Supporting information

New Reactivity of Ethynyl Benziodoxolone: Modulating Iron-Catalyzed Dehydration of Propargyl Alcohols

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Table of contents

Materials and methods S2
General procedure for the discovery of dehydration S2
General procedure for the optimization of the reaction conditions S2
General procedures for the dehydration of propargyl alcohols S3
Radical trapping and kinetic isotopic effect experiments S4
UV-Vis absorption experiment S5
Control experiments S5
Practical scale reaction and representative derivation of enyne 4e and 4j S6
References S7
Characterization data for compounds S7
Copies of 1H NMR and 13C NMR spectra S13
Materials and methods

All the chemicals were commercially, and used without further purification unless otherwise noted. FeCl₃ and other starting materials were purchased from Alfa Aesar, Energy Chemical, Adamas and other companies. All reactions were carried out under nitrogen atmosphere unless specified. 1,2-dichloroethane, dichloromethane, and acetonitrile were distilled from calcium hydride. Toluene was distilled from sodium. Thin-layer chromatography (TLC) was carried out on 0.25 mm Huanghai silica gel plates (HSGF-254) and visualized by exposure to UV light (254 nm) and/or KMnO₄ (aq.) was used as revealing system. Flash column chromatography was performed on Tsingdao silica gel (60, particle size 0.040–0.063 mm). ¹H NMR, and ¹³C NMR spectra were recorded on Bruker spectrometers (at 300, 400 or 500 MHz for ¹H NMR, at 75, 100 or 125 MHz for ¹³C NMR) and were reported relative to deuterated solvent or tetramethylsilane internal standard signals. Data for ¹H NMR spectra were reported as following: chemical shift (δ/ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (J/Hz) and integration. Data for ¹³C NMR spectra were reported in terms of chemical shift and coupling constant (J/Hz) when necessary. High Resolution Mass Spectrometry was conducted on Bruker Apex IV RTMS.

Propargyl alcohols were prepared according to known procedures. ¹⁻³ R-EBX were prepared according to Waser’s procedures.¹⁴ Arylbenziodoxolone was prepared according to Zhdankin and co-workers’ procedure.²

General Procedure for the Discovery of Dehydration

In a 10 mL flask with a magnetic stirring bar under N₂ atmosphere were placed a solution of propargyl alcohol 2a (0.3 mmol, 55.8 mg, 1.0 equiv) in dry DCE (1.5 mL), then TIPS-EBX (0.3 mmol, 129 mg, 1.0 equiv) was added followed by addition of AuCl₃ (0.015 mmol, 4.5 mg, 0.05 equiv) quickly. The solution was stirred at room temperature for about 12 h and followed by TLC. After that, the solvent was removed in vacuo and the residue was subjected to column chromatography (SiO₂, Hexanes) to afford enyne 4a as colorless oil (25.5 mg, 50%).

The control experiments were conducted under the similar condition without AuCl₃ or TIPS-EBX.

Optimization of the Reaction Conditions

<table>
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<th>entry</th>
<th>Lewis Acid (10 mol%)</th>
<th>R-EBX (20 mol%)</th>
<th>additive</th>
<th>solvent</th>
<th>temp (°C)</th>
<th>time (h)</th>
<th>yield (%)</th>
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<tr>
<td>1b</td>
<td>R = TMS</td>
<td>1c, R = TES</td>
<td>1d, R = TRDPS</td>
<td>1e, R = Ph</td>
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S2
1. FeCl₃  TIPS-EBX -  DCM  rt  6  54
2. FeBr₃  TIPS-EBX -  DCM  rt  12  53
3. FeCl₂  TIPS-EBX -  DCM  rt  12  <10
4. InCl₃  TIPS-EBX -  DCM  rt  12  trace
5. Ce(OTf)₃  TIPS-EBX -  DCM  rt  12  trace
6. La(OTf)₃  TIPS-EBX -  DCM  rt  12  trace
7. Dy(OTf)₃  TIPS-EBX -  DCM  rt  12  trace
8. Cu(OTf)₂  TIPS-EBX -  DCM  rt  24  <30
9. (CuOTf)₂•Ph  TIPS-EBX -  DCM  rt  24  <30
10. FeCl₃  TIPS-EBX  4 Å  MS  DCM  rt  >36  <b
11. FeCl₃  TIPS-EBX  MgSO₄  ACN  rt  24  44
12. FeCl₃  TIPS-EBX  Na₂SO₄  ACN  rt  24  48
13. FeCl₃  TIPS-EBX  MgSO₄  ACN  50  5  63
14. FeCl₃  TIPS-EBX -  DCE  50  2  76
15. FeCl₃ (5 mol %)  TIPS-EBX (10 mol %) -  DCE  50  3  68
16. Cu(OTf)₂  TIPS-EBX -  DCE  50  3  64
17. FeCl₃  TIPS-EBX -  PhMe  50  12  13
18. FeCl₃  TMS-EBX -  DCE  50  7  58
19. FeCl₃  TES-EBX -  DCE  50  1  65
20. FeCl₃  Ph-EBX -  DCE  50  5  55
21. FeCl₃  TBDPS-EBX -  DCE  50  1.2  76
22. FeCl₃  TIPS-EBX -  DCE/PhMe (v/v = 2:1)  50  5  88(83°)

