Supporting Information

Aerobic C-C and C-O Bond Formation Reactions Mediated by High-Valent Nickel Species

Sofia M. Smith,[†] Oriol Planas,[§] Laura Gómez,[#] Nigam P. Rath,[‖] Xavi Ribas,[§] and Liviu M. Mirica[*,†,‡]

[‡] Department of Chemistry, University of Illinois at Urbana-Champaign, 600 S. Mathews Avenue, Urbana, Illinois 61801, United States

[†] Department of Chemistry, Washington University in St. Louis, One Brookings Drive, St. Louis, Missouri 63130-4899, United States

[§] Institut de Química Computacional i Catàlisi (IQCC) and Departament de Química, Universitat de Girona, Campus de Montilivi, Girona E-17003, Catalonia, Spain

[#] Serveis Tècnics de Recerca (STR), Universitat de Girona, Parc Científic i Tecnològic, Girona E-17071, Catalonia, Spain

[‖] Department of Chemistry and Biochemistry, University of Missouri-St. Louis, One University Boulevard, St. Louis, Missouri 63121-4400, United States

* e-mail: mirica@illinois.edu

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I. General specifications

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk and glove box techniques if not indicated otherwise. All reagents for which synthesis is not given are commercially available from Aldrich, Acros or STREM and were used as received without further purification. Solvents were purified prior to use by passing through a column of activated alumina using an MBRAUN SPS. N,N'-R-2,11-diaza[3.3](2,6)pyridinophane (R= Me, TsMe, Ts and tBu) (^{R}N4),[1, 2] $(Py)_2Ni^{II}$(cycloneophyl),[3] (^{Me}N4)Ni^{III}(cycloneophyl),[4] ferrocenium hexafluorophosphate ($FcPF_6$),[5] acetylferrocene tetrafluoroborate ($^{Ac}FcBF_4$)[5] were prepared according to the literature procedures. Other abbreviations used throughout the paper and supporting information: silver hexafluoroantimony ($AgSbF_6$), 1-Fluoro-2,4,6-trimethylpyridinium triflate (NFTPT), 5-(trifluoromethyl)dibenzothiophenium trifluoromethanesulfonate (TDTT), meta-chloroperoxybenzoic acid (^{m}CPBA), xenon difluoride (XeF_2) and (diacetoxyiodo)benzene ($PhI(OAc)_2$).

^{1}H NMR spectra were recorded on a Varian Mercury-300 spectrometer (300.121 MHz), Agilent DD2-500 spectrometer (499.885 MHz) or Agilent DD2-600 spectrometer (599.736 MHz). Chemical shifts are reported in ppm and referenced to residual solvent resonance peaks.[6, 7] Abbreviations for the multiplicity of NMR signals are s (singlet), d (doublet), dd (doublet of doublets), t (triplet), m (multiplet). EPR spectra were recorded on a Bruker EMX-PLUS EPR or a JEOL JES-FA EPR spectrometer at X-band (~9.2 GHz) frequency in frozen solution at 77 K. The purchase of the Bruker EMX-PLUS EPR spectrometer was supported by the National Science Foundation (MRI, CHE-1429711). High resolution mass spectra (HRMS) were measured on a Bruker MicrOTOF-Q II^{TM} instrument using Cryospray ionization sources at Serveis Tècnics of the University of Girona. Samples were introduced into the mass spectrometer ion source by direct infusion and were externally calibrated using sodium triflate. The instrument was operated in the positive ion mode. Electrochemical-grade electrolytes from Fluka were used as the supporting electrolyte for electrochemical measurements. Cyclic voltammetry experiments were performed with a BASi EC Epsilon electrochemical workstation or a CHI 660D Electrochemical Analyzer. The electrochemical measurements were taken in a glove box under nitrogen. A glassy carbon disk electrode (d = 1.6 mm) was used as the working electrode for cyclic voltammetry. The auxiliary electrode was a Pt wire for cyclic voltammetry measurements. The non-aqueous references electrode used was a silver wire. The reference electrodes were calibrated against Cp_2Fe (Fc).

II. Synthesis of (^{R}N4)Ni(cycloneophyl) Complexes

Preparation of (^{Me}N4)Ni^{II}(cycloneophyl), 1

$$(^{Me}N4) + (Py)_2Ni(cycloneophyl) \xrightarrow{THF} (^{Me}N4)Ni(cycloneophyl)$$

A slightly modified procedure was used to make the (^{Me}N4)Ni(cycloneophyl) complex. A solution of ^{Me}N4 (61.6 mg, 0.23 mmol) and (Py)$_2$Ni^{II}(cycloneophyl) (87.8 mg, 0.25 mmol) in 5 ml THF was stirred at room temperature for 14 hours. The solution was evaporated and re-dissolved in a minimum amount of THF. After filtration the solution was evaporated to dryness and triturated with pentane five times. The solid was dried under vacuum to obtain an orange-yellow powder (76.1 mg, 0.17 mmol, 72%).

^{1}H NMR (300 MHz, MeCN-d$_3$), δ (ppm): 7.51 (m, 2H, I), 7.10 (m, 4H, H), 6.67 (m, 6H, G), 6.38 (t, *J* = 6.4 Hz, 1H, F), 5.88 (d, *J* = 5.9 Hz, 1H, E), 4.22 (m, 4H, D), 2.24 (s, 6H, C), 1.31 (s, 6H, B), 1.15 (s, 2H, A).

Note: further characterization was reported by Mirica and co-workers in 2016.[4]

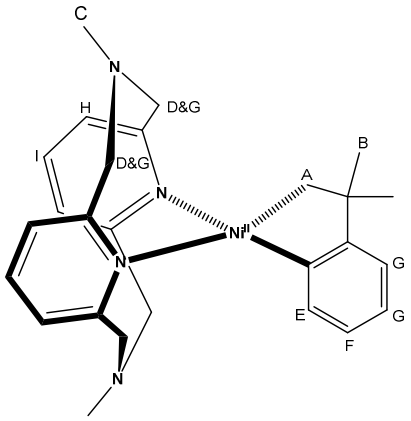


Figure S1. Proton structural assignments from NMR experiments for (^{Me}N4)Ni^{II}(cycloneophyl).

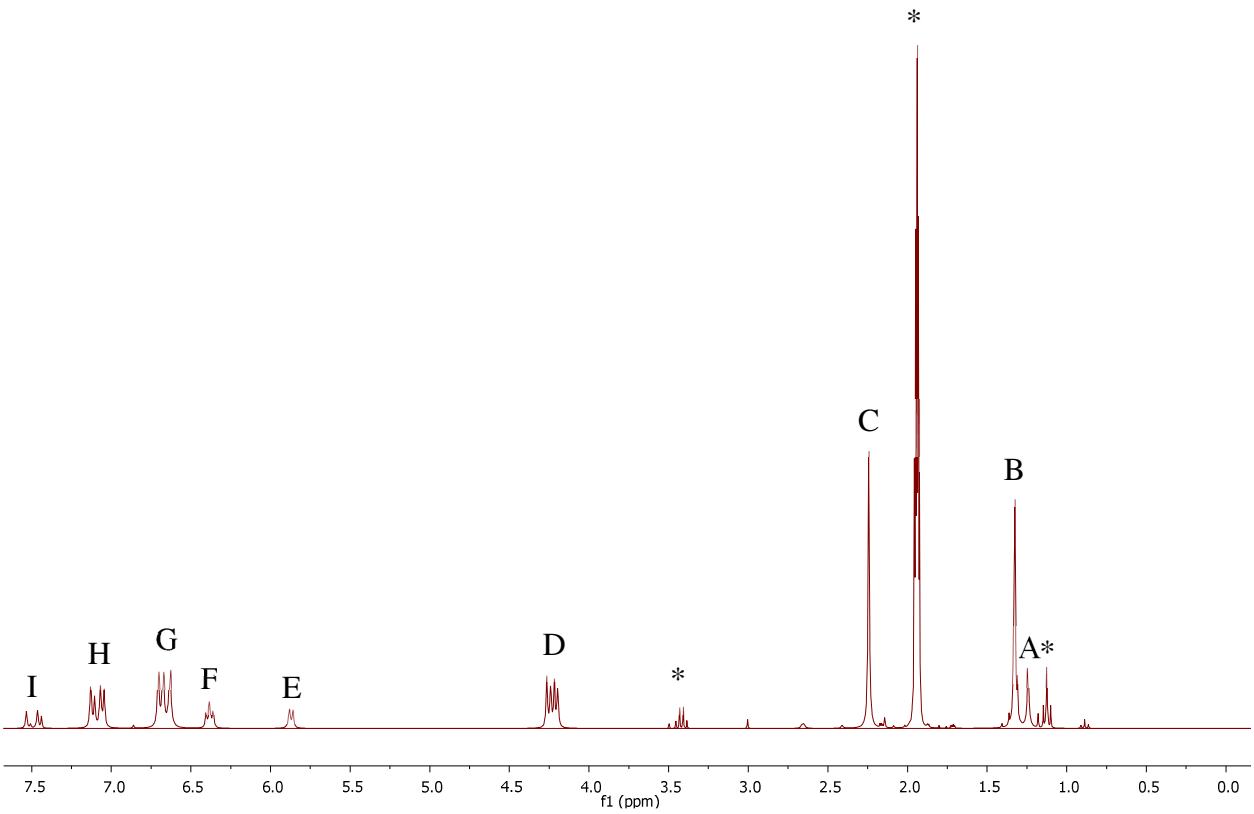


Figure S2. ^{1}H NMR spectrum of (^{Me}N4)Ni^{II}(cycloneophyl) in MeCN-d_3 (300 MHz). Peaks marked with an asterisk correspond to a trace amount of solvent (MeCN-d_3 and diethyl ether).

Preparation of (^{TsMe}N4)Ni^{II}(cycloneophyl), 2

$$(^{TsMe}N4) + (Py)_2Ni(cycloneophyl) \xrightarrow{THF} (^{TsMe}N4)Ni(cycloneophyl)$$

A solution of ^{TsMe}N4 (134.0 mg, 0.33 mmol) and $(Py)_2Ni^{II}$(cycloneophyl) (125.0 mg, 0.36 mmol) in 5 ml THF was stirred at room temperature for 14 hours. The solution was evaporated and re-dissolved in a minimum amount of THF. After filtration the solution was evaporated to dryness and triturated with pentane five times. The solid was dried under vacuum to obtain a yellow powder (159.5 mg, 0.27 mmol, 81%).

^{1}H NMR (600 MHz, THF-d_8), δ (ppm): 7.95 (d, *J* = 7.8 Hz, 2H, W), 7.90 (t, *J* = 7.0 Hz, 1H, V), 7.83 (t, *J* = 7.1 Hz, 1H, U), 7.78 (d, *J* = 7.5 Hz, 1H, T), 7.68 (d, *J* = 7.5 Hz, 1H, S), 7.65 (d, *J* = 7.8 Hz, 2H, R), 7.44 (d, *J* = 7.4 Hz, 1H, Q), 7.40 (d, *J* = 7.4 Hz, 1H, P), 7.05 (m, 4H, O), 6.85 (t, *J* = 7.2 Hz, 1H, N), 6.78 (d, *J* = 7.0 Hz, 1H, M), 6.52 (t, *J* = 7.0 Hz, 1H, L), 5.68 (d, *J* = 5.7 Hz, 1H, K), 5.21 (d, *J* = 14.4 Hz, 1H, J), 5.15 (d, *J* = 14.5 Hz, 1H, I), 4.27 (d, *J* = 14.2 Hz, 1H, H), 4.22 (d, *J* = 14.2 Hz, 1H, G), 2.41 (s, 3H, F), 2.26 (s, 3H, E), 1.40 (s, 3H, D), 1.21 (d, *J* = 9.7 Hz, 1H, C), 1.15 (s, 3H, B), 1.10 (d, *J* = 9.7 Hz, 1H, A).

^{13}C NMR (600 MHz, THF-d_8), δ (ppm): 170.32 (u), 159.88 (t), 159.76 (t), 159.66 (t), 159.54 (t), 159.47 (t), 144.59 (s), 138.89 (r), 137.31 (q'), 137.14 (q), 135.77 (p), 130.89 (o), 128.06 (n), 126.12 (m'), 126.01 (m), 125.59 (l'), 125.44 (l), 123.76 (k), 122.90 (j), 121.71 (i), 64.22 (h'), 64.16 (h), 58.40 (g'), 58.22 (g), 48.83 (f), 41.43 (e), 38.38 (d), 35.29 (c), 33.68 (b), 21.59 (a).

Elemental analysis: found C 61.63, H 6.04, N 8.58%; calculated $C_{32}H_{36}N_4NiO_2S$•1.5*H_2O C, 61.35, H 6.28, N 8.94%

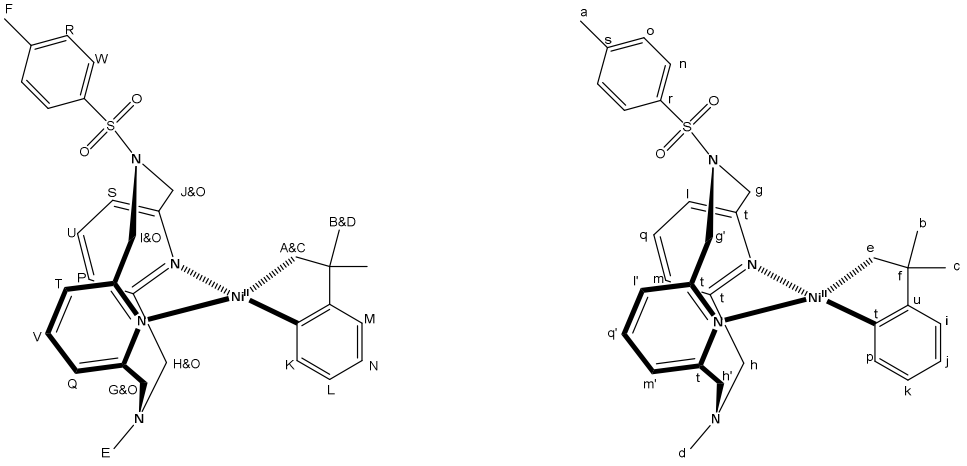


Figure S3. Proton (left) and carbon (right) structural assignments from NMR experiments for (^{TsMe}N4)Ni^{II}(cycloneophyl).

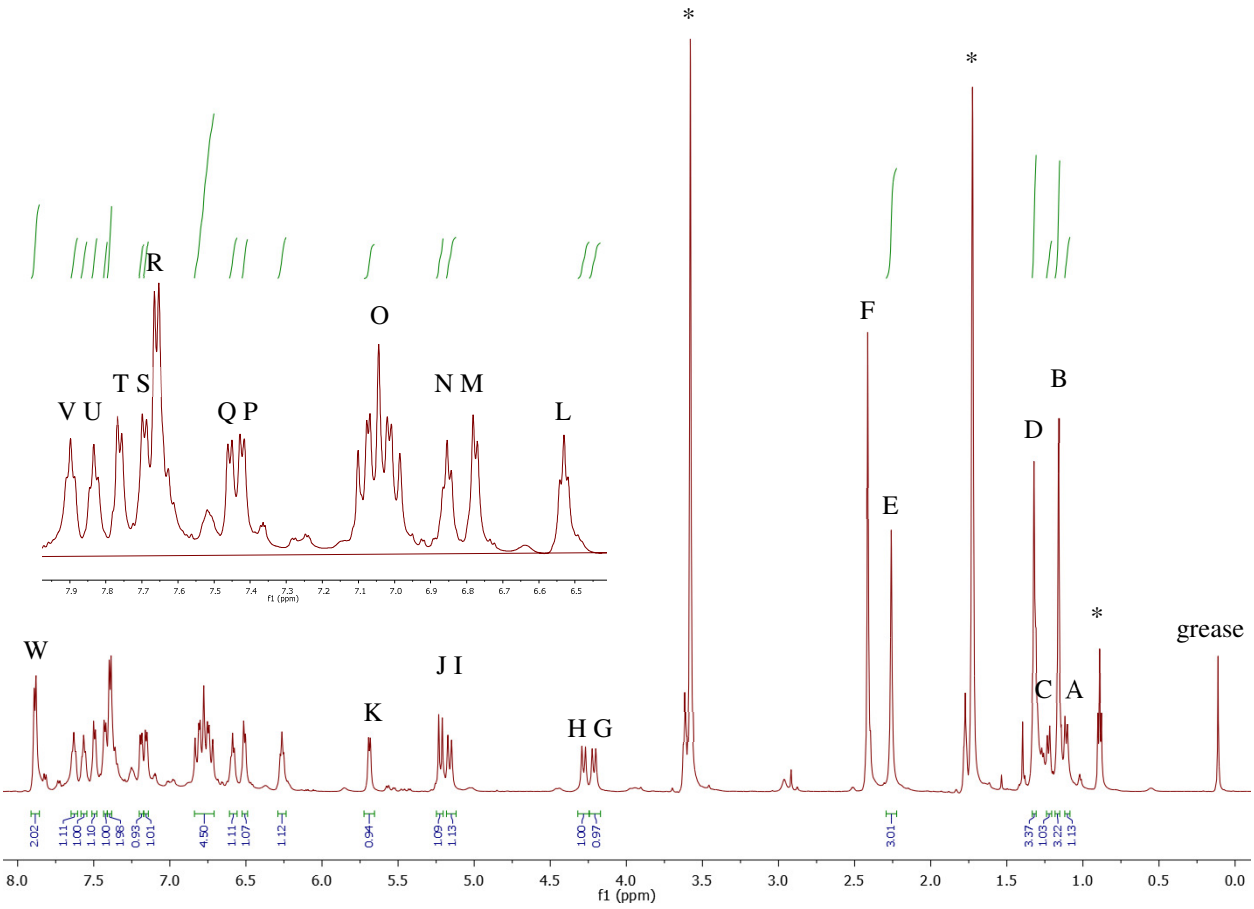


Figure S4. ^{1}H NMR spectrum of (^{TsMe}N4)Ni^{II}(cycloneophyl) in THF-d_8 (600 MHz). Peaks marked with an asterisk correspond to a trace amount of solvent (THF-d_8, THF and pentane).

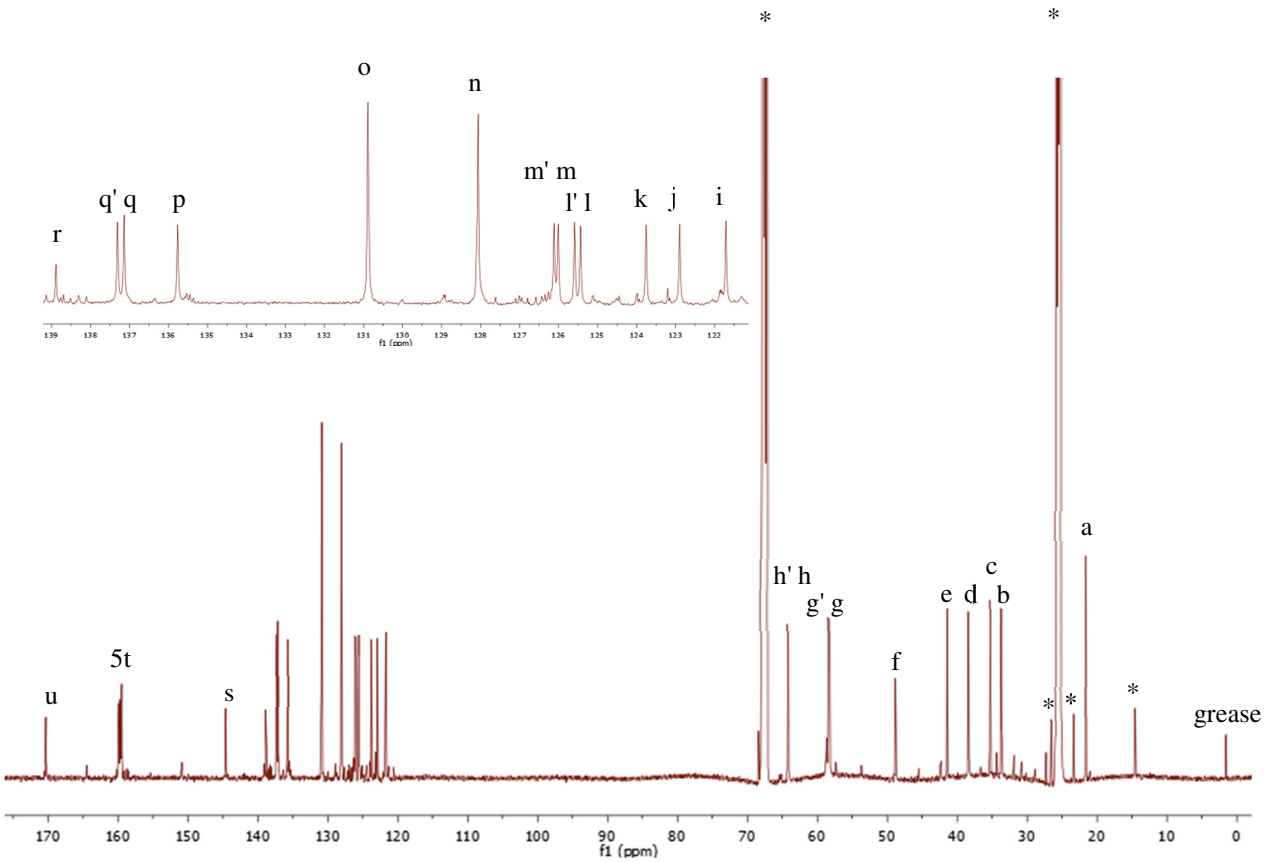


Figure S5. ^{13}C NMR spectrum of ($^{TsMe}N4$)Ni^{II}(cycloneophyl) in THF-d_8 (600 MHz). Peaks marked with an asterisk correspond to a trace amount of solvent (THF-d_8, THF and pentane).

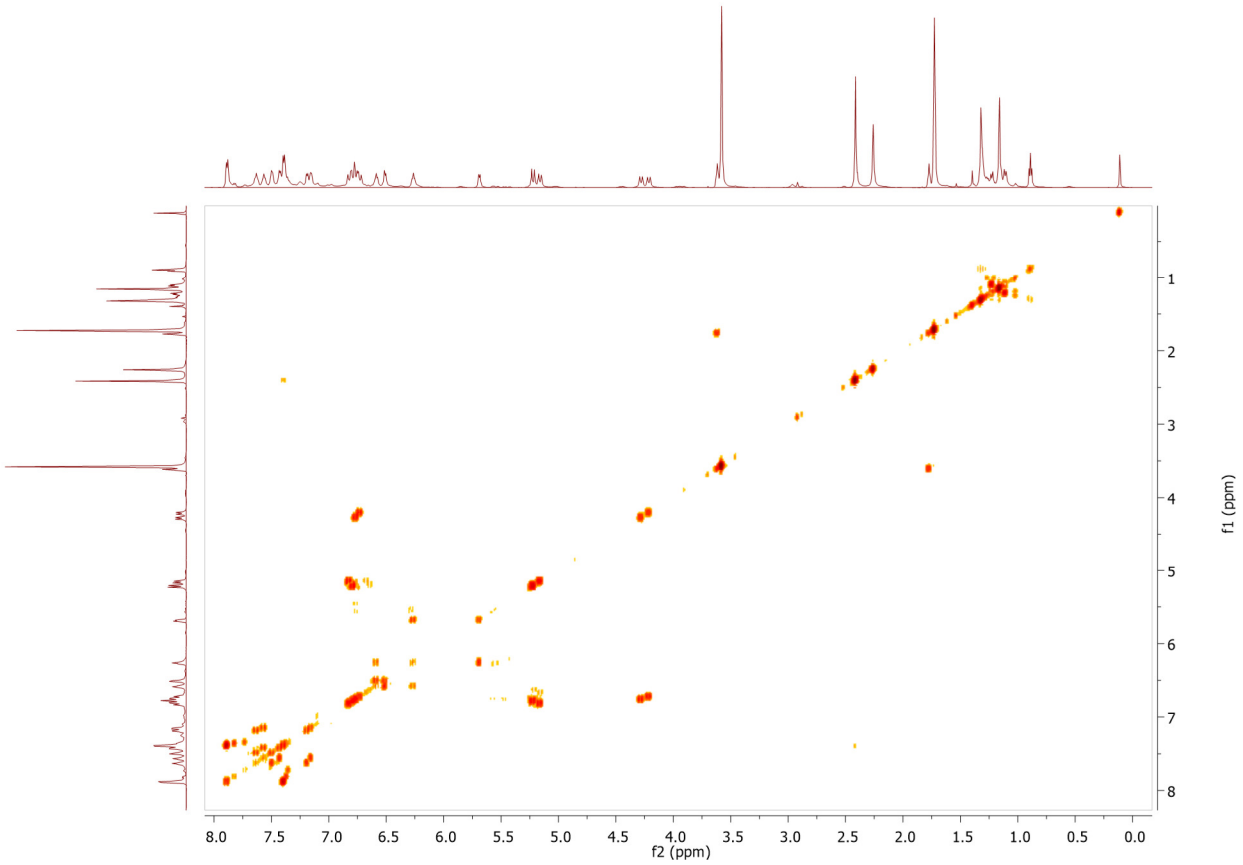


Figure S6. ^{1}H-^{1}H gCOSY spectrum of (^{TsMe}N4)Ni^{II}(cycloneophyl) in THF-d_8 (600 MHz).

