Supporting Information

A Computationally Designed Titanium-Mediated Amination of Allylic Alcohols for the Synthesis of Secondary Allylamines

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Computational Details

All calculations were performed using Gaussian 09, Revision A.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Full geometrical optimizations were carried out using Gaussian 09 suite of programs, employing the Minnesota density functional M06. The 6-31++G** basis set was used on nonmetallic atoms while the SDD basis set was employed on Ti and I. The solvent effect was dealt with using conductor-like polarizable continuum model (CPCM) in toluene. Frequency calculations were performed at the same level to identify all of the stationary points as minima (zero imaginary frequency) or transition states (one imaginary frequency) and intrinsic reaction coordinates (IRC) were calculated for each transition state to confirm that the structure indeed connects the two relevant minima.

Cartesian coordinates and energetics for all stationary points are given below.

Part I: structures in the reaction of titanium imido chloride

1. Reaction of allylic alcohol with aniline

Allylic alcohol

Zero-point correction=	0.084494 (Hartree/Particle)
Thermal correction to Energy=	0.089592
Thermal correction to Enthalpy=	0.090536
Thermal correction to Gibbs Free Energy=	0.057216
Sum of electronic and zero-point Energies=	-192.918092
Sum of electronic and thermal Energies=	-192.912995
Sum of electronic and thermal Enthalpies=	-192.912050
Sum of electronic and thermal Free Energies=	-192.945370

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	56.220	16.641	70.128
C	1.834349365927	0.073525298308	-0.213411627158
H	1.940368046369	1.075047352826	-0.629700530125
H	2.727004634983	-0.546202730171	-0.190163216651
C	0.664431794847	-0.363483215108	0.248592732148
H	0.570007125034	-1.373661427263	0.651134329022
C	-0.579072621731	0.457053031499	0.279157114469
H	-0.407982640663	1.417835829534	-0.232717964840
H	-0.845673516877	0.680112296366	1.325757608731
O	-1.620084660170	-0.282757023160	-0.343334026966
H	-2.458835527723	0.165403587157	-0.188663418597

Starting material

Zero-point correction=	0.287997 (Hartree/Particle)
Thermal correction to Energy=	0.308479
Thermal correction to Enthalpy=	0.309423
Thermal correction to Gibbs Free Energy=	0.237370
Sum of electronic and zero-point Energies=	-1534.960115
Sum of electronic and thermal Energies=	-1534.939634
Sum of electronic and thermal Enthalpies=	-1534.938689
Sum of electronic and thermal Free Energies=	-1535.010743

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin

Total	193.574	72.558	151.650
C	2.683464017109	0.082945243315	-1.010000357860
C	2.092343361779	0.000715362209	0.266174223340
C	2.926343237028	-0.088847703676	1.395593204408
C	4.309109921866	-0.092051729411	1.247564567541
C	4.886939354924	-0.005615511703	-0.019439780152
C	4.066496730249	0.080706029050	-1.145454975707
H	2.029968314777	0.147739380455	-1.879913120505
H	2.467263856258	-0.154205500865	2.380057915526
H	4.942458206405	-0.160348630102	2.129847514208
H	5.968774904550	-0.006585820427	-0.129166325370
H	4.509129917350	0.147404141148	-2.137410609374
N	0.722597040300	0.006769336410	0.389887498010
C	-0.194807442275	2.925705308290	-0.682497944518
H	-0.308082946366	4.014422282072	-0.587266695286
H	0.812814966648	2.632975546744	-0.375073295877
H	-0.335718851643	2.643449186055	-1.730864742921
C	-2.554980102747	2.681816385521	-0.157539970257
H	-2.795520587634	2.427520259700	-1.194845718559
H	-3.266682431063	2.180871660244	0.505709764403
H	-2.643098205297	3.768950710431	-0.027846021612
Cl	-2.109394735370	0.028415942575	2.192759036193
Cl	-1.434743532192	-0.015944351226	-2.112683055414
N	-1.189888261392	2.217990068894	0.141676407128
H	-0.995756078650	2.434442747118	1.120679029982
N	-1.187125309751	-2.206611862094	0.180134111757
H	-0.983192114718	-2.405892222868	1.160820856456
C	-2.553977889627	-2.678281670078	-0.098423001022
H	-3.261582725772	-2.166399607608	0.560776400933
H	-2.803424646731	-2.445699964502	-1.138741613548
H	-2.638725254783	-3.762837529827	0.053167897550
Ti	-0.943334937689	0.004757100881	0.154947094520
C	-0.199331426955	-2.928535737318	-0.641135512497
H	-0.355710833910	-2.670945316045	-1.693616562142
H	0.811367846703	-2.625918611039	-0.354000810230
H	-0.306929361373	-4.015197922547	-0.519892409085

Reaction complex

Zero-point correction=	0.279633 (Hartree/Particle)
Thermal correction to Energy=	0.299301
Thermal correction to Enthalpy=	0.300246
Thermal correction to Gibbs Free Energy=	0.231506

Sum of electronic and zero-point Energies= -1592.883498
Sum of electronic and thermal Energies= -1592.863829
Sum of electronic and thermal Enthalpies= -1592.862885
Sum of electronic and thermal Free Energies= -1592.931625

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	187.814	71.558	144.675
C	-2.327712252222	-1.153562240417	-0.920686540528
C	-1.751611550444	-0.736011808278	0.294490133201
C	-2.564107068608	-0.650815364288	1.438853118519
C	-3.915106060592	-0.969068112270	1.364070963256
C	-4.480481812279	-1.382347916818	0.156467997426
C	-3.679441454824	-1.473748112030	-0.982680415655
H	-1.693185935550	-1.208841945996	-1.805447834216
H	-2.114692551299	-0.323734211928	2.374292902399
H	-4.533726142209	-0.895893514569	2.256322271390
H	-5.537367915159	-1.632966440134	0.103979265195
H	-4.112108181009	-1.794988980118	-1.928188140943
N	-0.422685198552	-0.391476973250	0.347351300250
C	1.317622438446	-2.790512016004	-0.874706952317
H	1.780752183317	-3.786554083917	-0.876702973981
H	0.276702355893	-2.869552047275	-0.551320321518
H	1.340778557434	-2.382449830333	-1.890436145962
C	3.489255471996	-1.878358412475	-0.277530642459
H	3.637798790379	-1.495776323931	-1.292240541596
H	4.014655019489	-1.229367361368	0.429288664915
H	3.903840372677	-2.893176641681	-0.213994235309
Cl	2.314803837477	0.341472739289	2.217392218256
Cl	1.629723946638	0.496562786847	-2.057187553298
N	2.046430740324	-1.876837866552	0.023905714447
H	1.928847256084	-2.218873716164	0.979403064759
Ti	1.162670571765	0.134343403005	0.187998731549
C	0.070147910103	3.158738759985	-0.420197149687
H	0.671459820046	3.389121454745	-1.310268342516
H	-0.109322584548	4.079303325227	0.148016549603
O	0.837253010960	2.260615052244	0.421675740362
H	1.597798701878	2.720244799357	0.804496722713
C	-1.216678522261	2.508797960086	-0.790591232731
H	-1.155555080067	1.658433115498	-1.470678337212
C	-2.397014891531	2.927681437713	-0.336896482748
H	-2.478009509963	3.773362872345	0.345596152881
H	-3.323521273790	2.437054213454	-0.628622668436

TS [3,3]

Zero-point correction=	0.276211 (Hartree/Particle)
Thermal correction to Energy=	0.297274
Thermal correction to Enthalpy=	0.298219
Thermal correction to Gibbs Free Energy=	0.225121
Sum of electronic and zero-point Energies=	-1592.839156
Sum of electronic and thermal Energies=	-1592.818092
Sum of electronic and thermal Enthalpies=	-1592.817148
Sum of electronic and thermal Free Energies=	-1592.890245

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	186.542	75.622	153.846
C	0.4592277240	2.5581878193	-1.0012826852
C	0.1383344669	3.2896815059	0.1242876950
C	-1.2006669356	3.4740844365	0.4292814009
H	1.4909073930	2.3988746119	-1.3013448984
H	0.9065968057	3.5291054911	0.8570920649
H	-0.3045009207	2.3373874231	-1.7459431478
N	0.4748618469	0.4367845314	-0.2805710787
C	1.8258965014	0.1344588015	-0.2076745875
C	2.5097469587	0.1786885604	1.0201144043
C	2.5401760743	-0.2080223597	-1.3705865612
C	3.8658629767	-0.1252542454	1.0785218063
H	1.9508166223	0.4443822260	1.9161798194
C	3.8948054766	-0.5135997907	-1.3010329754
H	2.0070709895	-0.2336650860	-2.3206993477
C	4.5648139629	-0.4737883110	-0.0775511850
H	4.3813341424	-0.0915792103	2.0361755931
H	4.4325649892	-0.7835867980	-2.2076710761
H	5.6243699140	-0.7124104381	-0.0258901174
H	-1.5045994554	3.9923456256	1.3339428879
H	-1.9501537830	3.3750438431	-0.3522533972
C	-2.3864455822	-2.8174738025	-0.4505765027
H	-2.4053753076	-3.0937041419	0.6085473538
H	-3.2626249917	-2.2021369166	-0.6768697765
H	-2.4226755804	-3.7323830214	-1.0577007586
C	0.0342058230	-2.8853804951	-0.5009733375
H	0.9334610914	-2.3385219018	-0.7994188513
H	0.1105437498	-3.1263653530	0.5638128119
H	-0.0295908744	-3.8191874605	-1.0768659492

N	-1.1585379216	-2.0508671892	-0.7200661260
H	-1.1779288134	-1.7769515213	-1.7032105217
O	-1.7645672371	1.5935629391	1.0871911777
H	-2.6961056775	1.6632687478	1.3340446518
Ti	-1.1242990316	-0.0059308544	0.2505593830
Cl	-2.5872270110	0.4515684234	-1.5938943280
Cl	-0.9779533856	-1.1867390892	2.2309111592

TS [2+2]

Zero-point correction=	0.280537 (Hartree/Particle)
Thermal correction to Energy=	0.300308
Thermal correction to Enthalpy=	0.301252
Thermal correction to Gibbs Free Energy=	0.231249
Sum of electronic and zero-point Energies=	-1592.842449
Sum of electronic and thermal Energies=	-1592.822679
Sum of electronic and thermal Enthalpies=	-1592.821735
Sum of electronic and thermal Free Energies=	-1592.891737

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	188.446	72.325	147.332

C	0.2307452967	-1.7021113010	-1.3747451889
H	0.8253127649	-1.2838108874	-2.1837854713
H	0.7108386247	-2.5178063513	-0.8323155254
N	0.7860690651	-0.3835086880	-0.0517834107
C	-1.1734626068	-1.6920323552	-1.5056691239
H	-1.6303143014	-1.2089472734	-2.3664575364
C	2.1599314507	-0.2408037655	-0.0331417864
C	2.8373528727	-0.4403282232	1.1838256555
C	2.8988366863	0.1416466386	-1.1674042637
C	4.2129862745	-0.2597714471	1.2588027681
H	2.2557681075	-0.7302823799	2.0568276517
C	4.2766884514	0.3119749263	-1.0828877756
H	2.3889070167	0.3104442562	-2.1146166467
C	4.9396991891	0.1125108829	0.1273246893
H	4.7226439919	-0.4137468669	2.2074550687
H	4.8359564191	0.6067541415	-1.9682071356
H	6.0168003835	0.2470127108	0.1889009959
C	-1.9916973565	-2.6135242968	-0.6571855799
H	-1.7268787292	-3.6766102046	-0.7380335986
H	-3.0598951744	-2.4795889158	-0.8522002600
C	-0.4030515462	2.2271334166	-1.7042120681

H	-1.3879670752	2.1186837071	-2.1704300644
H	-0.0189388331	3.2351953279	-1.9106211754
H	0.2826461759	1.4926095576	-2.1412938806
C	-1.3805817652	3.0247897485	0.3694395259
H	-2.3877032318	2.9623005292	-0.0503342485
H	-1.4396951024	2.8388659223	1.4446716198
H	-0.9648492308	4.0246837114	0.1850223283
O	-1.6702306590	-2.1728875810	0.689130709
H	-2.4267783905	-2.1856250942	1.2917511954
N	-0.5341946322	1.9925887432	-0.2562616265
H	0.3959690210	2.0685763454	0.1569839285
Ti	-0.9478252671	-0.1692612353	0.1085437401
Cl	-1.2059789003	0.1854084241	2.3948429524
Cl	-3.2178839894	0.4650068768	-0.5544134620

[2+2] intermediate

Zero-point correction=	0.281745 (Hartree/Particle)
Thermal correction to Energy=	0.301456
Thermal correction to Enthalpy=	0.302400
Thermal correction to Gibbs Free Energy=	0.234159
Sum of electronic and zero-point Energies=	-1592.867662
Sum of electronic and thermal Energies=	-1592.847951
Sum of electronic and thermal Enthalpies=	-1592.847007
Sum of electronic and thermal Free Energies=	-1592.915248

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	189.167	72.872	143.626

C	0.2601679492	-2.0368150923	-0.8622805489
H	0.7032910933	-2.0527493381	-1.8728348595
H	0.5995987239	-2.9486680804	-0.3356144299
C	-1.2430033187	-1.8887493492	-0.9273379826
H	-1.6744157077	-1.8044095676	-1.9261425314
C	2.0039745203	-0.5049826151	0.0003423206
C	2.3882138387	0.5646708271	0.8369178870
C	3.0153815143	-1.1947853078	-0.6973102559
C	3.7214126321	0.9401382292	0.9448633492
H	1.6313938797	1.0642537539	1.4412646629
C	4.3470358131	-0.8101251534	-0.5769650342
H	2.7625354736	-2.0402263673	-1.3316501077
C	4.7121958322	0.2617725718	0.2348655282
H	3.9894600735	1.7651657188	1.6016699889

H	5.1090904398	-1.3592973899	-1.1264007287
H	5.7547378623	0.5569216857	0.3228171267
C	-0.1285865206	1.4884469644	-2.2779570232
H	-1.1339276149	1.3788462155	-2.6982436439
H	0.3745281978	2.3291526343	-2.7727310864
H	0.4431728837	0.5729755774	-2.4648963693
C	-0.8517963323	3.0328888681	-0.5388958060
H	-0.2772314295	3.8393098724	-1.0127698134
H	-1.8735114728	3.0388069329	-0.9278927596
H	-0.8862349715	3.1908964604	0.5423334472
C	-2.0759443181	-2.6052228587	0.0814169648
H	-1.7563315455	-3.6250094353	0.3458674020
H	-3.1338726782	-2.6142254937	-0.2036401711
N	0.6647534980	-0.8384767647	-0.1228983590
O	-1.8980595665	-1.7612394858	1.2590916865
H	-2.6669741199	-1.7139715854	1.8420308507
N	-0.2361573978	1.7232560811	-0.8248202837
H	0.7182363246	1.7477809734	-0.4531893178
Ti	-1.0783419847	-0.0481535558	0.1514510524
Cl	-0.9510680669	0.8317121248	2.2835825403
Cl	-3.1494825044	0.5882649492	-0.6994396954

