Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information for

Fluxionality by Quantum Tunnelling: Nonclassical 21-Homododecahedryl Cation Rearrangement Re-Revisited

Minima according to the exact exchange

We computed the energy difference between **M** and **TS1** with 23 functionals of different characteristics with the 6-31g(d) basis set and the error with reference to the G4 electronic energy (in the M06-2x/def2-TZVP geometry). G4 gives an energy of 5.15 kJ mol^{-1} for this reaction (**M** being the lower energy state), which compared well with the DLPNO-CCSD(T)/cc-pVQZ with tightPNO results of 7.3 kJ mol^{-1}.

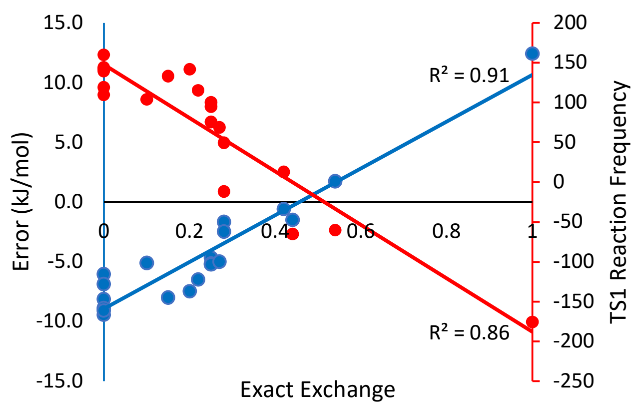
As we can see in Table S1 and Fig. S1, there is a correlation between the activation energy and the exact exchange of the functional (with some variability because they are entirely different functionals). Although accurate activation energies in main group chemistry are known to require large HF-exchange, in this particular low-barrier reaction, the effect is exacerbated, completely switching the minimum-transition state character of **M** and **TS1**. Without G4 and DLPNO-CCSD(T) results to confirm the nature of these states, it would not be easy to define which is which.

The selection of the functional was made accordingly, not only based on the error but also considering that any method giving **TS1** as a minimum (with all its frequencies being real) and **M** as a transition state (one imaginary frequency) should be discarded. According to this criterion, most of the functionals were inappropriate for this particular project, especially all the pure GGAs. We finally decided to use M06-2x, which also compared well with the G4 activation energy for **TS2**. As a note, we used a very small basis set due to the cost of the SCT tunnelling computations, which compute first and second derivatives all along the minimum energy pathway (it took more than a week on 32 cores). However, triple zeta basis sets provided similar results.

Table S1. Amount of exact exchange of different functionals (RS is for "range separated", with variable exact exchange), their **M** to **TS1** reaction error with the 6-31g(d) basis set compared to G4 in kJ mol^{-1}, and the reaction frequency at **TS1** in cm^{-1} (in red the imaginary frequencies).

	Functional	Ex.Exch.	Error	freq
GGA	B97D3	0	-6.0	160
	BB95	0	-6.9	119
	MN15L	0	-8.1	109
	PBE	0	-8.9	139
	M06-L	0	-9.4	142
	mPW-PW91	0	-9.1	144
Hybrid	TPSSh	0.1	-5.1	104
	τHCTHhyb	0.15	-8.0	133
	B3LYP	0.2	-7.5	142
	B98	0.22	-6.5	115
	PBE0	0.25	-4.7	95
	mPW1PW91	0.25	-5.1	100
	TPSS0	0.25	-5.2	75
	M06	0.27	-5.0	68
	B1B95	0.28	-1.7	12i
	PW6B95	0.28	-2.5	49
	BMK	0.42	-0.6	13
	MN15	0.44	-1.5	65i
	M06-2X	0.54	1.7	60i
	M06-HF	1	12.4	176i
RS	M11		4.6	108i
	ωB97X		-3.5	110
	ωB97XD		-3.7	97

Figure S1. Error of the functionals with respect to G4 (in blue) and **TS1** reaction frequency (in red) as a function of the exact exchange. Range separated functionals are not shown.



