Supporting Information

Enediynes from Aza-enediynes: *C,N*-Dialkynyl Imines Undergo Both Aza-Bergman Rearrangement and Conversion to Enediynes and Fumaronitriles.

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General.

All commercial chemicals were used without further purification unless otherwise noted. Methylene chloride and diethyl ether were re-distilled from calcium hydride. All reactions were performed under argon. Unless otherwise noted, organic extracts were dried with Na₂SO₄, filtered through a fritted glass funnel, and concentrated with a rotary evaporator (20-30 mmHg). *R_f* values are reported for thin-layer chromatography (TLC) performed on silica gel TLC plates, using the indicated mobile phase. Flash chromatography was performed with EM silica gel. ¹H NMR spectra were recorded at 400 and 300 MHz and ¹³C NMR spectra were recorded at 100 and 75 MHz in CDCl₃, unless otherwise noted. All mass spectra were obtained by chemical ionization with methane as the ionizing gas. The yields for compounds **11** and **12** are based on 2:1 stoichiometry between aza-enediyne **5** and **11/12**.

[1-¹³C]-1,3-Diphenyl-1-propynone ([1-¹³C]-**9**). To a mixture of phenyl acetylene (0.22 g, 2.2 mmol) and cuprous iodide (17.0 mg, 0.08 mmol) in triethylamine (5.0 mL) was added [1-¹³C]-benzoyl chloride (0.20 g, 1.4 mmol). The reaction mixture was stirred at room temperature under argon for 48 h. After filtering off the salt, the solvent was distilled off and the product was purified by flash chromatography (hexanes/EtOAc, 20:1) to afford 0.17 g (60% yield) of [1-¹³C]-**9** as a yellow oil: *R_f* 0.40 (EtOAc/hexanes, 1:9); ¹H NMR 7.32-7.53 (m, 5H), 7.56-7.70 (m, 3H), 8.16-8.23 (m, 2H); ¹³C NMR 86.78 (d, *J* = 91.8 Hz), 93.01 (d, *J* = 13.7 Hz), 119.98 (d, *J* = 1.7 Hz), 128.54 (d, *J* = 5.0 Hz), 128.60, 129.46 (d, *J* = 3.3 Hz), 130.73, 132.96, 134.05, 136.74 (d, *J* = 61.1 Hz), 177.89 (¹³C); HRMS *m/z* 208.0842 (calc'd 208.0843, C₁₄¹³CH₁₁O).

1,3-Diphenyl-1-propynone oxime mesitylate (**10**) and [1-¹³C]-**10**. To a solution of compound **9** (0.25 g, 1.21 mmol) in 6 mL dry CH₂Cl₂ was added *O*-mesitylenesulfonylhydroxyamine^{1,2} (0.50 g, 2.32 mmol). The reaction mixture was stirred at room temperature for 30 h, and poured into ice-water. The aqueous layer was extracted by CH₂Cl₂ (15 mL x 3). The residue upon drying and concentration of the organic layer was purified by flash chromatography (5% EtOAc in hexanes) to afford 0.34 g (70% yield) of a single isomer of **10** as a white solid: *R_f* 0.34 (10% EtOAc in hexanes); m.p 111.0-113.0 °C; ¹H NMR 2.25 (s, 3H), 2.73 (s, 6H), 6.94 (s, 2H), 7.30-7.50 (m, 6H), 7.61 (dd, 2H, *J* = 7.8, 1.5 Hz), 7.81 (dd, 2H, *J* =

7.8, 1.5 Hz); ^{13}C NMR 20.99, 22.77, 77.79, 104.29, 120.57, 127.29, 128.51, 128.59, 130.32, 130.47, 131.29, 131.40, 131.61, 132.44, 140.70, 143.69, 147.59; HRMS m/z 404.1304 (calc'd 404.1320, $\text{C}_{24}\text{H}_{22}\text{NO}_3\text{S}$). In the same way, $[1-^{13}\text{C}]\text{-10}$ was prepared from $[1-^{13}\text{C}]\text{-9}$: ^{13}C NMR (CDCl_3) 147.59; HRMS m/z 405.1354 (calc'd 405.1354, $\text{C}_{23}^{13}\text{CH}_{22}\text{NO}_3\text{S}$).