*a NMR yield using 1,3,5-trimethoxybenzene as the internal standard.  b Propargyl alcohol could not be fully converted and the yield was not determined.  c Isolated yield.

Reaction conditions: unless otherwise noted, 2b (0.1 mmol), R-EBX (0.02 mmol), Lewis acid (0.01 mmol), solvent (1mL or 1.5 mL).

**General Procedures for the Dehydration Reaction**

A 25 mL oven-dried round bottom flask was charged with a stir bar, FeCl₃ (4.8 mg, 0.03 mmol, 0.1 equiv) and DCE/PhMe (3 mL/1.5 mL) unless otherwise specified. Then TIPS-EBX (25.6 mg, 0.06 mmol, 0.2 equiv) was added and the resulting mixture was stirred for about 5 min at room temperature. To the resulting yellow solution was added propargyl alcohol 2 (0.3 mmol, 1.0 equiv). Or propargyl alcohol 2
and TIPS-EBX was premixed in solution, then added FeCl₃ quickly. The reaction solution was allowed to stir at 50 °C until progargyl alcohol 2 disappeared from the TLC, followed by evaporation of the solvent under reduced pressure. The residue was purified by column chromatography on silica gel (Hexanes) to afford the desired pure product 4 in 60-95% yield (most of the enynes are not stable at neat state).

**Radical Trapping and Kinetic Isotopic Effect**

Radical Trapping Experiment: A 10 mL oven-dried round bottom flask was charged with a stir bar, FeCl₃ (1.6 mg, 0.01 mmol, 0.1 equiv) and DCE/PhMe (1 mL/0.5 mL), then TIPS-EBX (8.4 mg, 0.02 mmol, 0.2 equiv) and BHT (24.2 mg, 0.11 mmol, 1.1 equiv) were added and the resulting mixture was stirred for 5 min. Then 2e (20.2 mg, 0.1 mmol, 1.0 equiv) was added and the resulting mixture was warmed to 50 °C and stirred for 1.5 h at this temperature. Upon completion of the reaction indicated by TLC, the reaction mixture was cooled to room temperature. Remove FeCl₃ through a short pad of silica gel (DCM eluted) and added 1,3,5-trimethoxybenzene (11.2 mg, 0.066 mmol) as the internal standard for NMR analysis. Then remove the solvent in vacuo and the residue was subjected to NMR analysis in CDCl₃.

Intermolecular Kinetic Isotopic Effect Experiment: A 10 mL oven-dried round bottom flask was charged with a stir bar, FeCl₃ (4.8 mg, 0.03 mmol, 0.1 equiv) and DCE/PhMe (2 mL/1 mL), then TIPS-EBX (25.6 mg, 0.06 mmol, 0.2 equiv) was added and the resulting mixture was stirred for 5 min. In another 25 mL oven-dried round bottom flask was placed 2d (32.2 mg, 0.159 mmol) and 2d-d₃ (30.8 mg, 0.150 mmol) in DCE/PhMe (1 mL/0.5 mL). The mixture in the first flask was transferred into the second one and the resulting mixture was allowed to warm to 50 °C and stirred for 3 h. After cooling down to room temperature, the solvent was removed and the resulting residue was subjected to silica gel (Hexanes to EtOAc/Hexanes = 20: 1) to afford enyne (28.4 mg, with some impurity, KIE = 1.11) and the recovered alcohol (34.3 mg).

