Cartesian Coordinates of Compounds

Mechanistic Aspects of Pincer Nickel(II)-Catalyzed C–H Bond Alkylation of Azoles with Alkyl Halides

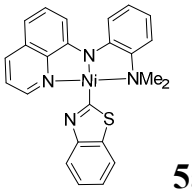
Ulhas N. Patel,[†,ǁ] Shailja Jain,[‡] Dilip K. Pandey,[†,ǁ] Rajesh G. Gonnade,[§] Kumar Vanka,[‡] and Benudhar Punji[*,†,ǁ]

[†]Organometallic Synthesis and Catalysis Group, Chemical Engineering Division, [‡]Physical and Materials Chemistry Division, and [§]Centre for Material Characterization, CSIR–National Chemical Laboratory (CSIR–NCL), Dr. Homi Bhabha Road, Pune 411 008, India.

[ǁ]Academy of Scientific and Innovative Research (AcSIR), New Delhi 110 020, India

[*]E-mail: b.punji@ncl.res.in

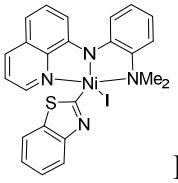
PBE/TZVP Optimized Geometries for all the Compounds and Transition States



5a

Ni	1.492448	2.102082	3.861018
S	3.506126	0.936830	1.735310
N	0.745076	3.726673	4.498162
N	0.285598	2.316868	2.419615
N	2.495036	2.051772	5.560718
N	2.343714	-0.647241	3.469840
C	-0.106423	4.341513	3.618418
C	-0.705975	5.613512	3.640782
H	-0.495560	6.320373	4.436748
C	-1.588218	6.012736	2.615018
H	-2.031977	7.008806	2.679025
C	-1.909825	5.193371	1.546550
H	-2.612643	5.512809	0.775748
C	-1.305585	3.912331	1.455834
C	-1.552029	2.986844	0.409654
H	-2.256930	3.249647	-0.382060
C	-0.904704	1.766356	0.406288
H	-1.081554	1.031159	-0.378851
C	0.020716	1.464375	1.420928
H	0.564007	0.522231	1.429794
C	-0.381391	3.521232	2.468200
C	1.196310	4.141025	5.732465
C	0.792282	5.265790	6.494241
H	0.005928	5.923473	6.136649
C	1.373906	5.532910	7.733475
H	1.042433	6.410566	8.292789
C	2.359851	4.698864	8.267140
H	2.814347	4.917083	9.234214
C	2.746957	3.562774	7.547448
H	3.492892	2.886490	7.968567
C	2.171564	3.290690	6.311947
C	3.968443	1.922617	5.363513
H	4.323091	2.771201	4.767792
H	4.174707	0.990413	4.828917
H	4.490269	1.906956	6.331733
C	1.971761	0.868081	6.315289
H	2.502559	0.768520	7.275529
H	2.112929	-0.033194	5.705600
H	0.903164	1.020896	6.507476
C	2.368377	0.609801	3.129968
C	3.179508	-1.451294	2.701334
C	3.336350	-2.837663	2.857314

H	2.771586	-3.355343	3.634518	C	1.124753	4.043470	5.765122
C	4.211185	-3.521918	2.014718	C	0.638594	5.135005	6.516436
H	4.338600	-4.600025	2.129290	C	1.066377	5.330193	7.829854
C	4.931376	-2.841088	1.016177	C	1.977840	4.455572	8.425633
H	5.610675	-3.395517	0.365947	C	2.451272	3.354227	7.701467
C	4.790296	-1.462304	0.843440	C	2.019767	3.148505	6.397115
H	5.350419	-0.938608	0.067243	N	0.133694	2.241991	2.455925
C	3.913032	-0.773718	1.688405	C	-0.268171	1.379316	1.516960



