Supporting information for

Displacement of η^5-cyclopentadienyl ligands from half-sandwich *C,C*-(NHC-cyanoalkyl)–nickel(II) metallacycles: further insight into the structure of the resulting Cp-free nickelacycles and a catalytic activity study

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Synthesis of 1-(2,6-diisopropylphenyl)-3-butylnitrile-imidazolium chloride

1-(2,6-Diisopropylphenyl)-1*H*-imidazole (1.80 g, 7.88 mmol) and 4-chlorobutyronitrile (745 µL, 7.88 mmol) were mixed in a 10 mL sealed vial with 4 mL of THF. The vial was then placed in a Discover CEM S-class microwave operating at 2.45 GHz and heated for 1 h at 180 °C. The solvent was then removed under vacuum. The resulting oily residue was extracted with CH_2Cl_2 (2 mL), and precipitated with pentane (25 mL) to give a whitish solid (1.456 g, 4.42 mmol, 56 %) that was washed with ethyl acetate (1 x 50 mL overnight, and 2 x 30 mL for 1 h) and dried under vacuum. Anal. Calcd for $C_{19}H_{26}N_3Cl$: C, 68.76; H, 7.90; N, 12.66. Found: C, 68.73; H, 7.94; N, 12.52. HR-MS (ESI): *m/z* $[M]^+$ calcd for $C_{19}H_{26}N_3$ 296.2121, found 296.2128. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 10.65 (t, ^4J n.r., 1H, NC*H*N), 8.44 (t, ^3J n.r., 1H, NC*H*), 7.55 (t, ^3J = 8.1, 1H, *p*-H_{Ar}), 7.31 (d, ^3J = 8.1, 2H, *m*-H_{Ar}), 7.20 (t, ^3J = 1.8, 1H, NC*H*), 5.04 (t , ^3J = 6.9, 2H, NCH_2), 2.78 (t, ^3J = 6.9, 2H, CH_2CN), 2.51 (quint., ^3J = 6.9, 2H, CH_2), 2.31 (sept., ^3J = 6.9, 2H, C*H*Me_2), 1.22 (d , ^3J = 6.9, 6H, CH*Me*$_2$), 1.16 (d , ^3J = 6.9, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ 145.5 (*o*-C_{Ar}), 139.0 (N*C*HN), 132.0, (*p*-C_{Ar}), 130.3 (*ipso*-C_{Ar}), 124.8 (*m*-C_{Ar}), 124.4 (N*C*H), 123.8 (N*C*H), 118.9 (CN), 48.9 (N*C*H_2), 28.8 (*C*HMe_2), 26.7 (CH_2), 24.5 (CH*Me*$_2$), 24.2 (CH*Me*$_2$), 14.4 (*C*H_2CN).

Synthesis of 1-(2,4,6-trimethylphenyl)-3-propylnitrile-imidazolium bromide[1]

1-Mesityl-1*H*-imidazole (934 mg, 5.01 mmol) and 3-bromopropionitrile (1.66 mL, 20.0 mmol) were refluxed for two days in ethyl acetate (150 mL). The resulting white suspension (in an orange solution) was cooled to room temperature, and the precipitate was collected by filtration, rinsed with ethyl acetate until the washings were colourless, and air-dried to afford a light whitish powder (285 mg, 0.890 mmol, yield 18 %). Anal. Calcd for $C_{15}H_{18}N_3Br$: C, 56.26; H, 5.67; N, 13.12. Found: C, 56.14; H, 5.59; N, 13.08. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 10.23 (t, ^4J n.r., 1H, NC*H*N), 8.40 (t, ^3J n.r., 1H, NC*H*), 7.19 (t, ^3J = 1.8, 1H, NC*H*), 7.01 (s, 2H, *m*-H), 5.18 (t, ^3J = 6.3 Hz, 2H, NCH_2), 3.49 (t, ^3J = 6.3 Hz, 2H, CH_2CN), 2.35 (s, 3H, *p*-Me), 2.08 (s, 6H, *o*-Me). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ 141.8 (*p*-C_{Ar}), 138.2 (N*C*HN), 134.4, (*o*-C_{Ar}), 130.6 (*ipso*-C_{Ar}), 130.1 (*m*-C_{Ar}), 124.2 (N*C*H), 123.4 (N*C*H), 116.8 (CN), 46.1 (N*C*H_2), 21.2 (*p*-Me), 20.7 (*C*H_2CN), 17.8 (*o*-Me). Note: Under the previously reported conditions,[1] we have observed the decomposition of 1-(2,4,6-trimethylphenyl)-3-propylnitrile-imidazolium bromide into acrylonitrile and 1-(2,4,6-trimethylphenyl)-imidazolium bromide salt in the reaction medium. This salt's solubility is too similar to that of 1-(2,4,6-trimethylphenyl)-3-propylnitrile-imidazolium bromide to allow a proper separation. The same degradation may be observed under the conditions reported here, if the reaction is carried out for longer than 3 days.

Figure S1. ^{1}H NMR spectrum of [NiBrCp{Mes-NHC-$(CH_2)_2$CN}] (**b**)

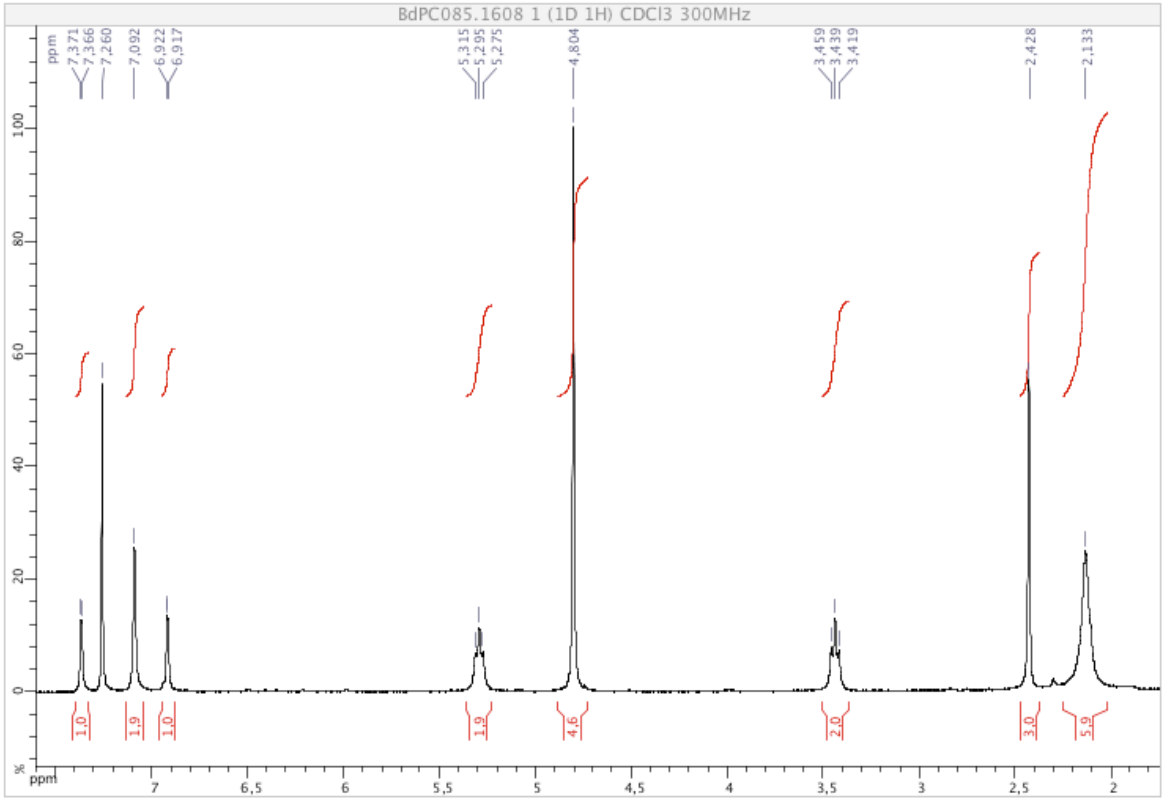


Figure S2. ^{13}C{^{1}H} NMR spectrum of [NiBrCp{Mes-NHC-$(CH_2)_2$CN}] (**b**)

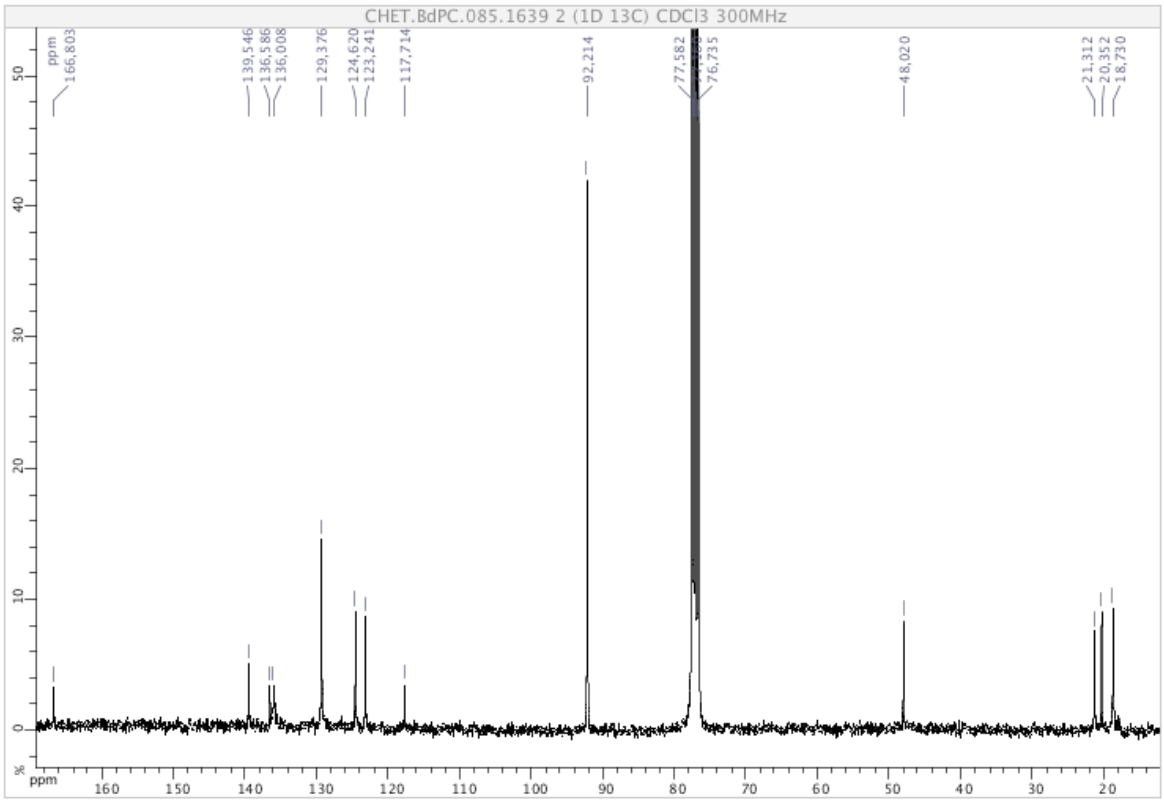


Figure S3. ^{1}H NMR spectrum of [NiClCp{DiPP-NHC-$(CH_2)_3$CN}] (**d**)

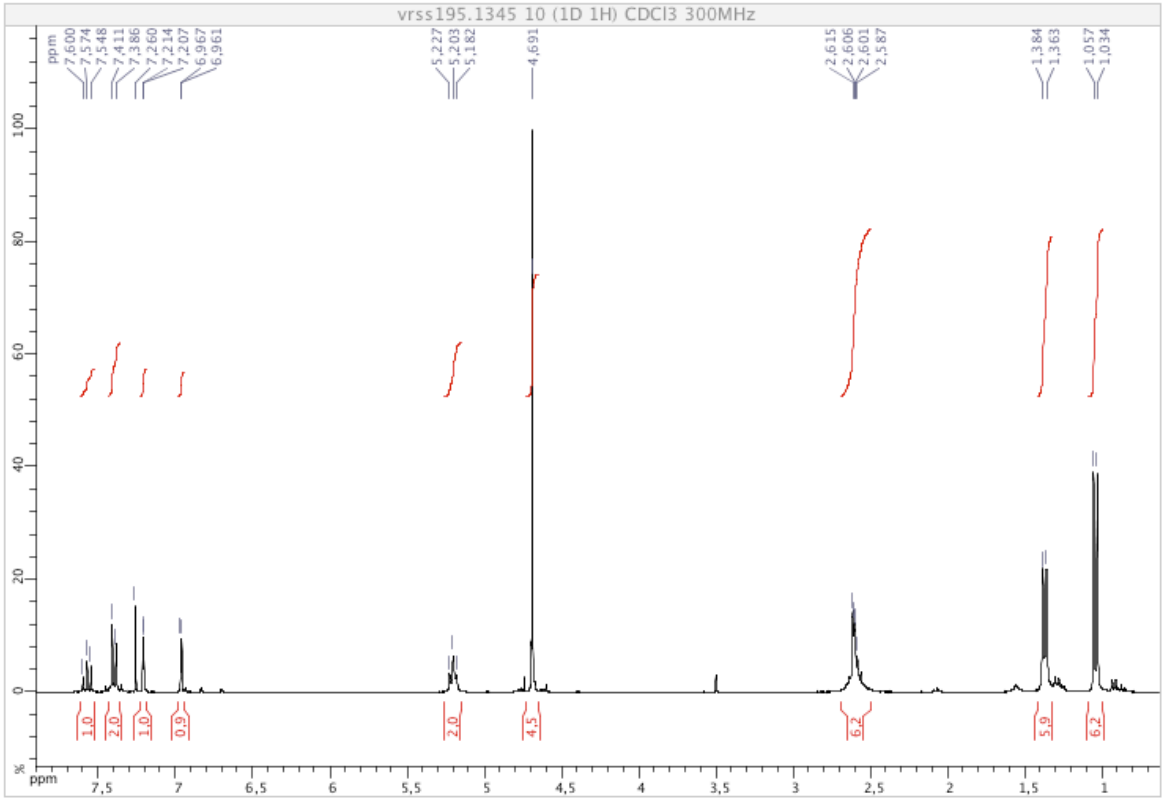


Figure S4. ^{13}C {^{1}H} NMR spectrum of [NiClCp{DiPP-NHC-$(CH_2)_3$CN}] (**d**)

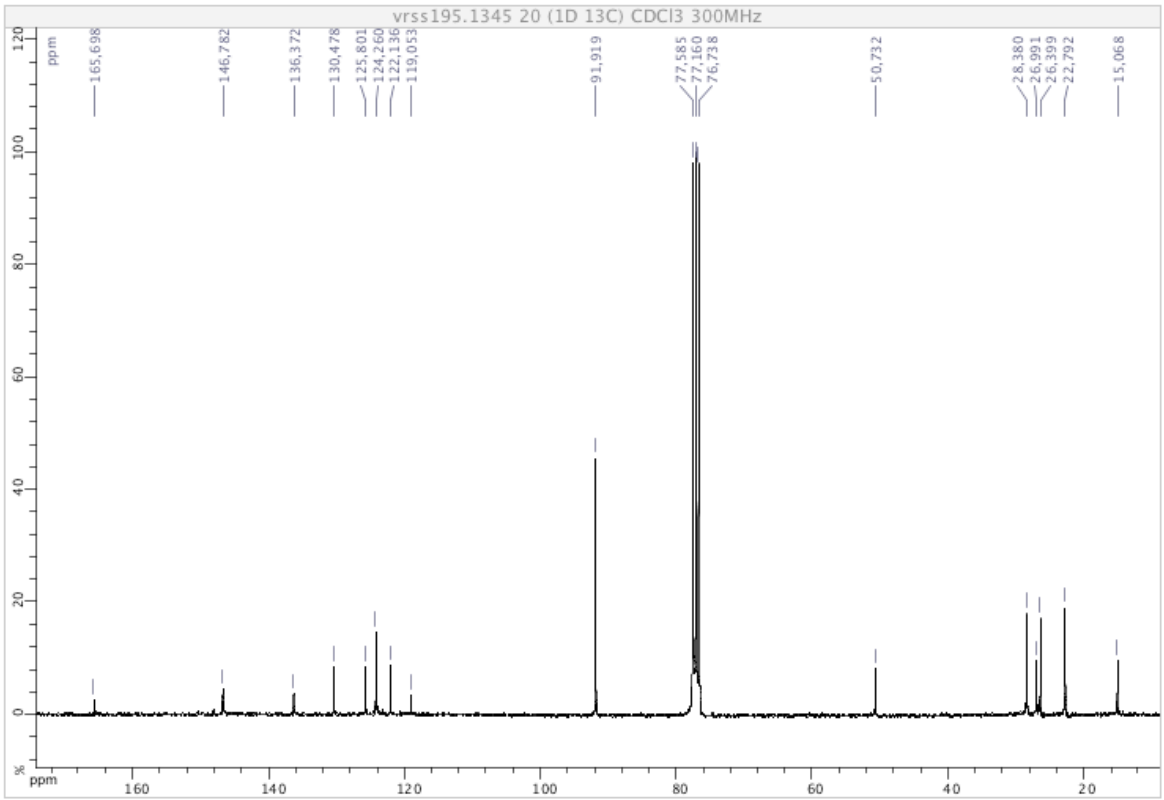


Figure S5. ^{1}H NMR spectrum of [NiCp{Mes-NHC-CH_2CH(CN)}] (**1b**)

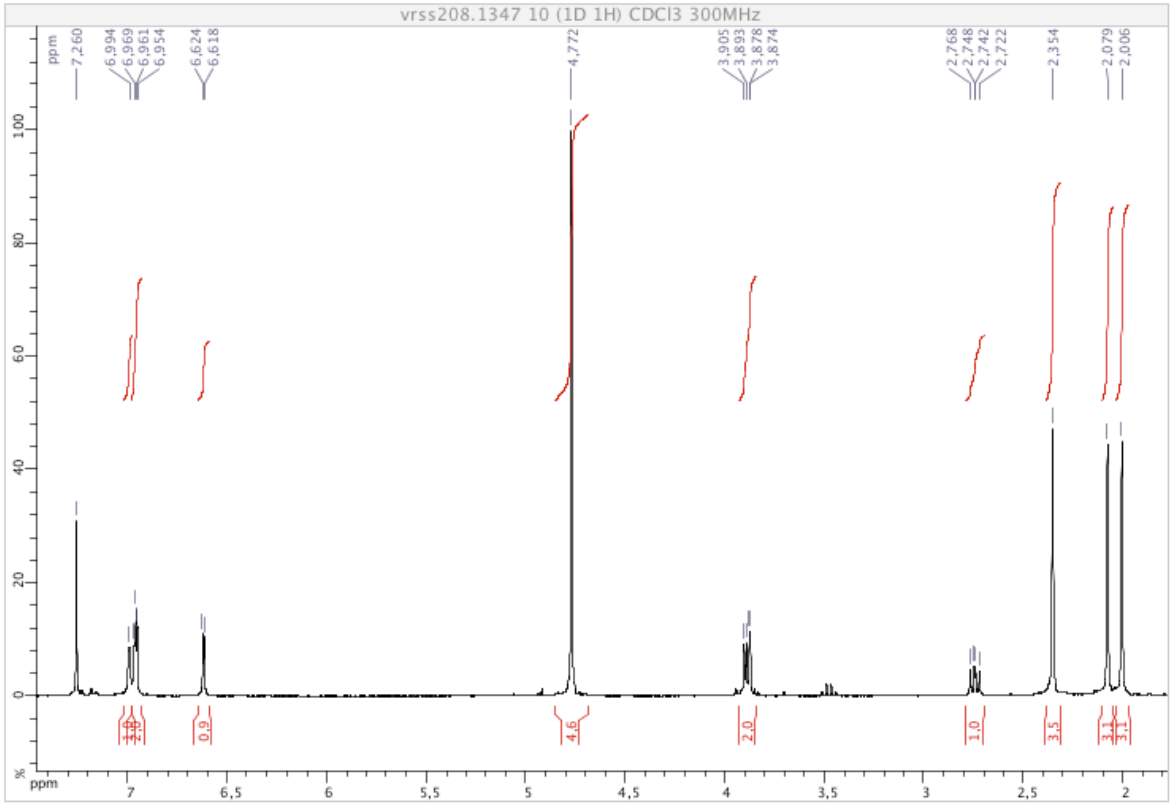


Figure S6. ^{13}C {^{1}H} NMR spectrum of [NiCp{Mes-NHC-CH_2CH(CN)}] (**1b**)

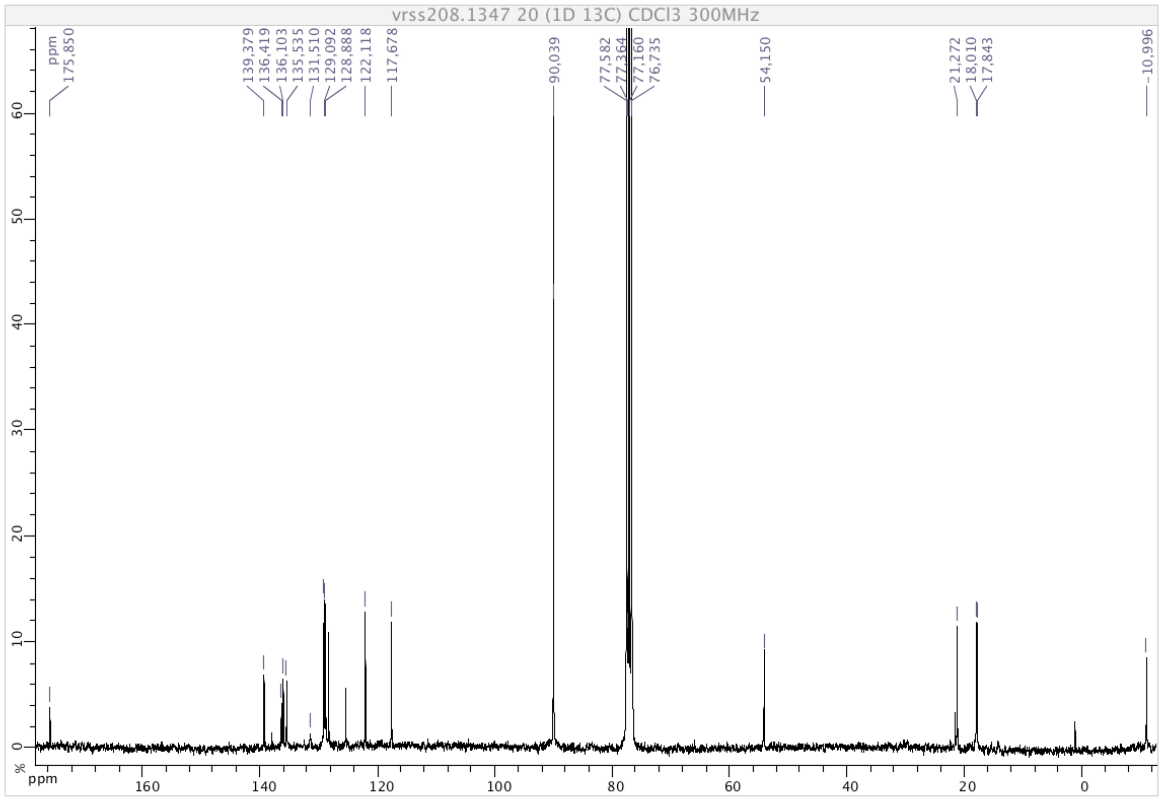


Figure S7. ^{1}H NMR spectrum of [NiCp{DiPP-NHC-$(CH_2)_2$CH(CN)}] (**1d**)

