Synthesis of Pyrroles from 1-Dialkylamino-3-phosphoryl (or phosphanyl)-allenes Through 1,5-Cyclization of Conjugated Azomethine Ylide Intermediates

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General Methods

Reactions were carried out in rigorously dried glassware and under argon. Solvents were dried by standard procedures and kept under argon. Column chromatography was performed under hydrostatic conditions on silica gel (Si60, 0.063–0.2 mm, Macherey-Nagel) with distilled eluents; for flash chromatography, pressurized nitrogen gas was applied. Melting points were determined with a melting point apparatus and are uncorrected.

IR spectra: Solids were measured in KBr pellets, liquids as films between NaCl or KBr plates. NMR spectroscopy: ^1H spectra were measured at 500.14, 400.13 or 200.13 MHz, ^{13}C spectra at 125.77 MHz, 100.62 or 50.32 MHz, and ^{31}P spectra at 202.46 MHz. All spectra were recorded at 300–303 K. CDCl_3 was used as the solvent unless stated otherwise, and the following references were applied: internal TMS for the ^1H spectra ($\delta = 0.00$ ppm), a solvent signal for the ^{13}C spectra [$\delta(\text{CDCl}_3) = 77.0$ ppm; $[\text{D}_5]\text{pyridine}$: $\delta = 123.5$ ppm], and external 85% H_3PO_4 ($\delta = 0.00$ ppm) for the ^{31}P spectra. Coupling constants are reported as absolute values; mc = centered multiplet. ^{13}C spectra were recorded ^1H -decoupled; if necessary, signals were assigned based on gs-HMQC ($^1J(\text{C},\text{H})$) and gs-HMBC ($^2J(\text{C},\text{H})$, $^3J(\text{C},\text{H})$) spectra.

1. Synthesis of Propynones **8b–e** from Phenylethynyl(trimethyl)silane

General Procedure: A solution of phenylethynyl(trimethyl)silane (17.43 g, 0.10 mol) and a carboxylic acid chloride (0.1 mol) in dichloromethane (250 mL) was cooled at 0 °C with an ice bath. Under vigorous stirring, anhydrous AlCl_3 (13.23 g, 0.10 mol) was added during 15 min in several portions, allowing the solution to cool to 0 °C after each addition. After complete addition, the mixture was brought to 20 °C within 2 hours and kept at this temperature for another hour. Water (250 mL) was gradually added. After separation of the water phase, the organic phase was extracted with water (2×250 mL) and a satd aqueous NaHCO_3 solution (250 mL), then dried (CaCl_2). The solvent was evaporated and the product was isolated and purified by vacuum distillation or recrystallization from ethyl acetate.

Propynones **8b–d** have already been prepared by other methods, but the reported NMR data are partially incomplete.

1-(4-Fluorophenyl)-3-phenyl-2-propyn-1-one (8b). From 4-fluorobenzoyl chloride; yield 80%. IR (KBr) 2200 (s), 1640 (s) cm^{-1} ; ^1H NMR (200.13 MHz) δ 7.10–7.80 (m, 7 H_{aryl}), 8.15–8.25 (m, 2 H_{aryl}); ^{13}C NMR (50.32 MHz) δ 86.4 (C-2), 93.1 (C-3), 115.6 (d, $^2J_{\text{C},\text{F}} = 22.1$

Hz, C-3,5_{p-F-Ph}), 119.7 (C-1_{Ph}), 128.5 (C-3,5_{Ph}), 130.7 (C-4_{Ph}), 132.0 (d, $^3J_{C,F} = 9.6$ Hz, C-2,6_{p-F-Ph}), 132.9 (C-2,6_{Ph}), 133.2 (C-1_{p-F-Ph}), 166.2 (d, $^1J_{C,F} = 256.6$ Hz, C-4_{p-F-Ph}), 176.1 (C-1). Anal. Calcd for C₁₅H₉FO (224.23): C, 80.35; H, 4.04. Found: C, 80.42; H, 3.98.

1-(3,4-Dichlorophenyl)-3-phenyl-2-propyn-1-one (8c). From 3,4-dichlorobenzoyl chloride; yield 65%. Mp 164 °C (lit.²: 163–165 °C); IR (KBr) 2202 (s), 1636 (s) cm⁻¹; ¹H NMR (500.14 MHz) δ 7.40–8.23 (m, 8 H_{aryl}); ¹³C NMR (125.77 MHz) δ 86.2 (C-2), 94.3 (C-3), 119.5, 128.3, 128.7, 130.7, 131.1, 133.1, 133.3, 136.4, 138.7 (C_{aryl}), 175.3 (C-1). Anal. Calcd for C₁₅H₈Cl₂O (275.13): C, 65.48; H, 2.93. Found: C 65.49; H, 2.92.

1-(1,3-Benzodioxol-5-yl)-3-phenyl-2-propyn-1-one (8d)

From 3,4-(methylenedioxy)benzoic acid chloride; yield 55%. Mp 103 °C (lit.³: 102–103 °C); IR (KBr) 2187 (s), 1625 (s), 1597 (s) cm⁻¹; ¹H NMR (200.13 MHz) δ 6.06 (s, CH₂), 6.89 (d, $^3J = 8.1$ Hz, 1H, H-7_{Bd}), 7.39–7.68 (m, 5 H), 7.88 (dd, 2H); ¹³C NMR (50.32 MHz) δ = 86.7 (C-2), 92.2 (C-3), 102.0 (CH₂), 107.9 (C-7_{Bd}), 108.2 (C-4_{Bd}), 120.1 (C-1_{Ph}), 127.1 (C-6_{Bd}), 128.5 (C-3,5_{Ph}), 130.6 (C-4_{Ph}), 132.0 (C-5_{Bd}), 132.8 (C-2,6_{Ph}), 148.1 (C-3a_{Bd}), 152.8 (C-7a_{Bd}), 176.0 (C-1) (Bd = benzodioxolyl). Anal. Calcd for C₁₆H₁₀O₃ (250.26): C, 76.79; H, 4.03. Found: C, 76.86; H, 4.02.

3-(2-Bromophenyl)-1-(4-chlorophenyl)-2-propyn-1-one (8e)

From 2-(2-bromophenyl)ethynyl-trimethylsilane⁴ (51.55 g, 0.203 mol), 4-chlorobenzoyl chloride (35.63 g, 0.203 mol) and AlCl₃ (27.15 g, 0.203 mol); yield 52.86 g (81%). Mp 164–165 °C; IR (KBr) 2198 (s), 1646 (s), 1583 (s), 1212 (s), 1005 (s), 752 (s) cm⁻¹; ¹H NMR (500.14 MHz) δ 7.36–8.26 (m, 8 H_{Ar}); ¹³C NMR (125.77 MHz) δ 90.0, 91.0 (C-2,3), 122.5, 126.8, 127.4, 129.1, 131.1, 132.0, 132.9, 135.3, 134.4, 140.9 (C_{aryl}), 176.5 (C-1). Anal. Calcd for C₁₅H₈BrClO (319.58): C, 56.37; H, 2.52. Found C, 56.43; H, 2.55.

