Supporting Information

Decarbonylative Transfer Hydrochlorination of Alkenes and Alkynes Based on a B(C₆F₅)₃-Initiated Grob Fragmentation

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Supporting Information

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1 General Information

Reactions

All reactions were performed in an MBraun glovebox or using conventional Schlenk techniques under a static pressure of argon (glovebox) or nitrogen. Glassware for reactions performed outside the glovebox was dried under vacuum using a heat gun. Glassware for reactions performed inside the glovebox was dried overnight in a 120 °C oven and plastic syringes were dried overnight in a 60 °C oven before being transferred into the glovebox. Liquids and solutions were transferred with either syringes or glass pipettes.

Reagents and Solvents

Standard reagents and solvents were purchased from ABCR, Acros, Alfa Aesar, Merck, Sigma-Aldrich or Tokyo Chemical Industry (TCI). Technical grade solvents for chromatography and extraction were distilled prior to use. Solvents for reactions: CH₂Cl₂, 1,2-F₂C₆H₄ and chlorobenzene were dried over CaH₂, toluene was dried over sodium/benzophenone, distilled, degassed by three freeze-pump-thaw cycles and stored in a glovebox over thermally activated 4 Å molecular sieves; C₆D₆ (purchased from Eurisotop) was degassed by three freeze-pump thaw cycles and stored in a glovebox over thermally activated 4 Å molecular sieves; THF were dried over sodium/benzophenone and freshly distilled prior to use. B(C₆F₅)₃ was purchased from Fluoropharm company and sublimed before use. BCl₃ (1.0M solution in toluene), BEt₃ (1.0M solution in hexane) were purchased from Sigma-Aldrich and used as received.

Chromatography

Analytical thin layer chromatography (TLC) was performed on Alugram® Xtra SIL G/UV₂₅₄ silica gel 60 pre-coated aluminium-backed plates. Flash column chromatography was performed on Grace 60 (40–63 μm, 230–400 mesh, ASTM) silica gel using the indicated solvents.

Nuclear Magnetic Resonance (NMR) Spectroscopy

¹H, ¹³C, and ¹⁹F NMR spectra were recorded in CDCl₃ or C₆D₆ on a Bruker AV400, AV500 or AV 700 instruments. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard (CHCl₃: δ = 7.26 ppm for ¹H NMR
and CDCl₃: δ = 77.16 ppm for ¹³C NMR; C₆D₅H: δ = 7.16 ppm for ¹H NMR and C₆D₆: δ = 128.06 ppm for ¹³C NMR). ¹⁹F chemical shifts are referenced in compliance with the unified scale as recommended by the IUPAC stating the chemical shift relative to CCl₃F.¹⁹ Data are reported as follows: chemical shift, multiplicity (br = broad signal, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration.

**Infrared Spectroscopy**

Infrared (IR) spectra were recorded on an Agilent Technologies Cary 630 FT-IR spectrometer equipped with an ATR unit or a Jasco FT/IR-4100 spectrometer and selected absorption maxima are reported in wavenumbers (cm⁻¹).

**Mass Spectrometry**

High resolution mass spectrometry (HRMS) analysis was performed by the Analytical Facility at the Institut für Chemie, Technische Universität Berlin.
2 Preparation of Surrogates

2.1 Synthesis of cyclohexa-2,5-diene-1-carbonyl Chloride (2aa)

\[ \text{Scheme S1. Synthesis of surrogate 2aa.} \]

2.1.1 Cyclohexa-2,5-diene-1-carboxylic Acid (5aa)

A 500-mL three-neck round bottom flask equipped with a dry ice condenser and a mechanical stirrer was flushed with N₂ for 10 min before being placed in a dry ice/acetone bath (–78 °C). Ammonia (approx. 200 mL) was condensed, and a solution of benzoic acid (10.0 g, 81.9 mmol, 1.0 equiv) in THF (50 mL) was then added dropwise. Then, lithium (2.27 g, 328 mmol, 4.0 equiv) was added portionwise until the deep dark blue of the solution persisted. The mixture was stirred at –78 °C for 1 h, removed from the cold bath and allowed to stir at room temperature overnight for the evaporation of ammonia. Water (100 mL) was added, and the aqueous phase was acidified with HCl (37%, aq.) under ice bath until pH = 2 was achieved. The mixture was extracted with Et₂O (3 × 150 mL), and the combined organic layers were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel with Et₂O/n-pentane = 1:10 as the eluent to afford 5aa as a colorless oil (9.05 g, 89%). The NMR spectroscopic data are in accordance with those reported in the literature. [52]
2.1.2 Cyclohexa-2,5-diene-1-carbonyl Chloride (2aa)

\[
\begin{align*}
\text{O} & \text{Cl} \\
\text{2aa} \\
\text{C}_2\text{H}_2\text{ClO} \\
M = 142.58\text{ g/mol}
\end{align*}
\]

To a solution of cyclohexa-2,5-diene-1-carboxylic acid (5aa, 5.70 g, 45.9 mmol, 1.0 equiv) in dry \(\text{CH}_2\text{Cl}_2\) (90 mL) was added oxalyl chloride (8.5 mL, 101 mmol, 2.2 equiv) dropwise under nitrogen atmosphere. The solution was heated at reflux for 1 h, cooled to room temperature and stirred overnight. The solvent and the excess of oxalyl chloride were removed under vacuum, and the crude product was purified by vacuum distillation (34 °C head, 5.6x10^{-1} mbar) at 50 °C oil-bath temperature to afford 2aa as a colorless liquid (3.99 g, 61%).

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta = 6.06–6.00\) (m, 2H), 5.88–5.83 (m, 2H), 4.18–4.11 (m, 1H), 2.77–2.71 (m, 2H) ppm. \(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)): \(\delta = 173.8, 129.0, 120.3, 53.1, 26.2\) ppm.

\text{HRMS} (APCI) calculated for C\(_7\)H\(_8\)ClO\(^+\) [M+H]\(^+\): 143.0259; found: 143.0258. \text{IR (ATR)}: \(\tilde{\nu} = 3042, 2877, 2817, 1784, 1419, 1012, 923, 784, 719\ \text{cm}^{-1}\).

2.2 Synthesis of 1-methylcyclohexa-2,5-diene-1-carbonyl Chloride (2ab)

\text{Scheme S2. Synthesis of surrogate 2ab.}

2.2.1 1-Methylcyclohexa-2,5-diene-1-carboxylic Acid (5ab)

\[
\begin{align*}
\text{Me} & \text{O} \text{H} \\
\text{5ab} \\
\text{C}_7\text{H}_{15}\text{O}_2 \\
M = 138.17\text{ g/mol}
\end{align*}
\]
A 500-mL three-neck round bottom flask equipped with a dry ice condenser and a mechanical stirrer was flushed with N₂ for 10 min before being placed in a dry ice/acetone bath (−78 °C). Ammonia (approx. 200 mL) was condensed, and a solution of benzoic acid (10.0 g, 81.9 mmol, 1.0 equiv) in THF (50 mL) was then added dropwise. Then, lithium (2.27 g, 328 mmol, 4.0 equiv) was added portionwise until the deep dark blue of the solution persisted. After the mixture was stirred at −78 °C for 1 h, iodomethane (20.4 mL, 328 mmol, 4.0 equiv) was added dropwise. After addition, the mixture was removed from the cold bath and allowed to stir at room temperature overnight for the evaporation of ammonia. Water (100 mL) was added, and the aqueous phase was acidified with HCl (37%, aq.) under ice bath until pH = 2 was achieved. The mixture was extracted with Et₂O (3 × 150 mL) and the combined organic layers were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel with Et₂O/n-pentane = 1:5 as the eluent to afford 5ab as an off-white solid (10.52 g, 93%). The NMR spectroscopic data are in accordance with those reported in the literature.\[^{[S2]}\]

### 2.2.2 1-Methylcyclohexa-2,5-diene-1-carbonyl Chloride (2ab)

![Structure of 1-Methylcyclohexa-2,5-diene-1-carbonyl Chloride (2ab)](image)

Acyl chloride 2ab was synthesized according to a literature procedure\[^{[S3]}\] with some modifications. To a solution of 1-methylcyclohexa-2,5-diene-1-carboxylic acid (5ab, 8.00 g, 57.9 mmol, 1.0 equiv) in dry CH₂Cl₂ (120 mL) was added oxalyl chloride (10.8 mL, 127.4 mmol, 2.2 equiv) dropwise under a nitrogen atmosphere. The solution was heated at reflux for 1 h, cooled to room temperature and stirred overnight. The solvent and the excess of oxalyl chloride were removed under vacuum, and the crude product was purified by vacuum distillation (37 °C head, 5.6x10⁻¹ mbar) at 55 °C oil-bath temperature to afford 2ab as a colorless liquid (6.45 g, 71%).

\[^{1}H\text{ NMR}\] (400 MHz, CDCl₃): δ = 6.00–5.95 (m, 2H), 5.74–5.69 (m, 2H), 2.75–2.71 (m, 2H), 1.44 (s, 3H) ppm. \[^{13}C\text{ NMR}\] (101 MHz, CDCl₃): δ = 177.3, 127.3, 126.9, 54.2, 26.9, 26.2 ppm. \[^{HRMS}\]
(APCI) calculated for C₈H₁₀ClO⁺ [M+H]⁺: 157.0415; found: 157.0414. IR (ATR): ν = 3034, 2981, 2874, 1780, 1452, 1417, 1012, 934, 902, 781, 708 cm⁻¹.

