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Cascade Cyclizations via *N*,4-Didehydro-2-(phenylamino)pyridine Biradicals/Zwitterions Generated from Enyne−Carbodiimides

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Thermolysis of the enyne−carbodiimides **7** having the central carbon−carbon double bond incorporated as part of the cyclopentene ring favors the formation of the corresponding *N*,4-didehydro-2-(phenylamino)pyridine intermediates, either as the σ,π-biradicals **8** or as the zwitterions **8′**, for subsequent synthetic elaborations. By placing appropriate substituents at the acetylenic terminus, a variety of the intramolecular decay routes are available for the initially formed σ,π-biradicals/zwitterions, leading to the 5,6-dihydrobenzo[*c*][1,8]naphthyridine **21**, the 1,2,3,4-tetrahydro-[1,8]naphthyridine **24** and related compounds **25** and **26**, the 5,6-dihydrobenz[*f*]isoquinoline **28**, and the benzofuro[3,2-*c*]pyridine **30**. Surprisingly, the use of the dimethylamino group of the 2-(dimethylamino)phenyl substituent to capture the carbocationic center in the zwitterion **8e′** furnished the 5*H*-pyrido[4,3-*b*]indole **32** in only 14% yield. The majority of the products were the 1*H*-pyrrolo[2,3-*b*]quinolines **34** and **35**, isolated in 48 and 7% yields, respectively. However, it was possible to redirect the reaction toward **32** by conducting thermolysis of the enyne−carbodiimide **7e** in the presence of 5 equiv of dimethylphenylsilyl chloride. Under this reaction condition, the 2-pyridone imine **37** was isolated in 86% yield, which on exposure to silica gel was converted to **32** in essentially quantitative yield. Thermolysis of the enyne−carbodiimide **42** having a methoxymethyl substituent at the acetylenic terminus led to the formation of **46′** as a pyridine analogue of *ortho*-quinone methide imine. An intramolecular hetero-Diels−Alder reaction of **46′** then furnished the tetrahydro[1,8]naphthyridino[2,1-*c*][1,4]benzoxazine **47**.

Introduction

Thermolysis of the benzannulated enyne−carbodiimides provides easy access to the corresponding heteroaromatic biradicals for subsequent synthetic elaborations.[1] Specifically, when **1a** was subjected to heating in γ-terpinene at 138 °C for 14 h, 2-(phenylamino)quinoline (**3a**) was produced as the major product along with a minor amount of the indoloquinoline **6a** (Scheme 1). Apparently, *N*,4-didehydro-2-(phenylamino)quinoline (**2a**) was formed preferentially, which behaved as a σ,π-biradical to abstract hydrogen atoms from γ-terpinene to produce **3a**. An alternative pathway involving the formation of the formal Diels−Alder adduct **5a** followed by tautomerization led to **6a**. The transformation from **1** to **5** could proceed either through a two-step biradical mechanism via **4** followed by an intramolecular radical−radical coupling or through a concerted Diels−Alder reaction. In the analogous enyne−allene[2] and enyne−ketenimine[3] systems, the kinetic, mechanistic, theoretical, and DNA-cleaving studies suggest a two-step biradical pathway. Unlike **1a**, thermolysis of the benzannulated enyne−carbodiimides **1b**−**f** having a substituent at the alkynyl terminus produced the indoloquinolines **6b**−**f** exclusively. In addition to providing easy access to indoloquinolines, this pathway was also adopted for the synthesis of 6*H*-indolo[2,3-*b*][1,6]naphthyridines and related compounds[4] as the aza analogues of the naturally occurring ellipticine alkaloids. Ellipticine and many of its derivatives have been found to exhibit potent antitumor activities.[5]

Compared with the analogous enyne−allene,[2,6] enyne−ketene,[7] and enyne−ketenimine[3] systems, the thermally induced cyclization reaction of enyne−carbodiimide ap-

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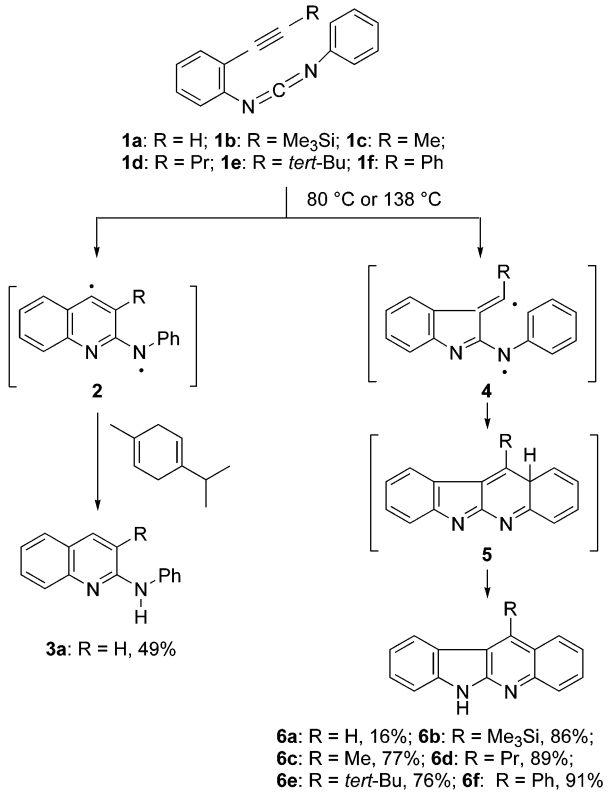
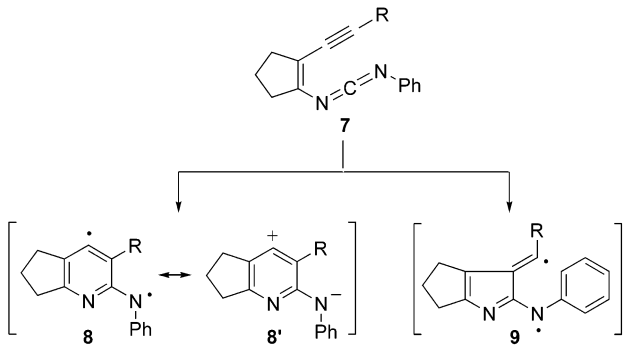
SCHEME 1



pears to have a greater propensity to proceed toward the Diels−Alder route. We are interested in exploring the possibility of redirecting the cyclization reaction toward the pathway leading to **2** and related biradicals even for the systems having a substituent at the alkynyl terminus. A success could provide many opportunities to exploit the chemical reactivities of these reactive biradical intermediates.

