Z-Selective Olefin Synthesis via Iron-Catalyzed Reductive Coupling of Alkyl Halides with Terminal Arylalkynes

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Supporting Online Material

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General Considerations

(A) General Analytical Information

Nuclear Magnetic Resonance spectra were recorded on a Bruker Avance 400 MHz instruments at ambient temperature. All $^1$H NMR spectra were measured in part per million (ppm) relative to the signals for tetramethylsilane (TMS) added into the deuterated chloroform (CDCl$_3$) (0 ppm) unless otherwise stated. Data for $^1$H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, sex = sextet, m = multiplet, ovrlp = overlap), coupling constants, and integration. All $^{13}$C NMR spectra were reported in ppm relative to CDCl$_3$ (77.16 ppm) unless otherwise stated, and were obtained with complete $^1$H decoupling. All GC analyses were performed on a Perkin-Elmer Clarus 400 GC system with a FID detector. All GC-MS analyses were performed on an Agilent Technologies 7890A GC system equipped with a 5975C MS detector. High-resolution mass spectra (HRMS) by electrospray ionization (ESI) method were performed at the EPFL ISIC Mass Spectroscopy Service with a Micro Mass QTOF Ultima spectrometer. HRMS by atmospheric pressure photoionization (APPI) method were performed on a hybrid linear ion trap Fourier transform ion cyclotron resonance mass spectrometer (LTQ FT-ICR MS, Thermo Scientific, Bremen, Germany) equipped with a 10 T superconducting superconducting agent (Oxford Instruments Nanoscience, Abingdon, UK).

(B) General Reagent Information

Unless otherwise noted, all chemicals used in the preparations of starting materials and in the iron-catalyzed reductive coupling of alkyl halides with terminal alkynes were commercially available and were used as received without further purifications. Tetrahydrofuran (THF) and $N$,$N$-dimethylformamide (DMF) were purified and dehydrated using a two-column solid-state purification system (Innovative Technology, NJ, USA) and transferred to the glove box without exposure to air. Anhydrous $N$-methylypyrrolidone (NMP) (99.8% purity) and anhydrous dimethylacetamide (DMA) (99.8% purity) were purchased from Aldrich Chemical Co. or Acros Chemicals. Iron(II) bromide (FeBr$_2$, 98% purity) was purchased from Aldrich Chemical Co. or Acros Chemicals. Iron(II) bromide [FeBr$_2$, 99.999% purity (containing 0.4-3.2 ppm of Co, Cu, Mn, and Cr), beads, -10 mesh] was purchased from Aldrich Chemical Co. All alkyl halides and alkynes (starting materials) and the corresponding alkylated olefin products were in form of racemic mixtures unless otherwise noted.

The following known starting materials (alkyl halides and terminal alkynes) were commercially available and used without further purifications:
The following known starting materials (alkyl halides/tosylates and terminal alkynes) were prepared according to the literature procedures.\textsuperscript{1-22}
(i) Alkyl Halides and Tosylates

- Iodocycloheptane
- Iodocyclooctane
- 4-Iodotetrahydro-2H-pyran
- tert-butyl 4-iodopiperidine-1-carboxylate
- 2-Iodobicyclo[2.2.1]heptane (d.r.: endo = 4.3:1)
- 2-Iodosnonane
- 3-Iodosnonane
- 5-Iodosnonane
- (3-Iodobutyl)benzene
- 6-Iodo-2-methylhept-2-ene
- 1-Iodo-3-methylcyclohexane (d.r.: trans:cis = 6.4:1)
- 1-Iodo-4-methylcyclohexane (d.r.: cis:trans = 10.3:1)
- 1-Iodoadamantane
- 3-Bromo-3-ethylpentane
- 1-(3-Iodopropoxy)-4-methoxybenzene
- 5-Iodopentyl acetate
- 2-((6-Iodohexyl)oxy)tetrahydro-2H-pyran
- 9-(3-Iodopropyl)-9H-carbazole
- 10-Iododec-1-ene
- 6-Iodo-1-yne
- 1-Chloro-6-iodohexane
- 6-Iodohexanenitrile
- 7-Iodoheptanenitrile
- 6-Iodohept-1-ene
- Octyl 4-methylbenzenesulfonate
- Isopentyl 4-methylbenzenesulfonate
- 3-Phenylpropyl 4-methylbenzenesulfonate
- 1-Iodosoundecane

(ii) Terminal Alkynes

- (4-Ethynylphenyl)-(methyl)sulfane
- N,N-Diethyl-4-ethynylbenzamido
- 2-Ethynylnaphthalene
- 2-Ethynyl-5-methylthiophene
- 5-Ethynyl-1,2,3-trimethoxybenzene
- Ethyl 2-(4-Ethynylphenoxy)acetate
(C) General Manipulation Considerations

All manipulations for the iron-catalyzed reductive coupling reactions of alkyl halides with terminal alkynes were set up in a 30 mL Teflon-screw cap test tubes under an inert nitrogen (N\textsubscript{2}) atmosphere using glove-box techniques. The test tubes were then sealed with air-tight electrical tapes and the reaction mixtures were stirred on bench-top. Flash column chromatography was performed using silica gel (Silicycle, ultra pure grade). The eluent for column chromatography is presented as a ratio of solvent volumes. Yields reported in the publication are of isolated materials unless otherwise noted. All new starting materials were characterized by \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectroscopies. All new olefin products were characterized by \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectroscopies and high-resolution mass spectrometry (HRMS); in case the molecular ions could not be detected by HRMS, GC-MS was used instead. The Z- and E-olefins are differentiated by the coupling constants of \(\alpha\)- and \(\beta\)-olefinic protons (\(3J_{HH}\) of Z-olefin \(\sim 12\) Hz; \(3J_{HH}\) of E-olefin \(\sim 16\) Hz) by \textsuperscript{1}H NMR spectroscopy. The Z to E ratio (Z:E) and diastereomeric ratio (d.r.) of the olefin products were determined by taking the ratio of the integrations of olefinic protons of both Z- and E-isomers and the ratio of \textit{exo}- and \textit{endo}-isomers of the Z-olefin products, respectively, by \textsuperscript{1}H NMR spectroscopy.
Supplementary Experimental Results

(A) Optimization of Z-Selective Olefin Synthesis via Fe-Catalyzed Reductive Coupling of Secondary Alkyl Iodide with Terminal Alkyne

(i) Optimizations of Reductant and Loading of Alkyl Iodide. The reaction of ethynylbenzene (1a) and iodocyclohexane (CyI, 2a) was chosen as the test reaction. In the presence of FeBr$_2$ catalyst (10 mol %) and Zn dust (2.5 equiv), the use of a high loading of CyI (2 equiv) could lead to a high yield of Z-olefin product in 97% yield at room temperature, in conjunction with a high Z to E isomeric ratio (Table S1, entry 1). In contrast, the use of lower loading of CyI (1.5 equiv) decreased the yield of Z-olefin to 79% yield (Table S1, entry 2). The use of chlorotrimethylsilane (TMSCl) as the activating agent of Zn could then promote the yield even when 1.5 equiv of CyI was used (Table S1, entry 3). Further screening showed that I$_2$ in 2 mol % could be used as activating agent of Zn (Table S1, entries 4-6) and a lower loading of Zn (1.5 equiv) (Table S1, entry 7) could be used to maintain the high yield. However, the use of manganese and magnesium instead of Zn only gave a trace of product (Table S1, entries 10 and 11). Therefore, Zn (1.5 equiv)/I$_2$ (2 mol %) and CyI (1.5 equiv) were utilized for further optimizations (Table S1, entry 7).

Table S1. Optimization of Reductant and Loading of Secondary Alkyl Iodide$^a$

| entry | CyI (equiv) | reductant (equiv) | additive (mol %) | yield of Z-product (%)$^b$ | Z : E$^c$ |
|-------|-------------|-------------------|------------------|---------------------------|----------|
| 1     | 2           | Zn (2.5)          | ---              | 97                        | 13.8     |
| 2     | 1.5         | Zn (2.5)          | ---              | 79                        | 13.8     |
| 3     | 1.5         | Zn (2.5)          | TMSCl (20)       | 85                        | 15.2     |
| 4     | 1.5         | Zn (2.5)          | TMSBr (10)       | 70                        | 17.4     |
| 5     | 1.5         | Zn (2.5)          | TMSI (10)        | 85                        | 17.4     |
| 6     | 1.5         | Zn (2.5)          | I$_2$ (2)        | 92                        | 14.0     |
| 7     | 1.5         | Zn (1.5)          | I$_2$ (2)        | 91                        | 13.4     |
| 8     | 1.5         | Zn (1.2)          | I$_2$ (2)        | 77                        | 12.6     |
| 9     | 1.2         | Zn (1.5)          | I$_2$ (2)        | 77                        | 12.6     |
| 10    | 1.5         | Mn (1.5)          | I$_2$ (2)        | 5                         | 2.9      |
| 11    | 1.5         | Mg (1.5)          | I$_2$ (2)        | 7                         | 1.3      |

$^a$ Reaction Conditions: alkyne (0.5 mmol), RI (1.5-2 equiv), FeBr$_2$ (10 mol %), Zn (1.2-2.5 equiv), additive (2-20 mol %), DMA (1 mL, 0.5 M), N$_2$ atm, rt, 16 h. $^b$ Determined by GC analysis using dodecane as internal standard. $^c$ Z : E isomeric ratio determined by GC analysis.
(ii) Optimization of Fe Catalyst. The nature, loading, and purity of Fe catalyst were then optimized. 10 mol % of FeBr$_2$ was found to be the optimal loading to give the highest yield (Table S2, entries 1-3). When FeBr$_2$ in extremely high purity (99.99% purity) was used, the yield of product remained the same, supporting that the reaction is indeed Fe-catalyzed (Table S2, entries 4). In dark conditions, the yield of product also remained the same, suggesting that light is not required to promote the Fe-catalyzed reaction (Table S2, entries 5). The use of other Fe salts generally did not enhance the yields (Table S2, entries 6-10). Although FeI$_2$ catalyzed as efficiently as FeBr$_2$ (Table S2, entries 1 and 8), FeBr$_2$ was selected as the optimal Fe catalyst due to its lower cost.

Table S2. Optimization of Fe Catalyst$^a$

![Chemical structure](image)

| entry | Fe catalyst (mol %) | GC yield of Z-product (%)$^b$ | Z : E$^c$ |
|-------|---------------------|-------------------------------|-----------|
| 1     | FeBr$_2$ (10)       | 91                            | 13.4      |
| 2     | FeBr$_2$ (5)        | 82                            | 14.0      |
| 3     | FeBr$_2$ (15)       | 69                            | 12.4      |
| 4     | FeBr$_2$ (10)$^d$   | 90                            | 12.4      |
| 5     | FeBr$_2$ (10)$^e$   | 88                            | 13.2      |
| 6     | FeBr$_3$ (10)       | 85                            | 12.8      |
| 7     | FeCl$_2$ (10)       | 82                            | 13.5      |
| 8     | FeI$_2$ (10)        | 92                            | 14.3      |
| 9     | Fe(OTf)$_2$ (10)    | 79                            | 13.6      |
| 10    | Fe(acac)$_3$ (10)   | 49                            | 11.2      |

*a. Reaction Conditions: alkyne (0.5 mmol), RI (1.5 equiv), Fe catalyst (5-10 mol %), Zn (1.5 equiv), I$_2$ (2 mol %), DMA (1 mL), 0.5 M, N$_2$ atm, rt, 16 h. b. Determined by GC analysis using dodecane as internal standard. c. Z:E isomeric ratio determined by GC analysis. d. 99.99% purity. e. Dark conditions.*
(iii) Effect of Transition Metal Catalyst. Other transition metals (Ni, Co, Cu, Ag, Pd, Cr, Mn) instead of FeBr$_2$ were also studied. However, they either catalyzed less efficiently than FeBr$_2$ (Table S3, entries 4, 7, and 8) or did not catalyze the reaction at all (Table S3, entries 2, 3, 5, 6). The results further demonstrate that these trace metals present in FeBr$_2$ unlikely catalyze the reaction.

Table S3. Effect of Other Transition Metal Catalyst$^a$

| entry | Fe catalyst (mol %) | GC yield of Z-product (%)$^b$ | Z: E$^c$ |
|-------|---------------------|-------------------------------|----------|
| 1     | FeBr$_2$ (10)       | 91                            | 13.4     |
| 2     | NiBr$_2$ (10)       | 1                             | 1.0      |
| 3     | CoBr$_2$ (10)       | 2                             | 0.4      |
| 4     | CuBr$_2$ (10)       | 73                            | 12.0     |
| 5     | AgNO$_3$ (10)       | 7                             | 1.9      |
| 6     | Pd(OAc)$_2$ (10)    | 8                             | 7.4      |
| 7     | CrCl$_2$ (10)       | 81                            | 17.8     |
| 8     | Mn(OAc)$_2$ • 4H$_2$O (10) | 24                      | 21.7     |

$^a$ Reaction Conditions: alkyne (0.5 mmol), RI (1.5 equiv), metal catalyst (10 mol %), Zn (1.5 equiv), I$_2$ (2 mol %), DMA (1 mL), N$_2$ atm, rt, 16 h. $^b$ Determined by GC analysis using dodecane as internal standard. $^c$ Z:E isomeric ratio determined by GC analysis.

(iv) Optimization of Solvent. By comparing different solvent, DMA was found to be the optimal solvent to give the highest product yield (Table S4, entries 1 and 4-6). 1 mL of DMA (when 0.5 mmol of alkyne was used, 0.5 M) was selected as the optimal solvent volume, since lower yields were obtained when more (1 mL) or less DMA (0.5 mL) was used (Table S4, entries 2, 3).
Table S4. Optimization of Solvent$^a$

![Chemical Structure]

| entry | solvent (mL) | concentration of alkyne (M) | GC yield of Z-product (%)$^b$ | $Z: E^c$ |
|-------|--------------|----------------------------|-------------------------------|---------|
| 1     | DMA (1)      | 0.5                        | 91                           | 13.4    |
| 2     | DMA (2)      | 0.25                       | 87                           | 12.0    |
| 3     | DMA (0.5)    | 1                          | 80                           | 14.6    |
| 4     | NMP (1)      | 0.5                        | 81                           | 11.2    |
| 5     | DMF (1)      | 0.5                        | 62                           | 14.1    |
| 6     | THF (1)      | 0.5                        | 5                            | 3.7     |

$^a$ Reaction Conditions: alkyne (0.5 mmol), RI (1.5 equiv), FeBr$_2$ (10 mol %), Zn (1.5 equiv), I$_2$ (2 mol %), solvent (1 mL, 0.5 M), N$_2$ atm, rt, 16 h. $^b$ Determined by GC analysis using dodecane as internal standard. $^c$ Z:E isomeric ratio determined by GC analysis.

(v) Effect of Additive. Bis[2-(N,N-dimethylamino)ethyl]ether (O-TMEDA) and N,N,N',N'-tetramethylethlenediamine (TEMDA) have been used as additives in Fe-catalyzed cross-coupling reactions. However, they did not promote the yield in this reaction protocol (Table S5, entries 2 and 3).

Table S5. Optimization: Effect of Additives$^a$

![Chemical Structure]

| entry | additive (equiv) | GC yield of Z-product (%)$^b$ | $Z: E^c$ |
|-------|------------------|-------------------------------|---------|
| 1     | none             | 91                            | 13.4    |
| 2     | O-TMEDA (1.5 equiv)$^d$ | 40        | 8.0    |
| 3     | TEMDA (1.5 equiv)$^e$   | 72                           | 13.1    |

$^a$ Reaction Conditions: alkyne (0.5 mmol), RI (1.5 equiv), FeBr$_2$ (10 mol %), Zn (1.5 equiv), I$_2$ (2 mol %), additive (1.5 equiv), DMA (1 mL, 0.5 M), N$_2$ atm, rt, 16 h. $^b$ Determined by GC analysis using dodecane as internal standard. $^c$ Z:E isomeric ratio determined by GC analysis. $^d$ Bis[2-(N,N-dimethylamino)ethyl]ether. $^e$ N,N,N',N'-tetramethylethlenediamine.
(vi) Effects of Fe Catalyst and Zinc Reductant. Both FeBr₂ catalyst and Zn reductant are crucial in the catalytic formation of Z-olefin (Table S6, entry 1). In the absence of FeBr₂, only a low yield of product was obtained (Table S6, entry 2). Additionally, in the absence of Zn, no product was formed (Table S6, entry 3).

| entry | FeBr₂ (mol%) | Zn (equiv) | GC yield of Z-product (%)<sup>b</sup> | Z : E<sup>c</sup> |
|-------|--------------|------------|--------------------------------------|-----------------|
| 1     | 10           | 1.5        | 91                                   | 13.4            |
| 2     | 0            | 1.5        | 34                                   | 14.3            |
| 3     | 10           | 0          | 0                                    | ---             |

Table S6. Control Experiment: Effect of Fe catalyst and Reductant<sup>a</sup>

<sup>a</sup> Reaction Conditions: alkyne (0.5 mmol), RI (1.5 equiv), FeBr₂ (0-10 mol %), Zn (0-1.5 equiv), I₂ (2 mol %), DMA (1 mL, 0.5 M), N₂ atm, rt, 16 h. b. Determined by GC analysis using dodecane as internal standard. c. Z : E isomeric ratio determined by GC analysis.

(vii) Effect of Reaction Temperature. At room temperature, the reaction provided higher product yield with the concomitant formation of smaller amounts of side-products via reduction and homocoupling of alkyl iodide [Figure S1(a)]. At higher temperature (80 °C), a lower yield was obtained and more side-products were formed [Figure S1(b)]. Thus, the reactions with alkyl iodides were carried out at room temperature.

Fig. S1. Effect of reaction temperature.
(B) Optimization of Z-Selective Olefin Synthesis via Fe-Catalyzed Reductive Coupling of Primary Alkyl Iodide with Terminal Alkyne

(i) Optimization of Reaction conditions. Under the similar conditions for reaction with secondary alkyl iodide (Tables S1-S6; Figure S1), the reaction protocol only gave a low yield of Z-olefin product in the presence of primary alkyl iodide (Table S7, entries 1 and 2). The use of iodomethylsilane as the activating reagent of Zn was found to enhance the yield to 32% (Table S7, entries 5). The addition of copper co-catalysts could generally further promote the yield (Table S7, entries 6-13), and CuBr₂ was the optimal Cu co-catalyst (Table S7, entry 6). By increasing the loading of alkyl iodide to 2 equiv and the concentration of substrates (1 M of alkyne in DMA), the yield could be further enhanced to 53% (Table S7, entry 16).

Table S7. Optimization: Reaction with Primary Alkyl Iodides

| entry | catalyst (mol %) | RI (equiv) | additive (mol %) | alkyne conc. (M) | GC yield (%)b |
|-------|-----------------|------------|-----------------|-----------------|--------------|
| 1     | FeBr₂ (10)      | 1.5        | I₂ (4 mol%)     | 0.5             | 23c          |
| 2     | FeBr₂ (10)      | 1.5        | I₂ (10 mol%)    | 0.5             | 27c          |
| 3     | FeBr₂ (10)      | 1.5        | TMSI (20)       | 0.5             | 21           |
| 4     | FeBr₂ (10)      | 1.5        | TMSBr (20)      | 0.5             | 25           |
| 5     | FeBr₂ (10)      | 1.5        | TMSI (20)       | 0.5             | 32           |
| 6     | FeBr₂ (10), CuBr₂ (10) | 1.5 | TMSI (20) | 0.5 | 43 |
| 7     | FeBr₂ (10), CuBr (15) | 1.5 | TMSI (20) | 0.5 | 37 |
| 8     | FeBr₂ (10), CuCl (20) | 1.5 | TMSI (20) | 0.5 | 26 |
| 9     | FeBr₂ (10), Cu (20) | 1.5 | TMSI (20) | 0.5 | 34 |
| 10    | FeBr₂ (10), CuF₂ (20) | 1.5 | TMSI (20) | 0.5 | 28 |
| 11    | FeBr₂ (10), Cu(acac) (20) | 1.5 | TMSI (20) | 0.5 | 18 |
| 12    | FeBr₂ (10), CuSO₄ (15) | 1.5 | TMSI (20) | 0.5 | 39 |
| 13    | FeBr₂ (10), Cu(OTf) (10) | 1.5 | TMSI (20) | 0.5 | 29 |
| 14    | FeBr₂ (10), CrCl₃ (10) | 1.5 | TMSI (20) | 0.5 | 33 |
| 15    | FeBr₂ (10), CuBr₂ (10) | 2 | TMSI (20) | 0.5 | 33 |
| 16    | FeBr₂ (10), CuBr₂ (10) | 2 | TMSI (20) | 1 | 53 |
| 17    | FeBr₂ (10), CuBr₂ (10) | 2 | TMSI (20) | 2 | 36 |

a. Reaction Conditions: alkyne (0.5-1 mmol), RI (1.5 equiv), FeBr₂ (10 mol %), Cu catalyst (10-20 mol %), Zn (2.5 equiv), I₂ or TMSX (4-20 mol %), DMA (0.5-2 M), N₂ atm, rt, 16 h. b. Uncorrected GC yield using dodecane as internal standard. c. 1-iodooctane was used instead of 1-iodoheptane.
(ii) Promoting Effect of CuBr$_2$ Co-catalyst. The effect of CuBr$_2$ as co-catalyst in Fe-catalyzed Z-olefin synthesis with primary alkyl iodide was further examined under identical conditions (Figure S2). In the presence of 10 mol % of CuBr$_2$ [Figure S2(a)], the reaction conversion is enhanced to give a higher yield of Z-olefin (9% yield enhancement when compared with no CuBr$_2$ added [Figure S2(b)]).

Fig. S2. Effect of CuBr$_2$ as co-catalyst.

(C) Mechanistic Study of Fe-Catalyzed Z-Olefin Synthesis

(i) Radical Mechanisms

(1) Radical Clock Experiments: Ring Cyclizations. Both secondary and primary alkyl radical clock substrates reacted to form the cyclized ring-substituted Z-olefins as major products (8a and 8b) (Fig. S3). The formation of alkyl radical is supported.

Fig. S3. The use of secondary and primary alkyl halides in radical clock experiments.
(2) Alkyl Radical Trapped by Radial Scavenger. When a radical trap, TEMPO, was added into the reaction mixture, no Z-olefin was formed and an alkyl-TEMPO adduct (8d) was formed in 14% yield (Fig. S4). The formation of alkyl radical is further supported.

Fig. S4. The effect of TEMPO as radical scavenger in Fe-catalyzed Z-olefin synthsis.

(3) Sluggish Reaction Under Air Conditions. When the reaction was conducted in air atmosphere, only a low yield of Z-olefin was formed (Fig. S5). Oxygen serves as a radical source and radical pathways should be involved in the reaction.

Fig. S5. The effect of oxygen as radical scavenger in Fe-catalyzed Z-olefin synthsis.

(4) Formation of Alkenyl Radical Intermediate. An alkenyl radical trap, P(OEt)_3, was added into the reaction mixture. Diethyl (E)-(2-cyclohexyl-1-phenylvinyl)phosphonate (8e) was formed in 8% yield, supporting the formation of alkenyl radical intermediate (Fig. S6).

Fig. S6. The use of P(OEt)_3 as alkenyl radical trap.
(ii) Source of α-Olefinic Hydrogen for Z-Olefin Synthesis. To identify the source of α-olefinic hydrogen of Z-olefin, two parallel reactions were conducted: (1) reaction in DMA-d₉ solvent followed by workup with H₂O, and (2) reaction in DMA-H₂ solvent followed by workup with D₂O (Fig. S7). α-H-olefin and α-D-enriched-olefin were formed, respectively, suggesting that the olefinic H should come from water rather than DMA. Moreover, the olefin product did not undergo α-olefinic H/D exchange with D₂O to give α-D-enriched-olefin under the reaction conditions. It is unlikely that the alkenyl radical intermediate (refer to Fig. S6) abstracts H radical from DMA solvent to form α-H-olefin followed by subsequent α-olefinic H/D exchange with D₂O to form the observed α-D-enriched olefin. Most likely, alkenyl anion intermediate is generated and then protonated by water to give α-H-olefin.

**Fig. S7.** Study of the source of α-olefinic hydrogen in Z-olefin.
(iii) Formation of Alkenyl Anion Intermediate

(1) Trapped with Electrophilic Iodinating Reagent. To support the formation of alkenyl anion intermediate, electrophilic iodinating reagents, IBr and ICl, were added instead of H₂O for workup at room temperature after the reaction (Fig. S8). α-iodo-olefin was formed as a major product in both reactions, supporting the formation of alkenyl anion intermediate. Moreover, α-iodo-olefin was not formed by H/I exchange of final olefin product with iodine monohalides, further supporting that iodo-olefin is likely formed by electrophilic iodination of alkenyl anion with iodine monohalides.

**Workup with IBr**

\[
\begin{align*}
\text{FeBr}_2 (10 \text{ mol %}) & \\
& 1) \text{ Zn (1.5 equiv), I}_2 (2 \text{ mol %}) \\
& \text{DMA (0.5 M), rt, 4 d} \\
& 2) \text{ IBr (3 equiv), rt, 1.5 d} \\
\end{align*}
\]

\[
\begin{align*}
\text{8f, 53\%} & \\
\text{3a, 22\%} & \\
\end{align*}
\]

**Workup with ICl**

\[
\begin{align*}
\text{FeBr}_2 (10 \text{ mol %}) & \\
& 1) \text{ Zn (1.5 equiv), I}_2 (2 \text{ mol %}) \\
& \text{DMA (0.5 M), rt, 16 h} \\
& 2) \text{ ICl (2 equiv), rt, 18 h} \\
\end{align*}
\]

\[
\begin{align*}
\text{8f, 41\% NMR yield} & \\
\text{3a, 11\% NMR yield} & \\
\end{align*}
\]

**No H/I exchange between olefin and IBr**

\[
\begin{align*}
\text{FeBr}_2 (10 \text{ mol %}) & \\
& \text{Zn (1.5 equiv), I}_2 (2 \text{ mol %}) \\
& \text{IBr (3 equiv)} \\
& \text{DMA, rt, 16 h} \\
\end{align*}
\]

\[
\begin{align*}
\text{8f, 0\%} & \\
\end{align*}
\]

**Fig. S8.** Effect of electrophilic iodinating reagent as alkenyl anion trap.

(2) Observation of a Downfield Alkenyl β-Olefinic H Signal (¹H NMR Experiment): The reaction profile of Fe-catalyzed reductive coupling of phenylacetylene and iodocyclohexane was monitored in a sealed NMR tube (Fig. S9a). The reaction mixture was mixed thoroughly with the aid of ultrasound and it was then left at room temperature. After 5 days, all ethynylbenzene and iodocyclohexane were consumed. A small amount of Z-olefin product was observed along with the major formation of a proposed alkenyl species bearing a downfield β-olefinic H. The alkenyl species is likely an alkenylzinc intermediate, which, upon the addition of excess water, was consumed to give the Z-olefin product in ~66% NMR yield using residual DMA protons as internal standard. The downfield β-olefinic H (δ 6.91 ppm) could be attributed to the interaction between the β-olefinic H and the anionic lone-pair at the α-olefinic carbon. Such downfield β-olefinic H is also observed in the ¹H NMR of α-iodo-olefin product,
(E)-(2-cyclohexyl-1-iodovinyl)benzene (8f), in which the lone pair of iodine could interact with the β-olefinic H (δ 6.31 ppm, in CDCl₃).
The source of α-hydrogen of Z-olefin formed in the course of reaction.

