Supporting Information

Palladium-Catalyzed Synthesis of Deuterated Alkenes through Deuterodechlorination of Alkenyl Chlorides

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**General.** All melting points are not corrected. IR spectra were expressed in cm⁻¹. ¹H and ¹³C NMR spectra were taken at 500 and 100 MHz, respectively. Chemical shift values are expressed in ppm relative to internal or external TMS. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded using electron ionization (EI) mass spectrometry. Deuteration degrees were determined with ¹H-NMR (500 MHz). All reactions were performed under an argon atmosphere unless otherwise specified. Toluene was distilled from sodium benzophenone ketyl under an argon atmosphere. Alkenyl chlorides 1a, 1c-1i, and 1k-1m were synthesized as new chemical compounds. On the other hand, 1b¹a, 1j¹b, α-duteriobenzhydrol², and unsymmetrical NHC precursors² were prepared as previously reported.

**Synthesis of alkenyl chlorides**

**1-(4-Chlorocyclohex-3-enyl)-4-methoxybenzene (1a).**

![Image](attachment://1a.png)

This alkenyl chloride was prepared on the basis of the previous report.¹ Under an argon atmosphere, the suspension of PCl₅ (2.34 g, 11.3 mmol) in cyclohexane (7.69 mL) was refluxed to dissolve PCl₅, and then 4-(4-methoxyphenyl)cyclohexanone³ (2.04 g, 10 mmol) in CH₂Cl₂ (1.23 mL) was added. The reaction mixture was refluxed for 1 h. After cooling to room temperature, the resulting mixture was poured into ice water (100 mL) containing NaOH (2.0 g). The biphasic mixture was stirred for 30 min and extracted with Et₂O. The combined organic layers were washed with satd. NaHCO₃ solution and dried over MgSO₄. Concentration and purification through silica gel column chromatography (hexane/benzene = 8/1) gave 1.60 g of the product (7.2 mmol, 72% yield) as white solids of mp 62 °C. ¹H-NMR (500 MHz, CDCl₃): δ 1.84-1.92 (m, 1H), 1.96-2.01 (m, 1H), 2.17-2.24 (m, 1H), 2.31-2.40 (m, 2H), 2.48-2.55 (m, 1H), 2.74-2.80 (m, 1H), 3.79 (s, 3H), 5.87-5.89 (m, 1H), 6.84-6.87 (m, 2H), 7.12-7.15 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ 30.9 (CH₂), 33.2 (CH₂), 34.0 (CH₂), 38.0 (CH), 55.2 (CH₃), 113.9 (CH), 124.2 (CH), 127.7 (CH), 131.8 (C) 137.7 (C), 158.1 (C). IR (ATR): 810, 1030, 1240, 1620 cm⁻¹. HRMS (EI) m/z: (M⁺) Calcd for C₁₃H₁₅Cl₃O: 222.0811; Found: 222.0811.

**3-(4-Chlorocyclohex-3-enyl)pyridine (1c).**

![Image](attachment://1c.png)
This alkenyl chloride was prepared from 4-(pyridin-3-yl)cyclohexanone with the same procedure as 1a. After silica gel column chromatography (hexane/AcOEt = 2/1), the product was converted to the corresponding hydrochloride salt with HCl solution (4 M in 1,4-dioxane). After recrystallization from (AcOEt/acetonitrile = 1/1), treatment with satd. NaHCO₃ solution and extraction gave 542 mg of the product (2.8 mmol, 28% yield) as brown oil. ¹H-NMR (500 MHz, CDCl₃): δ 1.90-1.99 (m, 1H), 2.00-2.06 (m, 1H), 2.22-2.29 (m, 1H), 2.36-2.43 (m, 1H), 2.50-2.59 (m, 1H), 2.84-2.90 (m, 1H), 5.89-5.91 (m, 1H), 7.24-7.26 (m, 1H), 7.52-7.54 (m, 1H), 8.48 (dd, J = 1.6, 4.8 Hz, 1H), 8.50 (d, J = 2.3 Hz, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ 30.1 (CH₂), 32.7 (CH₂), 33.3 (CH₂), 36.3 (CH), 123.4 (CH), 123.5 (CH), 131.8 (C), 134.0 (CH), 140.6 (C), 147.9 (CH), 148.9 (CH). IR (ATR): 710, 810, 1650, 2930 cm⁻¹. HRMS (EI) m/z: (M⁺) Calcd for C₁₁H₁₂Cl₃N: 193.0658; Found: 193.0661.

