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**The Reactivity of N-Phenyl-1-Aza-2-Cyano-1,3-Butadienes
in the Diels-Alder Reaction**

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EXPERIMENTAL SECTION

Full Experimental and Spectral Data, Complete with NMR Peak Assignments

NMR peak assignments were made on the basis of the following experiments:

H-irradiations: Compounds **7** to **10**, **13**, **19**, **20**, **22**, **23**, **29**, **31**, **33** to **36**;

J Modulation (Spin Echo): Compounds **4**, **7**, **8** to **10**, **18**, **21** to **23**, **33**, **35**, **36**;

2D (COSY): Compounds **35** to **40**;

2D (H-C): Compound **7**.

N-Phenyl-2-cyano-1-aza-1,3-butadiene 4. Triflic anhydride (4.4 g, 16.3 mmol, 1.2 equiv.) was added dropwise over 10 min to a cold (-60°C) solution of acrylanilide **1** (prepared in 82% yield according to ref. 7) (2.0 g, 13.6 mmol) and dry diisopropylethylamine (2.6 g, 20.4 mmol, 1.5 equiv.) in 40 mL of anhydrous CH₂Cl₂ and the resulting mixture was stirred for 1 h (argon atmosphere). A suspension of LiCN (0.6 g, 19.0 mmol, 1.4 equiv.; predried for 2 h at 80°C; 0.01 mm Hg) in 40 mL of anhydrous THF containing 12-crown-4 (0.27 g, 0.14 mmol, 0.1 equiv.) was then added dropwise over a period of 10 min and stirring was continued at -60°C for an additional 45 min. The reaction mixture was subsequently warmed to -20°C over a period of 15 min and quenched with 50 mL of water. The organic layer was removed and the aqueous phase washed with ether. The combined organic layers were washed with water, dried over sodium sulfate, and concentrated. N-Phenyl-2-cyano-1-aza-1,3-butadiene **4** was obtained as a yellow oil (1.5 g, 70%) after flash column purification (silica gel, 10:1 heptane/EtOAc): IR (neat) 2221, 1623, 1581 cm⁻¹; ¹H NMR (CDCl₃) δ 6.09 (d, J = 10.5 Hz, 1H, H-4), 6.33 (d, J = 17.5 Hz, 1H, H-4), 6.75 (dd, J = 10.5, 7.0 Hz, 1H, H-3), 7.13 (dd, J = 7.4, 1.5 Hz, 2H, *o*-H_{Ar}), 7.25 - 7.47 (m, 3H, *m*-, *p*-H_{Ar}); ¹³C NMR (CDCl₃) δ 109.8 (CN), 120.4 (C_{Ar}), 127.7 (C_{Ar}), 129.3 (C_{Ar}), 129.6 (C₄), 135.5 (*p*-C_{Ar}), 140.5 (N-C_{Ar}), 148.7 (C₂); MS m/z 156 (M⁺), 155, 130, 77; HRMS: calcd. for C₁₀H₈N₂ 156.0687, found 156.0703.

N-phenyl-2-cyano-1-aza-1,3-butadiene dimer 5. N-Phenyl-2-cyano-1-aza-1,3-butadiene **4** (75 mg, 0.48 mmol) in 0.4 mL of anhydrous benzene was placed in an argon flushed

10-mL capacity thick glass-walled tube, equipped with a Rotoflo tap and a magnetic stirring bar, and heated under closed conditions at 90°C (oil bath temperature) for 15 h. After cooling, the solvent was removed under vacuum, and the residue was flash column chromatographed (silica, 4:1 heptane ether). Compound **5** was obtained after subsequent recrystallization (pentane-ether) as a colorless solid (45 mg, 60%): m.p. 106-107°C; IR (neat) 2263, 2228, 1623, 1595, 1490 cm⁻¹; ¹H NMR (CDCl₃) δ 2.03 (m, 1H, H-3), 2.38 (m, 2H, H-4), 2.55 (m, 1H, H-3), 4.70 (t, J = 4.2, 3.5 Hz, 1H, H-2), 5.96 (t, J = 3.6, 4.1 Hz, 1H, H-5), 7.04 (d, J = 7.6 Hz, 2H, *o*-H_{Ar}), 7.19 - 7.45 (m, 8H, H_{Ar}); ¹³C NMR (CDCl₃) δ 19.8 (C3), 21.8 (C4), 64.5 (C2), 111.0, 115.4 (CN), 117.9 (CN), 120.1, 123.1, 123.5, 125.8, 127.8, 129.2, 129.5, 143.1, 145.1, 148.0; MS m/z 312 (M⁺), 220, 183, 155, 92, 77; Anal: Calcd. for C₂₀H₁₆N₄: C, 76.90; H, 5.16; N, 17.94. Found: C, 76.55; H, 5.42, N, 17.71.

N-Phenyl-1,2,3,4-tetrahydro-2-ethoxy-6-cyanopyridine 6. N-Phenyl-2-cyano-1-aza-1,3-butadiene **4** (78 mg, 0.5 mmol) and ethyl vinyl ether (1.2 mL, 20 mmol, 40 equiv.) were placed in an argon flushed 10-mL capacity thick glass-walled tube, equipped with a Rotoflo tap and a magnetic stirring bar, and heated under closed conditions at 90°C (oil bath temperature) for 36 h. After cooling, the excess dienophile was removed under vacuum and the residue was flash column chromatographed (silica, 6:1 heptane/EtOAc). Compound **6** was obtained as a pale yellow solid (104 mg, 91%): m.p. 54-56°C (heptane-EtOAc); IR (neat) 2228, 1630, 1595, 1490 cm⁻¹; ¹H NMR (CDCl₃) δ 1.26 (t, J = 7.0 Hz, 3H, Me), 1.61 (m, 1H, H-3), 1.97 (m, 1H, H-3), 2.19 (ddt, J = 19.3, 1.3, 5.1 Hz, 1H, H-4), 2.39 (m, 1H, H-4), 3.67 (m, 1H, OCH₂), 3.90 (m, 1H, OCH₂), 4.82 (t, J = 2.5 Hz, 1H, H-2), 6.02 (brt, 1H, H-5), 7.16 (m, 3H, *o*-, *p*-H_{Ar}), 7.36 (t, 2H, *m*-H_{Ar}); ¹³C NMR (CDCl₃) δ 15.2 (Me), 18.9 (C3), 24.0 (C4), 63.0 (CH₂O), 88.3 (C2), 115.5 (CN), 116.3, 123.3, 124.7, 125.2, 129.5, 144.9 (C6); MS m/z 228 (M⁺), 199, 196, 183, 155, 104, 77, 51. Anal: Calcd. for C₁₄H₁₆N₂O: C, 73.65; H, 7.06; N, 12.27. Found: C, 73.66; H, 6.93; N, 12.35.

