

Controllable stereoselective synthesis of trisubstituted alkenes by a catalytic three-component reaction of terminal alkynes, benzylic alcohols, and simple arenes

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Supporting information

Table of contents

General information.....	1
General procedure for the optimization of reaction conditions (Table 1).....	2
General procedure for the controllable stereoselective three-component synthesis of trisubstituted alkenes (Table 2).....	2
Analytical data for the products shown in Table 2.....	2
Reaction of (<i>R</i>)-1-phenylethanol with phenylacetylene (1a) and mesitylene (3a).....	14
Copies of ¹ H and ¹³ C NMR spectra.....	15

General information

The ¹H and ¹³C NMR spectra were recorded on a Bruker AC-300 FT spectrometer (300 MHz and 75 MHz, respectively) using tetramethylsilane as internal reference, and the chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. The 2D NOESY spectra were recorded on a Bruker AC-400 FT spectrometer (400 MHz). The high resolution mass spectra were recorded on a LC-TOF spectrometer (Micromass). High pressure liquid chromatography (HPLC) analyses were performed on an instrument equipped with an isostatic pump and a Chiralpak OD column (250 x 4.6 mm), and the UV detection was monitored at 254 nm. The melting points were uncorrected.

The chemicals were purchased from Acros, Alfa Aesar, AstaTech Pharmaceutical Co., Meryer, Sigma-Aldrich, TCI, and the Sinopharm Chemical Reagent Co., and used as received. All the solvents were untreated before use.

General procedure for the optimization of reaction conditions (Table 1)

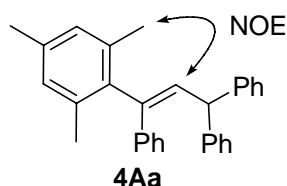
To a stirred solution of phenylacetylene (**1a**, 20.4 mg, 22 μ L, 0.20 mmol) in a solvent (0.20 mL) were added successively mesitylene (**3a**, 48.0 mg, 55 μ L, 0.40 mmol), benzhydrol (**2a**, 55.2 mg, 0.30 mmol), and catalyst (10-20 mol %). The resulting mixture was stirred at an ambient temperature of 10 $^{\circ}$ C for 21 h. The mixture was directly purified by silica gel column chromatography, eluting with petroleum ether, to give alkene product **4Aa**.

General procedure for the controllable stereoselective three-component synthesis of trisubstituted alkenes (Table 2)

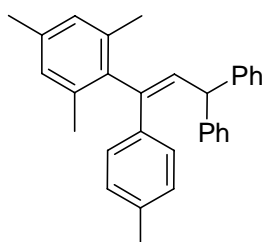
To a stirred solution of terminal alkyne **1** (0.20 mmol) in nitromethane (0.20 mL, precooled if the reaction was carried out at below ambient temperature) were added successively simple arene **3** (0.40 mmol), benzylic alcohol **2** (0.30 mmol), AgNO₃ (6.8 mg, 20 mol %), FeCl₃ (6.6 mg, 20 mol %), and Tf₂O (11.3 mg, 20 mol %). For entries 26, 29, 30 and 32-36, FeCl₃ (16.3 mg, 50 mol %) was used as the catalyst instead of Tf₂O/FeCl₃/AgNO₃ (1:1:1, 20 mol %). The resulting mixture was stirred at the temperature specified in Table 2 until no further transformation was observed by TLC analysis. The mixture was directly purified by silica gel column chromatography, eluting with petroleum ether, to give trisubstituted alkene **4A** and its isomer **4B** (if any).

The stereochemistry of trisubstituted alkenes **4Aa**, **4Bd**, **4Ak**, **4Al**, **4An**, **4Aq**, **4Au**, **4Ax**, **4Ba**, **4Bc**, **4Bm**, **4Bn**, and **4Bx** was determined by 2D NOESY analysis (*vide infra*), and the stereochemistry of the rest of trisubstituted alkenes shown in Table 2 was determined by analogy. The *E/Z* ratios were determined by integrating the vinyl proton signals in the ¹H NMR spectra.

Analytical data for the products shown in Table 2

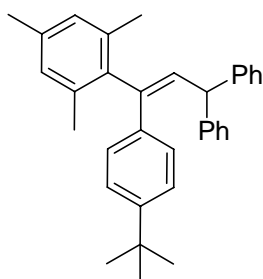


4Aa, obtained as a 96:4 mixture of *E/Z* isomers, white solid; m.p. 85 $^{\circ}$ C; ¹H NMR (300 MHz, CDCl₃): δ 7.33-7.05 (m, 15H), 6.84 (s, 2H), 5.95 (d, *J* = 10.5 Hz, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 2.26 (s, 3H), 2.06 (s, 6H); Partial ¹H NMR for the minor *Z*-isomer: 4.44 (d, *J* = 10.5 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 144.9, 139.2, 136.5, 133.4, 129.0, 128.7, 128.5, 128.2, 127.1, 126.4, 50.6, 21.1, 20.6; HRMS (EI): Calcd for C₃₀H₂₈ (M): 388.2191. Found: 388.2188.



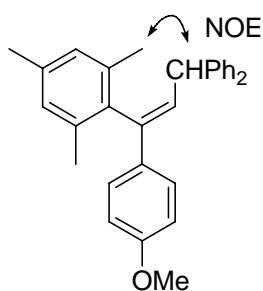
4Ab

4Ab, obtained as a 98:2 mixture of *E/Z* isomers, white solid; m.p. 97 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.33-7.10 (m, 10H), 7.10-6.95 (m, 4H), 6.83 (s, 2H), 5.91 (d, $J = 10.5$ Hz, 1H), 5.28 (d, $J = 10.5$ Hz, 1H), 2.31 (s, 3H), 2.26 (s, 3H), 2.05 (s, 6H); Partial ^1H NMR for the minor *Z*-isomer: 6.81 (d, $J = 10.8$ Hz, 1H), 4.42 (d, $J = 10.8$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 145.0, 140.6, 139.1, 136.8, 136.4, 136.2, 132.8, 130.3, 129.5, 128.9, 128.6, 128.5, 128.4, 126.4, 126.0, 50.7, 21.3, 21.1, 20.6; HRMS (EI): Calcd for $\text{C}_{31}\text{H}_{30}$ (M): 402.2348. Found: 402.2345.