2-(4-Chlorocyclohex-3-enyl)thiophene (1d).

This alkenyl chloride was prepared from 4-(thiophen-2-yl)cyclohexanone with the same procedure as 1a. Silica gel column chromatography (hexane) gave 1.47 g of the product (7.4 mmol, 74% yield) as yellow oil. ¹H-NMR (500 MHz, CDCl₃): δ 1.87-1.95 (m, 1H), 2.14-2.19 (m, 1H), 2.27-2.34 (m, 1H), 2.36-2.42 (m, 1H), 2.48-2.57 (m, 2H), 3.11-3.17 (m, 1H), 5.85-5.87 (m, 1H), 6.84 (dt, J = 1.0, 3.5 Hz, 1H), 6.94 (dd, J = 3.5, 5.1 Hz, 1H), 7.15 (dd, J = 1.2, 5.1 Hz, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ 31.7 (CH₂), 32.5 (CH₂), 34.0 (CH), 34.2 (CH₂), 122.6 (CH), 122.8 (CH), 123.3 (CH), 126.5 (CH), 131.7 (C), 149.2 (C). IR (ATR): 690, 810, 1660, 2920 cm⁻¹. HRMS (EI) m/z: (M⁺) Calcd for C₁₀H₁₁Cl₃S: 198.0270; Found: 198.0252.

1-Benzyl-4-chloro-1,2,3,6-tetrahydropyridine (1e).

This alkenyl chloride was prepared with the same procedure as 1a. Silica gel column chromatography (benzene) gave 853 mg of the product (4.1 mmol, 41% yield) as brown oil. ¹H-NMR (500 MHz, CDCl₃): δ 2.40-2.44 (m, 2H), 2.66 (t, J = 5.7 Hz, 2H), 3.01-3.03 (m, 2H), 3.59 (s, 2H), 5.74-5.76 (m, 1H), 7.25-7.28 (m, 1H), 7.30-7.34 (m, 4H). ¹³C-NMR (100 MHz, CDCl₃): δ 33.2 (CH₂), 50.0 (CH₂), 52.7 (CH₂), 61.8 (CH₂), 122.3 (CH), 127.2 (CH), 128.3 (CH), 128.9 (CH), 130.1 (C), 138.0 (C). IR (ATR): 1190, 1600, 1660, 2930 cm⁻¹. HRMS (EI) m/z: (M⁺) Calcd for C₁₂H₁₄Cl₃N: 207.0815; Found: 207.0818.
**2-(1-Chlorovinyl)naphthalene (1f).**

![2-(1-Chlorovinyl)naphthalene](image)

This alkenyl chloride was prepared with the same procedure as 1a. Silica gel column chromatography (hexane) and recrystallization gave 520 mg of the product (2.8 mmol, 28% yield) as white solids of mp 60 °C. \(^1\)H-NMR (500 MHz, CDCl\(_3\)): δ 5.62 (d, \(J = 1.8\) Hz, 1H), 5.92 (d, \(J = 1.8\) Hz, 1H), 7.49-7.52 (m, 2H), 7.71 (dd, \(J = 1.9, 8.6\) Hz, 1H), 7.81-7.84 (m, 2H), 7.87-7.89 (m, 1H), 8.14 (d, \(J = 1.5\) Hz, 1H). \(^1^3\)C-NMR (100 MHz, CDCl\(_3\)): δ 113.1 (CH\(_2\)), 123.5 (CH), 126.4 (CH), 126.6 (CH), 126.9 (CH), 127.6 (CH), 128.0 (CH), 128.6 (CH), 133.0 (C), 133.5 (C), 134.0 (C), 140.0 (C). IR (ATR): 820, 900, 1180, 3050 cm\(^{-1}\). HRMS (EI) \(m/z\): (M\(^+\)) Calcd for C\(_{12}\)H\(_9\)Cl\(_3\): 188.0393; Found: 188.0397.