2.3 Synthesis of 1-methylcyclohexa-2,5-diene-1-carbonyl Chloride (2ac)

\[
\begin{align*}
\text{Me} & \quad \text{Li} (4.0 \text{ equiv}) \text{ in NH₃} \\
\text{THF} & \quad \text{–78 °C for 1h} \\
\text{then MeI (4.0 equiv)} & \quad \text{THF} \\
\text{–78 °C to RT overnight} & \quad (\text{COCl})₂ \\
\text{CH₂Cl₂} & \quad \Delta \text{ for 1h then RT overnight}
\end{align*}
\]

Scheme S3. Synthesis of surrogate 2ac.

2.3.1 1,4-Dimethylcyclohexa-2,5-diene-1-carboxylic Acid (5ac)

A 500-mL three-neck round bottom flask equipped with a dry ice condenser and a mechanical stirrer was flushed with N₂ for 10 min before being placed in a dry ice/acetone bath (−78 °C). Ammonia (approx. 200 mL) was condensed, and a solution of 4-methylbenzoic acid (10.9 g, 80.0 mmol, 1.0 equiv) in THF (50 mL) was then added dropwise. Then, lithium (2.27 g, 328 mmol, 4.0 equiv) was added portionwise until the deep dark blue of the solution persisted. After the mixture was stirred at −78 °C for 1 h, iodomethane (19.9 mL, 320 mmol, 4.0 equiv) was added dropwise. After addition, the mixture was removed from the cold bath and allowed to stir at room temperature overnight for the evaporation of ammonia. Water (100 mL) was added, and the aqueous phase was acidified with HCl (37%, aq.) under ice bath until pH = 2 was achieved. The mixture was extracted with Et₂O (3 × 150 mL) and the combined organic layers were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel with Et₂O/n-pentane = 1:6 as the eluent to afford 5ac as a yellow oil (10.82 g, 89%). The NMR spectroscopic data are in
accordance with those reported in the literature.[54]

2.3.2 1,4-Dimethylcyclohexa-2,5-diene-1-carbonyl Chloride (2ac)

![Chemical Structure](image)

To a solution of 1,4-dimethylcyclohexa-2,5-diene-1-carboxylic acid (5ac, 3.50 g, 23.0 mmol, 1.00 equiv) in dry CH$_2$Cl$_2$ (45 mL) was added oxalyl chloride (4.3 mL, 50.6 mmol, 2.2 equiv) dropwise under a nitrogen atmosphere. The solution was heated at reflux for 1 h, cooled to room temperature and stirred overnight. The solvent and the excess of oxalyl chloride were removed under vacuum, and the crude product was purified by vacuum distillation (42 °C head, 5.6x10$^{-1}$ mbar) at 60 °C oil-bath temperature to afford 2ac as a colorless liquid (3.13 g, 80%, d.r. = 56:44).

$^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ = 5.53–5.42 (m, 4H), 2.45–2.38 (m, 0.56H, major diastereomer), 2.35–2.28 (m, 0.44H, minor diastereomer), 1.17 (s, 1.31H, minor diastereomer), 1.16 (s, 1.66H, major diastereomer), 0.85 (d, $J$ = 7.3 Hz, 1.38H, minor diastereomer), 0.75 (d, $J$ = 7.4 Hz, 1.71H, major diastereomer) ppm. $^{13}$C NMR (101 MHz, C$_6$D$_6$, both diastereomers): $\delta$ = 176.5, 176.4, 133.4, 133.0, 125.9, 125.8, 54.5, 54.4, 30.8, 30.6, 26.7, 26.6, 21.0, 20.4 ppm. HRMS (APCI) calculated for C$_9$H$_{12}$ClO$^+$ [M+H]$^+$: 171.0572; found: 171.0570. IR (ATR): $\tilde{\nu}$ = 3028, 2966, 2930, 2875, 1783, 1452, 1371, 940, 902, 788, 734 cm$^{-1}$. 
3 Preparation of Substrates

Figure S1. The collection of substrates.

3.1 General Procedure for the Synthesis of 1b–n and 1p

Scheme S4. Synthesis of alkene substrates.

According to a modified literature procedure, a dried Schlenk flask was charged with a solution of the indicated Grignard reagent (10.0 mmol, 1.0 equiv) in anhydrous THF (0.2M). The solution is cooled to −30 °C, and 3-bromo-2-methylprop-1-ene (12.0 mmol, 1.2 equiv) was
added dropwise under nitrogen atmosphere. The reaction mixture is stirred at −30 °C for 1 h, then slowly warmed to room temperature and stirred overnight. After addition of saturated aqueous NH₄Cl (15 mL), the mixture was extracted with tert-butyl methyl ether (3 × 20 mL). The combined organic phase was washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to give the desired product.

Alkenes 1b[S6], 1c[S5], 1d[S5], 1e[S7], 1f[S5], 1g[S8], 1h[S5], 1i[S7], 1j[S7], 1l–n[S5] and 1p[S9] were synthesized according to the general procedure and spectroscopic data were consistent with those reported.

1-Chloro-3-(2-methylallyl)benzene (1k) was prepared from 3-chlorophenylmagnesium bromide (10.0 mmol, 1.0 equiv) and 3-bromo-2-methylprop-1-ene (1.62 g, 12.0 mmol, 1.2 equiv) according to the general procedure. The title compound 1k was obtained as a colorless oil (1.09 g, 65%). Rf = 0.71 (n-pentane). 1H NMR (400 MHz, CDCl₃): δ = 7.24–7.17 (m, 3H), 7.09–7.06 (m, 1H), 4.85–4.84 (m, 1H), 4.76–4.75 (m, 1H), 3.30 (s, 2H), 1.68 (s, 3H) ppm. 13C NMR (101 MHz, CDCl₃): δ = 144.4, 141.9, 134.2, 129.6, 129.1, 127.2, 126.4, 112.7, 44.4, 22.1 ppm. HRMS (APCI) calculated for C₁₀H₁₂Cl⁺ [M+H]⁺: 167.0622; found: 167.0619. IR (ATR): ν = 3075, 2971, 2908, 1650, 1595, 1572, 1472, 1420, 1374, 1077, 890, 773, 726, 684 cm⁻¹.

Alkenes 1o[S10], 1q[S6], 1r[S11], 1s[S12], 1t[S13], 1u[S14], 1v[S15], 1w[S16], 1x[S17], 1a'[S18] and alkyne 6d[S19] were synthesized according to reported procedures. Alkenes 1y–z, b' and alkyne 6a–c were purchased from commercial suppliers and used as received.
4 Decarbonylative Transfer Hydrochlorination

4.1 General Procedure for the Decarbonylative Transfer Hydrochlorination

Method A (1.2 equiv of 2ab and 5.0 mol% of B(C₆F₅)₃)

In a glovebox, a 1.5-mL GLC vial equipped with a magnetic stir bar was charged with the indicated alkene or alkyne (1.0 equiv) and surrogate 2ab (1.2 equiv). CH₂Cl₂ (0.5 M) was added followed by the addition of B(C₆F₅)₃ (5.0 mol%). The vial was capped, and the solution was stirred in the glovebox at room temperature for 3 h or 24 h (for 1g, 1n, 1t, 1u, and 1x). The reaction was then removed from the glovebox, filtered through a small column (covered with 2.0 cm silica gel) eluting with n-pentane or n-pentane/Et₂O = 5:1 (for 3c, 3g, 3s, 3t, 3u, and 3x), and all volatiles were removed under reduced pressure to obtain the analytically pure alkyl or alkenyl chloride. If necessary, the crude product is purified by flash column chromatography on silica gel.

Method B (1.2 equiv of 2ab and 5.0 mol% of BCl₃)

For the substrates where the corresponding products are unstable towards silica gel.

In a glovebox, a 1.5-mL GLC vial equipped with a magnetic stir bar was charged with the indicated alkene (1.0 equiv) and surrogate 2ab (1.2 equiv). CH₂Cl₂ (0.5 M) was added followed by the addition of BCl₃ (5.0 mol%, 1.0 M in toluene). The vial was capped, and the solution was stirred in the glovebox at room temperature for 3 h. The reaction was then removed from the glovebox, methanol (0.5 mL/mmol) was added to the mixture, and the mixture was stirred for 5 min. All volatiles were removed under reduced pressure to afford the analytically pure alkyl chloride.