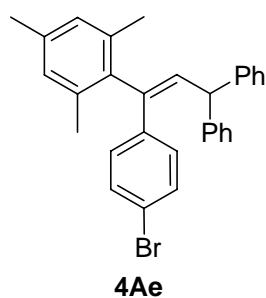
4Ac

4Ac, white solid; m.p. 136 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.33-7.12 (m, 12H), 7.12-7.02 (m, 2H), 6.83 (s, 2H), 5.92 (d, $J = 10.5$ Hz, 1H), 5.32 (d, $J = 10.5$ Hz, 1H), 2.25 (s, 3H), 2.07 (s, 6H), 1.28 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ 149.9, 145.1, 140.7, 139.0, 136.4, 136.0, 132.8, 128.6, 128.5, 128.4, 126.3, 125.0, 50.6, 34.6, 31.4, 21.1, 20.6; HRMS (EI): Calcd for $\text{C}_{34}\text{H}_{36}$ (M): 444.2817. Found: 444.2813.

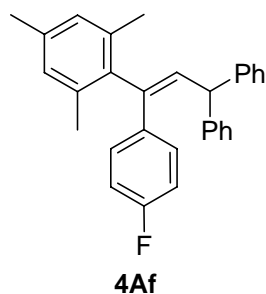


4Bd

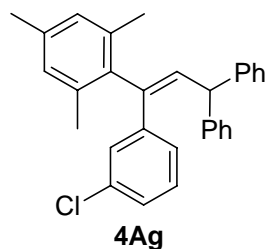
4Bd, obtained as a 98:2 mixture of *Z/E* isomers, white solid; m.p. 110 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.30-6.99 (m, 12H), 6.88 (s, 2H), 6.82-6.65 (m, 3H), 4.40 (d, $J = 10.2$ Hz, 1H), 3.77 (s, 3H), 2.33 (s, 3H), 1.85 (s, 6H); Partial ^1H NMR for the minor *E*-isomer: 5.85 (d, $J = 10.2$ Hz, 1H), 5.25 (d, $J = 10.2$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 159.1, 144.7, 139.1, 136.7, 135.4, 132.8, 128.5, 128.4, 127.2, 126.2, 113.9, 55.4, 50.7, 21.2, 20.0; HRMS (EI): Calcd for $\text{C}_{31}\text{H}_{30}\text{O}$ (M): 418.2297. Found: 418.2293.



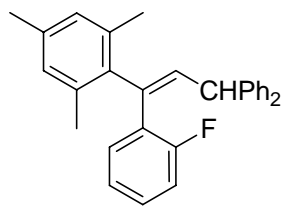
4Ae, obtained as a 97:3 mixture of *E/Z* isomers, white solid; m.p. 130 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.40-7.12 (m, 12H), 7.03-6.95 (m, 2H), 6.83 (s, 2H), 5.97 (d, $J = 10.5$ Hz, 1H), 5.19 (d, $J = 10.5$ Hz, 1H), 2.26 (s, 3H), 2.03 (s, 6H); Partial ^1H NMR for the minor *Z*-isomer: 4.40 (d, $J = 10.5$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 144.6, 138.1, 136.8, 136.4, 134.1, 131.4, 130.6, 128.8, 128.5, 128.4, 126.6, 121.2, 50.7, 21.1, 20.6; HRMS (EI): Calcd for $\text{C}_{30}\text{H}_{27}\text{Br}$ (M): 466.1296. Found: 466.1288.



4Af, obtained as a 98:2 mixture of *E/Z* isomers, white solid; m.p. 90 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.33-7.03 (m, 12H), 6.98-6.88 (m, 2H), 6.84 (s, 2H), 5.94 (d, $J = 10.8$ Hz, 1H), 5.20 (d, $J = 10.8$ Hz, 1H), 2.26 (s, 3H), 2.00 (s, 6H); Partial ^1H NMR for the minor *Z*-isomer: 6.77 (d, $J = 10.8$ Hz, 1H), 4.41 (d, $J = 10.8$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 161.8 (d, $^1J_{\text{CF}} = 254$ Hz), 144.7, 140.1, 138.2, 136.7, 136.4, 135.2, 133.5, 130.7, 130.6, 128.8, 128.5, 128.4, 126.5, 115.1 (d, $^2J_{\text{CF}} = 21$ Hz), 50.7, 21.1, 20.5; HRMS (EI): Calcd for $\text{C}_{30}\text{H}_{27}\text{F}$ (M): 406.2097. Found: 406.2093.

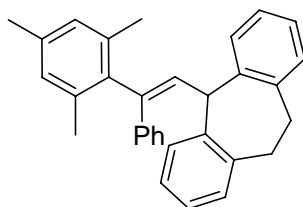


4Ag, obtained as a 95:5 mixture of *E/Z* isomers, white solid; m.p. 92 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.35-7.01 (m, 14H), 6.84 (s, 2H), 6.01 (d, $J = 10.5$ Hz, 1H), 5.20 (d, $J = 10.5$ Hz, 1H), 2.27 (s, 3H), 2.05 (s, 6H); Partial ^1H NMR for the minor *Z*-isomer: 4.41 (d, $J = 10.5$ Hz, 1H); HRMS (EI): Calcd for $\text{C}_{30}\text{H}_{27}\text{Cl}$ (M): 422.1801. Found: 422.1802.