**1-Chloro-2-methylprop-1-enylbenzene (1g).**

![1-Chloro-2-methylprop-1-enylbenzene](image)

This alkenyl chloride was prepared with the same procedure as 1a. Silica gel column chromatography (hexane/ AcOEt = 50/1) and Kugelrohr distillation (2 torr, 65 °C) gave 331 mg of the product (2.0 mmol, 20% yield) as colorless oil. \(^1\)H-NMR (500 MHz, CDCl\(_3\)): δ 1.75 (s, 3H), 2.01 (s, 3H), 7.26-7.30 (m, 1H), 7.31-7.36 (m, 4H). \(^1^3\)C-NMR (100 MHz, CDCl\(_3\)): δ 21.8 (CH\(_3\)), 22.0 (CH\(_3\)), 125.3 (C), 127.8 (CH), 128.1 (CH), 129.3 (CH), 130.6 (C), 139.4 (C). IR (ATR): 700, 1070, 1650 cm\(^{-1}\). HRMS (EI) \(m/z\): (M\(^+\)) Calcd for C\(_{10}\)H\(_{11}\)Cl: 166.0549; Found: 166.0551.

**1-(1-Chlorovinyl)-4-methoxybenzene (1h).**

![1-(1-Chlorovinyl)-4-methoxybenzene](image)

This alkenyl chloride was prepared with the same procedure as 1a. Silica gel column chromatography (hexane/ AcOEt = 50/1) gave 260 mg of the product (1.5 mmol, 15% yield) as white solids of mp 55 °C. \(^1\)H-NMR (500 MHz, CDCl\(_3\)): δ 3.83 (s, 3H), 5.41 (d, \(J = 1.7\) Hz, 1H), 5.65 (d, \(J = 1.7\) Hz, 1H), 6.87-6.90 (m, 2H), 7.55-7.58 (m, 2H). \(^1^3\)C-NMR (100 MHz, CDCl\(_3\)): δ 55.3 (CH\(_3\)), 110.8 (CH\(_2\)), 113.6 (CH), 127.8 (CH), 129.6 (C), 139.6 (C), 160.4 (C). IR (ATR): 870, 1250, 1610 cm\(^{-1}\). HRMS (EI) \(m/z\): (M\(^+\)) Calcd for C\(_9\)H\(_9\)ClO: 168.0342; Found: 168.0341.
4-(1-Chlorovinyl)benzonitrile (1i).

\[ \text{NC} \quad \text{Cl} \]

This alkenyl chloride was prepared with the same procedure as 1a. Silica gel column chromatography (hexane/AcOEt = 50/1) and recrystallization (hexane/AcOEt = 100/1) gave 599 mg of the product (3.7 mmol, 37% yield) as white solids of mp 54 °C. \( ^1 \text{H-NMR} \) (500 MHz, CDCl₃): \( \delta \) 5.70 (d, \( J = 2.2 \) Hz, 1H), 5.90 (d, \( J = 2.2 \) Hz, 1H), 7.66-7.68 (m, 2H), 7.73-7.75 (m, 2H). \( ^{13} \text{C-NMR} \) (100 MHz, CDCl₃): \( \delta \) 112.7 (C), 115.8 (CH₂), 118.3 (C), 127.0 (CH), 132.2 (CH), 138.1 (C), 141.0 (C). IR (ATR): 900, 1600, 1220, 2230 cm\(^{-1}\). HRMS (EI) m/z: (M⁺) Calcd for C₉H₆₃₅ClN: 163.0189; Found: 163.0174.

3,4-Dichloro-7-methoxy-2,2-dimethyl-2\( ^{1} \text{H} \)-chromene (1k).

\[ \text{MeO} \quad \text{Cl} \quad \text{Cl} \]