In Fig. S9a, a small amount of Z-olefin was observed in the course of reaction. Most likely, the in-situ formed alkenylzinc intermediate is partially protonated by the proton source. There are two possible proton sources: (1) the residue water in solvent and reagents; (2) the acidic C(sp)-H proton of phenylacetylene. Two sets of experiments were undergone to distinguish the source of proton:

1) Reaction under “extra-dry” conditions. Prior to the reaction, all liquid reagents [phenylacetylene, iodocyclohexane, DMA-d₉ solvent, I₂ solution (0.5 M in DMA)] were dried with 3Å molecular sieves, and solid reagents (Zn, FeBr₂) were dried in vacuo under heating with a heat gun, in attempt to eliminate most of residual water. The reductive coupling reaction was then undertaken using the typical procedure. After the reaction, the reaction mixture was analyzed by ¹H NMR spectroscopy without aqueous workup. Both alkenylzinc intermediate and a small amount Z-olefin were observed (Fig. S9b), and the ratio of alkenylzinc to Z-olefin is similar to that observed under the standard conditions (Fig. S9a). Thus, it is unlikely for the residual water to be the proton source for Z-olefin formation.

Fig. S9b. ¹H NMR spectra showing the species formed in the Fe-catalyzed reductive coupling reactions under dried conditions.
**(2) Effect of acidic phenylacetylene: use of phenylacetylene-d₁.** Phenylacetylene-d₁ [D% of PhCC-D ~ 80% D] was prepared, and it was used instead in the typical reaction (Fig. S9c). The D-incorporation of α-H of Z-olefin product was found to be 19%. α-H,β-D-Z-olefin ([M] = 187) and α-D,β-D-Z-olefin ([M] = 188) were also observed as major and minor species, respectively, by GC-MS analysis. Moreover, the reaction of *in-situ* formed alkenylzinc intermediate reacted with phenylacetylene-d₁ to form α-D-enriched Z-olefin with D% of 16% (Fig. S9d). The amount of phenylacetylene was also increased, likely due to the protonation of phenylacetylenide (formed after the deprotonation of phenylacetylene-d₁) during the aqueous workup. Both results further support that phenylacetylene acts as a mild proton donor for the protonation of alkenylzinc, forming a small amount of Z-olefin.

![Diagram](image1)

**Fig. S9c.** Iron-catalyzed reductive coupling using deuteroenriched phenylacetylene-d₁.

![Diagram](image2)

**Fig. S9d.** Reaction of alkenylzinc intermediate with phenylacetylene-d₁.

Based on the results from (1) and (2), we proposed phenylacetylene is likely the proton source to react with a small amount of alkenylzinc intermediate to generate the observed Z-olefin in Fig. S9a.

**(iv) Unlikely Intermediacy of Alkylzinc Reagent.** Since the *in-situ* formation of alkylzinc reagent is viable for the subsequent formation of Z-olefin, the intermediacy of alkylzinc reagent was thus studied (Fig. S10). Indeed, both secondary and primary alkyl iodides reacted with Zn at room temperature in DMA to give the corresponding alkylzinc reagents, which could be quenched by HCl, H₂O, or D₂O to give the protonated or deuteriated alkane products accordingly. The alkylzinc reagents could also be formed faster at elevated temperature (60-80 °C). When the alkylzinc reagents were subjected to the reactions with arylalkynes in the presence of FeBr₂ catalyst, only traces of Z-olefins were formed. On
the contrary, the Z-olefins were formed in high yields under the normal reaction conditions (4s and 6t in Fig S12). The results suggested that the in-situ formed alkylzinc reagent is unlikely the intermediate which leads to the Z-olefin formation.

**Formation of Alkylzinc Reagents with Secondary Alkyl Halides**

\[ \text{I}^- \quad \text{Zn (2 equiv)} \quad \text{I}_2 (3 \text{ mol }\%), \text{DMA} \quad \text{(i) rt, 16 h} \quad \text{(ii) 80 °C, 3 h} \]

\[ \text{I}^- \quad \text{Zn} \quad \text{(1.5 equiv)} \]

\[ \text{alkylzinc reagent formation determined by:} \]

\[ \text{HCl (aq)} \]

(i) 91% GC yield
(ii) 88% GC yield

(GCMS: M⁺ = 128 obs)

\[ \text{D}_2\text{O} \]

(i) 74% GC yield
(ii) 71% GC yield

(GCMS: M⁺ = 129 obs)

**Formation of Alkylzinc Reagents with Primary Alkyl Halides**

\[ \text{I}^- \quad \text{Zn (2.5 equiv)} \quad \text{TMSi (20 mol %), DMA} \quad \text{(i) rt, 16 h} \quad \text{(ii) 60 °C, 6 h} \]

\[ \text{I}^- \quad \text{Zn} \quad \text{(2 equiv)} \]

\[ \text{alkylzinc reagent formation determined by:} \]

\[ \text{H}_2\text{O} \]

(i) 87% GC yield
(ii) 83% GC yield

(GCMS: M⁺ = 142 obs)

\[ \text{D}_2\text{O} \]

(i) 88% GC yield
(ii) 83% GC yield

(GCMS: M⁺ = 143 obs)

**Unproductive Reaction with Alkylzinc Reagents**

\[ \text{I}^- \quad \text{Zn (2 equiv)} \quad \text{I}_2 (3 \text{ mol }\%), \text{DMA} \quad \text{80 °C, 3 h} \]

\[ \text{I}^- \quad \text{Zn} \quad \text{(1.5 equiv)} \]

\[ 1) \text{Me} \quad \text{FeBr}_2 (10 \text{ mol }\%), \text{rt, 16 h} \]

\[ \text{H}_2\text{O} \]

4s

< 5% GC yield
71% GC yield

\[ 2) \]

\[ \text{Me} \quad \text{H} \]

\[ \text{I}^- \quad \text{Zn} \quad \text{(2 equiv)} \quad \text{TMSi (20 mol %), DMA} \quad \text{60 °C, 6 h} \]

\[ \text{I}^- \quad \text{Zn} \quad \text{(2 equiv)} \]

\[ 1) \text{Me} \quad \text{FeBr}_2 (10 \text{ mol }\%), \text{CuBr}_2 (10 \text{ mol }\%), \text{rt, 16 h} \]

\[ \text{H}_2\text{O} \]

6t

< 5% GC yield
77% GC yield

**Fig. S10.** Study of alkylzinc reagents in Fe-catalyzed Z-olefin synthesis.
(v) **Unlikely Conversion of E-olefin to Z-olefin.** The E-olefin did not convert to Z-olefin under the reaction conditions (Fig. S11), suggesting that the formation Z-olefin does not go through the intermediacy of E-olefin.

![Conversion of E-olefin to Z-olefin](image)

Fig. S11. Study of Conversion of E-olefin to Z-olefin.

(D) **Supplementary Results of Z-olefin Synthesis via Fe-Catalyzed Reductive Cross-Coupling of Alkyl Halides with Terminal Alkynes.**

Additional substrate scope of Fe-catalyzed reductive coupling of alkyl halides with terminal alkynes were shown in Fig. S12. Notably, enynes could be used as substrates to give the Z-olefins in high Z to E ratios.
Fig. S12. Additional scope of Z-selective olefin synthesis via Fe-Catalyzed reductive coupling of alkyl halides with terminal alkynes.

a. R1 (2 equiv), Zn (2 equiv), I₂ (3 mol %). b. R1 (4 equiv), Zn (4 equiv), I₂ (10 mol %). c. R1 (5 equiv), Zn (5 equiv), I₂ (10 mol %). d. R1 (3 equiv), Zn (3.5 equiv), TMSI (30 mol %). e. R1 (5 equiv), Zn (5.5 equiv), TMSI (50 mol %). f. R1 (2 equiv), Zn (2.5 equiv), TMSI (20 mol %).
Experimental Section

Preparation of Alkyl Halides from Alkyl Alcohols (General Procedure A). A 1 L round-bottom flask equipped with a Teflon-coated magnetic stir bar was charged with triphenylphosphine (1.4 equiv), imidazole (1.4 equiv), and dichloromethane (~300 mL). The reaction mixture was stirred at room temperature until the white solids dissolved to form a clear solution. Iodine (1.4 equiv) was then added slowly in a few portions into the reaction mixture, and the resulting mixture was stirred until all iodine granules almost dissolved. Alkyl alcohol (1.0 equiv) was then slowly added into the reaction mixture, and the resulting mixture was stirred overnight. The reaction mixture was diluted with hexanes and filtered to remove the solid residues. The filtrate was concentrated in vacuo with the aid of a rotary evaporator. The residue was purified by flash column chromatography with silica gel using hexanes as an eluent to afford the alkyl iodide product.

3-Iodo-2-methylhexane (R1). Following the general procedure A, the title compound was prepared using 2-methylhexan-3-ol (5.81 g, 50 mmol), triphenylphosphine (18.4 g, 70 mmol), imidazole (4.77 g, 70 mmol), and iodine (17.8 g, 70 mmol). Since the reaction was not complete, more triphenylphosphine (7.9 g, 30 mmol), imidazole (2.4 g, 30 mmol), and iodine (7.6 g, 30 mmol) were added and the reaction was further stirred overnight. After work up, the crude product was purified by flash chromatography to afford the title compound (R1) as colorless oil (2.49 g, 11 mmol, 22%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 4.22-4.16 (m, 1 \text{ H}), 2.02-1.85 (m, 1 \text{ H}), 1.67-1.55 (m, 2 \text{ H}), 1.45-1.34 (m, 1 \text{ H}), 1.30-1.21 (m, 1 \text{ H}), 0.99 (d, \(J = 6.4 \text{ Hz}, 3 \text{ H}), 0.94-0.91 (\text{ovrlp}, 6 \text{ H}).\) \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 52.4, 40.7, 34.9, 23.3, 20.0, 13.4.\)

(Z)-8-Iodooc-3-ene (R2). Following the general procedure A, the title compound was prepared using (Z)-oct-5-en-1-ol (3.53 g, 27.5 mmol), triphenylphosphine (10.1 g, 38.5 mmol), imidazole (2.62 g, 38.5 mmol), and iodine (9.79 g, 38.5 mmol). After work up, the crude product was purified by flash chromatography to afford the title compound (R2) as colorless oil (5.71 g, 24.4 mmol, 89%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 5.41-5.35 (m, 1 \text{ H}), 5.32-5.26 (m, 1 \text{ H}), 3.18 (t, J = 7.0 \text{ Hz}, 2 \text{ H}), 2.07-1.98 (\text{ovrlp}, 4 \text{ H}), 1.82 (\text{qu}, J = 7.2 \text{ Hz}, 2 \text{ H}), 1.45 (\text{qu}, J = 7.4 \text{ Hz}, 2 \text{ H}), 0.95 (t, J = 7.5 \text{ Hz}, 3 \text{ H}).\) \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 132.4, 128.3, 33.1, 30.6, 26.0, 20.6, 14.5, 7.1.\)
Preparation of 2-Isopropyl-4-methylcyclohexyl 6-iodohexanoate [(±)-Menthyl 6-iodohexanoate] (R3). A 250 mL conical flask equipped with a Teflon-coated magnetic stir bar was charged with 6-bromohexanoic acid (2.54 g, 13 mmol, 1.0 equiv), (±)-menthol (2.24 g, 14.3 mmol, 1.1 equiv), N,N'-dicyclohexylcarbodiimide (DCC, 2.68 g, 1.0 equiv), 4-dimethylaminopyridine (32 mg, 0.20 mmol, 2 mol %), and dichloromethane (100 mL). The reaction mixture was stirred at room temperature overnight. The reaction mixture was then filtered, and the filtrate was washed with HCl solution [~1 M (aq), ~100 mL]. The organic fraction was dried in vacuo to give a crude alkyl bromide which was introduced into a 250 mL round-bottom flask equipped with a Teflon-coated magnetic stir bar, followed by the addition of NaI (9.74 g, 65 mmol, 5 equiv), acetone (70 mL), and water (7 mL). The reaction mixture was then heated at 60 °C until all alkyl bromide was consumed as determined by GC analysis. After cooling to room temperature, the reaction mixture was concentrated in vacuo and washed with CH₂Cl₂ (50 mL) and water (100 mL). The aqueous solution was further washed with CH₂Cl₂ (2 x 50 mL). The combined organic fractions were concentrated in vacuo, and the residue was purified by flash chromatography with silica gel using a mixture of hexanes/EtOAc (10:1) as an eluent to afford the tite compound (R3) as a pale-yellow oil (2.43 g, 6.39 mmol, 49%).

**1H NMR** (400 MHz, CDCl₃): δ 4.64-4.58 (m, 1 H), 3.11 (t, J = 7.0 Hz, 2 H), 2.23 (t, J = 7.5 Hz, 2 H), 1.94-1.88 (m, 1 H), 1.84-1.74 (ovrlp, 3 H), 1.63-1.54 (ovrlp, 4 H), 1.47-1.33 (ovrlp, 4 H), 1.04-0.78 (ovrlp, 9 H), 0.69 (d, J = 6.8 Hz, 3 H).

**13C NMR** (100 MHz, CDCl₃): δ 172.7, 73.8, 46.9, 40.9, 34.3, 34.2, 33.1, 31.3, 29.9, 26.2, 23.9, 23.3, 22.0, 20.7, 16.3, 6.4.

Preparation of Terminal Arylalkyne using Aryl Bromides and Trimethylsilylacetylene (General Procedure B).

A 250 mL conical flask equipped with a Teflon-coated magnetic stir bar was charged with 4-bromobenzoyl chloride, alcohol, triethylamine (Et₃N), and CH₂Cl₂ solvent. Alternatively, the flask was charged with 4-bromobenzoic acid, alcohol, N,N'-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), and CH₂Cl₂ solvent. The reaction mixture was stirred at room temperature overnight. The reaction mixture was then filtered (if solid was formed), and the filtrate was washed with HCl solution [~1 M (aq), ~100 mL]. The organic fraction was dried with anhydrous Na₂SO₄ and then dried in vacuo to give a crude alkyl 4-bromobenzoate, which was further purified by column chromatography to give a pure alkyl 4-bromobenzoate.

In a nitrogen-filled glove-box, a 30 mL test tube equipped with a Teflon-coated magnetic stir bar was charged with alkyl 4-bromobenzoate, Pd(PPh₃)₂Cl₂ catalyst, CuI co-catalyst, and THF solvent, followed by trimethylsilylacetylene and finally Et₃N. The reaction mixture was stirred at room temperature for 4 days. After the reaction, the dark reaction mixture was diluted with CH₂Cl₂ and filtered through silica
gel to obtain a brown solution. The dark brown solution was washed with HCl solution [~1 M (aq), ~100 mL], and the organic fraction was dried with anhydrous Na$_2$SO$_4$ and then dried in vacuo to give a crude internal alkyne. The internal alkyne was dissolved with anhydrous THF, and tetrabutyrammonium fluoride solution (TBAF, 1M in THF) was added. The resulting mixture was stirred at room temperature overnight. After the reaction, the reaction mixture was concentrated in vacuo to give a crude terminal alkyne. The residue was purified by flash chromatography with silica gel using a mixture of hexanes/EtOAc as an eluent to afford the pure terminal alkyne.

(3S,5S,8R,9S,10S,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-ethynylbenzoate (Cholestanyl 4-ethynylbenzoate) (S1). Following the general procedure B, alkyl 4-bromobenzoate was prepared using 4-bromobenzoyl chloride (720 mg, 3.28 mmol, 1.1 equiv), cholesterol (1.16 g, 2.98 mmol, 1 equiv), Et$_3$N (452 mg, 4.47 mmol, 1.5 equiv), and CH$_2$Cl$_2$ solvent (100 mL). After work up, the crude product was purified by flash chromatography using hexanes/EtOAc (15:1) as an eluent to afford the pure alkyl 4-bromobenzoate (249 mg, 0.44 mmol, 15%).

The corresponding internal alkyne was prepared using alkyl 4-bromobenzoate (249 mg, 0.44 mmol, 1 equiv), Pd(PPh$_3$)$_2$Cl$_2$ (15 mg, 5 mol %), CuI (8 mg, 10 mol %), THF solvent (2 mL), trimethylsilylacetylene (64 mg, 1.5 equiv) and Et$_3$N (71 mg, 1.6 equiv). After the addition of TBAB solution (1 mL) and subsequent work up, the crude product was purified by flash chromatography using hexanes/EtOAc (15:1) as an eluent to afford the title terminal alkyne (S1) as viscous brown oil (129 mg, 0.25 mmol, 57%, based on alkyl 4-bromobenzoate).

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.90 (d, $J$ = 8.2 Hz, 2 H), 7.46 (d, $J$ = 8.2 Hz, 2 H), 4.90-4.82 (m, 1 H), 3.14 (s, 1 H), 1.94-1.84 (ovrlp, 2 H), 1.78-1.54 (ovrlp, 5 H), 1.52-1.38 (ovrlp, 4 H), 1.31-1.12 (ovrlp, 11 H), 1.10-0.90 (ovrlp, 9 H), 0.83 (d, $J$ = 6.5 Hz, 3 H), 0.80-0.78 (ovrlp, 9 H), 0.58 (s, 3 H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 165.5, 132.1, 131.1, 129.5, 126.6, 83.0, 80.0, 74.8, 56.5, 56.4, 54.4, 44.8, 42.7, 40.1, 39.7, 36.9, 36.3, 36.0, 35.6, 34.2, 32.1, 29.9, 28.8, 28.4 28.2, 27.7, 24.4, 24.0, 23.0, 22.7, 21.4, 18.8, 12.4, 12.2. HRMS (APPI): Calcd for C$_{36}$H$_{52}$O$_2$ [M]: 516.3978; Found: 516.3967.

(3aR,5R,5aS,8aS,8bR)-2,2,7,7-Tetramethyltetrahydro-5H-bis[(1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-ethynylbenzoate (1,2:3,4-di-O-isopropylidyene-α-D-galactopyranosyl 4-ethynylbenzoate) (S2). Following the general procedure B, alkyl 4-bromobenzoate was prepared using 4-bromobenzoic acid (1.55 g, 7.69 mmol, 1 equiv), 1,2:3,4-di-O-isopropylidyene-α-D-galactopyranose (2.00 g, 7.69 mmol, 1 equiv), DCC (1.75 g, 8.46 mmol, 1.1 equiv), DMAP (47 mg, 0.38 mmol, 5 mol %), and CH$_2$Cl$_2$ solvent (300 mL). After work up, the crude product was purified by flash chromatography using hexanes/EtOAc (10:1) as an eluent to afford the pure alkyl 4-bromobenzoate (1.39 g, 3.14 mmol, 41%). The corresponding internal alkyne was prepared using alkyl 4-
bromobenzoate (1.39 g, 3.14 mmol, 1 equiv), Pd(PPh₃)₂Cl₂ (154 mg, 7 mol %), CuI (84 mg, 14 mol %), THF solvent (6 mL), trimethylsilylacetylene (493 mg, 1.6 equiv) and Et₃N (636 mg, 2 equiv). After the addition of TBAB solution (3.2 mL) and subsequent work up, the crude product was purified by flash chromatography using hexanes/EtOAc (10:1) as an eluent to afford the title terminal alkyne (S2) as viscous brown oil (856 mg, 2.20 mmol, 70%, based on alkyl 4-bromobenzoate). 

\[^1\text{H}\] NMR (400 MHz, CDCl₃): δ 8.00 (d, \(J = 7.7\) Hz, 2 H), 7.53 (d, \(J = 7.7\) Hz, 2 H), 5.57 (d, \(J = 3.6\) Hz, 1 H), 4.66 (d, \(J = 7.2\) Hz, 1 H), 4.53 (dd, \(J = 10.8\) Hz, \(J = 3.7\) Hz, 1 H), 4.33 (d, \(J = 10.1\) Hz, 2 H), 4.19 (s, 1 H), 3.31 (s, 1 H), 1.51 (s, 3 H), 1.48 (s, 3 H), 1.35 (s, 3 H), 1.33 (s, 3 H). 

\[^{13}\text{C}\] NMR (100 MHz, CDCl₃): δ 165.6, 132.0, 130.0, 129.5, 126.8, 109.6, 108.7, 96.3, 82.8, 80.4, 71.1, 70.7, 70.4, 66.1, 64.1, 26.0, 25.9, 24.9, 24.4. HRMS (APPI): Calcd for C₂₁H₂₅O₇ [M]: 389.1551; Found: 389.1592.

Following the general procedure B, alkyl 4-bromobenzoate was prepared using 4-bromobenzoyl chloride (926 mg, 4.22 mmol, 2 equiv), (+)-\(\alpha\)-Tocopherol (909 mg, 2.11 mmol, 1 equiv), Et₃N (534 mg, 5.28 mmol, 2.5 equiv), and CH₂Cl₂ solvent (100 mL). After work up, the crude product was purified by flash chromatography using hexanes/EtOAc (10:1) as an eluent to afford the pure aryl 4-bromobenzoate (1.17 g, 1.90 mmol, 90%). The corresponding internal alkyne was prepared using aryl 4-bromobenzoate (600 mg, 0.98 mmol, 1 equiv), Pd(PPh₃)₂Cl₂ (41 mg, 6 mol %), CuI (22 mg, 12 mol %), THF solvent (4 mL), trimethylsilylacetylene (154 mg, 1.6 equiv) and Et₃N (199 mg, 2 equiv). After the addition of TBAB solution (1 mL) and subsequent work up, the crude product was purified by flash chromatography using hexanes/EtOAc (15:1) as an eluent to afford the title terminal alkyne (S3) as viscous brown oil (257 mg, 0.46 mmol, 47%, based on aryl 4-bromobenzoate). 

\[^1\text{H}\] NMR (400 MHz, CDCl₃): δ 8.24 (d, \(J = 8.2\) Hz, 2 H), 7.65 (d, \(J = 8.2\) Hz, 2 H), 3.29 (s, 1 H), 2.66 (d, \(J = 6.5\) Hz, 2 H), 2.17 (s, 3 H), 2.09 (s, 3 H), 2.05 (s, 3 H), 1.93-1.78 (m, 2 H), 1.69-1.38 (ovrlp, 8 H), 1.35-1.26 (ovrlp, 10 H), 1.21-1.08 (ovrlp, 6 H), 0.92-0.89 (ovrlp, 12 H). 

\[^{13}\text{C}\] NMR (100 MHz, CDCl₃): δ 164.7, 149.7, 140.6, 132.0, 129.5, 126.8, 109.6, 108.7, 96.3, 82.8, 80.4, 71.1, 70.7, 70.4, 66.1, 64.1, 26.0, 25.9, 24.9, 24.4. HRMS (APPI): Calcd for C₃₈H₅₅O₃ [M]: 559.4155; Found: 559.4151.

\(\text{Ethyl 4-(2-Ethynylphenoxy)butanoate (S4). Following the general procedure B, the title compound was prepared using ethyl 4-(2-iodophenoxy)butanoate}^{23}\) (instead of alkyl 4-bromobenzoate) (2.80 g, 8.38 mmol, 1 equiv), Pd(PPh₃)₂Cl₂ (294 mg, 5 mol %), CuI (160 mg, 10 mol %), THF solvent (10 mL), trimethylsilylacetylene (1.23 g, 1.5 equiv) and Et₃N (1.71 g, 2 equiv). After the addition of TBAB
solution (6 mL) and subsequent work up, the crude product was purified by flash chromatography using hexanes/EtOAc (15:1) as an eluent to afford the title terminal alkyne (S4) as brown oil (1.48 g, 6.38 mmol, 76%). ¹H NMR (400 MHz, CDCl₃): δ 7.44 (dd, J = 7.5 Hz, J = 1.6 Hz, 1 H), 7.28 (t, J = 7.4 Hz, 1 H), 6.91-6.86 (ovrlp, 2 H), 4.14 (q, J = 7.1 Hz, 2 H), 4.08 (t, J = 6.1 Hz, 2 H), 3.27 (s, 1 H), 2.57 (t, J = 7.3 Hz, 2 H), 2.15 (qu, J = 6.4 Hz, 2 H), 1.25 (t, J = 7.1 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 173.3, 159.9, 134.1, 130.2, 120.6, 112.1, 111.8, 81.2, 80.0, 67.5, 60.5, 30.7, 24.5, 14.3.

Optimizations of Iron-Catalyzed Z-Olefin Synthesis with Arylalkyne and Secondary Alkyl Iodide (Tables S1-S6 and Fig. S1). An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with zinc powder (1.2-2.5 equiv) and DMA solvent (0.5-2 mL). Iodine (dissolved in DMA, 0.5 M, 2 mol %) or halotrimethylsilane (10-20 mol %) was then added into the reaction mixture, and the mixture was stirred at room temperature (~1-2 min, after which time the brown color decolorized when I₂ was added). Iron (or other transition metal catalyst) (5-15 mol %) was added into the reaction mixture, followed by the additions of phenylacetylene (51 mg, 0.5 mmol), other additives, and finally iodocyclohexane (1.2-2.5 equiv). The resulting mixture was stirred at room temperature for 16 h, or heated at 80 °C in a preheated oil bath. After the reaction, n-dodecane (109 μL, 0.50 mmol, 1.0 equiv) was added into the crude product mixture, and the crude product was washed with EtOAc (~5 mL) and water (~20 mL). A small portion of the organic fraction was filtered through a plug of silica gel and then subjected to GC analysis to determine the GC yield of Z-olefin and the Z to E ratio of olefin using n-dodecane as internal standard.

Optimizations of Iron-Catalyzed Z-Olefin Synthesis with Arylalkyne and Primary Alkyl Iodide (Tables S7 and Fig. S2). An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with zinc powder (2.0-2.5 equiv) and DMA solvent (0.5-1 mL). Iodine (dissolved in DMA, 0.5 M, 4-10 mol %) or halotrimethylsilane (20 mol %) was then added into the reaction mixture, and the mixture was stirred at room temperature (~1-2 min, after which time the brown color decolorized when I₂ was added). Iron(II) bromide (10 mol %) and copper catalyst (5-15 mol %) were added into the reaction mixture, followed by the additions of phenylacetylene (0.5-1.0 mmol) and finally 1-iodoheptane (or 1-iodooctane) (1.5-2 equiv). The resulting mixture was stirred at room temperature for 16 h. After the reaction, n-dodecane (1.0 equiv) was added into the crude product mixture, and the crude product was washed with EtOAc (~5 mL) and water (~20 mL). A small portion of the organic fraction was filtered through a plug of silica gel and then subjected to GC analysis to determine the GC yields of Z-olefin and co-products using n-dodecane as internal standard.

