A Heterocycle-Forming Double Michael Reaction. [5 + 1] Annulation Route to Highly Substituted and Functionalized Piperidines

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Supporting Information

Experimental details for the preparation and characterization of compounds **1–3**, **4b**, **5c**, and **10–13**, ^{1}H and ^{13}C NMR spectra of mono- and bicyclic compounds not subject to elemental analysis (**5c**, **11**, **12**), and data from X-ray crystallographic analysis of **3b**, **3c**, and **3e** (44 pages).

General procedure A (for synthesis of 1a–d,f). A solution of an alkene in methanol (50–70 mL) was ozonolyzed (72 V, 1.2 L/min) at –78 °C until the reaction mixture turned blue. After sparging with oxygen until the blue color was gone, the appropriate ammonium salt (3–4 equiv) and $NaBH_3CN$ (6 equiv) were added. The reaction mixture was allowed to warm to rt and stir overnight. The solvent was evaporated, and the residue was suspended in saturated aqueous $NaHCO_3$. The aqueous layer was extracted three times with ether. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash chromatography (10–30% EtOAc in petroleum ether as eluant) to afford **1a–d,f**. Because of their instability, these compounds were not subject to elemental analysis.

Triethyl 1-cyano-2-aza-1,5,5-pentanetricarboxylate (1a). Diethyl prenylmalonate[10] (1.65 g, 7.23 mmol) and ethyl cyanoglycinate hydrotosylate[8] (6.63 g, 22.1 mmol) were combined according to general procedure A to afford **1a** (783 mg, 2.48 mmol, 34% yield) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.33 (s, 1H), 4.31 (q, 7.1 Hz, 2H), 4.19 (q, 7.1 Hz, 4H), 3.52 (t, 7.1 Hz, 1H), 2.87 (dt, J_d = 11.9 Hz, J_t = 6.6 Hz, 2H), 2.12 (q, 6.8 Hz, 2H), 1.31 (t, 7.1 Hz, 9H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 169.2, 169.1, 164.7, 115.0, 63.2, 61.7, 61.5, 61.4, 52.1, 49.6, 44.7, 42.3, 13.9, 13.8. IR (neat): 3334, 2228, 1747, 1097, 1024 cm^{-1}.

Diethyl 1,5-dicyano-2-aza-1,5-pentanedicarboxylate (1b). Ethyl cinnamylcyanoacetate[10] (2.69 g, 11.7 mmol) and ethyl cyanoglycinate hydrotosylate[8] (10.8 g, 36.0 mmol) were combined according to general procedure A to afford **1b** (1.28 g, 4.78 mmol, 41% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.38 (s, 1H), 4.32 (q, 7.1 Hz, 4H), 3.80 (m, 1H), 3.01 (m, 2H), 2.21 (m, 2H), 1.38 (t, 7.1 Hz, 6H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 166.0, 164.6, 116.1, 114.8, 63.5, 63.0, 52.1, 50.8, 43.7, 34.9, 29.3, 29.2. IR (neat): 3334, 2244, 1747, 1257, 1025 cm^{-1}.

Ethyl 1-cyano-2-aza-5-nitro-1-hexanecarboxylate (1c). General procedure A was followed, except that instead of alkene ozonolysis, crude 3-nitro-1-butanal (921 mg, 7.86 mmol) was prepared[11] and combined with ethyl cyanoglycinate hydrotosylate[8] (4.64 g, 15.7 mmol), $NaBH_3CN$ (947 mg, 15.7 mmol) and AcOH (900 µL, 15.7 mmol) to afford **1c** (430 mg, 1.88 mmol, 24% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.77 (m, 1H), 4.35 (s, 1H), 4.31

(q, 7.1 Hz, 2H), 2.84 (m, 2H), 2.28 (m, 1H), 1.90 (m, 1H), 1.84 (bs, 1H), 1.58 (d, 6.8 Hz, 3H), 1.35 (t, 7.1 Hz, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 164.7, 114.9, 80.8, 63.5, 58.8, 52.5, 43.4, 34.6, 19.3. IR (neat): 3333, 2252, 1750, 1549.

Triethyl 5-cyano-2-aza-1,1,5-pentanetricarboxylate (1d). Ethyl cinnamylcyanoacetate[10] (695 mg, 3.04 mmol) and diethyl aminomalonate hydrochloride (2.55 g, 12.04 mmol) were combined according to general procedure A to afford **1d** (569 mg, 1.81 mmol, 60% yield) as an oil. ^1H NMR (200 MHz, $CDCl_3$): δ 4.25 (q, 7.1 Hz, 6H), 4.02 (s, 1H), 3.86 (dd, 7.2 Hz, 6.2 Hz, 1H), 2.85 (m, 2H), 2.08 (m, 2H), 1.29 (t, 7.1 Hz, 9H). $^{13}C\{H\}$ NMR (50 MHz, $CDCl_3$): δ 168.2, 168.1, 166.1, 116.3, 79.9, 77.6, 76.3, 64.5, 62.7, 61.8, 43.9, 34.8, 13.9, 13.8. IR (neat): 3329, 2238, 1736, 1019 cm^{-1}.

Diethyl 5,5-dicyano-2-aza-1,1-pentanedicarboxylate (1f). Prenylmalononitrile[10] (2.04 g, 15.2 mmol) and diethyl aminomalonate hydrochloride (9.68 g, 45.7 mmol) were combined according to general procedure A to afford **1f** (683 mg, 2.56 mmol, 17% yield) as an oil. ^1H NMR (400 MHz, $CDCl_3$): δ 4.35 (q, 7.1 Hz, 4H), 4.24 (s, 1H), 4.03 (t, 7.2 Hz, 1H), 2.91 (m, 2H), 2.17 (m, 2H), 1.29 (t, 7.1 Hz, 6H). $^{13}C\{H\}$ NMR (50 MHz, $CDCl_3$): δ 165.1, 112.4, 66.7, 62.1, 61.7, 61.6, 53.1, 49.2, 29.3, 26.6, 14.0, 13.8. IR (neat): 2251, 1752, 1203, 1028 cm^{-1}.

General procedure B (for synthesis of 2a–d). A solution of **1** in absolute ethanol (0.1–0.2 M) was cooled to 0 °C, and formalin, $NaBH_3CN$, and acetic acid (1.1–1.2 equiv each) were added. The solution was allowed to warm to rt and stir overnight. The solvent was evaporated, and the residue was suspended in saturated aqueous $NaHCO_3$. The aqueous layer was extracted three times with ether. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash chromatography (10% EtOAc in petroleum ether as eluant) to give **2** as a yellow oil.

Triethyl *N*-methyl-1-cyano-2-aza-1,5,5-pentanetricarboxylate (2a). Compound **1a** (2.57 g, 8.18 mmol) was transformed by general procedure B into **2a** (1.41 g, 4.29 mmol, 53% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 4.24 (s, 1H), 4.15 (q, 7.1 Hz, 2H), 4.09 (q, 7.1 Hz, 4H), 3.55 (t, 6.8 Hz, 1H), 2.61 (m, 2H), 2.37 (s, 3H), 2.06 (m, 2H), 1.34 (t, 7.1 Hz, 3H), 1.27 (t, 7.1 Hz, 6H).

$^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 169.4, 169.3, 164.1, 112.8, 62.5, 61.4, 60.2, 52.7, 49.4, 44.6, 42.3, 39.0, 26.3, 13.9, 13.8. IR (neat): 2229, 1745, 1219, 1025 cm^{-1}. Anal. Calcd for $C_{15}H_{24}N_2O_6$: C, 54.87; H, 7.37. Found: C, 54.78; H, 7.55.

Diethyl *N*-methyl-1,5-dicyano-2-aza-1,5-pentanedicarboxylate (2b). Compound **1b** (811 mg, 2.99 mmol) was transformed by general procedure B into **2b** (457 mg, 1.64 mmol, 55% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 4.38 (s, 1H), 4.31 (q, 7.1 Hz, 4H), 3.84 (m, 1H), 2.77 (m, 2H), 2.43 (s, 3H), 2.16 (m, 2H), 1.34 (t, 7.1 Hz, 6H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 166.1, 163.7, 116.4, 112.6, 63.4, 63.2, 60.3, 51.8, 51.3, 39.2, 38.8, 34.5, 13.9. IR (neat): 2250, 1743, 1216, 1023 cm^{-1}. Anal. Calcd for $C_{13}H_{19}N_3O_4$: C, 55.50; H, 6.81. Found: C, 55.61; H, 6.92.

Ethyl *N*-methyl-1-cyano-2-aza-5-nitro-1-hexanecarboxylate (2c). Compound **1c** (410 mg, 1.79 mmol) was transformed by general procedure B into **2c** (227 mg, 933 μmol, 52% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 4.75 (m, 1H), 4.34 (s, 1H), 4.31 (q, 7.1 Hz, 2H), 2.61 (m, 2H), 2.42 (s, 3H), 2.29 (m, 1H), 1.88 (m, 1H), 1.58 (d, 3.6 Hz, 3H), 1.35 (t, 7.1 Hz, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 163.9, 112.6, 80.9, 63.3, 60.7, 51.1, 39.3, 32.4, 19.7, 14.2. IR (neat): 2236, 1742, 1549, 1218, 1028 cm^{-1}. Anal. Calcd for $C_{10}H_{17}N_3O_4$: C, 49.37; H, 7.04. Found: C, 49.45; H, 6.99.

Triethyl *N*-methyl-5-cyano-2-aza-1,1,5-pentanetricarboxylate (2d). Compound **1d** (4.38 g, 13.9 mmol) was transformed by general procedure B into **2d** (2.24 g, 6.83 mmol, 49% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 4.24 (q, 7.1 Hz, 6H). 4.08 (s, 1H), 3.92 (dd, 8.1 Hz, 5.5 Hz, 1H), 2.88 (m, 2H), 2.46 (s, 3H), 2.12 (m, 2H), 1.30 (t, 7.1 Hz, 9H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 167.5, 167.4, 166.4, 116.9, 70.2, 62.7, 61.5, 61.4, 51.1, 39.1, 34.4, 28.1, 14.1, 14.0, 13.9. IR (neat): 2249, 1739, 1241, 1026 cm^{-1}. Anal. Calcd for $C_{15}H_{24}N_2O_6$: C, 54.87; H, 7.37. Found: C, 54.97; H, 7.13.

General procedure C (for synthesis of 2e,f). A solution of **1** in freshly distilled CH_2Cl_2 (10 mL) was treated with pyridine (1.0 equiv), trifluoroacetic anhydride (1.0 equiv), and DMAP (15 mol%). The solution was allowed to stir at rt overnight. Saturated aqueous $NaHCO_3$ was added and extracted three times with ether. The organic layers were combined and dried over $MgSO_4$,

filtered, and concentrated. The residue was purified by flash chromatography (30% EtOAc in petroleum ether as eluant).

Triethyl *N*-trifluoroacetyl-5-cyano-2-aza-1,1,5-pentanetricarboxylate (2e). Compound **1d** (1.47 g, 4.69 mmol) was treated according to general procedure C to afford **2e** (1.59 g, 3.89 mmol, 83% yield) as an oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.98 (s, 1H), 4.31 (q, 7.1 Hz, 6H), 3.69 (m, 3H), 2.35 (m, 2H), 1.33 (t, 7.1 Hz, 9H). ^{13}C{H} NMR (50 MHz, $CDCl_3$): δ 165.4, 165.0, 164.8, 164.7, 164.3, 157.6 (q, 36 Hz), 116.0 (q, 286 Hz), 115.8 (q, 286 Hz), 115.8, 115.3, 63.4, 63.2, 63.0, 62.9, 45.7, 45.5, 35.3, 34.3, 28.4, 27.1, 13.8. IR (neat): 2248, 1721, 1270, 1019 cm^{-1}. Anal. Calcd for $C_{16}H_{21}N_2O_7F_3$: C, 46.83; H, 5.16. Found: C, 46.85; H, 5.29.

Diethyl *N*-trifluoroacetyl-5,5-dicyano-2-aza-1,1-pentanedicarboxylate (2f). Compound **1f** (683 mg, 2.56 mmol) was treated according to general procedure C to afford **2f** (922 mg, 2.54 mmol, 99% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.21 (s, 1H), 4.35 (q, 7.1 Hz, 4H), 4.04 (t, 7.2 Hz, 1H), 3.72 (m, 2H), 2.52 (m, 2H), 1.34 (t, 7.1 Hz, 6H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 164.6, 164.4, 157.9 (q, 37 Hz), 115.6 (q, 290 Hz), 112.1, 111.5, 63.5, 63.0, 45.3, 44.4, 29.9, 28.7, 20.9, 13.9. IR (neat): 2987, 2913, 2253, 1751, 1701, 1186, 1029 cm^{-1}. Anal. Calcd for $C_{14}H_{16}N_3O_5F_3$: C, 46.29; H, 4.44. Found: C, 46.09; H, 4.20.

General procedure D (for synthesis of 3a–f and diastereomers). A solution of **2** in freshly distilled CH_2Cl_2 (80–330 mM) was cooled to 0 °C, *t*-BuOK (15 mol%) was added, and a solution of 3-butyn-2-one (1.1–1.3 equiv) in CH_2Cl_2 (2–5 mL) was added dropwise. The solution was allowed to warm to rt and stir for 2 h. Saturated aqueous $NaHCO_3$ was added, and the mixture was extracted three times with ether. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash chromatography (10–30% EtOAc in petroleum ether as eluant).