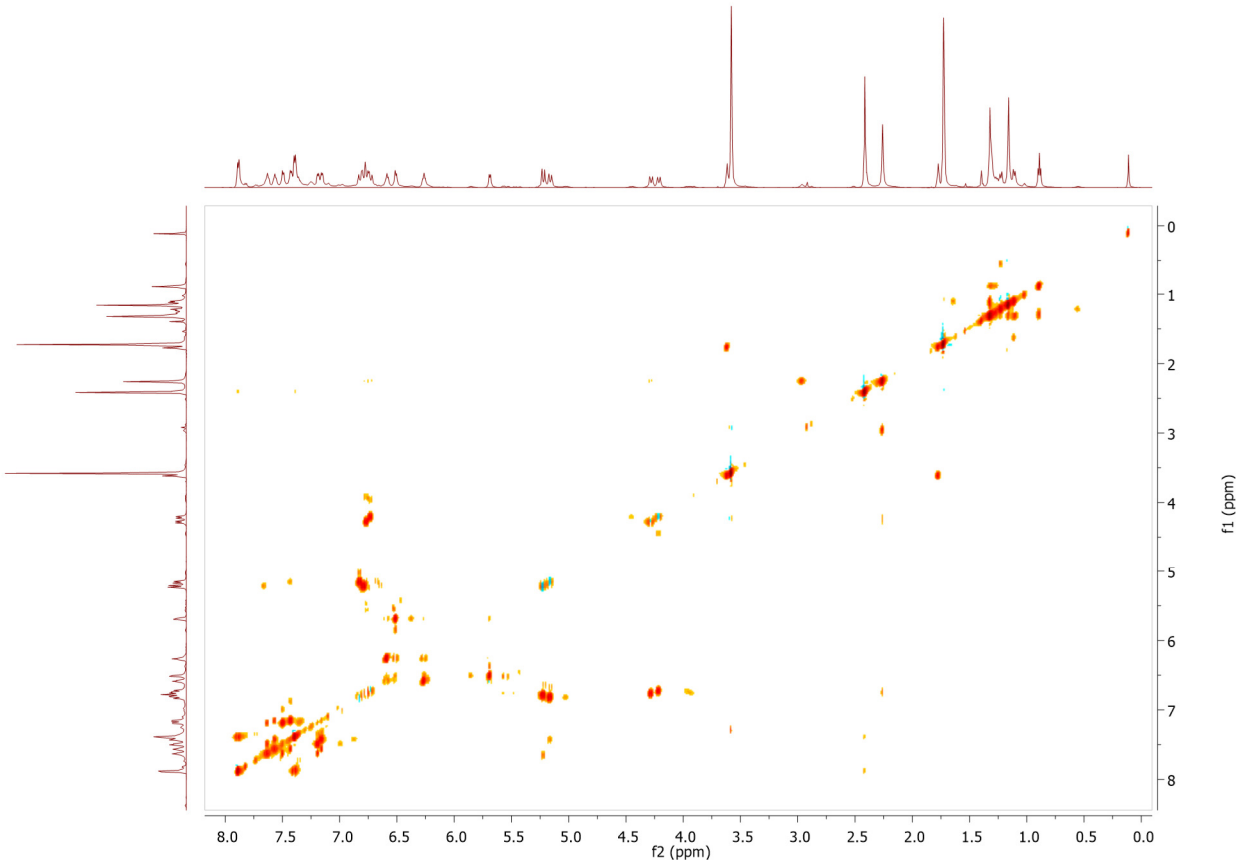


Figure S7. ^{1}H-^{1}H TOXY spectrum of (^{TsMe}N4)Ni^{II}(cycloneophyl) in THF-d_8 (600 MHz).

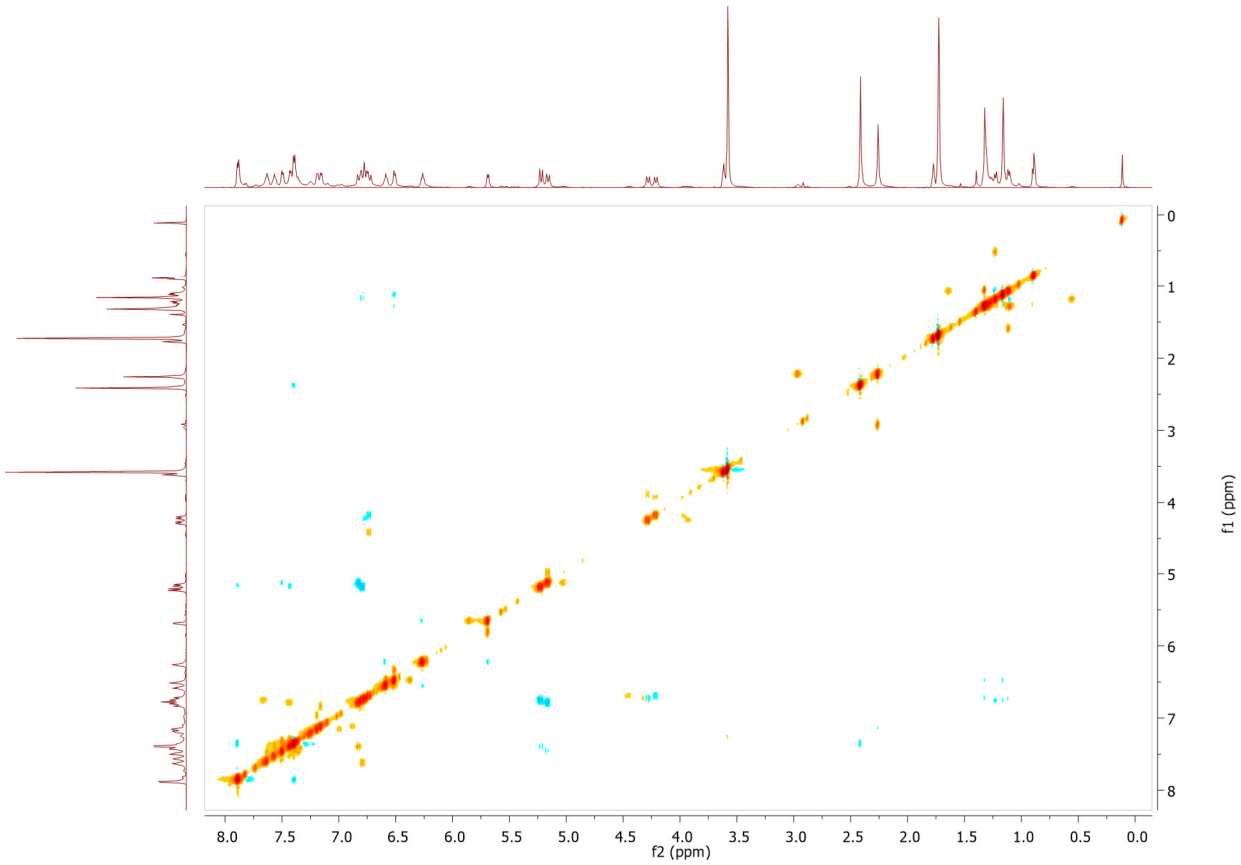


Figure S8. ^{1}H-^{1}H NOESY spectrum of (^{TsMe}N4)Ni^{II}(cycloneophyl) in THF-d_8 (600 MHz).

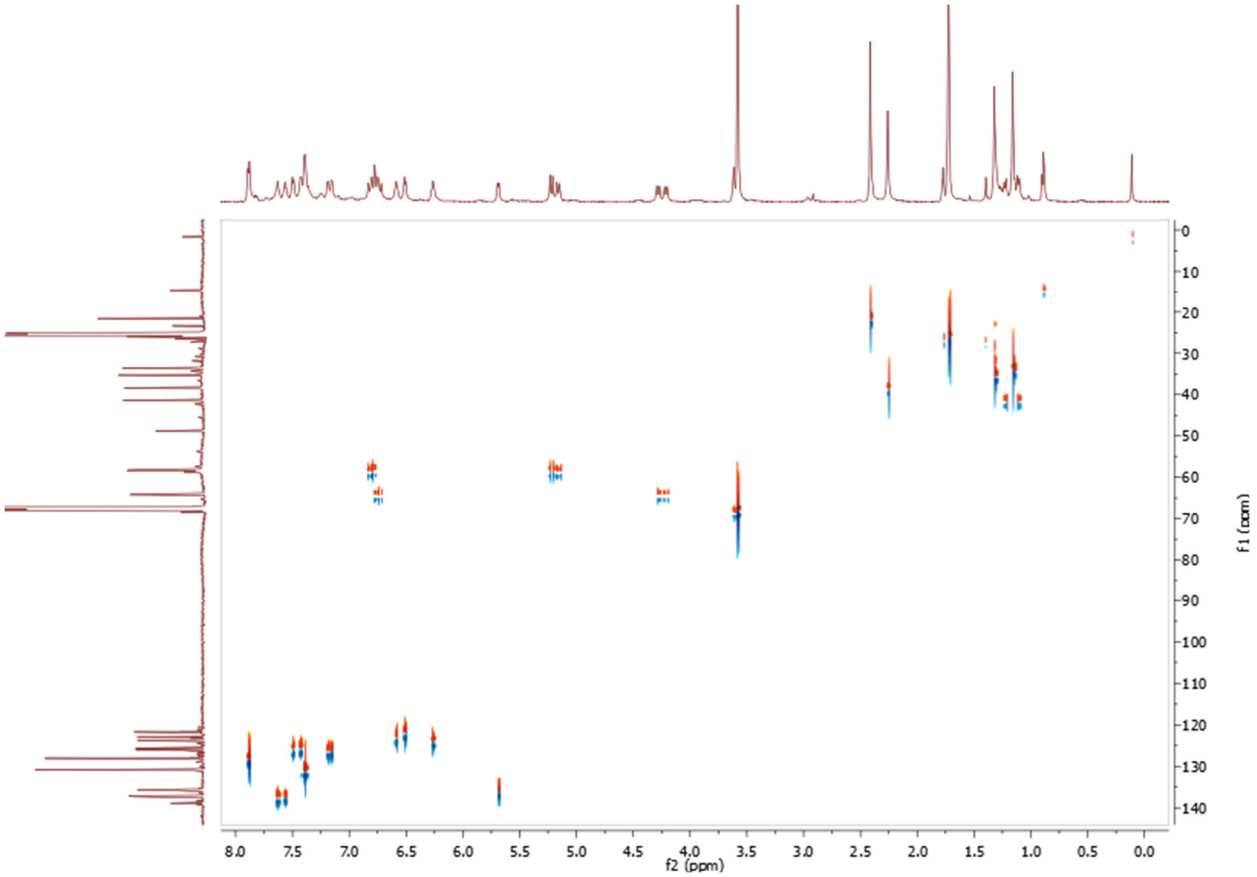


Figure S9. ^{1}H-^{13}C HSQC spectrum of (^{TsMe}N4)Ni^{II}(cycloneophyl) in THF-d$_8$ (600 MHz).

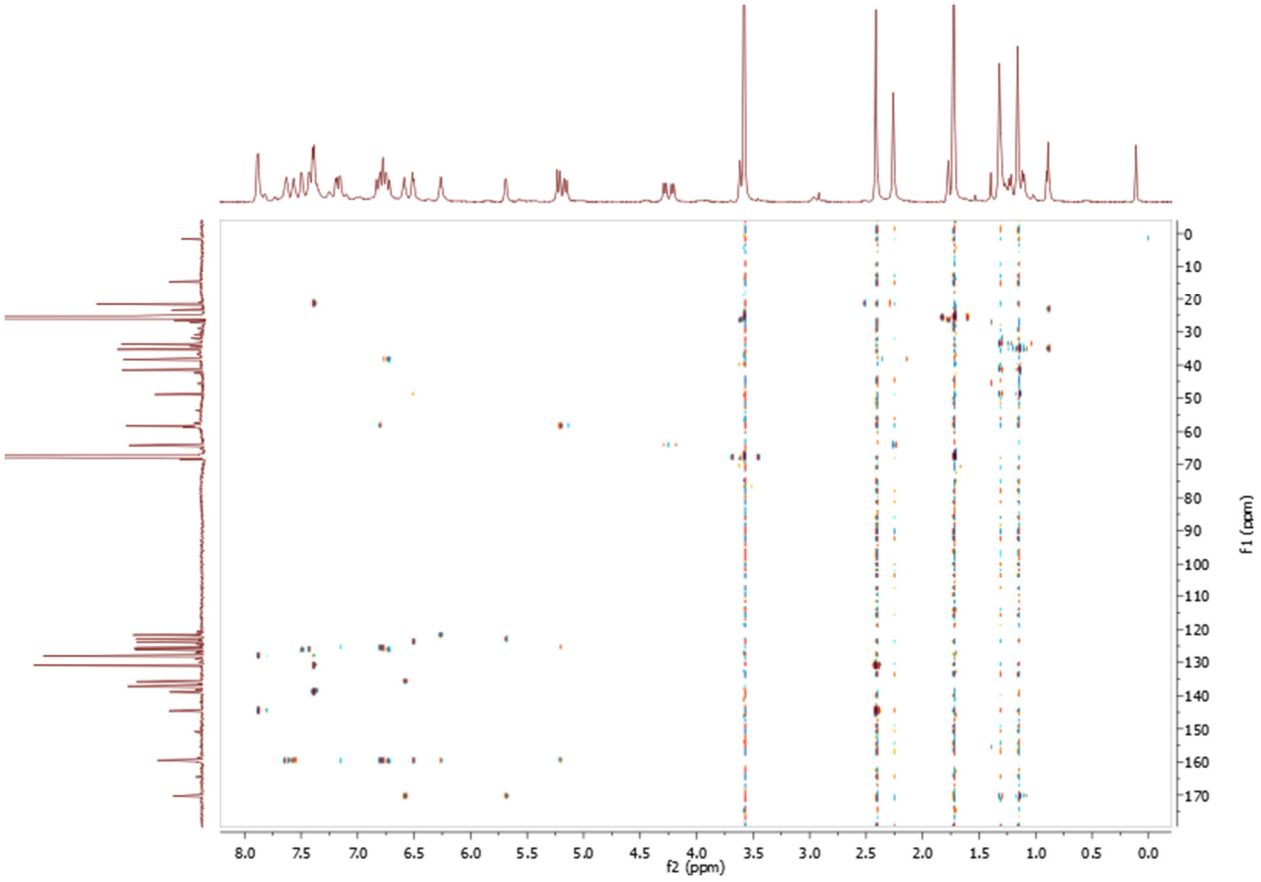


Figure S10. ^{1}H-^{13}C HMBC spectrum of (^{TsMe}N4)Ni^{II}(cycloneophyl) in THF-d_8 (600 MHz).

Preparation of (^{Ts}N4)Ni^{II}(cycloneophyl), 3

A solution of ^{Ts}N4 (111.1 mg, 0.203 mmol) and (Py)$_2$Ni^{II}(cycloneophyl) (77.6 mg, 0.224 mmol) in 5 mL of THF was stirred at room temperature for 14 hours. The solution was evaporated and re-dissolved in a minimum amount of THF. After filtration the solution was evaporated to dryness and triturated with pentane five times. The solid was dried under vacuum to obtain a yellow powder (100.5 mg, 0.136 mmol, 67%).

^{1}H NMR (500 MHz, THF-d$_8$), δ (ppm): 7.73 (d, *J* = 8.1 Hz, 4H, M), 7.70 (t, *J* = 7.7 Hz, 1H, L), 7.64 (t, *J* = 7.7 Hz, 1H, L'), 7.51 (d, *J* = 7.7 Hz, 2H, K), 7.46 (d, *J* = 7.6 Hz, 2H, K'), 7.35 (d, *J* = 8.0 Hz, 4H, J), 6.79 (d, *J* = 7.8 Hz, 2H, I), 6.76 (d, *J* = 7.8 Hz, 2H, I'), 6.57 (t, *J* = 7.0 Hz, 1H, H), 6.47 (d, *J* = 6.2 Hz, 1H, G), 6.23 (t, *J* = 7.0 Hz, 1H, F), 5.44 (d, *J* = 6.2 Hz, 1H, E), 5.25 (d, *J* = 14.8 Hz, 2H, D), 5.18 (d, *J* = 14.9 Hz, 2H, D'), 2.40 (s, 6H, C), 1.15 (s, 6H, B), 1.03 (s, 2H, A).

APT (500 MHz, THF-d$_8$), δ (ppm): 170.24 (v), 159.47 (u), 159.28 (t), 158.54 (s), 144.42 (r), 138.65 (q), 138.35 (p), 138.12 (o), 135. 24 (n), 130.73 (m), 127.92 (l), 126.21 (k), 126.12 (j), 123.81 (i), 123.03 (h), 121.68 (g), 58.62 (f), 58.48 (e), 48.58 (d), 42.38 (c), 34.21 (b), 21.43 (a).

Elemental analysis: found C 59.93, H 5.52, N 6.95%; calculated $C_{38}H_{40}N_4NiO_4S_2$•H_2O C, 60.25, H 5.59, N 7.40%

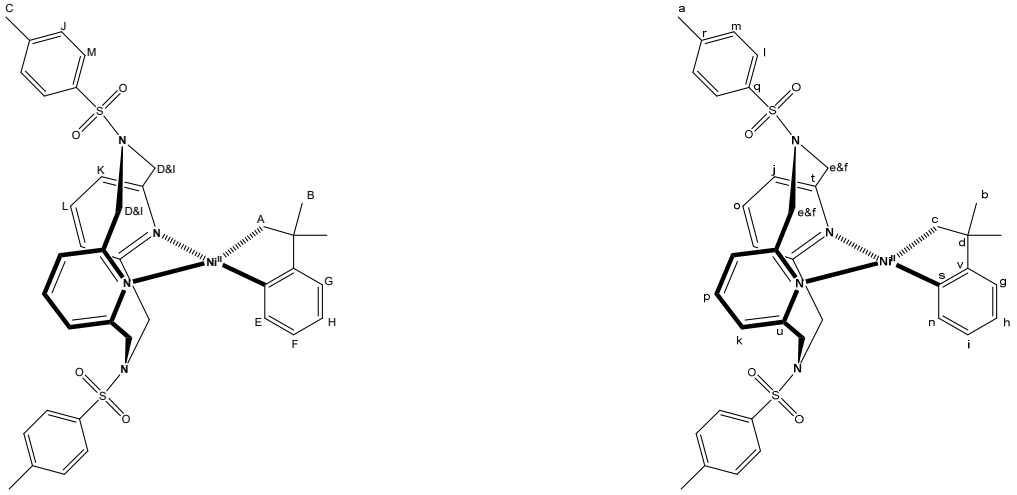


Figure S11. Proton (left) and carbon (right) structural assignments from NMR experiments for (^{Ts}N4)Ni^{II}(cycloneophyl)

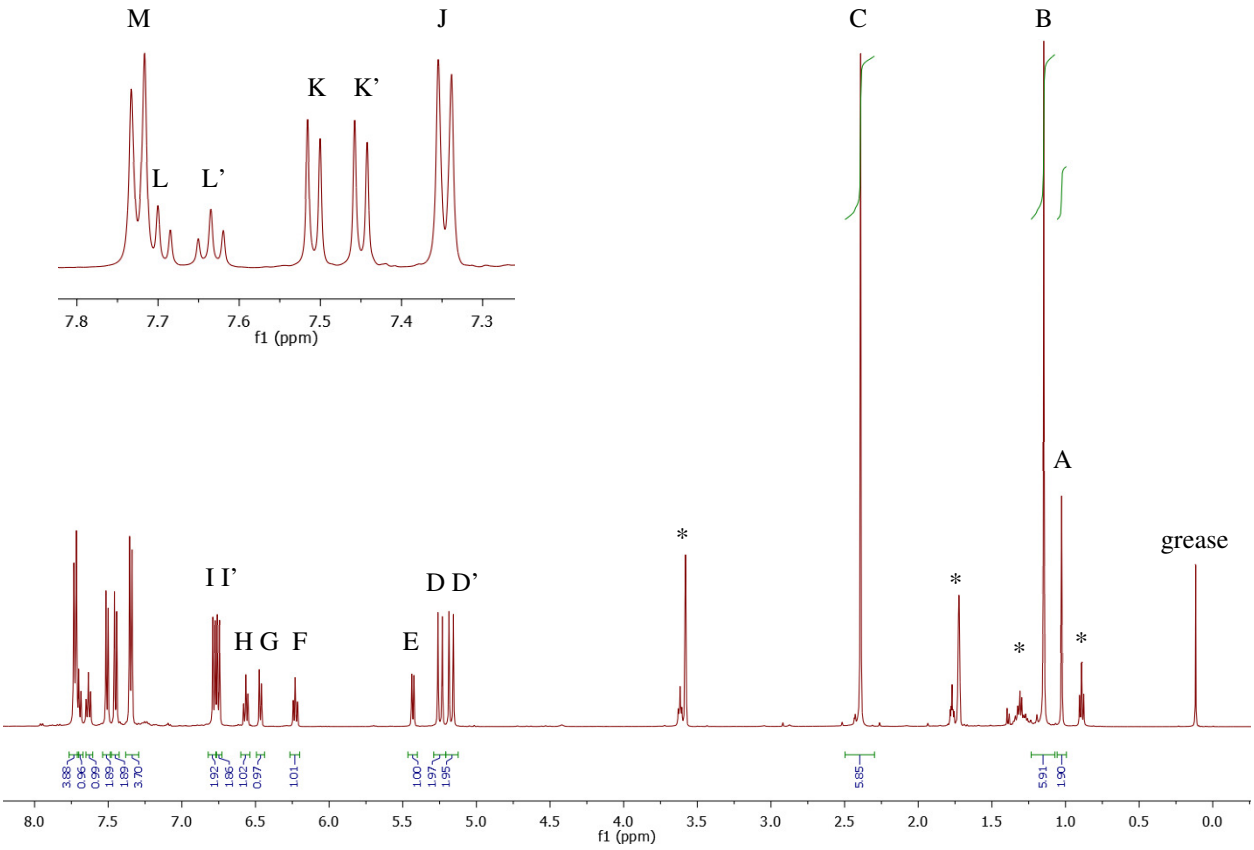


Figure S12. ^{1}H NMR spectrum of (^{Ts}N4)Ni^{II}(cycloneophyl) in THF-d_8 (500 MHz). Peaks marked with an asterisk correspond to a trace amount of solvent (THF-d_8 and pentane).

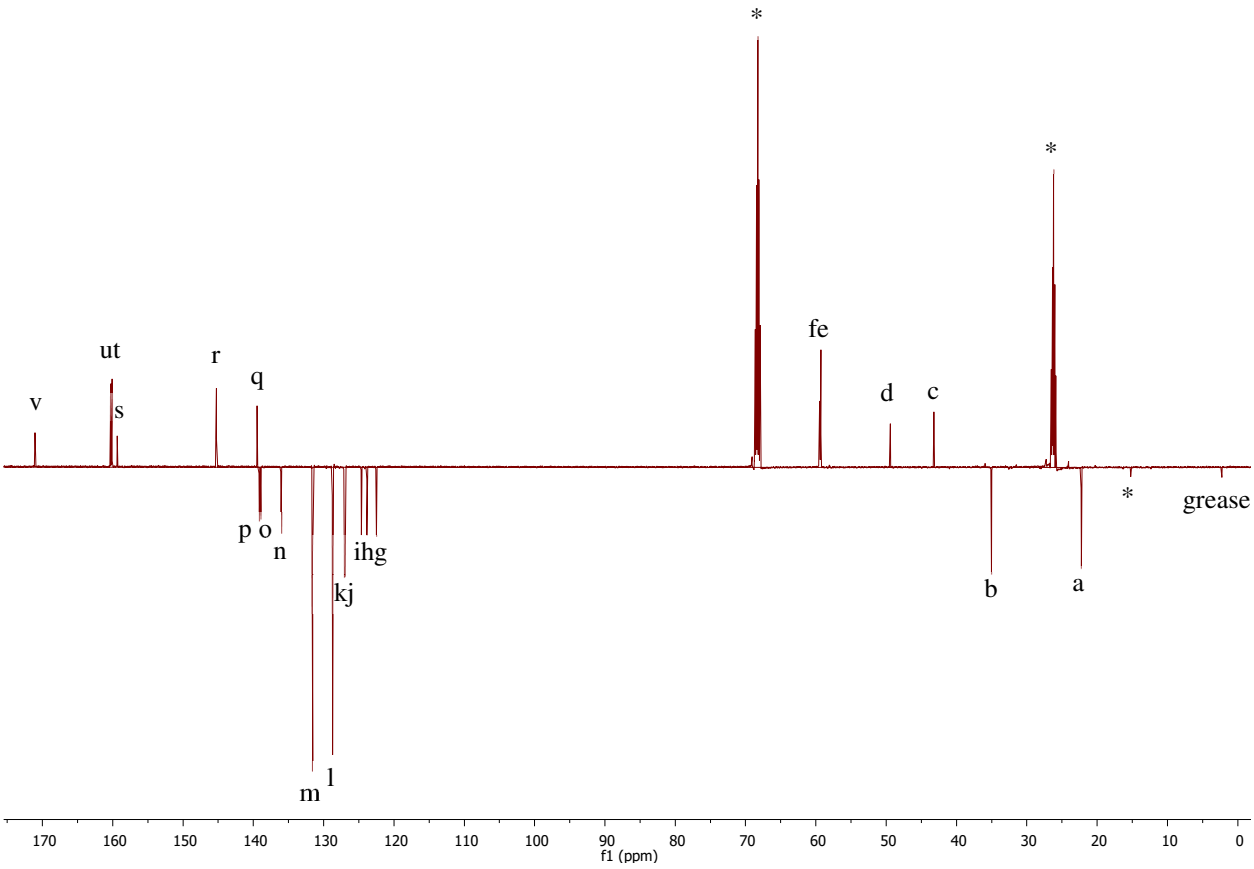


Figure S13. APT spectrum of (^{Ts}N4)Ni^{II}(cycloneophyl) in THF-d_8 (500 MHz). Peaks marked with an asterisk correspond to a trace amount of solvent (THF-d_8 and pentane).

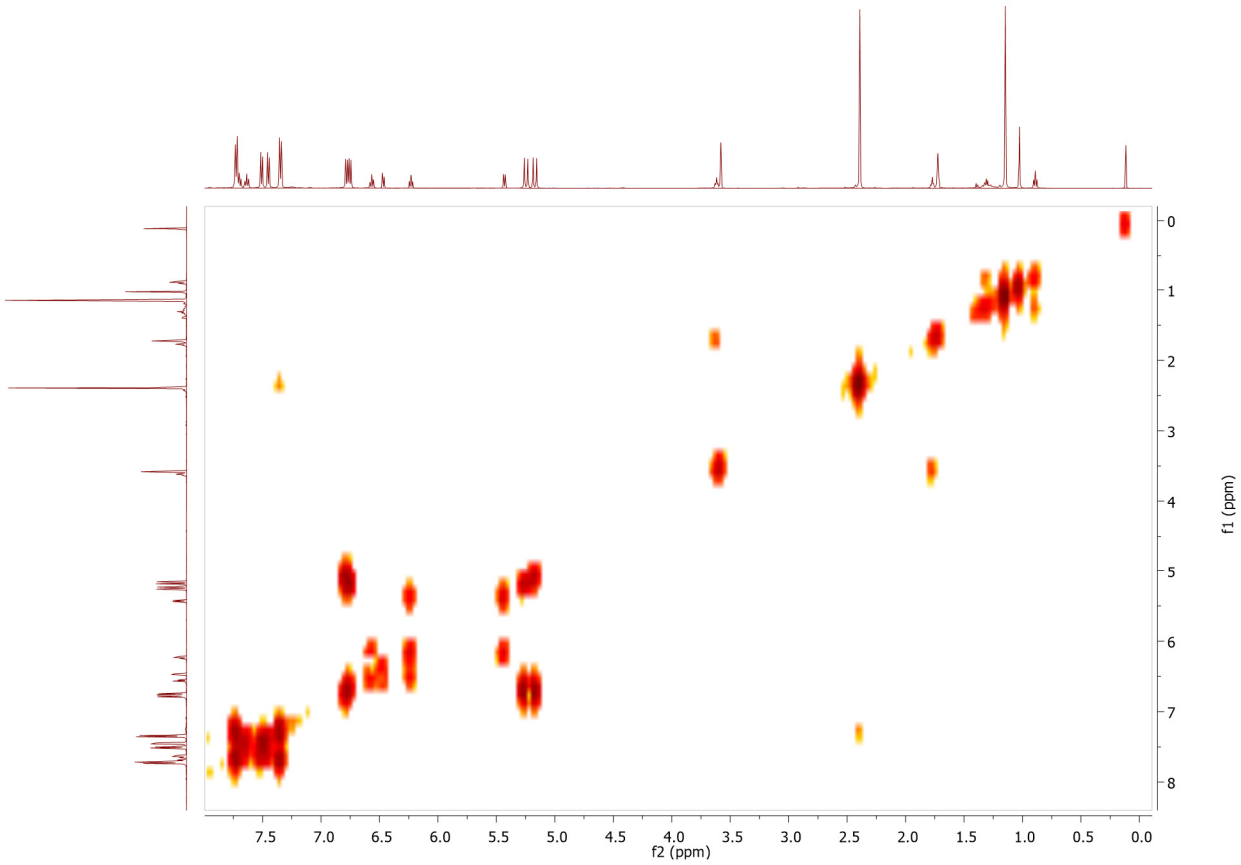


Figure S14. ^{1}H-^{1}H gCOSY spectrum of (^{Ts}N4)Ni^{II}(cycloneophyl) in THF-d_8 (500 MHz).

