Supplementary Information

Chromium-Catalyzed Migratory Arylmagnesiation of Unactivated Alkynes

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Material and Methods

General. All reactions dealing with air- or moisture-sensitive compound were performed by standard Schlenk techniques in oven-dried reaction vessels under nitrogen atmosphere. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates. $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were recorded on JEOL ECA-400 (400 MHz) or Bruker AV-400 (400 MHz) or Bruker AV-500 (500 MHz) NMR spectrometers. $^1$H and $^{13}$C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm) and CHCl$_3$ (77.0 ppm), respectively. Gas chromatographic (GC) analysis was performed on a Shimadzu GC-2010 system equipped with an FID detector and a capillary column, DB-5 (Agilent J&W, 0.25 mm i.d. x 30 m, 0.25 µm film thickness). High-resolution mass spectra (HRMS) were obtained with a Q-Tof Premier LC HR mass spectrometer.

Materials. Unless otherwise noted, commercial reagents were purchased from Aldrich, Alfa Aesar, and other commercial suppliers and were used as received. Anhydrous CrCl$_2$ (99.99%) was purchased from Aldrich and was used as received. THF, $i$-Pr$_2$O (diisopropyl ether), and $t$-BuOMe ($t$-butyl methyl ether) were distilled over Na/benzophenone. Grignard reagents were prepared from the corresponding halides and magnesium turnings in anhydrous THF (with a typical concentration of 1 M) and titrated before use. 2,2-Dimethyl-3-decyne was prepared according to the literature procedure.$^1$
Chromium-Catalyzed Migratory Arylmagnesiation of Alkynes

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\text{R-} \overset{\text{MgBr}}{\text{MgBr}} + \text{n-C}_6\text{H}_{11} = \overset{\text{CrCl}_2 (10 \text{ mol%})}{\text{n-C}_6\text{H}_{11}} \rightarrow \text{R} \overset{\text{D/H}}{\text{D/H}} \overset{\text{H/D}}{\text{H/D}} \overset{\text{n-C}_6\text{H}_{11}}{\text{n-C}_6\text{H}_{11}}
\]

**Typical procedure A (conditions A):** Inside a glovebox, a 10 mL Schlenk tube was charged with \( \text{CrCl}_2 \) (2.4 mg, 0.020 mmol). The Schlenk tube was taken out from the glovebox and submerged in an ice bath for 5 min prior to the addition of a Grignard reagent (0.60 mmol in THF). After stirring for 10 min at 0 °C, the resulting mixture was allowed to warm to room temperature and concentrated under reduced pressure, followed by the addition of \( \text{i-Pr}_2\text{O} \) (0.5 mL). After stirring for 5 min, 6-dodecyne (33.2 mg, 0.20 mmol) was added. The reaction mixture was stirred at 110 °C for 12 h, and then allowed to cool to room temperature, quenched by the addition of \( \text{D}_2\text{O} \) (0.5 mL), and diluted with ethyl acetate (1 mL). The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over \( \text{Na}_2\text{SO}_4 \) and concentrated under reduced pressure. The crude product was purified by silica gel chromatography to afford the desired product.

According to GCMS analysis of the crude product, the reaction was typically accompanied by two minor byproducts, that is, (1) a naphthalene derivative formed via annulation of the Grignard reagent and two molecules of the alkyne (ca. 10%), and (2) a cyclotrimerization product of the alkyne (< 5%). These byproducts are not always readily removable, and would account for (at least in part) impurities observed in \( ^1\text{H} \) and \( ^{13}\text{C} \) NMR spectra of some of the products.

**\((E)-1-(\text{Dodec}-6\text{-en}-6\text{-yl})\text{ benzene-2-d}\) (Table 2, entry 1):** Prepared according to typical procedure A. Silica gel chromatography (eluent: pentane) of the crude product afforded the title compound as a colorless oil (36.3 mg, 74%); \( ^1\text{H} \) NMR (400 MHz, DMSO-\( d_6 \)) \( \delta \) 7.51 – 7.24 (m, 3.14H), 7.26 – 7.16 (m, 1H), 5.63 (t, \( J = 7.3 \text{ Hz, 0.86H} \)), 2.46 (t, \( J = 7.0 \text{ Hz, 2H} \)), 2.16 (q, \( J = 7.2 \text{ Hz, 2H} \)), 1.46 – 1.38 (m, 2H), 1.37 – 1.27 (m, 4H), 1.26 – 1.17 (m, 6H), 0.87 (t, \( J = 6.8 \text{ Hz, 3H} \)), 0.80 (t, \( J = 6.8 \text{ Hz, 3H} \)); \( ^{13}\text{C} \) NMR (101 MHz, DMSO-\( d_6 \)) \( \delta \) 142.4, 139.5, 128.5, 128.2, 128.1,
126.4, 125.8, 31.02, 31.01, 29.0, 28.7, 27.9, 27.8, 22.0, 21.9, 13.9, 13.8; HRMS (ESI) Calcd for C_{18}H_{28}D [M + H]^+ 246.2332, found 246.2333. The $^1$H and $^{13}$C NMR spectral patterns, except for the deuterated positions, are in good agreement with the literature data for the non-deuterated derivative.\textsuperscript{2,3}

