Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information (ESI)

Structural investigation of doubly-dehydrogenated pyrene cations

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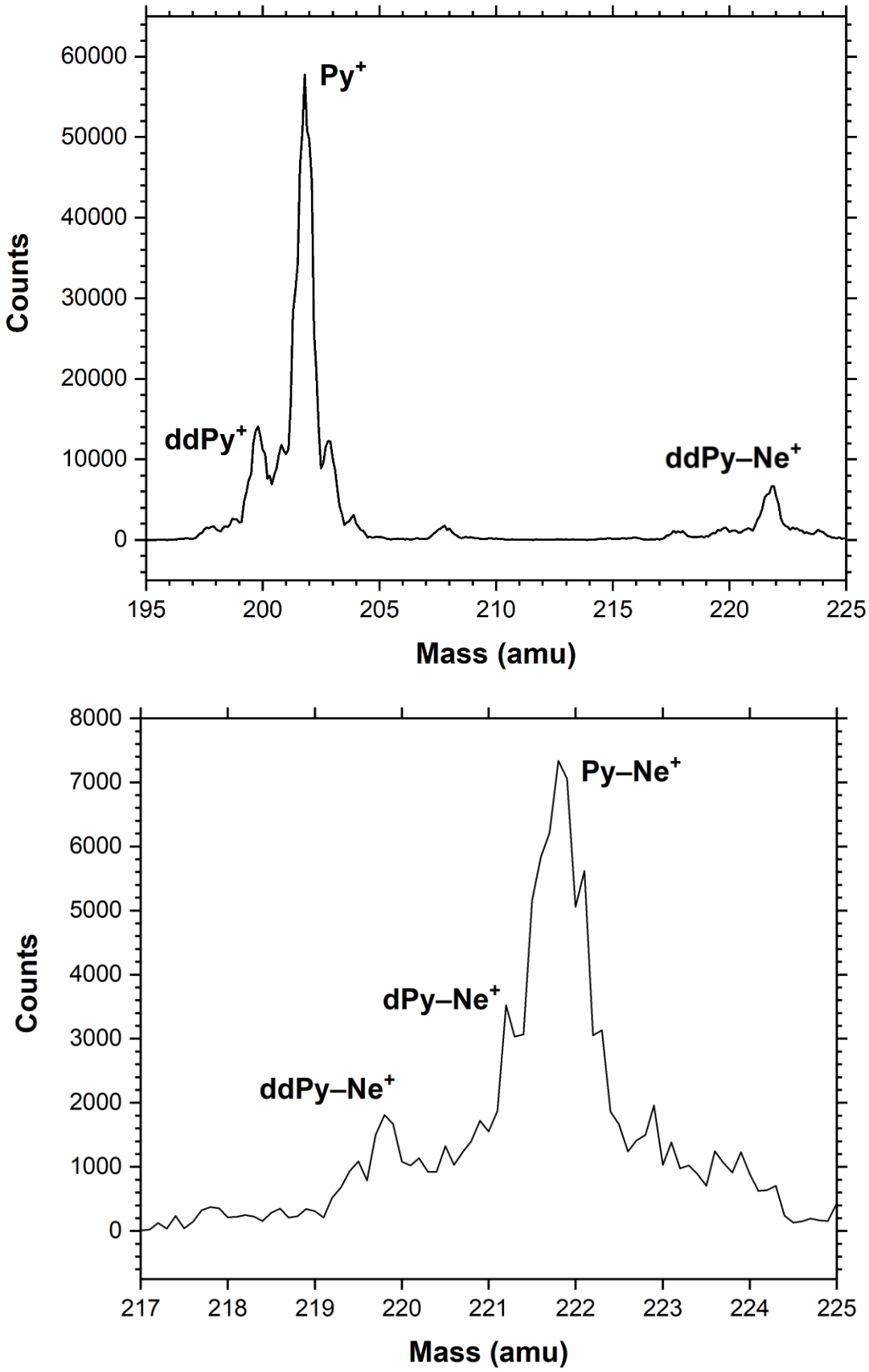

Fig. S1 Mass spectrum of pyrene showing Py^+ at 202 amu, $ddPy^+$ at 200 amu, $ddPy–Ne^+$ at 220 amu, $dPy–Ne^+$ at 221 amu, and $Py–Ne^+$ at 222 amu.

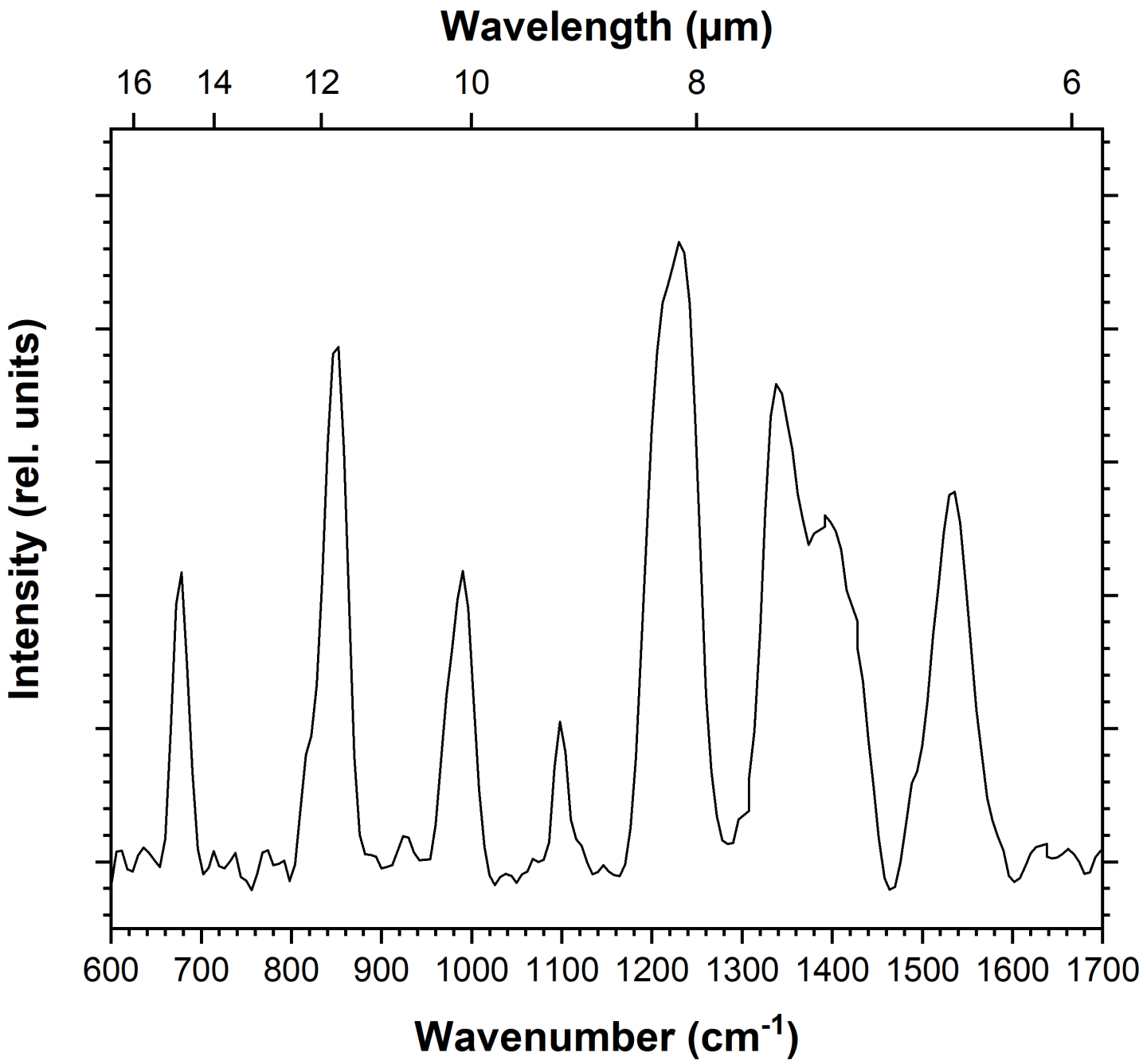

Fig. S2 IRMPD spectrum of Py^+ using FELIX and a Paul-type quadrupole ion trap (unpublished data). See Bouwman *et al.* for experimental details.[58]

The recorded IRMPD spectrum shows improvement in band resolution and strength in the 600–1300 cm^{-1} range compared to earlier IRMPD data presented in the literature,[19] but clearly lacks resolution compared to the Ne–tag experiments presented in this work.