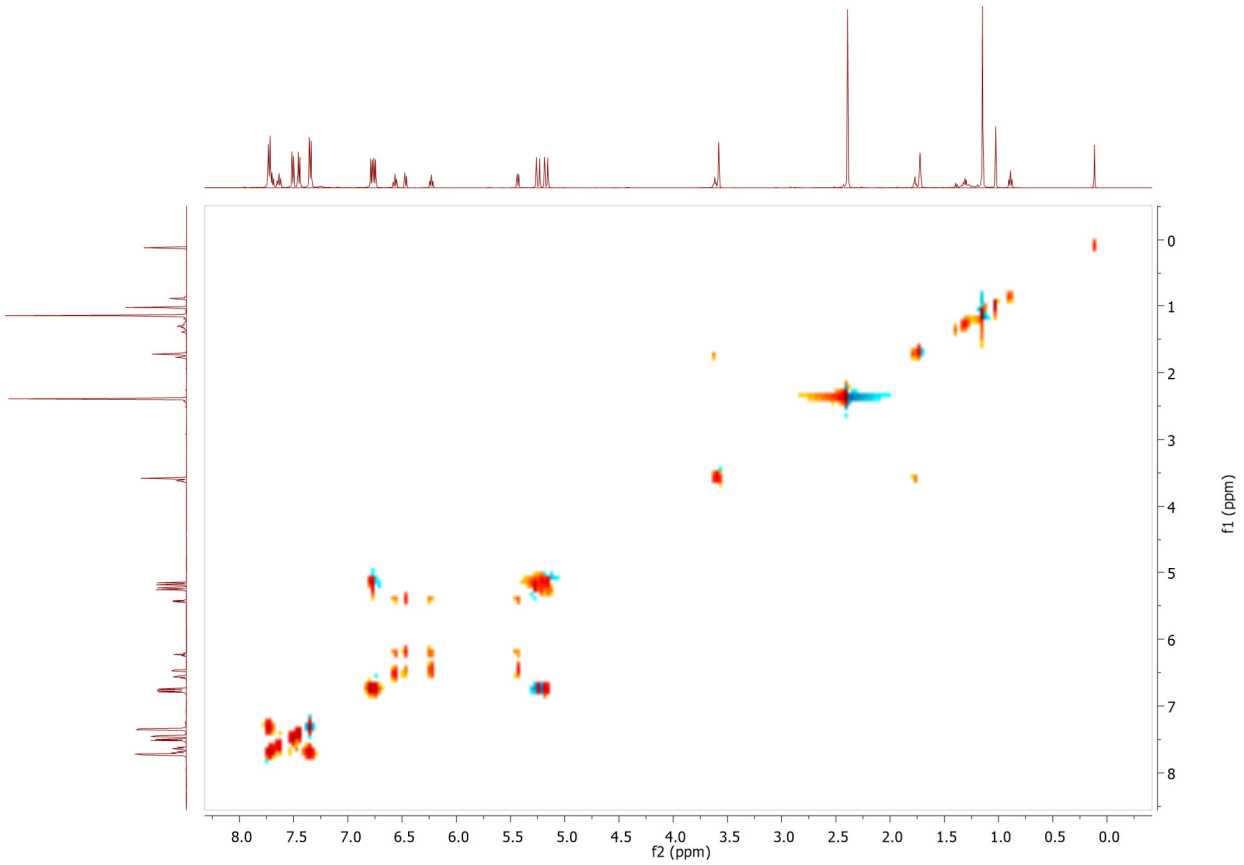


Figure S15. ^{1}H-^{1}H TOXY spectrum of (^{Ts}N4)Ni^{II}(cycloneophyl) in THF-d_8 (500 MHz).

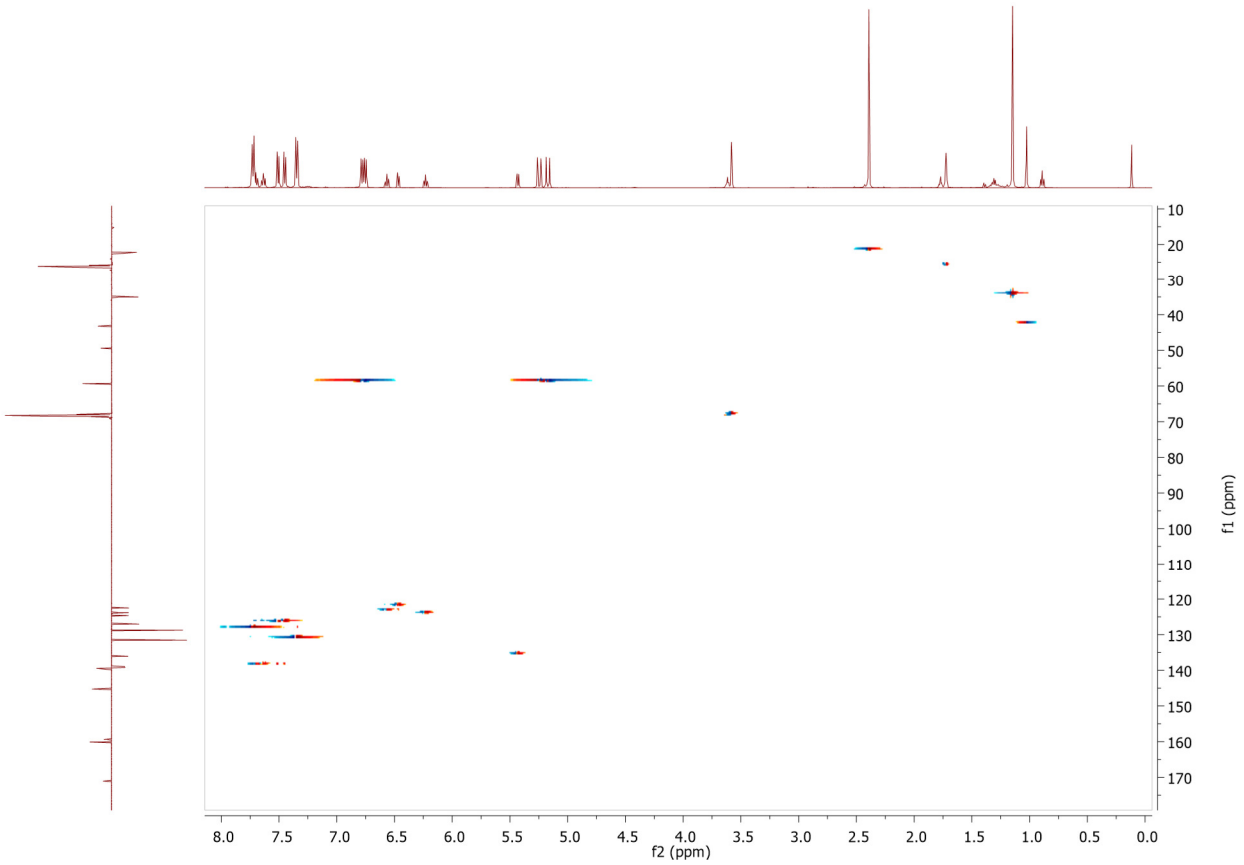


Figure S16. ^{1}H-^{13}C HSQC spectrum of (^{Ts}N4)Ni^{II}(cycloneophyl) in THF-d_8 (500 MHz).

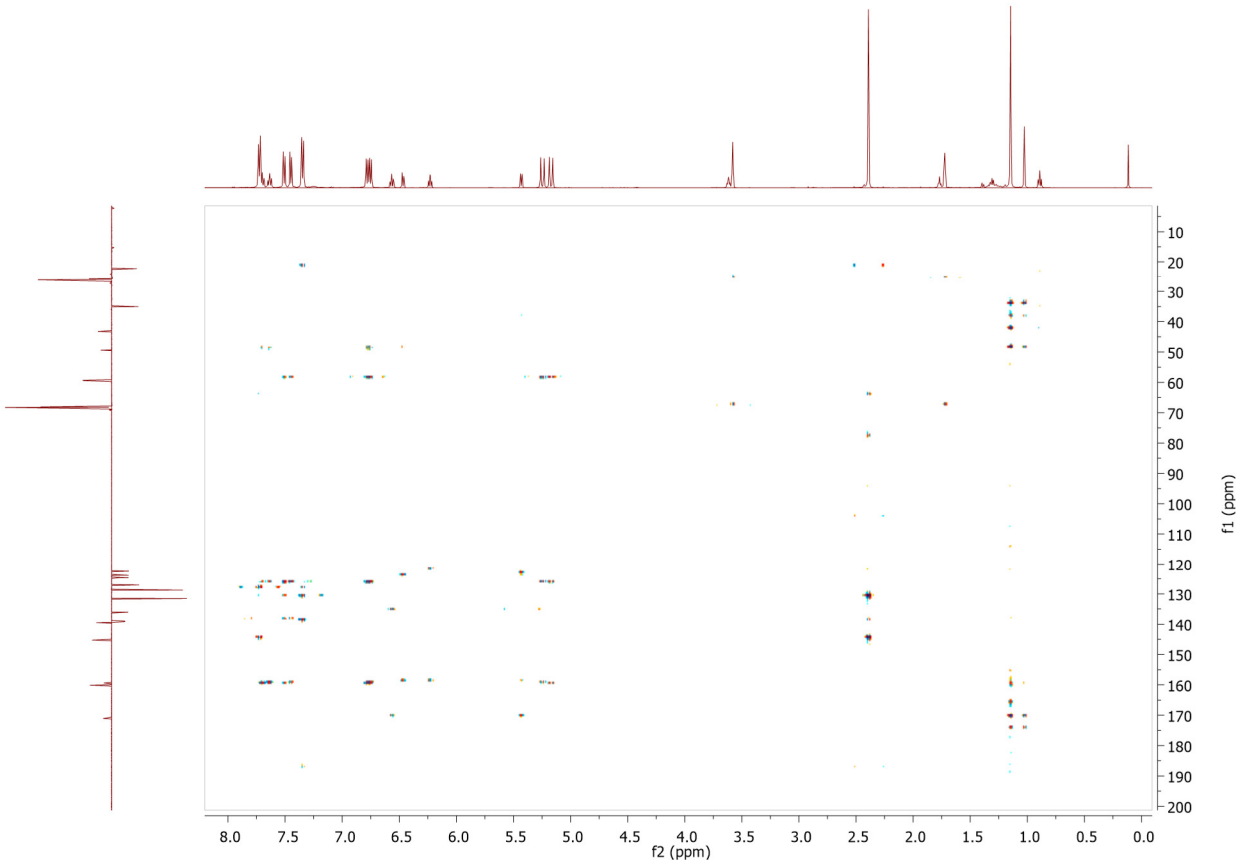


Figure S17. ^{1}H-^{13}C HMBC spectrum of (^{Ts}N4)Ni^{II}(cycloneophyl) in THF-d_8 (500 MHz).

Preparation of (^{tBu}N4)Ni^{II}(cycloneophyl), 4

$$(^{tBu}N4) + (Py)_2Ni(cycloneophyl) \xrightarrow{THF} (^{tBu}N4)Ni(cycloneophyl)$$

A solution of ^{tBu}N4 (100.7 mg, 0.200 mmol) and (Py)$_2$Ni^{II}(cycloneophyl) (69.8 mg, 0.200 mmol) in 5 mL of THF was stirred at room temperature for 14 hours. The solution was evaporated and re-dissolved in a minimum amount of THF. After filtration the solution was evaporated to dryness and triturated with pentane five times. The solid was dried under vacuum to obtain a yellow powder (78.7 mg, 0.145 mmol, 73%).

^{1}H NMR (500 MHz, THF-d$_8$), δ (ppm): 7.44 (t, *J* = 7.7 Hz, 1H, L), 7.39 (t, *J* = 7.7 Hz, 1H, K), 7.05 (d, *J* = 7.6 Hz, 2H, J), 7.00 (d, *J* = 7.6 Hz, 2H, I), 6.65 – 6.56 (m, 5H, H), 6.53 (d, *J* = 7.3 Hz, 1H, G), 6.29 (t, *J* = 7.2 Hz, 1H, F), 5.94 (d, *J* = 7.4 Hz, 1H, E), 4.65-4.55 (two d, *J* = 13.8 Hz, 4H, D), 1.38 (s, 18H, C), 1.34 (s, 6H, B), 1.27 (s, 2H, A).

APT (500 MHz, THF-d$_8$), δ (ppm): 169.81 (s), 162.54 (r), 162.48 (q), 161.10 (p), 136.97 (o), 136.88 (n), 136.45 (m), 123.92 (l), 123.79 (k), 123.14 (j), 122.08 (i), 121.32 (h), 60.26 (g), 60.13 (f), 57.70 (e), 48.95 (d), 40.60 (c), 34.43 (b), 28.51 (a).

Elemental analysis: found C 68.67, H 8.28, N 10.02%; calculated $C_{32}H_{44}N_4Ni \bullet H_2O$ C 68.46, H 8.26, N 9.98%

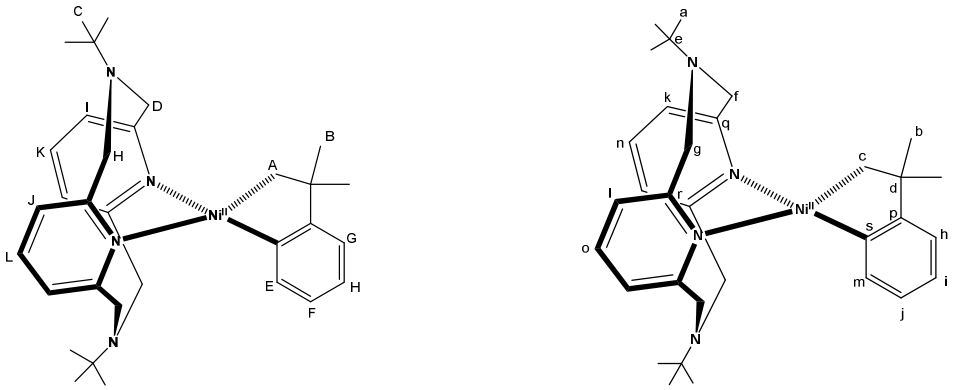


Figure S18. Proton (left) and carbon (right) structural assignments from NMR experiments for (^{tBu}N4)Ni^{II}(cycloneophyl)

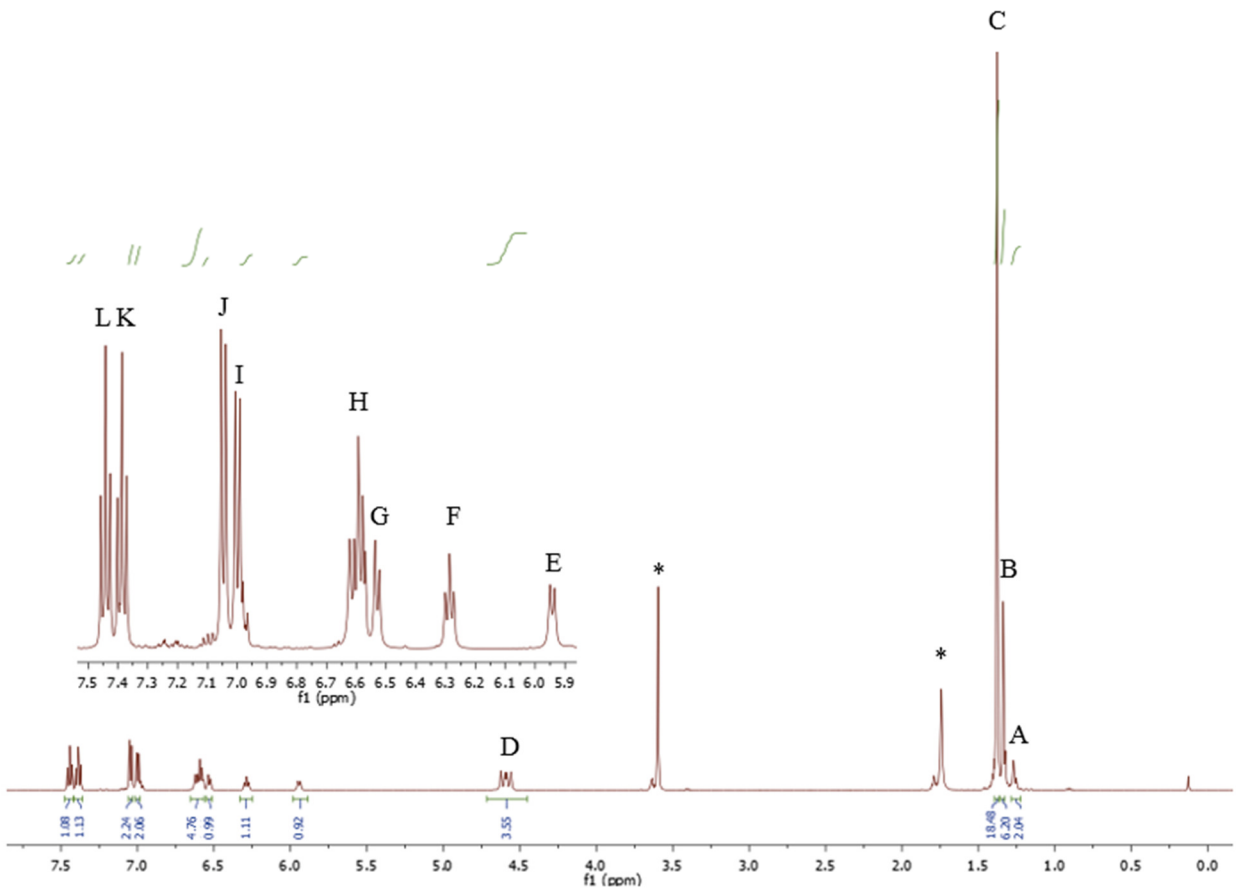


Figure S19. ^{1}H NMR spectrum of (^{tBu}N4)Ni^{II}(cycloneophyl) in THF-d_8 (500 MHz). Peaks marked with an asterisk correspond to a trace amount of solvent (THF-d_8).

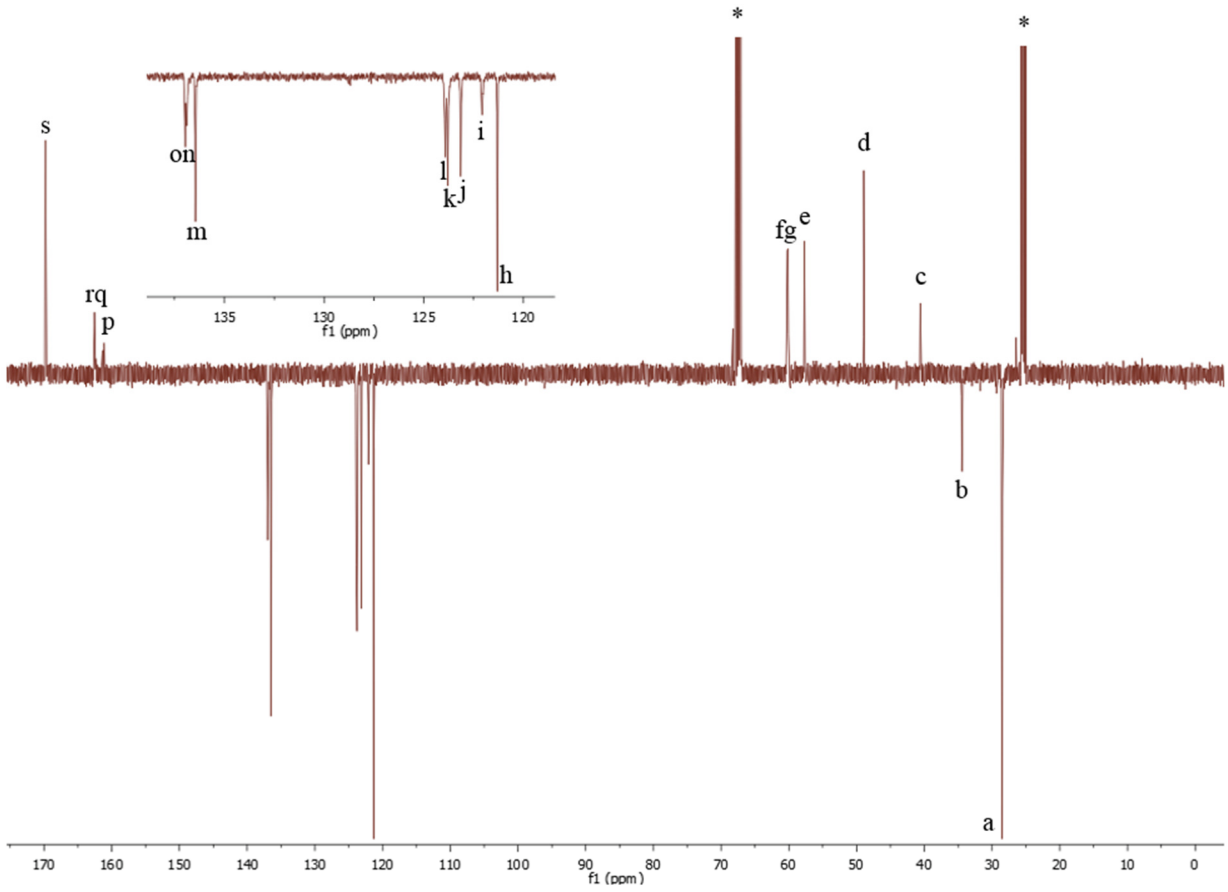


Figure S20. APT spectrum of (^{tBu}N4)Ni^{II}(cycloneophyl) in THF-d_8 (500 MHz). Peaks marked with an asterisk correspond to a trace amount of solvent (THF-d_8).

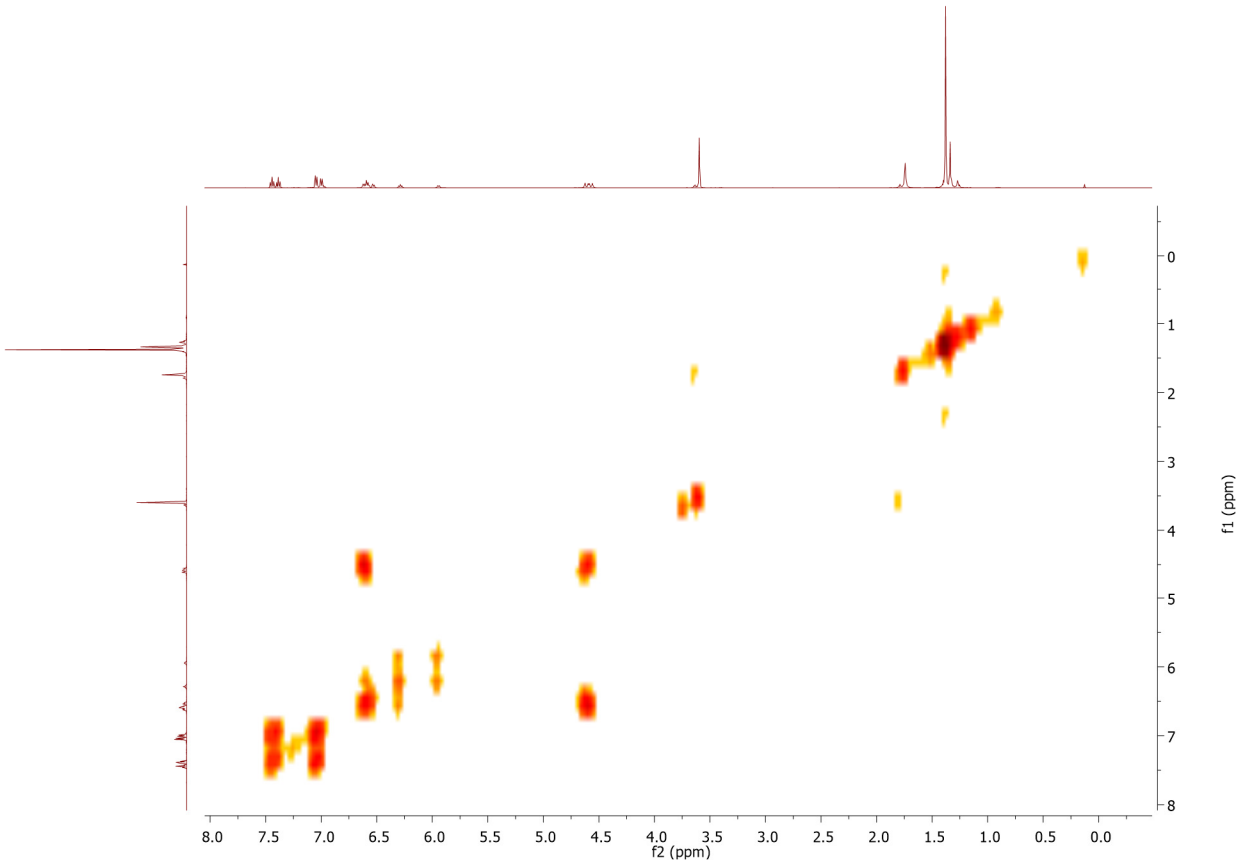


Figure S21. ^{1}H-^{1}H gCOSY spectrum of (^{tBu}N4)Ni^{II}(cycloneophyl) in THF-d_8 (500 MHz).

