1,2-Addition versus homoconjugate addition reactions of indoles and electron-rich arenes to α-cyclopropyl *N*-acyliminium ions: Synthetic and computational studies.

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Electronic Supplementary Information

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Experimental methods: The solvent for all ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) experiments was $CDCl_3$. Abbreviations used for recording of NMR data are: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, bs = broad singlet, bd = broad doublet, m = multiplet and app. = apparent. The recorded coupling constants (*J*) are measured in hertz. Chemical shifts are reported as parts per million (ppm) from tetramethylsilane and are corrected to 0.00 (TMS) ppm for ^{1}H NMR and 77.16 ppm ($CDCl_3$ centre line) for ^{13}C NMR. ^{1}H and ^{13}C NMR assignments are based upon gCOSY, gHSQC and gHMBC NMR correlations. *Ipso*-OCH_2Ph and *ipso*-NCH_2Ph refers to the *ipso* carbon of the aromatic ring. Mass and IR spectra, specific rotations and chromatography materials were as described previously (reference 2 of manuscript). PS refers to petroleum spirit fractions 40-60 °C. All reactions were stirred with a magnetic stirrer bar in the reaction mixture under an atmosphere of nitrogen. Glassware for all reactions was oven dried at 110 °C and cooled in a desiccator. Anhydrous THF and CH_2Cl_2 were obtained from an anhydrous solvent dispenser.

(5*R*)-1-Benzyl-4-(benzyloxy)-5-cyclopropyl-5-hydroxypyrrolidin-2-one (1)

A solution of (*S*)-1-benzyl-3-(benzyloxy)pyrrolidine-2,5-dione (2.0 g, 6.7 mmol) in THF (60 mL) was cooled to 0 °C, then cyclopropylmagnesium bromide in 2-methylfuran (8.8 mL, 1.0 M, 8.8 mmol) was added and the solution turned yellow. The solution was warmed to room temperature and over 30 min the reaction mixture turned a transparent dark orange, then deep purple as the reaction mixture was stirred for another 40 h. Saturated NH_4Cl solution (30 mL), was added and the organic layer was extracted with Et_2O (2 x 60 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo* giving a dark purple oil. Flash column chromatography (1:2 EtOAc/PS) yielded **1** as a white solid (0.724 g, 2.1 mmol, 63%) and as a mixture of diastereomers (dr = 90:10). A small amount of each diastereomer could be isolated pure by

further separation using column chromatography. ***Major diastereomer*** (4*S*,5R)-**1a**: $[\alpha]_D^{25}$ 13.4 ± 0.5 (*c* 10.3, $CHCl_3$). ν_{max}/cm^{-1} 3269, 2941, 2859, 2109, 1754, 1672, 1406, 1351, 1221, 1146, 1112, 1023, 982, 784, 696. δ_H 7.37 – 7.17 (10H, m, ArCH), 4.68 – 4.64 (2H, m, OCH_2Ph, NCH_2Ph), 4.57 (1H, d, *J* = 12.0 Hz, OCH_2Ph), 4.42 (1H, d, *J* = 15.0 Hz, NCH_2Ph), 4.02 (1H, dd, *J* = 4.0, 6.5 Hz, H4), 3.55 (1H, d, *J* = 4.0 Hz, OH), 2.73 (1H, dd, *J* = 6.5, 17.2 Hz, H3), 2.56 (1H, dd, *J* = 4.0, 17.2 Hz, H3), 0.83 – 0.78 (1H, m, H7), 0.68 – 0.62 (1H, m, H6), 0.34 – 0.28 (3H, m, H7 H7′). δ_C 171.5 (C2), 139.0 (*ipso*-OCH_2Ph), 136.8 (*ipso*-NCH_2Ph), 128.7 (ArCH), 128.4 (ArCH), 128.3 (ArCH), 127.9 (ArCH), 127.7 (ArCH), 126.9 (ArCH), 89.5 (C5), 77.9 (C4), 72.4 (OCH_2Ph), 42.7 (NCH_2Ph), 36.2 (C3), 17.7 (C6), 1.9 (C7), 0.7 (C7′). HRMS (ESI) *m/z* calcd for $C_{21}H_{24}NO_3$ $[M + H]^+$ 338.1756, found 338.1752. ***Minor diastereomer*** (4*S*,5*S*)-**1a**: $[\alpha]_D^{25}$ -21.1 ± 0.2 (*c* 11.5, $CHCl_3$). δ_H 7.42 – 7.18 (10H, m, ArCH), 4.75 (1H, d, *J* = 15.4 Hz, NCH_2Ph), 4.66 (d, *J* = 11.8 Hz, OCH_2Ph), 4.62 (d, *J* = 11.8 Hz, OCH_2Ph), 4.45 (1H, d, *J* = 15.4 Hz, NCH_2Ph), 3.80 (1H, dd, *J* = 5.5, 1.3 Hz, H4), 2.85 (1H, dd, *J* = 17.1, 5.5 Hz, H3), 2.54 (1H, dd, *J* = 17.1, 1.3 Hz, H3), 1.21 (1H, m, *J* = 7.2, 7.2 Hz, H6), 0.56 – 0.45 (3H, m, H7 H7′), 0.42 – 0.36 (1H, m, H7). δ_C 174.6 (C2), 138.7 (*ipso*-NCH_2Ph), 138.0 (*ipso*-OCH_2Ph), 128.9 (ArCH), 128.7 (ArCH), 128.0 (ArCH), 127.8 (ArCH), 127.7 (ArCH), 127.6 (ArCH), 93.3 (C5), 80.4 (C4), 72.3 (OCH_2Ph), 42.9 (NCH_2Ph), 36.5 (C3), 13.4 (C6), 1.6 (C7′), 0.9 (C7). LRMS (ESI) *m/z* calcd for $C_{21}H_{24}NO_3$ $[M + H]^+$ 338, found 338.

(5*R*)-4-(Benzyloxy)-5-cyclopropyl-5-hydroxy-1-methylpyrrolidin-2-one (*N*-Me analogue of 1)

The title compound was prepared according to the above procedure from (*S*)-3-(benzyloxy)-1-methylpyrrolidine-2,5-dione (0.75 g, 3.4 mmol), THF (30 mL) and 1.0 M cyclopropylmagnesium bromide in 2-methylfuran (3.75 mL, 0.1 M, 3.75 mmol). Column chromatography (1:1 EtOAc/PS as eluent) yielded the title compound as a white solid (0.595 g, 67%) and as a mixture of diastereomers (dr = 71:29). A small amount of the major diastereomer could be isolated pure by further separation using column chromatography. ***Major diastereomer*** [(4*S*,5*R*)-**1b**]: $[\alpha]_D^{25}$ 26.3 ± 0.3 (*c* 9.2, $CHCl_3$). ν_{max}/cm^{-1} 3317, 3009, 2928, 1671, 1434, 1394, 1339, 1207, 1176, 1075, 1024, 877, 807, 736, 697, 601. δ_H 7.45 – 7.28 (5H, m, ArC-), 4.66 (2H, d, *J* = 11.7 Hz, OCH_2Ph), 4.58 (1H, d, *J* = 11.7 Hz, OCH_2Ph), 4.00 (1H, dd, *J* = 6.6, 2.4 Hz, H4), 3.63 (1H, app. d, *J* = 5.4 Hz, OH), 2.84 (3H, s, NCH_3), 2.64 (1H, dd, *J* = 17.1, 6.6 Hz, H3), 2.48 (1H, dd, *J* = 17.1, 2.4 Hz, H3), 0.94 – 0.83 (1H, m, H6), 0.82 – 0.74 (1H, m, H7), 0.60 – 0.52 (1H, m, H7), 0.45 – 0.31 (2H, m, H7′). δ_C 170.8 (C2), 136.8 (*ipso*-

CH_2Ph), 128.7 (*m*-PhC), 128.3 (*p*-PhC), 128.0 (*o*-PhC), 89.0 (C5), 77.7 (C4), 72.5 (OCH_2Ph), 36.3 (C3), 24.8 (CH_3), 16.7 (C6), 1.3 (C7), -0.3 (C7′). HRMS (ESI) *m/z* calcd for $C_{15}H_{20}NO_3$ $[M + H]^+$ 262.1436, found 262.1443.

3-Cyclopropyl-3-hydroxy-2-methylisoindolin-1-one (10).

A solution of *N*-methylphthalimide (1.00 g, 6.21 mmol) in THF (55 mL) was cooled to 0 °C, then 1.0 M cyclopropylmagnesium bromide in 2-methylfuran (7.45 mL, 0.1 M, 7.45 mmol) was added dropwise over 10 min, where a fine white precipitate formed and the solution turned green. The solution was stirred for another 1.5 h. Saturated NH_4Cl solution (5 mL) was added giving a clear solution, after which a white precipitate formed. Water was then added to dissolve the white precipitate, and the aqueous layer was extracted with Et_2O (3 x 60 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude solid was dissolved in EtOAc and precipitated from solution with hexane, yielding **10** as a white solid (1.09 g, 5.36 mmol, 87%). Mp 179 ˚C. ν_{max}/cm^{-1} 3187, 2972, 2108, 1753, 1678, 1481, 1426, 1262, 1173, 1030, 757, 703, 685. δ_H 7.59 (1H, d, *J* = 7.3 Hz, H7), 7.52 (1H, app. t, *J* = 7.3 Hz, H5), 7.42 (1H, d, *J* = 7.3 Hz, H4), 7.37 – 7.31 (1H, m, H6), 4.00 (1H, s, OH), 2.79 (3H, s, CH_3), 1.03 – 0.95 (1H, m, H2′), 0.85 – 0.77 (1H, m, H1′), 0.74 – 0.68 (1H, m, H3′), 0.61 – 0.54 (1H, m, H2′), 0.51 – 0.44 (1H, m, H3′). δ_C 167.1 (C2), 148.3 (C3a), 132.1 (C5), 130.7 (C7a), 129.4 (C6), 123.0 (C4), 122.5 (C7), 88.4 (C3), 24.0 (CH_3), 16.8 (C1′), 1.0 (C2′), -0.2 (C3′). HRMS (ESI) *m/z* calcd for $C_{12}H_{14}NO_2$ $[M + H]^+$ 204.1025, found 204.1015.

General Procedure for the reactions of indoles and benzenes with cyclopropanols 1 (R = Bn, Me) and 10

Method A: A solution of **1** (1 mol. eq., mixture of diastereomers) and indole or benzene derivative (2 mol. eq. or 3 mol. eq.) in anhydrous CH_2Cl_2 (0.2 M) was cooled to 0 °C. $BF_3{\cdot}Et_2O$ (2 mol. eq.) was then added dropwise via syringe to the solution with vigorous stirring. The solution was warmed to room temperature and stirred for 12 h. The mixture was quenched with a saturated aqueous solution of $NaHCO_3$, a minimal amount of acetone was added to dissolve any solids, and the aqueous phase was then extracted with CH_2Cl_2 (3 x initially used volume of CH_2Cl_2). The organic layers were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo.* The crude product was purified by flash column chromatography.

Method B: A solution of **1** (1 mol. eq., mixture of diastereomers) and the indole (2 mol. eq.) in anhydrous CH_2Cl_2 (0.2 M) was cooled to 0 °C. $BF_3{\cdot}Et_2O$ (2 mol. eq., 0.3 mol/L in CH_2Cl_2) was then added via a syringe pump over 1 h to the solution with vigorous stirring. The solution was warmed to room temperature and stirred for 12 h. The mixture was then quenched with a

saturated aqueous solution of $NaHCO_3$, a minimal amount of acetone was added to dissolve any solids, and the aqueous phase was then extracted with CH_2Cl_2 (3 x initially used volume of CH_2Cl_2). The organic layers were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography.

1.3.2 General procedure for the addition of indoles to 10.

Method C: A solution of **10** (1 mol. eq.) and the indole (2 mol. eq.) in CH_2Cl_2 (0.2 M) was cooled to 0 °C. $BF_3{\cdot}Et_2O$ (2 mol. eq., 0.3 mol/L in CH_2Cl_2) was then added via syringe pump over 1 h to the solution with vigorous stirring. The solution was warmed to room temperature and stirred for 12 h. The mixture was quenched with a saturated aqueous solution of $NaHCO_3$, and the aqueous phase was then extracted with CH_2Cl_2 (3 x the initially used volume of CH_2Cl_2). The organic layers were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography.

(4*S*)-1-Benzyl-4-(benzyloxy)-5-cyclopropyl-5-(1*H*-indol-3-yl)pyrrolidin-2-one (3a)

Prepared following general method B, from **1** (0.050 g, 0.15 mmol), indole (0.035 g, 0.30 mmol), $BF_3{\cdot}Et_2O$ (0.046 g, 0.040 mL, 0.32 mmol) and CH_2Cl_2 (7.5 mL). This reaction was cooled to -40 °C, rather than 0 °C for both the $BF_3{\cdot}Et_2O$ addition, and for the duration of the reaction (26 h). Separation by column chromatography (1:1 EtOAc/PS) yielded **3a** as a colourless oil (0.048 g, 0.11 mmol, 74%) and as a mixture of diastereomers (dr = 94:6). A small amount of each diastereomer could be isolated pure by further chromatographic separation.

Major diastereomer (4*S*,5*S*)-**3a**:$[\alpha]_D^{25}$ -21.9 ± 0.3 (*c* 12.0, $CHCl_3$). ν_{max}/cm^{-1} 3265, 3005, 1662, 1434, 1408, 1354, 1094, 1026, 738, 698, 617, 465, 426. δ_H 8.34 (1H, bs, H1′), 7.70 (1H, d, *J* = 8.1 Hz, H4′), 7.39 (1H, d, *J* = 8.1 Hz, H7′), 7.23 – 7.18 (7H, m, ArCH), 7.17 – 7.13 (4H, m, ArCH), 7.09 (1H, dd, *J* = 15.3, 7.9 Hz, H5′), 6.84 (1H, d, *J* = 4.8 Hz, H2′), 5.13 (1H, d, *J* = 15.5 Hz, NCH_2Ph), 4.21 (1H, d, *J* = 12.0 Hz, OCH_2Ph), 4.12 (1H, dd, *J* = 12.0 Hz, OCH_2Ph), 3.83 (1H, d, *J* = 15.5 Hz, NCH_2Ph), 3.49 (1H, app. t, *J* = 7.3 Hz, H4), 2.83 (1H, dd, *J* = 16.7, 7.7 Hz, H3), 2.58 (1H, dd, *J* = 16.7, 6.8 Hz, H3), 1.29 – 1.18 (1H, m, H1″), 0.82 – 0.70 (2H, m, H2″), 0.15 – 0.06 (1H, m, H3″), -0.12— -0.20 (1H, m, H3″). δ_C 173.0 (C2), 139.2 (*ipso*-NCH_2Ph), 137.7 (*ipso*-OCH_2Ph)), 137.1 (C7′a), 128.2 (ArCH), 128.2 (ArCH), 128.1 (ArCH), 127.5 (ArCH), 127.3 (ArCH), 127.0 (C3′a), 126.9 (ArCH), 124.1 (ArCH), 122.2 (ArCH), 121.9 (C4′), 120.2 (C5′), 116.7 (C3′), 111.3 (C7′), 73.3 (C4), 71.3 (OCH_2Ph), 70.9 (C5), 44.7 (NCH_2Ph), 37.0 (C3), 18.4 (C1″), 5.3 (C2″), 2.4 (C3″). HRMS (ESI) *m/z* calcd for $C_{29}H_{28}N_2O_2$ $[M + H]^+$ 437.2229, found 437.2244. ***Minor diastereomer*** (4*S*,5*R*)-**3a**: $[\alpha]_D^{25}$ 30.5 ± 1.9 (*c* 1.05,

$CHCl_3$). δ_H 8.52 (1H, bs, H1′), 7.35 (1H, d, J = 8.3 Hz, H7′), 7.31 – 7.13 (12H, m, ArCH), 7.12 (1H, d, J = 1.8 Hz, H2′), 6.97 (1H, t, J = 7.5 Hz, ArCH), 4.97 (1H, d, J = 15.7 Hz, NCH_2Ph), 4.79 (1H, app. t, J = 5.5 Hz, H4), 4.61 (1H, d, J = 12.1 Hz, OCH_2Ph), 4.56 (1H, d, J = 12.1 Hz, OCH_2Ph), 4.17 (1H, d, J = 15.7 Hz, NCH_2Ph), 2.67 (1H, dd, J = 16.4, 4.9 Hz, H3), 2.50 (1H, dd, J = 16.4, 6.1 Hz, H3), 1.58 – 1.50 (1H, m, H1″), 0.42 – 0.32 (3H, m, H2″ H3″), 0.31 – 0.25 (1H, m, H3″). δ_C 174.5 (C2), 139.0 (*ipso*-OCH_2Ph), 138.2 (*ipso*-NCH_2Ph), 137.1 (C7′a), 128.5 (ArCH), 128.2 (ArCH), 127.7 (ArCH), 127.6 (ArCH), 126.9 (ArCH), 125.4 (C3′a), 124.5 (ArC), 122.3 (ArCH), 120.7 (ArCH), 120.0 (ArCH), 115.8 (C3′), 111.9 (C7′), 79.9 (C4), 72.0 (OCH_2Ph), 45.2 (NCH_2Ph), 37.3 (C3), 14.6 (C1″), 2.8 (C2″), 2.4 (C3″). LRMS (ESI) *m/z* calcd for $C_{29}H_{28}N_2O_2$ $[M + H]^+$ 437, found 437.

(4*S*)-4-(Benzyloxy)-5-cyclopropyl-5-(1*H*-indol-3-yl)-1-methylpyrrolidin-2-one (3b) Prepared following general method B, from the *N*-Me analogue of **1** (0.062 g, 0.24 mmol), indole (0.056 g, 0.47 mmol), $BF_3{\cdot}Et_2O$ (0.046 g, 0.040 mL, 0.32 mmol) and CH_2Cl_2 (7.5 mL). The reaction time was 3 h. Separation by column chromatography (3:2 EtOAc/PS) yielded **3b** as a white solid (0.085 g, 0.23 mmol, 98%) and as a mixture of diastereomers (dr = 90:10). A small amount of each diastereomer could be isolated pure by further chromatographic separation. ***Major diastereomer*** (4*S*,5*S*)-**3b**: $[\alpha]_D^{25}$ 70 ± 6 (*c* 1.2, $CHCl_3$). ν_{max}/cm^{-1} 3250, 3223, 3185, 3062, 3005, 2926, 2871, 1667, 1456, 1396, 1332, 1246, 1111, 1074, 1026, 766, 741, 698. δ_H 8.37 (1H, bs, H1′), 7.69 (1H, d, J = 7.8 Hz, H4′), 7.37 (1H, d, J = 8.3 Hz, H7′), 7.19 (1H, t, J = 7.6 Hz, H6′), 7.16 - 7.10 (3H, m, ArCH), 7.09 - 7.03 (1H, m, ArCH), 6.79 (2H, d, J = 7.3 Hz, ArCH), 4.15 (1H, d, J = 12.0 Hz, OCH_2Ph), 4.04 (1H, d, J = 12.0 Hz, OCH_2Ph), 3.65 (1H, app. t, J = 6.1 Hz, H4), 2.81 - 2.72 (4H, m, H3 CH_3), 2.53 (1H, dd, J = 5.4, 16.6 Hz, H3), 1.56 - 1.47 (1H, m, H4), 0.86 (1H, td, J = 4.9, 9.0 Hz, H2″), 0.75 - 0.68 (1H, m, H2″), 0.67 - 0.58 (1H, m, H3″), 0.37 (1H, app. dq, J = 10.0, 5.3 Hz, H3″). δ_C 172.8 (C2), 137.7 (*ipso*- OCH_2Ph), 137.0 (C7′a), 128.2 (ArCH), 127.5 (ArCH), 127.4 (ArCH), 127.2 (C2′), 123.5 (ArCH), 122.4 (ArCH), 122.3 (C4′), 120.1 (C5′), 116.2 (C3′a), 111.1 (C7′), 76.4 (C4), 71.7 (OCH_2Ph), 69.4 (C5), 37.3 (C3), 27.0 (NCH_3), 17.9 (C1″), 3.6 (C2″), 1.7 (C3″). HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O_2$ $[M+H]^+$ 361.1916, found 361.1919. ***Minor diastereomer*** (4*S*,5*R*)-**3b**: ν_{max}/cm^{-1} 3262, 3061, 3010, 2928, 2869, 1673, 1456, 1439, 1422, 1390, 1264, 1126, 767, 744, 699, 677. δ_H 8.45 (1H, bs, H1′), 7.44 (1H, d, J = 2.0 Hz, H2′), 7.41 (1H, d, J = 8.2 Hz, ArCH), 7.33 (1H, d, J = 7.8 Hz, ArCH), 7.23 – 7.16 (4H, m, ArCH), 7.10 – 7.03 (3H, m, ArCH), 4.73 (1H, t, J = 8.7 Hz, H4), 4.42 (1H, d, J = 11.9 Hz, OCH_2Ph), 4.33 (1H, d, J = 11.9 Hz, OCH_2Ph), 2.74 – 2.60 (2H, m, H3), 1.90 – 1.81 (1H, m, H1″), 0.75 (1H, dt, J = 8.9, 4.4 Hz H2″), 0.67 (1H, dd,

J = 9.2, 4.8 Hz H2″), 0.48 – 0.35 (2H, m H3″). δ_C 173.1 (C2), 137.9 (*ipso*-CH_2Ph), 137.2 (C7′a), 128.3 (ArCH), 127.7 (ArCH), 127.6 (ArCH), 125.2 (ArC), 124.8 (ArC), 122.5 (ArC), 120.3 (ArC), 119.9 (ArC), 117.4 (C3′), 111.8 (C7′), 81.1 (C4), 72.4 (OCH_2Ph), 67.6 (C5), 36.8 (CH_3), 28.4 (C3), 14.6 (C1″), 14.3 (C1″), 1.7 (C2″), 1.5 (C3″). LRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O_2$ $[M+H]^+$ 361, found 361.

(4*S*)-1-Benzyl-4-(benzyloxy)-5-(5-bromo-1*H*-indol-3-yl)-5-cyclopropylpyrrolidin-2-one (3c).

Prepared following general method A, from **1** (0.050 g, 0.15 mmol), 5-bromoindole (0.068 g, 0.45 mmol), $BF_3{\cdot}Et_2O$ (0.046 g, 0.040 mL, 0.32 mmol) and CH_2Cl_2 (7.5 mL). The reaction mixture was stirred for 2 h at room temperature rather than 12 h. Separation by column chromatography (1:1 EtOAc/PS) yielded **3c** as a yellow solid (0.070 g, 0.136 mmol, 92%) and as a mixture of diastereomers (dr > 95:5). A small amount of the major diastereomer could be isolated pure by further chromatographic separation. ***Major diastereomer*** (4*S*,5*S*)-**3c**: $[\alpha]_D^{25}$ 30.1 ± 2.0 (*c* 2.25, $CHCl_3$). ν_{max}/cm^{-1} 3409, 2968, 2921, 2860, 2106, 1753, 1686, 1502, 1414, 1380, 1346, 1258, 1224, 1007, 980, 797, 735, 695. δ_H 8.27 (1H, bs, H1′), 7.96 (1H, s, H4′), 7.27 (1H, dd, *J* = 8.5, 1.5 Hz, H6′), 7.24 – 7.16 (10H, m), 7.02 (1H, d, *J* = 2.6 Hz, H2′), 6.95 (1H, d, *J* = 6.6 Hz, H7′), 5.10 (1H, d, *J* = 15.2 Hz, NCH_2Ph), 4.28 (1H, d, *J* = 12.1 Hz, OCH_2Ph), 4.19 (1H, d, *J* = 12.1 Hz, OCH_2Ph), 3.93 (1H, d, *J* = 15.2 Hz, NCH_2Ph), 3.49 (1H, t, *J* = 7.4 Hz, H4), 2.79 (1H, dd, 16.6, 7.4 Hz, H3), 2.52 (1H, dd, *J* = 16.6, 7.4 Hz, H3), 1.24 – 1.18 (1H, m, H1″), 0.91 – 0.75 (2H, m, H2″), 0.13 – 0.08 (1H, d, *J* = 3.7 Hz, H3″), -0.09 – -0.15 (1H, m, H3″). δ_C 172.8 (C2), 139.0 (*ipso*-NCH_2Ph), 137.4 (*ipso*-OCH_2Ph), 135.8 (C7′a), 128.8 (C3′a), 128.3 (ArCH), 128.3 (ArCH), 127.6 (ArCH), 127.2 (C6′, C7′), 127.0 (ArCH), 125.2 (C4′), 124.4 (C2′), 112.7 (C3′), 73.4 (C4), 71.4 (OCH_2Ph), 70.4 (C5), 44.6 (NCH_2Ph), 36.1 (C3), 17.7 (C1″), 5.9 (C2″), 3.0 (C3″). HRMS (ESI) *m/z* calcd for $NaC_{29}H_{27}{}^{79}BrN_2O_2$ $[M + Na]^+$ 537.1154, found 537.1132.

(4*S*)-1-Benzyl-4-(benzyloxy)-5-(5-chloro-1*H*-indol-3-yl)-5-cyclopropylpyrrolidin-2-one (3d)

Prepared following general method A, from **1** (0.050 g, 0.15 mmol), 5-chloroindole (0.068 g, 0.45 mmol), $BF_3{\cdot}Et_2O$ (0.046 g, 0.040 mL, 0.32 mmol) and CH_2Cl_2 (7.5 mL). The reaction mixture was stirred for 2 h at room temperature rather than 12 h. Separation by column chromatography (1:1 EtOAc/PS) yielded compound **3d** as a yellow solid (0.059 g, 76%) and as a mixture of diastereomers (dr > 95:5). A small amount of the major diastereomer could be

isolated pure by further chromatographic separation. ***Major diastereomer*** (4*S,*5*S*)-**3d**: $[\alpha]_D^{25}$ 90 ± 6 (*c* 14.4, $CHCl_3$). ν_{max}/cm^{-1} 2926, 1666, 1402, 1270, 1069, 744, 697. δ_H 8.42 (1H, bs, H1′), 7.77 (1H, d, *J* = 1.7 Hz, H4′), 7.27 (1H, d, *J* = 8.7 Hz, H7′), 7.24 – 7.20 (5H, m. ArCH), 7.20 – 7.17 (3H, m, ArCH), 7.14 (1H, dd, *J* = 8.6, 1.7 Hz, H6′), 7.04 (1H, d, *J* = 1.7 Hz, H2′), 6.95 – 6.91 (2H, m, ArCH), 5.10 (1H, d, *J* = 15.4 Hz, NCH_2Ph), 4.26 (1H, d, *J* = 12.1 Hz, , OCH_2Ph), 4.17 (1H, d, *J* = 12.1 Hz, OCH_2Ph), 3.91 (1H, d, *J* = 15.4 Hz, NCH_2Ph), 3.49 (1H, app. t, *J* = 7.4 Hz, H4), 2.79 (1H, dd, *J* = 16.6, 7.4 Hz, H3), 2.52 (1H, dd, *J* = 16.6, 7.4 Hz, H3), 1.24 – 1.17 (1H, m, H1″), 0.87 – 0.47 (2H, m, H2″), 0.11 (1H, m, *J* = 9.2, 5.9 Hz, H3″), -0.09 – -0.17 (1H, m, H3″). δ_C 172.8 (C2), 138.9 (*ipso*-NCH_2Ph), 137.4 (*ipso*-OCH_2Ph), 135.6 (C7′a), 128.4 (ArCH), 128.3 (ArCH), 128.2 (ArCH), 128.1 (C5′a), 127.6 (ArCH), 127.2 (ArCH), 127.0 (ArCH), 125.7 (C3′a), 124.7 (C2′), 122.6 (C6′), 122.0 (C4′), 116.7 (C3′), 112.3 (C7′), 73.4 (C4), 71.4 (OCH_2Ph), 70.5 (C5), 44.6 (NCH_2Ph), 36.3 (C3), 17.7 (C1″), 5.8 (C2″), 2.9 (C3″). HRMS (ESI) *m/z* calcd for $NaC_{29}H_{27}{}^{35}ClN_2O_2$ $[M + Na]^+$ 493.1681, found 493.1659. ***Minor diastereomer*** [indicative peaks from mixture of diastereomers] δ_H 8.31 (1H, bs, H1′), 7.39 – 7.34 (1H, m, H7′), 7.32 – 7.13 (11H, m, ArCH), 6.98 (2H, app. t, *J* = 7.6 Hz, ArCH), 4.97 (1H, d, *J* = 15.5 Hz, NCH_2Ph), 4.80 (1H, app. t, *J* = 5.5 Hz, H4), 4.61 (1H, d, *J* = 12.2 Hz, OCH_2Ph), 4.56 (1H, d, *J* = 12.2 Hz, OCH_2Ph), 4.16 (1H, d, *J* = 15.5 Hz, NCH_2Ph), 2.68 (1H, dd, *J* = 16.5, 4.9 Hz, H3), 2.52 (1H, dd, *J* = 16.5, 6.1 Hz, H3), 1.58 – 1.51 (1H, m, H1″), 0.43 – 0.37 (2H, m, H2″), 0.37 – 0.26 (2H, m, H3″).

(4*S*)-1-Benzyl-4-(benzyloxy)-5-cyclopropyl-5-(5-fluoro-1*H*-indol-3-yl)pyrrolidin-2-one (3e).

Prepared following general method A, from **1** (0.050 g, 0.15 mmol), 5-fluoroindole (0.060 g, 0.44 mmol), $BF_3{\cdot}Et_2O$ (0.046 g, 0.040 mL, 0.32 mmol) and CH_2Cl_2 (7.5 mL). The reaction mixture was stirred at room temperature for 2 h rather than 12 h. Separation by column chromatography (1:1 EtOAc/PS) yielded compound **3e** as a yellow solid (0.055 g, 89%) and as a mixture of diastereomers (dr = 89:11). A small amount of the major diastereomer could be isolated pure by further chromatographic separation. ***Major diastereomer*** (4*S,*5*S*)-**3e**: $[\alpha]_D^{25}$ 7.5 ± 1.3 (*c* 5.1, $CHCl_3$). ν_{max}/cm^{-1} 3263, 2921, 2853, 1662, 1454, 1410, 1352, 1261, 1093, 1026, 930, 798, 737, 633. δ_H 8.63 (1H, bs, H1′), 7.40 (1H, dd, *J* = 10.5, 1.5 Hz, H4′), 7.27 (2H, dd, *J* = 8.5, 4.0 Hz H7′, ArCH), 7.23 – 7.16 (8H, m, ArCH), 7.00 (1H, d, *J* = 2.5 Hz, ArCH), 6.93 (1H, dd, *J* = 9.0, 2.0 Hz, H6′), 6.89 (1H, s, H2′), 5.10 (1H, d, *J* = 15.5 Hz, NCH_2Ph), 4.23 (1H, d, *J* = 12.0 Hz, OCH_2Ph), 4.15 (1H, d, *J* = 12.0 Hz, OCH_2Ph), 3.86 (1H, d, *J* = 15.5 Hz,

NCH_2Ph), 3.48 (1H, app. t, J = 7.5 Hz, H4), 2.81 (1H, dd, J = 16.5, 7.5 Hz, H3), 2.54 (1H, dd, J = 16.5, 7.5 Hz, H3), 1.24 – 1.18 (1H, m, H1″), 0.82 – 0.75 (2H, m, H2″), 0.12 – 0.10 (1H, m, H3″), -0.12 – -0.15 (1H, m, H3″). δ_C 173.0 (C2), 157.9 (d, J = 233.9 Hz, C5′), 138.9 (*ipso*-NCH_2Ph), 137.4 (*ipso*-OCH_2Ph), 128.5 (C7′a), 128.3 (ArCH), 128.2 (ArCH), 128.1 (ArCH), 127.6 (ArCH), 127.3 (ArCH), 126.9 (ArCH), 126.5 (ArCH), 116.6 (d, J = 4.8 Hz, C3′), 112.0 (d, J = 9.6 Hz, C7′), 110.5 (d, J = 26.9 Hz, C6′), 107.0 (d, J = 25.0 Hz, C4′), 73.3 (C4), 71.4 (OCH_2Ph), 70.7 (C5), 44.6 (NCH_2Ph), 36.7 (C3), 17.9 (C1″), 5.5 (C2″), 2.6 (C3″). HRMS (ESI) *m/z* calcd for $C_{29}H_{28}FN_2O_2$ $[M + H]^+$ 455.2135, found 455.2144.

(4*S*)-1-Benzyl-4-(benzyloxy)-5-cyclopropyl-5-(5-methoxy-1*H*-indol-3-yl)pyrrolidin-2-one (3f)

Prepared following general method B, from **1** (0.050 g, 0.15 mmol), 5-methoxyindole (0.044 g, 0.30 mmol), $BF_3{\cdot}Et_2O$ (0.046 g, 0.040 mL, 0.32 mmol) and CH_2Cl_2 (7.5 mL). This reaction was cooled to -40 °C rather than 0 °C for the $BF_3{\cdot}Et_2O$ addition and kept at that temperature for the duration of the reaction. Separation by column chromatography (1:1 EtOAc/PS) yielded compound **3f** as a colourless oil (0.059 g, 85%) and as a mixture of diastereomers (dr = 88:12). A small amount of each diastereomer could be isolated pure by further chromatographic separation. ***Major diastereomer*** (4*S,*5*S*)-**3f** $[\alpha]_D^{25}$ 5.8 ± 0.7 (*c* 3.0, $CHCl_3$). ν_{max}/cm^{-1} 2923, 1666, 1437,1295, 1213, 800, 745, 700. δ_H 8.42 (1H, bs, H1′), 7.25 (1H, d, J = 8.5 Hz, H7′), 7.22 – 7.20 (4H, m), 7.18 – 7.14 (5H, m, ArCH, H4′), 7.09 (1H, d, J = 2.4 Hz, H2′), 6.90 (2H, dd, J = 6.6, 2.9 Hz, ArCH), 6.86 (1H, dd, J = 8.9, 2.4 Hz, H6′), 5.12 (1H, d, J = 15.5 Hz, NCH_2Ph), 4.25 (1H, d, J = 11.8 Hz, OCH_2Ph), 4.14 (1H, d, J = 11.8 Hz, OCH_2Ph), 3.87 (1H, d, J = 15.5 Hz, NCH_2Ph), 3.73 (3H, s, OCH_3), 3.50 (1H, app. t, J = 7.4 Hz, H4), 2.83 (1H, dd, J = 16.6, 7.4 Hz. H3), 2.57 (1H, dd, J = 16.6, 7.4 Hz, H3), 1.24 – 1.20 (1H, m, H1″), 0.81 – 0.73 (2H, m, H2″), 0.16 – 0.04 (1H, m, H3″), -0.13 – -0.20 (1H, m, H3″). δ_C 173.0 (C2), 154.1 (C5′), 139.1 (*ipso*-NCH_2Ph), 137.6 (*ipso*-OCH_2Ph), 132.2 (C7′a), 128.4 (ArCH), 128.2 (ArCH), 128.2 (ArCH), 128.1 (ArCH), 127.6 (ArCH), 127.34 (ArCH), 127.33 (C3′a), 126.9 (ArCH), 124.6 (C2′), 116.1 (C3′), 112.6 (C6′), 112.0 (C7′), 103.6 (C4′), 73.5 (C4), 71.3 (OCH_2Ph), 70.8 (C5), 55.8 (OCH_3), 44.6 (NCH_2Ph), 36.7 (C3), 18.1 (C1″), 5.4 (C2″), 2.6 (C3″). HRMS (ESI) *m/z* calcd for $C_{30}H_{31}N_2O_3$ $[M + H]^+$ 467.2347, found 467.2335. ***Minor diastereomer*** (4*S*,5*R*)-**3f**: δ_H 8.25 (1H, bs, H1′), 7.29 – 7.22 (3H, m, ArCH), 7.22 – 7.19 (2H, m, ArCH), 7.19 – 7.12 (7H, m, ArCH), 6.82 (1H, dd, J = 8.7, 2.0 Hz, H6′), 6.69 (1H, s, H4′), 4.84 – 4.77 (2H, m, NCH_2Ph, H4), 4.55 (2H, s, OCH_2Ph), 4.22 (1H, d, J = 15.5 Hz, NCH_2Ph), 3.62 (3H, s, OCH_3), 2.70 (1H, dd, J = 16.3, 5.7 Hz, H3), 2.53 (1H, dd, J = 16.3, 6.4 Hz, H3), 1.67 – 1.54 (1H, m,

H1″), 0.50 – 0.38 (2H, m, H2″, H3″), 0.37 – 0.32 (1H, d, *J* = 5.4 Hz, H3‴). δ_C 174.3 (C2), 154.0 (C5′), 138.9 (*ipso*-NCH_2Ph), 138.2 (*ipso*-OCH_2Ph), 132.2 (C7′a), 128.5 (ArCH), 128.1 (ArCH), 127.9 (ArCH), 127.8 (ArCH), 127.5 (ArCH), 126.9 (ArCH), 125.8 (C3′a), 125.2 (ArCH), 115.8 (C3′), 112.5 (C6′), 112.4 (C7′), 102.8 (C4′), 79.6 (C4), 71.9 (OCH_2Ph), 56.0 (OCH_3), 45.2 (NCH_2Ph), 37.2 (C3), 14.7 (C1″), 2.7 (C2″), 2.3 (C3″). LRMS (ESI) *m/z* calcd for $C_{30}H_{31}N_2O_3$ $[M + H]^+$ 467, found 467.

3′-((3*S*)-1-Benzyl-3-(benzyloxy)-2-cyclopropyl-5-oxopyrrolidin-2-yl)-1*H*-indole-5′-carbonitrile (3g)

Prepared following general method B, from **1** (0.050 g, 0.148 mmol), 5-cyanoindole (0.042 g, 0.3 mmol), $BF_3{\cdot}Et_2O$ (0.046 g, 0.040 mL, 0.32 mmol) and CH_2Cl_2 (10.0 mL). Separation by column chromatography (1:1 EtOAc/PS) yielded compound **3g** as a yellow solid (0.048 g, 0.104 mmol, 70%) and as a mixture of diastereomers (93:7). A small amount of the major diastereromer could be isolated pure by further chromatographic separation. ***Major diastereomer*** (2*S*,3*S*)-**3g**: $[\alpha]_D^{25}$ 23.5 ± 0.2 (*c* 14.2, $CHCl_3$). ν_{max}/cm^{-1} 3241, 2922, 2218, 1664, 1434, 1406, 1348, 1096, 1073, 1026, 808, 735, 700, 640, 421. δ_H 8.66 (1H, bs, H1′), 8.17 (1H, s, H4′), 7.43 – 7.38 (2H, m, ArCH), 7.25 – 7.16 (8H, m, ArCH), 7.08 (1H, d, *J* = 1.7 Hz, ArCH), 6.96 – 6.89 (2H, m, ArCH), 5.07 (1H, d, *J* = 15.1 Hz, NCH_2Ph), 4.28 (1H, d, *J* = 11.7 Hz, OCH_2Ph), 4.18 (1H, d, *J* = 11.7 Hz, OCH_2Ph), 3.99 (1H, d, *J* = 15.1 Hz, NCH_2Ph), 3.51 (1H, app. t, *J* = 7.4 Hz, H3), 2.78 (1H, dd, *J* = 16.4, 7.4 Hz, H4), 2.48 (1H, dd, *J* = 16.4, 7.7 Hz, H4), 1.24 – 1.17 (1H, m, H1″), 0.95 – 0.77 (2H, m, H2″), 0.13 (1H, m, H3″), -0.03 – -0.11 (1H, m, H3″). δ_C 172.7 (C5), 139.0 (*ipso*-NCH_2Ph), 138.8 (C7′a), 137.1 (*ipso*-OCH_2Ph), 128.8 (ArCH), 128.5 (ArCH), 128.4 (ArCH), 128.3 (ArCH), 127.9 (ArCH), 127.4 (ArCH), 127.2 (ArCH), 127.1 (C3′a), 125.1 (ArCH), 125.0 (C3′a), 120.8 (NC), 118.4 (C3′), 112.2 (C7′), 103.1 (C5′), 73.4 (C3), 71.6 (OCH_2Ph), 70.3 (C2), 44.6 (NCH_2Ph), 35.9 (C4), 17.5 (C1″), 6.0 (C2″), 3.2 (C3″). HRMS (ESI) *m/z* calcd for $NaC_{30}H_{27}N_3O_2$ $[M+Na]^+$ 484.2001, found 484.1998.

Methyl 3-((3*S*)-1-benzyl-3-(benzyloxy)-2-cyclopropyl-5-oxopyrrolidin-2-yl)-1*H*-indole-5-carboxylate (3h)

Prepared following general method B, from **1** (0.050 g, 0.15 mmol), methyl indole-5-carboxylate (0.078 g, 0.45 mmol), $BF_3{\cdot}Et_2O$ (0.046 g, 0.040 mL, 0.32 mmol) and CH_2Cl_2 (7.5 mL). Separation by column chromatography (2:1 EtOAc/PS) yielded **3h** as a white foam (0.045 g, 0.090 mmol, 61%) and as a mixture of diastereomers (dr = 84:16). A small amount of the major diastereomer could be isolated pure by further chromatographic separation. ***Major***

diastereomer (2*S*,3*S*)-**3h**: $[\alpha]_D^{25}$ 35.2 ± 0.5 ° (*c* 17.0, $CHCl_3$). ν_{max}/cm^{-1} 3310, 2935, 2109, 1754, 1665, 1617, 1433, 1351, 1317, 1242, 1105, 907, 730, 703. δ_H 8.92 (1H, bs, H1′), 8.64 (1H, s, H4′), 7.89 (1H, d, *J* = 8.6 Hz, H6′), 7.35 (1H, d, *J* = 8.6 Hz, H7′), 7.28 – 7.16 (6H, m, ArCH), 7.13 (2H, d, *J* = 6.7 Hz, ArCH), 7.03 (1H, d, *J* = 2.0 Hz, ArCH), 6.95 – 6.91 (2H, m, ArCH), 5.10 (1H, d, *J* = 15.3 Hz, NCH_2Ph), 4.26 (1H, d, *J* = 11.8 Hz, OCH_2Ph), 4.18 (1H, d, *J* = 11.8 Hz, OCH_2Ph), 3.95 (1H, d, *J* = 15.3 Hz, NCH_2Ph), 3.90 (3H, s, $COOCH_3$), 3.53 (1H, t, *J* = 7.6 Hz, H3), 2.80 (1H, dd, *J* = 16.5, 7.6 Hz, H4), 2.53 (1H, dd, *J* = 16.5, 7.6 Hz, H4), 1.32 – 1.18 (1H, m, H1″), 0.94 – 0.82 (2H, m, H2″), 0.14 – 0.10 (1H, m, H3″), -0.10 – -0.16 (1H, m, H3″). δ_C 172.9 (C5), 168.4 (ArCOOMe), 140.0 (C7′a), 138.9 (*ipso*-NCH_2Ph), 137.4 (*ipso*-OCH_2Ph), 128.3 (ArCH), 128.2 (ArCH), 128.2 (ArCH), 127.6 (ArCH), 127.4 (ArCH), 127.0 (ArCH), 126.7 (ArCH), 125.7 (ArCH), 124.5 (ArCH), 123.5 (ArCH), 121.8 (ArCH), 118.1 (C6′), 111.1 (C7′), 73.3 (C4), 71.4 (OCH_2Ph), 70.6 (C2), 52.0 (OCH_3), 44.7 (NCH_2Ph), 36.0 (C4), 17.7 (C1″), 5.9 (C2″), 3.1 (C3″). HRMS (ESI) *m/z* calcd for $NaC_{31}H_{30}N_2O_4$ $[M + Na]^+$ 517.2103, found 517.2112.

