# SUPPORTING INFORMATION

## Application of β-phosphorylated nitroethenes in [3+2] cycloaddition reactions involving benzonitrile N-oxide in the light of DFT computational study

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**Table S1.** The relative enthalpies, Gibbs free energy (ΔH and ΔG values are in kcal/mol$^{-1}$) and entropies (ΔS values are in cal/mol$^{-1}$ K$^{-1}$), computed in toluene and nitromethane, for the stationary points involved in the [3+2] cycloaddition reactions of the benzonitrile N-oxide **1** and β-phosphorylated analogues of nitroethenes **2a-c**, as obtained via M062X/6-31+G(d) theory level.

| Reaction | Transition | Toluene (ε = 2.38) | | | Nitromethane (ε = 36.56) | | |
|---|---|---|---|---|---|---|---|
| | | ΔH | ΔG | ΔS | ΔH | ΔG | ΔS |
| 1 + 2a | **1 + 2a** → **MC$_{3a}$** | – 3.43 | 8.43 | – 39.81 | – 1.82 | 10.33 | – 40.75 |
| | **1 + 2a** → **TS$_{3a}$** | 9.04 | 23.20 | – 47.49 | 9.15 | 23.90 | – 49.49 |
| | **1 + 2a** → **3a** | – 43.63 | – 28.20 | – 51.74 | – 42.87 | – 26.72 | – 54.17 |
| | **1 + 2a** → **MC$_{4a}$** | – 5.77 | 4.11 | – 33.15 | – 3.40 | 5.79 | – 30.82 |
| | **1 + 2a** → **TS$_{4a}$** | 9.72 | 24.63 | – 49.99 | 10.03 | 24.83 | – 49.54 |
| | **1 + 2a** → **4a** | – 48.98 | – 33.60 | – 51.60 | – 48.00 | – 31.38 | – 55.76 |
| 1 + 2b | **1 + 2b** → **MC$_{3b}$** | – 7.90 | 6.18 | – 47.22 | – 3.85 | 10.17 | – 47.04 |
| | **1 + 2b** → **TS$_{3b}$** | 2.53 | 16.68 | – 47.45 | 3.88 | 18.45 | – 48.87 |
| | **1 + 2b** → **3b** | – 39.81 | – 24.38 | – 51.75 | – 37.34 | – 21.70 | – 52.45 |
| | **1 + 2b** → **MC$_{4b}$** | – 6.95 | 3.00 | – 33.35 | – 4.61 | 4.59 | – 30.87 |
| | **1 + 2b** → **TS$_{4b}$** | 5.47 | 19.59 | – 47.36 | 6.79 | 21.39 | 48.94 |
| | **1 + 2b** → **4b** | – 43.90 | – 28.53 | – 51.53 | – 41.35 | – 27.06 | – 49.93 |
| 1 + 2c | **1 + 2c** → **MC$_{3c}$** | – 5.56 | 8.03 | – 45.60 | – 3.79 | 10.75 | – 48.77 |
| | **1 + 2c** → **TS$_{3c}$** | 8.14 | 25.15 | – 47.08 | 8.28 | 24.64 | – 52.87 |
| | **1 + 2c** → **3c** | – 40.38 | – 25.49 | – 49.96 | – 38.08 | – 22.10 | – 53.58 |
| | **1 + 2c** → **MC$_{4c}$** | – 6.90 | 3.17 | – 33.74 | – 4.35 | 6.10 | – 35.05 |
| | **1 + 2c** → **TS$_{4c}$** | 6.45 | 22.53 | – 53.95 | 6.04 | 24.28 | – 51.12 |
| | **1 + 2c** → **4c** | – 44.40 | – 27.54 | – 56.54 | – 42.14 | – 25.79 | – 54.85 |

**Table S2.** The key parameters of the critical structures in the [3+2] cycloaddition reactions of the benzonitrile N-oxide **1** and $\beta$-phosphorylated analogues of nitroethenes **2a-c**, computed in toluene and nitromethane, as obtained via M062X/6-31+G(d) (PCM) calculations.

| Solvent | Reaction | Structure | C3–C4 r (Å) | $l_{C3–C4}$ | C5–O1 r (Å) | $l_{C5–O1}$ | GEDT (e) | Imaginary frequency ($cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| **Toluene** | **1 + 2a** | **MC$_{3a}$** | 3.918 | | 3.660 | | 0.0 | |
| **(ε = 2.38)** | | **TS$_{3a}$** | 2.238 | 0.523 | 2.091 | 0.550 | 0.26 | – 449.21 |
| | | **3a** | 1.515 | | 1.442 | | | |
| | | **MC$_{4a}$** | 3.858 | | 3.800 | | 0.0 | |
| | | **TS$_{4a}$** | 2.186 | 0.557 | 2.146 | 0.449 | 0.39 | – 449.51 |
| | | **4a** | 1.516 | | 1.383 | | | |
| | **1 + 2b** | **MC$_{3b}$** | 3.978 | | 3.482 | | 0.0 | |
| | | **TS$_{3b}$** | 2.410 | 0.426 | 1.889 | 0.681 | 0.45 | – 400.99 |
| | | **3b** | 1.531 | | 1.432 | | | |
| | | **MC$_{4b}$** | 3.787 | | 3.826 | | 0.0 | |
| | | **TS$_{4b}$** | 2.095 | 0.682 | 2.174 | 0.425 | 0.44 | – 439.15 |
| | | **4b** | 1.516 | | 1.381 | | | |
| | **1 + 2c** | **MC$_{3c}$** | 3.773 | | 3.769 | | 0.0 | |
| | | **TS$_{3c}$** | 2.149 | 0.579 | 2.138 | 0.517 | 0.31 | – 445.06 |
| | | **3c** | 1.512 | | 1.441 | | | |
| | | **MC$_{4c}$** | 3.952 | | 3.985 | | 0.0 | |
| | | **TS$_{4c}$** | 2.348 | 0.469 | 1.924 | 0.609 | 0.47 | – 430.14 |
| | | **4c** | 1.533 | | 1.383 | | | |
| **Nitromethane** | **1 + 2a** | **MC$_{3a}$** | 3.927 | | 3.649 | | 0.0 | |
| **(ε = 36.56)** | | **TS$_{3a}$** | 2.243 | 0.521 | 2.073 | 0.563 | 0.27 | – 451.08 |
| | | **3a** | 1.517 | | 1.443 | | | |
| | | **MC$_{4a}$** | 3.847 | | 3.786 | | 0.0 | |
| | | **TS$_{4a}$** | 2.191 | 0.553 | 2.136 | 0.455 | 0.41 | – 442.59 |
| | | **4a** | 1.514 | | 1.383 | | | |
| | **1 + 2b** | **MC$_{3b}$** | 4.039 | | 3.776 | | 0.0 | |
| | | **TS$_{3b}$** | 2.491 | 0.371 | 1.816 | 0.739 | 0.49 | – 457.02 |
| | | **3b** | 1.529 | | 1.440 | | | |
| | | **MC$_{4b}$** | 3.734 | | 3.832 | | 0.0 | |
| | | **TS$_{4b}$** | 2.068 | 0.636 | 2.180 | 0.419 | 0.47 | – 438.93 |
| | | **4b** | 1.516 | | 1.379 | | | |
| | **1 + 2c** | **MC$_{3c}$** | 3.768 | | 3.738 | | 0.0 | |
| | | **TS$_{3c}$** | 2.145 | 0.584 | 2.113 | 0.534 | 0.34 | – 448.65 |
| | | **3c** | 1.515 | | 1.442 | | | |
| | | **MC$_{4c}$** | 3.979 | | 3.947 | | 0.0 | |
| | | **TS$_{4c}$** | 2.371 | 0.454 | 1.890 | 0.631 | 0.49 | – 426.52 |
| | | **4c** | 1.534 | | 1.381 | | | |

