Highly Active Nickel Catalysts for C-H Functionalization Identified through Analysis of Off-Cycle Intermediates

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Supporting Information

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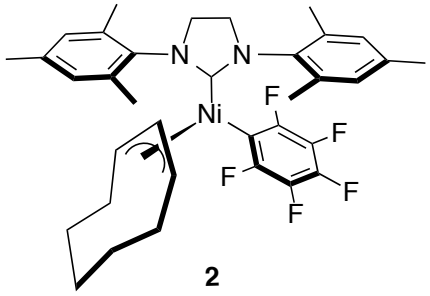
I. General Experimental Details

Unless otherwise stated, all operations were carried out under a nitrogen atmosphere in a glovebox or using standard Schlenk techniques. Tetrahydrofuran, diethyl ether, and toluene were purified under nitrogen using a solvent purification system (Innovative Technology, inc., Model # SPS-400-3 and PS-400-3). $Ni(COD)_2$ (Strem Chemicals, Inc.) and 1,3-Bis(2,4,6-trimethyphenyl)4,5-dihydroimidazol-2-ylidene (Frontier Scientific) were stored and weighed under an inert atmosphere glovebox. 4-octyne, pentafluorobenzene, benzoxazole and benzofuran (Aldrich) were distilled prior to use. C_6D_6 (Cambridge Isotopes) was distilled over sodium/benzophenone prior to use. Unless otherwise noted, all other chemicals were used as purchased and used without further purification. **7** and **1** were prepared following published procedures.[1,2]

^1H, ^{13}C, and ^{19}F NMR spectra were obtained in C_6D_6 or $CDCl_3$ (Cambridge Isotopes) using a Varian Unity 500 MHz NMR. ^1H, ^{13}C, and ^{19}F NMR spectra were referenced to respective solvent peaks (C_6H_6 or $CHCl_3$). High resolution mass spectra (HRMS were obtained at the University of Michigan Mass Spectrometry Laboratory on a VG-70-250-s spectrometer manufactured by Micromass Corp. (Manchester UK). Elemental analysis for H, C, and N were performed by Midwest Microlabs (Indiana). GCMS analysis was carried out on a HP 6980 Series GC system with HP-5MS column (30 m x 0.250 mm x 0.25 μm).

II. Synthesis of 2 and 3



2

(2). 1 (0.712g, 1.5 mmol) and $Ni(COD)_2$ (0.413g, 1.5 mmol) were dissolved in toluene. The yellow clear solution was heated to 60 °C, and over the course of 6 h the solution turned dark red, and was then allowed to cool to rt. Volatiles were pulled off in vacuo resulting in a red viscous oil. The crude was dissolved in a minimal amount of hexane and cooled to -78 °C. A yellow precipitate formed after several min, and the hexane was removed by cannula with a positive nitrogen pressure. The solid was washed twice with cold hexanes. Yield 0.702 g (73%).

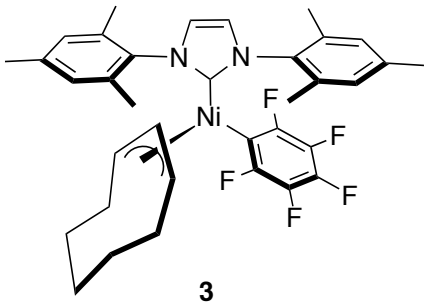
^{1}H NMR (C_6D_6, 500 MHz): δ 6.81 (2H, s), 6.69 (2H, s), 4.42 (1H, t, *J* = 12 Hz), 3.69 (1H, q, *J* = 10 Hz), 3.38 (1H, q, *J* = 10 Hz), 2.95 (4H, m), 2.28 (6H, s), 2.17 (6H, s), 1.98 (6H, s), 1.73-1.01 (10H, m).

^{13}C NMR (C_6D_6, 125 MHz): δ 214.13, 138.01, 136.99, 135.50, 135.76, 129.64, 129.21, 128,29, 107.47, 72.08, 69.22, 51.10, 30.84, 29.91, 27.69, 27.64, 23.12, 20.99, 18.18, 17.64.

^{19}F NMR (C_6D_6, 470MHz): δ -109.98 (1F, d, *J* = 47 Hz), -112.27 (1F, d, *J* = 52 Hz), -165.07 (1F, t, *J*=19 Hz), -165.74 (1F, m), -166.22 (1F, m).

HRMS (ESI+) (m/z): [M+Na] calcd for $C_{35}H_{39}F_5N_2NaNi$ 663.2285; found: 663.2289

Anal calcd for $C_{35}H_{39}F_5N_2Ni$: C (65.54 %), N (4.37 %), H (6.13 %); found: C (65.63 %), N (4.41 %), H (5.93 %).



3

(3). IMes (0.061g, 0.2 mmol) and $Ni(COD)_2$ (0.055g, 0.2 mmol) were dissolved in THF to form a dark brown solution. It was allowed to stir at rt for 30 min before the addition of

pentafluorobenzene (23 μL, 0.21 mmol). The reaction mixture immediately turned red and was heated to 55 °C and allowed to stir for 3 h. The solution was cooled and concentrated in vacuo. The product was precipitated with pentane at -20 °C, and an orange crystalline solid began to form. After filtration and washing with cold pentane, an orange solid was obtained. Yield 0.065 g (51 %).

^{1}H NMR (C_6D_6, 500 MHz): δ 6.79 (2H, s), 6.63 (2H, s), 6.00 (2H, s), 4.58 (1H, t, *J* = 10 Hz), 3.57 (1H, q, *J* = 15 Hz), 3.43 (1H, q, *J* = 15 Hz), 2.19 and 2.17 (12H, overlapping singlets), 1.66 (6H, s), 1.65-1.24 (10H, m).

^{13}C NMR (C_6D_6, 125 MHz): δ 185.11, 138.84, 136.89, 135.71, 134.87, 129.31, 128.82, 123.15, 107.16, 72.13, 68.02, 30.96, 30.15, 27.86, 27.56, 23.30, 21.00, 18.15, 17.68.

^{19}F NMR (C_6D_6, 470 MHz): δ -110.12 (1F, d, *J* = 47 Hz), -112.25 (1F, d, *J* = 47 Hz), -165.17 (1F, t, *J*=24 Hz), -165.53 (1F, m), -166.02 (1F, m).

Anal calcd for $C_{35}H_{39}F_5N_2Ni$: C (65.75 %), N (4.38 %), H (5.83 %); found: C (65.75 %), N (4.93 %), H (6.11 %).

III. General Alkenylation Procedure (Table 1, entries 1-6)

General procedure using Ni(COD)$_2$/IMes as a catalyst

Ni(COD)$_2$ (5.5 mg, 0.02 mmol) and IMes (6.0 mg. 0.02 mmol) were pre-stirred in 2 mL of toluene for 10 min. To the dark brown solution, substrate (0.20 mmol) was added, followed by addition of alkyne (0.30 mmol). The reaction mixture was stirred under a sealed nitrogen atmosphere. Upon completion, the reactions were quenched with methylene chloride and filtered through a silica plug eluting with methylene chloride.

General procedure using IMes(C_6H_{10})Ni (7) as a catalyst.

Complex **7**[1] (4.5 mg, 0.01 mmol) was dissolved in 2.0 mL of toluene, followed by addition of substrate (0.20 mmol) and alkyne (0.30 mmol). The reaction mixture was stirred under a sealed nitrogen atmosphere. Upon completion, the reactions were quenched methylene chloride and filtered through a silica plug eluting with methylene chloride.

***Table 1, entry 6 modification to general procedure: 0.04 mmol of $AlMe_3$ was added prior to addition of the alkyne.

Characterization

Products from Table 1, entries 1, 2, 3, and 6 were purified by column chromatography. The yields for entries 4 and 5 were determined by ^{1}H NMR with methylene bromide as an internal standard. ^{1}H NMR spectra for the alkenylation products from Table 1 (1-2[3], 3-5[4], 6[5]) match those reported in the literature.

IV. Intramolecular Alkylation Procedure (Table 1, entries 7-9)

General procedure using $Ni(COD)_2$/IMes as a catalyst

$Ni(COD)_2$ (5.5 mg, 0.02 mmol) and IMes (6.0 mg. 0.02 mmol) were pre-stirred in 0.3 mL of toluene for 10 min. To the dark brown solution, pyridinone (0.20 mmol) was added, followed by addition of $AlMe_3$ (0.04 mmol). The reaction mixture was then heated (temperature indicated in Table 1 of manuscript) and allowed to stir under a sealed nitrogen atmosphere. Upon completion, the reactions were quenched with methylene chloride and filtered through a silica plug eluting with methylene chloride.

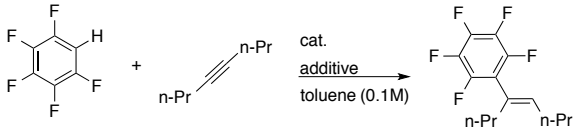
General procedure using IMes(C_6H_{10})Ni as a catalyst (7)

Catalyst **7** (9.0 mg, 0.02 mmol) dissolved in 0.3 mL of toluene, and pyridinone (0.20 mmol) was added followed by addition of $AlMe_3$ (0.04 mmol). The reaction mixture was then heated to 100 °C and allowed to stir under a sealed nitrogen atmosphere. Upon completion, the reactions were quenched with methylene chloride and filtered through a silica plug eluting with methylene chloride.

Characterization

The ^{1}H NMR of the cyclization products from Table 1 (entries 7, 8, 9) match those reported in the literature.[5] The yields for entries 7, 8 and 9 were determined using ^{1}H NMR with methylene bromide as an internal standard.

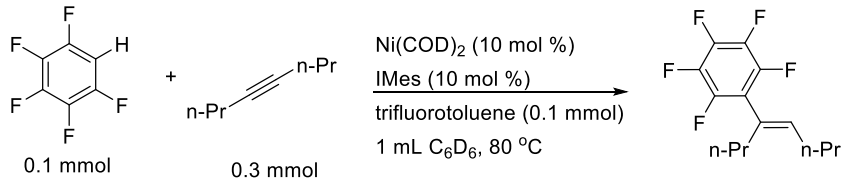
V. Experiments Probing the Role of 1,5-Dienes