(4*S*,5*S*)-1-Benzyl-4-(benzyloxy)-5-cyclopropyl-5-(5-nitro-1*H*-indol-3-yl)pyrrolidin-2-one (3i) and (1*S*,3′*S*)-1′-benzyl-3′-(benzyloxy)-6-nitro-2,3,4,9-tetrahydrospiro[carbazole-1,2′-pyrrolidin]-5′-one (5i).

Prepared following general method B, from **1** (0.050 g, 0.15 mmol), 5-nitroindole (0.068 g, 0.45 mmol), $BF_3{\cdot}Et_2O$ (0.046 g, 0.040 mL, 0.32 mmol) and CH_2Cl_2 (7.5 mL). Separation by column chromatography (3:2 PS/EtOAc) yielded compound **3i** as a yellow oil (0.040 g, 0.083 mmol, 56%) and as a mixture of diastereomers (dr > 95:5). A small amount of the major diastereomer could be isolated pure by further separation using column chromatography. The spirocycle **5i** was also isolated as a yellow oil (0.011 g, 0.023 mmol, 15%) and as a mixture of diastereomers (dr > 95:5). A small amount of the major diastereomer could be isolated pure by further chromatographic separation. ***Major diastereomer*** (4*S*,5*S*)-**3i**: $[\alpha]_D^{25}$ 113 ± 12 (*c* 12.5, $CHCl_3$). ν_{max}/cm^{-1} 3330, 2975, 2887, 1672, 1519, 1380, 1330, 1088, 1047, 881, 648. δ_H 9.01 (1H, bs, H1′), 8.85 (1H, d, *J* = 2.1 Hz, H4′), 8.05 (1H, dd, *J* = 8.8, 2.1 Hz, H6′), 7.36 (1H, d, *J* = 8.8 Hz, H7′), 7.25 – 7.18 (5H, m, ArCH), 7.17 – 7.14 (3H, m, ArCH), 7.06 (1H, d, *J* = 2.3 Hz, H2′), 6.98 – 6.96 (2H, m, ArCH), 5.07 (1H, d, *J* = 15.1 Hz, NCH_2Ph), 4.29 (1H, d, *J* = 11.7 Hz, OCH_2Ph), 4.21 (1H, d, *J* = 11.7 Hz, OCH_2Ph), 4.06 (1H, d, *J* = 15.1 Hz, NH_2Ph), 3.56 (1H, t, *J* = 7.7 Hz, H4), 2.79 (1H, dd, *J* = 16.4, 7.7 Hz, H3), 2.48 (1H, dd, *J* = 16.4, 7.7 Hz, H3), 1.30 – 1.18 (1H, m, H1″), 1.02 – 0.88 (2H, m, H2″), 0.16 (1H, dd, *J* = 9.4, 5.7 Hz,

H3″), -0.01 – -0.10 (1H, m, H3″). δ_C 172.7 (C2), 141.7 (C7′a), 140.4 (C5′), 138.6 (*ipso*-NCH_2Ph), 137.0 (*ipso*-OCH_2Ph), 128.4 (ArCH), 128.3 (ArCH), 127.9 (ArCH), 127.5 (ArCH), 127.2 (ArCH), 126.6 (C3′a), 125.7 (ArCH), 120.5 (C2′), 119.7 (C3′), 117.7 (C6′), 111.3 (C7′), 73.2 (C4), 71.6 (OCH_2Ph), 70.3 (C5), 44.7 (NCH_2Ph), 35.7 (C3), 17.3 (C1″), 6.1 (C2″), 3.3 (C3″). HRMS (ESI) *m/z* calcd for $NaC_{29}H_{27}N_3O_4$ $[M + Na]^+$ 504.1899, found 504.1891. ***Major diastereomer*** (1*S*,3′*S*)-**5i**: $[\alpha]_D^{25}$ 61.0 ± 5 (*c* 2.1, $CHCl_3$). ν_{max}/cm^{-1} 3330, 2975, 2887, 1654, 1522, 1360, 1088, 1044, 870, 740, 648. δ_H 8.74 (1H, bs, H9), 8.54 (1H, d, *J* = 1.5 Hz, H5), 8.08 (1H, d, *J* = 9.0, 1.5 Hz, H7), 7.22 – 7.18 (1H, m, ArCH), 7.16 – 7.12 (4H, m, ArCH), 7.06 (1H, d, *J* = 9.0 Hz, H8), 6.97 (2H, d, *J* = 7.3 Hz, ArCH), 6.82 (2H, d, *J* = 7.3 Hz, ArCH), 4.41 (1H, d, *J* = 15.2 Hz, NCH_2Ph), 4.23 (1H, d, *J* = 11.2 Hz, OCH_2Ph), 4.16 (1H, d, *J* = 15.2 Hz, NCH_2Ph), 3.98 (1H, d, *J* = 6.4 Hz, H3′), 3.93 (1H, d, *J* = 11.2 Hz, OCH_2Ph), 2.91 – 2.84 (2H, m, H4, H4′), 2.72 – 2.65 (2H, m, H4, H4′), 2.01 – 1.99 (1H, m, H3), 1.77 – 1.69 (2H, m, H2, H3), 1.68 – 1.62 (1H, m, H2). δ_C 173.7 (C5′), 141.5 (C8a), 139.4 (C6), 138.2 (*ipso*-NCH_2Ph), 136.9 (*ipso*-OCH_2Ph), 133.6 (C9a), 128.6 (ArCH), 128.5 (ArCH), 128.3 (ArCH), 128.2 (ArCH), 127.9 (ArCH), 127.6 (ArCH), 125.7 (C4b), 118.3 (C7), 118.1 (C4a), 116.4 (C5), 111.2 (C8), 79.5 (C3′), 72.2 (OCH_2Ph), 68.0 (C1), 44.6 (NCH_2Ph), 37.1 (C4′), 32.5 (C2), 21.5 (C3), 20.8 (C4). HRMS (ESI) *m/z* calcd for $C_{29}H_{28}N_3O_4$ $[M + H]^+$ 482.2080, found 482.2074.

(4*S*,5*S*)-1-Benzyl-4-(benzyloxy)-5-cyclopropyl-5-(7-fluoro-1*H*-indol-3-yl)pyrrolidin-2-one (3j) and (1*S*,3′*S*)-1′-benzyl-3′-(benzyloxy)-8-fluoro-2,3,4,9-tetrahydrospiro[carbazole-1,2′-pyrrolidin]-5′-one (5j).

Prepared following general method B, from **1** (0.050 g, 0.15 mmol), 7-fluoroindole (0.040 g, 0.30 mmol), $BF_3{\cdot}Et_2O$ (0.046 g, 0.040 mL, 0.32 mmol) and CH_2Cl_2 (7.5 mL). Separation by column chromatography (1:2 EtOAc/PS) yielded **3j** as a yellow solid (0.049 g, 0.11 mmol, 73%) and as a mixture of diastereomers (84:16). A small amount of the major diastereomer could be isolated pure by further chromatographic separation. Compound **5j** was also isolated as a yellow oil (0.003 g, 0.007 mmol, 5%) and as a pure diastereomer (dr >95:5). ***Major diastereomer*** (4*S*,5*S*)-**3j**: $[\alpha]_D^{25}$ -2.3 ± 0.2 (*c* 14.0, $CHCl_3$). ν_{max}/cm^{-1} 2875, 1666, 1353, 1234, 1091, 1025, 934, 847, 749, 701. δ_H 8.85 (1H, bs, H1′), 7.44 (1H, d, *J* = 8.1 Hz, H4′), 7.24 – 7.11 (10H, m, ArCH), 7.01 – 6.97 (1H, m, H5′), 6.90 (1H, dd, *J* = 10.8, 8.1 Hz, H6′, 6.87 – 6.82 (1H, m, ArCH), 5.12 (1H, d, *J* = 15.5 Hz, NCH_2Ph), 4.22 (1H, d, *J* = 12.0 Hz, OCH_2Ph), 4.11 (1H, d, *J* = 12.0 Hz OCH_2Ph), 3.81 (1H, d, *J* = 15.5 Hz, NCH_2Ph), 3.49 (1H, app. t, *J* = 7.2 Hz, H4), 2.85 (1H, dd, *J* = 16.7, 7.4 Hz, H3), 2.58 (1H, dd, *J* = 16.7, 6.6 Hz H3), 1.25 –

1.17 (1H, m, H1″), 0.82 – 0.68 (2H, m, H2″), 0.16 – 0.07 (1H, m, H3″), -0.11 – -0.21 (1H, m, H3″). δ_C 173.1 (C2), 149.8 (d, *J* = 243.8 Hz, C7′), 139.1 (*ipso*-NCH_2Ph), 137.6 (*ipso*-OCH_2Ph), 130.6 (d, *J* = 4.7 Hz, C7′a), 128.3 (ArCH), 128.3 (ArCH), 128.2 (ArCH), 127.7 (ArCH), 127.4 (ArCH), 127.0 (ArCH), 125.7 (d, *J* = 13.0 Hz, C3′a), 125.0 (ArCH), 120.3 (d, *J* = 6.5 Hz, C5′), 117.7 (d, *J* = 3.7 Hz, C4′), 117.6 (C3′), 106.8 (d, *J* = 15.8 Hz, C6′), 73.3 (C4), 71.5 (OCH_2Ph), 70.8 (C5), 44.8 (NCH_2Ph), 37.0 (C3), 18.5 (C1″), 5.4 (C2″), 2.5 (C3″). HRMS (ESI) *m/z* calcd for $NaC_{29}H_{27}FN_2O_2$ $[M+Na]^+$ 477.1954, found 477.1968. ***Major diastereomer*** (1*S*,3′*S*)-**5j**: $[\alpha]_D^{25}$ 71 ± 4 (*c* 1.5, $CDCl_3$). ν_{max}/cm^{-1} 3248, 2921, 2866, 2218, 2108, 1757, 1672, 1447, 1412, 1351, 1310, 1221, 1146, 1105, 1023, 730, 696. δ_H 7.56 (1H, bs, H9), 7.29 – 7.25 (4H, m, $CHCl_3$ and H5), 7.17 – 7.07 (4H, m, ArCH), 7.02 (1H, td, *J* = 7.6, 4.9 Hz, H6), 6.96 (2H, d, *J* = 7.4 Hz, ArCH), 6.87 (1H, dd, *J* = 10.9, 7.9 Hz, H7), 4.42 (1H, d, *J* = 12.1 Hz, OCH_2Ph), 4.38 (1H, d, *J* = 12.1 Hz, OCH_2Ph), 4.34 – 4.28 (2H, m, NCH_2Ph, H3′), 4.24 (1H, d, *J* = 15.1 Hz, NCH_2Ph), 2.83 (1H, dd, *J* = 16.8, 7.4 Hz, H4′), 2.80 – 2.74 (1H, m, H4), 2.71 (1H, dd, *J* = 16.8, 7.1 Hz, H4′), 2.68 – 2.63 (1H, m, H4), 2.48 – 2.42 (1H, m, H2), 2.04 – 1.98 (1H, m, H3), 1.97 – 1.90 (1H, m, H3), 1.76 (1H, td, *J* = 12.7, 3.2 Hz, H2,). δ_C 172.3 (C5′), 149.7 (C8), 138.1 (*ipso*-NCH_2Ph), 137.4 (*ipso*-OCH_2Ph), 133.1 (d, *J* = 3.7 Hz, C8′a), 128.5 (ArCH), 128.0 (ArCH), 127.6 (ArCH), 127.4 (ArCH), 120.1 (d, *J* = 6.5 Hz, C6), 114.7 (d, *J* = 3.7 Hz, C5), 107.8 (d, *J* = 15.8 Hz, C7), 79.8 (C3′), 72.4 (OCH_2Ph), 65.7 (C1), 44.1 (NCH_2Ph), 36.0 (C4′), 28.6 (C2), 21.6 (C3), 20.9 (C4). LRMS (ESI) *m/z* calcd for $NaC_{29}H_{27}FN_2O_2$ $[M+Na]^+$ 477, found 477.

(1*R*,3′*S*)-1′-Benzyl-3′-(benzyloxy)-8-nitro-2,3,4,9-tetrahydrospiro[carbazole-1,2′-pyrrolidin]-5′-one (5k) and (5*S*,9*S*)-6-benzyl-9-(benzyloxy)-1-oxa-6-azaspiro[4.4]nonan-7-one (6)

Prepared following general method B, from **1** (0.057 g, 0.169 mmol), 7-nitroindole (0.055 g, 0.33 mmol), $BF_3{\cdot}Et_2O$ (0.053 g, 0.045 mL, 0.37 mmol) and CH_2Cl_2 (8.5 mL). Separation by column chromatography (1:2 EtOAc/PS) yielded compound **5k** as a yellow oil (0.010 g, 0.021 mmol, 12%) and as a mixture of diastereomers (dr = 62:38). The spirofuran **6** was also isolated as a clear oil (0.028 g, 0.084 mmol, 49%) and as a mixture of diastereomers (dr = 75:25). Small amounts of the pure diastereomers of **5k** and the major diastereomer of **6** could be obtained after further purification by column chromatography. ***Major diastereomer*** (1*S*,3′*S*)-**5k**:$[\alpha]_D^{25}$ 90 ± 2 (*c* 12.0, $CHCl_3$). ν_{max}/cm^{-1} 2926, 1696, 1517, 1395, 1295, 1072, 733, 697. δ_H 9.28 (1H, bs, H9), 8.10 (1H, d, *J* = 8.1 Hz, H7), 7.85 (1H, d, *J* = 7.4 Hz, H5), 7.21 – 7.14 (2H, m, ArCH and

H6), 7.13 – 7.07 (3H, m, ArCH), 7.07 – 7.01 (2H, m, ArCH), 6.92 (2H, d, *J* = 7.4 Hz, *ortho*-H of $PhCH_2N$), 6.86 (2H, d, *J* = 7.4 Hz *ortho*-H of $PhCH_2O$), 4.38 (1H, d, *J* = 15.1 Hz, NCH_2Ph), 4.29 (1H, d, *J* = 11.8 Hz, OCH_2Ph), 4.21 (2H, d, *J* = 15.1 Hz, NCH_2Ph), 4.03 (1H, d, *J* = 11.8 Hz, OCH_2Ph), 3.99 (1H, d, *J* = 5.9 Hz, H3′), 2.92 (1H, dd, *J* = 17.6, 5.9 Hz, H4′), 2.83 (1H, bd, *J* = 15.8 Hz, H4), 2.76 (1H, d, *J* = 17.5 Hz, H4′), 2.72 – 2.64 (1H, m, H4), 2.04 – 1.98 (1H, m, H3), 1.86 – 1.79 (1H, m, H2), 1.77 – 1.69 (2H, m, H2 and H3). δ_C 173.5 (C5′), 138.0 (*ipso*-NCH_2Ph), 137.0 (*ipso*-OCH_2Ph), 130.2 (C9a), 129.5 (C4b), 128.6 (ArCH), 128.5 (ArCH), 128.2 (ArCH), 128.0 (ArCH), 127.6 (*ortho*C-$PhCH_2O$), 127.3 (ArCH), 126.7 (C5), 119.8 (C7), 118.6 (C6), 117.1 (C4a), 79.1 (C3′), 72.1 (OCH_2Ph), 67.7 (C1), 44.5 (NCH_2Ph), 37.1 (C4′), 32.4 (C2), 21.7 (C3), 21.0 (C4). HRMS (ESI) *m/z* calcd for $C_{29}H_{28}N_3O_4$ $[M + H]^+$ 482.2080, found 482.2084. ***Minor diastereomer*** (1*R*,3′*S*)-**5k**: ν_{max}/cm^{-1} 3064, 3032, 2957, 2919, 2850, 1706, 1669, 1454, 1402, 1356, 1314, 1271, 1125, 1112, 1071, 1028, 753, 699. δ_H 8.59 (1H, s, H9), 8.09 (1H, dd, *J* = 8.1, 0.9 Hz, H7), 7.83 (1H, d, *J* = 7.6 Hz, H5), 7.19 (1H, t, *J* = 7.9 Hz, H6), 7.14 – 7.11 (2H, m, ArH), 7.08 – 7.04 (2H, m), 7.01 (1H, d, *J* = 7.3 Hz), 6.94 (2H, t, *J* = 7.5 Hz), 6.86 – 6.81 (2H, d, *J* = 7.2 Hz, *o*-NCH_2ArH), 4.64 (1H, d, *J* = 15.0 Hz, NCH_2Ph)), 4.43 (1H, d, *J* = 12.1 Hz, OCH_2Ph), 4.40 – 4.33 (2H, m, OCH_2Ph H3′), 3.93 (1H, d, *J* = 15.0 Hz, NCH_2Ph), 2.88 (1H, dd, *J* = 16.6, 7.5 Hz, H4′), 2.82 (1H, dt, *J* = 15.7, 4.7 Hz, H4), 2.75 – 2.66 (2H, m, H4 H4′), 2.51 (1H, ddd, *J* = 13.7, 3.2, 2.1 Hz, H2), 2.19 – 2.10 (1H, m, H3), 2.06 – 1.97 (1H, m, H3), 1.85 (1H, ddd, *J* = 13.7, 11.9, 3.4 Hz, H2). δ_C 171.7 (C5′), 137.9 (*ipso*-NCH_2Ph), 137.2 (*ipso*-OCH_2Ph), 134.7 (C9a), 132.9 (C8a), 130.7 (C8), 129.9 (C4b), 128.5 (ArCH), 128.4 (ArCH), 128.01 (ArCH), 127.96 (s), 127.6 (s), 127.1 (s), 126.8 (C5), 119.7 (C7), 119.0 (C6), 118.1 (C4a), 79.7 (C3′), 72.6 (OCH_2Ph), 64.5 (C1), 44.0 (NCH_2Ph), 35.7 (C4′), 28.3 (C2), 21.7 (C3), 20.5 (C4). LRMS (ESI) *m/z* calcd for $C_{29}H_{28}N_3O_4$ $[M + H]^+$ 482, found 482. ***Major diastereomer*** (5*S*,9*S*)-**6**: $[\alpha]_D^{25}$ 56 ± 0.2 (*c* 8.0, $CHCl_3$). ν_{max}/cm^{-1} 3356, 3063, 22865, 1453, 1333, 1233, 1154, 1071, 1027, 7335, 604, 456. δ_H 7.44 – 7.29 (9H, m, ArCH), 7.28 – 7.24 (1H, m, ArCH), 4.74 – 4.65 (2H, m, NCH_2Ph and OCH_2Ph), 4.53 (1H, d, *J* = 11.8 Hz, OCH_2Ph), 4.31 (1H, d, *J* = 15.9 Hz, NCH_2Ph), 4.00 – 3.95 (1H, m, H9), 3.92 (1H, app. q, *J* = 7.0 Hz, H2), 3.79 (1H, dd, *J* = 14.0, 7.0 Hz, H2), 2.81 (1H, dd, *J* = 16.8, 6.0 Hz, H8), 2.52 (1H, dd, *J* = 16.8, 3.8 Hz, H8), 2.45 (1H, dt, *J* = 13.7, 7.0 Hz, H4), 1.96 – 1.86 (2H, m, H3), 1.83 – 1.75 (1H, m, H4). δ_C 172.8 (C7), 138.2 (*ipso*-NCH_2Ph), 137.7 (*ipso*-OCH_2Ph), 128.6 (ArCH), 128.6 (ArCH), 128.0 (ArCH), 127.7 (ArCH), 127.1 (ArCH), 103.3 (C5), 79.2 (C9), 71.8 (OCH_2Ph), 68.4 (C2), 42.6 (NCH_2Ph), 35.8 (C8), 28.5 (C4), 25.8 (C3). HRMS (ESI) *m/z* calcd for $C_{21}H_{24}NO_3$ $[M+H]^+$ 338.1756, found 338.1764. ***Minor diastereomer*** (5*S*,9*R*)-**6**: δ_H (in part

from the mixture) 4.79 (1H, d, J = 16.0 Hz), 4.72 (1H, d, J = 12.3 Hz), 4.54 (1H, d, J = 12.2 Hz).

(4*S*)-1-Benzyl-4-(benzyloxy)-5-cyclopropyl-5-(1-methyl-1*H*-indol-3-yl)pyrrolidin-2-one (3l)

Prepared following general method A, using **1** (0.050 g, 0.15 mmol), 1-methylindole (0.059 g, 0.45 mmol), $BF_3{\cdot}Et_2O$ (0.046 g, 0.040 mL, 0.32 mmol) and CH_2Cl_2 (7.5 mL). Separation by column chromatography (1:2 EtOAc/PS) yielded compound **3l** as a brown white solid (0.046 g, 0.010 mmol, 69%) and as a mixture of diastereomers (dr = 53:47). A small amount of each diastereomer could be isolated pure by further chromatographic separation. ***Major diastereomer*** (4*S*,5*S*)-**3l**: $[\alpha]_D^{25}$ 8.3 ± 1.6 (*c* 2.95, $CHCl_3$). ν_{max}/cm^{-1} 3242, 3078, 2900,2109, 1754, 1706, 1501, 1453, 1378, 1262, 1221, 1010, 976, 784, 743, 709, 696. δ_H 7.71 (1H, d, J = 8.2 Hz, H4′), 7.35 – 7.31 (1H, m, H7), 7.27 – 7.24 (2H, m, ArCH), 7.22 (3H, d, J = 3.7 Hz), 7.16 (4H, d, J = 4.9 Hz,), 7.13 – 7.08 (1H, d, J = 8.2 Hz, H5), 6.96 (1H, s, H2′), 6.89 (2H, d, J = 4.9 Hz, ArCH), 5.11 (1H, d, J = 15.3 Hz, NCH_2Ph), 4.25 (1H, d, J = 11.9 Hz, OCH_2Ph), 4.15 (1H, d, J = 11.9 Hz, OCH_2Ph), 3.88 (1H, d, J = 15.3 Hz, NCH_2Ph), 3.77 (3H, s, NCH_3), 3.47 (1H, app. t, J = 7.2 Hz, H4), 2.79 (1H, dd, J = 16.6, 7.5 Hz, H3), 2.56 (1H, dd, J = 16.6, 7.2 Hz, H3), 1.27 – 1.19 (1H, m, H1″), 0.84 – 0.72 (2H, m, H2″), 0.14 – 0.05 (1H, m, H3″), -0.15 – -0.21 (1H, m, H3″). δ_C 172.9 (C2), 139.2 (*ipso*-NCH_2Ph), 137.9 (C7′a) ,137.7 (*ipso*-OCH_2Ph), 128.7 (ArCH), 128.2 (ArCH), 128.2 (ArCH), 127.5 (ArCH), 127.4 (ArCH), 126.9 (ArCH), 122.1 (ArCH), 121.7(ArCH), 119.6 (ArCH), 114.9 (C3′), 109.4 (C5′), 73.2 (C4), 71.3 (OCH_2Ph), 70.8 (C5), 44.6 (NCH_2Ph), 36.6 (C3), 33.0 (NCH_3), 18.3 (C1″), 5.5 (C2″), 2.6 (C3″). HRMS (ESI) *m/z* calcd for $NaC_{30}H_{30}N_2O_2$ $[M + Na]^+$ 451.2386, found 451.2370. ***Minor diastereomer*** (4*S*,5*R*)-**3l**: Mp 162 ˚C. $[\alpha]_D^{25}$ 23 ± 2 (*c* 3.0, $CHCl_3$). δ_H 7.33 – 7.27 (5H, m, ArCH), 7.24 – 7.15 (8H, m, ArCH), 6.98 (1H, app. t, J = 7.5 Hz, ArCH), 6.95 (1H, s, H2′), 4.98 (1H, d, J = 15.6 Hz, NCH_2Ph), 4.77 (1H, app. t, J = 5.2 Hz, H4), 4.63 (1H, d, J = 12.0 Hz, OCH_2Ph), 4.56 (1H, d, J = 12.0 Hz, OCH_2Ph), 4.19 (1H, d, J = 15.6 Hz, NCH_2Ph), 3.75 (3H, s, NCH_3), 2.66 (1H, dd, J = 16.4, 4.7 Hz, H3), 2.50 (1H, dd, J = 16.4, 5.9 Hz, H3), 1.54 – 1.50 (1H, m, H1″), 0.38 (3H, m, J = 8.10 Hz, H2″ H3″), 0.31 – 0.25 (1H, m, H3″). δ_C 174.6 (C2 assigned from gHMBC), 139.2 (*ipso*-NCH_2Ph (assigned from gHMBC)), 138.6 (*ipso*-OCH_2Ph), 137.7 (C7′a), 129.1 (ArC), 128.5 (ArCH), 128.2 (ArCH), 127.8 (ArCH), 127.7 (ArCH), 127.6 (ArCH), 126.9 (ArCH), 121.9 (ArCH), 120.9 (ArCH), 119.5 (ArCH), 109.9

(C7′a), 80.0 (C5), 71.9 (OCH_2Ph) 45.1 (NCH_2Ph) 37.3 (C3), 31.1 (NCH_3), 14.6 (C1″), 3.4 (C3″), 2.8 (C2″). LRMS (ESI) *m/z* calcd for $NaC_{30}H_{30}N_2O_2$ $[M + Na]^+$ 451, found 451.

(4*S*)-1-Benzyl-4-(benzyloxy)-5-(5-bromo-1-methyl-1*H*-indol-3-yl)-5-cyclopropylpyrrolidin-2-one (3m)

Prepared following general method A, from **1** (0.050 g, 0.15 mmol), 3-bromo-1-methylindole (0.063 g, 0.30 mmol), $BF_3{\cdot}Et_2O$ (0.046 g, 0.040 mL, 0.32 mmol) and CH_2Cl_2 (7.5 mL). Separation by column chromatography (2:3 EtOAc/PS) yielded compound **3m** as a yellow solid (0.054 g, 0.10 mmol, 69%) and as a mixture of diastereomers (dr = 81:19). The diastereomers could not be separated. ***Major diastereomer*** (4*S*,5*S*)-**3m**: ν_{max}/cm^{-1} (on diastereomeric mixture) 2924, 1664, 1454, 1354, 1094, 884, 736, 700. δ_H 7.97 (1H, d, *J* = 1.5 Hz, H4′), 7.30 (1H, dd, *J* = 8.5, 1.8 Hz, H6′), 7.25 – 7.20 (5H, m, ArCH), 7.20 – 7.17 (2H, m, ArCH), 7.15 (2H, d, *J* = 1.5 Hz, H7′ ArCH), 6.97 (2H, d, *J* = 7.3 Hz, ArCH), 6.79 (1H, s, H2′), 5.08 (1H, d, *J* = 15.3 Hz, NCH_2Ph), 4.30 (1H, d, *J* = 12.0 Hz, OCH_2Ph), 4.20 (1H, d, *J* = 12.0 Hz, OCH_2Ph), 3.98 (1H, d, *J* = 15.3 Hz, NCH_2Ph), 3.70 (3H, s, NCH_3), 3.47 (1H, app. t, *J* = 7.6 Hz, H4), 2.77 (1H, dd, *J* = 16.5, 7.3 Hz, H3), 2.50 (1H, dd, *J* = 16.5, 7.9 Hz, H3), 1.23 – 1.17 (1H, m, H1″), 0.89 – 0.76 (2H, m, H2″), 0.14 – 0.05 (1H, m, H3″), -0.08 – -0.17 (1H, m, H3″). δ_C 172.7 (C2), 139.0 (*ipso*-NCH_2Ph), 137.4 (*ipso*-OCH_2Ph), 136.7 (C7′a), 129.2 (C3′a), 129.0 (C2′), 128.5 (ArCH), 128.4 (ArCH), 128.2 (ArCH), 127.6 (ArCH), 127.1 (ArCH), 127.0 (ArCH), 125.2 (C4′), 124.6 (C6′), 114.8 (C3′), 112.9 (C5′), 110.8 (C7′), 73.4 (C4), 71.3 (OCH_2Ph), 44.5 (NCH_2Ph), 33.1 ($ArNCH_3$), 17.6 (C1″), 6.0 (C2″), 3.0 (C3″). HRMS (ESI) (on diastereomeric mixture) *m/z* calcd for $NaC_{30}H_{30}{}^{35}BrN_2O_2$ $[M+H]^+$ 529.1491, found 529.1481. ***Minor diastereomer*** (4*S*,5*R*)-**3m**: (indicative peaks) δ_H 4.74 (1H, d, *J* = 15.3 Hz, NCH_2Ph), 4.67 (1H, t, *J* = 5.8 Hz, H4), 4.59 (1H, d, *J* = 12.2 Hz, OCH_2Ph), 4.52 (1H, d, *J* = 12.2 Hz, OCH_2Ph), 2.66 (1H, dd, *J*=16.5, 5.5 Hz, H3), 1.61 – 1.50 (1H, m, H1″), 0.39 – 0.36 (1H, m, H3″), 0.30 (1H, m, H3″)

(4*S*)-1-Benzyl-4-(benzyloxy)-5-cyclopropyl-5-(5-fluoro-1-methyl-1*H*-indol-3-yl)pyrrolidin-2-one (3n)

Prepared following general method A, from **1** (0.050 g, 0.15 mmol), 5-fluoro-1-methylindole (0.044 g, 0.3 mmol), $BF_3{\cdot}Et_2O$ (0.046 g, 0.040 mL, 0.32 mmol) and CH_2Cl_2 (7.5 mL). Separation by column chromatography (1:2 EtOAc/PS) yielded compound **3n** as a yellow oil (0.031 g, 0.066 mmol, 45%, 68:32). The diastereomers could not be separated. ***Major diastereomer*** (4*S*,5*S*)-**3n**: ν_{max}/cm^{-1} (on mixture of diastereomers) 3228, 3057, 2928, 2853,

2109, 1754, 1692, 1501, 1460, 1385, 1262, 1228, 1010, 976, 737, 696. δ_H 7.43 (1H, dd, *J* = 10.5, 2.4 Hz, H4′), 7.26 - 7.32 (2H, m, ArH), 7.16 - 7.25 (7H, m, ArH), 6.98 (2H, td, *J* = 8.9, 2.6 Hz, ArH), 6.92 - 6.96 (2H, m, ArH), 6.89 (1H, s, H2′), 5.09 (1H, d, *J* = 15.3 Hz, NCH_2Ph), 4.29 (1H, d, *J* = 12.1 Hz, OCH_2Ph), 4.18 (1H, d, *J* = 12.1 Hz, OCH_2Ph), 3.93 (1H, d, *J*=15.3 Hz, NCH_2Ph), 3.74 (3H, s, NCH_3), 3.46 (1H, t, *J* = 7.6 Hz, H4), 2.76 (1H, dd, *J*=16.6, 7.8 Hz, H3), 2.51 (1H, dd, *J*=16.5, 7.8 Hz, H3), 1.23 – 1.17 (1H, m, H1″), 0.84 – 0.76 (2H, m, H2″), 0.08 – 0.07 (1H, m, H3″), -0.12 – -0.18 (1H, m, H3″). δ_C 172.8 (C2), 157.8 (d, *J* = 233.5 Hz, C5′), 139.1 (*ipso*-NCH_2Ph), 137.5 (*ipso*-OCH_2Ph), 134.6 (C7′a), 129.6 (H2′), 129.3 (ArCH), 128.3 (ArCH), 128.2 (ArCH), 127.7 (ArCH), 127.3 (ArCH), 126.9 (ArCH), 115.0 (d, *J* = 4.6 Hz, C3′a), 107.4 (d, *J* = 24.8 Hz, H4′), 73.2 (C4), 71.3 (OCH_2Ph), 70.5 (C5), 44.5 (NCH_2Ph), 36.1 (C3), 33.3 (NCH_3), 17.7 (C1″), 5.8 (C2″), 2.8 (C3″). HRMS (ESI) *m/z* calcd for $C_{30}H_{30}N_2O_2F$ $[M + H]^+$ 469.2291, found 469.2303. ***Minor diastereomer*** (4*S*,5*R*)-**3n**: (indicative peaks) δ_H 4.87 (1H, d, *J* = 15.6 Hz, NCH_2Ph), 4.71 (1H, t, *J* = 5.4 Hz, H4), 4.64 (1H, d, *J* = 12.2 Hz, OCH_2Ph), 4.57 (1H, d, *J* = 12.2 Hz, OCH_2Ph), 1.54 - 1.61 (1H, m, H1″), 0.53 – 0.44 (2H, m, H2″), 0.44 – 0.37 (1H, m, H3″), 0.37 – 0.31 (1H, m, H3″).

(4*S*)-1-Benzyl-4-(benzyloxy)-5-cyclopropyl-5-(2-methyl-1*H*-indol-3-yl)pyrrolidin-2-one (3o)

Prepared following general method B, from **1** (0.050 g, 0.15 mmol), 2-methyl indole (0.059 g, 0.45 mmol), $BF_3{\cdot}Et_2O$ (0.046 g, 0.040 mL, 0.32 mmol) and CH_2Cl_2 (7.5 mL). This reaction was cooled to -40 °C rather than 0 °C for both the $BF_3{\cdot}Et_2O$ addition and the duration of the reaction (24 h). Separation by column chromatography (3:4 EtOAc/PS) yielded compound **3o** as a colourless oil (0.051 g, 0.11 mmol, 75%) and as a mixture of diastereomers (dr = 86:14). A small amount of the major diastereomer could be isolated pure by further chromatographic separation. ***Major diastereomer*** (4*S*,5*S*)-**3o**: δ_H 8.10 (1H, bs, H1′), 7.02 – 7.45 (10H, m, ArCH), 6.84 – 7.02 (1H, m, ArCH), 5.11 – 5.28 (1H, m, NCH_2Ph), 4.21 – 4.32 (1H, m, OCH_2Ph), 4.15 (1H, bs, OCH_2Ph), 3.68 – 3.86 (1H, m, NCH_2Ph), 3.43 (1H, bs, H4), 2.82 (1H, dd, *J* = 16.5, 7.7 Hz, H3), 2.49 (4H, dd, *J* = 16.5, 8.1 Hz, H3), 1.15 – 1.39 (1H, m, H1″), 0.64 – 0.92 (2H, m, H2″), -0.09 – -0.02 (1H, m, H3″), -0.39 (1H, bs, H3″). δ_C 172.8 (C2), 137.7 (s), 128.6 (ArCH), 128.3 (ArCH), 128.2 (ArCH), 127.7 (ArCH), 127.5 (ArCH), 126.8 (ArCH), 120.9 (s), 110.4 (C7′a), 73.4 (C4), 71.3 (OCH_2Ph), 45.5 (NCH_2Ph), 37.5 (CH_3), 29.8 (C1″), 8.8 (C2″), 4.5 (C3″). HRMS (ESI) *m/z* calcd for $NaC_{30}H_{30}N_2O_2$ $[M+Na]^+$ 473.2205, found 473.2228.

(4*S*)-1-Benzyl-4-(benzyloxy)-5-(2-methyl-5-nitro-1*H*-indol-3-yl)-5-(3-(2-methyl-5-nitro-1*H*-indol-3-yl)propyl)pyrrolidin-2-one (3p)

Prepared following general method B, from **1** (0.040 g, 0.119 mmol), 2-methyl-5-nitroindole (0.042 g, 0.24 mmol), $BF_3{\cdot}Et_2O$ (0.034 g, 0.032 mL, 0.26 mmol) and CH_2Cl_2 (6.0 mL). Separation by column chromatography (1:2 EtOAc/hexanes), yielded the major diastereomer of the bis-adduct **3p** as a yellow solid (0.021 g, 0.07 mmol, 27%, dr > 95:5) and its minor diastereomer **3p** as a yellow oil (0.009 g, 0.013 mmol, 10%, dr > 95:5). A mixture of the two diastereomers of **3p** was also isolated (0.011 g, 0.016 mmol, 9%, dr = 67:33) for a total combined yield of **3p** (0.041 g, 0.061 mmol, 51%, dr = 69:31). The spirocyclic furan **6** was also isolated as a colourless oil (0.006 g, 0.018 mmol, 15%, dr = 77:23). ***Major diastereomer*** (4*S*,5*S*)-**3p**: $[\alpha]_D^{25}$ 85.4 ± 0.8 (*c* 7.6, $CHCl_3$). ν_{max}/cm^{-1} 2973, 1663, 1514, 1320, 1052, 738, 699. δ_H 9.16 (1H, s, NHa), 8.50 (1H, s, NHb), 8.16 (1H, s, H4‴), 8.04 (1H, s, H4′), 7.93 (2H, app. t, *J* = 8.2 Hz, H6′ and H6‴), 7.29 – 7.24 (2H, m, ArCH), 7.24 – 7.17 (6H, m, ArCH), 7.16 – 7.10 (2H, m, ArCH), 6.95 (2H, d, *J* = 6.7 Hz, ArCH), 4.91 (1H, d, *J* = 15.1 Hz, NCH_2Ph), 4.38 (2H, d, *J* = 11.4 Hz, OCH_2Ph, H4), 4.25 (1H, d, *J* = 11.4 Hz, OCH_2Ph), 3.81 (1H, d, *J* = 15.1 Hz, NCH_2Ph), 2.80 (1H, dd, *J* = 17.1, 7.7 Hz, H3), 2.64 (1H, dd, *J* = 17.5, 6.4 Hz, H3), 2.38 – 2.34 (1H, m, H3″), 2.30 – 2.27 (1H, m, H2″), 2.24 (3H, s, H3″ $ArCH_3$), 2.19 (4H, s, $ArCH_3$ H3″), 2.00 (1H, t, *J* = 12.8 Hz, H2″), 1.90–1.82 (1H, m, H1″), 1.33 –1.29 (1H, m, H1″). δ_C 173.5 (C2), 141.6 (C7‴a), 141.3 (C7′a), 138.7 (either C7′a or C7‴a), 138.6 (either C7′a or C7‴a),), 137.8 (*ipso*-NCH_2Ph), 137.6 (*ipso*-OCH_2Ph), 136.3 (C2′), 135.1 (C2″), 129.0 (ArCH), 128.9 (ArCH), 128.6 (ArCH), 128.5 (ArCH), 128.3 (ArCH), 128.0 (ArCH), 127.9 (ArCH), 127.7 (ArCH), 127.6 (ArCH), 126.4 (ArCH), 117.3 (C6′ or C6‴), 116.9 (C6′ or C6‴), 116.5 (s), 115.3 (s), 115.2 (C3′), 113.7 (C3‴), 110.8 (s), 110.3 (s), 81.7 (C4), 72.6 (OCH_2Ph), 71.6 (C5), 45.0 (NCH_2Ph), 37.8 (s), 34.3 (C2″), 25.0 (C1″), 23.7 (C3″), 14.4 (CH_3), 11.8 (CH_3). HRMS (ESI) *m/z* calcd for $NaC_{39}H_{38}N_5O_6$ $[M+Na]^+$ 672.2822, found 672.2844. ***Minor diastereomer*** (4*S*,5*R*)-**3p**: δ_H 8.80 (1H, bs, NHa), 8.51 (1H, bs NH b), 8.33 (1H, bs), 8.22 (1H, bs), 8.01 (2H, d, *J* = 8.7 Hz,), 7.17 – 7.39 (11H, m), 7.12 – 6.99 (3H, m), 6.68 (2H, d, *J* = 7.1 Hz), 5.02 (1H, d, *J* = 13.8 Hz, NCH_2Ph), 4.04 (1H, d, *J* = 10.7 Hz, OCH_2Ph), 3.95 (1H, bs, H4), 3.70 (2H, m, NCH_2Ph OCH_2Ph), 2.97 (1H, dd, *J*=17.8, 7.7 Hz, H3), 2.62 – 2.51 (1H, m), 2.45 (2H, bs), 1.94 (1H, bs), 1.70 (1H, bs), 1.52 (1H, bs). δ_C 173.5 (C2), 142.8 (C7′a), 141.4 (C7‴a), 137.8 (either C7′a or C7‴a), 137.1 (either C7′a or C7‴a), 129.1 (ArCH), 128.6 (ArCH), 128.2 (ArCH), 127.7 (ArCH), 127.4 (ArCH), 117.0 (C6′ or C6‴), 116.8 (C6′ or C6‴), 115.0, 110.8, 110.3, 84.1 (C4), 79.6, 72.5 (OCH_2Ph, 44.9 (NCH_2Ph), 38.8, 38.7, 23.7 (C3″), 23.2, 15.2 (CH_3), 11.9 (CH_3).