Method C (3.0 equiv of 2ab and 20 mol% B(C₆F₅)₃)

In a glovebox, a 1.5-mL GLC vial equipped with a magnetic stir bar was charged with the indicated alkene (0.20 mmol, 1.0 equiv) and surrogate 2ab (3.0 equiv). CH₂Cl₂ (0.4 mL) was added followed by the addition of B(C₆F₅)₃ (20 mol%). The vial was capped, and the solution was stirred in the glovebox at room temperature for 24 h. The reaction was then removed from the glovebox, filtered through a small column (covered with 2.0 cm silica gel) eluting with n-
pentane or \( n \)-pentane/Et\(_2\)O = 5:1 (for 3a’), and all volatiles were removed under reduced pressure to obtain the analytically pure chloroalkane. If necessary, the crude product is purified by flash column chromatography on silica gel.

**Method D** (3.0 equiv of 2ab and 10 mol% of BCl\(_3\))

In a glovebox, a 1.5-mL GLC vial equipped with a magnetic stir bar was charged with 1b’ (28 mg, 0.20 mmol, 1.0 equiv) and surrogate 2ab (94 mg, 0.60 mmol, 3.0 equiv). C\(_6\)D\(_6\) (0.4 mL) was added followed by the addition of BCl\(_3\) (20 \( \mu \)L, 20 \( \mu \)mol, 10 mol%, 1.0 M in toluene). The vial was capped, and the solution was stirred in the glovebox at room temperature for 24 h. The reaction was then removed from the glovebox, methanol (0.1 mL) was added to the mixture, and the mixture was stirred for 5 min. All volatiles were removed under reduced pressure to afford the analytically pure alkyl chloride 3b’.

**Method E** (2.0 equiv of 2ab and 10 mol% of B(C\(_6\)F\(_5\))\(_3\))

In a glovebox, a 1.5-mL GLC vial equipped with a magnetic stir bar was charged with the indicated alkyne (1.0 equiv) and surrogate 2ab (2.0 equiv). CH\(_2\)Cl\(_2\) (0.5 M) was added followed by the addition of B(C\(_6\)F\(_5\))\(_3\) (10 mol%). The vial was capped, and the solution was stirred in the glovebox at room temperature for 24 h. The reaction was then removed from the glovebox, filtered through a small column (covered with 2.0 cm silica gel) eluting with \( n \)-pentane, and all volatiles were removed under reduced pressure to obtain the analytically pure alkenyl chloride.
4.2 Characterization Data of Alkyl Chlorides 3a–z and 3a’,b’ as well as Alkenyl Chlorides 7a–d

(2-Chloro-2-methylpropyl)benzene (3a). Prepared from (2-methylallyl)benzene (1a, 39.7 mg, 0.30 mmol, 1.0 equiv), 2ab (56.4 mg, 0.36 mmol, 1.2 equiv), and B(C$_6$F$_5$)$_3$ (7.7 mg, 15 µmol, 5.0 mol%) according to Method A. 3a was obtained as a colorless oil (39.6 mg, 78%). $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.33–7.24 (m, 5H), 3.07 (s, 2H), 1.57 (s, 6H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): δ = 137.1, 130.9, 128.1, 127.0, 70.2, 52.0, 32.3 ppm. HRMS (APCI) calculated for C$_{10}$H$_{14}$Cl: [M]+: 191.0812; found: 191.0806. IR (ATR): $\tilde{\nu}$ = 2972, 2926, 1494, 1452, 1385, 1368, 1206 cm$^{-1}$. The spectroscopic data are in accordance with those reported.$^{[520]}

1-(2-Chloro-2-methylpropyl)-4-methylbenzene (3b). Prepared from 1-methyl-4-(2-methylallyl)benzene (1b, 29.2 mg, 0.20 mmol, 1.0 equiv), 2ab (37.6 mg, 0.24 mmol, 1.2 equiv), and B(C$_6$F$_5$)$_3$ (5.1 mg, 10 µmol, 5.0 mol%) according to Method A. 3b was obtained as a colorless oil (34.4 mg, 94%). $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.18–7.13 (m, 4H), 3.06 (s, 2H), 2.36 (s, 3H), 1.59 (s, 6H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): δ = 136.5, 134.0, 130.8, 128.8, 70.4, 51.6, 32.2, 21.2 ppm. HRMS (APCI) calculated for C$_{11}$H$_{15}$Cl: [M]+: 182.0857; found: 182.0858. IR (ATR): $\tilde{\nu}$ = 2972, 2924, 1513, 1453, 1384, 1368, 1206, 1110, 839, 821, 794, 756 cm$^{-1}$.

1-(2-Chloro-2-methylpropyl)-4-methoxybenzene (3c). Prepared from 1-methoxy-4-(2-methylallyl)benzene (1c, 32.4 mg, 0.20 mmol, 1.0 equiv), 2ab (37.6 mg, 0.24 mmol, 1.2 equiv), and B(C$_6$F$_5$)$_3$ (5.1 mg, 10 µmol, 5.0 mol%) according to Method A. 3c was obtained as a colorless oil (38.3 mg, 96%). $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.20–7.16 (m, 2H), 6.87–6.84 (m, 2H), 3.81 (s, 3H), 3.02 (s, 2H), 1.56 (s, 6H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): δ = 158.7, 131.9, 129.2, 113.5, 70.6, 55.3, 51.1, 32.2 ppm. HRMS (LIFDI) calculated for C$_{11}$H$_{15}$ClO: [M]+: 198.0806; found: 198.0808. IR (ATR): $\tilde{\nu}$ = 2966, 2927, 1610, 1510, 1459, 1368, 1301, 1246, 1177, 1111, 1035, 840, 799, 760 cm$^{-1}$.
1-Chloro-4-(2-chloro-2-methylpropyl)benzene (3d). Prepared from 1-chloro-4-(2-methylallyl)benzene (1d, 33.3 mg, 0.20 mmol, 1.0 equiv), 2ab (37.6 mg, 0.24 mmol, 1.2 equiv), and B(C₆F₅)₃ (5.1 mg, 10 µmol, 5.0 mol%) according to Method A. 3d was obtained as a colorless oil (37.5 mg, 92%). ¹H NMR (400 MHz, CDCl₃): δ = 7.30–7.27 (m, 2H), 7.21–7.18 (m, 2H), 3.02 (s, 2H), 1.56 (s, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 135.5, 133.0, 132.2, 128.2, 69.7, 51.1, 32.3 ppm. HRMS (APCI) calculated for C₁₀H₁₂Cl₂⁺ [M⁺]: 202.0311; found: 202.0311. IR (ATR): ν = 2972, 2927, 1490, 1460, 1406, 1386, 1369, 1205, 1110, 1093, 1015, 845, 789, 720, 667 cm⁻¹.

1-Bromo-4-(2-chloro-2-methylpropyl)benzene (3e). Prepared from 1-bromo-4-(2-methylallyl)benzene (1e, 42.2 mg, 0.20 mmol, 1.0 equiv), 2ab (37.6 mg, 0.24 mmol, 1.2 equiv), and B(C₆F₅)₃ (5.1 mg, 10 µmol, 5.0 mol%) according to Method A. 3e was obtained as a colorless oil (49.4 mg, >99%). ¹H NMR (400 MHz, CDCl₃): δ = 7.46–7.42 (m, 2H), 7.16–7.12 (m, 2H), 3.01 (s, 2H), 1.56 (s, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 136.0, 132.6, 131.2, 121.1, 69.6, 51.2, 32.3 ppm. HRMS (APCI) calculated for C₁₀H₁₂BrCl⁺ [M⁺]: 245.9806; found: 245.9808. IR (ATR): ν = 2971, 2924, 1486, 1453, 1403, 1386, 1368, 1204, 1110, 1071, 1011, 842, 785, 714 cm⁻¹.