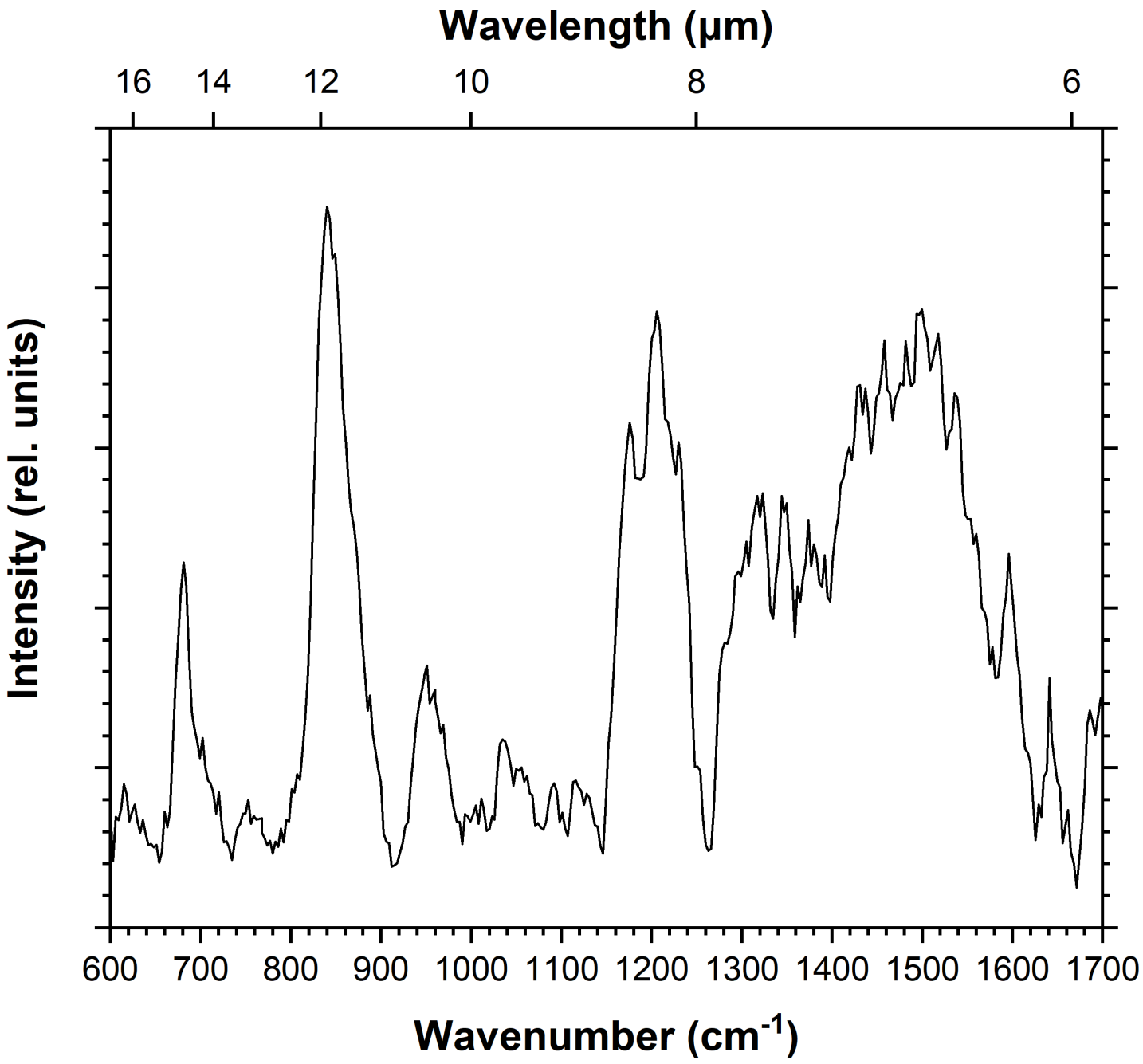

Fig. S3 IRMPD spectrum of $ddPy^+$ using FELIX and a Paul-type quadrupole ion trap (unpublished data).

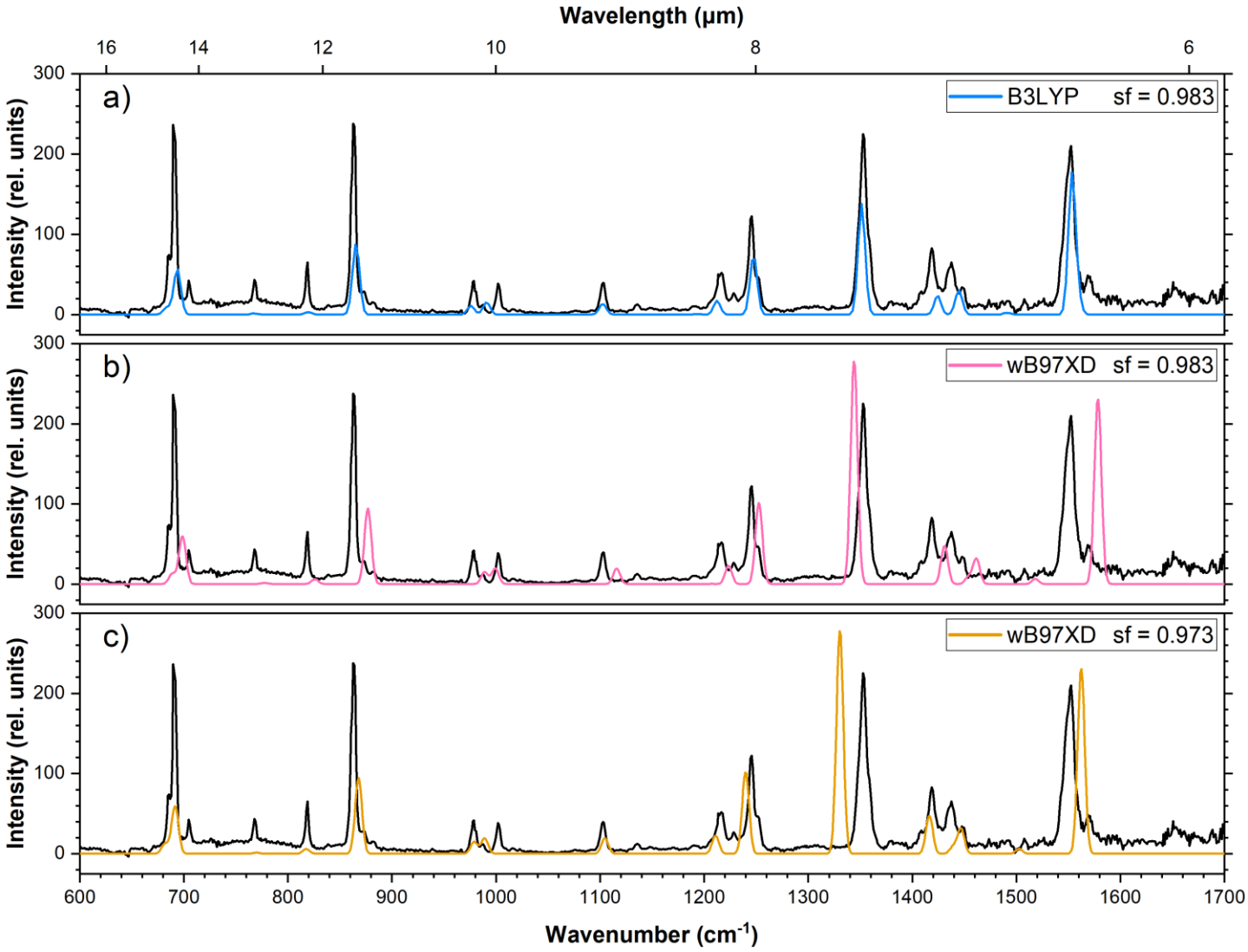

Fig. S4 IRPD spectrum of Py^+ (black) compared to computationally generated spectra using (a) B3LYP (blue, scaled by 0.983), (b) wB97XD (pink, scaled by 0.983), and (c) wB97XD (orange, scaled by 0.973). All functionals used the 6-311++G(2d,p) basis set.

For wB97XD, a scaling factor of 0.973 serves as a compromise between the C=C stretch region (~1500 cm^{-1}) and the bending modes (~700-1000 cm^{-1}) to achieve the best possible fit. In agreement with the literature, B3LYP/6-311++G(2d,p) is much preferred in vibrational analysis over wB97XD/6-311++G(2d,p) when scaled by a factor of 0.983 (blue trace, Fig. R1). Nevertheless, we take the empirically-determined scaling factor of 0.973 and apply it to our $ddPy^+$ calculations with wB97XD.

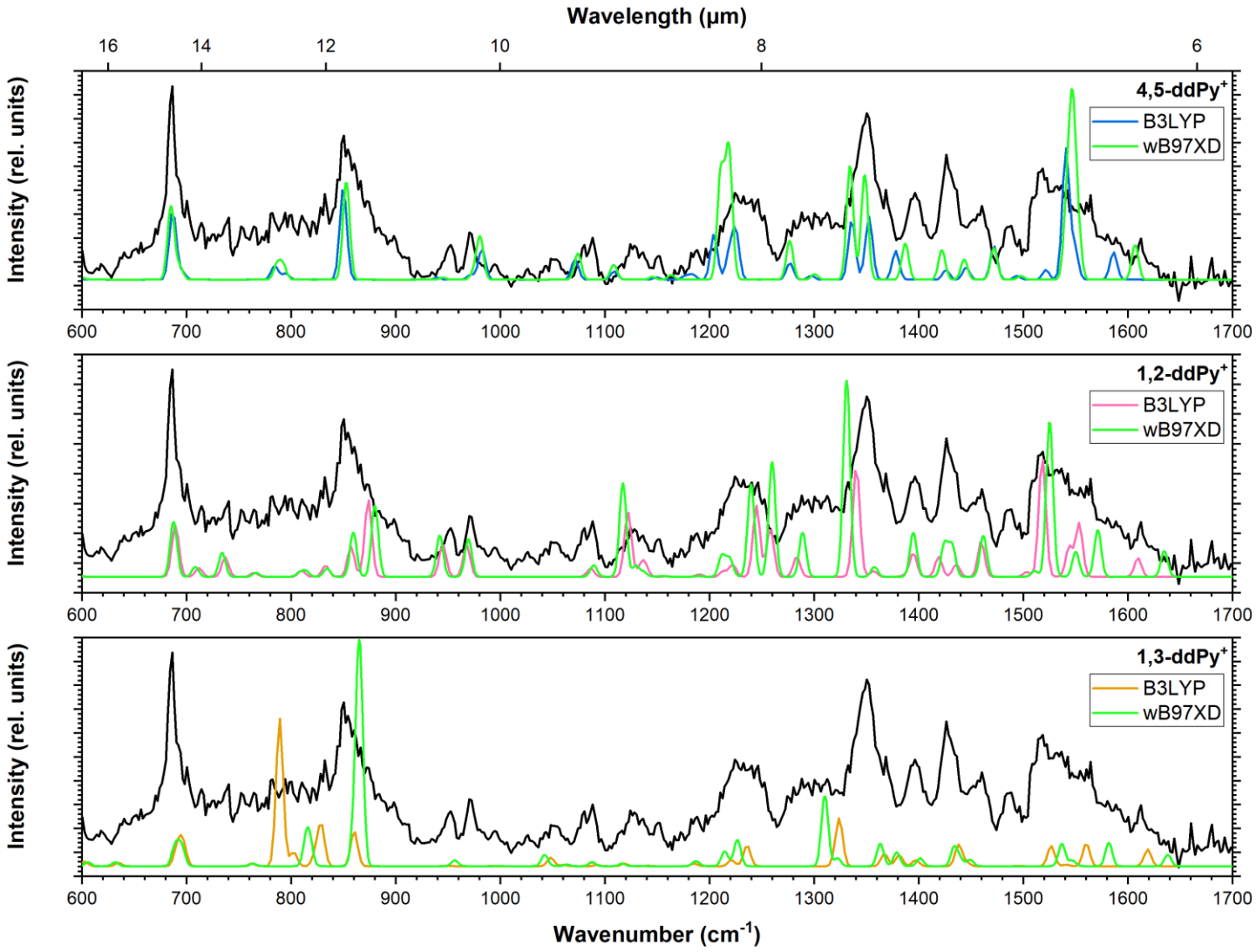

Fig. S5 IRPD spectrum of $ddPy^+$ (black) compared to computationally generated spectra of (a) 1,2–$ddPy^+$, (b) 4,5–$ddPy^+$, and (c) 1,3–$ddPy^+$. Calculations were performed using B3LYP (scaled by 0.983) and wB97XD (scaled by 0.973) with the 6-311++G(2d,p) basis set.

