Michael Addition of Imines to Alkynylcarbene Complexes with Subsequent Intramolecular Cyclization – An Efficient Three-Step Synthesis of 2*H*-Pyrroles

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Received November 23, 1993

Key Words: Chromium, [2-(methyleneamino)ethenyl]carbene complexes / Michael addition of imines / (1-alkynylcarbene)-chromium complexes / 2*H*-Pyrroles / Cyclization of {[2-(methyleneamino)ethenyl]carbene}chromium complexes

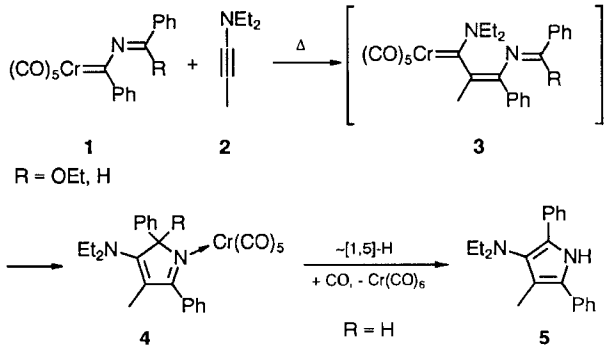
Imines **7**, **11**–**13** were added to (1-alkynylcarbene)chromium complexes **6a**–**d** to form {[2-(methyleneamino)ethenyl]-carbene}chromium complexes **8a**–**d**, **14a**–**d**, **15a**–**d**, **16a**–**d** in good to very good yields (63–98%) except for two cases (41–59%). The carbene ligands of the latter compounds cyclize to 2*H*-pyrroles **9a**–**d**, **17a**–**d**, **18a**–**d**, **19a**–**d** upon heating in tetrahydrofuran solution to 50–55°C.

Numerous investigations in recent years have uncovered manifold new reactions of Fischer carbene complexes[1]. Phenyl- and ethenyl(alkoxy)carbene complexes have gained the widest interest of all, because of their six-membered ring annulation with alkynes (the so-called Dötz reaction)[1,2]. A wide range of unsaturated carbenechromium complexes undergo this cycloaddition, but alkoxy{[2-(dialkylamino)ethenyl]carbene}chromium complexes yield a variety of different products. Depending on the substituents at the terminus of the ethenyl group they react with alkynes to give cyclopentadienes[3], coordinated fulvenes[4], 5-methylene-2-cyclopenten-1-ones[5], or cyclopenta[*b*]pyrans[6]. Moreover, alkoxy{[(2*Z*)-2-(dialkylamino)ethenyl]-carbene}chromium complexes rearrange to aminomethylene complexes[7], and monoalkylamino or amino derivatives rearrange to coordinated 1-aza-1,3-butadienes[8].

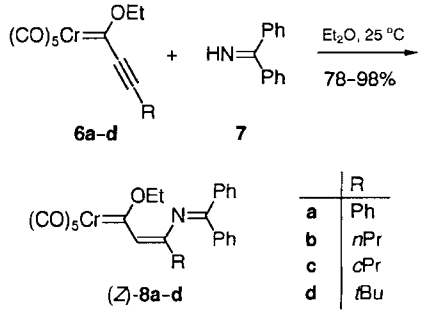
As Aumann et al. have shown for several examples, carbene ligands of [amino(3-aza-1,3-butadienyl)carbene]chromium complexes **3**, formed by insertion of alkynes, e.g. 1-(diethylamino)-1-propyne (**2**) into the chromium-carbon double bond of 1-(benzylideneamino) complexes **1** cyclize under the reaction conditions to the (initially coordinated) 2*H*-pyrrole **4**, which can undergo a 1,5-hydride shift to give pyrrole **5**, if R = H (Scheme 1)[9,10].

Although the Michael addition of dimethylamine to alkynylcarbene complexes was reported by Fischer et al. as early as 1972[11], the broad scope of this reaction with a variety of heteroatomic nucleophiles has been tested only recently[12,13]. However, the addition of imines to alkynylcarbene complexes[14], which would lead directly to complexes of type **3**, has not yet been tried.

Scheme 1



Scheme 2. (For detailed yields see Table 1)



When (alkynylcarbene)chromium complexes **6a**–**d**[11b,12,15] were treated with (diphenylmethylene)amine (**7**) in diethyl ether at 25°C, the Michael adducts **8a**–**d** were formed

[+] Crystal structure analysis.

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smoothly. As could be shown by 2D-NOESY-NMR measurements, the *Z* isomers were obtained as the sole products except for the cyclopropyl derivative **8c**, which gave a mixture of both isomers with a detectable amount of *E* isomer (ratio *Z*/*E* 94:6). The additions of **7** proceeded much slower than those of amines. With a threefold excess of **7** reactions were complete within one to two hours. Chromatography of the crude products afforded (*Z*)-**8a–d** in high yields (see Table 1).

Scheme 3

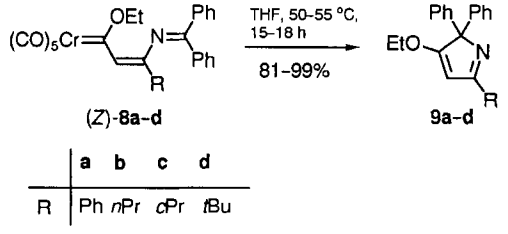


Table 1. Michael addition of (diphenylmethylene)amine (**7**) to (alkynylcarbene)chromium complexes **6a–d** and subsequent cyclization to 2*H*-pyrroles **9a–d**

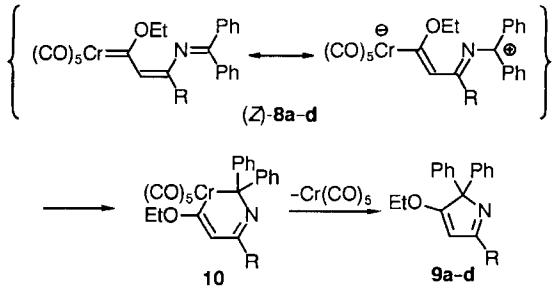
Starting material	R	Product	Yield (%)	*Z* Isomer (%)[a]	2*H*-Pyrrole	Yield (%)
6a[11b]	Ph	**8a**	81	>96	**9a**	80
6b[15]	*n*Pr	**8b**	78	>96	**9b**	88
6c[12a]	*c*Pr	**8c**	98	94	**9c**	96
6d[12a]	*t*Bu	**8d**	98	>96	**9d**	99

[a] Established on the basis of ^{1}H-NMR spectra.

When the alkoxy{(2*Z*)-2-[(diphenylmethylene)amino]-ethenyl}carbene complexes **8a–d** were heated to 50–55°C in tetrahydrofuran solution cyclization of their carbene ligands occurred cleanly to yield 2*H*-pyrroles **9a–d** within 15–18 h (see Table 1). The probable intermediate coordinated pyrroles like **4**, which have been obtained and fully characterized with a crystal structure analysis by Aumann et al. from 1-(benzylideneamino) complexes **1**[9a], could not be isolated in any of the above cases after column chromatography.

When the Michael additions were carried out with **6b, d** and only one equivalent of **7** under high pressure (10 kbar)[16], the adducts **8b,d** were not obtained in as high yields as above, but both the addition as well as the cyclization step were definitely accelerated. After 2 h under 10 kbar, unreacted starting materials **6b, d** (2, 3%), adducts **8b, d** (69, 71%), and 2*H*-pyrroles **9b, d** (15, 18%) were isolated.

Scheme 4



The formation of the 2*H*-pyrroles **9** could arise by a 6π electrocyclization of the 5-aza-1-chroma-1,3,5-hexatrienes **8** followed by reductive elimination of the pentacarbonylchromium unit from the 1-aza-5-chromacyclohexadiene **10**, as has been suggested before[9a]. The electrocyclization of trienes **8** ought to be favored by their zwitterionic character; all carbon 1,3,5-hexatrienes undergo electrocyclization only at temperatures above 120°C. To probe for this mechanistic concept and to widen the scope of this sequence, it was carried out with substituents of different electronic nature in the methyleneamino group.

Scheme 5. (For detailed yields see Tables 2 and 3)

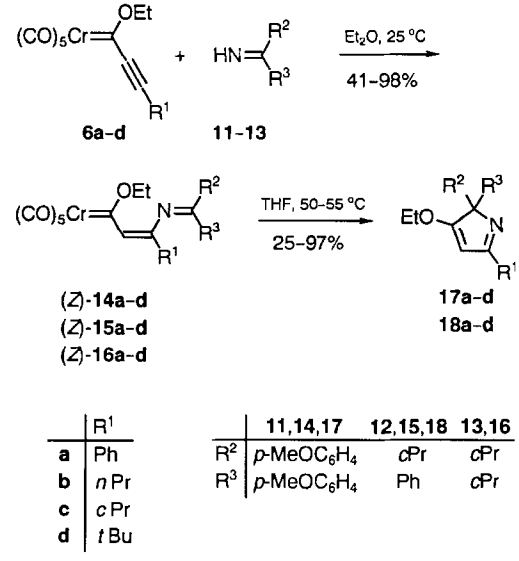


Table 2. Michael addition of imines **11–13** to (alkynylcarbene)chromium complexes **6a–d** (Scheme 5)

Starting material	R^1	Imine	R^2	R^3	Product	Yield (%)	(*Z*) Isomer (%)[a]
6a[12b]	Ph	**11**	*p*-MeOC$_6$H$_4$	*p*-MeOC$_6$H$_4$	**14a**	41	>96
		12	Ph	*c*Pr	**15a**	72	>96
		13	*c*Pr	*c*Pr	**16a**	85	>96
6b[15]	*n*Pr	**11**	*p*-MeOC$_6$H$_4$	*p*-MeOC$_6$H$_4$	**14b**	63	>96
		12	Ph	*c*Pr	**15b**	88	>96
		13	*c*Pr	*c*Pr	**16b**	81	>96
6c[12a]	*c*Pr	**11**	*p*-MeOC$_6$H$_4$	*p*-MeOC$_6$H$_4$	**14c**	64	94
		12	Ph	*c*Pr	**15c**	98	95
		13	*c*Pr	*c*Pr	**16c**	84	91
6d[12a]	*t*Bu	**11**	*p*-MeOC$_6$H$_4$	*p*-MeOC$_6$H$_4$	**14d**	59	>96
		12	Ph	*c*Pr	**15d**	85	>96
		13	*c*Pr	*c*Pr	**16d**	86	>96

[a] Established on the basis of ^{1}H-NMR spectra.

[Bis(*p*-methoxyphenyl)methylene]amine (**11**)[17], (cyclopropylphenylmethylene)amine (**12**)[18], and (dicyclopropylmethylene)amine (**13**)[17] were added to (alkynylcarbene)chromium complexes **6a–d** (Scheme 5 and Table 2). Surprisingly, the adducts **14a–d** of **11** with **6a–d** were obtained in poorer yield than all others, although the *p*-methoxy groups ought to increase the nucleophilicity of the nitrogen in **11**. Again, a second isomer besides the *Z* form was not detected in any case except for the cyclopropyl derivatives **14c–16c**, which each contained between 5 and 9% of the *E* isomer. It is noteworthy that even the addition of (cyclopropylphenylmethylene)amine (**12**) to **6a, b, d** leads to

only a single diastereomer (according to ^{1}H-NMR spectra). Yet the configuration around the N=C bond of this diastereomer remains unclear. The introduction of cyclopropyl groups as in **15** and **16** causes an increase in stability. The (dicyclopropylmethylene)amino derivatives **16a–d** are stable for several weeks even at room temperature. In comparison with the phenyl group this might be attributed to the stronger electron-donating ability[19] of the cyclopropyl group which would lead to a better compensation of the electron deficiency at the end of the conjugated system.