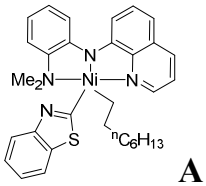
B

				C	-1.121103	1.768421	0.469918
				C	-1.563244	3.076020	0.395367
				C	-1.180765	4.006110	1.393749
C	3.680479	-0.860299	1.696512	C	-0.336090	3.530426	2.436108
S	3.049358	0.781516	1.689058	C	0.042515	4.356462	3.546308
C	2.121584	0.401164	3.224760	C	-0.338486	5.706943	3.500414
N	2.302843	-0.810506	3.629557	C	-1.134344	6.189266	2.440923
C	3.154695	-1.553695	2.820847	C	-1.572608	5.371241	1.413257
C	4.553463	-1.485858	0.800212	C	3.840633	2.370886	5.009359
C	4.898584	-2.817973	1.037896	H	-0.009710	6.404202	4.266561
C	4.384663	-3.513853	2.147497	H	-1.413330	7.244856	2.443551
C	3.513003	-2.892681	3.039795	H	-2.208382	5.757649	0.615319
Ni	1.231407	1.892472	4.002377	H	-2.214629	3.400771	-0.418685
N	2.499010	2.014801	5.574798	H	-1.414788	1.025567	-0.271341
C	2.604508	0.764357	6.376714	H	0.094613	0.358090	1.607708
N	0.780848	3.673876	4.478414	H	-0.113734	5.799319	6.099088

H	0.665088	6.170809	8.399166	H	0.436467	-0.770921	-0.805806
H	2.306726	4.611314	9.453804	H	0.490088	1.002987	-0.742368
H	3.143830	2.656968	8.173053	H	-0.620932	0.952279	1.532547
H	3.744043	3.272040	4.392050	H	-0.689184	-0.808147	1.459172
H	4.202635	1.542041	4.391605	H	1.822425	-0.906637	1.403947
H	4.548355	2.562333	5.830687	H	1.894320	0.856031	1.393674
H	3.432017	0.842424	7.097635	H	2.360516	0.139504	3.641455
H	2.783664	-0.074565	5.696536	H	0.771757	0.905678	3.662167
H	1.654803	0.600452	6.895694	H	-0.314998	-1.377287	3.583141
H	3.103408	-3.420964	3.902094	H	1.281639	-2.126437	3.612769
H	4.670834	-4.554687	2.309295	H	0.094729	-2.072272	5.847044
H	5.578240	-3.324530	0.350164	H	0.138566	-0.307186	5.821846
H	4.953777	-0.952364	-0.063092	H	2.610967	-2.131583	5.773784
I	-0.883778	0.627843	5.223935	H	2.647118	-0.358325	5.829735

Octyl Radical

C	-0.062184	0.118145	-0.388396	H	1.905549	-0.363450	8.220521
C	-0.094533	0.064065	1.140533	H	1.886357	-2.228507	8.171080
C	1.303893	0.000272	1.765786				
C	1.319159	0.015330	3.301534				



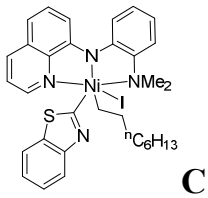
A

C	0.715934	-1.237965	3.948085	C	4.314704	-0.519398	2.812409
C	0.676126	-1.209456	5.482480	C	3.577229	0.650900	2.498102
C	2.075980	-1.243828	6.155879	C	2.466300	1.009359	3.321225
C	2.006634	-1.282354	7.640421	C	2.126821	0.258575	4.505884
H	-1.075793	0.163008	-0.814043	C	2.852993	-0.925128	4.734104

C	3.925640	-1.288475	3.897254	C	-2.308484	2.652740	6.149352
N	1.656809	2.073002	3.021608	H	2.585291	-1.584500	5.556582
C	1.948931	2.843389	1.970387	H	4.468212	-2.209199	4.124221
C	3.056571	2.592818	1.140614	H	5.166321	-0.802410	2.191615
C	3.860436	1.496816	1.395074	H	4.713045	1.267589	0.751787
Ni	0.279610	2.385333	4.488039	H	3.252932	3.257381	0.298776
N	1.080175	0.785091	5.209787	H	1.273462	3.677661	1.780744
C	0.580412	0.379072	6.434264	H	2.288542	-0.658440	7.281451
C	1.258457	-0.345102	7.439034	H	1.204148	-1.145127	9.434803
C	0.649303	-0.596989	8.670356	H	-1.112752	-0.334127	9.903660
C	-0.641428	-0.137647	8.939605	H	-2.329232	0.969038	8.173001
C	-1.325877	0.596828	7.962034	H	-1.372327	-0.062744	4.365319
C	-0.727846	0.855195	6.732590	H	-2.488864	1.256656	3.894407
N	-1.386128	1.606976	5.669660	H	-2.914914	0.166333	5.254896
C	-2.086129	0.681628	4.738825	H	-3.192426	2.225887	6.653358
C	-0.573915	3.878197	3.704393	H	-2.646421	3.237269	5.285737
S	-1.620715	3.410271	2.243800	H	-1.775849	3.317531	6.838988
C	-2.075209	5.098228	2.060325	H	-1.128506	7.843920	3.879876
C	-1.422905	5.868028	3.062854	H	-2.640485	8.928384	2.203162
N	-0.615619	5.151793	3.935732	H	-3.769897	7.561531	0.460741
C	-1.630234	7.255770	3.109633	H	-3.418968	5.100470	0.352724
C	-2.473747	7.850043	2.172323	C	1.034645	3.595493	5.891413
C	-3.113063	7.077523	1.186007	H	1.064936	2.948415	6.781612
C	-2.920928	5.695419	1.119710	C	2.396387	4.058842	5.440680

