Synthesis of Substituted Pyridine Derivatives via the Ruthenium–Catalyzed Cycloisomerization of 3-Azadienynes

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Supporting Information

General Procedures. All reactions were performed in oven-dried or flame-dried round bottomed flasks, modified Schlenk (Kjeldahl shape) flasks, or glass pressure vessels. The flasks were fitted with rubber septa and reactions were conducted under a positive pressure of argon. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Flash column chromatography was performed as described by Still et al. using silica gel (60–Å pore size, 32–63 µm, standard grade, Sorbent Technologies) or non-activated alumina gel (80–325 mesh, chromatographic grade, EM Science).¹ Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel or neutral alumina gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light and/or by exposure to an ethanolic phosphomolybdic acid (PMA), an acidic solution of *p*-anisaldehyde (anis), an aqueous solution of ceric ammonium molybdate (CAM), an aqueous solution of potassium permanganate (KMnO₄) or an ethanolic solution of ninhydrin followed by heating (<1 min) on a hot plate (~250 °C). Organic solutions were concentrated on Büchi R-200 rotary evaporators at ~10 Torr (house vacuum) at 25–35 °C, then at ~0.5 Torr (vacuum pump) unless otherwise indicated.

Materials. Commercial reagents and solvents were used as received with the following exceptions: Dichloromethane, diethyl ether, tetrahydrofuran, acetonitrile, and toluene were purchased from J.T. Baker (CycletainerTM) and were purified by the method of Grubbs et al. under positive argon pressure.² Ammonium hexafluorophosphate was dried at 150 °C under vacuum (~0.5 torr) for 24 h and stored in a glove box under an atmosphere of dinitrogen. The molarity of *n*-butyllithium solutions was determined by titration using diphenylacetic acid as an indicator (average of three determinations).³ Hünig's base and 2-chloropyridine were distilled from calcium hydride and stored sealed under an argon atmosphere. The starting amides were prepared by acylation of the corresponding anilines⁴ or via previously reported copper–catalyzed C–N bond-forming reactions.^{5,6} The ruthenium complex **5** (CpRu(PPh₃)₂Cl) is commercially available and was prepared on large scale

¹ Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

² Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

³ Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879–1880.

⁴ For a general procedure, see: DeRuiter, J.; Swearingen, B. E.; Wandrekar, V.; Mayfield, C. A. *J. Med. Chem.* **1989**, *32*, 1033–1038.

⁵ For the general procedure used for the synthesis of all *N*-vinyl amides, see: Jiang, L.; Job, G. E.; Klapars, A.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 3667–3669.

⁶ For related reports, see: (a) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805–818. (b) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852–860. (c) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046–2067. (d) Yang, B. H.; Buchwald, S. L. *J. Organomet. Chem.* **1999**, *576*, 125–146. (e) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131–209. (f) Beletskaya, I. P.; Cheprakov, A. V. *Coordin. Chem. Rev.* **2004**, *248*, 2337–2364. (g) Dehli, J. R.; Legros, J.; Bolm, C. *Chem. Commun.* **2005**, 973–986.

according to a literature procedure.⁷ 2-Dicyclohexyl-phosphino-2',6'-dimethoxy-1,1'-biphenyl (SPhos)⁸ is commercially available and we thank the Buchwald group for providing samples for initial studies. Solutions of Copper (I) (trimethylsilyl)-acetylide were prepared immediately prior to use according to literature procedure.⁹

Instrumentation. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded with a Varian inverse probe 500 INOVA spectrometer. Chemical shifts are recorded in parts per million from internal tetramethylsilane on the δ scale and are referenced from the residual protium in the NMR solvent (CHCl₃: δ 7.27, C₆HD₅: δ 7.16). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constant(s) in Hertz, integration, assignment]. Carbon-13 nuclear magnetic resonance spectra were recorded with a Varian 500 INOVA spectrometer and are recorded in parts per million from internal tetramethylsilane on the δ scale and are referenced from the carbon resonances of the solvent (CDCl₃: δ 77.2, benzene-*d*₆: δ 128.0). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constant(s) in Hertz, assignment]. Infrared data were obtained with a Perkin-Elmer 2000 FTIR and are reported as follows: [frequency of absorption (cm⁻¹), intensity of absorption (s = strong, m = medium, w = weak, br = broad), assignment]. Combustion analysis was performed by Atlantic Microlab, Incorporated. We are grateful to Dr. Li Li for obtaining the mass spectroscopic data at the Department of Chemistry's Instrumentation Facility, Massachusetts Institute of Technology.

⁷ (a) Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R. C. *Inorganic Syntheses* **1982**, 21, 78–83. Also, see: (b) Gilbert, J. D.; Wilkinson, G. *J. Chem. Soc. (A)* **1969**, 1749, (c) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. (A)* **1971**, 2376, and (d) Bruce, M. I.; Windsor, N. J., *Aust. J. Chem.* **1977**, 30, 1601.

⁸ (a) Walker, S. D.; Barder, T. E.; Martinelli, J. R.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2004**, 43, 1871. (b) Tomori, H.; Fox, J. M.; Buchwald, S. L. *J. Org. Chem.* **2000**, 65, 5334–5341.

⁹ Enda, J.; Kuwajima, I. *J. Am. Chem. Soc.* **1985**, 107, 5495–5501.

Supplementary notes on the single-step conversion of amides to the corresponding alkynyl imines:

- The choice of 2-chloropyridine as the base additive was particularly effective as the use of 2,6-lutidine, Et₃N, and ^tPr₂NEt, in place of 2-chloropyridine under identical conditions (4.0 equiv of base) gave markedly diminished yield of the desired alkynyl imine **3a** (Table S1).
- The use of 300-mol% of 2-chloropyridine gave satisfactory results (92% isolated yield of product **3a**), while further decrease in the amount of 2-chloropyridine led to significantly lower yield of product **3a** (i.e., Table S1, entry 7).
- The optimal solvent for activation of amides was found to be dichloromethane as compared to other solvents examined (i.e., diethyl ether, tetrahydrofuran, ^tbutyl methyl ether, toluene, acetonitrile, nitromethane, 1,2-dichloroethane).
- The use of copper acetylide provided the highest yield of the desired product as compared to the use of lithium acetylide, bromomagnesium acetylide, dichlorocerium acetylide, or cuprate derivatives under identical conditions. Approaches based on Sonogashira coupling after activation as described above provided the product **3a** in poor yield (<50%) and were not compatible with sensitive substrates (text ref. 8).
- With the exception of alkynyl imine in entry 15 of Table 1, all alkynyl imines described below could be stored for weeks under an argon atmosphere at 0 °C.
- A uniform and optimized set of conditions was used for all entries discussed in the text; please see experimental procedures for details.

Table S1.

Entry	Base Additive	x	Yield (%) ^a
1	pyridine	4	<10
2	2,6-lutidine	4	27
3	Et ₃ N	4	<4 ^b
4	^t Pr ₂ NEt	4	<20
5	2-chloropyridine	4	97
6	2-chloropyridine	3	92
7	2-chloropyridine	2	65

^aMass balance is the starting amide. ^bMixture of products; no recovered SM.

Supplementary notes on the metal catalyzed cycloisomerization of alkynyl imines:

- The combination of commercially available CpRu(PPh₃)₂Cl (10 mol%) and SPhos (10 mol%) in the presence of a stoichiometric quantity of ammonium hexafluorophosphate (1.0 equiv) provided a highly effective catalyst system for the clean desilylation and cycloisomerization of alkynyl imines (Tables S2 and 1).
- The use of other additives in place of ammonium hexafluorophosphate (i.e., trifluoroethanol, ⁱpropanol, ⁱpropanol-F₆, ^tbutanol, ammonium tetrafluoroborate, tetrabutylammonium fluoride, triethylamine trihydrogen-fluoride, and potassium fluoride) was found to be markedly less effective in providing cycloisomerization product **1a** (Table 1, entry 1).
- Lower catalyst loadings resulted in slower conversion of starting alkynyl imine to the corresponding azaheterocycle (i.e., entry 39, Table S2).
- Attempted crystallization or direct spectroscopic detection of a CpRu-SPhos derived complex under a variety of conditions has not been successful thus far.
- The cycloisomerization of the C-desilylated alkynyl imine **3a** under the optimized conditions was more rapid, but gave poor mass balance. The desilylation and cycloisomerization of alkynyl imine **3a** required at least 7 h. Complete conversion within 19 h was observed for all entries in Table 1.

Table S2.

Entry	Precatalyst	Phosphine	x	Yield (%) ^a
1	InBr ₃	-	-	0
2	In(OTf) ₃	-	-	0
3	Sc(OTf) ₃	-	-	0
4	Pd(OAc) ₂	-	-	<3
5	Pd(OAc) ₂	-	-	<6 ^b
6	Pd(OAc) ₂	-	-	<4 ^c
7	Pd(OAc) ₂	DPhos	10	0
8	Pd(OAc) ₂	XPhos	10	<4
9	Pd(OAc) ₂	SPhos	10	<3
10	K ₂ PtCl ₄	-	-	0
11	K ₂ PtCl ₄	-	-	0 ^b
12	(RhCl(COD)) ₂	-	-	0
13	RhCl(Ph ₃ P) ₂ CO	-	-	0
14	[Ru(<i>p</i> -cymene)Cl ₂] ₂	-	-	<2
15	CpRu(dppf)Cl	-	-	0
16	CpRu(EtO) ₃ P] ₂ Cl	-	-	<2
17	CpRu[(<i>p</i> -MeOC ₆ H ₄) ₃ P] ₂ Cl	-	-	36
18	CpRu(Me ₃ P) ₂ Cl	-	-	<1 ^d
19	CpRu(Me ₃ P) ₂ Cl	DPhos	10	≤10 ^d
20	CpRu(Me ₃ P) ₂ Cl	XPhos	10	19
21	CpRu(Me ₃ P) ₂ Cl	SPhos	10	19
22	[Ru(COD)Cl ₂] _n	-	-	0
23	[Ru(COD)Cl ₂] _n	SPhos	10	0
24	CpRu(COD)Cl	-	-	0
25	CpRu(COD)Cl	SPhos	10	<6
26	CpRu(COD)Cl	SPhos	20	<9
27	CpRu(COD)Cl	Ph ₃ P	10	38
28	CpRu(COD)Cl	Ph ₃ P	15	62
29	CpRu(COD)Cl	Ph ₃ P	20	77
30	CpRu(COD)Cl	(2-furyl) ₃ P	15	36
31	CpRu(COD)Cl	(2-furyl) ₃ P, Ph ₃ P	10, 10	67
32	CpRu(COD)Cl	(2-furyl) ₃ P, SPhos	10, 10	54
33	CpRu(COD)Cl	Ph ₃ P, SPhos	13, 13	88
34	CpRu(COD)Cl	Ph₃P, SPhos	15, 15	97
35	CpRu(Ph ₃ P) ₂ Cl	-	-	80
36	CpRu(Ph ₃ P) ₂ Cl	DPhos	10	30
37	CpRu(Ph ₃ P) ₂ Cl	XPhos	10	74
38	CpRu(Ph₃P)₂Cl	SPhos	10	95
39	CpRu(Ph ₃ P) ₂ Cl	SPhos	5	56
40	CpRu(Ph ₃ P) ₂ Cl	Ph ₃ P	10	80
41	CpRu(Ph ₃ P) ₂ Cl	Ph ₃ P	20	81
42	CpRu(Ph ₃ P) ₂ Cl	(2-furyl) ₃ P	10	76

^aMass balance is the starting silylated alkynyl imine **3a**. ^b2.2 mol% TFA additive. ^c10 mol% AgOAc additive. ^dSame result at 75 °C. ^e5 mol% Ru-complex.

Structures of DPhos, XPhos, and SPhos are shown in Figure S1.⁸

- To evaluate a potential loss of catalyst activity due to trace Cu-contamination from the imine synthesis step, necessitating the use of 10 mol% Ru-catalyst, an experiment based on the standard conditions (Table 1, entry 1) was conducted containing additional CuBr•SMe₂ (5 mol%). No change was observed and complete conversion was seen within the normal 7 h period for this substrate affording the product **1a** in 90% yield.
- When the conversion of **3a** to **1a** was conducted with 100 mol% of product **1a** present at the start of the experiment (under optimal conditions; i.e., Table 1, entry 1) the conversion to **1a** was not complete even after 22 h (typically complete in 7 h for **3a**) providing **1a** in 79% yield with the remaining substrate **3a** accounting for the mass balance.
- Due to ready availability of both precatalyst and ligand, a uniform and optimum set of conditions using 10 mol% of each was used for all entries (except entry 16) in Table 1.

Supplementary notes on the deuterium labeling experiments:

- The use of ammonium hexafluorophosphate-*d*₄ (>95%, 1.0 equiv) under optimal conditions for cycloisomerization of alkynyl imine **3a** (1 equiv) provided the corresponding quinoline **1a-d**₁ in 89% yield with 68% *d*-incorporation at C3 and 7% *d*-incorporation at C4 (Scheme S1).
- Similarly, the cycloisomerization of alkynyl imine **3a-d**₅ (98%, 1 equiv) in the presence of ammonium hexafluorophosphate (1.0 equiv) afforded the corresponding quinoline **1a-d**₅ in 76% yield with 2% *d*-incorporation at C3 and 68% *d*-incorporation at C4 (Scheme S1).
- Additionally, C-desilylation of alkynyl imine **3a** and complete deuterium incorporation at the terminal alkyne gave the azadienyne derivative **4a-d**₁ (>95%) that was converted to the quinoline **1a-d**₁ in 52% yield with 72% *d*-incorporation at C3 and 7% *d*-incorporation at C4 without the need for ammonium hexafluorophosphate (Scheme S1). As anticipated the conversion of alkynyl imine **4a-d**₁ to the desired product was significantly faster as compared to C-silylated alkynyl imine **3a** at the expense of poor mass recovery and lower yield.

Scheme S1.

- The results are most consistent with the intermediacy of a ruthenium vinylidene **8** (Scheme 3) prior to cycloisomerization step. Incomplete deuterium incorporation at the expected site and leakage to the alternate position (2-7%, Scheme S1) may in part be due to an intermolecular scrambling after cycloisomerization of **8** and prior to release of product **1** (i.e., the intermediate **9** or the metal hydride tautomer in Scheme 3).

N-Phenyl-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne (3a, Table 1, entry 1):

Trifluoromethanesulfonic anhydride (2.51 mL, 15.2 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2a** (2.50 g, 12.7 mmol, 1 equiv) and 2-chloropyridine (4.81 mL, 50.7 mmol, 4.00 equiv) in CH₂Cl₂ (25 mL) at –78 °C. After 5 min, the reaction mixture was warmed to 0 °C. After 20 min, the solution was cooled to –78 °C and a freshly prepared solution of copper (I) (trimethylsilyl)-acetylide (5.50 g, 34.2 mmol, 2.70 equiv) in THF (60 mL) at 0 °C was added via cannula. The reaction mixture was kept at –78 °C for 5 min and then warmed to 0 °C. After 10 min, the crude reaction mixture was filtered through celite (2 cm diam. × 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes→7% EtOAc/hexanes) to give the alkynyl imine **3a**¹⁰ as a yellow oil (3.42 g, 97%).