Triethyl (2*R,3*S*)-*N*-methyl-2-cyano-3-(2-oxopropyl)-2,4,4-piperidinetricarboxylate (3a).** Compound **2a** (1.41 g, 4.29 mmol) was treated according to general procedure D to afford **3a** (1.69 g, 4.27 mmol, 99% yield) as a pale yellow solid, mp 61–62 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.20 (q, 7.1 Hz, 6H), 3.51 (dd, 7.8 Hz, 1.8 Hz, 1H), 3.10 (dd, 19.0 Hz, 1.8 Hz, 1H), 2.96

(dd, 19.0 Hz, 7.8 Hz, 1H), 2.88 (ddd, 12.6 Hz, 4.9 Hz, 2.7 Hz, 1H), 2.79 (dt, J_t = 12.3 Hz, J_d = 2.6 Hz, 1H), 2.51 (dt, J_d = 13.4 Hz, J_t = 2.8 Hz, 1H), 2.29 (s, 3H), 2.13 (s, 3H), 2.04 (dt, J_t = 12.5 Hz, J_d = 4.8 Hz, 1H), 1.35 (t, 7.1 Hz, 6H), 1.21 (t, 7.1 Hz, 3H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 204.3, 170.2, 168.4, 166.7, 112.9, 72.9, 63.9, 62.2, 62.1, 54.8, 48.3, 43.6, 41.6, 39.5, 31.5, 29.3, 13.9, 13.8, 13.7. IR (neat): 2252, 1722, 1666, 1209, 1097, 1067, 1024 cm^{-1}. Anal. Calcd for $C_{19}H_{28}N_2O_7$: C, 57.56; H, 7.12. Found: C, 57.63; H, 7.26.

Diethyl (2*R, 3*S*, 4*R*)- and (2*R**, 3*R*, 4*R*)-*N*-methyl-1,5-dicyano-3-(2-oxopropyl)-1,5-piperidinedicarboxylate (3b and 4b).** Compound **2b** (220 mg, 783 μmol) was treated according to general procedure D to afford **3b** (191 mg, 544 μmol, 69% yield) as a pale yellow solid, mp 137–139 °C, and **4b** (20 mg, 57 μmol, 7% yield) as a pale yellow solid, mp 133–134 °C. Compound **3b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.23 (q, 7.1 Hz, 4H), 3.36 (dd, 5.61 Hz, 4.40 Hz, 1H), 2.96 (dd, 18.8 Hz, 5.6 Hz, 1H), 2.96 (m, 1H), 2.83 (dd, 18.8 Hz, 4.4 Hz, 1H), 2.80 (dt, J_t = 12.0 Hz, J_d = 4.4 Hz, 1H), 2.38 (dt, J_t = 11.2 Hz, J_d = 4.4 Hz, 1H), 2.37 (s, 3H), 2.23 (dt, J_d = 11.2 Hz, J_t = 2.4 Hz, 1H), 2.16 (s, 3H), 1.31 (t, 7.1 Hz, 6H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 165.1, 164.9, 118.0, 113.3, 76.4, 67.5, 64.0, 47.5, 45.5, 41.8, 40.9, 38.1, 29.7, 29.5, 27.7, 13.7, 13.6. IR (KBr): 2240, 1747, 1728, 1234, 1211, 1060 cm^{-1}. Anal. Calcd for $C_{17}H_{23}N_3O_5$: C, 58.44; H, 6.64. Found: C, 58.56; H, 6.68. Compound **4b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.29 (q, 7.1 Hz, 4H), 3.78 (ddd, 7.1 Hz, 2.7 Hz, 1.6 Hz, 1H), 3.44 (dd, 19.0 Hz, 7.1 Hz, 1H), 2.91 (dt, J_d = 13.0 Hz, J_t = 4.4 Hz, 1H), 2.75 (dd, 19.0 Hz, 2.7 Hz, 1H), 2.69 (ddd, 13.0 Hz, 11.4 Hz, 3.3 Hz, 1H), 2.51 (ddt, J_d = 13.7 Hz, J_t = 3.3 Hz, J_d = 1.6 Hz, 1H), 2.32 (s, 3H), 2.17 (s, 3H), 2.02 (ddd, 13.7 Hz, 11.2 Hz, 4.8 Hz, 1H), 1.39 (t, 7.1 Hz, 6H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 165.1, 164.9, 118.0, 113.4, 76.5, 67.5, 64.1, 47.5, 45.5, 41.8, 40.9, 38.1, 29.7, 29.5, 27.7, 13.7, 13.6. IR (KBr): 2243, 1749, 1739, 1239, 1214, 1063 cm^{-1}. Anal. Calcd for $C_{17}H_{23}N_3O_5$: C, 58.44; H, 6.64. Found: C, 58.40; H, 6.85.

Ethyl (2*R,3*R*,4*R*)- and (2*R**,3*R*,4*S*)-*N*-methyl-2-cyano-4-methyl-3-(2-oxopropyl)-4-nitro-2-piperidinecarboxylate (3c and 5c).** Compound **2c** (531 mg, 2.18 mmol) was treated according to general procedure D, except that after **2c** had been consumed (2 h), the solvent was

evaporated, the residue was taken up in THF, a catalytic amount of NaH was added, and the solution was allowed to reflux for 1 d. Workup as described in the general procedure afforded **3c** (342 mg, 1.09 mmol, 50% yield) as a solid, mp 127–128 °C, and **5c** (71 mg, 220 μmol, 10% yield) as a solid, mp 105–106 °C. Compound **3c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.23 (q, 7.1 Hz, 2H), 3.76 (dd, 7.7 Hz, 2.4 Hz, 1H), 2.99 (m, 1H), 2.86 (dd, 18.5 Hz, 7.5 Hz, 1H), 2.61 (m, 2H), 2.49 (dd, 18.6 Hz, 2.4 Hz, 1H), 2.35 (s, 3H), 2.13 (s, 3H), 2.04 (m, 1H), 1.79 (s, 3H), 1.37 (t, 7.1 Hz, 3H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 166.4, 113.9, 89.1, 73.3, 64.5, 48.1, 41.5, 41.4, 41.1, 36.7, 29.7, 18.3, 13.9. IR (KBr): 2229, 1732, 1726, 1554, 1291, 1040 cm^{-1}. Anal. Calcd for $C_{15}H_{21}N_2O_5$: C, 54.01; H, 6.80. Found: C, 53.74; H, 6.64. Compound **5c**: ^{1}H NMR (400 MHz, $CDCl_3$): 4.17 (q, 7.1 Hz, 2H), 3.27 (dd, 19.6 Hz, 3.1 Hz, 1H), 3.21 (dd, 5.7 Hz, 2.9 Hz, 1H), 3.05 (dd, 19.6 Hz, 5.7 Hz, 1H), 2.84 (ddd, 13.0 Hz, 5.1 Hz, 2.7 Hz, 1H), 2.75 (td, J_t = 12.5 Hz, J_d = 2.4 Hz, 1H), 2.59 (dt, J_d = 14.8 Hz, J_t = 2.6 Hz, 1H), 2.32 (s, 3H), 2.20 (s, 3H), 2.07 (ddd, 17.4 Hz, 12.3 Hz, 5.1 Hz, 1H), 1.54 (s, 3H), 1.33 (t, 7.1 Hz, 3H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 204.1, 166.7, 116.9, 85.4, 72.3, 63.9, 47.2, 41.9, 41.5, 41.2, 35.1, 29.5, 27.3, 13.7. IR (KBr): 1742, 1717, 1539, 1271, 1170 cm^{-1}.

Triethyl (3*R,4*S*)-*N*-methyl-4-cyano-3-(2-oxopropyl)-2,2,4-piperidinetricarboxylate (3d).** Compound **2d** (2.63 g, 8.01 mmol) was treated according to general procedure D to afford **3d** (2.29 g, 5.77 mmol, 72% yield) as a yellow solid, mp 55–56 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.30 (q, 7.1 Hz, 4H), 4.10 (q, 7.1 Hz, 2H), 3.49 (dd, 8.1 Hz, 2.0 Hz, 1H), 3.32 (td, J_t = 13.2 Hz, J_d = 2.8 Hz 1H), 3.05 (dd, 19.1 Hz, 8.1 Hz, 1H), 2.85 (ddd, 16.9 Hz, 5.1 Hz, 2.8 Hz, 1H), 2.83 (dd, 19.1 Hz, 2.0 Hz, 1H), 2.59 (s, 3H), 2.56 (td, J_t = 13.2 Hz, J_d = 4.9 Hz, 1H), 2.12 (s, 3H), 2.03 (dt, J_d = 13.6 Hz, J_t = 2.5 Hz, 1H), 1.39 (t, 7.1 Hz, 3H), 1.29 (t, 7.1 Hz, 6H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 204.3, 168.6, 167.4, 167.3, 117.2, 74.7, 63.5, 62.7, 61.6, 48.0, 46.4, 44.3, 41.5, 39.9, 32.3, 29.3, 39.9, 13.7. IR (KBr): 2243, 1733, 1229, 1023 cm^{-1}. Anal. Calcd for $C_{19}H_{28}N_2O_7$: C, 57.56; H, 7.12. Found: C, 57.50; H, 7.00.

Triethyl (3*R,4*S*)-*N*-trifluoroacetyl-4-cyano-3-(2-oxopropyl)-2,2,4-piperidinetricarboxylate (3e).** Compound **2e** (396 mg, 1.01 mmol) was treated according to

general procedure D to afford a 16:1 mixture of **3e** and **4e** (294 mg, 615 μmol, 61% yield; minor component identified by GC–MS) as a yellow solid. Recrystallization (2:1 heptane–CH_2Cl_2) gave pure **3e**, mp 97–98 °C, for characterization. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.37 (dq, J_d = 10.8 Hz, J_q = 7.1 Hz, 2H), 4.12 (m, 4 H), 4.08 (ddd, 14.4 Hz, 7.2 Hz, 3.6 Hz, 1H), 3.74 (ddd, 14.4 Hz, 9.6 Hz, 3.2 Hz, 1H), 3.62 (dd, 6.8 Hz, 2.8 Hz, 1H), 3.20 (dd, 19.6 Hz, 2.8 Hz, 1H), 3.12 (dd, 19.6 Hz, 6.8 Hz, 1H), 2.59 (ddd, 14.4 Hz, 9.6 Hz, 3.6 Hz, 1H), 2.30 (ddd, 14.4 Hz, 7.1 Hz, 3.2 Hz, 1H), 2.13 (s, 3H), 1.29 (t, 7.1 Hz, 9H). ^{13}C{H} NMR (50 MHz, $CDCl_3$): δ 203.4, 166.7, 164.9, 163.9, 157.8 (q, 39 Hz), 116.3, 116.1 (q, 290 Hz), 69.4, 64.1, 63.2, 63.1, 62.9, 46.4, 42.3, 39.6, 31.1, 29.3, 13.7, 13.6, 13.5. IR (KBr): 2238, 1741, 1705, 1194, 1053 cm^{-1}. Anal. Calcd for $C_{20}H_{25}N_2O_8F_3$: C, 50.21; H, 5.27. Found: C, 50.18; H, 5.23.

Diethyl *N*-trifluoroacetyl-4,4-dicyano-3-(2-oxopropyl)-2,2-piperidinedicarboxylate (3f). Compound **2f** (922 mg, 2.54 mmol) was treated according to general procedure D to afford **3f** (142 mg, 329 μmol, 13% yield) as a solid, mp 88–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.41 (dq, J_d = 10.8 Hz, J_q = 7.1 Hz, 2H), 4.24 (m, 3H), 3.83 (dd, 6.6 Hz, 2.8 Hz, 1H), 3.63 (ddd, 14.8 Hz, 9.6 Hz, 5.2 Hz, 1H), 3.36 (dd, 19.4 Hz, 2.6 Hz, 1H), 3.10 (dd, 19.4 Hz, 2.6 Hz, 1H), 2.61 (m, 2H), 2.31 (s, 3H), 1.35 (t, 7.1 Hz, 6H). ^{13}C{H} NMR (50 MHz, $CDCl_3$): δ 201.9, 163.9, 163.0, 157.9 (q), 115.6 (q), 113.4, 112.3, 69.2, 63.6, 63.5, 42.5, 40.6, 39.7, 39.6, 35.5, 33.0, 29.5, 13.5. IR (KBr): 2243, 1736, 1705, 1101, 1075, 1028 cm^{-1}. Anal. Calcd for $C_{18}H_{20}N_3O_6F_3$: C, 50.11; H, 4.64. Found: C, 50.17; H, 4.71.

Triethyl (4a*R,8a*S*)-1,6-dimethyl-1,2,3,4,4a,8a-7*H*-hexahydro[1,7]naphthyridin-8-one-4,4,8a-tricarboxylate (10).** A solution of **3a** (981 mg, 2.47 mmol) in absolute ethanol (8 mL) was cooled to 0 °C. Concentrated H_2SO_4 (35 mL) was added dropwise to the chilled solution. The reaction mixture was allowed to warm to rt and stir overnight. The solution was neutralized with $NaHCO_3$ and extracted three times with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash chromatography (10% EtOAc in petroleum ether as eluant) to afford **10** (423 mg, 1.07 mmol, 43% yield) as a solid, mp 130–131 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.54 (s, 1H), 4.86 (dq, J_d = 3.3 Hz, J_q = 1.8 Hz, 1H),

4.26 (q, 7.1 Hz, 2H), 4.13 (q, 7.1 Hz, 4H), 3.61 (dm, 1H), 3.35 (m, 1H), 2.86 (m 1H), 2.68 (s, 3H), 2.25 (ddd, 13.7 Hz, 5.5 Hz, 3.7 Hz, 1H), 2.03 (m, 1H), 1.75 (t, 1.3 Hz, 3H), 1.26 (t, 7.1 Hz, 9H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 170.5, 170.4, 170.1, 168.8, 133.8, 101.7, 69.5, 62.1, 61.8, 61.7, 54.9, 46.8, 41.4, 41.2, 30.7, 19.0, 14.3, 14.2, 14.1. IR (KBr): 3234, 3122, 1733, 1678 cm^{-1}. Anal. Calcd for $C_{19}H_{28}N_2O_7$: C, 57.59; H, 7.06. Found: C, 57.55; H, 7.09.

