Revisions for Final Thesis suggested by Examination Committee

Page i, 4, 7, 14, 31, 108, 111, 115, 128 – "ligand ~~manifold~~"

Page ii – "Chapter 7"

Page ii – Added footnotes for published and submitted chapters 2, 3, 4, 5. Footnote: "A version of this chapter has been published (citation)."

Page ii – Removed citation from in the text leaving just the co-authors for chapters 2, 3, 4, 5.

Page xviii – "pentyn-1-ol" to "pent-4-yn-1-ol"

Page xviii – "cyclopentadiene" to "cyclopentadienyl"

Page xviii – "pentamethylcyclopentadiene" to "pentamethylcyclopentadienyl"

Page xix, 212 – "equivalence" to "equivalent"

Page xix – "κ^2-PP kappa two through two phosphorus atoms"

Page xx – Subscripts included for abbreviations "*p*-CF_3-C_6H_4" and "*p*-MeO-C_6H_4"

Page xxi, 63, 64, 85, 104, 105, 123, 132, 133 – "T0" to "T_0"

Page xxii "PPh_3 triphenylphosphine" removed

Page xxii "PR_3 phosphine" removed

Page 1 – "how reactions are designed and performed in modern-day chemistry ~~is being performed~~"

Page 1 – "Homogenous catalysis operates with the catalyst and substrate in the same phase ~~whilst~~ as opposed to heterogeneous catalysis, which operates in difference phases"

Page 1 – "formation of many mol ~~equivalences~~ of product per mol of catalyst"

Page 1 – "ease of removal of catalyst"

Page 1 – "preferential" to "preferred"

Page 1 – "by altering ~~the~~ its steric and electronic properties"

Page 2 – "Alternatively, ~~a~~ numerous variants"

Page 2 – "electronic and steric properties~~, which~~ that alter the electron density

Page 2 – "~~Traditionally,~~ The metal causes a transformation of the substrate before releasing the product"

Page 3 – "soft σ-donor ligands (phosphines) that stabilize the Ru complexes generated."

Page 3 – "Oxidation states of +1 and +3 are uncommon unless hard σ-donor ligands (e.g. O^{2-}~~,~~), which destabilize the bonding and anti-bonding molecular orbitals, are used to decrease the ~~high crystal field~~ energy between the HOMO and LUMO. As the energy is decreased, ~~causing~~ a high ~~low~~-spin electron configuration is adopted as pairing electrons becomes unfavourable."

Page 3 – “Therefore, ruthenium does not normally perform one electron processes and remains a diamagnetic transition metal ~~unlike the first row d^8 metal iron~~. [22-24] One downside to ruthenium is cost ($9,500 USD/kg – Dec 18th 2018) as it is quite expensive. Two potential alternatives for Ru could be the other d^8 metals – iron and osmium. Iron ($0.068 USD/kg – Dec 18th 2018) is a cheap abundant metal, but iron complexes can be paramagnetic and perform one electron processes~~. However, an alternative to ruthenium is third row d^8 metal~~ Osmium is electronically similar to Ru (diamagnetic), but~~, which~~ it is far more expensive ($14,100 USD/kg – Dec 18th 2018).[12, 25]

Page 3 – “first row d^8 metal iron” and “third row d^8 metal”

Page 3, 9, 69, 70, 97, 114, 115, 116 – “metallocycle” to “metallacycle”

Page 4 – Made NHC ligand consistent with other NHCs in thesis.

Page 4 – “This change in ligand properties can cause~~s~~ a favourable change in catalytic rate.”

Page 4 – “stimuli” to “stimulus”

Page 5 – Figure 1-4: removal of charge in Figure 1-4c

Page 5 – “Another subset of MLC complexes is ~~are~~ proton-shuttling complexes”

Page 6 – Figure 1-5: L-B instead of L-BH3 in figure

Page 6 – “The hydroxy group is deprotonated by the base while~~whilst~~ a hydride is transferred to the ruthenium from the adjacent carbon.”

