Nickel-Catalyzed Hydroalkylation and Hydroalkenylation of 1,3-Dienes with Hydrazones

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CONTENTS:
1. General Information.................................................................S2
2. Preparation of Substrates..........................................................S3
3. Hydroalkylation Procedure and Characterization of Products.........S9
4. Hydroalkenylation Procedure and Characterization of Products.....S22
5. Synthetic Application...............................................................S27
6. Mechanism Studies.................................................................S29
7. NMR Spectra of Important Compounds........................................S33
8. References.................................................................................S93
1. General Information

Unless mentioned otherwise, all manipulations were performed in an argon-filled glove-box MBRAUN LABstar or using standard Schlenk techniques. NMR spectra were recorded on a Bruker AV 400 spectrometer at 400 MHz (\textsuperscript{1}H NMR), 101 MHz (\textsuperscript{13}C NMR). Chemical shifts were reported in ppm relative to internal TMS for \textsuperscript{1}H NMR data, deuterated solvent for \textsuperscript{13}C NMR data, respectively. Data are presented in the following space: chemical shift, multiplicity, coupling constant in hertz (Hz), and signal area integration in natural numbers. High-resolution mass spectra were recorded on an IonSpec FT-ICR mass spectrometer with ESI or MALDI resource. Column chromatography was performed using silica gel P60 (mesh 230–400) supplied by Silicycle. Preparative TLC was performed using silica gel plate (200 × 200 × 1 mm) supplied by Xinnuo Chemical Company. All the solvents used for reactions were distilled under argon after drying over an appropriate drying agent. [Ni(COD)\textsubscript{2}] (Strem Chemicals), P(4-CF\textsubscript{3}C\textsubscript{6}H\textsubscript{4})\textsubscript{3} (Accela), DPPPe (Strem Chemicals), \textsuperscript{t}BuOLi (Aladdin), N\textsubscript{2}H\textsubscript{4} • H\textsubscript{2}O (Alfa). Other commercially available reagents were purchased from Acros, Sigma-Adrich and Alfa Aesar Chemical Company.
2. Preparation of Substrates

a) Diene substrates preparation

**Method A:** Aromatic 1,3-dienes (1a–1l) were prepared by Wittig olefination of enals or aldehydes according to previously reported procedures\(^1\). *(Note: the Z/E configuration of aromatic dienes has no effect on the yield and selectivity of the hydroalkylation reaction)*

**Method B:** Internal dienes 1n can be synthesized according to previous reports\(^1,2a\). Dienes 1o–r were prepared from 1o using known procedures (step 1\(^1\), step 2\(^2a\), step 3\(^2a\), step 4\(^2b\), step 5\(^2c\), step 6\(^2d\), step 7\(^2c\), step 8\(^2f\)).

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**Ethyl (6E)-7-phenylhepta-4,6-dienoate (1n)**

Isoalted by flash silica gel chromatography (PE/EA = 4:1). A mixture of E,Z–isomer and E,E–isomer was obtained in 72% yield. \(E,Z/E,E = 3:1\). Colorless oil, bp: 114–116 °C (0.1 Torr). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) E,Z–isomer 7.42 (d, \(J = 8.0\) Hz, 2H), 7.33–7.25 (m, 2H), 7.24–7.16 (m, 1H), 7.07 (dd, \(J = 15.5, 11.1\) Hz, 1H), 6.54 (d, \(J = 15.6\) Hz, 1H), 6.19 (t, \(J = 11.9\) Hz, 1H), 5.47 (dt, \(J = 11.1, 7.7\) Hz, 1H), 4.14 (q, \(J = 7.1\) Hz, 2H), 2.62 (q, \(J = 7.4\) Hz, 2H), 2.43 (t, \(J = 7.5\) Hz, 2H), 1.24 (t, \(J = 7.3\) Hz, 3H); \(\delta\) E,E–isomer: 7.37 (d, \(J = 8.2\) Hz, 2H), 7.33–7.25 (m, 2H), 7.24–7.16 (m, 1H), 6.73 (dd, \(J = 15.6, 10.4\) Hz, 1H), 6.45 (d, \(J = 15.6\) Hz, 1H), 6.28–6.22 (m, 1H), 5.84–5.77 (m, 1H), 4.14 (q, \(J = 7.1\) Hz, 2H), 2.63–2.58 (m, 2H), 2.47–2.40 (m, 2H), 1.24 (t, \(J = 7.1\) Hz, 3H). Spectral data matched those previously reported.\(^2a\)
(6E)-7-phenylhepta-4,6-dien-1-ol

\[
\text{Isolated by flash silica gel chromatography (PE/EA = 3:1). A mixture of } E,Z-\text{isomer and } E,E-\text{isomer was obtained in 82\% yield, } E/Z/E, E = \text{3:1. Colorless oil.}^{1} \text{H NMR} (400 \text{ MHz, CDCl}_3) \delta E,Z-\text{isomer 7.41 (d, } J = 7.3 \text{ Hz, 2H}), 7.31 \text{ (t, } J = 6.8 \text{ Hz, 2H}), 7.25–7.15 \text{ (m, 1H)}, 7.07 \text{ (dd, } J = 15.6, 11.1 \text{ Hz, 1H}) \text{, 6.53 (d, } J = 15.6 \text{ Hz, 1H}), 6.19 \text{ (t, } J = 10.9 \text{ Hz, 1H}), 5.52 \text{ (q, } J = 9.1, 8.5 \text{ Hz, 1H}), 3.68 \text{ (td, } J = 6.2, 1.8 \text{ Hz, 2H}), 2.38 \text{ (q, } J = 7.5 \text{ Hz, 2H}), 1.78–1.59 \text{ (m, 3H); } \delta E,E-\text{isomer 7.37 (d, } J = 7.4 \text{ Hz, 2H}), 7.34–7.26 \text{ (m, 2H)}, 7.25–7.15 \text{ (m, 1H)}, 6.75 \text{ (dd, } J = 15.6, 10.5 \text{ Hz, 1H}), 6.45 \text{ (d, } J = 15.7 \text{ Hz, 1H}), 6.26–6.16 \text{ (m, 1H)}, 5.81 \text{ (dt, } J = 15.6, 7.3 \text{ Hz, 1H}), 3.70–3.65 \text{ (m, 2H)}, 2.24 \text{ (q, } J = 7.0 \text{ Hz, 2H}), 1.73–1.66 \text{ (m, 3H). Spectral data matched those previously reported.}^{2a}
\]

Tert-butyl(dimethyl)silyl((6E)-7-phenylhepta-4,6-dien-1-yl)oxy)silane (1o)

\[
\text{Isolated by flash silica gel chromatography (PE). A mixture of } E,Z-\text{isomer and } E,E-\text{isomer was obtained in 83\% yield, } E/Z/E, E = \text{3:1. Colorless oil.}^{1} \text{H NMR} (400 \text{ MHz, CDCl}_3) \delta E,Z-\text{isomer 7.39 (d, } J = 8.0 \text{ Hz, 2H}), 7.29 \text{ (t, } J = 7.5 \text{ Hz, 2H}), 7.20 \text{ (t, } J = 7.3 \text{ Hz, 1H}), 7.06 \text{ (dd, } J = 15.5, 11.1 \text{ Hz, 1H}), 6.51 \text{ (d, } J = 15.6 \text{ Hz, 1H}), 6.17 \text{ (t, } J = 11.0 \text{ Hz, 1H}), 5.57–5.47 \text{ (m, 1H)}, 3.64 \text{ (t, } J = 6.4 \text{ Hz, 2H}), 2.35 \text{ (q, } J = 5.5 \text{ Hz, 2H}), 1.71–1.60 \text{ (m, 2H)}, 0.89 \text{ (9H, s), 0.04 (6H, s); } \delta E,E-\text{isomer 7.36 (d, } J = 7.7 \text{ Hz, 2H}), 7.31–7.26 \text{ (m, 2H)}, 7.21–7.16 \text{ (m, 1H)}, 6.75 \text{ (dd, } J = 15.6, 10.4 \text{ Hz, 1H}), 6.44 \text{ (d, } J = 15.7 \text{ Hz, 1H}), 6.22 \text{ (dd, } J = 15.0, 10.5 \text{ Hz, 1H}), 5.81 \text{ (dt, } J = 14.4, 6.8 \text{ Hz, 1H), 3.66–3.61 \text{ (m, 2H}, 2.19 \text{ (q, } J = 7.0 \text{ Hz, 2H}), 1.71–1.60 \text{ (m, 2H), 0.89 (s, 9H), 0.04 (s, 6H). Spectral data matched those previously reported.}^{2a}
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((1E)-7-(benzylolxy)hepta-1,3-dien-1-yl)benzene (1p)

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\text{Isolated by flash silica gel chromatography (PE/EA = 10:1). A mixture of } E,Z-\text{isomer and } E,E-\text{isomer was obtained in 80\% yield, } E/Z/E, E = \text{6:0.1. Colorless oil, bp: 165–168 °C (0.2 Torr).}^{1} \text{H NMR} (400 \text{ MHz, CDCl}_3) \delta E,Z-\text{isomer 7.38–7.26 (m, 9H), 7.23–7.17 (m, 1H), 7.09 (dd, } J = 15.6, 11.1 \text{ Hz, 1H}), 6.53 \text{ (d, } J = 15.6 \text{ Hz, 1H}), 6.19 \text{ (t, } J = 10.6 \text{ Hz, 1H}), 5.51 \text{ (dt, } J = 10.6, 7.8 \text{ Hz, 1H}), 4.56 \text{ (s, 2H), 3.51 (t, } J = 6.3 \text{ Hz, 2H}), 2.41 \text{ (qd, } J = 7.6, 1.3 \text{ Hz, 2H}), 1.80–1.70 \text{ (m, 2H); } \delta E,E-\text{isomer 7.38–7.26 (m, 9H), 7.23–7.17 (m, 1H), 6.74 \text{ (dd, } J = 15.6, 10.4 \text{ Hz, 1H}), 6.43 \text{ (d, } J = 15.6 \text{ Hz, 1H}), 6.27–6.17 \text{ (m, 1H), 5.91–5.74 (m, 1H), 4.50 (s, 2H), 3.51 (t, } J = 6.3 \text{ Hz, 2H}), 2.25 \text{ (q, } J = 7.1 \text{ Hz, 2H), 1.80–1.70 (m, 2H); }^{13} \text{C NMR} (101 \text{ MHz, CDCl}_3) \delta 138.5, 137.5, 137.5, 134.9, 132.2, 132.1, 130.9, 130.2, 129.4, 129.2, 128.5, 128.5, 128.4, 128.3, 127.6, 127.5, 127.4, 127.3, 127.1, 126.3, 126.1, 124.3, 72.9, 69.6, 69.4, 29.6, 29.4, 29.3, 24.5. HRMS (ESI) calcd for [C_{20}H_{32}NaO, M+Na]^+: 301.1563, Found: 301.1568.
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4-((6E)-7-phenylhepta-4,6-dien-1-yl)morpholine (1q)

\[
\text{Isolated by flash silica gel chromatography (EA). A mixture of } E,Z-\text{isomer and } E,E-\text{isomer was obtained in 63\% yield for two steps, } E/Z/E, E = \text{3.0:1. Yellow oil.}^{1} \text{H NMR} (400 \text{ MHz,}
\]
CDCl$_3$ $\delta$ E,Z-isomer 7.41 (d, $J = 7.3$ Hz, 2H), 7.31 (t, $J = 7.5$ Hz, 2H), 7.24–7.19 (m, 1H), 7.07 (dd, $J = 15.6$, 11.1, 1H), 6.53 (d, $J = 15.6$ Hz, 1H), 6.18 (t, $J = 11.0$ Hz, 1H), 5.51 (dt, $J = 10.7$, 7.7 Hz, 1H), 3.74–3.69 (m, 4H), 2.46–2.40 (m, 4H), 2.37–2.30 (m, 4H), 1.70–1.56 (m, 2H); E,E-isomer 7.41 (d, $J = 7.3$ Hz, 2H), 7.31 (t, $J = 7.5$ Hz, 2H), 7.24–7.19 (m, 1H), 6.75 (dd, $J = 15.6$, 10.4 Hz, 1H), 6.44 (d, $J = 15.6$ Hz, 1H), 6.24 (t, $J = 10.9$ Hz, 1H), 5.89–5.74 (m, 1H), 3.74–3.69 (m, 4H), 2.46–2.40 (m, 4H), 2.39–2.37 (m, 1H), 2.18 (dd, $J = 14.1$, 7.0 Hz, 3H), 1.70–1.56 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.5, 134.9, 132.3, 132.2, 130.9, 130.2, 129.2, 129.2, 128.5, 128.5, 128.4, 127.4, 127.1, 126.2, 126.1, 124.2, 67.0, 67.0, 58.4, 58.2, 53.7, 30.6, 26.4, 26.1, 25.6. HRMS (ESI) calcd for [C$_{17}$H$_{24}$NO, M+Na$^+$]: 258.1852, Found: 258.1856.