Ethyl (2*R,3a*S*,4*R*,7a*R*)-4-cyano-2,5,7a-trimethylperhydropyrrolo[3,2-c]pyridine-4-carboxylate (11) and (1*R**,5*R*,8*S*)-1-cyano-2-methyl-8-(2-oxopropyl)-2,6-diazabicyclo[3.2.1]octan-7-one (12)**. Raney nickel (250 mg) was added to a solution of **3c** (240 mg, 743 μmol) in absolute ethanol (60 mL) in a Parr bomb. The bomb was pressurized to 1400 psi H_2, and the mixture was allowed to stir for 16 h. The reaction was filtered through Celite®, washing with EtOAc (3 × 15 mL), and the filtrate was concentrated. The residue was purified by flash chromatography (50% EtOAc in petroleum ether as eluant) to afford **11** (101 mg, 381 μmol, 51% yield) as an unstable solid, mp 141–142 °C, and **12** (30 mg, 127 μmol, 17% yield) as a solid, mp 146–148 °C. Compound **11**: ^1H NMR (400 MHz, $CDCl_3$): δ 4.38 (q, 7.1 Hz, 2H), 3.13 (ddd, 13.2 Hz, 7.7 Hz, 4.4 Hz, 1H), 2.83 (m, 1H), 2.74 (dt, J_d = 13.2 Hz, J_t = 8.2 Hz, 1H), 2.62 (dd, 12.3 Hz, 6.0 Hz, 1H), 2.43 (m, 1H), 2.41 (s, 3H), 2.14 (s, 3H), 2.09 (m, 2H), 1.81 (m, 1H), 1.54 (s, 3H), 1.38 (t, 7.1 Hz, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 165.8, 113.6, 71.7, 67.2, 63.8, 49.4, 47.6, 40.5, 32.9, 31.5, 16.1, 14.2, 13.2, 13.0. IR (KBr): 3213, 1754, 1324, 1058 cm^{-1}. $C_{14}H_{23}N_3O_2$. Compound **12**: ^1H NMR (400 MHz, $CDCl_3$): δ 6.78 (bs, 1H), 3.13 (dd, 18.5 Hz, 6.2 Hz, 1H), 2.96 (m, 2H), 2.51 (s, 3H), 2.48 (dd, 18.5 Hz, 4.9 Hz, 1H), 2.35 (dt, J_t = 12.1 Hz, J_d = 5.7 Hz, 1H), 2.26 (s, 3H), 1.73 (ddd, 18.5 Hz, 11.9 Hz, 6.6 Hz, 1H), 1.51 (m, 1H), 1.22 (s, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 204.6, 165.8, 115.4, 66.4, 57.5, 49.1, 48.2, 41.3, 37.9, 30.9, 30.4, 22.5. IR (KBr): 3200, 1729, 1706, 1354, 1177 cm^{-1}. $C_{12}H_{17}N_3O_2$.

Diethyl (4a*R,8a*S*)-7-acetoxy-4a-cyano-2-methyl-2,3,4,4a,8,8a-hexahydro-1*H*-isoquinolin-5-one-1,1-dicarboxylate (13).** Sodium metal (34 mg, 1.48 mmol) was dissolved in anhydrous ethanol (5 mL) under N_2. A solution of **3d** (246 mg, 621 μmol) in anhydrous ethanol (2 mL) was added, and the reaction mixture was heated to 90 °C for 1 h. After cooling to rt, the

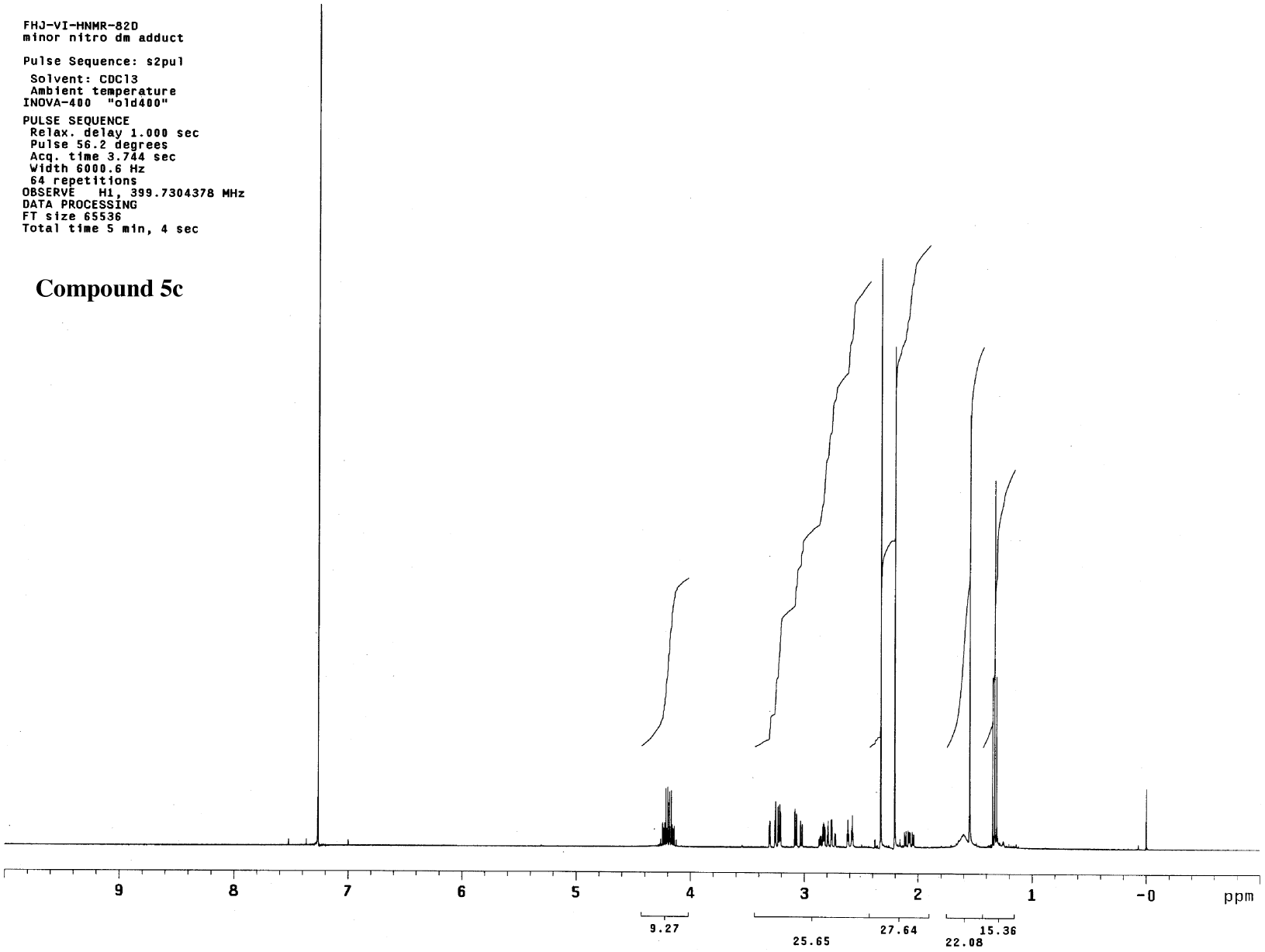
solvent was evaporated, Ac_2O (5 mL, 53 mmol) was added, and the mixture was allowed to stir overnight. The solvent was evaporated, and the slurry was suspended in saturated aqueous $NaHCO_3$. The aqueous layer was extracted three times with ether. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash chromatography (20% EtOAc in petroleum ether as eluant) to afford **13** (154 mg, 392 μmol, 63% yield) as a white solid, mp 93–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.15 (d, 2.4 Hz, 1H), 4.34 (q, 7.2 Hz, 4H), 3.57 (ddd, 18.4 Hz, 12.0 Hz, 2.4 Hz, 1H), 3.52 (td, J_t = 13.2 Hz, J_d = 2.8 Hz, 1H), 2.94 (dd, 12.0 Hz, 3.6 Hz, 1H), 2.89 (ddd, 13.2 Hz, 4.8 Hz, 2.0 Hz, 1H), 2.57 (s, 3H), 2.48 (dd, 18.8 Hz, 3.6 Hz, 1H), 2.41 (dt, J_d = 14.0 Hz, J_t = 2.4 Hz, 1H), 2.25 (s, 3H), 1.88 (td, J_t = 13.6 Hz, J_d = 5.2 Hz, 1H), 1.39 (t, 6.8 Hz, 3H), 1.34 (t, 7.2 Hz, 3H). ^{13}C{H} NMR (50 MHz, $CDCl_3$): δ . 189.1, 170.0, 168.2, 167.2, 166.6, 115.8, 113.3, 73.3, 62.8, 61.8, 47.3, 43.9, 43.5, 40.9, 30.2, 29.5, 21.3, 13.8. IR (KBr): 2256, 2231, 1779, 1733, 1689, 1646, 1232, 1138, 1097 cm^{-1}. Anal. Calcd for $C_{19}H_{24}N_2O_7$: C, 58.16; H, 6.16. Found: C, 58.13; H, 6.30.

FHJ-VI-HNMR-82D
minor nitro dm adduct

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "old400"

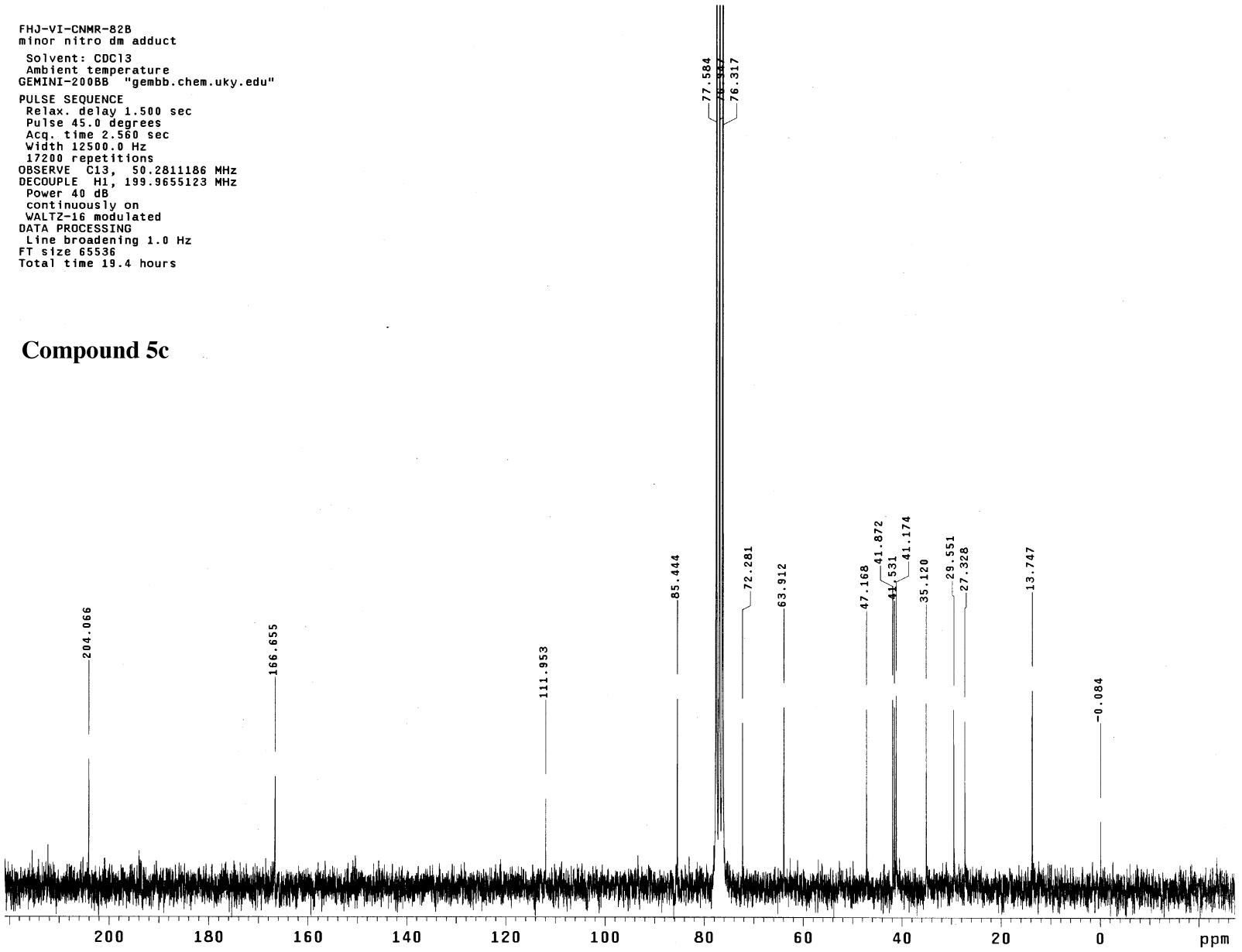
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 56.2 degrees
Acq. time 3.744 sec
Width 6000.6 Hz
64 repetitions
OBSERVE H1, 399.7304378 MHz
DATA PROCESSING
FT size 65536
Total time 5 min, 4 sec

Compound 5c



FHJ-VI-CNMR-82B
minor nitro dm adduct
Solvent: CDCl3
Ambient temperature
GEMINI-200BB "gembb.chem.uky.edu"
PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 2.560 sec
Width 12500.0 Hz
17200 repetitions
OBSERVE C13, 50.2811186 MHz
DECOUPLE H1, 199.9655123 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 19.4 hours

