

Supplementary Information for

Facile Kinetic Induction of a Dihydropyridide to Pyrrolide Ring Contraction

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General experimental procedures

All reactions dealing with air- and moisture-sensitive compounds were carried out under an argon atmosphere using standard Schlenk line and glovebox techniques in an MBraun Labmaster glovebox at $O_2, H_2O < 0.1$ ppm. NMR experiments using air-sensitive compounds were conducted in J. Youngs tap NMR tubes prepared and sealed in a glovebox under argon. All NMR data were acquired on a Bruker 300 Ultrashield™ for 1H (300 MHz) and $^{13}C\{^1H\}$ (75.48 MHz) spectra at room temperature or a Bruker 400 Ultrashield™ for 1H (400 MHz) and $^{13}C\{^1H\}$ (125.76 MHz) spectra. $^1H/^{13}C$ NMR spectra were referenced using residual solvent resonances. Elemental analyses of all moisture- and air-sensitive compounds were performed by Stephen Boyer of London Metropolitan Enterprises. Solvents for air- and moisture-sensitive reactions were provided by an Innovative Technology Solvent Purification System. C_6D_6 and toluene- d_8 were purchased from Fluorochem and dried over molten potassium prior to vacuum transfer into a sealed ampoule and storage in the glovebox under argon. Compounds **I** - **IV** were synthesised using literature procedures.¹

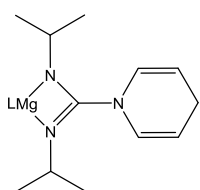
Reactions of Dihydropyridines with Carbodiimides

General Experimental procedure: Reactions of Dihydropyridines with Carbodiimides

Stoichiometric reactions between 30 mg of the dihydropyridide complex (**I** - **IV**) and carbodiimide were reacted together in 0.5 mL of either C_6D_6 or d_8 -toluene in a sealed Youngs tap NMR tube. In most cases an instant colour change was observed, although if no reaction had occurred at room temperature the NMR tube was heated to either 60°C or 80°C and regularly monitored by 1H NMR spectroscopy until completion. For scale-up experiments 50 – 100 mg of the dihydropyridide complex was again reacted with a stoichiometric amount of carbodiimide in 5 mL of toluene and left to stir overnight or heated to the appropriate temperature to effect the reaction. The desired product was crystallised from a toluene solution at -30 °C.

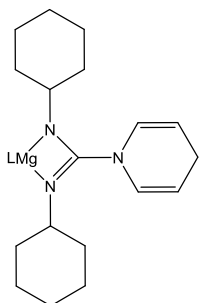
1,4-Dihydropyridide reactions, II

Synthesis of Compound 1



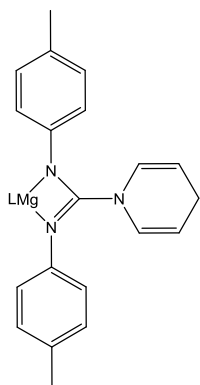
NMR Scale: 30 mg (0.05 mmol) **II** with 5.5 μL (0.05 mmol) of $i\text{PrNCNiPr}$. **Large Scale:** 50 mg (0.083 mmol) of **II** with 12.8 μL (0.083 mmol) of $i\text{PrNCNiPr}$, this was dissolved in toluene and left to stir at room temperature overnight. Solvent was removed *in vacuo* to yield yellow crystals of **1** (35 mg, 67% yield). ^1H NMR (300 MHz, d_8 -Tol, 300 K) δ_{H} (ppm): 7.11 – 6.94 (6H, m, Ar-*H*), 5.94 (2H, dt, $J_{\text{HH}} = 9$ Hz, NCH), 4.83 (1H, s, NC(CH₃)CH), 4.38 (2H, dt, $^3J = 9$ Hz, $^4J = 3$ Hz, NCHCH), 3.48 (2H, sept, $J_{\text{HH}} = 6$ Hz, NCH(CH₃)₂), 3.41 (4H, sept, $J_{\text{HH}} = 6$ Hz, CH(CH₃)₂), 2.89 (2H, m, NCHCHCH₂), 1.64 (6H, s, NC(CH₃)), 1.27 (12H, d, $J_{\text{HH}} = 6$ Hz, CH(CH₃)₂), 1.24 (12H, d, $J_{\text{HH}} = 6$ Hz, CH(CH₃)₂), 0.88 (6H, d, $J_{\text{HH}} = 6$ Hz, NCH(CH₃)₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, d_8 -Tol, 300 K) δ_{C} (ppm): 169.6 (NC(CH₃), 164.3 (CN₃), 145.6 (*ipso*-Ar), 142.6 (*o*-Ar), 129.3 (*p*-Ar), 128.1 (NCH), 123.8 (*m*-Ar), 99.0 (NCHCH), 94.9 (NC(CH₃)CH), 45.0 (NCH(CH₃)₂), 28.26 (CH(CH₃)₂), 26.0 (NCH(CH₃)₂), 25.4 (CH(CH₃)₂), 24.5 (CH(CH₃)₂), 24.3 (NC(CH₃)), 22.9 (NCHCHCH₂). HRMS (ESI) calcd. for hydrolysed product [M^+] C₁₂H₂₁N₃ m/z 207.32, found 208.1862.

Synthesis of Compound 2



NMR Scale: 30 mg (0.05 mmol) **II** with 6.8 mg (0.05 mmol) of CyNCNCy. **Large Scale:** 50 mg (0.083 mmol) of **II** with 17.2 mg (0.083 mmol) of CyNCNCy, this was dissolved in toluene and left to stir at room temperature overnight. Solvent was removed *in vacuo* to yield yellow crystals of **2** (30 mg, 52% yield). ^1H NMR (300 MHz, d_8 -Tol, 300 K) δ_{H} (ppm): 7.14 – 6.96 (6H, m, Ar-*H*), 6.00 (2H, dt, $J_{\text{HH}} = 9$ Hz, NCH), 4.85 (1H, s, NC(CH₃)CH), 4.40 (2H, dt, $^3J = 9$ Hz, $^4J = 3$ Hz, NCHCH), 3.44 (4H, sept, $J_{\text{HH}} = 6$ Hz, CH(CH₃)₂), 3.10 (2H, m, NCH(CH₂)₂), 2.87 (2H, m, NCHCHCH₂), 1.86 – 0.78 (20H, m, Cy-*H*), 1.65 (6H, s, NC(CH₃)), 1.33 (12H, d, $J_{\text{HH}} = 9$ Hz, CH(CH₃)₂), 1.26 (12H, d, $J_{\text{HH}} = 9$ Hz, CH(CH₃)₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, d_8 -Tol, 300 K) δ_{C} (ppm): 169.7 (NC(CH₃), 163.8 (CN₃), 145.6 (*ipso*-Ar), 142.6 (*o*-Ar), 128.1 (NCH), 125.3 (*o*-Ar), 123.9 (*m*-Ar), 99.1 (NCHCH), 94.8 (NC(CH₃)CH), 53.5 (NCH(CH₂)₂), 37.0 (CH(CH₂)₂), 28.7 (CH(CH₃)₂), 26.5 (CH(CH₂)₂), 26.0 (CH(CH₃)₂), 25.8 (CH(CH₂)₂(CH₂)₂), 25.6 (CH(CH₃)₂), 24.5 (NC(CH₃)), 24.3 (CH(CH₂)₄CH₂), 22.8 (NCHCHCH₂). HRMS (ESI) calcd. for hydrolysed product [M^+] C₁₈H₂₉N₃ m/z 287.45, found 288.2549.

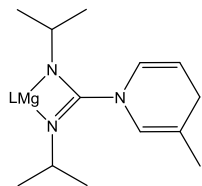
Synthesis of Compound 3



NMR Scale: 30 mg (0.05 mmol) **II** with 11.1 mg (0.05 mmol) of *p*-TolNCN*p*-Tol. ^1H NMR (300 MHz, d_8 -Tol, 300 K) δ_{H} (ppm): 7.11 – 6.99 (6H, m, Dipp-*H*), 6.81 (4H, m, *o*-*H* (*p*-Tol)), 6.67 (4H, m, *m*-*H* (*p*-Tol)), 6.00 (2H, d, $J_{\text{HH}} = 9$ Hz, NCHCH), 4.88 (1H, s, NC(CH₃)CH), 4.20 (2H, m, NCHCH), 3.64 (4H, m, CH(CH₃)₂), 2.68 (2H, s, NCHCHCH₂), 2.11 (6H, s, *p*-CH₃), 1.69 (6H, s, NC(CH₃)CH), 1.26 (12H, d, $J_{\text{HH}} = 6$ Hz, CH(CH₃)₂), 1.14 – 1.10 (12H, m, CH(CH₃)₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, d_8 -Tol, 300 K) δ_{C} (ppm): 168.3 (NC(CH₃)), 159.9 (*ipso*-C Dipp), 147.9 (*o*-C Dipp), 146.4 (*ipso*-C *p*-Tol), 143.0 (*o*-C *p*-Tol), 136.8(*p*-C *p*-Tol), 128.9 (*m*-C Dipp), 128.7 (*m*-C *p*-Tol), 124.9 (*p*-C Dipp), 124.0 (NCHCH), 100.7 (NCHCH), 97.6 (NC(CH₃)CH), 32.0 (CH(CH₃)₂), 27.9 (NCHCHCH₂), 25.0 (*p*-CH₃), 24.7 (NC(CH₃)), 21.2 (CH(CH₃)₂), 20.8 (CH(CH₃)₂). HRMS (ESI) calcd. for hydrolysed product $[\text{M}^+\text{H}^+]^+$ C₂₀H₂₁N₃ m/z 303.41, found 304.1814.

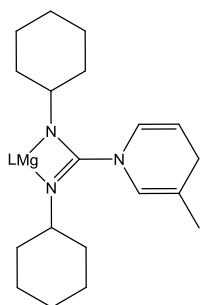
1,4-Dihydro-3-picolide reactions, III

Synthesis of Compound 4



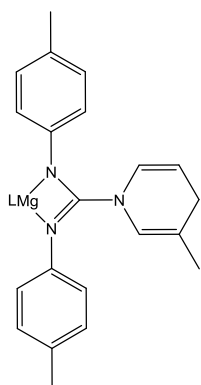
NMR Scale: 30 mg (0.048 mmol) **III** with 4.9 μL (0.048 mmol) of *i*PrNCNiPr.
Large Scale: 200 mg (0.32 mmol) of **III** with 49.3 μL (0.32 mmol) of *i*PrNCNiPr, this was dissolved in toluene and left to stir at room temperature overnight. Solvent was removed *in vacuo* to yield yellow crystals of **4** (140 mg, 66% yield). ^1H NMR (300 MHz, d_8 -Tol, 300 K) δ_{H} (ppm): 7.12 – 6.98 (6H, m, Ar), 6.02 (1H, dm, $^3J = 6$ Hz, $^4J = 3$ Hz, NCHCH), 5.87 (1H, m, NCHC(CH₃)), 4.85 (1H, s, NC(CH₃)CH), 4.46 (1H, dt, $^3J = 9$ Hz, $^4J = 3$ Hz, NCHCH), 3.43 (2H, sept, $J_{\text{HH}} = 6$ Hz, NCH(CH₃)₂), 3.33 (4H, sept, $J_{\text{HH}} = 6$ Hz, CH(CH₃)₂), 2.81 (2H, m, NC- HCHCH₂), 1.87 (3H, s, NCHC(CH₃)), 1.65 (6H, s, NC(CH₃)), 1.28 (12H, d, $J_{\text{HH}} = 6$ Hz, CH(CH₃)₂), 1.24 (12H, d, $J_{\text{HH}} = 6$ Hz, CH(CH₃)₂), 1.05 (12H, d, $J_{\text{HH}} = 6$ Hz, NCH(CH₃)₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, d_8 -Tol, 300 K) δ_{C} (ppm): 169.5 (NC(CH₃)), 164.5 (CN₃), 145.8 (*ipso*-Ar), 142.7 (*o*-Ar), 127.5 (NCH), 125.3 (*p*-Ar), 123.9 (*m*-Ar), 123.5 (NCHC(CH₃)), 107.1 (NCHC(CH₃)), 98.0 (NC(CH₃)CH), 95.0 (NCHCH), 45.0 (NCH(CH₃)₂), 28.3 (CH(CH₃)₂), 26.0(NCH(CH₃)₂), 25.4 (CH(CH₃)₂), 24.8 (NC(CH₃)), 24.3 (CH(CH₃)₂), 20.9 (NCHCHCH₂), 18.0 (NCHC(CH₃)).

Synthesis of Compound 5



NMR Scale: 30 mg (0.048 mmol) **III** with 11.5 mg (0.048 mmol) of CyNCNCy.
Large Scale: 200 mg (0.31 mmol) of **III** with 65.7 mg (0.31 mmol) of CyNCNCy, this was dissolved in toluene and left to stir at room temperature overnight. Solvent was removed *in vacuo* to yield yellow crystals of **5** (175 mg, 72% yield). ^1H NMR (300 MHz, d_8 -Tol, 300 K) δ_{H} (ppm): 7.15 – 7.07 (6H, m, Ar), 6.07 (1H, dm, $J_{\text{HH}} = 6$ Hz, NCHCH), 5.92 (1H, m, NCHC(CH₃)), 4.86 (1H, s, NC(CH₃)CH), 4.47 (1H, dt, $^3J = 6$ Hz, $^4J = 3$ Hz, NCHCH), 3.46 (4H, sept, $J_{\text{HH}} = 6$ Hz, CH(CH₃)₂), 3.12 (2H, m, NCH(CH₂)₂), 2.78 (2H, m, NCHCHCH₂), 1.83 (3H, s, NCHC(CH₃)), 1.73 (4H, m, Cy-H), 1.55 (4H, m, Cy-H), 1.66 (6H, s, NC(CH₃)), 1.34 (12H, d, $J_{\text{HH}} = 6$ Hz, CH(CH₃)₂), 1.26 (12H, d, $J_{\text{HH}} = 6$ Hz, CH(CH₃)₂), 1.29 – 0.99 (8H, m, Cy-H), 0.85 (4H, m, CH(CH₂)₂ (CH₂)₂CH₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, d_8 -Tol, 300 K) δ_{C} (ppm): 169.7 (NC(CH₃)), 164.0 (CN₃), 145.7 (*ipso*-Ar), 142.7 (*o*-Ar), 127.5 (NCH), 125.3 (*p*-Ar), 123.9 (*m*-Ar), 122.8 (NCHC(CH₃)), 107.3 (NCHC(CH₃)), 98.1 (NC(CH₃)CH), 94.9 (NCHCH), 53.6 (NCH(CH₂)₂), 37.0 (NCH(CH₂)₂), 28.4 (CH(CH₃)₂), 26.5 (CH(CH₂)₂(CH₂)₂), 26.1 (CH(CH₃)₂), 25.5 (CH(CH₃)₂), 24.6 (NC(CH₃)), 24.4 (CH(CH₂)₄CH₂), 20.9 (NCHCHCH₂) 18.0 (NCHC(CH₃)).