H	0.323239	4.420563	6.012166	H	0.075343	-0.418423	1.314322
C	3.077124	4.983609	6.471255	H	1.124826	-0.390737	-0.119728
H	3.056100	3.193381	5.256543	H	-0.433075	-1.242672	-0.176585
H	2.296166	4.597120	4.486072	C	-0.604922	0.932759	-0.267933
C	4.517578	5.358120	6.093405	C	-0.613295	1.061438	-1.795444
H	2.472140	5.900182	6.584487	H	-1.646164	0.961160	0.099576
H	3.079079	4.485885	7.455929	H	-0.098481	1.803402	0.180071
H	4.952889	5.962414	6.909113	C	-1.355846	2.293018	-2.333237
H	5.126963	4.438282	6.034461	H	0.428214	1.074212	-2.165761
C	4.648952	6.133495	4.777886	H	-1.075713	0.153870	-2.221172
C	6.086605	6.572667	4.481576	H	-1.438639	2.199737	-3.428502
H	4.289693	5.511623	3.939412	H	-2.391145	2.290894	-1.945766
H	3.983031	7.012886	4.814523	C	-0.693394	3.630957	-1.983470
C	6.272664	7.263224	3.122876	C	-1.432472	4.865109	-2.523410
H	6.434072	7.249281	5.283725	H	-0.618041	3.729540	-0.888382
H	6.742640	5.685638	4.524809	H	0.343974	3.632970	-2.363861
H	7.349859	7.427233	2.951522	H	-0.964078	5.773451	-2.107710
H	5.937378	6.579131	2.323129	C	-1.434707	4.964392	-4.059111
C	5.536033	8.600161	2.993750	H	-2.473769	4.856206	-2.155041
H	5.747744	9.081807	2.027244	C	-2.120196	6.239021	-4.508367
H	4.445753	8.474714	3.067015	H	-0.397354	4.943794	-4.430994
H	5.844699	9.297128	3.789392	H	-1.949238	4.096117	-4.496497
Octyl Iodide				I	-2.199955	6.420152	-6.710446
C	0.076730	-0.348913	0.216479	H	-3.170954	6.287845	-4.202509