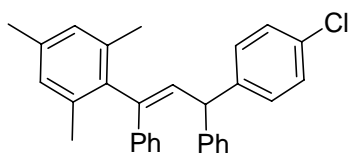
4Ah

4Ah, obtained as a 97:3 mixture of *Z/E* isomers, white solid; m.p. 102 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.38-6.94 (m, 14H), 6.82 (s, 2H), 6.10 (d, $J = 10.8$ Hz, 1H), 4.99 (d, $J = 10.8$ Hz, 1H), 2.25 (s, 3H), 2.05 (s, 6H); Partial ^1H NMR for the minor *E*-isomer: 6.52 (d, $J = 10.5$ Hz, 1H), 4.55 (d, $J = 10.5$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 160.0 (d, $^1J_{\text{CF}} = 246$ Hz), 144.1, 136.8, 133.1, 131.6, 131.0, 129.0, 128.6, 128.5, 126.4, 123.9, 116.0 (d, $^2J_{\text{CF}} = 23$ Hz), 51.0, 21.1, 20.6; HRMS (EI): Calcd for $\text{C}_{30}\text{H}_{27}\text{F}$ (M): 406.2097. Found: 406.2090.



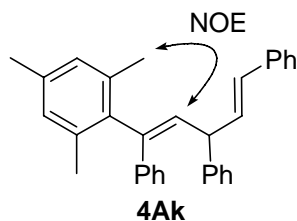
4Ai

4Ai, obtained as a 98:2 mixture of *E/Z* isomers, white solid; m.p. 112 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.33-7.18 (m, 6H), 7.18-7.05 (m, 7H), 6.88 (s, 2H), 6.55 (d, $J = 10.5$ Hz, 1H), 5.65 (d, $J = 10.5$ Hz, 1H), 3.33-3.05 (m, 4H), 2.29 (s, 3H), 2.16 (s, 6H); Partial ^1H NMR for the minor *Z*-isomer: 4.45 (d, $J = 10.5$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 142.5, 140.7, 140.1, 139.5, 138.8, 136.6, 136.4, 131.3, 130.3, 129.2, 128.5, 128.1, 127.2, 127.0, 126.6, 126.3, 45.9, 32.9, 21.1, 20.7; HRMS (EI): Calcd for $\text{C}_{32}\text{H}_{30}$ (M): 414.2348. Found: 414.2350.

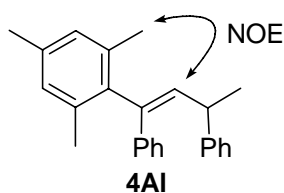


4Aj

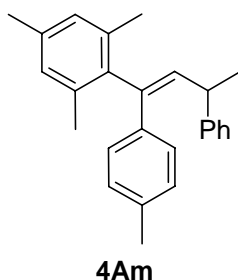
4Aj, obtained as a 97:3 mixture of *E/Z* isomers, white solid; m.p. 122 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.38-7.08 (m, 14H), 6.84 (s, 2H), 5.90 (d, $J = 10.5$ Hz, 1H), 5.24 (d, $J = 10.5$ Hz, 1H), 2.27 (s, 3H), 2.06 (s, 6H); Partial ^1H NMR for the minor *Z*-isomer: 6.78 (d, $J = 10.5$ Hz, 1H), 4.40 (d, $J = 10.5$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 144.4, 143.4, 140.2, 139.7, 139.0, 136.7, 136.3, 132.8, 132.2, 129.8, 129.0, 128.8, 128.5, 128.4, 128.3, 127.3, 126.6, 50.0, 21.1, 20.6; HRMS (EI): Calcd for $\text{C}_{30}\text{H}_{27}\text{Cl}$ (M): 422.1801. Found: 422.1797.



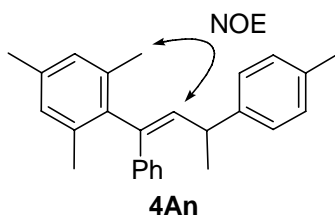
4Ak, obtained as a 93:7 mixture of *E/Z* isomers, yellow oil; ^1H NMR (300 MHz, CDCl_3): δ 7.41-7.11 (m, 15H), 6.86 (s, 2H), 6.60 (d, $J = 15.9$ Hz, 1H), 6.47 (dd, $J = 15.9, 5.4$ Hz, 1H), 5.75 (d, $J = 10.2$ Hz, 1H), 4.87-4.74 (m, 1H), 2.27 (s, 3H), 2.20 (s, 3H), 2.05 (s, 3H); Partial ^1H NMR for the minor *Z*-isomer: 5.25 (d, $J = 10.2$ Hz, 1H); HRMS (EI): Calcd for $\text{C}_{32}\text{H}_{30}$ (M): 414.2348. Found: 414.2343.



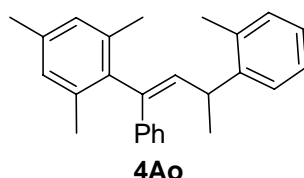
4Al, obtained as a 97:3 mixture of *E/Z* isomers, yellow oil; ^1H NMR (300 MHz, CDCl_3): δ 7.36-7.10 (m, 10H), 6.90 (s, 1H), 6.80 (s, 1H), 5.70 (d, $J = 10.5$ Hz, 1H), 4.14-3.98 (m, 1H), 2.30 (s, 3H), 2.27 (s, 3H), 1.96 (s, 3H), 1.41 (d, $J = 6.9$ Hz, 3H); Partial ^1H NMR for the minor *Z*-isomer: 6.45 (d, $J = 10.5$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 146.8, 139.6, 137.9, 136.6, 136.4, 136.3, 129.1, 128.7, 128.5, 128.4, 128.3, 128.1, 127.0, 126.9, 126.7, 126.1, 38.8, 23.3, 21.1, 20.7, 20.5; HRMS (EI): Calcd for $\text{C}_{25}\text{H}_{26}$ (M): 326.2035. Found: 326.2031.