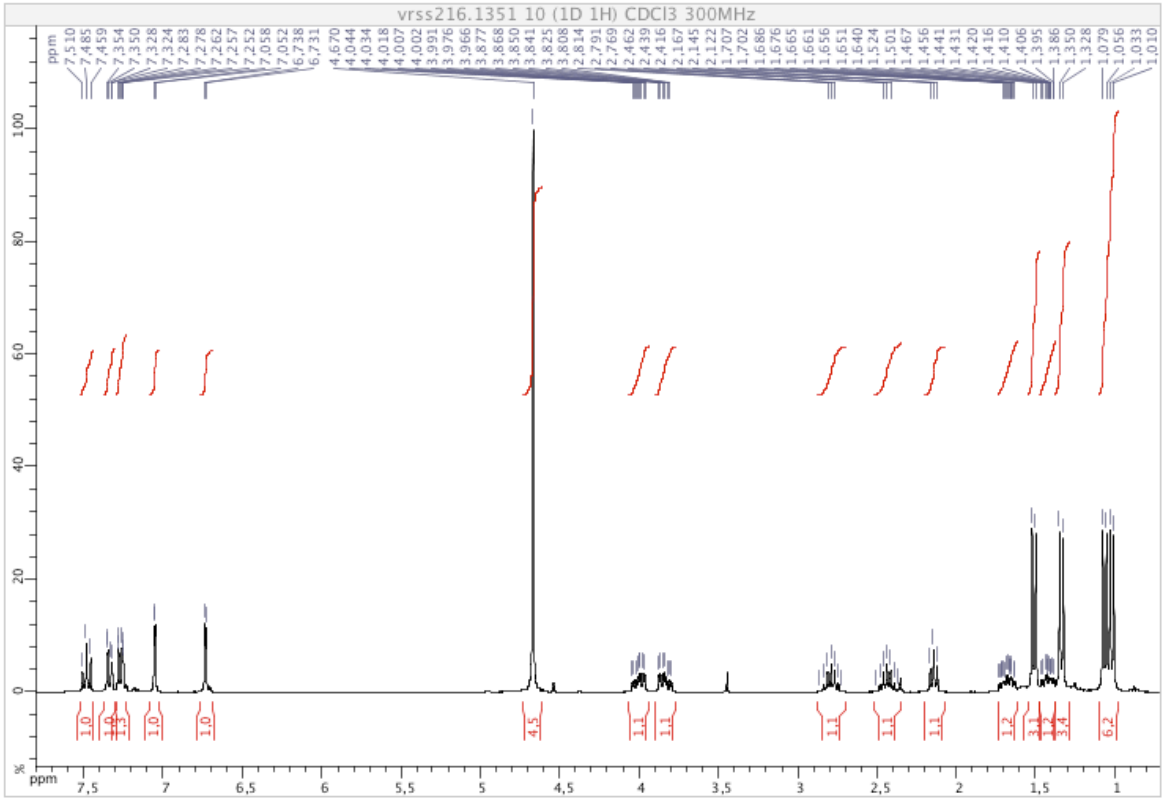


Figure S8. ^{13}C {^{1}H} NMR spectrum of [NiCp{DiPP-NHC-$(CH_2)_2$CH(CN)}] (**1d**)

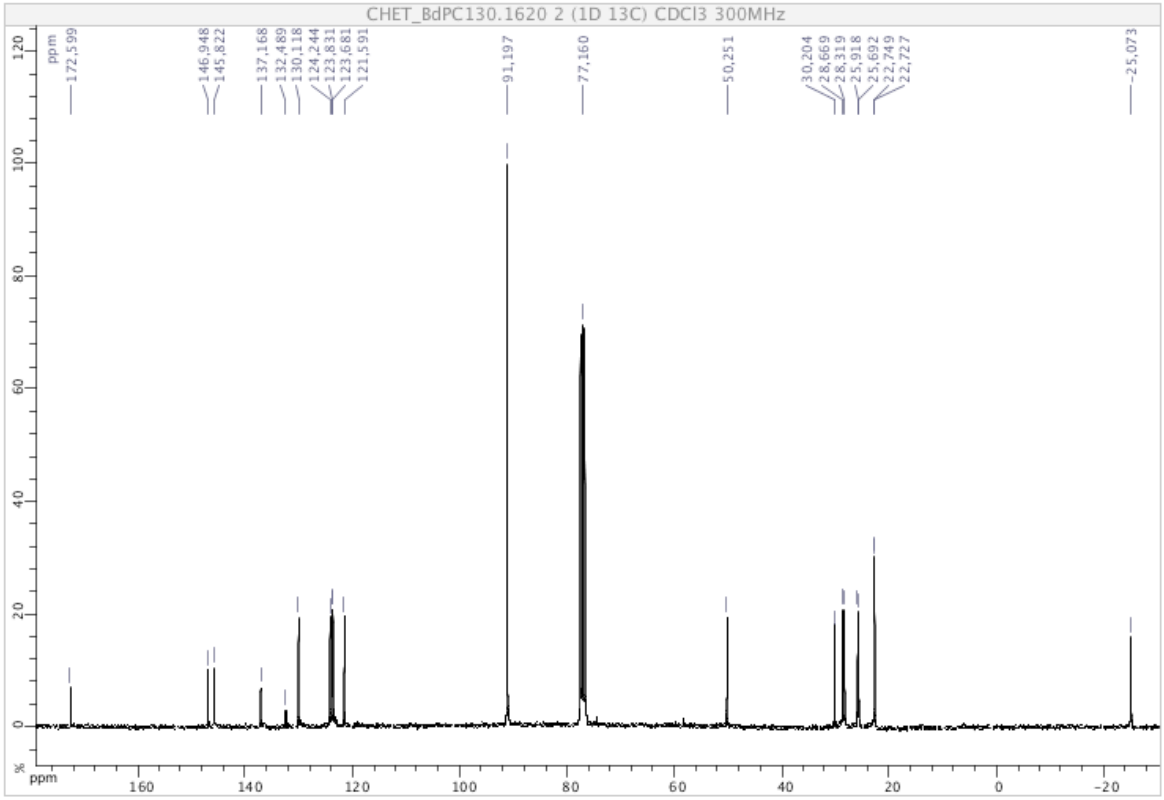


Table S1. X-ray crystallographic data and data collection parameters for **1a** and **1b**

Complex	**1a**	**1b**
Empirical formula	$C_{12}H_{13}N_3Ni$	$C_{20}H_{21}N_3Ni$
Formula weight	257.96	362.11
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Temperature (K)	173(2)	173(2)
a (Å)	8.4784(2)	9.3425(10)
b (Å)	17.3913(5)	13.7491(15)
c (Å)	8.5806(2)	14.2032(15)
α (°)	90	80.591(6)
β (°)	118.362(1)	86.833(7)
γ (°)	90	82.101(7)
V (Å^3)	1113.34(5)	1781.8(3)
Z	4	4
D_{calcd} (Mg.m^{-3})	1.539	1.350
Absorp coeff (mm^{-1})	1.716	1.592
Crystal form, colour	Prism, green	Needle, green
Crystal size (mm)	0.32 × 0.20 × 0.14	0.25 × 0.10 × 0.06
h, k, l_{max}	12, 17, 11	11, 16, 16
T_{min}, T_{max}	0.670, 0.747	0.617, 0.753
Reflns collected	16574	27037
Independent reflns, R_{int}	4192, 0.0196	6205, 0.0760
Reflns with I > 2σ(I)	3557	4232
R [$F^2 > 2\sigma(F^2)$]	0.0260	0.0883
$wR(F^2)$	0.0648	0.2721
GOF on F^2	1.050	1.066

Figure S9. ^{1}H NMR spectra of [Ni{Me-NHC-$CH_2CH(CN)$}($NCCH_3$)]$^{+}PF_6^{-}$ in CD_3CN (**2a**)

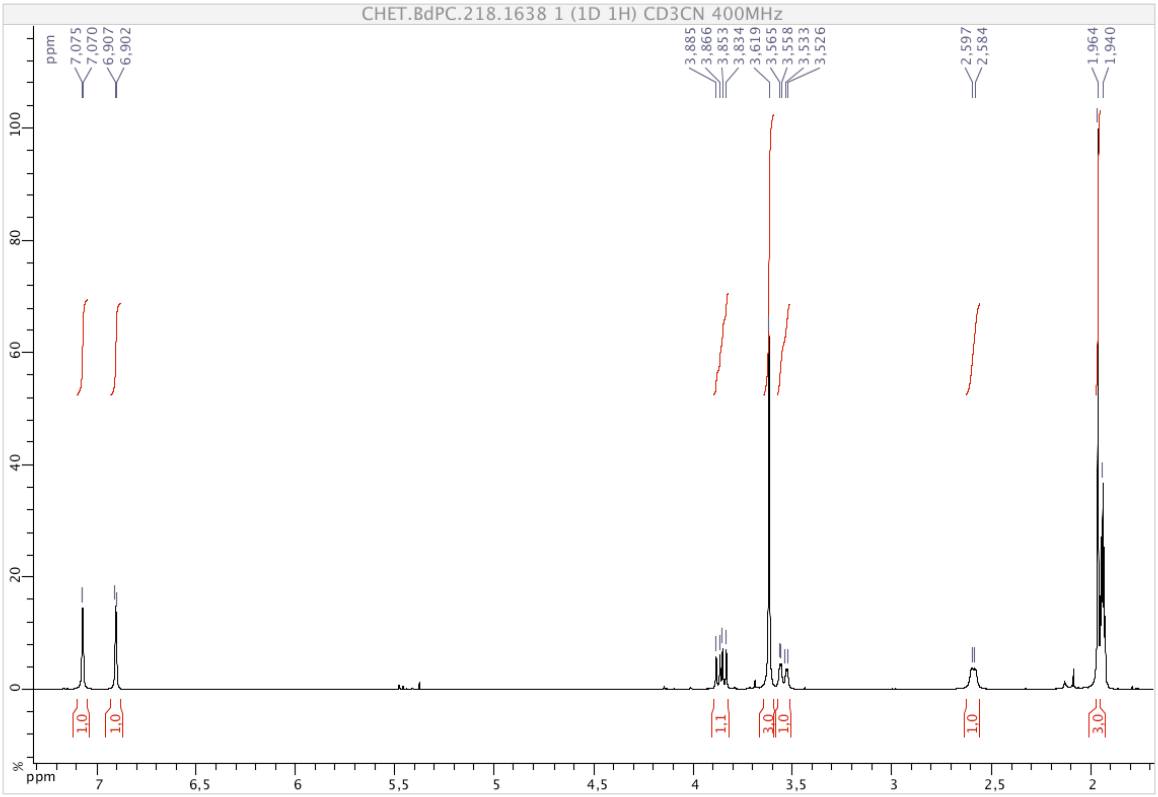


Figure S10. ^{1}H NMR spectra of [Ni{Me-NHC-$CH_2CH(CN)$}($NCCH_3$)]$^{+}PF_6^{-}$ in C_5D_5N (**2a**)

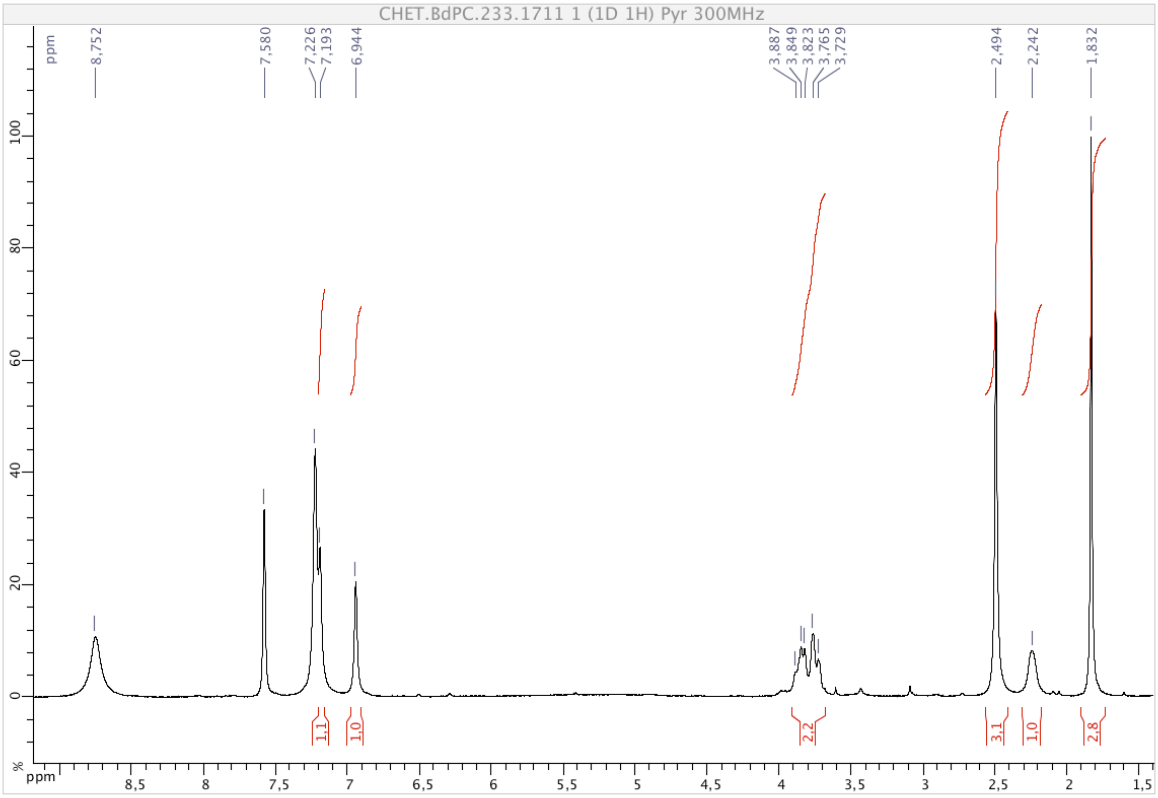


Figure S11. ^{13}C $\{^{1}H\}$ NMR spectrum of $[Ni\{Me\text{-}NHC\text{-}CH_2CH(CN)\}(NCCH_3)]^+PF_6^-$ (**2a**) in CD_3CN

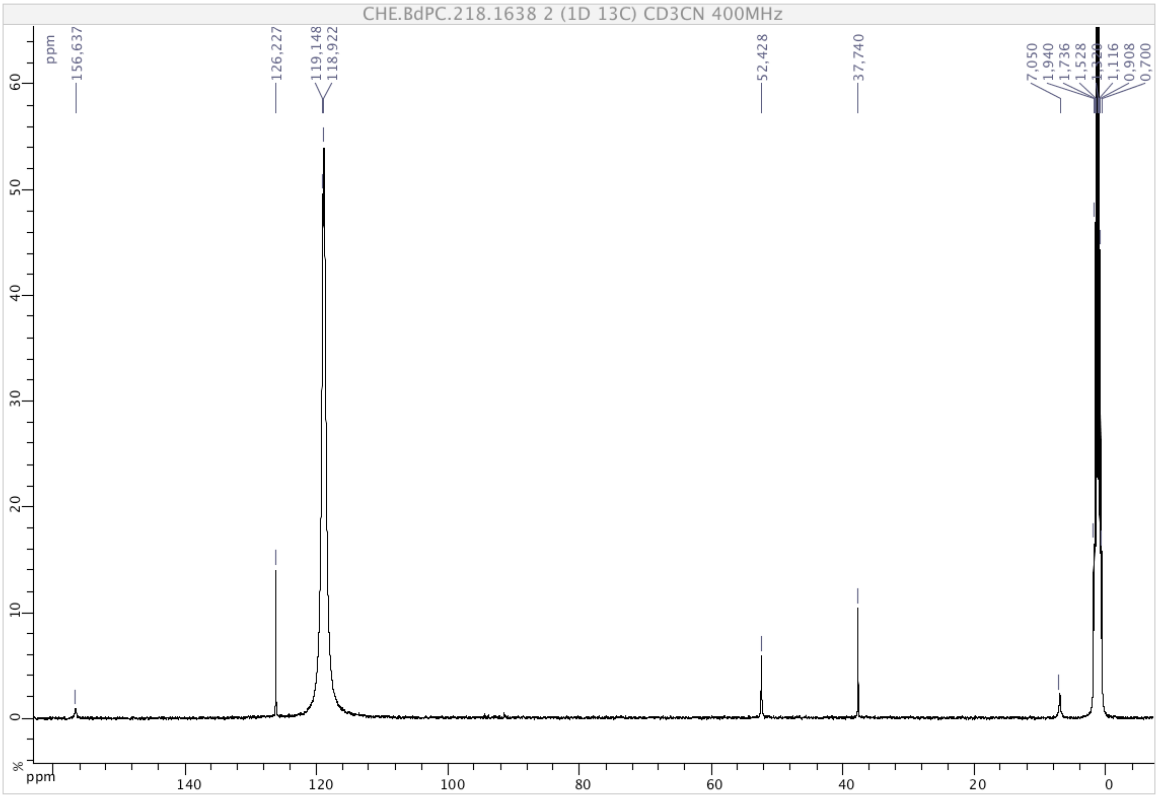


Figure S12. ^{13}C $\{^{1}H\}$ NMR spectrum of $[Ni\{Me\text{-}NHC\text{-}CH_2CH(CN)\}(NCCH_3)]^+PF_6^-$ (**2a**) in C_5D_5N

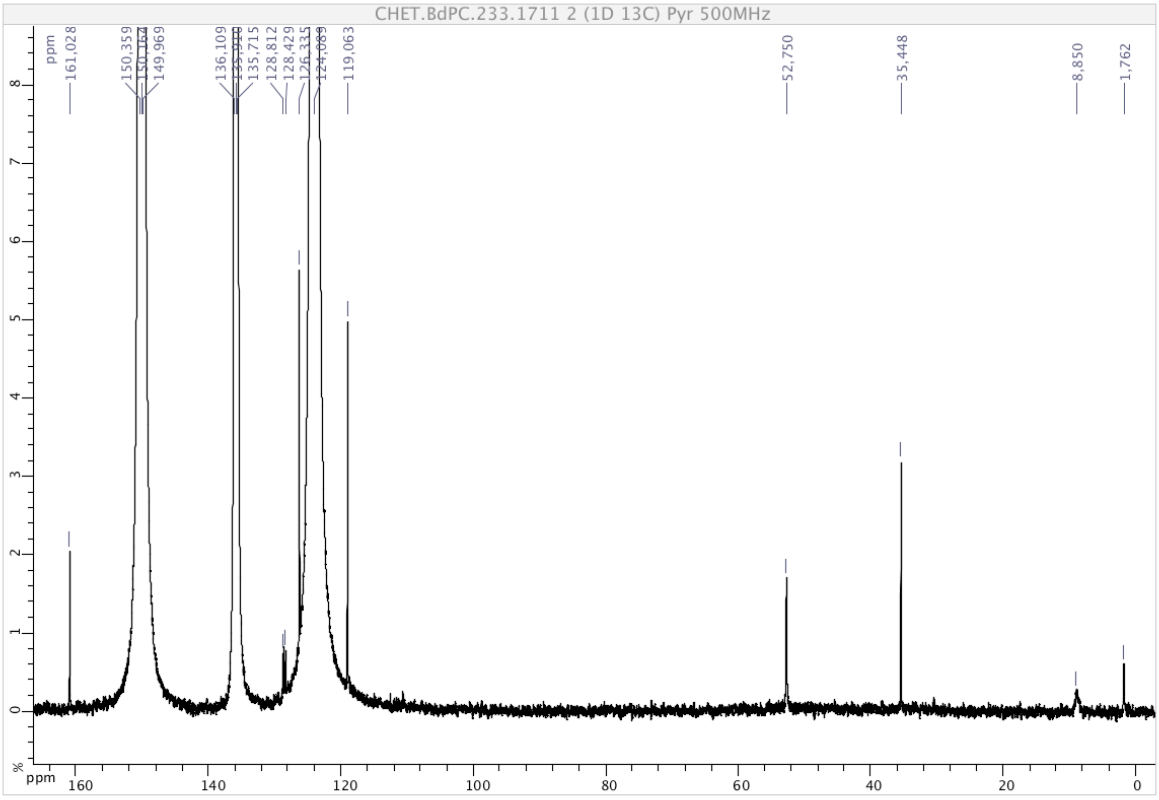


Figure S13. ^{1}H NMR spectrum of [Ni{Mes-NHC-$CH_2CH(CN)$}($NCCH_3$)]$^{+}PF_6^{-}$ (**2b**) in CD_3CN

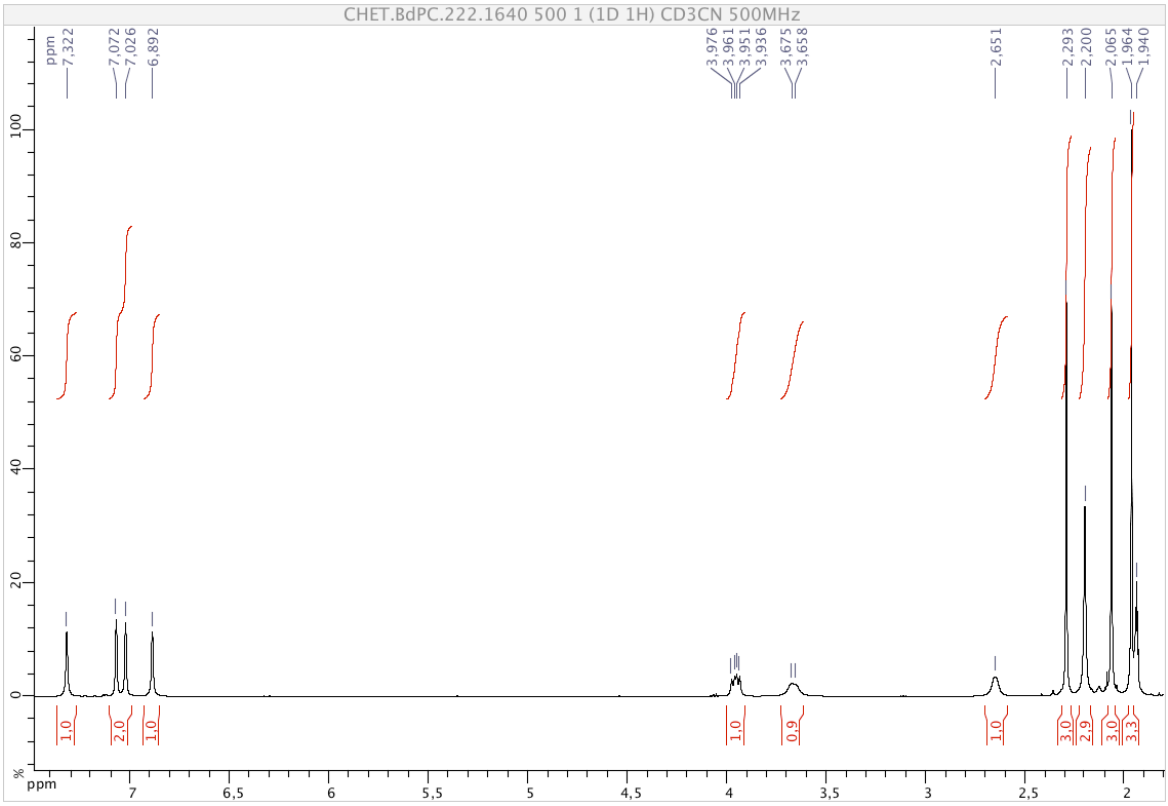


Figure S14. ^{1}H NMR spectrum of [Ni{Mes-NHC-$CH_2CH(CN)$}($NCCH_3$)]$^{+}PF_6^{-}$ (**2b**) in C_5D_5N