Example of Polyrate input files

.dat:

```
*GENERAL
TITLE
  DDHplus_m062x_001
END
DL ISPE

ATOMS
1 C
2 C
3 C
4 C
5 C
6 C
7 C
8 C
9 C
10 C
11 C
12 C
13 C
14 C
15 C
16 C
17 C
18 C
19 C
20 C
21 H
22 H
23 H
24 H
25 H
26 H
27 H
28 H
29 H
30 H
31 H
32 H
33 H
34 H
35 H
36 H
37 H
38 H
39 H
40 H
41 C
42 H
END
NOSUPERMOL
*SECOND
HESSCAL hhook
FPRINT
*OPTIMIZATION
PRINT
OPTMIN ohook
OPTTS ohook
*REACT1
INITGEO hooks
GEOM
1
2
3
4
5
6
7
8
9
10
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12
13
14
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16
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31
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35
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37
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39
40
41
42
END
SPECIES nonlinrp
*PROD1
INITGEO hooks
GEOM
1
2
3
4
5
6
7
8
9
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17
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21
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41
42
END
SPECIES nonlinrp
*START
INITGEO hooks
GEOM
1
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10
11
12
13
14
15
16
17
18
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36
37
38
39
40
41
42
END
SPECIES nonlints
PROJECT

*PATH
SYMMETRY
INTMU 3
SSTEP 0.001
RPM pagem
SRANGE
  SLP 4.24
  SLM -4.24
END
PRPATH
  coord 1 2
  xmol
  freq 120
END
*TUNNEL
ZCT
SCT
QRST
  harmonic
  mode 120
  states all
END
*RATE
FORWARDK
SIGMAF 1
TST
CVT
PRDELG
PRPART rtp
TEMP
8
10
12.5
13
13.5
14.1
14.7
15.4
16.1
16.9
17.9
18.9
20
21.3
22.7
24.4
26.3
28.6
31.3
34.5
38.5
43.5
50
58.8
77.36
END
ANALYSIS
8
10
12.5
13
13.5
14.1
14.7
15.4
16.1
16.9
17.9
18.9
20
21.3
22.7
24.4
26.3
28.6
31.3
34.5
38.5
43.5
50
58.8
77.36
END
GTLOG
```

.70:

```
*GRGENERAL
GRRESTART
*GRSTART
CHARGE 1
MULTIPLICITY 1
*GRCOMMON
GRENER
%mem=16gb
%nproc=8
#n m062x/6-31g(d)  units(au) fchk nosymm
END
GRFIRST
%mem=16gb
%nproc=8
#n m062x/6-31g(d)  units(au) fchk nosymm force
END

GRSEC
%mem=16gb
%nproc=8
#n m062x/6-31g(d)  units(au) fchk nosymm freq
END
```