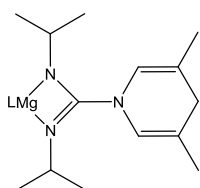
Synthesis of Compound 6



NMR Scale: 30 mg (0.048 mmol) **III** with 10.6 mg (0.048 mmol) of *p*-TolNCN*p*-Tol. ^1H NMR (300 MHz, d_8 -Tol, 300 K) δ_{H} (ppm): 7.10 – 6.98 (6H, m, Dipp-H), 6.76 (4H, m, *o*-H (*p*-Tol)), 6.52 (4H, m, *m*-H (*p*-Tol)), 6.08 (1H, m, NCHCH), 5.89 (1H, s, NCHC(CH₃)), 4.88 (1H, s, NC(CH₃)CH), 4.30 (1H, m, NCHCH), 3.63 (4H, m, CH(CH₃)₂), 2.59 (2H, s, NCHCHCH₂), 2.07 (6H, s, *p*-CH₃), 1.70 (6H, s, NC(CH₃)CH), 1.26 (12H, d, $J_{\text{HH}} = 6$ Hz, CH(CH₃)₂), 1.20 (3H, s, NCHC(CH₃)), 1.11 – 1.08 (12H, m, CH(CH₃)₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, d_8 -Tol, 300 K) δ_{C} (ppm): 168.2 (NC(CH₃)), 159.7 (*ipso*-C Dipp), 148.0 (*o*-C Dipp), 146.6 (*ipso*-C *p*-Tol), 143.1 (*o*-C *p*-Tol), 137.2 (*p*-C *p*-Tol), 128.8 (*m*-C Dipp), 128.6 (*m*-C *p*-Tol), 124.8 (*p*-C Dipp), 124.0 (NCHCH), 123.8 (NCH(CH₃)), 108.9 (NCHCH), 100.1 (NCHC(CH₃)), 97.5 (NC(CH₃)CH), 28.5 (NCHCHCH₂), 28.0 (CH(CH₃)₂), 25.1 (*p*-CH₃), 24.7 (NC(CH₃)), 20.8 (CH(CH₃)₂), 17.7 (NCHC(CH₃)). HRMS (ESI) calcd. for hydrolysed product $[\text{M}^+\text{H}^+]^+$ C₂₁H₂₃N₃ m/z 317.44, found 318.2011.

1,4-Dihydro-3,5-Lutidine reactions, IV

Synthesis of Compound 7



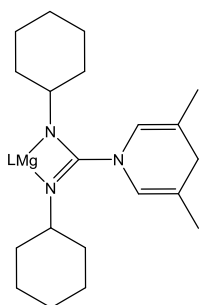
NMR Scale: 30 mg (0.046 mmol) **IV** with 4.7 μL (0.046 mmol) of iPrNCNiPr .

Large Scale: 50 mg (0.076 mmol) of **IV** with 11.7 μL (0.076 mmol) of iPrNCNiPr ,

this was dissolved in toluene and left to stir at room temperature overnight. Solvent was removed *in vacuo* to yield yellow crystals of **7** (40 mg, 78% yield). ^1H NMR

(300 MHz, $\text{d}_8\text{-Tol}$, 300 K) δ_{H} (ppm): 7.15 – 7.08 (6H, m, Ar), 5.94 (2H, s, NCH), 4.86 (1H, s, NC(CH₃)CH), 3.53 (2H, sept, $J_{\text{HH}} = 6$ Hz, NCH(CH₃)₂), 3.45 (4H, sept, $J_{\text{HH}} = 6$ Hz, CH(CH₃)₂), 2.65 (2H, s, NCHC(CH₃)CH₂), 1.53 (6H, s, NCHC(CH₃)), 1.30 (12H, d, $J_{\text{HH}} = 9$ Hz, CH(CH₃)₂), 1.25 (12H, d, $J_{\text{HH}} = 6$ Hz, CH(CH₃)₂), 0.86 (6H, d, $J_{\text{HH}} = 6$ Hz, NCH(CH₃)₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, $\text{d}_8\text{-Tol}$, 300 K) δ_{C} (ppm): 169.4 (NC(CH₃)), 164.7 (CN₃), 146.0 (*ipso*-Ar), 142.1 (*o*-Ar), 125.2 (*p*-Ar), 123.9 (*m*-Ar), 122.4 (NCH), 106.0 (NCHC(CH₃)), 95.1 (NC(CH₃)CH), 45.1 (NCH(CH₃)₂), 34.3 (NCHC(CH₃)CH₂), 28.2 (CH(CH₃)₂), 26.0 (CH(CH₃)₂), 25.3 (CH(CH₃)₂), 24.7 (CH(CH₃)₂), 24.4 (NC(CH₃)), 20.7 (NCHC(CH₃)). HRMS (ESI) calcd. for hydrolysed product [M^+] C₁₄H₂₅N₃ m/z 235.38, found 236.2214.

Synthesis of Compound 8



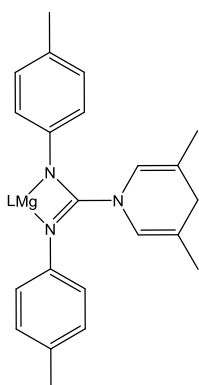
NMR Scale: 30 mg (0.046 mmol) **IV** with 6.3 mg (0.046 mmol) of CyNCNCy .

Large Scale: 50 mg (0.076 mmol) of **IV** with 15.7 mg (0.076 mmol) of CyNCNCy ,

this was dissolved in toluene and left to stir at room temperature overnight. Solvent was removed *in vacuo* to yield yellow crystals of **8** (30 mg, 52% yield). ^1H NMR

(300 MHz, $\text{d}_8\text{-Tol}$, 300 K) δ_{H} (ppm): 7.15 – 7.08 (6H, m, Ar), 6.01 (2H, s, NCH), 4.90 (1H, s, NC(CH₃)CH), 3.51 (2H, sept, $J_{\text{HH}} = 6$ Hz, NCH(CH₃)₂), 3.16 (2H, m, NCH(CH₂)₂), 2.62 (2H, s, NCHC(CH₃)CH₂), 1.89 (6H, s, NCHC(CH₃)), 1.75 – 1.55 (8H, m, Cy-H), 1.70 (6H, s, NC(CH₃)), 1.38 (12H, d, $J_{\text{HH}} = 6$ Hz, CH(CH₃)₂), 1.30 (12H, d, $J_{\text{HH}} = 6$ Hz, CH(CH₃)₂), 1.29 – 1.05 (8H, m, Cy-H), 0.90 (4H, m, CH(CH₂)₂(CH₂)₂CH₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, $\text{d}_8\text{-Tol}$, 300 K) δ_{C} (ppm): 169.6 (NC(CH₃)), 164.1 (CN₃), 145.8 (*ipso*-Ar), 142.7 (*o*-Ar), 125.2 (*p*-Ar), 123.9 (*m*-Ar), 122.4 (NCH), 106.3 (NCHC(CH₃)), 94.9 (NC(CH₃)CH), 53.7 (NCH(CH₂)₂), 37.0 (NCH(CH₂)₂), 35.4 (NCHC(CH₃)CH₂), 28.4 (CH(CH₃)₂), 26.5 (CH(CH₂)₂(CH₂)₂), 26.1 (CH(CH₃)₂), 25.5 (CH(CH₃)₂), 24.6 (NC(CH₃)), 24.4 (CH(CH₂)₄CH₂), 17.9 (NCHC(CH₃)).

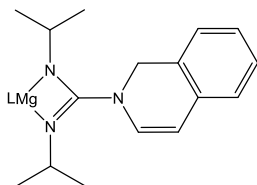
Synthesis of Compound 9



NMR Scale: 30 mg (0.046 mmol) **IV** with 10.1 mg (0.046 mmol) of *p*-TolNCN*p*-Tol. ^1H NMR (300 MHz, d_8 -Tol, 300 K) δ_{H} (ppm): 7.11 – 6.98 (6H, m, Dipp-*H*), 6.81 (4H, m, *o*-*H* (*p*-Tol)), 6.61 (4H, m, *m*-*H* (*p*-Tol)), 5.98 (2H, s, NCHC(CH₃)), 4.89 (1H, s, NC(CH₃)CH), 3.69 (4H, m, CH(CH₃)₂), 2.46 (2H, s, NCHC(CH₃)CH₂), 2.06 (6H, s, *p*-CH₃), 1.73 (6H, s, NC(CH₃)CH), 1.29 (6H, s, NCHC(CH₃)) 1.15 – 1.12 (12H, m, CH(CH₃)₂), 0.93 – 0.89 (12H, m, CH(CH₃)₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, d_8 -Tol, 300 K) δ_{C} (ppm): 168.0 (NC(CH₃)), 159.7 (*ipso*-C Dipp), 148.1 (*o*-C Dipp), 146.9 (*ipso*-C *p*-Tol), 143.2 (*o*-C *p*-Tol), 132.8 (*p*-C *p*-Tol), 128.6 (*m*-C Dipp), 128.4 (*m*-C *p*-Tol), 124.7 (*p*-C Dipp), 124.0 (NCHCH), 108.1 (NCHC(CH₃)), 97.5 (NC(CH₃)CH), 34.2 (CH(CH₃)₂), 28.0 (NCHC(CH₃)CH₂), 25.2 (*p*-CH₃), 24.7 (NC(CH₃)), 20.7 (CH(CH₃)₂), 20.6 (CH(CH₃)₂), 17.7 (NCHC(CH₃)). HRMS (ESI) calcd. for hydrolysed product $[\text{M}^+\text{H}^+]^+$ C₂₂H₂₅N₃ m/z 331.46, found 332.2207, $[\text{M}^+\text{Na}^+]^+$ C₂₂H₂₅N₃Na m/z 354.45, found 354.2028.

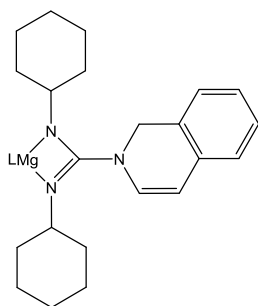
1,2-dihydro-*iso*-quinolide reactions, I

Synthesis of Compound 10



NMR Scale: 30 mg (0.043 mmol) **I** with 4.4 μL (0.043 mmol) of *i*PrNCNiPr.
Large Scale: 50 mg (0.071 mmol) of **I** with 11.0 μL (0.071 mmol) of *i*PrNCNiPr, this was dissolved in toluene and left to stir at room temperature overnight. Solvent was removed *in vacuo* to yield red crystals of **10** (30 mg, 61% yield). ^1H NMR (300 MHz, d_8 -Tol, 300 K) δ_{H} (ppm): 7.24 – 6.74 (10H, m, Ar-*H*, *i*Quin-*H*), 6.31 (1H, d, $J_{\text{HH}} = 6$ Hz, NCH), 5.50 (1H, d, $J_{\text{HH}} = 6$ Hz, NCHCH), 4.84 (1H, s, NC(CH₃)CH), 4.46 (2H, s, NCH₂), 3.44 (6H, m, CH(CH₃)₂, NCH(CH₃)₂), 1.65 (6H, s, NC(CH₃)), 1.30 (12H, d, $J_{\text{HH}} = 6$ Hz, CH(CH₃)₂), 1.25 (12H, d, $J_{\text{HH}} = 6$ Hz, CH(CH₃)₂), 0.79 (12H, d, $J_{\text{HH}} = 6$ Hz, CH(CH₃)₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, d_8 -Tol, 300 K) δ_{C} (ppm): 169.6 (NC(CH₃)), 165.4 (CN₃), 145.6 (*ipso*-Ar), 142.7 (*o*-Ar), 135.5 (*i*Quin(H)-C), 133.6 (*i*Quin(H)-C), 132.9 (NCH), 126.4 (*i*Quin(H)-C), 125.8 (*i*Quin(H)-C), 125.3 (*p*-Ar), 123.8 (*m*-Ar), 102.4 (NCHCH), 94.8 (NC(CH₃)CH), 52.4 (NCH₂), 45.1 (NCH(CH₃)₂), 28.3 (CH(CH₃)₂), 26.1 (CH(CH₃)₂), 25.4 (CH(CH₃)₂), 24.5 (NC(CH₃)), 24.3 (CH(CH₃)₂), 23.9 (CH(CH₃)₂). HRMS (ESI) calcd. for hydrolysed product $[\text{M}^+]$ C₁₆H₂₃N₃ m/z 257.38, found 258.2035.

Synthesis of Compound 11

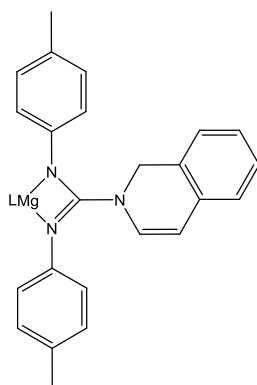


NMR Scale: 30 mg (0.043 mmol) **I** with 5.9 mg (0.043 mmol) of CyNCNCy.

Large Scale: 50 mg (0.071 mmol) of **I** with 14.6 mg (0.071 mmol) of CyNCNCy, this was dissolved in toluene and left to stir at room temperature overnight. Solvent was removed *in vacuo* to yield red crystals of **11** (37 mg, 67% yield). ¹H NMR (300 MHz, d₈-Tol, 300 K) δ_H(ppm): 7.10 – 6.74 (10H, m, Ar-*H*, iQuin(H)-*H*), 6.37 (1H, d, ³*J* = 9 Hz, NCH), 5.52 (1H, d, *J*_{HH} = 9 Hz, NCHCH), 4.87 (1H, s, NC(CH₃)CH), 4.52 (2H, s, NCH₂), 3.47 (4H, sept, *J*_{HH}

= 6 Hz, CH(CH₃)₂), 3.05 (2H, m, NCH(CH₂)₂), 1.66 (6H, s, NC(CH₃)), 1.58 – 1.38 (8H, m, Cy-*H*), 1.33 (12H, d, *J*_{HH} = 6 Hz, CH(CH₃)₂), 1.26 (12H, d, *J*_{HH} = 6 Hz, CH(CH₃)₂), 1.14 – 0.76 (12H, m, Cy-*H*). ¹³C{¹H} NMR (75.5 MHz, d₈-Tol, 300 K) δ_C (ppm): 169.6 (NC(CH₃)), 165.2 (CN₃), 145.8 (*ipso*-Ar), 142.7 (*o*-Ar), 136.0 (iQuin(H)-*C*), 133.7 (iQuin(H)-*C*), 132.9 (NCH), 127.7 (iQuin(H)-*C*), 126.4 (iQuin(H)-*C*), 125.3 (*p*-Ar), 123.8 (*m*-Ar), 102.4 (NCHCH), 94.9 (NC(CH₃)CH), 53.9 (NCH(CH₂)₂), 50.8 (NCH₂), 37.1 (Cy-*C*), 35.4 (Cy-*C*), 28.3 (CH(CH₃)₂), 26.4 (Cy-*C*), 26.0 (CH(CH₃)₂), 25.8 (Cy-*C*), 25.5 (CH(CH₃)₂), 24.6 (NC(CH₃)), 24.4 (CH(CH₃)₂), 23.9 (CH(CH₃)₂). HRMS (ESI) calcd. for hydrolysed product [M⁺] C₂₂H₃₁N₃ *m/z* 337.51, found 338.2714.

Synthesis of Compound 12

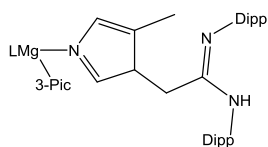


NMR Scale: 30 mg (0.043 mmol) **I** with 9.5 mg (0.043 mmol) of *p*-TolNCN*p*-Tol.