(3′*S*,6*R*)-1′-Benzyl-3′-(benzyloxy)-10-methyl-8,9-dihydro-7*H*-spiro[pyrido[1,2-*a*]indole-6,2′-pyrrolidin]-5′-one (7a) and 1′-benzyl-4′-(benzyloxy)-5′-((3*S*,3a*S*,8b*S*)-8b-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-3-yl)-1,5-dihydro-2*H*-pyrrol-2′-one (9a)

Prepared following general method A, from **1** (0.050 g, 0.15 mmol), 3-methylindole (0.059 g, 0.45 mmol), $BF_3{\cdot}Et_2O$ (0.046 g, 0.040 mL, 0.32 mmol) and CH_2Cl_2 (7.5 mL). Separation by column chromatography using gradient elution from 4:1 PS/EtOAc to 1:1 PS/EtOAc yielded compound **7a** as a clear oil (0.018 g, 0.040 mmol, 27%) and as a mixture diastereomers (dr >95:5). A small amount of the major diastereomer could be isolated pure by further chromatographic separation. Compound **9a** was also isolated as a clear oil (0.016 g, 0.036 mmol, 24%) and as a mixture of diastereomers (dr = 79:21). A small amount of the major diastereomer could be isolated pure by further chromatographic separation. ***Major diastereomer*** (3′*S*,6*R*)-**7a**: $[\alpha]_D^{25}$ 63 ± 6 (*c* 0.95, $CHCl_3$). ν_{max}/cm^{-1} 2923, 2851, 1634, 1454, 1396, 1319, 1107, 1027, 739, 692. δ_H 7.54 (1H, d, *J* = 7.7 Hz, H1), 7.24 – 7.17 (6H, m, ArCH), 7.15 (1H, app. t, *J* = 7.3 Hz, H2), 7.10 (2H, d, *J* = 7.3 Hz, ArCH), 7.06 (1H, app. t, *J* = 7.3 Hz, H3), 7.01 (2H, d, *J* = 3.6 Hz, ArCH), 6.94 (1H, d, *J* = 8.0 Hz, H4), 4.89 (1H, d, *J* = 15.6 Hz, NCH_2Ph), 4.70 (1H, app. t, *J* = 8.2 Hz, H3′), 4.27 (1H, d, *J* = 11.6 Hz, OCH_2Ph), 4.23 (1H, d, *J* = 11.6 Hz, OCH_2Ph), 3.50 (1H, d, *J* = 15.6 Hz, NCH_2Ph), 2.97 – 2.91 (1H, m, H9), 2.90 – 2.85 (1H, m, H4′), 2.70 (1H, dd, *J* = 16.9, 8.3 Hz, H4′), 2.53 – 2.47 (1H, m, H9), 2.41 (1H, d, *J* = 13.6 Hz, H7), 2.25 (3H, s, $ArCH_3$), 2.06 – 1.96 (1H, m, H8), 1.73 (1H, dd, *J* = 9.3, 4.0 Hz, H8), 1.66 (1H, td, *J* = 13.6, 3.0 Hz, H7). δ_C 171.1 (C2), 137.9 (*ipso*-NCH_2Ph), 137.3 (*ipso*-OCH_2Ph), 134.9 (C9a), 134.1 (C4a), 130.6 (C10a), 128.6 (ArCH), 128.5 (ArCH), 128.3 (ArCH), 128.0 (ArCH), 127.6 (ArCH), 127.4 (ArCH), 121.7 (C2), 120.2 (C3), 118.6 (C4), 111.7 (C1), 107.2 (C10), 82.2 (C6), 79.0 (C3′), 72.6 (OCH_2Ph), 43.4 (NCH_2Ph), 36.7 (C4′), 30.9 (C7), 22.4 (C9), 19.7 (C8), 8.5 ($ArCH_3$). HRMS (ESI) *m/z* calcd for $C_{30}H_{31}N_2O_2$ $[M + H]^+$ 451.2386, found 451.2389. ***Major diastereomer*** **9a**: ν_{max}/cm^{-1} 2937, 1662, 1619, 1454, 1210, 806, 741, 697. δ_H 7.40 – 7.32 (4H, m, ArCH), 7.32 – 7.27 (4H, m, ArCH), 7.18 (2H, d, *J* = 7.5 Hz, ArCH), 6.96 (1H, d, *J* = 7.5 Hz, H8), 6.92 (1H, app. t, *J* = 7.5 Hz, H6), 6.65 (1H, app. t, *J* = 7.3 Hz, H7), 6.24 (1H, d, *J* = 7.5 Hz, H5), 5.48 (1H, d, *J* = 16.2 Hz, NCH_2Ph), 5.27 (1H, s, H3′), 4.99 (1H, d, *J* = 11.7 Hz, OCH_2Ph), 4.93 (1H, d, *J* = 11.7 Hz, OCH_2Ph), 4.19 (1H, d, *J* = 6.5 Hz, H5′), 4.15 (1H, d, *J* = 16.2 Hz, NCH_2Ph), 3.87 (1H, d, *J* = 4.7 Hz, H3a), 2.16 (1H, dt, *J* = 11.9, 5.7 Hz, H3), 1.86 (1H, dd, *J* = 12.2, 6.5 Hz, H1), 1.80 – 1.72 (1H, m, H2), 1.68 (1H, dt, *J* = 12.5, 6.3 Hz, H2), 1.52 (1H, dt, *J* = 12.4, 6.1Hz, H1), 1.38 (3H, s, CH_3). δ_C 175.9 (C4′), 172.2 (C2′), 150.8 (C4a), 137.8 (*ipso*- NCH_2Ph), 137.2 (C8a), 134.7 (*ipso*-OCH_2Ph),

129.1 (ArCH), 128.9 (ArCH), 128.8 (ArCH), 128.0 (ArCH), 127.7 (ArCH), 127.5 (ArCH), 127.4 (ArCH), 122.7 (C8), 118.5 (C7), 108.6 (C5), 94.7 (C3′), 73.3 (OCH_2Ph), 71.9 (C3a), 59.4 (C5′), 53.5 (C8b), 49.0 (C3), 44.5 (NCH_2Ph), 42.3 (C1), 28.5 (C2), 28.4 (CH_3). HRMS (ESI) *m/z* calcd for $C_{30}H_{31}N_2O_2$ $[M + Na]^+$ 451.2386, found 451.2394.

(3′*S*)-1′-Benzyl-3′-(benzyloxy)-10-cyclohexyl-8,9-dihydro-7*H*-spiro[pyrido[1,2-*a*]indole-6,2′-pyrrolidin]-5′-one (7b), (3′*S*,9*R*)-1′-benzyl-3′-(benzyloxy)-10-cyclohexyl-7,8-dihydro-6*H*-spiro[pyrido[1,2-*a*]indole-9,2′-pyrrolidin]-5′-one (8b) and 1-benzyl-4-(benzyloxy)-5-((3a*S*,8b*R*)-8b-cyclohexyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-3-yl)-1,5-dihydro-2*H*-pyrrol-2-one (9b)

Prepared following general method B, from **1** (0.100 g, 0.296 mmol), 3-cyclohexylindole (0.08 g, 0.6 mmol), $BF_3{\cdot}Et_2O$ (0.09 g, 0.08 mL, 0.6 mmol) and CH_2Cl_2 (15.0 mL). Separation by column chromatography (1:6 EtOAc/PS to 2:1 EtOAc/PS) yielded several compounds. Compound **7b** (0.069 g, 0.133 mmol, 45%) was isolated as a mixture of diastereomers (73:27) and small amounts of both diastereomers, as colourless oils, could be isolated pure by further chromatographic separation. Compound **8b** was isolated as a colourless oil (0.008 g, 0.016 mmol, 5.3%) as a single isomer (dr > 95:5). Compound **9b** was isolated as a brown oil (0.036 g, 0.069, 24%) as a mixture of diastereromers (dr >95:5, analytical purity >85%). ***Major diastereomer*** (3′*S*,6*S*)-**7b**: $[\alpha]_D^{25}$ 72.7 ± 4.6 (*c* 1.35, $CHCl_3$). δ_H 7.76 (1H, d, J = 7.8 Hz, H1), 7.25 – 7.16 (8H, m, ArCH), 7.10 (1H, app. td, *J* = 7.5 0.9 Hz, H2), 7.08 – 7.06 (1H, m, ArCH), 7.03 – 7.00 (1H, m, H3), 6.99 – 6.97 (1H, m, ArCH), 6.94 (1H, d, *J* = 8.2 Hz, H4), 4.88 (1H, d, *J* = 15.4 Hz, NCH_2Ph), 4.77 (1H, app. t, *J* = 8.4 Hz, H3′), 4.28 (1H, d, *J* = 11.8 Hz, OCH_2Ph), 4.22 (1H, d, *J* = 11.8 Hz, OCH_2Ph), 3.47 (1H, d, *J* = 15.4 Hz, NCH_2Ph), 3.06 – 2.98 (1H, m, H9), 2.89 (1H, dd, *J* = 16.8, 8.1 Hz, H4′), 2.82 – 2.75 (1H, m, H1″), 2.71 (1H, dd, *J* = 16.8, 8.7 Hz, H4′), 2.54 – 2.46 (1H, m, H9), 2.43 – 2.37 (1H, m, H7), 2.03 – 1.94 (2H, m, H8, CH_2), 1.92 – 1.89 (2H, m, CH_2), 1.84 – 1.80 (3H, m, CH_2), 1.74 – 1.67 (1H, m, H8), 1.66 – 1.60 (1H, m, H7), 1.50 – 1.33 (3H, m, CH_2). δ_C 170.9 (C5′), 137.8 (*ipso*-NCH_2Ph), 137.2 (*ipso*-OCH_2Ph), 134.4 (C9a), 134.0 (C4a), 128.9 (C10a), 128.6 (ArCH), 128.5 (ArCH), 128.4 (ArCH), 127.9 (ArCH), 127.5 (ArCH), 121.2 (C3), 120.3 (C1), 119.8 (C2), 117.4 (C10), 112.0 (C4), 78.6 (C6), 72.4 (OCH_2Ph), 43.4 (NCH_2Ph), 36.55 (C4′), 36.53 (C1″), 33.14 (CH_2), 33.06 (CH_2), 30.8 (C7), 27.6 (CH_2), 27.5 (CH_2), 26.5 (CH_2), 22.9 (C9), 19.7 (C8). LRMS (ESI) *m/z* calcd for $C_{35}H_{39}N_2O_2$ $[M+H]^+$ 519, found 519. ***Minor diastereomer*** (3′*S*,6*R*)-**7b**: ν_{max}/cm^{-1} 2926, 2850, 1708, 1530, 1454, 1399, 1358, 1332, 1313, 1262, 1116, 974, 928, 906, 839, 771, 746, 701. δ_H 7.73 (1H, d, *J* = 7.8 Hz, H1), 7.31 – 7.18 (6H, m, ArCH), 7.17 – 7.07 (5H, m, ArCH),

6.55 (2H, d, *J* = 7.3 Hz, ArCH from *ortho*-OBn), 5.10 (1H, d, *J* = 16.1 Hz, NCH_2Ph), 4.16 (1H, dd, *J* = 8.1, 2.7 Hz, H3′), 3.86 (1H, d, *J* = 11.2 Hz, OCH_2Ph), 3.67 (1H, d, *J* = 15.6 Hz, NCH_2Ph), 3.61 (1H, d, *J* = 11.7 Hz, OCH_2Ph), 3.13 – 3.08 (1H, m, H9), 3.05 (1H, dd, *J* = 18.1, 7.8 Hz, H4′), 2.82 – 2.69 (2H, m, H4′ H1″), 2.65 – 2.55 (1H, m, H9), 2.06 – 1.67 (10H, m, H7 H8 CH_2), 1.64 – 1.60 (1H, m, H7), 1.49 – 1.32 (3H, m, CH_2). δ_C 172.7 (C5′), 138.3 (*ipso*-NCH_2Ph), 137.2 (C4a), 137.1 (*ipso*-OCH_2Ph), 132.6 (C9a), 128.7 (ArCH), 128.2 (ArCH), 128.0 (ArCH), 127.5 (ArCH), 127.4 (ArCH), 121.3 (C2), 119.4 (C1), 117.7 (C10), 113.8 (C4), 82.5 (C6), 79.5 (C3′), 71.8 (OCH_2Ph), 44.1 (NCH_2Ph), 38.3 (C4′), 36.6 (C1″), 36.4 (C7), 33.0 (CH_2), 32.8 (CH_2), 27.6 (CH_2), 27.5 (CH_2), 26.5 (CH_2), 22.9 (C9), 18.6 (C8). HRMS (ESI) *m/z* calcd for $C_{35}H_{39}N_2O_2$ $[M+H]^+$ 519.3012, found 519.3035. ***Major diastereomer*** (3′*S*,9*R*)-**8b**: ν_{max}/cm^{-1} 2927, 2851, 1694, 1457, 1402, 1349, 1328, 1206, 927, 742, 704. δ_H 7.87 (1H, d, *J* = 7.9 Hz, H1), 7.32 (1H, d, *J* = 7.9 Hz, H4)), 7.25 – 7.21 (8H, m, ArH), 7.17 – 7.13 (3H, m, ArH), 7.13 – 7.09 (2H, m, ArH), 5.06 (1H, d, *J* = 15.6 Hz, NCH_2Ph), 4.47 (1H, d, *J* = 11.8 Hz, OCH_2Ph), 4.40 (1H, app. t, *J* = 7.5 Hz, H3′), 4.33 (1H, d, *J* = 11.8 Hz, OCH_2Ph), 4.17 – 4.12 (1H, m, H6), 3.68 (1H, d, *J* = 15.6 Hz, NCH_2Ph), 3.60 (1H, td, *J* = 11.6, 4.5 Hz, H6), 2.82 (1H, dd, *J*=16.7, 7.5 Hz, H4′), 2.73 (1H, dd, *J* = 16.7, 7.3 Hz, H4′), 2.51 (1H, tt, *J* = 12.07, 3.19 Hz, H1″), 2.34 (1H, dt, *J*=13.69, 3.30 Hz, H8), 2.21 – 2.11 (2H, m, H7 H2″b), 2.03 – 1.93 (1H, m, H2″a), 1.88 – 1.74 (4H, m, H7 H2″b CH_2), 1.54 (1H, m, H2″a), 1.52 – 1.46 (1H, m, H8), 1.29 – 1.14 (4H, m, CH_2). δ_C 172.0 (C5′), 138.5 (*ipso*-NCH_2Ph), 137.4 (*ipso*-OCH_2Ph), 136.7 (C4a), 130.3 (C9a), 128.6 (ArCH), 128.6 (ArCH), 128.1 (ArCH), 128.0 (ArCH), 127.6 (ArCH), 127.3 (ArCH), 126.6 (C10a), 121.8 (C1), 121.7 (ArCH), 119.2 (ArCH), 118.6 (C10), 109.6 (C4), 82.3 (C3′), 72.5 (OCH_2Ph), 44.3 (NCH_2Ph), 42.0 (C6), 37.0 (C1″), 36.1 (C4′), 33.4 (C2″a), 33.2 (C2″b), 29.0 (C8), 27.6 (CH_2), 27.3 (CH_2), 26.4 (CH_2), 21.0 (C7). LRMS (ESI) *m/z* calcd for $C_{35}H_{39}N_2O_2$ $[M+H]^+$ 519, found 519. ***Major diastereomer*** **9b**: $[\alpha]_D^{25}$ -37.5 ± -4.0 (*c* 1.35, $CHCl_3$). ν_{max}/cm^{-1} 3390, 3031, 2927, 2851, 1665, 1621, 1484, 1452, 1403, 1337, 1262, 1227, 1198, 987, 977, 804, 741, 702. δ_H 7.39 – 7.14 (13H, m, ArH), 6.99 – 6.88 (2H, m, H8 H6), 6.65 – 6.54 (1H, m, H7), 6.22 (1H, d, *J* = 7.7 Hz, H5), 5.28 – 5.22 (2H, m, H3′ NCH_2Ph), 5.06 – 4.89 (2H, m, OCH_2Ph), 4.28 (1H, d, *J* = 16.3 Hz, NCH_2Ph), 4.23 (1H, d, *J* = 6.7 Hz, H5′), 3.86 (1H, d, *J* = 5.6 Hz, H3a), 1.96 – 1.87 (1H, m, H3), 1.76 – 1.67 (6H, m, CH_2 H2 H2″a), 1.66 – 1.58 (3H, m, CH_2), 1.54 – 1.49 (2H, m, CH_2 H2), 1.44 – 1.37 (1H, m, H1″), 1.22 – 1.02 (3H, m, CH_2), 1.01 – 0.94 (1H, m, CH_2), 0.66 – 0.55 (1H, m, H2″a). δ_C 176.1 (C4′), 172.3 (C2′), 151.9 (C4a), 138.0 (*ipso*-NCH_2Ph), 134.7 (*ipso*-OCH_2Ph), 134.6 (C8a), 128.9 (ArCH), 128.7 (ArCH), 128.7 (ArCH), 128.0 (ArCH), 127.5 (ArCH), 127.3 (C6), 127.1 (ArCH), 123.7 (C8),

118.1 (C7), 108.5 (C5), 94.7 (C3′), 73.2 (OCH_2Ph), 66.4 (C3a), 62.2 (C8b), 59.7 (C5′), 49.7 (C3), 46.6 (C1″), 44.7 (NCH_2Ph), 37.7 (CH_2), 28.8 (CH_2), 28.5 (C2″a), 27.5 (C2), 26.9 (CH_2), 26.7 (CH_2), 26.5 (CH_2). HRMS (ESI) *m/z* calcd for $C_{35}H_{39}N_2O_2$ $[M+H]^+$ 519.3012, found 519.3010.

3-Cyclopropyl-3-(1*H*-indol-3-yl)-2-methylisoindolin-1-one (11a)

Prepared following general method C, from **10** (0.050 g, 0.25 mmol), indole (0.035, 0.3 mmol), $BF_3{\cdot}Et_2O$ (0.07 g, 0.06 mL, 0.49 mmol) and CH_2Cl_2 (10 mL). The reaction mixture was quenched after 2 h. The crude product was dissolved in acetone then precipitated with hexane to yield compound **11a** as a white foam (0.064 g, 0.21 mmol, 86%). ν_{max}/cm^{-1} 3177, 2928, 2218, 1664, 1434, 1406, 1349, 1096, 1073, 1026, 808, 735, 700, 640, 421. δ_H 8.34 (1H, bs, H1′), 7.93 (1H, d, *J* = 7.7 Hz, H7), 7.65 (1H, d, *J* = 2.3 Hz, H2′), 7.45 – 7.38 (1H, m, H6), 7.37 – 7.30 (2H, m, H5, H7′), 7.10 (1H, app. t, *J* = 7.5 Hz, H6′), 7.03 (1H, d, *J* = 7.4 Hz, H4), 6.84 (1H, app. t, *J* = 7.7 Hz, H5′), 6.71 (1H, d, *J* = 8.1 Hz, H4′), 2.94 (3H, s, CH_3), 1.95 – 1.87 (1H, m, H1″), 0.83 (1H, s, H2″), 0.77 – 0.69 (1H, m, H2″), 0.42 (1H, bs, H3‴), -0.27 – -0.34 (1H, m, H3″). δ_C 168.2 (C1), 146.3 (C3a), 137.0 (C7′a), 132.9 (C7a), 131.0 (C5), 128.4 (C6), 125.0 (C3′a), 124.4 (C2′), 123.5 (C4), 123.4 (C7), 122.6 (C6′), 120.3 (C5′), 119.7 (C4′), 115.8 (C3′), 111.3 (C7′), 68.0 (C3), 25.6 (CH_3), 17.2 (C1″), 3.9 (C2″), 0.1 (C3″). HRMS (ESI) *m/z* calcd for $C_{20}H_{19}NO_2$ $[M+H]^+$ 303.1497, found 304.1491.

3-Cyclopropyl-2-methyl-3-(5-nitro-1*H*-indol-3-yl)isoindolin-1-one (11b)

Prepared following general method C, from **10** (0.050 g, 0.25 mmol), 5-nitroindole (0.081, 0.3 mmol), $BF_3{\cdot}Et_2O$ (0.07 g, 0.06 mL, 0.49 mmol) and CH_2Cl_2 (10 mL). The crude product was dissolved in acetone then precipitated with hexane to yield the title compound **11b** as a yellow foam (0.081 g, 0.23 mmol, 93%). Mp: decomposed at 246 ˚C before melting. ν_{max}/cm^{-1} 2977, 1661, 1520, 1474, 1334, 1052, 814, 743, 696. δ_H 9.37 (1H, bs, H1′), 8.03 (1H, dd, *J* = 7.4, 1.3 Hz, H6′), 7.98 (1H, d, *J* = 7.4 Hz, H7), 7.79 (1H, d, *J* = 2.4 Hz, H2′), 7.73 (1H, d, *J* = 1.3 Hz, H4′), 7.50 – 7.46 (1H, m, H6), 7.44 (1H, d, *J* = 9.1 Hz, H7′), 7.39 (1H, t, *J* = 7.4 Hz, H5), 7.06 (1H, d, *J* = 7.4 Hz, H4), 2.99 (3H, s, CH_3), 1.97 – 1.89 (1H, m, H1″), 0.96 – 0.89 (1H, m, H2″), 0.79 (1H, dq, *J* = 10.0, 5.2 Hz, H2″), 0.52 – 0.46 (1H, m, H3″), -0.27 (1H, dd, *J* = 9.7, 5.4 Hz, H3″). δ_C 168.1 (C1), 145.7 (C3a), 142.2 (C7′a), 140.1 (C5′), 132.6 (C7a), 131.3 (C5), 129.0 (C6), 127.4 (C2′), 124.5 (C3′a), 123.9 (C7), 123.4 (C4), 118.5 (C3′), 118.3 (C6′), 116.8 (C4′), 111.7 (C7′), 67.6 (C3), 25.6 (CH_3), 17.1 (C1″), 4.3 (C2″), 0.3 (C3″). HRMS (ESI) *m/z* calcd for $C_{20}H_{18}N_3O_3$ $[M+H]^+$ 348.1348 found 348.1365.

3-Cyclopropyl-2-methyl-3-(2-methyl-1*H*-indol-3-yl)isoindolin-1-one (11c)

Prepared following general method C, from **10** (0.050 g, 0.25 mmol), 2-methylindole (0.066, 0.5 mmol), $BF_3{\cdot}Et_2O$ (0.14 g, 0.12 mL, 0.97 mmol) and CH_2Cl_2 (10 mL). Separation by column chromatography (2:1 EtOAc/PS) yielded compound **11c** as a white foam (0.41 g, 0.13 mmol, 52%). ν_{max}/cm^{-1} 2974, 1676, 1456, 1389, 1332, 1022, 885, 744, 690. δ_H (DMSO-*d*6) 10.91 (1H, bs, H1′), 7.72 – 7.71 (1H, m, H7), 7.45 – 7.39 (2H, m, H6 H5), 7.23 (1H, d, *J* = 8.1 Hz, H7′), 7.15 – 7.12 (1H, m, H4), 6.93 (1H, t, *J* = 7.3 Hz, H6′), 6.73 (1H, bs, H5′), 3.17 (3H, s, $ArCH_3$), 2.80 (3H, s, NCH_3), 2.08 – 2.06 (1H, m, H1″), 0.87 (1H, bs, H2″), 0.67 – 0.62 (1H, m, H2″), 0.54 – 0.49 (1H, m, H3″), -0.42 – -0.47 (1H, m, H3″). δ_C (DMSO-*d*6) 166.4 (C1), 146.9 (C7a), 134.8 (C7′a), 131.9 (C3a), 130.6 (C6), 127.7 (C5), 123.3 (C4), 121.9 (C7), 119.8 (C6′), 118.5 (C5′), 110.3 (C7′), 107.6 (C3′), 68.3 (C3), 24.9 (NCH_3), 17.6 (C1″), 5.8 (C2″), 1.2 (C3″).

3-Cyclopropyl-2-methyl-3-(3-methyl-1*H*-indol-2-yl)isoindolin-1-one (11d)

Prepared following general method C, from **10** (0.050 g, 0.25 mmol), 3-methylindole (0.066, 0.5 mmol), $BF_3{\cdot}Et_2O$ (0.14 g, 0.12 mL, 0.97 mmol) and CH_2Cl_2 (10 mL). Separation by column chromatography (1:1 EtOAc/PS) yielded compound **11d** as a white foam (0.41 g, 0.13 mmol, 52%). ν_{max}/cm^{-1} 2974, 1676, 1456, 1389, 1332, 1022, 885, 744, 690. δ_H (DMSO-d_6) 10.73 (1H, bs, H1′), 7.81 – 7.68 (1H, m), 7.52 – 7.45 (1H, m), 7.42 (1H, d, *J* = 7.9 Hz, H7′), 7.36 (1H, d, *J* = 8.1 Hz, H4′), 7.23 – 7.16 (1H, m,), 7.07 (1H, t, *J* = 7.6 Hz, H5′), 7.00 – 6.93 (1H, m, H6′), 2.89 (3H, s, NCH_3), 2.08 – 2.00 (1H, m, H1″), 1.93 (3H, bs, $ArCH_3$), 1.03 – 0.92 (1H, m, H2″), 0.79 – 0.68 (1H, m, H2″), 0.57 – 0.46 (1H, m, H3″), -0.48 – -0.60 (1H, m, H3″). δ_C (DMSO-d_6) 166.6 (C1), 145.0 (C7a), 135.2 (s), 132.0 (s), 131.9 (s), 131.3 (s), 129.2 (s), 128.6 (s), 122.6 (s), 121.3 (s), 118.4 (C4′), 117.9 (C7′), 111.4 (s), 107.1 (C3′), 67.9 (C3), 25.4 (NCH_3), 15.9 (C1″), 8.4 ($ArCH_3$), 5.2 (C2″), 0.3 (C3″). HRMS (ESI) *m/z* calcd for $C_{21}H_{21}N_2O$ $[M + H]^+$ 317.1654, found 317.1649.

2-Methyl-3-(3-(1,2,3,4-tetrahydro-4a*H*-carbazol-4a-yl)propylidene)isoindolin-1-one (11e) Prepared following general method C, from **10** (0.100 g, 0.492 mmol), tetrahydrocarbazole (0.094, 0.55 mmol), $BF_3{\cdot}Et_2O$ (0.14 g, 0.12 mL, 0.97 mmol) and CH_2Cl_2 (25 mL). Separation by column chromatography (3:2 EtOAc/PS) yielded compound **11e** as a yellow foam (0.032 g, 0.090 mmol, 18%) and as a mixture of diastereomers (*E*/*Z* = 86:14 from ^{1}H NMR analysis of the crude reaction product). A small amount of each diastereomer could be isolated pure by further separation using column chromatography. (*E*)-**11e**: δ_H 7.79 (1H, dd, *J* = 5.1, 3.0 Hz, ArCH), 7.62 (1H, d, *J* = 7.8 Hz, H5″), 7.44 – 7.39 (2H, m, ArCH), 7.38 – 7.36 (1H, m, ArCH), 7.33 (1H, d, *J* = 7.1 Hz, H8″), 7.27 (1H, d, *J* = 7.4 Hz, ArCH), 7.22 – 7.17 (1H, m, ArCH), 5.14 (1H, t, *J* = 7.6 Hz, H1′), 3.13 (3H, s, CH_3), 2.94 (1H, d, *J* = 13.3 Hz, H1″),

2.56 (1H, td, *J* = 13.3, 5.6 Hz, H1″), 2.45 – 2.40 (1H, m, H3′), 2.37 (1H, d, *J* = 12.8 Hz, H4″), 2.22 (1H, app. d, *J* = 12.2 Hz, H2″), 2.11 – 2.03 (1H, m, H3′), 2.02 – 1.98 (1H, m, H2′), 1.97 – 1.91 (1H, m, H2′), 1.90 – 1.79 (1H, m, H3″), 1.72 (1H, d, *J* = 13.5 Hz, H3″), 1.52 – 1.39 (1H, m, H2″), 1.30 – 1.18 (1H, m, H4″). δ_C 189.0 (C9″b), 166.3 (C1), 155.2 (C8″a), 144.4 (C4″b), 136.4 (C3), 134.8 (C3a), 131.8 (ArCH), 130.7 (C7a), 128.7 (ArCH), 128.1 (ArCH), 125.1 (ArCH), 123.3 (ArCH), 123.0 (ArCH), 121.7 (C8″), 120.5 (C5″), 110.5 (C1′), 58.1 (C4″a), 38.4 (C4″), 34.5 (C3′), 30.4 (C1″), 29.1 (C2″), 25.8 (CH_3), 21.8 (C2′), 21.4 (C3″). HRMS (ESI) *m/z* calcd for $C_{24}H_{25}N_2O$ [M+H]+ 357.1961, found 357.1962LRMS (ESI) *m/z* calcd for $C_{36}H_{38}N_3O$ $[M+H]^+$ 528, found 528. (*Z*)-**11e**: ν_{max}/cm^{-1} 3356, 3226, 2951, 1672, 1431, 1389, 1047, 1023, 726, 699, 519, 473. δ_H (DMSO-d_6) 7.72 (1H, d, *J* = 7.3 Hz, H5″), 7.68 (1H, d, *J* = 7.3 Hz, H7), 7.47 (2H, app. t, *J* = 7.3 Hz, ArCH), 7.45 – 7.38 (3H, m, ArCH), 7.07 (1H, d, *J* = 7.6 Hz, H4), 5.30 (1H, t, *J* = 8.1 Hz, H1′), 3.11 (1H, d, *J* = 5.8 Hz, H1″), 3.03 (3H, s, CH_3), 2.97 (1H, d, *J* = 12.5 Hz, H1″), 2.68 – 2.56 (2H, m, H4″ and H3′), 2.41 (1H, d, *J* = 6.1 Hz, H3′), 2.27 (1H, bs, H4″), 2.21 – 2.10 (1H, m, H2′), 2.10 – 2.02 (1H, m, H2′), 1.96 – 1.86 (1H, m, H3″), 1.64 (1H, d, *J* = 13.4 Hz, H3″), 1.56 – 1.44 (1H, m, H2″), 1.24 (1H, m, *J* = 2.7 Hz, H4″). δ_C (DMSO-d_6) 195.7 (C9″b), 164.8 (C1), 146.4 (C4″a), 142.5 (C8″a), 135.28 (C3), 134.07 (ArC), 131.89 (ArCH), 129.82 (ArC), 128.87 (ArCH), 128.49 (ArCH), 127.09 (ArCH), 123.3 (C5″), 122.7 (C4), 122.6 (C7), 117.66 (C6″), 110.70 (C1′), 58.4 (C4″a), 33.53 (C4″), 29.79 (C2″), 29.09 (C1″), 25.45 (CH_3), 22.06 (C2′), 20.20 (C3″).

(3′*S*)-1′-Benzyl-3′-(benzyloxy)-6,7-dimethoxy-3,4-dihydro-2*H*-spiro[naphthalene-1,2′-pyrrolidin]-5′-one (12a)

Prepared following general method A, from **1** (0.050 g, 0.15 mmol), 1,2-dimethoxybenzene (0.041 g, 0.040 mL, 0.30 mmol), $BF_3{\cdot}Et_2O$ (0.046 g, 0.040 mL, 0.32 mmol) and CH_2Cl_2 (7.5 mL). Separation by column chromatography (3:1 EtOAc/PS) yielded **12a** (37 mg, 0.080 mmol, 54%) as a clear oil and as a mixture of diastereomers (dr = 90:10). ***Major diastereomer*** (*1S,3′S*)-**12a**: ν_{max}/cm^{-1} 2934, 2848, 1684, 1512, 1452, 1397, 1355, 1267, 1079, 738, 701. δ_H 7.28 – 7.16 (6H, m, ArCH), 7.11 – 7.09 (2H, m, ArCH), 6.96 – 6.95 (2H, m, ArCH), 6.62 (1H, s, H5), 6.59 (1H, s, H8), 4.57 (1H, d, *J* = 15.2 Hz, NCH_2Ph), 4.05 (1H, d, *J* = 11.5 Hz, OCH_2Ph), 3.96 (1H, d, *J* = 15.2 Hz, NCH_2Ph), 3.90 (3H, s, C7-OCH_3), 3.89 – 3.87 (1H, m, H3′), 3.85 (1H, d, *J* = 11.5 Hz, OCH_2Ph), 3.43 (3H, s, C6-OCH_3), 2.96 (1H, dd, *J* = 17.8, 6.9 Hz, H4′), 2.73 – 2.68 (2H, m, H4), 2.65 (1H, d, *J* = 17.8 Hz, H4′), 1.86 – 1.78 (1H, m, H3), 1.77 – 1.68 (1H, m, H3), 1.68 – 1.59 (1H, m, H2), 1.55 – 1.48 (1H, m, H2). δ_C 174.1 (C5′), 148.7 (C7), 146.7 (C6), 138.7 (*ipso*-NCH_2Ph), 137.7 (*ipso*-OCH_2Ph), 131.5 (C8a), 128.5 (ArCH), 128.4 (ArCH), 128.3 (ArCH), 127.7 (ArCH), 127.6 (ArCH), 127.1 (ArCH), 124.5 (C4a), 113.3 (C8),

111.0 (C5), 79.8 (C3′), 71.9 (OCH_2Ph), 70.4 (C1), 55.9 (C7-OCH_3), 55.7 ((C6-OCH_3), 44.4 (NCH_2Ph), 37.9 (C4′), 33.5 (C2), 29.2 (C4), 20.6 (C3). HRMS (ESI) *m/z* calcd for $C_{29}H_{31}NO_4Na$ $[M+Na]^+$ 480.2151, found 480.2125.

(3′*S*)-1′-Benzyl-3′-(benzyloxy)-5,6,7-trimethoxy-3,4-dihydro-2H-spiro[naphthalene-1,2′-pyrrolidin]-5′-one (12b)

Prepared following general method A, from **1** (0.050 g, 0.15 mmol), 1,2,3-trimethoxybenzene (0.050 g, 0.30 mmol), $BF_3{\cdot}Et_2O$ (0.046 g, 0.040 mL, 0.32 mmol) and CH_2Cl_2 (7.5 mL). The crude product mixture was separated by column chromatography (1:1 EtOAc/PS) yielding **12b** (42 mg, 0.086 mmol, 58%) as a clear oil and as a mixture of diastereomers (dr = 75:25). ***Major diastereomer*** (*1S,3′S*)-**12b**: ν_{max}/cm^{-1} 3384, 2934, 1683, 1493, 1453, 1403, 1343, 1327, 1270, 1191, 1108, 1075, 1028, 935, 699, 620, 497. δ_H 7.37 – 7.28 (5 H, m, ArCH), 7.25 - 7.16 (6H, m, ArCH), 7.11 (2H, d, *J* = 5.9 Hz, ArCH), 6.95 - 6.93 (2H, m, ArCH), 6.39 (1H, s, H8), 4.61 (1H, d, *J* = 15.1 Hz, NCH_2Ph), 4.16 (1H, d, *J* = 11.7 Hz, OCH_2Ph), 3.95 (1H, d, *J* = 15.1 Hz, NCH_2Ph), 3.93 – 3.90 (2H, m, OCH_2Ph, H3′), 3.91 - 3.88 (6H, m, C5-OCH_3 C6-OCH_3), 3.42 (3H, s, C7-OCH_3), 2.96 (1H, dd, *J* = 17.6, 7.3 Hz, H4′), 2.90 - 2.83 (1H, m, H4), 2.68 – 2.61 (1H, m, H4′), 2.52 - 2.39 (1H, m, H4), 1.91 - 1.80 (1H, m, H3), 1.74 - 1.66 (2H, m, H2 H3), 1.56 - 1.48 (1H, m, H2). δ_C 174.1 (C5′), 150.9 (C5 or C6), 150.8 (C5 or C6), 141.8 (C7), 138.6 (*ipso*-NCH_2Ph), 137.8 (*ipso*-OCH_2Ph), 128.5 (ArCH), 128.4 (ArCH), 128.4 (ArCH), 128.32 (C4a), 128.31 (ArCH), 128.0 (ArCH), 127.9 (ArCH), 127.7 (ArCH), 127.6 (ArCH), 127.4 (ArCH), 127.2 (ArCH), 125.9 (C8a), 109.1 (C8), 80.0 (C3′), 71.7 (OCH_2Ph), 70.5 (C1), 61.0 (OCH_3), 60.6 (OCH_3), 55.7 (a-OCH_3), 44.6 (NCH_2Ph), 37.6 (C4′), 33.7 (C2), 23.0 (C4), 19.7 (C3). HRMS (ESI) *m/z* calcd for $C_{30}H_{34}NO_5$ $[M+H]^+$ 488.2437, found 488.2450. ***Minor diastereomer*** (*1R,3′S*)-**12b**: (indicative peaks from mixture of diastereomers) δ_H 6.09 (1H, s, H8), 4.36 (1H, d, *J* = 11.7 Hz, OCH_2Ph), 3.55 (3H, s, OCH_3).

Gaussian Archive Entries for Computational Data

The calculations were performed using the Gaussian software package (see ref. 10 in paper).

Structure 12a (with Bn replaced by Me)

1\1\GINC-SPARTAN-RC106\FOpt\RM062X\6-31+G(d)\C17H23N1O4\UWILLE\28-May-
2019\0\\#p M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) nosymm ge
om=checkpoint guess=check opt=(readfc,maxcycle=500) scf=(qc,direct) fr
eq=noraman\\geom&freq\\0,1\C,0.6452815786,-0.0428136259,-0.3039671183\
C,1.9996555533,0.0148604765,-0.0309242384\C,2.66627015,1.2370527732,0.
1363488046\C,1.9409493299,2.4239331932,0.0053923017\C,0.5657875114,2.3
663050023,-0.2730401326\C,-0.0942193602,1.151184213,-0.4218558004\H,2.
5338408871,-0.9298833665,0.042623632\H,0.0192630984,3.3001962053,-0.36
47119195\C,2.5910880922,3.7890933756,0.1208357934\H,2.6401502933,4.228
5633065,-0.8857271838\H,1.9480174485,4.4499722514,0.7128875231\C,4.000
5342337,3.7424903089,0.7098504197\H,3.9500305031,3.6109392953,1.797227
9333\H,4.5128231589,4.6910317565,0.520378486\C,4.7815229958,2.58773220
4,0.0888161134\H,5.8319746129,2.5936577774,0.4020362717\H,4.7627680696
,2.6873203066,-1.0051184946\C,4.1517495107,1.2515439536,0.491161724\C,
4.3903314035,0.9508357523,2.0076147782\C,4.6779183012,-0.5504080429,2.
0821071221\H,5.2847358408,1.5124806943,2.3234585796\H,3.7572788806,-1.
1103249859,2.2913103972\H,5.4275290723,-0.8330589467,2.8243143346\O,3.
2892249975,1.369964325,2.7743756579\O,0.02045543,-1.259584549,-0.41710
71407\O,-1.4209792508,1.0102694832,-0.6725417523\C,-2.1892039117,2.193
3115673,-0.8239499445\H,-3.2079053388,1.8645138964,-1.026087672\H,-2.1
715402787,2.7921594986,0.0931120906\H,-1.8221497265,2.7935676024,-1.66
39101296\C,-0.3088676062,-1.6126477096,-1.7608595725\H,-0.9942891305,-
0.8796104934,-2.1968739515\H,0.602524649,-1.6794954003,-2.3661264534\H
,-0.7920706111,-2.589391516,-1.7147881458\C,3.5410265738,1.3014706316,
4.1652969766\H,2.6552204165,1.6906387549,4.6690705944\H,3.7147041342,0
.2673521509,4.4899528179\H,4.4133470454,1.9127720458,4.4346156151\C,5.
0607870974,0.0652302987,-1.5724188577\H,5.8935704676,0.7021584781,-1.8
868318891\H,5.2826303902,-0.969419389,-1.8380135793\H,4.1493546331,0.3
862689148,-2.0875472233\N,4.8589917535,0.1313487396,-0.1390539036\C,5.
1530890511,-0.9020804227,0.6862859253\O,5.6944128195,-1.9517102656,0.3
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769,0.2484985,8.3492783,18.91711,6.7331436,1.9842921\PG=C01 [X(C17H23N
1O4)]\\@

Sum of electronic and thermal Free Energies= -1016.576079 Hartrees

Data for Table 6

Entry 1

Reactant association complex

1\1\GINC-R731\FOpt\RM062X\6-31+G(d)\C17H21N2O2(1+)\ROOT\02-May-2016\0\
\# M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) freq=noraman scf=
(qc,direct) geom=checkpoint guess=check nosymm opt=(z-matrix,readfc,Ma
xcycle=500)\\freq&geom\\1,1\C,-0.4616661396,1.8256580869,1.2463647352\
C,0.960613301,1.2638191516,1.2033410349\H,-0.5070759026,2.7114637404,1
.8865769728\H,0.9379270913,0.1598455991,1.2132536643\H,-1.2208167008,1
.1146151322,1.576963196\C,-0.7333077531,2.2301286525,-0.1764259004\O,1
.8387629002,1.7404171606,2.1748046924\C,1.5969544416,1.1720308027,3.45
78751564\H,2.3449758073,1.5923234248,4.1289288053\H,0.5949982665,1.432
2546449,3.8189817778\H,1.7024543539,0.0813929238,3.4195854213\C,0.4752
819972,2.3997395111,-2.3580594744\H,0.0064137951,1.5568227653,-2.87110
00859\H,-0.128569239,3.2975436097,-2.4955756659\H,1.4741566609,2.57558
61817,-2.7425155021\C,2.8593265475,1.3500123038,-0.4869264964\O,-1.738

5697231,2.5834355001,-0.7148422184\N,0.5142489086,2.0997078379,-0.9234
08992\H,3.3932535473,0.9656258967,0.3741273512\C,3.2895894516,0.779372
5885,-1.852056512\H,2.5138120794,0.6379785392,-2.5955456898\H,4.006969
3235,-0.0294347596,-1.7737237398\C,3.7068986756,2.1417122941,-1.484834
494\H,4.7244694616,2.3032304123,-1.1466304659\H,3.2450229007,2.9972779
669,-1.9627839052\C,1.4858157265,1.6375956055,-0.1751387949\C,1.678953
1564,5.2170388839,-1.0112231908\C,1.3975322252,4.7680889848,1.18224448
19\C,0.3081758675,5.3791738382,-0.6856844375\C,2.0928663156,5.46006039
7,-2.335486441\H,1.4951862479,4.518525296,2.2297498418\C,-0.6511002417
,5.7664326912,-1.6299632716\C,1.1484586354,5.8384704213,-3.2758550489\
H,3.1397775411,5.3623612592,-2.6130409017\H,-0.6792152106,5.2296184002
,1.189661691\C,-0.2121683259,5.9901382778,-2.9258986872\H,-1.695911648
3,5.8820890024,-1.356519166\H,1.4555380809,6.0292077999,-4.299822686\H
,-0.9266373185,6.2916469257,-3.6860440089\N,0.1655383402,5.0841357098,
0.6521328195\C,2.3495617145,4.8208127237,0.198019389\H,3.4029888412,4.
6099968162,0.3245447463\\Version=ES64L-G09RevD.01\HF=-919.8426085\RMSD
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ole=-0.2430717,-5.0417603,5.284832,1.753808,-6.624607,1.2672514\PG=C01
[X(C17H21N2O2)]\\@

Sum of electronic and thermal Free Energies= -919.532637 Hartrees

TS1

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M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) freq=noraman scf=(
qc,direct) nosymm opt=(ts,noeigentest,z-matrix,calcfc,Maxcycle=500)\\f
req&geom\\1,1\C,-0.9215729097,1.6650878385,0.3351114082\C,0.1390087387
,2.3817582584,-0.2486299075\C,0.218318336,3.7715407367,-0.2209482852\C
,-0.7940206118,4.440590567,0.4616964398\C,-1.8358876881,3.7416715932,1
.0979401138\C,-1.9144347484,2.3543947988,1.0382048323\C,0.5596812362,0
.2042011316,-0.5916794974\H,1.0350892737,4.3061073342,-0.6956352901\H,
-0.7687237369,5.5242735529,0.5169504261\H,-2.5947566621,4.2985421103,1
.6386849745\H,-2.7284551513,1.8194306879,1.5205481084\H,1.1116188153,-
0.6645766044,-0.9240879589\H,1.8718872197,1.6653503427,-1.2936474978\N
,1.016800046,1.4409926391,-0.7970078659\C,-0.7109861254,0.2617919228,0
.0146755876\H,-1.1209661873,-0.5702761753,0.5706830269\C,-1.9438564148
,-0.026487621,-1.7435021579\C,-2.1429512756,-1.5401274331,-1.612873805
3\C,-3.2929385905,-1.6782250501,-0.6147356051\H,-2.484432889,-1.861581
1856,-2.6123123196\H,-4.0012971164,-2.4755642737,-0.8449889039\H,-2.92
43191728,-1.8295541236,0.4065296717\C,-1.1027277281,0.4085631316,-2.87
74738832\C,-1.7460447341,0.8446143027,-4.1830805942\C,-0.8973619978,1.
8043756446,-3.4151120175\H,-0.2548685258,-0.2595950749,-2.9961300521\H
,-2.8195786425,0.9966237429,-4.19367034\H,-1.3420920363,0.3896224487,-
5.0805584578\H,0.1010656294,2.012300049,-3.785283302\H,-1.376777608,2.
6453819342,-2.9315972172\C,-3.9805789865,-0.335680416,-0.7021662772\O,
-5.0632274653,-0.0159032736,-0.2778900195\O,-0.9478240375,-2.182653441
2,-1.2931510645\C,-3.5671884934,1.9267395225,-1.6476770642\H,-4.386386
3345,2.1309110277,-0.958391921\H,-2.7538727167,2.6199537362,-1.4442567
817\H,-3.926585153,2.0442560233,-2.6724352569\C,-1.0296514101,-3.59680
74623,-1.4272599409\H,-0.0397813651,-3.9891218266,-1.196005773\H,-1.76
05267146,-4.0139282613,-0.7250953846\H,-1.3062633335,-3.8711839712,-2.
45213909\N,-3.1347627303,0.5504121188,-1.4070400576\\Version=ES64L-G09
RevD.01\HF=-919.8269679\RMSD=0.000e+00\RMSF=6.949e-06\Dipole=2.3187267
,-0.7574471,-1.6811883\Quadrupole=-11.4885142,10.7661409,0.7223733,4.1
310254,5.2241551,-0.902256\PG=C01 [X(C17H21N2O2)]\\@

