Mechanism of Ni-Catalyzed Reductive 1,2-Dicarbofunctionalization of Alkenes

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1. General Considerations

1.1 Materials: Metals, ligands, solvents, and most substrates were obtained from commercial sources. All air- and moisture-sensitive manipulations were carried out in a glove box. THF was dried and deoxygenated by passing through alumina in a solvent purification system. N,N-dimethylacetamide (DMA) was dried over CaH_2, distilled, and degassed before use. Dimethylsulfoxide-d_6, acetone-d_6, dimethylacetamide-d_9 were purchased from Cambridge Isotope Laboratories, Inc. and stored with molecular sieve over 3 days before use. ^1H and ^{13}C NMR spectra were recorded on Bruker 400, 500, or 600 Avance spectrometers (400 MHz, 500 MHz, or 600 MHz). Chemical shifts are reported in ppm relative to tetramethylsilane, with the residual solvent resonance (CDCl$_3$, δ = 7.26;

DMA-d_9, δ = 1.83, 2.66, 2.84) as the internal reference. Spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration. ^{13}C NMR spectra were recorded on Bruker 400 and 600 Avance spectrometers (101 or 151 MHz). Chemical shifts were reported in ppm relative to tetramethylsilane with the solvent resonance used as the internal reference (CDCl$_3$, δ = 77.16). High resolution mass spectra (HRMS) were recorded on an Agilent 6224 TOF LC/MS (APCI source). GC data were obtained using a Shimadzu GC-2010 with a Shimadzu SH-Rxi-5Sil MS column (L 30 m, ID 0.25, DF 0.25). Reactions were monitored by thin-layer chromatography (TLC) on Merck TLC silica gel 60 F254 plates and compounds were visualized by UV light (254 nm) or staining with KMnO$_4$. Aryl bromides were purchased from commercial sources, with liquids dried over CaH$_2$, degassed, and distilled, and solids were dried overnight under reduced pressure (~20 mtorr) before being brought into a nitrogen-filled glove box and stored at –35°C. Zinc was washed with acid and grinded into powder.

2. General Kinetics Experimental Procedure

In a nitrogen-filled glove box, NiBr$_2$•DME, phenanthroline and naphthalene were separately dissolved in DMA to form stock solutions in concentration of 6.25 mM, 60 mM, and 0.2 M, respectively. To a 2 mL crimp-top vial was added **11** (15.9 mg, 0.05 mmol), PhBr (15.7mg, 0.1 mmol), and zinc powder (2.0 equiv.). After addition of stock solutions of NiBr$_2$•DME (0.8 mL), phenanthroline (0.1 mL) and naphthalene (internal standard, 0.1mL), the vial was sealed and removed from the glove box. The reaction was placed in a shaker and heated to 50 °C. The agitation speed was set to 850 rpm. The reaction progress was monitored by removing aliquots (~15 µL) from the reaction mixture via syringe. Each aliquot was quenched by saturated ammonium chloride (0.5 mL) in a 2 mL GC vial. The mixture was extracted by diethyl ether and the resulting organic layer was collected, washed with water twice, dried over Na$_2$SO$_4$, and analyzed by gas chromatography.

3. Kinetics Data

3.1.1. Kinetic plots for same excess experiment

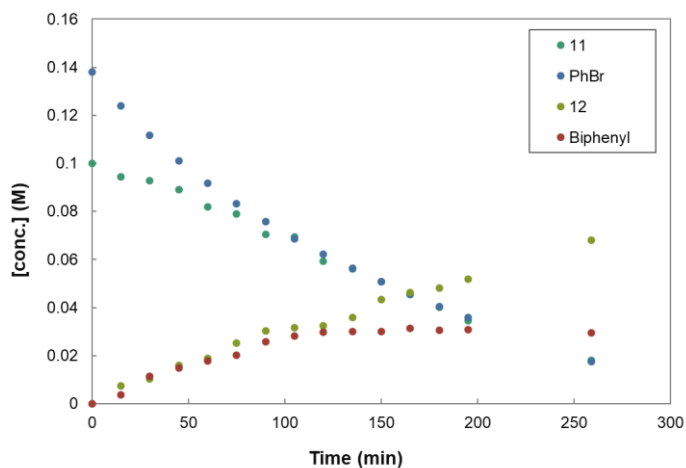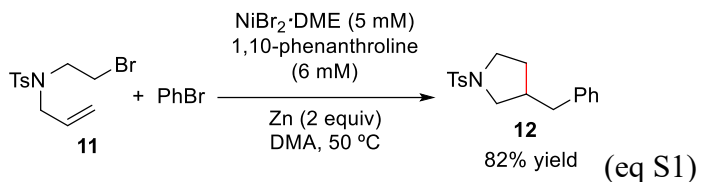Same excess studies were completed using general kinetics experimental procedure with an excess of 0.05 M.

(eq S1)

Figure S1-1. Time-course for the reaction shown in eq S1. Reaction conditions: [NiBr$_2$•DME] = 5.0 mM, [phenanthroline] = 6.0 mM, Zn = 0.10 mmol, solvent = DMA; [**11**]$_0$ = 0.10 M; [PhBr]$_0$ = 0.15 M.

3.1.2. Kinetic plots for different excess experiment

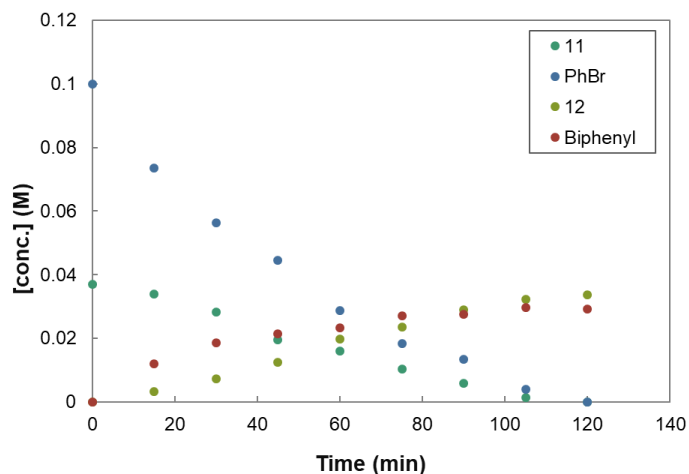Different excess studies were completed using general kinetics experimental procedure.

Figure S1-2. Time-course for the reaction shown in eq S1. Reaction conditions: [NiBr$_2$•DME] = 5.0 mM, [phenanthroline] = 6.0 mM, Zn = 0.10 mmol, solvent = DMA; [**11**]$_0$ = 0.037 M; [PhBr]$_0$ = 0.10 M. Mixing Speed at 900 rpm.
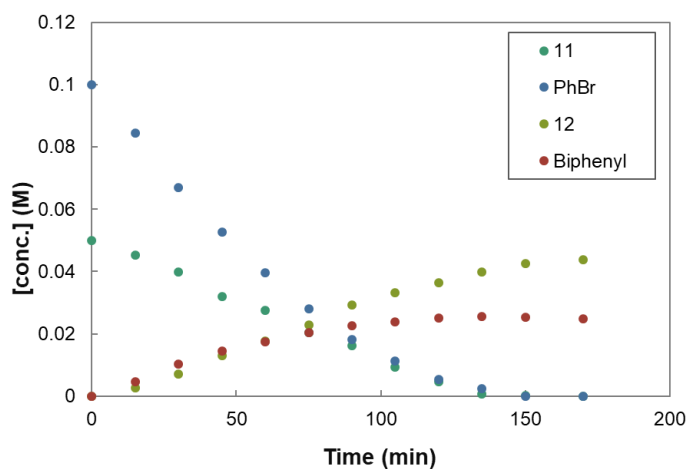
Figure S1-3. Time-course for the reaction shown in eq S1. Reaction conditions: [NiBr$_2$•DME] = 5.0 mM, [phenanthroline] = 6.0 mM, Zn = 0.10 mmol, solvent = DMA; [**11**]$_0$ = 0.050 M; [PhBr]$_0$ = 0.10 M. Mixing Speed at 900 rpm.
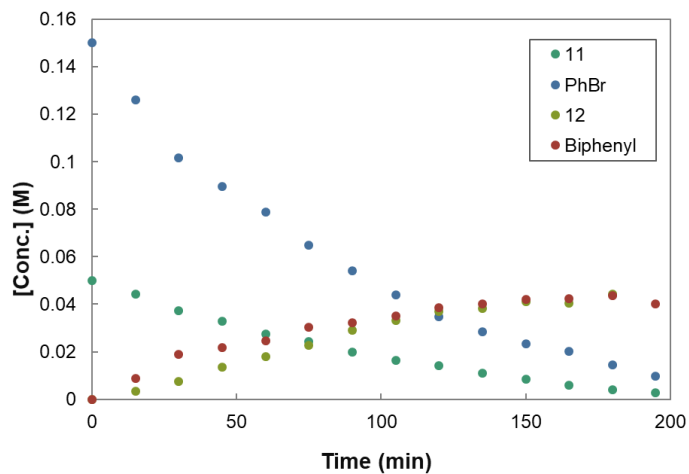
Figure S1-4. Time-course for the reaction shown in eq S1. Reaction conditions: [NiBr$_2$•DME] = 5.0 mM, [phenanthroline] = 6.0 mM, Zn = 0.10 mmol, solvent = DMA; [**11**]$_0$ = 0.050 M; [PhBr]$_0$ = 0.15 M. Mixing Speed at 900 rpm.

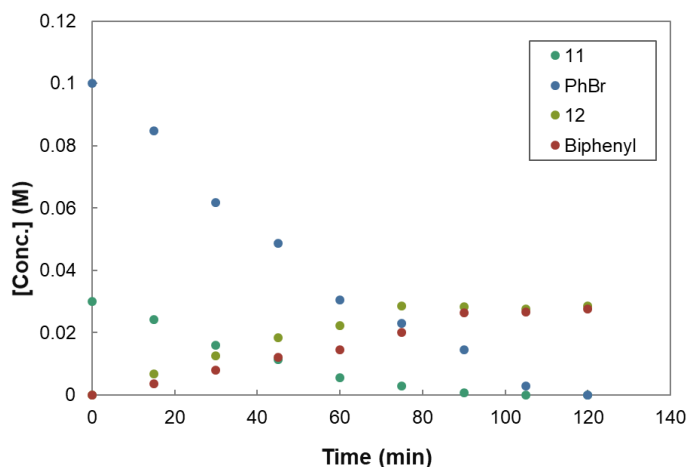**Figure S1-5.** Time-course for the reaction shown in eq S1. Reaction conditions: reaction scale = 0.025 mmol, [NiBr$_2$•DME] = 5.0 mM, [phenanthroline] = 6.0 mM, Zn = 0.050 mmol, solvent = DMA; [**11**]$_0$ = 0.030 M; [PhBr]$_0$ = 0.10 M. Mixing Speed at 1200 rpm.
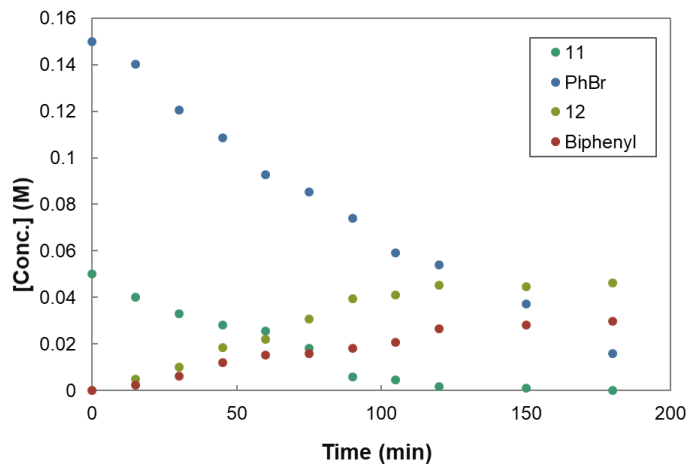

Figure S1-6. Time-course for the reaction shown in eq S1. Reaction conditions: reaction scale = 0.025 mmol, [NiBr$_2$•DME] = 5.0 mM, [phenanthroline] = 6.0 mM, Zn = 0.050 mmol, solvent = DMA; [**11**]$_0$ = 0.050 M; [PhBr]$_0$ = 0.15 M. Mixing Speed at 1200 rpm.

Table S1. Rate Constants of the formation of **12** in different excess experiments.

	Mixing Speed	**[11]$_0$ (M)**	**[PhBr]$_0$ (M)**	**k$_{obs}$ ($\times 10^{-4}$s^{-1})**
Entry 1	900 rpm	0.037	0.10	8.6
		0.050	0.10	8.6
		0.050	0.15	8.5
Entry 2	1200 rpm	0.037	0.10	12
		0.050	0.10	13
		0.050	0.15	12

3.2. Kinetic plots with different Ni loading

The study of kinetic orders in the catalyst was completed following the general procedure described above.
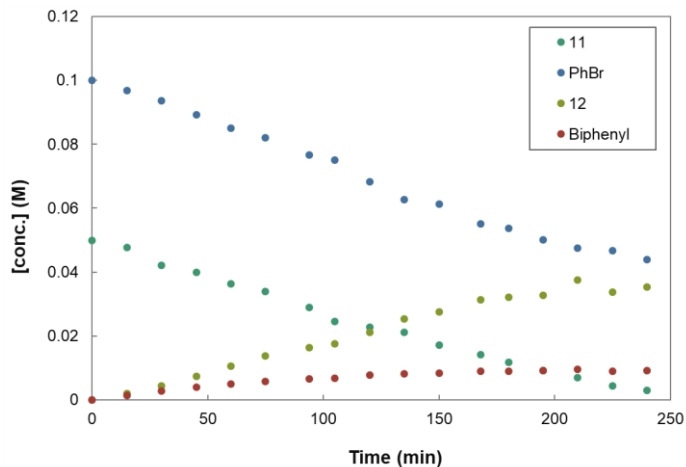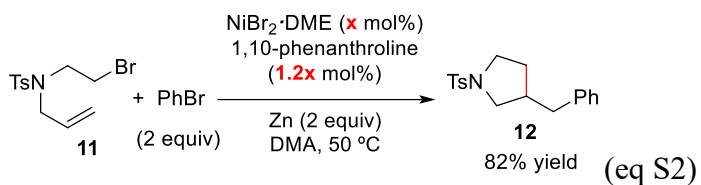

(eq S2)

Figure S2. Time-course for the reaction shown in eq S2 with 5% Ni loading. Reaction conditions: $[NiBr_2 \cdot DME] = 2.5$ mM, [phenanthroline] $= 3.0$ mM, Zn $= 0.10$ mmol, solvent $=$ DMA; $[\mathbf{11}]_0 = 0.050$ M; $[PhBr]_0 = 0.10$ M.

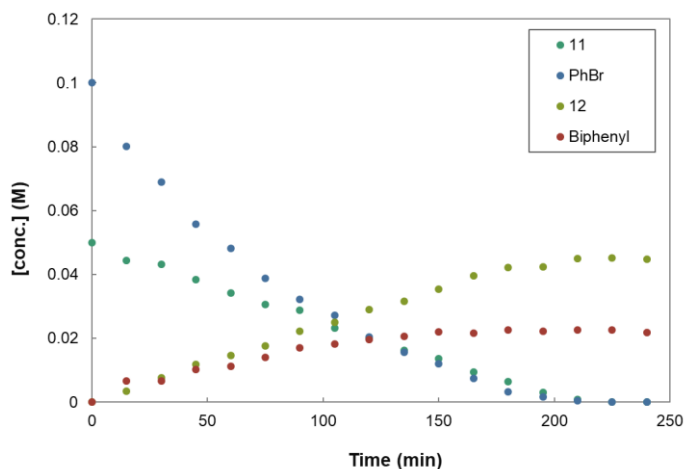**Figure S3.** Time-course for the reaction shown in eq S2 with 8% Ni loading. Reaction conditions: $[NiBr_2 \cdot DME] = 4.0$ mM, [phenanthroline] $= 4.8$ mM, Zn $= 0.10$ mmol, solvent $=$ DMA; $[\mathbf{11}]_0 = 0.050$ M; $[PhBr]_0 = 0.10$ M.

Figure S4. Time-course for the reaction shown in eq S2 with 10% Ni loading. Reaction conditions: $[NiBr_2 \cdot DME] = 5.0$ mM, [phenanthroline] = 6.0 mM, Zn = 0.10 mmol, solvent = DMA; $[11]_0 = 0.050$ M; $[PhBr]_0 = 0.10$ M.

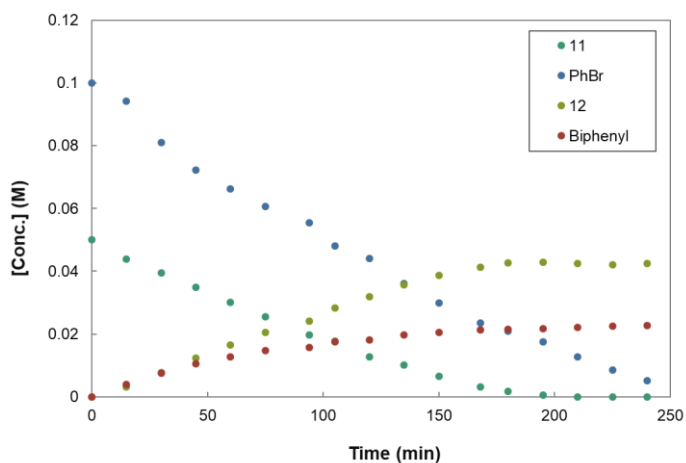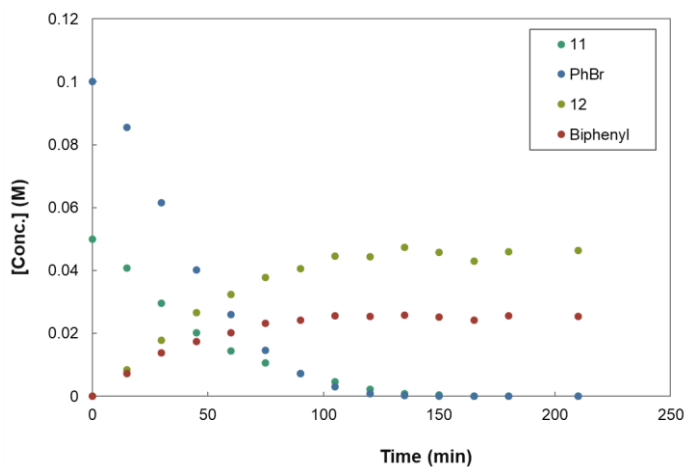**Figure S5.** Time-course for the reaction shown in eq S2 with 15% Ni loading. Reaction conditions: $[NiBr_2 \cdot DME] = 7.5$ mM, [phenanthroline] = 9.0 mM, Zn = 0.10 mmol, solvent = DMA; $[11]_0 = 0.050$ M; $[PhBr]_0 = 0.10$ M.

Figure S6-1. Various normalization analysis of product vs. [catalyst]$^{0.5}$·(time). The lack of overlay fitting suggests that the catalyst order is not 0.5.

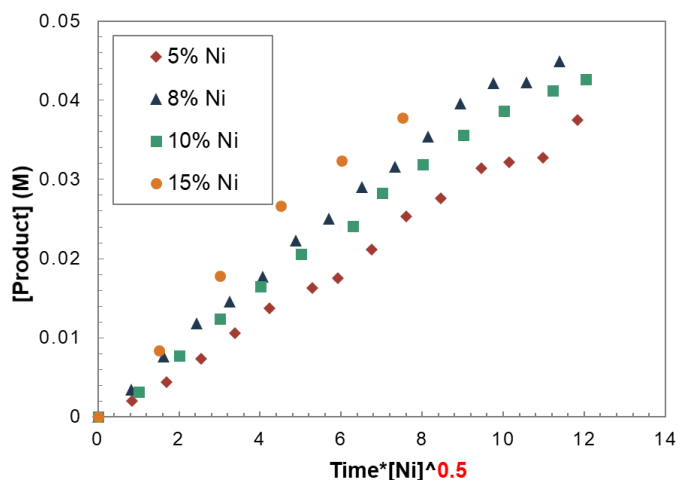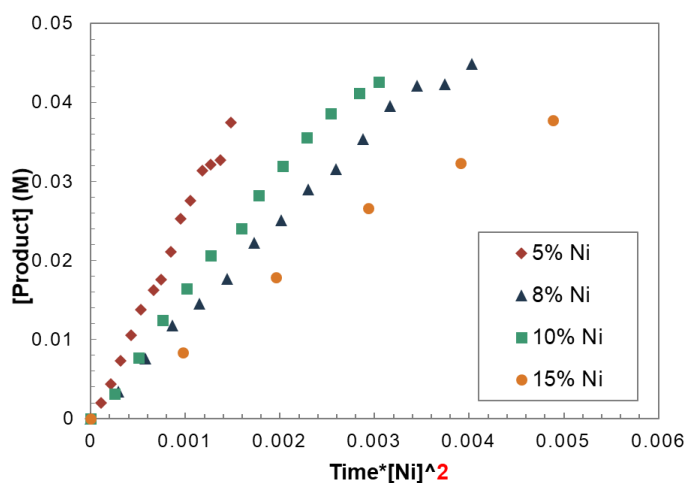**Figure S6-2.** Various normalization analysis of product vs. [catalyst]^2·(time). The lack of overlay fitting suggests that the catalyst order is not 2.

3.3. Kinetic Plots for Study of Agitation Speed

(eq S3)
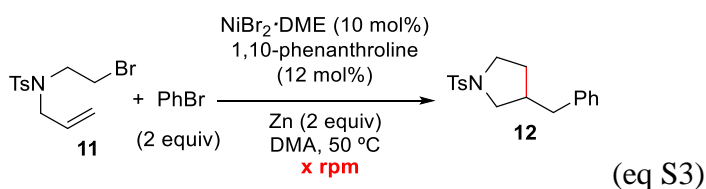
Reaction order in catalyst studies were elucidated by following general kinetics experimental procedures with the exception of agitation rate. All reactions were set up at 0.025 mmol scale. The first 2 hrs of the reaction progress was monitored.

Figure S7. Kinetic profile of the reaction shown in eq S3 with an agitation speed of 500 rpm. Reaction conditions: [NiBr$_2$•DME] = 5.0 mM, [phenanthroline] = 6.0 mM, Zn = 0.050 mmol, solvent = DMA; [**11**]$_0$ = 0.050 M; [PhBr]$_0$ = 0.10 M.

Figure S8. Kinetic profile of the reaction shown in eq S3 with an agitation speed of 700 rpm. Reaction conditions: [NiBr$_2$•DME] = 5.0 mM, [phenanthroline] = 6.0 mM, Zn = 0.050 mmol, solvent = DMA; [**11**]$_0$ = 0.050 M; [PhBr]$_0$ = 0.10 M.

Figure S9. Kinetic profile of the reaction shown in eq S3 with an agitation speed of 900 rpm. Reaction conditions: $[NiBr_2 \cdot DME]$ = 5.0 mM, [phenanthroline] = 6.0 mM, Zn = 0.050 mmol, solvent = DMA; $[\mathbf{11}]_0$ = 0.050 M; $[PhBr]_0$ = 0.10 M.
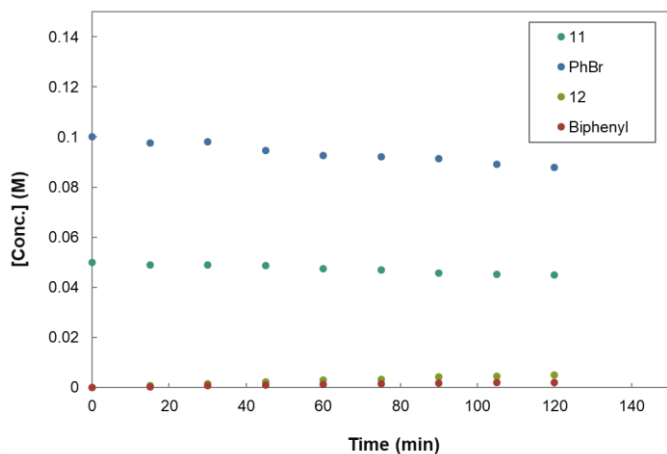

Figure S10. Kinetic profile of the reaction shown in eq S3 with an agitation speed of 1200 rpm. Reaction conditions: $[NiBr_2 \cdot DME]$ = 5.0 mM, [phenanthroline] = 6.0 mM, Zn = 0.050 mmol, solvent = DMA; $[\mathbf{11}]_0$ = 0.050 M; $[PhBr]_0$ = 0.10 M.
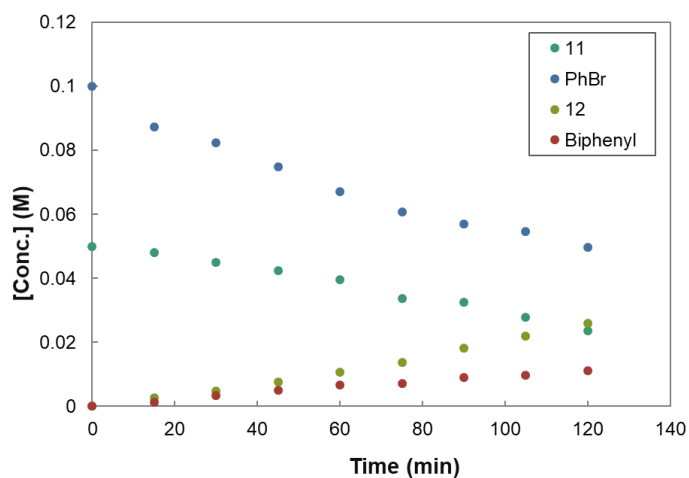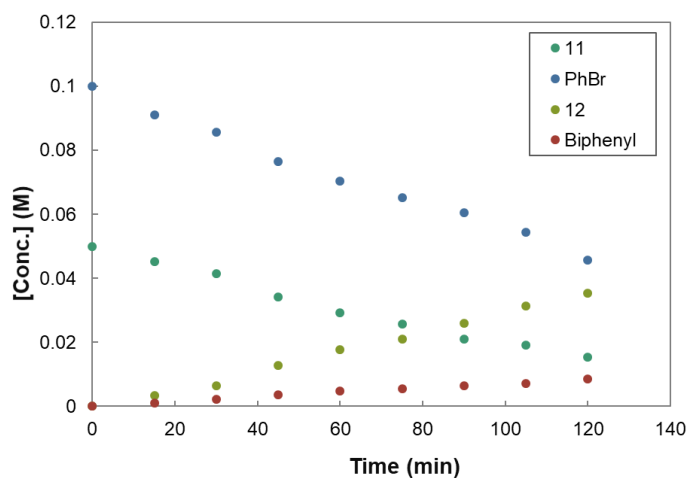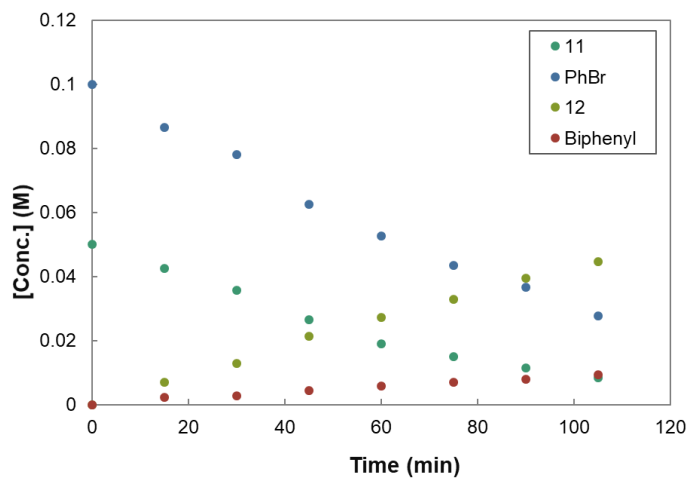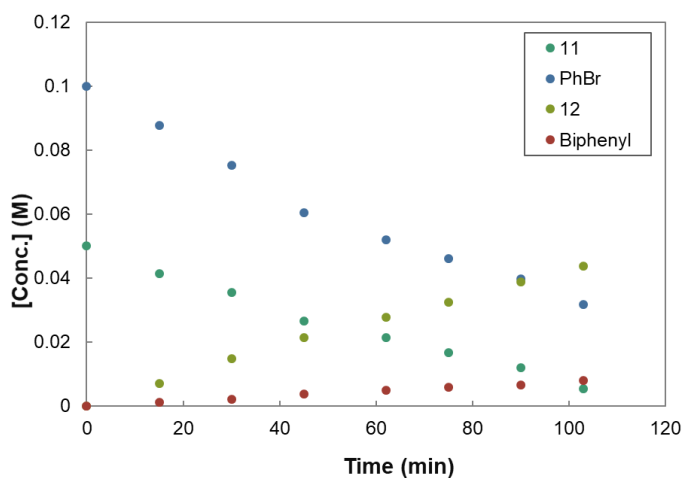
Figure S11. Kinetic profile of the reaction shown in eq S3 with an agitation speed of 1500 rpm. Reaction conditions: [NiBr$_2$•DME] = 5.0 mM, [phenanthroline] = 6.0 mM, Zn = 0.050 mmol, solvent = DMA; [**11**]$_0$ = 0.050 M; [PhBr]$_0$ = 0.10 M.
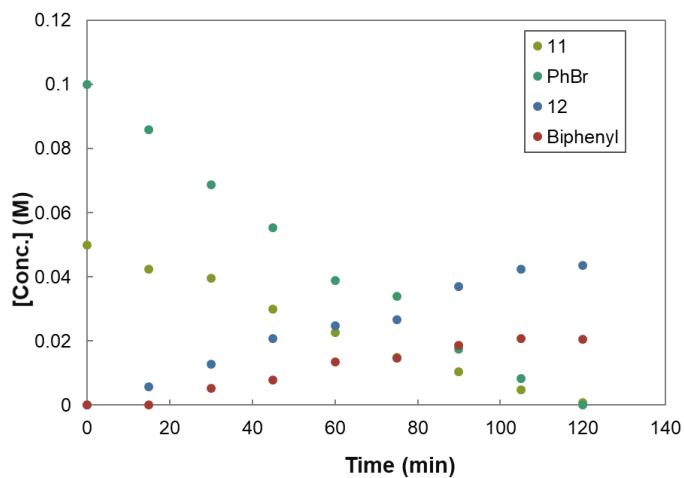
Figure S12. Time-course for the reaction shown in eq S3. Reaction conditions: reaction scale = 0.05 mmol, [NiBr$_2$•DME] = 5.0 mM, [phenanthroline] = 6.0 mM, Zn = 0.01 mmol, [TBAI] = 5.0 mM, solvent = DMA; [**11**]$_0$ = 0.050 M; [PhBr]$_0$ = 0.15 M. Mixing Speed at 900 rpm.

