Electronic Supplementary Information (ESI) for:

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

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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 (¹H NMR), 101 MHz (¹³C NMR). Chemical shifts were reported in ppm relative to internal TMS for ¹H NMR data, deuterated solvent for ¹³C 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)₂] (Strem Chemicals), P(4-CF₃C₆H₄)₃ (Accela), DPPPe (Strem Chemicals), ¹BuOLi (Aladdin), N₂H₄·H₂O (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 procedures¹. (*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^{2e} , step 8^{2f}).



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

Isolated 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). ¹H NMR (400 MHz, CDCl₃) δ *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); δ *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

Isolated by flash silica gel chromatography (PE/EA = 3:1). A mixture of *E*,*Z*–isomer and *E*,*E*–isomer was obtained in 82% yield, *E*,*Z*/*E*,*E* = 3:1. Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ *E*,*Z*–isomer 7.41 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 6.8 Hz, 2H), 7.25–7.15 (m, 1H), 7.07 (dd, *J* = 15.6, 11.1 Hz, 1H), 6.53 (d, *J* = 15.6 Hz, 1H), 6.19 (t, *J* = 10.9 Hz, 1H), 5.52 (q, *J* = 9.1, 8.5 Hz, 1H), 3.68 (td, *J* = 6.2, 1.8 Hz, 2H), 2.38 (q, *J* = 7.5 Hz, 2H), 1.78–1.59 (m, 3H); δ *E*,*E*–isomer 7.37 (d, *J* = 7.4 Hz, 2H), 7.34–7.26 (m, 2H), 7.25–7.15 (m, 1H), 6.75 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.45 (d, *J* = 15.7 Hz, 1H), 6.26–6.16 (m, 1H), 5.81 (dt, *J* = 15.6, 7.3 Hz, 1H), 3.70–3.65 (m, 2H), 2.24 (q, *J* = 7.0 Hz, 2H), 1.73–1.66 (m, 3H). Spectral data matched those previously reported.^{2a}

Tert-butyldimethyl(((6*E*)-7-phenylhepta-4,6-dien-1-yl)oxy)silane (10)

Ph OTBS Isolated by flash silica gel chromatography (PE). A mixture of *E*,*Z*–isomer and *E*,*E*–isomer was obtained in 83% yield, *E*,*Z*/*E*,*E* = 3:1. Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ *E*,*Z*–isomer 7.39 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.06 (dd, *J* = 15.5, 11.1 Hz, 1H), 6.51 (d, *J* = 15.6 Hz, 1H), 6.17 (t, *J* = 11.0 Hz, 1H), 5.57–5.47 (m, 1H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.35 (q, *J* = 5.5 Hz, 2H), 1.71–1.60 (m, 2H), 0.89 (9H, s), 0.04 (6H, s); δ *E*,*E*–isomer 7.36 (d, *J* = 7.7 Hz, 2H), 7.31–7.26 (m, 2H), 7.21–7.16 (m, 1H), 6.75 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.44 (d, *J* = 15.7 Hz, 1H), 6.22 (dd, *J* = 15.0, 10.5 Hz, 1H), 5.81 (dt, *J* = 14.4, 6.8 Hz, 1H), 3.66–3.61 (m, 2H), 2.19 (q, *J* = 7.0 Hz, 2H), 1.71–1.60 (m, 2H), 0.89 (s, 9H), 0.04 (s, 6H). Spectral data matched those previously reported.^{2a}

((1*E*)-7-(benzyloxy)hepta-1,3-dien-1-yl)benzene (1p)