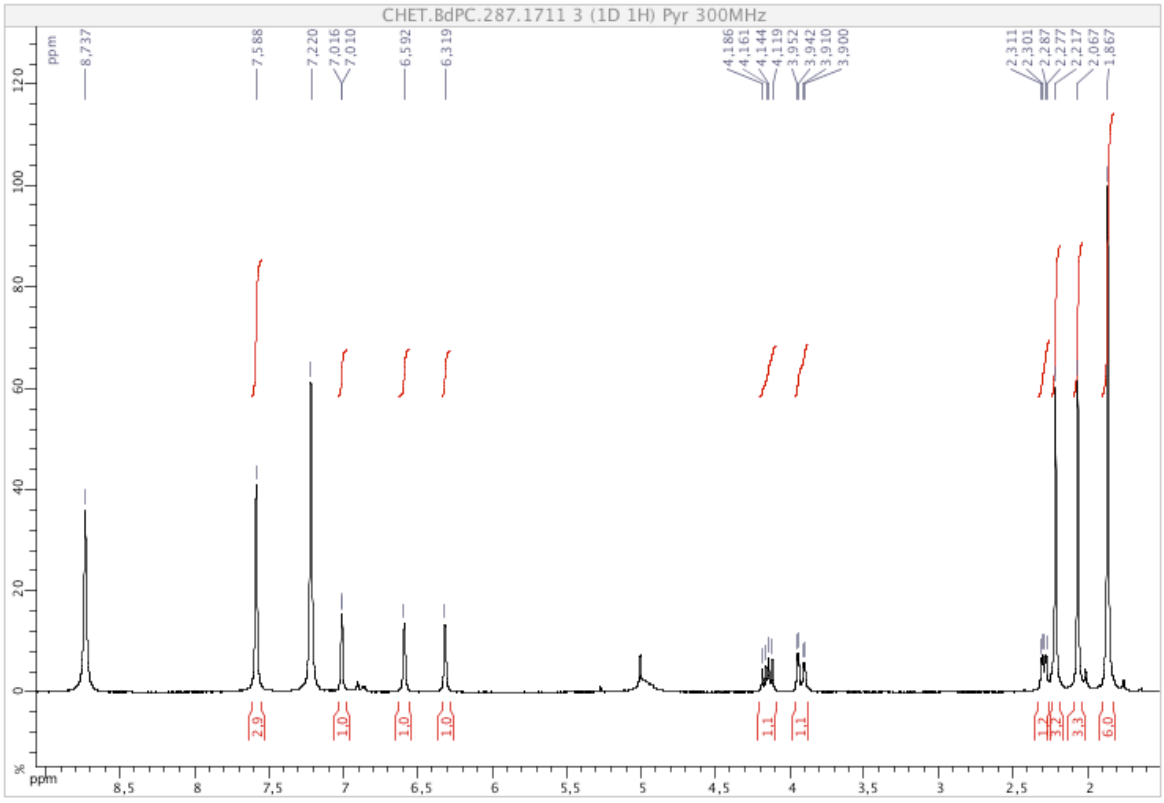


Figure S15. ^{13}C {^{1}H} NMR spectrum of [Ni{Mes-NHC-$CH_2CH(CN)$}($NCCH_3$)]$^{+}PF_6^{-}$ (**2b**) in CD_3CN

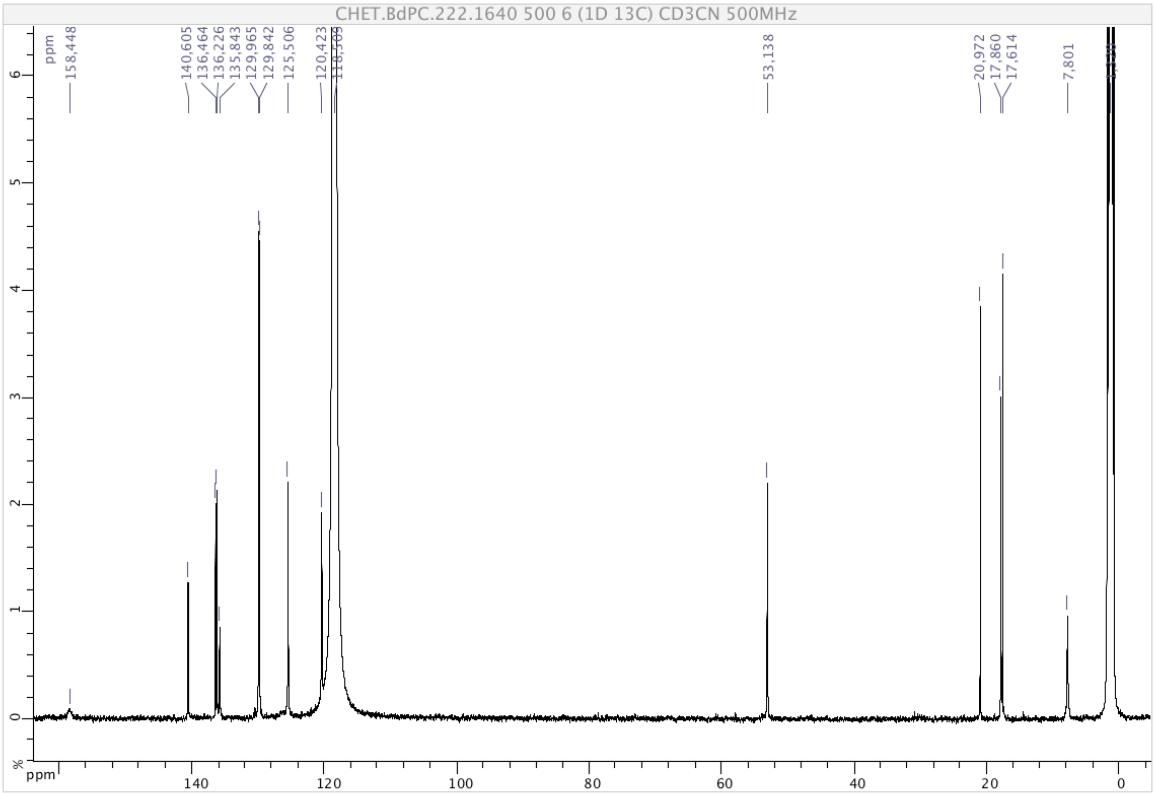


Figure S16. ^{13}C {^{1}H} NMR spectrum of [Ni{Mes-NHC-$CH_2CH(CN)$}($NCCH_3$)]$^{+}PF_6^{-}$ (**2b**) in C_5D_5N

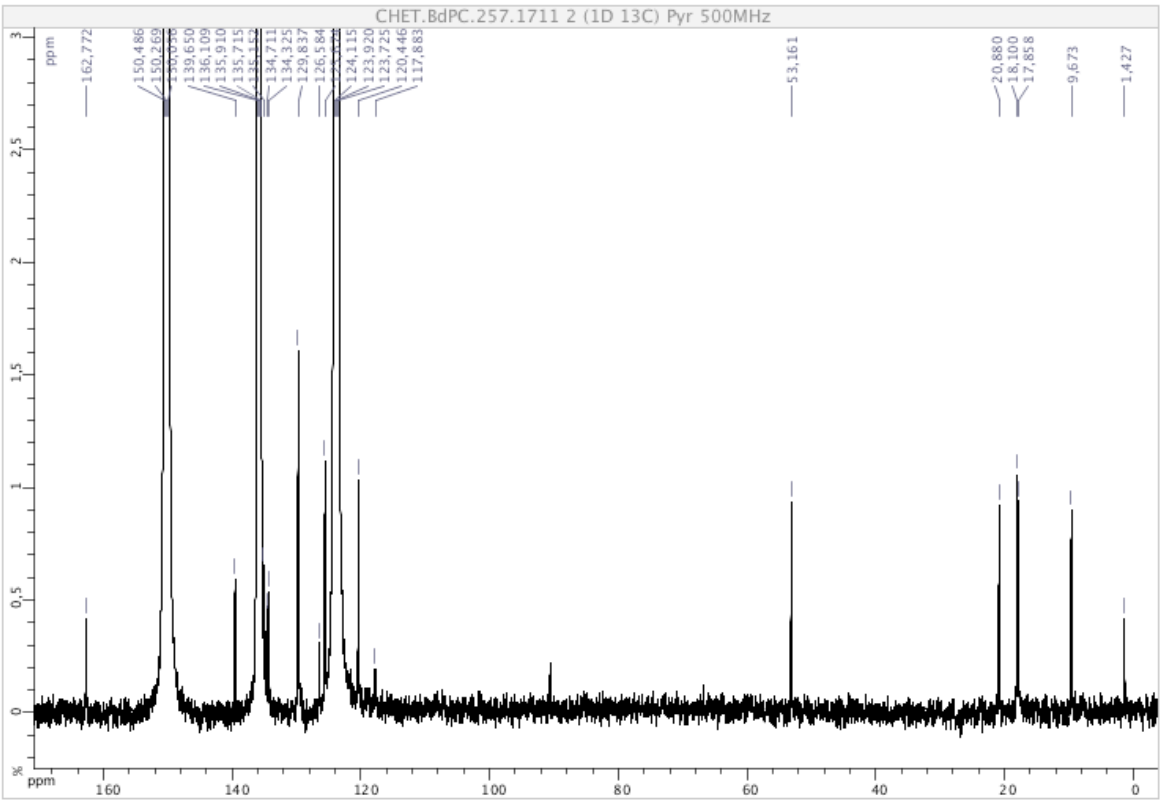


Figure S17. ^{1}H NMR spectrum of [Ni{Mes-NHC-$(CH_2)_2$CH(CN)}$(NCCH_3)$]$^{+}PF_6^{-}$ (**2c**) in CD_3CN (0.1 M)[2]

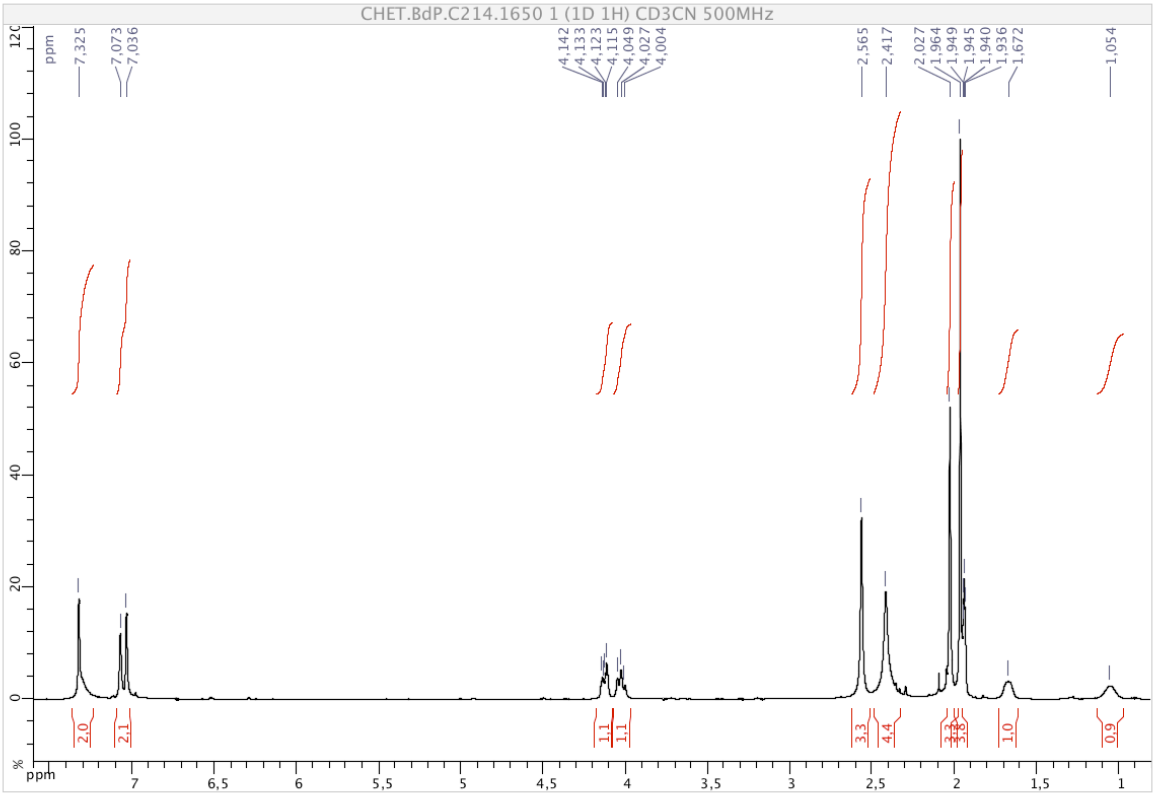


Figure S18. ^{1}H NMR spectrum of [Ni{Mes-NHC-$(CH_2)_2$CH(CN)}$(NCCH_3)$]$^{+}PF_6^{-}$ (**2c**) in C_5D_5N

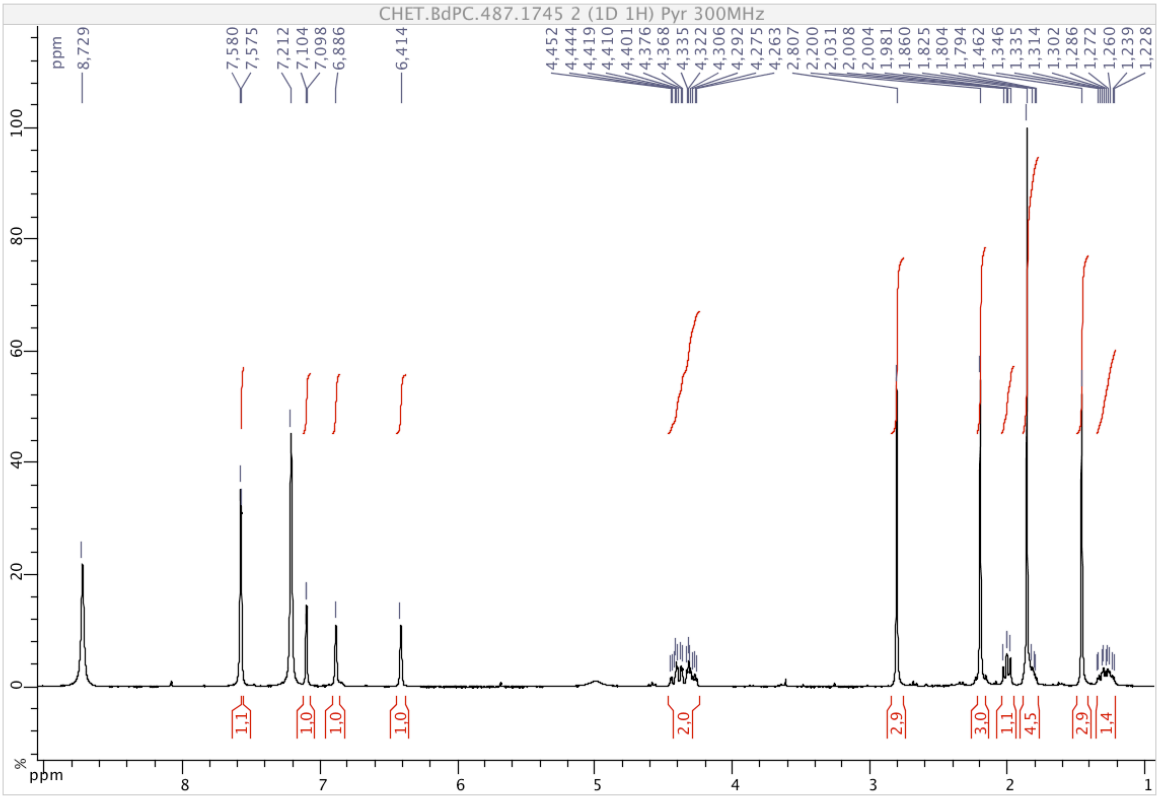


Figure S19. ^{13}C {^{1}H} NMR spectrum of [Ni{Mes-NHC-$(CH_2)_2$CH(CN)}$(NCCH_3)$]$^{+}PF_6^{-}$ (**2c**) in CD_3CN

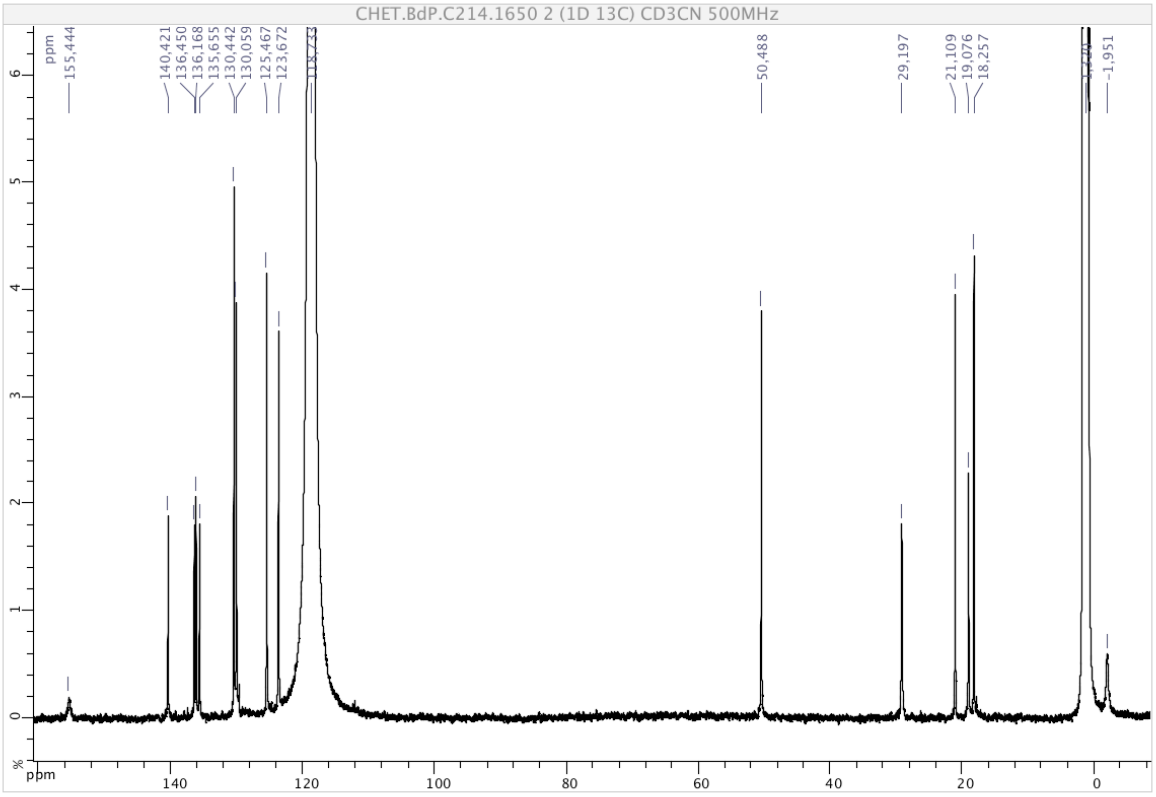


Figure S20. ^{13}C {^{1}H} NMR spectrum of [Ni{Mes-NHC-$(CH_2)_2$CH(CN)}$(NCCH_3)$]$^{+}PF_6^{-}$ (**2c**) in C_5D_5N

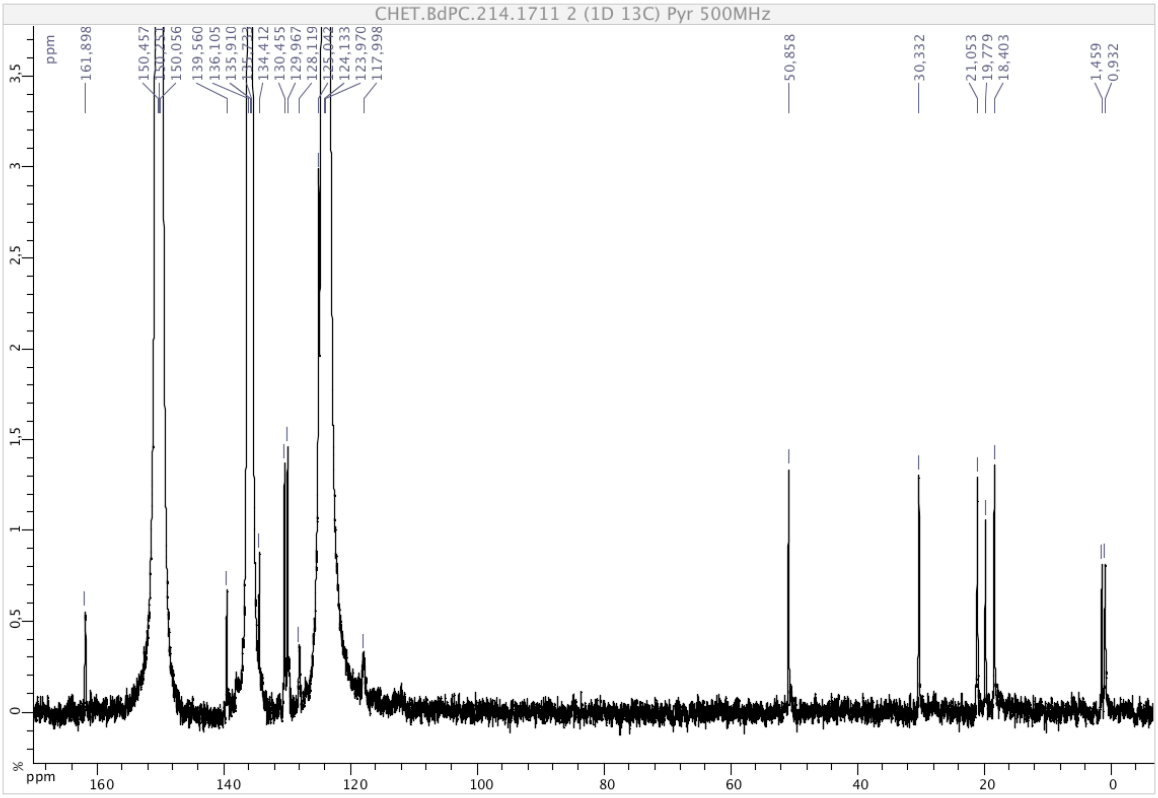


Figure S21. ^{1}H NMR spectrum of [Ni{DiPP-NHC-$(CH_2)_2$CH(CN)}$(NCCH_3)$]$^{+}PF_6^{-}$ (**2d**) in CD_3CN