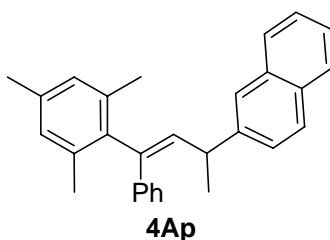
4Am, obtained as a 93:7 mixture of *E/Z* isomers, yellow oil; ^1H NMR (300 MHz, CDCl_3): δ 7.35-7.14 (m, 5H), 7.08-6.99 (m, 4H), 6.90 (s, 1H), 6.79 (s, 1H), 5.66 (d, $J = 10.5$ Hz, 1H), 4.13-3.98 (m, 1H), 2.31 (s, 3H), 2.30 (s, 3H), 2.27 (s, 3H), 1.95 (s, 3H), 1.40 (d, $J = 6.6$ Hz, 3H); Partial ^1H NMR for the minor *Z*-isomer: 6.41 (d, $J = 10.5$ Hz, 1H); HRMS (EI): Calcd for $\text{C}_{26}\text{H}_{28}$ (M): 340.2191. Found: 340.2192.



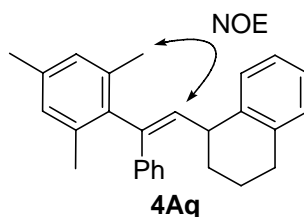
4An, obtained as a 96:4 mixture of *E/Z* isomers, yellow oil; ^1H NMR (300 MHz, CDCl_3): δ 7.32-7.09 (m, 9H), 6.91 (s, 1H), 6.80 (s, 1H), 5.69 (d, $J = 10.5$ Hz, 1H), 4.10-3.94 (m, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 2.27 (s, 3H), 1.96 (s, 3H), 1.39 (d, $J = 6.9$ Hz, 3H); Partial ^1H NMR for the minor *Z*-isomer: 6.43 (d, $J = 10.5$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 143.8, 140.7, 139.7, 137.6, 136.5, 136.4, 135.5, 129.4, 129.1, 128.9, 128.5, 128.4, 128.1, 126.9, 126.8, 38.4, 23.5, 21.2, 20.7, 20.6; HRMS (EI): Calcd for $\text{C}_{26}\text{H}_{28}$ (M): 340.2191. Found: 340.2185.



4Ao, obtained as a 95:5 mixture of *E/Z* isomers, white solid; m.p. 118 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.34-7.05 (m, 9H), 6.90 (s, 1H), 6.81 (s, 1H), 5.74 (d, $J = 10.2$ Hz, 1H), 4.25-4.10 (m, 1H), 2.28 (s, 6H), 2.16 (s, 3H), 1.90 (s, 3H), 1.38 (d, $J = 6.9$ Hz, 3H); Partial ^1H NMR for the minor *Z*-isomer: 6.64 (d, $J = 10.2$ Hz, 1H); HRMS (EI): Calcd for $\text{C}_{26}\text{H}_{28}$ (M): 340.2191. Found: 340.2192.

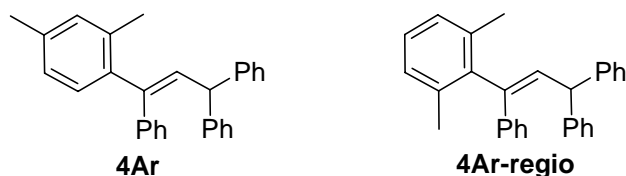


4Ap, obtained as a 93:7 mixture of *E/Z* isomers, yellow oil; ^1H NMR (300 MHz, CDCl_3): δ 7.88-7.67 (m, 4H), 7.50-7.34 (m, 3H), 7.30-7.10 (m, 5H), 6.92 (s, 1H), 6.81 (s, 1H), 5.81 (d, $J = 10.5$ Hz, 1H), 4.30-4.10 (m, 1H), 2.33 (s, 3H), 2.28 (s, 3H), 1.96 (s, 3H), 1.50 (d, $J = 6.9$ Hz, 3H); Partial ^1H NMR for the minor *Z*-isomer: 6.54 (d, $J = 10.5$ Hz, 1H); HRMS (EI): Calcd for $\text{C}_{29}\text{H}_{28}$ (M): 376.2191. Found: 376.2187.

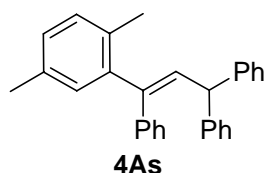


4Aq, obtained as a 98:2 mixture of *E/Z* isomers, white solid; m.p. 114 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.36-7.04 (m, 9H), 6.87 (s, 1H), 6.85 (s, 1H), 5.56-5.50 (m, 1H), 4.20-4.05 (m, 1H), 2.87-2.72 (m, 2H), 2.27 (s, 3H), 2.24 (s, 3H), 2.23 (s, 3H), 2.10-2.00 (m, 1H), 2.00-1.85 (m, 1H), 1.84-1.60 (m, 2H); Partial ^1H NMR for the minor *Z*-isomer: 6.40 (d, $J = 10.5$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 140.8, 139.6, 139.4, 138.8, 137.1, 136.3, 135.9, 129.3, 129.1, 128.8, 128.5, 128.2, 126.9, 126.1, 126.0, 125.8, 38.9, 30.8, 30.0, 29.7, 21.8, 21.1, 20.7; HRMS (EI): Calcd for

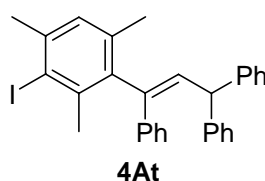
C₂₇H₂₈ (M): 352.2191. Found: 352.2186.



