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Supporting Information

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Catalytic Three-Component Coupling of Alkynes, Imines and Organoboron Reagents**

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Unless stated otherwise, all compounds were purchased from commercial suppliers (Aldrich, Alfa Aesar, or Strem) and used without further purification. THF, Et_2O and toluene were distilled from sodium/benzophenone ketyl. All other anhydrous grade solvents were purchased from Aldrich Chemical Co. Triethylborane, tributylborane, triphenylborane, and phenyl boronic acid were obtained neat and corresponding solutions were made prior to use. *trans*-Styrylboronic acid was prepared according to the procedures from H.C. Brown and coworkers[1] and a solution was made prior to use. Imines were made using known procedures from corresponding aldehydes and amines and prior to use, distilled or crystallized to >99% purity.

Analytical thin layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum plates precoated with a fluorescent indicator. The developed plates were analyzed under UV light and stained with 12-molybdophosphoric (PMA) stain. Flash chromatography was performed using silica gel 60 (40-63 μm) from Silicycle. All ^1H and ^{13}C NMR spectra were recorded using Bruker 400 MHz or Varian 500 MHz spectrometers at ambient temperature. IR spectra were recorded as a thin film between NaCl plates on a Perkin-Elmer Model 2000 FTIR instrument. Analytical chiral HPLC was performed on a Hewlett-Packard 1100 chromatograph equipped with a variable wavelength detector and Daicel Chiralcel OD column (0.46 cm x 25 cm).

Standard Experimental Procedure for Intermolecular Alkylative Coupling of Alkynes and Imines

In a glovebox, $Ni(cod)_2$ (14 mg, 0.05 mmol) and tricyclopentylphosphine (Cyp_3P, 14 μL, 0.05mmol) were placed into an oven-dried 50mL flask, with teflon coated stir bar, which was then sealed with a rubber septum. The flask was removed from the glovebox and placed under Ar atmosphere. Anhydrous MeOH (5 mL) was added followed by 200 μL of 3M MeOAc solution of RBX_2 (where X = OH, or R) and the flask was placed in 50 ^oC oil bath. After 2 min, imine (1.0 mmol) was added followed by alkyne (0.4 mmol). Reaction was stirred for an hour. Additional alkyne (1.60 mmol) and RBX_2 (3 M in MeOAc, 2.40 mmol, 800 μL) were added in 4 equal portions over 4 h. The reaction mixture was further stirred for 12 h at 50 ^oC, cooled to room temperature and opened to air. Concentration in vacuo and silica gel chromatography (hexanes: EtOAc) yielded allylic amines **1** and **2**. Unless otherwise stated, yield refers to the combined isolated yield of all allylic amine products. Ratios of regioisomers and alkylative coupling (AC), reductive coupling (RC) were determined by ^1H NMR.

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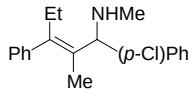
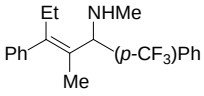
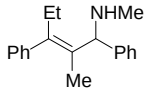
[1] H. C. Brown, S. K. Gupta, *J. Am. Chem. Soc.* **1971**, *164*, 4370-4371.

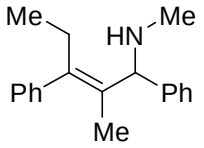
Standard Experimental Procedure for Asymmetric Intermolecular Alkylative Coupling of Alkynes and Imines