Substrate Scope for Iron-Catalyzed Z-Olefin Synthesis with Arylalkyne and Secondary/Tertiary Alkyl Iodides (General Procedure C). An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with zinc powder (98 mg, 1.5 mmol, 1.5 equiv) and DMA solvent (2 mL). Iodine (dissolved in DMA, 0.5 M, 2 mol %, 40 μL) was then added into the reaction mixture, and the mixture was stirred at room temperature until the brown color decolorized (~1-2 min). Iron(II) bromide (22 mg, 0.10 mmol, 10 mol %) was added into the reaction mixture, followed by the additions of arylacetylene (1.0 mmol, 1.0 equiv) and finally alkyl iodide (1.5 mmol, 1.5 mol %) or halotrimethylsilane (20 mol %) was then added into the reaction mixture, followed by the additions of phenylacetylene (51 mg, 0.5 mmol, 1.0 equiv) and other additives, and finally iodocyclohexane (1.2-2.5 equiv). The resulting mixture was stirred at room temperature for 16 h, or heated at 80 °C in a preheated oil bath. After the reaction, n-dodecane (109 μL, 0.50 mmol, 1.0 equiv) was added into the crude product mixture, and the crude product was washed with EtOAc (~5 mL) and water (~20 mL). A small portion of the organic fraction was filtered through a plug of silica gel and then subjected to GC analysis to determine the GC yield of Z-olefin and the Z to E ratio of olefin using n-dodecane as internal standard.
equiv). The resulting mixture was stirred at room temperature for 16 h. After the reaction, the crude product was washed with EtOAc (~10 mL) and water (~50 mL). The aqueous fraction was further washed with EtOAc (2 x ~10 mL). The combined organic fractions were concentrated in vacuo with the aid of a rotary evaporator. The crude product residue was purified by flash column chromatography with silica gel using a solvent mixture (EtOAc, hexanes) as an eluent to afford the isolated Z-olefin product.

Substrate Scope for Iron-Catalyzed Z-Olefin Synthesis with Arylalkyne and Secondary/Tertiary Alkyl Bromides at 60 °C (General Procedure D). An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with zinc powder (327 mg, 5 mmol, 5 equiv) and DMA solvent (2 mL). Iodine (dissolved in DMA, 0.5 M, 10 mol %, 200 μL) was then added into the reaction mixture, and the mixture was stirred at room temperature until the brown color decolorized (~1-2 min). Iron(II) bromide (22 mg, 0.10 mmol, 10 mol %) was added into the reaction mixture, followed by the additions of arylacetylene (1.0 mmol, 1.0 equiv) and finally alkyl bromide (5.0 mmol, 5 equiv). The resulting mixture was stirred at 60 °C for 16 h in a preheated oil-bath. After the reaction, the reaction mixture was cooled to room temperature, and the crude product was washed with EtOAc (~10 mL) and water (~50 mL). The aqueous fraction was further washed with EtOAc (2 x ~10 mL). The combined organic fractions were concentrated in vacuo with the aid of a rotary evaporator. The crude product residue was purified by flash column chromatography with silica gel using a solvent mixture (EtOAc, hexanes) as an eluent to afford the isolated Z-olefin product.

Substrate Scope for Iron-Catalyzed Z-Olefin Synthesis with Arylalkyne and Secondary/Tertiary Alkyl Bromides at Room Temperature (General Procedure E). An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with zinc powder (131-196 mg, 2-3 mmol, 2-3 equiv) and DMA solvent. Iodotrimethylsilane (TMSI) (20-30 mol %,) was then added into the reaction mixture, and the mixture was stirred at room temperature until the brown color decolorized (~1-2 min). Iron(II) bromide (22 mg, 0.10 mmol, 10 mol %) was added into the reaction mixture, followed by the additions of arylacetylene (1.0 mmol, 1.0 equiv) and finally alkyl bromide (2-3 mmol, 2-3 equiv). The resulting mixture was stirred at room temperature for 24 h. After the reaction, the crude product was washed with EtOAc (~10 mL) and water (~50 mL). The aqueous fraction was further washed with EtOAc (2 x ~10 mL). The combined organic fractions were concentrated in vacuo with the aid of a rotary evaporator. The crude product residue was purified by flash column chromatography with silica gel using a solvent mixture (EtOAc, hexanes) as an eluent to afford the isolated Z-olefin product.

Substrate Scope for Iron-Catalyzed Z-Olefin Synthesis with Arylalkyne and Primary Alkyl Iodide (General Procedure F). An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with zinc powder (2.5-3.5 equiv) and DMA solvent. Iodotrimethylsilane (TMSI) (20-30 mol %,) was then added into the reaction mixture, and the mixture was stirred at room temperature for ~2 min (Caution: white fume was generated when iodotrimethylsilane was once added; no more fume was produced upon prolonged stirring). Iron(II) bromide (10 mol %) and copper(II) bromide (10 mol %) were added into the reaction mixture, followed by the additions of arylacetylene (1.0 equiv) and finally alkyl iodide (2-3 equiv). The resulting mixture
was stirred at room temperature for 16 h. After the reaction, the crude product was washed with EtOAc (~10 mL) and water (~50 mL). The aqueous fraction was further washed with EtOAc (2 x ~10 mL). The combined organic fractions were concentrated \textit{in vacuo} with the aid of a rotary evaporator. The crude product residue was purified by flash column chromatography with silica gel using a solvent mixture (EtOAc, hexanes) as an eluent to afford the isolated Z-olefin product.

**Substrate Scope for Iron-Catalyzed Z-Olefin Synthesis with Arylalkyne and Primary Alkyl Tosylate (General Procedure G).** An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with zinc powder (3.5–5.5 equiv) and DMA solvent. Iodotrimethylsilane (TMSI) (30–50 mol %) was then added into the reaction mixture, and the mixture was stirred at room temperature for ~2 min (\textbf{Caution}: white fume was generated when iodotrimethylsilane was added; no more fume was produced upon prolonged stirring). Iron(II) bromide (10 mol %), copper(II) bromide (10 mol %), and tetrabutylammonium iodide (TBAI) (1–2 equiv) were added into the reaction mixture, followed by the additions of arylacetylene (1 equiv) and finally alkyl iodide (3–5 equiv). The resulting mixture was stirred at 60 °C for 3 days in a preheated oil-bath. After the reaction, the reaction mixture was cooled down to room temperature, and the crude product was washed with EtOAc (~10 mL) and water (~50 mL). The aqueous fraction was further washed with EtOAc (2 x ~10 mL). The combined organic fractions were concentrated \textit{in vacuo} with the aid of a rotary evaporator. The crude product residue was purified by flash column chromatography with silica gel using a solvent mixture (EtOAc, hexanes) as an eluent to afford the isolated Z-olefin product.

(Z)-(2-Cyclohexylvinyl)benzene (3a)\textsuperscript{24}

(i) \textbf{1 mmol scale.} Following the general procedure C, the title compound was prepared using ethynylbenzene (102 mg) and iodocyclohexane (315 mg, 194 \(\mu\)L). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (3a) as pale-yellow oil (147 mg, 0.79 mmol, 79%: Z:E = 15:1). \textbf{\(^1\)H NMR} (400 MHz, CDCl\(_3\)): \(\delta\) 7.32 (t, \(J = 7.4\) Hz, 2 H), 7.26-7.19 (ovrlp, 3 H), 6.31 (d, \(J = 11.6\) Hz, 1 H), 5.48 (t, \(J = 10.9\) Hz, 1 H), 2.61-2.54 (m, 1 H), 1.81-1.64 (ovrlp, 5 H), 1.32-1.11 (ovrlp, 5 H). \textbf{\(^{13}\)C NMR} (100 MHz, CDCl\(_3\)): \(\delta\) 139.1, 138.1, 128.7, 128.3, 127.0, 126.5, 37.0, 33.4, 26.2, 25.8.

(ii) \textbf{20 mmol scale.} Following the general procedure C, the title compound was prepared using ethynylbenzene (2.04 g, 20 mmol), iodocyclohexane (6.30 g, 30 mmol, 3.89 mL), FeBr\(_2\) (432 mg, 2.0 mmol), Zn (1.96 g, 30 mmol), I\(_2\) (dissolved in DMA, 0.5 M, 0.4 mmol, 800 \(\mu\)L), and DMA (40 mL) for 4 d. The reaction was performed in a Teflon-screw capped 500 mL Schlenk round-bottom flask. The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (3a) as pale-yellow oil (2.37 g, 12.7 mmol, 64%; Z:E = 16:1). Spectral and analytical data were identical to those reported for the same compound above.
(Z)-4-(2-Cyclohexylvinyl)-N,N-dimethylaniline (3b). Following the general procedure C, the title compound was prepared using 4-ethynyl-N,N-dimethylaniline (73 mg, 0.5 mmol, 1 equiv), iodocyclohexane (158 mg, 97 μL, 0.75 mmol, 1.5 equiv), FeBr₂ (11 mg, 0.05 mmol, 10 mol %), Zn (49 mg, 0.75 mmol, 1.5 equiv), I₂ (0.5 M solution in DMA, 20 μL), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (15:1) as an eluent to afford the title compound (3b) as pale-yellow oil (73 mg, 0.32 mmol, 64%; Z:E > 50:1). 

**1H NMR (400 MHz, CDCl₃):** δ 7.18 (d, J = 8.6 Hz, 2 H), 6.70 (d, J = 8.9 Hz, 2 H), 6.20 (d, J = 11.7 Hz, 1 H), 5.32 (dd, J = 11.6 Hz, J = 10.0 Hz, 1 H), 2.95 (s, 6 H), 2.66-2.57 (m, 1 H), 1.77-1.63 (ovrlp, 5 H), 1.35-1.10 (ovrlp, 5 H).

**13C NMR (100 MHz, CDCl₃):** δ 149.3, 136.2, 129.7, 126.7, 126.6, 112.4, 40.7, 37.1, 33.6, 26.3, 26.0.

**HRMS (ESI):** Calcd for C₁₆H₂₄N [M+H]: 230.1911; Found: 230.1909.

(Z)-1-(2-Cyclohexylvinyl)-4-methoxybenzene (3c). Following the general procedure C, the title compound was prepared using 1-ethynyl-4-methoxybenzene (132 mg) and iodocyclohexane (315 mg, 194 μL). The crude product was purified by flash chromatography using hexanes/EtOAc (20:1) as an eluent to afford the title compound (3c) as pale-yellow oil (194 mg, 0.90 mmol, 90%; Z:E = 12:1).

**1H NMR (400 MHz, CDCl₃):** δ 7.20 (d, J = 8.3 Hz, 2 H), 6.87 (d, J = 8.4 Hz, 2 H), 6.24 (d, J = 11.7 Hz, 1 H), 5.39 (t, J = 11.0 Hz, 1 H), 3.80 (s, 3 H), 2.60-2.52 (m, 1 H), 1.80-1.65 (ovrlp, 5 H), 1.33-1.11 (ovrlp, 5 H).

**13C NMR (100 MHz, CDCl₃):** δ 149.3, 136.2, 129.7, 126.7, 126.6, 112.4, 40.7, 37.1, 33.6, 26.3, 25.9.

**HRMS (ESI):** Calcd for C₁₅H₂₀O [M]: 216.1514; Found: 216.1514.

(Z)-(4-(2-Cyclohexylvinyl)phenyl)(methyl)sulfane (3d). Following the general procedure C, the title compound was prepared using 4-ethynylphenyl)(methyl)sulfane (94 mg, 0.63 mmol, 1 equiv), iodocyclohexane (200 mg, 123 μL, 0.95 mmol, 1.5 equiv), FeBr₂ (14 mg, 0.063 mmol, 10 mol %), Zn (62 mg, 0.95 mmol, 1.5 equiv), I₂ (0.5 M solution in DMA, 20 μL), and DMA (1.3 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (3d) as pale-yellow oil (105 mg, 0.45 mmol, 72%; Z:E > 50:1).

**1H NMR (400 MHz, CDCl₃):** δ 7.22 (d, J = 8.6 Hz, 2 H), 7.18 (d, J = 8.5 Hz, 2 H), 6.25 (d, J = 11.7 Hz, 1 H), 5.46 (dd, J = 11.6 Hz, J = 10.2 Hz, 1 H), 2.60-2.51 (m, 1 H), 2.49 (s, 3 H), 1.75-1.64 (ovrlp, 5 H), 1.32-1.11 (ovrlp, 5 H).

**13C NMR (100 MHz, CDCl₃):** δ 139.0, 136.4, 135.0, 129.9, 126.4, 113.7, 55.3, 37.0, 33.4, 26.2, 25.9.

**HRMS (APPI):** Calcd for C₁₅H₂₀S [M]: 232.1280; Found: 232.1275.
(Z)-1-((tert-Butyl)-4-(2-cyclohexylvinyl)benzene (3e). Following the general procedure C, the title compound was prepared using 1-((tert-butyl)-4-ethynylbenzene (158 mg) and iodo cyclohexane (315 mg, 194 μL). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (3e) as pale-yellow oil (210 mg, 0.87 mmol, 87%; Z:E = 14:1). \( ^1H \) NMR (400 MHz, CDCl\(_3\)): δ 7.35 (d, \( J = 8.0 \) Hz, 2 H), 7.21 (d, \( J = 8.0 \) Hz, 2 H), 6.27 (d, \( J = 11.7 \) Hz, 1 H), 5.44 (t, \( J = 11.0 \) Hz, 1 H), 2.65-2.58 (m, 1 H), 1.79-1.65 (ovrlp, 5 H), 1.33 (s, 9 H), 1.26-1.11 (ovrlp, 5 H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): δ 149.4, 138.6, 135.2, 128.5, 126.7, 125.3, 37.1, 34.6, 33.5, 31.5, 26.2, 25.9. HRMS (APPI): Calcd for C\(_{18}\)H\(_{26}\)[M]: 242.2029; Found: 242.2024.

(Br)-1-Bromo-4-(2-cyclohexylvinyl)benzene (3f). Following the general procedure C, the title compound was prepared using methyl 1-bromo-4-ethynylbenzene (91 mg, 0.5 mmol, 1 equiv), iodo cyclohexane (210 mg, 130 μL, 1.0 mmol, 2 equiv), FeBr\(_2\) (11 mg, 0.05 mmol, 10 mol %), Zn (65 mg, 1.0 mmol, 2 equiv), I\(_2\) (0.5 M solution in DMA, 3 mol %, 30 μL), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (3f) as pale-yellow oil (85 mg, 0.32 mmol, 64%; Z:E > 15:1). \( ^1H \) NMR (400 MHz, CDCl\(_3\)): δ 7.44 (d, \( J = 8.5 \) Hz, 2 H), 7.11 (d, \( J = 8.4 \) Hz, 2 H), 6.23 (d, \( J = 11.7 \) Hz, 1 H), 5.51 (dd, \( J = 11.6 \) Hz, \( J = 10.3 \) Hz, 1 H), 2.54-2.44 (m, 1 H), 1.80-1.65 (ovrlp, 5 H), 1.32-1.11 (ovrlp, 5 H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): δ 139.4, 136.9, 131.6, 131.4, 130.3, 125.8, 37.0, 33.2, 26.1, 25.8. HRMS (APPI): Calcd for C\(_{14}\)H\(_{17}\)Br [M]: 264.0508; Found: 264.0532.

(Chloro)-1-Chloro-4-(2-cyclohexylvinyl)benzene (3g). Following the general procedure C, the title compound was prepared using 1-chloro-4-ethynylbenzene (137 mg) and iodo cyclohexane (315 mg, 194 μL). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (3g) as pale-yellow oil (171 mg, 0.77 mmol, 77%; Z:E > 20:1). \( ^1H \) NMR (400 MHz, CDCl\(_3\)): δ 7.29 (d, \( J = 8.4 \) Hz, 2 H), 7.17 (d, \( J = 8.4 \) Hz, 2 H), 6.24 (d, \( J = 11.7 \) Hz, 1 H), 5.50 (dd, \( J = 11.6 \) Hz, \( J = 10.2 \) Hz, 1 H), 2.55-2.45 (m, 1 H), 1.74-1.64 (ovrlp, 5 H), 1.32-1.11 (ovrlp, 5 H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): δ 139.5, 136.3, 132.0, 129.8, 128.2, 125.6, 36.9, 33.1, 25.9, 25.6. HRMS (APPI): Calcd for C\(_{14}\)H\(_{17}\)Cl [M]: 220.1013; Found: 220.1016.
(Z)-1-(2-Cyclohexylvinyl)-4-fluorobenzene (3h). Following the general procedure C, the title compound was prepared using 1-ethynyl-4-fluorobenzene (120 mg) and iodocyclohexane (315 mg, 194 μL). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (3h) as pale-yellow oil (149 mg, 0.73 mmol, 73%; Z:E = 12:1). 1H NMR (400 MHz, CDCl3): δ 7.29 (dd, 3JCH = 7.7 Hz, 4JCF = 5.8 Hz, 2 H), 7.00 (dd, 3JCH = 8.4 Hz, 3JCF = 8.4 Hz, 2 H), 6.25 (d, J = 11.7 Hz, 1 H), 5.46 (t, J = 11.0 Hz, 1 H), 2.54-2.46 (m, 1 H), 1.80-1.65 (ovrlp, 5 H), 1.32-1.11 (ovrlp, 5 H). 13C NMR (100 MHz, CDCl3): δ 161.6 (1JCF = 244 Hz), 139.0, 134.1 (4JCF = 3.1 Hz), 130.2 (3JCF = 7.7 Hz), 125.9, 115.2 (2JCF = 21.1 Hz), 37.0, 33.3, 26.1, 25.8. HRMS (APPI): Calcd for C14H17F [M]: 204.1309; Found: 204.1310.

(Z)-4-(2-Cyclohexylvinyl)-N,N-diethylbenzamide (3i). Following the general procedure C, the title compound was prepared using N,N-diethyl-4-ethynylbenzamide (101 mg, 0.5 mmol, 1 equiv), iodocyclohexane (315 mg, 194 μL, 1.5 mmol, 3 equiv), FeBr2 (11 mg, 0.05 mmol, 10 mol %), Zn (98 mg, 1.5 mmol, 3 equiv), I2 (0.5 M solution in DMA, 5 mol %, 50 μL), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (10:1) as an eluent to afford the title compound (3i) as pale-yellow oil (67 mg, 0.23 mmol, 47%; Z:E = 10:1). 1H NMR (400 MHz, CDCl3): δ 7.34 (d, J = 8.1 Hz, 2 H), 7.26 (d, J = 8.0 Hz, 2 H), 6.30 (d, J = 11.7 Hz, 1 H), 5.52 (dd, J = 11.5 Hz, J = 10.3 Hz, 1 H), 3.55 (br s, 2 H), 3.30 (br s, 2 H), 2.59-2.51 (m, 1 H), 1.82-1.64 (ovrlp, 5 H), 1.31-1.09 (ovrlp, 11 H). 13C NMR (100 MHz, CDCl3): δ 171.2, 139.9, 138.9, 135.2, 128.5, 126.3, 126.2, 43.3, 39.2, 36.9, 33.2, 26.0, 25.7, 14.3, 12.9. HRMS (APPI): Calcd for C19H28NO [M]: 286.2177; Found: 286.2171.

Methyl (Z)-4-(2-Cyclohexylvinyl)benzoate (3j). Following the general procedure C, the title compound was prepared using methyl 4-ethynylbenzoate (80 mg, 0.5 mmol, 1 equiv), iodocyclohexane (315 mg, 194 μL, 1.5 mmol, 3 equiv), FeBr2 (11 mg, 0.05 mmol, 10 mol %), Zn (98 mg, 1.5 mmol, 3 equiv), I2 (0.5 M solution in DMA, 5 mol %, 50 μL), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (3j) as pale-yellow oil (68 mg, 0.28 mmol, 56%; Z:E > 20:1). 1H NMR (400 MHz, CDCl3): δ 8.00 (d, J = 8.4 Hz, 2 H), 7.31 (d, J = 8.3 Hz, 2 H), 6.33 (d, J = 11.7 Hz, 1 H), 5.59 (dd, J = 11.6 Hz, J = 10.3 Hz, 1 H), 3.92 (s, 3 H), 2.58-2.50 (m, 1 H), 1.74-1.65 (ovrlp, 5 H), 1.32-1.11 (ovrlp, 5 H). 13C NMR (100 MHz,
CDCl₃): δ 167.2, 142.8, 141.2, 129.7, 128.6, 128.1, 126.2, 52.2, 37.2, 33.2, 26.1, 25.7. **HRMS (ESI):** Calcd for C₁₆H₂₁O₂ [M+H]: 245.1542; Found: 245.1542.

(Z)-1-(4-(2-Cyclohexylvinyl)phenyl)ethan-1-one (3k). Following the general procedure C, the title compound was prepared using 1-(4-ethynylphenyl)ethan-1-one (144 mg) and iodocyclohexane (315 mg, 194 μL). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (3k) as pale-yellow oil (132 mg, 0.58 mmol, 58%; Z:E = 9.0:1 by comparing the ratio of aryl protons of Z- and E-isomers due to the overlapping of olefinic protons). **¹H NMR** (400 MHz, CDCl₃): δ 7.93 (d, J = 8.0 Hz, 2 H), 7.34 (d, J = 8.0 Hz, 2 H), 6.33 (d, J = 11.8 Hz, 1 H), 5.61 (d, J = 11.1 Hz, 1 H), 2.60-2.51 (ovrlp, 4 H), 1.79-1.66 (ovrlp, 5 H), 1.32-1.14 (ovrlp, 5 H). **¹³C NMR** (100 MHz, CDCl₃): δ 197.8, 141.4, 132.4, 131.8, 128.8, 128.5, 126.1, 37.3, 33.2, 26.7, 26.1, 25.7. **HRMS (ESI):** Calcd for C₁₆H₂₁O [M+H]: 229.1592; Found: 229.1592.

(Z)-4-(2-Cyclohexylvinyl)benzaldehyde (3l). Following the general procedure C, the title compound was prepared using methyl 4-ethynylbenzaldehyde (65 mg, 0.5 mmol, 1 equiv), iodocyclohexane (263 mg, 162 μL, 1.25 mmol, 2.5 equiv), FeBr₂ (11 mg, 0.05 mmol, 10 mol %), Zn (82 mg, 1.25 mmol, 2.5 equiv), I₂ (0.5 M solution in DMA, 5 mol %, 50 μL), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (3l) as pale-yellow oil (34 mg, 0.16 mmol, 32%; Z:E = 7.4:1 by comparing the ratio of aryl protons of Z- and E-isomers due to the overlapping of olefinic protons). **¹H NMR** (400 MHz, CDCl₃): δ 9.99 (s, 1 H), 7.85 (d, J = 8.2 Hz, 2 H), 7.40 (d, J = 8.2 Hz, 2 H), 6.35 (d, J = 11.8 Hz, 1 H), 5.64 (dd, J = 11.7 Hz, J = 10.4 Hz, 1 H), 2.60-2.51 (m, 1 H), 1.84-1.65 (ovrlp, 5 H), 1.30-1.18 (ovrlp, 5 H). **¹³C NMR** (100 MHz, CDCl₃): δ 192.0, 141.9, 134.6, 130.3, 129.9, 129.2, 126.1, 37.3, 33.2, 26.0, 25.7. **HRMS (APPI):** Calcd for C₁₅H₁₈O [M]: 214.1359; Found: 214.1358.

(Z)-4-(2-Cyclohexylvinyl)benzonitrile (3m). Following the general procedure C, the title compound was prepared using 4-ethynylbenzonitrile (64 mg, 0.5 mmol, 1 equiv), iodocyclohexane (525 mg, 324 μL, 2.5 mmol, 5 equiv), FeBr₂ (11 mg, 0.05 mmol), tetramethylethylenediamine (23 mg, 0.2 mmol), Zn (164 mg, 2.5 mmol, 5 equiv), I₂ (0.5 M solution in DMA, 10 mol %, 100 μL), and DMA (1 mL) for 4 d.
The crude product was purified by flash chromatography using hexanes/EtOAc (20:1) as an eluent to afford the title compound (3m) as pale-yellow oil (45 mg, 0.210 mmol, 43%; Z:E > 50:1). \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.61 (d, \( J = 8.3 \) Hz, 2 H), 7.33 (d, \( J = 8.2 \) Hz, 2 H), 6.30 (d, \( J = 11.8 \) Hz, 1 H), 5.64 (dd, \( J = 11.7 \) Hz, \( J = 10.6 \) Hz, 1 H), 2.54-2.44 (m, 1 H), 2.54-2.44 (m, 1 H), 1.79-1.63 (ovrlp, 5 H), 1.32-1.15 (ovrlp, 5 H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): \( \delta \) 142.8, 142.1, 132.1, 129.2, 125.5, 119.2, 110.0, 37.2, 33.1, 26.0, 25.6. HRMS (APPI): Calcd for C\(_{15}\)H\(_{18}\)N [M+H]: 212.1439; Found: 212.1439.

\((Z)-1-(3-Methylnon-1-en-1-yl)-4-(trifluoromethyl)benzene (3n)\). Following the general procedure C, the title compound was prepared using 1-ethynyl-4-(trifluoromethyl)benzene (85 mg, 0.5 mmol, 1 equiv), 2-iodooctane (360 mg, 1.5 mmol, 3 equiv), FeBr\(_2\) (11 mg, 0.05 mmol, 10 mol %), Zn (98 mg, 1.5 mmol, 3 equiv), I\(_2\) (0.5 M solution in DMA, 5 mol %, 50 \( \mu \)L), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (3n) as pale-yellow oil (95 mg, 0.33 mmol, 67%; Z:E = 17:1). \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.48 (d, \( J = 8.2 \) Hz, 2 H), 7.25 (d, \( J = 8.0 \) Hz, 2 H), 6.29 (d, \( J = 11.7 \) Hz, 1 H), 5.44 (dd, \( J = 11.5 \) Hz, \( J = 10.7 \) Hz, 1 H), 2.64-2.48 (m, 1 H), 2.54-2.48 (m, 1 H), 1.28-1.11 (ovrlp, 10 H), 2.96 (d, \( J = 6.6 \) Hz, 3 H), 0.76 (t, \( J = 6.7 \) Hz, 3 H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): \( \delta \) 141.7, 128.9, 128.6 (q, \( J = 32.1 \) Hz), 126.3, 125.2 (q, \( J = 3.6 \) Hz), 124.5 (q, \( J = 270 \) Hz), 37.7, 32.4, 32.0, 29.6, 27.5, 22.8, 21.1, 14.2. GCMS: \([M] = 284\) detected which corresponds to C\(_{17}\)H\(_{23}\)F\(_3\).

\((Z)-1-(2-Cyclohexylvinyl)-2-methylbenzene (3o)\). Following the general procedure C, the title compound was prepared using 1-ethynyl-2-methylbenzene (116 mg) and iodocyclohexane (315 mg, 194 \( \mu \)L). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (3o) as pale-yellow oil (150 mg, 0.75 mmol, 75%; Z:E = 19:1). \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.20-7.13 (ovrlp, 4 H), 6.29 (d, \( J = 11.7 \) Hz, 1 H), 5.52 (t, \( J = 10.9 \) Hz, 1 H), 2.36-2.29 (m, 1 H), 2.25 (s, 3 H), 1.72-1.60 (ovrlp, 5 H), 1.25-1.09 (ovrlp, 5 H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): \( \delta \) 138.8, 137.4, 136.3, 129.8, 129.0, 126.8, 126.1, 125.5, 36.9, 33.4, 26.2, 25.8, 20.2. HRMS (APPI): Calcd for C\(_{15}\)H\(_{20}\) [M]: 200.1560; Found: 200.1555.

