Supporting Information

Formation of 4*H*-1,2-Benzoxazines by Intramolecular Cyclization of Nitroalkanes. Scope of Aromatic Oxygen-functionalization Reaction Involving a Nitro Oxygen Atom, and Mechanistic Insights

Satoshi Nakamura, Hiromichi Sugimoto and Tomohiko Ohwada*

Graduate School of Pharmaceutical Sciences, The University of Tokyo,

7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

E-mail: ohwada@mol.f.u-tokyo.ac.jp; Fax: +81-3-5841-4735

General Methods

Melting points were determined with a Yanaco micro melting point apparatus without correction. ¹H- and ¹³C-NMR spectra were recorded on a Bruker ultra shield (400 MHz, AV400M). Chemical shifts were calibrated with 1% tetramethylsilane as an internal standard or with the solvent peak, and are shown in ppm (δ) values, and coupling constants are shown in hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, dt = double triplet, dq = double quartet, m = multiplet, and brs = broad singlet. Low-resolution mass spectra (LRMS) and high-resolution mass spectra (HRMS) were recorded on a JEOL JMS-O1SG-2 spectrometer or Bruker microTOF.

Cyclization reaction of 2-nitro-3-phenylpropane **1**.

Scheme S1.

To a suspension of *t*-BuONa (97%, 1.05 eq., 104.7 mg) in 3 mL of dry THF a solution of **1** (165.4 mg, 1.0 mmol) in 5 mL of dry THF was added. The mixture was stirred at r.t. overnight, then the solvent was removed by evaporation. To the residue, TFA (7.8 mL, 100 mmol, 100 equiv.) was added and the mixture was stirred at r.t. for 1 hr. The mixture was poured into ice-water (50 mL), and the whole was extracted with CHCl₃. The organic phase was washed with brine and dried over Na₂SO₄, and the solvent was evaporated under reduced pressure to give a residue (203.7 mg), which was column-chromatographed on silica gel (eluent n-hexane:ethyl acetate= 6:1). Removal of the solvent afforded 3-methyl-4*H*-1,2-benzoxazine **3** as a colorless amorphous solid (39.9 mg, 0.27 mmol).

Yield 27%. Mp. 45.0 - 46.0 °C (recrystallized from ether:n-hexane, colorless plates). ¹H-NMR (400 MHz, CDCl₃) δ (ppm) : 7.24 - 7.17 (m, total 1H), 7.04 - 6.97 (m, total 3H), 3.30 (s,

2H), 2.10 (s, 3H). ^{13}C -NMR (400 MHz, CDCl_3) δ (ppm): 156.6, 152.6, 128.0, 127.3, 123.5, 116.0, 114.1, 27.1, 20.9. Anal. Calcd. for $\text{C}_9\text{H}_9\text{NO}\cdot 1/16\text{H}_2\text{O}$: C, 72.89; H, 6.20; N, 9.44. Found: C, 73.05; H, 6.17; N, 9.42.

Synthesis of methyl 3-aryl-2-nitropropionates **4**.

Scheme S2.

Typical Procedure: **4a**

To ice-cooled dry THF (100 mL) a solution of TiCl_4 (9.0 mL, 82.0 mmol, 2.1 equiv.) in CCl_4 (20 mL) was added. Then, a solution of benzaldehyde (4.23 g, 39.8 mmol) and methyl nitroacetate (4.89 g, 41.0 mmol, 1.0 equiv.) in dry THF (40 mL) was added, and the whole was stirred for 2 hr at 0 °C. A solution of N-methylmorpholine (16.76 g, 166 mmol, 4.0 eq.) in dry THF (50 mL) was slowly added dropwise over 2 hr, and the whole was stirred powerfully for 20 hr at 18 °C. Then, water (200 mL) was added, and the whole was extracted with ether. The organic phase was washed with brine and dried over Na_2SO_4 , and the solvent was evaporated under reduced pressure to give a residue (7.77 g).

The residue was dissolved in a mixture of CHCl_3 (130 mL) and $i\text{PrOH}$ (40 mL). To this solution, SiO_2 (22.0 g) and NaBH_4 (6.10 g, 16.1 mmol) were added, and the whole was stirred at r.t. for 4 hr. Then, acetic acid (20 mL) was carefully added, and silica gel was removed by filtration. The solvent was evaporated under reduced pressure to give a residue (4.82 g), which was column-chromatographed on silica gel (eluent n-hexane:AcOEt=7:1-5:1). Removal of the solvent afforded **4a** as a white solid (2.92 g, 13.9 mmol).

Total yield 35%. Mp. 37.0 - 37.8 °C (recrystallized from n-hexane/ CHCl_3 , white powder). ^1H -NMR (400 MHz, CDCl_3) δ (ppm): 7.34 - 7.19 (m, total 5H), 5.35 (dd, J = 5.7, 9.5 Hz, 1H), 3.83 (s, 3H), 3.57 (dd, J = 9.5, 14.4 Hz, 1H), 3.48 (dd, J = 5.7, 14.7 Hz, 1H). ^{13}C -NMR (400 MHz, CDCl_3) δ (ppm): 164.5, 134.0, 129.0, 128.9, 127.9, 89.1, 53.7, 36.3. Anal. Calcd for $\text{C}_{10}\text{H}_{11}\text{NO}_4$: C, 57.41; H, 5.30; N, 6.70. Found: C, 57.41; H, 5.33; N, 6.63.

Methyl 3-(4-fluorophenyl)-2-nitropropionate (**4b**)

Total yield 58%. Yellow oil. ^1H -NMR (400 MHz, CDCl_3) δ (ppm): 7.23 - 7.16 (m, total 2H), 7.04 - 6.99 (m, total 2H), 5.31 (dd, J = 5.7, 9.5 Hz, 1H), 3.84 (s, 3H), 3.81 (dd, J = 3.5, 5.7 Hz, 1H), 3.46 (dd, J = 5.5, 14.8 Hz, 1H). ^{13}C -NMR (400 MHz, CDCl_3) δ (ppm): 164.3, 162.4 (d, J = 246.9 Hz), 130.6 (d, J = 8.3 Hz), 129.7 (d, J = 3.4 Hz), 116.0 (d, J = 21.5 Hz), 89.0, 53.7,

35.5. Anal. Calcd for $C_{10}H_{10}FNO_4$: C, 52.87; H, 4.44; N, 6.17. Found: C, 52.76; H, 4.63; N, 6.12.

Methyl 3-(4-chlorophenyl)-2-nitropropionate (4c)

Total yield 19%. Yellow oil. 1H -NMR (400 MHz, $CDCl_3$) δ (ppm): 7.31 - 7.25 (m, total 2H), 7.16 - 7.13 (m, total 2H), 5.31 (dd, $J = 5.7, 9.5$ Hz, 1H), 3.84 (s, 3H), 3.54 (dd, $J = 9.5, 14.7$ Hz, 1H), 3.45 (dd, $J = 5.7, 14.7$ Hz, 1H). ^{13}C -NMR (400 MHz, $CDCl_3$) δ (ppm): 164.3, 133.9, 132.4, 130.3, 129.2, 88.8, 53.8, 35.6. Anal. Calcd for $C_{10}H_{10}ClNO_4$: C, 49.30; H, 4.14; N, 5.75. Found: C, 49.49; H, 4.29; N, 5.64.

Methyl 3-(3-chlorophenyl)-2-nitropropionate (4d)

Total yield 25%. Yellow oil. 1H -NMR (400 MHz, $CDCl_3$) δ (ppm): 7.30 - 7.25 (m, total 2H), 7.22 (s, 1H), 7.10 - 7.09 (m, total 1H), 5.31 (dd, $J = 5.7, 9.5$ Hz, 1H), 3.89 (s, 3H), 3.52 (dd, $J = 9.5, 14.8$ Hz, 1H), 3.44 (dd, $J = 5.5, 14.7$ Hz, 1H). ^{13}C -NMR (400 MHz, $CDCl_3$) δ (ppm): 164.2, 135.9, 134.8, 130.3, 129.1, 128.2, 127.0, 88.6, 53.8, 35.8. Anal. Calcd for $C_{10}H_{10}ClNO_4$: C, 49.30; H, 4.14; N, 5.75. Found: C, 49.48; H, 4.29; N, 5.69.

Methyl 3-(3,5-dichlorophenyl)-2-nitropropionate (4e)

Total yield 28%. Yellow oil. 1H -NMR (400 MHz, $CDCl_3$) δ (ppm): 7.30 - 7.29 (m, total 1H), 7.11 (d, $J = 1.8$ Hz, 2H), 5.33 (dd, $J = 5.7, 9.5$ Hz, 1H), 3.85 (s, 3H), 3.54 (dd, $J = 9.5, 14.7$ Hz, 1H), 3.46 (dd, $J = 5.5, 14.7$ Hz, 1H). ^{13}C -NMR (400 MHz, $CDCl_3$) δ (ppm): 164.0, 137.3, 135.6, 128.3, 127.5, 88.2, 53.9, 35.5. Anal. Calcd for $C_{10}H_9Cl_2NO_4$: C, 43.19; H, 3.26; N, 5.04. Found: C, 43.26; H, 3.39; N, 4.88.

Methyl 3-(4-bromophenyl)-2-nitropropionate (4f)

Total yield 39%. Yellow oil. 1H -NMR (400 MHz, $CDCl_3$) δ (ppm): 7.45 (d, $J = 8.4$ Hz, 2H), 7.09 (d, $J = 8.2$ Hz, 2H), 5.31 (dd, $J = 6.2, 12.1$ Hz, 1H), 3.84 (s, 3H), 3.52 (dd, $J = 9.5, 14.7$ Hz, 1H), 3.44 (dd, $J = 5.7, 14.7$ Hz, 1H). ^{13}C -NMR (400 MHz, $CDCl_3$) δ (ppm): 164.2, 133.0, 132.2, 130.6, 122.0, 88.7, 53.8, 35.7. Anal. Calcd for $C_{10}H_{10}BrNO_4$: C, 41.69; H, 3.50; N, 4.86. Found: C, 41.50; H, 3.69; N, 4.61.

Methyl 3-(4-methoxycarbonylphenyl)-2-nitropropionate (4g)

Total yield 28%. Mp. 90.0 - 91.0 °C (recrystallized from n-hexane/ $CHCl_3$, colorless cubes). 1H -NMR (400 MHz, $CDCl_3$) δ (ppm): 7.99 (d, $J = 8.1$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 5.36 (dd, $J = 5.7, 9.3$ Hz, 1H), 3.91 (s, 3H), 3.62 (s, 3H), 3.62 (dd, $J = 9.5, 14.7$ Hz, 1H), 3.54 (dd, $J = 5.9, 14.5$ Hz, 1H). ^{13}C -NMR (400 MHz, $CDCl_3$) δ (ppm): 166.5, 164.2, 139.1, 130.3, 129.8, 128.9, 88.5, 53.8, 52.2, 36.1. Anal. Calcd for $C_{12}H_{13}NO_6$: C, 53.93; H, 4.90; N, 5.24. Found: C, 53.77; H, 4.97; N, 5.09.

Methyl 3-(4-diisopropylcarbamoylphenyl)-2-nitropropionate (4h)

Total yield 35%. Mp. 117.5 - 119.0 °C (recrystallized from n-hexane/ $CHCl_3$, white powder). 1H -NMR (400 MHz, $CDCl_3$) δ (ppm): 7.29 - 7.21 (m, total 5H), 5.35 (dd, $J = 5.7, 9.5$ Hz, 1H),

3.84 (s, 3H), 3.59 (dd, $J = 9.5, 14.7$ Hz, 1H), 3.49 (dd, $J = 5.7, 14.7$ Hz, 1H), 1.62 - 1.16 (m, total 14H). ^{13}C -NMR (400 MHz, CDCl_3) δ (ppm): 170.4, 164.4, 138.5, 134.6, 129.0, 128.7, 126.4, 88.8, 53.8, 36.0, 20.7. Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{O}_5$: C, 60.70; H, 7.19; N, 8.33. Found: C, 60.66; H, 7.13; N, 8.27.

Methyl 3-(4-trifluoromethylphenyl)-2-nitropropionate (4i)

Total yield 35%. Yellow oil. ^1H -NMR (400 MHz, CDCl_3) δ (ppm): 7.59 (d, $J = 8.1$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 5.36 (dd, $J = 5.7, 9.7$ Hz, 1H), 3.85 (s, 3H), 3.63 (dd, $J = 9.5, 14.7$ Hz, 1H), 3.55 (dd, $J = 5.7, 14.8$ Hz, 1H). ^{13}C -NMR (400 MHz, CDCl_3) δ (ppm): 164.1, 138.0, 130.3 (q, $J = 32.8$ Hz), 129.3, 126.0 (q, $J = 3.8$ Hz), 123.9 (q, $J = 272.1$ Hz), 88.5, 53.9, 35.9. Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{F}_3\text{NO}_4$: C, 47.66; H, 3.64; N, 5.05. Found: C, 47.54; H, 3.71; N, 4.90.

Methyl 3-(4-cyanophenyl)-2-nitropropionate (4j)

Total yield 37%. Mp. 56.0 - 57.0 °C (recrystallized from n-hexane/ CHCl_3 , white powder). ^1H -NMR (400 MHz, CDCl_3) δ (ppm): 7.64 - 7.62 (m, total 2H), 7.36 - 7.26 (m, total 2H), 5.35 (dd, $J = 5.5, 9.5$ Hz, 1H), 3.85 (s, 3H), 3.63 (dd, $J = 9.5, 14.7$ Hz, 1H), 3.55 (dd, $J = 5.7, 14.8$ Hz, 1H). ^{13}C -NMR (400 MHz, CDCl_3) δ (ppm): 163.9, 139.4, 132.7, 129.7, 118.2, 112.0, 88.1, 53.9, 36.0. Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_4$: C, 56.41; H, 4.30; N, 11.96. Found: C, 56.61; H, 4.48; N, 11.94.

Methyl 3-(4-nitrophenyl)-2-nitropropionate (4k)

Total yield 19%. Mp. 62.0 - 63.1 °C (recrystallized from ether, white powder). ^1H -NMR (400 MHz, CDCl_3) δ (ppm): 8.21 - 8.18 (m, total 2H), 7.42 - 7.39 (m, total 2H), 5.38 (dd, $J = 5.5, 9.5$ Hz, 1H), 3.86 (s, 3H), 3.68 (dd, $J = 5.5, 14.7$ Hz, 1H), 3.60 (dd, $J = 5.5, 14.7$ Hz, 1H). ^{13}C -NMR (400 MHz, CDCl_3) δ (ppm): 163.9, 147.7, 141.3, 129.9, 124.2, 88.1, 54.0, 35.8. Anal. Calcd for $\text{C}_{10}\text{H}_9\text{N}_2\text{O}_6$: C, 47.25; H, 3.97; N, 11.02. Found: C, 47.28; H, 4.16; N, 11.12.

