Supplementary Information

Tetrazine Metallation Boosts Rate and Regioselectivity of Inverse Electronic Demand Diels-Alder (iEDDA) Addition of Dienophiles

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1 Experimental

The ligand TzPy and the *trans*-cyclooctene were purchased or generously provided from TTI GmbH/TGU Varimol (www.varimol.de)

[ReCl(CO)3(TzPy)] was made by refluxing the $ReCl(CO)_5$ (100 mg, 0.277 mmol) with TzPy (44 mg, 0.277 mmol) in toluene for 3 h. After the reaction solution was cooled to room temperature, hexanes was over-layered and allowed to slowly diffuse into the solution to produce crystals of [**1**]. Yield: 97 mg (76.1%). IR (CH_2Cl_2): υ_{CO} = 2033, 1948, 1920 cm^{-1}. $\lambda_{max}(\epsilon)$ = 522 nm (2924 M^{-1} cm^{-1}). Elemental anal. Calcd (%) for $C_{10}H_5ClN_5O_3Re - 0.2C_7H_8 - 0.2H_2O$: C, 28.1; H, 1.53; N, 14.44. Found: C, 28.12; H, 1.45; N, 14.38 (max. diff: 0.08).

2 DFT Calculations

Calculations. All calculations reported herein were done with the ORCA program package. [**1**] The structure of [**1**], [**1**Fc] and [**1**Ci] was calculated using the molecular structure as a base. The structure of 1,4- and 4,5-dihydropyridazine of [**1**Fc] and [**1**Ci] were determined respectively by shifting the proton and finding the energy minimum structure, using the the same basis sets and level of theory as for the structures determined from the molecular structures.The geometry optimizations were carried out at the TPSS level of DFT.[2,3] Accurate triplet-ζ valence basis sets with one set of polarization functions on all atoms were used (def2-TZVP) and J-approximation as an auxiliary basis set with RI approximation. The SCF calculations were of spin-polarized type with Tight convergence (1 x 10^{-9} Eh in energy).

A DFT potential energy surface scan was performed in which the olefin was brought to the tetrazine moiety of [**1**]. The first energy minima was found after the dearomatization of the tetrazine moiety. This energy minima was then used to determine the energy of N_2 release by increasing the distance between the one of the uncoordinated nitrogen atoms and the carbon atom form 1.58 Åto 3.5 Å. The activation energy of the approach of the olefin to the tetrazine was confirmed by increasing the distance between the βC of the olefin and the carbon atom in the tetrazine from 1.5 Åto 3.5 Å. Only the *endo*- approach of the olefin was considered because attempt to calculate the *exo*-approach resulted in unreasonable activation energies. The Cl-face versus CO-face approach of the olefin to [**1**] was determined only for the first step to show the difference in activation energy.

3 References

1. F. Neese, "The orca program system," Wiley Interdisciplinary Reviews: Computational Molecular Science **2012**, 2, 73-78.

2. A. D. Becke, "Density-functional exchange-energy approximation with correct asymptotic behavior," *Phys. Rev. A*, **1988**, *38*, 3098-3100.

3. J. P. Perdew, "Density-functional approximation for the correlation energy of the inhomogeneous electron gas," *Phys. Rev. B*, **1986**, *33*, 8822-8824.

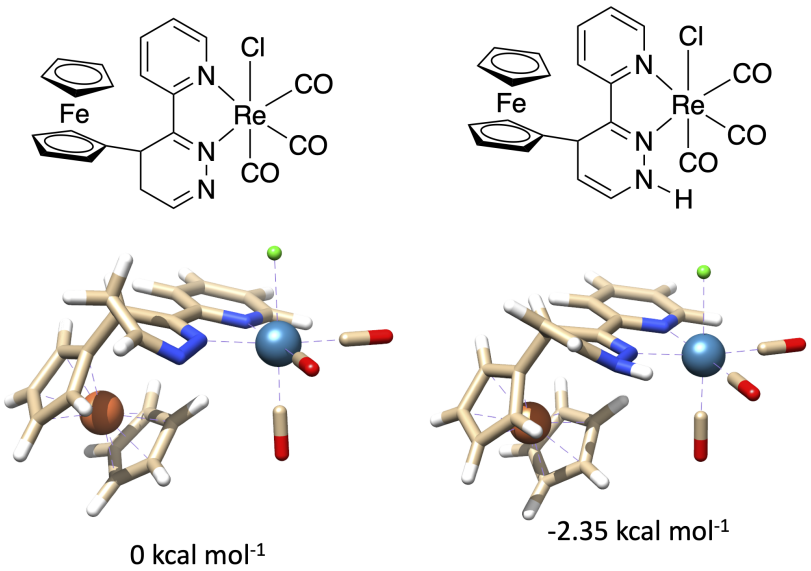

Figure S1: Molecular structures of 4,5-dhp (left) and 1,4-dhp (right) of [**1**Fc], difference in energy shown in kcal. Calculations were performed using TPSS basis set at def2-TZVP/J level of theory with TightSCF, in the gas-phase.

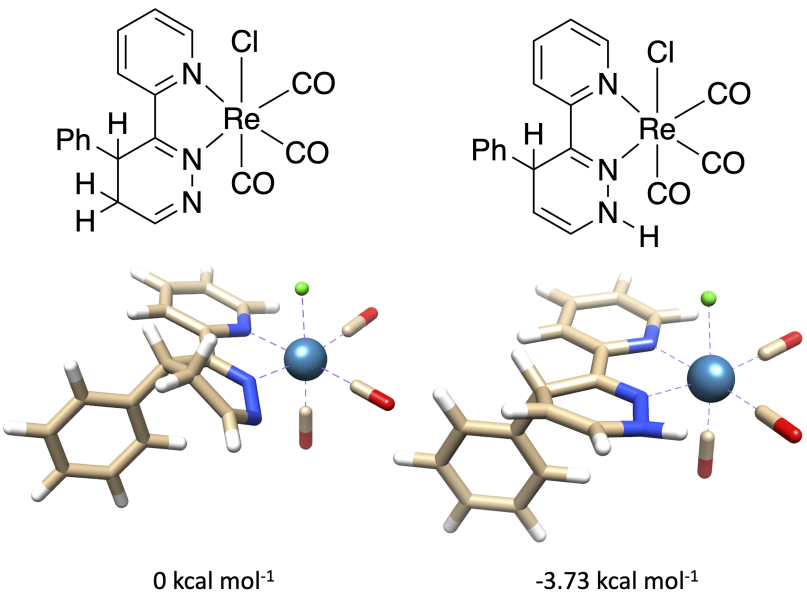

Figure S2: Molecular structures of 4,5-dhp (left) and 1,4-dhp (right) of [**1**Ci], difference in energy shown in kcal. Calculations were performed using TPSS basis set at def2-TZVP/J level of theory with TightSCF, in the gas-phase.

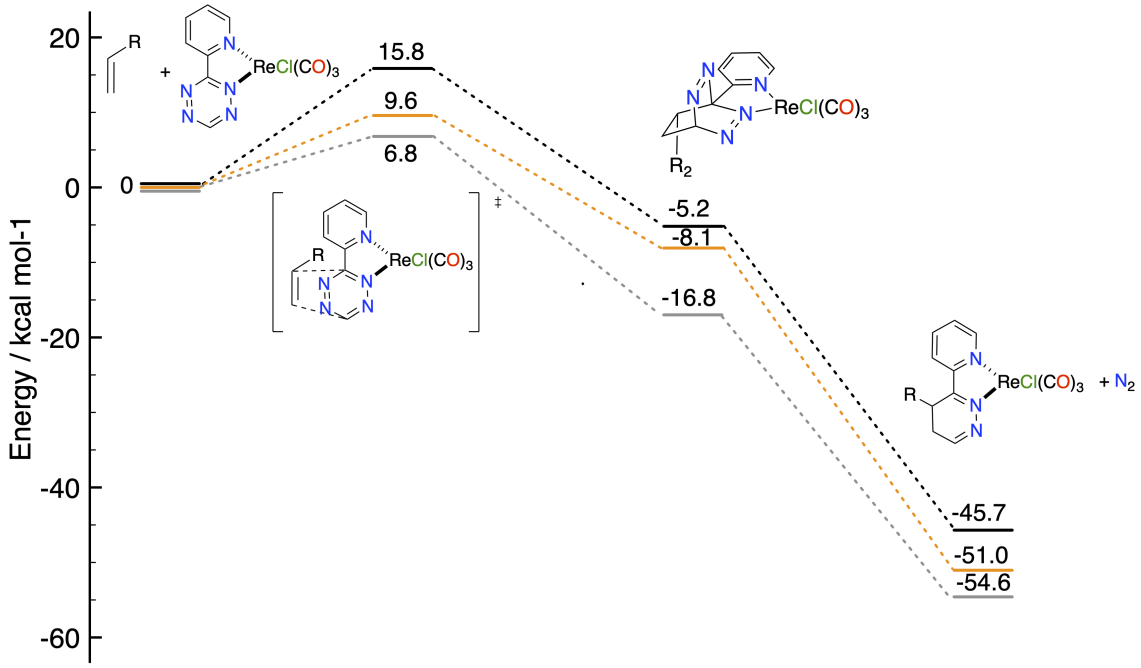

Figure S3: Potential energy surface scan between olefin and [**1**], and the three olefins discussed in the manuscript, styrene (gray), vinylferrocene (orange) and *trans*-cyclooctene (black). Calculations were performed using TPSS basis set at def2-TZVP/J level of theory with TightSCF, in the gas-phase.

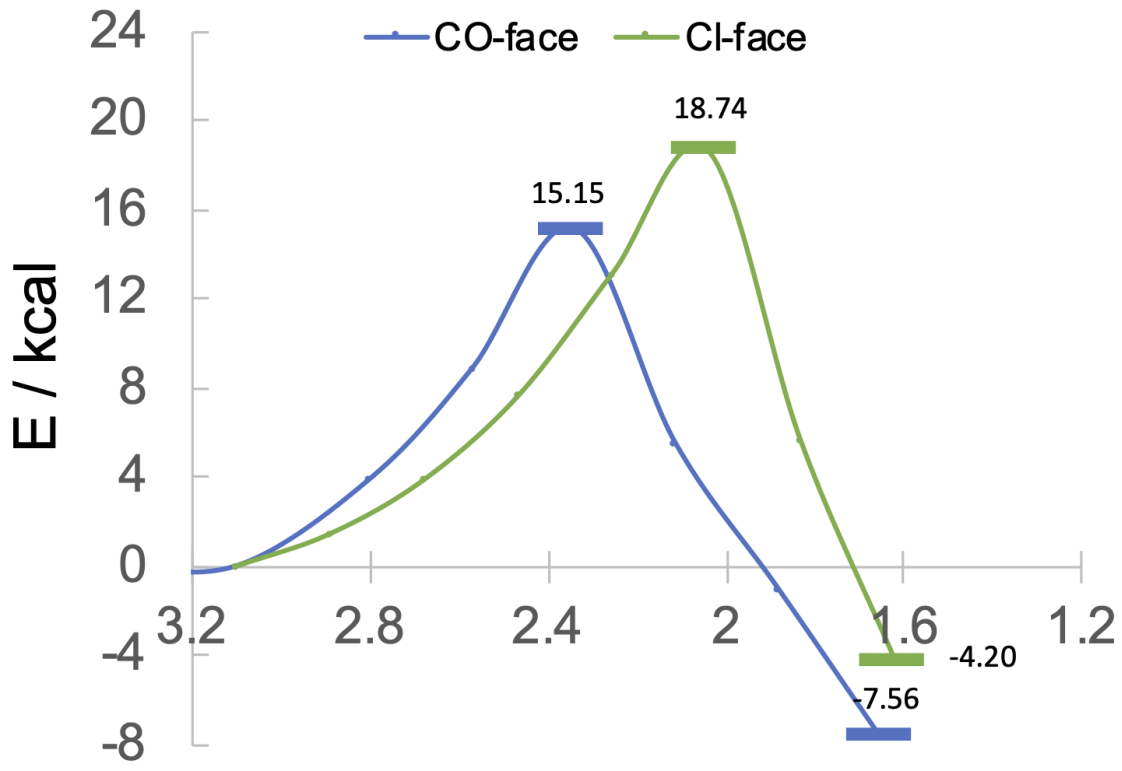

Figure S4: Potential energy surface scan between Ci and [**1**], from Cl-face (green) and CO-face (blue). Calculations were performed using TPSS basis set at def2-TZVP/J level of theory with TightSCF, in the gas-phase.

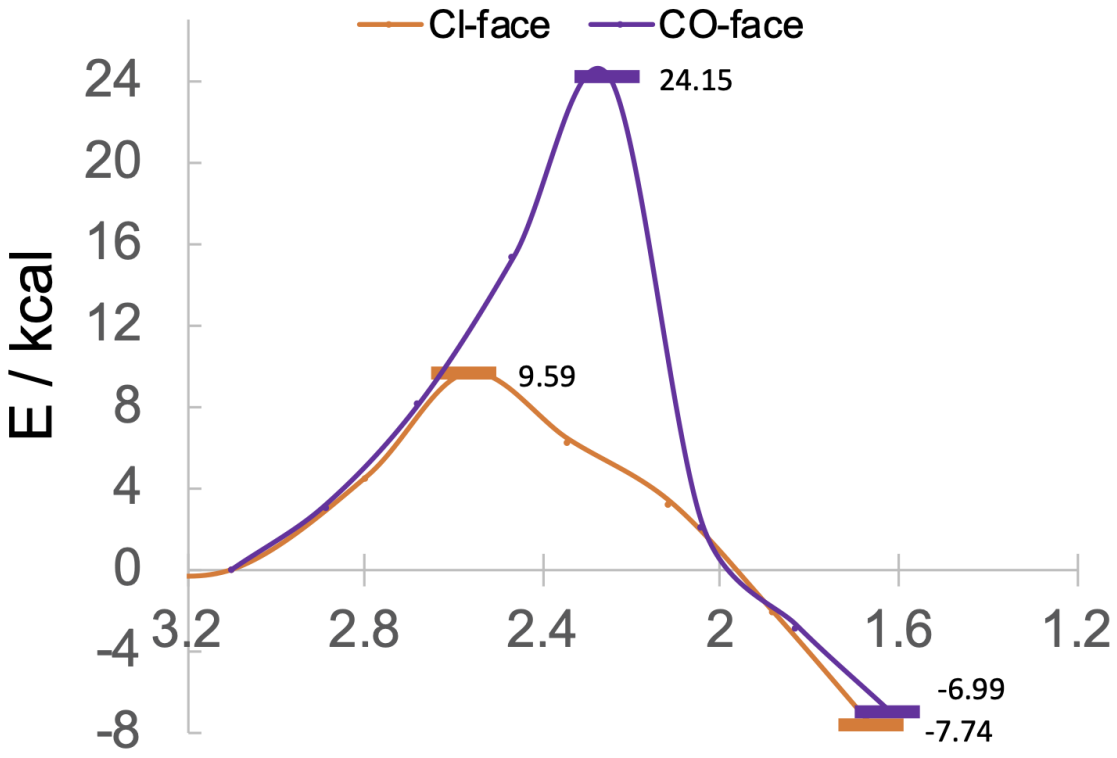

Figure S5: Potential energy surface scan between ViFc and [**1**], from Cl-face (grape) and CO-face (organge). Calculations were performed using TPSS basis set at def2-TZVP/J level of theory with TightSCF, in the gas-phase.

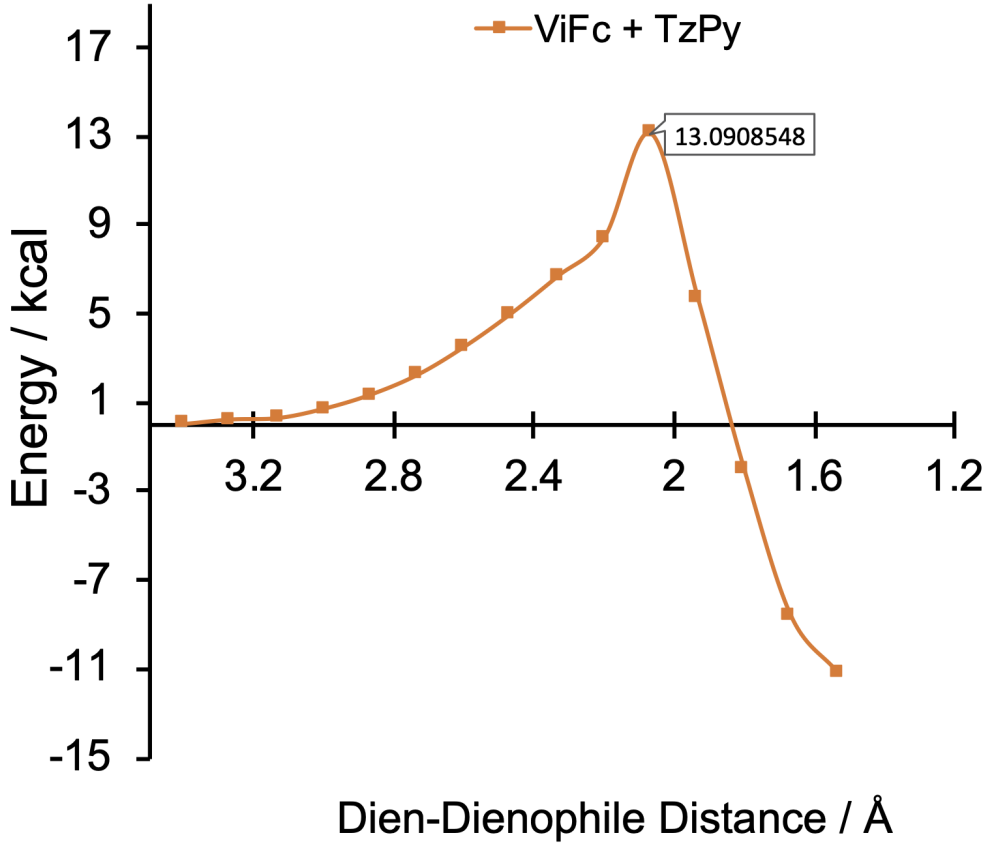

Figure S6: Potential energy surface scan between ViFc and TzPy. Calculations were performed using TPSS basis set at def2-TZVP/J level of theory with TightSCF, in the gas-phase.