1-(2-Chloro-2-methylpropyl)-4-(trifluoromethyl)benzene (3f). Prepared from 1-(2-methylallyl)-4-(trifluoromethyl)benzene (1f, 40.0 mg, 0.20 mmol, 1.0 equiv), 2ab (37.6 mg, 0.24 mmol, 1.2 equiv), and B(C₆F₅)₃ (5.1 mg, 10 µmol, 5.0 mol%) according to Method A. 3f was obtained as a colorless oil (43.5 mg, 92%). ¹H NMR (400 MHz, CDCl₃): δ = 7.57 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 3.11 (s, 2H), 1.59 (s, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 141.0, 131.3, 129.4 (q, J = 32.5 Hz), 125.0 (q, J = 3.8 Hz), 124.4 (q, J = 272.5 Hz), 69.3, 51.5, 32.4 ppm. ¹⁹F NMR (659 MHz, CDCl₃) δ = -62.44 (s, 3F) ppm. HRMS (APCI) calculated for C₁₁H₁₂F₃⁻ [M-Cl]⁻: 201.0886; found: 201.0888. IR (ATR): ν = 2975, 2928, 1619, 1417, 1322, 1162, 1114, 1067, 1019, 854, 802 cm⁻¹.
Methyl 4-(2-chloro-2-methylpropyl)benzoate (3g). Prepared from 1 methyl 4-(2-methylallyl)benzoate (1g, 38.0 mg, 0.20 mmol, 1.0 equiv), 2ab (37.6 mg, 0.24 mmol, 1.2 equiv), and B(C₆F₅)₃ (5.1 mg, 10 µmol, 5.0 mol%) according to Method A. 3g was obtained as a colorless oil (44.5 mg, 98%). ^1H NMR (400 MHz, CDCl₃): δ = 8.00–7.96 (m, 2H), 7.35–7.32 (m, 2H), 3.91 (s, 3H), 3.11 (s, 2H), 1.57 (s, 6H) ppm. ^13C NMR (101 MHz, CDCl₃): δ = 167.1, 142.3, 131.0, 129.3, 128.9, 69.5, 52.2, 51.7, 32.4 ppm. HRMS (APCI) calculated for C₁₂H₁₆ClO₂⁺ [M⁺H⁺]: 227.0834; found: 227.0835. IR (ATR): v = 2928, 1717, 1609, 1434, 1274, 1179, 1106, 1020, 864, 756, 707 cm⁻¹.

1-(2-Chloro-2-methylpropyl)-2-methylbenzene (3h). Prepared from 1-methyl-2-(2-methylallyl)benzene (1h, 29.2 mg, 0.20 mmol, 1.0 equiv), 2ab (37.6 mg, 0.24 mmol, 1.2 equiv), and B(C₆F₅)₃ (5.1 mg, 10 µmol, 5.0 mol%) according to Method A. 3h was obtained as a colorless oil (35.0 mg, 96%). ^1H NMR (400 MHz, CDCl₃): δ = 7.28–7.25 (m, 1H), 7.20–7.13 (m, 3H), 3.16 (s, 2H), 2.39 (s, 3H), 1.63 (s, 6H) ppm. ^13C NMR (101 MHz, CDCl₃): δ = 137.4, 135.6, 131.9, 130.7, 127.1, 125.5, 71.4, 47.7, 32.6, 20.7 ppm. HRMS (APCI) calculated for C₁₁H₁₅Cl⁺ [M⁺]: 182.0857; found: 182.0858. IR (ATR): v = 2971, 2926, 1493, 1457, 1383, 1368, 1117, 741 cm⁻¹.

1-Bromo-2-(2-chloro-2-methylpropyl)benzene (3i). Prepared from 1-bromo-2-(2-methylallyl)benzene (1i, 42.2 mg, 0.20 mmol, 1.0 equiv), 2ab (37.6 mg, 0.24 mmol, 1.2 equiv), and B(C₆F₅)₃ (5.1 mg, 10 µmol, 5.0 mol%) according to Method A. 3i was obtained as a colorless oil (46.9 mg, 95%). ^1H NMR (400 MHz, CDCl₃): δ = 7.58 (dd, J = 8.0, 1.3 Hz, 1H), 7.50 (dd, J = 7.7, 1.8 Hz, 1H), 7.28 (td, J = 7.5, 1.3 Hz, 1H), 7.13 (td, J = 7.7, 1.8 Hz, 1H), 3.33 (s, 2H), 1.65 (s, 6H) ppm. ^13C NMR (101 MHz, CDCl₃): δ = 136.7, 133.1, 133.0, 128.7, 127.1, 126.2, 71.0, 49.8, 32.6 ppm. HRMS (APCI) calculated for C₁₀H₁₂BrCl⁺ [M⁺]: 245.9806; found: 245.9807. IR (ATR): v = 2973, 2924, 1468, 1434, 1386, 1368, 1110, 1092, 1024, 746 cm⁻¹.
1-(2-Chloro-2-methylpropyl)-3-methylbenzene (3j). Prepared from 1-methyl-3-(2-methylallyl)benzene (1j, 29.2 mg, 0.20 mmol, 1.0 equiv), 2ab (37.6 mg, 0.24 mmol, 1.2 equiv), and B(C\(_6\)F\(_5\))\(_3\) (5.1 mg, 10 µmol, 5.0 mol%) according to Method A. 3j was obtained as a colorless oil (34.1 mg, 93%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ = 7.24–7.18 (m, 1H), 7.11–7.06 (m, 3H), 3.06 (s, 2H), 2.36 (s, 3H), 1.59 (s, 6H) ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): δ = 137.6, 137.0, 131.7, 128.0, 127.9, 127.7, 70.3, 51.9, 32.3 ppm. HRMS (APCI) calculated for C\(_{11}\)H\(_{15}\)Cl\(^+\) [M\(^+\)]: 182.0857; found: 182.0859. IR (ATR): \(\tilde{\nu}\) = 2972, 2924, 1606, 1487, 1454, 1384, 1368, 1107, 783, 742, 701 cm\(^{-1}\).

1-Chloro-3-(2-chloro-2-methylpropyl)benzene (3k). Prepared from 1-chloro-3-(2-methylallyl)benzene (1k, 33.3 mg, 0.20 mmol, 1.0 equiv), 2ab (37.6 mg, 0.24 mmol, 1.2 equiv), and B(C\(_6\)F\(_5\))\(_3\) (5.1 mg, 10 µmol, 5.0 mol%) according to Method A. 3k was obtained as a colorless oil (39.8 mg, 92%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ = 7.31–7.27 (m, 3H), 7.20–7.18 (m, 1H), 3.07 (s, 2H), 1.62 (s, 6H) ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): δ = 139.0, 133.8, 130.9, 129.3, 129.1, 127.2, 69.5, 51.4, 32.3 ppm. HRMS (APCI) calculated for C\(_{10}\)H\(_{12}\)Cl\(^+\) [M\(^+\)]: 202.0311; found: 202.0313. IR (ATR): \(\tilde{\nu}\) = 2972, 2927, 1596, 1572, 1473, 1428, 1386, 1369, 1205, 1107, 1089, 776, 706, 683 cm\(^{-1}\).

2-(2-Chloro-2-methylpropyl)-1,3,5-trimethylbenzene (3l). Prepared from 1,3,5-trimethyl-2-(2-methylallyl)benzene (1l, 34.9 mg, 0.20 mmol, 1.0 equiv), 2ab (37.6 mg, 0.24 mmol, 1.2 equiv), and BCl\(_3\) (10 µL, 10 µmol, 5.0 mol%, 1.0 M in toluene) according to Method B. 3l was obtained as a colorless oil (40.2 mg, 95%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ = 6.89 (s, 2H), 3.28 (s, 2H), 2.39 (s, 6H), 2.28 (s, 3H), 1.65 (s, 6H) ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): δ = 138.1, 136.0, 131.7, 129.5, 73.1, 43.5, 33.5, 21.8, 20.9 ppm. HRMS (APCI) calculated for C\(_{13}\)H\(_{15}\)Cl\(^+\) [M\(^+\)]: 210.1170; found: 210.1174. IR (ATR): \(\tilde{\nu}\) = 2970, 2921, 1611, 1455, 1381, 1368, 1108, 850 cm\(^{-1}\).
1-(2-Chloro-2-methylpropyl)naphthalene (3m). Prepared from 1-(2-methylallylnaphthalene (1m, 36.5 mg, 0.20 mmol, 1.0 equiv), 2ab (37.6 mg, 0.24 mmol, 1.2 equiv), and B(C₆F₅)₃ (5.1 mg, 10 μmol, 5.0 mol%) according to Method A. 3m was obtained as a colorless oil (42.9 mg, 98%). ¹H NMR (400 MHz, CDCl₃): δ = 8.14 (d, J = 8.4 Hz, 1H ), 7.87–7.85 (m, 1H), 7.81–7.78 (m, 1H), 7.54–7.43 (m, 4H), 3.63 (s, 2H), 1.64 (s, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 134.1, 133.5, 133.0, 129.8, 128.9, 127.9, 125.9, 125.5, 125.2, 124.9, 71.3, 47.0, 33.0 ppm. HRMS (APCI) calculated for C₁₄H₁₃Cl⁺ [M⁺]: 218.0857; found: 218.0860. IR (ATR): ν = 2972, 2927, 1594, 1509, 1450, 1386, 1104, 775 cm⁻¹.