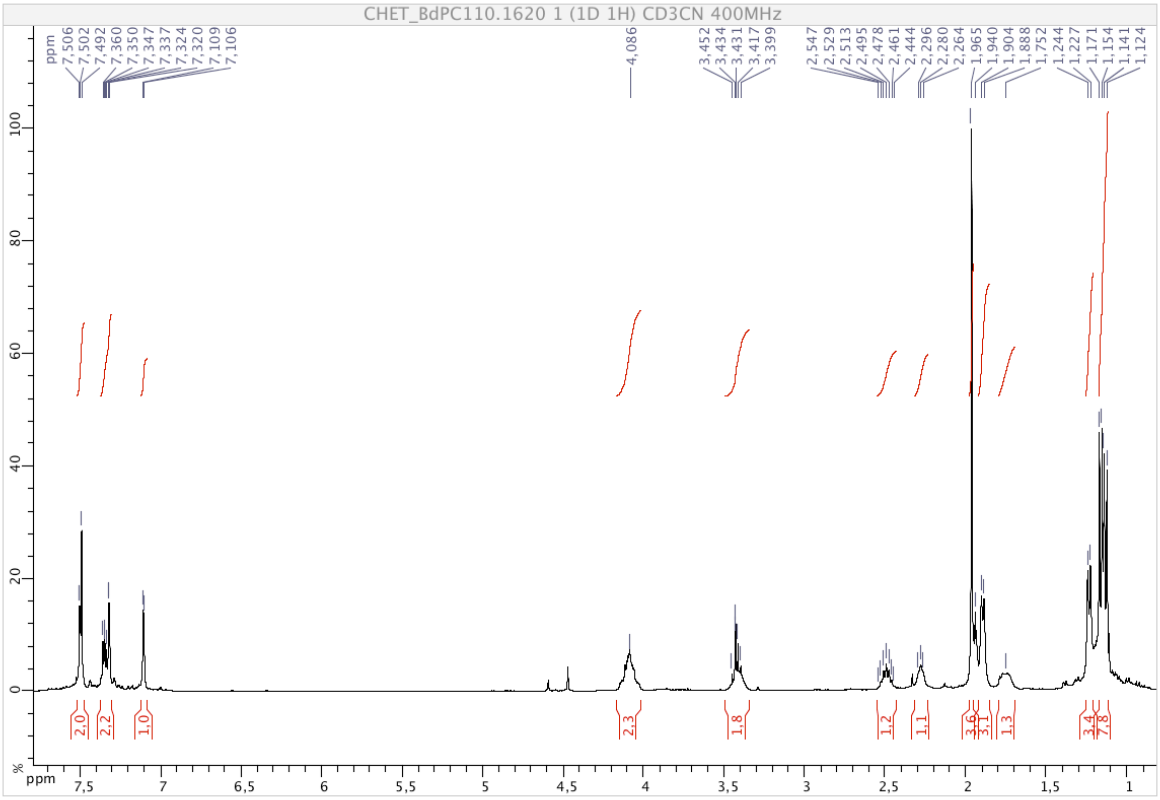


Figure S22. ^{1}H NMR spectrum of [Ni{DiPP-NHC-$(CH_2)_2$CH(CN)}$(NCCH_3)$]$^{+}PF_6^{-}$ (**2d**) in C_5D_5N

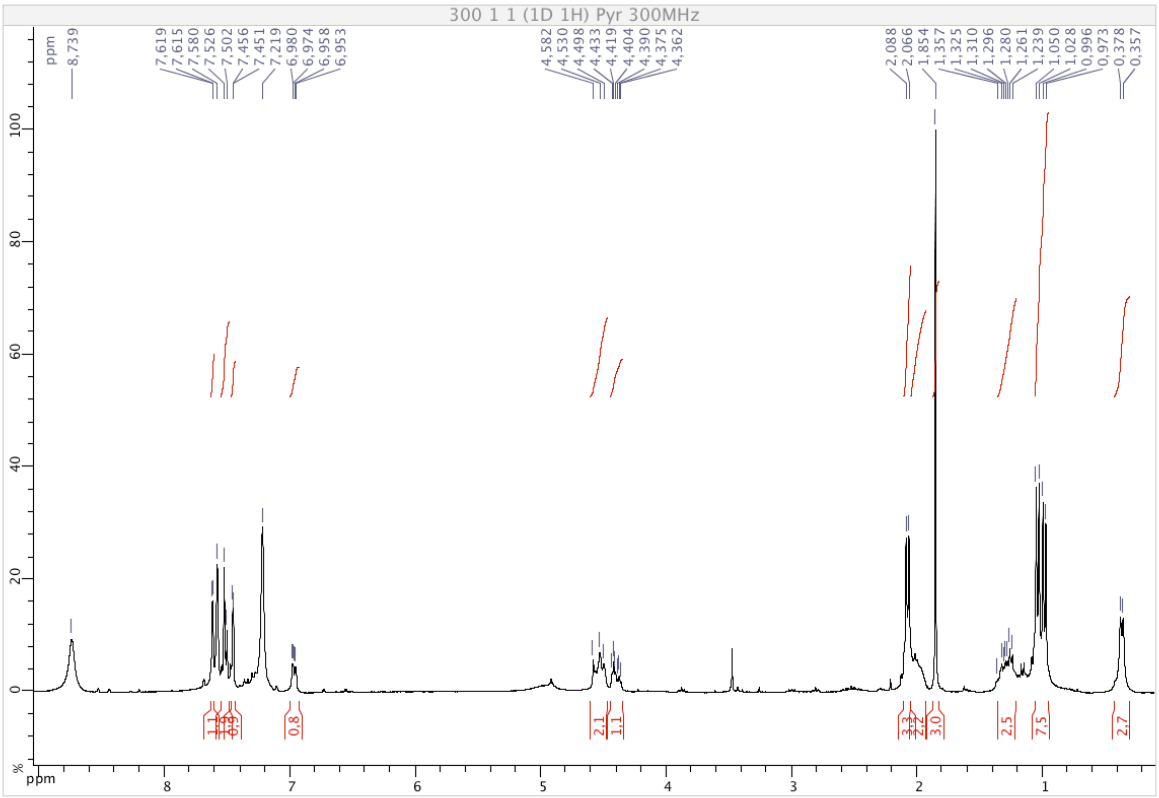


Figure S23. ^{13}C {^{1}H} NMR spectrum of **2d** in CD_3CN

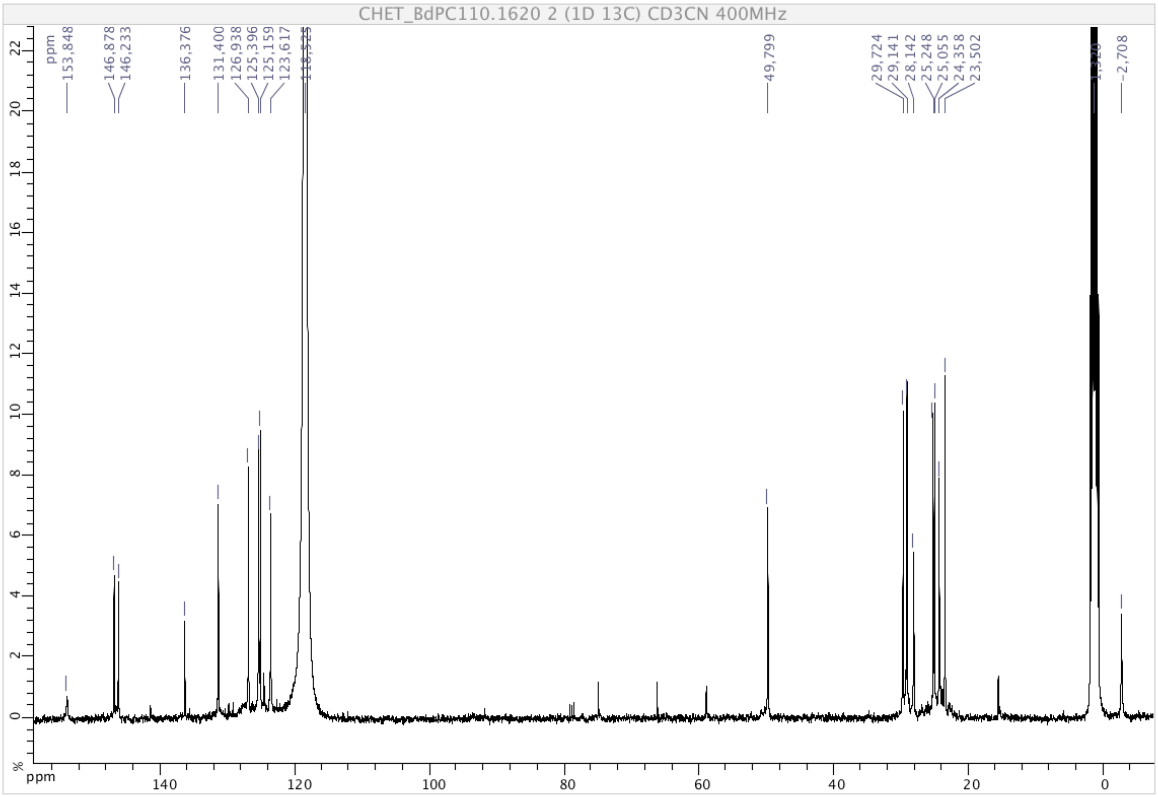


Figure S24. ^{13}C {^{1}H} NMR spectrum of **2d** in C_5D_5N

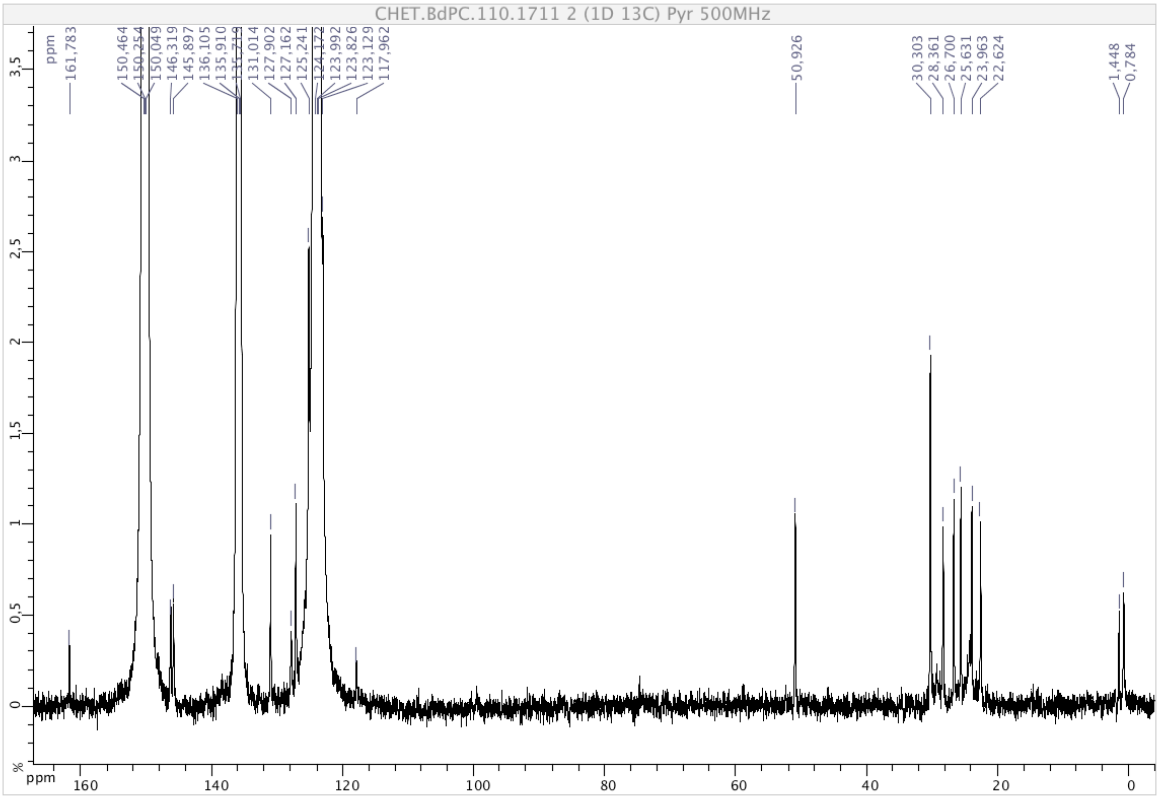


Figure S25. IR spectrum of [Ni{Me-NHC-$CH_2CH(CN)$}$(NCCH_3)$]$^+PF_6^-$ (**2a**)

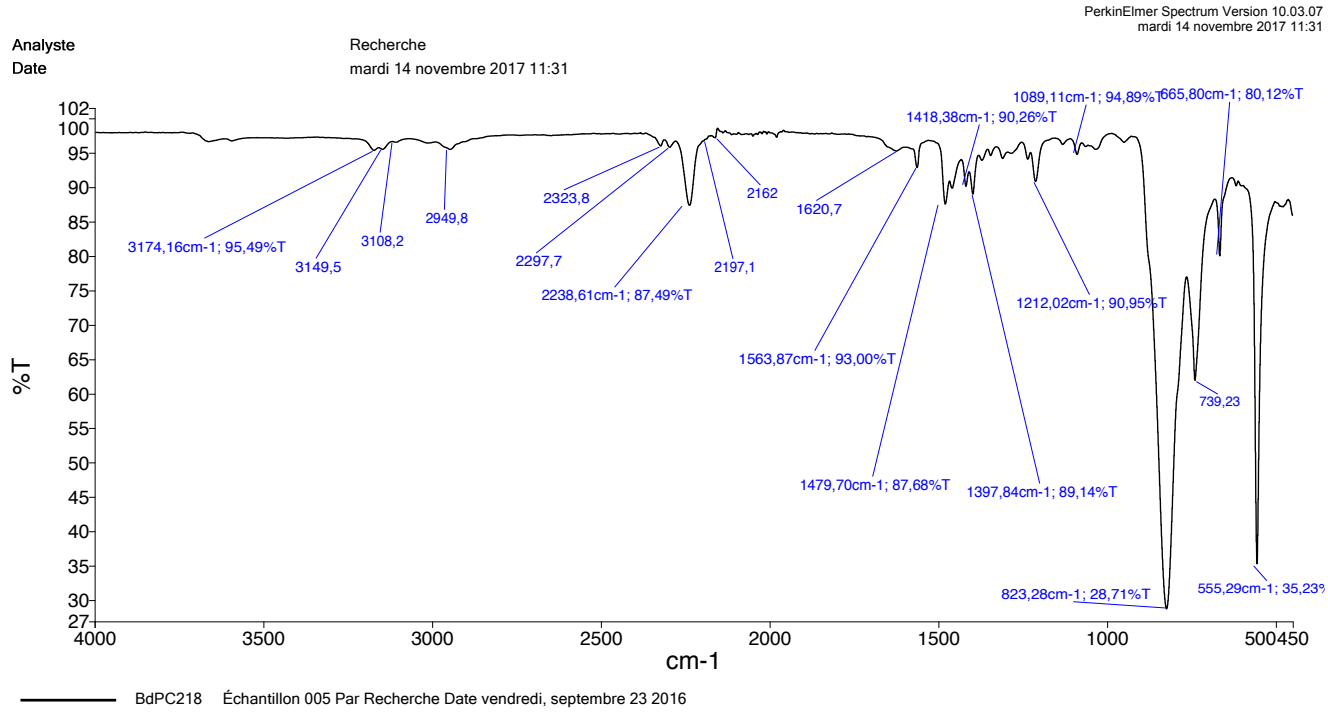


Figure S26. IR spectrum of [Ni{Mes-NHC-$CH_2CH(CN)$}$(NCCH_3)$]$^+PF_6^-$ (**2b**)

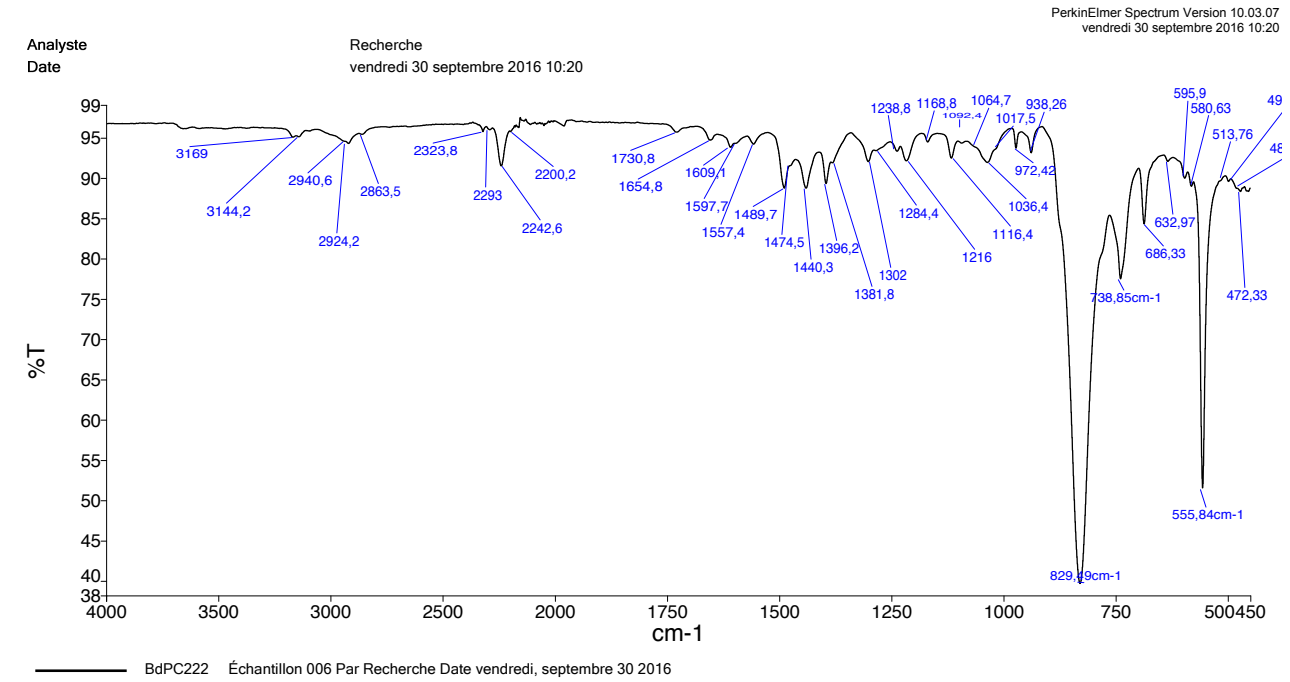


Figure S27. IR spectrum of [Ni{Mes-NHC-$(CH_2)_2CH(CN)$}$(NCCH_3)$]$^+PF_6^-$ (**2c**)

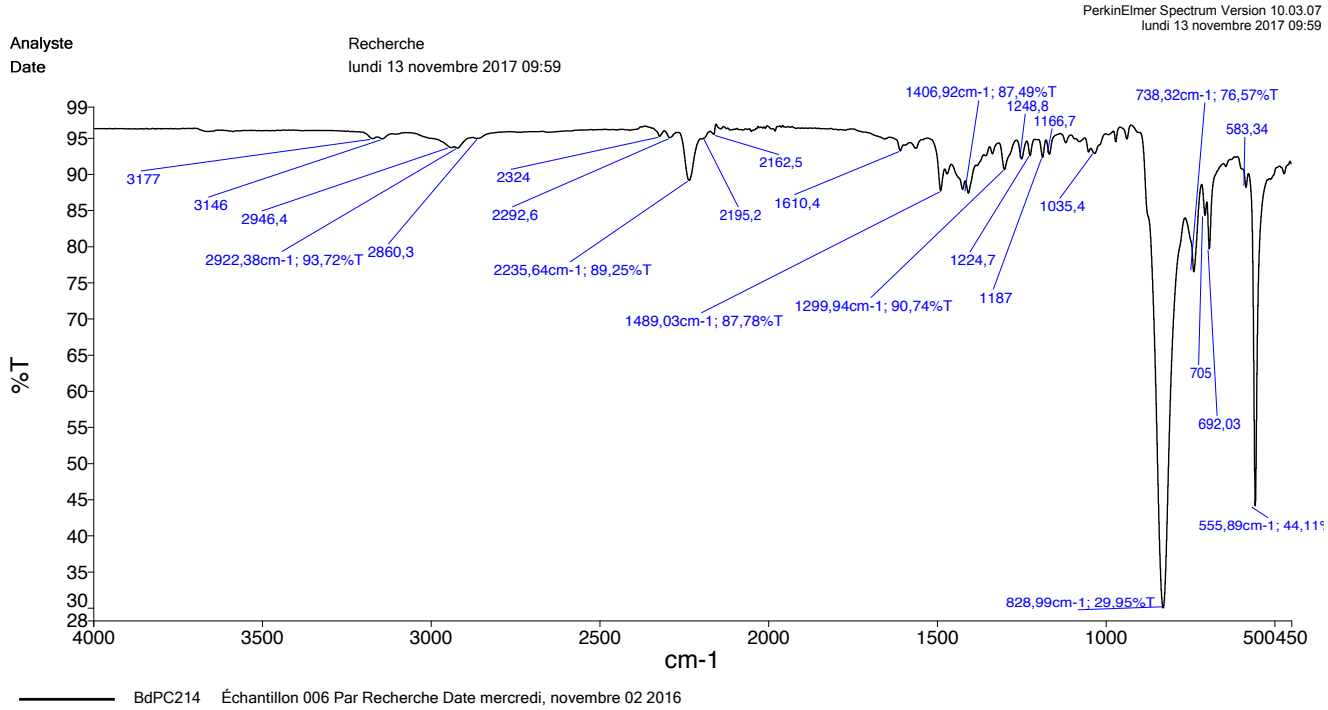
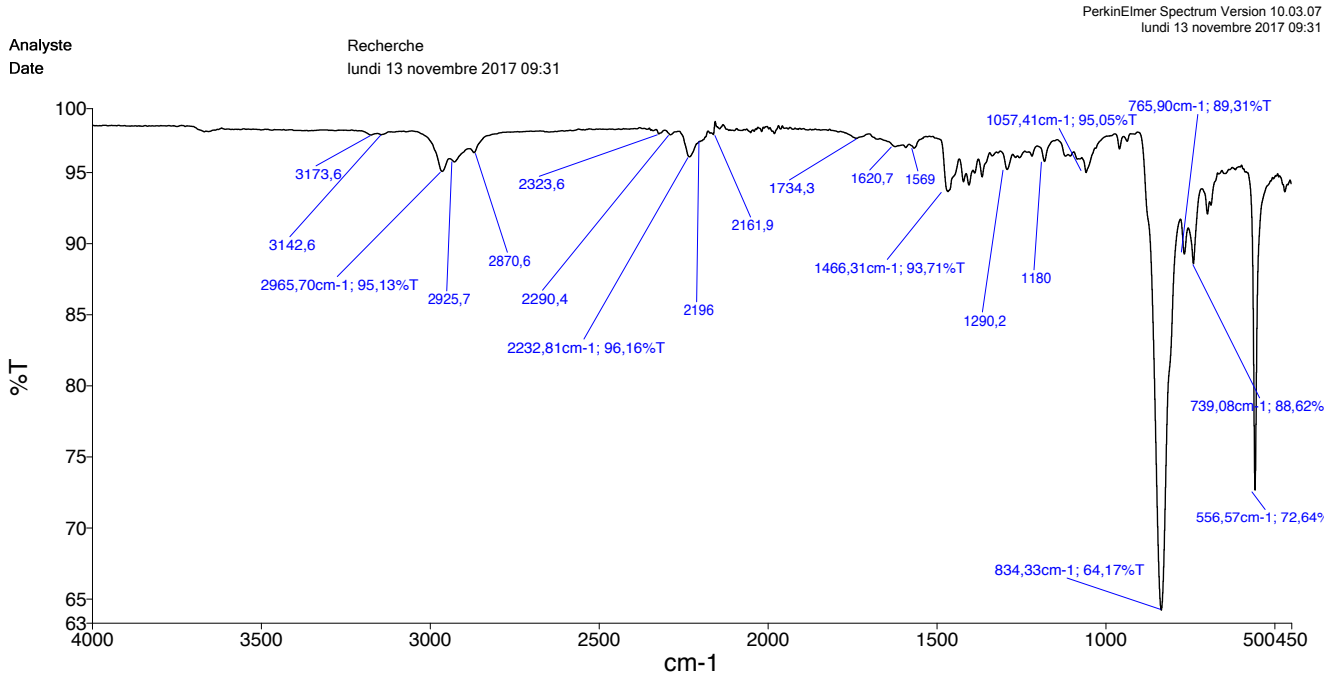