Diels-Alder Adduct 7. As described for **6**, a mixture of N-phenyl-2-cyano-1-aza-1,3-butadiene **4** (100 mg, 0.64 mmol) in freshly distilled 2,3-dihydrofuran (1.94 mL, 25.6 mmol, 40 equiv.) was heated under closed conditions at 90°C for 22 h. Compound **7** was obtained as a yellow oil (126 mg, 87%) after flash column chromatography (silica gel, 10:1 heptane/EtOAc): IR (neat) 2226, 1630, 1604, 1492, 1414 cm⁻¹; ¹H NMR (CDCl₃) δ 1.86 (m, 1H, H-8), 2.22 (m, 2H, H-4, H-8), 2.35 (ddd, J = 4.7, 6.3, 17.5 Hz, 1H, H-4), 2.63 (m, 1H, H-3), 3.80 (dt, J = 8.3, 6.4 Hz, 1H, H-7), 5.23 (d, J = 5.9 Hz, 1H, H-2), 5.95 (t, J = 5.1 Hz, 1H, H-5), 7.12 (t, J = 7.3, 1H, *p*-H_{Ar}), 7.22 (d, J = 7.6, 2H, *o*-H_{Ar}), 7.34 (t, J = 7.9, 2H, *m*-H_{Ar}); ¹³C NMR (CDCl₃) δ 24.0 (C7), 30.4 (C5), 37.7 (C6), 64.9 (C4), 89.9 (C2), 115.3 (CN), 121.6 (C8), 122.3 (*o*-C_{Ar}), 124.5 (*p*-C_{Ar}), 129.1 (*m*-C_{Ar}), 143.9 (C9, N-C_{Ar}); MS m/z 226 (M⁺), 225, 197, 195, 183, 181, 169, 155, 104, 77. HRMS: Calcd. for C₁₄H₁₄N₂O: 226.1106. Found: 226.1095. Anal: Calcd. for C₁₄H₁₄N₂O: C, 74.31; H, 6.24; N, 12.38. Found: C, 73.81; H, 6.38; N, 11.96.

Diels-Alder Adduct 8. As described for **6**, a mixture of N-phenyl-2-cyano-1-aza-1,3-butadiene **4** (70 mg, 0.45 mmol) in freshly distilled 3,4-dihydro-2H-pyran (4.6 g, 54 mmol, 120 equiv.) was heated under closed conditions at 120°C for 46 h. Compound **8** was obtained as a yellow

oil (27 mg, 25%) after flash column chromatography (silica gel, 4:1 heptane/ether).: IR (neat) 2225, 1625, 1600, 1500, 1413 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.36 (m, 1H, H-8), 1.83 (m, 3H, H-8, H-9), 2.10 (m, 2H, H-4), 2.56 (m, 1H, H-3), 3.61 (m, 1H, H-7), 4.09 (dd, $J = 3.6, 11.6$ Hz, 1H, H-7), 4.70 (d, $J = 0.8$ Hz, H-2), 5.71 (dd, $J = 3.0, 5.0$ Hz, H-5), 7.16 - 7.38 (m, 5H, H_{ar}); ^{13}C NMR (CDCl_3) δ 20.5 (C6), 22.7 (C8), 27.4 (C5), 30.7 (C7), 68.3 (C4), 88.4 (C2), 115.7 (CN), 116.3, 118.0 (C9), 123.9 (C_{ar}), 125.4 (C_{ar}), 129.2 (C_{ar}), 144.3 (C10); MS m/z 240 (M^+), 239, 181, 155, 97, 84, 77; HRMS: Calcd. for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}$: 240.1262. Found: 240.1262.

N-Phenyl-1,2,3,4-tetrahydro-2-carbomethoxy-6-cyanopyridine 9 and N-Phenyl-1,2,3,4-tetrahydro-3-carbomethoxy-6-cyanopyridine 10. As described for 6, a mixture of N-phenyl-2-cyano-1-aza-1,3-butadiene 4 (45 mg, 0.29 mmol) and methyl acrylate (1.04 ml, 11.5 mmol, 40 equiv.) was heated under closed conditions at 90°C for 40 h. Compounds 9 and 10, an inseparable 4:1 mixture of regioisomers, were obtained as a yellow oil (50 mg, 71%) after flash column chromatography (silica gel, 8:1 heptane/ethyl acetate). These regioisomers were separated by HPLC (silica gel; 93:7 heptane/ethyl acetate).

Compound 9: IR (neat) 2227, 1742, 1622, 1596, 1496 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.93 (m, 1H, H-3), 2.20-2.39 (m, 3H, H-3, 4), 3.78 (s, 3H, OMe), 4.44 (dd, $J = 2.8, 4.5$ Hz, 1H, H-2), 5.77 (dt, $J = 1.1, 4.5$ Hz, 1H, H-5), 7.12 (m, 3H, H_{ar}), 7.34 (t, 2H, H_{ar}); ^{13}C NMR (CDCl_3) δ 20.2 (C3), 22.8 (C4), 52.6 (OMe), 61.3 (C2), 115.7 (CN), 117.3, 120.5 (C5), 122.8 ($o\text{-C}_{\text{ar}}$), 124.7 ($p\text{-C}_{\text{ar}}$), 129.3 ($m\text{-C}_{\text{ar}}$), 145.1 (N- C_{ar}), 145.4 (C6), 171.7 (CO); MS m/z 242 (M^+), 184, 183, 181, 129, 104, 77, 51.

Compound 10: IR (neat) 2228, 1736, 1621, 1596, 1495 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.53 (m, 2H, H-4), 2.78 (m, 1H, H-3), 3.58 (s, 3H, OMe), 3.65 (m, 1H, H-2), 3.87 (ddd, $J = 0.7, 3.2, 12.6$ Hz, 1H, H-2), 5.88 (t, $J = 4.0$ Hz, 1H, H-5), 7.07 (m, 3H, H_{ar}), 7.34 (m, 2H, H_{ar}); ^{13}C NMR (CDCl_3) δ 26.0 (C4), 37.0 (C3), 52.1 (C2), 64.6 (OMe), 117.3 (CN), 120.1 (C5), 122.5 ($o\text{-C}_{\text{ar}}$), 124.4 ($p\text{-C}_{\text{ar}}$), 129.7 ($m\text{-C}_{\text{ar}}$), 145.2 (C6), 172.8 (CO); MS m/z 242 (M^+), 183, 181, 104, 77.

Anal. of mixture of regioisomers: Calcd. for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2$: C, 69.40; H, 5.82; N, 11.56. Found: C, 69.79; H, 5.73; N, 11.77.

N-Phenyl-1,2,3,4-tetrahydro-2-acetyl-6-cyanopyridine 11 and N-phenyl-1,2,3,4-tetrahydro-3-acetyl-6-cyanopyridine 12. As described for 6, a mixture of N-phenyl-2-cyano-1-aza-1,3-butadiene 4 (55 mg, 0.35 mmol) and methyl vinyl ketone (1.0 g, 14 mmol, 40 equiv.) in 1.0 mL of anhydrous benzene was heated under closed conditions at 90°C for 20 h. Compound 11 was obtained as a white solid (42 mg, 53%), and 12 was obtained as a yellow oil (10 mg, 12%) after flash column chromatography (silica gel, 3:1 heptane/ether, then 2:1 heptane/ether).