In a glovebox, $Ni(cod)_2$ (28 mg, 0.10 mmol) and (*S*)-(+)-(neomenthyl)diphenylphosphine [(*S*)-NMDPP, 64 mg, 0.20mmol] were placed into an oven-dried 50 mL flask, with teflon coated stir bar, which was sealed with a rubber septum. The flask was removed from the glovebox and placed under Ar atmosphere. Anhydrous MeOH (5 mL) was added followed by 200 μL of 3M MeOAc solution of R_3B and the flask was placed in 0 ^oC oil bath. After 10 min, imine (1.0 mmol) was added followed by alkyne (0.4 mmol). Reaction was stirred for an hour. Additional alkyne (1.60 mmol) and R_3B (3M MeOAc, 2.40 mmol, 800 μL) were added in 4 equal portions over 4 h. The reaction was further stirred for 20 h at 0 ^oC, and the flask was opened to the air and quenched with 5 mL water. The product was extracted with ethyl acetate, dried over $MgSO_4$ and concentrated *in vacuo*. Silica gel chromatography (hexanes:EtOAc) yielded allylic amines **1** and **2**. The corresponding acetamides were prepared [acetic anhydride (110%), triethylamine (120%) and 4-dimethylaminopyridine (DMAP, 5%) in CH_2Cl_2 (5 mL)]. 10 mL CH_2Cl_2 and 5 mL $NaHCO_3$ solution was added to the reaction flask and the organic layer was separated, dried with $MgSO_4$ and the solvent was removed under reduced pressure. The amides were analyzed by Chiralcel OD column to measure the enantiomeric excess.

Product	Chromatography conditions	Retention time of minor enantiomer of **1**	Retention time of major enantiomer of **1**	Retention time of minor enantiomer of **2**	Retention time of major enantiomer of **2**
	1% *i*-PrOH/Hexane (isocratic, 1mL/min)	15 min	17 min	28 min	32 min
	1% *i*-PrOH/Hexane flow rate 1mL/min for 45 min then 2% *i*-PrOH/Hexane	31 min	34 min	59 min	62 min
	1% *i*-PrOH/Hexane (isocratic, 1mL/min)	23 min	33 min	50 min	54 min

***N*-methyl-*N*-[(2*E*)-2-methyl-1,3-diphenylpent-2-enyl]amine (1a)**

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL) and *N*-[(1*E*)-phenylmethylene]methanamine (1.0 mmol, 119 mg), the standard procedure was used. Silica gel chromatography afforded the allylic amines as colorless oil (225 mg, 85% yield, AC : RC = 92:8, regioselectivity 91:9). R_f= 0.47 (2:3 hexanes: EtOAc).

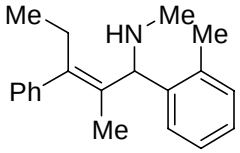


1a

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50-7.00 (m, 10H), 4.89 (s, 1H), 2.64 (m, 2H), 2.52 (s, 3H), 1.27 (s, 3H), 0.99 (t, *J*=7.5, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 142.8, 141.3, 131.4, 129.0, 128.4, 128.2, 127.0, 126.7, 126.3, 63.5, 34.6, 27.2, 14.1, 13.6. IR (film, CH_2Cl_2): 3333, 3024, 2969, 2931, 1600, 1575, 1491, 1441 cm^{-1}. HRMS (ESI) Calcd for $C_{19}H_{23}N$ $(M+Na)^+$ 288.1723 found 288.1734.

***N*-methyl-*N*-[(2*E*)-2-methyl-1-(2-methylphenyl)-3-phenylpent-2-enyl]amine (1b)**

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL) and *N*-[(1*E*)-(2-methylphenyl)methylene]methanamine (1.0 mmol, 133 mg), the standard procedure was used. Silica gel chromatography afforded the allylic amines as colorless oil (238 mg, 85% yield, AC : RC = 94:6, regioselectivity 90:10). R_f= 0.72 (3:2 hexanes: EtOAc).

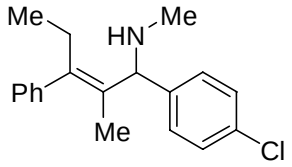


1b

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J*=7.56, 1H) 7.40-7.00 (m, 8H), 4.89 (s, 1H), 2.68 (m, 2H), 2.53 (s, 3H), 2.40 (s, 3H), 1.21 (s, 3H), 0.97 (t, *J*=7.5, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 141.1, 140.5, 136.2, 130.49, 130.46, 128.9, 128.2, 127.1, 126.5, 126.3, 125.9, 61.7, 35.1, 26.9, 19.8, 15.9, 13.1. IR (film, CH_2Cl_2): 3327, 3020, 2970, 2871, 1599, 1576, 1462, 1440, 754 cm^{-1}. HRMS (ESI) Calcd for $C_{20}H_{25}N$ $(M+H)^+$ 280.2060 found 280.2069.

