4-Iminocyclobutenones: Synthesis and Building-Blocks of Aminohydroquinones and Annulated Quinolines

Gerrit Oppermann,[a] Michael Stranberg,[b] Harold W. Moore,[b] Ernst Schaumann,*[a] Gunadi Adiwidjaja[c]

[a] Clausthal University of Technology, Institute of Organic Chemistry, Leibnizstr. 6, 38678 Clausthal-Zellerfeld, Germany
Fax +49(5323)722858; E-mail: ernst.schaumann@tu-clausthal.de

[b] Department of Chemistry, University of California, Irvine, CA 92717, USA

[c] Mineralogisch-Petrographisches Institut der Universität Hamburg, Grindelallee 46, 20146 Hamburg, Germany

Received 14 January 2010; revised 22 March 2010

Abstract: Two methods are presented for the synthesis of the title compounds starting from cyclobutenediones: an alkoxide substitution approach and a Staudinger reaction. Unsaturated lithiumorganyls may be added to the remaining carbonyl group and on heating lead to ring enlargement in a cascading process. 4-Alkenyl or 4-aryl derivatives yield aminophenols or -naphthols; 4-alkynyl compounds give cyclopenta-annulated quinolines.

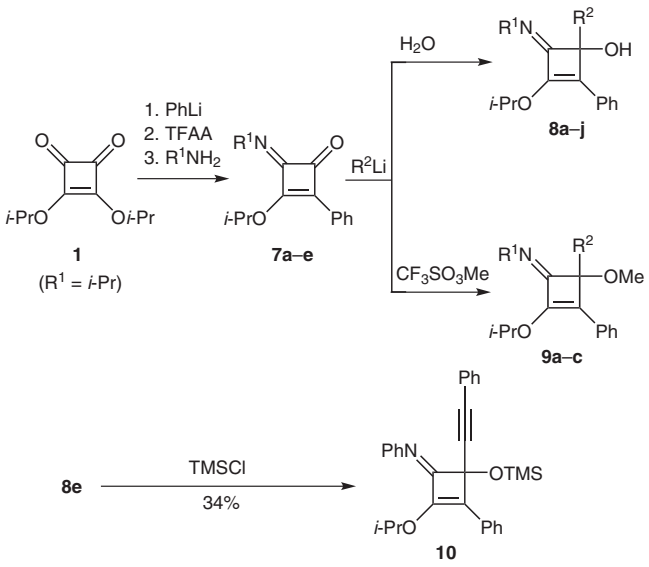
Key words: alkenes, Schiff bases, electrocyclic reactions, ring expansion, ring opening

Cyclobutenones have attracted wide attention as synthetic building-blocks primarily due to their facile electrocyclic ring opening to reactive conjugated ketenes, intermediates that lead to a variety of useful stable products. This chemistry has been studied by a number of research groups.[1–5]

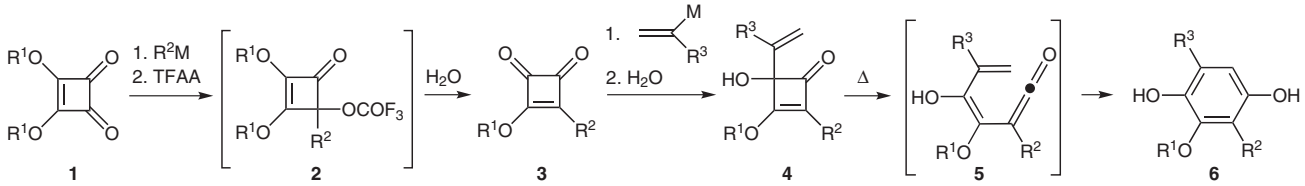
An important feature of the methodology rests on the simple substitution of an alkoxy group in the readily available dialkyl squarates **1** by a variety of other substituents upon treatment with carbanions to give **3** in a one-pot reaction sequence.[6–8] Subsequent 1,2-addition of unsaturated organometallics yields **4** which sets the stage for an electrocyclic cascade to, for example, hydroquinones **6** via the corresponding dienylketene **5** (Scheme 1).

Compared to cyclobutene(di)ones, the corresponding heteroanalogues have received relatively little attention. Thione derivatives have been prepared as such[9] or as thioacetals[10,11] and there are scattered reports on cyclobutenimines although no general synthesis is available.[12–14] The present study fills this gap and opens the door for a comparison of the cyclobutenone chemistry outlined in Scheme 1 with that of the nitrogen congeners.

The final step in the conversion of **1** into **3** involves the displacement of trifluoroacetate in **2** by water in an S_N2' reaction; analogously, alcohols can be used to supply cyclobutenone acetals.[6–8] We now find that amines can be employed to give iminocyclobutenones. Thus, treatment of **1** (R^1 = *i*-Pr) with anilines or 3-aminopyridine yields iminocyclobutenones **7**, the title compounds of the present study (Scheme 2). For the given examples, yields are good to excellent (Table 1); however, imines formed with alkylamines, with the exception of *N*-*tert*-butylamine, were found to be too sensitive to hydrolysis during work-up, thus giving cyclobutenediones **3** as the final product.



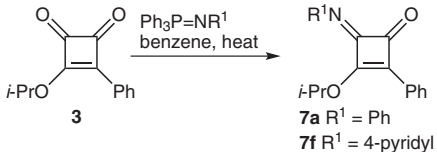
Scheme 2 Synthesis of iminocyclobutenones **7** and reaction with organometallics



Scheme 1 Modification of squarates **1** and electrocyclic ring opening to hydroquinones **6**

SYNTHESIS 2010, No. 12, pp 2027–2038
Advanced online publication: 05.05.2010
DOI: 10.1055/s-0029-1218767; Art ID: T01110SS

Another limitation of the method described in Scheme 2 was found in attempts to use 4-aminopyridine. Here, no reaction was observed apparently due to the reduced nucleophilicity of the conjugated amino group. However, we found that the Staudinger reaction[15] of cyclobutenediones **3** (R^1 = *i*-Pr, R^2 = Ph) with iminophosphoranes offers an alternative (Scheme 3). This method gave an even better yield of iminocyclobutenone **7a** and, furthermore allowed the synthesis of imine **7f** bearing the 4-pyridyl substituent (Table 1).



Scheme 3 Staudinger reaction of cyclobutenedione **3**

Table 1 Synthesis of Cyclobutenimines **7** from Diisopropyl Squarate (**1**) According to Scheme 2 or from Cyclobutenedione **3** (Scheme 3)

Compound	R^1	Method of scheme	Yield (%)
7a	Ph	2	83
		3	69
7b	4-$MeOC_6H_4$	2	85
7c	4-$F_3CC_6H_4$	2	71
7d	2,4,6-$Me_3C_6H_2$	2	52
7e	3-$H_2NC_6H_4N$	2	50
7f	4-$H_2NC_5H_4N$	3	68

In general, iminocyclobutenones **7** are characterized by IR absorptions at approximately 1690 cm^{-1} (imino stretch) and 1750 cm^{-1} (carbonyl stretch); the ^{13}C NMR spectra show resonances for the imino and carbonyl carbons at approximately 165 and 188 ppm, respectively. Interestingly, only one set of NMR data is observed though inversion at the imino nitrogen should be slow on the NMR time scale (vide infra for **16**, **22**, **27**). This indicates that only one isomer is formed, but there is no clue as to structure assignment.

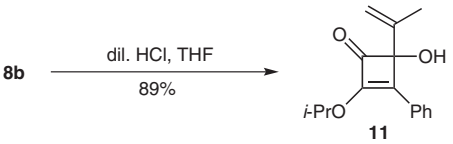
As noted above, additions of sp^2-hybridized carbon-based nucleophiles to cyclobutenediones provide 1,2-adducts and they can function as precursors to a variety of ring expanded products via an electrocyclic cascade (Scheme 1). It was of interest to study analogous reactions of iminocyclobutenones **8** and **9** where it is an open question as to whether a dienylketenimine intermediate **12** will allow ring-closure reactions similar to those observed for the more electrophilic[16] dienylketenes **5** (Scheme 1).

Lithiumorganyls give a smooth 1,2-addition to the carbonyl group in iminocyclobutenones **7** (Scheme 2). The reaction mixture may be quenched with water to give tertiary alcohols **8** or the alkoxide intermediate may be methylated to provide ethers **9** (Table 2); alcohol **8e** can be silylated to silyl ether **10** (Scheme 2). Products **8**, **9** can be isolated without competing hydrolysis of the imino unit. However, hydrolysis can be achieved by stirring with dilute hydrochloric acid to give the corresponding oxo compound as shown for the conversion of imine **8b** into cyclobutenone **11** (Scheme 4).

Table 2 Addition of Organometallics to Iminocyclobutenones **7**

Starting material	Reagent R^2Li	Product	Yield (%) of **8** or **9**
7a	H_2C=CHLi	**8a**	46
7a	H_2C=CMeLi	**8b**	82
7a	PhLi	**8c**	96
7a	$TMSCH_2C{\equiv}CLi$	**8d**	59
7a	$PhC{\equiv}CLi$	**8e**	89
7b	$PhC{\equiv}CLi$	**8f**	67
7c	$PhC{\equiv}CLi$	**8g**	–[a]
7d	$PhC{\equiv}CLi$	**8h**	86
7e	$PhC{\equiv}CLi$	**8i**	80
7f	$PhC{\equiv}CLi$	**8j**	36
7a	PhLi	**9a**	60
7a	3-MeC_6H_4Li	**9b**	70
7a	3-$MeOC_6H_4Li$	**9c**	87

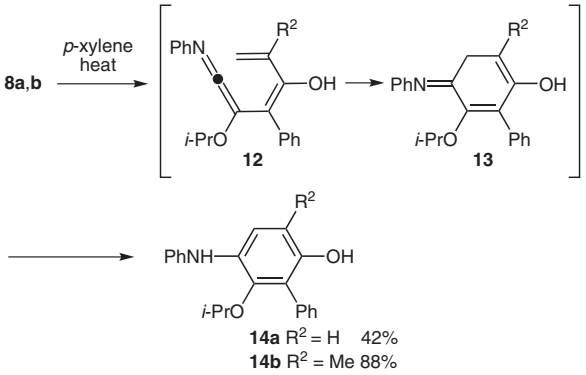
[a] The compound was generated and used in situ for the synthesis of **25d** (Table 4).



Scheme 4 Hydrolysis of iminocyclobutenone **8b**

It should be noted that product **11** is regioisomeric with **4** (R^1 = *i*-Pr, R^2 = Ph, R^3 = Me), formed directly from dione **3**. Thus, the imino group in **7** functions as a protective group for one oxo unit directing the addition of the lithiumorganyl to the otherwise less reactive vinylogous ester unit in **7**. In fact, the imino group appears to be a general and efficient protective group in cyclobutenone chemistry.

Thermolysis of cyclobutenimines **8a**,**b** in refluxing *p*-xylene followed by rapid workup to avoid oxidation gave aminophenols **14a**,**b** as the sole product (Scheme 5). This result is consistent with the paradigm that the ring expansion of iminocyclobutenes proceeds via a mechanism analogous to that described for the corresponding cyclobutenones (Scheme 1), that is, the switch from an intermediate dienylketene to a dienylketenimine does not change the reaction route. It may be noted that heat is required; the ring expansion is obviously not sufficiently supported by the oxy-anion, formed as an intermediate on



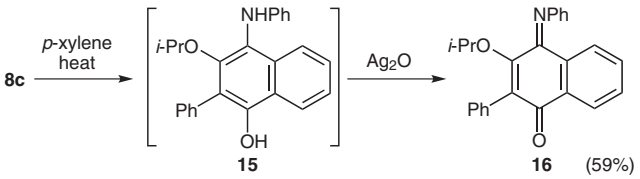
Scheme 5 Thermolysis of 4-alkenylcyclobutenimines **8a**,**b**

addition of lithiumorganyls to cyclobutenones **7** (Scheme 2).