Compound 11: mp $101\text{--}103^\circ\text{C}$; IR (neat) 2225, 1712, 1593, 1500 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.74 (m, 1H, H-3), 2.17 (m, 2H, H-3,4), 2.36 (s, 3H, Me), 2.37 (m, 1H, H-3), 4.24 (dd, $J = 3.2, 1.2$ Hz, 1H, H-2), 5.92 (t, $J = 4.0$ Hz, 1H, H-5), 7.12 (m, 3H, H_{ar}), 7.36 (t, 2H, H_{ar}); ^{13}C NMR (CDCl_3) δ 20.3, 20.9, 27.0, 68.7, 115.6, 117.3, 122.1, 124.2, 124.6, 129.5, 145.5, 208.7; MS m/z 226 (M^+), 183, 182, 166, 155, 143, 129, 104, 77, 51; Anal: Calcd. for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}$: C, 74.31; H, 6.23; N, 12.38; O, 7.07. Found: C, 74.15; H, 6.28; N, 12.53; O, 7.28.

Spectral data for **12**: IR (neat) 2227, 1709, 1622, 1596, 1496 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.15 (s, 3H, Me), 2.47 (m, 2H, H-4), 2.83 (m, 1H, H-3), 3.49 (m, 1H, H-2), 3.86 (dd, $J = 3.2$ Hz, 1H, H-2), 5.89 (t, $J = 4.1$ Hz, 1H, H-5), 7.09 (m, 3H, H_{ar}), 7.35 (t, 2H, H_{ar}); ^{13}C NMR (CDCl_3) δ 25.8, 28.7, 44.2, 51.7, 115.4, 118.3, 120.9, 122.9, 124.5, 129.4, 145.3, 207.4; MS m/z 226 (M^+), 183, 155, 147, 105, 93, 77, 55; HRMS: Calcd. for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}$: 226.1106. Found: 226.1104.

N-Phenyl-1,2,3,4-tetrahydro-2-phenyl-6-cyanopyridine 13. As described for **6**, N-phenyl-2-cyano-1-aza-1,3-butadiene **4** (64 mg, 0.41 mmol) and styrene (1.71 g, 16.4 mmol, 40 equiv.) was heated under closed conditions at 90°C for 23 h. Compound **13** was obtained as a pale yellow oil (81 mg, 76%) after flash column chromatography (silica gel, heptane): IR (neat) 2227, 1622, 1596, 1496 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.86 (m, 1H, H-3), 1.99 - 2.25 (m, 3H, H-3,4), 4.92 (t, $J = 3.4$ Hz, 1H, H-2), 5.76 (dt, $J = 1.6, 4.8$ Hz, 1H, H-5), 7.09 (m, 3H, H_{ar}), 7.22 - 7.41 (m, 7H, H_{ar}); ^{13}C NMR (CDCl_3) δ 19.5 (C3), 25.6 (C4), 62.5 (C2), 116.2 (CN), 117.0 (C- C_{ar}), 121.9, 122.1, 124.0, 125.9, 127.3, 128.9, 129.2 (C_{ar}), 140.8 (N- C_{ar}), 146.1 (C6); MS m/z 260 (M^+), 196, 183, 155, 130, 104, 84, 77, 51; Anal: Calcd. for $\text{C}_{18}\text{H}_{16}\text{N}_2$: C, 83.04; H, 6.19; N, 10.76. Found: C, 82.66; H, 5.81, N, 10.43.

N-Phenyl-1,2,3,4-tetrahydro-2-butyl-6-cyanopyridine 14. As described for **6**, a mixture of N-phenyl-2-cyano-1-aza-1,3-butadiene **4** (50 mg, 0.3 mmol) and 1-hexene (3.4 g, 36 mmol, 120 equiv.) was heated under closed conditions at 120°C for 48 h. Compound **14** was obtained as a light red oil (25 mg, 35%) after flash column chromatography (silica gel, 4:1 heptane/ether): IR (neat) 2227, 1625, 1595, 1492 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.95 (t, $J = 6.8$ Hz, 3H, Me), 1.50 (m, 4H), 1.69 (m, 2H), 2.21 (m, 2H, H-4), 3.68 (m, 1H, H-2), 5.90 (t, $J = 4.0$ Hz, 1H, H-5), 7.04 (m, 3H, H_{ar}), 7.32 (m, 2H, H_{ar}); ^{13}C NMR (CDCl_3) δ 14.2, 19.8, 22.9, 28.9, 30.6, 60.2, 116.2, 116.7, 122.4, 123.6, 123.7, 129.2, 146.7; MS m/z 240 (M^+), 183, 155, 130, 104, 77; HRMS: Calcd. for $\text{C}_{16}\text{H}_{20}\text{N}_2$: 240.1627. Found: 240.1629.

N-Phenyl-1,2,3,4-tetrahydro-*trans*-2-phenyl-3-methyl-6-cyanopyridine 15. As described for **6**, a mixture of N-phenyl-2-cyano-1-aza-1,3-butadiene **4** (50 mg, 0.32 mmol) and *trans*- β -methyl styrene (1.5 g, 12.8 mmol, 40 equiv.) was heated under closed conditions at 90°C for 20 h. Compound **15** was obtained as a light red oil (66 mg, 75%) after flash column chromatography (silica gel, 5:1 heptane/ether): IR (neat) 2227, 1616, 1596, 1496 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.07 (d, $J = 6.8$ Hz, 3H, Me), 1.92 (m, 1H, H-3), 2.43 (m, 2H, H-4), 4.59 (d, $J = 2.8$ Hz, 1H, H-2), 5.62 (dd, $J = 3.7$ Hz, 1H, H-5), 7.04 (m, 3H, H_{ar}), 7.30 (m, 7H, H_{ar}); ^{13}C NMR (CDCl_3) δ 19.3, 26.4, 32.3, 68.0, 115.9, 116.5, 118.4, 121.6, 123.9, 125.7, 127.3, 128.9, 129.1, 141.7, 146.2; MS m/z 274 (M^+), 194, 179, 176, 161, 136, 121, 105, 86, 84, 77. Anal: Calcd. for $\text{C}_{19}\text{H}_{18}\text{N}_2$: C, 83.18; H, 6.61; N, 10.21. Found: C, 83.17; H, 6.66; N, 9.92.

N-Phenyl-1,2,3,4-tetrahydro-*cis*-2-phenyl-3-methyl-6-cyanopyridine 16. As described for **6**, N-phenyl-2-cyano-1-aza-1,3-butadiene **4** (50 mg, 0.32 mmol) and *cis*- β -methyl styrene (1.5 g, 12.8 mmol, 40 equiv.) were heated under closed conditions at 90°C for 51 h.

Compound **16** was obtained as a light yellow oil (34 mg, 39%) after flash column chromatography (silica gel, 10:1 heptane/ethyl acetate): IR (neat) 2225, 1724, 1616, 1597, 1495 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.88 (d, J = 6.8 Hz, 3H, Me), 1.81 (ddd, J = 2.8, 11.8, 18.8 Hz, 1H, H-4), 2.13 - 2.34 (m, 2H, H-3,4), 4.57 (d, J = 4.1 Hz, 1H, H-2), 5.77 (dd, J = 2.8, 5.5 Hz, 1H, H-5), 7.05 (m, 3H, H_{Ar}), 7.29 (m, 7H, H_{Ar}); ^{13}C NMR (CDCl_3) δ 18.4 (Me), 27.4 (C4), 30.2 (C3), 68.5 (C2), 118.2 (CN), 118.8, 121.6, 122.7, 124.4, 125.8, 127.7, 127.8, 128.7, 129.0, 129.1 (C_{Ar}), 139.8 (N- C_{Ar}), 146.2 (C6); MS m/z 274 (M^+) 259, 156, 103, 91, 77; HRMS: Calcd. for $\text{C}_{19}\text{H}_{18}\text{N}_2$: 274.1470. Found: 274.1463.