Compound 5c



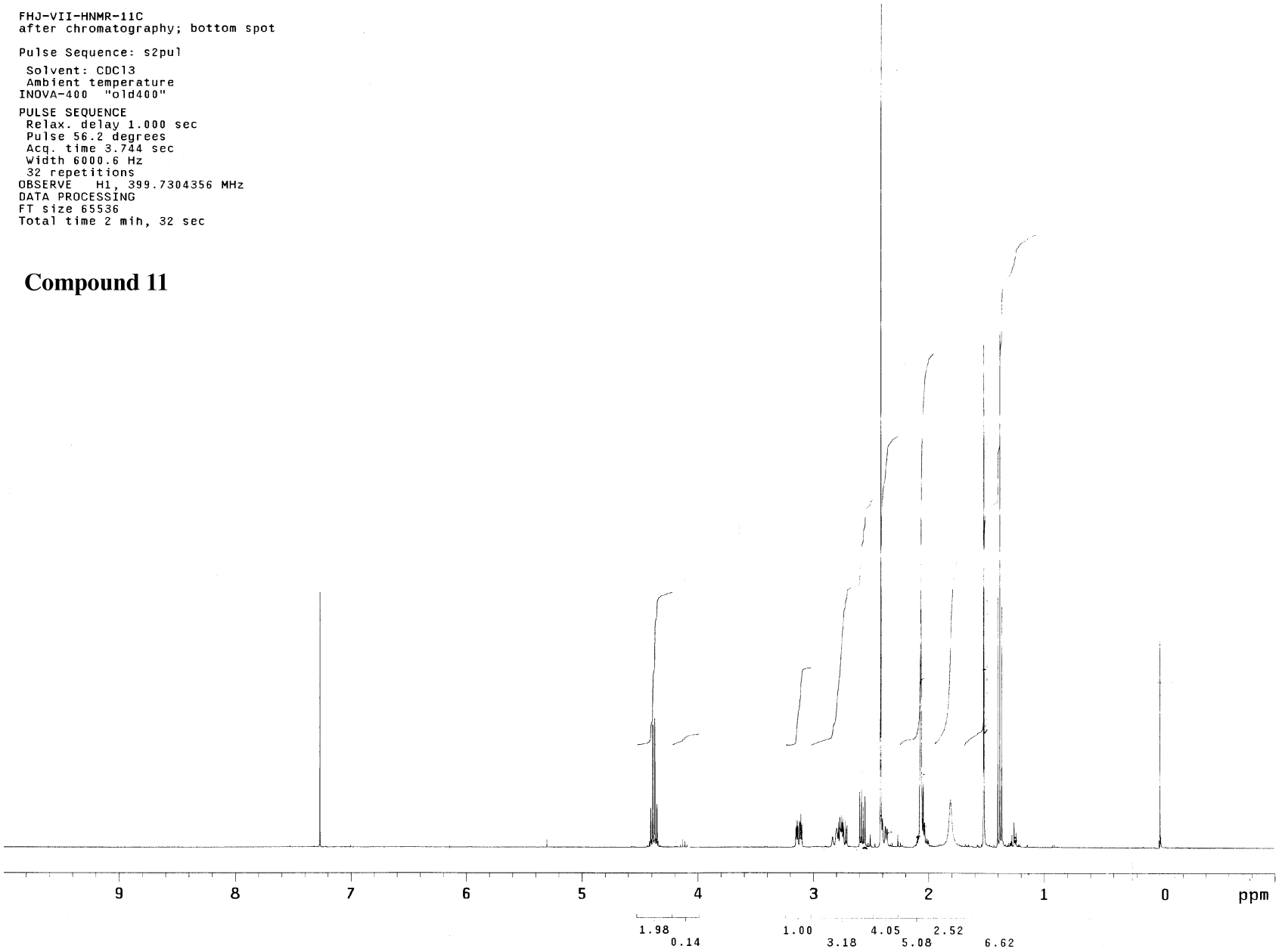
FHJ-VII-HNMR-11C
after chromatography; bottom spot

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
INOVA-400 "old400"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 56.2 degrees
Acq. time 3.744 sec
Width 6000.6 Hz
32 repetitions
OBSERVE H1, 399.7304356 MHz
DATA PROCESSING
FT size 65536
Total time 2 min, 32 sec

Compound 11

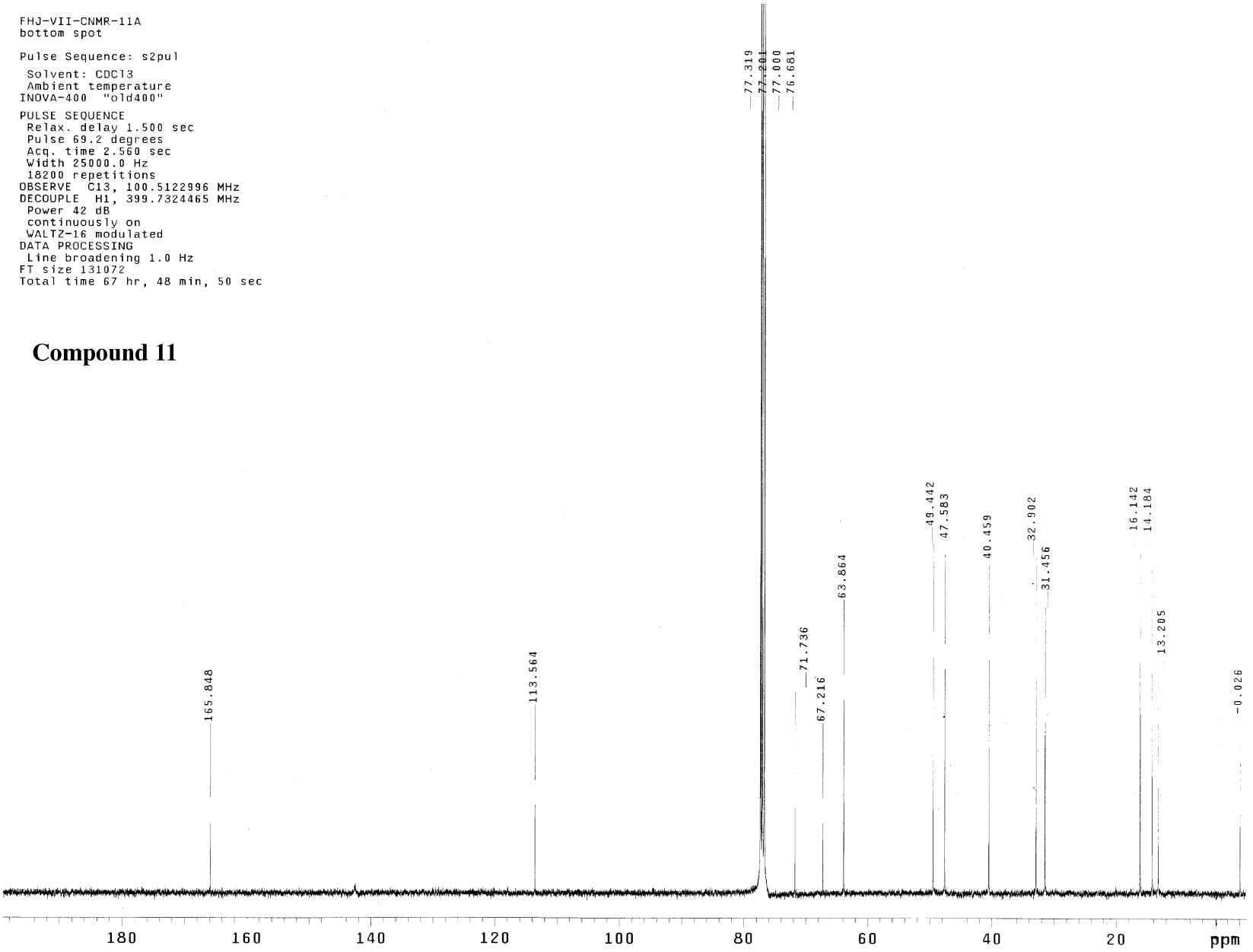


FHJ-VII-CNMR-11A
bottom spot

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "old400"

PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 69.2 degrees
Acq. time 2.560 sec
Width 25000.0 Hz
18200 repetitions
OBSERVE C13, 100.5122996 MHz
DECOUPLE H1, 399.7324465 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 67 hr, 48 min, 50 sec

Compound 11

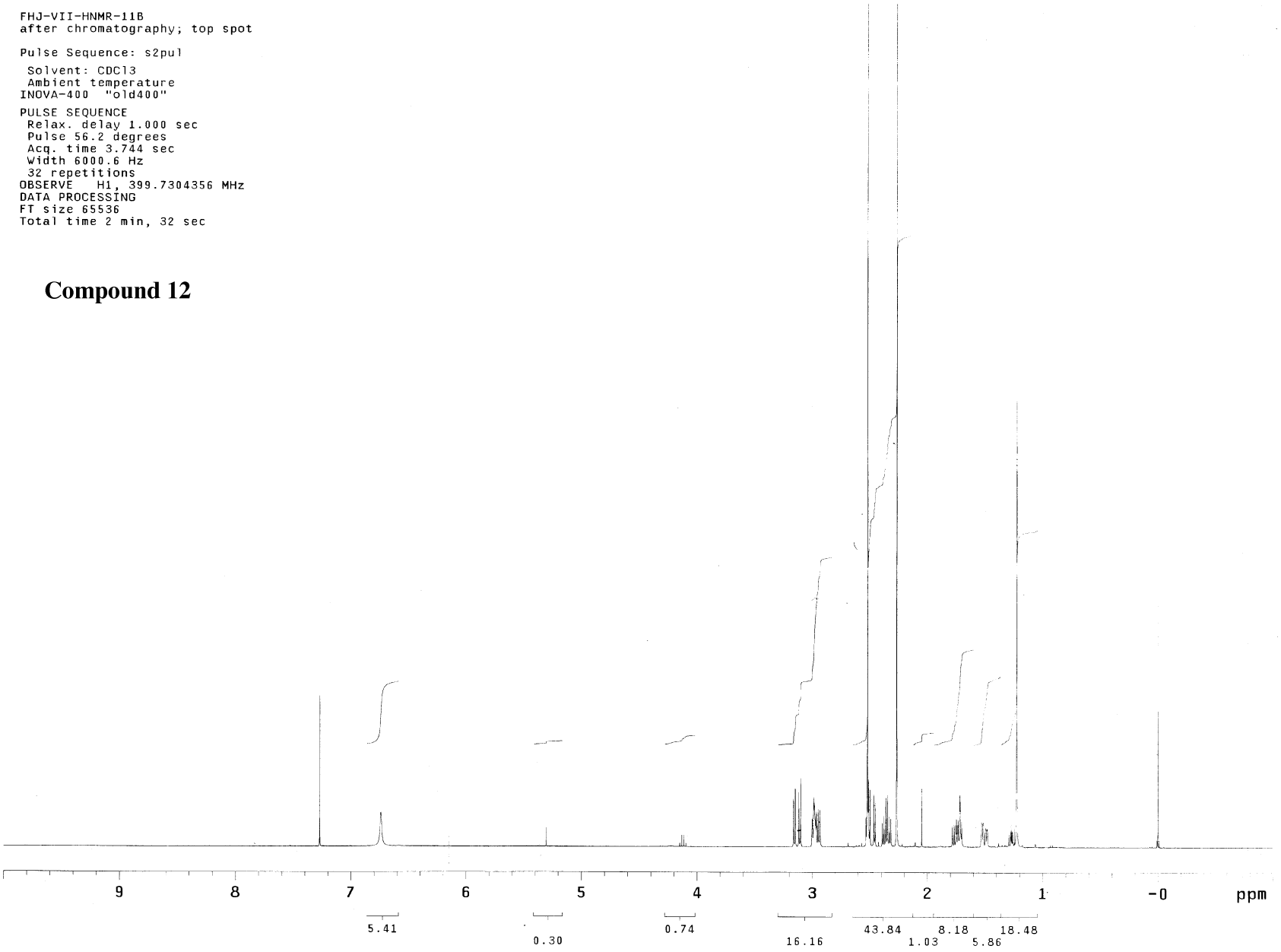


FHJ-VII-HNMR-11B
after chromatography; top spot

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "old400"

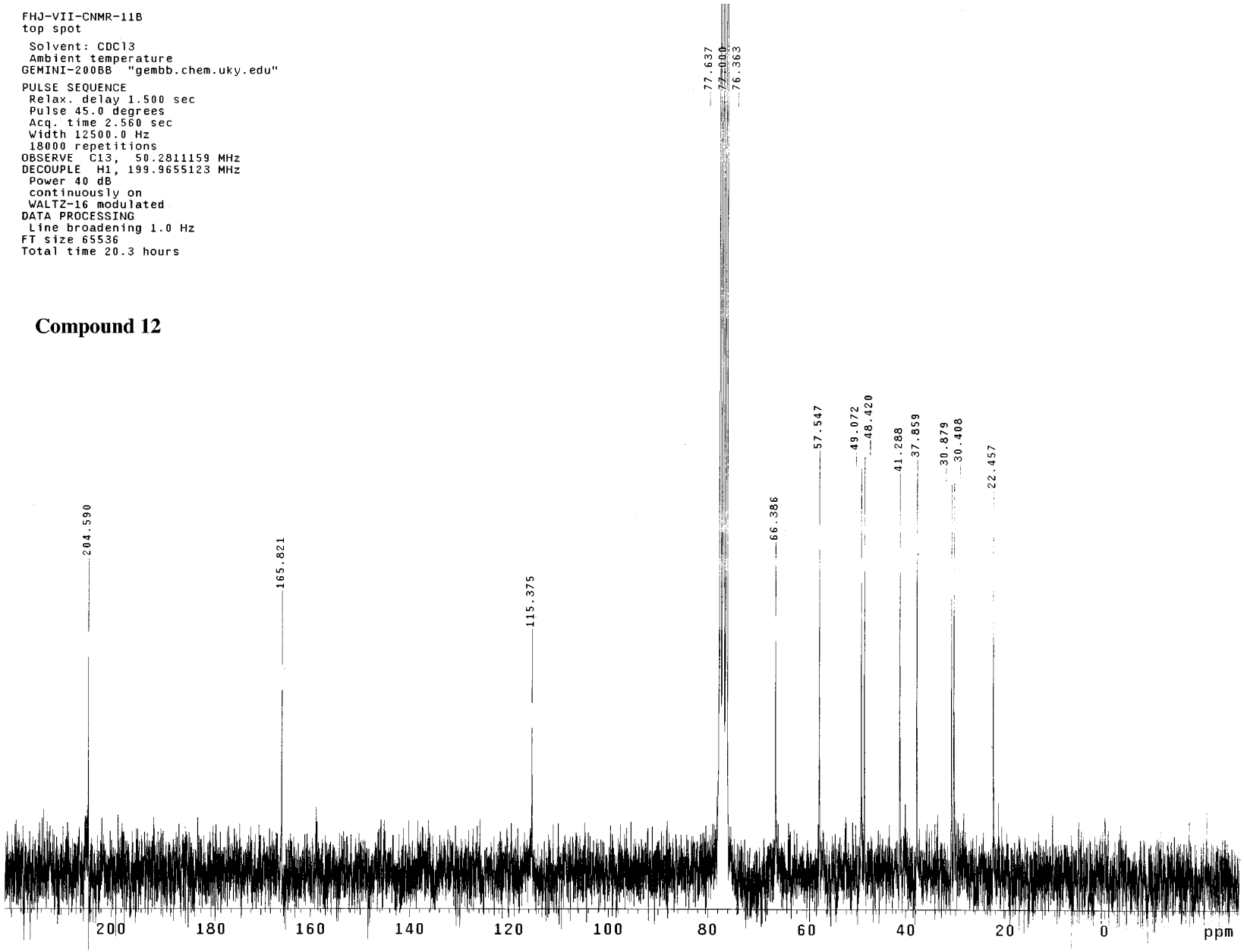
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 56.2 degrees
Acq. time 3.744 sec
Width 6000.6 Hz
32 repetitions
OBSERVE H1, 399.7304356 MHz
DATA PROCESSING
FT size 65536
Total time 2 min, 32 sec