ν_{imag} = -316.3573 cm^{-1}

Sum of electronic and thermal Free Energies= -919.514503 Hartrees

1,2-Adduct **13'**

1\1\GINC-R374\FOpt\RM062X\6-31+G(d)\C17H21N2O2(1+)\ROOT\02-May-2016\0\

\# M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) freq=noraman scf=
(qc,direct) geom=checkpoint guess=check nosymm opt=(z-matrix,readfc,Ma
xcycle=500)\\freq&geom\\1,1\C,-0.7921151397,2.0599215237,-0.1264183874
\C,0.5946675128,2.230027893,-0.1386781347\C,1.2506083655,3.4456921479,
-0.0412263886\C,0.4389960722,4.5714520408,0.0803220463\C,-0.9525092798
,4.4437809049,0.1091055847\C,-1.5789488093,3.1986824722,0.0097647814\C
,0.2960292278,0.0063474662,-0.3032274289\H,2.3329162431,3.5153683037,-
0.0539923526\H,0.8933959549,5.5532181458,0.160606263\H,-1.5661423486,5
.3331372343,0.2111827268\H,-2.6593289632,3.1492093998,0.0390118402\H,0
.5748010627,-1.038016652,-0.3568530334\H,2.1886690487,0.7712787246,-0.
2526947644\N,1.1827232919,0.9408292484,-0.2472680268\C,-1.0895070365,0
.5729296616,-0.2509736523\H,-1.5468273995,0.1635616264,0.6630687721\C,
-1.939714101,0.0805868932,-1.4791272894\C,-1.7076647011,-1.4371261272,
-1.7491558589\C,-3.0166325636,-1.8835882763,-2.3923074419\H,-0.8313472
929,-1.5912722839,-2.3950277763\H,-3.0162930746,-1.7423667851,-3.47698
32422\H,-3.2638755546,-2.9263661408,-2.1860505176\C,-1.5319797525,0.87
57700863,-2.7157327578\C,-2.3903922621,0.9613610477,-3.9484414128\C,-2
.1578564862,2.1830337075,-3.1072456034\H,-0.4608252408,0.8069588872,-2
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0.8794101449,-4.9103548798\H,-1.4951171952,2.9601097452,-3.4735183984\
H,-3.0019447969,2.5434820398,-2.5306372204\C,-4.0379027042,-0.96672309
47,-1.7507420695\O,-5.2466854857,-1.1407191513,-1.7107285669\O,-1.5161
047641,-2.0772445675,-0.5021300549\C,-4.1001791495,1.0663827042,-0.396
9745521\H,-3.5900808056,1.2227203367,0.5578689549\H,-4.2396155736,2.02
54110721,-0.902516165\H,-5.0841276565,0.6397074247,-0.1972978623\C,-1.
052102353,-3.414909805,-0.6088813674\H,-0.8791762504,-3.7682498958,0.4
078482576\H,-1.7906856095,-4.0628635144,-1.0930519918\H,-0.1136122028,
-3.4549099485,-1.1778152313\N,-3.3803054397,0.1046810243,-1.2096285232
\\Version=ES64L-G09RevD.01\HF=-919.8432394\RMSD=0.000e+00\RMSF=3.941e-
06\Dipole=5.5118121,0.7275868,0.9685305\Quadrupole=-17.9717226,19.9467
107,-1.9749881,-5.9792189,-5.0410349,1.5173956\PG=C01 [X(C17H21N2O2)]\\@
Sum of electronic and thermal Free Energies= -919.527093 Hartrees

TS2

1\1\GINC-R1582\FTS\RM062X\6-31+G(d)\C17H21N2O2(1+)\ROOT\02-May-2016\0\
\# M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) freq=noraman scf=
(qc,direct) nosymm opt=(ts,noeigentest,z-matrix,calcfc,Maxcycle=500)\\
freq&geom\\1,1\C,2.7342837703,0.2783922805,-5.0818125133\C,2.028845452
2,0.0214426954,-3.744443916\H,2.4306493673,1.2528779969,-5.4831980235\
H,1.8545830018,-1.0591814433,-3.6127082771\H,2.5742179097,-0.484744564
5,-5.8441510276\C,4.1953032673,0.3514990203,-4.7083791904\O,0.83923231
03,0.7277262276,-3.5447505134\C,-0.2300605303,0.2292304462,-4.33631406
28\H,-1.1114922761,0.8151639751,-4.0771564144\H,-0.0172099409,0.346500
7281,-5.4057767665\H,-0.4124373923,-0.8297190078,-4.115162794\C,5.5792
573729,0.5400996893,-2.6501367759\H,5.6423494052,-0.2372005515,-1.8866
317901\H,6.3350823938,0.3624609927,-3.4147127733\H,5.7549619187,1.5245
783094,-2.2070765602\C,2.7031126732,0.7410989349,-1.4199543371\O,5.159
6671182,0.3244492499,-5.4349139541\N,4.282161912,0.4779814243,-3.30971
4315\H,1.6488372279,0.6254404056,-1.1957409777\C,3.5694763925,1.319496
4059,-0.3259336232\H,4.6146694319,1.0244097446,-0.3206833784\H,3.10890
22603,1.2068037504,0.6533141969\C,3.2614833043,2.5779346876,-1.0112223
543\H,3.8208336339,2.8718714971,-1.8951883005\H,2.2831873714,3.0281573
148,-0.8833778057\C,3.0555210294,0.4505902119,-2.7089607678\C,3.743578
4572,5.3782280615,-0.8250865229\C,5.4055459756,4.0056236387,-0.1086489
571\C,4.8642982896,5.5238986254,-1.6702607994\C,2.5888051753,6.1324860
575,-1.0856147454\H,6.0455554178,3.3064603971,0.413398473\C,4.88047989
37,6.3939560871,-2.7639892578\C,2.5971579791,7.0052157743,-2.163888208
6\H,1.7115700304,6.0383029798,-0.4515932981\H,6.7703445421,4.557396875
5,-1.609014917\C,3.7298890978,7.1330642368,-2.9944450143\H,5.754384669
,6.4849030672,-3.4017338285\H,1.7160004131,7.602467437,-2.3774119128\H

,3.7001142761,7.8234359506,-3.8317070216\N,5.8510734073,4.6688879934,-
1.1993198494\C,4.0809736488,4.3565331698,0.1442554318\H,3.5338593423,4
.10676823,1.0436564471\\Version=ES64L-G09RevD.01\HF=-919.8056406\RMSD=
0.000e+00\RMSF=5.205e-06\Dipole=0.2734803,-1.2796923,1.8952224\Quadrup
ole=31.8193077,-8.0312956,-23.7880121,37.0460947,-7.4963418,-9.979668\
PG=C01 [X(C17H21N2O2)]\\@

ν_{imag} = - 569.6868 cm^{-1}

Sum of electronic and thermal Free Energies= -919.497396 Hartrees

Homoconjugate adduct **14'**

1\1\GINC-R109\FOpt\RM062X\6-31+G(d)\C17H21N2O2(1+)\ROOT\02-May-2016\0\
\# M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) freq=noraman scf=
(qc,direct) geom=checkpoint guess=check nosymm opt=(z-matrix,readfc,Ma
xcycle=500)\\freq&geom\\1,1\C,2.5894187286,-0.2143868959,-5.4407526867
\C,1.923115704,-0.4974937465,-4.0948620557\H,2.1846327204,0.713630307,
-5.862778967\H,2.0041013818,-1.5720472936,-3.8724021825\H,2.4900626583
,-1.0123395192,-6.1773321635\C,4.0388895181,0.0162497528,-5.0665269563
\O,0.578326214,-0.100729212,-4.063545838\C,-0.277297875,-1.0053894569,
-3.3815178882\H,-1.2695499507,-0.5526530675,-3.3696558235\H,-0.3220958
479,-1.9676793037,-3.9061643822\H,0.0561357636,-1.173835817,-2.3502019
312\C,5.3498659569,0.5405986461,-3.0449641665\H,5.414980413,-0.0686886
697,-2.1407600412\H,6.1486045895,0.2584958919,-3.7318188229\H,5.467443
441,1.5992025834,-2.7891820008\C,2.4059441908,0.8115479651,-1.97013547
47\O,5.0089289705,-0.0131610381,-5.8054200578\N,4.0900991698,0.2899695
064,-3.717370092\H,1.3509065419,0.6724031428,-1.746995991\C,3.17233746
97,1.6980247296,-1.0211142158\H,4.1951072574,1.3410915952,-0.869494336
8\H,2.6867337626,1.6688224131,-0.0394286946\C,3.1842592841,3.145575827
4,-1.52959226\H,3.7007913539,3.2114232527,-2.4947322299\H,2.1566582976
,3.4851018759,-1.6969312599\C,2.8158861618,0.2640155326,-3.119084033\C
,3.8303133506,5.5744756223,-1.0133997053\C,5.2886215913,3.901768567,-0
.3310121868\C,5.148516502,6.0236775207,-1.0780142387\C,2.8057668333,6.
4301761267,-1.3941354296\H,5.7712249969,2.9997762292,0.0290380776\C,5.
5233814349,7.2887920518,-1.4991555015\C,3.1487363346,7.7151792429,-1.8
231250762\H,1.7672999361,6.1152163916,-1.358548121\H,6.9934685543,5.00
30898454,-0.5840239157\C,4.4825257073,8.137761273,-1.8752280322\H,6.56
12246553,7.6018578571,-1.5359277686\H,2.3637428484,8.4017943101,-2.123
5759281\H,4.7131866251,9.1422658713,-2.2140851276\N,5.9769712882,4.949
4216979,-0.6445802031\C,3.8304162312,4.1451006964,-0.5361403542\H,3.32
93702227,4.0368917015,0.4384830524\\Version=ES64L-G09RevD.01\HF=-919.8
543775\RMSD=0.000e+00\RMSF=1.024e-05\Dipole=2.1137085,3.2811602,4.7993
77\Quadrupole=40.0236788,38.5271693,-78.5508481,88.3073526,8.4974694,-
11.2964527\PG=C01 [X(C17H21N2O2)]\\@

Sum of electronic and thermal Free Energies= -919.542568 Hartrees

Entry 2

Reactant association complex

See entry 1.

TS1 (anti)

1\1\GINC-SPARTAN-RC180\FTS\RM062X\6-31+G(d)\C17H21N2O2(1+)\UWILLE\23-J
an-2019\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm scrf=(cpcm,solvent=
dichloromethane) opt=(ts,noeigentest,calcfc,maxcycle=500) freq=noraman
\\freq&geom\\1,1\C,-0.8206800766,1.8869415917,0.2252262609\C,0.3920266
353,2.2823383671,-0.3680708667\C,-0.0764413634,4.5680810075,0.03097240
71\C,-1.6537682168,2.8671276321,0.7803245892\C,0.3350400445,0.04181396
4,-0.4498935555\H,0.1868135878,5.6186927564,-0.0405484899\H,-2.5767138
202,2.5936105356,1.2834579428\H,0.706135026,-0.9505511665,-0.673487338
1\H,1.9495409583,1.0952030806,-1.2432744383\N,1.0549020399,1.119836172

5,-0.7660778865\C,-0.9085471775,0.4398649233,0.0854954138\H,-1.5362236
683,-0.2008054754,0.6916425469\C,-1.9927512711,-0.0491689008,-1.740190
5776\C,-3.200911308,-2.1411282135,-1.938755238\H,-3.4226562578,-2.2588
886233,-3.0069809443\H,-3.3915992367,-3.0824615474,-1.4229287379\C,-1.
3057708634,0.74510551,-2.7751736551\C,-2.1361622789,1.3339643758,-3.91
08462643\C,-1.3839911384,2.2397073423,-3.0008532984\H,-0.3732891947,0.
2849572009,-3.0781527471\H,-3.2147838465,1.2813997907,-3.8000626055\H,
-1.7641316922,1.1578172534,-4.9138740419\H,-0.4653507493,2.6854610616,
-3.3679817038\H,-1.9285871254,2.8653381913,-2.3041998178\C,-4.06786124
42,-1.0321411843,-1.4034627419\O,-5.233563458,-1.0574292413,-1.0889339
658\C,-3.9989453542,1.3996402775,-1.1053205424\H,-4.4887615132,1.30780
96164,-0.1331627478\H,-3.287977202,2.2177084261,-1.0712680943\H,-4.760
0995026,1.587242565,-1.8665716417\N,-3.3071882868,0.1475375378,-1.3939
629592\C,-1.2735185042,4.1986581781,0.6736856622\H,-1.908536382,4.9710
367403,1.0961231627\C,-1.7858115995,-1.5826038912,-1.7516248863\H,-1.4
253898295,-1.9066241844,-0.7647656838\C,0.7848058471,3.612956451,-0.49
41668326\H,1.7185346229,3.8884161022,-0.9743539882\O,-0.8543237249,-1.
9256131999,-2.7301848576\C,-0.515330682,-3.3065524006,-2.7075810152\H,
-1.3839927206,-3.9275831227,-2.9537159449\H,0.2581205317,-3.4497143297
,-3.461214779\H,-0.1290420046,-3.5933361701,-1.7212090982\\Version=AM6
4L-G09RevB.01\HF=-919.8182602\RMSD=0.000e+00\RMSF=4.817e-06\Dipole=2.5
191082,-0.5345227,-0.4938065\Quadrupole=-10.8034787,11.7435297,-0.9400
51,-3.0205561,1.4403863,1.0792639\PG=C01 [X(C17H21N2O2)]\\@

ν_{imag} = - 308.1813 cm^{-1}

Sum of electronic and thermal Free Energies= -919.506041 Hartrees

1,2-Adduct **13' (*anti*)**

1\1\GINC-SPARTAN-RC180\FTS\RM062X\6-31+G(d)\C17H21N2O2(1+)\UWILLE\23-J
an-2019\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm scrf=(cpcm,solvent=
dichloromethane) opt=(ts,noeigentest,calcfc,maxcycle=500) freq=noraman
\\freq&geom\\1,1\C,-0.8206800766,1.8869415917,0.2252262609\C,0.3920266
353,2.2823383671,-0.3680708667\C,-0.0764413634,4.5680810075,0.03097240
71\C,-1.6537682168,2.8671276321,0.7803245892\C,0.3350400445,0.04181396
4,-0.4498935555\H,0.1868135878,5.6186927564,-0.0405484899\H,-2.5767138
202,2.5936105356,1.2834579428\H,0.706135026,-0.9505511665,-0.673487338
1\H,1.9495409583,1.0952030806,-1.2432744383\N,1.0549020399,1.119836172
5,-0.7660778865\C,-0.9085471775,0.4398649233,0.0854954138\H,-1.5362236
683,-0.2008054754,0.6916425469\C,-1.9927512711,-0.0491689008,-1.740190
5776\C,-3.200911308,-2.1411282135,-1.938755238\H,-3.4226562578,-2.2588
886233,-3.0069809443\H,-3.3915992367,-3.0824615474,-1.4229287379\C,-1.
3057708634,0.74510551,-2.7751736551\C,-2.1361622789,1.3339643758,-3.91
08462643\C,-1.3839911384,2.2397073423,-3.0008532984\H,-0.3732891947,0.
2849572009,-3.0781527471\H,-3.2147838465,1.2813997907,-3.8000626055\H,
-1.7641316922,1.1578172534,-4.9138740419\H,-0.4653507493,2.6854610616,
-3.3679817038\H,-1.9285871254,2.8653381913,-2.3041998178\C,-4.06786124
42,-1.0321411843,-1.4034627419\O,-5.233563458,-1.0574292413,-1.0889339
658\C,-3.9989453542,1.3996402775,-1.1053205424\H,-4.4887615132,1.30780
96164,-0.1331627478\H,-3.287977202,2.2177084261,-1.0712680943\H,-4.760
0995026,1.587242565,-1.8665716417\N,-3.3071882868,0.1475375378,-1.3939
629592\C,-1.2735185042,4.1986581781,0.6736856622\H,-1.908536382,4.9710
367403,1.0961231627\C,-1.7858115995,-1.5826038912,-1.7516248863\H,-1.4
253898295,-1.9066241844,-0.7647656838\C,0.7848058471,3.612956451,-0.49
41668326\H,1.7185346229,3.8884161022,-0.9743539882\O,-0.8543237249,-1.
9256131999,-2.7301848576\C,-0.515330682,-3.3065524006,-2.7075810152\H,
-1.3839927206,-3.9275831227,-2.9537159449\H,0.2581205317,-3.4497143297
,-3.461214779\H,-0.1290420046,-3.5933361701,-1.7212090982\\Version=AM6
4L-G09RevB.01\HF=-919.8182602\RMSD=0.000e+00\RMSF=4.817e-06\Dipole=2.5
191082,-0.5345227,-0.4938065\Quadrupole=-10.8034787,11.7435297,-0.9400
51,-3.0205561,1.4403863,1.0792639\PG=C01 [X(C17H21N2O2)]\\@

Sum of electronic and thermal Free Energies= - 919.522586 Hartrees

Entry 3

Reactant association complex

See entry 1.

***TS2* (formation of *E*-alkene)**

1\1\GINC-SPARTAN-RC055\FTS\RM062X\6-31+G(d)\C17H21N2O2(1+)\UWILLE\08-J
un-2019\0\\#p M062X/6-31+G* scf=(qc,direct) scrf=(cpcm,solvent=dichlor
omethane) nosymm freq=noraman opt=(ts,noeigentest,calcfc,maxcycle=500)
\\geom&freq\\1,1\C,4.004075634,0.4894479234,-4.2125131079\C,3.19886369
45,1.7739468318,-3.9637495476\H,4.9321878955,0.4907956706,-3.632804587
9\H,4.2525388604,0.3174641765,-5.2620357095\C,3.1224174116,-0.63322628
96,-3.7151149413\C,0.8718285488,-0.8733048587,-2.6507690426\H,-0.04979
79838,-0.7072877359,-3.2150848632\H,1.1681318776,-1.9188242131,-2.7253
405424\H,0.7161579912,-0.6073239738,-1.6019796436\C,0.8661896862,2.065
1616635,-2.8954305963\O,3.3460920838,-1.8206908878,-3.72737714\N,1.943
6178409,-0.0698586562,-3.2128644765\H,0.0087695046,1.6078297528,-2.414
8832378\C,0.8528380476,3.5655055389,-3.076382135\H,1.8430576694,4.0140
777733,-3.1233829718\H,0.1942651853,4.0640717788,-2.3677102285\C,0.245
5498979,3.2339548946,-4.3665228146\H,0.8702913481,2.9481421052,-5.2066
401358\H,-0.7920167987,2.9181147684,-4.4012993987\C,1.9046277175,1.285
7420846,-3.3235976424\C,-0.6259643499,4.4278425545,-6.8009333282\C,0.8
60243551,5.5852343489,-5.5325078076\C,0.6090499222,4.5011574022,-7.481
0564898\C,-1.6970359953,3.7479980073,-7.4014261254\H,1.3803829802,6.16
2209495,-4.7796281501\C,0.8164675928,3.9272788352,-8.7384147089\C,-1.5
037004968,3.1805468624,-8.6528365913\H,-2.6569855273,3.6739581089,-6.8
982087703\H,2.4497963862,5.420634486,-6.8964154349\C,-0.2608358598,3.2
690127409,-9.3132030234\H,1.7760917048,3.9976582545,-9.241395153\H,-2.
3231608482,2.6582201209,-9.136914319\H,-0.1449152606,2.8132189726,-10.
2916335113\N,1.4856367562,5.2102702325,-6.670421339\C,-0.4371503752,5.
0803182657,-5.5222041006\H,-1.2045180493,5.3529206187,-4.8097860523\O,
3.8163343425,2.6667921949,-3.0693763572\C,4.8659903096,3.4054443966,-3
.6780088588\H,4.4760614934,4.0125843097,-4.5059874364\H,5.2798303182,4
.0561726902,-2.9080773664\H,5.653506008,2.7421530732,-4.0558526207\H,2
.978388735,2.2893393719,-4.9113276724\\Version=AM64L-G09RevB.01\HF=-91
9.8095284\RMSD=0.000e+00\RMSF=7.486e-06\Dipole=-0.1467016,2.3101619,0.
5219946\Quadrupole=-30.9622788,-7.5510737,38.5133525,29.8681782,-30.80
12235,-66.4099241\PG=C01 [X(C17H21N2O2)]\\@

ν_{imag} = -564.8338 cm^{-1}

Sum of electronic and thermal Free Energies= -919.501621 Hartrees

Compound **14' (*E*-alkene)**

1\1\GINC-SPARTAN-RC018\FOpt\RM062X\6-31+G(d)\C17H21N2O2(1+)\UWILLE\09-
Jun-2019\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm scrf=(cpcm,solvent
=acetonitrile) freq=noraman opt=(calcfc,z-matrix,maxcycle=500)\\geom&f
req\\1,1\C,6.4292198183,4.3642804642,-2.7801777446\C,5.8608321575,3.32
16524987,-1.8056613815\H,7.4789626183,4.5938533731,-2.5813124978\H,5.1
533859556,3.7677625458,-1.0941152341\H,5.8670851435,5.3029512528,-2.76
65582958\C,6.2849968351,3.7400446213,-4.154821776\O,6.8732327554,2.633
7427875,-1.0923336513\C,7.3898497429,3.3916812188,-0.0121169888\H,8.16
0847843,2.7839061833,0.4627498189\H,7.8352385843,4.3340528787,-0.35492
29037\H,6.598053261,3.6145459054,0.7157143148\C,5.1462697284,1.7777902
938,-5.1532908757\H,4.0565418088,1.7830682329,-5.2587158066\H,5.602460
9176,2.1927527685,-6.0517441388\H,5.4876705795,0.7486792957,-5.0059650
191\C,4.3652458162,1.3157315644,-2.3303368769\O,6.7253915927,4.1793491
509,-5.2073629505\N,5.545140335,2.595820408,-4.0292908273\H,3.94363391
99,0.6496372896,-3.0808771412\C,3.9779723131,1.0614977982,-0.900318301
5\H,4.6236322839,1.6241126048,-0.2165122095\H,4.1209016195,-0.00143539
76,-0.6769781595\C,2.5117007608,1.4399803291,-0.6602278949\H,2.3654900
57,2.4952968229,-0.9150922431\H,1.8587061338,0.8465321299,-1.310665370

5\C,5.1662330236,2.3168726158,-2.7091143596\C,1.9847064208,-0.19611399
68,1.2883370843\C,0.6602822786,1.6841554467,0.9625843443\C,0.647654537
3,-0.4827604004,1.5708688246\C,2.9342686682,-1.1919336592,1.4839552748
\H,0.255260762,2.6666244118,0.7470484578\C,0.1827917837,-1.710945212,2
.0096220147\C,2.4995711292,-2.445223603,1.9257618463\H,3.9898403684,-1
.0067636307,1.3153304807\H,-1.1040328013,0.7861081161,1.4784452802\C,1
.1479536473,-2.7041284525,2.1778271557\H,-0.8670838251,-1.8883292712,2
.2172605921\H,3.2293299335,-3.2332680102,2.0810697196\H,0.84380082,-3.
6878088353,2.5198078338\N,-0.0960203891,0.7104295691,1.34641999\C,2.07
43269077,1.2358370185,0.8183277753\H,2.7195311524,1.852206867,1.460126
8228\\Version=AM64L-G09RevB.01\HF=-919.8701792\RMSD=0.000e+00\RMSF=5.0
75e-06\Dipole=-6.7572683,-1.266225,5.2204317\Quadrupole=-3.6037215,14.
612538,-11.0088165,-4.1015543,26.2490309,16.4300399\PG=C01 [X(C17H21N2
O2)]\\@
Sum of electronic and thermal Free Energies= -919.559235 Hartrees

Entry 4

Reactant association complex

1\1\GINC-R183\FOpt\RM062X\6-31+G(d)\C17H20N3O4(1+)\ROOT\03-May-2016\0\
\# M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) freq=noraman scf=
(qc,direct) geom=checkpoint guess=check nosymm opt=(z-matrix,readfc,Ma
xcycle=500)\\freq&geom\\1,1\C,-0.4608106637,1.8225519978,1.2117153826\
C,0.960115734,1.2560494791,1.1843338305\H,-0.5135537055,2.70508986,1.8
561969303\H,0.937980895,0.1529989937,1.2189177894\H,-1.2263619994,1.11
26820554,1.5303160021\C,-0.7167830798,2.2352279131,-0.2109470824\O,1.8
355367939,1.7582552768,2.1457978025\C,1.5944123024,1.2204451728,3.4426
262117\H,2.3415225141,1.6588170987,4.1030036194\H,0.5917832161,1.48734
32398,3.7967511322\H,1.7025430853,0.1296437077,3.4304943767\C,0.505181
443,2.3756211598,-2.3883453006\H,0.0538943395,1.5264396869,-2.90667570
44\H,-0.1152510347,3.2608799728,-2.5333550373\H,1.5053720222,2.5644729
968,-2.764264989\C,2.8660437628,1.30860709,-0.497615795\O,-1.708127758
3,2.6208125331,-0.7522597655\N,0.5325023589,2.079556373,-0.9525298809\
H,3.3905179252,0.9157728519,0.3652825291\C,3.3108722168,0.7526225198,-
1.8646479329\H,2.5429979079,0.6197955247,-2.6177155151\H,4.0249794276,
-0.0589149201,-1.7848577056\C,3.7283263199,2.1085495733,-1.4801427611\
H,4.7415385962,2.2652857706,-1.1273104464\H,3.2743661511,2.969218529,-
1.9559029759\C,1.4938457169,1.6056826339,-0.1974450449\C,1.6827162452,
5.2298120607,-1.0046262149\C,1.3930078673,4.7956829539,1.1843085419\C,
0.3094098576,5.4142699618,-0.6816101247\C,2.10624188,5.4572219446,-2.3
196796013\H,1.482581557,4.5487760555,2.2329488922\C,-0.6467446822,5.80
80239802,-1.6288961566\C,1.1457628567,5.8391889222,-3.2407249583\H,3.1
439468219,5.3534730554,-2.6187962688\H,-0.6838178582,5.2714240788,1.18
28529576\C,-0.2151885457,6.0203493814,-2.9236830915\H,-1.6896283949,5.
9389892575,-1.3590762451\H,-0.9078481583,6.3244525802,-3.6987704319\N,
0.1656143181,5.1331207662,0.6495234572\C,2.3480071307,4.829580879,0.20
50549076\H,3.3984604259,4.6071480827,0.3322073959\O,2.7404580413,5.869
3605681,-4.9088579628\O,0.7319700112,6.453298288,-5.4245428157\N,1.569
745942,6.0713877707,-4.6220643075\\Version=ES64L-G09RevD.01\HF=-1124.2
829124\RMSD=0.000e+00\RMSF=6.793e-06\Dipole=-0.1502515,-4.5589124,4.85
64549\Quadrupole=12.1464815,-0.1650151,-11.9814665,-6.3499751,4.040070
2,32.7712945\PG=C01 [X(C17H20N3O4)]\\@
Sum of electronic and thermal Free Energies= - 1123.973842 Hartrees

TS1

1\1\GINC-SPARTAN-RC113\FTS\RM062X\6-31+G(d)\C17H20N3O4(1+)\UWILLE\31-J
an-2019\0\\#p M062X/6-31+G* nosymm scf=(qc,direct) scrf=(cpcm,solvent=
dichloromethane) opt=(ts,noeigentest,calcfc,maxcycle=500) freq=noraman
\\geom&freq\\1,1\C,-0.9452893635,1.7023032335,0.3018171645\C,0.2180204

584,2.3214026078,-0.1954717328\C,0.4147726209,3.7001031828,-0.19011779
23\C,-0.5941594816,4.4761488483,0.3622196946\C,-1.7358771967,3.8552462
42,0.8849954826\C,-1.943918586,2.4828557923,0.8767453605\C,0.492361938
3,0.1120950603,-0.4581724379\H,1.3146176119,4.1522061674,-0.5925121794
\H,-0.5060068501,5.5548626744,0.4035240199\H,-2.8435984212,2.053909050
2,1.3043318208\H,1.0064466742,-0.8016614797,-0.72157726\H,1.9692322105
,1.4478797142,-1.0708031413\N,1.0559736758,1.3045321186,-0.6509764396\
C,-0.8219247235,0.2732072191,0.0383531481\H,-1.2983279155,-0.498860661
4,0.6290743287\C,-1.9992607939,-0.0284486136,-1.6681844257\C,-2.112393
5788,-1.5617323698,-1.6280056997\C,-3.2658694422,-1.8323939007,-0.6623
623881\H,-2.4179221477,-1.8405021223,-2.6515389211\H,-3.909370097,-2.6
659080633,-0.9482217001\H,-2.9042815063,-2.0111145855,0.3574474838\C,-
1.1825598287,0.5053634719,-2.7828801579\C,-1.8276891129,1.1181995619,-
4.0112951376\C,-0.9204019073,1.9452297405,-3.1614363838\H,-0.355738942
7,-0.1701734026,-2.9877386935\H,-2.8917940865,1.323142089,-3.973117231
7\H,-1.4664577614,0.7580182958,-4.9679238221\H,0.0805379655,2.14828993
48,-3.5280147993\H,-1.3425552726,2.7490016232,-2.5705575132\C,-4.04256
0739,-0.5393467084,-0.7056308337\O,-5.1626935346,-0.3131203079,-0.3190
094711\O,-0.889645833,-2.1536275143,-1.3204466082\C,-3.8297074295,1.76
24010624,-1.5467417385\H,-4.3996705626,2.0403632586,-0.6594723051\H,-3
.0536330112,2.5010713887,-1.7192516621\H,-4.5118383349,1.7231375068,-2
.400046892\C,-0.8879659061,-3.5628127879,-1.5227395439\H,0.1210917215,
-3.9071811174,-1.2984011095\H,-1.5995069673,-4.054569104,-0.8498499431
\H,-1.1387187456,-3.801987543,-2.5627072477\N,-3.2407127621,0.44147773
17,-1.3249542801\O,-2.5913947674,5.9092127072,1.4960680824\O,-3.791968
4653,4.1616124438,1.8852793834\N,-2.7828748024,4.7054895546,1.46743852
29\\Version=AM64L-G09RevB.01\HF=-1124.2630834\RMSD=0.000e+00\RMSF=4.82
8e-06\Dipole=4.4672697,-3.31518,-3.1049736\Quadrupole=-10.7783841,1.34
72172,9.4311669,20.5906526,13.6404336,-9.9550894\PG=C01 [X(C17H20N3O4)
]\\@

ν_{imag} = - 371.1627 cm^{-1}

Sum of electronic and thermal Free Energies= - 1123.950267 Hartrees

1,2-Adduct **13'**

1\1\GINC-SPARTAN-RC190\FOpt\RM062X\6-31+G(d)\C17H20N3O4(1+)\UWILLE\31-
Jan-2019\0\\#p M062X/6-31+G* scf=(qc,direct) scrf=(cpcm,solvent=dichlo
romethane) nosymm opt=(calcfc,maxcycle=500) freq=noraman\\geom&freq\\1
,1\C,-0.796256,2.061551,-0.114209\C,0.589947,2.240083,-0.130179\C,1.24
1255,3.458953,-0.039199\C,0.43295,4.584464,0.077761\C,-0.948771,4.4182
73,0.10542\C,-1.593996,3.188166,0.0183\C,0.295956,0.018337,-0.290402\H
,2.322111,3.538133,-0.05509\H,0.862198,5.576055,0.152024\H,-2.67342,3.
155541,0.056375\H,0.576611,-1.025931,-0.342253\H,2.189672,0.788177,-0.
244942\N,1.182751,0.954805,-0.237942\C,-1.090385,0.576962,-0.239473\H,
-1.549666,0.16432,0.672294\C,-1.941482,0.091576,-1.473993\C,-1.7047,-1
.424613,-1.749793\C,-3.014365,-1.871436,-2.390702\H,-0.830171,-1.57413
3,-2.399206\H,-3.01722,-1.723388,-3.474533\H,-3.25773,-2.91616,-2.1904
81\C,-1.533279,0.895896,-2.704191\C,-2.394958,0.991408,-3.933441\C,-2.
155953,2.208346,-3.087602\H,-0.463197,0.824168,-2.901743\H,-3.394985,0
.570444,-3.892905\H,-1.903684,0.91205,-4.896995\H,-1.490859,2.983937,-
3.452799\H,-2.999827,2.570691,-2.511448\C,-4.036497,-0.961045,-1.74203
4\O,-5.243661,-1.137778,-1.697798\O,-1.50664,-2.065009,-0.504331\C,-4.
101956,1.074288,-0.38953\H,-3.603884,1.220201,0.57364\H,-4.233509,2.03
6681,-0.891073\H,-5.090244,0.651828,-0.20302\C,-1.051923,-3.406677,-0.
612033\H,-0.864582,-3.754982,0.403791\H,-1.802586,-4.0522,-1.07996\H,-
0.123412,-3.454654,-1.1961\N,-3.379761,0.113012,-1.200925\O,-2.999585,
5.47284,0.216223\O,-1.228326,6.695947,0.351339\N,-1.790823,5.622812,0.
234905\\Version=AM64L-G09RevB.01\HF=-1124.2741452\RMSD=0.000e+00\RMSF=
2.940e-06\Dipole=6.7692931,-2.5576958,0.3568048\Polar=0.,0.,0.,0.,0.,0
.\Quadrupole=-10.9822932,-1.3145883,12.2968815,9.9052652,-3.6845607,-0
.9153481\PG=C01 [X(C17H20N3O4)]\\@

Sum of electronic and thermal Free Energies= -1123.958724 Hartrees

TS2

1\1\GINC-R101\FTS\RM062X\6-31+G(d)\C17H20N3O4(1+)\ROOT\03-May-2016\0\\
M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) freq=noraman scf=(
qc,direct) nosymm opt=(ts,noeigentest,z-matrix,calcfc,Maxcycle=500)\\f
req&geom\\1,1\C,2.7214247775,0.1919065359,-5.0814453528\C,2.0164950127
,-0.0386619505,-3.7388017465\H,2.4172694788,1.158263377,-5.5017606491\
H,1.845108675,-1.1167500796,-3.5848302688\H,2.5611543214,-0.585804775,
-5.8288587871\C,4.1826286854,0.2731743449,-4.7100553947\O,0.8245092804
,0.6680773799,-3.5547441943\C,-0.2411085607,0.1540083186,-4.3412349034
\H,-1.1253400545,0.7403380361,-4.0927094021\H,-0.0261990155,0.25625692
62,-5.4118455285\H,-0.4200893842,-0.9023095073,-4.1050912091\C,5.56628
94978,0.5063721963,-2.6581591031\H,5.626737563,-0.2496368283,-1.873292
7933\H,6.3220589785,0.3053162991,-3.4170824394\H,5.7463926011,1.502136
34,-2.2423261405\C,2.6911269863,0.7350135424,-1.4320609003\O,5.1466703
107,0.2305139793,-5.4369569911\N,4.2697688814,0.430797212,-3.315878069
1\H,1.6367087405,0.6264028329,-1.2040656336\C,3.5555267508,1.348296325
9,-0.3564495637\H,4.6014401082,1.054645121,-0.345471\H,3.0997020058,1.
2513122994,0.6270791775\C,3.2561200883,2.6094569347,-1.0473342619\H,3.
8034522538,2.8770868522,-1.9474154664\H,2.2682854971,3.0449503904,-0.9
389063345\C,3.0418196466,0.416949022,-2.7130472387\C,3.7197853074,5.40
04971322,-0.8426198876\C,5.3882797583,4.0343264611,-0.1459219346\C,4.8
547750657,5.5963662009,-1.6622818754\C,2.5623584107,6.1430984098,-1.08
46887845\H,6.0334413236,3.3304437147,0.3633687701\C,4.8808979355,6.507
0371445,-2.7232332944\C,2.608219026,7.0471174901,-2.1328470433\H,1.665
1109848,6.0298406761,-0.4866752154\H,6.7698025648,4.6591593841,-1.6011
806548\C,3.7329291329,7.2429418026,-2.9523706343\H,5.7632888356,6.6365
386816,-3.3408570015\H,3.6877982783,7.9691104013,-3.7547260266\N,5.841
4404081,4.7439675321,-1.2037292046\C,4.0512054635,4.346548959,0.094757
9447\H,3.5048565662,4.0847374992,0.9910618393\O,1.43846455,8.623232033
5,-3.3454001179\O,0.4386620769,7.6921653318,-1.6792265058\N,1.40806518
98,7.8462300128,-2.4049801818\\Version=ES64L-G09RevD.01\HF=-1124.24349
23\RMSD=0.000e+00\RMSF=3.935e-06\Dipole=2.9123053,-3.8149623,2.5133893
\Quadrupole=57.009079,-35.6223168,-21.3867622,60.4953187,-12.1026402,3
.3911752\PG=C01 [X(C17H20N3O4)]\\@

ν_{imag} = - 574.9038 cm^{-1}

Sum of electronic and thermal Free Energies= -1123.935969 Hartrees

Homoconjugate adduct **14'**

1\1\GINC-R101\FOpt\RM062X\6-31+G(d)\C17H20N3O4(1+)\ROOT\04-May-2016\0\
\# M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) freq=noraman scf=
(qc,direct) geom=checkpoint guess=check nosymm opt=(z-matrix,readfc,Ma
xcycle=500)\\freq&geom\\1,1\C,2.5851128365,-0.2340863,-5.4404106819\C,
1.9199097939,-0.5039352759,-4.0911709167\H,2.1824019841,0.691608437,-5
.8694837354\H,1.9966869175,-1.5769548121,-3.8602605988\H,2.4822662559,
-1.0377699911,-6.1702160385\C,4.0357493783,-0.0044328889,-5.0707111233
\O,0.5772816397,-0.1004705801,-4.0597540845\C,-0.2828681918,-0.9991183
693,-3.3753980777\H,-1.2729601043,-0.5417212957,-3.3656742832\H,-0.331
7547416,-1.9627632487,-3.8969681483\H,0.0493157172,-1.1656662352,-2.34
33743959\C,5.3518188058,0.5343415959,-3.0561067896\H,5.4199452559,-0.0
685042122,-2.1477809788\H,6.148596139,0.2475163263,-3.7432533884\H,5.4
699041785,1.5949386316,-2.808633847\C,2.4109227324,0.8153257649,-1.975
6404419\O,5.0044662577,-0.0407160371,-5.8106167192\N,4.0903121383,0.27
89248989,-3.7231523888\H,1.3557287785,0.6812120554,-1.7502291944\C,3.1
807038556,1.7032409663,-1.030897806\H,4.2058305711,1.3504337086,-0.886
6884951\H,2.7013819528,1.6723644514,-0.0462359587\C,3.1819669578,3.149
9973248,-1.541573741\H,3.6984930872,3.2200830245,-2.5059968891\H,2.152
0236062,3.4826279014,-1.7070811394\C,2.8178204561,0.2607579577,-3.1224

912544\C,3.8149199561,5.5835410661,-1.0186323987\C,5.277696768,3.92407
85006,-0.3332417093\C,5.1305720008,6.0440538015,-1.0742780851\C,2.7836
418287,6.4252059522,-1.4005801223\H,5.7636916617,3.0237131602,0.027268
7179\C,5.5020608026,7.3128600501,-1.4871748167\C,3.1511958528,7.702662
1309,-1.8152449817\H,1.7420616022,6.1253177061,-1.3818125751\H,6.98008
30315,5.0369602096,-0.5736758373\C,4.4664325174,8.1619950375,-1.866881
1266\H,6.5364986057,7.6352833934,-1.5169832576\H,4.6709577966,9.171638
7044,-2.2018236382\N,5.9637781379,4.9766317948,-0.6397342016\C,3.82046
04475,4.1546127327,-0.545083629\H,3.3155262321,4.0441066925,0.42748831
31\O,2.3992704191,9.7468570779,-2.5814378871\O,0.9324716204,8.21607020
07,-2.1867667494\N,2.0782899521,8.6274676005,-2.2261654573\\Version=ES
64L-G09RevD.01\HF=-1124.285456\RMSD=0.000e+00\RMSF=4.893e-06\Dipole=4.
1339503,0.2520138,5.3893079\Quadrupole=66.9178586,4.2381687,-71.156027
3,104.0392317,6.0455616,4.3991882\PG=C01 [X(C17H20N3O4)]\\@
Sum of electronic and thermal Free Energies= -1123.976135 Hartrees

Entry 5

Reactant association complex

See entry 4.