Methyl 3-(3-nitrophenyl)-2-nitropropionate (4l)

Total yield 39%. Yellow oil. ^1H -NMR (400 MHz, CDCl_3) δ (ppm): 8.16 - 8.11 (m, total 2H), 7.56 - 7.49 (m, total 2H), 5.38 (dd, $J = 5.6, 9.4$ Hz, 1H), 3.85 (s, 3H), 3.67 (dd, $J = 9.6, 14.8$ Hz, 1H), 3.58 (dd, $J = 5.6, 14.9$ Hz, 1H). ^{13}C -NMR (400 MHz, CDCl_3) δ (ppm): 163.9, 148.6, 136.0, 135.2, 130.1, 123.9, 123.1, 88.3, 54.0, 35.7. Anal. Calcd for $\text{C}_{10}\text{H}_9\text{N}_2\text{O}_6 \cdot 1/4\text{H}_2\text{O}$: C, 46.43; H, 4.09; N, 10.83. Found: C, 46.51; H, 3.99; N, 10.89.

Methyl 3-(4-methylphenyl)-2-nitropropionate (4m)

Total yield 64%. Mp. 32.1 - 32.7 °C (recrystallized from n-hexane/ CHCl_3 , white powder). ^1H -NMR (400 MHz, CDCl_3) δ (ppm): 7.13 - 7.07 (m, total 4H), 5.32 (dd, $J = 5.9, 9.5$ Hz, 1H), 3.83 (s, 3H), 3.52 (dd, $J = 9.5, 14.7$ Hz, 1H), 3.44 (dd, $J = 5.7, 14.5$ Hz, 1H), 2.32 (s, 3H). ^{13}C -NMR (400 MHz, CDCl_3) δ (ppm): 164.6, 137.6, 130.9, 129.7, 128.7, 89.2, 53.6, 35.9, 21.1. Anal. Calcd for $\text{C}_{11}\text{H}_{13}\text{NO}_4$: C, 59.19; H, 5.87; N, 6.27. Found: C, 59.14; H, 5.83; N, 6.17.

Methyl 3-(3,4-dimethylphenyl)-2-nitropropionate (4n)

Total yield 33%. Mp. 59.2 - 60.0 °C (recrystallized from n-hexane/CHCl₃, white powder). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.07 - 7.05 (m, total 1H), 6.95 - 6.90 (m, total 2H), 5.32 (dd, *J* = 5.7, 9.6 Hz, 1H), 3.82 (s, 3H), 3.48 (dd, *J* = 9.6, 14.6 Hz, 1H), 3.40 (dd, *J* = 5.7, 14.6 Hz, 1H), 2.22 (s, 3H), 2.21 (s, 3H). ¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 164.6, 137.2, 136.2, 131.3, 130.2, 130.0, 126.1, 89.3, 53.6, 35.9, 19.7, 19.4. Anal. Calcd for C₁₂H₁₅NO₄: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.77; H, 6.45; N, 5.80.

Methyl 3-(4-methoxyphenyl)-2-nitropropionate (4o)

Total yield 51%. Mp. 49.0 - 50.0 °C (recrystallized from ether, colorless cubes). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.14 - 7.11 (m, total 2H), 6.86 - 6.82 (m, total 2H), 5.30 (dd, *J* = 5.9, 9.5 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.50 (dd, *J* = 9.5, 14.7 Hz, 1H), 3.42 (dd, *J* = 5.9, 14.7 Hz, 1H). ¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 164.6, 159.2, 130.0, 125.9, 114.4, 89.3, 55.3, 53.6, 35.6. Anal. Calcd for C₁₁H₁₃NO₅: C, 55.23; H, 5.48; N, 5.86. Found: C, 55.35; H, 5.55; N, 5.79.

Methyl 3-(2-chlorophenyl)-2-nitropropionate (4p)

Total yield 59%. Yellow oil. ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.42 - 7.39 (m, total 1H), 7.26 - 7.23 (m, total 2H), 5.50 (t, *J* = 7.70 Hz, 1H), 3.83 (s, 3H), 3.68 (1H, dd, *J* = 7.7, 14.5 Hz), 3.59 (1H, dd, *J* = 7.5, 14.5 Hz). ¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 164.4, 134.1, 131.7, 131.6, 129.9, 129.6, 127.4, 86.8, 53.8, 34.4. Anal. Calcd for C₁₀H₁₀ClNO₄·1/8H₂O: C, 48.84; H, 4.20; N, 5.70. Found: C, 48.64; H, 4.25; N, 5.70.

Methyl 3-(2,6-dichlorophenyl)-2-nitropropionate (4q)

Total yield 44%. Mp. 51.8 - 52.5 °C (recrystallized from n-hexane/CHCl₃, white powder). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.34 - 7.32 (m, total 2H), 7.21 - 7.17 (m, total 1H), 5.52 (t, *J* = 7.7 Hz, 1H), 3.96 (dd, *J* = 7.7, 14.5 Hz, 1H), 3.86 (dd, *J* = 7.51, 14.5 Hz, 1H), 3.818 (s, 3H). ¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 164.2, 136.0, 130.2, 129.6, 128.6, 84.9, 53.7, 31.6. Anal. Calcd. for C₁₀H₈Cl₂NO₄: C, 43.19; H, 3.26; N, 5.04. Found: C, 43.03; H, 3.28; N, 5.07.

Methyl 3-(2,6-dibromophenyl)-2-nitropropionate (4r)

Total yield 53%. Mp. 63.0 - 64.0 °C (recrystallized from ether, colorless cubes). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.56 (d, *J* = 8.1 Hz, 2H), 7.03 (t, *J* = 8.1 Hz, 1H), 5.56 (t, *J* = 7.7 Hz, 1H), 4.00 (dd, *J* = 7.3, 14.7 Hz, 1H), 3.93 (dd, *J* = 7.9, 14.5 Hz, 1H), 3.82 (s, 3H). ¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 164.2, 133.2, 132.8, 130.4, 125.9, 85.0, 53.8, 36.7. Anal. Calcd. for C₁₀H₈Br₂NO₄: C, 32.73; H, 2.47; N, 3.82. Found: C, 32.71; H, 2.46; N, 3.82.

Methyl 3-(2,6-difluorophenyl)-2-nitropropionate (4s)

Total yield 15%. Colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ (ppm) : 7.33 - 7.26 (m, total 1H), 6.96 - 6.90 (m, total 2H), 5.47 (dd, *J* = 6.4, 9.2 Hz, 1H), 3.82 (s, 3H), 3.70 (dd, *J* = 9.3,

14.8 Hz, 1H), 3.52 (dd, $J = 6.4, 14.8$ Hz, 1H). ^{13}C -NMR (400 MHz, CDCl_3) δ (ppm): 164.1, 161.5 (dd, $J = 7.7, 249.1$ Hz), 129.9 (t, $J = 10.4$ Hz), 111.6 (dd, $J = 6.2, 19.3$ Hz), 109.9 (t, $J = 19.3$ Hz), 85.9, 53.8, 23.8 (t, $J = 2.5$ Hz). Anal. Calcd for $\text{C}_{10}\text{H}_9\text{NO}_4\text{F}_2$: C, 48.99; H, 3.70; N, 5.71. Found: C, 48.94; H, 3.95; N, 5.68.

The arylnitroalkylates below were synthesized according to the procedure described in references S1 and S2.

Methyl nitrophenylacetate (9)

Total yield 10%. Yellow oil. ^1H -NMR (400 MHz, CDCl_3) δ (ppm): 7.52 - 7.44 (m, total 5H), 6.18 (s, 1H), 3.87 (s, 3H).

Methyl 2-nitro-4-phenylbutyric acid (10)

Total yield 43%. Pale yellow oil. ^1H -NMR (400 MHz, CDCl_3) δ (ppm): 7.34 - 7.30 (m, total 2H), 7.27 - 7.22 (m, total 1H), 7.19 - 7.16 (m, total 2H), 5.08 (dd, $J = 5.1, 9.3$ Hz, 1H), 3.81 (s, 3H), 2.82 - 2.74 (m, total 1H), 2.69 - 2.59 (m, total 2H), 2.50 - 2.40 (m, total 1H). ^{13}C -NMR (400 MHz, CDCl_3) δ (ppm): 165.0, 138.8, 128.8, 128.5, 126.8, 86.9, 53.6, 31.9, 31.6. ESI-HRMS. Calcd. For $\text{C}_{11}\text{H}_{13}\text{NaNO}_4$ ($[\text{M}+\text{Na}]^+$); 246.0742. Found: 246.0750 (+0.8 mmu).

Methyl 2-nitro-5-phenylpentanoic acid (11)

Total yield 32%. ^1H -NMR (400 MHz, CDCl_3) δ (ppm): 7.29 - 7.15 (m, total 5H), 5.11 (dd, $J = 5.5, 9.5$ Hz, 1H), 3.82 (s, 3H), 2.68 (t, $J = 7.5$ Hz, 2H), 2.36 - 2.26 (m, total 1H), 2.21 - 2.12 (m, total 1H), 1.76 - 1.68 (m, total 2H). ^{13}C -NMR (400 MHz, CDCl_3) δ (ppm): 164.9, 140.6, 128.6, 128.3, 126.3, 87.8, 53.6, 34.9, 29.7, 27.2. ESI-HRMS. Calcd. For $\text{C}_{12}\text{H}_{15}\text{NNaO}_4$ ($[\text{M}+\text{Na}]^+$); 260.0899. Found: 260.0891 (-0.8 mmu).

Methyl 2-nitro-3-phenylbutyric acid (12)

Total yield 51%. A diastereomer mixture (almost 1:1). ^1H -NMR (400 MHz, CDCl_3) δ (ppm): 7.35 - 7.18 (m, total 5H of each diastereomer), 5.29 (d, $J = 10.3$ Hz, 1H), 5.25 (d, $J = 10.3$ Hz, 1H), 3.87 (s, 3H), 3.85 - 3.78 (m, 1H of each diastereomer), 3.57 (s, 3H), 1.43 (d, $J = 7.0$ Hz, 3H), 1.38 (d, $J = 7.0$ Hz, 3H). ^{13}C -NMR (400 MHz, CDCl_3) δ (ppm): 164.1, 163.7, 139.8, 138.9, 128.9, 128.7, 128.1, 127.9, 127.7, 127.3, 93.3, 93.1, 53.6, 53.2, 41.3, 41.2, 18.2. ESI-HRMS. Calcd. for $\text{C}_{11}\text{H}_{13}\text{NNaO}_4$ ($[\text{M}+\text{Na}]^+$); 246.0742. Found: 246.0772 (+3.0 mmu).

Methyl 2-nitro-3,3-diphenylpropionate (13)

Total yield 30%. Mp. 54.0 - 55.0 °C (recrystallized from ether, white powder). ^1H -NMR (400 MHz, CDCl_3) δ (ppm): 7.32 - 7.22 (m, total 10H), 5.95 (d, $J = 11.9$ Hz, 1H), 5.02 (d, $J = 11.9$ Hz, 1H), 3.60 (s, 3H). ^{13}C -NMR (400 MHz, CDCl_3) δ (ppm): 163.7, 138.2, 137.6, 129.1, 129.1, 128.1, 127.9, 127.8, 127.4, 91.0, 53.6, 52.2. Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{NO}_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.37; H, 5.46; N, 4.81.

Cyclization reaction of methyl 3-aryl-2-nitropropionates.

Scheme S3.

Typical procedure of 3-Methoxycarbonyl-4H-1,2-benzoxazine 5a.

To ice-cooled TFSA (0.45 mL, 5.00 mmol, 10 equiv.), a solution of methyl 2-nitro-3-phenylpropionate **4a** (106.3 mg, 0.51 mmol) in dry CHCl₃ (10 mL) was slowly added. The mixture was stirred at 50 °C for 30 min, then poured into ice-water (50 mL), and the whole was extracted with CHCl₃. The organic phase was washed with brine and dried over Na₂SO₄, and the solvent was evaporated under reduced pressure to give a residue (98.0 mg), which was column-chromatographed on silica gel (eluent: n-hexane - ethyl acetate (5:1)). Removal of the solvent afforded 3-methoxycarbonyl-4H-1,2-benzoxazine **5a** as a white powder (84.5 mg, 0.44 mmol).

Yield 85%. Mp. 64.0 - 65.0 °C (recrystallized from ether, colorless plates). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.27 - 7.22 (m, 1H), 7.12 - 7.04 (m, total 3H), 3.94 (s, 3H), 3.66 (s, 2H). ¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 163.2, 151.4, 149.3, 128.6, 128.1, 125.0, 114.8, 114.3, 53.2, 22.3. Anal. Calcd for C₁₀H₉NO₃: C, 62.82; H, 4.74; N, 7.33. Found: C, 62.74; H, 4.86; N, 7.32.

7-Fluoro-3-methoxycarbonyl-4H-1,2-benzoxazine (5b)

Yield 75%. Mp. 94.0 - 95.0 °C (recrystallized from ether, colorless needles). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.08 (dd, 1H, *J* = 5.9, 8.4 Hz), 6.86 - 6.78 (m, 2H), 3.94 (s, 3H), 3.63 (s, 2H). ¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 163.5, 162.0 (d, *J* = 191.5 Hz), 151.8 (d, *J* = 11.3 Hz), 149.5, 129.1 (d, *J* = 9.4 Hz), 112.3 (d, *J* = 21.9 Hz), 110.4 (d, *J* = 3.0 Hz), 102.1 (d, *J* = 25.6 Hz), 53.3, 21.9. Anal. Calcd for C₁₀H₈FNO₃: C, 57.42; H, 3.85; N, 6.70. Found: C, 57.63; H, 4.05; N, 6.70.

7-Chloro-3-methoxycarbonyl-4H-1,2-benzoxazine (5c)

Yield 93%. Mp. 96.0 - 97.0 °C (recrystallized from ether, colorless plates). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.10 - 7.03 (m, total 3H), 3.94 (s, 3H), 3.63 (s, 2H). ¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 162.9, 151.6, 149.4, 134.0, 129.0, 125.3, 114.7, 113.3, 53.3, 22.0. Anal. Calcd for C₁₀H₈ClNO₃: C, 53.23; H, 3.57; N, 6.21. Found: C, 53.17; H, 3.78; N, 6.06.