3-Aza-1,4,6-triphenyl-hex-3-ene-1,5-diyne (**5a**) and $[4-^{13}\text{C}]\text{-5a}$. To a solution of phenyl acetylene (262 mg, 2.57 mmol) in 3 mL of dry Et_2O at $-20\text{ }^\circ\text{C}$ was added dropwise a solution of *n*-butyllithium (2.57 mL, 1.6 M in hexanes, 2.57 mmol) such that the temperature was maintained at $-20\text{ }^\circ\text{C}$. This mixture was stirred for 20 min at $-20\text{ }^\circ\text{C}$. In a separate flask, a suspension of cuprous iodide (161 mg, 0.85 mmol) in 3 mL of dry Et_2O was cooled to $-40\text{ }^\circ\text{C}$. The phenylacetylide solution was added slowly via cannula to this suspension. After the addition was complete, the mixture was stirred at room temperature for 40 min. The resulting light yellow suspension was added to a solution of mesitylate **10** (285 mg, 0.71 mmol) in 3 mL of dry Et_2O at $0\text{ }^\circ\text{C}$. The reaction mixture was stirred at $0\text{ }^\circ\text{C}$ for 1 h, and then at room temperature for 24 h. The solvent was evaporated, and the product was purified by flash chromatography on silica gel (hexanes) to afford 115 mg (54%) of a single isomer of aza-enediyne **5a** as a red-yellow oil.: R_f 0.68 (50% CH_2Cl_2 in hexanes); ^1H NMR (CDCl_3) 7.22-7.59 (m, 11H), 7.70 (dd, 2H, $J = 7.5, 1.5\text{ Hz}$), 8.22 (dd, 2H, $J = 7.5, 1.5\text{ Hz}$); ^{13}C NMR (CDCl_3) 84.36, 93.94, 99.83, 102.07, 121.14, 124.70, 127.97, 128.24, 128.40, 128.55, 128.68, 130.33, 131.60, 132.09, 132.61, 135.82, 159.03; HRMS m/z 306.1272 (calcd 306.1282, $\text{C}_{23}\text{H}_{16}\text{N}$). In the same way, $[4-^{13}\text{C}]\text{-5a}$ was prepared from $[1-^{13}\text{C}]\text{-10}$: ^{13}C NMR 159.03; HRMS m/z 307.1323 (calcd 307.1316, $\text{C}_{22}^{13}\text{CH}_{16}\text{N}$).

3-Aza-1-(4-methylphenyl)-4,6-diphenyl-hex-3-ene-1,5-diyne (**5b**). Following the general procedure above for **5a**, **5b** was isolated in 55% yield after flash chromatography on silica gel (hexanes) as a yellow oil: R_f 0.70 (50% CH_2Cl_2 in hexanes); ^1H NMR (CDCl_3) 2.38 (s, 3H), 7.17 (d, 2H, $J = 8.1\text{ Hz}$), 7.42-7.4 (m, 8H), 7.69 (dd, 2H, $J = 8.1, 1.5$), 8.20 (dd, 2H, $J = 8.1, 1.5$); ^{13}C NMR (CDCl_3) 21.53, 84.40, 93.69, 100.42, 101.86, 121.22, 121.65, 127.88, 128.52, 128.66, 129.20, 130.25, 131.60, 131.94, 132.59, 135.89, 138.54, 158.44; HRMS m/z 320.1445 (calcd 320.1439, $\text{C}_{24}\text{H}_{18}\text{N}$).

3-Aza-4,6-diphenyl-1-triisopropylsilyl-hex-3-ene-1,5-diyne (**5g**). Following the general procedure above for **5a** but employing the cuprate derived from triisopropylacetylene, **5c** was isolated in 30% yield as an orange oil: $R_f = 0.64$ (10% EtOAc in hexanes); ^1H NMR (400 MHz, CDCl_3): 1.07-1.14 (m, 21H), 7.48-7.4 (m, 5H), 7.64 (dd, 3H, $J = 8.2, 1.4$), 8.17 (d, 2H, $J = 7.2$); ^{13}C NMR (75 MHz, CDCl_3): 11.59, 18.80, 84.14, 101.24, 106.96, 121.09, 128.03, 128.50, 128.69, 129.59, 130.17, 132.16, 132.52, 133.09, 134.13, 135.96, 160.15; IR (neat film): 3061, 3037, 2944, 2982, 2203, 2094, 1320, 1461, 1328, 1265, 1010, 883; HRMS (CI^+) m/z 386.2301 (calcd 386.2304, $\text{C}_{26}\text{H}_{32}\text{NSi}$).