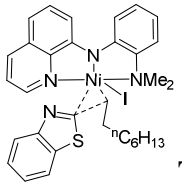
H	-1.595577	7.145501	-4.187518



C

C	-0.487230	7.949276	1.625450
C	0.061500	6.811448	2.228275
C	0.945892	6.919989	3.332252
C	1.282583	8.185524	3.838661
C	0.732490	9.316463	3.239368
C	-0.144600	9.199217	2.143821
N	1.411581	5.707437	3.822223
C	0.962588	4.675171	3.175753
S	-0.127609	5.109292	1.804310
Ni	1.354836	2.829032	3.621290
N	-0.341299	2.546830	4.737503
C	-0.738239	3.755367	5.515896
N	2.984980	2.747429	2.622447
C	3.527735	1.488102	2.663876
C	4.706104	1.168970	1.928385
C	5.278289	2.199201	1.139160
C	4.698014	3.451725	1.114773
C	3.547294	3.703023	1.882538
C	2.844850	0.516423	3.473206
C	3.352038	-0.792304	3.463074
C	4.513190	-1.105764	2.729600
C	5.196614	-0.160378	1.983790
N	1.750338	1.028096	4.113318
C	1.033448	0.548273	5.183586
C	1.309947	-0.600210	5.962896
C	0.536039	-0.899995	7.082751
C	-0.527794	-0.079917	7.467195
C	-0.809400	1.068073	6.718521
C	-0.039976	1.378982	5.602779
C	2.425285	3.345623	5.359428
C	3.849209	2.926571	5.608303
C	4.998889	3.709882	4.956880
C	4.863421	5.234472	5.022741
C	5.986284	5.985830	4.294586
C	7.383411	5.809444	4.896620
C	8.460229	6.627230	4.176489
C	9.855084	6.452984	4.780166
C	-1.497729	2.177745	3.856427
H	2.828273	-1.593430	3.977399
H	4.868644	-2.138114	2.743085
H	6.081873	-0.428531	1.405402
H	6.173507	1.986739	0.551299
H	5.115197	4.261422	0.516661
H	3.077491	4.683189	1.906362

H	2.154577	-1.238410	5.719466	H	7.358152	6.099484	5.963036
H	0.779216	-1.787602	7.670488	H	7.672766	4.744451	4.876905
H	-1.133447	-0.322696	8.340884	H	8.478914	6.338704	3.110882
H	-1.637606	1.711593	7.015818	H	8.177877	7.694501	4.197145
H	-1.260484	1.260879	3.311461	H	10.607184	7.050759	4.243888
H	-1.671759	2.984018	3.135847	H	9.871085	6.765237	5.836202
H	-2.387127	2.030506	4.489253	H	10.175319	5.399745	4.742294
H	-1.628355	3.544574	6.123740	I	0.364980	1.779368	0.964817
H	-0.978276	4.554583	4.808645				
H	0.080975	4.078552	6.163895				
H	1.964035	8.262204	4.687883				
H	0.984412	10.307246	3.621860				
H	-0.563332	10.099453	1.689923				
H	-1.164885	7.864830	0.774347				
H	1.755192	2.845790	6.067974				
H	2.263320	4.426959	5.300386				
H	3.950105	3.035071	6.710642				
H	3.984736	1.845460	5.435891				
H	5.930320	3.393903	5.454531				
H	3.900131	5.534846	4.580210				
H	4.829207	5.557417	6.079830				
H	5.115843	3.409642	3.905843				
H	5.740976	7.062123	4.278078				
H	6.004906	5.662878	3.237281				

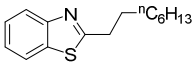


Ts_1

C	4.814247	0.694957	2.754742
C	3.706997	1.315404	3.379375
C	3.972647	2.269237	4.399240
C	5.268210	2.640435	4.740866
C	6.351056	2.035828	4.089678
C	6.111466	1.068407	3.107522
N	2.382589	1.246653	3.029084
C	1.768299	0.347137	2.209857
C	0.499987	0.811082	1.732708
C	-0.265016	0.043765	0.804555
C	0.239638	-1.216169	0.383142
C	1.445208	-1.676106	0.884516
C	2.205301	-0.922840	1.800293

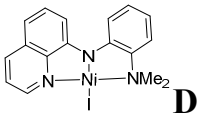
C	-1.521645	0.562754	0.409587	C	0.994689	0.578047	-3.136015
C	-1.957090	1.760077	0.939924	C	1.615308	-0.819654	-3.190262
C	-1.137969	2.469395	1.835623	C	2.966585	3.959047	5.886331
N	0.062715	2.022901	2.208662	H	3.121578	-1.345003	2.208301
Ni	1.299467	2.831102	3.541410	H	1.812973	-2.659619	0.585097
I	-0.872005	2.391168	5.312433	H	-0.355732	-1.823779	-0.300047
N	2.767261	2.728630	5.093083	H	-2.137680	0.000970	-0.295912
C	2.388181	1.630386	6.056250	H	-2.928071	2.180516	0.678030
C	0.717361	4.707742	3.340961	H	-1.430284	3.438426	2.228633
S	0.826646	5.958559	4.693945	H	4.660608	-0.014910	1.945172
C	-0.362084	6.939671	3.861300	H	6.952779	0.605645	2.587288
				H	7.370559	2.319187	4.353157
C	-0.740895	6.292067	2.653273	H	5.451210	3.386960	5.513598
N	-0.102944	5.097030	2.406446	H	2.154034	0.720443	5.497960
C	-1.693490	6.891653	1.812190	H	1.502745	1.939362	6.618223
C	-2.253540	8.110947	2.186984	H	3.242841	1.458330	6.728933
C	-1.873700	8.740055	3.386899	H	3.687832	3.782690	6.699627
C	-0.925800	8.162189	4.235874	H	2.003074	4.230041	6.330889
C	2.563586	4.321051	2.469534	H	3.332560	4.770219	5.248121
C	2.418738	4.728158	1.022376	H	-1.976275	6.393421	0.883339
C	1.883950	3.637517	0.097493	H	-2.996607	8.585064	1.543311
C	1.971057	3.979321	-1.390994	H	-2.325538	9.694483	3.663238
C	1.218933	2.978852	-2.280752	H	-0.637962	8.654952	5.165665
C	1.790509	1.556910	-2.267824	H	1.802855	5.634804	0.927338