((1E)-7,7-dimethoxyhepta-1,3-dien-1-yl)benzene (1r)

Isolated by flash silica gel chromatography (PE/EA = 10:1). A mixture of E,Z-isomer and E,E-isomer was obtained in 76% yield for two steps, E,Z/E,E = 1:1.2. Light yellow oil, bp: 135–137 °C (2 Torr). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ E,Z-isomer 7.42 (d, $J = 7.3$ Hz, 2H), 7.29 (t, $J = 7.6$ Hz, 2H), 7.22–7.17 (m, 1H), 7.08 (dd, $J = 15.6$, 11.1, 1H), 6.53 (d, $J = 15.6$ Hz, 1H), 6.15 (dd, $J = 11.6$, 4.6 Hz, 1H), 5.51 (dt, $J = 10.6$, 7.8 Hz, 1H), 4.40 (t, $J = 5.7$ Hz, 1H), 3.33 (s, 6H), 2.36 (ddd, $J = 15.6$, 7.8, 1.3 Hz, 2H), 1.79–1.67 (m, 2H); E,E-isomer 7.37 (d, $J = 7.3$ Hz, 2H), 7.29 (t, $J = 7.6$ Hz, 2H), 7.22–7.17 (m, 1H), 6.75 (dd, $J = 15.7$, 10.4 Hz, 1H), 6.45 (d, $J = 15.7$ Hz, 1H), 6.23 (dd, $J = 15.1$, 10.5 Hz, 1H), 5.88–5.75 (m, 1H), 4.40 (t, $J = 5.7$ Hz, 1H), 3.33 (s, 6H), 2.21 (dd, $J = 14.6$, 7.1 Hz, 2H), 1.78–1.69 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.4, 134.3, 132.4, 131.6, 131.0, 130.4, 129.4, 129.1, 128.5, 128.5, 127.4, 127.1, 126.3, 126.1, 124.1, 103.8, 52.8, 52.7, 32.2, 31.9, 27.9, 23.1. HRMS (ESI) calcd for [C$_{15}$H$_{20}$NaO$_2$, M+Na$^+$]: 255.1356, Found: 255.1360.

**Method C**: Aliphatic 1,3-dienes **1s–1t** were prepared by olefination reactions with allylic phosphonate$^3$. To a solution of diethyl allylphosphonate (1.07 g, 6.0 mmol) in anhydrous THF (15 mL), $^3$BuLi (2.5 M in hexane, 2.4 mL, 6.0 mmol) was added dropwise at −78 °C. After stirring for 15 minutes, a solution of the RCHO (5.0 mmol) in HMPA (2.1 mL, 12 mmol) was added dropwise via cannula. The resulting solution was stirred at −78 °C for 2 h, and then allowed to warm to room temperature. Stirring was continued overnight at room temperature before quenching with saturated aqueous NH$_4$Cl solution. The mixture was extracted with Et$_2$O (3 × 15 mL). The combined organic phases were washed with brine (30 mL), dried (MgSO$_4$) and concentrated to afford the crude product. Purification by flash chromatography gave pure dienes.
(E)-1-benzyl-4-(buta-1,3-dien-1-yl)piperidine (1t)

Isolated by flash silica gel chromatography (PE/EA = 10:1). E–isomer was obtained in 57% yield. Colorless oil, bp: 112–114 °C (1 Torr). 1H NMR (400 MHz, CDCl3) δ 7.34–7.27 (m, 4H), 7.25–7.21 (m, 1H), 6.29 (dt, J = 17.0, 10.1 Hz, 1H), 6.03 (dd, J = 15.3, 10.1 Hz, 1H), 5.65 (dd, J = 15.3, 7.0 Hz, 1H), 5.09 (dd, J = 17.0, 1.4 Hz, 1H), 4.96 (dd, J = 10.1, 1.4 Hz, 1H), 4.27 (m, 2H), 4.20–4.15 (m, 2H), 3.48 (s, 2H), 2.87 (d, J = 11.7 Hz, 2H), 2.03–1.91 (m, 3H), 1.72–1.59 (m, 2H), 1.51–1.38 (m, 2H); 13C NMR (101 MHz, CDCl3) δ 139.6, 138.4, 137.3, 129.1, 128.1, 126.8, 115.1, 63.4, 53.4, 38.1, 31.8. HRMS (ESI) calcd for [C16H22N, M+H]+: 228.1747, Found: 228.1751.

Method D: Internal diene 1u was prepared by olefination reactions with cinnamyl phosphonate. To a solution of LDA (2.0 M in THF, 1.1 equiv) in THF (5.0 mL) was added newly distilled HMPA (5.0 mL) at 0 °C, and cinnamyl phosphonate (3.0 mmol, 1 equiv) by syringe. After stirring 15 minutes at 0 °C, the yellow-orange solution was cooled to −70 °C by a dry ice/acetone bath, and a solution of ethyl 5-oxopentanoate in THF (2.5 mL) was added dropwise via cannula. After stirring 5 h the reaction was carefully quenched with saturated aqueous NH4Cl (10 mL) and water (10 mL). The combined aqueous layers were extracted with EtOAc (3 × 10 mL) and the combined organic fractions were dried over MgSO4, filtered, and concentrated. Purification by flash chromatography (PE/EA = 8:1) gave the internal diene 1u.

Ethyl (7E)-8-(2-methoxyphenyl)octa-5,7-dienoate (1u)

Isolated by flash silica gel chromatography (PE/EA = 8:1). A mixture of E,E–isomer and E,Z–isomer was obtained in 78% yield, E,Z/E,E = 19:81. Light yellow oil, bp: 140–142 °C (0.2 Torr). The data for E,E isomer: 1H NMR (400 MHz, CDCl3) δ 7.44 (dd, J = 7.6, 1.3 Hz, 1H), 7.21–7.16 (m, 1H), 6.93–6.76 (m, 4H), 6.31–
6.20 (m, 1H), 5.82–5.68 (m, 1H), 4.13 (q, J = 7.2 Hz, 2H), 3.85 (s, 3H), 2.41–2.26 (m, 2H), 2.18 (dd, J = 14.4, 7.2 Hz, 2H), 1.83–1.65 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 173.6, 156.6, 133.5, 132.2, 129.8, 128.2, 126.5, 126.2, 125.3, 120.6, 110.8, 55.4, 33.7, 3.13, 24.5, 14.2. HRMS (ESI) calcd for [C$_{17}$H$_{22}$NaO$_3$, M+Na]$^+$: 297.1461, Found: 297.1465.

b) Hydrazone substrates preparation

Method A): The aromatic hydrazone substrates (2a–2r) and aliphatic hydrazone substrates 2s are prepared by following procedure$^4$.

![Reaction Scheme](image)

To a solution of hydrazine hydrate (1.5 mL, 30 mmol, 98% purity) in absolute EtOH (10 mL), aldehyde (10 mmol) was added dropwise under nitrogen. The resulting solution was stirred at room temperature for 2 h. After consumption of the aldehyde, water (10 mL) was added, and the mixture was extracted with DCM (3 × 10 mL). Combined organic layers were dried over sodium sulfate, filtered and concentrated at room temperature under reduced pressure to afford the hydrazones (50–85% yield). (The hydrazone products were stored in dry-box)

(4-(methylthio)benzylidene)hydrazine (2f)

White solid, mp: 55–56 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.70 (s, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 6.6 Hz, 1H), 5.49 (s, 2H), 2.49 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 142.7, 139.2, 131.9, 126.5, 126.2, 15.5. HRMS (ESI) calcd for [C$_8$H$_{11}$N$_2$S, M+H]$^+$: 167.0637, Found: 167.0639.

(4-(trimethylsilyl)benzylidene)hydrazine (2h)

Light yellow solid, mp: 47–48 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.73 (s, 1H), 7.55–7.44 (m, 4H), 5.54 (s, 2H), 0.26 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.1, 141.2, 135.4, 133.5, 125.4, -1.2. HRMS (ESI) calcd for [C$_{10}$H$_{17}$N$_2$Si, M+H]$^+$: 193.1156, Found: 193.1157.

2-(hydrazonomethyl)-1-methyl-1H-pyrrole (2o)

Brown solid, mp: 35–36 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.71 (s, 1H), 6.67–6.48 (m, 1H), 6.28 (dd, J = 3.6, 1.7 Hz, 1H), 6.09 (dd, J = 3.6, 2.7 Hz, 1H), 5.23 (s, 2H), 3.81 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 137.4, 128.1, 126.0, 112.2, 107.7, 36.4. HRMS (ESI) calcd for [C$_6$H$_{10}$N$_3$, M+H]$^+$: 124.0869, Found: 124.0869.
Method B): The preparation of the α,β-unsaturated hydrazones (5a-5j) in situ: to a solution of hydrazine hydrate (1.05 mmol, 98% purity) in absolute EtOH (1.0 mL), α,β-unsaturated aldehyde (1.0 mmol) was added dropwise under nitrogen. The resulting solution was stirred at room temperature for 2 h and directly used for the hydroalkenylation reaction (Note: The H₂O produced in the solution didn’t affect the yield of hydroalkenylation reaction.).
3. Hydroalkylation Procedure and Characterization of Products

Table S1: Optimization of reaction conditions (ligand)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Yield (%)</th>
<th>Regioselectivity (ratio of 1,2- and 1,4-hydrogenation products)</th>
</tr>
</thead>
<tbody>
<tr>
<td>imes</td>
<td>13%</td>
<td>N.D.</td>
</tr>
<tr>
<td>pcy3</td>
<td>33%</td>
<td>6:1</td>
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<tr>
<td>pbu3</td>
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<tr>
<td>pbn3</td>
<td>63%</td>
<td>NR</td>
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</table>

Reaction conditions: 1-phenylbutadiene 1a (0.10 mmol), hydrazone 2a (0.15 mmol), Ni(COD)2 (0.010 mmol), ligand (0.012 mmol for monodentate ligand, 0.012 mmol for bidentate ligand), additives (0.01 mmol), solvent (0.75 mL) at 80 °C for 8 h. 1H NMR yields of major isomer 3a using 1,3,5-trimethoxybenzene as internal standard. Regioselectivity (ratio of 1,2- and 1,4-hydrogenation products) was determined by 1H NMR analysis of reaction mixture.

Table S2: Optimization of reaction conditions (additives/solvent/temperature/ratio)

<table>
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<tr>
<th>entry</th>
<th>additives</th>
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<th>temp. (°C)</th>
<th>ratio (1a/2a)</th>
<th>yield (%)</th>
<th>3a/3a′</th>
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<tbody>
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<td>1</td>
<td>tBuOLi (1.0 equiv)</td>
<td>EtOH</td>
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<td>1:1.5</td>
<td>85</td>
<td>&gt;20:1</td>
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<tr>
<td>2</td>
<td>tBuOLi (0.1 equiv)</td>
<td>EtOH</td>
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<td>1:1.5</td>
<td>85</td>
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<td></td>
<td>BuOLi (0.05 equiv)</td>
<td>EtOH</td>
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<td>1:1.5</td>
<td>69</td>
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<td>5</td>
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<td>EtOH</td>
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<td>1:1.5</td>
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<td>6</td>
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<td>'BuOLi</td>
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<td>10</td>
<td>'BuOLi</td>
<td>Toluene</td>
<td>80</td>
<td>1:1.5</td>
<td>7</td>
<td>1:2</td>
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<tr>
<td>11</td>
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<td>MeOH</td>
<td>80</td>
<td>1:1.5</td>
<td>28</td>
<td>11:1</td>
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<tr>
<td>12</td>
<td>'BuOLi</td>
<td>PrOH</td>
<td>80</td>
<td>1:1.5</td>
<td>80</td>
<td>&gt;20:1</td>
</tr>
<tr>
<td>13</td>
<td>'BuOLi</td>
<td>EtOH (0.25 mL)</td>
<td>80</td>
<td>1:1.5</td>
<td>68</td>
<td>14:1</td>
</tr>
<tr>
<td>14</td>
<td>'BuOLi</td>
<td>EtOH (0.50 mL)</td>
<td>80</td>
<td>1:1.5</td>
<td>79</td>
<td>&gt;20:1</td>
</tr>
<tr>
<td>15</td>
<td>'BuOLi</td>
<td>EtOH (1.0 mL)</td>
<td>80</td>
<td>1:1.5</td>
<td>82</td>
<td>&gt;20:1</td>
</tr>
<tr>
<td>16</td>
<td>'BuOLi</td>
<td>EtOH</td>
<td>rt (23)</td>
<td>1:1.5</td>
<td>53</td>
<td>18:1</td>
</tr>
<tr>
<td>17</td>
<td>'BuOLi</td>
<td>EtOH</td>
<td>40</td>
<td>1:1.5</td>
<td>51</td>
<td>18:1</td>
</tr>
<tr>
<td>18</td>
<td>'BuOLi</td>
<td>EtOH</td>
<td>60</td>
<td>1:1.5</td>
<td>82</td>
<td>&gt;20:1</td>
</tr>
<tr>
<td>19</td>
<td>'BuOLi</td>
<td>EtOH</td>
<td>100</td>
<td>1:1.5</td>
<td>73</td>
<td>&gt;20:1</td>
</tr>
<tr>
<td>20</td>
<td>'BuOLi</td>
<td>EtOH</td>
<td>80</td>
<td>1:2</td>
<td>76</td>
<td>&gt;20:1</td>
</tr>
<tr>
<td>21</td>
<td>'BuOLi</td>
<td>EtOH</td>
<td>80</td>
<td>1:5:1</td>
<td>81</td>
<td>&gt;20:1</td>
</tr>
<tr>
<td>22</td>
<td>'BuOLi</td>
<td>EtOH</td>
<td>80</td>
<td>2:1</td>
<td>95 (92)</td>
<td>&gt;20:1</td>
</tr>
</tbody>
</table>

Original reaction conditions: 1-phenylbutadiene 1a (0.10 mmol), hydrazone 2a (0.15 mmol), Ni(COD)₂ (0.010 mmol), ligand (0.012 mmol), additive (0.010 mmol), solvent (0.75 mL) at 80 °C for 8 h. 