¹H NMR (500 MHz, CDCl₃, 20 °C) δ: 8.21–8.18 (m, 2H, ArH (*o*-C=N)), 7.51–7.45 (m, 3H, ArH), 7.40–7.36 (m, 2H, ArH), 7.17 (tt, 1H, *J* = 7.5, 1.1 Hz, ArH), 7.14–7.11 (m, 2H, ArH), 0.14 (s, 9H, Si(CH₃)₃).

¹³C NMR (125 MHz, CDCl₃, 20 °C) δ: 151.7, 150.1, 137.0, 131.4, 128.6, 128.5, 128.3, 125.0, 120.9, 105.4, 97.5, –0.5.

FTIR (neat) cm^{–1}: 3063 (m), 3030 (w), 2960 (m), 1588 (s, C=N), 1565 (s).

HRMS (ESI): calcd for C₁₈H₂₀NSi [M+H]⁺: 278.1360, found: 278.1365.

Analysis: calcd for C₁₈H₁₉NSi: C, 77.93; H, 6.90; N, 5.05, found: C, 77.97; H, 6.87; N, 5.10.

TLC (20% EtOAc/hexanes), R_f: 0.59 (UV, CAM).

¹⁰ For a prior synthesis (characterization data not listed), see: Ito, Y.; Inouye, M.; Murakami, M. *Chem. Lett.* **1989**, 7, 1261–1264.

2-Phenylquinoline (1a, Table 1, entry 1):

An oven dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (587 mg, 3.60 mmol, 1.00 equiv), $\text{CpRuCl}(\text{PPh}_3)_2$ (262 mg, 0.35 mmol, 0.10 equiv) and SPhos (148 mg, 0.35 mmol, 0.10 equiv) under a nitrogen atmosphere in a glove-box and the flask sealed and brought out of the glove-box. Imine **3a** (1.00 g, 3.60 mmol, 1 equiv) and toluene (18 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105°C . After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 20-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (15→50 % EtOAc/Hexanes) to afford the quinoline **1a**¹¹ as a pale yellow solid (668 mg, 90%).

^1H NMR (500 MHz, CDCl_3 , 20°C) δ : 8.25 (d, 1H, $J = 8.5$ Hz, ArH), 8.21–8.16 (m, 3H, ArH), 7.90 (d, 1H, $J = 8.5$ Hz, ArH), 7.85 (d, 1H, $J = 8.2$ Hz, ArH), 7.75 (ddd, 1H, $J = 8.5, 7.0, 1.5$ Hz, ArH), 7.57–7.52 (m, 3H, ArH), 7.48 (tt, 1H, $J = 7.3, 1.2$ Hz, ArH).

^{13}C NMR (125 MHz, CDCl_3 , 20°C) δ : 157.5, 148.4, 139.8, 137.0, 129.9, 129.9, 129.5, 129.0, 127.8, 127.7, 127.3, 126.5, 119.2.

FTIR (neat) cm^{-1} : 3189 (s), 3055 (w), 2091 (s), 1617 (w), 1597 (s), 1491 (m), 1447 (s).

HRMS (EI): calcd for $\text{C}_{15}\text{H}_{11}\text{N}$ $[\text{M}]^+$: 205.0886, found: 205.0885.

TLC (20% EtOAc–hexanes), Rf: 0.51 (UV, CAM).

¹¹ Sangu, K.; Fuchibe, K.; Akiyama, T. *Org. Lett.* **2004**, *6*, 353–355.

N-(4-Methoxyphenyl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne (3b, Table 1, entry 2):

Trifluoromethanesulfonic anhydride (174 μ L, 1.06 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2b** (200 mg, 0.88 mmol, 1 equiv) and 2-chloropyridine (333 μ L, 3.52 mmol, 4.00 equiv) in CH_2Cl_2 (1.8 mL) at -78°C . After 5 min, the reaction mixture was warmed to 0°C . After 20 min, the solution was cooled to -78°C and a freshly prepared solution of copper (I) (trimethylsilyl)-acetylide (383 mg, 2.38 mmol, 2.70 equiv) in THF (5.0 mL) at 0°C was added via cannula. The reaction mixture was kept at -78°C for 5 min and then warmed to 0°C . After 10 min, the crude reaction mixture was filtered through celite (2 cm diam. $\times$ 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes $\rightarrow$ 10% EtOAc/hexanes) to afford the alkynyl imine **3b** as a yellow oil (240 mg, 89%).

^1H NMR (500 MHz, CDCl_3 , 20°C) δ : 8.21–8.15 (m, 2H, ArH (*o*-C=N)), 7.50–7.42 (m, 3H, ArH (*m*-C=N, *p*-C=N)), 7.31–7.25 (m, 2H, ArH), 6.96–6.90 (m, 2H, ArH), 3.83 (s, 3H, CH_3O), 0.21 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

^{13}C NMR (125 MHz, CDCl_3 , 20°C) δ : 157.7, 148.1, 144.2, 137.6, 131.0, 128.5, 128.1, 123.3, 113.7, 104.8, 98.1, 55.6, -0.4 .

FTIR (CDCl_3) cm^{-1} : 3066 (w), 2962 (m), 2838 (w), 1605 (m, C=N), 1559 (m), 1503 (s), 1251 (s).

HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{22}\text{NOSi}$ $[\text{M}+\text{H}]^+$: 308.1465, found: 308.1472.

TLC (20% EtOAc/hexanes), Rf: 0.49 (UV, CAM).

6-Methoxy-2-phenylquinoline (1b**, Table 1, entry 2):**

An oven dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (40 mg, 0.24 mmol, 1.0 equiv), $\text{CpRuCl}(\text{PPh}_3)_2$ (18 mg, 0.024 mmol, 0.10 equiv) and SPhos (10 mg, 0.024 mmol, 0.10 equiv) under a nitrogen atmosphere in a glove-box and the flask sealed and brought out of the glove-box. Imine **3b** (75 mg, 0.24 mmol, 1 equiv) and toluene (1.2 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at $105\text{ }^\circ\text{C}$. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (20 % EtOAc/Hexanes) to afford the quinoline **1b**¹¹ as a pale yellow solid (52 mg, 91%).

^1H NMR (500 MHz, CDCl_3 , $20\text{ }^\circ\text{C}$) δ : 8.16–8.10 (m, 3H, ArH), 8.08 (d, 1H, $J = 9.2\text{ Hz}$, ArH), 7.85 (d, 1H, $J = 8.9\text{ Hz}$, ArH), 7.56–7.50 (m, 2H, ArH), 7.48–7.42 (m, 1H, ArH), 7.40 (dd, 1H, $J = 9.2, 2.7\text{ Hz}$, ArH (CH_3OCCH)), 7.11 (d, 1H, $J = 3.1\text{ Hz}$, ArH(CH_3OCCH)), 3.99 (s, 3H, CH_3O).

^{13}C NMR (125 MHz, CDCl_3 , $20\text{ }^\circ\text{C}$) δ : 157.8, 155.2, 144.5, 139.9, 135.7, 131.3, 129.1, 129.0, 128.3, 127.5, 122.5, 119.4, 105.1, 55.7.

FTIR (neat) cm^{-1} : 3057 (w), 2958 (m), 2836 (w), 1621 (m), 1599 (m), 1493 (s).

HRMS (EI): calcd for $\text{C}_{16}\text{H}_{13}\text{NO}$ $[\text{M}]^+$: 235.0992, found: 235.0984.

TLC (20% EtOAc–hexanes), Rf: 0.39 (UV, CAM).

N-(2-Methoxyphenyl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne (3c, Table 1, entry 3):

Trifluoromethanesulfonic anhydride (218 μL , 1.32 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2c** (250 mg, 1.10 mmol, 1 equiv) and 2-chloropyridine (416 μL , 4.40 mmol, 4.00 equiv) in CH_2Cl_2 (2.2 mL) at -78°C . After 5 min, the reaction mixture was warmed to 0°C . After 20 min, the solution was cooled to -78°C and a freshly prepared solution of copper (I) (trimethylsilyl)-acetylide (477 mg, 2.97 mmol, 2.70 equiv) in THF (5.0 mL) at 0°C was added via cannula. The reaction mixture was kept at -78°C for 5 min and then warmed to 0°C . After 10 min, the crude reaction mixture was filtered through celite (2 cm diam. $\times$ 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes $\rightarrow$ 10% EtOAc/hexanes) to afford the alkynyl imine **3c** as a yellow oil (326 mg, 97%).

^1H NMR (500 MHz, CDCl_3 , 20°C) δ : 8.24–8.20 (m, 2H, ArH (*o*-C=N)), 7.52–7.44 (m, 3H, ArH (*p*-C=N, *m*-C=N)), 7.14 (ddd, 1H, $J = 8.3, 7.3, 1.8$ Hz, ArH), 7.01 (dd, 1H, $J = 7.6, 2.1$ Hz, ArH), 6.98–6.94 (m, 2H, ArH), 3.85 (s, 3H, OCH_3), 0.11 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

^{13}C NMR (125 MHz, CDCl_3 , 20°C) δ : 151.6, 150.5, 141.5, 136.8, 131.3, 128.4, 128.4, 125.7, 120.8, 120.5, 111.5, 104.9, 97.7, 55.9, -0.5 .

FTIR (neat) cm^{-1} : 3064 (w), 2959 (m), 2900 (w), 2834 (w), 1590 (s), 1567 (s), 1488 (s).

HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{22}\text{NOSi}$ $[\text{M}+\text{H}]^+$: 308.1465, found: 308.1477.

TLC (20% EtOAc/hexanes), Rf: 0.49 (UV, KMnO_4).

8-Methoxy-2-phenylquinoline (1c, Table 1, entry 3):

An oven dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (53 mg, 0.33 mmol, 1.0 equiv), CpRuCl(PPh₃)₂ (24 mg, 0.033 mmol, 0.10 equiv) and SPhos (13 mg, 0.033 mmol, 0.10 equiv) under a nitrogen atmosphere in a glove-box and the flask sealed and brought out of the glove-box. Imine **3c** (100 mg, 0.33 mmol, 1 equiv) and toluene (1.6 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105 °C. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (20 % EtOAc/Hexanes) to afford the quinoline **1c**¹² as a pale yellow solid (70 mg, 91%).

¹H NMR (500 MHz, CDCl₃, 20 °C) δ: 8.24–8.18 (m, 3H, ArH), 7.93 (d, 1H, *J* = 8.5 Hz, ArH), 7.53 (t, 2H, *J* = 7.5 Hz, ArH), 7.49–7.41 (m, 3H, ArH), 7.10 (dd, 1H, *J* = 7.6, 1.1 Hz, ArH), 4.13 (s, 3H, OCH₃).

¹³C NMR (125 MHz, CDCl₃, 20 °C) δ: 156.5, 155.7, 140.3, 140.0, 137.0, 129.4, 129.0, 128.5, 127.9, 126.7, 119.7, 119.5, 108.2, 56.3.

FTIR (neat) cm⁻¹: 3060 (m), 2934 (m), 2834 (w), 1599 (s), 1556 (s), 1467 (s), 1258 (s).

HRMS (ESI): calcd for C₁₆H₁₄NO [M+H]⁺: 236.1070, found: 236.1066.

TLC (20% EtOAc/hexanes), R_f: 0.23 (UV, KMnO₄).

¹² For a prior synthesis (characterization data not listed), see: Collin, J.; Jaber, N.; Lannou, M. I. *Tetrahedron Lett.* **2001**, 42, 7405–7407.

N-(3-Trifluoromethylphenyl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne (3d, Table 1, entry 4):

Trifluoromethanesulfonic anhydride (251 μL , 1.52 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2d** (337 mg, 1.27 mmol, 1 equiv) and 2-chloropyridine (481 μL , 5.08 mmol, 4.00 equiv) in CH_2Cl_2 (2.5 mL) at $-78\text{ }^{\circ}\text{C}$. After 5 min, the reaction mixture was warmed to $0\text{ }^{\circ}\text{C}$. After 20 min, the solution was cooled to $-78\text{ }^{\circ}\text{C}$ and a freshly prepared solution of copper (I) (trimethylsilyl)-acetylide (552 mg, 3.43 mmol, 2.70 equiv) in THF (7.0 mL) at $0\text{ }^{\circ}\text{C}$ was added via cannula. The reaction mixture was kept at $-78\text{ }^{\circ}\text{C}$ for 5 min and then warmed to $0\text{ }^{\circ}\text{C}$. After 10 min, the crude reaction mixture was filtered through celite (2 cm diam. $\times$ 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes $\rightarrow$ 7.5% EtOAc/hexanes) to afford the alkynyl imine **3d** as a pale yellow oil (321 mg, 73%). Desilylation of **3d** (see pages S19 and S38 for experimental procedures) afforded less than 10% yield of the corresponding terminal alkyne due to rapid nucleophilic addition (i.e., water and methanol) to this terminal alkynyl imine.

^1H NMR (500 MHz, CDCl_3 , $20\text{ }^{\circ}\text{C}$) δ : 8.20–8.17 (m, 2H, ArH (*o*-C=N)), 7.55–7.47 (m, 4H, ArH), 7.45–7.42 (m, 1H, ArH), 7.40 (s, 1H, ArH), 7.29–7.25 (m, 1H, ArH), 0.06 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

^{13}C NMR (125 MHz, CDCl_3 , $20\text{ }^{\circ}\text{C}$) δ : 152.3, 151.5, 136.6, 131.8, 131.1 (q, $J = 32.0\text{ Hz}$), 129.2, 128.6, 128.5, 124.6 (q, $J = 271.9\text{ Hz}$), 124.6, 121.5 (q, $J = 3.9\text{ Hz}$), 117.8 (q, $J = 3.8\text{ Hz}$), 106.8, 96.9, -0.7 .

FTIR (neat) cm^{-1} : 3067 (m), 2962 (m), 1589 (s, C=N), 1567 (s), 1330 (s).

HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{19}\text{F}_3\text{NSi}$ $[\text{M}+\text{H}]^+$: 346.1233, found: 346.1236.

TLC (20% EtOAc/hexanes), Rf: 0.57 (UV, CAM).

2-Phenyl-7-trifluoromethyl-quinoline (1d, Table 1, entry 4):

An oven dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (35 mg, 0.22 mmol, 1.0 equiv), $\text{CpRuCl}(\text{PPh}_3)_2$ (16 mg, 0.022 mmol, 0.10 equiv) and SPhos (9 mg, 0.022 mmol, 0.10 equiv) under a nitrogen atmosphere in a glove-box and the flask sealed and brought out of the glove-box. Imine **3d** (75 mg, 0.22 mmol, 1 equiv) and toluene (1.1 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at $105\text{ }^\circ\text{C}$. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (20 % EtOAc/Hexanes) to afford the quinoline **1d** as a pale yellow solid (53 mg, 89%).