***N*-[(2*E*)-1-(4-chlorophenyl)-2-methyl-3-phenylpent-2-enyl]-*N*-methylamine (1c)**

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL) and *N*-[(1*E*)-(4-chlorophenyl)methylene]-*N*-methylamine (1.0 mmol, 154 mg), the standard procedure was used. Silica gel chromatography afforded the allylic amines as colorless oil (284 mg, 95% yield, AC : RC = 96:4, regioselectivity 90:10). R_f= 0.53 (3:1 hexanes: EtOAc).

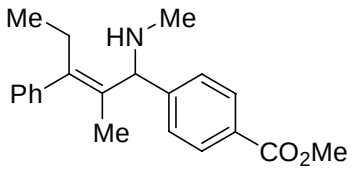


1c

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.00 (m, 9H), 4.79 (s, 1H), 2.55 (q, *J*=7.5, 2H), 2.44 (s, 3H), 1.18 (s, 3H), 0.95 (t, *J*=7.5, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 141.8, 141.2, 132.4, 130.8, 128.9, 128.5, 128.4, 128.2, 126.4, 62.9, 34.4, 27.2, 14.0, 13.6. IR (film, CH_2Cl_2): 3333, 3021, 2969, 2870, 1598, 1575, 1488, 1091, 1014, 766 cm^{-1}. HRMS (ESI) Calcd for $C_{19}H_{22}ClN$ $(M+H)^+$ 300.1514 found 300.1512.

methyl 4-[(2*E*)-2-methyl-1-(methylamino)-3-phenylpent-2-enyl]benzoate(1d)

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL) and methyl 4-[(*E*)-(methylimino)methyl]benzoate (1.0 mmol, 177 mg), the standard procedure was used. Silica gel chromatography afforded the allylic amines as colorless oil (284 mg, 82% yield, AC : RC = >96:4, regioselectivity 90:10). R_f= 0.42 (2:1 hexanes: EtOAc).

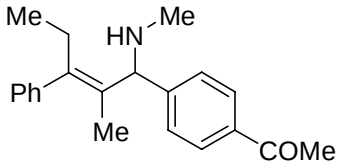


1d

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (m, 2H), 7.55 (m, 2H), 7.40-7.10 (m, 5H), 4.93 (s, 1H), 3.93 (s, 3H), 2.65 (q, *J*=7.5, 2H), 2.53 (s, 3H), 1.25 (s, 3H), 1.01 (t, *J*=7.5, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 148.3, 143.3, 141.9, 130.7, 129.7, 128.9, 128.6, 128.2, 127.0, 126.4, 63.5, 52.2, 34.5, 27.3, 14.1, 13.6. IR (film, CH_2Cl_2): 3336, 2969, 2871, 1722, 1609, 1436, 1279, 1109, 764 cm^{-1}. HRMS (ESI) Calcd for $C_{21}H_{25}NO_2$ $(M+Na)^+$ 346.1778 found 346.1775.

1-{4-[(2*E*)-2-methyl-1-(methylamino)-3-phenylpent-2-enyl]phenyl}ethanone(1e)

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL) and 1-{4-[(*E*)-(methylimino)methyl]phenyl}ethanone (1.0 mmol, 161 mg), the standard procedure was used. Silica gel chromatography afforded the allylic amines as colorless oil (257 mg, 78% yield, AC : RC = >96.4, regioselectivity 91:9). R_f= 0.28 (2:1 hexanes: EtOAc).