4 Kinetics

1st order kinetics fitted using equation 2-33 (p 23) and 2nd order kinetics fitted using equation 2-35 (p 24) from from Espenson "Chemical Kinetics" 1981 Mcgraw-Hill Education. The data was fitted using the corresponding equation on a MacBook Pro 2019 using Plot2 Pro Version 2.6.6 (9980) graphing program, for more information see micw.org.

P_t = absorption at time t
P_0 = initial absorption at time 0
P_∞ = absorption at time infinity (reaction end point)
k = rate constant
t = time

$$ln\frac{P_t - P_\infty}{P_0 - P_\infty} = -kt \quad \text{(2-33)}$$

$$P_t = (P_0 - P_\infty)e^{-kt} + P_\infty$$

P_t = absorption at time t

P_0 = initial absorption at time 0

P_∞ = absorption at time infinity (reaction end point)

k = rate constant

t = time

$[A]_0$ = initial concentration of [**1**]

$[B]_0$ = initial concentration of ViFc

$\Delta_0 = [B]_0 - [A]_0$

$$ln(1 + \frac{\Delta_0}{[A]_0} * \frac{P_0 - P_\infty}{P_t - P_\infty}) = ln\frac{[B]_0}{[A]_0} + \Delta_0 kt \quad \text{(2-35)}$$

$$P_t = [(P_0 - P_\infty) * (\frac{[B]_0}{\Delta_0} + \frac{[A]_0}{\Delta_0} e^{\Delta_0 kt})^{-1}] + P_\infty$$

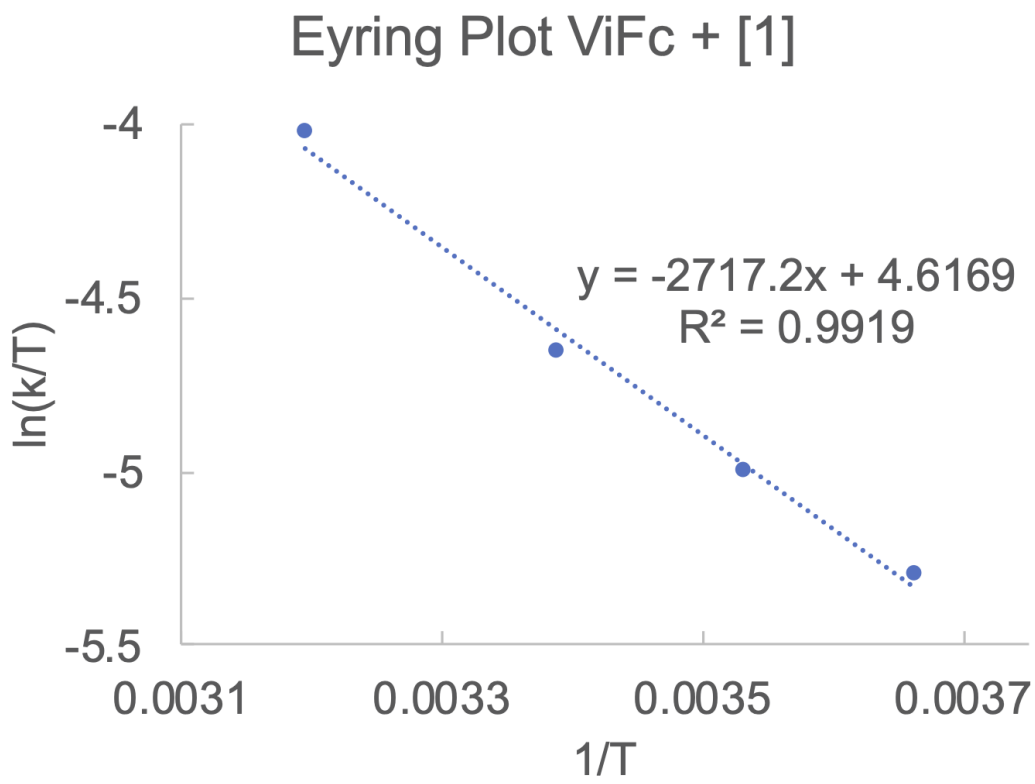

Figure S7: Eyring Plot of ViFc + [**1**]

Equations used for Eyring analysis

$y = mx + b$

$m = \frac{-\Delta H^\ddagger}{R}$

$b = ln(\frac{k'}{h}) + \frac{\Delta S^\ddagger}{R}$

$ln(\frac{k'}{h}) = 23.7638$

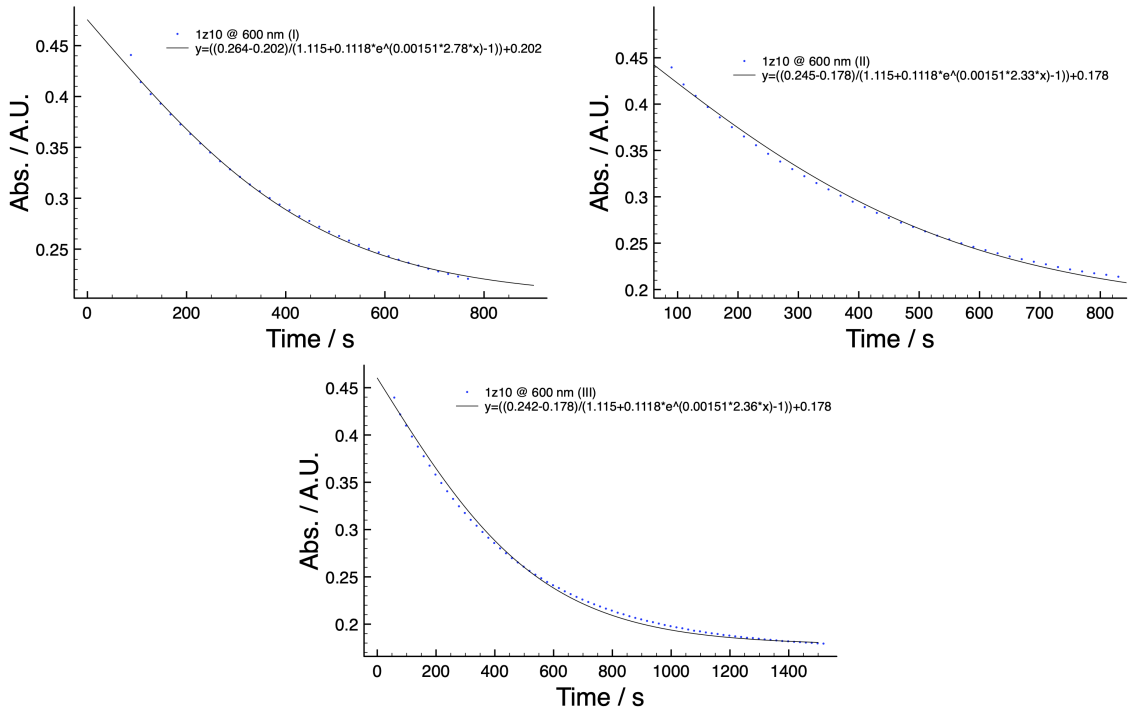

Figure S8: 2^{nd} order kinetics trace of ViFc + [**1**], 22C. Signal at 600 nm, 2nd order equation used to fit the data. Concentration of [**1**] = 0.000168 M, [ViFc] = 0.00167 M.

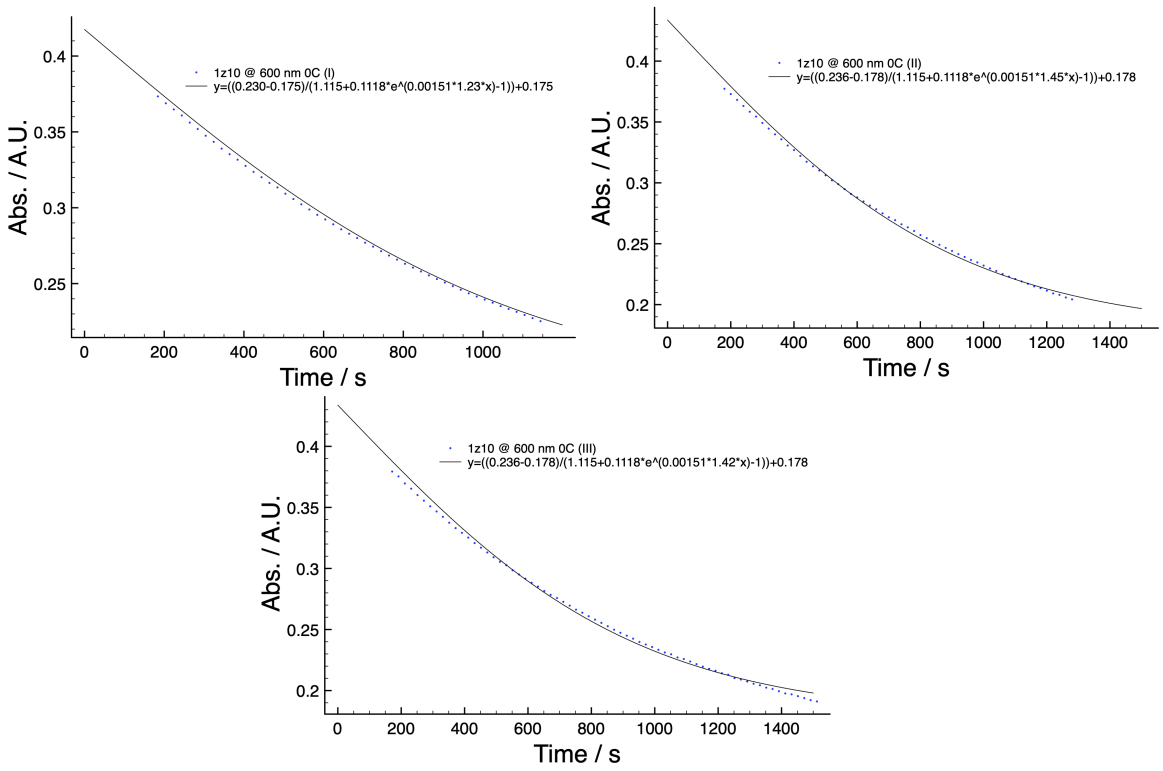

Figure S9: 2nd order kinetics trace of ViFc + [**1**], 0 C. Signal at 545 normalized and the 2nd order equation used to fit the data. Concentration of [**1**] = 0.000168 M, [ViFc] = 0.00167 M.

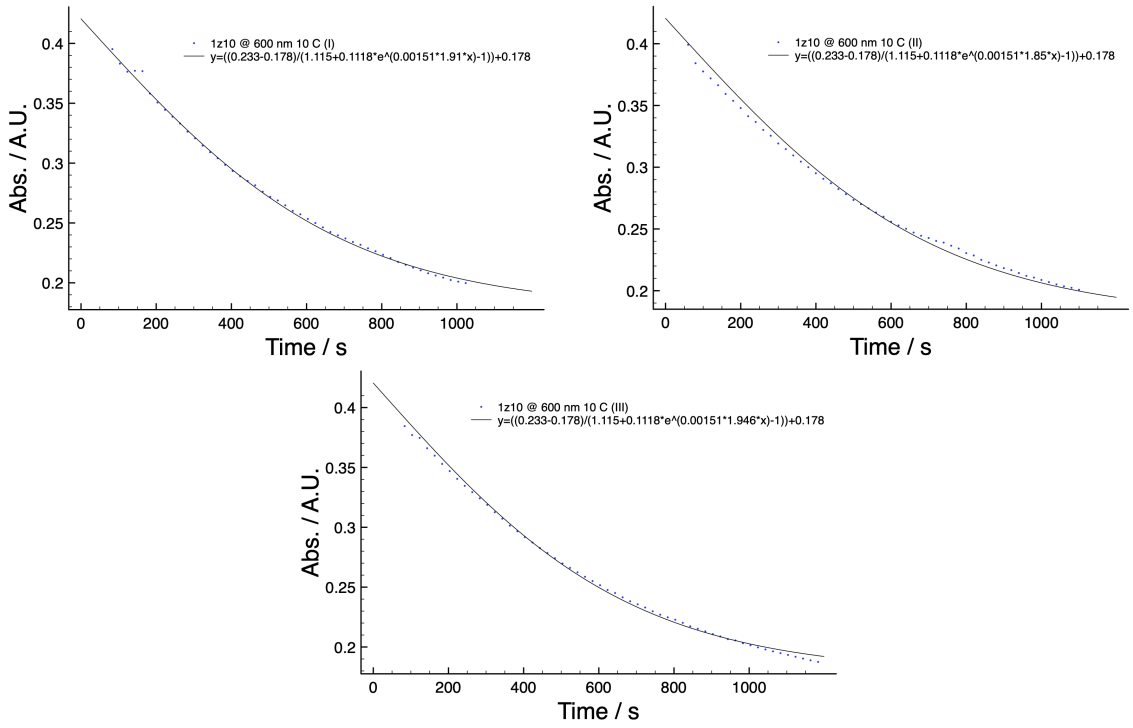

Figure S10: 2nd order kinetics trace off ViFc + [**1**], 10 C. Signal at 545 normalized and the 2nd order equation used to fit the data. Concentration of [**1**] = 0.000168 M, [ViFc] = 0.00167 M.

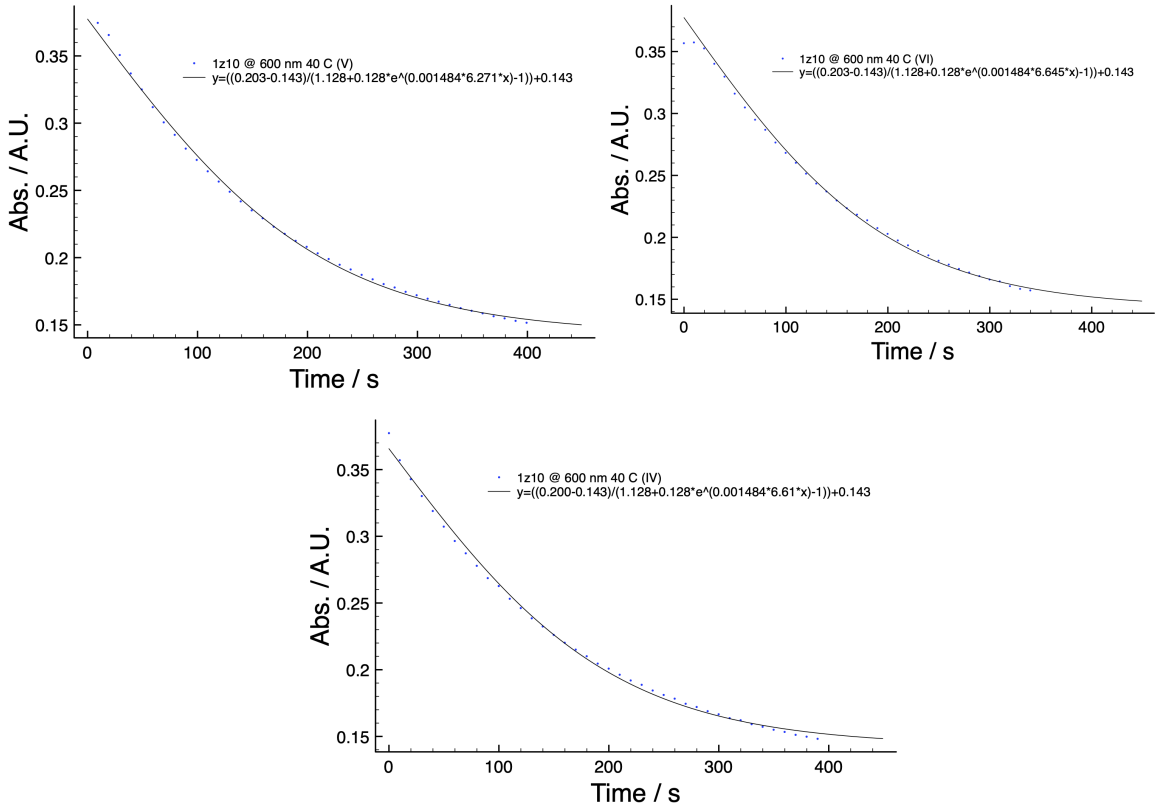

Figure S11: 2nd order kinetics trace of ViFc + [**1**], 44C. Signal at 545 normalized and the 2nd order equation used to fit the data. Concentration of [**1**] = 0.000190 M, [ViFc] = 0.00167 M.