While there are some minor differences in band positions and intensities for 4,5–$ddPy^+$ and 1,2–$ddPy^+$, it is the cyclopropenyl transition in 1,3–$ddPy^+$ that is the most strikingly dissimilar between the two computational methods.

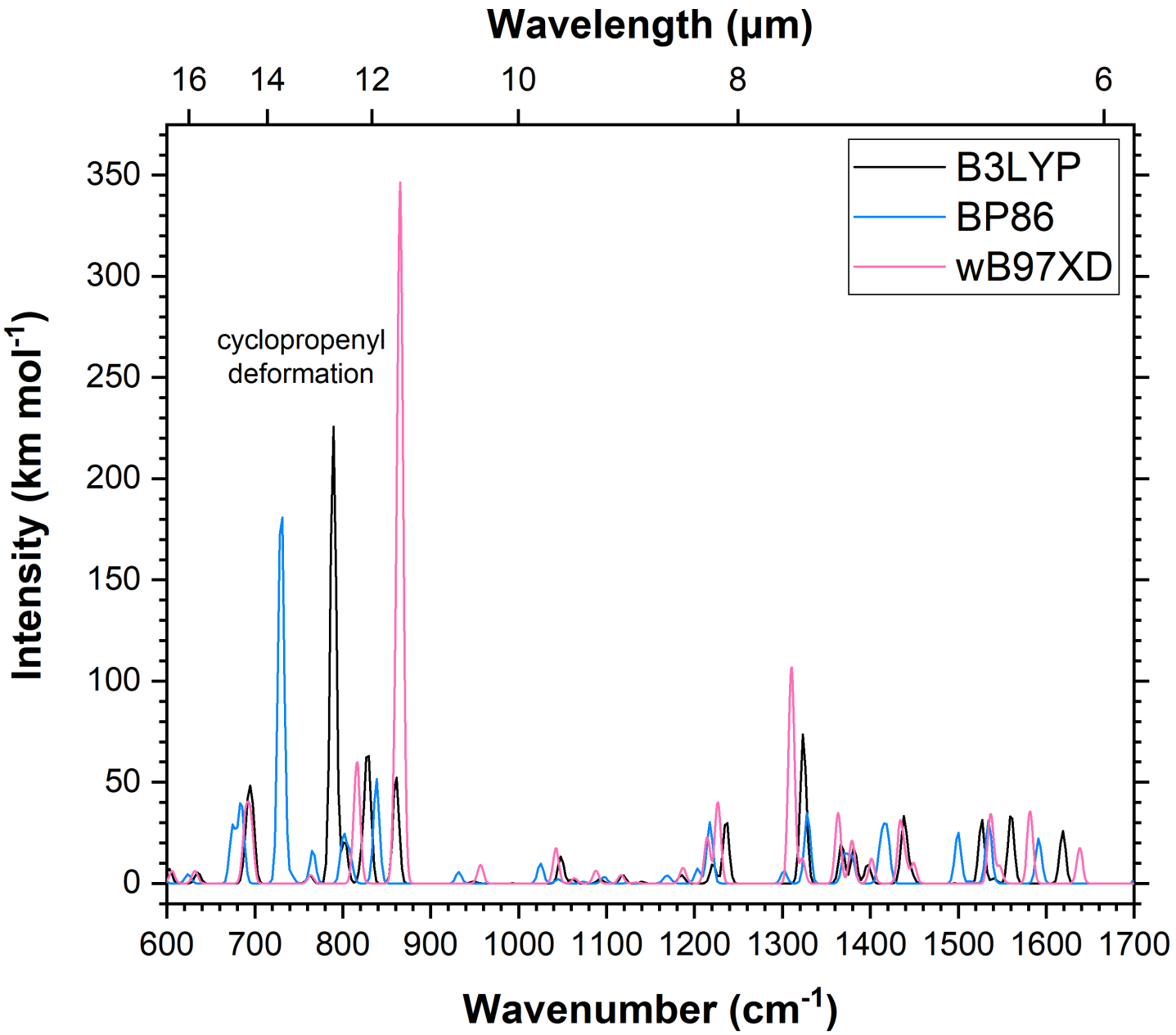

Fig. S6 Theoretical IR spectra for 1,3–ddPy^{+} using B3LYP (black), BP86 (blue), and wB97XD (pink). All calculations were performed with the 6-311++G(2d,p) basis set.

With wB97XD, the cyclopropenyl transition appears at 864 cm^{-1} even more intensely than for B3LYP. BP86 predicts this band at 721 cm^{-1}. This shows that the modelling of the cyclopropenyl vibrational mode is rather sensitive to the choice of computational method (with a shift of 69 cm^{-1} in B3LYP vs. BP86, and 74 cm^{-1} in B3LYP vs. wB97XD).

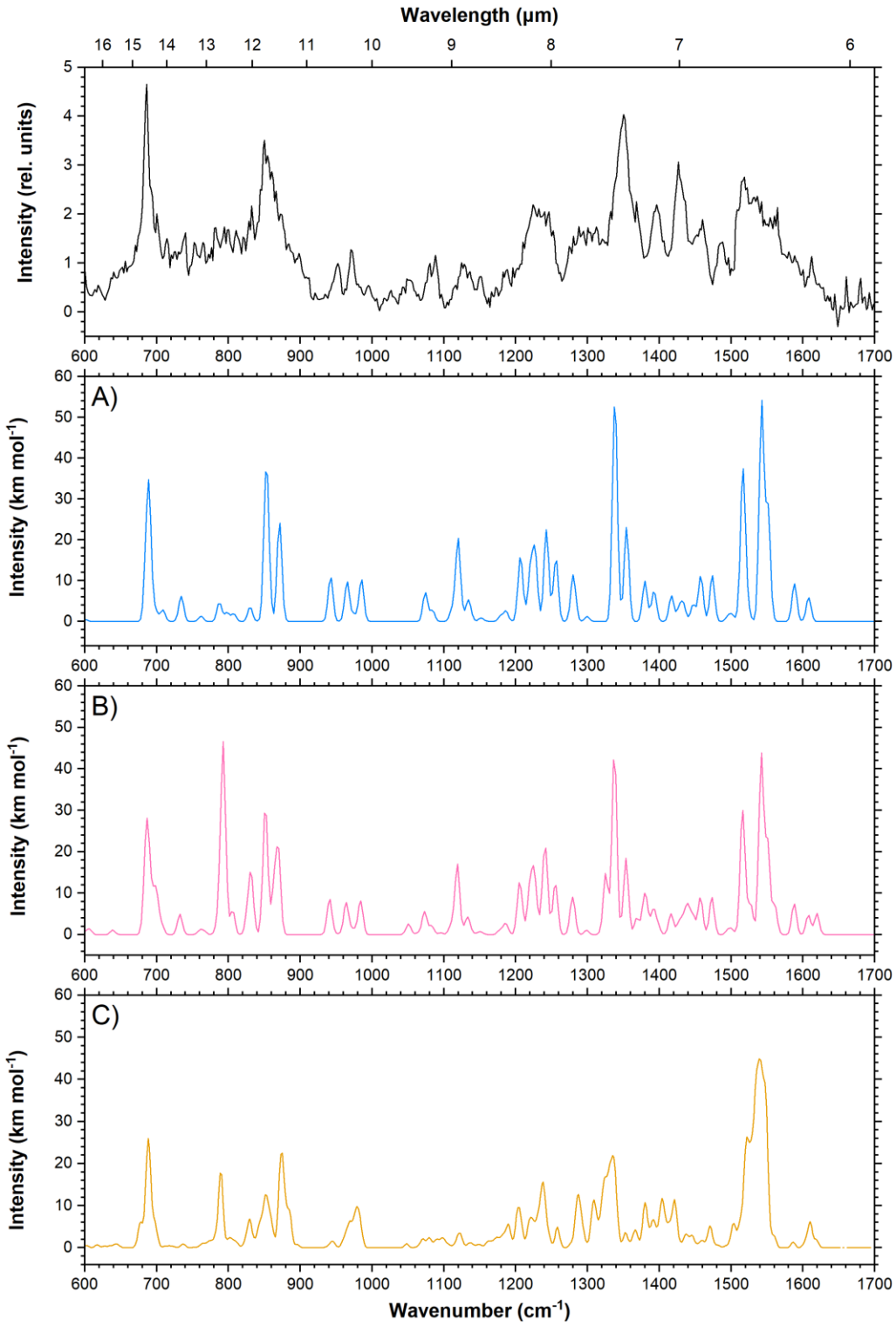

Fig. S7 IRPD spectrum of $ddPy^+$ (black) compared to computationally generated spectra using the B3LYP/6-311++G(2d,p) calculated spectra of the possible isomers (scaled by 0.983, convolved using a Gaussian profile with a FWHM of 8 cm^{-1}). Pink shows a 1:1 mixture (A) of 4,5–$ddPy^+$ and 1,2–$ddPy^+$. Blue shows a 1:1:0.5 mixture (B) of 4,5–$ddPy^+$: 1,2–$ddPy^+$: 1,3–$ddPy^+$. Green shows a homogeneous mixture (C) of all fourteen isomers.