**Table S3.** Cartesian coordinates of **1** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | 0.03649300 | -0.00000400 | 0.00000000 |
| C | -0.66031200 | 1.21625800 | 0.00000100 |
| C | -2.05123400 | 1.20906100 | 0.00000100 |
| C | -2.74721100 | 0.00000500 | 0.00000100 |
| C | -2.05124200 | -1.20905500 | 0.00000100 |
| C | -0.66031900 | -1.21626100 | 0.00000000 |
| H | -0.10942000 | 2.15134700 | 0.00000000 |
| H | -2.59240900 | 2.15004700 | 0.00000100 |
| H | -3.83294400 | 0.00000900 | 0.00000200 |
| H | -2.59242300 | -2.15003700 | 0.00000100 |
| H | -0.10943500 | -2.15135400 | 0.00000000 |
| C | 1.47261100 | -0.00000900 | -0.00000100 |
| N | 2.62994000 | -0.00000600 | -0.00000100 |
| O | 3.84929200 | 0.00000700 | -0.00000200 |

**Table S4.** Cartesian coordinates of **2a** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | 1.65129800 | -0.04922800 | 0.41622200 |
| C | 0.64867500 | -0.24887900 | -0.42663700 |
| H | 1.57906500 | 0.18940400 | 1.47078200 |
| H | 0.83034300 | -0.49057700 | -1.47107400 |
| N | 3.04291900 | -0.15586000 | -0.04740400 |
| O | 3.89887800 | 0.01649500 | 0.80229700 |
| O | 3.25454700 | -0.40260000 | -1.22025900 |
| P | -1.03358600 | -0.06291200 | 0.18919800 |
| O | -1.11130600 | 0.20220200 | 1.64284400 |
| O | -1.70946300 | -1.38467200 | -0.37757600 |
| O | -1.69650800 | 1.06923300 | -0.73213500 |
| H | -2.63654318 | -1.54872293 | -0.18993369 |
| H | -1.62088108 | 1.98709198 | -0.46118212 |

**Table S5.** Cartesian coordinates of **2b** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | -1.48493800 | -0.13469800 | -0.11650600 |
| C | -0.34979400 | -0.78384500 | 0.13172200 |
| H | -0.41307400 | -1.78623900 | 0.55017000 |
| N | -2.78519400 | -0.80523900 | 0.18246200 |
| O | -3.78831500 | -0.16305000 | -0.04487400 |
| O | -2.73987200 | -1.93335900 | 0.62624500 |
| P | 1.28865100 | -0.05915000 | -0.16321900 |
| O | 1.35597300 | 0.83089700 | -1.33784100 |
| O | 2.15496900 | -1.38681500 | -0.15878600 |
| O | 1.68044900 | 0.61862000 | 1.22933400 |
| C | -1.62570300 | 1.19399100 | -0.64070900 |
| N | -1.73134900 | 2.27509300 | -1.03456500 |
| H | 3.08904400 | -1.33273270 | -0.37367901 |
| H | 1.40433564 | 1.52123722 | 1.40438702 |

**Table S6.** Cartesian coordinates of **2c** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | 1.53344600 | -0.61102400 | -0.38825600 |
| C | 0.57014400 | 0.23699400 | -0.02619200 |
| N | 2.96197400 | -0.31244100 | -0.25474200 |
| O | 3.71412200 | -1.18758400 | -0.64400000 |
| O | 3.29413200 | 0.75501400 | 0.22196900 |
| P | -1.14830100 | -0.35709300 | -0.24542100 |
| O | -1.18453500 | -1.71643500 | -0.82072800 |
| O | -1.74990200 | 0.85680000 | -1.05841800 |
| O | -1.82901700 | -0.19309300 | 1.18558300 |
| H | 1.34300600 | -1.58883000 | -0.81517500 |
| C | 0.74412300 | 1.53981300 | 0.54362300 |
| N | 0.74817700 | 2.59688800 | 1.01403100 |
| H | -1.77608801 | -0.91239102 | 1.81915137 |
| H | -2.68637775 | 0.87697234 | -1.26867083 |