^1H NMR (500 MHz, CDCl_3 , $20\text{ }^\circ\text{C}$) δ : 8.46 (s, 1H, ArH), 8.30 (d, 1H, $J = 8.2\text{ Hz}$, ArH), 8.22–8.18 (m, 2H, ArH(*o*-C=N)), 8.03 (d, 1H, $J = 8.6\text{ Hz}$, ArH), 7.97 (d, 1H, $J = 8.6\text{ Hz}$, ArH), 7.72 (dd, 1H, $J = 8.5, 1.8\text{ Hz}$, ArH), 7.59–7.54 (m, 2H, ArH), 7.54–7.50 (m, 1H, ArH).

^{13}C NMR (125 MHz, CDCl_3 , $20\text{ }^\circ\text{C}$) δ : 158.9, 147.5, 139.1, 136.8, 131.7 (q, $J = 32.6\text{ Hz}$), 130.1, 129.2, 128.9, 127.8 (q, $J = 4.6\text{ Hz}$), 127.5, 125.3, 123.2, 122.1 (q, $J = 2.9\text{ Hz}$), 121.0.

FTIR (neat) cm^{-1} : 3067 (w), 3037 (w), 2917 (w), 1603 (s), 1316 (s).

HRMS (EI): calcd for $\text{C}_{16}\text{H}_{10}\text{F}_3\text{N}$ $[\text{M}]^+$: 273.0760, found: 273.0750.

TLC (20% EtOAc–hexanes), R_f: 0.46 (UV, CAM).

N-Phenyl-2-(thiophen-2-yl)-4-trimethylsilyl-1-azabut-1-en-3-yne (3e, Table 1, entry 5):

Trifluoromethanesulfonic anhydride (195 μL , 1.18 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2e** (200 mg, 0.98 mmol, 1 equiv) and 2-chloropyridine (372 μL , 3.94 mmol, 4.00 equiv) in CH_2Cl_2 (2.0 mL) at $-78\text{ }^{\circ}\text{C}$. After 5 min, the reaction mixture was warmed to $0\text{ }^{\circ}\text{C}$. After 20 min, the solution was cooled to $-78\text{ }^{\circ}\text{C}$ and a freshly prepared solution of copper (I) (trimethylsilyl)-acetylide (428 mg, 2.66 mmol, 2.70 equiv) in THF (5.0 mL) at $0\text{ }^{\circ}\text{C}$ was added via cannula. The reaction mixture was kept at $-78\text{ }^{\circ}\text{C}$ for 5 min and then warmed to $0\text{ }^{\circ}\text{C}$. After 10 min, the crude reaction mixture was filtered through celite (2 cm diam. $\times$ 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes $\rightarrow$ 7.5% EtOAc/hexanes) to afford the alkynyl imine **3e** as a pale yellow oil (227 mg, 81%).

^1H NMR (500 MHz, CDCl_3 , $20\text{ }^{\circ}\text{C}$) δ : 7.73 (dd, 1H, $J = 3.7, 1.2\text{ Hz}$, SCHCHCHCC=N), 7.48 (dd, 1H, $J = 5.0, 0.9\text{ Hz}$, SCHCHCHCC=N), 7.38–7.33 (m, 2H, ArH), 7.20–7.14 (m, 3H, ArH), 7.12 (dd, 1H, $J = 4.6, 3.7\text{ Hz}$, SCHCHCHCC=N), 0.16 (s, 9H, Si(CH₃)₃).

^{13}C NMR (125 MHz, CDCl_3 , $20\text{ }^{\circ}\text{C}$) δ : 150.5, 144.7, 144.0, 131.6, 130.6, 128.5, 127.7, 125.4, 121.6, 103.7, 96.7, -0.5 .

FTIR (neat) cm^{-1} : 3078 (m), 2960 (s), 1563 (s, C=N), 1425 (s), 1252 (s).

HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{18}\text{NSSi}$ $[\text{M}+\text{H}]^+$: 284.0924, found: 284.0937.

TLC (20% EtOAc/hexanes), R_f: 0.70 (UV, CAM).

2-Thiophen-2-ylquinoline (1e**, Table 1, entry 5):**

An oven dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (58 mg, 0.35 mmol, 1.0 equiv), $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$ (26 mg, 0.035 mmol, 0.10 equiv) and SPhos (15 mg, 0.035 mmol, 0.10 equiv) under a nitrogen atmosphere in a glove-box and the flask sealed and brought out of the glove-box. Imine **3e** (100 mg, 0.35 mmol, 1 equiv) and toluene (1.8 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at $105\text{ }^\circ\text{C}$. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (20 % EtOAc/Hexanes) to afford the quinoline **1e**¹³ as a pale yellow solid (56 mg, 75%).

^1H NMR (500 MHz, CDCl_3 , $20\text{ }^\circ\text{C}$):	8.16 (d, 1H, $J = 8.9\text{ Hz}$, ArH), 8.10 (d, 1H, $J = 9.2\text{ Hz}$, ArH), 7.82 (d, 1H, $J = 8.6\text{ Hz}$, ArH), 7.79 (d, 1H, $J = 7.9\text{ Hz}$, ArH (SCHCHCHCC=N)), 7.75 (dd, 1H, $J = 3.7, 0.9\text{ Hz}$, ArH (SCHCHCHCC=N)), 7.71 (ddd, 1H, $J = 8.5, 7.0, 1.5\text{ Hz}$, ArH), 7.52–7.47 (m, 2H, ArH), 7.18 (dd, 1H, $J = 4.9, 3.7\text{ Hz}$, ArH (SCHCHCHC=N)).
^{13}C NMR (125 MHz, CDCl_3 , $20\text{ }^\circ\text{C}$):	152.5, 148.3, 145.6, 136.8, 130.0, 129.4, 128.8, 128.3, 127.7, 127.3, 126.3, 126.0, 117.8.
FTIR (neat):	3079 (w), 3042 (w), 1962 (w), 1617 (m), 1597 (s), 1561 (m), 1502 (s).
HRMS (ESI):	calcd for $\text{C}_{13}\text{H}_{10}\text{NS}$ $[\text{M}+\text{H}]^+$: 212.0528, found: 212.0533.
TLC (20% EtOAc–hexanes), R_f :	0.40 (UV, KMnO_4).

¹³ Fürstner, A.; Leitner, A.; Méndez, M.; Krause, H. *J. Am. Chem. Soc.* **2002**, *124*, 13856–13863.

N-Phenyl-2-cyclohexyl-4-trimethylsilyl-1-azabut-1-en-3-yne (3f, Table 1, entry 6):

Trifluoromethanesulfonic anhydride (98 μL , 0.59 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2f** (100 mg, 0.49 mmol, 1 equiv) and 2-chloropyridine (186 μL , 1.97 mmol, 4.00 equiv) in CH_2Cl_2 (1.0 mL) at $-78\text{ }^\circ\text{C}$. After 5 min, the reaction mixture was warmed to $0\text{ }^\circ\text{C}$. After 20 min, the solution was cooled to $-78\text{ }^\circ\text{C}$ and a freshly prepared solution of copper (I) (trimethylsilyl)-acetylide (214 mg, 1.33 mmol, 2.70 equiv) in THF (3.0 mL) at $0\text{ }^\circ\text{C}$ was added via cannula. The reaction mixture was kept at $-78\text{ }^\circ\text{C}$ for 5 min and then warmed to $0\text{ }^\circ\text{C}$. After 10 min, the crude reaction mixture was filtered through celite (2 cm diam. $\times$ 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on neutralized silica gel (1% Et_3N /hexanes) to afford the alkynyl imine **3f** as a pale yellow oil (123 mg, 89%).

^1H NMR (500 MHz, CDCl_3 , 20°C): 7.32–7.28 (m, 2H, ArH), 7.12–7.07 (m, 1H, ArH), 6.96–6.93 (m, 2H, ArH), 2.47 (tt, 1H, $J = 23.2, 6.9\text{ Hz}$, $(\text{CH}_2)_2\text{CHC}=\text{N}$), 2.01 (br dd, 2H, $J = 12.6, 2.0\text{ Hz}$, $^6\text{C}_6\text{H}_{11}$), 1.86 (dt, 2H, $J = 13.1, 3.4\text{ Hz}$, $^6\text{C}_6\text{H}_{11}$), 1.76–1.69 (m, 1H, $^6\text{C}_6\text{H}_{11}$), 1.52 (qd, 2H, $J = 12.5, 3.4\text{ Hz}$, $^6\text{C}_6\text{H}_{11}$), 1.36 (qt, 2H, $J = 12.5, 3.2\text{ Hz}$, $^6\text{C}_6\text{H}_{11}$), 1.26 (qt, 1H, $J = 12.5, 3.2\text{ Hz}$, $^6\text{C}_6\text{H}_{11}$), 0.06 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

^{13}C NMR (125 MHz, CDCl_3 , 20°C): 159.6, 151.7, 128.4, 124.5, 120.6, 104.0, 98.2, 48.3, 30.3, 26.1, 26.0, -0.5 .

FTIR (neat): 3049 (w), 2933 (s), 2856 (m), 1660 (w), 1594 (s), 1484 (m).

HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{26}\text{NSi}$ $[\text{M}+\text{H}]^+$: 284.1829, found: 284.1836.

TLC (20% EtOAc –hexanes), R_f : 0.67 (UV, KMnO_4).

2-Cyclohexyl-quinoline (1f, Table 1, entry 6):

An oven dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (40 mg, 0.25 mmol, 1.0 equiv), $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$ (18 mg, 0.025 mmol, 0.10 equiv) and SPhos (10 mg, 0.025 mmol, 0.10 equiv) under a nitrogen atmosphere in a glove-box and the flask sealed and brought out of the glove-box. Imine **3f** (70 mg, 0.25 mmol, 1 equiv) and toluene (1.2 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105°C . After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (10 % EtOAc/Hexanes) to afford the quinoline **1f**¹⁴ as a pale yellow solid (36 mg, 69%).

^1H NMR (500 MHz, CDCl_3 , 20°C):	8.09 (d, 1H, $J = 8.5$ Hz, ArH), 8.06 (d, 1H, $J = 8.5$ Hz, ArH), 7.78 (d, 1H, $J = 8.2$ Hz, ArH), 7.69 (ddd, 1H, $J = 8.5, 7.0, 1.5$ Hz, ArH), 7.49 (ddd, 1H, $J = 7.9, 7.0, 1.2$ Hz, ArH), 7.35 (d, 1H, $J = 8.6$ Hz, ArH), 2.94 (tt, 1H, $J = 12.1, 3.4$ Hz, $(\text{CH}_2)_2\text{CHCN}$), 2.08–2.00 (m, 2H, $^6\text{C}_6\text{H}_{11}$), 1.98–1.87 (m, 2H, $^6\text{C}_6\text{H}_{11}$), 1.86–1.76 (m, 1H, $^6\text{C}_6\text{H}_{11}$), 1.64 (qd, 2H, $J = 12.5, 3.1$ Hz, $^6\text{C}_6\text{H}_{11}$), 1.49 (qt, 2H, $J = 13.1, 3.4$ Hz, $^6\text{C}_6\text{H}_{11}$), 1.35 (qt, 1H, $J = 12.8, 3.4$ Hz, $^6\text{C}_6\text{H}_{11}$).
^{13}C NMR (125 MHz, CDCl_3 , 20°C):	167.0, 148.0, 136.5, 129.4, 129.1, 127.6, 127.2, 125.8, 119.8, 47.9, 33.0, 26.7, 26.3.
FTIR (neat):	3058 (w), 2924 (s), 2850 (m), 1720 (w), 1619 (w), 1601 (m), 1502 (m).
HRMS (EI):	calcd for $\text{C}_{15}\text{H}_{17}\text{N}$ $[\text{M}]^+$: 211.1356, found: 211.1358.
TLC (20% EtOAc–hexanes), R_f :	0.50 (UV, KMnO_4).

¹⁴ For a prior synthesis (characterization data not listed), see: Ishikura, M.; Oda, I.; Kamada, M.; Terashima, M. *Synth. Comm.* **1987**, *17*, 959–967.

N-Phenyl-2-(*tert*-butyl)-4-trimethylsilyl-1-azabut-1-en-3-yne (3g, Table 1, entry 7):

Trifluoromethanesulfonyl anhydride (220 μ L, 1.33 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2g** (197 mg, 1.11 mmol, 1 equiv) and 2-chloropyridine (420 μ L, 4.44 mmol, 4.00 equiv) in CH_2Cl_2 (2.2 mL) at -78°C . After 5 min, the reaction mixture was warmed to 0°C . After 20 min, the solution was cooled to -78°C and a freshly prepared solution of copper (I) (trimethylsilyl)-acetylide (482 mg, 3.00 mmol, 2.70 equiv) in THF (5.0 mL) at 0°C was added via cannula. The reaction mixture was kept at -78°C for 5 min and then warmed to 0°C . After 10 min, the crude reaction mixture was filtered through celite (2 cm diam. $\times$ 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes $\rightarrow$ 7.5% EtOAc/hexanes) to afford the alkynyl imine **3g** as a pale yellow oil (236 mg, 83%).

^1H NMR (500 MHz, CDCl_3 , 20°C) δ : 7.32–7.28 (m, 2H, ArH), 7.11–7.06 (m, 1H, ArH), 6.92–6.88 (m, 2H, ArH), 1.31 (s, 9H, $\text{C}(\text{CH}_3)_3$), 0.50 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

^{13}C NMR (125 MHz, CDCl_3 , 20°C) δ : 162.9, 152.2, 128.5, 124.2, 120.3, 104.7, 97.3, 39.8, 28.0, -0.5 .

FTIR (neat) cm^{-1} : 3080 (w), 2967 (s), 2868 (m), 1931 (w), 1593 (s), 1477 (s).

HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{24}\text{NSi}$ $[\text{M}+\text{H}]^+$: 258.1673, found: 258.1675.

TLC (20% EtOAc–hexanes), R_f : 0.69 (UV, CAM).

(1-*tert*-Butyl-prop-2-ynylidene)-phenyl-amine (4g, Table 1, entry 7):

Anhydrous potassium carbonate (41 mg, 0.30 mmol, 0.2 equiv) was added to a solution of imine **3g** (380 mg, 1.48 mmol, 1 equiv) in methanol (5.0 mL) and stirred at 23 °C. After 25 min, the volatiles were removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (7.5 % EtOAc/hexanes) to afford the alkynyl imine **4g** as a yellow solid (259 mg, 95%).

¹ H NMR (500 MHz, CDCl ₃ , 20 °C):	7.32–7.28 (m, 2H, ArH), 7.12 (tt, 1H, <i>J</i> = 7.3, 2.3 Hz, ArH), 6.92–6.88 (m, 2H, ArH), 3.14 (s, 1H, C≡CH), 1.33 (s, 9H, C(CH ₃) ₃).
¹³ C NMR (125 MHz, CDCl ₃ , 20 °C):	161.9, 151.8, 128.7, 124.4, 119.9, 85.4, 76.2, 40.2, 27.8.
FTIR (neat):	2962 (s), 2925 (s), 1734 (m), 1717 (m), 1684 (s), 1653 (m).
HRMS (EI):	calcd for C ₁₃ H ₁₅ N [M] ⁺ : 185.1199, found: 185.1193.
TLC (20% EtOAc–hexanes), <i>R_f</i> :	0.66 (UV, KMnO ₄).