Page 7 – Figure 1-6: NH_2 instead of NH in figure

Page 8, 46, 58, 59 – “*p*-formaldehyde” to “paraformaldehyde”

Page 8 – “Additionally, primary phosphines can be ~~expensive or~~ difficult to synthesize preventing access to a wide variety of derivatives.”

Page 8 – “Route B is a generalized procedure from THP, a less hazardous starting material”

Page 9 – “the metallacycles ability” to “the metallacycles property”

Page 9 – “results in toxic TlCl byproduct”

Page 9 – “~~This~~ The H-bonding interaction between O_2 and the pendent amine demonstrates the metallacycles property to ring flip and interact with a potential substrate.”

Page 9 – “~~This method allows~~ Ligand substitution is ~~for~~ a fast, high yield reaction to synthesize ~~synthesis of~~ new Ru-($P^R_2N^{R'}_2$) complexes for catalytic testing.”

Page 10 – “~~This~~ Species **B** can be formed from”

Page 11 – “Some current routes to 5-membered *N*-heterocyclic”

Page 11 – “Fischer-Indole, Larock Indole, or Paal-Knorr reactions[68-73].” to “Fischer-indole, Larock indole, or Paal-Knorr reactions.[68-73]”

Page 11 – “Fischer-Indole” to “Fischer-indole”

Page 11 – “Buchwald-Hartwig”

Page 11 – “Some functional groups are not tolerant of acidic conditions and the high temperatures (>100 ˚C)”

Page 11 – “expand the structural space of the heterocycle from planar ~~the 2-dimensions heterocycles~~ (like aromatic rings) to non-planar ~~3-dimensional heterocycles~~ (like cyclohexyl rings)”

Page 11 – “~~However,~~ One ~~of the major flaws~~ drawback with the above methods is the lack of ring diversity synthetically possible. 5-Membered one heteroatom aromatized heterocycles, such as indoles, are the most common heterocyclic moieties.”

Page 11 – “New complimentary methods are needed for ~~synthesize~~ heterocyclic diversity,”

Page 12, 45 – “vinylidine” to “vinylidene”

Page 12 – “attacks the terminal carbon (Scheme 1-12)”

Page 12 – “pair of electrons to”

Page 12 – “Utilization of a Ru vinylidene ~~This pathway~~ produces the *endo-dig* product”

Page 13 – “6 membered rings that causes ~~a~~ a preferential formation”

Page 13 – Figure 1-12b,c: Changed the figure labels from “products” to “routes”

Page 13 – “Typically, strong exogenous bases are used in excess for bimolecular reaction to overcome the entropic challenge of the transition state required to facilitate proton transfer steps”

Page 14 – “Further advances with $RuCl(Cp)(PR_3)_2$ revealed that with an increase of electron density of the aryl substituent on the phosphine shifts the product selectivity ~~could be shifted away~~ from lactones to produce dihydropyrans.”

Page 14 – “However, an oxidant and excess base were”

Page 14 – “(1:4 ratio catalysts to ligand)” removed

Page 14 – “Instead, DMF, the oxidant, or added base” to “Instead, proton transfer steps are mediated by solvent, an oxidant, or exogenous base”

Page 15 – “acid base site” to “functional group”

Page 16 – Figure 1-15b: Figure was updated to include the charge on the complex

Page 16 – “Transfer hydrogenation is a reaction that utilizes”

Page 16 – “catalyst to perform ~~both~~ dehydrogenation (of isoproponal) and hydrogenation (of a ketone) to access ~~for the synthesis of~~ chiral alcohols ~~from aldehydes and ketones~~.”

Page 17 – “centre until equilibrium is reached resulting in incomplete conversion”

Page 17 – Figure 1-16: Figure was updated to include the charge on the complex

Page 17 – “(Figure 1-18a). [26, 108]” instead of “(Figure 1-18a) [26, 108].”