2. Synthesis of Enaminoketones 9b–k

(*E,Z*)-1-(4-Fluorophenyl)-3-morpholino-3-phenyl-2-propen-1-one (9b)

Alkynone **8b** (18.89 g, 0.084 mol) was dissolved in anhydrous ether (200 mL) and morpholine (7.33 g, 0.084 mol) was added rapidly. During 12 hours, a precipitate formed which was filtered off, washed with ether (50 mL), and dried at 0.01 mbar. When the mother liquor was concentrated, a second smaller batch of product was obtained. The combined yield of the yellow crystalline product was 22.58 g (86%), *E*-**9b**:*Z*-**9b** = 4.0 (¹H NMR). Mp 125–126 °C; IR (KBr) 1642 (s), 1588 (s), 1546 (vs), 1490 (s), 1450 (s), 1413 (s), 1202 (s), 1121 (s), 1020 (s), 928 (s), 799 (s), 633 (s) cm⁻¹; ¹H NMR (200.13 MHz), *E*-**9b**: δ 3.20 (mc, 4H, NCH₂), 3.71 (mc, 4H, OCH₂), 5.95 (s, 1H, 2-H), 6.94–7.93 (m, 9 H_{aryl}); *Z*-**9b**: δ 3.38 (m, 4H, NCH₂), 3.83 (m, 4H, OCH₂), 5.64 (s, 1H, 2-H), 6.94–7.93 (m, 9 H_{aryl}); ¹³C NMR (50.32 MHz), *E*- and *Z*-isomer: δ 47.9/51.9 (NCH₂), 66.1/66.9 (OCH₂), 96.3/97.4 (C-2), 114.52/114.67 (d, ²J_{C,F} = 21.5 Hz, C-2,6_{p-F-Ph}), 164.1 (d, ¹J_{C,F} = 250.9 Hz, C-4_{p-F-Ph}), 164.2/164.1 (C-3), 187.1/183.5 (C-1). Anal. Calcd for C₁₉H₁₈FO₂ (311.35): C, 73.29; H, 5.83; N, 4.50. Found C, 73.33; H, 5.75; N, 4.42.

(*E,Z*)-1-(3,4-Dichlorophenyl)-3-morpholino-3-phenyl-2-propen-1-one (9c)

Prepared by analogy to **9b**, from alkynone **8c** (27.51 g, 0.10 mol) and morpholine (8.71 g, 0.10 mol) in ethyl acetate (150 mL). After recrystallization from ethyl acetate, yellow crystals were obtained; yield 30.43 g (84%), *E*-**9c**:*Z*-**9c** = 3.8 (¹H NMR). Mp 140–141 °C; IR (KBr) 1625 (m), 1530 (vs), 1514 (vs), 1210 (s), 932 (m), 779 (m) cm⁻¹; ¹H NMR (200.13 MHz), *E*-**9c**: δ 3.27 (mc, 4H, NCH₂), 3.78 (mc, 4H, OCH₂), 5.93 (s, 1H, 2-H), 7.25–8.02 (m, 8 H_{aryl}); *Z*-**9c**: δ 3.45 (mc, 4H, NCH₂), 3.85 (mc, 4H, OCH₂), 5.58 (s, 1H, 2-H), 7.21–7.98 (m, 8 H_{aryl}); ¹³C NMR (50.32 MHz), *E*-**9c**: δ 48.1 (NCH₂), 66.4 (OCH₂), 95.7 (C-2), 126.8, 128.3, 128.7, 129.1, 129.5, 129.9, 132.1, 134.8, 135.5, 140.8 (all C_{aryl}), 165.2 (C-3), 186.0 (C-1); *Z*-

9c: δ 52.4 (NCH₂), 67.2 (OCH₂), 96.8 (C-2), 165.0 (C-3), 182.3 (C-1). Anal. Calcd. for C₁₉H₁₇Cl₂NO₂ (362.25): C, 62.99; H, 4.73; N, 3.87. Found C, 62.85; H, 4.76; N, 3.88.

(*E,Z*)-1,3-Diphenyl-3-{4-[3-(trifluoromethyl)phenyl]piperazino}-2-propen-1-one (9d)

A solution of alkynone **8a**⁵ (17.99 g, 0.087 mol) in ethyl acetate (200 mL) was prepared, 3-piperazino-benzotrifluoride hydrochloride⁶ (23.26 g, 0.087 mol) and triethylamine (8.80 g, 0.087 mol) were added and the mixture was heated at reflux for 2 hours. After cooling to 20 °C, the solution was extracted with water (3×100 mL), dried (Na₂SO₄), and the solvent was evaporated at 15 mbar. Ether (100 mL) was added to the residue, and the remaining solid (triethylammonium chloride) was filtered off. Evaporation of the solvent left an orange oil which solidified after some days; yield 34.55 g (91%), *E*-**9d**:*Z*-**9d** = 3.7 (¹H NMR). Mp 46 °C; IR (KBr) 1636 (m), 1613 (m), 1532 (vs), 1208 (s), 1113 (s), 949 (s), 696 (s) cm⁻¹; ¹H NMR (200.13 MHz) δ 3.20–3.55 (m, 8 H, NCH₂), 5.75 (s, 1H, 2-H, *Z*), 6.02 (s, 1H, 2-H, *E*), 7.00–7.95 (m, 14 H_{aryl}); ¹³C NMR (50.32 MHz), *E*-**9d**: δ 47.3 (NCH₂), 48.3 (NCH₂), 97.1 (C-2), 112.1–150.6 (all C_{aryl}, CF₃), 163.7 (C-3), 188.6 (C-1); *Z*-**9d**: δ 49.3 (NCH₂), 51.1 (NCH₂), 98.5 (C-2), 112.1–151.0 (all C_{aryl}, CF₃), 163.7 (C-3), 185.5 (C-1). Anal. Calcd for C₂₆H₂₃F₃N₂O (436.48): C, 71.55; H, 5.31; N, 6.42. Found C, 71.30; H, 4.96; N, 5.99.

(*E*)-3-(2,3-Dihydro-1*H*-2-isoindolyl)-1,3-diphenyl-2-propen-1-one (9e)

Isoindoline⁷ (9.11 g, 0.076 mol) was added to a solution of alkynone **8a**⁵ (15.76 g, 0.076 mol) in ether (250 mL). After 12 h, the solvent was evaporated at 15 mbar and the residue was recrystallized from ethyl acetate to give 22.63 g (91%) of **9e** as a light-brown crystalline solid. Mp 141–142 °C; IR (KBr) 1633 (s), 1523 (vs), 1459 (s), 1421 (s), 1210 (s), 944 (s), 767 (m), 760 (m), 701 (m) cm⁻¹; ¹H NMR (200.13 MHz) δ 4.40 (br s, 2H, NCH₂), 4.80 (br s, 2H, NCH₂), 5.98 (s, 1H, 2-H), 7.10–7.95 (m, 14 H_{aryl}); ¹³C NMR (50.32 MHz) δ 54.4/55.1 (C-1,₃isoindolyl), 94.1 (C-2), 122.4, 127.0, 127.5, 127.6, 127.8, 128.2, 128.7, 130.5, 136.1, 137.6,

141.4 (all C_{aryl}), 161.3 (C-3), 186.8 (C-1). Anal. Calcd for C₂₃H₁₉NO (325.41): C, 84.89; H, 5.88; N, 4.30. Found C, 84.63; H, 5.91; N, 4.38.