(*E*)- and (*Z*)-1,3,4,6-Tetraphenyl-3-hexene-1,5-diynes⁴ (**11a**) and $[1,4\text{-}^{13}\text{C}_2]\text{-11a}$. A benzene solution (2.5 mL) of **5a** (90 mg, 0.29 mmol) was stirred at 55 °C for 5 days under argon. The residue upon concentration of the organic layer was purified by flash chromatography to afford 38 mg (68 % yield) of (*Z*)-**11a** and (*E*)-**11a** (1:1 ratio judged by ^1H NMR) as a yellow solid and 15 mg (44 % yield) of **12**³ as a white solid. Recrystallization of the mixture of (*Z*)- and (*E*)-**11a** in hexanes/EtOAc afforded pure (*E*)-**11a** and a fraction enriched in (*Z*)-**11a**. Given the recent reports of dimerization of metal alkynylcarbene complexes to enediynes,⁵ thermolysis of **5b** as above, but in the presence of one equivalent of CuI was performed in order to rule out the possible involvement of copper species contaminating **5b**, which was prepared by cuprate coupling, in its thermal transformation to **11a**. These reactions proceeded at the same rate (TLC monitoring) and afforded the same yields of products as those in the absence of copper. (*E*)-**11a**: yellow prisms from hexanes/EtOAc m.p. 155.0-157.0 °C, lit.⁴ 156.2-157.2 °C; R_f 0.65 (10% EtOAc in hexanes); ^1H NMR⁴ 7.25-7.29 (m, 10H), 7.39 (t, 2H, $J = 8.0$ Hz), 7.45 (t, 4H, $J = 8.0$ Hz), 7.97 (d, 4H, $J = 8.0$ Hz); ^{13}C NMR⁴ 90.90, 98.53, 123.21, 127.83, 128.28 (2C), 128.45, 128.60, 129.23, 131.40, 139.01; HRMS m/z 381.1636 (calcd 381.1643, $\text{C}_{30}\text{H}_{21}$). (*Z*)-**11a** (80% (*Z*)-isomer): yellow needles from hexanes/EtOAc, mp 96-99 °C, lit.⁴ 105-106 °C; R_f 0.65 (10% EtOAc in hexanes); UV-Vis (cyclohexane): $\lambda_{\text{max}} = 362\text{ nm}$ (log $\epsilon = 4.50$), 269 nm (log $\epsilon = 4.53$), lit.⁴ 361 nm (log $\epsilon = 4.30$), 269 nm (log $\epsilon = 4.41$); IR (neat film): 3058, 2927, 2254 (w), 1463, 1379, 909, 740; ^1H NMR⁴ 7.18-7.21 (m, 6H), 7.28-7.34 (m, 10H), 7.52-7.55 (m, 4H); ^{13}C NMR⁴ 91.77, 96.84, 123.37, 127.83, 128.04, 128.36, 128.52, 129.23, 129.72, 131.65, 137.45. In the same way, 16 mg (60 % yield) of $[1,4\text{-}^{13}\text{C}_2]\text{-11b}$ was obtained from $[4\text{-}^{13}\text{C}]\text{-5b}$ as a 3:1 mixture of (*E*)/(*Z*) isomers after chromatography: ^{13}C NMR 96.84 (d, $J = 4.1$ Hz, (*Z*)-

isomer), 98.56 (d, $J = 4.6$ Hz, (*E*)-isomer), 128.62 (d, $J = 4.6$ Hz, (*E*)-isomer), 129.23 (d, $J = 4.1$ Hz, (*Z*)-isomer); HRMS m/z 383.1708 (calcd 383.1710, $C_{28}^{13}C_2H_{21}$).

(*E*)-Diphenylfumaronitrile (**12**):³ white needles from hexanes; R_f 0.40 (10% EtOAc in hexanes); m.p. 161.5-162.5 °C, lit.³ 161-162 °C; UV-Vis (EtOH): $\lambda_{max} = 340$ nm ($\log \epsilon = 4.29$), $\lambda_{max} = 237$ nm ($\log \epsilon = 4.25$), lit.⁶ 331 nm ($\log \epsilon = 3.91$), 238 nm ($\log \epsilon = 4.0$); 1H NMR 7.50-7.55 (m, 6H), 7.80-7.84 (m, 4H); ^{13}C NMR 116.6, 125.57, 128.67, 129.27, 131.70, 131.95; HRMS m/z 231.0924 (calcd 231.0922, $C_{16}H_{11}N_2$).