H	3.443564	5.005691	0.700827
H	2.419035	2.695343	0.304578
H	1.548291	4.986884	-1.550688
H	3.029111	4.035378	-1.704722
H	0.829777	3.465905	0.354171
H	1.210782	3.349584	-3.320673
H	0.161813	2.944242	-1.958995
H	2.839814	1.585050	-2.614064
H	1.818318	1.167433	-1.236000
H	-0.035602	0.511002	-2.743717
H	0.905830	0.985207	-4.158561
H	1.012107	-1.508872	-3.800251
H	2.626766	-0.785968	-3.624776
H	1.700232	-1.249156	-2.180095
H	3.236523	3.460705	2.558960
H	2.947048	5.130674	3.097453



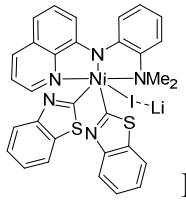
C	-0.388864	0.361632	0.966616
C	-0.051148	0.121460	2.299260
C	1.290927	-0.042453	2.689902
C	2.322115	0.031448	1.756835
C	2.007773	0.271242	0.409479
C	0.646586	0.431824	0.029539
H	-0.842974	0.061340	3.048094
H	1.525372	-0.229108	3.739387
H	3.366281	-0.092812	2.047614
N	2.930256	0.373745	-0.621197
S	0.563358	0.726041	-1.700114
C	2.353347	0.604666	-1.762524
C	3.059898	0.704644	-3.076074
H	-1.430399	0.488968	0.668680
H	4.103331	0.984919	-2.867185
C	3.022247	-0.613062	-3.875884
H	2.613795	1.511132	-3.680665
C	3.723423	-0.492896	-5.231078
H	3.494355	-1.408145	-3.275351
H	1.972655	-0.916229	-4.028297
C	3.677125	-1.784201	-6.053098
H	3.255537	0.323494	-5.810218
H	4.775460	-0.194902	-5.075154
C	4.348114	-1.655550	-7.424040
H	4.159577	-2.598477	-5.483554
H	2.624285	-2.089201	-6.190764
C	4.282822	-2.935215	-8.262688
H	3.872265	-0.830220	-7.983981
H	5.404587	-1.362375	-7.287932
C	4.931506	-2.796685	-9.643683
H	4.771604	-3.759330	-7.712144

H	3.226684	-3.235934	-8.386561
C	4.858671	-4.079546	-10.475331
H	4.441457	-1.972568	-10.191019
H	5.986264	-2.495469	-9.519451
H	5.326102	-3.949853	-11.462853
H	3.813625	-4.387279	-10.637250