.51:

```
*ISPEGEN
ENERXN -0.
ENESAD 1.23
MEPTYPER one
MEPTYPEP one
RCINFO
 SRC -8.0106
END
PCINFO
 SPC 8.0106
END
```

XYZ geometries

```
TS1
C   0.771681 -0.247467  2.066714
C  -0.769479 -0.108430  2.066985
C  -1.172996  1.195966  1.335001
C   0.248250  2.025320  1.242748
C   1.369509  0.982443  1.337118
C   1.140195 -1.509235  1.253540
C  -1.359240 -1.287454  1.254583
C  -1.867645  0.825809  0.000000
C   0.248250  2.025320 -1.242748
C   1.993729  0.496188  0.000000
C  -0.769479 -0.108430 -2.066985
C  -1.359240 -1.287454 -1.254583
C  -0.177832 -2.169535 -0.774955
C   1.140195 -1.509235 -1.253540
C   0.771681 -0.247467 -2.066714
C  -1.172996  1.195966 -1.335001
C  -2.059993 -0.712645 -0.000000
C  -0.177832 -2.169535  0.774955
C   1.926388 -1.054883 -0.000000
C   1.369509  0.982443 -1.337118
H   1.148454 -0.304503  3.089904
H  -1.158080 -0.081159  3.087610
H  -1.838381  1.818408  1.934428
H   0.224077  2.706916  2.094716
H   2.162781  1.431760  1.939726
H   1.730965 -2.202584  1.855065
H  -2.060594 -1.861769  1.862776
H  -2.841451  1.324008  0.000000
H   0.224077  2.706916 -2.094716
H   3.036607  0.820253  0.000000
H  -1.158080 -0.081159 -3.087610
H  -2.060594 -1.861769 -1.862776
H  -0.270010 -3.183794 -1.168343
H   1.730965 -2.202584 -1.855065
H   1.148454 -0.304503 -3.089904
H  -1.838381  1.818408 -1.934428
H  -3.124269 -0.955023 -0.000000
H  -0.270010 -3.183794  1.168343
H   2.934792 -1.473589 -0.000000
H   2.162781  1.431760 -1.939726
C   0.018304  2.685584  0.000000
H  -0.549843  3.618186  0.000000
```

```
TS2
C  -0.771368  2.070918 -0.189076
C   0.771368  2.070918 -0.189076
C   1.260468  1.335962  1.083703
C  -0.000000  1.240242  2.049149
C  -1.260468  1.335962  1.083703
C  -1.254188  1.254498 -1.411106
C   1.254188  1.254498 -1.411106
C   1.918860 -0.000000  0.661680
C  -0.000000 -1.240242  2.049149
C  -1.918860  0.000000  0.661680
C   0.771368 -2.070918 -0.189076
C   1.254188 -1.254498 -1.411106
C   0.000000 -0.774779 -2.185802
C  -1.254188 -1.254498 -1.411106
C  -0.771368 -2.070918 -0.189076
C   1.260468 -1.335962  1.083703
C   1.995732 -0.000000 -0.888260
C   0.000000  0.774779 -2.185802
C  -1.995732  0.000000 -0.888260
C  -1.260468 -1.335962  1.083703
H  -1.161911  3.090756 -0.203675
H   1.161911  3.090756 -0.203675
H   1.994503  1.934149  1.627550
H  -0.000000  2.098003  2.722327
H  -1.994503  1.934149  1.627550
H  -1.905630  1.854946 -2.048747
H   1.905630  1.854946 -2.048747
H   2.927693 -0.000000  1.084598
H  -0.000000 -2.098003  2.722327
H  -2.927693  0.000000  1.084598
H   1.161911 -3.090756 -0.203675
H   1.905630 -1.854946 -2.048747
H   0.000000 -1.168103 -3.204293
H  -1.905630 -1.854946 -2.048747
H  -1.161911 -3.090756 -0.203675
H   1.994503 -1.934149  1.627550
H   3.039071 -0.000000 -1.209526
H   0.000000  1.168103 -3.204293
H  -3.039071  0.000000 -1.209526
H  -1.994503 -1.934149  1.627550
C   0.000000  0.000000  2.767947
H   0.000000  0.000000  3.859870
```

```
SS
C  -0.260337 -0.912240  2.053552
C  -1.585231 -0.889438  1.250639
C  -1.846489  0.566548  0.778689
C  -0.820552  1.459950  1.520448
C   0.268439  0.536182  2.129370
C   0.767345 -1.751154  1.254143
C  -1.405012 -1.780447  0.000000
C  -1.846489  0.566548 -0.778689
C  -0.084699  2.456485 -0.689338
C   1.555605  0.624600  1.265902
C   0.268439  0.536182 -2.129370
C  -0.260337 -0.912240 -2.053552
C   0.767345 -1.751154 -1.254143
C   1.895608 -0.803404 -0.772291
C   1.555605  0.624600 -1.265902
C  -0.820552  1.459950 -1.520448
C  -1.585231 -0.889438 -1.250639
C   0.051466 -2.313191  0.000000
C   1.895608 -0.803404  0.772291
C   1.442168  1.524634 -0.000000
H  -0.416081 -1.320244  3.054041
H  -2.414377 -1.238864  1.869187
H  -2.839353  0.887474  1.099640
H  -1.323063  2.015934  2.317963
H   0.496312  0.833603  3.154900
H   1.178968 -2.554495  1.868166
H  -2.121278 -2.604195  0.000000
H  -2.839353  0.887474 -1.099640
H   0.417988  3.268346 -1.213120
H   2.368558  1.044126  1.864154
H   0.496312  0.833603 -3.154900
H  -0.416081 -1.320244 -3.054041
H   1.178968 -2.554495 -1.868166
H   2.865984 -1.112377 -1.165584
H   2.368558  1.044126 -1.864154
H  -1.323063  2.015934 -2.317963
H  -2.414377 -1.238864 -1.869187
H   0.065061 -3.404876  0.000000
H   2.865984 -1.112377  1.165584
H   2.178354  2.325726 -0.000000
C  -0.084699  2.456485  0.689338
H   0.417988  3.268346  1.213120
```