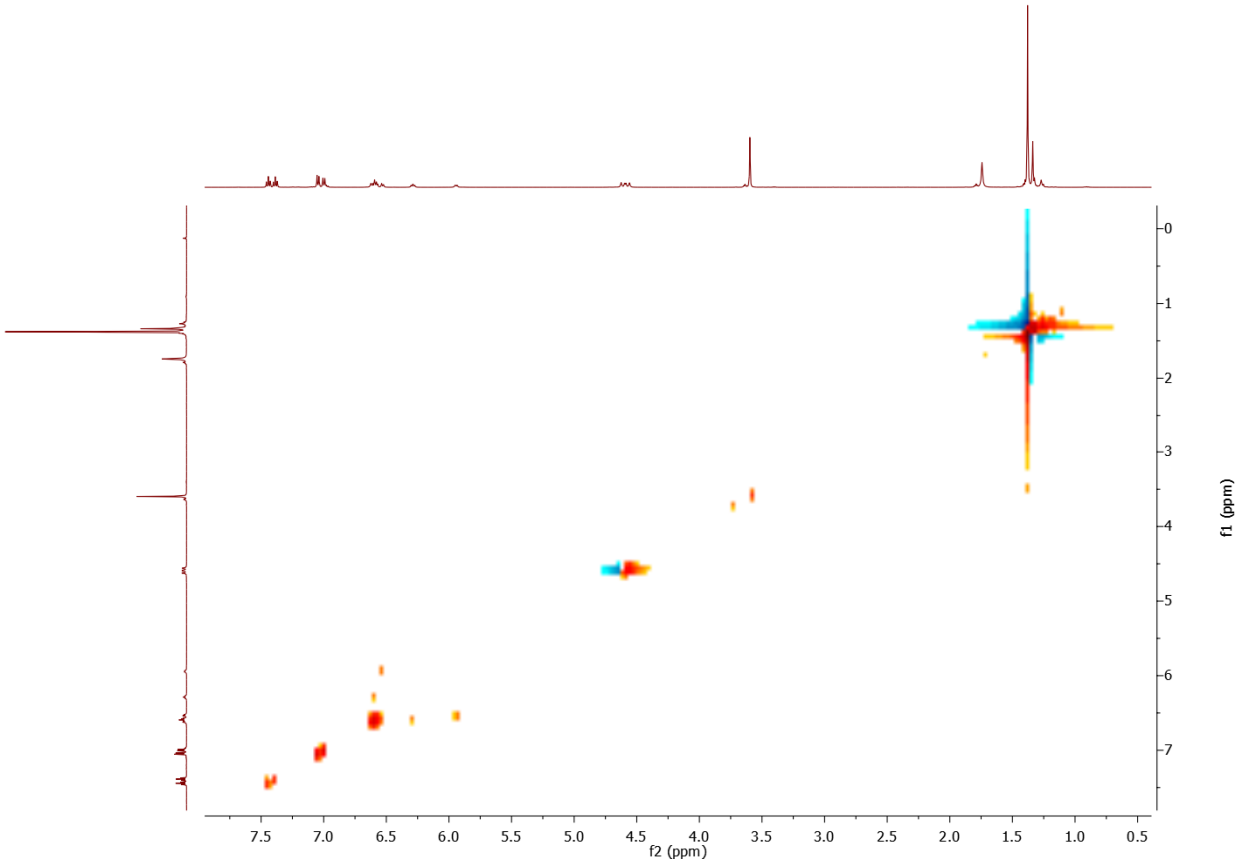


Figure S22. ^{1}H-^{1}H TOXY spectrum of (^{tBu}N4)Ni^{II}(cycloneophyl) in THF-d_8 (500 MHz).

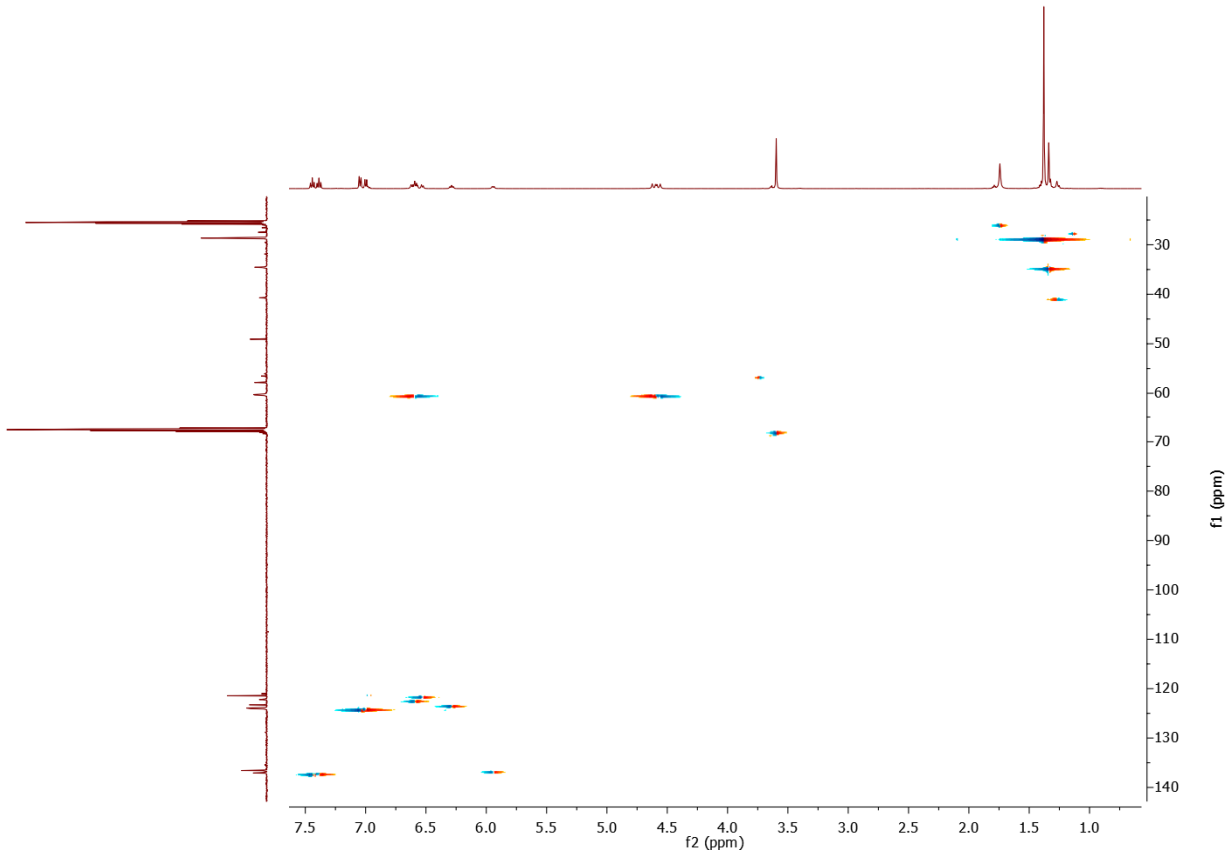


Figure S23. ^{1}H-^{13}C HSQC spectrum of (^{tBu}N4)Ni^{II}(cycloneophyl) in THF-d_8 (500 MHz).

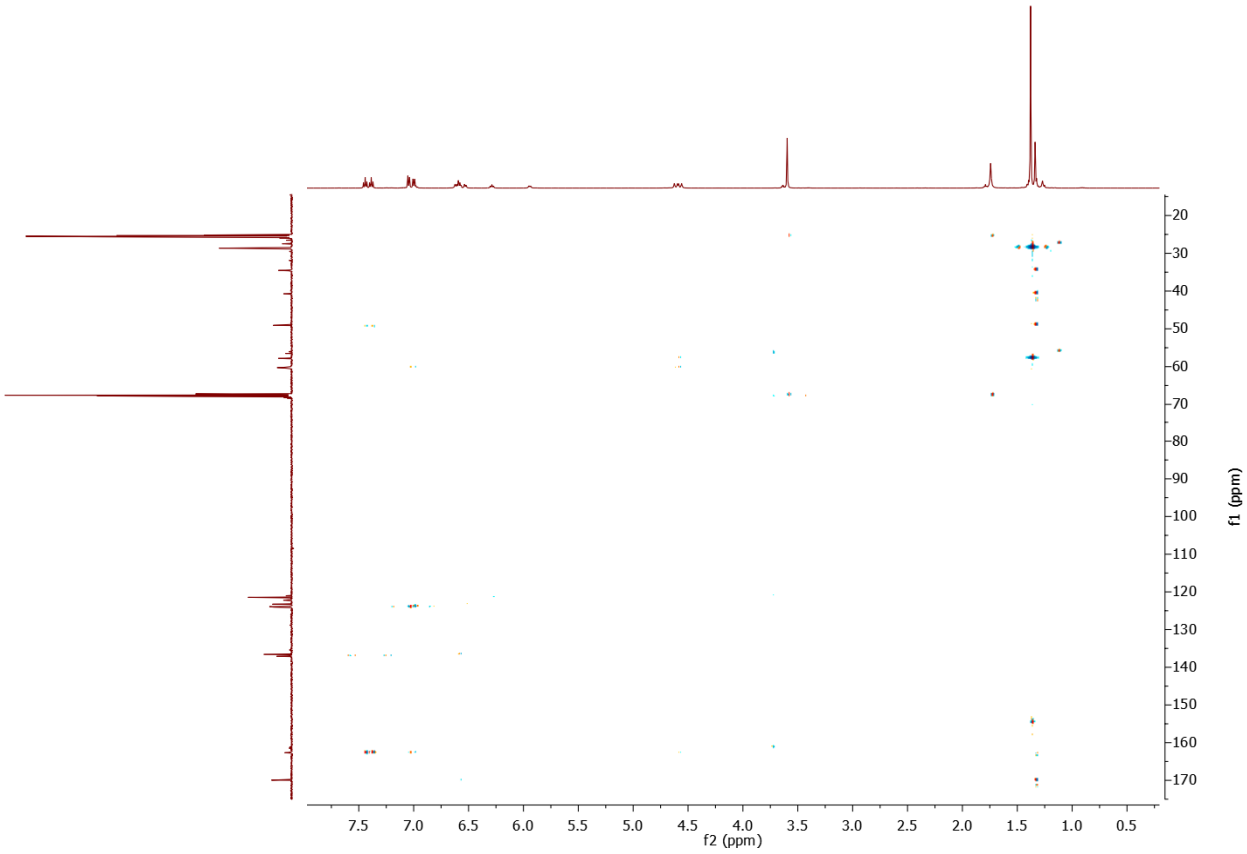


Figure S24. ^{1}H-^{13}C HMBC spectrum of (^{tBu}N4)Ni^{II}(cycloneophyl) in THF-d_8 (500 MHz).

III. Cyclic Voltammograms (CVs) of Isolated (^{R}N4)Ni^{II}(cycloneophyl) Complexes

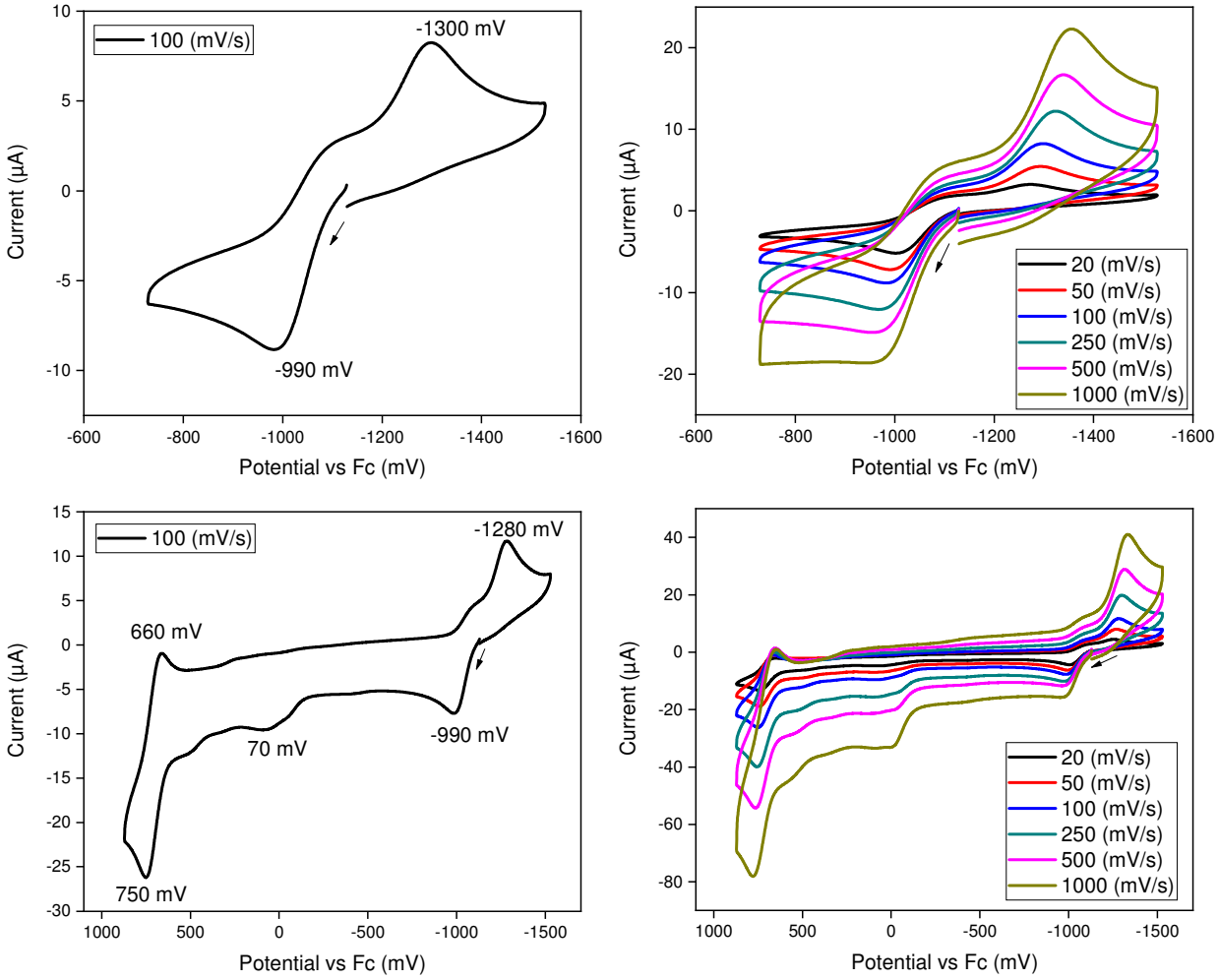


Figure S25. CVs of (^{TsMe}N4)Ni^{II}(cycloneophyl) in 0.1 M nBu$_4$NPF$_6$/MeCN at RT, at 100 mV/s scan rate (left) and variable scan rates (right).

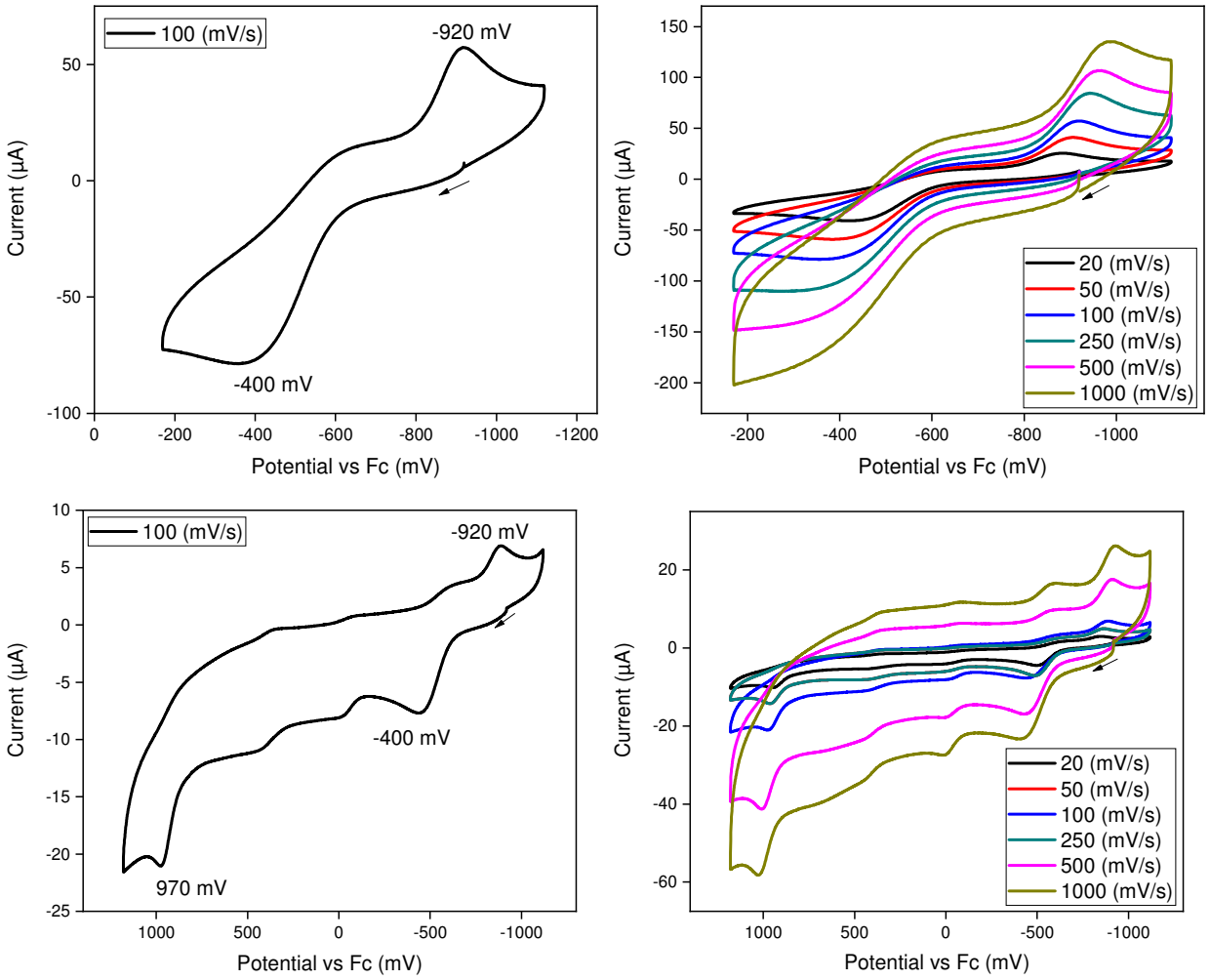


Figure S26. CVs of (^{Ts}N4)Ni^{II}(cycloneophyl) in 0.1 M *n*Bu$_4$NPF$_6$/MeCN at RT, at 100 mV/s scan rate (left) and variable scan rates (right).

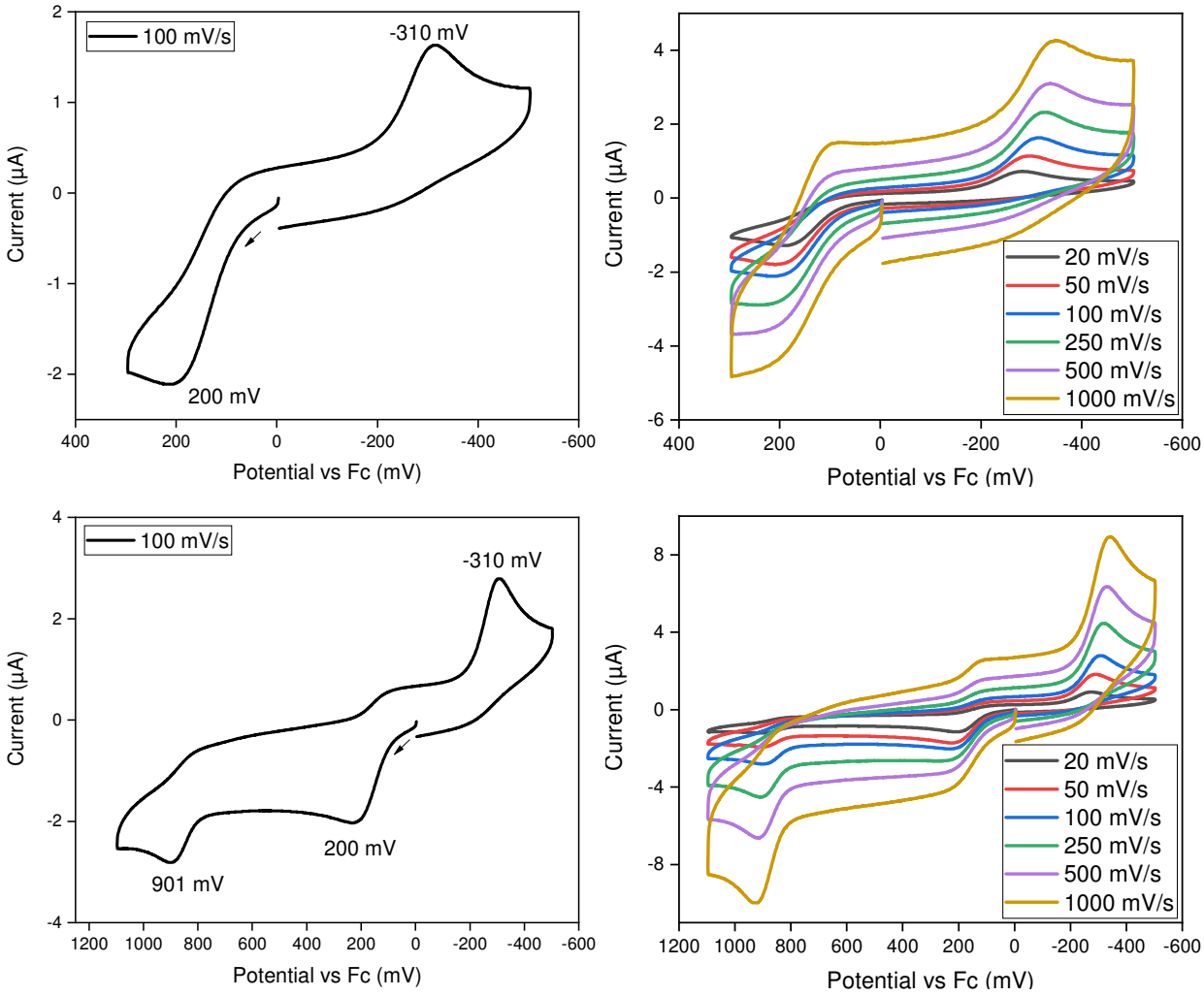


Figure S27. CVs of (^{tBu}N4)Ni^{II}(cycloneophyl) in 0.1 M *n*Bu$_4$NPF$_6$/MeCN at RT, at 100 mV/s scan rate (left) and variable scan rates (right).

IV. UV-Vis Spectra of Isolated (^{R}N4)Ni$^{II/III}$(cycloneophyl) Complexes

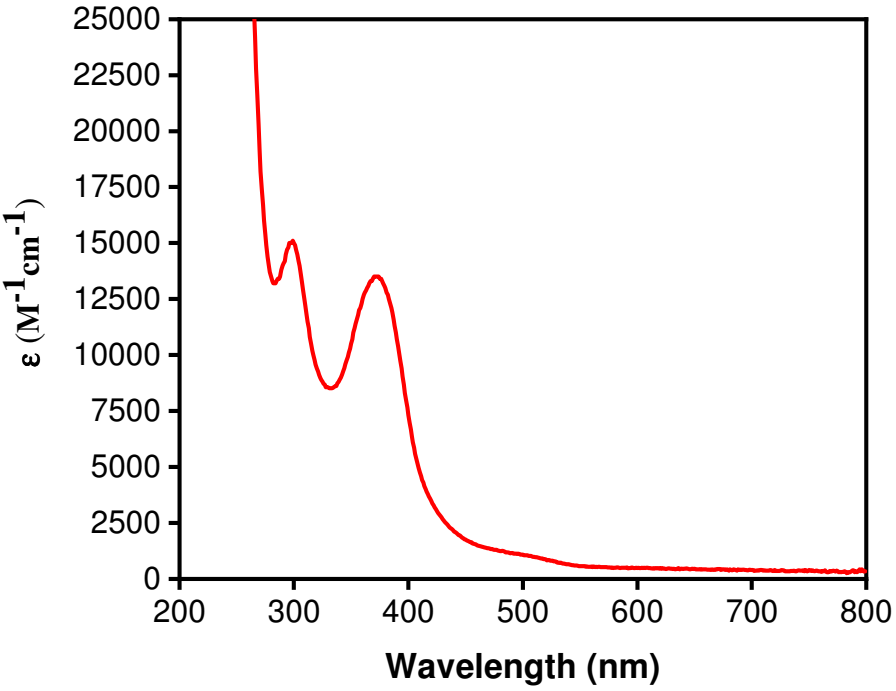


Figure S28. UV-visible spectrum of (^{TsMe}N4)Ni^{II}(cycloneophyl) in THF (1.25*10^{-4} M).

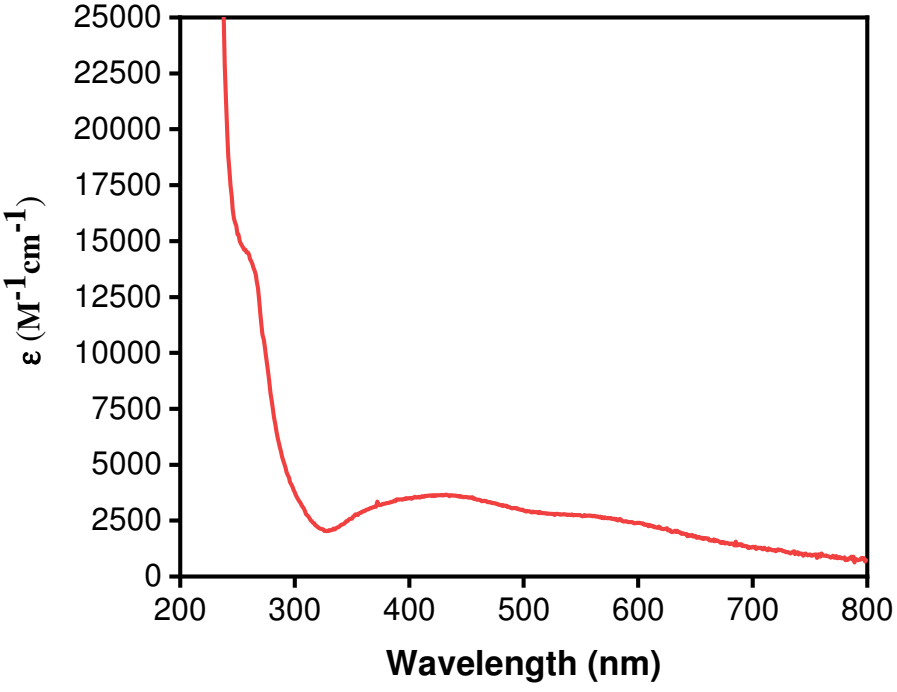


Figure S29. UV-visible spectrum of (^{TsMe}N4)Ni^{III}(cycloneophyl) in THF (6.25*10^{-5} M).

