Iridium-Catalyzed 1,5-(Aryl)aminomethylation of 1,3-Enynes by Alkenyl-to-Allyl 1,4-Iridium(I) Migration

Rebecca E. Ruscoe, Michael Callingham, Joshua A. Baker, Stamatis E. Korkis, and Hon Wai Lam*

*The GlaxoSmithKline Carbon Neutral Laboratories for Sustainable Chemistry, University of Nottingham, Jubilee Campus, Triumph Road, Nottingham, NG7 2TU, United Kingdom

and

School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom

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**General Information**

All air-sensitive reactions were carried out under an argon atmosphere using oven-dried apparatus. Anhydrous 1,4-dioxane was purchased from Sigma Aldrich and was dried further over activated molecular sieves. All commercially available reagents were used as received unless otherwise stated. Arylboronic acids were used as received unless the sample contained >10\% boroxine as determined by $^1$H NMR analysis. In this case, the boronic acid was stirred in a mixture of Et$_2$O and water for 30 min. The organic phase was separated, dried (Na$_2$SO$_4$), filtered and concentrated *in vacuo* to give the corresponding boronic acid, which was used without further purification. All petroleum ether used was 40-60 °C petroleum ether. Thin layer chromatography (TLC) was performed on Merck DFAufoilen 60F254 0.2 mm precoated plates. Compounds were visualized by exposure to UV light or by dipping the plates into solutions of potassium permanganate or vanillin followed by gentle heating. Flash column chromatography was carried out using silica gel (Fisher Scientific 60 Å particle size 35-70 micron). Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. Infra-red (IR) spectra were recorded on a Nicolet Avatar 360 FT instrument on compounds evaporated from CHCl$_3$. NMR spectra were acquired on Bruker Ascend 400 or Ascend 500 spectrometers. $^1$H and $^{13}$C NMR spectra were referenced to external tetramethylsilane via the residual protonated solvent ($^1$H) or the solvent itself ($^{13}$C). All chemical shifts are reported in parts per million (ppm). For CDCl$_3$, the shifts are referenced to 7.26 ppm for $^1$H NMR spectroscopy and 77.16 ppm for $^{13}$C NMR spectroscopy. Abbreviations used in the description of resonances are: s (singlet), d (doublet), t (triplet), q (quartet), app (apparent), br (broad) and m (multiplet). Coupling constants ($J$) are quoted to the nearest 0.1 Hz. HSQC and HMBC experiments were used to assist $^1$H NMR assignments where required. $^{13}$C NMR assignments were made using the DEPT sequence with secondary pulses at 135°. $^{19}$F NMR spectra were proton-decoupled and were referenced through the solvent lock ($^2$H) signal according to IUPAC recommended secondary referencing method the Bruker protocols. High-resolution mass spectra were recorded using electrospray ionization (ESI) or electron impact ionization (EI) techniques.
Preparation of 1,3-Enynes

Known 1,3-enynes were prepared according to literature procedures: 2a-d, 1, 2e, 2 2f, 3

(E)-Non-2-en-4-yn-2-ylbenzene (2g)

To a degassed solution of 1-bromo-2-phenyl-prop-1-ene 4 (1.60 g, 11.5 mmol) in pyrrolidine (30 mL) was added Pd(PPh)$_3$$_4$ (250 mg, 0.22 mmol), followed by CuI (210 mg, 1.09 mmol). Hex-1-yne (1.41 g, 10.9 mmol) was then added and the mixture was stirred for 16 h under a nitrogen atmosphere. 1 M Aqueous HCl solution (10 mL) was added slowly and the product was extracted with Et$_2$O (3 x 25 mL). The combined organic layers were washed with 1 M aqueous HCl solution (10 mL), dried (MgSO$_4$), filtered and concentrated in vacuo. The mixture was purified by column chromatography (1% Et$_2$O/petroleum ether) to give the enyne 2g (910 mg, 4.59 mmol, 43%) as a colorless oil. R$_f$ = 0.57 (1% Et$_2$O/petroleum ether); IR 2957, 2931, 2860, 2210, 1597, 1494, 1444, 1377, 1325, 1071, 1027, 910, 850, 753, 692, 615, 548, 480 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.44-7.40 (2H, m, ArH), 7.35-7.30 (2H, m, ArH), 7.29-7.26 (1H, m, ArH), 5.89-5.86 (1H, m, =CH), 2.43 (2H, td, $J$ = 7.0, 2.2 Hz, CH$_2$CH$_2$CH$_2$CH$_3$), 2.29 (3H, d, $J$ = 1.2 Hz, CH$_3$C=), 1.63-1.56 (2H, m, CH$_2$CH$_2$CH$_3$), 1.52-1.45 (2H, m, CH$_2$CH$_3$), 0.95 (3H, t, $J$ = 7.3 Hz, CH$_2$CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 146.8 (C), 141.4 (C), 128.5 (2 x CH), 127.9 (CH), 125.5 (2 x CH), 107.4 (CH), 96.6 (C), 79.2 (C), 31.2 (CH$_2$), 22.2 (CH$_2$), 19.6 (CH$_2$), 18.5 (CH$_3$), 13.8 (CH$_3$).

7-Methyl-1-morpholinooct-6-en-4-yn-1-one (S1)

A solution of 1-bromo-2-methylprop-1-ene (667 mg, 4.94 mmol) in pyrrolidine (15 mL) was degassed with argon for 15 min. Pd(PPh)$_3$$_4$ (116 mg, 0.10 mmol) and CuI (94.0 mg, 0.49 mmol) were added followed by 1-morpholinopent-4-yn-1-one 5 (750 mg, 4.49 mmol). The resulting solution was
degassed for a further 10 min before being heated to 60 °C for 2 h. The black solution was diluted with saturated aqueous NH₄Cl solution (20 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (15 mL), dried (Na₂SO₄), filtered and concentrated in vacuo. Purification of the residue by column chromatography (40% EtOAc/petroleum ether) gave 1,3-enedyne S1 (795 mg, 3.59 mmol, 80%) as a yellow oil. Rₚ = 0.59 (40% Et₂O/petroleum ether); IR 2857, 1646 (C=O), 1435, 1301, 1272, 1116, 1021, 847 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.21 (1H, app dd, J = 2.5, 1.1 Hz, =CH), 3.69-3.65 (4H, m, CH₂), 3.63 (2H, d, J = 5.0 Hz, CH₂), 3.51-3.46 (2H, m, CH₂), 2.70 (2H, ddd, J = 8.1, 6.8, 1.9 Hz, CH₂), 2.60-2.53 (2H, m, CH₂), 1.86 (3H, d, J = 1.1 Hz, CH₃), 1.77 (3H, d, J = 1.5 Hz, CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 170.1 (C), 147.6 (C), 105.3 (CH), 90.5 (C), 67.1 (CH₂), 66.8 (CH₂), 46.1 (CH₂), 42.2 (CH₂), 32.7 (CH₂), 24.8 (CH₃), 21.0 (CH₃), 15.9 (CH₂); HRMS (ESI) Exact mass calculated for C₁₃H₁₉N₂O [M+H]⁺: 222.1489, found: 222.1490.

7-Methyl-1-phenyloct-6-en-4-yn-1-one (2h)

PhLi (1.58 M in dibutyl ether, 4.3 mL, 6.78 mmol) was added to a solution of S1 (500 mg, 2.26 mmol) in THF (10 mL) at −78 °C. The resulting solution was stirred for 2 h, quenched carefully with saturated aqueous NH₄Cl solution (15 mL), and extracted with Et₂O (3 × 15 mL). The combined organic layers were dried (MgSO₄), filtered and concentrated in vacuo. Purification of the residue by column chromatography (10% Et₂O/petroleum ether) gave 1,3-enedyne 2h (437 mg, 2.06 mmol, 91%) as a yellow oil. Rₚ = 0.35 (10% Et₂O/petroleum ether); IR 2911, 2330 (C≡C), 1681 (C=O), 1578, 1447, 1409, 1360, 1290, 1203, 1046, 971, 821, 739, 689, 655, 567, 539, 489 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.00-7.95 (2H, m, ArH), 7.60-7.54 (1H, m, ArH), 7.40 (2H, d, J = 8.4, 7.1 Hz, ArH), 5.22 (1H, dt, J = 2.5, 1.1 Hz, =CH), 3.32-3.17 (2H, m, CH₂), 2.78 (2H, td, J = 7.5, 2.1 Hz, CH₂), 1.85 (3H, s, CH₃), 1.77 (3H, s, CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 198.3 (C), 147.5 (C), 136.8 (C), 133.3 (CH), 128.8 (2 × CH), 128.2 (2 × CH), 105.3 (CH), 90.6 (C), 79.1 (C), 38.3 (CH₂), 24.8 (CH₃), 20.9 (CH₃), 14.6 (CH₂); HRMS (ESI) Exact mass calculated for C₁₅H₁₇O [M+H]⁺: 213.1274, found: 213.1277.
3-(5-Methylhex-4-en-2-yn-1-yl)cyclohexan-1-one (2i)

A solution of 3-(prop-2-yn-1-yl)cyclohexan-1-one \(^6\) (378 mg, 2.76 mmol) in pyrrolidine (2 mL) was added to a mixture of 1-bromo-2-methylprop-1-ene (412 mg, 3.05 mmol), Pd(PPh\(_3\))\(_4\) (65.0 mg, 0.06 mmol) and CuI (53.0 mg, 0.28 mmol) in pyrrolidine (5 mL) under an atmosphere of argon. The resulting solution was stirred at room temperature for 18 h, quenched with saturated aqueous NH\(_4\)Cl solution (5 mL), extracted with Et\(_2\)O (3 × 5 mL), and the combined organic layers were washed with brine (10 mL), dried (MgSO\(_4\)), filtered and concentrated \textit{in vacuo}. Purification of the residue by column chromatography (10% Et\(_2\)O/petroleum ether) gave enyne 2i (434 mg, 2.28 mmol, 83%) as a colorless oil. \(R_f = 0.15\) (10% Et\(_2\)O/petroleum ether); IR 2929, 1710 (C=O), 1447, 1429, 1335, 1223, 1203, 1167, 1055, 868, 820, 732, 502, 488 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 5.28-5.17 (1H, m, =C\(\text{H}\)), 2.51-2.44 (1H, m, C\(\text{H}_2\)), 2.42-2.31 (3H, m, C\(\text{H}_2\)), 2.31-2.16 (2H, m, C\(\text{H}_2\)), 2.10-1.92 (3H, m, CH and C\(\text{H}_2\)), 1.86 (3H, s, CH\(_3\)), 1.78 (3H, d, \(J = 1.4\) Hz, CH\(_3\)), 1.72-1.64 (1H, m, CH\(_2\)), 1.62-1.45 (1H, m, CH\(_2\)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 211.6 (C), 147.5 (C), 105.3 (CH), 88.8 (C), 80.8 (C), 47.4 (CH\(_2\)), 41.3 (CH\(_3\)), 38.5 (CH), 30.6 (CH\(_2\)), 26.7 (CH\(_2\)), 25.1 (CH\(_2\)), 24.8 (CH\(_3\)), 21.0 (CH\(_3\)); HRMS (ESI) Exact mass calculated for C\(_{13}\)H\(_{19}\)O [M+H]\(^{+}\): 191.1430, found: 191.1436.