Rate constant and KIE tables at different temperatures

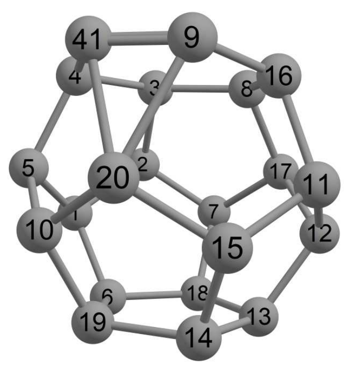
TS1	T	k(CVT)	k(SCT)	t1/2	KIE(A)	KIE(B)	KIE(C)	KIE(D)	KIE(E)	KIE(F)	KIE(H/D)
	8	2.41E-06	6.78E+05	1.02E-06	1.34	1.44	1.52	1.15	0.86	1.17	8.33
	10	7.03E-03	6.78E+05	1.02E-06	1.34	1.44	1.52	1.15	0.86	1.17	8.33
	12.5	4.35E+00	6.78E+05	1.02E-06	1.34	1.44	1.52	1.15	0.86	1.17	8.33
	13	1.17E+01	6.78E+05	1.02E-06	1.34	1.44	1.52	1.15	0.86	1.17	8.33
	13.5	2.95E+01	6.79E+05	1.02E-06	1.34	1.44	1.52	1.15	0.86	1.17	8.33
	14.1	8.20E+01	6.80E+05	1.02E-06	1.34	1.44	1.52	1.15	0.86	1.17	8.33
	14.7	2.10E+02	6.81E+05	1.02E-06	1.34	1.43	1.52	1.15	0.85	1.17	8.33
	15.4	5.74E+02	6.86E+05	1.01E-06	1.33	1.43	1.52	1.15	0.85	1.17	8.34
	16.1	1.44E+03	6.94E+05	9.99E-07	1.33	1.43	1.52	1.14	0.85	1.17	8.34
	16.9	3.76E+03	7.11E+05	9.75E-07	1.32	1.42	1.51	1.14	0.85	1.16	8.35
	17.9	1.11E+04	7.54E+05	9.19E-07	1.31	1.41	1.51	1.14	0.84	1.16	8.40
	18.9	2.94E+04	8.37E+05	8.28E-07	1.28	1.38	1.49	1.12	0.82	1.15	8.47
	20	7.66E+04	1.01E+06	6.86E-07	1.25	1.35	1.48	1.11	0.80	1.13	8.56
	21.3	2.10E+05	1.41E+06	4.92E-07	1.21	1.31	1.45	1.08	0.78	1.11	8.70
	22.7	5.50E+05	2.24E+06	3.09E-07	1.17	1.26	1.42	1.07	0.76	1.09	8.62
	24.4	1.53E+06	4.23E+06	1.64E-07	1.13	1.23	1.39	1.05	0.75	1.07	8.28
	26.3	4.14E+06	8.73E+06	7.94E-08	1.11	1.21	1.36	1.04	0.75	1.06	7.66
	28.6	1.16E+07	1.99E+07	3.48E-08	1.09	1.18	1.33	1.03	0.76	1.05	6.86
	31.3	3.24E+07	4.74E+07	1.46E-08	1.08	1.17	1.30	1.03	0.77	1.04	5.95
	34.5	8.96E+07	1.16E+08	5.98E-09	1.06	1.15	1.27	1.03	0.79	1.04	5.07
	38.5	2.54E+08	2.99E+08	2.32E-09	1.06	1.13	1.24	1.02	0.81	1.04	4.26
	43.5	7.24E+08	7.91E+08	8.76E-10	1.05	1.11	1.20	1.02	0.83	1.03	3.56
	50	2.09E+09	2.17E+09	3.19E-10	1.04	1.09	1.17	1.02	0.85	1.03	2.98
	58.8	6.17E+09	6.17E+09	1.12E-10	1.03	1.08	1.14	1.01	0.87	1.02	2.49
	77.36	2.80E+10	2.72E+10	2.55E-11	1.02	1.06	1.10	1.01	0.91	1.02	1.97
	100	8.52E+10	8.78E+10	7.89E-12	1.01	1.04	1.07	1.01	0.94	1.01	1.61
	125	1.86E+11	1.89E+11	3.67E-12	1.01	1.03	1.05	1.01	0.95	1.01	1.45
	150	3.15E+11	3.19E+11	2.17E-12	1.01	1.03	1.05	1.01	0.96	1.01	1.36
	175	4.61E+11	4.65E+11	1.49E-12	1.01	1.02	1.04	1.00	0.97	1.01	1.30
	200	6.16E+11	6.20E+11	1.12E-12	1.01	1.02	1.03	1.00	0.97	1.01	1.25
	225	7.72E+11	7.76E+11	8.93E-13	1.01	1.02	1.03	1.00	0.98	1.00	1.21
	250	9.27E+11	9.30E+11	7.45E-13	1.01	1.02	1.03	1.00	0.98	1.00	1.18
	275	1.08E+12	1.08E+12	6.42E-13	1.01	1.01	1.02	1.00	0.98	1.00	1.16
	300	1.22E+12	1.22E+12	5.68E-13	1.00	1.01	1.02	1.00	0.98	1.00	1.14