Compound 12



FHJ-VII-CNMR-11B
top spot
Solvent: CDCl3
Ambient temperature
GEMINI-200BB "gembb.chem.uky.edu"
PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 2.560 sec
Width 12500.0 Hz
18000 repetitions
OBSERVE C13, 50.2811159 MHz
DECOUPLE H1, 199.9655123 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 20.3 hours

Compound 12



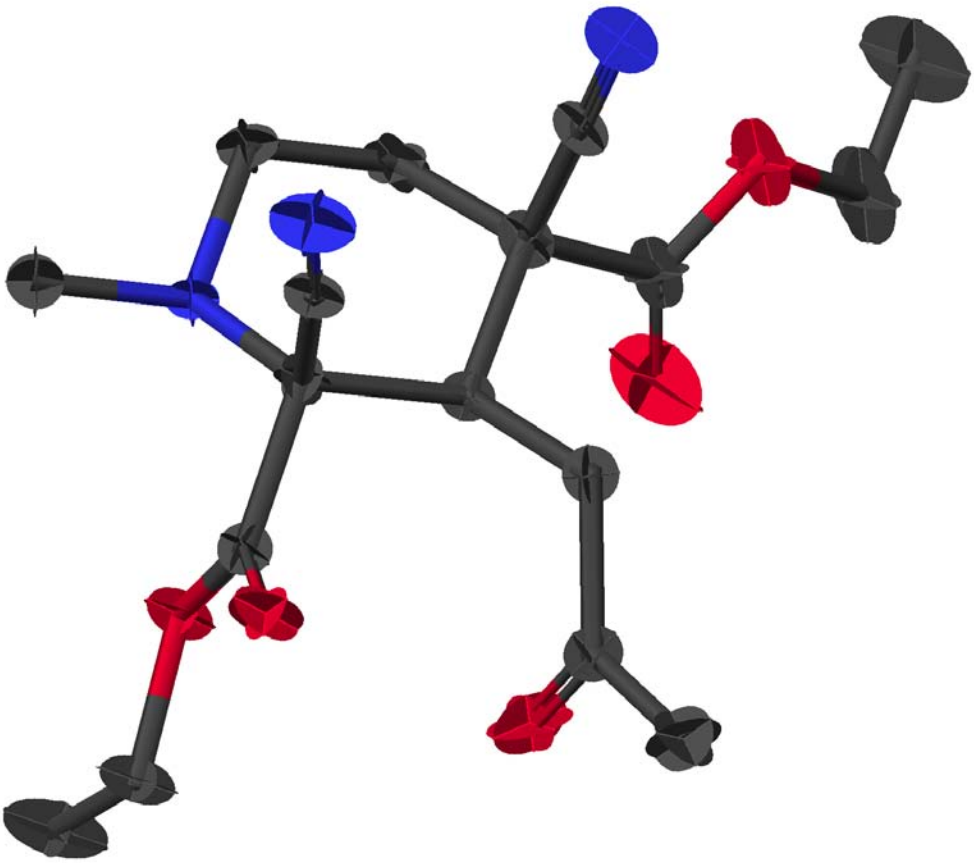


Figure 1. Thermal ellipsoid plot of **3b** (50% probability ellipsoids). One of the ethyl groups is disordered; only the major conformer is shown for clarity.

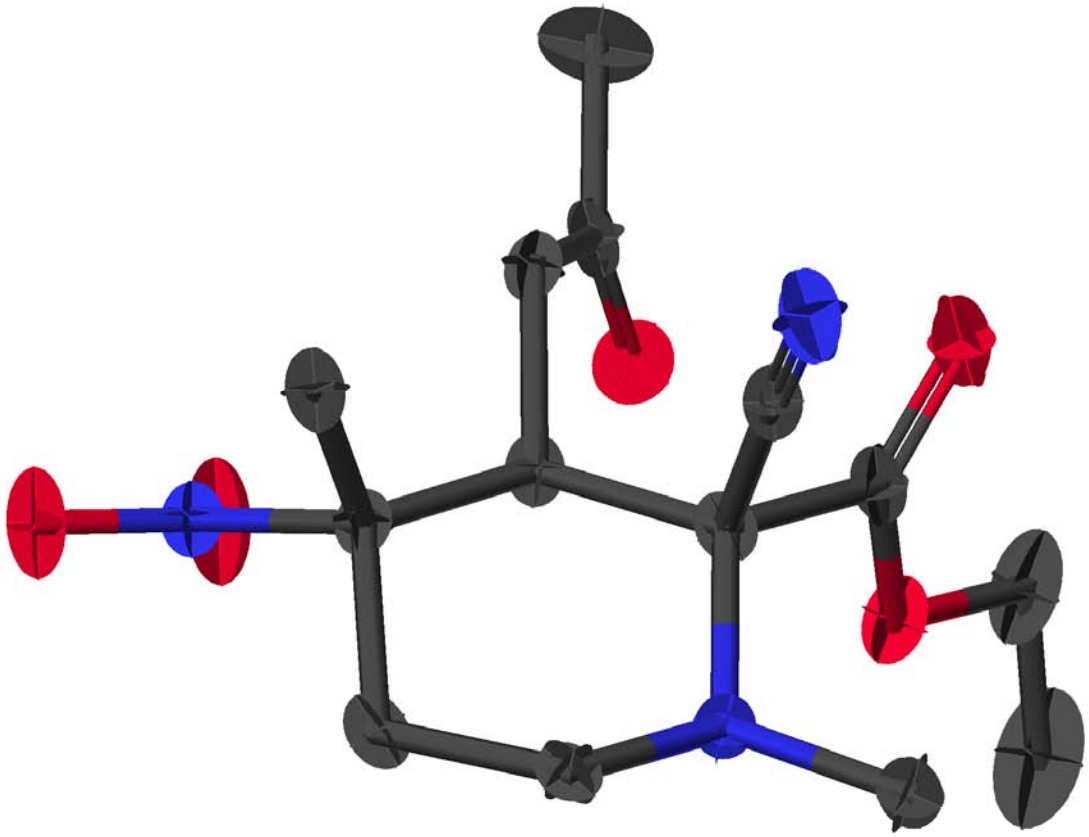


Figure 2. Thermal ellipsoid plot of **3c** (50% probability ellipsoids).

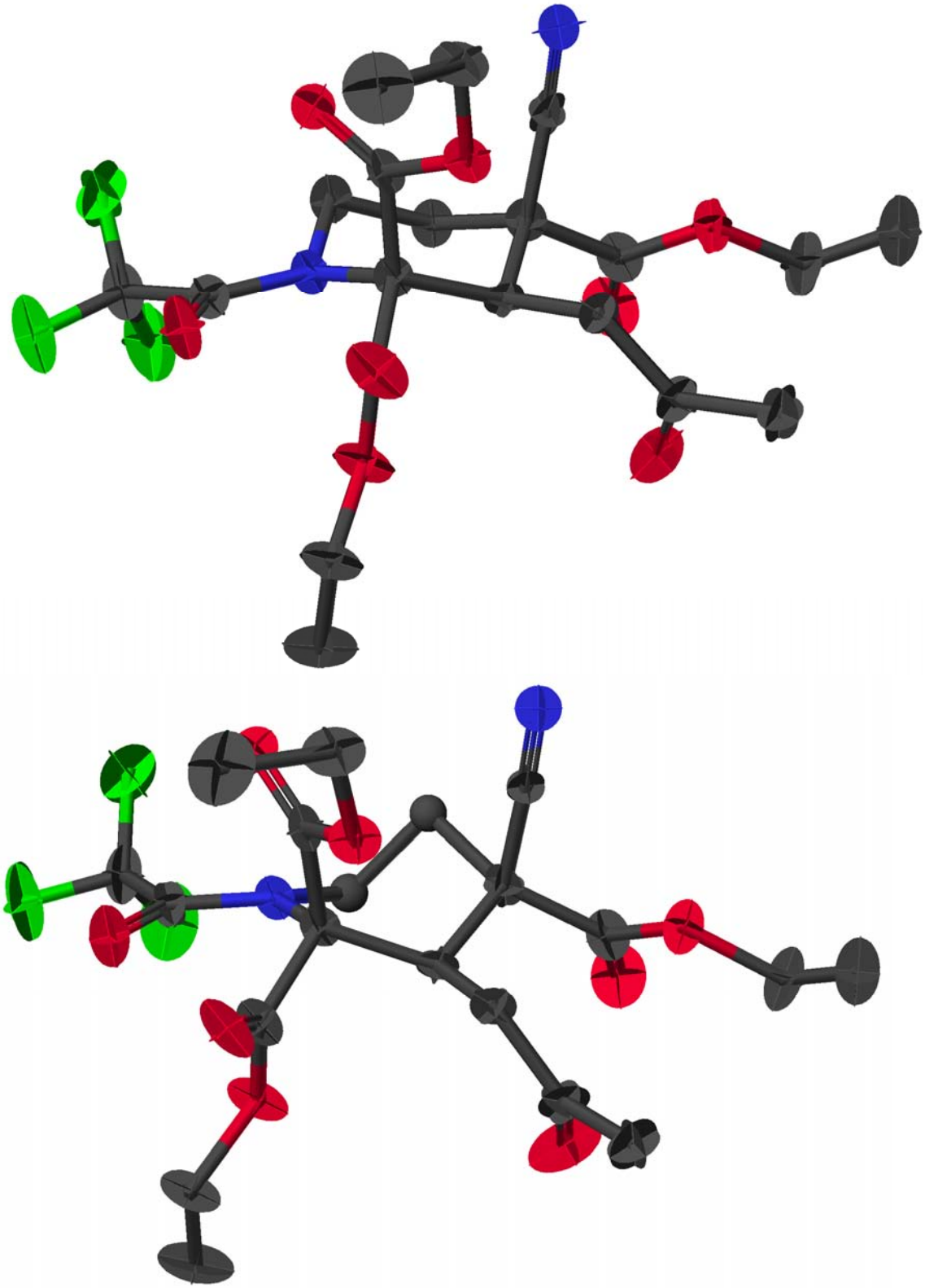


Figure 3. Thermal ellipsoid plot of the chair and twist-boat conformers of **3e** (50% probability ellipsoids). One of the ethyl groups is disordered; only one Et conformer in each structure is shown for clarity.

Table 1. Crystal data and structure refinement for **3b**, **3c**, and **3e**. Refinement method for all structures is full-matrix least-squares on F^2.

	3b	**3c**	**3e**
Empirical formula	$C_{17}H_{23}N_3O_5$	$C_{14}H_{21}N_3O_5$	$C_{20}H_{25}F_3N_2O_8$
Formula weight	349.38	311.34	478.42
Temp. (K)	173(1)	173(1)	173(1)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	C2/c
a (Å)	7.9260(16)	6.5630(4)	29.928(4)
b (Å)	8.6400(17)	10.7480(6)	9.4450(10)
c (Å)	26.257(5)	22.4950(12)	18.951(3)
α (°)	90	90	90
β (°)	93.35(3)	90	120.43(1)
γ (°)	90	90	90
V (Å^3)	1795.0(6)	1586.8(2)	4619.0(1)
Z	4	4	8
Calculated density (Mg/m^3)	1.293	1.303	1.376
μ (mm^{-1})	0.096	0.100	0.12
F(000)	744	664	2000
Crystal size (mm)	.38 × .36 × .26	.44 × .18 × .18	.44 × .40 × .13
Θ range (°)	1.55 to 25.00	1.81 to 25.41	1.58 to 25.00
Limiting indices	$-9 \le h \le 9$ $-10 \le k \le 10$ $-31 \le l \le 31$	$-7 \le h \le 7$ $-12 \le k \le 12$ $-27 \le l \le 27$	$-35 \le h \le 35$ $-10 \le k \le 11$ $-22 \le l \le 22$
Reflections collected / unique	7666 / 3065 [R(int) = 0.0319]	9541 / 1702 [R(int) = 0.0528]	7128 / 4082 [R(int) = 0.0224]
Completeness to Θ = 25.00°	96.9 %	99.8 %	100.0 %
Absorption correction	None	None	None
Data / restraints / parameters	3065 / 416 / 240	1702 / 0 / 204	4082 / 3 / 316
Goodness-of-fit on F^2	1.076	1.092	1.030
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0508 wR2 = 0.1081	R1 = 0.0435 wR2 = 0.0865	R1 = 0.0497 wR2 = 0.1181
R indices (all data)	R1 = 0.0704 wR2 = 0.1169	R1 = 0.0540 wR2 = 0.0897	R1 = 0.0705 wR2 = 0.1301
Extinction coefficient	0.0058(13)	0.0067(19)	
Largest diff. peak and hole (e·Å^{-3})	0.285 and –0.298	0.165 and –0.163	0.318 and –0.235

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **3b**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	7549(3)	10654(2)	81(1)	36(1)
N(1)	8540(2)	9845(2)	489(1)	26(1)
C(2)	7506(2)	8843(2)	787(1)	24(1)
C(3)	8583(2)	7992(2)	1220(1)	25(1)
C(4)	9736(2)	9117(2)	1540(1)	30(1)
C(5)	10701(2)	10182(2)	1186(1)	34(1)
C(6)	9515(2)	10980(2)	800(1)	31(1)
C(7)	6657(2)	7565(2)	449(1)	26(1)
O(7)	5261(2)	7099(2)	517(1)	33(1)
O(8)	7672(2)	7038(2)	106(1)	32(1)
C(8)	6995(3)	5717(2)	-193(1)	39(1)
C(9)	8170(3)	5347(3)	-592(1)	59(1)
C(10)	6080(2)	9731(2)	1001(1)	27(1)
N(10)	5026(2)	10501(2)	1138(1)	42(1)
C(11)	7501(2)	6990(2)	1553(1)	31(1)
C(12)	7162(2)	5358(2)	1360(1)	31(1)
O(12)	8000(2)	4783(2)	1038(1)	47(1)
C(13)	5773(3)	4510(3)	1596(1)	46(1)
C(14)	8750(3)	10067(2)	1885(1)	32(1)
N(14)	7981(2)	10815(2)	2144(1)	45(1)
C(15)	11090(3)	8189(3)	1848(1)	42(1)
O(15)	11753(2)	7080(2)	1686(1)	81(1)
O(16)	11478(2)	8827(2)	2295(1)	59(1)
C(16)	12864(10)	8240(12)	2644(4)	69(2)
C(17)	14416(5)	8966(6)	2480(3)	59(2)
C(16')	12970(20)	7980(20)	2527(10)	69(2)
C(17')	14040(20)	8981(12)	2824(8)	87(6)

Table 3. Bond lengths [Å] for **3b**.