In the starting material: H : D = 0.159 : 0.150 = 1.06; In the product: H : D = 0.54 : 0.46 = 1.174; So 1.06k_H/k_D = 1.174; k_H/k_D = 1.11.
Copy for NMR analysis of intermolecular kinetic isotopic effect experiment

UV-Vis absorption experiment:

**Materials and instrument:** MeCN (99.9% for HPLC, BCR international trading Ltd. Co), FeCl₃ (Alfa Aesar). UV-Vis absorption spectrums were recorded on Shimadzu UV-2600 UV-Vis spectrophotometer. TIPS-EBX, 2a and FeCl₃ were prepared as a MeCN solution (2.664 × 10⁻⁵ M), respectively. TIPS-EBX+ 2a, TIPS-EBX+ FeCl₃ were prepared as a 1:1 mixture in MeCN (2.664 × 10⁻⁵ M), respectively.

![Figure S1] UV-Vis absorption spectrum

Control Experiments
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<th>entry</th>
<th>1II (20 mol %)</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>yield (%)</th>
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<td>1a</td>
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<td>-</td>
<td>rt-50</td>
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<td>6</td>
<td>1i</td>
<td>50</td>
<td>12</td>
<td>4a (trace), 2a (&gt;90)c</td>
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<tr>
<td>7</td>
<td>1j</td>
<td>50</td>
<td>24</td>
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a NMR yield using 1,3,5-trimethoxybenzene as the internal standard. b DCE/PhMe (v/v = 2:1) was used as solvent. c Without FeCl₃. d Without 1II. e Isolated yield.

Reaction conditions: 2a (0.1 mmol), R-EBX (0.02 mmol), FeCl₃ (0.01 mmol), DCE/PhMe (1 mL/0.5 mL), 50 °C.

Millimole Scale Reaction and Derivation of Enyne 4e and 4j

Follow the general procedures for the dehydration reaction described above.

Enyne 4e (128 mg, 0.61 mmol, 1.0 equiv) was dissolved in freshly distilled DCM (5 mL), and the solution was bubbled for 10 min with Ar and cooled to 0 °C using an ice/water bath. Then to the solution was added bis[rhodium(α, α, α', α', -tetramethyl-1,3-benzenedipropionic acid)] (0.92 mg, 0.0012 mmol, 0.02 mol%). After that, the iodonium ylide (203 mg, 0.61 mmol, 1.0 equiv) was added in one portion at 0 °C. After 10 min, the ice/water bath was removed and the reaction mixture was stirred at room
temperature for another 1 h. Another portion of iodonium ylide (203 mg, 0.61 mmol, 1.0 equiv) was added and stirred for another hour. When TLC showed the completion of the reaction, DCM was removed in vacuo. The residue was purified by flash chromatography on silica gel (Hexanes/EtOAc = 50:1 to 20:1) to afford the desired product as yellowish oil (124 mg, 60%).

References:

Characterization Data for Compounds

(4-cyclopropylbut-1-en-3-yn-2-yl)benzene (4a): 5 h, yellowish oil (42.4 mg, 84% yield); 1H NMR 1H NMR (500 MHz, CDCl3) δ 7.66 – 7.59 (m, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.26 (m, 1H), 5.82 (d, J = 1.1 Hz, 1H), 5.56 (d, J = 0.9 Hz, 1H), 1.48 – 1.41 (m, 1H), 0.88 – 0.83 (m, 1H), 0.82 – 0.78 (m, 1H); 13C NMR (125 MHz, CDCl3) δ 137.9, 130.9, 128.3, 128.1, 126.1, 119.4, 95.1, 75.0, 8.7, 0.2; HRMS calculated for C13H13 (M + H+): 169.1012, found: 169.1014.

Hex-5-en-3-yn-1,5-diyl dibenzene (4b): 5 h, yellowish oil (57.7 mg, 83% yield); 1H NMR (400 MHz, CDCl3) δ 7.62 – 7.51 (m, 2H), 7.36 – 7.17 (m, 8H), 5.83 (d, J = 0.9 Hz, 1H), 2.92 (t, J = 7.4 Hz, 2H), 2.71 (t, J = 7.4 Hz, 2H); 13C NMR (101 MHz, CDCl3) δ 140.6, 137.5, 130.8, 128.6, 128.4, 128.2, 128.1, 126.3, 126.0, 119.5, 91.0, 80.5, 35.0, 21.6; HRMS calculated for C18H17 (M + H+): 233.1325, found: 233.1324.