Figure S28. IR spectrum of [Ni{DiPP-NHC-$(CH_2)_2CH(CN)$}$(NCCH_3)$]$^+PF_6^-$ (**2d**)



Optimisation of the phenylation of benzothiazole: influence of the base and of the solvent

Table S2. Coupling of benzothiazole and iodobenzene catalysed by **2c** in the presence of various bases and solvents.[a]

Entry	Base	Solvent	Temp. (°C)	Conversion (%)[b]
1	LiO*t*-Bu	1,4-dioxane	140	69
2	NaO*t*-Bu	1,4-dioxane	140	0
3	KO*t*-Bu	1,4-dioxane	140	0
4	LiOH	1,4-dioxane	140	0
5	NaOH	1,4-dioxane	140	11[c]
6	Cs_2CO_3	1,4-dioxane	140	0
7	K_3PO_4	1,4-dioxane	140	0
8	KOAc	1,4-dioxane	140	0
9	NEt_3	1,4-dioxane	140	0
10	LiO*t*-Bu	THF	70	0
11	LiO*t*-Bu	Toluene	110	20
12	LiO*t*-Bu	Diglyme	165	0
13	LiO*t*-Bu	Acetonitrile	85	0

[a] Reaction conditions: benzothiazole (1 equiv.), iodobenzene (1.5 equiv.), base (2 equiv.), **2c** (5 mol%), solvent (0.13 M), Δ, 18 h. [b] Conversion determined by GC; average value of two run; dodecane used as internal standard. [c] No conversion to 2-phenylbenzo[*d*]thiazole.

GC conditions

GC analyses were performed with an Agilent 7820A instrument equipped with a HP-5 column (cross-linked 5% phenyl silicone gum, 30 m × 0.32 mm × 0.25 μm). H_2/air was used as the vector gas. The GC conditions were: (i) 50 °C for 5 min, (ii) increase in temperature at a rate of 10 °C/min until 150 °C, (iii) isotherm for 5 min, and (iv) temperature increase at 20 °C/min until 240 °C. *n*-Dodecane was used as internal standard. Conversion was determined by considering instrument response factors.

Control experiments

Investigation of the mercury and radical scavenger effects

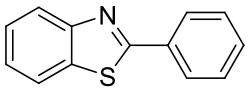
An oven dried Schlenk tube equipped with a magnetic stir bar was charged with **2c** (10 mg, 0.0201 mmol), LiO*t*-Bu (59 mg, 0.737 mmol, 2.0 equiv.), benzothiazole (40 µL, 0.369 mmol, 1.0 equiv.), iodobenzene (60 µL, 0.536 mmol, 1.5 equiv.), Hg (460 mg, 2.29 mmol) or TEMPO (3 mg, 0.0192 mmol), and 1,4-dioxane (3 mL), and sealed. The Schlenk tube was then introduced into an oil bath that was heated up to a temperature of 140 °C. After 36 h, the reaction medium was cooled to room temperature, and the volatiles were evaporated under high vacuum. The resulting brown residue was extracted with diethyl ether and filtered over a silica pad (2.5 × 1 cm). The collected filtrate was then concentrated under vacuum, and loaded onto a silica column (Merck Silica Gel 60 - mesh size 40-60 mm; 28 × 3.5 cm) pre-wet with petroleum ether (bp. 40-70 °C). Elution with a petroleum ether/ethyl acetate 98/2 gave 2-phenylbenzothiazole as a white solid (Hg: 4 mg, 0.0189 mmol, 5 %; TEMPO: 2 mg, 0.00947 mmol, 3 %).

Control experiment for the formation of 2,2'-bibenzothiazole

An oven dried Schlenk tube equipped with a magnetic stir bar was charged with **2c** (10 mg, 0.0201 mmol), LiO*t*-Bu (59 mg, 0.737 mmol), benzothiazole (40 µL, 0.369 mmol) and 1,4-dioxane (3 mL), and sealed. The Schlenk tube was then introduced into an oil bath that was heated up to a temperature of 140 °C. After 36 h, the reaction medium was cooled to room temperature, and the volatiles were evaporated under vacuum. The resulting brown residue was extracted with diethyl ether and filtered over a silica pad (43-60 µm, 2.5 × 2 cm) that was washed with Et_2O. The collected filtrate was then concentrated under vacuum to give a pale yellow solid. The solid dissolved in CH_2Cl_2 and loaded onto a silica column (43-60 µm; 15 × 2 cm) pre-wet with petroleum ether (bp. 40-70 °C). Elution with a petroleum ether/ethyl acetate mixture (9/1) afforded the homocoupling product (0.0186 mmol, 5 mg, 93 % based on **2c**) as a white solid after solvent removal.

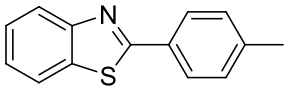
NMR data of the heteroarylation coupling products

2-phenylbenzo[*d*]thiazole[3]



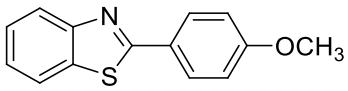
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.12-8.07 (m, 3H), 7.92 (d, ^3J = 7.8, 1H), 7.53-7.47 (m, 4H) 7.39 (ddd, ^3J = 8.1, ^3J = 7.2, ^4J = 1.2, 1 H). **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 168.2 (N*C*S), 154.3 (N*C*CH), 135.2, 133.8, 131.1, 129.1 (C_6H_5), 127.7 (C_6H_5), 126.4, 125.3, 123.4, 121.7.

2-(*p*-tolyl)benzo[*d*]thiazole[4]



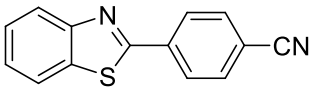
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.06 (d, ^3J = 8.1, 1H, C_6H_4NS), 7.99 (d, ^3J = 8.1, 2H, C_6H_4Me), 7.89 (d, ^3J = 8.1, C_6H_4NS), 7.49 (ddd, ^3J = 8.1, ^3J = 7.2, ^4J = 1.5, 1H, C_6H_4NS), 7.37 (ddd, ^3J = 8.1, ^3J = 7.2, ^4J = 1.2, 1H, C_6H_4NS), 7.30 (d, ^3J = 8.1, 2H, C_6H_4Me), 2.43 (s, 3H, CH_3). **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 168.4 (N*C*S), 154.3 (N*C*CH), 141.6, 135.1, 131.1, 129.9, 127.7, 126.4, 125.2, 123.2, 121.7, 21.7 (CH$_3$).

2-(4-methoxyphenyl)benzo[*d*]thiazole[3]



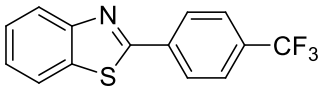
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.05 (d, ^3J = 9.0, 2H, C_6H_4OMe), 8.04 (m, 1H, C_6H_4NS), 7.88 (ddd, ^3J = 8.3, ^4J n.r., ^5J n.r., 1 H, C_6H_4NS), 7.47 (ddd, ^3J = 8.3, ^3J = 7.0, ^4J = 1.3, 1H, C_6H_4NS), 7.36 (ddd, ^3J = 8.3, ^3J = 7.0, ^4J = 1.0, 1H, C_6H_4NS), 7.01 (d, ^3J = 9.0, 2H, C_6H_4OMe), 3.89 (s, 3H, OCH_3). **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 168.1 (N*C*S), 162.1 (*C*OMe), 154.2 (N*C*CH), 134.9, 129.3 (C_6H_4OMe), 126.5, 126.4, 125.0, 122.9, 121.7, 114.5 (C_6H_4OMe), 55.6 (OCH$_3$).

2-(4-cyanophenyl)benzo[*d*]thiazole[5]



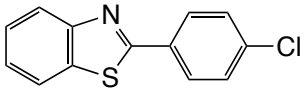
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.18 (d, ^3J = 8.0, 2H, C_6H_4CN), 8.10 (d, ^3J = 8.5, 1H, C_6H_4NS), 7.93 (d, ^3J = 8.5, 1H, C_6H_4NS), 7.77 (d, ^3J = 8.0, 2H, C_6H_4CN), 7.54 (dd, ^3J = 8.5, ^3J n.r., 1 H, C_6H_4NS), 7.45 (dd, ^3J = 8.5, ^3J n.r., 1H, C_6H_4NS). **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 165.4 (N*C*S), 154.1 (N*C*CH), 137.6, 135.4, 132.9 (C_6H_4CN), 128.0 (C_6H_4CN), 127.0, 126.2, 123.9, 121.9, 118.4 (*C*N), 114.2 (*C*CN).

2-(4-trifluoromethylphenyl)benzo[*d*]thiazole[6]



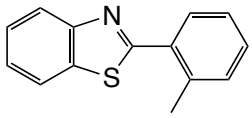
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.21 (d, ^{3}J = 8.1, 2H, $C_6H_4CF_3$), 8.11 (d, ^{3}J = 8.1, 1H, C_6H_4NS), 7.93 (ddd, ^{3}J = 8.1, ^{4}J n.r., ^{5}J n.r., 1 H, C_6H_4NS), 7.75 (d, ^{3}J = 8.1, 2H, $C_6H_4CF_3$), 7.53 (ddd, ^{3}J = 8.1, ^{3}J = 7.2, ^{4}J = 1.2, 1H, C_6H_4NS), 7.43 (ddd, ^{3}J = 8.1, ^{3}J = 7.2, ^{4}J = 1.2, 1H, C_6H_4NS). **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 166.2 (N*C*S), 154.2 (N*C*CH), 137.0, 135.4, 132.6 (q, $^{2}J_{C,F}$ = 32.6, *C*CF_3), 127.9 ($C_6H_4CF_3$), 126.8, 126.2 (q, $^{3}J_{C,F}$ = 3.6, $C_6H_4CF_3$) 124.0 (q, $^{1}J_{C,F}$ = 270.8, *C*F_3), 123.8, 121.9.

2-(4-chlorophenyl)benzo[*d*]thiazole[7]



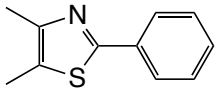
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07 (ddd, ^{3}J = 8.0, ^{4}J n.r., ^{5}J n.r., 1H, C_6H_4NS), 8.03 (d, ^{3}J = 8.6, 2H, C_6H_4Cl), 7.90 (ddd, ^{3}J = 8.0, ^{4}J n.r., ^{5}J n.r., 1 H, C_6H_4NS), 7.50 (ddd, ^{3}J = 8.0, ^{3}J = 7.2, ^{4}J = 0.8, 1H, C_6H_4NS), 7.46 (d, ^{3}J = 8.6, 2H, C_6H_4Cl), 7.41 (ddd, ^{3}J = 8.0, ^{3}J = 7.2, ^{4}J = 0.8, 1H, C_6H_4NS). **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 166.7 (N*C*S), 154.2 (N*C*CH), 137.2, 135.2, 132.3, 129.4 (C_6H_4Cl), 128.8 (C_6H_4Cl), 126.6, 125.6, 123.4, 121.8.

2-(*o*-tolyl)benzo[*d*]thiazole[6]



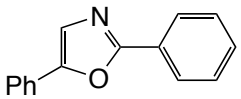
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.14 (d, ^{3}J = 8.0, 1H), 7.94 (d, ^{3}J = 8.0, 1H), 7.79 (dd, ^{3}J = 8.0, ^{4}J = 1.0, 1H), 7.53 (ddd, ^{3}J = 8.5, ^{3}J = 7.5, ^{4}J = 1.0, 1H), 7.44-7.31 (m, 4H), 2.69 (s, 3 H, CH_3). **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 168.1 (N*C*S), 153.9 (N*C*CH), 137.3, 135.7, 133.2, 131.6, 130.6, 130.1, 126.2, 126.2, 125.2, 123.5, 121.4, 21.5 (*C*H_3).

2-phenyl-4,5-dimethylthiazole[8]



^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.86 (d, ^{3}J = 7.0, 2H, C_6H_5), 7.41-7.36 (m, 3H, C_6H_5), 2.39 (s, 3H, CH_3), 2.39 (s, 3H, CH_3). **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 163.5 (N*C*S), 149.4 (N*C*CH_3), 134.1, 129.5 (C_6H_5), 128.9 (C_6H_5), 126.7, 126.2 (C_6H_5), 14.5 (NC*C*H_3), 11.6 (SC*C*H_3).

2,5-diphenyloxazole[8]



^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.12 (dd, ^{3}J = 8.0, ^{4}J = 2.0, 2H, C_6H_5), 7.73 (dd, ^{3}J = 8.5, ^{4}J = 1.5, 2H, C_6H_5), 7.51-7.43 (m, 6H, C_6H_5 and NC*H*), 7.34 (ddd, 1H, ^{3}J = 7.5, C_6H_5). **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 161.2 (N*C*O), 151.4 (O*C*Ph), 130.4, 129.0, 128.9, 128.5, 128.1, 127.6, 126.4, 124.3, 123.6.