¹H NMR (500 MHz, C₆D₆, 300 K) δ_H (ppm): 7.24 – 6.41 (18H, m, Ar-*H*), 6.07 (1H, d, *J*_{HH} = 5 Hz, NCHCH), 5.32 (1H, d, *J*_{HH} = 5 Hz, NCHCH), 4.94 (1H, s, NC(CH₃)CH), 4.40 (2H, s, NCH₂), 3.32 (4H, m, CH(CH₃)₂), 1.76 (6H, s, NC(CH₃)CH), 1.67 (6H, s, *p*-CH₃), 1.63 (12H, d, *J*_{HH} = 5 Hz, CH(CH₃)₂), 1.22 (12H, d, *J*_{HH} = 5 Hz, CH(CH₃)₂). ¹³C{¹H} NMR (125.75 MHz, d₈-Tol, 300 K) δ_C (ppm): 168.7 (NC(CH₃)CH), 161.9 (N₃C), 148.5 (*ipso*-*C* Ar), 147.0 (*ipso*-*C p*-Tol), 143.7 (*o*-*C p*-Tol), 143.1 (*o*-*C* Ar), 136.4

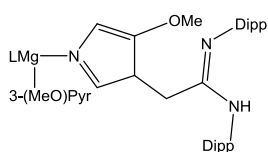
(iQuin(H)-*C*), 133.6 (iQuin(H)-*C*), 133.5 (*p*-*C p*-Tol), 130.4 (NCH), 129.8 (iQuin(H)-*C*), 129.0 (*p*-Ar-*C*), 128.7 (iQuin(H)-*C*), 127.8 (iQuin(H)-*C*), 126.9 (iQuin(H)-*C*), 126.6 (*m*-*C p*-Tol), 126.1 (*m*-*C* Ar), 105.4 (NCHCH), 94.6 (NC(CH₃)CH), 51.5 (NCH₂), 37.3 (CH(CH₃)₂), 29.0 (NC(CH₃)CH), 28.4 (*p*-CH₃ *p*-Tol), 25.5 (CH(CH₃)₂), 25.2 (CH(CH₃)₂), 24.4 (CH(CH₃)₂), 23.8 (CH(CH₃)₂). HRMS (ESI) calcd. for hydrolysed product [M⁺H⁺]⁺ C₂₄H₂₃N₃ *m/z* 353.47, found 354.1970.

Synthesis of Compound 13



NMR Scale: 30 mg (0.048 mmol) **III** with 17.3 mg (0.048 mmol) of DippNCNDipp. **Large Scale:** 200 mg (0.32 mmol) of **III** with 115.4 mg (0.32 mmol) of DippNCNDipp, this was dissolved in toluene and left to stir at room temperature overnight. Solvent was removed *in vacuo* to yield yellow crystals of **13** (220 mg, 69% yield). ^1H NMR (300 MHz, d_8 -Tol, 300 K) δ_{H} (ppm): 7.76 (1H, m, *o*-CH 3Pic), 7.13- 6.98 (12H, m, Ar-*H*), 6.67 (1H, s, *o*-CHC(CH₃) 3Pic), 6.64 (1H, m, *p*-*H*, 3Pic), 6.35 (1H, m, *m*-*H* 3Pic), 6.09 (1H, s, NCH), 5.89 (1H, s, NCH), 5.83 (1H, s, CH₂), 4.92 (1H, s, NC(CH₃)CH), 4.17 (1H, s, CH₂), 4.01 (1H, s, NH), 3.90 (2H, m, CH(CH₃)₂), 3.61 (2H, m, CH(CH₃)₂), 3.41 (4H, m, CH(CH₃)₂), 1.75 (6H, s, NC(CH₃)CH), 1.73 (3H, s, NCHC(CH₃), 1.61 (3H, s, *m*-CH₃ 3Pic), 1.38 – 1.09 (39H, m, CH(CH₃)₂, 3-CH₃ 3Pic), 1.23 (12H, d, $J_{\text{HH}} = 6$ Hz, CH(CH₃)₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.75 MHz, d_8 -Tol, 300 K) δ_{C} (ppm): 169.7 (NC(CH₃)CH), 150.5 (NCNH), 149.2 (*ipso*-C), 146.8 (*ipso*-C NCN), 146.7 (*ipso*-C NCNH), 145.2 (*o*-C), 143.4 (*o*-C NCN), 141.9 (*o*-C NCNH), 138.1 (*o*-C Pyr), 136.9 (*o*-C Pyr), 135.9 (*p*-C), 130.2 (*p*-C NCN), 128.7 (*p*-C NCNH), 127.6 (*p*-C Pyr), 126.6 (*m*-C(CH₃) Pyr), 126.2 (NCHCCH₂), 125.9 (NCHC(CH₃)C), 124.1 (*m*-C), 123.9 (*m*-C NCN), 123.6 (*m*-C NCNH), 120.0 (NCHC(CH₃)), 117.3 (NCH), 94.6 (NC(CH₃)CH), 70.0 (CH₂), 29.9 (CH(CH₃)₂), 28.7 (CH(CH₃)₂ NCN), 28.5 (CH(CH₃)₂ NCNH), 28.0 (NC(CH₃)CH), 26.6 (CH(CH₃)₂), 25.8 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 24.4 (CH₃), 23.8 (CH(CH₃)₂), 14.3 (3-CH₃ 3Pic). Elemental Analysis for C₆₆H₉₁MgN₆ (found): C 79.85 (79.98); H 9.24 (9.38); N 8.47 (8.19). HRMS (ESI) calcd. for hydrolysed product [M⁺H⁺]⁺ C₃₁H₄₃N₃ m/z 457.71, found 458.3667.

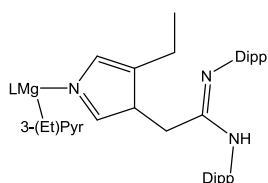
Synthesis of Compound 14



NMR Scale: 50 mg of [HC{(Me)CN(2,6-^{*i*}Pr₂C₆H₃)₂MgBu] (0.1 mmol), with 2 equivalents of 3-(MeO)pyridine (20.2 μL , 0.2 mmol) and 1 equivalent of PhSiH₃ (12.3 μL , 0.1 mmol) was heated for 2 days at 60 °C to form the dihydropyridide complex, 0.1 mmol of DippNCNDipp (36 mg) was then added. ^1H NMR (500 MHz, C₆D₆, 300 K) δ_{H} (ppm): 7.48 (1H, m, *o*-CH 3Pic), 7.13 – 6.95 (14H, m, Ar-*H*, *o*,*m*-CH 3Pic), 6.86 (1H, s, NCH), 6.68 (1H, d, $J_{\text{HH}} = 5$ Hz, *p*-CH 3Pic), 5.77 (1H, s, NCH), 5.47 (1H, s, CH₂), 4.89 (1H, s, N(CH₃)CH), 4.18 (1H, s, CH₂), 4.00 (1H, s, NH), 3.88 (2H, m, CH(CH₃)₂), 3.60 (2H, m, CH(CH₃)₂), 3.51 (2H, m, CH(CH₃)₂), 3.34 (3H, s, OCH₃), 3.28 (CH(CH₃)₂), 2.81 (3H, s, OCH₃ Pyr), 1.73 (6H, s, NC(CH₃)CH), 1.33 (12H, m, CH(CH₃)₂), 1.21 (12H, d, $J_{\text{HH}} = 5$ Hz, CH(CH₃)₂), 1.12 (24H, m, CH(CH₃)₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.75 MHz, d_8 -Tol, 300 K) δ_{C} (ppm): 169.7 (NC(CH₃)CH), 157.1 (NCNH), 149.4 (*ipso*-C), 147.5 (*ipso*-C NCN), 146.5 (*ipso*-C NCNH), 145.0 (*o*-C), 143.7 (*o*-C NCN), 142.3 (*o*-C NCNH), 137.3 (*o*-C Pyr), 136.7 (*o*-C Pyr), 135.9 (*p*-C), 130.2 (*p*-C NCN), 128.7 (*p*-C NCNH), 127.5 (*p*-C Pyr), 126.5 (*m*-C(CH₃) Pyr), 125.9 (NCHCCH₂), 125.8 (NCHC(CH₃)C) 124.1

(*m*-C), 123.9 (*m*-C), 123.6 (*m*-C NCN), 123.1 (*m*-C NCNH), 111.0 (NCHC(CH₃), 108.3 (NCH), 94.5 (NC(CH₃)CH), 74.4 (CH₂), 58.0 (OCH₃), 56.1 (OCH₃ Pyr), 29.9 (CH(CH₃)₂), 28.7 (CH(CH₃)₂ NCN), 28.6 (CH(CH₃)₂ NCNH), 28.0 (NC(CH₃)CH), 26.5 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 24.3 (CH(CH₃)₂), 23.7 (CH(CH₃)₂), 23.1 (CH(CH₃)₂).

Synthesis of Compound 15



NMR Scale: 50 mg of [HC{(Me)CN(2,6-ⁱPr₂C₆H₃)₂MgBu}] (0.1 mmol), with 2 equivalents of 3-(Et)pyridine (22.4 μL, 0.2 mmol) and 1 equivalent of PhSiH₃ (12.3 μL, 0.1 mmol) was heated for 2 days at 60 °C to form the dihydropyridide complex, 0.1 mmol of DippNCNDipp (36 mg) was then added. ¹H NMR (500 MHz, C₆D₆, 300 K) δ_H (ppm): 7.48 (1H, m, *o*-CH Pyr), 7.14 – 7.02 (13H, m, Ar-H, *o*-CH Pyr), 6.81 (1H, m, *p*-CH Pyr), 6.49 (1H, m, *m*-CH Pyr), 6.19 (1H, s, NCH), 5.86 (1H, s, NCH), 5.83 (1H, s, CH₂), 4.21 (1H, s, CH₂), 4.03 (1H, s, NH), 3.87 (2H, m, CH(CH₃)₂), 3.60 (2H, m, CH(CH₃)₂), 3.40 (2H, m, CH(CH₃)₂), 2.80 (2H, m, CH(CH₃)₂), 2.44 (2H, m, CH₂CH₃), 2.05 (2H, m, 3-CH₂CH₃ Pyr), 1.74 (6H, s, NC(CH₃)CH), 1.35 (12H, m, CH(CH₃)₂), 1.20 (12H, d, *J*_{HH} = 5 Hz, CH(CH₃)₂), 1.13 (12H, m, CH(CH₃)₂), 1.08 (3H, t, *J*_{HH} = 10 Hz, 3-CH₂CH₃), 0.93 (3H, t, *J*_{HH} = 10 Hz, 3-CH₂CH₃ Pyr), 0.77 (12H, m, CH(CH₃)₂). ¹³C{¹H} NMR (125.75 MHz, d₈-Tol, 300 K) δ_C (ppm): 169.7 (NC(CH₃)CH), 150.2 (NCNH), 149.2 (*ipso*-C), 146.9 (*ipso*-C NCN), 145.2 (*ipso*-C NCNH), 143.7 (*o*-C), 143.4 (*o*-C NCN), 142.8 (*o*-C NCNH), 137.4 (*o*-C Pyr), 136.8 (*o*-C Pyr), 135.9 (*p*-C), 130.2 (*p*-C NCN), 128.7 (*p*-C NCNH), 127.6 (*p*-C Pyr), 126.7 (*m*-C(CH₃) Pyr), 126.0 (NCHCCH₂), 125.2 (NCHC(CH₃)) 125.9 (NCHC(CH₃)C), 124.4 (*m*-C), 124.1 (*m*-C), 123.9 (*m*-C NCN), 123.6 (*m*-C NCNH), 119.5 (NCH), 108.3 (NCH), 94.5 (NC(CH₃)CH), 76.0 (CH₂), 29.9 (CH(CH₃)₂), 29.3 (CH₂CH₃), 28.9 (3-CH₂CH₃ Pyr), 28.6 (CH(CH₃)₂ NCN), 28.5 (CH(CH₃)₂ NCNH), 28.0 (NC(CH₃)CH), 26.5 (CH(CH₃)₂), 26.4 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 24.7 (CH₂CH₃), 24.5 (3-CH₂CH₃ Pyr), 23.7 (CH(CH₃)₂), 23.2 (CH(CH₃)₂).

Figure S1: Stacked ^1H NMR spectra showing **III** (bottom) and the resulting spectrum from the insertion of N,N' -di-*iso*-propylcarbodiimide to give compound **13** (top)

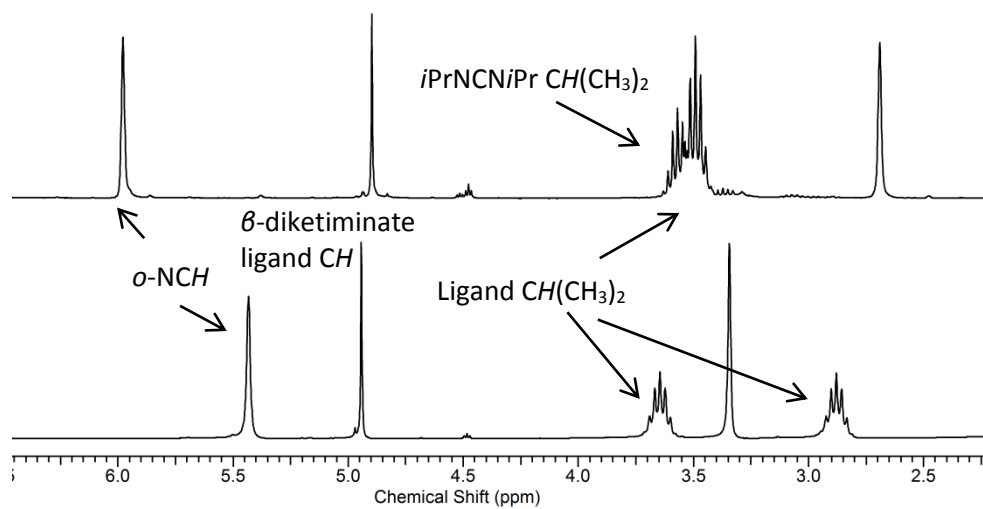


Figure S2: ^1H NMR spectrum for compound **13** illustrating the distinctive five (1H) singlet resonances

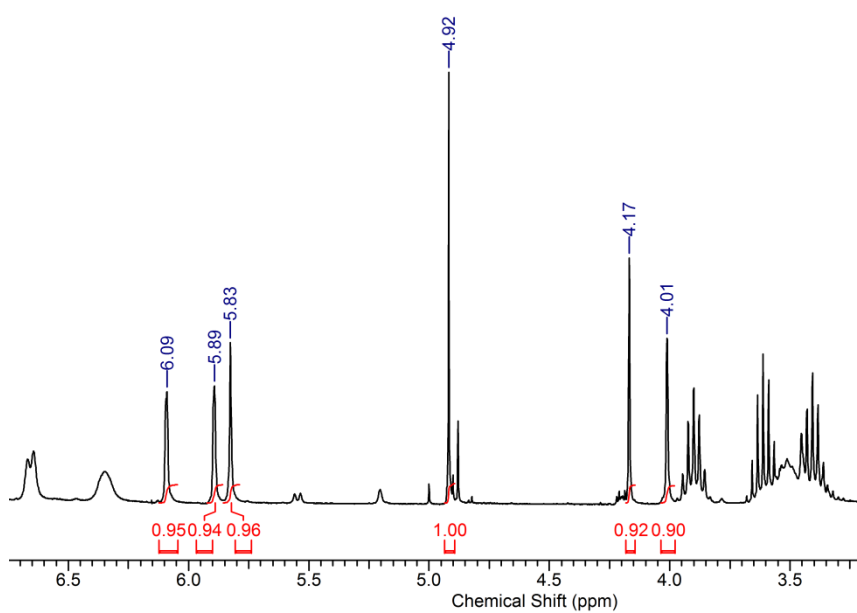


Figure S3: ^1H NMR spectrum of the reaction of **III-d₇** with DippNCNDipp to form compound **13-d₇**

