro-2H,2'H-4,4'-bipyran (11c)](image)

Under inert atmosphere, 4-bromo-3,6-dihydro-2H-pyran (2 mmol, 1.0 equiv.) was dissolved in a reaction tube in THF (5.0 mL) and the solution was cooled down to -78 °C before adding t-BuLi (4 mmol, 2 eq.) dropwise. The mixture was stirred for 30 min before tributylborate (270 µL, 1.0 mmol, 0.5 equiv.) was added dropwise at -78 °C. The mixture was stirred for 30 min at -78 °C before warming to 0 °C and stirred for another 1 h. Then, cooled back to -78 °C, iodine (1.522 g, 6.0 mmol, 3 equiv.), dissolved in THF (2.0 mL), was added dropwise to the solution. After 20 min a suspension of sodium methoxide (405 mg, 7.5 mmol, 3.75 equiv.) in methanol (2.0 mL) was added at once. The reaction was allowed to reach room temperature. After reaching room temperature the reaction is completed, providing 11c (0.88 mmol, 146 mg, 88%) as greenish oil. \( R_1 = 0.3 \) (hexane/Et\(_2\)O 8:2, UV, PAA, KMnO\(_4\)). \(^{1} \)H NMR (Benzene-\( d_6 \)) \( \delta 5.31 \) (s, 2H), 4.09 (d, \( J = 2.1 \) Hz, 4H), 3.65 (t, \( J = 5.6 \) Hz, 4H), 2.03 – 1.91 ppm (m, 4H).

\(^{13} \)C NMR (101 MHz, \( \text{C}_6\text{D}_6 \)) \( \delta 133.5, 121.0, 65.8, 64.4, 25.5 \) ppm LRMS (DEP/EI-Orbitrap): \( m/z \) [%]:

\[14\] V. Hornillos, M. Giannerini, C. Vila, M. Fananas-Mastral, B. L. Feringa, *Chem Sci* 2015, 6, 1394-1398.
166.1 (40), 137.1 (10), 121.1 (15). **HRMS (El-Orbitrap):** m/z: [M⁺] Calcd for C₁₀H₁₄O₂⁺: 166.0994; found: 166.0988. **IR** (Diamond-ATR, neat) \( \tilde{\nu}_{max} \): 2927 (w), 2848 (w), 1724 (w), 1671 (vw), 1627 cm⁻¹ (w).

**1,2-Dimethoxy-4-(1-phenylvinyl)benzene (12a)**

Using (1-bromovinyl)benzene and (3,4-dimethoxyphenyl)lithium according to general procedure **G (a)** provided 12a (0.50 mmol, 120 mg, 50%) as colourless oil. \( R_f = 0.4 \) (hexane/EtOAc 9:1, UV, PAA, KMnO₄). **¹H NMR** (400 MHz, CDCl₃) \( \delta \): 7.39 – 7.30 (m, 5H), 6.92 – 6.87 (m, 2H), 6.83 (d, \( J = 8.0 \) Hz, 1H), 5.40 (dd, \( J = 10.1, 1.3 \) Hz, 2H), 3.90 (s, 3H), 3.84 ppm (s, 3H).

**¹³C NMR** (101 MHz, CDCl₃) \( \delta \): 149.8, 148.9, 148.6, 141.7, 134.4, 128.4, 128.3, 127.9, 121.0, 113.3, 111.5, 110.8, 56.0 ppm. **LRMS** (DEP/El-Orbitrap): m/z [%]: 240.1 (100), 225.1 (10), 209.1 (5), 193.1 (10), 181.1 (10). **HRMS (El-Orbitrap):** m/z: [M⁺] Calcd for C₁₆H₁₆O₂⁺: 240.1150; found: 240.1140. **IR** (Diamond-ATR, neat) \( \tilde{\nu}_{max} \): 3055 (vw), 2999 (w), 2934 (w), 2835 (w), 1601 cm⁻¹ (w).

