*Supporting Information*

# Mechanisms and Origins of Regioselectivities of Nickel-Catalyzed β,δ-Vinylarylation of Alkenyl Esters with Vinyl Triflates and Arylzinc Reagents

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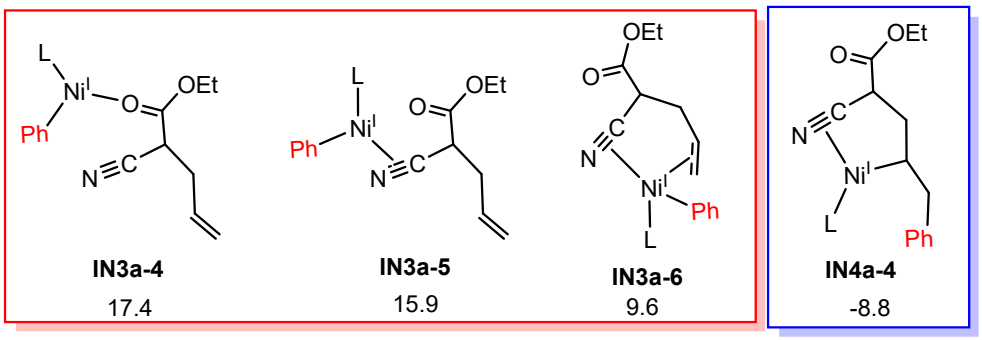
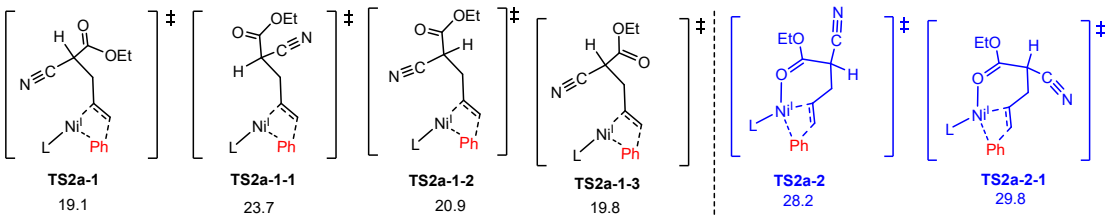
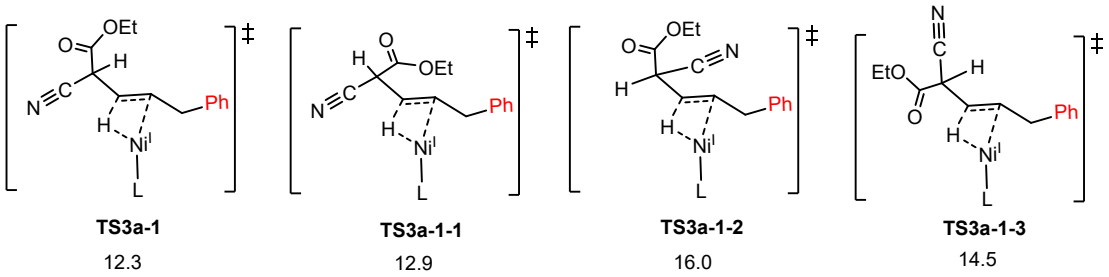


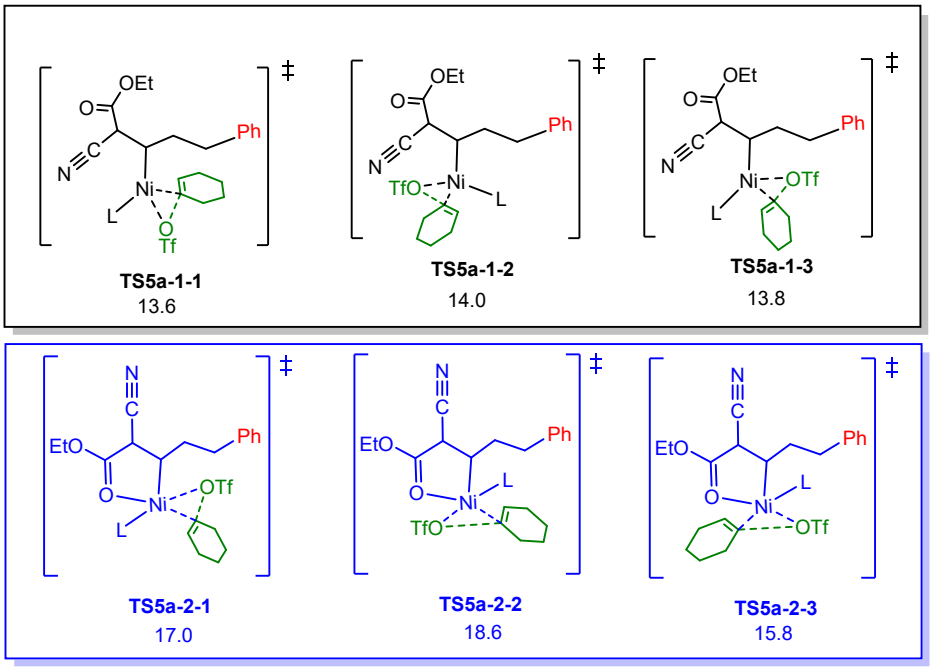

**Scheme S1** Other possible isomers of intermediate **IN3a-1** and **IN4a-1**. Values shown are relative free energies in kcal/mol.



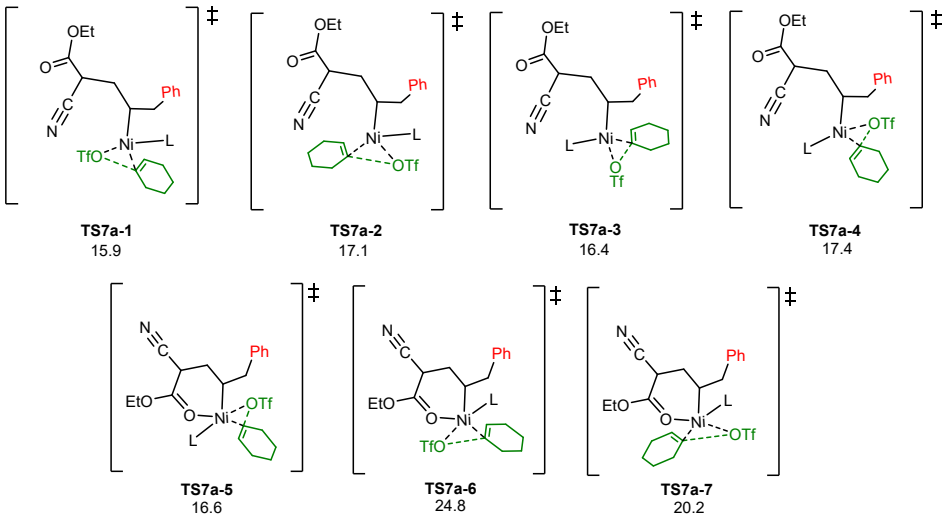

**Scheme S2** Other possible conformers of transition states **TS2a-1** and **TS2a-2**. Values shown are relative free energies in kcal/mol.



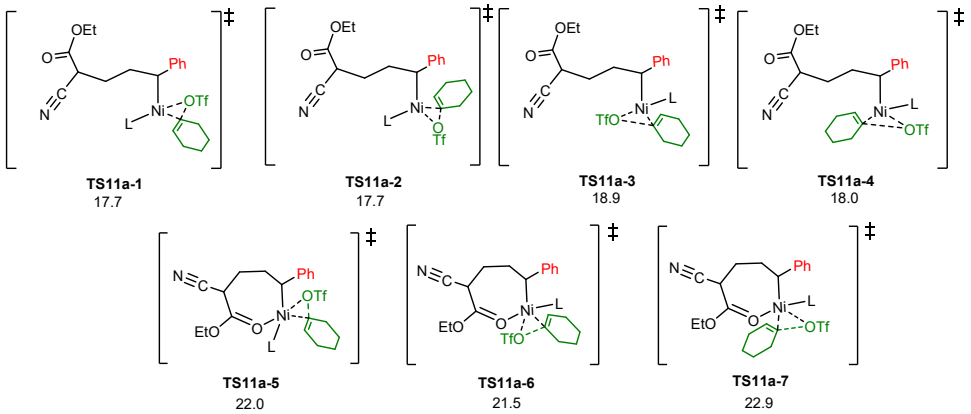

**Scheme S3** Other possible conformers of transition state **TS3a-1**. Values shown are relative free energies in kcal/mol.