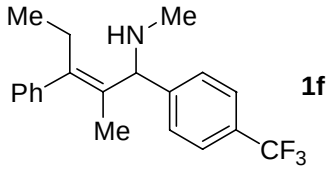


1e

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.90(m, 2H), 7.58 (m, 2H), 7.40-7.00 (m, 5H), 4.94 (s, 1H), 2.65 (m, 5H), 2.53 (s, 3H), 1.25 (s, 3H), 1.02 (t, *J*=7.5, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 148.6, 143.4, 142.1, 135.8, 130.7, 128.9, 128.6, 128.3, 127.3, 126.5, 63.6, 34.6, 27.3, 26.8, 14.2, 13.7. IR (film, CH_2Cl_2): 3335, 2969, 2932, 2870, 1682, 1605, 1571, 1268, 767 cm^{-1}. HRMS (ESI) Calcd for $C_{21}H_{25}NO$ $(M+Na)^+$ 330.1828 found 330.1817.

***N*-methyl-*N*-{(2*E*)-2-methyl-3-phenyl-1-[4-(trifluoromethyl)phenyl]pent-2-enyl}amine(1f)**

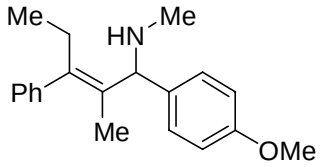
In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL) and *N*-{(1*E*)-[4-(trifluoromethyl)phenyl]methylene}methanamine (1.0 mmol, 187 mg), the standard procedure was used. Silica gel chromatography afforded the allylic amines as colorless oil (326 mg, 98% yield, AC : RC = 94:6, regioselectivity 89:11). R_f= 0.58 (1:2 hexanes: EtOAc).



1f

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.06 (m, 9H), 4.91 (s, 1H), 2.62 (q, *J*= 7.5, 2H), 2.51 (s, 3H), 1.52 (bs, 1H), 1.24 (s, 3H), 1.00 (t, *J*=7.5, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 143.4, 142.1, 130.7, 129.2, 128.9, 128.3, 127.4, 126.5, 125.4 (q, *J*=15) 123.2, 63.3, 34.6, 27.3, 14.1, 13.7. IR (film, CH_2Cl_2): 3332, 2971, 2872, 1618, 1599, 1411, 1325, 1163, 1124, 1067, 1017 cm^{-1}. HRMS (EI) Calcd for $C_{20}H_{22}F_3N$ $(M)^+$ 333.1699 found 333.1696.

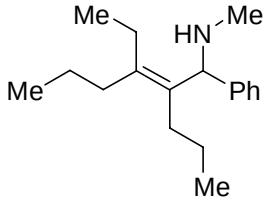
***N*-[(2*E*)-1-(4-methoxyphenyl)-2-methyl-3-phenylpent-2-enyl]-*N*-methylamine(1g)**
In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL) and *N*-[(1*E*)-(4-methoxyphenyl)methylene]-*N*-methylamine (1.0 mmol, 149 mg), the standard procedure was used. Silica gel chromatography afforded the allylic amines as colorless oil (203 mg, 64% yield, AC : RC = 86:14, regioselectivity 91:9). R_f= 0.78 (1:3 hexanes: EtOAc).



1g

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.10 (m, 7H), 6.92 (m, 2H), 4.85 (s, 1H), 3.84 (S, 3H), 2.62 (m, 2H), 2.52 (s, 3H), 1.61 (bs, 1H), 1.28 (s, 3H), 1.00 (t, *J*=7.5, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 143.8, 141.2, 134.8, 131.5, 129.0, 128.2, 128.0, 126.3, 113.7, 62.9, 55.4, 34.5, 27.2, 14.1, 13.7. IR (film, CH_2Cl_2): 3327, 3020, 2970, 2871, 1599, 1576, 1462, 1440, 754 cm^{-1}. HRMS (ESI) Calcd for $C_{20}H_{25}NO$ $(M+Na)^+$ 318.1828 found 318.1821.