Table S2. Rate Constants of the formation of **12** with and without TBAI as additives.

	TBAI	**Agitation rate (rpm)**	**k$_{obs}$ (×10^{-4}s^{-1})**
Entry 1	0	900	8.1
Entry 2	10%	900	12
Entry 3	0	1200	12

3.4. Kinetic plots for Zn loading experiments.

(eq S4)
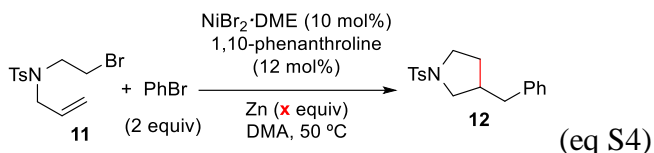
The study to elucidate the effect on Zn loading on rates was completed following the general procedure. All reactions were set up at 0.025 mmol scale. The first 2 hrs of the reaction progress was monitored.
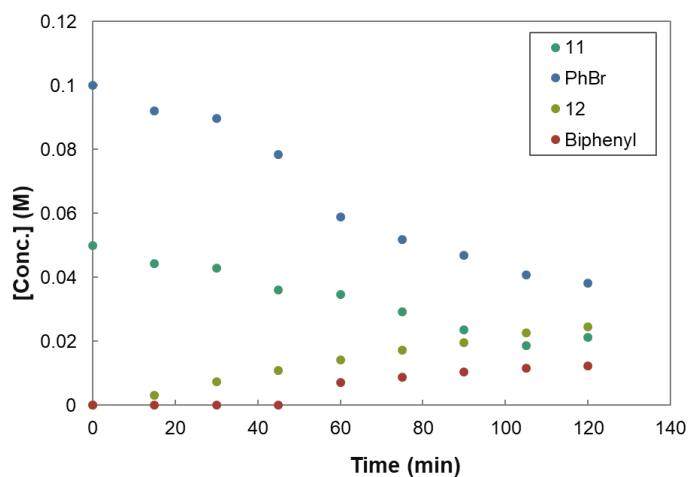
Figure S13. Kinetic profile for the reaction shown in eq S4 with 1 equiv. Zn loading. Reaction conditions: [NiBr$_2$•DME] = 5.0 mM, [phenanthroline] = 6.0 mM, Zn = 0.025 mmol, solvent = DMA; [**11**]$_0$ = 0.050 M; [PhBr]$_0$ = 0.10 M. Mixing Speed at 900 rpm.
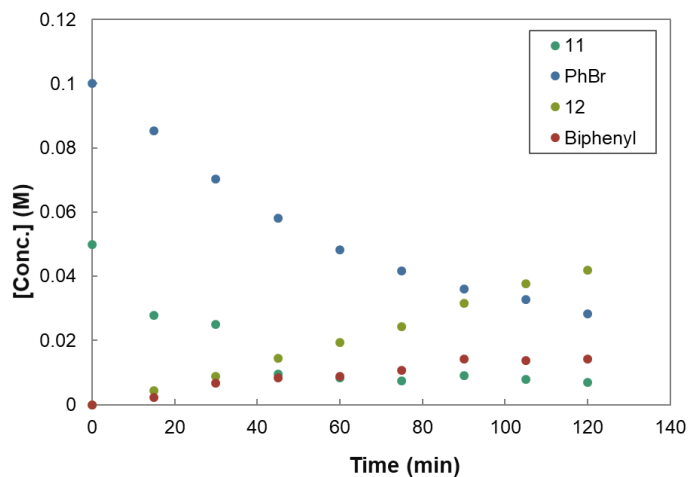
Figure S14. Kinetic profile for the reaction shown in eq S4 with 4 equiv. Zn loading.

Reaction conditions: [NiBr$_2$•DME] = 5.0 mM, [phenanthroline] = 6.0 mM, Zn = 0.10 mmol, solvent = DMA; [**11**]$_0$ = 0.050 M; [PhBr]$_0$ = 0.10 M. Mixing Speed at 900 rpm.
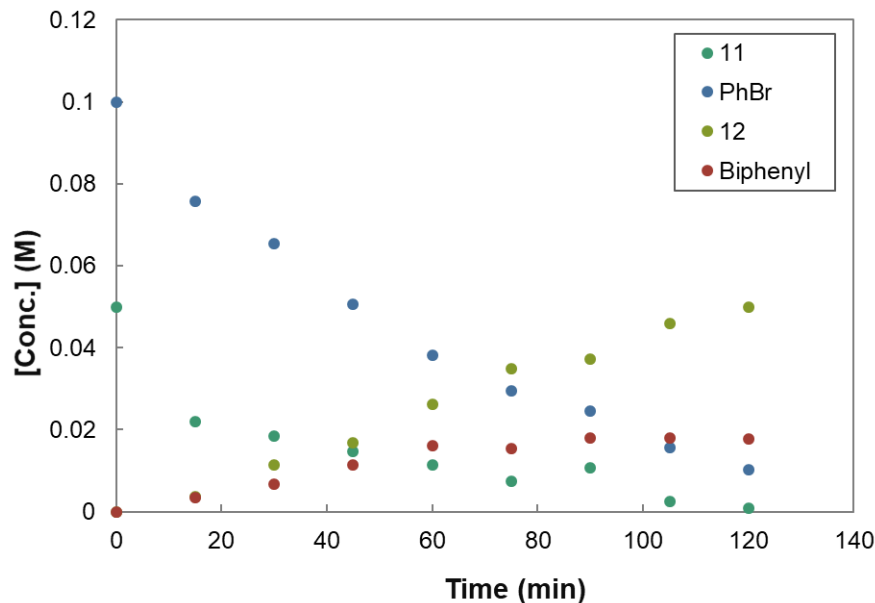
Figure S15. Kinetic profile for the reaction shown in eq S4 with 6 equiv. Zn loading. Reaction conditions: [NiBr$_2$•DME] = 5.0 mM, [phenanthroline] = 6.0 mM, Zn = 0.15 mmol, solvent = DMA; [**11**]$_0$ = 0.050 M; [PhBr]$_0$ = 0.10 M. Mixing Speed at 900 rpm.

Figure S16. The reaction rate vs. Zn loading for the reaction shown in eq S4.

3.5. Comparison of Activation Rates for Different Electrophiles

To a 2 mL crimp-top vial was added (Phen)NiBr$_2$ **14** (19.9 mg, 0.05 mmol), zinc (2.0 equiv.) and DMA 2 mL. The reaction was placed in a shaker, heated to 50 °C, and agitated

at a speed of 850 rpm. After reacting for 30mins, the resulting purple solution was cooled and filtered to remove Zn. This solution was divided into two 2 mL crimp-top vials, containing **11** (7.9 mg, 0.025 mmol) and PhBr (3.9 mg, 0.025 mmol), respectively. After charging with zinc (2.0 equiv.), both vials were placed in a shaker and allowed to react at 50 °C. The reaction progress was monitored in the same way as described in the general procedure.

4. NMR Spectroscopy Characterization of Catalyst Resting State

4.1. NMR study of the reaction mixture with (*o*-Tol)Br as the electrophile.

In a nitrogen-filled glove box, NiBr$_2$•DME, phenanthroline and 1,3,5-trimethoxybenzene were separately dissolved in DMA-d_9 to form stock solutions in concentration of 6.25 mM, 60 mM, and 0.2 M, respe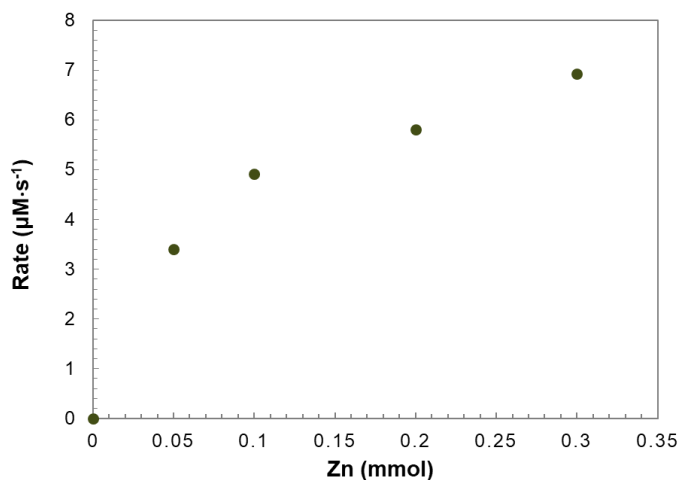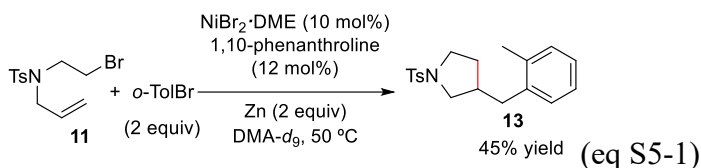ctively. To a 2 mL crimp-top vial was added **11** (15.9 mg, 0.05 mmol), PhBr (15.7mg, 0.1 mmol), and zinc powder (2.0 equiv.). After addition of stock solutions of NiBr$_2$•DME (0.8 mL), phenanthroline (0.1mL) and 1,3,5-trimethoxybenzene (internal standard, 0.06 mL), the vial was sealed and removed from the glove box. The reaction was placed in a shaker and heated to 50 °C. The agitation speed was set to 850 rpm. After reacting for 15 min, the mixture was cooled, followed by filtration with glass wool into a J-Young tube and analyzed by ^{1}H NMR spectroscopy.

(eq S5-1)

Figure S17-1. The diamagnetic region of the reaction shown in eq S5-1 at 21% conversion. Reaction conditions: [NiBr$_2$•DME] = 5.0 mM, [phenanthroline] = 6.0 mM, Zn = 0.10 mmol, solvent = DMA-d_9; [**11**]$_0$ = 0.050 M; [o-TolBr]$_0$ = 0.10 M. Agitation rate = 850 rpm. Probe temperature = 25 °C. **11**(✦). **13** (✦), (Phen)Ni(o-Tol)Br (✦).

4.2. NMR study of the reaction mixture with (Phen)Ni(o-Tol)Br as catalyst
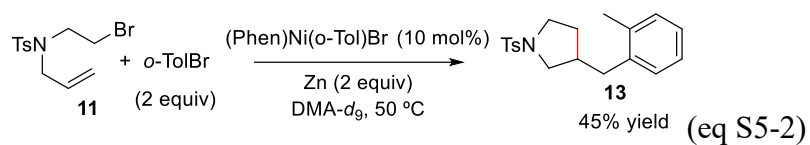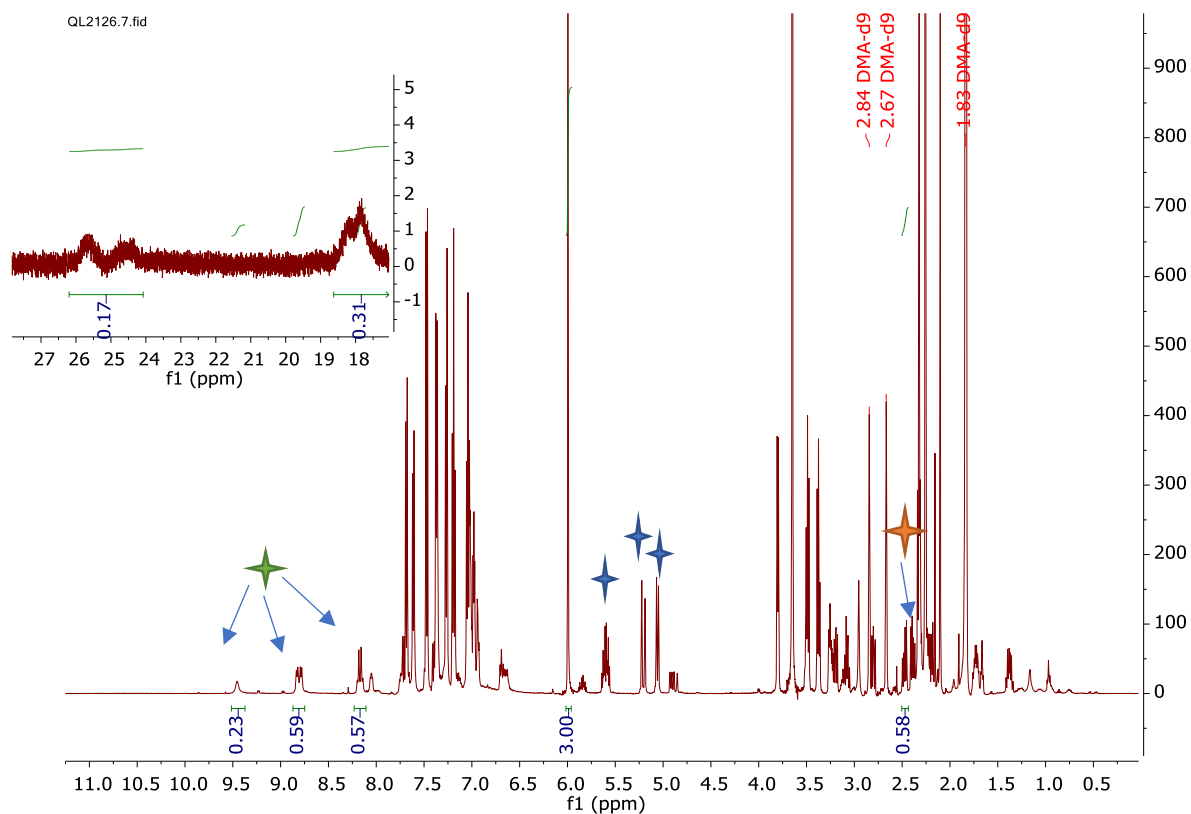
(eq S5-2)

Figure S17-2. ^{1}H NMR spectrum of the reaction shown in eq S5-2 at 25% conversion. Reaction conditions: [(Phen)Ni(o-Tol)Br] = 5.0 mM, Zn = 0.10 mmol, solvent = DMA-d_9; [**11**]$_0$ = 0.05 M; [o-TolBr]$_0$ = 0.1 M. Mixing Speed at 850 rpm. Probe temperature = 25 °C. **11**(✦), **13**(✦) (Phen)Ni(o-TolBr)Br is shown as (✦).

4.3. NMR study of the reaction mixture with PhBr as the electrophile.
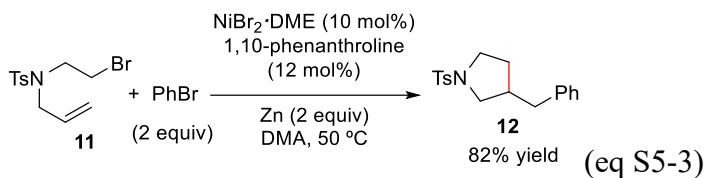
(eq S5-3)

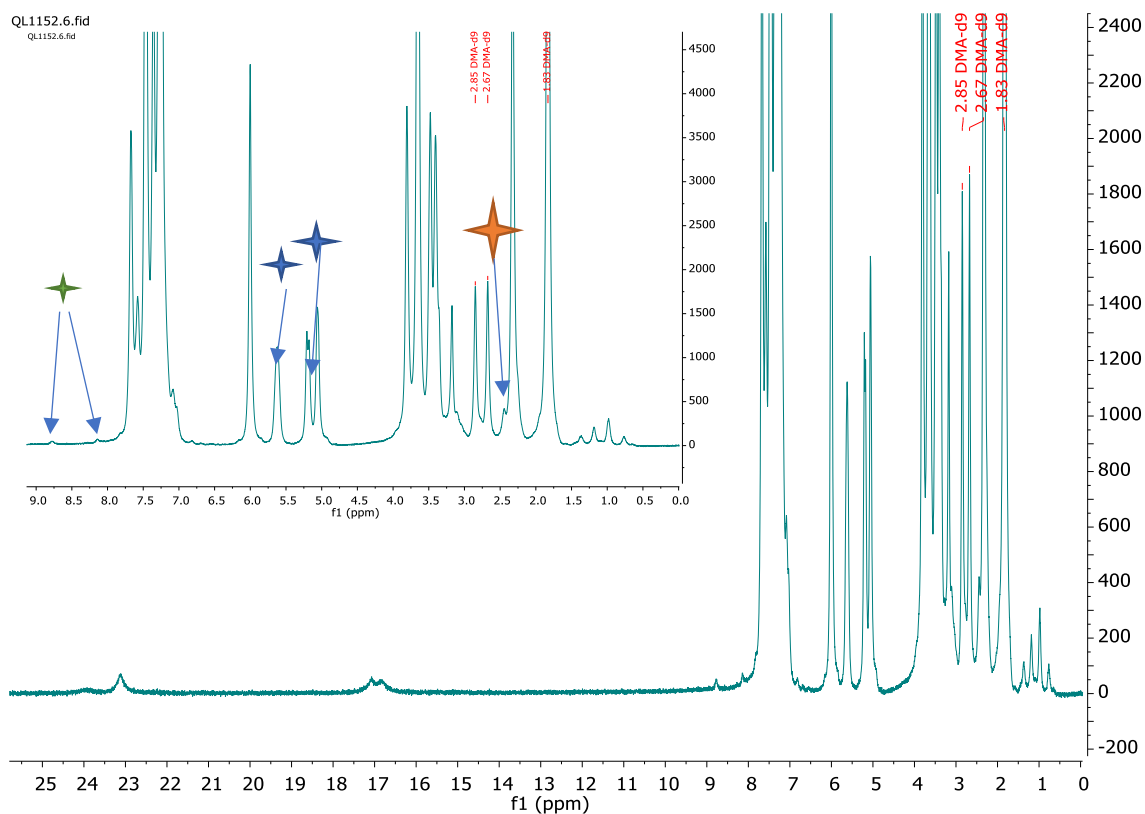**Figure S18**. ^{1}H NMR spectrum of the reaction shown in eq S5-3 at 17% conversion. Reaction conditions: [NiBr$_2$•DME] = 5.0 mM, [phenanthroline] = 6.0 mM, Zn = 0.10 mmol, solvent = DMA-d_9; [**11**]$_0$ = 0.05 M; [PhBr]$_0$ = 0.1 M. Mixing Speed at 850 rpm. Probe temperature = 50 °C. **11**(✦), **12** (✦) (Phen)Ni(Ph)Br **16** is shown as (✦).

Figure S19. Comparison of (a) (Phen)NiBr$_2$ **14** in DMA-d_9 and (b)the paramagnetic region of the reaction mixture shown in eq S5-3. Probe temperature = 50 °C.

No significant (Phen)NiPh(Br) **16** peaks were observed in diamagnetic region due to the low stability of **16** in DMA. The decomposition of **16** was also observed when dissolving the independently prepared **16** into DMA.

4.4. Stoichiometric Experiments to probe the activation of electrophiles

1,3,5-trimethoxybenzene as the internal standard was added to a 2 mL crimp-top vial and dissolved in DMA-d_9 to prepare stock solutions (0.22 M).

To a 2 mL crimp-top vial was added (Phen)NiBr$_2$ **14** (4.7 mg, 0.01 mmol), 1,3,5-trimethoxybenzene solution (30 μL) and DMA-d_9 0.6 mL. This green solution was filtered through glass wool into a J-Young tube and analyzed by ^{1}H NMR spectroscopy (Figure S6a). The solution was then transferred to a 2 mL crimp-top vial, recharged with activated zinc (2.0 equiv.), sealed, and placed in a shaker at 50°C for 30 min to give a purple mixture. The dark purple mixture **19** was cooled, followed by filtration with glass wool into a J-

Young tube. To the J-Young tube was then added (*o*-Tol)Br (1.7 mg, 0.01 mmol) to afford an orange solution. The orange mixture was then cooled to room temperature and analyzed by ^{1}H NMR spectroscopy. (Figure S6b).
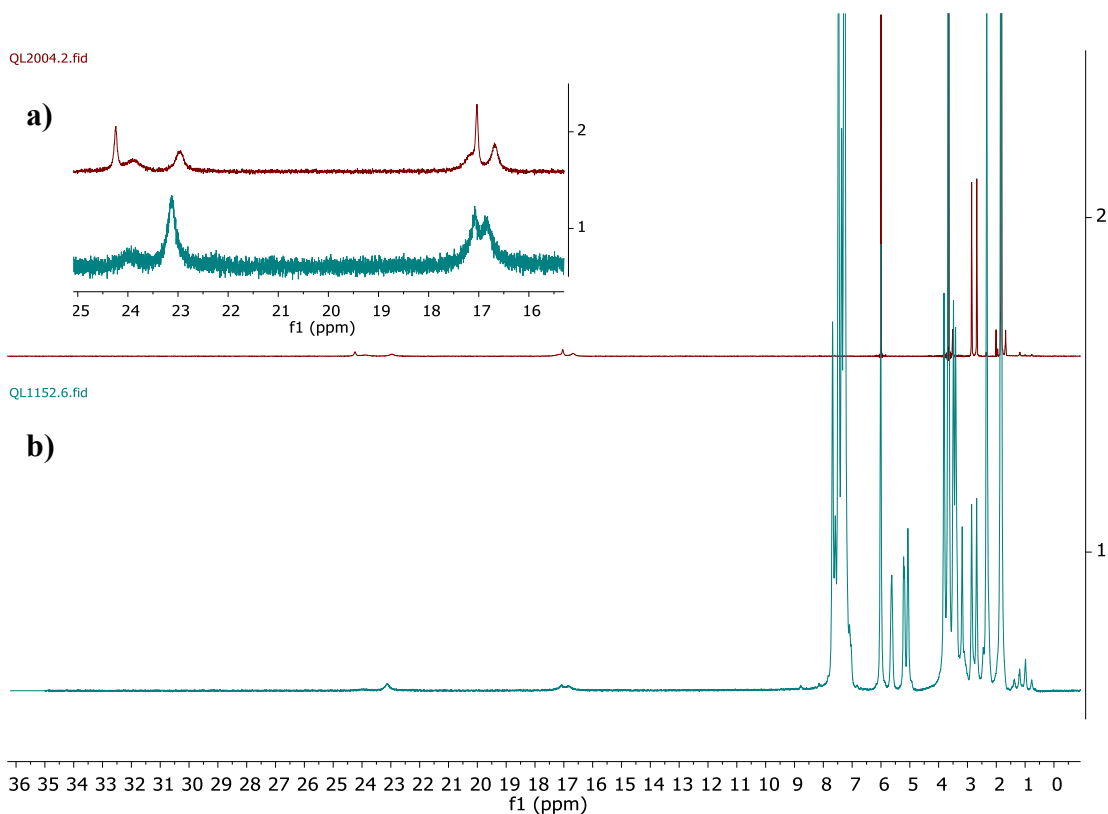

Figure S20. Comparison of (a) (Phen)NiBr$_2$ **14** in DMA-*d*$_9$ with (b) the paramagnetic region of the reaction mixture shown in eq S6. Reaction conditions: [**14**] = 0.015 M; [*o*-TolBr] = 0.015 M; Zn = 0.020 mmol, solvent = DMA-*d*$_9$. Probe temperature = 50 ºC.
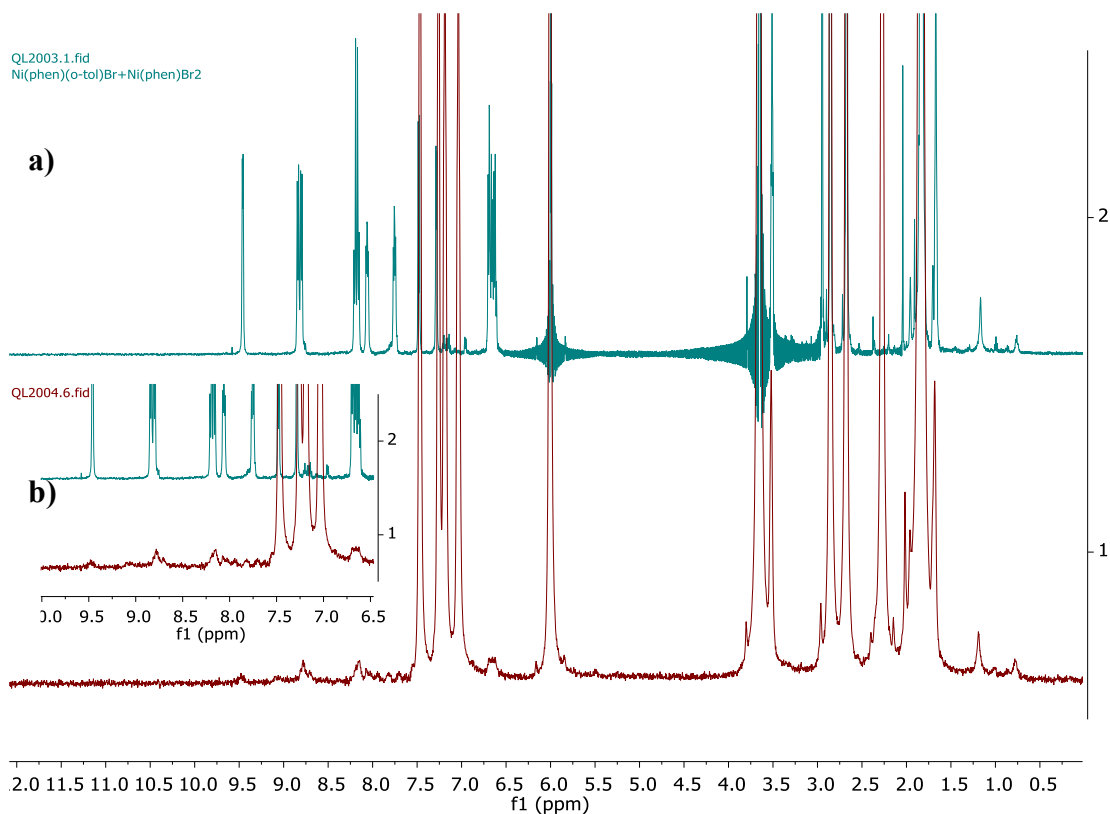
Figure S21. Comparison of (a) (Phen)Ni(*o*-Tol)Br **15** in DMA-*d*₉ with (b) the diamagnetic region of the reaction mixture shown in eq S6. Reaction conditions: [**14**] = 0.015 M; [*o*-TolBr] = 0.015 M; Zn = 0.020 mmol, solvent = DMA-*d*₉.