(E)-1-(Dodec-6-en-6-yl)-4-methoxybenzene-2-d (Table 2, entry 2): Prepared according to typical procedure A. Silica gel chromatography (eluent: hexane/\textit{Et}_2\text{O} = 200/1) of the crude product afforded the title compound as a colorless oil (35.8 mg, 65%); $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.26 (d, $J$ = 9.2 Hz, 1.09H), 6.91 – 6.77 (m, 2H), 5.55 (t, $J$ = 7.3 Hz, 0.92H), 3.73 (s, 3H), 2.42 (t, $J$ = 7.0 Hz, 2H), 2.13 (q, $J$ = 7.3 Hz, 2H), 1.43 – 1.35 (m, 2H), 1.33 – 1.26 (m, 4H), 1.25 – 1.19 (m, 6H), 0.87 (t, $J$ = 6.9 Hz, 3H), 0.81 (t, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (400 MHz, DMSO-$d_6$) $\delta$ 158.0, 138.8, 134.7, 126.87, 126.86, 113.6, 113.5, 55.0, 31.02, 31.00, 29.1, 28.7, 27.9, 27.8, 22.0, 21.9, 13.9, 13.8; HRMS (ESI) Calcd for C_{19}H_{30}DO [M + H]^+ 276.2438, found 276.2443.

(E)-1-(Dodec-6-en-6-yl)-4-fluorobenzene-2-d (Table 2, entry 3): Prepared according to typical procedure A. Silica gel chromatography (eluent: pentane) of the crude product afforded the title compound as a colorless oil (16.8 mg, 32%); $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.36 (dd, $J$ = 9.3, 5.5 Hz, 1.17H), 7.21 – 7.07 (m, 2H), 5.61 (t, $J$ = 7.3 Hz, 0.86H), 2.44 (t, $J$ = 6.8 Hz, 2H), 2.15 (q, $J$ = 7.2 Hz, 2H), 1.46 – 1.35 (m, 2H), 1.34 – 1.27 (m, 4H), 1.25 – 1.20 (m, 6H), 0.87 (t, $J$ = 6.8 Hz, 3H), 0.80 (t, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 162.7, 140.0, 139.3, 138.9,
129.1, 128.2 (d, $^3\text{J}_{\text{C-F}} = 8.2$ Hz), 115.4 (d, $^2\text{J}_{\text{C-F}} = 21.1$ Hz), 115.3 (d, $^2\text{J}_{\text{C-F}} = 21.1$ Hz), 31.5, 31.4, 29.4, 29.2, 28.4, 28.2, 22.5, 22.4, 14.4, 14.3; HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{27}\text{DF} [\text{M + H}]^+$ 264.2238, found 249.2235.

**{(E)-1-(Dodec-6-yl-7-d)-4-methylbenzene (Table 2, entry 4):}** Prepared according to typical procedure A. Silica gel chromatography (eluent: pentane) of the crude product afforded the title compound as a colorless oil (41.1 mg, 79%); $^1\text{H}$ NMR (400 MHz, DMSO-$_d6$) $\delta$ 7.21 (d, $J = 8.2$ Hz, 1.80 H), 7.10 (d, $J = 7.9$ Hz, 2H), 5.59 (t, $J = 7.3$ Hz, 0.21 H), 2.43 (t, $J = 7.0$ Hz, 2H), 2.27 (s, 3H), 2.14 (t, $J = 7.1$ Hz, 2H), 1.45 – 1.38 (m, 2H), 1.36 – 1.26 (m, 4H), 1.25 – 1.19 (m, 6H), 0.87 (t, $J = 6.8$ Hz, 3H), 0.81 (t, $J = 6.8$ Hz, 3H); HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{30}\text{D} [\text{M + H}]^+$ 260.2489, found 260.2483. The $^1\text{H}$ NMR spectral patterns, except for the deuterated positions, are in good agreement with the literature data for the non-deuterated derivative.\(^2\) The $^{13}\text{C}$ NMR spectrum is reported for the product with higher deuterium incorporation into the ortho position (Table 2, entry 11).

**{(E)-4-(Dodec-6-yl-7-d)-N,N-dimethylaniline (Table 2, entry 5):}** Prepared according to typical procedure A. Silica gel chromatography (eluent: hexane/Et$_2$O = 200/1) of the crude product afforded the title compound as a colorless oil (32.3 mg, 56%); $^1\text{H}$ NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 7.23 (d, $J = 8.0$ Hz, 1.55 H), 6.69 (d, $J = 7.8$ Hz, 2H), 5.57 (t, $J = 7.3$ Hz, 0.40 H), 2.92 (s, 6H), 2.45 (t, $J = 7.3$ Hz, 2H), 2.16 (td, $J = 7.2$, 1.7 Hz, 2H), 1.48 – 1.41 (m, 2H), 1.38 – 1.32 (m, 4H), 1.31 – 1.25 (m, 6H), 0.92 (t, $J = 7.2$ Hz, 3H), 0.87 (t, $J = 7.0$ Hz, 3H); HRMS (ESI)
Calcd for C_{20}H_{33}DN [M + H]^+ 289.2754, found 289.2755. The $^{13}$C NMR spectrum is reported for the product with higher deuterium incorporation into the ortho position (Table 2, entry 7).

(E)-1-(Dodec-6-en-6-yl)-4-methylbenzene-2-d (Table 2, entry 6): Prepared according to typical procedure A with a modification, that is, addition of CuBr (2.9 mg, 0.020 mmol) together with CrCl$_2$. Silica gel chromatography (eluent: pentane) of the crude product afforded the title compound as a colorless oil (29.0 mg, 56%); $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.22 (d, $J = 8.0$ Hz, 1.49H), 7.10 (d, $J = 7.8$ Hz, 2H), 5.59 (t, $J = 7.2$ Hz, 0.51H), 2.43 (t, $J = 6.8$ Hz, 2H), 2.27 (s, 3H), 2.14 (t, $J = 7.4$ Hz, 2H), 1.49 – 1.37 (m, 2H), 1.31 – 1.26 (m, 4H), 1.27 – 1.17 (m, 6H), 0.86 (t, $J = 7.0$ Hz, 3H), 0.80 (t, $J = 6.8$ Hz, 3H); HRMS (ESI) Calcd for C$_{19}$H$_{30}$D [M + H]$^+$ 260.2489, found 260.2485. The $^1$H NMR spectral patterns, except for the deuterated positions, are in good agreement with the literature data for the non-deuterated derivative. The $^{13}$C NMR spectrum is reported for the product with higher deuterium incorporation into the ortho position (Table 2, entry 7).