C(1)-N(1)	1.467(2)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
N(1)-C(2)	1.452(2)
N(1)-C(6)	1.467(2)
C(2)-C(10)	1.502(3)
C(2)-C(7)	1.545(2)
C(2)-C(3)	1.564(2)
C(3)-C(11)	1.529(3)
C(3)-C(4)	1.549(2)
C(3)-H(3)	1.0000
C(4)-C(14)	1.478(3)
C(4)-C(15)	1.533(3)
C(4)-C(5)	1.542(3)
C(5)-C(6)	1.509(3)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-O(7)	1.200(2)
C(7)-O(8)	1.324(2)
O(8)-C(8)	1.469(2)
C(8)-C(9)	1.478(3)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-N(10)	1.142(2)
C(11)-C(12)	1.517(3)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-O(12)	1.210(2)
C(12)-C(13)	1.488(3)
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-N(14)	1.142(2)
C(15)-O(15)	1.184(3)
C(15)-O(16)	1.317(2)
O(16)-C(16)	1.478(6)
O(16)-C(16')	1.492(13)
C(16)-C(17)	1.467(10)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(16')-C(17')	1.414(14)
C(16')-H(16C)	0.9900

C(16')-H(16D)	0.9900
C(17')-H(17D)	0.9800
C(17')-H(17E)	0.9800
C(17')-H(17F)	0.9800

Table 4. Bond angles [°] for **3b**.

N(1)-C(1)-H(1A)	109.5
N(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
N(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(2)-N(1)-C(1)	112.46(14)
C(2)-N(1)-C(6)	113.22(14)
C(1)-N(1)-C(6)	109.24(14)
N(1)-C(2)-C(10)	110.99(15)
N(1)-C(2)-C(7)	110.93(14)
C(10)-C(2)-C(7)	105.52(14)
N(1)-C(2)-C(3)	111.77(14)
C(10)-C(2)-C(3)	111.01(14)
C(7)-C(2)-C(3)	106.36(14)
C(11)-C(3)-C(4)	112.18(15)
C(11)-C(3)-C(2)	112.45(15)
C(4)-C(3)-C(2)	112.25(15)
C(11)-C(3)-H(3)	106.5
C(4)-C(3)-H(3)	106.5
C(2)-C(3)-H(3)	106.5
C(14)-C(4)-C(15)	110.21(16)
C(14)-C(4)-C(5)	109.68(16)
C(15)-C(4)-C(5)	105.91(16)
C(14)-C(4)-C(3)	111.36(15)
C(15)-C(4)-C(3)	109.35(16)
C(5)-C(4)-C(3)	110.19(15)
C(6)-C(5)-C(4)	111.48(15)
C(6)-C(5)-H(5A)	109.3
C(4)-C(5)-H(5A)	109.3
C(6)-C(5)-H(5B)	109.3
C(4)-C(5)-H(5B)	109.3
H(5A)-C(5)-H(5B)	108.0
N(1)-C(6)-C(5)	110.81(15)
N(1)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6A)	109.5
N(1)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	108.1
O(7)-C(7)-O(8)	125.95(17)
O(7)-C(7)-C(2)	121.98(16)
O(8)-C(7)-C(2)	112.01(15)
C(7)-O(8)-C(8)	114.45(14)
O(8)-C(8)-C(9)	108.79(16)
O(8)-C(8)-H(8A)	109.9
C(9)-C(8)-H(8A)	109.9
O(8)-C(8)-H(8B)	109.9
C(9)-C(8)-H(8B)	109.9
H(8A)-C(8)-H(8B)	108.3
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5

H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
N(10)-C(10)-C(2)	174.5(2)
C(12)-C(11)-C(3)	115.38(16)
C(12)-C(11)-H(11A)	108.4
C(3)-C(11)-H(11A)	108.4
C(12)-C(11)-H(11B)	108.4
C(3)-C(11)-H(11B)	108.4
H(11A)-C(11)-H(11B)	107.5
O(12)-C(12)-C(13)	122.54(18)
O(12)-C(12)-C(11)	121.40(18)
C(13)-C(12)-C(11)	116.05(17)
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
N(14)-C(14)-C(4)	178.9(2)
O(15)-C(15)-O(16)	125.0(2)
O(15)-C(15)-C(4)	122.99(19)
O(16)-C(15)-C(4)	111.86(19)
C(15)-O(16)-C(16)	122.3(4)
C(15)-O(16)-C(16')	107.2(9)
C(16)-O(16)-C(16')	15.3(12)
C(17)-C(16)-O(16)	106.1(6)
C(17)-C(16)-H(16A)	110.4
O(16)-C(16)-H(16A)	110.5
C(17)-C(16)-H(16B)	110.6
O(16)-C(16)-H(16B)	110.6
H(16A)-C(16)-H(16B)	108.7
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.4
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(17')-C(16')-O(16)	110.8(12)
C(17')-C(16')-H(16C)	109.4
O(16)-C(16')-H(16C)	109.5
C(17')-C(16')-H(16D)	109.6
O(16)-C(16')-H(16D)	109.5
H(16C)-C(16')-H(16D)	108.0
C(16')-C(17')-H(17D)	109.4
C(16')-C(17')-H(17E)	109.6
H(17D)-C(17')-H(17E)	109.5
C(16')-C(17')-H(17F)	109.4
H(17D)-C(17')-H(17F)	109.5
H(17E)-C(17')-H(17F)	109.5

Table 5. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **3b**. The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
C(1)	40(1)	38(1)	29(1)	6(1)	-4(1)	-5(1)
N(1)	27(1)	26(1)	23(1)	2(1)	-2(1)	-8(1)
C(2)	25(1)	24(1)	23(1)	-2(1)	2(1)	-4(1)
C(3)	30(1)	22(1)	24(1)	-3(1)	-1(1)	0(1)
C(4)	33(1)	30(1)	26(1)	-3(1)	-4(1)	-2(1)
C(5)	32(1)	37(1)	34(1)	-6(1)	-3(1)	-12(1)
C(6)	36(1)	28(1)	31(1)	-1(1)	0(1)	-12(1)
C(7)	29(1)	25(1)	23(1)	0(1)	0(1)	-3(1)
O(7)	29(1)	35(1)	36(1)	-7(1)	3(1)	-10(1)
O(8)	34(1)	34(1)	30(1)	-13(1)	7(1)	-13(1)
C(8)	44(1)	36(1)	38(1)	-19(1)	7(1)	-16(1)
C(9)	58(2)	64(2)	58(2)	-36(1)	22(1)	-23(1)
C(10)	28(1)	26(1)	26(1)	-2(1)	-3(1)	-6(1)
N(10)	35(1)	41(1)	49(1)	-10(1)	0(1)	0(1)
C(11)	40(1)	26(1)	25(1)	0(1)	3(1)	-2(1)
C(12)	39(1)	25(1)	28(1)	1(1)	1(1)	2(1)
O(12)	59(1)	28(1)	55(1)	-5(1)	21(1)	-1(1)
C(13)	58(1)	38(1)	42(1)	-4(1)	12(1)	-16(1)
C(14)	41(1)	30(1)	22(1)	-2(1)	-9(1)	-6(1)
N(14)	58(1)	42(1)	34(1)	-10(1)	-3(1)	-2(1)
C(15)	42(1)	44(1)	38(1)	-1(1)	-14(1)	2(1)
O(15)	88(1)	76(1)	74(1)	-25(1)	-39(1)	45(1)
O(16)	65(1)	66(1)	43(1)	0(1)	-30(1)	6(1)
C(16)	70(2)	84(4)	48(5)	3(3)	-35(3)	10(2)
C(17)	44(2)	61(3)	71(4)	-10(3)	-4(2)	19(2)
C(16')	70(2)	84(4)	48(5)	3(3)	-35(3)	10(2)
C(17')	79(8)	81(7)	92(12)	-29(7)	-64(9)	31(6)

Table 6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **3b**.

	x	y	z	U(eq)
H(1A)	8299	11309	-110	54
H(1B)	6690	11299	231	54
H(1C)	6996	9893	-150	54
H(3)	9350	7269	1046	30
H(5A)	11334	10970	1393	41
H(5B)	11529	9560	1005	41
H(6A)	8732	11655	979	38
H(6B)	10174	11640	575	38
H(8A)	5868	5979	-352	47
H(8B)	6872	4811	32	47
H(9A)	7732	4463	-794	89
H(9B)	9281	5086	-432	89
H(9C)	8275	6245	-816	89
H(11A)	8070	6925	1898	37
H(11B)	6403	7515	1586	37
H(13A)	5660	3475	1445	68
H(13B)	4711	5079	1534	68
H(13C)	6033	4417	1964	68
H(16A)	12671	8524	3001	83
H(16B)	12943	7098	2621	83
H(17A)	15379	8624	2703	88
H(17B)	14310	10094	2501	88
H(17C)	14594	8664	2128	88
H(16C)	12579	7128	2745	83
H(16D)	13612	7509	2254	83
H(17D)	14964	8386	2991	130
H(17E)	13385	9484	3083	130
H(17F)	14498	9770	2603	130

Table 7. Torsion angles [°] for **3b**.

C(1)-N(1)-C(2)-C(10)	-55.44(19)
C(6)-N(1)-C(2)-C(10)	68.98(18)
C(1)-N(1)-C(2)-C(7)	61.53(19)
C(6)-N(1)-C(2)-C(7)	-174.04(14)
C(1)-N(1)-C(2)-C(3)	-179.96(14)
C(6)-N(1)-C(2)-C(3)	-55.53(19)
N(1)-C(2)-C(3)-C(11)	177.33(14)
C(10)-C(2)-C(3)-C(11)	52.82(19)
C(7)-C(2)-C(3)-C(11)	-61.47(18)
N(1)-C(2)-C(3)-C(4)	49.71(19)
C(10)-C(2)-C(3)-C(4)	-74.80(18)
C(7)-C(2)-C(3)-C(4)	170.90(14)
C(11)-C(3)-C(4)-C(14)	-53.9(2)
C(2)-C(3)-C(4)-C(14)	73.86(19)
C(11)-C(3)-C(4)-C(15)	68.1(2)
C(2)-C(3)-C(4)-C(15)	-164.11(16)
C(11)-C(3)-C(4)-C(5)	-175.85(16)
C(2)-C(3)-C(4)-C(5)	-48.1(2)
C(14)-C(4)-C(5)-C(6)	-70.2(2)
C(15)-C(4)-C(5)-C(6)	170.89(16)
C(3)-C(4)-C(5)-C(6)	52.7(2)
C(2)-N(1)-C(6)-C(5)	60.3(2)
C(1)-N(1)-C(6)-C(5)	-173.55(15)
C(4)-C(5)-C(6)-N(1)	-58.3(2)
N(1)-C(2)-C(7)-O(7)	-144.43(17)
C(10)-C(2)-C(7)-O(7)	-24.2(2)
C(3)-C(2)-C(7)-O(7)	93.8(2)
N(1)-C(2)-C(7)-O(8)	38.2(2)
C(10)-C(2)-C(7)-O(8)	158.50(15)
C(3)-C(2)-C(7)-O(8)	-83.52(17)
O(7)-C(7)-O(8)-C(8)	-2.9(3)
C(2)-C(7)-O(8)-C(8)	174.36(15)
C(7)-O(8)-C(8)-C(9)	174.50(19)
N(1)-C(2)-C(10)-N(10)	13(2)
C(7)-C(2)-C(10)-N(10)	-107.4(19)
C(3)-C(2)-C(10)-N(10)	137.8(19)
C(4)-C(3)-C(11)-C(12)	-145.66(16)
C(2)-C(3)-C(11)-C(12)	86.7(2)
C(3)-C(11)-C(12)-O(12)	16.7(3)
C(3)-C(11)-C(12)-C(13)	-164.55(17)
C(15)-C(4)-C(14)-N(14)	158(11)
C(5)-C(4)-C(14)-N(14)	42(11)
C(3)-C(4)-C(14)-N(14)	-80(11)
C(14)-C(4)-C(15)-O(15)	160.7(2)
C(5)-C(4)-C(15)-O(15)	-80.7(3)
C(3)-C(4)-C(15)-O(15)	38.0(3)
C(14)-C(4)-C(15)-O(16)	-23.0(2)
C(5)-C(4)-C(15)-O(16)	95.6(2)
C(3)-C(4)-C(15)-O(16)	-145.67(18)
O(15)-C(15)-O(16)-C(16)	2.2(6)
C(4)-C(15)-O(16)-C(16)	-174.0(5)