**Preparation of Triazinanes**

Triazanine 1f is commercially available.

\[ \text{NH}_2 \quad \xrightarrow{\text{HCHO}_{\text{anhyd}} \text{(1.0 equiv)}} \quad 25^\circ \text{C}, 2 \text{h} \quad \text{Ph} \quad \xrightarrow{\text{1a \quad (1.0 equiv)}} \quad 25^\circ \text{C}, 2 \text{h} \quad \text{Ph} \]

1,3,5-Triphenyl-1,3,5-triazinane (1a)

A solution of aniline (5.00 mL, 54.9 mmol) and aqueous formaldehyde (37%, 4.20 mL, 54.9 mmol) was stirred at room temperature for 2 h. Et\(_2\)O (10 mL) and H\(_2\)O (10 mL) were added and the resulting precipitate was filtered. The solid was then washed with petroleum ether (10 mL) to give triazanine 1a (3.58 g, 11.3 mmol, 21%) as an off-white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.25-7.18 (6H, m, Ar\(\text{H}\)), 7.06-7.01 (6H, m, Ar\(\text{H}\)), 6.87 (3H, tt, \(J = 7.3, 1.1\) Hz, Ar\(\text{H}\)), 4.90 (6H, s, 3 × CH\(_2\)); \(^{13}\)C NMR
(101 MHz, CDCl$_3$) δ 148.6 (3 × C), 129.2 (6 × CH), 120.9 (3 × CH), 117.7 (6 × CH), 68.6 (3 × CH$_2$). These data are consistent with those reported previously.$^7$

1,3,5-Tris(4-methoxyphenyl)-1,3,5-triazinane (1b)

Aqueous formaldehyde (37%, 0.84 mL, 11 mmol) was added to a solution of $p$-anisidine (1.23 g, 10.0 mmol) in EtOAc (15 mL) and H$_2$O (15 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h, warmed to room temperature and then stirred for an additional 1 h. The resulting solid was filtered and washed with H$_2$O to give triazinane $1b$ (993 mg, 2.45 mmol, 25%) as a grey solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.05-6.99 (6H, m, ArH), 6.83-6.76 (6H, m, ArH), 4.69 (6H, s, 3 × CH$_2$), 3.76 (9H, s, 3 × CH$_3$); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 154.5 (3 × C), 142.6 (3 × C), 120.1 (6 × CH), 114.4 (6 × CH), 71.1 (3 × CH$_2$), 55.5 (3 × CH$_3$). These data are consistent with those reported previously.$^8$

1,3,5-Tris(4-fluorophenyl)-1,3,5-triazinane (1c)

$para$-Fluoroaniline (0.95 mL, 10.0 mmol) and aqueous formaldehyde (37%, 0.9 mL, 12.0 mmol) were added to a sealed vessel and irradiated in a Biotage Initiator microwave synthesizer at 100 °C for 10 min. A solid formed upon standing, which was filtered and recrystallized from iso-hexane (MP = 157-162 °C) to give triazinane $1c$ as a white solid (730 mg, 1.98 mmol, 20%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.00-6.95 (6H, m, ArH), 6.92-6.87 (6H, m, ArH), 4.76 (6H, s, 3 × CH$_2$); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 158.1 (d, $J_{C-F} = 240.8$ Hz, C), 145.2 (d, $J_{C-F} = 2.6$ Hz, C), 120.1 (d, $J_{C-F} = 7.7$ Hz, 6 × CH), 115.8 (d, $J_{C-F} = 22.1$ Hz, 6 × CH), 70.7 (3 × CH$_2$); $^{19}$F NMR (376 MHz, CDCl$_3$) δ –122.3 (s). These data are consistent with those reported previously.$^9$
1,3,5-Tris(3,5-dimethylphenyl)-1,3,5-triazinane (1d)

A solution of 3,5-dimethylaniline (606 mg, 5.0 mmol) and aqueous formaldehyde (37%, 0.42 mL, 5.50 mmol) was stirred at 25 °C for 2h. Et₂O (10 mL) and H₂O (10 mL) was added and the resulting precipitate was filtered. The solid was then washed with petroleum ether (10 mL) to give triazinane 1d (190 mg, 0.49 mmol, 10%) as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 6.62 (6H, s, ArH), 6.54 (3H, s, ArH), 4.77 (6H, s, 3 × CH₂), 2.25 (18H, s, 6 × CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 148.9 (3 × C), 138.8 (6 × C), 122.8 (3 × CH), 115.7 (6 × CH), 68.7 (3 × CH₂), 21.8 (6 × CH₃). These data are consistent with those reported previously.⁹

1,3,5-Tris(6-methoxypyridin-3-yl)-1,3,5-triazinane (1e)

Paraformaldehyde (532 mg, 17.7 mmol) was added to a solution of 5-amino-2-methoxypyridine (2.00 g, 16.1 mmol) in toluene (20 mL) and the mixture was heated at 110 °C for 30 min. The reaction was cooled to room temperature and concentrated in vacuo. Petroleum ether (20 mL) was added and the resulting solid was isolated by filtration and washed with additional petroleum ether to leave triazinane 1e (1.64 g, 4.02 mmol, 25%) as a red solid. ¹H NMR (400 MHz, CDCl₃) δ 7.95 (3H, dd, J = 3.0, 0.7 Hz, ArH), 7.39 (3H, dd, J = 8.9, 3.0 Hz, ArH), 6.61 (3H, dd, J = 8.9, 0.7 Hz, ArH), 4.72 (6H, s, 3 × CH₂), 3.87 (9H, s, 3 × CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 159.6 (3 × C), 139.2 (3 × C), 137.0 (3 × CH), 131.3 (3 × CH), 110.9 (3 × CH), 70.9 (3 × CH₂), 53.4 (3 × CH₃). These data are consistent with those reported previously.⁸
1,3,5-Triisopropyl-1,3,5-triazinane (1g)

A solution of isopropylamine (5.00 mL, 58.8 mmol) in toluene (15 mL) was cooled to 0 °C. Aqueous formaldehyde (37%, 5.25 mL, 70.4 mmol) was added dropwise. The mixture was warmed to room temperature and stirred for 4 h, washed with water (2 × 20 mL), dried (MgSO₄) and concentrated in vacuo to leave triazinane 1g (2.09 g, 9.80 mmol, 17%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 3.53 (6H, s, 3 × CH₂), 2.85 (3H, hept, J = 6.5 Hz, 3 × CH(CH₃)₂), 1.06 (18H, d, J = 6.5 Hz, 3 × CH(CH₃)₂); ¹³C NMR (126 MHz, CDCl₃) δ 68.6 (3 × CH₂), 49.9 (3 × CH), 20.0 (6 × CH₃). These data are consistent with those reported previously.¹⁰
Iridium-Catalyzed 1,5-(Aryl)aminomethylation of 1,3-Enynes: General Procedure

1,3-Enyne (0.30 mmol), triazinane (0.15 mmol), arylboronic acid (0.45 mmol), [Ir(cod)Cl]₂ (5.0 mg, 0.0075 mmol), anhydrous K₃PO₄ (95.5 mg, 0.45 mmol) and 4Å molecular sieves (100 mg) were added to an oven-dried microwave vial, which was sealed. The vessel was evacuated and refilled with argon and left to flush with argon for 15 min. Anhydrous 1,4-dioxane (3.0 mL) was added and the vial was sealed with parafilm, before being heated to 80 °C. After 24 h, the reaction was quenched with saturated aqueous NH₄Cl solution, extracted with EtOAc, dried (MgSO₄) and concentrated in vacuo. The crude product was purified by column chromatography to give the 1,5-(aryl)aminomethylation product.

1,5-Difunctionalized Products

N-[3Z,5Z]-3-methyl-6,8-diphenylocta-3,5-dien-1-yl]aniline (3a). The title compound was prepared according to the general procedure using enyne 2a (55.3 mg, 0.30 mmol), triazinane 1a (47.3 mg, 0.15 mmol) and PhB(OH)₂ (54.9 mg, 0.45 mmol) to give the crude product as a 4.9:1 mixture of inseparable E/Z isomers. Purification of the residue by column chromatography (5-10% EtOAc/petroleum ether) gave homoallylic amine 3a [86.3 mg, 0.24 mmol, 52% (4.9:1 E:Z)] as a brown oil. Rf = 0.42 (10% EtOAc/petroleum ether); IR 3024 (N-H), 2924, 1601 (C=C), 1504, 1452, 1316, 1262, 1179, 1153, 866, 746, 692 cm⁻¹; HRMS (ESI) Exact mass calculated for C₂₇H₃₀N [M+H]⁺: 368.2373, found: 368.2381.

NMR data of major E-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.54-7.49 (2H, m, ArH), 7.44-7.37 (2H, m, ArH), 7.35-7.29 (3H, m, ArH), 7.25-7.18 (5H, m, ArH), 6.79-6.73 (1H, m, ArH), 6.70-6.65 (2H, m, ArH), 6.61 (1H, d, J = 11.3 Hz, CH=CPh), 6.22 (1H, dq, J = 11.3, 1.3 Hz, CH₃C≡CH), 3.66 (1H, br s, N-H), 3.29 (2H, t, J = 6.8 Hz, CH₂), 2.51-2.43 (2H, m, NCH₂CH₂), 1.89 (3H, d, J = 1.3 Hz, CH₃C≡C=); ¹³C NMR (101 MHz, CDCl₃) δ 148.3 (C), 142.8 (C), 142.0 (C), 139.3 (C), 137.1 (C), 129.4 (2 × CH), 128.56 (2 × CH), 128.53 (2 × CH), 128.46 (2 × CH), 127.1 (CH), 126.4 (2 × CH), 126.0 (CH), 123.9 (CH), 123.3 (CH), 117.5 (CH), 113.1 (2 × CH), 41.8 (CH₂), 40.0 (CH₂), 35.4 (CH₂), 32.3 (CH₂), 16.6 (CH₃).