SCHEME 2



We have explored the strategy of using the enyne−carbodiimides **7** having the central carbon−carbon double bond incorporated as part of the cyclopentene ring to produce the σ,π-biradicals **8** (Scheme 2). It was anticipated that cyclization to form the σ,π-biradicals **9** would be disfavored because of emergence of ring strain in the resulting bicyclic ring system. The effect of ring strain in dictating the biradical-forming pathway was observed previously in the analogous enyne−allene system.[8] We now report our findings of thermolysis of **7** to generate the corresponding *N*,4-didehydro-2-(phenylamino)pyridine intermediates, either as the σ,π-biradicals **8** or as the zwitterions **8′**, for subsequent synthetic elaborations. Derivatives of several interesting heteroaromatic compounds such as 5,6-dihydrobenzo[*c*][1,8]naphthyridine,[9] benzofuro[3,2-*c*]pyridine,[10] 5*H*-pyrido[4,3-*b*]indole,[11] and 1*H*-pyrrolo[2,3-*b*]quinoline[12] were synthesized.

Results and Discussion

The synthetic sequence outlined in Scheme 3 provides an efficient route to a variety of the enyne−carbodiimides **7**. The commercially available ethyl 2-oxocyclopentanecarboxylate (**10**) was converted to the triflate **11** as reported previously.[13] The Pd-catalyzed cross-coupling reaction[14] between **11** and the terminal alkynes **12** then produced **13**. Saponification followed by treatment of the carboxylic acids **14** with diphenyl phosphorazidate (DPPA)[15] then afforded the isocyanates **15**. Condensation between **15** and aniline gave the urea derivatives **16**, which on treatment with dibromotriphenylphosphorane[16] furnished the enyne−carbodiimides **7** (Table 1).

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SCHEME 3

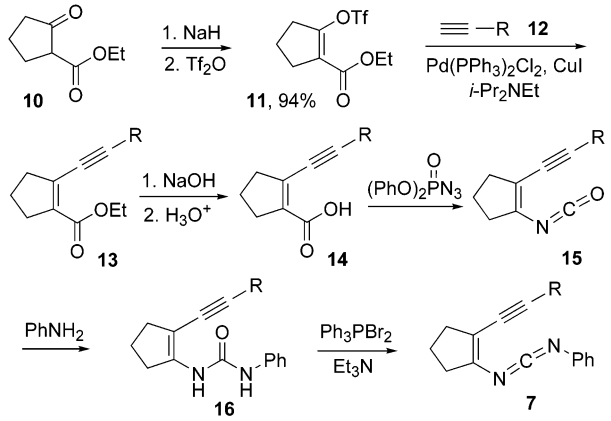
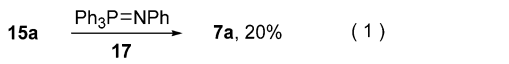


TABLE 1. Synthesis of 13−16 and the Enyne−Carbodiimides 7

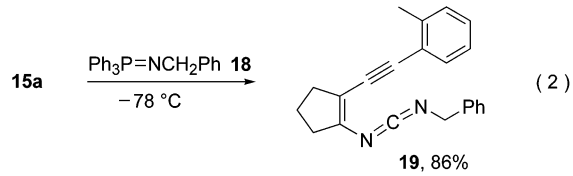
entry	R	**13**, yield (%)	**14**, yield (%)	**15**, yield (%)	**16**, yield (%)	**7**, yield (%)
a	2-methylphenyl	90	96	91	85	85
b	propyl	91	89	87	72	65
c	2-phenylethyl	98	92	86	72	72
d	2-methoxyphenyl	92	92	84	69	82
e	2-(dimethylamino)phenyl	91	85	87	76	50
f	methoxymethyl	91	80	68		

The use of the aza-Wittig reaction between the isocyanate **15a** and the iminophosphorane **17**,[17] derived from aniline and dibromotriphenylphosphorane, to form **7a** gave only 20% yield (eq 1). Attempts to improve the yield



(1)

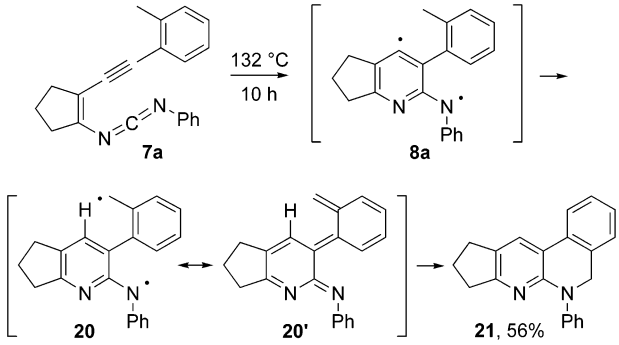
of the reaction by conducting the aza-Wittig reaction at −78 °C were unsuccessful. Interestingly, the reaction at −78 °C between **15a** and the iminophosphorane **18**,[18] derived from benzyl azide and triphenylphosphine, was very efficient in producing the enyne−carbodiimide **19** in 86% isolated yield (eq 2).

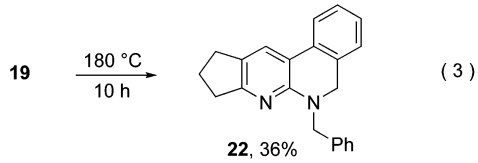


(2)

Thermolysis of **7a** under refluxing chlorobenzene at 132 °C produced the 5,6-dihydrobenzo[*c*][1,8]naphthyridine **21** in 56% yield (Scheme 4). Apparently, cycloaromatization of **7a** generated the *N*,4-didehydro-2-(phenylamino)pyridine *σ*,*π*-biradical **8a** as anticipated. A subsequent 1,5-hydrogen shift produced the *π*,*π*-biradical **20**, which could also be written as an *ortho*-quinodimethane derivative depicted in **20′**. Rotation around the central carbon−carbon bond followed by an intramolecular radical−radical coupling, or an electrocyclic reaction if the resulting biradical is also regarded as an *ortho*-quinodimethane derivative, then afforded **21**. This cascade sequence is reminiscent of those of several examples of the enyne−allene[8b] and enyne−ketene[7c,d] systems reported earlier. In the case of **19**, the cycloaromatization reaction requires heating at a substantially higher temperature (180 °C under refluxing 1,2-dichlorobenzene) to produce **22** in 36% yield (eq 3).