\((Z)-2-(2-Cyclohexylvinyl)naphthalene (3p)\). Following the general procedure C, the title compound was prepared using 2-ethynylnaphthalene (152 mg, 1.0 mmol, 1 equiv), iodocyclohexane (630 mg, 389 \( \mu \)L, 3 mmol, 3 equiv), Zn (196 mg, 3 mmol, 3 equiv), and I\(_2\) (0.5 M solution in DMA, 5 mol %, 100 \( \mu \)L). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent.
to afford the title compound (3p) as pale-yellow oil (116 mg, 0.49 mmol, 49%; Z:E = 14:1). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.81-7.76 (ovrlp, 3 H), 7.69 (s, 1 H), 7.48-7.43 (ovrlp, 2 H), 7.41 (dd, $J = 8.5$ Hz, $J = 1.8$ Hz, 1 H), 6.46 (d, $J = 11.7$ Hz, 1 H), 5.57 (dd, $J = 11.6$ Hz, $J = 10.2$ Hz, 1 H), 2.72-2.62 (m, 1 H), 1.83-1.65 (ovrlp, 5 H), 1.33-1.16 (ovrlp, 5 H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 139.6, 135.7, 133.5, 132.3, 128.1, 127.73, 127.70, 127.31, 127.29, 127.0, 126.1, 125.7, 37.2, 33.4, 26.2, 25.9. HRMS (APPI): Calcd for C$_{18}$H$_{20}$ [M]: 236.1560; Found: 236.1563.

(Z)-2-(2-Cyclohexylvinyl)-5-methylthiophene (3q). Following the general procedure C, the title compound was prepared using 2-ethynyl-5-methylthiophene (122 mg, 1.0 mmol, 1 equiv), iodo cyclohexane (630 mg, 389 μL, 3 mmol, 3 equiv), Zn (196 mg, 3 mmol, 3 equiv), and I$_2$ (0.5 M solution in DMA, 5 mol %, 100 μL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (3q) as pale-yellow oil (113 mg, 0.55 mmol, 55%; Z:E = 13:1). $^1$H NMR (400 MHz, CDCl$_3$): δ 6.72 (d, $J = 3.4$ Hz, 1 H), 6.63-6.61 (m, 1 H), 6.33 (d, $J = 11.5$ Hz, 1 H), 5.31 (dd, $J = 11.4$ Hz, $J = 10.1$ Hz, 1 H), 2.79-2.68 (m, 1 H), 2.47 (s, 3 H), 1.79-1.66 (ovrlp, 5 H), 1.43-1.32 (m, 2 H), 1.27-1.08 (ovrlp, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 139.6, 138.6, 135.7, 127.3, 124.9, 120.2, 38.1, 33.0, 26.2, 26.1, 15.5. HRMS (APPI): Calcd for C$_{13}$H$_{18}$S [M]: 206.1124; Found: 206.1125.

(Z)-3-(3-Methyldec-1-en-1-yl)pyridine (3r). Following the general procedure C, the title compound was prepared using 3-ethynlypyridine (52 mg, 0.5 mmol, 1 equiv), 2-iodononane (636 mg, 2.5 mmol, 5 equiv), FeBr$_2$ (11 mg, 0.05 mmol), tetramethyl ethylenediamine (23 mg, 0.2 mmol), Zn (164 mg, 2.5 mmol, 5 equiv), I$_2$ (0.5 M solution in DMA, 10 mol %, 100 μL), and DMA (1 mL) for 4 d. The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (3r) as pale-yellow oil (41 mg, 0.18 mmol, 35%; Z:E > 50:1). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.53-8.36 (ovrlp, 2 H), 7.56 (d, $J = 7.8$ Hz, 1 H), 7.26 (dd, $J = 7.6$ Hz, $J = 4.8$ Hz, 1 H), 6.31 (d, $J = 11.7$ Hz, 1 H), 5.57 (dd, $J = 11.4$ Hz, $J = 10.7$ Hz, 1 H), 2.70-2.59 (m, 1 H), 1.34-1.11 (ovrlp, 12 H), 1.04 (d, $J = 6.6$ Hz, 3 H), 0.86 (t, $J = 6.8$ Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 149.7, 147.4, 142.1, 135.8, 133.8, 123.8, 123.2, 37.6, 32.5, 31.9, 29.8, 29.4, 27.5, 22.8, 21.1, 14.2. HRMS (APPI): Calcd for C$_{16}$H$_{25}$N [M]: 231.1982; Found: 231.1976.
(Z)-1-(2-Cyclohexylvinyl)cyclohex-1-ene (3s, olefin) and (2-cyclohexylidenevinyl)cyclohexane (3s’, allene). Following the general procedure C, the title compound was prepared using 1-ethynlycyclohex-1-ene (106 mg, 1.0 mmol, 1 equiv), iodocyclohexane (420 mg, 259 µL, 2 mmol, 2 equiv), Zn (131 mg, 2 mmol, 2 equiv), and I₂ (0.5 M solution in DMA, 3 mol %, 60 µL). The crude product was purified by flash chromatography using hexanes as an eluent to afford an inseparable mixture of Z-olefin (3s) (51 mg, 0.27 mmol, 27%; Z:E = 6.6:1) and allene (3s’) (19 mg, 0.10 mmol, 10%) as colorless oil. Analysis of Z-olefin (3s): ¹H NMR (400 MHz, CDCl₃): δ 5.66-5.61 (ovrlp, 2 H), 5.09 (t, J = 11.1 Hz, 1 H), 2.55-2.47 (m, 1 H), 2.16-1.96 (ovrlp, 3 H), 1.71-1.56 (ovrlp, 9 H), 1.32-0.85 (ovrlp, 6 H). Analysis of allene (3s’): Analysis: Allene: HRMS (APPI): Calcd for C₁₄H₂₂ [M]: 190.1716; Found: 190.1713.

(Z)-1-(3-Methyldec-1-en-1-yl)cyclohex-1-ene (3t, olefin) and (3-methyldec-1-en-1-ylidene)cyclohexane (3t’, allene). Following the general procedure C, the title compound was prepared using 1-ethynlycyclohex-1-ene (106 mg, 1.0 mmol, 1 equiv), 2-iodononane (1.02 g, 4 mmol, 4 equiv), Zn (262 mg, 4 mmol, 4 equiv), and I₂ (0.5 M solution in DMA, 10 mol %, 200 µL) for 4 d. The crude product was purified by flash chromatography using hexanes as an eluent to afford an inseparable mixture of Z-olefin (3t) (51 84 mg, 0.36 mmol, 36%; Z:E = 15:1) and allene (3t’) (15 mg, 0.06 mmol, 6%) as colorless oil. Analysis of Z-olefin (3t): ¹H NMR (400 MHz, CDCl₃): δ 5.69 (d, J = 11.8 Hz, 1 H), 5.60 (s, 1 H), 5.01 (t, J = 11.1 Hz, 1 H), 2.72-2.65 (m, 1 H), 2.15-2.07 (ovrlp, 3 H), 1.70-1.56 (ovrlp, 4 H), 1.31-1.18 (ovrlp, 13 H), 0.95 (d, J = 6.6 Hz, 3 H), 0.88 (t, J = 6.6 Hz, 3 H). Analysis of allene (3t’): Analysis: Allene: HRMS (APPI): Calcd for C₁₇H₃₀ [M]: 234.2342; Found: 234.2337.

tert-Butyl (Z)-4-(4-Methoxystyryl)piperidine-1-carboxylate (4a). Following the general procedure C, the title compound was prepared using 1-ethynyl-4-methoxybenzene (132 mg, 1.0 mmol, 1 equiv), tert-butyl 4-iodopiperidine-1-carboxylate (622 mg, 2 mmol, 2 equiv), Zn (131 mg, 2 mmol, 2 equiv), and I₂ (0.5 M solution in DMA, 3 mol %, 60 µL). The crude product was purified by flash chromatography using hexanes/EtOAc (20:1) as an eluent to afford the title compound (4a) as pale-yellow oil (189 mg, 0.60 mmol, 60%; Z:E = 9:0.1). ¹H NMR (400 MHz, CDCl₃): δ 7.17 (d, J = 8.6 Hz, 2 H), 6.87 (d, J = 8.7 Hz, 2 H), 6.32 (d, J = 11.7 Hz, 1 H), 5.36 (dd, J = 11.4 Hz, J = 10.0 Hz, 1 H), 4.19-3.99 (m, 2 H), 3.80 (s, 3 H), 2.86-2.65 (ovrlp, 3 H), 1.72-1.62 (m, 2 H), 1.46 (s, 9 H), 1.40-1.30 (m, 2 H). Analysis of allene (3t’): Analysis: Allene: HRMS (APPI): Calcd for C₁₇H₃₀ [M]: 234.2342; Found: 234.2337.

HRMS (APPI): Calcd for C₁₉H₂₇NO₃Na [M+Na]: 340.1889; Found: 340.1903.
(Z)-1-Methoxy-4-(3-methyl-5-phenylpent-1-en-1-yl)benzene (4b). Following the general procedure C, the title compound was prepared using 1-ethynyl-4-methoxybenzene (66 mg, 0.5 mmol, 1 equiv), (3-iodobutyl)benzene (390 mg, 1.5 mmol, 3.0 equiv), FeBr$_2$ (11 mg, 0.05 mmol, 10 mol %), Zn (98 mg, 1.5 mmol, 3 equiv), I$_2$ (0.5 M solution in DMA, 5 mol %, 50 μL), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (4b) as pale-yellow oil (76 mg, 0.29 mmol, 57%; Z:E > 20:1). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.21 (t, $J$ = 7.6 Hz, 2 H), 7.16–7.12 (ovrlp, 3 H), 7.08 (d, $J$ = 7.7 Hz, 2 H), 6.82 (d, $J$ = 8.6 Hz, 2 H), 6.35 (d, $J$ = 11.6 Hz, 1 H), 5.39 (dd, $J$ = 11.4 Hz, 10.6 Hz, 1 H), 3.80 (s, 3 H), 2.84–2.73 (m, 1 H), 2.65–2.57 (m, 1 H), 2.56–2.48 (m, 1 H), 1.70–1.58 (m, 2 H), 1.08 (d, $J$ = 6.6 Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.3, 142.7, 137.8, 130.6, 129.9, 128.6, 128.3, 127.5, 125.7, 113.7, 55.4, 39.8, 33.8, 31.8, 21.2. HRMS (APPI): Calcd for C$_{19}$H$_{22}$O [M]: 266.1665; Found: 266.1659.

(i) From Alkyl Iodide.

1-((Z)-4-methoxystyrlyl) adamantane (4c). Following the general procedure C, the title compound was prepared using 1-ethynyl-4-methoxybenzene (66 mg, 0.5 mmol, 1 equiv), 1-iodoadamantane (655 mg, 2.5 mmol, 5 equiv), FeBr$_2$ (11 mg, 0.05 mmol, 10 mol %), Zn (164 mg, 2.5 mmol, 5 equiv), I$_2$ (0.5 M solution in DMA, 10 mol %, 100 μL), and DMA (1 mL) for 4 d. The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (4c) as pale-yellow, low-melting solid (93 mg, 0.35 mmol, 69%; Z:E > 50:1). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.10 (d, $J$ = 8.4 Hz, 2 H), 6.81 (d, $J$ = 8.7 Hz, 2 H), 6.33 (d, $J$ = 12.6 Hz, 1 H), 5.32 (d, $J$ = 12.6 Hz, 1 H), 3.81 (s, 3 H), 1.86 (s, 3 H), 1.68-1.55 (ovrlp, 12 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.0, 143.1, 132.1, 130.2, 126.8, 112.9, 55.3, 43.3, 37.0, 36.9, 28.7. HRMS (APPI): Calcd for C$_{19}$H$_{24}$O [M]: 268.1822; Found: 268.1815.

(2Z)-1-((tert-Butyl)-4-(2-cyclopentylvinyl)benzene (4d). Following the general procedure C, the title compound was prepared using 1-(tert-butyl)-4-ethynylbenzene (158 mg) and iodocyclopentane (294 mg). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (4d) as pale-yellow oil (127 mg, 0.56 mmol, 56%; Z:E = 15:1). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.35 (d, $J$ = 8.4 Hz, 2 H), 7.23 (d, $J$ = 8.4 Hz, 2 H), 6.32 (d, $J$ = 11.5 Hz, 1 H), 5.54 (dd, $J$ = 11.4 Hz, 10.1 Hz, 1 H), 2.99 (sex, $J$ = 8.5 Hz, 1 H), 1.91-1.84 (m, 2 H), 1.76-1.65 (m, 2 H), 1.63-1.55 (m, 2 H), 1.39-1.31
(Z)-(4-(tert-Butyl)styryl)cycloheptane (4d). Following the general procedure D, the title compound was prepared using 1-(tert-butyl)-4-ethynylbenzene (158 mg, 1.0 mmol, 1 equiv), bromocyclopentane (447 mg, 3.0 mmol, 3 equiv), Zn (196 mg, 3.0 mmol, 3 equiv), and I$_2$ (0.5 M solution in DMA, 5 mol %, 100 μL). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (4d) as pale-yellow oil (118 mg, 0.52 mmol, 52%; Z:E = 5.3:1). Spectral and analytical data were identical to those reported for the same compound above.

\[(Z)-(4-(tert-Butyl)styryl)cycloheptane (4d).

(Z)-(4-(tert-Butyl)styryl)cycloheptane (4e). Following the general procedure C, the title compound was prepared using 1-(tert-butyl)-4-ethynylbenzene (158 mg) and iodocycloheptane (336 mg). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (4e) as pale-yellow oil (124 mg, 0.55 mmol, 55%; Z:E = 16:1). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.35 (d, $J$ = 8.0 Hz, 2 H), 7.21 (d, $J$ = 8.0 Hz, 2 H), 6.20 (d, $J$ = 11.6 Hz, 1 H), 5.54 (t, $J$ = 11.0 Hz, 1 H), 2.83-2.73 (m, 1 H), 1.81-1.76 (m, 2 H), 1.73-1.67 (m, 2 H), 1.62-1.48 (ovrlp, 6 H), 1.44-1.39 (m, 2 H), 1.33 (s, 9 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 149.4, 139.4, 135.1, 128.5, 125.2, 125.1, 36.4, 34.6, 31.5, 28.6, 26.5. HRMS (APPI): Calcd for C$_{19}$H$_{28}$ [M]: 256.2186; Found: 256.2182.

(Z)-(4-(tert-Butyl)styryl)cyclooctane (4f). Following the general procedure C, the title compound was prepared using 1-(tert-butyl)-4-ethynylbenzene (158 mg) and iodocyclooctane (357 mg). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (4f) as pale-yellow oil (138 mg, 0.58 mmol, 58%; Z:E = 18:1). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.35 (d, $J$ = 8.0 Hz, 2 H), 7.22 (d, $J$ = 7.9 Hz, 2 H), 6.20 (d, $J$ = 11.7 Hz, 1 H), 5.55 (t, $J$ = 11.1 Hz, 1 H), 2.90-2.83 (m, 1 H), 1.76-1.67 (ovrlp, 4 H), 1.60-1.45 (ovrlp, 10 H), 1.32 (s, 9 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 149.3, 139.5, 135.2, 128.5, 125.2, 125.1, 36.4, 34.6, 32.8, 31.5, 27.4, 26.3, 25.2. HRMS (APPI): Calcd for C$_{20}$H$_{30}$ [M]: 270.2342; Found: 270.2336.

(Z)-1-(tert-butyl)-4-(3,3-dimethylbut-1-en-1-yl)benzene (4g).

(i) From Alkyl Iodide. Following the general procedure C, the title compound was prepared using 1-(tert-butyl)-4-ethynylbenzene (158 mg, 1.0 mmol, 1 equiv), 2-ido-2-methylpropane (552 mg, 3.0
mmol, 3 equiv), Zn (196 mg, 3.0 mmol, 3 equiv), and I₂ (0.5 M solution in DMA, 5 mol %, 100 μL). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (4g) as colorless oil (135 mg, 0.62 mmol, 62%; Z:E > 50:1). ¹H NMR (400 MHz, CDCl₃): δ 7.28 (d, J = 8.0 Hz, 2 H), 7.11 (d, J = 7.9 Hz, 2 H), 6.37 (d, J = 12.6 Hz, 1 H), 5.58 (d, J = 12.6 Hz, 1 H), 1.31 (s, 9 H), 0.99 (s, 9 H).

¹³C NMR (100 MHz, CDCl₃): δ 149.2, 142.6, 136.4, 128.8, 127.3, 124.6, 34.6, 34.2, 31.6, 31.4. HRMS (APPI): Calcd for C₁₆H₂₄ [M]: 216.1873; Found: 216.1874.

(ii) From Alkyl Bromide. Following the general procedure D, the title compound was prepared using 1-((tert-buty1)-4-ethynylbenzene (158 mg, 1.0 mmol, 1 equiv) and 2-bromo-2-methylpropane (685 mg). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (4g) as colorless oil (105 mg, 0.49 mmol, 49%; Z:E = 19:1). Spectral and analytical data were identical to those reported for the same compound above.

(Z)-4-(4-Methylstyril)tetrahydro-2H-pyran (4h). Following the general procedure C, the title compound was prepared using 1-ethynyl-4-methylbenzene (158 mg) and 4-iodotetrahydro-2H-pyran (318 mg). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (4h) as pale-yellow oil (124 mg, 0.61 mmol, 61%; Z:E = 16:1). ¹H NMR (400 MHz, CDCl₃): δ 7.17-7.12 (ovrlp 4 H), 6.36 (d, J = 11.6 Hz, 1 H), 5.44 (t, J = 10.9 Hz, 1 H), 3.95 (d, J = 10.5 Hz, 2 H), 3.41 (t, J = 10.9 Hz, 2 H), 2.87-2.77 (m, 1 H), 2.35 (s, 3 H), 1.68-1.49 (ovrlp, 4 H). ¹³C NMR (100 MHz, CDCl₃): δ 136.6, 136.3, 134.8, 129.1, 128.5, 128.2, 67.6, 34.3, 33.0, 21.3. HRMS (APPI): Calcd for C₁₄H₁₈O [M]: 202.1352; Found: 202.1349.

2-((Z)-4-Methylstyril)bicyclo[2.2.1]heptane (4i). Following the general procedure C, the title compound was prepared using 1-ethynyl-4-methylbenzene (116 mg) and 2-iodobicyclo[2.2.1]heptane (322 mg). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (4i) as colorless oil (150 mg, 0.71 mmol, 71%; Z:E = 19:1; exo:endo > 50:1). ¹H NMR (400 MHz, CDCl₃): δ 7.18 (d, J = 7.4 Hz, 2 H), 7.13 (d, J = 7.4 Hz, 2 H), 6.23 (d, J = 11.4 Hz, 1 H), 5.51 (t, J = 10.8 Hz, 1 H), 2.56 (t, J = 10.8 Hz, 1 H), 2.34 (s, 3 H), 2.27 (s, 1 H), 2.07 (s, 1 H), 1.62 (t, J = 10.2 Hz, 1 H), 1.55-1.46 (ovrlp, 3 H), 1.31-1.15 (ovrlp, 4 H). ¹³C NMR (100 MHz, CDCl₃): δ 138.4, 136.2, 135.0, 128.9, 128.8, 126.2, 43.5, 40.8, 40.1, 36.8, 36.3, 29.5, 29.1, 21.3. HRMS (APPI): Calcd for C₁₆H₂₀ [M]: 212.1560; Found: 212.1558. The exo-stereochemistry of 4i was determined by oxidizing 4i to bicyclo[2.2.1]heptane-2-carboxylic acid according to the literature procedure and comparing the characteristic proton chemical shift with the authentic compound. 26
(Z)-1-(3-Ethynon-1-en-1-yl)-4-methylbenzene (4j). Following the general procedure C, the title compound was prepared using 1-ethynyl-4-methylbenzene (116 mg) and 3-iodononane (381 mg). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (4j) as colorless oil (200 mg, 0.82 mmol, 82%; Z:E > 20:1). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.16 (d, $J$ = 7.7 Hz, 2 H), 7.11 (d, $J$ = 7.6 Hz, 2 H), 6.42 (d, $J$ = 11.7 Hz, 1 H), 5.32 (t, $J$ = 11.2 Hz, 1 H), 2.60-2.51 (m, 1 H), 2.33 (s, 3 H), 1.52-1.38 (m, 2 H), 1.32-1.17 (ovrlp, 10 H), 0.88-0.83 (ovrlp, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 137.9, 136.0, 135.4, 128.9, 128.8, 128.6, 39.1, 35.6, 32.0, 29.8, 28.6, 27.4, 22.8, 21.3, 14.3, 11.9. HRMS (APPI): Calcd for C$_{18}$H$_{28}$ [M]: 244.2186; Found: 244.2180.

(Z)-1-(3-Butylept-1-en-1-yl)-4-methylbenzene (4k). Following the general procedure C, the title compound was prepared using 1-ethynyl-4-methylbenzene (116 mg) and 5-iodononane (381 mg). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (4k) as colorless oil (166 mg, 0.68 mmol, 68%; Z:E > 20:1). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.16 (d, $J$ = 7.8 Hz, 2 H), 7.12 (d, $J$ = 7.8 Hz, 2 H), 6.39 (d, $J$ = 11.7 Hz, 1 H), 5.32 (t, $J$ = 11.2 Hz, 1 H), 2.65-2.58 (m, 1 H), 2.33 (s, 3 H), 1.44-1.32 (m, 4 H), 1.26-1.19 (ovrlp, 8 H), 0.85 (t, $J$ = 6.4 Hz, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 138.3, 136.0, 135.4, 128.9, 128.6, 128.5, 39.1, 35.6, 32.0, 29.8, 28.6, 27.4, 22.8, 21.3, 14.2. HRMS (ESI): Calcd for C$_{18}$H$_{28}$ [M]: 244.2183; Found: 244.2191.

(Z)-1-(3-Isopropylhex-1-en-1-yl)-4-methylbenzene (4l). Following the general procedure C, the title compound was prepared using 1-ethynyl-4-methylbenzene (116 mg) and 3-iodo-2-methylhexane (R1) (339 mg). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (4l) as colorless oil (150 mg, 0.69 mmol, 69%; Z:E > 50:1). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.16 (d, $J$ = 8.0 Hz, 2 H), 7.10 (d, $J$ = 8.0 Hz, 2 H), 6.46 (d, $J$ = 11.8 Hz, 1 H), 5.40 (d, $J$ = 11.6 Hz, 1 H), 2.53-2.47 (m, 1 H), 2.33 (s, 3 H), 1.66-1.58 (m, 1 H), 1.47-1.28 (m, 2 H), 1.25-1.11 (m, 2 H), 0.88 (t, $J$ = 6.6 Hz, 6 H), 0.82 (t, $J$ = 7.0 Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 141.8, 136.0, 135.5, 129.4, 128.9, 128.7, 43.2, 35.0, 32.3, 21.3, 20.8, 20.5, 19.6, 14.6. HRMS (APPI): Calcd for C$_{16}$H$_{24}$ [M]: 216.1873; Found: 216.1868.
(Z)-1-(3-Ethylhepta-1,6-dien-1-yl)-4-methylbenzene (4m). Following the general procedure C, the title compound was prepared using 1-ethynyl-4-methylbenzene (116 mg, 1.0 mmol, 1 equiv), 6-iodo-2-methylhept-2-ene (672 mg, 3.0 mmol, 3 equiv), Zn (196 mg, 3.0 mmol, 3 equiv), and I\(_2\) (0.5 M solution in DMA, 5 mol %, 100 \(\mu\)L). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (4m) as pale-yellow oil (115 mg, 0.54 mmol, 54%; \(Z:E > 50:1\)).

\[^1\text{H NMR}\] (400 MHz, CDCl\(_3\)): \(\delta\) 7.16 (d, \(J = 8.1\) Hz, 2 H), 7.11 (d, \(J = 8.1\) Hz, 2 H), 6.45 (d, \(J = 11.8\) Hz, 1 H), 5.80–5.70 (m, 1 H), 5.32 (dd, \(J = 11.5\) Hz, \(J = 10.8\) Hz, 1 H), 4.93–4.85 (ovrlp, 2 H), 2.65–2.55 (m, 1 H), 2.33 (s, 3 H), 2.13–2.03 (m, 1 H), 1.99–1.90 (m, 1 H), 1.55–1.44 (m, 2 H), 1.38–1.25 (m, 2 H), 0.88 (t, \(J = 7.4\) Hz, 3 H).

\[^{13}\text{C NMR}\] (100 MHz, CDCl\(_3\)): \(\delta\) 139.2, 137.3, 136.1, 135.3, 129.3, 128.9, 128.7, 114.3, 38.7, 34.9, 31.7, 28.5, 21.3, 11.8.

\[^\text{HRMS}\] (APPI): Calcd for \(C_{16}H_{22}\) [M]: 214.1716; Found: 214.1717.

(3S,5S,8R,9S,10S,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-((Z)-3-methylpent-1-en-1-yl)benzoate (4n). Following the general procedure C, the title compound was prepared using (cholestanyl 4-ethynylbenzoate) (S1) (113 mg, 0.22 mmol, 1 equiv), 2-iodobutane (143 mg, 0.66 mmol, 3 equiv), FeBr\(_2\) (4.8 mg, 0.022 mmol, 10 mol %), Zn (43 mg, 0.66 mmol, 3 equiv), I\(_2\) (0.5 M solution in DMA, 5 mol %, 22 \(\mu\)L), and DMA (1.5 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (4n) as a white solid (77 mg, 0.13 mmol, 61%; \(Z:E > 50:1\)).

\[^1\text{H NMR}\] (400 MHz, CDCl\(_3\)): \(\delta\) 7.91 (d, \(J = 8.2\) Hz, 2 H), 7.23 (d, \(J = 8.3\) Hz, 2 H), 6.33 (d, \(J = 11.7\) Hz, 1 H), 5.44 (t, \(J = 11.2\) Hz, 1 H), 4.90–4.82 (m, 1 H), 2.60–2.49 (m, 1 H), 1.92–1.85 (ovrlp, 2 H), 1.78–1.54 (ovrlp, 4 H), 1.48–1.38 (ovrlp, 4 H), 1.33–1.12 (ovrlp, 14 H), 1.10–0.90 (ovrlp, 12 H), 0.83 (d, \(J = 6.4\) Hz, 3 H), 0.80–0.75 (ovrlp, 12 H), 0.59 (s, 3 H).

\[^{13}\text{C NMR}\] (100 MHz, CDCl\(_3\)): \(\delta\) 166.2, 142.7, 141.3, 129.6, 129.0, 128.6, 127.1, 74.4, 56.6, 56.4, 54.4, 44.9, 42.8, 40.2, 39.7, 37.0, 36.3, 36.0, 35.7, 34.3, 34.1, 32.2, 30.4, 29.9, 28.8, 28.4, 28.2, 27.8, 24.4, 24.0, 23.0, 22.7, 21.4, 20.7, 18.8, 12.4, 12.2, 11.9.

\[^\text{HRMS}\] (APPI): Calcd for \(C_{40}H_{62}O_2\) [M]: 574.4767; Found: 574.4750.