TS2	T	CVT	SCT	t1/2	KIE(A)	KIE(B)	KIE(C)	KIE(D)	KIE(E)	KIE(F)	KIE(H/D)
	8	5.58E-90	1.17E-12	5.92E+11	1.68	1.45	1.00	0.90	1.13	0.89	1.03E+05
	10	8.70E-70	1.17E-12	5.92E+11	1.68	1.45	1.00	0.90	1.13	0.89	1.03E+05
	12.5	1.30E-53	1.22E-12	5.68E+11	1.69	1.44	1.00	0.89	1.12	0.89	9.76E+04
	13	4.01E-51	1.29E-12	5.37E+11	1.70	1.44	1.00	0.89	1.11	0.89	9.15E+04
	13.5	8.12E-49	1.45E-12	4.78E+11	1.73	1.43	1.00	0.90	1.10	0.90	8.06E+04
	14.1	2.90E-46	1.90E-12	3.65E+11	1.71	1.39	0.98	0.88	1.08	0.90	5.96E+04
	14.7	6.42E-44	3.20E-12	2.17E+11	1.66	1.35	0.95	0.87	1.06	0.92	4.19E+04
	15.4	2.06E-41	7.98E-12	8.69E+10	1.54	1.30	0.93	0.87	1.04	0.93	3.08E+04
	16.1	4.00E-39	2.38E-11	2.91E+10	1.47	1.29	0.91	0.86	1.03	0.94	2.58E+04
	16.9	9.69E-37	8.55E-11	8.11E+09	1.43	1.28	0.91	0.86	1.03	0.94	2.25E+04
	17.9	4.66E-34	3.90E-10	1.78E+09	1.42	1.28	0.90	0.86	1.03	0.94	1.88E+04
	18.9	1.17E-31	1.57E-09	4.41E+08	1.43	1.29	0.90	0.87	1.03	0.94	1.48E+04
	20	2.70E-29	6.27E-09	1.11E+08	1.43	1.29	0.91	0.87	1.04	0.94	1.06E+04
	21.3	8.17E-27	2.74E-08	2.53E+07	1.43	1.29	0.91	0.87	1.04	0.95	6.68E+03
	22.7	1.85E-24	1.13E-07	6.13E+06	1.41	1.29	0.91	0.87	1.03	0.95	4.02E+03
	24.4	5.83E-22	5.35E-07	1.30E+06	1.39	1.27	0.92	0.88	1.03	0.95	2.33E+03
	26.3	1.51E-19	2.57E-06	2.70E+05	1.35	1.24	0.93	0.90	1.02	0.96	1.41E+03
	28.6	4.71E-17	1.45E-05	4.78E+04	1.28	1.20	0.95	0.92	1.01	0.96	9.12E+02
	31.3	1.37E-14	9.10E-05	7.62E+03	1.23	1.16	0.97	0.94	1.00	0.97	6.55E+02
	34.5	3.63E-12	6.30E-04	1.10E+03	1.19	1.14	0.99	0.96	0.99	0.98	5.16E+02
	38.5	1.07E-09	5.05E-03	1.37E+02	1.17	1.13	1.00	0.98	0.99	0.99	4.11E+02
	43.5	3.02E-07	4.46E-02	1.55E+01	1.17	1.13	1.01	0.99	0.98	0.99	3.01E+02
	50	8.73E-05	4.64E-01	1.49E+00	1.16	1.13	1.01	0.99	0.98	0.99	1.68E+02
	58.8	2.59E-02	6.70E+00	1.03E-01	1.13	1.12	1.02	1.00	0.98	0.99	57.3
	77.36	6.31E+01	7.52E+02	9.22E-04	1.08	1.11	1.02	1.00	0.98	1.00	9.31
	100	1.75E+04	6.28E+04	1.10E-05	1.03	1.07	1.02	1.00	0.98	1.00	4.55
	125	8.37E+05	1.78E+06	3.89E-07	1.02	1.05	1.02	1.00	0.98	1.00	2.98
	150	1.12E+07	1.85E+07	3.75E-08	1.01	1.04	1.02	1.00	0.98	1.00	2.37
	175	7.14E+07	1.03E+08	6.73E-09	1.01	1.04	1.02	1.00	0.99	1.00	2.05
	200	2.89E+08	3.81E+08	1.82E-09	1.01	1.03	1.01	1.00	0.99	1.00	1.85
	225	8.60E+08	1.07E+09	6.48E-10	1.01	1.03	1.01	1.00	0.99	1.00	1.72
	250	2.06E+09	2.45E+09	2.83E-10	1.01	1.03	1.01	1.00	0.99	1.00	1.62
	275	4.23E+09	4.88E+09	1.42E-10	1.01	1.02	1.01	1.00	0.99	1.00	1.56
	300	7.70E+09	8.68E+09	7.99E-11	1.01	1.02	1.01	1.00	0.99	1.00	1.51