TS2 (formation of *E*-alkene)

1\1\GINC-SPARTAN-RC039\FTS\RM062X\6-31+G(d)\C17H20N3O4(1+)\UWILLE\11-J
un-2019\0\\#p M062X/6-31+G* scf=(qc,direct) scrf=(cpcm,solvent=dichlor
omethane) nosymm freq=noraman opt=(ts,noeigentest,calcfc,maxcycle=500)
\\geom&freq\\1,1\C,4.0394418062,0.4658469792,-4.1495436206\C,3.2329165
493,1.7520688516,-3.9152022392\H,4.9564944577,0.4613543434,-3.55293729
77\H,4.3076176389,0.2963490295,-5.194818866\C,3.1434908932,-0.65595559
9,-3.675711613\C,0.8545184429,-0.8959838829,-2.6985637727\H,-0.0460490
646,-0.7254357749,-3.2948037053\H,1.1506372544,-1.9419916298,-2.766781
7011\H,0.6617666965,-0.633834485,-1.6549775451\C,0.861818392,2.0440622
178,-2.9407525945\O,3.3706257862,-1.8431543403,-3.6750890341\N,1.94720
7112,-0.0931853188,-3.2190525755\H,-0.0153837496,1.5903224095,-2.49329
16597\C,0.8565751559,3.5428189367,-3.1303203024\H,1.8496295511,3.98833
92363,-3.1461750941\H,0.1833291642,4.0459053954,-2.4382551882\C,0.2791
204865,3.241507222,-4.4445324199\H,0.9250269963,2.9392290374,-5.263422
3356\H,-0.7544466914,2.9141220269,-4.500726852\C,1.911725044,1.2636292
639,-3.331766421\C,-0.6554681087,4.5098523156,-6.8034485341\C,0.943982
6409,5.5796313459,-5.6079618179\C,0.5271962347,4.5891535847,-7.5747223
578\C,-1.7857019949,3.8913906902,-7.3415219247\H,1.5325092475,6.117833
8176,-4.8769063908\C,0.6270463103,4.0725118931,-8.870304771\C,-1.67211
0766,3.3923760421,-8.6285002441\H,-2.7150959445,3.8036504552,-6.790354
9828\H,2.4228883364,5.444001186,-7.0941663076\C,-0.4989219516,3.467849
6477,-9.3986075153\H,1.5453105404,4.1434866078,-9.4431851779\H,-0.4892
914418,3.0531109419,-10.3990086417\N,1.4724595519,5.2427448032,-6.8058
440399\C,-0.3588460982,5.0970576528,-5.5130878089\H,-1.0721683203,5.38
05291991,-4.7505874957\O,3.8183088837,2.6262272531,-2.9807680668\C,4.9
027936396,3.3622722404,-3.5278752661\H,4.5598232487,3.9843231745,-4.36
54083614\H,5.2844753279,3.9985329804,-2.729645266\H,5.7021826271,2.696
9821524,-3.8759766819\H,3.0551847091,2.2837318013,-4.8624021557\N,-2.8
470081875,2.7434378137,-9.2211385184\O,-2.7388560496,2.2765345179,-10.
3433818727\O,-3.8734333569,2.7016219647,-8.5616759634\\Version=AM64L-G
09RevB.01\HF=-1124.2473051\RMSD=0.000e+00\RMSF=7.977e-07\Dipole=2.9594
182,3.4962747,2.4694006\Quadrupole=-35.5042719,18.4843496,17.0199223,3
8.0354807,-66.6497312,-81.2062357\PG=C01 [X(C17H20N3O4)]\\@

ν_{imag} = -572.8201 cm^{-1}

Sum of electronic and thermal Free Energies= -1123.941298 Hartrees

Compound **14' (*E*-alkene)**

1\1\GINC-SPARTAN-RC009\FOpt\RM062X\6-31+G(d)\C17H20N3O4(1+)\UWILLE\11-
Jun-2019\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm scrf=(cpcm,solvent
=acetonitrile) freq=noraman opt=(calcfc,z-matrix,maxcycle=500)\\geom&f
req\\1,1\C,6.4078110349,4.3758048963,-2.7863255801\C,5.8523286676,3.32
89919185,-1.8088234732\H,7.4554594489,4.6164390884,-2.5893994606\H,5.1
383005038,3.768527333,-1.0997138446\H,5.8361082712,5.3086255865,-2.773
7203884\C,6.2688514378,3.747313521,-4.1594549629\O,6.8725211808,2.6566
70402,-1.0921276229\C,7.3800079038,3.4259639645,-0.0154777997\H,8.1576
254927,2.8294453539,0.462759621\H,7.8148439044,4.3714519606,-0.3629937
816\H,6.5854073582,3.6435622508,0.7108343314\C,5.1551910013,1.76731884
88,-5.1521125392\H,4.0651969552,1.7544215767,-5.2536069708\H,5.6013786
97,2.1888917056,-6.0524846354\H,5.5143459958,0.7442557407,-5.005039170
6\C,4.3870376476,1.2989119122,-2.3279035857\O,6.7012250381,4.189916628
,-5.2136270608\N,5.5442957769,2.5931990295,-4.030310819\H,3.9743580692
,0.6245454189,-3.0757302185\C,4.0056876766,1.0435149133,-0.8965404579\
H,4.65308301,1.6057792263,-0.2143216584\H,4.1500831393,-0.0200031962,-
0.6764872399\C,2.5398142685,1.4229275271,-0.6537961457\H,2.3936644983,
2.4790409875,-0.9038104716\H,1.883488373,0.8316400976,-1.3022120201\C,
5.1719732355,2.3117671096,-2.7095954873\C,2.0099020247,-0.2121252421,1
.2931607263\C,0.6971532737,1.6710260041,0.9802165881\C,0.6716230621,-0
.4948648429,1.5787767001\C,2.9587184467,-1.2051574053,1.4788601752\H,0
.2974371074,2.6574226768,0.7716760211\C,0.1986338731,-1.7219298822,2.0
123269417\C,2.4889496854,-2.4427355202,1.9141186279\H,4.0178507918,-1.
0462020116,1.3166282792\H,-1.0739041423,0.7801038567,1.4972130305\C,1.
1497964969,-2.7246892796,2.1765062713\H,-0.8505191997,-1.8974747859,2.
2213015337\H,0.8617695093,-3.7129222946,2.5132962951\N,-0.0661955605,0
.7001554058,1.3617808877\C,2.1069532641,1.2189786844,0.8284310452\H,2.
7590987405,1.8288956115,1.4692310305\O,3.0655528735,-4.6024937903,2.49
38055029\O,4.646026365,-3.2641732167,1.8969910746\N,3.4747518021,-3.51
84737688,2.1174747115\\Version=AM64L-G09RevB.01\HF=-1124.3029835\RMSD=
0.000e+00\RMSF=3.382e-06\Dipole=-8.1987097,1.8139528,4.0965895\Quadrup
ole=-8.077703,8.6023326,-0.5246296,13.7351298,18.2805409,25.0847249\PG
=C01 [X(C17H20N3O4)]\\@
Sum of electronic and thermal Free Energies= -1123.993526 Hartrees

Entry 6

Reactant association complex

1\1\GINC-SPARTAN-RC210\FOpt\RM062X\6-31+G(d)\C17H20N3O4(1+)\UWILLE\28-
Jan-2019\0\\#p M062X/6-31+G* scf=(qc,direct) scrf=(cpcm,solvent=dichlo
romethane) nosymm opt=(calcfc,z-matrix,maxcycle=500) freq=noraman\\geo
m&freq\\1,1\C,-0.7785296623,1.8060567807,0.7467600443\C,0.6496022012,1
.3664081053,1.0721040077\H,-1.1116226414,2.6416416462,1.3695696109\H,0
.7014221291,0.2842313122,1.2685044352\H,-1.5163557905,1.0041551726,0.8
297091272\C,-0.71336279,2.2569535651,-0.6832558\O,1.274816222,2.083304
6909,2.0979135381\C,0.8714317306,1.6566626254,3.3970532094\H,1.4237854
464,2.2707749649,4.1072311548\H,-0.2045884115,1.8069465084,3.542221104
3\H,1.1197837486,0.5996485041,3.5455063721\C,0.9476118769,2.411245858,
-2.5497168102\H,0.6594853115,1.5542732887,-3.1624394034\H,0.338106635,
3.2730091506,-2.8256010889\H,1.9975789762,2.6502033409,-2.6854266827\C
,2.8265375631,1.2324683405,-0.2344689839\O,-1.5617825504,2.6652049226,
-1.4171712882\N,0.6666317965,2.1010036865,-1.1447431427\H,3.1564846353
,0.8515803882,0.7251761901\C,3.4255480508,0.5325544756,-1.4759903147\H
,2.7768897483,0.4386559287,-2.3399511411\H,4.0129995529,-0.3468351924,
-1.2389056994\C,3.9236917453,1.8612130966,-1.0947407272\H,4.8734603828
,1.9328019493,-0.5761171498\H,3.6651512146,2.7305540637,-1.6848250155\
C,1.4431719226,1.617712071,-0.2078490143\C,1.7640720522,5.459080068,-1
.3319633018\C,2.285712519,4.6485778974,0.7031631831\C,0.5657944254,5.2
810260794,-0.5852122118\C,1.7003536909,5.9508969253,-2.6426777558\H,2.

7425633182,4.2648836974,1.6042360378\C,-0.6694002525,5.6001748572,-1.1
735845232\H,2.6126757215,6.0889929585,-3.2160271801\H,0.2719043924,4.6
353298803,1.4044922289\C,-0.7190699756,6.0807663751,-2.4741603024\H,-1
.6836920106,6.3117003245,-2.9114459996\N,0.9130322035,4.7803294928,0.6
364147194\C,2.8440337031,5.0477464339,-0.4788615015\H,3.8984891687,5.0
613564816,-0.717017513\C,0.4649131437,6.2558862976,-3.2030840831\H,0.4
069173139,6.6343024737,-4.2176866934\O,-2.9594708114,5.690333126,-0.95
66950867\O,-1.8021778325,4.9233116344,0.6944698012\N,-1.8983288136,5.3
987587522,-0.4369653547\\Version=AM64L-G09RevB.01\HF=-1124.2842838\RMS
D=0.000e+00\RMSF=9.140e-06\Dipole=3.9117487,-4.121153,0.2981814\Quadru
pole=-3.2090003,-4.8885016,8.097502,27.1694876,-8.3468405,-10.4338436\
PG=C01 [X(C17H20N3O4)]\\@
Sum of electronic and thermal Free Energies= -1123.974499 Hartrees

TS1

1\1\GINC-SPARTAN-RC079\FTS\RM062X\6-31+G(d)\C17H20N3O4(1+)\UWILLE\28-J
an-2019\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm scrf=(cpcm,solvent=
dichloromethane) opt=(ts,noeigentest,calcfc,maxcycle=500) freq=noraman
\\geom&freq\\1,1\C,-0.9240866881,1.7047677744,0.3043980376\C,0.2430327
42,2.2998111169,-0.2074307329\C,0.3972668429,3.6863835003,-0.185077004
9\C,-0.5911947138,4.4764448189,0.3873591047\C,-1.906441623,2.497667913
5,0.8998544894\C,0.496046822,0.0944575167,-0.4572378063\H,-0.459040966
5,5.5521061984,0.4067100962\H,-2.7945262287,2.043383066,1.3305315191\H
,1.0022632148,-0.8241144847,-0.7185335856\H,1.9785706485,1.4416597818,
-1.0857613842\N,1.0701585718,1.2797180432,-0.6612291576\C,-0.815300102
7,0.272295642,0.0417462326\H,-1.2972851165,-0.4902609978,0.6406466616\
C,-1.9812337311,-0.0217842793,-1.6588787513\C,-2.1061187539,-1.5549394
66,-1.6254226818\C,-3.2639958472,-1.8207099583,-0.6637873663\H,-2.4111
277077,-1.8270274859,-2.6508582344\H,-3.9109595338,-2.6504924028,-0.95
27386989\H,-2.9062525699,-2.0026447556,0.3568395748\C,-1.1620184794,0.
5096348455,-2.7743297603\C,-1.8001277711,1.125181199,-4.004209665\C,-0
.8920265587,1.9488493706,-3.1512683426\H,-0.3370172796,-0.1684314587,-
2.9783804209\H,-2.8632064822,1.3360244856,-3.9701511528\H,-1.437132224
8,0.76361248,-4.9596389003\H,0.1111900484,2.1495443944,-3.5136900056\H
,-1.3168087002,2.7544349117,-2.5645426726\C,-4.033144881,-0.5232572503
,-0.707863415\O,-5.153561359,-0.2920679655,-0.3233565268\O,-0.88935724
,-2.1579932393,-1.3166371566\C,-3.8023767414,1.7787185787,-1.541319198
8\H,-4.3807689725,2.0518406946,-0.6585609701\H,-3.0198500534,2.5142464
769,-1.6961415307\H,-4.4739046115,1.7515202286,-2.4033862865\C,-0.8993
403695,-3.5667625444,-1.5215510115\H,0.107008005,-3.9198843738,-1.2987
227907\H,-1.6144588393,-4.0537207975,-0.8489851467\H,-1.1529172477,-3.
8017812407,-2.5617702932\N,-3.2245571258,0.4529740708,-1.3223647593\C,
-1.7291709333,3.8789400844,0.9389333544\H,-2.4826449071,4.5079581286,1
.3999431437\O,2.4251517458,3.5568258388,-1.2422189282\O,1.6828016388,5
.5157066203,-0.7227051053\N,1.5845560808,4.3049829201,-0.7539387706\\V
ersion=AM64L-G09RevB.01\HF=-1124.2618794\RMSD=0.000e+00\RMSF=6.755e-06
\Dipole=-0.3004601,-2.7377066,-0.6144406\Quadrupole=-9.8256077,3.83456
25,5.9910451,-12.7770364,9.1345132,7.479089\PG=C01 [X(C17H20N3O4)]\\@

ν_{imag} = - 373.2278 cm^{-1}

Sum of electronic and thermal Free Energies= -1123.948137 Hartrees

Compound **13'**

1\1\GINC-SPARTAN-RC087\FOpt\RM062X\6-31+G(d)\C17H20N3O4(1+)\UWILLE\27-
Jan-2019\0\\#p M062X/6-31+G* scf=(qc,direct) scrf=(cpcm,solvent=dichlo
romethane) nosymm freq=noraman opt=(calcfc,maxcycle=500)\\geom&freq\\1
,1\C,-1.9142647462,2.0507653728,0.0761767852\C,-0.602091158,2.47522904
74,0.2814707841\C,-0.2776520427,3.8099419498,0.4977982962\C,-1.2922295
093,4.7555572845,0.5140552832\C,-2.9310605898,3.0022671323,0.103368070
3\C,-0.4321448196,0.2573924256,0.0329026419\H,-1.0455341879,5.79738943

11,0.6827191425\H,-3.9679324786,2.72858873,-0.039425292\H,0.0534600221
,-0.709883439,0.0020847838\H,1.2484867823,1.4027869751,0.391680493\N,0
.2394364628,1.3395572042,0.2429501222\C,-1.8905206842,0.5426038207,-0.
1169463382\H,-2.3841023029,0.0138967806,0.7138805153\C,-2.4519282112,-
0.0490685267,-1.4655020219\C,-1.8716366128,-1.4719081609,-1.7303210067
\C,-2.9615035416,-2.1468333114,-2.5562049728\H,-0.9047961794,-1.410466
6296,-2.2499479503\H,-2.8516550209,-1.9534320784,-3.6271789158\H,-3.00
584072,-3.2271533514,-2.4076458587\C,-2.0598481619,0.8752068306,-2.612
8040634\C,-2.7409254919,0.8378321845,-3.9536951385\C,-2.8920742512,2.0
403821007,-3.0680442728\H,-0.9826584606,1.0406229496,-2.653133929\H,-3
.6228983991,0.2142728515,-4.0654391968\H,-2.113483315,0.9053964173,-4.
8356246957\H,-2.3666655424,2.9547490604,-3.3230410064\H,-3.8675043146,
2.1897981261,-2.6186556781\C,-4.227308156,-1.494330836,-2.0394138731\O
,-5.3664718722,-1.9155018756,-2.163803883\O,-1.7212001617,-2.118087115
9,-0.4810138048\C,-4.8916204891,0.4204203801,-0.6728348835\H,-4.547286
4071,0.6500516974,0.339692127\H,-5.176739457,1.3422479211,-1.187080348
1\H,-5.7752834718,-0.2150866353,-0.5995697092\C,-0.9511021827,-3.31030
71053,-0.5428945499\H,-0.8907406399,-3.6973125873,0.4741915741\H,-1.41
98908026,-4.0615942222,-1.1872404481\H,0.0591712064,-3.0986214529,-0.9
182617742\N,-3.8857420196,-0.3347912758,-1.3948268425\C,-2.6100773697,
4.3428907368,0.3200390936\H,-3.4025314156,5.0828116634,0.3397531492\O,
1.9625895358,3.3438472645,0.6927183052\O,1.3330145723,5.3978727205,0.8
944128336\N,1.1069446048,4.2217205453,0.7118104531\\Version=AM64L-G09R
evB.01\HF=-1124.2713786\RMSD=0.000e+00\RMSF=5.105e-06\Dipole=1.9665552
,0.1623559,0.9233885\Quadrupole=-13.967621,13.0744287,0.8931923,-31.05
81478,-7.4953918,-2.0082974\PG=C01 [X(C17H20N3O4)]\\@
Sum of electronic and thermal Free Energies= -1123.957969 Hartrees

TS2

1\1\GINC-SPARTAN-RC039\FTS\RM062X\6-31+G(d)\C17H20N3O4(1+)\UWILLE\28-J
an-2019\0\\#p M062X/6-31+G* nosymm scf=(qc,direct) scrf=(cpcm,solvent=
dichloromethane) opt=(ts,noeigentest,calcfc,maxcycle=500) freq=noraman
\\geom&freq\\1,1\C,2.7063247788,0.2188755122,-5.0862820022\C,2.0139270
616,-0.0192393312,-3.7385533306\H,2.3954784315,1.1858399173,-5.5002275
09\H,1.847710848,-1.0984631963,-3.5870770509\H,2.5421444942,-0.5564970
749,-5.8352755355\C,4.1705275468,0.3032973358,-4.7271565583\O,0.820691
5141,0.6822863327,-3.5414909063\C,-0.2498801792,0.1664777736,-4.319908
3278\H,-1.1339981956,0.7491197873,-4.0623331457\H,-0.0447832865,0.2720
494392,-5.3921135867\H,-0.4233145774,-0.8910256261,-4.0848589949\C,5.5
709743015,0.534590179,-2.686209721\H,5.6412953818,-0.2251188189,-1.905
7218904\H,6.3211874728,0.340718782,-3.4524723728\H,5.7506026921,1.5289
674414,-2.2670480933\C,2.7047694484,0.7469628001,-1.4350834547\O,5.128
0634611,0.2652748316,-5.4627975885\N,4.2692326717,0.4565697779,-3.3334
665741\H,1.6521644607,0.6344707092,-1.2005021828\C,3.5732920496,1.3586
789898,-0.3620853829\H,4.6201687173,1.0679019933,-0.3592621261\H,3.124
0497067,1.2546060555,0.6238130645\C,3.268810818,2.6247624735,-1.042204
7215\H,3.8135395045,2.8986126677,-1.942226275\H,2.2785428799,3.0541785
174,-0.9318597252\C,3.0465340937,0.4363670731,-2.7199689015\C,3.748197
9731,5.409798089,-0.8458371905\C,5.3860325857,4.0277125221,-0.10073463
55\C,4.9075010112,5.5795304843,-1.634815462\C,2.6013746236,6.164459416
1,-1.1189427508\H,6.0120983855,3.3203392398,0.4269319137\C,4.907827321
,6.4973326294,-2.6929156077\H,1.7056746673,6.0381274371,-0.5177541165\
H,6.8024459213,4.642986677,-1.5499579501\C,3.771378697,7.2469293843,-2
.9535690467\H,3.7875789813,7.9569922159,-3.7725342728\N,5.8731792403,4
.7236236171,-1.1531222245\C,4.0487806188,4.3588313196,0.1062912694\H,3
.4779207082,4.1098863822,0.9909058196\C,2.6253754165,7.0795353647,-2.1
655739386\H,1.7463518722,7.6755178525,-2.3842809396\O,7.0715533289,5.9
836849252,-3.2354653517\O,6.0625124488,7.4735162714,-4.4266924338\N,6.
0925121035,6.6699038301,-3.5135431887\\Version=AM64L-G09RevB.01\HF=-11
24.2426994\RMSD=0.000e+00\RMSF=3.440e-06\Dipole=-2.3381955,-2.3776268,

3.7072851\Quadrupole=12.6473801,7.4780772,-20.1254573,12.3029047,18.55
55646,9.015027\PG=C01 [X(C17H20N3O4)]\\@
ν_{imag} = - 571.1816 cm^{-1}
Sum of electronic and thermal Free Energies= -1123.934301 Hartrees

Compound **14'**

1\1\GINC-SPARTAN-RC022\FOpt\RM062X\6-31+G(d)\C17H20N3O4(1+)\UWILLE\28-
Jan-2019\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm scrf=(cpcm,solvent
=dichloromethane) opt=(calcfc,maxcycle=500) freq=noraman\\geom&freq\\1
,1\C,2.4112462546,-0.7903121448,-5.0883947637\C,1.7890915506,-0.623487
1927,-3.696738808\H,2.0705786665,0.0142908011,-5.7522026993\H,1.664714
0039,-1.6130117778,-3.2277265591\H,2.2195346254,-1.7499738801,-5.57078
3238\C,3.8937090872,-0.6064316112,-4.8420539575\O,0.5646040078,0.06158
07361,-3.6696472487\C,-0.4951453839,-0.699154169,-4.2234507353\H,-1.40
37625651,-0.1064483802,-4.1127025035\H,-0.3248436747,-0.9027456765,-5.
2882505828\H,-0.6107659479,-1.6513937901,-3.6893480403\C,5.379297558,0
.2550234284,-3.0780096968\H,5.5158995786,-0.2047072152,-2.0963441682\H
,6.1062105776,-0.1596311509,-3.7766135118\H,5.5342083807,1.336643274,-
3.0079023075\C,2.5710073801,0.8697241772,-1.8243730799\O,4.8040675622,
-0.8746537026,-5.6079102831\N,4.0597261547,-0.0537826055,-3.5921481846
\H,1.5216473369,0.8577982138,-1.5377631811\C,3.4580086291,1.761447697,
-0.9956104686\H,4.498584326,1.4298093192,-1.0007609128\H,3.1218228239,
1.7168211353,0.0471728193\C,3.3585271419,3.2117285316,-1.4868342781\H,
3.7666190792,3.3063892861,-2.4995510964\H,2.3067063603,3.5123336781,-1
.5336641081\C,2.8431866115,0.1538325169,-2.9214627095\C,3.9436361593,5
.6639060654,-0.9769892237\C,5.5476749521,4.0570813364,-0.5080603892\C,
5.2232581659,6.181521628,-1.1487556155\C,2.8331406112,6.4648127492,-1.
2175945761\H,6.1136009328,3.1719353526,-0.2398195403\C,5.425491284,7.4
967599408,-1.5516330818\H,1.8283059566,6.0745569126,-1.0907637609\H,7.
1586047587,5.2945855228,-0.8982779751\C,4.3213135894,8.3040104647,-1.7
898851991\H,4.4758982692,9.3297286546,-2.1047257752\N,6.1484477872,5.1
520240587,-0.8471919215\C,4.0689704637,4.2251177597,-0.5507923262\H,3.
6844991092,4.07548066,0.4707859592\C,3.0352094389,7.7847860762,-1.6237
858646\H,2.1816584448,8.4250713744,-1.816340744\O,7.7056658692,7.26467
38868,-1.4887321392\O,6.8994074135,9.1778294758,-2.0797435588\N,6.7741
896693,8.0269465831,-1.7217789646\\Version=AM64L-G09RevB.01\HF=-1124.2
863172\RMSD=0.000e+00\RMSF=4.630e-06\Dipole=-0.6016792,1.7983115,3.971
3782\Quadrupole=18.0227242,35.7311337,-53.7538579,58.2621053,13.215849
2,-11.1155827\PG=C01 [X(C17H20N3O4)]\\@
Sum of electronic and thermal Free Energies= - 1123.974869 Hartrees

Entry 7

Reactant association complex

1\1\GINC-R101\FOpt\RM062X\6-31+G(d)\C18H23N2O3(1+)\ROOT\04-May-2016\0\
\# M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) freq=noraman scf=
(qc,direct) geom=checkpoint guess=check nosymm opt=(z-matrix,readfc,Ma
xcycle=500)\\freq&geom\\1,1\C,-0.4614297817,1.8330765458,1.223303289\C
,0.9607900263,1.2703209493,1.1883857548\H,-0.5119971957,2.7151021261,1
.8682445872\H,0.9370088329,0.166322351,1.1941878402\H,-1.2234692004,1.
1202911029,1.5435424237\C,-0.7219542476,2.2454654146,-0.1993141026\O,1
.8325278648,1.7420614195,2.168001313\C,1.5790408546,1.1704279491,3.447
229262\H,2.3229221066,1.5864091762,4.1255149694\H,0.5750113277,1.43241
43601,3.8012434985\H,1.6816706544,0.0796301838,3.4064341022\C,0.501704
2209,2.4154555039,-2.3728986179\H,0.0462726911,1.5690819854,-2.8924042
347\H,-0.1103204935,3.3069823071,-2.5140252719\H,1.5023895514,2.603016
5398,-2.7475043688\C,2.87057564,1.3585039401,-0.4896575471\O,-1.722402
3012,2.6050112549,-0.7426120556\N,0.5299415379,2.1134419925,-0.9386447
045\H,3.3988296308,0.9705257337,0.373249258\C,3.3069536652,0.790503421

5,-1.8538048812\H,2.5347547543,0.652925858,-2.6016874605\H,4.022160965
,-0.0200933277,-1.7740603415\C,3.7251389896,2.1510290829,-1.4806151706
\H,4.7412346168,2.3092638287,-1.1364822702\H,3.2675209879,3.0088797125
,-1.9588496432\C,1.4957134404,1.6480202097,-0.1851521504\C,1.706168326
6,5.2248568423,-1.0075465233\C,1.3932520328,4.7698640272,1.1813052431\
C,0.337237094,5.3894891752,-0.6993432542\C,2.1584168292,5.4626592296,-
2.3253234098\H,1.4784905615,4.5165862487,2.228988413\C,-0.6000858995,5
.7841560265,-1.6646050516\C,1.2280906855,5.8447524649,-3.2792102138\H,
3.2117686885,5.3591102953,-2.5632316235\H,-0.679407051,5.2388478066,1.
1636429523\C,-0.1424129722,6.0046131426,-2.9483468475\H,-1.6503643435,
5.9076780557,-1.417330521\H,-0.8236645659,6.3098937175,-3.7364698829\N
,0.1721792736,5.0913981214,0.6378984639\C,2.3591922563,4.822813872,0.2
070016138\H,3.4100221642,4.6066687115,0.345955956\C,2.8755824996,5.930
7973113,-4.9891106695\H,3.2063293849,4.8975848739,-4.8275354086\H,2.90
33598352,6.1621235833,-6.0532719606\H,3.5369755097,6.6163479064,-4.446
899152\O,1.5282383516,6.0988348454,-4.585496257\\Version=ES64L-G09RevD
.01\HF=-1034.3238635\RMSD=0.000e+00\RMSF=9.022e-06\Dipole=0.9223448,-3
.7964035,1.9997762\Quadrupole=4.0133768,-7.9202715,3.9068947,8.1381214
,-12.870022,2.0713402\PG=C01 [X(C18H23N2O3)]\\@
Sum of electronic and thermal Free Energies= -1033.984222 Hartrees

TS1

1\1\GINC-R103\FTS\RM062X\6-31+G(d)\C18H23N2O3(1+)\ROOT\06-May-2016\0\\
M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) freq=noraman scf=(
qc,direct) nosymm opt=(ts,noeigentest,z-matrix,calcfc,Maxcycle=500)\\f
req&geom\\1,1\C,-1.093097904,1.6601685513,0.2664822553\C,0.0274402162,
2.3536077625,-0.2325327986\C,0.0814976308,3.7402035904,-0.2770068954\C
,-1.016596484,4.4453610378,0.2105552732\C,-2.1324211817,3.7662566769,0
.7410207055\C,-2.1756331655,2.3709497541,0.7775682084\C,0.4796878099,0
.1642496755,-0.4229245029\H,0.9430821313,4.2663225986,-0.6764665245\H,
-0.9936071545,5.5280283708,0.1835810193\H,-3.0457763991,1.8739160763,1
.1980707001\H,1.0620216241,-0.7152237282,-0.6588568557\H,1.8597795451,
1.5962036994,-1.0541357093\N,0.9573940652,1.3931705457,-0.6393779348\C
,-0.8399369973,0.2447695432,0.0596004474\H,-1.3110004834,-0.563212774,
0.6019999346\C,-1.9962991918,-0.1353423539,-1.7932962932\C,-2.05968085
45,-1.6628880752,-1.6749571446\C,-3.2328634883,-1.9197157966,-0.727902
7304\H,-2.3307986932,-2.0010061654,-2.6912298258\H,-3.8537698118,-2.77
56874172,-0.9969082727\H,-2.8938353494,-2.0512577617,0.3062883424\C,-1
.1193748017,0.3919869977,-2.8532865267\C,-1.7019547466,0.9792717174,-4
.1310245483\C,-0.8639945909,1.8313157099,-3.2404689653\H,-0.2714124479
,-0.2721167878,-2.99606547\H,-2.7704535279,1.161277354,-4.1589085666\H
,-1.2778915882,0.6070553224,-5.0568389107\H,0.1551120909,2.0447457141,
-3.5458406951\H,-1.3300603247,2.6320199394,-2.6795434637\C,-4.03437001
16,-0.6466452845,-0.8393295341\O,-5.1632631851,-0.4243697852,-0.480295
8745\O,-0.8294970645,-2.2044048027,-1.3113528436\C,-3.85249127,1.62092
22745,-1.7920771583\H,-4.471886961,1.9085761723,-0.9428007473\H,-3.088
3299758,2.3759556346,-1.9434960576\H,-4.4866097396,1.5299079995,-2.677
9663147\C,-0.7849251364,-3.619542898,-1.4549155712\H,0.2275389436,-3.9
258736173,-1.1935453206\H,-1.4983709071,-4.1040537871,-0.7784193751\H,
-1.0038967529,-3.9097144203,-2.489290484\N,-3.2400484694,0.3251697049,
-1.4934210422\O,-3.2285901993,4.3985313855,1.2365405206\C,-3.231598626
9,5.8182206405,1.2657252675\H,-4.1814305281,6.1038697201,1.7157622942\
H,-2.4061499153,6.1984825246,1.8771383643\H,-3.1663321289,6.2328267614
,0.2540226269\\Version=ES64L-G09RevD.01\HF=-1034.3083472\RMSD=0.000e+0
0\RMSF=5.192e-06\Dipole=2.711177,-0.8670709,-2.083051\Quadrupole=-16.1
528596,20.1943173,-4.0414577,-0.8501285,7.6501541,0.3133887\PG=C01 [X(
C18H23N2O3)]\\@

ν_{imag} = -289.2445 cm^{-1}

Sum of electronic and thermal Free Energies= -1033.964627 Hartrees

Compound **13'**

1\1\GINC-R93\FOpt\RM062X\6-31+G(d)\C18H23N2O3(1+)\ROOT\04-May-2016\0\\
M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) freq=noraman scf=(
qc,direct) geom=checkpoint guess=check nosymm opt=(z-matrix,readfc,Max
cycle=500)\\freq&geom\\1,1\C,-0.7943903471,2.0337906146,-0.1105771447\
C,0.5972076526,2.1935100566,-0.1381002695\C,1.2433113195,3.4112758594,
-0.0429174566\C,0.4459371371,4.5457369441,0.0890275255\C,-0.9506924635
,4.4195692426,0.1313908623\C,-1.5767744172,3.1626855063,0.0368900721\C
,0.2832461102,-0.0270182528,-0.3034084053\H,2.3250147462,3.489284419,-
0.0645364433\H,0.9205394299,5.5159127455,0.1657752482\H,-2.6575967033,
3.1389237392,0.0788336041\H,0.5572693583,-1.0721475526,-0.361550793\H,
2.1787186875,0.7293485148,-0.2689101155\N,1.1739333424,0.9044207592,-0
.2536665402\C,-1.1011839998,0.5476034246,-0.2395239011\H,-1.5604633715
,0.1389629318,0.6729540664\C,-1.9548726923,0.0698778898,-1.4698642751\
C,-1.7327370196,-1.4477248479,-1.7475186695\C,-3.0447528542,-1.8840583
789,-2.3914825402\H,-0.8573464364,-1.6035336967,-2.3940851714\H,-3.044
8694985,-1.7410218124,-3.4758733589\H,-3.297937256,-2.9257387955,-2.18
61495608\C,-1.5418585144,0.8678617009,-2.7030933089\C,-2.3964393747,0.
958809807,-3.93831252\C,-2.1628545653,2.1777899724,-3.0935979213\H,-0.
4704081243,0.7960759766,-2.8933734811\H,-3.3967283083,0.5378441729,-3.
9037301138\H,-1.8996674538,0.8774013548,-4.8990053248\H,-1.496618337,2
.9536405853,-3.4562107397\H,-3.0076207474,2.5397792362,-2.5190030223\C
,-4.0600116005,-0.9625715735,-1.7465827765\O,-5.2700186283,-1.12905204
05,-1.7073198631\O,-1.5461310563,-2.0970331498,-0.5043078696\C,-4.1078
781371,1.0648221697,-0.3831011619\H,-3.5972856752,1.2103143567,0.57325
97138\H,-4.2376948523,2.0284247934,-0.8824511448\H,-5.0958411628,0.645
7181509,-0.1871832995\C,-1.0659731438,-3.4276823363,-0.6218741115\H,-0
.9295062843,-3.803154923,0.3923450578\H,-1.7783867925,-4.0706397339,-1
.1502876669\H,-0.1054331915,-3.4464430363,-1.1544386791\N,-3.395540643
6,0.1021975075,-1.2012125902\O,-1.7936269522,5.4641783806,0.2620126549
\C,-1.2429990577,6.7737812955,0.3488247888\H,-2.0947261827,7.446081495
3,0.4355594987\H,-0.6057746506,6.8688480136,1.2338255639\H,-0.67246700
94,7.0152214733,-0.5535830137\\Version=ES64L-G09RevD.01\HF=-1034.32662
81\RMSD=0.000e+00\RMSF=2.818e-06\Dipole=5.909792,0.4889391,0.7640694\Q
uadrupole=-25.4487999,31.4906951,-6.0418952,-3.2465585,-5.0523702,2.42
90763\PG=C01 [X(C18H23N2O3)]\\@

Sum of electronic and thermal Free Energies= -1033.980994 Hartrees

TS2

1\1\GINC-R98\FTS\RM062X\6-31+G(d)\C18H23N2O3(1+)\ROOT\04-May-2016\0\\#
M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) freq=noraman scf=(q
c,direct) nosymm opt=(ts,noeigentest,z-matrix,calcfc,Maxcycle=500)\\fr
eq&geom\\1,1\C,2.8456908001,-0.0137747573,-5.0190526486\C,2.1454169967
,-0.2350160158,-3.6723278924\H,2.5187024955,0.9368693204,-5.4575966025
\H,1.9991982329,-1.3136780068,-3.4972609271\H,2.7046875306,-0.80914063
78,-5.7515791743\C,4.3038804846,0.110429106,-4.6487705528\O,0.93792730
83,0.4477645013,-3.5012839497\C,-0.1142431022,-0.0998993335,-4.2832142
746\H,-1.01148008,0.470420494,-4.0442783837\H,0.1011513989,-0.00709601
39,-5.3545658362\H,-0.2707250615,-1.1566927823,-4.0334731852\C,5.67876
90986,0.4223341207,-2.5990719625\H,5.755489073,-0.3139963032,-1.797281
105\H,6.4399618307,0.222238187,-3.3527095672\H,5.8320283959,1.43149010
54,-2.2064257525\C,2.7986811316,0.6041370936,-1.3802051081\O,5.2701874
613,0.0757925097,-5.3720514603\N,4.3848611037,0.299428239,-3.256221528
6\H,1.7497547473,0.4614184907,-1.146973661\C,3.6465723777,1.263853191,
-0.3179602804\H,4.7035745785,1.0150621861,-0.3052234871\H,3.1940416098
,1.1795284367,0.6677060666\C,3.2782064297,2.468213878,-1.0663901155\H,
3.8243378423,2.7462230066,-1.9634829847\H,2.2857088756,2.8888852206,-0
.9488772907\C,3.1593491834,0.2643576635,-2.6558384744\C,3.5427940268,5
.3017959674,-0.9305080444\C,5.3719530431,4.0998275305,-0.3225413497\C,
4.5851084199,5.5390868134,-1.8533099526\C,2.3085358656,5.9351002739,-1

.1018335497\H,6.1066308588,3.4673131599,0.1583315929\C,4.4281257909,6.
3972954521,-2.9393367034\C,2.1477991313,6.8000995308,-2.1806881698\H,1
.4833406338,5.7773757199,-0.4136413654\H,6.5760269644,4.749854932,-1.9
148664021\C,3.2006884895,7.0293853814,-3.0945825543\H,3.064728976,7.70
43671838,-3.9310948248\N,5.6796908973,4.783966518,-1.4453272971\C,4.03
98061495,4.3283001698,0.0193233754\H,3.5811770787,4.0431439654,0.95694
45688\H,5.2324990434,6.5745697856,-3.6462827052\O,0.9268071278,7.39460
64267,-2.2851571088\C,0.7079278771,8.2953234181,-3.3591357568\H,-0.314
8475592,8.6522861128,-3.2448049649\H,1.3990705348,9.1438243884,-3.3081
8084\H,0.8132989073,7.7899973705,-4.3255228097\\Version=ES64L-G09RevD.
01\HF=-1034.286173\RMSD=0.000e+00\RMSF=6.570e-06\Dipole=0.9834641,-1.7
071028,1.2341383\Quadrupole=24.4502359,-1.4240003,-23.0262356,39.19253
99,-11.031616,-21.8767256\PG=C01 [X(C18H23N2O3)]\\@

ν_{imag} = -575.9237cm^{-1}

Sum of electronic and thermal Free Energies= -1033.948355 Hartrees

Compound **14'**

1\1\GINC-R102\FOpt\RM062X\6-31+G(d)\C18H23N2O3(1+)\ROOT\07-May-2016\0\
\# M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) freq=noraman scf=
(qc,direct) nosymm opt=(z-matrix,calcfc,Maxcycle=500)\\freq&geom\\1,1\
C,2.4219828728,-0.6961103295,-5.1340946904\C,1.8003481543,-0.562444856
1,-3.7388205008\H,2.0834829679,0.1257046941,-5.7776119739\H,1.67347628
52,-1.5631194485,-3.2947976905\H,2.227701272,-1.6429830259,-5.64022182
19\C,3.9049100952,-0.5216990894,-4.8832601556\O,0.5769782396,0.1239226
085,-3.6948598967\C,-0.4844813432,-0.6225039428,-4.264245729\H,-1.3928
488997,-0.0330350005,-4.1352013134\H,-0.3178964407,-0.7990633599,-5.33
45407616\H,-0.598381374,-1.5881156672,-3.7542387971\C,5.3924880117,0.2
959648002,-3.1011306759\H,5.5310856884,-0.1877107541,-2.1313200027\H,6
.1186745734,-0.1004823495,-3.810958433\H,5.5457293211,1.3756638509,-3.
0035717679\C,2.5860653479,0.8784305354,-1.8272282383\O,4.8142917897,-0
.7728397128,-5.656659591\N,4.0723645884,-0.0008053719,-3.6207719682\H,
1.5361277756,0.8614290612,-1.5424109797\C,3.4746226187,1.7404558221,-0
.9692456798\H,4.5158957133,1.4116525558,-0.9926202843\H,3.144546782,1.
652887556,0.072974344\C,3.3716730054,3.2105359536,-1.3973313396\H,3.76
10016092,3.3429139031,-2.4136758775\H,2.3198898327,3.5156588052,-1.414
9801768\C,2.8559912418,0.1925027636,-2.9436620432\C,3.971196772,5.6373
72454,-0.8071352521\C,5.5891706197,4.0071625501,-0.4520601181\C,5.2499
05831,6.1646390512,-1.008034403\C,2.8642841178,6.4417362746,-0.9799041
264\H,6.159319676,3.1113107545,-0.2344908453\H,1.8508405891,6.07952103
56,-0.8378506934\H,7.1873327879,5.2187942566,-0.8480885242\C,4.3657930
346,8.2944080635,-1.5403876021\H,4.5151932717,9.3286428274,-1.82420397
07\N,6.1758058976,5.1131294521,-0.7740312678\C,4.1047010529,4.18081253
75,-0.4388436382\H,3.7506073062,3.9890214239,0.5858027277\C,3.07022449
55,7.7836643732,-1.348991206\C,5.4834159595,7.4781514023,-1.3707521926
\H,6.4847066699,7.8681846454,-1.5193747705\O,1.9481819917,8.5173931988
,-1.4976958113\C,2.0750685488,9.8855168366,-1.8679276126\H,2.561010322
9,9.9806736095,-2.8442134439\H,1.0584382105,10.2704564925,-1.925208436
4\H,2.6381411152,10.441527757,-1.1115537724\\Version=ES64L-G09RevD.01\
HF=-1034.3405838\RMSD=0.000e+00\RMSF=4.307e-06\Dipole=2.8386965,3.5292
443,3.6369737\Quadrupole=33.9653266,52.2413787,-86.2067052,103.7268816
,4.2263858,-21.2453995\PG=C01 [X(C18H23N2O3)]\\@

Sum of electronic and thermal Free Energies= -1033.998219 Hartrees

Entry 8

Reactant association complex

See entry 7.

***TS2* (formation of *E*-alkene)**

1\1\GINC-SPARTAN-RC071\FTS\RM062X\6-31+G(d)\C18H23N2O3(1+)\UWILLE\10-J
un-2019\0\\#p M062X/6-31+G* nosymm scrf=(cpcm,solvent=dichloromethane)
scf=(qc,direct) freq=noraman opt=(ts,noeigentest,calcfc,maxcycle=500)
\\geom&freq\\1,1\C,1.6348881565,2.1687622587,-1.6985340059\C,1.2535609
792,3.476849394,-2.4079217368\H,2.2589438271,2.3751538561,-0.822772745
7\H,2.1551634486,1.4488469892,-2.3332834176\C,0.3253582069,1.579868213
,-1.2274352703\C,-2.0866998105,2.2391103273,-1.2044896827\H,-2.6932193
016,2.2521846539,-2.1138777286\H,-2.1439407978,1.2573744289,-0.7360794
223\H,-2.445912648,3.0012000453,-0.5081340731\C,-1.0512314212,4.639696
6706,-2.5657113699\O,0.1371310961,0.5230973569,-0.6725358208\N,-0.6949
115119,2.4865499629,-1.5395662189\H,-2.1079300022,4.6206750441,-2.3243
094304\C,-0.5276813046,5.8415940376,-3.3193733474\H,0.5254624498,6.049
630152,-3.1450371646\H,-1.163250575,6.7164600332,-3.1976745326\C,-0.82
60811504,5.0103278203,-4.4850456556\H,-0.117620787,4.2576329689,-4.815
6646389\H,-1.8551665432,4.8870997009,-4.806680316\C,-0.2501661254,3.59
61781541,-2.1899399788\C,-0.6102750474,4.9785632736,-7.3125253222\C,0.
8562201681,6.3018073123,-6.1900302881\C,0.6926061692,4.4487307755,-7.4
437818998\C,-1.6870334752,4.3243416214,-7.9177693352\H,1.3576963352,7.
0691607912,-5.6154951371\C,0.9486177833,3.2859984261,-8.1665295917\C,-
1.4367244856,3.1659067291,-8.6491940609\H,-2.7031361319,4.6993839856,-
7.8392920449\H,2.5539561499,5.1581046764,-6.6555591444\C,-0.1277737016
,2.6487479218,-8.7714926134\H,1.9523925716,2.8834216928,-8.2609376832\
H,0.0561928863,1.7454523281,-9.3402777178\N,1.553368894,5.2853796433,-
6.7402864625\C,-0.5024221847,6.1389867788,-6.4527627422\H,-1.265991463
3,6.881505668,-6.2627290229\O,1.8746028608,4.6181706072,-1.8726983828\
C,3.2294097436,4.7420575882,-2.2815867607\H,3.2919867094,4.8394886315,
-3.3735466001\H,3.6186845405,5.6437983332,-1.8093849191\H,3.8230680702
,3.8777280753,-1.9601778063\H,1.463440985,3.4081844681,-3.4869996677\O
,-2.5254959465,2.5822323314,-9.2231309702\C,-2.3270682969,1.4168624496
,-10.0072215213\H,-3.3129397533,1.1330760321,-10.3735307443\H,-1.66617
25589,1.6222594922,-10.8565676857\H,-1.912910747,0.6012953392,-9.40418
63283\\Version=AM64L-G09RevB.01\HF=-1034.2899523\RMSD=0.000e+00\RMSF=4
.408e-06\Dipole=1.350544,1.9282269,0.0896417\Quadrupole=-42.3581634,16
.5565257,25.8016377,12.0287215,-16.5375071,-65.6006001\PG=C01 [X(C18H2
3N2O3)]\\@

ν_{imag} = -573.3500 cm^{-1}

Sum of electronic and thermal Free Energies= -1033.953103 Hartrees

Compound **14' (*E*-alkene)**

1\1\GINC-SPARTAN-RC094\FOpt\RM062X\6-31+G(d)\C18H23N2O3(1+)\UWILLE\09-
Jun-2019\0\\#p M062X/6-31+G* nosymm scf=(qc,direct) freq=noraman scrf=
(cpcm,solvent=dichloromethane) opt=(calcfc,maxcycle=500)\\geom&freq\\1
,1\C,6.4283491247,4.3226844423,-2.8097626727\C,5.8437671258,3.31426816
49,-1.8089109714\H,7.4786229698,4.5476731764,-2.6076213036\H,5.1132403
591,3.7828317704,-1.1352222091\H,5.8765223736,5.26712816,-2.831556772\
C,6.296419365,3.6575160603,-4.1664868058\O,6.8405054377,2.6659149353,-
1.0401418522\C,7.3278426961,3.4761309179,0.0147500283\H,8.0905901746,2
.896220469,0.5353468785\H,7.776301164,4.4044484971,-0.3609816305\H,6.5
178239873,3.728390835,0.712793074\C,5.1876500782,1.6525433093,-5.11258
00569\H,4.0981655022,1.6342130263,-5.2201694343\H,5.6380282293,2.05306
60959,-6.0205668276\H,5.5485664042,0.6342731185,-4.9382668071\C,4.3896
209376,1.2659142446,-2.2828584499\O,6.736300696,4.0696200157,-5.228201
7446\N,5.5676167857,2.5077458344,-4.0101917699\H,3.9902563225,0.566282
158,-3.0147331924\C,3.9833492603,1.0594389813,-0.8502102772\H,4.614551
885,1.651847519,-0.1781919405\H,4.1304771227,0.0066303281,-0.585278057
\C,2.5110881825,1.4365722418,-0.6468253088\H,2.362679698,2.4791884065,
-0.9488444575\H,1.8713479715,0.8130939231,-1.2822422648\C,5.1791205913
,2.2667578969,-2.6869474434\C,1.9508489636,-0.1211081257,1.3551075657\
C,0.6334145091,1.7492614511,0.9369811056\C,0.6047791189,-0.3922006233,
1.6279795076\C,2.8968563403,-1.09760668,1.5968670581\H,0.2336524313,2.