4.5. Bimolecular Oxidative Addition in DMSO-*d*₆

(eq S7)

Due to the low solubility of (Phen)NiBr₂ in DMA, we repeated the quantitative experiment in DMSO-*d*₆ using the same procedure.
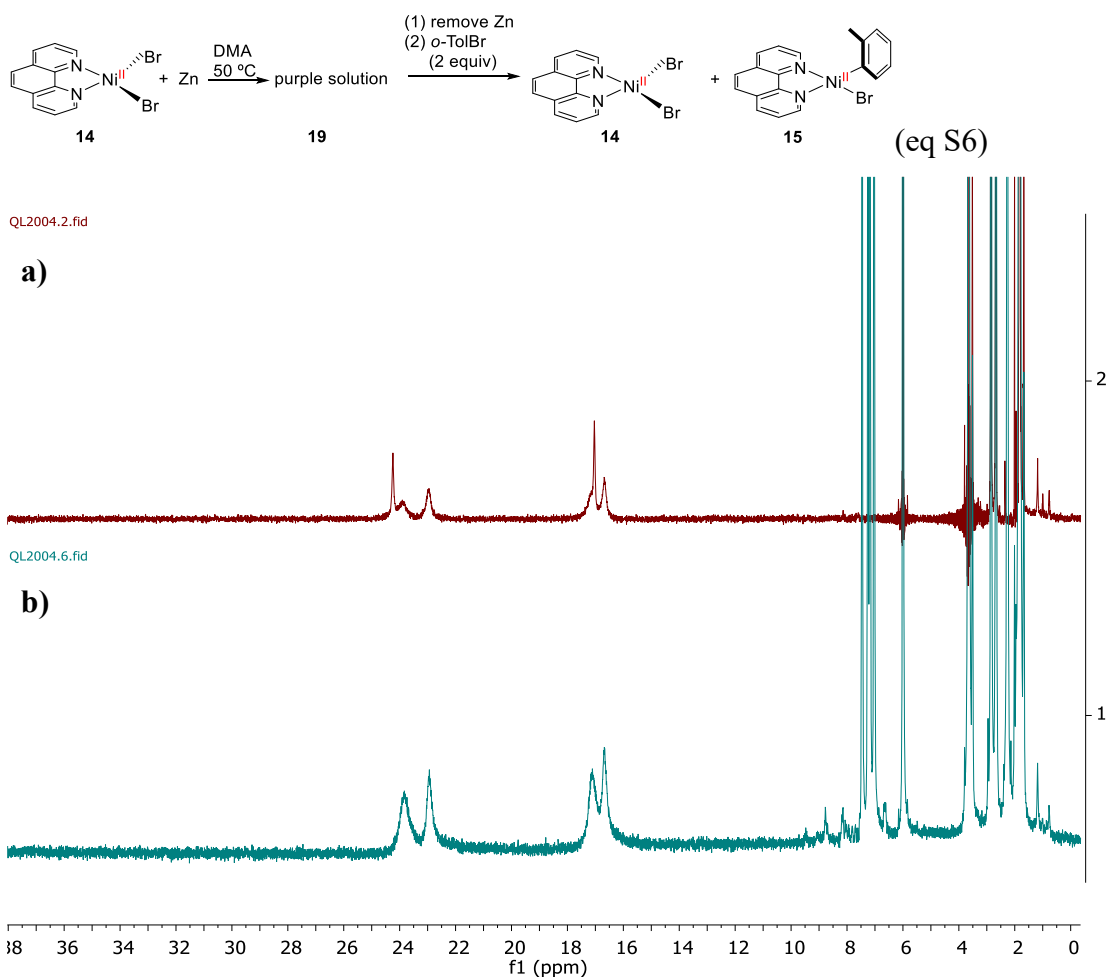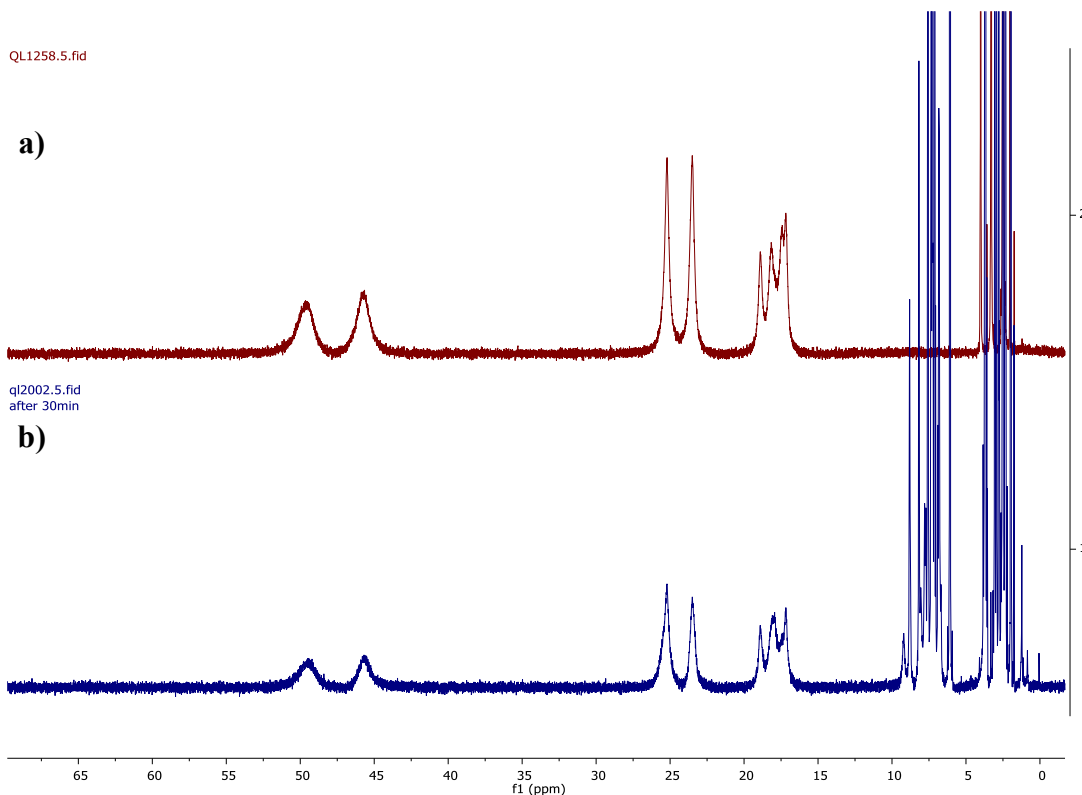
Figure S22. Comparison of (a) (Phen)NiBr$_2$ **14** in DMSO-d_6 with (b) the paramagnetic region of the reaction mixture shown in eq S7. Reaction conditions: [**14**] = 0.015 M; [o-TolBr] = 0.015 M; Zn = 0.020 mmol, solvent = DMSO-d_6. Probe temperature = 25 °C.
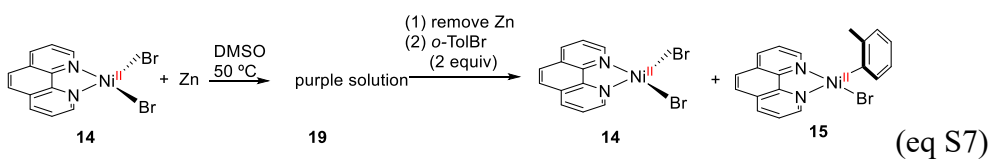
5. Stoichiometric Studies of Substrate Activation

5.1. Reaction of (Phen)Ni(Ar)Br with **11**

5.1.1. Activation of **11** by (Phen)Ni (o-Tol)Br **15**

(eq S8)
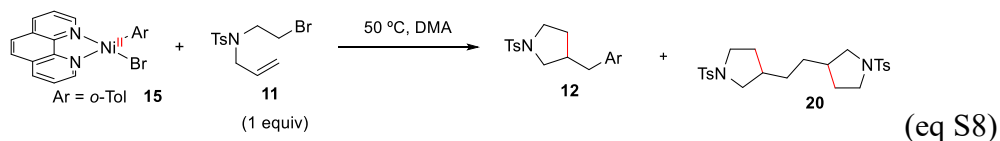
To a 2 mL crimp-top vial was added (Phen)Ni (o-Tol)Br **15** (8.2 mg, 0.02 mmol), **11** (6.4 mg, 0.02 mmol) and DMA (0.4 mL). The vial was sealed, removed from the glove box, and placed in a shaker at 50 °C with a mixing speed of 850 rpm. After reacting overnight, the mixture was quenched with saturated ammonium chloride, and extracted with diethyl ether. The organic phase was washed with water twice, dried over Na$_2$SO$_4$, filtered, concentrated under N$_2$ and analyzed by ^{1}H NMR spectroscopy.
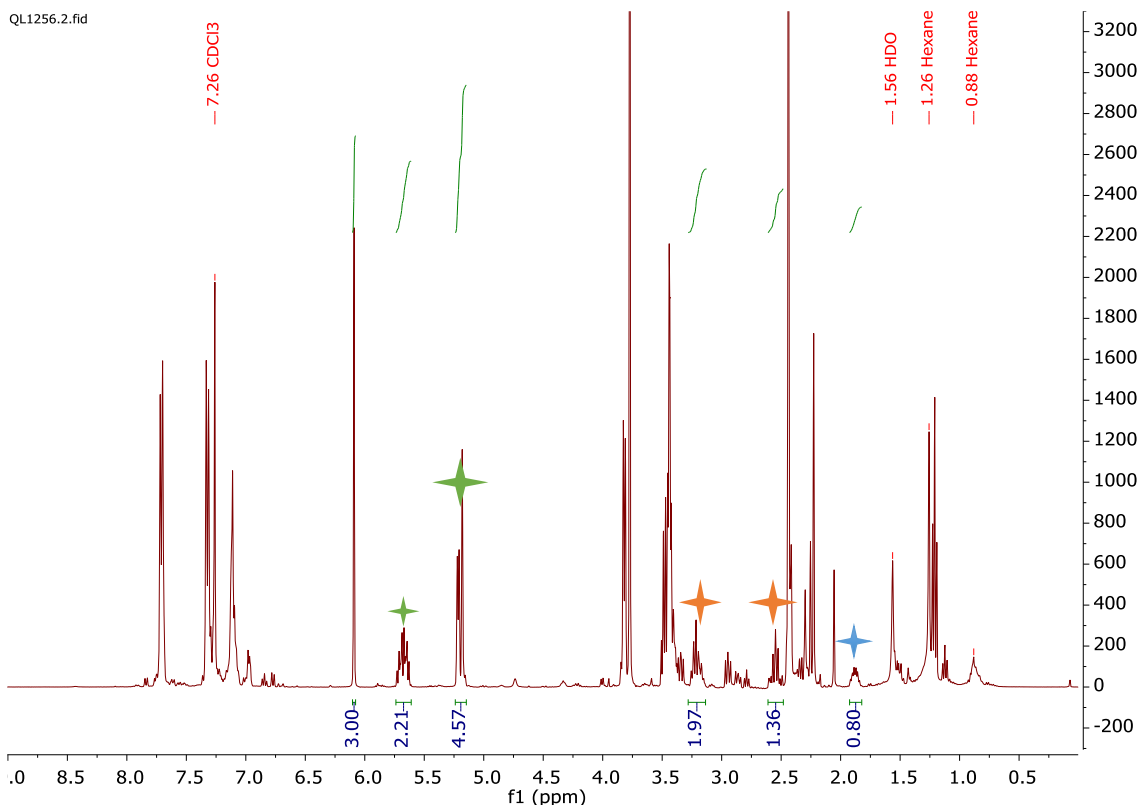
Figure S23. Crude ^{1}H NMR spectrum for the reaction shown in eq S8. Reaction conditions: [**15**] = 0.050 M; [**11**] = 0.050 M; solvent = DMA; **11** (+) , **12** (+) and **20** (+) were observed.

5.1.2. **11** activation with reduced product (Phen)Ni (*o*-Tol) **15-a**
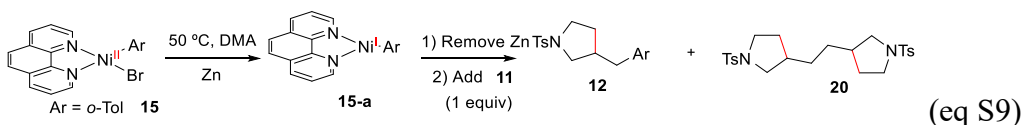
(eq S9)

To a 2 mL crimp-top vial was added (Phen)Ni(*o*-Tol)Br **15** (8.2 mg, 0.02 mmol), ground, activated zinc (2.0 equiv.) and DMA (0.4 mL), which was then placed in a shaker, heated to 50 °C with mixing speed at 850 rpm for 30 min. The resulting purple-red solution was filtered with glass wool into a new 2 mL crimp-top vial, followed by adding **11** (6.4 mg, 0.02 mmol) and placed back to the shaker. After 2 hrs, the mixture was quenched with saturated ammonium chloride. The mixture was extracted by diethyl ether and the resulting organic layer was collected, washed with water twice, dried over Na$_2$SO$_4$, filtered, concentrated under N$_2$ and analyzed by ^{1}H NMR spectroscopy.

Figure S24. Crude ^{1}H NMR spectrum for the reaction shown in eq S9. Reaction conditions: [**15**] = 0.050 M; [**11**] = 0.050 M; Zn = 0.040 mmol, solvent = DMA; **11** (✦) , **12** (✦) and **20** (✦) were observed.

5.1.3. **11** activation with (Phen)Ni (*o*-Tol)Br **15** and Zn

(eq S10)

To a 2 mL crimp-top vial was added (Phen)Ni(*o*-Tol)Br **15** (8.2 mg, 0.02 mmol), ground, activated zinc (2.0 equiv.) and DMA (0.4 mL), which was then placed in a shaker heated to 50 °C, with mixing speed at 850 rpm for 2 hrs. The mixture was quenched with saturated ammonium chloride. The mixture was extracted by diethyl ether and the resulting organic layer was collected, washed with water twice, dried over Na_2SO_4, filtered, concentrated under N_2 and analyzed by ^{1}H NMR spectroscopy.
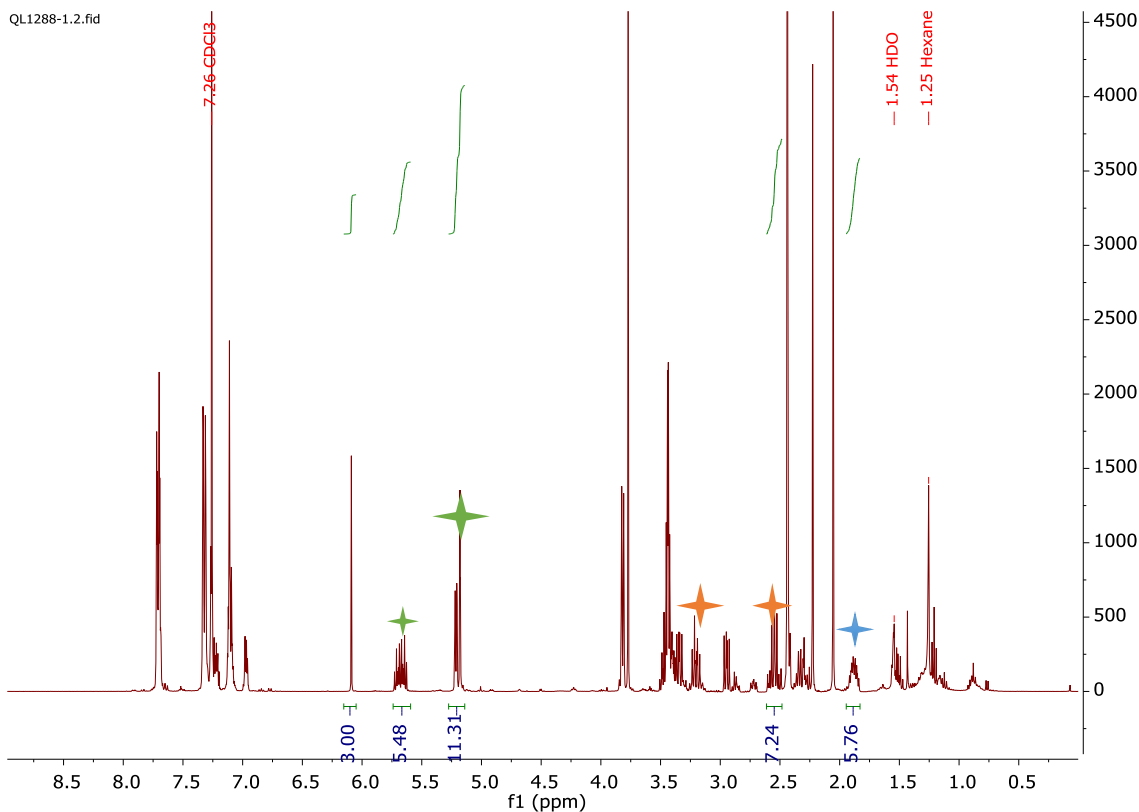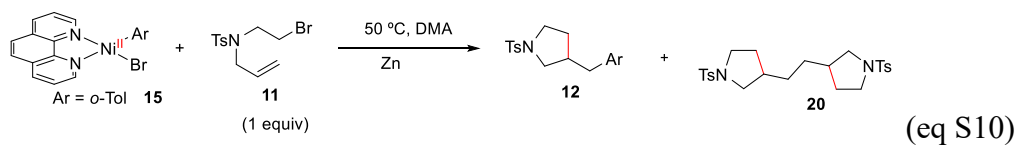
Figure S25. Crude ^{1}H NMR spectrum for the reaction shown in eq S10. Reaction conditions: [**15**] = 0.050 M; [**11**] = 0.050 M; Zn = 0.040 mmol, solvent = DMA; All **11** was consumed, **12** (✦) and **20** (✦) were observed.

5.1.4. **11** activation with reduced product (Phen)Ni (Mes) **21-a**

(eq S11)
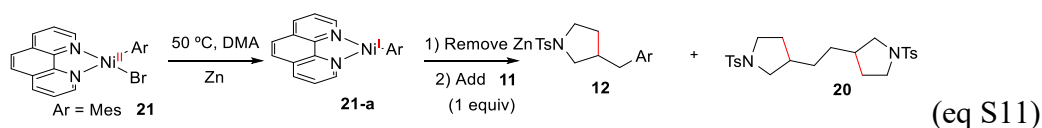
To a 2 mL crimp-top vial was added (Phen)Ni (Mes)Br **21** (8.6 mg, 0.02 mmol), ground, activated zinc (2.0 equiv.) and DMA (0.4 mL), which was then placed in a shaker heated to 50 °C, with mixing speed at 850 rpm overnight. The resulting purple-red solution was filtered with glass wool into a new 2 mL crimp-top vial, followed by adding **11** (6.4 mg, 0.02 mmol) and placed back to the shaker. After reacting overnight, the mixture was quenched with saturated ammonium chloride. The mixture was extracted by diethyl ether and the resulting organic layer was collected, washed with water twice, dried over Na$_2$SO$_4$, filtered, concentrated under N$_2$ and analyzed by ^{1}H NMR spectroscopy.
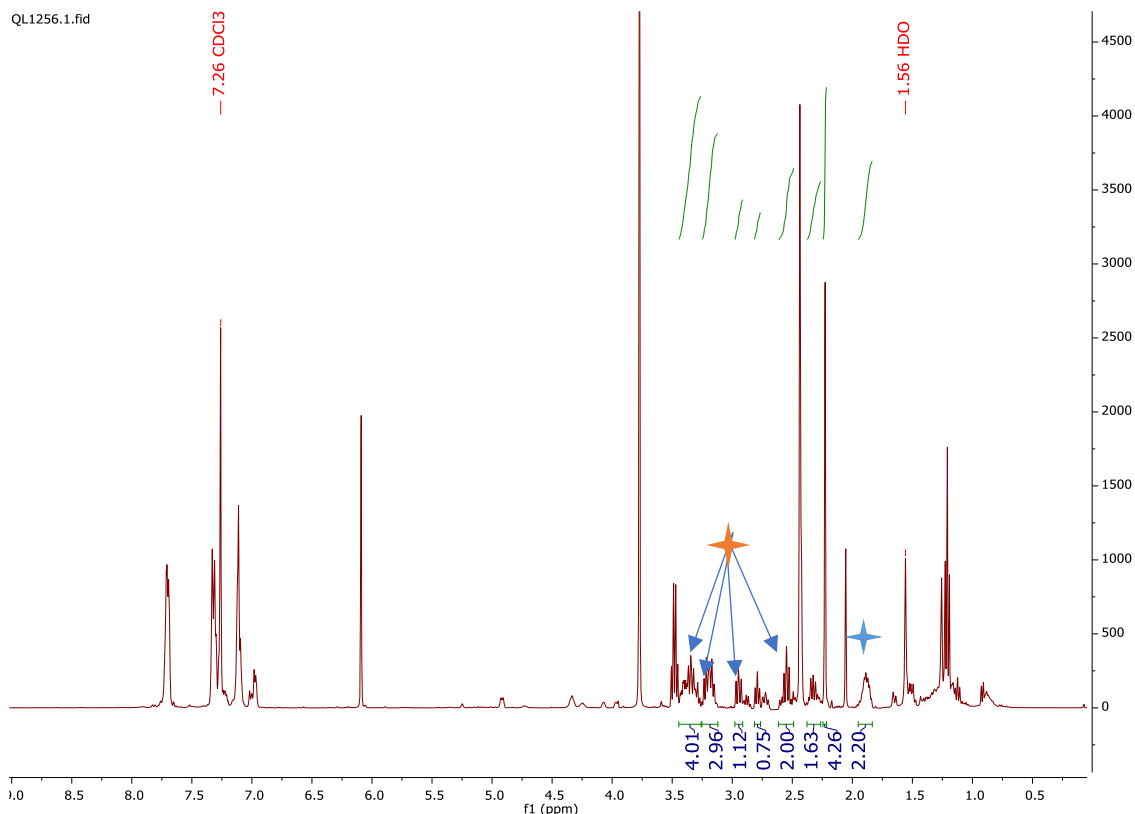
Figure S26. Crude ^{1}H NMR spectrum for the reaction shown in eq S11. Reaction conditions: [**21**] = 0.050 M; [**11**] = 0.050 M; Zn = 0.040 mmol (Filtered off before adding **11**), solvent = DMA; **11** (✦) and **20** (✦) were observed.

5.1.5. **11** activation with (Phen)Ni(Mes)Br **15** and Zn

(eq S12)
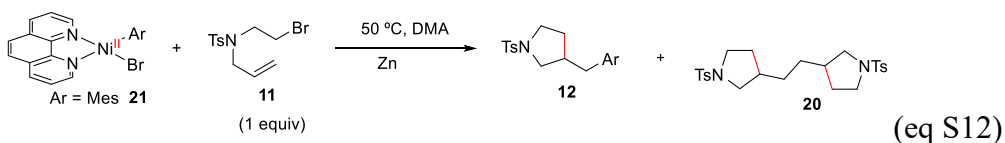
To a 2 mL crimp-top vial was added (Phen)Ni(Mes)Br (8.6 mg, 0.02 mmol), **11** (6.4 mg, 0.02 mmol), ground, activated zinc (2.0 equiv.) and DMA (0.4 mL), which was then placed in a shaker heated to 50 °C, with mixing speed at 850 rpm. After reacting overnight, the mixture was quenched with saturated ammonium chloride. The mixture was extracted by diethyl ether and the resulting organic layer was collected, washed with water twice, dried over Na$_2$SO$_4$, filtered, concentrated under N$_2$ and analyzed by ^{1}H NMR spectroscopy.
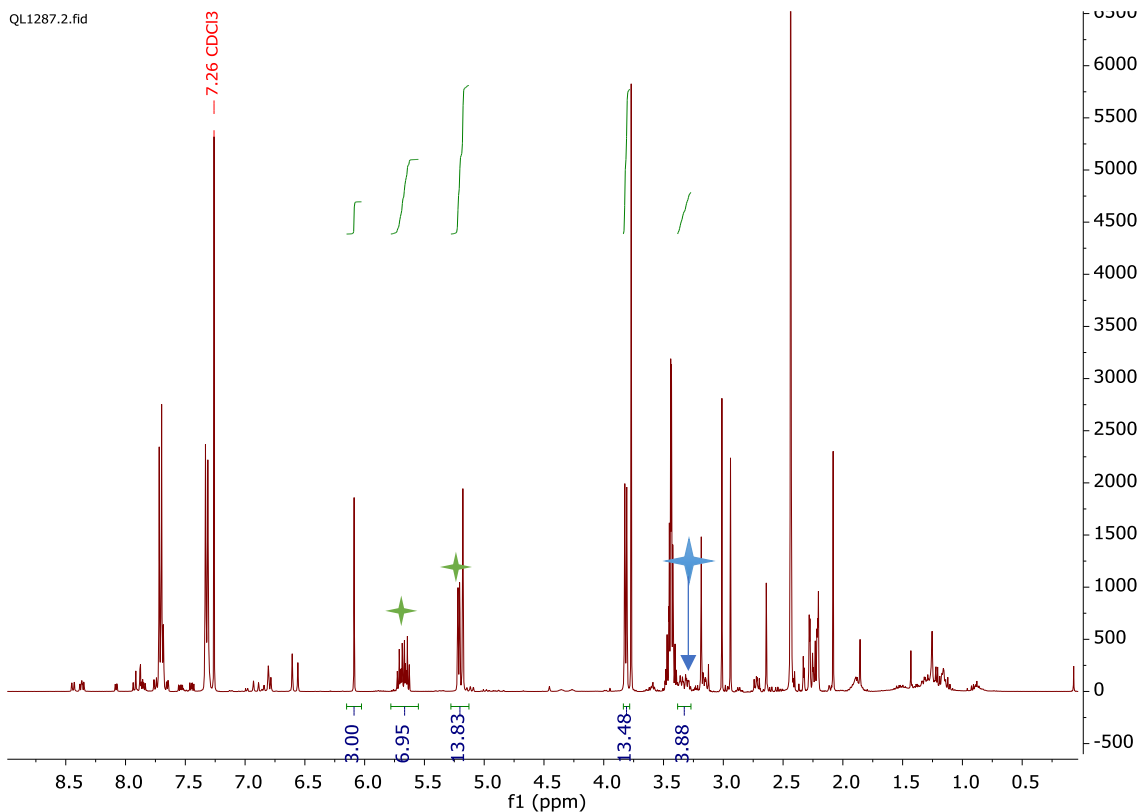
Figure S27. Crude ^{1}H NMR spectrum for the reaction shown in eq S12. Reaction conditions: [**21**] = 0.050 M; [**11**] = 0.050 M; Zn = 0.040 mmol, solvent = DMA; All **11** was consumed and corresponding **20** (✦) was observed.

5.1.6. **11** activation with (Phen)Ni (Mes)Br **21**

(eq S13)
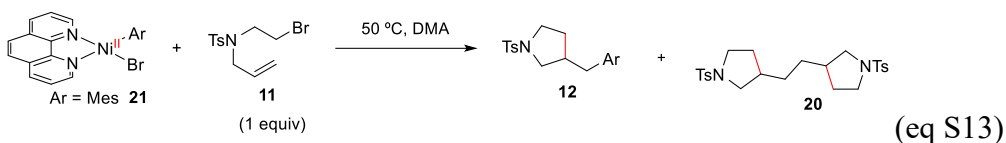
To a 2 mL crimp-top vial was added (Phen)Ni(Mes)Br (8.6 mg, 0.02 mmol), **11** (6.4 mg, 0.02 mmol) and DMA (0.4 mL), which was then placed in a shaker heated to 50 °C, with mixing speed at 850 rpm. After reacting overnight, the mixture was quenched with saturated ammonium chloride. The mixture was extracted by diethyl ether and the resulting organic layer was collected, washed with water twice, dried over Na$_2$SO$_4$, filtered, concentrated under N$_2$ and analyzed by ^{1}H NMR spectroscopy.

Figure S28. Crude ^{1}H NMR spectrum for the reaction shown in eq S13. Reaction conditions: [**21**] = 0.050 M; [**11**] = 0.050 M; solvent = DMA; **11** (✦) was remained.

5.2. Zn Activation Pathway

5.2.1. **1** activation with Zn.