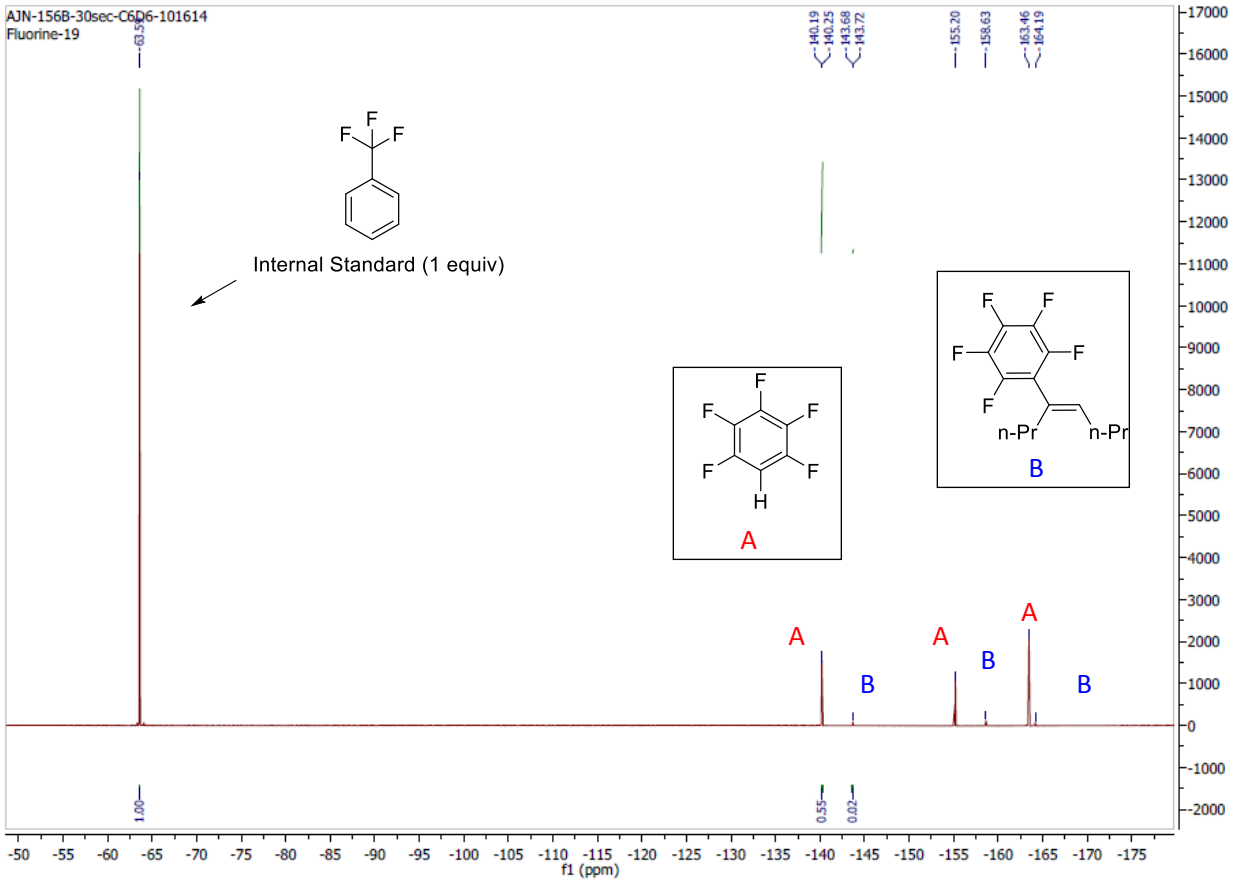
entry	pre-catalyst	additive	amount	temp	% yield
1	$Ni(COD)_2$/IMes (10 mol %)	none	--	rt	8
2	$Ni(COD)_2$/IMes (10 mol %)	1,5-hexadiene	10 mol %	rt	27
3	$Ni(COD)_2$/IMes (10 mol %)	1,5-hexadiene	20 mol %	rt	30
4	**7** (5 mol %)	none	--	rt	93
5	**7** (5 mol %)	COD	20 mol %	rt	50
6	**7** (5 mol %)	COD	40 mol %	rt	30

VI. Reaction Progression Monitored by ^{19}F NMR

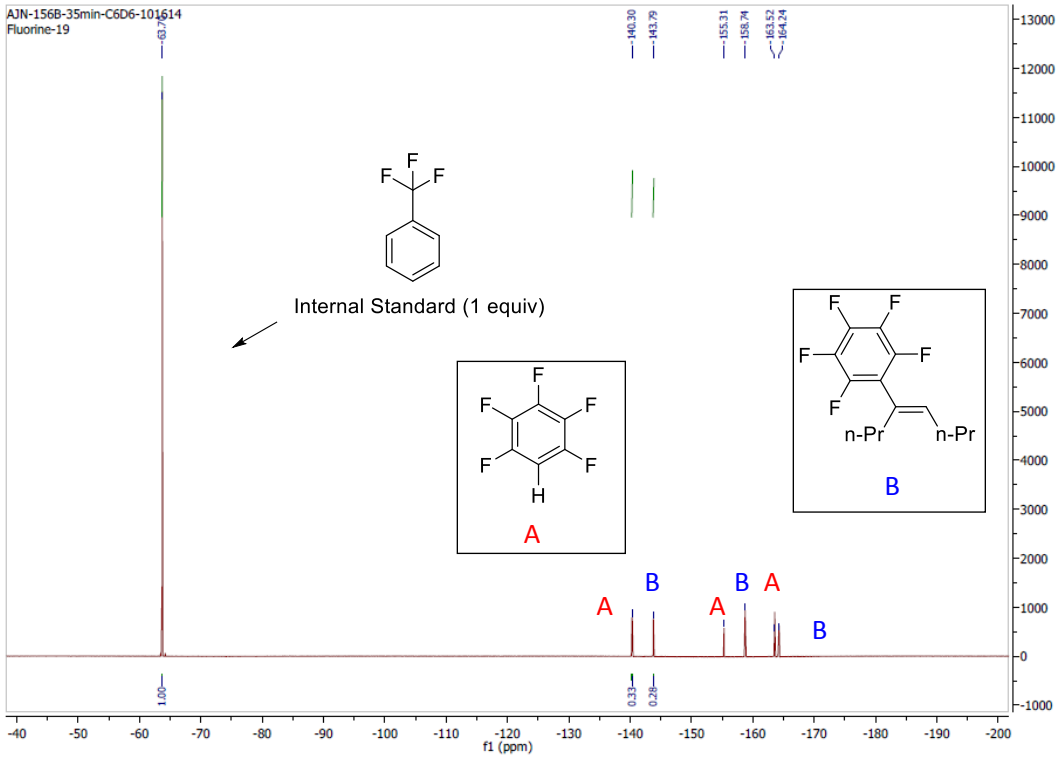
All reactions progression profiles described in Figure 2 were monitored by ^{19}F NMR and yields were calculated using α,α,α-trifluorotoluene as an internal standard. A representative spectrum is shown below with labeled starting material, product and internal standard peaks.



30 second time point (^{19}F NMR (C_6D_6, 470 MHz))

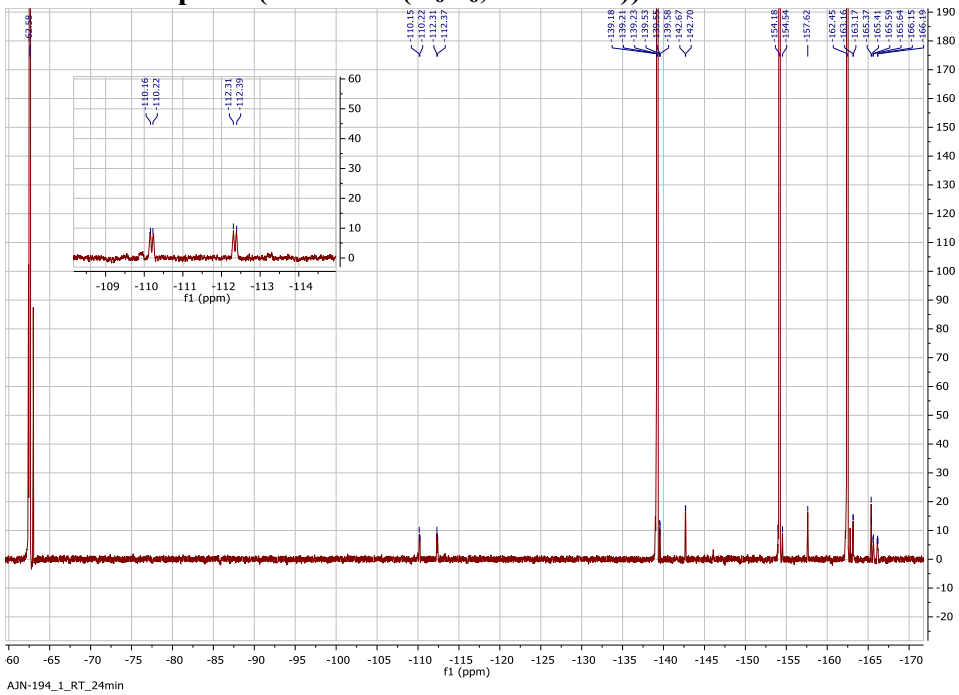


35 minute time point (^{19}F NMR (C_6D_6, 470 MHz))



In the room temperature reaction (Figure 2 of manuscript), small quantities of complex **3** were visible in the reaction by ^{19}F NMR (see S10 for authentic ^{19}F spectrum of **3**).

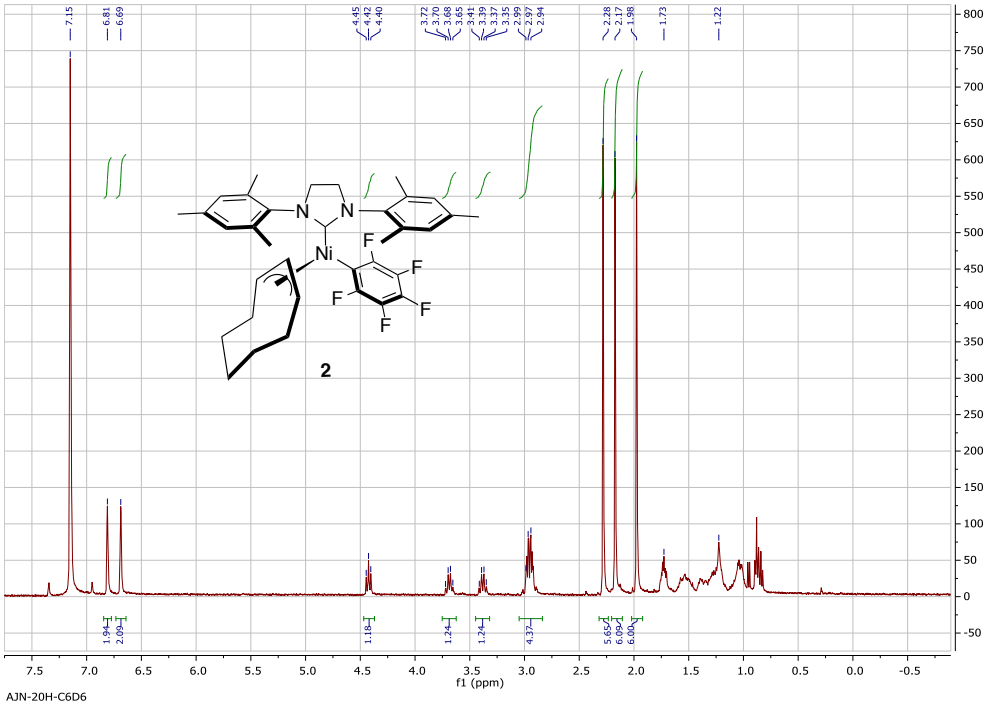
24-min time point (^{19}F NMR (C_6D_6, 470 MHz))