TS retro-[2+2]

Zero-point correction=	0.280248 (Hartree/Particle)
Thermal correction to Energy=	0.299633
Thermal correction to Enthalpy=	0.300577
Thermal correction to Gibbs Free Energy=	0.232608
Sum of electronic and zero-point Energies=	-1592.850290
Sum of electronic and thermal Energies=	-1592.830905
Sum of electronic and thermal Enthalpies=	-1592.829961
Sum of electronic and thermal Free Energies=	-1592.897930

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	188.022	72.289	143.052

C	0.2244891477	-2.0803683276	-0.8099064721
H	0.5125354636	-1.9961561531	-1.8712500535
H	0.7466447762	-2.9625438366	-0.3970315783
N	0.5758440783	-0.8814832898	-0.0587079326
C	-1.2724099980	-2.1706238087	-0.6895098531
H	-1.8809517500	-2.1428987365	-1.5894656101
C	-1.8487274717	-2.6721066433	0.4858782794

C	1.9265059097	-0.5407281801	0.0312627582
C	2.3647216753	0.4927461925	0.8833925015
C	2.9015243842	-1.2095565117	-0.7373481603
C	3.7067233030	0.8476100943	0.9457428279
H	1.6469357824	0.9894387180	1.5307462222
C	4.2432597903	-0.8476313944	-0.6619721409
H	2.6193561081	-2.0217393950	-1.4009279595
C	4.6595906380	0.1858125114	0.1727280416
H	4.0100775225	1.6467829113	1.6189884228
H	4.9694983151	-1.3852848509	-1.2682355771
H	5.7087889253	0.4648527264	0.2271258028
C	-0.9683687025	2.9907889710	-0.6421742907
H	-0.3597470755	3.8018308026	-1.0632284643
H	-1.9165646032	2.9340288021	-1.1844301927
H	-1.1735251508	3.1971617716	0.4112719116
C	0.0696896742	1.4274885316	-2.1751311376
H	-0.8546041383	1.2699313794	-2.7398695059
H	0.6159143399	2.2719366127	-2.6160170552
H	0.6906940061	0.5286734321	-2.2429825539
H	-1.2096949475	-3.1231804228	1.2458012744
H	-2.8750059560	-3.0262336578	0.4747745903
O	-2.2944140562	-1.1631988213	1.5081289928
H	-1.9759625321	-1.1577630122	2.4214520744
N	-0.2670794751	1.6998353148	-0.7654877969
H	0.6160948099	1.7876247274	-0.2563303009
Ti	-1.1821032193	-0.0974196352	0.2406473267
Cl	-2.9990523927	0.4155698929	-1.0746576290
Cl	-0.7251941810	1.1394982847	2.1882152383

Product complex

Zero-point correction=	0.279175 (Hartree/Particle)
Thermal correction to Energy=	0.299949
Thermal correction to Enthalpy=	0.300893
Thermal correction to Gibbs Free Energy=	0.229957
Sum of electronic and zero-point Energies=	-1592.898338
Sum of electronic and thermal Energies=	-1592.877564
Sum of electronic and thermal Enthalpies=	-1592.876619
Sum of electronic and thermal Free Energies=	-1592.947556

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	188.221	75.801	149.298

C	-0.4511486597	2.4550267487	-0.4887691453
H	-1.4386344290	2.9345371001	-0.4209804047
H	0.2047481847	2.9666867499	0.2268417312
N	-0.6023856378	1.0474685518	-0.0574344404
C	0.1046769934	2.6058778274	-1.8719792690
H	-0.3562895591	1.9946354625	-2.6529880348
C	1.1077034068	3.4270372152	-2.1781068027
C	-1.9183768554	0.5386488673	-0.0806480359
C	-2.3475163523	-0.3699015130	0.9001579188
C	-2.8289586116	0.9058395386	-1.0878863662
C	-3.6228134129	-0.9251366670	0.8475225542
H	-1.6787222147	-0.6178292392	1.7224806125
C	-4.1059415889	0.3566527858	-1.1251909956
H	-2.5338340582	1.6098301009	-1.8630226980
C	-4.5093915445	-0.5715893717	-0.1669889882
H	-3.9283496491	-1.6259288570	1.6216003948
H	-4.7877687475	0.6516517867	-1.9197996362
H	-5.5066409339	-1.0026711149	-0.2032652869
C	0.8581475311	-3.0559395545	-0.5559099328
H	0.3040006574	-3.9260361961	-0.9328576355
H	1.7675632593	-2.9297879826	-1.1517016198
H	1.1372872165	-3.2275482072	0.4864024279
C	-0.4353769616	-1.6757731835	-2.0496475851
H	0.4262230172	-1.5299538989	-2.7077356934
H	-0.9858121123	-2.5701387731	-2.3721010518
H	-1.0933520686	-0.8055385116	-2.1292323232
H	1.6001138399	4.0245854164	-1.4103110901
H	1.4753623346	3.5287577809	-3.1959723737
O	1.9734920978	1.4388685800	0.8599827429
H	2.8349270299	1.7675251982	0.5794919944
N	0.0448485302	-1.8299388040	-0.6642776331
H	-0.7800602980	-1.9616078421	-0.0732503447
Ti	0.9872162668	0.0548178521	0.2900611929
Cl	2.4885488198	-0.2492243350	-1.4531736749
Cl	0.8875180396	-1.1256627713	2.2282125821

TS of product complex dissociation

Zero-point correction=	0.314575 (Hartree/Particle)
Thermal correction to Energy=	0.337693
Thermal correction to Enthalpy=	0.338637
Thermal correction to Gibbs Free Energy=	0.262691
Sum of electronic and zero-point Energies=	-1669.642025
Sum of electronic and thermal Energies=	-1669.618906

Sum of electronic and thermal Enthalpies= -1669.617962
Sum of electronic and thermal Free Energies= -1669.693908

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	211.906	83.794	159.842

C	-0.16308	2.33355	0.45004
H	-1.11764	2.81259	0.72268
H	0.56474	2.55458	1.24289
N	-0.3871	0.85706	0.4341
C	0.36812	2.88164	-0.83981
H	-0.178	2.62799	-1.75253
C	1.45428	3.64885	-0.91248
C	-1.71491	0.43864	0.1112
C	-2.20025	-0.77508	0.62397
C	-2.55591	1.19676	-0.71784
C	-3.46959	-1.23517	0.28399
H	-1.57937	-1.3718	1.29456
C	-3.82736	0.73457	-1.04361
H	-2.2203	2.14603	-1.12986
C	-4.28787	-0.48693	-0.55782
H	-3.81916	-2.18327	0.68928
H	-4.45952	1.33681	-1.69379
H	-5.27872	-0.84732	-0.82593
C	1.09858	-2.81992	-1.61393
H	0.54286	-3.45695	-2.31522
H	2.03503	-2.50472	-2.0862
H	1.32924	-3.39087	-0.70968
C	-0.1107	-0.92956	-2.50563
H	0.78084	-0.56915	-3.03003
H	-0.6586	-1.61524	-3.16648
H	-0.75484	-0.07619	-2.26833
H	2.03131	3.90706	-0.02254
H	1.81175	4.04829	-1.85926
O	2.07155	0.76871	1.54699
H	2.96691	1.13704	1.58934
N	0.30578	-1.61921	-1.26789
H	-0.54787	-1.95635	-0.81114
Cl	2.85483	0.01311	-1.19332
Cl	0.9535	-2.0444	1.70008
Ti	1.24489	-0.2792	0.33666
H	-1.57726	0.70788	3.31156
O	-0.62424	0.5889	3.11414

H	-0.45411	0.65159	2.0845
H	-0.10358	1.26651	3.59379

Allylamine

Zero-point correction=	0.177851 (Hartree/Particle)
Thermal correction to Energy=	0.187150
Thermal correction to Enthalpy=	0.188094
Thermal correction to Gibbs Free Energy=	0.142752
Sum of electronic and zero-point Energies=	-403.840204
Sum of electronic and thermal Energies=	-403.830905
Sum of electronic and thermal Enthalpies=	-403.829961
Sum of electronic and thermal Free Energies=	-403.875304

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	117.438	35.967	95.431

C	2.00581	-0.03497	-0.83464
H	1.7425	-0.93209	-1.40973
H	2.77531	0.48301	-1.42089
N	0.83857	0.82712	-0.76138
C	2.55222	-0.40182	0.51258
H	1.84616	-0.86758	1.20546
C	3.80545	-0.15936	0.8971
C	-0.40641	0.37081	-0.35161
C	-1.34881	1.29289	0.13707
C	-0.78519	-0.97786	-0.44837
C	-2.62058	0.88166	0.50793
H	-1.06771	2.34334	0.22318
C	-2.06668	-1.37592	-0.07612
H	-0.08493	-1.72194	-0.82051
C	-2.99537	-0.45855	0.40555
H	-3.32524	1.61782	0.89005
H	-2.33658	-2.42624	-0.16275
H	-3.99058	-0.77981	0.70068
H	4.52187	0.31295	0.22278
H	4.16392	-0.42116	1.88993
H	1.04264	1.78056	-0.48545

TiCl2O

Zero-point correction=	0.005535 (Hartree/Particle)
Thermal correction to Energy=	0.010846
Thermal correction to Enthalpy=	0.011790

Thermal correction to Gibbs Free Energy=	-0.025213
Sum of electronic and zero-point Energies=	-1054.091331
Sum of electronic and thermal Energies=	-1054.086020
Sum of electronic and thermal Enthalpies=	-1054.085076
Sum of electronic and thermal Free Energies=	-1054.122080

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	6.806	14.707	77.881

O	1.97057	1.09426	1.27752
Cl	3.02222	-0.71255	-1.02881
Cl	0.97674	-1.80336	1.82696
Ti	1.43217	-0.13261	0.42251

2. Reaction of 2-methylallyl alcohol with aniline

2-methylallyl alcohol

Zero-point correction=	0.112608 (Hartree/Particle)
Thermal correction to Energy=	0.118993
Thermal correction to Enthalpy=	0.119937
Thermal correction to Gibbs Free Energy=	0.083191
Sum of electronic and zero-point Energies=	-232.180420
Sum of electronic and thermal Energies=	-232.174036
Sum of electronic and thermal Enthalpies=	-232.173092
Sum of electronic and thermal Free Energies=	-232.209838

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	74.669	22.032	77.339

C	-1.50684	-1.00216	-0.19683
H	-1.29119	-2.06921	-0.19987
H	-2.5307	-0.7033	-0.4142
C	-0.55829	-0.09948	0.06717
C	0.83052	-0.53061	0.42878
H	0.91804	-1.62518	0.35296
H	1.03072	-0.24765	1.47736
O	1.7566	0.11845	-0.43237
H	2.64969	-0.05812	-0.11789
C	-0.80712	1.37559	0.06241
H	-0.199	1.86917	-0.70465
H	-1.86045	1.60391	-0.12808

H	-0.51957	1.82273	1.02408

TS [3,3]

Zero-point correction=	0.304561 (Hartree/Particle)
Thermal correction to Energy=	0.326766
Thermal correction to Enthalpy=	0.327710
Thermal correction to Gibbs Free Energy=	0.253290
Sum of electronic and zero-point Energies=	-1632.100636
Sum of electronic and thermal Energies=	-1632.078431
Sum of electronic and thermal Enthalpies=	-1632.077486
Sum of electronic and thermal Free Energies=	-1632.151906

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	205.049	80.896	156.630

C	0.7697600433	2.8288184528	-0.6534134644
C	0.0737430037	3.4357500847	0.3718269335
C	-1.2836992258	3.6339318239	0.1581579843
H	1.8423402387	2.6630176537	-0.5843469152
H	0.3223443221	2.7160666699	-1.6393120983
N	0.5337785988	0.6244782423	-0.2257375186
C	1.8345043681	0.1666563083	-0.3563851285
C	2.6676458618	0.0351673673	0.7681138707
C	2.3349073819	-0.1820560758	-1.6234835795
C	3.9567773978	-0.4668771917	0.6270205651
H	2.2721569549	0.3133553134	1.7443723137
C	3.6260312596	-0.6834463053	-1.7530857263
H	1.6815170292	-0.0691789334	-2.4890744899
C	4.4415134869	-0.8319100932	-0.6303138457
H	4.5890037333	-0.5766656212	1.5058043382
H	3.9988615464	-0.9611225565	-2.7369470304
H	-1.9066777029	4.1032630993	0.9154690857
H	-1.6873732649	3.5836190079	-0.8502851113
C	-2.1291366579	-2.7945829487	-0.3213670405
H	-2.3117255445	-2.9106641238	0.7519821947
H	-2.9613059261	-2.2451680718	-0.771934855
H	-2.0646344818	-3.7901750137	-0.7809173471
C	0.2611793741	-2.8120339538	0.026107739
H	1.2062632161	-2.3206024059	-0.221604781
H	0.170936742	-2.8691338651	1.1147899226
H	0.2679311831	-3.8292660951	-0.389499019
N	-0.8750909666	-2.0414312089	-0.5094518487

H	-0.7360724392	-1.9254139463	-1.5148279794
O	-2.0166821311	1.735340151	0.5881146607
H	-2.9577053787	1.7983535598	0.3772568724
Ti	-1.093598879	0.1293899803	0.122356305
Cl	-2.242937138	0.192110987	-1.9880586802
Cl	-1.0941872783	-0.7287588226	2.2857795766
H	5.4498006449	-1.2252612991	-0.734619825
C	0.660095006	3.553169345	1.7473291274
H	0.3634077601	2.6853162192	2.3550985292
H	1.7545213244	3.5745837103	1.7154443877
H	0.3112369875	4.4529156961	2.2654243376

TS [2+2]

Zero-point correction=	0.308305 (Hartree/Particle)
Thermal correction to Energy=	0.329460
Thermal correction to Enthalpy=	0.330404
Thermal correction to Gibbs Free Energy=	0.258672
Sum of electronic and zero-point Energies=	-1632.099784
Sum of electronic and thermal Energies=	-1632.078629
Sum of electronic and thermal Enthalpies=	-1632.077685
Sum of electronic and thermal Free Energies=	-1632.149417