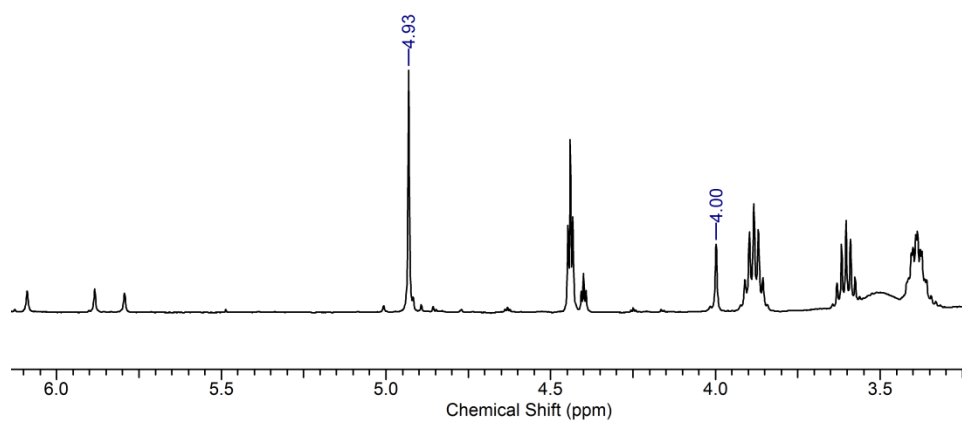
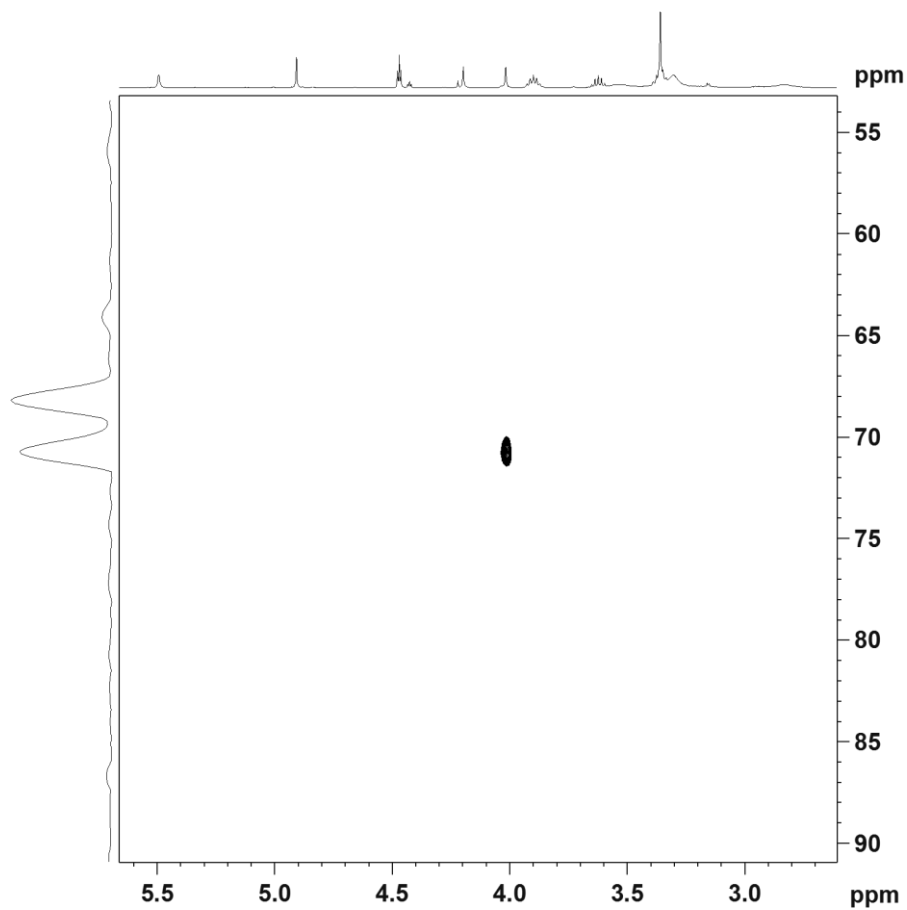
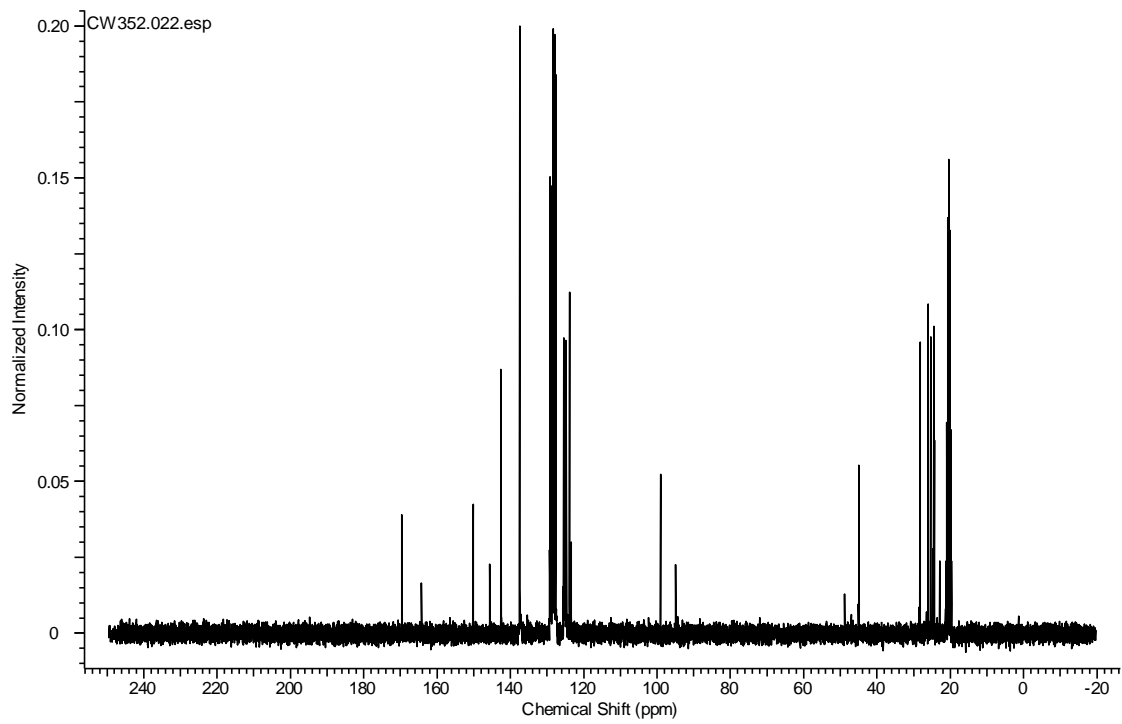
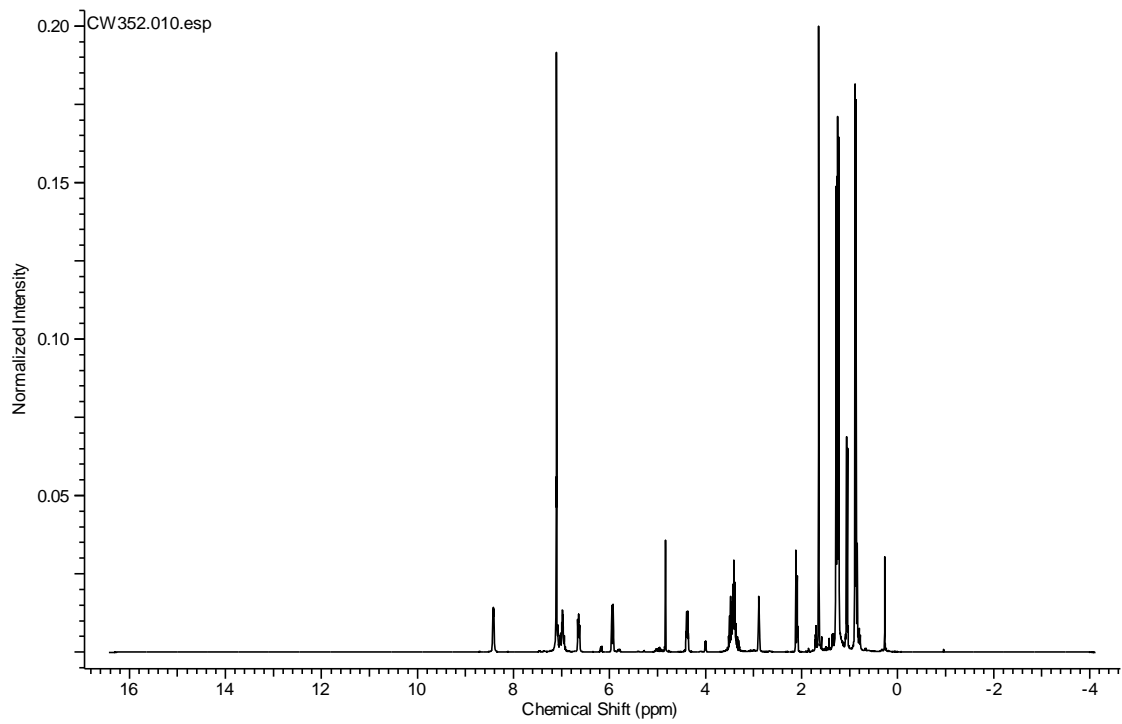


Figure S4: ^1H - ^{14}N HSQC for compound **13-d₇**

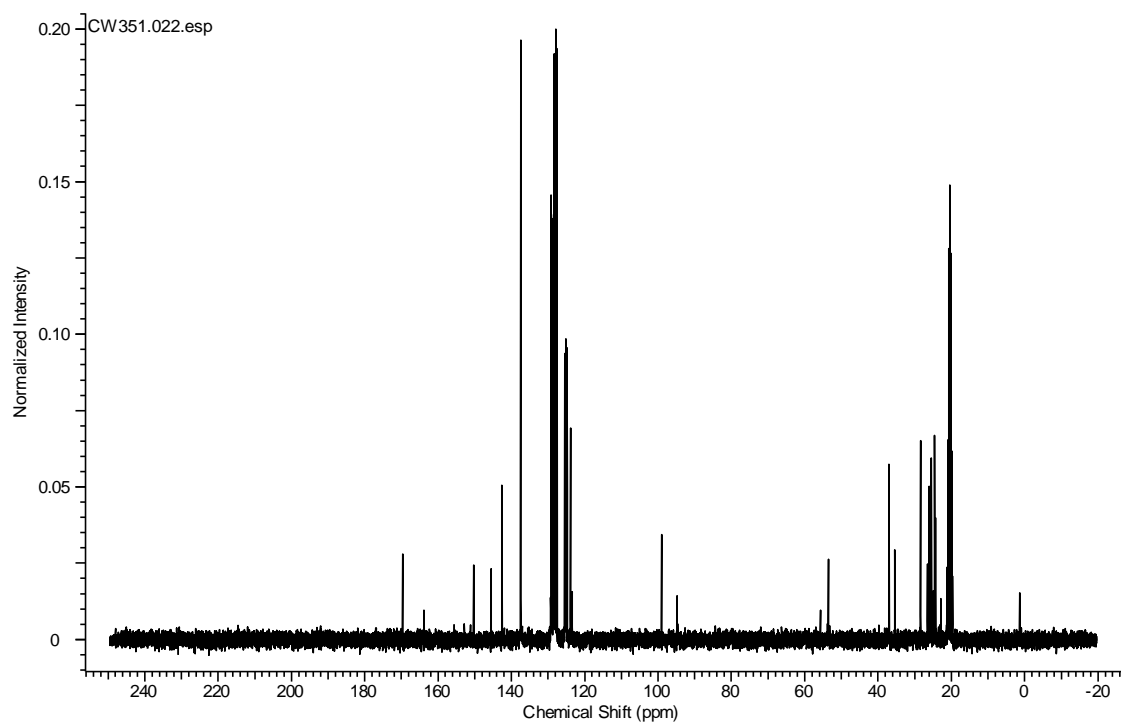
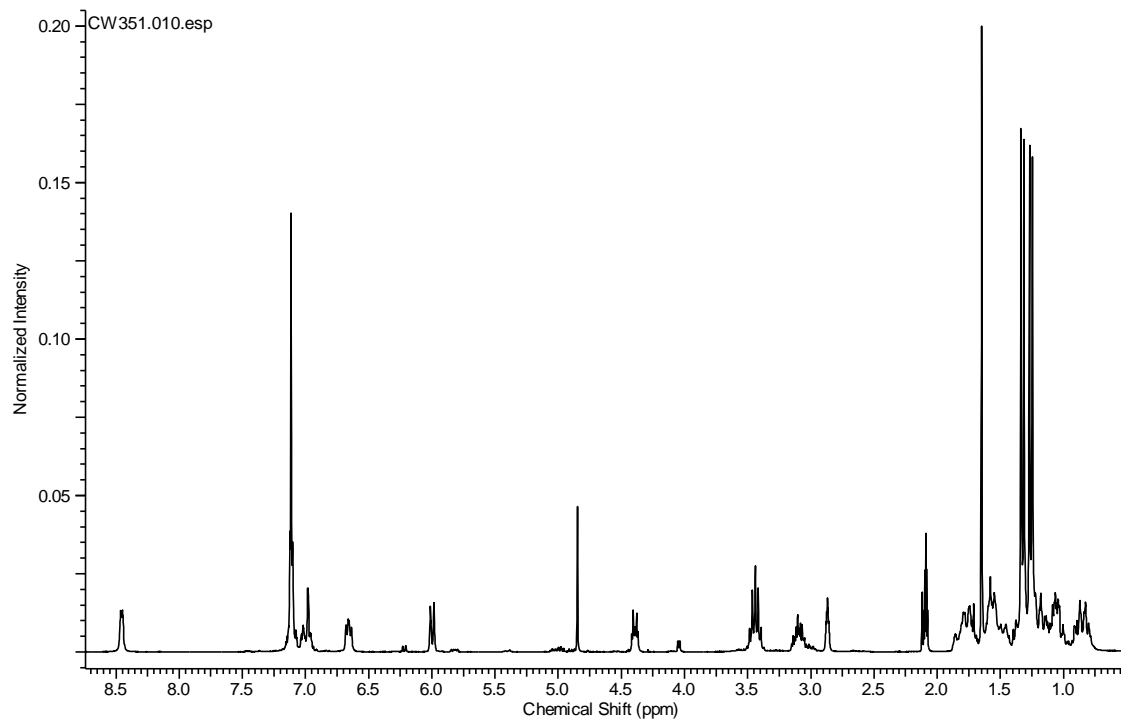