10% (eq S14)
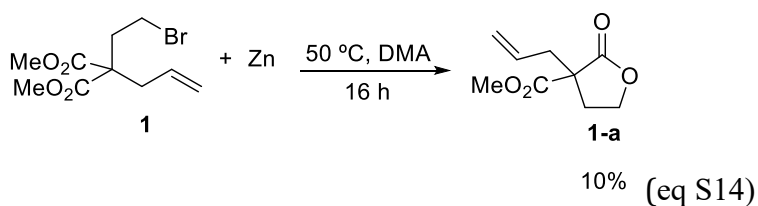
To a 2 mL crimp-top vial was added **1** (7.0 mg, 0.025 mmol), ground, activated zinc (2.0 equiv.) and DMA 0.5mL, which was then placed in a shaker heated to 50°C, with mixing speed at 850 rpm. After reacting overnight, the mixture was quenched with saturated ammonium chloride. The mixture was extracted by diethyl ether and the resulting organic layer was collected, washed with water twice, dried over Na_2SO_4, filtered, concentrated under N_2 and analyzed by ^{1}H NMR spectroscopy.
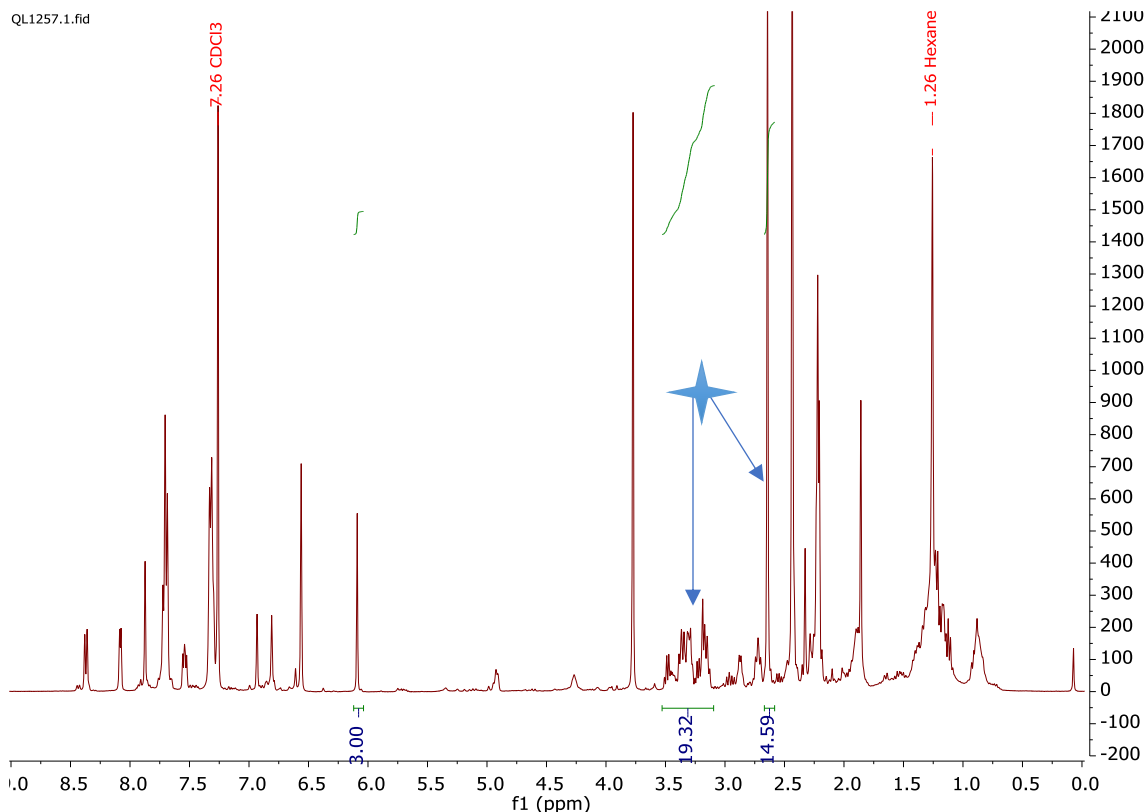
Figure S29. Crude ^{1}H NMR spectrum for the reaction shown in eq S14. Reaction conditions: [**1**] = 0.050 M; Zn = 0.050 mmol; solvent = DMA; **1** (✦) and **1-a** (✦) were observed.

5.2.2. The activation of **11** with Zn.

To a 2 mL crimp-top vial was added **11** (6.4 mg, 0.02 mmol), ground, activated zinc (2.0 equiv.) and DMA (0.4 mL), which was then placed in a shaker heated to 50 °C, with mixing speed at 850 rpm. After reacting overnight, the mixture was quenched with saturated ammonium chloride. The mixture was extracted by diethyl ether and the resulting organic layer was collected, washed with water twice, dried over Na$_2$SO$_4$, filtered, concentrated under N$_2$ and analyzed by ^{1}H NMR spectroscopy.
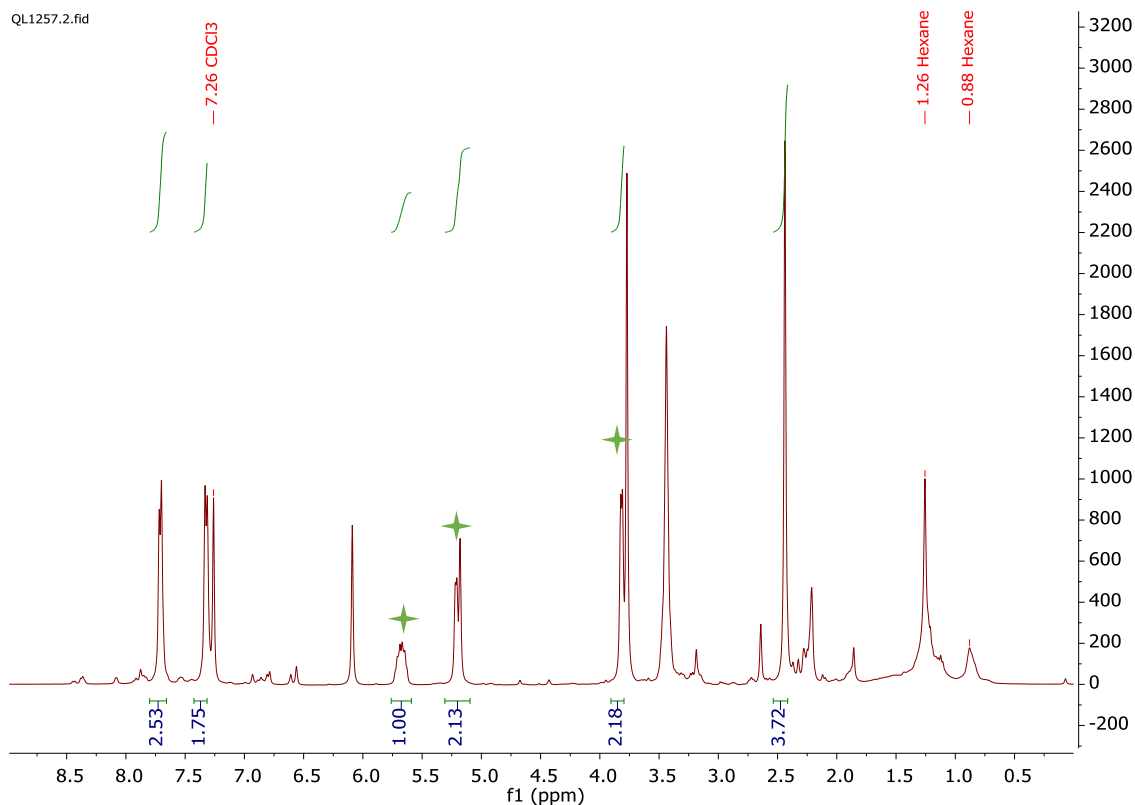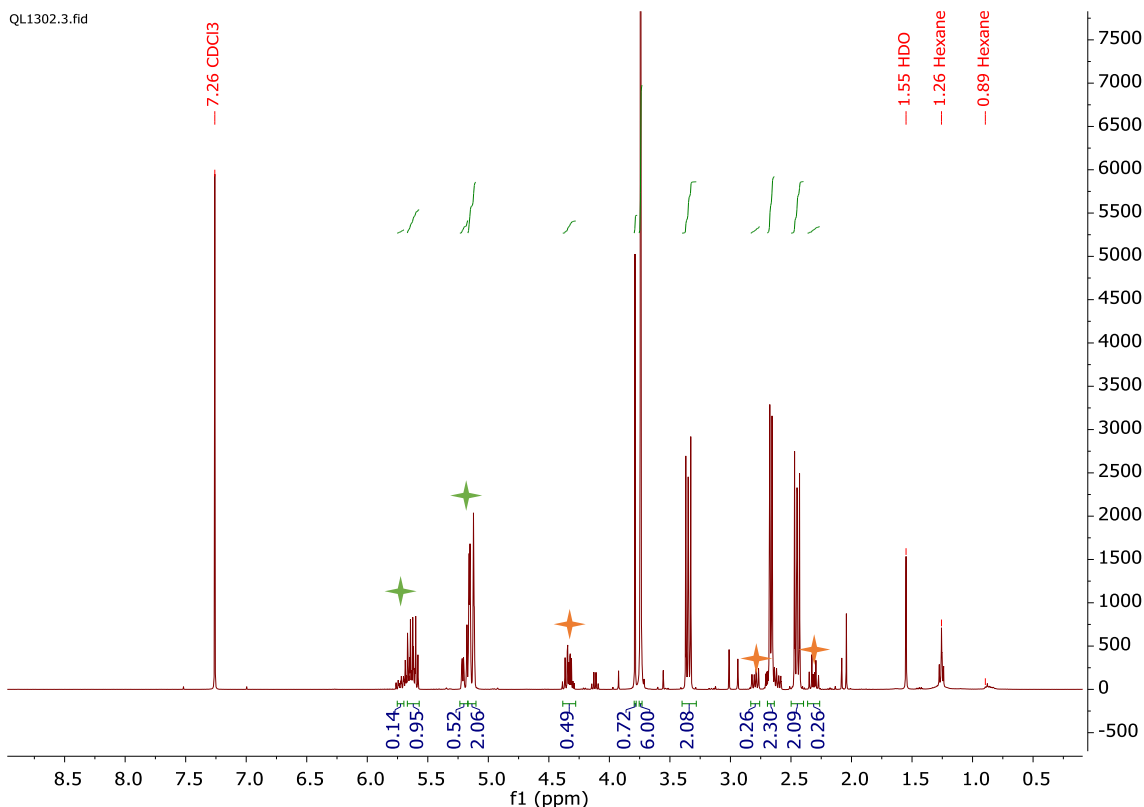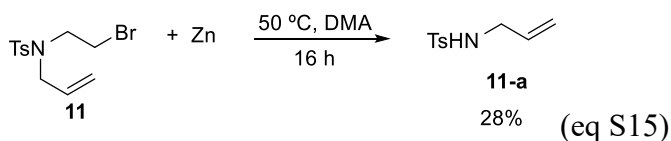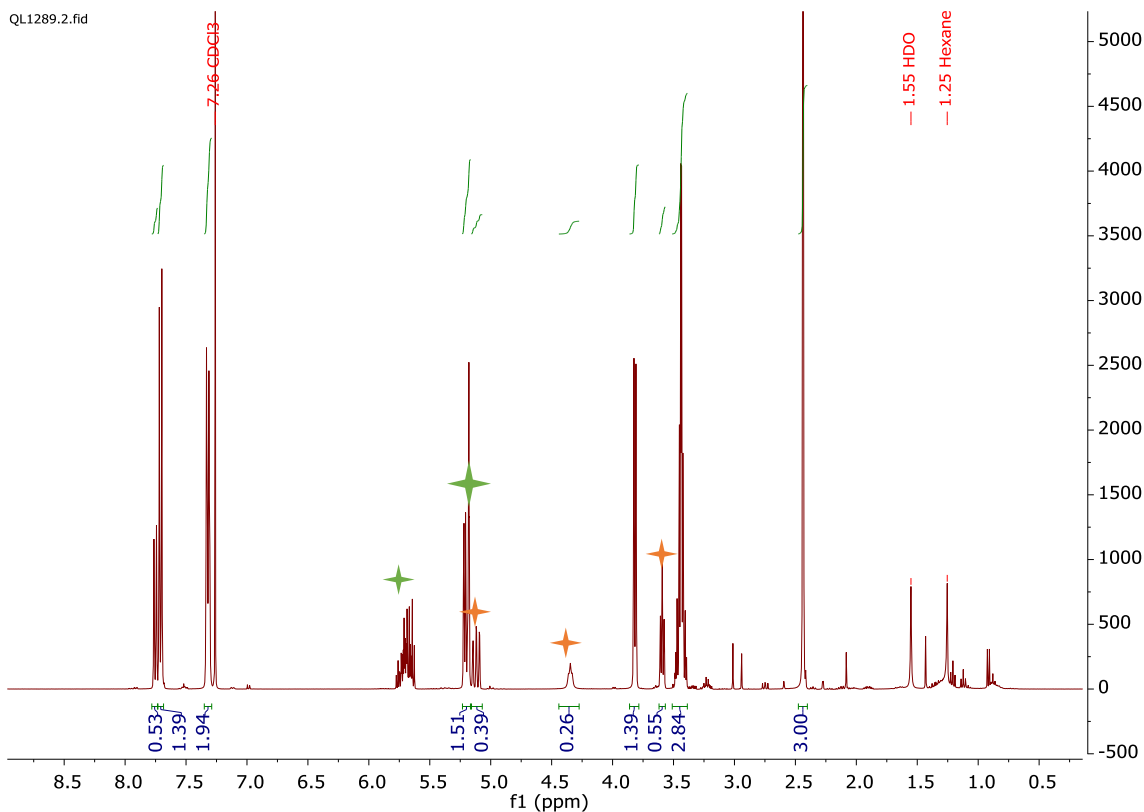
Figure S30. Crude ^{1}H NMR spectrum for the reaction shown in eq S15. Reaction conditions: [**11**] = 0.050 M; Zn = 0.040 mmol; solvent = DMA; **11** (✦) and **11-a** (✦) were observed.

6. Ni Loading Control Experiments of Radical Capture and Cyclization Rate

(eq S16)
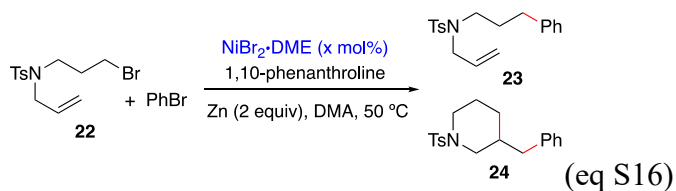
	Ni loading(mM)	23/24 Ratio	Yield of 23 (%)	Yield of 24 (%)
Trial 1	1.0	0.33	8.4	25
	2.5	0.62	13	21
	5.0	1.3	8.1	6.3
	7.5	1.4	5.9	4.1
	10	2.4	10	4.0
Trial 2	1.0	0.23	5.6	25
	2.5	0.49	13	27
	5.0	1.0	13	12

	7.5	0.80	4.9	6.2
	1.0	0.36	10	28
	2.5	0.68	18	26
Trial 3[a]	5.0	0.90	12	13
	7.5	1.6	14	8.6
	10	2.5	20	8.1

Table S3. Ratio of **23/24** and yields of **23** and **24** from three independent trials. Reaction conditions: [**23**] = 0.050 M, [PhBr] = 0.10 M, Zn = 0.10 mmol, solvent = DMA, agitation rate = 900 rpm. The yield and ratio are determined by GC analysis with 1,3,5-trimethoxybenzene as internal standard.

[a]:[PhBr] = 0.20 M.

7. Calculation of Radical Capture and Cyclization Rate

The rate for cyclization of hept-6-enyl is estimated from previous experiments in radical initiation and capture by Bu_3SnH.[1] The Thorpe-Ingold effect of tosylamine in substrate **22** is not accounted for due to the lack of available data. At steady state, [**16**] is estimated to be 0.0025 M with 0.0050 M catalyst loading, given the distribution of **16** and **14** based on NMR measurements. Eq S17 reveals that the lower limit for k_2 is 10^7 Ms^{-1}.

$$\frac{24}{23} = \frac{k_4}{k_2[Ni]} = \frac{k_4}{k_2 * 0.0025M} = 1.1 \text{ (eq S17)}.$$

$$k_2 = \frac{k_4}{0.0025M} * 1.1$$

$$k_4 > 2.7 * 10^4 \ s^{-1}$$

$$k_2 > 1.2 * 10^7 \ Ms^{-1}$$

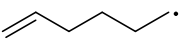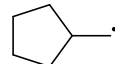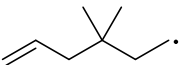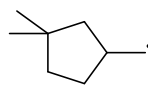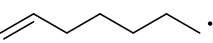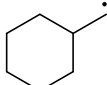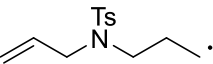The upper limit of k_2 is estimated based on lack of direct coupling product with substrate **11**. The radical cyclization rate of gem-dimethyl hexa-5-enyl is estimated to be 1.6 x $10^7 s^{-1}$. According to eq S19, the upper limit of k_2 is 6.4 x 10^9 Ms^{-1}
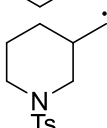
$$k_2[Ni] < k_{5-exo} \text{ (eq S18)}.$$

$$k_{5-exo} = 1.6 * 10^7 \ s^{-1}$$

$k_2 < 6.4 * 10^9 \ Ms^{-1}$ (eq S19).

Radical clock	Cyclized product	Cyclization rate $_{(50\,°C)}$ (s^{-1})
		10^6
		1.6×10^7
		2.7×10^4
		$k_4 \sim 2.7 \times 10^4$

8. Synthesis and Characterization of Radical Clock Substrates and Ni Complexes

Compound **1** and **11** were synthesized following the literature report[2].

Radical Clock Synthesis

Aldehyde **S1**:
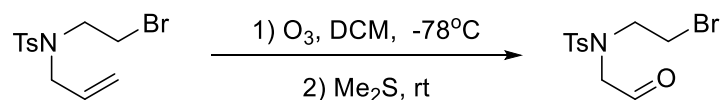
A solution of **11** in DCM (954 mg, 3 mmol, 0.2 M) was cooled to -78 °C. Ozone was allowed to bubble through the solution for 10 min until the solution became blue. After addition of excess Me$_2$S, the reaction was warmed to rt and stirred overnight. The resulting mixture was washed with water. The combined organic layers were dried over MgSO$_4$, filtered, and concentrated by rotary evaporation to afford 1.15 g (99% yield) light yellow oil, which was used without further purification.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.64 (t, J = 1.1 Hz, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.02 (d, J = 1.1 Hz, 2H), 3.60 – 3.47 (m, 4H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.5, 144.5, 135.5, 130.2, 127.5, 58.8, 51.7, 30.0, 21.7.

HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for C$_{11}$H$_{15}$NO$_3$SBr 319.9951, found 319.9948.

Radical Clock **9**:
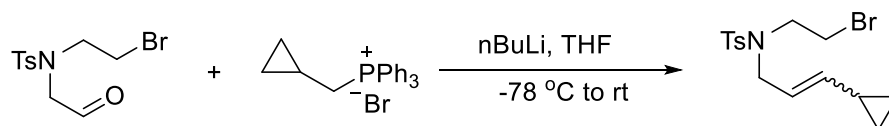
A solution of (cyclopropylmethyl)triphenylphosphonium bromide in THF (1.02 mL, 1.6 M in Hexane, 1.05 eq, synthesized based on the literature procedure[3]) was cooled to -78 °C, followed by dropwise addition of *n*BuLi. The mixture was stirred for 1 h, followed by dropwise addition of the aldehyde (1.56 mmol, 500 mg, in 3 mL THF). The resulting mixture was warmed to rt and stirred overnight. The reaction was washed with sat. NH4Cl and extracted with ethyl acetate. The combined organic layers were dried over Na2SO4, filtered, concentrated by rotary evaporation and purified by column chromatography (hexane: ethyl acetate = 20 ~ 8:1) to give 70.6 mg (13% yield) of a mixture of the *E/Z* isomers in a ratio of 1:1.6 of as a light yellow oil.

**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.71 (dd, J = 10.4, 8.3 Hz, 2H), 7.39 – 7.26 (m, 2H), 5.38 – 5.25 (dt, J = 10.5 Hz, 6.8Hz, 0.27H, *E* isomer), 5.25 – 5.02 (m, 1H), 4.93 (t, J = 10.5 Hz, 0.67H, *Z* isomer), 3.98 (dd, J = 7.3, 1.3 Hz, 1.4H, *Z* isomer), 3.74 (dd, J = 6.9, 1.2 Hz, 0.6H, *E* isomer), 3.57 – 3.30 (m, 4H), 2.43 (s, 3H), 1.52 – 1.42 (m, 0.75H*, Z* isomer), 1.39 – 1.27 (m, 0.25H, *E* isomer), 0.86 – 0.64 (m, 2H), 0.35 (ddt, J = 17.5, 6.5, 4.5 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.7, 140.5, 140.1, 136.6, 130.0, 129.9, 127.4, 127.4, 121.5, 121.3, 51.3, 49.0, 48.7, 46.1, 29.7, 29.6, 21.7, 13.5, 9.7, 7.4, 7.0.

HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for C15H21NO2SBr 358.0471, found 358.0454.

Radical Clock Experiment:
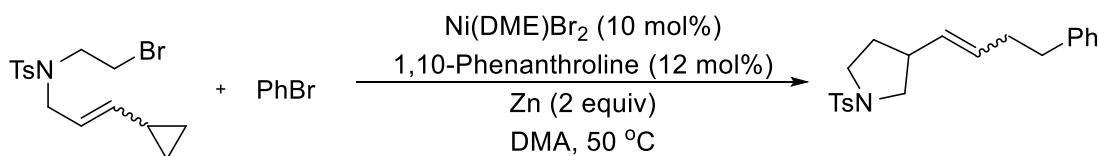
The reaction was set up in accordance with the standard procedure[3].

The mixture was quenched with sat. NH4Cl, and extracted by diethyl ether twice and the resulting organic layer was collected, washed with brine, dried over Na2SO4, filtered and concentrated by rotary evaporation and purified by column chromatography (hexane: ethyl acetate = 20 ~ 10:1). Colorless oil was collected. 84% yield (NMR) and *E/Z* isomer ratio is 2:1 (GC)

E isomer:

¹H NMR (400 MHz, Chloroform-*d*): δ 7.78 – 7.67 (m, 2H), 7.39 – 7.25 (m, 4H), 7.25 – 7.15 (m, 1H), 7.21 – 7.10 (m, 2H), 5.46 (dtd, J = 15.4, 6.7, 1.0 Hz, 1H), 5.29 – 5.04 (m, 1H), 3.55 – 3.10 (m, 3H), 2.88 (dd, J = 9.9, 8.2f Hz, 1H), 2.87 – 2.55 (m, 3H), 2.45 (s, 3H), 2.37 – 2.20 (m, 2H), 1.92 (dtd, J = 13.5, 6.8, 3.8 Hz, 1H), 1.57 – 1.32 (m, 1H).

¹³C NMR (101 MHz, Chloroform-*d*, 25 °C): δ 143.45, 141.76, 134.15, 131.14, 130.08, 129.76, 128.57, 128.41, 127.68, 125.99, 53.10, 47.61, 41.73, 35.80, 34.32, 32.13, 21.67.

Z isomer:

¹H NMR (400 MHz, Chloroform-*d*): δ 7.69 (d, J = 8.3 Hz, 2H), 7.36 – 7.27 (m, 4H), 7.22 – 7.16 (m, 1H), 7.15 – 7.10 (m, 2H), 5.41 (dtd, J = 10.7, 7.5, 1.0 Hz, 1H), 5.08 (dd, J = 10.7, 9.0 Hz, 1H), 3.36 – 3.24 (m, 2H), 3.17 (ddd, J = 9.9, 9.0, 7.1 Hz, 1H), 2.81 – 2.73 (m, 1H), 2.70 (dd, J = 9.4, 8.5 Hz, 1H), 2.61 (q, J = 7.3 Hz, 2H), 2.43 (s, 3H), 2.29 (qd, J = 7.4, 1.5 Hz, 1H), 1.73 (dtd, J = 13.0, 6.8, 3.4 Hz, 1H), 1.38 (dt, J = 12.4, 8.8 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 143.47, 141.60, 134.09, 130.96, 129.91, 128.63, 128.44, 127.21, 126.14, 116.97, 66.00, 53.18, 47.71, 36.88, 35.89, 32.38, 29.66.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{24}NO_2S$ 356.1684 and 357.1718, found 356.1685 and 357.1711.

Alcohol **S2**:
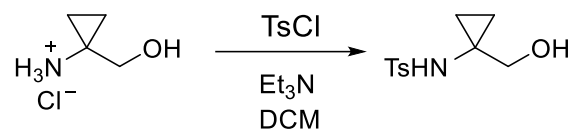
To a solution of amine (185.4 g, 1.5 mmol, 1 equiv.) and toluenesulfonyl chloride (314.6 g, 1.1 equiv.) in DCM (3 mL, 0.45 M) at 0°C was added triethylamine (1.04 mL, 7.5 mmol, 5 equiv.). The reaction mixture was warmed to ambient temperature and stirred for 24 hours. The reaction was quenched with $NaHCO_3$ solution and washed with H_2O. The aqueous layer was extracted with CH_2Cl_2 (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product, sulfonamide (306.8 mg, 85% yield), was used in the next step without further purification.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H),

5.20 (bs, 1H), 3.43 (d, J = 6.0 Hz, 2H), 2.44 (s, 3H), 0.84 – 0.74 (m, 2H), 0.64 (t, J = 3.6 Hz, 2H).

Allylamine **S3**:
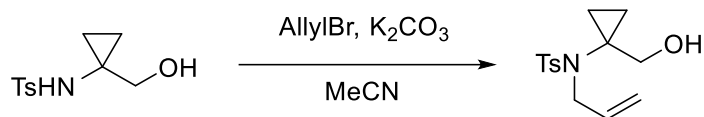
To a solution of sulfonamide (96.2 mg, 0.32 mmol) in MeCN (0.5 M) was added allyl bromide (5 equiv.), K_2CO_3 (5 equiv.). The reaction mixture was heated to reflux and stirred for 16 hours. The reaction was quenched with the NH_4Cl solution and the aqueous layer was extracted with DCM (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography (Hexane: ethyl acetate 1:1). **S3** was obtained as a colorless oil (78.6 mg, 85%)

1H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.67 (m, 2H), 7.33 – 7.24 (m, 2H), 5.89 (ddtd, J = 16.7, 10.1, 6.3, 1.5 Hz, 1H), 5.25 – 5.10 (m, 2H), 3.98 (dq, J = 6.4, 1.5 Hz, 2H), 3.59 (d, J = 5.8 Hz, 2H), 2.76 (td, J = 5.9, 1.8 Hz, 1H), 2.43(s, 3H), 0.95 – 0.76 (m, 4H). HRMS (ESI-TOF) m/z: $[M+H-H_2O]^+$ calcd for $C_{14}H_{18}NO_2S$ 264.1053, found 264.1056.

Radical Clock **7**:
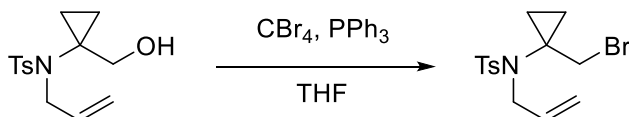
To a solution of triphenylphosphine (3 equiv.) in THF (0.25 M) at 0°C was added CBr_4 (3 equiv.). This solution was stirred at 0 °C for 5 minutes until the solution transforms into a bright yellow color. The solution of the alcohol (298.1mg, 1.1mmol) in THF (5 mL) was then added dropwise. The reaction mixture was warmed to ambient temperature and was stirred for 16 hours. After quenching with H_2O, the aqueous layer was extracted with ethyl acetate (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography (hexane: ethyl acetate = 20 ~ 10:1) to afford **7** as a white solid (308.6 mg, 84%)

1H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.67 (m, 2H), 7.29 (d, J = 8.0 Hz, 2H), 5.86

– 5.73 (m, 1H), 5.18 – 5.03 (m, 2H), 4.11 (dt, J = 6.0, 1.6 Hz, 2H), 3.62 (bs, 1H), 2.43 (s, 3H), 1.29 (bs, 2H), 0.96 (bs, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.7, 138.3, 135.8, 129.8, 127.7, 117.3, 53.3, 42.3, 41.6, 32.7, 21.7.

HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $C_{14}H_{19}NO_2SBr$ 344.0320 and 346.0299, found 344.0318 and 346.0293.
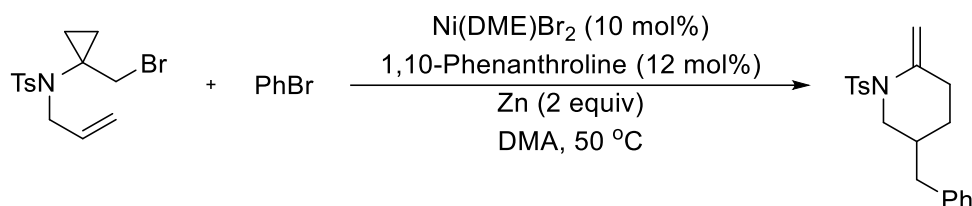
The reaction was set up based on the standard procedure[2]. The product **8** was purified by column chromatography (hexane: ethyl acetate = 20 ~ 10:1). Colorless oil was collected. 48% yield (NMR).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.61 (m, 2H), 7.34 – 7.13 (m, 5H), 7.13 – 7.04 (m, 2H), 5.03 (d, J = 1.5 Hz, 1H), 4.81 (d, J = 1.8 Hz, 1H), 4.05 (ddd, J = 13.2, 4.0, 2.1 Hz, 1H), 2.84 (dd, J = 13.1, 10.6 Hz, 1H), 2.52 (dd, J = 13.6, 6.8 Hz, 1H), 2.43 (s, 3H), 2.40 (dd, J = 13.6, 6.8 Hz, 1H), 2.16 (dt, J = 13.8, 4.0 Hz, 1H), 1.86 (dddd, J = 13.8, 12.1, 4.7, 1.7 Hz, 1H), 1.68 (dddq, J = 18.3, 11.0, 7.5, 3.9 Hz, 2H), 1.32 – 1.12 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.4, 142.8, 139.2, 129.7, 129.1, 128.6, 127.4, 126.5, 108.6, 52.6, 39.9, 36.6, 31.1, 29.9, 21.7.
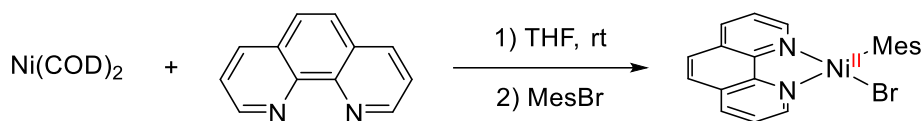
HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $C_{20}H_{24}NO_2S$ 342.1521, found 342.1524.