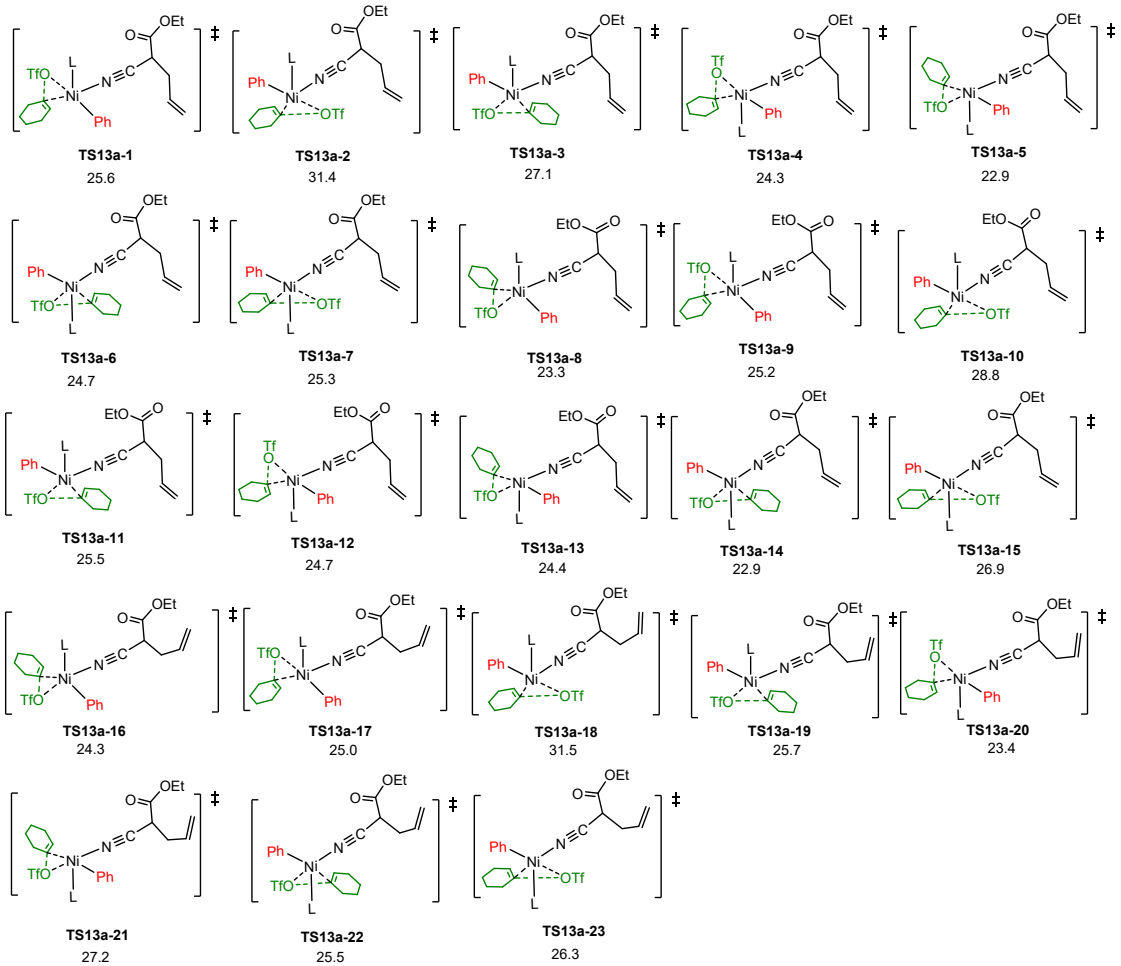

**Scheme S4** Other possible isomers of transition states **TS5a-1 and TS5a-2**. Values shown are relative free energies in kcal/mol.



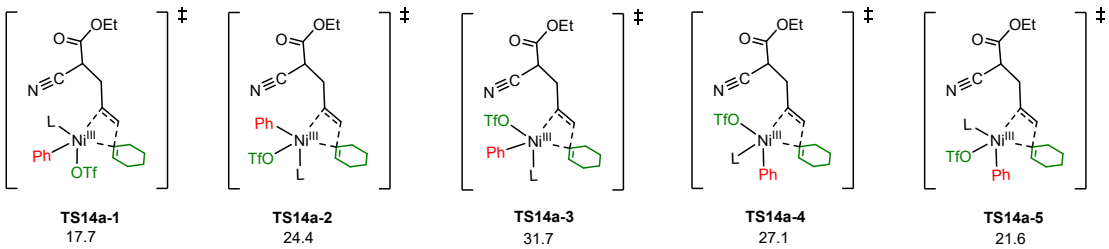

**Scheme S5** Other possible isomers of transition states **TS7a**. Values shown are relative free energies in kcal/mol.



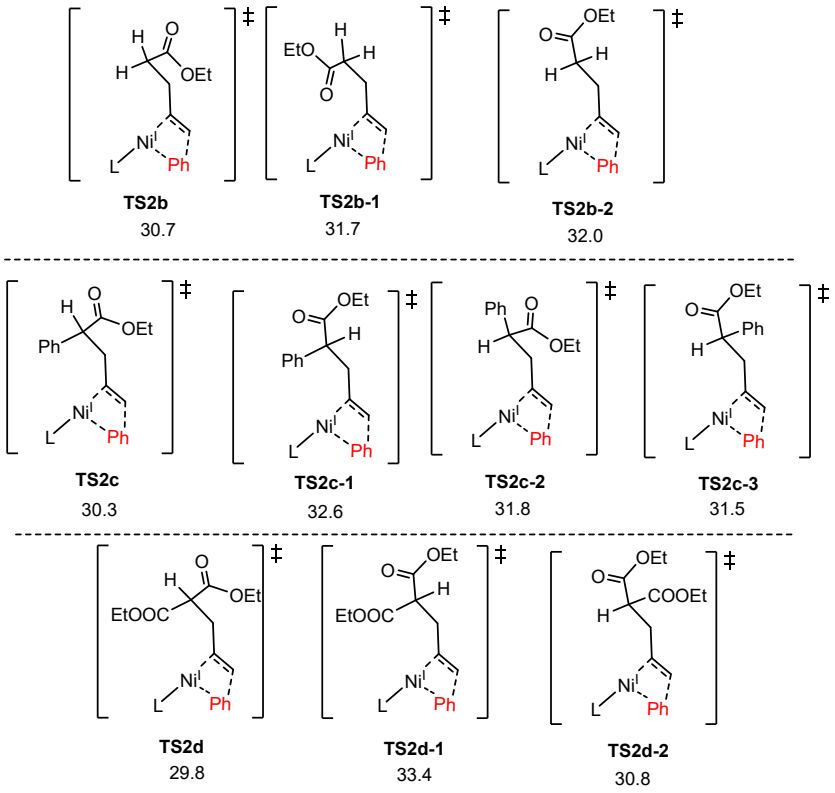

**Scheme S6** Other possible isomers of transition states **TS11a**. Values shown are relative free energies in kcal/mol.




**Scheme S7** Other possible isomers and conformers of transition state **TS13a**. Values shown are relative free energies in kcal/mol.




**Scheme S8** Other possible isomers of transition state **TS14a**. Values shown are relative free energies in kcal/mol.




**Scheme S9** Conformers for transition states of the carbometallation step. Values shown are relative free energies in kcal/mol.