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	206.739	77.998	150.973

C	0.2334177403	-1.6677591446	-1.2895660177
H	0.8791386399	-1.3288869703	-2.0992035592
H	0.6633854408,	-2.456706741	-0.6705998179
N	0.7956519458	-0.2762609481	-0.0582564614
C	-1.1660539981	-1.6282710097	-1.5094324781
C	2.1751625549	-0.2076698987	-0.0272694025
C	2.8465393069	-0.6161473577	1.1382047965
C	2.9247104356	0.2875891143	-1.1092711941
C	4.2308995236	-0.5236627891	1.2186960278
H	2.2543075369	-0.9916577523	1.9705980907
C	4.3101057558	0.372897771	-1.0200413821
H	2.4109440351	0.6066469454	-2.0153019947
C	4.9683786069	-0.0311831035	0.1412279551
H	4.7389689137	-0.8387041261	2.127457439
H	4.8797619624	0.7606471186	-1.8619138425
C	-2.0015532812	-2.5268057591	-0.641581714
H	-1.7841031762	-3.6012038421	-0.7367040082

H	-3.068930524	-2.3496895799	-0.816672592
C	-0.5688510819	2.329768843	-1.7218961482
H	-1.5885906319	2.1998616025	-2.0996759358
H	-0.2260716219	3.3466545436	-1.9561715592
H	0.090266486	1.6119649085	-2.2232751675
C	-1.3603882053	3.1101484587	0.4349321732
H	-2.4051194724	3.025221066	0.1256352006
H	-1.2989732958	2.9375858916	1.5122081566
H	-0.9875412903	4.1157739114	0.1973980015
O	-1.6367382384	-2.0990607829	0.6920580624
H	-2.376614451	-2.111774224	1.3150370342
N	-0.5659225086	2.0874664283	-0.2694473434
H	0.3973082745	2.1687940519	0.0568793611
Ti	-0.9364485784	-0.0782875749	0.1197847601
Cl	-1.1405836114	0.2300405471	2.4238937166
Cl	-3.242885161	0.5259411817	-0.4236106292
H	6.051490047	0.0378425768	0.2058504277
C	-1.7039996748	-1.2069693194	-2.8511343646
H	-1.0705266216	-0.4383115128	-3.3126140165
H	-1.7369446477	-2.0566496682	-3.5497003818
H	-2.7176216544	-0.7994194161	-2.7640139726

TS retro-[2+2]

Zero-point correction=	0.308397 (Hartree/Particle)
Thermal correction to Energy=	0.329029
Thermal correction to Enthalpy=	0.329973
Thermal correction to Gibbs Free Energy=	0.259843
Sum of electronic and zero-point Energies=	-1632.105622
Sum of electronic and thermal Energies=	-1632.084990
Sum of electronic and thermal Enthalpies=	-1632.084045
Sum of electronic and thermal Free Energies=	-1632.154175

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	206.469	77.653	147.601

C	0.1710630483	-2.0374547616	-0.8471607664
H	0.4124346515	-1.9043960308	-1.9170942785
H	0.7235423441	-2.9320948664	-0.5029291533
N	0.5335837462	-0.8715489747	-0.057495043
C	-1.32811384	-2.1597309911	-0.6866215474
C	-1.789639316	-2.6231187773	0.5584400503
C	1.8867745836	-0.5398199994	0.0330946854

C	2.3381293999	0.4287417839	0.9514644463
C	2.8482925578	-1.1532371655	-0.7959037893
C	3.6821677054	0.7747617138	1.0220042782
H	1.6267901474	0.8823643781	1.6367401312
C	4.1921352787	-0.8006260087	-0.7122899418
H	2.5527027806	-1.9127105778	-1.5142968852
C	4.6224874642	0.1676820563	0.1905536012
H	3.9971339849	1.5226215539	1.74698547
H	4.9089951083	-1.2931035931	-1.3662197284
C	-0.8740833354	3.0402525178	-0.6353778748
H	-0.2324047948	3.8245262746	-1.0583036841
H	-1.8262812336	3.0272448207	-1.1730656377
H	-1.0647717195	3.2527389473	0.4194417902
C	0.0714902818	1.4370635519	-2.1818061078
H	-0.8681316783	1.3258100385	-2.7330063671
H	0.6507248762	2.2564970893	-2.6278444909
H	0.6487403971	0.5108596212	-2.2647581192
H	-1.0735641167	-2.939780641	1.3168956231
H	-2.7718169501	-3.084825028	0.6271590514
O	-2.3553110276	-1.0938526431	1.4931903595
H	-2.0790383955	-1.0310179788	2.4184336937
N	-0.2325188965	1.7193764048	-0.7666593633
H	0.6603498112	1.7676804782	-0.2688751033
Ti	-1.2105833585	-0.0510265983	0.2384005394
Cl	-3.0110573305	0.5525884885	-1.0442071815
Cl	-0.7677261583	1.1895202147	2.1867054856
H	5.6733874501	0.438830439	0.2522434522
C	-2.1443388904	-2.4164450482	-1.9283505984
H	-1.8960540445	-3.3968544749	-2.3645098429
H	-3.2183556114	-2.4048051582	-1.7126278052
H	-1.9601704095	-1.6594420055	-2.7012707383

Part II: structures in the reaction of titanium imido iodide

Starting material

Zero-point correction=	0.286647 (Hartree/Particle)
Thermal correction to Energy=	0.307932
Thermal correction to Enthalpy=	0.308876
Thermal correction to Gibbs Free Energy=	0.232293
Sum of electronic and zero-point Energies=	-637.397524
Sum of electronic and thermal Energies=	-637.376239
Sum of electronic and thermal Enthalpies=	-637.375295

Sum of electronic and thermal Free Energies= -637.451878

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	193.230	73.302	161.182
C	2.722922122069	0.036339689191	-1.045836731332
C	2.086066837590	-0.003535498073	0.208268365859
C	2.868429329930	-0.033940216379	1.375371613407
C	4.256030837514	-0.024688467339	1.282917262674
C	4.883465906167	0.014436264576	0.037101031907
C	4.110449810996	0.044919066164	-1.124562690221
H	2.103260915438	0.060030252599	-1.941858694289
H	2.367864275038	-0.064335091446	2.341349138267
H	4.853704192591	-0.048313361691	2.191797957887
H	5.968887367406	0.021336708169	-0.027874773168
H	4.593232453982	0.075531151412	-2.099134479471
N	0.711205722720	-0.011588467472	0.274746286152
C	-0.208114063554	2.994091987475	-0.514114752219
H	-0.331756483757	4.065237108625	-0.303774200521
H	0.794288375793	2.675425383910	-0.215505020985
H	-0.323127378375	2.826552760703	-1.590252627304
C	-2.578700356381	2.702074605029	-0.063852486527
H	-2.794339638596	2.578743515634	-1.129966346010
H	-3.309748946239	2.128229978298	0.514962882308
H	-2.666741895643	3.764768958227	0.197897521513
N	-1.219362837916	2.200268553968	0.210942332168
H	-1.045542067693	2.331812549565	1.209731043215
N	-1.208958900258	-2.222777119648	0.045988793034
H	-1.032289464359	-2.428020891549	1.031716572069
C	-2.566590119901	-2.709160576415	-0.263018635793
H	-3.299043375338	-2.182421984199	0.357186582195
H	-2.784530501174	-2.509096961584	-1.316981745381
H	-2.649784770107	-3.788585612151	-0.079627806243
Ti	-0.950132233838	-0.009070735005	0.091025111389
C	-0.195959430456	-2.955503400256	-0.738340694899
H	-0.315054739853	-2.709361108478	-1.798643324723
H	0.805714095798	-2.654478324114	-0.419751453106
H	-0.313662481865	-4.039780220172	-0.607629576176
I	-2.130600514399	-0.104907140021	2.617120926385
I	-1.445152863254	0.089285552379	-2.606993631868

Reaction complex

Zero-point correction=	0.279029 (Hartree/Particle)
Thermal correction to Energy=	0.300575
Thermal correction to Enthalpy=	0.301519
Thermal correction to Gibbs Free Energy=	0.224781
Sum of electronic and zero-point Energies=	-695.320886
Sum of electronic and thermal Energies=	-695.299340
Sum of electronic and thermal Enthalpies=	-695.298396
Sum of electronic and thermal Free Energies=	-695.375134

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	188.614	74.478	161.508
C	-2.373646227100	-1.128578878275	-0.996993987138
C	-1.739927239323	-0.727664551618	0.191853004650
C	-2.485762924598	-0.654040134237	1.380301773213
C	-3.839780592050	-0.966415278186	1.372079846977
C	-4.468582475592	-1.357519077452	0.188549636284
C	-3.729325011889	-1.438730722390	-0.992206360920
H	-1.783582423573	-1.175547400493	-1.912229619695
H	-1.983468742332	-0.337819379064	2.292866024923
H	-4.411367653765	-0.902843988567	2.295597300035
H	-5.528658089323	-1.599596800173	0.187032364525
H	-4.213911854410	-1.743748688327	-1.917368262541
N	-0.408740929187	-0.382898615280	0.182503038127
C	1.370998827582	-2.842131059639	-0.835463072975
H	1.813035986907	-3.842180708081	-0.729774235658
H	0.314826777557	-2.874171762634	-0.555731359431
H	1.448737145651	-2.525293414486	-1.880745216917
C	3.534186910039	-1.912287780568	-0.231596667292
H	3.725449374179	-1.601666176144	-1.263773516970
H	4.048342030471	-1.225300726818	0.448217975297
H	3.926788023405	-2.927007382507	-0.084064421105
N	2.080013608280	-1.869577679634	0.020721238697
H	1.933921175485	-2.161025065215	0.989869412817
Ti	1.171519378699	0.145958907995	0.109060270318
C	0.014062667160	3.172627196120	-0.438022622813
H	0.574043643953	3.438566324871	-1.345791202901
H	-0.144056252148	4.068800699420	0.172871589038
O	0.837885984676	2.255037712819	0.333833131776
H	1.577372578762	2.730882668176	0.738936747321
C	-1.280601872581	2.522180036336	-0.772166315432
H	-1.238792195434	1.685647199723	-1.471040638908
C	-2.446539763488	2.929361224070	-0.273208967679

H	-2.507767570709	3.760081473336	0.429122372845
H	-3.381422104421	2.446762030639	-0.550420405021
I	2.252912420619	0.347772281308	2.664040281474
I	1.762145678418	0.549897834883	-2.542980554545

TS [3,3]

Zero-point correction=	0.275180 (Hartree/Particle)
Thermal correction to Energy=	0.296938
Thermal correction to Enthalpy=	0.297882
Thermal correction to Gibbs Free Energy=	0.221387
Sum of electronic and zero-point Energies=	-695.281212
Sum of electronic and thermal Energies=	-695.259454
Sum of electronic and thermal Enthalpies=	-695.258510
Sum of electronic and thermal Free Energies=	-695.335005

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	186.331	76.203	160.997

C	-0.3293516498	1.5107667461	2.7900864641
C	-0.4194316021	0.3694894641	3.5598887844
C	-1.5184651319	-0.4513865130	3.4174197363
H	0.5304497911	2.1754514980	2.8510797946
H	0.4594397414	0.0197530197	4.1158371968
H	-1.2138892146	1.8974236985	2.2810165874
N	0.4021641132	0.9076964013	0.7172279741
C	1.1018197743	2.0446897461	0.3398746746
C	2.4894279462	2.1297298746	0.5389301517
C	0.4238713210	3.1227197447	-0.2539764133
C	3.1845016743	3.2594997413	0.1203398763
H	3.0024297647	1.2873041645	0.9994964655
C	1.1309036467	4.2471379460	-0.6688931321
H	-0.6537013465	3.0449739874	-0.3967613486
C	2.5115464613	4.3201064963	-0.4875196744
H	4.2606565464	3.3117906149	0.26632978131
H	0.5999187412	5.0716161318	-1.13945643234
H	3.0600046799	5.2001697461	-0.81511976222
H	-1.6119037981	-1.3753679541	3.98263049174
H	-2.4225997467	-0.0684497461	2.94437979643
C	-0.3608397613	-1.4188803497	-2.88593797936
H	0.3297996131	-2.2536179416	-2.72717974613
H	-1.3692174936	-1.7244498763	-2.58643967464
H	-0.3691779749	-1.1573697466	-3.95244794637

C	1.3977996310	0.2091994637	-2.53176946315
H	1.6941455135	1.0995398746	-1.97168131378
H	2.1450213138	-0.5719313984	-2.37119746020
H	1.3584894613	0.4544779411	-3.60096796346
N	0.0800094137	-0.2714596436	-2.06706973443
H	-0.5904997497	0.4840564654	-2.23240646377
O	-1.0477246419	-1.4249079641	1.62943941461
H	-1.6634797413	-2.1653936165	1.54361974131
Ti	-0.2536516457	-0.5823313133	0.13879064974
I	-2.8943519654	0.2701467961	-0.58391654936
I	1.8625379841	-2.3650706548	0.06577791101

TS [2+2]

Zero-point correction=	0.279681 (Hartree/Particle)
Thermal correction to Energy=	0.300130
Thermal correction to Enthalpy=	0.301074
Thermal correction to Gibbs Free Energy=	0.227454
Sum of electronic and zero-point Energies=	-695.283758
Sum of electronic and thermal Energies=	-695.263310
Sum of electronic and thermal Enthalpies=	-695.262366
Sum of electronic and thermal Free Energies=	-695.335986

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	188.334	72.756	154.948

C	0.246037350268	-1.582048623327	-1.386426404215
H	0.815716607197	-1.134416326621	-2.198814730842
H	0.753621644301	-2.402939593450	-0.876901189407
N	0.800637677325	-0.298170779528	-0.049710566744
C	-1.166362010762	-1.610350643482	-1.479944285902
H	-1.662067722711	-1.166725504464	-2.341057976640
C	2.182220211295	-0.231880841198	0.011658241166
C	2.834022323446	-0.732399472483	1.150798671055
C	2.939110358662	0.357695020090	-1.014432304957
C	4.216040727912	-0.633164296261	1.260198682859
H	2.231820404926	-1.180699917812	1.938708038537
C	4.322072664018	0.446317589549	-0.896709009010
H	2.436037669131	0.746126058718	-1.898880151556
C	4.964033478296	-0.046358049991	0.239189876973
H	4.713493761579	-1.016045611604	2.148352192052
H	4.901479955286	0.906442108105	-1.694019837263
H	6.045066096488	0.027179834582	0.328553745900

C	-1.902297616551	-2.588355783439	-0.616840243280
H	-1.569027321815	-3.630532465585	-0.714732709871
H	-2.983190266197	-2.523736588629	-0.775129651608
C	-0.597741174907	2.178782238948	-1.849696205836
H	-1.629049514684	2.089907342382	-2.207838622261
H	-0.194595198732	3.152984490702	-2.156399368304
H	0.006516452757	1.389707515689	-2.310795027073
C	-1.321922221410	3.154974554779	0.247706793701
H	-2.370169800179	3.115644220262	-0.058057347361
H	-1.269746154044	3.059940594068	1.335116861979
H	-0.886272124526	4.114306505386	-0.062151502086
O	-1.563538906662	-2.131701468666	0.720878182853
H	-2.299475351843	-2.199675023022	1.346287100521
N	-0.587103165510	2.039208605086	-0.380831892035
H	0.383157301194	2.116430097469	-0.072477522542
Ti	-0.922191495581	-0.104139876326	0.120625596297
I	-3.729166388685	0.496722081731	-0.348878221057
I	-0.994849119090	0.304286908661	2.853274106365