6-Chloro-3-methoxycarbonyl-4H-1,2-benzoxazine (5d)

Yield 69%. Mp. 111.0 - 112.0 °C (recrystallized from ether, colorless cubes). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.21 (dd, *J* = 2.4, 8.6 Hz, 1H), 7.11 (d, *J* = 2.56 Hz, 1H), 7.00 (d, *J* = 8.79 Hz, 1H), 3.94 (s, 3H), 3.64 (s, 2H). ¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 162.9, 149.9,

148.8, 129.8, 128.7, 127.8, 118.6, 116.5, 115.7, 53.3, 22.3. Anal. Calcd for $C_{10}H_8ClNO_3$: C, 53.23; H, 3.57; N, 6.21. Found: C, 53.20; H, 3.71; N, 6.22.

8-Chloro-3-methoxycarbonyl-4*H*-1,2-benzoxazine (5d')

Yield 9%. Mp. 89.0 - 90.0 °C (recrystallized from n-hexane/ethyl acetate, yellow powder). 1H -NMR (400 MHz, $CDCl_3$) δ (ppm): 7.31 - 7.29 (m, 1H), 7.04 - 7.02 (m, total 2H), 3.95 (s, 3H), 3.68 (s, 2H). ^{13}C -NMR (400 MHz, $CDCl_3$) δ (ppm): 162.7, 150.0, 147.4, 129.5, 126.3, 125.1, 120.3, 116.9, 53.3, 22.7. Anal. Calcd for $C_{10}H_8ClNO_3$: C, 53.23; H, 3.57; N, 6.21. Found: 53.36; H, 3.78; N, 6.04.

6,8-Dichloro-3-methoxycarbonyl-4*H*-1,2-benzoxazine (5e)

Yield 38%. Mp. 83.0 - 84.0 °C (recrystallized from ether, colorless needles). 1H -NMR (400 MHz, $CDCl_3$) δ (ppm): 7.31 (d, $J = 2.4$ Hz, 1H), 7.30 - 7.02 (m, total 1H), 3.95 (s, 3H), 3.65 (s, 2H). ^{13}C -NMR (400 MHz, $CDCl_3$) δ (ppm): 162.5, 149.6, 146.2, 129.7, 129.3, 126.2, 121.3, 118.1, 53.5, 22.7. Anal. Calcd for $C_{10}H_7Cl_2NO_3$: C, 46.07; H, 2.71; N, 5.39. Found: C, 46.11; H, 2.89; N, 5.39.

7-Bromo-3-methoxycarbonyl-4*H*-1,2-benzoxazine (5f)

Yield 88%. Mp. 110.0 - 111.0 °C (recrystallized from ether, colorless cubes). 1H -NMR (400 MHz, $CDCl_3$) δ (ppm): 7.24 - 7.22 (m, total 2H), 7.20 (d, $J = 1.83$ Hz, 1H), 3.92 (s, 3H), 3.59 (s, 2H). ^{13}C -NMR (400 MHz, $CDCl_3$) δ (ppm): 162.9, 151.7, 149.3, 129.3, 128.1, 121.5, 117.6, 113.8, 53.3, 22.1. Anal. Calcd for $C_{10}H_8BrNO_3$: C, 44.47; H, 2.99; N, 5.19. Found: C, 44.36; H, 3.03; N, 5.17.

3,7-Dimethoxycarbonyl-4*H*-1,2-benzoxazine (5g)

Yield 85%. Dec. 144.0 - 146.0 °C (recrystallized from n-hexane/ $CHCl_3$, colorless needles). 1H -NMR (400 MHz, $CDCl_3$) δ (ppm): 7.78 (dd, $J = 1.7, 7.9$ Hz, 1H), 7.72 (d, $J = 1.7$ Hz, 1H), 7.256 - 7.18 (m, total 1H), 3.95 (s, 3H), 3.92 (s, 3H), 3.71 (s, 2H). ^{13}C -NMR (400 MHz, $CDCl_3$) δ (ppm): 166.0, 162.9, 151.2, 149.0, 130.9, 128.2, 126.0, 119.9, 115.5, 53.3, 52.4, 22.5. Anal. Calcd for $C_{12}H_{11}NO_5$: C, 57.83; H, 4.45; N, 5.62. Found: C, 57.74; H, 4.53; N, 5.52.

7-Diisopropylcarbamoyl-3-methoxycarbonyl-4*H*-1,2-benzoxazine (5h)

Yield 98%. Dec. 123.0 - 124.0 °C (recrystallized from ether, colorless plates). 1H -NMR (400 MHz, $CDCl_3/TMS$) δ (ppm): 7.13 (d, $J = 7.7$ Hz, 1H), 7.05 (dd, $J = 1.5, 7.9$ Hz, 1H), 7.00 (d, $J = 1.1$ Hz, 1H), 3.94 (s, 3H), 3.67 (s, 2H), 1.59 - 1.19 (m, total 14H). ^{13}C -NMR (400 MHz, $CDCl_3$) δ (ppm): 169.4, 163.0, 151.2, 149.3, 139.5, 128.4, 122.3, 115.2, 111.6, 53.3, 22.2, 20.6. Anal. Calcd for $C_{17}H_{22}N_2O_4$: C, 64.13; H, 6.97; N, 8.80. Found: C, 64.12; H, 6.80; N, 8.63.

7-Trifluoromethyl-3-methoxycarbonyl-4*H*-1,2-benzoxazine (5i)

Yield 88%. Mp. 98.0 - 99.0 °C (recrystallized from ether, colorless plates). 1H -NMR (400

MHz, CDCl₃) δ (ppm): 7.34 - 7.21 (m, total 3H), 3.93 (s, 3H), 3.68 (s, 2H). ¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 162.8, 151.3, 149.2, 131.3 (q, J = 33.4 Hz), 128.8, 123.4 (q, J = 272.3 Hz), 121.6 (q, J = 3.6 Hz), 118.9, 111.7 (q, J = 4.0 Hz), 53.4, 22.3. Anal. Calcd for C₁₁H₈F₃NO₃: C, 50.97; H, 3.11; N, 5.40. Found: C, 50.95; H, 3.27; N, 5.30.

7-Cyano-3-methoxycarbonyl-4H-1,2-benzoxazine (5j)

Yield 59%. Dec. 140.0 - 143.0 °C (recrystallized from n-hexane/CHCl₃, colorless needles). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.41 - 7.36 (m, total 2H), 7.26 - 7.23 (m, total 1H), 3.96 (s, 3H), 3.71 (s, 2H). ¹³C-NMR (400 MHz, DMSO-*d*₆) δ (ppm): 162.9, 151.4, 151.2, 130.4, 128.9, 122.7, 118.5, 117.8, 111.4, 53.5, 22.8. Anal. Calcd for C₁₁H₈N₂O₃: C, 61.11; H, 3.73; N, 12.96. Found: C, 60.92; H, 3.90; N, 12.76.

7-Nitro-3-methoxycarbonyl-4H-1,2-benzoxazine (5k)

Yield 81%. Dec. 145.0 - 146.0 °C (recrystallized from n-hexane/CHCl₃, colorless needles). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.99 (dd, J = 2.2, 8.2 Hz, 1H), 7.94 (d, J = 2.4 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 3.97 (s, 3H), 3.76 (s, 2H). ¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 162.5, 151.4, 149.2, 148.2, 129.0, 122.1, 119.7, 110.1, 53.5, 22.6. Anal. Calcd for C₁₀H₈N₂O₅·1/8H₂O: C, 50.37; H, 3.49; N, 11.75. Found: C, 50.27; H, 3.43; N, 11.74.

6-Nitro-3-methoxycarbonyl-4H-1,2-benzoxazine (5l)

Yield 23%. Dec. 134.0-135.0 °C (recrystallized from ether, yellow powder). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.89 (dd, J = 7.8, 0.7 Hz, 1H), 7.41 (dd, J = 7.8, 1.0 Hz, 1H), 7.25 (d, J = 7.8 Hz, 1H), 3.97 (s, 3H), 3.73 (s, 2H). ¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 162.3, 155.4, 149.4, 144.4, 124.7, 124.3, 116.0, 115.2, 53.6, 22.4. Anal. Calcd for C₁₀H₈N₂O₅·1/4H₂O: C, 49.90; H, 3.58; N, 11.64. Found: C, 50.11; H, 3.58; N, 11.39.

8-Nitro-3-methoxycarbonyl-4H-1,2-benzoxazine (5l')

Yield 51%. Dec. 144.0-146.0 °C (recrystallized from ether, yellow cubes). ¹H-NMR (400 MHz, DMSO-*d*₆) δ (ppm): 8.17 (dd, J = 2.7 Hz, 9.0 Hz, 1H), 8.09 (d, J = 2.7 Hz, 1H), 7.19 (d, J = 8.8 Hz, 1H), 3.98 (s, 3H), 3.77 (s, 2H). ¹³C-NMR (400 MHz, DMSO-*d*₆) δ (ppm): 162.2, 153.3, 144.3, 136.8, 134.3, 125.0, 124.5, 120.2, 53.6, 22.8. Anal. Calcd for C₁₀H₈N₂O₅: C, 50.85; H, 3.41; N, 11.86. Found: C, 50.64; H, 3.50; N, 11.61.

7-Methyl-3-methoxycarbonyl-4H-1,2-benzoxazine (5m)

Yield 16%. Mp. 94.5 - 95.0 °C (recrystallized from n-hexane/CHCl₃, white powder). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.26 (d, J = 2.0 Hz, 1H), 6.99 - 6.87 (m, total 2H), 3.93 (s, 3H), 3.61 (s, 2H). ¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 163.3, 151.1, 149.2, 138.9, 127.8, 125.9, 114.5, 111.5, 53.2, 22.0, 21.2. Anal. Calcd for C₁₁H₁₁NO₃: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.23; H, 5.46; N, 6.61.

6,7-Dimethyl-3-methoxycarbonyl-4H-1,2-benzoxazine (5n) and 7,8-Dimethyl-3-methoxycarbonyl-4H-1,2-benzoxazine (5n')

Yield **5n** (1%) and **5n'** (3%). **5n** and **5n'** could not be separated by column-chromatography on silica gel. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm): 6.89 - 6.87 (m, total 1H of **5n'**), 6.82 - 6.80 (m, total 3H of **5n** and **5n'**), 3.91 (s, 3H of **5n'**), 3.90 (s, 3H of **5n**), 2.24 (s, 3H of **5n'**), 2.23 (s, 3H of **5n'**), 2.21 (s, 3H of **5n**), 2.18 (s, 3H of **5n**). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) δ (ppm): 163.4 (**5n'**), 163.3 (**5n**), 149.6 (**5n'**), 149.5 (**5n**), 149.3 (**5n**), 148.8 (**5n'**), 137.4 (**5n'**), 137.2 (**5n**), 133.4 (**5n**), 128.7 (**5n**), 126.0 (**5n'**), 124.5 (**5n'**), 122.7 (**5n'**), 114.9 (**5n**), 112.1 (**5n'**), 111.4 (**5n**), 53.1 (**5n'**), 53.1 (**5n**), 22.6 (**5n'**), 21.8 (**5n**), 19.7 (**5n'**), 19.6 (**5n**), 19.1 (**5n**), 11.4 (**5n'**). Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.40; H, 5.96; N, 6.41.

7-Methoxy-3-methoxycarbonyl-4H-1,2-benzoxazine (5o)

Only a trace amount of **5o** could be detected. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) : 7.00 (d, $J = 8.2$ Hz, 1H), 6.67 (dd, $J = 2.6, 8.4$ Hz, 1H), 6.60 (d, $J = 2.6$ Hz, 1H), 3.93 (s, 3H), 3.79 (s, 3H), 3.60 (s, 2H). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) δ (ppm): 163.3, 159.9, 151.8, 149.4, 128.6, 111.9, 106.3, 99.2, 55.5, 53.2, 21.8. ESI-HRMS. Calcd for $\text{C}_{11}\text{H}_{12}\text{NO}_4$ ($[\text{M}+\text{H}]^+$); 222.0766. Found: 222.0747 (-1.9 mmu).

5-Chloro-3-methoxycarbonyl-4H-1,2-benzoxazine (5p)

Yield 41%. Mp. 74.0 – 75.0 °C (recrystallized from $\text{CH}_2\text{Cl}_2/\text{n-hexane}$, colorless needles). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm): 7.18 – 7.10 (m, total 2H), 6.93 – 6.90 (m, total 1H), 3.92 (s, 3H), 3.63 (s, 2H). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) δ (ppm): 162.8, 151.8, 148.7, 133.4, 128.8, 125.0, 113.8, 112.5, 53.3, 20.8. Anal. Calcd for $\text{C}_{10}\text{H}_8\text{ClNO}_3$: C, 53.23; H, 3.57; N, 6.21. Found: C, 53.24; H, 3.71; N, 6.01.

5,8-Dichloro-3-methoxycarbonyl-4H-1,2-benzoxazine (5q)

Yield 50%. Mp. 94.6 - 95.5 °C (recrystallized from $\text{CHCl}_3/\text{n-hexane}$, white powder). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm): 7.47 (dd, $J = 0.6, 8.6$ Hz, 1H), 7.29 (dd, $J = 0.4, 8.6$ Hz, 1H), 3.84 (d, $J = 0.4$ Hz, 3H), 3.68 (2H, s). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) δ (ppm): 162.5, 149.4, 147.8, 131.5, 129.7, 129.6, 127.5, 125.1, 118.7, 115.6, 53.5, 21.4. Anal. Calcd for $\text{C}_{10}\text{H}_7\text{Cl}_2\text{NO}_3$: C, 46.07; H, 2.71; N, 5.39. Found: C, 46.07; H, 2.79; N, 5.33.

5,8-Dibromo-3-methoxycarbonyl-4H-1,2-benzoxazine (5r)

Yield 68%. Mp. 118.0 - 119.0 °C (recrystallized from ether, colorless needles). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm): 7.37 (d, $J = 8.6$ Hz, 1H), 7.21 (d, $J = 8.6$ Hz, 1H), 3.96 (s, 3H), 3.67 (d, $J = 0.6$ Hz, 2H). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) δ (ppm): 162.5, 149.8, 149.1, 133.2, 128.7, 122.2, 117.3, 107.6, 53.5, 24.1. Anal. Calcd for $\text{C}_{10}\text{H}_7\text{Br}_2\text{NO}_3$: C, 34.42; H, 2.02; N, 4.01. Found: C, 34.39; H, 2.20; N, 3.90.