2,3,5-Triphenyl-pent-2-en-4-ynenitrile **7a** and [5- ^{13}C]-**7a**. A solution of aza-enediyne **5a** (22 mg) in benzene (0.45 mM) was stirred at 90 °C for 24 hours. The solvent was evaporated, and the product was purified by flash chromatography on silica gel (1% EtOAc in hexanes) to afford 18.6 mg (85% yield) of nitrile **7a** as a light-yellow solid mp: 132-134 °C; R_f 0.50 (10% EtOAc in hexanes); 1H NMR 7.22-7.40 (m, 13H), 7.62-7.66 (m, 2H); ^{13}C NMR 89.47, 100.48, 118.24, 119.24, 121.91, 128.49, 128.60, 129.05, 129.42, 129.48, 129.65, 132.23, 132.87, 135.32, 137.34, 138.26; IR (KBr): 2185 cm^{-1} ; HRMS m/z 306.1284 (calcd 306.1283, $C_{23}H_{16}N$). In the same way, starting from [4- ^{13}C]-**5a**, 10 mg (24% yield) of [5- ^{13}C]-**7a** was isolated: ^{13}C NMR 100.47; HRMS m/z 307.1317 (calcd 307.1316, $C_{22}^{13}CH_{16}N$).

(*E*) and (*Z*)-3,6-Dimethyl-1,4-diphenyl-3-hexene-1,5-diynes (**11c**), and diphenylfumaronitrile (**12**) from **5c**. Flash chromatography of a sample of aza-enediyne **5c** (20 mg) stored in a -10 °C freezer for 24 months afforded 1.2 mg (14 % yield) of (*Z*)-, and (*E*)-**11c** (1:1 ratio as judged by 1H NMR) as a yellow solid, 2.8 mg (35 % yield) of (*E*)-1,2-dicyano-1,2-diphenylethylene **12** as a white solid, along with 3.5 mg of aza-enediyne **5c** (18 % recovered). **11c**: R_f 0.60 (10% EtOAc in hexanes); UV-Vis (cyclohexane): $\lambda_{max} = 319$ nm ($\log \epsilon = 3.95$); IR (neat film): 3055, 2923, 2852, 2219 (w), 1720 (w), 1598 (w), 1489 (w), 1442 (w), 1265 cm^{-1} ; 1H NMR 2.01 (s, 3H), 2.08 (s, 3H), 2.09 (s, 3H), 2.30 (s, 3H), 7.23-7.36 (m, 16H), 7.49-7.51 (m, 2H), 7.77 (d, 2H, $J = 7.6$ Hz); HRMS m/z 257.1323 (calcd 257.1330, $C_{20}H_{17}$).

NMR Kinetics. A solution of **5b** or [4- ^{13}C]-**5b** (20 mg, 120 mM) containing 12 mg (120 mM) of 2,5-dimethylfuran as an internal standard in the case of 1H NMR kinetics in d_6 -benzene or d_8 -THF was transferred to a NMR tube. After degassing by three freeze-pump-thaw cycles, the NMR tube was flame-

sealed and an initial ^1H or ^{13}C NMR spectra was acquired. The NMR tube was transferred to an oil bath maintained at $70 \pm 1\text{ }^\circ\text{C}$ in the dark and additional spectra were acquired over the next 22 h. Each time a spectrum was acquired, the tube was insert into an ice-water bath for transfer to and from the spectrometer. An additional spectrum was acquired after 3 d at $70\text{ }^\circ\text{C}$. For each spectrum, peak area ratios of signals for **5b** (7.45 ppm) or $[4\text{-}^{13}\text{C}]\text{-5b}$ (159 ppm) and 2,5-dimethylfuran (^1H NMR) or solvent (^{13}C NMR) were obtained. These were then fit to an equation for parallel first- and second-order decay using a non-linear least squares fitting program:

$$y = Ak_1 / [(Ak_2 + k_1)\exp(k_1 t) - Ak_2]$$

where y is the concentration of **5b**, A is the initial concentration of **5b**, k_1 is the first-order rate constant, k_2 is the second-order rate constant, and t is time in seconds.

ESI-MS. A solution of **5a** in benzene (200 mM) was stored at -10°C , and at various time intervals, an aliquot was removed, diluted to $10\text{ }\mu\text{M}$ in MeOH, and analyzed by positive mode ESI-MS. In all spectra, the most abundant ion corresponds to a protonated dimer of **5a** at m/z 611. While the ion corresponding to protonated **5a** ($m/z = 306$) is in relatively low abundance, there is an ion corresponding to adduction of methanol to **5a** at m/z 338. Over the course of 11 days, the relatively intensity of the **5a** and **5a**-methanol adduct ions decreases and an ion corresponding to the enediyne **11a** grows in intensity. Collisionally activated dissociation of the dimer ion demonstrates sequential loss of phenyl and m/z 27 fragments, indicating that this ion is not due to non-covalent association between two **5a** molecules.

References.

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Figure S1.

Thermolysis of **5a** in d_6 -benzene @ 70 °C
Disappearance of **5a** followed by ^1H NMR (7.45 ppm)

Figure S2.