(E)-4-(Dodec-6-en-6-yl)-N,N-dimethylaniline-3-d (Table 2, entry 7): Prepared according to typical procedure A with a modification, that is, addition of CuBr (2.9 mg, 0.020 mmol) together with CrCl$_2$ and use of tBuOMe instead of $i$-Pr$_2$O. Silica gel chromatography (eluent: hexane/Et$_2$O = 200/1) of the crude product afforded the title compound as a colorless oil (36.8 mg, 64%); $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 7.23 (d, $J = 9.1$ Hz, 1.13H), 6.81 – 6.57 (m, 2H), 5.56 (t, $J = 7.2$ Hz, 0.87H), 2.92 (s, 6H), 2.44 (t, $J = 7.3$ Hz, 2H), 2.16 (q, $J = 7.3$ Hz, 2H), 1.48 – 1.39
(E)-1-(Dodec-6-en-6-yl-7-d) benzene-2,3,4,5-d_4 (Table 1, entry 5): Prepared according to typical procedure B with pentadeuterated phenylmagnesium bromide. The reaction was quenched with H_2O. Silica gel chromatography (eluent: pentane) of the crude product afforded the title compound as a colorless oil (31.4 mg, 63%); ^1H NMR (400 MHz, CDCl_3) δ 7.34 (s, 0.64H), 5.65 (t, J = 7.3 Hz, 0.29H), 2.48 (t, J = 7.4 Hz, 2H), 2.18 (t, J = 7.4 Hz, 2H), 1.48 – 1.41 (m, 2H), 1.37 – 1.32 (m, 6H), 1.30 – 1.24 (m, 6H), 0.91 (t, J = 6.8 Hz, 3H), 0.86 (t, J = 6.8 Hz,
(E)-1-(Dodec-6-en-6-yl) benzene-2-d (Table 2, entry 8): Prepared according to typical procedure B. Silica gel chromatography (eluent: pentane) of the crude product afforded the title compound as a colorless oil (25.5 mg, 52%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 – 7.28 (m, 3.23H), 7.21 (t, $J = 6.5$ Hz, 1H), 5.65 (t, $J = 7.3$ Hz, 0.76H), 2.48 (t, $J = 7.4$ Hz, 2H), 2.19 (q, $J = 7.2$ Hz, 2H), 1.49 – 1.38 (m, 2H), 1.39 – 1.32 (m, 6H), 1.31 – 1.24 (m, 4H), 0.92 (t, $J = 6.9$ Hz, 3H), 0.86 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.4, 140.0, 136.7, 129.1, 128.1, 128.0, 126.3, 31.9, 31.7, 29.7, 29.6, 28.5, 28.4, 22.6, 22.5, 14.08, 14.05; HRMS (ESI) Calcd for C$_{18}$H$_{28}$D [M + H]$^+$ 246.2332, found 246.2329. The $^1$H and $^{13}$C NMR spectral patterns, except for the deuterated positions, are in good agreement with the literature data for the non-deuterated derivative.$^{2,3}$

(E)-1-(Dodec-6-en-6-yl)-4-methoxybenzene-2-d (Table 2, entry 9): Prepared according to typical procedure B. Silica gel chromatography (eluent: hexane/Et$_2$O = 200/1) of the crude product afforded the title compound as a colorless oil (40.7 mg, 74%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28 (d, $J = 9.2$ Hz, ~1H; overlapped with CHCl$_3$), 6.84 (d, $J = 9.4$ Hz, 2H), 5.58 (t, $J = 7.3$ Hz, 0.87H), 3.81 (s, 3H), 2.45 (t, $J = 7.3$ Hz, 2H), 2.17 (q, $J = 7.3$ Hz, 2H), 1.49 – 1.42 (m, 2H), 1.39 – 1.31 (m, 6H), 1.30 – 1.25 (m, 4H), 0.92 (t, $J = 6.8$ Hz, 3H), 0.87 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 158.4, 139.5, 136.1, 127.9, 127.4, 113.6, 113.5, 55.4, 32.0, 31.8,
29.9, 29.8, 28.7, 28.6, 22.8, 22.7, 14.24, 14.22; HRMS (ESI) Calcd for C_{19}H_{30}DO \ [M + H]^+ 276.2438, found 276.2434.