Ph OBn Isolated by flash silica gel chromatography (PE/EA = 10:1). A mixture of *E*,*Z*–isomer and *E*,*E*–isomer was obtained in 80% yield, *E*,*Z*/*E*,*E* = 6.0:1. Colorless oil, bp: 165–168 °C (0.2 Torr). ¹H NMR (400 MHz, CDCl₃) δ *E*,*Z*–isomer 7.38–7.26 (m, 9H), 7.23–7.17 (m, 1H), 7.09 (dd, *J* = 15.6, 11.1, 1H), 6.53 (d, *J* = 15.6 Hz, 1H), 6.19 (t, *J* = 10.6 Hz, 1H), 5.51 (dt, *J* = 10.6, 7.8 Hz, 1H), 4.56 (s, 2H), 3.51 (t, *J* = 6.3 Hz, 2H), 2.41 (qd, *J* = 7.6, 1.3 Hz, 2H), 1.80–1.70 (m, 2H); δ *E*,*E*–isomer 7.38–7.26 (m, 9H), 7.23–7.17 (m, 1H), 6.74 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.43 (d, *J* = 15.6 Hz, 1H), 6.27–6.17 (m, 1H), 5.91–5.74 (m, 1H), 4.50 (s, 2H), 3.51 (t, *J* = 6.3 Hz, 2H), 1.80–1.70 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 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, 127.6, 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 [C₂₀H₂₂NaO, M+Na]⁺: 301.1563, Found: 301.1568.

4-((6E)-7-phenylhepta-4,6-dien-1-yl)morpholine (1q)

Photomorphic Normal Soluted by flash silica gel chromatography (EA). A mixture of *E*,*Z*–isomer and *E*,*E*–isomer was obtained in 63% yield for two steps, *E*,*Z*/*E*,*E* = 3.0:1. Yellow oil. ¹H NMR (400 MHz,

CDCl₃) δ *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); δ *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); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₁₇H₂₄NO, M+H]⁺: 258.1852, Found: 258.1856.

((1*E*)-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). ¹H NMR (400 MHz, CDCl₃) δ *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); δ *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); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₁₅H₂₀NaO₂, M+Na]⁺: 255.1356, Found: 255.1360.

Method C: Aliphatic 1,3-dienes **1s–1t** were prepared by olefination reactions with allylic phosphonate³. To a solution of diethyl allylphosphonate (1.07 g, 6.0 mmol) in anhydrous THF (15 mL), "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 NH₄Cl solution. The mixture was extracted with Et₂O (3 × 15 mL). The combined organic phases were washed with brine (30 mL), dried (MgSO₄) 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)

BnN

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), 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, 129.0, 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 (7*E*)-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); ¹³C NMR (101 MHz, CDCl₃) δ 173.6, 156.6, 133.5, 132.2, 129.8, 128.2, 126.5, 126.2, 125.3, 120.6, 110.8, 60.2, 55.4, 33.7, 3.13, 24.5, 14.2. HRMS (ESI) calcd for [C₁₇H₂₂NaO₃, 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 procedure⁴.

$$R-CHO \xrightarrow{N_2H_4 \cdot H_2O (3 \text{ equiv})}_{EtOH, \text{ rt, 2-24 h}} R^{NNH_2}$$

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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (101 MHz, CDCl₃) δ 142.7, 139.2, 131.9, 126.5, 126.2, 15.5. HRMS (ESI) calcd for [C₈H₁₁N₂S, M+H]⁺: 167.0637, Found: 167.0639.

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



Light yellow solid, mp: 47–48 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (s, 1H), 7.55–7.44 (m, 4H), 5.54 (s, 2H), 0.26 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 143.1, 141.2, 135.4, 133.5, 125.4, -1.2. HRMS

(ESI) calcd for $[C_{10}H_{17}N_2Si, M+H]^+$: 193.1156, Found: 193.1157.

2-(hydrazonomethyl)-1-methyl-1H-pyrrole (20)

Brown solid, mp: 35–36 °C. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (101 MHz, CDCl₃) δ 137.4, 128.1, 126.0, 112.2, 107.7, 36.4. HRMS (ESI) calcd for [C₆H₁₀N₃, 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)

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.