[2+2] intermediate

Zero-point correction=	0.280907 (Hartree/Particle)
Thermal correction to Energy=	0.301352
Thermal correction to Enthalpy=	0.302297
Thermal correction to Gibbs Free Energy=	0.229515
Sum of electronic and zero-point Energies=	-695.303760
Sum of electronic and thermal Energies=	-695.283314
Sum of electronic and thermal Enthalpies=	-695.282370
Sum of electronic and thermal Free Energies=	-695.355151

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	189.101	73.414	153.181

C	0.261551455167	-1.994988866970	-0.864399624965
H	0.720026840380	-1.998309496249	-1.867120003555
H	0.591195575647	-2.908710693283	-0.336703088129
C	-1.244022795573	-1.862222198226	-0.957416295736
H	-1.654300056653	-1.790178810132	-1.965324564233
C	2.018406485654	-0.486710159154	0.009497101027
C	2.418188133769	0.614013217392	0.795189773972
C	3.020467688884	-1.234501934538	-0.639812341404
C	3.758330696371	0.964033166871	0.901282859598

H	1.670705170083	1.161891399330	1.368826208238
C	4.359457946977	-0.876362482425	-0.520133230781
H	2.758097010801	-2.105599166186	-1.233589863556
C	4.740392535034	0.226642118845	0.240573572662
H	4.037605016238	1.815025288951	1.518919201014
H	5.113973489533	-1.471698274823	-1.030182496288
H	5.788686037110	0.500609893734	0.328635503177
C	-0.166378332810	1.492705786336	-2.270476554538
H	-1.170713695013	1.439779181906	-2.703471519095
H	0.389465626867	2.305200089564	-2.756131405631
H	0.357654548567	0.547888347957	-2.451825130449
C	-0.851586453520	3.073719065921	-0.555521296641
H	-0.248445506332	3.847204111708	-1.048407896800
H	-1.872722281817	3.107660611073	-0.944435909168
H	-0.878835153733	3.260785218133	0.521472844633
C	-2.059546791452	-2.624268440402	0.033554033241
H	-1.735423536480	-3.654674997016	0.245414118625
H	-3.123733346293	-2.618962030355	-0.227888394792
N	0.671481564642	-0.799091088937	-0.111905570692
O	-1.844427896013	-1.826633233531	1.233403717238
H	-2.594088530241	-1.807209063220	1.843769379943
N	-0.279623241706	1.736725480952	-0.816204681117
H	0.677513169150	1.750041764568	-0.450320228123
Ti	-1.075253585182	-0.064450678381	0.162014822977
I	-3.609088697234	0.639067916754	-0.727022077742
I	-1.017939860851	0.925445323718	2.714738147053

TS retro-[2+2]

Zero-point correction=	0.278658 (Hartree/Particle)
Thermal correction to Energy=	0.298884
Thermal correction to Enthalpy=	0.299829
Thermal correction to Gibbs Free Energy=	0.227673
Sum of electronic and zero-point Energies=	-695.282666
Sum of electronic and thermal Energies=	-695.262440
Sum of electronic and thermal Enthalpies=	-695.261495
Sum of electronic and thermal Free Energies=	-695.333652

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	187.553	73.323	151.865

C	0.244724430676	-2.037561302578	-0.813582764016
H	0.592832918046	-1.939248738291	-1.854922950408

H	0.716107996691	-2.943291545918	-0.392172856481
N	0.593312012254	-0.861538895794	-0.019333556452
C	-1.256294214030	-2.089072894428	-0.766139275565
H	-1.827211499698	-1.967087070690	-1.683080229069
C	-1.886071482071	-2.671234165605	0.342013215174
C	1.946843624113	-0.525746940754	0.071129569850
C	2.383113725253	0.534645501905	0.888458982620
C	2.924600071767	-1.222772832211	-0.669218453092
C	3.725120298747	0.888593326322	0.949013164386
H	1.667015333035	1.059747175594	1.515729680923
C	4.266249309205	-0.861213774853	-0.597641257505
H	2.646076658420	-2.057800991542	-1.304905469816
C	4.680560809994	0.198057830845	0.204982876737
H	4.025584692752	1.709495915173	1.596704705554
H	4.994773026893	-1.420746238452	-1.180750193284
H	5.730213432537	0.475798766076	0.256756447755
C	-0.918208836704	3.025149136964	-0.723722725461
H	-0.258958964227	3.763883762357	-1.197828948109
H	-1.873923996361	3.001053487323	-1.254776699656
H	-1.098701663056	3.308240798432	0.315946913763
C	-0.020267487793	1.326185507402	-2.186333461044
H	-0.966253596988	1.154025011730	-2.710895736871
H	0.519962890765	2.138876595937	-2.689113756282
H	0.589104885605	0.419230980699	-2.232877077947
H	-1.301882022640	-3.261195753015	1.048275860440
H	-2.944680990116	-2.910131253309	0.292753028022
O	-2.157216635413	-1.259514034324	1.571589170265
H	-1.780924259505	-1.402277460373	2.450714160434
N	-0.302906606783	1.683387642520	-0.778879593723
H	0.604488579402	1.758405970926	-0.309643007967
Ti	-1.169359107387	-0.104815661252	0.304921616853
I	-3.519847829795	0.538326763784	-0.953873433645
I	-0.840228933582	1.451829050246	2.606412333535

Product complex

Zero-point correction=	0.277184 (Hartree/Particle)
Thermal correction to Energy=	0.299213
Thermal correction to Enthalpy=	0.300157
Thermal correction to Gibbs Free Energy=	0.222561
Sum of electronic and zero-point Energies=	-695.335472
Sum of electronic and thermal Energies=	-695.313442
Sum of electronic and thermal Enthalpies=	-695.312498
Sum of electronic and thermal Free Energies=	-695.390094

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	187.759	76.966	163.314
C	0.5620789413	1.4976197946	2.3562179613
H	0.0775013456	2.4246597461	2.6966397644
H	0.3418479417	0.7206597413	3.0991797431
N	-0.0844703198	1.1148506949	1.0783594614
C	2.0440879416	1.6950306402	2.2597784136
H	2.4040574612	2.3209398763	1.4422397615
C	2.9157597425	1.1585897436	3.1113974631
C	-0.7695297641	2.1511406499	0.3895574600
C	-2.1106697461	1.9848274633	0.0224997314
C	-0.1200374613	3.3525465987	0.0669937982
C	-2.7748294136	2.9794946355	-0.6920064619
H	-2.6339579657	1.0773993166	0.3202413160
C	-0.7941479841	4.3473034602	-0.6305897463
H	0.9208796416	3.4992087465	0.3492366777
C	-2.1203564145	4.1617145614	-1.0261096439
H	-3.8158439416	2.8301265252	-0.9716064947
H	-0.2766064691	5.2715749698	-0.8769835787
H	-2.6403064673	4.9400298466	-1.5785067482
C	-0.4825036486	-1.5505064671	-2.6579497466
H	-0.9259684134	-1.3780642650	-3.6470603641
H	0.5663064681	-1.8373813649	-2.7806274634
H	-1.0214394137	-2.3591494131	-2.1566697413
C	-0.0114994136	0.8165623360	-2.6295597641
H	1.0183397461	0.5906112146	-2.9184997423
H	-0.6174591346	0.9675397167	-3.5328946180
H	-0.0131665149	1.7370984152	-2.0381332561
H	2.5882472972	0.5035898748	3.9182484108
H	3.9835141313	1.3450097467	3.0271498417
O	0.7820094691	-1.4405294135	1.7193334968
H	1.3971064657	-2.1404906460	1.9644394137
N	-0.5474979619	-0.3173497374	-1.8411203181
H	-1.5417861349	-0.1251700216	-1.6916198746
Ti	0.1214279611	-0.5806296414	0.3272706549
I	2.6564675137	-0.7056054004	-0.8196604883
I	-2.3233574581	-1.8838171675	0.5618901969

Part III: structures in the reaction of $PhN=Ti(NMe_2)_2(HNMe_2)_2$

Starting material

Zero-point correction=	0.438022 (Hartree/Particle)
Thermal correction to Energy=	0.464347
Thermal correction to Enthalpy=	0.465291
Thermal correction to Gibbs Free Energy=	0.383297
Sum of electronic and zero-point Energies=	-941.254251
Sum of electronic and thermal Energies=	-941.227926
Sum of electronic and thermal Enthalpies=	-941.226981
Sum of electronic and thermal Free Energies=	-941.308975

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	291.382	98.098	172.570

C	3.05304	-0.10377	-1.07001
C	2.31994	0.00162	0.13556
C	3.06775	0.08322	1.33362
C	4.45505	0.04986	1.32319
C	5.15717	-0.06452	0.1238
C	4.44102	-0.13904	-1.06984
H	2.49919	-0.16361	-2.00788
H	2.52295	0.17409	2.274
H	4.99799	0.1133	2.26636
H	6.24533	-0.09349	0.11977
H	4.97267	-0.22588	-2.01763
N	0.95652	0.02073	0.14524
C	-0.06154	3.03572	-0.58705
H	-0.0174	4.11085	-0.34847
H	0.95377	2.62826	-0.64186
H	-0.54049	2.91239	-1.56586
C	-2.17905	2.85968	0.55236
H	-2.74414	2.66948	-0.36999
H	-2.69588	2.38062	1.39002
H	-2.15187	3.94781	0.72574
N	-0.83802	2.29269	0.40842
H	-0.35849	2.35201	1.30727
N	-0.82008	-2.23009	-0.17164
H	-0.2286	-2.48979	0.6201
C	-2.1244	-2.87331	-0.00864
H	-2.55366	-2.59825	0.96084
H	-2.79591	-2.52238	-0.80386
H	-2.05482	-3.971	-0.07628
Ti	-0.77086	0.04153	0.08227

C	-0.16451	-2.67519	-1.4042
H	-0.75387	-2.32337	-2.2606
H	0.83499	-2.23223	-1.46583
H	-0.08576	-3.7738	-1.45259
N	-1.56994	-0.23643	1.8683
N	-1.53081	0.26138	-1.72065
C	-0.88866	-0.74892	3.02984
H	-1.11289	-0.15826	3.94103
H	-1.18726	-1.79522	3.26174
H	0.19779	-0.73593	2.88043
C	-2.98949	-0.19359	2.10827
H	-3.40078	-1.17942	2.41539
H	-3.26057	0.51614	2.91708
H	-3.54657	0.11836	1.20938
C	-2.93668	0.07049	-1.96361
H	-3.41304	0.95884	-2.42775
H	-3.13345	-0.78307	-2.64758
H	-3.4886	-0.13395	-1.03028
C	-0.84365	0.51108	-2.96008
H	-0.96793	-0.32257	-3.68372
H	-1.2262	1.41939	-3.47202
H	0.23295	0.64893	-2.79385

Reaction complex

Zero-point correction=	0.437554 (Hartree/Particle)
Thermal correction to Energy=	0.465075
Thermal correction to Enthalpy=	0.466019
Thermal correction to Gibbs Free Energy=	0.380408
Sum of electronic and zero-point Energies=	-941.223984
Sum of electronic and thermal Energies=	-941.196463
Sum of electronic and thermal Enthalpies=	-941.195519
Sum of electronic and thermal Free Energies=	-941.281131

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	291.839	100.023	180.184

C	-2.70132	-1.05856	-1.08781
C	-2.00092	-0.83615	0.1197
C	-2.76333	-0.77223	1.30913
C	-4.14439	-0.9094	1.28608
C	-4.81919	-1.12333	0.08296
C	-4.08376	-1.19715	-1.10057

H	-2.12928	-1.10889	-2.01692
H	-2.23362	-0.59098	2.24649
H	-4.70497	-0.8481	2.22049
H	-5.90268	-1.23019	0.06854
H	-4.59518	-1.36217	-2.04992
N	-0.64972	-0.64968	0.13984
C	1.11221	-2.59023	-1.71015
H	1.56675	-3.54636	-2.0163
H	0.07075	-2.74849	-1.41464
H	1.13005	-1.90357	-2.56545
C	3.26623	-1.8337	-0.92151
H	3.36255	-1.13338	-1.76116
H	3.80076	-1.42304	-0.05708
H	3.72347	-2.795	-1.20498
N	1.84479	-1.9756	-0.59933
H	1.75656	-2.57717	0.22161
Ti	0.96613	-0.05797	0.16558
C	-0.11949	3.032	0.32644
H	0.60114	3.38915	-0.42475
H	-0.33431	3.84603	1.03167
O	0.46978	1.93754	1.05153
H	1.1227	2.25531	1.69482
C	-1.37426	2.55307	-0.31853
H	-1.25631	1.77268	-1.07207
C	-2.5842	3.00184	0.00657
H	-2.72614	3.76691	0.77112
H	-3.483	2.61661	-0.47382
N	1.45634	0.87855	-1.48717
N	1.91338	-0.36336	1.86951
C	0.82293	0.86234	-2.77945
H	0.5478	1.88329	-3.12554
H	1.488	0.43931	-3.56395
H	-0.09426	0.25835	-2.75712
C	2.63366	1.70862	-1.51754
H	3.40975	1.32456	-2.20979
H	2.40792	2.74324	-1.84867
H	3.10124	1.78531	-0.52275
C	3.1914	0.2301	2.17253
H	3.16657	0.85324	3.09272
H	3.98588	-0.52742	2.33548
H	3.54063	0.87926	1.35099
C	1.4934	-1.23762	2.93558
H	2.19775	-2.08629	3.07943
H	1.43967	-0.712	3.91103

H	0.4993	-1.65215	2.7251

TS [3,3]

Zero-point correction=	0.437901 (Hartree/Particle)
Thermal correction to Energy=	0.462880
Thermal correction to Enthalpy=	0.463824
Thermal correction to Gibbs Free Energy=	0.385203
Sum of electronic and zero-point Energies=	-941.172630
Sum of electronic and thermal Energies=	-941.147651
Sum of electronic and thermal Enthalpies=	-941.146707
Sum of electronic and thermal Free Energies=	-941.225328