**2-(1-(3,4-Dimethoxyphenyl)vinyl)benzo[b]thiophene (12b)**

Using 2-(1-bromovinyl)benzene and (3,4-dimethoxyphenyl)lithium according to general procedure **G (a)** provided 12b (0.52 mmol, 154 mg, 52%) as colorless oil. \( R_f = 0.3 \) (hexane/EtOAc 9:1, UV, PAA, KMnO₄). **¹H NMR** (400 MHz, CDCl₃) \( \delta \): 7.82 – 7.76 (m, 1H), 7.68 – 7.64 (m, 1H), 7.36 – 7.28 (m, 2H), 7.13 (s, 1H), 7.06 (dd, \( J = 8.2, 2.1 \) Hz, 1H), 7.00 (d, \( J = 2.0 \) Hz, 1H), 6.90 (d, \( J = 8.3 \) Hz, 1H), 5.65 (s, 1H), 5.36 (s, 1H), 3.93 (s, 3H), 3.88 ppm (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) \( \delta \): 149.2, 148.7, 145.1, 143.6, 140.2, 139.6, 133.4, 124.8, 124.5, 123.8, 123.6, 122.3, 121.1, 115.3, 111.8, 110.9, 56.1 ppm. **LRMS** (DEP/El-Orbitrap): m/z [%]: 296.1 (100), 281.1 (10), 265.1 (10), 249.0 (10), 237.1 (5). **HRMS (El-Orbitrap):** m/z: [M⁺] Calcd for C₁₈H₁₆O₂S⁺: 296.0871; found: 296.0864. **IR** (Diamond-ATR, neat) \( \tilde{\nu}_{max} \): 3056 (vw), 3000 (w), 2933 (w), 2835 (w), 1601 cm⁻¹ (w).

**4-(Prop-1-en-2-yl)benzonitrile (12c)**

Using 2-bromoprop-1-ene and (4-cyanophenyl)lithium according to general procedure **G (a)** provided 12c (0.35 mmol, 50 mg, 35%) as yellowish oil. \( R_f = 0.5 \) (hexane/EtOAc 9:1, UV, PAA, KMnO₄). **¹H NMR** (400 MHz, CDCl₃) \( \delta \): 7.60 (d, \( J = 8.5 \) Hz, 2H), 7.53 (d, \( J = 8.5 \) Hz, 2H), 5.46 (s, 1H), 5.25–5.24 (m, 1H), 2.15 ppm (s, 3H). **LRMS** (DEP/El-Orbitrap): m/z [%]: 143.1 (100), 127.9 (50), 116.0 (60). Analytical data was in agreement with the literature.¹⁵

¹⁵ G. Pratsch, L. E. Overman *J. Org. Chem.* **2015**, *80*, 11388–11397.
Using 2-bromoprop-1-ene and lithium (4-carboxylatophenyl)lithium according to general procedure G (a) provided 12d (0.53 mmol, 86 mg, 53%) as white solid. \( R_f = 0.3 \) (CH\(_2\)Cl\(_2\)/MeOH 99:1, UV, PAA, KMnO\(_4\)). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.08 (d, \( J = 8.0 \) Hz, 2H), 7.56 (d, \( J = 8.4 \) Hz, 2H), 5.50 (s, 1H), 5.24-5.21 (m, 1H), 2.19 ppm (s, 3H). \( \text{LRMS (DEP/EI-Orbitrap):} \) \( m/z \) [%]: 162.1 (5), 144.0 (5), 133.1 (5), 120.1 (50), 105.0 (100). \textbf{Melting Point:} 158-160 °C. Analytical data was in agreement with the literature.\(^{16}\)

For the following preparation a modified procedure by Keay et al was used.\(^{17}\) In a dry Schlenk-flask \( N^\prime \)-cycloheptylidene-4-methylbenzenesulfonohydrazide (1.0 mmol, 1.0 eq.) was added under nitrogen stream. Then, hexane (2 mL) was added resulting in a suspension. After cooling down to -78 °C, TMEDA (1 mL) was added and the mixture was further stirred for 10 minutes. Then, \( n \)-BuLi (3.0 mol, 3.0 eq.) was added at -78 °C resulting in a red colored solution. After 10 minutes of stirring, the reaction mixture was allowed to reach 0 °C for 15 minutes (N\(_2\) evolving) before cooling down to -78 °C again. B(OBu)\(_3\) was added and after 5 minutes of stirring the solution was allowed to warm to 0 °C. The solvent was