V. Simulation of EPR Spectra of Isolated (^{R}N4)Ni^{III}(cycloneophyl) Complexes

General procedure for the isolation of the Ni^{III} complexes for EPR. An EPR tube was charged with a solution of a complex (^{TsMe}N4)Ni^{II}(cycloneophyl), (^{Ts}N4)Ni^{II}(cycloneophyl) or (^{tBu}N4)Ni^{II}(cycloneophyl) in MeCN or THF. A PrCN (butyronitrile) or methylTHF (MeTHF) solution containing one equivalent of ferrocenium hexafluorophosphate ($FcPF_6$) or acetylferrocenium tetrafluoroborate ($^{Ac}FcBF_4$) was then added. The resulting solution of 1:3 MeCN:PrCN or 1:3 THF:MeTHF was shaken for 5 seconds and then frozen in liquid nitrogen. (lw = linewidth)

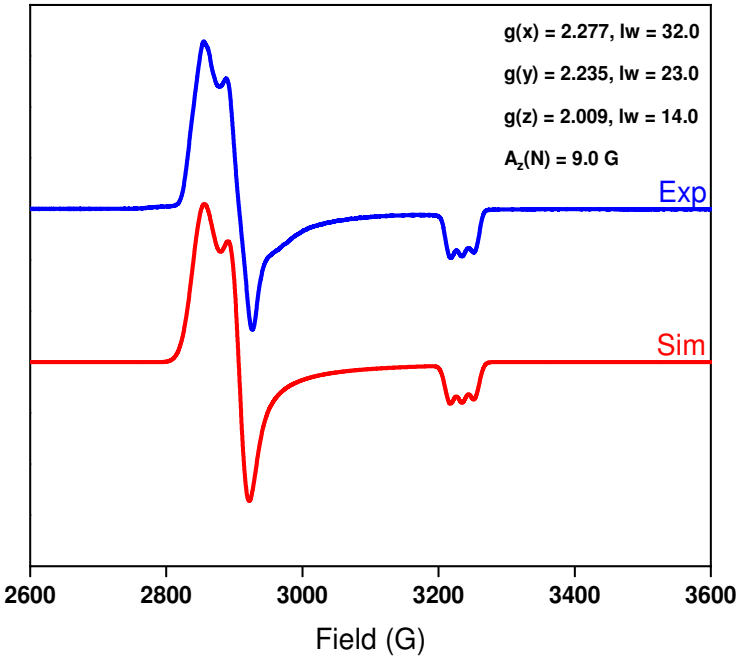


Figure S30. Experimental and simulated EPR spectra of isolated [(^{TsMe}N4)Ni^{III}(cycloneophyl)]PF_6 in frozen 1:3 MeCN:PrCN (77 K). Experimental conditions: frequency ≈ 9.097 GHz, power = 1 mW, modulation frequency = 100 kHz, modulation amplitude = 3 G, time constant = 0.3 s.

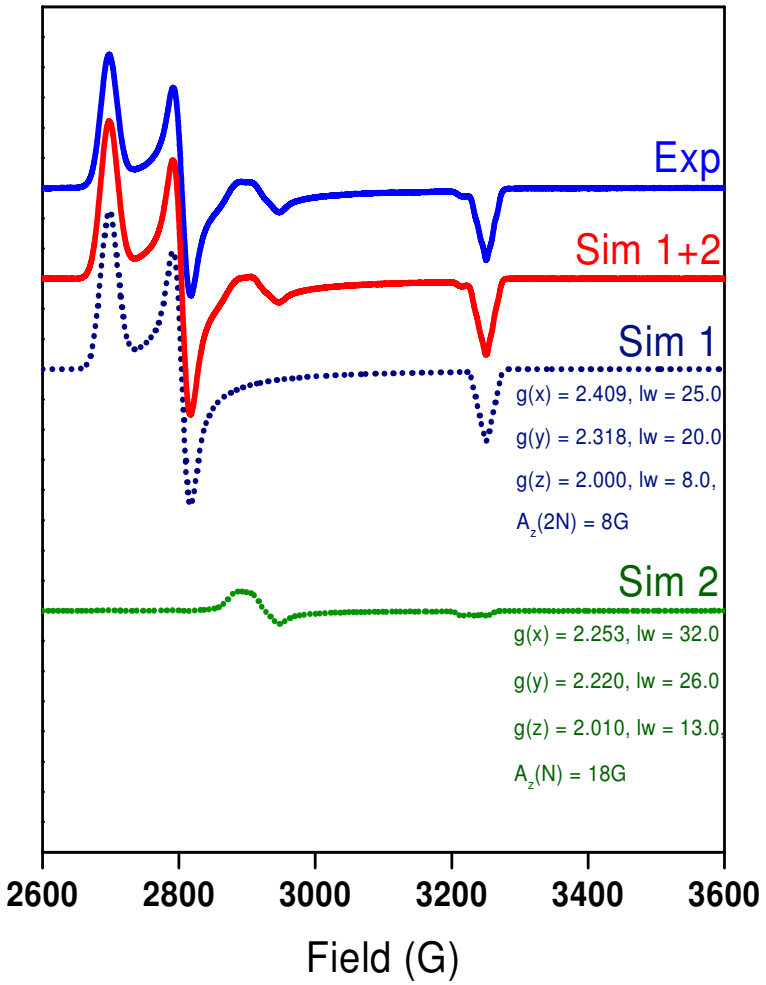


Figure S31. Experimental and simulated EPR spectra of isolated [(^{Ts}N4)Ni^{III}(cycloneophyl)]PF_6 in frozen 1:3 MeCN:PrCN (77 K). The simulation of the simulations 1 and 2 were added together in a 19:1 ratio to result in the experimental spectra. Experimental conditions: frequency ≈ 9.097 GHz, power = 1 mW, modulation frequency = 100 kHz, modulation amplitude = 3 G, time constant = 0.3 s.

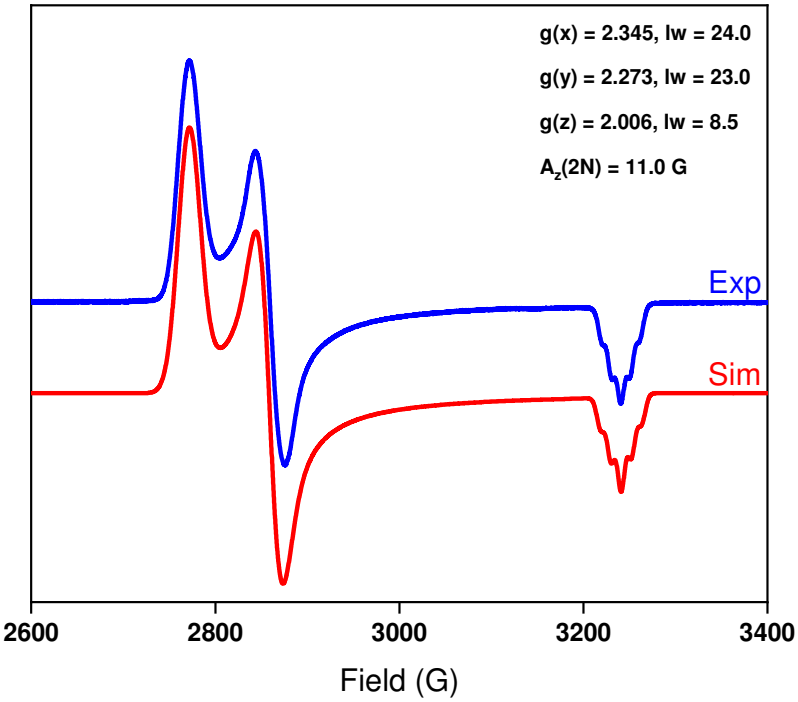


Figure S32. Experimental and simulated EPR spectra of isolated [(^{tBu}N4)Ni^{III}(cycloneophyl)]PF_6 in frozen 1:3 MeCN:PrCN (77 K). Experimental conditions: frequency ≈ 9.097 GHz, power = 1 mW, modulation frequency = 100 kHz, modulation amplitude = 3 G, time constant = 0.3 s.

VI. Reactivity of (^{R}N)Ni(cycloneophyl) Complexes

General procedure for the reactivity studies of (^{R}N4)Ni(cycloneophyl) complexes (R = Me, TsMe, Ts and tBu). In N_2-filled glove box, a solution of 5-7 mg of (^{R}N4)Ni(cycloneophyl) complex in 2.0 mL of MeCN was added into a 5 mL vial containing 1,3,5-trimethoxybenzene as an internal standard. To this solution different oxidants were added (bubbled O_2 + 10% water, H_2O_2, ^{m}CPBA, $PhI(OAc)_2$, NFTPT, TDTT and XeF_2) and stirred for 14 hours at 70 °C. Then 1 mL of 14% perchloric acid was added and stirred for an additional 4 hours at 70 °C. To this solution 3 mL of a saturated potassium carbonate solution was added. The solution was then extracted 3 times with 1 mL of diethyl ether and dried over potassium carbonate for 30 minutes. The solution was filtered and the yield of product(s) were obtained by GC/FID using 1,3,5-trimethoxybenzene as the internal standard. The identity of the products was confirmed by GC-MS.

Scheme S1. General reaction for the formation of the different GC-MS products.

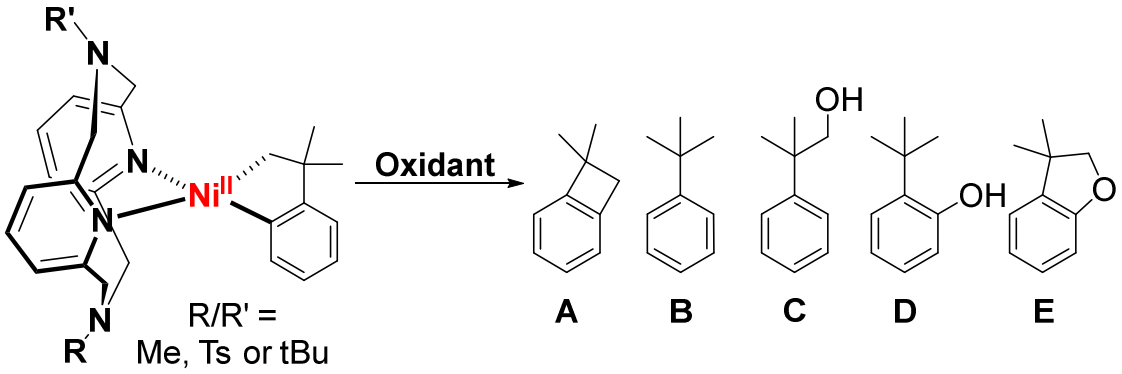


Table S1. Yields of the products from the reaction of (^{R}N4)Ni^{II}(cycloneophyl) with a variety of oxidants in MeCN.

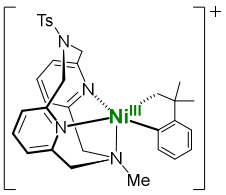
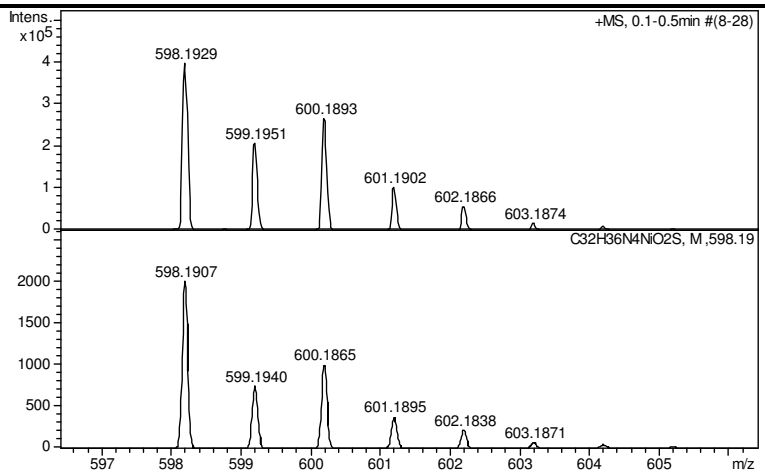
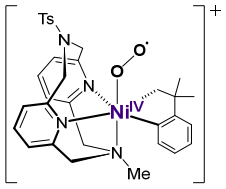
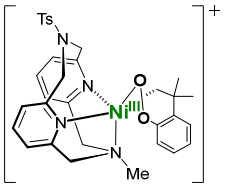
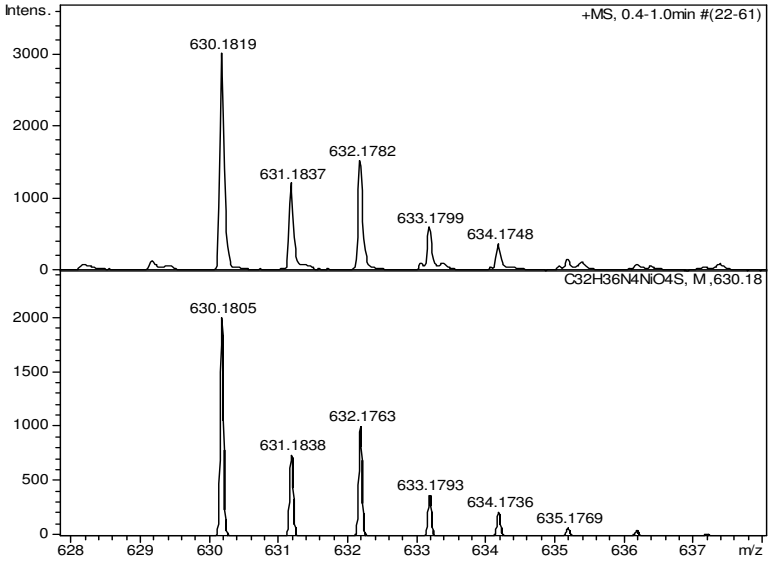
		Yields (%)					
Starting Complex	**Oxidants**	**A**	**B**	**C**	**D**	**E**	**Sum (%)**
(^{Ts}N4)Ni^{II}(cycloneophyl)	O_2	69	12	2	5	5	93
(^{TsMe}N4)Ni^{II}(cycloneophyl)	O_2	41	12	2	17	22	94
(^{Me}N4)Ni^{II}(cycloneophyl)	O_2	35	12	8	3	6	64
(^{tBu}N4)Ni^{II}(cycloneophyl)	O_2	27	6	0	0	0	33
(^{Ts}N4)Ni^{II}(cycloneophyl)	2 equiv. H_2O_2	65	12	0	6	3	86
(^{TsMe}N4)Ni^{II}(cycloneophyl)	2 equiv. H_2O_2	48	1	1	3	7	60
(^{Me}N4)Ni^{II}(cycloneophyl)	2 equiv. H_2O_2	45	2	0	2	6	55
(^{tBu}N4)Ni^{II}(cycloneophyl)	2 equiv. H_2O_2	17	0	0	0	0	17
(^{TsMe}N4)Ni^{II}(cycloneophyl)	2 equiv. *m*CPBA	37	11	4	7	11	70
(^{Ts}N4)Ni^{II}(cycloneophyl)	2 equiv. PhI(OAc)$_2$	42	10	n/a	n/a	n/a	52
(^{TsMe}N4)Ni^{II}(cycloneophyl)	2 equiv. PhI(OAc)$_2$	24	13	n/a	n/a	n/a	37
(^{Me}N4)Ni^{II}(cycloneophyl)	2 equiv. PhI(OAc)$_2$	4	22	n/a	n/a	n/a	26
(^{Ts}N4)Ni^{II}(cycloneophyl)	1 equiv. NFTPT	96	4	n/a	n/a	n/a	100
(^{TsMe}N4)Ni^{II}(cycloneophyl)	1 equiv. NFTPT	32	27	n/a	n/a	n/a	59
(^{Me}N4)Ni^{II}(cycloneophyl)	1 equiv. NFTPT	17	39	n/a	n/a	n/a	56
(^{tBu}N4)Ni^{II}(cycloneophyl)	1 equiv. NFTPT	14	44	n/a	n/a	n/a	48
(^{Ts}N4)Ni^{II}(cycloneophyl)	1 equiv. TDTT	42	9	n/a	n/a	n/a	51
(^{TsMe}N4)Ni^{II}(cycloneophyl)	1 equiv. TDTT	33	15	n/a	n/a	n/a	48
(^{Me}N4)Ni^{II}(cycloneophyl)	1 equiv. TDTT	7	19	n/a	n/a	n/a	26
(^{tBu}N4)Ni^{II}(cycloneophyl)	1 equiv. TDTT	6	20	n/a	n/a	n/a	26
(^{Ts}N4)Ni^{II}(cycloneophyl)	1 equiv. XeF_2	99	1	n/a	n/a	n/a	100
(^{TsMe}N4)Ni^{II}(cycloneophyl)	1 equiv. XeF_2	50	16	n/a	n/a	n/a	66
(^{Me}N4)Ni^{II}(cycloneophyl)	1 equiv. XeF_2	20	40	n/a	n/a	n/a	60

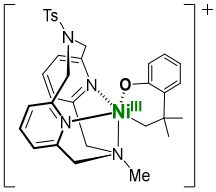
VII. Cryo-ESI-MS of (^{R}N)Ni(cycloneophyl) Intermediates

General procedure for the oxidation studies of (^{R}N4)Ni(cycloneophyl) intermediates (R = Me, TsMe and Ts) studied by low temperature MS. A solution of 1mM (^{R}N4)Ni^{II}(cycloneophyl) complex in 10% H_2O/acetone was saturated with O_2. To a second solution of 1 mM (^{R}N4)Ni^{II}(cycloneophyl) complex in acetone, 1mM of H_2O_2 was added. To both solutions a drop of perchloric acid was added as the proton source, and then the reaction mixture was analyzed first at -80 °C by cryo-ESI-MS, and then at RT.

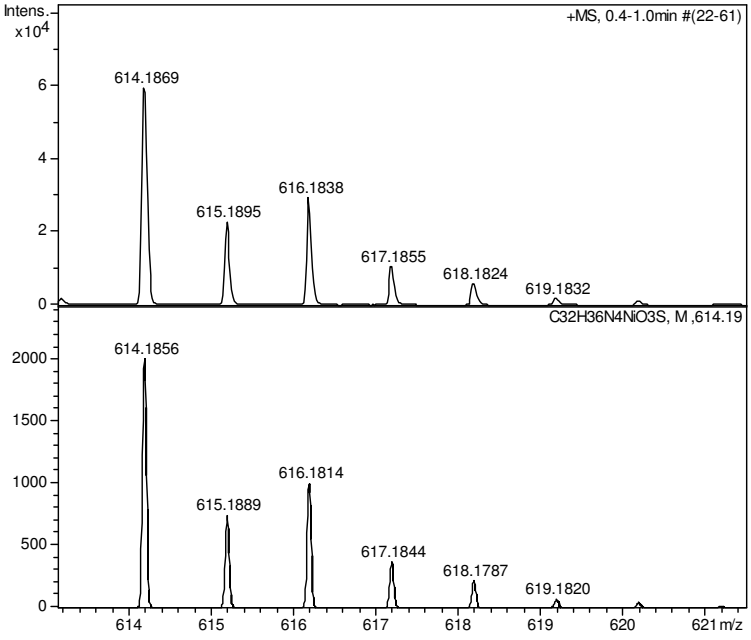
To a second solution of 1 mM (or 0.13 mM) of (^{R}N4)Ni^{II}(cycloneophyl) in acetone, one equivalent of aqueous H_2O_2 was added. To both solutions a drop of perchloric acid was added as the proton source, and the reaction mixtures were analyzed first at -80 °C by cryo-ESI-MS, and then at RT.

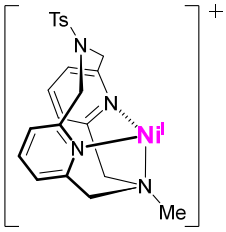
Table S2. Cryo-ESI-MS results for the oxidation of (^{TsMe}N4)Ni^{II}(cycloneophyl) with O_2 in 10% H_2O/acetone.

Proposed Intermediates	Chemical Formula and m/z	Spectra
	$C_{32}H_{36}N_4NiO_2S$, 598.1912	
 OR  Proposed structures	$C_{32}H_{36}N_4NiO_4S$, 630.1805 <u>Note</u>: this m/z value corresponds to complex **2**$^+$+O_2	

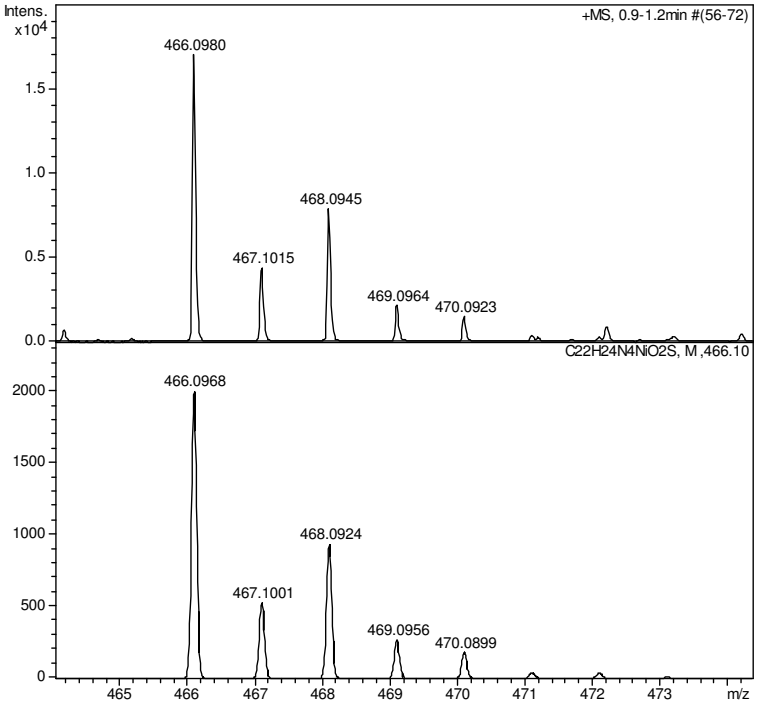


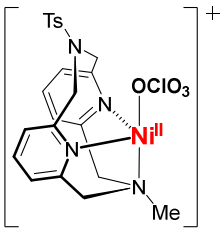
$C_{32}H_{36}N_4NiO_3S$, 614.1856





$C_{22}H_{24}N_4NiO_2S$, 466.0968





$C_{22}H_{24}ClN_4NiO_6S$,
565.0453

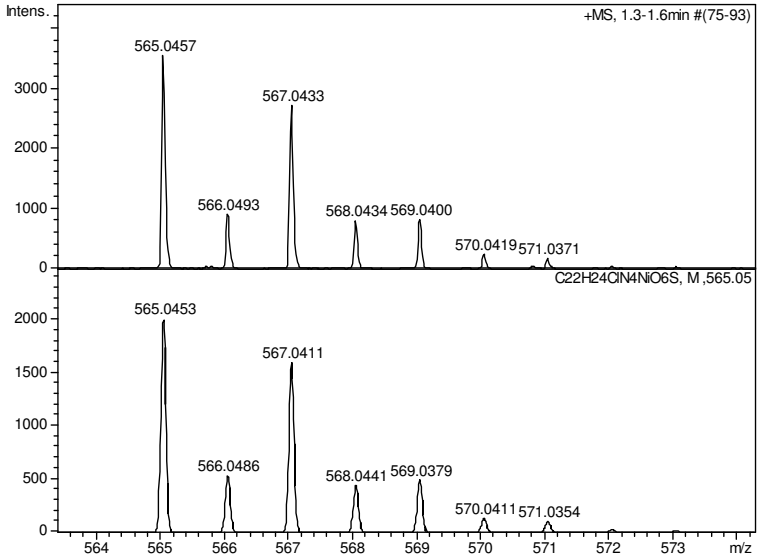
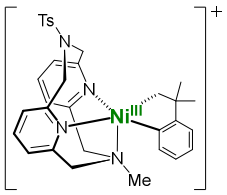
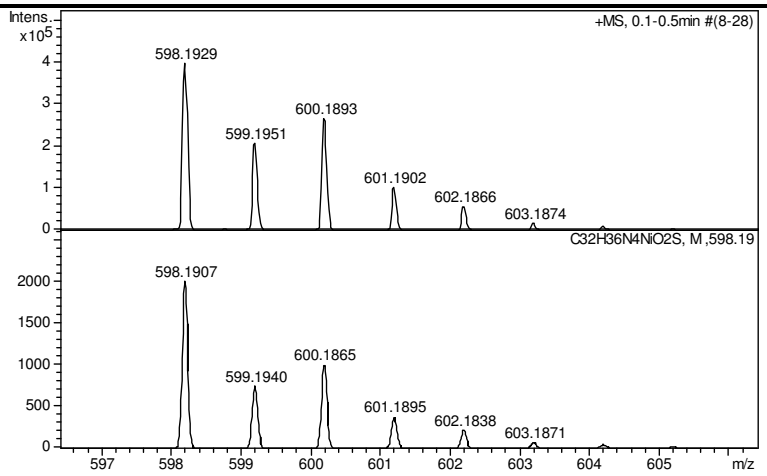
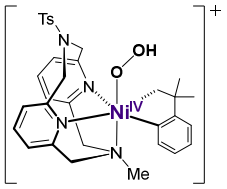
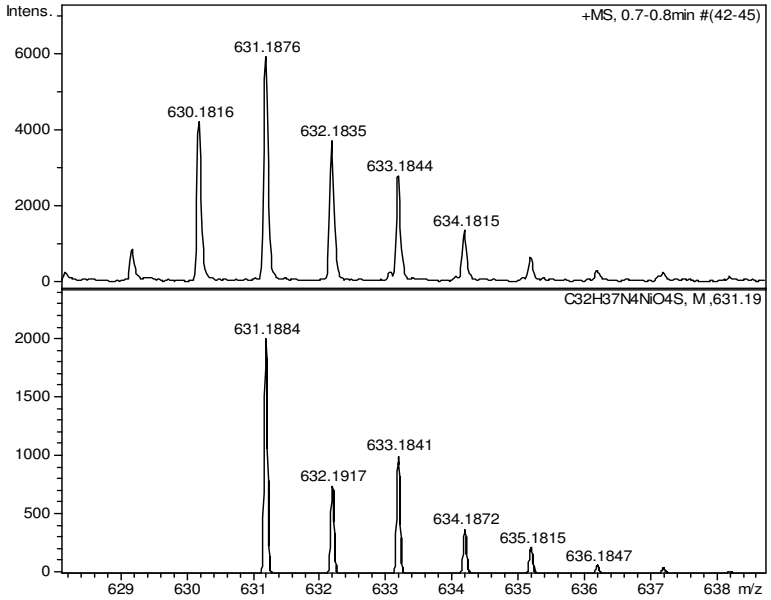
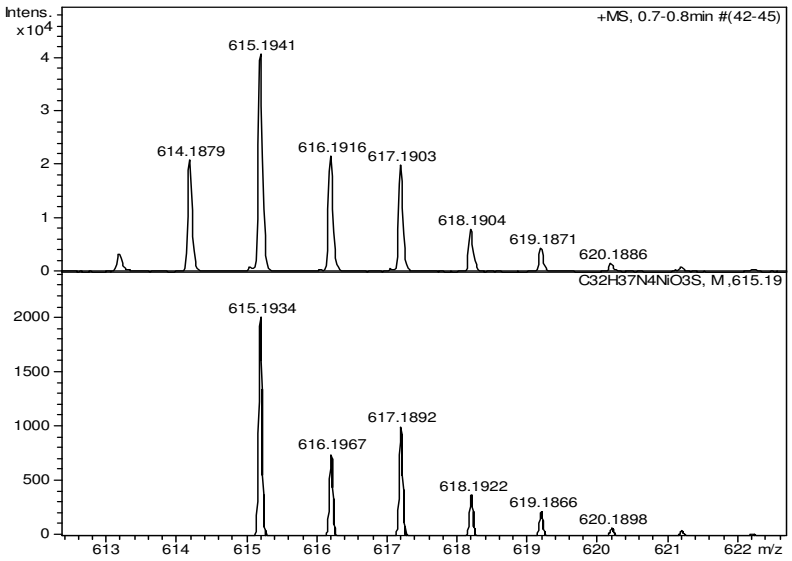


Table S3. Cryo-ESI-MS results for the oxidation of (^{TsMe}N4)Ni^{II}(cycloneophyl) with H_2O_2 in 10% H_2O/acetone.