(3-Ethyl-1-phenyl-2-propyl-hex-2-enyl)-methyl-amine (1h)
In the alkylative coupling of 4-octyne (2.0 mmol, 293 μL) and *N*-[(1*E*)-phenylmethylene]methanamine (1.0 mmol, 119 mg), the standard procedure was used. Silica gel chromatography afforded the allylic amines as colorless oil (236 mg, 91% yield, AC : RC = 94:6). R_f= 0.50 (1:3 hexanes: EtOAc).

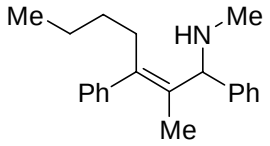


1h

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (m, 2H), 7.29 (m, 2H), 7.20 (m, 1H), 4.69 (s, 1H), 2.41 (s, 3H), 2.29 (m, 2H), 2.03 (m, 2H), 1.85 (m, 1H), 1.73 (m, 1H), 1.45 (m, 1H), 1.15 (m, 1H), 1.09 (t, *J*= 7.75, 3H), 0.94 (t, *J*= 7.25, 3H), 0.68 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 139.4, 134.6, 128.1, 127.2, 126.4, 64.2, 34.9, 34.1, 30.4, 24.2, 24.1, 22.2, 15.0, 14.7, 14.5. IR (film, CH_2Cl_2): 3419, 2959, 2870, 1644, 1492, 1451, 1030, 739 cm^{-1}. HRMS (ESI) Calcd for $C_{18}H_{29}N$ $(M+H)^+$ 260.2386 found 260.2382.

***N*-methyl-*N*-[(2*E*)-2-methyl-1,3-diphenylhept-2-enyl]amine (1i)**

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), *N*-[(1*E*)-phenylmethylene]methanamine (1.0 mmol, 119 mg) and Bu_3B (3M MeOAc, 1mL), the standard procedure was used. Silica gel chromatography afforded the allylic amines as colorless oil (206 mg, 70% yield, AC : RC = 90:10, regioselectivity 91:9). R_f= 0.42 (1:2 hexanes: EtOAc).



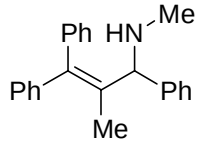
1i

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.10 (m, 10H), 4.90 (s, 1H), 2.62 (m, 2H), 2.53 (s, 3H), 1.61 (bs, 1H), 1.43 (m, 4H), 1.28 (s, 3H), 0.89 (t, *J*= 7.5, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 142.8, 140.1, 131.8, 128.9, 128.4, 128.2, 127.0, 126.7, 126.2, 63.5, 34.6, 34.0, 31.1, 23.1, 14.3, 14.2. IR (film, CH_2Cl_2): 3334, 3024, 2954, 2858, 1599, 1574, 1491, 1148, 1102, 1029, 745 cm^{-1}. HRMS (ESI) Calcd for $C_{21}H_{27}N$ $(M+H)^+$ 294.2216 found 294.2224.

***N*,2-dimethyl-1,3,3-triphenylprop-2-en-1-amine (1j)**

Procedure using Ph_3B: In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), *N*-[(1*E*)-phenylmethylene]methanamine (1.0 mmol, 119 mg) and Ph_3B (1M MeOAc, 1mL), the standard procedure was used. Silica gel chromatography afforded the allylic amines as colorless oil (203 mg, 65% yield, AC : RC = >97%, regioselectivity 93:7). R_f= 0.62 (3:1 hexanes: EtOAc).

Procedure using phenyl boronic acid: In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), *N*-[(1*E*)-phenylmethylene]methanamine (1.0 mmol, 119 mg) and phenyl boronic acid (3M MeOAc, 1mL), the standard procedure was used. Silica gel chromatography afforded the allylic amines as colorless oil (225 mg, 72% yield, AC : RC = >97%, regioselectivity 92:8). R_f= 0.62 (3:1 hexanes: EtOAc).