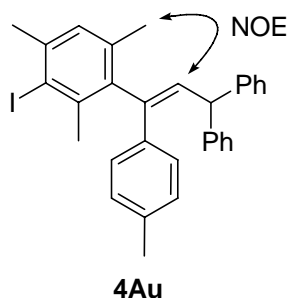
4Ar, obtained as a 85:15 mixture of regioisomers (**4Ar-regio** is the minor one) and as a 97:3 mixture of *E/Z* isomers, yellow oil; ¹H NMR (300 MHz, CDCl₃): δ 7.34-7.03 (m, 16H), 7.03-6.88 (m, 2H), 6.14 (d, *J* = 10.8 Hz, 1H), 5.09 (d, *J* = 10.8 Hz, 1H), 2.30 (s, 3H), 1.96 (s, 3H); Partial ¹H NMR for the minor regioisomer: 5.94 (d, *J* = 10.8 Hz, 1H), 5.29 (d, *J* = 10.8 Hz, 1H), 2.10 (s, 6H); Partial ¹H NMR for the minor *Z*-isomer: 6.62 (d, *J* = 10.8 Hz, 1H), 4.60 (d, *J* = 10.8 Hz, 1H); HRMS (EI): Calcd for C₂₉H₂₆ (M): 374.2035. Found: 374.2037.



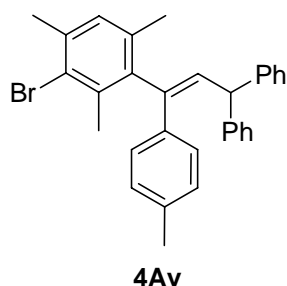
4As, obtained as a 96:4 mixture of *E/Z* isomers, white solid; m.p. 90 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.36-7.11 (m, 15H), 7.04-6.96 (m, 3H), 6.14 (d, *J* = 10.5 Hz, 1H), 5.10 (d, *J* = 10.5 Hz, 1H), 2.28 (s, 3H), 1.96 (s, 3H); Partial ¹H NMR for the minor *Z*-isomer: 6.67 (d, *J* = 10.5 Hz, 1H), 4.56 (d, *J* = 10.5 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 144.9, 143.4, 141.9, 140.0, 135.1, 133.1, 130.8, 130.3, 129.3, 128.7, 128.5, 128.2, 128.1, 127.1, 126.4, 50.3, 21.0, 20.1; HRMS (EI): Calcd for C₂₉H₂₆ (M): 374.2035. Found: 374.2028.



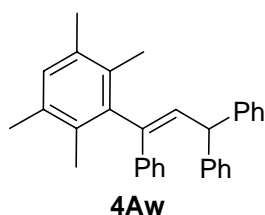
4At, obtained as a 98:2 mixture of *E/Z* isomers, white solid; m.p. 70 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.40-7.09 (m, 15H), 6.94 (s, 1H), 5.91 (d, *J* = 10.5 Hz, 1H), 5.29 (d, *J* = 10.5 Hz, 1H), 2.43 (s, 3H), 2.34 (s, 3H), 2.02 (s, 3H); Partial ¹H NMR for the minor *Z*-isomer: 4.35 (d, *J* = 10.5 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 144.7, 144.6, 141.2, 140.9, 139.8, 139.7, 138.6, 136.3, 133.8, 129.0, 128.8, 128.4, 128.3, 127.4, 126.6, 126.5, 106.6, 50.6, 30.0, 28.0, 20.4; HRMS (EI): Calcd for C₃₀H₂₇I (M): 514.1157. Found: 514.1154.



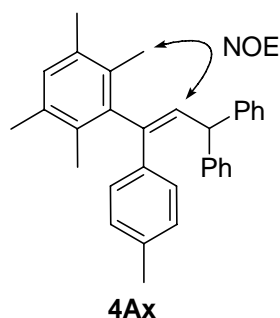
4Au, obtained as a 99:1 mixture of *E/Z* isomers, white solid; m.p. 61 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.35-7.10 (m, 10H), 7.07 (d, $J = 8.1$ Hz, 2H), 7.01 (d, $J = 8.1$ Hz, 2H), 6.93 (s, 1H), 5.86 (d, $J = 10.5$ Hz, 1H), 5.29 (d, $J = 10.5$ Hz, 1H), 2.42 (s, 3H), 2.34 (s, 3H), 2.32 (s, 3H), 2.01 (s, 3H); Partial ^1H NMR for the minor *Z*-isomer: 6.55 (d, $J = 10.5$ Hz, 1H), 4.32 (d, $J = 10.5$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 144.8, 144.7, 141.4, 140.7, 139.8, 139.6, 137.1, 136.3, 135.6, 133.2, 129.0, 128.8, 128.7, 128.4, 126.5, 106.6, 50.6, 30.0, 27.9, 21.3, 20.3; HRMS (EI): Calcd for $\text{C}_{31}\text{H}_{29}\text{I}$ (M): 528.1314. Found: 528.1309.



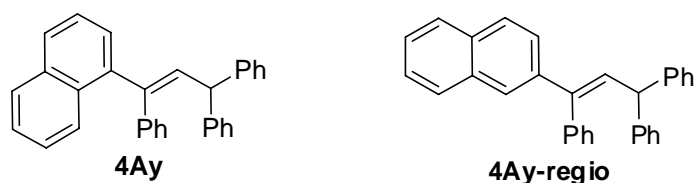
4Av, obtained as a 93:7 mixture of *E/Z* isomers, white solid; m.p. 42 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.36-7.13 (m, 10H), 7.04 (d, $J = 8.4$ Hz, 2H), 6.99 (d, $J = 8.4$ Hz, 2H), 6.91 (s, 1H), 5.88 (d, $J = 10.5$ Hz, 1H), 5.29 (d, $J = 10.5$ Hz, 1H), 2.36 (s, 3H), 2.32 (s, 3H), 2.25 (s, 3H), 2.01 (s, 3H); Partial ^1H NMR for the minor *Z*-isomer: 6.82 (d, $J = 10.5$ Hz, 1H), 4.36 (d, $J = 10.5$ Hz, 1H); HRMS (EI): Calcd for $\text{C}_{31}\text{H}_{29}\text{Br}$ (M): 480.1453. Found: 480.1444.