((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-((Z)-2-cyclohexylvinyl)benzoate (4o). Following the general procedure C, the title
compound was prepared using 1,2:3,4-di-O-isopropylpylidene-α-D-galactopyranosyl 4-ethynylbenzoate) (S2) (97 mg, 0.25 mmol, 1 equiv), 2-iodocyclohexane (158 mg, 0.75 mmol, 3 equiv), FeBr₂ (5.4 mg, 0.025 mmol, 10 mol %), Zn (49 mg, 0.75 mmol, 3 equiv), I₂ (0.5 M solution in DMA, 5 mol %, 25 μL), and DMA (2 mL) for 24 h. The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (4o) as a pale-yellow oil [53 mg, 0.11 mmol, 45%; Z: E = 9.6:1 (using aryl C-H for the estimation of Z:E due to the overlapping of olefinic H)].

1H NMR (400 MHz, CDCl₃): δ 7.81 (d, J = 8.1 Hz, 2 H), 7.30 (d, J = 8.2 Hz, 2 H), 6.33 (d, J = 11.8 Hz, 1 H), 5.61-5.56 (ovrlp, 2 H), 4.66 (dd, J = 7.8 Hz, J = 2.0 Hz, 1 H), 4.54 (dd, J = 11.4 Hz, J = 4.8 Hz, 1 H), 4.42 (dd, J = 11.4 Hz, J = 7.6 Hz, 1 H), 4.36-4.33 (m, 2 H), 4.19 (t, J = 5.6 Hz, 1 H), 2.58-2.50 (m, 1 H), 1.79-1.66 (ovrlp, 5 H), 1.53 (s, 3 H), 1.48 (s, 3 H), 1.36 (s, 3 H), 1.34 (s, 3 H), 1.30-1.11 (ovrlp, 5 H).

13C NMR (100 MHz, CDCl₃): δ 166.4, 142.9, 141.1, 129.8, 128.6, 128.0, 126.2, 109.8, 108.9, 96.5, 71.3, 70.8, 66.3, 63.9, 37.2, 33.2, 26.2, 26.10, 26.07, 25.7, 25.1, 24.6. HRMS (APPI): Calcd for C₂₇H₃₇O₇ [M+H]: 473.2534; Found: 473.2528.

Following the general procedure C, the title compound was prepared using (±)-α-Tocopheryl 4-ethynylbenzoate (S3) (56 mg, 0.10 mmol, 1 equiv), iodocyclohexane (126 mg, 0.60 mmol, 6 equiv), FeBr₂ (4 mg, 0.02 mmol, 20 mol %), Zn (39 mg, 0.60 mmol, 6 equiv), I₂ (0.5 M solution in DMA, 10 mol %, 20 μL), and DMA (1 mL) for 24 h. The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (4p) (33 mg, 0.051 mmol, 51%; Z: E > 50:1) as pale-yellow oil. 1H NMR (400 MHz, CDCl₃): δ 8.20 (d, J = 7.8 Hz, 2 H), 7.39 (d, J = 8.0 Hz, 2 H), 6.35 (d, J = 11.7 Hz, 1 H), 5.63 (t, J = 11.0 Hz, 1 H), 2.64-2.56 (ovrlp, 3 H), 2.12 (s, 3 H), 2.07 (s, 3 H), 2.02 (s, 3 H), 1.88-1.67 (ovrlp, 7 H), 1.56-1.19 (ovrlp, 23 H), 1.16-1.04 (ovrlp, 6 H), 0.90-0.84 (ovrlp, 12 H). 13C NMR (100 MHz, CDCl₃): δ 165.2, 149.6, 143.4, 141.4, 140.8, 130.3, 128.8, 127.6, 127.1, 126.2, 125.3, 123.2, 117.6, 75.2, 39.5, 37.7, 37.6, 37.5, 37.4, 37.3, 33.3, 32.94, 32.88, 28.1, 26.1, 25.7, 25.0, 24.6, 22.9, 22.8, 21.2, 20.8, 19.91, 19.85, 19.80, 19.76, 13.2, 12.4, 12.0. HRMS (APPI): Calcd for C₄₄H₆₇O₃ [M+H]: 643.5085; Found: 643.5090.

5-(3-Ethynylnon-1-en-1-yl)-1,2,3-trimethoxybenzene (4q). Following the general procedure C, the title compound was prepared using 5-ethynyl-1,2,3-trimethoxybenzene (96 mg, 0.50 mmol, 1 equiv), 3-iodononane (635 mg, 2.5 mmol, 5 equiv), FeBr₂ (11 mg, 0.050 mmol, 10 mol %), Zn (164 mg, 2.5 mmol, 5 equiv), I₂ (0.5 M solution in DMA, 10 mol %, 100 μL), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title
compound (4q) (99 mg, 0.31 mmol, 62%; Z:E > 20:1) as pale-yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.41 (s, 2 H), 6.32 (d, $J$ = 11.7 Hz, 1 H), 5.25 (t, $J$ = 11.4 Hz, 1 H), 3.77 (s, ovrlp, 9 H), 2.54-2.45 (m, 1 H), 1.44-1.33 (ovrlp, 2 H), 1.26-1.13 (ovrlp, 10 H), 0.82 (t, $J$ = 7.4 Hz, 3 H), 0.77 (d, $J$ = 6.7 Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 152.8, 138.1, 133.9, 128.9, 105.7, 60.9, 56.0, 39.3, 35.6, 32.0, 29.6, 28.5, 27.5, 22.7, 14.1, 12.0. HRMS (APPI): Calcd for C$_{20}$H$_{33}$O$_3$ [M+H]: 321.2432; Found: 321.2430.

(Z)-5-(3,3-Dimethylbut-1-en-1-yl)-1,2,3-trimethoxybenzene (4r). Following the general procedure C, the title compound was prepared using 5-ethynyl-1,2,3-trimethoxybenzene (96 mg, 0.50 mmol, 1 equiv), 2-iodo-2-methylpropane (460 mg, 2.5 mmol, 5 equiv), FeBr$_2$ (11 mg, 0.050 mmol, 10 mol %), Zn (164 mg, 2.5 mmol, 5 equiv), I$_2$ (0.5 M solution in DMA, 10 mol %, 100 $\mu$L), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (4r) (70 mg, 0.28 mmol, 56%; Z:E > 20:1) as pale-yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.32 (s, 2 H), 6.27 (d, $J$ = 12.5 Hz, 1 H), 5.53 (d, $J$ = 12.5 Hz, 1 H), 3.77 (s, 3 H), 3.76 (s, 6 H), 0.94 (s, 9 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 152.5, 142.7, 134.9, 127.2, 106.2, 61.0, 56.1, 34.1, 31.2. HRMS (APPI): Calcd for C$_{15}$H$_{23}$O$_3$ [M]: 251.1649; Found: 251.1647.

(Z)-1-Methyl-4-(3-methyldec-1-en-1-yl)benzene (4s). Following the general procedure C, the title compound was prepared using 1-ethynyl-4-methylbenzene (116 mg) and 2-iodononane (381 mg). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (4s) as colorless oil (210 mg, 0.86 mmol, 86%; Z:E > 20:1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.16 (d, $J$ = 7.8 Hz, 2 H), 7.12 (d, $J$ = 7.9 Hz, 2 H), 6.32 (d, $J$ = 11.6 Hz, 1 H), 5.37 (t, $J$ = 11.0 Hz, 1 H), 2.77-2.69 (m, 1 H), 2.33 (s, 3 H), 1.32-1.19 (ovrlp, 12 H), 1.02 (d, $J$ = 6.5 Hz, 3 H), 0.86 (d, $J$ = 6.4 Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.2, 136.1, 135.3, 128.9, 128.6, 127.3, 37.8, 32.3, 32.0, 29.9, 29.5, 27.5, 22.8, 21.3, 21.2, 14.3. HRMS (APPI): Calcd for C$_{18}$H$_{28}$ [M]: 244.2186; Found: 244.2181.

(Z)-1-Methyl-2-(2-(3-methylcyclohexyl)vinyl)benzene (4t). Following the general procedure C, the title compound was prepared using 1-ethynyl-2-methylbenzene (116 mg) and 1-iodo-3-methylcyclohexane (d.r.: trans:cis = 6.4:1) (336 mg). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (4t) as colorless oil (165 mg, 0.77 mmol, 77%; Z:E > 20:1; d.r. = 1.8:1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.18-7.11 (ovrlp, 5 H), 6.34 (d, $J$ = 11.6 Hz, 2 H), 7.12-7.07 (m, 4 H), 5.24 (t, $J$ = 11.0 Hz, 1 H), 3.74 (s, 3 H), 2.77-2.67 (m, 2 H), 2.21 (s, 3 H), 1.20-1.07 (ovrlp, 12 H), 0.92 (d, $J$ = 6.5 Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.2, 136.1, 135.3, 128.6, 127.3, 37.8, 32.3, 32.0, 29.9, 29.5, 27.5, 22.8, 21.3, 21.2, 14.3. HRMS (APPI): Calcd for C$_{18}$H$_{28}$ [M]: 244.2186; Found: 244.2181.
0.64 H), 6.30 (d, J = 11.6 Hz, 0.36 H), 5.82 (t, J = 11.1 Hz, 0.36 H), 5.48 (t, J = 11.2 Hz, 0.36 H), 2.76-2.67 (m, 0.64 H), 2.40-2.30 (m, 0.36 H), 2.25 (s, 3 H), 1.87-1.02 (m, 9 H), 0.95-0.75 (ovrlp, 4 H). 

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta\) 138.8, 137.41, 137.36, 127.2, 136.31, 136.29, 130.2, 129.8, 128.98, 128.95, 126.8, 126.5, 126.1, 125.53, 125.46, 42.2, 39.9, 37.0, 34.8, 33.7, 33.0, 32.4, 32.0, 31.6, 27.5, 23.0, 20.9, 20.1 (observed complexity due to the inseparable mixture of both diasteromers).

HRMS (APPI): Calcd for C\(_{16}\)H\(_{22}\) [M]: 214.1716; Found: 214.1732.

\((Z)-1\text{-Methyl-2-(2-(4-methylcyclohexyl)vinyl)benzene (4u)}\). Following the general procedure C, the title compound was prepared using 1-ethynyl-2-methylbenzene (116 mg) and 1-iodo-4-methylcyclohexane (d.r.: cis:trans = 10.3:1) (336 mg). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (4u) as colorless oil (158 mg, 0.74 mmol, 74%; Z:E > 20:1; d.r. = 2.1:1). 

\(^{1}\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta\) 7.18-7.11 (ovrlp, 4 H), 6.36-6.30 (ovrlp, 1 H), 5.83 (t, J = 11.2 Hz, 0.68 H), 5.49 (t, J = 11.2 Hz, 0.32 H), 2.57-2.49 (m, 0.68 H), 2.34-2.30 (m, 0.32 H), 1.66-1.11 (m, 9 H), 0.95-0.83 (ovrlp, 4 H). 

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta\) 138.9, 137.4, 137.0, 136.3, 129.8, 128.98, 128.96, 126.8, 126.5, 126.3, 125.51, 125.49, 36.8, 34.6, 34.1, 33.4, 32.3, 30.7, 29.9, 29.6, 22.9, 20.4, 20.2 (observed complexity due to the inseparable mixture of both diasteroisomers). HRMS (APPI): Calcd for C\(_{16}\)H\(_{22}\) [M]: 214.1716; Found: 214.1732.

\((Z)-1\text{-Methyl-2-(4-iodo-3,3-dimethylcyclohexyl)benzene (5a)}\).

(i) From Alkyl Iodide. Following the general procedure C, the title compound was prepared using 1-ethynyl-2-(3,3-dimethylcyclohexyl)benzene (158 mg) and 2-iodobutane (276 mg). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (5a) as colorless oil (175 mg, 0.81 mmol, 81%; Z:E > 50:1). 

\(^{1}\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta\) 7.34 (d, J = 8.0 Hz, 2 H), 7.22 (d, J = 8.0 Hz, 2 H), 6.33 (d, J = 11.6 Hz, 1 H), 5.39 (t, J = 11.1 Hz, 1 H), 2.74-2.66 (m, 1 H), 1.40-1.32 (ovrlp, 11 H), 1.03 (d, J = 6.5 Hz, 3 H), 0.87 (t, J = 7.3 Hz, 3 H). 

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta\) 149.4, 139.0, 135.2, 128.5, 127.4, 125.2, 34.6, 34.0, 31.5, 30.6, 20.8, 12.0. HRMS (APPI): Calcd for C\(_{16}\)H\(_{24}\) [M]: 216.1873; Found: 216.1868.

(ii) From Alkyl Bromide. Following the general procedure D, the title compound was prepared using 1-ethynyl-2-(3,3-dimethylcyclohexyl)benzene (158 mg) and 2-bromobutane (685 mg). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (5a) as pale-yellow oil (118 mg, 0.55 mmol, 55%; Z:E = 8.7:1). Spectral and analytical data were identical to those reported for the same compound above.
(Z)-1-(tert-butyl)-4-(3-ethylpent-1-en-1-yl)benzene (5b). Following the general procedure D, the title compound was prepared using 1-(tert-butyl)-4-ethynylbenzene (158 mg) and 3-bromopentane (755 mg). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (5a) as pale-yellow oil (118 mg, 0.510 mmol, 51%; Z:E = 10:1). $^{1}$H NMR (400 MHz, CDCl$_3$): δ 7.33 (d, $J$ = 8.4 Hz, 2 H), 7.22 (d, $J$ = 8.4 Hz, 2 H), 6.44 (d, $J$ = 11.8 Hz, 1 H), 5.33 (t, $J$ = 11.6 Hz, 1 H), 2.59-2.49 (m, 1 H), 1.54-1.43 (ovrlp, 2 H), 1.34-1.25 (ovrlp, 11 H), 0.87 (t, $J$ = 7.4 Hz, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 149.3, 137.6, 135.4, 128.9, 128.5, 125.1, 40.7, 34.6, 31.5, 28.2, 11.9. HRMS (ESI): Calcd for C$_{17}$H$_{26}$ [M]: 230.2033; Found: 230.2034.

(Z)-1-(2-cyclopentylvinyl)-4-methoxybenzene (5c). Following the general procedure D, the title compound was prepared using 1-ethynyl-4-methoxybenzene (132 mg) and bromocyclopentane (745 mg). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (5a) as pale-yellow oil (132 mg, 0.65 mmol, 65%; Z:E = 9.3:1). $^{1}$H NMR (400 MHz, CDCl$_3$): δ 7.22 (d, $J$ = 8.6 Hz, 2 H), 6.87 (d, $J$ = 8.8 Hz, 2 H), 6.29 (d, $J$ = 11.5 Hz, 1 H), 5.49 (dd, $J$ = 11.4 Hz, $J$ = 10.0 Hz, 1 H), 3.80 (s, 3 H), 3.00-2.89 (m, 1 H), 1.90-1.83 (m, 2 H), 1.74-1.66 (m, 2 H), 1.62-1.55 (m, 2 H), 1.42-1.29 (m, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.3, 137.1, 130.7, 129.9, 126.9, 113.7, 55.4, 39.0, 34.3, 25.7.

(Z)-1-(2-cyclopentylvinyl)-4-methylbenzene (5d). Following the general procedure D, the title compound was prepared using 1-ethynyl-4-methylbenzene (116 mg) and bromocyclopentane (745 mg). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (5d) as pale-yellow oil (114 mg, 0.61 mmol, 61%; Z:E = 14:1). $^{1}$H NMR (400 MHz, CDCl$_3$): δ 7.18 (d, $J$ = 8.1 Hz, 2 H), 7.13 (d, $J$ = 8.0 Hz, 2 H), 6.32 (d, $J$ = 11.5 Hz, 1 H), 5.53 (t, $J$ = 11.0 Hz, 1 H), 3.00-2.90 (m, 1 H), 2.34 (s, 3 H), 1.90-1.82 (m, 2 H), 1.74-1.66 (m, 2 H), 1.62-1.54 (m, 2 H), 1.39-1.29 (m, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 137.9, 136.2, 135.2, 128.9, 128.7, 127.3, 39.0, 34.4, 25.7, 21.3. HRMS (APPI): Calcd for C$_{14}$H$_{18}$ [M]: 186.1403; Found: 186.1397.
(Z)-(4-methylstyryl)cycloheptane (5e). Following the general procedure D, the title compound was prepared using 1-ethyl-4-methylbenzene (116 mg) and bromocycloheptane (885 mg). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (5a) as pale-yellow oil (126 mg, 0.59 mmol, 59%; Z:E = 8.4:1). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.19-7.10 (ovrlp, 4 H), 6.21 (d, $J = 11.6$ Hz, 1 H), 5.54 (dd, $J = 11.4$ Hz, $J = 10.7$ Hz, 1 H), 2.78-2.69 (m, 1 H), 2.34 (s, 3 H), 1.81-1.66 (m, 4 H), 1.61-1.35 (ovrlp, 8 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 139.3, 136.1, 135.2, 129.0, 128.7, 125.2, 38.3, 35.4, 28.6, 26.5, 21.3. HRMS (APPI): Calcd for C$_{16}$H$_{22}$ [M]: 214.1716; Found: 214.1710.

(Z)-styrylcyclooctane (5f). Following the general procedure E, the title compound was prepared using ethynylbenzene (102 mg, 1.0 mmol, 1 equiv), bromocyclooctane (354 mg, 2.0 mmol, 2 equiv), Zn (196 mg, 2.5 mmol, 2.5 equiv), and I$_2$ (0.5 M solution in DMA, 5 mol %, 100 μL). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (5f) as pale-yellow oil (104 mg, 0.52 mmol, 52%; Z:E = 12:1). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.31 (t, $J = 7.6$ Hz, 2 H), 7.26 (d, $J = 7.8$ Hz, 2 H), 7.20 (t, $J = 7.2$ Hz, 1 H), 6.25 (d, $J = 11.5$ Hz, 1 H), 5.59 (t, $J = 11.6$ Hz, 1 H), 2.87-2.79 (m, 1 H), 1.73-1.66 (ovrlp, 4 H), 1.59-1.44 (ovrlp, 10 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 140.0, 138.1, 128.8, 128.3, 126.4, 125.4, 36.2, 32.8, 27.4, 26.4, 25.2.

(Z)-1-(3,3-dimethylpent-1-en-1-yl)-4-methylbenzene (5g). Following the general procedure E, the title compound was prepared using 1-ethyl-4-methylbenzene (116 mg, 1.0 mmol, 1 equiv), 2-bromo-2-methylbutane (453 mg, 3 mmol, 3 equiv), Zn (196 mg, 3.0 mmol, 3 equiv), and I$_2$ (0.5 M solution in DMA, 5 mol %, 100 μL). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (5g) as pale-yellow oil (111 mg, 0.59 mmol, 59%; Z:E > 50:1). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.09-7.04 (ovrlp, 4 H), 6.43 (d, $J = 12.7$ Hz, 1 H), 5.46 (d, $J = 12.7$ Hz, 1 H), 2.33 (s, 3 H), 1.31 (q, $J = 7.5$ Hz, 2 H), 0.90 (d, 6 H), 0.82 (t, $J = 7.4$ Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 141.4, 136.6, 135.8, 128.8, 128.3, 128.1, 37.6, 36.8, 28.6, 21.3, 9.3. HRMS (APPI): Calcd for C$_{14}$H$_{20}$ [M]: 188.1560; Found: 188.1557.
(Z)-(3,3-diethylpent-1-en-1-yl)benzene (5h). Following the general procedure E, the title compound was prepared using ethynylbenzene (102 mg, 1.0 mmol, 1 equiv), 3-bromo-3-ethylpentane (537 mg, 3 mmol, 3 equiv), Zn (196 mg, 3.0 mmol, 3 equiv), and I₂ (0.5 M solution in DMA, 5 mol %, 100 µL). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (5h) as pale-yellow oil (84 mg, 0.42 mmol, 42%; Z:E > 20:1). **¹H NMR** (400 MHz, CDCl₃): δ 7.25 (t, J = 7.4 Hz, 2 H), 7.21-7.16 (ovrlp, 3 H), 6.56 (d, J = 13.0 Hz, 1 H), 5.28 (d, J = 13.0 Hz, 1 H), 1.25 (d, J = 7.4 Hz, 6 H), 0.73 (t, J = 7.4 Hz, 9 H). **¹³C NMR** (100 MHz, CDCl₃): δ 140.4, 140.1, 129.3, 128.5, 127.6, 126.2, 44.0, 29.1, 8.3. **HRMS** (APPI): Calcd for C₁₅H₂₂ [M]: 202.1716; Found: 202.1731.

(Z)-(4-methoxystyryl)cycloheptane (5i). Following the general procedure D, the title compound was prepared using 1-ethynyl-4-methoxybenzene (132 mg, 1.0 mmol, 1 equiv), bromocyclopentane (531 mg, 3.0 mmol, 3 equiv), Zn (196 mg, 3.0 mmol, 3 equiv), and I₂ (0.5 M solution in DMA, 5 mol %, 100 µL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (5i) as pale-yellow oil (144 mg, 0.63 mmol, 63%; Z:E = 6.0:1). **¹H NMR** (400 MHz, CDCl₃): δ 7.19 (d, J = 8.7 Hz, 2 H), 6.87 (d, J = 8.7 Hz, 2 H), 6.18 (d, J = 11.6 Hz, 1 H), 5.50 (dd, J = 11.4 Hz, J = 10.5 Hz, 1 H), 3.81 (s, 3 H), 2.77-2.68 (m, 1 H), 1.80-1.66 (ovrlp, 4 H), 1.60-1.36 (ovrlp, 8 H). **¹³C NMR** (100 MHz, CDCl₃): δ 158.2, 138.6, 130.7, 129.9, 124.8, 113.7, 55.4, 38.3, 35.4, 28.6, 26.5. **HRMS** (APPI): Calcd for C₁₆H₂₂O [M]: 230.1665; Found: 230.1663.

(Z)-(4-methylstyryl)cyclooctane (5j). Following the general procedure D, the title compound was prepared using 1-ethynyl-4-methylbenzene (116 mg, 1.0 mmol, 1 equiv) and bromocyclooctane (885 mg, 5.0 mmol, 5 equiv). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (5j) as pale-yellow oil (126 mg, 0.59 mmol, 59%; Z:E = 5.9:1). **¹H NMR** (400 MHz, CDCl₃): δ 7.16 (d, J = 8.2 Hz, 2 H), 7.13 (d, J = 8.2 Hz, 2 H), 6.23 (d, J = 11.6 Hz, 1 H), 5.54 (dd, J = 11.5 Hz, J = 10.6 Hz, 1 H), 2.89-2.79 (m, 1 H), 2.34 (s, 3 H), 1.76-1.66 (ovrlp, 4 H), 1.62-1.42 (ovrlp, 10 H). **¹³C NMR** (100 MHz, CDCl₃): δ 139.5, 136.1, 135.2, 129.0, 128.7, 125.2, 32.8, 27.4, 26.4, 25.2, 21.3. **GCMS** [M] = 228 detected which corresponds to C₁₇H₂₄.
(i) 1 mmol Scale. Following the general procedure F, the title compound was prepared using 1-ethynyl-4-methoxybenzene (132 mg, 1.0 mmol, 1 equiv), 1-iodoheptane (678 mg, 3 mmol, 3 equiv), FeBr₂ (22 mg, 0.10 mmol, 10 mol %), CuBr₂ (22 mg, 0.10 mmol, 10 mol %), Zn (229 mg, 3.5 mmol, 3.5 equiv), TMSI (60 mg, 0.30 mmol, 30 mol %), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (6a) (119 mg, 0.51 mmol, 51%; Z:E = 7.7:1) as pale-yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.22 (d, J = 8.7 Hz, 2 H), 6.87 (d, J = 8.7 Hz, 2 H), 6.33 (d, J = 11.6 Hz, 1 H), 5.57 (dd, J = 11.6 Hz, J = 7.2 Hz, 1 H), 3.81 (s, 3 H), 2.31 (qd, J = 7.2 Hz, J = 1.7 Hz, 2 H), 1.44 (qu, J = 7.1 Hz, 2 H), 1.35-1.21 (ovrlp, 8 H), 0.87 (t, J = 6.9 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 158.2, 131.9, 130.7, 130.1, 128.2, 113.6, 55.4, 32.0, 30.2, 29.5, 29.4, 28.8, 22.8, 14.3. HRMS (APPI): Calcd for C₁₆H₂₄O [M]: 232.1822; Found: 232.1818.

(ii) 8 mmol Scale. Following the general procedure F, the title compound was prepared using 1-ethynyl-4-methoxybenzene (1.06 g, 8.0 mmol, 1 equiv), 1-iodoheptane (3.62 mg, 16 mmol, 2 equiv), FeBr₂ (173 mg, 0.80 mmol, 10 mol %), CuBr₂ (179 mg, 0.80 mmol, 10 mol %), Zn (1.31 g, 20 mmol, 2.5 equiv), TMSI (320 mg, 1.6 mmol, 20 mol %), and DMA (8 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (6a) (860 mg, 3.7 mmol, 46%; Z:E = 7.6:1) as pale-yellow oil. Spectral and analytical data were identical to those reported for the same compound above.

(Z)-1-chloro-4-(non-1-en-1-yl)benzene (6b). Following the general procedure F, the title compound was prepared using 1-chloro-4-ethylbenzene (137 mg, 1.0 mmol, 1 equiv), 1-iodoheptane (452 mg, 2 mmol, 2 equiv), FeBr₂ (22 mg, 0.10 mmol, 10 mol %), CuBr₂ (22 mg, 0.10 mmol, 10 mol %), Zn (164 mg, 2.5 mmol, 2.5 equiv), TMSI (40 mg, 0.20 mmol, 20 mol %), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (6b) (138 mg, 0.58 mmol, 58%; Z:E = 8.1:1) as pale-yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.28 (d, J = 8.5 Hz, 2 H), 7.19 (d, J = 8.4 Hz, 2 H), 6.34 (d, J = 11.7 Hz, 1 H), 5.68 (dt, J = 11.6 Hz, J = 7.3 Hz, 1 H), 2.28 (qd, J = 7.4 Hz, J = 1.7 Hz, 2 H), 1.43 (qu, J = 7.5 Hz, 2 H), 1.34-1.20 (ovrlp, 8 H), 0.87 (t, J = 7.0 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 136.4, 134.1, 132.1, 130.1, 128.4, 127.6, 32.0, 30.0, 29.4, 29.3, 28.7, 22.8, 14.3. HRMS (APPI): Calcd for C₁₅H₂₁Cl [M]: 236.1326; Found: 236.1325.

(Z)-dec-1-en-1-ylbenzene (6c).

(i) 1 mmol Scale: Following the general procedure F, the title compound was prepared using ethynylbenzene (102 mg, 1.0 mmol, 1 equiv), 1-iodoheptane (720 mg, 3 mmol, 3 equiv), FeBr₂ (22 mg, 0.10 mmol, 10 mol %), CuBr₂ (22 mg, 0.10 mmol, 10 mol %), Zn (229 mg, 3.5 mmol, 3.5 equiv), TMSI (60 mg, 0.30 mmol, 30 mol %), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (6c) (119 mg, 0.55 mmol,
55%; Z:E = 8.7:1) as pale-yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.32 (t, $J = 7.6$ Hz, 2 H), 7.27 (d, $J = 6.8$ Hz, 2 H), 7.21 (t, $J = 7.1$ Hz, 1 H), 6.40 (d, $J = 11.6$ Hz, 1 H), 5.66 (dt, $J = 11.6$ Hz, $J = 7.3$ Hz, 1 H), 2.32 (qd, $J = 7.4$ Hz, $J = 1.6$ Hz, 2 H), 1.44 (qu, $J = 7.5$ Hz, 2 H), 1.33-1.22 (ovrlp, 10 H) 0.87 (t, $J = 6.7$ Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.0, 133.4, 128.9, 128.8, 128.2, 126.5, 32.1, 30.1, 29.8, 29.7, 29.52, 29.50, 28.8, 22.8, 14.3. HRMS (APPI): Calcd for C$_{16}$H$_{24}$ [M]: 216.1873; Found: 216.1868.