2-(2-Chloro-2-methylpropyl)thiophene (3n). Prepared from 2-(2-methylallyl)thiophene (1n, 41.5 mg, 0.30 mmol, 1.0 equiv), 2ab (56.4 mg, 0.36 mmol, 1.2 equiv), and B(C₆F₅)₃ (7.7 mg, 15 μmol, 5.0 mol%) according to Method A. 3n was obtained as a colorless oil (32.7 mg, 62%). ¹H NMR (500 MHz, CDCl₃): δ = 7.21 (dd, J = 5.1, 1.2 Hz, 1H ), 6.98 (dd, J = 5.1, 3.5 Hz, 1H ), 6.93–6.92 (m, 1H), 3.30 (s, 2H), 1.62 (s, 6H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 138.7, 127.9, 126.7, 124.8, 69.5, 46.2, 32.1 ppm. HRMS (LIFDI) calculated for C₇H₇Cl⁺ [M⁺]: 174.0265; found: 174.0269. IR (ATR): ν = 2959, 2923, 1807, 1453, 1385, 1369, 1111, 1018, 694 cm⁻¹.

(3-chloro-3-methylbutyl)benzene (3o). Prepared from (3-methylbut-3-en-1-yl)benzene (1o, 29.2 mg, 0.20 mmol, 1.0 equiv) or (3-methylbut-2-en-1-yl)benzene (1s, 29.2 mg, 0.20 mmol, 1.0 equiv), 2ab (37.6 mg, 0.24 mmol, 1.2 equiv), and B(C₆F₅)₃ (5.1 mg, 10 μmol, 5.0 mol%) according to Method A. 3o was obtained as a colorless oil (from 1o: 34.2 mg, 94%; from 1v: 33.8 mg, 93%). ¹H NMR (400 MHz, CDCl₃): δ = 7.34–7.29 (m, 2H), 7.24–7.20 (m, 3H), 2.87–2.83 (m, 2H), 2.09–2.05 (m, 2H), 1.67 (s, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 141.9, 128.6, 128.5, 126.1, 70.7, 48.1, 32.6, 31.8 ppm. HRMS (APCI) calculated for C₁₁H₁₅Cl⁺ [M⁺]: 182.0857; found: 182.0857. IR (ATR): ν = 2972, 2926, 1496, 1453, 1369, 1111, 746, 698 cm⁻¹. The spectroscopic data are in accordance with those reported.[S21]
2-Chloro-2-methylnonane (3p). Prepared from 2-methylnon-1-ene (1p, 42.1 mg, 0.30 mmol, 1.0 equiv) or 2-methylnon-2-ene (1t, 42.1 mg, 0.30 mmol, 1.0 equiv), 2ab (56.4 mg, 0.36 mmol, 1.2 equiv), and B(C₆F₅)₃ (7.7 mg, 15 µmol, 5.0 mol%) according to Method A. 3p was obtained as a colorless oil (from 1p: 41.6 mg, 78%; from 1w: 34.8 mg, 66%). ¹H NMR (400 MHz, CDCl₃): δ = 1.75–1.71 (m, 2H), 1.56 (s, 6H), 1.50–1.43 (m, 2H), 1.35–1.23 (m, 8H), 0.89 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 71.5, 46.3, 32.6, 32.0, 29.8, 29.4, 25.3, 22.8, 14.2 ppm. HRMS (APCI) calculated for C₁₀H₂₁⁺ [M-Cl]⁺: 141.1638; found: 141.1637. IR (ATR): ν = 2924, 2854, 1463 cm⁻¹.

(2-Chloro-2-methylpropane-1,3-diyl)dibenzene (3q). Prepared from (2-methylene)propane-1,3-diyl)dibenzene (1q, 41.7 mg, 0.20 mmol, 1.0 equiv), 2ab (37.6 mg, 0.24 mmol, 1.2 equiv), and B(C₆F₅)₃ (5.1 mg, 10 µmol, 5.0 mol%) according to Method A. 3q was obtained as a colorless oil (49.5 mg, quant.). ¹H NMR (400 MHz, CDCl₃): δ = 7.36–7.28 (m, 10H), 3.18 (d, J = 13.8 Hz, 2H), 3.09 (d, J = 13.8 Hz, 2H), 1.46 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 136.7, 131.4, 128.1, 127.1, 72.9, 50.7, 29.1 ppm. HRMS (APCI) calculated for C₁₆H₁₇Cl⁺ [M]⁺: 244.1014; found: 244.1015. IR (ATR): ν = 3027, 2921, 1492, 1451, 1377, 1082, 750, 736, 697 cm⁻¹.

1-Chloro-1-methylcyclooctane (3r). Prepared from methylenecyclooctane (1r, 37.3 mg, 0.30 mmol, 1.0 equiv), 2ab (56.4 mg, 0.36 mmol, 1.2 equiv), and BCl₃ (15 µL, 15 µmol, 5.0 mol%, 1.0 M in toluene) according to Method B. 3r was obtained as a colorless oil (35.6 mg, 74%). ¹H NMR (400 MHz, CDCl₃): δ = 2.21–2.11 (m, 2H), 1.91–1.82 (m, 2H), 1.75–1.41 (m, 13H). ¹³C NMR (101 MHz, CDCl₃): δ = 76.8, 40.4, 32.7, 28.2, 24.9, 23.7 ppm. HRMS (LIFDI) calculated for C₉H₁₇⁺ [M-Cl]⁺: 125.1325; found: 125.1325. IR (ATR): ν = 2918, 2852, 1445, 1109 cm⁻¹.
**3s**

**tert-Butyl(3-chloro-3-methylbutoxy)diphenylsilane (3s).** Prepared from *tert*-butyl((3-methylbut-3-en-1-yl)oxy)diphenylsilane (1s, 32.5 mg, 0.10 mmol, 1.0 equiv), 2ab (18.8 mg, 0.12 mmol, 1.2 equiv), and B(C$_6$F$_5$)$_3$ (2.6 mg, 5 µmol, 5.0 mol%) according to **Method A.** 3s was obtained as a colorless oil (36.1 mg, 100%).

**1H NMR** (400 MHz, CDCl$_3$): δ = 7.70–7.68 (m, 4H), 7.45–7.38 (m, 6H), 3.91 (t, $J = 6.8$ Hz, 2H), 2.08 (t, $J = 6.8$ Hz, 2H), 1.60 (s, 6H), 1.07 (s, 9H) ppm.

**13C NMR** (101 MHz, CDCl$_3$): δ = 135.7, 133.8, 129.8, 127.8, 69.7, 61.2, 48.1, 33.2, 27.0, 19.3 ppm.

**HRMS** (APCI) calculated for C$_{21}$H$_{30}$ClOSi$^+$ [M+H]$^+$: 361.1749; found: 361.1748.

**IR** (ATR): $\tilde{\nu}$ = 2929, 2888, 2855, 1470, 1427, 1388, 1107, 833, 738, 701 cm$^{-1}$. The spectroscopic data are in accordance with those reported.

**3t**

**((3-Chloro-3-methylbutoxy)methyl)benzene (3t).** Prepared from ((3-methylbut-3-en-1-yl)oxy)methyl)benzene (1t, 35.3 mg, 0.20 mmol, 1.0 equiv), 2ab (37.6 mg, 0.24 mmol, 1.2 equiv), and B(C$_6$F$_5$)$_3$ (10.2 mg, 20 µmol, 10.0 mol%) according to **Method A.** The crude product needs to be purified by flash column chromatography on silica gel with Et$_2$O/n-pentane = 1:50 as the eluent to afford 3t as a colorless oil (30.8 mg, 72%). $R_f = 0.42$ (50:1 n-pentane:Et$_2$O).

**1H NMR** (400 MHz, CDCl$_3$): δ = 7.38–7.27 (m, 5H), 4.52 (s, 2H), 3.72 (t, $J = 6.7$ Hz, 2H), 2.12 (t, $J = 6.7$ Hz, 2H), 1.62 (s, 6H) ppm.

**13C NMR** (101 MHz, CDCl$_3$): δ = 138.5, 128.5, 127.8, 127.7, 73.2, 69.6, 67.6, 45.3, 33.1 ppm.

**HRMS** (APCI) calculated for C$_{12}$H$_{18}$ClO$_2$ [M+H]$^+$: 213.1041; found: 213.1043. **IR** (ATR): $\tilde{\nu}$ = 2970, 2888, 2855, 1470, 1427, 1388, 1107, 833, 738, 687 cm$^{-1}$. The spectroscopic data are in accordance with those reported.

**3u**

**3-Chloro-3-methylbutyl pivalate (3u).** Prepared from 3-methylbut-3-en-1-yl pivalate (1u, 34.1 mg, 0.20 mmol, 1.0 equiv), 2ab (37.6 mg, 0.24 mmol, 1.2 equiv), and B(C$_6$F$_5$)$_3$ (10.2 mg, 20 µmol, 10.0 mol%) according to **Method A.** 3u was obtained as a light yellow oil (38.9 mg, 94%).

**1H NMR** (400 MHz, CDCl$_3$): δ = 4.29 (t, $J = 6.8$ Hz, 2H), 2.10 (t, $J = 6.8$ Hz, 2H), 1.62 (s, 6H), 1.19 (s, 9H) ppm.