N-(*p*-Methoxyphenyl)-2-cyano-1-aza-1,3-butadiene 18. Following the procedure described for the preparation of N-phenyl-2-cyano-1-aza-1,3-butadiene **4**, *p*-methoxy acrylanilide **17** (1.0 g, 5.65 mmol) in CH_2Cl_2 (40 mL) containing diisopropylethylamine (1.75 g, 13.56 mmol, 2.4 equiv.) was treated with triflic anhydride (1.91 g, 1.14 mL, 6.78 mmol, 1.2 equiv.) at -73°C , and then with LiCN (0.56 g, 16.95 mmol, 3.0 equiv.), and 12-crown-4 (0.10 g, 0.57 mmol, 0.1 equiv.). N-(*p*-Methoxyphenyl)-2-cyano-1-aza-1,3-butadiene **18** was obtained as a yellow low melting crystalline solid (0.83 g, 79%) after flash column purification (silica gel, 5:1 heptane/EtOAc): mp. $52 - 54^\circ\text{C}$; IR (neat) 2220, 1609, 1503, 1250 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.84 (s, 3H, OMe), 6.05 (d, J = 10.5 Hz, 1H, H-4), 6.29 (d, J = 17.5 Hz, 1H, H-4), 6.75 (dd, J = 10.6, 17.5 Hz, 1H, H-3), 6.94 (m, 2H, H_{Ar}), 7.27 (m, 2H, H_{Ar}); ^{13}C NMR (CDCl_3) δ 55.6 (OMe), 110.7 (CN), 114.6 (*m*- C_{Ar}), 123.3 (*o*- C_{Ar}), 128.2 (C4), 136.0 (C3), 137.5 (N- C_{Ar}), 141.4 (C2), 159.1 (O- C_{Ar}); MS m/z 186 (M^+), 171, 160, 143, 85; Anal: Calcd. for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}$: C, 70.95; H, 5.41; N, 15.04. Found: C, 70.65; H, 5.24; N, 14.76.

N-(*p*-Methoxyphenyl)-1,2,3,4-tetrahydro-2-ethoxy-6-cyanopyridine 19. As described for **6**, a mixture of N-(*p*-methoxyphenyl)-2-cyanoazadiene **18** (100 mg, 0.54 mmol) and ethyl vinyl ether (1.6 g, 21.6 mmol, 40 equiv.) was heated under closed conditions at 90°C for 30 h. Compound **19** was obtained as a pale yellow oil (93 mg, 67%) after flash column chromatography (silica gel, 4:1 heptane/ether): IR (neat) 2227, 1622, 1510 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.26 (t, J = 7.0 Hz, 3H, Me), 1.59 (m, 1H, H-3), 1.95 (m, 1H, H-3), 2.16 (ddt, J = 1.0, 18.2, 5.1 Hz, 1H, H-4), 2.40 (m, 1H, H-4), 3.62 (m, 1H, OCH_2), 3.79 (s, 3H, OMe), 3.90 (m, 1H, OCH_2), 4.68 (t, J = 2.4 Hz, 1H, H-2), 5.90 (dd, J = 3.0, 1.0 Hz, 1H, H-5), 6.89 (m, 2H, H_{Ar}), 7.08 (m, 2H, H_{Ar}); ^{13}C NMR (CDCl_3) δ 15.3 (Me), 18.6 (C3), 23.9 (C4), 55.6 (Ar-OMe), 63.1 (CH_2O), 88.4 (C2), 114.8 X 2 (CN, C_{Ar}), 116.5, 122.7, 125.7 (C_{Ar}), 138.3 (N- C_{Ar}), 157.4 (O- C_{Ar}); MS m/z 259 (M^+), 214, 187, 172; Anal: Calcd. for $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_2$: C, 69.47; N, 7.38; O, 10.80. Found: C, 69.57; H, 7.08; N, 10.89.

N-(*p*-Methoxyphenyl)-2-cyano-1-aza-1,3-butadiene Dimer 20. N-(*p*-Methoxyphenyl)-2-cyanoazadiene **18** (206 mg, 1.10 mmol) in 3.0 mL of anhydrous benzene was placed in an argon flushed 10-mL capacity thick glass-walled tube, equipped with a Rotoflo tap and a magnetic stirring bar, and heated under closed conditions at 100°C (oil bath temperature) for 36 hr. After cooling, the solvent was removed and the residue was flash column chromatographed (silica; 6/1 heptane/ether). Compound **20** was obtained after subsequent recrystallization (pentane-ether) as a

bright yellow solid (127 mg, 62%). m.p. = 97-98°C; IR (neat) 2227, 2221, 1622, 1510 cm⁻¹; ¹H NMR (CDCl₃), δ: 2.02 (m, 1H, H-3), 2.34 (m, 2H, H-4), 2.47 (m, 1H, H-3), 3.78 (s, 3H, OMe), 3.81 (s, 3H, OMe), 4.53 (t, J = 4.0 Hz, 1H, H-2), 5.82 (t, J = 4.0 Hz, 1H, H-5), 6.92 (m, 4H, H_{ar}), 7.20 (m, 4H, H_{ar}). ¹³C NMR (CDCl₃), δ 19.8 (C3), 22.2 (C4), 55.6 (OMe), 65.1 (OMe), 111.9 (CN), 114.6 (*m*-Car), 114.9 (*m*-Car), 115.6 (CC(CN)=N), 118.9 (6-CN), 120.5 (C5), 122.9 (*o*-Car), 126.3 (*o*-Car), 138.4 (N-Car), 140.0 (N-Car), 140.6 (C6), 158.0 (O-Car), 160.0 (O-Car); MS, m/z 373 (M⁺), 250, 213, 123. HRMS: Calcd. for C₂₂H₂₀N₄O₂: 372.1587. Found: 372.1590. Anal.: Calcd. for C₂₂H₂₀N₄O₂: C, 70.95; H, 5.41; N, 15.04. Found: C, 70.85; H, 5.65; N, 15.10.

N-(*p*-Methoxyphenyl)-2-cyano-1,4-dihydropyridine 21. Procedure 1: N-(*p*-Methoxyphenyl)-1,2,3,4-tetrahydro-2-ethoxy-6-cyanopyridine **19** was treated with dry HCl in CH₂Cl₂ for 1 h at room temperature. The mixture was then concentrated and separated by preparative TLC on SiO₂ (heptane - EtOAc, 5:1). Compound **21** was obtained as a colorless oil (20%).