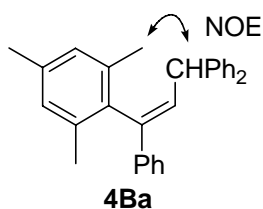
4Aw, obtained as a 96:4 mixture of *E/Z* isomers, white solid; m.p. 115 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.35-7.10 (m, 15H), 6.90 (s, 1H), 5.93 (d, $J = 10.5$ Hz, 1H), 5.30 (d, $J = 10.5$ Hz, 1H), 2.19 (s, 6H), 2.02 (s, 6H); Partial ^1H NMR for the minor *Z*-isomer: 4.35 (d, $J = 10.5$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 145.0, 143.3, 142.4, 140.3, 139.3, 133.8, 133.0, 132.3, 130.5, 129.8, 129.0, 128.7, 128.5, 128.2, 127.6, 127.4, 127.1, 126.4, 50.7, 20.3, 17.0; HRMS (EI): Calcd for $\text{C}_{31}\text{H}_{30}$ (M): 402.2348. Found: 402.2342.



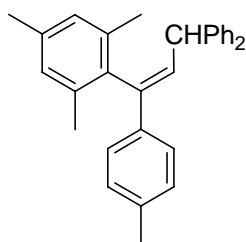
4Ax, obtained as a 97:3 mixture of *E/Z* isomers, white solid; m.p. 118 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.40-7.15 (m, 10H), 7.08-6.99 (m, 4H), 6.89 (s, 1H), 5.88 (d, $J = 10.5$ Hz, 1H), 5.30 (d, $J = 10.5$ Hz, 1H), 2.31 (s, 3H), 2.18 (s, 6H), 2.01 (s, 6H); Partial ^1H NMR for the minor *Z*-isomer: 6.81 (d, $J = 10.5$ Hz, 1H), 4.33 (d, $J = 10.5$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 145.1, 143.5, 140.2, 136.8, 136.4, 133.7, 132.5, 132.3, 130.4, 129.0, 128.9, 128.6, 128.5, 127.6, 127.4, 126.3, 50.7, 21.3, 20.3, 17.0; HRMS (EI): Calcd for $\text{C}_{32}\text{H}_{32}$ (M): 416.2504. Found: 416.2496.



4Ay, obtained as a 93:7 mixture of regioisomers (**4Ay-regio** is the minor one) and as a 93:7 mixture of *E/Z* isomers, yellow oil; ^1H NMR (300 MHz, CDCl_3): δ 7.88-7.74 (m, 3H), 7.45-7.12 (m, 19H), 6.37 (d, $J = 10.8$ Hz, 1H), 5.24 (d, $J = 10.8$ Hz, 1H); Partial ^1H NMR for the minor regioisomer: 6.64 (d, $J = 10.8$ Hz, 1H), 4.86 (d, $J = 10.8$ Hz, 1H); Partial ^1H NMR for the minor *Z*-isomer: 6.85 (d, $J = 10.8$ Hz, 1H), 4.46 (d, $J = 10.8$ Hz, 1H); HRMS (EI): Calcd for $\text{C}_{31}\text{H}_{24}$ (M): 396.1878. Found: 396.1880.

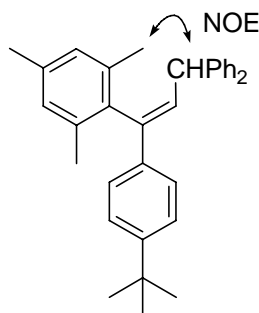


4Ba, obtained as a 97:3 mixture of *Z/E* isomers, white solid; m.p. 83 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.33-7.08 (m, 15H), 6.89 (s, 2H), 6.86 (d, $J = 10.2$ Hz, 1H), 4.44 (d, $J = 10.2$ Hz, 1H), 2.33 (s, 3H), 1.86 (s, 6H); Partial ^1H NMR for the minor *E*-isomer: 5.95 (d, $J = 10.2$ Hz, 1H), 5.28 (d, $J = 10.2$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 144.5, 140.2, 139.7, 136.8, 135.3, 130.4, 129.7, 129.0, 128.5, 128.4, 127.3, 126.8, 126.3, 126.1, 50.8, 21.3, 20.6, 20.0; HRMS (EI): Calcd for $\text{C}_{30}\text{H}_{28}$ (M): 388.2191. Found: 388.2188.



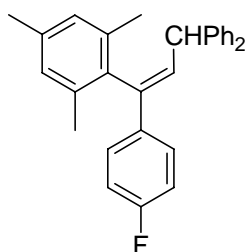
4Bb

4Bb, obtained as a 97:3 mixture of *Z/E* isomers, yellow oil; ^1H NMR (300 MHz, CDCl_3): δ 7.30-6.99 (m, 14H), 6.88 (s, 2H), 6.81 (d, $J = 10.5$ Hz, 1H), 4.42 (d, $J = 10.5$ Hz, 1H), 2.33 (s, 3H), 2.30 (s, 3H), 1.85 (s, 6H); Partial ^1H NMR for the minor *E*-isomer: 5.91 (d, $J = 10.5$ Hz, 1H), 5.28 (d, $J = 10.5$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 144.7, 139.5, 137.3, 137.1, 136.8, 136.6, 135.4, 129.5, 129.3, 128.9, 128.6, 128.5, 128.4, 128.0, 126.2, 126.0, 50.7, 21.3, 21.2, 20.0; HRMS (EI): Calcd for $\text{C}_{31}\text{H}_{30}$ (M): 402.2348. Found: 402.2343.