Fable S2 : Optimization of reaction co	nditions (additives/so	lvent/temperature/ratio)
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4	2 NNH ₂	Ni(COD) ₂ (10 m P(4-CF ₃ C ₆ H ₄) ₃ (12	nol %) 2 mol %)	Ph +	<u>^</u>	
Ph' ~ 3 3 1a	1 Ph additives (1 2a solvent, Te		iol %) , 8 h	Ph Me 3a (1,2-addition)	Ph Ph 3a' (1,4-addition)	
entry	additives	solvent	temp. (°C)	ratio (1a / 2a)	yield (%) ^a	3a/3a' ^b
1	^t BuOLi (1.0 equiv)	EtOH	80	1:1.5	85	>20:1
2	'BuOLi (0.1 equiv)	EtOH	80	1:1.5	85	>20:1

3	^t BuOLi (0.05 equiv)	EtOH	80	1:1.5	69	15:1
4	none	EtOH	80	1:1.5	30	6:1
5	Na ₂ CO ₃	EtOH	80	1:1.5	43	9:1
6	^t BuONa	EtOH	80	1:1.5	78	19:1
7	NaOH	EtOH	80	1:1.5	82	>20:1
8	NaOEt	EtOH	80	1:1.5	81	>20:1
9	K ₃ PO ₄	EtOH	80	1:1.5	75	19:1
10	^t BuOLi	THF	80	1:1.5	7	2:1
11	^t BuOLi	Toluene	80	1:1.5	7	1:2
12	^t BuOLi	MeOH	80	1:1.5	28	11:1
13	^t BuOLi	"PrOH	80	1:1.5	80	>20:1
14	^t BuOLi	ⁱ PrOH	80	1:1.5	71	16:1
15	'BuOLi	EtOH (0.25 mL)	80	1:1.5	68	14:1
16	'BuOLi	EtOH (0.50 mL)	80	1:1.5	79	>20:1
17	'BuOLi	EtOH (1.0 mL)	80	1:1.5	82	>20:1
18	'BuOLi	EtOH	rt (23)	1:1.5	53	18:1
19	'BuOLi	EtOH	40	1:1.5	51	18:1
20	'BuOLi	EtOH	60	1:1.5	82	>20:1
21	'BuOLi	EtOH	100	1:1.5	73	>20:1
22	^t BuOLi	EtOH	80	1:2	76	>20:1
23	'BuOLi	EtOH	80	1.5:1	81	>20:1
24	^t BuOLi	EtOH	80	2:1	95 (92) ^c	>20:1

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. ^{*a*} ¹H NMR yields of major isomer **3a** using 1,3,5-trimethoxybenzene as internal standard. ^{*b*} Regioselectivity was determined by ¹H NMR analysis of reaction mixture. ^{*c*} Isolated yield in the parentheses. ^{*d*} 83% yield when using 5 mol % catalyst in the optimized condition.

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-CF₃C₆H₄)₃ (0.024 mmol), 'BuOLi (0.020 mmol), EtOH (1.5 mL) at 80 °C for 8 h. Isolated yields.

Regioselectivity was determined by ¹H NMR analysis, isomers were determined by ¹H 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-CF₃C₆H₄)₃ (11.2 mg, 0.024 mmol), 1,3-diene **1** (0.40 mmol), hydrazone **2** (0.20 mmol) and '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. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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 calcd for [C₁₈H₂₀, 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. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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, 127.4, 127.1, 125.9, 115.3 (d, J = 21.5 Hz), 43.6, 38.8, 19.7; ¹⁹F NMR (376 MHz, CDCl₃) δ –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. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) 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)

 F_{3C} Ph (2:1 Me prep δ 7.5

(2:1 *Z/E*)–**1f** was used. 95% yield, **3f**/**3f**' >20:1. Isolated by preparative TLC (PE). Colorless oil. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (101 MHz, CDCl₃) 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; ¹⁹F NMR (376 MHz, CDCl₃) δ –58.1. HRMS (EI) m/z calcd for [C₁₈H₁₇F₃, 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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (101 MHz, CDCl₃) 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 [C₁₉H₂₂O₂, 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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (101 MHz, CDCl₃) 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 [C₁₈H₂₀, 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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (101 MHz, CDCl₃) 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 [C₁₈H₂₀, M]⁺: 236.1565, Found: 236.1558.

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



E–**1j** was used. 76% yield, **3**j/**3**j' >20:1. Isolated by preparative TLC (PE). Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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* calcd for [C₁₅H₁₆O, M]⁺: 212.1201, Found: 212.1196.

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



(1:1 Z/E)–**1k** was used. 96% yield, **3k**/**3k**' >20:1. Isolated by preparative TLC (PE). Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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 calcd for [C₁₅H₁₆S, M]⁺: 228.0973, Found: 228.0971.