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	290.462	95.109	165.473

C	0.6282	2.65688	-0.24807
C	-0.11661	3.19131	0.86044
C	-1.46174	3.16537	0.84032
H	1.69641	2.93508	-0.26391
H	0.41603	3.41819	1.78432
H	0.13019	2.67156	-1.22695
N	0.74575	0.80843	0.06248
C	2.08416	0.44478	0.11077
C	2.54063	-0.56882	0.97096
C	3.02674	1.02113	-0.7683
C	3.87173	-0.96545	0.97754
H	1.80476	-1.06681	1.60069
C	4.35794	0.62627	-0.7539
H	2.68163	1.77408	-1.47982
C	4.79504	-0.36389	0.12544
H	4.19106	-1.75527	1.65682
H	5.06107	1.08903	-1.44616
H	5.8392	-0.67079	0.13626
H	-2.06637	3.5085	1.67246
H	-1.99153	2.97721	-0.09261
C	-1.26132	-2.70299	-1.63727
H	-1.32106	-3.3597	-0.76159
H	-2.22422	-2.20214	-1.78806
H	-1.02876	-3.32111	-2.5192
C	1.07647	-2.3671	-1.28232
H	1.8862	-1.63341	-1.25816
H	1.0977	-2.93942	-0.34593

H	1.24557	-3.05914	-2.12341
N	-0.22279	-1.69758	-1.39533
H	-0.19599	-1.08742	-2.21331
O	-1.87908	1.09876	1.33179
H	-2.82457	1.09591	1.51581
Ti	-0.92073	-0.06117	0.19391
N	-2.07807	0.30554	-1.34176
N	-1.16315	-1.5843	1.43559
C	-0.89783	-1.32319	2.84332
H	-1.05491	-2.24015	3.43752
H	0.12829	-0.98798	3.04237
H	-1.57526	-0.54658	3.24517
C	-2.51456	-2.11804	1.37839
H	-2.59425	-3.06515	1.94088
H	-3.26073	-1.42609	1.82537
H	-2.83166	-2.32702	0.34896
C	-3.47115	0.63521	-1.15143
H	-3.64254	1.72907	-1.14924
H	-4.11225	0.20474	-1.94257
H	-3.85064	0.22973	-0.2032
C	-1.52263	1.02097	-2.47528
H	-0.45418	1.23399	-2.32205
H	-1.60752	0.4516	-3.42128
H	-2.03558	1.98583	-2.63988

TS [2+2]

Zero-point correction=	0.435858 (Hartree/Particle)
Thermal correction to Energy=	0.460863
Thermal correction to Enthalpy=	0.461807
Thermal correction to Gibbs Free Energy=	0.383691
Sum of electronic and zero-point Energies=	-941.176351
Sum of electronic and thermal Energies=	-941.151346
Sum of electronic and thermal Enthalpies=	-941.150402
Sum of electronic and thermal Free Energies=	-941.228518

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	289.196	95.517	164.409

C	0.71338	-0.86013	-1.89329
H	1.22706	-0.06377	-2.4365
H	1.34761	-1.7313	-1.69543
N	1.0556	-0.14213	-0.1298

C	-0.65561	-1.07387	-2.11289
H	-1.2412	-0.41099	-2.74845
C	2.42182	-0.06579	-0.05426
C	3.17657	-1.18523	0.36275
C	3.12906	1.10621	-0.40003
C	4.56229	-1.12156	0.45549
H	2.63922	-2.09857	0.62587
C	4.5158	1.16205	-0.30445
H	2.5657	1.97859	-0.73716
C	5.24348	0.0515	0.12551
H	5.11877	-1.99779	0.78884
H	5.0358	2.08327	-0.56841
H	6.3287	0.09947	0.20094
C	-1.23904	-2.35249	-1.62485
H	-0.73517	-3.25937	-1.99627
H	-2.31157	-2.42296	-1.84462
C	-0.3434	2.65057	-1.50963
H	-1.21874	2.59393	-2.16682
H	-0.03507	3.7054	-1.43954
H	0.47211	2.07014	-1.95513
C	-1.72199	2.90312	0.46983
H	-2.67807	2.76747	-0.0461
H	-1.83548	2.56116	1.50275
H	-1.46029	3.97303	0.46466
O	-1.03723	-2.34776	-0.16905
H	-1.80024	-2.73579	0.28707
N	-0.68191	2.1039	-0.19021
H	0.16137	2.16428	0.3843
Ti	-0.76574	-0.14527	0.04494
N	-0.88691	-0.10007	1.98626
N	-2.80206	-0.04298	-0.22704
C	0.23355	-0.45606	2.83796
H	0.41355	0.32514	3.60074
H	0.0387	-1.3966	3.38804
H	1.14994	-0.58721	2.25392
C	-2.0442	0.14908	2.8193
H	-2.35848	-0.75347	3.3799
H	-1.81143	0.92086	3.57828
H	-2.89139	0.50249	2.22203
C	-3.70543	-1.00835	0.34121
H	-3.28568	-1.49393	1.2345
H	-4.66589	-0.55002	0.658
H	-3.98466	-1.81093	-0.38236
C	-3.44236	0.54684	-1.37052

H	-3.7186	-0.21099	-2.13947
H	-4.38496	1.07097	-1.10474
H	-2.79414	1.27902	-1.8722

[2+2] intermediate

Zero-point correction=	0.441964 (Hartree/Particle)
Thermal correction to Energy=	0.467300
Thermal correction to Enthalpy=	0.468244
Thermal correction to Gibbs Free Energy=	0.389177
Sum of electronic and zero-point Energies=	-941.208615
Sum of electronic and thermal Energies=	-941.183279
Sum of electronic and thermal Enthalpies=	-941.182335
Sum of electronic and thermal Free Energies=	-941.261403

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	293.235	96.424	166.412

C	0.74522	2.24161	0.1477
H	1.22454	2.51065	1.11017
H	1.1512	2.94872	-0.60982
C	-0.75903	2.2821	0.28779
H	-1.11246	2.69413	1.23683
C	2.32742	0.42008	-0.20916
C	2.64684	-0.87753	-0.6789
C	3.40725	1.20277	0.26424
C	3.94298	-1.36998	-0.63941
H	1.85678	-1.47358	-1.13504
C	4.70256	0.6989	0.29308
H	3.23158	2.22029	0.60617
C	4.98891	-0.59122	-0.14468
H	4.14131	-2.37258	-1.01883
H	5.50591	1.33499	0.66562
H	6.00642	-0.97638	-0.11788
C	0.37743	-0.36389	2.6171
H	-0.53719	0.11299	2.99004
H	0.80757	-0.97367	3.42507
H	1.09748	0.40743	2.32709
C	-0.74526	-2.36075	1.87754
H	-0.19171	-2.96836	2.60874
H	-1.67148	-2.00012	2.33732
H	-1.00878	-2.98529	1.01784
C	-1.52457	2.75115	-0.89563

H	-1.13306	3.6459	-1.41594
H	-2.58243	2.92183	-0.64187
N	1.02624	0.85631	-0.22106
O	-1.41916	1.62416	-1.80331
H	-2.15238	1.60107	-2.43433
N	0.04288	-1.19712	1.44913
H	0.93367	-1.51978	1.0563
Ti	-0.86686	0.12095	-0.11857
N	-1.24179	-1.1604	-1.52662
N	-2.59119	0.01106	0.82203
C	-2.18089	-1.06563	-2.61878
H	-1.68718	-0.90428	-3.59474
H	-2.77096	-1.99731	-2.70844
H	-2.90692	-0.25881	-2.45589
C	-0.5675	-2.43695	-1.59312
H	-1.28766	-3.27612	-1.51059
H	-0.02205	-2.57149	-2.54631
H	0.16472	-2.55982	-0.78534
C	-3.60229	-0.98146	0.50375
H	-3.86878	-1.59027	1.3916
H	-4.54383	-0.50559	0.16636
H	-3.26083	-1.66415	-0.28157
C	-3.07973	0.78312	1.94114
H	-2.36672	1.55353	2.25018
H	-4.0359	1.28831	1.70015
H	-3.28577	0.14072	2.82188

TS retro-[2+2]

Zero-point correction=	0.440242 (Hartree/Particle)
Thermal correction to Energy=	0.465197
Thermal correction to Enthalpy=	0.466141
Thermal correction to Gibbs Free Energy=	0.388702
Sum of electronic and zero-point Energies=	-941.205738
Sum of electronic and thermal Energies=	-941.180784
Sum of electronic and thermal Enthalpies=	-941.179840
Sum of electronic and thermal Free Energies=	-941.257279

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	291.915	96.012	162.985

C	-0.61899	-2.26691	-0.29299
H	-1.07318	-2.71968	0.61045

H	-1.04099	-2.81789	-1.15922
N	-0.9007	-0.84101	-0.38396
C	0.88059	-2.36118	-0.24276
H	1.37763	-2.60941	0.69595
C	1.61801	-2.38472	-1.43017
C	-2.20727	-0.42586	-0.23122
C	-2.52785	0.95238	-0.16157
C	-3.28746	-1.33226	-0.11837
C	-3.83427	1.386	0.01176
H	-1.72672	1.68282	-0.27859
C	-4.59226	-0.88247	0.04968
H	-3.10588	-2.40302	-0.17918
C	-4.88475	0.47615	0.12108
H	-4.03447	2.45667	0.0562
H	-5.39503	-1.61601	0.12729
H	-5.90855	0.81996	0.25543
C	0.79811	1.68036	2.53905
H	0.19079	2.08289	3.36509
H	1.73015	1.28035	2.95304
H	1.0472	2.49473	1.85101
C	-0.41347	-0.40248	2.74
H	0.42621	-0.95207	3.18125
H	-0.99381	0.04597	3.56137
H	-1.05224	-1.10556	2.1961
H	1.13237	-2.7031	-2.35747
H	2.68112	-2.62053	-1.38539
O	1.85707	-0.65953	-2.01081
H	1.24196	-0.52113	-2.74858
N	0.08322	0.62439	1.81569
H	-0.74993	1.05337	1.40507
Ti	0.97027	-0.03557	-0.24157
N	0.58086	1.64885	-1.10079
N	2.69997	-0.04353	0.61945
C	1.51716	2.7481	-0.98308
H	0.98832	3.71284	-0.87356
H	2.17162	2.62525	-0.11018
H	2.16168	2.83222	-1.88029
C	-0.19647	1.79398	-2.31044
H	-0.90379	0.96356	-2.42584
H	-0.77661	2.73501	-2.31264
H	0.45852	1.82363	-3.20388
C	3.87111	0.34086	-0.14376
H	3.60128	0.88045	-1.05693
H	4.53134	0.99123	0.45959

H	4.46429	-0.54382	-0.44679
C	3.11204	-0.76091	1.79777
H	3.6791	-1.67687	1.53566
H	3.77366	-0.14904	2.43966
H	2.25275	-1.07117	2.40374

Product complex

Zero-point correction=	0.438022 (Hartree/Particle)
Thermal correction to Energy=	0.464347
Thermal correction to Enthalpy=	0.465291
Thermal correction to Gibbs Free Energy=	0.383297
Sum of electronic and zero-point Energies=	-941.254251
Sum of electronic and thermal Energies=	-941.227926
Sum of electronic and thermal Enthalpies=	-941.226981
Sum of electronic and thermal Free Energies=	-941.308975

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	291.382	98.098	172.570

C	0.80238	2.00496	-1.33742
H	1.75411	2.16946	-1.87126
H	0.00993	2.04631	-2.09674
N	0.80237	0.65859	-0.75532
C	0.5717	3.10574	-0.34434
H	1.23774	3.13625	0.52417
C	-0.3952	4.01498	-0.45809
C	2.04727	0.14566	-0.40804
C	2.2468	-1.2508	-0.29706
C	3.17319	0.95926	-0.14901
C	3.47433	-1.78652	0.07093
H	1.42095	-1.92285	-0.53299
C	4.40014	0.41176	0.20806
H	3.08967	2.04224	-0.21199
C	4.56802	-0.96374	0.3309
H	3.57876	-2.86951	0.13597
H	5.23705	1.0824	0.40214
H	5.52989	-1.38639	0.6141
C	-0.94366	-1.68941	2.46886
H	-0.50566	-1.9861	3.43602
H	-1.90262	-1.18679	2.65648
H	-1.13021	-2.59062	1.87672
C	0.45332	0.2602	2.60581

H	-0.37984	0.8521	3.0005
H	1.00315	-0.16231	3.46233
H	1.12343	0.9216	2.04596
H	-1.08461	4.00129	-1.30542
H	-0.54063	4.80504	0.27704
O	-1.73576	0.48714	-2.02829
H	-2.42995	1.15802	-1.96855
N	-0.06432	-0.7884	1.72536
H	0.74035	-1.33026	1.40385
Ti	-1.02188	-0.13472	-0.41534
N	-1.13938	-1.99018	-0.8498
N	-2.44299	0.57698	0.65136
C	-2.22308	-2.88352	-0.51688
H	-2.99969	-2.89442	-1.30753
H	-1.86393	-3.92269	-0.40235
H	-2.70812	-2.59433	0.42468
C	-0.57252	-2.33249	-2.14079
H	-0.1125	-3.33694	-2.11823
H	-1.34761	-2.32657	-2.93004
H	0.20447	-1.61549	-2.4396
C	-2.44923	1.7533	1.48311
H	-2.84934	1.54026	2.49377
H	-1.44043	2.171	1.5928
H	-3.08327	2.54896	1.04632
C	-3.78451	0.15276	0.32448
H	-4.34258	-0.14433	1.23263
H	-4.36235	0.96078	-0.16744
H	-3.78224	-0.71131	-0.35391

Experimental Section

General Considerations. All the starting materials including amines and alcohols, $TiCl_4$, $HNEt_2$ and solvents were dried and distilled prior to use according to standard procedures. BuLi is used as 1.6 M solution in hexanes. All reactions were performed under an atmosphere of argon using standard Schlenck techniques. NMR spectra were recorded on a Bruker 400 spectrometer using $CDCl_3$ as solvent, and the chemical shifts were reported in ppm with respect to the reference (internal $SiMe_4$ for ^1H NMR spectra). The products are known compounds and were identified by comparison with the reported NMR spectra of the compounds in literature.

Reaction of 2-methylbut-3-en-2-ol with aniline (entry 1). To a solution of 3.12 mL (5 mmol) of BuLi in 20 mL of dry toluene was added 0.52 mL (5mmol) of $HNEt_2$ at -20 ^oC, and the mixture was stirred for 1 hour at that temperature. To the mixture was added 0.11 mL (1 mmol) of $TiCl_4$ and the mixture was stirred for about 2 h at 80 ^oC until the brown precipitates disappeared and a light yellow solution remained over white precipitates of lithium salt. The mixture was cooled to room temperature and 0.27 mL (3 mmol) of aniline and 0.51 mL (4 mmol) of TMSCl. The mixture was stirred for 1 h at 80 ^oC, cooled to room temperature and to the solution was added 0.10 mL (1 mmol) of 2-methylbut-3-en-2-ol. After refluxing for 24 h, the solution was acidified with 5% HCl, neutralized with saturated $NaHCO_3$ solution, extracted with diethyl ether and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was isolated by column chromatography on silica using CH_2Cl_2/hexanes (1:4 v/v) as eluent to give brown liquid (85 mg, yield 53%). ^1H NMR: (400MHz, $CDCl_3$) δ = 7.17 (t, J = 7.6 Hz, 2H), 6.70 (t, J = 7.2 Hz, 1H), 6.60 (d, J = 7.9 Hz, 2H), 5.31 (t, J = 6.3 Hz, 1H), 3.68 (d, J = 6.7 Hz, 2H), 1.74 (s, 3H), 1.71 (s, 3H).