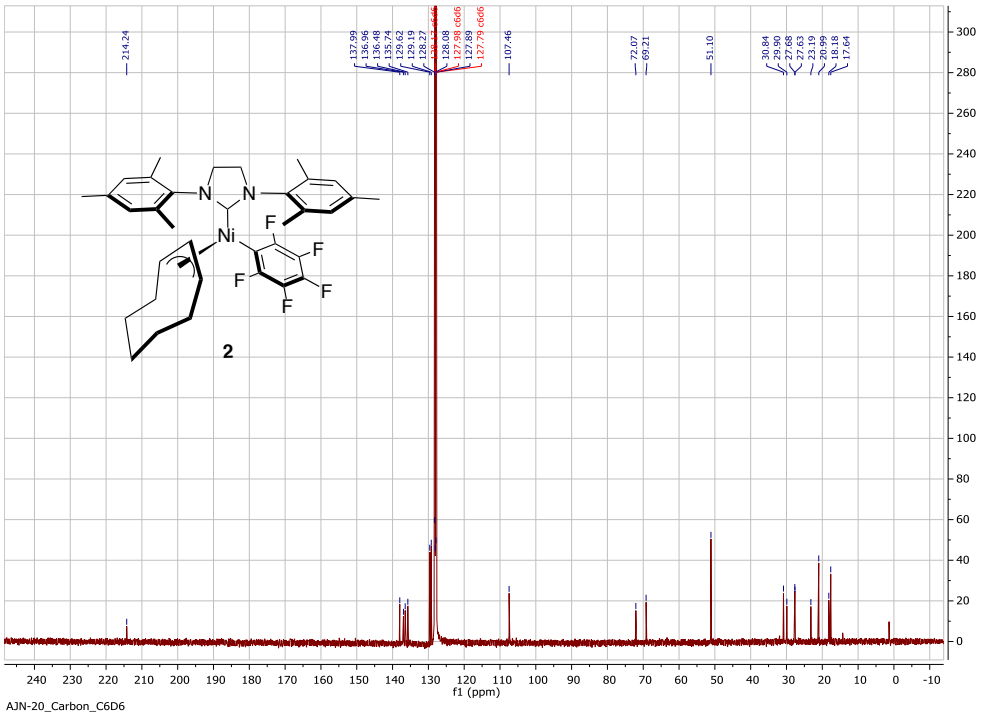
VII. NMR Spectra for 2 and 3

a. NMR details for 2

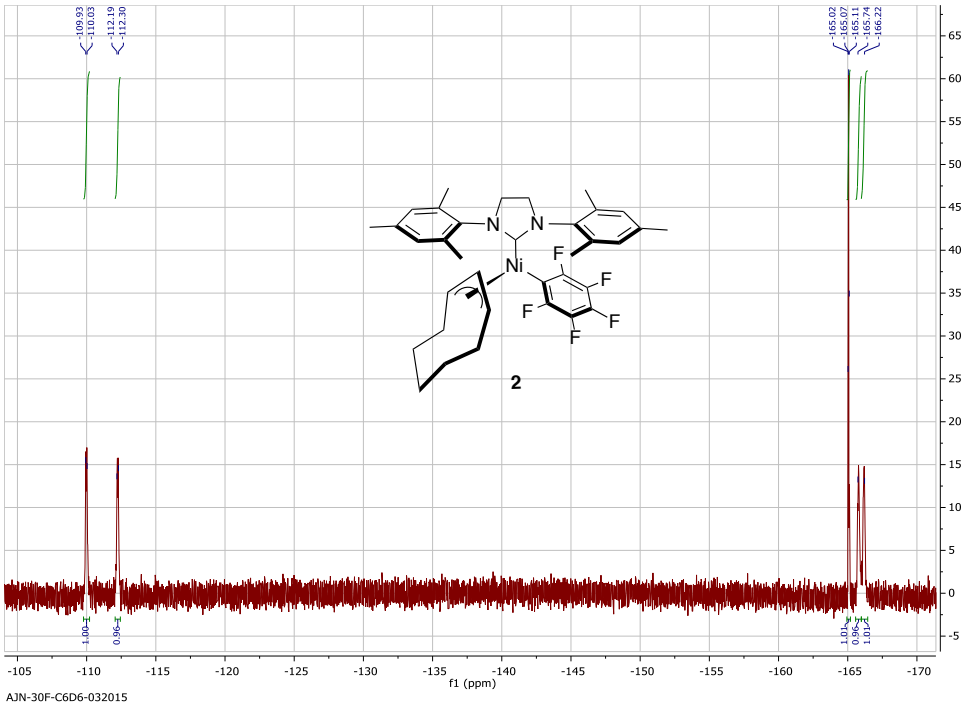
^{1}H NMR (C_6D_6, 500 MHz)



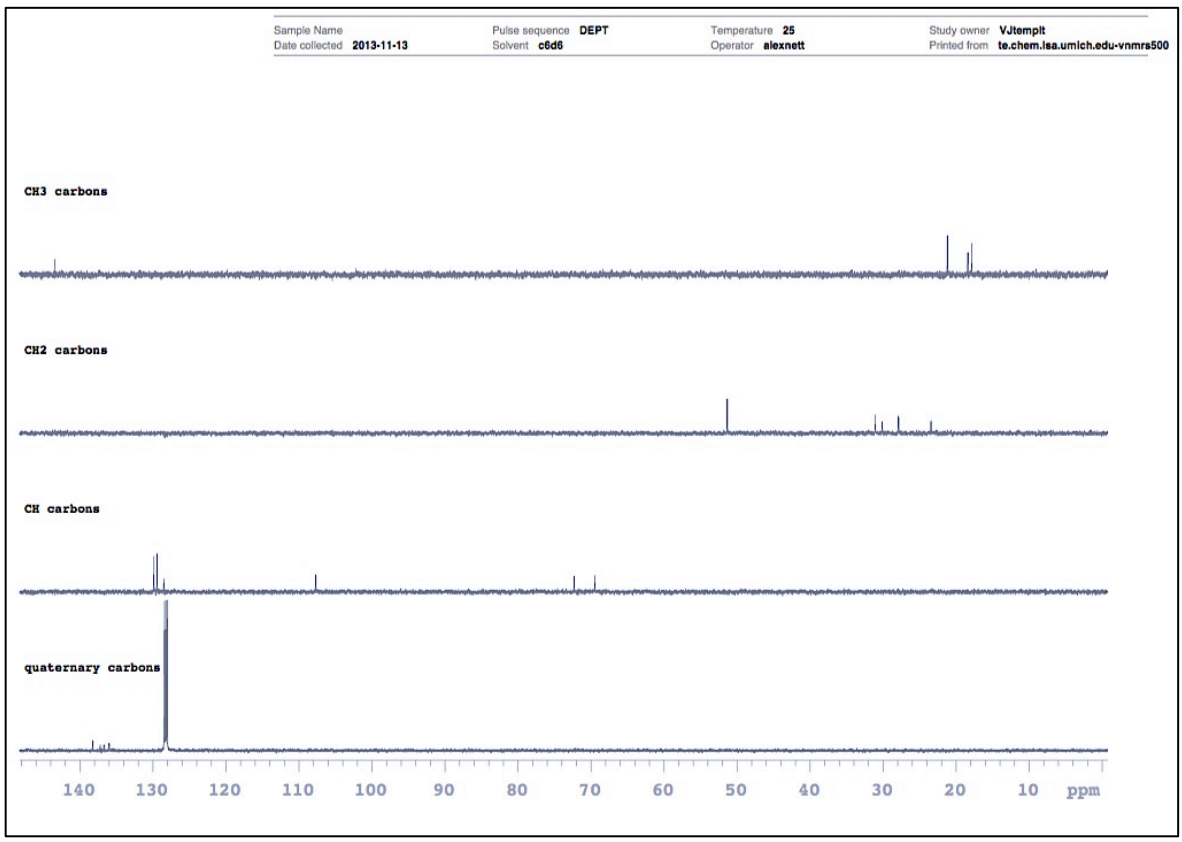
^{13}C NMR (C_6D_6, 125 MHz)



^{19}F NMR (C_6D_6, 470 MHz)