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\text{F} \\
\text{H/D (0.91H)}
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\((E)-1-(\text{Dodec-6-en-6-yl})-4\text{-fluorobenzene-2-d (Table 2, entry 10)}: \) Prepared according to typical procedure B. Silica gel chromatography (eluent: pentane) of the crude product afforded the title compound as a colorless oil (31.6 mg, 60%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.32 – 7.24 (m, \(\sim\)1H; overlapped with CHCl\(_3\)), 7.00 – 6.94 (m, 2H), 5.58 (t, \(J = 7.3\) Hz, 0.91H), 2.44 (t, \(J = 7.3\) Hz, 2H), 2.16 (q, \(J = 7.3\) Hz, 2H), 1.46 – 1.39 (m, 2H), 1.36 – 1.30 (m, 6H), 1.30 – 1.24 (m, 4H), 0.91 (t, \(J = 6.8\) Hz, 3H), 0.85 (t, \(J = 6.8\) Hz, 3H); \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 162.7, 140.0, 139.3, 138.9, 129.1, 128.2(d, \(^3J_{C-F} = 8.2\) Hz), 115.4 (d, \(^2J_{C-F} = 21.1\) Hz), 115.3 (d, \(^2J_{C-F} = 21.1\) Hz), 31.5, 31.4, 29.4, 29.2, 28.4, 28.2, 22.5, 22.4, 14.4, 14.3; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 161.7 (d, \(^1J_{C-F} = 245.4\) Hz), 139.4(d, \(^4J_{C-F} = 3.2\) Hz), 139.1, 136.7, 129.1, 127.7 (\(^3J_{C-F} = 7.8\) Hz), 114.8 (d, \(^2J_{C-F} = 21.2\) Hz), 114.7 (d, \(^2J_{C-F} = 21.2\) Hz), 31.8, 31.6, 29.8, 29.6, 28.5, 28.3, 22.6, 22.5, 14.1, 14.0; HRMS (ESI) Calcd for C\(_{18}\)H\(_{27}\)DF \([\text{M + H}]^+\) 264.2238, found 249.2233.

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\begin{center}
\text{Me} \\
\text{H/D (0.16H)} \\
\text{H/D (0.78H)}
\end{center}
\]

\((E)-1-(\text{Dodec-6-en-6-yl})-4\text{-methylbenzene-2-d (Table 2, entry 11)}: \) Prepared according to typical procedure B. Silica gel chromatography (eluent: pentane) of the crude product afforded the title compound as a colorless oil (25.9 mg, 50%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.23 (d, \(J = 8.4\) Hz, 1.16H), 7.13 – 7.09 (m, 2H), 5.61 (t, \(J = 7.3\) Hz, 0.78H), 2.46 (t, \(J = 7.5\) Hz, 2H), 2.33 (s, \(3\)H), 2.17 (q, \(J = 7.3\) Hz, 2H), 1.48 – 1.41 (m, 2H), 1.39 – 1.31 (m, 6H), 1.29 – 1.20 (m, 4H), 0.91 (t, \(J = 6.8\) Hz, 3H), 0.86 (t, \(J = 6.9\) Hz, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 140.5, 139.8,
135.9, 128.8, 128.7, 128.4, 126.1, 31.9, 31.7, 29.7, 29.6, 28.52, 28.45, 22.6, 22.5, 21.0, 14.09, 14.08; HRMS (ESI) Calcd for C\textsubscript{19}H\textsubscript{30}D [M + H]\textsuperscript{+} 260.2489, found 260.2484. The \textsuperscript{1}H and \textsuperscript{13}C NMR spectral patterns, except for the deuterated positions, are in good agreement with the literature data for the non-deuterated derivative.\textsuperscript{2}

(E)-4-(Dodec-6-en-6-yl)-N,N-dimethylaniline-3-d (Table 2, entry 12): Prepared according to typical procedure B. Silica gel chromatography (eluent: hexane/Et\textsubscript{2}O = 200/1) of the crude product afforded the title compound as a colorless oil (35.2 mg, 61%); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.25 (d, \(J = 8.4\) Hz, ~1H; overlapped with CHCl\textsubscript{3}), 6.69 (d, \(J = 8.3\) Hz, 2H), 5.56 (t, \(J = 7.2\) Hz, 0.65H), 2.94 (s, 6H), 2.44 (t, \(J = 7.6\) Hz, 2H), 2.16 (q, \(J = 7.1\) Hz, 2H), 1.47 – 1.39 (m, 2H), 1.36 – 1.31 (m, 6H), 1.29 – 1.26 (m, 4H), 0.91 (t, \(J = 6.8\) Hz, 3H), 0.85 (t, \(J = 6.4\) Hz, 3H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 139.35, 139.29, 129.2, 126.9, 126.5, 112.7, 40.9, 31.9, 31.7, 29.8, 29.5, 28.6, 28.5, 22.64, 22.55, 14.09, 14.06; HRMS (ESI) Calcd for C\textsubscript{20}H\textsubscript{33}DN [M + H]\textsuperscript{+} 289.2754, found 289.2751.

(E)-4-(Dodec-6-en-6-yl)phenyl-3-d trimethylsilane (Table 2, entry 13): Prepared according to typical procedure B. Silica gel chromatography (eluent: pentane) of the crude product afforded the title compound as a colorless oil (38.1 mg, 60%); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.46 (d, \(J = 7.8\) Hz, 2H), 7.33 (d, \(J = 8.0\) Hz, 1.34H), 5.68 (t, \(J = 7.3\) Hz, 0.66H), 2.48 (t, \(J = 7.5\) Hz, 2H), 2.19 (q, \(J = 7.2\) Hz, 2H), 1.47 – 1.42 (m, 2H), 1.38 – 1.32 (m, 6H), 1.30 – 1.23 (m, 4H), 0.90 (t, \(J = 6.8\) Hz, 3H), 0.86 (t, \(J = 6.9\) Hz, 3H), 0.27 (s, 9H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 143.8, 139.9,
138.0, 133.2, 133.1, 129.3, 125.6, 31.9, 31.6, 29.7, 29.6, 28.6, 28.5, 22.6, 22.5, 14.12, 14.08, -1.1; HRMS (ESI) Calcd for C_{21}H_{36}DSi [M + H]^+ 318.2727, found 318.2722.