Figure S29. ^{1}H NMR spectrum of 2-phenylbenzo[*d*]thiazole

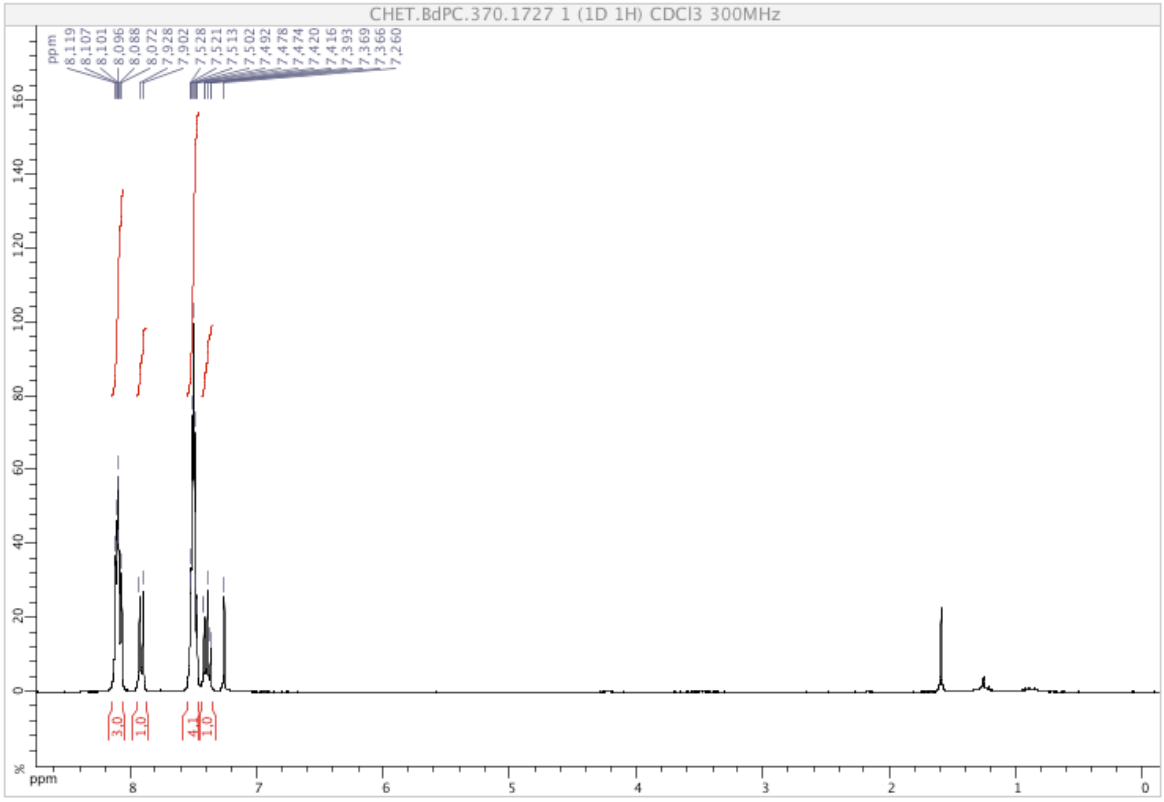


Figure S30. ^{13}C {^{1}H} NMR spectrum of 2-phenylbenzo[*d*]thiazole

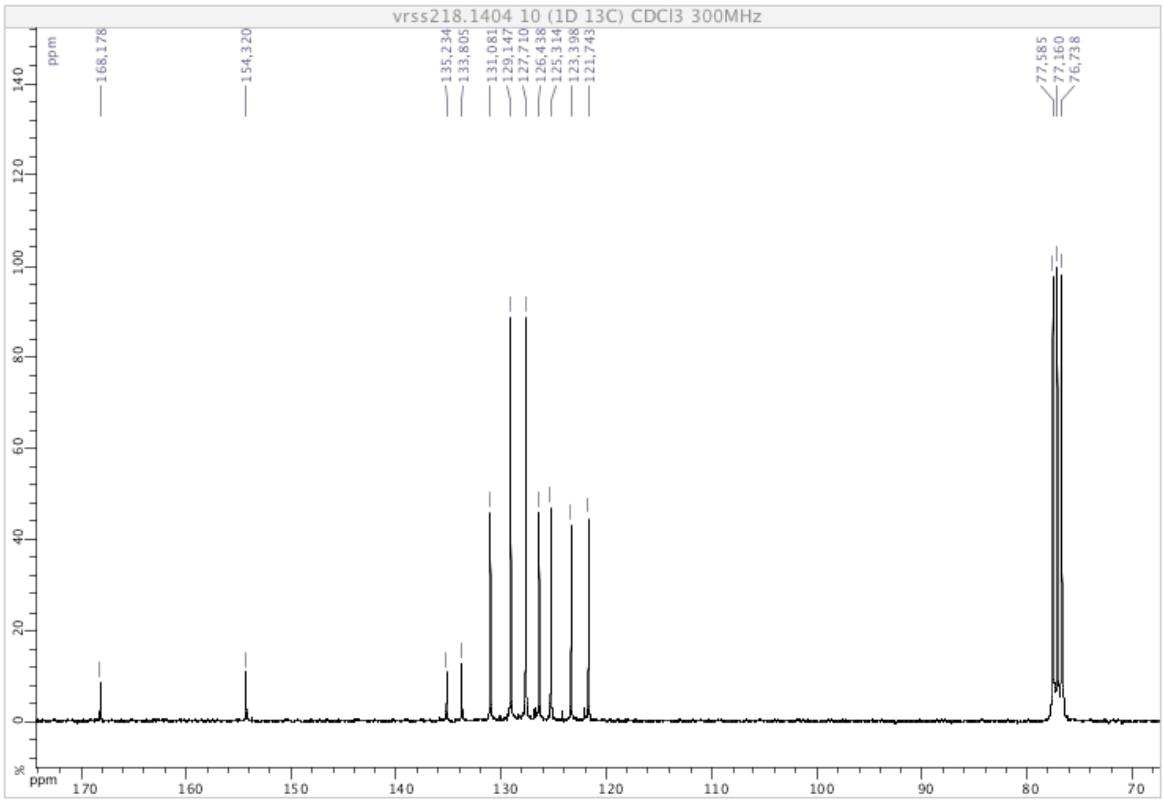


Figure S31. ^{1}H NMR spectrum of 2-(*p*-tolyl)benzo[*d*]thiazole

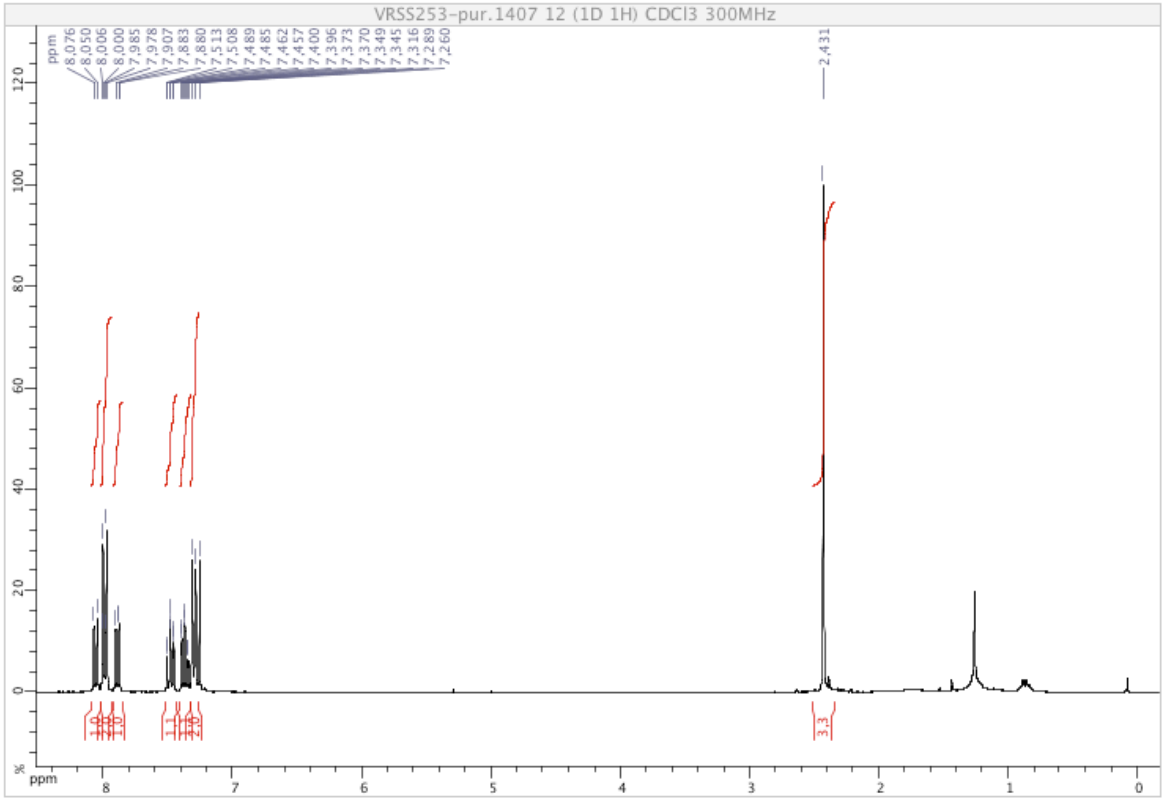


Figure S32. ^{13}C {^{1}H} NMR spectrum of 2-(*p*-tolyl)benzo[*d*]thiazole

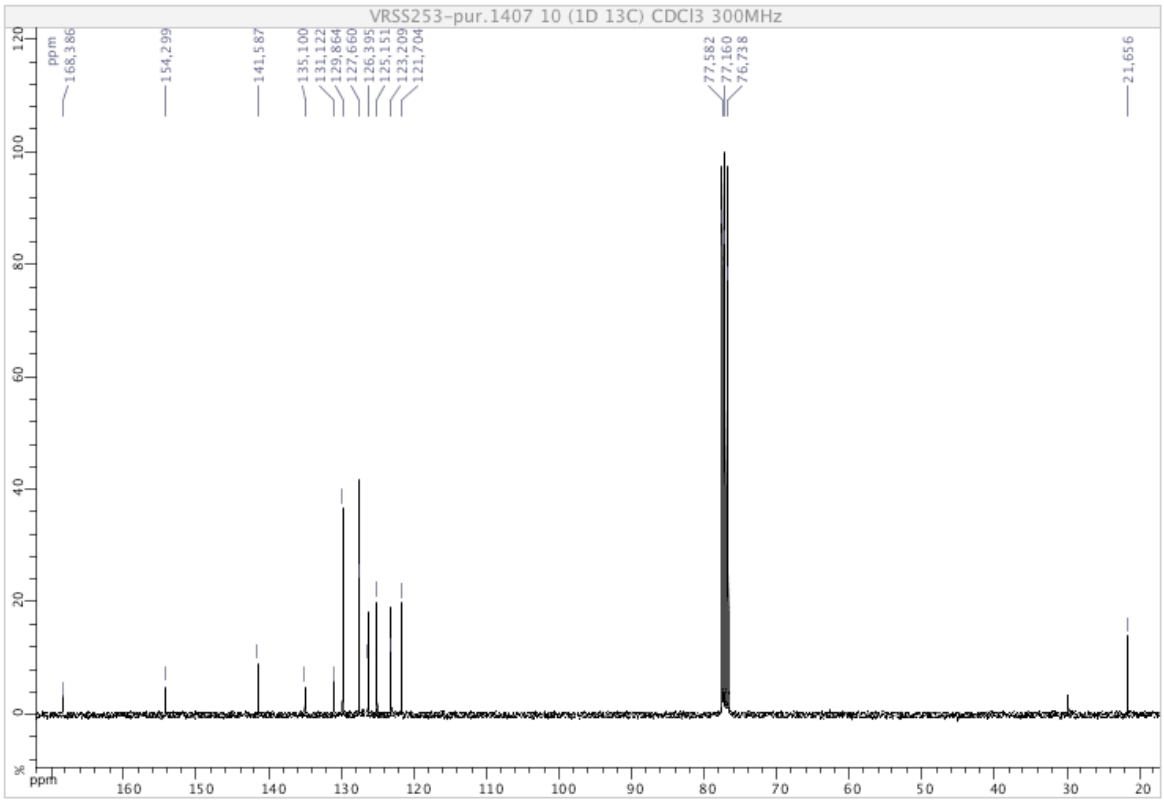


Figure S33. ^{1}H NMR spectrum of 2-(4-methoxyphenyl)benzo[*d*]thiazole

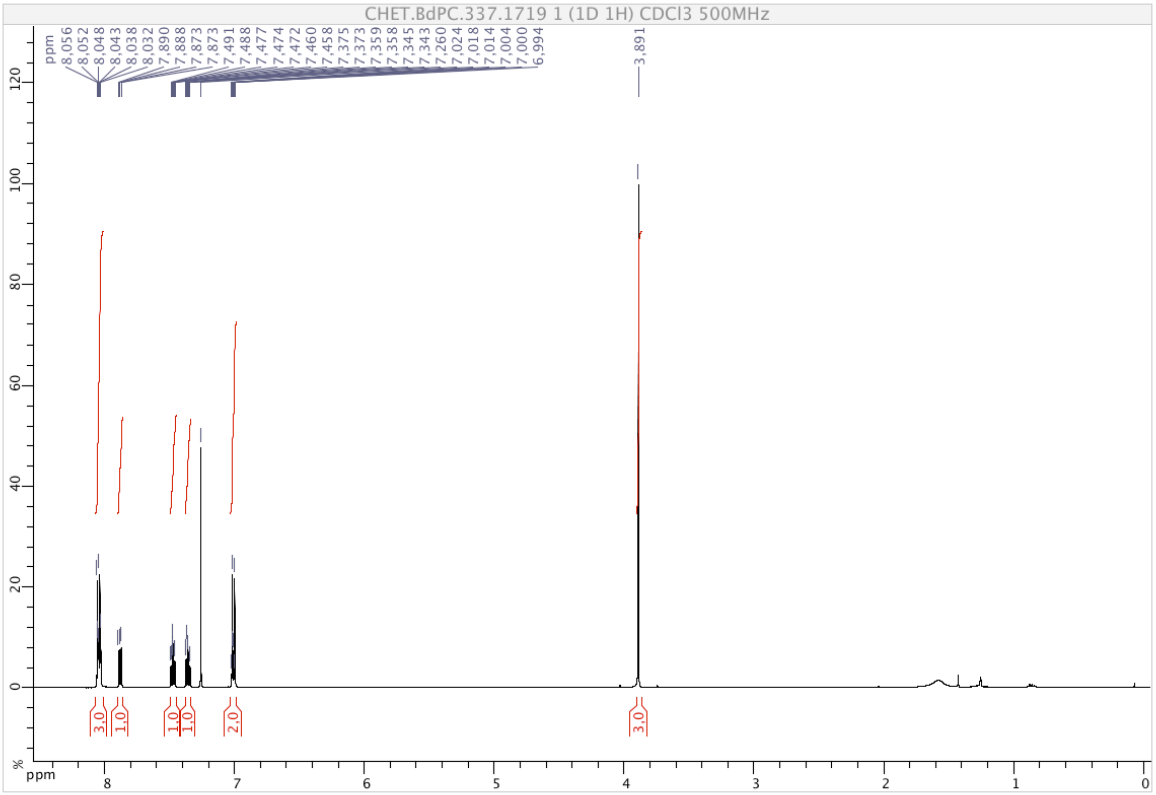


Figure S34. ^{13}C {^{1}H} NMR spectrum of 2-(4-methoxyphenyl)benzo[*d*]thiazole

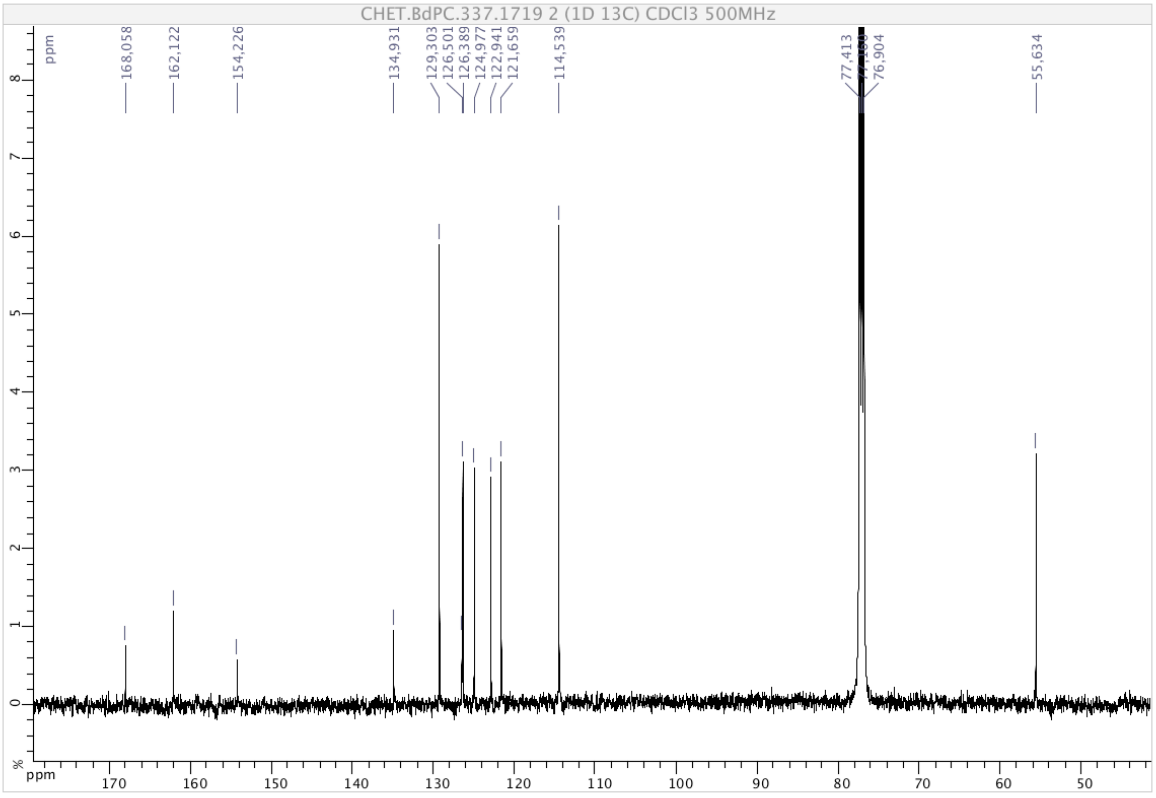


Figure S35. ^{1}H NMR spectrum of 2-(4-cyanophenyl)benzo[*d*]thiazole

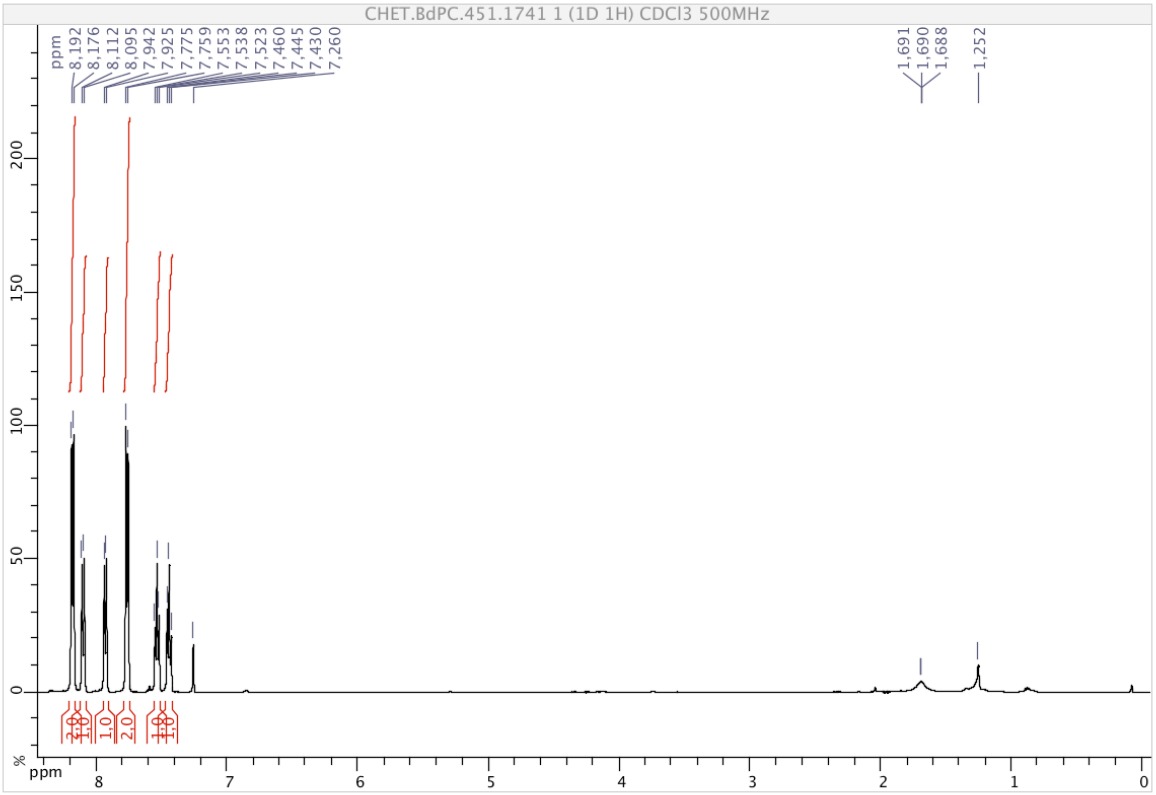


Figure S36. ^{13}C {^{1}H} NMR spectrum of 2-(4-cyanophenyl)benzo[*d*]thiazole

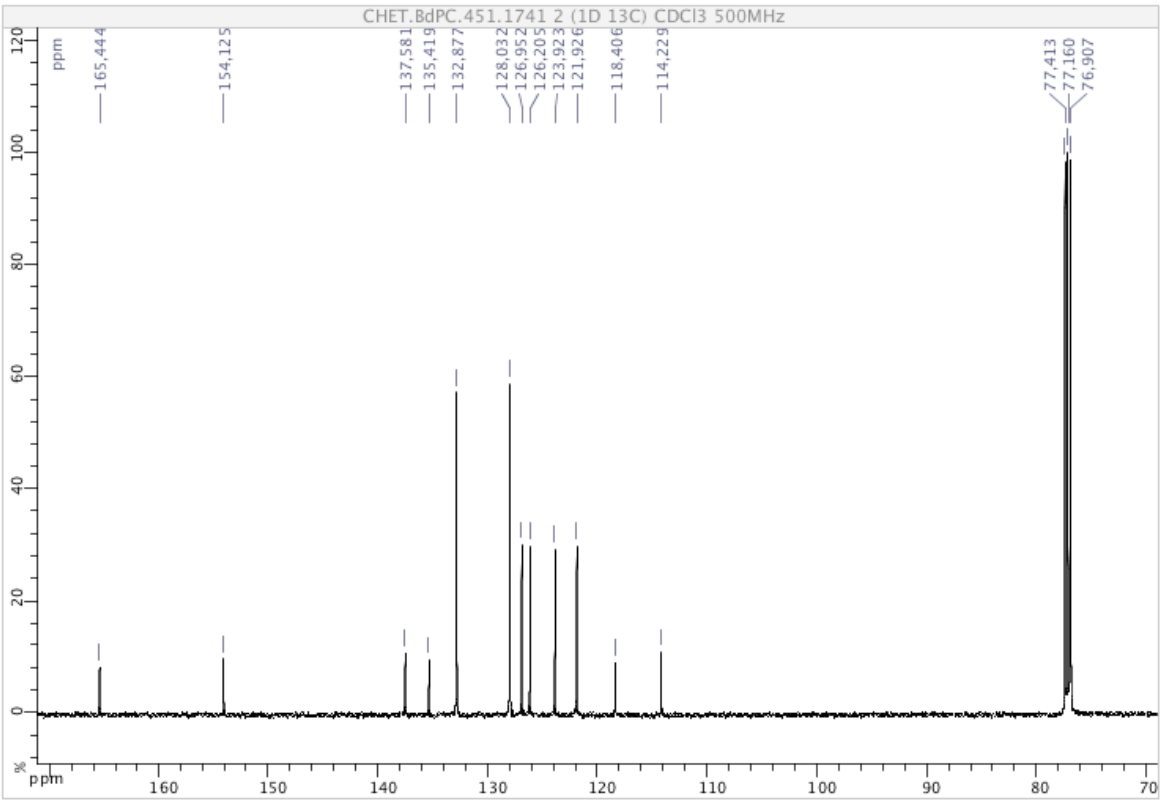


Figure S37. ^{1}H NMR spectrum of 2-(4-trifluoromethylphenyl)benzo[*d*]thiazole

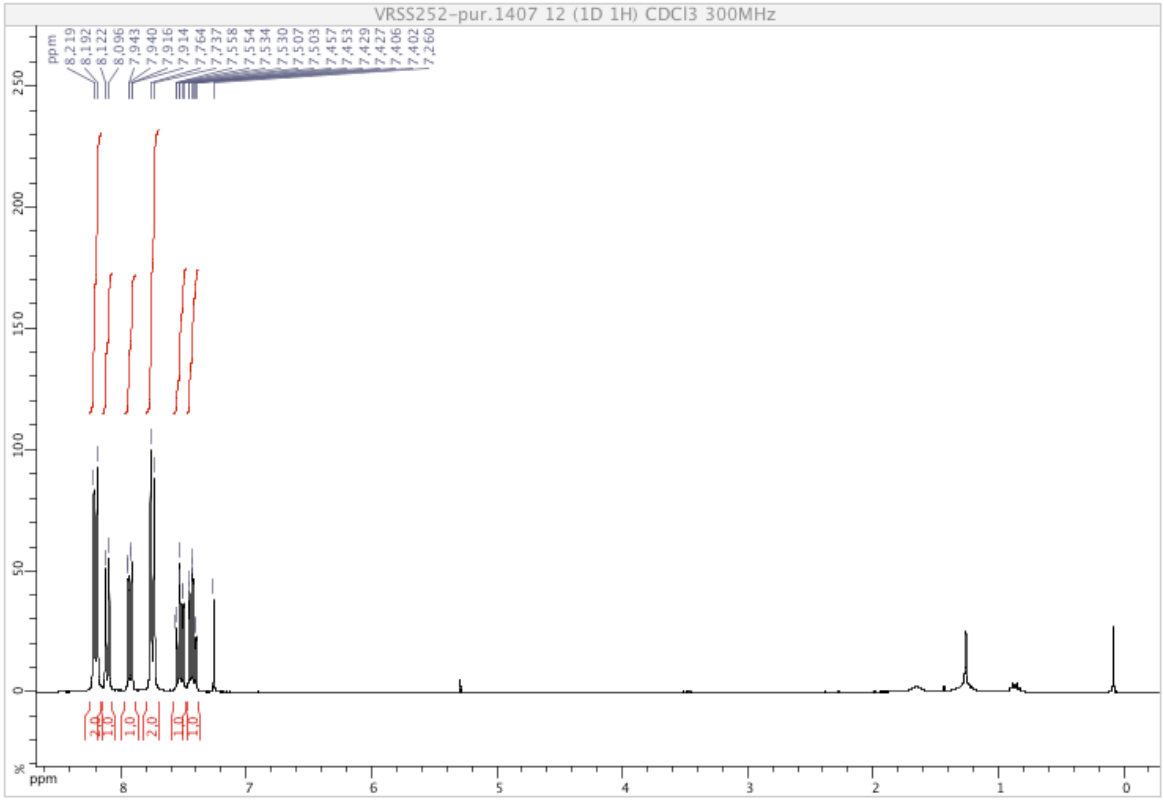


Figure S38. ^{13}C {^{1}H} NMR spectrum of 2-(4-trifluoromethylphenyl)benzo[*d*]thiazole