**Table S7.** Cartesian coordinates of **3a** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | -0.04505400 | 0.91717100 | -0.16014500 |
| C | -1.27007500 | 0.54636300 | -0.98526400 |
| H | -0.21054200 | 0.96701200 | 0.91594800 |
| H | -1.68803800 | 1.38566400 | -1.54640800 |
| N | 0.45555900 | -0.86116800 | -1.57165800 |
| O | -0.80781600 | -0.44658300 | -1.92286700 |
| C | 0.92421500 | -0.15670000 | -0.61166200 |
| C | 2.26211800 | -0.36535600 | -0.04080400 |
| C | 2.66763900 | 0.36394600 | 1.08213700 |
| C | 3.13944900 | -1.29532700 | -0.61802400 |
| C | 3.93483800 | 0.16220500 | 1.62684300 |
| H | 2.00476200 | 1.09345800 | 1.53891500 |
| C | 4.39976600 | -1.49275700 | -0.06914400 |
| H | 2.82540300 | -1.85292300 | -1.49486800 |
| C | 4.80096100 | -0.76512300 | 1.05478000 |
| H | 4.24074700 | 0.73409800 | 2.49726800 |
| H | 5.07545500 | -2.21345000 | -0.51959700 |
| H | 5.78836100 | -0.92070400 | 1.47899800 |
| N | 0.50140100 | 2.27983400 | -0.55002400 |
| O | 0.62016300 | 2.50437300 | -1.73712100 |
| O | 0.78805500 | 3.04031400 | 0.35290900 |
| O | -3.79572100 | -0.65144400 | -0.70850100 |
| P | -2.56020200 | -0.29071100 | 0.01628500 |
| O | -1.76907900 | -1.51614500 | 0.67894300 |
| O | -2.68152200 | 0.74088000 | 1.22533600 |
| H | -1.78183337 | -2.38326707 | 0.26719473 |
| H | -3.35540307 | 0.60360982 | 1.89514284 |

**Table S8.** Cartesian coordinates of **4a** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | 0.82623500 | -0.22032400 | -0.42049900 |
| C | 1.98740900 | -1.02882100 | 0.13569400 |
| H | 0.75277400 | -0.29096100 | -1.50944700 |
| H | 2.93626200 | -0.50306600 | 0.25002500 |
| N | 0.13767500 | -1.60783700 | 1.31473400 |
| O | 1.54510000 | -1.52922700 | 1.34727700 |
| C | -0.29665300 | -0.90183400 | 0.33677900 |
| C | -1.73191300 | -0.77542900 | 0.04373500 |
| C | -2.16514600 | 0.03004700 | -1.01358100 |
| C | -2.67206700 | -1.46503000 | 0.82276100 |
| C | -3.52648000 | 0.14916200 | -1.28812100 |
| H | -1.44766100 | 0.57535900 | -1.61978000 |
| C | -4.02697000 | -1.34298200 | 0.54368100 |
| H | -2.33141500 | -2.09405700 | 1.63924300 |
| C | -4.45800500 | -0.53530500 | -0.51197600 |
| H | -3.85495500 | 0.77653100 | -2.11102600 |
| H | -4.75095200 | -1.88064100 | 1.14837800 |
| H | -5.51834800 | -0.44393500 | -0.72810000 |
| N | 2.28507600 | -2.20010800 | -0.83084600 |
| O | 2.60282800 | -1.86442000 | -1.95690600 |
| O | 2.20371300 | -3.33092300 | -0.41554800 |
| O | 2.43065400 | 1.92422800 | 0.29715900 |
| O | 0.00550300 | 1.86057500 | 1.21937100 |
| O | 0.29538200 | 2.25274100 | -1.21269300 |
| P | 1.02198300 | 1.55956400 | 0.02213700 |
| H | 0.29047454 | 1.73487970 | 2.12744143 |
| H | 0.21568384 | 3.20933068 | -1.22627200 |

**Table S9.** Cartesian coordinates of **3b** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | 0.09816900 | 0.34197500 | -0.23179000 |
| C | -1.01640500 | -0.43534300 | -0.96128200 |
| H | -0.99864800 | -0.14109200 | -2.01729600 |
| N | 0.73694700 | -1.86449600 | -0.61005700 |
| O | -0.61320200 | -1.80553600 | -0.86354400 |
| C | 1.20159600 | -0.71731000 | -0.28803200 |
| C | 2.61591300 | -0.47904200 | 0.03175800 |
| C | 3.03143300 | 0.72805000 | 0.60457300 |
| C | 3.55976100 | -1.47779400 | -0.24851000 |
| C | 4.37805800 | 0.93112900 | 0.89975700 |
| H | 2.32058800 | 1.51567400 | 0.83875500 |
| C | 4.89943000 | -1.26833400 | 0.05015200 |
| H | 3.23362700 | -2.40765500 | -0.70376500 |
| C | 5.31209200 | -0.06350400 | 0.62451900 |
| H | 4.69201200 | 1.86974400 | 1.34533300 |
| H | 5.62643000 | -2.04415600 | -0.16940000 |
| H | 6.36119500 | 0.09864900 | 0.85267300 |
| N | 0.48486400 | 1.57828600 | -1.06396200 |
| O | 0.80144600 | 1.35323200 | -2.21074000 |
| O | 0.45341100 | 2.65642200 | -0.51808200 |
| O | -3.75061600 | -0.85654100 | -1.21040700 |
| P | -2.72834800 | -0.28697500 | -0.31188400 |
| O | -2.68281500 | -0.90579400 | 1.15492200 |
| O | -2.70150700 | 1.28075900 | -0.05099600 |
| C | -0.16430200 | 0.76880600 | 1.14870100 |
| N | -0.33412300 | 1.04396100 | 2.25664000 |
| H | -2.96134349 | -1.81263483 | 1.30210077 |
| H | -3.35785377 | 1.70430430 | 0.50705266 |