Page 17 – Figure 1-18e: Figure was updated to include the charge on the complex

Page 17 – “Increasing the temperature to 157 ˚C improved the rate”

Page 18 – “Further advances in performance were demonstrated by Gusev”

Page 18 – “Amines ~~re~~present a difficult”

Page 19 – “1) outersphere MLC (Figure ~~Scheme~~ 1-20a); 2) innersphere MLC (Figure 1-20b); and 3) innersphere non-MLC (Figure ~~Scheme~~ 1-20c).”

Page 19 – “1-(phenylmethyl)-*N*-phenylmethanimine”

Page 19 – “whilst” to “while”

Page 19 – “β-Hydride”

Page 19 – “the carbon adjacent to the amine”

Page 19 – “The hydride transfer and deprotonation steps can occur in a stepwise or concert process

Page 19 – “Whereas if an external base”

Page 19, 20, 21, 99, 109, 110, 121, 122, 123, 125, 138 – “innersphere” to “inner-sphere”

Page 19, 20, 21, 22, 99, 100, 109, 110, 112, 117, 121, 128, 138, 139, 140 – “outersphere” to “outer-sphere”

Page 20 – “The NNN pincer ~~This~~ ligand”

Page 20 – “Substrate deprotonation ~~This~~ generates”

Page 21 – “triazolydiene” to “triazolidene”

Page 21 – “under closed conditions for 24 h (Figure 1-22c). ~~Full conversion of indole requires 24 h.~~”

Page 22 – Changed NHC to be consistent with other figures.

Page 22 – “The potential scope for both alcohols and amines is limited since the reaction requires high temperatures to proceed with electronically biased substrate due to the thermodynamic driving force of aromaticity.”

Page 22 – Caption of Figure 1-22: “Albecht” to “Albrecht”

Page 23 – “A series of [Ru(Cp)($P^{R}_{2}N^{R'}_{2}$)(NCMe)]PF_6 complexes was ~~were~~ prepared to probe”

Page 23, 33 – “t-Bu” to “*t*-Bu”

Page 24 – “dehydrogenation of benzylamine ($BnNH_2$) and nitrogen heterocycles.

Page 24 – “through varying the number of basic functional groups.”

Page 24-30 – Altered the boldness of the comma after the year.

Page 25 – “Vol.” to “Ed.”

Page 25 – "Vol. 2nd~~, completely rev. and enlarg~~."

Page 29 – "*Nat. Chem.*"

Page 31 – "The bisphosphine $P^{R}_{2}N^{R'}_{2}$ (3,7-R'-1,5-R-3,7-diaza-1,5-diphosphacyclooctane) MLC ligand family is ~~are~~ highly tunable

Page 31 – "Catalyst performance however is limited by both low conscription, due to acetonitrile lability, and by competitive deactivation, caused by nucleophilic deactivation of the Ruthenium vinylidene by the pendent amine."

Page 31, 44, 89 – "1,5-R'-3,7-R-1,5-diaza-3,7-diphosphacyclooctane" to "3,7-R'-1,5-R-3,7-diaza-1,5-diphosphacyclooctane"

Page 33 – Figure 2-2: Inserted a better quality image.

Page 33 – "In both cases, poor or no product yield was observed with either catalyst, which ~~. This~~ prompted catalytic testing at increased temperatures."

Page 34 – "$^{31}P\{^{1}H\}$" superscript

Page 34 – "~~This indicates~~ Therefore, conscription of **2-1a** into the catalytic cycle is low, presumably due to poor MeCN lability.

Page 35 – "that could be a π-bound alkyne species (**2-4a**)," bold compound number

Page 35 – "Ru–vinylidene"

Page 35 – "~~This~~ The active catalyst would be the dominant species at low temperatures, which would avoid the elevated temperatures required to promote acetonitrile dissociation from the precatalysts **2-1a/2-1b**."