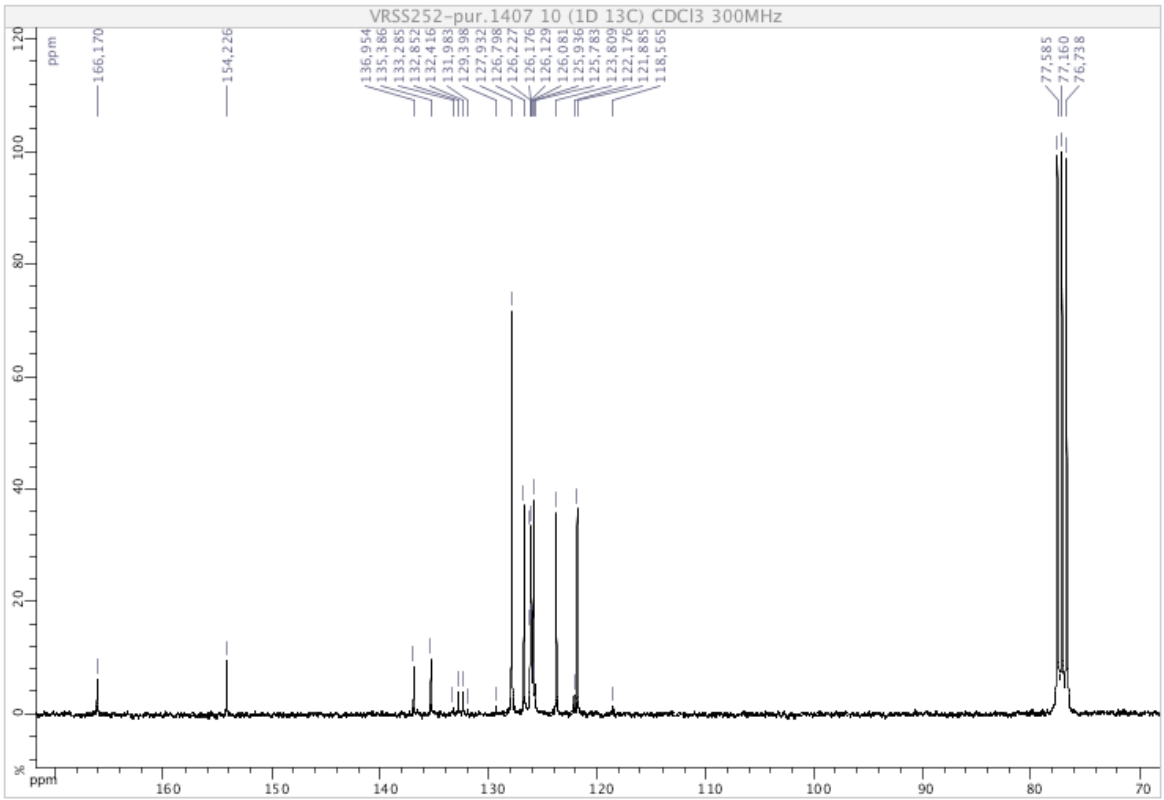


Figure S39. ^{1}H NMR spectrum of 2-(4-chlorophenyl)benzo[*d*]thiazole

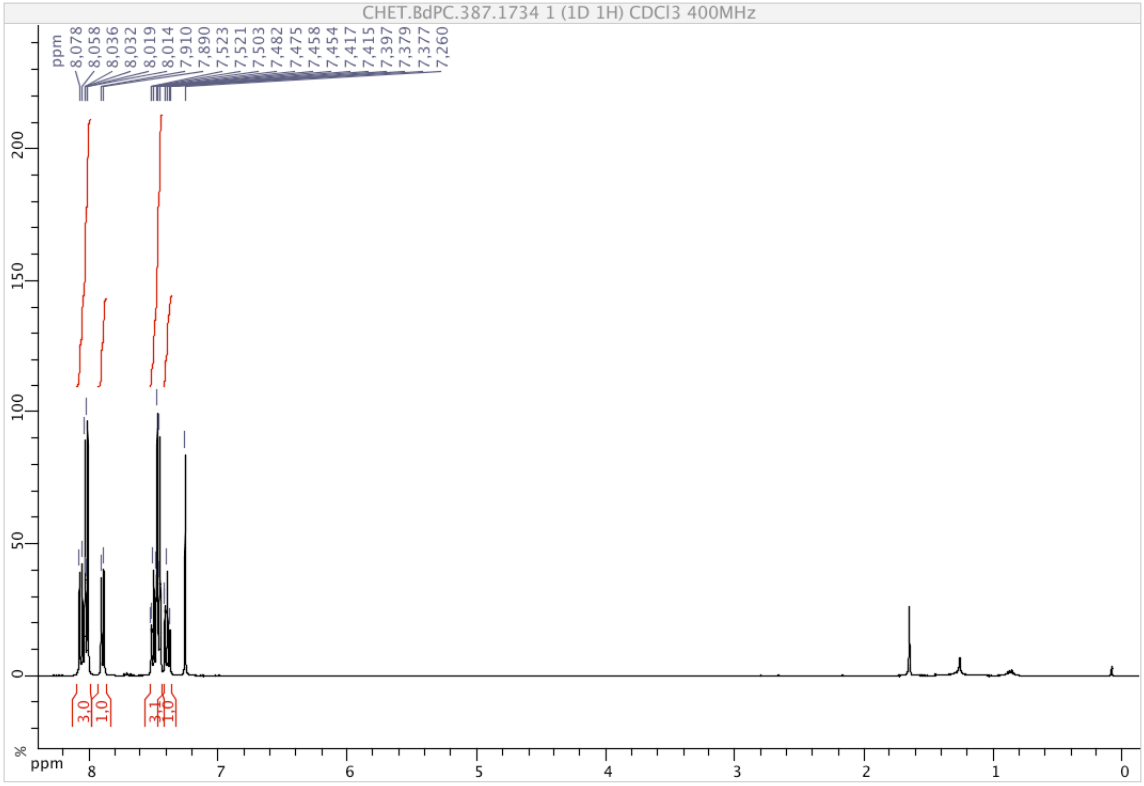


Figure S40. ^{13}C {^{1}H} NMR spectrum of 2-(4-chlorophenyl)benzo[*d*]thiazole

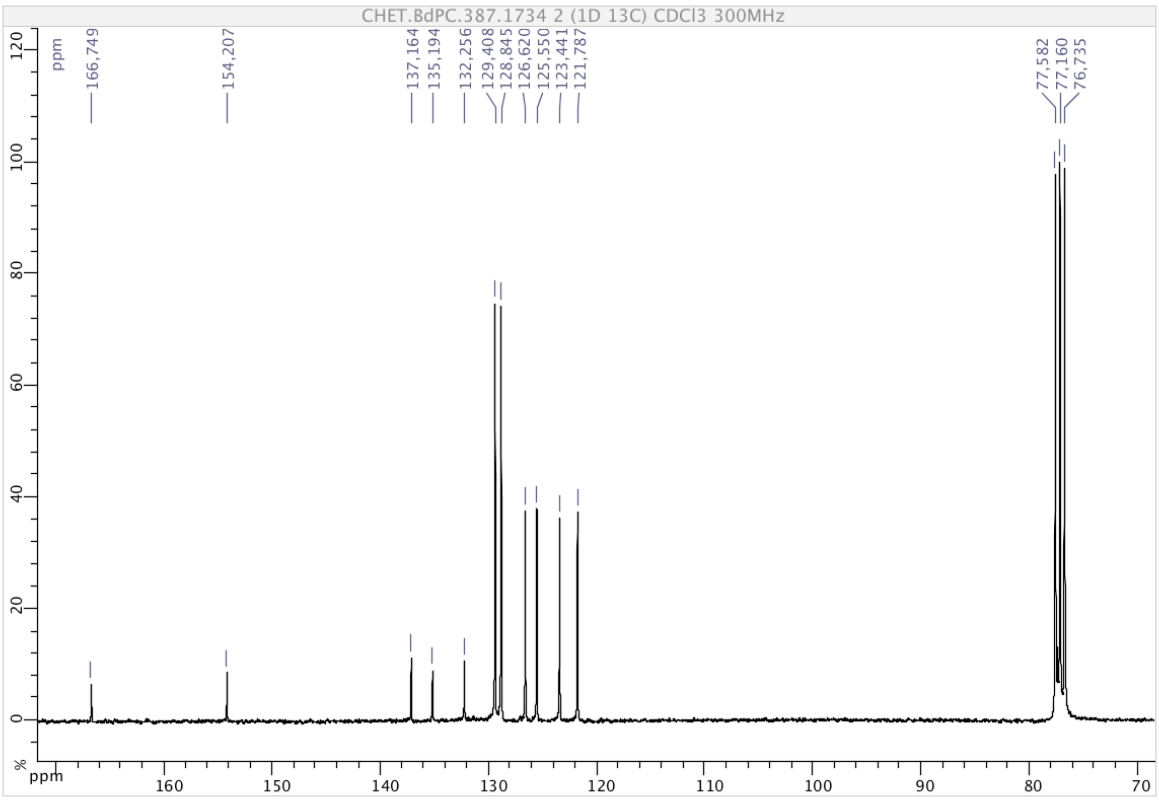


Figure S41. ^{1}H NMR spectrum of 2-(*o*-tolyl)benzo[*d*]thiazole

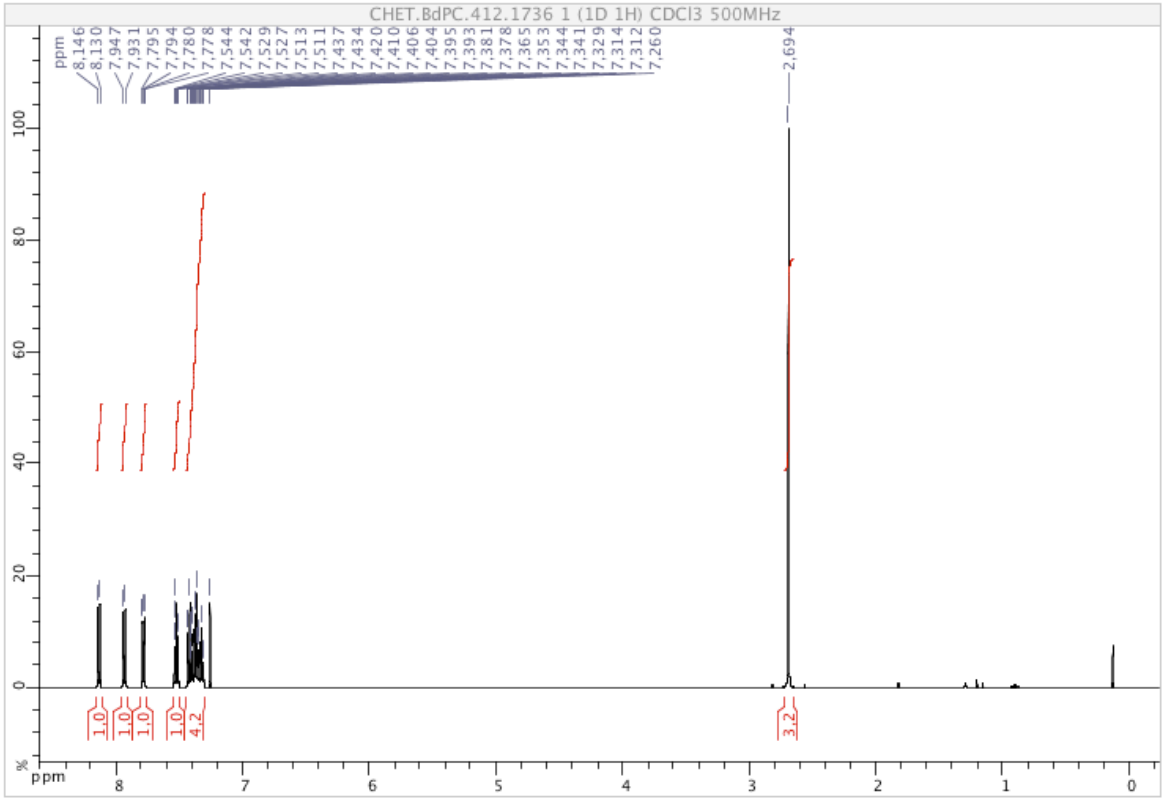


Figure S42. ^{13}C {^{1}H} NMR spectrum of 2-(*o*-tolyl)benzo[*d*]thiazole

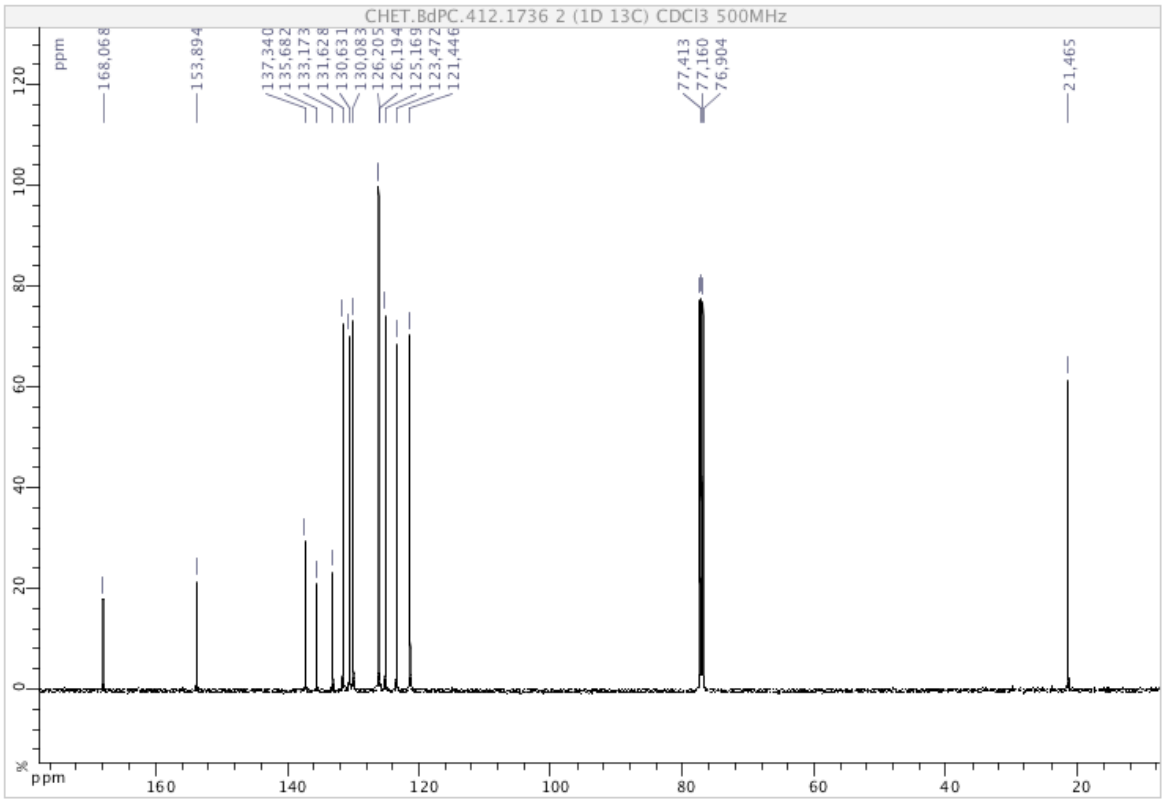


Figure S43. ^{1}H NMR spectrum of 2-phenyl-4,5-dimethylthiazole

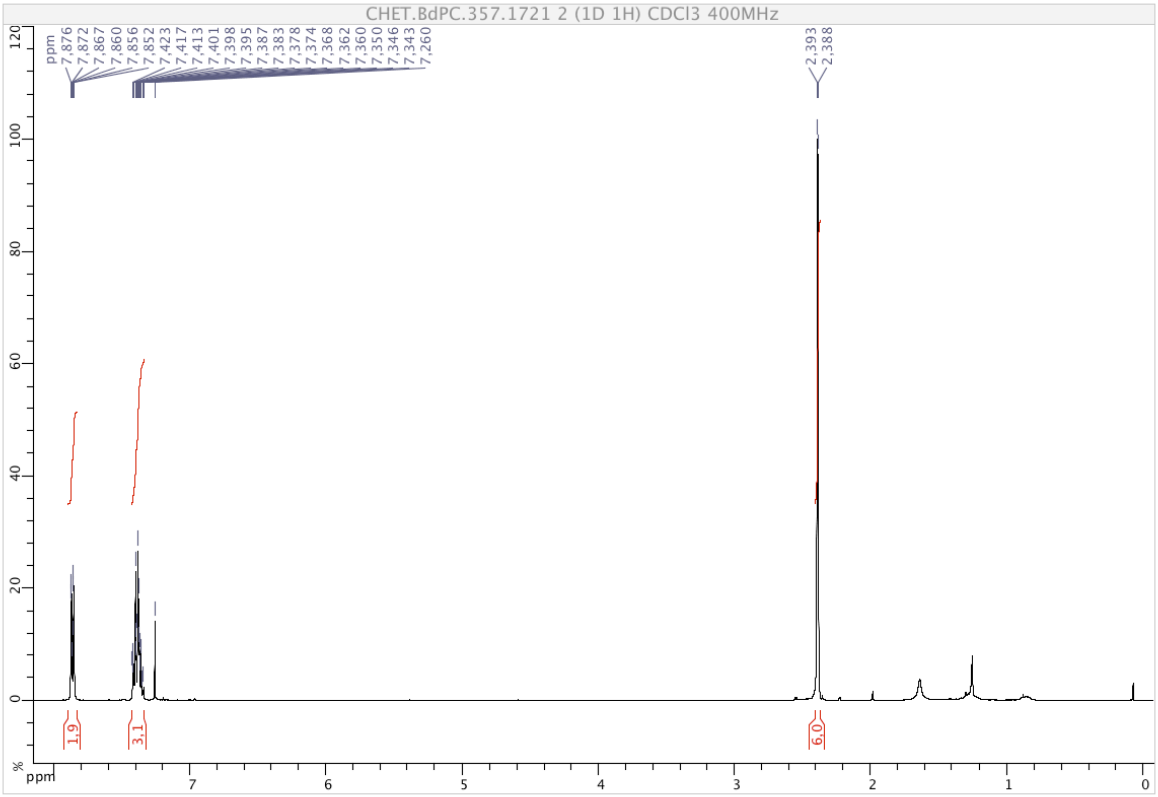


Figure S44. ^{13}C {^{1}H} NMR spectrum of 2-phenyl-4,5-dimethylthiazole

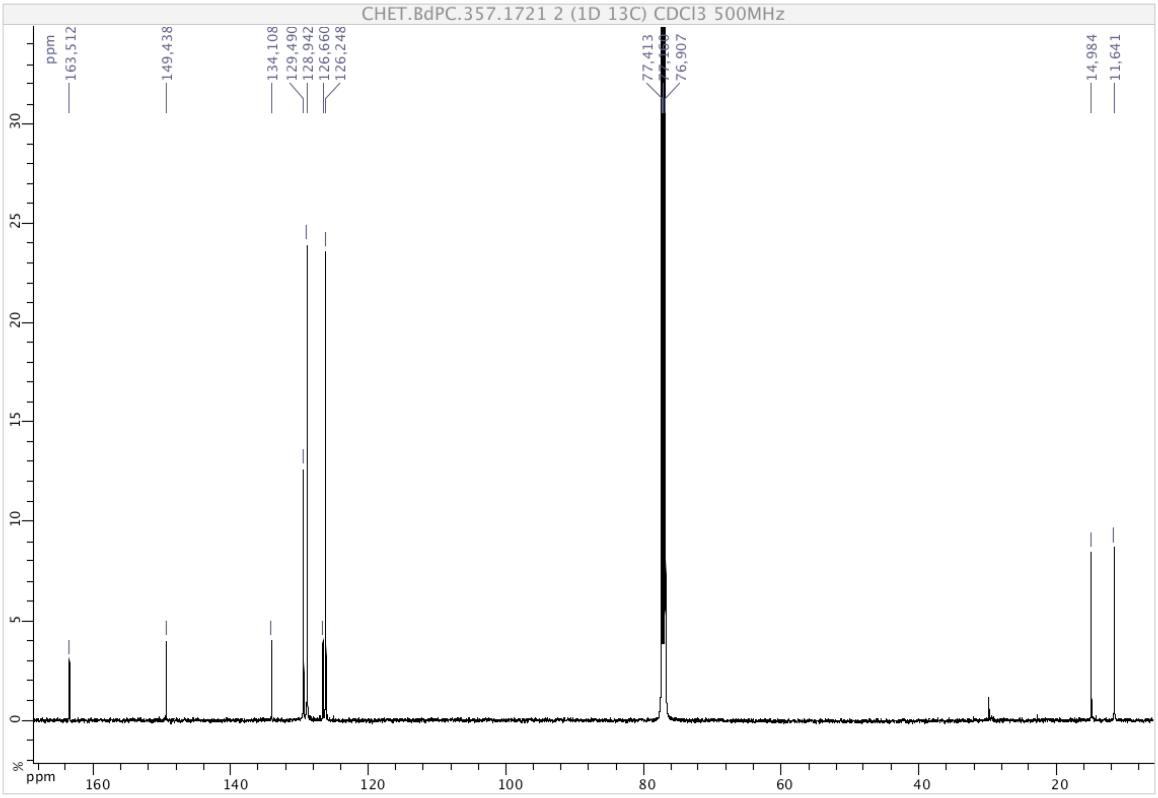


Figure S45. ^{1}H NMR spectrum of 2,5-diphenyloxazole

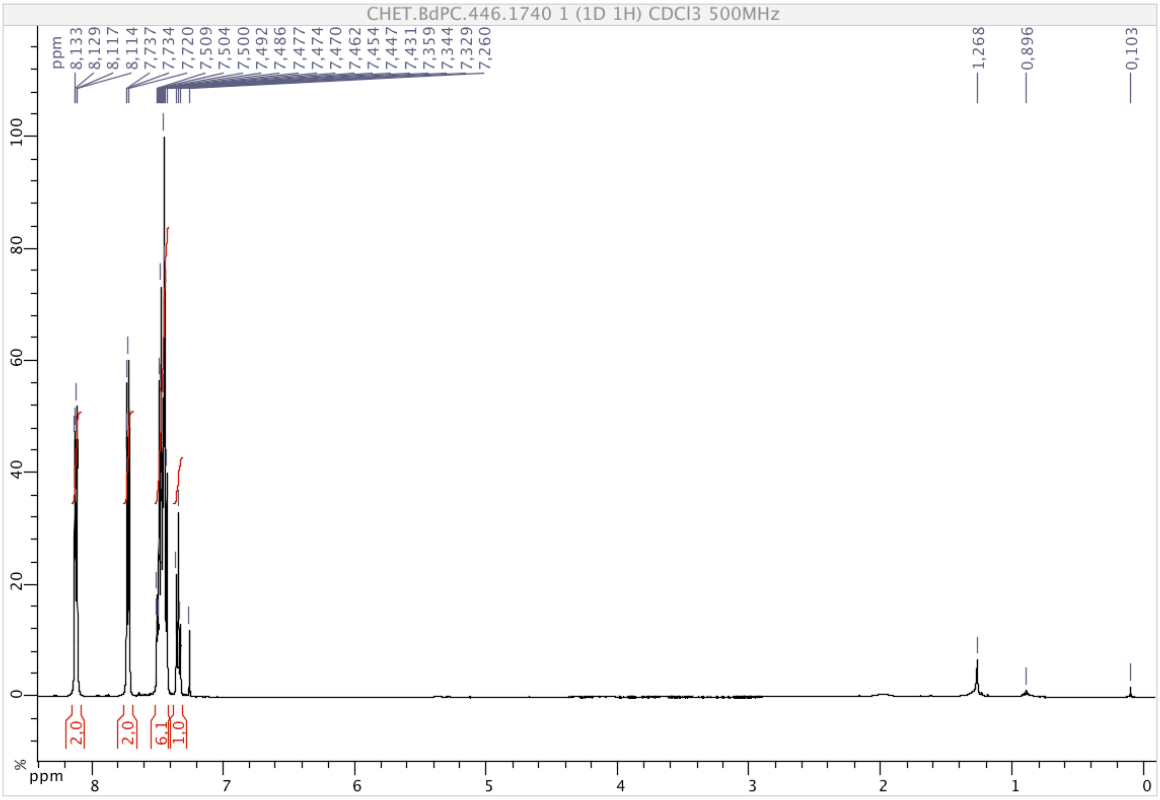
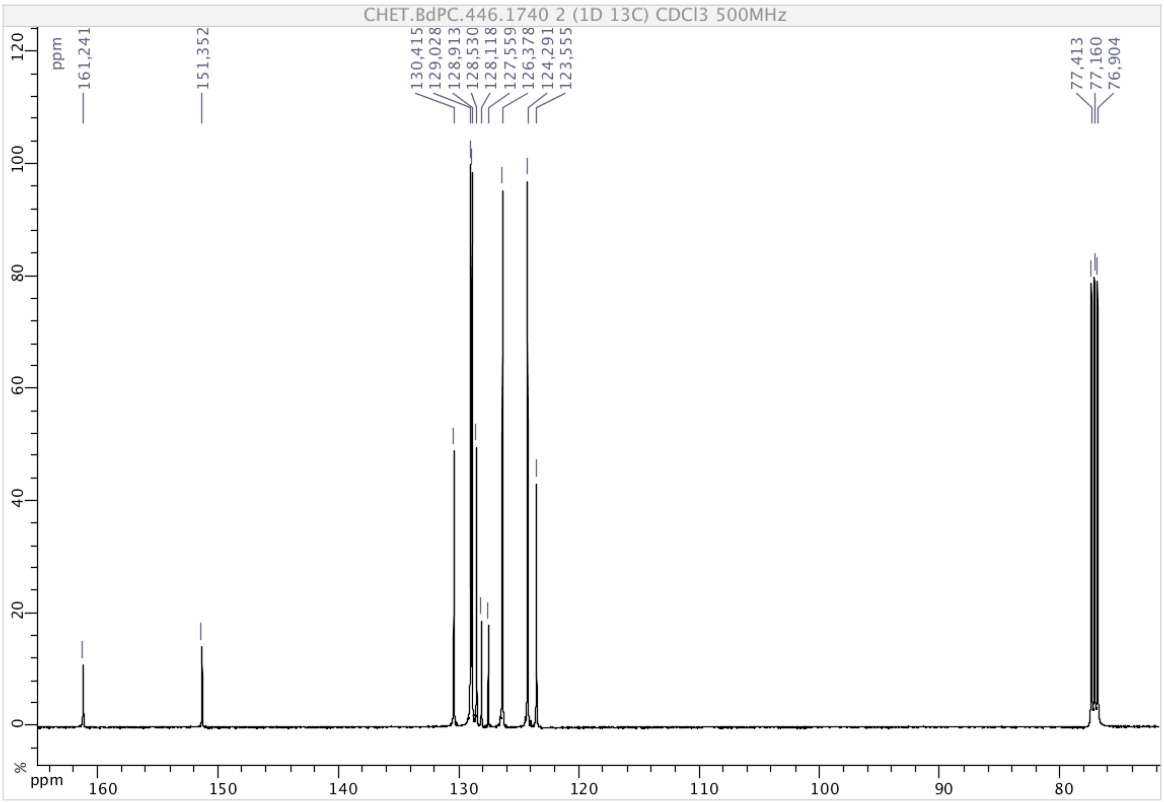