4Bc

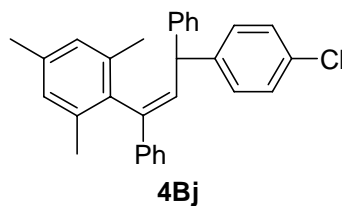
4Bc, obtained as a 97:3 mixture of *Z/E* isomers, white solid; m.p. 135 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.30-6.99 (m, 14H), 6.88 (s, 2H), 6.82 (d, $J = 10.5$ Hz, 1H), 4.42 (d, $J = 10.5$ Hz, 1H), 2.33 (s, 3H), 1.86 (s, 6H), 1.28 (s, 9H); Partial ^1H NMR for the minor *E*-isomer: 5.92 (d, $J = 10.5$ Hz, 1H), 5.32 (d, $J = 10.5$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 150.2, 144.7, 139.5, 137.3, 136.8, 136.6, 135.4, 129.6, 128.6, 128.5, 128.4, 128.0, 126.2, 125.8, 125.4, 125.1, 50.7, 34.6, 31.4, 21.3, 20.1; HRMS (EI): Calcd for $\text{C}_{34}\text{H}_{36}$ (M): 444.2817. Found: 444.2811.



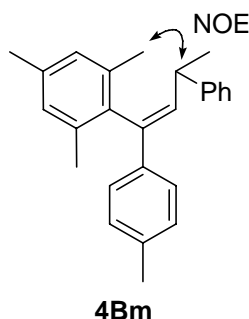
4Bf

4Bf, obtained as a 94:6 mixture of *Z/E* isomers, white solid; m.p. 72 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.30-7.05 (m, 12H), 6.97-6.85 (m, 4H), 6.78 (d, $J = 10.5$ Hz, 1H), 4.41 (d, $J = 10.5$ Hz, 1H), 2.34 (s, 3H), 1.84 (s, 6H); Partial ^1H NMR for the minor *E*-isomer: 5.94 (d, $J = 10.5$ Hz, 1H), 5.20 (d, $J = 10.5$ Hz, 1H), 2.27 (s, 3H), 2.04 (s,

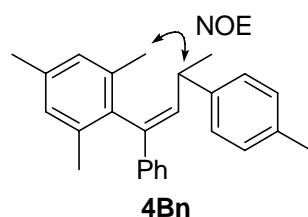
3H); HRMS (EI): Calcd for C₃₀H₂₇F (M): 406.2097. Found: 406.2094.



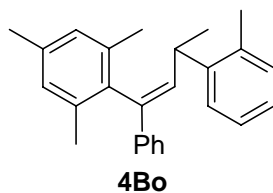
4Bj, obtained as a 93:7 mixture of *Z/E* isomers, white solid; m.p. 40 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.34-6.98 (m, 14H), 6.89 (s, 2H), 6.78 (d, *J* = 10.5 Hz, 1H), 4.40 (d, *J* = 10.5 Hz, 1H), 2.33 (s, 3H), 1.85 (s, 6H); Partial ¹H NMR for the minor *E*-isomer: 5.90 (d, *J* = 10.5 Hz, 1H), 5.24 (d, *J* = 10.5 Hz, 1H), 2.26 (s, 3H), 2.05 (s, 3H); HRMS (EI): Calcd for C₃₀H₂₇Cl (M): 422.1801. Found: 422.1794.



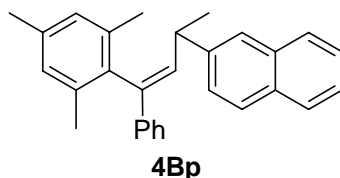
4Bm, obtained as a 99:1 mixture of *Z/E* isomers, white solid; m.p. 98 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.33-6.98 (m, 9H), 6.95 (s, 1H), 6.86 (s, 1H), 6.41 (d, *J* = 9.9 Hz, 1H), 3.28-3.09 (m, 1H), 2.34 (s, 3H), 2.29 (s, 3H), 2.16 (s, 3H), 1.74 (s, 3H), 1.32 (d, *J* = 6.9 Hz, 3H); Partial ¹H NMR for the minor *E*-isomer: 5.66 (d, *J* = 9.9 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 146.4, 137.6, 137.5, 136.8, 136.7, 136.4, 136.1, 135.9, 132.3, 129.2, 128.5, 128.4, 128.2, 127.1, 126.0, 125.9, 40.2, 22.7, 21.3, 21.2, 20.2, 19.9; HRMS (EI): Calcd for C₂₆H₂₈ (M): 340.2191. Found: 340.2184.



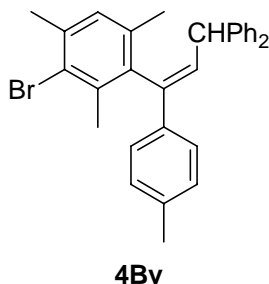
4Bn, obtained as a 98:2 mixture of *Z/E* isomers, yellow oil; ¹H NMR (300 MHz, CDCl₃): δ 7.35-7.10 (m, 5H), 7.10-6.92 (m, 5H), 6.88 (s, 1H), 6.43 (d, *J* = 9.9 Hz, 1H), 3.26-3.11 (m, 1H), 2.34 (s, 3H), 2.29 (s, 3H), 2.16 (s, 3H), 1.78 (s, 3H), 1.31 (d, *J* = 6.9 Hz, 3H); Partial ¹H NMR for the minor *E*-isomer: 5.69 (d, *J* = 9.9 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 143.2, 140.4, 137.5, 136.9, 136.5, 136.2, 135.8, 135.5, 133.5, 129.2, 128.4, 128.3, 127.0, 126.0, 39.8, 22.6, 21.3, 21.1, 20.2, 20.0; HRMS (EI): Calcd for C₂₆H₂₈ (M): 340.2191. Found: 340.2192.