ZPE and symmetry corrected concentration percentage at 4 K for ^{13}C and D substituted HDC at different positions.

As explained in the main text, the energy differences for the ^{13}C monosubstituted cases is almost negligible, and we would probably see a complete scrambling of the marked carbon position. However, with deuteration there is a larger ZPE differences, and at liquid He conditions most of the deuterium will be bonded to the equivalent carbons 3 and 8, and to 20 (see numeration in the figure). At least that would be in gas phase, where anisotropies of the medium will not affect the results.

	^{13}C			D		
C position	ZPE (Ha)	Rel. ZPE (kJ mol-1)	%	ZPE (Ha)	Rel. ZPE (kJ mol-1)	%
9/41	0.381403	0.058	2	0.378211	0.396	0
4/16	0.381383	0.005	11	0.378132	0.189	0
7	0.381381	0.000	6	0.378113	0.139	1
18	0.381382	0.003	6	0.378111	0.134	1
1/12	0.381381	0.000	12	0.378114	0.142	1
14/19	0.381382	0.003	11	0.378113	0.139	1
6/13	0.381382	0.003	11	0.378112	0.137	1
5/11	0.381383	0.005	11	0.378109	0.129	1
10/15	0.381388	0.018	7	0.378108	0.126	2
2/17	0.381381	0.000	12	0.378108	0.126	2
20	0.381423	0.110	0	0.378060	0.000	35
3/8	0.381384	0.008	10	0.378063	0.008	56



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Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.