**Table S10.** Cartesian coordinates of **4b** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | 0.50874500 | -0.23047200 | -0.51889500 |
| C | 1.70606300 | -0.98145500 | 0.06074100 |
| H | 0.36587100 | -0.46141700 | -1.57756200 |
| N | -0.03059800 | -1.32669600 | 1.46538800 |
| O | 1.37788500 | -1.24893700 | 1.37512200 |
| C | -0.54231500 | -0.78748000 | 0.42084600 |
| C | -1.99975300 | -0.72061800 | 0.23150900 |
| C | -2.54070000 | -0.49201500 | -1.03747500 |
| C | -2.85045900 | -0.91365700 | 1.32795300 |
| C | -3.92197700 | -0.46504900 | -1.21058600 |
| H | -1.89094400 | -0.33253800 | -1.89273200 |
| C | -4.22822600 | -0.88123700 | 1.15023800 |
| H | -2.42339100 | -1.08100300 | 2.31179800 |
| C | -4.76631400 | -0.65826300 | -0.11882500 |
| H | -4.33712100 | -0.29341400 | -2.19887700 |
| H | -4.88473000 | -1.02758600 | 2.00246500 |
| H | -5.84338900 | -0.63421600 | -0.25530200 |
| N | 1.81980800 | -2.35997300 | -0.71863600 |
| O | 1.90005100 | -2.26466800 | -1.92473900 |
| O | 1.82527000 | -3.36475400 | -0.05757900 |
| O | 1.81210600 | 2.16024400 | -1.11411100 |
| O | 0.66525800 | 1.89916700 | 1.20344500 |
| O | -0.79956700 | 2.01186500 | -0.80763700 |
| P | 0.66782100 | 1.60396400 | -0.36500300 |
| C | 3.04962400 | -0.39392000 | -0.00592700 |
| N | 4.12341200 | 0.02707100 | -0.01246500 |
| H | 1.47884373 | 2.05560647 | 1.68842433 |
| H | -1.05525628 | 2.93717072 | -0.80195173 |

**Table S11.** Cartesian coordinates of **3c** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | 0.04050100 | 0.74234400 | 0.20204900 |
| C | -1.20360000 | 0.50888100 | -0.67604400 |
| N | 0.60664500 | -0.50334400 | -1.68097500 |
| O | -0.70626300 | -0.12291200 | -1.87214100 |
| C | 1.05906500 | -0.06756500 | -0.56820700 |
| C | 2.43927700 | -0.29341300 | -0.12059700 |
| C | 2.83525900 | 0.09244400 | 1.16440600 |
| C | 3.36721500 | -0.88847100 | -0.98724500 |
| C | 4.14698700 | -0.12300500 | 1.58315800 |
| H | 2.13089700 | 0.56004300 | 1.84775800 |
| C | 4.67163400 | -1.10120000 | -0.56305500 |
| H | 3.05779600 | -1.17187200 | -1.98833200 |
| C | 5.06433700 | -0.72039400 | 0.72314000 |
| H | 4.44819400 | 0.17969200 | 2.58097500 |
| H | 5.38823900 | -1.55884100 | -1.23800700 |
| H | 6.08666800 | -0.88559900 | 1.04966600 |
| N | 0.47559800 | 2.19524000 | 0.22704800 |
| O | 0.75262100 | 2.69670700 | -0.84180000 |
| O | 0.51131200 | 2.73837000 | 1.31183100 |
| O | -3.52608400 | -1.08607900 | -0.69263900 |
| P | -2.33064400 | -0.75507600 | 0.10177100 |
| O | -1.31372000 | -1.94830800 | 0.39136800 |
| O | -2.52430700 | -0.07144900 | 1.52002100 |
| H | -0.10187800 | 0.45521100 | 1.24371500 |
| C | -1.96371100 | 1.71107500 | -1.02161300 |
| N | -2.60506800 | 2.64280300 | -1.25292200 |
| H | -1.24003714 | -2.69179934 | -0.21145160 |
| H | -3.22540622 | -0.37014919 | 2.10383439 |

**Table S12.** Cartesian coordinates of **4c** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | 0.74221000 | -0.28260600 | -0.29321500 |
| C | 1.81049100 | -1.16896300 | 0.38184200 |
| N | -0.11343200 | -1.34780400 | 1.59247800 |
| O | 1.29131500 | -1.43163400 | 1.63666600 |
| C | -0.47042800 | -0.74837100 | 0.52117500 |
| C | -1.88190800 | -0.52819000 | 0.18028600 |
| C | -2.25633900 | 0.45161800 | -0.74506900 |
| C | -2.86159700 | -1.31629000 | 0.80070800 |
| C | -3.60411900 | 0.64996600 | -1.03541400 |
| H | -1.50943600 | 1.06882200 | -1.23634800 |
| C | -4.20339200 | -1.11225500 | 0.50506600 |
| H | -2.55964700 | -2.09013300 | 1.49958800 |
| C | -4.57715700 | -0.12850700 | -0.41264600 |
| H | -3.89102000 | 1.41208100 | -1.75329300 |
| H | -4.95919400 | -1.72789000 | 0.98289200 |
| H | -5.62637100 | 0.02493600 | -0.64680700 |
| N | 1.97863800 | -2.47998000 | -0.40143400 |
| O | 2.76860700 | -2.42470600 | -1.32176300 |
| O | 1.30960400 | -3.43242700 | -0.07237900 |
| O | 2.61552300 | 1.64492000 | 0.44744600 |
| O | 0.17860300 | 1.90635400 | 1.30980300 |
| O | 0.58088500 | 2.25943100 | -1.11403000 |
| P | 1.17757800 | 1.50363000 | 0.14056000 |
| H | 2.80473700 | -0.72826800 | 0.44485100 |
| C | 0.61013600 | -0.45717000 | -1.73486100 |
| N | 0.48311300 | -0.59977500 | -2.87401300 |
| H | 0.68281647 | 3.21177216 | -1.17927031 |
| H | 0.42264076 | 1.81768649 | 2.23402356 |