(*E,Z*)-1-(1,3-Benzodioxol-5-yl)-3-morpholino-3-phenyl-2-propen-1-one (9f)

Prepared by analogy to **9b**, from alkynone **8d** (10.00 g, 0.04 mol) and morpholine (3.48 g, 0.04 mol) in ethyl acetate (150 mL); yellow crystals, yield 12.28 g (91%), *E*-**9f**:*Z*-**9f** = 4.0 (¹H NMR). Mp 122–123 °C; IR (KBr) 1621 (m), 1600 (s), 1522 (vs), 1243 (vs), 1112 (vs), 882 (s), 781 (s) cm⁻¹; ¹H NMR (200.13 MHz), *E*-**9f**: δ 3.17 (mc, 4H, NCH₂), 3.70 (mc, 4H, OCH₂), 5.91 (s, 1H, 2-H), 5.92 (s, 2H, OCH₂O), 6.76 (d, ³J = 8.1 Hz, 1H, 6-H_{Bd}), 7.20–7.50 (m, 7 H_{aryl}); *Z*-**9f**: δ 3.34 (mc, 4H, NCH₂), 3.81 (mc, 4H, OCH₂), 5.48 (s, 1H, 2-H), 5.93 (s, 2H, OCH₂O), 6.77 (d, ³J = 8.1 Hz, 1H, 6-H_{Bd}), 7.20–7.50 (m, 7 H_{aryl}); ¹³C NMR (50.32 MHz), *E*-**9f**: δ 48.0 (NCH₂), 66.2 (OCH₂), 96.9 (C-2), 101.2 (C-2_{Bd}), 107.1 (C-7_{Bd}), 107.8 (C-4_{Bd}), 122.8 (C-6_{Bd}), 128.3 (C-2,6_{Ph}), 128.3 (C-3,5_{Ph}), 135.5 (C-4_{Ph}), 135.9 (C-5_{Bd}), 147.3 (C-3_{aBd}), 149.8 (C-7_{aBd}), 163.7 (C-3), 187.1 (C-1); *Z*-**9f**: δ 51.8 (NCH₂), 67.0 (OCH₂), 97.9 (C-2), 101.2 (C-2_{Bd}), 107.2 (C-7_{Bd}), 107.8 (C-4_{Bd}), 123.0 (C-6_{Bd}), 138.3 (C-5_{Bd}), 147.5 (C-3_{aBd}), 149.8 (C-7_{aBd}), 163.3 (C-3), 184.0 (C-1); further C_{aryl} signals of both isomers are superimposed (Bd = benzodioxolyl). Anal. Calcd for C₂₀H₁₉NO₄ (337.37): C, 71.20; H, 5.67; N, 4.15. Found C, 71.18; H, 5.65; N, 4.13.

(*E*)-1-(1,3-Benzodioxol-5-yl)-3-phenyl-3-(1,2,3,4-tetrahydro-2-isoquinolinyl)-2-propen-1-one (9g)

1,2,3,4-Tetrahydroisoquinoline (6.51 g, 0.049 mol) was added to a solution of alkynone **8d** (12.23 g, 0.049 mol) in ether (250 mL). After 12 h, the precipitate was removed by filtration and discarded, and the solvent was evaporated at 0.01 mbar. The product was left as an orange cake-like solid (15.36 g, 82%) which could not be crystallized, mp 51–52 °C. ¹H NMR (200.13 MHz) δ = 2.82 (pseudo-t, 2H, NCH₂CH₂), 3.38 (pseudo-t, 2H, NCH₂CH₂), 4.47 (s, 2H, NCH₂-Ar), 5.85 (s, 1H, H_{olefin}), 5.90 (s, 2H, OCH₂O), 6.60–7.90 (m, 12 H_{aryl}); ¹³C NMR

(50.32 MHz) δ 28.4 (C-4_{THI}), 44.9 (C-3_{THI}), 49.0 (C-1_{THI}), 94.4 (C-2), 100.6 (OCH₂O), 106.5, 107.2, 122.0, 125.5, 125.7, 126.0, 127.6, 127.7, 127.9, 128.5, 132.1, 133.7, 135.4, 136.1, 146.8, 149.0 (all C_{aryl}), 162.4 (C-3), 185.3 (C-1). Anal. Calcd for C₂₅H₂₁NO₃ (383.44): C, 78.31; H, 5.52; N, 3.65. Found: C, 78.20; H, 5.61; N, 3.70.

(*E,Z*)-3-(2-Bromophenyl)-1-(4-chlorophenyl)-3-morpholino-2-propen-1-one (9h)

Prepared by analogy to **9b** from alkynone **8e** (52.86 g, 0.165 mol) and morpholine (14.41 g, 0.165 mol) in ethyl acetate (300 mL); light-yellow solid, yield 62.88 g (93.5%), *E*-**9i**:*Z*-**9i** = 18.0 (¹H NMR). Mp 130 °C; IR (KBr) 1622 (m), 1589 (m), 1567 (m), 1517 (vs), 1208 (s), 914 (s) cm⁻¹; ¹H NMR (200.13 MHz), *E*-**9h**: δ 3.27 (m, 4H, NCH₂), 3.74 (m, 4H, OCH₂), 6.03 (s, 1H_{olefin}), 7.10–7.80 (m, 8 H_{aryl}); *Z*-**9h**: δ 5.50 (s, 1H_{olefin}) (*E*- and *Z* configuration was established by NOESY experiments); ¹³C NMR (50.32 MHz), *E*-**9h**: δ 47.0 (NCH₂), 66.1 (OCH₂), [66.5 (OCH₂, *Z*-**9h**)], 94.3 (C-2), [96.4 (C-2, *Z*-**9h**)], 121.7, 127.5, 127.9, 128.7, 129.3, 129.6, 132.5, 136.6, 137.0, 139.1 (all C_{aryl}), 161.1 (C-3), 185.6 (C-1). Anal. Calcd for C₁₉H₁₇BrClNO₂ (406.71): C, 56.11; H, 4.21; N, 3.44. Found C, 56.13; H, 4.23; N, 3.40.

(*E*)-3-(1-Azepanyl)-1,3-diphenyl-2-propen-1-one (9i)

Alkynone **8a**⁵ (7.00 g, 0.034 mol) was dissolved in anhydrous ether (200 mL) and perhydroazepine (3.37 g, 0.034 mol) was added rapidly. After 12 h, the solvent was evaporated at 15 mbar. The residual light-brown oil solidified after several days, yielding 9.22 g (89%) of a waxy yellow solid, mp 54 °C. IR (KBr) 1630 (m), 1518 (s), 1222 (m), 1201 (m), 893 (s), 766 (s), 700 (s) cm⁻¹; ¹H NMR (200.13 MHz) δ 1.3–2.1 (m, br, 8 H), 3.0–3.8 (m, br, 4H, NCH₂), 5.97 (s, 1H_{olefin}), 7.2–8.3 (several m, 10 H_{aryl}); ¹³C NMR (50.32 MHz) δ 26.6 (br), 30.0 (br), 50.9 (2 NCH₂), 92.5 (C-2), 127.5–132.0 (C_{aryl}), 137.2 (C_{aryl}), 142.1 (C_{aryl}), 163.9 (C-3), 186.9 (C-1). Anal. Calcd for C₂₁H₂₃NO (305.42): C, 82.58; H, 7.59; N, 4.59. Found: C, 82.20; H, 7.77; N, 4.80.