Page 36 – "The cationic precatalysts $[Ru(Cp)(P^{R}_{2}N^{Bn}_{2})(MeCN)]PF_{6}$ (**2-1a**: R = *t*-Bu; **2-1b**: R = Ph) are active ~~catalysts~~ for the cyclization of ethynylbenzyl"

Page 36 – "The work discussed in this chapter represents"

Page 37 – "^{1}H and $^{13}C\{^{1}H\}$ spectra"

Page 38 – "^{1}H NMR"; "$^{31}P\{^{1}H\}$ NMR"; "$^{13}C\{^{1}H\}$ NMR" in 2.4.2; 2.4.3; 2.4.4; 2.4.5; 4.4.3, 5.4.2, 5.4.3, and 6.4.2

Page 38 – "heated to ~~at~~ 70"

Page 38 – "RT" to "room temperature"

Page 39 – "X-ray quality crystals were grown by vapor diffusion in THF and diethyl ether."

Page 39 – "indicate a maximum conversion of 77% to ~~of~~ **2-5a** from ~~with the balance being~~ **2-1a** (23% remaining)"

Page 39 – All sig figs. in 2.4.6. for volume e.g. "1.118 mL" to "1.12 mL"

Page 41 – "Adv. Synth. Catal." to "*Adv. Synth. Catal.*"

Page 42 – “Organometallics” to “*Organometallics*”

Page 43 – “A family of [CpRu(PP)(MeCN)]PF_6 complexes (**2-1b**, **3-2a-d** and **3-4**) ~~were~~ was prepared”

Page 43 – “The catalytic performance of **2-1b**, **3-2a-d** and **3-4** ~~were~~ was assessed”

Page 43 – “contain a~~n~~ Brønsted acidic or basic site”

Page 44 – Scheme 3-1: Edited complex A to show a Cl ligand.

Page 44 – “intermolecular hydration of alkynes.[1e, 2a]” fixed font

Page 46 – Scheme 3-3: Fixed labels for consistency

Page 46 – “*t*-Bu”

Page 46, 51, 52, 53, 54, 55, 56, 59, 61 – “*p*-CF_3-Ph” to “*p*-CF_3-C_6H_4”

Page 46, 51, 52, 54, 55, 56, 59, 61 – “*p*-MeOPh” to “*p*-MeO-C_6H_4”

Page 47 – Scheme 3-4: Fixed labels for consistency

Page 46 – Scheme 3-3: Fixed caption “p-CH_2O” to “paraformaldehyde

Page 49 – Scheme 3-6: “Catalysis of the cyclization of 2-ethynylaniline”

Page 49 – Table 3-1: “Catalysis of the cyclization of 2-ethynylaniline”

Page 49 – Scheme 3-7: Scheme was updated to include an anion

Page 50 – “The minor ~~This~~ signal”

Page 50 – “With optimal conditions identified, a screen of catalysts was undertaken using **2-1b, 3-2a-d** and **3-4**.” Moved

Page 50 – “Evidence of a deactivated vinyl ammonium compound (analogous to **2-2a**), or other deactivation species, is ~~are~~ not observed.”

Page 51, 101 – “chlorofro~~r~~m-d_1”

Page 57, 102 – “tetrahydronaphthalene”

Page 60 – “by ^{1}H NMR” superscript

Page 63 – All sig figs. in 3.4.6. for volume e.g. “12.390 mL” to “12.39 mL”

Page 66 – “give *O*– and *N*– Heterocycles”

Page 66 – “A series of [Ru(Cp/Cp*)($P^R{}_2N^{R'}{}_2$)(MeCN)]PF_6 complexes was ~~were~~ prepared,”

Page 66 – “more active ~~that~~ than previous catalysts”

Page 68 – “A group of complexes ~~were~~ was prepared”

Page 69 – “Coalescence to one major signal is observed in the ^{31}P {^{1}H} NMR on cooling to –90 ˚C in CH_2Cl_2.”