Figure S46. ^{13}C {^{1}H} NMR spectrum of 2,5-diphenyloxazole



Atomic coordinates of the optimized species

MeCN

N	-1.427715	1.193832	-0.459424
C	-0.580767	0.429062	-0.258035
C	0.482216	-0.529377	-0.003451
H	0.612743	-1.186861	-0.866843
H	1.423761	-0.007471	0.185739
H	0.238362	-1.140785	0.869113

1a

Ni	-0.272647	-0.209182	-1.137850
C	-0.542099	0.358694	0.606996
C	-1.028270	1.166789	2.656421
H	-1.609169	1.687254	3.401882
C	0.175100	0.546072	2.743576
H	0.841705	0.414162	3.581226
C	-2.676287	1.612568	0.830668
H	-2.556095	2.684339	0.645735
H	-3.488204	1.458752	1.545482
H	-2.922189	1.113806	-0.105022
C	1.561649	-0.727273	0.996752
H	1.418051	-1.767405	1.309969
H	2.489120	-0.356489	1.447154
C	1.536826	-0.634877	-0.530980
H	1.845165	-1.583341	-0.979033
C	2.371641	0.429734	-1.032692
C	-2.133713	-0.578722	-2.190067
H	-3.088555	-0.773205	-1.717101
C	-1.198046	-1.549616	-2.587087
H	-1.280970	-2.619528	-2.453325
C	-0.073723	-0.846717	-3.116048
H	0.836157	-1.301700	-3.487573
C	-0.378582	0.548482	-3.175528
H	0.279684	1.326497	-3.536921
C	-1.628189	0.720125	-2.562365
H	-2.135938	1.663631	-2.407075
N	-1.454121	1.038012	1.346576
N	0.447322	0.068314	1.484208
N	3.028378	1.303323	-1.436479

2a-NCMe-CN$^+$

Ni	1.199780	-0.675716	0.768489
C	-0.284609	0.075771	1.620305
C	-2.192552	0.937507	2.411839
H	-3.037871	1.607778	2.440814
C	-1.841181	-0.076032	3.245899
H	-2.320660	-0.455739	4.134699
C	-1.242175	1.989987	0.349231
H	-1.275970	2.999410	0.764318
H	-2.112813	1.829199	-0.290667
H	-0.331698	1.873439	-0.235767
C	0.197133	-1.660848	3.211178
H	-0.190043	-2.627925	2.877299
H	0.238822	-1.655823	4.303644
C	1.534077	-1.325522	2.575137
H	2.179671	-0.666901	3.157691
C	2.218030	-2.154331	1.666116
C	1.285489	0.059879	-3.632604
H	1.614255	1.074778	-3.872417
H	2.015426	-0.655229	-4.022609
N	-1.227686	1.015424	1.426110
C	1.179217	-0.098471	-2.198401
N	-0.666230	-0.581021	2.745128
N	1.102428	-0.233190	-1.054167
N	2.630232	-2.397038	0.582459
H	0.315127	-0.126687	-4.100724

2a-NCMe$^+$

Ni	-2.380057	-0.431532	-0.277869
C	-0.564798	-0.540868	0.106895
C	1.639296	-0.440683	0.465390
H	2.612032	0.021696	0.534994
C	1.257307	-1.730343	0.664085
H	1.831270	-2.601113	0.940266
C	0.500456	1.691546	-0.191621
H	1.101423	1.882789	-1.083255
H	0.896942	2.264789	0.648890
H	-0.525257	2.008931	-0.381790
C	-1.056682	-2.842394	0.520179
H	-1.251731	-3.075520	1.570911
H	-0.655842	-3.735941	0.032593
C	-2.334770	-2.337797	-0.159225
H	-3.236086	-2.618183	0.392957
C	-2.455410	-2.692384	-1.552074
N	0.508891	0.273360	0.124074
N	-0.095769	-1.759802	0.434575
N	-2.561626	-2.935104	-2.684605
C	-6.671339	-0.044402	-1.494969
H	-6.843793	0.961683	-1.887722
H	-6.859587	-0.776200	-2.286101
C	-5.302124	-0.163384	-1.048346
N	-4.205621	-0.266428	-0.698972
H	-7.352623	-0.227714	-0.659459

2a-(NCMe)$_2^+$

Ni	-1.511499	1.471288	0.885355
C	0.290048	1.039560	1.213484
C	2.493811	0.742021	1.513824
H	3.534942	1.023168	1.546960
C	1.894187	-0.456491	1.733227
H	2.308858	-1.417546	1.993496
C	1.764004	3.036233	0.875063
H	2.833928	3.157381	0.704841
H	1.460437	3.684131	1.700419
H	1.231251	3.315295	-0.033895
C	-0.566472	-1.157583	1.625008
H	-0.806841	-1.336389	2.677395
H	-0.295677	-2.112203	1.163658
C	-1.730796	-0.457274	0.925864
H	-2.677040	-0.682498	1.424736
C	-1.835497	-0.764003	-0.482629
N	1.500624	1.645093	1.194740
N	0.554426	-0.242697	1.537887
N	-1.926572	-0.949271	-1.627659
C	-5.830285	1.582428	-0.347527
H	-6.125269	2.569661	-0.712147
H	-5.910109	0.859034	-1.164183
C	-4.462911	1.614645	0.126411
N	-3.368530	1.622174	0.492488
H	-6.498859	1.283429	0.464239
C	-1.487694	5.990218	0.858420
H	-2.141875	6.325828	1.667806
H	-0.490784	6.413815	1.007446
C	-1.417647	4.543337	0.853893
N	-1.355826	3.390387	0.849569
H	-1.887032	6.344630	-0.095788

2c-NCMe$^+$

Ni	-0.882173	-0.434265	-0.268614
C	-1.854474	0.619728	0.885898
C	-2.126333	2.282453	2.367402
H	-1.844696	3.141569	2.956226
C	-3.305994	1.614467	2.264676
H	-4.253096	1.777231	2.755712
C	0.129683	1.955829	1.243059
C	0.434708	2.805942	0.167686
C	1.781718	3.061597	-0.084602
H	2.042474	3.718424	-0.910773
C	2.799094	2.510733	0.698482
C	2.446691	1.672672	1.759290
H	3.228856	1.239542	2.377884
C	1.116971	1.381160	2.059754
C	-0.643793	3.429355	-0.672962
H	-1.245112	2.674551	-1.191748
H	-0.210157	4.086634	-1.428758
H	-1.332531	4.025670	-0.065376
C	4.238265	2.841166	0.428707
H	4.408589	3.064273	-0.627522
H	4.900436	2.021943	0.720200
H	4.541568	3.725011	1.001730
C	0.760825	0.502369	3.225647
H	0.234643	1.065351	4.004219
H	1.659761	0.077052	3.675611

H	0.106679	-0.325336	2.931787
C	-4.081820	-0.409664	0.944216
H	-5.079955	0.029644	1.013301
H	-4.032746	-1.247322	1.649995
C	-3.805597	-0.871341	-0.474263
H	-3.927007	-0.031179	-1.166038
H	-4.574899	-1.608815	-0.736559
C	-2.427980	-1.507569	-0.663847
H	-2.276074	-2.351127	0.025290
C	-2.253134	-1.961472	-2.024102
C	1.779886	-2.635769	-3.108404
H	1.068189	-3.032472	-3.840337
H	2.482303	-1.965870	-3.611230
N	-1.249304	1.650784	1.510151
C	1.031771	-1.911253	-2.108337
N	-3.113011	0.602112	1.347490
N	0.379289	-1.346676	-1.341098
N	-2.094628	-2.306138	-3.123348
H	2.328713	-3.460987	-2.647197

2c-NCMe-CN$^+$

Ni	0.636166	-1.233518	0.879529
C	-0.808676	-0.330459	1.662792
C	-2.492622	1.114735	2.063678
H	-3.118245	1.974647	1.882717
C	-2.505254	0.191425	3.052209
H	-3.150798	0.082638	3.910058
C	-1.120805	1.560648	0.060740
C	-1.939118	1.454656	-1.070021
C	-1.621487	2.249032	-2.172858
H	-2.253547	2.192010	-3.056699
C	-0.532924	3.124751	-2.164874
C	0.256473	3.190910	-1.014649
H	1.104534	3.871090	-0.990089
C	-0.021026	2.426045	0.117744
C	-3.107995	0.511347	-1.111900
H	-2.819336	-0.500694	-0.808368
H	-3.525833	0.458864	-2.119419
H	-3.914100	0.828634	-0.441679
C	-0.238181	4.003214	-3.347139
H	-0.698984	3.620485	-4.261448
H	0.837714	4.101117	-3.517327
H	-0.631402	5.012818	-3.182881
C	0.837197	2.533454	1.345761
H	0.234303	2.647780	2.252305
H	1.506065	3.393402	1.274736
H	1.458321	1.639956	1.479919
C	-1.115250	-1.737707	3.745437
H	-2.034286	-2.259673	4.025453
H	-0.723296	-1.248451	4.644828
C	-0.095210	-2.727203	3.207758
H	-0.544917	-3.372536	2.446712
H	0.207128	-3.370382	4.043116
C	1.076344	-1.971596	2.632456
H	1.584332	-1.288717	3.316301
C	1.911579	-2.547254	1.654290
C	0.613841	-0.538417	-3.528023
H	0.015501	0.327132	-3.823352
H	1.654024	-0.381614	-3.826284
N	-1.451628	0.780537	1.220319
C	0.541590	-0.704443	-2.092838
N	-1.469674	-0.682082	2.793679
N	0.483172	-0.834701	-0.948274
N	2.289801	-2.635079	0.534734
H	0.233008	-1.435705	-4.023348

2c-(NCMe)$_2^+$

Ni	0.510102	-0.738816	0.513931
C	-0.290557	0.557480	1.609190
C	-1.284767	2.413864	2.411033
H	-1.744805	3.387788	2.358622
C	-1.093289	1.570205	3.453178
H	-1.337484	1.669018	4.499374
C	-0.868599	2.358067	-0.024050
C	-1.786921	1.830959	-0.941887
C	-1.852546	2.428293	-2.201918
H	-2.561343	2.034332	-2.926427
C	-1.060396	3.522827	-2.549011
C	-0.170869	4.024127	-1.595192
H	0.440756	4.890616	-1.840071
C	-0.058775	3.462349	-0.323235
C	-2.688385	0.678962	-0.600595
H	-2.175221	-0.286638	-0.673618
H	-3.538738	0.644551	-1.285004
H	-3.079446	0.759539	0.418068
C	-1.195383	4.173435	-3.895918
H	-1.437554	3.442790	-4.672224
H	-0.279411	4.694283	-4.187230
H	-2.001915	4.915481	-3.885589
C	0.907748	4.032293	0.678264
H	0.397824	4.627352	1.443875
H	1.624329	4.695543	0.187505
H	1.463145	3.248804	1.204189
C	-0.255060	-0.797949	3.656958
H	-0.636725	-0.673626	4.672730
H	0.820807	-0.991779	3.719244
C	-0.983301	-1.904811	2.914506
H	-2.037495	-1.623283	2.821700
H	-0.949614	-2.822956	3.512487
C	-0.364809	-2.158079	1.538294
H	0.483275	-2.846896	1.648944
C	-1.301102	-2.728811	0.600324
C	1.486932	-4.105534	-2.298946
C	3.113105	2.102762	-1.850864
H	1.771396	-3.746386	-3.291125
H	2.497503	2.904918	-2.267481
H	2.256268	-4.787210	-1.926895
H	3.888277	2.533640	-1.211591
C	1.328020	-2.991199	-1.389823
N	-0.783127	1.782906	1.287498
C	2.267049	1.220210	-1.075483
N	-0.483342	0.448243	2.938563
N	1.573957	0.533131	-0.460332
N	1.158335	-2.116874	-0.656146
N	-2.037852	-3.146098	-0.199021
H	0.533455	-4.638387	-2.366391
H	3.587440	1.548465	-2.664708

Int

Ni	-0.866172	-0.992900	-0.469476
C	-0.669538	0.243831	0.928895
C	-0.484039	2.156996	2.110375
H	-0.400442	3.222487	2.255633
C	-0.506175	1.131830	2.992668
H	-0.446384	1.124775	4.069917
C	-0.574755	2.393125	-0.342794
C	-1.725873	3.116794	-0.676650
C	-1.678705	3.914649	-1.820889
H	-2.558622	4.495734	-2.089474
C	-0.532264	4.001922	-2.614404
C	0.588570	3.255809	-2.244308
H	1.490482	3.315296	-2.849003
C	0.597793	2.449793	-1.106301
C	-2.977970	3.029142	0.149292
H	-3.265927	1.988303	0.331391
H	-3.807958	3.530462	-0.353129
H	-2.856067	3.502982	1.129217
C	-0.489656	4.905530	-3.813764
H	-1.491626	5.122681	-4.193232
H	0.099928	4.470215	-4.625402
H	-0.025566	5.864359	-3.556176
C	1.824750	1.671678	-0.726040
H	2.073479	1.799416	0.332215
H	2.683630	1.993475	-1.318499
H	1.685641	0.597481	-0.894531
C	-0.531951	-1.342585	2.896358
H	-1.184206	-1.328793	3.773794
H	0.503960	-1.472299	3.226561
C	-0.911150	-2.488269	1.973937
H	-1.985556	-2.489321	1.763625
H	-0.678103	-3.419773	2.503929
C	-0.112078	-2.365879	0.701413
H	0.969982	-2.320373	0.841921
C	-0.546687	-2.950115	-0.502491
C	5.273149	-2.700465	2.942297
C	-2.870448	0.978838	-3.937268
H	5.711077	-3.273394	2.120883
H	-2.326957	0.674842	-4.835917
H	5.875673	-1.803965	3.109119

H	-3.897420	0.609102	-4.000556
C	3.906921	-2.330472	2.617367
N	-0.587789	1.598643	0.851865
C	-2.222338	0.425132	-2.768166
N	-0.619352	-0.027063	2.255351
N	-1.705167	-0.013698	-1.835205
N	2.816542	-2.036036	2.358560
N	-1.005846	-2.860675	-1.592519
H	5.290447	-3.312229	3.847910
H	-2.875343	2.069383	-3.866609

TS1

Ni	-0.736486	-1.011384	0.029324
C	-1.021580	0.313121	1.328508
C	-1.306929	2.299218	2.362099
H	-1.341919	3.374563	2.439107
C	-1.503689	1.329141	3.283659
H	-1.748921	1.389543	4.332734
C	-0.716375	2.385142	-0.031417
C	-1.774097	2.966682	-0.740577
C	-1.458680	3.696526	-1.887303
H	-2.264968	4.169139	-2.444703
C	-0.140552	3.852165	-2.324082
C	0.879040	3.249910	-1.584555
H	1.910786	3.367437	-1.907453
C	0.620751	2.518082	-0.425195
C	-3.201130	2.799044	-0.301391
H	-3.453033	1.743463	-0.152530
H	-3.885763	3.211658	-1.045461
H	-3.400592	3.311242	0.645913
C	0.178488	4.681484	-3.535507
H	-0.674543	4.749759	-4.215891
H	1.029453	4.274535	-4.088575
H	0.442228	5.704217	-3.242899
C	1.741446	1.905274	0.364620
H	1.663165	2.151532	1.428693
H	2.705954	2.271108	0.006338
H	1.750822	0.811884	0.289947
C	-1.330007	-1.138233	3.379403
H	-2.202863	-1.135132	4.038012
H	-0.433820	-1.149397	4.010775
C	-1.347203	-2.368227	2.488367
H	-2.321754	-2.482306	2.003052
H	-1.201648	-3.241006	3.136767
C	-0.251054	-2.247847	1.462169
H	0.765622	-2.093517	1.829521
C	-0.307721	-2.937349	0.236849
C	5.290268	-2.514521	0.225339
C	-1.806516	0.574769	-4.003526
H	5.798908	-2.899314	1.112955
H	-0.998865	0.293094	-4.684431
H	5.208175	-3.317721	-0.511388
H	-2.731273	0.090665	-4.328806
C	3.968478	-2.028249	0.580635
N	-1.015824	1.662528	1.171945
C	-1.478181	0.150242	-2.659810
N	-1.324381	0.124031	2.637149
N	-1.216705	-0.185579	-1.587763
N	2.914212	-1.641506	0.866534
N	-0.453966	-2.954310	-0.939580
H	5.887350	-1.703807	-0.199853
H	-1.933216	1.660108	-4.020026

(2c-NCMe)$_2^+$

Ni	-1.340864	-0.264468	0.317199
Ni	1.395344	-0.052499	0.456313
C	-1.753046	1.213783	1.400384
C	2.525757	-1.033928	1.543700
C	-2.345595	3.241202	2.180253
C	3.645266	-2.785077	2.393235
H	3.995701	-3.804344	2.445454
H	-2.650570	4.273919	2.115077
C	-2.173376	2.427778	3.249599
C	3.910642	-1.706873	3.174172
H	4.532863	-1.605183	4.050338
H	-2.287896	2.614414	4.306468
C	-2.267325	3.029810	-0.269307
C	2.311147	-3.181035	0.325081
C	-3.345487	2.569679	-1.047706
C	2.915892	-3.063288	-0.938269
C	-3.566325	3.190934	-2.276525
C	2.489081	-3.936437	-1.936840
H	2.957825	-3.876940	-2.916242
H	-4.405222	2.856829	-2.882352
C	-2.786013	4.262846	-2.724428
C	1.521998	-4.919070	-1.700718
C	0.944299	-4.991983	-0.431647
C	-1.729923	4.688117	-1.916220
H	0.202169	-5.760444	-0.225462
H	-1.112819	5.522834	-2.241448
C	-1.450247	4.093258	-0.681897
C	1.325716	-4.136610	0.604570
C	-4.278206	1.491538	-0.572515
C	4.017206	-2.074480	-1.203528
H	-3.835394	0.490655	-0.630311
H	3.658925	-1.038293	-1.188842
H	-5.183918	1.475877	-1.181819
H	4.465441	-2.253479	-2.182534
H	-4.580385	1.649890	0.467658
H	4.812213	-2.150613	-0.454402
C	1.158880	-5.902000	-2.777093
C	-3.108847	4.962344	-4.012790
H	1.966894	-6.628645	-2.916644
H	-3.470210	4.264587	-4.772876
H	1.007609	-5.410586	-3.743181
H	-2.243965	5.496332	-4.413585
H	-3.901691	5.701625	-3.852259
H	0.259144	-6.470798	-2.526980
C	0.727688	-4.288363	1.975485
C	-0.321875	4.637721	0.150928
H	-0.621620	5.562487	0.656814
H	1.374505	-4.885442	2.628323
H	-0.233023	-4.806090	1.923319
H	0.537256	4.884143	-0.478611
H	0.009030	3.939771	0.923029
H	0.576776	-3.324802	2.472384
C	-1.725629	-0.037801	3.513914
C	3.252297	0.731615	3.099492
H	4.097099	0.832669	3.783785
H	-1.960329	0.194429	4.554645
H	-0.701612	-0.425520	3.473060
H	2.337125	0.951021	3.661115
C	3.414715	1.653131	1.906379
C	-2.720786	-1.020872	2.923859
H	-3.712223	-0.556849	2.921991
H	4.333575	1.390024	1.372649
H	3.539828	2.681342	2.268204
H	-2.784369	-1.905713	3.568389
C	-2.320223	-1.452240	1.514789
C	2.221199	1.606659	0.957987
H	1.336600	2.084084	1.404864
H	-1.559533	-2.243287	1.569309
C	2.513486	2.218088	-0.315075
C	-3.430903	-1.933419	0.730919
C	-1.966380	-3.595105	-2.544225
C	0.050524	1.941306	-3.153584
H	-3.012310	-3.798645	-2.287282
H	1.010766	2.472083	-3.222087
H	-1.904353	-3.268612	-3.585642
H	-0.044112	1.228422	-3.977188
C	-1.492177	-2.556582	-1.660156
N	-2.081025	2.487367	1.050207
N	2.792803	-2.352615	1.397066
C	0.053342	1.257637	-1.893861
N	-1.808336	1.198786	2.747266
N	3.214856	-0.648929	2.633279
N	0.119272	0.712723	-0.866712
N	-1.190146	-1.718439	-0.923624
N	-4.298600	-2.298903	0.047051
N	2.723630	2.677237	-1.363668
H	-1.369727	-4.500430	-2.409713
H	-0.769171	2.669933	-3.170657

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