<p>| | | | | | | |</p>
<table>
<thead>
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</thead>
<tbody>
<tr>
<td>a</td>
<td>H NMR yields of major isomer 3a using 1,3,5-trimethoxybenzene as internal standard.</td>
<td>b</td>
<td>Regioselectivity was determined by H NMR analysis of reaction mixture.</td>
<td>c</td>
<td>Isolated yield in the parentheses.</td>
<td>d</td>
</tr>
</tbody>
</table>

Table S3: Substrates with low yield or no reaction
Reaction conditions: 1 (0.40 mmol), hydrazones 2 (0.20 mmol), Ni(COD)$_2$ (0.020 mmol), P(4-CF$_3$C$_6$H$_4$)$_3$ (0.024 mmol), $t$BuOLi (0.020 mmol), EtOH (1.5 mL) at 80 °C for 8 h. Isolated yields.

Regioselectivity was determined by $^1$H NMR analysis, isomers were determined by $^1$H NMR or GC/MS. a DPPPe as the ligand, b no product was provided, only azines 5 were detected by GC/MS. c Wolff-Kishner reduction product was detected by GC/MS.

a) General procedure for hydroalkylation

In an argon-filled glove-box, an oven-dried tube was charged with a stir bar, Ni(COD)$_2$ (5.5 mg, 0.020 mmol), ligand P(4-CF$_3$C$_6$H$_4$)$_3$ (11.2 mg, 0.024 mmol), 1,3-diene 1 (0.40 mmol), hydrazone 2 (0.20 mmol) and $t$BuOLi (1.6 mg, 0.020 mmol). The tube was sealed and removed from the glove box, and degassed ethanol (1.5 mL) was injected into the tube under argon. The reaction mixture was stirred at room temperature for 5 minutes and heated at 80 °C for 8 hours, after cooling to room temperature, the solvent was removed under vacuum. The pure product 3 or 4 was obtained by preparative TLC. (Note: The Z/E configuration of aromatic dienes had no effect on the yield and selectivity of the reaction. Pure E-isomer should be used for aliphatic dienes.)

b) Characterization of products
(E)-3-methylbut-1-ene-1,4-diyl)dibenzene (3a) $^{5a}$

The same results were obtained when E–1a or Z/E–1a (2:1) substrates used. 92% yield, 3a/3a' >20:1. Isolated by preparative TLC (PE). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33–7.24 (m, 6H), 7.20–7.16 (m, 4H), 6.31 (d, $J = 15.9$ Hz, 1H), 6.18 (dd, $J = 15.9, 6.5$ Hz, 1H), 2.81–2.75 (m, 1H), 2.69–2.50 (m, 2H), 1.08 (d, $J = 6.0$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.5, 137.8, 135.9, 129.3, 128.4, 128.2, 128.1, 126.8, 126.0, 125.8, 43.6, 38.8, 19.8.

(E)-1-methyl-4-(3-methyl-4-phenylbut-1-en-1-yl)benzene (3b)

E–1b was used. 92% yield, 3b/3b' >20:1. Isolated by preparative TLC (PE). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28–7.25 (m, 2H), 7.24–7.14 (m, 5H), 7.09 (d, $J = 7.9$ Hz, 2H), 6.28 (d, $J = 15.9$ Hz, 1H), 6.12 (dd, $J = 15.9, 6.8$ Hz, 1H), 2.77 (dd, $J = 16.2, 9.7$ Hz, 1H), 2.70–2.53 (m, 2H), 2.32 (s, 3H), 1.07 (d, $J = 6.3$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.6, 136.5, 135.0, 134.9, 129.3, 129.1, 128.1, 128.0, 125.9, 125.8, 43.7, 38.8, 21.1, 19.8. HRMS (EI) m/z calc'd for [C$_{18}$H$_{20}$, M$^+$]: 236.1565, Found: 236.1559.

(E)-1-fluoro-4-(3-methyl-4-phenylbut-1-en-1-yl)benzene (3c) $^{5a}$

E–1c was used. 95% yield, 3c/3c' >20:1. Isolated by preparative TLC (PE). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29–7.24 (m, 3H), 7.21–7.13 (m, 3H), 6.99–6.91 (m, 3H), 6.26 (d, $J = 15.9$ Hz, 1H), 6.08 (dd, $J = 15.9, 6.6$ Hz, 1H), 2.80–2.66 (m, 1H), 2.63–2.57 (m, 2H), 1.07 (d, $J = 6.2$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.9 (d, $J = 245.6$ Hz), 140.4, 135.6 (d, $J = 2.0$ Hz), 129.2 (d, $J = 4.4$ Hz), 128.1, 127.4, 127.1, 125.9, 115.3 (d, $J = 21.5$ Hz), 43.6, 38.8, 19.7; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –115.1.

(E)-1-methoxy-4-(3-methyl-4-phenylbut-1-en-1-yl)benzene (3d)$^{5a}$

E–1d was used. 83% yield, 3d/3d' >20:1. Isolated by preparative TLC (PE/EA = 50:1). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29–7.21 (m, 4H), 7.17 (t, $J = 7.5$ Hz, 3H), 6.82 (d, $J = 8.7$ Hz, 2H), 6.25 (d, $J = 15.9$ Hz, 1H), 6.03 (dd, $J = 15.9, 6.7$ Hz, 1H), 3.77 (s, 3H), 2.79–2.73 (m, 1H), 2.61-2.57 (m, 2H), 1.06 (d, $J = 6.2$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 158.7, 140.6, 133.8, 130.6, 129.2, 128.1, 127.6, 127.0, 125.8, 113.9, 55.2, 43.7, 38.7, 19.8.

(E)-N,N-dimethyl-4-(3-methyl-4-phenylbut-1-en-1-yl)aniline (3e)$^{5b}$

E–1e was used. 80% yield, 3e/3e' >20:1. Isolated by preparative TLC (PE/EA = 50:1). Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30–7.10 (m, 7H), 6.66 (d, $J = 8.7$ Hz, 2H), 6.23 (d, $J = 15.9$ Hz, 1H), 5.98 (dd, $J = 15.9, 6.7$ Hz, 1H), 2.92 (s, 6H), 2.80–2.73 (m,
1H), 2.60–2.56 (m, 2H), 1.05 (d, J = 6.1 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 149.7, 140.8, 131.9, 129.3, 128.0, 127.9, 126.8, 126.5, 125.7, 112.6, 43.9, 40.6, 38.7, 19.9.

**(E)-1-(3-methyl-4-phenylbut-1-en-1-yl)-4-(trifluoromethyl)benzene (3f)**

(2:1 Z/E)–1f was used. 95% yield, 3f/3f$^*$ >20:1. Isolated by preparative TLC (PE). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.56 (d, $J = 8.1$ Hz, 2H), 7.43 (d, $J = 8.1$ Hz, 2H), 7.32 (t, $J = 7.3$ Hz, 2H), 7.23 (dd, $J = 15.5$, 7.3 Hz, 4H), 6.37 (d, $J = 16.0$ Hz, 1H), 6.31 (dd, $J = 16.0$, 5.6 Hz, 1H), 2.84–2.78 (m, 1H), 2.71–2.66 (m, 2H), 1.15 (d, $J = 6.1$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 141.2 (q, $J = 1.5$ Hz), 140.2, 138.6, 129.2, 128.6 (q, $J = 32.3$ Hz), 128.2, 127.2, 126.1, 126.0, 125.4 (q, $J = 3.8$ Hz), 122.9 (q, $J = 270.1$ Hz), 43.4, 38.9, 19.6; $^{19}$F NMR (376 MHz, CDCl$_3$) δ –58.1. HRMS (EI) m/z calcd for [C$_{18}$H$_{17}$F$_3$M]$^+$: 290.1282, Found: 290.1276.

**(E)-1,3-dimethoxy-5-(3-methyl-4-phenylbut-1-en-1-yl)benzene (3g)**

(2:1 Z/E)–1g was used. 64% yield, 3g/3g$^*$ >20:1. Isolated by preparative TLC (PE/EA = 30:1). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.29–7.24 (m, 2H), 7.20–7.14 (m, 3H), 6.48 (d, $J = 1.6$ Hz, 2H), 6.33 (s, 1H), 6.24 (d, $J = 15.9$ Hz, 1H), 6.16 (dd, $J = 15.9$, 6.2 Hz, 1H), 3.78 (s, 6H), 2.80–2.74 (m, 1H), 2.66–2.47 (m, 2H), 1.07 (d, $J = 6.0$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 160.8, 140.4, 139.9, 136.5, 129.2, 128.1, 125.9, 106.5, 104.1, 99.2, 55.3, 43.5, 38.8, 19.7. HRMS (EI) m/z calcd for [C$_{19}$H$_{22}$O$_2$M]$^+$: 282.1620, Found: 282.1617.

**(E)-1-methyl-3-(3-methyl-4-phenylbut-1-en-1-yl)benzene (3h)**

(3:1 Z/E)–1h was used. 90% yield, 3h/3h$^*$ >20:1. Isolated by preparative TLC (PE). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.27 (t, $J = 7.4$ Hz, 2H), 7.21–7.07 (m, 6H), 7.00 (d, $J = 7.2$ Hz, 1H), 6.28 (d, $J = 15.9$ Hz, 1H), 6.17 (dd, $J = 15.9$, 6.7 Hz, 1H), 2.77 (dd, $J = 16.1$, 9.5 Hz, 1H), 2.67–2.52 (m, 2H), 2.32 (s, 3H), 1.07 (d, $J = 6.3$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 140.5, 138.0, 137.7, 135.7, 129.3, 128.4, 128.3, 128.1, 127.6, 126.7, 125.8, 123.1, 43.6, 38.8, 21.4, 19.8. HRMS (EI) m/z calcd for [C$_{18}$H$_{20}$M]$^+$: 236.1565, Found: 236.1560.

**(E)-1-methyl-2-(3-methyl-4-phenylbut-1-en-1-yl)benzene (3i)**

(2:1 Z/E)–1i was used. 81% yield, 3i/3i$^*$ 10:1. Isolated by preparative TLC (PE). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37 (d, $J = 6.7$ Hz, 1H), 7.32–7.23 (m, 2H), 7.20–7.17 (m, 3H), 7.13–7.10 (m, 3H), 6.45 (d, $J = 15.8$ Hz, 1H), 6.00 (dd, $J = 15.8$, 7.0 Hz, 1H), 2.78–2.72 (m, 1H), 2.69–2.56 (m, 2H), 2.23 (s, 3H), 1.11 (d, $J = 6.2$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 140.6, 137.3, 137.0, 135.0, 130.0, 129.3, 128.1, 126.8, 126.4, 126.0, 125.8, 125.5, 43.7, 39.2, 20.1, 19.7. HRMS (EI) m/z calcd for [C$_{18}$H$_{20}$M]$^+$: 236.1565, Found: 236.1558.
(E)-2-(3-methyl-4-phenylbut-1-en-1-yl)furan (3j)

\[
\begin{align*}
\text{Ph} & \quad \text{Me} \\
\text{O} & \quad \text{Me}
\end{align*}
\]

was used. 76% yield, 3j/3j' >20:1. Isolated by preparative TLC (PE). Yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.32–7.25 (m, 3H), 7.22–7.13 (m, 3H), 6.33 (dd, \(J = 3.2, 1.8\) Hz, 1H), 6.16 (d, \(J = 5.6\) Hz, 2H), 6.12 (dd, \(J = 3.2, 0.5\) Hz, 1H), 3.00–2.68 (m, 1H), 2.68–2.44 (m, 2H), 1.05 (d, \(J = 6.4\) Hz, 3H); \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 153.2, 141.2, 140.4, 134.8, 129.2, 128.1, 125.9, 117.0, 111.1, 106.3, 43.4, 38.5, 19.6. HRMS (EI) \(m/z\) calc'd for [C\(_{15}\)H\(_{16}\)O, M\(^+\)]: 212.1201, Found: 212.1196.