(E)-(3-ethylbut-1-ene-1,4-diyl)dibenzene (3l)



(1:1.5 *E*,*Z*/*E*,*E*)–**11** was used. 83% yield, **31**/**31**' 20:1. Isolated by preparative TLC (PE). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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 calcd for [C₁₈H₂₀, M]⁺: 236.1565, Found: 236.1560.

(E)-(3-benzylbut-1-ene-1,4-diyl)dibenzene (3m)



E,*E*–**1m** was used. 69% yield, **3m**/**3m**' >20:1. Isolated by preparative TLC (PE/EA = 100:1). Light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101

MHz, CDCl₃) δ 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* calcd for [C₂₃H₂₂, M]⁺: 298.1722, Found: 298.1718.

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



(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. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₂₂H₂₆, M]⁺: 322.1933, Found: 322.1927.

(E)-((5-benzyl-7-phenylhept-6-en-1-yl)oxy)(tert-butyl)dimethylsilane (30)



(3:1 *E*,*Z*/*E*,*E*)–**10** was used. 69% yield, **30/30**' >20:1. Isolated by preparative TLC (PE). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₂₆H₃₈NaOSi, M+Na]⁺: 417.2584, Found: 417.2584.

(E)-(3-(4-(benzyloxy)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, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₂₇H₃₀NaO, M+Na]⁺: 393.2189, Found: 393.2194.

(E)-4-(5-benzyl-7-phenylhept-6-en-1-yl)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 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.23 (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); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₂₄H₃₂NO, M+H]⁺: 350.2478, Found: 350.2481.

(E)-(3-(4,4-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 [C₂₂H₂₈NaO₂, M+Na]⁺: 347.1982, Found: 347.1985.

Ethyl (E)-4-(4-cyclohexyl-2-methylbut-3-en-1-yl)benzoate (3s)



(1:15 *Z/E*)–**1s** was used. DPPPe (*1*,5-*Bis(diphenylphosphin-o)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, 135.4, 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)-2-methylbut-3-en-1-yl)benzoate (3t)



E–1t was used. DPPPe (*1*,5-*Bis*(*diphenylphosphino*)*pentane*) as the ligand. 70% yield, $3t/3t' 13:1.^{1}H$ 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, 32.2, 20.2, 14.3. HRMS (ESI) calcd for [C₂₆H₂₈NO₂, M+H]⁺: 392.2584, Found: 392.2588.

(E)-1-methyl-4-(2-methyl-4-phenylbut-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 (EI) 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 NMR (400 MHz, CDCl₃) δ 7.53 (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, 2H), 7.32–7.26 (m, 6H), 7.24–7.15 (m, 2H), 7.32–7.26 (m, 6H), 7.24–7.15 (m, 2H), 6.30 (m, 2H), 7.32–7.26 (m, 6H), 7.24–7.15 (m, 2H), 6.30 (m, 2H), 7.32–7.26 (m, 6H), 7.24–7.15 (m, 2H), 6.30 (m, 2H), 7.32–7.26 (m, 6H), 7.24–7.15 (m, 2H), 6.30 (m, 2H), 7.32–7.26 (m, 6H), 7.24–7.15 (m, 2H), 6.30 (m, 2H), 7.32–7.26 (m, 6H), 7.24–7.15 (m, 2H), 7.32–7.26 (m, 6H), 7.24–7.15 (m, 2H), 7.32–7.26 (m, 6H), 7.24–7.15 (m, 2H), 7.32–7.26 (m, 6H), 7.32–7.26 (m, 6H), 7.24–7.15 (m, 2H), 7.32–7.26 (m, 6H), 7.32–7.26 (m, 6H), 7.34–7.15 (m, 2H), 7.32–7.26 (m, 6H), 7.32–7.26 (m, 6H), 7.34–7.15 (m, 2H), 7.32–7.26 (m, 6H), 7.34–7.15 (m, 2H), 7.34–7.15

1H), 2.71–2.59 (m, 2H), 1.10 (d, J = 5.6 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 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; ¹⁹F NMR (376 MHz, CDCl₃) δ –62.3. HRMS (EI) m/z calcd for [C₁₈H₁₇F₃, M]⁺: 290.1282, 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 NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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; ¹⁹F NMR (376 MHz, CDCl₃) δ –117.1. HRMS (EI) m/z calcd for [C₁₇H₁₇F, M]⁺: 240.1314, 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 NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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. HRMS (EI) *m*/*z* calcd for [C₁₈H₁₇N, M]⁺: 247.1361, Found: 247.1356.