O(15)-C(15)-O(16)-C(16')	4.5(11)
C(4)-C(15)-O(16)-C(16')	-171.7(10)
C(15)-O(16)-C(16)-C(17)	84.8(8)
C(16')-O(16)-C(16)-C(17)	76(5)
C(15)-O(16)-C(16')-C(17')	146(2)
C(16)-O(16)-C(16')-C(17')	-41(3)

Table 8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **3c**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N(1)	2942(3)	8664(2)	8804(1)	26(1)
C(1)	2348(4)	7442(2)	8568(1)	33(1)
C(2)	5078(4)	8951(2)	8699(1)	24(1)
C(3)	5606(4)	10286(2)	8930(1)	24(1)
N(4)	4903(4)	11893(2)	9697(1)	32(1)
O(4A)	4883(4)	12609(2)	9281(1)	53(1)
O(4B)	4796(4)	12228(2)	10213(1)	47(1)
C(4)	4956(4)	10468(2)	9581(1)	24(1)
C(5)	2743(4)	10062(2)	9663(1)	29(1)
C(6)	2431(4)	8743(2)	9436(1)	27(1)
O(7)	7227(3)	8571(2)	7854(1)	39(1)
C(7)	5604(5)	8928(2)	8030(1)	28(1)
O(8)	4121(3)	9381(2)	7703(1)	33(1)
C(8)	4530(6)	9435(3)	7063(1)	46(1)
C(9)	2577(7)	9804(3)	6774(1)	68(1)
N(10)	7318(4)	7215(2)	9208(1)	36(1)
C(10)	6422(4)	7990(2)	8977(1)	26(1)
C(11)	7840(4)	10627(2)	8820(1)	26(1)
O(12)	6891(3)	11590(2)	7905(1)	36(1)
C(12)	8245(4)	11308(2)	8243(1)	29(1)
C(13)	10433(5)	11618(3)	8128(1)	51(1)
C(14)	6347(4)	9911(2)	10050(1)	31(1)

Table 9. Bond lengths [Å] for **3c**.

N(1)-C(2)	1.455(3)
N(1)-C(6)	1.461(3)
N(1)-C(1)	1.470(3)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(10)	1.495(4)
C(2)-C(7)	1.546(3)
C(2)-C(3)	1.564(3)
C(3)-C(11)	1.531(4)
C(3)-C(4)	1.539(3)
C(3)-H(3)	1.0000
N(4)-O(4A)	1.212(3)
N(4)-O(4B)	1.216(3)
N(4)-C(4)	1.555(3)
C(4)-C(14)	1.518(4)
C(4)-C(5)	1.528(4)
C(5)-C(6)	1.521(3)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
O(7)-C(7)	1.199(3)
C(7)-O(8)	1.313(3)
O(8)-C(8)	1.465(3)
C(8)-C(9)	1.491(5)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
N(10)-C(10)	1.145(3)
C(11)-C(12)	1.513(3)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
O(12)-C(12)	1.208(3)
C(12)-C(13)	1.497(4)
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800

Table 10. Bond angles [°] for **3c**.

C(2)-N(1)-C(6)	111.5(2)
C(2)-N(1)-C(1)	112.8(2)
C(6)-N(1)-C(1)	110.06(19)
N(1)-C(1)-H(1A)	109.5
N(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
N(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
N(1)-C(2)-C(10)	110.7(2)
N(1)-C(2)-C(7)	111.7(2)
C(10)-C(2)-C(7)	105.3(2)
N(1)-C(2)-C(3)	110.8(2)
C(10)-C(2)-C(3)	111.4(2)
C(7)-C(2)-C(3)	106.75(19)
C(11)-C(3)-C(4)	112.9(2)
C(11)-C(3)-C(2)	112.2(2)
C(4)-C(3)-C(2)	111.7(2)
C(11)-C(3)-H(3)	106.5
C(4)-C(3)-H(3)	106.5
C(2)-C(3)-H(3)	106.5
O(4A)-N(4)-O(4B)	123.3(2)
O(4A)-N(4)-C(4)	119.7(2)
O(4B)-N(4)-C(4)	116.9(2)
C(14)-C(4)-C(5)	112.0(2)
C(14)-C(4)-C(3)	116.4(2)
C(5)-C(4)-C(3)	110.0(2)
C(14)-C(4)-N(4)	106.6(2)
C(5)-C(4)-N(4)	103.9(2)
C(3)-C(4)-N(4)	106.95(19)
C(6)-C(5)-C(4)	110.7(2)
C(6)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5A)	109.5
C(6)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	108.1
N(1)-C(6)-C(5)	110.5(2)
N(1)-C(6)-H(6A)	109.6
C(5)-C(6)-H(6A)	109.6
N(1)-C(6)-H(6B)	109.6
C(5)-C(6)-H(6B)	109.6
H(6A)-C(6)-H(6B)	108.1
O(7)-C(7)-O(8)	126.4(2)
O(7)-C(7)-C(2)	121.6(3)
O(8)-C(7)-C(2)	111.9(2)
C(7)-O(8)-C(8)	115.4(2)
O(8)-C(8)-C(9)	106.3(3)
O(8)-C(8)-H(8A)	110.5
C(9)-C(8)-H(8A)	110.5
O(8)-C(8)-H(8B)	110.5
C(9)-C(8)-H(8B)	110.5

H(8A)-C(8)-H(8B)	108.7
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
N(10)-C(10)-C(2)	174.7(3)
C(12)-C(11)-C(3)	114.9(2)
C(12)-C(11)-H(11A)	108.5
C(3)-C(11)-H(11A)	108.5
C(12)-C(11)-H(11B)	108.5
C(3)-C(11)-H(11B)	108.5
H(11A)-C(11)-H(11B)	107.5
O(12)-C(12)-C(13)	122.7(3)
O(12)-C(12)-C(11)	122.1(2)
C(13)-C(12)-C(11)	115.1(3)
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(4)-C(14)-H(14A)	109.5
C(4)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(4)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5

Table 11. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **3c**. The anisotropic displacement factor exponent takes the form:
$-2\pi^2$ [h^2 a^{*2} U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
N(1)	30(1)	24(1)	22(1)	-3(1)	2(1)	-5(1)
C(1)	37(2)	31(1)	30(1)	-5(1)	3(1)	-7(1)
C(2)	27(1)	22(1)	22(1)	0(1)	3(1)	3(1)
C(3)	30(2)	22(1)	21(1)	-1(1)	-1(1)	1(1)
N(4)	32(1)	28(1)	34(1)	-9(1)	2(1)	0(1)
O(4A)	92(2)	25(1)	43(1)	0(1)	4(1)	4(1)
O(4B)	68(2)	37(1)	38(1)	-18(1)	4(1)	1(1)
C(4)	26(1)	21(1)	26(1)	-4(1)	1(1)	0(1)
C(5)	31(2)	31(1)	26(1)	-3(1)	6(1)	3(1)
C(6)	27(2)	30(1)	25(1)	-3(1)	4(1)	-2(1)
O(7)	48(1)	38(1)	33(1)	-6(1)	13(1)	1(1)
C(7)	37(2)	21(1)	26(1)	-3(1)	7(1)	-4(1)
O(8)	46(1)	32(1)	22(1)	3(1)	-4(1)	-4(1)
C(8)	80(3)	41(2)	18(1)	4(1)	1(2)	-19(2)
C(9)	121(3)	49(2)	34(2)	8(2)	-26(2)	3(2)
N(10)	44(2)	33(1)	31(1)	0(1)	0(1)	7(1)
C(10)	33(2)	22(1)	22(1)	-4(1)	4(1)	-2(1)
C(11)	29(2)	23(1)	28(1)	-2(1)	0(1)	0(1)
O(12)	44(1)	32(1)	34(1)	6(1)	-2(1)	-2(1)
C(12)	36(2)	22(1)	29(1)	-1(1)	5(1)	0(1)
C(13)	41(2)	57(2)	56(2)	22(2)	10(2)	-2(2)
C(14)	38(2)	33(2)	23(1)	-3(1)	0(1)	1(1)

Table 12. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **3c**.

	x	y	z	U(eq)
H(1A)	3063	6786	8787	49
H(1B)	2711	7394	8146	49
H(1C)	874	7331	8613	49
H(3)	4773	10879	8688	29
H(5A)	2380	10102	10090	35
H(5B)	1835	10637	9444	35
H(6A)	3302	8163	9664	32
H(6B)	993	8495	9495	32
H(8A)	4984	8613	6916	56
H(8B)	5607	10054	6977	56
H(9A)	2214	10650	6897	102
H(9B)	1497	9227	6895	102
H(9C)	2737	9776	6342	102
H(11A)	8318	11153	9153	32
H(11B)	8660	9854	8823	32
H(13A)	10537	12114	7763	77
H(13B)	11216	10848	8081	77
H(13C)	10979	12096	8463	77
H(14A)	7715	10266	10009	47
H(14B)	6413	9007	9997	47
H(14C)	5809	10101	10446	47

Table 13. Torsion angles [°] for **3c**.

C(6)-N(1)-C(2)-C(10)	65.6(3)
C(1)-N(1)-C(2)-C(10)	-58.8(3)
C(6)-N(1)-C(2)-C(7)	-177.4(2)
C(1)-N(1)-C(2)-C(7)	58.2(3)
C(6)-N(1)-C(2)-C(3)	-58.5(2)
C(1)-N(1)-C(2)-C(3)	177.07(19)
N(1)-C(2)-C(3)-C(11)	-179.4(2)
C(10)-C(2)-C(3)-C(11)	56.9(3)
C(7)-C(2)-C(3)-C(11)	-57.5(3)
N(1)-C(2)-C(3)-C(4)	52.7(3)
C(10)-C(2)-C(3)-C(4)	-71.0(3)
C(7)-C(2)-C(3)-C(4)	174.5(2)
C(11)-C(3)-C(4)-C(14)	-48.9(3)
C(2)-C(3)-C(4)-C(14)	78.7(3)
C(11)-C(3)-C(4)-C(5)	-177.7(2)
C(2)-C(3)-C(4)-C(5)	-50.1(3)
C(11)-C(3)-C(4)-N(4)	70.1(3)
C(2)-C(3)-C(4)-N(4)	-162.3(2)
O(4A)-N(4)-C(4)-C(14)	141.6(3)
O(4B)-N(4)-C(4)-C(14)	-41.4(3)
O(4A)-N(4)-C(4)-C(5)	-99.9(3)
O(4B)-N(4)-C(4)-C(5)	77.1(3)
O(4A)-N(4)-C(4)-C(3)	16.4(4)
O(4B)-N(4)-C(4)-C(3)	-166.6(2)
C(14)-C(4)-C(5)-C(6)	-77.7(3)
C(3)-C(4)-C(5)-C(6)	53.5(3)
N(4)-C(4)-C(5)-C(6)	167.71(19)
C(2)-N(1)-C(6)-C(5)	62.5(3)
C(1)-N(1)-C(6)-C(5)	-171.6(2)
C(4)-C(5)-C(6)-N(1)	-59.6(3)
N(1)-C(2)-C(7)-O(7)	-145.0(2)
C(10)-C(2)-C(7)-O(7)	-24.7(3)
C(3)-C(2)-C(7)-O(7)	93.8(3)
N(1)-C(2)-C(7)-O(8)	37.6(3)
C(10)-C(2)-C(7)-O(8)	157.8(2)
C(3)-C(2)-C(7)-O(8)	-83.7(3)
O(7)-C(7)-O(8)-C(8)	0.5(4)
C(2)-C(7)-O(8)-C(8)	177.8(2)
C(7)-O(8)-C(8)-C(9)	172.3(2)
N(1)-C(2)-C(10)-N(10)	-6(3)
C(7)-C(2)-C(10)-N(10)	-127(3)
C(3)-C(2)-C(10)-N(10)	118(3)
C(4)-C(3)-C(11)-C(12)	-140.0(2)
C(2)-C(3)-C(11)-C(12)	92.7(2)
C(3)-C(11)-C(12)-O(12)	2.0(4)
C(3)-C(11)-C(12)-C(13)	-178.7(2)

Table 14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **3e**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
F(009)	2085(1)	997(2)	9282(1)	71(1)
F(010)	1361(1)	1387(2)	9217(1)	73(1)
F(011)	1706(1)	2989(2)	8854(1)	73(1)
O(007)	936(1)	331(2)	7782(1)	49(1)
O(009)	1655(1)	-1390(2)	7301(1)	39(1)
O(010)	1167(1)	-1421(2)	5931(1)	37(1)
O(012)	324(1)	-237(2)	5994(1)	49(1)
O(013)	467(1)	2041(2)	6380(1)	46(1)
O(016)	750(1)	3678(2)	4753(1)	68(1)
O(019)	1944(1)	4405(2)	5956(1)	57(1)
O(020)	1837(1)	2670(2)	5075(1)	41(1)
N(001)	1491(1)	1347(2)	7445(1)	29(1)
N(018)	2299(1)	-298(3)	6225(1)	53(1)
C(002)	1196(1)	739(2)	6610(1)	28(1)
C(003)	1262(1)	1713(2)	6001(1)	27(1)
C(004)	1840(1)	2011(2)	6288(1)	32(1)
C(005)	2103(1)	2626(4)	7167(2)	33(1)
C(006)	2048(1)	1659(3)	7741(2)	34(1)
C(007)	1322(1)	1014(2)	7964(1)	34(1)
C(008)	1627(1)	1610(3)	8837(2)	47(1)
C(009)	1368(1)	-816(2)	6661(1)	30(1)
C(010)	1264(1)	-2943(3)	5933(2)	47(1)
C(011)	912(1)	-3769(3)	6125(2)	68(1)
C(012)	609(1)	748(3)	6307(1)	36(1)
C(013)	-75(1)	2116(4)	6196(2)	50(1)
C(014)	-152(1)	3614(5)	6343(2)	67(1)
C(015)	936(1)	1244(2)	5104(1)	32(1)
C(016)	712(1)	2466(3)	4515(1)	41(1)
C(017)	434(1)	2121(3)	3620(1)	48(1)
C(018)	2098(1)	716(3)	6235(1)	37(1)
C(019)	1882(1)	3182(3)	5763(1)	38(1)
C(020)	1843(1)	3746(3)	4517(2)	54(1)
C(021)	1740(1)	3012(3)	3763(2)	59(1)
C(05B)	2189(6)	1840(20)	7260(10)	24(5)
C(06B)	1850(6)	2528(19)	7554(9)	27(5)
C(13B)	-74(5)	2759(18)	5877(9)	38(5)
C(14B)	-213(8)	2710(30)	6550(12)	72(7)

Table 15. Bond lengths [Å] for **3e**.