2-*tert*-Butyl-quinoline (1g**, Table 1, entry 7):**

An oven dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (62 mg, 0.38 mmol, 1.0 equiv), $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$ (28 mg, 0.038 mmol, 0.10 equiv) and SPhos (16 mg, 0.038 mmol, 0.10 equiv) under a nitrogen atmosphere in a glove-box and the flask sealed and brought out of the glove-box. Imine **4g** (70 mg, 0.38 mmol, 1 equiv) and toluene (1.9 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105°C . After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (7.5 % EtOAc/Hexanes) to afford the quinoline **1g** as a pale yellow solid (51 mg, 73%).

^1H NMR (500 MHz, CDCl_3 , 20°C): 8.09 (d, 1H, $J = 8.2$ Hz, ArH), 8.07 (d, 1H, $J = 8.5$ Hz, ArH), 7.78 (dd, 1H, $J = 7.9, 1.2$ Hz, ArH), 7.65 (ddd, 1H, $J = 8.5, 7.0, 1.5$ Hz, ArH), 7.54 (d, 1H, $J = 8.9$ Hz, ArH), 7.48 (ddd, 1H, $J = 8.1, 6.7, 0.9$ Hz, ArH), 1.49 (s, 9H, $\text{C}(\text{CH}_3)_3$).

^{13}C NMR (125 MHz, CDCl_3 , 20°C): 147.6, 136.1, 129.6, 129.2, 127.4, 126.6, 125.8, 118.5, 100.0, 38.3, 30.4.

FTIR (neat): 3061 (w), 2960 (s), 2868 (m), 1619 (m), 1601 (s), 1565 (w), 1503 (s).

HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{16}\text{N}$ $[\text{M}+\text{H}]^+$: 186.1277, found: 186.1283.

TLC (20% EtOAc–hexanes), R_f : 0.46 (UV, KMnO_4)

N-Phenyl-2-(morpholin-4-yl)-4-trimethylsilyl-1-azabut-1-en-3-yne (3h, Table 1, entry 8):

Trifluoromethanesulfonic anhydride (144 μL , 0.87 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2h** (150 mg, 0.73 mmol, 1 equiv) and 2-chloropyridine (275 μL , 2.91 mmol, 4.00 equiv) in CH_2Cl_2 (1.5 mL) at -78°C . After 5 min, the reaction mixture was warmed to 0°C . After 20 min, the solution was cooled to -78°C and Hünig's base (190 μL , 1.09 mmol, 1.50 equiv) was added via syringe followed by a freshly prepared solution of copper (I) (trimethylsilyl)-acetylide (316 mg, 1.96 mmol, 2.70 equiv) in THF (3.0 mL) at 0°C via cannula. The reaction mixture was kept at -78°C for 5 min and then warmed to 0°C . After 10 min, the crude reaction mixture was filtered through celite (2 cm diam. $\times$ 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on neutralized silica gel (50% EtOAc/hexanes) to afford the alkynyl imidate **3h** as a burgandy colored oil (166 mg, 80%).

^1H NMR (500 MHz, CDCl_3 , 20°C): 7.27–7.23 (m, 2H, ArH), 7.01 (tt, 1H, $J = 7.3, 1.1$ Hz, ArH), 6.92–6.88 (m, 2H, ArH), 3.79–3.75 (m, 4H, $\text{OCH}_2\text{CH}_2\text{N}$), 3.69–3.66 (m, 4H, $\text{OCH}_2\text{CH}_2\text{N}$), 0.04 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

^{13}C NMR (125 MHz, CDCl_3 , 20°C): 151.2, 144.2, 128.5, 122.9, 122.3, 104.2, 93.2, 66.8, 45.9, -0.7 .

FTIR (neat): 2967 (m), 2924 (w), 2861 (m), 1577 (s, $\text{C}=\text{N}$), 1420 (m), 1247 (s).

HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{23}\text{N}_2\text{OSi}$ $[\text{M}+\text{H}]^+$: 287.1574, found: 287.1580.

TLC (50% EtOAc–hexanes), R_f : 0.70 (UV, KMnO_4).

2-Morpholin-4-yl-quinoline (1h, Table 1, entry 8):

An oven dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (43 mg, 0.26 mmol, 1.0 equiv), CpRu(PPh₃)₂Cl (19 mg, 0.026 mmol, 0.10 equiv) and SPhos (11 mg, 0.026 mmol, 0.10 equiv) under a nitrogen atmosphere in a glove-box and the flask sealed and brought out of the glove-box. Imine **3h** (75 mg, 0.26 mmol, 1 equiv) and toluene (1.3 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105 °C. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (20 % EtOAc/Hexanes) to afford the quinoline **1h** as a pale yellow solid (35 mg, 62%).

¹H NMR (500 MHz, CDCl₃, 20°C): 7.95 (d, 1H, *J* = 8.7 Hz, ArH), 7.74 (d, 1H, *J* = 7.6 Hz, ArH), 7.65 (dd, 1H, *J* = 7.9, 1.5 Hz, ArH), 7.56 (ddd, 1H, *J* = 8.5, 7.0, 1.5 Hz, ArH), 7.27 (ddd, 1H, *J* = 8.0, 6.7, 0.9 Hz, ArH), 6.99 (d, 1H, *J* = 9.2 Hz, ArH), 3.87 (t, 4H, *J* = 4.9, OCH₂CH₂N), 3.73 (t, 4H, *J* = 4.9 Hz, OCH₂CH₂N).

¹³C NMR (125 MHz, CDCl₃, 20°C): 157.6, 147.8, 137.7, 129.8, 127.4, 126.9, 123.4, 122.8, 109.4, 67.0, 45.7.

FTIR (neat): 3047 (w), 2972 (w), 2917 (w), 2858 (m), 1617 (s), 1605 (m).

HRMS (ESI): calcd for C₁₃H₁₄N₂O [M]⁺: 215.1179, found: 215.1178.

TLC (20% EtOAc–hexanes), *R_f*: 0.21 (UV, KMnO₄).

N-(trans-β-Styryl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne (3i, Table 1, entry 9):

Trifluoromethanesulfonic anhydride (133 μL , 0.81 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2i** (150 mg, 0.67 mmol, 1 equiv) and 2-chloropyridine (254 μL , 2.69 mmol, 4.00 equiv) in CH_2Cl_2 (1.3 mL) at $-78\text{ }^\circ\text{C}$. After 5 min, the reaction mixture was warmed to $0\text{ }^\circ\text{C}$. After 20 min, the solution was cooled to $-78\text{ }^\circ\text{C}$ and a freshly prepared solution of copper (I) (trimethylsilyl)-acetylide (292 mg, 1.81 mmol, 2.70 equiv) in THF (5.0 mL) at $0\text{ }^\circ\text{C}$ was added via cannula. The reaction mixture was kept at $-78\text{ }^\circ\text{C}$ for 5 min and then warmed to $0\text{ }^\circ\text{C}$. After 10 min, the crude reaction mixture was filtered through celite (2 cm diam. $\times$ 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes $\rightarrow$ 7.5% EtOAc/hexanes) to afford the alkynyl imine **3i** as a pale yellow solid (159 mg, 78%).

^1H NMR (500 MHz, CDCl_3 , $20\text{ }^\circ\text{C}$):	8.34 (d, 1H, $J = 13.1\text{ Hz}$, NCHCHC), 8.18–8.13 (m, 2H, ArH), 7.56 (d, 2H, $J = 7.3\text{ Hz}$, ArH), 7.48–7.42 (m, 3H, ArH), 7.39 (t, 2H, $J = 7.6\text{ Hz}$, ArH), 7.31 (tt, 1H, $J = 7.3, 1.2\text{ Hz}$, ArH), 7.16 (d, 1H, $J = 13.4\text{ Hz}$, NCHCHC), 0.39 (s, 9H, $\text{Si}(\text{CH}_3)_3$).
^{13}C NMR (125 MHz, CDCl_3 , $20\text{ }^\circ\text{C}$) δ :	148.0, 139.7, 137.1, 136.7, 133.8, 131.0, 129.0, 128.6, 128.5, 128.0, 127.4, 108.7, 96.8, 0.0.
FTIR (CDCl_3) cm^{-1} :	3155 (m), 3062 (m), 3028 (m), 2963 (m), 2902 (m), 1815 (m), 1794 (m), 1643 (w), 1622 (m), 1490 (s).
HRMS (ESI):	calcd for $\text{C}_{20}\text{H}_{22}\text{NSi}$ $[\text{M}+\text{H}]^+$: 304.1516, found: 304.1526.
TLC (20% EtOAc–hexanes), R_f :	0.59 (UV, CAM).

2,5-Diphenyl-pyridine (1i, Table 1, entry 9):¹⁵

An oven dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (40 mg, 0.25 mmol, 1.0 equiv), CpRu(PPh₃)₂Cl (18 mg, 0.025 mmol, 0.10 equiv) and SPhos (10 mg, 0.025 mmol, 0.10 equiv) under a nitrogen atmosphere in a glove-box and the flask sealed and brought out of the glove-box. Imine **3i** (75 mg, 0.25 mmol, 1 equiv) and toluene (1.3 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105 °C. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on neutralized silica gel (20 % EtOAc/Hexanes) to afford the pyridine **1i** as a pale yellow solid (44 mg, 77%).

¹H NMR (500 MHz, CDCl₃, 20 °C): 8.96 (d, 1H, *J* = 2.5 Hz, ArH), 8.08–8.05 (m, 2H, ArH), 7.98 (dd, 1H, *J* = 8.2, 2.5 Hz, ArH), 7.83 (d, 1H, *J* = 8.2 Hz, ArH), 7.68–7.64 (m, 2H, ArH), 7.54–7.50 (m, 4H, ArH), 7.47–7.42 (m, 2H, ArH).

¹³C NMR (125 MHz, CDCl₃, 20 °C) δ: 156.4, 148.3, 139.2, 137.9, 135.3, 135.1, 129.3, 129.2, 129.0, 128.3, 127.2, 127.0, 120.6.

FTIR (CH₂Cl₂) cm^{−1}: 2926 (w), 1735 (s), 1654 (s), 1594 (w), 1472 (s), 1371 (s).

HRMS (ESI): calcd for C₁₇H₁₄N [M+H]⁺: 232.1121, found: 232.1126.

TLC (20% EtOAc–hexanes), *R*_f: 0.43 (UV, CAM).

¹⁵ Berthiol, F.; Kondolff, I.; Doucet, H.; Santelli, M. *J. Organomet. Chem.* **2004**, 689, 2786–2798.

(2-Naphthalen-1-yl-vinyl)-[1-phenyl-3-(trimethyl-silanyl)-prop-2-ynylidene]-amine (3j, Table 1, entry 10):

Trifluoromethanesulfonic anhydride (127 μ L, 0.77 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2j** (175 mg, 0.64 mmol, 1 equiv) and 2-chloropyridine (242 μ L, 2.56 mmol, 4.00 equiv) in CH_2Cl_2 (1.3 mL) at -78°C . After 5 min, the reaction mixture was warmed to 0°C . After 20 min, the solution was cooled to -78°C and a freshly prepared solution of copper (I) (trimethylsilyl)-acetylide (278 mg, 1.73 mmol, 2.70 equiv) in THF (4.0 mL) at 0°C was added via cannula. The reaction mixture was kept at -78°C for 5 min and then warmed to 0°C . After 10 min, the crude reaction mixture was filtered through celite (2 cm diam. $\times$ 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes $\rightarrow$ 7.5% EtOAc/hexanes) to afford the alkynyl imine **3j** as a pale yellow oil (197 mg, 87%).

^1H NMR (500 MHz, CDCl_3 , 20°C): 8.39 (dd, 1H, $J = 12.8, 0.6$ Hz, NCHCHC), 8.31 (d, 1H, $J = 8.2$ Hz, 8.22–8.18 (m, 2H, ArH), 7.94 (d, 1H, $J = 13.1$ Hz, NCHCHC), 7.89 (d, 1H, $J = 7.9$ Hz, ArH), 7.85 (d, 2H, $J = 7.6$ Hz, ArH), 7.60–7.47 (m, 6H, ArH), 0.38 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

^{13}C NMR (125 MHz, CDCl_3 , 20°C) δ : 148.8, 142.4, 137.7, 134.6, 134.3, 132.3, 131.6, 131.2, 129.5, 129.4, 129.2, 128.7, 127.1, 126.8, 126.4, 124.8, 124.6, 109.3, 97.5, 0.6.

FTIR (neat) cm^{-1} : 3059 (m), 2959 (m), 2141 (w), 1810 (w), 1692 (m), 1644 (w), 1590 (w), 1251 (s).

HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{24}\text{NSi}$ $[\text{M}+\text{H}]^+$: 354.1673, found: 354.1675.

TLC (20% EtOAc–hexanes), R_f : 0.77 (UV, CAM).

5-Naphthalen-1-yl-2-phenyl-pyridine (1j, Table 1, entry 10):

An oven dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (28 mg, 0.17 mmol, 1.0 equiv), $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$ (12 mg, 0.017 mmol, 0.10 equiv) and SPhos (7 mg, 0.017 mmol, 0.10 equiv) under a nitrogen atmosphere in a glove-box and the flask sealed and brought out of the glove-box. Imine **3j** (60 mg, 0.17 mmol, 1 equiv) and toluene (0.9 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at $105\text{ }^\circ\text{C}$. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on neutralized silica gel (7.5 % EtOAc/Hexanes) to afford the pyridine **1j** as a pale brown solid (44 mg, 88%).

^1H NMR (500 MHz, CDCl_3 , $20\text{ }^\circ\text{C}$): 8.87–8.84 (m, 1H, ArH), 8.11 (d, 2H, $J = 7.02\text{ Hz}$, ArH), 7.98–7.87 (m, 5H, ArH), 7.61–7.46 (m, 7H, ArH).

^{13}C NMR (125 MHz, CDCl_3 , $20\text{ }^\circ\text{C}$): 156.4, 150.6, 139.3, 138.4, 136.4, 134.9, 134.0, 131.7, 129.3, 129.0, 128.7, 128.7, 127.6, 127.1, 126.7, 126.3, 125.6, 125.6, 120.1.

FTIR (neat): 3058 (m), 2930 (w), 1950 (w), 1595 (m), 1548 (m), 1476 (s), 1396 (m).

HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{16}\text{N}$ $[\text{M}+\text{H}]^+$: 282.1277, found: 282.1289.

TLC (15% EtOAc–hexanes), R_f : 0.46 (UV, KMnO_4).

