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

Supporting Information

Study on Unusual S_N2 Mechanism in Methylation of Benzyne through Nickel-complexation

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Supporting Information

1. General Remarkds

1.1 Orbital analysis on the Ni complex

The Ni complex and the related complex were analyzed by the three orbital analyses; canonical Kohn-Sham orbital, natural bond orbital (NBO) and Pipek-Mezey (PM) localized orbital. The related complexes were derived from the Ni^0 ($3d^{10}$) center and the unsaturated compounds (cyclohexyne, diphenylacetylene and stilbene, see Figure S1). Thus, these complexes could form the η^2 structure or metallacycle. The resulting Kohn-Sham, NBO3, NBO6 and PM localized orbitals are shown in Figure S2, S3, S4 and S5 respectively. These orbitals indicated that the Ni centers do not exist as the absolute Ni^0 ($3d^{10}$) state at these complexes, especially at the complexes consisting of benzyne or cyclohexyne. Then, it was suggested that these two complexes form the metallacycle rather than the η^2 structure. The details were described hereafter.

NBO3 and NBO6 were considered respectively, because these analyses showed the different results at the complexes consisting of benzyne or cyclohexyne (Figure S3a, S3b, S4a and S4b). The difference appeared at the orbitals consisting of the Ni-3d orbital distributing within the P–Ni–P plane and/or C-2p orbital of benzyne (or cyclohexyne) directing to the Ni center. For example, at the benzyne–Ni complex, one NBO3 orbital consisted of these Ni-3d and C-2p orbitals showing the 1.78 electron occupation number (Figure S3a). And another NBO3 orbital consisted of the C-2p orbital showing the 1.25 occupation. These results indicated that the total population of these C-2p orbitals is close to 3.0 rather than 2.0 and is redundant compared to that of benzyne monomer. Thus, these results also indicated that some electrons are shifted from the Ni^0 ($3d^{10}$) center to the benzyne so that the metallacycle is formed. In fact, such a shift was represented by the NBO3 orbital with the 1.78 occupation because the orbital was represented by the direct interaction between the Ni-3d orbital distributing within the P–Ni–P plane and the C-2p orbital of benzyne. Then, these NBO3 orbitals indicated that the Ni-center exists as Ni^{II} ($3d^8$) rather than Ni^0 ($3d^{10}$) making the metallacycle with the benzyne. The same trend was indicated from NBO3 on the cyclohexyne complex (Figure S3b).

The NBO6 orbitals were different from the NBO3 orbitals at the complex consisting of benzyne or cyclohexyne. At first, at the benzyne–Ni complex, the NBO6 orbitals were localized at either of the Ni center or benzyne (Figure S4a). Then, one NBO6 orbital represented the π^* orbital of the benzyne showing the occupation as 0.88 but not 0.0. And, one NBO6 orbital represented the Ni-3d orbital within the P–Ni–P plane showing the occupation as 1.42 but not 2.0. These results indicated that the electrons of the Ni^0 ($3d^{10}$) center were partially shifted to the π^* orbital of benzyne after the formation of the benzyne–Ni complex. In other words, the interaction between the Ni center and benzyne was represented by the shift of the occupation number but not by the orbital interaction in NBO6 analysis. In addition, it is worth noting that the 0.88 occupation of the π^* orbital at the benzyne–Ni complex was larger than that (0.61) of the π^* orbital at the stilbene-Ni complex. Thus, from a comparative perspective, the metallacycle structure was assumed in the benzyne-Ni complex rather than the stilbene–Ni complex.

The PM localized orbitals were similar to the NBO3 orbitals at the complex consisting of benzyne or cyclohexyne. For example, at the Ni-benzyne complex, the two PM localized orbitals were represented by the interaction between the C-2p orbitals of the benzyne and the Ni-3d orbital within the P–Ni–P. Both PM localized orbitals showed the occupation number as 2.00 and corresponded to the Ni-C bonding orbital making the metallacycle structure. Such a Ni–C bonding orbital was not found in the stilbene–Ni complex. Thus, the stilbene–Ni complex was suggested to form the η^2 structure based on the results of the PM localized orbitals.

1.2 Multidimensional energy profile for methylation of benzyne–Ni complex

The methylation of benzyne–Ni complex was discussed in the text based on the optimized structures. In order to complement these results, a multidimensional energy profile was also investigated. The profile was scanned by considering the three coordinates; (i) the distance of two carbon atoms which form the C–C bond during the methylation, (ii) the C–I distance of iodomethane (MeI) which dissociates during the methylation and (iii) the I–Ni distance which varies after the MeI dissociation. These three coordinates are changed during the methylation of benzyne–Ni complex. In order to simplify the profile to be two-dimensional, the former two coordinates (i) and (ii) were considered as the axes of the two-dimensional profile. The later coordinate (iii) was considered as the parameter by respecting the heavy mass of I and Ni atoms. In addition, the cyclohexyl groups of the benzyne–Ni complex were simplified to the Me groups to suppress the computational time.

Three energy profiles were drawn by changing the I–Ni distance to 5.0, 3.8 and 2.6 [Å], respectively (Figure S6). The profiles and the axes were illustrated so that the transition state of the benzyne methylation is clarified. When the I–Ni distance is 5.0 Å, the profile showed the two local minima and the one plateau region (Figure S6a). The first minimum was represented by the long C-C distance (> 3.5 Å) and the short C–I distance (~ 2.1 Å) reflecting the initial state (structure (A) of Figure 2 in the text). The second minimum was represented by the short C–C distance (~ 1.5Å) and the long C–I distance (> 3.5 Å) reflecting the intermediate state of S_N2 reaction (structure (C) of Figure 2 in the text). And the plateau was represented by the middle C–C distance (~ 2.7 Å) and the long C–I distance (> 3.5 Å) reflecting the intermediate state of oxidative addition (structure (K) of Figure 2 in the text). The two minima were divided by one mountain peak being similar to the energy curve among the structures (A, B and C) shown in Figure 2 of the text. And also, the local minimum reflecting the initial state was connected to the plateau region by the uphill energy path being similar to the change among the structures (A, J and K) shown in Figure 2 of the text. Then, it was found that the energy profile (Figure S6a) presented the same trend compared to the energy curve shown in Figure 2 of the text as long as the I–Ni distance is long (~5.0 Å).

The energy profile with the 3.8 I-Ni distance [Å] (Figure S6b) showed the same shape compared to that with the 5.0 I–Ni distance [Å] (Figure S6a). On the other hand, the energy profile with the 2.6 I–Ni distance [Å] (Figure S6c) showed the different shape (Figure S6a). First of all, the profile with the 2.6 I–Ni distance [Å] indicated the deep valley at around the region represented by the short C–C distance (<2.0 Å) and long C–I distance (>3.0 Å). The deep region corresponded to the low energy of the final state of the benzyne methylation being similar to that in the text (structure (D) of Figure 2 in the text). Meanwhile, the profile with the 2.6 I–Ni distance [Å] indicated the high energy at around the region represented by long C–C distance (>3.0 Å) and short C–I distance (<2.5 Å). This

result indicated that the I and Ni atoms are less contacted in the initial state of the benzyne methylation. This is because the iodine atom is saturated by the Me–I bond in the initial state unless the Me–I bond is cleaved by the benzyne methylation. The high energy of the initial state also supported the result in the text that the benzyne methylation at the present Ni complex favors S_N2 reaction rather than σ-bond metathesis.

Three profiles indicated the several inflection points of the energy change. And these inflection points were assumed to correspond to the optimized structures and the TS structures discussed in the text. Thus, it was confirmed that the results investigated in the text sufficiently covers the mechanism of the benzyne methylation at the present Ni complex.

1.3 Experimental details

$^{31}P\{^{1}H\}$ NMR (160 MHz) analyses were taken on a JEOL 400SS spectrometer. To a mixture of benzyne–Ni(dcpe) complex (10.0 mg, 17.9 μmol) and vacuum dried 3A molecular sieves (10 mg, powdered) in THF-d_8 (200 μL) was added iodomethane (300 μL, 4.82mmol) at 273 K (Figure S10). After warming the mixture to each temperatures (283 K, 293 K, 303 K), $^{31}P\{^{1}H\}$ NMR (160 MHz) analysis was performed at regular time intervals. Experiments were carried out three times at each temperature. Values of reaction rate constants (k) for the methylation of benzyne–Ni(dcpe) complex are provided in Table S14. The activation energy (E_a) was determined to be E_a = 66.4 [kJ/mol] = 15.9 [kcal/mol]. Intensity data of X-ray crystallographical analyses were collected on a Rigaku XtaLABmini. The structure was solved by direct methods (SHELXS-2014) and refined by the full-matrix least-squares on F^2 (SHELXL-2014). Crystal structure of ***o*-tolyl(dcpe)Ni complex** is shown in Figure S11 and Table S15. CCDC 1557998 (compound ***o*-tolyl(dcpe)Ni complex**) contain the supplementary crystallographic data for these structures. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

2. Figures

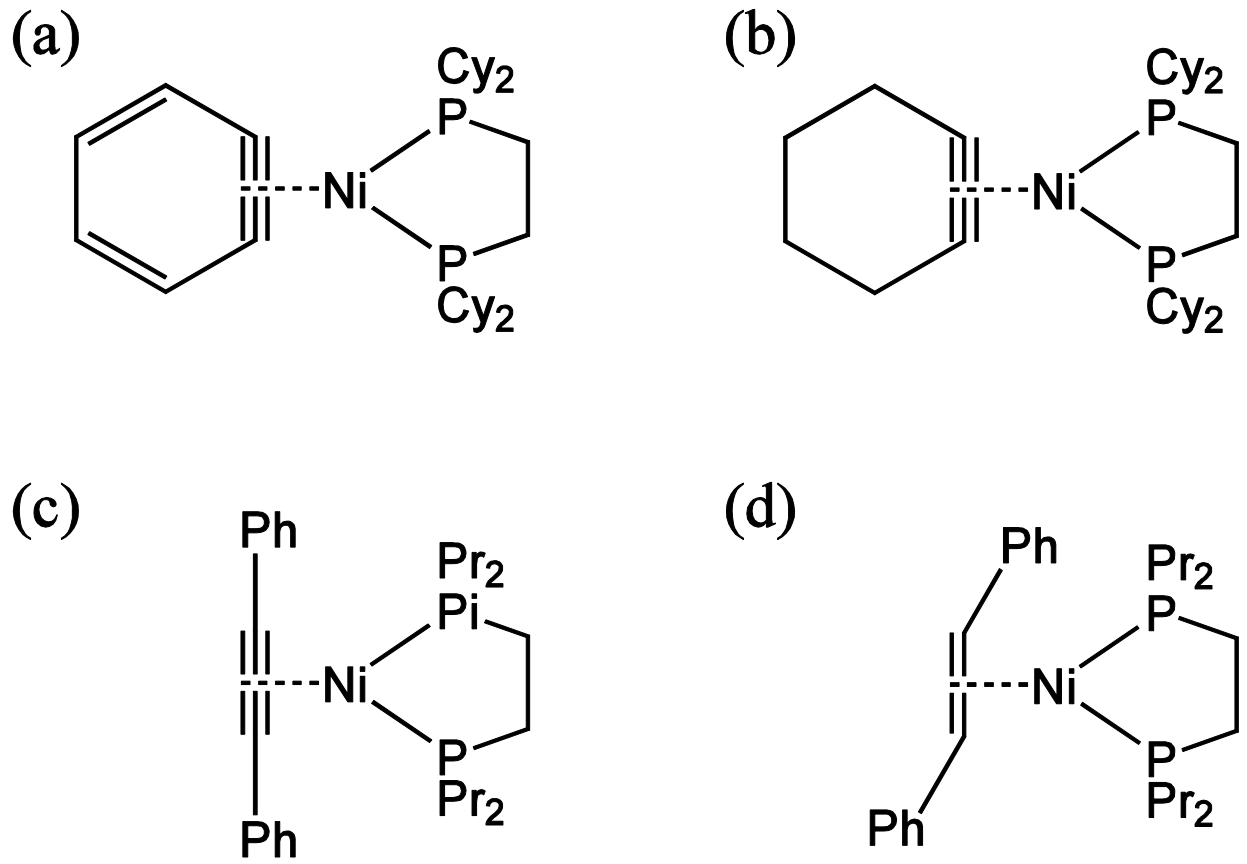


Figure S1. Ni complexes investigated by orbital analyses; (a) Ni complex with benzyne,[1] (b) Ni complex with Cyclohexyne,[2] (c) Ni complex with diphenylacetylene[3] and (d) Ni complex with stilbene.[4]