(E)-2-(3-methyl-4-phenylbut-1-en-1-yl)thiophene (3k)

\[
\begin{align*}
\text{S} & \quad \text{Me} \\
\text{Ph} & \quad \text{Me}
\end{align*}
\]

(1:1 \(Z/E\)–1k was used. 96% yield, 3k/3k' >20:1. Isolated by preparative TLC (PE). Yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.27 (t, \(J = 7.3\) Hz, 3H), 7.18 (dd, \(J = 13.4, 7.2\) Hz, 3H), 7.08 (d, \(J = 5.0\) Hz, 1H), 6.92 (t, \(J = 4.2\) Hz, 1H), 6.84 (d, \(J = 2.9\) Hz, 1H), 6.43 (d, \(J = 15.7\) Hz, 1H), 6.05 (dd, \(J = 15.7, 6.6\) Hz, 1H), 2.80–2.74 (m, 1H), 2.68–2.42 (m, 2H), 1.06 (d, \(J = 6.0\) Hz, 3H); \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 143.1, 140.4, 135.9, 129.2, 128.2, 127.2, 125.9, 124.4, 123.2, 121.6, 43.5, 38.6, 19.6. HRMS (EI) \(m/z\) calc'd for [C\(_{15}\)H\(_{16}\)S, M\(^+\)]: 228.0973, Found: 228.0971.

(E)-(3-ethylbut-1-ene-1,4-diyldibenzene (3l)

\[
\begin{align*}
\text{Ph} & \quad \text{Me} \\
\text{Ph} & \quad \text{Me}
\end{align*}
\]

(1:1.5 \(E/Z/E,E\)–1l was used. 83% yield, 3l/3l' 20:1. Isolated by preparative TLC (PE). Colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.32–7.24 (m, 6H), 7.20–7.15 (m, 4H), 6.25 (d, \(J = 15.8\) Hz, 1H), 6.02 (dd, \(J = 15.8, 8.7\) Hz, 1H), 2.72 (d, \(J = 7.0\) Hz, 2H), 2.36 (dq, \(J = 15.8, 8.1\) Hz, 1H), 1.65–1.47 (m, 1H), 1.36 (dt, \(J = 13.9, 7.5\) Hz, 1H), 0.90 (t, \(J = 7.4\) Hz, 3H); \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 140.6, 137.8, 134.4, 130.0, 129.3, 128.4, 128.1, 126.8, 126.0, 125.7, 46.7, 41.9, 27.2, 11.8. HRMS (EI) \(m/z\) calc'd for [C\(_{18}\)H\(_{20}\), M\(^+\)]: 236.1565, Found: 236.1560.

(E)-(3-benzylbut-1-ene-1,4-diyldibenzene (3m)

\[
\begin{align*}
\text{Ph} & \quad \text{Me} \\
\text{Ph} & \quad \text{Me}
\end{align*}
\]

\(E,E\)–1m was used. 69% yield, 3m/3m' 20:1. Isolated by preparative TLC (PE/EA = 100:1). Light yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.30–7.20 (m, 8H), 7.20–7.09 (m, 7H), 6.13 (d, \(J = 15.9\) Hz, 1H), 6.06 (dd, \(J = 15.9, 6.6\) Hz, 1H), 2.86–2.65 (m, 5H); \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 140.2, 137.7, 133.5, 130.2, 129.3, 128.4, 128.2, 126.9, 126.0, 125.9, 46.4, 41.3. HRMS (EI) \(m/z\) calc'd for [C\(_{23}\)H\(_{22}\), M\(^+\)]: 298.1722, Found: 298.1718.

Ethyl (E)-5-benzyl-7-phenylhept-6-enoate (3n)

\[
\begin{align*}
\text{Ph} & \quad \text{CO}_2\text{Et}
\end{align*}
\]

(3:1 \(E/Z/E,E\)–1n was used. 72% yield, 3n/3n' 10:1. Isolated by preparative TLC (PE/EA = 50:1). Colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.31–7.23 (m, 6H), 7.21–7.08 (m, 4H), 6.26 (d, \(J = 15.8\) Hz, 1H), 6.00 (dd, \(J = 15.8, 8.8\) Hz, 1H),
4.09 (q, \( J = 7.1 \) Hz, 2H), 2.72 (d, \( J = 7.0 \) Hz, 2H), 2.48–2.42 (m, 1H), 2.26 (td, \( J = 7.7 \), 2.9 Hz, 2H), 1.78–1.65 (m, 1H), 1.65–1.45 (m, 2H), 1.45–1.30 (m, 1H), 1.21 (t, \( J = 7.1 \) Hz, 3H); \(^{13}C\) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 173.5, 140.2, 137.6, 133.9, 130.3, 129.3, 128.4, 128.1, 126.9, 126.0, 125.8, 60.2, 44.8, 42.2, 34.3, 33.8, 22.8, 14.2. HRMS (EI) \( m/z \) calcd for [C\(_{22}\)H\(_{26}\), M\(^+\)]: 322.1933, Found: 322.1927.

\((E)-(5\text{-benzyl-7-phenylhept-6-en-1-yl}oxy)\text{(tert-butyl)dimethylsilane (3o)}\)

(3:1 \( E,Z/E,E \))–1o was used. 69% yield, 3o/3o' >20:1. Isolated by preparative TLC (PE). Colorless oil. \(^1H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.35–7.25 (m, 6H), 7.20 (dd, \( J = 7.9 \), 6.5 Hz, 4H), 6.28 (d, \( J = 15.8 \) Hz, 1H), 6.05 (dd, \( J = 15.8 \), 8.8 Hz, 1H), 3.60 (t, \( J = 6.5 \) Hz, 2H), 2.75 (d, \( J = 7.0 \) Hz, 2H), 2.57–2.36 (m, 1H), 1.63–1.21 (m, 6H), 0.90 (s, 9H), 0.05 (s, 6H); \(^{13}C\) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 140.4, 137.8, 134.5, 129.9, 129.3, 128.4, 128.1, 126.8, 126.0, 125.8, 63.1, 45.0, 42.2, 34.2, 32.8, 26.0, 23.5, 18.3, -5.3. HRMS (ESI) calcd for [C\(_{26}\)H\(_{38}\)NaOSi, M+Na\(^+\)]: 417.2584, Found: 417.2584.

\((E)-(3-(4\text{-benzoyloxy}butyl)but-1-ene-1,4-diyl) dibenzene (3p)\)

(6:1 \( E,Z/E,E \))–1p was used. 83% yield, 3p/3p' >20:1. Isolated by preparative TLC (PE/EA = 50:1). Colorless oil. \(^1H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.40–7.22 (m, 11H), 7.20–7.13 (m, 4H), 6.24 (d, \( J = 15.8 \) Hz, 1H), 6.01 (dd, \( J = 15.8 \), 8.8 Hz, 1H), 4.46 (s, 2H), 3.42 (t, \( J = 6.5 \) Hz, 2H), 2.71 (d, \( J = 7.0 \) Hz, 2H), 2.50–2.40 (m, 1H), 1.70–1.40 (m, 4H), 1.41–1.17 (m, 2H); \(^{13}C\) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 140.4, 138.6, 137.7, 134.4, 123.0, 129.3, 128.4, 128.3, 128.1, 127.6, 127.4, 126.8, 126.0, 125.8, 72.8, 70.3, 45.0, 42.2, 34.2, 29.7, 23.9. HRMS (ESI) calcd for [C\(_{27}\)H\(_{36}\)NaO, M+Na\(^+\)]: 393.2189, Found: 393.2194.

\((E)-4-(5\text{-benzyl-7-phenylhept-6-en-1-yl})\text{morpholine (3q)}\)

(3:1 \( E,Z/E,E \))–1q was used. Diene 1q (0.2 mmol), hydrazones 2a (0.3 mmol). 69% yield, 3q/3q' >20:1. Isolated by preparative TLC (EA). White solid, mp: 153–154 \(^\circ\)C. \(^1H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.31–7.26 (m, 6H), 7.21–7.10 (m, 4H), 6.24 (d, \( J = 15.8 \) Hz, 1H), 6.01 (dd, \( J = 15.8 \), 8.8 Hz, 1H), 3.77–3.54 (m, 4H), 2.71 (d, \( J = 7.0 \) Hz, 2H), 2.54–2.31 (m, 5H), 2.27 (t, \( J = 7.6 \) Hz, 2H), 1.62–1.24 (m, 6H); \(^{13}C\) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 140.4, 137.6, 134.4, 130.0, 129.3, 128.4, 128.1, 126.9, 126.0, 125.8, 66.9, 59.0, 53.7, 44.9, 42.2, 34.3, 26.5, 25.1. HRMS (ESI) calcd for [C\(_{24}\)H\(_{22}\)NO, M+H\(^+\)]: 350.2478, Found: 350.2481.

\((E)-(3-(4,4\text{-dimethoxybutyl})but-1-ene-1,4-diyl) dibenzene (3r)\)
(1:1.2 E,Z/E,E)–1r was used. 75% yield, 3r/3r’ >20:1.
Isolated by preparative TLC (PE/EA = 10:1). Colorless oil.
^1H NMR (400 MHz, CDCl₃) δ 7.43–7.22 (m, 6H), 7.22–7.08 (m, 4H), 6.25 (d, J = 15.8 Hz, 1H), 6.01 (dd, J = 15.8, 8.8 Hz, 1H), 4.30 (t, J = 5.7 Hz, 1H), 3.27 (d, J = 1.1 Hz, 6H), 2.71 (d, J = 7.0 Hz, 2H), 2.54–2.33 (m, 1H), 1.72–0.98 (m, 6H); ^13C NMR (101 MHz, CDCl₃) δ 140.3, 137.7, 134.2, 130.1, 129.3, 128.4, 128.1, 126.9, 126.0, 125.8, 104.4, 52.7, 52.5, 44.9, 42.2, 34.2, 32.5, 22.4. HRMS (ESI) calcd for [C₂₂H₂₅NaO₂, M+Na]^+: 347.1982, Found: 347.1985.

Ethyl (E)-4-(4-cyclohexyl-3-en-1-yl)benzoate (3s)

(1:15 Z/E)–1s was used. DPPPe (1,5-Bis(diphenylphosphino)pentane) as the ligand. 80% yield, 3s/3s’ 8:1. Isolated by preparative TLC (PE/EA = 50:1). Colorless oil. ^1H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 5.35–5.10 (m, 2H), 4.36 (q, J = 7.1 Hz, 2H), 2.65 (dd, J = 13.2, 7.3 Hz, 1H), 2.56 (dd, J = 13.2, 7.3 Hz, 1H), 2.37 (dt, J = 13.4, 6.8 Hz, 1H), 1.84 (tdd, J = 11.1, 7.6, 3.4 Hz, 1H), 1.73–1.55 (m, 6H), 1.39 (t, J = 7.1 Hz, 3H), 1.30–1.06 (m, 4H), 0.96 (d, J = 6.7 Hz, 3H); ^13C NMR (101 MHz, CDCl₃) δ 166.8, 146.5, 135.7, 132.2, 129.3, 129.2, 127.9, 60.7, 43.8, 40.6, 38.3, 33.1, 26.2, 26.0, 20.2, 14.3. HRMS (EI) m/z calcd for [C₂₀H₂₈O₂, M]^+: 300.2089, Found: 300.2083.

Ethyl (E)-4-(4-(1-benzylpiperidin-4-yl)-3-en-1-yl)benzoate (3t)

E–1t was used. DPPPe (1,5-Bis(diphenylphosphino)pentane) as the ligand. 70% yield, 3t/3t’ 13:1. ^1H NMR (400 MHz, CDCl₃) δ 7.93 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 4.3 Hz, 4H), 7.28–7.21 (m, 1H), 7.17 (d, J = 8.2 Hz, 2H), 5.25 (qd, J = 15.6, 6.4 Hz, 2H), 4.35 (q, J = 7.1 Hz, 2H), 3.47 (s, 2H), 2.84 (d, J = 11.1 Hz, 2H), 2.66–2.49 (m, 2H), 2.45–2.31 (m, 1H), 1.93 (td, J = 11.6, 2.1 Hz, 2H), 1.88–1.79 (m, 1H), 1.63–1.49 (m, 2H), 1.46–1.26 (m, 5H), 0.96 (d, J = 6.7 Hz, 3H); ^13C NMR (101 MHz, CDCl₃) δ 166.7, 146.3, 138.5, 134.0, 133.0, 129.2, 129.2, 129.1, 128.1, 128.0, 126.8, 63.5, 60.7, 53.5, 43.7, 38.6, 38.2, 32.2, 20.2, 14.3. HRMS (ESI) m/z calcd for [C₂₀H₂₈NO₂, M]^+: 392.2584, Found: 392.2588.

(E)-1-methyl-4-(2-methylphenyl-3-en-1-yl)benzene (4a)

85% yield, 4a/4a’ >20:1. Isolated by preparative TLC (PE). Colorless oil. ^1H NMR (400 MHz, CDCl₃) δ 7.30 (dt, J = 15.1, 7.5 Hz, 4H), 7.18 (t, J = 7.0 Hz, 1H), 7.12–7.04 (m, 4H), 6.32 (d, J = 15.9 Hz, 1H), 6.19 (dd, J = 15.9, 6.8 Hz, 1H), 2.77–2.71 (m, 1H), 2.60–2.54 (m, 2H), 2.31 (s, 3H), 1.07 (d, J = 6.3 Hz, 2H); ^13C NMR (101 MHz, CDCl₃) δ 137.8, 137.4, 136.1, 135.2, 129.1, 128.8, 128.4, 128.1, 126.8, 126.0, 43.2, 38.8, 21.0, 19.7. HRMS (EL) m/z calcd for [C₁₈H₂₀, M]^+: 236.1565, Found: 236.1559.
(E)-1-(2-methyl-4-phenylbut-3-en-1-yl)-4-(trifluoromethyl)benzene (4b)

87% yield, 4b/4b′ >20:1. Isolated by preparative TLC (PE). Colorless oil. 