## Section 2. Optimization with D3 dispersion correction

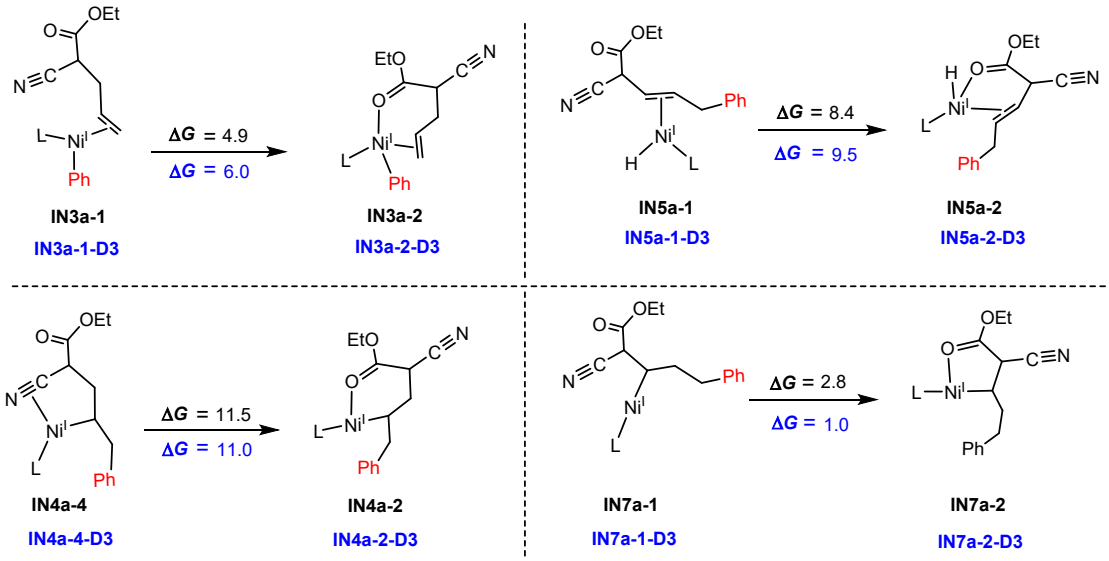



**Fig. S1** Calculated free energy difference for key species using the M06/BS2//B3LYP/BS1 and M06/BS2//B3LYP-D3/BS1 levels. Values shown are relative free energies in kcal/mol.

## Section 3. Optimization with M06 and B97D methods

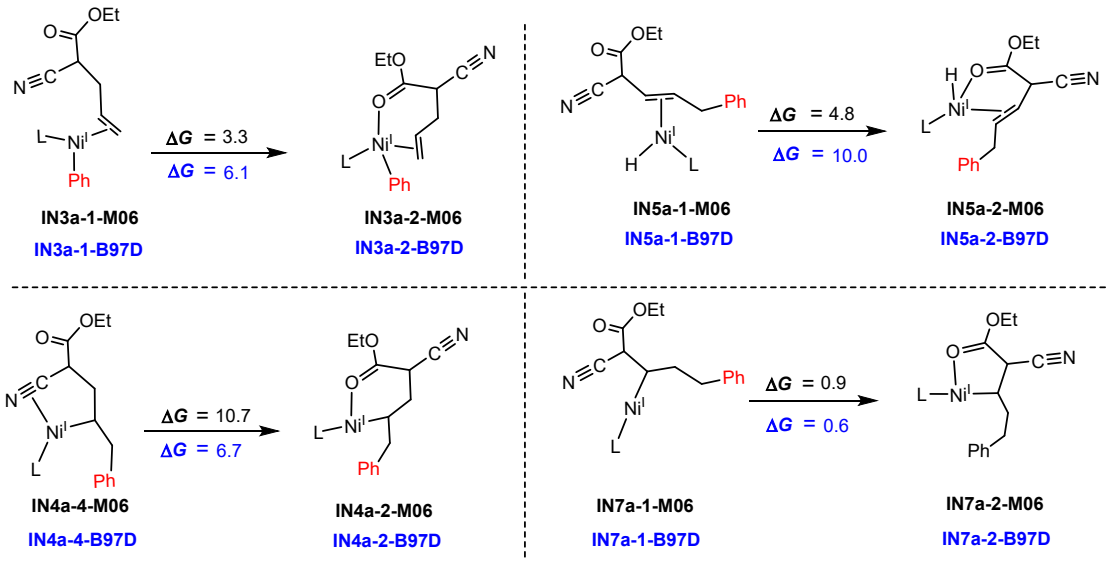
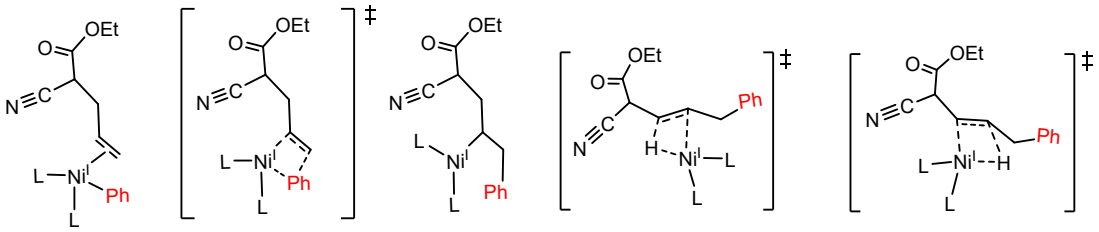


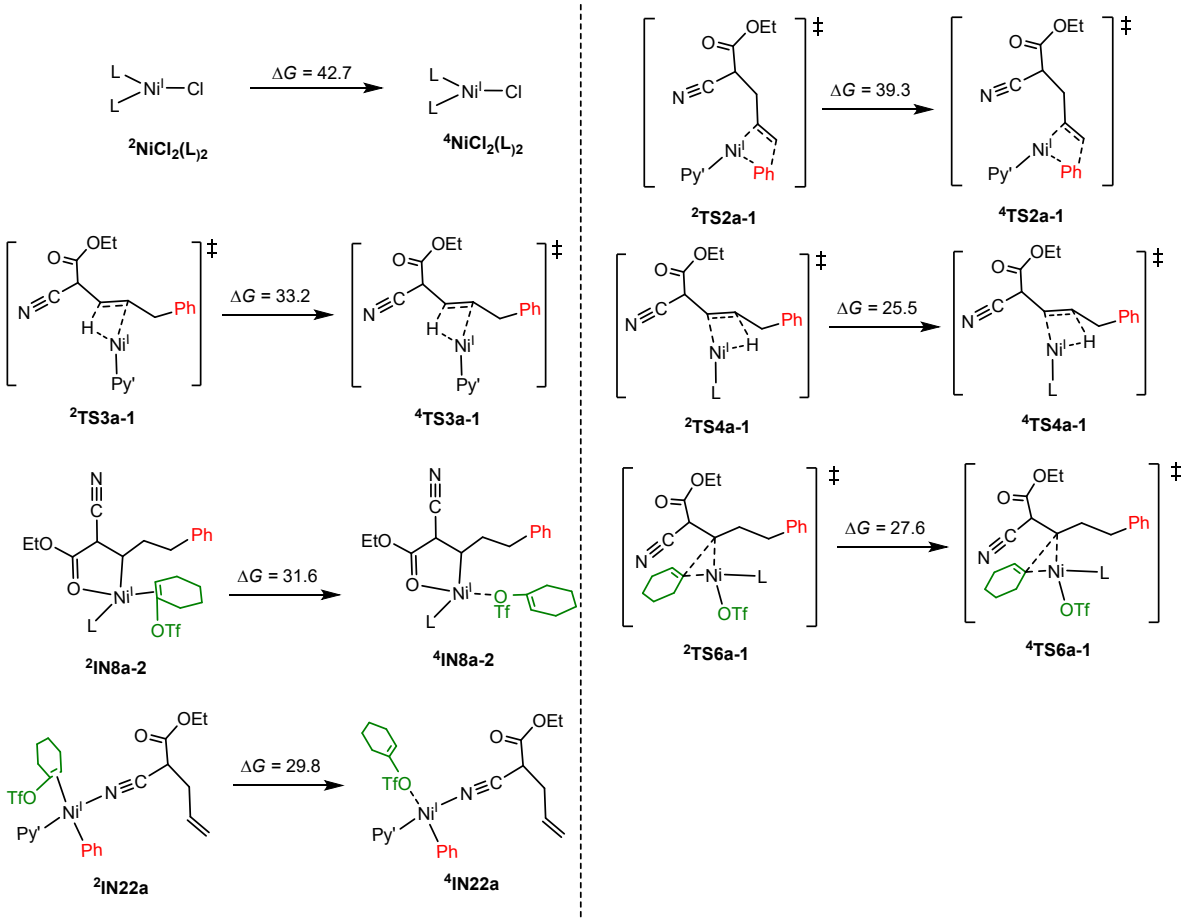

**Fig. S2** Calculated free energy difference for key species using the M06/BS2//M06/BS1 and M06/BS2//B97D/BS1 levels. Values shown are relative free energies in kcal/mol.

## Section 4. Two-4-PhPy-coordination mode




**Scheme S10** Two-4-PhPy-coordination mode for key intermediates and transition states. Values shown are relative free energies in kcal/mol.

## Section 5. Optimization along quartet state




**Scheme S11** Optimized key intermediates and transition states in quartet state. Values shown are relative free energies in kcal/mol.