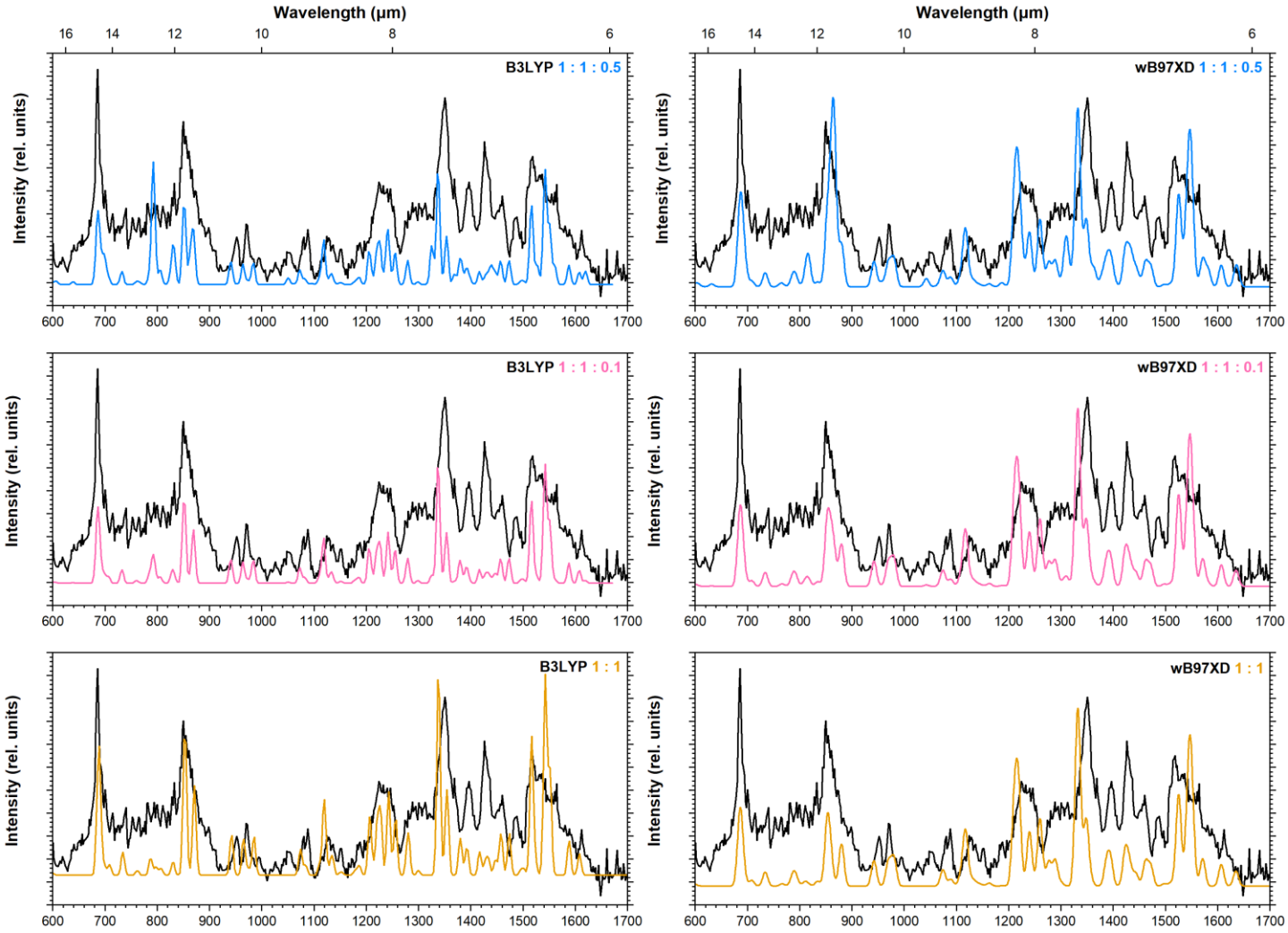

Fig. S8 IRPD spectrum of $ddPy^+$ (black) compared to computationally generated spectra with mixtures of 4,5–$ddPy^+$, 1,2–$ddPy^+$, and 1,3–$ddPy^+$. Left panels show B3LYP/6-311++G(2d,p) spectra scaled by 0.983, while right panels show wB97XD/6-311++G(2d,p) spectra scaled by 0.973. Blue spectra show a 1:1:0.5 mixture of all three isomers. Pink spectra show a 1:1:0.1 mixture of all three isomers. Orange spectra show a 1:1 mixture of only 4,5–$ddPy^+$ and 1,2–$ddPy^+$.

We see that the calculated spectra match better with the experimentally recorded $ddPy^+$ spectrum with diminishing quantities of 1,3–$ddPy^+$.

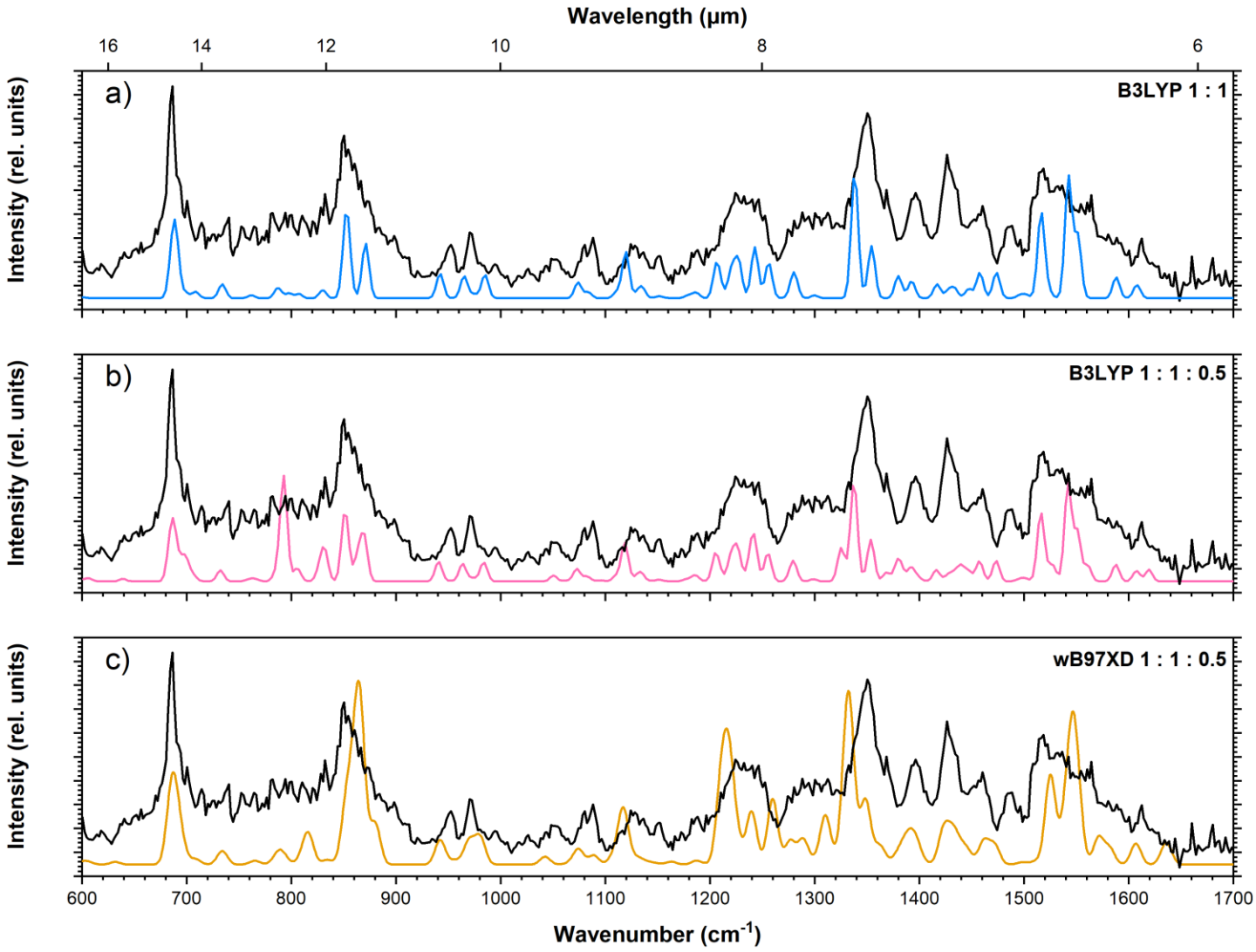

Fig. S9 IRPD spectrum of $ddPy^+$ (black) compared to computationally generated spectra of (a, b) B3LYP (scaled by 0.983), and (c) wB97XD (scaled by 0.973). Blue shows a 1:1 mixture of 4,5–$ddPy^+$ and 1,2–$ddPy^+$. Pink and orange show a 1:1:0.5 mixture of 4,5–$ddPy^+$: 1,2–$ddPy^+$: 1,3–$ddPy^+$. All calculations were performed with the 6-311++G(2d,p) basis set.