1-bromo-4-(4-cyclopropylbut-1-en-3-yn-2-yl)benzene (4c): 2 h, DCE as solvent, yellowish oil (67.0 mg, 90% yield); 1H NMR (400 MHz, CDCl3) δ 7.55 – 7.41 (m, 4H), 5.81 (d, J = 0.6 Hz, 1H), 5.58 (s, 1H), 1.49 – 1.41 (m, 1H), 0.92 – 0.84 (m, 2H), 0.84 – 0.76 (m, 2H); 13C NMR (125 MHz, CDCl3) δ 136.8, 131.3, 129.9, 127.7, 122.2, 119.8, 95.6, 74.5, 8.7, 0.2; HRMS calculated for C13H12Br (M + H+): 247.0122, found: 247.0116.

Oct-1-en-3-yn-2-yl benzene (4d): 5 h, colorless oil (47.5 mg, 85% yield); 1H NMR (400 MHz, CDCl3) δ 7.65 (dd, J = 5.3, 3.3 Hz, 2H), 7.40 – 7.25 (m, 3H), 5.83 (s, 1H), 5.57 (s, 1H), 2.41 (t, J = 7.0 Hz, 2H), 1.59 (dq, J = 12.1, 6.9 Hz, 2H), 1.54 – 1.41 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 137.8, 131.0, 128.2, 128.0, 126.0, 119.3, 92.0, 79.7, 30.8, 22.0, 19.1, 13.6; HRMS
calculated for C$_{14}$H$_{17}$ (M + H$^+$): 185.1325, found: 185.1325.

(4-cyclohexylbut-1-en-3-yn-2-yl)benzene (4e): 2 h, colorless oil (59 mg, 93% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 – 7.60 (m, 2H), 7.39 – 7.25 (m, 3H), 5.84 (d, $J$ = 1.2 Hz, 1H), 5.58 (d, $J$ = 0.8 Hz, 1H), 2.71 – 2.53 (m, 1H), 1.93 – 1.85 (m, 2H), 1.81 – 1.69 (m, 2H), 1.64 – 1.48 (m, 3H), 1.45 – 1.27 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.8, 130.9, 128.2, 128.0, 126.0, 119.1, 96.0, 79.6, 32.6, 29.7, 25.9, 24.9; HRMS calculated for C$_{16}$H$_{17}$ (M + H$^+$): 185.1325, found: 185.1325.

(5-methylhex-1-en-3-yn-2-yl)benzene (4f): 4 h, colorless oil (48.4 mg, 90%); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.75 – 7.62 (m, 2H), 7.39 – 7.34 (m, 2H), 7.34 – 7.29 (m, 1H), 5.86 (d, $J$ = 1.1 Hz, 1H), 5.61 (d, $J$ = 0.6 Hz, 1H), 2.81 (dt, $J$ = 13.7, 6.9 Hz, 1H), 1.30 (d, $J$ = 6.9 Hz, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 137.9, 130.9, 128.3, 128.09, 126.1, 119.3, 97.4, 79.0, 23.0, 21.2; HRMS calculated for C$_{13}$H$_{15}$ (M + H$^+$): 171.1168, found: 171.1168.

but-3-en-1-yn-1,3-diyl dibenzene (4g): 11 h, colorless oil (50.4 mg, 82%); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.77 – 7.72 (m, 2H), 7.58 – 7.53 (m, 2H), 7.43 – 7.38 (m, 2H), 7.38 – 7.32 (m, 4H), 6.00 (d, $J$ = 0.9 Hz, 1H), 5.78 (d, $J$ = 0.8 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 137.3, 131.7, 130.7, 130.7, 128.4, 128.4, 126.1, 123.2, 120.6, 90.8, 88.6; HRMS calculated for C$_{16}$H$_{13}$ (M + H$^+$): 205.1017, found: 205.1011.

trimethyl(3-phenylbut-3-en-1-yn-1-yl) silane (4h): 24 h, yellowish oil (52.7 mg, 87%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 – 7.62 (m, 2H), 7.44 – 7.29 (m, 3H), 7.43 – 7.38 (m, 2H), 7.38 – 7.32 (m, 4H), 6.00 (d, $J$ = 0.9 Hz, 1H), 5.78 (d, $J$ = 0.8 Hz, 1H), 0.27 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.9, 130.6, 128.4, 128.3, 126.0, 121.4, 104.1, 95.9, -0.1; HRMS calculated for C$_{13}$H$_{17}$Si (M + H$^+$): 210.1100, found: 210.1092.