Characteristic NMR data of minor Z-isomer: ¹H NMR (400 MHz, CDCl₃) δ 6.31 (1H, dd, J = 11.5, 1.5 Hz, CH₃C≡CH), 2.60 (2H, t, J = 6.8 Hz, CH₂), 1.93 (3H, d, J = 1.5 Hz, CH₃C≡C=); ¹³C NMR (101 MHz, CDCl₃) δ 124.1 (CH), 123.6 (CH), 24.4 (CH₃).
4-Methoxy-N-[(3Z,5Z)-3-methyl-6,8-diphenylocta-3,5-dien-1-yl]aniline (3b). The title compound was prepared according to the general procedure using enyne 1a (55.3 mg, 0.30 mmol), triazinane 1b (60.8 mg, 0.15 mmol) and PhB(OH)$_2$ (54.9 mg, 0.45 mmol) to give the crude product as a 5.2:1 mixture of inseparable E/Z isomers. Purification of the residue by column chromatography (5-10% EtOAc/petroleum ether) gave *homoallylic amine* 3b [88.2 mg, 0.22 mmol, 74% (6.0:1 E:Z)] as a brown oil. $R_t = 2.9$ (10% EtOAc/petroleum ether); IR 3395 (N-H), 3025, 2930, 1510 (C=C), 1443, 1234, 1036, 817, 753, 696 cm$^{-1}$; HRMS (ESI) Exact mass calculated for C$_{28}$H$_{32}$NO [M+H]$^+$: 398.2478, found: 398.2472.

**NMR data of major E-isomer:** $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.47 (2H, dd, J = 8.3, 1.3 Hz, ArH), 7.40-7.33 (2H, m, ArH), 7.30-7.27 (3H, m, ArH), 7.22-7.14 (3H, m, ArH), 6.81-6.77 (2H, m, ArH), 6.63-6.59 (2H, m, ArH), 6.56 (1H, $J$ = 11.3 Hz, HC=CPh), 6.21-6.16 (1H, m, CH$_3$C=CH), 3.75 (3H, s, OCH$_3$), 3.36 (1H, br s, NH), 3.21 (2H, t, $J$ = 6.7 Hz, NCH$_2$), 2.96-2.90 (2H, m, CH$_3$Ph), 2.74-2.67 (2H, m, CH$_2$CH$_2$Ph), 2.42 (2H, t, $J$ = 6.7 Hz, NCH$_2$CH$_2$), 1.85 (3H, d, $J$ = 1.3 Hz, CH$_3$C=); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 152.3 (C), 142.9 (C), 142.6 (C), 142.1 (C), 139.3 (C), 137.2 (C), 128.6 (2 $\times$ CH), 128.53 (2 $\times$ CH), 128.48 (2 $\times$ CH), 127.1 (CH), 126.4 (2 $\times$ CH), 126.1 (CH), 124.0 (CH), 123.3 (CH), 115.1 (2 $\times$ CH), 114.5 (2 $\times$ CH), 56.0 (CH$_3$), 42.8 (CH$_2$), 40.1 (CH$_2$), 35.5 (CH$_2$), 32.3 (CH$_2$), 16.6 (CH$_3$).

**Characteristic NMR data of minor Z-isomer:** $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.51 (1H, d, $J$ = 11.5 Hz, HC=CPh), 6.25 (1H, dd, $J$ = 11.5, 1.5 Hz, CH$_3$C=CH), 2.54 (2H, t, $J$ = 6.8 Hz, CH$_2$), 1.88 (3H, d, $J$ = 1.5 Hz, CH$_3$C=); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 124.2 (CH), 123.7 (CH), 24.5 (CH$_3$).

4-Fluoro-N-[(3Z,5Z)-3-methyl-6,8-diphenylocta-3,5-dien-1-yl]aniline (3c). The title compound was prepared according to the general procedure using enyne 2a (55.3 mg, 0.30 mmol), triazinane 1c (60.8 mg, 0.15 mmol) and PhB(OH)$_2$ (54.9 mg, 0.45 mmol) to give the crude product as a 3.7:1 mixture of inseparable E/Z isomers. Purification of the residue by column chromatography (10-50% EtOAc/petroleum ether) gave *homoallylic amine* 3c [88.2 mg, 0.22 mmol, 74% (4.6:1 E:Z)] as a brown oil. $R_t = 0.57$ (50% EtOAc/petroleum ether); IR 3405 (N-H), 3026, 2922, 2360, 1596 (C=C), 1509, 1110, 818, 763, 696 cm$^{-1}$; HRMS (ESI) Exact mass calculated for C$_{29}$H$_{34}$NF [M+H]$^+$: 386.2279, found: 386.2280.

**NMR data of major E-isomer:** $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.52-7.46 (2H, m, ArH), 7.42-7.36 (2H, m, ArH), 7.33-7.27 (3H, m, ArH), 7.25-7.21 (1H, m, ArH), 7.20-7.16 (2H, m, ArH), 6.96-6.89 (2H, m, ArH), 6.61-6.55 (3H, m, ArH and HC=CPh), 6.20 (1H, dq, $J$ = 11.3, 1.3 Hz, CH$_3$C=CH), 3.55
(1H, br s, NH), 3.23 (2H, td, J = 6.7, 2.0 Hz, NCH$_2$), 2.99-2.92 (2H, m, CH$_2$Ph), 2.77-2.69 (2H, m, CH$_2$CH$_2$Ph), 2.44 (2H, t, J = 6.7 Hz, NCH$_2$CH$_2$), 1.87 (3H, d, J = 1.3 Hz, CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 155.9 (d, $J_{C\text{-}F}$ = 235.0 Hz, CF), 144.6 (d, $J_{C\text{-}F}$ = 1.8 Hz, C), 142.7 (C), 141.9 (C), 139.3 (C), 136.8 (C), 128.5 (2 × CH), 128.4 (4 × CH), 127.1 (CH), 126.3 (2 × CH), 126.0 (CH), 123.8 (CH), 123.3 (CH), 115.7 (d, $J_{C\text{-}F}$ = 22.5 Hz, 2 × CH), 113.8 (d, $J_{C\text{-}F}$ = 7.3 Hz, 2 × CH), 42.3 (CH$_2$), 39.8 (CH$_3$), 35.3 (CH$_2$), 32.2 (CH$_2$), 16.5 (CH$_3$); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ −128.1 (s)

Characteristic NMR data of minor Z-isomer: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.28 (1H, dd, J = 11.5, 1.5 Hz, CH$_3$C=CH), 2.55 (2H, t, J = 6.7 Hz, CH$_2$), 1.90 (3H, d, J = 1.5 Hz, CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 124.3 (CH), 123.6 (CH), 31.9 (CH$_2$), 24.4 (CH$_3$); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ −128.2 (s).

3,5-Dimethyl-N-[(3Z,5Z)-3-methyl-6,8-diphenylocta-3,5-dien-1-yl]aniline (3d). The title compound was prepared according to the general procedure on a 0.26 mmol scale, using enyne 2a (47.9 mg, 0.26 mmol), triazinane 1d (51.0 mg, 0.13 mmol) and PhB(OH)$_2$ (47.6 mg, 0.39 mmol) to give the crude product as a 3.6:1 mixture of inseparable E/Z isomers. Purification of the residue by column chromatography (5% EtOAc/petroleum ether) gave homoaallyl amine 3d [65.5 mg, 0.17 mmol, 64% (4.8:1 E:Z)] as a brown oil. $R_f$ = 0.32 (5% EtOAc/petroleum ether); IR 3401, (N-H), 3025, 2916, 1599 (C=C), 1494, 1445, 1375, 1334, 1303, 1186, 1108, 1078, 1029, 820, 753, 695 cm$^{-1}$; HRMS (ESI) Exact mass calculated for C$_{29}$H$_{33}$N [M+H]$^+$: 396.2686, found: 396.2674.

NMR data of major E-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50-7.45 (2H, m, ArH), 7.41-7.34 (2H, m, ArH), 7.32-7.26 (3H, m, ArH), 7.23-7.14 (3H, m, ArH), 6.57 (1H, d, J = 11.3 Hz, HC=CH), 6.39 (1H, br s, NH), 6.29 (2H, d, J = 1.5 Hz, ArH), 6.20 (1H, dq, J = 11.3, 1.3 Hz, CH$_3$C=CH), 3.53 (1H, br s, NH), 3.24 (2H, t, J = 6.7 Hz, NCH$_2$), 2.99-2.91 (2H, m, CH$_2$Ph), 2.76-2.68 (2H, m, CH$_2$CH$_2$Ph), 2.43 (2H, t, J = 6.7 Hz, NCH$_2$CH$_2$), 2.25 (6H, s, 2 × ArCH$_3$), 1.85 (3H, d, J = 1.3 Hz, CH$_3$C=); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.4 (C), 142.9 (C), 142.1 (C), 139.2 (C), 139.0 (2 × C), 137.2 (C), 128.6 (CH), 128.54 (3 × CH), 128.48 (2 × CH), 127.1 (CH), 126.4 (2 × CH), 126.1 (CH), 124.0 (CH), 123.3 (CH), 119.6 (CH), 111.0 (2 × CH), 41.8 (CH$_2$), 40.1 (CH$_2$), 35.4 (CH$_2$), 32.3 (CH$_2$), 21.7 (2 × CH$_3$), 16.6 (CH$_3$).

Characteristic NMR data of minor Z-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.55 (2H, t, J = 6.9 Hz, CH$_2$), 2.22 (6H, s, 2 × ArCH$_3$), 1.89 (3H, d, J = 1.3 Hz, CH$_3$C=); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 126.3 (CH), 111.0 (CH).
6-Methoxy-N-[(3Z,5Z)-3-methyl-6,8-diphenylocta-3,5-dien-1-yl]pyridin-3-amine (3e). The title compound was prepared according to the general procedure using enyne 2a (55.3 mg, 0.30 mmol), triazinane 1e (61.3 mg, 0.15 mmol), PhB(OH)\(_2\) (54.9 mg, 0.45 mmol) to give the crude product as a 5.6:1 mixture of inseparable E/Z isomers. Purification of the residue by column chromatography (10-50% EtOAc/petroleum ether) gave homoallylic amine 3e [69.4 mg, 0.17 mmol, 58% (7.7:1 E:Z)] as a brown oil. R\(_f\) = 0.48 (50% EtOAc/petroleum ether); IR 3271 (N\_O\), 2926, 2360, 1578, 1420, 1394, 1392, 1367, 1305 (CH), 1286 (2 × CH), 1285 (2 × CH), 1284 (2 × CH), 1271 (CH), 1264 (2 × CH), 1261 (CH), 1260 (CH), 1238 (CH), 1234 (CH), 1109 (CH), 53.4 (CH\(_3\)), 42.6 (CH\(_2\)), 40.0 (CH\(_2\)), 35.4 (CH\(_2\)), 32.2 (CH\(_2\)), 16.6 (CH\(_3\)).