To emphasize once again the regiocontrol available with iminocyclobutenones as compared to the related cyclobutenones, note that aminophenol **14b** (arising from **8b**, Scheme 5) bears a substitution pattern different from that of the hydroquinone that would arise form the corresponding cyclobutenone **4** (Scheme 1).

The thermolysis studies were extended to include the ring expansion of 4-aryl analogues. This resulted in a viable route to aminonaphthols as shown for the ring expansion of **8c** (Scheme 6). However, the initially formed air-sensitive aminonaphthol **15** was not isolated, but oxidized (Ag_2O)[17] directly to iminonaphthoquinone **16**, isolated in 59% yield (Scheme 6). The NMR spectra of **16** are quite complex obviously due to slow inversion at the imino nitrogen and formation of *E*/*Z* isomers.

The ring expansion studies were further expanded to include the ethers **9** (Scheme 7). For example, thermolysis



Scheme 6 Thermolysis of 4-phenylcyclobutenimine **8c**

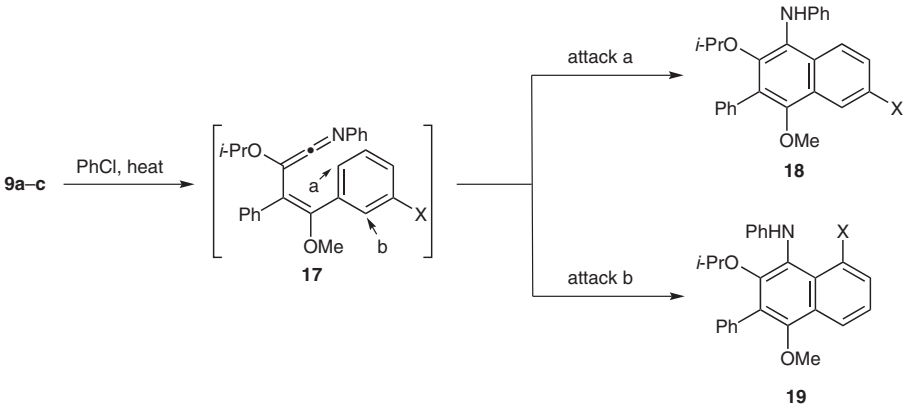
of **9a** gave aminonaphthalene **18** (X = H) in 81% yield. For the 3-tolyl and 3-methoxy derivatives **9b**,**c** there are two possible options for ring closure, *p*- ('attack a') or *o*-substitution ('attack b') relative to substituent X. Not unexpectedly, mixtures of **18**/**19** were formed with a clear preference for the '*p*-product' **18** (Table 3). This is in line with the smaller steric shielding of position 'a' and with a polarized transition state of the electrocyclic process. The same competition of two substitution pathways was observed earlier for the cyclization of the ketene congeners of ketenimines **17**.[18] In that case, the cyclization was found to be less selective, demonstrating the higher electrophilicity and thus lower selectivity for the ketene attack as compared to the ketenimine. In addition, the smaller carbonyl group in ketenes relative to the imino unit in **17** would be expected to further reduce selectivity.

Table 3 Products of the Ring Expansion of 4-Aryl-4-methoxycyclobutenimines **9**

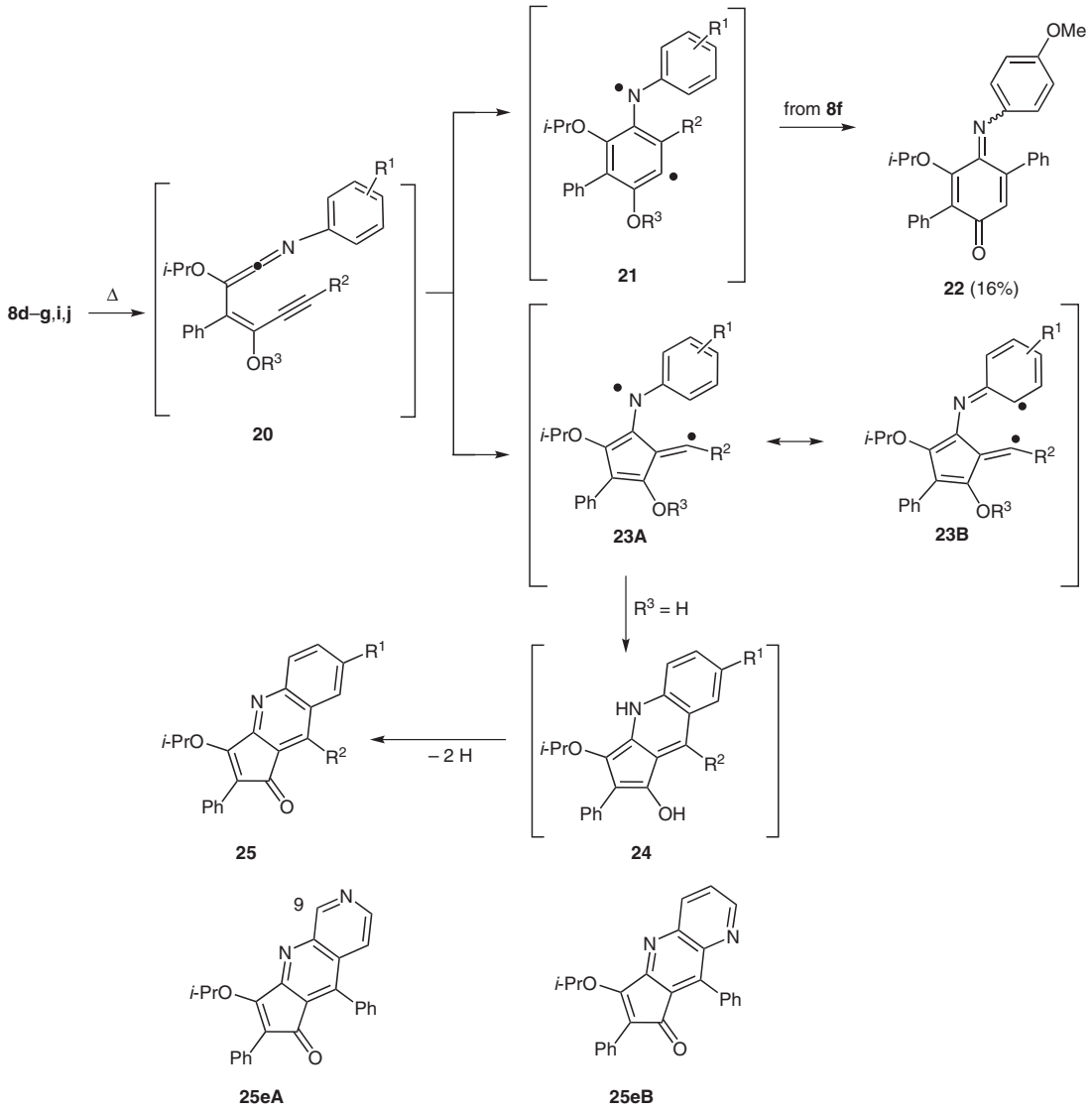
Starting material	Substituent X	Product **18**	Yield (%)	Product **19**	Yield (%)
9a	H	**18a**	81	–	–
9b	Me	**18b**	40	**19a**	11
9c	OMe	**18c**	57	**19b**	18

While there is no reason to doubt the concerted nature of the electrocyclizations of dienylketenes such as **5** or dienylketenimines such as **12**, ring closure of the corresponding enynylketene intermediates arising from **8d–j** and **10** is likely proceed via a diradical intermediate as was observed for the corresponding 4-alkynylcyclobutenones.[19,20]

Interestingly, the phenyl group on the imino nitrogen allows additional delocalization of an unpaired electron and apparently this opens additional avenues for cyclization. For example, thermolysis of 4-alkynylcyclobutenimines **8d–g** results in a novel cyclization mode, yielding cyclopenta-annulated quinolines **25** (Scheme 8, Table 4). This unusual structure was unambiguously established by an X-ray structural analysis of **25a** (Figure 1).[21]



Scheme 7 Aminonaphthyl ethers from ethers **9**



Scheme 8 Ring enlargement of 4-alkynylcyclobutenimines

Table 4 Cyclopenta[*b*]quinolin-1-ones **25a**–**d**, Cyclopenta [*b*][1,n]-naphthyridin-4-ones **25e**,**f** (n = 5–7) and Cyclopentenes **26**,**27**

Starting material	Product	R^1	R^2	R^3	Yield (%)
8d	**25a**	H	CH_2TMS	H	12
8e	**25b**	H	Ph	H	49
8f	**25c**	4-OMe	Ph	H	49
8g	**25d**	4-CF_3	Ph	H	36
8h	**27**	2,4,6-Me_3	Ph	H	53
8i	**25eA**	3-aza	Ph	H	12
	25eB				7
8j	**25f**	4-aza	Ph	H	22
10	**26**	H	Ph	TMS	19

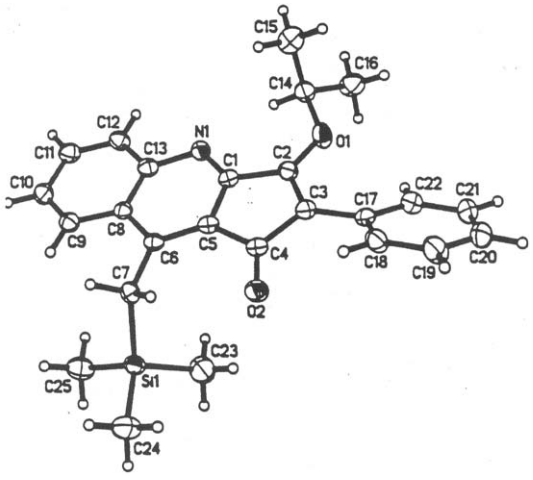
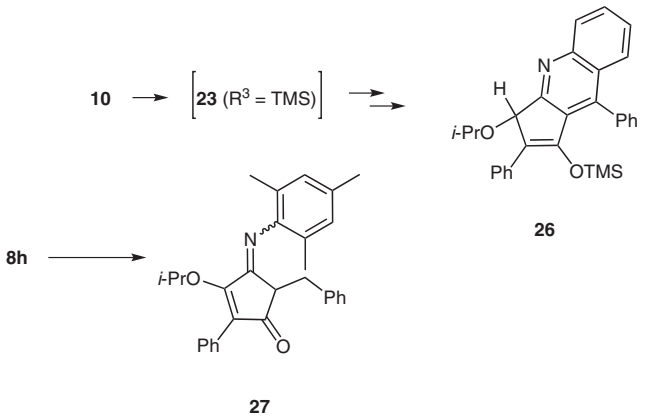


Figure 1 X-ray crystal structure of compound **25a**

Formation of **25** arises from diradical ring closure on the *o*-position in the *N*-phenyl substituent. Moreover, the primary cyclization product **24** apparently undergoes dehydrogenation. Possible hydrogen acceptors might be iminoquinones as formed from diradical **21**. In fact, an iminoquinone **22** could be isolated from **8f**; other dehydrogenation partners are conceivable and may also account for the relatively low yield of **25** in the complex product mixture.

Interestingly, 4-pyridyl derivatives **8i**,**j** follow the same pathway as 4-aryl derivatives **8d**–**g** (Table 4). However, starting from the unsymmetrical 4-(3-pyridyl) compound **8i**, two cyclization modes are possible and both were confirmed by the isolation of **25eA** and **25eB** (Scheme 8, Table 4). A characteristic spectroscopic feature of **25eA** is a broad singlet in the ^{1}H NMR spectrum at δ = 9.44 for H-9 (Scheme 8).

The dehydrogenation of intermediate **24** was suppressed by starting with the silyl ether **10** (R^3 = TMS). Here, **26**, a silylated tautomer of alcohol **24**, was isolated (Scheme 9). Evidence for the suggested structure comes from the ^{1}H NMR spectrum showing the cyclopentyl methine hydrogen at 5.53 ppm and from NOE experiments.



Scheme 9 Ring enlargement of 4-silyl ether **10** and of *N*-mesityl derivative **8h**

In accord with the suggested mechanism, *N*-mesityl derivative **8h** where methyl substitution prevents the cyclization to a **25**-type product gives cyclopentene **27**. This is assumed to arise via a H-atom abstraction from the proximal hydroxy group in a diradical intermediate analogous to **23A** (R^3 = H).