5-Fluoro-3-methoxycarbonyl-8-trifluoromethylsulfonfyl-4H-1,2-benzoxazine (5s)

Yield 46%. Mp. 93.0 - 94.0 °C (recrystallized from ether, white powders). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm): 7.29 – 7.24 (m, total 1H), 6.94 (dd, $J = 2.0, 8.9$ Hz, 1H), 3.94 (s, 3H),

3.71 (s, 2H). ^{13}C -NMR (400 MHz, CDCl_3) δ (ppm): 162.3, 150.9 (d, $J = 255.1$ Hz), 150.5 (d, $J = 5.9$ Hz), 147.7, 132.8 (d, 13.1 Hz), 122.7, 118.7 (q, $J = 320.9$ Hz), 110.4 (d, $J = 4.1$ Hz), 106.1 (d, $J = 19.6$ Hz), 53.6, 17.4. ESI-HRMS. Calcd for $\text{C}_{11}\text{H}_7\text{F}_4\text{NNaO}_6\text{S}$ ($[\text{M}+\text{Na}]^+$): 379.9828. Found: 379.9873 (+4.5 mmu). Anal. Calcd for $\text{C}_{11}\text{H}_7\text{F}_4\text{NO}_6\text{S}$: C, 36.98; H, 1.98; N, 3.92. Found: C, 36.89; H, 2.13; N, 4.01.

8-Oxo-1-oxa-2-aza-spiro[4,5]deca-2,6,9-triene-3-carboxylic acid methyl ester 6

Yield 55%. Mp. 94.5 – 96.0 °C (recrystallized from n-hexane/ CHCl_3 , colorless needles). ^1H -NMR (400 MHz, CDCl_3) δ (ppm): 6.83 (d, $J = 10.1$ Hz, 2H), 6.27 (d, $J = 10.1$ Hz, 2H), 3.91 (s, 3H), 3.35 (s, 2H). ^{13}C -NMR (400 MHz, CDCl_3) δ (ppm): 184.14, 160.02, 150.92, 143.51, 129.63, 129.38, 129.10, 83.11, 53.14, 43.43. Anal. Calcd for $\text{C}_{10}\text{H}_9\text{NO}_4$: C, 57.97; H, 4.38; N, 6.76. Found: C, 57.71; H, 4.47; N, 6.76. ESI-HRMS. Calcd for $\text{C}_{10}\text{H}_9\text{NO}_4$ ($[\text{M}+\text{H}]^+$): 207.0532. Found: 207.0497 (-3.5 mmu).

Superacid-Catalyzed Reaction of Methyl 3-Aryl-2-nitropropionates with Aromatic Solvents.

Scheme S4.

Typical Procedure (7a and 8a).

To a solution of **4a** (102.7 mg, 0.49 mmol) in dry benzene (2.5 mL) was added TFSA (4.5 mL, 50 mmol, 100 equiv.) under an Ar atmosphere at 0 °C. The reaction mixture was stirred overnight at 20 °C and poured into ice-water (50 mL), and the whole was extracted with CHCl_3 . The organic phase was washed with brine, dried over Na_2SO_4 , and evaporated to give a residue (101.5 mg), which was column-chromatographed on silica-gel (eluent: n-hexane:ethyl acetate=5:1). Removal of the solvent afforded 3-methoxycarbonyl-4*H*-1,2-benzoxazine (62.6 mg, 0.33 mmol) and **7a** and **8a** (34.6 mg, total 0.13 mmol).

Mixture of **7a** and **8a**. Total yield 26% (*o*:*p* = 1:12 on the ^1H -NMR spectra). ^1H -NMR (400 MHz, CDCl_3) δ (ppm) : 10.89 (brs, 1H), 7.57 - 7.57 (m, total 1H), 7.56 - 7.55 (m, total 1H), 7.55 - 7.24 (m, total 7H), 4.010(s, 2H of **7a**), 3.94 (s, 2H of **8a**), 3.81 (s, 3H of **7a**), 3.71 (s, 3H of **8a**).

Methyl 3-biphenyl-4-yl-2-hydroxyiminopropionate (7a)

Mp. 144.5 - 145.5 °C (recrystallized from n-hexane - CHCl₃, white powder). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 10.89 (brs, 1H), 7.57 - 7.50 (m, total 2H), 7.44 - 7.37 (m, total 2H), 7.34 - 7.33 (m, total 4H), 4.03 (s, 2H), 3.85 (s, 3H). ¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 164.2, 152.0, 141.1, 139.9, 135.4, 129.8, 129.1, 127.6, 127.5, 127.3, 53.0, 30.5. Anal. Calcd for C₁₆H₁₅NO₃; C, 71.36; H, 5.61; N, 5.20. Found: C, 71.11; H, 5.85; N, 5.23.

Methyl 2-hydroxyimino-3-(2',4',6'-trimethylbiphenyl-4-yl)propionate (7a')

Yield 10%. ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 10.89 (brs, 1H), 7.36 - 7.34 (m, total 2H), 7.05 - 7.03 (m, total 2H), 6.923 - 6.92 (m, total 2H), 4.04 (s, 2H), 3.87 (s, 3H), 2.32 (s, 3H), 1.98 (s, 6H). ¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 163.8, 151.1, 139.4, 138.7, 136.5, 136.0, 133.6, 129.5, 129.1, 128.0, 52.8, 30.3, 21.0, 20.8. ESI-HRMS. Calcd For C₁₉H₂₁NNaO₃ ([M+Na]⁺): 334.1419. Found: 334.1411 (-0.8 mmu).

Methyl 3-(3,5-dichlorobiphenyl-4-yl)-2-hydroxyiminopropionate (7q)

Yield 42%. Mp. 182.0 - 183.0 °C (colorless needles, recrystallized from ether). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 10.95 (brs, 1H), 8.99 - 7.30 (m, total 7H), 4.30 (s, 2H), 3.84 (s, 3H). ¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 163.3, 149.2, 141.6, 138.1, 136.0, 131.5, 129.0, 128.3, 126.9, 126.6, 52.8, 27.8. Anal. Calcd for C₁₆H₁₃Cl₂NO₃; C, 56.82; H, 3.87; N, 4.14. Found: C, 56.66; H, 4.11; N, 4.06.

Methyl 3-(3,5-dibromobiphenyl-4-yl)-2-hydroxyiminopropionate (7r)

Yield 41%. Mp. 172-173 °C (colorless needles, recrystallized from ether). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.77 (brs, 2H), 7.57 - 7.38 (m, total 5H), 4.38 (s, 2H), 3.83 (s, 3H). ¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 163.1, 149.1, 142.3, 137.8, 134.5, 130.5, 129.0, 128.3, 126.9, 125.8, 52.8, 33.6. Anal. Calcd for C₁₆H₁₃Br₂NO₃; C, 45.00; H, 3.07; N, 3.28. Found: C, 44.87; H, 3.17; N, 3.15.

Methyl 3-(3,5-difluorobiphenyl-4-yl)-2-hydroxyiminopropionate (7s)

Yield 43%. Mp. 161 - 162 °C (white powder, recrystallized from ether). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 8.18 (brs, 1H), 7.57 - 7.40 (m, total 5H), 7.15 - 7.09 (m, total 2H), 4.06 (s, 2H), 3.89 (s, 3H). ¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 163.3, 161.5 (dd, *J* = 9.1, 247.8 Hz), 149.6, 142.1, 138.6, 127.9 (d, *J* = 216.6 Hz), 128.3, 110.6 (t, *J* = 20.1 Hz), 109.6 (d, *J* = 26.3 Hz), 109.6 (d, *J* = 12.1 Hz), 52.9, 18.6 (t, *J* = 3.1 Hz). Anal. Calcd for C₁₆H₁₃F₂NO₃·1/8H₂O; C, 62.49; H, 4.34; N, 4.55. Found: C, 62.39; H, 4.46; N, 4.37.

Acidity-dependence of the cyclization reaction

Scheme S5.

Typical Procedure.

Distilled TFSA and TFA were mixed in various weight ratios under an Ar atmosphere. To dry CHCl_3 (10 mL) was added **4a** or the sodium salt of **4a** (1.0 mmol) and the mixture was cooled to 0 °C. To this mixture the combined acid (10 mL, excess amount) was added and the whole was stirred at 50 °C for 30 min. Then the mixture was poured into ice-water (50 mL) and the whole was extracted with CHCl_3 . The organic phase was washed with brine and dried over Na_2SO_4 , then the solvent was evaporated under reduced pressure to give a residue. The residue was column-chromatographed on silica gel (eluent: n-hexane - ethyl acetate (5:1). Removal of the solvent afforded **4a** and **5a**. The yield ratio was consistent with that calculated from the ^1H -NMR spectra of the crude mixture.

Reaction rate determination in TFSA/TFA reaction medium. Typical Procedure.

Distilled TFSA and TFA was mixed (1:1 (w/w)) under an Ar atmosphere. The substrate (0.05 mmol) was dissolved in the combined acid (0.8 mL) in a NMR tube under an Ar atmosphere. Magnetic field locking and external standard peaks were obtained by using a capillary tube filled with acetone/acetone- d_6 . The ^1H -NMR spectra were obtained at 30.0 ± 0.1 °C every 3 min to get 15 spectra. The integration value ($S_{\alpha\text{-H}}$) of the α -proton with respect to the nitro group of the substrate, compared with that of acetone in the capillary tube, was obtained. The ratios of disappearance of the starting substrate against time were plotted to give first-order kinetics (regression coefficient $r > 0.99$). The rate constants were obtained on the basis of the middle 10 data in the total of 15 data.

Figure S1. Reaction Rate Determination.

Table S1. Experimental and Theoretical Acidity of the α -Proton of the Nitro Group of Methyl 3-Aryl-2-nitropropionates.

entry	R	Experimental		Theoretical		
		^{13}C -NMR chemical shift (ppm) ^a		natural population		proton affinity (kcal/mol) ^b
				α -proton	α -carbon	
1	H	4a	88.3	0.22166	-0.09086	345.3
2	F	4b	88.3	-	-	-
3	Cl	4c	88.0	0.22312	-0.09096	341.9
4	CO ₂ Me	4g	87.6	-	-	-
5	CF ₃	4i	87.8	-	-	-
6	CN	4j	87.3	0.22497	-0.09046	337.8
7	NO ₂	4k	87.3	0.22583	-0.09037	337.6

^a Measured in TFA. Acetone/acetone- d_6 in a capillary tube was used as external standard for calibration of the chemical shift on ^{13}C -NMR spectrum (205.0 ppm). ^b All the structures are optimized at the B3LYP/6-31+G* level. Proton affinity (PA) is defined as $PA = -H_{298} = -\Delta E_{\text{elec}} - \Delta ZPE + 5/2RT$. ΔE_{elec} is the difference of the electronic energy at 0 K between the substrate and its *aci*-nitro anion. E_{elec} is calculated at the MP2/6-311G**//B3LYP/6-31+G* level. ΔZPE is the difference of zero-point energy between the substrate and its *aci*-nitro anion, which is scaled by the factor of 0.925. ZPE is calculated at the RHF/6-311G**//B3LYP/6-31+G* level. R is the gas constant. T is temperature (here 298.15 K).

Deuterium Labeling Experiment.

Scheme S7.

Typical Procedure.

CDCl_3 (10 mL) was added to the substrate (1.0 mmol), and the solution was cooled to 0 °C. To this solution was added TFSA-*d* (10 or 50 equiv.). The reaction mixture was stirred for 30 min at 50 °C, then poured into 20 mL of D_2O , and extracted with CHCl_3 . The organic phase was washed with brine, dried over Na_2SO_4 , and evaporated under reduced pressure to give a residue. The residue was column-chromatographed on silica gel (eluent: n-hexane – ethyl acetate (5:1)). Removal of the solvent afforded the 4*H*-1,2-benzoxazines. ^1H -NMR spectra of the crude product and those of the separated cyclized products indicated that no proton or deuterium on the benzyl positions was exchanged under the reaction conditions.

Computational Methods.

In order to evaluate the chemical features of these possible reaction mechanisms quantitatively, we carried out computational studies by using the Gaussian 98 and Gaussian 03 suites of programs.³ All the structures were optimized at the B3LYP/6-31+G* level and the total energies with respect to the structures were calculated at the MP2/6-311G** level. The total energies were corrected with the zero-point energy (ZPE) calculated at the RHF/6-311G** level, which was scaled by the factor of 0.925.⁴

Reaction Pathway of Methyl 2-Nitro-3-phenylpropionate derivatives. Figure S2 shows the Friedel-Crafts type reaction coordinate of the methyl arylnitropropionates. Hydrochloric acid (HCl) was employed as an model Brønsted acid instead of TFSA in order to simplify the calculation. *O*-Protonated *aci*-nitro species **22-H** can afford the nitroso cation **23-H** by elimination of water. This process is moderately endothermic (18.4 kcal/mol) because of the formation of the cationic intermediate. A C-O bond formation between the aromatic carbon atom and the oxygen atom of the nitroso group is achieved in intramolecular electrophilic aromatic substitution through the transition structure represented by TS-**24-H**. Re-

aromatization of TS-**24**-H by deprotonation directly affords the 4*H*-1,2-benzoxazine skeleton **25**-H.⁵ To investigate the influence of the substituent of the benzene ring upon the cyclization reaction, the reaction pathway was also calculated with a substrate, in which the *p*-position of the benzene ring was substituted with an electron-withdrawing cyano group. The transition state TS-**24**-CN was higher-lying (by 3.8 kcal/mol) than that of TS-**24**-H. The energy difference apparently indicates that the electron-withdrawing substituent retards the cyclization.

Figure S2. Reaction Coordinate of Cyclization of Protonated *aci* Methyl 3-Aryl-2-nitropropionates: Friedel-Crafts Type Reaction.^{a, b}

^a A gray-colored sphere represents carbon; light blue, hydrogen; blue, nitrogen; red, oxygen; green, chloride. All of the structures were obtained at the B3LYP/6-31+G* level. Values in the chemical structures are bond length (black) and natural charge (red), respectively. ^b E_0 is calculated as $E_{\text{elec}} + \text{ZPE}$. E_{elec} is the electronic energy, which is calculated at the MP2/6-311G**//B3LYP/6-31+G* level. ZPE is the zero-point energy, which is calculated at the RHF/6-311G**//B3LYP/6-31+G* level and scaled by the factor of 0.925.