NMR data of major E-isomer: \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.61 (1H, d, J = 3.0 Hz, ArH), 7.50-7.46 (2H, m, ArH), 7.40-7.34 (3H, m, ArH), 7.31-7.26 (3H, m, ArH), 7.23-7.15 (3H, m, ArH), 6.99 (1H, dd, J = 8.8, 3.0 Hz, ArH), 6.64 (1H, d, J = 8.8 Hz, ArH), 6.57 (1H, d, J = 11.3 Hz, HC=CPh), 6.17 (1H, dq, J = 11.3, 1.3 Hz, CH\(_3\)=C(CH\(_3\))\,), 3.89 (3H, s, OCH\(_3\)), 3.34 (1H, br s, NH), 3.21 (2H, t, J = 6.6 Hz, NCH\(_2\)CH\(_2\)), 2.98-2.90 (2H, m, CH\(_2\)Ph), 2.76-2.67 (2H, m, CH\(_2\)CH\(_2\)Ph), 2.43 (2H, t, J = 6.6 Hz, NCH\(_2\)CH\(_2\)), 1.86 (3H, d, J = 1.3 Hz, CH\(_3\)C=); \(^1^3\)C NMR (126 MHz, CDCl\(_3\)) δ 157.5 (C), 142.8 (C), 142.0 (C), 139.4 (C), 139.2 (C), 136.7 (C), 130.5 (CH), 128.6 (2 × CH), 128.5 (2 × CH), 128.4 (2 × CH), 127.1 (CH), 126.4 (2 × CH), 126.1 (CH), 126.0 (CH), 123.8 (CH), 123.4 (CH), 110.9 (CH), 53.4 (CH\(_3\)), 42.6 (CH\(_2\)), 40.0 (CH\(_2\)), 35.4 (CH\(_2\)), 32.2 (CH\(_2\)), 16.6 (CH\(_3\)).

Characteristic NMR data of minor Z-isomer: \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.58 (1H, d, J = 3.0 Hz, ArH), 6.93 (1H, dd, J = 8.8, 3.0 Hz, ArH), 6.49 (1H, d, J = 11.5 Hz, HC=CPh), 6.27 (1H, dd, J = 11.5, 1.5 Hz, CH\(_3\)=C(CH\(_3\))\,), 3.88 (3H, s, OCH\(_3\)), 2.55 (2H, t, J = 6.7 Hz, CH\(_2\)), 1.89 (3H, d, J = 1.5 Hz, CH\(_3\)C=); \(^1^3\)C NMR (126 MHz, CDCl\(_3\)) δ 124.4 (CH), 31.9 (CH\(_2\)), 24.4 (CH\(_3\)).

(3Z,5Z)-N-Isopropyl-3-methyl-6,8-diphenylocta-3,5-dien-1-amine (3g). The title compound was prepared according to the general procedure using enyne 2a (55.3 mg, 0.30 mmol), triazinane 1g (32.0 mg, 0.15 mmol), and PhB(OH)\(_2\) (54.9 mg, 0.45 mmol) to give the crude product as a 5.0:1 mixture of inseparable E/Z isomers. Purification of the residue by column chromatography using Et\(_3\)N-neutralized silica gel (50% EtOAc/petroleum ether) gave homoallylic amine 3g [58.3 mg, 0.18 mmol, 58% (6.8:1 E:Z)] as a dark yellow oil. R\(_f\) = 0.45 (50% EtOAc/petroleum ether); R\(_f\) = 0.45 (50% EtOAc/petroleum ether); IR 3026, 2962, 1596, 1494, 1444, 1378, 1336, 1173, 1078, 1029, 883, 752, 696 cm\(^{-1}\); HRMS (ESI) Exact mass calculated for C\(_{24}\)H\(_{33}\)N\(_3\) [M+H]+: 334.2529, found: 334.2527.

NMR data of major E-isomer: \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.47-7.44 (2H, m, ArH), 7.36 (2H, t, J = 7.7 Hz, ArH), 7.30-7.26 (3H, m, ArH), 7.19 (3H, d, J = 7.3 Hz, ArH), 6.56 (1H, d, J = 11.4 Hz,
HC=CPh), 6.20 (1H, dq, J = 11.4, 1.3 Hz, CH₃C=CH), 2.97-2.89 (2H, m, NCH₂), 2.83 (1H, hept, J = 6.3 Hz, (CH₃)₂CH), 2.76-2.67 (4H, m, CH₂Ph and NCH₂CH₂H₂), 2.33 (2H, t, J = 7.0 Hz, CH₂CH₂Ph), 1.83 (3H, d, J = 1.3 Hz, CH₃C=), 1.08 (6H, d, J = 6.3 Hz, (CH₃)₂CH), NH not observed; ¹³C NMR (126 MHz, CDCl₃) δ 143.0 (C), 142.1 (C), 138.9 (C), 138.0 (C), 128.54 (2 × CH), 128.50 (2 × CH), 128.46 (2 × CH), 127.0 (CH), 126.4 (2 × CH), 126.0 (CH), 124.1 (CH), 122.7 (CH), 48.8 (CH), 45.5 (CH₂), 41.0 (CH₂), 35.4 (CH₂), 32.2 (CH₂), 23.1 (2 × CH₃), 16.8 (CH₃).

**Characteristic NMR data of minor Z-isomer:** ¹H NMR (500 MHz, CDCl₃) δ 6.31-6.27 (1H, m, CH₂C=CH), 2.16 (2H, t, J = 7.0 Hz, CH₂), 1.77 (3H, d, J = 1.4 Hz, CH₃C=), 1.01 (6H, d, J = 6.2 Hz, (CH₃)₂CH); ¹³C NMR (126 MHz, CDCl₃) δ 123.2 (CH), 40.4 (CH₂), 23.0 (CH₃).

![N-(3Z,5Z)-3-Methyl-8-phenyl-6-[4-(trimethylsilyl)phenyl]octa-3,5-dien-1-yl]aniline (3h).](image)

N-[(3Z,5Z)-3-Methyl-8-phenyl-6-[4-(trimethylsilyl)phenyl]octa-3,5-dien-1-yl]aniline (3h). The title compound was prepared according to the general procedure using enyne 2a (55.3 mg, 0.30 mmol), triazinane 1a (47.3 mg, 0.15 mmol), and (4-(trimethylsilyl)phenyl)boronic acid (87.3 mg, 0.45 mmol) to give the crude product as a 4:6:1 mixture of inseparable E/Z isomers. Purification of the residue by column chromatography (5-10% EtOAc/petroleum ether) gave homoallylic amine 3h [99.5 mg, 0.27 mmol, 75% (4:6:1 E:Z)] as a brown gum. Rₓ = 0.37 (10% EtOAc/petroleum ether); Rₓ = 0.37 (10% EtOAc/petroleum ether); IR 3408 (N-H), 3023, 2952, 1601 (C=C), 1495, 1317, 1247, 1178, 1110, 837, 819, 747, 693 cm⁻¹; HRMS (ESI) Exact mass calculated for C₃₀H₃₈NSi [M+H]^+: 440.2768, found: 440.2767.

**NMR data of major E-isomer:** ¹H NMR (CDCl₃) δ 7.53 (2H, d, J = 8.2 Hz, ArH), 7.48-7.44 (2H, m, ArH), 7.24-7.13 (6H, m, ArH), 6.75-6.69 (1H, m, ArH), 6.67-6.55 (4H, m, CH₃C=CH and ArH), 6.18 (1H, dq, J = 11.4, 1.4 Hz, CH₃C=CH), 3.67 (1H, br s, NH), 3.25 (2H, t, J = 6.7 Hz, NCH₂), 2.98-2.87 (2H, m, CH₂Ph), 2.77-2.67 (2H, m, CH₂CH₂Ph), 2.44 (2H, t, J = 6.7 Hz, NCH₂CH₂), 1.85 (3H, d, J = 1.3 Hz, CH₃C=), 0.30 (9H, s, Si(CH₃)₃); ¹³C NMR (101 MHz, CDCl₃) δ 148.3 (C), 143.2 (C), 142.1 (C), 139.3 (C), 139.2 (C), 137.2 (C), 133.7 (2 × CH), 129.4 (CH), 128.6 (CH), 128.5 (3 × CH), 126.1 (CH), 125.7 (2 × CH), 124.1 (CH), 123.4 (CH), 117.5 (CH), 113.1 (3 × CH), 41.8 (CH₂), 40.0 (CH₂), 35.5 (CH₂), 32.2 (CH₂), 16.6 (CH₃), -0.9 (3 × CH₃).

**Characteristic NMR data of minor Z-isomer:** ¹H NMR (400 MHz, CDCl₃) δ 6.26 (1H, d, J = 11.5 Hz, CH₃C=CH), 2.55 (2H, t, J = 6.9 Hz, CH₂), 1.88 (3H, d, J = 1.4 Hz, CH₃C=), 0.27 (9H, s, Si(CH₃)₃); ¹³C NMR (101 MHz, CDCl₃) δ 124.2 (CH), 123.7 (CH), 32.1 (CH₂), 24.5 (CH₃).
N-[(3Z,5Z)-6-(2-Fluorophenyl)-3-methyl-8-phenylcta-3,5-dien-1-yl]aniline (3i). The title compound was prepared according to the general procedure using enyne 2a (55.3 mg, 0.30 mmol), triazinane 1a (47.3 mg, 0.15 mmol), and (2-fluorophenyl)boronic acid (63.0 mg, 0.45 mmol) to give the crude product as a 3.8:1 mixture of inseparable E/Z isomers. Purification of the residue by column chromatography (5-10% EtOAc/petroleum ether) gave homoallylic amine 3i [55.6 mg, 0.14 mmol, 48% (5.7:1 E:Z)] as a brown oil. \( R_f = 0.15 \) (5% EtOAc/petroleum ether); IR 3406 (N-H), 3025, 2922, 1601, 1504, 1447, 1377, 1315, 1263, 1211, 1179, 1153, 1102, 1072, 1029, 992, 866, 817, 747, 692 cm\(^{-1}\); HRMS (ESI) Exact mass calculated for \( \text{C}_{27}\text{H}_{28}\text{FN}^{+} \): 386.2279, found: 386.2032.

NMR data of major E-isomer: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.32-7.28 (1H, m, ArH), 7.27-7.24 (2H, m, ArH), 7.23-7.06 (8H, m, ArH), 6.74 (1H, dd, \( J = 7.9, 6.7 \) Hz, ArH), 6.68-6.63 (2H, m, ArH), 6.43 (1H, d, \( J = 11.4 \) Hz, CH\(_3\)C=CHCH\(_3\)), 6.22 (1H, dq, \( J = 11.4, 1.4 \) Hz, CH\(_3\)C=CH), 3.65 (1H, br s, NH), 3.27 (2H, t, \( J = 6.7 \) Hz, NCH\(_2\)CH\(_3\)), 2.96-2.90 (2H, m, CH\(_2\)Ph), 2.73-2.65 (2H, m, CH\(_2\)CH\(_2\)Ph), 2.45 (2H, t, \( J = 6.7 \) Hz, NCH\(_2\)CH\(_2\)CH\(_3\)), 1.83 (3H, d, \( J = 1.4 \) Hz, CH\(_3\)C=); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 160.3 (d, \( J_{CF} = 246.3 \) Hz, CF), 148.3 (C), 142.0 (C), 137.7 (C), 135.6 (C), 131.5 (d, \( J_{CF} = 13.7 \) Hz, C), 130.52 (CH), 130.49 (CH), 129.4 (2 \( \times \) CH), 128.6 (2 \( \times \) CH), 128.4 (2 \( \times \) CH), 127.0 (d, \( J_{CF} = 2.8 \) Hz, CH), 126.0 (CH), 124.2 (d, \( J_{CF} = 3.4 \) Hz, CH), 122.7 (CH), 117.5 (CH), 115.9 (d, \( J_{CF} = 22.8 \) Hz, CH), 113.1 (2 \( \times \) CH), 41.8 (CH\(_2\)), 40.0 (CH\(_2\)), 35.1 (CH\(_2\)), 33.1 (d, \( J_{CF} = 2.8 \) Hz, CH\(_2\)), 16.6 (CH\(_3\)); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -114.7 (s).