SCHEME 4

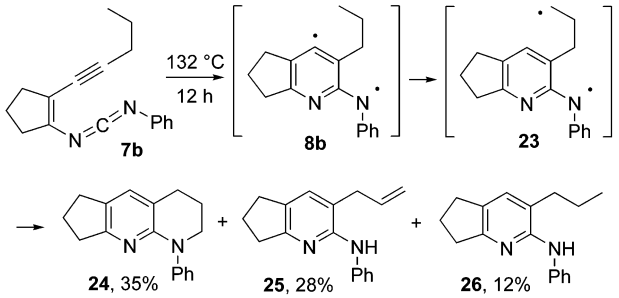




(3)

When **7b** was subjected to thermolysis, **24** (35%) was isolated along with **25** (28%) and **26** (12%) (Scheme 5). As observed previously in an enyne−ketene system,[7d] cycloaromatization of **7b** generated the *σ*,*π*-biradical **8b**, which underwent a 1,5-hydrogen shift to furnish **23**. An intramolecular radical−radical coupling then afforded **24**. In addition, **23** could also undergo a second intramolecular 1,5-hydrogen shift to produce **25** or could abstract hydrogen atoms from elsewhere to give **26**.

SCHEME 5



The aryl radical center of the *σ*,*π*-biradical **8c**, generated from **7c**, was captured by the carbon−carbon double bond of the phenyl substituent in a 6-*endo* radical cyclization reaction to give **27** (Scheme 6). A subsequent tautomerization then produced **28** in 73% yield.

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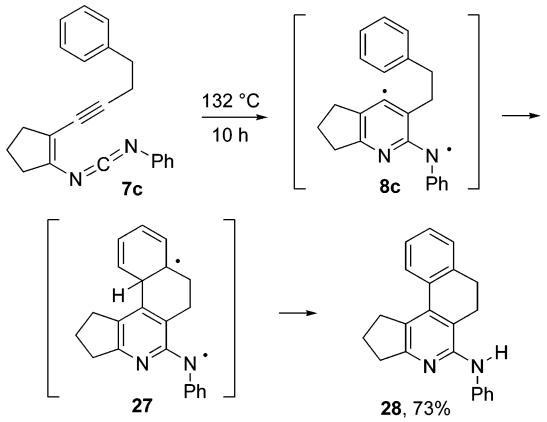
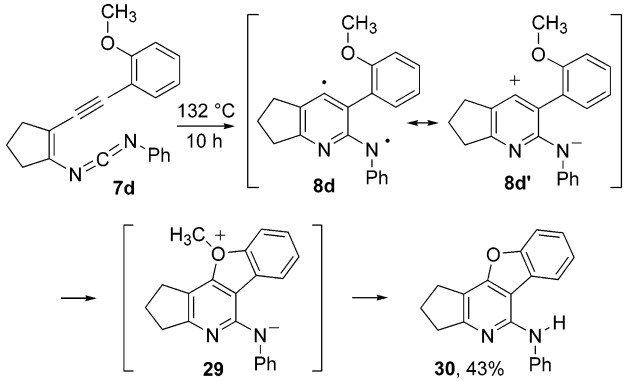
SCHEME 6



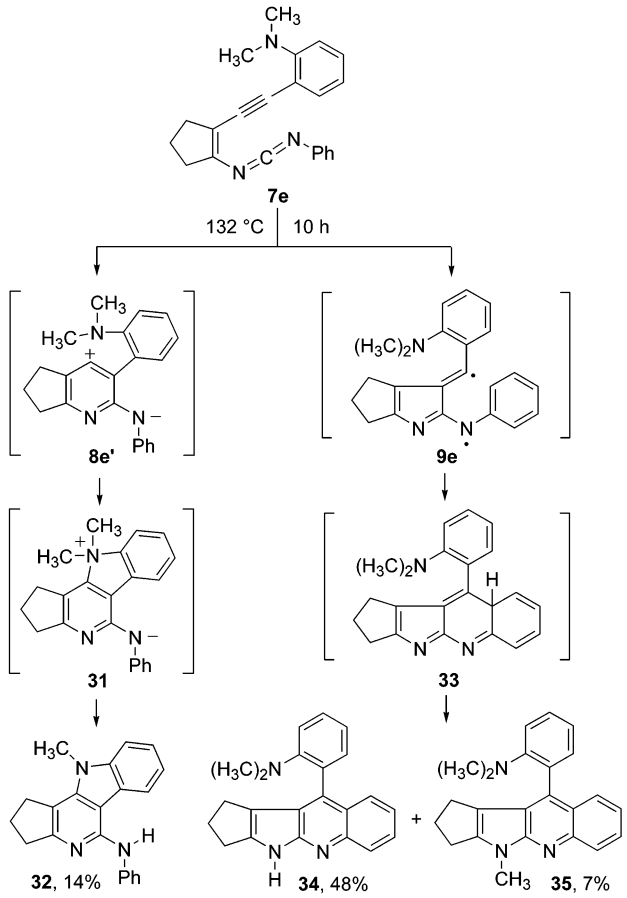
SCHEME 7



The transformation from **7d** to the benzofuro[3,2-*c*]-pyridine **30** can be best accounted for by regarding the initially formed σ,π-biradical **8d** as the zwitterion **8d′** (Scheme 7). The carbocationic center of **8d′** was then captured by the lone-pair electrons on the oxygen atom to give the oxonium ion in **29**, which was converted to **30** perhaps during workup and purification by column chromatography. The structure of **30** was unequivocally established by the X-ray structure analysis. The dual chemical property of the cycloaromatized intermediate as the σ,π-biradical **8d** and as the zwitterion **8d′** resembles that of the biradical/zwitterion intermediate derived from the Moore cyclization reaction of the enyne−ketene system.[7,19]

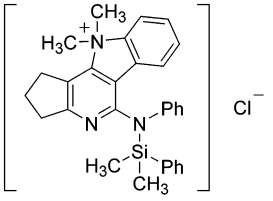
The use of the dimethylamino group to capture the carbocationic center in **8e′** was also successful, leading to the formation of the 5*H*-pyrido[4,3-*b*]indole **32** (Scheme 8). Surprisingly, **32** was produced only as a minor product in 14% yield. The 1*H*-pyrrolo[2,3-*b*]quinoline **34** and the methylated derivative **35**, both derived via the Diels−Alder route through **33**, combine to give a total of 55% yield. The extra methyl group in **35** could come from **31**. The structures of **32** and **34** were unequivocally established by the X-ray structure analysis. The reason for such a switch is not clear at the present time. Perhaps the 2-(dimethylamino)phenyl group is too sterically demanding, making the generation of **8e′** less favorable. In the enyne−allene system, the presence of a sterically demanding group such as the *tert*-butyl group or the

SCHEME 8



trimethylsilyl group at the alkynyl terminus causes the cyclization reaction to adopt the Diels−Alder route.[6h,i]

In several cases of the enyne−ketene system, it was reported that the efficiency of the zwitterion pathway could be greatly enhanced by conducting thermolysis in the presence of trimethylsilyl chloride.[19] Indeed, it was gratifying to observe that when **7e** was heated in the presence of 1.2 equiv of dimethylphenylsilyl chloride, **32** was produced as the major product in 70% isolated yield after purification by column chromatography along with only 14% of **34**. With 5 equiv of dimethylphenylsilyl chloride, **34** was not detected, and only **32** was isolated in 84% yield. This dramatic change in favor of **32** is presumably due to silylation of the amide anion in **31** to form **36**, preventing **31** from reverting back to **7e** and eventually producing **34** and **35**. However, other pathways including an initial silylation of one of the nitrogen atoms of the carbodiimide moiety in **7e** to promote a cationic reaction mechanism leading to a silylated adduct such as **36** could not be completely ruled out.