(E)-1-(tert-Butyl)-4-(dodec-6-en-6-yl)benzene-3-d (Table 2, entry 14): Prepared according to typical procedure B. Silica gel chromatography (eluent: pentane) of the crude product afforded the title compound as a colorless oil (35.6 mg, 59%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.32–7.28 (m, 3.39H), 5.65 (t, \(J = 7.3\) Hz, 0.62H), 2.47 (d, \(J = 7.6\) Hz, 2H), 2.18 (q, \(J = 7.2\) Hz, 2H), 1.48–1.40 (m, 2H), 1.34–1.32 (m, 15H), 1.29–1.27 (m, 4H), 0.90 (t, \(J = 6.8\) Hz, 3H), 0.86 (t, \(J = 6.8\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 149.1, 140.3, 140.3, 139.6, 136.7, 128.4, 125.7, 125.0, 124.9, 34.4, 32.9, 32.0, 31.7, 31.4, 29.6, 28.6, 28.5, 22.6, 22.5, 14.1(2C); HRMS (ESI) Calcd for C\(_{22}\)H\(_{36}\)D [M + H]^+ 302.2958, found 302.2954.

(E)-1-(Dodec-6-en-6-yl)-3-methylbenzene-6-d (Table 2, entry 15): Prepared according to typical procedure B. Silica gel chromatography (eluent: pentane) of the crude product afforded the title compound as a colorless oil (33.2 mg, 64%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.23–7.12 (m, 2.30H), 7.03 (d, \(J = 7.4\) Hz, 1H), 5.63 (t, \(J = 7.3\) Hz, 0.62H), 2.47 (t, \(J = 7.4\) Hz, 2H), 2.35 (s, 3H), 2.18 (q, \(J = 7.2\) Hz, 2H), 1.45 (t, \(J = 7.1\) Hz, 2H), 1.38–1.30 (m, 6H), 1.30–1.25 (m, 4H), 0.92 (t, \(J = 6.8\) Hz, 3H), 0.86 (t, \(J = 6.9\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 140.1, 137.5, 128.9, 128.0, 127.9, 127.1, 123.4, 31.9, 31.7, 29.7, 29.6, 28.54, 28.46, 22.6, 22.5, 21.5, 14.09, 14.07; HRMS (ESI) Calcd for C\(_{19}\)H\(_{30}\)D [M + H]^+ 260.2489, found 260.2484. The \(^1\)H and \(^{13}\)C NMR spectral patterns, except for the deuterated positions, are in good agreement with the literature data for the non-deuterated derivative.\(^2\)
(E)-1-(Dodec-6-en-6-yl)-3-methoxylbenzene-6-d (Table 2, entry 16): Prepared according to typical procedure B. Silica gel chromatography (eluent: hexane/Et₂O = 200/1) of the crude product afforded the title compound as a colorless oil (41.8 mg, 76%); ^1H NMR (400 MHz, CDCl₃) δ 7.24 – 7.19 (m, 1H), 6.94 (d, J = 8.0 Hz, 0.35H), 6.88 (d, J = 2.6 Hz, 0.85H), 6.77 (dd, J = 8.2, 2.5 Hz, 1H), 5.65 (t, J = 7.3 Hz, 0.82H), 3.82 (s, 3H), 2.45 (t, J = 7.4 Hz, 2H), 2.17 (q, J = 7.2 Hz, 2H), 1.48 – 1.41 (m, 2H), 1.37 – 1.32 (m, 6H), 1.29 – 1.25 (m, 4H), 0.91 (t, J = 6.9 Hz, 3H), 0.86 (t, J = 6.8 Hz, 3H); ^13C NMR (101 MHz, CDCl₃) δ 159.5, 145.1, 139.9, 129.3, 129.0, 128.9, 112.3, 111.4, 55.2, 31.9, 31.7, 29.8, 29.6, 28.5, 28.4, 22.6, 22.5, 14.07, 14.06; HRMS (ESI) Calcd for C₁₉H₂₃D [M + H]^+ 276.2438, found 276.2433. The ^1H and ^13C NMR spectral patterns, except for the deuterated positions, are in good agreement with the literature data for the non-deuterated derivative.

(E)-1-(Dodec-6-en-6-yl-7-d)-2-methylbenzene (Table 2, entry 17): Prepared according to typical procedure B. Silica gel chromatography (eluent: pentane) of the crude product afforded the title compound as a colorless oil (42.0 mg, 81%); ^1H NMR (400 MHz, CDCl₃) δ 7.20 – 7.10 (m, 2.78H), 7.07 – 7.00 (m, 1H), 5.24 (t, J = 7.3 Hz, 0.15H), 2.33 (t, J = 7.0 Hz, 2H), 2.27 (s, 3H), 2.17 (t, J = 7.0 Hz, 2H), 1.46 – 1.39 (m, 2H), 1.38 – 1.31 (m, 4H), 1.28 – 1.21 (m, 6H), 0.92 (t, J = 7.0 Hz, 3H), 0.85 (t, J = 6.8 Hz, 3H); ^13C NMR (101 MHz, CDCl₃) δ 144.7, 140.4, 135.2, 129.9, 129.8, 129.0, 126.2, 125.1, 32.0, 31.7, 31.6, 29.6, 29.5, 27.9, 22.6, 22.5, 19.9, 14.1, 14.06; HRMS (ESI) Calcd for C₁₉H₂₃D [M + H]^+ 260.2489, found 260.2485. The ^1H and ^13C NMR spectral patterns, except for the deuterated positions, are in good agreement with the literature data for the non-deuterated derivative.
(E)-1-(Dec-5-en-5-yl)-4-methoxybenzene-2-d (Table 2, entry 18): Prepared according to typical procedure B. Silica gel chromatography (eluent: hexane/Et₂O = 200/1) of the crude product afforded the title compound as a colorless oil (31.6 mg, 64%); ¹H NMR (400 MHz, DMSO-d₆) δ 7.26 (d, J = 9.0 Hz, 1.24H), 6.97 – 6.62 (m, 2H), 5.55 (t, J = 7.3 Hz, 0.85H), 3.73 (s, 3H), 2.43 (t, J = 7.2 Hz, 2H), 2.14 (q, J = 7.2 Hz, 2H), 1.44 – 1.32 (m, 4H), 1.27 – 1.17 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H), 0.82 (t, J = 7.0 Hz, 3H); ¹³C NMR (101 MHz, DMSO-d₆) δ 158.5, 139.3, 135.2, 127.4, 127.3, 114.1, 114.0, 55.5, 32.1, 31.0, 29.0, 28.1, 22.4, 22.3, 14.34, 14.29; HRMS (ESI) Calcd for C₁₇H₂₆DO [M + H]+ 248.2125, found 248.2122.