Page 69 – “(Figure 4-2)”

Page 69 – “are ~~very~~ similar”

Page 69 – “~~This~~ The coplanar arrangement suggests that the nitrogen lone pair is ~~there is~~ delocalized ~~of the lone pair~~ into the π-system, which ~~This~~ is supported by the planar geometry found for N3 (sum of bonding angles = 359.05˚).”

Page 70 – “The close proximity of the pendent amine to the acetonitrile ~~This conformation~~ is uncommon for solid-state structures”

Page 71 – “from 1 to 3 mol% had”

Page 71 – “catalysts **2-1a,b**” space

Page 71 – “at 1 mol% (Figure 4-3b, red bars), the 1 mol% ~~this~~ data will”

Page 71 – “~~This~~ Therefore, incomplete conversion is likely due to competitive formation of a vinyl ammonium deactivation complex by nucleophilic attack of the pendent amine on the vinylidene alpha carbon.

Page 71 – “~~It is notable that~~ Therefore, the C-H/π interaction observed in the solid-state structure of ~~**2d**~~ **4-2b** does not hinder MeCN lability.”

Page 72 – “iso-chromene” to “isochromene”

Page 73 – “~~This~~ The hypothesis that the thermal initiation was higher for the Cp analogue (**4-1b**) was further supported by the observation that complete conversion”

Page 75 – “A number of additives were significantly detrimental to catalyst activity (>50% change in activity relative to control), including: benzyl amine, benzonitrile, sodium iodide, phenyl acetylene, and 1,2-ethanedithiol ~~and potassium carbonate~~ (Table 4-2, Entries 10-15)”

Page 77 – “Benzyl amine” to “Benzylamine”

Page 78 – “1,2-Ethandithiol”

Page 79 – “good to excellent yields of CF_3 derivatives can be obtained ~~achieved~~”

Page 79 – “or increased steric hinderance of the amine”

Page 81 – “ A group of [Ru(Cp/Cp*)($P^R_2N^{R'}_2$)(MeCN)]PF_6 complexes was ~~were~~ prepared”

Page 81 – Within the first paragraph of 4.4.1 General Procedure, Materials and Instrumentation: “2-Ethynyl” to “2-ethynyl”

Page 82, 101 – “degassed by bubbling with N_2”

Page 82 – “Elemental analysis was performed by Canadian Microanalytical Service Ltd”

Page 82 – “Tris(hydroxymethyl)phosphine”

Page 83 – “[Ru(Cp)(-$NCCH_3)_3$]PF_6 or [Ru(Cp*)(-$NCCH_3)_3$]PF_6”

Page 83 – " acetonitrile (20 mL) were ~~was~~ added."

Page 83- 84 – Fixed coupling constants to 1 d.p.

Page 86 – "To a 200 mL Schlenk flask, $Pd(PPh_3)_2Cl_2$ (0.01 equiv.)," X = I

Page 86 – "To a 200 mL Schlenk flask, $Pd(PPh_3)_2Cl_2$ (0.03 equiv.)," X = Br

Page 87 – "D. B. Grotjahn, *Top. Catal.* **2010**, *53*, 1009-1014; (b) A. J. Arita, J. Cantada, D. B. Grotjahn, A. L. Cooksy, *Organometallics* **2013**, *32*, 6867-6870."

Page 88, 89 – Removal of comman after jornal name for reference 24, 25, 27, and 28

Page 89 – Bold year for reference 26

Page 90 – "~~This system~~ The Milstein pincer catalyst is proposed to operate"

Page 90 – "Other high-boiling polar solvents affords improved product formation (Entries 4-6) with the sustainable[11]"

Page 91 – "Addition of mercury to test for heterogenous Ru nanoparticles does not negatively"

Page 93, 94, 95 – "Brønsted"

Page 96 – "and the Shvo catalysts"

Page 90 – "This system is proposed to operates through a"

Page 95 – "Scheme 5-3, Table 5-3"

Page 96 – "Scheme 5-4"

Page 96 – "Scheme 5-2a"

Page 96 – Scheme 5-3: "Conditions: 250 mM Sub., 3 mol% **[Ru]**, 110 ˚C, anisole, 48 h, in a sealed vial."