Ethyl 1-[(*E,Z*)-3-Oxo-1,3-diphenyl-1-propenyl]piperidine-3-carboxylate (9j**)**

Alkynone **8a**⁵ (3.09 g, 0.015 mol) was dissolved in anhydrous ether (100 mL) and ethyl piperidine-3-carboxylate⁵ (2.36 g, 0.015 mol) was added. After 12 h, the precipitate was removed by filtration and discarded, the solvent was evaporated, and the residue was kept at 0.01 mbar to remove last traces of volatiles. A yellow oil (4.41 g, 81%) was obtained which was used without purification. *E*-**9j**:*Z*-**9j** = 3.8 (¹H NMR). IR (KBr) 1724 (vs), 1620 (s), 1597 (s), 1523 (vs), 1208 (s), 756 (s), 702 (s) cm⁻¹; ¹H NMR (200.13 MHz) δ 1.18 (t, *J* = 7.1 Hz, 3H, CH₃), 1.42–2.10 (m, 4H, 2 CH₂), 2.50–3.75 (m, 5 H_{alkyl}), 4.05 (q, 2H, CH₂CH₃), 5.71 (*Z*-**9j**) 6.06 (*E*-**9j**) (s, 1H_{olefin}), 7.15–8.00 (m, 10 H_{aryl}); ¹³C NMR (50.32 MHz), *E*-**9j**: δ 13.6 (CH₃), 23.5, 26.5, 40.6, 48.0, 49.3 (5 C_{alkyl}), 60.0 (CH₂CH₃), 96.0 (C-2), 126.6–130.2 (C_{aryl}), 136.0 (C_{aryl}), 140.8 (C_{aryl}), 163.6 (C-3), 172.1 (C=O), 187.8 (C-1); *Z*-**9j**: δ 13.6 (CH₃), 24.2, 25.9, 41.4, 51.2, 53.3 (5 C_{alkyl}), 60.0 (CH₂CH₃), 98.4 (C-2), 126.6–130.2 (C_{aryl}), 138.6 (C_{aryl}), 140.5 (C_{aryl}), 164.3 (C-3), 172.4 (C=O), 184.7 (C-1). Anal. Calcd for C₂₃H₂₅NO₃ (363.46): C, 76.01; H, 6.93; N, 3.85. Found: C, 75.79; H, 7.06; N, 3.99.

(*E,Z*)-3-[Benzyl(methyl)amino]-1,3-diphenyl-2-propen-1-one (9k**)**

Benzyl(methyl)amine (3.03 g, 0.025 mol) was added to a solution of alkynone **8a**⁵ (5.15 g, 0.025 mol) in ether (100 mL). After 12 h, the precipitate was removed by filtration. The solvent was evaporated at 15 mbar and the residual oil was kept at 0.01 mbar to remove last traces of volatiles. The yellow oil which was left (7.37 g, 90%) was used without purification for further transformations; *E*-**9k**:*Z*-**9k** = 15.0 (¹H NMR). IR (KBr) 1636 (s), 1517 (vs), 1449 (s), 1205 (s), 932 (m), 767 (m), 698 (s) cm⁻¹; ¹H NMR (200.13 MHz), *E*-**9k**: δ 3.96 (s, CH₃, *E*), 3.97 (s, CH₃, *Z*), 4.31 (br s, NCH₂, *E*), 4.53 (s, NCH₂, *Z*), 5.77 (s, 2-H, *Z*), 6.02 (s, 2-H, *E*), 7.10–7.95 (15 H_{aryl}); ¹³C NMR (50.32 MHz), *E*-**9k**: δ 30.0 (CH₃), 55.5 (NCH₂), 94.6 (C-2), 126.7, 127.3, 127.4, 127.7, 127.9, 128.4, 128.6, 129.5, 130.5, 136.4, 136.7, 141.4 (all C_{aryl}),

164.3 (C-3), 187.4 (C-1). Anal. Calcd for $C_{23}H_{21}NO$ (327.42): C, 84.37; H, 6.46; N, 4.28. Found C, 84.43; H, 6.33; N, 4.28.

3. 1H and ^{13}C NMR data of compounds 2b-e, 5a, 6a-k, 7a, 7b, 7d, 7f, 13–17 With Peak Assignments

4-[3-(4-Fluorophenyl)-1-phenyl-2-propynylidene]morpholinium

Trifluoromethanesulfonate (2b)

1H NMR (500.14 MHz) δ 3.91 (pseudo-t, 2H, NCH_2), 4.17 (pseudo-t, 2H, NCH_2), 4.25 (pseudo-t, 2H, OCH_2), 4.67 (pseudo-t, 2H, OCH_2), 7.15 (mc, 2 H_{aryl}), 7.54–7.86 (m, 7 H_{aryl}); ^{13}C NMR (125.77 MHz) δ = 54.0 (NCH_2), 56.5 (NCH_2), 66.1 (OCH_2), 66.3 (OCH_2), 83.8 (C-2), 114.3 (d, $J \sim 5$ Hz, C-1_{p-F-Ph}), 116.6 (d, $^2J_{C,F} = 22.6$ Hz, C-3,5_{p-F-Ph}), 120.6 (C-3), 129.2, 129.5, 130.0, 133.7 ($4 \times C_{Ph}$), 135.5 (d, $^3J_{C,F} = 9.5$ Hz, C-2,6_{p-F-Ph}), 162.0 (C-1), 165.4 (d, $^1J_{C,F} = 258.4$ Hz, C-4_{p-F-Ph}).

4-[3-(3,4-Dichlorophenyl)-1-phenyl-2-propynylidene]morpholinium

Trifluoromethanesulfonate (2c)

1H NMR (400.13 MHz) δ = 3.90 (pseudo-t, 2H, NCH_2), 4.13 (pseudo-t, 2H, NCH_2), 4.21 (pseudo-t, 2H, OCH_2), 4.64 (pseudo-t, 2H, OCH_2), 7.45–7.85 (m, 8 H_{aryl}); ^{13}C NMR (100.61 MHz) δ 54.5 (NCH_2), 57.2 (NCH_2), 66.3 (OCH_2), 66.5 (OCH_2), 84.5 (C-2), 118.1 (C-3), 118.1, 129.3, 129.8, 130.2, 131.3, 132.7, 133.7, 133.9, 134.7, 138.3 (C_{aryl}), 162.4 (C-1).

1-(1,3-Diphenyl-2-propynylidene)-4-[3-(trifluoromethyl)phenyl]hexahydro-1-pyrazinium
Trifluoromethanesulfonate (**2d**)

^1H NMR (500.14 MHz) δ 3.51 (pseudo-t, 2H, NCH_2), 3.78 (pseudo-t, 2H, NCH_2), 4.40 (pseudo-t, 2H, NCH_2), 4.80 (pseudo-t, 2H, NCH_2), 7.07–7.85 (m, 14 H_{aryl}); ^{13}C NMR (125.77 MHz) δ 48.2, 48.7, 53.2, 56.0 ($4\times\text{NCH}_2$), 84.0 (C-2), 112.5, 117.2, 117.9/119.5 (C_{aryl} , C-3), 121.9, 122.6 (CF_3), 133.8, 129.0–133.8, 149.0, 162.6 (C-1). $\text{C}_{27}\text{H}_{22}\text{F}_6\text{N}_2\text{O}_3\text{S}$ (568.53).