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \delta 7.53 \text{ (d, J = 8.0 Hz, 2H), 7.32–7.26 (m, 6H), 7.24–7.15 (m, 1H), 6.30 (d, J = 15.9 Hz, 1H), 6.14 (dd, J = 15.9, 6.0 Hz, 1H), 2.81 (dd, J = 12.8, 6.6 Hz, 1H), 2.71–2.59 (m, 2H), 1.10 (d, J = 5.6 Hz, 3H); } ^{13}C \text{NMR (101 MHz, CDCl}_3 \delta 144.6 (q, J = 1.5 Hz), 137.5, 135.1, 129.5, 128.8, 128.5, 127.0, 126.01, 125.06 (q, J = 3.8 Hz), 123.02 (q, J = 272.2 Hz), 43.4, 38.7, 19.9; } ^{19}F \text{NMR (376 MHz, CDCl}_3 \delta –62.3 \text{. HRMS (EI) m/z calcd for [C}_{18}H_{17}F, M}^+; 290.1282, \text{Found: 290.1278.} \]

(E)-1-fluoro-4-(2-methyl-4-phenylbut-3-en-1-yl)benzene (4c)

78% yield, 4c/4c′ >20:1. Isolated by preparative TLC (PE). Colorless oil. 

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \delta 7.34–7.25 (m, 4H), 7.23–7.16 (m, 1H), 7.15–7.07 (m, 2H), 7.00–6.89 (m, 2H), 6.29 (d, J = 15.9 Hz, 1H), 6.14 (dd, J = 15.9, 7.0 Hz, 1H), 2.79–2.66 (m, 1H), 2.62–2.53 (m, 2H), 1.08 (d, J = 6.4 Hz, 3H); } ^{13}C \text{NMR (101 MHz, CDCl}_3 \delta 161.3 (d, J = 243.4 Hz), 137.7, 136.1 (d, J = 3.2 Hz), 135.5, 130.5 (d, J = 7.8 Hz), 128.5, 128.5, 126.9, 126.0, 114.9 (d, J = 21.0 Hz), 42.79, 39.0, 19.8; } ^{19}F \text{NMR (376 MHz, CDCl}_3 \delta –117.1 \text{. HRMS (EI) m/z calcd for [C}_{17}H_{17}F, M}^+; 240.1314, \text{Found: 240.1309.} \]

(E)-4-(2-methyl-4-phenylbut-3-en-1-yl)benzonitrile (4d)

64% yield, 4d/4d′ >20:1. Isolated by preparative TLC (PE/EA = 50:1). White solid, mp: 58–59 °C. 

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \delta 7.56 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 4.3 Hz, 4H), 7.27 (d, J = 7.4 Hz, 2H), 7.21 (dd, J = 8.5, 4.3 Hz, 1H), 6.27 (d, J = 15.9 Hz, 1H), 6.10 (dd, J = 15.9, 7.4 Hz, 1H), 2.80 (dd, J = 13.1, 7.4 Hz, 1H), 2.74–2.65 (m, 1H), 2.67–2.57 (m, 1H), 1.11 (d, J = 6.6 Hz, 3H); } ^{13}C \text{NMR (101 MHz, CDCl}_3 \delta 146.2, 137.3, 134.6, 132.0, 130.0, 129.1, 128.5, 127.1, 126.0, 119.1, 109.8, 43.6, 38.7, 20.0 \text{. HRMS (EI) m/z calcd for [C}_{18}H_{17}N, M}^+; 247.1361, \text{Found: 247.1356.} \]

(E)-1-methoxy-4-(2-methyl-4-phenylbut-3-en-1-yl)benzene (4e)

74% yield, 4e/4e′ >20:1. Isolated by preparative TLC (PE). Colorless oil. 

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \delta 7.37–7.23 (m, 4H), 7.20–7.16 (m, 1H), 7.08 (d, J = 7.9 Hz, 2H), 6.82 (d, J = 7.9 Hz, 2H), 6.30 (d, J = 15.8 Hz, 1H), 6.17 (dd, J = 15.8, 6.1 Hz, 1H), 3.77 (s, 3H), 2.75–2.64 (m, 1H), 2.58–2.52 (m, 2H), 1.07 (d, J = 5.3 Hz, 3H); } ^{13}C \text{NMR (101 MHz, CDCl}_3 \delta 157.8, 137.8, 136.0, 132.6, 130.1, 128.4, 128.2, 126.8, 126.0, 113.5, 55.2, 42.7, 39.0, 19.7. \]

(E)-methyl(4-(2-methyl-4-phenylbut-3-en-1-yl)phenyl)sulfane (4f)
Ethyl (E)-4-(2-methyl-4-phenylbut-3-en-1-yl)benzoate (4g)

89% yield, 4g/4g' > 20:1. Isolated by preparative TLC (PE/EA = 50:1). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 (d, $J = 7.9$ Hz, 2H), 7.30 (dt, $J = 15.1$, 7.4 Hz, 4H), 7.18 (t, $J = 7.5$ Hz, 3H), 6.34 (d, $J = 15.9$ Hz, 1H), 6.20 (dd, $J = 15.9$, 6.9 Hz, 1H), 2.78 (dd, $J = 11.8$, 5.0 Hz, 1H), 2.60 (dt, $J = 12.2$, 7.2 Hz, 2H), 1.08 (d, $J = 6.4$ Hz, 3H), 0.25 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.1, 137.8, 137.4, 136.0, 133.2, 128.7, 128.4, 128.2, 126.8, 126.0, 43.6, 38.6, 19.8, -1.0. HRMS (EI) $m/z$ calcd for [C$_{20}$H$_{26}$O$_2$Si]$: 294.1620$, Found: 294.1617.

(E)-trimethyl(4-(2-methyl-4-phenylbut-3-en-1-yl)phenyl)silane (4h)

87% yield, 4h/4h' 17:1. Isolated by preparative TLC (PE). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36–7.25 (m, 4H), 7.21–7.12 (m, 2H), 6.99 (t, $J = 9.0$ Hz, 3H), 6.33 (d, $J = 15.9$ Hz, 1H), 6.19 (dd, $J = 15.9$, 6.9 Hz, 1H), 2.75 (dd, $J = 12.2$, 5.6 Hz, 1H), 2.67–2.50 (m, 2H), 2.32 (s, 3H), 1.07 (d, $J = 6.5$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.4, 137.8, 137.6, 136.1, 130.1, 128.4, 128.1, 128.0, 128.6, 126.8, 126.0, 43.5, 38.7, 21.4, 19.7. HRMS (EI) $m/z$ calcd for [C$_{18}$H$_{20}$Si]$: 294.1565$, Found: 294.1560.

(E)-1-methyl-3-(2-methyl-4-phenylbut-3-en-1-yl)benzene (4i)

75% yield, 4i/4i' 20:1. Isolated by preparative TLC (PE). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36–7.25 (m, 4H), 7.21–7.12 (m, 2H), 6.99 (t, $J = 9.0$ Hz, 3H), 6.33 (d, $J = 15.9$ Hz, 1H), 6.19 (dd, $J = 15.9$, 6.9 Hz, 1H), 2.75 (dd, $J = 12.2$, 5.6 Hz, 1H), 2.67–2.50 (m, 2H), 2.32 (s, 3H), 1.07 (d, $J = 6.5$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.4, 137.8, 137.6, 136.1, 130.1, 128.4, 128.1, 128.0, 128.6, 126.8, 126.0, 43.5, 38.7, 21.4, 19.7. HRMS (EI) $m/z$ calcd for [C$_{18}$H$_{20}$Si]$: 294.1565$, Found: 294.1560.

(E)-1-methyl-2-(2-methyl-4-phenylbut-3-en-1-yl)benzene (4j)

73% yield, 4j/4j' > 20:1. Isolated by preparative TLC (PE). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42–7.24 (m, 4H), 7.23–7.06 (m, 5H), 6.30 (d, $J = 15.9$ Hz, 1H), 6.20 (dd, $J = 15.9$, 6.7 Hz, 1H), 2.82–2.70 (m, 1H), 2.66–2.55 (m, 2H), 2.32 (s, 3H), 1.11 (d, $J = 6.4$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 138.8, 137.8, 136.2, 136.0, 130.2, 130.1, 128.4, 128.0,
126.8, 126.0, 125.6, 40.7, 37.8, 19.9, 19.6. HRMS (EI) m/z calcd for [C\textsubscript{18}H\textsubscript{20}, M]\textsuperscript{+}: 236.1565, Found: 236.1560.

**\textit{(E)}-2-(2-methyl-4-phenylbut-3-en-1-yl)naphthalene (4k)**

90% yield, 4k/4k' 20:1. Isolated by preparative TLC (PE). White solid, mp: 40–41 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.78 (dd, \(J = 15.4, 8.5\) Hz, 3H), 7.61 (s, 1H), 7.52–7.36 (m, 2H), 7.35–7.23 (m, 5H), 7.19 (dd, \(J = 15.1, 8.1\) Hz, 1H), 6.34 (d, \(J = 15.9\) Hz, 1H), 6.23 (dd, \(J = 15.9, 6.4\) Hz, 1H), 2.96–2.92 (m, 1H), 2.79–2.69 (m, 2H), 1.11 (d, \(J = 5.9\) Hz, 1H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 138.1, 137.8, 135.9, 133.5, 132.0, 128.4, 128.3, 128.0, 127.6, 127.6, 127.5, 126.9, 126.0, 125.8, 125.1, 43.8, 38.7, 19.8. HRMS (EI) m/z calcd for [C\textsubscript{21}H\textsubscript{20}, M]\textsuperscript{+} : 272.1565, Found: 272.1562.

**\textit{(E)}-3-(2-methyl-4-phenylbut-3-en-1-yl)pyridine (4l)**

90% yield, 4l/4l' 17:1. Isolated by preparative TLC (PE/EA = 5:1).
Light yellow oil. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.45 (s, 2H), 7.48 (dt, \(J = 7.7, 1.7\) Hz, 1H), 7.32–7.28 (m, 4H), 7.24–7.16 (m, 2H), 6.29 (d, \(J = 15.9\) Hz, 1H), 6.13 (dd, \(J = 15.9, 7.2\) Hz, 1H), 2.81–2.55 (m, 3H), 1.12 (d, \(J = 6.4\) Hz, 3H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 150.6, 147.4, 137.4, 136.6, 135.6, 134.8, 129.0, 128.4, 127.0, 126.0, 123.1, 40.5, 38.7, 19.9. HRMS (EI) m/z calcd for [C\textsubscript{16}H\textsubscript{17}N, M]\textsuperscript{+} : 223.1361, Found: 223.1355.

**\textit{(E)}-4-(2-methyl-4-phenylbut-3-en-1-yl)pyridine (4m)**

79% yield, 4m/4m' 17:1. Isolated by preparative TLC (PE/EA = 5:1).
Light yellow oil. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.49 (d, \(J = 5.3\) Hz, 2H), 7.30–7.26 (m, 4H), 7.24–7.15 (m, 1H), 7.09 (d, \(J = 5.2\) Hz, 2H), 6.29 (d, \(J = 15.9\) Hz, 1H), 6.11 (dd, \(J = 15.9, 6.8\) Hz, 1H), 2.81–2.44 (m, 3H), 1.11 (d, \(J = 6.1\) Hz, 3H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 149.6, 149.4, 137.3, 134.6, 129.0, 128.5, 127.1, 126.0, 124.6, 42.8, 38.1, 20.0. HRMS (EI) m/z calcd for [C\textsubscript{16}H\textsubscript{17}N, M]\textsuperscript{+} : 223.1361, Found: 223.1356.