Characteristic NMR data of minor Z-isomer: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 6.63-6.59 (2H, m, ArH), 6.39 (1H, d, \( J = 11.5 \) Hz, CH\(_3\)C=CHCH\(_3\)), 6.31-6.27 (1H, m, CH\(_3\)C=CH), 2.53 (2H, t, \( J = 6.9 \) Hz, CH\(_2\)), 1.90 (3H, d, \( J = 1.3 \) Hz, CH\(_3\)C=); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 126.6 (CH), 123.5 (CH), 32.0 (CH\(_2\)), 24.3 (CH\(_3\)); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -114.8 (s).

N-[(3Z,5Z)-6-(3,5-Dimethylphenyl)-3-methyl-8-phenylcta-3,5-dien-1-yl]aniline (3j). The title compound was prepared according to the general procedure using enyne 2a (55.3 mg, 0.30 mmol), triazinane 1a (47.3 mg, 0.15 mmol), and (3,5-dimethylphenyl)boronic acid (67.5 mg, 0.45 mmol) to give the crude product as a 3.0:1 mixture of inseparable E/Z isomers. Purification of the residue by column chromatography (5-10% EtOAc/petroleum ether) gave homoallylic amine 3j [82.2 mg, 0.21 mmol, 69% (4.6:1 E:Z)] as a pale brown oil. \( R_f = 0.14 \) (5% EtOAc/petroleum ether); IR 3393 (N-H), 3024, 2920, 1601, 1505, 1453, 1375, 1316, 1262, 1178, 1030, 908, 856, 747, 693, 507 cm\(^{-1}\); HRMS (ESI) Exact mass calculated for \( \text{C}_{29}\text{H}_{34}\text{N}^{+} \): 396.2686, found: 396.2688.
NMR data of major E-isomer: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.33-7.26 (2H, m, ArH), 7.23-7.14 (5H, m, ArH), 7.07 (2H, br s, ArH), 6.94 (1H, s, ArH), 6.75-6.70 (1H, m, ArH), 6.66-6.62 (2H, m, ArH), 6.53 (1H, d, $J = 11.3$ Hz, CH$_3$=CHCH), 6.17 (1H, dq, $J = 11.3$, 1.4 Hz, CH$_3$=CH), 3.66 (1H, br s, NH), 3.25 (2H, t, $J = 6.7$ Hz, NCH$_2$), 2.96-2.88 (2H, m, CH$_2$Ph), 2.75-2.67 (2H, m, CH$_2$CH$_2$Ph), 2.44 (2H, t, $J = 6.7$ Hz, NCH$_2$CH$_2$), 2.36 (6H, s, 2 × ArCH$_3$), 1.86 (3H, d, $J = 1.4$ Hz, CH$_2$C=); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 148.3 (C), 143.0 (C), 142.2 (C), 139.7 (C), 138.0 (2 × C), 136.7 (C), 129.4 (2 × CH), 128.9 (CH), 128.6 (2 × CH), 128.5 (2 × CH), 126.0 (CH), 124.4 (2 × CH), 123.6 (CH), 123.4 (CH), 117.5 (CH), 113.1 (2 × CH), 41.8 (CH$_2$), 40.0 (CH$_2$), 35.5 (CH$_2$), 32.4 (CH$_2$), 21.6 (2 × CH$_3$), 16.6 (CH$_3$).

Characteristic NMR data of minor Z-isomer: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.01 (2H, d, $J = 1.5$ Hz, ArH), 6.26 (1H, dd, $J = 11.6$, 1.5 Hz, CH$_3$=CH), 2.56 (2H, t, $J = 6.9$ Hz, CH$_2$), 2.34 (6H, s, 2 × ArCH$_3$), 1.88 (3H, d, $J = 1.5$ Hz, CH$_3$C=); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 124.1 (CH), 32.1 (CH$_2$), 24.3 (CH$_3$), 21.3 (2 × CH$_3$).

NMR data of major E-isomer: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.46-7.40 (2H, m, ArH), 7.33-7.26 (2H, m, ArH), 7.25-7.14 (3H, m, ArH), 7.11-7.03 (2H, m, ArH), 6.85-6.78 (2H, m, ArH), 6.66-6.60 (2H, m, ArH), 6.51 (1H, d, $J = 11.3$ Hz, CH$_3$C=CHCH), 6.18 (1H, dq, $J = 11.3$, 1.3 Hz, CH$_3$C=CH), 3.78 (3H, s, OCH$_3$), 3.24 (2H, t, $J = 6.6$ Hz, NCH$_2$), 2.97-2.89 (2H, m, CH$_2$Ph), 2.75-2.67 (2H, m, CH$_2$CH$_2$Ph), 2.45 (2H, t, $J = 6.6$ Hz, NCH$_2$CH$_2$), 1.87 (3H, d, $J = 1.3$ Hz, CH$_3$C=), NH not observed; $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.2 (d, $J_{C,F} = 246.0$ Hz, CF), 152.3 (C), 142.6 (C), 141.9 (C), 139.0 (C), 138.2 (C), 137.3 (C), 128.5 (5 × CH), 127.9 (d, $J_{C,F} = 7.8$ Hz, 2 × CH), 126.1 (CH), 123.9 (CH), 123.4 (CH), 115.5 (CH), 115.3 (CH), 115.1 (2 × CH), 114.5 (CH), 55.9 (CH$_3$), 42.8 (CH$_2$), 40.1 (CH$_2$), 35.3 (CH$_2$), 32.4 (CH$_2$), 16.6 (CH$_3$); $^{19}$F NMR (376 MHz, CDCl$_3$) δ –115.8 (s).

N-[(3E,5E)-6-(4-Fluorophenyl)-3-methyl-8-phenylocta-3,5-dien-1-yl]-4-methoxyaniline (3k). The title compound was prepared according to the general procedure using enyne 2a (55.3 mg, 0.30 mmol), triazinane 1b (60.8 mg, 0.15 mmol), and (4-fluorophenyl)boronic acid (63.0 mg, 0.45 mmol) to give the crude product as a 4:7:1 mixture of inseparable E/Z isomers. Purification of the residue by column chromatography (5-10% EtOAc/petroleum ether) gave homallylic amine 3k [105 mg, 0.25 mmol, 84% (6:1 E:Z)] as a brown oil. R$_f$ = 0.24 (10% EtOAc/petroleum ether); IR 3406 (N-H), 2929, 1503, 1453, 1232, 1036, 816, 749, 698 cm$^{-1}$; HRMS (ESI) Exact mass calculated for C$_{28}$H$_{31}$FNO [M+H]$^+$: 416.2384, found: 416.2698.
Characteristic NMR data of minor Z-isomer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.43 (1H, d, \(J = 11.5\) Hz, CH\(_3\)=CHCH), 6.28-6.22 (1H, m, CH\(_3\)=CH), 2.55 (2H, t, \(J = 6.7\) Hz, CH\(_2\)), 1.90 (3H, d, \(J = 1.4\) Hz, CH\(_3\)=C); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 124.1 (CH), 123.7 (CH), 32.0 (CH\(_2\)), 25.8 (CH\(_3\)); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) –115.9 (s).

\(1-(4-[(3E,5E)-8-\{4\)-Methoxyphenyl\}amino]-6-methyl-1-phenylocta-3,5-dien-3-yl\}phenyl\}ethan-1-one (3l).\) The title compound was prepared according to the general procedure using enyne 2a (55.3 mg, 0.30 mmol), triazinane 1b (60.8 mg, 0.15 mmol), and (4-acetophenyl)boronic acid (73.8 mg, 0.45 mmol) to give the crude product as a 4:2:1 mixture of inseparable E/Z isomers. Purification of the residue by column chromatography (5-30% EtOAc/petroleum ether) gave homoallylic amine 3l [92.8 mg, 0.21 mmol, 70% (5.1:1 E:Z)] as a brown oil. \(R_t = 0.27\) (30% EtOAc/petroleum ether); IR 3392 (N-H), 2929, 1677 (C=O), 1598, 1511, 1357, 1236, 956, 819, 750 cm\(^{-1}\); HRMS (ESI) Exact mass calculated for C\(_{30}\)H\(_{33}\)NO\(_2\) [M+H]\(^+\): 440.2584, found: 440.2578.

NMR data of major E-isomer: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.97-7.92 (2H, m, ArH), 7.58-7.51 (2H, m, ArH), 7.31-7.25 (2H, m, ArH), 7.22-7.17 (1H, m, ArH), 7.17-7.12 (2H, m, ArH), 6.83-6.74 (2H, m, ArH), 6.68 (1H, d, \(J = 11.3\) Hz, CH\(_3\)=CHCH), 6.61 (2H, d, \(J = 8.9\) Hz, ArH), 6.23-6.16 (1H, m, CH\(_3\)=CH), 3.75 (3H, s, OCH\(_3\)), 3.22 (2H, t, \(J = 6.7\) Hz, NCH\(_2\)), 2.94 (2H, dd, \(J = 9.7, 6.4\) Hz, CH\(_3\)Ph), 2.73-2.67 (2H, m, CH\(_2\)CH\(_2\)Ph), 2.62 (3H, s, CH\(_3\)C=O), 2.44 (2H, t, \(J = 6.7\) Hz, NCH\(_2\)CH\(_2\)), 1.88 (3H, d, \(J = 1.3\) Hz, CH\(_3\)=C), NH not observed; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 197.8 (C), 152.3 (C), 147.6 (C), 142.4 (C), 141.6 (C), 139.2 (C), 138.0 (C), 135.6 (C), 128.8 (2 \(\times\) CH), 128.5 (2 \(\times\) CH), 128.5 (2 \(\times\) CH), 126.3 (2 \(\times\) CH), 126.2 (CH), 125.8 (CH), 123.1 (CH), 115.1 (2 \(\times\) CH), 114.5 (2 \(\times\) CH), 55.9 (CH\(_3\)), 42.8 (CH\(_2\)), 40.2 (CH\(_2\)), 35.4 (CH\(_2\)), 31.9 (CH\(_2\)), 26.7 (CH\(_3\)), 16.8 (CH\(_3\)).