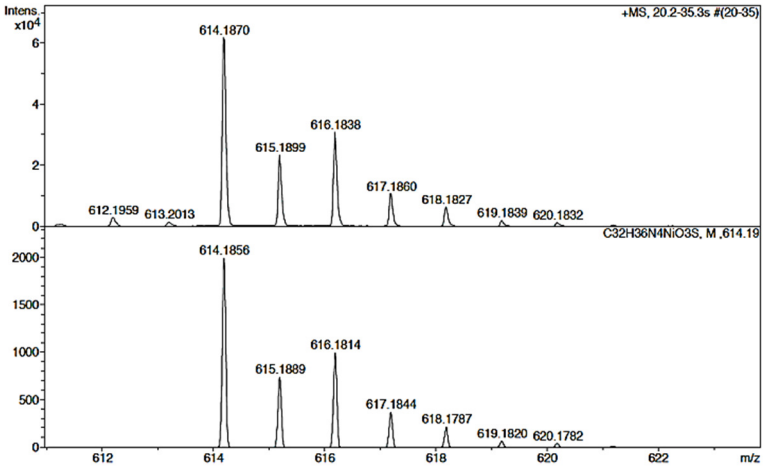
Intermediates	Chemical Formula and m/z	Spectra
	$C_{32}H_{36}N_4NiO_2S$, 598.1907	
	$C_{32}H_{37}N_4NiO_4S$, 631.1884 Note: The experimental isotopic pattern is best simulated with a 49:51 mixture of the m/z 630.1805 (complex **2**$^+$+O_2, see Table S32) and this m/z 631.1884 species	

$C_{32}H_{37}N_4NiO_3S$, 615.1934

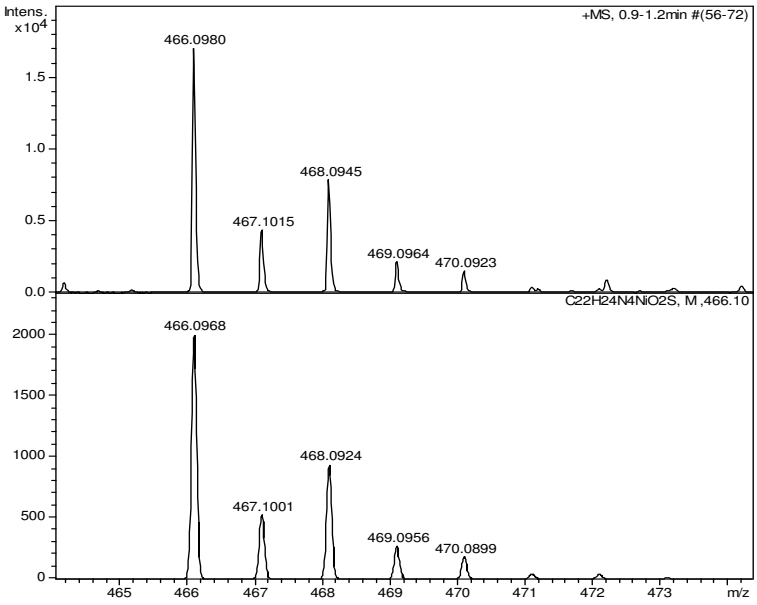
<u>Note</u>: The experimental isotopic pattern is best simulated with a 39:61 mixture of the m/z 614.1856 species (see below), and this m/z 615.1934 species

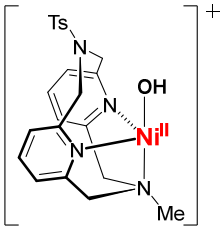


$C_{32}H_{36}N_4NiO_3S$, 614.1856



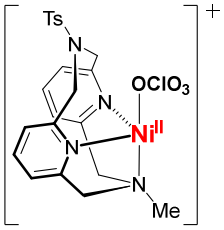
$C_{22}H_{24}N_4NiO_2S$, 466.0968





$C_{22}H_{25}N_4NiO_3S$, 483.0995

Not observed



$C_{22}H_{24}ClN_4NiO_6S$, 565.0453

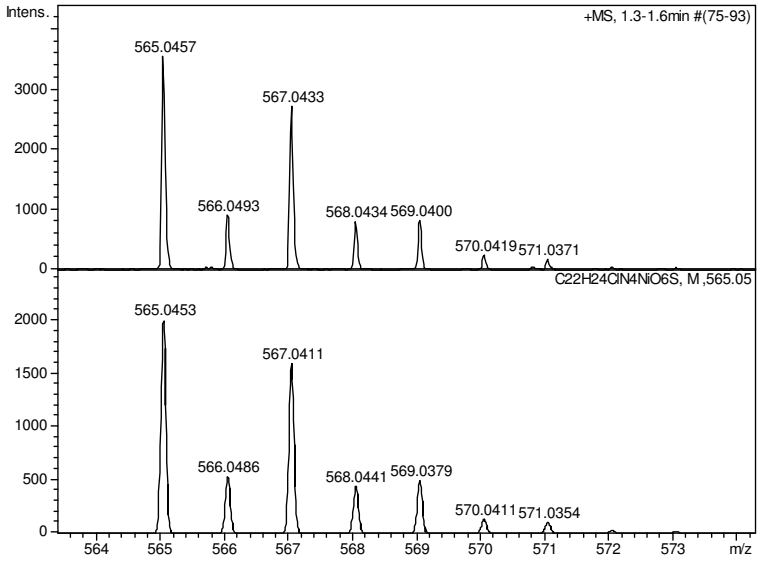
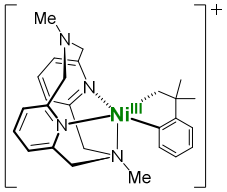
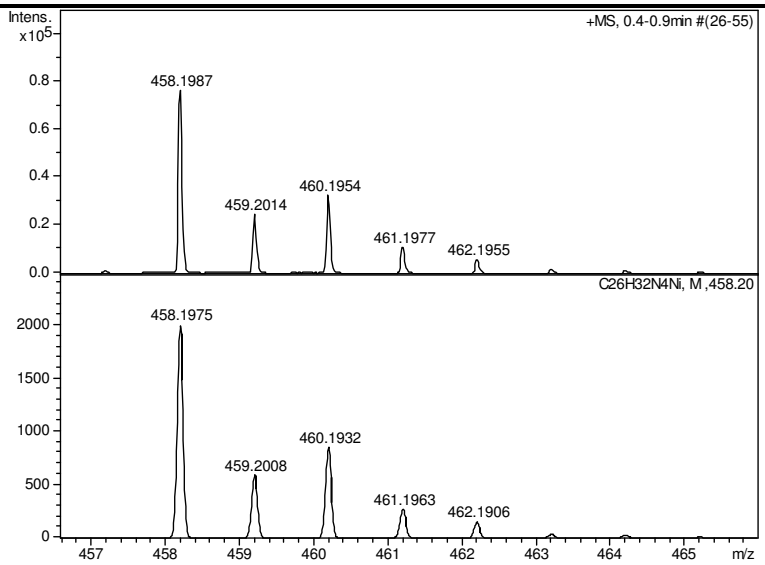
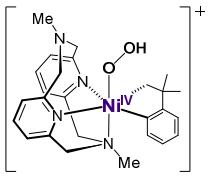
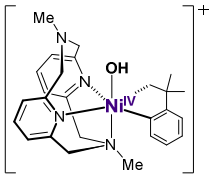
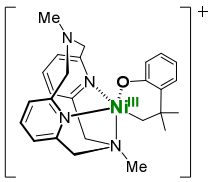
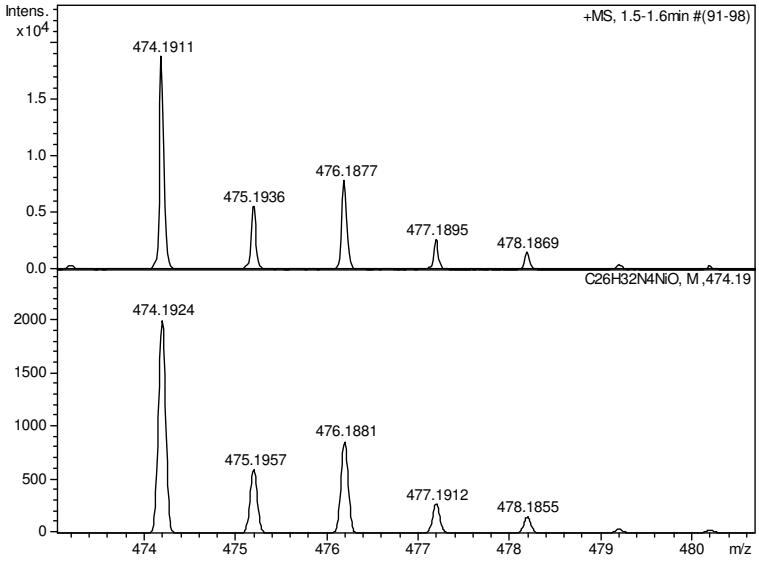
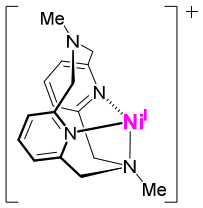
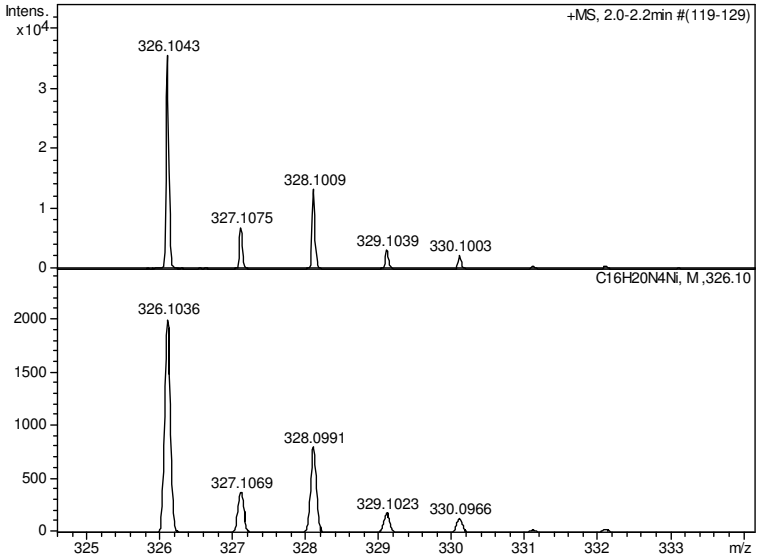


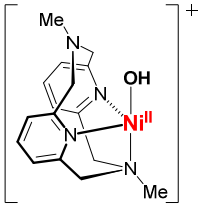
Table S4. Cryo-ESI-MS results for the oxidation of (^{Me}N4)Ni^{II}(cycloneophyl) with H_2O_2 in 10% H_2O/acetone.

Intermediates	Chemical Formula and m/z	Spectra
	$C_{26}H_{32}N_4Ni$, 458.1975	
	$C_{26}H_{33}N_4NiO_2$, 491.1952	Not observed
	$C_{26}H_{33}N_4NiO$, 475.2002	Not observed
	$C_{26}H_{32}N_4NiO$, 474.1924	



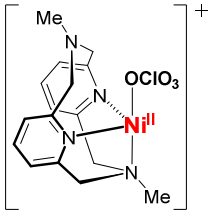
$C_{16}H_{20}N_4Ni$,
326.1036





$C_{16}H_{21}N_4NiO$,
343.1063

Not observed



$C_{16}H_{20}ClN_4NiO_4$,
425.0521

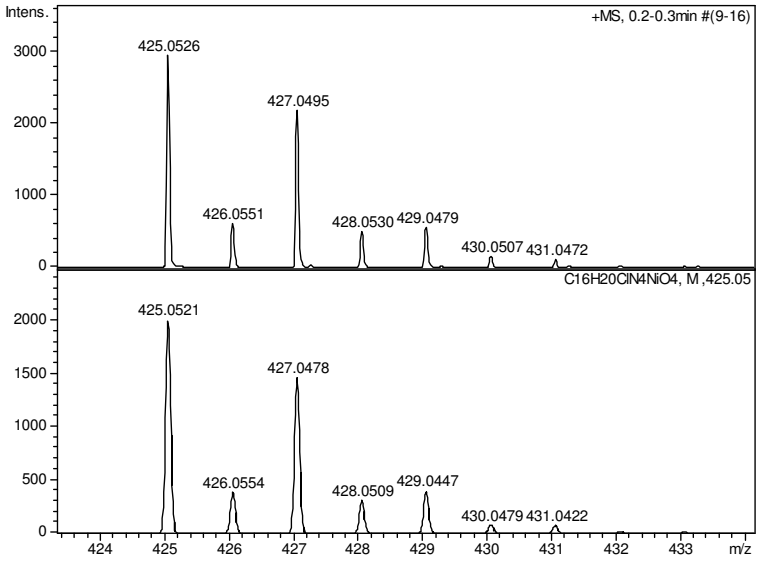
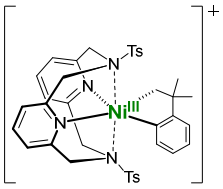
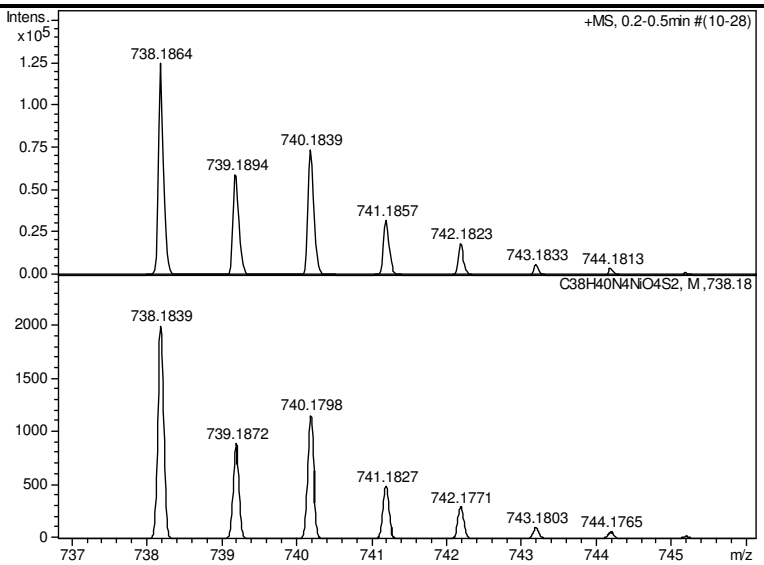
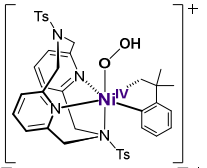
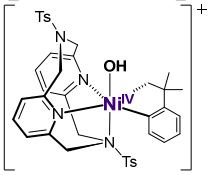
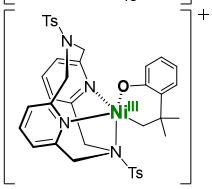
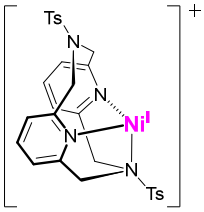
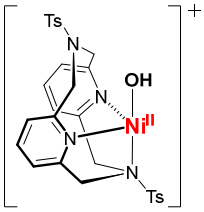
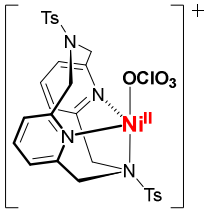
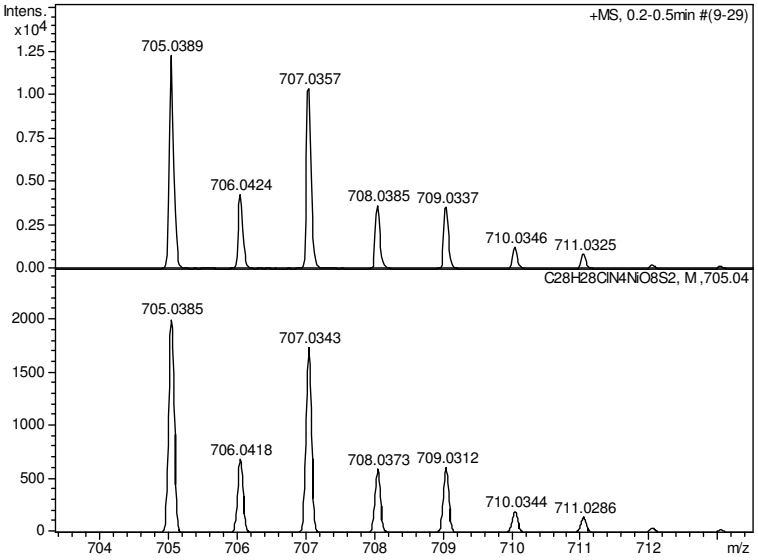


Table S5. Cryo-ESI-MS results for the oxidation of (^{Ts}N4)Ni^{II}(cycloneophyl) with H_2O_2 in 10% H_2O/acetone.

Intermediates	Chemical Formula and m/z	Spectra
	$C_{38}H_{40}N_4NiO_4S_2$, 738.1839 <u>Note</u>: the signal corresponding to this species is very weak.	
	$C_{38}H_{31}N_4NiO_6S_2$, 771.1816	Not observed
	$C_{38}H_{41}N_4NiO_5S_2$, 755.1866	Not observed
	$C_{38}H_{40}N_4NiO_5S_2$, 754.1788	Not observed
	$C_{28}H_{28}N_4NiO_4S_2$, 606.0900	Not observed
	$C_{28}H_{29}N_4NiO_5S_2$, 623.0927	Not observed

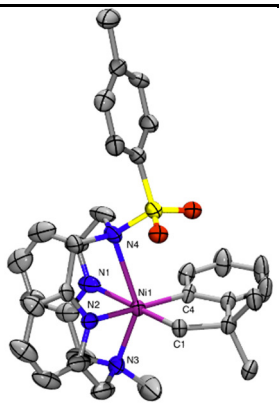
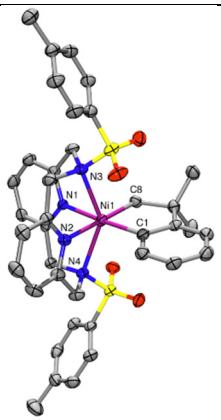
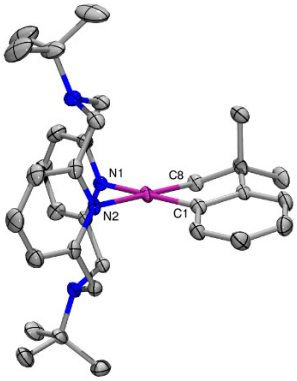


$C_{28}H_{28}ClN_4NiO_8S_2$,
705.0385



VIII. ORTEP Representations of Isolated (^{R}N4)Ni(cycloneophyl) Complexes

Table S6. ORTEP representation with 50% probability thermal ellipsoids.

Complex Name	Structure	Bond lengts (Å)	
(^{TsMe}N4)Ni^{III}(cycloneophyl)BF_4 (**2^{+}·BF_4**)		Ni(1)-C(1)	1.938(9)
		Ni(1)-C(4)	1.938(4)
		Ni(1)-N(1)	2.182(5)
		Ni(1)-N(2)	1.867(4)
		Ni(1)-N(3)	2.199(4)
		Ni(1)-N(4)	2.527
(^{Ts}N4)Ni^{III}(cycloneophyl) SbF_6 (**3^{+}·SbF_6**)		Ni(1)-C(1)	1.933(3)
		Ni(1)-C(8)	1.982(3)
		Ni(1)-N(1)	1.993(3)
		Ni(1)-N(2)	2.010(3)
		Ni(1)-N(3)	2.360(3)
		Ni(1)-N(4)	2.436(3)
(^{tBu}N4)Ni^{II}(cycloneophyl) (**4**)		Ni(1)-C(1)	1.887(3)
		Ni(1)-C(8)	1.938(3)
		Ni(1)-N(1)	1.944(3)
		Ni(1)-N(2)	1.976(2)

IX. X-ray Structure Determinations of (^{R}N4)Ni(cycloneophyl) Complexes

X-ray quality crystals of [(^{TsMe}N4)Ni^{III}(cycloneophyl)]BF_4 and [(^{Ts}N4)Ni^{III}(cycloneophyl)] SbF_6 were obtained by a slow diethyl ether diffusion into acetonitrile at -35 °C. X-ray quality crystals of (^{tBu}N4)Ni^{II}(cycloneophyl) were obtained by a slow pentane diffusion into tetrahydrofuran at -35 °C.

Suitable crystals of appropriate dimensions were mounted on Mitgen loops in random orientations. Preliminary examination and data collection were performed using a Bruker Kappa Apex-II Charge Coupled Device (CCD) Detector system single crystal X-Ray diffractometer equipped with an Oxford Cryostream LT device. Data were collected using graphite monochromated Mo Kα radiation (λ= 0.71073 Å) from a fine focus sealed tube X-Ray source. Preliminary unit cell constants were determined with a set of 36 narrow frame scans.

Typical data sets consist of a combination of ω and ϕ scan frames with typical scan width of 0.5° and counting time of 15-30 seconds/frame at a crystal to detector distance of ~4.0 cm. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. Apex II and SAINT software packages (*Bruker Analytical X-Ray, Madison, WI, 2008*) were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by global refinement of reflections from the complete data set. Data were corrected for systematic errors using SADABS (*Bruker Analytical X-Ray, Madison, WI, 2008*) based on the Laue symmetry using equivalent reflections.

Structure solutions and refinement were carried out using the SHELXTL- PLUS software package (*Sheldrick, G. M. (2008), Bruker-SHELXTL, Acta Cryst. A64,112-122*). The structures were refined with full matrix least-squares refinement by minimizing $\Sigma w(F_o^2-F_c^2)^2$. All non-hydrogen atoms were refined anisotropically to convergence. Typically, H atoms are added at the calculated positions in the final refinement cycles.

Acknowledgement: Funding from the National Science Foundation (MRI, CHE-0420497) for the purchase of the ApexII diffractometer is acknowledged.

Crystal data and structure refinement for lm9017. (^{TsMe}N4)Ni^{III}(cycloneophyl)$^{+}$

Identification code	l9017/lt/SMS_TsMeN4Ni(Neophyl)_ThBF4	
Empirical formula	C32 H36 B F4 N4 Ni O2 S	
Formula weight	686.23	
Temperature	143(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 21.2777(18) Å	α = 90°.
	b = 8.9357(7) Å	β = 112.115(4)°.
	c = 17.3493(15) Å	γ = 90°.
Volume	3056.0(4) Å^3	
Z	4	
Density (calculated)	1.492 Mg/m^3	
Absorption coefficient	0.766 mm^{-1}	
F(000)	1428	
Crystal size	0.593 x 0.251 x 0.104 mm^3	
Theta range for data collection	2.066 to 25.770°.	
Index ranges	-25≤h≤25, -10≤k≤10, -21≤l≤11	
Reflections collected	22586	
Independent reflections	5805 [R(int) = 0.0689]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7453 and 0.6336	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5805 / 183 / 513	
Goodness-of-fit on F^2	1.013	
Final R indices [I>2sigma(I)]	R1 = 0.0598, wR2 = 0.1125	
R indices (all data)	R1 = 0.1351, wR2 = 0.1415	
Largest diff. peak and hole	0.657 and -0.497 e.Å^{-3}	

Bond lengths [Å] and angles [°] for lm9017.