Page 97 – "N-H-N"

Page 98 – Scheme 5-4: Fixed spacing of the reaction scheme

Page 98 – "~~This is~~ As amine adducts **5-1** and **5-2** are isolable and **5-**3 is not further supports that a hydrogen bond is a stabilizing force ~~in amine adducts **5-1** and **5-2**~~."

Page 99 – "Scheme 5-5"

Page 100 – "Scheme 5-6; see ~~S.I.~~ Appendices D10 for conversion curve"

Page 104, 105 – "were prepared: benzylamine"

Page 105 – "were prepared: indoline"

Page 105 – "To each of these vials the catalyst stock **2-1b** (250 µL to set A), and **2-3** (250 µL) to set B." to "To each vial in set A, 250 µL of the catalyst stock **2-1b** was added. To each vial in set B, 250 µL of the catalyst stock **2-3** was added."

Page 105 – “1.50~~0~~ mL”

Page 108 - “These complexes have a~~n acid/base site~~ functional group present”

Page 108 – “The entropic release of H_2 from the catalyst is used to make acceptorless dehydrogenation more favorable.[25, 26, 31, 32] However, H_2 release and H_2 binding are in equilibrium. As the reaction proceeds in a closed (capped) system, the H_2 pressure increases until the rate of H_2 binding is equal to the rate of H_2 release causing an incomplete reaction.[26] Open conditions, under a flow of N_2, can be employed to release H_2 and allow AD reactions to go to completion ~~since an equilibrium exists between H_2 release and binding, preventing complete conversion~~.”

Page 106 – “Figure 6-2”

Page 111 – “Indoline was chosen as the substrate since only one product (indole) can be formed following acceptorless dehydrogenation. Indoline is additionally not as thermodynamically challenging as other AD substrates due to the aromatization of the heterocyclic ring system.”

Page 111 – “14 catalyst derivatives”

Page 113 – “However, the Ru complex does not exhibit the same chemical structure as other Ru($P^R_2N^{R'}_2$) complexes as observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy possibly due to either decomposition or different confirmations existing as many $^{31}P\{^1H\}$ signals are observed (3-20 ppm) upfield of the typical Ru($P^R_2N^{R'}_2$) singlet observed between 33-54 ppm.”

Page 114, 128 – “A Goldilocks”

Page 116, 117, 124, 132, 235-244 - “REACTIR” to “ReactIR”

Page 117 – “in which the concentration of the species”

Page 117 – “tet~~et~~rahydronaphthalene”

Page 118, 119 – “AD of indoline for catalyst variable time normalization analysis”

Page 120 – “$\sum[Sub]^{\text{reaction order of Sub}}\Delta t$”

Page 121, 123 – “AD of indoline for substrate variable time normalization analysis”

Page 125 – “This substituents of the indoline can alters the electronic properties of the amine on the substrate and the donor ability of the hydridic C-H” to “The substituents can alter the electronic properties of the amine and the donor ability of the hydridic C-H of indoline”

Page 125 – “H_2 release in case”

Page 125 – “a greater amount of product was produced at 110 ˚C than with the 5-Cl substituent”

Page 125 – “also present as detected by GC-FID”

Page 125 – “2-Me~~-indoline~~”

Page 130-131 – Fixed the d.p. of the coupling constants

Page 130 – “relative to ~~the internal standard (~~tetrahydronaphthalene~~)~~,”