Procedure 2: N-(*p*-Methoxyphenyl)-1,2,3,4-tetrahydro-2-ethoxy-6-cyanopyridine **19** (57 mg, 0.22 mmol) in CH₂Cl₂ (5 ml) was absorbed on 1.0 g of acidic Al₂O₃ (Janssen Chimica, 50-200 micron). The solvent was then evaporated under reduced pressure, and the mixture was stirred under nitrogen at room temperature for 10 min. The adsorbent was washed several times with CH₂Cl₂, and the combined washings evaporated giving compound **21** (44 mg, 94%) (TLC and NMR pure): IR (film) 2231, 1669, 1606, 1513 cm⁻¹; ¹H NMR (CDCl₃) δ: 3.11 (m, 2H, H-4), 3.80 (s, 3H, OMe), 4.49 (ddd, J = 8.1, 5.5, 3.0 Hz, 1H, H-3), 5.39 (m, 1H, H-5), 5.99 (dt, J = 8.1, 1.2 Hz, 1H, H-2), 6.89 (d, J = 8.9 Hz, 2H, H_{ar}), 7.14 (d, J = 8.9 Hz, 2H, H_{ar}). ¹³C NMR (CDCl₃), δ: 29.82 (C4), 55.62 (OMe), 98.20 (C3), 114.72 (*m*-Car), 115.77 (C5), 118.57 (CN), 126.70 (*o*-Car), 128.35 (N-Car), 131.75 (C2), 136.28 (C6), 158.45 (O-Car); MS (CI, isobutane, 170°C), m/z: 269 (M+57), 213 (M+H), 124, 105.

N-(*p*-Methoxyphenyl)-1,2,3,4-tetrahydro-2-carbomethoxy-6-cyanopyridine 22 and N-(*p*-Methoxyphenyl)-1,2,3,4-tetrahydro-3-carbomethoxy-6-cyanopyridine 23. As described for **6**, a mixture of N-(*p*-methoxyphenyl)-2-cyanoazadiene **18** (110 mg, 0.59 mmol) and methyl acrylate (2.03 g, 2.13 ml, 23.7 mmol, 40 equiv.) was heated under closed conditions at 90°C for 40 h. Compounds **22** and **23**, an inseparable 7:1 mixture of regioisomers, were obtained as a yellow oil (134 mg, 83%) after flash column chromatography (silica gel, 4:1 heptane/ethyl acetate).

Compound **22**: ¹H NMR (CDCl₃) δ 1.95 (m, 1H, H-3), 2.17-2.34 (m, 3H, H-3,4), 3.75 (s, 3H, CO₂Me), 3.78 (s, 3H, OMe), 4.33 (dd, J = 3.1, 4.4 Hz, 1H, H-2), 5.64 (dt, J = 1.1, 4.2 Hz, 1H, H-5), 6.87 (dt, J = 2.7, 8.9 Hz, 2H, H-3', 5'), 7.10 (dt, J = 2.7, 8.9 Hz, 2H, H-2', 6'); ¹³C NMR (CDCl₃) δ 20.0 (C3), 22.7 (C4), 55.5 (Ar-OMe), 61.7 (OMe), 114.5 (*m*-Car), 115.8 (CN), 117.7 (C5), 125.6 (*o*-Car), 138.5 (C6), 157.4 (O-Car), 171.8 (CO).

Compound **23**: ¹H NMR (CDCl₃) δ 2.50 (m, 2H, H-4), 2.77 (m, 1H, H-3), 3.54 (m, 2H, H-2), 3.62 (s, 3H, CO₂Me), 3.78 (s, 3H, OMe), 5.78 (t, J = 4.0, 1H, H-5), 6.87 (dt, J = 2.1, 8.9 Hz, 2H, H-3', 5'), 7.01 (dt, J = 2.1, 8.9 Hz, 2H, H-2', 6'); ¹³C NMR (CDCl₃) δ 25.8 (C4), 36.7 (C3), 52.5 (Ar-OMe), 52.7 (C2), 61.7 (OMe), 115.8 (CN), 118.3 (*m*-Car), 118.9 (C5), 124.7 (*o*-Car), 138.9 (C6), 157.3 (O-Car), 173.0 (CO).

For the mixture of regioisomers: IR (neat) 2225, 1744, 1613, 1506, 1450 cm^{-1} ; MS m/z 272 (M^+), 257, 213, 134, 92; HRMS: Calcd. for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_3$: 272.1161. Found: 272.1151.

N-(*p*-Methoxyphenyl)-1,2,3,4-tetrahydro-2-acetyl-6-cyanopyridine 24 and N-(*p*-Methoxyphenyl)-1,2,3,4-tetrahydro-3-acetyl-6-cyanopyridine 25. As described for **6**, a mixture of N-(*p*-methoxyphenyl)-2-cyanoazadiene **18** (100 mg, 0.54 mmol) and methyl vinyl ketone (1.1 g, 21.6 mmol, 40 equiv.) were heated under closed conditions at 75°C for 24 h. Compound **24** was obtained as a white solid (78 mg, 56%), and **25** as a yellow oil (10 mg, 7%) after flash column chromatography (silica gel, 4:1 heptane/ether).

Compound **24**: IR (neat) 2259, 2227, 1717, 1618, 1508 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.75 (m, 1H, H-3), 2.17 (m, 3H, H-3,4), 2.33 (s, 3H, Me), 3.79 (s, 3H, OMe), 4.11 (t, $J = 4.0$ Hz, 1H, H-2), 5.79 (t, $J = 4.0$ Hz, 1H, H-5), 6.88 (m, 2H, H_{Ar}), 7.06 (m, 2H, H_{Ar}); ^{13}C NMR (CDCl_3) δ 20.2 (C3), 20.7 (C4), 27.1 (Me), 55.6 (OMe), 114.8, 115.8, 118.3, 121.5, 124.7, 139.1, 157.3 (O-C_{Ar}), 208.8 (CO); MS m/z 256 (M^+), 213, 134, 92; Anal: Calcd. for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2$: C, 70.28; H, 6.29; N, 10.93. Found: C, 69.88; H, 6.46; N, 10.78.

Compound **25**: IR (neat) 2228, 1711, 1621, 1514 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.17 (s, 3H, Me), 2.44 (m, 2H, H-4), 2.82 (m, 1H, H-3), 3.44 (m, 1H, H-2), 3.75 (dd, $J = 3.0, 10.0$ Hz, 1H, H-2), 3.80 (s, 3H, OMe), 5.81 (t, $J = 4.2$ Hz, 1H, H-5), 6.89 (m, 2H, H_{Ar}), 7.01 (m, 2H, H_{Ar}); ^{13}C NMR (CDCl_3) δ 25.4 (C4), 28.6 (Me), 44.1 (C3), 52.4 (C2), 55.6 (OMe), 114.8, 118.7, 115.5, 119.3, 124.9, 139.0, 157.3 (O-C_{Ar}), 207.6 (CO); MS m/z 256 (M^+), 213, 134, 84; HRMS: Calcd. for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2$: 256.1212. Found: 256.1210.