The structure of **27** was established by a single-crystal X-ray investigation (Figure 2).[22] Interestingly, the observed *E*-configuration of the exocyclic C=C unit in **27** speaks against an intramolecular hydrogen transfer from the hydroxy group in **23A** (R^3 = H). Although the yields of products **22** (16%), **25** (7–49%), **26** (19%), **27** (53%) have yet to be optimized, these unusual structures give new evidence of the versatility of iminocyclobutenone chemistry.

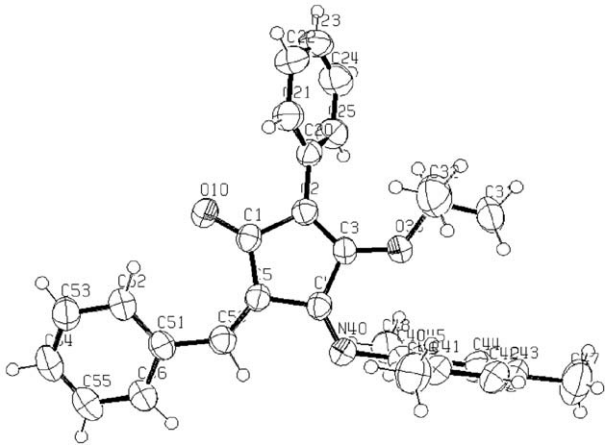


Figure 2 X-ray crystal structure of compound **27**

All air- or water-sensitive reactions were carried out in oven dried glassware under a slight positive pressure of N_2 or argon (as indicated), which was dried by passage through a column of KOH/Drierite. Air and moisture-sensitive liquids were transferred via syringe through a rubber septum. THF was degassed with N_2 and then passed through two 4 × 36 inch columns of anhyd neutral A-2 alumina (8 × 14 mesh; LaRoche Chemicals; activated under a flow of argon at 350 °C for 3 h) to remove H_2O. Xylenes, toluene, benzene, Et_3N, and CH_2Cl_2 were distilled from CaH_2 at atmospheric pressure. Unless specified as anhyd, all solvents were unpurified reagent grade. Petroleum ether (PE) used refers to the fraction boiling in the range 60–70 °C. Flash or column chromatography was performed using Merck silica gel (230–400 mesh). Radial chromatography was performed on glass plates coated with Merck silica gel, TLC grade 7749, with gypsum binder and fluorescent indicator. Sublimation was performed using a Büchi oven model GHR-51 equipped with a sublimation assembly. Analytical TLC analyses were performed on E. Merck silica gel 60 F_{254} coated on plastic or glass. Melting points were taken on a Büchi 510 or Dr. Totolli melting point apparatus and are not corrected.

IR spectra were recorded on a Perkin-Elmer 1620 single beam or a Bruker Vektor 22 FT spectrophotometer. IR recordings were taken in $CDCl_3$ unless otherwise specified. ^{1}H and ^{13}C NMR spectra were recorded on Bruker ARX 400 (100 MHz), GN 500 MHz or Omega 500 MHz NMR instruments in $CDCl_3$. All NMR recording were referenced to $CHCl_3$ resonances (7.26 and 77.0 ppm), unless otherwise specified. Mass spectra were recorded on a Hewlett Packard instrument HP 5989B. High-resolution mass spectra (HRMS) were obtained on a VG Analytic 7070E spectrometer. Elemental analyses were performed by Robertson Laboratories, Inc., Madison, NJ. Recrystallization of compounds were carried out at r.t., unless otherwise indicated.

3-Isopropoxy-4-*N*-(phenyl)imino-2-phenylcyclobut-2-en-1-ones 7a-e; General Procedure

Under N_2, a 100 mL one-necked round-bottomed flask equipped with a magnetic stirring bar and rubber septum was charged with THF (30 mL) and PhBr (2.0 mL, 19 mmol) and cooled to ca. –78 °C for 15 min. Then *n*-BuLi (11.3 mL of a 1.6 M solution in hexane, 18.1 mmol) was added in a dropwise manner. The reaction mixture was stirred for 30 min at ca. –78 °C, then transferred via cannula under positive pressure of N_2 to a 250 mL one-necked round-bottomed flask equipped with a magnetic stirring bar and rubber septum, charged with THF (40 mL) and **1**[8,23] (R^1 = *i*-Pr; 3.0 g, 15.1 mmol) and also kept at –78 °C. The resulting solution was treated with

TFAA (2.7 mL, 19.4 mmol) followed by the addition of a freshly distilled arylamine (for **7a**–**d**; 20 mmol or the quantity given below) or pyridylamine (for **7e**; 20 mmol or the quantity given below) in a dropwise manner and subsequently warmed to r.t. This solution was stirred for ca. 2 h when TLC analysis indicated no change in the product pattern. This was followed by a brine quench (15 mL) and the aqueous phase was extracted with Et_2O (2 × 50 mL). The combined organic layers were washed with brine (2 × 50 mL), dried ($MgSO_4$), filtered, and concentrated to a viscous dark yellow oil. Column chromatography of the oil (elution with 20:1 mixture of hexanes–EtOAc) furnished the product. Note that occasionally after chromatography there was an impurity that had a similar R_f value as **7**, which could be removed by sublimation in a Büchi microsublimation oven attachment at 100 °C (0.1–0.2 mm Hg) or the desired product was obtained by recrystallization from CH_2Cl_2–pentane.

3-Isopropoxy-2-phenyl-4-*N*-phenyliminocyclobut-2-en-1-one (7a)

Prepared using aniline (2.8 mL, 29 mmol); yellow solid; yield: 3.65 g (83%); mp 91–93 °C.

IR (KBr): 3061, 2984, 2341, 2252, 1756, 1666, 1566, 1494, 1410, 762, 692 cm^{-1}.

^1H NMR (200 MHz): δ = 7.90–8.00 (m, 2 H), 7.15–7.50 (m, 8 H), 7.22–7.20 (m, 1 H), 6.16 (sept, *J* = 6.2 Hz, 1 H), 1.59 (d, *J* = 6.2 Hz, 6 H).

^{13}C NMR (50 MHz): δ = 187.3, 185.8, 167.9, 153.8, 145.8, 130.3, 128.8, 128.7, 128.6, 126.9, 126.2, 123.6, 78.8, 23.2.

HRMS (EI): *m*/*z* calcd for $C_{19}H_{17}NO_2$: 291.1259; found: 291.1253.

Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.12; H, 5.85; N, 4.66.

3-Isopropoxy-2-phenyl-4-*N*-(4-methoxyphenyl)iminocyclobut-2-en-1-one (7b)

Prepared using PhBr (290 μL, 2.75 mmol), *n*-BuLi (1.6 mL of a 1.6 M solution in hexane, 2.6 mmol), **1** (R^1 = *i*-Pr; 400 mg, 20.2 mmol), followed by TFAA (390 μL, 2.8 mmol) and a solution of THF (100 mL) containing *p*-anisidine (340 mg, 276 mmol); yellow solid; yield: 0.55 g (85%); mp 94–96 °C.

IR: 3060, 2982, 2835, 1759, 1672, 1603, 1566, 1506, 1495, 1465, 1448, 1408, 1337, 1295, 1248, 1174, 1089, 1033 cm^{-1}.

^1H NMR (500 MHz): δ = 7.95–7.93 (m, 2 H), 7.52–7.51 (m, 2 H), 7.44–7.37 (m, 3 H), 6.90–6.89 (m, 2 H), 6.18 (sept, *J* = 6.2 Hz, 1 H), 3.82 (s, 3 H), 1.57 (d, *J* = 6.2 Hz, 6 H).

^{13}C NMR (125 Hz): δ = 187.3, 186.9, 165.6, 158.3, 151.8, 139.3, 129.9, 129.0, 128.7, 126.6, 125.9, 113.9, 78.5, 55.4, 23.3.

HRMS (CI): *m*/*z* calcd for $C_{20}H_{19}NO_3$ $[M + H]^+$: 322.1445; found: 322.1408.

3-Isoproxy-2-phenyl-4-*N*-(4-trifluoromethyl)phenyliminocyclobut-2-ene-1-one (7c)

Prepared using PhBr (580 μL, 5.5 mmol), *n*-BuLi (11.3 mL of a 1.6 M solution in hexane, 18.1 mmol), **1** (R^1 = *i*-Pr; 1.0 g, 5.1 mmol), then TFAA (800 μL, 5.8 mmol) and 4-(trifluoromethyl)aniline [prepared from the hydrochloride (1.2 g, 6.1 mmol) and Et_3N (874 μL, 6.3 mmol) in THF (10 mL)]; yellow solid; yield: 1.3 g (71%); mp 97–98 °C.

IR: 3021, 1767, 1681, 1571, 1496, 1413, 1324, 1210, 1168, 1126, 1066, 1041 cm^{-1}.

^1H NMR (500 MHz): δ = 7.98–7.60 (m, 2 H), 7.62 (d, *J* = 10 Hz, 2 H), 7.48–7.42 (m, 5 H), 6.10 (sept, *J* = 6.2 Hz, 1 H), 1.62 (d, *J* = 6.2 Hz, 6 H).

^{13}C NMR (125 MHz): δ = 186.1, 185.2, 169.7, 155.7, 148.9, 130.7, 128.8, 127.1, 125.8, 125.80, 123.3, 79.2, 23.3.

HRMS (CI): *m*/*z* calcd for $C_{20}H_{16}F_3NO_2$: 359.1133; found: 359.1132.

3-Isopropoxy-2-phenyl-4-*N*-(2,4,6-trimethylphenyl)iminocyclobut-2-en-1-one (7d)

Prepared from PhLi (11 mL, 2 M in Bu_2O, 22 mmol) and **1** (R^1 = *i*-Pr; 3.96 g, 20 mmol), then TFAA (3.7 mL, 5.56 g, 26.6 mmol) and 2,4,6-trimethylaniline (5.6 mL, 5.4 g, 40 mmol); yellow solid; yield: 3.47 g (52%); mp 101 °C.

IR (KBr): 2981, 1772, 1693, 1582, 1407, 1338, 1089, 1049, 788, 759, 693 cm^{-1}.

^1H NMR (200 MHz): δ = 7.95–7.85 (m, 2 H), 7.50–7.30 (m, 4 H), 6.84 (d, *J* = 0.5 Hz, 2 H), 6.06 (sept, *J* = 6.2 Hz, 1 H), 2.26 (s, 3 H), 2.13 (s, 6 H), 1.62 (d, *J* = 6.2 Hz, 6 H).

^{13}C NMR (50 MHz): δ = 186.4, 185.8, 168.3, 154.5, 143.3, 133.1, 130.3, 128.8, 128.7, 128.5, 126.9, 126.5, 79.2, 23.2, 20.8, 18.3.

MS (70 eV): *m*/*z* (%) = 333 (75, $[M]^+$), 290 (20), 262 (40), 234 (23), 204 (5), 145 (100), 117 (20), 89 (30), 77 (6).

3-Isopropoxy-2-phenyl-4-*N*-(3-pyridyl)iminocyclobut-2-en-1-one (7e)

Prepared from PhLi (3 mL, 2 M in Bu_2O, 6 mmol) and **1** (R^1 = *i*-Pr; 1.2 g, 6.1 mmol), then TFAA (1.1 mL, 1.66 g, 7.9 mmol) and 3-pyridylamine (1.13 g, 12 mmol); yellow solid; yield: 0.88 g (50%); mp 109 °C.

IR (KBr): 1758, 1668, 1556, 1420, 1088, 1025, 798, 704, 688 cm^{-1}.

^1H NMR (200 MHz): δ = 8.62 (d, *J* = 2.1 Hz, 1 H), 8.43 (dd, *J* = 1.5, 4.7 Hz, 1 H), 8.0–7.80 (m, 3 H), 7.55–7.35 (m, 3 H), 7.35–7.28 (m, 1 H), 6.13 (sept, *J* = 6.2 Hz, 1 H), 1.61 (d, *J* = 6.2 Hz, 6 H).