Table 3. 2*H*-Pyrroles **17a–d** and **18a–d** by cyclization of {[2-(methyleneamino)ethenyl]carbene}chromium complexes **14a–d** and **15a–d**

Starting material	R^1	R^2	R^3	Product	Yield (%)
14a	Ph	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**17a**	25
14b	*n*Pr	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**17b**	57
14c	*c*Pr	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**17c**	65
14d	*t*Bu	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**17d**	78
15a	Ph	Ph	*c*Pr	**18a**	62
15b	*n*Pr	Ph	*c*Pr	**18b**	88
15c	*c*Pr	Ph	*c*Pr	**18c**	97
15d	*t*Bu	Ph	*c*Pr	**18d**	85

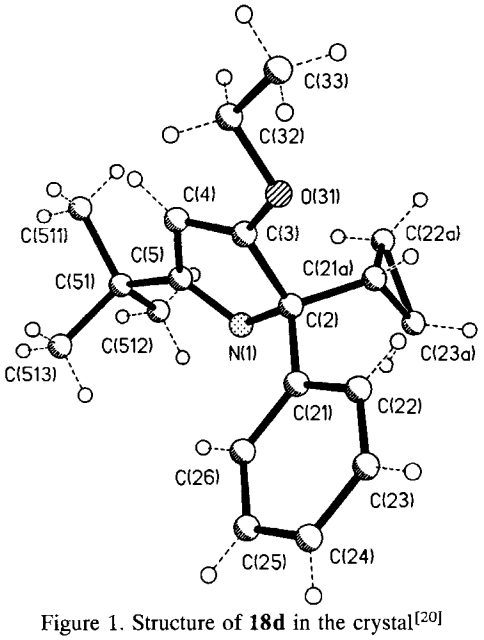


Figure 1. Structure of **18d** in the crystal[20]

Cyclization by heating of the [bis(*p*-methoxyphenyl)methylene]amino derivatives **14a–d** in tetrahydrofuran solution gave the 2*H*-pyrroles **17a–d** only in moderate yield (Scheme 5 and Table 3). This indicates that the groups with stronger electron-donating ability disfavor the electrocyclization of an azachromatriene (Scheme 3). However, the (cyclopropylphenylmethylene)amino derivatives **15b–d** were cyclized to the 2*H*-pyrroles **18b–d** in excellent yield.

Crystals suitable for X-ray diffraction were obtained for compound **18d**. The structure analysis (Figure 1) revealed that the ring of **18d** is planar (max. deviation ±0.66 pm), the lengths of the C(5)=N and C(3)=C(4) bonds are 129.4 and 133.7 pm, respectively.

Scheme 6

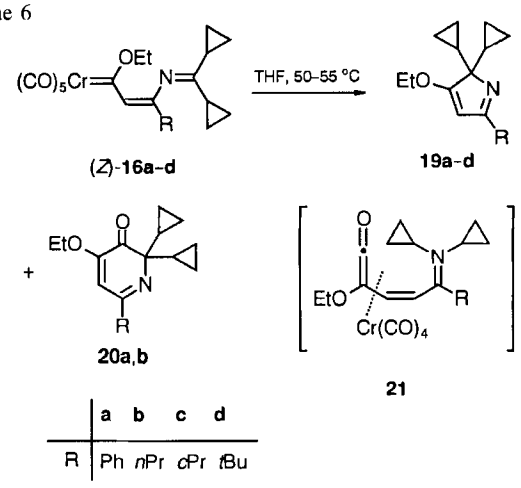
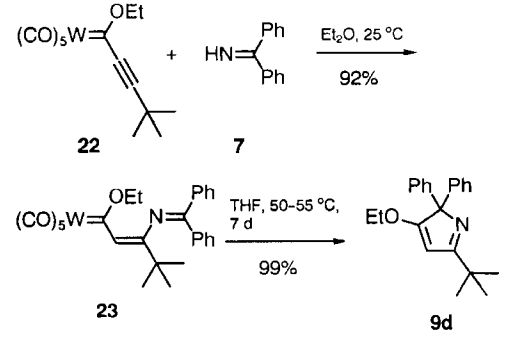


Table 4. Cyclization of {[(2*Z*)-2-[(dicyclopropylmethylene)-amino]ethenyl}carbene)chromium complexes **16a–d**

Starting material	R	2*H*-Pyrrole	Yield (%)	3(2*H*)-Pyridinone	Yield (%)
16a	Ph	**19a**	45	**20a**	21
16b	*n*Pr	**19b**	63	**20b**	22
16c	*c*Pr	**19c**	81	**20c**	0
16d	*t*Bu	**19d**	92	**20d**	0

Scheme 7



The (dicyclopropylmethylene)amino derivatives **16c, d** (R = *c*Pr, *t*Bu) yielded the 2*H*-pyrroles **19c, d** in high yields of 81 and 92%, respectively, whereas **16a, b** each gave a mixture of a 2*H*-pyrrole **19a, b** and a new compound. The ^{1}H- and ^{13}C-NMR, IR, and mass spectra disclosed these new compounds as the 3(2*H*)-pyridinones **20a, b** (Scheme 6 and Table 4).

The formation of **20** may be rationalized as starting with a carbonyl insertion into the chromium-carbon bond in **16** to give a 3-azabutadienyl-ketene complex **21**, which subsequently cyclizes as in the third and fourth step of the Dötz reaction[1,2]. Recently, there have been several reports on (2-phenylethenyl)-, (1,3-butadienyl)-, or (biphenyl-2-yl)carbene complexes reacting with C≡X (X = O, NR) to yield analogous six-membered ring dienones[21]. However, it is not at all understood, why this reaction occurs only with these two examples, but this may be ascribed to the elec-

tronic peculiarity of the cyclopropyl groups[19] and the bulkiness of the substituents R in **16c, d**. This type of cyclocarbonylation has been described before[9c], and 3-hydroxypyridines were isolated as rearrangement products of (2*H*)-pyridinone intermediates.

Eventually, by analogy with **5** the tungsten complex **23** was prepared by addition of (diphenylmethylene)amine (**7**) to the (alkynylcarbene)tungsten complex **22** in 92% yield. Cyclization of **23** proceeded cleanly and quantitatively to afford the 2*H*-pyrrole **9d**, yet it took much longer (7 days) than that of the chromium counterpart, which took only 18 h.

This new three-step high-yield synthesis of 2*H*-pyrroles from easily prepared starting materials complements existing methods for the synthesis of 2*H*-pyrroles[22].

This work was supported by the *Volkswagen-Stiftung* and the *Fonds der Chemischen Industrie*. Generous gifts of chemicals by the *Hoechst AG* and *Hüls AG* are gratefully acknowledged. M. D. is indebted to the *Deutsche Forschungsgemeinschaft* (Graduiertenkolleg "Kinetik und Selektivität chemischer Prozesse in verdichteter fluider Phase") for a graduate fellowship.

Experimental

All operations were performed under nitrogen. Solvents were dried by distillation from sodium or potassium/benzophenone. – ^{1}H NMR: Bruker AM 250 (250 MHz). – ^{13}C NMR: Bruker AM 250 (62.9 MHz), multiplicities were determined by DEPT (Distortionless Enhancement by Polarization Transfer) measurements. Chemical shifts refer to $\delta_{TMS} = 0.00$ according to the chemical shifts of residual solvent signals. – IR: Bruker IFS 66, Perkin-Elmer 298. – MS: Varian MAT CH 7, MAT 731. – HRMS: Varian MAT 311 A. – Melting points: Büchi 510, uncorrected. – Elemental analysis: Mikroanalytisches Laboratorium des Instituts für Organische Chemie der Universität Göttingen.

Molecular composition and bulk purity were determined by microanalyses for representative examples of new compounds, for all others except for the methoxy-substituted compounds **14a–d** molecular masses were confirmed by high-resolution mass spectrometry with preselected ion peak matching at $R \approx 10000$ to be within ±2 ppm of the exact masses.

General Procedure for the Preparation of {[2-(Methyleneamino)ethenyl]carbene}chromium Complexes: The imine (15 mmol) was added to a solution of 5 mmol of **6** in 50 ml of diethyl ether. The solution was stirred until no starting material could be detected by TLC. The solvent was removed under reduced pressure, and the residue was purified by chromatography on 100 g of silica gel (40 × 3 cm) to afford the pure complex.

Pentacarbonyl{(2Z)-3-[(diphenylmethylene)amino]-1-ethoxy-3-phenyl-2-propenylidene}chromium (**8a**): To a solution of 1.00 g (2.86 mmol) of pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)chromium (**6a**)[11b] in 50 ml of diethyl ether was added 1.53 g (8.43 mmol) of (diphenylmethylene)amine (**7**) at 20°C. After 30 min purification (50 g of silica gel, 30 × 1.5 cm) yielded 1.22 g (81%) of **8a** ($R_f = 0.21$, pentane), orange-red oil. – IR (film): $\tilde{\nu}$ = 2059 cm^{-1} (C=O), 1916 (C=O), 1639, 1508, 1475, 1261, 996, 665. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.30 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 4.89 (q, ^3J = 7.1 Hz, 2H, OCH_2), 7.16 (s, 1H, 2-H), 7.29–7.55 (m, 15H, Ph). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 15.38 (+, OCH_2CH_3), 76.02 (–, OCH_2), 122.72 (+, C-2), 127.83, 128.29, 128.44, 128.74, 130.40, 130.60 (+, Ph), 136.31, 137.70 (C_{quat}, Ph), 146.66 (C_{quat}, C-3), 164.66 (C_{quat}, C=N), 217.38, 224.36 (C_{quat}, C=O), 321.37 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 339 (2) [M^+ – $Cr(CO)_5$], 261 (1), 208 (3), 152 (7), 105 (100), 74 (81), 60 (62), 46 (45).

Pentacarbonyl{(2Z)-3-[(diphenylmethylene)amino]-1-ethoxy-2-hexenylidene}chromium (**8b**)

Variant A: To a solution of 141 mg (0.45 mmol) of pentacarbonyl(1-ethoxy-2-hexynylidene)chromium (**6b**)[15] in 10 ml of diethyl ether was added 240 mg (1.32 mmol) of **7** at 20°C. After 1 h purification (20 g of silica gel, 16 × 1.5 cm) yielded 176 mg (78%) of **8b** ($R_f = 0.37$, pentane), red oil. – IR (film): $\tilde{\nu}$ = 2965 cm^{-1}, 2052 (C=O), 1911 (C=O), 1645, 1517, 1240, 1137, 1030, 668. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.67 (t, ^3J = 7.3 Hz, 3H, 6-H), 0.78 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 1.33 (tq, ^3J = 7.3, ^3J = 7.3 Hz, 2H, 5-H), 1.66 (t, ^3J = 7.3 Hz, 2H, 4-H), 4.60 (q, ^3J = 7.1 Hz, 2H, OCH_2), 6.91 (s, 1H, 2-H), 7.03–7.12 (m, 6H, Ph), 7.23–7.36 (m, 4H, Ph). – ^{13}C NMR (62.9 MHz, C_6D_6, plus DEPT): δ = 13.62, 15.01 (+, OCH_2CH_3, C-6), 21.61 (–, C-5), 39.80 (–, C-4), 76.03 (–, OCH_2), 125.40 (+, C-2), 128.54, 128.83, 130.67 (+, Ph), 136.78 (C_{quat}, Ph), 151.75 (C_{quat}, C-3), 160.30 (C_{quat}, C=N), 218.32, 224.41 (C_{quat}, C=O), 317.94 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 497 (<1) [M^+], 385 (6) [M^+ – 4 CO], 357 (26) [M^+ – 5 CO], 305 (41) [M^+ – $Cr(CO)_5$], 276 (100), 248 (56), 165 (43).