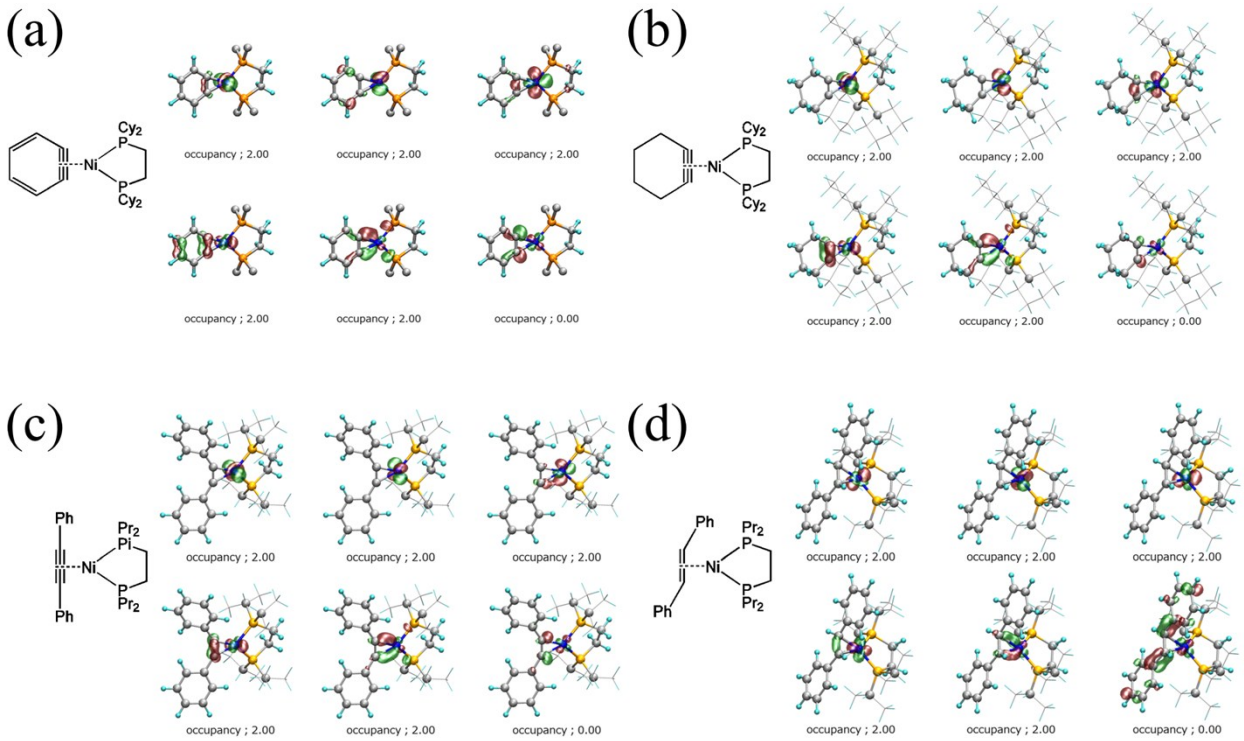


Figure S2. Kohn-Sham orbitals consisting of the Ni-3d orbitals and the π orbital of the unsaturated compounds; (a) Ni complex with benzyne (cyclohexyl groups are represented transparently except for the linking carbon atoms), (b) Ni-complex with Cyclohexyne, (c) Ni-complex with diphenylacetylene and (d) Ni-complex with stilbene.

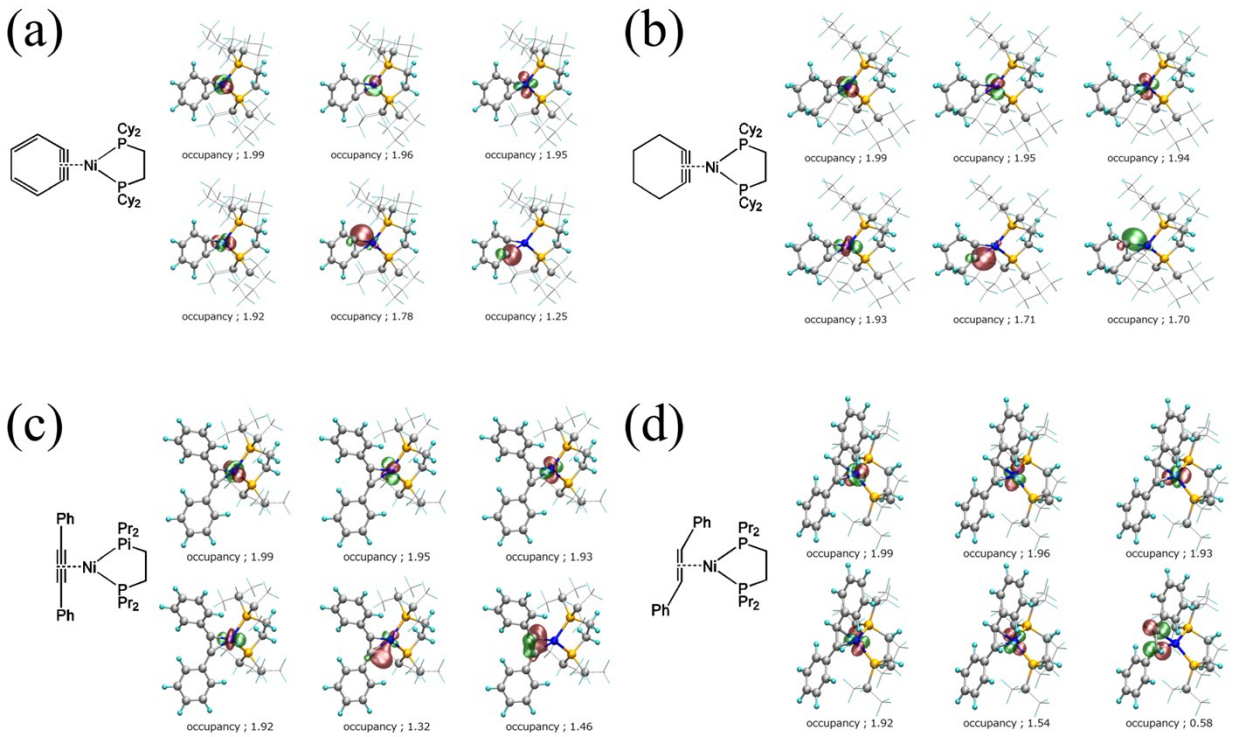


Figure S3. NBO3 orbitals consisting of the Ni-3d orbitals and the π orbital of the unsaturated compounds; (a) Ni complex with benzyne, (b) Ni complex with Cyclohexyne, (c) Ni complex with diphenylacetylene and (d) Ni complex with stilbene.

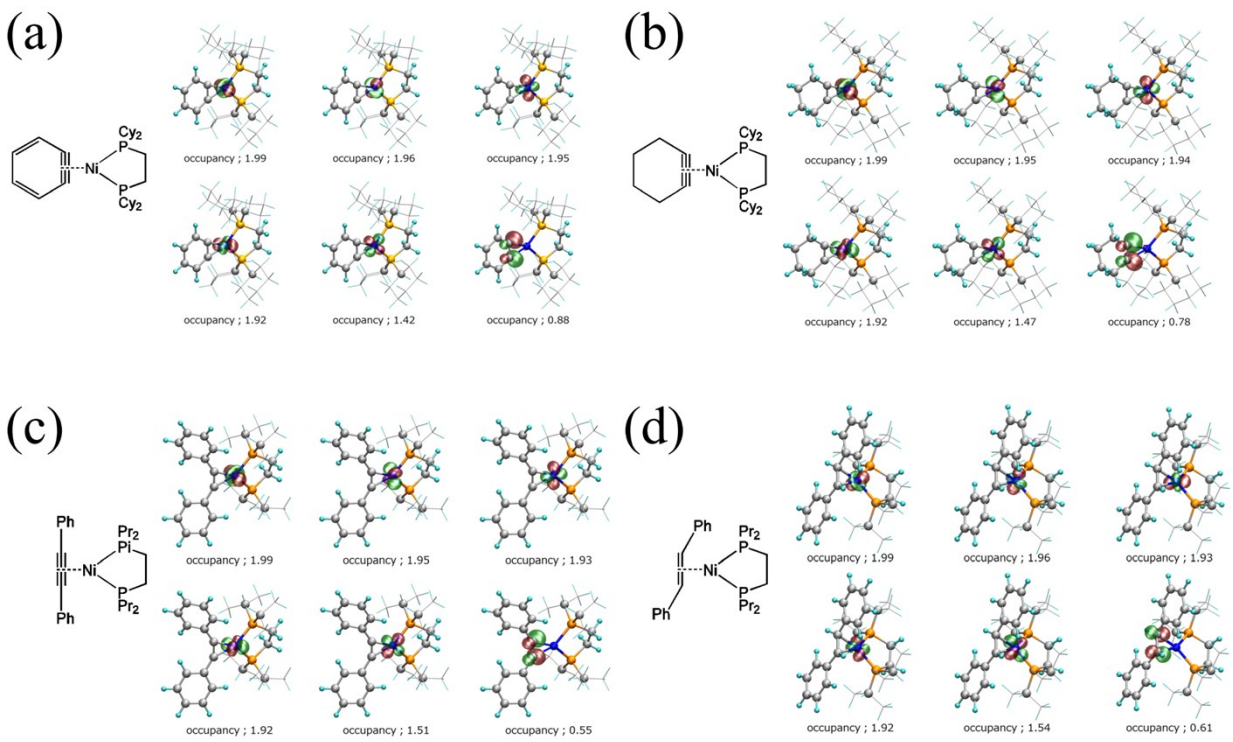


Figure S4. NBO6 orbitals consisting of the Ni-3d orbitals and the π orbital of the unsaturated compounds; (a) Ni complex with benzyne, (b) Ni complex with Cyclohexyne, (c) Ni complex with diphenylacetylene and (d) Ni complex with stilbene.

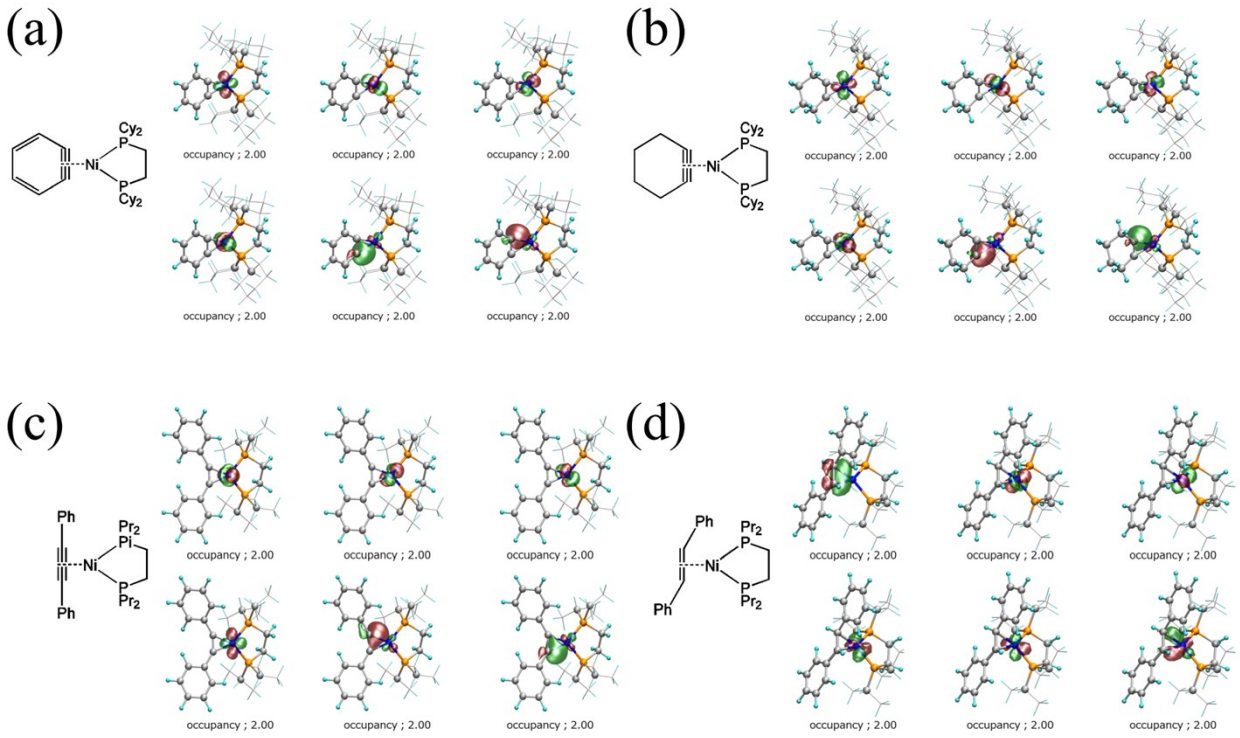
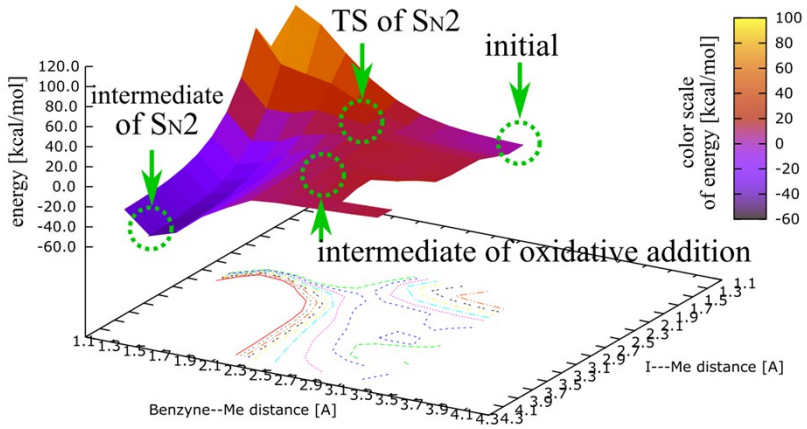
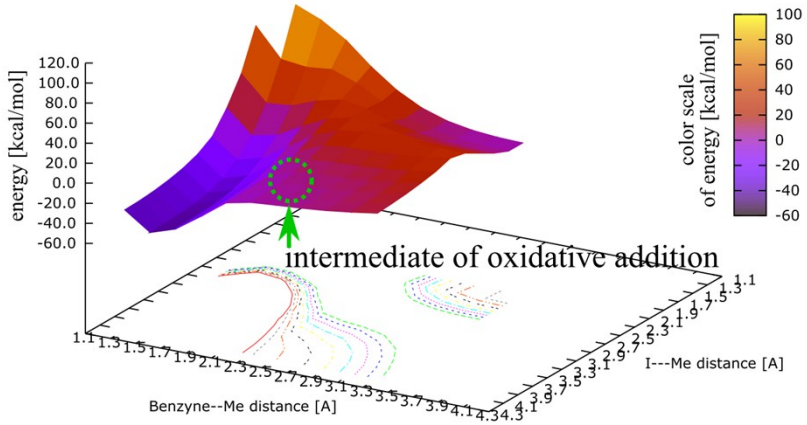