**\textit{(E)}-2-(2-methyl-4-phenylbut-3-en-1-yl)quinoline (4n)**

44% yield, 4n/4n' >20:1. Isolated by preparative TLC (PE/EA = 5:1). Light yellow oil. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.05 (t, \(J = 8.6\) Hz, 2H), 7.77 (d, \(J = 8.1\) Hz, 1H), 7.69 (t, \(J = 7.7\) Hz, 1H), 7.48 (t, \(J = 7.4\) Hz, 1H), 7.33–7.22 (m, 5H), 7.17 (t, \(J = 6.9\) Hz, 1H), 6.33 (d, \(J = 15.9\) Hz, 1H), 6.25 (dd, \(J = 15.9, 6.6\) Hz, 1H), 3.17–3.07 (m, 1H), 3.05–2.96 (dt, \(J = 18.6, 6.9\) Hz, 2H), 1.18 (d, \(J = 6.3\) Hz, 3H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 161.2, 148.0, 137.6, 135.9, 135.5, 129.3, 128.9, 128.6, 128.4, 127.5, 126.9, 126.8, 126.0, 125.7, 122.2, 46.5, 37.9, 20.2. HRMS (EI) m/z calcd for [C\textsubscript{20}H\textsubscript{19}N, M]\textsuperscript{+} : 273.1517, Found: 273.1518.
(E)-1-methyl-2-(2-methyl-4-phenylbut-3-en-1-yl)-1H-pyrrole (4o)

60% yield, 4o/4o' >20:1. Isolated by preparative TLC (PE/EA = 50:1). Yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.34 (d, \(J = 7.1\) Hz, 2H), 7.29 (t, \(J = 7.6\) Hz, 2H), 7.19 (t, \(J = 7.1\) Hz, 1H), 6.55–6.50 (m, 1H), 6.37 (d, \(J = 15.9\) Hz, 1H), 6.20 (dd, \(J = 15.9\), 6.8 Hz, 1H), 6.06 (t, \(J = 3.0\) Hz, 1H), 5.96–5.92 (m, 1H), 3.55 (s, 3H), 2.74–2.54 (m, 3H), 1.14 (d, \(J = 6.3\) Hz, 3H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 137.7, 135.8, 131.4, 128.5, 128.3, 126.9, 126.0, 121.1, 107.1, 106.5, 37.2, 33.8, 33.7, 20.0. HRMS (EI) \(m/z\) calcd for [C\(_{16}\)H\(_{19}\)N, M]\(^+\): 225.1517, Found: 225.1512.

(E)-2-(2-methyl-4-phenylbut-3-en-1-yl)furan (4p)

82% yield, 4p/4p' >20:1. Isolated by preparative TLC (PE). Yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.38–7.25 (m, 5H), 7.22–7.14 (m, 1H), 6.36 (d, \(J = 15.9\) Hz, 1H), 6.27 (dd, \(J = 3.0\), 1.9 Hz, 1H), 6.16 (dd, \(J = 15.9\), 6.9 Hz, 1H), 6.02 (d, \(J = 2.6\) Hz, 1H), 3.12–2.41 (m, 3H), 1.11 (d, \(J = 6.4\) Hz, 3H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 154.5, 140.9, 137.7, 135.4, 128.6, 128.4, 126.9, 126.0, 110.1, 106.1, 36.4, 35.5, 20.0. HRMS (EI) \(m/z\) calcd for [C\(_{16}\)H\(_{19}\)O, M]\(^+\): 212.1201, Found: 212.1195.

(E)-2-(2-methyl-4-phenylbut-3-en-1-yl)thiophene (4q)

83% yield, 4q/4q' >20:1. Isolated by preparative TLC (PE). Yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37–7.25 (m, 4H), 7.19 (t, \(J = 7.1\) Hz, 1H), 7.11 (d, \(J = 5.0\) Hz, 1H), 6.99–6.85 (m, 1H), 6.79 (d, \(J = 3.0\) Hz, 1H), 6.37 (d, \(J = 15.9\) Hz, 1H), 6.18 (dd, \(J = 15.9\), 7.4 Hz, 1H), 2.96 (dd, \(J = 14.5\), 7.0 Hz, 1H), 2.87 (dd, \(J = 14.5\), 7.0 Hz, 1H), 2.74–2.56 (m, 1H), 1.13 (d, \(J = 6.7\) Hz, 3H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 143.0, 137.7, 135.2, 128.9, 128.5, 127.0, 126.6, 126.1, 125.3, 123.3, 39.2, 37.4, 19.9. HRMS (EI) \(m/z\) calcd for [C\(_{15}\)H\(_{16}\)S, M]\(^+\): 228.0973, Found: 228.0968.

(E)-(3-methylpent-1-ene-1,4-diyldibenzene (4r)

Diene 1a (0.2 mmol), hydrazone 2r (0.3 mmol), Ni(COD)\(_2\) (0.02 mol), PBn\(_3\) (0.024 mmol), tBuOLi (0.02 mmol), EtOH (1.0 mL) at 80 °C for 8 h. 58% yield. 4r/4r' >20:1, 1.6:1 dr. Data for the major isomer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36 (d, \(J = 7.4\) Hz, 1H), 7.33–7.24 (m, 5H), 7.19 (dd, \(J = 14.6\), 7.4 Hz, 4H), \(\delta\) 6.38 (d, \(J = 15.8\) Hz, 1H), 6.12 (dd, \(J = 15.8\), 8.6 Hz, 1H), 2.64–2.55 (m, 1H), 2.45 (td, \(J = 15.1\), 7.0 Hz, 1H), 1.25 (d, \(J = 7.0\) Hz, 3H), 0.91 (d, \(J = 6.7\) Hz, 3H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 146.2, 137.8, 135.2, 129.4, 128.5, 128.2, 127.7, 126.9, 126.0, 125.9, 46.0, 44.4, 20.1, 18.1. The minor isomer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36 (d, \(J = 7.4\) Hz, 1H), 7.33–7.24 (m, 5H), 7.19 (dd, \(J = 14.6\), 7.4 Hz, 4H), 6.27 (d, \(J = 15.9\) Hz, 1H), 6.02 (dd, \(J = 15.9\), 8.0 Hz, 1H), 2.80 (p, \(J = 7.0\) Hz, 1H), 2.52 (dd, \(J = 13.8\), 7.0 Hz, 1H), 1.29 (d, \(J = 7.0\) Hz, 3H), 1.05 (d, \(J = 6.8\) Hz, 3H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 145.1, 137.9, 134.6, 129.0, 128.4, 128.1, 127.9,
126.8, 126.0, 125.9, 45.3, 43.3, 19.3, 17.4. HRMS (EI) m/z calcd for [C$_{18}$H$_{20}$, M]$^+$: 236.1565, Found: 236.1560.
4. Hydroalkenylation Procedure and Characterization of Products

a) General procedure for hydroalkenylation

\[
\begin{align*}
R^1 & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
R^2 & \quad \text{H} \\
\end{align*}
\]

In an argon-filled glove-box, an oven-dried tube was charged with a stir bar, Ni(COD)_2 (5.5 mg, 0.020 mmol), ligand P(4-CF_3C_6H_4)_3 (11.2 mg, 0.024 mmol), 1,3-diene 1 (0.40 mmol) and tBuOLi (1.6 mg, 0.020 mmol). The tube was sealed and removed from the glove box, and the degassed \( \alpha,\beta \)-unsaturated hydrazone solution 5 (0.20 mmol, 1.0 M in EtOH) and degassed ethanol (Note that the total dosage of EtOH was 1.5 mL) were injected into the tube under argon. The mixture was stirred at room temperature for 5 minutes and heated at 80 °C for 8 hours. After cooling to room temperature, the solvent was removed under vacuum. The pure product 6 was obtained by preparative TLC.

b) Characterization of products

((1\(E\),4\(E\))-3-methylhexa-1,4-diene-1,6-diyl)dibenzene (6a)

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

55% yield. Isolated by preparative TLC (PE). Colorless oil. \(^1\)H NMR (400 MHz, CDCl_3) \( \delta \) 7.38–7.32 (m, 2H), 7.31–7.27 (m, 4H), 7.23–7.14 (m, 4H), 6.36 (d, \( J = 15.9 \) Hz, 1H), 6.17 (dd, \( J = 15.9, 6.9 \) Hz, 1H), 5.67–5.52 (m, 2H), 3.37 (d, \( J = 6.4 \) Hz, 2H), 3.09–2.97 (m, 1H), 1.19 (d, \( J = 6.9 \) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl_3) \( \delta \) 140.8, 137.7, 135.5, 134.8, 128.5, 128.5, 128.4, 128.3, 128.0, 126.9, 126.0, 125.9, 39.6, 39.0, 20.3. HRMS (EI) \( m/z \) calcd for [C_{19}H_{20}, M]^+: 248.1565, Found: 248.1560.

1-methoxy-4-((2\(E\),5\(E\))-4-methyl-6-phenylhexa-2,5-dien-1-yl)benzene (6b)

\[
\text{Ph} \quad \text{Me} \quad \text{OMe}
\]

63% yield. Isolated by preparative TLC (PE). Colorless oil. \(^1\)H NMR (400 MHz, CDCl_3) \( \delta \) 7.35 (d, \( J = 7.3 \) Hz, 2H), 7.29 (t, \( J = 7.3 \) Hz, 2H), 7.19 (t, \( J = 7.6 \) Hz, 1H), 7.11 (d, \( J = 8.4 \) Hz, 2H), 6.84 (d, \( J = 8.4 \) Hz, 2H), 6.35 (d, \( J = 15.9 \) Hz, 1H), 6.17 (dd, \( J = 15.9, 6.9 \) Hz, 1H), 5.70–5.44 (m, 2H), 3.78 (s, 3H), 3.30 (d, \( J = 6.3 \) Hz, 2H), 3.07–2.98 (m, 1H), 1.19 (d, \( J = 6.9 \) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl_3) \( \delta \) 157.9, 137.7, 135.2, 134.9, 132.8, 129.4, 128.4, 128.2, 127.8, 126.9, 126.0, 113.8, 55.2, 39.6, 38.1, 20.4. HRMS (EI) \( m/z \) calcd for [C_{20}H_{22}O, M]^+: 278.1671, Found: 278.1668.

((1\(E\),4\(E\))-6-cyclopropyl-3-methylhexa-1,4-diene-1,6-diyl)dibenzene (6c)
75% yield, 1.5:1 dr. Colorless oil. Isolated by preparative TLC (PE). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ the major isomer 7.37–7.27 (m, 8H), 7.20 (dd, $J = 13.8, 7.0$ Hz, 2H), 6.34 (d, $J = 6.7$ Hz, 1H), 6.20 (dd, $J = 6.7, 3.0$ Hz, 1H), 5.64 (d, $J = 6.7$ Hz, 1H), 5.57 (t, $J = 6.1$ Hz, 1H), 3.06–3.01 (m, 1H), 2.60 (t, $J = 7.7$ Hz, 1H), 1.19 (dd, $J = 6.7, 4.5$ Hz, 3H), 1.13–0.98 (m, 1H), 0.67–0.55 (m, 1H), 0.53–0.46 (m, 1H), 0.30–0.18 (m, 2H); $\delta$ the minor isomer 7.37–7.27 (m, 8H), 7.20 (dd, $J = 13.8, 7.0$ Hz, 2H), 6.38 (d, $J = 6.6$ Hz, 1H), 6.16 (dd, $J = 6.7, 3.0$ Hz, 1H), 5.68 (d, $J = 6.6$ Hz, 1H), 5.53 (t, $J = 6.1$ Hz, 1H), 3.06–3.01 (m, 1H), 2.60 (t, $J = 7.7$ Hz, 1H), 1.19 (dd, $J = 6.7, 4.5$ Hz, 3H), 1.13–0.98 (m, 1H), 0.67–0.55 (m, 1H), 0.53–0.46 (m, 1H), 0.30–0.18 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.8, 137.8, 135.0 (135.0), 134.1, 132.0, 131.9, 128.5, 128.3 (128.3), 128.2, 127.8, 126.9, 126.1, 52.7 (52.7), 39.6, 20.4 (20.4), 16.3 (16.3), 4.5, 4.2 (4.1). HRMS (EI) m/z calcd for [C$_{22}$H$_{24}$, M]$^+$: 288.1878, Found: 288.1876.

((1$E$,4$E$)-3,6-dimethylhepta-1,4-dien-1-yl)benzene (6d)

84% yield. Isolated by preparative TLC (PE). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39–7.33 (m, 2H), 7.31–7.25 (m, 2H), 7.22–7.16 (m, 1H), 6.34 (d, $J = 15.9$ Hz, 1H), 6.17 (dd, $J = 15.9, 6.9$ Hz, 1H), 5.40 (qd, $J = 15.6, 5.9$ Hz, 2H), 3.04–2.84 (m, 1H), 2.32–2.19 (m, 1H), 1.16 (d, $J = 6.9$ Hz, 3H), 0.98 (d, $J = 6.8$ Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.8, 136.7, 135.4, 130.9, 128.4, 128.0, 126.8, 126.0, 39.6, 31.0, 22.6, 22.6, 20.5. HRMS (EI) m/z calcd for [C$_{15}$H$_{20}$, M]$^+$: 200.1565, Found: 200.1560.

((1$E$,4$E$)-3,5-dimethylhexa-1,4-diene-1,6-diyldibenzene (6e)

62% yield. Isolated by preparative TLC (PE). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 (d, $J = 7.3$ Hz, 2H), 7.28 (t, $J = 7.6$ Hz, 4H), 7.22–7.15 (m, 4H), 6.34 (d, $J = 15.9$ Hz, 1H), 6.17 (dd, $J = 15.9, 6.4$ Hz, 1H), 5.20 (d, $J = 8.9$ Hz, 1H), 3.35–3.19 (m, 3H), 1.59 (s, 3H), 1.17 (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.2, 137.8, 135.1, 134.2, 130.4, 128.8, 128.4, 128.2, 127.6, 126.8, 126.0, 126.0, 46.2, 35.7, 21.1, 16.0. HRMS (EI) m/z calcd for [C$_{20}$H$_{22}$, M]$^+$: 262.1722, Found: 262.1718.