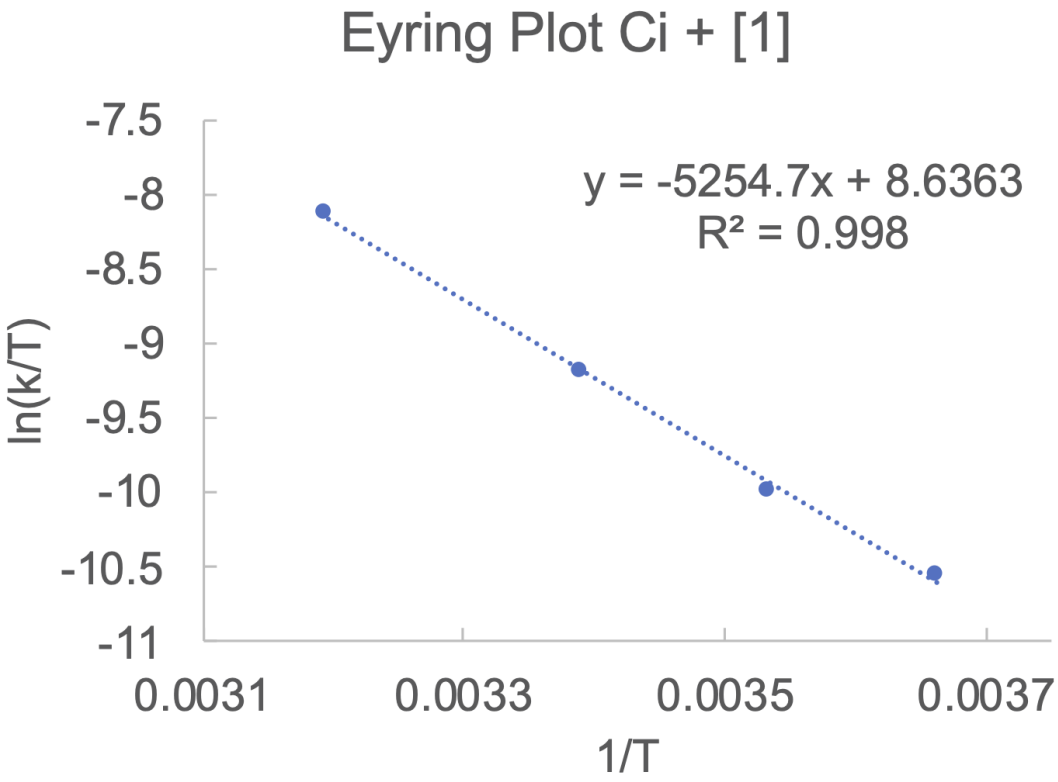

Figure S12: Eyring Plot of Ci + [**1**]

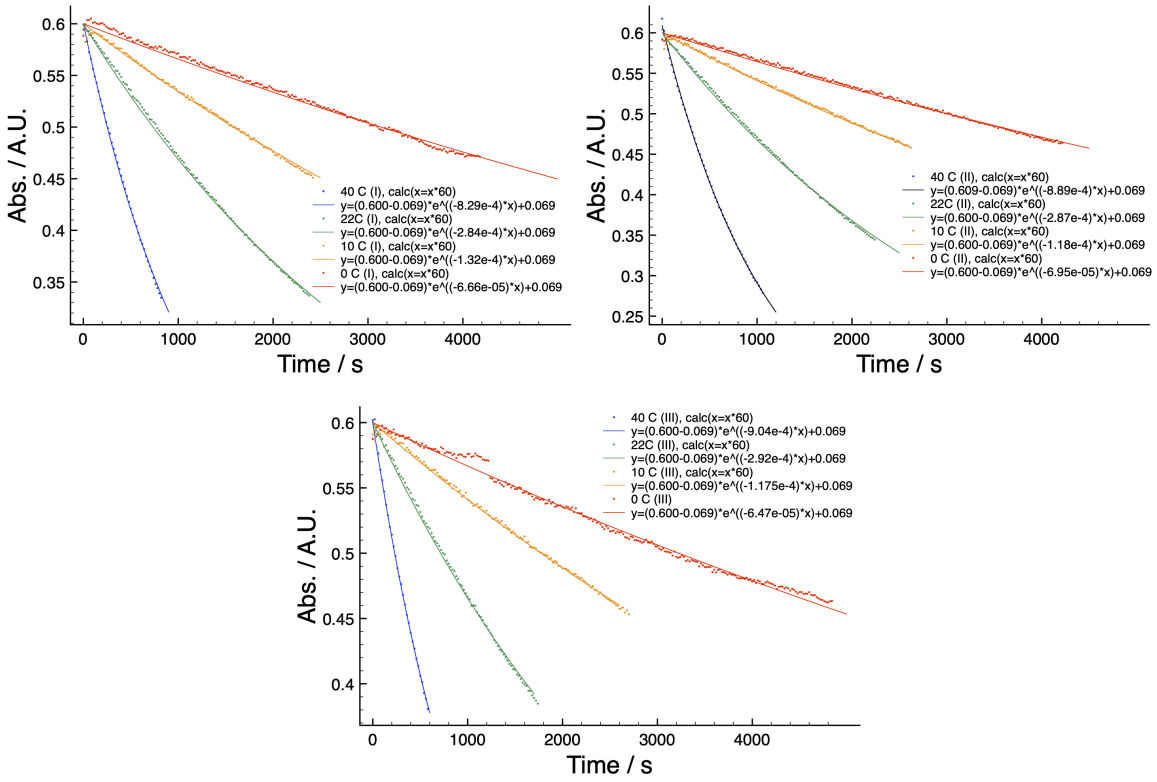

Figure S13: Pseudo 1st order kinetics trace of Ci + [**1**], at different temperatures. Signal at 545 normalized and the 1st order equation used to fit the data, run at 50 equiv. Ci. Concentration of [**1**] = 0.000190 M, [Ci] = 0.00949 M.

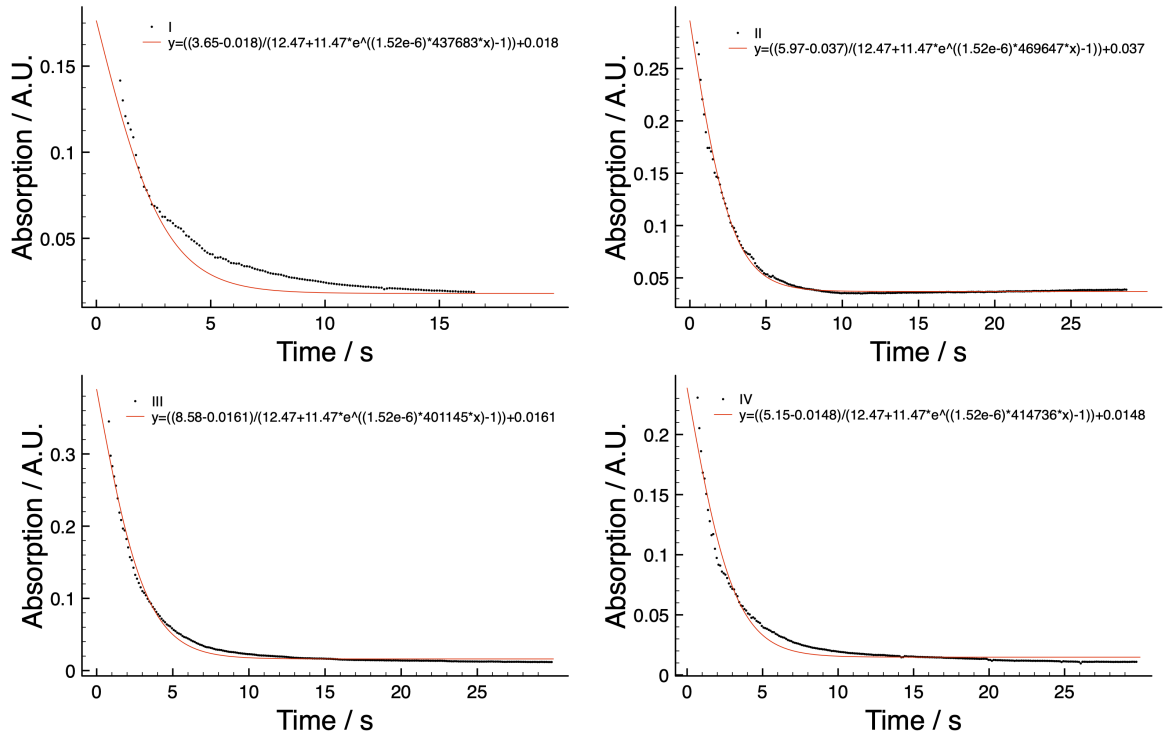

Figure S14: 2nd order kinetics trace of TCO + [**1**], at room temperature. 2nd order equation used to fit the data, Concentration [**1**] = 3.45 x 10^{-5} M, [TCO] = 3.79 x 10^{-5}.

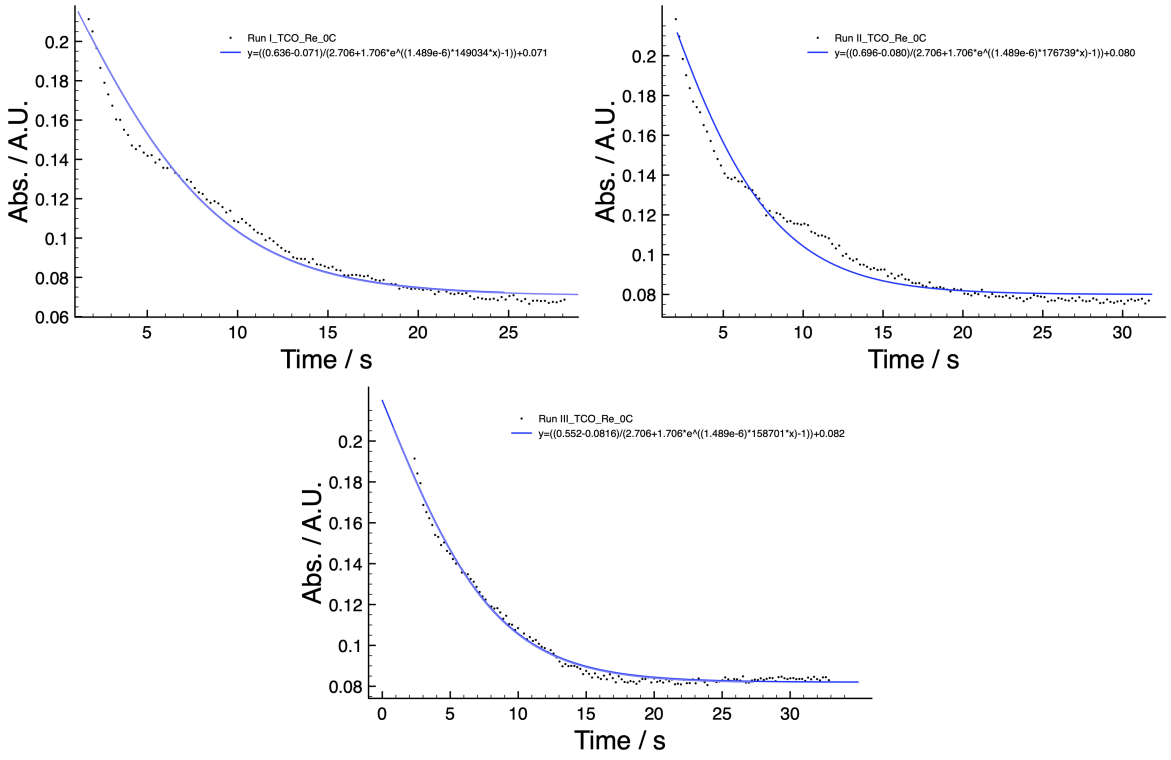

Figure S15: 2nd order kinetics trace of TCO + [**1**], at 0 C. 2nd order equation used to fit the data, Concentration [**1**] = 2.54 x 10^{-6} M, [TCO] = 4.03 x 10^{-6}.

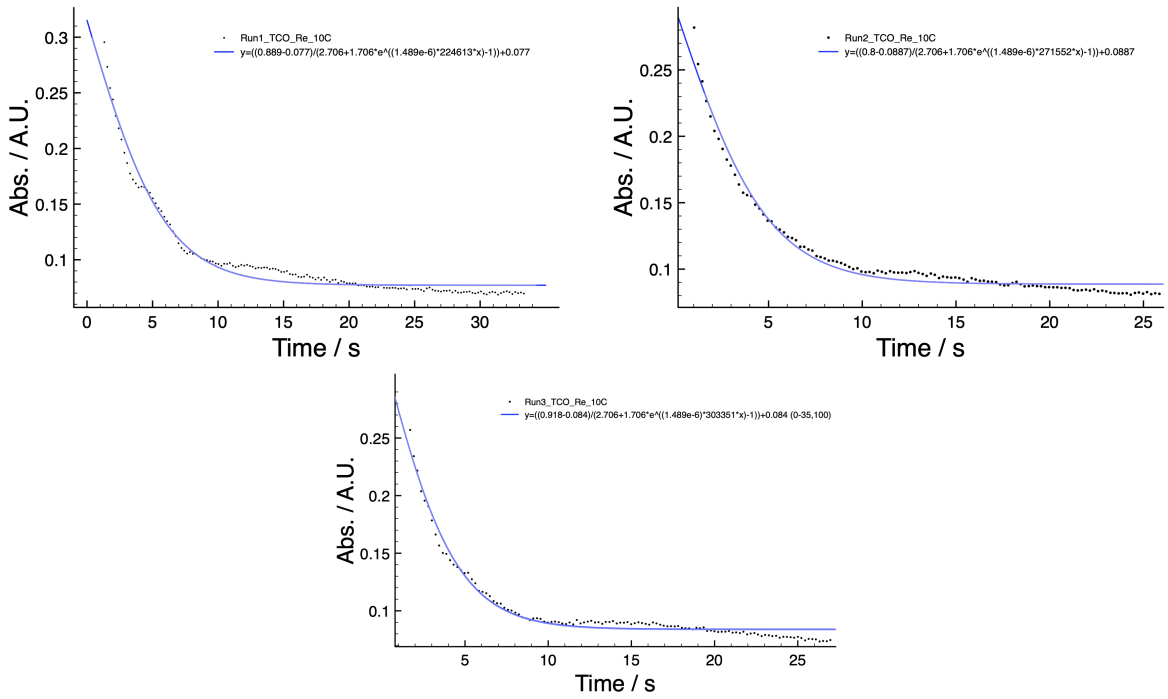

Figure S16: 2nd order kinetics trace of TCO + [**1**], at 10 C. 2nd order equation used to fit the data, Concentration [**1**] = 2.54 x 10^{-6} M, [TCO] = 4.03 x 10^{-6}.