Thermolysis of [1- ^{13}C]-**5a** in d_6 -benzene @ 70 °C
Disappearance of [1- ^{13}C]-**5a** followed by ^{13}C NMR (159 ppm)

Figure S3.

Thermolysis of [1-¹³C]-**5a** in *d*₈-THF @ 70 °C
Disappearance of [1-¹³C]-**5a** followed by ¹³C NMR (159 ppm)

Figure S4. ^1H NMR of 1,3-diphenylpropynone mesitylate (**10**)

Figure S5. ^1H NMR of 1,4,6-triphenyl-3-aza-3-ene-1,5-diyne (**5a**)

Figure S6. ^1H NMR of 1-(4-methylphenyl)-4,6-diphenyl-3-aza-3-ene-1,5-diyne (**5b**)

Figure S7. ^1H NMR of 3-Aza-4,6-diphenyl-1-triisopropylsilyl-hex-3-ene-1,5-diyne (**5g**)

Figure S8. ^1H NMR of (*E*)-1,3,4,6-tetraphenyl-3-hexene-1,5-diyne (**11a**)

1F-6-83-1-h

Pulse Sequence: zgpg30
Solvent: CDCl3
Acq. time 2.856 sec
Width 5002.3 Hz
F2 400.146 MHz
F1 100.625 MHz
Data 400.2608861 MHz
SFO 400.146 MHz
Line broadening 0.3 Hz
FT size 32768
Total time 0 min, 41 sec

Relax. delay 2.800 sec
Pulse 15.8 degrees
Acq. time 2.856 sec
Width 5002.3 Hz
F2 400.146 MHz
F1 100.625 MHz
Data 400.2608861 MHz
SFO 400.146 MHz
Line broadening 0.3 Hz
FT size 32768
Total time 0 min, 41 sec

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6.896
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Figure S10. ^1H NMR of (*E*)-1,2-dicyano-1,2-diphenylethylene (**12**)

Figure S11. ^1H NMR of (*E*)-1,2-dicyano-1,2-di(4-methylphenyl)ethylene (**13**)

S19

Figure S13. ^1H NMR of (*E*) and (*Z*)-3,6-dimethyl-1,4-diphenyl-3-hexene-1,5-diyne (**11c**)

Figure S14. Representative ^{13}C NMR spectra from thermolysis of $[4\text{-}^{13}\text{C}]\text{-5a}$ in $d_6\text{-THF}$ at 70°C

1F-7-81-thf-2-C
Pulse Sequence: zgpg1
Solvent: thf
Pulse delay: 2.000 sec
Relaxation delay: 2.000 sec
Acq time: 1.777 sec
Width: 19399.9 Hz
84 repetitions
SOLVENT: C13, 75.4702761 MHz
RECOUPLE: H1, 399.1426046 MHz
Power: 40 dB
continuously on
waltz-16 modulated
Single precision data
128 F2 points
Time: 0.000000 sec
FT size: 65536
Total time: 4 min, 2 sec

Time: 3618
sec

17-7-81-147-5-C

Pulse Sequence: zgpg30

Solvent: 1H2O

Ambient temperature

UNITY800-300 MHz

Relax. delay 2.000 sec

Pulse 35.0 degree

Acq. time 1.277 sec

Width 10000.0 Hz

64 repetitions

DECOUPLE CH2 75.4702781 MHz

DECOUPLE H1 200.1433216 MHz

Power 0.00

continuously on

CH2 is modulated

with 10000.0 Hz

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 6 min, 2 sec

Time: 40173 sec

$$111-7-91-134-0-0-0$$

Pulse Sequence: cfoul

Solvent: tef

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Relax. delay 2.000 sec

Publication 200 - 0 Supply
Date: 4/10/2007 1:27:23 PM

Width 10000.0 Hz

64 repetitions 74.438261 mm2

DECOUPLE_H1: 300.1420244 MHz

Power 40 dB
 Input 1 mV/div

WAL72-16 modulated

Using the prediction data
 CARP, INTERFACING

Line broadening 1.0 nm

1977 6 11 200 00 05 2000

TOTAL TIME 6 MIN, 4 SEC

Figure S15. Positive mode ESI-MS spectrum of **5a** in benzene day 0.

Figure S16. Positive Mode ESI-MS of **5a** in benzene, day 5.

Figure S17. Positive mode ESI-MS spectrum of **5a** in benzene, day 11

Figure S18. CAD spectra of $[\text{dimer}+\text{H}]^{1+}$ at m/z 611. a. MS^2 at m/z 611. b. MS^3 of m/z 533. c. MS^4 of m/z 457. In this labeling system P= parent ion and Ph= phenyl group.