Page 130 – "[Ru(Cp/Cp*)(NCCH$_3$)$_3$]PF$_6$ (1 equiv., 5 mM), ligand P–P (1.05 equiv., 5 mM)"

Page 131 – Insert a section for "Synthesis of [Ru(Cp)(P$^{Me}_2$N$^{Bn}_2$)(NCMe)]PF$_6$"

"[Ru(Cp)(NCMe)$_3$]PF$_6$ (257 mg, 0.592 mmol, 1 equiv.) and P$^{Me}_2$N$^{Bn}_2$ (213 mg, 0.595 mmol, 1 equiv.) were combined in a 100 mL Schlenk flask with acetonitrile (10 mL) and heated at 70 °C for 4 h. A bright orange solution formed. The solvent was removed under vacuum to afford an orange powder. Yield: 414 mg (98%). ^{1}H NMR (400 MHz, acetone-d_6) δ: 7.82-7.23 (m, Ph-*H*, 10H), 4.88 (s, Cp-*H*, 5H), 4.03 (s, NC*H*$_2$Ph, 2H), 3.76 (s, NC*H*$_2$Ph), 3.41 (m, C*H*$_3$P, 6H), 3.17 (m, NC*H*$_2$P, 4H), 2.97 (m, NC*H*$_2$P, 4H), 2.43 (s, RuCNC*H*$_3$, 3H). ^{31}P{^{1}H} NMR (162 MHz, acetone-d_6) δ: 39.2 (s, Ru*P*), -144.2 (sept, $^1J_{P\text{-}F}$ = 707 Hz, *P*F$_6$). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ: 138.5 (s, CH$_2$(Ph-*C*)), 137.8 (s, CH$_2$(Ph-*C*)), 132.6, 131.8, 130.5, 129.8, 129.3, and 128.5 (s, Ph-*C*), 129.0 (s, Ru*C*NCH$_3$), 82.2 (s, *Cp*), 65.7 (s, NCH$_2$Ph), 64.9 (s, NCH$_2$Ph), 53.1 (NCH$_2$P), 52.5 (NCH$_2$P), 52.3 (*C*H$_3$P), 4.2 (s, *C*H$_3$CN).*This species would convert to another under mild conditions in solvent (quickly) and as a solid (slowly)."

Page 131 – "**1c**" to "**3-1a"**

Page 132 – **"**The vials were tightly capped under N$_2$, electrical taped, and removed"

Page 132 – "General Procedure for the Catalytic Cyclization of Substrates under Closed Conditions

A representative procedure is given for one ~~four~~ substrate. In a glovebox, the following stock solutions were prepared: ~~tetrahydronaphthalene (26 mg, 0.2 mmol, 0.4 M) in anisole (2.5 mL);~~ 4-chloroindoline (77 mg, 0.50 mmol, 1.00 M) and tetrahydronaphthalene (26 mg, 0.2 mmol, 0.4 M) in anisole ~~tetrahydronaphthalene stock solution~~ (0.50 mL); ~~5-chloroindoline (77 mg, 0.50 mmol, 1.00 M) in tetrahydronaphthalene stock solution (0.50 mL); 6-chloroindoline (77 mg, 0.50 mmol, 1.00 M) in tetrahydronaphthalene stock solution (0.50 mL); 5-fluoroindoline (69 mg, 0.50 mmol, 1.00 M) in tetrahydronaphthalene stock solution (0.50 mL);~~ **3-1a** (10 mg, 0.011 mmol, 5 mM) in anisole (2.20 mL). ~~Four~~ In a 4 mL vial containing a stir bar, ~~were charged with~~ the substrate/tetrahydronaphthalene stock solution (125 µL, 4-chloroindoline~~, B = 5-chloroindoline, C = 6-chloroindoline, D = 5-fluoroindoline~~) and additional anisole (125 µL). To the ~~each~~ vial, **3-1a** stock solution (250 µL) was added giving a final volume of 500 µL. The final concentrations for ~~all~~ the vial were 0.250 M in substrate and 2.5 mM in catalyst. A final vial was charged with substrate/internal standard stock solution (100 µL) for use as the time = 0 sample, required for accurate quantification of substrate and product. The vial was ~~were~~ tightly capped under N$_2$, electrical taped, and removed from the glove box and heated to 110 °C with stirring. After 24 hours ~~all~~ the vial was ~~were~~ removed from the heat, cooled, and exposed to air to quench. A 40 µL aliquot was diluted to 10 mM (960 µL) in acetonitrile and analyzed by GC-FID. A 10 µL aliquot of the T$_0$ sample was diluted with acetonitrile (990 µL) and analyzed by GC-FID."