Figure S5. Pipek-Mezey localized orbitals consisting of the Ni-3d orbitals and the π orbital of the unsaturated compounds; (a) Ni complex with benzyne, (b) Ni complex with Cyclohexyne, (c) Ni complex with diphenylacetylene and (d) Ni complex with stilbene.

(a) I···Ni; 5.0 [Å]



(b) I···Ni; 3.8 [Å]



(c) I···Ni; 2.6 [Å]

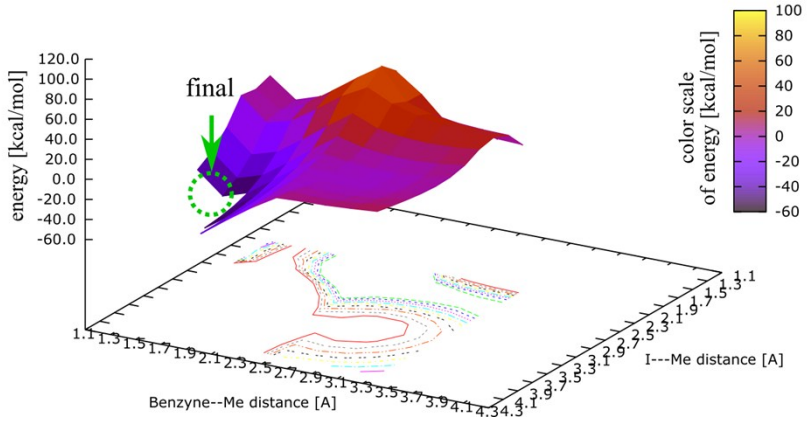


Figure S6. Two dimensional energy profile on the benzyne methylation of the benzyne–Ni complex; (a) profile obtained with the 5.0 I–Ni distance [Å], (b) profile obtained with the 3.8 I–Ni distance [Å] and (c) profile obtained with the 2.6 I–Ni distance [Å].

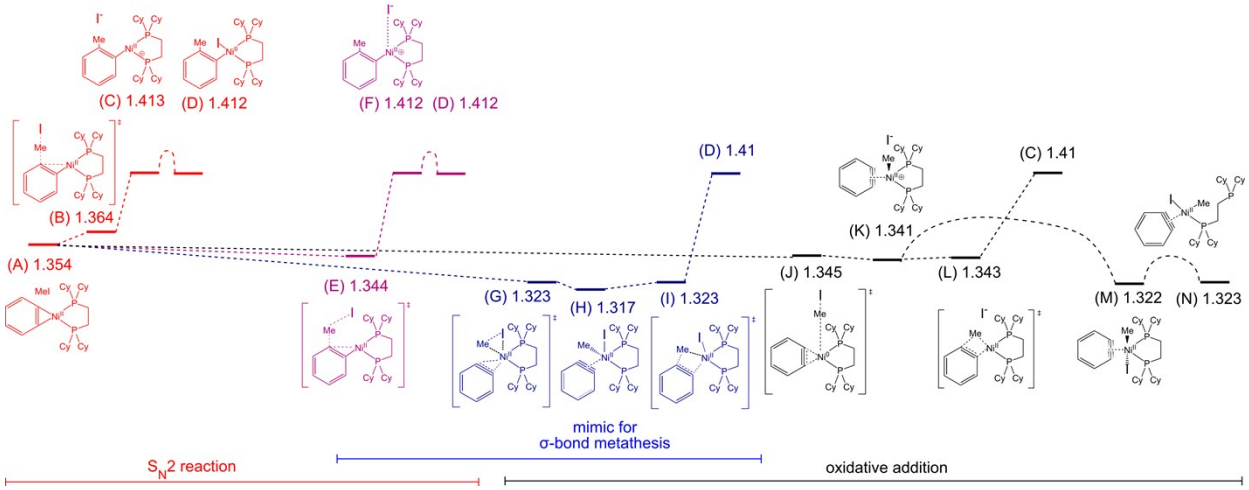


Figure S7. DFT optimized structures and the distance (d_{CC}) of two carbon atoms which form a C≡C triple bond in a benzyne monomer. The transition states are labeled by double dagger. The structures (A–N, Figure 2) correspond to the following states; (A) initial state, (B) transition state (TS) of S_N2 reaction, (C) intermediate state of S_N2 reaction, (D) final state, (E) TS state of mimic for σ-bond metathesis, (F) intermediate state of mimic for σ-bond metathesis, (G) TS state of mimic for σ-bond metathesis, (H) intermediate state of mimic for σ-bond metathesis (I) TS state from σ-bond metathesis to final state, (J) TS state of oxidative addition, (K) intermediate state of oxidative addition, (L) TS state from oxidative addition to S_N2 reaction, (M) intermediate state of oxidative addition and (N) intermediate state of oxidative addition.

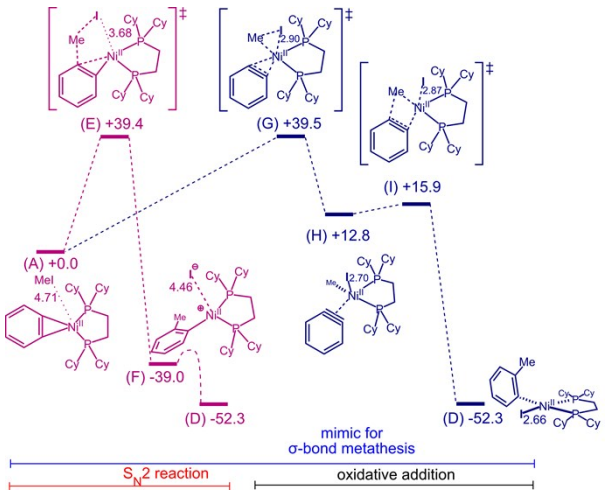


Figure S8. Gibbs free energies [kcal/mol] and I–Ni^{II} distances [Å] mimicking σ-bond metathesis.

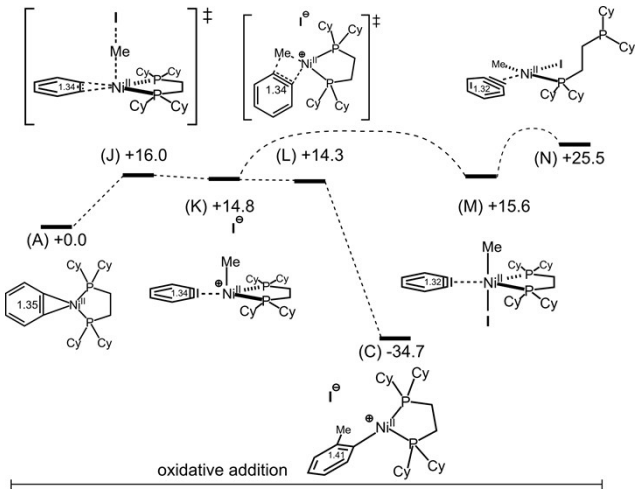


Figure S9. Gibbs free energies [kcal/mol] and d_{CC} distances [Å] for oxidative addition.

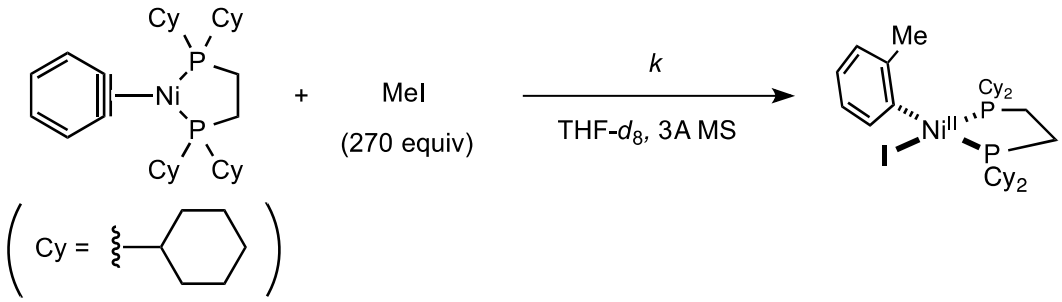


Figure S10. Schematic representation of sample preparation.

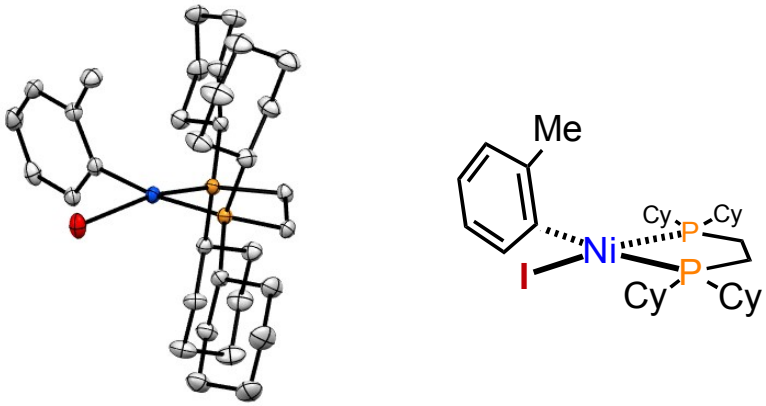


Figure S11. ORTEP diagram of the X-ray structure of ***o*-tolyl(dcpe)Ni complex**. Ellipsoids are drawn at 50% probability; hydrogen atoms are omitted for clarity.

Table S1. Coordinates of the benzyne–Ni complex in the state (A) (see the text for the detail).