^{13}C NMR (50 MHz): δ = 186.2, 185.4, 170.1, 155.3, 147.0, 146.2, 142.0, 130.7, 129.7, 128.9, 128.6, 127.1, 123.3, 79.2, 23.2.

MS (70 eV): *m*/*z* (%) = 292 (87, $[M]^+$), 250 (53), 221 (47), 194 (23), 145 (100), 78 (11).

3-Alkoxy-4-*N*-(het)arylimino-2-phenylcyclobut-2-en-1-ones via the Aza-Wittig Reaction; 3-Isopropoxy-2-phenyl-4-*N*-phenyliminocyclobut-2-en-1-one (7a); Typical Procedure

Under N_2, a 100 mL one-necked round-bottomed flask equipped with a magnetic stirring bar and reflux condenser was charged with benzene (50 mL), **3**[8] (690 mg, 3.2 mmol), and *N*-(triphenylphosphoranylidene)aniline (1.3 g, 3.7 mmol), and the mixture was refluxed until TLC analysis indicated consumption of starting material (ca. 18 h). Concentration of the reaction solution in vacuo followed by column chromatography (elution with a 10:1 mixture of hexanes–EtOAc) gave 644 mg (69%) of **7a**; yellow solid with identical properties to the material prepared as given above.

3-Isopropoxy-2-phenyl-4-*N*-(4-pyridylimino)cyclobut-2-en-1-one (7f)

Prepared analogously from **3** (1.2 g, 5.6 mmol) and (4-pyridylimino)phosphorane[24] (5.5 g, 15.7 mmol) in toluene (80 mL) at 85–90 °C; yellow solid; yield: 1.11 g (68%); mp 118 °C (dec.).

IR (KBr): 3055, 2984, 1764, 1666, 1568, 1413, 1342, 1088, 1037, 834, 798, 760, 696 cm^{-1}.

^1H NMR (200 MHz): δ = 8.56 (dd, *J* = 1.5, 4.5 Hz, 2 H), 8.00–7.90 (m, 2 H), 7.50–7.40 (m, 3 H), 7.15 (dd, *J* = 1.5, 4.5 Hz, 2 H), 6.03 (sept, *J* = 6.2 Hz, 1 H), 1.60 (d, *J* = 6.2 Hz, 6 H).

^{13}C NMR (50 MHz): δ = 185.5, 184.5, 171.0, 157.2, 152.8, 150.4, 131.1, 128.9, 128.4, 127.2, 117.4, 79.4, 23.2.

MS (70 eV): *m*/*z* (%) = 292 (48, $[M]^+$), 250 (42), 221 (50), 194 (27), 145 (96), 89 (100).

4-Substituted Cyclobutenimines 8a–f,h,j, 9a–c; General Procedure

A 250 mL one-necked round-bottomed flask equipped with a magnetic stirring bar and rubber septum was charged with THF (200 mL) and **7** (1.9 mmol or the amount given below). After 15 min at ca. –78 °C, the corresponding organyllithium compound (2.1 mmol) was added in a dropwise manner. Upon consumption of starting material as confirmed by TLC analysis, at –20 °C brine (20 mL) (for **8a–f,h–j**) or methyl triflate (for **9a–c**) was added and the reaction was allowed to warm to r.t. The aqueous phase was extracted with Et_2O (2 × 100 mL), dried ($MgSO_4$), filtered, and concentrated to a viscous yellow oil. Column chromatography (elution with a 10:1 mixture of hexanes–EtOAc) gave the pure product **8** or **9**.

3-Isopropoxy-2-phenyl-4-phenylimino-1-vinylcyclobut-2-en-1-ol (8a)

Prepared from **7a** (496 mg, 1.77 mmol) and vinyllithium (900 μL, 2.3 M in Et_2O, 2.1 mmol); yellow oil; yield: 260 mg (46%).

IR: 3586, 3083, 2982, 2935, 1697, 1606, 1590, 1104 cm^{-1}.

^1H NMR (500 MHz): δ = 7.69–7.67 (m, 2 H), 7.38–7.35 (m, 2 H), 7.32–7.28 (m, 3 H), 7.21–7.20 (m, 2 H), 7.13–7.09 (m, 1 H), 6.00 (dd, *J* = 10.8, 17.2 Hz, 1 H), 5.61 (sept, *J* = 6.4 Hz, 1 H), 5.39 (dd, *J* = 1.4, 17.2 Hz, 1 H), 5.15 (dd, *J* = 1.4, 10.8 Hz, 1 H), 2.41 (s, 1 H), 1.49–1.46 (m, 6 H).

^{13}C NMR (125 MHz): δ = 164.5, 151.1, 147.4, 138.4, 137.8, 130.6, 128.5, 128.4, 128.39, 127.4, 124.5, 122.5, 116.2, 84.4, 74.2, 23.2, 23.1.

HRMS (EI): *m*/*z* calcd for $C_{21}H_{21}NO_2$: 319.1572; found: 319.1562.

Anal. Calcd for $C_{21}H_{21}NO_2$: C, 78.97, H; 6.63; N, 4.39. Found: C, 78.82; H, 6.69; N, 4.28.

3-Isopropoxy-2-phenyl-4-phenylimino-2-propenylcyclobut-2-en-1-ol (8b)

Prepared from **7a** (516 mg, 1.77 mmol), 2-bromopropene (210 μL, 2.4 mmol), and *t*-BuLi (2.5 mL, 1.6 M in pentane, 4.0 mmol) using a 5:1 mixture of hexanes–EtOAc for chromatography; yellow solid; yield: 482 mg (82%); mp 104–106 °C.

IR: 3588, 3065, 2981, 2937, 1698, 1590, 1488, 1448, 1386, 1104 cm^{-1}.

^1H NMR (500 MHz): δ = 7.65 (dd, *J* = 8.4, 1.5 Hz, 2 H), 7.35 (t, *J* = 7.3 Hz, 2 H), 7.29–7.26 (m, 3 H), 7.15 (t, *J* = 8.4 Hz, 2 H), 7.09 (t, *J* = 7.3 Hz, 1 H), 5.60 (sept, *J* = 6.2 Hz, 1 H), 5.30 (s, 1 H), 4.98 (s, 1 H), 2.26 (s, 1 H), 1.64 (s, 3 H), 1.47 (d, *J* = 6.2 Hz, 3 H), 1.45 (d, *J* = 6.2 Hz, 3 H).

^{13}C NMR (125 MHz): δ = 164.5, 151.7, 147.2, 143.4, 138.0, 128.6, 128.5, 127.0, 124.5, 122.3, 113.6, 86.4, 74.1, 23.2, 23.1, 19.6.

HRMS (EI): *m*/*z* calcd for $C_{22}H_{23}NO_2$: 333.1729; found: 333.1732.

Anal. Calcd for $C_{22}H_{23}NO_2$: C, 79.25; H, 6.95; N, 4.20. Found: C, 79.29; H, 6.80; N, 4.11.

3-Isopropoxy-1,2-diphenyl-4-phenyliminocyclobut-2-en-1-ol (8c)

Prepared from **7a** (800 mg, 2.75 mmol), PhBr (345 μL, 3.28 mmol), and *n*-BuLi (2.1 mL of a 1.6 M solution in hexane, 3.4 mmol); yellow solid; yield: 970 mg (96%); mp 149–150 °C.

IR: 3436, 3061, 2978, 1692, 1588, 1489, 1448, 1384, 1341, 1170, 1103, 1014 cm^{-1}.

^1H NMR (500 MHz): δ = 7.52–750 (m, 2 H), 7.35–7.33 (m, 2 H), 7.28–7.25 (m, 3 H), 7.22–7.15 (m, 3 H), 7.10–7.07 (m, 2 H), 6.97–6.94 (m, 1 H), 6.79–6.77 (m, 2 H), 5.65 (sept, *J* = 6.2 Hz, 1 H), 2.41 (s, 1 H), 1.51 (d, *J* = 6.2 Hz, 3 H), 1.509 (d, *J* = 6.2 Hz, 3 H).

^{13}C NMR (125 MHz): δ = 164.7, 152.5, 147.2, 140.1, 139.0, 130.1, 128.6, 128.4, 128.3, 128.1, 127.7, 127.1, 125.6, 124.0, 122.0, 74.4, 55.2, 23.2, 23.2.

HRMS (EI): *m*/*z* calcd for $C_{25}H_{23}NO_2$: 369.1729; found: 369.1717.

Anal. Calcd for $C_{25}H_{23}NO_2$: C, 81.27; H, 6.27; N, 3.79. Found: C, 81.08; H, 6.18; N, 3.75.

3-Isoproxy-2-phenyl-4-phenylimino-1-(3-trimethylsilylprop-1-ynyl)cyclobut-2-en-1-ol (8d)

Prepared from **7a** (400 mg, 1.37 mmol), trimethyl(propargyl)silane (0.8 mL, 5.5 mmol), and *n*-BuLi (3.9 mL of a 1.6 M solution in hexane, 6.2 mmol) and using gradient elution with 20:1 → 15:1 mixtures of hexanes–EtOAc for chromatography; dark yellow oil; yield: 328 mg (59%).

IR: 3519, 3404, 3060, 2978, 2884, 2225, 1943, 1695, 1587, 1489, 1449, 1387, 1346, 1250, 1132, 1104, 1074, 1006 cm^{-1}.

^1H NMR (500 MHz): δ = 7.83 (d, *J* = 6.9 Hz, 2 H), 7.44–7.39 (m, 4 H), 7.38–7.35 (m, 2 H), 7.33–730 (m, 1 H), 7.15 (m, 1 H), 5.61 (sept, *J* = 6.1 Hz, 1 H), 2.44 (s, 1 H), 1.49 (d, *J* = 6.1 Hz, 3 H), 1.48 (s, 2 H), 1.46 (d, *J* = 6.1 Hz, 3 H), 0.01 (s, 9 H).

^{13}C NMR (125 MHz): δ = 161.8, 151.4, 147.1, 139.0, 130.1, 128.6, 128.4, 128.37, 127.5, 124.5, 122.9, 87.0, 74.9, 74.3, 23.1, 23.0, 7.3, –2.2.

HRMS (EI): *m*/*z* calcd for $C_{25}H_{29}NO_2Si$: 403.1968; found: 403.1971.

3-Isopropoxy-2-phenyl-1-phenylethynyl-4-phenyliminocyclobut-2-en-1-ol (8e)

Prepared from **7a** (400 mg, 1.37 mmol), phenylacetylene (1.6 mL, 14.6 mmol), and *n*-BuLi (9.2 mL of a 1.6 M solution in hexane, 15.8 mmol) and using radial chromatography with gradient elution of 10:1 → 5:1 mixtures of hexanes–EtOAc; dark yellow oil; yield: 479 mg (89%).

IR: 3519, 3393, 3061, 2980, 2933, 2227, 1696, 1589, 1489, 1448, 1389, 1346, 1245, 1141, 1102, 1068 cm^{-1}.

^1H NMR (500 MHz): δ = 7.82 (m, 2 H), 7.40–7.29 (m, 6 H), 7.28–7.22 (m, 6 H), 7.14–7.11 (m, 1 H), 5.56 (sept, *J* = 6.1 Hz, 1 H), 5.53 (s, 1 H), 1.47 (d, *J* = 6.1 Hz, 3 H), 1.44 (d, *J* = 6.1 Hz, 3 H).

^{13}C NMR (125 MHz): δ = 161.1, 151.7, 147.4, 137.9, 131.6, 130.0, 128.7, 128.6, 128.5, 128.1, 127.5, 124.6, 122.4, 122.2, 87.7, 87.0, 74.8, 74.7, 23.2, 23.1.

HRMS (CI): *m*/*z* calcd for $C_{27}H_{23}NO_2$ $[M + H]^+$: 394.1737; found: 394.1759.