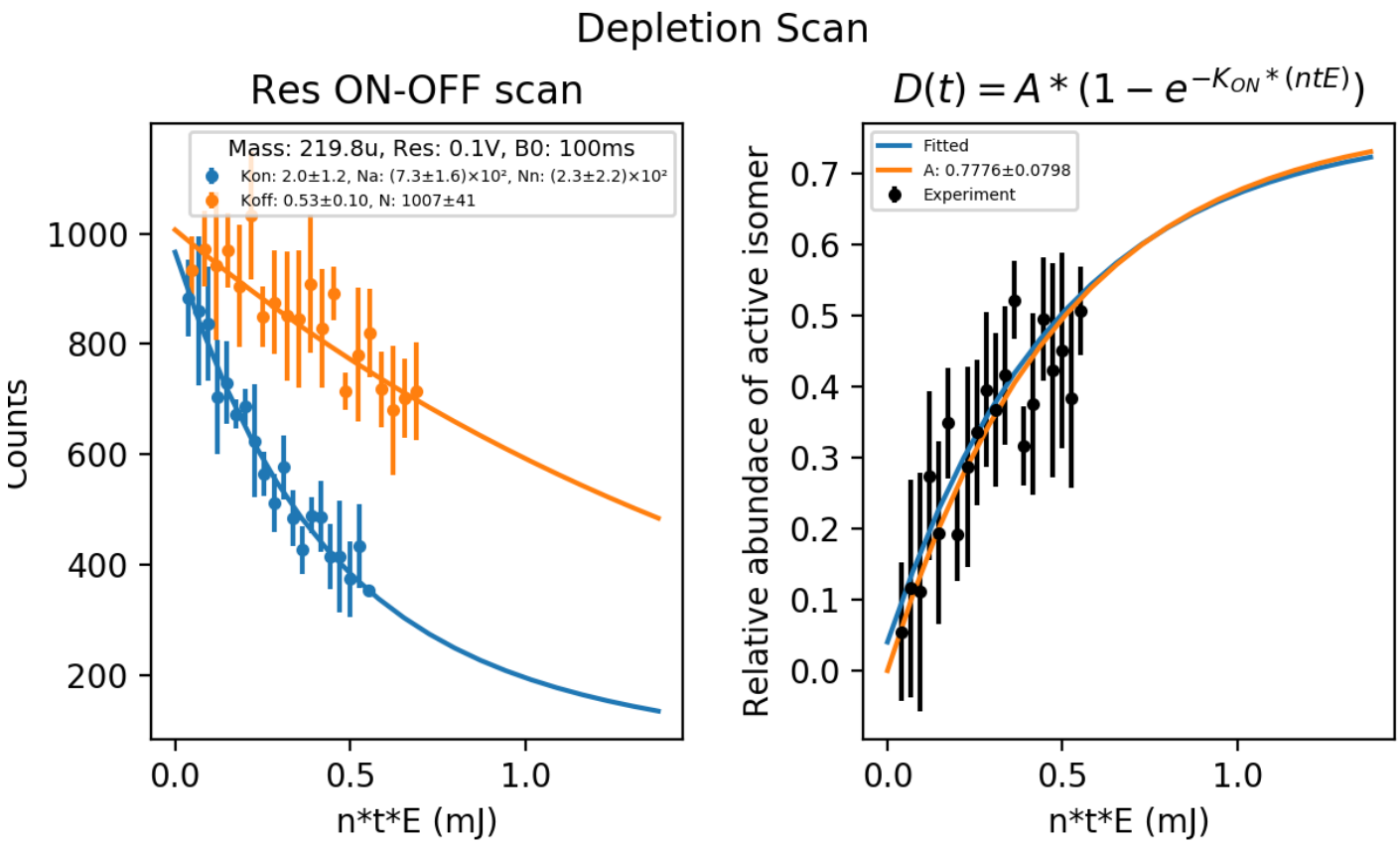

Fig. S10 Depletion scan of the vibrational band at 1245 cm^{-1} in the ddPy^{+} spectrum. **Left:** Blue shows the exponential decay of the complex counts ($N_{on}(ntE) = N_a\, e^{-(K_{off}+K_{on})\, ntE} + N_n\, e^{-(K_{off})\, ntE}$) on resonance as a function of total deposited energy, with t trapping time (in s), E energy (in mJ) per macropulse at $n = 10$ Hz rate, N_a total number of active isomers, N_n total number of inactive isomers at $t = 0$ s, and K_{on} and K_{off}, the on- and off-resonance decay rate constants. Orange shows the exponential decay of the complex counts off-resonance ($N_{off} = (N_a + N_n)\, e^{-(K_{off})\, ntE}$) due to other loss mechanisms with the rate constant K_{off}. **Right:** The relative depletion $D = 1 - N_{on}/N_{off}$, which has been fitted with an exponential function $D(ntE) = A(1 - e^{-(K_{on})\, ntE})$, where A is the constant for relative abundance of the active isomer $A = \frac{N_a}{N_a + N_n}$.

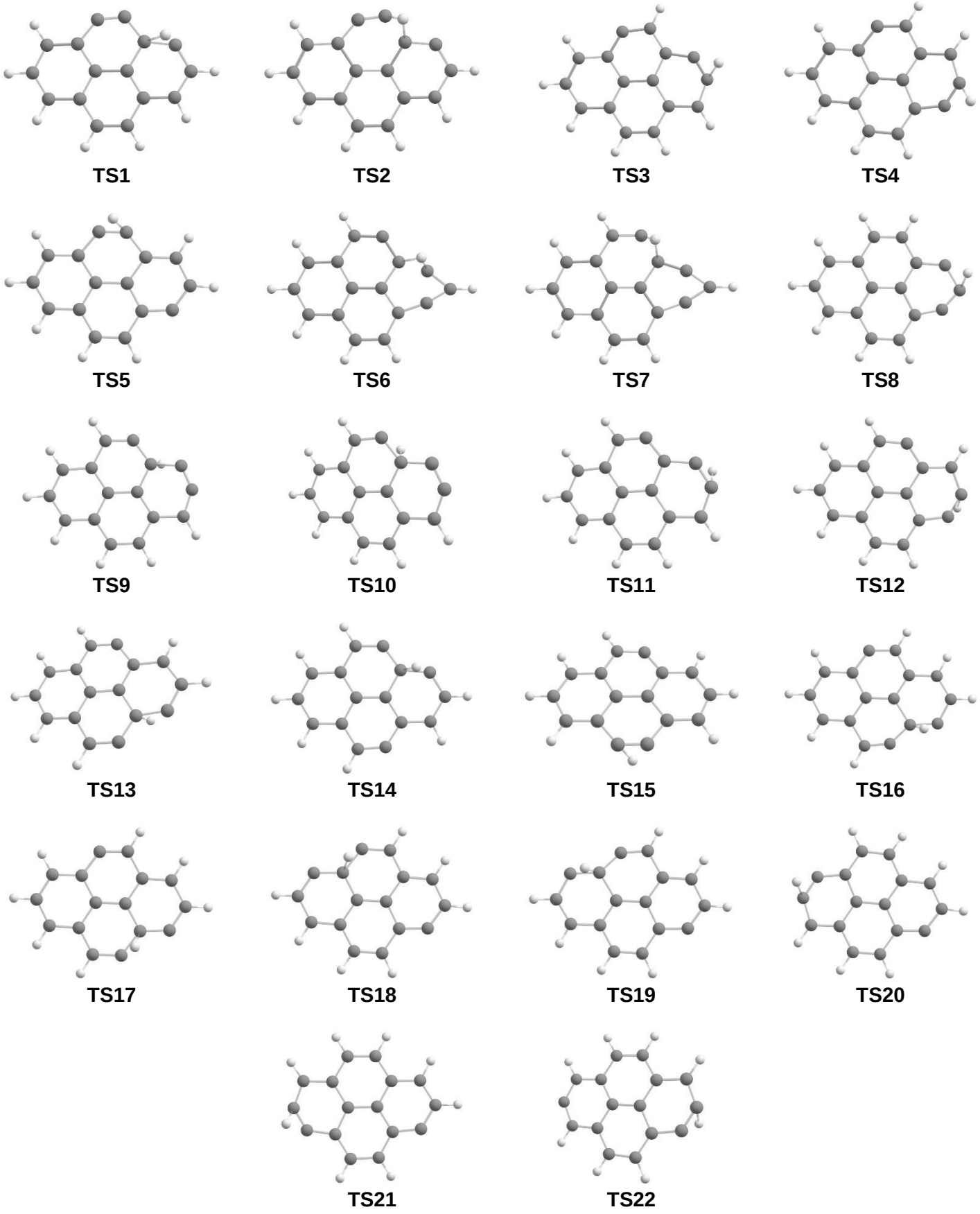

Fig. S11 Chemical structures of transition states in hydrogen migration pathways.

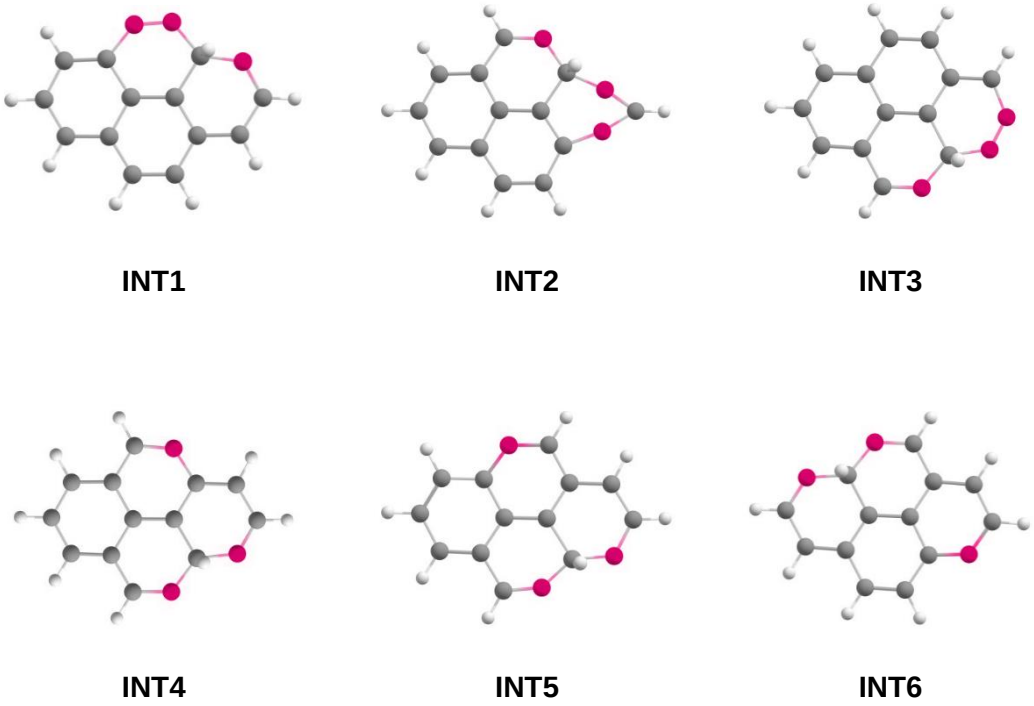

Fig. S12 Chemical structures of intermediates in hydrogen migration pathways.