2-(1,3-Diphenyl-2-propynylidene)-2,3-dihydro-1H-isoindolium
Trifluoromethanesulfonate (**2e**)

^1H NMR (500.14 MHz) δ 5.45 (s, 2H, NCH_2), 5.79 (s, 2H, NCH_2), 7.10–8.05 (m, 14 H_{aryl}); ^{13}C NMR (125.77 MHz) δ 60.5 (NCH_2), 63.4 (NCH_2), 84.6 (C-2), 117.6 or 120.1 (C-3), 122.3, 122.6, 128.6, 129.0, 129.46, 129.53, 130.3, 131.5, 132.6, 133.4, 133.8, 134.5 (all C_{aryl} , 1 signal not detected) 160.5 (C-1).

Diphenyl(6-phenyl-3,4,6,12b-tetrahydro-1H-benzo[*c*][1,4]oxazino[4,3-*a*]azepin-8-yl)phosphane (**5a**)

^1H NMR (CDCl_3 , 500.14 MHz) δ 2.15–2.39 (2 m, 2H, 4-H), 3.25 (mc, 6-H), 3.60 (ddd, 2J , $^3J_{\text{Hax,Hax}} = 10.9$, 10.6 Hz, $^3J_{\text{Hax,Heq}} = 3.4$ Hz, 3- H^{ax}), 3.79 (d, $^2J = 11.0$ Hz, 3- H^{eq}), 3.97 (mc, 12b-H), 4.13 (dd, $^2J_{\text{H,H}} = 11.8$ Hz, $^3J_{\text{Hax,Heq}} = 3.5$ Hz, 1- H^{ax}), 4.41 (d, $^2J_{\text{H,H}} = 11.8$ Hz, 1- H^{eq}), 5.80 (dd, $^3J_{\text{H,H}} = 5.9$ Hz, $^3J_{\text{H,P}} = 6.0$ Hz, 7-H), ca. 7.05–7.90 (m, 19 H_{aryl}).

6,8-Diphenyl-3,4-dihydro-1H-pyrrolo[2,1-c][1,4]oxazine (6a)

^1H NMR (500.14 MHz) δ 4.03–4.06 (mc, 4H, $\text{NCH}_2\text{CH}_2\text{O}$), 5.15 (s, 2H, 1- H_2), 6.57 (s, 7-H), 7.25 (t, $J = 7.0$ Hz, 1H, p- H_{aryl}), 7.35–7.51 (m, 9 H_{aryl}); ^{13}C NMR (125.77 MHz) δ 44.2 (C-2), 64.4 (C-3), 65.1 (C-5), 107.7 (C-7), 119.5 (C-6), 123.5 (C-5a), 125.3, 126.7, 127.0, 128.4, 128.5, 128.6, 132.4, 135.8 (all C_{aryl}), 133.7 (C-8).

Diphenyl-(6-phenyl-3,4,6,12b-tetrahydro-1H-benzo[c][1,4]oxazino[4,3-a]azepin-8-yl)phosphanoxide (7a)

^1H NMR (500.14 MHz) δ 2.21–2.33 (m, 2H, 4-H), 3.31 (dd, $^3J_{\text{H,H}} = 5.9$ Hz, $^4J_{\text{H,P}} = 3.3$ Hz, 6-H), 3.56 (dt, 2J , $^3J_{\text{Hax,Hax}} = 10.8$, 10.6 Hz, $^3J_{\text{Hax,Heq}} = 3.5$ Hz, 3- H^{ax}), 3.70–3.85 (m, 2H, 3- H^{eq} , 12b-H), 4.07 (dd, $^2J_{\text{H,H}} = 12.0$ Hz, $^3J_{\text{Hax,Heq}} = 3.5$ Hz, 1- H^{ax}), 4.38 (d, $^2J_{\text{H,H}} = 12.0$ Hz, 1- H^{eq}), 6.57 (dd, $^3J_{\text{H,H}} = 5.9$ Hz, $^3J_{\text{H,P}} = 18.0$ Hz, 1H, 7-H), 6.85–8.00 (m, 19 H_{aryl}); ^{13}C NMR (50.32 MHz) δ 46.8 (C-4), 56.2 (C-12b), 64.9 (C-3), 67.0 (d, $^3J_{\text{C,P}} = 13.4$ Hz, C-6), 68.9 (C-1), 125.1–146.3 (C_{aryl} , 1 C_{olefin}); ^{31}P NMR $\delta = 28.2$.

Diphenyl-[1-(4-fluorophenyl)-3-morpholino-3-phenyl-1,2-propadienyl]phosphane (3b):

^1H NMR (200.13 MHz) δ 2.30–2.45 (m, 4H, NCH_2), 3.50–3.60 (m, 4H, OCH_2), 7.1–7.8 (m, 19 H_{aryl}); ^{13}C NMR (50.32 MHz) δ 50.4 (NCH_2), 66.7 (OCH_2), 111.0 (d, $J_{\text{C,P}} = 19.5$ Hz, C-1), 115.2 (d, $J_{\text{C,F}} = 21.6$ Hz, C-3, 5- F-Ph), 126.8–135.5 (all C_{aryl} , C-3), 163.0 (d, $J_{\text{C,F}} = 251$ Hz, C-4- F-Ph), 205.1 (C-2); ^{31}P NMR (CDCl_3 , 202.46 MHz) $\delta -3.0$. Data for **3c**: ^1H NMR (CDCl_3 ,

500.14 MHz) δ 2.31–2.42 (2 m, 4H, NCH₂), 3.55–3.61 (m, 4H, OCH₂), 7.17–7.77 (m, 18 H_{aryl}); ¹³C NMR (CDCl₃, 125.77 MHz) δ 50.5 (NCH₂), 66.7 (OCH₂), 110.3 (d, ¹J_{C,P} = 20.1 Hz, C-1), 126.2–137.9 (all C_{aryl}, C-3), 206.5 (C-2); ³¹P NMR δ -6.9.