## Section 6. Other possible pathways to afford product 2a

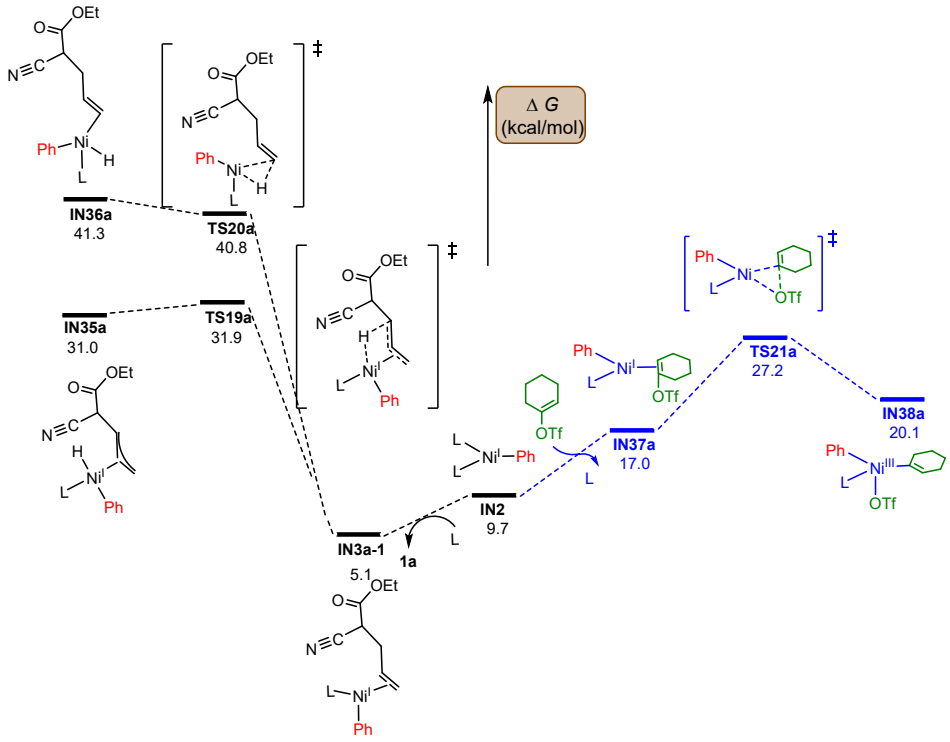



**Fig. S3** Calculated energy profiles for β-H elimination, δ-H elimination and oxidative addition steps from **IN2**, respectively. Values shown are relative free energies in kcal/mol.

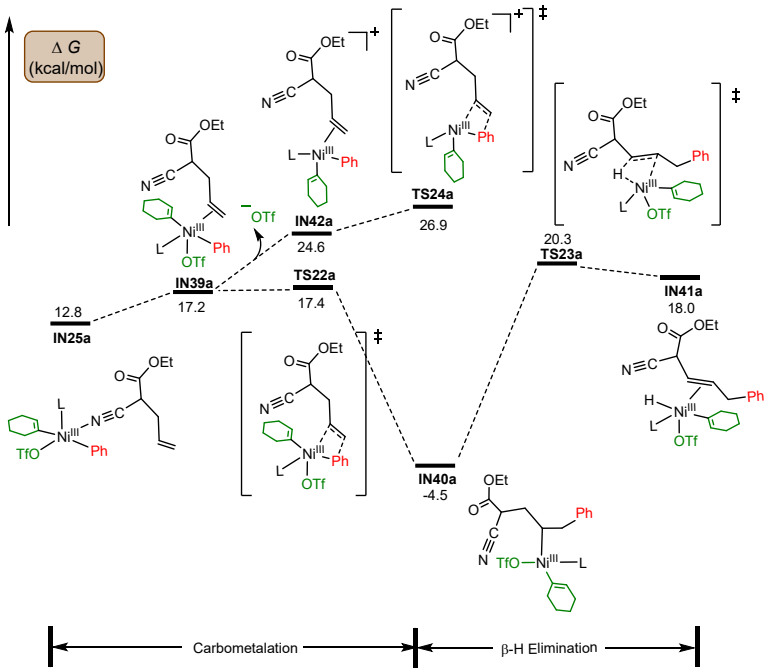



**Fig. S4** Calculated energy profiles for carbometallation and β-H elimination steps

from **IN25a**, respectively. Values shown are relative free energies in kcal/mol.

## Section 7. Other possible pathways to afford product 4a

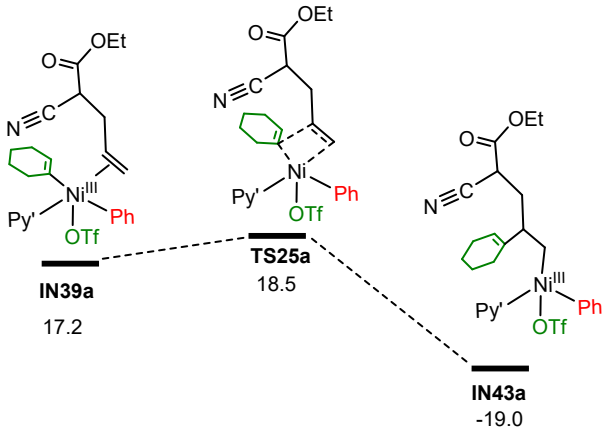



**Fig. S5** Calculated energy profiles for carbometallation step from **IN39a**. Values shown are relative free energies in kcal/mol.

## Section 8. Other possible pathways to afford regioisomer 5a

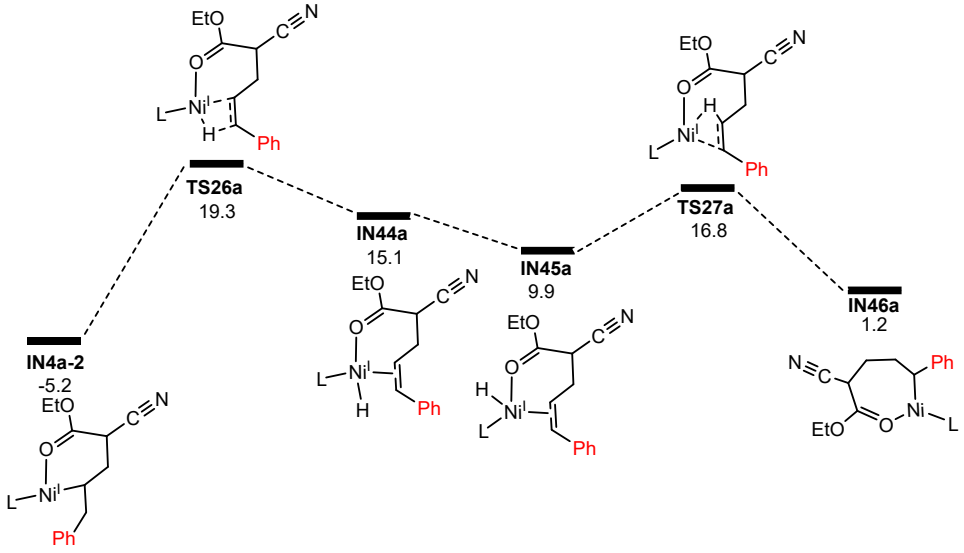



**Fig. S6** Calculated energy profiles for β-H elimination and Ni-H reinsertion steps from **IN4a-2**, respectively. Values shown are relative free energies in kcal/mol.