Variant B: To a solution of 111 mg (0.35 mmol) of **6b**[15] in 5 ml of diethyl ether was added 63 mg (0.35 mmol) of **7** at 20°C. After 2 h under high pressure (10 kbar) the solvent was removed under reduced pressure. Purification (12 g of silica gel, 11 × 1 cm, pentane/diethyl ether, 50:1) of the residue yielded fraction I: 2 mg (2%) of **6b** ($R_f = 0.75$). – II: 121 mg (69%) of **8b** ($R_f = 0.41$). – III: 16 mg (15%) of 3-Ethoxy-2,2-diphenyl-5-propyl-2*H*-pyrrole (**9b**) ($R_f = 0.03$).

Pentacarbonyl{(2E/Z)-3-cyclopropyl-1-ethoxy-3-[(diphenylmethylene)amino]-2-propenylidene}chromium (**8c**): To a solution of 1.00 g (3.18 mmol) of pentacarbonyl(3-cyclopropyl-1-ethoxy-2-propynylidene)chromium (**6c**)[12a] in 50 ml of diethyl ether was added 1.73 g (9.54 mmol) of **7** at 20°C. After 20 min purification (50 g of silica gel, 30 × 1.5 cm) yielded 1.54 g (98%) of **8c** ($R_f = 0.22$, pentane), orange-red oil. – IR (film): $\tilde{\nu}$ = 2049 cm^{-1} (C=O), 1900 (C=O), 1631, 1482, 1238, 902, 665. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.71–0.90 (m, 4H, *c*Pr-CH_2), 1.12 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 1.40–1.51 (m, 1H, *c*Pr-CH), 4.70 [q, ^3J = 7.1 Hz, 2H, OCH_2, (*Z*)-**8c**], 4.90 [q, ^3J = 7.1 Hz, OCH_2, (*E*)-**8c**], 6.47 [s, 2-H, (*E*)-**8c**], 6.69 [s, 1H, 2-H, (*Z*)-**8c**], 7.32–7.53 (m, 10H, Ph). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): (*Z*)-**8c**: δ = 9.76 (–, *c*Pr-CH_2), 15.22, 18.17 (+, OCH_2CH_3, *c*Pr-CH), 75.48 (–, OCH_2), 122.49 (+, C-2), 128.33, 128.81, 130.72 (+, Ph), 136.15 (C_{quat}, Ph), 154.61 (C_{quat}, C-3), 162.58 (C_{quat}, C=N), 217.71, 224.14 (C_{quat}, C=O), 313.89 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 495 (2) [M^+], 439 (1) [M^+ – 2 CO], 383 (22) [M^+ – 4 CO], 355 (100) [M^+ – 5 CO], 303 (25) [M^+ – $Cr(CO)_5$], 274 (37), 105 (18), 77 (17). – $C_{26}H_{21}CrNO_6$: calcd. 495.0774 (correct HRMS).

Pentacarbonyl[(2Z)-3-[(diphenylmethylene)amino]-1-ethoxy-4,4-dimethyl-2-pentenylidene]chromium (**8d**)

Variant A: To a solution of 1.00 g (3.03 mmol) of pentacarbonyl(1-ethoxy-4,4-dimethyl-2-pentynylidene)chromium (**6d**)[12a] in 50 ml of diethyl ether was added 1.65 mg (9.11 mmol) of **7** at 20°C. After 1 h purification (50 g of silica gel, 30 × 1.5 cm) yielded 1.52 g (98%) of **8d** ($R_f = 0.27$, pentane), red oil. – IR (film): $\tilde{\nu}$ = 2972 cm^{-1}, 2050 (C=O), 1978 (C=O), 1920 (C=O), 1658, 1494, 1276, 694, 666, 644. – UV (pentane): λ_{max} (lg ε) = 249 nm (4.36), 457 (1.62). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.03 [s and t, ^3J = 7.1

Hz, 12H, $C(CH_3)_3$, OCH_2CH_3], 4.79 (q, ^3J = 7.1 Hz, 2H, OCH_2), 6.91 (s, 1H, 2-H), 7.36–7.61 (m, 10H, Ph). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 15.02 (+, OCH_2CH_3), 29.64 [+, $C(CH_3)_3$], 39.31 [C_{quat}, $C(CH_3)_3$], 75.61 (–, OCH_2), 121.94 (+, C-2), 128.37, 129.08, 130.69 (+, Ph), 136.76 (C_{quat}, Ph), 156.66 (C_{quat}, C-3), 158.35 (C_{quat}, C=N), 217.94, 224.31 (C_{quat}, C=O), 314.66 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 511 (<1) [M^+], 371 (6) [M^+ – 5 CO], 319 (67) [M^+ – $Cr(CO)_5$], 304 (100), 290 (25), 219 (51), 107 (42), 80 (78), 52 (63) [Cr^+]. – $C_{27}H_{25}CrNO_6$ (511.5): calcd. C 63.40, H 4.93, N 2.74; found C 63.62, H 5.05, N 2.73.

Variant B: To a solution of 106 mg (0.32 mmol) of **6d**[12a] in 5 ml of diethyl ether was added 58 mg (0.32 mmol) of **7** at 20°C. After 2 h under high pressure (10 kbar) the solvent was removed under reduced pressure. Purification (12 g of silica gel, 11 × 1 cm, pentane/diethyl ether, 50:1) of the residue yielded fraction I: 3 mg (3%) of **6d** (R_f = 0.72). – II: 117 mg (71%) of **8d** (R_f = 0.43). – III: 18 mg (18%) of 5-*tert*-Butyl-3-ethoxy-2,2-diphenyl-2*H*-pyrrole (**9d**) (R_f = 0.02).

{(2Z)-3-{[Bis(4-methoxyphenyl)methylene]amino}-1-ethoxy-3-phenyl-2-propenylidene}pentacarbonylchromium (**14a**): To a solution of 190 mg (0.54 mmol) of **6a**[11b] in 20 ml of diethyl ether was added 390 mg (1.62 mmol) of [bis(4-methoxyphenyl)methylene]amine (**11**) at 20°C. After 2 h purification (30 g of silica gel, 30 × 1.5 cm) yielded 131 mg (41%) of **14a** (R_f = 0.26, pentane/diethyl ether, 15:1), red oil. – IR (film): $\tilde{\nu}$ = 2050 cm^{-1} (C=O), 1924 (C=O), 1602, 1507, 1253, 1033, 665. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.28 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 3.47 (s, 6H, OCH_3), 4.85 (q, ^3J = 7.1 Hz, 2H, OCH_2), 6.81–6.92 (m, 4H, Ar), 7.21 (s, 1H, 2-H), 7.30–7.41 (m, 7H, Ar), 7.51–7.60 (m, 2H, Ar). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 15.11 (+, OCH_2CH_3), 55.38 (+, OCH_3), 75.90 (–, OCH_2), 113.64 (+, C-2), 122.62, 127.92, 128.71, 129.15 (+, Ar), 130.22 (C_{quat}, Ar), 130.49 (+, Ar), 137.84, 146.97 (C_{quat}, Ar), 161.48, 163.43 (C_{quat}, C-3, C=N), 217.57, 224.31 (C_{quat}, C=O), 319.45 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 479 (<1) [M^+ – 4 CO], 451 (4) [M^+ – 5 CO], 399 (18) [M^+ – $Cr(CO)_5$], 370 (20) [M^+ – $Cr(CO)_5$ – C_2H_5], 355 (22), 220 (51), 80 (93), 52 (100) [Cr^+].

{(2Z)-3-{[Bis(4-methoxyphenyl)methylene]amino}-1-ethoxy-2-hexenylidene}pentacarbonylchromium (**14b**): To a solution of 695 mg (2.20 mmol) of **6b**[15] in 50 ml of diethyl ether was added 1.59 g (6.60 mmol) of **11** at 20°C. After 2 h purification (40 g of silica gel, 30 × 1.5 cm) yielded 773 mg (63%) of **14b** (R_f = 0.37, pentane/diethyl ether, 50:1), red oil. – IR (film): $\tilde{\nu}$ = 2052 cm^{-1} (C=O), 1930 (C=O), 1604, 1509, 1170, 908, 734, 668. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.89 (t, ^3J = 7.2 Hz, 3H, 6-H), 1.30 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 1.50 (tq, ^3J = 7.2, ^3J = 7.2 Hz, 2H, 5-H), 1.95 (t, ^3J = 7.2 Hz, 2H, 4-H), 3.86 (s, 6H, OCH_3), 4.77 (q, ^3J = 7.1 Hz, 2H, OCH_2), 6.72 (s, 1H, 2-H), 6.72–6.92 (m, 4H, C_6H_4), 7.26–7.41 (m, 4-H, C_6H_4). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.73, 15.19 (+, C-6, OCH_2CH_3), 21.45 (–, C-5), 39.84 (–, C-4), 55.35 (+, OCH_3), 75.52 (–, OCH_2), 113.68 (+, C-2), 125.33 (+, C_6H_4), 129.30 (C_{quat}, C_6H_4), 130.00 (+, C_6H_4), 139.94 (C_{quat}, C_6H_4), 152.22, 161.42 (C_{quat}, C-3, C=N), 217.89, 224.17 (C_{quat}, C=O), 315.18 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 501 (<1) [M^+ – 2 CO], 445 (3) [M^+ – 4 CO], 261 (1), 208 (3), 152 (7), 105 (100), 74 (81), 60 (62), 46 (45).

{(2E/Z)-3-{[Bis(4-methoxyphenyl)methylene]-amino}-3-cyclopropyl-1-ethoxy-2-propenylidene}pentacarbonylchromium (**14c**): To a solution of 431 mg (1.37 mmol) of **6c**[12a] in 35 ml of diethyl ether was added 990 mg (4.10 mmol) of **11** at 20°C. After 3 h purification (40 g of silica gel, 30 × 1.5 cm) yielded 487 mg (64%) of **14c** (R_f = 0.26, pentane/diethyl ether, 15:1), red oil. – IR (film): $\tilde{\nu}$ = 2253 cm^{-1}, 2051 (C=O), 1930 (C=O), 1603, 906, 734, 695. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.71–0.92 (m, 4H, *c*Pr-CH_2), 1.11 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 1.42–1.58 (m, 1H, *c*Pr-CH), 3.86 (s, 6H, OCH_3), 4.68 [q, ^3J = 7.1 Hz, 2H, OCH_2, (*Z*)-**14c**], 4.87 [q, ^3J = 7.1 Hz, OCH_2, (*E*)-**14c**], 6.42 [s, 2-H, (*E*)-**14c**], 6.72 [s, 1H, 2-H, (*Z*)-**14c**], 6.39–6.99 (m, 4H, C_6H_4), 7.38–7.45 (m, 4H, C_6H_4). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): (*Z*)-**14c**: δ = 9.69 (–, *c*Pr-CH_2), 15.31 (+, OCH_2CH_3), 18.31 (+, *c*Pr-CH), 55.41 (+, OCH_3), 75.35 (–, OCH_2), 113.69 (+, C-2), 122.71 (+, C_6H_4), 128.98 (C_{quat}, C_6H_4), 130.83 (+, C_6H_4), 155.39, 161.34, 161.54 (C_{quat}, C_6H_4, C-3, C=N), 217.95, 224.18 (C_{quat}, C=O), 311.75 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 443 (8) [M^+ – 4 CO], 415 (32) [M^+ – 5 CO], 363 (58) [M^+ – $Cr(CO)_5$], 334 (100) [M^+ – $Cr(CO)_5$ – C_2H_5], 240 (10), 135 (7), 77 (3), 52 (6) [Cr^+].