Characteristic NMR data of minor Z-isomer: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.47 (2H, d, \(J = 8.0\) Hz, ArH), 7.38-7.33 (2H, m, ArH), 6.28-6.24 (1H, m, CH\(_3\)=CH), 1.90 (3H, d, \(J = 1.4\) Hz, CH\(_3\)=C); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 127.2(CH), 124.1 (CH), 24.5 (CH\(_3\)).

4-Methoxy-N-[(3E,5E)-3-methyl-8-phenyl-6-(m-tolylocta-3,5-dien-1-yl)aniline (3m).\) The title compound was prepared according to the general procedure using enyne 2a (55.3 mg, 0.30 mmol), triazinane 1b (60.8 mg, 0.15 mmol), and m-tolylboronic acid (61.2 mg, 0.45 mmol) to give the crude product as a 4:8:1 mixture of inseparable E/Z isomers. Purification of the residue by column chromatography (5-10% EtOAc/petroleum ether) gave

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 homoallylic amine 3m [103.3 mg, 0.25 mmol, 83% (5.7:1 E:Z)] as a brown oil. R_f = 0.28 (10% EtOAc/petroleum ether); IR 3390 (N-H), 2925, 1601 (C=O), 1510, 1453, 1235, 1178, 1037, 878, 784, 750, 698 cm⁻¹; HRMS (ESI) Exact mass calculated for C_{29}H_{33}NO [M+H]^+: 412.2635, found: 412.2630.

NMR data of major E-isomer: ^1H NMR (400 MHz, CDCl₃) δ 7.32-7.26 (5H, m, ArH), 7.25-7.04 (4H, m, ArH), 6.79 (2H, d, J = 8.9 Hz, ArH), 6.63-6.57 (2H, m, ArH), 6.57-6.51 (1H, m, CH₂=CHCH), 6.17 (1H, dq, J = 11.4, 1.3 Hz, CH₃C=CHH), 3.75 (3H, s, OCH₃), 3.21 (2H, t, J = 6.6 Hz, NCH₂), 2.96-2.88 (2H, m, CH₂Ph), 2.74-2.67 (2H, m, CH₂CH₂Ph), 2.44 (2H, t, NCH₂CH₂), 2.42 (3H, s, ArCH₃), 1.85 (3H, d, J = 1.3 Hz, CH₃=C=), NH not observed; ^13C NMR (101 MHz, CDCl₃) δ 152.3 (C), 142.9 (C), 142.6 (C), 142.1 (C), 139.5 (C), 138.1 (C), 137.0 (C), 128.6 (2 × CH), 128.48 (2 × CH), 128.46 (CH), 127.9 (CH), 127.2 (CH), 126.0 (CH), 123.8 (CH), 123.6 (CH), 123.4 (CH), 115.1 (2 × CH), 114.5 (2 × CH), 56.0 (CH₃), 42.8 (CH₂), 40.1 (CH₂), 35.5 (CH₂), 32.3 (CH₂), 21.8 (CH₃), 16.6 (CH₃).

Characteristic NMR data of minor Z-isomer: ^1H NMR (500 MHz, CDCl₃) δ 6.77 (2H, d, J = 8.8 Hz, ArH), 6.53 (1H, d, J = 11.5 Hz, CH₃C=CHCH), 6.27 (1H, d, J = 11.5 Hz, CH₃C=CH), 3.75 (3H, s, OCH₃), 2.56 (2H, t, J = 7.0 Hz, CH₂), 1.90 (3H, s, CH₃C=); ^13C NMR (101 MHz, CDCl₃) δ 124.2 (CH), 55.9 (CH₃), 32.0 (CH₂), 24.5 (CH₃).

Ethyl 3-[[3E,5E]-8-[(4-methoxyphenyl)amino]-6-methyl-1-phenylhexa-3,5-dien-3-yl]benzoate (3n). The title compound was prepared according to the general procedure using enyne 2a (55.3 mg, 0.30 mmol), triazinane 1b (60.8 mg, 0.15 mmol), and 3-[ethoxycarbonyl]phenylboronic acid (87.3 mg, 0.45 mmol) to give the crude product as a 4.5:1 mixture of inseparable E/Z isomers. Purification of the residue by column chromatography (10-30% EtOAc/petroleum ether) gave homoallylic amine 3n [92.1 mg, 0.20 mmol, 65% (6.6:1 E:Z)] as a brown oil. R_f = 0.33 (10% EtOAc/petroleum ether); IR 3385 (N-H), 2932, 1715 (C=O), 1601 (C=C), 1510, 1453, 1367, 1285, 1234, 1179, 1108, 1034, 818, 755, 698 cm⁻¹; HRMS (ESI) Exact mass calculated for C₃₁H₃₆NO₃ [M+H]^+: 470.2690, found: 470.2698.

NMR data of major E-isomer: ^1H NMR (500 MHz, CDCl₃) δ 8.15 (1H, t, J = 1.8 Hz, ArH), 7.95 (1H, dt, J = 7.9, 1.4 Hz, ArH), 7.63 (1H, dt, J = 7.9, 1.4 Hz, ArH), 7.43 (1H, t, J = 7.9 Hz, ArH), 7.28-7.24 (3H, m, ArH), 7.18-7.13 (2H, m, ArH), 6.80 (2H, d, J = 8.9 Hz, ArH), 6.64-6.56 (3H, m, ArH and CH₃C=CHCH), 6.19 (1H, dq, J = 11.3, 1.3 Hz, CH₃C=CH), 4.42 (2H, q, J = 7.1 Hz, CH₂CH₃), 3.75 (3H, s, OCH₃), 3.22 (2H, t, J = 6.7 Hz, NCH₂), 2.98-2.92 (2H, m, CH₂Ph), 2.73-2.67 (2H, m, CH₂CH₂Ph), 2.44 (2H, t, J = 6.7 Hz, NCH₂CH₂), 1.87 (3H, d, J = 1.3 Hz, CH₃C=), 1.43 (3H, t, J = 7.1 Hz, CH₂CH₃), NH not observed; ^13C NMR (126 MHz, CDCl₃) δ 166.9 (C), 152.3 (C), 143.2 (C),
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142.5 (C), 141.8 (C), 138.3 (C), 138.1 (C), 130.8 (C), 130.7 (CH), 128.6 (CH), 128.53 (2 × CH), 128.5 (2 × CH), 128.1 (CH), 127.5 (CH), 126.1 (CH), 124.8 (CH), 123.1 (CH), 115.1 (2 × CH), 114.5 (2 × CH), 61.2 (CH₂), 56.0 (CH₃), 42.8 (CH₂), 40.1 (CH₂), 35.3 (CH₂), 32.3 (CH₂), 16.8 (CH₃), 14.5 (CH₃).

Characteristic NMR data of minor Z-isomer: ¹H NMR (500 MHz, CDCl₃) δ 6.73 (2H, d, J = 8.9 Hz, ArH), 6.56 (2H, d, J = 8.9 Hz, ArH), 6.52 (1H, d, J = 11.5 Hz, CH₃C=CHCH), 6.26 (1H, dd, J = 11.5, 1.5 Hz, CH₃C=CH), 2.55 (2H, t, J = 6.9 Hz, CH₂), 1.89 (3H, d, J = 1.5 Hz, CH₃C=); ¹³C NMR (126 MHz, CDCl₃) δ 115.0 (CH), 114.3 (CH), 32.2 (CH₂), 24.5 (CH₃).

4-Methoxy-N-[(3E,5E)-3-methyl-8-phenyl-6-(o-tolylocta-3,5-dien-1-yl]aniline (3o). The title compound was prepared according to the general procedure using enyne 2a (55.3 mg, 0.30 mmol), triazinane 1b (60.8 mg, 0.15 mmol), and o-tolylboronic acid (61.2 mg, 0.45 mmol) to give the crude product as a 2:5:1 mixture of inseparable E/Z isomers. Purification of the residue by column chromatography (5-10% EtOAc/petroleum ether) gave homoallylic amine 3o [20 mg, 0.05 mmol, 16% (5:6:1 E:Z)] as a brown oil. R₁ = 0.30 (10% EtOAc/petroleum ether); IR 3312 (NH), 2919, 1602 (C=O), 1510, 1453, 1236, 1035, 817, 752, 730, 698 cm⁻¹; HRMS (ESI) Exact mass calculated for C₂₀H₃₅NO[M+H]⁺: 412.2635, found: 412.2634.

NMR data of major E-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.26 -7.10 (9H, m, ArH), 6.79 (2H, d, J = 8.9 Hz, ArH), 6.62 (2H, d, J = 8.9 Hz, ArH), 6.23 (1H, dq, J = 11.3, 1.3 Hz, CH₃C=CH), 6.14 (1H, d, J = 11.3 Hz, CH₃C=CHCH), 3.75 (3H, s, OCH₃), 3.40 (1H, br s, NH), 3.22 (2H, t, J = 6.7 Hz, NCH₂), 2.83-2.75 (2H, m, PhCH₂), 2.66-2.58 (2H, m, CH₂CH₂Ph), 2.43 (2H, t, J = 6.7 Hz, NCH₂CH₂), 2.30 (3H, s, ArCH₃), 1.78 (3H, d, J = 1.3 Hz, CH₃C=); ¹³C NMR (101 MHz, CDCl₃) δ 152.3 (C), 144.2 (C), 142.6 (C), 142.1 (C), 140.7 (C), 140.7 (C), 136.3 (C), 135.3 (C), 130.4 (CH), 129.1 (4 x CH), 128.5 (CH), 126.9 (CH), 126.0 (CH), 125.6 (CH), 125.4 (CH), 122.7 (CH), 115.1 (2 × CH), 114.5 (2 × CH), 56.0 (CH₃), 42.9 (CH₂), 40.1 (CH₂), 34.8 (CH₂), 34.4 (CH₂), 20.4 (CH₃), 16.5 (CH₃).

Characteristic NMR data of minor Z-isomer: ¹H NMR (400 MHz, CDCl₃) δ 6.73 (2H, d, J = 8.8 Hz, ArH), 6.53 (2H, d, J = 8.8 Hz, ArH), 6.30 (1H, d, J = 12.1 Hz, CH₃C=CH), 3.73 (3H, s, OCH₃); ¹³C NMR (101 MHz, CDCl₃) δ 115.0 (CH), 114.3 (CH).