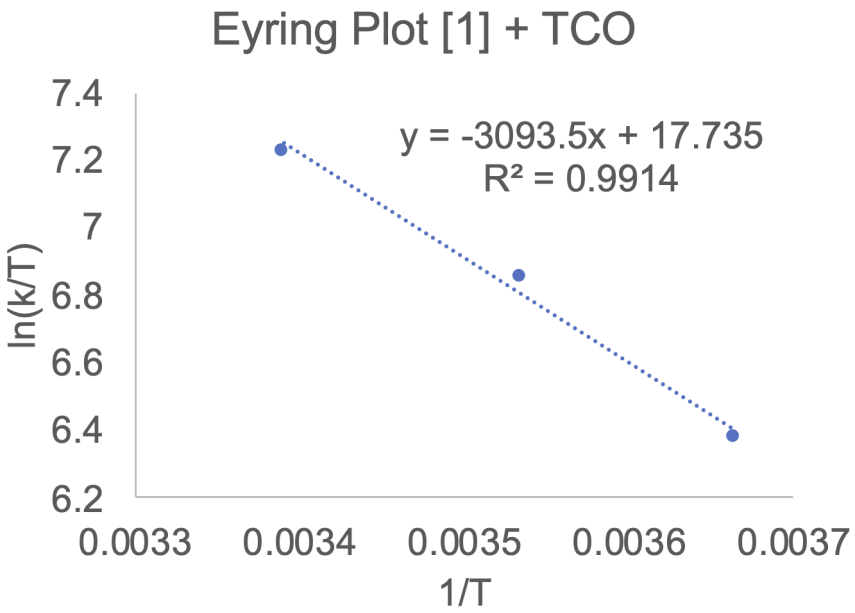

Figure S17: Eyring Plot of TCO + [**1**]

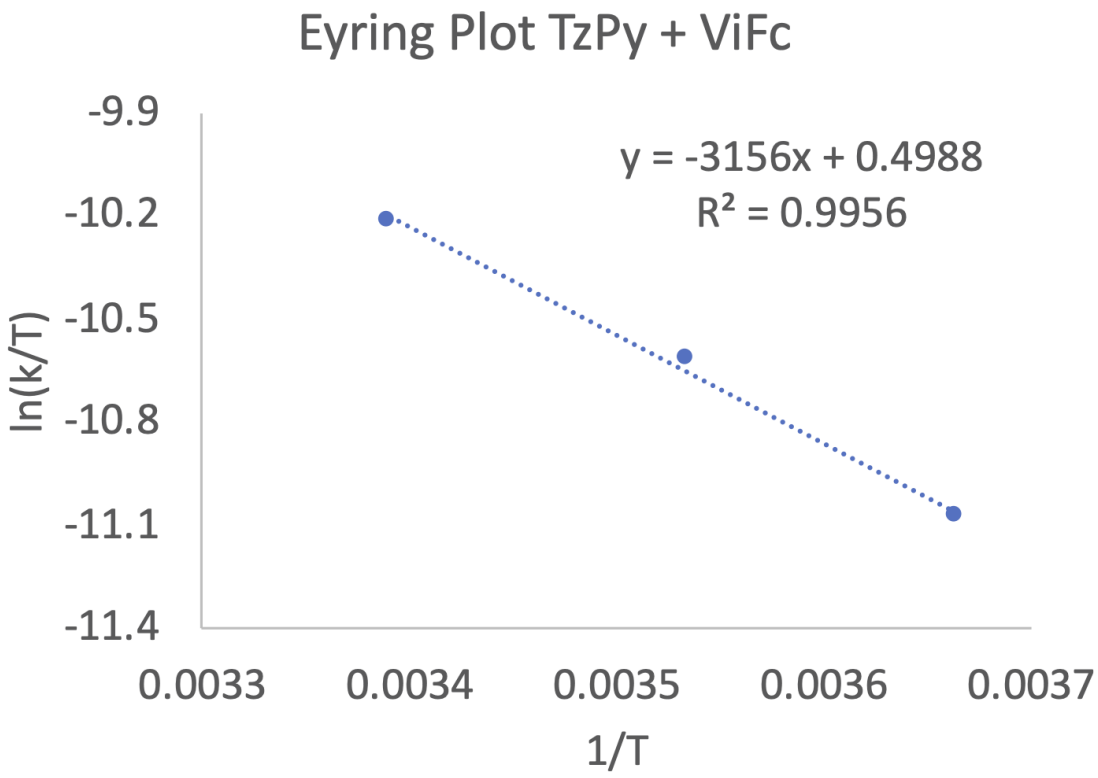

Figure S18: Eyring Plot of ViFc + TzPy

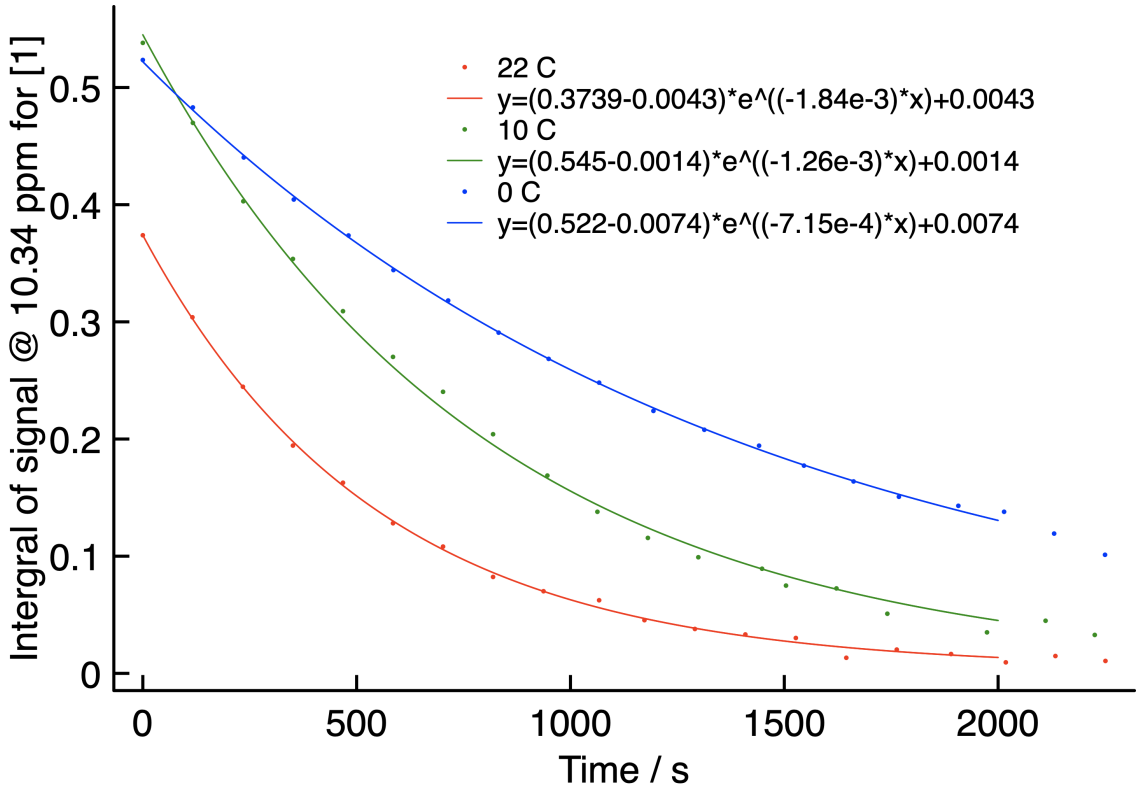

Figure S19: Pseudo 1st order kinetics trace of TzPy + ViFc (xs), at different temperatures. Signal at 9 ppm normalized and the 1st order equation used to fit the data, run at 4 equiv. ViFc. Concentration of TzPy = 0.042439M M, ViFc = 0.169747M

5 NMR Spectroscopy

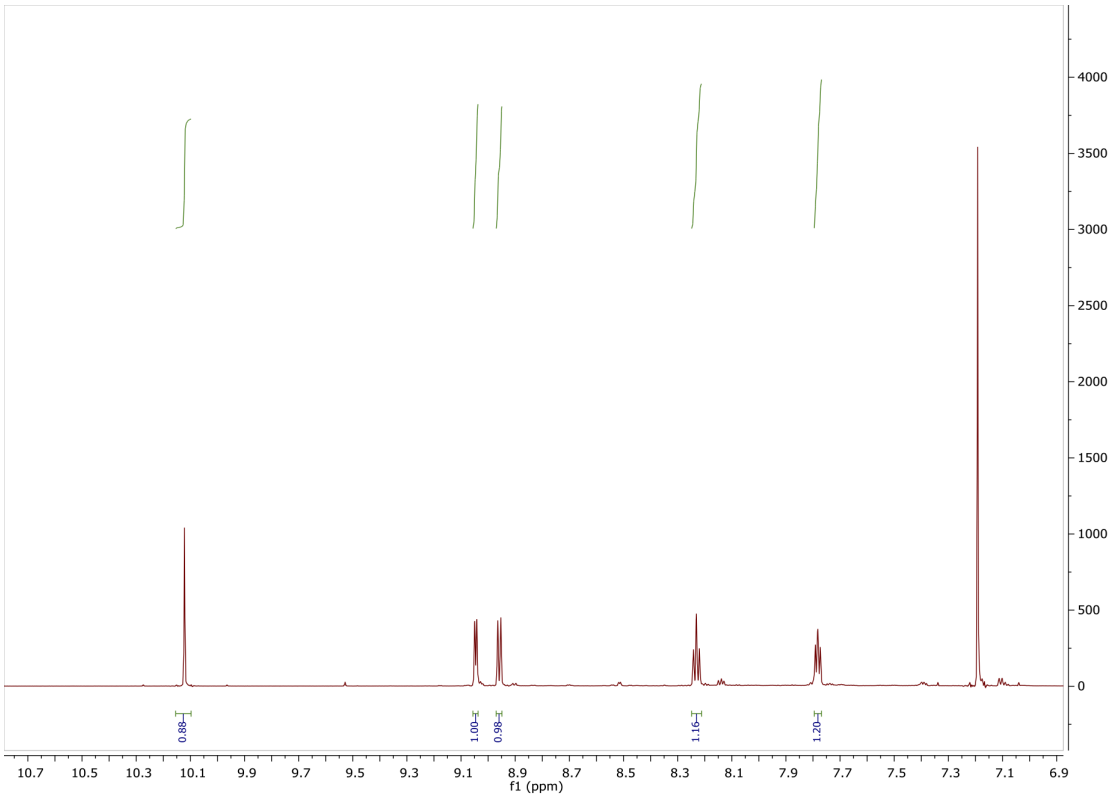

Figure S20: 1H NMR of [**1**](700 MHz, Chloroform-d) δ 10.19 (s, 1H), 9.11 (d, J = 5.3 Hz, 1H), 9.03 (d, J = 7.9 Hz, 1H), 8.30 (t, J = 7.8 Hz, 1H), 7.85 (t, J = 6.5 Hz, 1H).

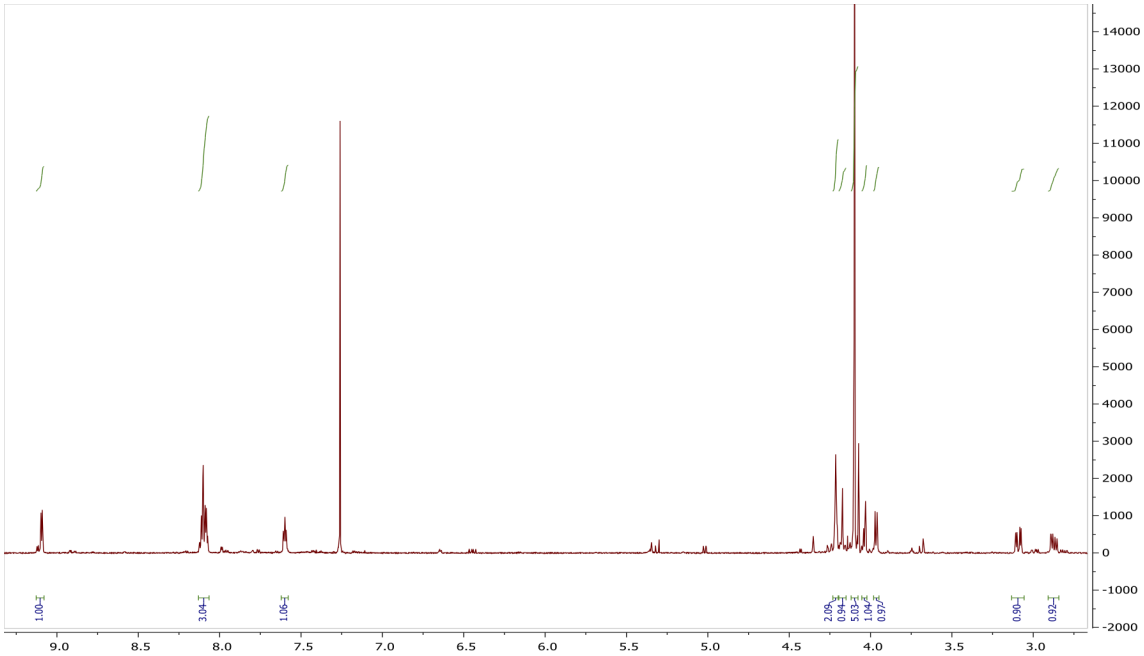

Figure S21: 1H NMR of [**1**Fc] (700 MHz, Chloroform-d) δ 9.09 (d, J = 5.3 Hz, 1H), 8.13 – 8.07 (m, 3H), 7.60 (ddd, J = 7.2, 5.5, 2.1 Hz, 1H), 4.22 – 4.20 (m, 2H), 4.17 (s, 1H), 4.10 (s, 5H), 4.04 – 4.02 (m, 1H), 3.97 (d, J = 8.9 Hz, 1H), 3.09 (dd, J = 18.3, 5.4 Hz, 1H), 2.87 (ddd, J = 18.1, 8.7, 1.3 Hz, 1H)). Major Product

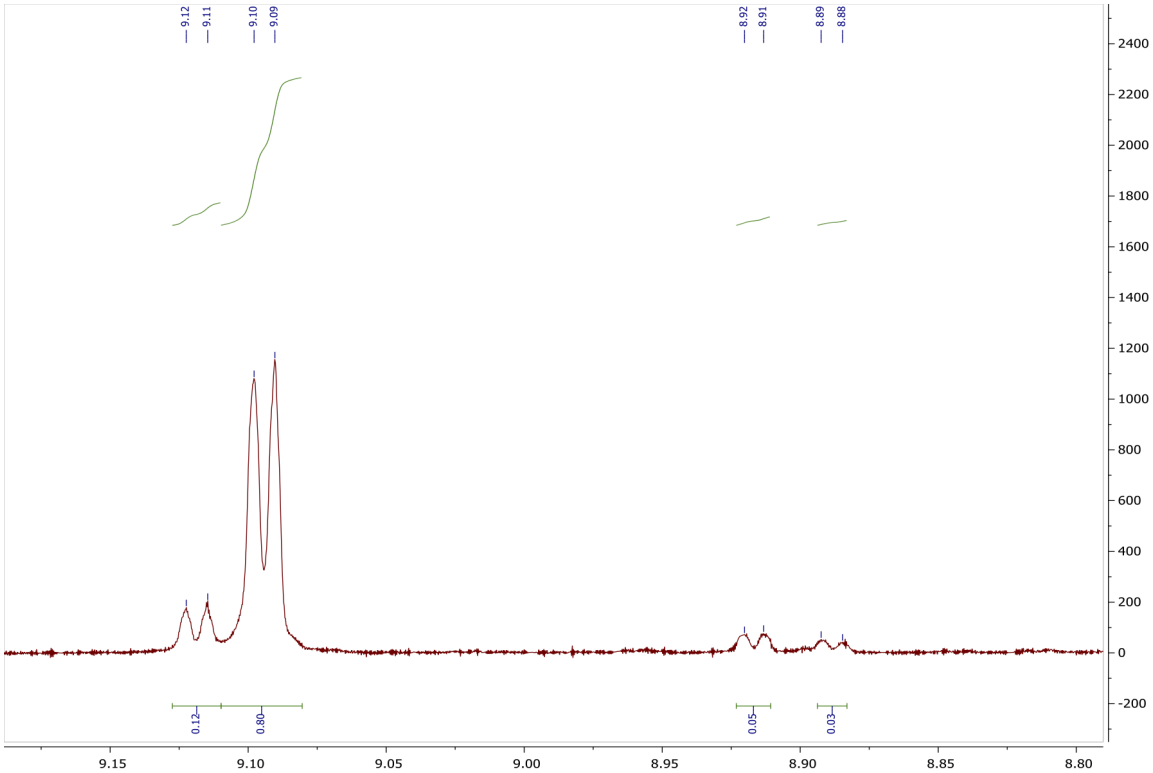

Figure S22: 1H NMR of [**1**Fc] (700 MHz, Chloroform-d) zoom of low field signals showing signals from minor products, ratio 0.12:0.8:0.08

Figure S23: COSY NMR of [**1**Fc] (700 MHz, Chloroform-d) cross signals of major product

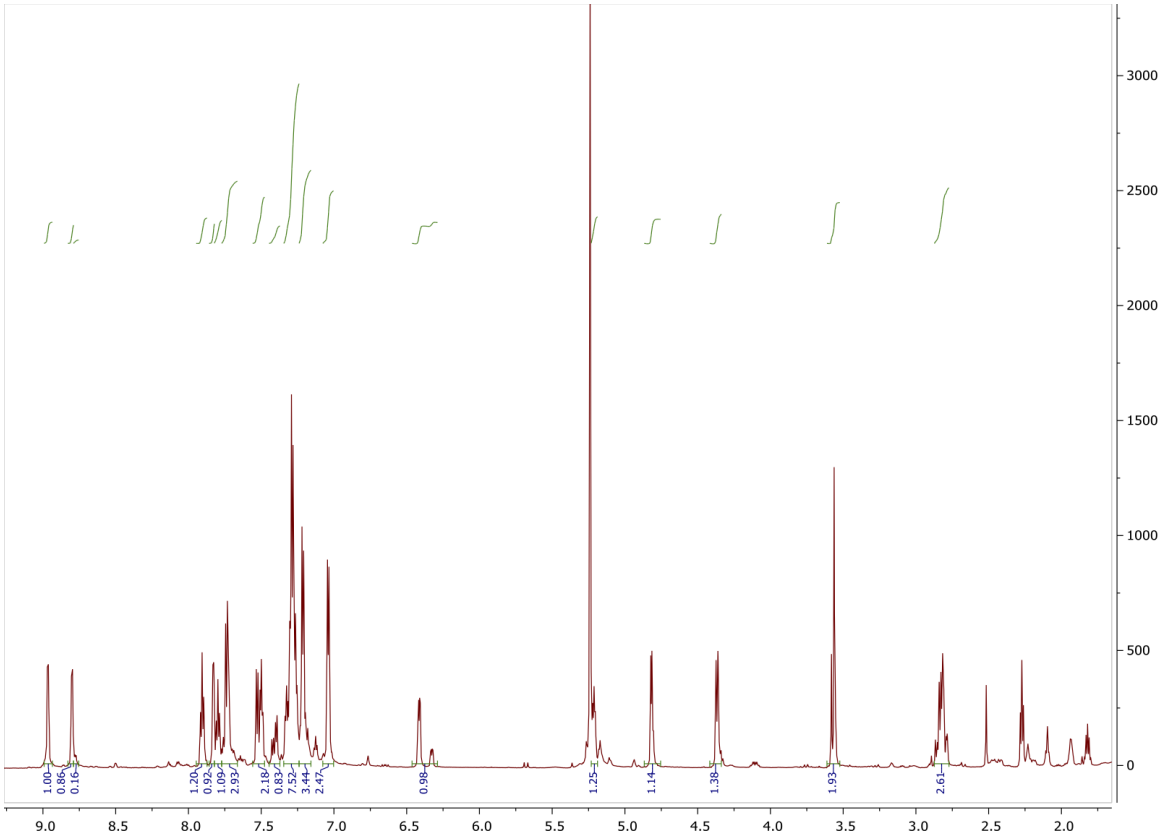

Figure S24: 1H NMR of [**1**Ci] (700 MHz, Methylene Chloride-d2) δ 8.97 (d, J = 5.4 Hz, 1H), 8.80 (d, J = 5.4 Hz, 1H), 7.91 (t, J = 7.8 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.80 (t, J = 7.9 Hz, 1H), 7.74 (q, J = 8.4, 5.7 Hz, 3H), 7.56 – 7.48 (m, 2H), 7.41 (dd, J = 17.3, 8.0 Hz, 1H), 7.29 (tt, J = 19.5, 7.1 Hz, 8H), 7.24 – 7.16 (m, 3H), 7.04 (d J = 7.2 Hz, 2H), 6.37 (ddd, J = 60.5, 7.7, 3.4 Hz, 1H), 5.23 – 5.19 (m, 1H), 4.81 (dd, J = 8.3, 5.2 Hz, 1H), 4.37 (d, J = 9.0 Hz, 1H), 3.61 – 3.52 (m, 2H), 2.87 – 2.77 (m, 3H).