Complex (Phen)NiBr$_2$ **14** was synthesized by literature report.[4]

^{1}H NMR (500 MHz, DMSO-*d$_6$*) δ 48.83 (bs, 2H), 45.77(bs, 2H), 25.28 (bs, 2H), 23.52 (bs, 2H), 19.86 – 16.77 (m, 4H).

UV-Vis (DMSO, 23 °C): 635 nm (3.3 M^{-1}cm^{-1})

Complex (Phen)Ni (Mes)Br **21** was synthesized followed by modified literature report.[5]

To a 20 mL scintillation vial was added phenanthroline (36 mg, 0.2 mmol), Ni(cod)$_2$ (55 mg, 0.2 mmol) and THF (8 mL). MesBr (47.8 mg, 1.2 equiv.) was added the next day after stirring the reaction mixture at room temperature overnight. After stirring at room temperature overnight an additional day, the solution changed from dark purple to red and was then concentrated under reduced pressure. The solid was washed several times with dry n-pentane and then dried under vacuum for 2 hrs to give complex **21** (60 mg, 69% yield) as a red solid. ^{1}H NMR matched the literature report[6].

Complex (Phen)Ni (*o*-Tol)Br **15**

Following the same procedure reported for (Phen)Ni(Mes)Br, using (*o*-Tol)Br in place of MesBr, complex **15** was afforded (64.1 mg, 78%) as a red solid.

^{1}H NMR (500 MHz, Acetone-d_6) δ 9.61 (dd, J = 5.1, 1.5 Hz, 1H), 8.93 – 8.63 (m, 2H), 8.27 – 8.11 (m, 2H), 8.06 (dd, J = 8.2, 5.0 Hz, 1H), 7.80 – 7.64 (m, 1H), 7.60 (dd, J = 7.3, 1.4 Hz, 1H), 7.43 (dd, J = 5.4, 1.4 Hz, 1H), 6.95 – 6.61 (m, 4H), 3.06 (s, 3H).

^{1}H NMR (500 MHz, DMA-d_9) δ 9.5 (d, J = 4.7 Hz, 1H), 8.8 (dd, J = 19.5, 8.0 Hz, 2H), 8.2 (q, J = 8.8 Hz, 2H), 8.1 (dd, J = 8.1, 4.8 Hz, 1H), 7.8 – 7.7 (m, 1H), 7.5 (d, J = 7.2 Hz, 1H), 7.3 (d, J = 4.9 Hz, 1H), 6.7 – 6.6 (m, 3H), 3.0 (s, 3H).

UV-Vis (THF, 23 °C): 532 nm (shoulder, 2164.5 M^{-1}cm^{-1}); 487 nm (3304.1 M^{-1}cm^{-1}); 451 nm (shoulder, 2835.6 M^{-1}cm^{-1}).

Complex (Phen)Ni(Ph)Br **16**

Following the same procedure reported for (Phen)Ni(Mes)Br, except for a shortened stirring time (5 min) following the addition of PhBr, complex **16** was afforded (54.1mg, 68%) as a red solid.
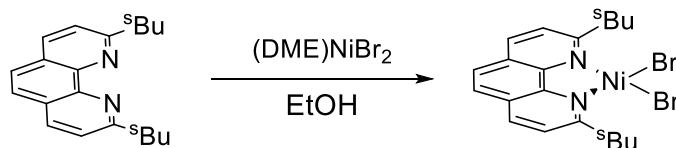
NMR shows PhBr residue due to low stability of **16** in solution.

^{1}H NMR (500 MHz, Acetone-d_6) δ 9.61 (s, 1H), 8.78 (m, 2H), 8.19 (d, J = 7.6 Hz, 2H), 8.05 (s, 1H), 7.74 (s, 1H), 7.58 (d, J = 7.2 Hz, 3H), 6.92 (t, J = 7.3 Hz, 2H), 6.78 (t, J = 7.3 Hz, 1H).

UV-Vis (DMA, 23 °C): 510 nm (shoulder); 466 nm (shoulder); 401 nm.

phen* was synthesized following the literature report[7].

Complex (phen*)NiBr₂ **17** was synthesized following a modified literature procedure[8].

To a stirred solution of (s-Bu)₂Phen (160 mg, 0.60 mmol) in EtOH (5 mL) was added NiBr₂(DME) (572 mg, 1.8 mmol) at room temperature. After stirring for overnight at room temperature, the purple solid was collected after filtration and washed with Et₂O. The solid was dissolved in CH₃CN and heated to reflux. After cooling to room temperature, crystallization in the fridge overnight gave grape-purple crystals.
The crystals were filtered and washed with Et₂O and dried under reduced pressure for overnight to afford **17** (167 mg, 54%) as a purple crystal.
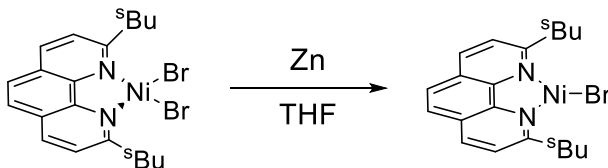
¹H NMR (500 MHz, Acetone-d_6) δ 80.93 (s, 2H), 50.06 – 40.10 (bs, 1H), 27.00 (s, 2H), 25.73 (s, 2H), 14.11 (s, 1H), 13.92 (s, 1H), 12.59 (s, 1H), 12.43 (s, 1H), 11.01 (s, 3H), 10.80 (s, 3H), 2.85 (s, 3H), 2.57 (s, 3H).

UV-Vis (Acetone, 23 °C): 520 nm (237.4 M^{-1} cm^{-1})

HRMS (ESI-TOF) m/z: [M-Br]$^+$ calcd for $C_{20}H_{24}N_2NiBr$ 429.0476 and 431.0456, found 429.0492 and 431.0499.

Elemental Analysis: C : 47.23 % H : 4.55 % N : 5.48 %

Complex (phen*)NiBr **18**:

To a 20 mL vial was added (phen*)NiBr₂ (10.4 mg, 0.02 mmol), zinc (50.0 equiv.) and THF (2 mL). The reaction was allowed to stir for 2 hrs at r.t. The resulting dark blue solution was filtered with glass wool, concentrated, extracted with Et₂O, washed with pentane and dried under vacuum, to yield **18** ((8.5 mg, 98%) as a black solid.
The X-ray quality crystals were obtained by cooling the acetone solution at -35ºC for 3 days.
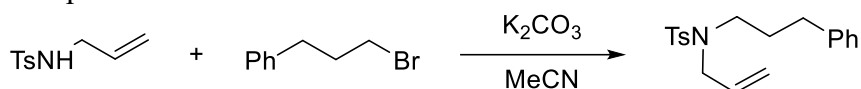
¹H NMR (500 MHz, Acetone-d_6) δ 37.64 – 33.94 (m, 2H), 26.43 – 23.01 (m, 2H), 11.64

(s, 2H), 3.87 – 3.07 (m, 2H), 2.01 – 1.59 (m, 6H), 0.57 – -0.57 (m, 10H), -17.46 – -24.55 (m, 2H).

UV-Vis (THF, 23 °C): 663 nm; 603 nm(shoulder); 474 nm(shoulder); 434 nm;

Evan's Method (C_6D_6) μ_{eff} = 1.87 μB

Compound **23**:

To a solution of sulfonamide (689.3 mg, 3.11 mmol) in MeCN (0.5 M) was added 1-Bromo-3-phenylpropane (1 equiv.), K_2CO_3 (3 equiv.). The reaction mixture was heated to reflux and stirred for 16 hours. The reaction mixture was filtered and concentrated. The crude product was purified by flash chromatography (Hexane: ethyl acetate 20-5:1). **23** was obtained as a colorless oil (607.2 mg, 59%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.64 (m, 2H), 7.32 – 7.24 (m, 4H), 7.23 – 7.09 (m, 3H), 5.63 (ddt, J = 16.7, 9.9, 6.4 Hz, 1H), 5.18 – 5.02 (m, 2H), 3.78 (dt, J = 6.6, 1.4 Hz, 2H), 3.24 – 3.03 (m, 2H), 2.59 (t, J = 7.8 Hz, 2H), 2.42 (s, 3H), 1.84 (tt, J = 9.0, 6.7 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.3, 141.5, 137.2, 133.4, 129.8, 128.5, 128.5, 127.3, 126.1, 118.9, 50.9, 47.1, 33.0, 29.9, 21.7.

9. Crystallographic data for Ni(phen*)Br 18
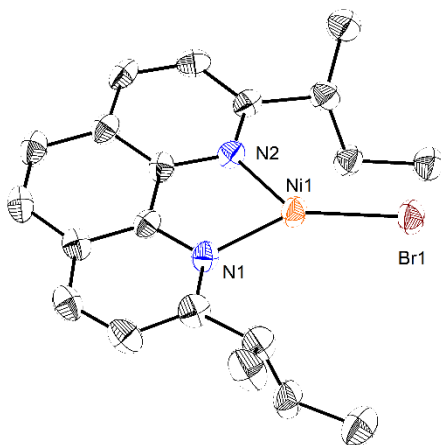
Formula: $C_{20}H_{24}BrN_2Ni$, M_r = 431.02, black needle, 0.030mm x 0.070mm x 0.360 mm, space group P 1 21/n 1, a = 7.7077(11) Å, b = 19.398(3) Å, c = 12.6503(19) Å, α = 90°, β

$= 106.8787(18)°$, $\gamma = 90°$, $V = 1809.9(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.582$ g/cm^3, $\mu = 3.283$ mm^{-1}, $F(000) = 884$, $T = 100(2)$ K, $R^1 = 0.0465$, $wR^2 = 0.0969$, 3201 independent reflections.

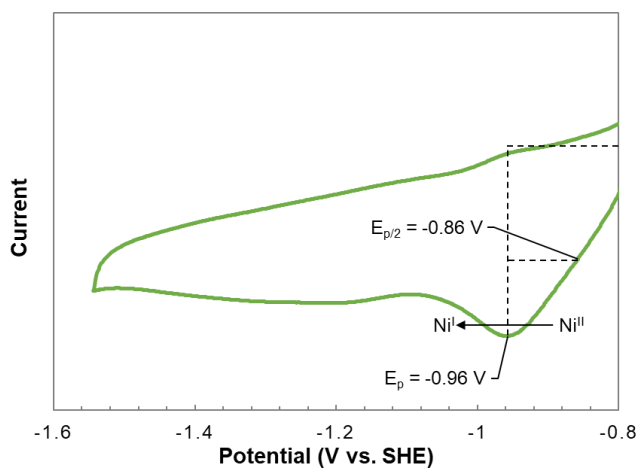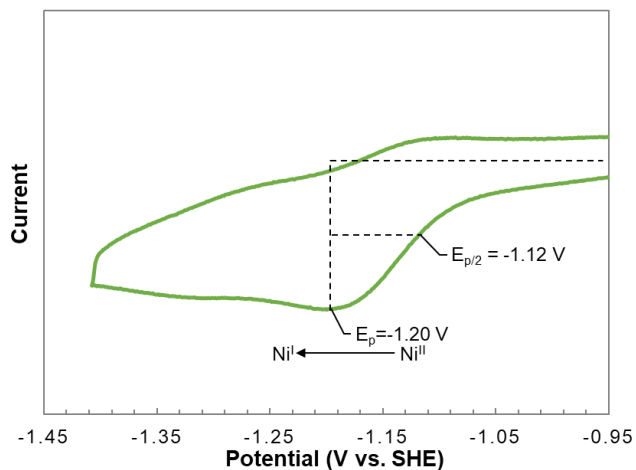## 10. Electrochemical Analysis

(Phen)NiBr$_2$ **14**:

Figure S31. Cyclic voltammetry (CV) of (Phen)NiBr$_2$ **14**. Solvent = DMA, temperature = 25 °C, concentration = 1 – 2 mM. Fc was added as the internal standard. Electrolyte = NBu$_4$Br (0.4 M), scan rate = 650 mV/s. Ni^{II}/Ni^I $E_{p/2}$ = –0.86 V vs. SHE

(Phen)Ni (*o*-Tol)Br **15**:

Figure S32. Cyclic voltammetry (CV) of (Phen)Ni (*o*-Tol)Br **15**. Solvent = DMA, temperature = 25 °C, concentration = 1 – 2 mM. Fc was added as the internal standard. Electrolyte = NBu$_4$Br (0.4 M), scan rate = 650 mV/s. Ni^{II}/Ni^I $E_{P/2}$ = –1.12 V vs. SHE
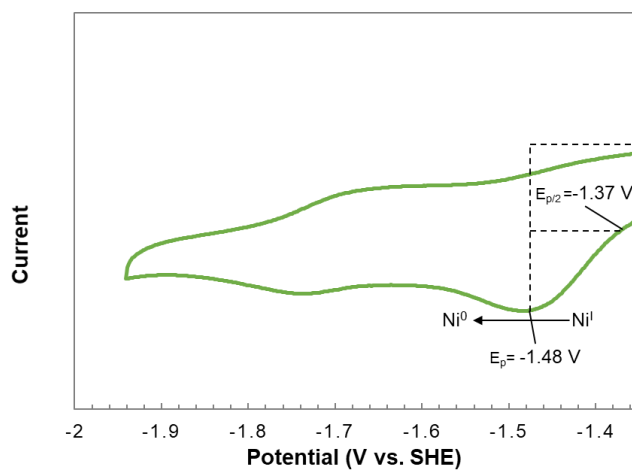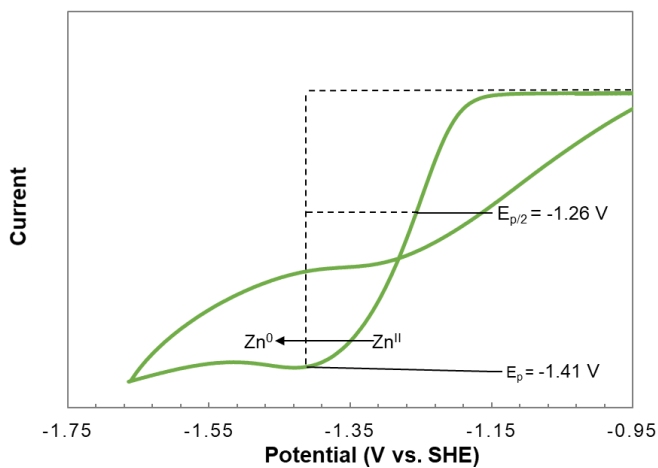
Ni(phen*)Br$_2$ **17** :
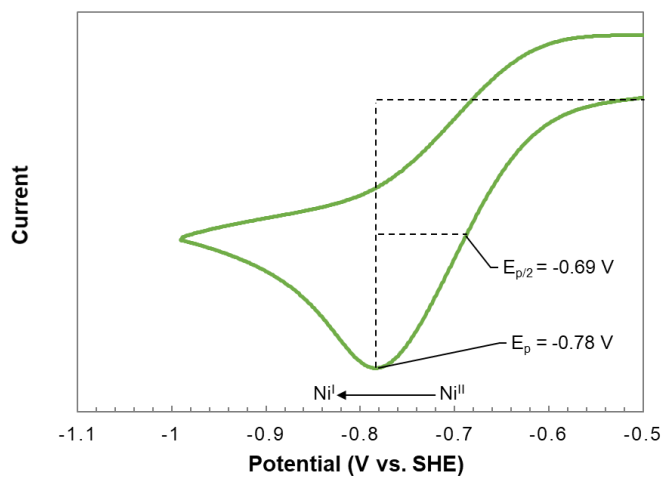
Figure S33. Cyclic voltammetry (CV) of Ni(phen*)Br$_2$ **17**. Solvent = THF, temperature = 25 °C, concentration = 1 mM. Fc was added as the internal standard. Electrolyte = NBu$_4$PF$_6$ (0.4 M), scan rate = 50 mV/s. Ni^{II}/Ni^{I} E$_{P/2}$ = –0.69 V vs. SHE

Ni(phen*)Br **18**:

Figure S34. Cyclic voltammetry (CV) of Ni(phen*)Br **18**. Solvent = THF, temperature = 25 °C, concentration = 1 mM. Fc was added as the internal standard. Electrolyte = NBu$_4$PF$_6$ (0.4 M), scan rate = 50 mV/s. Ni^{I}/Ni^{0} E$_{P/2}$ = –1.37 V vs. SHE

ZnBr₂:
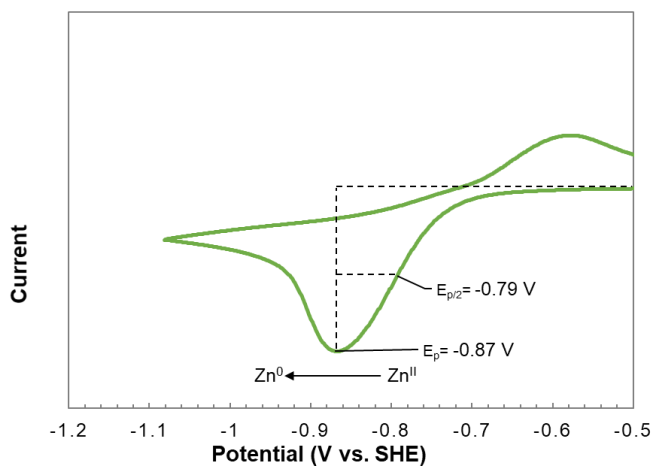
Figure S35. Cyclic voltammetry (CV) of ZnBr$_2$. Solvent = THF, temperature = 25 °C, concentration = 1 mM. Fc was added as the internal standard. Electrolyte = NBu$_4$PF$_6$ (0.4 M), scan rate = 50 mV/s Zn^{II}/Zn^0 E$_{P/2}$ = –0.79 V vs. SHE

Figure S36. Cyclic voltammetry (CV) of ZnBr$_2$. Solvent = DMA, temperature = 25 °C, concentration = 1 – 2 mM. Fc was added as the internal standard. Electrolyte = NBu$_4$BF$_4$ (0.4 M), scan rate = 120 mV/s. Zn^{II}/Zn^0 E$_{P/2}$ = –1.26 V vs. SHE

11. NMR Spectra
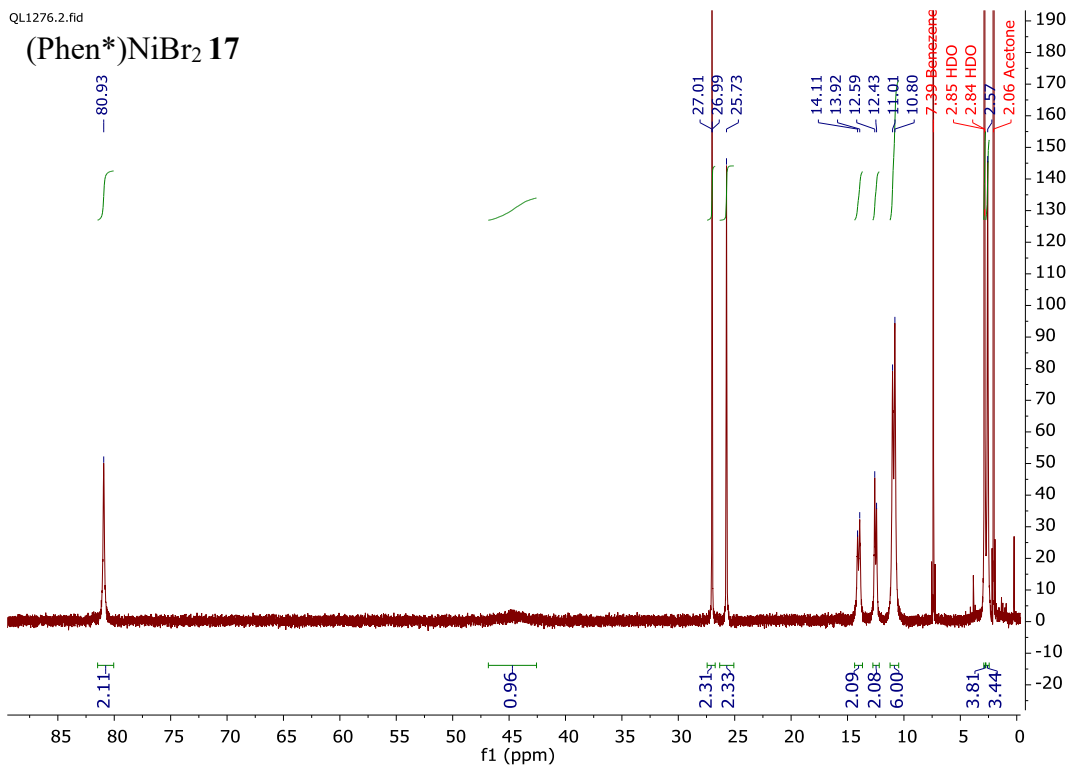
Figure S37. (Phen*)NiBr$_2$ **17** in Acetone-d_6. Probe temperature = 25 °C.
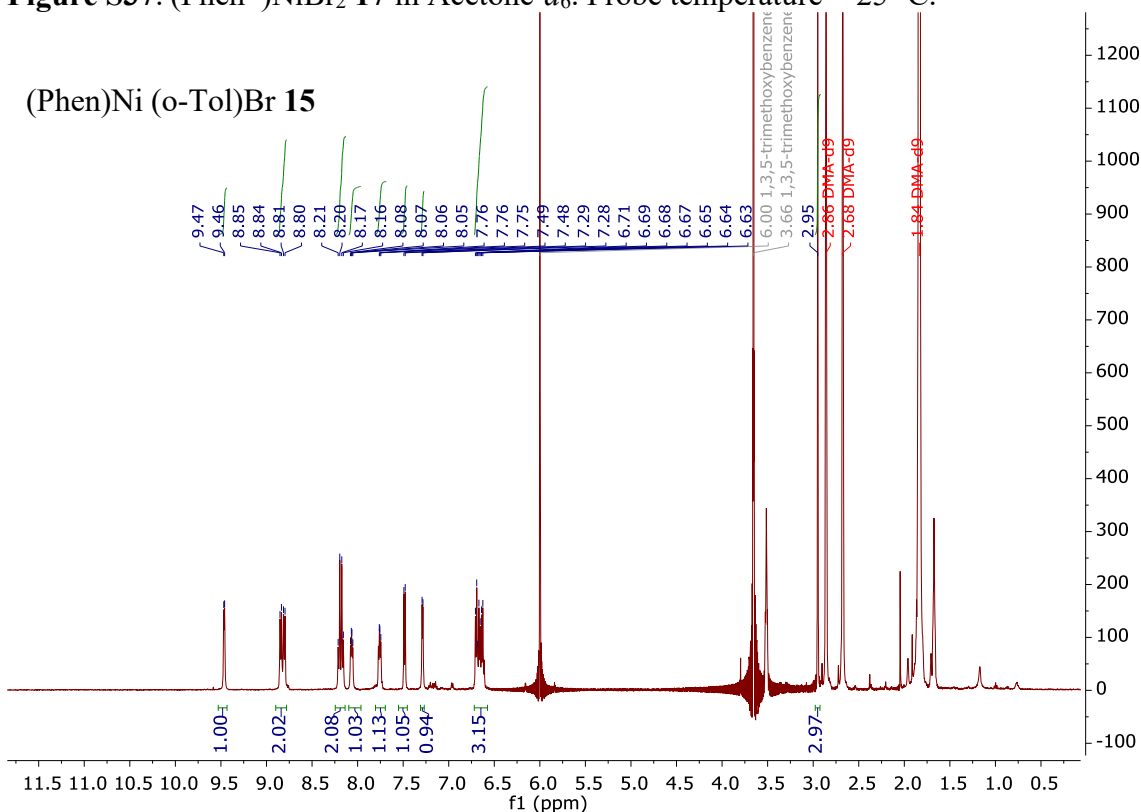
Figure S38. (Phen)Ni (o-Tol)Br **15** in DMA-d_9. Probe temperature = 25 °C.
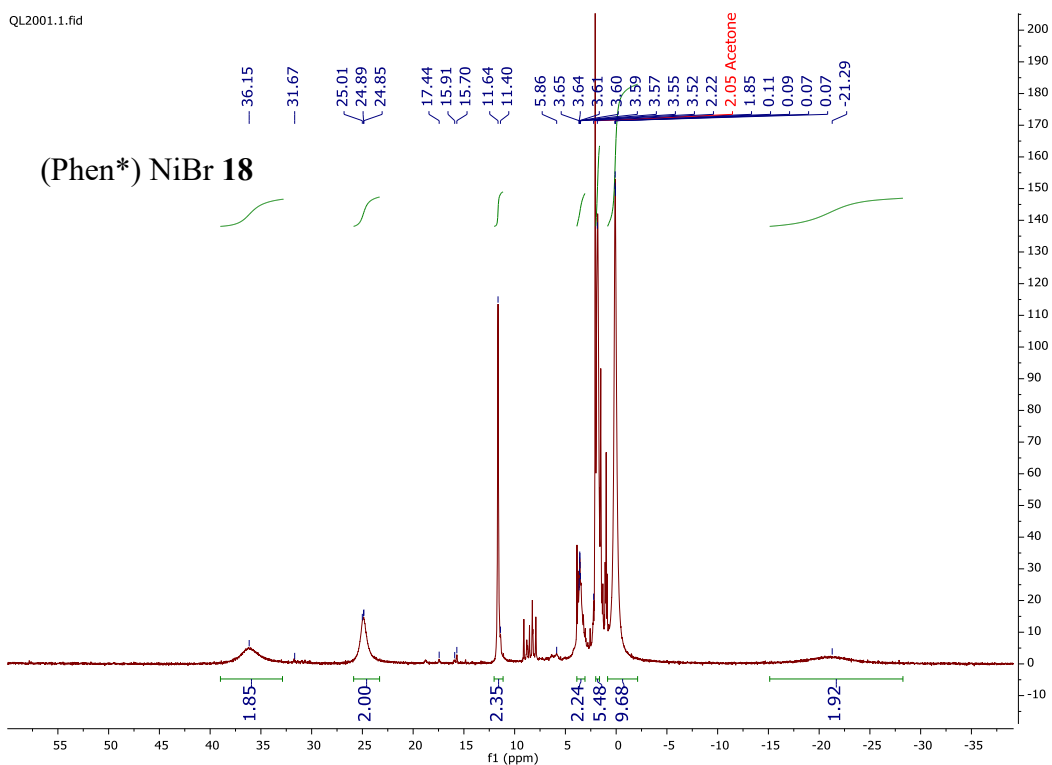
Figure S39. (Phen*)NiBr **18** in Acetone-d_6. Probe temperature = 25 °C.
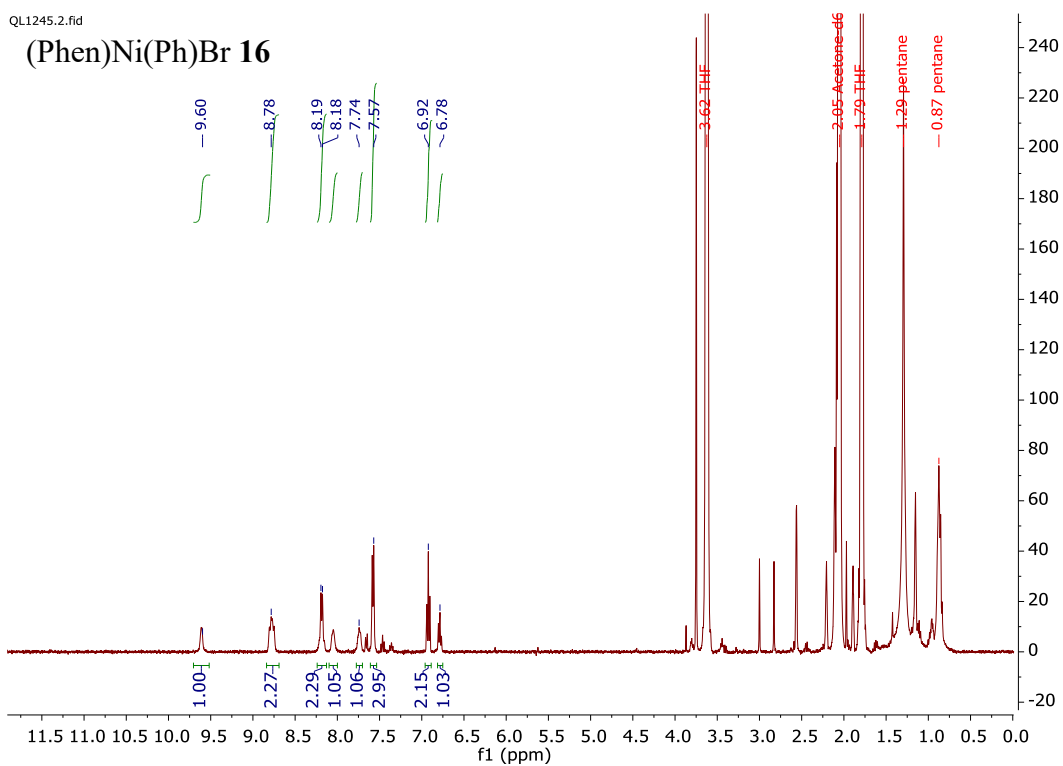

Figure S40. (Phen)Ni(Ph)Br **16** in Acetone-d_6. Probe temperature = 25 °C.