(E)-1-(2,2-dimethyldec-3-en-4-yl)-4-methoxybenzene-2-d (Table 2, entry 19): Prepared according to typical procedure B. Silica gel chromatography (eluent: hexane/Et₂O = 200/1) of the crude product afforded a mixture of the title compound and minor unknown impurities as a colorless oil (7.7 mg, 14%); ¹H NMR (400 MHz, CDCl₃) δ 7.21 (d, J = 9.1 Hz, 1.15H), 6.95 – 6.66 (m, 2H), 5.50 (s, 0.77H), 3.80 (s, 3H), 2.56 (t, J = 7.4 Hz, 2H), 1.50 – 1.22 (m, 8H), 1.19 (s, 9H), 0.84 (d, J = 7.8 Hz, 3H); HRMS (ESI) Calcd for C₁₉H₃₀DO [M + H]+ 276.2438, found 276.2434.
(E)-1-Methoxy-4-(1-phenylprop-1-en-2-yl-1-d)benzene (Table 2, entry 20): Prepared according to typical procedure B. Silica gel chromatography (eluent: hexane/Et₂O = 200/1) of the crude product afforded a mixture of the title compound and minor unknown impurities as a colorless oil (11.3 mg, 25%); ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 8.8 Hz, 2H), 7.40 – 7.35 (m, 4H), 7.27 – 7.22 (m, 1H), 6.92 (d, J = 8.6 Hz, 2H), 3.85 (s, 3H), 2.27 (s, 3H); HRMS (ESI) Calcd for C₁₆H₁₆DO [M + H]⁺ 226.1342, found 226.1340. The ¹H NMR spectral patterns, except for the olefinic position, are in good agreement with the literature data for the non-deuterated derivative.

(E)-1-Methoxy-4-(1-phenylbut-1-en-2-yl-1-d)benzene (Table 2, entry 21): Prepared according to typical procedure B. Silica gel chromatography (eluent: hexane/Et₂O = 200/1) of the crude product afforded a mixture of the title compound and minor unknown impurities as a colorless oil (8.6 mg, 18%); ¹H NMR (400 MHz, acetone-d₆) δ 7.45 – 7.34 (m, 4H), 7.34 – 7.27 (m, 1H), 7.21 (d, J = 8.7 Hz, 2H), 6.98 (d, J = 8.6 Hz, 2H), 3.84 (s, 3H), 2.33 (q, J = 7.4 Hz, 2H), 0.82 (t, J = 7.4 Hz, 3H); HRMS (ESI) Calcd for C₁₇H₁₈DO [M + H]⁺ 240.1499, found 240.1494. The ¹H NMR spectral patterns, except for the olefinic position, are in good agreement with the literature data for the non-deuterated derivative.
(E)-(2-(4-Methoxyphenyl)prop-1-en-1-yl-1-d)trimethylsilane (Table 2, entry 22): Prepared according to typical procedure B. Silica gel chromatography (eluent: hexane/Et₂O = 200/1) of the crude product afforded a mixture of the title compound and minor unknown impurities as a colorless oil (11.5 mg, 26%); ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 8.8 Hz, 1.66H), 6.85 (d, J = 8.5 Hz, 2H), 5.84 (s, 0.43H), 3.81 (s, 3H), 2.19 (s, 3H), 0.18 (s, 9H); HRMS (ESI) Calcd for C₁₃H₂₀DOSi [M + H]⁺ 222.1424, found 222.1420. The ¹H NMR spectral patterns, except for the olefinic position, are in good agreement with the literature data for the non-deuterated derivative.⁷
Electrophilic Trapping of ortho-AlkenylarylMagnesium Bromide

(E)-2-(Dodec-6-en-6-yl)-5-methoxybenzoic acid (3): After the reaction of 4-methoxyphenylmagnesium bromide and 6-dodecylene under conditions B, a CO2-filled balloon was attached to the Schlenk tube. The reaction mixture was stirred at room temperature for 9 h, followed by the addition of saturated aqueous NH4Cl (2 mL) and ethyl acetate (1 mL). The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over Na2SO4 and concentrated under reduced pressure. Silica gel chromatography (eluent: hexane/ethyl acetate = 5/1) of the crude product afforded the title compound as a colorless oil (39.6 mg, 62%); 1H NMR (400 MHz, CDCl3) δ 7.45 (d, J = 2.8 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H), 7.01 (dd, J = 8.5, 2.8 Hz, 1H), 5.29 (t, J = 7.3 Hz, 1H), 3.84 (s, 3H), 2.37 (t, J = 7.1 Hz, 2H), 2.15 (q, J = 7.2 Hz, 2H), 1.45 – 1.38 (m, 2H), 1.36 – 1.30 (m, 4H), 1.27 – 1.18 (m, 6H), 0.90 (t, J = 6.8 Hz, 3H), 0.84 (t, J = 6.8 Hz, 3H); 13C NMR (101 MHz, CDCl3) δ 172.5, 157.9, 140.9, 139.2, 131.9, 129.6, 129.4, 118.5, 114.8, 55.5, 32.4, 31.9, 31.5, 29.3, 28.22, 28.15, 22.6, 22.5, 14.1, 14.0; HRMS (ESI) Calcd for C20H31O3 [M + H]+ 319.2273, found 319.2270.