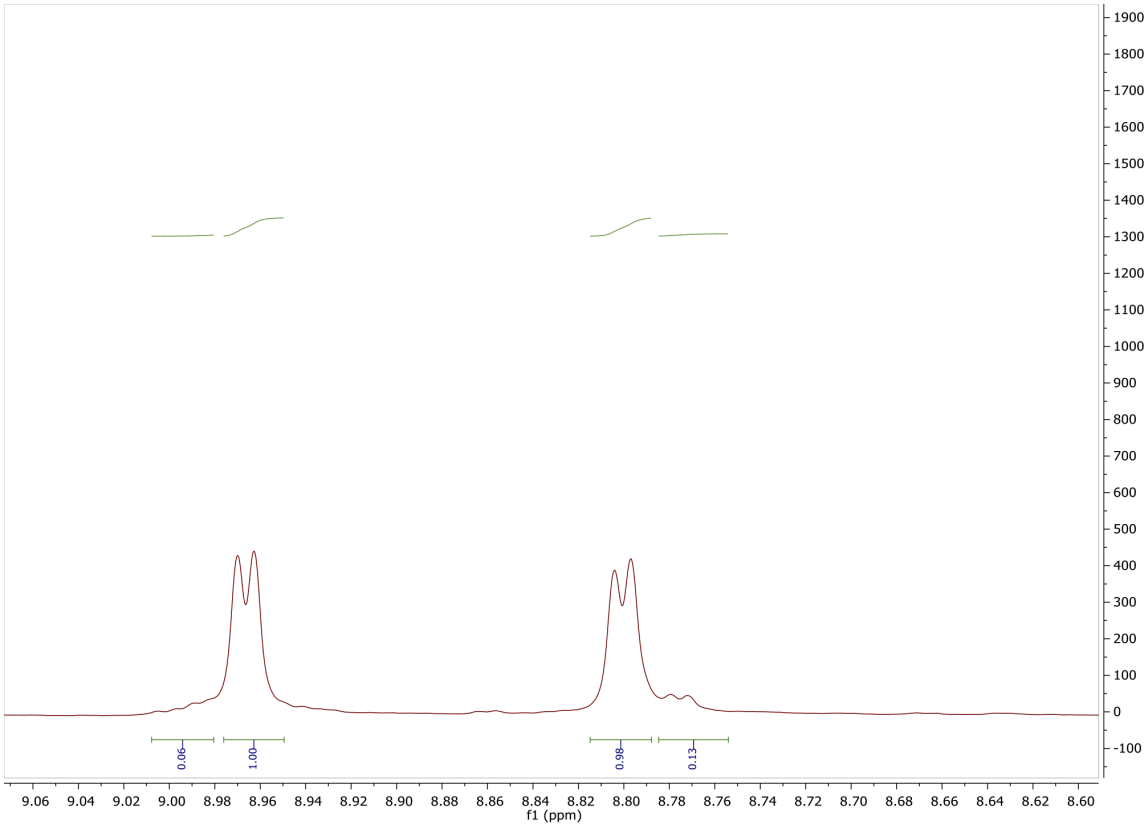

Figure S25: 1H NMR of [**1**Ci] (700 MHz, Chloroform-d) zoom of low field signals showing signals from minor products product ratio 0.03:0.46:0.46:0.05

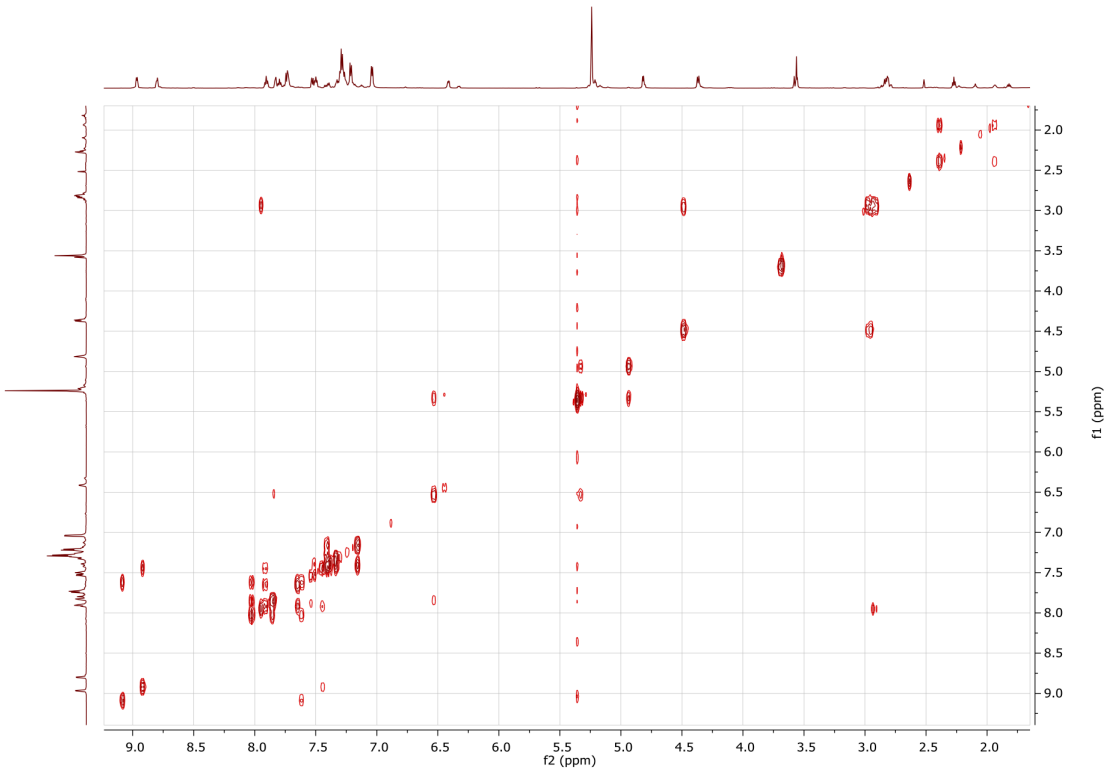

Figure S26: COSY NMR of [**1**Ci] (700 MHz, Chloroform-d)

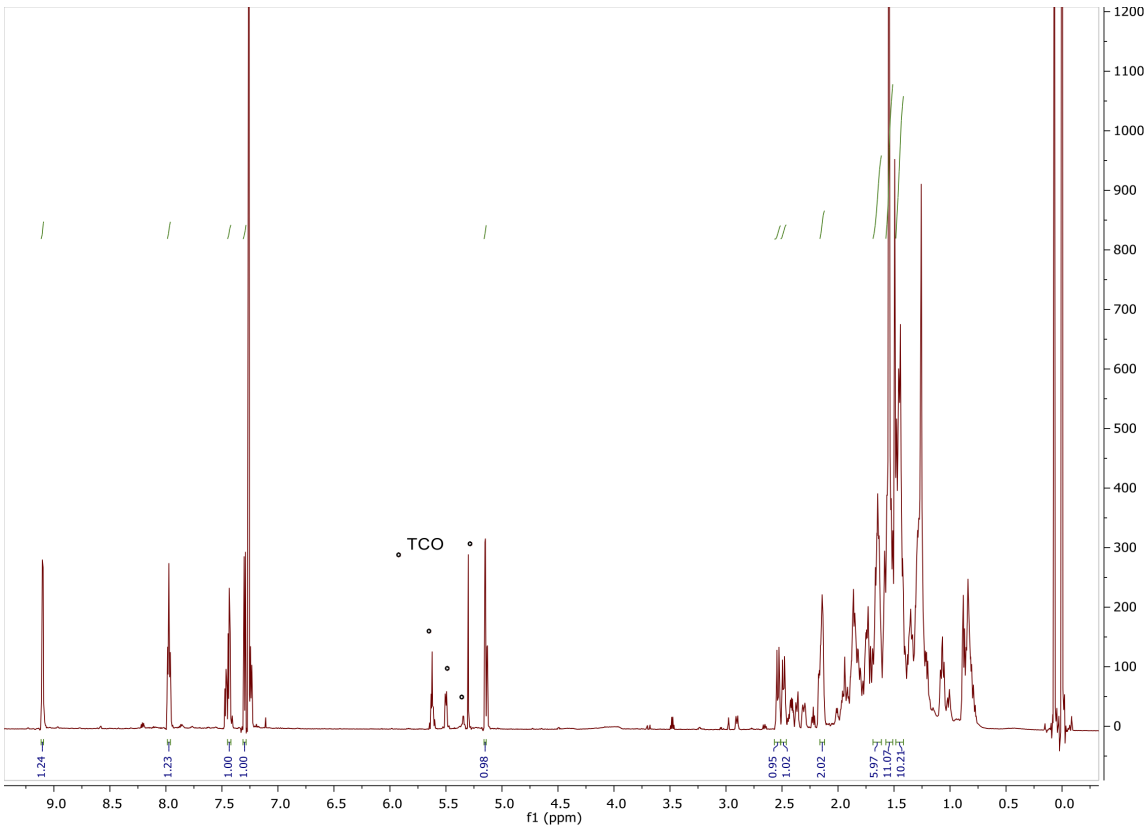

Figure S27: 1H NMR of [**1**TCO] (700 MHz, Chloroform-d) δ 9.10 (d, J = 4.9 Hz, 1H), 7.97 (t, J = 7.8 Hz, 1H), 7.43 (t, J = 6.0 Hz, 1H), 7.30 (d, J = 8.1 Hz, 1H), 5.15 (d, J = 2.5 Hz, 1H), 2.54 (dt, J = 11.7, 5.4 Hz, 1H), 2.49 (dt, J = 12.0, 4.7 Hz, 1H), 2.16 – 2.12 (m, 2H), 1.90 – 1.79 (m, 1H), 1.64 (m, 1H), 1.61 – 1.50 (m, 4H), 1.50 – 1.40 (m, 4H). TCO signals based on reported spectrum, *J. Am. Chem. Soc.*, **2008**, *130*, 3760-3761

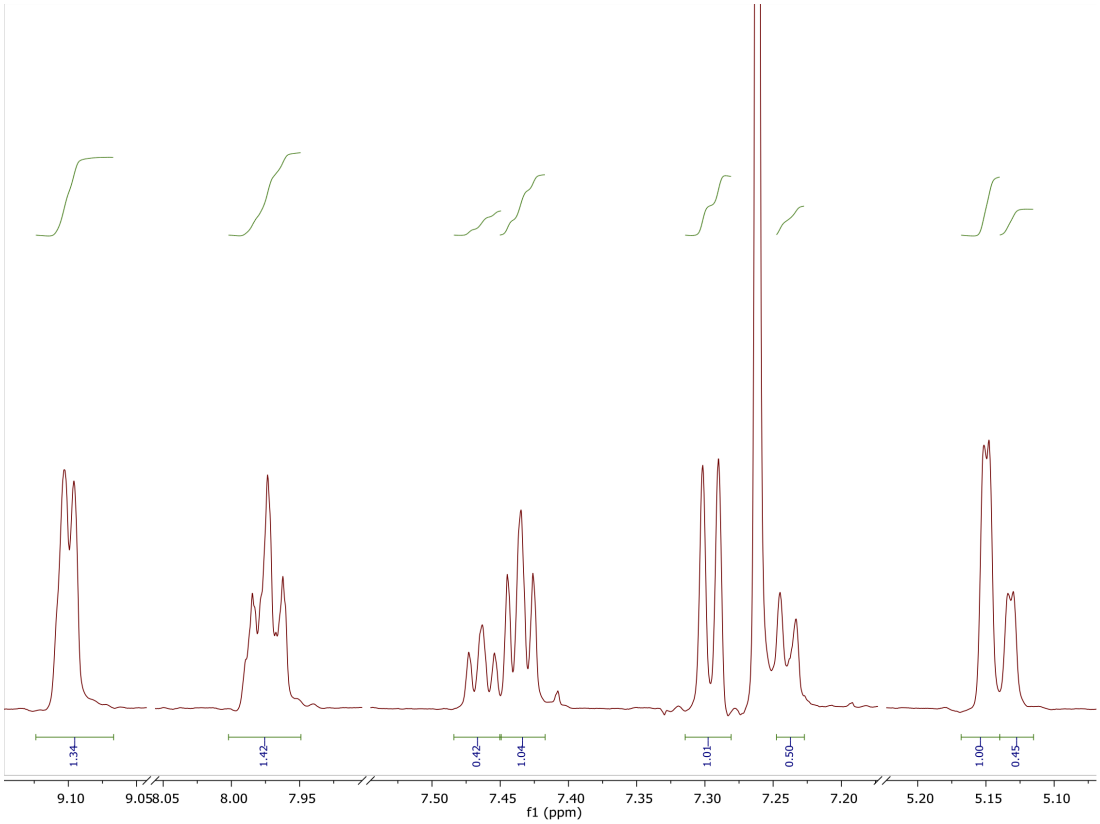

Figure S28: 1H NMR of [**1**TCO] (700 MHz, Chloroform-d) zoom of low field signals showing signals from minor products 0.71:0.29

Figure S29: COSY NMR of [**1**TCO] (700 MHz, Chloroform-d)

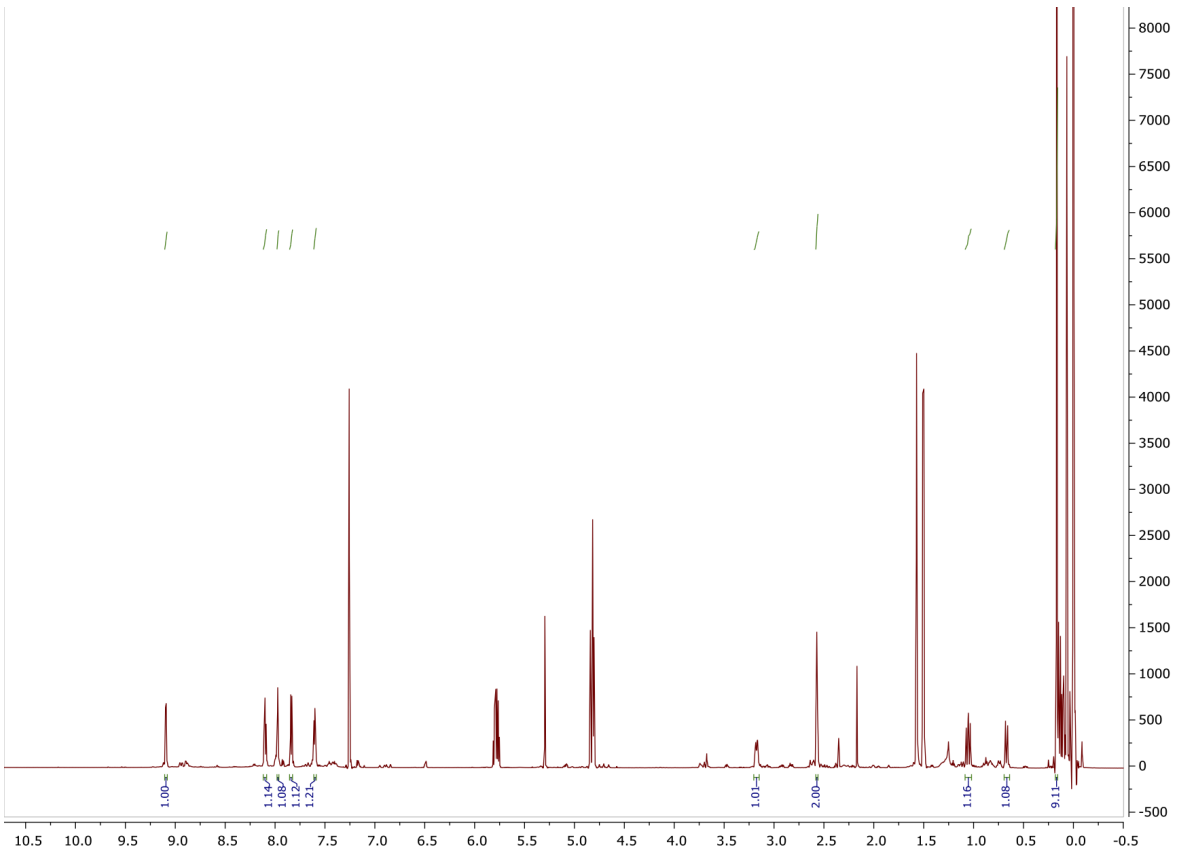

Figure S30: 1H NMR of [**1**Allyl-TMS] (700 MHz, Chloroform-d) δ 9.09 (d, J = 5.2 Hz, 1H), 8.10 (t, J = 7.8 Hz, 1H), 7.97 (t, J = 3.1 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.61 – 7.59 (m, 1H), 3.20 – 3.15 (m, 1H), 2.59 – 2.56 (t, J = 2.6 Hz, 2H), 1.05 (dd, J = 15.0, 13.1 Hz, 1H), 0.67 (dd, J = 15.2, 2.6 Hz, 1H), 0.17 (s, 9H).