(5-methylhexa-1,5-dien-3-yn-2-yl) benzene (4i): 12 h, yellowish oil (51.2 mg, 82%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 – 7.62 (m, 2H), 7.41 – 7.27 (m, 3H), 5.92 (d, $J$ = 0.9 Hz, 1H), 5.66 (d, $J$ = 0.8 Hz, 1H), 5.40 (dd, $J$ = 1.8, 0.9 Hz, 1H), 5.34 – 5.28 (m, 1H), 2.00 – 1.98 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.2, 130.5, 128.3, 128.2, 126.7, 126.0, 122.2, 120.5, 92.0, 87.5, 23.4; HRMS calculated for C$_{13}$H$_{13}$ (M + H$^+$): 169.1017, found: 169.1011.
(Z)-non-2-en-4-yn-3-ylbenzene (4j): 5 h, colorless oil (58.9 mg, 95%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.58 (dt, \(J = 3.2, 1.9\) Hz, 2H), 7.40 – 7.28 (m, 2H), 7.28 – 7.19 (m, 1H), 6.40 (q, \(J = 6.9\) Hz, 1H), 2.48 (t, \(J = 7.0\) Hz, 2H), 2.05 (d, \(J = 6.9\) Hz, 3H), 1.67 – 1.57 (m, 2H), 1.56 – 1.44 (m, 2H), 0.97 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 138.9, 131.5, 128.2, 127.1, 125.8, 124.7, 96.7, 77.6, 31.0, 22.0, 19.3, 16.7, 13.6; HRMS calculated for C\(_{15}\)H\(_{19}\) (M + H\(^{+}\)): 199.1487, found: 199.1482.

(2-methylnon-2-en-4-yn-3-yl)benzene (4k): 5 h, colorless oil (42.9 mg, 66%); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.37 – 7.28 (m, 4H), 7.27 – 7.21 (m, 1H), 2.38 (t, \(J = 7.0\) Hz, 2H), 2.12 (s, 3H), 1.79 (s, 3H), 1.62 – 1.51 (m, 2H), 1.50 – 1.38 (m, 2H), 0.93 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 140.8, 140.2, 129.1, 127.9, 126.5, 119.4, 93.1, 81.3, 31.1, 23.8, 22.0, 21.3, 19.3, 13.6; HRMS calculated for C\(_{16}\)H\(_{21}\) (M + H\(^{+}\)): 213.1643, found: 213.1636.

(\(E\))-\((3\)-methylene\(\)\(-1\)-en-4-\(\)yn\(-1\)-\(\)yl)\)benzene (4l): 23 h, PhMe as solvent, room temperature, colorless oil (41.4 mg, 60%); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.44 (d, \(J = 7.5\) Hz, 2H), 7.33 (t, \(J = 7.5\) Hz, 2H), 7.27 – 7.22 (m, 1H), 6.98 (d, \(J = 15.7\) Hz, 1H), 6.76 (d, \(J = 15.7\) Hz, 1H), 5.48 (d, \(J = 15.1\) Hz, 2H), 2.45 (t, \(J = 7.0\) Hz, 2H), 1.68 – 1.58 (m, 2H), 1.58 – 1.47 (m, 2H), 0.98 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 136.9, 132.5, 130.2, 128.9, 128.6, 127.8, 126.8, 122.6, 92.9, 77.4, 30.8, 22.0, 19.0, 13.6; HRMS calculated for C\(_{16}\)H\(_{19}\) (M + H\(^{+}\)): 211.1487, found: 211.1471.

(3-heptylidene\(\)\(-1\),4\(-\)di\(\)yne\(-1\),5\(-\)di\(\)yl)\)dibenzene (4m): 24 h, colorless oil (51.8 mg, 82%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.54 – 7.44 (m, 4H), 7.37 – 7.27 (m, 6H), 6.47 (t, \(J = 7.8\) Hz, 1H), 2.49 (q, \(J = 7.5\) Hz, 2H), 1.55 – 1.45 (m, 2H), 1.42 – 1.34 (m, 2H), 1.34 – 1.23 (m, 4H), 0.89 (t, \(J = 6.9\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 149.7, 131.6, 131.6, 128.4, 128.3, 128.2, 128.2, 123.0, 105.6, 92.7, 87.5, 86.5, 84.9, 31.6, 31.0, 28.9, 28.6, 22.6, 14.1; HRMS calculated for C\(_{24}\)H\(_{25}\) (M + H\(^{+}\)): 313.1956, found: 313.1948.