Ni(1)-N(2)	1.867(4)	C(6)-H(6)	0.9500
Ni(1)-C(1)	1.938(9)	C(7)-C(8)	1.3900
Ni(1)-C(4)	1.938(4)	C(7)-H(7)	0.9500
Ni(1)-N(1)	2.182(5)	C(8)-H(8)	0.9500
Ni(1)-N(3)	2.199(4)	C(9)-H(9A)	0.9800
Ni(1')-N(1)	1.683(5)	C(9)-H(9B)	0.9800
Ni(1')-C(4')	1.925(6)	C(9)-H(9C)	0.9800
Ni(1')-C(1')	1.947(12)	C(10)-H(10A)	0.9800
Ni(1')-N(3)	2.126(4)	C(10)-H(10B)	0.9800
Ni(1')-N(2)	2.217(5)	C(10)-H(10C)	0.9800
S(1)-O(1)	1.421(5)	C(1')-C(2')	1.503(14)
S(1)-O(2)	1.445(3)	C(1')-H(1'1)	0.9900
S(1)-O(1')	1.465(7)	C(1')-H(1'2)	0.9900
S(1)-N(4)	1.671(4)	C(2')-C(3')	1.508(11)
S(1)-C(26)	1.752(4)	C(2')-C(9')	1.542(13)
N(1)-C(15)	1.338(6)	C(2')-C(10')	1.565(15)
N(1)-C(11)	1.348(6)	C(3')-C(4')	1.3900
N(2)-C(22)	1.344(5)	C(3')-C(8')	1.3900
N(2)-C(18)	1.358(5)	C(4')-C(5')	1.3900
N(3)-C(17)	1.468(6)	C(5')-C(6')	1.3900
N(3)-C(16)	1.476(6)	C(5')-H(5')	0.9500
N(3)-C(25)	1.478(6)	C(6')-C(7')	1.3900
N(4)-C(23)	1.469(5)	C(6')-H(6')	0.9500
N(4)-C(24)	1.483(6)	C(7')-C(8')	1.3900
C(1)-C(2)	1.551(10)	C(7')-H(7')	0.9500
C(1)-H(1A)	0.9900	C(8')-H(8')	0.9500
C(1)-H(1B)	0.9900	C(9')-H(9'1)	0.9800
C(2)-C(3)	1.509(8)	C(9')-H(9'2)	0.9800
C(2)-C(9)	1.531(10)	C(9')-H(9'3)	0.9800
C(2)-C(10)	1.538(10)	C(10')-H(10D)	0.9800
C(3)-C(4)	1.3900	C(10')-H(10E)	0.9800
C(3)-C(8)	1.3900	C(10')-H(10F)	0.9800
C(4)-C(5)	1.3900	C(11)-C(12)	1.369(7)
C(5)-C(6)	1.3900	C(11)-C(24)	1.497(7)
C(5)-H(5)	0.9500	C(12)-C(13)	1.382(7)
C(6)-C(7)	1.3900	C(12)-H(12)	0.9500

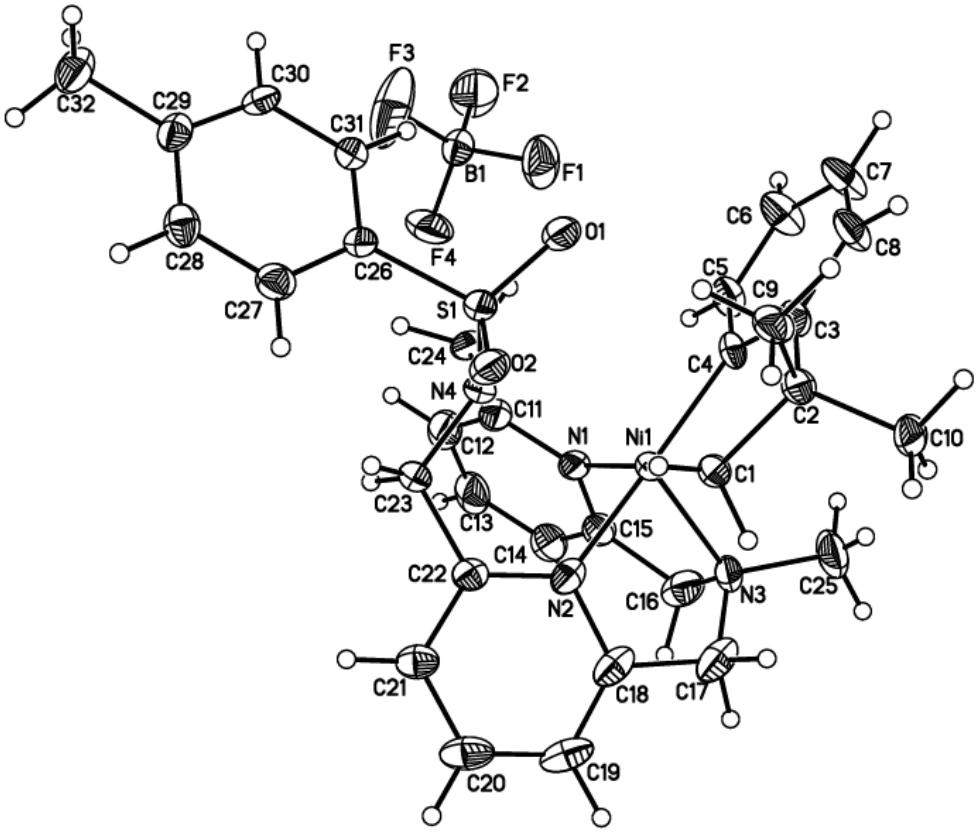
C(13)-C(14)	1.380(7)	C(32)-H(32B)	0.9800
C(13)-H(13)	0.9500	C(32)-H(32C)	0.9800
C(14)-C(15)	1.386(7)	B(1)-F(4)	1.333(6)
C(14)-H(14)	0.9500	B(1)-F(3')	1.337(7)
C(15)-C(16)	1.500(6)	B(1)-F(2')	1.349(7)
C(16)-H(16A)	0.9900	B(1)-F(3)	1.350(6)
C(16)-H(16B)	0.9900	B(1)-F(4')	1.350(7)
C(17)-C(18)	1.495(6)	B(1)-F(2)	1.361(6)
C(17)-H(17A)	0.9900	B(1)-F(1)	1.368(4)
C(17)-H(17B)	0.9900		
C(18)-C(19)	1.361(6)	N(2)-Ni(1)-C(1)	93.7(3)
C(19)-C(20)	1.370(7)	N(2)-Ni(1)-C(4)	175.0(2)
C(19)-H(19)	0.9500	C(1)-Ni(1)-C(4)	82.2(3)
C(20)-C(21)	1.367(6)	N(2)-Ni(1)-N(1)	82.71(15)
C(20)-H(20)	0.9500	C(1)-Ni(1)-N(1)	175.6(3)
C(21)-C(22)	1.376(5)	C(4)-Ni(1)-N(1)	101.3(2)
C(21)-H(21)	0.9500	N(2)-Ni(1)-N(3)	81.54(16)
C(22)-C(23)	1.504(5)	C(1)-Ni(1)-N(3)	105.0(3)
C(23)-H(23A)	0.9900	C(4)-Ni(1)-N(3)	102.2(2)
C(23)-H(23B)	0.9900	N(1)-Ni(1)-N(3)	77.08(17)
C(24)-H(24A)	0.9900	N(1)-Ni(1')-C(4')	170.4(3)
C(24)-H(24B)	0.9900	N(1)-Ni(1')-C(1')	91.5(4)
C(25)-H(25A)	0.9800	C(4')-Ni(1')-C(1')	81.5(4)
C(25)-H(25B)	0.9800	N(1)-Ni(1')-N(3)	90.8(2)
C(25)-H(25C)	0.9800	C(4')-Ni(1')-N(3)	97.5(3)
C(26)-C(31)	1.374(6)	C(1')-Ni(1')-N(3)	107.0(4)
C(26)-C(27)	1.390(6)	N(1)-Ni(1')-N(2)	85.90(17)
C(27)-C(28)	1.378(6)	C(4')-Ni(1')-N(2)	100.7(3)
C(27)-H(27)	0.9500	C(1')-Ni(1')-N(2)	176.3(4)
C(28)-C(29)	1.382(6)	N(3)-Ni(1')-N(2)	75.75(16)
C(28)-H(28)	0.9500	O(1)-S(1)-O(2)	112.8(3)
C(29)-C(30)	1.387(6)	O(2)-S(1)-O(1')	131.3(4)
C(29)-C(32)	1.496(6)	O(1)-S(1)-N(4)	111.0(4)
C(30)-C(31)	1.375(6)	O(2)-S(1)-N(4)	105.1(2)
C(30)-H(30)	0.9500	O(1')-S(1)-N(4)	98.3(5)
C(31)-H(31)	0.9500	O(1)-S(1)-C(26)	110.5(4)
C(32)-H(32A)	0.9800	O(2)-S(1)-C(26)	108.8(2)

O(1')-S(1)-C(26)	103.1(5)	C(4)-C(3)-C(2)	116.6(4)
N(4)-S(1)-C(26)	108.4(2)	C(8)-C(3)-C(2)	123.4(4)
C(15)-N(1)-C(11)	119.9(5)	C(5)-C(4)-C(3)	120.0
C(15)-N(1)-Ni(1')	116.6(3)	C(5)-C(4)-Ni(1)	121.9(3)
C(11)-N(1)-Ni(1')	123.6(4)	C(3)-C(4)-Ni(1)	117.9(3)
C(15)-N(1)-Ni(1)	117.2(3)	C(4)-C(5)-C(6)	120.0
C(11)-N(1)-Ni(1)	121.5(4)	C(4)-C(5)-H(5)	120.0
C(22)-N(2)-C(18)	118.0(4)	C(6)-C(5)-H(5)	120.0
C(22)-N(2)-Ni(1)	126.4(3)	C(5)-C(6)-C(7)	120.0
C(18)-N(2)-Ni(1)	115.4(3)	C(5)-C(6)-H(6)	120.0
C(22)-N(2)-Ni(1')	124.4(3)	C(7)-C(6)-H(6)	120.0
C(18)-N(2)-Ni(1')	116.2(3)	C(6)-C(7)-C(8)	120.0
C(17)-N(3)-C(16)	111.1(4)	C(6)-C(7)-H(7)	120.0
C(17)-N(3)-C(25)	110.0(4)	C(8)-C(7)-H(7)	120.0
C(16)-N(3)-C(25)	109.4(5)	C(7)-C(8)-C(3)	120.0
C(17)-N(3)-Ni(1')	112.8(3)	C(7)-C(8)-H(8)	120.0
C(16)-N(3)-Ni(1')	99.8(3)	C(3)-C(8)-H(8)	120.0
C(25)-N(3)-Ni(1')	113.4(3)	C(2)-C(9)-H(9A)	109.5
C(17)-N(3)-Ni(1)	97.3(3)	C(2)-C(9)-H(9B)	109.5
C(16)-N(3)-Ni(1)	113.2(3)	H(9A)-C(9)-H(9B)	109.5
C(25)-N(3)-Ni(1)	115.3(3)	C(2)-C(9)-H(9C)	109.5
C(23)-N(4)-C(24)	113.9(4)	H(9A)-C(9)-H(9C)	109.5
C(23)-N(4)-S(1)	113.5(3)	H(9B)-C(9)-H(9C)	109.5
C(24)-N(4)-S(1)	114.4(3)	C(2)-C(10)-H(10A)	109.5
C(2)-C(1)-Ni(1)	118.1(6)	C(2)-C(10)-H(10B)	109.5
C(2)-C(1)-H(1A)	107.8	H(10A)-C(10)-H(10B)	109.5
Ni(1)-C(1)-H(1A)	107.8	C(2)-C(10)-H(10C)	109.5
C(2)-C(1)-H(1B)	107.8	H(10A)-C(10)-H(10C)	109.5
Ni(1)-C(1)-H(1B)	107.8	H(10B)-C(10)-H(10C)	109.5
H(1A)-C(1)-H(1B)	107.1	C(2')-C(1')-Ni(1')	118.8(8)
C(3)-C(2)-C(9)	112.1(6)	C(2')-C(1')-H(1'1)	107.6
C(3)-C(2)-C(10)	110.5(6)	Ni(1')-C(1')-H(1'1)	107.6
C(9)-C(2)-C(10)	107.6(6)	C(2')-C(1')-H(1'2)	107.6
C(3)-C(2)-C(1)	104.9(6)	Ni(1')-C(1')-H(1'2)	107.6
C(9)-C(2)-C(1)	110.2(7)	H(1'1)-C(1')-H(1'2)	107.0
C(10)-C(2)-C(1)	111.6(6)	C(1')-C(2')-C(3')	105.0(8)
C(4)-C(3)-C(8)	120.0	C(1')-C(2')-C(9')	114.1(10)

C(3')-C(2')-C(9')	110.9(8)	C(11)-C(12)-C(13)	120.3(5)
C(1')-C(2')-C(10')	109.0(9)	C(11)-C(12)-H(12)	119.9
C(3')-C(2')-C(10')	113.4(9)	C(13)-C(12)-H(12)	119.9
C(9')-C(2')-C(10')	104.8(8)	C(14)-C(13)-C(12)	118.6(6)
C(4')-C(3')-C(8')	120.0	C(14)-C(13)-H(13)	120.7
C(4')-C(3')-C(2')	116.4(6)	C(12)-C(13)-H(13)	120.7
C(8')-C(3')-C(2')	123.6(6)	C(13)-C(14)-C(15)	119.0(5)
C(3')-C(4')-C(5')	120.0	C(13)-C(14)-H(14)	120.5
C(3')-C(4')-Ni(1')	117.7(4)	C(15)-C(14)-H(14)	120.5
C(5')-C(4')-Ni(1')	122.1(4)	N(1)-C(15)-C(14)	121.5(5)
C(4')-C(5')-C(6')	120.0	N(1)-C(15)-C(16)	117.3(5)
C(4')-C(5')-H(5')	120.0	C(14)-C(15)-C(16)	121.2(5)
C(6')-C(5')-H(5')	120.0	N(3)-C(16)-C(15)	114.5(4)
C(7')-C(6')-C(5')	120.0	N(3)-C(16)-H(16A)	108.6
C(7')-C(6')-H(6')	120.0	C(15)-C(16)-H(16A)	108.6
C(5')-C(6')-H(6')	120.0	N(3)-C(16)-H(16B)	108.6
C(8')-C(7')-C(6')	120.0	C(15)-C(16)-H(16B)	108.6
C(8')-C(7')-H(7')	120.0	H(16A)-C(16)-H(16B)	107.6
C(6')-C(7')-H(7')	120.0	N(3)-C(17)-C(18)	111.8(4)
C(7')-C(8')-C(3')	120.0	N(3)-C(17)-H(17A)	109.3
C(7')-C(8')-H(8')	120.0	C(18)-C(17)-H(17A)	109.3
C(3')-C(8')-H(8')	120.0	N(3)-C(17)-H(17B)	109.3
C(2')-C(9')-H(9'1)	109.5	C(18)-C(17)-H(17B)	109.3
C(2')-C(9')-H(9'2)	109.5	H(17A)-C(17)-H(17B)	107.9
H(9'1)-C(9')-H(9'2)	109.5	N(2)-C(18)-C(19)	122.1(4)
C(2')-C(9')-H(9'3)	109.5	N(2)-C(18)-C(17)	113.9(4)
H(9'1)-C(9')-H(9'3)	109.5	C(19)-C(18)-C(17)	124.0(4)
H(9'2)-C(9')-H(9'3)	109.5	C(18)-C(19)-C(20)	119.1(4)
C(2')-C(10')-H(10D)	109.5	C(18)-C(19)-H(19)	120.4
C(2')-C(10')-H(10E)	109.5	C(20)-C(19)-H(19)	120.4
H(10D)-C(10')-H(10E)	109.5	C(21)-C(20)-C(19)	119.7(4)
C(2')-C(10')-H(10F)	109.5	C(21)-C(20)-H(20)	120.2
H(10D)-C(10')-H(10F)	109.5	C(19)-C(20)-H(20)	120.2
H(10E)-C(10')-H(10F)	109.5	C(20)-C(21)-C(22)	119.1(4)
N(1)-C(11)-C(12)	120.8(5)	C(20)-C(21)-H(21)	120.5
N(1)-C(11)-C(24)	115.2(5)	C(22)-C(21)-H(21)	120.5
C(12)-C(11)-C(24)	124.0(5)	N(2)-C(22)-C(21)	121.8(4)

N(2)-C(22)-C(23)	118.7(4)	C(29)-C(28)-H(28)	119.0
C(21)-C(22)-C(23)	119.3(4)	C(28)-C(29)-C(30)	118.2(4)
N(4)-C(23)-C(22)	114.2(3)	C(28)-C(29)-C(32)	121.0(4)
N(4)-C(23)-H(23A)	108.7	C(30)-C(29)-C(32)	120.8(4)
C(22)-C(23)-H(23A)	108.7	C(31)-C(30)-C(29)	120.8(4)
N(4)-C(23)-H(23B)	108.7	C(31)-C(30)-H(30)	119.6
C(22)-C(23)-H(23B)	108.7	C(29)-C(30)-H(30)	119.6
H(23A)-C(23)-H(23B)	107.6	C(26)-C(31)-C(30)	119.9(4)
N(4)-C(24)-C(11)	110.1(4)	C(26)-C(31)-H(31)	120.1
N(4)-C(24)-H(24A)	109.6	C(30)-C(31)-H(31)	120.1
C(11)-C(24)-H(24A)	109.6	C(29)-C(32)-H(32A)	109.5
N(4)-C(24)-H(24B)	109.6	C(29)-C(32)-H(32B)	109.5
C(11)-C(24)-H(24B)	109.6	H(32A)-C(32)-H(32B)	109.5
H(24A)-C(24)-H(24B)	108.2	C(29)-C(32)-H(32C)	109.5
N(3)-C(25)-H(25A)	109.5	H(32A)-C(32)-H(32C)	109.5
N(3)-C(25)-H(25B)	109.5	H(32B)-C(32)-H(32C)	109.5
H(25A)-C(25)-H(25B)	109.5	F(3')-B(1)-F(2')	109.3(10)
N(3)-C(25)-H(25C)	109.5	F(4)-B(1)-F(3)	110.2(6)
H(25A)-C(25)-H(25C)	109.5	F(3')-B(1)-F(4')	110.9(10)
H(25B)-C(25)-H(25C)	109.5	F(2')-B(1)-F(4')	107.1(10)
C(31)-C(26)-C(27)	120.7(4)	F(4)-B(1)-F(2)	108.0(6)
C(31)-C(26)-S(1)	119.7(3)	F(3)-B(1)-F(2)	108.9(6)
C(27)-C(26)-S(1)	119.6(3)	F(4)-B(1)-F(1)	107.8(5)
C(28)-C(27)-C(26)	118.3(4)	F(3')-B(1)-F(1)	107.0(7)
C(28)-C(27)-H(27)	120.9	F(2')-B(1)-F(1)	117.7(10)
C(26)-C(27)-H(27)	120.9	F(3)-B(1)-F(1)	114.2(5)
C(27)-C(28)-C(29)	122.0(4)	F(4')-B(1)-F(1)	104.8(7)
C(27)-C(28)-H(28)	119.0	F(2)-B(1)-F(1)	107.4(5)

Projection view with 30% probability ellipsoids- disorder components omitted for clarity:



Crystal data and structure refinement for lm8417. (^{Ts}N4)Ni^{III}(cycloneophyl)$^{+}$

Identification code	l8417/lt/x8/SMS_Ts2N4NiMe2-AgSbF6	
Empirical formula	C42 H46 F6 N6 Ni O4 S2 Sb	
Formula weight	1057.43	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.5650(6) Å	α = 90°.
	b = 16.4096(7) Å	β = 93.577(2)°.
	c = 19.6099(10) Å	γ = 90°.
Volume	4356.6(3) Å^3	
Z	4	
Density (calculated)	1.612 Mg/m^3	
Absorption coefficient	1.223 mm^{-1}	
F(000)	2148	
Crystal size	0.444 x 0.247 x 0.219 mm^3	
Theta range for data collection	1.504 to 27.568°.	
Index ranges	-16≤h≤17, -21≤k≤21, -25≤l≤25	
Reflections collected	58394	
Independent reflections	10068 [R(int) = 0.0604]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7041 and 0.6356	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10068 / 162 / 596	
Goodness-of-fit on F^2	1.318	
Final R indices [I>2sigma(I)]	R1 = 0.0489, wR2 = 0.1138	
R indices (all data)	R1 = 0.0814, wR2 = 0.1262	
Largest diff. peak and hole	1.565 and -1.358 e.Å^{-3}	

Bond lengths [Å] and angles [°] for lm8417.

Sb(1)-F(6')	1.811(7)	C(3)-C(4)	1.382(5)
Sb(1)-F(5)	1.816(3)	C(3)-H(3)	0.9500
Sb(1)-F(3)	1.836(4)	C(4)-C(5)	1.385(5)
Sb(1)-F(4)	1.840(4)	C(4)-H(4)	0.9500
Sb(1)-F(3')	1.842(8)	C(5)-C(6)	1.400(5)
Sb(1)-F(5')	1.845(7)	C(5)-H(5)	0.9500
Sb(1)-F(4')	1.848(7)	C(6)-C(7)	1.504(5)
Sb(1)-F(2)	1.852(3)	C(7)-C(9)	1.531(5)
Sb(1)-F(1)	1.853(3)	C(7)-C(10)	1.533(5)
Sb(1)-F(6)	1.867(4)	C(7)-C(8)	1.542(5)
Ni(1)-C(1)	1.933(3)	C(8)-H(8A)	0.9900
Ni(1)-C(8)	1.982(3)	C(8)-H(8B)	0.9900
Ni(1)-N(1)	1.993(3)	C(9)-H(9A)	0.9800
Ni(1)-N(2)	2.010(3)	C(9)-H(9B)	0.9800
Ni(1)-N(3)	2.360(3)	C(9)-H(9C)	0.9800
Ni(1)-N(4)	2.436(3)	C(10)-H(10A)	0.9800
S(1)-O(2)	1.421(3)	C(10)-H(10B)	0.9800
S(1)-O(1)	1.430(3)	C(10)-H(10C)	0.9800
S(1)-N(3)	1.698(3)	C(11)-C(12)	1.389(5)
S(1)-C(25)	1.746(4)	C(11)-C(24)	1.508(5)
S(2)-O(3)	1.417(2)	C(12)-C(13)	1.380(5)
S(2)-O(4)	1.420(3)	C(12)-H(12)	0.9500
S(2)-N(4)	1.692(3)	C(13)-C(14)	1.376(5)
S(2)-C(32)	1.755(3)	C(13)-H(13)	0.9500
N(1)-C(11)	1.336(4)	C(14)-C(15)	1.382(5)
N(1)-C(15)	1.350(4)	C(14)-H(14)	0.9500
N(2)-C(18)	1.347(4)	C(15)-C(16)	1.503(5)
N(2)-C(22)	1.348(4)	C(16)-H(16A)	0.9900
N(3)-C(17)	1.488(4)	C(16)-H(16B)	0.9900
N(3)-C(16)	1.490(4)	C(17)-C(18)	1.495(5)
N(4)-C(24)	1.493(4)	C(17)-H(17A)	0.9900
N(4)-C(23)	1.495(4)	C(17)-H(17B)	0.9900
C(1)-C(6)	1.389(5)	C(18)-C(19)	1.365(5)
C(1)-C(2)	1.391(5)	C(19)-C(20)	1.384(5)
C(2)-C(3)	1.386(5)	C(19)-H(19)	0.9500
C(2)-H(2)	0.9500	C(20)-C(21)	1.385(5)

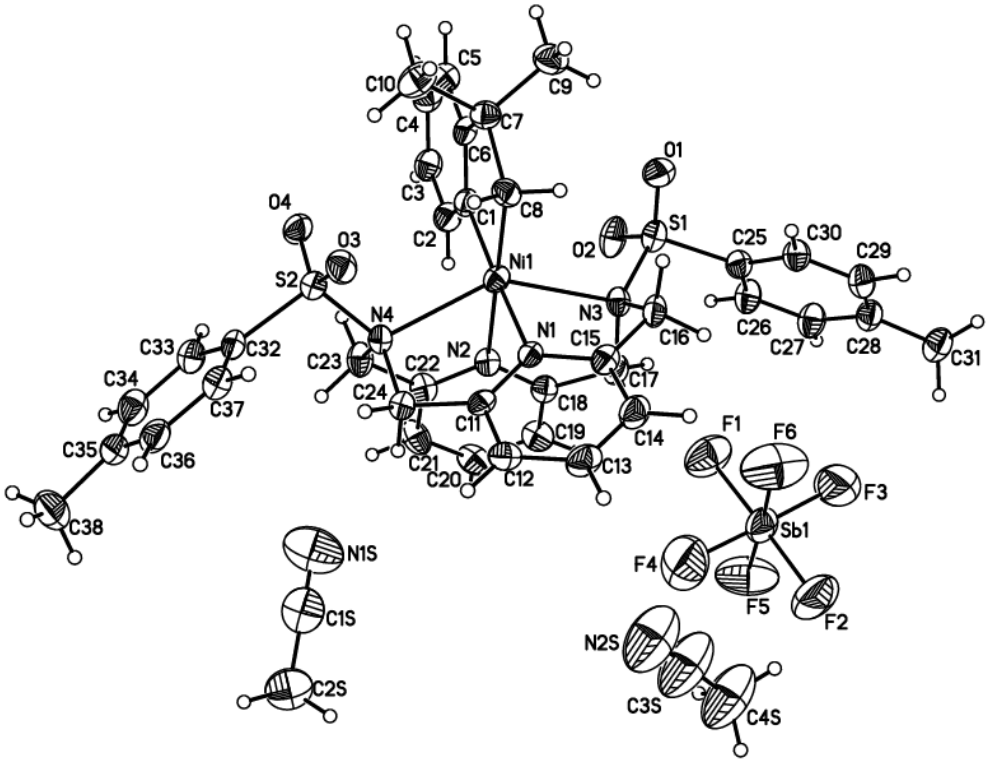
C(20)-H(20)	0.9500	C(1S)-C(2S)	1.471(8)
C(21)-C(22)	1.369(5)	C(2S)-H(2SA)	0.9800
C(21)-H(21)	0.9500	C(2S)-H(2SB)	0.9800
C(22)-C(23)	1.501(5)	C(2S)-H(2SC)	0.9800
C(23)-H(23A)	0.9900	N(2S)-C(3S)	1.123(7)
C(23)-H(23B)	0.9900	C(3S)-C(4S)	1.438(8)
C(24)-H(24A)	0.9900	C(4S)-H(4SA)	0.9800
C(24)-H(24B)	0.9900	C(4S)-H(4SB)	0.9800
C(25)-C(30)	1.383(5)	C(4S)-H(4SC)	0.9800
C(25)-C(26)	1.384(5)		
C(26)-C(27)	1.378(5)	F(5)-Sb(1)-F(3)	92.4(3)
C(26)-H(26)	0.9500	F(5)-Sb(1)-F(4)	91.3(3)
C(27)-C(28)	1.389(5)	F(3)-Sb(1)-F(4)	176.3(3)
C(27)-H(27)	0.9500	F(6')-Sb(1)-F(3')	88.8(12)
C(28)-C(29)	1.379(5)	F(6')-Sb(1)-F(5')	175.2(8)
C(28)-C(31)	1.498(5)	F(3')-Sb(1)-F(5')	93.0(13)
C(29)-C(30)	1.366(5)	F(6')-Sb(1)-F(4')	87.3(10)
C(29)-H(29)	0.9500	F(3')-Sb(1)-F(4')	176.1(11)
C(30)-H(30)	0.9500	F(5')-Sb(1)-F(4')	90.9(11)
C(31)-H(31A)	0.9800	F(6')-Sb(1)-F(2)	78.6(5)
C(31)-H(31B)	0.9800	F(5)-Sb(1)-F(2)	90.1(2)
C(31)-H(31C)	0.9800	F(3)-Sb(1)-F(2)	92.2(2)
C(32)-C(33)	1.377(5)	F(4)-Sb(1)-F(2)	87.6(2)
C(32)-C(37)	1.381(5)	F(3')-Sb(1)-F(2)	91.3(8)
C(33)-C(34)	1.381(5)	F(5')-Sb(1)-F(2)	96.9(6)
C(33)-H(33)	0.9500	F(4')-Sb(1)-F(2)	88.2(6)
C(34)-C(35)	1.382(6)	F(6')-Sb(1)-F(1)	102.5(5)
C(34)-H(34)	0.9500	F(5)-Sb(1)-F(1)	90.70(18)
C(35)-C(36)	1.378(5)	F(3)-Sb(1)-F(1)	89.8(2)
C(35)-C(38)	1.501(6)	F(4)-Sb(1)-F(1)	90.32(19)
C(36)-C(37)	1.389(5)	F(3')-Sb(1)-F(1)	90.7(7)
C(36)-H(36)	0.9500	F(5')-Sb(1)-F(1)	81.9(6)
C(37)-H(37)	0.9500	F(4')-Sb(1)-F(1)	89.9(6)
C(38)-H(38A)	0.9800	F(2)-Sb(1)-F(1)	177.75(18)
C(38)-H(38B)	0.9800	F(5)-Sb(1)-F(6)	177.1(2)
C(38)-H(38C)	0.9800	F(3)-Sb(1)-F(6)	88.3(3)
N(1S)-C(1S)	1.134(6)	F(4)-Sb(1)-F(6)	88.0(3)