[2-(3,4-Dimethoxy-phenyl)-vinyl]-[1-phenyl-3-(trimethyl-silanyl)-prop-2-ynylidene]-amine (3k**, Table 1, entry 11):**

Trifluoromethanesulfonic anhydride (122 μL , 0.74 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2k** (175 mg, 0.62 mmol, 1 equiv) and 2-chloropyridine (234 μL , 2.47 mmol, 4.00 equiv) in CH_2Cl_2 (1.2 mL) at -78°C . After 5 min, the reaction mixture was warmed to 0°C . After 20 min, the solution was cooled to -78°C and a freshly prepared solution of copper (I) (trimethylsilyl)-acetylide (268 mg, 1.67 mmol, 2.70 equiv) in THF (4.0 mL) at 0°C was added via cannula. The reaction mixture was kept at -78°C for 5 min and then warmed to 0°C . After 10 min, the crude reaction mixture was filtered through celite (2 cm diam. $\times$ 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (15% EtOAc/hexanes) to afford the alkynyl imine **3k** as a yellow oil (216 mg, 96%).

^1H NMR (500 MHz, CDCl_3 , 20°C):	8.26 (d, 1H, $J = 13.1$ Hz, NCHCHC), 8.16–8.12 (m, 2H, NCHCHC , ArH), 7.46–7.42 (m, 3H, ArH), 7.14–7.08 (m, 3H, ArH), 6.86 (d, 1H, $J = 8.2$ Hz, ArH), 3.96 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 0.38 (s, 9H, $\text{Si}(\text{CH}_3)_3$).
^{13}C NMR (125 MHz, CDCl_3 , 20°C) δ :	149.6, 149.2, 146.6, 138.2, 137.1, 133.8, 130.7, 129.6, 128.5, 127.8, 121.4, 111.3, 108.8, 108.1, 96.9, 56.1, 55.8, -0.0 .
FTIR (neat) cm^{-1} :	3057 (w), 2958 (m), 2835 (w), 1599 (s), 1578 (m), 1512 (s), 1267 (s).
HRMS (ESI):	calcd for $\text{C}_{22}\text{H}_{26}\text{NO}_2\text{Si}$ $[\text{M}+\text{H}]^+$: 364.1727, found: 364.1733.
TLC (20% EtOAc–hexanes), R_f :	0.52 (UV, CAM).

5-(3,4-Dimethoxy-phenyl)-2-phenyl-pyridine (1k, Table 1, entry 11):

An oven dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (45 mg, 0.28 mmol, 1.0 equiv), CpRu(PPh₃)₂Cl (20 mg, 0.028 mmol, 0.10 equiv) and SPhos (11 mg, 0.028 mmol, 0.10 equiv) under a nitrogen atmosphere in a glove-box and the flask sealed and brought out of the glove-box. Imine **3k** (100 mg, 0.28 mmol, 1 equiv) and toluene (1.4 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105 °C. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on neutralized silica gel (30 % EtOAc/Hexanes) to afford the pyridine **1k** as a yellow solid (64 mg, 79%).

¹ H NMR (500 MHz, CDCl ₃ , 20°C):	8.92 (d, 1H, <i>J</i> = 2.1 Hz, ArH), 8.07–8.03 (m, 2H, ArH), 7.93 (dd, 1H, <i>J</i> = 8.2, 2.5 Hz, ArH), 7.81 (d, 1H, <i>J</i> = 8.2 Hz, ArH), 7.53–7.49 (m, 2H, ArH), 7.44 (tt, 1H, <i>J</i> = 7.3, 1.1 Hz, ArH), 7.22 (dd, 1H, <i>J</i> = 8.2, 2.1 Hz, ArH), 7.15 (d, 1H, <i>J</i> = 1.8 Hz, ArH), 7.02 (d, 1H, <i>J</i> = 8.2 Hz, ArH), 3.99 (s, 3H, OCH ₃), 3.96 (s, 3H, OCH ₃).
¹³ C NMR (125 MHz, CDCl ₃ , 20°C):	155.7, 149.5, 149.3, 147.9, 139.1, 134.8, 134.8, 130.5, 129.0, 128.9, 126.8, 120.3, 119.5, 111.8, 110.1, 56.1, 56.1.
FTIR (neat):	3055 (w), 3005 (w), 2966 (m), 2837 (m), 1602 (s), 1590 (s), 1522 (s), 1150 (s), 1022 (s).
HRMS (ESI):	calcd for C ₁₉ H ₁₈ NO ₂ [M+H] ⁺ : 292.1332, found: 292.1337.
TLC (20% EtOAc–hexanes), <i>R</i> _f :	0.19 (UV, KMnO ₄).

N-(Cyclohexen-1-yl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne (3I, Table 1, entry 12):

Trifluoromethanesulfonic anhydride (148 μL , 0.89 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2I** (150 mg, 0.75 mmol, 1 equiv) and 2-chloropyridine (282 μL , 2.98 mmol, 4.00 equiv) in CH_2Cl_2 (1.5 mL) at $-78\text{ }^{\circ}\text{C}$. After 5 min, the reaction mixture was warmed to $0\text{ }^{\circ}\text{C}$. After 20 min, the solution was cooled to $-78\text{ }^{\circ}\text{C}$ and a freshly prepared solution of copper (I) (trimethylsilyl)-acetylide (323 mg, 2.01 mmol, 2.70 equiv) in THF (3.0 mL) at $0\text{ }^{\circ}\text{C}$ was added via cannula. The reaction mixture was kept at $-78\text{ }^{\circ}\text{C}$ for 5 min and then warmed to $0\text{ }^{\circ}\text{C}$. After 10 min, the crude reaction mixture was filtered through celite (2 cm diam. $\times$ 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes $\rightarrow$ 7.5% EtOAc/hexanes) to afford the alkynyl imine **3I** as a yellow oil (157 mg, 75%).

^1H NMR (500 MHz, CDCl_3 , $20\text{ }^{\circ}\text{C}$) δ : 8.09–8.05 (m, 2H, ArH), 7.48–7.39 (m, 3H, ArH), 5.21 (t, 1H, $J = 4.0\text{ Hz}$, $\text{NC}=\text{CH}$), 2.29–2.23 (m, 2H, CH_2), 2.22–2.16 (m, 2H, CH_2), 1.82–1.75 (m, 2H, CH_2), 1.70–1.64 (m, 2H, CH_2), 0.28 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

^{13}C NMR (125 MHz, CDCl_3 , $20\text{ }^{\circ}\text{C}$) δ : 148.7, 147.5, 137.2, 130.8, 128.4, 128.0, 110.3, 103.7, 97.6, 27.9, 24.7, 23.1, 22.5, -0.1 .

FTIR (neat) cm^{-1} : 3063 (w), 2927 (s), 2857 (m), 1663 (m), 1562 (m), 1448 (m), 1273 (s), 1251 (s).

HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{24}\text{NSi}$ $[\text{M}+\text{H}]^+$: 282.1673, found: 282.1685.

TLC (20% EtOAc/hexanes), Rf: 0.61 (UV, KMnO_4).

2-Phenyl-5,6,7,8-tetrahydro-quinoline (1I**, Table 1, entry 12):**

An oven dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (43 mg, 0.27 mmol, 1.0 equiv), $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$ (19 mg, 0.027 mmol, 0.10 equiv) and SPhos (11 mg, 0.027 mmol, 0.10 equiv) under a nitrogen atmosphere in a glove-box and the flask sealed and brought out of the glove-box. Imine **3I** (75 mg, 0.27 mmol, 1 equiv) and toluene (1.3 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105°C . After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (20 % EtOAc/Hexanes) to afford the pyridine **1I** as a pale yellow solid (41 mg, 73%).

^1H NMR (500 MHz, CDCl_3 , 20°C): 7.97–7.94 (m, 2H, ArH), 7.48–7.36 (m, 5H, ArH), 3.00 (t, 2H, $J = 6.4$ Hz, CH_2), 2.82 (t, 2H, $J = 6.4$ Hz, CH_2), 1.98–1.92 (m, 2H, CH_2), 1.89–1.83 (m, 2H, CH_2).

^{13}C NMR (125 MHz, CDCl_3 , 20°C): 157.4, 154.9, 140.1, 137.6, 130.9, 128.8, 128.5, 127.0, 118.1, 33.1, 28.8, 23.4, 23.0.

FTIR (neat): 3061 (w), 3032 (w), 2935 (s), 2860 (m), 1590 (m), 1566 (m), 1460 (s), 1434 (m), 1253 (m).

HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{16}\text{N}$ $[\text{M}+\text{H}]^+$: 210.1277, found: 210.1279.

TLC (20% EtOAc–hexanes), R_f : 0.48 (UV, KMnO_4).

N-(Thiophen-2-yl)-2-(phenyl)-4-trimethylsilyl-1-azabut-1-en-3-yne (3m, Table 1, entry 13):

Trifluoromethanesulfonic anhydride (195 μL , 1.18 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2m** (200 mg, 0.98 mmol, 1 equiv) and 2-chloropyridine (372 μL , 3.94 mmol, 4.00 equiv) in CH_2Cl_2 (2.0 mL) at $-78\text{ }^\circ\text{C}$. After 10 min, a freshly prepared solution of copper (I) (trimethylsilyl)-acetylide (428 mg, 2.66 mmol, 2.70 equiv) in THF (5.0 mL) at $0\text{ }^\circ\text{C}$ was added via cannula. The reaction mixture was kept at $-78\text{ }^\circ\text{C}$ for 10 min and then warmed to $0\text{ }^\circ\text{C}$. After 10 min, the crude reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes $\rightarrow$ 7.5% EtOAc/hexanes) to afford the alkynyl imine **3m** as a yellow oil (181 mg, 65%).

^1H NMR (500 MHz, CDCl_3 , $20\text{ }^\circ\text{C}$) δ : 8.19–8.13 (m, 2H, ArH), 7.48–7.43 (m, 3H, ArH), 7.42 (dd, 1H, $J = 3.8, 1.4\text{ Hz}$, CHS), 7.32 (dd, 1H, $J = 5.5, 1.4\text{ Hz}$, CHCHCHS), 7.07 (dd, 1H, $J = 5.5, 3.8\text{ Hz}$, CHCHS), 0.40 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

^{13}C NMR (125 MHz, CDCl_3 , $20\text{ }^\circ\text{C}$) δ : 152.2, 140.9, 137.7, 130.6, 129.2, 128.5, 127.9, 125.4, 125.3, 112.0, 99.2, -0.6 .

FTIR (neat) cm^{-1} : 3064 (m), 2960 (s), 2144 (m), 2067 (m), 1537 (m), 1412 (s), 1272 (s), 1253 (s).

HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{18}\text{NSSi}$ $[\text{M}+\text{H}]^+$: 284.0924, found: 284.0934.

TLC (20% EtOAc–hexanes), R_f : 0.63 (UV, CAM).

6-Phenyl-thieno[2,3-*b*]pyridine (1m**, Table 1, entry 13):**

An oven dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (35 mg, 0.21 mmol, 1.0 equiv), $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$ (15 mg, 0.021 mmol, 0.10 equiv) and SPhos (9 mg, 0.021 mmol, 0.10 equiv) under a nitrogen atmosphere in a glove-box and the flask sealed and brought out of the glove-box. Imine **1m** (60 mg, 0.21 mmol, 1 equiv) and toluene (1.1 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105°C . After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (20 % EtOAc/Hexanes) to afford the thienopyridine **1m**¹⁶ as a pale yellow solid (44 mg, 99%).

^1H NMR (500 MHz, CDCl_3 , 20°C): 8.15 (d, 1H, $J = 8.2$ Hz, ArH), 8.11–8.09 (m, 2H, ArH), 7.78 (d, 1H, $J = 8.6$ Hz, ArH), 7.54–7.49 (m, 3H, ArH, SCH), 7.44 (tt, 1H, $J = 7.3, 1.2$ Hz, ArH), 7.30 (d, 1H, $J = 5.8$ Hz, SCHCH).

^{13}C NMR (125 MHz, CDCl_3 , 20°C): 162.4, 154.7, 139.4, 131.7, 131.3, 129.1, 129.0, 127.4, 127.2, 121.5, 117.0.

FTIR (CH_2Cl_2): 3025 (w), 1714 (w), 1574 (s), 1558 (m), 1480 (m), 1333 (m).

HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{10}\text{NS}$ $[\text{M}+\text{H}]^+$: 212.0534, found: 212.0535.

TLC (20% EtOAc–hexanes), R_f : 0.45 (UV, KMnO_4).

¹⁶ Taylor, E. C.; Macor, J. E. *J. Org. Chem.* **1987**, 52, 4280–4287.

[1-Phenyl-3-(trimethyl-silanyl)-prop-2-ynylidene]-thiophen-3-yl-amine (3n, Table 1, entry 14):

Trifluoromethanesulfonic anhydride (294 μL , 1.77 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2n** (300 mg, 1.48 mmol, 1 equiv) and 2-chloropyridine (559 μL , 5.90 mmol, 4.00 equiv) in CH_2Cl_2 (3.0 mL) at $-78\text{ }^{\circ}\text{C}$. After 5 min, the reaction mixture was warmed to $0\text{ }^{\circ}\text{C}$. After 20 min, the solution was cooled to $-78\text{ }^{\circ}\text{C}$ and a freshly prepared solution of copper (I) (trimethylsilyl)-acetylide (641 mg, 3.99 mmol, 2.70 equiv) in THF (5.0 mL) at $0\text{ }^{\circ}\text{C}$ was added via cannula. The reaction mixture was kept at $-78\text{ }^{\circ}\text{C}$ for 5 min and then warmed to $0\text{ }^{\circ}\text{C}$. After 10 min, the crude reaction mixture was filtered through celite (2 cm diam. $\times$ 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes $\rightarrow$ 10% EtOAc/hexanes) to afford the alkynyl imine **3n** as a yellow oil (411 mg, 98%).

^1H NMR (500 MHz, CDCl_3 , $20\text{ }^{\circ}\text{C}$) δ : 8.17 (dd, 2H, $J = 7.6, 1.8\text{ Hz}$, ArH), 7.50–7.43 (m, 4H, ArH, CHS), 7.38 (d, 1H, $J = 5.2\text{ Hz}$, CHS), 7.31 (dd, 1H, $J = 5.2, 3.4\text{ Hz}$, CHCHS), 0.29 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

^{13}C NMR (125 MHz, CDCl_3 , $20\text{ }^{\circ}\text{C}$) δ : 149.9, 147.4, 137.6, 131.0, 128.5, 128.1, 124.9, 124.2, 115.6, 106.1, 98.8, -0.4 .

FTIR (neat) cm^{-1} : 3740 (w), 3108 (m), 3063 (m), 2960 (s), 2899 (m), 2147 (m), 1645 (w), 1586 (m), 1556 (s), 1271 (s).

HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{18}\text{NSSi}$ $[\text{M}+\text{H}]^+$: 284.0929, found: 284.0933.

TLC (20% EtOAc/hexanes), Rf: 0.74 (UV, KMnO_4).