(ii) 15 mmol Scale: Following the general procedure F, the title compound was prepared using ethynylbenzene (1.53 g, 15 mmol, 1 equiv), 1-iodooctane (7.20 g, 30 mmol, 2 equiv), FeBr$_2$ (324 mg, 1.5 mmol, 10 mol %), CuBr$_2$ (336 mg, 1.5 mmol, 10 mol %), Zn (2.45 g, 37.5 mmol, 2.5 equiv), TMSI (600 mg, 3.0 mmol, 20 mol %), and DMA (15 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (6c) (2.01 g, 9.31.0 mmol, 62%; Z:E = 8.3:1) as pale-yellow oil.

(Z)-oct-1-en-7-yn-1-ylbenzene (6d). Following the general procedure F, the title compound was prepared using ethynylbenzene (56 mg, 0.50 mmol, 1 equiv), 6-iodohex-1-yne (312 mg, 1.5 mmol, 3 equiv), FeBr$_2$ (11 mg, 0.05 mmol, 10 mol %), CuBr$_2$ (11 mg, 0.05 mmol, 10 mol %), Zn (115 mg, 1.75 mmol, 3.5 equiv), TMSI (30 mg, 0.15 mmol, 20 mol %), and DMA (0.5 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (6d) (49 mg, 0.27 mmol, 53%; Z:E = 5.3:1) as pale-yellow oil.

(Z)-1-methyl-4-(4-methylpent-1-en-1-yl)benzene (6e). Following the general procedure F, the title compound was prepared using 1-ethyl-4-methylbenzene (116 mg, 1.0 mmol, 1 equiv), 1-iodo-2-methylpropane (552 mg, 3.0 mmol, 3 equiv), FeBr$_2$ (22 mg, 0.10 mmol, 10 mol %), CuBr$_2$ (22 mg, 0.10 mmol, 10 mol %), Zn (229 mg, 3.5 mmol, 3.5 equiv), TMSI (60 mg, 0.30 mmol, 30 mol %), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (6e) (82 mg, 0.47 mmol, 47%; Z:E = 13:1) as volatile, pale-yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.18 (d, $J = 8.1$ Hz, 2 H), 7.13 (d, $J = 8.1$ Hz, 2 H), 6.40 (d, $J = 11.7$ Hz, 1 H), 5.64 (dt, $J = 11.7$ Hz, $J = 7.2$ Hz, 1 H), 2.34 (s, 3 H), 2.22 (td, $J = 7.1$ Hz, $J = 1.9$ Hz, 2 H), 1.76-1.65 (m, 1 H), 0.92 (d, $J = 6.6$ Hz, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 136.2, 135.1, 131.5, 129.2, 128.91, 128.86, 37.8, 29.2, 22.6, 21.3. HRMS (APPI): Calcd for C$_{13}$H$_{16}$ [M]: 184.1247; Found: 184.1261.
(Z)-1-(tert-butyl)-4-(4,4-dimethylpent-1-en-1-yl)benzene (6f). Following the general procedure F, the title compound was prepared using 1-(tert-butyl)-4-ethynylbenzene (79 mg, 0.50 mmol, 1 equiv), 1-iodo-2,2-dimethylpropane (297 mg, 1.5 mmol, 3 equiv), FeBr$_2$ (11 mg, 0.05 mmol, 10 mol %), CuBr$_2$ (11 mg, 0.05 mmol, 10 mol %), Zn (115 mg, 1.75 mmol, 3.5 equiv), TMSI (20 mg, 0.10 mmol, 20 mol %), and DMA (0.5 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (6f) (61 mg, 0.27 mmol, 53%; Z: E = 9.7:1) as pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.28 (d, $J = 8.0$ Hz, 2 H), 7.17 (d, $J = 8.4$ Hz, 2 H), 6.38 (d, $J = 11.8$ Hz, 1 H), 5.64 (d, $J = 11.8$ Hz, $J = 6.8$ Hz, 1 H), 2.20 (d, $J = 6.8$ Hz, 2 H), 1.25 (s, 9 H), 0.86 (s, 9 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 149.4, 135.2, 129.7, 129.2, 128.7, 125.1, 42.3, 34.6, 31.5, 31.2, 29.5. HRMS (APPI): Calcd for C$_{17}$H$_{26}$[M]: 230.2029; Found: 230.2050.

(Z)-1-(tert-butyl)-4-(5-(4-methoxyphenoxy)pent-1-en-1-yl)benzene (6g). Following the general procedure F, the title compound was prepared using 1-(tert-butyl)-4-ethynylbenzene (158 mg, 1.0 mmol, 1 equiv), 1-(3-iodopropoxy)-4-methoxybenzene (584 mg, 2.0 mmol, 2 equiv), FeBr$_2$ (22 mg, 0.10 mmol, 10 mol %), CuBr$_2$ (22 mg, 0.10 mmol, 10 mol %), Zn (164 mg, 2.5 mmol, 2.5 equiv), TMSI (40 mg, 0.20 mmol, 20 mol %), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (6g) (129 mg, 0.40 mmol, 40%; Z: E = 4.6:1) as pale-yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.34 (d, $J = 8.4$ Hz, 2 H), 7.23 (d, $J = 8.5$ Hz, 2 H), 6.83-6.81 (ovrlp, 4 H), 6.42 (d, $J = 11.6$ Hz, 1 H), 5.65 (dt, $J = 11.6$ Hz, $J = 7.3$ Hz, 1 H), 3.93 (t, $J = 6.4$ Hz, 2 H), 3.76 (s, 3 H), 2.53 (qd, $J = 7.4$ Hz, $J = 1.7$ Hz, 2 H), 1.92 (qu, $J = 7.7$ Hz, 2 H), 1.32 (s, 9 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 153.8, 153.3, 149.6, 134.8, 131.3, 129.5, 128.6, 125.2, 115.6, 114.7, 68.1, 55.9, 34.6, 31.5, 29.8, 25.4. HRMS (APPI): Calcd for C$_{22}$H$_{28}$O$_2$ [M]: 324.2091; Found: 324.2089.

(Z)-1-(tert-butyl)-4-(8-chlorooct-1-en-1-yl)benzene (6h). Following the general procedure F, the title compound was prepared using 1-(tert-butyl)-4-ethynylbenzene (158 mg, 1.0 mmol, 1 equiv), 1-chloro-6-iodohexane (493 mg, 2 mmol, 2 equiv), FeBr$_2$ (22 mg, 0.10 mmol, 10 mol %), CuBr$_2$ (22 mg, 0.10 mmol, 10 mol %), Zn (164 mg, 2.5 mmol, 2.5 equiv), TMSI (40 mg, 0.20 mmol, 20 mol %), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (6h) (175 mg, 0.63 mmol, 63%; Z: E = 7.1:1) as pale-yellow oil. $^1$H NMR (400
MHz, CDCl$_3$): δ 7.28 (d, $J = 8.4$ Hz, 2 H), 7.15 (d, $J = 8.3$ Hz, 2 H), 6.30 (d, $J = 11.6$ Hz, 1 H), 5.53 (dt, $J = 11.6$ Hz, $J = 7.2$ Hz, 1 H), 3.44 (t, $J = 6.8$ Hz, 2 H), 2.28 (qd, $J = 7.2$ Hz, $J = 1.8$ Hz, 2 H), 1.69 (qu, $J = 6.8$ Hz, 2 H), 1.43-1.36 (ovrlp, 4 H), 1.34-1.22 (ovrlp, 11 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 149.5, 135.0, 132.4, 128.8, 128.6, 125.2, 45.2, 34.6, 32.7, 31.5, 30.0, 28.7, 26.9. HRMS (APPI): Calcd for C$_{18}$H$_{27}$Cl [M]: 278.1796; Found: 278.1821.

(Z)-7-(4-chlorophenyl)hept-6-en-1-yl acetate (6i). Following the general procedure F, the title compound was prepared using 1-chloro-4-ethynylbenzene (137 mg, 1.0 mmol, 1 equiv), 5-iodopentyl acetate (512 mg, 2 mmol, 2 equiv), FeBr$_2$ (22 mg, 0.10 mmol, 10 mol %), CuBr$_2$ (22 mg, 0.10 mmol, 10 mol %), Zn (164 mg, 2.5 mmol, 2.5 equiv), TMSI (40 mg, 0.20 mmol, 20 mol %), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (6i) (148 mg, 0.55 mmol, 55%; Z:E = 9.6:1) as pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.29 (d, $J = 8.4$ Hz, 2 H), 7.18 (d, $J = 8.4$ Hz, 2 H), 6.36 (d, $J = 11.4$ Hz, 1 H), 5.66 (dt, $J = 11.4$ Hz, $J = 7.3$ Hz, 1 H), 4.04 (t, $J = 6.7$ Hz, 2 H), 2.30 (qd, $J = 7.3$ Hz, $J = 1.7$ Hz, 2 H), 2.04 (s, 3 H), 1.61 (qu, $J = 7.1$ Hz, 2 H), 1.47 (qu, $J = 7.2$ Hz, 2 H), 1.37 (qu, $J = 7.2$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 171.3, 136.2, 133.5, 132.3, 130.1, 128.4, 128.0, 64.6, 29.6, 28.6, 28.5, 25.7, 21.1. HRMS (ESI): Calcd for C$_{15}$H$_{19}$ClO$_2$Na [M+Na]: 289.0971; Found: 289.0971.

(Z)-8-(4-chlorophenyl)oct-7-enenitrile (6j). Following the general procedure F, the title compound was prepared using 1-chloro-4-ethynylbenzene (68 mg, 0.50 mmol, 1 equiv), 6-iodohexanenitrile (223 mg, 1.0 mmol, 2 equiv), FeBr$_2$ (11 mg, 0.05 mmol, 10 mol %), CuBr$_2$ (11 mg, 0.05 mmol, 10 mol %), Zn (82 mg, 1.25 mmol, 2.5 equiv), TMSI (20 mg, 0.10 mmol, 20 mol %), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (15:1) as an eluent to afford the title compound (6j) (55 mg, 0.47 mmol, 47%; Z:E = 12:1) as pale-yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.22 (d, $J = 8.7$ Hz, 2 H), 7.10 (d, $J = 8.4$ Hz, 2 H), 6.30 (d, $J = 11.6$ Hz, 1 H), 5.57 (dt, $J = 11.6$ Hz, $J = 7.2$ Hz, 1 H), 2.27-2.21 (ovrlp, 4 H), 1.56 (qu, $J = 7.1$ Hz, 2 H), 1.44-1.38 (ovrlp, 4 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 136.0, 133.0, 132.3, 130.1, 128.4, 128.3, 119.8, 29.0, 28.3, 28.2, 25.3, 17.2. HRMS (APPI): Calcd for C$_{14}$H$_{16}$ClN [M]: 233.0966; Found: 233.0970.
(Z)-9-(4-Methoxyphenyl)non-8-enenitrile (6k). Following the general procedure F, the title compound was prepared using 1-ethynyl-4-methoxybenzene (132 mg, 1.0 mmol, 1 equiv), 7-iodohexanenitrile (711 mg, 3.0 mmol, 3 equiv), FeBr₂ (22 mg, 0.10 mmol, 10 mol %), CuBr₂ (22 mg, 0.10 mmol, 10 mol %), Zn (229 mg, 3.5 mmol, 3.5 equiv), TMSI (60 mg, 0.30 mmol, 30 mol %), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (15:1) as an eluent to afford the title compound (6k) (124 mg, 0.51 mmol, 51%; Z:E = 6.7:1) as pale yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.21 (d, J = 8.6 Hz, 2 H), 6.87 (d, J = 8.8 Hz, 2 H), 6.35 (d, J = 11.5 Hz, 1 H), 5.54 (dt, J = 11.6 Hz, J = 7.2 Hz, 1 H), 3.81 (s, 3 H), v2.36-2.16 (ovrlp, 4 H), 1.64 (qu, J = 6.8 Hz, 2 H), 1.51-1.33 (ovrlp, 6 H). ¹³C NMR (100 MHz, CDCl₃): δ 158.3, 131.2, 130.6, 130.0, 128.6, 119.9, 113.6, 55.3, 29.7, 28.7, 28.51, 28.48, 25.4, 17.2. HRMS (APPI): Calcd for C₁₆H₂₁NO [M]: 243.1618; Found: 243.1612.

(Z)-2-((8-(4-methoxyphenyl)oct-7-en-1-yl)oxy)tetrahydro-2H-pyran (6l). Following the general procedure F, the title compound was prepared using 1-ethynyl-4-methoxybenzene (66 mg, 0.50 mmol, 1 equiv), 2-((6-iodohexyl)oxy)tetrahydro-2H-pyran (382 mg, 1.0 mmol, 2 equiv), FeBr₂ (11 mg, 0.05 mmol, 10 mol %), CuBr₂ (11 mg, 0.05 mmol, 10 mol %), Zn (82 mg, 1.75 mmol, 2.5 equiv), TMSI (20 mg, 0.10 mmol, 20 mol %), and DMA (0.5 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (20:1) as an eluent to afford the title compound (6l) (80 mg, 0.50 mmol, 50%; Z:E = 4.2:1) as pale-yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.14 (d, J = 8.7 Hz, 2 H), 6.79 (d, J = 8.8 Hz, 2 H), 6.26 (d, J = 11.6 Hz, 1 H), 5.49 (dt, J = 11.6 Hz, J = 7.2 Hz, 2 H), 4.51-4.49 (m, 1 H), 3.82-3.76 (m, 1 H), 3.74 (s, 3 H), 3.69-3.62 (m, 1 H), 3.46-3.40 (m, 1 H), 3.34-3.27 (m, 1 H), 2.24 (qd, J = 7.2 Hz, J = 1.7 Hz, 2 H), 1.79-1.71 (m, 1 H), 1.67-1.61 (m, 1 H), 1.55-1.43 (ovrlp, 6 H), 1.39-1.27 (ovrlp, 6 H). ¹³C NMR (100 MHz, CDCl₃): δ 158.2, 131.7, 130.6, 130.0, 128.3, 113.6, 99.0, 67.4, 62.5, 55.4, 30.9, 30.1, 29.8, 29.3, 28.7, 26.3, 25.6, 19.8. HRMS (APPI): Calcd for C₂₀H₃₁O₃ [M+H]: 319.2224; Found: 319.2254.

(Z)-9-(5-(4-methoxyphenyl)pent-4-en-1-yl)-9H-carbazole (6m). Following the general procedure F, the title compound was prepared using 1-ethynyl-4-methoxybenzene (66 mg, 0.50 mmol, 1 equiv), 9-(3-iodopropyl)-9H-carbazole (503 mg, 1.5 mmol, 3 equiv), FeBr₂ (11 mg, 0.10 mmol, 10 mol %),
CuBr₂ (11 mg, 0.10 mmol, 10 mol %), Zn (115 mg, 1.75 mmol, 3.5 equiv), TMSI (20 mg, 0.10 mmol, 20 mol %), and DMA (0.5 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (1:30) as an eluent to afford the title compound (6m) (68 mg, 0.20 mmol, 40%; Z:E = 4.1:1) as pale-yellow oil. A pure Z-olefin (6m) could be obtained by purification using thin-layer chromatography using hexane/EtOAc (100:1) as an eluent.

**1H NMR** (400 MHz, CDCl₃): δ 8.09 (d, J = 7.8 Hz, 2 H), 7.43 (t, J = 8.1 Hz, 2 H), 7.37 (d, J = 8.0 Hz, 2 H), 7.21 (t, J = 7.0 Hz, 2 H), 7.09 (d, J = 8.6 Hz, 2 H), 6.76 (d, J = 8.7 Hz, 2 H), 6.39 (d, J = 11.6 Hz, 1 H), 5.57 (dt, J = 11.6 Hz, J = 7.2 Hz, 1 H), 4.32 (t, J = 7.2 Hz, 2 H), 3.79 (s, 3 H), 2.40 (qd, J = 7.5 Hz, J = 1.3 Hz, 2 H), 2.03 (qu, J = 7.4 Hz, 2 H).

**13C NMR** (100 MHz, CDCl₃): δ 158.4, 140.5, 130.0, 129.7, 129.6, 125.7, 123.0, 120.5, 118.9, 113.7, 108.7, 55.4, 42.6, 29.2, 26.5.

**HRMS** (ESI): Calcd for C₂₄H₂₄NO [M+H]: 342.1860; Found: 342.1858.

**(Z)-1-(dodeca-1,11-dien-1-yl)-4-methoxybenzene (6n).** Following the general procedure F, the title compound was prepared using 1-ethynyl-4-methoxybenzene (66 mg, 0.50 mmol, 1 equiv), 10-iododec-1-ene (399 mg, 1.5 mmol, 3 equiv), FeBr₂ (11 mg, 0.05 mmol, 10 mol %), CuBr₂ (22 mg, 0.05 mmol, 10 mol %), Zn (115 mg, 1.75 mmol, 3.5 equiv), TMSI (30 mg, 0.15 mmol, 30 mol %), and DMA (0.5 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (6n) (81 mg, 0.30 mmol, 59%; Z:E = 8.2:1) as pale-yellow oil.

**1H NMR** (400 MHz, CDCl₃): δ 7.14 (d, J = 8.4 Hz, 2 H), 6.79 (d, J = 8.4 Hz, 2 H), 6.26 (d, J = 11.6 Hz, 1 H), 5.78-5.68 (m, 1 H), 5.49 (dt, J = 11.4 Hz, J = 7.0 Hz, 1 H), 4.91 (d, J = 17.2 Hz, 1 H), 4.85 (d, J = 10.0 Hz, 1 H), 3.73 (s, 3 H), 2.23 (q, J = 7.1 Hz, 2 H), 1.96 (d, J = 6.2 Hz, 2 H), 1.36-1.14 (ovrlp, 12 H).

**13C NMR** (100 MHz, CDCl₃): δ 158.2, 139.4, 131.8, 130.6, 130.0, 128.2, 114.2, 113.6, 55.4, 34.0, 30.2, 29.60, 29.59, 29.5, 29.3, 29.1, 28.8. **HRMS** (APPI): Calcd for C₁₉H₂₈O [M]: 272.2135; Found: 272.2132.

**(2)-Isopropyl-4-methylcyclohexyl (Z)-8-(4-methoxyphenyl)oct-7-enoate (6o).** Following the general procedure F, the title compound was prepared using 1-ethynyl-4-methoxybenzene (66 mg, 0.50 mmol, 1 equiv), menthyl 6-iodohexanoate (R₃) (380 mg, 1.0 mmol, 2 equiv), FeBr₂ (11 mg, 0.050 mmol, 10 mol %), CuBr₂ (11 mg, 0.050 mmol, 10 mol %), Zn (82 mg, 1.25 mmol, 2.5 equiv), TMSI (20 mg, 0.10 mmol, 20 mol %), and DMA (0.5 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (6o) (97 mg, 0.25 mmol, 50%; Z:E = 4.0:1) as pale-yellow oil.

**1H NMR** (400 MHz, CDCl₃): δ 7.21 (d, J = 8.6 Hz, 2 H), 6.87 (d, J = 8.8 Hz, 2 H), 6.34 (d, J = 11.6 Hz, 1 H), 5.55 (dt, J = 11.6 Hz, J = 7.2 Hz, 1 H), 4.67 (td, J = 10.8 Hz, J = 4.4 Hz, J = 9.3 Hz, 2 H).
(Z)-5-(Dec-1-en-1-yl)-1,2,3-trimethoxybenzene (6p). Following the general procedure F, the title compound was prepared using 5-ethynyl-1,2,3-trimethoxybenzene (96 mg, 0.50 mmol, 1 equiv), 1-iodooctane (600 mg, 2.5 mmol, 5 equiv), FeBr₂ (11 mg, 0.050 mmol, 10 mol %), CuBr₂ (11 mg, 0.050 mmol, 10 mol %), Zn (180 mg, 2.75 mmol, 5.5 equiv), TMSI (50 mg, 0.25 mmol, 50 mol %), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (6p) (78 mg, 0.26 mmol, 51%; Z: E = 6.8:1) as pale yellow oil.

\[ ^1H \text{NMR} (400 MHz, CDCl}_3\]: δ 6.50 (s, 2 H), 6.33 (d, \( J = 11.6 \text{ Hz}, 1 \text{ H} \)), 5.63 (dt, \( J = 11.6 \text{ Hz}, J = 7.3 \text{ Hz}, 1 \text{ H} \)), 3.87-3.83 (ovrlp, 9 H), 2.34 (qd, \( J = 7.4 \text{ Hz}, J = 1.6 \text{ Hz}, 2 \text{ H} \)), 1.46 (qu, \( J = 7.3 \text{ Hz}, 2 \text{ H} \)), 1.35-1.22 (ovrlp, 10 H), 0.87 (t, \( J = 7.0 \text{ Hz}, 3 \text{ H} \)).

\[ ^13C \text{NMR} (100 MHz, CDCl}_3\): δ 153.0, 135.6, 133.1, 128.8, 106.0, 61.0, 56.1, 32.0, 30.1, 29.7, 29.6, 29.4, 28.9, 22.8, 14.2. HRMS (APPI): Calcd for C₁₉H₃₁O₄ [M]: 307.2277; Found: 307.2273.

(Z)-1-(dec-1-en-1-yl)-4-methoxybenzene (6q). Following the general procedure G, the title compound was prepared using 1-ethynyl-4-methoxybenzene (66 mg, 0.50 mmol, 1 equiv), octyl 4-methylbenzenesulfonate (427 mg, 1.5 mmol, 3 equiv), FeBr₂ (11 mg, 0.050 mmol, 10 mol %), CuBr₂ (11 mg, 0.050 mmol, 10 mol %), TBAI (185 mg, 0.5 mmol, 1 equiv), Zn (115 mg, 1.75 mmol, 3.5 equiv), TMSI (60 mg, 0.30 mmol, 30 mol %), and DMA (0.5 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (6q) (64 mg, 0.26 mmol, 52%; Z: E = 6.1:1) as pale-yellow oil.

\[ ^1H \text{NMR} (400 MHz, CDCl}_3\]: δ 7.22 (d, \( J = 8.7 \text{ Hz}, 2 \text{ H} \)), 6.87 (d, \( J = 8.7 \text{ Hz}, 2 \text{ H} \)), 6.33 (d, \( J = 11.6 \text{ Hz}, 1 \text{ H} \)), 5.57 (dt, \( J = 11.6 \text{ Hz}, J = 7.2 \text{ Hz}, 1 \text{ H} \)), 3.81 (s, 3 H), 2.31 (qd, \( J = 7.5 \text{ Hz}, J = 1.7 \text{ Hz}, 2 \text{ H} \)), 1.44 (qu, \( J = 7.3 \text{ Hz}, 2 \text{ H} \)), 1.34-1.22 (ovrlp, 10 H), 0.88 (t, \( J = 7.0 \text{ Hz}, 3 \text{ H} \)).

\[ ^13C \text{NMR} (100 MHz, CDCl}_3\): δ 158.2, 131.9, 130.7, 130.0, 128.2, 113.7, 55.4, 32.0, 30.2, 29.6, 29.5, 29.4, 28.8, 22.8, 14.3. HRMS (APPI): Calcd for C₁₅H₂₆O [M]: 246.1978; Found: 246.1972.
(Z)-1-Methoxy-4-(5-methylhex-1-en-1-yl)benzene (6r). Following the general procedure G, the title compound was prepared using 1-ethynyl-4-methoxybenzene (66 mg, 0.50 mmol, 1 equiv), isopentyl 4-methylbenzenesulfonate (606 mg, 2.5 mmol, 5 equiv), FeBr$_2$ (11 mg, 0.050 mmol, 10 mol %), CuBr$_2$ (11 mg, 0.050 mmol, 10 mol %), TBAI (369 mg, 1.0 mmol, 2 equiv), Zn (180 mg, 2.75 mmol, 5.5 equiv), TMSI (50 mg, 0.25 mmol, 50 mol %), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (6r) (57 mg, 0.28 mmol, 56%; Z:E = 8.7:1) as pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.26 (d, $J = 8.6$ Hz, 2 H), 6.90 (d, $J = 8.7$ Hz, 2 H), 6.36 (d, $J = 11.6$ Hz, 1 H), 5.59 (dt, $J = 11.6$ Hz, $J = 7.2$ Hz, 1 H), 3.84 (s, 3 H), 2.35 (qd, $J = 7.4$ Hz, $J = 1.8$ Hz, 2 H), 1.68-1.56 (m, 1 H), 1.37 (q, $J = 8.6$ Hz, 2 H), 0.91 (d, $J = 6.6$ Hz, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.2, 131.9, 130.6, 130.0, 128.1, 113.7, 55.4, 39.3, 27.9, 26.7, 22.7. HRMS (ESI): Calcd for C$_{14}$H$_{21}$O [M+H]: 205.1588; Found: 205.1592.

(Z)-1-Methoxy-4-(5-phenylpent-1-en-1-yl)benzene (6s). Following the general procedure G, the title compound was prepared using 1-ethynyl-4-methoxybenzene (66 mg, 0.50 mmol, 1 equiv), 3-phenylpropyl 4-methylbenzenesulfonate (726 mg, 2.5 mmol, 5 equiv), FeBr$_2$ (11 mg, 0.050 mmol, 10 mol %), CuBr$_2$ (11 mg, 0.050 mmol, 10 mol %), TBAI (369 mg, 1.0 mmol, 2 equiv), Zn (180 mg, 2.75 mmol, 5.5 equiv), TMSI (50 mg, 0.25 mmol, 50 mol %), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (6s) (50 mg, 0.20 mmol, 40%; Z:E = 6.1:1) as pale-yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.26 (d, $J = 8.6$ Hz, 2 H), 6.90 (d, $J = 8.7$ Hz, 2 H), 6.36 (d, $J = 11.6$ Hz, 1 H), 5.59 (dt, $J = 11.6$ Hz, $J = 7.2$ Hz, 1 H), 3.84 (s, 3 H), 2.35 (qd, $J = 7.4$ Hz, $J = 1.8$ Hz, 2 H), 1.68-1.56 (m, 1 H), 1.37 (q, $J = 8.6$ Hz, 2 H), 0.91 (d, $J = 6.6$ Hz, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.3, 142.4, 131.1, 130.5, 130.0, 128.7, 128.6, 128.4, 125.8, 113.7, 55.4, 39.3, 27.9, 26.7, 22.7. HRMS (ESI): Calcd for C$_{18}$H$_{21}$O [M+H]: 253.1593; Found: 253.1592.