Another conceivable reaction pathway, aromatic 1,3-dipolar cycloaddition, was also obtained theoretically, as shown in Figure S3. In this reaction pathway, **22**-H can directly afford the tricyclic cycloadduct species **29**-H via the transition state TS-**27**-H. At the

transition state, two bonds are formed synchronously; one is a C-C bond between the ipso aromatic carbon atom and the α -carbon atom of the *aci*-nitro moiety, and the other is a C-O bond between the aromatic carbon atom and the oxygen atom of the *aci*-nitro moiety. The *O*-protonated *aci*-nitro species **26-H** is also conceivable as a possible starting structure of the 1,3-dipolar cycloaddition. The energy difference between the isomers **22-H** and **26-H** was 4.0 kcal/mol, so these species can be in equilibrium in a strong Brønsted acid. The corresponding cycloadduct species **30-H** was generated via transition state TS-**28-H**. In a comparison between these two 1,3-dipolar cycloaddition pathways, the latter would be energetically favored over the former by 3.9 kcal/mol (**22-H** to TS-**27-H**: 44.3 kcal/mol, **26-H** to TS-**28-H**: 40.4 kcal/mol). The substitution by an electron-withdrawing group did not change the magnitude of the activation energy of the relevant 1,3-dipolar cycloaddition significantly (within ± 0.6 kcal/mol). Similar cycloaddition of diradical species was also investigated and showed almost the same activation energy.

Figure S3. Reaction Coordinate of Cyclization of Protonated *aci*-Methyl 3-Aryl-2-nitropropionates: 1,3-Dipolar Addition.^{a, b}

^a A gray-colored sphere represents a carbon; light blue, hydrogen; blue, nitrogen; red, oxygen; green, chloride. All of the structures were obtained at the B3LYP/6-31+G* level. Values in the chemical structures are bond length (black) and natural charge (red), respectively. ^b E_0 is calculated as $E_{\text{elec}} + \text{ZPE}$. E_{elec} is the electronic energy, which is calculated at the MP2/6-311G**//B3LYP/6-31+G* level. ZPE is the zero-point energy, which is calculated at the RHF/6-311G**//B3LYP/6-31+G* level and scaled by the factor of 0.925.

We also simulated the subsequent reaction from the tricyclic cycloadduct **30-H**, which affords the 4*H*-1,2-benzoxazine skeleton. Structure optimization was carried out with fixation of the bond length (1.1 Å to 1.5 Å) between the eliminating aromatic hydrogen atom, which is located on the ipso position of the introduced oxygen atom, and the chloride atom (Figure S4). When the position of chloride was changed from **30-H** so that the hydrogen approached the hydroxyl group on the nitrogen and the chloride approached the eliminating aromatic hydrogen, cleavage of the N-O bond occurred simultaneously accompanied with the elimination of water. Re-aromatization by deprotonation of the aromatic hydrogen is represented by a series of the structures of **31-H**; the bond length between the aromatic carbon and the hydrogen was fixed to 1.1 Å, 1.3 Å, 1.5 Å respectively, with full optimization of all other geometrical parameters. The whole process is significantly exothermic, which means that the formation of the 4*H*-1,2-benzoxazine skeleton is thermodynamically favored once the intermediate **30-H** is formed.

Figure S4. Plausible Reaction Coordinate of Dehydration from [3+2]-Cycloadduct of Protonated *aci*-Methyl 2-Nitro-3-phenylpropionate.^{a, b, c}

^a A gray-colored sphere represents a carbon; light blue, hydrogen; blue, nitrogen; red, oxygen; green, chloride. All of the structures were obtained at the B3LYP/6-31+G* level. ^b E_0 is calculated as $E_{elec} + ZPE$. E_{elec} is the electronic energy, which is calculated at the MP2/6-311G**//B3LYP/6-31+G* level. ZPE is the zero-point energy, which is calculated at the RHF/6-311G**//B3LYP/6-31+G* level and scaled by the factor of 0.925. ^c The series of structures of **22-H** was optimized with a fixed bond length between C1 and H2 as written

under the structures (1.1 Å, 1.3 Å, 1.5 Å, and the optimized structure without restriction of the bond length).

As compared with the difference of the reaction energy in the present theoretical studies, the energy level of the transition states of the Friedel-Crafts type reaction was much higher than those of 1,3-dipolar cycloaddition in all cases. That is, the total energy of the Friedel-Crafts type transition state (Figure S2) was 54.9 kcal/mol, which is 12.6 kcal/mol higher than that of the 1,3-dipolar cycloaddition (42.3 kcal/mol, see Figure 1). With respect to the calculated energetics, aromatic 1,3-dipolar cycloaddition reactions are still energy-demanding processes, probably because a strained intermediate with a cyclopropane ring fused in a tricyclic system is formed, in spite of entropic feasibility. Under the highly acidic reaction condition, however, the reactive species is likely to be a bare cation, the energy levels of which should be much higher, and therefore the required activation energy should be lower than the calculated value. The effect of substituents on the benzene ring would provide an alternative criterion to evaluate the results of the theoretical studies. In the case of the Friedel-Crafts type reaction, the required activation energy became much higher when the benzene ring was substituted with a cyano group on its *p*-position. Experimentally, however, the cyclization reaction of the substrates with strongly electron-withdrawing substituents, such as a trifluoromethyl or nitro group, was found to proceed efficiently. The following experimental information also seems inconsistent with the possibility of the Friedel-Crafts type cyclization: if the cationic species such as **23-H**, formed via elimination of water, were involved in the reaction, a Nef-type product (the nitro group is converted to a carbonyl group) should be detected when the reaction is quenched with water. However, no Nef product (the keto-ester) was detected.

In this context, we also investigated the reaction pathway of the naked cationic species. In the 1,3-dipolar addition pathway, the transition structures of two monocationic species **18** and **19** were obtained (Table S2), but the activation energies (47.4 kcal/mol and 46.2 kcal/mol) were still large. The values are almost equivalent to the activation energy in the case of the neutral *aci*-nitro species (**17** and **17-TS**, 43.8 kcal/mol), which suggests that monoprotection does not efficiently facilitate the cyclization. In the case of the dicationic species (**20**), however, the activation energy was significantly reduced (**20** to **20-TS**: 28.7 kcal/mol). These results would indicate possible intermediacy of the dicationic species in the cyclization reaction, together with the experimental data on the acidity dependence of the reaction rate.

ΔE_0 (kcal/mol)					
neutral					
path A (17→17-TS)	43.8				
monocation					
path B (18→18-TS)	47.4				
path C (19→19-TS)	46.2				
dication					
path D (20→20-TS)	28.7				
		19	19-TS	20	20-TS

Table S2. The Monocationic and Dicationic species and their energy gap.^{a,b}

^a A gray-colored sphere represents a carbon; light blue, hydrogen; blue, nitrogen; red, oxygen. All of the structures were obtained at the B3LYP/6-31+G* level. ^b E_0 is calculated as $E_{elec} + ZPE$. E_{elec} is the electronic energy, which is calculated at the MP2/6-311G**//B3LYP/6-31+G* level. ZPE is the zero-point energy, which is calculated at the RHF/6-311G**//B3LYP/6-31+G* level and scaled by the factor of 0.925.

The Optimized Geometries

22-H

Total Energy (a.u.) = -1201.6549738 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 0 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 141.03688 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.942899	-1.233478	-0.215509
2	8	0	0.005386	-2.404596	-1.104719
3	7	0	-0.638809	-1.388941	-0.780169
4	8	0	-1.911766	-1.631091	-0.265173
5	1	0	-1.941964	-2.610821	-0.276796
6	6	0	-0.235180	-0.132200	-0.889929
7	6	0	-1.098596	0.985067	-0.453657

8	8	0	-2.203836	0.927404	0.062458
9	1	0	-3.626226	-0.176194	0.738950
10	17	0	-4.696543	-0.716645	1.256259
11	8	0	-0.490617	2.164918	-0.708049
12	6	0	-1.230158	3.344871	-0.331191
13	1	0	-1.418565	3.345279	0.745153
14	1	0	-0.591622	4.181372	-0.615003
15	1	0	-2.181475	3.382049	-0.867414
16	6	0	1.150170	0.072653	-1.466569
17	1	0	1.307864	-0.678938	-2.246169
18	1	0	1.172412	1.056155	-1.939393
19	6	0	2.263366	-0.025180	-0.427129
20	1	0	2.669222	-2.109061	-0.797097
21	6	0	2.629433	1.097283	0.330784
22	1	0	2.117075	2.042402	0.168992
23	6	0	3.648177	1.013610	1.283005
24	6	0	3.962364	-1.318197	0.737053
25	1	0	4.480569	-2.262035	0.887267
26	6	0	4.317165	-0.196156	1.490288
27	1	0	3.922531	1.894492	1.858265
28	1	0	5.111904	-0.261868	2.228995

22-CN

Total Energy (a.u.) = -1293.6902904 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 0 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 140.50805 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.451198	-1.038981	-1.023275
2	8	0	-0.530824	-2.310879	-1.174006
3	7	0	-1.181626	-1.344312	-0.735952
4	8	0	-2.314034	-1.668976	0.004537
5	6	0	-0.892874	-0.063070	-0.912421

6	6	0	-1.748347	0.999637	-0.344253
7	8	0	-2.800187	0.873418	0.261292
8	17	0	-5.176307	-0.937371	1.491229
9	8	0	-1.205080	2.212228	-0.593563
10	6	0	-1.956568	3.347164	-0.110891
11	6	0	0.353744	0.221337	-1.722912
12	6	0	1.643819	0.102421	-0.918809
13	6	0	2.047723	1.141583	-0.065705
14	6	0	3.634198	-1.146599	-0.294320
15	6	0	3.226702	1.047032	0.668498
16	6	0	4.029022	-0.102323	0.558128
17	6	0	5.247984	-0.204265	1.308718
18	7	0	6.236638	-0.285180	1.917702
19	1	0	4.253917	-2.033666	-0.382074
20	1	0	3.534505	1.857068	1.322642
21	1	0	1.434824	2.034681	0.018700
22	1	0	2.147516	-1.851724	-1.675948
23	1	0	0.383686	-0.479012	-2.563672
24	1	0	0.265324	1.230238	-2.129662
25	1	0	-2.053327	3.300702	0.976404
26	1	0	-1.377364	4.219191	-0.413918
27	1	0	-2.949975	3.362298	-0.565311
28	1	0	-4.156148	-0.318966	0.963290
29	1	0	-2.289438	-2.649003	-0.016228

23-H

Total Energy (a.u.) = -1201.6250725 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 0 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 140.67778 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.204507	-1.860555	-0.457464
2	8	0	2.535234	-0.360047	-1.218667

3	7	0	1.672136	0.467008	-0.984899
4	6	0	0.674164	0.754068	-0.245845
5	8	0	3.158620	0.436597	1.976803
6	17	0	2.767818	-2.168218	-0.088428
7	6	0	-1.187418	-0.798565	0.459871
8	6	0	0.130146	-0.149994	0.854682
9	6	0	0.068228	2.094018	-0.582467
10	8	0	0.342685	2.744419	-1.567063
11	8	0	-0.802209	2.467718	0.367600
12	6	0	-1.450609	3.740515	0.155403
13	6	0	-2.397350	-0.367761	1.020611
14	6	0	-3.601605	-0.988012	0.676566
15	6	0	-2.407494	-2.477630	-0.805673
16	6	0	-3.610346	-2.042051	-0.240595
17	1	0	-2.404111	-3.302668	-1.513319
18	1	0	-4.546479	-2.524433	-0.509710
19	1	0	-0.270624	-2.216753	-0.886427
20	1	0	-4.531078	-0.648141	1.126593
21	1	0	-2.394553	0.452455	1.733832
22	1	0	0.011644	0.473868	1.744965
23	1	0	0.874933	-0.911405	1.083782
24	1	0	-2.021065	3.718713	-0.776191
25	1	0	-2.109520	3.871479	1.013278
26	1	0	-0.704721	4.537637	0.110775
27	1	0	3.372399	-0.431495	1.589022
28	1	0	4.011412	0.837708	2.201039

23-CN

Total Energy (a.u.) = -1293.6599951 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 0 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 140.17504 (RHF/6-311G**//B3LYP/6-31+G*)

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	6	0	-1.288126	-1.206634	-0.305129
2	8	0	2.667411	-1.259497	-1.275632
3	6	0	1.438627	0.506446	-0.268557
4	6	0	-0.829029	-0.217304	0.578882
5	7	0	2.209567	-0.153594	-1.040660
6	8	0	3.679572	-0.684029	1.847578
7	6	0	1.377133	1.971883	-0.623365
8	8	0	1.862817	2.457417	-1.620637
9	8	0	0.720234	2.657311	0.325523
10	6	0	0.597871	4.079409	0.097357
11	6	0	0.653827	-0.096039	0.889875
12	6	0	-1.761900	0.633582	1.187663
13	6	0	-2.646261	-1.343909	-0.578113
14	6	0	-3.574567	-0.485170	0.036863
15	6	0	-3.124370	0.504760	0.926348
16	6	0	-4.976344	-0.620265	-0.239216
17	7	0	-6.113717	-0.726760	-0.462328
18	1	0	-2.994183	-2.114458	-1.259055
19	1	0	-3.841367	1.163839	1.406204
20	1	0	-0.578916	-1.886813	-0.770009
21	1	0	-1.418601	1.401920	1.874429
22	1	0	1.069198	-1.074623	1.128360
23	1	0	0.820936	0.550823	1.755113
24	1	0	3.591526	-1.592400	1.507764
25	1	0	4.605823	-0.594047	2.117085
26	1	0	0.055659	4.263099	-0.833087
27	1	0	0.042494	4.459016	0.954402
28	1	0	1.589201	4.535020	0.041432
29	17	0	2.220343	-2.981122	-0.107766

TS-24-H

Total Energy (a.u.) = -1201.5594678 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 1 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 141.10463 (RHF/6-311G**//B3LYP/6-31+G*)