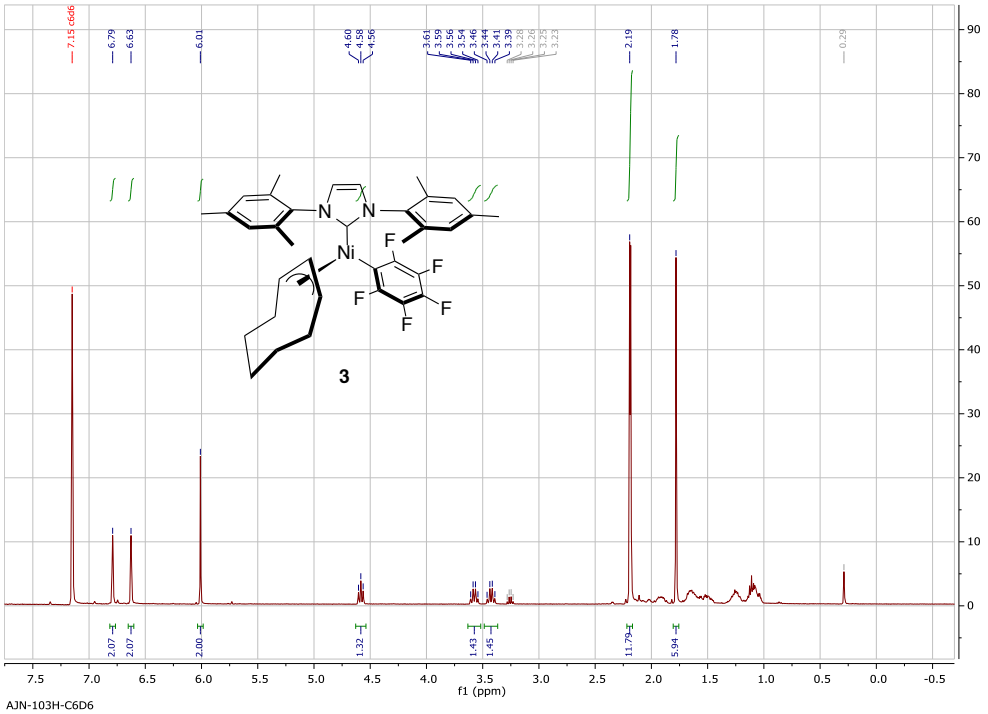


^{13}C DEPT NMR Spectra

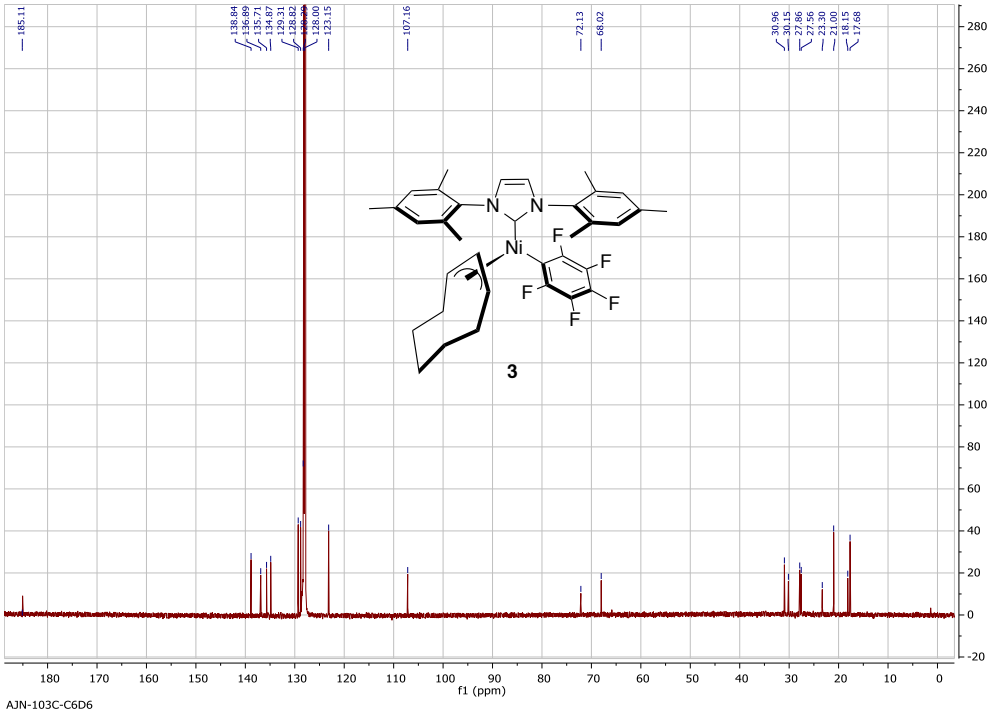


b. NMR spectra for 3

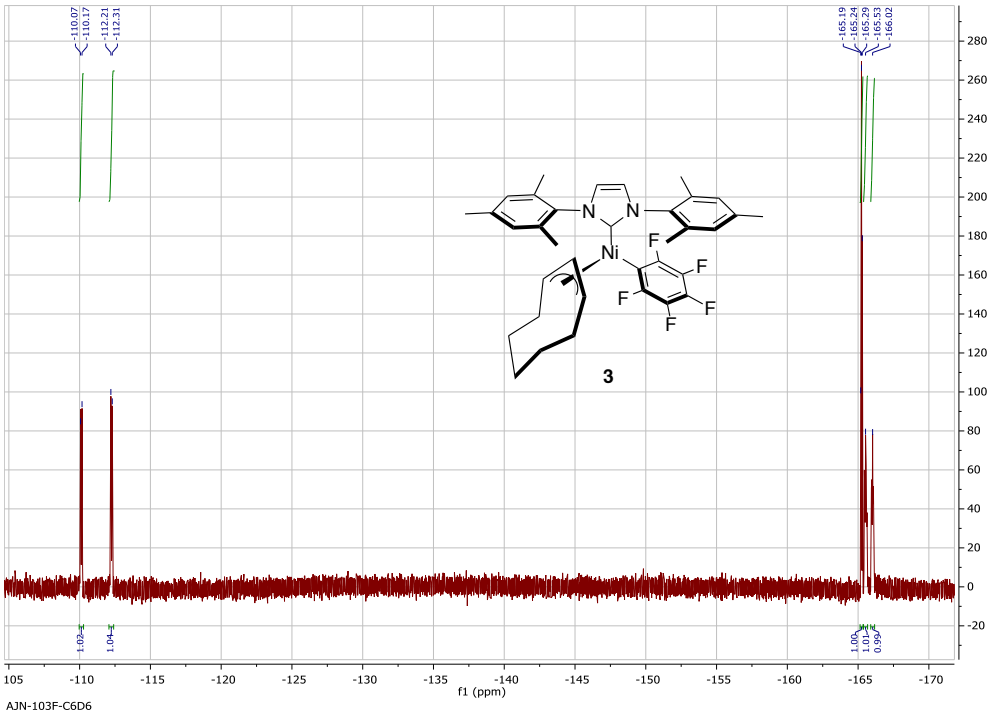
^{1}H NMR (C_6D_6, 500 MHz)



^{13}C NMR (C_6D_6, 125 MHz)



^{19}F NMR (C_6D_6, 470 MHz)



VIII. X-ray Notes

Note from CIF file concerning Level A Alert:

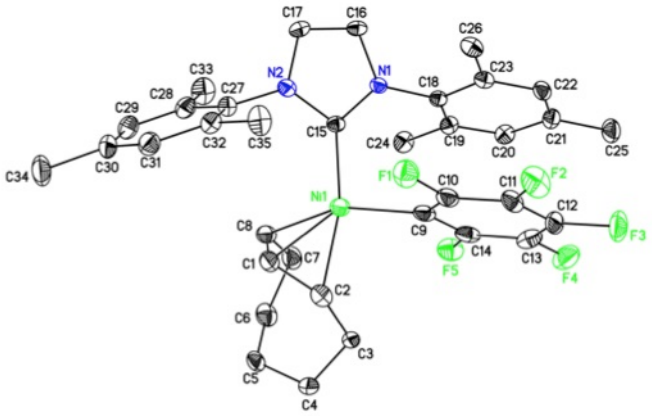
"The crystal is likely a non-merhhedral twin. Attempts at processing the data with the Twinsolve suite did not produce any improvement in the model. This is seemingly due to deficiencies in the available software. The raw images have been archived locally and this data may be revisited if software improvements become available.

The large residual electron density is 0.94 A from the nickel atoms and likely reflects the unresolved twinning issue.

Refinement of F^2^ against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2^, conventional R-factors R are based on F, with F set to zero for negative F^2^. The threshold expression of F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2^ are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger."

ORTEP of 3

For further details concerning the X-ray structure refer to CIF file.



IX. Computational Details

The automated reaction discovery tools developed in the Zimmerman group[6] was used to locate intermediates and products in the proposed mechanism. These tools start from the initial catalyst structure and locate plausible reaction routes without substantial guidance from chemical intuition. After identifying thermodynamically reasonable intermediates, the minimum energy paths and transition states connecting these intermediates were optimized using a recently developed version of the Growing String Method[7,8]. Besides locating the exact transition states, this method provides a comparable path to an IRC calculation, except in non-mass-weighted coordinates. Herein we report only the most kinetically and thermodynamically favorable reaction paths.

All geometries were optimized using the spin-restricted B3LYP density functional and the LANL2DZ basis set.[9,10] Frequency computations were performed at the same level of theory for all stationary points in order to obtain free energy corrections at 298K.[11,12] With the exception of solvent computations, all density functional calculations were performed using Q-Chem 4.0.[13] The SMD model for toluene was used with a ωB97X-D exchange functional with a cc-pVTZ basis set, and performed using the GAMESS software package.[14]

XYZ's for intermediates and transition states in Figure 2.

<u>Formation of π-allyl complex 3</u>

4
Total free energy (kcal/mol) = -2179035.531
80

C 3.494800 2.923116 2.683451

C 2.156650 3.050766 3.048074
C 1.247772 3.574771 2.132237
C 1.649977 3.983361 0.866596
H 0.934352 4.377139 0.159273
C 2.989250 3.846246 0.522665
C 3.917007 3.318573 1.416950
F -0.082677 3.667401 2.490150
F 1.746794 2.651009 4.300388
F 4.398649 2.401313 3.575439
F 5.235365 3.173828 1.058093
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H 0.164479 -2.433243 -2.534993
H 3.750534 -1.463805 -1.930842
C 1.040360 -1.833111 -2.296427
H 0.433579 -0.416363 -3.760820
C 1.852220 -2.240864 -1.254331
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H 1.530800 -3.107478 -0.676089
H 3.174014 0.353374 -2.695402
C 2.089379 0.508718 -2.684382
H 1.901527 1.362913 -3.347665
C 3.332655 -0.597208 0.035405
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H 3.286549 -1.021863 1.047709
H 0.946529 1.710316 -1.211284
H 1.920279 0.905610 0.825455
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H -3.043396 0.178225 -5.041537
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H -3.154839 -1.909848 -3.944860
H -4.029536 -1.771804 -2.410842
H -4.635397 0.108599 0.079639
H -3.783363 -1.284111 2.318343

4t
Total free energy (kcal/mol) = -2179027.082
80

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C -1.911700 -2.519399 1.462583
H -1.036530 -1.927709 1.697437
C -1.786113 -3.822045 0.995544

C -2.899530 -4.583200 0.650310
F -3.356461 -0.683021 2.006199
F -5.573581 -2.164138 1.338308
F -5.278635 -4.760725 0.422344
F -2.753822 -5.862511 0.171734
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H 3.849795 -0.979325 -1.249999
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C 2.468989 -3.367049 4.493356

C -1.302228 3.785496 -3.791519
C 2.165531 -2.058625 3.798987
H -1.495276 3.609122 -5.944163
C 0.777511 1.309643 0.214192
C -0.177916 3.019643 -1.337507
C 1.524035 0.269794 2.364157
N 0.392243 2.620273 -0.075341
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N 1.152478 1.403256 1.559233
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C 0.668355 3.470888 -2.369452
C 1.000793 2.712848 2.056836
C 0.526718 3.471164 1.036393
C 2.803257 -0.300499 2.215220
H 0.728552 4.203710 -4.386530
H 4.072731 -1.929214 2.808078
H 2.576232 2.549317 -1.958332
C 2.165130 3.542667 -2.174204
C 3.849695 0.361233 1.350232
H 3.494786 0.478575 0.322147
H 2.654750 3.931060 -3.072230
H 2.436269 4.190711 -1.332000
H 4.773662 -0.224419 1.340423
H 4.089519 1.365074 1.723550
H 1.238016 2.968738 3.075146
H 0.274360 4.516781 0.990392

5
Total free energy (kcal/mol) = -2179037.30
80

C 3.318799 0.170637 5.029619
C 3.642118 0.970630 3.935872
C 2.691960 1.170533 2.937593
C 1.429750 0.596114 3.002655
H 0.712613 0.734629 2.193502
C 1.128100 -0.188705 4.106718
C 2.057022 -0.410758 5.119389
F 3.034134 1.949663 1.847172
F 4.890589 1.543239 3.848503
F 4.248319 -0.051195 6.018219
F 1.751660 -1.225550 6.189124

F -0.115613 -0.781995 4.211806
H -3.446011 -0.397682 3.078995
C -2.799551 -0.119191 2.228379
H -3.515364 -1.631790 0.830656
H -4.406978 2.127340 0.851873
C -3.485426 -0.547069 0.952166
H -1.897661 -0.736727 2.341113
C -4.058874 0.180516 -0.020158
H -5.026809 1.920064 -0.769915
C -4.173319 1.682976 -0.119999
H -4.484133 -0.368244 -0.861889
H -3.269754 1.992650 2.509040
C -2.378000 1.358527 2.418379
H -1.892533 1.402431 3.403135
C -2.931882 2.389039 -0.720047
Ni -0.504107 0.718638 0.032148
H -3.201787 3.448746 -0.871201
C -1.394706 1.949898 1.403263
C -1.636518 2.362721 0.075481
H -2.744122 1.988020 -1.725942
H -0.552742 2.457988 1.881937
H -0.912296 3.081142 -0.323721
H 4.796113 -0.989937 0.828301
H 2.132246 3.296595 -3.131193
C 3.866720 -1.003284 0.251066
H 1.711177 2.277089 -1.737830
H 3.490298 0.024642 0.195254
H 4.138548 -2.413732 2.550649
C 1.780745 2.304966 -2.832033
H 0.246983 3.931133 -4.380272
H 4.112620 -1.310195 -0.771846
H -1.522743 4.623648 -5.830962
C 3.158863 -2.569053 2.106609
H 2.542095 1.571443 -3.123330
C -0.226470 2.964931 -4.228778
C 2.855235 -1.923277 0.898531
C 0.439643 2.000901 -3.456949
H 3.651883 -4.130640 4.224713
H 2.171769 -3.461265 4.921835
C -2.182299 3.774635 -5.626890
C 2.569408 -4.047270 4.082787
C -1.477108 2.714728 -4.809257
C 2.234726 -3.400073 2.756508
H -3.065328 4.160247 -5.100615
C 0.466735 -0.422754 -1.144879
C -0.186760 0.755080 -3.269632