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\(^{16}\) B. Yang, Z. Lu \textit{ACS Catal.}, 2017, 7, 8362–8365; R. L. Letsinger, S. B. Hamilton \textit{J. Am. Chem. Soc.} 1959, 81, 3009-3012.

\(^{17}\) M. S. Passafaro, B. A. Keay, \textit{Tetrahedron Lett.} 1996, 37, 429–432.
removed in vacuo with the Schlenk line. At 0 °C phenylmagnesium bromide (3.0 mmol, 3.0 eq.) was added. The resulting mixture was allowed to reach room temperature after 10 minutes and was stirred for 1 h. After cooling down to -78 °C, iodine (4.0 mmol, 4.0 eq., dissolved in 4 mL THF) was added and stirred for 20 minutes, followed by portionwise addition of sodium methanolate (8.0 mmol, 8.0 eq., dissolved in 5 mL MeOH). The resulting mixture was allowed to reach 0 °C after 10 minutes and was stirred for further 30 minutes. The reaction was then quenched by the addition of saturated solution of Na₂S₂O₃ and extracted with diethyl ether (3 x 20 mL). The combined organic phases were dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel yielding 13 as a colorless liquid (0.29 mmol, 50 mg, 29 %). \( R_f = 0.89 \) (hexane, UV, PAA, KMnO₄). \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 7.29 – 7.18 (m, 4H), 7.16 – 7.07 (m, 1H), 6.02 (t, \( J = 6.8 \) Hz, 1H), 2.59 – 2.45 (m, 2H), 2.29 – 2.15 (m, 2H), 1.76 (p, \( J = 5.9 \) Hz, 2H), 1.61 – 1.52 (m, 2H), 1.52 – 1.40 ppm (m, 2H). \(^{13}\)C NMR (101 MHz, CDCl₃) \( \delta \) 145.1, 130.6, 128.2, 126.4, 125.8, 33.0, 32.9, 29., 27.1, 26.9 ppm. LRMS (DEP/EI-Orbitrap): \text{m/z} [\%]: 172.1 (50), 155.1 (9), 144.1 (74), 143.1 (34), 141.1 (15), 130.1 (23), 129.1 (100). HRMS (EI-Orbitrap): \text{m/z}: [M⁺] Calcld for C_{13}H_{18}: 172.1252; found: 172.1246. IR (Diamond-ATR, neat) \( \tilde{\nu}_{\text{max}} \): 3056 (w), 3024 (w), 2916 (m), 2846 (w), 1639 cm\(^{-1}\) (w).
4. NMR-Spectra

6-Chloro-3-(3,4-dihydro-2H-pyran-6-yl)-2-methylpyridine (8a)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
1,2-Dichloro-4-(1-ethoxyvinyl)benzene (8b)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, Benzene-d$_6$)
2-Chloro-4-(1-ethoxyvinyl)-1-fluorobenzene (8c)

$^1$H NMR (400 MHz, Benzene-d$_6$) and $^{13}$C NMR (101 MHz, Benzene-d$_6$)
6-Phenyl-3,4-dihydro-2H-pyran (8d)

$^1$H NMR (400 MHz, Benzene-d$_6$) and $^{13}$C NMR (101 MHz, Benzene-d$_6$)
5-(3,4-Dihydro-2H-pyran-6-yl)-2,4-dimethoxypyrimidine (8e)

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

![NMR Spectra](image-url)

![Chemical Structure](image-url)
4-(3,4-Dihydro-2H-pyran-6-yl)-3,5-dimethylisoxazole (8f)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
1,3-Dimethoxy-2-vinylbenzene (9a)

