**Acetonitrile Derivatives as Carbonyl Synthons. The One-Pot
Preparation of Diheteroaryl Ketones *via* a Strategy of Sequential S_NAr
Substitution and Oxidation**

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Supporting Materials

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General Procedure: Preparation of Compound **8b**

General procedure for the preparation of hetero diaryl ketones: NaHMDS (2.5 mL, 1.0 M in THF, 2.5 mmol) was added to a solution of 2-chloro-quinoxaline (164 mg, 1.0 mmol) and benzyl nitrile (140 mg, 1.2 mmol) in dry THF (20 mL). After stirring for 10 h at room temperature, saturated NH_4OAc solution (5 mL) and Na_2O_2 (340 mg, 4 mmol) were added and the mixture stirred a further 10 h at room temperature. Insoluble solids were filtered off and washed with MeOH. Concentration of the filtrate *in vacuo* afforded a residue which was purified by silica gel chromatography to provide phenyl-quinoxalin-2-yl-methanone **8b** (140 mg, 60%).

HRMS Results

Compound Number	Formula [M+H]	Theoretic m/z.	Observed m/z	Deviation in ppm
8a	C ₁₂ H ₉ ClNO	218.0373	218.0377	-1.8
8d	C ₁₂ H ₁₀ ClN ₂ O ₂	249.0431	249.0432	-0.6
8c	C ₁₁ H ₆ F ₃ ClNOS	291.9811	291.9800	3.6
8b	C ₁₅ H ₁₁ N ₂ O	235.0871	235.0869	1.0
8i	C ₁₆ H ₁₂ NO	234.0919	234.0922	-1.2
8j	C ₁₄ H ₁₀ N ₃ O	236.0824	236.0823	0.4
8k	C ₁₄ H ₁₀ N ₃ O	236.0824	236.0827	-1.2
8l	C ₁₄ H ₁₀ N ₃ O	236.0824	236.0824	-0.2
8n	C ₁₂ H ₁₁ N ₂ O ₂	215.0821	215.0826	-2.6
8o	C ₁₇ H ₁₃ N ₂ O	261.1028	261.1022	-2.3
9a	C ₂₆ H ₁₇ Cl ₂ N ₄	455.0830	455.0842	-2.7
9d	C ₂₆ H ₁₉ Cl ₂ N ₆ O ₂	517.0947	517.0930	3.3
Compound Number	Formula [M-H]	Theoretic m/z.	Observed m/z	Deviation in ppm
8m	C ₁₇ H ₉ N ₂ OS	289.0436	289.0440	1.5

Supporting Material: Spectra

(4-Chloro-phenyl)-pyridin-2-yl-methanone, 8a

^1H NMR (500 MHz, CDCl_3) δ 8.73 (s, 1H), 8.04 (m, 3H), 7.94 (m, 1H), 7.54 (m, 1H), 7.46 (d, 2H, $J = 8.5$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 192.2, 154.5, 148.4, 139.7, 137.7, 134.6, 132.5, 128.6, 126.6, 124.9; HRMS m/z : $(\text{M}+\text{H})^+$ calcd. for $\text{C}_{12}\text{H}_9\text{ClNO}$: 218.0373. Found 218.0377.

Phenyl-quinoxalin-2-yl-methanone, 8b

^1H NMR (500 MHz, CDCl_3) δ 9.45 (s, 1H), 8.20 (m, 4H), 7.85 (m, 2H), 7.62 (m, 1H), 7.50 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 192.4, 148.7, 145.3, 143.1, 140.5, 135.5, 133.7, 132.1, 131.3, 130.9, 130.5, 129.4, 128.5, 128.4; HRMS m/z : $(\text{M}+\text{H})^+$ calcd. for $\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}$: 235.0871. Found 235.0869.