**Table S13.** Cartesian coordinates of **TS$_{3a}$** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | -0.17360300 | 1.03286700 | 0.33429000 |
| C | -1.30656100 | 1.08142800 | -0.43373400 |
| H | -0.05998400 | 0.45650600 | 1.24469900 |
| H | -1.49332900 | 1.93216100 | -1.08223900 |
| N | 0.31189200 | -0.47060200 | -1.75399400 |
| O | -0.83285000 | -0.12382400 | -2.07537400 |
| C | 1.11178000 | -0.34455600 | -0.87323700 |
| C | 2.41573400 | -0.57527000 | -0.30933800 |
| C | 3.44858700 | 0.33111800 | -0.58669500 |
| C | 2.62074300 | -1.65714100 | 0.55798000 |
| C | 4.69901200 | 0.13192800 | -0.01208900 |
| H | 3.26280300 | 1.17682300 | -1.24289200 |
| C | 3.87609000 | -1.84531900 | 1.12348800 |
| H | 1.80135000 | -2.33587000 | 0.77592400 |
| C | 4.91188500 | -0.95328200 | 0.83788500 |
| H | 5.50451900 | 0.82799600 | -0.22222100 |
| H | 4.04739100 | -2.68426400 | 1.79043300 |
| H | 5.88936300 | -1.10233300 | 1.28661300 |
| N | 0.78449700 | 2.12690000 | 0.25607300 |
| O | 0.76494900 | 2.85961700 | -0.72201100 |
| O | 1.58700600 | 2.21648000 | 1.17270800 |
| O | -3.76920200 | -0.05932700 | -1.04788600 |
| P | -2.68387300 | -0.01251300 | -0.04512100 |
| O | -2.00689500 | -1.43260200 | 0.28986000 |
| O | -3.07495300 | 0.50597500 | 1.41604300 |
| H | -2.03993323 | -2.15779632 | -0.33831329 |
| H | -3.83927449 | 0.11404920 | 1.84476998 |

**Table S14.** Cartesian coordinates of **TS$_{4a}$** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | 1.13711600 | -0.06579900 | -0.51004600 |
| C | 2.22649300 | -0.78167100 | -0.09205800 |
| H | 0.67998300 | -0.31053400 | -1.46704700 |
| H | 2.99910000 | -0.42588000 | 0.57638100 |
| N | 0.19550600 | -1.82828700 | 1.14294700 |
| O | 1.37271400 | -2.08770500 | 1.38190800 |
| C | -0.50651000 | -1.12280800 | 0.47210300 |
| C | -1.88344100 | -0.89066200 | 0.08690700 |
| C | -2.22422500 | 0.16132400 | -0.76888300 |
| C | -2.87329400 | -1.75815100 | 0.57478700 |
| C | -3.55481100 | 0.34211400 | -1.13445600 |
| H | -1.46306200 | 0.83796900 | -1.14330100 |
| C | -4.19878900 | -1.56057600 | 0.20835400 |
| H | -2.59496800 | -2.57690000 | 1.23104500 |
| C | -4.54209900 | -0.51208100 | -0.64667000 |
| H | -3.81884900 | 1.15756000 | -1.80038800 |
| H | -4.96352800 | -2.23120800 | 0.58744800 |
| H | -5.57860900 | -0.36355100 | -0.93384200 |
| N | 2.62455600 | -1.96886600 | -0.84834100 |
| O | 1.81717000 | -2.45328800 | -1.62532200 |
| O | 3.74282500 | -2.40246000 | -0.63791200 |
| O | 2.28816800 | 2.11642900 | 0.72973800 |
| O | -0.24451700 | 1.75547000 | 1.05952900 |
| O | 0.50883600 | 2.36704100 | -1.21423800 |
| P | 1.03970200 | 1.63030700 | 0.09855100 |
| H | -0.12699143 | 1.60781287 | 2.00079682 |
| H | 0.37168406 | 3.31672684 | -1.18446964 |

**Table S15.** Cartesian coordinates of **TS$_{3b}$** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | -0.16249000 | 0.97389700 | 0.30889600 |
| C | -1.26328900 | 1.02597900 | -0.53901700 |
| H | -1.41201400 | 1.95082500 | -1.09006200 |
| N | 0.32348500 | -0.39331600 | -1.90618900 |
| O | -0.84145100 | 0.03689500 | -2.09183400 |
| C | 1.21447700 | -0.38960600 | -1.12345500 |
| C | 2.50611600 | -0.59142800 | -0.55731900 |
| C | 3.51535400 | 0.34943100 | -0.82378300 |
| C | 2.71978000 | -1.66012400 | 0.32849800 |
| C | 4.75583900 | 0.19328200 | -0.22010600 |
| H | 3.31362500 | 1.18482600 | -1.48805000 |
| C | 3.96673700 | -1.79949700 | 0.92245900 |
| H | 1.91358000 | -2.35398700 | 0.54396100 |
| C | 4.97924600 | -0.87784300 | 0.64685500 |
| H | 5.54431900 | 0.91225300 | -0.41584400 |
| H | 4.14763200 | -2.62003500 | 1.60877500 |
| H | 5.95002100 | -0.99117400 | 1.11989200 |
| N | 0.82751200 | 2.03818900 | 0.23303800 |
| O | 0.78687700 | 2.78303100 | -0.73765600 |
| O | 1.66925500 | 2.09263600 | 1.11395400 |
| O | -3.82115700 | 0.22207100 | -1.21671300 |
| P | -2.76350200 | 0.05254500 | -0.19928200 |
| O | -2.26206600 | -1.45117300 | 0.01474300 |
| O | -3.06445500 | 0.53062500 | 1.28663600 |
| C | -0.03456900 | 0.11523900 | 1.44436100 |
| N | 0.08111100 | -0.61349600 | 2.33692600 |
| H | -3.78074808 | 0.12037800 | 1.77676009 |
| H | -2.34358697 | -2.10791876 | -0.68069883 |