F(2)-Sb(1)-F(6)	92.62(19)	C(16)-N(3)-S(1)	114.0(2)
F(1)-Sb(1)-F(6)	86.51(17)	C(17)-N(3)-Ni(1)	105.52(19)
C(1)-Ni(1)-C(8)	80.86(14)	C(16)-N(3)-Ni(1)	100.17(19)
C(1)-Ni(1)-N(1)	174.20(12)	S(1)-N(3)-Ni(1)	113.85(13)
C(8)-Ni(1)-N(1)	93.35(12)	C(24)-N(4)-C(23)	113.3(3)
C(1)-Ni(1)-N(2)	99.71(13)	C(24)-N(4)-S(2)	111.6(2)
C(8)-Ni(1)-N(2)	179.42(13)	C(23)-N(4)-S(2)	112.3(2)
N(1)-Ni(1)-N(2)	86.08(11)	C(24)-N(4)-Ni(1)	103.77(19)
C(1)-Ni(1)-N(3)	105.67(12)	C(23)-N(4)-Ni(1)	98.9(2)
C(8)-Ni(1)-N(3)	101.66(12)	S(2)-N(4)-Ni(1)	116.15(14)
N(1)-Ni(1)-N(3)	75.73(10)	C(6)-C(1)-C(2)	118.6(3)
N(2)-Ni(1)-N(3)	78.29(10)	C(6)-C(1)-Ni(1)	119.5(3)
C(1)-Ni(1)-N(4)	102.89(12)	C(2)-C(1)-Ni(1)	121.9(3)
C(8)-Ni(1)-N(4)	105.30(12)	C(3)-C(2)-C(1)	121.2(3)
N(1)-Ni(1)-N(4)	78.20(10)	C(3)-C(2)-H(2)	119.4
N(2)-Ni(1)-N(4)	74.50(10)	C(1)-C(2)-H(2)	119.4
N(3)-Ni(1)-N(4)	143.25(9)	C(4)-C(3)-C(2)	119.8(3)
O(2)-S(1)-O(1)	121.13(17)	C(4)-C(3)-H(3)	120.1
O(2)-S(1)-N(3)	105.01(15)	C(2)-C(3)-H(3)	120.1
O(1)-S(1)-N(3)	105.87(15)	C(3)-C(4)-C(5)	120.1(4)
O(2)-S(1)-C(25)	108.76(17)	C(3)-C(4)-H(4)	119.9
O(1)-S(1)-C(25)	109.17(17)	C(5)-C(4)-H(4)	119.9
N(3)-S(1)-C(25)	105.79(16)	C(4)-C(5)-C(6)	119.8(3)
O(3)-S(2)-O(4)	121.07(16)	C(4)-C(5)-H(5)	120.1
O(3)-S(2)-N(4)	105.28(14)	C(6)-C(5)-H(5)	120.1
O(4)-S(2)-N(4)	105.94(15)	C(1)-C(6)-C(5)	120.5(3)
O(3)-S(2)-C(32)	108.71(16)	C(1)-C(6)-C(7)	116.3(3)
O(4)-S(2)-C(32)	109.17(16)	C(5)-C(6)-C(7)	123.2(3)
N(4)-S(2)-C(32)	105.54(15)	C(6)-C(7)-C(9)	112.1(3)
C(11)-N(1)-C(15)	119.6(3)	C(6)-C(7)-C(10)	109.6(3)
C(11)-N(1)-Ni(1)	121.8(2)	C(9)-C(7)-C(10)	107.7(3)
C(15)-N(1)-Ni(1)	118.6(2)	C(6)-C(7)-C(8)	105.3(3)
C(18)-N(2)-C(22)	118.7(3)	C(9)-C(7)-C(8)	111.4(3)
C(18)-N(2)-Ni(1)	121.1(2)	C(10)-C(7)-C(8)	110.8(3)
C(22)-N(2)-Ni(1)	120.2(2)	C(7)-C(8)-Ni(1)	117.9(2)
C(17)-N(3)-C(16)	112.4(3)	C(7)-C(8)-H(8A)	107.8
C(17)-N(3)-S(1)	110.3(2)	Ni(1)-C(8)-H(8A)	107.8

C(7)-C(8)-H(8B)	107.8	N(3)-C(17)-H(17A)	108.6
Ni(1)-C(8)-H(8B)	107.8	C(18)-C(17)-H(17A)	108.6
H(8A)-C(8)-H(8B)	107.2	N(3)-C(17)-H(17B)	108.6
C(7)-C(9)-H(9A)	109.5	C(18)-C(17)-H(17B)	108.6
C(7)-C(9)-H(9B)	109.5	H(17A)-C(17)-H(17B)	107.6
H(9A)-C(9)-H(9B)	109.5	N(2)-C(18)-C(19)	121.9(3)
C(7)-C(9)-H(9C)	109.5	N(2)-C(18)-C(17)	116.9(3)
H(9A)-C(9)-H(9C)	109.5	C(19)-C(18)-C(17)	120.8(3)
H(9B)-C(9)-H(9C)	109.5	C(18)-C(19)-C(20)	119.2(3)
C(7)-C(10)-H(10A)	109.5	C(18)-C(19)-H(19)	120.4
C(7)-C(10)-H(10B)	109.5	C(20)-C(19)-H(19)	120.4
H(10A)-C(10)-H(10B)	109.5	C(19)-C(20)-C(21)	118.9(3)
C(7)-C(10)-H(10C)	109.5	C(19)-C(20)-H(20)	120.5
H(10A)-C(10)-H(10C)	109.5	C(21)-C(20)-H(20)	120.5
H(10B)-C(10)-H(10C)	109.5	C(22)-C(21)-C(20)	119.0(3)
N(1)-C(11)-C(12)	121.8(3)	C(22)-C(21)-H(21)	120.5
N(1)-C(11)-C(24)	118.7(3)	C(20)-C(21)-H(21)	120.5
C(12)-C(11)-C(24)	119.2(3)	N(2)-C(22)-C(21)	121.9(3)
C(13)-C(12)-C(11)	118.4(4)	N(2)-C(22)-C(23)	116.2(3)
C(13)-C(12)-H(12)	120.8	C(21)-C(22)-C(23)	121.9(3)
C(11)-C(12)-H(12)	120.8	N(4)-C(23)-C(22)	110.3(3)
C(14)-C(13)-C(12)	119.7(3)	N(4)-C(23)-H(23A)	109.6
C(14)-C(13)-H(13)	120.2	C(22)-C(23)-H(23A)	109.6
C(12)-C(13)-H(13)	120.2	N(4)-C(23)-H(23B)	109.6
C(13)-C(14)-C(15)	119.4(3)	C(22)-C(23)-H(23B)	109.6
C(13)-C(14)-H(14)	120.3	H(23A)-C(23)-H(23B)	108.1
C(15)-C(14)-H(14)	120.3	N(4)-C(24)-C(11)	114.9(3)
N(1)-C(15)-C(14)	120.9(3)	N(4)-C(24)-H(24A)	108.5
N(1)-C(15)-C(16)	116.5(3)	C(11)-C(24)-H(24A)	108.5
C(14)-C(15)-C(16)	122.5(3)	N(4)-C(24)-H(24B)	108.5
N(3)-C(16)-C(15)	108.9(3)	C(11)-C(24)-H(24B)	108.5
N(3)-C(16)-H(16A)	109.9	H(24A)-C(24)-H(24B)	107.5
C(15)-C(16)-H(16A)	109.9	C(30)-C(25)-C(26)	120.4(3)
N(3)-C(16)-H(16B)	109.9	C(30)-C(25)-S(1)	120.3(3)
C(15)-C(16)-H(16B)	109.9	C(26)-C(25)-S(1)	119.3(3)
H(16A)-C(16)-H(16B)	108.3	C(27)-C(26)-C(25)	119.4(3)
N(3)-C(17)-C(18)	114.6(3)	C(27)-C(26)-H(26)	120.3

C(25)-C(26)-H(26)	120.3	C(36)-C(35)-C(38)	120.8(4)
C(26)-C(27)-C(28)	121.1(3)	C(34)-C(35)-C(38)	120.7(4)
C(26)-C(27)-H(27)	119.4	C(35)-C(36)-C(37)	121.4(4)
C(28)-C(27)-H(27)	119.4	C(35)-C(36)-H(36)	119.3
C(29)-C(28)-C(27)	117.7(3)	C(37)-C(36)-H(36)	119.3
C(29)-C(28)-C(31)	122.3(3)	C(32)-C(37)-C(36)	118.3(3)
C(27)-C(28)-C(31)	120.0(3)	C(32)-C(37)-H(37)	120.9
C(30)-C(29)-C(28)	122.5(3)	C(36)-C(37)-H(37)	120.9
C(30)-C(29)-H(29)	118.8	C(35)-C(38)-H(38A)	109.5
C(28)-C(29)-H(29)	118.8	C(35)-C(38)-H(38B)	109.5
C(29)-C(30)-C(25)	118.9(3)	H(38A)-C(38)-H(38B)	109.5
C(29)-C(30)-H(30)	120.6	C(35)-C(38)-H(38C)	109.5
C(25)-C(30)-H(30)	120.6	H(38A)-C(38)-H(38C)	109.5
C(28)-C(31)-H(31A)	109.5	H(38B)-C(38)-H(38C)	109.5
C(28)-C(31)-H(31B)	109.5	N(1S)-C(1S)-C(2S)	179.4(6)
H(31A)-C(31)-H(31B)	109.5	C(1S)-C(2S)-H(2SA)	109.5
C(28)-C(31)-H(31C)	109.5	C(1S)-C(2S)-H(2SB)	109.5
H(31A)-C(31)-H(31C)	109.5	H(2SA)-C(2S)-H(2SB)	109.5
H(31B)-C(31)-H(31C)	109.5	C(1S)-C(2S)-H(2SC)	109.5
C(33)-C(32)-C(37)	121.6(3)	H(2SA)-C(2S)-H(2SC)	109.5
C(33)-C(32)-S(2)	119.4(3)	H(2SB)-C(2S)-H(2SC)	109.5
C(37)-C(32)-S(2)	118.9(3)	N(2S)-C(3S)-C(4S)	179.7(8)
C(32)-C(33)-C(34)	118.6(3)	C(3S)-C(4S)-H(4SA)	109.5
C(32)-C(33)-H(33)	120.7	C(3S)-C(4S)-H(4SB)	109.5
C(34)-C(33)-H(33)	120.7	H(4SA)-C(4S)-H(4SB)	109.5
C(33)-C(34)-C(35)	121.4(4)	C(3S)-C(4S)-H(4SC)	109.5
C(33)-C(34)-H(34)	119.3	H(4SA)-C(4S)-H(4SC)	109.5
C(35)-C(34)-H(34)	119.3	H(4SB)-C(4S)-H(4SC)	109.5
C(36)-C(35)-C(34)	118.6(4)		

Projection view with 50% probability ellipsoids- disorder components of the anion omitted for clarity:



Crystal data and structure refinement for lm2418. (^{tBu}N4)Ni^{II}(cycloneophyl)

Identification code	l2418/lt/x8/3SMS117	
Empirical formula	C_{32} H_{44} N_4 Ni	
Formula weight	543.42	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.4391(6) Å	α= 90°.
	b = 23.9058(13) Å	β= 92.174(4)°.
	c = 12.7167(8) Å	γ = 90°.
Volume	2867.4(3) Å^3	
Z	4	
Density (calculated)	1.259 Mg/m^3	
Absorption coefficient	0.704 mm^{-1}	
F(000)	1168	
Crystal size	0.377 x 0.249 x 0.162 mm^3	
Theta range for data collection	1.704 to 30.631°.	
Index ranges	-12≤h≤13, -34≤k≤34, -14≤l≤18	
Reflections collected	49624	
Independent reflections	8789 [R(int) = 0.086]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8253 and 0.7156	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8789 / 0 / 342	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0603, wR2 = 0.1255	
R indices (all data)	R1 = 0.1170, wR2 = 0.1477	
Largest diff. peak and hole	1.811 and -0.908 e.Å^{-3}	

Bond lengths [Å] and angles [°] for lm2418.

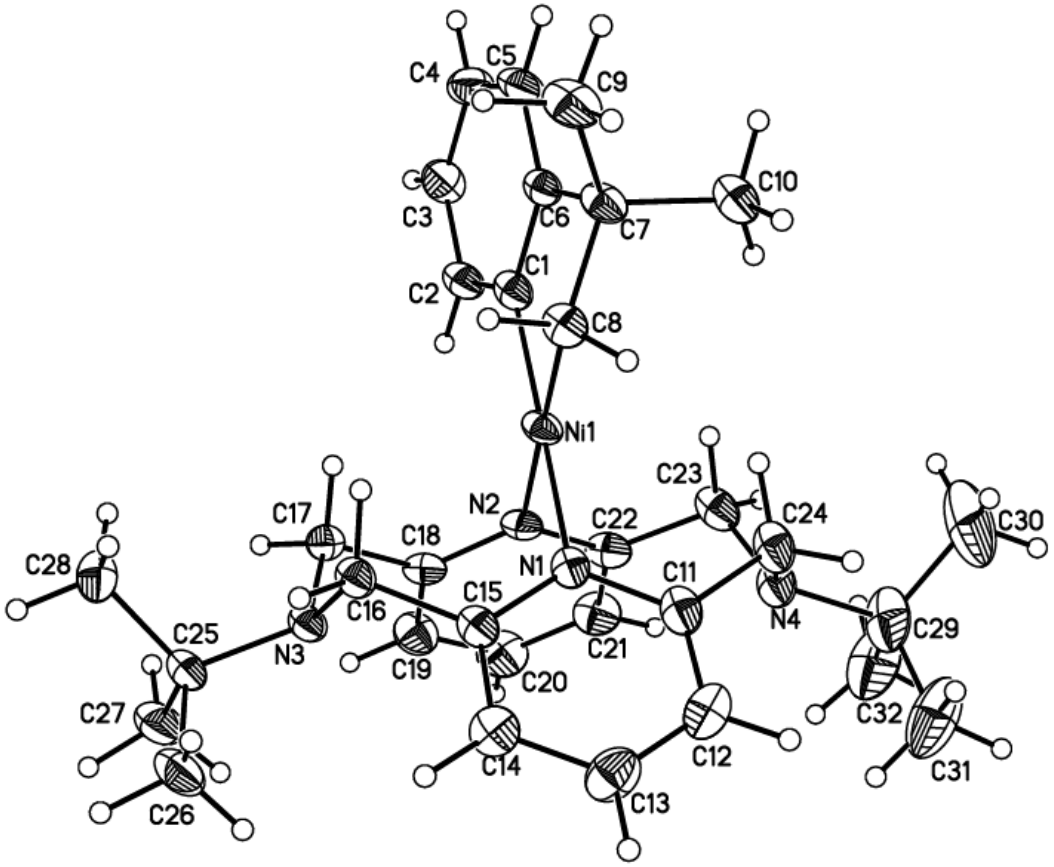
Ni(1)-C(1)	1.887(3)	C(10)-H(10B)	0.9800
Ni(1)-C(8)	1.938(3)	C(10)-H(10C)	0.9800
Ni(1)-N(1)	1.944(3)	C(11)-C(12)	1.381(5)
Ni(1)-N(2)	1.976(2)	C(11)-C(24)	1.507(4)
N(1)-C(11)	1.351(4)	C(12)-C(13)	1.374(5)
N(1)-C(15)	1.352(3)	C(12)-H(12)	0.9500
N(2)-C(22)	1.349(3)	C(13)-C(14)	1.379(4)
N(2)-C(18)	1.352(4)	C(13)-H(13)	0.9500
N(3)-C(16)	1.475(3)	C(14)-C(15)	1.375(4)
N(3)-C(17)	1.483(4)	C(14)-H(14)	0.9500
N(3)-C(25)	1.496(4)	C(15)-C(16)	1.501(4)
N(4)-C(23)	1.467(4)	C(16)-H(16A)	0.9900
N(4)-C(24)	1.480(3)	C(16)-H(16B)	0.9900
N(4)-C(29)	1.491(4)	C(17)-C(18)	1.500(4)
C(1)-C(2)	1.400(4)	C(17)-H(17A)	0.9900
C(1)-C(6)	1.420(4)	C(17)-H(17B)	0.9900
C(2)-C(3)	1.400(5)	C(18)-C(19)	1.385(4)
C(2)-H(2)	0.9500	C(19)-C(20)	1.387(4)
C(3)-C(4)	1.373(4)	C(19)-H(19)	0.9500
C(3)-H(3)	0.9500	C(20)-C(21)	1.378(5)
C(4)-C(5)	1.388(5)	C(20)-H(20)	0.9500
C(4)-H(4)	0.9500	C(21)-C(22)	1.391(4)
C(5)-C(6)	1.384(4)	C(21)-H(21)	0.9500
C(5)-H(5)	0.9500	C(22)-C(23)	1.503(4)
C(6)-C(7)	1.515(4)	C(23)-H(23A)	0.9900
C(7)-C(8)	1.519(4)	C(23)-H(23B)	0.9900
C(7)-C(10)	1.530(4)	C(24)-H(24A)	0.9900
C(7)-C(9)	1.530(4)	C(24)-H(24B)	0.9900
C(8)-H(8A)	0.9900	C(25)-C(28)	1.521(4)
C(8)-H(8B)	0.9900	C(25)-C(27)	1.527(4)
C(9)-H(9A)	0.9800	C(25)-C(26)	1.534(5)
C(9)-H(9B)	0.9800	C(26)-H(26A)	0.9800
C(9)-H(9C)	0.9800	C(26)-H(26B)	0.9800
C(10)-H(10A)	0.9800	C(26)-H(26C)	0.9800

C(27)-H(27A)	0.9800	C(23)-N(4)-C(29)	116.1(3)
C(27)-H(27B)	0.9800	C(24)-N(4)-C(29)	113.7(2)
C(27)-H(27C)	0.9800	C(2)-C(1)-C(6)	116.5(3)
C(28)-H(28A)	0.9800	C(2)-C(1)-Ni(1)	126.4(2)
C(28)-H(28B)	0.9800	C(6)-C(1)-Ni(1)	117.1(2)
C(28)-H(28C)	0.9800	C(1)-C(2)-C(3)	121.5(3)
C(29)-C(31)	1.528(6)	C(1)-C(2)-H(2)	119.3
C(29)-C(30)	1.532(6)	C(3)-C(2)-H(2)	119.3
C(29)-C(32)	1.533(4)	C(4)-C(3)-C(2)	120.5(3)
C(30)-H(30A)	0.9800	C(4)-C(3)-H(3)	119.8
C(30)-H(30B)	0.9800	C(2)-C(3)-H(3)	119.8
C(30)-H(30C)	0.9800	C(3)-C(4)-C(5)	119.8(3)
C(31)-H(31A)	0.9800	C(3)-C(4)-H(4)	120.1
C(31)-H(31B)	0.9800	C(5)-C(4)-H(4)	120.1
C(31)-H(31C)	0.9800	C(6)-C(5)-C(4)	120.1(3)
C(32)-H(32A)	0.9800	C(6)-C(5)-H(5)	119.9
C(32)-H(32B)	0.9800	C(4)-C(5)-H(5)	119.9
C(32)-H(32C)	0.9800	C(5)-C(6)-C(1)	121.7(3)
		C(5)-C(6)-C(7)	125.1(3)
C(1)-Ni(1)-C(8)	82.44(12)	C(1)-C(6)-C(7)	113.2(3)
C(1)-Ni(1)-N(1)	173.36(10)	C(6)-C(7)-C(8)	104.4(2)
C(8)-Ni(1)-N(1)	91.31(11)	C(6)-C(7)-C(10)	109.3(2)
C(1)-Ni(1)-N(2)	98.51(11)	C(8)-C(7)-C(10)	110.9(3)
C(8)-Ni(1)-N(2)	179.05(12)	C(6)-C(7)-C(9)	112.8(3)
N(1)-Ni(1)-N(2)	87.74(9)	C(8)-C(7)-C(9)	111.1(2)
C(11)-N(1)-C(15)	118.9(3)	C(10)-C(7)-C(9)	108.4(2)
C(11)-N(1)-Ni(1)	121.2(2)	C(7)-C(8)-Ni(1)	112.88(18)
C(15)-N(1)-Ni(1)	119.90(19)	C(7)-C(8)-H(8A)	109.0
C(22)-N(2)-C(18)	119.6(2)	Ni(1)-C(8)-H(8A)	109.0
C(22)-N(2)-Ni(1)	118.76(19)	C(7)-C(8)-H(8B)	109.0
C(18)-N(2)-Ni(1)	121.41(18)	Ni(1)-C(8)-H(8B)	109.0
C(16)-N(3)-C(17)	111.4(2)	H(8A)-C(8)-H(8B)	107.8
C(16)-N(3)-C(25)	113.8(2)	C(7)-C(9)-H(9A)	109.5
C(17)-N(3)-C(25)	114.6(2)	C(7)-C(9)-H(9B)	109.5
C(23)-N(4)-C(24)	112.2(2)	H(9A)-C(9)-H(9B)	109.5

C(7)-C(9)-H(9C)	109.5	H(17A)-C(17)-H(17B)	107.8
H(9A)-C(9)-H(9C)	109.5	N(2)-C(18)-C(19)	120.9(3)
H(9B)-C(9)-H(9C)	109.5	N(2)-C(18)-C(17)	117.9(2)
C(7)-C(10)-H(10A)	109.5	C(19)-C(18)-C(17)	121.2(3)
C(7)-C(10)-H(10B)	109.5	C(18)-C(19)-C(20)	120.2(3)
H(10A)-C(10)-H(10B)	109.5	C(18)-C(19)-H(19)	119.9
C(7)-C(10)-H(10C)	109.5	C(20)-C(19)-H(19)	119.9
H(10A)-C(10)-H(10C)	109.5	C(21)-C(20)-C(19)	118.0(3)
H(10B)-C(10)-H(10C)	109.5	C(21)-C(20)-H(20)	121.0
N(1)-C(11)-C(12)	121.4(3)	C(19)-C(20)-H(20)	121.0
N(1)-C(11)-C(24)	116.8(3)	C(20)-C(21)-C(22)	120.3(3)
C(12)-C(11)-C(24)	121.8(3)	C(20)-C(21)-H(21)	119.9
C(13)-C(12)-C(11)	119.4(3)	C(22)-C(21)-H(21)	119.9
C(13)-C(12)-H(12)	120.3	N(2)-C(22)-C(21)	120.8(3)
C(11)-C(12)-H(12)	120.3	N(2)-C(22)-C(23)	117.6(2)
C(12)-C(13)-C(14)	119.1(3)	C(21)-C(22)-C(23)	121.5(3)
C(12)-C(13)-H(13)	120.5	N(4)-C(23)-C(22)	112.0(3)
C(14)-C(13)-H(13)	120.5	N(4)-C(23)-H(23A)	109.2
C(15)-C(14)-C(13)	119.6(3)	C(22)-C(23)-H(23A)	109.2
C(15)-C(14)-H(14)	120.2	N(4)-C(23)-H(23B)	109.2
C(13)-C(14)-H(14)	120.2	C(22)-C(23)-H(23B)	109.2
N(1)-C(15)-C(14)	121.4(3)	H(23A)-C(23)-H(23B)	107.9
N(1)-C(15)-C(16)	117.8(3)	N(4)-C(24)-C(11)	112.5(2)
C(14)-C(15)-C(16)	120.8(3)	N(4)-C(24)-H(24A)	109.1
N(3)-C(16)-C(15)	112.8(2)	C(11)-C(24)-H(24A)	109.1
N(3)-C(16)-H(16A)	109.0	N(4)-C(24)-H(24B)	109.1
C(15)-C(16)-H(16A)	109.0	C(11)-C(24)-H(24B)	109.1
N(3)-C(16)-H(16B)	109.0	H(24A)-C(24)-H(24B)	107.8
C(15)-C(16)-H(16B)	109.0	N(3)-C(25)-C(28)	112.5(2)
H(16A)-C(16)-H(16B)	107.8	N(3)-C(25)-C(27)	108.8(2)
N(3)-C(17)-C(18)	112.7(2)	C(28)-C(25)-C(27)	110.7(3)
N(3)-C(17)-H(17A)	109.1	N(3)-C(25)-C(26)	108.9(2)
C(18)-C(17)-H(17A)	109.1	C(28)-C(25)-C(26)	109.7(3)
N(3)-C(17)-H(17B)	109.1	C(27)-C(25)-C(26)	106.0(3)
C(18)-C(17)-H(17B)	109.1	C(25)-C(26)-H(26A)	109.5

C(25)-C(26)-H(26B)	109.5	C(31)-C(29)-C(32)	106.6(3)
H(26A)-C(26)-H(26B)	109.5	C(30)-C(29)-C(32)	109.7(3)
C(25)-C(26)-H(26C)	109.5	C(29)-C(30)-H(30A)	109.5
H(26A)-C(26)-H(26C)	109.5	C(29)-C(30)-H(30B)	109.5
H(26B)-C(26)-H(26C)	109.5	H(30A)-C(30)-H(30B)	109.5
C(25)-C(27)-H(27A)	109.5	C(29)-C(30)-H(30C)	109.5
C(25)-C(27)-H(27B)	109.5	H(30A)-C(30)-H(30C)	109.5
H(27A)-C(27)-H(27B)	109.5	H(30B)-C(30)-H(30C)	109.5
C(25)-C(27)-H(27C)	109.5	C(29)-C(31)-H(31A)	109.5
H(27A)-C(27)-H(27C)	109.5	C(29)-C(31)-H(31B)	109.5
H(27B)-C(27)-H(27C)	109.5	H(31A)-C(31)-H(31B)	109.5
C(25)-C(28)-H(28A)	109.5	C(29)-C(31)-H(31C)	109.5
C(25)-C(28)-H(28B)	109.5	H(31A)-C(31)-H(31C)	109.5
H(28A)-C(28)-H(28B)	109.5	H(31B)-C(31)-H(31C)	109.5
C(25)-C(28)-H(28C)	109.5	C(29)-C(32)-H(32A)	109.5
H(28A)-C(28)-H(28C)	109.5	C(29)-C(32)-H(32B)	109.5
H(28B)-C(28)-H(28C)	109.5	H(32A)-C(32)-H(32B)	109.5
N(4)-C(29)-C(31)	109.1(3)	C(29)-C(32)-H(32C)	109.5
N(4)-C(29)-C(30)	111.7(3)	H(32A)-C(32)-H(32C)	109.5
C(31)-C(29)-C(30)	110.6(4)	H(32B)-C(32)-H(32C)	109.5
N(4)-C(29)-C(32)	109.0(3)		

Projection view with 50% probability ellipsoids:



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