(3-Chloro-5-trifluoromethyl-pyridin-2-yl)-thiophen-2-yl-methanone, 8c

^1H NMR (500 MHz, CDCl_3) δ 8.83 (s, 1H), 8.09 (s, 1H), 7.80 (d, 1H, $J = 5.00$ Hz), 7.61 (d, 1H, $J = 4.00$ Hz), 7.15 (dd, 1H, $J = 5.00, 4.00$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 182.9, 156.4, 143.6, 141.4, 136.7, 135.8, 130.4, 129.0, 128.7, 123.4, 121.3; HRMS m/z : $(\text{M}+\text{H})^+$ calcd. for $\text{C}_{11}\text{H}_6\text{F}_3\text{ClNOS}$: 291.9811. Found 291.9800.

(6-Chloro-pyridazin-3-yl)-(4-methoxy-phenyl)-methanone, 8d

^1H NMR (500 MHz, CDCl_3) δ 8.24 (d, 2H, $J = 11.5$ Hz), 8.09 (d, 1H, $J = 15.00$ Hz), 7.70 (d, 1H, $J = 14.50$ Hz), 6.95 (d, 2H, $J = 11.5$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 188.7, 164.5, 158.4, 157.4, 134.1, 130.0, 129.2, 127.9, 113.9, 55.7; HRMS m/z : $(\text{M}+\text{H})^+$ calcd. for $\text{C}_{12}\text{H}_{10}\text{ClN}_2\text{O}_2$: 249.0431. Found 249.0432.

Phenyl-quinolin-2-yl-methanone, 8i

^1H NMR (500 MHz, CDCl_3) δ 8.26 (m, 4H), 8.08 (d, 1H, $J = 14.00$ Hz), 7.84 - 7.49 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 193.9, 154.8, 146.8, 137.2, 136.3, 133.2, 131.5, 130.6, 130.2, 129.0, 128.5, 128.2, 127.8, 120.9; HRMS m/z : $(\text{M}+\text{H})^+$ calcd. for $\text{C}_{16}\text{H}_{12}\text{NO}$: 234.0919. Found 234.0922.

Pyridin-2-yl-quinoxalin-2-yl-methanone, 8j

^1H NMR (500 MHz, CDCl_3) δ 9.46(s, 1H), 8.74 (d, 1H, $J = 6.50$ Hz), 8.26 (d, 1H, $J = 13.00$ Hz), 8.16 (m, 2H), 7.84 (m, 3H), 7.25 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 192.0, 153.4, 149.4, 149.3, 145.4, 143.2, 141.4, 137.1, 132.0, 130.7, 130.6, 129.4, 127.2, 125.3; HRMS m/z : $(\text{M}+\text{H})^+$ calcd. for $\text{C}_{14}\text{H}_{10}\text{N}_3\text{O}$: 236.0824. Found 236.0823.

Pyridin-3-yl-quinoxalin-2-yl-methanone, 8k

^1H NMR (500 MHz, CDCl_3) δ 9.50 (m, 2H), 8.80 (d, 1H, $J = 5.50$ Hz), 8.52 (d, 1H, $J = 13.00$ Hz), 8.14 (m, 2H), 7.85 (m, 2H), 7.46 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 190.9, 153.5, 152.5, 147.3, 145.1, 143.5, 140.4, 138.3, 132.6, 131.4, 131.1, 130.5, 129.5, 123.4; HRMS m/z : $(\text{M}+\text{H})^+$ calcd. for $\text{C}_{14}\text{H}_{10}\text{N}_3\text{O}$: 236.0824. Found 236.0824.

Pyridin-4-yl-quinoxalin-2-yl-methanone, 8l

^1H NMR (500 MHz, CDCl_3) δ 9.46 (s, 1H), 8.79 (d, 2H, $J = 4.50$ Hz), 8.09 (m, 2H), 7.98 (d, 2H, $J = 4.50$ Hz), 7.85 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 191.4, 150.4, 146.9, 144.9, 143.6, 141.9, 140.4, 132.7, 131.1, 130.6, 129.6, 123.9; HRMS m/z : $(\text{M}+\text{H})^+$ calcd. for $\text{C}_{14}\text{H}_{10}\text{N}_3\text{O}$: 236.0824. Found 236.0824.