7225551076,0.6752117697\C,0.148545732,-1.6040641656,2.1098857245\C,2.4
625218399,-2.3440383124,2.0863040287\H,3.9586457992,-0.9389801693,1.44
08748212\H,-1.1392235898,0.8726023599,1.458347107\C,1.1031528757,-2.59
56859222,2.3341667124\H,-0.9013804427,-1.7849880097,2.3148307528\H,0.7
776641907,-3.5567569455,2.7120878314\N,-0.1293866484,0.7905998234,1.34
65877716\C,2.0503229699,1.2929874355,0.8310512538\H,2.6890559143,1.929
9326554,1.4587457421\O,3.4407723226,-3.2489405162,2.2957455762\C,3.083
5039567,-4.5267802075,2.8096116921\H,2.4110233085,-5.0481791837,2.1208
737004\H,4.017162866,-5.0792523224,2.9000621513\H,2.6134953577,-4.4308
694071,3.7935525159\\Version=AM64L-G09RevB.01\HF=-1034.3450435\RMSD=0.
000e+00\RMSF=3.337e-06\Dipole=-6.8252805,-0.9426727,4.7653811\Quadrupo
le=-10.2236422,21.2772737,-11.0536314,-4.7882123,25.1702533,9.498388\P
G=C01 [X(C18H23N2O3)]\\@
Sum of electronic and thermal Free Energies= -1034.004256 Hartrees

Entry 9

Reactant association complex

1\1\GINC-SPARTAN-RC031\FOpt\RM062X\6-31+G(d)\C18H23N2O3(1+)\UWILLE\30-
Jan-2019\0\\#p M062X/6-31+G* scf=(qc,direct) scrf=(cpcm,solvent=dichlo
romethane) nosymm freq=noraman opt=(calcfc,maxcycle=500)\\geom&freq\\1
,1\C,-0.4489168659,1.7458038826,1.1408431654\C,0.9896221246,1.22656182
36,1.1942733664\H,-0.5539968851,2.6503171945,1.7469494572\H,0.99875085
41,0.1233670421,1.2376824755\H,-1.2049736397,1.0230800437,1.452705497\
C,-0.6520616825,2.0994223965,-0.3065387417\O,1.7970860811,1.7586495922
,2.1976803423\C,1.4963734174,1.225142224,3.4829861992\H,2.200575466,1.
6786768368,4.1793614096\H,0.4723584542,1.4779900902,3.7820383124\H,1.6
216522846,0.1358882037,3.484395082\C,0.6727887309,2.2362440116,-2.4216
823434\H,0.2806933523,1.3536405417,-2.9324682636\H,0.0329868349,3.0952
179391,-2.6267066617\H,1.6822590284,2.4551025018,-2.75146213\C,2.97806
59349,1.3270518503,-0.3898979442\O,-1.6339640196,2.4064551745,-0.91184
72413\N,0.6397227139,1.9844758468,-0.9782987066\H,3.4754855659,0.98178
92531,0.5087337934\C,3.5034008686,0.7417736319,-1.7147822303\H,2.77518
77959,0.5549043575,-2.49545488\H,4.24347342,-0.0383247153,-1.578647065
\C,3.8522501239,2.1261559899,-1.3591614247\H,4.8434571476,2.330298115,
-0.9695710593\H,3.3887696028,2.9550177854,-1.8811422118\C,1.5805542162
,1.5761311907,-0.1632968038\C,1.6702025381,5.1426772336,-1.1021478986\
C,1.3858755236,4.7585843396,1.1085115164\C,0.300408946,5.247266678,-0.
7846224425\C,2.077881347,5.3568269502,-2.4388750463\H,1.4854610571,4.5
505986465,2.1646753916\C,-0.6838808117,5.555761634,-1.7400528331\H,3.1
266164697,5.3036188938,-2.7182444031\H,-0.7157974759,5.1236788121,1.07
07856388\C,-0.2649849262,5.7504408252,-3.0474676273\H,-0.9805045234,5.
9872312939,-3.8267952556\N,0.1471518464,4.9980116013,0.5580227508\C,2.
3436647996,4.8222075495,0.1278132696\H,3.4045616972,4.665864791,0.2704
986429\O,-1.9540880924,5.6327258329,-1.2728215747\C,-2.9819018444,5.86
8754501 1,-2.2251366253\H,-3.9161580539,5.8670385217,-1.6656853527\H,-2
.8440378879,6.8396776544,-2.7123968562\H,-2.9981454982,5.0733639914,-2
.9784125709\C,1.1101687404,5.6517549796,-3.3797369082\H,1.3991232236,5
.8207434658,-4.4129062087\\Version=AM64L-G09RevB.01\HF=-1034.3253296\R
MSD=0.000e+00\RMSF=5.747e-06\Dipole=0.9204342,-3.4994622,1.0535937\Qua
drupole=2.0092728,-6.6248926,4.6156198,-3.0737529,-2.484437,-4.7987993
\PG=C01 [X(C18H23N2O3)]\\@
Sum of electronic and thermal Free Energies= -1033.985058 Hartrees

TS1

1\1\GINC-SPARTAN-RC008\FTS\RM062X\6-31+G(d)\C18H23N2O3(1+)\UWILLE\30-J
an-2019\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm scrf=(cpcm,solvent=
dichloromethane) opt=(ts,noeigentest,calcfc,maxcycle=500) freq=noraman
\\geom&freq\\1,1\C,-0.9575749212,1.6615255852,0.3468843394\C,0.0640335

8,2.4120071109,-0.2474168529\C,0.0954930036,3.8105581318,-0.2201749009
\C,-0.9302349158,4.4463910477,0.4781830525\C,-1.9310364919,3.694300704
4,1.1245406409\C,-1.9693737718,2.3076169923,1.0687265421\C,0.572429501
7,0.2681644036,-0.6175151258\H,-0.9563390101,5.5277583031,0.5472868428
\H,-2.698446211,4.2294493698,1.6753148329\H,-2.7568966874,1.7458846109
,1.5623697258\H,1.1530934392,-0.5757250955,-0.9648864427\H,1.813904607
8,1.7989781764,-1.3170243391\N,0.977098874,1.5233656571,-0.8141954567\
C,-0.6952443365,0.2717374082,0.0031186001\H,-1.0649538985,-0.581413227
9,0.5552704803\C,-1.9306934715,-0.0196079115,-1.7403622818\C,-2.128421
795,-1.5324970211,-1.6025467144\C,-3.2722977106,-1.6649986015,-0.59636
31159\H,-2.4764058576,-1.8589154181,-2.5980155673\H,-3.9798012251,-2.4
663940977,-0.814701765\H,-2.8971699739,-1.8051814454,0.4241088717\C,-1
.1012159158,0.4092911774,-2.8869015794\C,-1.7599269826,0.8142085524,-4
.1941731908\C,-0.9203858756,1.7993010728,-3.4469447359\H,-0.2452885735
,-0.2489058966,-3.0021665462\H,-2.8360101386,0.9483847692,-4.200209496
5\H,-1.3545724701,0.3523296397,-5.0875054157\H,0.0715748238,2.01714645
99,-3.8286034371\H,-1.4102362832,2.6400393601,-2.9732348348\C,-3.96434
89995,-0.3245962199,-0.6920667177\O,-5.0468074274,-0.0059089611,-0.265
5025847\O,-0.9301607914,-2.1725149487,-1.2884072325\C,-3.5531698294,1.
9328317795,-1.6547373884\H,-4.3939811427,2.1308587947,-0.9902556521\H,
-2.7482613597,2.6280499704,-1.4227987823\H,-3.8797196527,2.0546385984,
-2.6899022335\C,-1.0109320096,-3.5870497262,-1.4175876252\H,-0.0194921
206,-3.9776436603,-1.1901873201\H,-1.7378599395,-4.0028371461,-0.71051
93826\H,-1.2924304459,-3.8651508196,-2.4401791529\N,-3.1241208882,0.55
70164646,-1.40687095\O,1.1244848945,4.4030172986,-0.8633781809\C,1.189
1093059,5.8253854323,-0.8252910014\H,1.2845224257,6.1780220153,0.20652
65097\H,2.076288516,6.0981775048,-1.3937939613\H,0.3001961517,6.263047
8057,-1.2904824736\\Version=AM64L-G09RevB.01\HF=-1034.3095694\RMSD=0.0
00e+00\RMSF=5.930e-06\Dipole=1.8282388,-0.6839642,-1.6002486\Quadrupol
e=-17.4715277,21.6018694,-4.1303417,5.0566454,5.7001138,-1.5529625\PG=
C01 [X(C18H23N2O3)]\\@

ν_{imag} = - 320.9239 cm^{-1}

Sum of electronic and thermal Free Energies= -1033.965825 Hartrees

Compound **13'**

1\1\GINC-SPARTAN-RC040\FOpt\RM062X\6-31+G(d)\C18H23N2O3(1+)\UWILLE\30-
Jan-2019\0\\#p M062X/6-31+G* scf=(qc,direct) scrf=(cpcm,solvent=dichlo
romethane) nosymm freq=noraman opt=(calcfc,maxcycle=500)\\geom&freq\\1
,1\C,-0.8735964421,2.0593410566,-0.0573957489\C,0.5080021412,2.2275726
181,-0.0327653936\C,1.1693200402,3.4472811112,0.098212997\C,0.35677037
53,4.5760137539,0.2128500489\C,-1.6694118207,3.1941992741,0.0705488492
\C,0.2456327336,0.0128103523,-0.227321538\H,0.7930301361,5.5624235001,
0.3180584781\H,-2.7496966227,3.1503343025,0.0690108299\H,0.5371876943,
-1.0276110175,-0.2836159724\H,2.1294101039,0.8179262109,-0.1159541481\
N,1.1187782305,0.9582796782,-0.1373337952\C,-1.1474425839,0.5675932832
,-0.2069931241\H,-1.6278039826,0.1452634138,0.6890551839\C,-1.95695597
29,0.0831890867,-1.4646343639\C,-1.7015499588,-1.4284594825,-1.7460525
232\C,-2.9884713494,-1.8824713476,-2.4277220358\H,-0.8060550566,-1.564
351565,-2.3693442482\H,-2.9624316776,-1.7333387137,-3.5109590614\H,-3.
2292737673,-2.9293807901,-2.2343257876\C,-1.5223227409,0.8977949502,-2
.6793000481\C,-2.3424117853,0.9829033244,-3.9379881786\C,-2.1576553224
,2.1986215179,-3.0764473428\H,-0.4445957937,0.848139953,-2.838290726\H
,-3.3345067473,0.5416446714,-3.9365479214\H,-1.8158807648,0.9207211624
,-4.8841403745\H,-1.4975552466,2.9912780482,-3.4128676721\H,-3.0250255
825,2.5378854463,-2.5222067481\C,-4.036045367,-0.9820550407,-1.8047218
835\O,-5.243580276,-1.1691104444,-1.7983241528\O,-1.5387789973,-2.0840
613103,-0.5027142664\C,-4.1537455546,1.0371209128,-0.4324929087\H,-3.6
687503759,1.1888696521,0.5361013862\H,-4.2880572784,1.9999170373,-0.93
19494449\H,-5.1384978803,0.5999192962,-0.2619301844\C,-1.0251833899,-3
.4026358446,-0.616781856\H,-0.9235178121,-3.7891365477,0.3972879296\H,

-1.7001999783,-4.0528200661,-1.1839301056\H,-0.0428633704,-3.393521438
1,-1.1084954818\N,-3.4044217288,0.0903773003,-1.236063261\C,-1.0346369
478,4.4313729787,0.2008049259\H,-1.6446885801,5.3241158859,0.296501302
1\O,2.5135719625,3.4060812378,0.1058958772\C,3.2110492406,4.6434286069
,0.2491610051\H,4.2686848799,4.388305712,0.2347172349\H,2.9760388803,5
.3114840805,-0.5845087302\H,2.9540743364,5.1181391921,1.2006879791\\Ve
rsion=AM64L-G09RevB.01\HF=-1034.3258122\RMSD=0.000e+00\RMSF=1.726e-06\
Dipole=5.0108298,0.9858277,1.0030662\Quadrupole=-20.1065263,26.8801895
,-6.7736632,0.2069546,-4.5881511,2.6666114\PG=C01 [X(C18H23N2O3)]\\@
Sum of electronic and thermal Free Energies= -1033.979610 Hartrees

TS2

1\1\GINC-SPARTAN-RC013\FTS\RM062X\6-31+G(d)\C18H23N2O3(1+)\UWILLE\31-J
an-2019\0\\#p M062X/6-31+G* nosymm scf=(qc,direct) scrf=(cpcm,solvent=
dichloromethane) opt=(ts,noeigentest,calcfc,maxcycle=500) freq=noraman
\\geom&freq\\1,1\C,2.706792,0.267224,-5.079892\C,2.023164,0.005219,-3.
732176\H,2.384715,1.236262,-5.480044\H,1.863826,-1.077064,-3.595342\H,
2.546335,-0.500333,-5.837705\C,4.171715,0.360794,-4.727087\O,0.82807,0
.697732,-3.517372\C,-0.245815,0.186507,-4.294337\H,-1.129986,0.763688,
-4.025031\H,-0.047977,0.304094,-5.366638\H,-0.414268,-0.873921,-4.0691
54\C,5.581586,0.573914,-2.688806\H,5.66646,-0.200469,-1.924519\H,6.329
099,0.405076,-3.463462\H,5.749376,1.56198,-2.250624\C,2.720561,0.73898
1,-1.419138\O,5.126089,0.344466,-5.467008\N,4.276447,0.491653,-3.33016
\H,1.670847,0.61116,-1.18052\C,3.594206,1.330016,-0.337757\H,4.642644,
1.04663,-0.344359\H,3.146665,1.215162,0.647231\C,3.263779,2.582578,-1.
023107\H,3.810089,2.880414,-1.913997\H,2.282634,3.023453,-0.884783\C,3
.058855,0.449813,-2.71219\C,3.695573,5.38189,-0.829357\C,5.411958,4.04
2654,-0.163142\C,4.790516,5.54852,-1.692057\C,2.516699,6.114804,-1.062
137\H,6.080426,3.354463,0.337101\C,4.773352,6.425591,-2.788148\C,2.498
789,6.984638,-2.13837\H,1.653596,6.007414,-0.412517\H,6.719941,4.64088
4,-1.704158\C,3.607904,7.147601,-3.000442\H,1.606526,7.570038,-2.33902
1\H,3.535573,7.844345,-3.827661\N,5.812847,4.721267,-1.260901\C,4.0850
62,4.363586,0.124671\H,3.566142,4.097048,1.035956\O,5.906794,6.47546,-
3.527186\C,5.924034,7.369935,-4.633374\H,5.777063,8.401422,-4.296778\H
,6.908051,7.265138,-5.087231\H,5.149792,7.10081,-5.359365\\Version=AM6
4L-G09RevB.01\HF=-1034.2881217\RMSD=0.000e+00\RMSF=4.070e-06\Dipole=-0
.2162208,-1.5241471,1.6290168\Polar=0.,0.,0.,0.,0.,0.\Quadrupole=22.33
44064,-0.4079392,-21.9264672,41.9157685,-13.1204475,-21.2973137\PG=C01
[X(C18H23N2O3)]\\@

ν_{imag} = - 571.3501 cm^{-1}

Sum of electronic and thermal Free Energies= -1033.949316 Hartrees

Compound **14'**

1\1\GINC-SPARTAN-RC016\FOpt\RM062X\6-31+G(d)\C18H23N2O3(1+)\UWILLE\30-
Jan-2019\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm scrf=(cpcm,solvent
=dichloromethane) opt=(calcfc,maxcycle=500) freq=noraman\\geom&freq\\1
,1\C,2.4662960112,-0.6362135304,-5.1665915719\C,1.8339539335,-0.534844
3579,-3.7735013598\H,2.1231710183,0.1933983823,-5.7975144966\H,1.71168
62105,-1.5447749546,-3.3496609878\H,2.2854980541,-1.5757491923,-5.6910
991477\C,3.9455732516,-0.4501325687,-4.9031148337\O,0.6047761001,0.141
0938008,-3.725389386\C,-0.4465447837,-0.6028329694,-4.3164470183\H,-1.
3604110377,-0.0228737472,-4.1833861357\H,-0.2707810046,-0.7583574952,-
5.388537952\H,-0.55675479,-1.5784378454,-3.8251308843\C,5.4124701123,0
.3514352433,-3.0960309323\H,5.5531432215,-0.1540000403,-2.1375986715\H
,6.1481403795,-0.0167727496,-3.8113231298\H,5.5486866006,1.4304962492,
-2.970323948\C,2.5940800392,0.8693349895,-1.8249454106\O,4.8622000285,
-0.6765525195,-5.6755404446\N,4.099466539,0.0487927423,-3.6300616831\H
,1.5429292341,0.8341869483,-1.5463266037\C,3.4674498026,1.7238896715,-
0.94404164\H,4.5128901375,1.4083642035,-0.9673786105\H,3.1318306853,1.

612357747,0.0940438968\C,3.3473936361,3.1998689867,-1.3458498615\H,3.7
422602506,3.3565977607,-2.3564851477\H,2.2917646044,3.4908225544,-1.36
61371748\C,2.8774680124,0.2131219251,-2.9559067891\C,3.8927895436,5.62
49330887,-0.7139181734\C,5.5451722824,4.0193134449,-0.37418229\C,5.158
2577396,6.1649237797,-0.9057768129\C,2.7730925416,6.4282855854,-0.8863
707143\H,6.1320578345,3.1326207602,-0.1633773\H,1.7687335446,6.0426574
119,-0.7472662057\H,7.1174902671,5.2837359302,-0.7575135849\C,4.271794
3003,8.2938847905,-1.4323219209\H,4.3780563986,9.3356807206,-1.7115254
717\N,6.110131151,5.140804198,-0.6836231743\C,4.0582174806,4.166308355
6,-0.3647615979\H,3.7017273406,3.9487546293,0.6540248975\C,5.402042532
8,7.4898771468,-1.2640115969\C,2.9896766811,7.760573808,-1.2446527309\
H,2.1367086705,8.4169364253,-1.3859302122\O,6.6881985823,7.855931827,-
1.4107885642\C,6.948775698,9.2030670125,-1.8036198373\H,8.0314767572,9
.2849738977,-1.875226127\H,6.4931689967,9.410518773,-2.7763624057\H,6.
5703594098,9.9009841805,-1.0510782531\\Version=AM64L-G09RevB.01\HF=-10
34.3396066\RMSD=0.000e+00\RMSF=3.084e-06\Dipole=1.7907065,3.6197183,3.
6888465\Quadrupole=32.6604467,52.7298193,-85.390266,107.6063746,4.4372
987,-19.3387955\PG=C01 [X(C18H23N2O3)]\\@
Sum of electronic and thermal Free Energies= - 033.997699 Hartrees

Entry 10

Reactant association complex

1\1\GINC-R105\FOpt\RM062X\6-31+G(d)\C17H24N1O4(1+)\ROOT\05-May-2016\0\
\# M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) freq=noraman scf=
(qc,direct) geom=checkpoint guess=check nosymm opt=(z-matrix,readfc,Ma
xcycle=500)\\freq&geom\\1,1\C,-0.6689451858,2.109374174,0.6584989075\C
,0.8034334381,1.7136633544,0.7923250447\H,-0.8495562229,3.1083452676,1
.0678325193\H,0.8891131837,0.6484442687,1.0703259\H,-1.3689688564,1.41
02131737,1.1199758101\C,-0.9050987731,2.1479123582,-0.8244204463\O,1.5
815499618,2.4998531015,1.6393708128\C,1.3220946008,2.2455815379,3.0163
200485\H,1.9897786464,2.8945435748,3.5816652151\H,0.2820935532,2.48321
38224,3.2690212962\H,1.5292970105,1.1965760832,3.2583161249\C,0.436410
353,1.9518340934,-2.953323729\H,-0.5908940178,1.8556498473,-3.30329204
63\H,0.8544397212,2.8937274128,-3.3095406021\H,1.0210507501,1.10538743
99,-3.3092480115\C,2.7655791235,1.5953326287,-0.8277375591\O,-1.909088
2558,2.295123036,-1.4515579736\N,0.3861589878,1.9527276316,-1.48783554
2\H,3.3234893775,1.6968981499,0.0963053508\C,3.2474604953,0.4503597206
,-1.7503315616\H,2.4889533056,-0.103233253,-2.2919363289\H,4.03267966,
-0.1546946616,-1.3122962173\C,3.5267329076,1.8502448378,-2.1181627521\
H,4.5271044965,2.2391257392,-1.9621504334\H,2.9896568363,2.2907651614,
-2.9484130857\C,1.3569315982,1.7960918576,-0.6221029803\C,2.3087353053
,5.0521778208,-1.845842171\C,-0.2598897323,5.4196384809,-0.8198296014\
C,1.2645393659,5.3953836435,-2.7060280749\H,3.3152334302,4.9199837736,
-2.2284314353\C,-0.0354619487,5.5669809167,-2.1827346288\H,-1.26881561
65,5.5802060504,-0.44811949\C,0.7923171521,5.0975790673,0.0430525048\H
,0.6182486474,5.0013253649,1.1100743758\C,2.0675358732,4.9029111395,-0
.4753583422\H,2.8901342356,4.63949798,0.1834481336\O,-1.0607206623,5.9
64398164,-2.9978155952\O,1.3929847059,5.5747241466,-4.0442528558\C,-1.
5549507003,4.9489996642,-3.8734028758\H,-1.9511519588,4.1107150757,-3.
2895818939\H,-2.3594843167,5.4067925421,-4.4494787981\H,-0.7683516889,
4.6024769745,-4.5509332686\C,2.704125646,5.5607036394,-4.5931919484\H,
2.5849655525,5.7897912936,-5.6511201434\H,3.3315793447,6.3211030324,-4
.1165247873\H,3.1702056736,4.5750978706,-4.484388866\\Version=ES64L-G0
9RevD.01\HF=-1017.2658097\RMSD=0.000e+00\RMSF=2.548e-06\Dipole=2.14320
92,-4.225519,1.2156229\Quadrupole=5.9701382,-18.4957413,12.5256032,16.
9941928,-15.1273598,-3.7365244\PG=C01 [X(C17H24N1O4)]\\@
Sum of electronic and thermal Free Energies= -1016.922146 Hartrees

TS1

1\1\GINC-R160\FTS\RM062X\6-31+G(d)\C17H24N1O4(1+)\ROOT\10-May-2016\0\\
M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) scf=(qc,direct) no
symm freq=noraman opt=(ts,noeigentest,z-matrix,calcfc,Maxcycle=500)\\f
req&geom\\1,1\C,-1.6502109305,-0.917615299,-0.7088812539\C,-2.60099396
85,-1.9678725727,1.2766130288\H,-3.347712575,-2.7323689049,1.502296608
3\H,-1.9847193114,-1.8232125043,2.1695598013\C,-1.3722516508,-1.114635
9917,-2.1699422445\C,-2.5151089914,-1.3885414222,-3.1190079304\C,-1.64
80416397,-0.1780884594,-3.3113837976\H,-0.5066344293,-1.7586147603,-2.
3033421188\H,-3.5221623532,-1.2283827613,-2.7449497385\H,-2.4076028613
,-2.2296179515,-3.7948401886\H,-0.9217694436,-0.1916725024,-4.11726664
92\H,-2.0924525802,0.7920365633,-3.1297974372\C,-3.2985802294,-0.67608
09019,0.9204927829\O,-4.2230779173,-0.1489199843,1.4975510138\C,-3.352
1097711,1.0031511959,-0.8762730014\H,-3.8533688102,1.5651639769,-0.087
4719086\H,-2.6058492968,1.6399359974,-1.343071844\H,-4.094394699,0.695
1737378,-1.6184884312\N,-2.7288378324,-0.1640552499,-0.2543649217\C,-1
.7677251152,-2.2689267185,0.0300177183\C,-0.0570200792,1.1730501962,-0
.7126168494\C,-0.1027750959,-0.1914252013,1.3283108547\C,-0.5297066084
,2.2475038258,-0.0131888503\H,0.1967378986,1.2590587522,-1.7634283815\
C,-0.6241269801,0.8623644484,2.0362622916\H,0.1624425026,-1.1135779446
,1.8335244205\C,-0.9094040787,2.0707599789,1.3632949198\H,-0.797596376
7,0.7805252926,3.1026620639\C,0.0050816654,-0.132072723,-0.0959775551\
H,0.6665212265,-0.8638537478,-0.5532594387\O,-1.4855135702,3.109974421
4,1.9195060423\C,-1.9333790439,3.0284331267,3.2817206249\H,-2.42223017
75,3.979720169,3.4769363387\H,-2.644303911,2.2061085614,3.3922160326\H
,-1.0790346492,2.8999400674,3.9498437069\O,-0.5087566211,-2.8368858652
,0.2364967995\C,-0.578608973,-4.1889641468,0.669573345\H,-1.123686494,
-4.7996199247,-0.0602755678\H,0.4481811196,-4.5442868568,0.7518180372\
H,-1.0694012321,-4.2625252566,1.6473678229\H,-2.3539319975,-2.90841938
54,-0.6498719869\O,-0.7366423095,3.4873985762,-0.4961387681\C,-0.31819
03906,3.7386902438,-1.8336989856\H,-0.5219613365,4.7922011821,-2.01481
31174\H,0.752299676,3.5386778768,-1.9457579952\H,-0.8881757575,3.12768
68465,-2.5425672923\\Version=ES64L-G09RevD.01\HF=-1017.2444085\RMSD=0.
000e+00\RMSF=7.317e-06\Dipole=1.1811022,-0.8527242,-0.4367353\Quadrupo
le=-17.0132232,8.3430914,8.6701318,3.091528,3.5556519,0.5879787\PG=C01
[X(C17H24N1O4)]\\@

ν_{imag} = -352.5723 cm^{-1}

Sum of electronic and thermal Free Energies= --1016.898502 Hartrees

Compound **13'**

1\1\GINC-R115\FOpt\RM062X\6-31+G(d)\C17H24N1O4(1+)\ROOT\05-May-2016\0\
\# M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) freq=noraman scf=
(qc,direct) geom=checkpoint guess=check nosymm opt=(z-matrix,readfc,Ma
xcycle=500)\\freq&geom\\1,1\C,-1.7134631314,-0.9676070166,-0.635054937
6\C,-2.8096779772,-3.1114062759,-0.2420862351\H,-3.0763309848,-3.56611
86645,-1.2017239255\H,-2.8985792791,-3.876085102,0.532646696\C,-1.5566
91825,-0.8199813712,-2.1448209878\C,-2.6355572312,-1.2826854907,-3.084
3910246\C,-2.3137414374,0.1818699673,-2.9685144807\H,-0.5378162575,-1.
0180365893,-2.4753845682\H,-3.5808563169,-1.605941194,-2.6580199173\H,
-2.3307121331,-1.8155574156,-3.9783168785\H,-1.7772358701,0.6586374929
,-3.7825533029\H,-3.0483959717,0.8155866377,-2.4836813537\C,-3.7548858
862,-1.9604165626,0.0345785286\O,-4.9285683089,-2.0329348999,0.3743085
289\C,-3.7855854069,0.4763094006,-0.0211324502\H,-4.1840705044,0.55533
04479,0.9943454798\H,-3.0938058797,1.3004583073,-0.201186387\H,-4.6174
51126,0.5528979203,-0.728491795\N,-3.0914292986,-0.7922287214,-0.18004
30974\C,-1.4238517294,-2.4618626775,-0.2764441522\C,-0.4376863706,1.28
28150541,-0.5898429131\C,-1.1006292725,0.1999689687,1.5510405813\C,-0.
4133754926,2.4872861633,0.0231498965\H,-0.1865887245,1.2447802414,-1.6
454427896\C,-1.0917026614,1.4041466523,2.1730908668\H,-1.3608940254,-0
.6929046571,2.1095071848\C,-0.75578051,2.5748508751,1.4271682891\H,-1.

3491005615,1.4831902301,3.2221529311\C,-0.7406345612,0.0176338871,0.12
43591648\H,0.2216485857,-0.5358296239,0.1586754614\O,-0.7403521411,3.7
672434852,1.9223557773\O,-0.1612304417,3.6354059807,-0.653356885\C,1.1
642333186,4.1583528061,-0.4683196926\H,1.2069310708,5.0769161442,-1.05
12917359\H,1.3508901756,4.3785345189,0.5864393637\H,1.9006261604,3.440
8010088,-0.842089458\C,-1.0753551057,4.010035922,3.3079774456\H,-0.977
8033082,5.0848980951,3.4315693602\H,-2.1020492318,3.6931692344,3.49478
69118\H,-0.369620609,3.4834291348,3.9519560754\O,-0.784832987,-2.53756
91506,0.9797770391\C,-0.1724500744,-3.7942032489,1.2226671143\H,0.5907
099153,-4.0002097484,0.4621290656\H,0.2952837587,-3.7316505807,2.20540
34458\H,-0.9090912291,-4.6061693448,1.2242893637\H,-0.7686801221,-2.89
79452411,-1.0413375999\\Version=ES64L-G09RevD.01\HF=-1017.245479\RMSD=
0.000e+00\RMSF=6.021e-06\Dipole=3.6223326,2.1036052,1.5869581\Quadrupo
le=-30.6650271,19.0991971,11.5658299,-8.976587,-1.6214877,19.6478984\P
G=C01 [X(C17H24N1O4)]\\@

Sum of electronic and thermal Free Energies= -1016.899221 Hartrees

TS2

1\1\GINC-R146\FTS\RM062X\6-31+G(d)\C17H24N1O4(1+)\ROOT\10-May-2016\0\\
M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) freq=noraman scf=(
qc,direct) nosymm opt=(ts,noeigentest,z-matrix,calcfc,Maxcycle=500)\\f
req&geom\\1,1\C,1.6780292363,-0.9660148589,-1.7890257556\C,1.612304798
8,-0.4936222071,-0.3310230194\H,1.4085826963,-0.142596826,-2.461794133
6\H,1.3359335702,-1.3368803374,0.3230982976\H,1.0599355625,-1.83309797
16,-2.0242406985\C,3.1394299339,-1.2869013842,-1.9949368422\O,0.771071
7763,0.5964425293,-0.0869260142\C,-0.6043503678,0.2543180996,-0.179658
1458\H,-1.1691401574,1.1508081925,0.075083771\H,-0.864663435,-0.062387
8912,-1.1968555274\H,-0.8504142189,-0.5494696431,0.5255008861\C,5.3064
865227,-0.883315674,-0.8492826817\H,5.5754295888,-1.3104433898,0.11854
79661\H,5.600083344,-1.5688983868,-1.643834554\H,5.8210252301,0.069627
7738,-1.0014460669\C,3.3675986061,0.7033424224,1.0305850081\O,3.651989
638,-1.9001122339,-2.9024992838\N,3.8619745368,-0.7249910251,-0.932661
6073\H,2.5214307121,1.0538013683,1.6115918977\C,4.7105249804,1.2932731
261,1.3835403913\H,5.5817795883,0.682162764,1.1622244051\H,4.727391818
8,1.6532516807,2.4108920366\C,4.4181247989,2.3375719533,0.3838751381\H
,4.5446800172,2.0928741643,-0.6661373855\H,3.6765720121,3.0969740688,0
.6171322315\C,3.0494563745,-0.1110282549,-0.0144601482\C,5.5755679687,
4.5117352676,-0.6374044101\C,5.951753812,4.2132332949,1.7458340623\C,4
.8211369852,5.6491123214,-0.3846169144\H,5.7339044881,4.195559035,-1.6
643327635\C,5.2128319469,5.3432451992,2.0105154954\H,6.39719398,3.6786
706763,2.5801784543\C,4.6204280847,6.0690499549,0.9379627504\H,4.39200
32292,6.2036284139,-1.2104366162\C,6.0903173269,3.734506511,0.41861918
44\H,6.8037248903,2.9421474303,0.2093439015\O,3.8919568266,7.129045700
4,1.295598177\O,5.00347419,5.743584767,3.2973028486\C,5.744905118,6.90
8571213,3.6793485233\H,5.4713829422,7.7639030887,3.0558388182\H,5.4832
454768,7.1082000333,4.7181297573\H,6.8186261093,6.7092622214,3.5982809
635\C,3.2700701354,7.9076738864,0.2738496771\H,2.7409933221,8.70332699
62,0.7941793956\H,4.0229695708,8.3352905403,-0.3943442772\H,2.56193843
12,7.2967853925,-0.2936561966\\Version=ES64L-G09RevD.01\HF=-1017.22308
83\RMSD=0.000e+00\RMSF=2.494e-06\Dipole=0.3192043,0.6254555,0.1188056\
Quadrupole=32.4238085,16.7444658,-49.1682742,51.4781262,12.0459971,-4.
5143495\PG=C01 [X(C17H24N1O4)]\\@

ν_{imag} = -556.5533 cm^{-1}

Sum of electronic and thermal Free Energies= -1016.883514 Hartrees

Compound **14'**

1\1\GINC-R144\FOpt\RM062X\6-31+G(d)\C17H24N1O4(1+)\ROOT\16-May-2016\0\
\# M062X/6-31+G* freq=noraman nosymm scrf=(cpcm,solvent=dichloromethan
e) geom=checkpoint guess=check opt=(z-matrix,readfc,maxcycle=500)\\fre
q&geom\\1,1\C,2.2000049995,-2.1339187412,-1.406970799\C,1.9753518665,-

1.5985174949,0.0124866795\H,1.6260321539,-1.5392963805,-2.1288268863\H
,2.074712069,-2.4231611533,0.7372934803\H,1.9598438664,-3.1886402104,-
1.5495643032\C,3.6739367413,-1.8873838235,-1.6513787388\O,0.751329627,
-0.9440200403,0.2165849857\C,-0.3488483922,-1.8373923688,0.2070837056\
H,-1.2386114238,-1.2482797312,0.4311043986\H,-0.4674144437,-2.31244333
64,-0.7749631871\H,-0.2233885135,-2.6160245369,0.970699812\C,5.5158824
438,-0.5822683663,-0.6667513754\H,5.9527075454,-0.7808482723,0.3147542
571\H,6.049247984,-1.1571114298,-1.4241651723\H,5.6054135625,0.4826032
802,-0.9038348949\C,3.1145889297,0.365021644,1.1120351975\O,4.35787410
57,-2.3569720205,-2.5454471142\N,4.1311140961,-1.0121590074,-0.6925015
594\H,2.1913140692,0.4364045443,1.6820421693\C,4.139264762,1.439537305
4,1.3690956349\H,5.1641235322,1.0743317636,1.2581264434\H,4.0345695952
,1.7639403865,2.4091855524\C,3.9188415042,2.6349434367,0.431287409\H,3
.9022096795,2.2887773936,-0.6078799103\H,2.950352286,3.1045210846,0.63
46781602\C,3.1304806046,-0.6303398798,0.2176151596\C,4.8315989095,4.76
22307587,-0.478441309\C,5.2008907392,4.2359869005,1.9227526384\C,4.732
7033142,6.0829635247,-0.191768988\H,4.7335779971,4.4315877896,-1.50974
81335\C,5.1127493053,5.5486519592,2.2275782817\H,5.393339815,3.5330965
755,2.7291776577\C,4.8599850814,6.5045082529,1.167386517\H,4.559095661
5,6.8122969439,-0.9731057018\C,5.0440749573,3.7186207197,0.5449616292\
H,5.9804509867,3.1918688096,0.280025251\O,4.766061886,7.7335493954,1.5
516916547\C,4.5245973579,8.8006130767,0.6064160759\H,4.4951200761,9.70
33225585,1.2098098888\H,5.3455499206,8.8441953268,-0.110701416\H,3.566
7903832,8.6379935604,0.1107116649\O,5.1909787263,6.0064712554,3.501789
4215\C,6.4617584823,6.5790798006,3.8489507164\H,6.3728189967,6.9005305
106,4.8854965917\H,7.2460276926,5.8219788552,3.7558014803\H,6.68785845
95,7.4387793854,3.2118389616\\Version=ES64L-G09RevD.01\HF=-1017.254979
9\RMSD=5.816e-09\RMSF=5.293e-06\Dipole=1.5876915,6.2619978,0.8507036\Q
uadrupole=17.3797539,61.8711991,-79.2509529,113.3687085,24.1011768,1.9
378924\PG=C01 [X(C17H24N1O4)]\\@
Sum of electronic and thermal Free Energies= -1016.912485 Hartrees

Entry 11

Reactant association complex

See entry 10.