C	0.148469	-3.665826	-0.358458
H	0.429071	-4.714005	-0.429758
H	1.005613	-3.001708	-0.401140
H	-0.599883	-3.378455	-1.090963
I	-0.759840	-3.385577	1.615475
C	-0.852670	-0.584296	-1.830139
C	0.458395	-0.724247	-2.137164
C	0.914473	-1.631492	-3.091007
C	-0.067124	-2.412379	-3.727251
C	-1.427868	-2.271210	-3.404518
C	-1.852361	-1.342317	-2.436052
H	1.966652	-1.762682	-3.345433
H	0.225666	-3.143609	-4.478630
H	-2.160472	-2.895821	-3.912649
H	-2.910206	-1.253116	-2.188865
Ni	0.213394	0.558972	-0.779237
P	-0.920033	1.834561	0.617677
P	2.116466	1.351436	0.015473
C	0.304172	2.485401	1.879976
H	-0.052279	3.418734	2.332014
H	0.339815	1.738698	2.675196
C	1.719126	2.665968	1.294121
H	1.789632	3.633724	0.796920
H	2.469303	2.666371	2.093612
C	-2.371557	1.184670	1.616152
C	-3.110739	0.096148	0.810654
C	-1.977922	0.635327	2.999888
C	-4.340246	-0.427992	1.563428
C	-3.204284	0.100061	3.755535
C	-3.958782	-0.961760	2.948629
H	-3.050892	2.035960	1.771388
H	-2.412522	-0.724733	0.618174
H	-3.404161	0.474676	-0.172352
H	-1.244119	-0.173293	2.874751
H	-1.501734	1.414314	3.603981
H	-4.824909	-1.214855	0.971908
H	-5.075809	0.382739	1.674483
H	-2.888861	-0.306729	4.724588
H	-3.881618	0.939345	3.971536
H	-4.852174	-1.289404	3.494804
H	-3.317802	-1.844938	2.826188
C	-1.617488	3.376014	-0.178661
C	-0.521333	4.118185	-0.967738
C	-2.805676	3.027814	-1.095782
C	-2.228946	4.953216	-2.642183
C	-3.336966	4.257952	-1.844577
C	-1.066964	5.338067	-1.721459
H	-1.976766	4.029676	0.630772
H	-0.068273	3.418527	-1.684053
H	0.276031	4.440791	-0.291889
H	-2.481920	2.267896	-1.820016
H	-3.616959	2.583490	-0.510288
H	-0.256867	5.805079	-2.295488

H	-1.413167	6.087712	-0.995183
H	-4.157442	3.956224	-2.507282
H	-3.760467	4.968457	-1.119713
H	-2.622801	5.840109	-3.153570
H	-1.861778	4.271221	-3.422908
C	3.079121	0.075959	0.976883
C	2.206999	-0.537972	2.086016
C	3.608600	-1.016060	0.029345
C	2.935355	-1.658484	2.839818
C	4.340051	-2.126990	0.793750
C	3.451426	-2.738600	1.882464
H	3.935449	0.592376	1.436896
H	1.291807	-0.940707	1.634103
H	1.894907	0.236443	2.795648
H	2.760535	-1.436729	-0.526987
H	4.282894	-0.578608	-0.715113
H	2.257282	-2.098804	3.580989
H	3.782700	-1.231060	3.395445
H	4.672985	-2.900748	0.090739
H	5.246007	-1.710369	1.257713
H	4.001814	-3.507976	2.437974
H	2.594378	-3.241135	1.413983
C	3.431969	2.076789	-1.114563
C	3.261697	1.492540	-2.531352
C	3.450986	3.614043	-1.169332
C	4.346675	2.001594	-3.487484
C	4.531653	4.124341	-2.134630
C	4.365429	3.533918	-3.539243
H	4.400269	1.745006	-0.712829
H	2.270770	1.776910	-2.907601
H	3.260148	0.399183	-2.495444
H	2.469203	3.981163	-1.498858
H	3.632178	4.031447	-0.173228
H	4.181730	1.585885	-4.489257
H	5.328698	1.637361	-3.151488
H	4.503281	5.220432	-2.171881
H	5.520326	3.847070	-1.741096
H	5.168681	3.887137	-4.197591
H	3.419673	3.891271	-3.972049

Table S2. Coordinates of the benzyne–Ni complex in the state (B) (see the text for the detail).

C	-1.23940000	-2.05140000	-0.66940000
H	-0.78690000	-2.71020000	-1.38850000
H	-0.63300000	-1.61510000	0.10730000
H	-2.28720000	-1.81090000	-0.72890000
I	-1.76630000	-4.18970000	0.90920000
C	-0.84590000	-0.50590000	-2.36160000
C	0.49050000	-0.33710000	-2.56560000
C	1.11260000	-0.60010000	-3.78410000
C	0.27220000	-0.99770000	-4.83780000
C	-1.11480000	-1.13550000	-4.65120000
C	-1.70050000	-0.89850000	-3.40090000
H	2.18090000	-0.48030000	-3.95440000
H	0.69700000	-1.18630000	-5.82170000
H	-1.73670000	-1.44150000	-5.48980000
H	-2.76930000	-1.05600000	-3.26020000
Ni	0.06190000	0.46060000	-0.93300000
P	-1.18830000	1.76150000	0.48620000
P	1.94330000	1.26360000	-0.04050000
C	0.05260000	2.58270000	1.63300000
H	-0.32790000	3.54820000	1.98600000
H	0.12210000	1.93590000	2.51180000
C	1.44480000	2.74360000	0.99900000
H	1.44900000	3.60160000	0.31960000
H	2.20070000	2.95000000	1.76610000
C	-2.49130000	1.21880000	1.74230000
C	-3.85470000	0.85640000	1.11580000
C	-1.99290000	0.05950000	2.63230000
C	-4.88540000	0.48010000	2.19640000
C	-3.02320000	-0.30320000	3.71630000
C	-4.38410000	-0.65350000	3.10030000
H	-2.64070000	2.10360000	2.38150000
H	-3.72950000	0.01040000	0.42480000
H	-4.24550000	1.69260000	0.52730000
H	-1.80920000	-0.82530000	2.00910000
H	-1.04010000	0.31170000	3.11150000

H	-5.83030000	0.19800000	1.71520000
H	-5.09850000	1.36780000	2.81020000
H	-2.64520000	-1.14320000	4.31180000
H	-3.13940000	0.54670000	4.40500000
H	-5.11770000	-0.86170000	3.88940000
H	-4.28520000	-1.57520000	2.50980000
C	-2.04850000	3.18630000	-0.41370000
C	-1.11440000	4.36840000	-0.75010000
C	-2.74120000	2.69490000	-1.70470000
C	-2.60180000	5.02350000	-2.71060000
C	-3.51330000	3.82830000	-2.40060000
C	-1.88160000	5.50750000	-1.44490000
H	-2.81610000	3.55560000	0.28360000
H	-0.31330000	4.01810000	-1.41560000
H	-0.63530000	4.75960000	0.15400000
H	-1.97320000	2.29870000	-2.38130000
H	-3.41800000	1.86000000	-1.49490000
H	-1.18650000	6.32170000	-1.68640000
H	-2.61920000	5.92250000	-0.74240000
H	-3.97130000	3.44760000	-3.32230000
H	-4.33910000	4.15760000	-1.75260000
H	-3.18160000	5.84260000	-3.15440000
H	-1.85480000	4.72350000	-3.46020000
C	2.89900000	0.11870000	1.11620000
C	2.31770000	0.05000000	2.54480000
C	3.00010000	-1.30760000	0.52900000
C	3.16000000	-0.87180000	3.44540000
C	3.84490000	-2.22940000	1.42410000
C	3.29320000	-2.28230000	2.85510000
H	3.91090000	0.54600000	1.18760000
H	1.28930000	-0.33530000	2.50240000
H	2.27110000	1.04730000	2.99580000
H	1.98630000	-1.71990000	0.43800000
H	3.41550000	-1.28800000	-0.48330000
H	2.70910000	-0.91550000	4.44490000
H	4.16060000	-0.43250000	3.57070000
H	3.87440000	-3.23570000	0.98790000

H	4.88240000	-1.86420000	1.44470000
H	3.93890000	-2.90050000	3.49140000
H	2.30570000	-2.76570000	2.84340000
C	3.27480000	2.03990000	-1.12630000
C	4.26360000	1.02720000	-1.74010000
C	2.64260000	2.91050000	-2.23440000
C	5.32870000	1.72950000	-2.60130000
C	3.71290000	3.61050000	-3.08940000
C	4.69760000	2.60120000	-3.69470000
H	3.84340000	2.69690000	-0.44920000
H	3.71300000	0.30760000	-2.36040000
H	4.76500000	0.45220000	-0.95460000
H	2.02240000	2.27020000	-2.87510000
H	1.97340000	3.66370000	-1.80240000
H	5.99200000	0.97660000	-3.04510000
H	5.95670000	2.35850000	-1.95320000
H	3.22480000	4.19240000	-3.88140000
H	4.26490000	4.32880000	-2.46570000
H	5.47780000	3.12290000	-4.26320000
H	4.16360000	1.95800000	-4.40950000

Table S3. Coordinates of the benzyne–Ni complex in the state (C) (see the text for the detail).

C	-0.28950000	-2.75740000	-0.31620000
H	0.26560000	-3.65040000	-0.00470000
H	-0.07980000	-1.96590000	0.41100000
H	-1.35630000	-3.00350000	-0.24020000
I	0.29250000	-1.84360000	5.89530000
C	0.08110000	-2.34260000	-1.72740000
C	0.46570000	-1.02320000	-2.06020000
C	0.80140000	-0.71410000	-3.39050000
C	0.72140000	-1.67940000	-4.39760000
C	0.32720000	-2.98000000	-4.07270000
C	0.00960000	-3.30080000	-2.75320000
H	1.11300000	0.29200000	-3.65490000
H	0.97110000	-1.42020000	-5.42350000
H	0.27340000	-3.74420000	-4.84350000
H	-0.29370000	-4.31660000	-2.50530000
Ni	-0.08550000	0.30670000	-0.86080000
P	-1.14630000	1.78790000	0.58070000
P	1.90290000	0.95430000	-0.18730000
C	0.21340000	2.17980000	1.79030000
H	0.00190000	3.07700000	2.38040000
H	0.25240000	1.33890000	2.48900000
C	1.55930000	2.32020000	1.06090000
H	1.58480000	3.25790000	0.49840000
H	2.38800000	2.36370000	1.77650000
C	-2.59050000	1.13270000	1.58120000
C	-3.73790000	0.71910000	0.62980000
C	-2.21150000	-0.03670000	2.51200000
C	-4.95760000	0.19690000	1.40810000
C	-3.43790000	-0.55710000	3.28210000
C	-4.57810000	-0.96210000	2.33940000
H	-2.93660000	1.97310000	2.20150000
H	-3.37560000	-0.07180000	-0.04430000
H	-4.04190000	1.55930000	-0.00580000
H	-1.78130000	-0.85610000	1.91820000
H	-1.44560000	0.26530000	3.23280000
H	-5.73500000	-0.11500000	0.69940000

H	-5.38380000	1.01880000	2.00160000
H	-3.13230000	-1.40020000	3.91220000
H	-3.79180000	0.23000000	3.96360000
H	-5.45250000	-1.28650000	2.91700000
H	-4.26290000	-1.82540000	1.73470000
C	-1.84170000	3.39390000	-0.13890000
C	-1.07250000	4.67980000	0.22650000
C	-2.01330000	3.27340000	-1.67040000
C	-1.94440000	5.80490000	-1.88400000
C	-2.69520000	4.51940000	-2.25970000
C	-1.76810000	5.92000000	-0.36320000
H	-2.84260000	3.48180000	0.30700000
H	-0.04820000	4.63170000	-0.16700000
H	-0.99330000	4.78710000	1.31400000
H	-1.02490000	3.14390000	-2.13320000
H	-2.59410000	2.37630000	-1.92060000
H	-1.18870000	6.81670000	-0.11090000
H	-2.75320000	6.03850000	0.11040000
H	-2.76450000	4.41980000	-3.35000000
H	-3.72670000	4.57710000	-1.88300000
H	-2.47750000	6.68220000	-2.27050000
H	-0.95510000	5.80150000	-2.36490000
C	3.03970000	-0.24620000	0.70550000
C	2.58140000	-0.55550000	2.14810000
C	3.28540000	-1.56370000	-0.06160000
C	3.61620000	-1.43500000	2.87330000
C	4.32930000	-2.43340000	0.66070000
C	3.90910000	-2.73020000	2.10620000
H	3.99050000	0.30770000	0.76400000
H	1.61420000	-1.07520000	2.12570000
H	2.43380000	0.36300000	2.72480000
H	2.34220000	-2.11520000	-0.12950000
H	3.60590000	-1.37440000	-1.08930000
H	3.24600000	-1.65900000	3.87970000
H	4.54790000	-0.86260000	2.99300000
H	4.47040000	-3.36640000	0.10090000
H	5.29970000	-1.91520000	0.65770000

H	4.68930000	-3.30550000	2.61990000
H	3.00740000	-3.35910000	2.10030000
C	2.99500000	1.89800000	-1.40010000
C	3.95630000	1.04560000	-2.25250000
C	2.15720000	2.84630000	-2.28510000
C	4.83660000	1.93610000	-3.14960000
C	3.05250000	3.72440000	-3.17570000
C	4.00090000	2.87370000	-4.03000000
H	3.61270000	2.51680000	-0.72950000
H	3.38550000	0.34740000	-2.87720000
H	4.60360000	0.44460000	-1.60690000
H	1.48710000	2.25260000	-2.91990000
H	1.51450000	3.48690000	-1.67090000
H	5.47910000	1.29790000	-3.76820000
H	5.50620000	2.53470000	-2.51500000
H	2.42220000	4.35740000	-3.81220000
H	3.64070000	4.40220000	-2.54030000
H	4.65710000	3.51920000	-4.62630000
H	3.41240000	2.27730000	-4.74250000

Table S4. Coordinates of the benzyne–Ni complex in the state (D) (see the text for the detail).