Reaction of cinnamic alcohol with aniline (entry 2). The reaction was carried out as above-mentioned procedure in entry 1, using cinnamic alcohol (0.10 mL, 1 mmol) instead of 2-methylbut-3-en-2-ol. Isolation by column chromatography on silica using CH_2Cl_2/hexanes (1:8 v/v) as eluent gave brown liquid (80 mg, yield 38%). ^1H NMR: (400MHz, $CDCl_3$) δ = 7.17-7.30 (m, 7H), 6.63 (t, J = 7.4 Hz, 1H), 6.52 (d, J = 7.8 Hz, 2H), 5.96 (ddd, J = 16.9, 10.2, 5.9 Hz, 1 H), 5.20 (d, J = 17.1 Hz, 1H), 5.15 (d, J = 10.2 Hz, 1H), 4.86 (d, J = 5.8 Hz, 1 H), 3.96 (brs, 1H).

Reaction of 1-phenylprop-2-en-1-ol with aniline (entry 3). The reaction was carried out as above-mentioned procedure in entry 1, using 1-phenylprop-2-en-1-ol (0.13 g, 1 mmol) instead of 2-methylbut-3-en-2-ol. Isolation by column chromatography on silica using CH_2Cl_2/hexanes (1:4 v/v) as eluent gave brown liquid (51 mg, yield 24%). ^1H NMR: (400MHz, $CDCl_3$) δ = 7.37 (d, J = 7.5 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.23 (d, J = 6.8 Hz, 1H), 7.19 (t, J = 7.7 Hz, 2H), 6.73 (t, J = 7.3 Hz,

1H), 6.67 (d, J = 8.0 Hz, 2H), 6.62 (d, J = 16.1 Hz, 1H), 6.33 (dt, J = 15.9, 5.7 Hz, 1H), 3.94 (d, J = 5.7 Hz, 2H), 3.84 (brs, 1H).

Reaction of 2-methylbut-3-en-2-ol with aniline employing $Ti(NMe_2)_4$ (entry 4). To a solution of 224 mg (1 mmol) of $Ti(NMe_2)_4$ in 20 mL of dry toluene was added 0.27 mL (3 mmol) of aniline and 0.10 mL (1 mmol) of 2-methylbut-3-en-2-ol. After refluxing for 24 h, the reaction mixture was worked up and purified as in entry 1 to give brown liquid (80 mg, yield 50%). The product has same ^{1}H NMR as that in entry 1.

Reaction of 2-methylbut-3-en-2-ol with aniline without TMSCl (entry 5). To a solution of 3.12 mL (5 mmol) of BuLi in 20 mL of dry toluene was added 0.52 mL (5mmol) of $HNEt_2$ at -20 ^{o}C, and the mixture was stirred for 1 hour at that temperature. To the mixture was added 0.11 mL (1 mmol) of $TiCl_4$ and the mixture was stirred for about 2 h at 80 ^{o}C until the brown precipitates disappeared and a light yellow solution remained over white precipitates of lithium salt. The mixture was cooled to room temperature and 0.27 mL (3 mmol) of aniline was added. The mixture was stirred for 1 h at 80 ^{o}C, cooled to room temperature and to the solution was added 0.10 mL (1 mmol) of 2-methylbut-3-en-2-ol. After refluxing for 24 h, the reaction mixture was worked up and isolated as in entry 1. No S_N2' product was obtained while over 80% of 2-methylbut-3-en-2-ol was recovered.

Reaction of 2-methylbut-3-en-2-ol with aniline (entry 6). The reaction was carried out as above-mentioned procedure in entry 1, using TMSI instead of TMSCl. After refluxing for 12 h, aqueous work-up and isolation by column chromatography on silica using CH_2Cl_2/hexanes (1:4 v/v) as eluent gave brown liquid (122 mg, yield 76%). The product has same ^{1}H NMR as that in entry 1.

Reaction of 2-methylbut-3-en-2-ol with aniline at 80 ^{o}C (entry 7). The reaction was carried out as above-mentioned procedure in entry 4 but at 80 ^{o}C. After refluxing for 12 h, aqueous work-up and isolation by column chromatography on silica using CH_2Cl_2/hexanes (1:4 v/v) as eluent gave brown liquid (81 mg, yield 50%). The product has same ^{1}H NMR as that in entry 1.

Reaction of 1-phenylprop-2-en-1-ol with aniline (entry 8). The reaction was carried out as above-mentioned procedure in entry 3, using TMSI instead of TMSCl. After refluxing for 12 h, aqueous work-up and isolation by column chromatography on silica using CH_2Cl_2/hexanes (1:4 v/v) as eluent gave brown liquid (162 mg, yield 76%). The product has same ^{1}H NMR as that in entry 3.

Reaction of but-3-en-2-ol with aniline (entry 9). The reaction was carried out as above-mentioned procedure in entry 4, using but-3-en-2-ol instead of 2-methylbut-3-3n-2-ol. Isolation by column chromatography on silica using CH_2Cl_2/hexanes (1:4 v/v) as eluent gave brown liquid (104 mg, yield 71%), *cis:trans* = 1:10 according to NMR spectrum. ^{1}H NMR: (400MHz, $CDCl_3$) δ = 7.17 (dd, J = 8.5, 1.2 Hz, 2H), 6.70

(t, J = 7.3 Hz, 1H), 6.62 (dd, J = 8.6, 1.0 Hz, 2H), 5.76-5.68 (m, 1H), 5.64-5.56 (m, 1H), 3.68 (d, J = 5.7 Hz, 2H), 1.70 (dd, J = 6.3, 1.2 Hz, 3H).

Reaction of 2-methylbut-3-en-2-ol with 4-chloroaniline (entry 10). The reaction was carried out as above-mentioned procedure in entry 4, using 4-chloroaniline instead of aniline. Isolation by column chromatography on silica using CH_2Cl_2/hexanes (1:4 v/v) as eluent gave brown liquid (132 mg, yield 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.11 (d, J = 8.8 Hz, 2H), 6.52 (d, J = 8.8 Hz, 2H), 5.30 (t, J = 6.6 Hz, 1H), 3.65 (d, J = 6.7 Hz, 2H), 3.60 (brs, 1H), 1.75 (s, 3H), 1.71 (s, 3H).

Reaction of 2-methylbut-3-en-2-ol with 4-bromoaniline (entry 11). The reaction was carried out as above-mentioned procedure in entry 4, using 4-bromoaniline instead of aniline. Isolation by column chromatography on silica using CH_2Cl_2/hexanes (1:4 v/v) as eluent gave brown liquid (173 mg, yield 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.24 (d, J = 8.2 Hz, 2H), 6.48 (d, J = 8.2 Hz, 2H), 5.29 (t, J = 5.9 Hz, 1H), 3.64 (d, J = 6.5 Hz, 2H), 3.62 (brs, 1H), 1.75 (s, 3H), 1.71 (s, 3H).

Reaction of 2-methylbut-3-en-2-ol with 4-methylaniline (entry 12). The reaction was carried out as above-mentioned procedure in entry 4, using 4-methylaniline instead of aniline. Isolation by column chromatography on silica using CH_2Cl_2/hexanes (1:8 v/v) as eluent gave brown liquid (75 mg, yield 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.99 (d, J = 8.3 Hz, 2H), 6.54 (d, J = 8.3 Hz, 2H), 5.32 (dd, J = 9.5, 4.0 Hz, 1H), 3.66 (d, J = 6.7 Hz, 2H), 3.46 (brs, 1H), 2.24 (s, 3H), 1.74 (s, 3H), 1.70 (s, 3H).

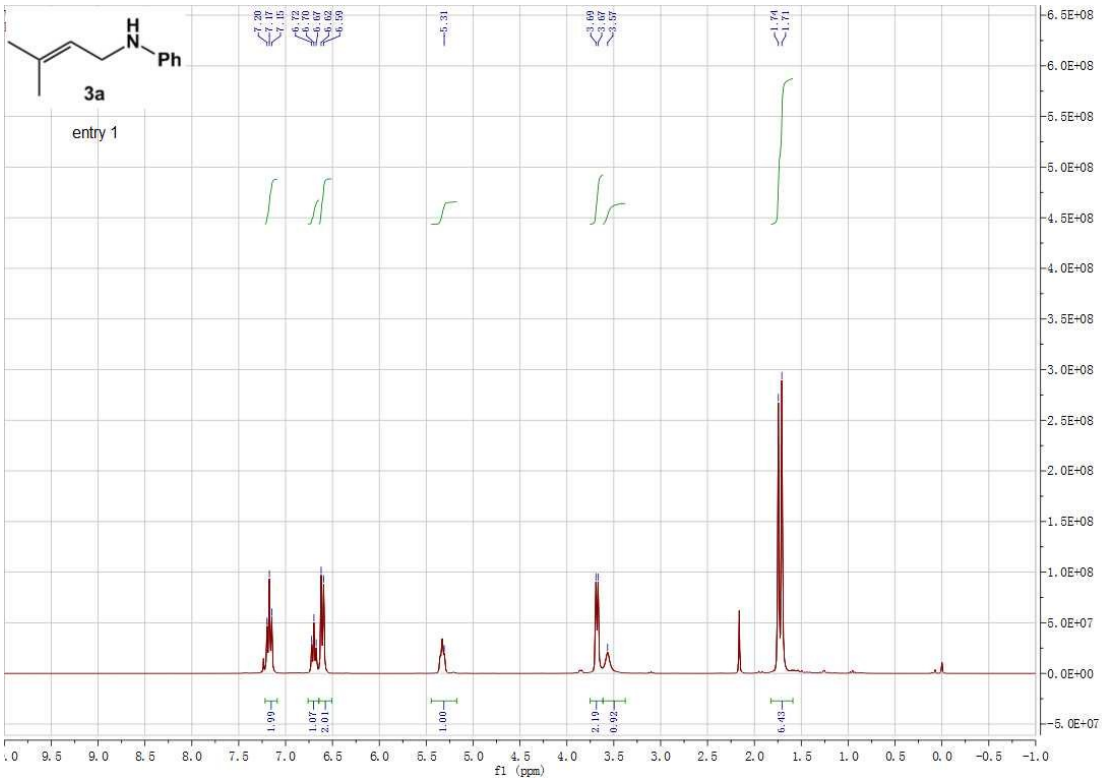
Reaction of 2-methylbut-3-en-2-ol with 2-iodoaniline (entry 13). The reaction was carried out as above-mentioned procedure in entry 4, using 2-iodoaniline instead of aniline. Isolation by column chromatography on silica using CH_2Cl_2/hexanes (1:4 v/v) as eluent gave brown liquid (81 mg, yield 28%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (d, J = 7.7 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 6.56 (d, J = 8.1 Hz, 1H), 6.44 (t, J = 7.4 Hz, 1H), 5.34 (t, J = 6.2 Hz, 1H), 4.09 (s, 1H), 3.72 (d, J = 5.4 Hz, 2H), 1.77 (s, 3H), 1.73 (s, 3H).

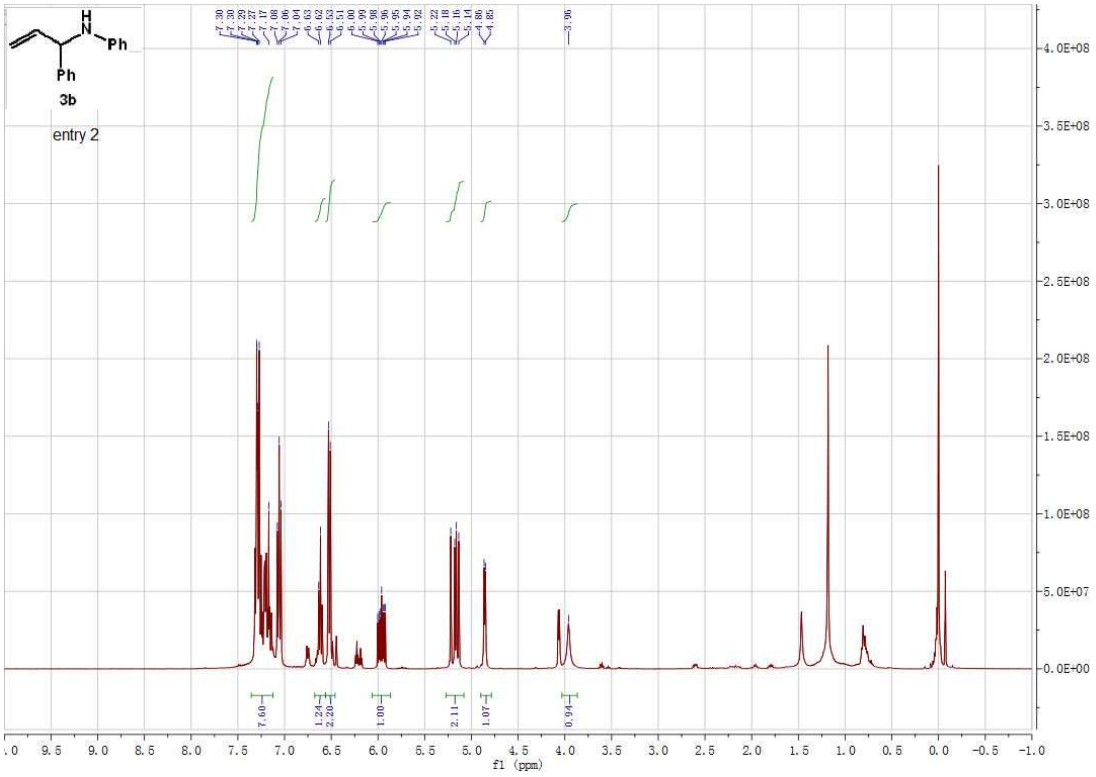
Reaction of 2-methylbut-3-en-2-ol with 2-trifluoromethylaniline (entry 14). The reaction was carried out as above-mentioned procedure in entry 4, using 2-trifluoromethylaniline instead of aniline. Isolation by column chromatography on silica using CH_2Cl_2/hexanes (1:4 v/v) as eluent gave brown liquid (88 mg, yield 38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 (d, J = 7.8 Hz, 1H), 7.36 (t, J = 7.8 Hz, 1H), 6.71 (d, J = 7.9 Hz, 1H), 6.70 (t, J = 7.4 Hz, 1H), 5.32 (tt, J = 6.7, 1.3 Hz, 1H), 4.27 (brs, 1H), 3.73 (t, J = 5.6 Hz, 2H), 1.76 (s, 3H), 1.72 (s, 3H).