Although it was initially assumed that the putative intermediate **36** or the corresponding demethylated ad-

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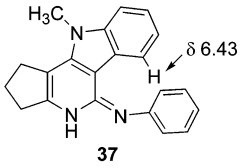
duct would be converted directly to **32** during workup, we were surprised to observe that its tautomer, the 2-pyridone imine **37**, precipitated out of the chlorobenzene solution as a yellow solid in 86% yield when the solution was allowed to cool to room temperature after thermolysis. It is worth noting that the (*E*)- configuration



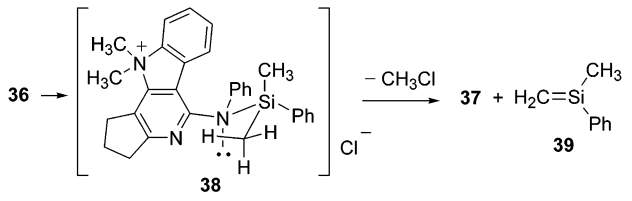
37

was assigned to the carbon−nitrogen double bond in **37** in order to account for the observation of an upfield-shifted aromatic ^{1}H NMR signal at δ 6.43 (doublet). Such an assignment would allow the magnetic ring current of the phenyl substituent on the nitrogen to shield the neighboring aromatic hydrogen, causing its ^{1}H NMR signal to shift upfield to δ 6.43. On exposure to silica gel, **37** was converted to **32** in essentially quantitative yield.

It was reported that in equilibrium, the parent 2-aminopyridine predominates over the tautomeric isomer 2-pyridone imine.[20] Therefore, it was quite unexpected that **37** was produced in excellent yield. This serendipitous discovery could provide a unique pathway for easy access to a variety of highly labile 2-pyridone imines.

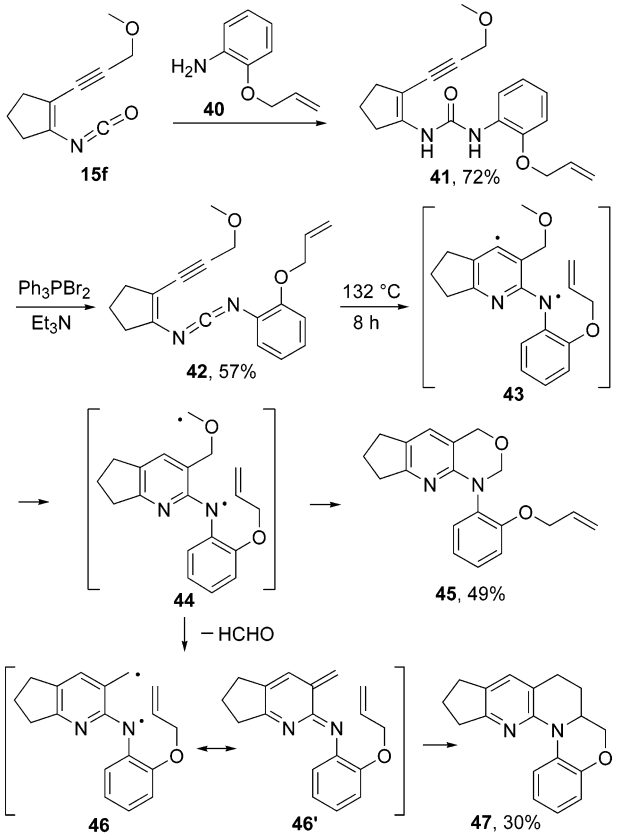
While it is difficult to exclude the possibility of hydrolysis of **36** and/or the corresponding demethylated adduct to form **37** due to the presence of trace amount of water during the period when the reaction mixture was allowed to cool to room temperature, it is hard to imagine that such a condition would not also induce the transformation of **37** to **32**. Hydrogen chloride would be generated from reaction between water and the excess dimethylphenylsilyl chloride, creating an acidic condition that should also convert **37** to **32**, as observed when **37** was passed through a silica gel column. One possible alternative is for the putative intermediate **36** to undergo a retro-ene reaction through a chairlike transition state as depicted in **38** (Scheme 9) to afford **37** directly during thermolysis with concomitant formation of 2-phenyl-2-silapropene (**39**). It was reported that such a retro-ene reaction took place with allyltrimethylsilane to produce propene and transient 2-methyl-2-silapropene, albeit at a much higher temperature (600 °C).[21] Clearly, additional studies will be needed to determine the exact reaction pathway and at what stage methyl chloride was eliminated from **36**.

SCHEME 9



The enyne−carbodiimide **42** was likewise synthesized by condensation of the isocyanate **15f** with the aniline **40**[22] followed by treatment of the resulting urea derivative **41** with dibromotriphenylphosphorane (Scheme 10).

SCHEME 10



It was anticipated that **44**, derived from **42** via a 1,5-hydrogen shift of the initially formed σ,π-biradical **43**, would have the propensity to lose a molecule of formaldehyde to form **46**, which could also be regarded as a pyridine analogue of *ortho*-quinone methide imine depicted in **46′**. It is worth noting that a similar fragmentation process was observed in several cases of the biradicals derived from enyne−ketenes.[7b,d] The isolation of **47** suggests that **46′** was indeed produced and then captured in an intramolecular hetero-Diels−Alder reaction. However, unlike the enyne−ketene system, the fragmentation process of **44** is relatively slow compared to the intramolecular radical−radical coupling pathway. As a result, **45** was produced predominantly.