C	-0.17570000	-2.91820000	-0.32350000
H	0.07510000	-3.92910000	0.01850000
H	0.09200000	-2.21320000	0.47240000
H	-1.26630000	-2.86250000	-0.43800000
I	-2.50050000	-0.39580000	-2.42810000
C	0.51680000	-2.58390000	-1.62730000
C	0.58920000	-1.25640000	-2.10730000
C	1.18030000	-1.03750000	-3.36000000
C	1.70590000	-2.08600000	-4.12570000
C	1.64850000	-3.39150000	-3.63880000
C	1.05170000	-3.62800000	-2.39830000
H	1.22060000	-0.03240000	-3.77150000
H	2.15470000	-1.87880000	-5.09520000
H	2.05600000	-4.21760000	-4.21660000
H	0.99270000	-4.64710000	-2.01810000
Ni	-0.24550000	0.17640000	-1.10720000
P	-1.28780000	1.73150000	0.38580000
P	1.76680000	0.84720000	-0.27780000
C	0.06240000	2.10150000	1.62620000
H	-0.17470000	2.99330000	2.21800000
H	0.08340000	1.25860000	2.32480000
C	1.41790000	2.24680000	0.92870000
H	1.43950000	3.17140000	0.34450000
H	2.23700000	2.31700000	1.65400000
C	-2.60940000	1.05000000	1.55300000
C	-4.05880000	1.14110000	1.03170000
C	-2.28360000	-0.40070000	1.96770000
C	-5.05740000	0.61550000	2.07880000
C	-3.28220000	-0.92480000	3.01390000
C	-4.72890000	-0.81980000	2.51180000
H	-2.53510000	1.69040000	2.44690000
H	-4.15060000	0.55470000	0.10960000
H	-4.31670000	2.17590000	0.78090000
H	-2.31920000	-1.03870000	1.07600000
H	-1.26450000	-0.47480000	2.36680000
H	-6.07460000	0.66810000	1.67040000

H	-5.03850000	1.27390000	2.96020000
H	-3.03840000	-1.96480000	3.26590000
H	-3.17500000	-0.34250000	3.94110000
H	-5.42730000	-1.15250000	3.29020000
H	-4.86430000	-1.49660000	1.65580000
C	-1.97780000	3.43730000	-0.07670000
C	-0.93610000	4.57550000	-0.12720000
C	-2.76790000	3.40130000	-1.40230000
C	-2.43400000	5.90450000	-1.69970000
C	-3.44660000	4.75130000	-1.68910000
C	-1.61470000	5.93010000	-0.40250000
H	-2.67590000	3.67810000	0.73920000
H	-0.21020000	4.37640000	-0.92720000
H	-0.37430000	4.64230000	0.81040000
H	-2.07500000	3.15870000	-2.21900000
H	-3.51190000	2.60020000	-1.39280000
H	-0.85210000	6.71810000	-0.44560000
H	-2.27450000	6.17740000	0.44210000
H	-3.97570000	4.69820000	-2.64890000
H	-4.21030000	4.94350000	-0.92070000
H	-2.94680000	6.86390000	-1.84370000
H	-1.75290000	5.78030000	-2.55450000
C	2.94500000	-0.24290000	0.72580000
C	2.41070000	-0.55970000	2.14180000
C	3.37680000	-1.55640000	0.03900000
C	3.46560000	-1.30480000	2.98070000
C	4.45340000	-2.27970000	0.86660000
C	3.95950000	-2.58170000	2.28780000
H	3.83540000	0.39590000	0.84290000
H	1.50780000	-1.18060000	2.05870000
H	2.12280000	0.35330000	2.67250000
H	2.50600000	-2.20910000	-0.06550000
H	3.74480000	-1.37770000	-0.97380000
H	3.04530000	-1.54040000	3.96660000
H	4.31850000	-0.63280000	3.15580000
H	4.74070000	-3.20790000	0.35700000
H	5.35820000	-1.65590000	0.91750000

H	4.75570000	-3.04990000	2.88030000
H	3.13610000	-3.30890000	2.23690000
C	2.89720000	1.79640000	-1.46810000
C	3.97780000	0.98520000	-2.21100000
C	2.05060000	2.62680000	-2.45770000
C	4.84140000	1.89750000	-3.10300000
C	2.92830000	3.52820000	-3.34180000
C	3.99410000	2.71450000	-4.08720000
H	3.42470000	2.49740000	-0.80200000
H	3.50800000	0.20900000	-2.82570000
H	4.62940000	0.47790000	-1.49280000
H	1.46920000	1.94890000	-3.09370000
H	1.32130000	3.24310000	-1.92040000
H	5.57420000	1.28470000	-3.64280000
H	5.41650000	2.58540000	-2.46560000
H	2.29330000	4.07340000	-4.05130000
H	3.42050000	4.28450000	-2.71290000
H	4.63530000	3.37850000	-4.68040000
H	3.50070000	2.03490000	-4.79720000

Table S5. Coordinates of the benzyne–Ni complex in the state (E) (see the text for the detail).

C	-2.23749217	-0.90184707	-1.47283011
H	-2.30189218	0.15967501	-1.62165812
H	-2.33815118	-1.53103512	-2.34400618
H	-2.58929820	-1.28782810	-0.52855604
I	-0.28721802	-2.93896522	-0.66224905
C	-0.24947702	0.18274301	-2.97628423
C	1.08060408	0.11270001	-2.79579621
C	1.96476915	-0.11755001	-3.84594529
C	1.38275811	-0.28407802	-5.11581339
C	-0.00758000	-0.21224002	-5.29558542
C	-0.86893207	0.01997700	-4.20721632
H	3.04532823	-0.16896001	-3.72493128
H	2.01923816	-0.47273304	-5.97762245
H	-0.42356503	-0.34317603	-6.29230951
H	-1.94795715	0.06127400	-4.35539233
Ni	0.40252303	0.64259705	-1.11491608
P	-0.76022006	1.85179714	0.38256903
P	2.26092317	1.14774509	-0.06209400
C	0.44729803	2.50540919	1.65112112
H	0.13217501	3.49418127	2.00117915
H	0.38592303	1.83131514	2.50974019
C	1.89203314	2.54769619	1.12234409
H	2.05759116	3.47216327	0.56236204
H	2.60858420	2.54401520	1.95067015
C	-2.15332716	1.16675109	1.40980011
C	-1.71059913	-0.11712101	2.13727016
C	-2.78117921	2.16800417	2.39574918
C	-2.88551622	-0.75496406	2.89039122
C	-3.94936230	1.52461312	3.15965124
C	-3.51962027	0.23664102	3.87370330
H	-2.92387022	0.88281507	0.68047705
H	-0.92000507	0.12510701	2.85990522
H	-1.27749510	-0.82764307	1.42666911
H	-2.01839516	2.49967419	3.11316124
H	-3.13387124	3.06198123	1.87009914
H	-2.54265619	-1.65422813	3.41585126

H	-3.64349528	-1.08321708	2.16441717
H	-4.36149433	2.24310617	3.87878430
H	-4.75447836	1.29228210	2.44791819
H	-4.37896933	-0.22128902	4.37842233
H	-2.78771621	0.48452304	4.65614835
C	-1.47063611	3.36966626	-0.43125703
C	-0.36189703	4.16710132	-1.14397409
C	-2.57173420	2.96335522	-1.42867511
C	-2.01921415	4.94885438	-2.89573322
C	-3.13387724	4.17745132	-2.17977517
C	-0.92820107	5.37283641	-1.90575515
H	-1.90977015	4.00629731	0.34873003
H	0.15840001	3.50232327	-1.84525914
H	0.38322803	4.50958734	-0.41753603
H	-2.13727316	2.26240817	-2.15526316
H	-3.38465826	2.43824319	-0.91307407
H	-0.11458301	5.89062645	-2.42833119
H	-1.35016410	6.08961747	-1.18650409
H	-3.89434630	3.84643629	-2.89742822
H	-3.63902228	4.84425337	-1.46631711
H	-2.43033518	5.82649245	-3.40904326
H	-1.57560212	4.30523433	-3.66914628
C	3.03737423	-0.17224601	0.99043107
C	2.02463516	-0.69939305	2.02215916
C	3.58445628	-1.32040410	0.12262601
C	2.62836020	-1.81963414	2.88043222
C	4.19014732	-2.43123518	0.99303108
C	3.17275424	-2.95922323	2.01107915
H	3.87320730	0.29531302	1.53053312
H	1.14642109	-1.08127508	1.48972511
H	1.68533513	0.11516001	2.67197320
H	2.76389021	-1.73478313	-0.47493004
H	4.33971533	-0.94462307	-0.57729605
H	1.86810014	-2.19689917	3.57557227
H	3.44336527	-1.40760111	3.49378427
H	4.54712335	-3.24575425	0.35102203
H	5.06896639	-2.03781316	1.52532611

H	3.63004028	-3.73263828	2.64068020
H	2.33916718	-3.43001426	1.47329711
C	3.63988628	1.79728414	-1.12625009
C	3.13923224	2.90500722	-2.07177116
C	4.88405637	2.25794717	-0.34704803
C	4.25205132	3.35215326	-3.02850523
C	5.99299447	2.71686821	-1.30672610
C	5.49848341	3.81053529	-2.26119617
H	3.91995030	0.93899007	-1.75177914
H	2.80631521	3.77225029	-1.48534111
H	2.27387917	2.54433719	-2.63463220
H	4.61034735	3.08962523	0.31683902
H	5.26040540	1.45181811	0.29173802
H	3.88290230	4.15662232	-3.67639028
H	4.51555735	2.51160419	-3.68640128
H	6.85721855	3.07104123	-0.73150905
H	6.33572950	1.85193014	-1.89252915
H	6.29547446	4.09269231	-2.95991123
H	5.25248740	4.71154836	-1.68033013

Table S6. Coordinates of the benzyne–Ni complex in the state (F) (see the text for the detail).

C	-2.09453400	-0.79505600	-1.88377800
H	-2.88398100	-0.33199400	-2.48507800
H	-2.43744400	-1.75813300	-1.49097700
H	-2.01872600	-0.14992500	-0.98196400
I	-1.40397300	-3.86658100	0.60454900
C	-0.80676100	-0.96862300	-2.67253700
C	0.42141300	-0.60827500	-2.08958200
C	1.59795900	-0.86098700	-2.80319000
C	1.55659400	-1.43507500	-4.07639000
C	0.32985400	-1.76408700	-4.65769600
C	-0.85035000	-1.53082900	-3.95334200
H	2.56882200	-0.62776200	-2.38542500
H	2.48279200	-1.62508100	-4.61268300
H	0.29367300	-2.20590300	-5.64953000
H	-1.81217800	-1.79534000	-4.38888800
Ni	-0.19594800	0.27166100	-0.53626800
P	-1.24764100	1.53587700	1.05687300
P	1.70610700	0.75097500	0.37145500
C	0.03627400	2.06974800	2.28347600
H	-0.21016200	3.05160900	2.69998400
H	0.00004400	1.35405600	3.10751800
C	1.43567400	2.08529200	1.65194600
H	1.60149700	3.03408600	1.13457000
H	2.21236200	2.00185500	2.41930400
C	-2.63995100	0.81239700	2.04606100
C	-2.19316900	-0.47358800	2.76605700
C	-3.29282000	1.80383700	3.02677900
C	-3.37226400	-1.12326700	3.50124400
C	-4.46411300	1.14171000	3.76931800
C	-4.02989700	-0.14536600	4.48199700
H	-3.38756000	0.52334500	1.29406900
H	-1.41073900	-0.23418800	3.49899400
H	-1.76624000	-1.18490200	2.05268900
H	-2.54298400	2.13944100	3.75638800
H	-3.64936300	2.69654600	2.50135100
H	-3.02401500	-2.02242300	4.02213600

H	-4.11257900	-1.45717500	2.76106100
H	-4.89425600	1.85303000	4.48485700
H	-5.25488800	0.90484100	3.04346500
H	-4.89207900	-0.61484300	4.97091100
H	-3.31318000	0.10642900	5.27730800
C	-1.91931400	3.09268900	0.29639600
C	-0.81924500	3.84532500	-0.47520800
C	-3.10824700	2.76646200	-0.62900300
C	-2.55332500	4.76556000	-2.07973600
C	-3.65345200	4.03200500	-1.30398700
C	-1.37052200	5.10080600	-1.16417900
H	-2.27143700	3.73518600	1.11417100
H	-0.38792200	3.17460300	-1.22958200
H	-0.00605200	4.12955200	0.20096100
H	-2.77663900	2.06323200	-1.40477700
H	-3.90734600	2.26793700	-0.06945200
H	-0.56846400	5.58664200	-1.73266600
H	-1.69583700	5.81794000	-0.39733700
H	-4.48167600	3.76383100	-1.97033900
H	-4.06664000	4.70054200	-0.53561300
H	-2.95227000	5.67950500	-2.53533100
H	-2.20407500	4.12581400	-2.90322500
C	2.44582600	-0.67719900	1.29173000
C	1.43612600	-1.25628000	2.29809000
C	2.96113500	-1.77450100	0.34345800
C	2.04136600	-2.42857400	3.08209400
C	3.57298500	-2.93624400	1.13979200
C	2.56474800	-3.51622800	2.13744000
H	3.29773400	-0.25670700	1.84605500
H	0.55579500	-1.61200400	1.75097800
H	1.10285000	-0.48280300	2.99787400
H	2.12420600	-2.14627700	-0.25871900
H	3.70615800	-1.36833500	-0.35015400
H	1.27870300	-2.84125900	3.75276800
H	2.86149200	-2.05992600	3.71598200
H	3.91341400	-3.71175700	0.44341700
H	4.46324900	-2.57778500	1.67758300

H	3.02377700	-4.32992100	2.71227500
H	1.71538700	-3.94160600	1.58763300
C	3.04989600	1.45275300	-0.69225800
C	2.50019800	2.51208000	-1.66317100
C	4.24961600	1.99045200	0.11247500
C	3.60574400	3.01325900	-2.60167100
C	5.34788100	2.48283000	-0.84286700
C	4.81249000	3.54108700	-1.81500000
H	3.41293500	0.61100300	-1.28838500
H	2.09883300	3.36083300	-1.09404700
H	1.67048000	2.08851400	-2.23851400
H	3.92980000	2.82410600	0.74969700
H	4.65037400	1.21473000	0.77403400
H	3.20503600	3.79317700	-3.25986400
H	3.92469300	2.18443500	-3.24919500
H	6.18560100	2.88460000	-0.26075800
H	5.73760200	1.62715200	-1.41188600
H	5.60503400	3.85798000	-2.50307100
H	4.51084000	4.43255100	-1.24607000

Table S7. Coordinates of the benzyne–Ni complex in the state (G) (see the text for the detail).