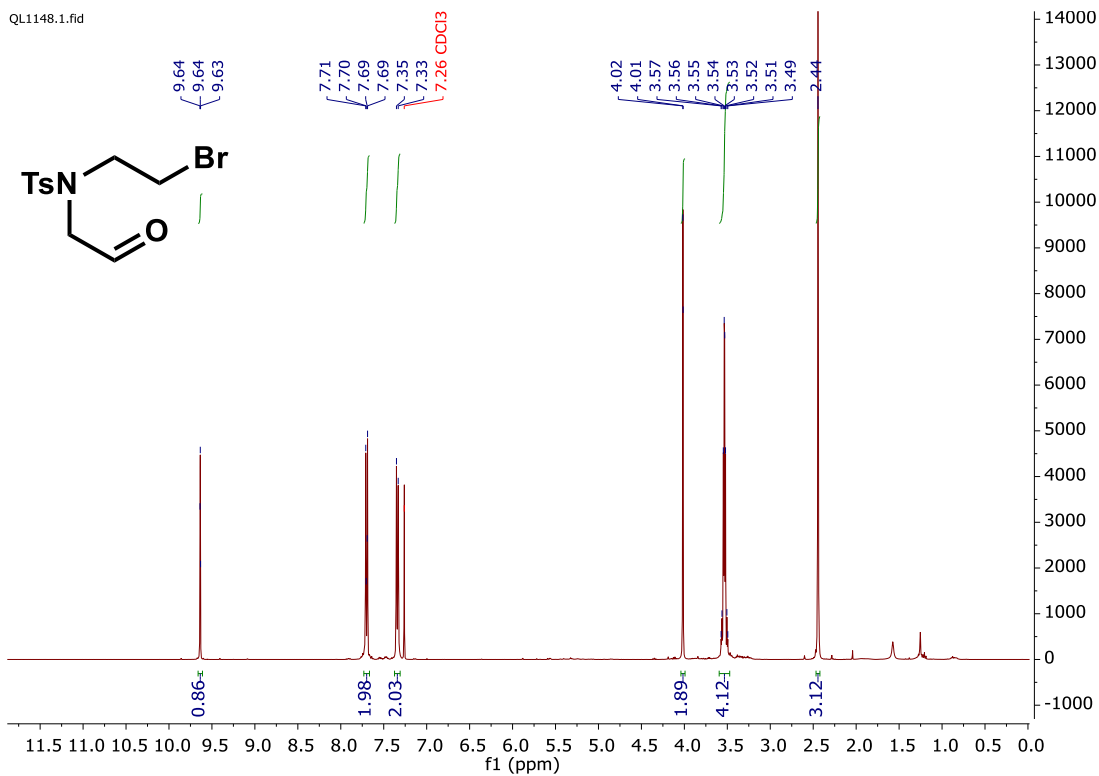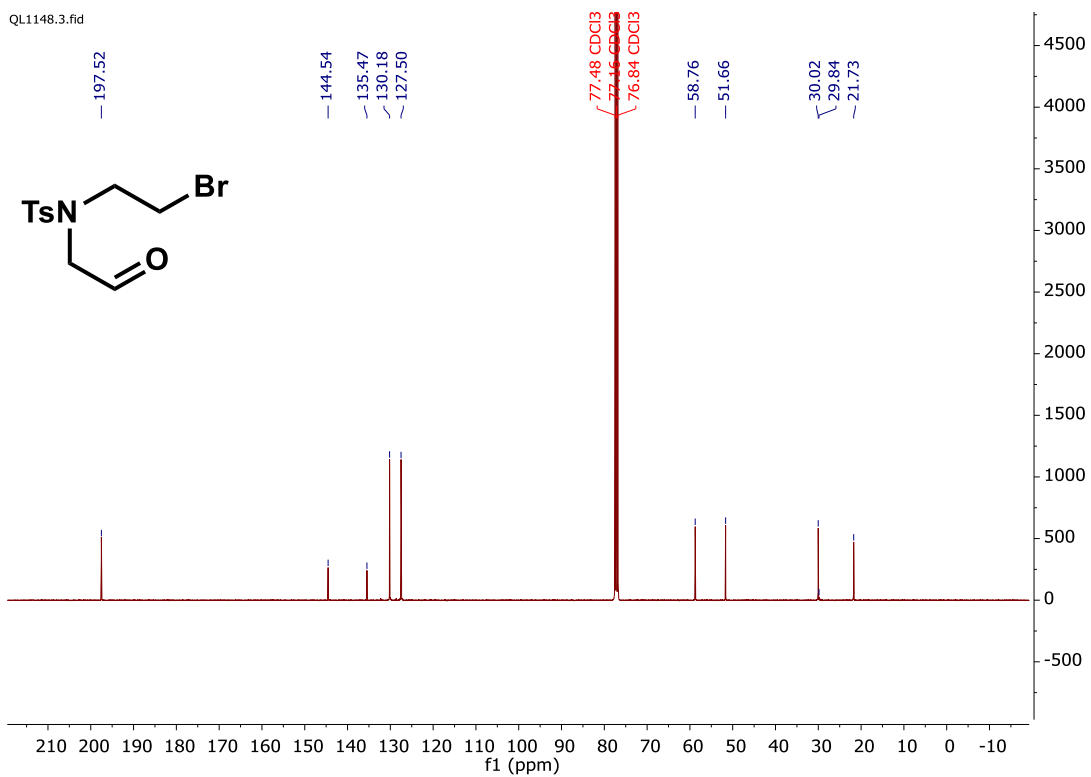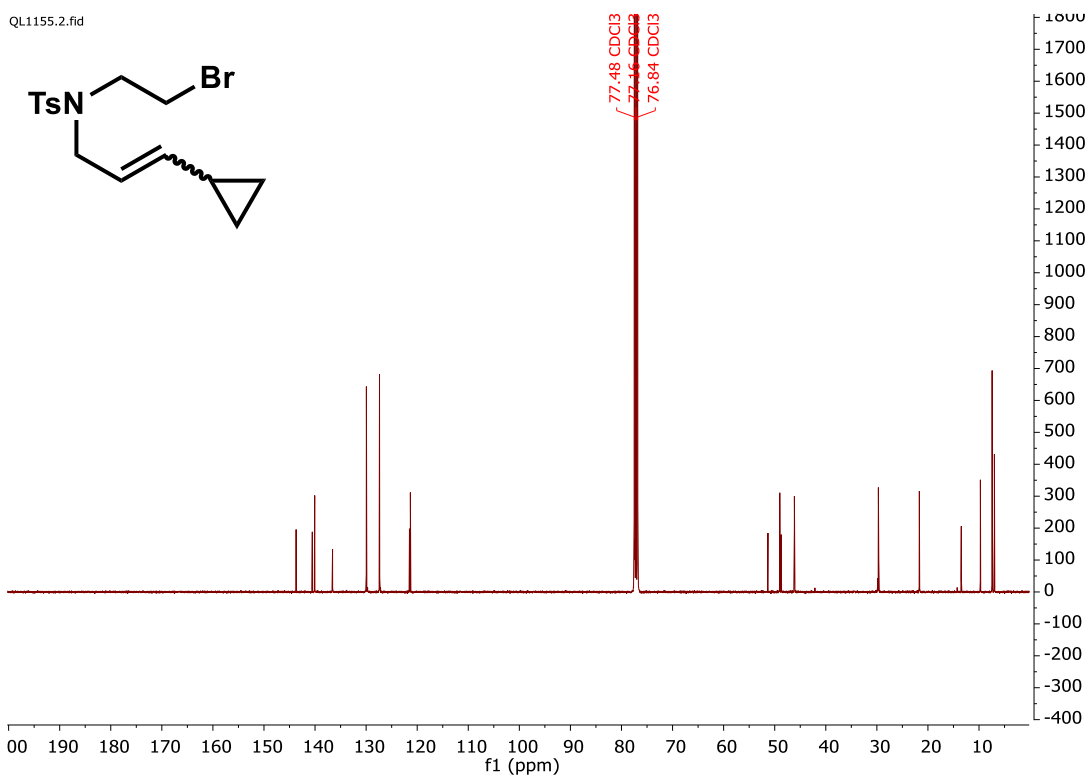**Figure S41**. ^{1}H NMR of **S1** in CDCl$_3$. Probe temperature = 25 ^{o}C.

Figure S42. ^{13}C NMR of **S1** in CDCl$_3$. Probe temperature = 25 ^{o}C.

Figure S43. ^{1}H NMR of **9** in CDCl$_3$. Probe temperature = 25 ^{o}C.

Figure S44. ^{13}C NMR of **9** in CDCl$_3$. Probe temperature = 25 ^{o}C.
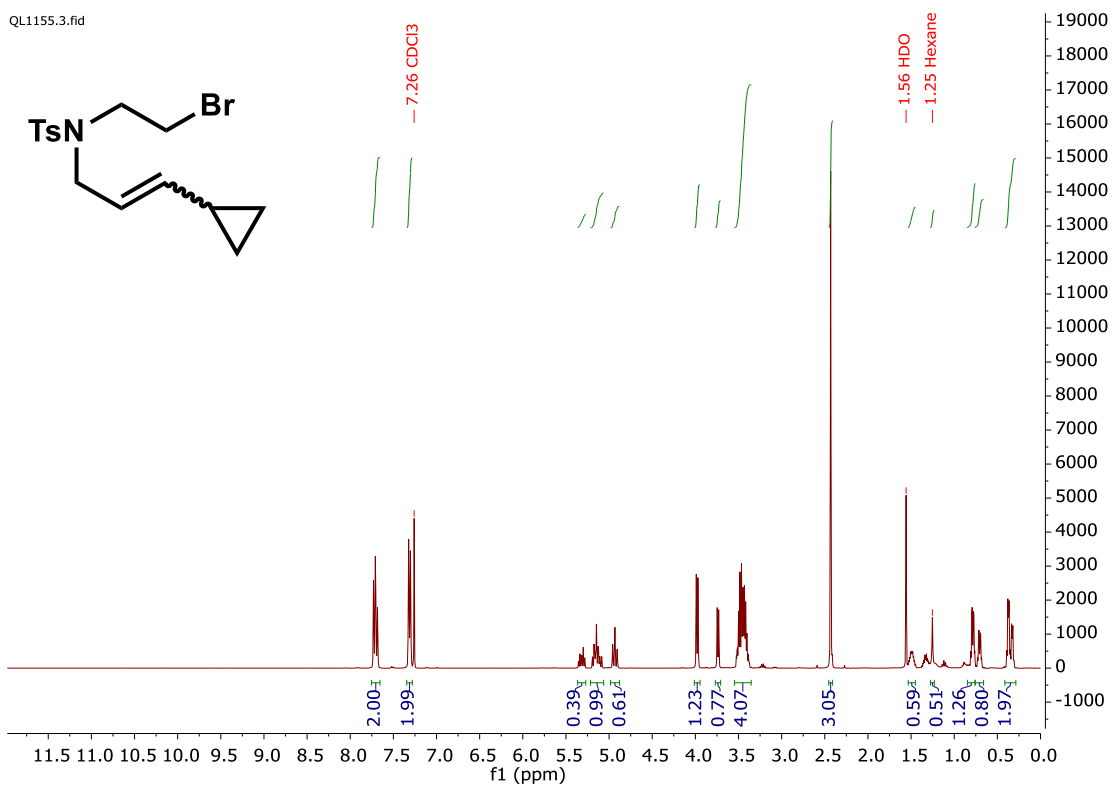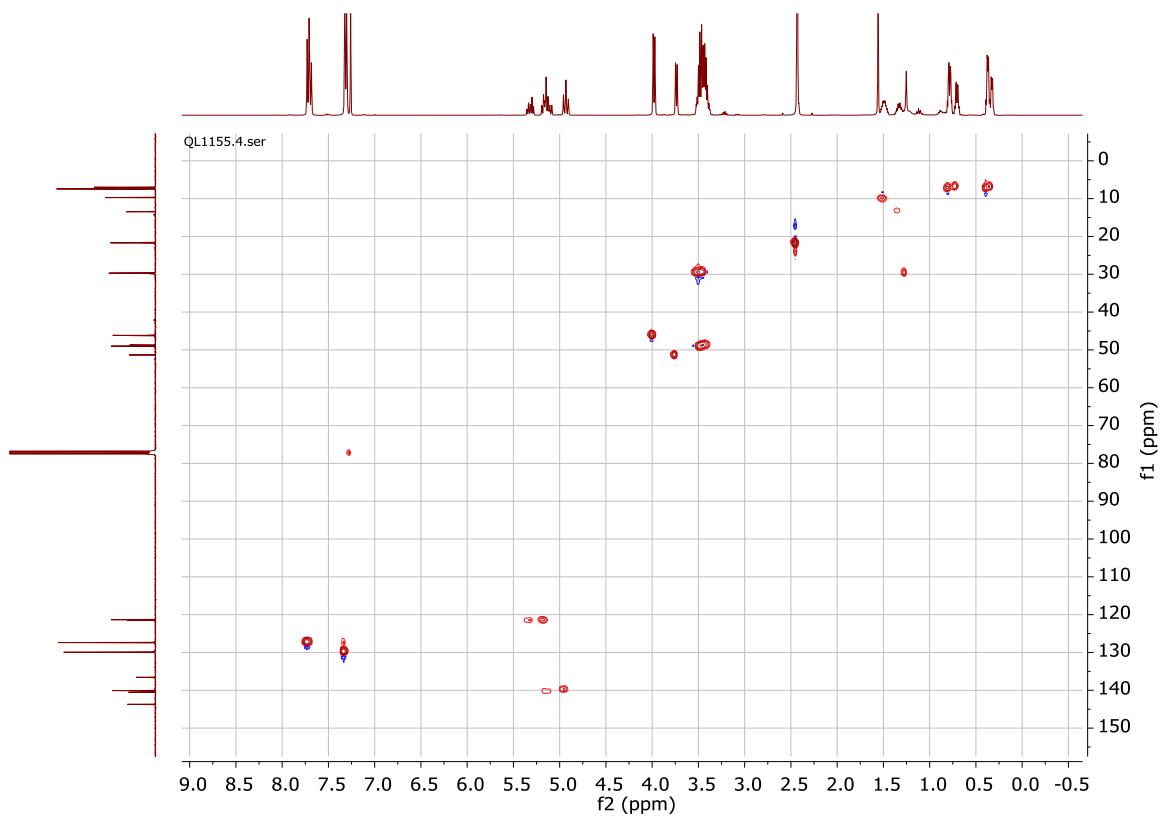
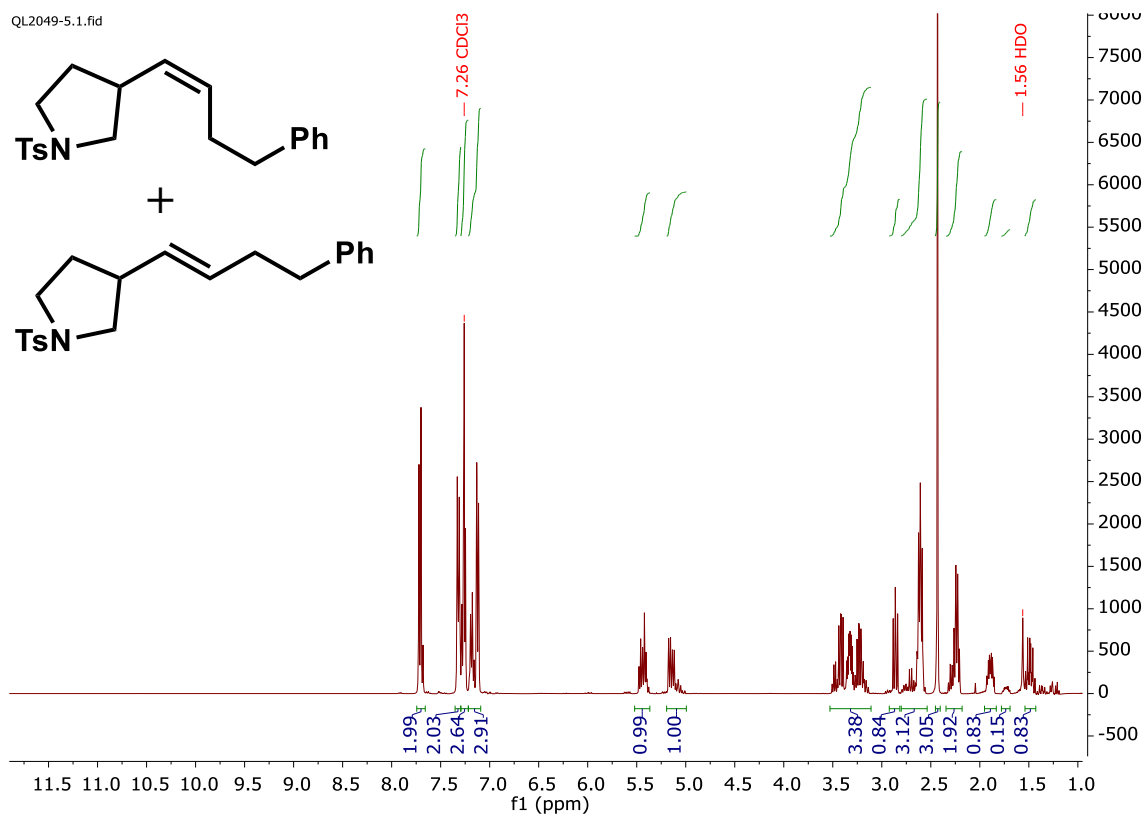**Figure S45**. HSQC of **9** in CDCl$_3$. Probe temperature = 25 °C.

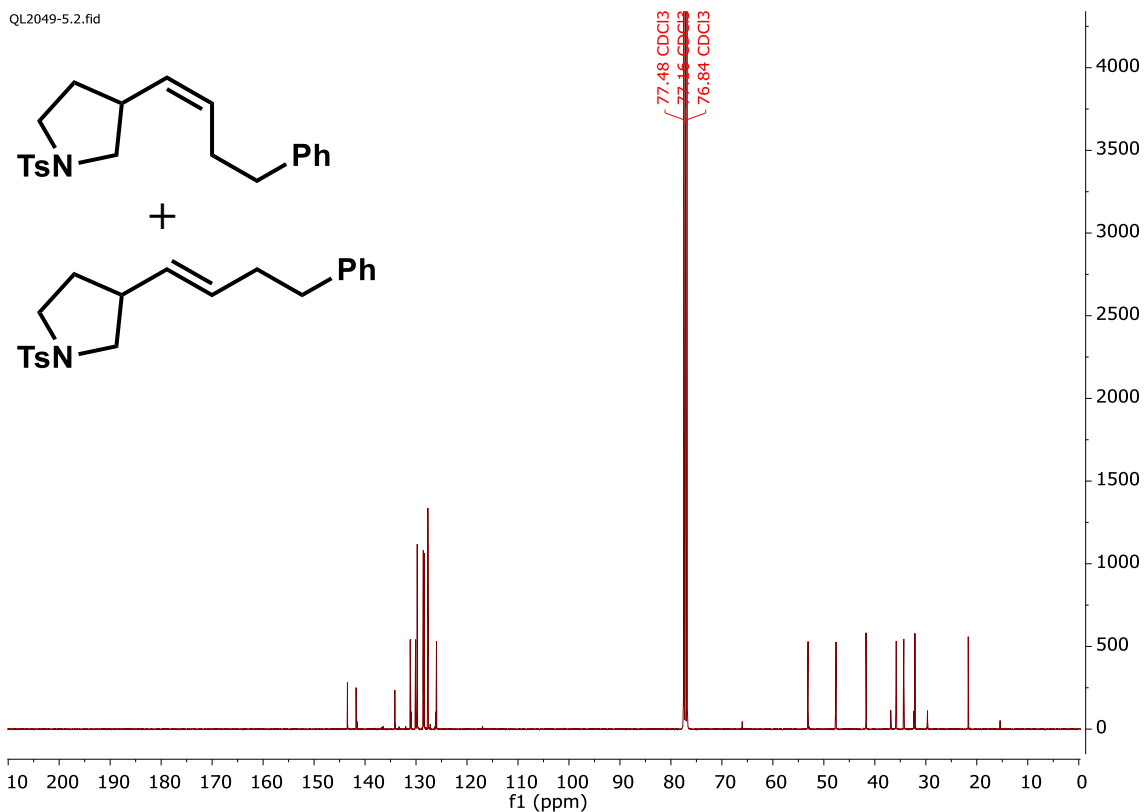**Figure S46**. ^{1}H NMR of **10** in CDCl$_3$. Probe temperature = 25 °C.

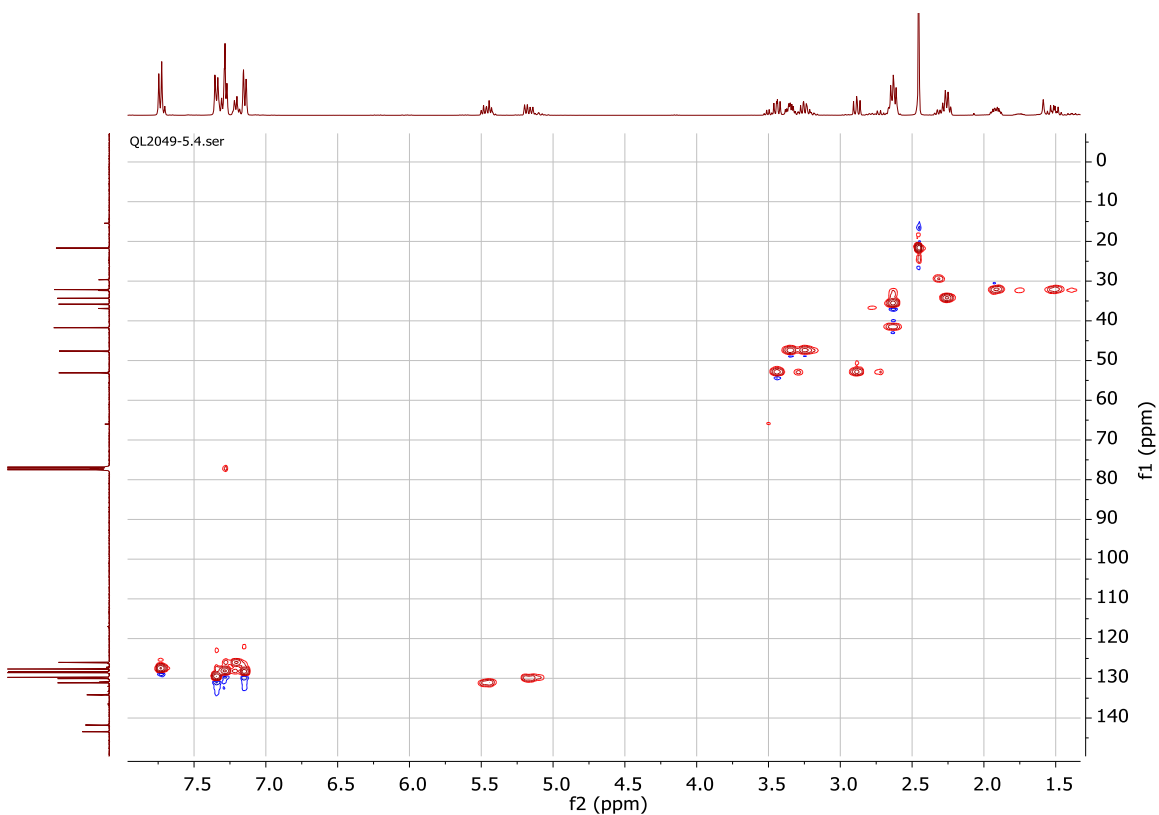**Figure S47**. ^{13}C NMR of **10** in CDCl$_3$. Probe temperature = 25 ºC.

Figure S48. HSQC of **10** in CDCl$_3$. Probe temperature = 25 ºC.
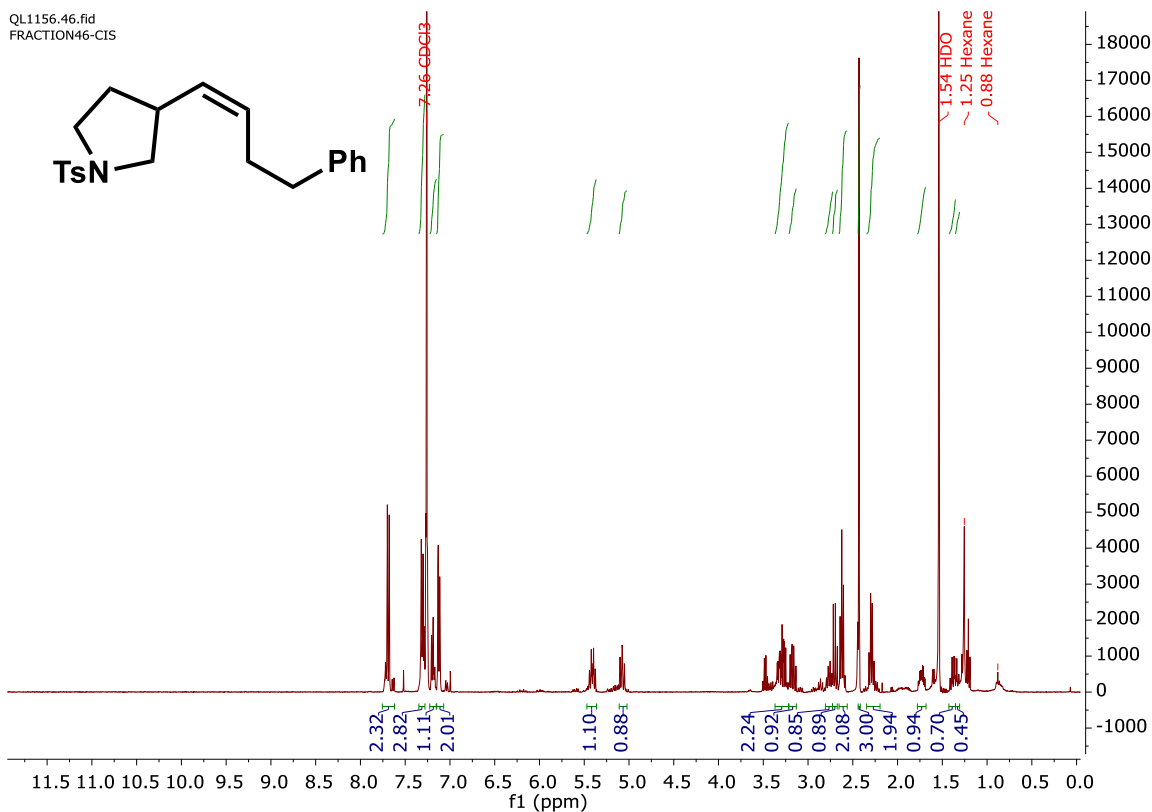
Figure S49. ^{1}H NMR of **10-cis** in CDCl$_3$. Probe temperature = 25 ^{o}C.
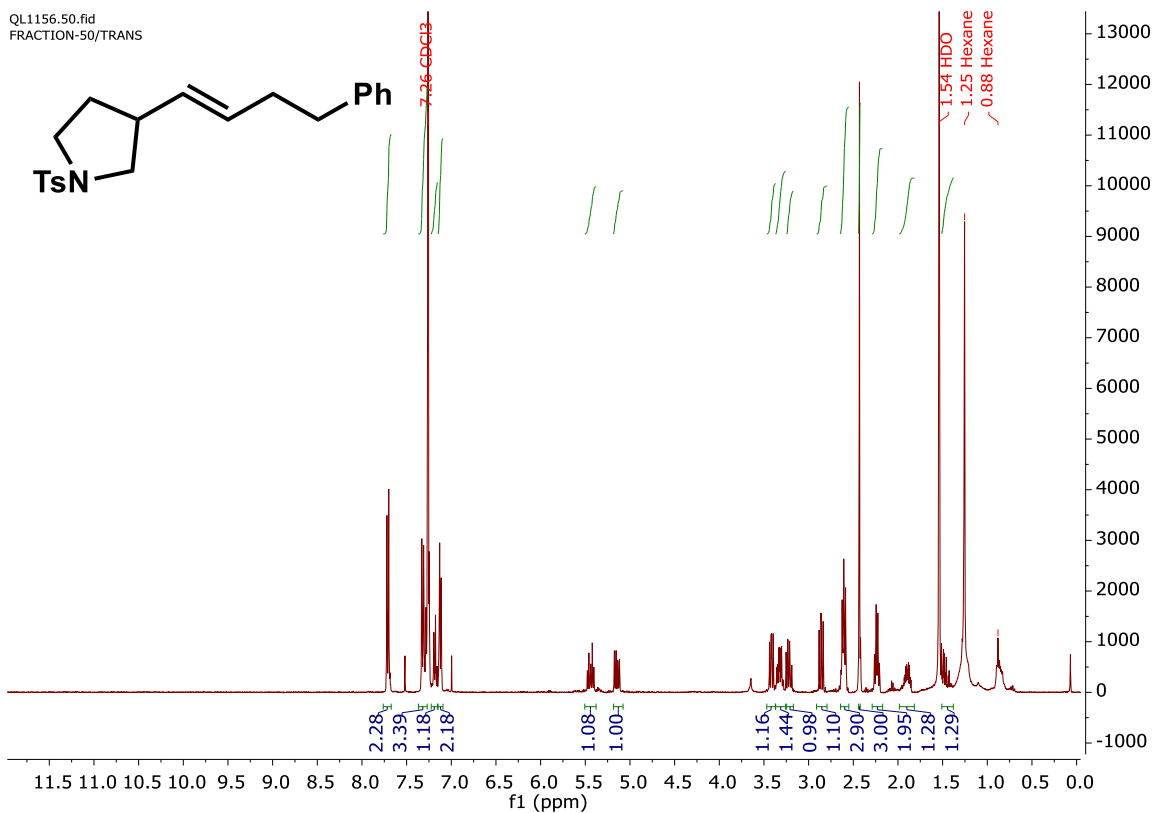