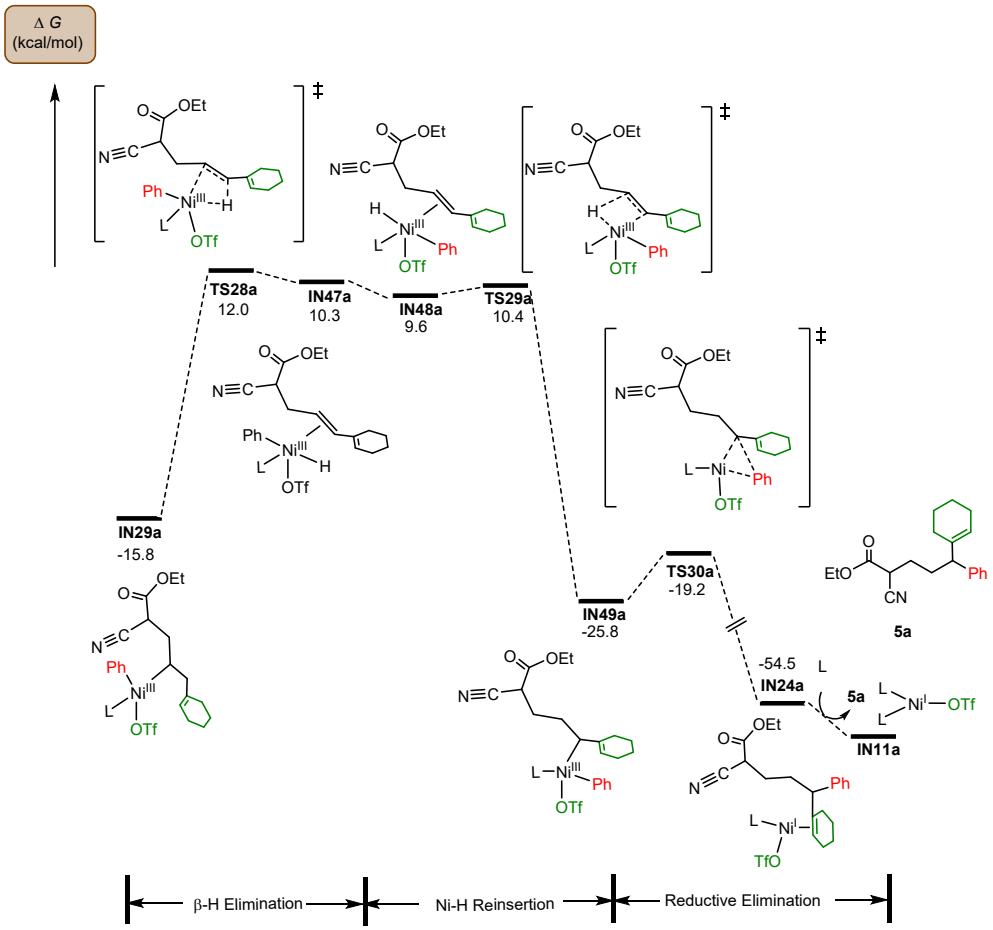



**Fig. S7** Calculated energy profiles for affording regioisomer **5a** from **IN29a**. Values shown are relative free energies in kcal/mol.

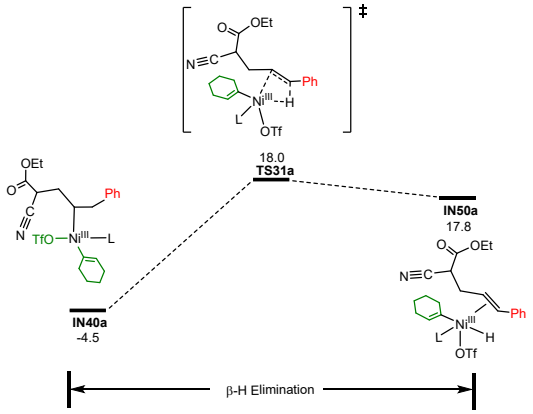



**Fig. S8** Calculated energy profiles for β-H elimination step from **IN40a**. Values shown are relative free energies in kcal/mol.

## Section 9. Other possible pathways to afford regioisomer 6a

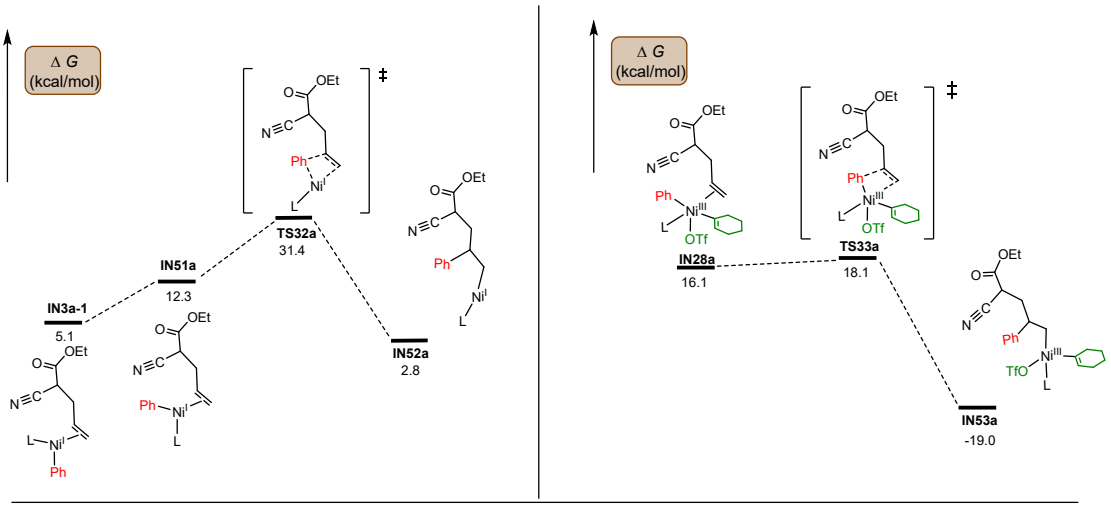



**Fig. S9** Calculated energy profiles for carbometallation step from **IN3a-1** and **IN28a**, respectively. Values shown are relative free energies in kcal/mol.

## Section 10. Other possible pathways to afford regioisomer 7a

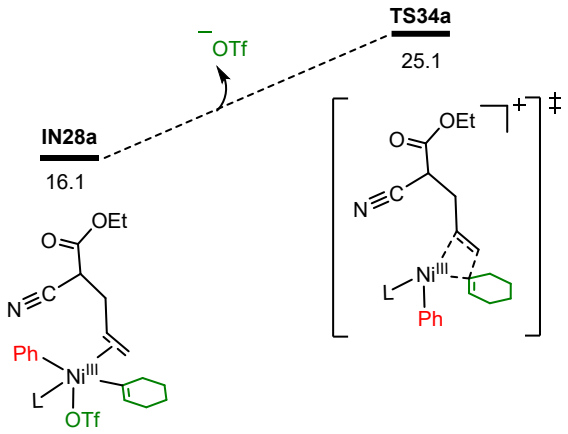



**Fig. S10** Calculated energy profiles for carbometallation step from **IN28a**. Values shown are relative free energies in kcal/mol.

## Section 11. Pathway to afford 8a

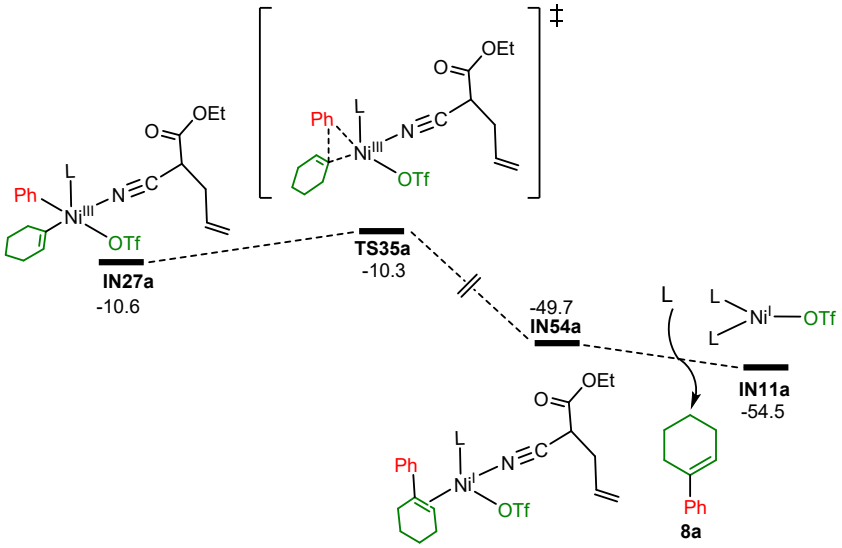



**Fig. S11** Calculated energy profiles for oxidative addition step from **IN27a**, respectively. Values shown are relative free energies in kcal/mol.