N-phenyl-2-cyano-4-methyl-1-aza-1,3-butadiene 27. Following the procedure described for the preparation of N-phenyl-2-cyano-1-aza-1,3-butadiene **4**, crotonilide **26** (1.777 g, 11.04 mmol) in CH_2Cl_2 (60 mL) containing diisopropylethylamine (3.418 g, 26.50 mmol, 2.4 equiv.) was treated with triflic anhydride (3.735 g, 2.23 mL, 13.25 mmol, 1.2 equiv.) at -73°C , and then with LiCN (1.093 g, 33.12 mmol, 3.0 equiv.), and 12-crown-4 (0.194 g, 1.1 mmol, 0.1 equiv.). N-phenyl-2-cyano-4-methyl-1-aza-1,3-butadiene **27**, a 5:1 mixture of isomers, was obtained as a yellow low melting crystalline solid (1.181 g, 63%) after flash column purification (silica gel, 15:1 heptane/EtOAc): mp. 35°C ; IR (neat) 2228, 1645, 1581, 1490, 1441, 1251 cm^{-1} ; ^1H NMR (CDCl_3) major isomer - δ 2.05 (dd, $J = 1.6, 6.8$ Hz, 3H, Me), 6.52 (ddd, $J = 1.5, 3.0, 15.9$ Hz, 1H, H-4), 6.96 (m, 1H, H-3), 7.08 (d, $J = 7.3, 2\text{H}$, $o\text{-H}_{\text{Ar}}$), 7.27 (t, $J = 7.4, 1\text{H}$, $p\text{-H}_{\text{Ar}}$), 7.42 (t, $J = 7.3, 2\text{H}$, $m\text{-H}_{\text{Ar}}$); minor isomer - δ 1.91 (dd, $J = 1.6, 6.9$ Hz, 3H, Me), 6.21 (ddd, $J = 1.5, 3.1, 15.6$ Hz, 1H, H-4), 6.90 (m, 1H, H-3), 7.08 (d, $J = 7.3, 2\text{H}$, $o\text{-H}_{\text{Ar}}$), 7.27 (t, $J = 7.4, 1\text{H}$, $p\text{-H}_{\text{Ar}}$), 7.42 (t, $J = 7.3, 2\text{H}$, $m\text{-H}_{\text{Ar}}$); ^{13}C NMR (CDCl_3) δ 18.8 (Me), 110.3 (CN), 119.9 (C4), 120.4 (C4), 122.8, 125.9, 127.2, 129.3, 130.8 (C_{Ar}), 140.4 (N-C_{Ar}), 144.6 (C3), 146.1 (C3), 147.9 (C2), 149.1 (C2); MS (CI) m/z 227 ($\text{M}+57^+$), 171 ($\text{M}+\text{H}$), 144; Anal: Calcd. for $\text{C}_{11}\text{H}_{10}\text{N}_2$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.50; H, 5.81; N, 16.41.

N-Phenyl-1,2,3,4-tetrahydro-*cis*-2-phenyl-4-methyl-6-cyanopyridine 29, and its *trans* isomer 30. As described for **6**, N-phenyl-2-cyano-4-methyl-1-aza-1,3-butadiene **27** (141 mg, 0.83 mmol) and styrene (3.45 g, 33.2 mmol, 40 equiv.) were heated under closed

conditions at 120°C for 30 h. Compound **29** was obtained as a white solid (141 mg, 62%), and **30** (admixture with **29**) as a pale yellow oil (33 mg, 15% from NMR) after flash column chromatography (silica gel, heptane/EtOAc, 97:3, then 95:5).

Compound **29** (major isomer). IR (neat) 2228, 1616, 1602, 1497, 1413 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.85 (d, $J = 7.2$ Hz, 3H, Me), 2.05 (m, 1H, H-3), 2.25 (ddd, $J = 4.5, 5.8, 13.5$ Hz, 1H, H-3), 2.61 (ddd, $J = 3.4, 6.8, 13.4$ Hz, 1H, H-4), 4.70 (dd, $J = 4.1, 7.7$ Hz, 1H, H-2), 5.69 (d, $J = 3.2$ Hz, 1H, H-5), 7.03 (m, 3H, H_{ar}), 7.25 (m, 7H, H_{ar}); ^{13}C NMR (CDCl_3) δ 20.9 (Me), 28.3 (C3), 38.6 (C4), 63.2 (C2), 116.2 (CN), 119.2 (C-C_{ar}), 124.5, 125.2, 126.4, 127.1, 127.4, 128.6, 129.0 (C5 + C_{ar}), 141.2 (N-C_{ar}), 145.4 (C6); MS m/z 274 (M^+), 259, 180, 168, 104, 91, 77; Anal: Calcd. for $\text{C}_{19}\text{H}_{18}\text{N}_2$: C, 83.18; H, 6.61; N, 10.21. Found: C, 83.16; H, 6.85; N, 10.16.

Compound **30** (minor isomer). ^1H NMR (CDCl_3) δ 1.07 (d, $J = 6.9$ Hz, 3H, Me), 1.77 (m, 1H, H-3), 1.96-2.28 (m, 2H, H-3, H-4), 4.88 (t, $J = 3.5$ Hz, 1H, H-2), 5.61 (d, $J = 1.5$ Hz, 1H, H-5), 6.87-7.38 (m, 10H, H_{ar}); ^{13}C NMR (CDCl_3) δ 19.5 (Me), 25.3 (C3), 34.8 (C4), 63.0 (C2), 116.3 (CN), 119.2 (C-C_{ar}), 124.1-129.2, 7 peaks (C5 + C_{ar}), 141.4 (N-C_{ar}), 145.9 (C6).

N-Phenyl-1,2,3,4-tetrahydro-*cis*-2-(3-nitrophenyl)-4-methyl-6-cyanopyridine **31 and its *trans* isomer **32**.** As described for **6**, N-phenyl-2-cyano-4-methyl-1-aza-1,3-butadiene **27** (37 mg, 0.22 mmol) and 3-nitrostyrene (1.3 g, 8.8 mmol, 40 equiv.) were heated under closed conditions at 90°C for 22 h. Compounds **31** (31 mg, 44%) and **32** (11 mg, 16%) were obtained as yellow oils after two flash column chromatographies (silica gel, 50:1 heptane/EtOAc):

Compound **31** (major isomer). IR (neat) 2228, 1609, 1595, 1532, 1356 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.94 (d, $J = 7.2$ Hz, 3H, Me), 2.02 (dt, $J = 8.4, 13.6$ Hz, 1H, H-3), 2.26 (dddd, $J = 0.6, 3.8, 5.7, 13.7$ Hz, 1H, H-3), 2.71 (m, 1H, H-4), 4.77 (dd, $J = 3.7, 8.7$ Hz, 1H, H-2), 5.69 (dd, $J = 2.5, 3.7$ Hz, 1H, H-5), 6.98-7.61 (m, 8H, H_{ar}), 8.01 (m, 1H, H_{ar}); ^{13}C NMR (CDCl_3) δ 20.9 (Me), 28.4 (C3), 39.0 (C4), 63.0 (C2), 115.7 (CN), 119.8, 122.3, 122.4, 122.7, 125.5, 125.8, 126.3, 129.4, 129.7, 133.2 (C5 + C_{ar}), 143.7 (N-C_{ar}), 144.8 (C6), 148.5 (C_{ar}-NO₂); MS m/z 319 (M^+), 304, 197, 169, 155, 93, 77. HRMS: Calcd. for $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_2$: 319.1321. Found: 319.1302.