C	0	-1.90019200	-1.03267900	-1.55200000
H	0	-1.45783700	-1.36963500	-2.48074600
H	0	-2.21943100	-0.00167000	-1.55111200
H	0	-2.61275700	-1.71318800	-1.10292400
I	0	-0.17054700	-2.04054000	0.09499900
C	0	0.82377900	0.10364400	-2.64643200
C	0	-0.05925000	1.09504600	-2.78013200
C	0	-0.28638900	1.72427300	-3.99707100
C	0	0.50400200	1.27648800	-5.07897800
C	0	1.43151000	0.23966400	-4.92089800
C	0	1.61225000	-0.39299700	-3.67032800
H	0	-1.00176400	2.53175000	-4.14310800
H	0	0.39303000	1.74732600	-6.05380200
H	0	2.02037100	-0.08473200	-5.77628400
H	0	2.33330000	-1.19933700	-3.55238500
Ni	0	0.10523600	0.45977700	-0.92122700
P	0	-1.04350500	1.84398600	0.50836900
P	0	2.12351600	1.32641000	-0.03442300
C	0	0.22058800	2.74536300	1.55407500
H	0	-0.16947400	3.73096800	1.83361100
H	0	0.30934400	2.17408500	2.47837400
C	0	1.59764600	2.86433000	0.89652900
H	0	1.58808400	3.66792300	0.15704200
H	0	2.35989300	3.12998600	1.63863700
C	0	-2.22650500	1.32240200	1.87990300
C	0	-3.55709600	0.75206200	1.35559200
C	0	-1.57683100	0.32539500	2.86058300
C	0	-4.50223000	0.35658200	2.49999200
C	0	-2.52883700	-0.05187600	4.00400500
C	0	-3.84250500	-0.62921400	3.46839200
H	0	-2.44808800	2.25189900	2.42807500
H	0	-3.35295700	-0.12808500	0.73240900
H	0	-4.06316900	1.48478500	0.72271400
H	0	-1.29293500	-0.57777900	2.31210500
H	0	-0.65545700	0.73287300	3.28695600
H	0	-5.42265900	-0.06905400	2.08158300

H	0	-4.79477300	1.26267300	3.05033400
H	0	-2.03338300	-0.77243900	4.66639200
H	0	-2.74430200	0.83989000	4.61078500
H	0	-4.52366300	-0.86884300	4.29418400
H	0	-3.63508700	-1.57188600	2.94179700
C	0	-1.96845400	3.23393900	-0.34947500
C	0	-0.99111300	4.26773600	-0.94181700
C	0	-2.88608800	2.70639600	-1.47081100
C	0	-2.67171200	4.88829300	-2.74239100
C	0	-3.63896500	3.84530500	-2.17316400
C	0	-1.73228500	5.41078600	-1.65074600
H	0	-2.58160400	3.72963300	0.41896900
H	0	-0.33363700	3.75447000	-1.65550400
H	0	-0.35461100	4.69086600	-0.15886400
H	0	-2.25982400	2.17634200	-2.19561500
H	0	-3.60683400	1.97910800	-1.08816600
H	0	-1.00336400	6.11271300	-2.07468200
H	0	-2.31769400	5.97237000	-0.90840500
H	0	-4.26907900	3.43202200	-2.97040300
H	0	-4.31539500	4.33098300	-1.45478900
H	0	-3.22615500	5.71770900	-3.19857200
H	0	-2.07398100	4.42927900	-3.54224500
C	0	3.17571200	0.39066500	1.20453400
C	0	2.46054900	0.27148100	2.56515900
C	0	3.52238500	-1.01734100	0.67699700
C	0	3.29336900	-0.53119200	3.57524400
C	0	4.36820000	-1.80586300	1.68496000
C	0	3.65310700	-1.91967200	3.03576100
H	0	4.10575900	0.96261900	1.35262900
H	0	1.49262500	-0.22500400	2.41925300
H	0	2.25582700	1.26411100	2.97929600
H	0	2.58826400	-1.55489100	0.48968100
H	0	4.04091600	-0.96400500	-0.28232500
H	0	2.74232500	-0.61562800	4.52030100
H	0	4.21840800	0.02118600	3.79629700
H	0	4.58726800	-2.80253800	1.28215900
H	0	5.33574300	-1.30142300	1.82622700

H	0	4.27668100	-2.46012900	3.75873500
H	0	2.73243400	-2.50689500	2.90598800
C	0	3.39940000	2.14362200	-1.15674500
C	0	4.41420000	1.16435800	-1.77180000
C	0	2.72674800	2.98298900	-2.26128800
C	0	5.42609000	1.88225000	-2.67786100
C	0	3.75982400	3.70950000	-3.13244200
C	0	4.73498300	2.71104200	-3.76460100
H	0	3.95434300	2.82750900	-0.49406300
H	0	3.87609500	0.40584900	-2.35327300
H	0	4.96338700	0.64380300	-0.98267800
H	0	2.13112500	2.32619400	-2.89682500
H	0	2.03141000	3.71063900	-1.82926600
H	0	6.10189300	1.14307900	-3.12597100
H	0	6.04951300	2.54684800	-2.06155200
H	0	3.24058800	4.28459800	-3.90935800
H	0	4.32128900	4.43272300	-2.52255100
H	0	5.47920400	3.23286900	-4.37918900
H	0	4.17648000	2.04133000	-4.43412700

Table S8. Coordinates of the benzyne–Ni complex in the state (H) (see the text for the detail).

C	-1.77390000	-0.41650000	-1.60680000
H	-1.55080000	-1.23710000	-2.28350000
H	-2.29970000	0.38660000	-2.11550000
H	-2.30660000	-0.77270000	-0.72780000
I	0.43140000	-2.24120000	-0.07050000
C	0.62760000	0.00210000	-2.84570000
C	0.22910000	1.24970000	-2.70660000
C	0.23100000	2.18230000	-3.72910000
C	0.71460000	1.68090000	-4.95960000
C	1.11680000	0.34570000	-5.10540000
C	1.07120000	-0.56370000	-4.02460000
H	-0.09550000	3.21410000	-3.63400000
H	0.76700000	2.34750000	-5.81700000
H	1.47330000	0.00330000	-6.07380000
H	1.38280000	-1.59830000	-4.13560000
Ni	0.01440000	0.25880000	-1.01750000
P	-1.06000000	1.66240000	0.49410000
P	2.11660000	1.19310000	-0.07330000
C	0.20680000	2.35880000	1.66410000
H	-0.18470000	3.27290000	2.12600000
H	0.30930000	1.62070000	2.46270000
C	1.55780000	2.61950000	0.99530000
H	1.48000000	3.49470000	0.35280000
H	2.32530000	2.84350000	1.74580000
C	-2.31260000	1.05780000	1.75070000
C	-3.76520000	0.96500000	1.24930000
C	-1.86500000	-0.27810000	2.37010000
C	-4.70500000	0.52660000	2.38290000
C	-2.80720000	-0.70670000	3.50240000
C	-4.25720000	-0.79760000	3.01220000
H	-2.29060000	1.82920000	2.53690000
H	-3.83220000	0.24500000	0.42500000
H	-4.10030000	1.93100000	0.85960000
H	-1.84910000	-1.04760000	1.59150000
H	-0.83730000	-0.21100000	2.74400000
H	-5.72870000	0.44390000	1.99820000

H	-4.71950000	1.30850000	3.15620000
H	-2.47810000	-1.67070000	3.90840000
H	-2.74570000	0.02220000	4.32380000
H	-4.92490000	-1.07130000	3.83820000
H	-4.33390000	-1.59810000	2.26250000
C	-1.87390000	3.19580000	-0.22640000
C	-0.86070000	4.29890000	-0.58490000
C	-2.75760000	2.88240000	-1.44830000
C	-2.46590000	5.23470000	-2.32720000
C	-3.47260000	4.13870000	-1.96280000
C	-1.55800000	5.55210000	-1.13550000
H	-2.51400000	3.58120000	0.58200000
H	-0.15230000	3.91000000	-1.32730000
H	-0.27940000	4.58750000	0.29480000
H	-2.12270000	2.48160000	-2.24530000
H	-3.49110000	2.10830000	-1.21010000
H	-0.80110000	6.29560000	-1.41380000
H	-2.16140000	6.00110000	-0.33350000
H	-4.08920000	3.87880000	-2.83160000
H	-4.15750000	4.51320000	-1.18810000
H	-2.98570000	6.14100000	-2.66080000
H	-1.85240000	4.89330000	-3.17360000
C	3.24640000	0.30250000	1.14470000
C	2.50310000	-0.14760000	2.41620000
C	4.03680000	-0.84840000	0.49510000
C	3.43290000	-0.87710000	3.39650000
C	4.94010000	-1.56560000	1.50850000
C	4.14670000	-2.05350000	2.72440000
H	3.96820000	1.08060000	1.43990000
H	1.67670000	-0.80950000	2.13840000
H	2.07270000	0.72170000	2.92350000
H	3.33560000	-1.56730000	0.05870000
H	4.65500000	-0.45990000	-0.31960000
H	2.85050000	-1.21940000	4.26090000
H	4.18510000	-0.17200000	3.78050000
H	5.44580000	-2.40410000	1.01400000
H	5.72820000	-0.87670000	1.84770000

H	4.81080000	-2.55630000	3.43840000
H	3.40180000	-2.79390000	2.40110000
C	3.41530000	1.97210000	-1.20410000
C	3.70980000	1.09100000	-2.43430000
C	3.09900000	3.40770000	-1.66510000
C	4.88120000	1.64900000	-3.25120000
C	4.23780000	3.97630000	-2.52880000
C	4.56930000	3.07350000	-3.72220000
H	4.32470000	2.01720000	-0.58630000
H	2.82740000	1.07190000	-3.07210000
H	3.90330000	0.05460000	-2.14410000
H	2.16690000	3.40690000	-2.24250000
H	2.95200000	4.07160000	-0.80820000
H	5.07280000	0.99480000	-4.11060000
H	5.79680000	1.65210000	-2.64180000
H	3.96580000	4.98270000	-2.87110000
H	5.13490000	4.08830000	-1.90280000
H	5.41090000	3.48940000	-4.28990000
H	3.70690000	3.04050000	-4.40310000

Table S9. Coordinates of the benzyne–Ni complex in the state (I) (see the text for the detail).