Benzo[b]thiophen-3-yl-quinoxalin-2-yl-methanone, 8m

^1H NMR (500 MHz, CDCl_3) δ 9.58 (s, 1H), 9.32 (s, 1H), 8.87 (d, 1H, $J = 13.50$ Hz), 8.20 (m, 2H), 7.90 (m, 3H), 7.44 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 185.4, 149.3, 143.7, 143.2, 140.4, 139.3, 137.8, 132.3, 132.1, 130.9, 130.4, 129.5, 126.2, 125.7, 125.6, 122.4; HRMS m/z : $(\text{M}-\text{H})^+$ calcd. for $\text{C}_{17}\text{H}_9\text{N}_2\text{OS}$: 289.0436. Found 289.0440.

(6-Methoxy-pyridazin-3-yl)-phenyl-methanone, 8n

^1H NMR (500 MHz, CDCl_3) δ 8.16 (d, 2H, $J = 14.50$ Hz), 8.09 (d, 1H, $J = 15.5$ Hz), 7.55 (t, 1H, $J = 12.00$ Hz), 7.46 (t, 2H, $J = 11.00$ Hz), 7.09 (d, 1H, $J = 15.5$ Hz), 4.20 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 191.2, 165.5, 154.2, 135.9, 133.2, 131.4, 130.5, 128.2, 117.8, 55.6; HRMS m/z : $(\text{M}+\text{H})^+$ calcd. for $\text{C}_{12}\text{H}_{11}\text{N}_2\text{O}_2$: 215.0821. Found 215.0826.

Phenyl-(6-phenyl-pyridazin-3-yl)-methanone, 8o

^1H NMR (500 MHz, CDCl_3) δ 8.25 (m, 5H), 8.06 (d, 1H, $J = 14.5$ Hz), 7.51 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 191.8, 160.0, 156.3, 135.7, 135.5, 133.6, 131.5, 131.0, 129.3, 128.4, 128.3, 127.6, 124.5; HRMS m/z : $(\text{M}+\text{H})^+$ calcd. for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{O}$: 261.1028. Found 261.1022.

3-Bis-(4-chloro-phenyl)-2,3-di-pyridin-2-yl-succinonitrile, 9a

^1H NMR (500 MHz, CDCl_3) δ 8.32 (d, 2H, $J = 4.00$ Hz), 7.64 (m, 4H), 7.21 (d, 4H, $J = 9.00$ Hz), 7.13 (m, 2H), 6.99 (d, 4H, $J = 9.00$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 156.3, 147.5, 137.3, 135.7, 134.0, 131.5, 128.2, 124.0, 122.6, 120.5, 60.4; HRMS m/z : $(\text{M}+\text{H})^+$ calcd. for $\text{C}_{26}\text{H}_{17}\text{Cl}_2\text{N}_4$: 455.0830. Found 455.0842.

2,3-Bis-(6-chloro-pyridazin-3-yl)-2,3-bis-(4-methoxy-phenyl)-succinonitrile, 9d

^1H NMR (500 MHz, CDCl_3) δ 7.73 (d, 2H, $J = 9.00$ Hz), 7.54 (d, 2H, $J = 8.50$ Hz), 6.91 (d, 4H, $J = 8.50$ Hz), 6.77 (d, 4H, $J = 9.00$ Hz), 3.79 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 160.7, 158.5, 156.7, 131.6, 129.9, 129.7, 125.0, 113.7, 109.6, 59.5, 55.4; HRMS m/z : $(\text{M}+\text{H})^+$ calcd. for $\text{C}_{26}\text{H}_{19}\text{Cl}_2\text{N}_6\text{O}_2$: 517.0947. Found 517.0930.