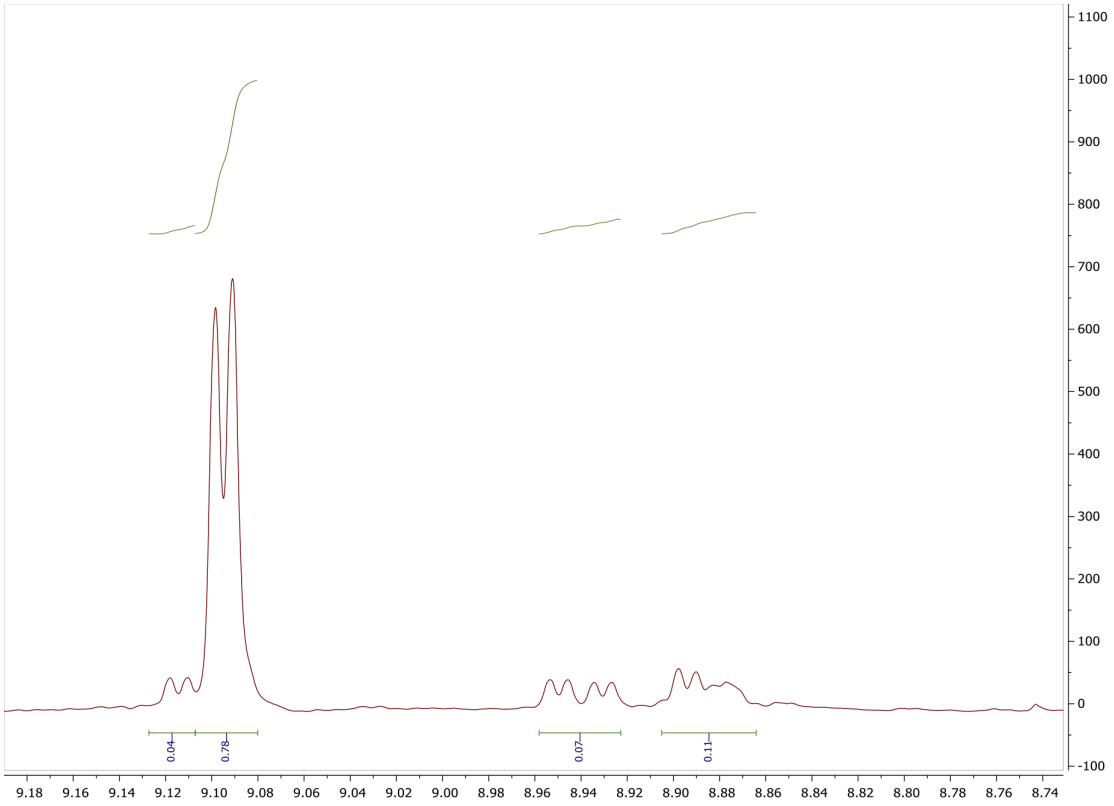

Figure S31: 1H NMR of [**1**Allyltrimethylsilane] (700 MHz, Chloroform-d) zoom of low field signals showing signals from minor products 0.72:0.04:0.07:0.11

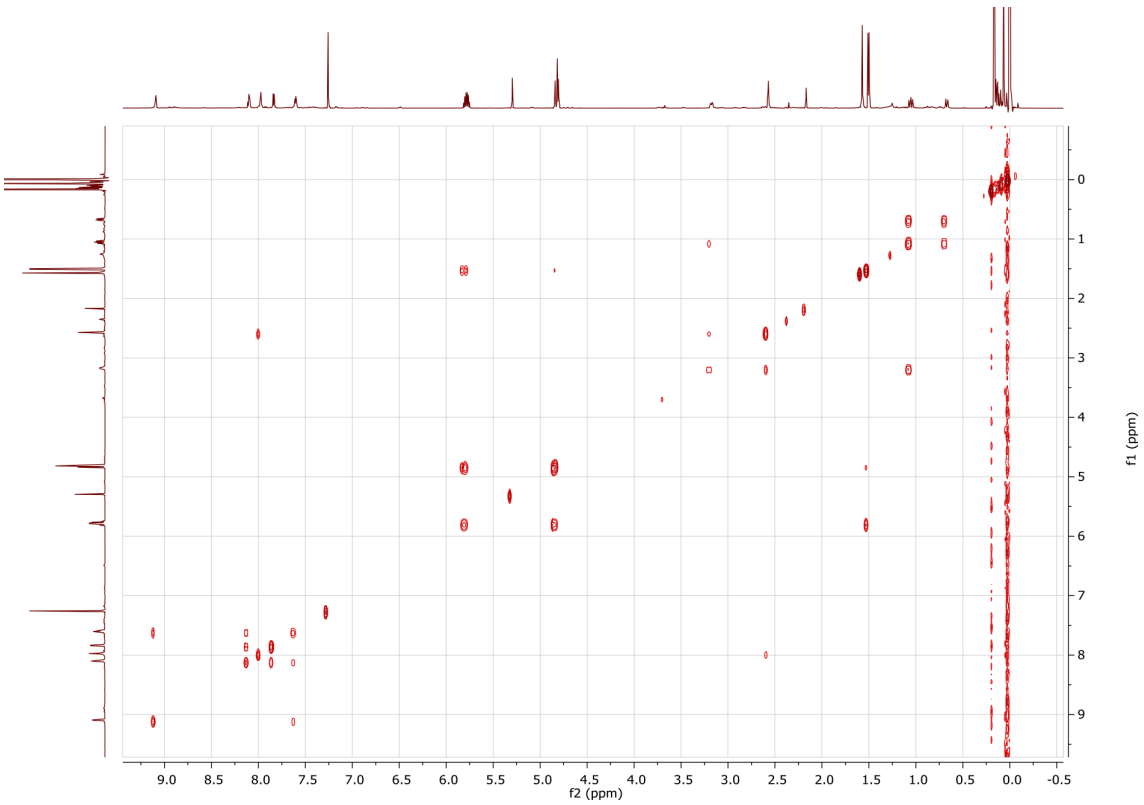

Figure S32: COSY NMR of [**1**Allyltrimethylsilane] (700 MHz, Chloroform-d)

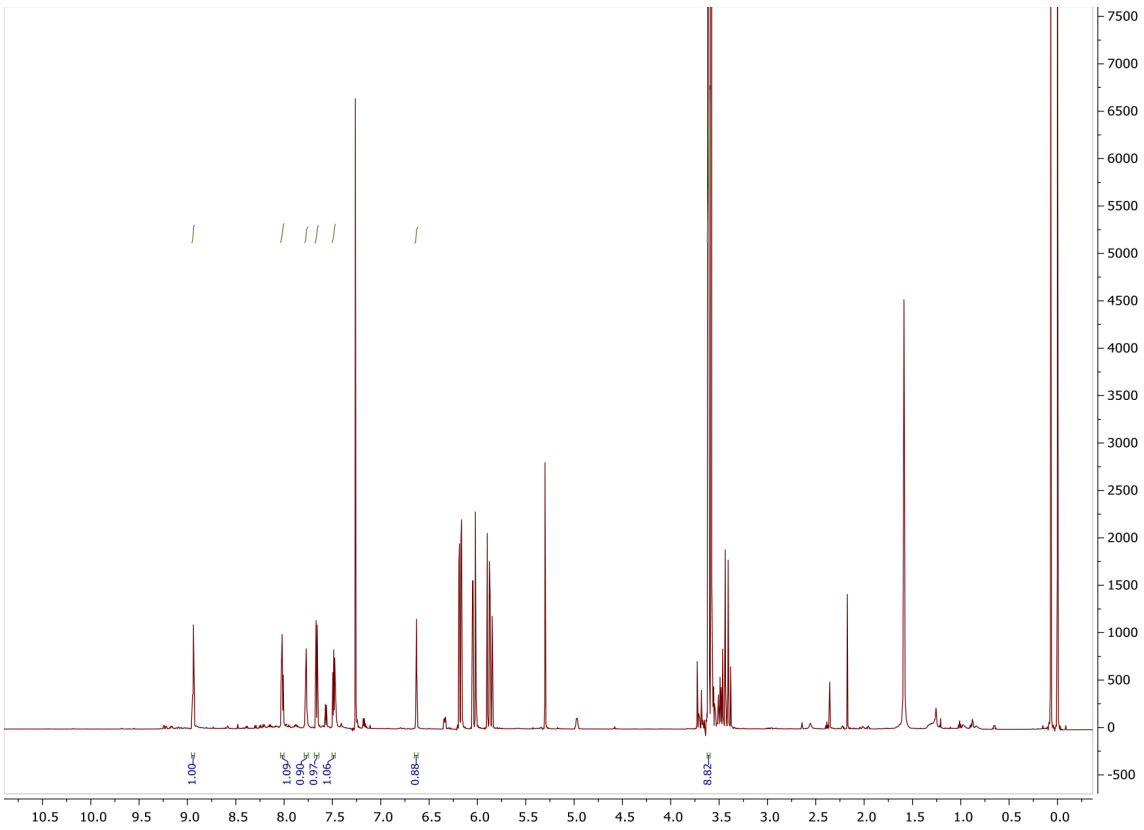

Figure S33: 1H NMR of [**1**Vinyltrimethoxysilane] (700 MHz, Chloroform-d) δ 8.94 (d, J = 5.3 Hz, 1H), 8.02 (t, J = 7.9 Hz, 1H), 7.77 (d, J = 2.7 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 6.8, 5.6 Hz, 1H), 6.63 (d, J = 3.1 Hz, 1H), 3.61 (s, 9H).

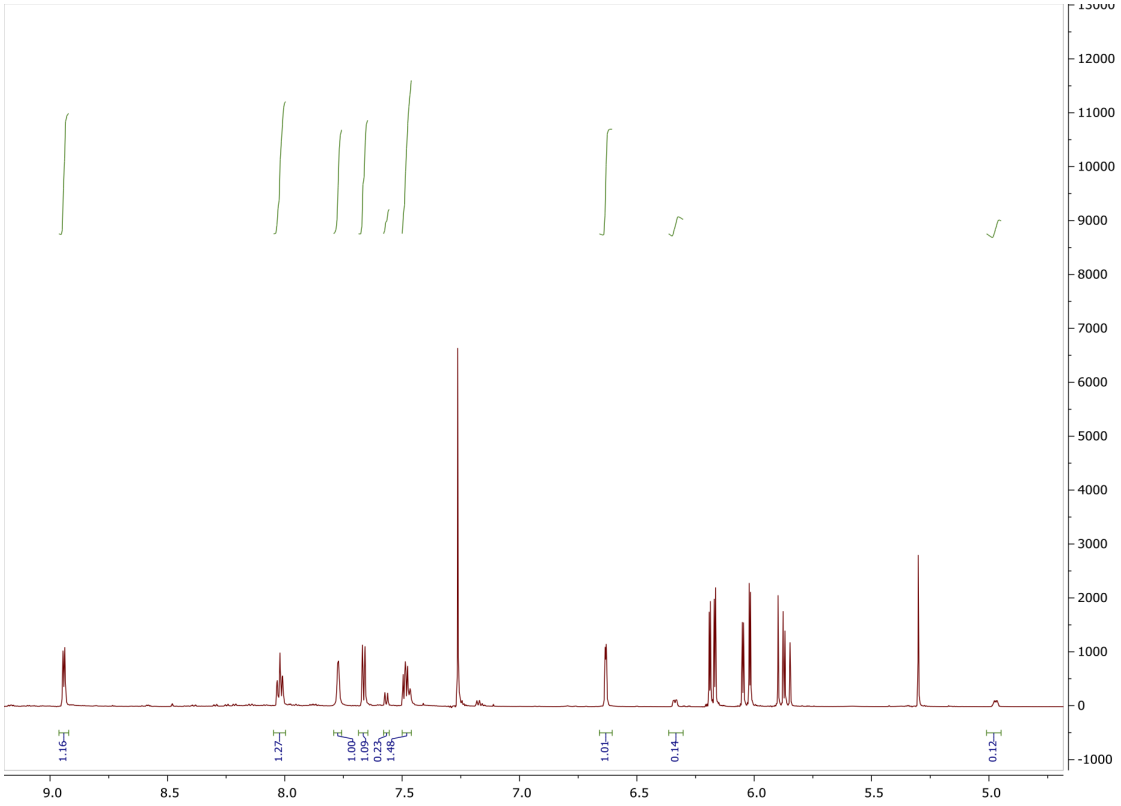

Figure S34: 1H NMR of [**1**Vinyltrimethoxysilane] (700 MHz, Chloroform-d) zoom of low field signals showing signals from minor products 0.82:0.18

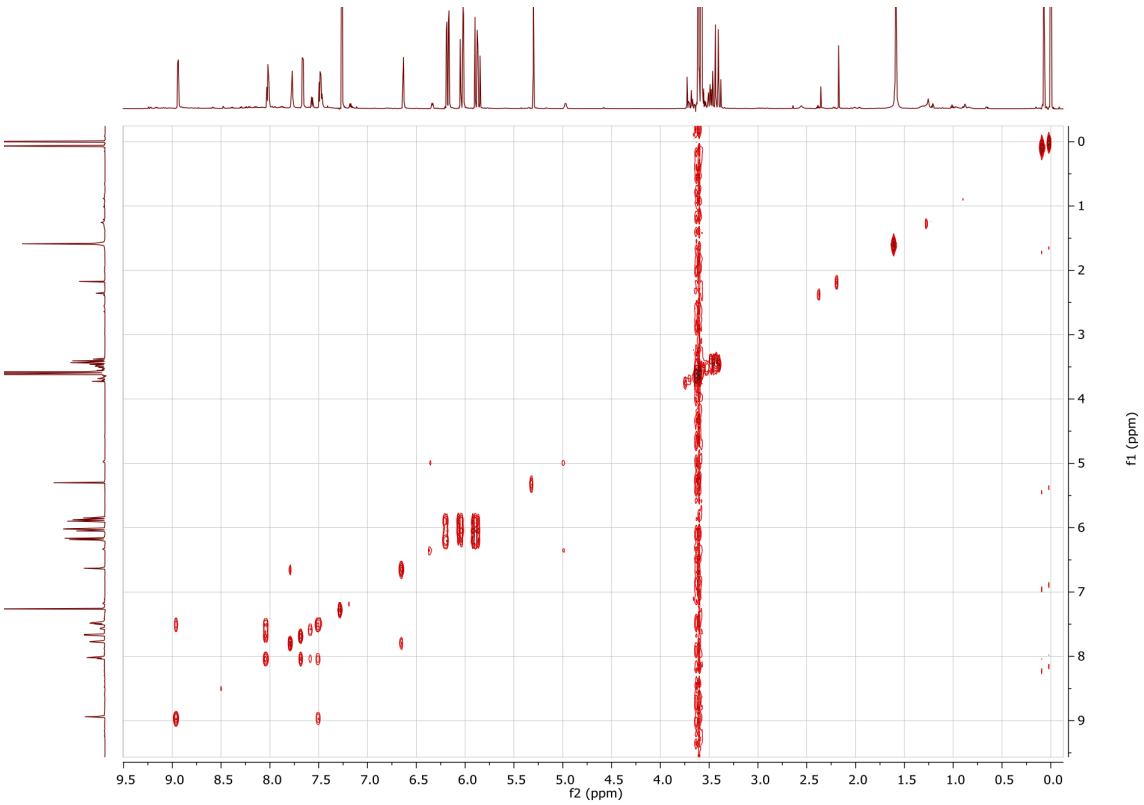

Figure S35: COSY NMR of [**1**Vinyltrimethoxysilane] (700 MHz, Chloroform-d)