{(2Z)-3-{[Bis(4-methoxyphenyl)methylene]amino}-1-ethoxy-4,4-dimethyl-2-pentenylidene}pentacarbonylchromium (**14d**): To a solution of 445 mg (1.35 mmol) of **6d**[12a] in 30 ml of diethyl ether was added 970 mg (4.03 mmol) of **11** at 20°C. After 3 h purification (40 g of silica gel, 30 × 1.5 cm) yielded 455 mg (59%) of **14d** (R_f = 0.23, pentane/diethyl ether, 15:1), red oil. – IR (film): $\tilde{\nu}$ = 2976 cm^{-1}, 2049 (C=O), 1923 (C=O), 1652, 1603, 1506, 1383, 698, 666. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.00–1.11 [m, 12H, $C(CH_3)_3$, OCH_2CH_3], 3.89 (s, 6H, OCH_3), 4.72 (q, ^3J = 7.1 Hz, 2H, OCH_2), 6.88–6.99 (m, 5H, 2-H, C_6H_4), 7.39–7.47 (m, 4H, C_6H_4). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 15.11 (+, OCH_2CH_3), 29.64 [+, $C(CH_3)_3$], 39.31 [C_{quat}, $C(CH_3)_3$], 55.33 (+, OCH_3), 75.40 (–, OCH_2), 113.69 (+, C-2), 121.63 (+, C_6H_4), 129.54 (C_{quat}, C_6H_4), 131.00 (+, C_6H_4), 156.80 (C_{quat}, C_6H_4), 157.34, 161.52 (C_{quat}, C-3, C=N), 218.18, 224.34 (C_{quat}, C=O), 311.55 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 571 (<1) [M^+], 459 (1) [M^+ – 4 CO], 379 (12) [M^+ – $Cr(CO)_5$], 281 (21), 207 (62), 108 (100), 86 (99), 52 (99) [Cr^+].

Pentacarbonyl{(2Z)-3-[(cyclopropylphenylmethylene)amino]-1-ethoxy-3-phenyl-2-propenylidene}chromium (**15a**): To a solution of 304 mg (0.87 mmol) of **6a**[11b] in 20 ml of diethyl ether was added 370 mg (2.55 mmol) of (cyclopropylphenylmethylene)amine (**12**) at 20°C. After 2 h purification (35 g of silica gel, 30 × 1.5 cm) yielded 311 mg (72%) of **15a** (R_f = 0.16, pentane), red oil. – IR (film): $\tilde{\nu}$ = 2050 cm^{-1} (C=O), 1918 (C=O), 1653, 1616, 1095, 667. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.02–1.05 (m, 4H, *c*Pr-CH_2), 1.43 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 1.98 (m_c, 1H, *c*Pr-CH), 4.89 (q, ^3J = 7.1 Hz, 2H, OCH_2), 7.17 (s, 1H, 2-H), 7.33–7.40 (m, 6H, Ph), 7.52–7.57 (m, 4H, Ph). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 8.36, 9.47 (–, *c*Pr-CH_2), 15.49, 17.44 (+, OCH_2CH_3, *c*Pr-CH), 76.02 (–, OCH_2), 121.43 (C-2), 126.39, 127.16, 127.77, 128.43, 128.64, 128.81 (+, Ph), 130.10, 130.47 (C_{quat}, Ph), 145.57 (C_{quat}, C-3), 166.78 (C_{quat}, C=N), 217.59, 224.36 (C_{quat}, C=O), 318.39 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 411 (13) [M^+ – 3 CO], 383 (55) [M^+ – 4 CO], 355 (70) [M^+ – 5 CO], 303 (35) [M^+ – $Cr(CO)_5$], 274 (45), 220 (25), 155 (20), 52 (100) [Cr^+].

Pentacarbonyl{(2Z)-3-[(cyclopropylphenylmethylene)amino]-1-ethoxy-2-hexenylidene}chromium (**15b**): To a solution of 408 (1.29 mmol) of **6b**[15] in 20 ml of diethyl ether was added 560 mg (3.87 mmol) of **12** at 20°C. After 1.5 h purification (30 g of silica gel, 25 × 1.5 cm) yielded 524 mg (88%) of **15b** (R_f = 0.12, pentane), red oil. – IR (film): $\tilde{\nu}$ = 2051 cm^{-1} (C=O), 1973 (C=O), 1914 (C=O), 1669 (C=N), 1506, 1448, 1244, 1135, 668. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 7.2 Hz, 3H, 6-H), 1.08 (m_c, 4H, *c*Pr-CH_2), 1.37 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 1.41–1.70 (m, 3H, 5-H, *c*Pr-CH), 2.00 (t, ^3J = 7.2 Hz, 2H, 4-H), 4.83 (q, ^3J = 7.1 Hz, 2H, OCH_2), 6.62 (s, 1H, 2-H), 7.32–7.63 (m, 5H, Ph). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 9.49 (–, *c*Pr-CH_2),

13.67, 15.30, 17.14 (+, C-6, OCH_2CH_3, *c*Pr-CH), 21.49 (−, C-5), 40.15 (−, C-4), 75.68 (−, OCH_2), 123.04 (+, C-2), 127.24, 128.44, 130.32 (+, Ph), 137.00 (C_{quat}, Ph), 151.04, 162.36 (C_{quat}, C-3, C=N), 217.84, 224.26 (C_{quat}, C=O), 324.26 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 461 (10) [M^+], 377 (3) [M^+ – 3 CO], 349 (18) [M^+ – 4 CO], 321 (72) [M^+ – 5 CO], 269 (17) [M^+ – $Cr(CO)_5$], 240 (35), 155 (19), 125 (60), 95 (100), 52 (40) [Cr^+]. – $C_{23}H_{23}CrNO_6$: calcd. 461.0930 (correct HRMS).

Pentacarbonyl{(2E/Z)-3-cyclopropyl-3-[(cyclopropylphenylmethylene)amino]-1-ethoxy-2-propenylidene}chromium (**15c**): To a solution of 900 mg (2.86 mmol) of **6c**[12a] in 40 ml of diethyl ether was added 1.24 g (8.54 mmol) of **12** at 20°C. After 80 min purification (50 g of silica gel, 30 × 1.5 cm) yielded 1.29 g (98%) of **15c** (R_f = 0.19, pentane), red oil. – IR (KBr): $\tilde{\nu}$ = 2052 cm^{-1} (C=O), 1967 (C=O), 1915 (C=O), 1895, 1681, 1450, 1340, 1248, 1037, 905, 662. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.61–0.72 (m, 2H, *c*Pr-CH_2), 0.80–0.95 (m, 2H, *c*Pr-CH_2), 0.96–1.11 (m, 4H, *c*Pr-CH_2), 1.31 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 1.51 (m_c, 1H, *c*Pr-CH), 1.98 (m_c, 1H, *c*Pr-CH), 4.72 [q, ^3J = 7.1 Hz, 2H, OCH_2, (*Z*)-**15c**], 4.91 [q, ^3J = 7.1 Hz, OCH_2, (*E*)-**15c**], 6.49 [s, 2-H, (*E*)-**15c**], 6.71 [s, 1H, 2-H, (*Z*)-**15c**], 7.36–7.50 (m, 3H, Ph), 7.50–7.65 (m, 2H, Ph). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): (*Z*)-**15c**: δ = 9.53, 9.95 (−, *c*Pr-CH_2), 15.30, 17.15, 17.89 (+, OCH_2CH_3, *c*Pr-CH), 75.43 (−, OCH_2), 121.38 (+, C-2), 127.29, 128.50, 130.66 (+, Ph), 136.80 (C_{quat}, Ph), 154.36 (C_{quat}, C-3), 165.24 (C_{quat}, C=N), 217.94, 224.20 (C_{quat}, C=O), 310.12 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 459 (1) [M^+], 431 (1) [M^+ – CO], 403 (1) [M^+ – 2 CO], 375 (3) [M^+ – 3 CO], 347 (15) [M^+ – 4 CO], 319 (25) [M^+ – 5 CO], 267 (40) [M^+ – $Cr(CO)_5$], 238 (100), 220 (25), 128 (30), 52 (58) [Cr^+]. – $C_{23}H_{21}CrNO_6$ (459.4): calcd. C 60.13, H 4.61, N 3.05; found C 60.25, H 4.80, N 3.01; calcd. 459.0774 (correct HRMS).

Pentacarbonyl{(2Z)-3-[(cyclopropylphenylmethylene)amino]-1-ethoxy-4,4-dimethyl-2-pentenylidene}chromium (**15d**): To a solution of 1.00 g (3.03 mmol) of **6d**[12a] in 50 ml of diethyl ether was added 1.31 g (9.02 mmol) of **12** at 20°C. After 1 h purification (50 g of silica gel, 30 × 1.5 cm) yielded 1.22 g (85%) of **15d** (R_f = 0.15, pentane), red oil. – IR (film): $\tilde{\nu}$ = 2050 cm^{-1} (C=O), 1982 (C=O), 1927 (C=O), 1488, 1219, 1100, 1054. – ^1H NMR (250 MHz, $CDCl_3$)[20]: δ = 0.61–1.78 [bs, 16H, $C(CH_3)_3$, OCH_2CH_3, *c*Pr-CH_2], 1.80–2.09 (bs, 1H, *c*Pr-CH), 4.55–4.90 (bs, 2H, OCH_2), 6.62–6.69 (bs, 1H, 2-H), 7.15–7.79 (m, 5H, Ph). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 8.63, 10.38 (−, *c*Pr-CH_2), 15.36 (+, OCH_2CH_3), 17.33 (+, *c*Pr-CH), 29.60 [+, $C(CH_3)_3$], 39.14 [C_{quat}, $C(CH_3)_3$], 75.54 (−, OCH_2), 118.66 (+, C-2), 127.53, 128.01, 130.66 (+, Ph), 137.81 (C_{quat}, Ph), 156.47 (C_{quat}, C-3), 160.67 (C_{quat}, C=N), 218.17, 224.37 (C_{quat}, C=O), 311.10 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 475 (8) [M^+], 419 (3) [M^+ – 2 CO], 363 (22) [M^+ – 4 CO], 335 (100) [M^+ – 5 CO], 283 (55) [M^+ – $Cr(CO)_5$], 268 (96), 254 (41), 198 (8), 97 (16), 57 (17).