NMR Spectra

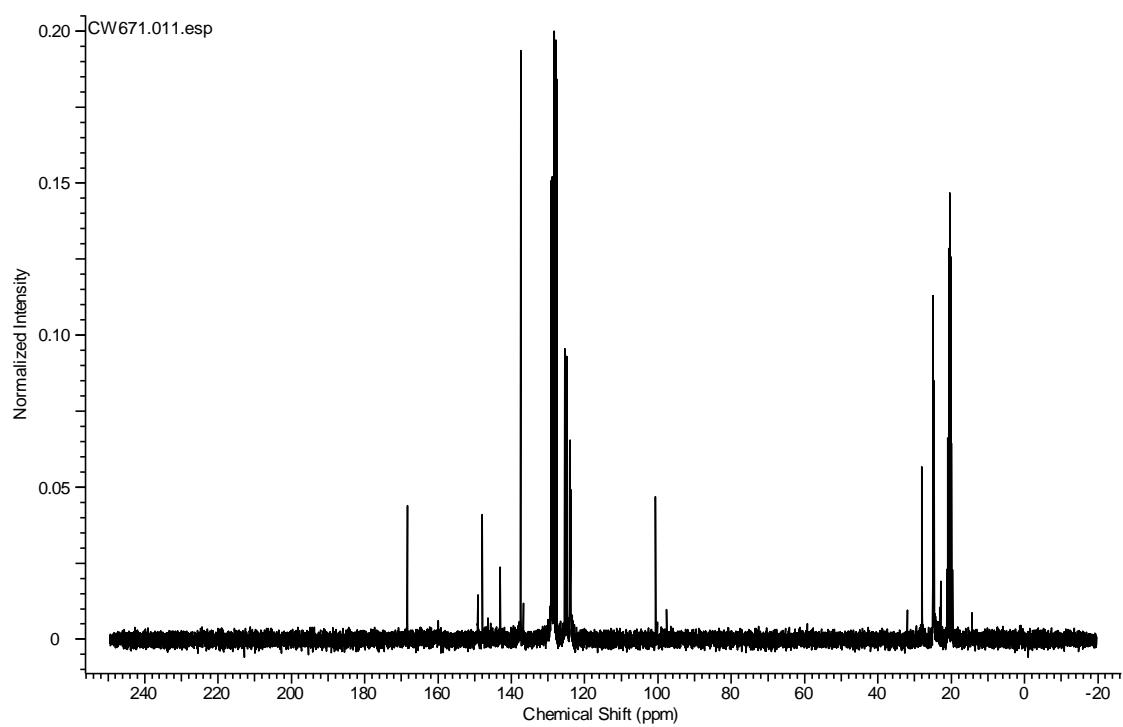
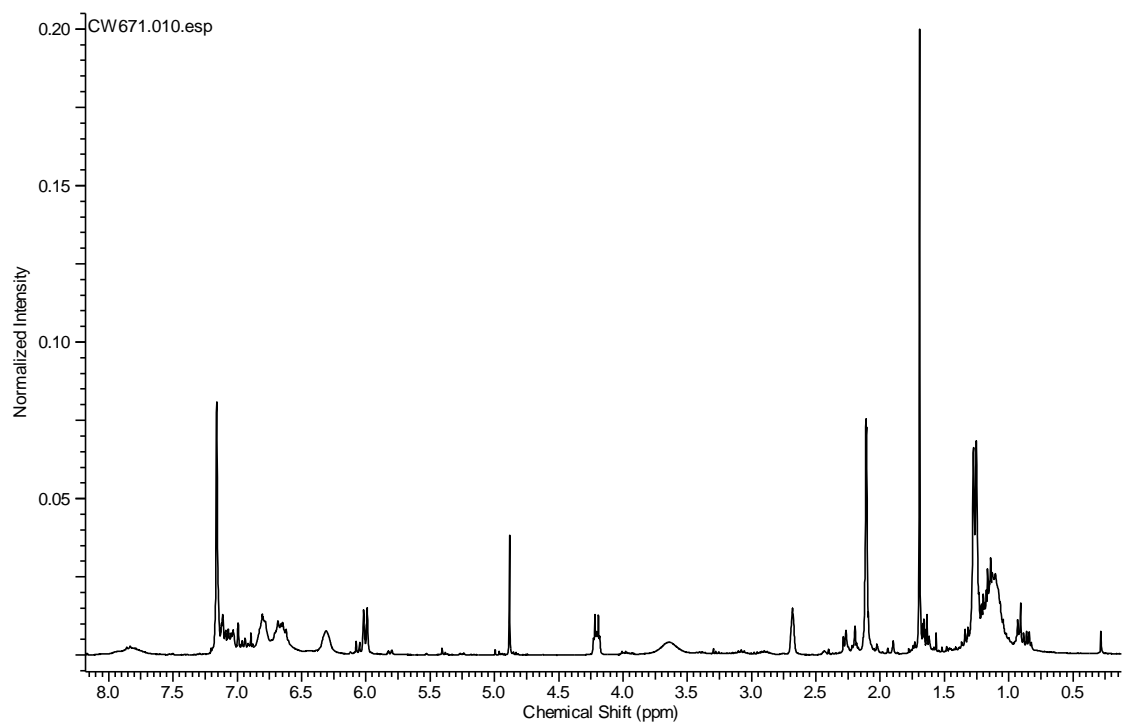
Compound 1



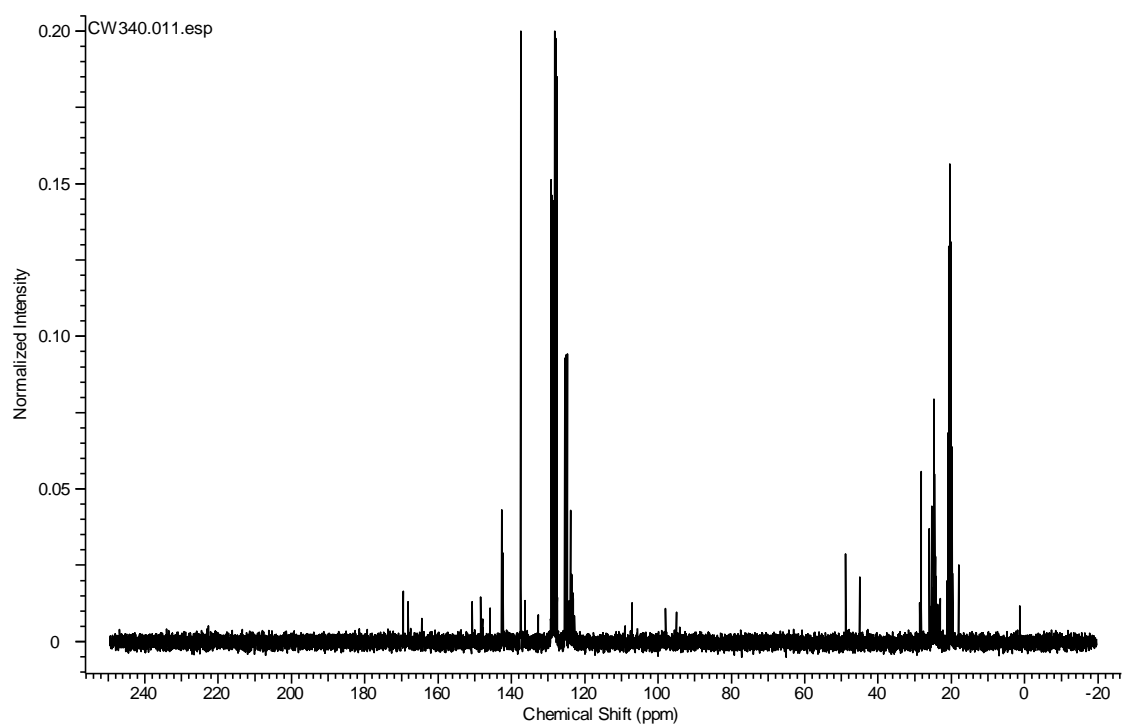
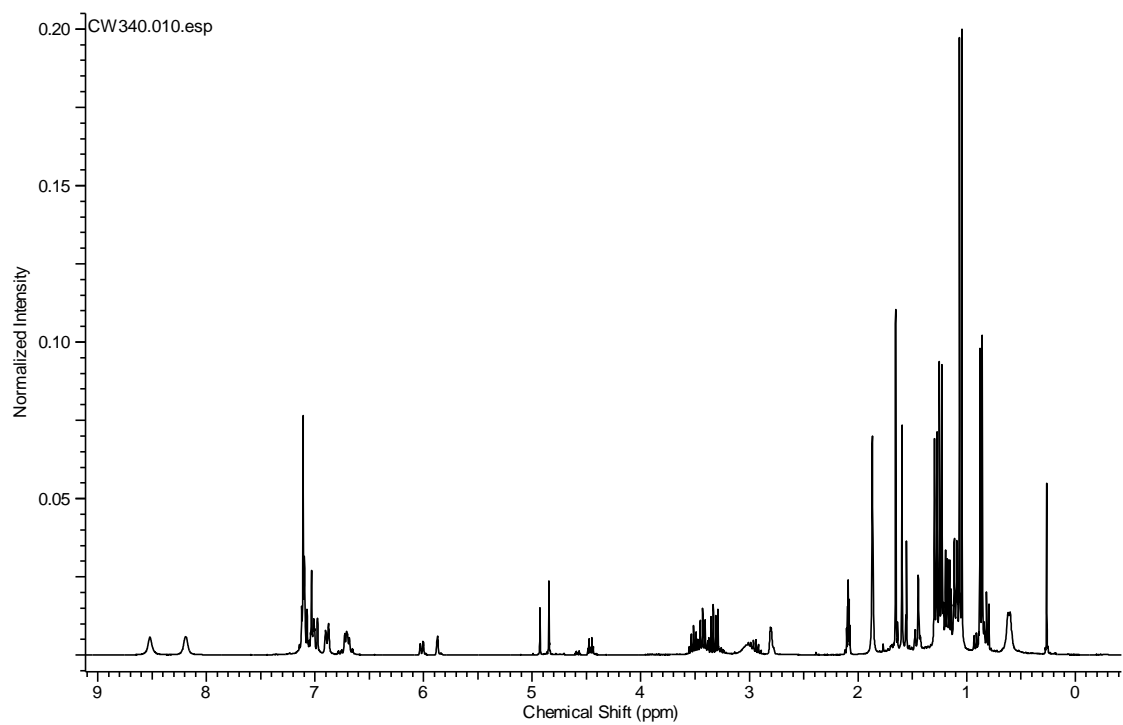
Compound 2



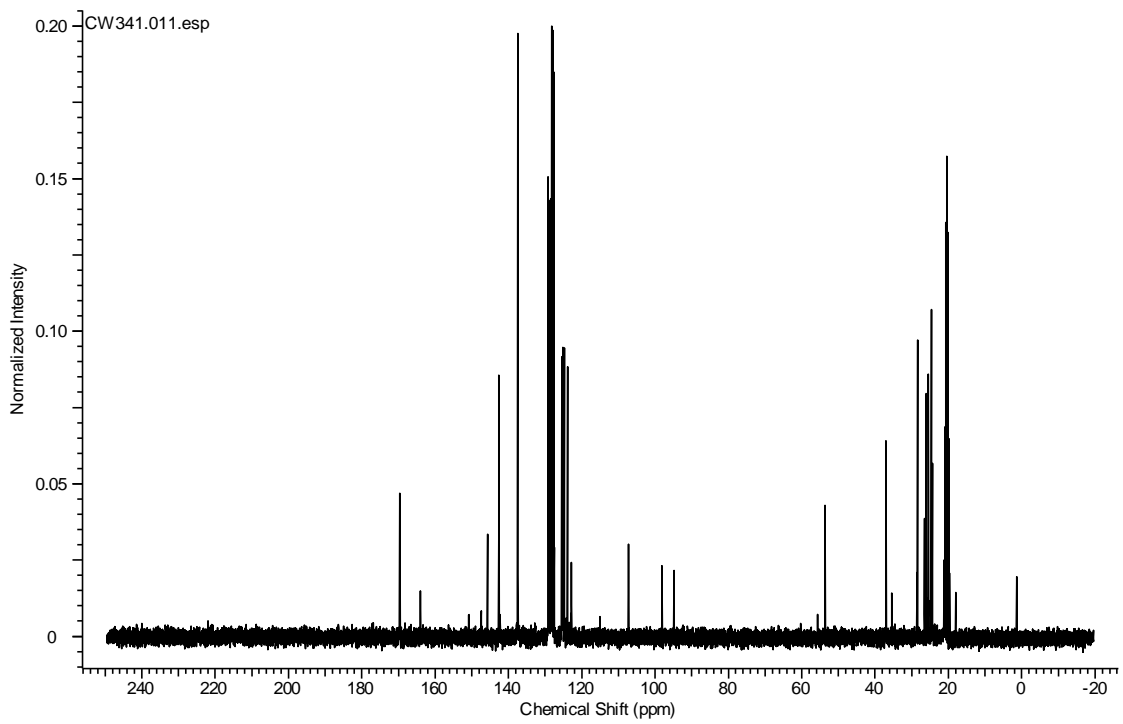
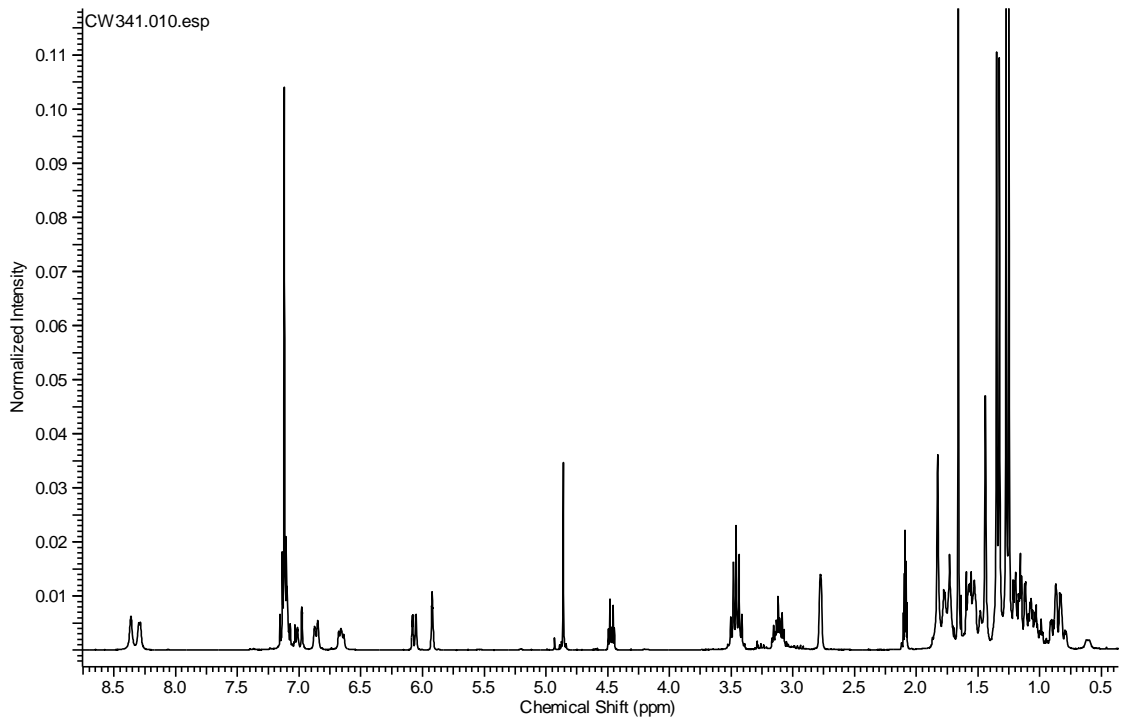
Compound 3