Conclusions

Thermolysis of the enyne−carbodiimides **7** provides easy access to the σ,π-biradicals **8**, which also behave as the zwitterions **8′** under certain reaction conditions. The presence of two reactive centers in **8**/**8′** affords many opportunities for intramolecular decay, leading to a variety of heteroaromatic compounds. The reaction sequence outlined in Scheme 10 represents a novel pathway

(20) (a) Elguero, J.; Marzin, C.; Katritzky, A. R.; Linda, P. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1976; Suppl. 1, pp 153, 206. (b) Pietrzycki, W.; Sepioł, J.; Tomasik, P.; Brzózka, Ł. *Bull. Soc. Chim. Belg.* **1993**, *102*, 709−717. (c) Alkorta, I.; Elguero, J. *J. Org. Chem.* **2002**, *67*, 1515−1519.

(21) (a) Barton, T. J.; Burns, S. A.; Davidson, I. M. T.; Ijadi-Maghsoodi, S.; Wood, I. T. *J. Am. Chem. Soc.* **1984**, *106*, 6367−6372. (b) Dubac, J.; Laporterie, A. *Chem. Rev.* **1987**, *87*, 319−334.

(22) (a) Abbas, A. A.; Elwahy, A. H. M. *Synthesis* **2001**, 1331−1336. (b) Tiffany, B. D. *J. Am. Chem. Soc.* **1948**, *70*, 592−594.

to the pyridine analogues of *ortho*-quinone methide imine for the hetero-Diels−Alder reactions.

Experimental Section

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Triethylamine, aniline, and benzene were distilled over CaH_2 prior to use. 1-Pentyne, methyl propargyl ether, 4-phenyl-1-butyne, (trimethylsilyl)-acetylene, $Pd(PPh_3)_2Cl_2$, copper(I) iodide, *N*,*N*-diisopropylethylamine, sodium hydride, trifluoromethanesulfonic anhydride, diphenyl phosphorazidate (DPPA), dibromotriphenylphosphorane, sodium azide, triphenylphosphine, benzyl chloride, ethyl 2-oxocyclopetanecarboxylate (**10**), dimethylphenylsilyl chloride, *N*,*N*-dimethylformamide (DMF), chlorobenzene (anhydrous), 1,2-dichlorobenzene (anhydrous), 2-iodotoluene, 2-iodoanisole, and 2-iodoaniline were purchased from chemical suppliers and were used as received. (2-Methylphenyl)acetylene (**12a**) and 2-ethynylanisole (**12d**) were prepared from 2-iodotoluene and 2-iodoanisole, respectively, using the procedure described for **12e**. Ethyl 2-[[(trifluoromethyl)sulfonyl]oxy]-1-cyclopentene-1-carboxylate (**11**),[13] 2-aminophenyl allyl ether (**40**),[22] *N*,*N*-dimethyl-2-iodoaniline,[23] *N*-(triphenylphosphoranylidene)-benzenamine (**17**),[17] and *N*-(triphenylphosphoranylidene)-benzenemethanamine (**18**)[18] were prepared according to the reported procedures. Melting points are uncorrected. ^{1}H (270 MHz) and ^{13}C (67.9 MHz) NMR spectra were recorded in $CDCl_3$ using $CHCl_3$ (^{1}H δ 7.26) and $CDCl_3$ (^{13}C δ 77.00) as internal standards unless otherwise indicated.

Ethyl 2-[(2-Methylphenyl)ethynyl]-1-cyclopentenecarboxylate (13a). The following procedure is representative for the preparation of the esters **13**. To a mixture of the enol triflate **11** (4.324 g, 15.0 mmol), *N*,*N*-diisopropylethylamine (2.6 mL, 15.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.316 g, 0.45 mmol), and copper(I) iodide (0.143 g, 0.75 mmol) in 30 mL of DMF was added slowly a solution of (2-methylphenyl)acetylene (1.742 g, 15.0 mmol) in 5 mL of DMF. After 2 h of stirring at room temperature, 50 mL of a saturated aqueous ammonium chloride solution and 50 mL of diethyl ether were added. The organic layer was separated, and the aqueous layer was back-extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/5% diethyl ether in hexanes, R_f = 0.33) afforded 3.459 g of **13a** (13.6 mmol, 90% yield) as a yellow liquid: IR (neat) 2197, 1700, 757 cm^{-1}; ^{1}H NMR δ 7.47 (1 H, d, J = 7.5 Hz), 7.24−7.11 (3 H, m), 4.27 (2 H, q, J = 7.1 Hz), 2.76 (4 H, t, J = 7.7 Hz), 2.50 (3 H, s), 1.96 (2 H, quintet, J = 7.7 Hz), 1.32 (3 H, t, J = 7.1 Hz); ^{13}C NMR δ 164.5, 140.5, 137.4, 134.2, 132.1, 129.3, 128.7, 125.4, 122.7, 98.6, 89.4, 60.1, 39.4, 33.3, 22.1, 20.5, 14.3; MS *m*/*z* 254 (M$^+$), 239, 225, 208.

2-[(2-Methylphenyl)ethynyl]-1-cyclopentenecarboxylic Acid (14a). The following procedure is representative for the hydrolysis of the carboxylic esters **13** to the carboxylic acids **14**. A solution of 4.274 g of the ester **13a** (16.80 mmol) in 10 mL of THF and 60 mL of a 1 M aqueous sodium hydroxide solution was heated at 70 °C for 16 h. The reaction mixture was cooled in an ice−water bath and acidified with a dilute HCl solution. Filtration afforded 3.634 g of **14a** (16.06 mmol, 96% yield) as a white solid: mp 142−143 °C; IR (KBr) 3300−2500 (br), 2198, 1655, 759 cm^{-1}; ^{1}H NMR δ 12.15 (1 H, s br), 7.49 (1 H, d, J = 7.2 Hz), 7.28−7.12 (3 H, m), 2.81 (4 H, t, J = 7.4 Hz), 2.48 (3 H, s), 2.01 (2 H, quintet, J = 7.6 Hz); ^{13}C NMR δ 169.9, 141.0, 137.5, 136.8, 132.3, 129.5, 129.0, 125.5, 122.5, 100.5, 89.2, 39.6, 33.0, 22.2, 20.5; MS *m*/*z* 226 (M$^+$), 208, 197.