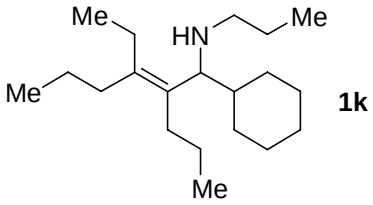


1j

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.20 (m, 15H), 4.60 (s, 1H), 2.45 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 142.9, 142.5, 141.0, 135.4, 129.5, 129.4, 128.4, 128.3, 128.2, 127.2, 126.8, 126.7, 126.6, 65.1, 34.3, 14.1. IR (film, CH_2Cl_2): 3334, 3056, 3024, 2931, 2789, 1598, 1576, 1490, 1442, 754 cm^{-1}. HRMS (ESI) Calcd for $C_{23}H_{23}N$ $(M)^+$ 313.1825 found 313.1825.

(1-Cyclohexyl-3-ethyl-2-propyl-hex-2-enyl)-propyl-amine (1k)

In the alkylative coupling of 4-octyne (2.0 mmol, 293 μL) and *N*-[(1*E*)-cyclohexylmethylene]-*N*-propylamine (1.0 mmol, 153 mg), the standard procedure was used. Silica gel chromatography afforded the allylic amines as colorless oil (153 mg, 52% yield, AC : RC = >96:4). R_f= 0.68 (1:2 hexanes: EtOAc).

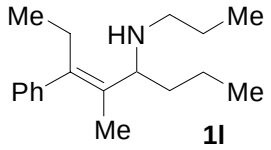


1k

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.16 (d, *J*= 9.5, 1H), 2.42 (m, 1H), 2.28 (m, 1H), 2.14-1.89 (m, 6H), 1.82-1.74 (m, 2H), 1.65(m, 2H), 1.55 (m, 1H), 1.48-1.31 (m, 7H), 1.26-1.19 (m, 2H), 1.13 (m, 2H), 0.94-0.87 (m, 12H), 0.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.6, 132.7, 49.8, 41.1, 33.9, 31.4, 31.0, 26.9, 26.7, 26.6, 24.5, 23.7, 23.3, 22.1, 15.4, 14.8, 13.8, 12.1. IR (film, CH_2Cl_2): 3419, 2957, 2870, 1733, 1455, 1376, 1260, 1092, 1020, 803 cm^{-1}. HRMS (ESI) Calcd for $C_{20}H_{39}N$ $(M+H)^+$ 294.3155 found 294.3151.

***N*-[(2*E*)-2-methyl-3-phenyl-1-propylpent-2-enyl]-*N*-propylamine (1l)**

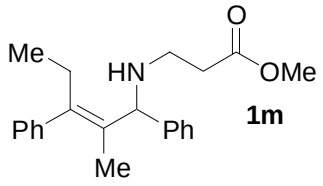
In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL) and *N*-[(1*E*)-butylidene]-*N*-propylamine (1.0 mmol, 113 mg), the standard procedure was used. Silica gel chromatography afforded the allylic amines as colorless oil (78 mg, 30% yield, AC : RC = 90:10, regioselectivity 91:9). R_f= 0.18 (1:3 hexanes: EtOAc).



1l

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (m, 2H), 7.22 (m, 1H), 7.08 (m, 2H), 3.74 (dd, *J*= 5.8, 8.2, 1H), 2.49 (m, 4H), 1.48 (m, 7H), 1.34 (s, 3H), 0.93 (m, 6H), 0.86 (t, *J*= 7.5, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 141.1, 131.3, 129.1, 128.2, 126.1, 57.8, 49.4, 36.9, 26.7, 23.8, 20.0, 14.7, 13.5, 13.1, 12.2. HRMS (ESI) Calcd for $C_{18}H_{29}N$ $(M+H)^+$ 260.2373 found 260.2369.