Figure S50. ^{1}H NMR of **10-trans** in CDCl$_3$. Probe temperature = 25 ^{o}C.
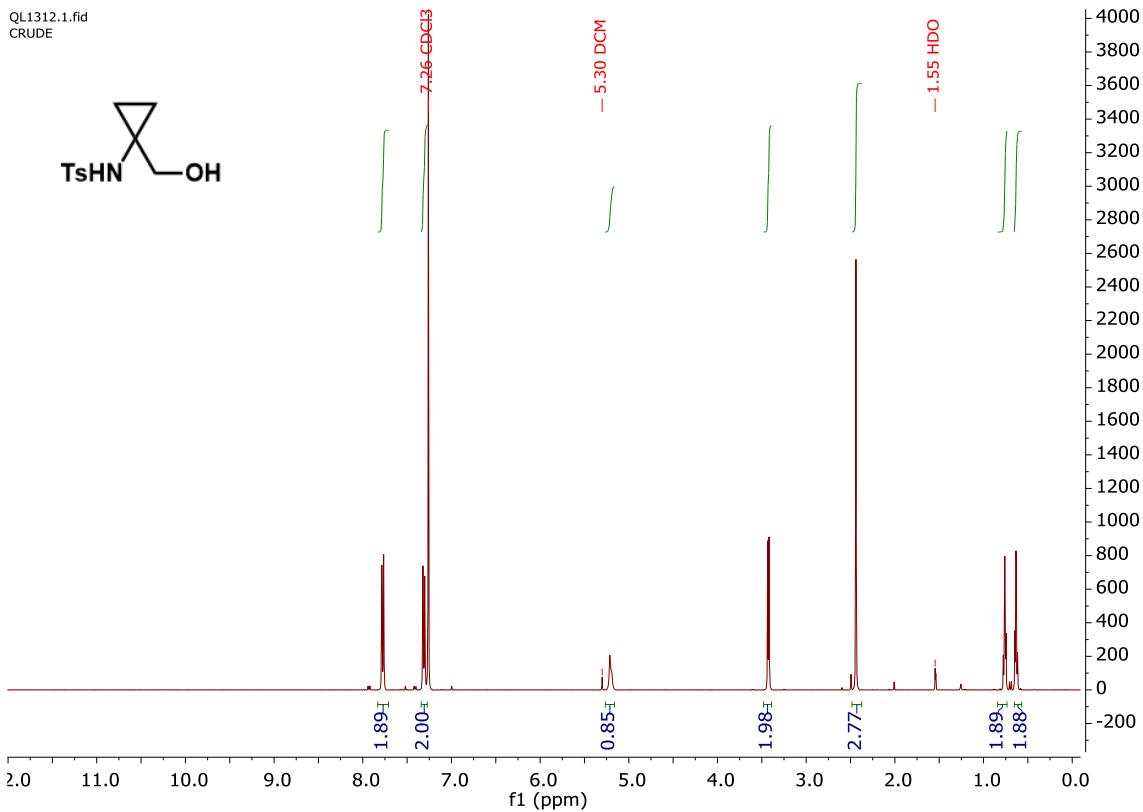
Figure S51. ^{1}H NMR of **S2** in CDCl$_3$. Probe temperature = 25 ^{o}C.
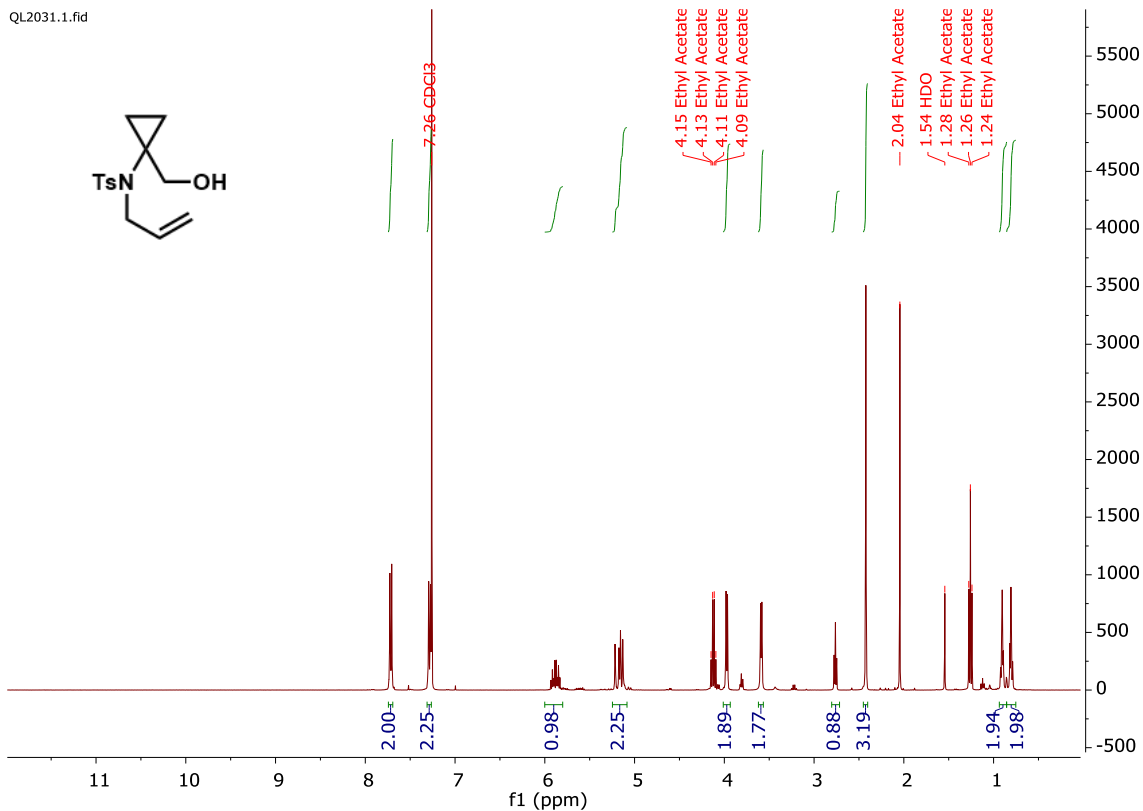
Figure S52. ^{1}H NMR of **S3** in CDCl$_3$. Probe temperature = 25 ^{o}C.

S50

Figure S53. ^{1}H NMR of **7** in CDCl$_3$. Probe temperature = 25 ^{o}C.

Figure S54. ^{13}C NMR of **7** in CDCl$_3$. Probe temperature = 25 ^{o}C.

S51
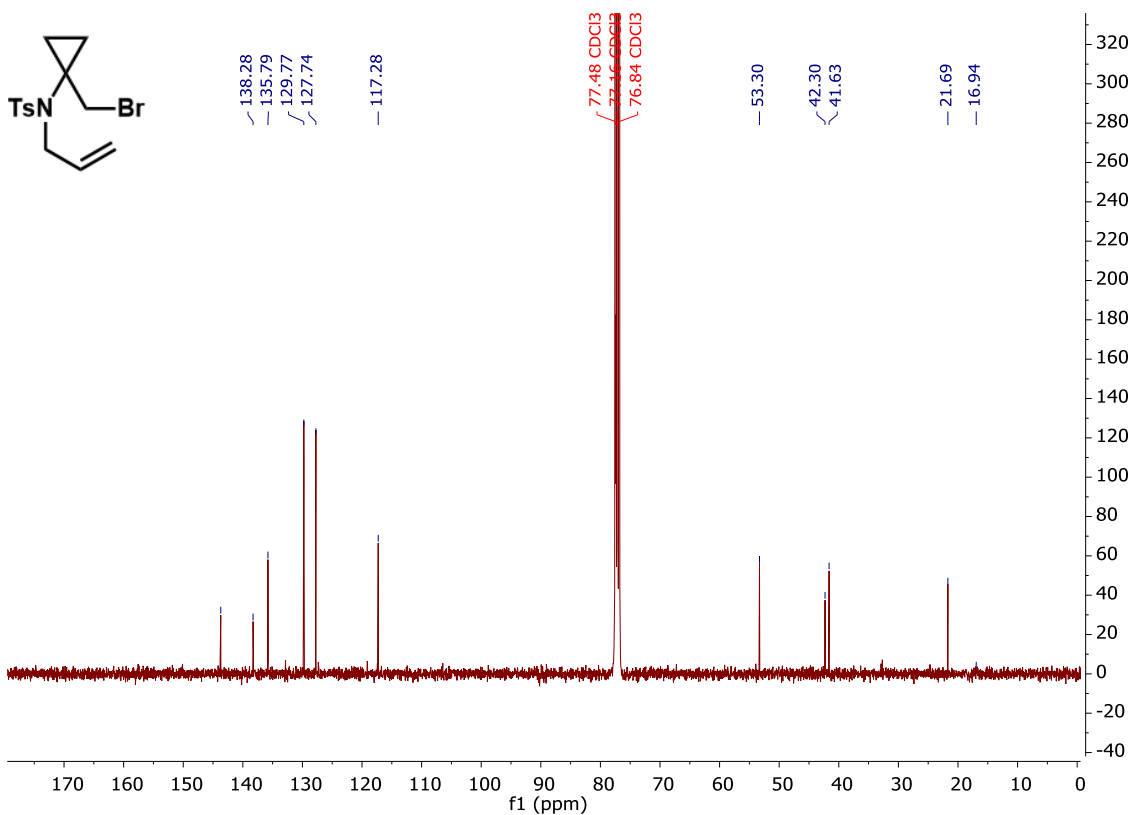
Figure S55. HSQC of **7** in CDCl₃. Probe temperature = 25 °C.

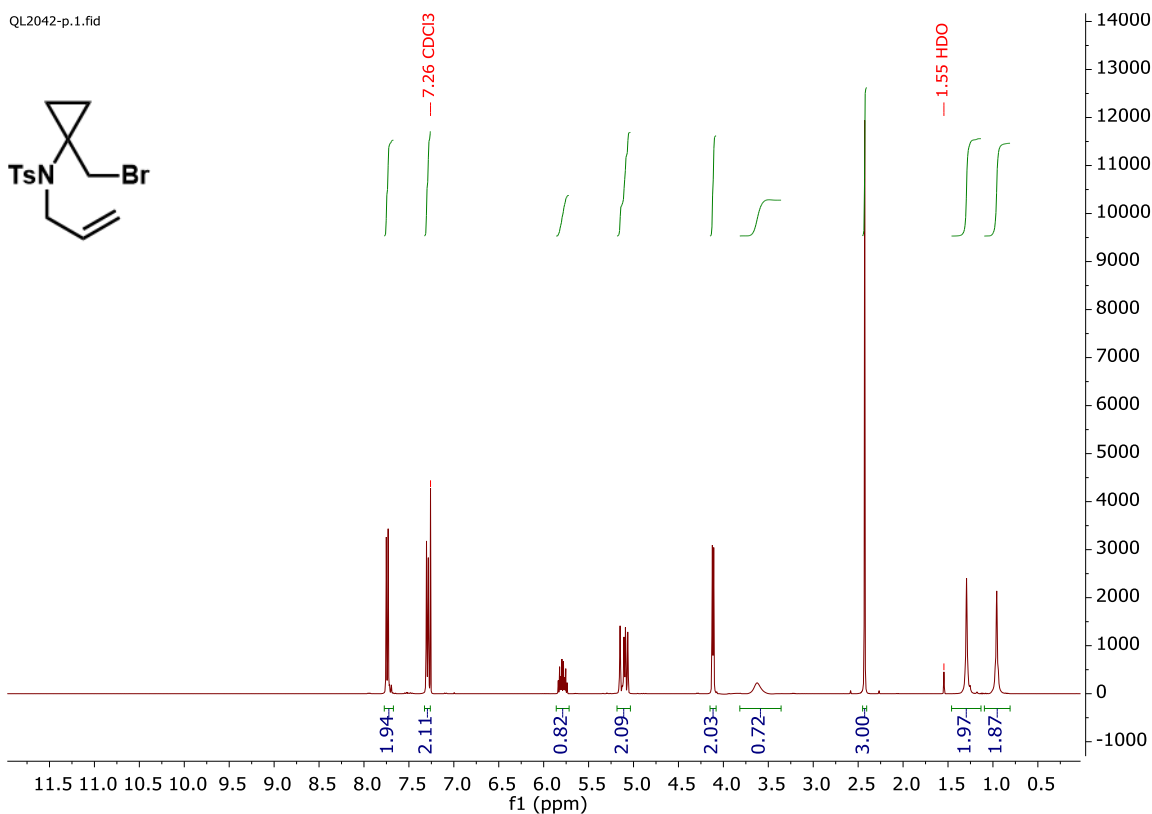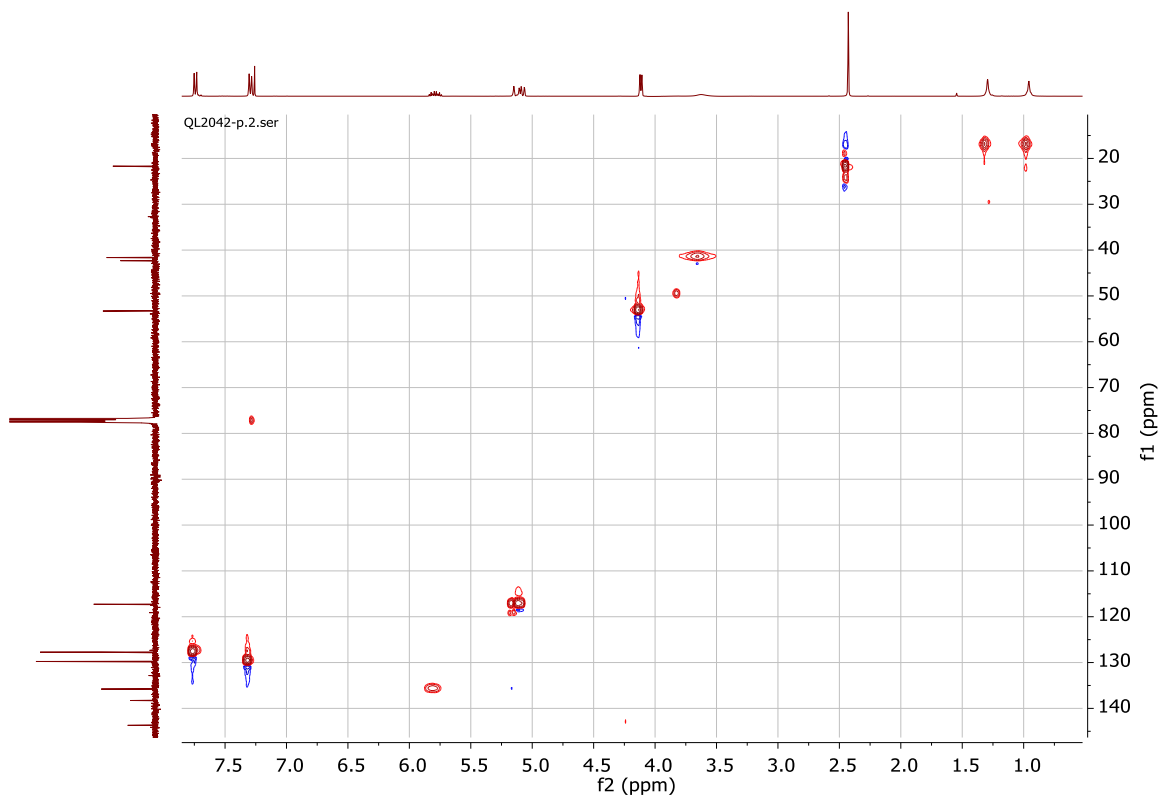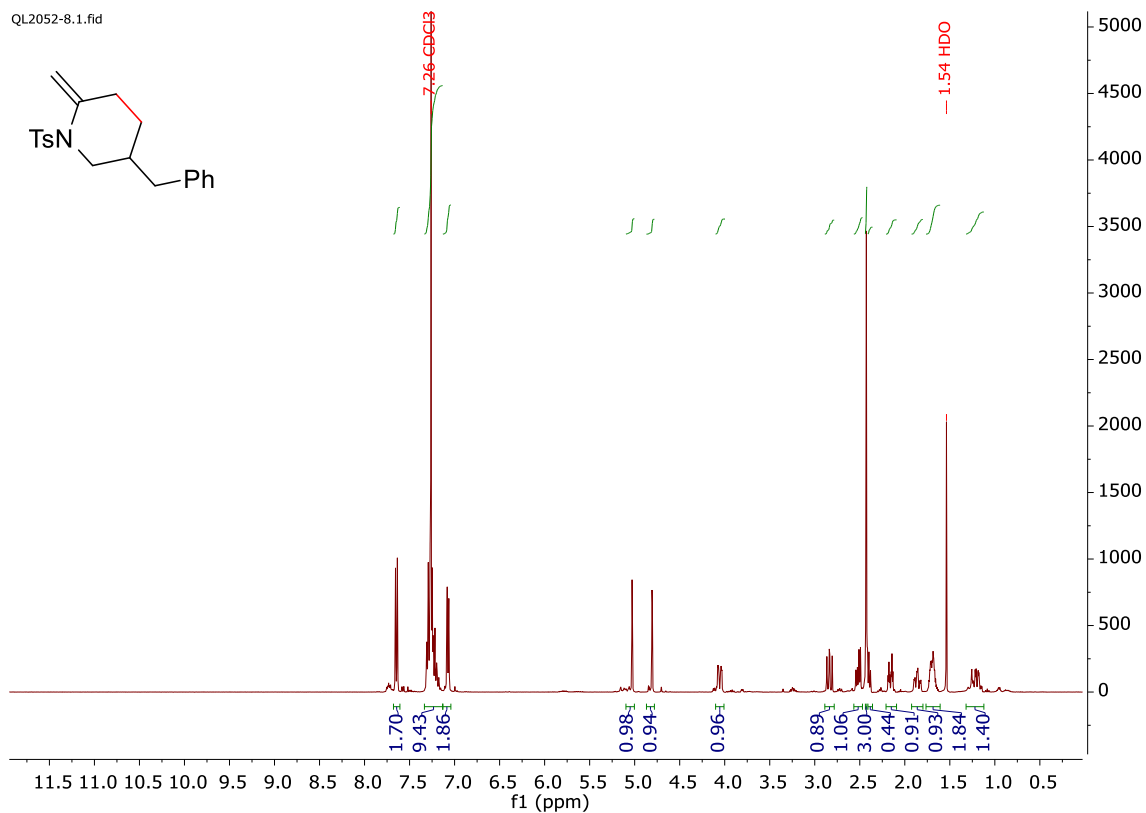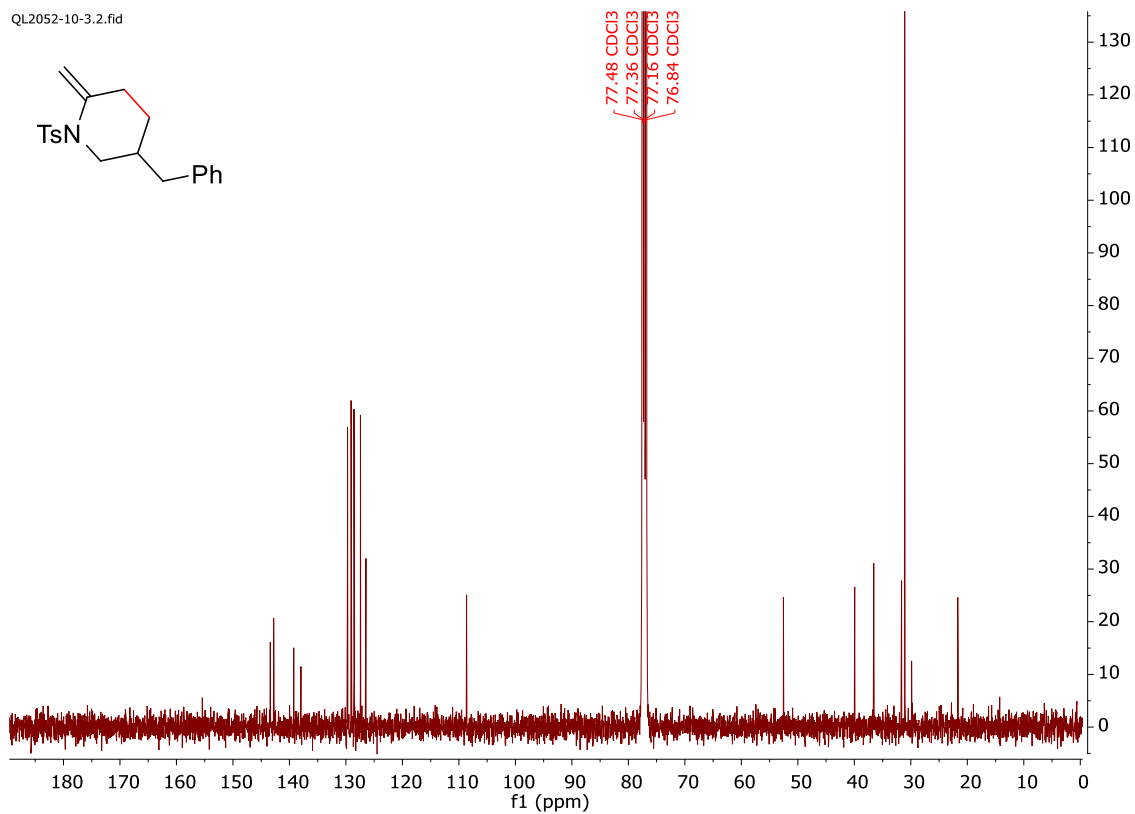**Figure S56**. ¹H NMR of **8** in CDCl₃. Probe temperature = 25 °C.

Figure S57. ^{13}C NMR of **8** in CDCl$_3$. Probe temperature = 25 ^{o}C.
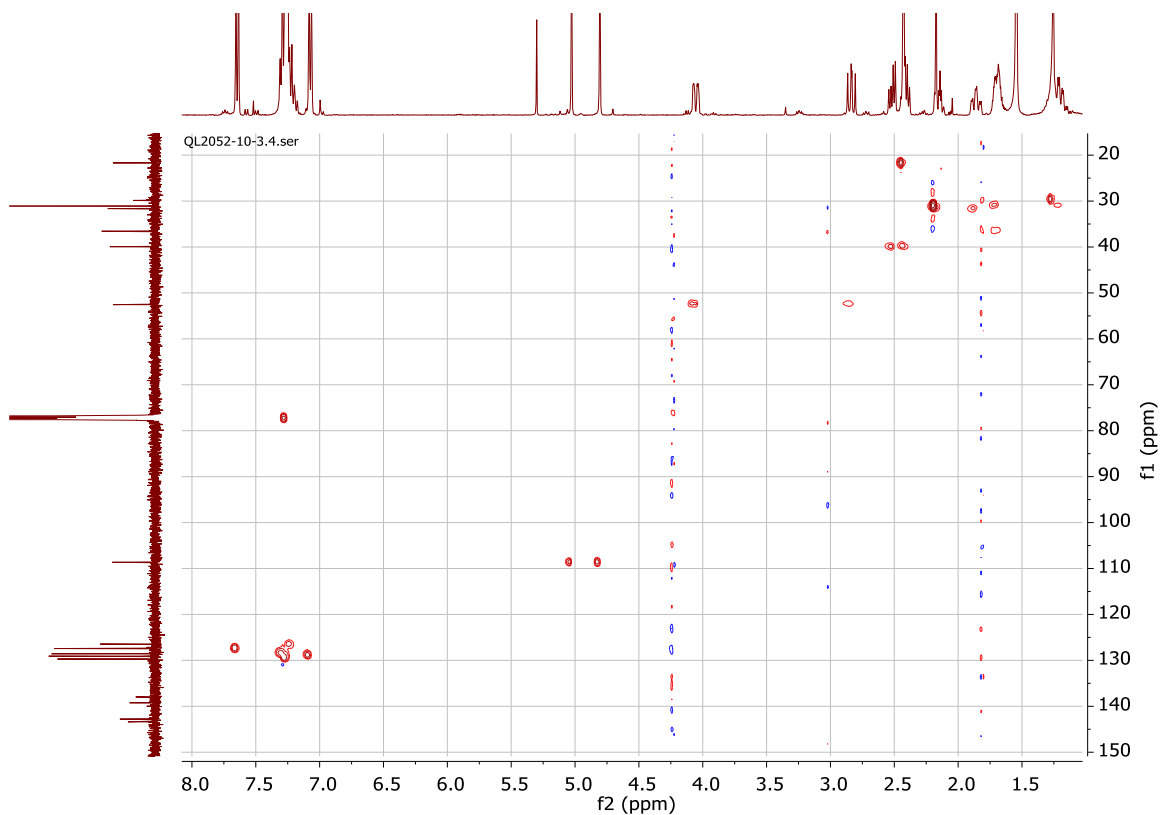
Figure S58. HSQC of **8** in CDCl$_3$. Probe temperature = 25 ^{o}C.
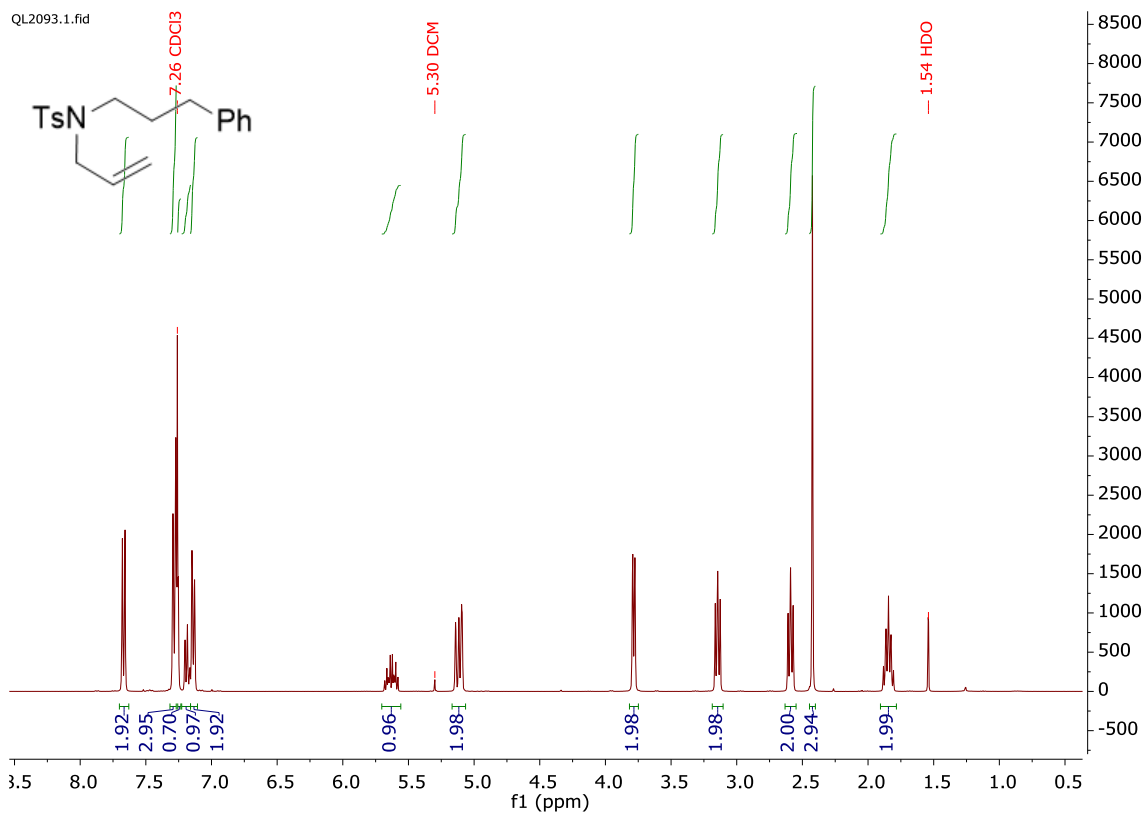
Figure S59-1. ^{1}H NMR of **23** in CDCl$_3$. Probe temperature = 25 ^{o}C.
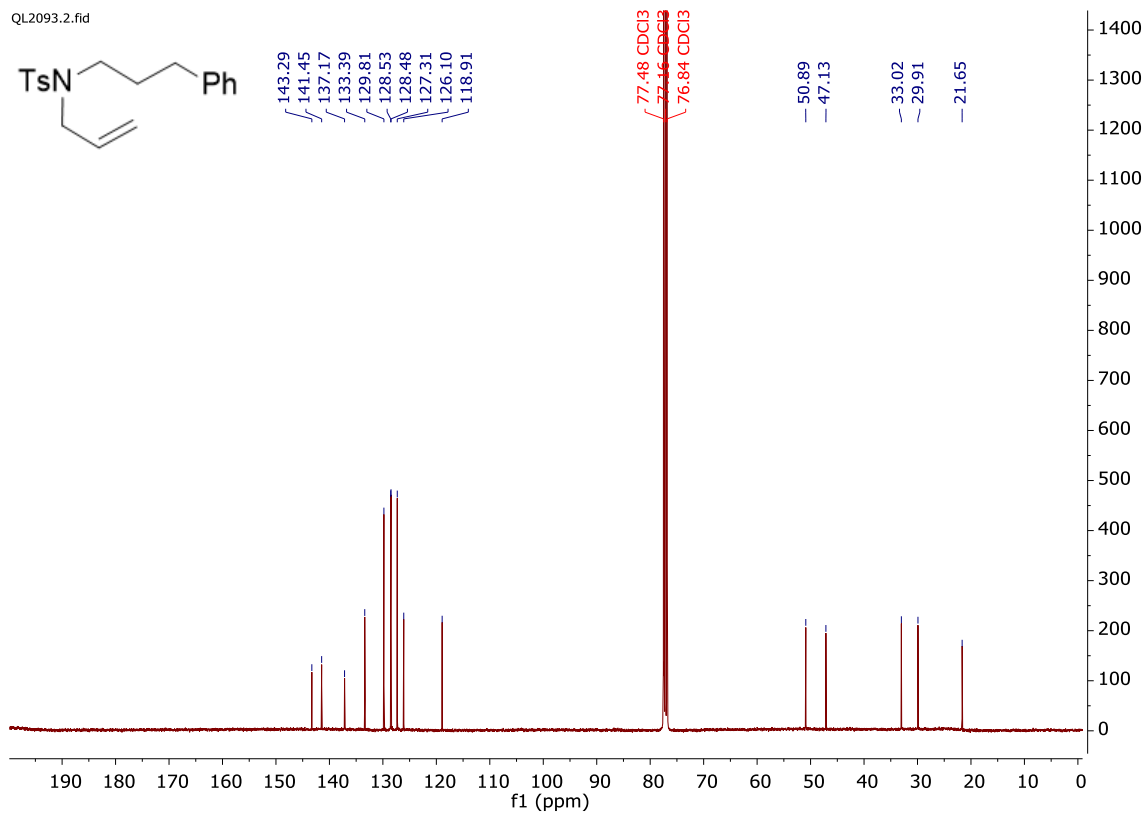
Figure S59-2. ^{13}C NMR of **23** in CDCl$_3$. Probe temperature = 25 ^{o}C.