## Section 12. α-H elimination step

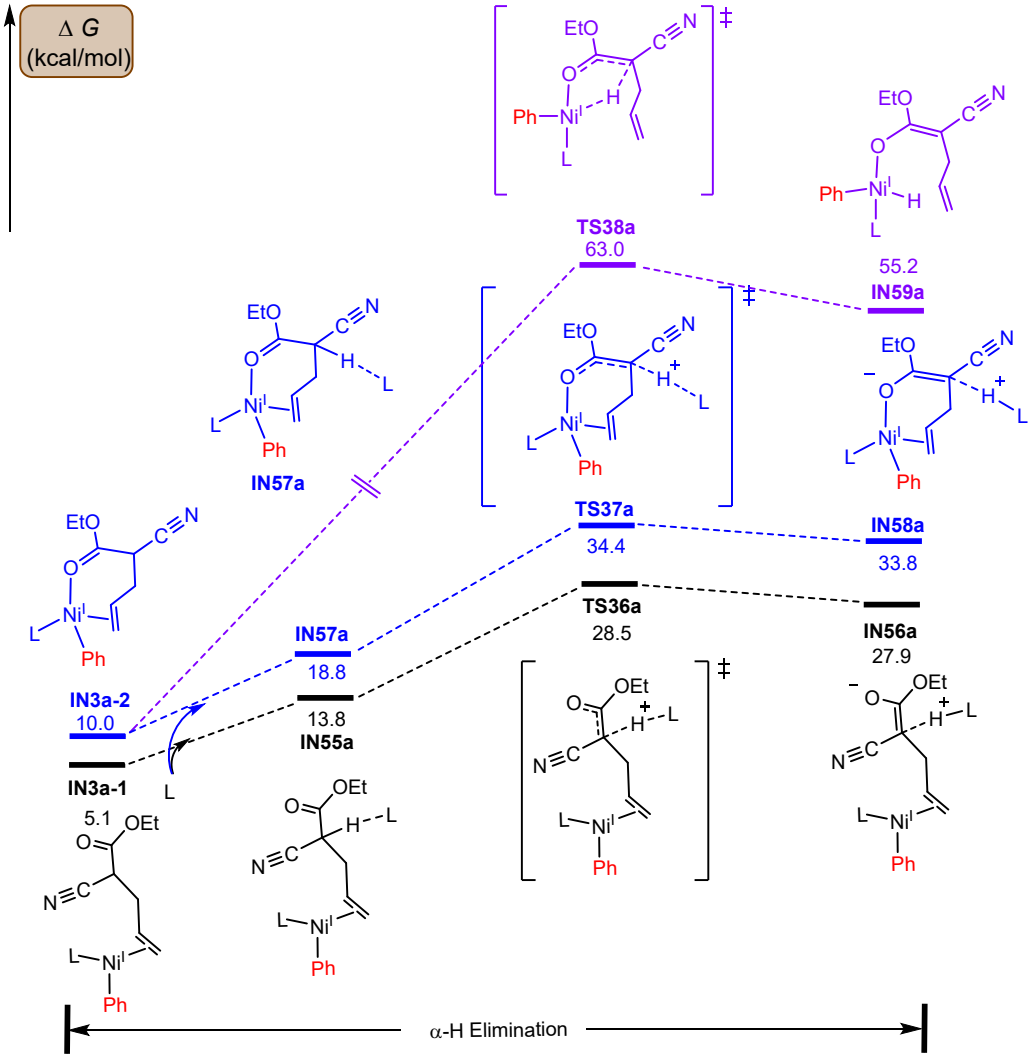



**Fig. S12** Calculated energy profiles for α-H elimination step from **IN3a-1** and **IN3a-2**, respectively. Values shown are relative free energies in kcal/mol.

## Section 13. Relaxed energy scans for MECP

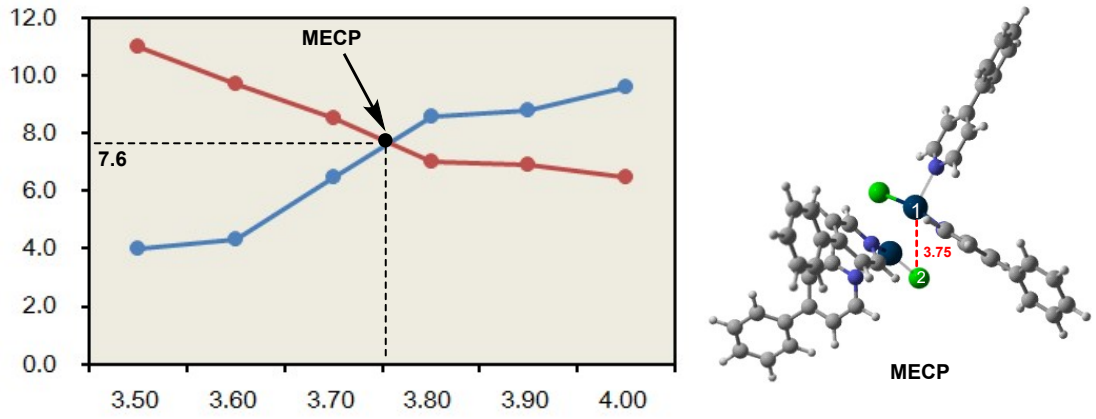



**Fig. S13** Relaxed energy scan in the singlet (blue line) and triplet (red line) states for the comproportionation of $Ni^{II}$ with $Ni^{0}$. The structure of MECP is show. Energies are relative to **$^{1}$INf** and in kcal/mol. Distance of Ni1-Cl2 is given in angstroms.

## Section 14. Calculated Ph-migration processes for substrates lacking an α-H

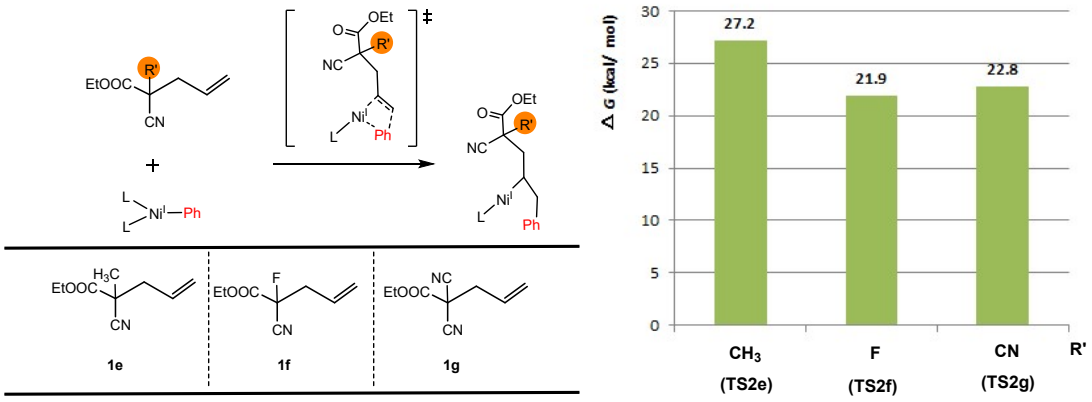



**Fig. S14** Calculated Ph-migration processes for three substrates with different $C_{\alpha}$ position of substituents. Values shown are relative free energies in kcal/mol.