1-[(2-Isocyanato-1-cyclopentenyl)ethynyl]-2-methylbenzene (15a). The following procedure is representative for the preparation of the isocyanates **15** from the acids **14**. To a solution of 1.253 g of **14a** (5.5 mmol) in 40 mL of anhydrous benzene was added a solution of 0.83 mL of triethylamine (6.0 mmol) and 1.514 g of DPPA (5.5 mmol) in 5 mL of benzene. After 6 h of stirring at room temperature, the reaction mixture was then washed with brine and water, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/5% diethyl ether in hexanes, R_f = 0.72) afforded 1.117 g of **15a** (5.00 mmol, 91% yield) as a pale yellow solid: mp 63−65 °C; IR 2254, 2159, 757 cm^{-1}; ^{1}H NMR δ 7.48 (1 H, d, J = 7.3 Hz), 7.27−7.11 (3 H, m), 2.62 (2 H, tt, J = 7.3, 2.4 Hz), 2.52 (2 H, tt, J = 7.3, 2.4 Hz), 2.48 (3 H, s), 2.00 (2 H, quintet, J = 7.6 Hz); ^{13}C NMR δ 139.9, 136.6, 131.7, 129.4, 128.3, 127.4, 125.5, 122.7, 115.1, 96.3, 87.3, 34.6, 33.9, 21.0, 20.6; MS *m*/*z* 223 (M$^+$), 194, 167.

***N*-[2-[(2-Methylphenyl)ethynyl]-1-cyclopentenyl]-*N*′-phenylurea (16a).** The following procedure is representative for the preparation of the ureas **16** from the isocyanates **15**. A solution of 0.250 g of **15a** (1.12 mmol) and 0.115 g of aniline (1.23 mmol) in 5 mL of methylene chloride was stirred at room temperature for 8 h before 5 mL of hexanes was added. Filtration afforded 0.302 g of **16a** (0.954 mmol, 85% yield) as a white solid: mp 198−199 °C; IR (KBr) 3302, 2187, 1644 cm^{-1}; ^{1}H NMR δ (DMSO-d_6) 9.34 (1 H, s), 8.35 (1 H, s), 7.57 (1 H, d, J = 6.9 Hz), 7.50 (2 H, d, J = 7.9 Hz), 7.38−7.27 (5 H, m), 7.05 (1 H, t, J = 7.2 Hz), 3.09 (2 H, t, J = 7.2 Hz), 2.53 (2 H, t, J = 7.4 Hz), 1.98 (2 H, quintet, J = 7.3 Hz); ^{13}C NMR δ (DMSO-d_6) 151.3, 146.4, 139.4, 139.0, 131.3, 129.5, 128.8, 128.1, 125.8, 123.1, 122.0, 118.1, 96.6, 94.0, 89.1, 32.8, 32.4, 21.6, 20.5.

***N*-[2-[(2-Methylphenyl)ethynyl]-1-cyclopentenyl]-*N*′-phenylcarbodiimide (7a).** The following procedure is representative for the preparation of the carbodiimides **7** from the ureas **16**. To a solution of 0.241 g of dibromotriphenylphosphorane (0.57 mmol) and 0.115 g of triethylamine (1.14 mmol) in 10 mL of methylene chloride was added a suspension of 0.090 g of the urea **16a** (0.285 mmol) in 5 mL of methylene chloride over a period of 45 min. After 1 h of stirring at room temperature, the solvent was removed, and the residue was taken up with diethyl ether. The diethyl ether solution was concentrated, and the residue was purified by flash column chromatography (silica gel/5% diethyl ether in hexanes, R_f = 0.53) to afford 0.072 g of **7a** (0.241 mmol, 85% yield) as a yellow liquid: IR (neat) 2130, 1628, 1593 cm^{-1}; ^{1}H NMR δ 7.31−7.23 (3 H, m), 7.18−7.03 (6 H, m), 2.68−2.57 (4 H, m), 2.43 (3 H, s), 2.02 (2 H, quintet, J = 7.5 Hz); ^{13}C NMR δ 141.9, 139.9, 138.4, 134.9, 131.7, 129.3, 129.2, 128.1, 125.4, 125.3, 124.1, 123.0, 113.4, 95.8, 88.2, 34.8, 34.6, 21.2, 20.7.

***N*-[2-[(2-Methylphenyl)ethynyl]-1-cyclopentenyl]-*N*′-(phenylmethyl)carbodiimide (19).** To a solution of 0.492 g of *N*-(triphenylphosphoranylidene)benzylamine (**18**, 1.34 mmol) in 20 mL of methylene chloride at −78 °C was added slowly a solution of 0.276 g of **15a** (1.24 mmol) in 5 mL of methylene chloride. After the reaction mixture was allowed to warm to room temperature, the solvent was removed in vacuo, and the residue was purified by flash column chromatography (silica gel/5% diethyl ether in hexanes, R_f = 0.30) to afford 0.332 g of **19** (1.06 mmol, 86% yield) as a yellow liquid: IR (neat) 2124, 1626, 756 cm^{-1}; ^{1}H NMR δ 7.41 (1 H, d, J = 7.5 Hz), 7.37−7.28 (5 H, m), 7.18 (2 H, d, J = 3.8 Hz), 7.14−7.07 (1 H, m), 4.50 (2 H, s), 2.58 (2 H, tt, J = 7.3, 2.2 Hz), 2.44 (3 H, s), 2.42 (2 H, tt, J = 8.1, 2.0 Hz), 1.94 (2 H, quintet, J = 7.5 Hz); ^{13}C NMR δ 143.8, 139.9, 137.6, 137.2, 131.6, 129.3, 128.6, 128.0, 127.7, 127.3, 125.4, 123.3, 111.3, 95.0, 88.6, 50.6, 34.6, 34.5, 21.1, 20.8.

5,8,9,10-Tetrahydro-6-phenyl-6*H*-benzo[*f*]cyclopenta-[*b*][1,8]naphthyridine (21). A solution of 0.072 g of **7a** (0.241 mmol) in 5 mL of chlorobenzene was heated under reflux for 10 h. The solvent was then removed in vacuo. Purification of the residue by flash column chromatography (silica gel/20% diethyl ether in hexanes, R_f = 0.30) afforded 0.040 g of **21** (0.0134 mmol, 56% yield) as a yellow solid: IR 1593, 1417 cm^{-1}; ^{1}H NMR δ 7.85 (1 H, s), 7.72 (1 H, d, J = 7.5 Hz), 7.39−7.33 (5 H, m), 7.25 (1 H, td, J = 7.3, 1.1 Hz), 7.15 (1 H, d, J = 7.3

(23) Bunnett, J. F.; Mitchel, E.; Galli, C. *Tetrahedron* **1985**, *41*, 4119−4132.

Hz), 7.12−7.06 (1 H, m), 4.91 (2 H, s), 2.91 (2 H, t, J = 7.5 Hz), 2.85 (2 H, t, J = 7.7 Hz), 2.09 (2 H, quintet, J = 7.5 Hz); ^{13}C NMR δ 163.9, 153.9, 145.2, 132.1, 131.4, 128.9, 128.4, 127.7, 127.4, 127.2, 125.6, 123.0, 122.2, 116.2, 52.7, 34.4, 30.2, 23.3; MS m/z 298 (M^+), 297.