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	6	0	1.290304	1.144516	0.188097
2	8	0	1.073503	-0.011697	1.585870
3	7	0	0.193355	-0.827106	1.325588
4	6	0	-0.564041	-0.540119	0.162067
5	8	0	1.296593	-2.842210	0.436807
6	17	0	3.465775	-1.124368	-0.882932
7	6	0	0.038938	0.799145	-0.553518
8	6	0	0.077452	-0.538278	-1.216170
9	6	0	-2.029949	-0.833836	0.360599
10	8	0	-2.512593	-1.103347	1.436705
11	8	0	-2.716974	-0.741068	-0.789954
12	6	0	-4.139266	-0.992704	-0.691908
13	6	0	-0.916784	1.873305	-0.845738
14	6	0	-0.694877	3.124186	-0.375707
15	6	0	1.434663	2.491948	0.680589
16	6	0	0.487310	3.430289	0.402516
17	1	0	2.349496	2.753487	1.203844
18	1	0	0.637546	4.456263	0.728955
19	1	0	2.198055	0.600069	-0.127052
20	1	0	-1.399650	3.921644	-0.592447
21	1	0	-1.800440	1.628742	-1.426189
22	1	0	-0.633319	-0.748897	-2.009779
23	1	0	1.067946	-0.989961	-1.303939
24	1	0	-4.598903	-0.284707	0.001633
25	1	0	-4.521668	-0.856567	-1.702862
26	1	0	-4.310650	-2.013548	-0.343930
27	1	0	2.120377	-2.445149	0.033036
28	1	0	1.592812	-3.281518	1.249080

TS-24-CN

Total Energy (a.u.) = -1293.587966 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 1 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 140.40395 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.021478	0.959517	-0.003958
2	8	0	0.005622	1.083304	1.525312
3	6	0	1.150949	-0.279100	0.166040
4	6	0	-0.235281	-0.112771	-0.677134
5	7	0	1.075972	0.515194	1.345359
6	8	0	2.690650	2.160773	0.664132
7	6	0	1.856329	-1.589843	0.421643
8	8	0	2.168401	-1.967690	1.527049
9	8	0	2.070344	-2.267375	-0.717006
10	6	0	2.735041	-3.547066	-0.570737
11	6	0	1.087419	0.343917	-1.213085
12	6	0	-0.927671	-1.348811	-1.052895
13	6	0	-2.388238	0.684204	0.348367
14	6	0	-2.962608	-0.509957	-0.001779
15	6	0	-2.225967	-1.536690	-0.723401
16	6	0	-4.344701	-0.756372	0.297100
17	7	0	-5.460517	-0.982948	0.535568
18	1	0	-2.970981	1.462927	0.829872
19	1	0	-2.746023	-2.447469	-1.000940
20	1	0	-0.748884	1.999537	-0.266070
21	1	0	-0.366395	-2.110293	-1.584002
22	1	0	1.210281	1.427130	-1.280244
23	1	0	1.577419	-0.256768	-1.973560
24	1	0	2.101699	2.839173	0.221154
25	1	0	2.940144	2.548948	1.517670
26	1	0	2.144698	-4.204274	0.071720
27	1	0	2.806432	-3.945875	-1.581839
28	1	0	3.726500	-3.399663	-0.137690
29	17	0	0.540825	3.732155	-0.818789

25-H

Total Energy (a.u.) = -1201.7021258 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 0 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 140.01546 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.337437	-0.970106	0.812246
2	8	0	-0.507200	-0.720723	1.891999
3	7	0	0.797959	-0.263374	1.652158
4	6	0	1.309711	-0.507884	0.502279
5	8	0	1.014070	2.218904	-0.981066
6	17	0	-2.482888	2.686497	-0.159851
7	6	0	-0.829253	-1.242043	-0.457042
8	6	0	0.667555	-1.281444	-0.622323
9	6	0	2.702295	0.042132	0.336864
10	8	0	3.123226	1.059860	0.844403
11	8	0	3.420326	-0.753701	-0.477239
12	6	0	4.768895	-0.319041	-0.754202
13	6	0	-1.734405	-1.462107	-1.500835
14	6	0	-3.112100	-1.439063	-1.272218
15	6	0	-2.712911	-0.923746	1.063621
16	6	0	-3.599747	-1.174968	0.013475
17	1	0	-3.062395	-0.710248	2.069525
18	1	0	-4.670086	-1.154390	0.199496
19	1	0	-2.593019	1.434145	0.166076
20	1	0	-3.801630	-1.621188	-2.091319
21	1	0	-1.351582	-1.658456	-2.499876
22	1	0	1.046665	-2.314776	-0.603175
23	1	0	0.973035	-0.853302	-1.582059
24	1	0	5.344833	-0.267154	0.172908
25	1	0	5.180050	-1.072441	-1.425775
26	1	0	4.753160	0.663616	-1.231932
27	1	0	0.125728	2.562625	-0.793740
28	1	0	1.539640	2.399633	-0.183753

25-CN

Total Energy (a.u.) = -1293.7377095 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 0 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 139.74226 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.271154	-0.036465	-0.333158
2	8	0	0.384357	0.807758	-0.989322
3	6	0	-1.416102	-0.416874	-0.255594
4	6	0	0.822295	-0.961668	0.608304
5	7	0	-0.971301	0.407293	-1.127007
6	8	0	-2.641775	1.763517	1.543382
7	6	0	-2.880934	-0.742238	-0.435705
8	8	0	-3.740114	0.075176	-0.688397
9	8	0	-3.103514	-2.051723	-0.247132
10	6	0	-4.477870	-2.485731	-0.373460
11	6	0	-0.651743	-0.991933	0.909172
12	6	0	1.763325	-1.798630	1.217190
13	6	0	2.615354	0.090466	-0.671095
14	6	0	3.547481	-0.735419	-0.025863
15	6	0	3.118598	-1.687994	0.917361
16	6	0	4.942545	-0.618977	-0.343654
17	7	0	6.074765	-0.531014	-0.597015
18	1	0	2.924274	0.814278	-1.417603
19	1	0	3.846072	-2.328961	1.404215
20	1	0	0.140912	2.717651	-0.430197
21	1	0	1.430563	-2.534328	1.945143
22	1	0	-0.897067	-0.370876	1.785120
23	1	0	-1.000126	-2.006038	1.125331
24	1	0	-2.149980	2.588428	1.399306
25	1	0	-3.212328	1.667086	0.761356
26	1	0	-4.844122	-2.274639	-1.380684

27	1	0	-4.455985	-3.558193	-0.183248
28	1	0	-5.100331	-1.969331	0.360961
29	17	0	-0.089552	3.863289	0.145249

26-H

Total Energy (a.u.) = -1201.6483742 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 0 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 140.91976 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.632518	-2.044861	-0.006207
2	8	0	1.649309	-1.164529	0.442989
3	17	0	4.627332	-1.835795	-0.210568
4	7	0	1.348552	0.046310	0.231261
5	8	0	2.305453	0.801601	-0.444368
6	6	0	0.245899	0.641700	0.625483
7	6	0	-1.831136	-0.800370	0.610738
8	6	0	-0.729356	-0.163533	1.451489
9	8	0	-0.891564	2.665598	1.032431
10	6	0	-0.100799	2.062123	0.327731
11	8	0	0.462569	2.574095	-0.771522
12	6	0	0.110519	3.939117	-1.079352
13	6	0	-3.059189	-0.146112	0.438302
14	6	0	-4.069406	-0.722611	-0.336903
15	6	0	-3.863422	-1.961650	-0.949448
16	6	0	-2.642247	-2.621054	-0.780993
17	1	0	-2.475352	-3.587880	-1.249450
18	1	0	-4.649740	-2.412425	-1.549591
19	1	0	-5.018005	-0.205089	-0.456850
20	1	0	-3.224756	0.817078	0.915358
21	1	0	-0.684940	-2.560809	0.123433
22	1	0	3.394697	-1.815596	0.237684
23	1	0	3.019484	0.150935	-0.618557

24	1	0	-0.174970	-0.932986	1.994671
25	1	0	-1.171455	0.524439	2.176740
26	1	0	-0.965156	4.021003	-1.254484
27	1	0	0.671179	4.177047	-1.982918
28	1	0	0.398291	4.598017	-0.256486

26-CN

Total Energy (a.u.) = -1293.6851541 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 0 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 140.40012 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.891761	0.898742	1.081554
2	8	0	-1.286171	1.536341	0.710111
3	7	0	-1.677810	0.419685	0.275085
4	8	0	-2.713452	0.451691	-0.650174
5	6	0	-1.166408	-0.745128	0.619887
6	6	0	-1.605233	-2.068840	0.100332
7	8	0	-2.779420	-2.093076	-0.537127
8	6	0	-3.198257	-3.383769	-1.030514
9	8	0	-0.917131	-3.058897	0.294208
10	6	0	-0.012207	-0.709824	1.595844
11	6	0	1.323919	-0.375211	0.941994
12	6	0	2.011134	-1.348646	0.199197
13	6	0	3.237555	-1.058161	-0.392370
14	6	0	3.118902	1.201794	0.494509
15	6	0	3.799462	0.222875	-0.248296
16	6	0	5.064919	0.527097	-0.853081
17	7	0	6.091237	0.773289	-1.344100
18	17	0	-3.013806	3.905085	-0.467497
19	1	0	-2.132810	3.232488	0.223004
20	1	0	-2.899285	1.412444	-0.744588
21	1	0	-2.466367	-3.770089	-1.743956

22	1	0	-4.156244	-3.200282	-1.516072
23	1	0	-3.308114	-4.087351	-0.201678
24	1	0	0.046595	-1.697250	2.059169
25	1	0	-0.235113	0.025877	2.374479
26	1	0	1.580794	-2.340313	0.090684
27	1	0	1.367520	1.659684	1.651779
28	1	0	3.766475	-1.816771	-0.961206
29	1	0	3.553348	2.190246	0.608463

TS-27-H

Total Energy (a.u.) = -1201.5833156 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 1 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 140.34805 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.141249	-1.166137	0.729036
2	8	0	-0.630081	-1.879777	1.075188
3	7	0	0.359647	-1.116583	0.617941
4	8	0	0.643271	-1.388803	-0.754842
5	1	0	1.393513	-2.013594	-0.713879
6	6	0	0.112276	0.237519	0.799786
7	6	0	1.017104	1.213004	0.164157
8	8	0	2.142708	0.982804	-0.261841
9	1	0	3.206410	-0.453020	-0.323888
10	17	0	3.950509	-1.537861	-0.419262
11	8	0	0.490687	2.452510	0.150824
12	6	0	1.326111	3.490081	-0.405474
13	1	0	1.564745	3.263068	-1.447043
14	1	0	0.731919	4.400910	-0.332748
15	1	0	2.250362	3.581054	0.170251
16	6	0	-0.889504	0.660633	1.837501
17	1	0	-0.925135	0.038476	2.734215
18	1	0	-0.825297	1.722097	2.067216

19	6	0	-1.822184	0.274492	0.745550
20	1	0	-2.548987	-1.557375	1.665585
21	6	0	-2.376181	1.144489	-0.248774
22	1	0	-2.208479	2.213790	-0.161301
23	6	0	-3.074202	0.621252	-1.303660
24	6	0	-2.795690	-1.662872	-0.478794
25	1	0	-2.969929	-2.732044	-0.562246
26	6	0	-3.235345	-0.800562	-1.438589
27	1	0	-3.496900	1.279320	-2.057616
28	1	0	-3.747911	-1.188228	-2.315740

TS-27-CN

Total Energy (a.u.) = -1293.6194705 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 1 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 139.88869 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.629293	-0.511057	1.519872
2	8	0	-0.200257	-1.447519	1.675121
3	7	0	0.745987	-0.951325	0.887525
4	8	0	0.656617	-1.468006	-0.437040
5	6	0	0.741806	0.436872	0.862202
6	6	0	1.615837	1.123085	-0.118359
7	8	0	2.580202	0.625728	-0.681588
8	17	0	3.884438	-2.223141	-0.691843
9	8	0	1.271455	2.411361	-0.280762
10	6	0	2.102154	3.183372	-1.178059
11	6	0	0.107933	1.189243	1.996923
12	6	0	-1.087342	0.820659	1.189816
13	6	0	-1.714881	1.620197	0.176079
14	6	0	-2.607098	-1.053785	0.586542
15	6	0	-2.697716	1.092728	-0.609914
16	6	0	-3.104864	-0.282274	-0.431898

17	6	0	-4.092385	-0.826314	-1.322290
18	7	0	-4.896077	-1.248699	-2.050416
19	1	0	-2.970653	-2.064203	0.744044
20	1	0	-3.173421	1.686356	-1.383151
21	1	0	-1.374430	2.639845	0.027059
22	1	0	-1.863958	-0.676650	2.574157
23	1	0	0.181604	0.716153	2.977495
24	1	0	0.385061	2.240939	2.011253
25	1	0	2.071661	2.751374	-2.180712
26	1	0	1.670143	4.183701	-1.172000
27	1	0	3.132565	3.200476	-0.815757
28	1	0	3.394179	-1.003208	-0.671393
29	1	0	1.293372	-2.210103	-0.440767

TS-28-H

Total Energy (a.u.) = -1201.5831054 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 1 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 140.23321 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.109860	1.438367	0.700900
2	8	0	-1.409551	-0.352299	0.791073
3	17	0	-4.025269	-1.788724	-0.141604
4	7	0	-0.321464	-0.985996	0.355227
5	8	0	-0.350383	-1.126441	-1.074364
6	6	0	0.842656	-0.308242	0.724210
7	6	0	0.357100	1.429793	0.841078
8	6	0	0.859453	0.558948	1.945278
9	8	0	3.158741	-0.007870	0.258831
10	6	0	2.169103	-0.711624	0.166897
11	8	0	2.172907	-1.945462	-0.357603
12	6	0	3.440830	-2.400807	-0.874528
13	6	0	1.155003	2.304114	0.009999

14	6	0	0.570131	2.978995	-1.021249
15	6	0	-0.836926	2.842080	-1.281025
16	6	0	-1.650374	2.114782	-0.459821
17	1	0	-2.724428	2.086945	-0.621284
18	1	0	-1.266592	3.370479	-2.128792
19	1	0	1.169828	3.619317	-1.661799
20	1	0	2.222969	2.359850	0.191391
21	1	0	-1.685286	1.531734	1.621676
22	1	0	-2.940544	-1.144929	0.240882
23	1	0	-0.671255	-2.036851	-1.203698
24	1	0	0.137347	0.318377	2.724564
25	1	0	1.865081	0.751258	2.312401
26	1	0	3.773986	-1.746750	-1.684068
27	1	0	3.250077	-3.408394	-1.243509
28	1	0	4.192234	-2.412600	-0.081018