This alkenyl chloride was prepared on the basis of the previous report.⁷ 7-Methoxy-2,2-dimethylchroman-4-one⁸ (412 mg, 2.0 mmol) and PCl₅ (833 mg, 4.0 mmol) were dissolved in CCl₄ (2.0 mL). The reaction mixture was stirred for 8 h at room temperature. Then, 10% NaOH solution was added at 0 °C, and the resulting mixture was extracted with AcOEt. The combined organic layers were dried over Na₂SO₄. Concentration and purification through silica gel column chromatography (hexane/benzene = 20/1) gave 370 mg of the product (1.43 mmol, 71% yield) as white solids of mp 38-39 °C. \( ^1 \text{H-NMR} \) (500 MHz, CDCl₃): \( \delta \) 1.55 (s, 6H), 3.79 (s, 3H), 6.41 (d, \( J = 2.5 \) Hz, 1H), 6.53 (dd, \( J = 2.5, 8.6 \) Hz, 1H), 7.33 (d, \( J = 8.6 \) Hz, 1H). \( ^{13} \text{C-NMR} \) (100 MHz, CDCl₃): \( \delta \) 25.8 (CH₃), 55.4 (CH₃), 81.1 (C), 102.1 (CH), 107.6 (CH), 114.0 (C), 124.4 (C), 125.6 (CH), 127.2 (C), 152.7 (C), 161.6 (C). IR (ATR): 840, 960, 1030, 1200, 1280, 1500 cm\(^{-1}\). HRMS (EI) m/z: (M⁺) Calcd for C₁₂H₁₂³⁵Cl₂O₂: 258.0214; Found: 258.0214.

5-Allyl-10-chloro-5\( ^{1} \text{H} \)-dibenzo[\( b,f \)]azepine (1l).

\[ \text{Cl} \]

10-Methoxy-5\( ^{1} \text{H} \)-dibenzo[\( b,f \)]azepine (483 mg, 2.16 mmol) was dissolved in DMF (8 mL) and
60% NaH in mineral oil (346 mg, 8.64 mmol) was added at 0 °C. The reaction mixture was stirred for 30 min at room temperature. Then, allyl bromide (784 mg, 6.48 mmol) was added, and the reaction mixture was stirred for 4 h at room temperature. After 10% HCl (5.0 mL) was added, the mixture was stirred for 1 h. The resulting mixture was extracted with AcOEt. The combined organic layers were dried over Na2SO4. Concentration and purification through silica gel column chromatography (hexane/AcOEt = 10/1) gave 509 mg of 5,11-dihydro-5-(2-propen-1-yl)-10H-dibenzo[b,f]azepin-10-one (2.04 mmol, 94% yield) as yellow solids of mp 102-103 °C. 

\[ ^1H-NMR \ (500 \text{ MHz, } \text{CDCl}_3); \delta \text{ values: } 3.97 (s, 2H), 4.65 (d, J = 5.5 \text{ Hz}, 2H), 5.21 (dd, J = 1.3, 10.4, 1H), 5.32 (dd, J = 1.4, 17.3 \text{ Hz}, 1H), 5.82-5.90 \text{ (m, 1H)}, 6.99 (t, J = 7.8 \text{ Hz}, 1H), 7.14-7.17 \text{ (m, 1H)}, 7.19-7.24 \text{ (m, 3H)}, 7.30-7.32 \text{ (m, 1H)}, 7.46-7.49 \text{ (m, 1H)}, 8.15 (dd, J = 1.8, 7.8 \text{ Hz}, 1H). \]

\[ ^13C-NMR \ (100 \text{ MHz, } \text{CDCl}_3); \delta \text{ values: } 49.1 \text{ (CH2)}, 54.3 \text{ (CH2)}, 118.0 \text{ (CH2)}, 118.1 \text{ (CH)}, 120.2 \text{ (CH)}, 122.0 \text{ (CH)}, 125.8 \text{ (CH)}, 126.0 \text{ (C)}, 127.1 \text{ (CH)}, 128.5 \text{ (CH)}, 130.4 \text{ (C)}, 131.1 \text{ (CH)}, 133.6 \text{ (CH)}, 134.4 \text{ (CH)}, 147.2 \text{ (C)}, 149.3 \text{ (C)}, 190.8 \text{ (C)}. \]

IR (ATR): 780, 1120, 1220, 1450, 1660 cm\(^{-1}\). HRMS (EI) \(m/z\): (M\(^+\)) Calcd for C\(_{17}\)H\(_{15}\)NO: 249.1154; Found: 249.1145.