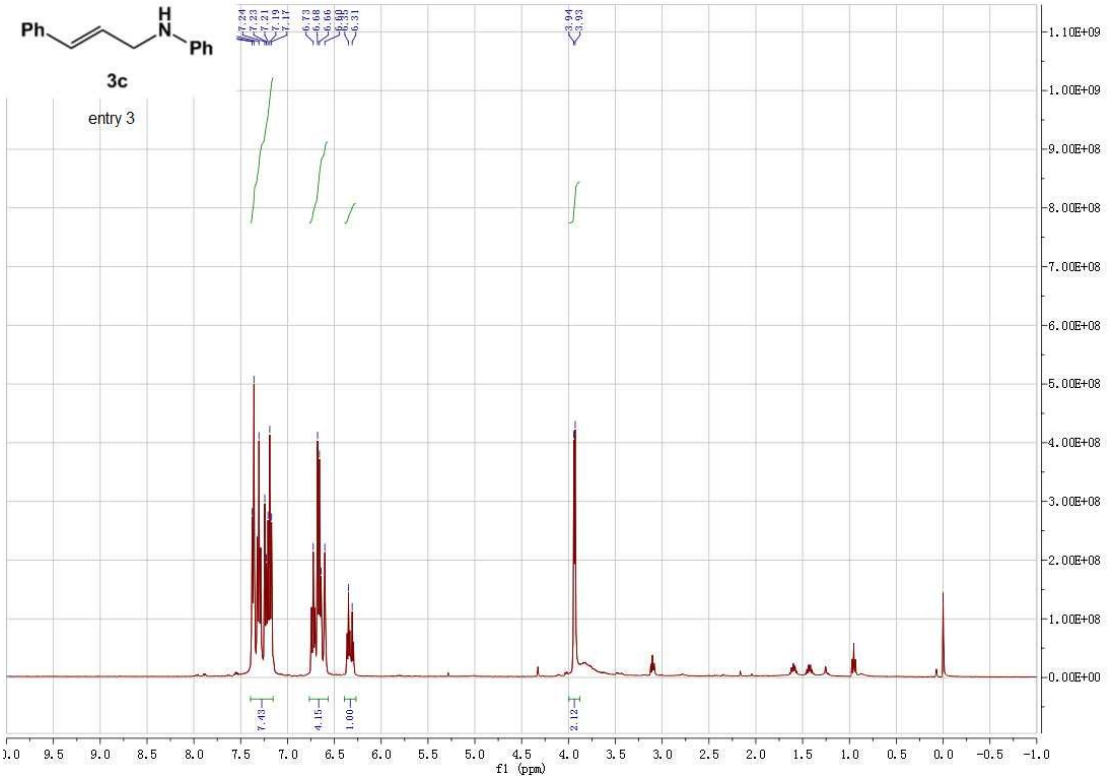
Reaction of 2-methylbut-3-en-2-ol with pyridine-2-amine (entry 15). The reaction was carried out as above-mentioned procedure in entry 4, using pyridine-2-amine instead of aniline. Isolation by column chromatography on silica using CH_2Cl_2/hexanes (1:4 v/v) as eluent gave brown liquid (62 mg, yield 38%). ^{1}H NMR

(400 MHz, $CDCl_3$) δ = 8.02 (d, J = 3.7 Hz, 1H), 7.34 (t, J = 7.1 Hz, 1H), 6.49 (t, J = 6.2 Hz, 1H), 6.30 (d, J = 8.4 Hz, 1H), 5.25 (t, J = 6.5 Hz, 1H), 4.36 (s, 1H), 3.77 (t, J = 5.7 Hz, 2H), 1.68 (s, 3H), 1.64 (s, 3H).

1H NMR of the Products



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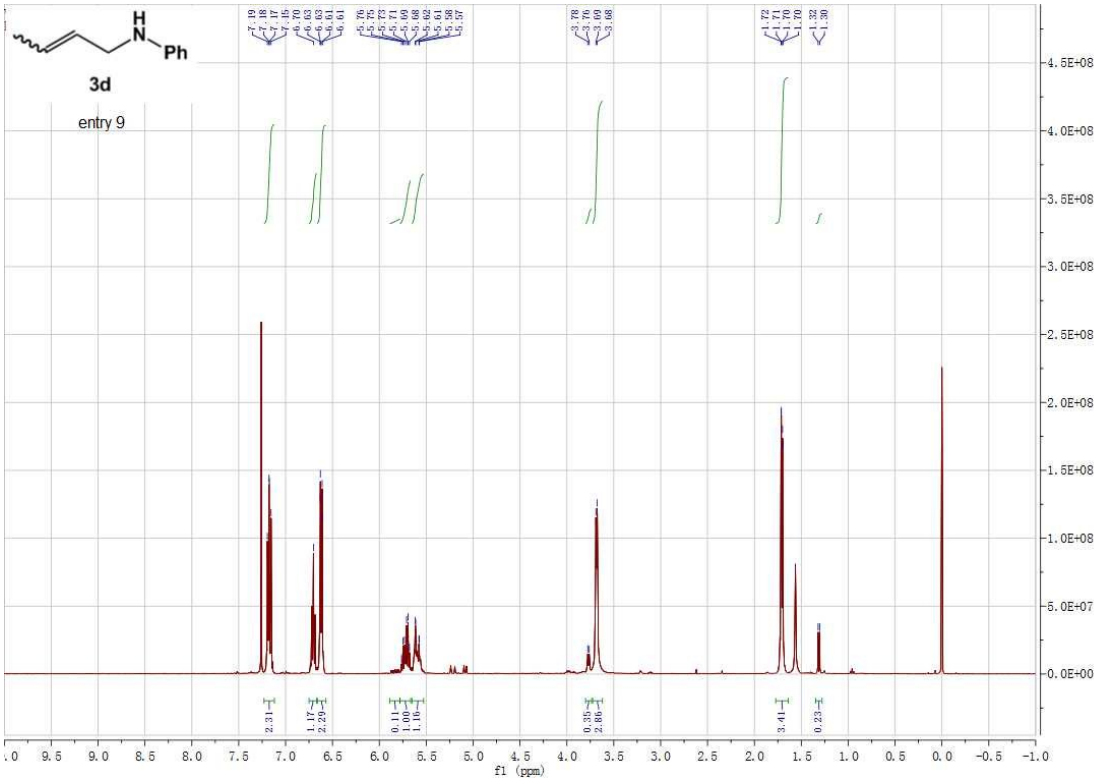
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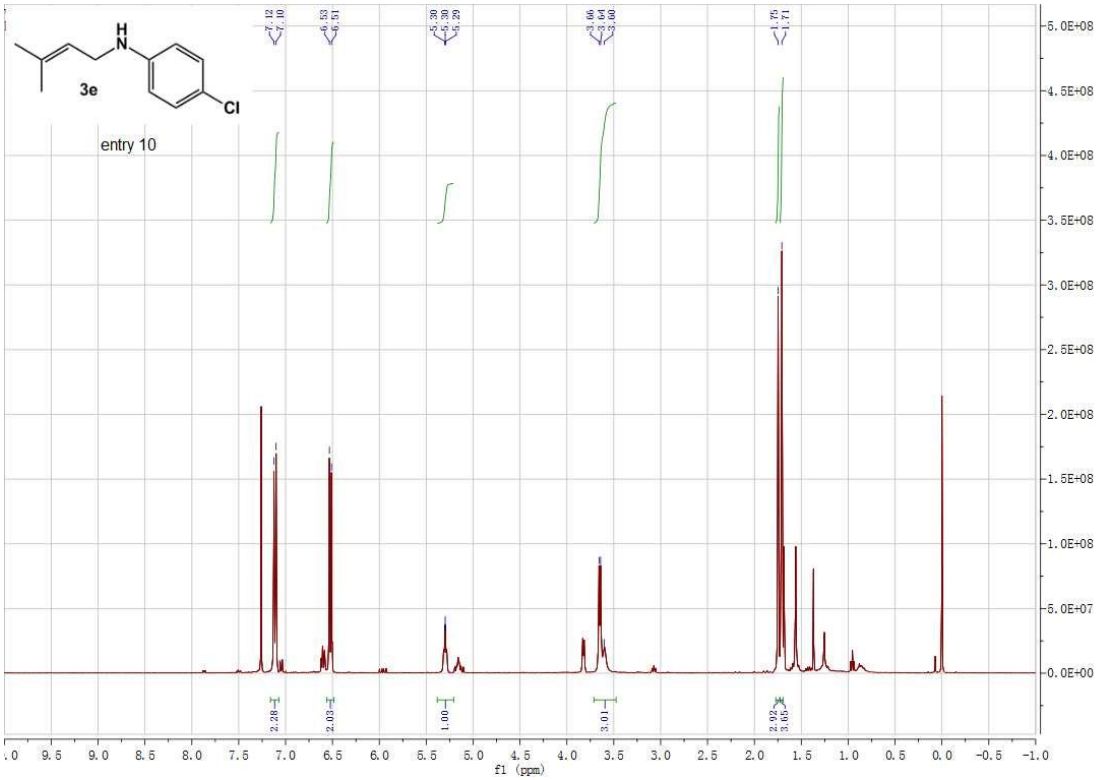
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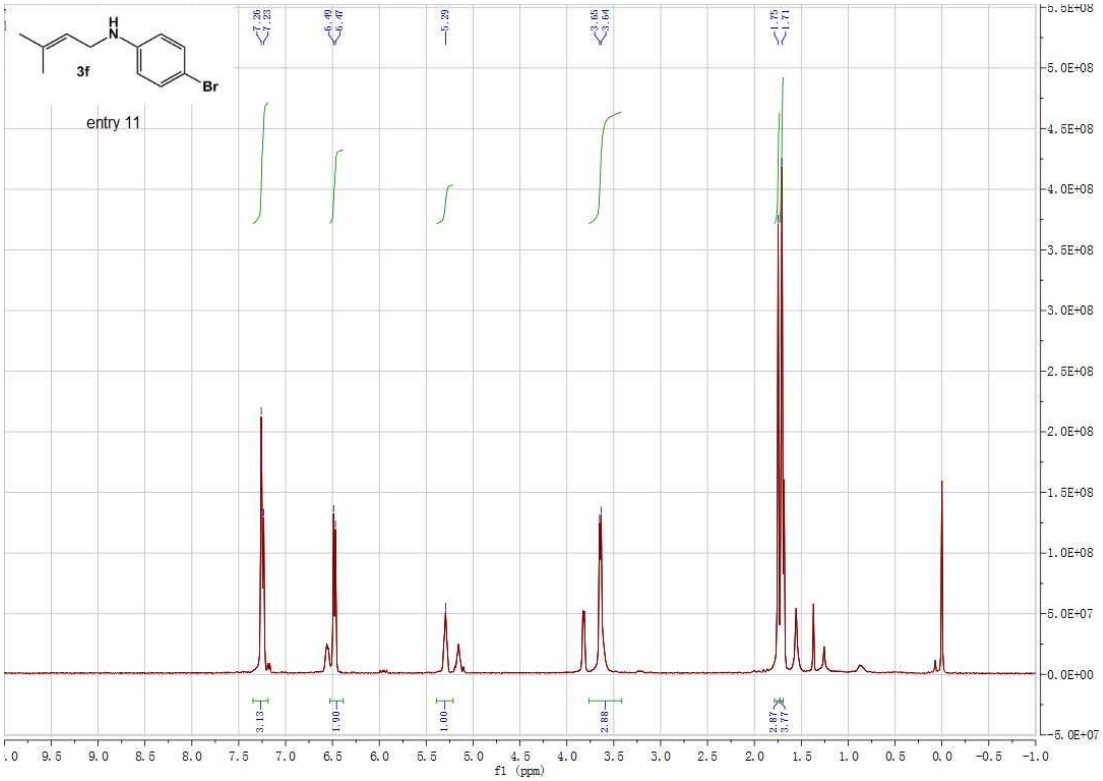
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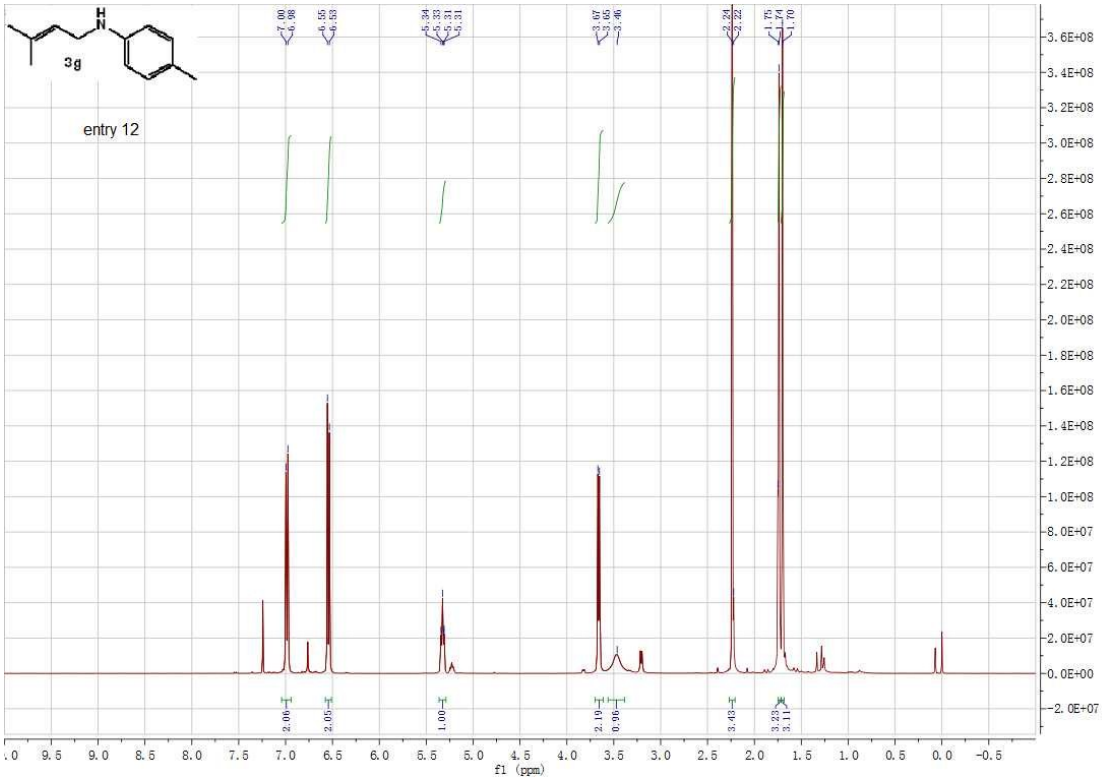
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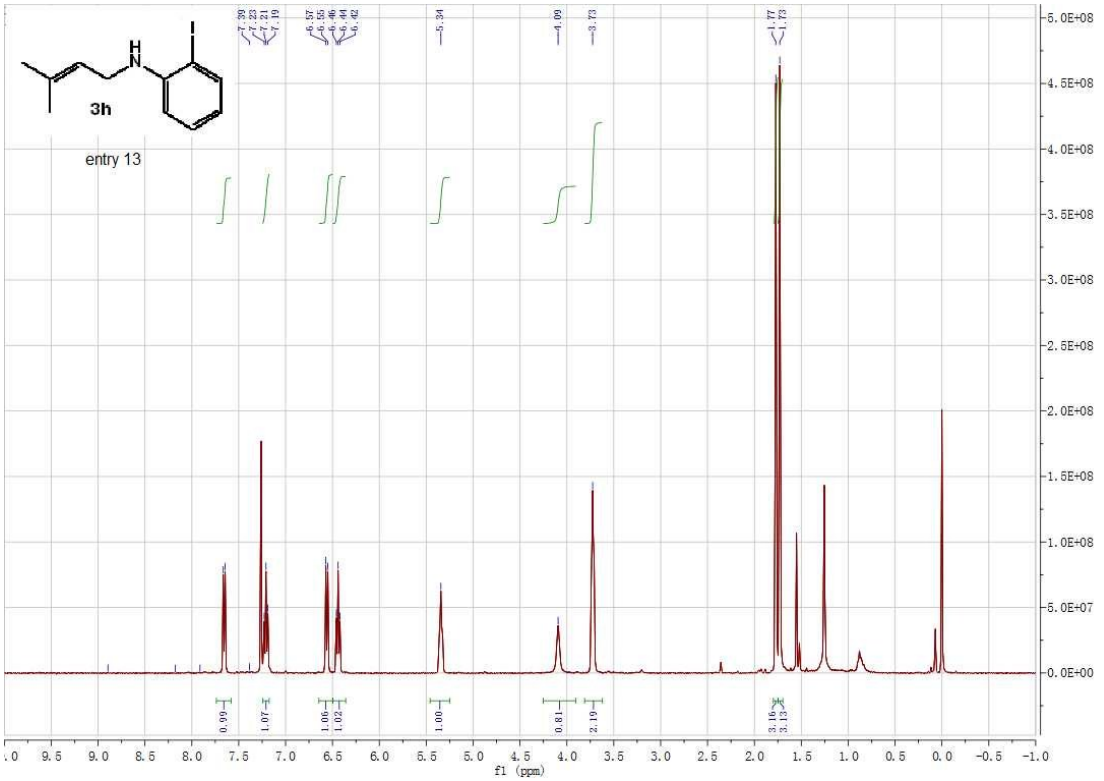
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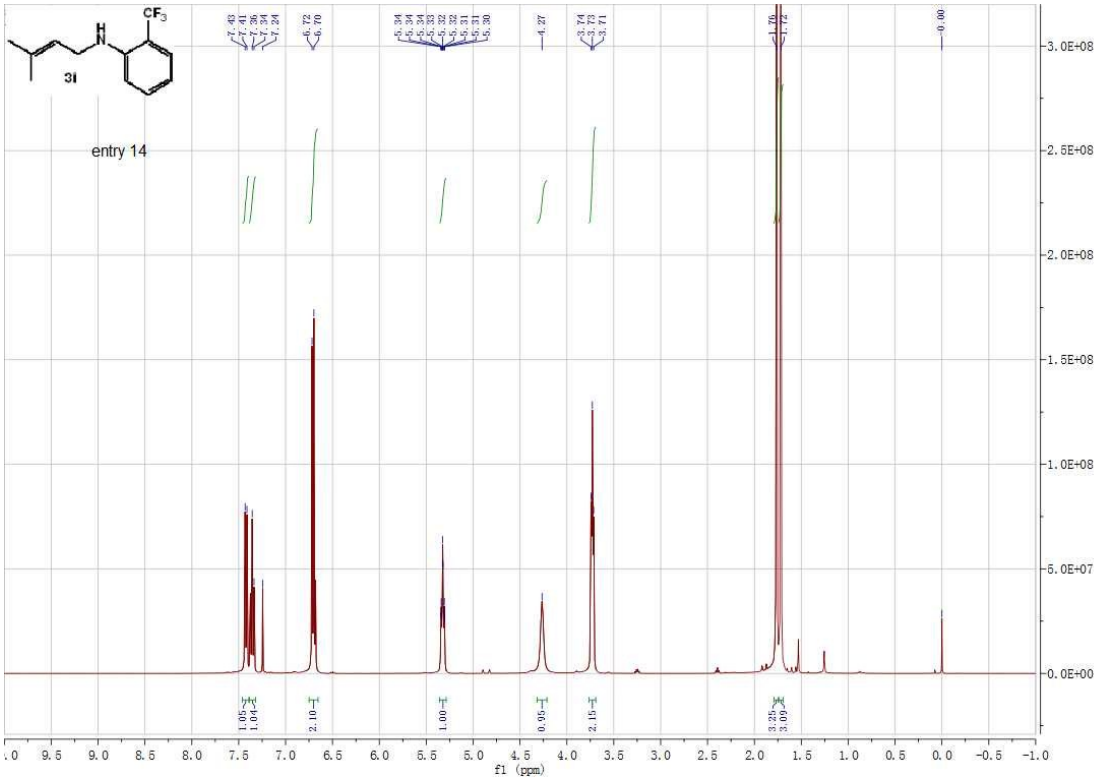
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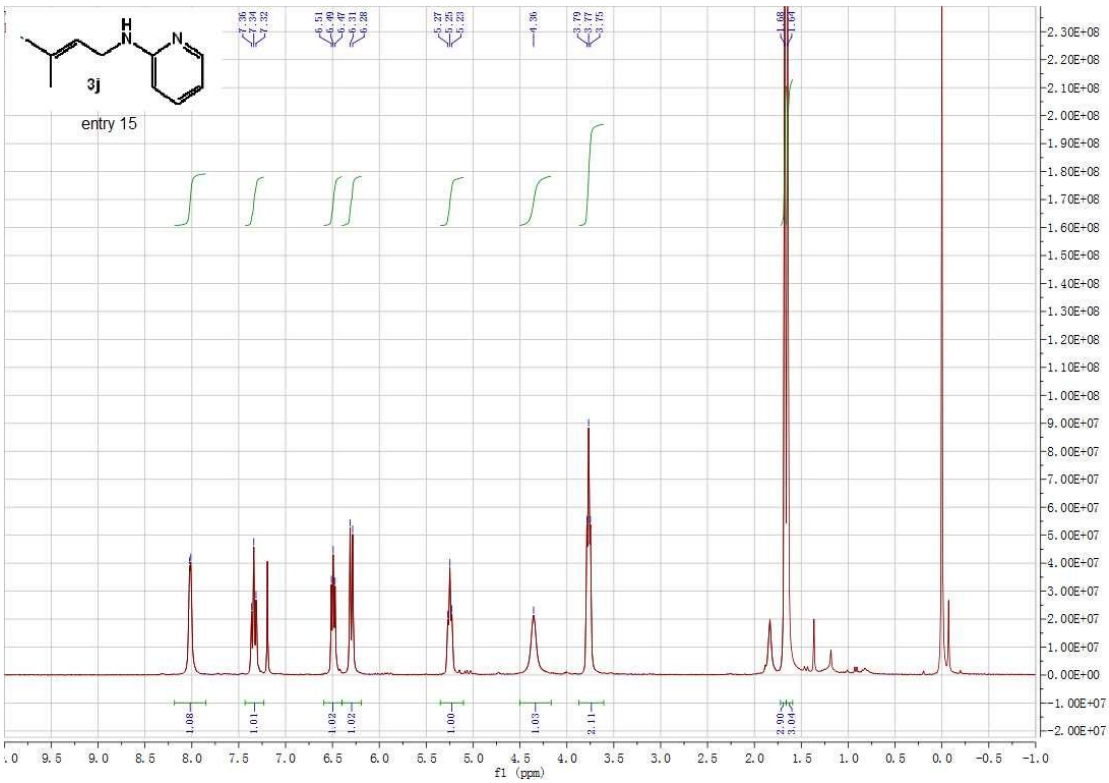
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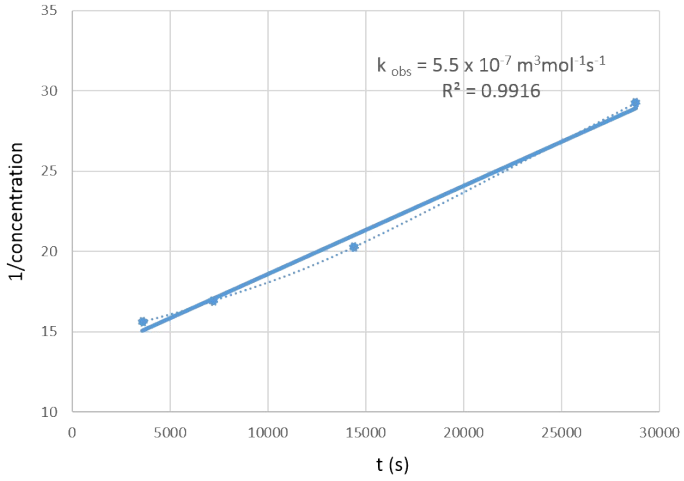
Kinetic experiments