2,3,6,7-Tetrahydro-*N*-phenyl-1*H*-benzo[*f*]cyclopent[*c*]-isoquinolin-5-amine (28). The same procedure was repeated as described for **21** except that 0.132 g of **7c** (0.422 mmol) was used to afford 0.097 g of **28** (0.309 mmol, 73% yield) as a yellow solid: mp 83−85 °C; IR 3370, 1601, 1578 cm^{-1}; ^{1}H NMR δ 7.73 (1 H, dd, J = 6.2, 2.3 Hz), 7.38−7.21 (5 H, m), 7.16−7.12 (2 H, m), 6.91 (1 H, tt, J = 7.2, 1.2 Hz), 6.24 (1 H, s), 3.23 (2 H, t, J = 7.1 Hz), 3.00 (2 H, t, J = 7.5 Hz), 2.82−2.77 (2 H, m), 2.63−2.58 (2 H, m), 2.14 (2 H, quintet, J = 7.4 Hz); ^{13}C NMR δ 162.9, 151.3, 142.7, 140.2, 139.0, 133.4, 128.8, 128.4, 127.8, 127.0, 126.4, 126.2, 120.7, 117.8, 117.5, 34.2, 32.6, 28.9, 24.0, 23.4; MS m/z 312 (M^+), 311.

2,3-Dihydro-*N*-phenyl-1*H*-benzofuro[2,3-*d*]cyclopenta-[*b*]pyridin-5-amine (30). The same procedure was repeated as described for **21** except that 0.127 g of **7d** (0.40 mmol) was used to afford 0.052 g of **30** (0.172 mmol, 43% yield) as brown crystals: mp 174−175 °C; IR 3431, 1642, 1600 cm^{-1}; ^{1}H NMR δ 7.59 (1 H, d, J = 8.1 Hz), 7.51−7.45 (3 H, m), 7.41 (1 H, td, J = 7.8, 1.4 Hz), 7.35−7.27 (3 H, m), 7.02 (1 H, t, J = 7.3 Hz), 6.77 (1 H, s), 3.17 (2 H, t, J = 7.4 Hz), 3.10 (2 H, t, J = 7.9 Hz), 2.26 (2 H, quintet, J = 7.5 Hz); ^{13}C NMR δ 163.5, 159.8, 155.2, 149.9, 141.0, 129.1, 126.0, 123.3, 122.1, 121.9, 121.0, 118.7, 112.9, 111.4, 105.9, 34.9, 27.1, 23.2; MS m/z 300 (M^+), 299. The structure of **30** was established by X-ray structure analysis.

1,2,3,10-Tetrahydro-10-methyl-*N*-phenylcyclopenta-[1′,2′:5,6]pyrido[4,3-*b*]indol-5-amine (32), 2-(1,2,3,4-Tetrahydrocyclopenta[1′,2′:4,5]pyrrolo[2,3-*b*]quinolin-10-yl)-*N*,*N*-dimethylbenzenamine (34), and 2-(1,2,3,4-Tetrahydro-4-methylcyclopenta[1′,2′:4,5]pyrrolo[2,3-*b*]quinolin-10-yl)-*N*,*N*-dimethylbenzenamine (35). The same procedure was repeated as described for **21** except that 0.073 g of **7e** (0.22 mmol) was used to afford 0.010 g of **32** (0.03 mmol, 14% yield) as a brown solid, 0.035 g of **34** (0.107 mmol, 48%) as brown crystals, and 0.005 g of **35** (0.015 mmol, 7%) as a brown solid. Compound **32**: mp 177−178 °C; IR 3460, 1601, 1574 cm^{-1}; ^{1}H NMR δ 7.78 (1 H, d, J = 7.7 Hz), 7.55 (2 H, d, J = 7.7 Hz), 7.48−7.39 (2 H, m), 7.34−7.23 (3 H, m), 6.97 (1 H, t, J = 7.3 Hz), 6.87 (1 H, s br), 4.01 (3 H, s), 3.41 (2 H, t, J = 7.3 Hz), 3.09 (2 H, t, J = 7.7 Hz), 2.26 (2 H, quintet, J = 7.5 Hz); ^{13}C NMR δ 159.5, 149.6, 144.6, 141.4, 140.3, 129.0, 124.6, 121.5, 121.2, 120.8, 120.3, 118.6, 110.7, 108.6, 104.5, 34.1, 30.8, 29.5, 23.1; MS m/z 313 (M^+), 312. **Compound 34:** mp 260−261 °C dec; IR 3149, 758, 732 cm^{-1}; ^{1}H NMR δ 11.8 (1 H, s br), 8.11 (1 H, d, J = 8.2 Hz), 7.82 (1 H, dd, J = 8.5, 1.4 Hz), 7.62 (1 H, ddd, J = 8.5, 6.9, 1.5 Hz), 7.43 (1 H, ddd, J = 8.4, 7.2, 1.7 Hz), 7.33 (1 H, ddd, J = 8.3, 6.9, 1.1 Hz), 7.22 (1 H, dd, J = 7.4, 1.7 Hz), 7.14 (1 H, d, J = 8.2 Hz), 7.05 (1 H, td, J = 7.3, 1.0 Hz), 3.14−3.07 (2 H, m), 2.49−2.37 (10 H, m); ^{13}C NMR δ 154.6, 152.4, 148.7, 143.2, 138.2, 132.9, 128.9, 128.4, 127.1, 126.6, 126.4, 122.9, 122.6, 120.1, 119.1, 117.1, 43.2, 27.6, 26.8, 25.4; MS m/z 327 (M^+), 312, 298. **Compound 35:** mp 130−131 °C; IR 1594, 1446, 758 cm^{-1}; ^{1}H NMR δ 8.15 (1 H, d, J = 8.5 Hz), 7.77 (1 H, dd, J = 8.5, 1.2 Hz), 7.58 (1 H, ddd, J = 8.4, 6.8, 1.4 Hz), 7.40 (1 H, ddd, J = 8.4, 7.2, 1.7 Hz), 7.29 (1 H, ddd, J = 8.5, 7.0, 1.2 Hz), 7.18 (1 H, dd, J = 7.5, 1.8 Hz), 7.12 (1 H, d, J = 7.5 Hz), 7.02 (1 H, td, J = 7.4, 1.1 Hz), 3.90 (3 H, m), 2.98−2.91 (2 H, m), 2.44−2.33 (4 H, m), 2.41 (6 H, s); ^{13}C NMR δ 153.4, 152.4, 150.7, 144.0, 137.6, 132.9, 128.74, 128.68, 127.6, 126.7, 126.4, 122.8, 122.4, 120.1, 118.3, 117.0, 115.0, 43.1, 29.6, 27.0, 25.65, 25.61; MS m/z 341 (M^+), 326, 312. The structures of **32** and **34** were established by X-ray structure analysis.