$^1H$ NMR (400 MHz, CDCl$_3$)
2,2-Difluoro-5-vinylbenzo[d][1,3]dioxole (9b)

$^1$H NMR (400 MHz, CDCl$_3$)
4-(4-Vinylbenzyl)morpholine (9c)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
1-Fluoro-4-vinynaphthalene (9d)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
1-Methyl-5-vinyl-1H-indole (9e)

$^1$H NMR (400 MHz, CDCl$_3$)
6-Chloro-2-methyl-3-vinylpyridine (9f)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
1-Methoxy-4-(prop-1-en-2-yl)benzene (9g)

$^1$H NMR (400 MHz, CDCl$_3$)
1,2-Dimethoxy-4-(prop-1-en-2-yl)benzene (9h)

\[ ^1H \text{NMR} \ (400 \text{ MHz, CDCl}_3) \]
2-(3-(Prop-1-en-2-yl)phenyl)-1,3-dioxolane (9j)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
1-Phenyl-4-(prop-1-en-2-yl)naphthalene (9k)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
1-Bromo-3-methoxy-5-(prop-1-en-2-yl)benzene (9l)

$^1$H NMR (400 MHz, CDCl₃) and $^{13}$C NMR (101 MHz, CDCl₃)
6-Chloro-2-methyl-3-(prop-1-en-2-yl)pyridine (9m)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
2,4-Dimethoxy-5-(prop-1-en-2-yl)pyrimidine (9n)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
5-(Prop-1-en-2-yl)benzofuran (9o)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
3-(Prop-1-en-2-yl)benzo[b]thiophene (9p)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
1,3,5-Trimethyl-4-(prop-1-en-2-yl)-1H-pyrazole (9q)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
6-Chloro-2-methyl-3-(1-phenylvinyl)pyridine (9r)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
2,4-Dimethoxy-5-(1-phenylvinyl)pyrimidine (9s)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
1,2-Dichloro-4-(1-phenylvinyl)benzene (9t)

$^1$H NMR (400 MHz, CDCl$_3$)
1-(1-Phenylvinyl)-4-(trifluoromethyl)benzene (9u)

$^1$H NMR (400 MHz, CDCl$_3$)
2,4-Dimethoxy-5-(1-(4-methoxyphenyl)vinyl)pyrimidine (9v)

$^{1}H$ NMR (400 MHz, CDCl$_3$) and $^{13}C$ NMR (101 MHz, CDCl$_3$)
9-Vinylphenanthrene (10a)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
1-Phenyl-4-vinylnaphthalene (10b)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
3-Bromo-9-phenyl-6-(prop-1-en-2-yl)-9H-carbazole (10c)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
9-Phenyl-3,6-divinyl-9H-carbazole (10d)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
2,8-Di(prop-1-en-2-yl)dibenzo[\textit{b,d}]thiophene (10e)

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) and \textbf{\textsuperscript{13}C NMR} (101 MHz, CDCl\textsubscript{3})
4,4'-Oxybis(prop-1-en-2-ylbenzene) (10f)

$^1$H NMR (400 MHz, CDCl₃) and $^{13}$C NMR (101 MHz, CDCl₃)
(4-(Cyclohexylidinemethyl)phenyl)(methyl)sulfane (11a)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
Trimethyl(3-(1-phenylvinyl)phenyl)silane (11b)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
3,3',6,6'-Tetrahydro-2H,2'H-4,4'-bipyran (11c)

$^1$H NMR (400 MHz, Benzene-d$_6$) and $^{13}$C NMR (101 MHz, Benzene-d$_6$)
1,2-Dimethoxy-4-(1-phenylvinyl)benzene (12a)

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$)
2-(1-(3,4-Dimethoxyphenyl)vinyl)benzo[b]thiophene (12b)

$^1H$ NMR (400 MHz, CDCl$_3$) and $^{13}C$ NMR (101 MHz, CDCl$_3$)
4-(Prop-1-en-2-yl)benzonitrile (12c)

$^1$H NMR (200 MHz, CDCl$_3$)
1-Phenylcyclohept-1-ene (13)

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