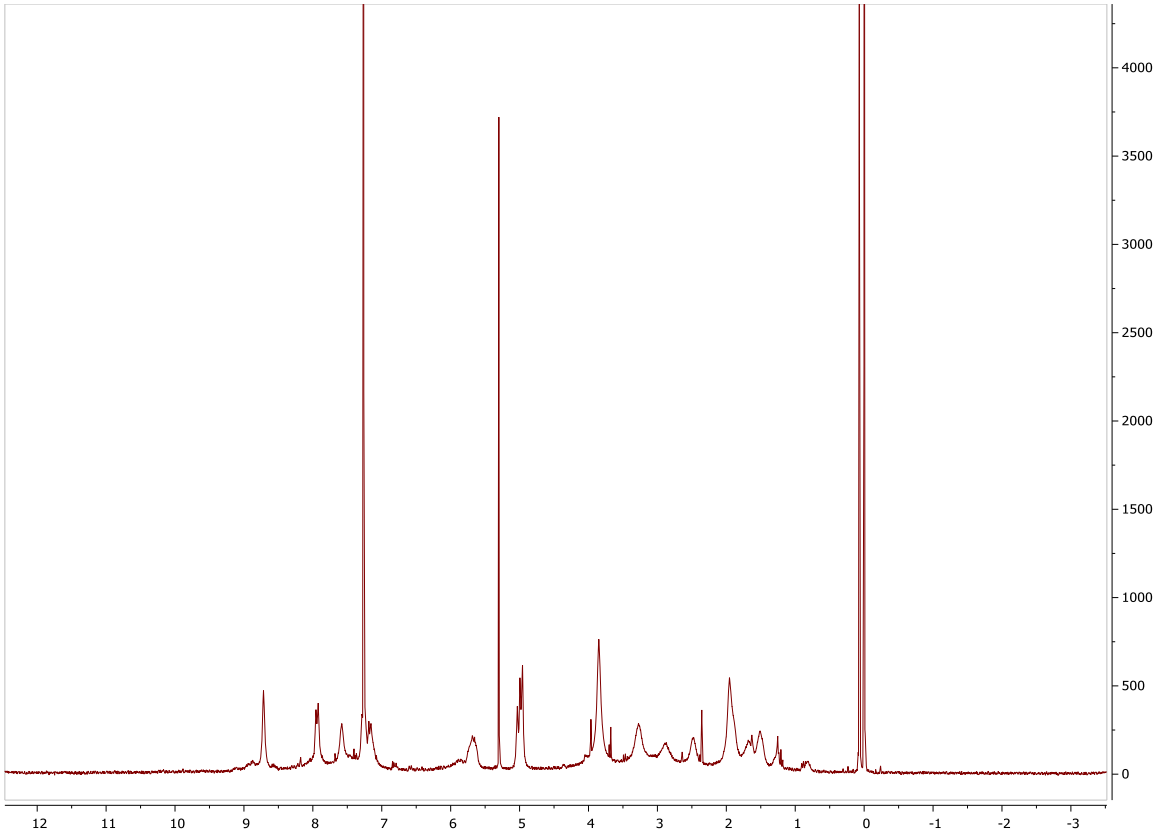

Figure S36: 1H NMR of [**1**Quinine] from reaction of [**1**] and quinine at 40 C

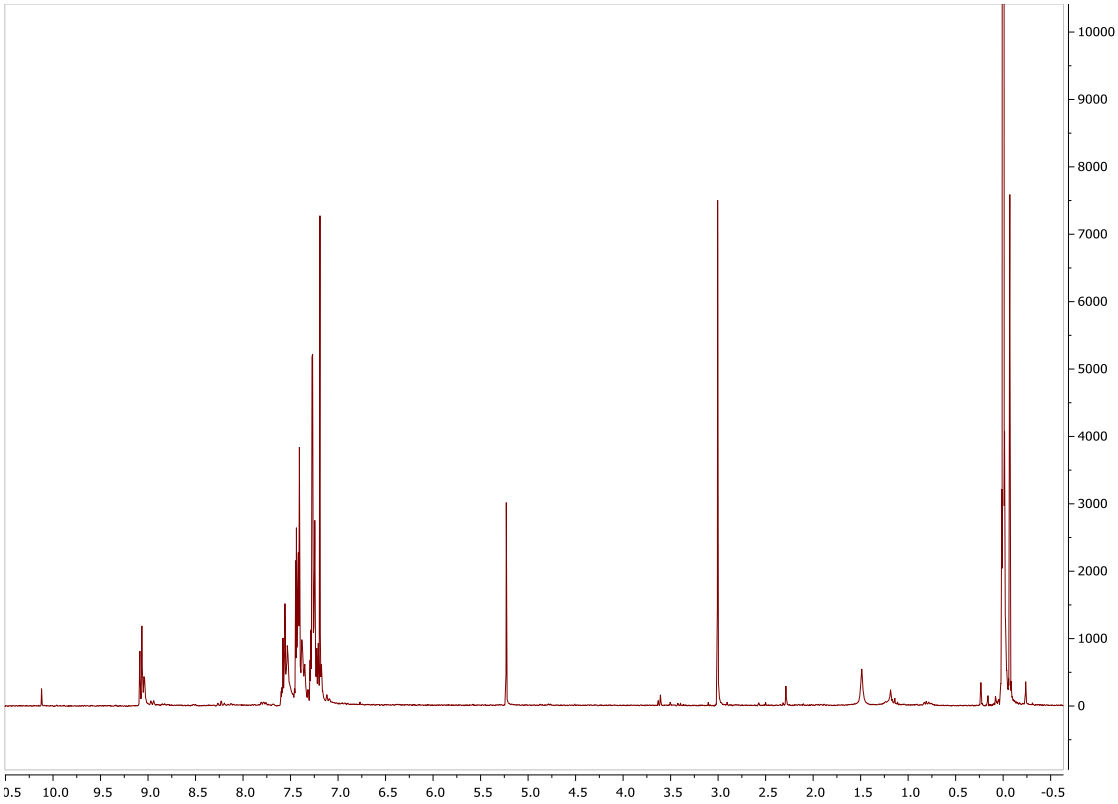

Figure S37: 1H NMR of [**1**PhCCH] from the reaction between [**1**] and phenylacetylene at 50 C for 60 h, approx. 85 % conversion

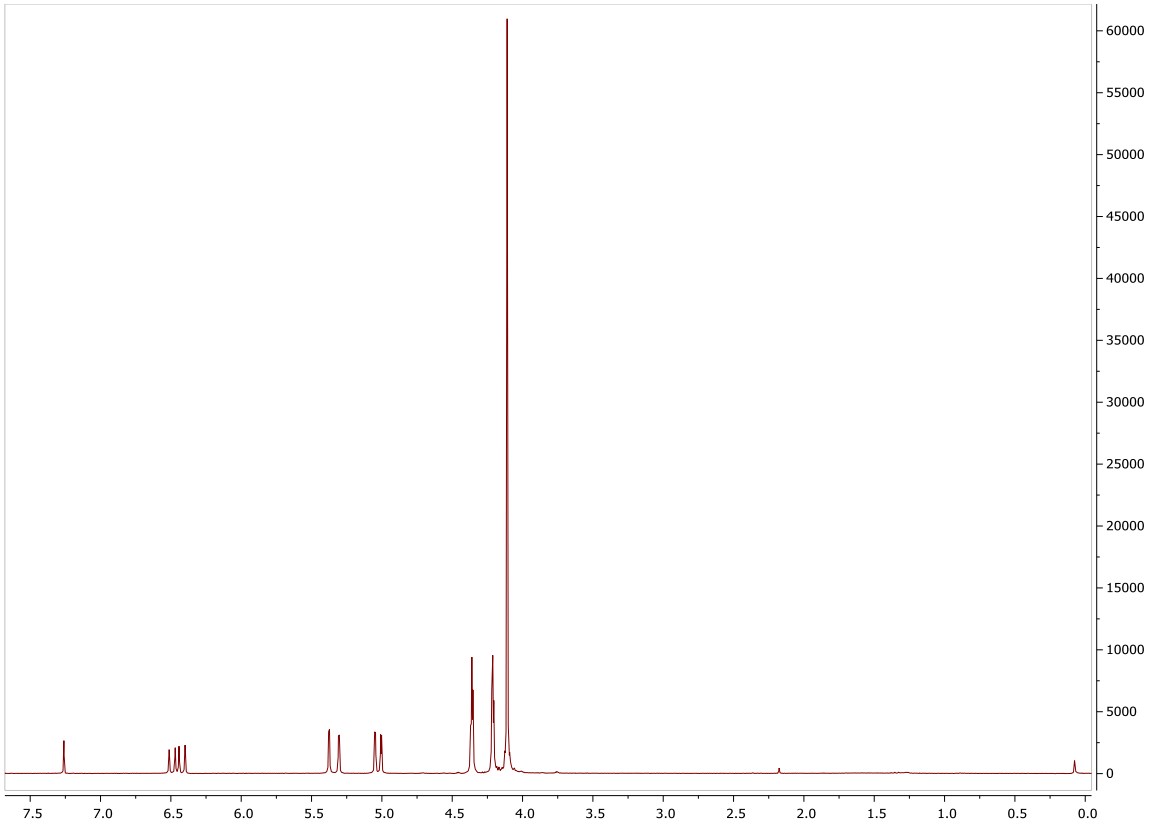

Figure S38: 1H NMR of ViFc (400 MHz, Chloroform-d)

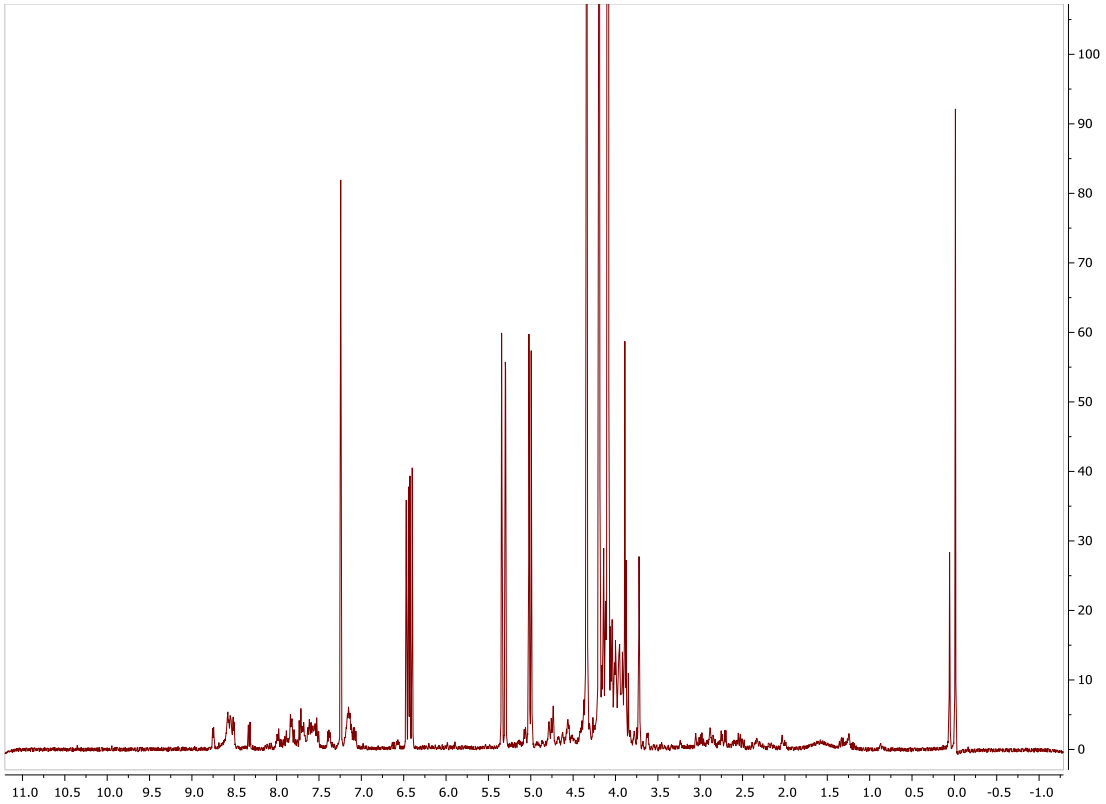

Figure S39: 1H NMR of *in situ* reaction between TzPy and ViFc (400 MHz, Chloroform-d) after 1 h

6 Crystallography

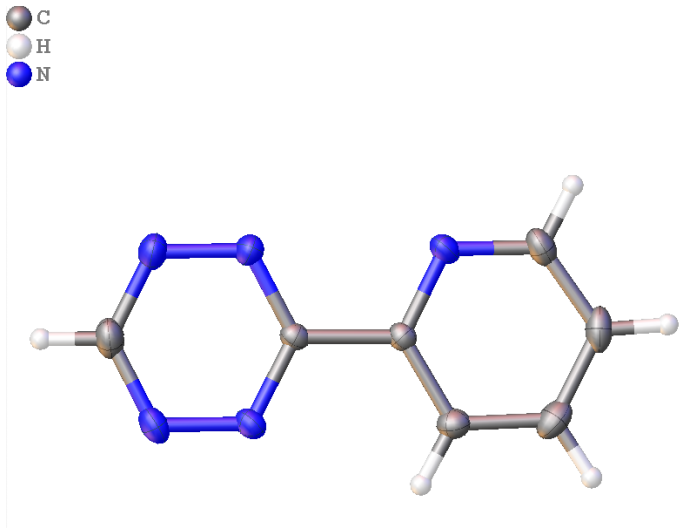

Figure S40: Molecular structure of TzPy determined crystallographically. Ellipsoids are shown at 50% probability.

Table S1: Crystallographic Information for Complexes Reported Herein

Identification code	ac488 [**1**]	ac479a [**1**Fc]
Empirical formula	$C_{10}H_5N_5O_3ClRe$	$C_{22}H_{17}ClFeN_3O_3Re$
Formula weight	464.842	648.90
Temperature/K	135.0	135.02
Crystal system	monoclinic	monoclinic
Space group	C2/c	$P2_1/c$
a/Å	16.0600(8)	12.9074(3)
b/Å	13.0072(8)	12.0184(3)
c/Å	13.9753(7)	14.9765(4)
$\alpha/^\circ$	90	90
$\beta/^\circ$	99.720(6)	113.9810(10)
$\gamma/^\circ$	90	90
Volume/Å^3	2877.5(3)	2122.71(9)
Z	8	4
$\rho_{calc}/(g/cm^3)$	2.146	2.0303
μ/mm^{-1}	18.383	6.537
F(000)	1698.7	1247.1
Crystal size/mm^3	0.146 × 0.065 × 0.029	0.286 × 0.105 × 0.035
Radiation	Cu Kα (λ = 1.54178)	Mo Kα (λ = 0.71073)
2Θ range/$^\circ$ for data collection	10.32 to 132.66	3.46 to 66.34
Index ranges	-18 ≤ h ≤ 18	-19 ≤ h ≤19
	-10 ≤ k ≤ 15	-18 ≤ k ≤ 18
	-16 ≤ l ≤ 16	-22 ≤ l ≤ 23
Reflections collected	17080	58206
Independent reflections	2412	8110
	[R_{int} = 0.0685, R_{sigma} = 0.0440]	[R_{int} = 0.0419, R_{sigma} = 0.0268]
Data/restraints/parameters	2412/0/195	8110/0/280
Goodness-of-fit on F^2	1.046	0.994
Final R indexes [I>= 2σ (I)]	R_1 = 0.0750, wR_2 = 0.1901	R_1 = 0.0197, wR_2 = 0.0374
Final R indexes [all data]	R_1 = 0.0888, wR_2 = 0.2250	R_1 = 0.0329, wR_2 = 0.0415
Largest diff. peak/hole/eÅ^{-3}	6.27/-2.57	0.83/-0.85