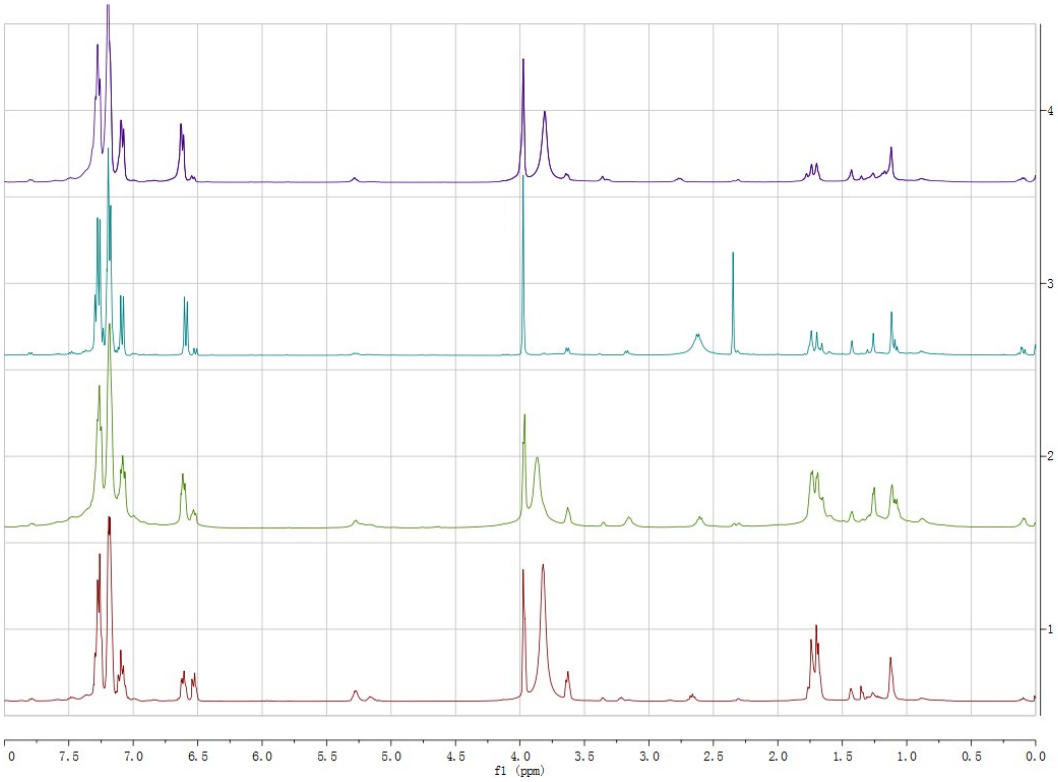
The reaction of 2-methylbut-3-en-2-ol with 4-chloroaniline was selected in the kinetic study for the simplification of NMR. Diphenylmethane was added into the reaction mixture as an internal standard for integral. To a solution of 3.12 mL (5 mmol) of BuLi in 6 mL of dry toluene was added 0.52 mL (5mmol) of $HNEt_2$ at -20 ^oC, and the mixture was stirred for 1 hour at that temperature. To the mixture was added 0.11 mL (1 mmol) of $TiCl_4$ and the mixture was stirred for about 2 h at 80 ^oC until the brown precipitates disappeared and a light yellow solution remained over white precipitates of lithium salt. The mixture was cooled to room temperature and 128 mg (1 mmol) of 4-chloroaniline and 0.51 mL (4 mmol) of TMSCl. The mixture was stirred for 1 h at 80 ^oC, cooled to room temperature and to the solution was added 0.10 mL (1 mmol) of 2-methylbut-3-en-2-ol and 168 mg (1 mmol) of diphenylmethane. The mixture was divided into four portions for parallel experiments that were terminated after 1 h, 2 h, 4 h and 8 h respectively. After refluxing for a certain period of time, the solution was acidified with 5% HCl, neutralized with saturated $NaHCO_3$ solution, extracted with diethyl ether and dried over Na_2SO_4, and the solvent was removed under reduced pressure. Proton spectra were obtained under consistent conditions and the integral of the signals at 6.59 and 6.52 ppm were adopted to measure the amount of 4-chloroaniline and the product, using diphenylmethane as the internal standard for integral. The concentration of 4-chloroaniline at different reaction time were listed in Table S1 and the data were used to gain the second order rate constant (Figure S1).

Table S1.

Time (h)	1	2	4	8
Concentration (mol/L)	0.064	0.059	0.049	0.034

Figure S1. Change of 4-chloroaniline concentration over time.





Correlation of reaction barriers with Arrhenius equation

Correlation of reaction barriers between the designed reaction and the $Ti(NMe_2)_4$-mediated reaction in literature was derived with Arrhenius equation.

$$k = Ae^{-Ea/RT}$$

$$\ln \frac{k_2}{k_1} = \frac{E_{a1}}{RT_1} - \frac{E_{a2}}{RT_2}$$

to gain a similar reaction rate, where $k_2 = k_1$,

$$\frac{E_{a1}}{RT_1} = \frac{E_{a2}}{RT_2}$$

Where E_{a1} = 43.1 kcal/mol and T_1 = 433 K (160 ^oC) for the $Ti(NMe_2)_4$-mediated reaction in literature, and an expected T_2 = 383 K (110 ^oC) for the designed reaction, giving an E_{a2} = 38.1 kcal/mol.