(Z)-Dodec-1-en-1-ylbenzene (6t). Following the general procedure F, the title compound was prepared using ethynylbenzene (102 mg, 1.0 mmol, 1 equiv), 1-iododecane (805 mg, 3 mmol, 3 equiv), FeBr$_2$ (22 mg, 0.10 mmol, 10 mol %), CuBr$_2$ (22 mg, 0.10 mmol, 10 mol %), Zn (229 mg, 3.5 mmol, 3.5 equiv), TMSI (60 mg, 0.30 mmol, 30 mol %), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (6t) (158 mg, 0.65 mmol, 65%; Z:E = 4.9:1) as pale-yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.33 (t, $J = 7.2$ Hz, 2 H), 7.29 (d, $J = 7.0$ Hz, 2 H), 7.21 (t, $J = 7.1$ Hz, 1 H), 6.40 (d, $J = 11.6$ Hz, 1 H), 5.66 (dt, $J = 11.6$ Hz, $J = 7.3$ Hz, 1 H), 2.32 (qd, $J = 7.5$ Hz, $J = 1.7$ Hz, 2 H), 1.44 (qu, $J = 7.2$ Hz, 2 H), 1.33-1.23 (ovrlp, 14 H) 0.88 (t,
\[ J = 7.0 \text{ Hz}, \text{3 H}. \]

\( ^{13} \text{C NMR} \) (100 MHz, CDCl\(_3\)): \( \delta \) 138.0, 133.4, 128.9, 128.8, 128.2, 126.5, 32.1, 30.1, 29.8, 29.7, 29.52, 29.50, 28.8, 22.8, 14.3. HRMS (APPI): Calcd for C\(_{18}\)H\(_{28}\) [M]: 244.2186; Found: 244.2188.

(Z)-1-Methoxy-4-(octadec-1-en-1-yl)benzene (6u). Following the general procedure F, the title compound was prepared using 1-ethynyl-4-methoxybenzene (132 mg, 1.0 mmol, 1 equiv), 1-iodohexadecane (1.76 g, 5 mmol, 5 equiv), FeBr\(_2\) (22 mg, 0.10 mmol, 10 mol %), CuBr\(_2\) (22 mg, 0.10 mmol, 10 mol %), Zn (360 mg, 5.5 mmol, 5.5 equiv), TMSI (100 mg, 0.50 mmol, 50 mol %), and DMA (2 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (6u) (180 mg, 0.50 mmol, 50%; Z:E = 13:1) as pale-yellow oil.

\( ^{1} \text{H NMR} \) (400 MHz, CDCl\(_3\)): \( \delta \) 7.22 (d, \( J = 8.6 \text{ Hz}, \text{2 H} \)), 6.86 (d, \( J = 8.8 \text{ Hz}, \text{2 H} \)), 6.33 (d, \( J = 11.6 \text{ Hz}, \text{1 H} \)), 5.56 (dd, \( J = 11.6 \text{ Hz}, J = 7.2 \text{ Hz}, \text{1 H} \)), 3.80 (s, 3 H), 2.31 (qd, \( J = 7.2 \text{ Hz}, J = 1.8 \text{ Hz}, \text{2 H} \)), 1.44 (qu, \( J = 7.4 \text{ Hz}, \text{2 H} \)), 1.34-1.22 (ovrlp, 26 H), 0.88 (t, \( J = 7.0 \text{ Hz}, \text{3 H} \)). \( ^{13} \text{C NMR} \) (100 MHz, CDCl\(_3\)): \( \delta \) 158.2, 131.9, 130.7, 130.0, 128.2, 113.6, 55.4, 32.1, 30.2, 29.9, 29.83, 29.79, 29.7, 29.6, 29.5, 28.8, 22.9, 14.3. HRMS (APPI): Calcd for C\(_{25}\)H\(_{42}\)O [M]: 358.3230; Found: 358.3221.

(Z)-7-Phenylept-6-en-1-yl acetate (6v). Following the general procedure F, the title compound was prepared using ethynylbenzene (102 mg, 1.0 mmol, 1 equiv), 5-iodopentyl acetate (512 mg, 2 mmol, 2 equiv), FeBr\(_2\) (22 mg, 0.10 mmol, 10 mol %), CuBr\(_2\) (22 mg, 0.10 mmol, 10 mol %), Zn (164 mg, 2.5 mmol, 2.5 equiv), TMSI (40 mg, 0.20 mmol, 20 mol %), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (6v) (120 mg, 0.52 mmol, 52%; Z:E = 7.3:1) as pale-yellow oil.

\( ^{1} \text{H NMR} \) (400 MHz, CDCl\(_3\)): \( \delta \) 7.33 (t, \( J = 7.5 \text{ Hz}, \text{2 H} \)), 7.26 (d, \( J = 8.1 \text{ Hz}, \text{2 H} \)), 7.21 (t, \( J = 7.2 \text{ Hz}, \text{1 H} \)), 6.42 (d, \( J = 11.6 \text{ Hz}, \text{1 H} \)), 5.64 (dt, \( J = 11.7 \text{ Hz}, J = 7.2 \text{ Hz}, \text{1 H} \)), 4.04 (t, \( J = 6.7 \text{ Hz}, \text{2 H} \)), 2.34 (qt, \( J = 7.2 \text{ Hz}, J = 1.8 \text{ Hz}, \text{2 H} \)), 2.03 (s, 3 H), 1.61 (qu, \( J = 7.5 \text{ Hz}, \text{2 H} \)), 1.48 (qu, \( J = 7.0 \text{ Hz}, \text{2 H} \)), 1.38 (qu, \( J = 6.8 \text{ Hz}, \text{2 H} \)). \( ^{13} \text{C NMR} \) (100 MHz, CDCl\(_3\)): \( \delta \) 171.3, 137.8, 132.8, 129.1, 128.8, 128.2, 126.6, 64.6, 29.7, 28.58, 28.57, 25.7, 21.1.
(Z)-2-((8-Phenyloct-7-en-1-yl)oxy)tetrahydro-2H-pyran (7a). Following the general procedure F, the title compound was prepared using ethynylbenzene (31 mg, 0.30 mmol, 1 equiv), 2-((6-iodohexyl)oxy)tetrahydro-2H-pyran (281 mg, 0.90 mmol, 3 equiv), FeBr$_2$ (6.5 mg, 0.030 mmol, 10 mol %), CuBr$_2$ (6.7 mg, 0.030 mmol, 10 mol %), Zn (69 mg, 1.05 mmol, 3.5 equiv), TMSI (18 mg, 0.09 mmol, 30 mol %), and DMA (0.5 mL) for 18 h. The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (7a) (38 mg, 0.13 mmol, 44%; Z:E = 7.6:1) as pale yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.33 (t, $J = 7.5$ Hz, 2 H), 7.27 (d, $J = 8.2$ Hz, 2 H), 7.21 (t, $J = 7.1$ Hz, 1 H), 6.40 (d, $J = 11.6$ Hz, 1 H), 5.66 (dt, $J = 11.6$ Hz, $J = 7.3$ Hz, 1 H), 4.58 - 4.55 (m, 1 H), 3.89 - 3.84 (m, 1 H), 3.75 - 3.69 (m, 1 H), 3.52 - 3.47 (m, 1 H), 3.40 - 3.34 (m, 1 H), 2.33 (qd, $J = 7.4$ Hz, $J = 1.6$ Hz, 2 H), 1.87 - 1.78 (m, 1 H), 1.74 - 1.68 (m, 1 H), 1.60 - 1.43 (ovrlp, 8 H), 1.39 - 1.32 (ovrlp, 4 H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 137.9, 133.3, 128.9, 128.2, 126.5, 99.0, 67.7, 62.5, 30.9, 30.1, 29.8, 29.3, 28.7, 26.3, 25.6, 19.8.

Ethyl (Z)-4-(2-(Tridec-1-en-1-yl)phenoxy)butanoate (7b). Following the general procedure F, the title compound was prepared using ethyl 4-(2-ethynlyphenoxy)butanoate (S4) (116 mg, 0.50 mmol, 1 equiv), 1-iodoundecane (705 mg, 2.5 mmol, 5 equiv), FeBr$_2$ (11 mg, 0.050 mmol, 10 mol %), CuBr$_2$ (11 mg, 0.050 mmol, 10 mol %), Zn (180 mg, 2.75 mmol, 5.5 equiv), TMSI (50 mg, 0.25 mmol, 50 mol %), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (6c) (82 mg, 0.21 mmol, 42%; Z:E = 7.6:1) as pale yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.25 (dd, $J = 7.3$ Hz, $J = 1.1$ Hz, 1 H), 7.18 (td, $J = 7.8$ Hz, $J = 1.5$ Hz, 1 H), 6.91 (t, $J = 7.6$ Hz, 1 H), 6.84 (d, $J = 8.3$ Hz, 1 H), 6.51 (d, $J = 11.6$ Hz, 1 H), 5.68 (td, $J = 11.6$ Hz, $J = 7.3$ Hz, 1 H), 4.14 (q, $J = 7.1$ Hz, 2 H), 4.00 (t, $J = 6.0$ Hz, 2 H), 2.52 (t, $J = 7.4$ Hz, 2 H), 2.25 (qt, $J = 7.4$ Hz, $J = 1.6$ Hz, 2 H), 2.12 (qu, $J = 6.3$ Hz, 2 H), 1.41 (qu, $J = 7.5$ Hz, 2 H), 1.31-1.20 (ovrlp, 19 H), 0.88 (t, $J = 7.0$ Hz, 3 H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 173.3, 156.3, 132.9, 131.9, 130.1, 127.9, 124.0, 120.2, 110.6, 67.1, 60.5, 32.0, 31.0, 30.1, 29.83, 29.79, 29.77, 29.7, 29.51, 29.49, 28.9, 24.8, 22.8, 14.3, 14.2. HRMS (ESI): Calcd for C$_{25}$H$_{40}$O$_3$Na [M+Na]: 411.2877; Found: 411.2875.

Ethyl (Z)-2-(4-(Tridec-1-en-1-yl)phenoxy)acetate (7c). Following the general procedure F, the title compound was prepared using ethyl 2-(4-ethynlyphenoxy)acetate (102 mg, 0.50 mmol, 1 equiv), 1-iodoundecane (705 mg, 2.5 mmol, 5 equiv), FeBr$_2$ (11 mg, 0.050 mmol, 10 mol %), CuBr$_2$ (11 mg, 0.050 mmol, 10 mol %), Zn (180 mg, 2.75 mmol, 5.5 equiv), TMSI (50 mg, 0.25 mmol, 50 mol %), and DMA (0.5 mL) for 18 h. The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (7c) (38 mg, 0.13 mmol, 44%; Z:E = 7.6:1) as pale yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.33 (t, $J = 7.5$ Hz, 2 H), 7.27 (d, $J = 8.2$ Hz, 2 H), 7.21 (t, $J = 7.1$ Hz, 1 H), 6.40 (d, $J = 11.6$ Hz, 1 H), 5.66 (dt, $J = 11.6$ Hz, $J = 7.3$ Hz, 1 H), 4.58 - 4.55 (m, 1 H), 3.89 - 3.84 (m, 1 H), 3.75 - 3.69 (m, 1 H), 3.52 - 3.47 (m, 1 H), 3.40 - 3.34 (m, 1 H), 2.33 (qd, $J = 7.4$ Hz, $J = 1.6$ Hz, 2 H), 1.87 - 1.78 (m, 1 H), 1.74 - 1.68 (m, 1 H), 1.60 - 1.43 (ovrlp, 8 H), 1.39 - 1.32 (ovrlp, 4 H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 137.9, 133.3, 128.9, 128.2, 126.5, 99.0, 67.7, 62.5, 30.9, 30.1, 29.8, 29.3, 28.7, 26.3, 25.6, 19.8.
and DMA (1 mL). The crude product was purified by flash chromatography using hexanes/EtOAc (30:1) as an eluent to afford the title compound (6c) (78 mg, 0.22 mmol, 43%; Z:E = 8.6:1) as pale-yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.22 (d, \(J = 8.7\) Hz, 2 H), 6.87 (d, \(J = 8.7\) Hz, 2 H), 6.32 (d, \(J = 11.6\) Hz, 1 H), 5.58 (dt, \(J = 11.6\) Hz, 1 H), 4.62 (s, 2 H), 4.28 (q, \(J = 7.2\) Hz, 2 H), 2.30 (qd, \(J = 7.5\) Hz, \(J = 1.2\) Hz, 2 H), 1.43 (qu, \(J = 7.4\) Hz, 2 H), 1.34-1.18 (ovrlp, 19 H), 0.88 (t, \(J = 6.6\) Hz, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 169.1, 156.5, 132.3, 131.7, 130.1, 128.0, 114.4, 65.6, 61.5, 32.1, 30.2, 29.80, 29.79, 29.7, 29.53, 29.50, 28.8, 22.8, 14.32, 14.28. HRMS (ESI): Calcd for C\(_{23}\)H\(_{36}\)O\(_3\) [M+Na]: 383.2560; Found: 383.2562.

Mechanistic Study of Fe-Catalyzed Reductive Cross-Coupling of Alkyl Halides with Terminal Alkynes.

(a) Radical Clock Experiment (Fig. S3; Fig. 6A).

(i) Reaction with 6-iodohept-1-ene: Preparation of (Z)-1-chloro-4-(3-(2-methylcyclopentyl)prop-1-en-1-yl)benzene (8a, first compound) and (Z)-1-chloro-4-(3-methyl2,7-dien-1-yl)benzene (8a’, second compound). Following the general procedure C, the title compounds were prepared using 1-chloro-4-ethynylbenzene (68 mg, 0.50 mmol, 1 equiv), 6-iodohept-1-ene (224 mg, 1.0 mmol, 2 equiv), FeBr\(_2\) (11 mg, 0.05 mmol, 10 mol %), Zn (82 mg, 1.25 mmol, 2.5 equiv), TMSI (20 mg, 0.10 mmol, 20 mol %) (instead of I\(_2\)), DMA (1 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford an inseparable mixture of 8a and 8a’ (\(~45\) mg, \(~0.19\) mmol, total yield \(~38\%\); 8a:8a’ = 6.3:1) as a pale-yellow oil. \(~10\%\) of unidentified compounds were co-isolated. The 8a to 8a’ ratio was determined by taking the ratio of the methyl groups of alkyl substituents of Z-olefin products (See the NMR spectra of 8a/8a’ for details; Z:E of 8a could not be determined by \(^1\)H NMR due to the overlapping of olefinic proton signals from 8a/8a’ with other unknown species). The chemical shifts of the methyl groups are referenced to the structurally similar compounds. \(^{4,29}\)

(ii) Reaction with 6-bromohex-1-ene: Preparation of (Z)-1-(tert-butyl)-4-(3-cyclopentylprop-1-en-1-yl)benzene (8b, first compound) and (Z)-1-(tert-butyl)-4-(octa-1,7-dien-1-yl)benzene (8b’, second compound). Following the general procedure F, the title compounds were prepared using 1-(tert-butyl)-4-ethynylbenzene (79 mg, 0.50 mmol, 1 equiv), 6-bromohex-1-ene (163 mg, 1.0 mmol, 2 equiv), FeBr\(_3\) (11 mg, 0.05 mmol, 10 mol %), CuBr\(_2\) (11 mg, 0.05 mmol, 10 mol %), Zn (82 mg, 1.25 mmol, 2.5 equiv), TMSI (20 mg, 0.10 mmol, 20 mol %), DMA (0.5 mL). The crude product was purified by flash

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chromatography using hexanes as an eluent to afford an inseparable mixture of 8b (48 mg, 0.20 mmol, 40%; Z:E = 7.0:1) and 8b* (2 mg, 0.008 mmol, 2%) as pale-yellow oil. *Analysis of 8b: ^1^H NMR (400 MHz, CDCl$_3$): δ 7.35 (d, $J$ = 8.4 Hz, 2 H), 7.21 (d, $J$ = 8.5 Hz, 2 H), 6.37 d, $J$ = 11.7 Hz, 1 H), 5.66 (dt, $J$ = 11.7 Hz, $J$ = 7.1 Hz, 1 H), 2.37 (td, $J$ = 7.1 Hz, $J$ = 1.8 Hz, 2 H), 1.97-1.86 (m, 1 H), 1.83-1.74 (m, 2 H), 1.64-1.46 (ovrlp, 4 H), 1.32 (s, 9 H), 1.20-1.11 (ovrlp, 2 H). ^13^C NMR (100 MHz, CDCl$_3$): δ 149.4, 135.2, 132.1, 128.7, 125.1, 40.8, 35.0, 34.6, 32.5, 31.5, 25.3. HRMS (ESI): Calcd for C$_{18}$H$_{26}$ [M]: 242.2034; Found: 242.2034.

(iii) Reaction with (Z)-8-iodooct-3-ene: Preparation of (Z)-1-(3-cyclopentylpent-1-en-1-yl)-4-methylbenzene (8c). Following the general procedure F, the title compound was prepared using 1-ethynyl-4-methylbenzene (116 mg, 1.0 mmol, 1 equiv), (Z)-8-iodooct-3-ene (R2) (476 mg, 2.0 mmol, 2 equiv), FeBr$_2$ (22 mg, 0.10 mmol, 10 mol %), CuBr$_2$ (22 mg, 0.10 mmol, 10 mol %), Zn (164 mg, 2.5 mmol, 2.5 equiv), TMSI (40 mg, 0.20 mmol, 20 mol %), and DMA (1 mL). The crude product was purified by flash chromatography using hexanes as an eluent to afford the title compound (8c) (159 mg, 0.70 mmol, 70%; Z:E > 50:1) as pale-yellow oil. ^1^H NMR (400 MHz, CDCl$_3$): δ 7.19 (d, $J$ = 8.0 Hz, 2 H), 7.12 (d, $J$ = 8.0 Hz, 2 H), 6.46 (d, $J$ = 11.8 Hz, 1 H), 5.39 (t, $J$ = 11.5 Hz, 1 H), 2.53-2.45 (m, 1 H), 2.34 (s, 3 H), 1.80-1.66 (m, 2 H), 1.64-1.46 (ovrlp, 5 H), 1.31-1.20 (m, 2 H), 1.17-1.08 (m, 2 H), 0.87 (t, $J$ = 7.4 Hz, 3 H). ^13^C NMR (100 MHz, CDCl$_3$): δ 136.6, 135.9, 135.6, 129.0, 128.9, 128.7, 45.0, 43.9, 30.6, 30.4, 27.2, 25.4, 25.3, 21.3, 11.9. HRMS (APPI): Calcd for C$_{17}$H$_{24}$ [M]: 228.1873; Found: 228.1868.

(b) Reaction with Radical Scavenger (Fig. S4): Formation of 1-(Cyclohexyloxy)-2,2,6,6-tetramethylpiperidine (8d). Following the general procedure C, the title compound was prepared using ethynylbenzene (51 mg, 0.50 mmol, 1 equiv), iodocyclohexane (158 mg, 0.75 mmol, 1.5 equiv), FeBr$_2$ (11 mg, 0.050 mmol, 10 mol %), Zn (49 mg, 0.75 mmol, 1.5 equiv), I$_2$ (0.5 M solution in DMA, 20 μL), DMA (1 mL), and 2,2,6,6-tetramethylpiperidinooxy (TEMPO, 117 mg, 0.75 mmol, 1.5 equiv). After the reaction, 1,3,5-trimethoxybenzene (42 mg, 0.25 mmol) was added into the reaction mixture, and the reaction mixture was washed with water (~20 mL) and EtOAc (~4 mL). A fraction of organic layer was dried in vacuo, and the residue was analyzed by ^1^H NMR spectroscopy. The ^1^H NMR yield of cyclohexyl-TEMPO adduct, 1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine (8d), was estimated to be 14% with respect to iodocyclohexane using 1,3,5-trimethoxybenzene as internal standard.
(c) Reaction with Alkenyl Radical Trap (Fig. S6; Fig. 6B): Formation of Diethyl (E)-(2-Cyclohexyl-1-phenylvinyl)phosphonate (8e). Following the general procedure C, the title compound was prepared using ethynylbenzene (102 mg, 1.0 mmol, 1 equiv), iodocyclohexane (315 mg, 1.5 mmol, 1.5 equiv), and triethyl phosphite (P(OEt)₃; 2.49 g, 15 mmol, 15 equiv) was added, and the reaction mixture was washed with water (~20 mL) and EtOAc (~4 mL). A small fraction of organic layer was subjected to GC analysis. The GC yield of (Z)-(2-cyclohexylvinyl)benzene (3a) was estimated to be 8% using dodecane as internal standard. Then, all organic fraction was concentrated in vacuo and the residue was purified by flash chromatography using hexanes/EtOAc (4:1) as an eluent to afford 8e (27 mg, 0.08 mmol, 8%; E:Z = 13:1) as pale-yellow oil. The stereochemistry of 6p was defined by comparing the chemical shift of β-olefinic H and the P-H coupling constant in the ¹H NMR spectroscopy of structurally similar compound.³¹ Analysis of diethyl (E)-(2-cyclohexyl-1-phenylvinyl)phosphonate (8e): ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.28 (ovrlp, 3 H), 7.19 (d, J = 6.6 Hz, 2 H), 6.66 (dd, J₆₃ = 23.3 Hz, J₆₅ = 10.2 Hz, 1 H), 4.15-3.97 (m, 4 H), 2.17-2.07 (m, 1 H), 1.81-1.57 (ovrlp, 5 H), 1.36-1.09 (ovrlp, 11 H). ³¹P NMR (162 MHz, CDCl₃) δ 19.0. HRMS (APPI): Calcd for C₁₈H₂₈O₃P [M+H]: 323.1776; Found: 323.1732. ¹³C NMR spectroscopy was not taken due to the low concentration of sample.

(d) Study of the Source of α-Olefinic Hydrogen for Z-Olefin Synthesis (Fig. S7).

(i) Reaction in DMA-d₉ followed by Workup with H₂O. Following the general procedure C, the reaction was undergone using ethynylbenzene (26 mg, 0.25 mmol, 1 equiv), iodocyclohexane (79 mg, 0.375 mmol, 1.5 equiv), FeBr₂ (5 mg, 0.025 mmol, 10 mol %), Zn (25 mg, 0.375 mmol, 1.5 equiv), I₂ (0.5 M solution in DMA, 10 μL, 2 mol %), and DMA-d₉ (0.5 mL; 97% deuterium-enriched after incorporating the DMA-H₂ source from I₂ solution). After the reaction, 1,3,5-trimethoxybenzene (14 mg, 0.083 mmol) was added, and the reaction mixture was washed with H₂O (~20 mL) and EtOAc (~5 mL). A fraction of organic layer was dried in vacuo, and the residue was analyzed by ¹H NMR spectroscopy. The ¹H NMR yield of (Z)-(2-cyclohexylvinyl)benzene (3a) was estimated to be 76% (Z:E = 12:1) using 1,3,5-trimethoxybenzene as internal standard. No D-incorporation of α-olefinic H was observed by ¹H NMR spectroscopy. M = 186 was also detected by GC-MS analysis.

(ii) Reaction in DMA-H₂O followed by Workup with D₂O. Following the general procedure C, the reaction was undergone using ethynylbenzene (51 mg, 0.50 mmol, 1 equiv), iodocyclohexane (158 mg, 0.75 mmol, 1.5 equiv), FeBr₂ (11 mg, 0.05 mmol, 10 mol %), Zn (49 mg, 0.75 mmol, 1.5 equiv), I₂ (0.5 M solution in DMA, 20 μL, 2 mol %), and DMA-H₂O (1 mL). After the reaction, D₂O (100 mg, 90 μL, 5.0 mmol, 10 equiv) was added, and the reaction mixture was stirred at room temperature for 30 min. 1,3,5-Trimethoxybenzene (28 mg, 0.17 mmol) was then added, and the reaction mixture was washed with H₂O (~20 mL) and EtOAc (~5 mL). A fraction of organic layer was dried in vacuo, and the residue was analyzed by ¹H NMR spectroscopy. The ¹H NMR yield of (Z)-(2-cyclohexylvinyl)benzene (3a) (Z:E = 12:1) was estimated to be 63% using 1,3,5-trimethoxybenzene as internal standard. The D-incorporation
of α-olefinic H was estimated to be ~41% by 1H NMR spectroscopy (by comparing the ratio of integrations of α- and β-olefinic H of 3a). M = 187 was also detected by GC-MS analysis.

(e) Reaction with Electrophilic Iodinating Reagents (Fig. S8; Fig. 6C): Preparation of (E)-(2-cyclohexyl-1-iodovinyl)benzene (8f).

(i) Reaction with Iodine Monobromide. Following the general procedure C, the title compound was prepared using ethynylbenzene (2.04 g, 20 mmol), iodocyclohexane (6.30 g, 30 mmol, 3.89 mL), FeBr₂ (432 mg, 2.0 mmol), Zn (1.96 g, 30 mmol), I₂ (0.4 mmol, 800 μL solution in DMA (0.5 M)), and DMA (40 mL) for 4 d. The reaction was performed in a Teflon-screw capped 500 mL Schlenk round-bottom flask. After the reaction, IBr (12.4 g, 2.81 mL, 60 mmol, 3 equiv) was added instead of H₂O, and the reaction mixture was stirred at room temperature for 1.5 d. After workup, the crude product was purified by flash chromatography using hexanes as an eluent to afford an inseparable mixture of (E)-(2-cyclohexyl-1-iodovinyl)benzene (8f) (3.31 g, 10.6 mmol, 53%; E:Z = 18:1) and (Z)-(2-cyclohexylvinyl)benzene (3a) (0.82 g, 4.4 mmol, 22%). The stereochemistry of 8f was defined by comparing with the chemical shift of β-olefinic H in the 1H NMR spectroscopy of structurally similar compound. The pure 8f could be obtained by heating the product mixture in vacuo overnight to remove the more volatile 3a. Analysis of (E)-(2-cyclohexyl-1-iodovinyl)benzene (8f): 1H NMR (400 MHz, CDCl₃): δ 7.35-7.22 (ovrlp, 5 H), 6.31 (d, J = 10.3 Hz, 1 H), 2.07-1.98 (m, 1 H), 1.81-1.52 (ovrlp, 5 H), 1.22-1.04 (ovrlp, 5 H). 13C NMR (100 MHz, CDCl₃): δ 149.2, 142.3, 128.6, 128.3, 128.0, 93.7, 41.3, 32.8, 25.8, 25.5. GCMS: [M] = 312 detected which corresponds to C₁₄H₁₇I.

(ii) Reaction with Iodine Monochloride. Following the general procedure C, the title compound was prepared using ethynylbenzene (102 mg, 1.0 mmol, 1 equiv) and iodocyclohexane (315 mg, 194 μL, 1.5 mmol, 1.5 equiv). After the reaction, ICl (325 mg, 2.0 mmol, 2 equiv) was added instead of H₂O, and the reaction mixture was stirred at room temperature for 18 h. 1,3,5-Trimethoxybenzene (56 mg, 0.33 mmol) was then added, and the reaction mixture was washed with H₂O (~20 mL) and EtOAc (~5 mL). A fraction of organic layer was dried in vacuo, and the residue was analyzed by 1H NMR spectroscopy. The 1H NMR yields of (E)-(2-cyclohexyl-1-iodovinyl)benzene (8f) and (Z)-(2-cyclohexylvinyl)benzene (3a) were estimated to be 41% (E:Z > 20:1) and 11%, respectively, using 1,3,5-trimethoxybenzene as internal standard.

(f) NMR study of the Reaction Profile of Fe-Catalyzed Z-Olefin Synthesis (Fig. S9).