10-Fluoro-6-phenyl-3,4,6,12b-tetrahydro-1H-benzo[c][1,4]oxazino[4,3-a]azepin-8-yl(diphenyl)phosphanoxide (7b)

¹H NMR (200.13 MHz) δ = 2.23–2.37 (m, 2H, 4-H), 3.29 (dd, ³J_{H,H} = 5.8 Hz, ³J_{H,P} = 3.3 Hz, 1H, 6-H), 3.53 (dt, ²J_{H,H} = ³J_{Hax,Hax} = 10.9 Hz, ³J_{Hax,Heq} = 4.1 Hz, 1H, 3-H^{ax}), 3.62–3.74 (m, 2H, 3-H^{eq}, 1H, 12b-H), 4.08 (dd, ²J_{H,H} = 12.1 Hz, ³J_{Hax,Heq} = 3.0 Hz, 1H, 1-H^{ax}), 4.35 (d, ²J_{H,H} = 12.1 Hz, 1H, 1-H^{eq}), 6.51 (dd, ³J_{H,H} = 5.9 Hz, ³J_{H,P} = 17.8 Hz, 1H, 7-H), 6.83 (t, *J* = 7.4 Hz, 1 H_{aryl}), 7.20–7.80 (m, 17 H_{aryl}); ¹³C NMR (50.32 MHz) δ 46.8 (C-4), 56.0 (C-12b), 66.9 (C-3), 67.4 (d, ³J_{C,P} = 13.4 Hz, C-6), 68.7 (C-1), 114.4 (d, ²J_{C,F} = 21.5 Hz, C-10), 116.3 (d, ²J_{C,F} = 22.3 Hz, C-12), 127.6–132.4, 137.3, 138.1, 140.3, 140.9, 145.9 (d, ²J_{C,P} = 8.8 Hz, C-7), 161.9 (d, ¹J_{C,F} = 249.0 Hz, C-11); ³¹P NMR δ 28.3; MS (EI, 70 eV) *m/z* (rel. int., %) 495 (M⁺, 35), 294 (M⁺ – POPh₂, 100).

Diphenyl{6-phenyl-2-[3-(trifluoromethyl)phenyl]-1,2,3,4,6,12b-hexahydrobenzo[c]pyrazino[1,2-a]azepin-8-yl}phosphanoxide (7d)

7d

¹H NMR (200.13 MHz) δ 2.44–2.54 (m, 2H, 4-H), 2.89 (pseudo-t, 1H, 3-H^{ax}), 3.41–3.48 (m, 3H, 1-H_{ax}, 6-H, 3-H^{eq}), 4.09 (d, ²J = 12.3 Hz, 1H, 1-H^{eq}), 4.14 (s, 1H, 12b-H), 6.64 (dd, ³J_{H,H} = 5.9 Hz, ³J_{H,P} = 18.6 Hz, 1H, 7-H), 7.12–7.90 (m, 23 H_{aryl}); ¹³C NMR (50.32 MHz) δ 46.0

(C-4), 48.3 (C-3), 51.2 (C-1), 55.8 (C-12b), 66.9 (d, C-6); 112.0, 116.1, 118.9, 127.3–138.0, 141.0, 146.6, 151.1 (C_{aryl}, C_{olefin}, CF₃); ³¹P NMR δ 28.3.

8-(4-Fluorophenyl)-6-phenyl-3,4-dihydro-1H-pyrrolo[2,1-c][1,4]oxazine (6b)

¹H NMR (500.14 MHz) δ 4.01–4.06 (m, 4H, NCH₂CH₂O), 5.08 (s, 2H, 1-H₂), 6.49 (s, 1H, 7-H), 7.08–7.50 (several m, 9 H_{aryl}); ¹³C NMR (125.77 MHz) δ 44.1 (C-4), 64.2 (C-3), 64.8 (C-1), 107.6 (C-7), 115.3 (d, ²J_{C,F} = 21.3 Hz, C-3,5_{p-F-Ph}), 128.0 (d, ³J_{C,F} = 7.7 Hz, C-2,6_{p-F-Ph}), 131.9 (d, ⁴J_{C,F} = 3.1 Hz, C-1_{p-F-Ph}), 160.1 (d, ¹J_{C,F} = 244.3 Hz, C-4_{p-F-Ph}), 118.5, 123.2, 126.9, 128.3, 128.5, 132.3, 133.7 (all C_{aryl}).

8-(3,4-Dichlorophenyl)-6-phenyl-3,4-dihydro-1H-pyrrolo[2,1-c][1,4]oxazine (6c)

¹H NMR (500.14 MHz) δ 3.97 (s, 4H, NCH₂CH₂O), 5.00 (s, 2H, 1-H₂), 6.40 (s, 1H, 7-H), 7.05 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.27–7.39 (m, 7 H_{aryl}); ¹³C NMR (125.77 MHz) 44.1 (C-4), 64.2 (C-3), 64.7 (C-1), 107.4 (C-7), 117.1, 124.1, 125.7, 127.2, 128.1, 128.4, 128.5, 128.7, 130.4, 132.0, 132.5, 134.0, 136.0 (all C_{aryl}).

6,8-Diphenyl-2-[3-(trifluoromethyl)phenyl]-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine (6d)

¹H NMR (200.13 MHz) δ 3.31 (pseudo-t, 2H, NCH₂), 3.97 (pseudo-t, 2H, 3-H₂), 4.58 (s, 2H, 1-H₂), 6.42 (s, 1H, 7-H), 6.82–7.48 (m, 14 H_{aryl}); ¹³C NMR (50.32 MHz) δ 43.9, 45.9, 46.1

(C-1, C-3, C-4), 108.0 (C-7), 110.8, 115.3, 117.6, 120.2, 123.3, 125.4, 126.8, 126.9, 128.0, 128.5, 128.6, 129.7, 131.3, 132.2, 133.3, 135.8, 149.6 (all C_{aryl}, CF₃).

1,3-Diphenyl-1-{4-[3-(trifluoromethyl)phenyl]piperazino}-2-propynyl(diphenyl)phosphanoxide (10)

¹H NMR (200.13 MHz) δ 2.72–2.85 (m, 2H, NCH₂), 3.08–3.30 (m, 6H, 3 NCH₂), 7.00–7.72 (m, 22 H_{aryl}), 8.05–8.15 (m, 2 H_{aryl}); ¹³C NMR (50.32 MHz) δ 48.7 (2 C, NCH₂), 49.2 (d, ³J_{C,P} = 5.0 Hz, 2 NCH₂), 71.4 (d, ¹J_{C,P} = 81.7 Hz, C-1), 84.0 (C-3), 94.3 (d, ²J_{C,P} = 8.3 Hz, C-2), 111.7, 115.5, 118.4, 121.5, 122.0, 126.9–135.2, 151.1 (CCF₃); ³¹P NMR δ 30.2.

1,3-Diphenyl-5H-pyrrolo[2,1-a]isoindole (6e).

¹H NMR (500.14 MHz) δ 5.13 (s, 2H, CH₂), 6.76 (s, 1H, 2-H), 7.17–7.79 (m, 14 H_{aryl}); ¹³C NMR (125.77 MHz) δ 51.1 (C-5), 111.5 (C-2), 118.8, 119.1, 122.8, 124.9, 125.2, 126.0, 126.4, 127.8, 127.9, 128.6, 128.8, 131.1, 132.6, 133.2, 135.6, 136.3, 140.0 (all C_{aryl}).