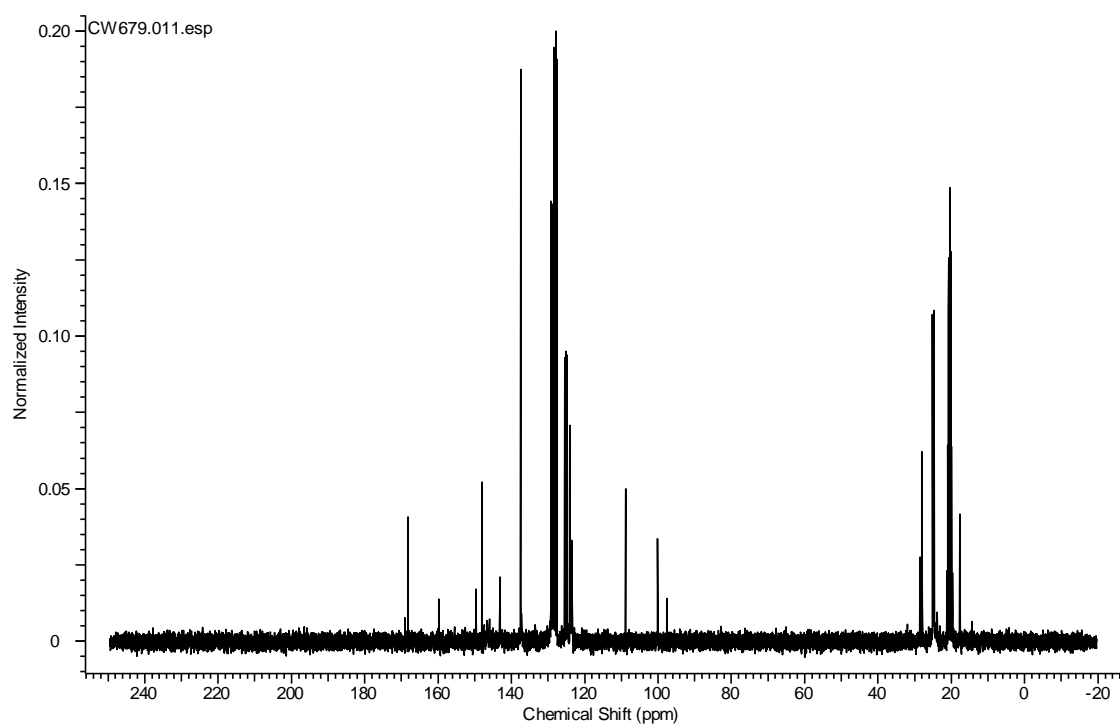
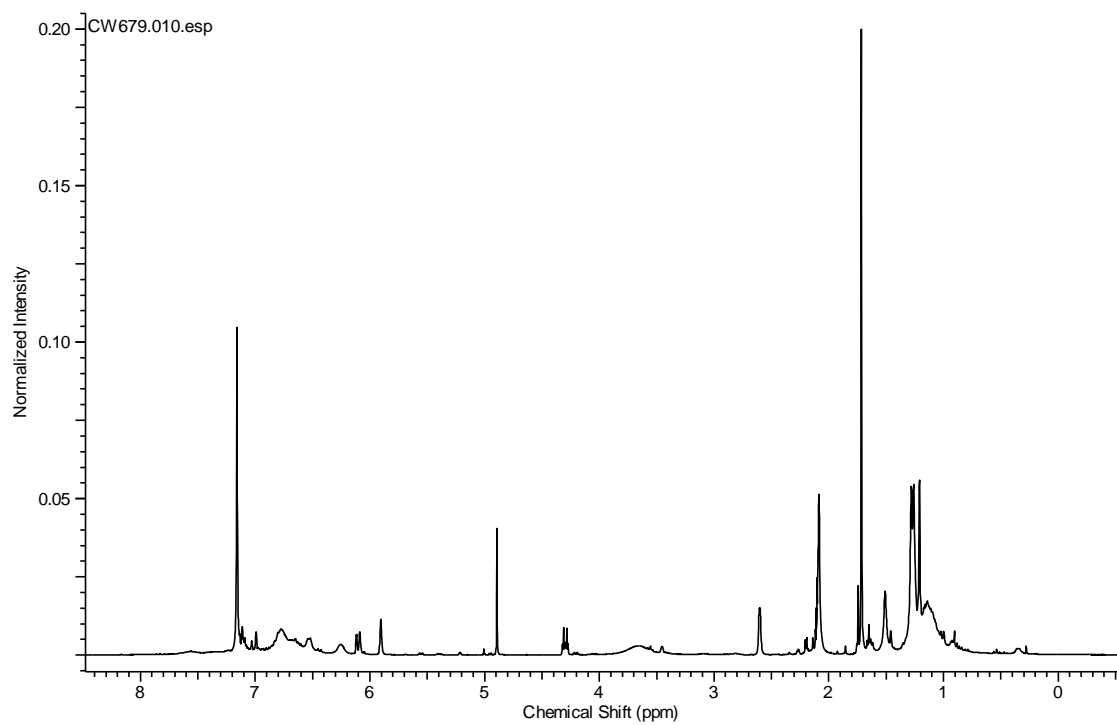
Compound 4



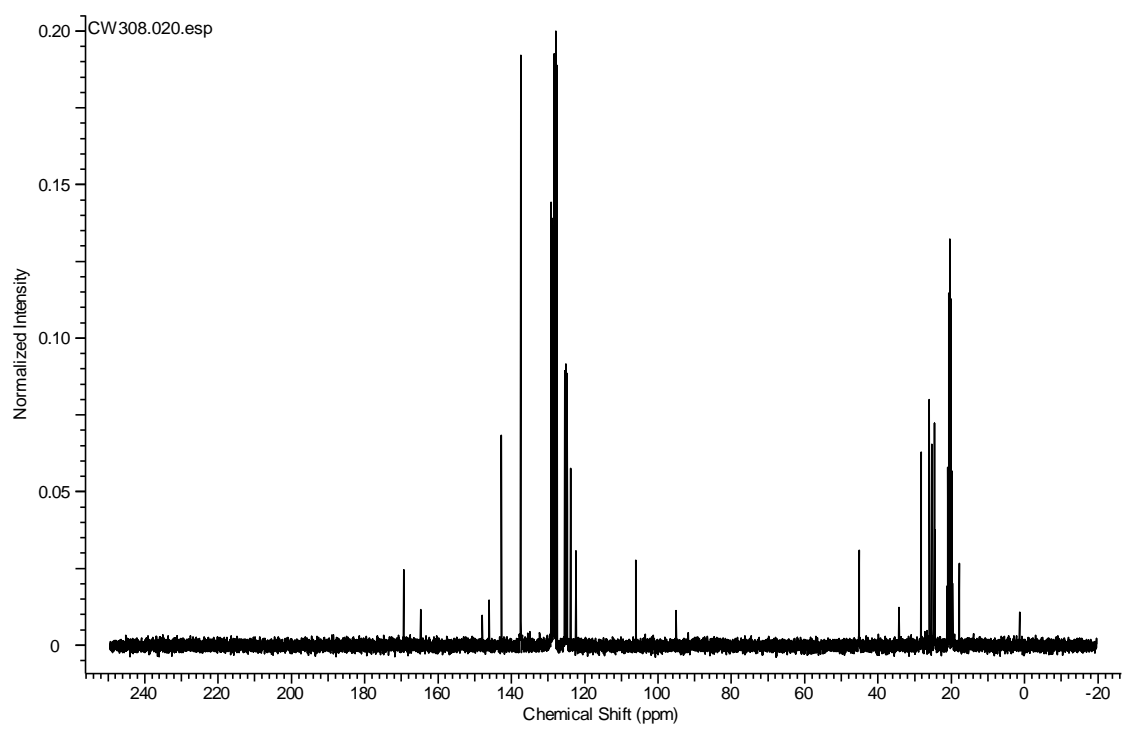
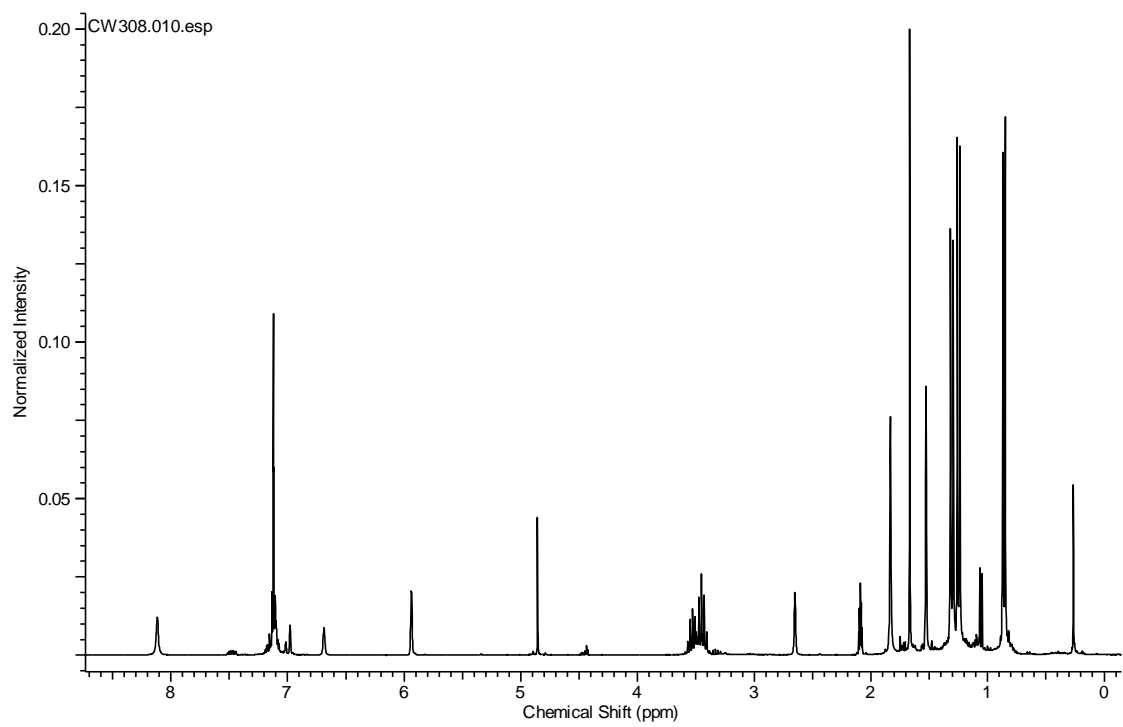
Compound 5



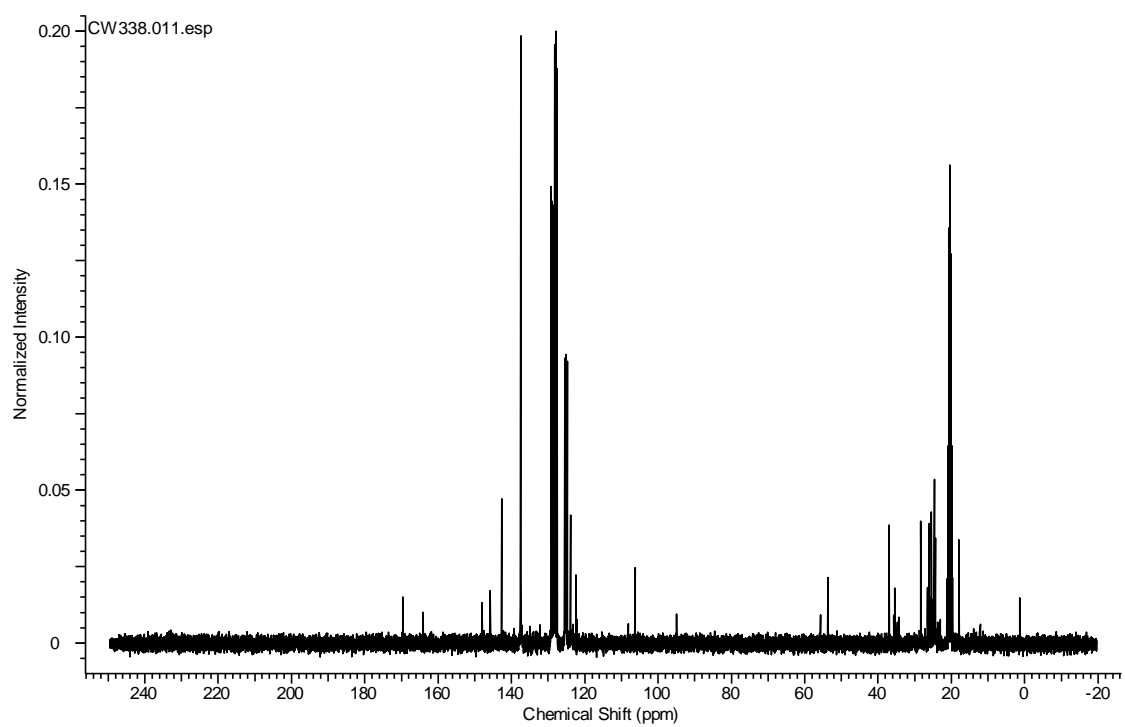
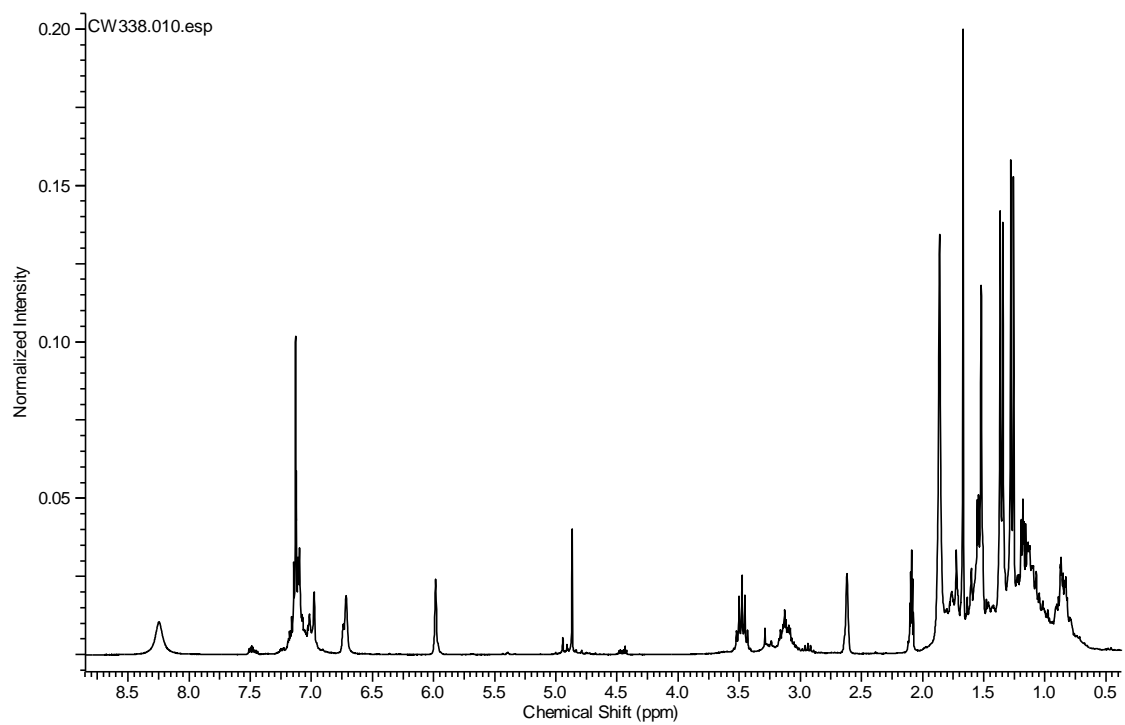
Compound 6