(*E*)-1-methoxy-4-(2-methyl-4-phenylbut-3-en-1-yl)benzene (4e)^{5c}



74% yield, **4e**/**4e**' >20:1. Isolated by preparative TLC (PE). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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)



93% yield, **4f**/**4f**' 13:1. Isolated by preparative TLC (PE). Light yellow solid, mp: 36–37 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.38–7.25 (m, 4H), 7.20–7.17 (m, 3H), 7.13–7.08 (m, 2H), 6.30 (d, *J* = 15.9 Hz, 1H), 6.16 (dd, *J* = 15.9, 6.8 Hz, 1H), 2.82–2.66 (m, 1H),

2.64–2.51 (m, 2H), 2.46 (s, 3H), 1.07 (d, J = 6.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 137.7, 137.6, 135.7, 135.3, 129.8, 128.4, 128.3, 126.9, 126.8, 126.0, 43.0, 38.8, 19.8, 16.2. HRMS (EI) m/z calcd for [C₁₈H₂₀S, M]⁺: 268.1286, Found: 268.1280.

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. ¹H NMR (400 MHz, CDCl₃) 7.96 (d, *J* = 8.3 Hz, 2H), 7.63–7.09 (m, 7H), 6.29 (d, *J* = 15.9 Hz, 1H), 6.14 (dd, *J* = 15.9, 7.1 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.80 (dd, *J* =

12.8, 6.7 Hz, 1H), 2.65 (ddd, J = 25.6, 13.3, 7.0 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H), 1.09 (d, J = 6.5 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.7, 145.9, 137.5, 135.2, 129.4, 129.2, 128.6, 128.4, 128.2, 127.0, 126.0, 60.8, 43.6, 38.7, 19.9, 14.3. HRMS (EI) m/z calcd for [C₂₀H₂₂O₂, M]⁺: 294.1620, Found: 294.1617.

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



MS

87% yield, **4h**/**4h**' 17:1. Isolated by preparative TLC (PE). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₂₀H₂₆Si, M]⁺: 294.1804, Found: 294.1801.

(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. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 140.4, 137.8, 137.6, 136.1, 130.1, 128.4, 128.1, 128.0, 126.8, 126.6, 126.3, 126.0, 43.5, 38.7, 21.4, 19.7. HRMS (EI) m/z calcd for [C₁₈H₂₀, M]⁺: 236.1565, Found: 236.1560.

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

Me 73% yield, 4j/4j' > 20:1. Isolated by preparative TLC (PE). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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 $[C_{18}H_{20}, M]^+$: 236.1565, Found: 236.1560.

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



90% yield, **4**k/**4**k' 20:1. Isolated by preparative TLC (PE). White solid, mp: 40–41 °C. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₂₁H₂₀, M]⁺: 272.1565, Found: 272.1562.

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

90% yield, **4***I*/**4***I*' 17:1. Isolated by preparative TLC (PE/EA = 5:1). Light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₁₆H₁₇N, M]⁺: 223.1361, Found: 223.1355.

(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. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₁₆H₁₇N, M]⁺: 223.1361, Found: 223.1356.

(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. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₂₀H₁₉N, M]⁺: 273.1517, Found: 273.1518.

(E)-1-methyl-2-(2-methyl-4-phenylbut-3-en-1-yl)-1H-pyrrole (40)

60% yield, 4o/4o' >20:1. Isolated by preparative TLC (PE/EA = 50:1). Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 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), 3.53 (s, 3H), 2.74–2.54 (m, 3H), 1.14 (d, J = 6.3 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₁₆H₁₉N, 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. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₁₆H₁₉O, 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. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₁₅H₁₆S, M]⁺: 228.0973, Found: 228.0968.