C	0	-1.69600000	-0.12323600	-1.85067600
H	0	-1.56934400	-1.00623600	-2.47187000
H	0	-2.19290200	0.68138500	-2.38986300
H	0	-2.23096000	-0.38065500	-0.94438500
I	0	-0.17761500	-2.14434500	0.56787000
C	0	1.14343400	-0.30641700	-2.42919700
C	0	0.21626400	0.53646400	-2.85389100
C	0	0.03929100	0.96235100	-4.15413600
C	0	1.01335000	0.45534500	-5.04361700
C	0	2.00974000	-0.43128500	-4.61350000
C	0	2.10498300	-0.84579500	-3.26443500
H	0	-0.74612800	1.63444200	-4.48814800
H	0	0.98281800	0.75511100	-6.08795300
H	0	2.72413900	-0.81579600	-5.33690800
H	0	2.87753700	-1.53739300	-2.94186100
Ni	0	0.09875600	0.32773700	-0.91848200
P	0	-0.98105900	1.72469700	0.59569900
P	0	2.12915700	1.21528200	-0.10562600
C	0	0.34538900	2.41972400	1.70647100
H	0	-0.01637800	3.33327100	2.19299000
H	0	0.50230600	1.67588200	2.48867200
C	0	1.66974900	2.65606800	0.98711000
H	0	1.61881800	3.53840400	0.34454600
H	0	2.47574000	2.83888300	1.70708000
C	0	-2.30522700	1.19134900	1.83086700
C	0	-3.32387100	0.20650900	1.22381700
C	0	-1.74694100	0.61217500	3.14691700
C	0	-4.46073700	-0.10247200	2.20668400
C	0	-2.88046100	0.27029300	4.12787800
C	0	-3.91161700	-0.68086000	3.51394700
H	0	-2.82816200	2.12801300	2.07720300
H	0	-2.79751700	-0.72361200	0.98487700
H	0	-3.74225100	0.59352800	0.29152500
H	0	-1.16191600	-0.28830400	2.92399600
H	0	-1.07929600	1.32768900	3.63433200
H	0	-5.16391700	-0.80333900	1.74053200

H	0	-5.02426500	0.81826700	2.41933400
H	0	-2.44911300	-0.16388300	5.03822900
H	0	-3.38337200	1.20093500	4.42975300
H	0	-4.72508900	-0.87093700	4.22495800
H	0	-3.43434400	-1.64854400	3.30601700
C	0	-1.74911200	3.26429100	-0.16111400
C	0	-0.86149500	3.81966000	-1.28773300
C	0	-3.19233000	3.05417800	-0.65923100
C	0	-2.87888200	4.84074100	-2.43177300
C	0	-3.76452700	4.33183300	-1.29046500
C	0	-1.45223200	5.08135600	-1.93054200
H	0	-1.78132700	3.99981300	0.65712700
H	0	-0.72383800	3.04259400	-2.04963500
H	0	0.13187500	4.05360200	-0.89865300
H	0	-3.21099200	2.25090200	-1.40455400
H	0	-3.83882800	2.74111300	0.16496500
H	0	-0.80227100	5.40960700	-2.75095500
H	0	-1.46233500	5.89356500	-1.18952000
H	0	-4.78239100	4.13507000	-1.64809300
H	0	-3.84469000	5.11119400	-0.51900700
H	0	-3.29532900	5.76029000	-2.86033700
H	0	-2.85999700	4.09319400	-3.23838600
C	0	3.24798000	0.15981700	0.95219900
C	0	2.69453700	-0.04952700	2.37438300
C	0	3.54600100	-1.19063500	0.27137900
C	0	3.64262200	-0.91881700	3.21324200
C	0	4.49400900	-2.04500200	1.12298100
C	0	3.93009700	-2.26121000	2.53179800
H	0	4.18460100	0.73253000	1.03805700
H	0	1.71372300	-0.53393500	2.31246600
H	0	2.55806100	0.91525800	2.87508700
H	0	2.60091300	-1.72174800	0.12943700
H	0	3.97532500	-1.03742800	-0.72163700
H	0	3.20729500	-1.07730400	4.20761000
H	0	4.58943800	-0.37902100	3.36382100
H	0	4.66189900	-3.00841300	0.62601400
H	0	5.47450200	-1.55009800	1.19355200

H	0	4.62762400	-2.85300400	3.13761100
H	0	2.99711800	-2.83617800	2.45921500
C	0	3.34060600	2.11707200	-1.23863900
C	0	4.49195300	1.27844400	-1.82048700
C	0	2.61658500	2.88697800	-2.35704100
C	0	5.45413100	2.15715400	-2.63588700
C	0	3.58799200	3.76384700	-3.15777800
C	0	4.72439300	2.92106400	-3.74557500
H	0	3.79710300	2.85440500	-0.55913500
H	0	4.08406100	0.49685400	-2.46831300
H	0	5.05271400	0.78468100	-1.02201000
H	0	2.14277800	2.17338400	-3.03422400
H	0	1.81527300	3.50551500	-1.94394500
H	0	6.24795600	1.52880700	-3.05806900
H	0	5.94449200	2.87577100	-1.96293000
H	0	3.03989300	4.28199900	-3.95439000
H	0	4.00899100	4.54138300	-2.50361300
H	0	5.42751400	3.55351500	-4.30119600
H	0	4.30255700	2.20203400	-4.46249200

Table S10. Coordinates of the benzyne–Ni complex in the state (K) (see the text for the detail).

C	0.13670000	2.01350000	-2.74930000
H	0.55950000	1.48160000	-3.58930000
H	0.76630000	2.77120000	-2.30710000
H	-0.91410000	2.25010000	-2.83110000
I	0.40220000	4.42800000	-4.68430000
C	-0.72510000	-0.56570000	-2.12850000
C	0.59450000	-0.78590000	-2.22590000
C	1.15620000	-1.81700000	-2.97350000
C	0.22420000	-2.65570000	-3.60280000
C	-1.16400000	-2.42680000	-3.50160000
C	-1.68230000	-1.34920000	-2.76810000
H	2.22490000	-1.98700000	-3.07770000
H	0.57510000	-3.50270000	-4.18740000
H	-1.84500000	-3.10490000	-4.01050000
H	-2.75340000	-1.17120000	-2.71220000
Ni	0.25400000	0.71720000	-1.16110000
P	-0.92300000	1.98440000	0.36320000
P	2.20710000	1.37240000	-0.18150000
C	0.34600000	2.52100000	1.63100000
H	0.01270000	3.44180000	2.12250000
H	0.38030000	1.75080000	2.39990000
C	1.74710000	2.71910000	1.02510000
H	1.76610000	3.65300000	0.45950000
H	2.49940000	2.80760000	1.81730000
C	-2.25290000	1.04430000	1.30350000
C	-2.96480000	0.05060000	0.36320000
C	-1.75380000	0.30470000	2.55780000
C	-4.13290000	-0.64700000	1.06960000
C	-2.90800000	-0.42320000	3.26530000
C	-3.64970000	-1.38060000	2.32590000
H	-2.97850000	1.80430000	1.62720000
H	-2.23590000	-0.69860000	0.03580000
H	-3.30980000	0.55100000	-0.54730000
H	-0.98440000	-0.42420000	2.26950000
H	-1.29130000	1.00160000	3.26360000
H	-4.61530000	-1.34780000	0.37740000

H	-4.89210000	0.09840000	1.34760000
H	-2.51700000	-0.96410000	4.13560000
H	-3.61490000	0.32540000	3.65070000
H	-4.49330000	-1.84690000	2.84900000
H	-2.97210000	-2.19370000	2.02760000
C	-1.79490000	3.58830000	-0.04080000
C	-0.83910000	4.66690000	-0.58160000
C	-3.00010000	3.37960000	-0.97630000
C	-2.76500000	5.76760000	-1.80490000
C	-3.72280000	4.70590000	-1.25440000
C	-1.58300000	5.98280000	-0.85280000
H	-2.18050000	3.93540000	0.93060000
H	-0.38040000	4.33110000	-1.51640000
H	-0.02840000	4.84710000	0.13280000
H	-2.66260000	2.94470000	-1.92530000
H	-3.70510000	2.66780000	-0.53550000
H	-0.88130000	6.71270000	-1.27310000
H	-1.94780000	6.39810000	0.09800000
H	-4.54790000	4.53050000	-1.95510000
H	-4.17310000	5.06990000	-0.31940000
H	-3.29920000	6.71190000	-1.96640000
H	-2.38190000	5.44440000	-2.78210000
C	2.98060000	0.02670000	0.85360000
C	1.92140000	-0.61300000	1.77180000
C	3.65330000	-1.04210000	-0.02880000
C	2.48370000	-1.78630000	2.58480000
C	4.21060000	-2.20470000	0.80480000
C	3.12430000	-2.84040000	1.67800000
H	3.75040000	0.50700000	1.47560000
H	1.08790000	-0.97040000	1.15060000
H	1.51330000	0.13240000	2.45950000
H	2.91360000	-1.43000000	-0.74060000
H	4.46270000	-0.59520000	-0.61400000
H	1.68030000	-2.22790000	3.18670000
H	3.23720000	-1.40780000	3.29030000
H	4.65330000	-2.95100000	0.13440000
H	5.02240000	-1.83510000	1.44770000

H	3.54380000	-3.65680000	2.27790000
H	2.35170000	-3.28270000	1.03220000
C	3.61620000	2.04110000	-1.21740000
C	3.66390000	1.32320000	-2.58380000
C	3.57000000	3.56810000	-1.42270000
C	4.86300000	1.79650000	-3.41480000
C	4.75460000	4.04580000	-2.27670000
C	4.81930000	3.31440000	-3.62190000
H	4.53620000	1.80360000	-0.66340000
H	2.74320000	1.54440000	-3.13280000
H	3.69260000	0.23810000	-2.45410000
H	2.63440000	3.85200000	-1.92400000
H	3.59190000	4.08680000	-0.45910000
H	4.86500000	1.27750000	-4.38090000
H	5.79620000	1.51940000	-2.90270000
H	4.67440000	5.12830000	-2.43150000
H	5.68750000	3.87190000	-1.72090000
H	5.69310000	3.64950000	-4.19390000
H	3.92920000	3.57100000	-4.21270000

Table S11. Coordinates of the benzyne–Ni complex in the state (L) (see the text for the detail).

C	0	-0.100052	1.892330	-2.780966
H	0	0.314196	1.398226	-3.649451
H	0	0.530846	2.669387	-2.363372
H	0	-1.146839	2.147910	-2.869158
I	0	0.382441	4.507250	-4.642619
C	0	-0.639913	-0.511701	-2.189027
C	0	0.666828	-0.814327	-2.130981
C	0	1.219459	-1.910281	-2.787900
C	0	0.297804	-2.703694	-3.488126
C	0	-1.072455	-2.374384	-3.547131
C	0	-1.583799	-1.233671	-2.911052
H	0	2.277440	-2.159443	-2.780079
H	0	0.644992	-3.594195	-4.006441
H	0	-1.744174	-3.022137	-4.104997
H	0	-2.635123	-0.968241	-2.982711
Ni	0	0.276586	0.734469	-1.136164
P	0	-0.889885	2.020266	0.362787
P	0	2.220548	1.347957	-0.122735
C	0	0.363949	2.527207	1.656424
H	0	0.032386	3.448687	2.147440
H	0	0.379307	1.751331	2.420511
C	0	1.771719	2.712723	1.065847
H	0	1.801998	3.640272	0.491443
H	0	2.517869	2.799837	1.863712
C	0	-2.227414	1.049473	1.255330
C	0	-2.956824	0.121638	0.262385
C	0	-1.729424	0.231637	2.460365
C	0	-4.127922	-0.604819	0.934057
C	0	-2.886406	-0.527382	3.129867
C	0	-3.642731	-1.418731	2.138923
H	0	-2.939072	1.800858	1.626746
H	0	-2.239814	-0.616275	-0.113010
H	0	-3.302036	0.678727	-0.614270
H	0	-0.967440	-0.484360	2.124727
H	0	-1.257617	0.881072	3.203983
H	0	-4.622464	-1.257111	0.204176

H	0	-4.876936	0.129993	1.262919
H	0	-2.495022	-1.123574	3.963043
H	0	-3.584314	0.202465	3.564471
H	0	-4.486802	-1.909171	2.638576
H	0	-2.974473	-2.217527	1.785676
C	0	-1.745196	3.641278	-0.005795
C	0	-0.777578	4.696116	-0.572475
C	0	-2.992306	3.481313	-0.894516
C	0	-2.715422	5.870149	-1.706571
C	0	-3.682527	4.833901	-1.124830
C	0	-1.488099	6.037415	-0.803871
H	0	-2.084022	3.987690	0.983370
H	0	-0.363564	4.355533	-1.526656
H	0	0.064075	4.845891	0.112549
H	0	-2.707271	3.052490	-1.862466
H	0	-3.701770	2.786510	-0.434504
H	0	-0.780121	6.746097	-1.248758
H	0	-1.798765	6.457447	0.164054
H	0	-4.543301	4.693423	-1.789532
H	0	-4.078492	5.200489	-0.166498
H	0	-3.225181	6.832612	-1.836479
H	0	-2.384991	5.544688	-2.701979
C	0	3.024057	0.035095	0.927457
C	0	1.971545	-0.599389	1.856475
C	0	3.711769	-1.040097	0.065933
C	0	2.542173	-1.755407	2.688086
C	0	4.283614	-2.178615	0.922539
C	0	3.201519	-2.814664	1.800923
H	0	3.786853	0.539119	1.538841
H	0	1.140746	-0.966861	1.237431
H	0	1.557773	0.153683	2.532783
H	0	2.977456	-1.453343	-0.636208
H	0	4.513956	-0.592739	-0.529244
H	0	1.740143	-2.198113	3.291041
H	0	3.286459	-1.358571	3.393273
H	0	4.740510	-2.930134	0.267534
H	0	5.086603	-1.785574	1.562386

H	0	3.628585	-3.615914	2.415664
H	0	2.438425	-3.277374	1.158094
C	0	3.579938	2.003012	-1.228987
C	0	3.578799	1.235766	-2.569076
C	0	3.481273	3.519830	-1.484049
C	0	4.710144	1.714610	-3.486641
C	0	4.597721	3.999267	-2.424292
C	0	4.605501	3.221345	-3.744356
H	0	4.527168	1.804636	-0.706832
H	0	2.617260	1.400748	-3.067010
H	0	3.655211	0.158256	-2.400847
H	0	2.509545	3.761314	-1.936088
H	0	3.547468	4.072086	-0.541303
H	0	4.671431	1.159986	-4.432076
H	0	5.680454	1.484063	-3.022477
H	0	4.472823	5.072133	-2.612512
H	0	5.567203	3.874736	-1.919869
H	0	5.433410	3.560620	-4.378878
H	0	3.674412	3.430101	-4.288324

Table S12. Coordinates of the benzyne–Ni complex in the state (M) (see the text for the detail).