Pentacarbonyl{(2Z)-3-[(dicyclopropylmethylene)amino]-1-ethoxy-3-phenyl-2-propenylidene}chromium (**16a**): To a solution of 350 mg (1.00 mmol) of **6a**[11b] in 20 ml of diethyl ether was added 2.00 g (18.3 mmol) of (dicyclopropylmethylene)amine (**13**) at 20°C. After 4 h purification (40 g of silica gel, 30 × 1.5 cm) yielded 388 mg (85%) of **16a** (R_f = 0.16, pentane), red oil. – IR (KBr): $\tilde{\nu}$ = 2963 cm^{-1}, 2053 (C=O), 1911 (C=O), 1260, 1094, 799, 659, 462. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.86–0.91 (m, 4H, *c*Pr-CH_2), 1.03–1.06 (m, 4H, *c*Pr-CH_2), 1.05–1.33 (m, 2H, *c*Pr-CH), 1.59 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 4.98 (q, ^3J = 7.1 Hz, 2H, OCH_2), 7.32 (s, 1H, 2-H), 7.38–7.42 (m, 3H, Ph), 7.54–7.57 (m, 2H, Ph). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 8.25 (−, *c*Pr-CH_2), 13.59, 15.59 (+, OCH_2CH_3, *c*Pr-CH), 76.23 (−, OCH_2), 122.65 (+, C-2), 126.39, 127.72, 128.32 (+, Ph), 146.40 (C_{quat}, Ph), 146.40 (C_{quat}, C-3), 172.79 (C_{quat}, C=N), 217.74, 224.36 (C_{quat}, C=O), 319.88 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 459 (3) [M^+], 375 (2) [M^+ – 3 CO], 267 (35) [M^+ – $Cr(CO)_5$], 238 (100), 222 (36), 210 (37), 167 (31), 80 (35), 52 (32) [Cr^+]. – $C_{23}H_{21}CrNO_6$: calcd. 459.0774 (correct HRMS).

Pentacarbonyl{(2Z)-3-[(dicyclopropylmethylene)amino]-1-ethoxy-2-hexenylidene}chromium (**16b**): To a solution of 760 mg (2.40 mmol) of **6b**[15] in 20 ml of diethyl ether was added 2.00 g (18.3 mmol) of **13** at 20°C. After 3.5 h purification (30 g of silica gel, 25 × 1.5 cm) yielded 827 mg (81%) of **16b** (R_f = 0.25, pentane/diethyl ether 50:1), red oil. – IR (KBr): $\tilde{\nu}$ = 2959 cm^{-1}, 2925, 2875, 2052 (C=O), 1935 (C=O), 1457, 1380, 1033, 738, 481. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.72–1.10 (m, 11H, *c*Pr-CH_2, 6-H), 1.12–1.31 (m, 2H, 5-H, *c*Pr-CH), 1.39–1.62 (m, 5H, 5-H, *c*Pr-CH, OCH_2CH_3), 2.11 (t, ^3J = 7.2 Hz, 2H, 4-H), 4.89 (q, ^3J = 7.1 Hz, 2H, OCH_2), 6.68 (s, 1H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 8.03, 8.43 (−, *c*Pr-CH_2), 13.28, 13.86, 15.45 (+, C-6, OCH_2CH_3, *c*Pr-CH), 21.11 (−, C-5), 40.60 (−, C-4), 75.66 (−, OCH_2), 123.69 (+, C-2), 152.54, 169.20 (C_{quat}, C-3, C=N), 217.89, 224.19 (C_{quat}, C=O), 319.01 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 425 (35) [M^+], 369 (5) [M^+ – 2 CO], 341 (12) [M^+ – 3 CO], 313 (10) [M^+ – 4 CO], 285 (55) [M^+ – 5 CO], 269 (17), 241 (80), 213 (100), 121 (79), 73 (48), 52 (68) [Cr^+]. – $C_{20}H_{23}CrNO_6$ (425.4): calcd. C 56.47, H 5.45, N 3.29; found C 56.65, H 5.45, N 3.32.

Pentacarbonyl{(2E/Z)-3-cyclopropyl-3-[(dicyclopropylmethylene)amino]-1-ethoxy-2-propenylidene}chromium (**16c**): To a solution of 120 mg (0.38 mmol) of **6c**[12a] in 15 ml of diethyl ether was added 1.50 g (13.8 mmol) of **13** at 20°C. After 2.5 h purification (25 g of silica gel, 20 × 1.5 cm) yielded 136 mg (84%) of **16c** (R_f = 0.28, pentane), red oil. – IR (film): $\tilde{\nu}$ = 2960 cm^{-1}, 2926, 2052 (C=O), 1973 (C=O), 1933 (C=O), 1507, 901, 669. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.62–0.67 (m, 2H, *c*Pr-CH_2), 0.82–0.92 (m, 8H, *c*Pr-CH), 1.21–1.27 (m, 2H, *c*Pr-CH_2), 1.45–1.51 (m, 5H, OCH_2CH_3, *c*Pr-CH_2), 1.98 (m_c, 1H, *c*Pr-CH), 4.83 [q, ^3J = 7.1 Hz, 2H, OCH_2, (*Z*)-**16c**], 4.96 [q, ^3J = 7.1 Hz, 2H, OCH_2, (*E*)-**16c**)], 6.70 [s, 1H, 2-H, (*E*)-**16c**], 6.87 [s, 1H, 2-H, (*Z*)-**16c**]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): (*Z*)-**16c**: δ = 8.34, 8.69 (−, *c*Pr-CH_2), 13.35, 15.49, 18.04 (+, OCH_2CH_3, *c*Pr-CH), 75.39 (−, OCH_2), 123.37 (+, C-2), 155.98 (C_{quat}, C-3), 172.79 (C_{quat}, C=N), 218.03, 224.17 (C_{quat}, C=O), 312.81 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 423 (5) [M^+], 367 (3) [M^+ – 2 CO], 339 (1) [M^+ – 3 CO], 231 (100) [M^+ – $Cr(CO)_5$], 202 (91), 175 (55), 119 (38), 91 (45), 77 (58). – $C_{20}H_{21}CrNO_6$: calcd. 423.0774 (correct HRMS).

Pentacarbonyl{(2Z)-3-[(dicyclopropylmethylene)amino]-1-ethoxy-4,4-dimethyl-2-pentenylidene}chromium (**16d**): To a solution of 620 mg (1.88 mmol) of **6d**[12a] in 20 ml of diethyl ether was added 2.50 g (22.9 mmol) of **13** at 20°C. After 4 h purification (40 g of silica gel, 30 × 1.5 cm) yielded 709 mg (86%) of **16d** (R_f = 0.30, pentane), orange crystals, m.p. 101°C. – IR (KBr): $\tilde{\nu}$ = 2048 cm^{-1} (C=O), 1921 (C=O), 1392, 1363, 998, 743, 635, 527. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.81–0.93 (m, 6H, *c*Pr-CH_2), 0.94–1.15 (m, 2H, *c*Pr-CH_2), 1.16 [s, 9H, $C(CH_3)_3$], 1.20–1.29 (m, 2H, *c*Pr-CH), 1.23 (t ^3J = 7.1 Hz, 3H, OCH_2CH_3), 4.87 (q, ^3J = 7.1 Hz, 2H, OCH_2), 6.87 (s, 1H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 7.02, 8.85 (−, *c*Pr-CH_2), 13.21, 15.36, 17.33 (+, OCH_2CH_3, *c*Pr-CH), 29.16 [+, $C(CH_3)_3$], 39.64 (C_{quat}, $C(CH_3)_3$], 75.99 (−, OCH_2), 129.12 (+, C-2), 158.76 (C_{quat}, C-3), 169.69 (C_{quat}, C=N), 217.86, 224.20 (C_{quat}, C=O), 317.75 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 439 (100) [M^+], 317 (11), 255 (5), 183 (16), 141 (19), 105 (41), 77 (35), 55 (16). – $C_{21}H_{25}CrNO_6$ (439.4): calcd. C 57.40, H 5.73, N 3.19; found C 57.47, H 5.78, N 3.20.

Pentacarbonyl(1-ethoxy-4,4-dimethyl-2-pentynylidene)tungsten (**22**) was prepared according to the previously published method[7] from 0.82 g (10.0 mmol) of 3,3-dimethyl-2-butyne and 3.52 g (10.0 mmol) of hexacarbonyltungsten, yield 4.46 g (97%) of **22** (R_f = 0.31, pentane), reddish black oil. – IR (film): $\tilde{\nu}$ = 2970 cm^{-1}, 2166 (C≡C), 2069 (C=O), 1945 (C=O), 1454, 1365, 1265, 1217, 1088, 645, 564. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.36 [s, 9H, $C(CH_3)_3$], 1.53 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 4.60 (q, ^3J = 7.1 Hz, 2H, OCH_2). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.67 (OCH_2CH_3), 29.80 [$C(CH_3)_3$], 30.11 (C-4), 75.93 (OCH_2), 90.02 (C-3), 197.60, 250.80 (C=O), 290.41 (C-1), C-2 not observed. – MS (70 eV), *m/z* (%): 462 (52) [M^+], 378 (75) [M^+ – 3 CO], 350 (66) [M^+ – 4 CO], 322 (100) [M^+ – 5 CO], 263 (83), 41 (47). – $C_{14}H_{14}O_6W$ (462.1): calcd. C 36.39, H 3.05; found C 37.17, H 3.08.

Pentacarbonyl{(2Z)-3-[(diphenylmethylene)amino]-1-ethoxy-4,4-dimethyl-2-pentenylidene}tungsten (**23**): To a solution of 711 mg (1.54 mmol) of **22** in 30 ml of diethyl ether was added 0.84 g (4.62 mmol) of **7** at 20°C. After 4 h purification (40 g of silica gel, 25 × 1.5 cm) yielded 911 mg (92%) of **23** (R_f = 0.41, pentane), red oil. – IR (film): $\tilde{\nu}$ = 2972 cm^{-1}, 2059 (C=O), 1909 (C=O), 1498, 1221, 1058, 694, 597. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.99 [s and t, ^3J = 7.1 Hz, 12H, $C(CH_3)_3$, OCH_2CH_3], 4.55 (q, ^3J = 7.1 Hz, 2H, OCH_2), 6.92 (s, 1H, 2-H), 7.38–7.52 (m, 10H, Ph). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.81 (+, OCH_2CH_3), 29.48 [+, $C(CH_3)_3$], 39.44 [C_{quat}, $C(CH_3)_3$], 78.31 (–, OCH_2), 121.56 (+, C-2), 128.38, 129.08, 130.75 (+, Ph), 136.66 (C_{quat}, Ph), 157.84 (C_{quat}, C-3), 160.40 (C_{quat}, C=N), 198.75, 204.09 (C_{quat}, C=O), 290.27 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 643 (<1) [M^+], 615 (1) [M^+ – CO], 587 (6) [M^+ – 2 CO], 559 (3) [M^+ – 3 CO], 531 (2) [M^+ – 4 CO], 319 (76) [M^+ – $W(CO)_5$], 304 (100), 165 (25), 105 (10), 77 (12). – $C_{27}H_{25}NO_6W$ (643.4): calcd. C 50.41, H 3.92, N 2.18; found C 51.09, H 4.31, N 2.18; calcd. 643.1191 (correct HRMS).

3-Ethoxy-2,2,5-triphenyl-2H-pyrrole (**9a**): A solution of 430 mg (0.81 mmol) of **8a** in 20 ml of tetrahydrofuran was stirred at 50–55°C for 15 h. The solvent was evaporated under reduced pressure. Impurities were removed by chromatography (15 g of silica gel, petroleum ether/diethyl ether, 10:1), elution with diethyl ether (plus 5% triethylamine) yielded 220 mg (80%) of **9a** (R_f = 0.24), colorless crystals, m.p. 154°C. – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 3056, 1960, 1618, 1578, 1058, 694. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.52 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 4.22 (q, ^3J = 7.0 Hz, 2H, OCH_2), 5.95 (s, 1H, 4-H), 7.29–7.59 (m, 13H, Ph), 8.05–8.13 (m, 2H, Ph). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.23 (+, OCH_2CH_3), 67.95 (–, OCH_2), 84.78 (C_{quat}, C-2), 95.01 (+, C-4), 127.13, 127.44, 127.93, 127.96, 128.38, 130.32 (+, Ph), 134.75, 141.36 (C_{quat}, Ph), 172.42, 184.38 (C_{quat}, C-5, -3). – MS (70 eV), *m/z* (%): 339 (100) [M^+], 310 (96) [M^+ – C_2H_5], 180 (82), 165 (22), 105 (25), 77 (43). – $C_{24}H_{21}NO$: calcd. 339.1623 (correct HRMS).