A solution of **7e** (0.112 g, 0.342 mmol) and dimethylphenylsilyl chloride (0.070 g, 0.41 mmol) in 10 mL of chlorobenzene was heated under reflux at 132 °C for 3 h. After the reaction mixture was allowed to cool to room temperature, the solvent was removed in vacuo. The residue was purified by flash column chromatography (silica gel) to afford 0.075 g of **32** (0.24 mmol, 70%) and 0.016 g of **34** (0.049 mmol, 14%).

2-Pyridone Imine 37. A solution of 0.0722 g of **7e** (0.22 mmol) and 0.188 g of dimethylphenylsilyl chloride (1.1 mmol) in 8 mL of chlorobenzene was heated under reflux at 132 °C for 3 h. A yellow solid appeared as the reaction mixture was allowed to cool to room temperature. Suction filtration gave 0.0593 g of **37** (0.189 mmol, 86%) as a yellow solid: mp 268−270 °C dec without melting; IR (KBr) 3418, 1634, 756 cm^{-1}; ^{1}H NMR δ 10.02 (1 H, s), 7.43 (2 H, d, J = 3.8 Hz), 7.25 (2 H, t, J = 7.5 Hz), 7.14 (1 H, t, J = 7.4 Hz), 7.05−6.94 (3 H, m), 6.43 (1 H, d, J = 8.1 Hz), 4.09 (3 H, s), 3.46 (2 H, t, J = 7.3 Hz), 3.32 (2 H, t, J = 7.8 Hz), 2.40 (2 H, quintet, J = 7.6 Hz); ^{13}C NMR δ 149.1, 146.4, 146.3, 140.6, 138.7, 129.4, 126.5, 124.9, 124.7, 122.0, 121.5, 120.5, 112.8, 109.2, 105.0, 31.3, 30.7, 29.8, 23.1; MS m/z 313 (M^+), 312.

To a solution of 8.2 mg of **37** in 4 mL of methylene chloride was added a small amount of silica gel. After 5 h, silica gel was removed by filtration, and the filtrate was pumped to dryness in vacuo to give 8.0 mg of **32** (98%). The ^{1}H NMR spectrum indicates that the product was essentially pure without the need for further purification.

1,2,4,6,7,8-Hexahydro-1-[2-(2-propenyloxy)phenyl]-cyclopenta[1′,2′:5,6]pyrido[2,3-*d*][1,3]oxazine (45) and 6a,7,8,10,11,12-Hexahydro-6*H*-cyclopenta[1′,2′:6,7][1,8]-naphthyridino[2,1-*c*][1,4]benzoxazine (47). A solution of 0.086 g of **42** (0.278 mmol) in 10 mL of chlorobenzene was heated under reflux for 8 h. The solvent was then removed in vacuo. The residue was purified by flash column chromatography to afford 0.042 g of **45** (0.136 mmol, 49% yield) as a light yellow oil and 0.023 g of **47** (0.083 mmol, 30% yield) as a pale yellow oil. **Compound 45:** IR 1608, 1573, 1425 cm^{-1}; ^{1}H NMR δ 7.19 (1 H, dd, J = 8.2, 1.5 Hz), 7.16−7.09 (1 H, m), 7.08 (1 H, s), 6.96−6.90 (2 H, m), 5.93 (1 H, ddt, J = 17.2, 10.5, 5.3 Hz), 5.29 (1 H, dq, J = 17.3, 1.6 Hz), 5.17 (1 H, dq, J = 10.6, 1.4 Hz), 5.06 (2 H, s), 4.91 (2 H, s), 4.52 (2 H, dt, J = 5.0, 1.6 Hz), 2.82 (2 H, t, J = 7.3 Hz), 2.80 (2 H, t, J = 7.5 Hz), 2.03 (2 H, quintet, J = 7.5 Hz); ^{13}C NMR δ 162.7, 153.4, 152.3, 134.2, 133.3, 128.9, 128.2, 127.7, 126.0, 121.1, 116.8, 115.0, 113.9, 81.8, 69.1, 67.7, 34.2, 30.0, 23.2; MS m/z 308 (M^+), 293, 277. **Compound 47:** IR 1571, 1494, 1420 cm^{-1}; ^{1}H NMR δ 7.98−7.91 (1 H, m), 7.16 (1 H, s), 6.90−6.82 (3 H, m), 4.44 (1 H, dd, J = 10.2, 1.9 Hz), 3.95 (1 H, t, J = 9.8 Hz), 3.87−3.76 (1 H, m), 2.92 (2 H, t, J = 7.2 Hz), 2.82 (2 H, t, J = 7.3 Hz), 2.72 (2 H, tt, J = 15.2, 3.9 Hz), 2.28−2.19 (1 H, m), 2.08 (2 H, quintet, J = 7.5 Hz), 1.46 (1 H, qd, J = 12.3, 4.8 Hz); ^{13}C NMR δ 161.2, 151.1, 145.9, 132.3, 128.2, 127.7, 122.2, 121.2, 120.0, 118.8, 116.9, 70.3, 53.3, 34.2, 30.1, 26.3, 25.1, 23.3; MS m/z 278 (M^+), 277.

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Supporting Information Available: Experimental procedures and spectroscopic data for *N*,*N*-dimethyl-2-[(trimethylsilyl)ethynyl]aniline, **7b**−**e**, **12e**, **13b**−**f**, **14b**−**f**, **15b**−**f**, **16b**−**e**, **24**−**26**, **41**, and **42**; ^{1}H and ^{13}C NMR spectra for *N*,*N*-dimethyl-2-[(trimethylsilyl)ethynyl]aniline, **7a**−**e**, **12e**, **13a**−**f**, **14a**−**f**, **15a**−**f**, **16a**−**e**, **19**, **21**, **22**, **24**−**26**, **28**, **30**, **32**, **34**, **35**, **37**, **41**, **42**, **45**, and **47**; and ORTEP drawings and tables of crystallographic data for the X-ray diffraction analyses of **30**, **32**, and **34**. This material is available free of charge via the Internet at http://pubs.acs.org.

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