3-Isopropoxy-4-(4-methoxy)phenylimino-2-phenyl-1-(phenylethynyl)cyclobut-2-en-1-ol (8f)

Prepared from **7b** (400 mg, 1.24 mmol), phenylacetylene (1.4 mL, 12.8 mmol), and *n*-BuLi (8.6 mL of a 1.6 M solution in hexane, 13.8 mmol) and using radial chromatography with gradient elution of 10:1 → 5:1 mixtures of hexanes–EtOAc; dark red oil; yield: 354 mg (67%).

IR: 3368, 3060, 2978, 2933, 2191, 1762 (overtone), 1688, 1607, 1551, 1505, 1445, 1386, 1349, 1295, 1247, 1176, 1102, 1066, 1033 cm^{-1}.

^1H NMR (500 MHz): δ = 7.83 (d, *J* = 7.3 Hz, 2 H), 7.44 (d, *J* = 8.8 Hz, 2 H), 7.41 (t, *J* = 7.6 Hz, 2 H), 7.32–7.24 (m, 8 H), 5.61 (sept, *J* = 6.0 Hz, 1 H), 3.80 (s, 3 H), 2.49 (s, 1 H), 1.48, 1.44 (d each, *J* = 6.0 Hz, 3 H).

^{13}C NMR (125 MHz): δ = 159.4, 157.2, 152.2, 140.0, 137.5, 131.7, 130.1, 128.7, 128.5, 128.5, 128.2, 127.3, 124.7, 122.3, 113.9, 87.8, 87.2, 75.1, 74.8, 55.4, 23.2, 23.1.

HRMS (CI): *m*/*z* calcd for $C_{28}H_{25}NO_3$: 423.1834; found: 423.1678.

3-Isopropoxy-4-(2,4,6-trimethylphenyl)imino-2-phenyl-1-phenylethynylcyclobut-2-en-1-ol (8h)

Prepared from **7d** (740 mg, 2.2 mmol), phenylacetylene (2.9 mL, 26.4 mmol), and *n*-BuLi (14.0 mL of a 1.6 M solution in hexane, 22.4 mmol); red oil; yield: 652 mg (68%).

IR (film): 3407, 2997, 2916, 1707, 1616, 1387, 1347, 1102, 982, 757, 690 cm^{-1}.

^1H NMR (200 MHz): δ = 7.95–7.85 (m, 2 H), 7.45–7.20 (m, 8 H), 6.85 (s, 2 H), 5.57 (sept, *J* = 6.1 Hz, 1 H), 2.28 (s, 3 H), 2.22 (s, 6 H), 1.50 (m, 6 H).

^{13}C NMR (50 MHz): δ = 160.1, 151.0, 143.6, 137.2, 132.5, 132.1, 131.6, 130.0, 128.7, 128.6, 128.6, 128.5, 128.2, 127.5, 122.2, 86.3, 77.2, 75.1, 74.4, 23.2, 23.1, 20.8, 18.5.

MS (70 eV): *m*/*z* (%) = 436 (5, $[M + H]^+$), 392 (8), 378 (90), 316 (3), 202 (100).

3-Isopropoxy-2-phenyl-1-phenylethynyl-4-(3-pyridyl)iminocyclobut-2-en-1-ol (8i)

Prepared from **7e** (238mg, 0.82 mmol), phenylacetylene (0.82 g, 8.0 mmol), and *n*-BuLi (5.0 mL of a 1.6 M solution in hexane, 8.0 mmol) and using consecutive flash and radial chromatography with 1:2 → 2:1 mixtures of hexanes–EtOAc; red oil; yield: 258 mg (80%).

IR (film): 3059, 2980, 1696, 1601, 1571, 1491, 1387, 1102, 989, 756, 691 cm^{-1}.

^1H NMR (200 MHz): δ = 8.55 (d, *J* = 2.0 Hz, 1 H), 8.00 (dd, *J* = 1.5, 4.8 Hz, 1 H), 7.90 (dd, *J* = 1.5, 8.1 Hz, 2 H), 7.65–7.55 (m, 1 H), 7.05–7.25 (m, 8 H), 7.14 (dd, *J* = 4.8, 8.1 Hz, 1 H), 5.47 (sept, *J* = 6.2 Hz, 1 H), 1.45 (dd, *J* = 2.4, 6.2 Hz, 6 H).

^{13}C NMR (50 MHz): δ = 164.5, 150.8, 144.3, 144.1, 142.8, 140.0, 131.7, 130.0, 130.0, 128.9, 128.7, 128.7, 128.3, 127.8, 127.1, 123.1, 122.2, 88.3, 79.2, 73.8, 23.3, 23.1.

MS (70 eV): *m*/*z* (%) = 395 (100, $[M + H]^+$), 251 (68), 275 (53).

3-Isopropoxy-2-phenyl-1-phenylethynyl-4-(4-pyridyl)iminocyclobut-2-en-1-ol (8j)

Prepared from **7f** (650 mg, 2.2 mmol), phenylacetylene (2.83 g, 27.7 mmol), and *n*-BuLi (13.8 mL of a 1.6 M solution in hexane, 22 mmol) and using flash chromatography with a 1:1 mixture of hexanes–EtOAc; red oil; yield: 310 mg (36%).

IR (film): 3407, 3083, 2978, 1709, 1589, 1394, 1105, 988, 758, 691 cm^{-1}.

^1H NMR (200 MHz): δ = 8.09 (dd, *J* = 1.5 Hz, 4.7 Hz, 2 H), 7.94 (d, *J* = 1.5 Hz, 1 H), 7.90 (d, *J* = 1.3 Hz, 1 H), 7.50–7.20 (m, 8 H), 7.01 (dd, *J* = 1.5, 4.8 Hz, 2 H), 5.41 (sept, *J* = 6.2 Hz, 1 H), 1.46 (dd, *J* = 6.2, 8.8 Hz, 6 H).

^{13}C NMR (50 MHz): δ = 164.6, 156.4, 149.8, 148.5, 140.8, 131.3, 129.9, 129.0, 128.7, 128.6, 128.6, 128.0, 122.4, 117.0, 89.7, 86.1, 79.7, 73.2, 23.3, 23.1.

2-Isopropoxy-4-methoxy-3,4,*N*-triphenylcyclobut-2-en-1-imine (9a)

Prepared from **7a** (500 mg, 1.72 mmol), PhBr (216 μL, 2.1 mmol), *n*-BuLi (1.4 mL of a 1.6 M solution in hexane, 2.2 mmol), and methyl triflate (225 μL, 2.0 mmol); yellow solid; yield: 341 mg (60%); mp 149–150 °C.

IR: 3061, 2979, 2932, 2826, 1694, 1682, 1607, 1590, 1487, 1447, 1384, 1347, 1313, 1242, 1193, 1145, 1102, 1086, 1032, 1011 cm^{-1}.

^1H NMR (500 MHz): δ = 7.52 (d, *J* = 7.3 Hz, 2 H), 7.41 (d, *J* = 7.1 Hz, 2 H), 7.23 (t, *J* = 7.2 Hz, 2 H), 7.18–7.13 (m, 4 H), 7.11–7.06 (m, 3 H), 6.95 (t, *J* = 7.4 Hz, 1 H), 6.77 (d, *J* = 7.5 Hz, 2 H), 5.73 (sept, *J* = 6.2 Hz, 1 H), 3.36 (s, 3 H), 1.48 (d, *J* = 6.2 Hz, 6 H).

^{13}C NMR (125 MHz): δ = 163.2, 152.5, 146.9, 140.3, 137.2, 130.9, 128.5, 128.4, 128.1, 127.9, 127.2, 127.1, 125.9, 124.3, 122.0, 90.6, 74.0, 51.5, 23.2, 23.1.

HRMS (EI): *m*/*z* calcd for $C_{26}H_{25}NO_2$: 383.1885; found: 383.1890.

2-Isopropoxy-4-methoxy-3,*N*-diphenyl-4-(3-methylphenyl)cyclobut-2-en-1-imine (9b)

Prepared from **7a** (400 mg, 1.37 mmol), 3-bromotoluene (206 μL, 1.7 mmol), *n*-BuLi (1.2 mL of a 1.6 M solution in hexane, 1.92 mmol), and methyl triflate (180 μL, 1.6 mmol) using radial chromatography (elution with 50:1 mixture of hexanes–EtOAc); yellow solid; yield: 380 mg (70%); mp 108–110 °C.

IR: 3060, 3028, 2979, 2932, 2825, 1692, 1608, 1587, 1488, 1383, 1345, 1170, 1144, 1102, 1086, 1011 cm^{-1}.

^1H NMR (400 MHz): δ = 7.53 (d, *J* = 7.2 Hz, 2 H), 7.25 (m, 2 H), 7.19–7.17 (m, 3 H), 7.11–7.04 (m, 3 H), 7.00–6.93 (m, 2 H), 6.93 (sept, *J* = 6.0 Hz, 1 H), 6.76 (d, *J* = 7.6 Hz, 2 H), 3.36 (s, 3 H), 2.20 (s, 3 H), 1.50 (d, *J* = 6.0 Hz, 3 H), 1.49 (d, *J* = 6.0 Hz, 3 H).

^{13}C NMR (125 MHz): δ = 163.3, 152.3, 147.0, 140.2, 137.3, 137.1, 131.0, 128.5, 128.4, 128.0, 127.9, 127.7, 127.3, 126.8, 124.2, 122.9, 122.0, 90.6, 74.0, 51.5, 23.3, 23.1, 21.5.

HRMS (EI): *m*/*z* calcd for $C_{27}H_{27}NO_2$: 397.2042; found: 397.2038.

2-Isopropxy-4-methoxy-3,*N*-diphenyl-4-(3-methoxyphenyl)cyclobut-2-en-1-imine (9c)

Prepared from **7a** (411 mg, 1.41 mmol), 3-bromoanisole (211 μL, 1.7 mmol), *n*-BuLi (1.2 mL of a 1.6 M solution in hexane, 1.92 mmol), and methyl triflate (180 μL, 1.6 mmol) using column chromatography (elution with 20:1 mixture of hexanes–EtOAc) and recrystallization from pentane–CH_2Cl_2; yellow solid; yield: 504 mg (87%); mp 109–110 °C.

IR: 3060, 2979, 2934, 2829, 1692, 1589, 1486, 1449, 1383, 1343, 1283, 1164, 1081, 1048 cm^{-1}.

^1H NMR (500 MHz): δ = 7.53 (m, 2 H), 7.27–7.19 (m, 3 H), 7.13–7.01 (m, 3 H), 7.00–6.96 (m, 2 H), 6.76 (m, 2 H), 6.70 (dd, *J* = 1.2, 8.0 Hz, 1 H), 5.70 (sept, *J* = 6.0 Hz, 1 H), 3.67 (s, 3 H), 3.36 (s, 3 H), 1.5 (d, *J* = 6.0 Hz, 6 H).

^{13}C NMR (125 MHz): δ = 163.0, 159.3, 152.4, 147.0, 142.1, 137.0, 130.9, 128.8, 128.5, 128.4, 128.2, 127.3, 124.3, 122.0, 118.3, 113.0, 111.5, 90.4, 74.1, 55.1, 51.6, 23.2, 23.1.

HRMS (EI): *m*/*z* calcd for $C_{27}H_{27}NO_3$: 413.1991; found: 413.1981.

2-Isopropoxy-3,*N*-diphenyl-4-phenylethynyl-4-trimethylsilyloxycyclobut-2-en-1-imine (10)

A 50 mL one-necked round-bottomed flask equipped with a magnetic stirring bar and rubber septum was charged with CH_2Cl_2 (25 mL), **8a** (212 mg, 0.66 mmol), TMSCl (98 μL, 0.77 mmol) and Et_3N (233 μL, 1.67 mmol) and stirred overnight. The crude reaction mixture was concentrated followed by column chromatography (gradient elution with 10:1 → 5:1 hexanes–EtOAc); yellow oil; yield: 103 mg (34%).

IR: 3061, 2978, 2225, 1758 (overtone), 1690, 1606, 1581, 1491, 1448, 1386, 1350, 1252, 1176, 1102, 1008 cm^{-1}.