**Table S16.** Cartesian coordinates of **TS$_{4b}$** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | 0.88281100 | -0.23952300 | -0.69771000 |
| C | 2.15867200 | -0.43210300 | -0.20470700 |
| H | 0.58512400 | -0.88583000 | -1.52218900 |
| N | 0.51788700 | -1.60625200 | 1.42829100 |
| O | 1.72665800 | -1.57428700 | 1.59446400 |
| C | -0.34864600 | -1.21978500 | 0.68540000 |
| C | -1.78512000 | -1.18407100 | 0.49084700 |
| C | -2.35811200 | -1.89087700 | -0.57075800 |
| C | -2.57030700 | -0.39237900 | 1.33719800 |
| C | -3.73179900 | -1.81554600 | -0.77532900 |
| H | -1.73106800 | -2.49073900 | -1.22377100 |
| C | -3.94395100 | -0.33028500 | 1.12686800 |
| H | -2.09777500 | 0.16620500 | 2.13918300 |
| C | -4.52244200 | -1.03690700 | 0.07126600 |
| H | -4.18615700 | -2.36442800 | -1.59403000 |
| H | -4.56291200 | 0.27377800 | 1.78297400 |
| H | -5.59457900 | -0.98117100 | -0.09214300 |
| N | 2.93995900 | -1.58355100 | -0.68934600 |
| O | 2.32864100 | -2.45215900 | -1.28563200 |
| O | 4.12825100 | -1.59141400 | -0.44219500 |
| O | 0.98598500 | 2.46441100 | -1.40174900 |
| O | -0.04527200 | 1.74861200 | 0.86040000 |
| O | -1.25191000 | 1.10659600 | -1.27938900 |
| P | 0.19316100 | 1.43707800 | -0.69424600 |
| C | 2.91247400 | 0.56905400 | 0.49079500 |
| N | 3.46119400 | 1.41161700 | 1.06242300 |
| H | -1.93292794 | 1.78296137 | -1.26082957 |
| H | 0.27984863 | 2.56341523 | 1.25026186 |

**Table S17.** Cartesian coordinates of **TS$_{3c}$** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | -0.07713600 | 0.68392700 | 0.58390800 |
| C | -1.26472400 | 0.87844100 | -0.09553600 |
| N | 0.40963900 | -0.17621900 | -1.79706000 |
| O | -0.75966900 | 0.13025100 | -2.03306800 |
| C | 1.20677500 | -0.19339700 | -0.89903000 |
| C | 2.54404300 | -0.46753500 | -0.43443300 |
| C | 2.83968900 | -1.71790100 | 0.12536000 |
| C | 3.51019000 | 0.54632300 | -0.48947300 |
| C | 4.12224000 | -1.96123900 | 0.60143900 |
| H | 2.06883600 | -2.48169700 | 0.17797100 |
| C | 4.78816600 | 0.28963300 | -0.00548100 |
| H | 3.25372600 | 1.51636800 | -0.90640200 |
| C | 5.09294600 | -0.95960800 | 0.53519200 |
| H | 4.36435100 | -2.92919900 | 1.02845800 |
| H | 5.54435300 | 1.06680800 | -0.04734100 |
| H | 6.09213500 | -1.15294400 | 0.91365400 |
| N | 0.82516600 | 1.79741400 | 0.87132200 |
| O | 0.86269600 | 2.73336300 | 0.09178200 |
| O | 1.52325300 | 1.67739900 | 1.86345700 |
| O | -3.62930900 | -0.37396500 | -0.91249400 |
| P | -2.51818000 | -0.44002900 | 0.05359200 |
| O | -1.64717600 | -1.78502200 | 0.02757800 |
| O | -2.87265100 | -0.29522700 | 1.59964100 |
| H | 0.04548100 | -0.12295300 | 1.29733100 |
| C | -1.72838100 | 2.14981500 | -0.57055800 |
| N | -2.18791900 | 3.14436300 | -0.94232200 |
| H | -3.58993533 | -0.82681018 | 1.95251847 |
| H | -1.63514300 | -2.35688545 | -0.74341318 |

**Table S18.** Cartesian coordinates of **$TS_{4c}$** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | 1.15763700 | -0.03587900 | 0.43565100 |
| C | 2.34262300 | 0.13884400 | -0.26483500 |
| N | 0.68378000 | 1.27476500 | -1.80280000 |
| O | 1.90474000 | 1.04589000 | -1.90457200 |
| C | -0.24703300 | 1.06857800 | -1.08755200 |
| C | -1.63588100 | 1.14198300 | -0.73998300 |
| C | -2.53381300 | 0.23307400 | -1.32002800 |
| C | -2.06356500 | 2.07657500 | 0.21315800 |
| C | -3.87267200 | 0.28153500 | -0.95753100 |
| H | -2.16894300 | -0.49703200 | -2.03585700 |
| C | -3.40675900 | 2.10582300 | 0.57308100 |
| H | -1.34952800 | 2.76051900 | 0.65996500 |
| C | -4.30614500 | 1.21329000 | -0.01066500 |
| H | -4.57912100 | -0.41070700 | -1.40421500 |
| H | -3.75089900 | 2.82516600 | 1.30899500 |
| H | -5.35364700 | 1.24204600 | 0.27456100 |
| N | 3.29333200 | 1.18724000 | 0.14313300 |
| O | 2.84127200 | 2.20611900 | 0.62803800 |
| O | 4.46931300 | 0.95201200 | -0.05975200 |
| O | 1.14448500 | -2.75676900 | 1.08742500 |
| O | 0.26504500 | -1.85960800 | -1.20325500 |
| O | -1.09530000 | -1.46620000 | 0.86430800 |
| P | 0.40869500 | -1.68575900 | 0.37993500 |
| H | 2.84564700 | -0.68093900 | -0.76131100 |
| C | 0.74393100 | 0.76704200 | 1.54654400 |
| N | 0.29769800 | 1.32757500 | 2.45808900 |
| H | -1.36497215 | -1.66398031 | 1.76417459 |
| H | 0.02171091 | -2.72332856 | -1.54439325 |