Table S0 DFT calculated energies (Δ*E*, given in eV) of selected isomers and transition states (shown in Fig. 7 in the manuscript). Energies presented are relative to 4,5–ddPy$^+$.

	Δ*E* (eV)	
Isomer	**B3LYP**	**wB97XD**
4,5–ddPy$^+$	0.00	0.00
1,2–ddPy$^+$	0.05	0.04
1,3–ddPy$^+$	0.28	0.04
TS1	3.45	3.36
TS8	2.90	2.84
TS9	3.84	3.86

Atomic number	Coordinates (Å)		
	X	Y	Z
6	−0.005 003	0.621 296	−2.509 953
6	0.010 855	−0.595 086	−2.404 226
6	0.004 561	−1.500 971	−1.323 322
6	−0.031 210	−0.721 300	−0.095 388
6	−0.050 843	0.696 648	−0.087 362
6	−0.086 898	1.474 240	−1.368 204
6	−0.017 168	1.413 845	1.134 165
6	−0.012 805	0.685 802	2.361 645
6	−0.024 520	−0.674 659	2.362 040
6	−0.026 108	−1.421 285	1.146 156
6	0.026 301	−2.880 991	−1.284 487
6	0.016 395	−3.538 027	−0.048 637
6	−0.006 424	−2.828 087	1.137 174
6	0.020 342	2.887 443	−1.227 645
6	0.039 143	3.583 346	−0.032 919
6	0.031 189	2.832 248	1.130 181
1	0.052 054	−3.445 039	−2.207 400
1	0.032 439	−4.620 143	−0.024 854
1	−0.003 049	−3.357 019	2.082 473
1	−0.021 234	−1.216 980	3.299 962
1	0.002 460	1.235 779	3.294 191
1	0.070 938	4.665 469	−0.012 971
1	0.058 109	3.350 088	2.082 818
1	−1.161 362	2.104 244	−1.398 549

Table 1: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS1**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	−0.014 620	0.614 626	−2.523 821
6	−0.018 154	−0.614 474	−2.361 863
6	−0.011 796	−1.521 948	−1.315 244
6	−0.026 453	−0.724 566	−0.080 481
6	−0.044 603	0.689 688	−0.075 947
6	−0.074 033	1.478 901	−1.330 771
6	−0.022 716	1.410 272	1.150 752
6	−0.012 131	0.672 055	2.379 727
6	−0.007 288	−0.683 096	2.381 409
6	−0.008 962	−1.432 033	1.160 399
6	0.014 129	−2.910 453	−1.277 690
6	0.023 951	−3.552 493	−0.045 844
6	0.013 879	−2.831 662	1.143 686
6	−0.018 133	2.869 658	−1.222 087
6	0.019 723	3.560 400	−0.053 752
6	0.008 137	2.813 667	1.136 120
1	0.021 666	−3.473 140	−2.201 298
1	0.041 165	−4.634 318	−0.011 585
1	0.026 529	−3.363 135	2.087 626
1	0.004 812	−1.228 797	3.316 997
1	−0.003 194	1.222 210	3.312 459
1	0.061 184	4.642 812	−0.026 754
1	0.029 589	3.343 496	2.081 914
1	−1.117 387	1.224 360	−2.016 737

Table 2: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS2**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	2.643 269	−0.481 661	0.020 455
6	0.018 973	0.673 282	−0.000 752
6	2.418 952	0.847 435	0.023 939
6	0.147 736	−0.740 749	0.013 163
6	1.185 376	1.508 980	0.010 289
6	1.486 061	−1.294 332	0.009 771
6	−1.056 698	−1.565 916	0.016 351
6	1.041 040	2.908 188	0.006 881
6	1.376 576	−2.700 224	−0.077 338
6	−2.333 541	−0.908 862	0.015 900
6	−0.219 127	3.475 302	−0.004 811
6	−2.429 525	0.441 919	−0.001 918
6	−1.361 883	2.673 062	−0.010 439
6	−1.268 937	1.281 960	−0.008 380
1	−3.406 222	0.911 600	−0.005 868
1	−2.341 497	3.135 969	−0.015 950
1	−3.224 959	−1.522 689	0.023 199
1	−0.323 317	4.552 773	−0.008 195
1	1.927 914	3.528 234	0.013 719
6	−1.014 332	−2.976 088	0.008 091
6	0.320 896	−3.386 416	−0.027 394
1	3.631 863	−0.923 873	0.011 429
1	1.039 848	−3.430 105	1.016 141
1	−1.885 524	−3.609 894	0.051 291

Table 3: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS3**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	2.543 953	−0.622 300	0.015 973
6	−0.020 163	0.656 475	−0.003 458
6	2.381 124	0.700 995	−0.004 182
6	0.050 995	−0.761 127	0.009 696
6	1.180 221	1.440 356	−0.011 042
6	1.349 590	−1.438 785	0.016 150
6	−1.206 835	−1.470 179	0.003 971
6	1.100 803	2.830 129	−0.012 388
6	1.478 720	−2.840 788	0.011 770
6	−2.449 716	−0.811 170	0.015 474
6	−0.142 318	3.466 314	−0.007 346
6	−2.479 222	0.555 231	0.020 259
6	−1.311 284	2.729 845	0.003 218
6	−1.281 957	1.321 530	0.006 958
1	−3.429 907	1.074 625	0.024 222
1	−2.270 052	3.234 008	0.009 193
6	−3.361 193	−1.393 407	0.010 128
6	−0.187 343	4.547 847	−0.010 508
1	2.013 558	3.411 893	−0.017 084
1	−0.927 573	−2.853 137	−0.082 131
1	0.201 487	−3.410 469	−0.030 828
1	3.516 523	−1.100 024	0.024 142
1	2.419 809	−3.365 059	0.058 356
1	−0.515 796	−3.546 232	1.008 106

Table 4: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS4**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	−2.436 737	0.631 261	−0.010 540
6	0.043 762	−0.735 985	0.015 107
6	−2.430 403	−0.723 115	−0.010 819
6	0.025 806	0.699 271	0.015 875
6	−1.194 783	−1.447 883	−0.000 466
6	−1.218 622	1.387 509	0.000 163
6	1.225 282	1.520 453	0.014 401
6	−1.095 171	−2.830 306	−0.001 259
6	−1.223 424	2.794 620	−0.001 125
6	2.343 831	0.629 022	−0.013 843
6	0.031 812	−3.598 165	0.002 058
6	2.359 237	−0.622 712	−0.012 239
6	1.259 777	−2.920 928	0.008 209
6	1.259 061	−1.537 023	0.012 560
1	2.194 471	−3.466 983	0.003 709
1	−0.004 310	−4.680 689	−0.005 516
6	1.186 839	2.900 893	0.011 068
6	−0.054 895	3.536 347	0.004 572
1	−3.354 417	−1.286 269	−0.020 883
1	−3.374 600	1.173 123	−0.020 577
1	−2.178 473	3.306 425	−0.008 537
1	−0.101 790	4.617 399	−0.001 808
1	2.106 260	3.471 148	0.007 660
1	2.698 949	0.004 286	1.079 092

Table 5: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS5**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	2.470 163	−0.701 693	0.016 224
6	0.016 796	0.624 181	−0.070 839
6	2.453 506	0.634 074	−0.008 762
6	−0.003 164	−0.760 044	−0.052 673
6	1.255 035	1.413 875	−0.076 815
6	1.225 021	−1.476 527	−0.023 793
6	−1.274 980	−1.393 141	−0.022 082
6	0.857 957	2.779 200	−0.026 490
6	1.157 191	−2.859 447	0.002 074
6	−2.448 273	−0.572 739	0.004 107
6	0.027 240	3.902 325	0.043 206
6	−2.403 394	0.802 336	0.013 171
6	−0.652 982	2.767 522	−0.015 085
6	−1.132 526	1.431 645	−0.023 053
1	−3.313 486	1.385 925	0.043 522
1	−3.413 105	−1.065 409	0.026 216
1	0.043 357	4.982 643	0.089 854
1	1.306 147	2.213 305	−1.160 778
6	−1.285 900	−2.803 797	−0.000 378
6	−0.094 757	−3.505 405	0.005 734
1	3.409 024	−1.242 358	0.090 757
1	2.063 289	−3.452 702	0.027 852
1	−0.119 532	−4.587 832	0.025 448
1	−2.228 974	−3.336 112	0.020 264

Table 6: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS6**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	0.027 914	−0.590 009	2.447 129
6	0.075 890	0.777 121	2.440 231
6	0.076 786	1.456 110	1.184 536
6	0.011 819	0.677 466	0.008 989
6	−0.028 577	−0.707 181	−0.011 699
6	−0.020 033	−1.377 928	1.242 292
6	−0.051 645	−1.401 829	−1.265 528
6	0.037 532	−0.620 569	−2.477 352
6	0.041 299	0.743 938	−2.446 611
6	0.004 584	1.510 593	−1.192 305
6	0.120 276	2.789 650	0.738 168
6	0.127 464	3.945 105	0.032 124
6	0.078 108	2.842 924	−0.751 062
6	−0.059 176	−2.781 744	1.206 201
6	−0.093 767	−3.460 296	−0.007 180
6	−0.091 506	−2.795 320	−1.236 348
1	−1.030 689	1.296 640	−1.981 387
1	0.140 826	−1.133 673	−3.428 259
1	−0.121 888	−4.542 911	−0.001 017
1	−0.113 315	−3.361 786	−2.158 913
1	−0.063 565	−3.342 604	2.133 012
1	0.028 321	−1.114 984	3.394 503
1	0.111 703	1.333 067	3.367 722
1	0.141 384	5.027 535	0.050 031