## Section 15. Optimized structures of TS5a-2, TS7a and TS11a

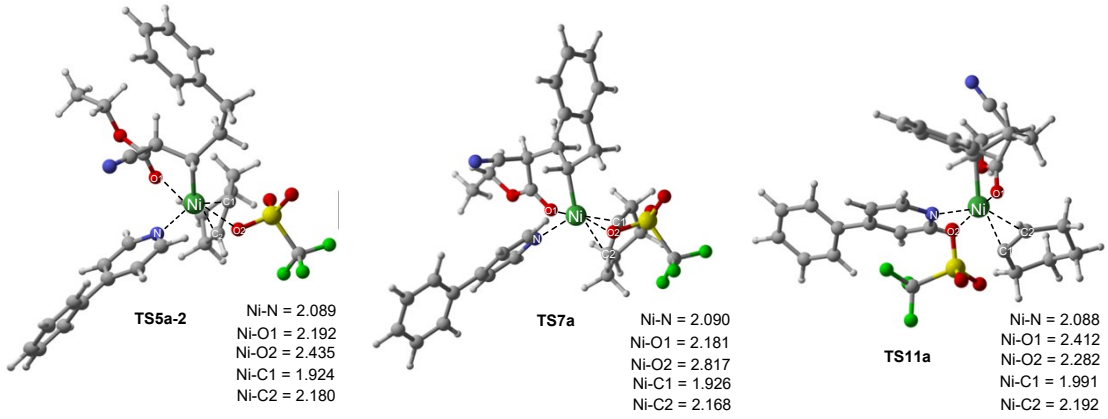



**Fig. S15** Optimized structures of **TS5a-2**, **TS7a** and **TS11a** along with interatomic distances (in angstroms).

## Section 16. Energies (in hartree) of All TSs and Intermediates.

| Geometry | $E_0$ | E | $H_{353.15}$ | $G_{353.15}$ | $E_{(sol,M06)}$ |
|---|---|---|---|---|---|
| 1a | -516.456370 | -516.440027 | -516.438909 | -516.506770 | -516.444743 |
| 1b | -424.232083 | -424.218012 | -424.216894 | -424.279251 | -424.249780 |
| 1c | -655.198602 | -655.178152 | -655.177033 | -655.255526 | -655.176042 |
| 1d | -691.350366 | -691.328552 | -691.327433 | -691.409598 | -691.368612 |
| 1e | -555.752405 | -555.734109 | -555.732991 | -555.803916 | -555.748430 |
| 1f | -615.694112 | -615.676640 | -615.675521 | -615.745520 | -615.681416 |
| 1g | -608.687623 | -608.668844 | -608.667726 | -608.740763 | -608.6446672 |
| 1h | -520.792271 | -520.774534 | -520.773415 | -520.844736 | -520.760875 |
| 2a | -981.952362 | -981.921613 | -981.920495 | -982.021801 | -981.927886 |
| 3a | -747.441045 | -747.418336 | -747.417218 | -747.502775 | -747.385300 |
| 4a | -981.969542 | -981.938597 | -981.937479 | -982.041936 | -981.945684 |
| 5a | -981.959786 | -981.928902 | -981.927784 | -982.029989 | -981.934521 |
| 6a | -981.967326 | -981.936479 | -981.935361 | -982.037066 | -981.945419 |
| 7a | -981.970675 | -981.939721 | -981.938602 | -982.041839 | -981.946571 |
| 8a | -465.480142 | -465.466285 | -465.465167 | -465.524864 | -465.452253 |
| $^1NiCl_2L_2$ | -2049.850884 | -2049.817652 | -2049.816534 | -2049.926846 | -2049.706394 |
| $^3NiCl_2L_2$ | -2049.825881 | -2049.791806 | -2049.790688 | -2049.905467 | -2049.699410 |
| $^2NiClL_2$ | -1589.616899 | -1589.585474 | -1589.584356 | -1589.691374 | -1589.470057 |
| $NiHL_2$ | -1783.977728 | -1783.953658 | -1783.952540 | -1784.036759 | -1129.771129 |
| $Ph_2Zn$ | -690.279288 | -690.263561 | -690.262443 | -690.329488 | -690.234900 |
| PhZnCl | -918.984410 | -918.974209 | -918.973091 | -919.026074 | -918.975145 |
| Ph-Ph | -463.127090 | -463.114714 | -463.113595 | -463.170160 | -463.053761 |

| | | | | | |
|---|---|---|---|---|---|
| 4-PhPy | -479.176056 | -479.163918 | -479.162800 | -479.219097 | -479.096557 |
| $ZnCl_2$ | -1147.676799 | -1147.670982 | -1147.669863 | -1147.710595 | -1147.700701 |
| cyclohexenyl triflate | -1195.282107 | -1195.263981 | -1195.262863 | -1195.334945 | -1195.292094 |
| $^-$OTf | -961.531547 | -961.522154 | -961.521035 | -961.571627 | -961.550777 |
| PhZnOTf | -1420.147292 | -1420.128091 | -1420.126973 | -1420.203646 | -1420.140780 |
| $^1$INa | -2740.133900 | -2740.082147 | -2740.081028 | -2740.241872 | -2739.951457 |
| $^3$INa | -2740.160688 | -2740.108274 | -2740.107156 | -2740.271999 | -2739.965399 |
| $^1$TSa | -2740.102239 | -2740.051647 | -2740.050529 | -2740.201567 | -2739.936521 |
| $^3$TSa | -2740.142840 | -2740.094783 | -2740.093665 | -2740.238901 | -2739.964205 |
| $^1$INb | -2740.140812 | -2740.089383 | -2740.088265 | -2740.245628 | -2739.968843 |
| $^3$INb | -2740.142967 | -2740.091106 | -2740.089987 | -2740.245956 | -2739.967456 |
| $^1$TSb | -2740.115412 | -2740.064786 | -2740.063668 | -2740.217108 | -2739.948136 |
| $^3$TSb | -2740.129818 | -2740.079607 | -2740.078489 | -2740.231234 | -2739.950616 |
| $^1$INc | -2740.134439 | -2740.083841 | -2740.082722 | -2740.231503 | -2739.973642 |
| $^3$INc | -2740.136747 | -2740.084814 | -2740.083695 | -2740.240229 | -2739.956971 |
| $^1$INd | -1592.447185 | -1592.403326 | -1592.402207 | -1592.537296 | -1592.240233 |
| $^3$INd | -1592.432459 | -1592.387664 | -1592.386545 | -1592.526339 | -1592.210460 |
| $^1$TSc | -1592.414885 | -1592.371560 | -1592.370441 | -1592.503218 | -1592.216987 |
| $^3$TSc | -1592.383082 | -1592.339117 | -1592.337999 | -1592.474091 | -1592.171923 |
| $^1$INe | -1592.452492 | -1592.409073 | -1592.407955 | -1592.541337 | -1592.256100 |
| $^3$INe | -1592.443375 | -1592.398989 | -1592.397871 | -1592.536036 | -1592.237534 |
| $^1NiL_2$ | -1129.327416 | -1129.298817 | -1129.297699 | -1129.396456 | -1129.186178 |
| $^3NiL_2$ | -1129.317633 | -1129.289073 | -1129.287955 | -1129.388285 | -1129.166492 |
| $^1$INf | -3179.199153 | -3179.134565 | -3179.133447 | -3179.319611 | -3178.934333 |
| MECP | -3179.197337 | -3179.135743 | -3179.134624 | -3179.312943 | -3178.933717 |
| $^3$INf | -3179.243456 | -3179.177446 | -3179.176328 | -3179.373636 | -3178.963654 |
| TS1 | -2279.871402 | -2279.825164 | -2279.824046 | -2279.966212 | -2279.71897 |
| IN1 | -2279.896272 | -2279.846606 | -2279.845487 | -2279.996745 | -2279.724435 |
| IN2 | -1360.888290 | -1360.851035 | -1360.849917 | -1360.974329 | -1360.705736 |
| IN3a-1 | -1398.175485 | -1398.135118 | -1398.134000 | -1398.262039 | -1398.068617 |
| TS2a-1 | -1398.140100 | -1398.100720 | -1398.099601 | -1398.227074 | -1398.045576 |
| IN4a-1 | -1398.197093 | -1398.157748 | -1398.156629 | -1398.283755 | -1398.087865 |
| IN3a-2 | -1398.170371 | -1398.129957 | -1398.128839 | -1398.257971 | -1398.059603 |
| TS2a-2 | -1398.130145 | -1398.091031 | -1398.089913 | -1398.214618 | -1398.034639 |
| IN4a-2 | -1398.185181 | -1398.146113 | -1398.144995 | -1398.269765 | -1398.077403 |
| IN3a-3 | -1877.355901 | -1877.300850 | -1877.299732 | -1877.464130 | -1877.178510 |
| TS2a-3 | -1877.308089 | -1877.254310 | -1877.253191 | -1877.412949 | -1877.1407645 |
| IN4a-3 | -1877.385169 | -1877.331261 | -1877.330142 | -1877.491130 | -1877.209635 |
| TS3a-1 | -1398.141906 | -1398.102733 | -1398.101615 | -1398.228583 | -1398.054215 |
| IN5a-1 | -1398.180693 | -1398.140578 | -1398.139459 | -1398.268701 | -1398.064375 |
| TS3a-2 | -1398.140622 | -1398.101517 | -1398.100398 | -1398.226412 | -1398.038259 |
| IN5a-2 | -1398.173804 | -1398.134559 | -1398.133440 | -1398.258079 | -1398.055795 |