1-methyl-4-(oct-1-en-3-\(\)yn-2-\(\)yl)\)benzene (4n): 3 h, yellowish oil (53.3 mg, 82%); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.55 (d, \(J = 8.2\) Hz, 2H), 7.15 (d, \(J = 8.0\) Hz, 2H), 5.80 (d, \(J = 0.5\) Hz, 1H), 5.53 (s, 1H), 2.42 (t, \(J = 7.1\) Hz, 2H), 2.36 (s, 3H), 1.64 – 1.56 (m, 21H), 1.49 (dq, \(J = 14.3, 7.2\) Hz, 2H), 0.95 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 137.3, 135.1, 130.8, 128.9, 126.0, 118.4, 91.8, 79.9, 49.4, 30.9, 22.0, 21.1, 19.1, 13.6; HRMS calculated for C\(_{15}\)H\(_{19}\) (M + H\(^{+}\)): 199.1487, found: 199.1480.

1-methoxy-4-(oct-1-en-3-\(\)yn-2-\(\)yl)\)benzene (4o): 4 h, PhMe was used as solvent, yellowish oil (65.0
mg, 88%); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.65 - 7.56\) (m, 2H), 6.95 - 6.79 (m, 2H), 5.75 (d, \(J = 0.7\) Hz, 1H), 5.49 (s, 1H), 3.82 (d, \(J = 6.0\) Hz, 3H), 2.43 (t, \(J = 7.1\) Hz, 2H), 1.68 - 1.58 (m, 2H), 1.56 - 1.43 (m, 2H), 0.97 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta 159.7, 130.5, 130.4, 127.3, 117.4, 113.6, 91.7, 80.0, 55.3, 30.9, 22.1, 19.1, 13.6; HRMS calculated for C\(_{18}\)H\(_{39}\)O (M + H\(^+\)): 215.1436, found: 215.1431.

1-fluoro-4-(oct-1-en-3-yn-2-yl)benzene (4p): 7 h, colorless oil (4p): 7 h, colorless oil (54.6 mg, 90%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.68 - 7.58\) (m, 2H), 7.09 - 6.99 (m, 2H), 5.78 (s, 1H), 5.56 (s, 1H), 2.43 (t, \(J = 7.1\) Hz, 2H), 1.66 - 1.55 (m, 2H), 1.55 - 1.43 (m, 8.3, 5.9 Hz, 2H), 0.96 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 162.7\) (d, \(J = 247.3\) Hz), 133.9 (d, \(J = 3.2\) Hz), 129.9, 127.8 (d, \(J = 8.1\) Hz), 119.0, 115.1 (d, \(J = 21.6\) Hz), 92.2, 79.6, 30.8, 22.0, 19.1, 13.6; HRMS calculated for C\(_{14}\)H\(_{16}\)F (M + H\(^+\)): 203.1236, found: 203.1227.

1-chloro-4-(oct-1-en-3-yn-2-yl)benzene (4q): 15 h, colorless oil (55.6 mg, 85%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.63 - 7.51\) (m, 2H), 7.34 - 7.27 (m, 2H), 5.80 (d, \(J = 0.8\) Hz, 1H), 5.57 (s, 1H), 2.40 (t, \(J = 7.0\) Hz, 2H), 1.64 - 1.52 (m, 2H), 1.52 - 1.40 (m, 2H), 0.94 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 136.3, 133.9, 129.9, 128.3, 127.3, 119.6, 92.4, 79.3, 30.7, 22.0, 19.0, 13.6; HRMS calculated for C\(_{14}\)H\(_{16}\)Cl (M + H\(^+\)): 219.0941, not found; calculated for C\(_{14}\)H\(_{16}\)Cl (M + H\(^+\)): 219.0941, found: 219.0935.

1-bromo-4-(oct-1-en-3-yn-2-yl)benzene (4r): 5 h, colorless oil (70 mg, 87%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.55 - 7.48\) (m, 2H), 7.47 - 7.41 (m, 2H), 5.81 (d, \(J = 0.8\) Hz, 1H), 5.58 (s, 1H), 2.40 (t, \(J = 7.0\) Hz, 2H), 1.64 - 1.52 (m, 2H), 1.52 - 1.40 (m, 2H), 0.94 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 136.7, 131.3, 123.0, 127.7, 122.1, 119.7, 92.5, 79.2, 30.7, 22.0, 19.0, 13.6; HRMS calculated for C\(_{14}\)H\(_{16}\)Br (M + H\(^+\)): 263.0435, found: 263.0425.