Table 7: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS7**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	2.463 283	0.751 563	0.005 552
6	2.567 544	−0.603 427	−0.018 586
6	1.382 083	−1.391 349	−0.056 091
6	0.058 181	−0.746 876	−0.047 791
6	0.000 673	0.659 592	−0.013 926
6	1.199 978	1.428 812	0.004 740
6	−1.271 886	1.299 590	−0.005 738
6	−2.451 820	0.501 289	−0.019 421
6	−2.397 421	−0.863 297	−0.033 630
6	−1.140 389	−1.523 253	−0.039 293
6	1.149 481	−2.715 794	−0.085 564
6	0.237 270	−3.620 215	0.007 466
6	−0.996 600	−2.936 846	0.017 390
6	1.102 730	2.820 033	0.027 282
6	−0.143 775	3.447 451	0.030 610
6	−1.312 456	2.705 128	0.014 857
1	−0.547 007	−3.744 627	−0.994 463
1	−3.302 147	−1.456 250	−0.029 359
1	−3.414 080	0.999 017	−0.013 754
1	−0.195 921	4.528 603	0.048 227
1	−2.273 042	3.206 002	0.021 450
1	2.006 589	3.417 139	0.044 132
1	3.365 606	1.351 338	0.026 227
1	3.529 404	−1.096 400	−0.017 000

Table 8: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS8**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	0.025 596	0.637 905	−2.524 888
6	−0.005 367	−0.693 366	−2.553 609
6	0.015 542	−1.419 718	−1.302 602
6	0.031 856	−0.691 842	−0.068 414
6	0.040 384	0.718 062	−0.049 715
6	0.088 691	1.438 449	−1.352 707
6	0.001 189	1.428 087	1.191 783
6	−0.010 398	0.687 469	2.409 098
6	0.003 230	−0.673 782	2.390 690
6	0.016 819	−1.406 479	1.168 951
6	0.002 165	−2.811 884	−1.271 466
6	0.001 548	−3.496 870	−0.057 370
6	0.005 801	−2.808 461	1.144 922
6	−0.014 895	2.873 854	−1.194 337
6	−0.000 817	3.344 082	−0.031 354
6	−0.020 294	2.869 085	1.227 612
1	−0.011 160	−3.364 578	−2.202 924
1	−0.008 294	−4.579 506	−0.056 443
1	−0.003 790	−3.352 932	2.081 285
1	−0.042 636	3.421 613	2.157 178
1	1.150 306	2.110 965	−1.404 576
1	−0.058 400	−1.246 258	−3.485 940
1	−0.005 052	−1.223 667	3.324 291
1	−0.030 104	1.225 909	3.348 033

Table 9: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS9**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	0.018 402	0.616 527	−2.527 091
6	0.002 737	−0.742 052	−2.538 540
6	0.017 744	−1.442 377	−1.300 018
6	0.027 648	−0.698 018	−0.061 560
6	0.042 187	0.707 636	−0.046 259
6	0.085 295	1.449 827	−1.338 620
6	0.005 989	1.427 986	1.200 171
6	−0.005 289	0.675 681	2.420 880
6	−0.001 533	−0.678 531	2.406 752
6	0.006 793	−1.414 309	1.178 610
6	0.002 411	−2.845 962	−1.265 274
6	−0.011 252	−3.512 523	−0.054 634
6	−0.009 978	−2.808 099	1.150 386
6	0.031 960	2.848 916	−1.188 884
6	−0.006 956	3.338 556	−0.056 838
6	−0.019 107	2.844 800	1.223 214
1	−0.002 377	−3.399 317	−2.195 966
1	−0.025 513	−4.595 037	−0.039 168
1	−0.023 478	−3.352 695	2.086 886
1	−0.039 303	3.406 035	2.147 378
1	1.145 482	1.141 911	−1.946 347
1	−0.049 076	−1.289 815	−3.473 385
1	−0.012 417	−1.231 221	3.338 245
1	−0.020 071	1.216 941	3.358 570

Table 10: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS10**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	−2.476 391	0.927 146	0.033 197
6	−2.564 451	−0.414 097	0.034 699
6	−1.498 571	−1.294 380	0.016 531
6	−0.148 032	−0.753 316	0.017 407
6	−0.016 333	0.659 110	−0.000 850
6	−1.167 455	1.508 245	0.009 054
6	1.283 862	1.247 031	−0.014 429
6	2.433 795	0.392 542	−0.007 102
6	2.325 478	−0.957 231	0.016 367
6	1.041 686	−1.599 066	0.022 616
6	−1.407 785	−2.697 874	−0.070 077
6	−0.365 570	−3.405 089	−0.025 264
6	0.974 962	−3.006 688	0.022 988
6	−0.993 599	2.904 010	−0.001 695
6	0.273 468	3.454 752	−0.019 322
6	1.403 228	2.635 201	−0.023 552
1	−1.108 178	−3.454 715	1.009 736
1	1.836 726	−3.653 187	0.070 851
1	3.210 337	−1.580 560	0.024 021
1	3.415 340	0.851 790	−0.015 080
1	0.392 399	4.530 779	−0.028 538
1	2.390 618	3.080 933	−0.033 707
1	−1.866 959	3.544 488	0.004 359
1	−3.351 064	1.568 259	0.043 751

Table 11: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS11**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	−2.457 766	0.783 170	−0.005 114
6	−2.481 591	−0.550 711	0.019 419
6	−1.376 272	−1.428 246	0.026 120
6	−0.063 941	−0.769 475	0.019 896
6	0.012 612	0.647 169	−0.000 320
6	−1.173 017	1.443 690	−0.013 231
6	1.288 567	1.289 178	0.007 125
6	2.474 262	0.505 265	0.024 726
6	2.431 250	−0.861 628	0.026 901
6	1.180 083	−1.502 089	0.018 557
6	−1.540 592	−2.828 241	0.024 359
6	−0.272 220	−3.420 597	−0.010 092
6	0.862 638	−2.876 515	−0.054 932
6	−1.061 809	2.831 498	−0.022 333
6	0.190 174	3.450 668	−0.019 805
6	1.346 654	2.696 055	−0.004 312
1	3.336 325	−1.453 906	0.024 654
1	3.431 372	1.012 661	0.026 023
1	0.250 888	4.531 521	−0.029 132
1	2.314 335	3.182 712	−0.000 610
1	−1.961 038	3.435 636	−0.031 620
1	−3.364 230	1.379 472	−0.012 474
1	−2.495 088	−3.326 983	0.066 554
1	0.436 469	−3.552 543	1.037 121

Table 12: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS12**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	0.008 960	2.479 103	−0.670 830
6	−0.052 163	−0.011 300	0.723 871
6	−0.022 260	2.447 570	0.656 631
6	−0.035 119	0.000 633	−0.686 034
6	−0.106 868	1.268 238	1.469 082
6	−0.013 828	1.232 567	−1.412 080
6	−0.016 408	−1.238 477	−1.401 154
6	−0.002 730	1.135 642	2.888 296
6	0.004 099	1.205 895	−2.801 151
6	−0.005 886	−2.470 340	−0.662 005
6	0.023 815	−0.047 892	3.598 313
6	0.008 463	−2.401 920	0.676 792
6	0.040 174	−1.227 522	2.870 424
6	−0.004 175	−1.231 068	1.456 393
1	0.078 944	−2.176 437	3.392 353
1	−0.002 124	−3.414 395	−1.196 136
1	0.047 148	−0.048 395	4.680 985
1	−1.185 747	1.291 578	2.080 394
6	−0.001 406	−1.213 756	−2.803 758
6	0.004 996	−0.010 325	−3.487 547
1	0.065 198	3.416 003	−1.215 933
1	0.021 937	2.137 338	−3.353 600
1	0.018 459	−0.009 728	−4.570 253
1	0.011 086	−2.149 237	−3.349 440

Table 13: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS13**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	0.008 960	2.479 103	−0.670 830
6	−0.052 163	−0.011 300	0.723 871
6	−0.022 260	2.447 570	0.656 631
6	−0.035 119	0.000 633	−0.686 034
6	−0.106 868	1.268 238	1.469 082
6	−0.013 828	1.232 567	−1.412 080
6	−0.016 408	−1.238 477	−1.401 154
6	−0.002 730	1.135 642	2.888 296
6	0.004 099	1.205 895	−2.801 151
6	−0.005 886	−2.470 340	−0.662 005
6	0.023 815	−0.047 892	3.598 313
6	0.008 463	−2.401 920	0.676 792
6	0.040 174	−1.227 522	2.870 424
6	−0.004 175	−1.231 068	1.456 393
1	0.078 944	−2.176 437	3.392 353
1	−0.002 124	−3.414 395	−1.196 136
1	0.047 148	−0.048 395	4.680 985
1	−1.185 747	1.291 578	2.080 394
6	−0.001 406	−1.213 756	−2.803 758
6	0.004 996	−0.010 325	−3.487 547
1	0.065 198	3.416 003	−1.215 933
1	0.021 937	2.137 338	−3.353 600
1	0.018 459	−0.009 728	−4.570 253
1	0.011 086	−2.149 237	−3.349 440