5-Phenyl-thieno[3,2-*b*]pyridine (1n**, Table 1, entry 14):**

An oven dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (58 mg, 0.35 mmol, 1.0 equiv), $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$ (26 mg, 0.035 mmol, 0.10 equiv) and SPhos (15 mg, 0.035 mmol, 0.10 equiv) under a nitrogen atmosphere in a glove-box and the flask sealed and brought out of the glove-box. Imine **3n** (100 mg, 0.35 mmol, 1 equiv) and toluene (1.8 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105°C . After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (15 % EtOAc/Hexanes) to afford the thienopyridine **1n** as a pale yellow solid (73 mg, 97%).

^1H NMR (500 MHz, CDCl_3 , 20°C):	8.26 (d, 1H, $J = 8.6$ Hz, ArH), 8.08 (d, 1H, $J = 7.3$ Hz, ArH), 7.78 (d, 1H, $J = 5.5$ Hz, CHS), 7.73 (d, 1H, $J = 8.5$ Hz, ArH), 7.65 (d, 1H, $J = 5.5$ Hz, CHCHS), 7.52 (t, 2H, $J = 7.0$ Hz, ArH), 7.45 (t, 1H, $J = 7.3$ Hz, ArH).
^{13}C NMR (125 MHz, CDCl_3 , 20°C):	156.4, 155.5, 139.8, 131.7, 131.0, 131.0, 129.0, 128.9, 127.4, 125.5, 116.5.
FTIR (neat):	3071 (s), 1906 (w), 1564 (s), 1544 (s), 1397 (s), 1280 (s), 1158 (s).
HRMS (ESI):	calcd for $\text{C}_{13}\text{H}_{10}\text{NS}$ $[\text{M}+\text{H}]^+$: 212.0534, found: 212.0534.
TLC (20% EtOAc–hexanes), R_f :	0.53 (UV, KMnO_4).

(5,6-Dihydro-4H-pyran-3-yl)-[1-phenyl-3-(trimethyl-silanyl)-prop-2-ynylidene]-amine (3o, Table 1, entry 15):

Trifluoromethanesulfonic anhydride (292 μ L, 1.77 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2o** (300 mg, 1.48 mmol, 1 equiv) and 2-chloropyridine (559 μ L, 5.90 mmol, 4.00 equiv) in CH_2Cl_2 (3.0 mL) at -78°C . After 5 min, the reaction mixture was warmed to 0°C . After 20 min, the solution was cooled to -78°C and a freshly prepared solution of copper (I) (trimethylsilyl)-acetylide (641 mg, 3.99 mmol, 2.70 equiv) in THF (5.0 mL) at 0°C was added via cannula. The reaction mixture was kept at -78°C for 5 min and then warmed to 0°C . After 10 min, the crude reaction mixture was filtered through celite (2 cm diam. $\times$ 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (5% EtOAc/hexanes) to afford the alkynyl imine **3o** as a pale yellow oil (416 mg, 99%).

^1H NMR (500 MHz, C_6D_6 , 20°C) δ : 8.44–8.40 (m, 2H, ArH), 7.44 (bs, 1H, NC=CHO), 7.24–7.20 (m, 2H, ArH), 7.12–7.08 (m, 1H, ArH), 3.58 (t, 2H, $J = 5.2$ Hz, CH_2O), 2.80 (t, 2H, $J = 6.4$ Hz, NCCH_2), 1.46–1.40 (m, 2H, $\text{CH}_2\text{CH}_2\text{O}$), 0.14 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

^{13}C NMR (125 MHz, C_6D_6 , 20°C) δ : 149.7, 139.9, 138.2, 134.3, 129.9, 127.9, 103.2, 102.1, 100.5, 66.6, 24.8, 22.5, -0.2 .

FTIR (neat) cm^{-1} : 3063 (w), 2960 (m), 2920 (m), 2850 (w), 1783 (w), 1724 (s), 1675 (w), 1251 (s), 1176 (s).

HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{22}\text{NOSi}$ $[\text{M}+\text{H}]^+$: 284.1465, found: 284.1471.

TLC (20% EtOAc/hexanes), Rf: 0.67 (UV, KMnO_4).

6-Phenyl-3,4-dihydro-2H-pyrano[3,2-*b*]pyridine (1o**, Table 1, entry 15):**

An oven dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (52 mg, 0.32 mmol, 1.0 equiv), $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$ (23 mg, 0.032 mmol, 0.10 equiv) and SPhos (13 mg, 0.032 mmol, 0.10 equiv) under a nitrogen atmosphere in a glove-box and the flask sealed and brought out of the glove-box. Imine **3o** (90 mg, 0.32 mmol, 1 equiv) and toluene (1.6 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105°C . After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (1 % $\text{Et}_3\text{N}/\text{CH}_2\text{Cl}_2$) to afford the dihydropyranopyridine **1o** as a pale yellow solid (47 mg, 70%).

^1H NMR (500 MHz, CDCl_3 , 20°C): 7.92–7.89 (m, 2H, ArH), 7.49–7.47 (m, 1H, ArH), 7.46–7.42 (m, 2H, ArH), 7.35 (tt, 1H, $J = 7.3, 1.5$ Hz, ArH), 7.16 (d, 1H, $J = 8.6$, ArH), 4.24 (t, 2H, $J = 5.5$ Hz, CH_2O), 3.05 (t, 2H, $J = 6.6$ Hz, NCCH_2), 2.19–2.14 (m, 2H, $\text{CH}_2\text{CH}_2\text{O}$).

^{13}C NMR (125 MHz, C_6D_6 , 20°C): 151.5, 149.6, 144.0, 140.3, 129.2, 128.5, 127.1, 124.6, 119.6, 66.6, 29.2, 22.8.

FTIR (neat): 3061 (w), 3034 (w), 2949 (m), 2874 (m), 1575 (m), 1471 (s), 1458 (s), 1258 (s).

HRMS (EI): calcd for $\text{C}_{14}\text{H}_{13}\text{NO}$ $[\text{M}]^+$: 211.0992, found: 211.0987.

TLC (20% EtOAc–hexanes), R_f : 0.40 (UV, KMnO_4).

N-(N-Triisopropylsilylpyrrol-3-yl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne (3p, Table 1, entry 16):

Trifluoromethanesulfonic anhydride (175 μ L, 1.05 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2p** (300 mg, 0.88 mmol, 1 equiv) and 2-chloropyridine (332 μ L, 3.50 mmol, 4.00 equiv) in CH_2Cl_2 (1.8 mL) at -78°C . After 5 min, the reaction mixture was warmed to 0°C . After 20 min, the solution was cooled to -78°C and a freshly prepared solution of copper (I) (trimethylsilyl)-acetylide (380 mg, 2.37 mmol, 2.70 equiv) in THF (5.0 mL) at 0°C was added via cannula. The reaction mixture was kept at -78°C for 5 min and then warmed to 0°C . After 10 min, the crude reaction mixture was filtered through celite (2 cm diam. $\times$ 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes $\rightarrow$ 10% EtOAc/hexanes) to afford the alkynyl imine **3p** as a yellow oil (304 mg, 82%).

^1H NMR (500 MHz, C_6D_6 , 20°C) δ : 8.63–8.60 (m, 2H, ArH), 7.74 (dd, 1H, $J = 3.1, 1.2$ Hz, CHN), 7.50 (dd, 1H, $J = 2.4, 1.5$ Hz, CHN), 7.29–7.24 (m, 2H, ArH), 7.14 (tt, 1H, $J = 7.3, 1.2$ Hz, ArH), 6.73 (dd, 1H, $J = 3.1, 2.1$ Hz, CHCHN), 1.17 (septet, 3H, $J = 7.3$ Hz, $\text{Si}(\text{CH}(\text{CH}_3)_2)_3$), 0.95 (d, 18, $J = 7.3$ Hz, $\text{Si}(\text{CH}(\text{CH}_3)_2)_3$), 0.22 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

^{13}C NMR (125 MHz, CDCl_3 , 20°C) δ : 140.1, 139.2, 138.4, 129.5, 128.3, 127.4, 125.1, 124.4, 105.8, 105.2, 101.0, 18.0, 11.8, -0.2 .

FTIR (Neat) cm^{-1} : 2948 (m), 2868 (m), 2141 (w), 1547 (w), 1514 (w), 1488 (m), 1252 (s), 1099 (s).

HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{39}\text{N}_2\text{Si}_2$ $[\text{M}+\text{H}]^+$: 423.2646, found: 423.2656.

TLC (20% EtOAc/hexanes), Rf: 0.76 (UV, KMnO_4).

(1-Phenyl-prop-2-ynylidene)-[1-(triisopropyl-silanyl)-1H-pyrrol-3-yl]-amine (4p**, Table 1, entry 16):**

Anhydrous potassium carbonate (23 mg, 0.17 mmol, 0.2 equiv) was added to a solution of imine **3p** (380 mg, 0.83 mmol, 1 equiv) stirred in methanol (2.8 mL) at 23 °C. After 25 min, the volatiles were removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (7.5 % EtOAc/hexanes) to afford the alkynyl imine **4p** as a yellow solid (274 mg, 94%).

1H NMR (500 MHz, $CDCl_3$, 20°C): 8.16–8.12 (m, 2H, ArH), 7.44–7.36 (m, 3H, ArH), 7.29 (t, 1H, $J = 1.8$ Hz, CHN), 7.18 (dd, 1H, $J = 3.1, 1.2$ Hz, CHCHN), 6.77 (dd, 1H, $J = 2.7, 2.1$ Hz, CHCHN), 3.69 (s, 1H, $C\equiv CH$), 1.48 (septet, 3H, $J = 7.6$ Hz, Si(CH(CH₃)₂)₃), 1.14 (d, 18H, $J = 7.5$ Hz, Si(CH(CH₃)₂)₃).

^{13}C NMR (125 MHz, C_6D_6 , 20°C): 139.8, 139.7, 139.4, 130.1, 128.8, 128.0, 125.4, 124.6, 107.2, 86.7, 80.4, 18.1, 12.0.

FTIR (neat): 3296 (m, $C\equiv C-H$), 2947 (s), 2868 (s), 2088 (w, $C\equiv C$), 1547 (w), 1488 (s), 1098 (s).

HRMS (ESI): calcd for $C_{22}H_{31}N_2Si$ [M+H]: 351.2251, found: 351.2264.

TLC (30% EtOAc–hexanes), R_f : 0.83 (UV, $KMnO_4$).

5-Phenyl-1-(triisopropyl-silanyl)-1*H*-pyrrolo[3,2-*b*]pyridine (1p**, Table 1, entry 16):**

An oven dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (33 mg, 0.20 mmol, 1.0 equiv), CpRu(PPh₃)₂Cl (7.3 mg, 0.01 mmol, 0.05 equiv)¹⁷ and SPhos (4.1 mg, 0.01 mmol, 0.05 equiv) under a nitrogen atmosphere in a glove-box and the flask sealed and brought out of the glove-box. Imine **3p** (70 mg, 0.20 mmol, 1 equiv) and toluene (1.0 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 90 °C. After 4 h, the reaction vessel was allowed to cool to ambient temperature and was diluted with dichloromethane (3 mL). This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on basic alumina (15 % EtOAc/Hexanes) to afford the azaindole **1p** as a pale brown solid (46 mg, 65%).

¹H NMR (500 MHz, CDCl₃, 20°C): 8.46–8.42 (m, 2H, ArH), 7.58 (dd, 1H, *J* = 8.7, 0.9 Hz, ArH), 7.53 (d, 1H, *J* = 8.5 Hz, ArH), 7.39–7.34 (m, 2H, ArH), 7.22 (tt, 1H, *J* = 7.3, 1.2 Hz, ArH), 7.14 (d, 1H, *J* = 3.4 Hz, NCHCHC), 7.11 (dd, 1H, *J* = 3.4, 0.6 Hz, NCHCHC), 1.32 (septet, 3H, *J* = 7.6 Hz, Si(CH(CH₃)₂)₃), 0.93 (d, 18H, *J* = 7.6 Hz, Si(CH(CH₃)₂)₃).

¹³C NMR (125 MHz, CDCl₃, 20°C): 151.9, 151.4, 141.8, 135.5, 133.3, 129.2, 128.5, 127.8, 121.3, 114.5, 107.8, 18.3, 13.0.

FTIR (neat): 3062 (w), 2948 (m), 2868 (m), 1561 (w), 1510 (w), 1465 (m), 1407 (s), 1138 (m).

HRMS (ESI): calcd for C₂₂H₃₁N₂Si [M+H]: 351.2251, found: 351.2245.

TLC (20% EtOAc–hexanes), *R*_f: 0.58 (UV, KMnO₄).

¹⁷ Use of higher catalyst loadings led to more *N*-desilylation of the product without improvement in yield of **1p**.

3-Deutero-2-phenylquinoline (**1a-d₁**, Scheme S1):

An oven dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (d_4) (42 mg, 0.25 mmol, 1.0 equiv), $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$ (18 mg, 0.025 mmol, 0.10 equiv) and SPhos (10 mg, 0.025 mmol, 0.10 equiv) under a nitrogen atmosphere in a glove-box and the flask sealed and brought out of the glove-box. Freshly distilled benzene (2×3 mL) was added to the pressure vessel and subsequently removed in vacuo. Imine **3a** (70 mg, 0.25 mmol, 1 equiv) and toluene (1.3 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105°C . After 21 h, the reaction vessel was allowed to cool to ambient temperature and was diluted with dichloromethane (5 mL). This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (5 % EtOAc/Hexanes) to afford the quinoline **1a-d₁** as a pale yellow solid (46 mg, 89%). ^1H and ^{13}C NMR analysis indicates the presence of **1a-C3-H²**, **1a-C4-H²**, and **1a** in a ratio of 68 : 7 : 25.

^1H NMR (500 MHz, CDCl_3 , 20°C ; resonances corresponding to the C3-H² noted by *) δ : 8.25 (d, 1H, $J = 8.2$ Hz, C4-H*), 8.24 (s, 1H, C4-H), 8.21–8.16 (m, 6H, C8-H, C8-H*, C10-H, C10-H*), 7.91 (d, 1H, $J = 8.6$ Hz, C3-H), 7.85 (dd, 1H, $J = 8.2, 1.2$ Hz, C5-H, C5-H*), 7.74 (ddd, 1H, $J = 8.2, 6.7, 1.2$ Hz, C7-H, C7-H*), 7.57–7.52 (m, 6H, C6-H*, C6-H, C11-H, C11-H*), 7.48 (tt, 1H, $J = 7.6, 1.2$ Hz, C12-H, C12-H*).

^{13}C NMR (125 MHz, CDCl_3 , 20°C ; resonances corresponding to the C3-H² noted by *) δ : 157.5 (C2), 157.4 (C2*), 148.5 (C8'), 148.4 (C8'*), 139.9 (C9), 139.8 (C9*), 136.9 (C4*), 136.8 (C4), 129.9 (C7, C7*), 129.8 (C8, C8*), 129.5 (C12, C12*), 129.0 (C11, C11*), 127.7 (C10, C10*), 127.6 (C5, C5*), 127.3 ((4', 4'*), 126.4 (6, 6*), 119.1 (C3), 119.0 (t, $J = 21$ Hz, C3*).