(E)-(2-(Dodec-6-en-6-yl)-5-methoxyphenyl)(phenyl)methanol (4): The reaction of 4-methoxyphenylmagnesium bromide and 6-dodecylene under conditions B was quenched by the addition of benzaldehyde (64 mg, 0.60 mmol) at room temperature. After stirring for 12 h, the reaction mixture was quenched by the addition of saturated aqueous NH4Cl (2 mL) and then diluted with ethyl acetate (1 mL). The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over Na2SO4 and concentrated under reduced
pressure. Silica gel chromatography (eluent: hexane/ethyl acetate = 20/1) of the crude product afforded the title compound as a colorless oil (45.6 mg, 60%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.39 – 7.28 (m, 4H), 7.25 – 7.20 (m, 1H), 7.01 (d, \(J = 8.4\) Hz, 1H), 6.93 (d, \(J = 2.7\) Hz, 1H), 6.78 (dd, \(J = 8.4, 2.8\) Hz, 1H), 6.02 (d, \(J = 3.8\) Hz, 1H), 5.19 (t, \(J = 7.2\) Hz, 1H), 3.75 (s, 3H), 2.45 – 2.18 (m, 2H), 2.13 (t, \(J = 7.0\) Hz, 2H), 2.10 (d, \(J = 3.8\) Hz, 1H), 1.38 – 1.33 (m, 10H), 0.88 (t, \(J = 6.9\) Hz, 3H), 0.84 (t, \(J = 6.8\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 158.4, 143.9, 142.3, 139.0, 136.4, 131.5, 130.4, 128.2, 127.2, 126.7, 112.9, 112.3, 110.0, 72.6, 55.2, 32.8, 32.0, 31.6, 29.4, 28.1, 27.9, 22.6, 22.5, 14.1 (2C); HRMS (ESI) Calcd for C\(_{26}\)H\(_{37}\)O\(_2\) [M + H]\(^+\) 381.2794, found 381.2792.

**MeO**

\(\text{(E)-1-(Dodec-6-en-6-yl)-2-iodo-4-methoxybenzene (5):}\) The reaction of 4-methoxyphenylmagnesium bromide and 6-dodecyne under conditions B was quenched by the addition of iodine (XX mg, 1.2 mmol) at room temperature. After stirring for 3 h, the reaction mixture was quenched by the addition of saturated aqueous NH\(_4\)Cl (2 mL) and then diluted with ethyl acetate (1 mL). The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over Na\(_2\)SO\(_4\) and concentrated under reduced pressure. Silica gel chromatography (eluent: hexane/Et\(_2\)O = 200/1) of the crude product afforded the title compound as a colorless oil (50.4 mg, 63%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37 (d, \(J = 2.6\) Hz, 1H), 6.99 (d, \(J = 8.4\) Hz, 1H), 6.83 (dd, \(J = 8.4, 2.6\) Hz, 1H), 5.25 (t, \(J = 7.3\) Hz, 1H), 3.78 (s, 3H), 2.34 (t, \(J = 7.0\) Hz, 2H), 2.15 (q, \(J = 7.2\) Hz, 2H), 1.52 – 1.49 (m, 2H), 1.47 – 1.33 (m, 10H), 0.91 (t, \(J = 6.7\) Hz, 3H), 0.86 (t, \(J = 6.9\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 158.1, 142.7, 141.7, 136.7, 131.6, 129.7, 124.0, 113.8, 55.5, 32.9, 31.9, 31.6, 29.2, 28.0, 27.7, 22.6, 22.6, 14.1, 14.1; HRMS (ESI) Calcd for C\(_{26}\)H\(_{37}\)O\(_2\) [M + H]\(^+\) 401.1341, found 401.1338.
(E)-2-(2-(Dodec-6-en-6-yl)-5-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6): The reaction of 4-methoxyphenylmagnesium bromide and 6-dodecyne under conditions B was quenched by the addition of trimethyl borate (104 mg, 1.0 mmol) at 0 °C. After stirring at room temperature for 6 h, the reaction mixture was hydrolyzed by the addition of aqueous HCl (1.0 M, 4 mL) and additional stirring for 3 h. The resulting mixture was extracted with dichloromethane (3 x 10 mL), and the combined organic layer was dried over MgSO\(_4\) and concentrated under reduced pressure. The residue was dissolved in Et\(_2\)O (5 mL) and treated with pinacol (118 mg, 1.0 mmol) in the presence of 4Å molecular sieves (200 mg) at room temperature for 6 h. The mixture was concentrated under reduced pressure, and the residue was subjected to silica gel chromatography (eluent: hexane/Et\(_2\)O = 30/1) to afford the title compound as a colorless oil (24.0 mg, 30%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.14 (d, \(J = 2.9\) Hz, 1H), 7.08 (d, \(J = 8.4\) Hz, 1H), 6.86 (dd, \(J = 8.4, 2.9\) Hz, 1H), 5.20 (t, \(J = 7.2\) Hz, 1H), 3.81 (s, 3H), 2.37 (t, \(J = 7.0\) Hz, 2H), 2.11 (q, \(J = 7.2\) Hz, 2H), 1.45 – 1.39 (m, 2H), 1.35 – 1.32 (m, 4H), 1.30 (s, 12H), 1.26 – 1.22 (m, 6H), 0.90 (t, \(J = 7.0\) Hz, 3H), 0.83 (t, \(J = 6.9\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 157.4, 143.5, 142.1, 129.2, 128.9, 118.8, 115.6, 110.0, 83.4 (2C), 55.3, 32.8, 31.9, 31.7, 29.5, 28.4, 28.0, 24.8 (4C), 22.65, 22.6, 14.1 (2C); HRMS (ESI) Calcd for C\(_{25}\)H\(_{42}\)BO\(_3\)[M + H]\(^+\) 401.3227, found 401.3223.
References