3-Ethoxy-2,2-diphenyl-5-propyl-2H-pyrrole (**9b**): A solution of 440 mg (0.89 mmol) of **8b** in 20 ml of tetrahydrofuran was stirred at 50–55°C for 16 h. The solvent was evaporated under reduced pressure. Impurities were removed by chromatography (15 g of silica gel, petroleum ether/diethyl ether, 10:1), elution with diethyl ether (plus 5% triethylamine) yielded 239 mg (88%) of **9b**, brown oil. – IR (film): $\tilde{\nu}$ = 3078 cm^{-1}, 3050, 1619, 1573, 1052, 687. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.96 (t, ^3J = 7.0 Hz, 3H, $CH_2CH_2CH_3$), 1.36 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 1.70 (tq, ^3J = 7.0, ^3J = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 2.53 (t, ^3J = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 4.03 (q, ^3J = 7.0 Hz, 2H, OCH_2), 5.31 (s, 1H, 4-H), 7.12–7.48 (m, 10H, Ph). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.76, 14.01 (+, $CH_2CH_2CH_3$, OCH_2CH_3), 20.46 (–, $CH_2CH_2CH_3$), 35.83 (–, $CH_2CH_2CH_3$), 67.61 (–, OCH_2), 83.63 (C_{quat}, C-2), 96.78 (+, C-4), 126.84, 127.22, 127.62 (+, Ph), 141.26 (C_{quat}, Ph), 176.62, 183.34 (C_{quat}, C-5, -3). – MS (70 eV), *m/z* (%): 305 (6) [M^+], 276 (7) [M^+ – C_2H_5], 179 (38), 105 (100), 77 (68), 59 (75). – $C_{21}H_{23}NO$: calcd. 305.1779 (correct HRMS).

5-Cyclopropyl-3-ethoxy-2,2-diphenyl-2H-pyrrole (**9c**): A solution of 468 mg (0.95 mmol) of **8c** in 20 ml of tetrahydrofuran was stirred at 50–55°C for 16 h. The solvent was evaporated under reduced pressure. Impurities were removed by chromatography (12 g of silica gel, petroleum ether/diethyl ether, 10:1), elution with diethyl ether (plus 5% triethylamine) yielded 275 mg (96%) of **9c**, light yellow oil. – IR (film): $\tilde{\nu}$ = 3058 cm^{-1}, 2976, 1620, 1543, 1110, 1043, 760, 699. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.82–1.01 (m, 4H, *c*Pr-CH_2), 1.36 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 1.97 (m_c, 1H, *c*Pr-CH), 3.98 (q, ^3J = 7.1 Hz, 2H, OCH_2), 5.02 (s, 1H, 4-H), 7.18–7.33 (m, 10H, Ph). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 7.32 (–, *c*Pr-CH_2), 13.99, 14.29 (+, OCH_2CH_3, *c*Pr-CH), 67.56 (–, OCH_2), 83.43 (C_{quat}, C-2), 93.74 (+, C-4), 126.81, 127.60, 127.70 (+, Ph), 141.37 (C_{quat}, Ph), 171.59, 183.29 (C_{quat}, C-5, -3). – MS (70 eV), *m/z* (%): 303 (22) [M^+], 274 (41) [M^+ – C_2H_5], 177 (63), 126 (75), 105 (79), 98 (100), 77 (57), 69 (65). – $C_{21}H_{21}NO$: calcd. 303.1623 (correct HRMS).

5-tert-Butyl-3-ethoxy-2,2-diphenyl-2H-pyrrole (**9d**)

Variant A: A solution of 530 mg (1.04 mmol) of **8d** in 20 ml of tetrahydrofuran was stirred at 50–55°C for 18 h. The solvent was removed under reduced pressure. Purification by filtration (5 g of silica gel, diethyl ether) yielded 328 mg (99%) of **9d**, colorless oil. – IR (film): $\tilde{\nu}$ = 2985 cm^{-1}, 1699, 1616, 1068, 627, 645. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.23 [s, 9H, $C(CH_3)_3$], 1.32 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 4.00 (q, ^3J = 7.1 Hz, 2H, OCH_2), 5.40 (s, 1H, 4-H), 7.12–7.41 (m, 10H, Ph). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.01 (+, OCH_2CH_3), 28.12 [+, $C(CH_3)_3$], 35.52 [C_{quat}, $C(CH_3)_3$], 67.54 (–, OCH_2), 83.06 (C_{quat}, C-2), 94.73 (+, C-4), 126.87, 127.74, 127.77 (+, Ph), 141.29 (C_{quat}, Ph), 182.82, 183.35 (C_{quat}, C-5, -3). – MS (70 eV), *m/z* (%): 319 (57) [M^+], 304 (62) [M^+ – CH_3], 290 (20), 165 (5), 105 (100), 86 (57), 84 (73). – $C_{22}H_{25}NO$ (319.5): calcd. C 82.72, H 7.89, N 4.38; found C 82.12, H 7.87, N 4.33; calcd. 319.1936 (correct HRMS).

Variant B: A solution of 924 mg (1.44 mmol) of **23** in 20 ml of tetrahydrofuran was stirred at 50–55°C for 7 d. The solvent was removed under reduced pressure. Purification by filtration (5 g of silica gel) yielded 458 mg (99%) of **9d**, colorless oil.

3-Ethoxy-2,2-bis(4-methoxyphenyl)-5-phenyl-2H-pyrrole (**17a**): A solution of 126 mg (0.21 mmol) of **14a** in 10 ml of tetrahydrofuran was stirred at 50–55°C for 16 h. The solvent was evaporated under reduced pressure. Impurities were removed by chromatography (10 g of silica gel, petroleum ether/diethyl ether, 10:1), elution with diethyl ether (plus 5% triethylamine) yielded 21 mg (25%) of **17a**, colorless oil. – IR (film): $\tilde{\nu}$ = 2977 cm^{-1}, 2805, 1444, 1122, 735. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.43 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 3.78 (s, 6H, OCH_3), 4.16 (q, ^3J = 7.1 Hz, 2H, OCH_2), 5.87 (s, 1H, 4-H), 6.78–6.88 (m, 4H, Ar), 7.31–7.39 (m, 4H, Ar), 7.40–7.51 (m, 3H, Ar), 8.00–8.11 (m, 2H, Ar). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.22 (+, OCH_2CH_3), 55.42 (+, OCH_3), 68.30 (–, OCH_2), 83.36 (C_{quat}, C-2), 94.44 (+, C-4), 113.54, 127.94, 128.56, 129.02 (+, Ar), 131.05, 132.78, 158.96 (C_{quat}, Ar), 171.81, 185.28 (C_{quat}, C-5, -3). – MS (70 eV), *m/z* (%): 399 (1) [M^+], 370 (4) [M^+ – C_2H_5], 142 (9), 170 (10), 135 (25), 86 (85), 84 (100), 77 (33), 47 (42). – $C_{26}H_{25}NO_3$: calcd. 399.1834 (correct HRMS).

3-Ethoxy-2,2-bis(4-methoxyphenyl)-5-propyl-2H-pyrrole (**17b**): A solution of 485 mg (0.87 mmol) of **14b** in 18 ml of tetrahydrofuran was stirred at 50−55°C for 16 h. The solvent was evaporated under reduced pressure. Impurities were removed by chromatography (20 g of silica gel, petroleum ether/diethyl ether, 8:1), elution with diethyl ether (plus 5% triethylamine) yielded 180 mg (57%) of **17b**, light yellow oil. − IR (film): $\tilde{\nu}$ = 2962 cm^{-1}, 1625, 1607, 1508, 1176, 908, 734. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.98 (t, ^3J = 7.0 Hz, 3H, $CH_2CH_2CH_3$), 1.39 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 1.70 (tq, ^3J = 7.0, ^3J = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 2.51 (t, ^3J = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 3.77 (s, 6H, OCH_3), 4.01 (q, ^3J = 7.0 Hz, 2H, OCH_2), 5.28 (s, 1H, 4-H), 6.77−6.83 (m, 4H, C_6H_4), 7.22−7.30 (m, 4H, C_6H_4). − ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.88, 14.17 (+, $CH_2CH_2CH_3$, OCH_2CH_3), 20.56 (−, $CH_2CH_2CH_3$), 35.98 (−, $CH_2CH_2CH_3$), 55.08 (+, OCH_3), 67.66 (−, OCH_2), 82.86 (C_{quat}, C-2), 96.47 (+, C-4), 113.24, 128.80 (+, C_6H_4), 133.76, 158.54 (C_{quat}, C_6H_4), 176.08, 183.98 (C_{quat}, C-5, -3). − MS (70 eV), *m/z* (%): 365 (15) [M^+], 336 (18) [$M^+ - C_2H_5$], 171 (38), 135 (23), 113 (40), 87 (100), 84 (98). − $C_{23}H_{27}NO_3$: calcd. 365.1990 (correct HRMS).

5-Cyclopropyl-3-ethoxy-2,2-bis(4-methoxyphenyl)-2H-pyrrole (**17c**): A solution of 269 mg (0.48 mmol) of **14c** in 12 ml of tetrahydrofuran was stirred at 50−55°C for 18 h. The solvent was evaporated under reduced pressure. Impurities were removed by chromatography (15 g of silica gel, petroleum ether/diethyl ether, 10:1), elution with diethyl ether (plus 5% triethylamine) yielded 113 mg (65%) of **17c**, brown oil. − IR (film): $\tilde{\nu}$ = 2837 cm^{-1}, 1622, 1605, 1508, 1249, 1110, 909, 732, 648. − ^1H NMR (250 MHz, $CDCl_3$)[23]: δ = 0.95−1.18 (bs, 4H, *c*Pr-CH_2), 1.36−1.62 (bs, 3H, OCH_2CH_3), 2.00−2.16 (bs, 1H, *c*Pr-CH), 3.80−4.01 (bs, 6H, OCH_3), 4.03−4.19 (bs, 2H, OCH_2), 5.12 (s, 1H, 4-H), 6.82−7.12 (bs, 4H, C_6H_4), 7.32−7.50 (bs, 4H, C_6H_4). − ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 7.38 (−, *c*Pr-CH_2), 14.14 (+, OCH_2CH_3), 14.35 (+, *c*Pr-CH), 55.08 (+, OCH_3), 67.63 (−, OCH_2), 82.64 (C_{quat}, C-2), 93.48 (+, C-4), 113.23, 128.78 (+, C_6H_4), 133.79, 158.53 (C_{quat}, C_6H_4), 177.16, 183.93 (C_{quat}, C-5, -3). − MS (70 eV), *m/z* (%): 363 (42) [M^+], 334 (100) [$M^+ - C_2H_5$], 242 (20), 135 (45), 84 (22), 77 (18), 57 (22), 43 (15). − $C_{23}H_{25}NO_3$: calcd. 363.1834 (correct HRMS).