Table 14: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS14**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	−2.341 937	0.656 015	−0.013 966
6	−0.035 478	−0.717 393	0.016 093
6	−2.358 454	−0.596 583	−0.014 008
6	−0.025 470	0.722 197	0.014 974
6	−1.254 195	−1.508 147	0.016 295
6	−1.220 024	1.545 224	0.015 508
6	1.218 000	1.427 994	−0.000 686
6	−1.253 473	−2.889 550	0.016 260
6	−1.180 984	2.926 593	0.014 395
6	2.370 606	0.615 988	−0.010 392
6	−0.031 054	−3.560 110	0.010 704
6	2.434 870	−0.715 349	−0.010 601
6	1.157 909	−2.851 053	0.003 160
6	1.187 712	−1.445 620	0.001 809
1	3.371 063	−1.262 155	−0.021 409
1	2.099 092	−3.387 713	−0.003 278
1	−0.013 731	−4.642 129	0.006 683
1	−2.188 815	−3.433 181	0.013 975
6	1.231 148	2.833 334	0.000 088
6	0.057 741	3.567 748	0.008 075
1	−2.709 032	0.033 675	1.074 214
1	−2.101 956	3.494 409	0.012 121
1	0.099 335	4.648 966	0.003 573
1	2.188 195	3.339 349	−0.006 852

Table 15: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS15**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	0.016 945	0.584 948	−2.374 832
6	−0.042 232	−0.702 415	−2.537 306
6	0.006 405	−1.476 138	−1.291 543
6	0.043 855	−0.719 295	−0.089 377
6	0.054 856	0.697 139	−0.077 563
6	0.155 740	1.552 291	−1.365 683
6	−0.011 300	1.422 465	1.133 171
6	−0.023 295	0.693 219	2.372 163
6	0.006 950	−0.644 721	2.308 244
6	0.031 141	−1.436 891	1.154 915
6	−0.001 326	−2.858 997	−1.270 325
6	0.010 968	−3.538 431	−0.044 902
6	0.022 926	−2.844 268	1.147 072
6	0.005 705	2.964 598	−1.265 917
6	0.018 623	3.580 331	−0.007 308
6	−0.043 263	2.840 434	1.147 226
1	−0.025 767	−3.415 583	−2.198 802
1	0.001 487	−4.620 913	−0.039 198
1	0.020 749	−3.370 655	2.092 616
1	−0.052 774	1.239 399	3.307 807
1	0.017 410	4.663 532	0.041 140
1	−0.105 024	3.340 318	2.107 985
1	1.222 904	2.113 592	−1.436 098
1	−0.117 186	−1.197 977	−3.500 420

Table 16: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS16**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	−2.406 935	0.656 084	−0.010 367
6	−0.037 353	−0.710 040	−0.037 182
6	−2.500 287	−0.674 825	−0.009 761
6	0.002 504	0.698 009	−0.020 732
6	−1.267 862	−1.431 806	−0.013 418
6	−1.230 864	1.435 796	−0.008 143
6	1.243 784	1.423 865	−0.003 948
6	−1.260 070	−2.829 103	0.017 471
6	−1.193 274	2.830 343	0.010 512
6	2.467 698	0.689 552	0.012 204
6	−0.061 805	−3.569 824	0.023 154
6	2.428 357	−0.664 999	0.004 023
6	1.101 018	−2.879 820	−0.015 850
6	1.220 259	−1.481 067	−0.067 933
1	1.852 901	−1.196 570	−1.122 522
1	3.415 412	1.215 663	0.058 340
1	−0.083 759	−4.652 739	0.059 331
1	−2.204 476	−3.360 822	0.038 493
6	1.227 198	2.825 842	0.011 658
6	0.023 567	3.511 042	0.019 014
1	−3.448 296	−1.200 953	−0.003 324
1	−2.125 224	3.380 848	0.019 378
1	0.026 117	4.593 616	0.033 805
1	2.164 517	3.367 907	0.021 649

Table 17: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS17**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	0.003 032	0.627 115	−2.505 843
6	−0.007 174	−0.728 627	−2.528 744
6	0.005 423	−1.448 798	−1.298 659
6	0.022 127	−0.702 386	−0.064 570
6	0.039 366	0.702 900	−0.044 356
6	0.073 529	1.460 314	−1.310 027
6	0.013 770	1.426 101	1.182 889
6	0.007 333	0.685 048	2.411 455
6	0.007 507	−0.670 358	2.415 842
6	0.007 611	−1.406 545	1.188 182
6	−0.011 219	−2.852 979	−1.276 451
6	−0.019 953	−3.533 434	−0.062 638
6	−0.012 932	−2.779 013	1.084 827
6	0.018 050	2.859 799	−1.200 882
6	−0.019 719	3.556 228	−0.040 660
6	−0.015 533	2.825 101	1.162 527
1	−0.021 094	−3.402 964	−2.209 788
1	−0.034 791	−4.616 645	−0.033 427
1	−0.038 153	3.364 741	2.102 387
1	1.131 206	1.169 924	−1.929 133
1	−0.050 502	−1.263 158	−3.471 863
1	0.001 015	−1.222 208	3.346 595
1	−0.000 350	1.235 666	3.343 881
1	−0.056 137	4.639 263	−0.026 324

Table 18: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS18**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	0.013 959	0.593 558	−2.364 401
6	−0.041 500	−0.695 286	−2.523 926
6	0.006 690	−1.470 530	−1.280 503
6	0.043 219	−0.708 894	−0.077 323
6	0.052 644	0.703 478	−0.068 991
6	0.150 796	1.562 050	−1.357 338
6	−0.014 147	1.418 245	1.145 826
6	−0.024 245	0.688 819	2.373 277
6	0.007 884	−0.671 151	2.392 792
6	0.033 074	−1.406 197	1.178 209
6	−0.000 521	−2.854 717	−1.268 475
6	0.014 396	−3.544 795	−0.038 954
6	0.028 762	−2.791 382	1.091 097
6	−0.001 797	2.971 675	−1.248 672
6	0.010 180	3.582 491	0.012 919
6	−0.048 400	2.837 238	1.163 652
1	−0.025 178	−3.410 732	−2.197 878
1	0.006 881	−4.628 062	−0.016 429
1	−0.109 788	3.333 405	2.126 396
1	1.216 979	2.126 882	−1.425 846
1	−0.114 059	−1.188 783	−3.488 300
1	0.000 331	−1.212 271	3.330 052
1	−0.055 095	1.249 466	3.298 960
1	0.006 556	4.665 421	0.065 328

Table 19: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS19**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	2.509 572	−0.635 072	0.016 572
6	−0.017 378	0.672 126	−0.002 555
6	2.458 559	0.718 432	−0.004 508
6	0.024 381	−0.743 619	0.014 166
6	1.207 752	1.415 662	−0.012 775
6	1.313 088	−1.429 944	0.020 073
6	−1.246 586	−1.431 689	0.012 277
6	1.071 284	2.782 394	−0.018 245
6	1.422 801	−2.835 715	0.018 188
6	−2.475 541	−0.750 335	0.023 469
6	−0.101 615	3.500 576	−0.014 374
6	−2.477 445	0.617 688	0.024 511
6	−1.284 774	2.774 134	0.000 194
6	−1.268 122	1.363 482	0.007 509
1	−2.236 649	3.292 381	0.005 949
1	−0.110 996	4.583 896	−0.021 788
6	−0.979 601	−2.816 299	−0.068 066
6	0.139 556	−3.392 541	−0.020 617
1	3.372 086	1.299 521	−0.009 958
1	3.463 460	−1.146 423	0.025 174
1	2.357 440	−3.371 501	0.063 298
1	−3.419 044	1.153 217	0.028 301
1	−3.398 891	−1.313 457	0.020 937
1	−0.575 761	−3.510 754	1.022 642

Table 20: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS20**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	−2.602 901	0.487 316	0.036 326
6	−0.011 935	−0.697 047	0.001 817
6	−2.483 399	−0.874 754	0.032 435
6	−0.109 524	0.715 944	0.023 952
6	−1.204 888	−1.493 725	0.010 919
6	−1.440 154	1.279 468	0.026 074
6	1.108 233	1.522 207	0.030 402
6	−1.008 741	−2.867 781	−0.002 843
6	−1.307 318	2.683 377	−0.049 794
6	2.370 974	0.841 034	0.021 943
6	0.186 286	−3.519 622	−0.021 153
6	2.439 691	−0.512 275	−0.004 714
6	1.344 918	−2.726 430	−0.024 199
6	1.265 359	−1.332 833	−0.013 194
1	2.317 787	−3.204 499	−0.035 295
1	0.255 605	−4.600 853	−0.031 909
6	1.083 274	2.932 545	0.032 550
6	−0.247 491	3.362 348	−0.000 427
1	−3.365 093	−1.502 518	0.035 178
1	−3.573 248	0.965 054	0.037 034
1	3.408 052	−0.998 679	−0.014 274
1	3.274 962	1.436 109	0.030 826
1	1.962 329	3.555 343	0.078 239
1	−0.966 888	3.408 126	1.044 388

Table 21: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS21**.

Atomic number	Coordinates (Å)		
	X	Y	Z
6	0.008 763	2.453 628	0.669 733
6	−0.011 467	−0.018 541	−0.709 738
6	−0.012 472	2.467 511	−0.684 075
6	0.005 138	−0.014 288	0.708 147
6	−0.016 827	1.247 121	−1.439 635
6	0.015 809	1.228 945	1.412 769
6	−0.003 312	−1.252 260	1.425 928
6	−0.012 765	1.314 531	−2.847 425
6	0.021 833	1.219 950	2.813 276
6	−0.018 536	−2.483 771	0.716 990
6	0.023 911	0.015 237	−3.365 925
6	−0.017 274	−2.518 948	−0.649 169
6	0.067 980	−1.085 071	−2.754 896
6	−0.007 814	−1.307 821	−1.363 072
1	−0.013 292	−3.456 984	−1.187 729
1	−1.024 071	−0.700 074	−3.451 275
1	−0.020 705	−3.408 643	1.280 790
1	−0.054 019	2.233 013	−3.410 874
6	0.005 013	−1.225 352	2.841 254
6	0.017 877	−0.003 484	3.439 885
1	−0.020 498	3.405 710	−1.223 833
1	0.014 804	3.388 553	1.217 554
1	0.029 029	2.151 102	3.368 596
1	0.000 901	−2.151 177	3.405 187

Table 22: B3LYP/6-311++G(2d,p) optimised structure of transition state **TS22**.