D

C	3.624827	-6.307718	2.181206
C	2.831583	-5.184550	2.522873
C	3.252216	-3.916887	2.027330
N	4.351316	-3.767795	1.209926
C	5.087062	-4.851195	0.928506
C	4.753970	-6.131128	1.406713
C	2.578637	-2.704090	2.376705
C	1.394846	-2.818226	3.123467
C	0.954742	-4.080517	3.573048
C	1.650809	-5.247213	3.308414
N	3.206891	-1.596589	1.867601
Ni	4.554000	-1.954063	0.616655
I	6.195354	-2.500632	-1.299858
C	2.968578	-0.267194	2.146073
C	3.659248	0.633323	1.309913
C	3.511863	2.010729	1.432312
C	2.689013	2.537815	2.433970
C	2.040631	1.662268	3.310423
C	2.172744	0.280037	3.181819
N	4.552501	0.017534	0.297603
C	4.033417	0.342267	-1.068258
C	5.937221	0.557563	0.473227
H	1.423268	2.059709	4.118746
H	2.573279	3.617426	2.534879
H	4.043872	2.687094	0.760976
H	1.686733	-0.367595	3.906279
H	0.788116	-1.945791	3.349242
H	0.030288	-4.125608	4.152934
H	1.307086	-6.211622	3.685204
H	3.337239	-7.298424	2.539871
H	5.394565	-6.970609	1.135556
H	5.950845	-4.693723	0.285903
H	3.025345	-0.077238	-1.167218
H	5.941812	1.650404	0.343728
H	3.992248	1.433377	-1.206668
H	4.692500	-0.107356	-1.817747
H	6.596145	0.093423	-0.267460
H	6.285098	0.307432	1.482275



E

C	11.174682	2.855950	1.640513
C	10.576301	2.427806	2.835599
C	11.377774	2.200943	3.985926
C	12.762583	2.403344	3.953129
C	13.340074	2.831542	2.756171
C	12.553924	3.055985	1.610212
S	10.351160	1.673266	5.312432
C	8.926913	1.794058	4.222807
N	9.219726	2.185063	3.019662
Ni	7.162266	1.228123	4.695522
I	8.057711	-0.154115	7.472057
N	5.334969	0.474938	5.107721
C	4.295129	1.088548	4.376798
C	4.681823	2.100091	3.439859
C	3.704799	2.842158	2.702966
C	2.332498	2.535072	2.878811
C	1.971025	1.521316	3.745551
C	2.933647	0.805779	4.489672
C	4.181297	3.841324	1.815910
C	5.538708	4.037000	1.670367
C	6.437659	3.230272	2.401514
N	6.022505	2.296193	3.247835
C	5.378637	-0.951331	5.085470
C	4.457289	-1.778242	5.747818
C	4.597837	-3.168140	5.722250
C	5.666474	-3.749476	5.040100
C	6.599759	-2.937288	4.387461
C	6.462333	-1.549647	4.416219
N	7.398320	-0.640008	3.732807
C	6.983710	-0.468967	2.308671
C	7.035852	2.819192	5.795765
S	5.337886	3.257896	6.509936
C	6.095170	4.579526	7.388742
C	7.472585	4.645463	7.048351
N	7.921019	3.665356	6.175947
C	8.275953	5.651798	7.604264
C	7.702178	6.566579	8.485500
C	6.337665	6.491291	8.815147
C	5.518892	5.499653	8.268445
C	8.791901	-1.159482	3.759222
H	2.594074	0.029595	5.173563
H	0.916603	1.270527	3.877944
H	1.581287	3.097079	2.320739
H	3.462693	4.442127	1.253401
H	5.934852	4.794436	0.993314

H	7.522626	3.311462	2.297195	H	8.864831	-2.116314	3.220528
H	3.648988	-1.329348	6.327021	H	7.104934	-1.419573	1.764401
H	3.880666	-3.793276	6.257308	H	7.614273	0.308111	1.857641
H	5.789903	-4.833401	5.025816	H	5.934310	-0.160320	2.266765
H	7.438827	-3.402186	3.870284	H	10.554509	3.026481	0.758607
H	1.581287	3.097079	2.320739	H	13.031364	3.390574	0.687320
H	3.462693	4.442127	1.253401	H	14.418325	2.996076	2.711603
H	5.934852	4.794436	0.993314	H	13.377293	2.231728	4.838177
H	7.522626	3.311462	2.297195	H	4.460228	5.447385	8.526100
H	3.648988	-1.329348	6.327021	H	5.907944	7.215630	9.509562
H	3.880666	-3.793276	6.257308	H	8.319773	7.350957	8.926700
H	5.789903	-4.833401	5.025816	H	9.333664	5.694502	7.341071
H	7.438827	-3.402186	3.870284	H	9.441743	-0.435602	3.259797
H	9.108639	-1.281689	4.800650	Li	5.700135	0.860353	7.087511