S54

(Phen)NiBr$_2$ **14**

4.01 MeOH
2.50 DMSO

2.00
2.05

2.25
2.17

4.68

f1 (ppm)
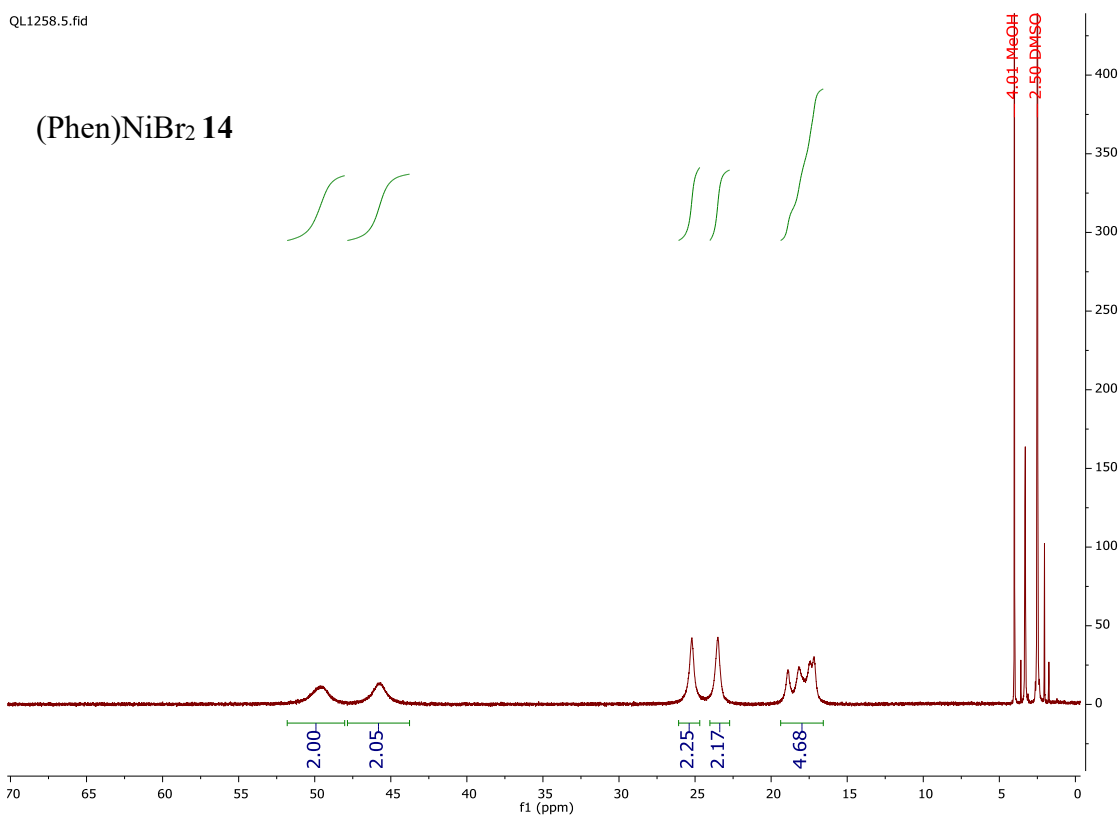
Figure S60. ^{1}H NMR of **14** in DMSO-d_6. Probe temperature = 25 °C.

2.94 DMA
2.78 DMA
2.50 DMSO
1.95 DMA

0.89

1.69

1.25

4.00

f1 (ppm)

Figure S61. ^{1}H NMR of **19** in DMSO-d_6. Probe temperature = 25 °C.
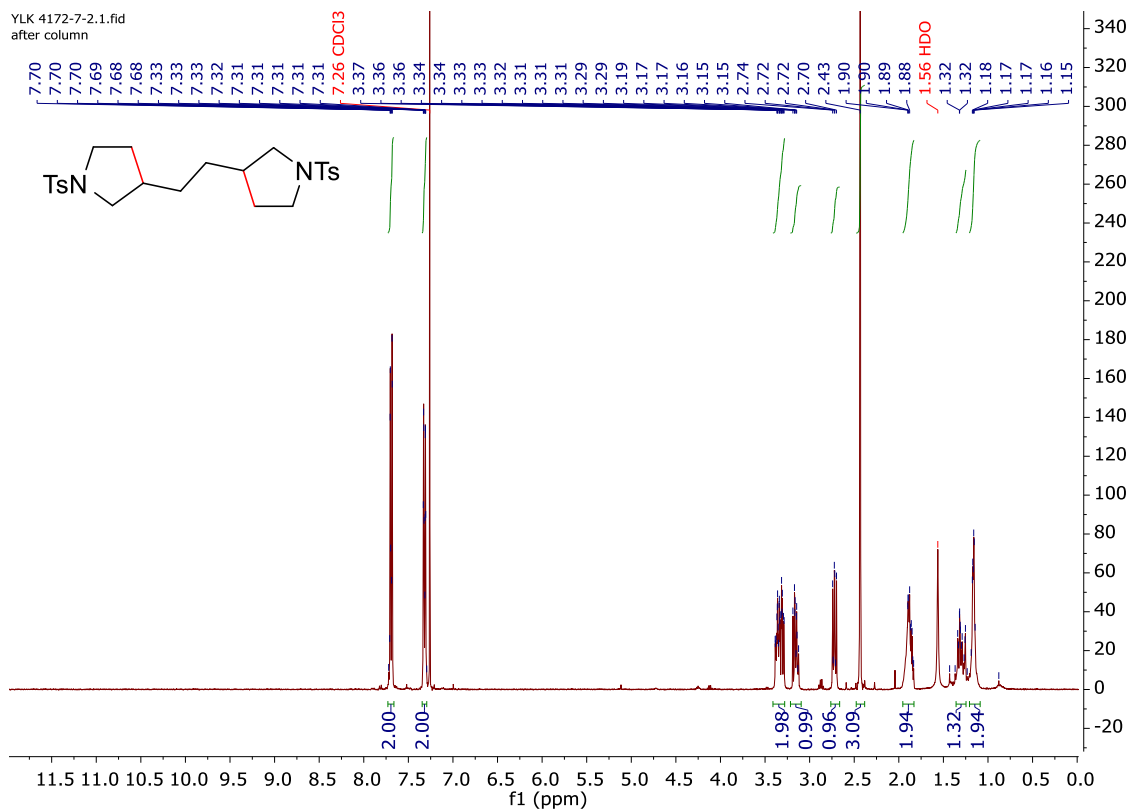
Figure S62. ^{1}H NMR of **20** in CDCl$_3$. Probe temperature = 25 °C.
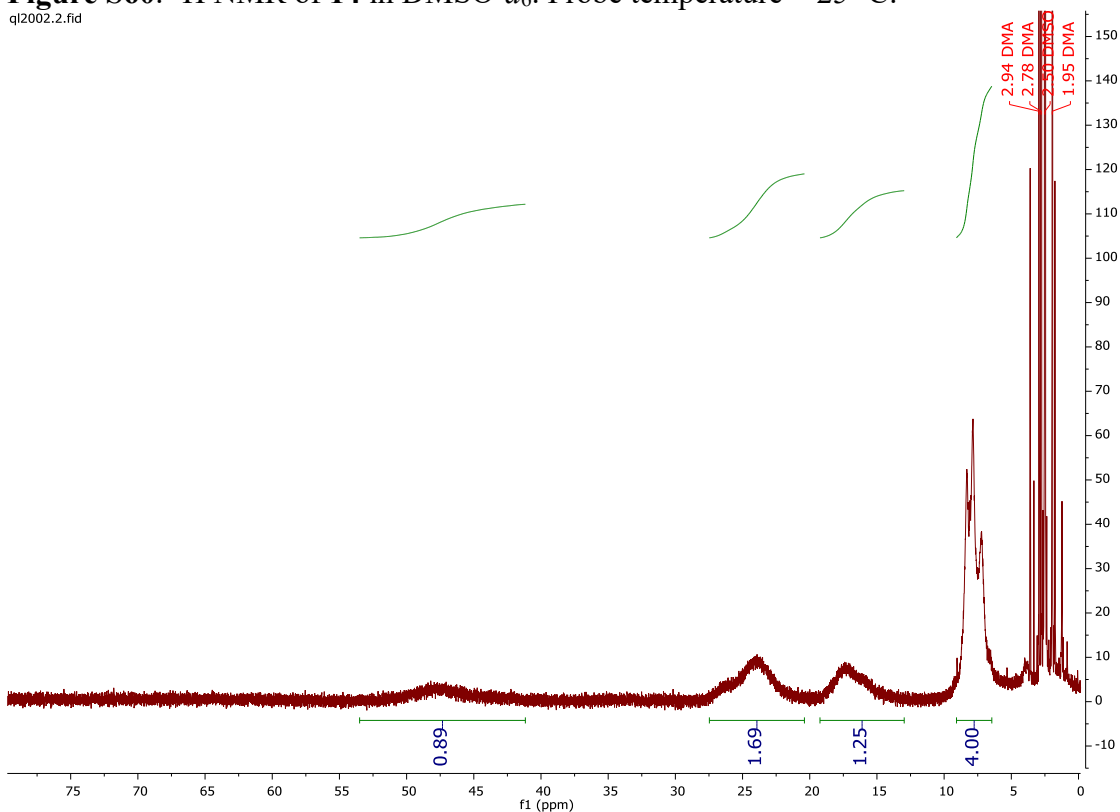
12. UV/Vis Spectra

(Phen)NiBr$_2$ **14** (DMA, 23 °C)

(Phen)Ni(Ph)Br **16** (DMA, 23 °C)

(Phen)Ni(o-Tol)Br **15** (THF, 23 °C)

(Phen*)NiBr$_2$ **17** (Acetone, 23 °C)

(Phen*)NiBr **18** (THF, 23 °C)
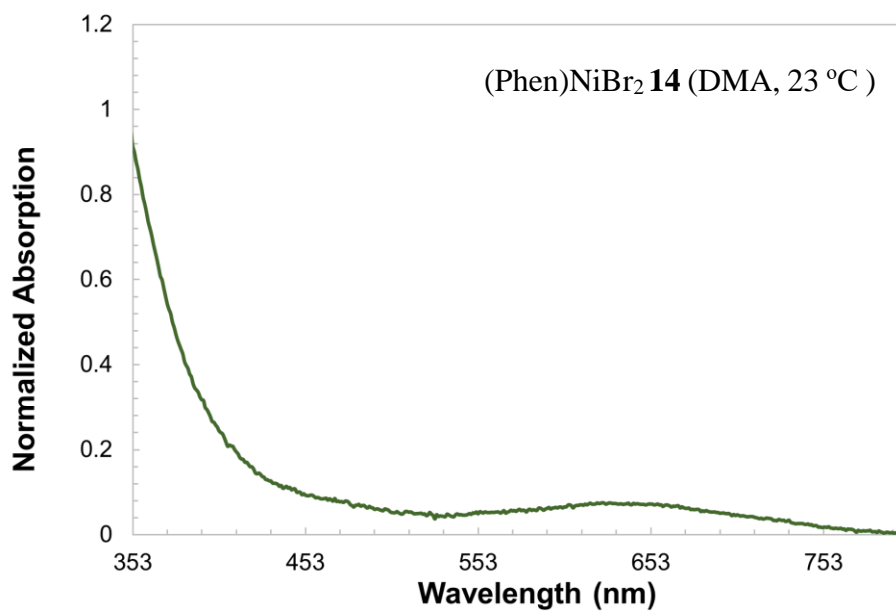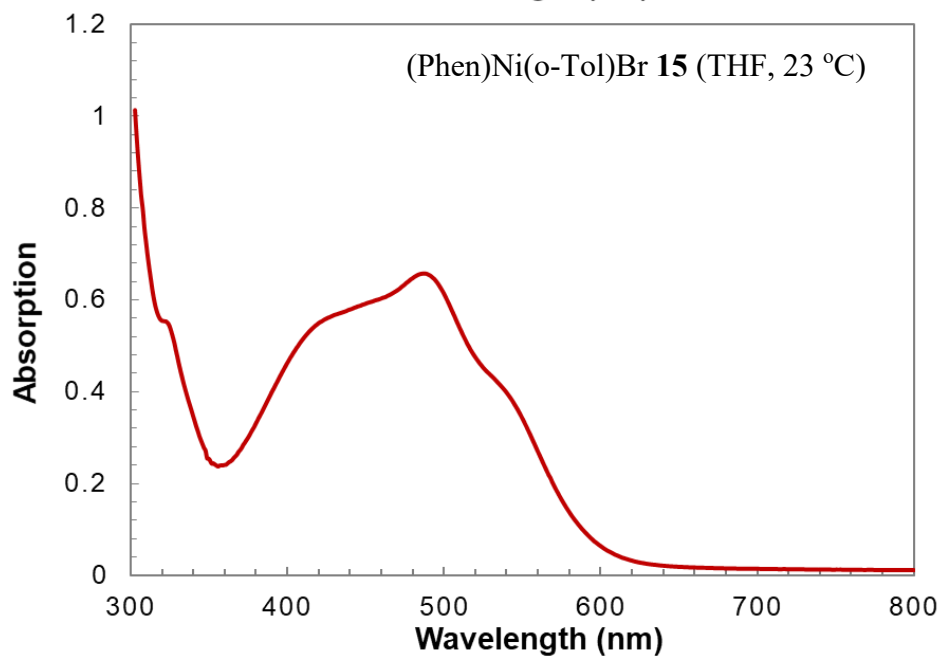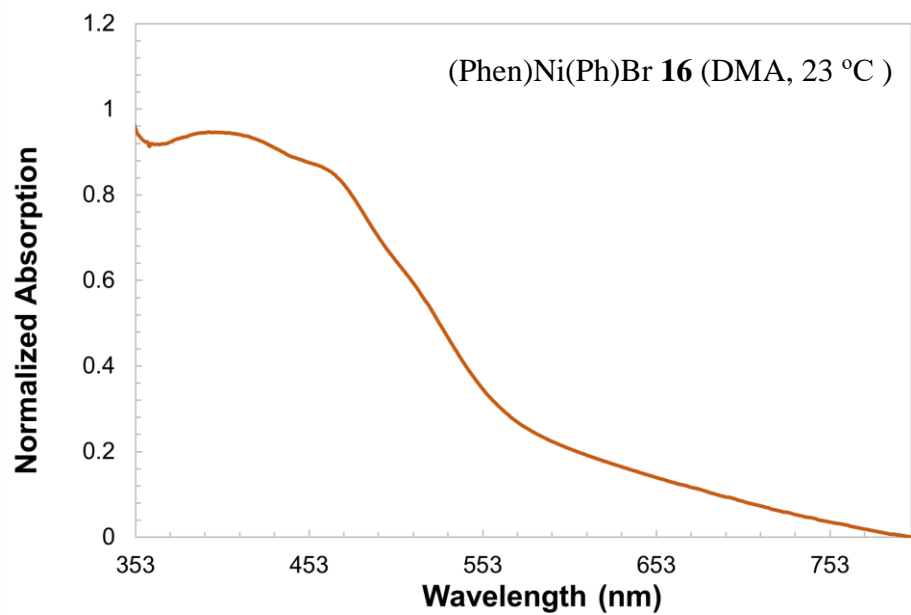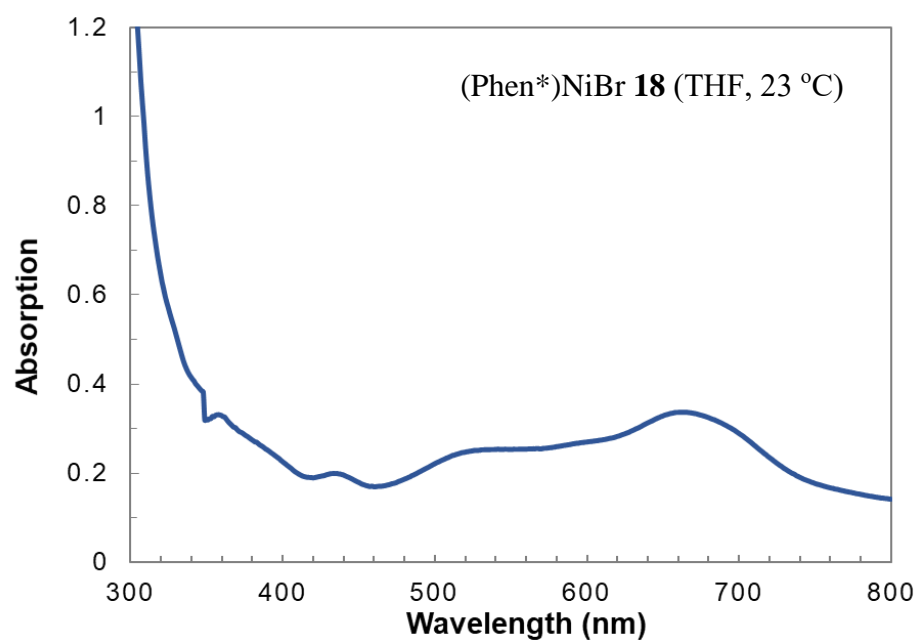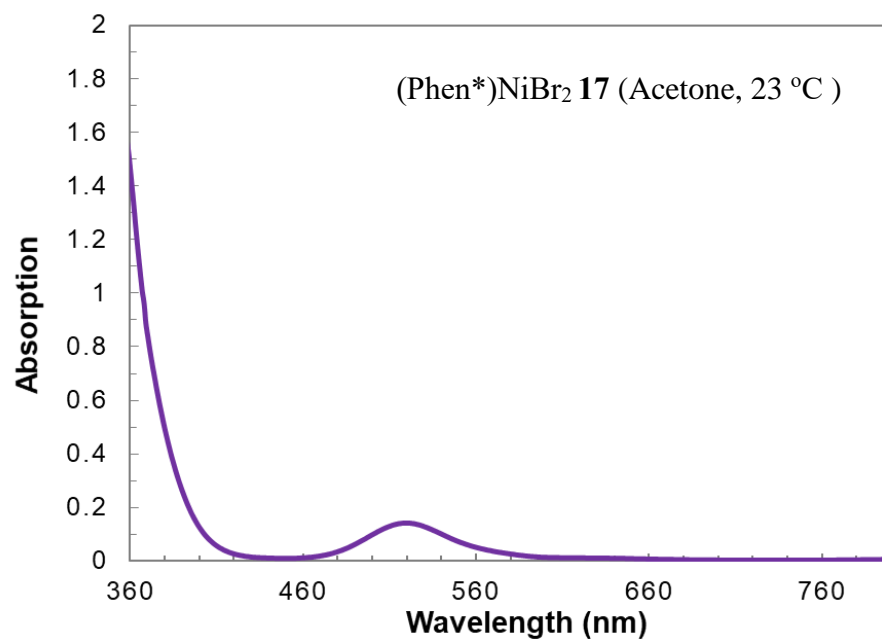
13. EPR Experiments

Figure S63. X-Band EPR Spectrum of reaction mixture of **21** with MesMgBr. Temperature = 10 K, solvent = DMA. The spectrum is simulated with Easyspin. Spectroscopic parameters: g = 2.009. Microwave frequency = 9.380 GHz, power = 0.063 mW, modulation amplitude = 1 mT/100 kHz.
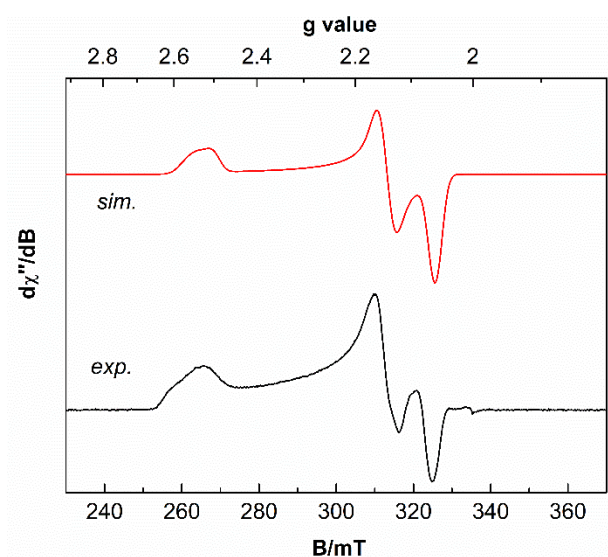
Figure S64. X-Band EPR Spectrum of reaction mixture of **18** with MesMgBr. Temperature = 10 K, solvent = Toluene/THF. The spectrum is simulated with Easyspin. Spectroscopic parameters: g = [2.5305 2.1411 2.0581]. Microwave frequency = 9.380 GHz, power = 0.63 mW, modulation amplitude = 1 mT/100 kHz.

14. DFT Calculations

Input File for Energy and MullikenSpin Density Calculation of Ni(phen*)Br 18

! UKS B3LYP RIJCOSX SlowConv TightSCF def2-SV(P) def2-SVP/J Normalprint UCO
OPT

%basis NewGTO 28 "def2-TZVP(-f)" end
NewGTO 7 "def2-TZVP(-f)" end
NewGTO 8 "def2-TZVP(-f)" end
NewGTO 35 "def2-TZVP(-f)" end
NewAuxGTO 28 "def2-TZVP/J" end
NewAuxGTO 7 "def2-TZVP/J" end
NewAuxGTO 8 "def2-TZVP/J" end
NewAuxGTO 35 "def2-TZVP/J" end
end

%scf
MaxIter 1500
TolE 1E-7
TolErr 1E-6
end

* xyz 0 2
```
Ni      0.00000      0.00000      0.00000
Br      0.00000     -0.00000      2.28773
N      -1.05759      0.82425     -1.44167
N       1.13883     -0.61617     -1.48181
C      -2.20549      1.50709     -1.37578
C      -2.82435      2.00313     -2.54333
H      -3.66243      2.44531     -2.48147
C      -2.22754      1.85205     -3.75834
H      -2.64652      2.19638     -4.53769
C      -0.99194      1.18727     -3.85949
C      -0.46228      0.67014     -2.65555
C       2.24621     -1.38288     -1.45950
C       2.99748     -1.57942     -2.62719
H       3.78079     -2.11586     -2.58874
C       2.63000     -1.01923     -3.81804
H       3.15854     -1.14804     -4.59731
C       1.45764     -0.24996     -3.86953
C       0.74996     -0.08111     -2.67419
C      -0.24609      1.01155     -5.06143
H      -0.58728      1.36249     -5.87646
C       0.92555      0.36114     -5.06608
H       1.41923      0.29960     -5.87603
C      -2.80532      1.68298     -0.01524
```
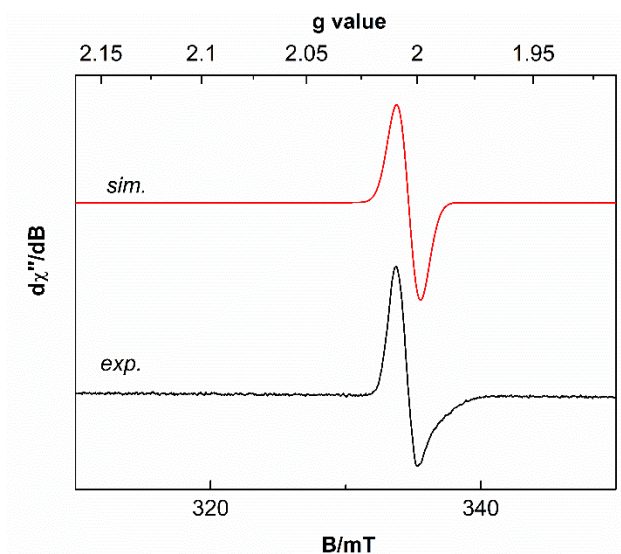
```
H     -2.04255    1.68016    0.63089
C     -3.52537    3.02309    0.17133
H     -3.86751    3.08502    1.08659
H     -4.27044    3.08437   -0.46218
H     -2.89607    3.75686    0.00678
C     -3.65342    0.47729    0.32146
H     -4.44619    0.46469   -0.27176
H     -3.13065   -0.34465    0.14463
C     -4.11401    0.46662    1.75667
H     -4.59154   -0.36891    1.94023
H     -4.71323    1.22654    1.91256
H     -3.33696    0.53649    2.34932
C      2.55416   -2.04041   -0.13644
H      2.42492   -1.34636    0.57187
C      3.98748   -2.53252   -0.02149
H      4.17630   -2.77126    0.90981
H      4.59976   -1.82308   -0.30782
H      4.10878   -3.31947   -0.59215
C      1.51903   -3.15053    0.12489
H      0.61056   -2.77621   -0.00148
H      1.64405   -3.86847   -0.54409
C      1.60882   -3.75653    1.52041
H      2.58652   -4.16485    1.66971
H      0.87912   -4.53278    1.61980
H      1.42387   -2.99742    2.25147
*

%plots format cube
dim1 100 dim2 100 dim3 100
SpinDens("Ni(disBuphen)Br.cube");
end
```

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