^1H NMR (500 MHz): δ = 7.85 (d, *J* = 7.7 Hz, 2 H), 7.48 (d, *J* = 8.0 Hz, 2 H), 7.39–7.26 (m, 9 H), 7.17–7.15 (m, 2 H), 5.65 (sept, *J* = 6.1 Hz, 1 H), 1.52, 1.46 (d each, *J* = 6.1 Hz, 3 H), –0.06 (s, 9 H).

^{13}C NMR (125 MHz): δ = 161.1, 151.9, 146.9, 139.6, 131.6, 130.5, 128.5, 128.4, 128.3, 128.2, 127.6, 124.8, 123.6, 122.7, 88.9, 86.5, 74.6, 23.5, 23.2, 1.3.

HRMS (EI): *m*/*z* calcd for $C_{30}H_{31}NO_2Si$: 465.2124; found: 465.2123.

Hydrolysis of 8b; 4-Hydroxy-2-isopropoxy-3-phenyl-4-(prop-2-enyl)cyclobut-2-en-1-one (11)

A 25 mL one-necked round-bottomed flask equipped with a magnetic stirring bar was charged with THF (5 mL), **8b** (35 mg, 0.1 mmol), and 10% aq HCl (2.0 mL) and the mixture was stirred. After complete conversion into the ketone via TLC analysis, 5% $NaHCO_3$ (10 mL) was added to the reaction mixture. The aqueous layer was extracted with Et_2O (2 × 20 mL), and the combined organic layers washed with brine (2 × 20 mL), dried ($MgSO_4$), filtered, concentrated, and purified by radial chromatography (elution with 20:1 hexanes–EtOAc); yellow oil; yield: 23 mg (89%).

IR: 3597, 3457, 2981, 1754, 1377 cm^{-1}.

^1H NMR (500 MHz): δ = 7.75 (d, *J* = 1.8 Hz, 2 H), 7.74–7.38 (m, 3 H), 5.41 (s, 1 H), 5.20 (s, 1 H), 5.16 (sept, *J* = 6.1 Hz, 1 H), 2.53 (s, 1 H), 1.76 (s, 3 H), 1.42, 1.40 (d each, *J* = 6.1 Hz, 3 H).

^{13}C NMR (125 MHz): δ = 188.2, 152.3, 150.3, 141.8, 130.4, 129.8, 128.8, 128.3, 114.2, 90.6, 75.0, 23.0, 22.96, 19.9.

HRMS (EI): *m*/*z* calcd for $C_{16}H_{18}O_3$ $[M + H]^+$: 259.1334; found: 259.1334.

4-(*N*-Phenylamino)-3-isopropoxy-2-phenylphenol (14a)

A 100 mL round-bottomed flask equipped with a stirring bar and reflux condenser was charged with a solution of **8a** (223 mg, 0.7 mmol) in *p*-xylene (50 mL) and refluxed for 1.5 h. When TLC analysis had confirmed consumption of starting material, the solvent was evaporated followed by column chromatography (elution with 10:1 hexanes–EtOAc); yellow oil; yield: 93.8 mg (42%).

IR: 3552, 3422, 3061, 2976, 2931, 1601, 1506, 1470, 1441, 1340, 1273, 1171, 1106, 1014 cm^{-1}.

^1H NMR (500 MHz): δ = 7.53–7.45 (m, 2 H), 7.43–7.40 (m, 3 H), 7.37–7.23 (m, 2 H), 7.04 (d, *J* = 8.1 Hz, 2 H), 6.86 (t, *J* = 7.3 Hz, 1 H), 6.73 (d, *J* = 8.7 Hz, 1 H), 5.90 (s, 1 H), 4.78 (s, 1 H), 3.66 (sept, *J* = 6.1 Hz, 1 H), 0.88 (d, *J* = 6.2 Hz, 6 H).

^{13}C NMR (125 MHz): δ = 147.7, 146.2, 144.5, 133.3, 130.6, 130.2, 129.3, 129.2, 129.1, 128.0, 123.0, 119.8, 119.3, 116.3, 110.6, 75.5, 22.2.

HRMS (EI): *m*/*z* calcd for $C_{21}H_{21}NO_2$: 319.1572; found: 319.1572.

4-(*N*-Phenylamino)-3-isopropoxy-5-methyl-2-phenylphenol (14b)

Prepared analogous to **14a** from **8b** (165 mg, 0.5 mmol) by refluxing in *p*-xylene (20 mL) for 1 h; yellow oil; yield: 146 mg (88%).

IR: 3553, 3421, 2976, 1598, 1466 cm^{-1}.

^1H NMR (500 MHz): δ = 7.62 (t, *J* = 7.6 Hz, 2 H), 7.56–7.51 (m, 3 H), 7.36 (t, *J* = 7.51 Hz, 3 H), 7.26–7.15 (m, 2 H), 6.97 (t, *J* = 7.3 Hz, 1 H), 6.01 (s, 1 H), 5.97 (s, 1 H), 3.73 (sept, *J* = 6.2 Hz, 1 H), 2.35 (s, 3 H), 0.98 (d, *J* = 6.2 Hz, 6 H).

^{13}C NMR (125 MHz): δ = 145.6, 144.7, 144.1, 133.5, 130.7, 129.4, 129.3, 128.1, 122.4, 120.8, 119.7, 119.6, 116.1, 75.6, 22.3, 16.2.

HRMS (EI): *m*/*z* calcd for $C_{22}H_{23}NO_2$: 333.1729; found: 333.1732.

3-Isopropoxy-2,*N*-diphenyl-*p*-naphthaquinonimine (16)

A 100 mL round-bottomed flask equipped with a stirring bar, reflux condenser, and gas inlet/outlet (argon) was charged with a solution of **8c** (253 mg, 0.7 mmol) in *p*-xylene (60 mL) and refluxed for 15 h. Upon consumption of starting material, the solvent was removed in vacuo to give an oil, which was dissolved in a mixture of freshly distilled benzene (70 mL), $KHCO_3$ (392 mg, 2.8 mmol), and Ag_2O (381 mg, 2.8 mmol) under a blanket of N_2 and stirred for 2 h. The reaction mixture was filtered through a bed of Celite, concentrated, and the product isolated as a viscous red oil. Column chromatography (gradient elution with 10:1 → 5:1 mixtures of hexanes–EtOAc); red-wine colored oil; yield: 150 mg (59%); complex *E*/*Z* mixture.

IR: 3060, 2978, 2932, 1648, 1591, 1484, 1446, 1361, 1298, 1274, 1231, 1181, 1097 cm^{-1}.

^1H NMR (500 MHz): δ = 8.39 (d, *J* = 7.5 Hz, 2 H), 8.20 (d, *J* = 7.7 Hz, 2 H), 7.69 (t, *J* = 6.9 Hz, 2 H), 7.64 (t, *J* = 7.2 Hz, 2 H), 7.50–7.36 (m, 12 H), 7.16 (m, 2 H), 7.10 (t, *J* = 7.1 Hz, 2 H), 6.93 (d, *J* = 7.4 Hz, 2 H), 6.85 (br, 2 H), 4.92 (br, 1 H), 3.62 (br, 1 H), 1.20 (br, 6 H), 0.57–0.47 (br, 6 H).

^{13}C NMR (125 MHz): δ = 185.1, 155.2, 151.6, 150.9, 134.8, 132.6, 132.4, 131.2, 131.1, 131.0, 129.5, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.3, 127.2, 126.1, 125.6, 124.2, 123.5, 118.3, 117.7, 76.4, 74.7, 22.6, 20.9.

HRMS (EI): *m*/*z* calcd for $C_{25}H_{21}NO_2$: 367.1572; found: 367.1572.

Anal Calcd for $C_{25}H_{21}NO_2$: C, 81.72; H, 5.76; N, 3.81. Found: C, 81.42; H, 5.51; N, 3.58.

Thermolysis of 4-Aryl-4-methoxycyclobutenimines; General Procedure

A 100 mL round-bottomed flask equipped with a stirring bar and reflux condenser was charged with **9** (0.6 mmol) in PhCl (40 mL) and refluxed for 9.5 days. Upon consumption of starting material, the solvent was removed in vacuo to a viscous yellow oil and product **18**,**19** isolated by column chromatography (gradient elution with 30:1 → 20:1 hexanes–EtOAc).

2-Isopropoxy-4-methoxy-1-(*N*-phenylamino)-3-phenylnaphthalene (18a)

Prepared from **9a** (211 mg, 5.5 mmol); amorphous solid; yield: 171 mg (81%).

IR: 3390, 3054, 2975, 2931, 2842, 1600, 1498, 1455, 1364, 1301, 1238, 1212, 1180, 1152, 1104, 1079, 1038, 1005 cm^{-1}.

^1H NMR (500 MHz): δ = 8.17 (d, *J* = 8.4 Hz, 1 H), 7.85 (d, *J* = 8.3 Hz, 1 H), 7.58–7.57 (m, 2 H), 7.44 (t, *J* = 7.2 Hz, 3 H), 7.40–7.34 (m, 2 H), 7.13 (t, *J* = 7.5 Hz, 2 H), 6.78 (t, *J* = 7.3 Hz, 1 H), 6.68–6.67 (m, 2 H), 6.14 (s, 1 H), 3.67 (sept, *J* = 6.1 Hz, 1 H), 3.47 (s, 3 H), 0.79 (d, *J* = 6.1 Hz, 6 H).

^{13}C NMR (125 MHz): δ = 151.1, 147.2, 146.9, 134.6, 130.9, 129.9, 128.9, 127.8, 127.6, 127.1, 126.9, 126.2, 125.8, 125.0, 124.8, 122.7, 119.1, 115.1, 75.5, 61.1, 22.2.

HRMS (EI): *m*/*z* calcd for $C_{26}H_{25}NO_2$: 383.1885; found: 383.1880.

2-Isopropoxy-4-methoxy-6-methyl-3-phenyl-1-(*N*-phenylamino)naphthalene (18b) and 3-Isopropoxy-1-methoxy-5-methyl-2-phenyl-4-(*N*-phenylamino)naphthalene (19a)

Prepared from **9b** (298 mg, 0.75 mmol); oil; yield: 151 mg (51%) as a mixture in a 3.8:1 ratio.

IR: 3390, 3054, 2975, 2931, 1600, 1497, 1449, 1412, 1365, 1301, 1192, 1104, 1077, 1031 cm^{-1}.

^1H NMR (500 MHz): δ = 8.0 (d, *J* = 8.3 Hz, 1 H), 7.93 (s, 1 H), 7.75 (d, *J* = 8.6 Hz, 1 H), 7.59–7.56 (m, 3 H), 7.44 (t, *J* = 7.4 Hz, 3 H), 7.37–7.33 (m, 2 H), 7.25–7.21 (m, 2 H), 7.15–7.08 (t, 3 H), 6.78 (t, *J* = 7.3 Hz, 1 H), 6.75 (t, *J* = 7.3 Hz, 1 H), 6.67 (d, *J* = 7.6 Hz, 2 H), 6.52 (d, *J* = 7.7 Hz, 2 H), 3.62 (sept, *J* = 5.8 Hz, 2 H), 3.45 (s, 3 H), 2.71 (s, 3 H), 2.52 (s, 3 H), 0.78 (d, *J* = 5.8 Hz, 6 H), 0.74 (d, *J* = 5.8 Hz, 6 H).

^{13}C NMR (100 MHz): δ = 151.6, 150.6, 148.8, 148.7, 147.0, 146.4, 134.9, 134.7, 134.6, 131.3, 130.9, 130.8, 130.3, 129.1, 128.9, 128.4, 128.1, 128.0, 127.8, 127.6, 127.1, 127.07, 126.9, 126.86, 125.9, 124.8, 121.6, 121.0, 119.0, 118.8, 115.5, 114.2, 75.5, 75.0, 61.1, 60.9, 23.3, 21.8.

HRMS (EI): *m*/*z* calcd for $C_{27}H_{27}NO_2$: 397.2042; found: 397.2040.