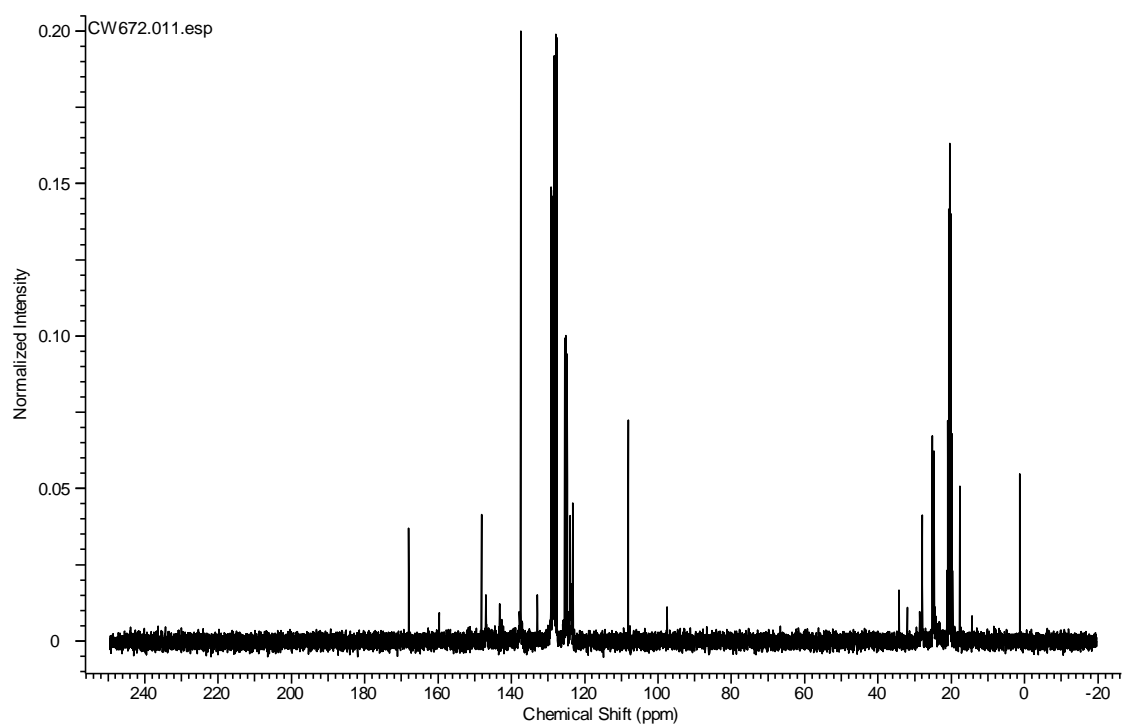
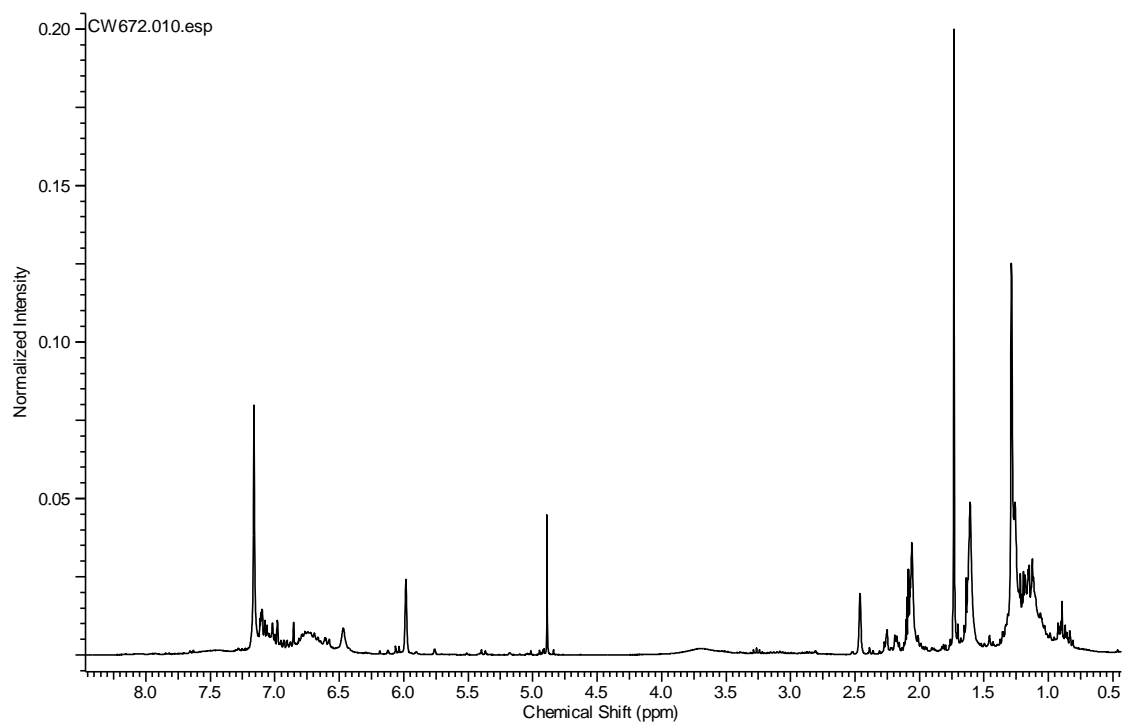
Compound 7



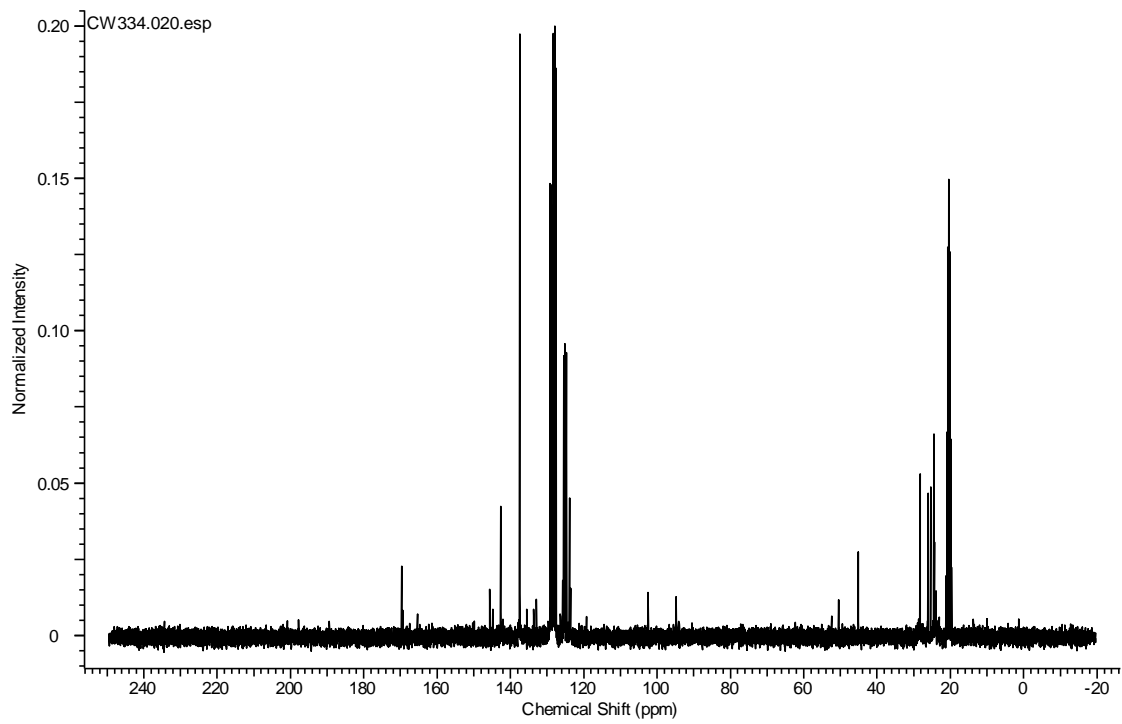
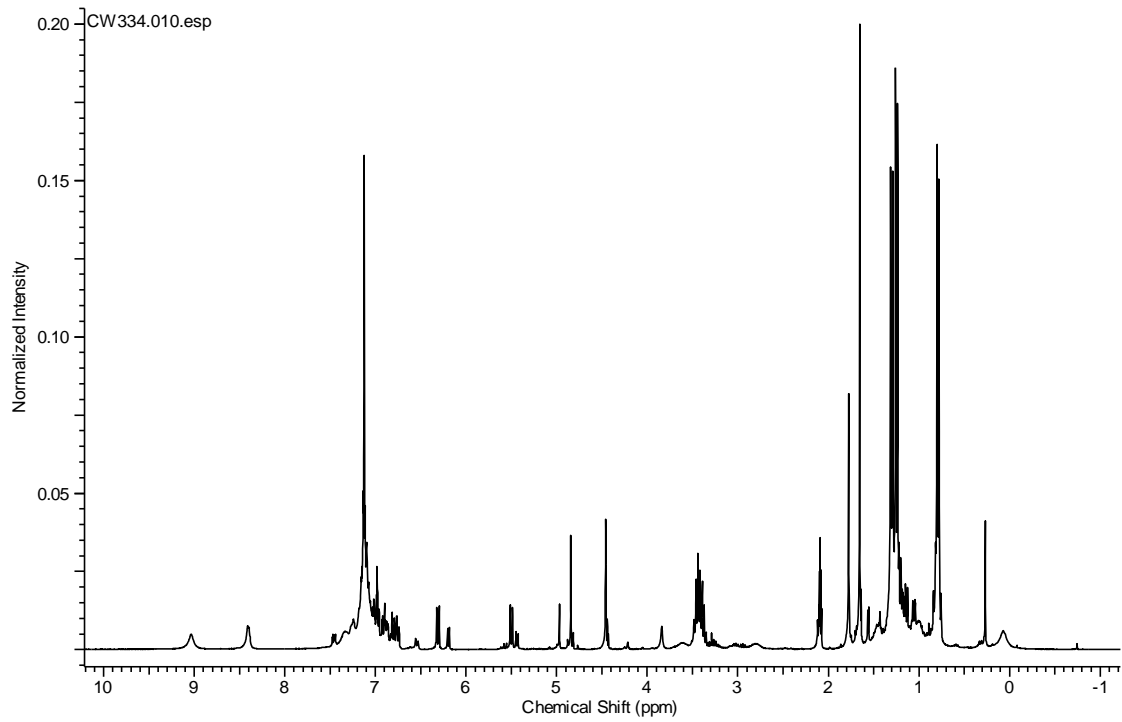
Compound 8



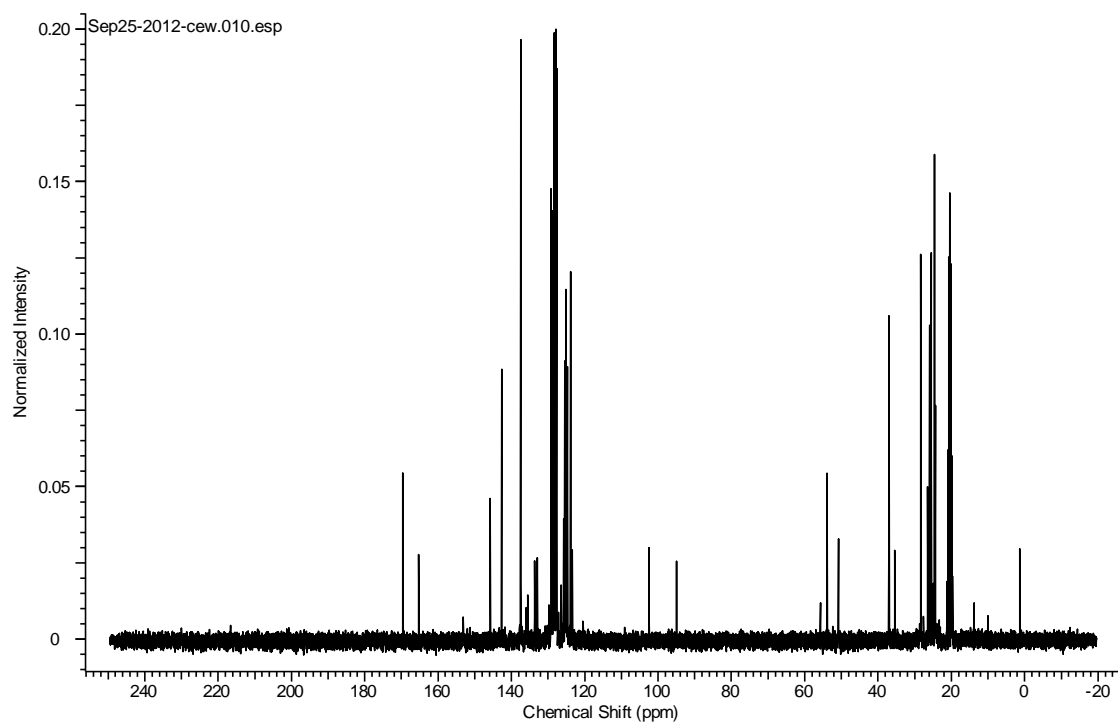
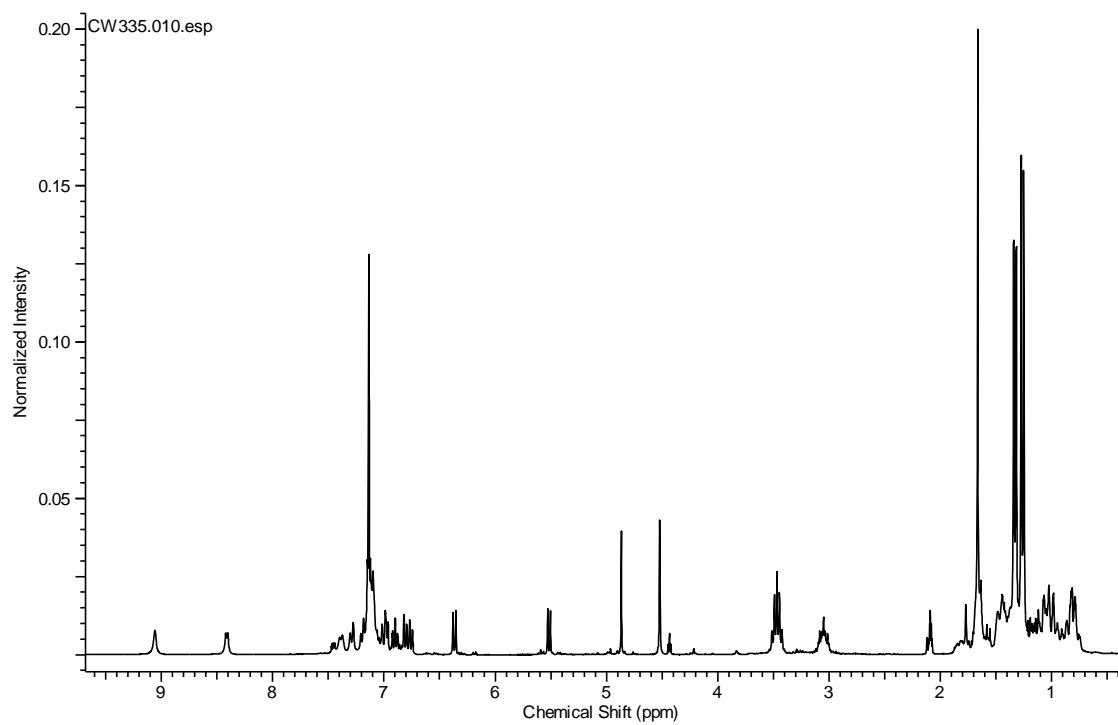
Compound 9