**13C NMR** (101 MHz, CDCl$_3$): δ = 178.6, 68.7, 61.6, 44.2, 38.8, 33.0, 27.3 ppm. **HRMS** (APCI) calculated for C$_{10}$H$_{19}$ClO$_2$ [M+H]$^+$: 207.1147; found: 207.1146. **IR** (ATR): $\tilde{\nu}$ = 2960, 2921, 2852, 1730, 1459, 1368, 1113, 1028, 736, 687 cm$^{-1}$. The spectroscopic data are in accordance with those reported.
2-(4-Chloro-4-methylpentyl)isoindoline-1,3-dione (3x).
Prepared from 2-(4-methylpent-3-en-1-yl)isoindoline-1,3-dione (1x, 22.7 mg, 0.10 mmol, 1.0 equiv), 2ab (18.8 mg, 0.12 mmol, 1.2 equiv), and B(C₆F₅)₃ (5.1 mg, 10 µmol, 10.0 mol%) according to Method A. 3x was obtained as a white solid (24.6 mg, 93%). M.P. = 86–88 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.86–7.81 (m, 2H), 7.73–7.68 (m, 2H), 3.71 (t, J = 6.9 Hz, 2H), 1.94–1.85 (m, 2H), 1.80–1.76 (m, 2H), 1.55 (s, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 168.5, 134.1, 132.2, 123.4, 70.2, 43.1, 38.0, 32.5, 24.7 ppm. HRMS (APCI) calculated for C₁₄H₁₅ClNO₂⁺ [M+H]⁺: 266.0942; found: 266.0941. IR (ATR): v = 2971, 2930, 1772, 1707, 1466, 1437, 1395, 1360, 1083, 1030, 719 cm⁻¹. The spectroscopic data are in accordance with those reported.[S22]

1-(2-Chloropropyl)naphthalene (3y). Prepared from 1-allylnaphthalene (1y, 41.7 mg, 0.20 mmol, 1.0 equiv), 2ab (94.0 mg, 0.60 mmol, 3.0 equiv), and B(C₆F₅)₃ (20.5 mg, 40 µmol, 20 mol%) according to Method C. 3y was obtained as a colorless oil (40.1 mg, 98%). ¹H NMR (400 MHz, CDCl₃): δ = 8.04–8.02 (m, 1H), 7.91–7.89 (m, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.59–7.50 (m, 2H), 7.47–7.44 (m, 1H), 7.41–7.39 (m, 1H), 4.49–4.41 (m, 1H), 3.66 (dd, J = 14.1, 6.5 Hz, 1H), 3.41 (dd, J = 14.1, 7.8 Hz, 1H), 1.57 (d, J = 6.5 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 134.2, 134.1, 132.0, 129.1, 128.0, 127.9, 126.3, 125.8, 125.5, 123.6, 57.7, 44.1, 25.1 ppm. HRMS (APCI) calculated for C₁₃H₁₃Cl⁺ [M⁺]⁺: 204.0701; found: 204.0701. IR (ATR): v = 2971, 2925, 1595, 1509, 1443, 1394, 1376, 1013, 792, 773 cm⁻¹.

(3-Chlorobutyl)benzene (3z). Prepared from but-3-en-1-ylbenzene (1z, 26.4 mg, 0.20 mmol, 1.0 equiv), 2ab (94.0 mg, 0.60 mmol, 3.0 equiv), and B(C₆F₅)₃ (20.5 mg, 40 µmol, 20 mol%) according to Method C. 3z was obtained as a colorless oil (29.6 mg, 88%). ¹H NMR (400 MHz, CDCl₃): δ = 7.33–7.27 (m, 2H), 7.24–7.19 (m, 3H), 4.05–3.97 (m, 1H), 2.90–2.83 (m, 1H), 2.80–2.72 (m, 1H), 2.06–2.00 (m, 2H), 1.54 (d, J = 6.6 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 141.2, 128.6, 128.6, 126.2, 58.1, 42.0, 33.0, 25.6 ppm. HRMS (LIFDI) calculated for C₁₀H₁₃Cl⁺ [M⁺]: 168.0701; found: 168.0700. IR (ATR): v = 2969, 2925, 1494, 1452, 746, 689 cm⁻¹. The spectroscopic data are in accordance with those reported.[S21]
5-Chlorohexyl pivalate (3a’). Prepared from hex-5-en-1-yl pivalate (1a’, 36.9 mg, 0.20 mmol, 1.0 equiv), 2ab (94.0 mg, 0.60 mmol, 3.0 equiv), and B(C₆F₅)₃ (20.5 mg, 40 µmol, 20.0 mol%) according to Method C. The crude product needs to be purified by flash column chromatography on silica gel with Et₂O/n-pentane = 1:50 as the eluent to afford 3a’ as a colorless oil (35.7 mg, 81%). Rᵣ = 0.30 (50:1 n-pentane:Et₂O). ¹H NMR (400 MHz, CDCl₃): δ = 4.10–3.98 (m, 3H), 1.79–1.44 (m, 9H), 1.20 (s, 9H) ppm. ³¹C NMR (101 MHz, CDCl₃): δ = 178.7, 64.1, 58.6, 40.0, 38.9, 28.3, 27.3, 25.5, 23.2 ppm. HRMS (APCI) calculated for C₁₃H₂₂ClO₂⁺ [M⁺H]⁺: 221.1303; found: 221.1303. IR (ATR): ν = 2969, 2933, 2870, 1727, 1479, 1459, 1284, 1155 cm⁻¹.

1-Chloro-3-(1-chloroethyl)benzene (3b’). Prepared from 1-chloro-3-vinylbenzene (1b’, 28 mg, 0.20 mmol, 1.0 equiv), 2ab (94 mg, 0.60 mmol, 3.0 equiv), and BCl₃ (20 µL, 20 µmol, 10 mol%, 1.0 M in toluene) according to Method D. 3b’ was obtained as a colorless oil (22.9 mg, 65%). ¹H NMR (400 MHz, CDCl₃): δ = 7.42–7.41 (m, 1H), 7.30–7.27 (m, 3H), 5.04 (q, J = 6.8 Hz, 1H) 1.83 (d, J = 6.8 Hz, 3H) ppm. ³¹C NMR (101 MHz, CDCl₃): δ = 144.9, 134.6, 130.1, 128.5, 126.9, 124.9, 57.8, 26.6 ppm. HRMS (LIFDI) calculated for C₆H₅Cl₂⁺ [M⁺Cl]⁺: 173.9998; found: 173.9997. IR (ATR): ν = 2962, 2925, 2854, 1595, 1573, 1476, 1431, 1082, 786, 696 cm⁻¹. The spectroscopic data are in accordance with those reported.⁵²₃

(1-Chloroprop-1-en-1-yl)benzene (7a). Prepared from prop-1-yn-1-ylbenzene (6a, 34.85 mg, 0.30 mmol, 1.0 equiv), 2ab (56.4 mg, 0.36 mmol, 1.2 equiv), and B(C₆F₅)₃ (7.7 mg, 15 µmol, 5.0 mol%) according to Method A. 7a was obtained as a yellow oil (27.4 mg, 60%, E/Z = 72:28 ), the ratio of E/Z was determined by ¹H NMR analysis according to the reported literature.⁵²¹ (E)-7a: ¹H NMR (400 MHz, CDCl₃): δ = 7.43–7.34 (m, 5H), 6.05 (q, J = 7.3 Hz, 1H), 1.74 (d, J = 7.3 Hz, 3H) ppm. ³¹C NMR (101 MHz, CDCl₃): (E-7a) δ = 137.2, 131.0, 129.0, 128.5, 128.3, 124.7, 15.5 ppm. (Z)-7a: ¹H NMR (400 MHz, CDCl₃): δ = 7.58–7.55 (m, 2H), 7.34–7.30 (m, 3H), 6.21 (q, J = 6.7 Hz, 1H), 1.97 (d, J = 6.7 Hz, 3H) ppm. ³¹C NMR (101 MHz, CDCl₃): δ = 138.6, 133.9, 129.0, 128.4, 126.4, 122.5, 15.3 ppm. HRMS (APCI) calculated for C₅H₁₀Cl⁺ [M⁺H]⁺: 153.0466; found: 153.0466. IR (ATR): ν =3058, 3023,
(1-Chloropent-1-en-1-yl)benzene (7b). Prepared from pent-1-yn-1-ylbenzene (6b, 43.3 mg, 0.30 mmol, 1.0 equiv), 2ab (56.4 mg, 0.36 mmol, 1.2 equiv), and B(C₆F₅)₃ (7.7 mg, 15 µmol, 5.0 mol%) according to Method A. 7b was obtained as a yellow oil (49.8 mg, 92%, E/Z = 85:15), the stereochemistry of 7b was determined by 2D-NMR analysis and the ratio of E/Z was determined by ¹H NMR analysis. (E)-7b: ¹H NMR (400 MHz, CDCl₃): δ = 7.41–7.33 (m, 5H), 5.98 (t, J = 7.8 Hz, 1H ), 2.12–2.06 (m, 2H ), 1.44 (dq J = 7.4 Hz, 2H ), 0.90 (t, J = 7.4 Hz, 3H ) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 137.5, 130.4, 128.9, 128.5, 128.3, 126.5, 31.9, 22.9, 13.8 ppm. (Z)-7b: ¹H NMR (400 MHz, CDCl₃): δ = 7.60–7.57 (m, 2H ), 7.33–7.30 (m, 3H), 6.16 (t, J = 7.0 Hz, 1H ), 2.42–2.36 (m, 2H ), 1.55 (dq J = 7.4 Hz, 2H ), 1.01 (t, J = 7.4 Hz, 3H ) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 138.6, 132.9, 130.5, 128.4, 128.3, 128.1, 31.8, 22.0, 14.0 ppm. HRMS (APCI) calculated for C₁₁H₁₄Cl⁺ [M+H]⁺: 181.0779; found: 181.0777. IR (ATR): ʋ = 2958, 2928, 2859, 1442, 758, 695 cm⁻¹.