N-[(3Z,5Z)-8-[(tert-Butyldimethylsilyl)oxy]-3-methyl-6-phenylocta-3,5-dien-1-yl]aniline (3p). The title compound was prepared according to the general procedure using enyne 2b (71.5 mg, 0.30 mmol), triazinane 1b (47.3 mg, 0.15 mmol), and PhB(OH)₂ (54.9 mg, 0.45 mmol) to give the crude product as a 3:1:1
mixture of inseparable E/Z isomers. Purification of the residue by column chromatography (10% EtOAc/petroleum ether) gave homoallylic amine 3p [49.0 mg, 0.12 mmol, 39% (6.5:1 E:Z)] as a brown oil. Data for major isomer: Rf = 0.47 (10% EtOAc/petroleum ether); IR 3405 (N-H), 3051, 2953, 2927, 2855, 1601 (C=C), 1505, 1360, 1095, 834, 774, 747, 692 cm\(^{-1}\); HRMS (ESI) Exact mass calculated for C\(_{27}H_{40}NOSi\) [M+H]\(^+\): 422.2874, found: 422.2876.

**NMR data of major E-isomer:** \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.49-7.45 (2H, m, ArH), 7.39-7.33 (3H, m, ArH), 7.25-7.18 (2H, m, ArH), 6.75-6.69 (1H, m, ArH), 6.69-6.60 (3H, m, HC=CPh and ArH), 6.35 (1H, dq, \(J = 11.3, 1.3\) Hz, CH\(_3\)C=CH), 3.74-3.62 (2H, m, CH\(_2\)O), 3.30 (2H, \(t, J = 6.8\) Hz, NCH\(_2\)), 2.93 (2H, \(t, J = 7.4\) Hz, CH\(_2\)CH\(_2\)O), 2.50 (2H, \(t, J = 6.8\) Hz, NCH\(_2\)CH\(_2\)), 1.90 (3H, d, \(J = 1.3\) Hz, CH\(_3\)=), 0.90 (9H, s, C(CH\(_3\))\(_3\)), 0.04 (6H, s, Si(CH\(_3\))\(_2\)), NH not observed; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 148.3 (C), 142.2 (C), 141.9 (C), 139.3 (C), 132.4 (CH), 129.4 (2 × CH), 128.5 (2 × CH), 127.1 (CH), 126.4 (2 × CH), 125.0 (CH), 123.8 (CH), 117.6 (CH), 113.0 (2 × CH), 62.5 (CH\(_2\)), 41.9 (CH\(_2\)), 40.2 (CH\(_2\)), 34.0 (CH\(_2\)), 26.1 (3 × CH\(_3\)), 18.5 (C), 16.6 (CH\(_3\)), -5.12 (2 × CH\(_3\)).

Characteristic NMR data of minor Z-isomer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.40 (1H, app d, \(J = 11.7\) Hz, CH\(_3\)C=CH), 2.58 (2H, \(t, J = 6.9\) Hz, CH\(_2\)), 1.93 (3H, d, \(J = 1.4\) Hz, CH\(_3\)C=), 0.89 (9H, s, C(CH\(_3\))\(_3\)), 0.03 (6H, s, 2 × CH\(_3\)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 124.7 (CH), 32.1 (CH\(_2\)), 24.4 (CH\(_3\)).

**N-[3Z,5Z]-6,8-Diphenylocta-3,5-dien-1-yl]aniline (3q).** The title compound was prepared according to the general procedure using enyne 2c (51.0 mg, 0.30 mmol), triazinane 1a (47.3 mg, 0.15 mmol), and PhB(OH)\(_2\) (54.9 mg, 0.45 mmol) to give the crude product as a 3:3:1 mixture of inseparable E/Z isomers. Purification of the residue by column chromatography (5% EtOAc/petroleum ether) gave homoallylic amine 3q [38.4 mg, 0.11 mmol, 36% (10:1:1 E:Z)] as a brown oil. Rf = 0.27 (5% EtOAc/petroleum ether); IR 3405 (N-H), 3053, 3023, 2922, 2857, 1601 (C=C), 1504, 1317, 963, 748, 693 cm\(^{-1}\); HRMS (ESI) Exact mass calculated for C\(_{26}H_{28}N\) [M+H]\(^+\): 354.2216, found: 354.2209.

**NMR data of major E-isomer:** \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.48-7.44 (2H, m, ArH), 7.39-7.35 (2H, m, ArH), 7.29 (3H, td, \(J = 7.3, 5.3\) Hz, ArH), 7.23-7.16 (5H, m, ArH), 6.73 (1H, tt, \(J = 7.3, 1.1\) Hz, ArH), 6.66-6.62 (2H, m, ArH), 6.43-6.35 (2H, m, HC=CPh and NCH\(_2\)CH\(_2\)=), 5.78 (1H, dt, \(J = 13.8, 7.4\) Hz, CH\(_2\)CH=C=), 3.67 (1H, br s, NH), 3.21 (2H, \(t, J = 6.7\) Hz, NCH\(_2\)), 2.98-2.91 (2H, m, CH\(_3\)Ph), 2.74-2.69 (2H, m, CH\(_2\)CH\(_2\)Ph), 2.46 (2H, q, \(J = 6.7\) Hz, NCH\(_2\)CH\(_2\)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 148.3 (C), 142.2 (C), 141.9 (C), 139.3 (C), 132.4 (CH), 129.4 (2 × CH), 129.1 (CH), 128.6 (4 × CH), 128.5 (2 × CH), 127.8 (CH), 127.2 (CH), 126.4 (2 × CH), 126.1 (CH), 117.6 (CH), 113.1 (2 × CH), 43.5 (CH\(_2\)), 35.4 (CH\(_2\)), 33.0 (CH\(_2\)), 32.2 (CH\(_2\)).
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Characteristic NMR data of minor Z-isomer: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.59-5.51 (1H, m, CH$_2$CH=CH), 2.62-2.56 (2H, m, CH$_2$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 27.7 (CH$_2$).

$N$-[(3Z,5E)-3,6,8-Triphenylocta-3,5-dien-1-yl]aniline (3r). The title compound was prepared according to the general procedure using enyne 2d (73.9 mg, 0.30 mmol), triazinane 1a (47.3 mg, 0.15 mmol), and PhB(OH)$_2$ (54.9 mg, 0.45 mmol) to give the crude product as a 2.6:1 mixture of inseparable Z/E isomers. Purification of the residue by column chromatography (5% EtOAc/petroleum ether) gave homoallylic amine 3r [93.6 mg, 0.22 mmol, 73% (2.7:1 Z:E)] as a brown oil. IR 3407 (N-H), 3023, 2928, 1600 (C=C), 1504, 1452, 1319, 876, 746, 692 cm$^{-1}$; $R_f$ = 0.27 (5% EtOAc/petroleum ether); HRMS (ESI) Exact mass calculated for C$_{32}$H$_{32}$N$_{3}$ [M+H$^+$]: 430.2529, found: 430.2532. Exact mass calculated for C$_{32}$H$_{31}$NNa [M+Na$^+$]: 452.2349, found: 452.2347.

NMR data of major E-isomer: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.42-7.28 (13H, m, ArH), 7.27-7.14 (6H, m, ArH), 6.77-6.67 (2H, m, HC=CH$_2$CH$_2$Ph and ArH), 6.59 (1H, dt, $J = 8.8$, 1.8 Hz, NCH$_2$CH$_2$C=CH), 3.68 (1H, br s, NH), 3.24 (1H, t, $J = 6.8$ Hz, NCH$_2$), 3.09-2.98 (4H, m, CH$_2$Ph and CH$_2$CH$_2$Ph), 2.78 (2H, dd, $J = 8.6$, 6.8 Hz, NCH$_2$CH$_2$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 148.0 (C), 142.4 (2 × C), 142.1 (C), 141.9 (C), 139.3 (C), 129.4 (2 × CH), 128.7 (CH), 128.66 (2 × CH), 128.65 (2 × CH), 128.5 (3 × CH), 127.5 (CH), 127.4 (CH), 126.5 (4 × CH), 126.1 (CH), 125.8 (CH), 124.2 (CH), 117.5 (CH), 113.0 (2 × CH), 42.7 (CH$_2$), 35.3 (CH$_2$), 32.1 (CH$_2$), 29.8 (CH$_2$).

Characteristic NMR data of minor Z-isomer: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.42 (1H, d, $J = 3.5$ Hz, =CH), 3.15 (2H, t, $J = 6.8$ Hz, CH$_2$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 113.1 (CH), 42.5 (CH$_2$), 39.2 (CH$_2$).

$N$-[(3Z,5E)-3,6-Diphenylocta-3,5-dien-1-yl]-4-methoxylaniline (3s). The title compound was prepared according to the general procedure using enyne 2h (59.5 mg, 0.30 mmol), triazinane 1b (60.8 mg, 0.15 mmol), and PhB(OH)$_2$ (54.9 mg, 0.45 mmol) to give the crude product as a 1.2:1 mixture of inseparable E/Z isomers. Purification of the residue by column chromatography (5% EtOAc/petroleum ether) gave homoallylic amine 3s [88.3 mg, 0.22 mmol, 72% (2.0:1 E:Z)] as a brown oil. $R_f$ = 0.18 (10% EtOAc/petroleum ether); IR 3390 (N-H), 2928, 2857, 1594 (C=C), 1510, 1440, 1234, 1178, 1034, 817, 758, 696 cm$^{-1}$; HRMS (ESI) Exact mass calculated for C$_{29}$H$_{34}$NO [M+H$^+$]: 412.2635, found: 412.2628.

NMR data of major Z-isomer: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.51-7.47 (2H, m, ArH), 7.41-7.27 (8H, m, ArH), 6.86 (1H, d, $J = 11.5$ Hz, PhC=CH), 6.75-6.71 (2H, m, ArH), 6.67 (d, $J = 11.5$ Hz,
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PhC=CH), 6.56-6.52 (2H, m, ArH), 3.73 (3H, s, OCH₃), 3.22 (2H, t, J = 7.0 Hz, NCH₂), 3.03 (2H, t, J = 7.0 Hz, NCH₂CH₂), 2.77-2.70 (2H, m, CH₂CH₂CH₂), 1.49-1.34 (4H, m, CH₂CH₂CH₂), 0.91 (3H, t, J = 7.2 Hz, CH₃), NH not observed; ¹³C NMR (126 MHz, CDCl₃) δ 152.2 (C), 143.8 (C), 142.9 (C), 142.6 (C), 142.2 (C), 139.0 (C), 128.7 (2 × CH), 128.5 (2 × CH), 127.4 (CH), 127.3 (CH), 126.4 (2 × CH), 126.4 (2 × CH), 125.9 (CH), 123.5 (CH), 115.0 (2 × CH), 114.4 (2 × CH), 55.9 (CH₃), 43.8 (CH₂), 31.6 (CH₂), 30.0 (2 × CH₂), 22.9 (CH₂), 14.1 (CH₃).