TS-28-CN

Total Energy (a.u.) = -1293.6188794 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 1 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 139.73205 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.227017	-0.015659	1.286739
2	8	0	0.360594	1.488939	0.848334
3	7	0	-0.745004	1.160970	0.181954
4	8	0	-0.473893	0.993811	-1.213206
5	6	0	-1.317056	-0.007495	0.684217
6	6	0	-2.435328	-0.687652	-0.041184
7	8	0	-3.066643	0.112780	-0.907370
8	6	0	-4.183036	-0.477686	-1.608983
9	8	0	-2.769139	-1.831801	0.206526
10	6	0	-1.088026	-0.408985	2.108720
11	6	0	0.082991	-0.942426	1.351133

12	6	0	0.206638	-2.266170	0.785991
13	6	0	1.288399	-2.589000	0.024694
14	6	0	2.312263	-0.382633	0.401458
15	6	0	2.327895	-1.612584	-0.208452
16	6	0	3.429163	-1.971678	-1.057791
17	7	0	4.314601	-2.279466	-1.747530
18	17	0	1.282217	4.307434	-0.263049
19	1	0	0.991590	3.138265	0.255427
20	1	0	-0.691383	1.864176	-1.594266
21	1	0	-3.843117	-1.326960	-2.206422
22	1	0	-4.567117	0.317550	-2.247164
23	1	0	-4.943593	-0.809291	-0.897982
24	1	0	-1.818811	-1.131022	2.465566
25	1	0	-0.870016	0.392635	2.813321
26	1	0	-0.602524	-2.972834	0.934452
27	1	0	1.523579	0.460469	2.221411
28	1	0	1.380084	-3.572087	-0.424402
29	1	0	3.143556	0.304165	0.277396

29-H

Total Energy (a.u.) = -1201.5991817 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 0 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 141.84275 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.905757	-1.312579	0.657676
2	8	0	-0.647884	-1.945086	1.081113
3	7	0	0.451421	-1.153259	0.675816
4	8	0	0.655580	-1.398073	-0.722972
5	1	0	1.467416	-1.939248	-0.731373
6	6	0	-0.043255	0.217657	0.746065
7	6	0	0.854261	1.252993	0.162300
8	8	0	2.032027	1.094983	-0.116868

9	1	0	3.196835	-0.301824	-0.227687
10	17	0	4.010613	-1.312584	-0.440789
11	8	0	0.237168	2.438244	0.032726
12	6	0	1.045496	3.526949	-0.465470
13	1	0	1.421715	3.288583	-1.462794
14	1	0	0.374732	4.385273	-0.498406
15	1	0	1.884985	3.713224	0.208627
16	6	0	-0.879569	0.572137	1.958825
17	1	0	-0.863602	-0.126418	2.792164
18	1	0	-0.878068	1.624441	2.228231
19	6	0	-1.609688	0.179708	0.711213
20	1	0	-2.594019	-1.625705	1.456277
21	6	0	-2.445028	1.067207	-0.123335
22	1	0	-2.460718	2.129341	0.098309
23	6	0	-3.127566	0.548462	-1.165774
24	6	0	-2.433277	-1.753405	-0.677289
25	1	0	-2.373440	-2.812800	-0.911280
26	6	0	-3.041755	-0.874086	-1.496423
27	1	0	-3.731074	1.194861	-1.797924
28	1	0	-3.483430	-1.213785	-2.430176

29-CN

Total Energy (a.u.) = -1293.6336105 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 0 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 141.33869 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.443186	-0.632442	1.496909
2	8	0	-0.241710	-1.420727	1.783427
3	7	0	0.830067	-0.961694	0.979842
4	8	0	0.619163	-1.485744	-0.335077
5	6	0	0.597056	0.472963	0.849272
6	6	0	1.472011	1.174729	-0.134740

7	8	0	2.508245	0.728746	-0.597435
8	17	0	3.884057	-2.100646	-0.768645
9	8	0	1.023727	2.407765	-0.412985
10	6	0	1.838708	3.195872	-1.311471
11	6	0	0.155858	1.204962	2.098012
12	6	0	-0.912978	0.750439	1.150074
13	6	0	-1.779522	1.620170	0.331571
14	6	0	-2.331735	-1.199388	0.429960
15	6	0	-2.768803	1.080861	-0.406404
16	6	0	-2.982676	-0.375477	-0.425510
17	6	0	-3.907992	-0.910177	-1.384812
18	7	0	-4.668621	-1.315234	-2.167046
19	1	0	-2.490020	-2.273239	0.419074
20	1	0	-3.406305	1.701225	-1.028268
21	1	0	-1.581346	2.686502	0.311621
22	1	0	-1.969436	-0.650208	2.462385
23	1	0	0.263424	0.683238	3.045940
24	1	0	0.388014	2.265876	2.116795
25	1	0	1.926509	2.690679	-2.275627
26	1	0	1.310038	4.142982	-1.415113
27	1	0	2.832074	3.347511	-0.882818
28	1	0	3.369430	-0.901171	-0.628420
29	1	0	1.302685	-2.179304	-0.408773

30-H

Total Energy (a.u.) = -1201.5987139 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 0 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 141.70346 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.076345	1.209357	0.603122
2	8	0	-1.420576	-0.225553	0.755386
3	17	0	-4.174884	-1.566823	-0.070570

4	7	0	-0.337144	-1.048115	0.328634
5	8	0	-0.383134	-1.073194	-1.104440
6	6	0	0.847466	-0.262563	0.657801
7	6	0	0.429703	1.236544	0.809724
8	6	0	0.859870	0.432746	2.000518
9	8	0	3.164663	0.011070	0.172548
10	6	0	2.174289	-0.693544	0.117859
11	8	0	2.169995	-1.949170	-0.352494
12	6	0	3.433295	-2.436658	-0.849699
13	6	0	1.185079	2.347427	0.195750
14	6	0	0.622958	3.058688	-0.803379
15	6	0	-0.715332	2.740850	-1.300540
16	6	0	-1.509310	1.843553	-0.684622
17	1	0	-2.510100	1.620346	-1.044640
18	1	0	-1.067175	3.251542	-2.193771
19	1	0	1.178546	3.861542	-1.280629
20	1	0	2.202610	2.525659	0.526105
21	1	0	-1.621392	1.650647	1.449574
22	1	0	-3.046538	-0.998593	0.281486
23	1	0	-0.710663	-1.969652	-1.293248
24	1	0	0.105435	0.142493	2.727843
25	1	0	1.852711	0.624218	2.397698
26	1	0	3.774741	-1.817360	-1.682840
27	1	0	3.233644	-3.455834	-1.180447
28	1	0	4.183592	-2.425825	-0.055073

30-CN

Total Energy (a.u.) = -1293.6323564 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 0 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 141.15824 (RHF/6-311G**//B3LYP/6-31+G*)

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-1.085193	0.153332	1.092145

2	8	0	-0.890639	-1.262825	0.723432
3	7	0	0.338758	-1.424094	0.018436
4	8	0	0.103574	-0.965571	-1.316593
5	6	0	1.215678	-0.420800	0.612656
6	6	0	2.520724	-0.110494	-0.054097
7	8	0	2.891330	-1.041541	-0.941002
8	6	0	4.162481	-0.821118	-1.590286
9	8	0	3.191200	0.858772	0.246607
10	6	0	1.168757	-0.267274	2.114649
11	6	0	0.328895	0.668944	1.296563
12	6	0	0.559594	2.116017	1.124708
13	6	0	-0.331982	2.862685	0.445650
14	6	0	-1.871765	0.960329	0.105203
15	6	0	-1.528947	2.246040	-0.148120
16	6	0	-2.339864	3.048885	-1.020858
17	7	0	-2.981822	3.722359	-1.719764
18	17	0	-3.034311	-3.461696	-0.207189
19	1	0	-2.169437	-2.575245	0.208908
20	1	0	0.054589	-1.792755	-1.827120
21	1	0	4.140788	0.117546	-2.149048
22	1	0	4.288191	-1.670239	-2.261552
23	1	0	4.964617	-0.788365	-0.848985
24	1	0	2.076789	0.136532	2.553359
25	1	0	0.667722	-1.041602	2.690260
26	1	0	1.480398	2.543540	1.505672
27	1	0	-1.643998	0.065317	2.034692
28	1	0	-0.168771	3.923548	0.286273
29	1	0	-2.760164	0.512747	-0.329756

31-H

$C^1 - H^2 = 1.10 \text{ \AA}$

Total Energy (a.u.) = -1201.6116152 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 2 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 139.67681 (RHF/6-311G**//B3LYP/6-31+G*)

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	6	0	1.574683	0.491570	-0.330489
2	1	0	1.911523	0.691161	0.697471
3	8	0	0.392543	1.311695	-0.407999
4	7	0	-0.848141	0.738863	-0.285049
5	8	0	-3.479036	2.610198	-1.082354
6	8	0	-3.292872	-0.143518	-0.084788
7	8	0	-2.550166	-2.193125	0.532467
8	17	0	2.138601	1.059693	2.375423
9	6	0	-4.666033	-0.586390	-0.009618
10	6	0	-2.348108	-1.036891	0.211330
11	6	0	-0.957378	-0.475849	0.115568
12	6	0	0.189977	-1.381116	0.495527
13	6	0	1.410947	-0.936703	-0.234725
14	6	0	2.453599	-1.756517	-0.638703
15	6	0	2.657299	1.017020	-1.124095
16	6	0	3.690543	0.181361	-1.488233
17	6	0	3.590453	-1.202675	-1.240230
18	1	0	-4.831047	-1.409436	-0.709169
19	1	0	-4.895838	-0.913338	1.007334
20	1	0	-5.252693	0.288825	-0.285130
21	1	0	-2.944206	3.417039	-1.055626
22	1	0	-2.885033	1.902829	-0.774547
23	1	0	0.374940	-1.278190	1.579664
24	1	0	-0.063676	-2.426267	0.302948
25	1	0	2.383317	-2.830526	-0.489501
26	1	0	2.676281	2.084667	-1.320087
27	1	0	4.562883	0.578795	-1.997857
28	1	0	4.404683	-1.857251	-1.538944

$C^1 - H^2 = 1.30 \text{ \AA}$

Total Energy (a.u.) = -1201.6542633 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 2 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 137.50526 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.522049	0.473253	-0.385249
2	1	0	1.970763	0.675124	0.818040
3	17	0	2.280678	0.991642	2.262048
4	8	0	0.383493	1.312782	-0.306480
5	7	0	-0.876684	0.750687	-0.214765
6	1	0	-2.845150	1.961195	-0.672962
7	8	0	-3.444969	2.675698	-0.952335
8	1	0	-2.900632	3.476566	-0.950431
9	6	0	-0.988769	-0.485134	0.114460
10	6	0	-2.386190	-1.036931	0.192604
11	8	0	-2.597639	-2.201151	0.476179
12	8	0	-3.322672	-0.126010	-0.072793
13	6	0	-4.699600	-0.557942	-0.009959
14	1	0	-4.874031	-1.354345	-0.737563
15	1	0	-4.930954	-0.918357	0.995337
16	1	0	-5.278402	0.331873	-0.253436
17	6	0	0.150535	-1.415984	0.443785
18	1	0	0.309327	-1.409679	1.534940
19	1	0	-0.107265	-2.441543	0.166901
20	6	0	1.386083	-0.930809	-0.249925
21	6	0	2.455750	-1.738063	-0.628715
22	6	0	2.608775	1.026178	-1.113338
23	6	0	3.671005	0.205393	-1.454605
24	6	0	3.595525	-1.175858	-1.210047
25	1	0	4.426790	-1.817668	-1.487675
26	1	0	4.546576	0.626179	-1.939647
27	1	0	2.615792	2.094264	-1.306194
28	1	0	2.395765	-2.811493	-0.469406

$C^1 - H^2 = 1.50 \text{ \AA}$

Total Energy (a.u.) = -1201.6773799 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 2 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 139.10772 (RHF/6-311G**//B3LYP/6-31+G*)

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
<hr/>					
1	6	0	1.505883	0.438209	-0.487478
2	1	0	1.977396	0.747418	0.902509
3	17	0	2.221859	1.100308	2.232975
4	8	0	0.383962	1.278241	-0.413066
5	7	0	-0.882353	0.723196	-0.288937
6	1	0	-2.867557	1.940323	-0.684481
7	8	0	-3.471015	2.668306	-0.917574
8	1	0	-2.908782	3.455083	-0.967564
9	6	0	-0.989632	-0.504258	0.071788
10	6	0	-2.389219	-1.045338	0.191321
11	8	0	-2.601456	-2.195985	0.524786
12	8	0	-3.326188	-0.141300	-0.095963
13	6	0	-4.703751	-0.561813	0.012673
14	1	0	-4.898496	-1.383130	-0.681333
15	1	0	-4.914923	-0.883999	1.035231
16	1	0	-5.282904	0.322343	-0.249844
17	6	0	0.145149	-1.434134	0.414137
18	1	0	0.263978	-1.457014	1.509434
19	1	0	-0.105091	-2.454562	0.109891
20	6	0	1.404021	-0.940920	-0.239671
21	6	0	2.512181	-1.743421	-0.517138
22	6	0	2.625575	0.987996	-1.141264
23	6	0	3.725123	0.173799	-1.383450
24	6	0	3.668795	-1.192373	-1.072530
25	1	0	4.526579	-1.828559	-1.270433
26	1	0	4.617620	0.595095	-1.836454
27	1	0	2.623704	2.044912	-1.388168
28	1	0	2.466176	-2.806099	-0.292593

without restriction of the bond length

Total Energy (a.u.) = -1201.700328 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 0 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 139.83429 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.172378	0.196926	-0.811367
2	1	0	3.593919	0.973166	0.803557
3	17	0	4.018884	1.329718	1.975133
4	8	0	0.134164	1.116235	-0.730724
5	7	0	-1.140827	0.691386	-0.377637
6	1	0	-3.039570	2.039581	-0.636745
7	8	0	-3.602549	2.802714	-0.859710
8	1	0	-2.989675	3.486259	-1.167316
9	6	0	-1.291553	-0.487475	0.109221
10	6	0	-2.699124	-0.874633	0.477043
11	8	0	-2.953663	-1.959464	0.965967
12	8	0	-3.593499	0.080189	0.216191
13	6	0	-4.970511	-0.197582	0.550176
14	1	0	-5.324445	-1.062196	-0.016776
15	1	0	-5.062112	-0.395647	1.620923
16	1	0	-5.509811	0.705832	0.268799
17	6	0	-0.212651	-1.500582	0.384758
18	1	0	-0.071208	-1.575588	1.473701
19	1	0	-0.556818	-2.491063	0.066232
20	6	0	1.063176	-1.097325	-0.308468
21	6	0	2.155351	-1.959209	-0.464878
22	6	0	2.334863	0.654390	-1.438590
23	6	0	3.418923	-0.216156	-1.568208
24	6	0	3.329308	-1.527719	-1.084288
25	1	0	4.169867	-2.207284	-1.188792
26	1	0	4.327068	0.127101	-2.056071
27	1	0	2.367339	1.669369	-1.823380