Compound **32** (minor isomer). IR (neat) 2228, 1602, 1532, 1497, 1349 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.13 (d, $J = 6.9$ Hz, 3H, Me), 1.84 (ddd, $J = 4.2, 11.4, 12.9$, 1H, H-3), 2.02 (m, 1H, H-3), 2.26 (m, 1H, H-4), 4.96 (t, $J = 3.5$ Hz, 1H, H-2), 5.68 (dd, $J = 1.4, 2.5$ Hz, 1H, H-5), 7.04-7.73 (m, 8H, H_{ar}), 8.17 (m, 1H, H_{ar}); ^{13}C NMR (CDCl_3) δ 19.5 (Me), 25.2 (C3), 34.3 (C4), 62.7 (C2), 115.8 (CN), 116.6, 121.0, 122.4, 122.6, 125.0, 127.5, 129.5, 130.0, 132.2 (C5 + C_{ar}), 143.7 (N-C_{ar}), 145.6 (C6), 148.9 (C_{ar}-NO₂).

N-Phenyl-1,2,3,4-tetrahydro-*cis*-2-(4-bromophenyl)-4-methyl-6-cyanopyridine **33 and its *trans* isomer **34**.** As described for **6**, N-phenyl-2-cyano-4-methyl-1-aza-1,3-butadiene **27** (116 mg, 0.68 mmol) and 4-bromostyrene (5.0 g, 27.2 mmol, 40 equiv.) were heated under closed conditions at 90°C for 44 h. Compounds **33** (120 mg, 50%) and **34** (43 mg, 18%) were obtained as pale yellow oils after repetitive flash column chromatography (silica gel, 97:3 heptane/EtOAc):

Compound **33** (major isomer). IR (neat) 2228, 1623, 1595, 1497 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.86 (d, $J = 7.2$ Hz, 3H, Me), 1.97 (m, 1H, H-3), 2.20 (ddd, $J = 4.1, 5.9, 13.6$ Hz, 1H, H-3), 2.61

(ddd, $J = 3.2, 7.3, 13.7$ Hz, 1H, H-4), 4.64 (dd, $J = 3.9, 8.0$ Hz, 1H, H-2), 5.67 (d, $J = 3.1$ Hz, 1H, H-5), 6.97 (d, $J = 7.4$, 2H, o -H_{ar}), 7.04 (t, $J = 7.4$, p -H_{ar}), 7.11 (d, $J = 8.4$, 2H, α -H_{ar}), 7.21 (t, $J = 7.7$, m -H_{ar}), 7.38 (d, $J = 8.4$, 2H, β -H_{ar}); ^{13}C NMR (CDCl_3) δ 20.9 (Me), 28.2 (C3), 38.5 (C4), 62.7 (C2), 116.0 (CN), 119.3 (C-C_{ar}), 121.2 (C_{ar}-Br), 124.7 (o -C_{ar}), 125.5, 126.2 (C5 + p -C_{ar}), 128.8, 129.1 (o -C_{ar} + m -C_{ar}), 131.7 (m -C_{ar}), 140.3 (N-C_{ar}), 145.1 (C6); MS m/z 354, 352 (M^+), 353, 351, 339, 337, 231, 182, 184, 169, 77; Anal: Calcd. for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{Br}$: C, 64.60; H, 4.85; N, 7.93. Found: C, 64.44; H, 5.01; N, 7.64.

Compound **34** (minor isomer). IR (neat) 2228, 1625, 1595, 1490 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.09 (d, $J = 6.8$ Hz, 3H, Me), 1.77 (ddd, $J = 4.3, 11.0, 12.6$, 1H, H-3), 2.06 (m, 1H, H-3), 2.19 (m, 1H, H-4), 4.83 (dd, $J = 3.3, 3.6$ Hz, 1H, H-2), 5.62 (dd, $J = 1.6, 2.5$ Hz, 1H, H-5), 7.02-7.33 (m, 7H, H_{ar}), 7.50 (d, $J = 8.5$, H_{ar}); ^{13}C NMR (CDCl_3) δ 19.5 (Me), 25.2 (C3), 34.6 (C4), 62.6 (C2), 116.0 (CN), 120.4 (C-C_{ar}), 121.2 (C_{ar}-Br), 124.4, 127.4, 127.7, 129.3, 132.0 (C5 + C_{ar}), 140.5 (N-C_{ar}), 145.8 (C6); MS m/z 354, 352 (M^+), 353, 351, 339, 337, 231, 195, 182, 169, 93, 77.

N-Phenyl-1,2,3,4-tetrahydro-*cis*-2-ethoxy-4-methyl-6-cyanopyridine 35 and its *trans* isomer 36. As described for **6**, N-phenyl-2-cyano-4-methyl-1-aza-1,3-butadiene **27** (60 mg, 0.35 mmol) and ethyl vinyl ether (1.02 g, 14.0 mmol, 40 equiv.) were heated under closed conditions at 120°C for 34 h. Compounds **35** and **36** (73 mg, 88%) were obtained as a 2:1 mixture of isomers after flash column chromatography (silica gel, 20:1 heptane/EtOAc):

Compound **35** (major isomer). ^1H NMR (CDCl_3) δ 1.23 (d, $J = 5.8$ Hz, 3H, 4-Me), 1.26 (d, $J = 5.3$ Hz, 3H, Me), 1.95 (m, 1H, H-3), 2.42 (m, 1H, H-4), 3.58 (m, 1H, CH_2O), 3.84 (m, 1H, CH_2O), 4.88 (t, $J = 2.9$ Hz, 1H, H-2), 6.03 (d, $J = 4.2$ Hz, 1H, H-5), 7.06-7.45 (m, 5H, H_{ar}); ^{13}C NMR (CDCl_3) δ 15.3 (Me), 21.6 (Me), 26.3 (C3), 31.9 (C4), 63.1 (OCH_2), 88.8 (C2), 119.9 (CN), 120.4, 122.7, 124.4, 127.2, 129.3, 129.5, 130.8, 131.7 (C5 + C_{ar}), 144.5 (C6).

Compound **36** (minor isomer). ^1H NMR (CDCl_3) δ 1.14 (d, $J = 7.2$ Hz, 3H, 4-Me), 1.23 (d, $J = 6.7$ Hz, 3H, Me), 1.77-2.07 (m, 1H, H-3), 2.72 (m, 1H, H-4), 3.59 (m, 1H, CH_2O), 3.87 (m, 1H, CH_2O), 4.75 (t, $J = 2.6$ Hz, 1H, H-2), 5.83 (dd, $J = 1.4, 2.5$ Hz, 1H, H-5), 7.11 (m, 3H, H_{ar}), 7.37 (m, 2H, H_{ar}); ^{13}C NMR (CDCl_3) δ 18.9 (Me), 19.4 (Me), 24.8 (C3), 33.0 (C4), 63.2 (OCH_2), 89.1 (C2), 116.4 (CN), 120.4, 123.6, 124.9, 129.6, 130.5, 131.8 (C5 + C_{ar}), 144.5 (C6).

For the mixture of isomers: IR (neat) 2228, 1645, 1631, 1595, 1490 cm^{-1} ; MS (FAB) m/z 242 (M^+). Anal: Calcd. for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}$: C, 74.35; H, 7.49; N, 11.56. Found: C, 74.29; H, 7.20; N, 11.78.