((1$E$,4$E$)-3,5-dimethylhepta-1,4-dien-1-yl)benzene (6f)

84% yield. Isolated by preparative TLC (PE). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37–7.32 (m, 2H), 7.30–7.26 (m, 2H), 7.20–7.15 (m, 1H), 6.33 (d, $J = 15.9$ Hz, 1H), 6.15 (dd, $J = 15.9, 6.5$ Hz, 1H), 5.08–4.98 (m, 1H), 3.29–3.14 (m, 1H), 2.02 (q, $J = 7.4$ Hz, 2H), 1.66 (d, $J = 1.2$ Hz, 3H), 1.13 (d, $J = 6.8$ Hz, 3H), 1.01 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.9, 136.7, 135.5, 128.4, 127.2, 126.8, 126.7, 126.0, 35.6, 32.3, 21.2, 16.2, 12.7. HRMS (EI) m/z calcd for [C$_{15}$H$_{20}$, M]$^+$: 200.1565, Found: 200.1560.

((1$E$,4$E$)-3,6,10-trimethylundeca-1,4,9-trien-1-yl)benzene (6g)
55% yield, 1:1 dr. Isolated by preparative TLC (PE).
Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 (d, $J = 7.6$ Hz, 2H), 7.29 (t, $J = 7.4$ Hz, 2H), 7.19 (t, $J = 7.2$ Hz, 1H), 6.35 (d, $J = 15.9$ Hz, 1H), 6.17 (dd, $J = 15.9$, 6.8 Hz, 1H), 5.35 (qd, $J = 15.4$, 6.8 Hz, 2H), 5.10 (t, $J = 6.8$ Hz, 1H), 3.07–2.91 (m, 1H), 2.10 (dt, $J = 13.7$, 6.8 Hz, 1H), 1.96 (d, $J = 7.3$ Hz, 2H), 1.68 (s, 3H), 1.59 (s, 3H), 1.30 (q, $J = 7.4$ Hz, 2H), 1.17 (d, $J = 6.8$ Hz, 3H), 0.98 (d, $J = 6.7$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.8, 135.4, 135.3, 132.3, 131.2, 128.4, 128.0 (127.9), 126.8, 126.0, 124.8 (124.77), 39.7 (39.6), 37.2, 36.3, 25.8 (25.8), 25.7, 20.9 (20.8), 20.6 (20.5), 17.7. HRMS (EI) $m/z$ calcld for [C$_{20}$H$_{28}$, M]$^+$: 268.2191, Found: 268.2188.

(E)-(4-cyclopentylidene-3-methylbut-1-en-1-yl)benzene (6h)

1a (0.2 mmol), $\alpha$, $\beta$-unsaturated hydrazones 5 (0.4 mmol). 65% yield. Isolated by preparative TLC (PE). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37–7.31 (m, 2H), 7.32–7.24 (m, 2H), 7.21–7.13 (m, 1H), 6.33 (d, $J = 15.9$ Hz, 1H), 6.15 (dd, $J = 15.9$, 6.8 Hz, 1H), 5.25–5.13 (m, 1H), 3.17–2.99 (m, 1H), 2.32–2.13 (m, 4H), 1.73–1.55 (m, 4H), 1.14 (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.0, 137.9, 135.2, 128.4, 127.1, 126.7, 126.0, 123.6, 37.7, 33.7, 28.6, 26.4, 20.9. HRMS (EI) $m/z$ calcld for [C$_{16}$H$_{20}$, M]$^+$: 212.1565, Found: 212.1560.

(E)-(4-cyclohexylidene-3-methylbut-1-en-1-yl)benzene (6i)

1a (0.2 mmol), $\alpha$, $\beta$-unsaturated hydrazones 5 (0.4 mmol). 81% yield. Isolated by preparative TLC (PE). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 (d, $J = 7.6$ Hz, 2H), 7.28 (t, $J = 7.6$ Hz, 2H), 7.17 (t, $J = 7.2$ Hz, 1H), 6.33 (d, $J = 15.9$ Hz, 1H), 6.16 (dd, $J = 15.9$, 6.3 Hz, 1H), 4.99 (d, $J = 8.8$ Hz, 1H), 3.31–3.22 (m, 1H), 2.26–2.13 (m, 2H), 2.12–2.06 (m, 2H), 1.57–1.48 (m, 6H), 1.13 (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 139.4, 138.0, 135.9, 128.5, 127.3, 126.8, 126.0, 125.1, 37.2, 34.7, 29.2, 28.8, 20.8, 26.9, 21.5. HRMS (EI) $m/z$ calcld for [C$_{17}$H$_{22}$, M]$^+$: 226.1722, Found: 226.1714.

(E)-(3-methyl-4-(4-(prop-1-en-2-yl)cyclohexylidene)but-1-en-1-yl)benzene (6j)

71% yield. Isolated by preparative TLC (PE). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ the major isomer 7.37–7.31 (m, 2H), 7.31–7.25 (m, 2H), 7.21–7.15 (m, 1H), 6.31 (d, $J = 15.0$ Hz, 1H), 6.18 (dd, $J = 15.0$, 6.3 Hz, 1H), 5.03 (d, $J = 7.5$ Hz, 1H), 4.69 (s, 2H), 3.34–3.22 (m, 1H), 2.68 (d, $J = 13.9$ Hz, 1H), 2.28–2.2 (m, 1H), 2.15–2.03 (m, 2H), 1.85–1.76 (m, 3H), 1.72 (s, 3H), 1.36–1.18 (m, 2H), 1.17–1.11 (m, 3H). $\delta$ the minor isomer 7.31–7.25 (m, 2H), 7.21–7.15 (m, 1H), 6.35 (d, $J = 15.3$ Hz, 1H), 6.14 (dd, $J = 15.3$, 6.2 Hz, 1H), 5.01 (d, $J = 7.9$ Hz, 1H), 4.67 (s, 2H), 3.34–3.22 (m, 1H), 2.68 (d, $J = 13.9$ Hz, 1H), 2.28–2.2 (m, 1H), 2.15–2.03 (m, 2H), 1.85–1.76 (m, 3H), 1.71 (s, 3H), 1.36–1.18 (m, 2H), 1.17–1.11 (m, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 150.3 (150.2), 138.4 (138.4), 137.9 (137.9), 135.8 (135.6), 128.4
(E)-(3-(cyclohexyldenemethyl)pent-1-en-1-yl)benzene (6k)

48% yield. Isolated by preparative TLC (PE). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 (d, $J = 7.6$ Hz, 2H), 7.28 (t, $J = 7.6$ Hz, 2H), 7.17 (t, $J = 7.2$ Hz, 1H), 6.33 (d, $J = 15.9$ Hz, 1H), 6.11 (dd, $J = 15.9$, 7.1 Hz, 1H), 4.96 (d, $J = 9.1$ Hz, 1H), 3.13–2.86 (m, 1H), 2.26–2.00 (m, 4H), 1.56–1.46 (m, 1H), 1.43–1.30 (m, 1H), 0.90 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.2, 138.0, 134.7, 128.4, 128.2, 126.7, 126.0, 123.7, 42.4, 37.4, 29.3, 28.9, 28.8, 27.9, 26.9, 11.9. HRMS (EI) m/z calcd for [C$_{18}$H$_{26}$O, M]$^+$: 240.1872, Found: 240.1872.

(E)-5-(4-cyclohexyldiene-3-methylbut-1-en-1-yl)benzo[d][1,3]dioxole (6l)

Diene (0.2 mmol, $E$-isomer), $\alpha,\beta$-unsaturated hydrazones 5 (0.4 mmol). 70% yield. Isolated by preparative TLC (PE). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.90 (d, $J = 1.3$ Hz, 1H), 6.78–6.70 (m, 2H), 6.24 (d, $J = 15.9$ Hz, 1H), 5.99 (dd, $J = 15.9$, 6.6 Hz, 1H), 5.92 (s, 2H), 4.97 (d, $J = 8.8$ Hz, 1H), 3.31–3.14 (m, 1H), 2.22–2.12 (m, 2H), 2.10–2.05 (m, 2H), 1.56–1.47 (m, 6H), 1.11 (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.9, 146.5, 139.3, 134.2, 132.6, 126.9, 125.2, 120.3, 108.2, 105.0, 100.9, 37.2, 34.6, 29.2, 28.7, 28.0, 26.9, 21.5. HRMS (EI) m/z calcd for [C$_{18}$H$_{25}$O, M]$^+$: 270.1620, Found: 270.1616.

(E)-2-(4-cyclohexyldiene-3-methylbut-1-en-1-yl)furan (6m)

Diene (0.2 mmol), $\alpha,\beta$-unsaturated hydrazones 5 (0.4 mmol). 73% yield. Isolated by preparative TLC (PE). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30–7.28 (m, 1H), 6.34–6.31 (m, 1H), 6.16–6.11 (m, 3H), 4.95 (d, $J = 8.8$ Hz, 1H), 3.28–3.19 (m, 1H), 2.22–2.12 (m, 2H), 2.11–2.06 (m, 2H), 1.54 (s, 6H), 1.11 (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 153.5, 141.2, 139.6, 134.9, 124.8, 116.2, 111.1, 106.1, 37.2, 34.3, 29.2, 28.7, 27.9, 26.9, 21.3. HRMS (EI) m/z calcd for [C$_{12}$H$_{20}$O, M]$^+$: 216.1514, Found: 216.1508.

(E)-2-(4-cyclohexyldiene-3-methylbut-1-en-1-yl)thiophene (6n)

Diene (0.2 mmol), $\alpha,\beta$-unsaturated hydrazones 5 (0.4 mmol). 72% yield. Isolated by preparative TLC (PE). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.07 (d, $J = 5.0$ Hz, 1H), 6.96–6.90 (m, 1H), 6.86 (d, $J = 3.3$ Hz, 1H), 6.45 (d, $J = 15.7$ Hz, 1H), 6.02 (dd, $J = 15.7$, 6.2 Hz, 1H), 4.96 (d, $J = 8.9$ Hz, 1H), 3.35–3.14 (m, 1H), 2.21–2.13 (m, 2H), 2.11–2.06 (m, 2H), 1.57–1.48 (m, 6H), 1.11 (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.3, 139.6,
135.8, 127.2, 124.8, 124.3, 123.0, 120.7, 37.2, 34.4, 29.1, 28.7, 27.9, 26.9, 21.3. HRMS (EI) $m/z$ calcd for [C$_{15}$H$_{20}$S, M]$^+$: 232.1286, Found: 232.1282.
5. Synthetic Application

![Chemical Structure]

**Ethyl (E)-4-(7-ethoxy-2-(2-methoxystyryl)-7-oxoheptyl)benzoate (7)**

The hydroalkylation was conducted in a modified procedure. In an argon-filled glove box, an oven-dried tube was charged with a stir bar, Ni(COD)$_2$ (87.0 mg, 0.317 mmol), ligand P(4-CF$_3$C$_6$H$_4$)$_3$ (178 mg, 0.380 mmol), 1,3-diene 1u (1.30 g, 4.76 mmol), hydrazone 2g (0.610 g, 3.17 mmol) and tBuOLi (25.0 mg, 0.317 mmol). The tube was sealed and removed from the glove box, and degassed ethanol (32.0 mL) was injected into the tube under argon. The mixture was stirred at room temperature for 5 minutes and heated at 80 °C for 8 hours. After cooling to room temperature, the solvent was evaporated under vacuum. The pure product 7 was obtained by flash silica gel chromatography (PE/EA = 15:1) as light yellow oil (1.06 g, 2.42 mmol, 76% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 7.9$ Hz, 2H), 7.36 (d, $J = 7.5$ Hz, 1H), 7.25–7.10 (m, 3H), 6.89 (t, $J = 7.5$ Hz, 1H), 6.83 (d, $J = 8.2$ Hz, 1H), 6.56 (d, $J = 16.0$ Hz, 1H), 5.95 (dd, $J = 16.0$, 8.8 Hz, 1H), 4.35 (q, $J = 7.1$ Hz, 2H), 4.09 (q, $J = 7.1$ Hz, 2H), 3.79 (s, 3H), 2.77 (d, $J = 6.9$ Hz, 2H), 2.53–2.43 (d, $J = 4.3$ Hz, 1H), 2.25 (t, $J = 7.5$ Hz, 2H), 1.66–1.52 (m, 2H), 1.51–1.30 (m, 7H), 1.22 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 173.7, 166.7, 156.3, 146.0, 134.1, 129.4, 129.3, 128.1, 128.0, 126.5, 126.3, 125.0, 120.5, 110.9, 60.7, 60.1, 55.4, 44.9, 42.2, 34.2, 34.2, 26.8, 24.9, 14.3, 14.2. HRMS (ESI) calcd for [C$_{27}$H$_{34}$NaO$_5$, M+Na]$^+$: 461.2298, Found: 461.2303.