C	0.23210000	1.85370000	-2.45230000
H	0.85170000	1.55590000	-3.29380000
H	0.65160000	2.71510000	-1.93870000
H	-0.78840000	2.04740000	-2.77590000
I	-0.01700000	-2.03050000	0.48280000
C	-0.91130000	-0.61350000	-2.55350000
C	0.37020000	-0.87380000	-2.72370000
C	0.88640000	-1.66530000	-3.73470000
C	-0.10310000	-2.21240000	-4.58240000
C	-1.46670000	-1.93640000	-4.40210000
C	-1.92550000	-1.09560000	-3.36280000
H	1.94190000	-1.87420000	-3.88790000
H	0.20130000	-2.86500000	-5.39790000
H	-2.19100000	-2.38080000	-5.08130000
H	-2.98290000	-0.87730000	-3.23780000
Ni	0.14260000	0.32010000	-1.19450000
P	-1.11290000	1.74040000	0.36470000
P	2.21820000	1.08850000	-0.15200000
C	0.24650000	2.28820000	1.53070000
H	-0.06830000	3.18010000	2.08690000
H	0.36950000	1.48520000	2.26020000
C	1.59220000	2.56270000	0.82400000
H	1.48730000	3.39790000	0.12790000
H	2.34040000	2.86760000	1.56550000
C	-2.50810000	1.07420000	1.47840000
C	-3.36540000	0.00780000	0.75950000
C	-2.05700000	0.56790000	2.86470000
C	-4.57290000	-0.40420000	1.61840000
C	-3.26740000	0.13810000	3.71470000
C	-4.13290000	-0.90820000	2.99970000
H	-3.14770000	1.95170000	1.65190000
H	-2.74280000	-0.86890000	0.55350000
H	-3.71320000	0.38100000	-0.21110000
H	-1.37460000	-0.28130000	2.74160000
H	-1.51030000	1.35200000	3.40110000
H	-5.14770000	-1.17830000	1.09410000

H	-5.24620000	0.45750000	1.74300000
H	-2.91360000	-0.25020000	4.67840000
H	-3.88160000	1.02290000	3.94010000
H	-5.00890000	-1.15790000	3.61230000
H	-3.55600000	-1.83580000	2.87910000
C	-1.93700000	3.39480000	-0.10890000
C	-1.01540000	4.55460000	-0.54170000
C	-3.08680000	3.20590000	-1.12290000
C	-2.96280000	5.67590000	-1.73200000
C	-3.87690000	4.51070000	-1.33020000
C	-1.82280000	5.85400000	-0.72040000
H	-2.38820000	3.70770000	0.84540000
H	-0.51910000	4.32010000	-1.48940000
H	-0.23030000	4.72160000	0.20420000
H	-2.67620000	2.87350000	-2.08540000
H	-3.77280000	2.42050000	-0.78900000
H	-1.14990000	6.66040000	-1.03820000
H	-2.24060000	6.15730000	0.25090000
H	-4.65280000	4.35180000	-2.08960000
H	-4.39970000	4.76530000	-0.39660000
H	-3.54420000	6.60260000	-1.81760000
H	-2.53690000	5.47880000	-2.72690000
C	3.32080000	0.20840000	1.12210000
C	2.68910000	-0.03200000	2.50720000
C	3.93480000	-1.09060000	0.55760000
C	3.70750000	-0.65870000	3.47840000
C	4.94400000	-1.70780000	1.54170000
C	4.31250000	-1.95280000	2.91830000
H	4.13820000	0.93300000	1.26640000
H	1.82200000	-0.69300000	2.40680000
H	2.33540000	0.91340000	2.93370000
H	3.13020000	-1.80850000	0.35910000
H	4.43620000	-0.89690000	-0.39770000
H	3.21830000	-0.84940000	4.44210000
H	4.51460000	0.06340000	3.67410000
H	5.33340000	-2.64550000	1.12520000
H	5.80500000	-1.03150000	1.65270000

H	5.05980000	-2.35510000	3.61440000
H	3.52400000	-2.71300000	2.82550000
C	3.60540000	1.75950000	-1.27790000
C	3.74660000	0.94120000	-2.58180000
C	3.56530000	3.27110000	-1.59020000
C	4.99490000	1.37110000	-3.37100000
C	4.81070000	3.69820000	-2.38890000
C	4.97810000	2.87610000	-3.67470000
H	4.51960000	1.58980000	-0.69180000
H	2.85860000	1.08650000	-3.20610000
H	3.79350000	-0.13130000	-2.36160000
H	2.66830000	3.51430000	-2.17360000
H	3.51560000	3.85610000	-0.66500000
H	5.05830000	0.79390000	-4.30210000
H	5.89530000	1.12680000	-2.78820000
H	4.74450000	4.76810000	-2.62380000
H	5.70210000	3.57000000	-1.75760000
H	5.89810000	3.17060000	-4.19530000
H	4.14530000	3.09770000	-4.35840000

Table S13. Coordinates of the benzyne–Ni complex in the state (N) (see the text for the detail).

C	-0.10660000	-0.00630000	0.19470000
H	-0.36400000	0.76930000	0.91340000
H	0.60060000	-0.73440000	0.58420000
H	-0.99550000	-0.47710000	-0.22550000
I	-1.48620000	2.33820000	-1.86650000
C	1.47510000	-0.66850000	-2.47490000
C	0.37020000	-0.30610000	-3.10200000
C	-0.04830000	-0.82210000	-4.32770000
C	0.80880000	-1.79190000	-4.86050000
C	1.98210000	-2.19480000	-4.18430000
C	2.35140000	-1.64620000	-2.95050000
H	-0.95500000	-0.51730000	-4.84230000
H	0.56880000	-2.25370000	-5.81510000
H	2.61380000	-2.95450000	-4.63840000
H	3.25240000	-1.97210000	-2.43980000
Ni	0.57340000	0.70200000	-1.47880000
P	0.66440000	5.66100000	1.46100000
P	2.16490000	1.68980000	-0.25110000
C	1.14640000	4.32210000	0.23710000
H	0.29020000	4.07830000	-0.39690000
H	1.90930000	4.76760000	-0.40760000
C	1.71830000	3.07050000	0.90240000
H	2.63580000	3.32480000	1.44830000
H	1.02150000	2.65920000	1.63470000
C	0.46860000	7.03460000	0.17810000
C	-0.42250000	8.19650000	0.64930000
C	1.85360000	7.57050000	-0.23410000
C	-0.52810000	9.29550000	-0.41970000
C	1.74560000	8.65920000	-1.31110000
C	0.85110000	9.81310000	-0.84380000
H	-0.00770000	6.58140000	-0.70490000
H	-0.00610000	8.62530000	1.57260000
H	-1.42650000	7.83430000	0.89060000
H	2.35110000	7.98700000	0.65350000
H	2.49500000	6.75900000	-0.59860000
H	-1.14780000	10.11900000	-0.04310000

H	-1.04640000	8.88690000	-1.29910000
H	2.74600000	9.02860000	-1.56950000
H	1.32390000	8.21930000	-2.22640000
H	0.74970000	10.56540000	-1.63600000
H	1.32790000	10.31480000	0.01090000
C	-1.13940000	5.22620000	1.81670000
C	-1.38270000	3.72200000	2.03600000
C	-1.62510000	6.00720000	3.05480000
C	-3.36500000	4.23420000	3.54380000
C	-3.10570000	5.73340000	3.35280000
C	-2.85970000	3.43130000	2.33950000
H	-1.73230000	5.53340000	0.94200000
H	-0.76670000	3.37140000	2.87800000
H	-1.08970000	3.15230000	1.14990000
H	-1.01770000	5.70000000	3.91840000
H	-1.46090000	7.08250000	2.93160000
H	-2.99520000	2.35580000	2.51130000
H	-3.45800000	3.68400000	1.45270000
H	-3.41860000	6.29250000	4.24380000
H	-3.71570000	6.10480000	2.51650000
H	-4.43370000	4.04730000	3.70690000
H	-2.84220000	3.89300000	4.44960000
C	3.28570000	0.63490000	0.81210000
C	2.78300000	0.46940000	2.26280000
C	3.58230000	-0.73900000	0.18430000
C	3.79410000	-0.32850000	3.10000000
C	4.58940000	-1.53000000	1.02940000
C	4.10170000	-1.69250000	2.47280000
H	4.22470000	1.20690000	0.85630000
H	1.81960000	-0.05400000	2.26850000
H	2.61850000	1.44310000	2.73120000
H	2.64910000	-1.30800000	0.10010000
H	3.96140000	-0.62100000	-0.83130000
H	3.40560000	-0.45110000	4.11790000
H	4.72450000	0.25130000	3.18400000
H	4.76260000	-2.51000000	0.56870000
H	5.55500000	-1.00390000	1.02670000

H	4.84880000	-2.22670000	3.07170000
H	3.19030000	-2.30770000	2.47860000
C	3.26060000	2.53720000	-1.51440000
C	4.42290000	1.68220000	-2.04900000
C	2.42770000	3.07440000	-2.69820000
C	5.30050000	2.50450000	-3.00630000
C	3.29980000	3.91080000	-3.64230000
C	4.48800000	3.09480000	-4.16480000
H	3.69080000	3.38960000	-0.96720000
H	4.01520000	0.81390000	-2.58230000
H	5.04270000	1.30360000	-1.23050000
H	2.01650000	2.21950000	-3.25080000
H	1.57080000	3.65680000	-2.35350000
H	6.11030000	1.87190000	-3.38940000
H	5.77620000	3.31950000	-2.44240000
H	2.68930000	4.27810000	-4.47560000
H	3.66790000	4.79620000	-3.10340000
H	5.13040000	3.71480000	-4.80160000
H	4.11020000	2.27630000	-4.79420000

Table S14. Values of k at each temperature

temp. (K)	k_{1st} (min^{-1})	k_{2nd} (min^{-1})	k_{3rd} (min^{-1})
283	6.272×10^{-3}	6.120×10^{-3}	6.111×10^{-3}
293	1.485×10^{-2}	1.602×10^{-2}	1.687×10^{-2}
303	3.921×10^{-2}	4.121×10^{-2}	3.873×10^{-2}

Table S15. Crystal data and structure refinement for *o*-tolyl(dcpe)Ni complex

Identification code compound ***o*-tolyl(dcpe)Ni complex**
Empirical formula $C_{34}H_{57}Cl_2INiP_2 \cdot CH_2Cl_2$
Formula weight 784.2754
Temperature 173 K
Wavelength 0.71075 Å
Crystal system Monoclinic
Space group $P2_1/c$
Unit cell dimensions $a = 12.0708(9)$ Å $\alpha = 90°$
$b = 12.3284(3)$ Å $\beta = 101.264(4)°$
$c = 20.9551(5)$ Å $\gamma = 90°$
$V = 3629.2(5)$ Å^3
Z 4
D_X 1.435 g/m^3
μ 1.643 mm^{-1}
$F(000)$ 1624
Crystal size $0.440 \times 0.130 \times 0.050$ mm^3
Theta range for data collection 1.70 to 27.50°
Index ranges $-15 \le h \le 15, -24 \le k \le 24, -21 \le l \le 24$
Reflections collected 38170
Independent reflections 8324 [$R_{int} = 0.0583$]
Completeness 100.0%
Absorption correction Multi-scan
Max. and min. transmission 0.676 and 0.921
Refinement method Full-matrix least-squares on F^2
Data / restraints / parameters 8323 / 3 / 390
Goodness-of-fit on $F2$ 1.004
Final R indices [$I > 2\sigma(I)$] $R(F) = 0.0301$, $wR(F^2) = 0.0648$
R indices (all data) $R(F) = 0.0465$, $wR(F^2) = 0.0704$
Largest diff. peak and hole 0.47 and –0.64 e Å^{-3}

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