28 1 0 2.083624 -2.975639 -0.084136

17

Total Energy (a.u.) = -741.3981996 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 0 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 134.94702 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.455945	0.947945	0.188437
2	8	0	-0.390556	2.659592	0.135282
3	7	0	-1.118929	1.654406	-0.015942
4	8	0	-2.245700	1.871694	-0.820898
5	6	0	-0.925941	0.458822	0.511038
6	6	0	-1.791271	-0.728921	0.305254
7	8	0	-1.536462	-1.783381	0.867522
8	8	0	-2.836782	-0.570140	-0.519231
9	6	0	0.300682	0.302455	1.382312
10	6	0	1.836049	-1.385765	0.264233
11	6	0	1.558111	-0.050215	0.593659
12	6	0	2.985269	-1.715274	-0.458641
13	6	0	3.873712	-0.713772	-0.861633
14	6	0	3.605817	0.618188	-0.534942
15	1	0	4.769753	-0.970281	-1.421383
16	1	0	4.293450	1.403449	-0.839634
17	1	0	3.188707	-2.755380	-0.701850
18	1	0	1.148287	-2.166703	0.578833
19	1	0	2.250409	1.985010	0.438722
20	1	0	0.456806	1.234570	1.932889
21	1	0	0.083410	-0.492003	2.099841
22	1	0	-4.085148	-2.062310	0.243422
23	6	0	-3.660571	-1.737101	-0.709769
24	1	0	-3.072327	-2.550587	-1.141971
25	1	0	-4.445100	-1.418090	-1.395952

26 1 0 -2.106552 2.811185 -1.062423

17-TS

Total Energy (a.u.) = -741.3271143 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 1 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 134.03155 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

1	6	0	-2.029509	-0.621485	0.578556
2	8	0	-0.945572	-2.002386	0.484352
3	7	0	0.261835	-1.589733	0.123908
4	8	0	0.384378	-1.515321	-1.309520
5	6	0	0.595407	-0.360911	0.680774
6	6	0	1.789422	0.404826	0.237444
7	8	0	1.949064	1.582885	0.510661
8	8	0	2.699253	-0.338660	-0.414056
9	6	0	-0.082051	0.090719	1.939720
10	6	0	-1.186498	1.730386	0.233896
11	6	0	-1.080017	0.458618	0.897334
12	6	0	-2.065303	1.886434	-0.801334
13	6	0	-2.879734	0.786343	-1.239521
14	6	0	-2.874340	-0.412535	-0.587703
15	1	0	-3.539831	0.930856	-2.091823
16	1	0	-3.541917	-1.215458	-0.888716
17	1	0	-2.141357	2.842514	-1.311609
18	1	0	-0.527924	2.535835	0.543180
19	1	0	-2.520078	-1.088360	1.435185
20	1	0	-0.387003	-0.696187	2.630805
21	1	0	0.449153	0.910321	2.419551
22	1	0	4.410264	0.780204	0.024699
23	6	0	3.885176	0.361374	-0.837820
24	1	0	3.622392	1.165938	-1.529403
25	1	0	4.496636	-0.391828	-1.335025
26	1	0	0.714520	-2.400471	-1.543758

18

Total Energy (a.u.) = -741.7453213 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 0 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 142.96558 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.503793	0.742764	0.581045
2	8	0	-0.126945	2.666102	0.285897
3	1	0	-1.731958	3.133838	-1.136967
4	1	0	-2.972539	0.790523	-1.160294
5	8	0	-2.983813	-0.132124	-0.818109
6	8	0	-1.933455	2.190266	-0.944771
7	7	0	-0.931857	1.807435	-0.017476
8	6	0	-0.963065	0.538547	0.420530
9	6	0	-1.990968	-0.371151	-0.007473
10	8	0	-1.922941	-1.563682	0.482652
11	6	0	-2.930880	-2.576074	0.129394
12	1	0	-2.899870	-2.748235	-0.947090
13	1	0	-2.620840	-3.457107	0.685951
14	1	0	-3.913699	-2.225933	0.447046
15	6	0	0.162028	0.116463	1.348258
16	1	0	0.322170	0.920613	2.073241
17	1	0	-0.176006	-0.759989	1.905209
18	6	0	1.453776	-0.185553	0.594470
19	6	0	1.607379	-1.403613	-0.086217
20	1	0	0.814097	-2.147832	-0.057899
21	6	0	3.686947	0.458940	-0.106720
22	1	0	4.498058	1.181530	-0.101530
23	6	0	3.829700	-0.751577	-0.788815
24	6	0	2.788431	-1.684928	-0.774905
25	1	0	2.901347	-2.635773	-1.288248
26	1	0	4.751598	-0.972964	-1.318909

27 1 0 2.405039 1.681875 1.119060

18-TS

Total Energy (a.u.) = -741.6701885 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 1 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 141.91778 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.034853	-0.342196	0.754635
2	8	0	-1.170129	-1.749232	0.779939
3	1	0	-0.186838	-2.804561	-1.273649
4	1	0	1.793069	-1.488744	-1.397232
5	8	0	2.467092	-0.852893	-1.051982
6	8	0	0.047421	-1.859965	-1.173378
7	7	0	0.052640	-1.675200	0.276152
8	6	0	0.753598	-0.510548	0.614783
9	6	0	1.944123	-0.176765	-0.051222
10	8	0	2.611532	0.871322	0.362285
11	6	0	3.850388	1.251146	-0.313826
12	1	0	3.651523	1.440186	-1.369938
13	1	0	4.166256	2.157878	0.197604
14	1	0	4.587814	0.455904	-0.194646
15	6	0	0.149548	0.348574	1.708371
16	1	0	-0.090470	-0.216658	2.614051
17	1	0	0.812398	1.179049	1.949178
18	6	0	-1.029576	0.731127	0.878956
19	6	0	-1.141334	1.883726	0.091284
20	1	0	-0.434070	2.698181	0.223625
21	6	0	-2.986116	-0.246799	-0.354662
22	1	0	-3.688171	-1.062581	-0.499905
23	6	0	-3.037799	0.886775	-1.114438
24	6	0	-2.148196	1.974981	-0.860285
25	1	0	-2.249304	2.885009	-1.444884

26	1	0	-3.776775	0.982491	-1.904361
27	1	0	-2.519934	-0.573732	1.710596

19

Total Energy (a.u.) = -741.7381204 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 0 (B3LYP/6-31+G*)

Zero-point energy (kcal / m ol) = 143.17432 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.232378	1.057132	-0.137515
2	8	0	-0.742954	2.747825	0.249635
3	7	0	-1.342161	1.555346	0.025203
4	8	0	-2.359590	1.706926	-0.858824
5	1	0	-2.708313	0.785073	-1.031288
6	6	0	-0.895255	0.474296	0.589904
7	6	0	1.536538	0.091699	0.608350
8	6	0	0.330579	0.502456	1.460344
9	6	0	-1.584143	-0.859094	0.362006
10	8	0	-1.301153	-1.822662	1.021080
11	8	0	-2.517388	-0.824173	-0.611000
12	6	0	-3.238025	-2.077814	-0.887300
13	1	0	-2.514794	-2.836139	-1.187431
14	1	0	-3.919942	-1.831662	-1.698368
15	1	0	-3.773590	-2.381933	0.012379
16	1	0	0.465787	1.495554	1.892499
17	1	0	0.168881	-0.214305	2.269271
18	6	0	1.959220	-1.245384	0.578357
19	1	0	1.432339	-1.996685	1.160317
20	1	0	1.929711	2.100655	-0.100963
21	6	0	3.071728	-1.609982	-0.182874
22	6	0	3.342500	0.686997	-0.898422
23	1	0	3.886924	1.441570	-1.458931
24	6	0	3.761563	-0.646766	-0.924799

25	1	0	3.403357	-2.644307	-0.188341
26	1	0	4.628627	-0.932176	-1.513530
27	1	0	-1.337688	3.422369	-0.147461

19-TS

Total Energy (a.u.) = -741.6615669 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 1 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 142.47807 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.000625	-0.590205	0.549381
2	8	0	-1.125634	-1.963777	0.473585
3	7	0	0.413522	-1.660909	0.134286
4	8	0	0.447880	-1.634758	-1.242318
5	1	0	0.961148	-2.430629	-1.488295
6	6	0	0.502995	-0.290059	0.609100
7	6	0	-0.899809	0.415334	0.809206
8	6	0	-0.020568	0.053905	1.977052
9	6	0	1.731650	0.485116	0.158559
10	8	0	1.835599	1.672602	0.365786
11	8	0	2.662436	-0.300349	-0.374357
12	6	0	3.914830	0.348765	-0.745116
13	1	0	3.723656	1.102464	-1.510916
14	1	0	4.540614	-0.454632	-1.129432
15	1	0	4.362918	0.810965	0.136037
16	1	0	-0.352127	-0.755652	2.624091
17	1	0	0.515202	0.855310	2.477541
18	6	0	-1.100974	1.772100	0.257267
19	1	0	-0.443706	2.562194	0.599534
20	1	0	-2.557865	-0.880076	1.445529
21	6	0	-2.018748	1.972457	-0.712462
22	6	0	-2.843305	-0.348677	-0.628492
23	1	0	-3.573294	-1.103177	-0.912034

24	6	0	-2.851285	0.882438	-1.196452
25	1	0	-2.148475	2.958519	-1.146982
26	1	0	-3.550891	1.086972	-2.002600
27	1	0	-1.419052	-2.522686	-0.282304

20

Total Energy (a.u.) = -741.9122611 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 0 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 150.14036 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.996605	0.944712	0.142145
2	8	0	-0.529812	2.876771	0.649358
3	7	0	-1.174562	1.821497	0.071040
4	8	0	-1.321193	1.979015	-1.315175
5	6	0	-0.879876	0.579622	0.505130
6	6	0	-1.590568	-0.559706	-0.158064
7	8	0	-2.103694	-0.515864	-1.337500
8	8	0	-1.732431	-1.607262	0.546257
9	6	0	-2.466467	-2.806479	0.023203
10	6	0	0.024586	0.328294	1.654754
11	6	0	1.169747	-0.065858	0.717688
12	6	0	1.468859	-1.438565	0.480932
13	6	0	2.597719	-1.782379	-0.243640
14	6	0	3.419352	-0.774351	-0.788092
15	6	0	3.118249	0.584650	-0.588868
16	1	0	3.772378	1.351493	-0.992420
17	1	0	4.298904	-1.052092	-1.362574
18	1	0	2.860096	-2.827137	-0.380390
19	1	0	1.785842	1.993528	0.327183
20	1	0	0.855869	-2.214517	0.930237
21	1	0	0.225800	1.219793	2.245856
22	1	0	-0.307530	-0.489777	2.293730

23	1	0	-2.402681	-3.516916	0.843192
24	1	0	-1.952648	-3.152544	-0.874268
25	1	0	-3.494033	-2.504899	-0.182116
26	1	0	-1.928192	2.740840	-1.453849
27	1	0	-1.212722	3.433312	1.087082
28	1	0	-1.931343	0.347524	-1.793583

20-TS

Total Energy (a.u.) = -741.8667382 (MP2/6-311G**//B3LYP/6-31+G*)

Number of Imaginary Frequencies = 1 (B3LYP/6-31+G*)

Zero-point energy (kcal / mol) = 150.33272 (RHF/6-311G**//B3LYP/6-31+G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.072197	0.126369	0.616896
2	8	0	1.606494	1.727384	0.357601
3	7	0	0.090728	1.946933	0.197991
4	8	0	-0.065084	2.182327	-1.161158
5	6	0	-0.449831	0.625814	0.523128
6	6	0	-1.716570	0.211881	-0.136097
7	8	0	-2.157271	0.667251	-1.257503
8	8	0	-2.394912	-0.681774	0.465616
9	6	0	-3.676906	-1.205848	-0.107694
10	6	0	-0.134997	0.096694	1.902533
11	6	0	0.713383	-0.512321	0.838844
12	6	0	0.531835	-1.867305	0.288295
13	6	0	1.406579	-2.342104	-0.626948
14	6	0	2.547450	-1.550725	-1.070358
15	6	0	2.867080	-0.360077	-0.502388
16	1	0	3.786733	0.161160	-0.752030
17	1	0	3.201620	-1.969746	-1.830219
18	1	0	1.278762	-3.339916	-1.036253
19	1	0	2.634892	0.315249	1.537359
20	1	0	-0.316386	-2.453462	0.627324

21	1	0	0.324453	0.803369	2.592588
22	1	0	-0.903273	-0.520126	2.360600
23	1	0	-3.978064	-1.968082	0.606053
24	1	0	-3.468805	-1.617363	-1.095217
25	1	0	-4.385290	-0.378270	-0.147855
26	1	0	-0.028480	3.158577	-1.263309
27	1	0	1.889512	2.346032	1.072683
28	1	0	-1.545901	1.338277	-1.651367

References and Notes

- 1) Kornblum, N.; Blackwood, R. K.; Powers, J. W. *J. Am. Chem. Soc.* **1957**, *79*, 2507-2509.
- 2) Crumbie, R. L.; Nimitz, J. S.; Mosher, H. S. *J. Org. Chem.* **1982**, *47*, 4040-4045.
- 3) (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; GoMpe.erts, R.; Martin, R. L.; Fox, D. J.; Keith, T. A.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Gaussian, Inc.: Pittsburgh, PA, **1998**. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Jr., T. V.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Lyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Peterson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; GoMpe.erts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, G.; Dapprich, S.; Daniels, A. K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Gaussian, Inc.; Pittsburgh, PA, **2003**.

- 4) Scott, A.P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502-16513.
- 5) Intramolecular ipso-attack of the aromatic moiety upon the oxygen atom in the dehydrated cationic intermediate **23-H** is also conceivable, affording the spiro species with a five-six ring system. However, we could not find a corresponding transition state or intermediate in the calculation.