Table S2: Crystallographic Information 2 for Complexes Reported Herein

Identification code	ac484 [**1**Ci]	TzPy	stams02 [**1**TCO]
Empirical formula	$C_{18}H_{13}ClN_3O_3Re$	$C_7H_5N_5$	$C_{36}H_{38}Cl_2N_6O_6Re_2$
Formula weight	540.981	159.16	1094.02
Temperature/K	135.0	135(2)	100
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	C2/c
a/Å	9.0781(7)	7.2794(4)	17.9274(18)
b/Å	10.9568(10)	9.3608(4)	12.2202(9)
c/Å	22.080(2)	10.4528(5)	17.9025(19)
$\alpha/^\circ$	90	90	90
$\beta/^\circ$	92.870(2)	96.970(3)	103.284(8)
$\gamma/^\circ$	90	90	90
Volume/Å^3	2193.5(3)	707.00(6)	3817.1(6)
Z	4	4	4
$\rho_{calc}/(g/cm^3)$	1.638	1.495	1.904
μ/mm^{-1}	5.681	0.103	6.529
F(000)	1030.6	328	2112.0
Crystal size/mm^3	0.149 × 0.127 × 0.085	0.647 × 0.248 × 0.165	
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range/$^\circ$ for data collection	3.7 to 56.62	2.819 to 28.338	4.07 to 63.838
Index ranges	-9 ≤ h ≤ 12	-9 ≤ h ≤ 9	-25 ≤ h ≤ 26
	-14 ≤ k ≤ 14	-12 ≤ k ≤ 12	-17 ≤ k ≤ 17
	-29 ≤ l ≤ 29	-13 ≤ l ≤ 13	-26 ≤ l ≤ 25
Reflections collected	22804	13031	24957
Independent reflections	5438	1759	6069
	[R_{int} = 0.0703, R_{sigma} = 0.0744]	[R_{int} = 0.0262]	[R_{int} = 0.2298, R_{sigma} = 0.3791]
Data/restraints/parameters	5438/36/211	1759/0/110	6069/36/235
Goodness-of-fit on F^2	0.957	1.079	0.948
Final R indexes [I>= 2σ (I)]	R_1 = 0.0395, wR_2 = 0.0731	R_1 = 0.0432, wR_2 = 0.1227	R_1 = 0.0675, wR_2 = 0.1271
Final R indexes [all data]	R_1 = 0.0630, wR_2 = 0.0785	R_1 = 0.0611, wR_2 = 0.1396	R_1 = 0.1927, wR_2 = 0.1503
Largest diff. peak/hole/eÅ^{-3}	2.20/-1.69	0.434/-0.222	3.83/-1.60

7 XYZ Coordinates from DFT calculations

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Coordinates from ORCA-job TPSS-Re-tzpy
Re 0.45312857971257 9.50548855528947 4.36894768089622
Cl -1.15399358688330 11.36181241617654 4.01369499166142
C 1.25116725081583 10.37301756215786 5.91061448436461
O 1.70647549292669 10.87838284941238 6.85071267770601
O 2.50269950964509 10.88873419914539 2.47376549845189
O 2.41950544599235 7.14207213609889 4.73091200995003
C 1.74770263087134 10.37876401247920 3.18940574407375
C -2.08808746135165 7.94431526553578 4.68968568344493
N -3.18148591052866 7.38814144049383 5.21797324204466
N -3.32448658878812 7.40714448445461 6.53665883778184
C -2.33612901600564 7.98489791213714 7.24411227372241
H -2.43902286567569 7.98680714602697 8.32353464388922
N -1.24529608612629 8.57390327583050 6.75346901679622
N -1.11570959925189 8.55874780351854 5.42689040286478
C -1.87663653766782 7.91054443104493 3.24577620726812
N -0.72998565175394 8.51124195655138 2.82564392804747
C -0.45268178161498 8.50728618999339 1.50868461599515
H 0.46550803661249 8.99693306462370 1.20935009883169
C -1.29609981399070 7.91269504124572 0.57610327629191
H -1.02542699551762 7.93879589138762 -0.47325325020143
C -2.47085515810148 7.29970301761300 1.00773184136395
H -3.14535305969810 6.83168482557462 0.29907542857590
C -2.76596504517789 7.29729344180766 2.36733082052897
H -3.66383375940376 6.83459916604284 2.75895602574743
C 1.67431197096113 8.02612391535802 4.59489381990288

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Coordinates from ORCA-job TPSS-Re-Fc

Cl	0.18506648428448	3.42122874274687	2.37172639840736
Re	2.22737466596789	4.42327635795717	3.39591800713869
Fe	1.43300403995904	9.87644711039803	4.63049781825045
N	0.79448516353345	5.12838345065919	4.87995962126592
N	1.41469265774342	6.25101417726888	2.62161369572687
N	1.94857111717107	6.80087844611940	1.43594308355795
O	3.94767051284486	3.70956414963615	0.91691507427927
O	2.97819193506709	1.74565635492876	4.77574691335317
O	4.74222196322722	5.69397727454627	4.66022476546823
C	3.31018810710239	3.96117440926495	1.85590830545138
C	2.70745398417633	2.74471261989844	4.24303159279017
C	3.77832978927707	5.23111741539400	4.18802758232102
C	0.54326672556538	4.53566444677405	6.06169949786220
H	1.17683453378633	3.69598771767171	6.31974861369018
C	-0.47023423155839	4.96510562112339	6.91054702268779
H	-0.62631282006818	4.45388432759609	7.85350949743076
C	-1.26897846735625	6.03961491524205	6.52281881956456
H	-2.07306208816891	6.39253769730084	7.15958102266574
C	-1.01761738117111	6.65814985150897	5.30328667969521
H	-1.62199122451858	7.49492174480699	4.97719163396085
C	0.02473671150415	6.19461118508862	4.49939632893614
C	0.39827261158778	6.80661314624178	3.23233602230492
C	-0.35086481249832	7.96834672751861	2.63370660328478
H	-1.39815112769356	7.87148864185846	2.92789606997869
C	-0.26864270817345	7.81221649102815	1.10323752354818
H	-0.91812428568241	6.98571407611627	0.78262895310182
H	-0.60852828300989	8.71795436793290	0.59672647805410
C	1.14022039396773	7.49807857838809	0.71744248412602
H	1.56026588006825	7.88689500725299	-0.20819261336962
C	0.14296703025518	9.31604441289558	3.12328781203716
C	1.25323649084852	10.07765047121335	2.61482793430375
H	1.97279618130582	9.74672014596102	1.87890185405257
C	1.24425708610187	11.35842648335701	3.25362108859701
H	1.96704866369714	12.14769809464944	3.09621251327280
C	0.14935823127169	11.38899783310134	4.17466656872301
H	-0.10595386257669	12.20707509231319	4.83469273603917
C	-0.52538180835356	10.13046357391614	4.09854800000443
H	-1.39968345945149	9.84236658300189	4.66735281096197
C	2.33814853808139	8.25376000592948	5.50648490656935
H	2.24717840462632	7.21506519836525	5.22938868638274
C	3.31496248113259	9.16201289433031	4.99323368411958
H	4.05744973178189	8.93479981665295	4.24041770096251
C	3.11697118001489	10.42779717777203	5.63264220407231
H	3.67636026912532	11.33308480769109	5.43827443617293
C	2.01242754610704	10.29995082864123	6.53657348980869
H	1.59634500783786	11.09089728314819	7.14618134455327
C	1.52631974453519	8.95516957330203	6.45461747622283
H	0.68945369672416	8.54684367149037	7.00426625761112

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Coordinates from ORCA-job TPSS-Re-Fc-tH

Cl	0.34564263366766	3.31878125651867	2.27450205004789
Re	2.29202190699586	4.43663184074747	3.35856484882548
Fe	1.46320864549179	9.89320524615512	4.71230361751859
N	0.79817594182267	5.09335344130777	4.80159652293330
N	1.37516203367355	6.21983703441998	2.51632200590007
N	1.67696546918145	6.65791357388724	1.26624081265933
O	4.17558823509742	3.72739138273111	1.00026211734426
O	3.15640747960945	1.83148417746677	4.79509989307592
O	4.66821109826900	5.88733036744934	4.69471005117509
C	3.47118669916481	3.98356592374757	1.89203264126208
C	2.84248489754490	2.80777910456443	4.24516637609977
C	3.75481643805592	5.35562424353996	4.19631999539078
C	0.53907535487829	4.48102051364937	5.97355942276233
H	1.15708252545369	3.62334843595449	6.20949315958542
C	-0.45741027394220	4.91269092637931	6.83774607499144
H	-0.62460671188146	4.38160670866670	7.76761808845682
C	-1.21882608757829	6.02666537762274	6.48327348891335
H	-2.00197345474636	6.39442833708704	7.13792343196106
C	-0.95515218644659	6.67041982767244	5.28138384901697
H	-1.51870749231147	7.54885802391672	4.99536855708038
C	0.05618194977246	6.18744918186501	4.44400792362772
C	0.39746111141868	6.80253246087288	3.17481489141849
C	-0.33197523358937	8.02094790769919	2.65281674080250
H	-1.37064734958043	7.96387081663897	2.99159181164077
C	-0.29624184392265	7.96710937906645	1.14382852151789
H	-1.06788853331596	8.47238911275172	0.57589186832940
C	0.72502233809545	7.35782928833106	0.52919326398714
H	0.89184164717015	7.34085193891802	-0.54086917559172
C	0.22974164778461	9.34367719184999	3.15393014073858
C	1.41590704650597	10.00217931163979	2.67851762658755
H	2.14159104802903	9.58269015854307	1.99495506390960
C	1.46198632765159	11.30980005086397	3.25781009852184
H	2.24701875873677	12.04017746102386	3.11335509644251
C	0.31810367594586	11.46044249774078	4.10734610536824
H	0.08584089785719	12.32585311971288	4.71370619678705
C	-0.43828067132280	10.24773273770182	4.04594102756193
H	-1.36026789593793	10.04176578167371	4.57462064111159
C	2.21373448042692	8.26798855363865	5.72188725299103
H	2.07659003052617	7.22409296371757	5.48849448387703
C	3.27258131437630	9.09425150876137	5.23245407078872
H	4.04827543166630	8.78908419754321	4.54373566512433
C	3.10849289789493	10.39966366471135	5.79764789612175
H	3.73116595020543	11.26178283262347	5.59898487245173
C	1.94232636669312	10.37898065359012	6.63042591393362
H	1.53463518689756	11.22153169178796	7.17300013825415
C	1.38515965799322	9.06019669470074	6.57953765389265
H	0.49188277838103	8.72600677213997	7.08936342082605
H	2.31905783164033	6.04513632640814	0.78040378397750

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Coordinates from ORCA-job TPSS-RePh

Re	6.89105283696937	7.22458141202392	-0.06295340986764
Cl	4.92662458137780	7.63855887782010	-1.48253117854742
C	8.11536969219838	7.23730848008968	-1.56882052228602
C	6.72313829617657	5.30240368625229	-0.24466585888967
C	8.37169726314148	6.98479966025638	1.15327765179797
C	5.18615140999834	8.73438745892209	1.94113262095716
C	4.21819789511823	9.05600422522366	3.06165784814094
H	3.63052884795612	9.93699782027597	2.76842815022404
C	3.28509210098784	7.88337578150841	3.25039970029021
H	2.36648532397389	8.03079731405715	3.80528956888416
C	3.60662786516611	6.67288871176695	2.78450200758995
H	3.00650275156859	5.78258273817300	2.92840254220972
C	4.95724497935758	9.40962088408533	4.35321523531426
C	4.47126630858280	10.42134418100895	5.18677858288191
H	3.57517185296865	10.96863929360141	4.89967666827383
C	5.12524124242656	10.73261408468202	6.37843230841232
H	4.73893209801998	11.52113255339399	7.01814711099737
C	6.27767118287915	10.03597021440936	6.74373623279754
H	6.79152881568678	10.28010056222149	7.66886648828861
C	6.77045748787628	9.02757371222774	5.91415745630605
H	7.67021596434963	8.48534135596645	6.18996863245070
C	6.11257443821873	8.71442605132512	4.72624383793231
H	6.50547040227282	7.93079034649111	4.08355323916782
N	6.80431059644939	9.36717578549403	0.29791199933847
C	7.50715497573113	10.29339623943798	-0.37872375842756
H	8.16816951517534	9.91381666885523	-1.14876066572872
C	7.40022468440671	11.65299480512700	-0.11913051857406
H	7.98831125178514	12.35567774559327	-0.69872284432867
C	6.53895282540330	12.08061069006645	0.89123851120060
H	6.44273526173373	13.13519463753096	1.12916272401437
C	5.80728409292026	11.13433966494738	1.59563429295125
H	5.14726329213998	11.43257044735286	2.40135148862670
C	5.93868219284137	9.77826181468508	1.27384958364519
N	5.45155989217174	7.51541093541877	1.53056745150656
N	4.77598835381458	6.46541314947870	2.06063514063966
H	4.87976162776429	5.62895797549016	1.50016235776653
O	8.84851250900037	7.28295607039207	-2.46720974824314
O	6.59036721627884	4.14911520012032	-0.31830948441094
O	9.25692007511214	6.85040176422712	1.90090355669765

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Coordinates from ORCA-job TPSS-RePh008

Re	0.53170039229605	9.24918329245092	4.88281412771571
Cl	-1.78317902640154	9.57885356308625	5.66235755564654
C	1.25916313142971	9.74481323976439	6.62509297580367
O	1.68147032463724	10.00849360354930	7.66943942251896
O	0.72637501954494	12.16908182771469	3.83269370728179
O	3.41228177091741	8.71348742907327	3.87553244709015
C	0.66582142837705	11.09034608453969	4.25631097739870
C	-0.77500344943389	6.58858646148313	4.59697799231497
C	-0.10158296500698	5.74636331165821	7.08468122194539
H	0.33399765272931	5.29041202398760	7.97170734310426
N	0.64341677907633	6.60531889836098	6.48836122501640
N	0.09666343359091	7.22181849547444	5.35025428439984
C	-1.07212317496472	7.22602751430280	3.33162795728325
N	-0.46766645229564	8.44000928927459	3.13891156849929
C	-0.64953227716470	9.06898478601185	1.96290021572976
H	-0.16161240682519	10.03140110294641	1.86311333704420
C	-1.42062384880654	8.53447702585431	0.93992295107552
H	-1.53401490469037	9.08707287553504	0.01389028953188
C	-2.03907807675630	7.29665792665235	1.12888299492313
H	-2.64692209243989	6.85470773791360	0.34602854836706
C	-1.86086843664295	6.63804389159452	2.33702511378717
H	-2.31329285236365	5.66885746608393	2.51489637137389
C	2.32902997896181	8.91529402130646	4.25424450661363
C	-1.45443768055170	5.34114100132645	6.58687495872019
H	-1.74628618580348	4.37184963180629	6.99783411612095
H	-2.19432376408060	6.08919039835124	6.90313208649436
C	-1.40679169991476	5.29710936920389	5.04006981417041
C	-0.71364890091001	4.05904703261940	4.48906637307613
C	-1.44976115184596	2.87896514047853	4.32817787452214
H	-2.51061970347651	2.87067412318903	4.57072816185979
C	-0.83732805668002	1.71901637938198	3.85789703249636
H	-1.42139154196084	0.81160390523484	3.73371821984310
C	0.52219071047278	1.72679128648329	3.54207573805661
H	1.00114024255003	0.82445089950622	3.17365891093454
C	1.26098604955940	2.89945234905646	3.69558106651603
H	2.31845362842801	2.91427228902793	3.44873436222346
C	0.64664660267210	4.06065696474707	4.16465985081942
H	1.23049052003485	4.97003726924921	4.27674402946890
H	-2.44086287211658	5.29620501335475	4.68003546608577

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Coordinates from ORCA-job TPSS-RePh-H

Re	6.41570146318435	7.39300985919715	-0.16627945323268
Cl	4.12766557053690	8.16305556357702	-0.71312700031688
C	7.02690464734859	7.74234554727203	-1.98159068619912
C	6.02947154594971	5.53627801910191	-0.62734804977434
C	8.20317964501872	6.87038934702610	0.34113987365711
C	5.12210421901139	8.51271803987318	2.27896864996614
C	4.10918823304092	8.55541115826354	3.26148680462434
C	3.78183998501883	7.34325089685113	3.85996982638456
H	3.00570405359298	7.29802119781880	4.61742739962774
C	4.41140192987832	6.18272286101678	3.41299113958489
H	4.20958016266764	5.21220838517987	3.85581361913273
C	3.33183554542309	9.77544748371250	3.56490596152546
C	2.75508711744005	10.49751546432772	2.50689320029900
H	2.91242916229634	10.15979306171946	1.48540563021166
C	1.97848360486106	11.62051314885835	2.77488965092224
H	1.52523445626048	12.16770850957048	1.95370684995374
C	1.77647182136708	12.03935930364682	4.09243453141178
H	1.17463872412774	12.91994818039014	4.29697514512101
C	2.34228124291291	11.32128384778202	5.14629886385348
H	2.18651448505419	11.64334058594608	6.17170184866757
C	3.10985396596422	10.18693989774646	4.88573241383200
H	3.56004559689035	9.63212594597656	5.70465466831571
N	6.58965712178901	9.39595454461146	0.61382339748962
C	7.34349770472162	10.37483422527641	0.07499712775207
H	7.90695429775571	10.09820357692076	-0.80811835149011
C	7.39906477941956	11.65219586785614	0.60917714344833
H	8.01781033262256	12.40512102543396	0.13370160164826
C	6.66304607742080	11.93117704256843	1.76137820019795
H	6.70193693823840	12.91298876251662	2.22211634992848
C	5.88097403014071	10.93025658327164	2.32061983762086
H	5.31308511142742	11.11740189210662	3.22195424279512
C	5.83453643618735	9.66846368895205	1.71721352885488
N	5.56164868803297	7.31185833935899	1.79671442508151
N	5.23285699091557	6.15254189604517	2.36413612110899
O	7.40312936878001	8.00015462450892	-3.04892431598857
O	5.78576257671053	4.43062523299212	-0.86571935238148
O	9.28566236799191	6.56314639272667	0.64450915636593