Characteristic NMR data of minor E-isomer: ¹H NMR (500 MHz, CDCl₃) δ 6.37 (1H, d, J = 11.3 Hz, =CH), 3.75 (3H, s, OCH₃), 3.12 (2H, t, J = 6.7 Hz, NCH₂), 2.83 (2H, t, J = 6.7 Hz, NCH₂CH₂); ¹³C NMR (126 MHz, CDCl₃) δ 124.2 (CH), 41.0 (CH₂), 30.0 (2 × CH₂), 22.9 (CH₂), 14.1 (CH₃).

N-[[(3E,5E)-6-Cyclohexyl-3-methyl-6-phenylhexa-3,5-dien-1-yl]-4-methoxyaniline (3t). The title compound was prepared according to the general procedure using enyne 2e (48.7 mg, 0.30 mmol), triazinane 1b (60.8 mg, 0.15 mmol), and PhB(OH)₂ (54.9 mg, 0.45 mmol) to give the crude product as a 4.8:1 mixture of inseparable E/Z isomers. Purification of the residue by column chromatography (5-10% EtOAc/petroleum ether) gave homoallylic amine 3t [57.1 mg, 0.15 mmol, 51% (6.1:1 E:Z)] as a brown oil. Rₕ = 0.14 (5% EtOAc/petroleum ether); IR 3398 (N-H), 2925, 2851, 1593 (C=C), 1510, 1441, 1236, 1178, 1117, 1037, 908, 892, 817, 757, 732, 701 cm⁻¹; HRMS (ESI) Exact mass calculated for C₂₆H₃₄N⁵O⁶ [M+H]+: 376.2635, found: 376.2632.

NMR data of major E-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.25 (3H, m, ArH), 7.24-7.19 (2H, m, ArH), 6.83-6.78 (2H, m, ArH), 6.65-6.60 (2H, m, ArH), 6.33 (1H, dq, J = 11.5, 1.3 Hz, CH₃C=CH), 6.10 (1H, d, J = 11.5 Hz, HC=CPh), 3.76 (3H, s, OCH₃), 3.23 (2H, t, J = 6.6 Hz, NCH₂), 2.84-2.72 (1H, m, CH), 2.49-2.42 (2H, m, NCH₂CH₂), 1.80-1.62 (9H, m, CH₃C= and 3 × CH₂), 1.40-1.28 (4H, m, 2 × CH₂), NH not observed; ¹³C NMR (126 MHz, CDCl₃) δ 152.3 (C), 147.0 (C), 144.2 (C), 142.6 (C), 136.1 (C), 128.5 (2 × CH), 127.7 (2 × CH), 126.5 (CH), 124.0 (CH), 122.7 (CH), 115.1 (2 × CH), 114.6 (2 × CH), 56.0 (CH₃), 42.8 (CH₂), 40.9 (CH), 40.1 (CH₂), 32.3 (2 × CH₂), 26.9 (2 × CH₂), 26.2 (CH₂), 16.3 (CH₃).

Characteristic NMR data of minor Z-isomer: ¹H NMR (400 MHz, CDCl₃) δ 6.43-6.38 (1H, m, HC=CPh), 6.27 (1H, app d, J = 11.6 Hz, CH₃C=CH), 3.18 (2H, td, J = 6.8, 3.0 Hz, NCH₂), 1.91 (3H, d, J = 1.4 Hz, CH₃C=); ¹³C NMR (126 MHz, CDCl₃) δ 123.8 (CH), 123.2 (CH), 50.9 (CH₂), 24.5 (CH₃).
(4E,6E)-9-[(4-Methoxyphenyl)amino]-7-methyl-1,4-diphenylnona-4,6-dien-1-one (3u). The title compound was prepared according to the general procedure using enyne 2f (63.7 mg, 0.30 mmol), triazinane 1b (60.8 mg, 0.15 mmol), and PhB(OH)₂ (54.9 mg, 0.45 mmol) to give the crude product as a 4.1:1 mixture of inseparable E/Z isomers. Purification of the residue by column chromatography (10-30% EtOAc/petroleum ether) gave homoallylic amine 3u [89.1 mg, 0.21 mmol, 70% (5.2:1 E:Z)] as a brown oil. Rₜ = 0.23 (10% EtOAc/petroleum ether); IR 3394 (N-H), 3053, 2906, 1681 (C=O), 1600 (C=C), 1505, 1203, 979, 867, 748, 691 cm⁻¹; HRMS (ESI) Exact mass calculated for C₂₉H₃₂NO₂ [M+H]⁺: 426.2428, found: 426.2427.

NMR data of major E-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.93-7.87 (2H, m, ArH), 7.56-7.51 (1H, m, ArH), 7.47-7.26 (7H, m, ArH), 6.79-6.73 (2H, m, ArH), 6.64-6.54 (3H, m, CH₃C=CH and ArH), 6.33 (1H, dq, J = 11.4, 1.3 Hz, HC=CPH), 3.73 (3H, s, OCH₃), 3.22 (2H, t, J = 6.7 Hz, NCH₂), 3.13-3.02 (4H, m, CH₂CH₂C=O), 2.45 (2H, t, J = 6.7 Hz, NCH₂CH₂), 1.88 (3H, d, J = 1.3 Hz, CH₃C=), NH not observed; ¹³C NMR (126 MHz, CDCl₃) δ 199.7 (C), 152.2 (C), 142.6 (C), 142.3 (C), 138.6 (C), 137.8 (C), 136.9 (C), 133.2 (CH), 128.7 (4 × CH), 128.2 (2 × CH), 127.3 (CH), 126.4 (2 × CH), 124.3 (CH), 123.3 (CH), 115.0 (2 × CH), 114.4 (2 × CH), 55.9 (CH₃), 42.9 (CH₂), 40.3 (CH₂), 37.9 (CH₃), 24.3 (CH₂), 16.6 (CH₃).

Characteristic NMR data of minor Z-isomer: ¹H NMR (400 MHz, CDCl₃) δ 6.40-6.35 (1H, m, CH₃C=CH), 2.56 (2H, t, J = 6.8 Hz, CH₂), 1.91 (3H, d, J = 1.3 Hz, CH₃C=); ¹³C NMR (126 MHz, CDCl₃) δ 124.0 (CH), 32.2 (CH₂), 24.5 (CH₃).

3-[(2E,4E)-7-[(4-Methoxyphenyl)amino]-5-methyl-2-phenylhepta-2,4-dien-1-yl]cyclohexan-1-one (3v). The title compound was prepared according to the general procedure using enyne 2i (52.9 mg, 0.30 mmol), triazinane 1b (60.8 mg, 0.15 mmol), and PhB(OH)₂ (54.9 mg, 0.45 mmol) to give the crude product as a 3.2:1 mixture of inseparable E/Z isomers. Purification of the residue by column chromatography (10-30% EtOAc/petroleum ether) gave homoallylic amine 3v [72.1 mg, 0.18 mmol, 60% (5.5:1 E:Z)] as a dark yellow oil. Rₜ = 0.28 (30% EtOAc/petroleum ether); IR 3372 (N-H), 2930, 1707 (C=O), 1511, 1235, 1036, 819, 750, 699 cm⁻¹; HRMS (ESI) Exact mass calculated for C₂₇H₃₄NO₂ [M+H]⁺: 404.2577, found: 404.2584.

NMR data of major E-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.42-7.28 (4H, m, ArH), 7.27-7.23 (1H, m, ArH), 6.82-6.77 (2H, m, ArH), 6.63-6.56 (3H, m, ArH and HC=CPH), 6.22 (1H, dq, J = 11.4, 1.3
Supplementary Information

Hz, CH₃C=CH), 3.75 (3H, s, OCH₃), 3.23 (2H, t, \( J = 6.6 \) Hz, NCH₂), 2.67 (2H, dd, \( J = 11.2, 6.7 \) Hz, =C(Ph)CH₂), 2.46 (2H, t, \( J = 6.6 \) Hz, NCH₂CH₂), 2.40-2.31 (1H, m, CH₂C=O), 2.33-2.26 (1H, m, CHCH₂CH₂), 2.25-2.15 (1H, m, CH₂C=O), 2.04-1.94 (2H, m, CH₂C=O), 1.88-1.79 (5H, m, CH₃C= and 2 of CHCH₂CH₂), 1.57-1.47 (1H, m, CHCH₂CH₂), 1.37-1.26 (1H, m, CHCH₂CH₂), NH not observed; ¹³C NMR (101 MHz, CDCl₃) \( \delta \) 211.6 (C), 152.2 (C), 142.9 (C), 142.5 (C), 137.5 (C), 137.4 (C), 128.5 (2 × CH), 127.1 (CH), 126.3 (2× CH), 125.3 (CH), 123.2 (CH), 114.9 (2 × CH), 114.3 (2 × CH), 55.8 (CH₃), 47.9 (CH₂), 42.5 (CH₂), 41.3 (CH₂), 40.0 (CH₂), 38.2 (CH), 36.3 (CH₂), 31.3 (CH₂), 25.1 (CH₂), 16.6 (CH₃).

Characteristic NMR data of minor Z-isomer: ¹H NMR (500 MHz, CDCl₃) \( \delta \) 6.30 (1H, dd, \( J = 11.4, 1.5 \) Hz, CH₃C=CH), 2.55 (2H, t, \( J = 6.9 \) Hz, CH₂), 1.92 (3H, d, \( J = 1.5 \) Hz, CH₃C=); ¹³C NMR (101 MHz, CDCl₃) \( \delta \) 124.1 (CH), 32.2 (CH₂), 24.3 (CH₃).
Supplementary Information

NMR Spectra
Supplementary Information

3a
4.9:1 mixture of E/Z isomers
Supplementary Information

3b
6.0:1 mixture of E/Z isomers
3c
4:6:1 mixture of E/Z isomers
Supplementary Information

4.8.1 mixture of E/Z isomers
Supplementary Information

3e

7.7:1 mixture of E/Z isomers

Chemical shifts and other experimental details are provided in the supplementary information.
Supplementary Information

NOESY Spectrum

[Chemical structure and spectrum diagrams with annotations]

1.86 (2H, d)
3.21 (2H, t)
6.17 (1H, dd)
6.57 (1H, d)
2.89-2.90 (2H, m)
2.43 (2H, t)
6.17 (1H, dq)
2.75-2.67 (2H, m)
3g

6.8:1 mixture of E/Z isomers
Supplementary Information

4.6:1 mixture of E/Z isomers
5.7:1 mixture of E/Z isomers
Supplementary Information

4:6:1 mixture of E/Z isomers
Supplementary Information

31
5:1:1 mixture of E/Z isomers
3m
5.7:1 mixture of E/Z isomers
3n
6.6:1 mixture of E/Z isomers
5.6:1 mixture of E/Z isomers
Supplementary Information

6:5:1 mixture of E/Z isomers
2:7:1 mixture of Z/E isomers
Supplementary Information

![Chemical Structure]

2.0:1 mixture of Z/E isomers
3t
6.1:1 mixture of E/Z isomers
Supplementary Information

5.2:1 mixture of E/Z isomers
5.5:1 mixture of E/Z isomers
References