**1H and 13C NMR Spectra**

*Figure S1.* $^1H$ NMR spectrum (400 MHz, CDCl$_3$) of the crude product in Scheme 2.

*Figure S2.* $^1H$ NMR spectrum (400 MHz, CDCl$_3$) of 2-$d_5$ (Table 1, entry 1, crude mixture).
Figure S3. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 2-$d_5$ (Table 1, entry 5).

Figure S4. $^{13}$C NMR spectrum (101 MHz, CDCl$_3$) of 2-$d_5$ (Table 1, entry 5).
Figure S5. $^1$H NMR spectrum (400 MHz, DMSO-$d_6$) of the product in Table 2, entry 1.

Figure S6. $^{13}$C NMR spectrum (101 MHz, DMSO-$d_6$) of the product in Table 2, entry 1.
Figure S7. $^1$H NMR spectrum (400 MHz, DMSO-$d_6$) of the product in Table 2, entry 2.

Figure S8. $^{13}$C NMR spectrum (101 MHz, DMSO-$d_6$) of the product in Table 2, entry 2.
Figure S9. $^1$H NMR spectrum (400 MHz, DMSO-$d_6$) of the product in Table 2, entry 3.

Figure S10. $^{13}$C NMR spectrum (101 MHz, DMSO-$d_6$) of the product in Table 2, entry 3.
**Figure S11.** $^1$H NMR spectrum (400 MHz, DMSO-$d_6$) of the product in Table 2, entry 4.

**Figure S12.** $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$) of the product in Table 2, entry 5.
Figure S13. $^1$H NMR spectrum (400 MHz, DMSO-$d_6$) of the product in Table 2, entry 6.

Figure S14. $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$) of the product in Table 2, entry 7.
Figure S15. $^{13}$C NMR spectrum (101 MHz, CD$_2$Cl$_2$) of the product in Table 2, entry 7.

Figure S16. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of the product in Table 2, entry 8.
Figure S17. $^{13}$C NMR spectrum (101 MHz, CDCl$_3$) of the product in Table 2, entry 8.

Figure S18. $^{13}$C NMR spectrum (400 MHz, CDCl$_3$) of the product in Table 2, entry 9.
Figure S19. $^{13}$C NMR spectrum (101 MHz, CDCl$_3$) of the product in Table 2, entry 9.

Figure S20. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of the product in Table 2, entry 10.
Figure S21. $^{13}$C NMR spectrum (101 MHz, CDCl$_3$) of the product in Table 2, entry 10.

Figure S22. $^1$H NMR spectrum (500 MHz, CDCl$_3$) of the product in Table 2, entry 11.
Figure S23. $^{13}$C NMR spectrum (126 MHz, CDCl$_3$) of the product in Table 2, entry 11.

Figure S24. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of the product in Table 2, entry 12.
Figure S25. $^{13}$C NMR spectrum (101 MHz, CDCl$_3$) of the product in Table 2, entry 12.

Figure S26. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of the product in Table 2, entry 13.
Figure S27. $^{13}$C NMR spectrum (400 MHz, CDCl$_3$) of the product in Table 2, entry 13.

Figure S28. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of the product in Table 2, entry 14.
Figure S29. $^{13}$C NMR spectrum (101 MHz, CDCl$_3$) of the product in Table 2, entry 14.

Figure S30. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of the product in Table 2, entry 15.
Figure S31. $^{13}$C NMR spectrum (101 MHz, CDCl$_3$) of the product in Table 2, entry 15.

Figure S32. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of the product in Table 2, entry 16.
Figure S33. $^{13}$C NMR spectrum (101 MHz, CDCl$_3$) of the product in Table 2, entry 16.

Figure S34. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of the product in Table 2, entry 17.
Figure S35. $^{13}$C NMR spectrum (101 MHz, CDCl$_3$) of the product in Table 2, entry 17.

Figure S36. $^1$H NMR spectrum (400 MHz, DMSO-$d_6$) of the product in Table 2, entry 18.
Figure S37. $^{13}$C NMR spectrum (400 MHz, DMSO-$d_6$) of the product in Table 2, entry 18.

Figure S38. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of the product in Table 2, entry 19.
Figure S39. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of the product in Table 2, entry 20.

Figure S40. $^1$H NMR spectrum (400 MHz, acetone-$d_6$) of the product in Table 2, entry 21.
Figure S41. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of the product in Table 2, entry 22.

Figure S42. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 3.
Figure S43. $^{13}$C NMR spectrum (101 MHz, CDCl$_3$) of compound 3.

Figure S44. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 4.
Figure S45. $^{13}$C NMR spectrum (101 MHz, CDCl$_3$) of compound 4.

Figure S46. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 5.
Figure S47. $^{13}$C NMR spectrum (101 MHz, CDCl$_3$) of compound 5.

Figure S48. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 6.
Figure S49. $^{13}$C NMR spectrum (101 MHz, CDCl$_3$) of compound 6.