(E)-4-(6-carboxy-2-(2-methoxystyryl)hexyl)benzoic acid (8)

To a solution of substrate 7 (1.06 g, 2.42 mmol) in ethanol (36.0 ml) and tetrahydrofuran (36.0 ml) was added NaOH (2.0 M, 18.2 ml, 36.3 mmol). The mixture was stirred overnight at room temperature. The solvents were evaporated under vacuum, and 10 mL H$_2$O was added to the residue. The aqueous solution was adjusted to pH 2–4 via addition of 6 N HCl. The
resulting aqueous solution was extracted with EtOAc (20 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate, and concentrated to give a light yellow solid. The solid was washed with a little amount of MeOH and petroleum ether, dried to give the title product 8 (0.88 g, 95% yield). White solid, mp: 151–152 °C. $^1$H NMR (400 MHz, DMSO) δ 12.38 (s, 2H), 7.82 (d, $J = 7.7$ Hz, 2H), 7.38 (d, $J = 7.4$ Hz, 1H), 7.29 (d, $J = 7.6$ Hz, 2H), 7.17 (t, $J = 7.6$ Hz, 1H), 6.92 (d, $J = 8.1$ Hz, 1H), 6.87 (t, $J = 7.4$ Hz, 1H), 6.42 (d, $J = 15.8$ Hz, 1H), 6.01 (dd, $J = 15.8, 8.7$ Hz, 1H), 3.72 (s, 3H), 2.79 (dd, $J = 12.7, 5.6$ Hz, 1H), 2.73–2.62 (m, 1H), 2.50–2.38 (m, 1H), 2.16 (t, $J = 6.9$ Hz, 2H), 1.57–1.17 (m, 6H); $^{13}$C NMR (101 MHz, DMSO) δ 174.5, 167.4, 155.8, 145.9, 134.3, 129.4, 129.2, 128.3, 128.2, 125.9, 125.7, 124.1, 120.5, 111.3, 55.4, 44.7, 41.4, 34.1, 33.6, 26.4, 24.6. HRMS (ESI) calcd for [C$_{23}$H$_{25}$O$_5$, M-H]: 381.1707, Found: 381.1705.
6. Mechanism Studies

a) Labelling experiment of hydroalkylation in ethanol-D

In an argon-filled glove-box, an oven-dried tube charged with a stir bar, Ni(COD)\(_2\) (5.5 mg, 0.020 mmol), ligand P(4-CF\(_3\)C\(_6\)H\(_4\))\(_3\) (11.2 mg, 0.024 mmol), 1,3-diene 1a (0.40 mmol), hydrazone 2a (0.20 mmol) and 1BuOLi (1.6 mg, 0.020 mmol) were added. The tube was sealed and removed from the glove box, and degassed ethanol-D (1.5 mL) was injected into the tube under argon. The mixture was stirred at room temperature for 5 minutes and heated at 80 °C for 1 hour. The reaction was concentrated and 1,3,5-trimethoxybenzene was added as internal standard. The deuterium incorporation was analyzed by \(^1\)H NMR. The 3a was obtained in 71% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.38–7.27 (m, 6H), 7.26–7.22 (m, 4H), 6.35 (d, \(J = 15.9\) Hz, 1H), 6.23 (dd, \(J = 15.9, 7.1\) Hz, 1H), 2.83–2.77 (m, 0.5H), 2.68–2.61 (m, 1.5H), 1.14–1.09 (m, 1.98 H); 32% 1,3-diene was recovered with < 5% deuterium into the terminal diene C–H bonds.
In an argon-filled glove-box, an oven-dried tube charged with a stir bar, Ni(COD)$_2$ (5.5 mg, 0.020 mmol), ligand P(4-CF$_3$C$_6$H$_4$)$_3$ (11.2 mg, 0.024 mmol), 1,3-diene 1a (0.40 mmol), hydrazone 5d (0.20 mmol, EtOH of 5d solution was evaporated before use) and tBuOLi (1.6 mg, 0.020 mmol) were added. The tube was sealed and removed from the glove box, and degassed ethanol-D (1.5 mL) was injected into the tube under argon. The reaction mixture was stirred at room temperature for 5 minutes and heated at 80 °C for 1 hour. The reaction was concentrated and 1,3,5-trimethoxybenzene was added as internal standard. The deuterium incorporation was analyzed by $^1$H NMR. The product 6d was obtained in 67% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38–7.33 (m, 2H), 7.29 (t, $J = 7.6$ Hz, 2H), 7.21–7.15 (m, 1H), 6.34 (d, $J = 16.0$ Hz, 1H), 6.17 (dd, $J = 16.0$, 6.9 Hz, 1H), 5.48–5.31 (m, 2H), 3.04–2.89 (m, 1H), 2.35–2.24 (m, 2H), 1.15 (t, $J = 6.8$ Hz, 1.94H), 0.98 (s, 6H); 28% 1,3-diene was recovered with < 5% deuterium into the terminal diene C−H bonds.
c) Labelling experiment using deuterated phenyl hydrazone 2a’

In an argon-filled glove-box, an oven-dried tube charged with a stir bar, Ni(COD)$_2$ (5.5 mg, 0.020 mmol), ligand P(4-CF$_3$C$_6$H$_4$)$_3$ (11.2 mg, 0.024 mmol), 1,3-diene 1a (0.40
mmol), hydrazone D-2a’ (0.20 mmol) and 'BuOLi (1.6 mg, 0.020 mmol) were added. The tube was sealed and removed from the glove box, and degassed ethanol (1.5 mL) was injected into the tube under argon. The mixture was stirred at room temperature for 5 minutes and heated at 80 °C for 8 hours. After cooling to room temperature, the solvent was removed under vacuum. The pure product 3a was obtained as light yellow oil in 90% yield by preparative TLC (PE). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37–7.23 (m, 6H), 7.21–7.15 (m, 4H), 6.31 (d, \(J = 15.9\) Hz, 1H), 6.19 (dd, \(J = 15.9, 7.0\) Hz, 1H), 2.78–2.73 (m, 0.5H), 2.64–2.57 (m, 1.5H), 1.08 (d, \(J = 6.4\) Hz, 3H).

![NMR spectrum of 3a](image)
7. NMR Spectra of Important Compounds

\[ \text{((1E)-7-(benzyloxy)hepta-1,3-dien-1-yl)benzene (1p)} \]
4-((6E)-7-phenylhepta-4,6-dien-1-yl)morpholine (1q)
((1\textit{E})-7,7-dimethoxyhepta-1,3-dien-1-yl)benzene (1r)
(E)-1-benzyl-4-(buta-1,3-dien-1-yl)piperidine (1s)
Ethyl (7E)-8-(2-methoxyphenyl)octa-5,7-dienoate (1t)
(4-(methylthio)benzylidene)hydrazine (2f)
(4-(trimethylsilyl)benzylidene)hydrazine (2h)
2-(hydrazonomethyl)-1-methyl-1H-pyrrole (2o)
(E)-(3-methylbut-1-ene-1,4-diyl)dibenzene (3a)
(E)-1-(3-methyl-4-phenylbut-1-en-1-yl)-4-(trifluoromethyl)benzene (3f)
(E)-1,3-dimethoxy-5-(3-methyl-4-phenylbut-1-en-1-yl)benzene (3g)
(E)-1-methyl-3-(3-methyl-4-phenylbut-1-en-1-yl)benzene (3h)
\( (E)-1\text{-methyl-2-}(3\text{-methyl-4-phenylbut-1-en-1-yl})\text{benzene (3i)} \)
(E)-2-(3-methyl-4-phenylbut-1-en-1-yl)furan (3j)
(E)-2-(3-methyl-4-phenylbut-1-en-1-yl)thiophene (3k)
(E)-(3-benzylbut-1-ene-1,4-diyl)dibenzene (3m)
Ethyl (E)-5-benzyl-7-phenylhept-6-enoate (3n)
(E)-((5-benzyl-7-phenylhept-6-en-1-yl)oxy)(tert-butyl)dimethylsilane (3o)
(E)-(3-(4-(benzyloxy)butyl)but-1-ene-1,4-diyl)dibenzene (3p)
(E)-4-(5-benzyl-7-phenylhept-6-en-1-yl)morpholine (3q)
(E)-(3-(4,4-dimethoxybutyl)but-1-ene-1,4-diyl) dibenzene (3r)
Ethyl \((E)-4-(4\text{-cyclohexyl}-2\text{-methylbut}-3\text{-en}-1\text{-yl})\)benzoate (3s)
Ethyl (E)-4-(4-(1-benzylpiperidin-4-yl)-2-methylbut-3-en-1-yl)benzoate (3t)
(E)-1-methyl-4-(2-methyl-4-phenylbut-3-en-1-yl)benzene (4a)
(E)-1-(2-methyl-4-phenylbut-3-en-1-yl)-4-(trifluoromethyl)benzene (4b)
(E)-1-fluoro-4-(2-methyl-4-phenylbut-3-en-1-yl)benzene (4c)
(E)-4-(2-methyl-4-phenylbut-3-en-1-yl)benzonitrile (4d)
(E)-methyl(4-(2-methyl-4-phenylbut-3-en-1-yl)phenyl)sulfane (4f)
Ethyl (E)-4-(2-methyl-4-phenylbut-3-en-1-yl)benzoate (4g)
(E)-trimethyl(4-(2-methyl-4-phenylbut-3-en-1-yl)phenyl)silane (4h)
(E)-1-methyl-3-(2-methyl-4-phenylbut-3-en-1-yl)benzene (4i)
(E)-1-methyl-2-(2-methyl-4-phenylbut-3-en-1-yl)benzene (4j)
(E)-2-(2-methyl-4-phenylbut-3-en-1-yl)naphthalene (4k)
(E)-3-(2-methyl-4-phenylbut-3-en-1-yl)pyridine (4l)

68
(E)-4-(2-methyl-4-phenylbut-3-en-1-yl)pyridine (4m)

\[
\text{[Chemical structure image]}
\]

(17:1)
(E)-2-(2-methyl-4-phenylbut-3-en-1-yl)quinoline (4n)
(E)-1-methyl-2-(2-methyl-4-phenylbut-3-en-1-yl)-1H-pyrrole (4o)
(E)-2-(2-methyl-4-phenylbut-3-en-1-yl)furan (4p)
(E)-2-(2-methyl-4-phenylbut-3-en-1-yl)thiophene (4q)
(E)-(3-methylpent-1-ene-1,4-diyl)dibenzene (4r)
((1E,4E)-3-methylhexa-1,4-diene-1,6-diyl)dibenzene (6a)
1-methoxy-4-((2E,5E)-4-methyl-6-phenylhexa-2,5-dien-1-yl)benzene (6b)
((1E,4E)-3,6-dimethylhepta-1,4-dien-1-yl)benzene (6d)
(1E,4E)-3,5-dimethylhexa-1,4-diene-1,6-diyldibenzene (6e)
((1E,4E)-3,5-dimethylhepta-1,4-dien-1-yl)benzene (6f)
(E)-(4-cyclopentylidene-3-methylbut-1-en-1-yl)benzene (6h)
(E)-(4-cyclohexylidene-3-methylbut-1-en-1-yl)benzene (6i)
(E)-(3-methyl-4-(4-(prop-1-en-2-yl)cyclohexylidene)but-1-en-1-yl)benzene (6j)
(E)-(3-(cyclohexyldienemethyl)pent-1-en-1-yl)benzene (6k)

Parameter Table
1. Name
   2. Molecular Formula
   3. Molecular Weight
   4. Density
   5. Melting Point
   6. Boiling Point
   7. Vapor Pressure
   8. Solubility
   9. Solvent
   10. Reactivity
   11. Stability
   12. Toxicity
   13. Regulation
   14. Compliance
   15. Certification
   16. Analysis
   17. Storage
   18. Transportation
   19. Shipping
   20. Handling
   21. Disposal
   22. Emergency Response
   23. Regulatory
   24. Safety Data Sheet

Diagram:
- Structure of (E)-(3-(cyclohexyldienemethyl)pent-1-en-1-yl)benzene (6k)

Chemical Spectra:
- NMR spectrum showing peaks at various chemical shifts
- Mass spectrum showing molecular ion and fragmentation patterns

Analysis:
- Mass spectral data indicating molecular weight
- NMR spectral data showing proton and carbon resonances

Safety:
- Non-flammable
- Non-toxic
- Non-corrosive
- Non-irritating

Handling:
- Store in a cool, dry place
- Avoid direct sunlight
- Keep away from heat and ignition sources
(E)-5-(4-cyclohexylidene-3-methylbut-1-en-1-yl)benzo[d][1,3]dioxole (6l)
(E)-2-(4-cyclohexylidene-3-methylbut-1-en-1-yl)furan (6m)
(E)-2-(4-cyclohexylidene-3-methylbut-1-en-1-yl)thiophene (6n)
Ethyl (E)-4-(7-ethoxy-2-(2-methoxystyril)-7-oxoheptyl)benzoate (7)
(E)-4-(6-carboxy-2-(2-methoxystyryl)hexyl)benzoic acid (8)
GC-MS chromatograph of azine 5:
GC-MS (EI) m/z calcd for C_{10}H_{16}N_{2}: 164.13, Found: 164.20
8. References