1-methoxy-2-(oct-1-en-3-yn-2-yl)benzene (4s): 0.5 h, colorless oil (58.0 mg, 90%); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.51\) (dd, \(J = 7.6, 1.7\) Hz, 1H), 7.33 - 7.15 (m, 1H), 6.95 (td, \(J = 7.5, 1.0\) Hz, 1H), 6.91 (d, \(J = 8.2\) Hz, 1H), 5.87 (d, \(J = 2.1\) Hz, 1H), 5.75 (d, \(J = 2.0\) Hz, 1H), 3.86 (s, 3H), 2.36 (t, \(J = 7.0\) Hz, 2H), 1.61 - 1.51 (m, 2H), 1.51 - 1.40 (m, 2H), 0.93 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta 157.0, 130.3, 128.9, 128.3, 128.0, 124.3, 120.5, 111.4, 90.0, 81.0, 55.6, 30.8, 22.0, 19.1, 13.6; HRMS calculated for C\(_{15}\)H\(_{16}\)O (M + H\(^+\)): 215.1436, found: 215.1429.

1-methyl-3-(oct-1-en-3-yn-2-yl)benzene (4t): 1 h, colorless to yellowish oil (57.4 mg, 90%); \(^1\)H NMR
(500 MHz, CDCl$_3$) δ 7.45 (dd, $J = 8.9$, 0.5 Hz, 2H), 7.22 (t, $J = 7.6$ Hz, 1H), 7.10 (d, $J = 7.5$ Hz, 1H), 5.81 (d, $J = 1.1$ Hz, 1H), 5.55 (s, 1H), 2.41 (t, $J = 7.0$ Hz, 2H), 2.36 (s, 3H), 1.65 – 1.54 (m, 2H), 1.54 – 1.44 (m, 2H), 0.95 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 137.8, 137.8, 131.1, 128.9, 128.2, 126.8, 123.2, 119.2, 91.9, 79.9, 30.86, 22.07, 21.5, 19.1, 13.6; HRMS calculated for C$_{15}$H$_{19}$ (M + H$^+$): 199.1487, found: 199.1481.

1-methoxy-3-(oct-1-en-3-yn-2-yl)benzene (4u): 5 h, colorless oil (51.1 mg, 81%); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.27 – 7.22 (m, 2H), 7.22 – 7.20 (m, 1H), 6.87 – 6.81 (m, 1H), 5.83 (d, $J = 1.0$ Hz, 1H), 5.58 (s, 1H), 3.82 (s, 3H), 2.41 (t, $J = 7.0$ Hz, 2H), 1.64 – 1.55 (m, 2H), 1.55 – 1.41 (m, 2H), 0.94 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.5, 139.3, 130.8, 129.2, 119.5, 118.4, 113.6, 111.9, 91.9, 79.7, 55.2, 30.8, 22.0, 19.0, 13.6; HRMS calculated for C$_{15}$H$_{19}$O (M + H$^+$): 215.1436, found: 215.1431.

2,4-dimethyl-1-(oct-1-en-3-yn-2-yl)benzene (4v): 0.5 h, colorless oil (57.8 mg, 90%); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.65 – 7.52 (m, 2H), 7.19 (d, $J = 8.4$ Hz, 2H), 7.19 (d, $J = 10.1$, 2.3 Hz, 2H), 5.66 (d, $J = 2.0$ Hz, 1H), 5.37 (d, $J = 2.0$ Hz, 1H), 2.41 (s, 3H), 2.37 – 2.29 (m, 5H), 1.60 – 1.50 (m, 21H), 1.49 – 1.37 (m, 2H), 0.93 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 137.3, 137.2, 135.2, 132.2, 131.1, 128.6, 126.4, 123.4, 91.6, 80.8, 30.8, 22.0, 21.0, 20.1, 19.1, 13.6; HRMS calculated for C$_{16}$H$_{21}$ (M + H$^+$): 213.1643, found: 213.1636.