C 1.583506 -2.140365 0.331063
N 0.498851 -0.275429 -2.528155
H -2.528082 3.376413 -6.588370
N 1.272330 -1.540583 -0.943419
H 2.139714 -5.052174 4.158282
C -2.070396 1.460053 -4.600270
C 0.980714 -3.595012 2.158644
C -1.447149 0.468161 -3.831280
C 1.769048 -2.053886 -2.156504
C 1.286315 -1.262363 -3.145783
C 0.636310 -2.985309 0.944520
H -3.042527 1.247747 -5.037754
H 0.255224 -4.243454 2.641469
H -2.263912 -1.029993 -2.511854
C -2.127807 -0.858989 -3.586349
C -0.710079 -3.244616 0.310167
H -1.287678 -2.318442 0.215883
H -3.111579 -0.880825 -4.064200
H -1.544590 -1.701619 -3.977123
H -1.288719 -3.954693 0.908098
H -0.604421 -3.657147 -0.700822
H 2.402652 -2.923306 -2.188731
H 1.420302 -1.299958 -4.213166

5t
Total free energy (kcal/mol) = -2179024.10
80

C -0.954040 4.110729 -1.705321
C -0.924951 3.937178 -0.324068
C -0.232261 2.853106 0.205046
C 0.434931 1.905283 -0.567850
H 1.684228 1.428069 -0.058469
C 0.355248 2.113159 -1.945533
C -0.309235 3.189309 -2.524163
F -0.225210 2.732370 1.598520
F -1.584158 4.838555 0.490046
F -1.625598 5.179013 -2.257504
F -0.355951 3.355420 -3.897931
F 0.940136 1.193830 -2.819496
H 4.760777 0.745982 -2.431525
C 3.868890 0.496843 -1.830738
H 3.048356 -1.129812 -3.031616
H 5.192833 -1.356416 0.149789

C 3.517613 -0.953218 -2.062654
H 3.059147 1.086692 -2.269778
C 3.704292 -2.018823 -1.268383
H 4.761777 -3.045214 0.267778
C 4.343423 -2.043037 0.099052
H 3.355128 -2.984913 -1.635505
H 5.053767 0.616495 0.002877
C 4.114299 1.015931 -0.395605
H 4.282570 2.097530 -0.496331
C 3.360350 -1.765985 1.262044
Ni 1.007814 0.090577 0.399728
H 3.901244 -1.957018 2.203291
C 3.016742 0.830237 0.670419
C 2.708463 -0.386215 1.383392
H 2.576460 -2.531211 1.218662
H 2.971149 1.712467 1.319268
H 2.398972 -0.203403 2.414072
H -4.013376 2.066485 0.174621
H -0.258001 1.133004 5.018411
C -3.446096 1.153144 0.375482
H -0.082592 1.095880 3.256306
H -2.634803 1.406752 1.067349
H -3.920350 1.983702 -2.167808
C -0.398122 0.513782 4.127597
H 1.381532 -0.187885 6.054082
H -4.112420 0.460607 0.904452
H 2.771702 -1.620592 7.412190
C -3.261525 1.119830 -2.149928
H -1.472297 0.327523 4.009949
C 1.260247 -0.980045 5.320831
C -2.915677 0.558807 -0.912327
C 0.376926 -0.776830 4.249005
H -4.035798 1.824578 -4.629062
H -2.297458 1.997584 -4.921181
C 2.951426 -2.353345 6.619588
C -3.088061 1.279017 -4.673283
C 1.982980 -2.171677 5.471776
C -2.769692 0.605441 -3.357859
H 3.990134 -2.229059 6.285451
C -0.486814 -0.948934 1.029971
C 0.238012 -1.811867 3.304746
C -2.047066 -0.550734 -0.909968
N -0.691732 -1.653193 2.211686
H 2.870836 -3.354453 7.058465
N -1.688481 -1.138869 0.357470
H -3.145960 0.556178 -5.494125

C 1.791758 -3.191722 4.528715
C -1.923928 -0.512717 -3.312541
C 0.919492 -3.038101 3.441879
C -2.588622 -1.921923 1.095044
C -1.968135 -2.239897 2.256878
C -1.546993 -1.108613 -2.099991
H 2.331242 -4.128711 4.638434
H -1.534301 -0.923448 -4.239395
H 0.752611 -3.816080 1.422970
C 0.715996 -4.169857 2.458182
C -0.619049 -2.301609 -2.085149
H 0.363031 -2.033384 -1.676495
H 1.486472 -4.935295 2.587751
H -0.258962 -4.655549 2.594290
H -0.470466 -2.684616 -3.098924
H -1.015545 -3.115870 -1.466563
H -3.566554 -2.170485 0.720294
H -2.297191 -2.814082 3.104663

6
Total free energy (kcal/mol) = -2179042.87
80

C -1.728296 4.366455 -2.053595
C -1.911645 4.155678 -0.690047
C -1.252336 3.091289 -0.078651
C -0.415158 2.202382 -0.741324
H 1.901957 1.727405 -0.090350
C -0.254568 2.475886 -2.096465
C -0.889424 3.515951 -2.768257
F -1.514366 2.914135 1.292473
F -2.752956 4.992151 0.022355
F -2.383379 5.399230 -2.695314
F -0.738211 3.700025 -4.134162
F 0.576434 1.648982 -2.870676
H 4.675311 1.597555 -2.465890
C 3.731504 1.300239 -1.978548
H 2.822670 0.223513 -3.641511
H 4.576902 -1.268237 -0.517480
C 3.223710 0.044771 -2.644638
H 3.018772 2.101260 -2.221298
C 3.200646 -1.218952 -2.193901
H 3.894258 -2.809366 -0.964272
C 3.650845 -1.743723 -0.851386
H 2.770724 -1.971868 -2.855810

H 4.765098 0.630923 -0.163839
C 3.964745 1.316105 -0.454424
H 4.335170 2.321982 -0.210725
C 2.569419 -1.648549 0.257697
Ni 0.554524 0.671530 0.101049
H 2.935394 -2.235264 1.114823
C 2.723772 1.074507 0.445992
C 2.132166 -0.272085 0.794036
H 1.687830 -2.189017 -0.113030
H 2.856838 1.642135 1.374245
H 1.978110 -0.338638 1.871589
H -4.739904 1.967447 -0.507253
H -0.777008 1.497420 4.497387
C -4.094928 1.114919 -0.277184
H -0.457834 1.473860 2.755356
H -3.398137 1.426779 0.507195
H -4.504755 1.932984 -2.822373
C -0.834162 0.882376 3.594757
H 0.846934 0.244249 5.610830
H -4.730361 0.326055 0.144823
H 2.106607 -1.224009 7.123950
C -3.714372 1.189276 -2.772603
H -1.891995 0.689808 3.381309
C 0.773507 -0.566813 4.892133
C -3.369226 0.656398 -1.523781
C -0.058704 -0.398094 3.776228
H -4.409748 1.808198 -5.316547
H -2.737690 2.384697 -5.384051
C 2.407659 -1.891226 6.309824
C -3.363188 1.490462 -5.264527
C 1.494929 -1.748713 5.111932
C -3.047713 0.815050 -3.949364
H 3.444907 -1.641138 6.048842
C -0.831946 -0.563832 0.560417
C -0.145925 -1.455958 2.850063
C -2.320986 -0.285757 -1.476271
N -1.019276 -1.333935 1.703172
H 2.407716 -2.916764 6.694711
N -1.959376 -0.850260 -0.194505
H -3.163078 0.831558 -6.115767
C 1.354470 -2.792277 4.186817
C -2.042192 -0.156108 -3.863367
C 0.537577 -2.672739 3.052803
C -2.802363 -1.762408 0.456879
C -2.222375 -2.056790 1.644231
C -1.664531 -0.725458 -2.639100

H 1.892325 -3.723028 4.346821
H -1.523417 -0.468039 -4.765126
H 0.280158 -3.523823 1.069293
C 0.394095 -3.846030 2.107019
C -0.558275 -1.750861 -2.587718
H 0.374317 -1.298975 -2.231746
H 1.272284 -4.495950 2.168012
H -0.482427 -4.459231 2.356136
H -0.371434 -2.163023 -3.584160
H -0.801031 -2.579749 -1.913514
H -3.719896 -2.101954 0.009777
H -2.535694 -2.696982 2.449578

3
Total free energy (kcal/mol) = -2179098.44
80

C	-1.07646525	-0.27934595	4.59377921
C	-1.64727144	-0.89220880	3.48140442
C	-1.08118540	-0.68027695	2.22748596
C	0.05668045	0.08743342	2.00328545
H	-2.03309736	0.85474963	-0.16847907
C	0.56543361	0.70538200	3.14130141
C	0.03973697	0.53544537	4.42021984
F	-1.72030433	-1.29770682	1.14049337
F	-2.74712025	-1.71856101	3.63798482
F	-1.60967802	-0.47766242	5.85212296
F	0.61300676	1.15444838	5.51640913
F	1.67061759	1.55696148	3.02935435
H	-3.18294455	2.51898073	-3.24938154
C	-2.59103125	1.90324209	-2.55611356
H	-0.70950045	2.32099186	-3.56144272
H	1.69697191	0.95071307	-2.44118050
C	-1.32198654	1.44566465	-3.30365774
H	-3.20621010	1.01652980	-2.33461229
C	-0.43727118	0.40067135	-2.55430339
H	-1.06604925	-0.16872926	-1.85928241
C	0.77862015	1.00525693	-1.86105516
H	-0.07083365	-0.33248154	-3.28009818
H	-1.81314343	3.60935937	-1.44832390
C	-2.40497708	2.70435356	-1.25165535
H	-3.40069894	3.04976786	-0.93935707
C	0.73937479	2.02173301	-0.88738057
Ni	0.76734338	0.29602297	0.20700270

H	1.66500836	2.56491185	-0.70161002
C	-1.77144802	1.91335779	-0.07013190
C	-0.26758869	2.12394868	0.10651987
H	-1.64702836	1.00486891	-4.25681970
H	-2.24258599	2.24030696	0.86485363
H	-0.02031366	2.81002327	0.91385146
H	2.22746639	-3.36583452	-3.07671595
C	1.35530824	-2.69853710	-3.06156098
C	0.29025658	-3.21239359	-2.11829786
C	-0.88526765	-3.78549958	-2.61926571
C	-1.61503727	-4.33023423	-0.39002566
H	-1.04081968	-3.80889469	-3.69433719
C	-1.85688056	-4.33512009	-1.76926710
H	-2.34913852	-4.76819656	0.28063983
H	-3.47265498	-5.77809891	-1.74507579
C	-3.14047745	-4.91064994	-2.32537224
H	-3.02252393	-5.22294821	-3.36816312
H	-3.95067231	-4.16978438	-2.29416441
H	1.71425244	-1.70831815	-2.76753383
H	0.97008099	-2.63589319	-4.08340754
C	0.47286815	-3.18092575	-0.72063480
C	-0.45352267	-3.76798771	0.15976980
H	0.23444299	-4.81546269	1.92075437
C	-0.21354396	-3.84955294	1.64947152
H	-1.15514437	-3.75710082	2.19766694
H	0.45883486	-3.06432117	1.99937590
H	5.16888194	-0.58531014	-1.80270384
C	4.55846156	0.30183958	-1.58574486
C	4.02891215	-0.10880583	0.87462260
C	3.83151142	-2.54873094	0.39399201
N	3.25996063	-1.26888025	0.47812977
C	2.85500693	-3.38552452	-0.03294788
C	1.92121215	-1.27838146	0.11433643
N	1.69630246	-2.60802994	-0.20286487
C	4.21013595	0.16183810	2.24293682
C	3.63836625	-0.73460450	3.31586609
H	4.29255814	-1.59698962	3.50426425
H	5.85816950	2.40934653	-0.48045016
C	5.38769426	1.79116042	0.27935294
H	7.13154689	3.57611978	1.33448927
C	4.64155099	0.67651059	-0.12356776
C	6.32510381	3.35369961	2.04172464
C	5.55287697	2.11899402	1.63369660
H	5.66911574	4.23395384	2.07645389
H	6.76716152	3.23908977	3.03682074
C	4.97257335	1.28431093	2.59646121