Page 132 – Added a new section

– "General Procedure for the Catalytic Cyclization of Substrates under Open Conditions

A representative procedure is given for one substrate. In a glovebox, the following stock solutions were prepared: 4-chloroindoline (77 mg, 0.50 mmol, 1.00 M) and tetrahydronaphthalene (26 mg, 0.2 mmol, 0.4 M) in anisole (0.50 mL); **3-1a** (10 mg, 0.011 mmol, 5 mM) in anisole (2.20 mL). To a 100 mL Schlenk tube containing a stir bar, the substrate/tetrahydronaphthalene stock solution (200 µL, 4-chloroindoline) and additional anisole (200 µL). To the 100 mL Schlenk tube, **3-1a** stock solution (400 µL) was added giving a

final volume of 800 µL. The final concentrations for the Schlenk tube were 0.250 M in substrate and 2.5 mM in catalyst. A final vial was charged with substrate/internal standard stock solution (100 µL) for use as the time = 0 sample, required for accurate quantification of substrate and product. The Schlenk tube was removed from the glove box and put under a flow of N_2. Following set up of the ReactIR and an initial IR spectrum, the Schlenk tube was heated to 125 °C with stirring. After 24 hours, the Schlenk tube was removed from the heat, cooled, and exposed to air to quench. A 40 µL aliquot was diluted to 10 mM (960 µL) in acetonitrile and analyzed by GC-FID. A 10 µL aliquot of the T_0 sample was diluted with acetonitrile (990 µL) and analyzed by GC-FID."

Page 133-135 – Removed issue numbers from references to match other sections.

Page 135 – "*Can. J. ~~of~~ Chem.*"

Page 137 – "while catalyst 4-1b was"

Page 139 – "*para*" italicized

Page 139 – "*N*" italicized of N-benzyl-phenylimine

Page 156 – Fixed the Space Group

Page 171, 172, 173 – "in *proteo*-THF" italicized

Page 184 – 212 Inserted page numbers.

Page 215 – Fixed footnote reference format

Page 216 – Fixed Figure C-38

Page 245 – Removal of contact information

Page 249 – "Cyclization and Competitive Deactivation"

For the variable normalization time analysis:

$$-\frac{d[A]}{dt} = f\left([A], kinetic\ const.\right) \cdot [cat]_T{}^n$$

$$\int_{[A]_0}^{[A]_t} f^{-1}([A], kinetic\ const.)\, d[A] = \int_0^t -[cat]_T{}^n\, dt$$

$$F^{-1}([A]_t, [A]_0, kinetic\ const.) = -\boldsymbol{t}[\boldsymbol{cat}]_{\boldsymbol{T}}{}^{\boldsymbol{n}}$$

$$[A]_t = G\left([A]_0, v_A, kinetic\ constant, \boldsymbol{t}[\boldsymbol{cat}]_{\boldsymbol{T}}{}^{\boldsymbol{n}}\right)$$

$$[P]_t = [A]_0 - G\left([A]_0, v_A, kinetic\ constant, \boldsymbol{t}[\boldsymbol{cat}]_{\boldsymbol{T}}{}^{\boldsymbol{n}}\right)$$

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