5-tert-Butyl-3-ethoxy-2,2-bis(4-methoxyphenyl)-2H-pyrrole (**17d**): A solution of 380 mg (0.66 mmol) of **14d** in 16 ml of tetrahydrofuran was stirred at 50−55°C for 20 h. The solvent was evaporated under reduced pressure. Impurities were removed by chromatography (20 g of silica gel, petroleum ether/diethyl ether, 10:1), elution with diethyl ether (plus 5% triethylamine) yielded 197 mg (78%) of **17d**, yellow oil. − IR (film): $\tilde{\nu}$ = 2964 cm^{-1}, 2837, 1623, 1508, 1248, 908, 734. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.39 [s, 9H, $C(CH_3)_3$], 1.50 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 3.92 (s, 6H, OCH_3), 4.15 (q, ^3J = 7.1 Hz, 2H, OCH_2), 5.52 (s, 1H, 4-H), 6.90−6.99 (m, 4H, C_6H_4), 7.36−7.48 (m, 4H, C_6H_4). − ^{13}C-NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.00 (+, OCH_2CH_3), 27.96 [+, $C(CH_3)_3$], 35.29 [C_{quat}, $C(CH_3)_3$], 54.83 (+, OCH_3), 67.30 (−, OCH_2), 81.96 (C_{quat}, C-2), 94.06 (+, C-4), 112.97, 128.58 (+, C_6H_4), 133.44, 158.29 (C_{quat}, C_6H_4), 182.09, 183.63 (C_{quat}, C-5, -3). − MS (70 eV), *m/z* (%): 379 (100) [M^+], 364 (87) [$M^+ - CH_3$], 350 (35) [$M^+ - C_2H_5$], 240 (10), 135 (18), 48 (18). − $C_{24}H_{29}NO_3$: calcd. 379.2147 (correct HRMS).

2-Cyclopropyl-3-ethoxy-2,5-diphenyl-2H-pyrrole (**18a**): A solution of 390 mg (0.78 mmol) of **15a** in 16 ml of tetrahydrofuran was stirred at 50−55°C for 20 h. The solvent was evaporated under reduced pressure. Impurities were removed by chromatography (12 g of silica gel, petroleum ether/diethyl ether, 10:1), elution with diethyl ether (plus 5% triethylamine) yielded 147 mg (62%) of **18a**, white crystals, m.p. 88°C. − IR (KBr): $\tilde{\nu}$ = 2839 cm^{-1}, 1621, 1462, 1302, 830, 787. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.18 (m_c, 1H, *c*Pr-CH_2), 0.31 (m_c, 1H, *c*Pr-CH_2), 0.54 (m_c, 1H, *c*Pr-CH_2), 0.76 (m_c, 1H, *c*Pr-CH_2), 1.30 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 1.60 (m_c, 1H, *c*Pr-CH), 4.02 (m_c, 2H, OCH_2), 5.65 (s, 1H, 4-H), 7.10−7.28 (m, 3H, Ph), 7.30−7.39 (m, 3H, Ph), 7.42−7.53 (m, 2H, Ph), 7.80−7.90 (m, 2H, Ph). − ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 0.27, 2.71 (*c*Pr-CH_2), 14.23, 17.60 (+, OCH_2CH_3, *c*Pr-CH), 67.66 (−, OCH_2), 79.54 (C_{quat}, C-2), 93.84 (+, C-4), 124.07, 126.84, 127.30, 128.12, 128.37, 130.19 (+, Ph), 134.85, 140.38 (C_{quat}, Ph), 172.67, 186.28 (C_{quat}, C-5, -3). − MS (70 eV), *m/z* (%): 303 (91) [M^+], 274 (100) [$M^+ - C_2H_5$], 246 (20), 144 (8), 102 (5), 77 (3). − $C_{21}H_{21}NO$: calcd. 303.1623 (correct HRMS).

2-Cyclopropyl-3-ethoxy-2-phenyl-5-propyl-2H-pyrrole (**18b**): A solution of 407 mg (0.88 mmol) of **15b** in 18 ml of tetrahydrofuran was stirred at 50−55°C for 24 h. The solvent was evaporated under reduced pressure. Impurities were removed by chromatography (10 g of silica gel, petroleum ether/diethyl ether, 10:1), elution with diethyl ether (plus 5% triethylamine) yielded 210 mg (88%) of **18b**, light brown oil. − IR (film): $\tilde{\nu}$ = 2962 cm^{-1}, 2932, 1623, 1048, 909, 733. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.18 (m_c, 1H, *c*Pr-CH_2), 0.31 (m_c, 1H, *c*Pr-CH_2), 0.59 (m_c, 1H, *c*Pr-CH_2), 0.71 (m_c, 1H, *c*Pr-CH_2), 0.98 (t, ^3J = 7.0 Hz, 3H, $CH_2CH_2CH_3$), 1.37 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 1.50 (m_c, 1H, *c*Pr-CH), 1.66 (tq, ^3J = 7.0, ^3J = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 2.47 (t, ^3J = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 4.03 (m_c, 2H, OCH_2), 5.21 (s, 1H, 4-H), 7.16−7.38 (m, 3H, Ph), 7.50−7.61 (m, 2H, Ph). − ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 0.14, 2.67 (−, *c*Pr-CH_2), 13.96, 14.17 (+, $CH_2CH_2CH_3$, OCH_2CH_3), 17.19 (+, *c*Pr-CH), 20.76 (−, $CH_2CH_2CH_3$), 36.01 (−, $CH_2CH_2CH_3$), 67.46 (−, OCH_2), 78.61 (C_{quat}, C-2), 95.84 (+, C-4), 126.29, 126.71, 128.00 (+, Ph), 128.44 (C_{quat}, Ph), 177.88, 185.39 (C_{quat}, C-5, -3). − MS (70 eV), *m/z* (%): 269 (43) [M^+], 240 (100) [$M^+ - C_2H_5$], 200 (42), 105 (40), 77 (26), 55 (18), 41 (23). − $C_{18}H_{23}NO$: calcd. 269.1779 (correct HRMS).

2,5-Dicyclopropyl-3-ethoxy-2-phenyl-2H-pyrrole (**18c**): A solution of 400 mg (0.87 mmol) of **15c** in 18 ml of tetrahydrofuran was stirred at 50−55°C for 16 h. The solvent was evaporated under reduced pressure. Impurities were removed by chromatography (16 g of silica gel, petroleum ether/diethyl ether, 10:1), elution with diethyl ether (plus 5% triethylamine) yielded 228 mg (97%) of **18c**, colorless oil. − IR (film): $\tilde{\nu}$ = 2962 cm^{-1}, 1621, 1304, 1100, 697. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.18 (m_c, 1H, *c*Pr-CH_2), 0.32 (m_c, 1H, *c*Pr-CH_2), 0.54 (m_c, 1H, *c*Pr-CH_2), 0.73 (m_c, 1H, *c*Pr-CH_2), 0.80−1.08 (m, 4H, *c*Pr-CH_2), 1.31 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 1.54 (m_c, 1H, *c*Pr-CH), 1.82 (m_c, 1H, *c*Pr-CH), 3.92 (m_c, 2H, OCH_2), 4.95 (s, 1H, 4-H), 7.16−7.35 (m, 3H, Ph), 7.50−7.58 (m, 2H, Ph). − ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 0.06, 2.59, 7.38, 7.42 (−, *c*Pr-CH_2), 14.06, 14.07, 17.10 (+, OCH_2CH_3, *c*Pr-CH), 67.33 (−, OCH_2), 78.26 (C_{quat}, C-2), 92.93 (+, C-4), 126.61, 126.80, 127.91 (+, Ph), 140.52 (C_{quat}, Ph), 178.85, 185.25 (C_{quat}, C-5, -3). − MS (70 eV), *m/z* (%): 267 (99) [M^+], 238 (100) [$M^+ - C_2H_5$], 222 (15), 164 (12), 109 (39), 77 (37), 41 (44). − $C_{18}H_{21}NO$: calcd. 267.1623 (correct HRMS).

5-tert-Butyl-2-cyclopropyl-3-ethoxy-2-phenyl-2H-pyrrole (**18d**): A solution of 321 mg (0.68 mmol) of **15d** in 12 ml of tetrahydrofuran was stirred at 50−55°C for 18 h. The solvent was evaporated under reduced pressure. Impurities were removed by chromatography (10 g of silica gel, petroleum ether/diethyl ether, 8:1), elution with diethyl ether (plus 5% triethylamine) yielded 162 mg (85%) of **18d**, white crystals, m.p. 29°C. − IR (film): $\tilde{\nu}$ = 3086 cm^{-1}, 2962, 2930, 1621, 1561, 1099. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.11 (m_c,

1H, *c*Pr-CH_2), 0.22 (m_c, 1H, *c*Pr-CH_2), 0.56 (m_c, 1H, *c*Pr-CH_2), 0.61 (m_c, 1H, *c*Pr-CH_2), 1.21 [s, 9H, $C(CH_3)_3$], 1.30 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 1.60 (m_c, 1H, *c*Pr-CH), 3.92 (m_c, 2H, OCH_2), 5.25 (s, 1H, 4-H), 7.13–7.37 (m, 3H, Ph), 7.40–7.53 (m, 2H, Ph). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 0.06, 2.34 (–, *c*Pr-CH_2), 14.07, 16.78 (+, OCH_2CH_3, *c*Pr-CH), 28.24 [+, $C(CH_3)_3$], 35.49 [C_{quat}, $C(CH_3)_3$], 67.18 (–, OCH_2), 77.51 (C_{quat}, C-2), 93.27 (+, C-4), 126.52, 126.73, 127.88 (+, Ph), 140.52 (C_{quat}, Ph), 184.45, 185.10 (C_{quat}, C-5, -3). – MS (70 eV), *m/z* (%): 283 (75) [M^+], 268 (100) [$M^+ - CH_3$], 254 (57) [$M^+ - C_2H_5$], 226 (12) [$M^+ - C_4H_9$], 198 (8), 128 (9), 57 (7). – $C_{19}H_{25}NO$ (283.4): calcd. C 80.52, H 8.89, N 4.94; found C 80.31, H 9.16, N 4.93.