***TS2* (formation of *E*-alkene)**

1\1\GINC-SPARTAN-RC099\FTS\RM062X\6-31+G(d)\C17H24N1O4(1+)\UWILLE\10-J
un-2019\0\\#p M062X/6-31+G* scf=(qc,direct) scrf=(cpcm,solvent=dichlor
omethane) nosymm opt=(ts,noeigentest,calcfc,maxcycle=500) freq=noraman
\\geom&freq\\1,1\C,3.241321109,0.8350934823,0.9861571103\H,2.414847563
5,1.2288140052,1.5681013772\C,4.6200607852,1.3595380657,1.3032035782\H
,5.4226647149,0.6857906837,1.0078011818\H,4.7082084394,1.6794735468,2.
3405589061\C,4.349193953,2.44935213,0.3494846829\H,4.4520373905,2.2404
702586,-0.7099524111\H,3.6396249624,3.2260084409,0.6237088063\C,3.0016
342801,-0.0621929659,-0.0105414316\C,5.5587093455,4.6168893307,-0.6101
151041\C,5.9130720347,4.2599472364,1.7680958403\C,4.8116613618,5.75501
32801,-0.3369586501\H,5.7227839288,4.3234045506,-1.6428248224\C,5.1816
182582,5.3901384755,2.0530161889\H,6.3468300962,3.7022894691,2.5933906
123\C,4.6032334445,6.1453957806,0.9932359639\H,4.394660117,6.332634431
4,-1.1531248493\C,6.0574161551,3.8108812964,0.4313823955\H,6.757884562
4,3.0108801471,0.2097200193\O,3.8792643931,7.2022349809,1.3700973541\O
,4.9647235186,5.7622481471,3.347030977\C,5.7143948267,6.9098529395,3.7
636532657\H,5.4546757392,7.7828990791,3.1590703474\H,5.4456391379,7.08
68189276,4.8047656587\H,6.7867512239,6.7017749189,3.6867974376\C,3.265
0602886,8.0038120351,0.3617498862\H,2.7337792619,8.7890577923,0.895552
499\H,4.0227436956,8.444675461,-0.2923789028\H,2.5597020673,7.40642242
55,-0.2233653319\C,4.0409430271,-0.7512340687,-0.8876593597\H,4.559715

5778,-0.0061918352,-1.5095555339\C,3.2200700255,-1.7135436383,-1.76011
08616\H,3.4646621388,-2.7545906828,-1.5257738651\H,3.3484307855,-1.562
4566755,-2.8338901355\C,1.7787777442,-1.4619718515,-1.3797307838\O,4.9
663143261,-1.3955810912,-0.0465710886\O,0.7851857304,-1.9698858903,-1.
8473123859\N,1.7594662066,-0.5128004172,-0.3565113138\C,0.5281554992,-
0.0518572584,0.2588075925\H,0.4344462441,1.0304217635,0.1334768875\H,-
0.2994674251,-0.5547014521,-0.2396062646\H,0.5249399318,-0.3017656607,
1.3230879105\C,6.1155867685,-1.8473795869,-0.7483798791\H,6.7667334227
,-2.3201903708,-0.0134354747\H,5.8485652366,-2.5785889512,-1.521068566
3\H,6.6369691054,-1.001684685,-1.2151804634\\Version=AM64L-G09RevB.01\
HF=-1017.2272548\RMSD=0.000e+00\RMSF=2.411e-06\Dipole=1.5433989,1.6104
752,-0.9395735\Quadrupole=34.8450718,13.8465521,-48.6916239,44.4254104
,-5.5753911,0.6217515\PG=C01 [X(C17H24N1O4)]\\@

ν_{imag} = -550.9912 cm^{-1}

Sum of electronic and thermal Free Energies= -1016.889171 Hartrees

Compound **14' (*E*-alkene)**

1\1\GINC-SPARTAN-RC027\FOpt\RM062X\6-31+G(d)\C17H24N1O4(1+)\UWILLE\10-
Jun-2019\0\\#p M062X/6-31+G* freq=noraman scrf=(cpcm,solvent=dichlorom
ethane) scf=(qc,direct) nosymm opt=(calcfc,maxcycle=500)\\geom&freq\\1
,1\C,2.95825149,0.416521933,0.9334248581\H,2.0377430503,0.6568693181,1
.4620056839\C,4.0998498097,1.3830351255,1.0799698309\H,5.0286324467,0.
9421858168,0.7010999965\H,4.2558048385,1.5849716032,2.146361281\C,3.80
69843233,2.6896380102,0.3324692419\H,3.6571572111,2.46823843,-0.729444
1685\H,2.8868791763,3.1522300416,0.7065497069\C,3.023013025,-0.6931048
927,0.1896943642\C,4.744282456,4.8287666835,-0.5236864609\C,5.19279792
99,4.1821979812,1.8333564569\C,4.6764498596,6.1355360455,-0.1725429295
\H,4.6071426241,4.5505881545,-1.5659373578\C,5.1314166996,5.4795476206
,2.2034357328\H,5.4008500007,3.4402639424,2.5996881267\C,4.8528218758,
6.4888897932,1.2007324458\H,4.4906536679,6.9027964264,-0.9138106714\C,
4.9713927235,3.7328709392,0.4403776078\H,5.8777008272,3.1926125611,0.1
096676786\O,4.7828039909,7.6978631603,1.6484630102\C,4.5175512171,8.81
17946945,0.7662768637\H,4.5075133314,9.6829716184,1.4149478947\H,5.317
7016263,8.8910797672,0.0289922674\H,3.5455825981,8.6762662702,0.290467
7337\O,5.2571799112,5.873530758,3.4953071395\C,6.5439179375,6.41843288
36,3.8273495667\H,6.4893888306,6.6974976866,4.8784612161\H,7.316682600
7,5.6581276207,3.6801006216\H,6.7609039421,7.3017145631,3.2199886317\C
,2.2822251744,-2.6254347273,-0.8536547857\C,4.2248759898,-1.1968862338
,-0.5934214523\H,4.6288775817,-0.4059285153,-1.2406508418\C,3.67152167
63,-2.3756483683,-1.4087570263\H,3.5836687928,-2.150409453,-2.47576207
93\H,4.2799527338,-3.2774214551,-1.3018137367\C,0.7130309277,-1.506418
1199,0.7045768581\H,0.8638332718,-1.4864145018,1.7882668375\H,0.201265
167,-0.5890566517,0.3958481268\H,0.1093048234,-2.3718143164,0.43226097
48\O,1.533655252,-3.54436914,-1.1457117517\O,5.2164863173,-1.591714777
1,0.3368542355\C,6.4751217841,-1.8184351731,-0.2727415509\H,7.16185020
02,-2.120649223,0.5185898222\H,6.42257786,-2.6137778298,-1.0267761434\
H,6.8440262238,-0.8994002437,-0.7483920477\N,1.987072073,-1.6205390365
,0.0298057316\\Version=AM64L-G09RevB.01\HF=-1017.2599086\RMSD=0.000e+0
0\RMSF=4.920e-06\Dipole=2.6930187,7.9613561,-0.6213389\Quadrupole=29.8
430033,46.1164177,-75.9594209,102.9775296,4.9001714,6.7543411\PG=C01 [
X(C17H24N1O4)]\\@

Sum of electronic and thermal Free Energies= -1016.919000 Hartrees

Data for Scheme 4

Reactant association complex

1\1\GINC-R265\FOpt\RM062X\6-31+G(d)\C18H23N2O2(1+)\ROOT\18-Aug-2016\0\
\# M062X/6-31+G* geom=checkpoint guess=check nosymm freq=noraman scrf=
(cpcm,solvent=dichloromethane) scf=(qc,direct) opt=(readfc,z-matrix,Ma

xcycle=500)\\freq&geom\\1,1\C,-0.4005782909,1.7921735335,1.3558602931\
C,1.0564235923,1.3542267865,1.1881572563\H,-0.4770580815,2.6603882556,
2.0170219254\H,1.1206044198,0.2518693139,1.1654581189\H,-1.0662561346,
1.0113924877,1.7288751125\C,-0.8261155239,2.1871311315,-0.0326581081\O
,1.9712792612,1.870004942,2.1021442166\C,1.8903624372,1.239009716,3.37
57555967\H,2.6552746109,1.7015102807,3.998592384\H,0.9049872469,1.3969
269785,3.8298719754\H,2.0848577331,0.1637866721,3.2850609653\C,0.21894
238,2.4358812066,-2.3205398891\H,0.5398027713,1.5748758486,-2.90709270
48\H,-0.8381454715,2.6271565801,-2.4993469945\H,0.7920150734,3.3259307
091,-2.576453496\C,2.7845534394,1.6042416274,-0.6656025973\O,-1.899057
4806,2.4836476119,-0.4636827901\N,0.356545245,2.1369366804,-0.89119883
54\H,3.4664848051,1.5062284827,0.1723869333\C,3.0583478984,0.626435448
7,-1.8329095295\H,2.1975089829,0.2226454571,-2.3541269603\H,3.84899316
36,-0.0858917326,-1.6282983286\C,3.3850298033,2.0578234105,-1.98505955
63\H,4.4247963986,2.3579975125,-1.9081717079\H,2.7853794486,2.66650172
42,-2.6485544647\C,1.4274409052,1.7852222782,-0.2219977321\C,1.7599239
462,5.1981979754,-0.8856491985\C,1.1776240376,4.751632429,1.2380495043
\C,0.3542129736,5.3387129212,-0.7665393807\C,2.3680557707,5.4374734655
,-2.1310210185\H,1.137370564,4.5179921272,2.2937577187\C,-0.4560711196
,5.7115736864,-1.8459561311\C,1.5705323682,5.801725513,-3.2063475134\H
,3.4452335095,5.3397123454,-2.2467182239\H,-0.8905263703,5.1700277062,
0.9478401959\C,0.1716339504,5.9392959943,-3.0622030972\H,-1.5318844317
,5.8131683638,-1.7345505816\H,2.024363849,5.9890211233,-4.1749404378\H
,-0.4245084491,6.2283121029,-3.9225075198\N,0.0238277357,5.0369495806,
0.5358230984\C,2.2677456631,4.8157486227,0.408306935\C,3.7009848714,4.
5994054037,0.780119577\H,4.2029408302,3.9358293525,0.0670957759\H,4.25
59348574,5.5447322827,0.7855618888\H,3.7782278089,4.1495490614,1.77381
53267\\Version=ES64L-G09RevD.01\HF=-959.1421705\RMSD=0.000e+00\RMSF=2.
432e-05\Dipole=0.3409053,-3.2039705,0.9914621\Quadrupole=-1.1922243,-4
.1007365,5.2929608,2.8859272,-4.7710589,0.2560152\PG=C01 [X(C18H23N2O2
)]\\@

Sum of electronic and thermal Free Energies= - 958.803006 Hartrees

TS1

1\1\GINC-R265\FTS\RM062X\6-31+G(d)\C18H23N2O2(1+)\ROOT\18-Aug-2016\0\\
# M062X/6-31+G* nosymm freq=noraman scf=(qc,direct) geom=checkpoint gu
ess=check scrf=(cpcm,solvent=dichloromethane) opt=(ts,noeigentest,read
fc,z-matrix,Maxcycle=500)\\freq&geom\\1,1\C,-0.8871108837,1.771148401,
0.2802378854\C,0.3013557491,2.2359768589,-0.3064190531\C,0.5978985551,
3.5857552256,-0.4634380782\C,-0.3408433947,4.4899546416,0.0248982066\C
,-1.5153177604,4.0520173238,0.6617212768\C,-1.7962272338,2.6959691946,
0.8009745386\C,0.4109054702,-0.0052391193,-0.2932754956\H,1.5162730247
,3.9179203853,-0.937454305\H,-0.1526843938,5.554667272,-0.0716818073\H
,-2.2106431692,4.7863240705,1.0562110501\H,-2.7011814033,2.3659719411,
1.3049116032\H,0.8587182424,-0.9778098669,-0.435532608\H,1.9572802677,
1.1293184099,-1.1073291482\N,1.0525926228,1.1081119183,-0.6491005979\C
,-0.8735567321,0.3067802969,0.218540002\C,-1.9944372339,-0.0672511447,
-1.643458024\C,-2.0292987111,-1.6078046178,-1.7734932915\C,-3.30049995
04,-2.0550147762,-1.0500076409\H,-2.1570415985,-1.774317909,-2.8568959
407\H,-3.8891895354,-2.7831305018,-1.612245573\H,-3.0938570349,-2.4722
736711,-0.0607323704\C,-1.1843536935,0.5907814718,-2.6940825282\C,-1.8
712347928,1.1824418617,-3.9167985621\C,-1.0434469512,2.0542463827,-3.0
350492518\H,-0.3046836289,-0.0078380477,-2.915409\H,-2.9500757458,1.29
19628167,-3.8726338435\H,-1.4804786376,0.8792414926,-4.881695155\H,-0.
0578531057,2.3463095324,-3.3834431987\H,-1.5276135213,2.8059533119,-2.
4234524215\C,-4.0863209443,-0.7767703123,-0.916672151\O,-5.2364687551,
-0.6264077069,-0.5804277945\O,-0.8408935469,-2.2035054663,-1.354543311
7\C,-3.9002129593,1.6207032862,-1.3698252295\H,-4.4308420977,1.7971365
186,-0.4332871797\H,-3.1514457547,2.3922063846,-1.5057399075\H,-4.6238
86065,1.6367643538,-2.1892142144\C,-0.7511224934,-3.5725199208,-1.7306

651453\H,0.2238210394,-3.9245682216,-1.3945313693\H,-1.5375480726,-4.1
639671289,-1.2476077737\H,-0.8290863127,-3.6783656387,-2.8193349588\N,
-3.2688381316,0.3024584282,-1.3077223908\C,-1.6006587317,-0.5323134264
,1.2316875108\H,-2.6829704102,-0.3659814835,1.1830641319\H,-1.38903275
85,-1.594579304,1.0966048963\H,-1.2846908226,-0.2441075122,2.239802216
3\\Version=ES64L-G09RevD.01\HF=-959.1207322\RMSD=0.000e+00\RMSF=2.507e
-06\Dipole=2.4790765,-0.68628,-1.4232456\Quadrupole=-11.6716889,10.711
5808,0.9601081,0.0688372,4.436358,0.6883694\PG=C01 [X(C18H23N2O2)]\\@

ν_{imag} = -301.7306 cm^{-1}

Sum of electronic and thermal Free Energies= -958.779176 Hartrees

Compound **13'**

1\1\GINC-R148\FOpt\RM062X\6-31+G(d)\C18H23N2O2(1+)\ROOT\25-Aug-2016\0\
\# M062X/6-31+G* scf=(qc,direct) scrf=(cpcm,solvent=dichloromethane) n
osymm freq=noraman opt=(calcfc,z-matrix,Maxcycle=500)\\freq&geom\\1,1\
C,-0.7787815185,2.0312333077,-0.0648937412\C,0.60483568,2.1413550758,-
0.2120645729\C,1.3169490748,3.3284792944,-0.2267669907\C,0.5706539648,
4.49329021,-0.0594905066\C,-0.8102681037,4.4256128257,0.1422570911\C,-
1.4920169137,3.2053612419,0.1504614354\C,0.2058443628,-0.0712258889,-0
.1866439081\H,2.3950342742,3.3474781624,-0.3463440055\H,1.0707531201,5
.456005999,-0.0629655582\H,-1.3700957876,5.341192168,0.3038899955\H,-2
.5583045509,3.2106022308,0.339923723\H,0.4402826069,-1.1274775896,-0.1
711894037\H,2.126043326,0.6075054519,-0.335940767\N,1.1302733353,0.822
3643536,-0.2751447988\C,-1.1641223135,0.5482296946,-0.0889640056\C,-1.
9846443484,0.0668688458,-1.3777189407\C,-1.6975685357,-1.4339764751,-1
.7405938836\C,-2.9808653891,-1.8968447356,-2.4238213572\H,-0.814977653
8,-1.4985947298,-2.3928899113\H,-2.9696974692,-1.7180513322,-3.5031128
082\H,-3.1940158483,-2.9538801149,-2.2551069399\C,-1.5647041573,0.9176
102469,-2.5759288413\C,-2.4014945645,1.0295263265,-3.8216474958\C,-2.2
004369593,2.2281981162,-2.938833605\H,-0.4896425763,0.8734704359,-2.75
29019733\H,-3.3945882006,0.5892625461,-3.8130106876\H,-1.8916356693,0.
9852127797,-4.7779327111\H,-1.5372702504,3.0209927926,-3.2697345598\H,
-3.0582220785,2.5691933994,-2.3699524471\C,-4.0396265089,-1.0254260902
,-1.7885457019\O,-5.251072461,-1.1876100766,-1.8317198945\O,-1.4820401
972,-2.1866890086,-0.562747001\C,-4.2923336755,1.0763556397,-0.6388728
58\H,-3.6895469269,1.9033391493,-0.2826949394\H,-4.974937983,1.4410078
112,-1.4130364172\H,-4.8860868014,0.6810603026,0.1901853119\C,-0.90376
43178,-3.460697373,-0.806480762\H,-0.7847480558,-3.9415623519,0.164545
3099\H,-1.5449029714,-4.0821864875,-1.4406723244\H,0.0776777101,-3.354
6562911,-1.2886761186\N,-3.4333184153,0.031495373,-1.1734580294\C,-1.8
17082511,0.126743195,1.2491289706\H,-1.1274357473,0.3175494145,2.07644
85938\H,-2.7132449813,0.7266739069,1.4184846036\H,-2.0858260128,-0.928
2357519,1.2287914321\\Version=ES64L-G09RevD.01\HF=-959.1337838\RMSD=0.
000e+00\RMSF=8.950e-06\Dipole=5.4284147,0.7889153,0.9127387\Quadrupole
=-17.9884428,19.6116283,-1.6231855,-7.480464,-6.8675462,0.9357022\PG=C
01 [X(C18H23N2O2)]\\@

Sum of electronic and thermal Free Energies= - 958.790935 Hartrees

TS2 (formation of *Z*-alkene)

1\1\GINC-R305\FTS\RM062X\6-31+G(d)\C18H23N2O2(1+)\ROOT\18-Aug-2016\0\\
# M062X/6-31+G* scf=(qc,direct) nosymm freq=noraman geom=checkpoint gu
ess=check scrf=(cpcm,solvent=dichloromethane) opt=(ts,noeigentest,read
fc,z-matrix,Maxcycle=500)\\freq&geom\\1,1\C,2.7791328951,0.2917400322,
-5.0966154553\C,2.0509319736,0.0421288173,-3.7701276008\H,2.497171619,
1.2723437448,-5.4989923199\H,1.8615063865,-1.0364830417,-3.6429481827\
H,2.6176995609,-0.4664920254,-5.8635307305\C,4.2358405544,0.3403134046
,-4.7017557366\O,0.866869055,0.7622543502,-3.5871371256\C,-0.196804306
4,0.2761778919,-4.3937323674\H,-1.0757521314,0.8703005943,-4.144894603
9\H,0.0312629439,0.3932904567,-5.4600904413\H,-0.392673747,-0.78130151

57,-4.1771574285\C,5.5920928716,0.5054315991,-2.6239304685\H,5.6320970
067,-0.2762932363,-1.8632061479\H,6.356722958,0.3200883289,-3.37788662
45\H,5.7756613627,1.485020454,-2.1733964442\C,2.7018230819,0.753545398
8,-1.4368614234\O,5.2097840268,0.2971961243,-5.4152070793\N,4.30433042
85,0.4659766725,-3.303008521\H,1.6423525922,0.6588489834,-1.2277513775
\C,3.5631161457,1.3132846049,-0.328107534\H,4.60064949,0.9926923642,-0
.3035392822\H,3.0802303799,1.2046819632,0.6412846042\C,3.3000544539,2.
5835978367,-1.0110888332\H,3.873725426,2.862295693,-1.8911425501\H,2.3
265958706,3.0496190739,-0.8993251191\C,3.0676937142,0.4574310303,-2.71
953349\C,3.7242773163,5.3713563046,-0.7984559986\C,5.3740544459,3.9714
635465,-0.1317066051\C,4.7992902724,5.4589089465,-1.7074540255\C,2.581
2449238,6.1567907025,-1.0094523324\H,6.0174545955,3.2674995879,0.38176
56707\C,4.7775899986,6.2983849483,-2.824397001\C,2.5520248079,6.999437
1445,-2.1119251882\H,1.740473114,6.1099445935,-0.3222760267\H,6.674602
6849,4.4314813608,-1.7216332916\C,3.6375230115,7.0667401038,-3.0095979
776\H,5.615906759,6.3469667161,-3.5125878683\H,1.6793974459,7.62022554
31,-2.2908269968\H,3.5808180052,7.7355152892,-3.8629170247\N,5.7850372
26,4.5888725665,-1.264614466\C,4.0770597207,4.3716822346,0.1940116379\
C,3.3708763355,4.1197076596,1.4936640377\H,3.4373397225,4.9991980372,2
.1425893943\H,2.3077087493,3.9043490432,1.3416949723\H,3.8198832562,3.
2754460699,2.0243843757\\Version=ES64L-G09RevD.01\HF=-959.1043362\RMSD
=0.000e+00\RMSF=3.061e-06\Dipole=0.2362354,-1.2910514,1.7001389\Quadru
pole=29.5048084,-7.062726,-22.4420823,36.2715747,-6.2178501,-8.4680577
\PG=C01 [X(C18H23N2O2)]\\@

$\tilde{\nu}_{imag}$ = - 548.6337 cm^{-1}

Sum of electronic and thermal Free Energies= - 958.769473 Hartrees

Compound **14'** (*Z*-alkene)

1\1\GINC-R321\FOpt\RM062X\6-31+G(d)\C18H23N2O2(1+)\ROOT\18-Aug-2016\0\
\# M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) scf=(qc,direct) n
osymm freq=noraman geom=checkpoint guess=check opt=(z-matrix,readfc,Ma
xcycle=500)\\freq&geom\\1,1\C,2.621719812,-0.0639955253,-5.4522971723\
C,1.9587945926,-0.4217933829,-4.1228512579\H,2.1991813762,0.873513324,
-5.8340810274\H,2.0603531604,-1.5037116087,-3.9503992176\H,2.540093778
2,-0.8302092464,-6.2240116685\C,4.0656033875,0.1783231903,-5.063787897
8\O,0.6062470247,-0.0536422729,-4.0772219685\C,-0.2315753686,-1.002652
153,-3.4346038222\H,-1.2336859765,-0.5727671957,-3.4102560781\H,-0.252
5511058,-1.944466083,-3.9963542941\H,0.1007719653,-1.2036917056,-2.408
7901253\C,5.3622144954,0.6336584238,-3.0163263657\H,5.4384111654,-0.01
73186684,-2.1424928099\H,6.1677851409,0.4024457332,-3.7140572906\H,5.4
575574329,1.6807771106,-2.7090866659\C,2.4112858686,0.7924076925,-1.93
67999929\O,5.0373664452,0.2017572372,-5.8005563428\N,4.1089141183,0.39
04651811,-3.7033311074\H,1.3589868431,0.619544498,-1.7245999839\C,3.15
50564736,1.6431029319,-0.9372897603\H,4.1851533117,1.3010232271,-0.798
9321145\H,2.6614952286,1.5414319447,0.0335651797\C,3.1356356847,3.1134
327152,-1.3791888994\H,3.6117845642,3.2122402287,-2.3627238254\H,2.097
4140442,3.4449438573,-1.501491776\C,2.8345962601,0.3105308918,-3.10986
77993\C,3.8206551964,5.509452301,-0.9902693654\C,5.2712016499,3.846785
4608,-0.2819532664\C,5.1418802607,5.9062236389,-1.1838835817\C,2.79728
23978,6.3733458778,-1.354358284\H,5.7501089009,2.9604315292,0.12192435
27\C,5.5228079555,7.1233032696,-1.7236802226\C,3.1454200134,7.61239456
49,-1.9003249737\H,1.7540251308,6.1023687504,-1.2197053926\H,6.9871819
619,4.8640013175,-0.7374610348\C,4.4831313524,7.9812350665,-2.08339417
28\H,6.5643471439,7.3941791503,-1.8603121977\H,2.3608700033,8.30431468
62,-2.1896938513\H,4.7175846078,8.9500217404,-2.5119462855\N,5.9678348
948,4.8402465973,-0.7244924589\C,3.8026554512,4.1189325582,-0.39490212
21\C,3.1515913308,4.0818806289,1.0041690408\H,2.0785482396,4.262195013
9,0.8929299225\H,3.2955686117,3.1116005755,1.4842087106\H,3.5723481652
,4.8581579367,1.6483492646\\Version=ES64L-G09RevD.01\HF=-959.1501297\R
MSD=0.000e+00\RMSF=8.846e-06\Dipole=2.0559069,2.9241195,4.5557517\Quad

rupole=39.6406784,36.0875296,-75.728208,84.7464848,7.9855541,-10.00573
94\PG=C01 [X(C18H23N2O2)]\\@
Sum of electronic and thermal Free Energies= - 958.811879 Hartrees

TS2 (formation of *E*-alkene)

1\1\GINC-SPARTAN-RC037\FTS\RM062X\6-31+G(d)\C18H23N2O2(1+)\UWILLE\09-J
un-2019\0\\#p M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) nosymm
scf=(qc,direct) freq=noraman opt=(ts,noeigentest,calcfc,maxcycle=500)
\\geom&freq\\1,1\C,4.0481872961,0.51756823,-4.210908176\C,3.2310191006
,1.7916815238,-3.9483076667\H,4.9706182225,0.5146989777,-3.622418348\H
,4.3082642528,0.3662474364,-5.2609153715\C,3.1690197317,-0.6202667942,
-3.7440557795\C,0.9015092619,-0.8967291774,-2.7268979899\H,-0.01061393
18,-0.7293422968,-3.3061646406\H,1.2081523226,-1.9384251791,-2.8125829
329\H,0.7232176811,-0.6490175695,-1.6772488574\C,0.8768064555,2.046400
2797,-2.9228032085\O,3.4047737772,-1.8055225515,-3.7700167384\N,1.9768
669994,-0.0756821423,-3.2551585844\H,0.011510684,1.5765115824,-2.46927
66122\C,0.8594453655,3.5507303638,-3.0746629497\H,1.8477521382,4.00603
83398,-3.0862997398\H,0.1817133127,4.0266586684,-2.3680078401\C,0.2843
159529,3.2497402924,-4.3871682997\H,0.9299749118,2.9748176654,-5.21540
59258\H,-0.750502664,2.927347315,-4.4488380962\C,1.9282860637,1.282192
9005,-3.3434598383\C,-0.6567297786,4.4350486912,-6.7892339901\C,0.8634
827935,5.5321237924,-5.5216056912\C,0.5891825862,4.4244409865,-7.45132
49325\C,-1.7599830866,3.811027279,-7.3902752637\H,1.3977899894,6.09766
40891,-4.7685694744\C,0.778766993,3.8086975999,-8.6912481743\C,-1.5839
779526,3.2020796367,-8.6251805413\H,-2.7307842754,3.8093753826,-6.9015
599872\H,2.471065931,5.2451976062,-6.848625912\C,-0.3283352177,3.20041
83624,-9.2661758436\H,1.7466747176,3.809978138,-9.183241911\H,-2.42602
6737,2.7182257532,-9.1104341427\H,-0.2253234432,2.7153944734,-10.23199
84746\N,1.490146449,5.1038581752,-6.6431299596\C,-0.4658418348,5.11081
1468,-5.519145958\O,3.8269335853,2.6668925138,-3.0219678869\C,4.883422
9594,3.4254848611,-3.5928471029\H,4.5060111784,4.0494476433,-4.4141281
67\H,5.2779404542,4.0606985119,-2.8000518969\H,5.6826711222,2.77600363
65,-3.9700650512\H,3.0251217467,2.3278175728,-4.8877085763\C,-1.546409
682,5.5733399096,-4.5873146559\H,-2.1309754294,6.3772406699,-5.0467544
778\H,-2.2405409273,4.7623100779,-4.3422795831\H,-1.1231262258,5.95539
60347,-3.6541981902\\Version=AM64L-G09RevB.01\HF=-959.108229\RMSD=0.00
0e+00\RMSF=4.571e-06\Dipole=-0.0198121,2.1652466,0.4840163\Quadrupole=
-30.7617598,-6.0798382,36.841598,27.6787507,-28.5586826,-66.5987383\PG
=C01 [X(C18H23N2O2)]\\@

ν_{imag} = -540.7735 cm^{-1}

Sum of electronic and thermal Free Energies= -958.775016 Hartrees

Compound **14'** (*E*-alkene)

1\1\GINC-SPARTAN-RC071\FOpt\RM062X\6-31+G(d)\C18H23N2O2(1+)\UWILLE\08-
Jun-2019\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm scrf=(cpcm,solvent
=dichloromethane) freq=noraman opt=(calcfc,maxcycle=500)\\geom&freq\\1
,1\C,6.541090671,4.0966964245,-2.7031253788\C,5.5012983852,3.318784313
6,-1.8834308586\H,7.5543576172,3.7991179133,-2.4051865191\H,4.60475271
9,3.9474611567,-1.7479838644\H,6.4603732177,5.1828448641,-2.6375302258
\C,6.3158734815,3.6242050206,-4.1261567638\O,5.9476568689,2.8702124564
,-0.6286630339\C,6.1994468591,3.9368733816,0.2694152825\H,6.4566674763
,3.4901007902,1.2309284981\H,7.0350300475,4.5590824542,-0.0742355158\H
,5.3067061004,4.5678078214,0.3837472041\C,5.2005316688,1.7196360994,-5
.2502159902\H,4.1187799627,1.5671632147,-5.307085224\H,5.5436019266,2.
2661059698,-6.1285065423\H,5.6994401145,0.7457050797,-5.2077513753\C,4
.5559999332,0.983983831,-2.4566528989\O,6.7700447071,4.120705545,-5.14
42771407\N,5.5245658742,2.5059605379,-4.0799596233\H,4.3668830045,0.26
68639154,-3.2516106949\C,4.1248687909,0.5920674424,-1.0629467982\H,4.9
637739436,0.6968734553,-0.3701010137\H,3.8324150598,-0.461558772,-1.07
54314868\C,2.937690892,1.4342707369,-0.5786251399\H,3.1536540086,2.500

322447,-0.7125329465\H,2.0591769187,1.1986958529,-1.1912229502\C,5.142
6145865,2.143621792,-2.7783724562\C,2.2313501043,-0.2017068323,1.27923
93394\C,1.2827249484,1.9079246789,1.1535195415\C,0.8727320145,-0.26101
27653,1.5888683714\C,2.9872554225,-1.3641222307,1.3656064101\H,1.06926
84018,2.9650763571,1.030555463\C,0.2008065008,-1.4152403332,1.95498757
05\C,2.3412929624,-2.5486667963,1.7320895664\H,4.053836075,-1.35935577
81,1.1623062226\H,-0.6114123291,1.3181685736,1.6569881347\C,0.97133388
96,-2.5767212929,2.0150682464\H,-0.858440477,-1.4168182323,2.188835419
5\H,2.9159213388,-3.4668296712,1.8009717605\H,0.5003323539,-3.51282518
63,2.2963544821\N,0.3617177456,1.065526401,1.4850264351\C,2.5941773121
,1.225863691,0.9312948135\C,3.679372394,1.8255220584,1.8455971341\H,4.
6251760117,1.3030688405,1.6840199551\H,3.8245373476,2.8843517054,1.613
6740083\H,3.4026857177,1.7229090489,2.8981013827\\Version=AM64L-G09Rev
B.01\HF=-959.1567692\RMSD=0.000e+00\RMSF=3.796e-06\Dipole=-5.4475266,-
0.90313,4.747764\Quadrupole=-0.3238083,12.135955,-11.8121467,-0.817519
3,21.228609,18.0766232\PG=C01 [X(C18H23N2O2)]\\@
Sum of electronic and thermal Free Energies= --958.816082 Hartrees

TS3 (*Z*-alkene)

1\1\GINC-SPARTAN-RC079\FTS\RM062X\6-31+G(d)\C18H23N2O2(1+)\UWILLE\27-M
ay-2019\0\\#p M062X/6-31+G* scf=(qc,direct) scrf=(cpcm,solvent=dichlor
omethane) nosymm freq=noraman opt=(ts,noeigentest,calcfc,maxcycle=500)
\\geom&freq\\1,1\C,1.5172209906,0.0178649248,-4.2727470085\C,1.7404388
101,-0.4215936374,-2.8210229362\H,0.9499339608,0.9564646843,-4.2995946
363\H,1.7825635559,-1.5215506085,-2.7689199618\H,1.015753359,-0.714825
2335,-4.9068027617\C,2.9149509092,0.2930864444,-4.7840643642\O,0.79370
05561,0.0540778338,-1.9020089708\C,-0.4676775164,-0.5770602512,-2.0458
96319\H,-1.1165951125,-0.1700055607,-1.27005548\H,-0.9068935794,-0.369
3016703,-3.0297988012\H,-0.3749895756,-1.6630262279,-1.9150177652\C,5.
182159059,0.6274059179,-3.8731623508\H,5.7757634963,-0.1462455105,-3.3
802200071\H,5.3895446377,0.6159308012,-4.9433362448\H,5.4441845327,1.6
125795503,-3.4751125288\C,3.5378769585,0.3113126825,-1.2233323838\O,3.
2568139654,0.4551094301,-5.9415041084\N,3.7684129044,0.3555162376,-3.7
010719789\H,2.8008346956,0.0501326065,-0.4677501543\C,4.8171531127,0.9
003751635,-0.6855985736\H,5.6602720309,0.8063997316,-1.3729312369\H,5.
0843755968,0.3753574788,0.2354801065\C,4.541117476,2.3754709946,-0.394
7205271\H,4.2883236633,2.8948770358,-1.3208080673\H,3.7595538622,2.563
3131516,0.3426313851\C,3.1191560698,0.1287559105,-2.4831559731\C,5.896
1433229,3.8463965423,-0.2692319472\C,4.9736610659,4.6153362163,1.69023
71219\H,5.3773825318,2.8144937628,2.7616381481\C,5.2086098502,4.957936
5457,0.3421581528\C,4.3053970412,5.4797551449,2.5637201235\C,4.7999905
129,6.2041016737,-0.1588170225\C,3.9101760964,6.7035389755,2.047947086
6\H,4.1136320741,5.2079668324,3.5962408181\C,4.1551908479,7.0698505823
,0.7055037513\H,4.9870761049,6.4759768863,-1.1934174186\H,3.3958281222
,7.4052068134,2.6976091318\H,3.8261545933,8.0415979381,0.3531013573\C,
5.9868177807,2.854196271,0.7408627578\H,6.6254259458,1.9802629386,0.73
7959414\C,6.6238166062,3.8575992348,-1.5726769843\H,6.9955279801,2.86
43457451,-1.8346495138\H,5.9885219172,4.2362428123,-2.3781168539\H,7.4
851527126,4.5265382418,-1.4779715559\N,5.5019413847,3.3588229928,1.916
9334436\\Version=AM64L-G09RevB.01\HF=-959.1142441\RMSD=0.000e+00\RMSF=
1.850e-06\Dipole=2.1006531,0.9688177,4.0150612\Quadrupole=55.0005649,1
.3367864,-56.3373512,56.426761,13.7279052,10.6176763\PG=C01 [X(C18H23N
2O2)]\\@

ν_{imag} = - 384.6057 cm^{-1}

Sum of electronic and thermal Free Energies= - 958.777771 Hartrees

Compound **17'** (*Z*-alkene)

1\1\GINC-SPARTAN-RC147\FOpt\RM062X\6-31+G(d)\C18H23N2O2(1+)\UWILLE\16-
May-2019\0\\#p M062X/6-31+G* nosymm scrf=(cpcm,solvent=dichloromethane

) scf=(qc,direct) opt=(calcfc,maxcycle=500) freq=noraman\\geom&freq\\1
,1\C,2.1779671821,0.6252605821,-5.466774462\C,1.5878798575,0.219150632
7,-4.1165809805\H,1.996287064,1.6928548424,-5.641284965\H,1.4112671383
,-0.8670495473,-4.1145261202\H,1.8040316771,0.0567819182,-6.3190171038
\C,3.6647900645,0.4086759719,-5.2696376116\O,0.3974235144,0.8988781266
,-3.8214166322\C,-0.5776734469,0.1002403449,-3.1680053106\H,-1.4268555
29,0.7507169355,-2.9552508026\H,-0.9025653755,-0.7226773428,-3.8163842
951\H,-0.1946662693,-0.3140428357,-2.2274922359\C,5.242200515,0.118843
5922,-3.3942924138\H,5.2025252928,-0.6687772108,-2.6382740242\H,5.8637
881249,-0.2078130522,-4.2286215068\H,5.682680535,1.0234987251,-2.96244
43265\C,2.5967326169,0.9057349327,-1.8832426201\O,4.518304647,0.298933
448,-6.1340487147\N,3.9104366012,0.3638812788,-3.9152281397\H,1.571085
868,0.9818287224,-1.5312621538\C,3.6671803618,1.3719347937,-0.92907797
15\H,4.5620322203,0.7432804853,-0.9673398735\H,3.2746285159,1.29476505
49,0.0903311591\C,4.0554078876,2.8271091216,-1.2282287894\H,4.40484571
78,2.9057656501,-2.2642823796\H,3.1852604694,3.4854678774,-1.124397342
\C,2.7344061116,0.5214046583,-3.156592416\C,5.5808860828,4.7559898348,
-0.6255883406\C,4.9372879545,4.646826744,1.5552564203\H,4.528097434,2.
6124184315,1.6396150154\C,5.4198018176,5.5175126335,0.5038464457\C,4.6
863991692,5.1459830078,2.8600656748\C,5.6401114514,6.9104178006,0.7737
507292\C,4.9140903641,6.4796505836,3.0605647738\H,4.3308094615,4.49520
93064,3.650680631\C,5.3877381242,7.3684637162,2.0286213204\H,5.9998234
707,7.5681532662,-0.0107850633\H,4.73332828,6.8980725892,4.046378315\H
,5.5423102676,8.4128090634,2.2759233429\C,5.1841556199,3.3470988326,-0
.3157202823\H,6.064361865,2.6920786858,-0.4127584348\C,6.0207607608,5.
181014656,-1.9765720929\H,6.7166829089,4.4549134247,-2.407307292\H,5.1
493876227,5.2313685103,-2.6427965074\H,6.4906973676,6.1653587098,-1.95
53395442\N,4.7979616152,3.4156644976,1.083811921\\Version=AM64L-G09Rev
B.01\HF=-959.1453716\RMSD=0.000e+00\RMSF=2.641e-06\Dipole=1.4005343,2.
5348906,5.3611962\Quadrupole=32.2350743,29.0431345,-61.2782088,82.0612
632,24.9596113,17.2142107\PG=C01 [X(C18H23N2O2)]\\@
Sum of electronic and thermal Free Energies= - 958.809457 Hartrees

TS4 (*Z* alkene)

1\1\GINC-SPARTAN-RC041\FTS\RM062X\6-31+G(d)\C18H23N2O2(1+)\UWILLE\13-J
un-2019\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm scrf=(cpcm,solvent=
dichloromethane) freq=noraman opt=(ts,noeigentest,calcfc,maxcycle=500)
\\geom&freq\\1,1\C,3.6396029582,1.1617910313,-1.3555425361\C,2.4017241
474,1.576144354,-0.591331302\H,1.9751849034,0.7061225544,-0.0818746555
\H,1.6249590216,1.996522029,-1.2310473418\C,2.8693395942,2.6261491187,
0.417367818\H,2.0326715051,3.1086956037,0.9322267896\H,3.5010596992,2.
1579475284,1.1824287225\C,3.802813767,0.8653440329,-2.6984902755\C,2.9
062685009,4.5320985633,-1.2982926384\C,4.6443833503,2.956275972,-1.344
3840116\C,3.537621144,4.5526012191,-2.5443886269\C,1.7651860468,5.2927
155887,-1.0939926184\H,5.5983069698,2.5422967474,-1.0297741086\C,3.083
6197182,5.3207352383,-3.6070035786\C,1.2788096084,6.0694823024,-2.1526
407317\H,1.2567760183,5.2904784479,-0.1330260251\H,5.3251576757,3.5879
700935,-3.2298204835\C,1.9342818969,6.0853925991,-3.3864337864\H,3.587
0770263,5.3169366628,-4.5689718338\H,0.3835898263,6.6671027205,-2.0128
107007\H,1.5418561157,6.6956157865,-4.1940143807\N,4.6314479471,3.6684
368457,-2.4961319066\C,3.7018378142,3.652409736,-0.3513116753\C,4.5480
42589,4.5296426992,0.5935566474\H,3.8796939781,5.1014375049,1.24421658
77\H,5.1961361099,3.9069558376,1.2173611589\H,5.1659500609,5.234140457
4,0.028614621\H,4.355601858,0.6133676935,-0.7419161977\C,1.7659429805,
1.913012366,-3.7496809889\H,1.5064409491,2.1195429802,-4.7873630752\H,
1.020703775,1.2475259615,-3.309279074\H,1.8131946408,2.8520749851,-3.1
962816308\N,3.0696259839,1.255686972,-3.7584619626\C,3.6243356507,0.81
39983896,-4.9943411645\O,3.1377613779,1.079934071,-6.0615749917\C,4.83
79964265,-0.025238187,-4.6884962729\H,5.6682029221,0.249824225,-5.3402
84465\H,4.575726632,-1.0735670557,-4.8742837831\C,5.0821636431,0.20576

05283,-3.1956323544\H,5.9099152353,0.9239022396,-3.056615555\O,5.32068
57774,-0.9443471386,-2.4367815176\C,6.5986628565,-1.5124661306,-2.6910
516354\H,6.6970076348,-2.3694606404,-2.0253805927\H,6.6821672242,-1.84
89845679,-3.7313823265\H,7.3915964392,-0.7846639664,-2.4782195398\\Ver
sion=AM64L-G09RevB.01\HF=-959.1544312\RMSD=0.000e+00\RMSF=5.961e-06\Di
pole=1.6298151,-0.2554687,0.9561417\Quadrupole=41.5896231,-12.7440537,
-28.8455694,26.0825484,-37.8591617,-13.5129803\PG=C01 [X(C18H23N2O2)]\
\@

ν_{imag} = -313.7811 cm^{-1}

Sum of electronic and thermal Free Energies= - 958.812122 Hartrees

TS4 (*E* alkene)

1\1\GINC-SPARTAN-RC006\FTS\RM062X\6-31+G(d)\C18H23N2O2(1+)\UWILLE\26-F
eb-2019\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm scrf=(cpcm,solvent=
dichloromethane) freq=noraman opt=(ts,noeigentest,calcfc,maxcycle=500)
\\geom&freq\\1,1\C,3.0522646518,1.708766211,-4.4953525239\C,2.50003168
59,1.1487954419,-3.1780046004\H,3.0022262213,2.8055587454,-4.482150521
4\H,2.1430706428,0.1155248003,-3.345575752\H,2.5668390657,1.336362338,
-5.3983846095\C,4.5048588554,1.2961522631,-4.4659814051\O,1.5030556442
,1.8938569812,-2.5563769179\C,0.3237609054,2.0109155514,-3.3355814408\
H,-0.4093149214,2.5271191364,-2.7144736002\H,0.5081136038,2.6001086678
,-4.2422889846\H,-0.0612451494,1.0211574233,-3.612859724\C,6.118439910
7,0.3923997791,-2.7736672129\H,6.0247446276,-0.6607343783,-2.494657301
8\H,6.7719136326,0.4896872611,-3.6399360455\H,6.5390138654,0.948324317
4,-1.9343421833\C,3.8529452255,0.9653101525,-0.9384000586\O,5.30940340
78,1.2909396113,-5.3659837806\N,4.8112631106,0.9135035272,-3.146382270
7\C,2.6663948508,1.1063562049,-0.0121196288\H,2.939768765,0.6666054013
,0.9505919697\H,1.8049834325,0.5486489978,-0.3890362075\C,2.2839617579
,2.5960337878,0.1886956171\H,1.3664928905,2.8303800729,-0.354922401\H,
2.0912610607,2.7846197628,1.2486553536\C,3.7386473103,1.0081067716,-2.
311810351\C,3.2460738102,4.1743159873,-1.6717212696\C,4.7294566053,2.8
258203807,-0.5032876996\C,4.4745672319,4.1237269037,-2.3357548103\C,2.
1861716479,4.8561167739,-2.2562245662\H,5.3237900388,2.4488164539,0.32
36078653\C,4.7013150225,4.7266296501,-3.5693427482\C,2.3828989367,5.46
53374938,-3.497727226\H,1.218862958,4.9083658354,-1.7624169364\H,6.356
4949592,3.2763512371,-1.7458126296\C,3.6261538141,5.4059271988,-4.1415
463893\H,5.6667022761,4.6663360775,-4.0631191386\H,1.5616941679,5.9931
967445,-3.9725100866\H,3.7545870319,5.8864638756,-5.1063798316\N,5.369
967502,3.385631779,-1.5414479309\C,3.4018408878,3.5390211531,-0.298989
3271\C,3.6379599619,4.6743767569,0.7292879996\H,2.7150955419,5.2526687
797,0.8336302303\H,3.8984843084,4.2543718076,1.7054421927\H,4.43550648
57,5.3486963288,0.4027202051\H,4.7329877582,0.4510569531,-0.5571413221
\\Version=AM64L-G09RevB.01\HF=-959.1525974\RMSD=0.000e+00\RMSF=5.308e-
06\Dipole=0.5124395,-0.7012636,1.7830299\Quadrupole=34.3966481,-8.4863
427,-25.9103054,29.9315798,-8.570538,-13.6467199\PG=C01 [X(C18H23N2O2)
]\\@

ν_{imag} = - 261.1308 cm^{-1}

Sum of electronic and thermal Free Energies= - 958.811133 Hartrees

TS5 (*Z* alkene)

1\1\GINC-SPARTAN-RC004\FTS\RM062X\6-31+G(d)\C18H23N2O2(1+)\UWILLE\14-J
un-2019\0\\#p M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) nosymm
scf=(qc,direct) freq=noraman opt=(ts,noeigentest,calcfc,maxcycle=500)
\\geom&freq\\1,1\C,2.6056909664,1.7520302773,-2.5636861246\C,1.4147537
566,1.9072809333,-1.6430507802\H,1.4221424725,1.1529467941,-0.85110274
88\H,0.4678897586,1.8087343793,-2.1841689789\C,1.5486794388,3.29690207
43,-1.0182989074\H,1.2986050136,4.0589131205,-1.763383269\H,0.86282965
45,3.4228167048,-0.1761507326\C,3.1736222255,0.5838901885,-3.035235657
6\C,3.7211900783,4.6681453345,-1.1847960272\C,3.9111244433,2.332619725