(E)-(3-methylpent-1-ene-1,4-diyl)dibenzene (4r)

Diene **1a** (0.2 mmol), hydrazone **2r** (0.3 mmol), Ni(COD)₂ (0.02 mol), PBn₃ (0.024 mmol), 'BuOLi (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: ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, *J* = 7.4 Hz, 1H), 7.33–7.24 (m,

5H), 7.19 (dd, J = 14.6, 7.4 Hz, 4H), δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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: ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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

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-CF₃C₆H₄)₃ (11.2 mg, 0.024 mmol), 1,3-diene **1** (0.40 mmol) and 'BuOLi (1.6 mg, 0.020 mmol). The tube was sealed and removed from the glove box, and the degassed α , β -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

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

55% yield. Isolated by preparative TLC (PE). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₁₉H₂₀, M]⁺: 248.1565, Found: 248.1560.

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

63% yield. Isolated by preparative TLC (PE). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₂₀H₂₂O, 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). ¹H NMR (400 MHz, CDCl₃) δ 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); δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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/zcalcd for [C₂₂H₂₄, M]⁺: 288.1878, Found: 288.1876.

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

Me NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₁₅H₂₀, M]⁺: 200.1565, Found: 200.1560.

((1E,4E)-3,5-dimethylhexa-1,4-diene-1,6-diyl)dibenzene (6e)

^{Me} Me Ph ^{Me} Me Ph ^{Me} Me ^{Ph} ^{Colorless oil. ¹H ^C}</sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup></sup>

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

Me Me 84% yield. Isolated by preparative TLC (PE). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₁₅H₂₀, M]⁺: 200.1565, Found: 200.1560.

((1*E*,4*E*)-3,6,10-trimethylundeca-1,4,9-trien-1-yl)benzene (6g)

Me 55% yield, 1:1 *dr*. Isolated by preparative TLC (PE). Me Me 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); ¹³C NMR (101 MHz, CDCl₃) δ 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* calcd for [C₂₀H₂₈, M]⁺: 268.2191, Found: 268.2188.

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

Ph

1a (0.2 mmol), α,β-unsaturated hydrazones **5** (0.4 mmol). 65% yield. Isolated by preparative TLC (PE). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 143.0, 137.9, 135.2, 128.4, 127.1, 126.7, 126.0, 123.6, 37.7, 33.7, 28.6, 26.4, 26.4, 20.9. HRMS (EI) m/z calcd for [C₁₆H₂₀, M]⁺: 212.1565, Found: 212.1560.

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

1a (0.2 mmol), α,β-unsaturated hydrazones **5** (0.4 mmol). 81% yield. Isolated by preparative TLC (PE). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 139.4, 138.0, 135.9, 128.5, 127.3, 126.8, 126.0, 125.1, 37.2, 34.7, 29.2, 28.8, 28.0, 26.9, 21.5. HRMS (EI) m/z calcd for [C₁₇H₂₂, M]⁺: 226.1722, Found: 226.1714.

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

Ph

71% yield. Isolated by preparative TLC (PE). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 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). δ the minor isomer 7.37–7.31 (m, 2H), 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); ¹³C NMR (101 MHz, CDCl₃) δ 150.3 (150.2), 138.4 (138.4), 137.9 (137.9), 135.8 (135.6), 128.4

(128.4), 127.3, 126.8, 126.0, 125.6 (125.5), 108.4 (108.4), 45.6 (45.6), 36.6 (36.6), 34.9 (34.7), 33.4 (33.4), 32.7 (32.6), 28.6 (28.5), 21.6 (21.2), 21.0 (20.9). HRMS (EI) m/z calcd for [C₂₀H₂₆, M]⁺: 266.2035, Found: 266.2030.

(E)-(3-(cyclohexylidenemethyl)pent-1-en-1-yl)benzene (6k)

^{Me} ^{Ph} ^{A8%} yield. Isolated by preparative TLC (PE). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 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, 7H), 1.43–1.30 (m, 1H), 0.90 (t, J = 7.3 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₁₈H₂₄, M]⁺: 240.1878, Found: 240.1872.