(E)-(1-Chloroethene-1,2-diyl)dibenzene (7c). Prepared from 1,2-diphenylethyne (6c, 35.6 mg, 0.20 mmol, 1.0 equiv), 2ab (62.6 mg, 0.40 mmol, 2.0 equiv), and B(C₆F₅)₃ (10.2 mg, 20 µmol, 10 mol%) according to Method E. 7c was obtained as a colorless oil (41.4 mg, 96%, E/Z = 96:4), the ratio of E/Z was determined by ¹H NMR analysis according to the reported literature.[⁵²⁵] ¹H NMR (400 MHz, CDCl₃): (E-7c) δ = 7.43–7.39 (m, 2H), 7.36–7.32 (m, 3H), 7.18–7.15 (m, 3H), 7.04–7.01 (m, 2H ), 6.97 (s, 1H ) ppm. ¹³C NMR (101 MHz, CDCl₃): (E-7c) δ = 137.9, 135.5, 133.2, 131.7, 129.3, 129.0, 128.9, 128.7, 128.4, 127.5. HRMS (APCI) calculated for C₁₄H₁₂Cl⁺ [M+H]⁺: 215.0623; found: 215.0625. IR (ATR): ʋ = 1492, 1443, 932, 898, 754, 712, 688 cm⁻¹.

4,4′-(1-Chloroethene-1,2-diyl)bis(methylbenzene) (7d). Prepared from 1,2-di-p-tolylethyne (6d, 20.6 mg, 0.1 mmol, 1.0 equiv), 2ab (56.4 mg, 0.2 mmol, 2.0 equiv), and B(C₆F₅)₃ (5.1 mg, 10 µmol, 10 mol%) according to Method E. 7d was obtained as a colorless oil (23.1 mg, 95%, E/Z = 85:15), the ratio of E/Z was determined by ¹H NMR analysis.
according to the reported literature.\textsuperscript{[S26]} (E)-7d: \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ = 7.30–7.28 (m, 2H), 7.14–7.12 (m, 2H), 6.98–6.96 (m, 2H), 6.92–6.91 (m, 2H ), 6.88 (s, 1H ), 2.37 (s, 3H ), 2.27 (s, 3H ) ppm. \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): (E-7d) δ = 139.0, 137.3, 135.2, 132.8, 132.5, 129.4, 129.2, 129.1, 128.8, 128.6, 21.5, 21.3 ppm. (Z)-7d: \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ = 7.66–7.64 (m, 2H), 7.61–7.58 (m, 2H), 7.22–7.20 (m, 4H), 7.01 (s, 1H ), 2.40 (s, 3H ), 2.39 (s, 3H ) ppm. \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): δ = 138.8, 138.0, 136.8, 129.5, 129.1, 126.7, 125.3, 29.9 ppm (Due to the low concentration of the minor isomer, not all signals could be detected).

HRMS (APCI) calculated for C\textsubscript{16}H\textsubscript{16}Cl\textsuperscript{+} [M+H]\textsuperscript{+}: 243.0936; found: 243.0934. IR (ATR): \tilde{\nu} = 2918, 1510, 913, 808, 789, 751, 713 cm\textsuperscript{-1}. 


5 Scale-Up Experiment

In a glovebox, a 10-mL sealed tube equipped with a magnetic stir bar was charged with 1-(2-methylallyl)naphthalene (1m, 364 mg, 2.00 mmol, 1.0 equiv) and surrogate 2ab (375.9 mg, 24.00 mmol, 1.2 equiv). CH$_2$Cl$_2$ (4 mL) was added followed by the addition of B(C$_6$F$_5$)$_3$ (51.2 mg, 100 µmol, 5.0 mol%). The tube was sealed and removed from the glovebox. The solution was stirred at room temperature for 3 h, and then filtered through a short column (covered with 2.0 cm silica gel) eluting with n-pentane, and all volatiles were removed under reduced pressure to afford 3m as a colorless oil (408.3 mg, 93%).