H	5.10206814	1.51448618	3.64986489
H	3.52943746	-0.18597272	4.25468657
H	4.92575652	1.11693866	-2.21618997
H	3.53544682	0.06561776	-1.88748426
H	2.65707096	-1.12404193	3.03657824
H	2.85954510	-4.44307897	-0.23099690
H	4.86239435	-2.72636293	0.64559387

Formation of 12

11
Total free energy (kcal/mol) = -2179785.204
82

C 0.793604 -4.428807 5.791195
C 0.100319 -4.742830 4.624283
C 0.303686 -3.974989 3.482628
C 1.201154 -2.910705 3.469131
C 1.864601 -2.604205 4.651437
C 1.679122 -3.352664 5.810411
F -0.394683 -4.292647 2.337695
F -0.748939 -5.829281 4.606782
F 0.613814 -5.191476 6.920795
F 2.374829 -3.054214 6.960899
F 2.754204 -1.547255 4.691765
Ni 2.830146 -2.783280 1.425665
H 3.580653 -5.624214 -1.492747
C 2.550030 -5.270832 -1.369565
C 1.828961 -6.020125 -0.275215
C 0.559827 -6.568567 -0.501149
C 0.459900 -7.397496 1.758230
H 0.109622 -6.452271 -1.482946
C -0.143912 -7.250210 0.501069
H -0.073547 -7.913090 2.551511
H -1.728751 -8.697939 0.814605
C -1.535050 -7.783929 0.242785
H -1.687441 -8.008036 -0.818269
H -2.296591 -7.048590 0.535349
H 2.599995 -4.202437 -1.125824
H 2.030905 -5.386265 -2.325429
C 2.397609 -6.176671 1.004390
C 1.730708 -6.874790 2.030429
H 3.054078 -7.910900 3.413347
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H 1.576085 -7.275413 4.141917
H 2.909578 -6.181921 3.718019
H 7.513247 -3.978652 -0.339155
C 6.927624 -3.054600 -0.243711

C 6.148614 -3.186126 2.173739
C 5.887007 -5.633585 1.707733
N 5.356750 -4.338181 1.812017
C 4.857767 -6.451611 1.370654
C 3.995677 -4.309126 1.534131
N 3.713446 -5.644377 1.270357
C 6.159516 -2.747565 3.511628
C 5.396447 -3.479712 4.591501
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C 7.680374 -1.431839 1.549671
H 9.254455 0.505616 2.483319
C 6.914735 -2.548911 1.180469
C 8.482292 0.290102 3.228750
C 7.691189 -0.946334 2.863784
H 7.829627 1.171260 3.290860
H 8.971810 0.180979 4.203053
C 6.932784 -1.621651 3.830578
H 6.938111 -1.266035 4.857335
H 5.239346 -2.838495 5.462544
H 7.369478 -2.312095 -0.913984
H 5.915404 -3.275995 -0.595180
H 4.420005 -3.812853 4.233013
H 4.823783 -7.512457 1.193171
H 6.928132 -5.840600 1.885032
C 2.852428 -1.570154 -0.055581
C 1.922718 -1.181749 0.747374
C 3.629306 -1.304377 -1.299338
C 0.910317 -0.110676 1.010399
H 1.321851 -2.300316 2.553005
H 0.773346 0.504632 0.106370
C 1.301702 0.821159 2.183774
H -0.072707 -0.555570 1.229985
C 4.662154 -0.161963 -1.132416
H 2.934441 -1.032382 -2.111969
H 4.152502 -2.209174 -1.637337
C 5.476815 0.091146 -2.410312
H 5.330715 -0.408369 -0.297947
H 4.129981 0.753384 -0.841200
H 6.031287 -0.807545 -2.710208
H 6.202568 0.900021 -2.264881
H 4.826366 0.373081 -3.248173
H 2.266010 1.291376 1.949278
H 1.471438 0.220600 3.086583
C 0.241382 1.897333 2.459681
H 0.078937 2.530008 1.577521
H 0.540556 2.550270 3.288038
H -0.722832 1.443260 2.723401

11t
Total free energy (kcal/mol) = -2179777.932
82

C 0.816742 -3.564532 6.103555
C 0.207720 -4.183360 5.013704
C 0.639694 -3.871901 3.727722
C 1.673842 -2.976455 3.469053
C 2.239008 -2.367753 4.586140
C 1.843314 -2.646407 5.890477
F -0.003959 -4.503157 2.669036
F -0.800722 -5.103670 5.226412
F 0.407215 -3.861138 7.384394
F 2.459493 -2.044758 6.970427
F 3.271382 -1.446536 4.414837
Ni 2.754323 -2.933371 1.690221
H 3.718285 -5.649230 -1.597277
C 2.671768 -5.330282 -1.526034
C 1.919727 -6.094132 -0.462199
C 0.679785 -6.679512 -0.749664
C 0.484580 -7.486980 1.511043
H 0.277744 -6.584720 -1.754579
C -0.054423 -7.374570 0.222186
H -0.074301 -8.012599 2.280120
H -1.603907 -8.872940 0.466404
C -1.411138 -7.958097 -0.104289
H -1.498834 -8.196972 -1.169369
H -2.212493 -7.247737 0.139404
H 2.672802 -4.258761 -1.296760
H 2.205528 -5.470885 -2.505491
C 2.425271 -6.223778 0.845865
C 1.720698 -6.918871 1.846017
H 3.014210 -7.859120 3.319355
C 2.267476 -7.056633 3.248908
H 1.463069 -7.290158 3.952288
H 2.753748 -6.134779 3.580317
H 7.555824 -3.813233 -0.401048
C 6.884511 -2.960308 -0.232271
C 6.129901 -3.230578 2.186716
C 5.913275 -5.635704 1.521236
N 5.351798 -4.371959 1.767670
C 4.895504 -6.450023 1.143386
C 3.984627 -4.369358 1.546877
N 3.724915 -5.673977 1.160551
C 6.152435 -2.862018 3.545691
C 5.435916 -3.667953 4.604219
H 6.016728 -4.559582 4.877271
H 8.209817 -0.877512 0.895788
C 7.633669 -1.427192 1.635113
H 9.193279 0.482723 2.651539
C 6.878745 -2.534027 1.218717

C 8.434709 0.215541 3.394177
C 7.653639 -1.009258 2.972589
H 7.772178 1.082825 3.515612
H 8.939530 0.058653 4.353997
C 6.915557 -1.744232 3.911507
H 6.930014 -1.443223 4.955230
H 5.290363 -3.072066 5.508921
H 7.226702 -2.142801 -0.873761
H 5.887572 -3.263664 -0.565058
H 4.456789 -4.008097 4.261325
H 4.883305 -7.489032 0.863086
H 6.965881 -5.823455 1.642296
C 2.712504 -1.797386 0.136631
C 1.766140 -1.350024 0.906579
C 3.406549 -1.453223 -1.141700
C 0.843758 -0.177817 1.078715
H 1.529435 -2.148253 2.248043
H 0.949036 0.472482 0.197589
C 1.117333 0.656080 2.351435
H -0.204920 -0.512352 1.094687
C 4.362699 -0.242351 -0.988855
H 2.661910 -1.209596 -1.917133
H 3.979378 -2.308352 -1.523739
C 5.028260 0.146323 -2.317613
H 5.123880 -0.480627 -0.235701
H 3.792213 0.608557 -0.593575
H 5.624430 -0.682999 -2.719766
H 5.694531 1.007864 -2.192525
H 4.277013 0.410096 -3.072907
H 2.166430 0.978986 2.346688
H 0.995514 0.020481 3.237312
C 0.190247 1.876688 2.455405
H 0.321298 2.544650 1.594699
H 0.396275 2.456197 3.362528
H -0.863961 1.573166 2.484070

12
Total free energy (kcal/mol) = -2179795.265
82

C 1.161634 -3.561281 6.476581
C 0.543461 -4.291857 5.465277
C 0.994572 -4.149357 4.154238
C 2.050290 -3.324541 3.782758
C 2.610357 -2.596336 4.827102
C 2.206115 -2.697479 6.155791
F 0.308893 -4.879990 3.178239
F -0.503752 -5.139841 5.777828

F 0.736378 -3.683906 7.783655
F 2.822386 -1.966907 7.155973
F 3.646052 -1.692122 4.555311
Ni 2.647200 -2.970503 1.927442
H 3.586370 -5.421282 -1.612752
C 2.536672 -5.123392 -1.502729
C 1.819292 -5.964775 -0.474614
C 0.595211 -6.570068 -0.787395
C 0.485933 -7.581909 1.393937
H 0.172288 -6.412183 -1.775495
C -0.091063 -7.372590 0.135235
H -0.030314 -8.201933 2.121181
H -1.577442 -8.945019 0.278420
C -1.433478 -7.976263 -0.211926
H -1.541304 -8.122009 -1.291926
H -2.253381 -7.322028 0.113701
H 2.526799 -4.068212 -1.214873
H 2.054175 -5.214899 -2.480082
C 2.351202 -6.174113 0.812358
C 1.706075 -6.995486 1.755694
H 3.019567 -8.087083 3.095655
C 2.296544 -7.260376 3.121818
H 1.508953 -7.530152 3.830381
H 2.817581 -6.384213 3.515984
H 7.387869 -3.633431 -0.409463
C 6.702745 -2.808361 -0.170510
C 6.095000 -3.237079 2.266561
C 5.833940 -5.595433 1.500477
N 5.278316 -4.344592 1.818373
C 4.815717 -6.385038 1.081696
C 3.910590 -4.335998 1.608933
N 3.643702 -5.613011 1.149814
C 6.268018 -3.011573 3.645262
C 5.681208 -3.933855 4.687330
H 6.339697 -4.796450 4.860600
H 8.060309 -0.774137 1.004387
C 7.548504 -1.387403 1.741001
H 9.168699 0.460061 2.768038
C 6.764224 -2.461924 1.299524
C 8.501250 0.102517 3.558661
C 7.692961 -1.091785 3.103690
H 7.844584 0.936773 3.838921
H 9.111817 -0.136294 4.436808
C 7.062733 -1.925614 4.037155
H 7.185302 -1.727077 5.097975
H 5.561964 -3.410363 5.639207
H 6.995468 -1.952494 -0.784929
H 5.702368 -3.125583 -0.473190
H 4.705132 -4.319381 4.388456
H 4.797912 -7.407491 0.747446
H 6.887353 -5.787289 1.604405