1-(7-chlorohept-1-en-3-yn-2-yl)-4-ethylbenzene (4w): 3 h, colorless oil (61.5 mg, 89%); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.65 – 7.52 (m, 2H), 7.19 (d, $J = 8.4$ Hz, 2H), 5.83 (d, $J = 1.0$ Hz, 1H), 5.56 (s, 1H), 3.78 – 3.65 (m, 2H), 2.77 – 2.57 (m, 4H), 2.06 (dq, $J = 13.2$, 6.6 Hz, 2H), 1.25 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.5, 135.0, 130.5, 127.8, 126.0, 119.1, 89.4, 80.9, 43.7, 31.4, 28.5, 16.8, 15.5; HRMS calculated for C$_{15}$H$_{18}$Cl (M + H$^+$): 233.1097, found: 233.1097.

2-(oct-1-en-3-yn-2-yl)naphthalene (4x): 4 h, PhMe/DCE (1:2) as solvent, yellowish oil (53.6 mg, 76%); $^1$H NMR (500 MHz, CDCl$_3$) δ 8.16 (s, 1H), 7.91 – 7.74 (m, 4H), 7.56 – 7.43 (m, 2H), 6.00 (s, 1H), 5.70 (s, 1H), 2.50 (t, $J = 7.0$ Hz, 2H), 1.72 – 1.61 (m, 2H), 1.62 – 1.44 (m, 2H), 1.00 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.5, 135.0, 130.5, 127.8, 126.0, 119.1, 89.4, 80.9, 43.7, 31.4, 28.5, 16.8, 15.5; HRMS calculated for C$_{18}$H$_{19}$ (M + H$^+$): 235.1487, found: 235.1482.

1-(but-1-en-3-yn-2-yl)-4-methoxybenzene (4y): 6 h, white solid (36.3 mg, 77%); $^1$H NMR (400
MHz, CDCl$_3$) δ 7.67 – 7.54 (m, 2H), 6.97 – 6.81 (m, 2H), 5.89 (s, 1H), 5.67 (s, 1H), 3.83 (s, 3H), 3.11 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.8, 129.2, 129.0, 127.2, 120.2, 113.7, 83.0, 78.3, 55.3; HRMS calculated for C$_{11}$H$_{11}$O (M + H$^+$): 159.0810, found: 159.0806.

cyclopent-1-en-1-ylbenzene (4z): 10 h, white solid (38.1 mg, 88%); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.53 – 7.40 (m, 2H), 7.38 – 7.28 (m, 2H), 7.24 (dd, $J = 14.1, 6.7$ Hz, 1H), 6.30 – 6.14 (m, 1H), 2.77 – 2.70 (m, 2H), 2.59 – 2.51 (m, 2H), 2.14 – 1.96 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 142.5, 136.9, 128.3, 126.8, 126.1, 125.6, 33.4, 33.2, 23.4; HRMS calculated for C$_{11}$H$_{13}$ (M + H$^+$): 145.1017, found: 145.1013.

2-phenyloct-3-yn-1,1,1-d3-2-ol (2d-d$_3$): $^1$H NMR (500 MHz, CDCl$_3$) δ 7.75 – 7.59 (m, 2H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.28 (dd, $J = 13.9, 6.5$ Hz, 1H), 2.38 (s, 1H), 2.29 (t, $J = 7.1$ Hz, 2H), 1.59 – 1.50 (m, 2H), 1.50 – 1.38 (m, 2H), 0.94 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 146.2, 128.2, 127.5, 125.0, 85.7, 83.8, 69.9, 30.8, 22.0, 18.4, 13.6; HRMS calculated for C$_{14}$H$_{15}$D$_3$ONa (M + Na$^+$): 228.1444, found: 228.1445.

2-phenyloct-3-yn-2-ol (2d): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.68 (dd, $J = 5.2, 3.3$ Hz, 2H), 7.41 – 7.33 (m, 2H), 7.33 – 7.26 (m, 1H), 2.45 (s, 1H), 2.30 (t, $J = 7.0$ Hz, 2H), 1.76 (s, 3H), 1.57 (dq, $J = 11.9, 6.9$ Hz, 2H), 1.46 (dq, $J = 14.0, 7.0$ Hz, 2H), 0.95 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 146.3, 128.2, 127.5, 125.0, 85.6, 83.8, 70.0, 33.6, 30.7, 22.0, 18.4, 13.6.

S12
Copies of $^1$H NMR and $^{13}$C NMR Spectra