Scheme 5. Scale-up experiment.
6 NMR Spectra

Figure S2. Cyclohexa-2,5-diene-1-carbonyl chloride (2aa): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S3. Cyclohexa-2,5-diene-1-carbonyl chloride (2aa): $^{13}\text{C}^{('}{\text{H}})$ NMR (101 MHz, CDCl$_3$, 298 K)
Figure S4. 1-Methylcyclohexa-2,5-diene-1-carbonyl chloride (2ab): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S5. 1-Methylcyclohexa-2,5-diene-1-carbonyl chloride (2ab): $^{13}\text{C}^{(1\text{H})}$ NMR (101 MHz, CDCl$_3$, 298 K)
Figure S6. 1,4-Dimethylcyclohexa-2,5-diene-1-carbonyl chloride (2ac): \(^1\)H NMR spectrum (500 MHz, \(\text{C}_6\text{D}_6\), 298 K)
Figure S7. 1,4-Dimethylcyclohexa-2,5-diene-1-carbonyl chloride (2ac): $^{13}$C($^1$H) NMR (101 MHz, C$_6$D$_6$, 298 K)
Figure S8. 1-Chloro-3-(2-methylallyl)benzene (1k): ¹H NMR spectrum (400 MHz, CDCl₃, 298 K)
Figure S9. 1-Chloro-3-(2-methylallyl)benzene (1k): $^{13}\text{C}\{}^1\text{H}\}$ NMR (101 MHz, CDCl$_3$, 298 K)
Figure S10. (2-Chloro-2-methylpropyl)benzene (3a): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S11. (2-Chloro-2-methylpropyl)benzene (3a): $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K)
Figure S12. 1-(2-Chloro-2-methylpropyl)-4-methylbenzene (3b): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S13. 1-(2-Chloro-2-methylpropyl)-4-methylbenzene (3b): $^{13}$C{H} NMR (101 MHz, CDCl$_3$, 298 K)
Figure S14. 1-(2-Chloro-2-methylpropyl)-4-methoxybenzene (3c): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S15. 1-(2-Chloro-2-methylpropyl)-4-methoxybenzene (3c): $^{13}$C{\textsuperscript{1}H} NMR (101 MHz, CDCl$_3$, 298 K)
Figure S16. 1-Chloro-4-(2-chloro-2-methylpropyl)benzene (3d): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S17. 1-Chloro-4-(2-chloro-2-methylpropyl)benzene (3d): $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K)
Figure S18. 1-Bromo-4-(2-chloro-2-methylpropyl)benzene (3e): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S19. 1-Bromo-4-(2-chloro-2-methylpropyl)benzene (3e): $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K)
Figure S20. 1-(2-Chloro-2-methylpropyl)-4-(trifluoromethyl)benzene (3f): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S21. 1-(2-Chloro-2-methylpropyl)-4-(trifluoromethyl)benzene (3f): $^{13}$C$^{1}$H NMR (101 MHz, CDCl$_3$, 298 K)
Figure S22. 1-(2-Chloro-2-methylpropyl)-4-(trifluoromethyl)benzene (3f): $^{19}$F NMR (695 MHz, CDCl$_3$, 298 K)
Figure S23. Methyl 4-(2-chloro-2-methylpropyl)benzoate (3g): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S24. Methyl 4-(2-chloro-2-methylpropyl)benzoate (3g): $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K)
Figure S25. 1-(2-Chloro-2-methylpropyl)-2-methylbenzene (3h): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S26. 1-(2-Chloro-2-methylpropyl)-2-methylbenzene (3h): $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K)
Figure S27. 1-Bromo-2-(2-chloro-2-methylpropyl)benzene (3i): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S28. 1-Bromo-2-(2-chloro-2-methylpropyl)benzene (3i): $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl$_3$, 298 K)
Figure S29. 1-(2-Chloro-2-methylpropyl)-3-methylbenzene (3j): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S30. 1-(2-Chloro-2-methylpropyl)-3-methylbenzene (3j): $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K)
Figure S31. 1-Chloro-3-(2-chloro-2-methylpropyl)benzene (3k): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S32. 1-Chloro-3-(2-chloro-2-methylpropyl)benzene (3k): $^{13}$C{H} NMR (101 MHz, CDCl₃, 298 K)
Figure S33. 2-(2-Chloro-2-methylpropyl)-1,3,5-trimethylbenzene (3l): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S34. 2-(2-Chloro-2-methylpropyl)-1,3,5-trimethylbenzene (3I) : $^{13}$C$^{1}$H NMR (101 MHz, CDCl$_3$, 298 K)
Figure S35. 1-(2-Chloro-2-methylpropyl)naphthalene (3m): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S36. 1-(2-Chloro-2-methylpropyl)naphthalene (3m): $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K)
Figure S37. 2-(2-Chloro-2-methylpropyl)thiophene (3n): $^1$H NMR spectrum (500 MHz, CDCl$_3$, 298 K)
Figure S38. 2-(2-Chloro-2-methylpropyl)thiophene (3n): $^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 298 K)
Figure S39. (3-Chloro-3-methylbutyl)benzene (3o): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S40. (3-Chloro-3-methylbutyl)benzene (3o): $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K)
Figure S41. 2-Chloro-2-methylnonane (3p): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S42. 2-Chloro-2-methylnonane (3p): $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K)
Figure S43. (2-Chloro-2-methylpropane-1,3-diyl)dibenzene (3q): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S44. (2-Chloro-2-methylpropane-1,3-diyl)dibenzene (3q): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S45. 1-Chloro-1-methylcyclooctane (3r): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S46. 1-Chloro-1-methylcyclooctane (3r): $^{13}\text{C}(^1\text{H})$ NMR (101 MHz, CDCl$_3$, 298 K)
Figure S47. tert-Butyl(3-chloro-3-methylbutoxy)diphenylsilane (3s): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S48. tert-Butyl(3-chloro-3-methylbutoxy)diphenylsilane (3s): $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K)
Figure S49. ((3-Chloro-3-methylbutoxy)methyl)benzene (3t): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S50. ((3-Chloro-3-methylbutoxy)methyl)benzene (3t): $^{13}$C{H} NMR (101 MHz, CDCl$_3$, 298 K)
Figure S51. 3-Chloro-3-methylbutyl pivalate (3u): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S52. 3-Chloro-3-methylbutyl pivalate (3u): $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K)
Figure S53. 2-(4-Chloro-4-methylpentyl)isoindoline-1,3-dione (3x): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S54. 2-(4-Chloro-4-methylpentyl)isoindoline-1,3-dione (3x): $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K)
Figure S55. 1-(2-Chloropropyl)naphthalene (3y): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S56. 1-(2-Chloropropyl)naphthalene (3y): $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K)
Figure S57. 1-Chloro-3-(1-chloroethyl)benzene (3z): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S58. 1-Chloro-3-(1-chloroethyl)benzene (3z): $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K)
Figure S59. 5-Chlorohexyl pivalate (3a'): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S60. 5-Chlorohexyl pivalate (3a'): $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K)
Figure S61. 1-Chloro-3-(1-chloroethyl)benzene (3b'): $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S62. 1-Chloro-3-(1-chloroethyl)benzene (3b): $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K)
Figure S63. \((E/Z)-(1\text{-Chloroprop-1-en-1-yl})\text{benzene [}(E/Z)-7a\): \(\text{H NMR spectrum (400 MHz, CDCl}_3, 298 K)\)
Figure S64. \((E/Z)\)-(1-Chloroprop-1-en-1-yl)benzene \([E/Z]-7a]\): \(^{13}\text{C}(^1\text{H})\) NMR (101 MHz, CDCl$_3$, 298 K)
Figure S65. (E/Z)-(1-Chloropent-1-en-1-yl)benzene [(E/Z)-7b]: $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S66. \((E/Z)-(1\text{-Chloropent-1-en-1-yl})benzene\) [(E/Z)-7b]: \(^{13}\text{C}\{^1\text{H}\} NMR (101 \text{ MHz, CDCl}_3, 298 \text{ K})\)
Figure S67. (E)-(1-Chloroethene-1,2-diyldibenzene [(E)-7c]: $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K)
Figure S68. (E)-(1-Chloroethene-1,2-diyl)dibenzene [(E)-7c]: $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$, 298 K)
Figure S69. (E/Z)-4,4'-[(1-Chloroethene-1,2-diyl)bismethylbenzene] [(E/Z)-7d]: $^1$H NMR spectrum (500 MHz, CDCl$_3$, 298 K)
Figure S70. (E/Z)-4,4'-(1-Chloroethene-1,2-diyl)bis(methylbenzene) [(E/Z)-7d]: $^{13}$C$\{^1$H$\}$ NMR (125 MHz, CDCl$_3$, 298 K)
7 References

[S1] P. R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow, P. Granger, *Pure Appl. Chem.* **2001**, *73*, 1795–1818.

[S2] D. Kuck, J. Schneider, H. F. Grutzmacher, *J. Chem. Soc. Perkin Trans. 2* **1985**, 689–696.

[S3] A. F. Bella, A. M. Z. Slawin, J. C. Walton, *J. Org. Chem.* **2004**, *69*, 5926–5933.

[S4] T. Krüger, K. Vorndran, T. Linker, *Chem. Eur. J.* **2009**, *15*, 12082–12091.

[S5] C. M. R. Volla, D. Marković, S. R. Dubbaka, P. Vogel, *Eur. J. Org. Chem.* **2009**, *6281–6288*.

[S6] C. Tabélé, C. Curti, N. Primas, Y. Kabri, V. Remusat, P. Vanelle, *Synthesis* **2015**, *47*, 3339–3346.

[S7] C. Dong, L. Zhang, X. Xue, H. Li, Z. Yu, W. Tang, L. Xu, *RSC Adv.* **2014**, *4*, 11152–11158.

[S8] C. Tabélé, C. Curti, N. Primas, Y. Kabri, V. Remusat, P. Vanelle, *Synthesis* **2015**, *47*, 3339–3346.

[S9] M. Davi, H. Lebel, *Org. Lett.* **2009**, *11*, 41–44.

[S10] H. Lebel, D. Guay, V. Paquet, K. Huard, *Org. Lett.* **2004**, *6*, 3047–3058.

[S11] N. Millius, G. Lapointe, P. Renaud, *Molecules* **2019**, *24*, 4184.

[S12] M. Fujiu, K. Negishi, J. Guang, P. G. Williard, S. Kuroki, K. Mikami, *Dalton Trans.* **2015**, *44*, 19464–19468.

[S13] P. A. Cleary, K. A. Woerpel, *Org. Lett.* **2005**, *7*, 2478–2481.

[S14] S. W. Lardy, V. A. Schmidt, *J. Am. Chem. Soc.* **2018**, *140*, 12318–12322.

[S15] L. Xu, Z. Liu, W. Dong, J. Song, M. Mao, J. Xu, H. Ren, *Org. Biomol. Chem.* **2015**, *13*, 6333–6337.

[S16] H. Albright, H. L. Vonesh, C. S. Schindler, *Org. Lett.* **2020**, *22*, 3155–3160.

[S17] S. Skvorcova, A. Jirgensons, *Org. Lett.* **2017**, *19*, 2478–2481.

[S18] W. B. Reid, J. J. Spillane, S. B. Krause, D. A. Watson, *J. Am. Chem. Soc.* **2016**, *138*, 5539–5542.

[S19] K. Park, G. Bae, J. Moon, J. Choe, K. H. Song, S. Lee, *J. Org. Chem.* **2010**, *75*, 6244–6251.

[S20] C.-H. Lee, S.-M. Lee, B.-H. Min, D.-S. Kim, C.-H. Jun, *Org. Lett.* **2018**, *20*, 2468–2471.

[S21] B. Gaspar, E. M. Carreira, *Angew. Chem. Int. Ed.* **2008**, *47*, 5758–5760.

[S22] F. T. Schevenels, M. Shen, S. A. Snyder, *J. Am. Chem. Soc.* **2017**, *139*, 6329–6337.

[S23] L. Han, J.-B. Xia, L. You, C. Chen, *Tetrahedron* **2017**, *73*, 3696–3701.

[S24] P. J. Kropp, S. D. Crawford, *J. Org. Chem.* **1994**, *59*, 3102–3112.

[S25] S. Dérien, H. Klein, C. Bruneau, *Angew. Chem. Int. Ed.* **2015**, *54*, 12112–12115.

[S26] P. Yu, A. Bismuto, B. Morandi, *Angew. Chem. Int. Ed.* **2020**, *59*, 2904–2910.