C 2.622999 -1.895511 0.353610
C 1.557210 -1.341654 0.940912
C 3.304285 -1.448456 -0.908982
C 0.738786 -0.107346 0.626489
H 1.178620 -1.831405 1.891860
H 1.078222 0.312783 -0.329253
C 0.828173 0.972971 1.729376
H -0.317245 -0.388026 0.492974
C 4.188002 -0.190358 -0.701199
H 2.551613 -1.215844 -1.680413
H 3.928208 -2.248201 -1.324652
C 4.854678 0.276210 -2.004129
H 4.944998 -0.404879 0.062445
H 3.564967 0.617291 -0.294825
H 5.509531 -0.501750 -2.417553
H 5.462123 1.174303 -1.842012
H 4.102669 0.513564 -2.767440
H 1.880884 1.253757 1.867802
H 0.496879 0.540030 2.684031
C -0.012163 2.218028 1.405625
H 0.324928 2.690349 0.474306
H 0.060100 2.964837 2.204434
H -1.071493 1.958933 1.283951

Formation of π-allyl complex 8

(All energies include 4-octyne, in order to allow comparison to **11**)

7

Total free energy (kcal/mol) = -2130490.993

76

Ni -0.493618 0.413579 -0.653519
H 1.004422 -4.476495 0.362178
H -4.275618 -2.667506 -1.341825
C 1.295709 -3.762603 -0.419281
H -2.637587 -1.985226 -1.285305
H 1.785342 -4.327474 -1.218034
H 3.965831 -3.501012 -0.831659
C -3.468919 -2.351387 -0.674125
H -5.897666 -1.139154 -0.620617
H 0.373456 -3.330012 -0.818873
H -7.560712 0.539701 -0.076038
C 3.584905 -2.707717 -0.194521
H -3.104961 -3.235674 -0.137018
C -5.250623 -0.762661 0.166794
C 2.216735 -2.689114 0.115476
C -3.951875 -1.282218 0.278451

H 6.214520 -2.732419 -0.509653
H 6.205609 -0.980662 -0.752815
C -7.144528 0.749106 0.914401
C 5.941291 -1.777832 -0.049097
C -5.732381 0.220619 1.041069
C 4.468637 -1.737857 0.296474
H -7.181600 1.832396 1.075296
C -0.661039 -0.884628 0.756597
C -3.121856 -0.780052 1.296721
C 1.734325 -1.654629 0.940025
N -1.789276 -1.307839 1.456106
H -7.810689 0.288190 1.656393
N 0.344982 -1.662684 1.325304
H 6.563607 -1.641972 0.843054
C -4.880359 0.688315 2.053123
C 3.951072 -0.720386 1.114497
C -3.574870 0.201475 2.202310
C -0.148323 -2.519547 2.326969
C -1.482932 -2.300704 2.406018
C 2.591616 -0.659625 1.449870
H -5.235883 1.453336 2.738075
H 4.622188 0.038443 1.506861
H -1.731192 1.100179 2.882133
C -2.675213 0.730243 3.296120
C 2.069025 0.442164 2.343216
H 1.299330 1.030680 1.831244
H -3.159703 1.550961 3.833127
H -2.422227 -0.046569 4.028272
H 2.880755 1.111531 2.643401
H 1.609562 0.040529 3.255165
H 0.495813 -3.187518 2.872215
H -2.238610 -2.743272 3.031975
H -1.820119 3.334181 -2.830237
C -1.798251 2.353960 -2.331327
H -2.824223 2.149836 -1.998611
H -2.105096 0.478013 -3.428625
H -0.841667 -1.459573 -2.471088
C -0.011249 -0.781024 -2.282384
C -1.312762 1.225808 -3.293838
C -0.084638 0.562364 -2.671749
H 0.952563 -1.260764 -2.135525
C -0.867420 2.392440 -1.116776
H 0.847376 1.108434 -2.809079
H -2.318568 1.921709 0.419108
C -1.275991 2.135415 0.197563
H 0.064411 2.934226 -1.268394
H -1.076771 1.615688 -4.294934
H -0.685925 2.493523 1.038462
F 6.015988 1.811221 0.205184
C 4.996397 2.258450 -0.613005
C 4.087649 3.193167 -0.131790

H 4.172556 3.585537 0.871818
C 3.059870 3.603845 -0.972716
F 2.131129 4.517195 -0.524642
C 2.935892 3.100474 -2.264640
F 1.899851 3.498308 -3.075946
C 3.852766 2.159757 -2.724578
F 3.725286 1.640002 -3.987717
C 4.894212 1.740996 -1.901024
F 5.800247 0.811831 -2.360066

7t
Total free energy (kcal/mol) = -2130472.026

76

Ni -1.221795 0.061587 -0.651367
H 0.289273 -4.364552 0.845785
H -4.881243 -3.256874 -0.092534
C 0.662183 -3.823930 -0.033219
H -3.249495 -2.619347 -0.384959
H 1.115368 -4.555021 -0.708972
H 3.301939 -3.688392 -0.678814
C -4.028186 -2.756672 0.375081
H -6.468133 -1.563798 0.261957
H -0.206671 -3.385207 -0.535055
H -8.109656 0.197052 0.382180
C 2.997794 -2.843923 -0.066963
H -3.616057 -3.428251 1.137624
C -5.750572 -0.949617 0.799278
C 1.662293 -2.758243 0.350737
C -4.441067 -1.424936 0.958686
H 5.503162 -2.794549 -0.905957
H 5.778188 -1.080922 -0.553631
C -7.578025 0.778248 1.142096
C 5.388870 -2.017456 -0.143914
C -6.153876 0.295131 1.307250
C 3.945794 -1.878209 0.288215
H -7.611439 1.832690 0.844889
C -1.107779 -0.890339 0.992628
C -3.520869 -0.614905 1.649793
C 1.285023 -1.658726 1.142259
N -2.178412 -1.100364 1.861857
H -8.141785 0.688945 2.080697
N -0.071011 -1.575136 1.626097
H 6.031302 -2.289100 0.704222
C -5.206309 1.077875 1.985106

C 3.532567 -0.792315 1.078089
C -3.887127 0.644110 2.168787
C -0.489416 -2.171872 2.829552
C -1.810317 -1.873153 2.977108
C 2.209879 -0.668664 1.523526
H -5.496410 2.049387 2.376236
H 4.252465 -0.025213 1.350785
H -2.027101 1.728417 2.219280
C -2.877628 1.516386 2.877676
C 1.784562 0.490578 2.393884
H 0.994769 1.073825 1.905412
H -3.329214 2.466110 3.178266
H -2.477429 1.032423 3.777338
H 2.628842 1.150669 2.604617
H 1.377582 0.144715 3.351647
H 0.183273 -2.737925 3.450848
H -2.512167 -2.128237 3.752430
H -3.520718 0.710143 -3.617282
C -2.717115 0.155938 -3.101749
H -3.222659 -0.547098 -2.424373
H -2.494041 -1.572717 -4.407546
H -0.852760 -3.020088 -3.060239
C -0.146493 -2.206333 -3.209623
C -1.925777 -0.665662 -4.162738
C -0.526392 -1.032027 -3.723636
H 0.884107 -2.403091 -2.931832
C -1.851722 1.094678 -2.268549
H 0.217336 -0.256020 -3.897208
H -3.332838 1.479260 -0.701320
C -2.320469 1.664521 -1.062554
H -1.053286 1.612308 -2.802004
H -1.853855 -0.079745 -5.089916
H -1.867395 2.581143 -0.684901
F 3.833532 2.941809 0.999419
C 3.372951 2.858524 -0.300540
C 2.127724 3.374585 -0.628037
H 1.508885 3.850239 0.119469
C 1.689521 3.249234 -1.937207
F 0.458973 3.755465 -2.301869
C 2.466420 2.613865 -2.903859
F 2.014777 2.484992 -4.193457
C 3.713343 2.110444 -2.555713
F 4.488178 1.489691 -3.500159
C 4.176026 2.235253 -1.253640
F 5.416016 1.745737 -0.916833

9
Total free energy (kcal/mol) = -2130478.993

76

Ni 0.635427 0.525218 -0.546789
H 1.433184 -3.537582 -0.721058
H -3.576622 -2.657696 -0.989135
C 2.187527 -2.877581 -1.164813
H -1.827771 -2.495058 -0.741303
H 2.715212 -3.433663 -1.944777
H 4.897181 -2.858533 -1.282083
C -2.802969 -2.443093 -0.246204
H -5.001633 -0.864931 -0.446568
H 1.646002 -2.047582 -1.636317
H -6.224808 1.318106 -0.458636
C 4.540162 -2.426681 -0.351478
H -2.828198 -3.249274 0.498374
C -4.239622 -0.404047 0.176124
C 3.156021 -2.362116 -0.126599
C -3.032555 -1.086637 0.382581
H 7.166412 -2.270278 -0.720968
H 7.452428 -1.083976 0.563647
C -5.805097 1.557743 0.524043
C 6.956540 -2.031929 0.326096
C -4.483736 0.854312 0.744218
C 5.467749 -1.952717 0.586248
H -5.694764 2.644980 0.589747
C 0.402125 -0.821757 0.792510
C -2.048613 -0.469310 1.179080
C 2.706702 -1.789135 1.078661
N -0.798596 -1.152766 1.408145
H -6.546359 1.257827 1.277525
N 1.292051 -1.728342 1.355881
H 7.427950 -2.807582 0.943999
C -3.482706 1.432991 1.537592
C 4.981355 -1.398553 1.780590
C -2.258705 0.790696 1.772724
C 0.656215 -2.585096 2.271547
C -0.651812 -2.225214 2.303411
C 3.608825 -1.300207 2.046609
H -3.653689 2.408773 1.983828
H 5.682812 -1.013820 2.516242
H -0.355686 1.780878 1.988991
C -1.194597 1.452754 2.615363
C 3.128781 -0.656371 3.329635

H 2.374577 0.112051 3.132683
H -1.598722 2.325505 3.136429
H -0.783481 0.765399 3.363396
H 3.962404 -0.177979 3.850750
H 2.677785 -1.385786 4.013482
H 1.191818 -3.355727 2.798408
H -1.480708 -2.616585 2.867420
H -2.708312 0.989235 -3.714619
C -1.812492 0.508964 -4.139582
H -1.265334 1.286873 -4.687232
H -1.473778 -0.802721 -2.439855
H 1.353848 1.636145 -2.822981
C 0.612053 1.858219 -2.054219
C -0.932814 0.000203 -2.960432
C -0.586611 1.105708 -1.980552
H 0.622318 2.890133 -1.697981
C -2.224815 -0.595579 -5.077227
H -1.455418 1.563269 -1.498763
H -1.284890 0.084068 -6.854177
C -1.889832 -0.679786 -6.370689
H -2.833046 -1.387096 -4.633658
H -0.017320 -0.446329 -3.369298
H -2.207579 -1.509338 -6.995800
F 2.889392 2.391227 2.006259
C 3.866100 2.181563 1.048421
C 3.510932 2.107211 -0.291294
H 2.470969 2.185075 -0.601504
C 4.512612 1.864234 -1.223636
F 4.195060 1.765547 -2.562917
C 5.839138 1.690076 -0.837439
F 6.818563 1.423148 -1.766356
C 6.167995 1.762436 0.513073
F 7.465867 1.530711 0.914244
C 5.182543 2.007192 1.464508
F 5.509485 2.019664 2.803196