N-Phenyl-1,2,3,4-tetrahydro-*cis*-2-carbomethoxy-4-methyl-6-cyanopyridine 37, its *trans*- isomer 38, and N-Phenyl-1,2,3,4-tetrahydro-*cis*-3-carbomethoxy-6-cyanopyridine 39 and its *trans*- isomer 40. As described for **6**, N-phenyl-2-cyano-4-methyl-1-aza-1,3-butadiene **27** (120 mg, 0.70 mmol) and methyl acrylate (2.43 g, 28.0 mmol, 40 equiv.) were heated under closed conditions at 120°C for 40 h. Compounds **37** - **40** (64 mg, 36%, mixture of isomers, 5:1:2.6:2) were obtained as a yellow oil after flash column chromatography (silica gel, 20:1 heptane/EtOAc):

For the mixture of isomers: IR (neat) 2231, 1738, 1619, 1606, 1500 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.02 (d, $J = 7.3$ Hz, 4-Me), 1.03 (d, $J = 6.6$ Hz, 4-Me), 1.14 (d, $J = 6.9$ Hz, 4-Me), 1.29 (dd, $J = 6.4, 13.3$ Hz, H-4), 1.43 (d, $J = 6.7$ Hz, H-3), 1.64 (ddd, $J = 4.7, 11.3, 13.1$ Hz, H-3), 2.21 (t, $J = 5.1$ Hz, H-3), 2.30-2.54 (m, H-5), 2.85 (m, H-2, H-3), 3.56 (dd, $J = 11.1, 12.8$ Hz, H-2), 3.59 (s, Me), 3.68 (s, Me), 3.73 (s, Me), 3.77 (s, Me), 3.82 (dd, $J = 1.3, 2.7$ Hz, H-2), 4.36 (t, $J = 5.0$ Hz, H-2), 4.41 (dd, $J = 2.9, 4.6$ Hz, H-2), 5.58 (dd, $J = 1.5, 2.5$ Hz, H-5), 5.72 (d, $J = 4.1$ Hz, H-5), 5.76 (d, $J = 3.8$ Hz, H-5), 5.79 (d, $J = 4.5$ Hz, H-5), 7.10 (m, H_{ar}), 7.26 (m, H_{ar}), 7.34 (m, H_{ar}); ^{13}C NMR (CDCl_3) δ 15.9, 17.4, 19.8, 21.2, 26.2, 26.6, 27.8, 30.0, 31.5, 31.7, 32.2, 41.5, 44.6, 47.4, 50.4, 51.6, 51.8, 52.1, 52.4, 52.7, 57.2, 59.8, 61.8, 115.5, 115.7, 116.6, 117.2, 117.7, 119.7, 119.9, 120.0, 122.2, 122.4, 122.6, 122.9, 123.0, 123.5, 123.9, 124.5, 124.9, 125.0, 125.5, 125.7, 125.8, 127.1, 127.3, 128.4, 129.3, 129.6, 129.8, 134.2, 144.8, 145.0, 145.4, 172.0; MS m/z 256 (M^+), 241, 205, 197, 181, 169, 93, 77. Anal: Calcd. for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.49; H, 6.25; N, 10.99.

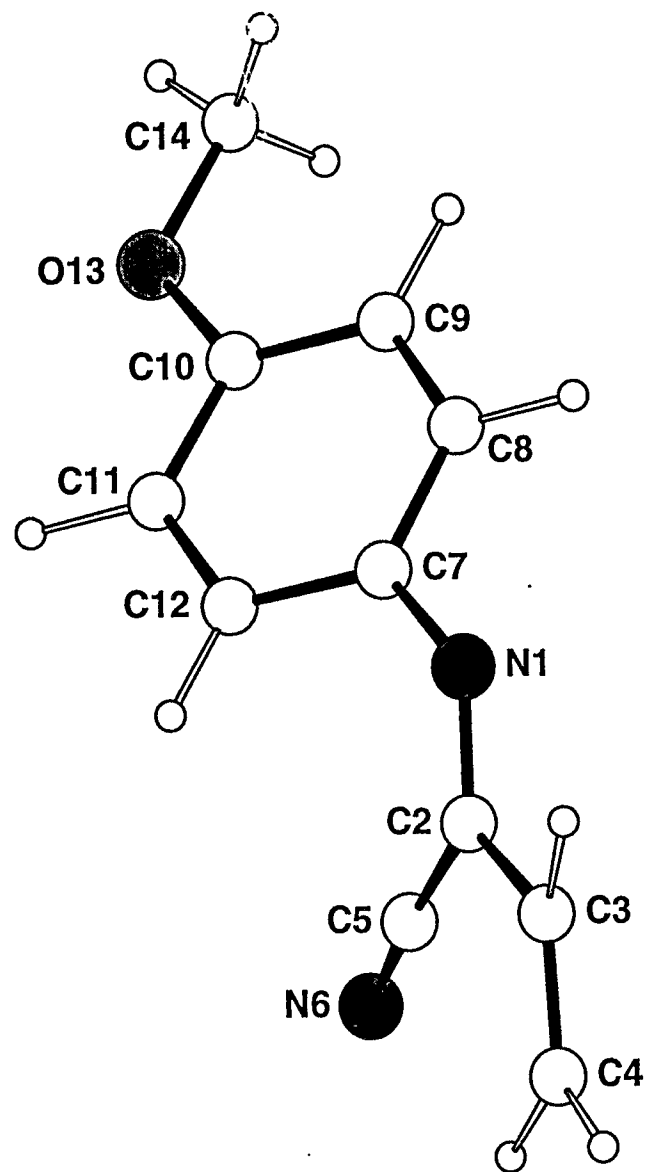
X-ray structure analysis of compound 18

Crystal data. $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}$, molecular weight 186.21 monoclinic system; space group $\text{P } 2_1/a$; $Z = 4$; $a = 6.918(1)$, $b = 10.948(1)$, $c = 13.677(3)$ Å, $\beta = 102.90(2)^\circ$; $V = 1009.7(5)$ Å³; $d_c = 1.22$ g cm^{-3} ; $F(000) = 292$; $\mu(\text{Cu K}\alpha) = 1.5418$ Å; $m = 0.62$ mm⁻¹ (absorption ignored). Data were collected on a CAD4 Enraf-Nonius diffractometer using graphite monochromated Cu K α radiation. From the 2193 reflexions measured by the (q -2 q) scan technique up to $q = 70^\circ$, 2030 were independent ($R_{\text{int}} = 0.102$) and 1087 were considered as observed with $I > 3.0\sigma(I)$, $s(I)$ from counting statistics.

The structure was solved by direct methods and refined by full matrix least-squares with TEXAN⁴⁶, minimizing the function $\text{Sw}(\text{Fo} - |\text{Fcl}|)^2$. Convergence was reached at $R = 0.064$ and $R_w = 0.072$ (with $R_w = \{\text{Sw}(\text{Fo} - |\text{Fcl}|)^2 / \text{SwFo}^2\}^{1/2}$ and $w = 4\text{Fo}^2 / [s^2(I) + 0.0009 \text{Fo}^4] / L_p$). No residual was higher than $0.19 \text{ e } \text{\AA}^{-3}$ in the final difference map.⁴⁹

References

47. TEXAN (1985). *TEXRAY* Structure Analysis Package Molecular Structure Corporation.



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