8,-1.0913259588\C,4.9330239156,4.2528877754,-1.7411599869\C,3.3599262926,6.0052693627,-1.2459518728\H,3.9591404128,1.3697425667,-0.5894821786\C,5.8154131843,5.1245920542,-2.3635576506\C,4.2324415152,6.907131993,-1.8668489799\H,2.4196084382,6.3495670252,-0.8221014596\H,5.8165667744,2.3169147601,-1.9213136046\C,5.4410545774,6.4700534495,-2.4159127203\H,6.7529166517,4.7788191433,-2.7879128201\H,3.9676321288,7.9583334676,-1.9218695334\H,6.1028144536,7.1858663693,-2.8937530764\N,5.0597251077,2.868745138,-1.5338721749\C,3.0195036285,3.4739421431,-0.5687542873\C,3.1425221787,3.5007094872,0.9688580156\H,2.621903366,4.3823606868,1.3539133426\H,2.6836041204,2.6066046138,1.4036086315\H,4.190041959,3.550867149,1.2815553238\C,1.9531820949,-1.2091595405,-1.7345184349\H,1.9210275821,-2.288647369,-1.8800853668\H,2.1753621227,-0.998472484,-0.6866005012\H,0.996451593,-0.7721404375,-2.0190636451\N,3.0053150632,-0.6917191274,-2.6057763403\C,3.9653204863,-1.5775423491,-3.1487435515\O,3.9714316742,-2.7614964077,-2.9224062633\C,4.9174797913,-0.7718433022,-3.9963217103\H,5.140900692,-1.2978573469,-4.9250811918\H,5.8479761997,-0.6314554237,-3.4326569689\C,4.1963296225,0.5689813931,-4.1642038832\H,3.6287444288,0.5756748967,-5.1097481734\O,5.0105391126,1.7019272872,-4.0830972174\C,5.8306906772,1.8726063195,-5.2320565877\H,6.3704542277,2.8095041541,-5.0950800277\H,6.5474047242,1.0486106857,-5.3290770819\H,5.2142158902,1.9306496706,-6.1370172931\H,2.7917835042,2.6011096638,-3.2248435444\\Version=AM64L-G09RevB.01\HF=-959.1492097\RMSD=0.000e+00\RMSF=3.731e-06\Dipole=-0.1848499,-0.0951841,-0.2929926\Quadrupole=26.0548695,-20.8837491,-5.1711204,32.0342847,-42.0397067,-15.8861221\PG=C01 [X(C18H23N2O2)]\\@

ν_{imag} = - 339.1911 cm^{-1}

Sum of electronic and thermal Free Energies= - 958.808980 Hartrees

TS5 (*E* alkene)

1\1\GINC-R1091\FTS\RM062X\6-31+G(d)\C18H23N2O2(1+)\ROOT\17-Aug-2016\0\\# M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) scf=verytight nosymm freq=noraman geom=checkpoint guess=check opt=(ts,noeigentest,readfc,z-matrix,Maxcycle=500)\\freq&geom\\1,1\C,4.0005902716,-0.8377737709,-3.6567296618\C,2.8940976615,-0.0144868825,-2.9805767224\H,3.5878984874,-1.5138609245,-4.411515983\H,2.902675089,-0.156226993,-1.888107889\H,4.6020459375,-1.4263745239,-2.9600341227\C,4.8830472434,0.1782247094,-4.3469086307\O,1.6043443516,-0.2593245204,-3.4816944741\C,1.0388647211,-1.4599414042,-2.9747636016\H,0.0510443277,-1.5553071574,-3.4248147772\H,1.6461047286,-2.3324008406,-3.2446456875\H,0.9441498053,-1.4069500744,-1.8826082488\C,4.9036563809,2.6566841211,-4.7119098292\H,5.8161638831,2.3707742562,-5.2336709803\H,4.174244285,3.049780028,-5.4254499073\H,5.1320363935,3.4200721854,-3.9659994516\C,2.5928855321,2.5384560585,-2.848514002\O,5.863317633,-0.0169985025,-5.0231616063\N,4.3673489465,1.4587901764,-4.0773964082\H,2.8723698553,3.4990737114,-3.286027641\C,1.2961266785,2.5214925529,-2.0880305608\H,1.1920771427,1.5839914517,-1.5281125271\H,0.4340729555,2.589816092,-2.758869668\C,1.3509701413,3.7220103073,-1.1327512282\H,1.1197274861,4.6396623355,-1.6830206371\H,0.6088343047,3.6257539142,-0.3362320183\C,3.2433030884,1.4251843074,-3.3158473441\C,3.5855248683,5.0420765905,-0.9607712983\C,3.7018320067,2.717861454,-1.0664942797\C,4.8655979593,4.6382367478,-1.3527480606\C,3.2678198035,6.3915457618,-0.9532919205\H,3.6257730968,1.6921713069,-0.7176517945\C,5.8536193533,5.5278051367,-1.7473883737\C,4.2464446206,7.3121556249,-1.346154933\H,2.2809572944,6.7306166676,-0.6485212651\H,5.7558434497,2.6766977415,-1.4338174932\C,5.5184727711,6.8847778582,-1.7352551178\H,6.8385656443,5.188985958,-2.0533892432\H,4.0140275509,8.3723184179,-1.3492011607\H,6.2607206745,7.6159967322,-2.0398606868\N,4.9191037966,3.2295198713,-1.2816982904\C,2.7806221325,3.8238423997,-0.5450293645\C,2.7622202344,3.710402337,0.9969896985\H,2.203777406,4.5576710082,1.4053965706\H,2.2657756664,2.7840709345,1.3027356174\H,3.7749584015,3.7295468397,1.4109130209\\Version=ES64L-G09RevD.01\HF=-959.15224

02\RMSD=3.520e-09\RMSF=6.618e-06\Dipole=-0.356491,-0.2735247,1.7057892
\Quadrupole=14.7561108,13.8670509,-28.6231617,39.9485348,-15.789259,-1
5.7045582\PG=C01 [X(C18H23N2O2)]\\@

ν_{imag} = - 261.6978 cm^{-1}

Sum of electronic and thermal Free Energies= - 958.812223 Hartrees

Compound ***syn,syn,syn*-16'**

1\1\GINC-SPARTAN-RC078\FOpt\RM062X\6-31+G(d)\C18H23N2O2(1+)\UWILLE\20-
Feb-2019\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm scrf=(cpcm,solvent
=dichloromethane) opt=(calcfc,maxcycle=500) freq=noraman\\geom&freq\\1
,1\C,3.0456623292,1.372551275,-4.6744551514\C,2.5447027038,1.151268768
5,-3.2410746782\H,3.028060873,2.4492971545,-4.8936022565\H,2.116152689
4,0.1350765718,-3.1473687776\H,2.508516478,0.8310749165,-5.4531859949\
C,4.4792593709,0.9332171256,-4.6143444012\O,1.6660509421,2.1022989199,
-2.7528302814\C,0.3740852454,2.0377833544,-3.3413300185\H,-0.222921587
7,2.8062265228,-2.8497706554\H,0.4213088071,2.2476797341,-4.4163431112
\H,-0.0782757132,1.0522257801,-3.1761203077\C,6.1971736713,0.499443021
1,-2.791666537\H,6.16651902,-0.5046635342,-2.3622439172\H,6.8136704009
,0.4988478122,-3.6889503527\H,6.5720473676,1.2255259817,-2.0749786415\
C,3.9603157651,1.2458389184,-0.9541499827\O,5.2659292175,0.6729121456,
-5.4719207217\N,4.8402864177,0.8737104153,-3.1975255645\C,2.6563543007
,1.1818647864,-0.1390690705\H,2.8884494816,0.6812049168,0.8049452794\H
,1.885077086,0.5864930074,-0.6345518337\C,2.1998359093,2.6345038717,0.
1276773 572\H,1.3129410612,2.8815412573,-0.4600112272\H,1.9413650708,2.
7598829421,1.1833454153\C,3.8198582259,1.116438136,-2.4208279948\C,3.2
523565184,4.2844953856,-1.5748561762\C,4.5992724703,2.6514935753,-0.55
48089564\C,4.4327342928,4.1259316846,-2.3055333159\C,2.2214470329,5.06
55510872,-2.0820426658\H,5.2346633146,2.4785055655,0.3170471812\C,4.60
19377066,4.7082570578,-3.5596395069\C,2.379520366,5.6677986344,-3.3330
202372\H,1.2983710147,5.1973865355,-1.5208997644\H,6.2114810293,3.7222
113566,-1.3422270255\C,3.5592428455,5.4889014065,-4.0633480651\H,5.517
6343812,4.5551523059,-4.124804011\H,1.5787182344,6.2742120701,-3.74587
21026\H,3.6647108349,5.9555365847,-5.0384514051\N,5.3517626122,3.26759
11998,-1.6386990803\C,3.3763880134,3.5609058591,-0.2452383701\C,3.6987
266093,4.5746799636,0.8598768391\H,2.8586962582,5.2641341021,0.9965272
86\H,3.8829221885,4.061492078,1.8101900599\H,4.5847987642,5.1662441636
,0.6029697573\H,4.6657015393,0.4649992533,-0.6458929155\\Version=AM64L
-G09RevB.01\HF=-959.1636579\RMSD=0.000e+00\RMSF=1.004e-05\Dipole=0.042
6941,-2.2705731,0.6068657\Quadrupole=29.8940819,-19.4157654,-10.478316
5,17.4931185,-16.8158432,-11.2319137\PG=C01 [X(C18H23N2O2)]\\@

Sum of electronic and thermal Free Energies= - 958.819139 Hartrees

Compound ***syn,syn,anti*-16'**

1\1\GINC-SPARTAN-RC123\FOpt\RM062X\6-31+G(d)\C18H23N2O2(1+)\UWILLE\13-
Jun-2019\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm scrf=(cpcm,solvent
=dichloromethane) freq=noraman opt=(calcfc,maxcycle=500)\\geom&freq\\1
,1\C,3.0000580944,1.8328420275,-2.3467144252\C,1.5316910383,1.91446314
86,-1.892284647\H,1.3071224174,1.1572407288,-1.137391829\H,0.833292724
6,1.7850682885,-2.722545652\C,1.4718270758,3.311692591,-1.2573889407\H
,1.3036669728,4.0655688245,-2.0328189631\H,0.6528857431,3.3885015193,-
0.5366589782\C,3.5215470755,0.5553690994,-2.8632145544\C,3.6170646282,
4.7254165474,-1.1215173622\C,3.772420162,2.3554859001,-1.076728897\C,4
.884374525,4.319626506,-1.5547605887\C,3.2403581761,6.0574073278,-1.20
8642976\H,3.8435074221,1.5539971246,-0.3332948976\C,5.789905662,5.2295
188139,-2.0959463772\C,4.1408006937,6.9870267273,-1.7436759119\H,2.255
1831194,6.3754109642,-0.8731462513\H,5.6746809914,2.4591602726,-1.9754
281955\C,5.3989470536,6.5687167257,-2.1835369451\H,6.7699578756,4.9081
160687,-2.4374573397\H,3.8593436464,8.0326517285,-1.8205614143\H,6.089
5077653,7.2947786391,-2.6031583273\N,5.0729623678,2.9499499284,-1.3205
595843\C,2.8548499425,3.5289078741,-0.5876420085\C,2.7651197906,3.5602

374654,0.9413137623\H,2.2014188997,4.4404970407,1.2672768274\H,2.25459
25955,2.66490259,1.3152874193\H,3.7640645688,3.6055907534,1.3882056552
\C,2.5505592,-1.0852191937,-1.2416136832\H,2.8849548462,-2.0893134882,
-0.986150627\H,2.7051329659,-0.4152853787,-0.3980626053\H,1.4999125404
,-1.1110062172,-1.5338166422\N,3.3574155164,-0.6419780749,-2.383154565
8\C,4.1119211596,-1.6504292547,-3.1553032663\O,4.0162686644,-2.8097094
94,-2.9062968934\C,4.919834934,-0.9104618821,-4.1828512773\H,4.8076877
309,-1.3858477099,-5.1582454294\H,5.9738213221,-0.9542663887,-3.884902
1641\C,4.4017923334,0.5265867318,-4.1015247596\H,3.7492652632,0.764485
8577,-4.9578993971\O,5.3804681319,1.5078946244,-3.9346463544\C,6.05664
64204,1.8416823162,-5.1455487673\H,6.7728122508,2.6226558961,-4.893085
1682\H,6.5874473085,0.9706156882,-5.5457196918\H,5.3413903943,2.215552
9063,-5.8861411756\H,3.17073699,2.5771128363,-3.1346381296\\Version=AM
64L-G09RevB.01\HF=-959.1627304\RMSD=0.000e+00\RMSF=3.618e-06\Dipole=-0
.9215938,-3.1736966,-1.9748045\Quadrupole=19.2286816,-32.7921704,13.56
34889,4.6448561,-52.8264415,-9.2713466\PG=C01 [X(C18H23N2O2)]\\@
Sum of electronic and thermal Free Energies= - 958.820486 Hartrees

Compound **18**

1\1\GINC-SPARTAN-RC150\FOpt\RM062X\6-31+G(d)\C18H23N2O2(1+)\UWILLE\22-
May-2019\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm scrf=(cpcm,solvent
=dichloromethane) freq=noraman opt=(calcfc,maxcycle=500)\\geom&freq\\1
,1\C,0.3808210156,-1.7792401888,-3.70543328\C,0.8744557312,-0.39246089
61,-4.1322535972\H,1.1169907648,-2.2788789646,-3.065604479\H,0.7274098
326,-0.2352847657,-5.2101060015\H,0.1267352478,-2.4399504466,-4.538627
0857\C,-0.8471592016,-1.5020569945,-2.8845020433\O,2.1879625727,-0.080
8602219,-3.767521582\C,3.148210619,-0.6859623341,-4.6283705818\H,4.125
9028649,-0.3432795638,-4.2921103439\H,3.099059858,-1.7790063387,-4.561
1382557\H,2.9792358511,-0.3750071725,-5.666454126\C,-1.9672942822,0.51
21323617,-1.8418112189\H,-2.9236818857,0.5021965696,-2.3687586164\H,-2
.0339492783,-0.1255077115,-0.9608052544\H,-1.6956429221,1.5261887065,-
1.5548003027\O,-1.6703900731,-2.2184651088,-2.4073811455\N,-0.93163756
32,-0.0440064559,-2.711983252\C,-1.0213780871,2.8495256737,-4.03181639
37\H,-0.9868120289,3.8597623453,-3.616041198\H,-1.9764417148,2.4201319
903,-3.7122449073\C,-0.9690864768,2.9456645973,-5.5643825529\H,-1.8719
93686,3.4683767122,-5.904685576\H,-0.1169346733,3.56440522,-5.85936441
57\C,-0.0259076182,0.5819375749,-3.3999026643\C,0.0726395269,1.1483272
582,-7.1407923701\C,-1.3961179649,-0.5477548648,-6.608362514\H,-2.6175
31822,0.7278506433,-5.4431992352\C,-0.2596651071,-0.2347198852,-7.3909
613546\C,-1.9737411724,-1.8225792518,-6.5998320114\C,0.3331946441,-1.2
423262227,-8.1709121907\C,-1.3751980019,-2.794913808,-7.3894428442\H,-
2.8503325982,-2.0424874384,-5.9966636654\C,-0.2295121196,-2.5104161325
,-8.1631802965\H,1.2153519774,-1.0287694594,-8.7692956083\H,-1.7949342
341,-3.7962880543,-7.4092245792\H,0.2138941511,-3.3000911263,-8.762339
5429\C,-0.8495380931,1.6159042366,-6.2370455676\C,1.2317165499,1.87494
61558,-7.7506005097\H,1.3327844005,2.8869696353,-7.3512417155\H,2.1733
555634,1.3461666986,-7.5632397043\H,1.116443602,1.954518921,-8.8374367
614\N,-1.7204878491,0.5853072106,-5.8908230788\C,0.1618847306,2.054931
2766,-3.4217933024\H,1.0881574513,2.2670757218,-3.9630161912\H,0.31178
2419,2.3707292979,-2.3806133626\\Version=AM64L-G09RevB.01\HF=-959.1766
497\RMSD=0.000e+00\RMSF=5.690e-06\Dipole=-0.1376458,1.7578632,2.601087
7\Quadrupole=-13.7129724,-13.8091219,27.5220943,-8.227498,-2.6450628,-
8.6439571\PG=C01 [X(C18H23N2O2)]\\@
Sum of electronic and thermal Free Energies= - 958.836685 Hartrees

TS6

1\1\GINC-SPARTAN-RC147\FTS\RM062X\6-31+G(d)\C18H23N2O2(1+)\UWILLE\21-M
ay-2019\0\\#p M062X/6-31+G* scf=(qc,direct) scrf=(cpcm,solvent=dichlor
omethane) nosymm freq=noraman opt=(ts,noeigentest,calcfc,maxcycle=500)
\\geom&freq\\1,1\C,0.4286668901,-1.8502626263,-4.0101757394\C,0.862356

2943,-0.4203766379,-4.3544352839\H,1.1632928786,-2.3382210722,-3.36235
26855\H,1.0402488753,-0.2746814633,-5.4277280803\H,0.2583331252,-2.484
7755603,-4.8831647592\C,-0.8609820763,-1.6854471848,-3.2426775661\O,1.
9842192865,-0.0014841706,-3.620358143\C,3.2089002524,-0.4434246943,-4.
1917930236\H,4.0047067359,-0.072824694,-3.5463511872\H,3.2548853561,-1
.5382993824,-4.2340511532\H,3.3278430527,-0.0335547087,-5.2021422702\C
,-2.3198743247,0.1818993998,-2.4386398166\H,-3.1851343923,0.228816763,
-3.1070424725\H,-2.5325552728,-0.5245473309,-1.636870386\H,-2.12021545
22,1.1682288753,-2.0193979867\O,-1.5680433122,-2.5210461973,-2.7437191
67\N,-1.1455295624,-0.2955956136,-3.157400665\C,-0.9204775659,2.977815
7213,-4.191013991\H,-0.7160129691,3.934426512,-3.7044893083\H,-1.98318
21471,2.7710510425,-4.0173336144\C,-0.6183586994,3.0967137078,-5.69166
5429\H,-1.3666469613,3.740014081,-6.1705715763\H,0.3562747923,3.573985
8794,-5.8388208388\C,-0.306192174,0.4627590874,-3.8874215849\C,0.00546
23858,1.2217340929,-7.4184466433\C,-1.2991698678,-0.4389801348,-6.4687
887858\H,-2.2598759217,0.9786034443,-5.2957157626\C,-0.4232673666,-0.1
738767545,-7.5322851514\C,-1.9578661023,-1.6500683879,-6.3071118675\C,
-0.1455551605,-1.1836827152,-8.4537511632\C,-1.679698674,-2.645354233,
-7.2457769515\H,-2.6655142277,-1.8199160018,-5.4996099452\C,-0.7785555
128,-2.4171776258,-8.2947688674\H,0.5347219859,-1.0110880695,-9.282814
7936\H,-2.1724788155,-3.6085268345,-7.160900239\H,-0.5822228762,-3.213
0138175,-9.0065026256\C,-0.6114988281,1.744757043,-6.3329158909\C,0.93
87052991,1.9082503853,-8.3613250517\H,1.1429896489,2.9335396361,-8.044
4494327\H,1.8906038252,1.3700041518,-8.4245078133\H,0.5123617585,1.941
3489544,-9.3698714668\N,-1.3363220221,0.7151774813,-5.6441726681\C,-0.
035252539,1.9115957804,-3.5376641659\H,1.0071017916,2.1057182612,-3.80
45631901\H,-0.09324441,1.9786266112,-2.4450907963\\Version=AM64L-G09Re
vB.01\HF=-959.1649372\RMSD=0.000e+00\RMSF=3.406e-06\Dipole=0.0166787,1
.9827247,0.0698257\Quadrupole=-31.0287707,-32.4486811,63.4774518,-6.87
10077,1.0073264,-10.7722927\PG=C01 [X(C18H23N2O2)]\\@

ν_{imag} = - 210.9669 cm^{-1}

Sum of electronic and thermal Free Energies= - 958.822636 Hartrees

Compound **19**

1\1\GINC-SPARTAN-RC009\FOpt\RM062X\6-31+G(d)\C18H23N2O2(1+)\UWILLE\16-
May-2019\0\\#p M062X/6-31+G* scrf=(cpcm,solvent=dichloromethane) scf=(
qc,direct) nosymm freq=noraman opt=(calcfc,maxcycle=500)\\geom&freq\\1
,1\C,0.8910379453,-1.4810299822,-3.3048844464\C,0.863182831,-0.3213367
916,-4.3025873782\H,1.4260660346,-1.1868435198,-2.3937765621\H,0.86046
17179,-0.7273493423,-5.324113283\H,1.3380719229,-2.3970926198,-3.69397
23641\C,-0.5610400735,-1.6988762661,-2.9462342298\O,1.9016223951,0.606
6442697,-4.1720382132\C,3.1158849414,0.1557927911,-4.754226597\H,3.847
9902183,0.9500284454,-4.6099425679\H,3.470801515,-0.7602037962,-4.2669
915998\H,2.9798972828,-0.0307493841,-5.8278603295\C,-2.670429002,-0.42
57109444,-2.9898317723\H,-3.2367842526,0.1068376913,-3.7588132534\H,-3
.1190394101,-1.4094579531,-2.8457325663\H,-2.73192291,0.1308486145,-2.
0499930997\O,-1.0382083974,-2.6251985508,-2.3203866331\N,-1.2908027531
,-0.6241958822,-3.4078331109\C,-0.587679883,2.9799568962,-4.1342685659
\H,-0.237735424,3.8403334532,-3.5595939317\H,-1.6477378946,3.168437627
7,-4.3458714183\C,0.1872110406,2.8836569512,-5.449452954\H,-0.01259218
14,3.7606708758,-6.073893223\H,1.2643154724,2.8531466897,-5.2501944375
\C,-0.5024514744,0.3809880414,-4.050835755\C,0.1146944358,1.1228885891
,-7.3786899508\C,-1.3132912949,-0.42443511,-6.3852399841\H,-2.02089984
57,1.169897631,-5.3001498736\C,-0.5713154231,-0.1650900583,-7.53732033
73\C,-2.0906587041,-1.5551604657,-6.2150692557\C,-0.5842433216,-1.0813
800222,-8.583116669\C,-2.0920005904,-2.4718534304,-7.272483099\H,-2.67
64475758,-1.739421052,-5.3219489419\C,-1.3508885086,-2.2390081315,-8.4
335881471\H,-0.0167876273,-0.8993971744,-9.4908095626\H,-2.6836530467,
-3.3769289245,-7.1842271591\H,-1.3765542228,-2.9701656501,-9.235456571
\C,-0.2080059732,1.6422264517,-6.1858026131\C,1.0244497259,1.724761115

1,-8.3967279951\H,1.4370004572,2.674122271,-8.0494106463\H,1.853069875
2,1.0421784601,-8.6131533216\H,0.4856414681,1.8985809665,-9.3340443112
\N,-1.1179936665,0.7004968738,-5.4594399559\C,-0.4397505278,1.71497560
5,-3.2742824027\H,0.5191199923,1.7267382465,-2.7511390252\H,-1.2252783
272,1.7059684946,-2.5146895257\\Version=AM64L-G09RevB.01\HF=-959.17281
81\RMSD=0.000e+00\RMSF=4.074e-06\Dipole=-0.1629922,2.2025556,-1.573979
1\Quadrupole=-38.0604176,-47.4339503,85.494368,-2.2955253,6.2581597,-1
0.3729509\PG=C01 [X(C18H23N2O2)]\\@
Sum of electronic and thermal Free Energies= - 958.828848 Hartrees

Data for Scheme 5

Reactant association complex

See Table 6, entry 1.

Compound **20'** (pre-*anti*)

1\1\GINC-SPARTAN-RC122\FOpt\RM062X\6-31+G(d)\C17H21N2O2(1+)\UWILLE\30-
May-2019\0\\#p M062X/6-31+G* scf=(qc,direct) scrf=(cpcm,solvent=dichlo
romethane) nosymm freq=noraman opt=(calcfc,maxcycle=500)\\geom&freq\\1
,1\C,1.715354481,0.8057532274,-4.0825021882\C,2.0194185234,1.354184067
2,-2.6878157543\H,0.884448923,1.3215559119,-4.5767909531\H,1.501438811
7,-0.2664931016,-4.0669731734\C,2.9761286751,1.0524771092,-4.865788645
3\C,5.2350766869,2.127491166,-4.4608028755\H,5.8832286917,2.3288518562
,-3.6094476259\H,5.6088645553,1.2763210117,-5.0298661587\H,5.173236497
,3.0015719862,-5.1112586931\O,3.2913490748,0.7761391482,-5.9813136206\
N,3.8980097422,1.7866964581,-3.9846540098\C,4.2919119724,4.2715943531,
-1.9079419418\H,5.0738622127,4.396948416,-2.6642511441\H,4.70461215,4.
6353709079,-0.96229605\C,3.0611583265,5.1023538669,-2.299266764\H,2.25
48114184,4.9332216469,-1.5753679411\H,3.3278513073,6.1625210712,-2.222
3324701\C,3.3616468906,2.0540477966,-2.8332157683\C,1.3115835149,4.236
3799337,-4.097548609\C,3.3392695741,4.8770148421,-4.8347115204\C,1.389
9518829,3.9878989019,-5.4919897146\C,0.1035687174,3.9566526529,-3.4280
355808\H,4.3380602734,5.2722556764,-4.9709680733\C,0.3256330157,3.4430
419828,-6.2235467616\C,-0.9515905319,3.4163879397,-4.144276444\H,-0.00
24626841,4.1658187959,-2.3658142449\H,2.9674404449,4.3759134064,-6.863
1037704\C,-0.8394054533,3.1568711283,-5.5304156733\H,0.4136239699,3.25
64609696,-7.2897340966\H,-1.8864616649,3.1951743505,-3.6383117234\H,-1
.686070642,2.7328486565,-6.061668234\N,2.6401320163,4.3804188629,-5.90
60288778\C,2.5849162146,4.7782044161,-3.6882337749\C,3.9947377884,2.76
90885522,-1.6952644953\H,4.9319917778,2.247779729,-1.4577064515\H,3.33
09324031,2.642463388,-0.8354850861\H,1.2610319027,2.0640818674,-2.3372
957881\O,2.2657625881,0.364198974,-1.7219375722\C,1.0738638915,-0.1306
482432,-1.1178248869\H,0.4136514859,-0.5826869539,-1.8672199824\H,1.38
48470215,-0.889431095,-0.4007182733\H,0.5451504729,0.677774217,-0.6007
544576\\Version=AM64L-G09RevB.01\HF=-919.8787123\RMSD=0.000e+00\RMSF=2
.533e-06\Dipole=1.8375004,-0.3108968,1.0350589\Quadrupole=9.8894935,-1
6.48847,6.5989764,39.9047624,-41.262578,-35.0618543\PG=C01 [X(C17H21N2
O2)]\\@
Sum of electronic and thermal Free Energies= - 919.563865 Hartrees

***TS7*$_{\text{anti}}$**

1\1\GINC-SPARTAN-RC052\FTS\RM062X\6-31+G(d)\C17H21N2O2(1+)\UWILLE\05-J
un-2019\0\\#p M062X/6-31+G* freq=noraman scrf=(cpcm,solvent=dichlorome
thane) scf=(qc,direct) nosymm opt=(ts,noeigentest,calcfc,maxcycle=500)
\\geom&freq\\1,1\C,2.5915112637,0.4747154124,-4.4586029215\C,2.3037127
22,1.4504243858,-3.3140979015\H,1.9908771682,0.66285025,-5.352678464\H
,2.4330417655,-0.5642431782,-4.1571567775\C,4.0522356595,0.6863345333,
-4.7809504825\C,5.8854354109,2.2355087444,-4.1130537042\H,6.4692623908
,1.4492424374,-4.590408678\H,5.9396859863,3.1399975041,-4.7287502252\H

,6.2890681179,2.4444629861,-3.1210167234\O,4.7525096791,0.0680973159,-
5.5463616422\N,4.5148671044,1.7652900956,-4.0090438366\C,4.2221420857,
4.55960159,-2.0737723473\H,5.0154298409,4.7450604315,-2.8072114153\H,4
.5996549927,4.9030839379,-1.1077900317\C,2.949474475,5.3340628429,-2.4
400907119\H,2.2670300119,5.3744434309,-1.5844289912\H,3.2006220086,6.3
696358678,-2.7032721859\C,3.5266265659,2.3812816109,-3.2825887008\C,0.
9086867673,4.5385519868,-3.9016894191\C,2.9943786754,3.9319863176,-4.5
623324739\C,0.8205729352,3.7908169874,-5.112333155\C,-0.2762245619,4.9
761836409,-3.2582113883\H,4.0116771511,4.1297609436,-4.8798318634\C,-0
.41731797,3.4769675334,-5.7013677812\C,-1.4837590256,4.6736064569,-3.8
409603646\H,-0.2242029086,5.5429047501,-2.3334145909\H,2.3317373785,3.
0421031733,-6.3900353888\C,-1.5469936094,3.9316421156,-5.0539948677\H,
-0.4754686039,2.9042026629,-6.6209380064\H,-2.4085093524,5.0000643104,
-3.3767960557\H,-2.5216087646,3.7143609308,-5.4808327957\N,2.083287574
2,3.4524317265,-5.4983599072\C,2.2803874087,4.6765645877,-3.5960746936
\C,3.8894775206,3.0671314714,-1.9823080752\H,4.7245128039,2.5069267863
,-1.5460701446\H,3.0371794099,2.9376815076,-1.3080748706\H,1.378370566
3,2.0204222907,-3.4652594211\O,2.2695002223,0.8103777145,-2.060973093\
C,1.0089184089,0.2187575706,-1.7789472399\H,0.753943155,-0.5482069603,
-2.5204209839\H,1.0947377929,-0.2440772331,-0.796049044\H,0.223002777,
0.9841605296,-1.7617416357\\Version=AM64L-G09RevB.01\HF=-919.8615963\R
MSD=0.000e+00\RMSF=6.442e-06\Dipole=-0.2859913,1.4942846,0.1754159\Qua
drupole=-10.1530671,0.0157223,10.1373448,36.4719318,-22.7842977,-47.89
16226\PG=C01 [X(C17H21N2O2)]\\@

ν_{imag} = - 345.7924 cm^{-1}

Sum of electronic and thermal Free Energies= - 919.547100 Hartrees

Compound *anti*-**21'**

1\1\GINC-SPARTAN-RC122\FOpt\RM062X\6-31+G(d)\C17H21N2O2(1+)\UWILLE\29-
May-2019\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=dichloromethane)\\geom&freq\\1
,1\C,2.6750688444,0.3094073114,-4.4199359427\C,2.3778180609,1.24058376
8,-3.2415003271\H,2.0247990773,0.4794522404,-5.2835380553\H,2.58675325
68,-0.7444168849,-4.1461634506\C,4.1101461453,0.6253902723,-4.79711850
85\C,5.7662595857,2.4041608954,-4.3706061648\H,6.263659923,2.591876951
7,-3.4155450621\H,6.3742306076,1.7218986713,-4.9654893633\H,5.67005173
61,3.3511569591,-4.9153787473\O,4.8239575721,-0.0254925804,-5.54563303
85\N,4.4761848158,1.7781652567,-4.1639730443\C,4.0972704006,4.45310826
93,-1.9632879158\H,4.8277329805,4.7881030237,-2.7104082859\H,4.4965149
506,4.7357037696,-0.9863011424\C,2.7486601642,5.1507612315,-2.18548244
77\H,2.1074125383,5.0591647599,-1.2995435094\H,2.8744556436,6.22680189
54,-2.3656506155\C,3.4163818498,2.3959697974,-3.3806403174\C,0.7863565
056,4.6797391975,-3.8559746533\C,2.8138273433,3.599226184,-4.215162114
5\C,0.7095168643,3.870655576,-5.0526619145\C,-0.3488006449,5.447784717
1,-3.4354464069\H,3.6627335577,4.1337421279,-4.6688033299\C,-0.4713802
884,3.8338137466,-5.8337341663\C,-1.4765210449,5.3917797209,-4.1955326
249\H,-0.2939799674,6.0522955726,-2.53581093\H,2.1133012959,2.74298851
45,-6.0953997572\C,-1.5256125083,4.5860047744,-5.3877648763\H,-0.53103
00608,3.2330110973,-6.7341510238\H,-2.3582489942,5.9573060416,-3.91577
69702\H,-2.4492434648,4.5780029384,-5.9588532959\N,1.8677394456,3.2376
41408,-5.2449334825\C,2.0599393043,4.5488478669,-3.3577584743\C,3.8939
53929,2.9368240523,-2.0128262496\H,4.7985548385,2.3966379761,-1.721704
4152\H,3.1318175958,2.673806826,-1.2726481008\H,1.3532021237,1.6399399
535,-3.2511181125\O,2.6213436991,0.5830347741,-2.0198656412\C,1.549732
1507,-0.2490735736,-1.6095736815\H,1.3556953997,-1.0479779578,-2.33559
42582\H,1.8442574011,-0.6943464785,-0.6589186233\H,0.6349606868,0.3416
898166,-1.4720881685\\Version=AM64L-G09RevB.01\HF=-919.8760876\RMSD=0.
000e+00\RMSF=5.080e-06\Dipole=-2.7160906,3.3820262,0.0663793\Quadrupol
e=-34.1564753,22.7660263,11.390449,28.1927628,-0.7323317,-65.5448641\P
G=C01 [X(C17H21N2O2)]\\@

Sum of electronic and thermal Free Energies= - 919.559729 Hartrees

Compound **20'** (pre-*syn*)

1\1\GINC-SPARTAN-RC120\FOpt\RM062X\6-31+G(d)\C17H21N2O2(1+)\UWILLE\22-
May-2019\0\\#p M062X/6-31+G* scf=(qc,direct) scrf=(cpcm,solvent=dichlo
romethane) nosymm freq=noraman opt=(calcfc,maxcycle=500)\\geom&freq\\1
,1\C,1.6308909492,0.9088084942,-3.9994876331\C,2.0686808348,1.28456712
67,-2.5762326688\H,0.8882748415,1.623754412,-4.3782069401\H,2.33589267
29,0.3656443775,-2.0190434498\H,1.2376079451,-0.103159273,-4.107185631
5\C,2.8960914336,1.0571700752,-4.7999309046\O,1.2143335775,2.074744805
5,-1.8207189492\C,0.0043733272,1.4117182335,-1.4751724837\H,-0.5569964
854,2.100327606,-0.8440117346\H,-0.5826058243,1.1806705863,-2.37208471
99\H,0.2168011782,0.4895115751,-0.9209420128\C,5.1887696225,2.07438541
81,-4.4774123654\H,5.8185959143,2.4605368558,-3.6785076579\H,5.6154471
799,1.1582053976,-4.8878896532\H,5.0797585011,2.813073927,-5.272373374
6\O,3.1853833373,0.7272016325,-5.9084796642\N,3.8683501442,1.750705089
7,-3.9462130174\C,4.2256654104,4.2823837795,-1.8949414179\H,4.99792549
9,4.4563454386,-2.6512537914\H,4.6171005994,4.6731289465,-0.9511576737
\C,2.9423332338,5.030808827,-2.2830951376\H,2.1300189755,4.7486088375,
-1.6029698394\H,3.1163540211,6.1030579759,-2.1353927093\C,3.3832377822
,2.0066480247,-2.7679630791\C,1.2558872906,4.284081059,-4.1857029487\C
,3.3503020163,4.8217859881,-4.8070764948\C,1.3929276526,4.0440397854,-
5.5759210372\C,0.0058921444,4.0558882355,-3.5782752029\H,4.3760806092,
5.1579690032,-4.8900148034\C,0.347457814,3.5347983157,-6.3601480581\C,
-1.0341454412,3.5641390334,-4.3478757363\H,-0.1328745761,4.2484334343,
-2.5183943892\H,3.0558853735,4.3658458234,-6.8610383469\C,-0.860856656
1,3.2942876211,-5.7261535344\H,0.4817790052,3.3410147797,-7.4202201291
\H,-2.0016524771,3.3798158994,-3.8898398814\H,-1.6947628606,2.90044978
68,-6.2996057993\N,2.680274597,4.3776362454,-5.9222276811\C,2.53344302
05,4.7488291241,-3.7033029396\C,4.0404663797,2.7605173235,-1.669621945
9\H,5.0242853275,2.3060441134,-1.4939488481\H,3.4330925898,2.602139299
4,-0.7754623947\\Version=AM64L-G09RevB.01\HF=-919.8782785\RMSD=0.000e+
00\RMSF=9.653e-06\Dipole=2.5383498,-1.5183487,1.3986992\Quadrupole=17.
9592191,-22.2445153,4.2852961,35.9213202,-42.5854838,-28.8149524\PG=C0
1 [X(C17H21N2O2)]\\@

Sum of electronic and thermal Free Energies= - 919.563617 Hartrees

***TS7*$_{syn}$**

1\1\GINC-SPARTAN-RC011\FTS\RM062X\6-31+G(d)\C17H21N2O2(1+)\UWILLE\17-M
ay-2019\0\\#p M062X/6-31+G* scf=(qc,direct) scrf=(cpcm,solvent=dichlor
omethane) nosymm freq=noraman opt=(ts,noeigentest,calcfc,maxcycle=500)
\\geom&freq\\1,1\C,2.4613419935,0.4766383083,-4.4514939399\C,2.3045762
449,1.3056940867,-3.1740487466\H,1.8280948944,0.8614893287,-5.25735958
84\H,2.5137283766,0.6591381866,-2.3007921525\H,2.2556824374,-0.5879790
691,-4.3256817727\C,3.915382826,0.6798141525,-4.8121723837\O,1.1055860
212,1.9810608098,-2.9903095952\C,-0.0128510816,1.1206468611,-2.8394307
69\H,-0.8728081788,1.76393818,-2.6498037278\H,-0.1889766741,0.54126245
47,-3.7537139693\H,0.1330549616,0.4366112809,-1.9937324924\C,5.7997495
624,2.1647324124,-4.1399313676\H,6.1787669482,2.5257326571,-3.18366881
59\H,6.4028521816,1.3242391805,-4.4825647521\H,5.8551406031,2.96576349
99,-4.8859021998\O,4.583722979,0.099767688,-5.6316466858\N,4.430133056
,1.7024927178,-3.9874522781\C,4.1507702248,4.4936824379,-2.0079109243\
H,4.9272121353,4.6976258272,-2.7545484485\H,4.5471155021,4.8248765233,
-1.0450500167\C,2.8675313574,5.2632665111,-2.3317134885\H,2.1864563118
,5.2468848609,-1.4728927185\H,3.1045967189,6.3171021433,-2.5286769125\
C,3.4740913668,2.2884446537,-3.2090956162\C,0.8318627957,4.6865602427,
-3.8992490241\C,2.8827289019,3.9057089769,-4.4847116263\C,0.729223265,
3.9659314032,-5.1200927309\C,-0.3311993371,5.2146404995,-3.294832089\H
,3.9183362684,4.0503926769,-4.7695767359\C,-0.5049869599,3.7659301236,

-5.7594433294\C,-1.5405817723,5.0255515362,-3.9266724995\H,-0.26733486
,5.7575841859,-2.3561277315\H,2.2226836851,3.1270599055,-6.3602059462\
C,-1.6200855661,4.3063930779,-5.1492422364\H,-0.5767147321,3.209233535
3,-6.6883509759\H,-2.4509380352,5.4241529623,-3.4908631814\H,-2.592092
687,4.175287364,-5.6156040798\N,1.9720980601,3.516243957,-5.4604720263
\C,2.1958720407,4.6751307319,-3.523689742\C,3.8504367511,2.9928441514,
-1.9263432333\H,4.7096897573,2.4525624501,-1.5101024209\H,3.0116506558
,2.8478715263,-1.2360880294\\Version=AM64L-G09RevB.01\HF=-919.8591349\
RMSD=0.000e+00\RMSF=7.093e-06\Dipole=0.7788641,0.26179,0.9249331\Quadr
upole=-0.3654444,-5.190055,5.5554994,33.6369173,-23.2955749,-39.564341
7\PG=C01 [X(C17H21N2O2)]\\@

ν_{imag} = - 336.8471 cm^{-1}

Sum of electronic and thermal Free Energies= - 919.544356 Hartrees

Compound *syn*-**21'**

1\1\GINC-SPARTAN-RC016\FOpt\RM062X\6-31+G(d)\C17H21N2O2(1+)\UWILLE\16-
May-2019\0\\#p M062X/6-31+G* nosymm scrf=(cpcm,solvent=dichloromethane
) opt=(calcfc,maxcycle=500) scf=(qc,direct) freq=noraman\\geom&freq\\1
,1\C,2.5089268578,0.3204890278,-4.2951080512\C,2.4036681231,1.24666548
41,-3.0828185028\H,1.7672639821,0.5691298394,-5.0629196894\H,2.7562372
22,0.7012169069,-2.1933112792\H,2.4101385343,-0.7405040817,-4.05655544
41\C,3.9026038161,0.6108025794,-4.8265424339\O,1.149999359,1.812777566
5,-2.8242932289\C,0.1850505466,0.8663483833,-2.3929298914\H,-0.7301693
969,1.4207941885,-2.1836243671\H,-0.010760393,0.1212928152,-3.17324810
48\H,0.5245481284,0.3580545524,-1.4815282333\C,5.636048214,2.341230905
3,-4.606911422\H,6.0622570636,2.9029150114,-3.7731046203\H,6.331252124
9,1.5530593663,-4.8984648616\H,5.4941303764,3.0141559637,-5.4615174785
\O,4.5070265082,-0.0242796107,-5.6772180417\N,4.3868587715,1.725160543
9,-4.1989503752\C,4.0007110905,4.4514675617,-1.8515510336\H,4.67390285
26,4.9231838727,-2.5780334585\H,4.3812733711,4.7083583509,-0.859989611
1\C,2.5797336276,5.0037928142,-2.0150555458\H,1.9417808073,4.683055551
3,-1.1790281525\H,2.5639619454,6.1005707965,-2.0094027104\C,3.41607318
91,2.3893525478,-3.3420964341\C,0.7701998817,4.7212487852,-3.891779926
9\C,2.7861439101,3.5903549249,-4.1306885065\C,0.7644260516,3.952498862
9,-5.1126822667\C,-0.3677929858,5.5123873414,-3.5356673365\H,3.6380922
238,4.1782414264,-4.5154335819\C,-0.3473886718,3.9867045203,-5.9888631
661\C,-1.4328935083,5.5237303762,-4.3855820052\H,-0.3668515367,6.08359
90837,-2.6127913796\H,2.2090426048,2.8133973468,-6.0829158207\C,-1.410
9098772,4.7611320978,-5.6046431411\H,-0.3529017129,3.4166579293,-6.910
9863092\H,-2.3153967235,6.109953174,-4.1549166036\H,-2.2844757847,4.80
35472193,-6.2484559108\N,1.9085505304,3.2756398301,-5.2319660761\C,1.9
826198009,4.5033933204,-3.2810947889\C,3.9953439974,2.9266013315,-2.00
59595753\H,4.9984403944,2.5135624036,-1.8637982129\H,3.3748296841,2.52
02640895,-1.1988324208\\Version=AM64L-G09RevB.01\HF=-919.8796917\RMSD=
0.000e+00\RMSF=6.738e-06\Dipole=-1.5287279,2.599519,0.7929874\Quadrupo
le=-24.1305976,18.3623061,5.7682915,27.5795022,-3.6909789,-61.384503\P
G=C01 [X(C17H21N2O2)]\\@

Sum of electronic and thermal Free Energies= - 919.563148 Hartrees