8-(1,3-Benzodioxol-5-yl)-6-phenyl-3,4-dihydro-1H-pyrrolo[2,1-c][1,4]oxazine (6f) and Diphenyl(6-phenyl-3,4,6,13b-tetrahydro-1H-[1,3]dioxolo[4',5':4,5]benzo[c][1,4]oxazino[4,3-a]azepin-8-yl)phosphanoxide (7f)

6f

7f

Data for **6f**: ^1H NMR (500.14 MHz) δ 4.01 (s, 4H, $\text{NCH}_2\text{CH}_2\text{O}$), 5.03 (s, 2H, 1- H_2), 5.94 (s, 2H, OCH_2O), 6.40 (s, 1H, 7-H), 6.74 (d, $^3J = 8.0$ Hz, 1H, 6- H_{Bd}), 6.82 (d, $^3J = 8.0$ Hz, 1H, 7- H_{Bd}), 6.83 (s, 1H, 4- H_{Bd}), 7.25–7.45 (m, 5 H_{aryl}); ^{13}C NMR (125.77 MHz) δ 44.2 (C-4), 64.3 (C-3), 64.9 (C-1), 100.8 (C-2 $_{\text{Bd}}$), 107.5 (C-4 $_{\text{Bd}}$), 107.7 (C-7), 108.4 (C-7 $_{\text{Bd}}$), 119.3 (C-8), 119.9 (C-6 $_{\text{Bd}}$), 123.0 (C-8a), 126.9 (C-4 $_{\text{Ph}}$), 128.4, 128.5 (C-2,3,5,6 $_{\text{Ph}}$), 129.9 (C-5 $_{\text{Bd}}$), 132.4 (C-1 $_{\text{Ph}}$), 133.5 (C-6), 145.4 (C-7a $_{\text{Bd}}$), 147.8 (C-3a $_{\text{Bd}}$) (Bd = benzodioxolyl).

Data for **7f**: ^1H NMR (200.13 MHz) δ 2.20–2.42 (m, 2H, 4- H_2), 3.28 (dd, $^3J_{\text{H,H}} = 5.9$ Hz, $^4J_{\text{H,P}} = 3.4$ Hz, 1H, 6-H), 3.57 (dt, $^2J = 10.9$ Hz, $^3J_{\text{Hax,Hax}} = 10.9$ Hz, $^3J_{\text{Hax,Heq}} = 3.1$ Hz, 1H, 3- H^{ax}), 3.72–3.78 (m, 2H, 12b-H, 3- H^{eq}), 4.07 (dd, $^2J = 11.9$ Hz, $^3J_{\text{Hax,Heq}} = 3.5$ Hz, 1H, 1- H^{ax}), 4.32 (d, $^2J = 11.9$ Hz, 1H, 1- H^{eq}), 5.93/5.96 (AB system, $^2J = 5.9$ Hz, 2H, OCH_2O), 6.46 (dd, $^3J_{\text{H,H}} = 5.9$ Hz, $^3J_{\text{H,P}} = 18.2$ Hz, 1H, 7-H), 7.03 (s, 1 H_{aryl}), 7.20–7.80 (m, 16 H_{aryl}); ^{13}C NMR (50.32 MHz) δ 46.8 (C-4), 56.1 (C-13b), 66.9 (C-3), 67.7 (d, $^3J_{\text{C,P}} = 13.3$ Hz, C-6), 69.1 (C-1), 101.2 (C-11), 108.3 (C-13), 109.6 (C-9), 127.6–147.5 (C $_{\text{aryl}}$, C $_{\text{olefin}}$); ^{31}P NMR δ 28.3.

6-(2-Bromophenyl)-8-(4-chlorophenyl)-3,4-dihydro-1H-pyrrolo[2,1-c][1,4]oxazine (6h)

^1H NMR (500.14 MHz) δ 3.76 (pseudo-t, 2H, NCH_2), 4.00 (pseudo-t, 2H, 3- H_2), 5.02 (s, 2H, 1-H), 6.37 (s, 1H, 7-H), 7.20–7.45 (m, 7 H_{aryl}), 7.63 (d, $J = 7.9$ Hz, 1 H_{aryl}); ^{13}C NMR (125.77 MHz) δ 43.3 (C-4), 64.2 (C-3), 64.8 (C-1), 108.1 (C-7), 117.7, 123.0, 125.3, 127.2, 127.7, 128.6, 129.8, 130.7, 131.8, 132.8, 132.9, 133.5, 134.3 (all C $_{\text{aryl}}$).

1-(1,3-Benzodioxol-5-yl)-3-phenyl-5,6-dihydropyrrolo[2,1-a]isoquinoline (6g)

^1H NMR (200.13 MHz) δ 2.88 (t, $^3J = 6.1$ Hz, 2H, 6- H_2), 3.98 (t, $^3J = 6.1$ Hz, 2H, 5- H_2), 5.83 (s, 2H, 2- $\text{H}_{\text{benzodioxol}}$), 6.28 (s, 1H, 2-H), 6.70–7.40 (m, 12 H_{aryl}); ^{13}C NMR (50.32 MHz) δ

30.1 (C-6), 42.2 (C-5), 100.7 (C-2_{benzodioxolyl}), 108.3, 109.5, 111.0, 122.1, 122.4, 124.3, 125.4, 125.5 (2C), 126.8, 127.5, 128.3, 128.5, 129.8, 131.2, 132.2, 132.3, 133.2, 146.0, 147.5 (all C_{aryl}).

1,3-Diphenyl-6,7,8,9-tetrahydro-5H-pyrrolo[1,2-*a*]azepine (6i)

¹H NMR (200.13 MHz) δ 1.68–1.92 (m, 6H), 2.90–2.95 (m, 2H, 9-H₂), 3.98–4.02 (m, 2H, 5-H₂), 6.23 (s, 1H, 2-H), 7.15–7.42 (m, 10 H_{aryl}); ¹³C NMR (50.32 MHz) δ 25.8 (CH₂), 27.8 (CH₂), 29.5 (CH₂), 31.1 (C-6,-7,-8,-9), 46.4 (C-5), 108.0 (C-2), 121.5, 125.2, 126.6, 128.3, 128.4, 128.6, 129.1, 133.3, 133.4, 133.6, 137.5 (all C_{aryl}).

Ethyl 1,3-Diphenyl-5,6,7,8-tetrahydroindolizine-8-carboxylate (6jA) and Ethyl 1,3-Diphenyl-5,6,7,8-tetrahydroindolizine-6-carboxylate (6jB)

6jA: R¹ = CO₂Et, R² = H (11%)

6jB: R¹ = H, R² = CO₂Et (25%)

Data for **6jA**: ¹H NMR (500.14 MHz) δ 1.17 (t, ³J = 7.1 Hz, CH₃), 1.91 (mc, 1H, 6-H), 2.21 (mc, 3H, 7-H₂, 6-H), 3.97–3.99 (m, 1H, 5-H), 4.08 (q, ³J = 7.1 Hz, OCH₂), 4.14–4.18 (m, 1H, 5-H), 4.34–4.37 (m, 1H, 8-H), 6.56 (s, 1H, 2-H), 7.30–7.58 (m, 10 H_{aryl}); ¹³C NMR (CDCl₃, 125.77 MHz) δ 13.6 (CH₃), 20.9 (C-6), 25.0 (C-7), 40.1 (C-8), 44.4 (C-5), 60.4 (OCH₂), 108.7 (C-2), 122.2, 123.0, 125.1, 126.4, 127.4, 127.9, 128.0, 128.4, 132.8, 133.2, 136.4 (all C_{aryl}), 173.3 (C=O).