5-Allyl-10-chloro-5H-dibenzo[b,f]azepine (11) was prepared from 5,11-dihydro-5-(2-propen-1-y1)-10H-dibenzo[b,f]azepin-10-one (499 mg, 2.0 mmol) with the same procedure as 1a. Silica gel column chromatography (hexane/AcOEt = 50/1) gave 299 mg of the product (1.12 mmol, 56% yield) as a yellow oil. 

\[ ^1H-NMR \ (500 \text{ MHz, } \text{CDCl}_3); \delta \text{ values: } 4.40 (d, J = 5.6 \text{ Hz}, 2H), 5.11 (dd, J = 1.5, 10.3 \text{ Hz}, 1H), 5.30 (dd, J = 1.5, 17.1 \text{ Hz}, 1H), 5.74-5.82 \text{ (m, 1H)}, 6.98-7.03 \text{ (m, 3H)}, 7.06-7.09 \text{ (m, 2H)}, 7.14 (s, 1H), 7.23-7.27 \text{ (m, 1H)}, 7.30-7.33 \text{ (m, 1H)}, 7.61 (dd, J = 1.5, 8.1 \text{ Hz}, 1H). \]

\[ ^13C-NMR \ (100 \text{ MHz, } \text{CDCl}_3); \delta \text{ values: } 53.1 \text{ (CH2)}, 117.9 \text{ (CH2)}, 120.1 \text{ (CH)}, 120.4 \text{ (CH)}, 123.6 \text{ (CH)}, 123.7 \text{ (CH)}, 128.6 \text{ (CH)}, 128.90 \text{ (CH)}, 128.92 \text{ (CH)}, 130.2 \text{ (CH)}, 130.8 \text{ (CH)}, 131.8 \text{ (C)}, 132.6 \text{ (C)}, 133.8 \text{ (C)}, 134.7 \text{ (CH)}, 150.4 \text{ (C)}, 151.5 \text{ (C)}. \]

IR (ATR): 840, 930, 1230, 1480 cm\(^{-1}\). HRMS (EI) \(m/z\): (M\(^+\)) Calcd for C\(_{17}\)H\(_{14}\)Cl\(_3\)N: 267.0815; Found: 267.0815.

\((8R,9S,13S,14S)-17\)-Chloro-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6H-cyclopenta[α]phenanthrene (1m).

This vinyl chloride was prepared from estrone 3-methyl ether\(^9\) with the same procedure as 1a. Silica gel column chromatography (hexane/AcOEt = 50/1) and recrystallization (hexane/AcOEt = 100/1) gave 539 mg of the product (1.8 mmol, 18% yield) as white solids of mp 115 °C. 

\[ ^1H-NMR \ (500 \text{ MHz, } \text{CDCl}_3); \delta \text{ values: } 0.90 (s, 3H), 1.39-1.64 \text{ (m, 4H)}, 1.69-1.75 \text{ (m, 1H)}, 1.87-1.94 \text{ (m, 2H)}, 2.03 \text{ (dd, J = 1.7, 11.3, 14.7 Hz, 1H)}, 2.25 \text{ (dd, J = 3.2, 6.4, 14.7 Hz, 1H)}, 2.26-2.31 \text{ (m, 1H)}, \]
2.37-2.41 (m, 1H), 2.85-2.95 (m, 2H), 3.78 (s, 3H), 5.66 (dd, $J = 1.7, 3.2$ Hz, 1H), 6.64 (d, $J = 2.7$ Hz, 1H), 6.72 (dd, $J = 2.8, 8.6$ Hz, 1H), 7.20 (d, $J = 8.6$ Hz, 1H). $^{13}$C-NMR (100 MHz, CDCl₃): δ15.0 (CH₃), 26.1 (CH₂), 27.1 (CH₂), 29.5 (CH₂), 30.2 (CH₂), 33.6 (CH₂), 37.3 (CH), 44.1 (CH), 47.8 (C), 54.9 (CH), 55.1 (CH₃), 111.4 (CH), 113.9 (CH), 124.5 (CH), 126.0 (CH), 132.5 (C), 137.8 (C), 144.9 (C), 157.6 (C). IR (ATR): 900, 1230, 1500, 1610, 2920 cm⁻¹. HRMS (EI) $m/z$: (M⁺) Calcd for C₁₉H₂₃ClO: 302.1437; Found: 302.1446.
References


hydrogenated sample
\[ \text{D NMR (2e) exp} \]

\[ \text{\(^{1}H\) NMR (60 MHz, CHCl\textsubscript{3})} \]

\[ \text{D NMR (2f) exp} \]

\[ \text{\(^{1}H\) NMR (60 MHz, CHCl\textsubscript{3})} \]