**Table S19.** Cartesian coordinates of **MC$_{3a}$** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | 0.80285043 | 1.81534239 | -0.49941265 |
| C | 1.79515343 | 1.34263439 | 0.25365635 |
| H | 0.56305043 | 1.51828539 | -1.51107865 |
| H | 1.97189243 | 1.73558639 | 1.24839535 |
| N | -0.73644143 | -0.99290339 | 1.87160165 |
| O | 0.30067657 | -1.13118039 | 2.49918065 |
| C | -1.64452043 | -0.74516739 | 1.17715665 |
| C | -2.56164294 | -0.80785319 | 0.08357490 |
| C | -3.61564136 | 0.11077751 | -0.05955660 |
| C | -2.37581410 | -1.82951839 | -0.86613412 |
| C | -4.47525403 | -0.00568474 | -1.14947974 |
| H | -3.76134596 | 0.89238370 | 0.67791707 |
| C | -3.24420046 | -1.93338789 | -1.94497086 |
| H | -1.55702206 | -2.53149206 | -0.74366991 |
| C | -4.29529073 | -1.02368821 | -2.08821522 |
| H | -5.29283082 | 0.70043207 | -1.26153457 |
| H | -3.10224128 | -2.72517305 | -2.67489088 |
| H | -4.97387877 | -1.10954897 | -2.93219126 |
| N | -0.06524157 | 2.89145539 | -0.02449965 |
| O | 0.02649143 | 3.26888739 | 1.13939935 |
| O | -0.84908457 | 3.35578839 | -0.86155665 |
| O | 4.00250943 | -0.33212161 | 0.57131335 |
| P | 2.91399543 | 0.05473439 | -0.35621265 |
| O | 2.00599543 | -1.17372261 | -0.89788965 |
| O | 3.31993643 | 0.79222939 | -1.73594865 |
| H | 2.05511782 | -2.03944991 | -0.48593914 |
| H | 4.02084933 | 0.43044339 | -2.28315245 |

**Table S20.** Cartesian coordinates of **MC$_{4a}$** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | 1.60584987 | 0.12718538 | -0.99341267 |
| C | 2.51049487 | -0.78498462 | -0.64363367 |
| H | 0.84387587 | -0.12197262 | -1.72393867 |
| H | 3.33907387 | -0.64675162 | 0.03693133 |
| N | -0.44633687 | -1.95717538 | 1.63120567 |
| O | 0.52812813 | -2.52179838 | 2.09382867 |
| C | -1.28326987 | -1.32429238 | 1.11252067 |
| C | -2.15717302 | -0.74361788 | 0.14212303 |
| C | -3.01993234 | 0.32299278 | 0.45407143 |
| C | -2.13064352 | -1.26520290 | -1.16454879 |
| C | -3.84075108 | 0.85373017 | -0.53782743 |
| H | -3.05389426 | 0.71835435 | 1.46100290 |
| C | -2.96034926 | -0.72900386 | -2.14181037 |
| H | -1.45867823 | -2.08491580 | -1.39792510 |
| C | -3.81658297 | 0.33055003 | -1.83229826 |
| H | -4.50509431 | 1.67845553 | -0.29622391 |
| H | -2.93647334 | -1.13704825 | -3.14814828 |
| H | -4.46237071 | 0.74797318 | -2.59959776 |
| N | 2.47178987 | -2.12930362 | -1.22875667 |
| O | 1.49855287 | -2.44701262 | -1.91295167 |
| O | 3.44400587 | -2.84258362 | -0.99378367 |
| O | 2.97664887 | 2.10366238 | 0.37611333 |
| O | 0.38255787 | 2.06328338 | 0.59993233 |
| O | 1.30470087 | 2.58743938 | -1.65475267 |
| P | 1.69974687 | 1.79027238 | -0.30967367 |
| H | 0.44821784 | 2.11212355 | 1.55643816 |
| H | 1.38785473 | 3.54337215 | -1.68438333 |

**Table S21.** Cartesian coordinates of **MC**$_{\text{зь}}$ in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | 0.81884923 | 1.83208079 | -0.51037261 |
| C | 1.81115223 | 1.35937279 | 0.24269639 |
| H | 1.98789123 | 1.75232479 | 1.23743539 |
| N | -0.75244023 | -1.00964179 | 1.88256161 |
| O | 0.28467777 | -1.14791879 | 2.51014061 |
| C | -1.66051923 | -0.76190579 | 1.18811661 |
| C | -2.57764174 | -0.82459159 | 0.09453486 |
| C | -3.63164016 | 0.09403911 | -0.04859664 |
| C | -2.39181290 | -1.84625679 | -0.85517416 |
| C | -4.49125283 | -0.02242314 | -1.13851978 |
| H | -3.77734476 | 0.87564530 | 0.68887703 |
| C | -3.26019926 | -1.95012629 | -1.93401090 |
| H | -1.57302086 | -2.54823046 | -0.73270995 |
| C | -4.31128953 | -1.04042661 | -2.07725526 |
| H | -5.30882962 | 0.68369367 | -1.25057461 |
| H | -3.11824008 | -2.74191145 | -2.66393092 |
| H | -4.98987757 | -1.12628737 | -2.92123130 |
| N | -0.04924277 | 2.90819379 | -0.03545961 |
| O | 0.04249023 | 3.28562579 | 1.12843939 |
| O | -0.83308577 | 3.37252679 | -0.87251661 |
| O | 4.01850823 | -0.31538321 | 0.56035339 |
| P | 2.92999423 | 0.07147279 | -0.36717261 |
| O | 2.02199423 | -1.15698421 | -0.90884961 |
| O | 3.33593523 | 0.80896779 | -1.74690861 |
| H | 2.07111662 | -2.02271151 | -0.49689910 |
| H | 4.03684813 | 0.44718179 | -2.29411241 |
| C | 0.47732406 | 1.40900973 | -1.95119579 |
| N | 0.22007134 | 1.09033282 | -3.03649118 |