FTIR (CDCl_3) cm^{-1} : 3056 (m), 2918 (w), 2248 (w, C–D), 1962 (w), 1616 (m), 1589 (s), 1552 (s), 1589 (s), 1490 (s).

HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{11}\text{DN}$ $[\text{M}+\text{H}]$: 207.1027, found: 207.1036.

TLC (20% EtOAc–hexanes), R_f : 0.51 (UV, CAM).

Solvent: CDCl₃
 Ambient temperature
 INOVA-500 "rocky"
 PULSE SEQUENCE
 Relax delay 2.000 sec
 Pulse 90.0 degrees
 Acq. time 3.200 sec
 Width 10000.0 Hz
 16 repetitions
 OBSERVE H1, 500.2312691 MHz
 DATA PROCESSING
 FT size 131072
 Total time 1 minute

N-Phenyl-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne

Solvent: CDCl₃
 Ambient temperature
 User: 1-14-87
 INOVA-500 "rocky"
 PULSE SEQUENCE
 Pulse 65.4 degrees
 Acq. time 1.736 sec
 Width 37735.8 Hz
 576 repetitions
 OBSERVE C13, 125.7832286 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 37 dB
 continuously on
 VOLTAGE modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FI size 131072
 Total time 16 minutes

N-Phenyl-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne

Solvent: CCl₃
 Temp. 20.0 C / 293.1 K
 User: 1-14-87
 INOVA-500 "rocky"
 PULSE SEQUENCE
 Relax. delay 0.763 sec
 Pulse 65.4 degrees
 Acq. time 1.736 sec
 Width 37735.8 Hz
 100 repetitions
 OBSERVE C13, 125.7832332 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 44 dB
 continuously on
 VOLTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 131072
 Total time 4 minutes

2-Phenylquinoline

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 INOVA-500 "bulwinkle"
 PULSE SEQUENCE
 Relax. delay 2.000 sec
 Pulse 85.8 degrees
 Acq. time 3.277 sec
 Width 9998.8 Hz
 16 repetitions
 OBSERVE H1, 499.7537722 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 24 sec

N-(4-Methoxyphenyl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne

Solvent: CDCl₃
 Ambient temperature
 User: 1-14-87
 INOVA-500 "rocky"
 PULSE SEQUENCE
 Pulse 65.4 degrees
 Acq. time 1.736 sec
 Width 37735.8 Hz
 136 repetitions
 OBSERVE C13, 125.7832337 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 44 dB
 Continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 131072
 Total time 3 minutes

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 File: mh-1-200A
 INOVA-500 "zippy"
 PULSE SEQUENCE
 Relax delay 1.000 sec
 Pulse 85.8 degrees
 Acq. time 3.277 sec
 Width 3998.8 Hz
 16 repetitions
 OBSERVE H1, 499.7537722 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 8 sec

6-Methoxy-2-phenylquinoline

Pulse Sequence: s2pu1
 Solvent: CDCl3
 Ambient temperature
 User: j-14-87
 INOVA-500 "bottle" "bottle"
 PULSE SEQUENCE
 Relax. delay 3.000 sec
 Pulse 54.0 degrees
 Acq. time 0.869 sec
 Width 3718.1 Hz
 272 repetitions
 OBSERVE C13, 125.6631648 MHz
 DECOUPLE H1, 499.7562709 MHz
 Power 34 dB
 Continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total time 1 hr, 4 min, 41 sec

6-Methoxy-2-phenylquinoline

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 INOVA-500 "bulwinkle"
 PULSE SEQUENCE
 Relax delay 1.000 sec
 Pulse 85.8 degrees
 Acq. time 3.277 sec
 Width 998.8 Hz
 16 repetitions
 OBSERVE M1, 499.746521 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 8 sec

N-(2-Methoxyphenyl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne

S49

Solvent: CDCl₃
 Ambient temperature
 User: 1-14-87
 INOVA-500 "rocky"
 PULSE SEQUENCE
 Pulse 55.4 degrees
 Acq. time 1.736 sec
 Width 37735.8 Hz
 56 repetitions
 OBSERVE C13, 125.7832360 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 37 dB, 500.2332753 MHz
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 131072
 Total time 1 minutes

N-(2-Methoxyphenyl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INDVA-500 "bullwinkle"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1 499.744521 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec

8-Methoxy-2-phenylquinoline

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 User: 1-14-87
 INOVA-500 "bullwinkle"
 PULSE SEQUENCE
 Pulse 34.0 degrees
 Acq. time 0.869 sec
 Width 37718.1 Hz
 384 Repetitions
 OBSERVE C13, 125.6608716 MHz
 DECOUPLE H1, 493.7471508 MHz
 Power 34 dB
 Continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total time 243 hr, 47 min, 34 sec

8-Methoxy-2-phenylquinoline

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 File: mh-I-192column3
 INOVA-500 "zippy"
 PULSE SEQUENCE
 Pulse 85.8 degrees
 Acq. time 3.277 sec
 Width 9998.8 Hz
 16 repetitions
 OBSERVE H1, 499.7537721 MHz
 DATA PROCESSING
 FT size 65536
 Total time 0 min, 52 sec

N-(3-Trifluoromethylphenyl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne

S53

Pulse Sequence: s2pu1
 Solvent: CDCl3
 Ambient temperature
 User: 1-14-87
 INOVA-500 "bullwinkle"
 PULSE SEQUENCE
 Pulse 54.0 degrees
 Acq. time 0.959 sec
 Width 50314.5 Hz
 1008 repetitions
 OBSERVE C13, 125.6631663 MHz
 DECOUPLE H1, 499.7562705 MHz
 Power 34 dB
 Continuously on
 127-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 F1 size 131072
 Total time 2 hr, 41 min, 20 sec

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"
PULSE SEQUENCE
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.753725 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 52 sec

2-Phenyl-7-trifluoromethyl-quinoline

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: :
File: :
INOVA-500 "zippy"
PULSE SEQUENCE
Relax. delay 1.00 sec
Pulse 48.4 degrees
Acq. time 2.001 sec
Width 31397.2 Hz
440 repetitions
OBSERVE C13, 125.660747 MHz
DECOUPLE H1, 499.7471509 MHz
Power 34 dB
continuously on
VOLTAGE-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 336025 hr, 31 min, 7 sec

2-Phenyl-7-trifluoromethyl-quinoline

Solvent: CDCl3
Ambient temperature
INNOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 90.0 degrees
Acq. time 3.200 sec
Width 10000.0 Hz
16 repetitions
OBSERVE H1, 500.2312700 MHz
DATA PROCESSING
FT size 131072
Total time 1 minute

N-Phenyl-2-(thiophen-2-yl)-4-trimethylsilyl-1-azabut-1-en-3-yne

Solvent: CDCl₃
 Ambient temperature
 User: 1-14-87
 INOVA-500 "rocky"
 PULSE SEQUENCE
 Pulse 65.4 degrees
 Acq. time 1.736 sec
 Width 37735.8 Hz
 256 repetitions
 OBSERVE C13, 125.7832280 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 37 dB
 Continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 131072
 Total time 7 minutes

N-Phenyl-2-(thiophen-2-yl)-4-trimethylsilyl-1-azabut-1-en-3-yne

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 INOVA-500 "bullwinkle"
 PULSE SEQUENCE
 Relax delay 2.000 sec
 Pulse 65.6 degrees
 Acq. time 3.277 sec
 Width 998.8 Hz
 16 repetitions
 OBSERVE H1, 499.7446543 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 24 sec

2-Thiophen-2-ylquinoline

Solvent: CDCl₃
 Ambient temperature
 User: 1-14-87
 INOVA-500 "rocky"
 PULSE SEQUENCE
 Pulse 65.4 degrees
 Acq. time 1.736 sec
 Width 37735.8 Hz
 120 repetitions
 OBSERVE C13, 125.7832337 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 131872
 Total time 3 minutes

2-Thiophen-2-ylquinoline

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 INOVA-500 "bullwinkle"
 PULSE SEQUENCE
 Relax . delay 2.000 sec
 Pulse 85.8 degrees
 Acq. time 3.277 sec
 Width 998.8 Hz
 16 repetitions
 OBSERVE H1, 499.753719 MHz
 DATA PROCESSING
 FI size 65536
 Total time 1 min, 24 sec

N-Phenyl-2-cyclohexyl-4-trimethylsilyl-1-azabut-1-en-3-yne

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 User: 1-14-87
 INOVA-500 "bullwinkle"
 PULSE SEQUENCE
 Pulse 54.0 degrees
 Acq time 0.863 sec
 Width 3718.1 Hz
 208 repetitions
 OBSERVE C13, 125.6631654 MHz
 DECOUPLE H1, 499.7562709 MHz
 Power 34 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total time 243 hr, 47 min, 34 sec

N-Phenyl-2-cyclohexyl-4-trimethylsilyl-1-azabut-1-en-3-yne

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 INOVA-500 "bullwinkle"
 PULSE SEQUENCE
 Relax delay 1.000 sec
 Pulse 85.8 degrees
 Acq. time 3.277 sec
 Width 338.8 Hz
 16 repetitions
 OBSERVE H1, 433.746540 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 8 sec

2-Cyclohexyl-quinoline

Solvent: CDCl₃
 Ambient temperature
 User: 1-14-87
 INOVA-500 "rocky"
 PULSE SEQUENCE
 Pulse 55.4 degrees
 Acq. time 1.736 sec
 Width 37735.8 Hz
 416 repetitions
 OBSERVE C13, 125.7832274 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 131972
 Total time 12 minutes

2-Cyclohexyl-quinoline

Solvent: CDCl₃
 Ambient temperature
 INOVA-500 "rocky"
 PULSE SEQUENCE
 Relax - delay 2.000 sec
 Pulse 90.0 degrees
 Acq. time 3.200 sec
 Width 10000.0 Hz
 16 repetitions
 OBSERVE H1, 500.2312702 MHz
 DATA PROCESSING
 FT size 131072
 Total time 1 minute

N-Phenyl-2-(*tert*-butyl)-4-trimethylsilyl-1-azabut-1-en-3-yne

Solvent: CDCl₃
 Ambient temperature
 User: j-14-87
 INOVA-500 "Rocky"
 PULSE SEQUENCE
 Pulse 65.4 degrees
 Acq. time 1.736 sec
 Width 37735.8 Hz
 160 repetitions
 OBSERVE C13, 125.7832268 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 37 dB
 Continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 131072
 Total time 4 minutes

N-Phenyl-2-(*tert*-butyl)-4-trimethylsilyl-1-azabut-1-en-3-yne

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 INOVA-500 "bulwinkle"
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 85.8 degrees
 Acq. time 3.277 sec
 Width 3336.8 Hz
 16 repetitions
 OBSERVE H1, 499.744521 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 8 sec

(1-*tert*-Butyl-prop-2-ynylidene)-phenyl-amine

Solvent: CDCl₃
 Ambient temperature
 User: 1-14-87
 INOVA-500 "Rocky"
 PULSE SEQUENCE
 Relax. delay 0.763 sec
 Pulse 65.4 degrees
 Acq. time 1.736 sec
 Width 37735.8 Hz
 32 repetitions
 OBSERVE C13, 125.7832291 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 131072
 Total time 1 minute

(1-*tert*-Butyl-prop-2-ynylidene)-phenyl-amine

Pulse Sequence: s2pu1
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 998.8 Hz
16 repetitions
OBSERVE H1, 499.7446552 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec

2-tert-Butyl-quinoline

Solvent: CDCl₃
 Ambient temperature
 User: 1-14-87
 INOVA-500 "Rocky"
 PULSE SEQUENCE
 Relax. delay 0.763 sec
 Pulse 65.4 degrees
 Acq. time 1.000 sec
 Width 37735.8 Hz
 3112 repetitions
 OBSERVE C13, 125.7832263 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 37 dB, continuously on
 VALT2-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FI size 131072
 Total time 31 minutes

2-tert-Butyl-quinoline

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 File: mh-11-110fr12-14
 INOVA-500 "Zippy"
 PULSE SEQUENCE
 Relax. delay 2.000 sec
 Pulse 85.8 degrees
 Acq. time 3.277 sec
 Width 998.8 Hz
 16 repetitions
 OBSERVE H1 499.7537708 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 24 sec

N-Phenyl-2-(morpholin-4-yl)-4-trimethylsilyl-1-azabut-1-en-3-yne

Pulse Sequence: s2pu)
 Solvent: CDCl₃
 Ambient temperature
 User: 1-14-87
 INOVA-500 "bullwinkle"
 PULSE SEQUENCE
 Pulse 54.0 degrees
 Acq. time 0.869 sec
 Width 37718.1 Hz
 880 repetitions
 OBSERVE C13, 125.6631607 MHz
 DECOUPLE H1, 499.7562709 MHz
 Power 34 dB,
 continuously on
 VALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total time 243 hr, 47 min, 34 sec

N-Phenyl-2-(morpholin-4-yl)-4-trimethylsilyl-1-azabut-1-en-3-yne

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 File: mh-II-281
 INOVA-500 "Zippy"
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 95.8 degrees
 Acq. time 3.277 sec
 Width 3998.8 Hz
 16 repetitions
 OBSERVE H1, 499.746521 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 8 sec

Solvent: CDCl₃
 Ambient temperature
 User: l-14-87
 INOVA-500 "rocky"
 PULSE SEQUENCE
 Relax. delay 0.763 sec
 Pulse 65.4 degrees
 Acq. time 1.736 sec
 Width 37735.8 Hz
 8 repetitions
 OBSERVE C13, 125.7832383 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 37 dB, continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 131072
 Total time 1 minute

2-Morpholin-4-yl-quinoline

Pulse Sequence: s2pu1
 Solvent: CDCl3
 Ambient temperature
 INOVA-500 "bullwinkle"
 PULSE SEQUENCE
 Relax . delay 2.000 sec
 Pulse 85.8 degrees
 Acq. time 3.277 sec
 Width 9998.8 Hz
 16 repetitions
 OBSERVE H1, 499.7537722 MHZ
 DATA PROCESSING
 File size 65536
 Total time 1 min, 24 sec

N-(*trans*- β -Styryl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne

Pulse Sequence: s2pul
 Solvent: CDCl₃
 Ambient temperature
 User: i-14-87
 INOVA-500 "bullwinkle"
 PULSE SEQUENCE
 Pulse 54.0 degrees
 Acq. time 0.869 sec
 Width 37718.1 Hz
 2144 repetitions
 OBSERVE C13, 125.6631607 MHz
 DECOUPLE H1, 499.7562709 MHz
 Power 34 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total time 24 hr, 22 min, 46 sec

N-(*trans*- β -Styryl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 INOVA-500 "bulwinkle"
 PULSE SEQUENCE
 Relax. delay 2.000 sec
 Pulse 85.8 degrees
 Acq. time 3.277 sec
 Width 998.8 Hz
 16 Repetitions
 OBSERVE H1, 499.7448540 MHz
 DATA PROCESSING
 F1 size 65536
 Total time 1 min, 24 sec