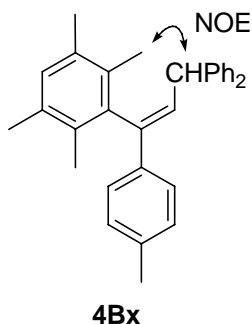
4Bo, obtained as a 97:3 mixture of *Z/E* isomers, white solid; m.p. 131 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.33-7.07 (m, 7H), 7.07-6.88 (m, 3H), 6.79 (s, 1H), 6.64 (d, $J = 9.6$ Hz, 1H), 3.52-3.37 (m, 1H), 2.32 (s, 3H), 2.18 (s, 3H), 1.78 (s, 3H), 1.47 (s, 3H), 1.29 (d, $J = 6.9$ Hz, 3H); Partial ^1H NMR for the minor *E*-isomer: 5.74 (d, $J = 9.6$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 145.2, 140.3, 138.2, 137.0, 136.5, 136.0, 135.9, 135.0, 133.4, 130.2, 128.5, 128.4, 128.2, 127.0, 126.6, 126.3, 126.0, 125.6, 35.2, 23.3, 21.2, 20.1, 19.3, 18.9; HRMS (EI): Calcd for $\text{C}_{26}\text{H}_{28}$ (M): 340.2191. Found: 340.2184.



4Bp, obtained as a 95:5 mixture of *Z/E* isomers, yellow oil; ^1H NMR (300 MHz, CDCl_3): δ 7.83-7.69 (m, 3H), 7.52-7.34 (m, 3H), 7.34-7.11 (m, 6H), 6.98 (s, 1H), 6.87 (s, 1H), 6.54 (d, $J = 9.9$ Hz, 1H), 3.46-3.32 (m, 1H), 2.36 (s, 3H), 2.20 (s, 3H), 1.70 (s, 3H), 1.42 (d, $J = 6.9$ Hz, 3H); Partial ^1H NMR for the minor *E*-isomer: 5.81 (d, $J = 10.5$ Hz, 1H); HRMS (EI): Calcd for $\text{C}_{29}\text{H}_{28}$ (M): 376.2191. Found: 376.2187.

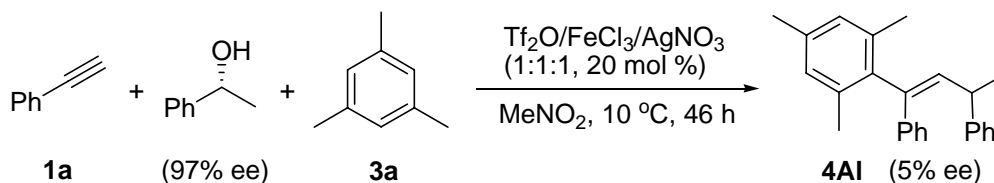


4Bv, obtained as a 96:4 mixture of *Z/E* isomers, white solid; m.p. 42 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.30-7.02 (m, 14H), 7.00 (s, 1H), 6.82 (d, $J = 10.2$ Hz, 1H), 4.36 (d, $J = 10.2$ Hz, 1H), 2.44 (s, 3H), 2.30 (s, 3H), 2.00 (s, 3H), 1.81 (s, 3H); Partial ^1H NMR for the minor *E*-isomer: 5.88 (d, $J = 10.2$ Hz, 1H), 5.29 (d, $J = 10.2$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 144.3, 144.2, 139.7, 137.4, 137.1, 136.8, 135.6, 130.0, 129.4, 129.0, 128.7, 128.6, 128.4, 128.3, 126.4, 126.0, 50.8, 24.1, 21.4, 21.2, 19.8; HRMS (EI): Calcd for $\text{C}_{31}\text{H}_{29}\text{Br}$ (M): 480.1453. Found: 480.1448.



4Bx, obtained as a 98:2 mixture of *Z/E* isomers, white solid; m.p. 110 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.32-7.10 (m, 10H), 7.10-6.98 (m, 4H), 6.97 (s, 1H), 6.81 (d, *J* = 10.2 Hz, 1H), 4.33 (d, *J* = 10.2 Hz, 1H), 2.30 (s, 3H), 2.20 (s, 6H), 1.75 (s, 6H); Partial ¹H NMR for the minor *Z/E* isomer: 5.88 (d, *J* = 10.2 Hz, 1H), 5.30 (d, *J* = 10.2 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 144.6, 141.0, 137.6, 137.0, 133.8, 132.5, 130.4, 129.4, 129.2, 129.0, 128.6, 128.5, 128.4, 126.2, 126.1, 50.7, 21.2, 20.3, 16.6; HRMS (EI): Calcd for C₃₂H₃₂ (M): 416.2504. Found: 416.2498.

Reaction of (*R*)-1-phenylethanol with phenylacetylene (1a**) and mesitylene (**3a**)**



To a stirred solution of phenylacetylene (**1a**, 20.4 mg, 22 μL, 0.20 mmol) in nitromethane (0.20 mL) at 10 °C were added successively mesitylene (**3a**, 48.0 mg, 55 μL, 0.40 mmol), (*R*)-1-phenylethanol (97% ee, 36.6 mg, 0.30 mmol), AgNO₃ (6.8 mg, 20 mol %), FeCl₃ (6.6 mg, 20 mol %), and Tf₂O (11.3 mg, 20 mol %). The resulting mixture was stirred at 10 °C for 46 h. The mixture was directly purified by silica gel column chromatography, eluting with petroleum ether, to give alkene **4AI** (31.1 mg, 47%) as a 96:4 mixture of *E/Z* isomers. The ee of alkene **4AI** was determined to be 5% by chiral HPLC [Chiralpak OD column, *n*-hexane/*i*-PrOH = 99.9:0.1, flow rate = 0.4 mL/min, *t*₁ = 17.4 min (minor), *t*₂ = 18.7 min (major)].