**Table S22.** Cartesian coordinates of **MC$_{4b}$** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | 1.57268213 | 0.11052209 | -0.96923609 |
| C | 2.47732713 | -0.80164791 | -0.61945709 |
| H | 0.81070813 | -0.13863591 | -1.69976209 |
| N | -0.41316913 | -1.94051209 | 1.60702909 |
| O | 0.56129587 | -2.50513509 | 2.06965209 |
| C | -1.25010213 | -1.30762909 | 1.08834409 |
| C | -2.12400528 | -0.72695459 | 0.11794645 |
| C | -2.98676460 | 0.33965607 | 0.42989485 |
| C | -2.09747578 | -1.24853961 | -1.18872537 |
| C | -3.80758334 | 0.87039346 | -0.56200401 |
| H | -3.02072652 | 0.73501764 | 1.43682632 |
| C | -2.92718152 | -0.71234057 | -2.16598695 |
| H | -1.42551049 | -2.06825251 | -1.42210168 |
| C | -3.78341523 | 0.34721332 | -1.85647484 |
| H | -4.47192657 | 1.69511882 | -0.32040049 |
| H | -2.90330560 | -1.12038496 | -3.17232486 |
| H | -4.42920297 | 0.76463647 | -2.62377434 |
| N | 2.43862213 | -2.14596691 | -1.20458009 |
| O | 1.46538513 | -2.46367591 | -1.88877509 |
| O | 3.41083813 | -2.85924691 | -0.96960709 |
| O | 2.94348113 | 2.08699909 | 0.40028991 |
| O | 0.34939013 | 2.04662009 | 0.62410891 |
| O | 1.27153313 | 2.57077609 | -1.63057609 |
| P | 1.66657913 | 1.77360909 | -0.28549709 |
| H | 0.41505010 | 2.09546026 | 1.58061474 |
| H | 1.35468699 | 3.52670886 | -1.66020675 |
| C | 3.65759554 | -0.60474207 | 0.34997294 |
| N | 4.54662888 | -0.45642339 | 1.08019297 |

**Table S23.** Cartesian coordinates of **MC$_{3c}$** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | 0.75639663 | 1.76674108 | -0.46758951 |
| C | 1.74869963 | 1.29403308 | 0.28547949 |
| N | -0.68998763 | -0.94430208 | 1.83977851 |
| O | 0.34713037 | -1.08257908 | 2.46735751 |
| C | -1.59806663 | -0.69656608 | 1.14533351 |
| C | -2.51518914 | -0.75925188 | 0.05175176 |
| C | -3.56918756 | 0.15937882 | -0.09137974 |
| C | -2.32936030 | -1.78091708 | -0.89795726 |
| C | -4.42880023 | 0.04291657 | -1.18130288 |
| H | -3.71489216 | 0.94098501 | 0.64609393 |
| C | -3.19774666 | -1.88478658 | -1.97679400 |
| H | -1.51056826 | -2.48289075 | -0.77549305 |
| C | -4.24883693 | -0.97508690 | -2.12003836 |
| H | -5.24637702 | 0.74903338 | -1.29335771 |
| H | -3.05578748 | -2.67657174 | -2.70671402 |
| H | -4.92742497 | -1.06094766 | -2.96401440 |
| N | -0.11169537 | 2.84285408 | 0.00732349 |
| O | -0.01996237 | 3.22028608 | 1.17122249 |
| O | -0.89553837 | 3.30718708 | -0.82973351 |
| O | 3.95605563 | -0.38072292 | 0.60313649 |
| P | 2.86754163 | 0.00613308 | -0.32438951 |
| O | 1.95954163 | -1.22232392 | -0.86606651 |
| O | 3.27348263 | 0.74362808 | -1.70412551 |
| H | 2.00866402 | -2.08805122 | -0.45411600 |
| H | 3.97439553 | 0.38184208 | -2.25132931 |
| H | 0.51910316 | 1.47278911 | -1.46868094 |
| C | 1.99977597 | 1.85226273 | 1.69861088 |
| N | 2.18889841 | 2.27274740 | 2.76304751 |

**Table S24.** Cartesian coordinates of **MC$_{4c}$** in toluene according to M062X/6-31+G(d) (PCM) calculations.

| | | | |
|---|---|---|---|
| C | 1.64755705 | 0.14813883 | -1.02381382 |
| C | 2.55220205 | -0.76403117 | -0.67403482 |
| N | -0.48804405 | -1.97812883 | 1.66160682 |
| O | 0.48642095 | -2.54275183 | 2.12422982 |
| C | -1.32497705 | -1.34524583 | 1.14292182 |
| C | -2.19888020 | -0.76457133 | 0.17252418 |
| C | -3.06163952 | 0.30203933 | 0.48447258 |
| C | -2.17235070 | -1.28615635 | -1.13414764 |
| C | -3.88245826 | 0.83277672 | -0.50742628 |
| H | -3.09560144 | 0.69740090 | 1.49140405 |
| C | -3.00205644 | -0.74995731 | -2.11140922 |
| H | -1.50038541 | -2.10586925 | -1.36752395 |
| C | -3.85829015 | 0.30959658 | -1.80189711 |
| H | -4.54680149 | 1.65750208 | -0.26582276 |
| H | -2.97818052 | -1.15800170 | -3.11774713 |
| H | -4.50407789 | 0.72701973 | -2.56919661 |
| N | 2.51349705 | -2.10835017 | -1.25915782 |
| O | 1.54026005 | -2.42605917 | -1.94335282 |
| O | 3.48571305 | -2.82163017 | -1.02418482 |
| O | 3.01835605 | 2.12461583 | 0.34571218 |
| O | 0.42426505 | 2.08423683 | 0.56953118 |
| O | 1.34640805 | 2.60839283 | -1.68515382 |
| P | 1.74145405 | 1.81122583 | -0.34007482 |
| H | 0.48992502 | 2.13307700 | 1.52603701 |
| H | 1.42956191 | 3.56432560 | -1.71478448 |
| H | 3.37225867 | -0.62721997 | -0.00046980 |
| C | 0.56564448 | -0.20563593 | -2.06107396 |
| N | -0.24930265 | -0.47211562 | -2.84238680 |