2,2-Dicyclopropyl-3-ethoxy-5-phenyl-2H-pyrrole (**19a**) *and 2,2-Dicyclopropyl-4-ethoxy-6-phenyl-3(2H)-pyridinone* (**20a**): A solution of 380 mg (0.83 mmol) of **16a** in 18 ml of tetrahydrofuran was stirred at 50–55°C for 20 h. The solvent was removed under reduced pressure. Flash chromatography (20 g of flash silica gel, 15 × 1.5 cm, pentane/diethyl ether, 5:1) yielded fraction I: 100 mg (45%) of **19a** (R_f = 0.29), white solid. – IR (KBr): $\tilde{\nu}$ = 2963 cm^{-1}, 1610, 1524, 1446, 1319, 1024, 759, 439, 407. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.15–0.36 (m, 4H, *c*Pr-CH_2), 0.44 (m_c, 2H, *c*Pr-CH_2), 0.69 (m_c, 2H, *c*Pr-CH_2), 1.25 (m_c, 2H, *c*Pr-CH), 1.40 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 4.00 (q, ^3J = 7.1 Hz, 2H, OCH_2), 5.61 (s, 1H, 4-H), 7.30–7.49 (m, 3H, Ph), 7.77–7.90 (m, 2H, Ph). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –0.81, 1.29 (–, *c*Pr-CH_2), 14.20, 16.34 (+, OCH_2CH_3, *c*Pr-CH), 67.19 (–, OCH_2), 76.24 (C_{quat}, C-2), 93.43 (+, C-4), 127.11, 128.22, 129.83 (+, Ph), 135.15 (C_{quat}, Ph), 172.27, 186.87 (C_{quat}, C-5, -3). – MS (70 eV), *m/z* (%): 267 (17) [M^+], 238 (100) [$M^+ - C_2H_5$], 222 (30) [$M^+ - OC_2H_5$], 210 (28), 164 (19), 102 (22), 77 (15), 41 (10). – $C_{18}H_{21}NO$: calcd. 267.1623 (correct HRMS). – II: 52 mg (21%) of **20a** (R_f = 0.22), yellow crystals, m.p. 112°C. – IR (KBr): $\tilde{\nu}$ = 1680 cm^{-1} (C=O), 1636, 1570, 1229, 859, 697, 638. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = –0.01 (m_c, 2H, *c*Pr-CH_2), 0.26 (m_c, 2H, *c*Pr-CH_2), 0.46 (m_c, 2H, *c*Pr-CH_2), 0.88 (m_c, 2H, *c*Pr-CH_2), 1.36–1.59 (m, 5H, *c*Pr-CH, OCH_2CH_3), 4.03 (q, ^3J = 7.1 Hz, 2H, OCH_2), 6.45 (s, 1H, 5-H), 7.33–7.56 (m, 3H, Ph), 7.62–7.85 (m, 2H, Ph). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –0.20, –0.10 (*c*Pr-CH_2), 14.02 (*c*Pr-CH), 19.71 (OCH_2CH_3), 64.41 (OCH_2), 69.89 (C-2), 102.57 (C-5), 126.34, 128.46, 130.06, 139.05 (Ph), 154.32 (C-4), 160.03 (C-6), 203.53 (C-3). – MS (70 eV), *m/z* (%): 295 (17) [M^+], 266 (75) [$M^+ - C_2H_5$], 210 (18), 91 (100), 85 (52), 77 (18), 55 (12), 41 (13). – $C_{19}H_{21}NO_2$ (295.4): calcd. C 77.26, H 7.17, N 4.74; found C 77.33, H 7.33, N 4.85.

2,2-Dicyclopropyl-4-ethoxy-6-propyl-3(2H)-pyridinone (**20b**) *and 2,2-Dicyclopropyl-3-ethoxy-5-propyl-2H-pyrrole* (**19b**): A solution of 400 mg (0.94 mmol) of **16b** in 15 ml of tetrahydrofuran was stirred at 50–55°C for 20 h. The solvent was removed under reduced pressure. Flash chromatography (20 g of flash silica gel, 15 × 1.5 cm, pentane/diethyl ether, 10:1) yielded fraction I: 18 mg unidentified product (R_f = 0.34), yellow oil. – II: 54 mg (22%) of **20b** (R_f = 0.13), yellow oil. – IR (film): $\tilde{\nu}$ = 3086 cm^{-1}, 3006, 2961, 2933, 1733 (C=O), 1652, 1587, 1376, 1154, 1085, 1023, 837. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = –1.11 (m_c, 2H, *c*Pr-CH_2), 0.19 (m_c, 2H, *c*Pr-CH_2), 0.36 (m_c, 2H, *c*Pr-CH_2), 0.73 (m_c, 2H, *c*Pr-CH_2), 0.92 (t, ^3J = 7.0 Hz, 3H, $CH_2CH_2CH_3$), 1.31–1.52 (m, 5H, OCH_2CH_3, *c*Pr-CH), 1.55 (tq, ^3J = 7.0, ^3J = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 2.31 (t, ^3J = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 4.03 (q, ^3J = 7.1 Hz, 2H, OCH_2), 5.72 (s, 1H, 5-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –0.44, –0.10 (–, *c*Pr-CH_2), 13.67, 13.97, 19.97 (+, $CH_2CH_2CH_3$, OCH_2CH_3, *c*Pr-CH), 20.14 (–, $CH_2CH_2CH_3$), 42.28 (–, $CH_2CH_2CH_3$), 64.14 (–, OCH_2), 69.26 (C_{quat}, C-2), 104.91 (+, C-5), 153.54, 164.11 (C_{quat}, C-6, -4), 203.91 (C_{quat}, C-3). – MS (70 eV), *m/z* (%): 261 (18) [M^+], 232 (62) [$M^+ - C_2H_5$], 218 (42), 190 (100), 162 (38), 148 (20), 77 (25), 55 (30), 41 (86). – $C_{16}H_{23}NO_2$: calcd. 261.1728 (correct HRMS). – III: 3 mg unidentified product (R_f = 0.03), blue oil. – IV (elution with diethyl ether): 138 mg (63%) of **19b**, colorless oil. – IR (film): $\tilde{\nu}$ = 2954 cm^{-1}, 1620, 1037, 909, 733, 699, 654. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.03–0.20 (m, 4H, *c*Pr-CH_2), 0.33 (m_c, 2H, *c*Pr-CH_2), 0.53 (m_c, 2H, *c*Pr-CH_2), 0.87 (t, ^3J = 7.0 Hz, 3H, $CH_2CH_2CH_3$), 1.08 (m_c, 2H, *c*Pr-CH), 1.33 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 1.53 (tq, ^3J = 7.0, ^3J = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 2.31 (t, ^3J = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 3.86 (q, ^3J = 7.1 Hz, 2H, OCH_2), 5.02 (s, 1H, 4-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –0.97, 1.16 (–, *c*Pr-CH_2), 13.79, 14.18, 15.83 (+, $CH_2CH_2CH_3$, OCH_2CH_3, *c*Pr-CH), 20.85 (–, $CH_2CH_2CH_3$), 35.85 (–, $CH_2CH_2CH_3$), 67.04 (–, OCH_2), 75.19 (C_{quat}, C-2), 95.17 (+, C-4), 177.62, 186.19 (C_{quat}, C-5, -3). – MS (70 eV), *m/z* (%): 233 (18) [M^+], 205 (100) [$M^+ - C_2H_4$], 164 (68), 148 (8), 91 (5), 77 (5), 55 (4), 44 (3). – $C_{15}H_{23}NO$: calcd. 233.1779 (correct HRMS).

2,2,5-Tricyclopropyl-3-ethoxy-2H-pyrrole (**19c**): A solution of 131 mg (0.31 mmol) of **16c** in 12 ml of tetrahydrofuran was stirred at 50–55°C for 20 h. The solvent was evaporated under reduced pressure. Impurities were removed by chromatography (10 g of silica gel, petroleum ether/diethyl ether, 10:1), elution with diethyl ether (plus 5% triethylamine) yielded 58 mg (81%) of **19c**, brown oil. – IR (film): $\tilde{\nu}$ = 2985 cm^{-1}, 1620, 1540, 1457, 1031, 907. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.02–0.30 (m, 3H, *c*Pr-CH_2), 0.41 (m_c, 2H, *c*Pr-CH_2), 0.62 (m_c, 2H, *c*Pr-CH_2), 0.80–1.08 (m, 8H, *c*Pr-CH_2, *c*Pr-CH), 1.39 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 3.95 (q, ^3J = 7.1 Hz, 2H, OCH_2), 4.32 (s, 1H, 4-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –0.68, 1.62, 8.62 (–, *c*Pr-CH_2), 14.08, 14.30, 15.91 (+, OCH_2CH_3, *c*Pr-CH), 67.78 (–, OCH_2), 75.23 (C_{quat}, C-2), 91.88 (+, C-4), 181.04, 186.96 (C_{quat}, C-5, -3). – MS (70 eV), *m/z* (%): 231 (32) [M^+], 202 (100) [$M^+ - C_2H_5$], 186 (42) [$M^+ - OC_2H_5$], 164 (40), 146 (5), 77 (11), 41 (34). – $C_{15}H_{21}NO$: calcd. 231.1623 (correct HRMS).

5-tert-Butyl-2,2-dicyclopropyl-3-ethoxy-2H-pyrrole (**19d**): A solution of 477 mg (1.09 mmol) of **16d** in 15 ml of tetrahydrofuran was stirred at 50–55°C for 16 h. The solvent was evaporated under reduced pressure. Impurities were removed by chromatography (10 g of silica gel, petroleum ether/diethyl ether, 10:1), elution with diethyl ether (plus 5% triethylamine) yielded 247 mg (92%) of **19d**, colorless oil. – IR (film): $\tilde{\nu}$ = 3007 cm^{-1}, 1637, 1614, 1447, 1092, 1026, 766, 693. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = –0.05–0.20 (m, 4H, *c*Pr-CH_2), 0.30 (m_c, 2H, *c*Pr-CH_2), 0.56 (m_c, 2H, *c*Pr-CH_2), 1.08–1.20 [s and m, 11H, $C(CH_3)_3$, *c*Pr-CH], 1.31 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 3.83 (q, ^3J = 7.1 Hz, 2H, OCH_2), 5.09 (s, 1H, 4-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –1.04, 1.10 (–, *c*Pr-CH_2), 14.22, 15.91 (+, OCH_2CH_3, *c*Pr-CH), 28.28 [+, $C(CH_3)_3$], 35.33 [C_{quat}, $C(CH_3)_3$], 66.78 (–, OCH_2), 74.23 (C_{quat}, C-2), 93.00 (+, C-4), 183.75, 185.46 (C_{quat}, C-5, -3). – MS (70 eV), *m/z* (%): 247 (17) [M^+], 232 (20) [$M^+ - CH_3$], 218 (23), 190 (18) [$M^+ - C_4H_9$], 95 (18), 81 (9), 57 (100) [$C(CH_3)_3^+$], 53 (22), 41 (74). – $C_{16}H_{25}NO$: calcd. 247.1936 (correct HRMS).

X-ray Structure Analysis of 5-tert-Butyl-2-cyclopropyl-3-ethoxy-2-phenyl-2H-pyrrole (**18d**): Formula $C_{19}H_{25}NO$, molecular mass 283.40, triclinic, space group *P*1, *Z* = 2, *a* = 870.3(2), *b* = 987.2(2), *c* = 1020.5(2) pm, α = 73.82(3), β = 84.51(3), γ = 78.15(3)°, *V* = 0.8234(3) nm^3, $\rho_{calcd.}$ = 1.143 Mg m^{-3}, μ(Mo-K_α) = 0.070 nm^{-1}, crystal dimensions 0.60 × 0.60 × 0.40 mm, 2149 unique reflections were measured with a Stoe-Siemens four-circle diffractometer with graphit-monochromated Mo-K_α radiation (λ = 71.073 pm) at 150(2) K, 2Θ-range: 3.53–22.50°. The structure was solved by di-

rect methods (SHELXL-92[24]) and refined on F^2 by full-matrix least-squares techniques (SHELXL-92[25]). All nonhydrogen atoms were refined anisotropically, the hydrogen atoms were included in calculated positions and refined by using a riding model. R values: $R_1 = |\Sigma(F_o - F_c)|/\Sigma F_o$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$. $R_1 = 0.0381$ [for $F > 4\sigma(F)$], $wR_2 = 0.1037$ (for all data) with 191 parameters and 0 restraints, $w = 1/[\sigma^2(F_o^2) + (0.08P)^2 + 0.47P$, $P = (F_o^2 + 2F_c^2)/3$. Largest difference peak 0.164 $e^- nm^{-3} \cdot 10^3$.

[1] Cf. W. D. Wulff in *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, vol. 5, p. 1065–1113.

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