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

Me

Diene (0.2 mmol, *E*-isomer), α,β-unsaturated hydrazones **5** (0.4 mmol). 70% yield. Isolated by preparative TLC (PE). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 147.9, 146.5, 139.3, 134.2, 132.6, 126.9, 125.2, 120.3, 108.2, 105.5, 100.9, 37.2, 34.6, 29.2, 28.7, 28.0, 26.9, 21.5. HRMS (EI) *m*/*z* calcd for [C₁₈H₂₂O, M]⁺: 270.1620, Found: 270.1616.

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

Me Me Diene (0.2 mmol), α,β-unsaturated hydrazones **5** (0.4 mmol). 73% yield. Isolated by preparative TLC (PE). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₁₅H₂₀O, M]⁺: 216.1514, Found: 216.1508.

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

Me Die yiel (400

Diene (0.2 mmol), α , β -unsaturated hydrazones **5** (0.4 mmol). 72% yield. Isolated by preparative TLC (PE). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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 [C₁₅H₂₀S, M]⁺: 232.1286, Found: 232.1282.

5. Synthetic Application

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-CF₃C₆H₄)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 ^{*i*}BuOLi (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). ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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, 26.8, 24.9, 14.3, 14.2. HRMS (ESI) calcd for [C₂₇H₃₄NaO₅, 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_2O 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. ¹H 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); ¹³C 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 [C₂₃H₂₅O₅, 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-CF₃C₆H₄)₃ (11.2 mg, 0.024 mmol), 1,3-diene **1a** (0.40 mmol), hydrazone **2a** (0.20 mmol) and ^{*t*}BuOLi (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 ¹H NMR. The **3a** was obtained in 71% yield. ¹H NMR (400 MHz, CDCl₃) 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.

b) Labelling experiment of hydroalkenylation 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-CF₃C₆H₄)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 'BuOLi (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 ¹H NMR. The product **6d** was obtained in 67% yield. ¹H NMR (400 MHz, CDCl₃) 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-CF₃C₆H₄)₃ (11.2 mg, 0.024 mmol), 1,3-diene **1a** (0.40

mmol), hydrazone **D-2a'** (0.20 mmol) and ^{*t*}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). ¹H NMR (400 MHz, CDCl₃) δ 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).

7. NMR Spectra of Important Compounds

((1E)-7-(benzyloxy)hepta-1,3-dien-1-yl)benzene (1p)

33

4-((6*E*)-7-phenylhepta-4,6-dien-1-yl)morpholine (1q)

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

(E)-1-benzyl-4-(buta-1,3-dien-1-yl)piperidine (1s)




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



2-(hydrazonomethyl)-1-methyl-1H-pyrrole (20)







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



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





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



(E)-(3-ethylbut-1-ene-1,4-diyl)dibenzene (3l)



(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 (30)



(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-cyclohexyl-2-methylbut-3-en-1-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)



$(E) \hbox{-} 1 \hbox{-} methyl \hbox{-} 2 \hbox{-} (2 \hbox{-} methyl \hbox{-} 4 \hbox{-} phenyl but \hbox{-} 3 \hbox{-} en \hbox{-} 1 \hbox{-} yl) benzene (4j)$



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



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



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



(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 (40)






(*E*)-(3-methylpent-1-ene-1,4-diyl)dibenzene (4r)



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



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



((1*E*,4*E*)-6-cyclopropyl-3-methylhexa-1,4-diene-1,6-diyl)dibenzene (6c)



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



((1E,4E)-3,5-dimethylhexa-1,4-diene-1,6-diyl)dibenzene (6e)



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



((1E,4E)-3,6,10-trimethylundeca-1,4,9-trien-1-yl)benzene (6g)





(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-(cyclohexylidenemethyl)pent-1-en-1-yl)benzene (6k)



(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-methoxystyryl)-7-oxoheptyl)benzoate (7)



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

GC-MS chromatograph of azine **5**: ._N__ GC-MS (EI) *m*/*z* calcd for C₁₀H₁₆N₂: 164.13, Found: 164.20

文件 : E:\DATA\CL\CL-6-113-PPH3.D 操作员 : CL 已采集 : 14 Mar 2019 14:36 ,使用采集方法 TEST-1.M 仪器: 5975 样品名称 : 其他信息 : 样品瓶号 : 0



8. References

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