2-Isopropoxy-4,6-dimethoxy-3-phenyl-1-(*N*-phenylamino)naphthalene (18c) and 3-Isopropoxy-1,5-dimethoxy-2-phenyl-4-(*N*-phenylamino)naphthalene (19b)

Prepared from **9c** (148 mg, 0.36 mmol) by refluxing for 35 days; oil; yield: 151 mg (48%) as a mixture in a 3.8:1 ratio. Crude ^{1}H NMR showed a 3.1:1 mixture of isomers. Radial chromatography (elution with 20:1 hexanes–EtOAc) gave one major fraction containing both isomers **18c** and **19b**; oil; yield: 111 mg (75%).

IR: 3406, 3055, 2972, 2930, 2840, 1600, 1496, 1446, 1401, 1371, 1303, 1227, 1176, 1105, 1060, 1011 cm^{-1}.

^{1}H NMR (500 MHz): δ = 7.81–7.79 (d, *J* = 8.4 Hz, 1 H), 7.58–7.57 (m, 2 H), 7.47–7.42 (m, 3 H), 7.38–7.30 (m, 1 H), 7.20 (t, *J* = 7.2 Hz, 2 H), 7.07 (dd, *J* = 2.6, 9.2 Hz, 1 H), 6.83–6.78 (m, 1 H), 6.67 (d, *J* = 8.2 Hz, 2 H) and further overlapping signals.

^{13}C NMR (125 MHz): δ = 156.6, 149.1, 145.8, 145.5, 134.7, 131.3, 128.3, 127.5, 124.7, 123.6, 120.6, 118.8, 115.9, 115.8, 106.4, 73.7, 60.9, 56.2, 22.2.

HRMS (EI): *m*/*z* calcd $C_{27}H_{27}NO_3$: 413.1991; found: 413.1994.

A minute amount of **18c** crystallized out of solution upon standing; mp 174–176 °C.

18c

IR: 3390, 3051, 2973, 2932, 2837, 1598, 1497, 1420, 1372, 1300, 1224, 1176, 1106, 1073, 1014 cm^{-1}.

^{1}H NMR (500 MHz): δ = 7.75 (d, *J* = 4.2 Hz, 1 H), 7.58–7.57 (m, 2 H), 7.47–7.44 (m, 3 H), 7.38–7.35 (m, 1 H), 7.16–7.13 (m, 2 H) 7.08 (dd, *J* = 2.6, 9.2 Hz, 1 H), 6.81–6.78 (m, 1 H), 6.69–6.67 (m, 2 H), 6.12 (s, 1 H), 3.94 (s, 3 H), 3.61 (sept, *J* = 6.0 Hz, 1 H), 3.45 (s, 3 H), 0.78 (d, *J* = 6.0 Hz, 6 H).

^{13}C NMR (125 MHz): δ = 157.4, 149.9, 147.0, 145.2, 134.7, 130.9, 128.9, 128.1, 127.9, 127.1, 126.8, 126.6, 125.1, 119.2, 118.7, 115.5, 100.9, 75.5, 60.7, 55.4, 22.2.

HRMS (EI): *m*/*z* calcd for $C_{27}H_{27}NO_3$: 413.1991; found: 413.1992.

Iminoquinone 22 and 3-Isopropoxy-2-phenylcyclopenta[*b*]quinolin-1-ones 25; General Procedure

A 100 mL round-bottomed flask equipped with a stirring bar, refluxing condenser, and gas inlet/outlet (argon) was charged with **8d–g,i,j** or **10** (0.34 mmol) and refluxed for 60 min followed by column chromatography (gradient elution 20:1 → 10:1 hexanes–EtOAc) to give a complex mixture of at least three compounds on TLC. The least polar fraction contained **25**.

2-Isopropoxy-*N*-(4-methoxyphenyl)-3,6-diphenyl-*p*-benzoquinonemonoimine (22)

Prepared from **8f** (100 mg, 0.24 mmol) by chromatography along with **25c** (vide infra); yellow oil; yield: 16 mg (16%); mixture of *E*/*Z* diastereomers.

IR: 2978, 1692, 1624, 1585, 1498, 1446, 1378, 1307, 1245, 1161, 1092, 1061, 1034 cm^{-1}.

^{1}H NMR (500 MHz): δ = 8.43–8.41 (m, 2 H), 8.02 (d, *J* = 7.9 Hz, 2 H), 7.69 (s, 1 H), 7.60 (s, 1 H), 7.47–7.35 (m, 8 H), 7.09 (t, *J* = 7.2 Hz, 2 H), 6.92 (t, *J* = 7.6 Hz, 2 H), 6.88–6.86 (m, 6 H), 6.70 (d, *J* = 8.7 Hz, 2 H), 6.37 (d, *J* = 8.7 Hz, 2 H), 6.10 (sept, *J* = 5.9 Hz, 1 H), 4.24 (sept, *J* = 6.0 Hz, 1 H), 3.83 (s, 3 H), 3.62 (s, 3 H), 1.49 (d, *J* = 6.0 Hz, 6 H), 0.71 (d, *J* = 5.9 Hz, 6 H).

^{13}C NMR (125 MHz): δ = 172.3, 158.0, 156.3, 154.8, 144.4, 142.0, 136.6, 135.1, 133.5, 133.5, 130.8, 130.2, 129.8, 129.7, 129.3, 129.2, 128.7, 128.2, 128.1, 127.3, 126.0, 123.2, 119.8, 113.4, 75.9, 74.9, 55.7, 55.4, 23.8, 21.5.

HRMS (EI): *m*/*z* calcd for $C_{28}H_{25}NO_3$: 423.1834; found: 423.1832.

3-Isopropoxy-2-phenyl-9-(trimethylsilylmethyl)cyclopenta[*b*]quinolin-1-one (25a)

Prepared from **8d** (100 mg, 0.25 mmol), reflux time 90 min, followed by radial chromatography (gradient elution with 200:1 → 100:1 → 100:10 pentane–EtOAc) to give one major fraction, which contained a mixture of three compounds; recrystallized from CH_2Cl_2–pentane; yellow solid; yield: 12 mg (17%); mp 135–136 °C.

IR: 3076, 2957, 1688, 1602, 1577, 1525, 1493, 1464, 1392, 1336, 1249, 1189, 1141, 1096, 1006 cm^{-1}.

^{1}H NMR (500 MHz): δ = 8.01 (dd, *J* = 1.2, 8.4 Hz, 1 H), 7.94 (dd, *J* = 1.2, 8.4 Hz, 1 H), 7.89 (dd, *J* = 1.2, 8.4 Hz, 2 H), 7.68–7.65 (m, 1 H), 7.52–7.49 (m, 1 H), 7.44–741 (m, 2 H), 7.33–7.29 (m, 1 H), 6.38 (sept, *J* = 6.0 Hz, 1 H), 3.22 (br s, 2 H), 1.49 (d, *J* = 6.2 Hz, 6 H), 0.03 (s, 9 H).

^{13}C NMR (125 MHz): δ = 192.2, 168.2, 159.6, 148.4, 145.7, 130.8, 130.3, 129.1, 128.0, 127.9, 127.4, 126.6, 125.6, 121.3, 120.0, 75.6, 23.3, 18.8, –0.7.

HRMS (EI): *m*/*z* calcd for $C_{25}H_{27}NO_2Si$: 401.1811; found: 401.1817.

3-Isopropoxy-2,9-diphenylcyclopenta[*b*]quinolin-1-one (25b)

Prepared from of **8e** (139 mg, 0.35 mmol) and isolated by column chromatography (gradient elution 7:1 → 5:1 hexanes–EtOAc) plus recrystallization from CH_2Cl_2–pentane; yellow solid; yield: 67 mg (49%); mp 204–206 °C.

IR: 3057, 2982, 2927, 1693, 1620, 1551, 1491, 1459, 1388, 1337, 1298, 1124, 1056 cm^{-1}.

^{1}H NMR (500 MHz): δ = 8.10 (d, *J* = 8.2 Hz, 1 H), 7.89–7.87 (m, 2 H), 7.70–7.67 (m, 1 H), 7.64 (d, *J* = 7.8 Hz, 1 H), 7.52–7.51 (m, 3 H), 7.45–7.34 (m, 5 H), 7.27 (t, *J* = 7.3 Hz, 1 H), 6.47 (sept, *J* = 6.1 Hz, 1 H), 1.53 (d, *J* = 6.1 Hz, 6 H).

^{13}C NMR (125 MHz): δ = 189.5, 169.0, 159.5, 148.9, 143.1, 133.0, 130.6, 130.5, 130.4, 129.5, 129.1, 128.7, 128.0, 127.9, 127.6, 127.4, 122.0, 121.9, 75.9, 23.3.

HRMS (EI): *m*/*z* calcd for $C_{27}H_{21}NO_2$: 391.1572; found: 391.1565.

3-Isopropoxy-2,9-diphenyl-7-methoxycyclopenta[*b*]quinolin-1-one (25c)

Prepared from of **8f** (100 mg, 0.24 mmol) along with **22** (vide supra) and isolated by column chromatography (gradient elution 10:1 → 5:1 hexanes–EtOAc) plus recrystallization from CH_2Cl_2–pentane; yellow solid; yield: 52 mg (49%); mp 204–206 °C.

IR: 1684, 1651, 1618, 1559, 1523, 1457, 1394, 1338, 1294, 1258, 1136, 1088, 1030 cm^{-1}.

^{1}H NMR (500 MHz): δ = 8.00 (d, *J* = 9.1 Hz, 1 H), 7.86 (dd, *J* = 1.2, 8.8 Hz, 2 H), 7.52–7.51 (m, 2 H), 7.40–7.38 (m, 2 H), 7.36–7.32 (m, 2 H), 7.31 (m, 1 H), 7.27–7.25 (m, 2 H), 6.96 (m, 1 H), 6.44 (sept, *J* = 6.0 Hz, 1 H), 3.74 (s, 3 H), 1.52 (d, *J* = 6.0 Hz, 6 H).

^{13}C NMR (125 MHz): δ = 189.7, 169.5, 158.7, 157.1, 144.3, 142.0, 133.2, 131.6, 130.6, 129.3, 129.1, 129.07, 128.6, 128.1, 127.8, 127.4, 122.3, 121.1, 120.8, 107.8, 75.8, 55.5, 23.3.

HRMS (EI): *m*/*z* calcd for $C_{28}H_{23}NO_3$: 421.1678; found: 421.1673.

Anal. Calcd for $C_{28}H_{23}NO_3$: C, 79.79; H, 5.55; N, 3.32. Found: C, 79.50; H, 5.77; N, 3.18.

3-Isopropoxy-2-phenyl-9-propyl-7-(trifluoromethyl)cyclopenta[*b*]quinolin-1-one (25d)

Starting from **7c** (360 mg, 1.0 mmol), crude **8g** (269 mg, 0.58 mmol) was prepared and refluxed for 1.5 h following the General Procedure. After chromatography (gradient elution 10:1 → 7:1 hexanes–EtOAc), the product was obtained by recrystallization

from CH_2Cl_2–pentane; yellow solid; yield: 96 mg (36%); mp 215–218 °C.

IR: 2985, 2361, 1696, 1615, 1560, 1424, 1394, 1311, 1282, 1179, 1152, 1121, 1089 cm^{-1}.

^1H NMR (500 MHz): δ = 8.2 (d, *J* = 10 Hz, 1 H), 7.91–7.87 (m, 4 H), 7.56–7.54 (m, 3 H), 7.40–7.36 (m, 4 H), 7.31–7.28 (m, 1 H), 6.42 (sept, *J* = 5.0 Hz, 1 H), 1.54 (d, *J* = 5.0 Hz, 6 H).

^{13}C NMR (100 MHz): δ = 188.8, 168.5, 161.5, 150.3, 143.3, 131.9, 131.2, 130.1, 129.5, 129.2, 128.3, 128.0, 127.95, 127.6, 126.5, 126.47, 125.4, 123.1, 122.7, 76.3, 23.2.