(i) Observation of in-situ Alkenylzinc Intermediate (Fig. S9a). In a nitrogen-filled glove-box, an oven-dried Teflon-screw capped J. Young NMR type was charged with zinc powder (4.9 mg, 0.075 mmol, 1.5 equiv) and DMA-d9 solvent (0.6 mL). Iodine (dissolved in DMA, 0.5 M, 10 mol %, 10 μL) was then added into the reaction mixture, and the mixture was agitated at room temperature until the brown color decolorized (~3 min). FeBr₂ (0.2 mg, 2 mol %) was added into the reaction mixture, followed by the additions of ethynylbenzene (5.1 mg, 5.5 μL, 0.050 mmol, 1.0 equiv) and finally iodocyclohexane (10
µL, 0.075 mmol, 1.5 equiv). The reaction mixture was mixed homogeneously with the aid of ultrasound at 40-50 °C for 3 h and was then left for reaction at room temperature. The course of reaction was monitored by ¹H NMR spectroscopy. After 5 days, all reactants were consumed to give a small amount of 3a along with a proposed alkenyl-zinc species. Upon the addition of H₂O (9 µL, 0.50 mmol, 10 equiv), the alkenyl-zinc species was consumed and 3a was formed in ~66% NMR yield using the residual DMA proton as internal standard.

(ii) Reaction under dry conditions (Fig. S9b). DMA-d₉ solvent, I₂ solution (0.5 M solution in DMA), ethynylbenzene, and iodocyclohexane were dried with activated, powdered 3Å molecular sieves and stored in a nitrogen-filled glovebox prior to use. In the glovebox, an oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with FeBr₂ (2.6 mg, 0.012 mmol, 4 mol %) and Zn (29 mg, 0.45 mmol, 1.5 equiv). The tube and the solids inside were then dried under vacuo with the aid of a hot gun. The tube was then cooled to room temperature, and was immediately transferred to the glovebox. DMA-d₉ (0.5 mL) and I₂ (0.5 M solution in DMA, 12 µL, 2 mol %) were transferred into the tube, and the reaction mixture was stirred until the brown solution was decolorized. Ethynylbenzene (31 mg, 0.30 mmol, 1 equiv) and iodocyclohexane (95 mg, 0.45 mmol, 1.5 equiv) were finally transferred into the tube, and the resulting reaction mixture was stirred at room temperature for 16 h. After the reaction, the reaction mixture was transferred into a J. Young NMR tube in the glovebox, and the reaction mixture was monitored by ¹H NMR spectroscopy. An alkenylzinc intermediate and Z-olefin were observed in around 2:1 ratio (Fig. S9b).

(iii) Reaction with Phenylacetylene-d₁ (Fig. S9c). Phenylacetylene-d₁ ([~80% D in C(sp)-H, by ¹H NMR spectroscopy] was prepared according to the experimental procedure.³³ DMA solvent, I₂ solution (0.5 M solution in DMA), and iodocyclohexane were dried with activated, powdered 3Å molecular sieves and stored in a nitrogen-filled glovebox prior to use. In the glovebox, an oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with FeBr₂ (5.4 mg, 0.025 mmol, 5 mol %) and Zn (25 mg, 0.38 mmol, 1.5 equiv). The tube and the solids inside were then dried under vacuo with the aid of a hot gun. The tube was then cooled to room temperature, and was immediately transferred to the glovebox. DMA (0.5 mL) and I₂ (0.5 M solution in DMA, 10 µL, 2 mol %) were transferred into the tube, and the reaction mixture was stirred until the brown solution was decolorized. Phenylacetylene-d₁ (26 mg, 0.25 mmol, 1 equiv) and iodocyclohexane (79 mg, 0.38 mmol, 1.5 equiv) were finally transferred into the tube, and the resulting reaction mixture was stirred at room temperature for 16 h. After the reaction, 1,3,5-trimethoxybenzene (14 mg, 0.083 mmol) was added into the reaction mixture. The reaction mixture was washed with EtOAc (~5 mL) and water (~10 mL). A portion of organic fraction was dried and was then analyzed by ¹H NMR spectroscopy. The total ¹H NMR yield of Z-olefin was estimated to be ~79%, where the ¹H NMR yields of α-H,β-β-D-Z-olefin and α-D,β-D-Z-olefin were estimated to be ~64% and ~15%, respectively. The formation of α-H,β-β-D-Z-olefin ([M] = 187) and α-D,β-D-Z-olefin ([M] = 188) were further established by GC-MS analysis.

(iv) Reaction of in-situ formed Alkenylzinc Intermediate with Phenylacetylene-d₁ (Fig. S9d). Phenylacetylene-d₁ ([~80% D in C(sp)-H, by ¹H NMR spectroscopy] was prepared according to the experimental procedure.³³ DMA solvent, I₂ solution (0.5 M solution in DMA), ethynylbenzene, and iodocyclohexane were dried with activated, powdered 3Å molecular sieves and stored in a nitrogen-filled glovebox prior to use. In the glovebox, an oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with FeBr₂ (5.4 mg, 0.025 mmol, 5 mol %) and Zn (25 mg, 0.38 mmol, 1.5 equiv). The tube and the solids inside were then dried under vacuo with
the aid of a hot gun. The tube was then cooled to room temperature, and was immediately transferred to the glovebox. DMA (0.5 mL) and I₂ (0.5 M solution in DMA, 10 μL, 2 mol %) were transferred into the tube, and the reaction mixture was stirred until the brown solution was decolorized. Ethynylbenzene (26 mg, 0.25 mmol, 1 equiv) and iodocyclohexane (79 mg, 0.38 mmol, 1.5 equiv) were finally transferred into the tube, and the resulting reaction mixture was stirred at room temperature for 16 h. After the reaction, the in-situ formed alkenylzinc intermediate was prepared, and phenylacetylene-d₁ (51 mg, 0.50 mmol, 2 equiv) was added in the glovebox. The reaction mixture was further stirred at room temperature for 12 h. After the reaction, 1,3,5-trimethoxybenzene (14 mg, 0.083 mmol) was added into the reaction mixture. The reaction mixture was washed with EtOAc (~5 mL) and water (~10 mL). A portion of organic fraction was dried and was then analyzed by ¹H NMR spectroscopy. The total ¹H NMR yield of α-H-Z-olefin was estimated to be ~81%, where the ¹H NMR yields of α-H-Z-olefin and α-D-Z-olefin were estimated to be ~68% and ~13%, respectively. The formation of α-H-Z-olefin ([M] = 186) and α-D-Z-olefin ([M] = 187) were further established by GC-MS analysis. Additionally, the amount of ethynylbenzene ([M] = 102) was increased as detected by GC-MS analysis.

(g) Study of Alkylzinc Reagent as Viable Intermediate (Fig. S10).

(i) Preparation of alkylzinc reagent with secondary alkyl iodide. An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with zinc powder (131 mg, 2.0 mmol, 2.0 equiv) and DMA solvent (2 mL). Iodine (dissolved in DMA, 0.5 M, 3 mol %, 60 μL) was then added into the reaction mixture, and the mixture was stirred at room temperature until the brown color decolorized (~1-2 min). 2-Iodononane (381 mg, 1.5 mmol, 1.5 equiv) was added into the reaction mixture, and the mixture was heated at 80 °C for 3 h in a preheated oil bath, or stirred at room temperature for 16 h.

(ii) Preparation of alkylzinc reagent with primary alkyl iodide. An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with zinc powder (164 mg, 2.5 mmol, 2.5 equiv) and DMA solvent (1 mL). Iodotrimethylsilane (40 mg, 0.20 mmol, 20 mol %) was then added into the reaction mixture, and the mixture was stirred at room temperature for ~2 min (Caution: white fume was generated when iodotrimethylsilane was once added; no more fume was produced upon prolonged stirring). 1-Iododecane (526 mg, 2.0 mmol, 2 equiv) was added into the reaction mixture, and the mixture was heated at 60 °C for 6 h in a preheated oil bath, or stirred at room temperature for 16 h.

(iii) Protonation of alkylzinc reagent to test their formation. In the reaction mixture from (i) was added HCl solution (~1 M aqueous solution, 3 mL) or D₂O (20 equiv, 270 μL). In the reaction mixture from (ii) was added H₂O (2 mL) or D₂O (2 mL). The reaction mixture was then stirred at room temperature for 15 min. From (i), none or nonane-d₁ was formed in about 70-90% by GC analysis using dodecane as internal standard. From (ii), decane or decane-d₁ was formed in about 80-90% by GC analysis using dodecane as internal standard. The products were further established by GC-MS analysis.

(iv) Use of alkylzinc reagent in Fe-Catalyzed Olefination. In the reaction mixture from (i) (prepared from heating at 80 °C) was added 1-ethynyl-4-methylbenzene (116 mg, 1.0 mmol, 1 equiv) followed by FeBr₂ (22 mg, 0.10 mmol, 10 mol %). In the reaction mixture from (ii) (prepared from heating at 60 °C) was added ethynylbenzene (102 mg, 1.0 mmol, 1 equiv) followed by FeBr₂ (22 mg, 0.10 mmol, 10 mol %) and CuBr₂ (22 mg, 0.10 mmol, 10 mol %). The resulting mixture was stirred at room temperature for
16 h. After the reaction, dodecane (226 μL, 1.0 mmol) was added as internal standard, and the reaction mixture was washed with additional water (~20 mL) and EtOAc (~5 mL). A small fraction of organic layer was subjected to GC analysis to determine the GC yield of nonane/decane formed, and then subjected to GC-MS analysis to determine the formation of (Z)-1-methyl-4-(3-methyldec-1-en-1-yl)benzene (4s) and (Z)-dodec-1-en-1-ylbenzene (6t) in trace amount.

**(h) Study of Conversion of E-Olefin to Z-Olefin (Fig. S11).** (i) An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with zinc powder (65 mg, 1.0 mmol, 2 equiv) and DMA solvent (1 mL). Iodine (dissolved in DMA, 0.5 M, 3 mol %, 30 μL) was then added into the reaction mixture, and the mixture was stirred at room temperature until the brown color decolorized (~1-2 min). (ii) An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with zinc powder (65 mg, 1.0 mmol, 2 equiv) and DMA solvent (0.5 mL). Iodotrimethylsilane (20 mg, 0.10 mmol, 20 mol %) was then added into the reaction mixture, and the mixture was stirred at room temperature (~2 min). In the reaction mixture of (i) was added iron(II) bromide (11 mg, 0.05 mmol, 10 mol %) and (E)-prop-1-en-1-ylbenzene (66 mg, 0.50 mmol, 1 equiv). In the reaction mixture of (ii) was added iron(II) bromide (11 mg, 0.05 mmol, 10 mol %), copper(II) bromide (11 mg, 0.05 mmol, 10 mol %) and (E)-prop-1-en-1-ylbenzene (66 mg, 0.50 mmol, 1 equiv). The resulting mixture from (i) or (ii) was stirred at room temperature for 16 h. After the reaction, 1,3,5-trimethoxybenzene (28 mg, 0.17 mmol) was added, and the reaction mixture was washed with water (~20 mL) and EtOAc (~5 mL). A fraction of organic layer was dried in vacuo, and the residue was analyzed by 1H NMR spectroscopy. No (Z)-prop-1-en-1-ylbenzene was generated and the substrate remained unreacted. The recovery yield of unreacted (E)-prop-1-en-1-ylbenzene was not determined due to its low volatility.
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NMR Spectra

3-Iodo-2-methylhexane (R1)
(Z)-8-Iodoct-3-ene (R2)

CWC067-sup-SM (H1).1/fd
(±)-Menthy 6-iodohexanoate) (R3)
Cholestanyl 4-ethynylbenzoate (S1)
1,2:3,4-Di-\(\alpha\)-isopropylpylidene-\(\alpha\)-D-galactopyranosyl 4-ethynylbenzoate (S2)
(±)-α-Tocopheryl 4-ethynylbenzoate (S3)
Ethyl 4-(2-ethynylphenoxy)butanoate (S4)

OEtO

OEtO

CWC11031-sap-SM (H1).1.fd

CWC11031-sap-SM (C13).1.fd

E77

S72
(Z)-(2-Cyclohexylvinyl)benzene (1 mmol Scale) (3a)
(Z)-(2-Cyclohexylvinyl)benzene (20 mmol Scale) (3a)
(Z)-4-(2-Cyclohexylvinyl)-N,N-dimethylaniline (3b)
(Z)-1-(2-Cyclohexylvinyl)-4-methoxybenzene (3c)
(Z)-(4-(2-Cyclohexylvinyl)phenyl)(methyl)sulfane (3d)
(Z)-1-(tert-Butyl)-4-(2-cyclohexylvinyl)benzene (3e)
(Z)-1-Bromo-4-(2-cyclohexylvinyl)benzene (3f)
(Z)-1-Chloro-4-(2-cyclohexylvinyl)benzene (3g)
(Z)-1-(2-Cyclohexylvinyl)-4-fluorobenzene (3h)
(Z)-4-(2-Cyclohexylvinyl)-N,N-diethylbenzamide (3i)
Methyl (Z)-4-(2-Cyclohexylvinyl)benzoate (3j)
(Z)-1-(4-(2-Cyclohexylvinyl)phenyl)ethan-1-one (3k)

See image for chemical structures and spectra.
(Z)-4-(2-Cyclohexylvinyl)benzaldehyde (3l)
(Z)-4-(2-Cyclohexylvinyl)benzonitrile (3m)

\[
\begin{align*}
\text{NC} & \quad \text{NC} \\
\end{align*}
\]
(Z)-1-(3-Methyl-1-en-1-yl)-4-(trifluoromethyl)benzene (3n)
(Z)-1-(2-Cyclohexylvinyl)-2-methylbenzene (3o)
(Z)-2-(2-Cyclohexylvinyl)naphthalene (3p)
(Z)-2-(2-Cyclohexylnvinyl)-5-methylthiophene (3q)

\[
\text{Me} \quad \text{S} \quad \text{Me} \\
\text{C}_6\text{H}_{12} \quad \text{S} \quad \text{C}_2\text{H}_4 \quad \text{C}_6\text{H}_{12} \\
\text{S} \quad \text{Me} \\
\text{C}_6\text{H}_{12} \quad \text{S} \quad \text{C}_2\text{H}_4 \quad \text{C}_6\text{H}_{12}
\]
(Z)-3-(3-Methyldec-1-en-1-yl)pyridine (3r)
(Z)-1-(2-Cyclohexylvinyl)cyclohex-1-ene (3s) and (2-cyclohexylidenevinyl)cyclohexane (3s')

\[ (3s : 1) \]

\[ (Z)-H \]

\[ (E)-H \]

vinyl H of allene

\[ (3.1 : 1) \]
(Z)-1-((3-Methyldec-1-en-1-yl)cyclohex-1-ene (3t) and (3-methyldec-1-en-1-ylidene)cyclohexane (3t')
**tert-Butyl (Z)-4-(4-methoxystyryl)piperidine-1-carboxylate (4a)**

![NMeO Boc](image)

![NMeO Boc](image)
(Z)-1-Methoxy-4-(3-methyl-5-phenylpent-1-en-1-yl)benzene (4b)
1-((Z)-4-Methoxystyryl)adamantine (4c)

MeO

MeO

S96
(Z)-1-(tert-Butyl)-4-(2-cyclopentylvinyl)benzene (from alkyl iodide) (4d)
(Z)-1-(tert-Butyl)-4-(2-cyclopentylvinyl)benzene (from alkyl bromide) (4d)

CWC8117C-sep (H1).1/3d

[Chemical structure image]
(Z)-(4-(tert-Butyl)styryl)cycloheptane (4e)
(Z)-(4-(tert-Butyl)styryl)cyclooctane (4f)
(Z)-1-(tert-Butyl)-4-(3,3-dimethylbut-1-en-1-yl)benzene (from alkyl iodide) (4g)
(Z)-1-(tert-Butyl)-4-(3,3-dimethylbut-1-en-1-yl)benzene (from alkyl bromide) (4g)
(Z)-4-(4-Methylstyryl)tetrahydro-2H-pyran (4h)

CWC7063A-MePhyran (C13J) 1.3d

S103
2-((Z)-4-Methylstyryl)bicyclo[2.2.1]heptane (4i)
(Z)-1-(3-Ethynon-1-en-1-yl)-4-methylbenzene (4j)

\[
\text{Me} \quad \text{(Z)-1-(3-Ethynon-1-en-1-yl)-4-methylbenzene (4j)}
\]

**CWF083C-MePh 3-Nor (C13), 1.1fd**

**Me**

\[
\text{Me} \quad \text{(Z)-1-(3-Ethynon-1-en-1-yl)-4-methylbenzene (4j)}
\]
(Z)-1-(3-Butylhept-1-en-1-yl)-4-methylbenzene (4k)
(Z)-1-(3-Isopropylhex-1-en-1-yl)-4-methylbenzene (4l)
(Z)-1-(3-Ethylhepta-1,6-dien-1-yl)-4-methylbenzene (4m)
(3S,5S,8R,9S,10S,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-((Z)-3-methylpent-1-en-1-yl)benzoate (4n)
((3\textit{a}R,5\textit{a}R,5\textit{a}S,8\textit{a}S,8\textit{b}R)-2,2,7,7-tetramethyltetrahydro-5\textit{H}-bis([1,3]dioxolo)[4,5-\textit{b}:4',5'-\textit{d}]pyran-5-yl)methyl 4-((Z)-2-cyclohexylvinyl)benzoate (4o)
(2,5,7,8-Tetramethyl-2-4,8,12-trimethyltridecyl)chroman-6-yl 4-((Z)-2-cyclohexylvinyl)benzoate (4p)
5-(3-Ethynon-1-en-1-yl)-1,2,3-trimethoxybenzene (4q)

\[
\begin{align*}
\text{MeO} & \quad \text{OMe} \\
\text{MeO} & \quad \text{MeO}
\end{align*}
\]
(Z)-5-(3,3-Dimethylbut-1-en-1-yl)-1,2,3-trimethoxybenzene (4r)
(Z)-1-Methyl-4-(3-methyldec-1-en-1-yl)benzene (4s)

CWC7933D-smp MePh 2-Non (M1),1,1,2d
(Z)-1-Methyl-2-(2-(3-methylcyclohexyl)vinyl)benzene (4t)
(Z)-1-Methyl-2-(2-(4-methylcyclohexyl)vinyl)benzene (4u)
(Z)-1-(tert-Butyl)-4-(3-methylpent-1-en-1-yl)benzene (from alkyl iodide) (5a)
(Z)-1-(tert-Butyl)-4-(3-methylpent-1-en-1-yl)benzene (from alkyl bromide) (5a)
(Z)-1-(tert-Butyl)-4-(3-ethylpent-1-en-1-yl)benzene (5b)
(Z)-1-(2-Cyclopentylvinyl)-4-methoxybenzene (5c)
(Z)-1-(2-Cyclopentylvinyl)-4-methylbenzene (5d)

Catalyst: (H3) (Z)-1,5-d

S121
(Z)-(4-Methylstyryl)cycloheptane (5e)
(Z)-1-(3,3-Dimethylpent-1-en-1-yl)-4-methylbenzene (5g)
(Z)-(3,3-Diethylpent-1-en-1-yl)benzene (5h)
(Z)-(4-Methoxystyryl)cycloheptane (5i)
(Z)-1-Methoxy-4-(non-1-en-1-yl)benzene (1 mmol Scale) (6a)
(Z)-1-Methoxy-4-(non-1-en-1-yl)benzene (8 mmol Scale) (6a)
(Z)-1-Chloro-4-(non-1-en-1-yl)benzene (6b)
(Z)-Dec-1-en-1-ylbenzene (1 mmol) (6c)
(Z)-Dec-1-en-1-ylbenzene (15 mmol) (6c)
(Z)-Oct-1-en-7-yn-1-ylbenzene (6d)
(Z)-1-Methyl-4-(4-methylpent-1-en-1-yl)benzene (6e)

CWC0052- Sep MePh CH2OHMe2 (H1) Me

Me

CWC0052- Sep MePh CH2OHMe2 (C13) 1.8d

Me

S134
(Z)-1-\textit{(tert-Butyl)}-4-(4,4-dimethylpent-1-en-1-yl)benzene (6f)
(Z)-1-(tert-Butyl)-4-(5-(4-methoxyphenoxy)pent-1-en-1-yl)benzene (6g)
(Z)-1-(tert-Butyl)-4-(8-chlorooct-1-en-1-yl)benzene (6h)
(Z)-7-(4-Chlorophenyl)hept-6-en-1-yl acetate (6i)
(Z)-8-(4-Chlorophenyl)oct-7-enenitrile (6j)
(Z)-9-(4-Methoxyphenyl)non-8-enenitrile (6k)

\[ \text{MeO} - \text{CN} \]
(Z)-2-((8-(4-Methoxyphenyl)oct-7-en-1-yl)oxy)tetrahydro-2H-pyran (6l)
(Z)-9-((4-Methoxyphenyl)pent-4-en-1-yl)-9H-carbazole (Z-isomer + E-isomer) (6m)

(Z: E = 4.1 : 1)
(Z)-9-((5-(4-Methoxyphenyl)pent-4-en-1-yl)-9H-carbazole (pure Z-isomer) (6m)
(Z)-1-(Dodeca-1,11-dien-1-yl)-4-methoxybenzene (6n)

\[
\text{MeO} \quad \begin{array}{c}
\text{MeO} \\
\end{array}
\]

\[
\text{MeO} \quad \begin{array}{c}
\text{MeO} \\
\end{array}
\]

\[
\text{MeO} \quad \begin{array}{c}
\text{MeO} \\
\end{array}
\]
2-Isopropyl-4-methylcyclohexyl (Z)-8-(4-methoxyphenyl)oct-7-enoate (60)
(Z)-5-(Dec-1-en-1-yl)-1,2,3-trimethoxybenzene (6p)

CWC11003F-Sep (H1) (t) 1/5d

CWC11003F-Sep (C13) (t) 1/5d

S146
(Z)-1-(Dec-1-en-1-yl)-4-methoxybenzene (6q)
(Z)-1-Methoxy-4-(5-methylhex-1-en-1-yl)benzene (6r)

![Chemical structure and NMR spectra]
(Z)-1-Methoxy-4-(5-phenylpent-1-en-1-yl)benzene (6s)
(Z)-Dodec-1-en-1-ylbenzene (6t)
(Z)-1-Methoxy-4-(octadec-1-en-1-yl)benzene (6u)
(Z)-7-Phenylept-6-en-1-yl acetate (6v)
\((Z)-2-((8\text{-Phenyloct-7-en-1-yl})\text{oxy})\text{tetrahydro-}2\text{-}H\text{-pyran (7a)}\)
Ethyl (Z)-4-(2-(Tridec-1-en-1-yl)phenoxy)butanoate (7b) (26)
Ethyl (Z)-2-(4-(Tridec-1-en-1-yl)phenoxy)acetate (7c)
(Z)-1-Chloro-4-(3-(2-methylcyclopentyl)prop-1-en-1-yl)benzene (8a) and (Z)-1-Chloro-4-(3-methylocta-1,7-dien-1-yl)benzene (8a’)

6.3 : 1
(Z)-1-(tert-butyl)-4-(3-cyclopentylprop-1-en-1-yl)benzene (8b, first compound) and (Z)-1-(tert-butyl)-4-(octa-1,7-dien-1-yl)benzene (8b’)

(Z)-cyclic isomer (Z': E = 7.0 : 1) (20 : 1) acyclic isomer

(Z)-cyclic isomer (Z)-acyclic isomer's terminal olefin H

(E)-cyclic isomer
(Z)-1-(3-Cyclopentylpent-1-en-1-yl)-4-methylbenzene (8c)
1-(Cyclohexyloxy)-2,2,6,6-tetramethylpiperidine (TEMPO-Cy) (8d)

\[
\text{TEMPO (1.5 equiv)} \quad \begin{align*}
\text{FeBr}_2 (10 \text{ mol} \%) \\
\text{Zn (1.5 equiv), } I_2 (2 \text{ mol} \%) \\
\text{DMA (0.5 M), rt, 16 h}
\end{align*}
\] 

\[
\text{H}_2\text{O}
\]

0% TEMPO-Cy

14% NMR yield
(w.r.t. CyI, 61% conv.)

CWOI065A (H1).1.fid
Diethyl (E)-(2-Cyclohexyl-1-phenylvinyl)phosphonate (8e)
Reaction in DMA-\textsubscript{d} \textsubscript{9} followed by Workup with H\textsubscript{2}O (Fig. S7)

\[
\begin{align*}
\text{H} \quad \text{equiv} & \quad \text{equiv} \\
\text{(1)} & \quad \text{(1.5)} \\
\text{FeBr}_2 (10 \text{ mol } \% ) & \quad \text{Zn (1.5 equiv), I}_2 (2 \text{ mol } \% ) \\
\text{DMAB-\textsubscript{d} \textsubscript{9} (97\% D, 0.5 M), r.t., 16 h} & \quad \text{H}_2\text{O (excess), r.t.} \\
\end{align*}
\]

\[
\begin{align*}
\text{76\% NMR yield} \\
(100\% \text{ H incorporation, } Z:E = 12:1) \\
(\text{GCMS: } M^* = 186 \text{ obs})
\end{align*}
\]
Reaction in DMA-H$_2$ followed by Workup with D$_2$O (Fig. S7)

FeBr$_2$ (10 mol %)
1) Zn (1.5 equiv), I$_2$ (2 mol%)
DMA (0.5 M), rt, 16 h

2) D$_2$O (10 equiv), rt, 30 min

63% NMR yield
(~41% D incorporation, Z:E = 12:1)
(GCMS: M$^+$ = 187 obs)

H$_a$: ~59% H (~41% D)
H$_b$: 100% H

OMe
MeO

(internal standard)
Reaction with Phenylacetylene-d1 (Fig. S9c)

\[
\begin{align*}
\text{FeBr}_3 (10 \text{ mol} \%) & \quad \text{Zn (1.5 equiv), I}_2 (2 \text{ mol} \%) \\
\text{DMA (0.5 M), rt, 16 h} & \quad \text{H}_2\text{O}
\end{align*}
\]

\(-80\% \text{ D-incorporation}

\text{~64\% NMR yield} \quad \text{~15\% NMR yield} \quad \text{~80\% beta-D-incorporation}

\text{OMe}

\text{(internal standard)}
Reaction with of Alkenylzinc Reagent with Phenylacetylene-$d_1$ (Fig. S9d)

\[
\text{PhCH} = \text{Ph} + \text{I} \xrightarrow{\text{FeBr}_2 (10 \text{ mol } \%)} \text{PhCH} = \text{Zn} \xrightarrow{\text{Zn} (1.5 \text{ equiv}), \text{I}_2 (2 \text{ mol } \%)} \xrightarrow{\text{DMA} (0.5 \text{ M}), \text{rt}, 16 \text{ h}} \text{PhCD} = \text{Zn} \xrightarrow{\text{H}_2\text{O}} \text{PhCD} + \text{PhCH}_2
\]

-80% D-incorporation

\[\text{H} / \text{D} \approx 16\% \text{ alpha-D-incorporation} \]

NMR yield \(\approx 13\%\)

H/D

\[\text{MeO} \quad \text{OMe} \quad \text{(internal standard)}\]
(E)-(2-Cyclohexyl-1-iodovinyl)benzene (8f)