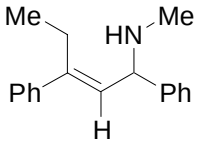
3-(2-Methyl-1,3-diphenyl-pent-2-enylamino)-propionic acid methyl ester (1m)
In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), and methyl 3-{[(1*E*)-phenylmethylene]amino}propanoate (1.0 mmol, 191 mg) the standard procedure was used. Silica gel chromatography afforded the allylic amines as colorless oil (230 mg, 75% yield, AC : RC = 94:6, regioselectivity 91:9). R_f= 0.58 (4:1 hexanes: EtOAc).



1m

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (m, 2H), 7.37 (m, 4H), 7.28 (m, 2H), 7.14 (m, 2H), 5.02 (s, 1H), 3.75 (s, 3H), 3.05 (m, 1H), 2.90 (m, 1H), 2.65 (m, 4H), 1.31 (s, 3H), 1.01 (t, *J*= 7.5, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 143.6, 142.7, 141.0, 131.6, 129.0, 128.3, 128.2, 127.0, 126.7, 126.3, 61.6, 51.7, 43.0, 35.0, 27.1, 14.2, 13.7. IR (film, CH_2Cl_2): 3449, 3024, 2966, 1736, 1600, 1491, 1438, 1371, 1173, 766 cm^{-1}. HRMS (ESI) Calcd for $C_{22}H_{27}NO_2$ $(M+Na)^+$ 360.1934 found 360.1925.

***N*-[(2*E*)-1,3-diphenylpent-2-enyl]-*N*-methylamine (1n)**
In the alkylative coupling of phenylacetylene (2.0 mmol, 220 μL), and *N*-[(1*E*)-phenylmethylene]methanamine (1.0 mmol, 119 mg), the standard procedure was used. Silica gel chromatography afforded the allylic amines as colorless oil (88 mg, 35% yield, AC : RC > 95:5, regioselectivity > 98:2). R $_f$= 0.12 (1:4 hexanes: EtOAc).

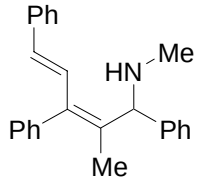


1n

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.5-7.2 (m, 10H), 5.79 (d, *J*= 9.2, 1H), 4.52 (d, *J*= 9.2, 1H), 2.68 (q, *J*= 7.5, 2H), 2.46 (s, 3H), 1.59 (bs, 1H), 1.00 (t, *J*= 7.5, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 143.1, 142.4, 130.9, 128.7, 128.4, 127.4, 127.3, 127.2, 126.7, 62.9, 34.7, 23.6, 13.8. IR (film, CH_2Cl_2): 3322, 3025, 2968, 2871, 1599, 1491, 1451, 1029, 760 cm^{-1}. HRMS (ESI) Calcd for $C_{18}H_{21}N$ $(M+H)^+$ 252.1747 found 252.1740.

Methyl-(2-methyl-1,3,5-triphenyl-penta-2,4-dienyl)-amine (1o)

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), *N*-[(1*E*)-phenylmethylene]methanamine (1.0 mmol, 119 mg) and *trans*-styrylbornoic acid (3M MeOAc, 1mL), the standard procedure was used. Silica gel chromatography afforded the allylic amines as colorless oil (230 mg, 68% yield, AC: RC = >97%, regioselectivity 91:9). R_f= 0.45 (1:1 hexanes: EtOAc).



1o

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J*= 15.7, 1H), 7.52 (m, 2H), 7.58-7.28 (m, 10H), 7.24 (m, 1H), 7.18 (m, 2H), 6.03 (d, *J*= 15.7, 1H), 5.32 (s, 1H), 2.58 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3, 140.9, 139.2, 137.9, 137.8, 132.3, 129.9, 128.7, 128.5, 127.5, 127.1, 126.92, 126.89, 128.81, 126.5, 63.1, 34.6, 15.4. IR (film, CH_2Cl_2): 3330, 3024, 2932, 1599, 1574, 1492, 1448, 1014, 957, 752 cm^{-1}. HRMS (ESI) Calcd for $C_{25}H_{25}N$ $(M+H)^+$ 340.2060 found 340.2069.