HRMS (EI): *m*/*z* calcd for $C_{28}H_{20}F_3NO_2$: 459.1446; found: 459.1535.

2-Isopropoxy-3,5-diphenylcyclopenta[*b*][1,5]naphthyridin-4-one (25eB) and 2-Isopropoxy-3,5-diphenylcyclopenta[*b*][1,7]naphthyridin-4-one (25eA)

Prepared from **8i** (420 mg, 1.06 mmol) following the General Procedure, but using *p*-xylene (100 mL) as solvent. Isolation from the crude red oil by radial chromatography (eluent: PE–EtOAc, 25:1) and recrystallization from EtOAc–PE.

25eA

Sticky orange colored mass; yield: 51 mg (12%).

IR (KBr): 3441, 2987, 2961, 2927, 1696, 1619, 1547, 1393, 1341, 1301, 904, 776, 692 cm^{-1}.

^1H NMR (200 MHz): δ = 9.44 (br s, 1 H), 8.56 (br d, 1 H, *J* = 5.0 Hz), 7.30–7.60 (m, 9 H), 7.89 (m, 2 H), 6.49 (sept, 1 H, *J* = 6.2 Hz), 1.56 (d, 6 H, *J* = 6.2 Hz).

^{13}C NMR (50 MHz): δ = 188.4, 168.9, 160.6, 153.6, 145.9, 141.6, 132.4, 131.4, 129.9, 129.5, 129.3, 129.2, 128.2, 128.0, 127.9, 127.5, 125.0, 123.3, 120.0, 76.6, 23.4.

MS (70 eV): *m*/*z* (%) = 392 (2, $[M]^+$), 350 (100), 321 (25).

25eB

Sticky orange colored mass; yield: 28 mg (7%).

IR (KBr): 3443, 3056, 3020, 2988, 1698, 1620, 1552, 1498, 1399, 1383, 1296, 1088, 785, 696, 689 cm^{-1}.

^1H NMR (200 MHz): δ = 1.52 (d, *J* = 6.1 Hz, 6 H), 6.32 (sept, *J* = 6.1 Hz, 1 H), 7.27–7.50 (m, 8 H), 7.60 (dd, *J* = 4.3, 8.3 Hz, 1 H), 7.80–7.90 (m, 2 H), 8.38 (dd, *J* = 1.8, 8.3 Hz, 1 H), 8.88 (dd, *J* = 1.8, 4.3 Hz, 1 H).

^{13}C NMR (50 MHz): δ = 188.8, 168.3, 160.2, 150.6, 144.8, 143.8, 137.7, 131.5, 130.5, 130.1, 129.3, 129.2, 129.1, 128.0, 127.9, 127.5, 127.1, 124.8, 122.9, 76.2, 23.3.

MS (70 eV): *m*/*z* (%) = 393 (3, $[M + H]^+$), 350 (100).

2-Isopropoxy-3,5-diphenylcyclopenta[*b*][1,6]naphthyridin-4-one (25f)

Prepared from **8j** (280 mg, 0.71 mmol) following the General Procedure, but using *p*-xylene (40 mL) as solvent and refluxing for 30 min. Isolation by column chromatography (eluent: PE–EtOAc, 1:1); semi-solid yellow material; yield: 62 mg (22%).

IR (KBr): 3445, 3060, 2972, 1701, 1611, 1563, 1425, 1393, 1302, 1091, 836, 790, 702 cm^{-1}.

^1H NMR (200 MHz): δ = 9.00 (s, 1 H), 8.77 (d, *J* = 5.7 Hz, 1 H), 7.80–7.95 (m, 3 H), 7.30–7.60 (m, 8 H), 6.35 (sept, *J* = 6.2 Hz, 1 H), 1.53 (d, *J* = 6.2 Hz, 6 H).

^{13}C NMR (100 MHz): δ = 188.5, 168.0, 163.6, 152.2, 152.2, 148.9, 143.0, 131.0, 129.9, 129.6, 129.3, 129.3, 128.2, 128.1, 128.0, 123.9, 123.0, 122.8, 122.7, 76.3, 23.3.

MS (70 eV): *m*/*z* (%) = 393 (42, $[M + H]^+$), 249 (56), 221 (47), 193 (21), 145 (100), 89 (89), 78 (56).

2-Isopropoxy-3,5-diphenyl-4-(trimethylsilyloxy)-2*H*-cyclopenta[*b*]quinoline (26)

Prepared from **10** (100 mg, 0.22 mmol) following the General Procedure, but refluxing for 1.5 h and using *p*-xylene (100 mL) as solvent. Isolation by radial chromatography (eluent: hexanes–EtOAc, 10:1); oil; yield: 20 mg (19%).

IR: 3059, 2970, 1592, 1492, 1444, 1388, 1308, 1253, 1176, 1119, 1076, 1043 cm^{-1}.

^1H NMR (500 MHz): δ = 8.17–8.15 (m, 1 H), 7.74–7.73 (m, 2 H), 7.64–7.61 (m, 2 H), 7.53–7.45 (m, 3 H), 7.42–7.36 (m, 4 H), 7.25–7.23 (m, 2 H), 5.53 (s, 1 H), 4.29 (sept, *J* = 6.1 Hz, 1 H), 1.15, 1.12 (d each, *J* = 6.1 Hz, 3 H), –0.49 (s, 9 H).

^{13}C NMR (125 MHz): δ = 164.7, 150.9, 146.7, 137.5, 134.9, 134.4, 131.6, 131.3, 129.7, 129.2, 128.9, 128.2, 128.1, 128.05, 127.99, 127.93, 127.5, 127.1, 126.8, 126.3, 125.9, 78.4, 70.2, 23.8, 22.8, –0.24.

HRMS (EI): *m*/*z* calcd for $C_{30}H_{31}NO_2Si$: 465.2124; found: 465.2121.

(*E*/*Z*)-5-Benzylidene-3-isopropoxy-2-phenyl-4-(2,4,6-trimethylphenylimino)cyclopent-2-en-1-one (27)

Obtained from **8h** (550 mg, 1.26 mmol) following the General Procedure, but using *p*-xylene (100 mL) as solvent and refluxing for 30 min. Isolation from the crude red oil by radial chromatography (eluent: PE–EtOAc, 25:1) and recrystallization from EtOAc–PE; red crystals; two diastereomers in a 1:0.6 ratio (as far as possible, isomer signals are indicated by subscripts 1 or 2 in the ^1H NMR spectrum); yield: 290 mg (53%); mp 147 °C.

IR (KBr): 3069, 2972, 2910, 1693, 1644, 1626, 1589, 1488, 1381, 1308, 1248, 1127, 1095, 1076, 1036, 770, 753, 697 cm^{-1}.

^1H NMR (400 MHz): δ = 8.43 (br s, 2 H_2), 8.03 (s, *J* = 7.3 Hz, 2 H_2), 7.87 (s, 1 H_1), 7.67 (d, *J* = 7.1 Hz, 2 H_2), 7.55–7.30 (m, H_1 and H_2), 6.99 (s, 2 H_2), 6.86 (s, 2 H_1), 6.78 (s, 1 H_2), 6.28 (sept, *J* = 6.1 Hz), 4.30 (sept, *J* = 6.0 Hz, 1 H_1), 2.86 (s, 3 H_1), 2.31 (s, 3 H_2), 2.27 (s, 3 H_1), 2.13 (s, 6 H_2), 2.10 (s, 3 H_1), 1.49 (d, *J* = 6.1 Hz, 6 H_2), 0.68 (d, *J* = 6.0 Hz, 6 H_1).

MS (70 eV): *m*/*z* (%) = 435 (100, $[M]^+$), 392 (48), 378 (90), 348 (34), 346 (13), 314 (19), 234 (16), 191 (16), 179 (19).

Acknowledgment

We thank the Fonds der Chemischen Industrie, Frankfurt, Germany as well as the National Institutes of Health for generous financial support.

References

(1) (a) Moore, H. W.; Yerxa, B. R. *Chemtracts* **1992**, *5*, 273. (b) Moore, H. W.; Yerxa, B. R. *Adv. Strain Org. Chem.* **1995**, *4*, 81.
(2) Liebeskind, L. S. *Tetrahedron* **1989**, *45*, 3053.
(3) (a) Paquette, L. A.; Morwick, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 1230. (b) Paquette, L. A.; Hamme, A. T.; Kuo, L. H.; Doyon, J.; Krezholz, R. *J. Am. Chem. Soc.* **1997**, *119*, 1242.
(4) Yamamoto, Y.; Nunokawa, K.; Okamoto, K.; Ohno, M.; Eguchi, S. *Synthesis* **1995**, 571.
(5) Zora, M.; Herndon, J. W.; Li, Y.; Rossi, J. *Tetrahedron* **2001**, *57*, 5097.
(6) Gayo, L. M.; Winters, M. P.; Moore, H. W. *J. Org. Chem.* **1992**, *57*, 6896.

(7) Reed, M. W.; Pollart, D.; Perri, S. T.; Foland, L.; Moore, H. W. *J. Org. Chem.* **1988**, *53*, 2477.
(8) Liebeskind, L. S.; Fengl, R. W.; Wirtz, K. R.; Shawe, T. T. *J. Org. Chem.* **1988**, *53*, 2482.
(9) Müller, M.; Heileman, M. J.; Moore, H. W.; Schaumann, E.; Adiwidjaja, G. *Synthesis* **1997**, 50.
(10) Regenhardt, W.; Schaumann, E.; Moore, H. W. *Synthesis* **2001**, 1076.
(11) Benda, K.; Regenhardt, W.; Schaumann, E.; Adiwidjaja, G. *Eur. J. Org. Chem.* **2009**, 1016.
(12) Ried, W.; Kunstmann, W. *Angew. Int., Ed. Engl.* **1968**, *7*, 135; *Angew. Chem.* **1968**, *80*, 121.
(13) (a) Obata, N.; Takizawa, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2017. (b) Obata, N.; Takizawa, T. *Tetrahedron Lett.* **1970**, 2231.
(14) Chickos, J. S. *J. Org. Chem.* **1973**, *38*, 3642.
(15) Palacios, F.; Alonso, C.; Aparicio, D.; Rubiales, G.; de los Santos, J. M. *Tetrahedron* **2006**, *63*, 523.
(16) Tidwell, T. T. *Ketenes*; Wiley-VCH: Weinheim, **2006**.
(17) Carreño, M. C.; Ribagorda, M. In *Science of Synthesis*, Vol. 28; Griesbeck, A. G., Ed.; Thieme: Stuttgart, **2006**, 629.
(18) Foland, L.; Karlsson, J. O.; Perri, S. T.; Schwabe, R.; Xu, S. L.; Patil, S.; Moore, H. W. *J. Am Chem. Soc.* **1989**, *111*, 975.
(19) Moore, H. W.; Perri, S. T. *J. Org. Chem.* **1988**, *53*, 996.
(20) Karlsson, J. O.; Nguyen, N. V.; Foland, L. D.; Moore, H. W. *J. Am. Chem. Soc.* **1985**, *107*, 3392.
(21) Unit cell parameters: a = 10.4030(13) Å, b = 13.3488(11) Å, c = 25.005(2) Å, α = 84.276(7)°, β = 87.124(9)°, γ = 70.792(9)°, V = 3262.2(6) Å^3, Z = 6; triclinic, space group $P1$, R = 0.0452, R_w = 0.0761. CCDC 758016 contains the supplementary cyrstallographic data for this compound. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
(22) Unit cell parameters: a = 9.4990(10) Å, b = 17.7990(10) Å, c = 14.7910(10) Å, α = β = γ = 90°, V = 2500.8(3) Å^3, Z = 4; orthorhombic, space group Pna2(1), R = 0.0542, R_w = 0.1274. CCDC 75 80 17. To obtain the data, see ref. 21.
(23) Lui, H.; Tomooka, C. S.; Moore, H. W. *Synth. Commun.* **1997**, *27*, 2177.
(24) Boedeker, J.; Koeckritz, A.; Koeckritz, P.; Radeglia, R. *J. Prakt. Chem.* **1985**, *327*, 723.