| | | | | | |
|---|---|---|---|---|---|
| IN6a-1 | -1398.177871 | -1398.137924 | -1398.136805 | -1398.264681 | -1398.064628 |
| IN6a-2 | -1398.176959 | -1398.137710 | -1398.136592 | -1398.260278 | -1398.058918 |
| TS4a-1 | -1398.159245 | -1398.119905 | -1398.118786 | -1398.246582 | -1398.054838 |
| IN7a-1 | -1398.200836 | -1398.161457 | -1398.160339 | -1398.288582 | -1398.090341 |
| TS4a-2 | -1398.146166 | -1398.107165 | -1398.106046 | -1398.230332 | -1398.041118 |
| IN7a-2 | -1398.195135 | -1398.155985 | -1398.154866 | -1398.280526 | -1398.088297 |
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| TS2a-2-1 | -1398.127599 | -1398.088354 | -1398.087235 | -1398.213854 | -1398.029168 |
| TS3a-1-1 | -1398.154031 | -1398.114799 | -1398.113680 | -1398.240266 | -1398.053694 |
| TS3a-1-2 | -1398.152841 | -1398.113634 | -1398.112516 | -1398.239131 | -1398.048811 |
| TS3a-1-3 | -1398.152775 | -1398.113515 | -1398.112397 | -1398.239476 | -1398.050712 |
| TS2b-1 | -1305.901926 | -1305.865137 | -1305.864018 | -1305.982863 | -1305.835423 |
| TS2b-2 | -1305.901544 | -1305.864564 | -1305.863446 | -1305.984393 | -1305.831116 |
| TS2c-1 | -1536.864452 | -1536.821174 | -1536.820056 | -1536.954288 | -1536.759565 |
| TS2c-2 | -1536.867963 | -1536.824464 | -1536.823346 | -1536.960417 | -1536.757848 |
| TS2c-3 | -1536.868936 | -1536.825463 | -1536.824344 | -1536.960241 | -1536.759609 |
| TS2d-1 | -1573.018135 | -1572.973581 | -1572.972462 | -1573.110526 | -1572.950641 |
| TS2d-2 | -1573.020180 | -1572.975288 | -1572.974169 | -1573.116537 | -1572.950196 |
| TS2e | -1437.425894 | -1437.384585 | -1437.383467 | -1437.512417 | -1437.338233 |
| TS2f | -1497.370593 | -1497.330116 | -1497.328998 | -1497.457444 | -1497.271410 |
| TS2g | -1490.364621 | -1490.322775 | -1490.321657 | -1490.453822 | -1490.237160 |
| $^4NiClL_2$ | -1589.556950 | -1589.526269 | -1589.525151 | -1589.630205 | -1360.653042 |
| $^4$TS2a-1 | -1398.090296 | -1398.050412 | -1398.049294 | -1398.176116 | -1397.984317 |
| $^4$TS3a-1 | -1398.097413 | -1398.057325 | -1398.056207 | -1398.186757 | -1397.979947 |
| $^4$TS4a-1 | -1398.099613 | -1398.059795 | -1398.058677 | -1398.186817 | -1397.980651 |
| $^4$IN8a-2 | -2593.438663 | -2593.378507 | -2593.377389 | -2593.553791 | -2593.333642 |
| $^4$TS6a-1 | -2593.463431 | -2593.403289 | -2593.402170 | -2593.579856 | -2593.369061 |
| $^4$IN22a | -2593.425156 | -2593.362872 | -2593.361753 | -2593.546418 | -2593.3131686 |

$E_0$ = Sum of electronic and zero-point energies calculated by B3LYP in solvent

E = Sum of electronic and thermal energies calculated by B3LYP in solvent

$H_{353.15}$ = Sum of electronic and thermal enthalpies calculated by B3LYP in solvent

$G_{353.15}$ = Sum of electronic and thermal free energies calculated by B3LYP in solvent

$E_{(M06)}$ = Single point energies calculated by M06 in solvent

## Section 17. Calculated imaginary frequencies of all transition states species.

| Species | Frequency |
|---|---|

| | |
|---|---|
| $^{1}$TSa | -131.33 |
| $^{3}$TSa | -47.76 |
| $^{1}$TSb | -71.75 |
| $^{3}$TSb | -81.21 |
| $^{1}$TSc | -252.56 |
| $^{3}$TSc | -257.67 |
| TS1 | -73.32 |
| TS2a-1 | -359.19 |
| TS2a-2 | -336.60 |
| TS2a-3 | -350.42 |
| TS3a-1 | -941.87 |
| TS3a-2 | -879.42 |
| TS4a-1 | -874.38 |
| TS4a-2 | -831.87 |
| TS5a-1 | -310.14 |
| TS5a-2 | -289.56 |
| TS6a-1 | -217.43 |
| TS6a-2 | -259.21 |
| TS7a | --274.82 |
| TS8a | -214.50 |
| TS9a | -917.39 |
| TS10a | -891.68 |
| TS11a | -266.88 |
| TS12a | -236.96 |
| TS13a | -273.28 |
| TS14a | -164.50 |
| TS15a | -262.84 |
| TS16a | -107.16 |
| TS17a | -31.22 |
| TS18a | -204.13 |
| TS19a | -820.11 |
| TS20a | -407.95 |
| TS21a | -318.52 |
| TS22a | -114.82 |
| TS23a | -52.84 |
| TS24a | -219.10 |
| TS25a | -97.34 |
| TS26a | -855.15 |
| TS27a | -938.36 |
| TS28a | -256.22 |
| TS29a | -29.12 |
| TS30a | -211.46 |
| TS31a | -47.25 |

| | |
|---|---|
| TS32a | -346.90 |
| TS33a | -163.52 |
| TS34a | -171.17 |
| TS35a | -172.13 |
| TS36a | -890.11 |
| TS37a | -1223.77 |
| TS38a | -469.10 |
| TS3a-3 | -867.11 |
| TS4a-3 | -849.58 |
| TS5a-1-1 | -295.66 |
| TS5a-1-2 | -330.08 |
| TS5a-1-3 | -261.11 |
| TS5a-2-1 | -267.57 |
| TS5a-2-2 | -248.56 |
| TS5a-2-3 | -272.42 |
| TS7a-1 | -324.03 |
| TS7a-2 | -251.77 |
| TS7a-3 | -246.26 |
| TS7a-4 | -334.79 |
| TS7a-5 | -267.87 |
| TS7a-6 | -166.41 |
| TS7a-7 | -265.91 |
| TS11a-1 | -335.21 |
| TS11a-2 | -330.62 |
| TS11a-3 | -251.93 |
| TS11a-4 | -311.16 |
| TS11a-5 | -283.55 |
| TS11a-6 | -248.84 |
| TS11a-7 | -202.56 |
| TS13a-1 | -245.31 |
| TS13a-2 | -259.66 |
| TS13a-3 | -238.34 |
| TS13a-4 | -258.70 |
| TS13a-5 | -239.46 |
| TS13a-6 | -292.30 |
| TS13a-7 | -182.97 |
| TS13a-8 | -275.74 |
| TS13a-9 | -248.40 |
| TS13a-10 | -268.77 |
| TS13a-11 | -242.72 |
| TS13a-12 | -260.65 |
| TS13a-13 | -241.10 |
| TS13a-14 | -289.78 |

| | |
|---|---|
| TS13a-15 | -180.23 |
| TS13a-16 | -281.94 |
| TS13a-17 | -242.92 |
| TS13a-18 | -264.51 |
| TS13a-19 | -246.05 |
| TS13a-20 | -255.28 |
| TS13a-21 | -241.28 |
| TS13a-22 | -288.72 |
| TS13a-23 | -184.32 |
| TS8a-1 | -339.89 |
| TS8a-2 | -102.01 |
| TS8a-3 | -423.98 |
| TS8a-4 | -397.09 |
| TS8a-5 | -412.55 |
| TS2b | -381.67 |
| TS2c | -351.18 |
| TS2d | -352.38 |
| TS1h | -391.86 |
| TS2h | -321.93 |
| TS3h | -377.57 |
| TS4h | -378.88 |
| TS2a-1-1 | -361.82 |
| TS2a-1-2 | -346.79 |
| TS2a-1-3 | -362.22 |
| TS2a-2-1 | -365.78 |
| TS3a-1-1 | -941.87 |
| TS3a-1-2 | -918.13 |
| TS3a-1-3 | -898.09 |
| TS2b-1 | -355.94 |
| TS2b-2 | -391.25 |
| TS2c-1 | -350.53 |
| TS2c-2 | -368.80 |
| TS2c-3 | -358.75 |
| TS2d-1 | -350.49 |
| TS2d-2 | -380.04 |
| TS2e | -348.90 |
| TS2f | -342.03 |
| TS2g | -336.89 |
| $^{4}$TS2a-1 | -369.51 |
| $^{4}$TS3a-1 | -907.52 |
| $^{4}$TS4a-1 | -906.72 |
| $^{4}$TS6a-1 | -408.83 |