F(009)-C(008)	1.326(3)
F(010)-C(008)	1.331(3)
F(011)-C(008)	1.322(3)
O(007)-C(007)	1.212(3)
O(009)-C(009)	1.203(2)
O(010)-C(009)	1.326(3)
O(010)-C(010)	1.466(3)
O(012)-C(012)	1.196(3)
O(013)-C(012)	1.323(3)
O(013)-C(013)	1.477(3)
O(013)-C(13B)	1.557(12)
O(016)-C(016)	1.214(3)
O(019)-C(019)	1.198(3)
O(020)-C(019)	1.333(3)
O(020)-C(020)	1.473(3)
N(001)-C(007)	1.350(3)
N(001)-C(002)	1.482(2)
N(001)-C(06B)	1.489(16)
N(001)-C(006)	1.493(3)
N(018)-C(018)	1.136(3)
C(002)-C(009)	1.543(3)
C(002)-C(012)	1.547(3)
C(002)-C(003)	1.567(3)
C(003)-C(015)	1.535(3)
C(003)-C(004)	1.553(3)
C(003)-H(003)	1.0000
C(004)-C(018)	1.477(4)
C(004)-C(019)	1.534(3)
C(004)-C(005)	1.551(3)
C(004)-C(05B)	1.600(17)
C(005)-C(006)	1.492(4)
C(005)-H(05A)	0.9900
C(005)-H(05B)	0.9900
C(006)-H(06A)	0.9900
C(006)-H(06B)	0.9900
C(007)-C(008)	1.537(3)
C(010)-C(011)	1.497(4)
C(010)-H(10A)	0.9900
C(010)-H(10B)	0.9900
C(011)-H(11A)	0.9800
C(011)-H(11B)	0.9800
C(011)-H(11C)	0.9800
C(013)-C(014)	1.483(5)
C(013)-H(13A)	0.9900
C(013)-H(13B)	0.9900
C(014)-H(14A)	0.9800
C(014)-H(14B)	0.9800
C(014)-H(14C)	0.9800
C(015)-C(016)	1.506(3)
C(015)-H(15A)	0.9900

C(015)-H(15B)	0.9900
C(016)-C(017)	1.499(3)
C(017)-H(17A)	0.9800
C(017)-H(17B)	0.9800
C(017)-H(17C)	0.9800
C(020)-C(021)	1.474(4)
C(020)-H(20A)	0.9900
C(020)-H(20B)	0.9900
C(021)-H(21A)	0.9800
C(021)-H(21B)	0.9800
C(021)-H(21C)	0.9800
C(05B)-C(06B)	1.527(17)
C(13B)-C(14B)	1.529(18)

Table 16. Bond angles [°] for **3e**.

C(009)-O(010)-C(010)	115.79(18)
C(012)-O(013)-C(013)	113.1(2)
C(012)-O(013)-C(13B)	128.9(6)
C(013)-O(013)-C(13B)	32.7(6)
C(019)-O(020)-C(020)	114.86(19)
C(007)-N(001)-C(002)	116.50(17)
C(007)-N(001)-C(06B)	125.7(6)
C(002)-N(001)-C(06B)	115.9(6)
C(007)-N(001)-C(006)	121.98(17)
C(002)-N(001)-C(006)	115.23(16)
C(06B)-N(001)-C(006)	37.8(6)
N(001)-C(002)-C(009)	107.59(16)
N(001)-C(002)-C(012)	110.18(16)
C(009)-C(002)-C(012)	108.05(17)
N(001)-C(002)-C(003)	109.24(16)
C(009)-C(002)-C(003)	116.16(17)
C(012)-C(002)-C(003)	105.55(16)
C(015)-C(003)-C(004)	114.30(17)
C(015)-C(003)-C(002)	113.58(17)
C(004)-C(003)-C(002)	112.53(16)
C(015)-C(003)-H(003)	105.1
C(004)-C(003)-H(003)	105.1
C(002)-C(003)-H(003)	105.1
C(018)-C(004)-C(019)	109.60(18)
C(018)-C(004)-C(005)	112.7(2)
C(019)-C(004)-C(005)	105.3(2)
C(018)-C(004)-C(003)	110.67(18)
C(019)-C(004)-C(003)	110.18(17)
C(005)-C(004)-C(003)	108.30(17)
C(018)-C(004)-C(05B)	86.4(7)
C(019)-C(004)-C(05B)	126.8(7)
C(005)-C(004)-C(05B)	28.5(6)
C(003)-C(004)-C(05B)	110.3(6)
C(006)-C(005)-C(004)	111.7(2)
C(006)-C(005)-H(05A)	109.3
C(004)-C(005)-H(05A)	109.3
C(006)-C(005)-H(05B)	109.3
C(004)-C(005)-H(05B)	109.3
H(05A)-C(005)-H(05B)	107.9
C(005)-C(006)-N(001)	111.2(2)
C(005)-C(006)-H(06A)	109.4
N(001)-C(006)-H(06A)	109.4
C(005)-C(006)-H(06B)	109.4
N(001)-C(006)-H(06B)	109.4
H(06A)-C(006)-H(06B)	108.0
O(007)-C(007)-N(001)	124.9(2)
O(007)-C(007)-C(008)	117.4(2)
N(001)-C(007)-C(008)	117.59(19)
F(011)-C(008)-F(009)	107.4(2)
F(011)-C(008)-F(010)	107.0(2)

F(009)-C(008)-F(010)	107.3(2)
F(011)-C(008)-C(007)	112.8(2)
F(009)-C(008)-C(007)	112.5(2)
F(010)-C(008)-C(007)	109.5(2)
O(009)-C(009)-O(010)	124.9(2)
O(009)-C(009)-C(002)	122.49(19)
O(010)-C(009)-C(002)	112.59(18)
O(010)-C(010)-C(011)	110.4(2)
O(010)-C(010)-H(10A)	109.6
C(011)-C(010)-H(10A)	109.6
O(010)-C(010)-H(10B)	109.6
C(011)-C(010)-H(10B)	109.6
H(10A)-C(010)-H(10B)	108.1
C(010)-C(011)-H(11A)	109.5
C(010)-C(011)-H(11B)	109.5
H(11A)-C(011)-H(11B)	109.5
C(010)-C(011)-H(11C)	109.5
H(11A)-C(011)-H(11C)	109.5
H(11B)-C(011)-H(11C)	109.5
O(012)-C(012)-O(013)	125.78(19)
O(012)-C(012)-C(002)	124.6(2)
O(013)-C(012)-C(002)	109.31(18)
O(013)-C(013)-C(014)	105.0(3)
O(013)-C(013)-H(13A)	110.7
C(014)-C(013)-H(13A)	110.7
O(013)-C(013)-H(13B)	110.7
C(014)-C(013)-H(13B)	110.7
H(13A)-C(013)-H(13B)	108.8
C(013)-C(014)-H(14A)	109.5
C(013)-C(014)-H(14B)	109.5
H(14A)-C(014)-H(14B)	109.5
C(013)-C(014)-H(14C)	109.5
H(14A)-C(014)-H(14C)	109.5
H(14B)-C(014)-H(14C)	109.5
C(016)-C(015)-C(003)	113.21(18)
C(016)-C(015)-H(15A)	108.9
C(003)-C(015)-H(15A)	108.9
C(016)-C(015)-H(15B)	108.9
C(003)-C(015)-H(15B)	108.9
H(15A)-C(015)-H(15B)	107.7
O(016)-C(016)-C(017)	121.3(2)
O(016)-C(016)-C(015)	121.6(2)
C(017)-C(016)-C(015)	117.1(2)
C(016)-C(017)-H(17A)	109.5
C(016)-C(017)-H(17B)	109.5
H(17A)-C(017)-H(17B)	109.5
C(016)-C(017)-H(17C)	109.5
H(17A)-C(017)-H(17C)	109.5
H(17B)-C(017)-H(17C)	109.5
N(018)-C(018)-C(004)	177.0(2)
O(019)-C(019)-O(020)	124.8(2)
O(019)-C(019)-C(004)	123.3(2)
O(020)-C(019)-C(004)	111.9(2)
O(020)-C(020)-C(021)	107.4(2)

O(020)-C(020)-H(20A)	110.2
C(021)-C(020)-H(20A)	110.2
O(020)-C(020)-H(20B)	110.2
C(021)-C(020)-H(20B)	110.2
H(20A)-C(020)-H(20B)	108.5
C(020)-C(021)-H(21A)	109.5
C(020)-C(021)-H(21B)	109.5
H(21A)-C(021)-H(21B)	109.5
C(020)-C(021)-H(21C)	109.5
H(21A)-C(021)-H(21C)	109.5
H(21B)-C(021)-H(21C)	109.5
C(06B)-C(05B)-C(004)	102.1(12)
N(001)-C(06B)-C(05B)	101.4(13)
C(14B)-C(13B)-O(013)	96.5(13)

Table 17. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **3e**. The anisotropic displacement factor exponent takes the form:
$-2\pi^2$ [h^2 a^{*2} U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
F(009)	62(1)	105(1)	35(1)	3(1)	16(1)	4(1)
F(010)	86(1)	106(2)	51(1)	-14(1)	52(1)	-20(1)
F(011)	115(1)	56(1)	62(1)	-27(1)	54(1)	-21(1)
O(007)	46(1)	62(1)	47(1)	-6(1)	31(1)	-16(1)
O(009)	44(1)	37(1)	34(1)	2(1)	18(1)	1(1)
O(010)	40(1)	32(1)	35(1)	-8(1)	16(1)	-1(1)
O(012)	32(1)	61(1)	57(1)	-24(1)	25(1)	-18(1)
O(013)	25(1)	54(1)	54(1)	-13(1)	17(1)	5(1)
O(016)	91(2)	46(1)	39(1)	3(1)	14(1)	20(1)
O(019)	77(1)	39(1)	65(1)	-13(1)	44(1)	-14(1)
O(020)	56(1)	37(1)	37(1)	2(1)	28(1)	-5(1)
N(001)	27(1)	34(1)	26(1)	-7(1)	14(1)	-6(1)
N(018)	48(1)	57(2)	65(2)	24(1)	36(1)	17(1)
C(002)	24(1)	32(1)	26(1)	-6(1)	12(1)	-5(1)
C(003)	24(1)	28(1)	26(1)	-2(1)	11(1)	1(1)
C(004)	27(1)	41(1)	28(1)	-1(1)	13(1)	-6(1)
C(005)	31(1)	37(2)	30(1)	-4(1)	14(1)	-9(1)
C(006)	27(1)	42(2)	28(1)	-6(1)	11(1)	-9(1)
C(007)	37(1)	33(1)	36(1)	-2(1)	22(1)	-1(1)
C(008)	61(2)	53(2)	40(1)	-4(1)	33(1)	-6(1)
C(009)	28(1)	33(1)	31(1)	-4(1)	17(1)	-6(1)
C(010)	58(2)	31(1)	47(1)	-10(1)	23(1)	4(1)
C(011)	93(2)	35(2)	79(2)	-13(2)	47(2)	-17(2)
C(012)	28(1)	48(2)	36(1)	-11(1)	19(1)	-4(1)
C(013)	28(2)	58(2)	61(2)	-1(2)	22(2)	10(1)
C(014)	50(2)	60(3)	83(3)	-7(2)	27(2)	21(2)
C(015)	26(1)	38(1)	27(1)	-5(1)	11(1)	0(1)
C(016)	35(1)	49(2)	31(1)	-1(1)	11(1)	6(1)
C(017)	44(1)	64(2)	28(1)	3(1)	12(1)	-1(1)
C(018)	25(1)	56(2)	30(1)	13(1)	14(1)	2(1)
C(019)	39(1)	39(2)	39(1)	-6(1)	22(1)	-7(1)
C(020)	75(2)	46(2)	51(2)	12(1)	38(1)	-9(1)
C(021)	63(2)	77(2)	43(2)	0(1)	32(1)	-18(2)

Table 18. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **3e**.

	x	y	z	U(eq)
H(003)	1116	2650	6026	33
H(05A)	2476	2783	7369	39
H(05B)	1945	3553	7155	39
H(06A)	2207	2103	8289	40
H(06B)	2233	763	7793	40
H(10A)	1630	-3151	6347	56
H(10B)	1206	-3229	5390	56
H(11A)	981	-4783	6124	101
H(11B)	551	-3571	5711	101
H(11C)	973	-3494	6665	101
H(13A)	-129	1477	6560	59
H(13B)	-318	1847	5621	59
H(14A)	-508	3744	6228	101
H(14B)	-92	4229	5984	101
H(14C)	91	3859	6915	101
H(15A)	1155	669	4960	38
H(15B)	649	636	5042	38
H(17A)	306	2996	3301	72
H(17B)	141	1494	3488	72
H(17C)	672	1645	3485	72
H(20A)	2185	4222	4774	65
H(20B)	1574	4471	4391	65
H(21A)	1735	3704	3373	88
H(21B)	1404	2532	3520	88
H(21C)	2013	2313	3894	88