2,5-Diphenyl-pyridine

Solvent: CDCl₃
 Ambient temperature
 User: 1-14-87
 INOVA-500 "rocky"
 PULSE SEQUENCE
 Pulse 65.4 degrees
 Acq. time 1.736 Sec
 Width 37735.8 Hz
 584 repetitions
 OBSERVE C13, 125.7832274 MHz
 DECOUPLE H1, 500.232753 MHz
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 131072
 Total time 16 minutes

2,5-Diphenyl-pyridine

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 INOVA-500 "bulwinkle"
 PULSE SEQUENCE
 Relax delay 1.000 sec
 Pulse 85.6 degrees
 Acq. time 3.277 sec
 Width 998.8 Hz
 16 repetitions
 OBSERVE H1, 499.746540 MHz
 DATA PROCESSING
 FT size 85536
 Total time 1 min, 8 sec

(2-Naphthalen-1-yl-vinyl)-[1-phenyl-3-(trimethyl-silanyl)-prop-2-ynylidene]-amine

Solvent: CDCl₃
 Ambient temperature
 User: 1-14-87
 File: mh-III-194carbon
 INOVA-500 "rocky"
 PULSE SEQUENCE
 Relax. delay 0.763 sec
 Pulse 65.4 degrees
 Acq. time 1.236 sec
 Width 37735.8 Hz
 8 repetitions
 OBSERVE C13, 125.7831641 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 37 dB
 Continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 131072
 Total time 1 minute

(2-Naphthalen-1-yl-vinyl)-[1-phenyl-3-(trimethyl-silanyl)-prop-2-ynylidene]-amine

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bottlewinkle"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9988.8 Hz
16 repetitions
OBSERVE H1, 499.7446540 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec

5-Naphthalen-1-yl-2-phenyl-pyridine

Solvent: CDCl₃
 Ambient temperature
 User: 1-14-87
 , INOVA-500 "rocky"
 PULSE SEQUENCE
 Relax. delay 0.763 sec
 Pulse 65.4 degrees
 Acq. time 1.736 sec
 Width 37735.8 Hz
 32 repetitions
 OBSERVE C13, 125.78326 MHz
 DECOUPLE H1, 500.232753 MHz
 Power 37 dB
 Continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 131072
 Total time 1 minute

5-Naphthalen-1-yl-2-phenyl-pyridine

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 INOVA-500 "bullwinkle"
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 85.8 degrees
 Acq. time 3.277 sec
 Width 9998.8 Hz
 16 repetitions
 OBSERVE H1, 499.746521 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 8 sec

[2-(3,4-Dimethoxy-phenyl)-vinyl]-[1-phenyl-3-(trimethyl-silanyl)-prop-2-ynylidene]-amine

Solvent: CDCl₃
 Ambient temperature
 User: 1-14-87
 INOVA-500 "rocky"

PULSE SEQUENCE
 Relax. delay 0.763 sec
 Pulse 65.4 degrees
 Acq. time 1.736 sec
 Width 37735.8 Hz
 24 repetitions
 OBSERVE C13, 125.7832395 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 131072
 Total time 1 minute

[2-(3,4-Dimethoxy-phenyl)-vinyl]-[1-phenyl-3-(trimethyl-silanyl)-prop-2-ynylidene]-
 amine

DATA CHANNEL: 220.1

0.013

Ambient temperature

INDVA-500 "bullwinkle"

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 85.8 degrees

Acq. time 3.277 sec

Width 9998.8 Hz

16 repetitions

OBSERVE H1 499.746540 MHz

DATA PROCESSING

FT size 65536

Total time 1 min, 8 sec

5-(3,4-Dimethoxy-phenyl)-2-phenyl-pyridine

Solvent: CDCl₃
 Ambient temperature
 User: 1-14-87
 File: mh-III-211carbon
 INOVA-500 "rocky"
 PULSE SEQUENCE
 Relax. delay 0.763 sec
 Pulse 65.4 degrees
 Acq. time 1.736 sec
 Width 37735.8 Hz
 16 repetitions
 OBSERVE C13, 125.7832418 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 131072
 Total time 1 minute

5-(3,4-Dimethoxy-phenyl)-2-phenyl-pyridine

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 INOVA-500 "bulwinkle"
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 65.8 degrees
 Acq. time 3.277 sec
 Width 999.8 Hz
 16 repetitions
 OBSERVE H1 499.7446521 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 8 sec

N-(Cyclohexen-1-yl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne

Solvent: CDCl₃
 Ambient temperature
 User: 1-14-87
 INOVA-500 "rocky"
 PULSE SEQUENCE
 Relax delay 0.763 sec
 Pulse 65.4 degrees
 Acq. time 1.000 sec
 Width 37735.8 Hz
 344 repetitions
 OBSERVE C13, 125.7632263 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 37 dB
 continuously on
 VOLTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 131072
 Total time 10 minutes

N-(Cyclohexen-1-yl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 INOVA-500 "bullwinkle"
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 85.8 degrees
 Acq. time 3.277 sec
 Width 9998.8 Hz
 16 repetitions
 OBSERVE H1 499.746521 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 8 sec

2-Phenyl-5,6,7,8-tetrahydro-quinoline

Solvent: CDCl₃
 Ambient temperature
 User: 1-14-87
 INOVA-500 "rocky"
 PULSE SEQUENCE
 Relax. delay 0.763 sec
 Pulse 65.4 degrees
 Acq. time 1.736 sec
 Width 37735.8 Hz
 24 repetitions
 OBSERVE C13, 125.7832303 MHz
 DECOUPLE H1, 500.2332753 MHz
 continuously On
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FI size 131072
 Total time 1 minute

2-Phenyl-5,6,7,8-tetrahydro-quinoline

Solvent: CDCl3
 Ambient temperature
 INOVA-500 "rocky"
 PULSE SEQUENCE
 Relax delay 2.000 sec
 Pulse 90.0 degrees
 Acq. time 3.200 sec
 Width 10000.0 Hz
 16 repetitions
 OBSERVE H1, 500.2312695 MHz
 DATA PROCESSING
 FT size 131072
 Total time 1 minute

N-(Thiophen-2-yl)-2-(phenyl)-4-trimethylsilyl-1-azabut-1-en-3-yne

Solvent: CDCl₃
 Ambient temperature
 User: J-14-87
 INOVA-500 "rocky"
 PULSE SEQUENCE
 Pulse 65.4 degrees
 Acq. time 1.736 sec
 Width 37735.8 Hz
 1192 repetitions
 OBSERVE C13, 125.7832268 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 6.3 Hz
 FT size 131872
 Total time 34 minutes

N-(Thiophen-2-yl)-2-(phenyl)-4-trimethylsilyl-1-azabut-1-en-3-yne

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INNOVA-500 "bulwinkle"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 998.8 Hz
16 repetitions
OBSERVE H1, 499.7446552 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec

6-Phenyl-thieno[2,3-*b*]pyridine

Solvent: CDCl₃
 Ambient temperature
 User: 1-14-87
 INOVA-500 "Rocky"
 PULSE SEQUENCE
 Pulse 65.4 degrees
 Acq. time 1.736 sec
 Width 37735.8 Hz
 208 repetitions
 OBSERVE C13, 125.7832314 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 131072
 Total time 6 minutes

6-Phenyl-thieno[2,3-*b*]pyridine

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INNOVA-500 "bullwinkle"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.746521 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec

[1-Phenyl-3-(trimethyl-silanyl)-prop-2-ynylidene]-thiophen-3-yl-amine

Solvent: CDCl₃
 Ambient temperature
 User: 1-14-87
 INOVA-500 "rocky"
 PULSE SEQUENCE
 Relax. delay 0.763 sec
 Pulse 65.4 degrees
 Acq. time 1.736 sec
 Width 37735.8 Hz
 24 repetitions
 OBSERVE C13, 125.7832418 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 37 dB
 Continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 131072
 Total time 1 minute

[1-Phenyl-3-(trimethyl-silanyl)-prop-2-ynylidene]-thiophen-3-yl-amine

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 File: mh-111-113
 INOVA-500 "zippy"
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 90.0 degrees
 Acq. time 3.277 sec
 Width 9998.8 Hz
 16 Repetitions
 OBSERVE H1, 499.746549 MHz
 DATA PROCESSING
 F1 size 65536
 Total time 1 min, 8 sec

5-Phenyl-thieno[3,2-*b*]pyridine

Solvent: CDCl₃
 Ambient temperature
 User: J-14-87
 INOVA-500 "rocky"
 PULSE SEQUENCE
 Relax. delay 0.763 sec
 Pulse 65.4 degrees
 Acq. time 1.736 sec
 Width 37735.8 Hz
 16 repetitions
 OBSERVE C13, 125.7832458 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 131072
 Total time 1 minute

5-Phenyl-thieno[3,2-*b*]pyridine

Pulse Sequence: s2pul
 Solvent: Benzene
 Ambient temperature
 INOVA-500 "bullwinkle"
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 85.8 degrees
 Acq. time 3.277 sec
 Width 998.8 Hz
 16 repetitions
 OBSERVE H1, 499.7446971 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 8 sec

(5,6-Dihydro-4H-pyran-3-yl)-[1-phenyl-3-(trimethyl-silanyl)-prop-2-ynylidene]-amine

Solvent: Benzene
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Pulse 65.4 degrees
Acq. time 1.000 sec
Width 37735.8 Hz
744 repetitions
OBSERVE C13, 125.7831721 MHz
DECOUPLE H1, 500.2333204 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 12 minutes

(5,6-Dihydro-4H-pyran-3-yl)-[1-phenyl-3-(trimethyl-silanyl)-prop-2-ynylidene]-amine
S100

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 INOVA-500 "bullwinkle"
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 85.8 degrees
 Acq. time 3.277 sec
 Width 9998.8 Hz
 16 repetitions
 OBSERVE H1, 499.7446540 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 8 sec

6-Phenyl-3,4-dihydro-2H-pyrano[3,2-b]pyridine

Pulse Sequence: s2pul
 Solvent: Benzene
 Ambient temperature
 User: 1-14-87
 File: mh-III-oxygen
 INOVA-500 "zippy"
 PULSE SEQUENCE
 Pulse 65.4 degrees
 Acq. time 1.000 sec
 Width 37735.8 Hz
 100000 repetitions
 OBSERVE C13, 125.7831761 MHz
 DECOUPLE H1, 500.233204 MHz
 Power 37 dB
 Continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 131072
 Total time 280 hr, 14 min, 55 sec

6-Phenyl-3,4-dihydro-2H-pyrano[3,2-b]pyridine

Pulse Sequence: s2p.
 Solvent: Benzene
 Ambient temperature
 INOVA-500 "Bullwinkle"
 PULSE SEQUENCE
 Relax delay 1.000 sec
 Pulse 85.8 degrees
 Acq. time 3.277 sec
 Width 998.6 Hz
 16 repetitions
 OBSERVE H1, 499.7446837 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 8 sec

N-(N-Triisopropylsilylpyrrol-3-yl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne

Solvent: CDCl₃
Ambient temperature
User: 1-14-87
INOVA-500 "Rocky"
PULSE SEQUENCE
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.6 Hz
40 repetitions
OBSERVE C13, 125.7832309 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FI size 131072
Total time 1 minute

N-(*N*-Triisopropylsilylpyrrol-3-yl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 INOVA-500 "bulwinkle"
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 85.8 degrees
 Acq. time 3.277 sec
 Width 998.8 Hz
 16 repetitions
 OBSERVE H1, 499.7446521 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 8 sec

(1-Phenyl-prop-2-ynylidene)-[1-(triisopropyl-silanyl)-1H-pyrrol-3-yl]-amine

Pulse Sequence: s2pu1
 Solvent: Benzene
 Ambient temperature
 Mercury-300 "mrhat"

Pulse 30.3 degrees
 Acq. time 2.501 sec
 Width 22624.4 Hz
 214 repetitions
 OBSERVE C13, 75.4598148 MHz
 DECOUPLE H1, 300.1001963 MHz
 Power 39 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 262144
 Total time 261 hr, 9 min, 1 sec

(1-Phenyl-prop-2-ynylidene)-[1-(triisopropyl-silanyl)-1H-pyrrol-3-yl]-amine

Pulse Sequence: s2pu1
 Solvent: Benzene
 Ambient temperature
 INOVA-500 "bullwinkle"
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 85.8 degrees
 Acq. time 3.277 sec
 Width 9998.8 Hz
 16 repetitions
 OBSERVE H1, 499.7466834 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 8 sec

5-Phenyl-1-(triisopropyl-silanyl)-1*H*-pyrrolo[3,2-*b*]pyridine

Pulse Sequence: s2pul
 Solvent: Benzene
 Ambient temperature
 Mercury-300 "mrhat"

Pulse 30.3 degrees
 Acq. time 2.501 sec
 Width 22624.4 Hz
 257 repetitions
 OBSERVE C13, 75.4598150 MHz
 DECOUPLE H1, 300.1001963 MHz
 Power 39 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 262144
 Total time 261 hr, 9 min, 1 sec

5-Phenyl-1-(triisopropyl-silanyl)-1H-pyrrolo[3,2-b]pyridine

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 File: mh-III-295
 INOVA-500 "Zippy"
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 85.8 degrees
 Acq. time 3.277 sec
 Width 9998.8 Hz
 16 repetitions
 OBSERVE H1 499.748549 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 8 sec

3-Deutero-2-phenylquinoline

Pulse Sequence: s2pu1
 Solvent: CDCl3
 Ambient temperature
 User: 1-14-87
 File: mh-111-235carbon
 INOVA-500 "Zippy"
 PULSE SEQUENCE
 Pulse 65.4 degrees
 Acq. time 1.000 sec
 Width 37735.8 Hz
 1376 repetitions
 OBSERVE C13, 125.7832371 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 line broadening 0.3 Hz
 FT size 131072
 Total time 2802 hr, 29 min, 10 sec

3-Deutero-2-phenylquinoline

Pulse Sequence: HMQDEC

2-Phenylquinoline Homo-nuclear Decoupling NMR

S111

Pulse Sequence: HSQC

Solvent: CDCl₃

Ambient temperature

User: 1-14-87

INQVA-500 "bullwinkle"

PULSE SEQUENCE: HSQC

Relax. delay 1.000 sec

Acq. time 0.100 sec

Width 5783.7 Hz

20 Width 19329.7 Hz

4 repetitions

2 x 128 increments

OBSERVE H1, 499.7537722 MHz

DECOUPLE C13, 125.6781982 MHz

Power 52 dB

on during acquisition

off during delay

GARP-1 modulated

DATA PROCESSING

Sq. sine bell 0.100 sec

Shifted by -0.100 sec

F1 DATA PROCESSING

Gauss apodization 0.012 sec

F1 size 2048 x 2048

Total time 23 min, 6 sec

2-Phenylquinoline HSQC

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