9t

Total free energy (kcal/mol) = -2130449.495

76

Ni 0.512317 0.392020 -0.347800
H 0.806918 -4.516707 -1.745046
H -3.556098 -0.888348 -2.410610
C 1.254051 -3.591052 -2.129727
H -1.847360 -0.691303 -1.983681

H 1.658338 -3.805483 -3.123088
H 3.908274 -3.343486 -2.652181
C -2.799705 -1.117733 -1.654442
H -4.857995 0.545036 -1.120460
H 0.442171 -2.866772 -2.237235
H -6.254109 2.074907 0.120037
C 3.675010 -3.045747 -1.633959
H -2.669261 -2.205942 -1.621452
C -4.324381 0.278239 -0.212377
C 2.340260 -3.083927 -1.206678
C -3.211948 -0.568066 -0.308600
H 6.265798 -2.875618 -2.273310
H 6.328253 -1.342506 -1.385568
C -5.984133 1.677836 1.103541
C 6.116691 -2.417053 -1.291224
C -4.771737 0.776387 1.020196
C 4.704827 -2.611973 -0.786810
H -5.805568 2.527044 1.772897
C -0.102152 -1.361106 0.335524
C -2.517102 -0.901871 0.872205
C 2.044632 -2.646979 0.099152
N -1.356489 -1.757775 0.777118
H -6.857044 1.136479 1.492671
N 0.655949 -2.516554 0.486411
H 6.858410 -2.835648 -0.601498
C -4.086936 0.386563 2.176811
C 4.386854 -2.318066 0.545433
C -2.964829 -0.456819 2.135258
C -0.106258 -3.575425 1.008393
C -1.365608 -3.103252 1.185874
C 3.068367 -2.339275 1.017138
H -4.430242 0.742724 3.145040
H 5.180219 -2.045745 1.236145
H -1.915096 0.007356 3.975714
C -2.320182 -0.861119 3.445612
C 2.788765 -2.059398 2.474652
H 2.197751 -1.154172 2.611101
H -3.066758 -1.322132 4.104326
H -1.499088 -1.563691 3.312904
H 3.726655 -1.951807 3.027213
H 2.220142 -2.876276 2.935615
H 0.319426 -4.546647 1.191266
H -2.255398 -3.578725 1.558381
H 0.759722 3.821206 -2.049240
C 0.085713 3.581397 -2.875856
H 0.568395 3.946145 -3.791899

H -1.070866 1.747667 -2.564818
H 0.076829 -0.668680 -2.719158
C 0.927049 -0.178270 -2.251404
C -0.084481 2.040596 -2.948505
C 1.007580 1.220930 -2.264550
H 1.830581 -0.776666 -2.186789
C -1.212331 4.323464 -2.680388
H 1.997061 1.676870 -2.268937
H -1.040482 5.707939 -4.277597
C -1.627770 5.347235 -3.436182
H -1.818373 4.003100 -1.830871
H -0.083650 1.747571 -4.010739
H -2.562304 5.866438 -3.243497
F 1.131906 3.888011 0.021660
C 0.855126 3.206281 1.204003
C 0.717362 1.809875 1.191718
H 1.300608 1.614127 -0.184573
C 0.526915 1.280560 2.473038
F 0.415749 -0.092673 2.688933
C 0.441589 2.035596 3.640902
F 0.269252 1.392933 4.852501
C 0.574443 3.416323 3.581495
F 0.515277 4.181677 4.724671
C 0.792660 4.004558 2.341183
F 0.982143 5.366617 2.249130

10
Total free energy (kcal/mol) = -2130492.182
76

Ni 0.527954 0.457215 -0.118332
H 0.779793 -4.396382 -2.004257
H -3.464254 -0.419937 -2.147358
C 1.326807 -3.517348 -2.367146
H -1.755118 -0.172294 -1.748961
H 1.716310 -3.752540 -3.361824
H 3.985620 -3.702603 -2.838216
C -2.660714 -0.723201 -1.469765
H -4.724477 0.781792 -0.584803
H 0.599323 -2.705029 -2.467261
H -6.081233 2.055961 0.934578
C 3.788286 -3.292063 -1.852117
H -2.455838 -1.787063 -1.637646
C -4.155183 0.370673 0.243690

C 2.457533 -3.133427 -1.440045
C -3.046117 -0.441053 -0.036528
H 6.330499 -3.416832 -2.551865
H 6.850350 -2.162381 -1.418007
C -5.727077 1.559733 1.842572
C 6.292017 -3.101731 -1.504364
C -4.536170 0.674356 1.556074
C 4.864652 -2.931740 -1.031006
H -5.475314 2.337348 2.572918
C 0.077575 -1.325087 0.326328
C -2.310401 -0.949381 1.048561
C 2.219345 -2.598634 -0.159087
N -1.145835 -1.769258 0.797187
H -6.563938 0.980943 2.256301
N 0.849949 -2.472918 0.295849
H 6.830388 -3.852982 -0.911515
C -3.792072 0.126251 2.611905
C 4.586303 -2.415410 0.243355
C -2.681258 -0.695284 2.387059
C 0.122139 -3.587020 0.749857
C -1.124327 -3.149308 1.053294
C 3.273981 -2.247890 0.706316
H -4.074737 0.355444 3.635748
H 5.406051 -2.136611 0.899520
H -2.174794 -0.751527 4.481501
C -1.909564 -1.270522 3.556383
C 3.017748 -1.698361 2.086865
H 2.605963 -0.686737 2.047321
H -2.132718 -2.335038 3.703489
H -0.829139 -1.178567 3.418059
H 3.945132 -1.669440 2.665800
H 2.289452 -2.302269 2.639669
H 0.568323 -4.564258 0.811978
H -1.990890 -3.671089 1.419481
H 0.206466 4.121043 -1.519498
C 0.506307 3.953926 -2.563410
H 1.512881 4.377843 -2.689156
H -0.478597 2.033306 -2.779196
H 0.626844 -0.250242 -2.619383
C 1.308249 0.148048 -1.864005
C 0.546465 2.426758 -2.811901
C 1.408724 1.645197 -1.804665
H 2.248772 -0.398137 -1.829593
C -0.475109 4.640429 -3.480678
H 2.446875 1.997994 -1.798199
H 0.870505 5.686963 -4.747187

C -0.160901 5.443282 -4.504067
H -1.523882 4.421396 -3.273540
H 0.930082 2.235660 -3.822988
H -0.919200 5.889687 -5.140290
F -1.467177 2.762397 -0.232559
C -1.126740 2.510856 1.110906
C -0.195137 1.516816 1.396128
H 1.044360 2.017636 -0.754849
C 0.077701 1.366551 2.749123
F 0.977104 0.373166 3.174578
C -0.536242 2.101466 3.760001
F -0.252268 1.869408 5.094040
C -1.473295 3.070436 3.414392
F -2.105817 3.808778 4.395388
C -1.777326 3.280074 2.071028
F -2.719968 4.232758 1.728028

8
Total free energy (kcal/mol) =
76

C	-0.7572756600	-0.8406075700	5.0561229700
C	-1.4323737500	-1.4828799000	4.0210822100
C	-1.0687099300	-1.2100311600	2.7051316100
C	-0.0403626900	-0.3461357200	2.3409915200
C	0.5771603700	0.2928639000	3.4111296600
C	0.2548487600	0.0644616900	4.7474870100
F	-1.8099872400	-1.8557070000	1.7047851400
F	-2.4395936900	-2.3851909300	4.3144818800
F	-1.0882038400	-1.0981410000	6.3715076700
F	0.9296330100	0.7097465700	5.7684222100
F	1.5852689400	1.2368635800	3.1667297900
H	-0.6413205000	5.1285873100	3.2001059300
C	-1.3347063000	4.3178159100	2.9486002800
H	0.1811677000	3.0026679900	2.1308974200
H	-1.9753499400	0.5422651700	0.1325395900
C	-0.7765929300	3.4363645700	1.8188788800
H	-2.2919367100	4.7717190100	2.6618382700
C	-1.7468978900	2.3061556500	1.4333180600
H	-1.9913265000	1.7251722000	2.3333828300
C	-1.2752426200	1.3500932700	0.3583602000
H	-2.7001751600	2.7542499100	1.1038186500
C	-0.2935009300	1.6408858000	-0.6006164600
Ni	0.3839662700	-0.0238509300	0.4673985000

H	0.3015571000	2.5447536400	-0.4920808800
C	0.1576747100	0.6323827400	-1.4876127100
H	-0.5720641700	4.0665428700	0.9414248300
H	1.7708704500	-3.0753632900	-3.2952819400
C	0.8754274100	-2.4788163300	-3.0741050600
C	-0.0032403000	-3.1691201300	-2.0548974800
C	-1.2038798300	-3.7734276500	-2.4495841600
C	-1.5668138900	-4.6050018600	-0.2191345600
H	-1.5143058600	-3.6929150400	-3.4876441700
C	-2.0068554000	-4.4818400600	-1.5428200100
H	-2.1672481500	-5.1642188400	0.4928212600
H	-3.5393654700	-6.0112929600	-1.4394278900
C	-3.3250433300	-5.0820342900	-1.9779913500
H	-3.3330221800	-5.3002214900	-3.0509475000
H	-4.1551194900	-4.3915234400	-1.7770268000
H	1.2196312200	-1.5035811400	-2.7217084200
H	0.3355852100	-2.3329673700	-4.0142038800
C	0.3782928600	-3.2714128300	-0.7013959800
C	-0.3757280200	-4.0137640800	0.2257813600
H	0.7116115400	-5.1111627300	1.7406724400
C	0.0793460100	-4.2168627600	1.6522980100
H	-0.7802445700	-4.3509720200	2.3140038100
H	0.6582234900	-3.3672752200	2.0198129200
H	4.6678727700	-0.1624107000	-1.9467977800
C	4.0479336200	0.6535386300	-1.5510958500
C	3.8359951200	-0.0829428300	0.8789093000
C	3.7872263700	-2.4576189100	0.1195362400
N	3.1230227800	-1.2553324500	0.4177077500
C	2.8453878400	-3.3302233300	-0.3152325200
C	1.7631872300	-1.3546254500	0.1801841700
N	1.6154496100	-2.6521406900	-0.2791914200
C	4.1356634200	0.0509229600	2.2475212300
C	3.7216877000	-0.9877815300	3.2644407200
H	4.4747362500	-1.7829503400	3.3513876400
H	5.3408727500	2.7054313100	-0.3372648900
C	4.9982806100	1.9705399600	0.3858957600
H	6.5168510500	3.9045251700	1.3921722600
C	4.2837019500	0.8555726900	-0.0717388200
C	6.0300946700	3.3832117300	2.2224140600
C	5.2877794700	2.1549030900	1.7453591500
H	5.3457806400	4.0939533700	2.7041172100
H	6.7993677400	3.1261678500	2.9595719200
C	4.8590036100	1.1797176500	2.6554219800
H	5.0778522900	1.3025535000	3.7123628500
H	3.6050303900	-0.5304951700	4.2508548300
H	4.2966396400	1.5603568400	-2.1098640000

H	3.0068974600	0.3943133900	-1.7573146700
H	2.7738168800	-1.4604612000	2.9988157900
H	-1.5035957000	3.7301869100	3.8595795800
H	2.9186138200	-4.3533260400	-0.6403312800
H	4.8501611500	-2.5630238400	0.2488169900
H	0.9848657200	0.8438875400	-2.1557399400
H	-0.5372749700	-0.1280841500	-1.8413439400

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