Data for **6jB**: ¹H NMR (500.14 MHz) δ 1.18 (t, ³J = 7.1 Hz, CH₃), 1.84–1.92 (mc, 1H, 7-H), 2.15–2.22 (mc, 1H, 7-H), 2.74–2.80 (mc, 1H, 6-H), 2.90–2.97 (mc, 1H, 8-H), 3.07–3.13 (m, 1H, 8-H), 4.03–4.14 (m, 4H, 5-H₂, OCH₂), 6.43 (s, 1H, 2-H), 7.12–7.43 (m, 10 H_{aryl}); ¹³C NMR (125.77 MHz) δ 13.9 (CH₃), 22.6 (C-8), 24.0 (C-7), 39.9 (C-6), 45.6 (C-5), 60.7

(OCH₂), 108.3 (C-2), 120.1, 124.8, 125.7, 126.6, 126.9, 128.2, 128.3, 128.5, 132.8, 133.1, 136.4 (all C_{aryl}), 172.5 (C=O).

***N*-[2-(2-Oxo-3,5-diphenyl-2,5-dihydro-1*H*-pyrrolyl)ethyl]-*N*-[3-(trifluoromethyl)phenyl] Formamide (13)**

¹H NMR (500.14 MHz) δ 2.98 (mc, 1H, N_{ring}CH), 3.73 (m, *J* = 14.0 Hz, 1H, N_{formamide}CH), 4.00 (m, 1H, N_{ring}CH), 4.14 (m, 1H, N_{formamide}CH), 5.24 (d, ³*J* = 1.9 Hz, 5-H_{lactame}), 7.10–7.55 (m, 14 H_{aryl}, 1 H_{olefin}), 8.28 (s, 1H, CHO); ¹³C NMR (125.77 MHz) δ 38.0 (N_{ring}CH₂), 43.1 (N_{formamide}CH₂), 63.8 (C-5_{lactame}), 120.5–134.6 (C_{aryl}, 1 C_{olefin}, CF₃), 140.93/140.95 (C-4_{lactame}, C-1_{CF3-Ph}), 162.0 (CHO), 170.3 (C-2_{lactame}).

***N*-[2-(2-Hydroxy-5-oxo-2,4-diphenyl-2,5-dihydro-1*H*-pyrrolyl)ethyl]-*N*-[3-(trifluoromethyl)phenyl] Formamide (14)**

¹H NMR (500.14 MHz) δ 2.86 (broadened d, ²*J* = 14.8 Hz, 1H, N_{ring}CH), 3.32 (broadened d, ²*J* = 14.3 Hz, 1H, N_{formamide}CH), 3.98 (mc, 1H, N_{ring}CH), 4.76 (mc, 1H, N_{formamide}CH), 6.03 (s, 1H, OH), 7.06 (s, 1 H_{olefin}), 7.32–7.88 (14 H_{aryl}), 8.18 (s, 1H, CHO); ¹³C NMR (125.77 MHz) δ 37.3 (N_{ring}CH₂), 46.3 (N_{formamide}CH₂), 90.4 (C-2_{lactame}), 122.3 (m, C-2_A), 124.5 (m, C-4_A), 125.9, 126.7, 127.4, 128.4, 128.7, 128.9 (6 C_{aryl}), 129.4 (C-5_A), 130.4 (C-6_A), 130.7 (C-4_{lactame}), 132.1 (q, ²*J*_{C,F} = 32.9 Hz, C-3_A), 133.2 (C-1_C), 137.2 (C-1_B), 141.1 (C-1_A), 144.5 (C-3_{lactame}), 163.8 (CHO), 169.7 (C-5_{lactame}).

Diphenyl-[3,5-diphenyl-1-{2-[3-(trifluormethyl)anilino]ethyl}-1*H*-pyrrol-2-yl]methylphosphanoxide (15)

^1H NMR (500.14 MHz) δ = 3.16 (t, $^3J_{\text{H,H}}$ = 6.0 Hz, 2H, ArNHCH_2), 3.88 (d, $^2J_{\text{P,H}}$ = 12.8 Hz, 2H, PCH_2), 4.49 (t, $^3J_{\text{H,H}}$ = 6.0 Hz, 2H, $\text{N}_{\text{pyrrole}}\text{CH}_2$), 6.14 (s, 1H, 4- $\text{H}_{\text{pyrrole}}$), 6.35 (d, J = 8.1 Hz, 1 H_{aryl}), 6.50 (s, 1 H_{aryl}), 6.81–7.45 (m, 22 H_{aryl}); ^{13}C NMR (125.77 MHz) δ 28.5 (d, $^1J_{\text{C,P}}$ = 67.4 Hz, PCH_2), 43.7 (ArNHCH_2), 44.4 ($\text{N}_{\text{pyrrole}}\text{CH}_2$), 108.7 (C-2_A), 110.7 (C-4_{pyrrole}), 113.4 (C-4_A), 115.2 (C-6_A), 120.1 (d, $^2J_{\text{C,P}}$ = 10.2 Hz, C-2_{pyrrole}), 125.6 (d, C-3_{pyrrole}), 129.5 (C-5_A), 135.3 (C-5_{pyrrole}), 147.8 (C-1_A), 125.7–136.6 (C_{aryl} , CF_3); ^{31}P NMR δ 30.5.

7-Bromo-6-(2-bromophenyl)-8-(4-chlorophenyl)-3,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]oxazine (16)

^1H NMR (200.13 MHz) δ 3.52–3.64 and 3.74–3.85 (2 m, AA' of AA'BB', NCH_2CH_2), 3.92–3.12 (m, 2H, NCH_2CH_2), 4.80/4.89 (AB system, 2J = 14.4 Hz, 2H, 1- H_2), 7.22–7.45 (m, 7 H_{aryl}), 7.68 (d, J = 7.9 Hz, 1 H_{aryl}); ^{13}C NMR (50.32 MHz) δ 43.4 (C-4), 64.0 (C-3), 64.4 (C-1), 97.1 (C-7), 117.2, 123.6, 126.0, 127.5, 128.4, 130.0, 130.5, 130.6, 131.9, 132.0, 132.2, 132.9, 133.7 (all C_{aryl}).

2-[8-(4-Chlorophenyl)-3,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]oxazin-6-yl]benzoic acid (17)

^1H NMR ($[\text{D}_5]$ pyridine, 200.13 MHz) δ 3.88 (s, 4H, $\text{NCH}_2\text{CH}_2\text{O}$), 5.05 (s, 2H, OCH_2), 6.65 (s, 1H, 7-H), 7.20–7.60 (m, 7 H_{aryl}), 8.34 (d, $J = 6.6$ Hz, 1 H_{aryl}); ^{13}C NMR ($[\text{D}_5]$ pyridine, 125.77 MHz) δ 43.6 (C-4), 64.3 (C-3), 65.1 (C-1), 107.7 (C-7), 117.7, 127.9, 128.1, 128.3, 128.4, 129.0, 130.3, 130.5, 131.3, 132.9, 133.0, 133.1, 134.7 (all C_{aryl}), 170.3 (COO^-).

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¹H-NMR
Reisser Probe Piperazin-Salz CDCl₃ 304K

¹H-NMR
Reissar Probe D₁-Cl-Allen 303K CDCl₃

Allene **3c** (¹H, 500.14 MHz, CDCl₃)

¹H-NMR
Reisser Probe B 3 303K

¹H-NMR
Reisser Probe F1/4 1006 CDC13 303K