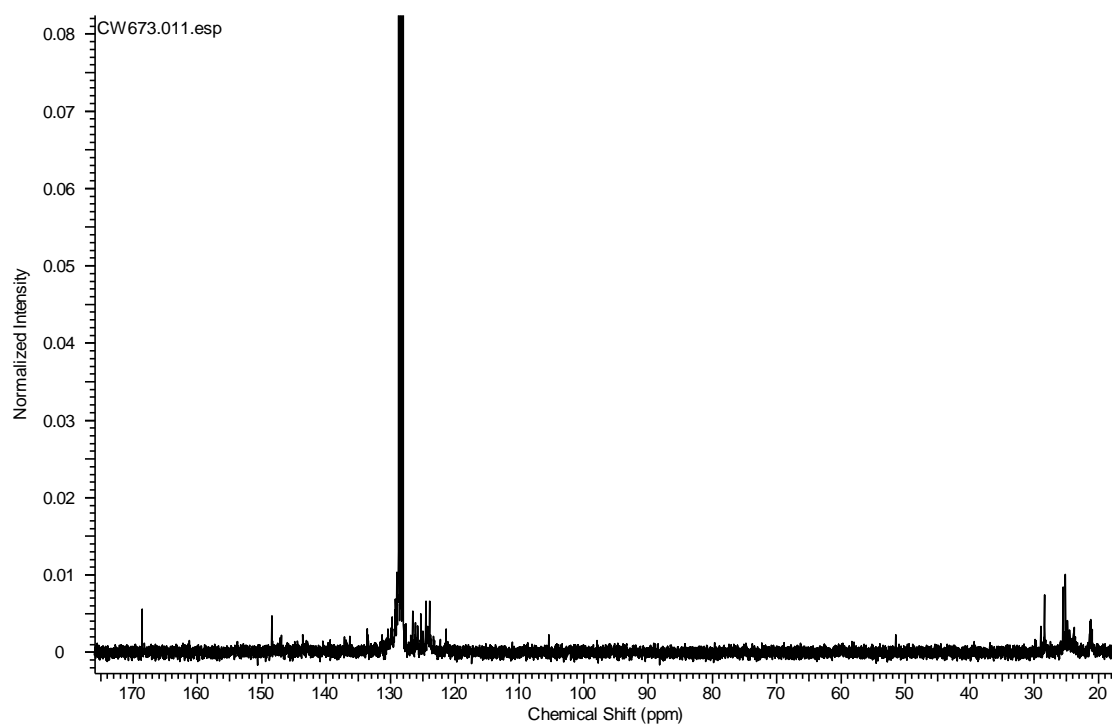
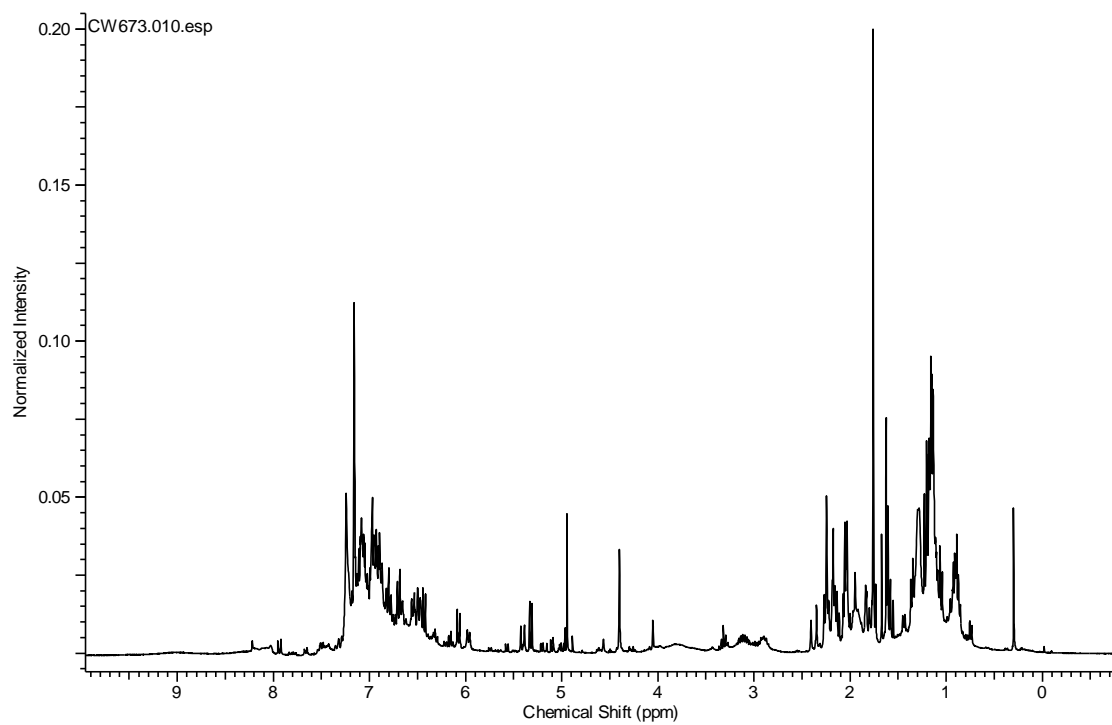
Compound 10



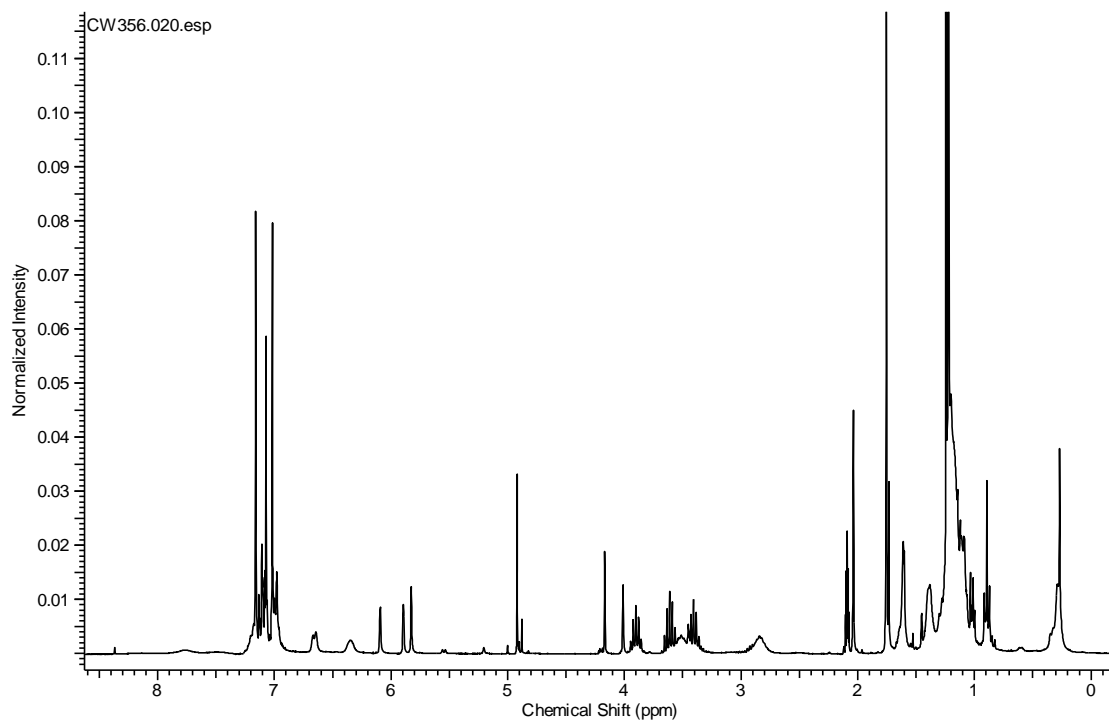
Compound 11



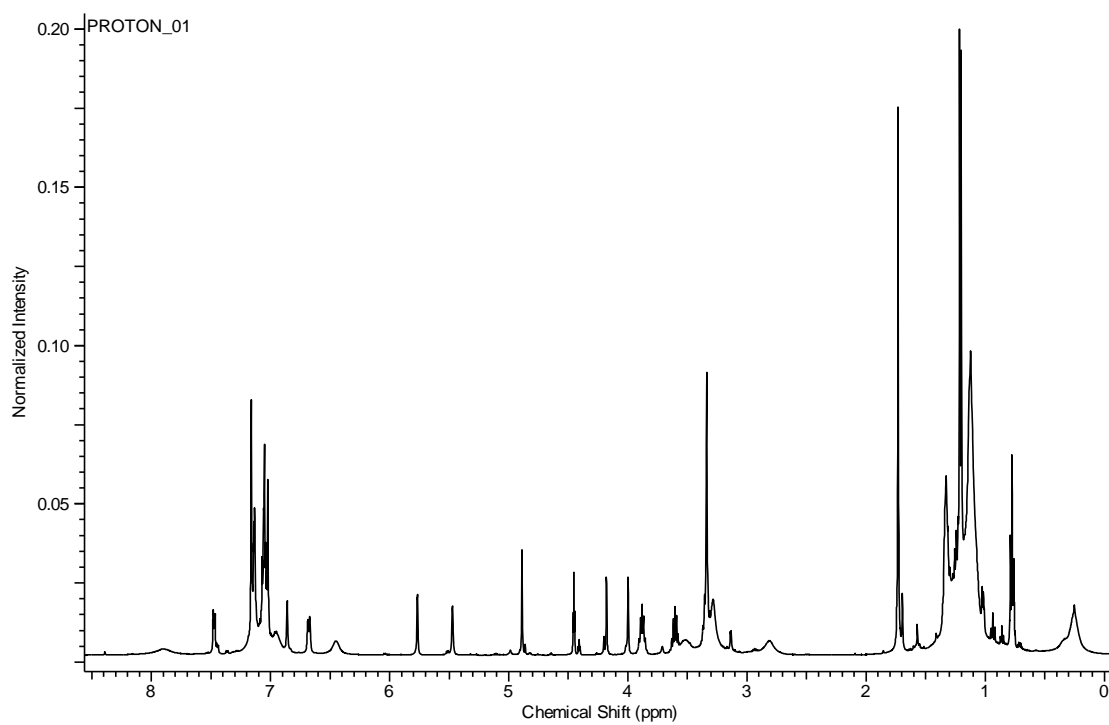
Compound 12

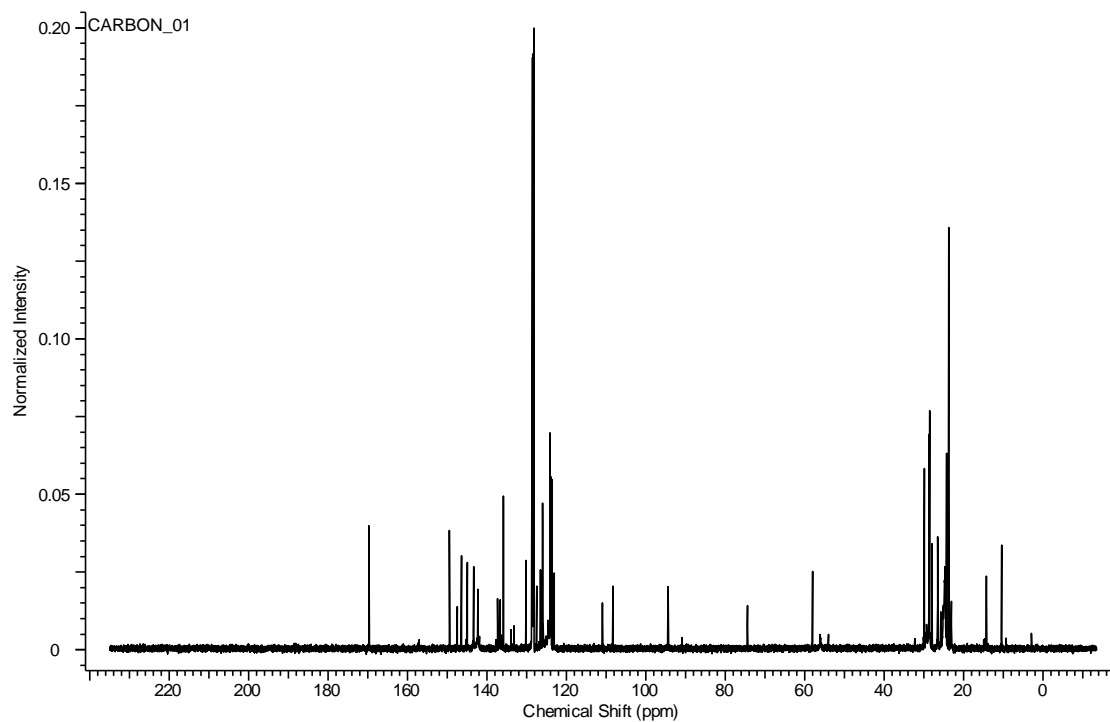


Compound 13

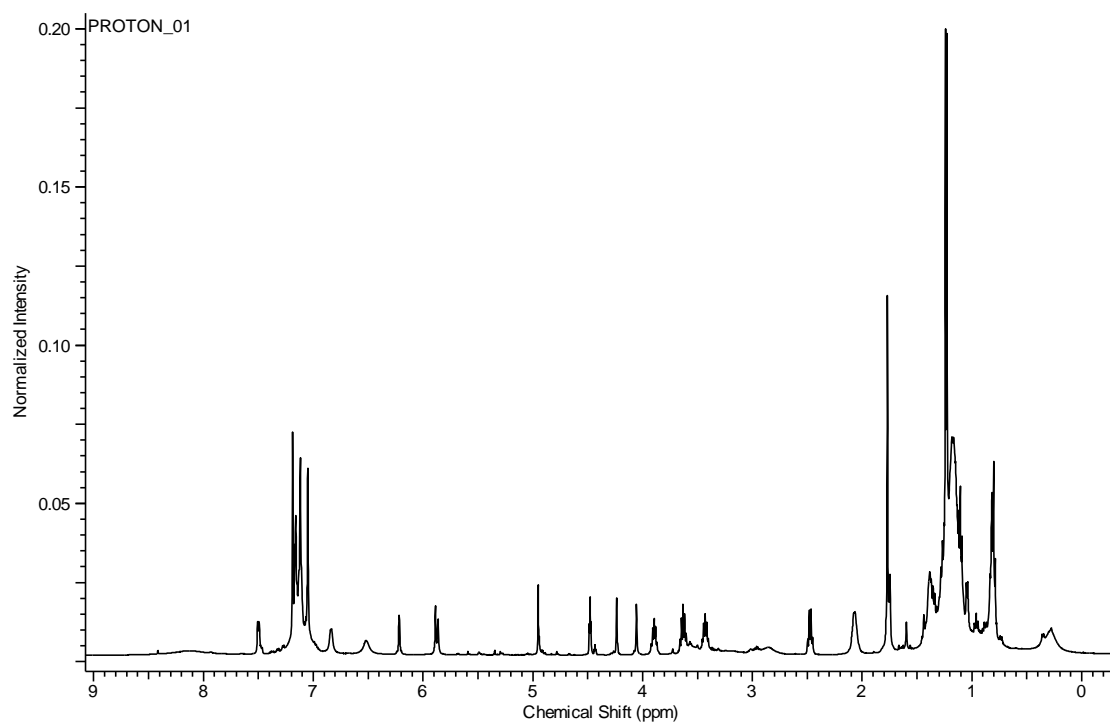


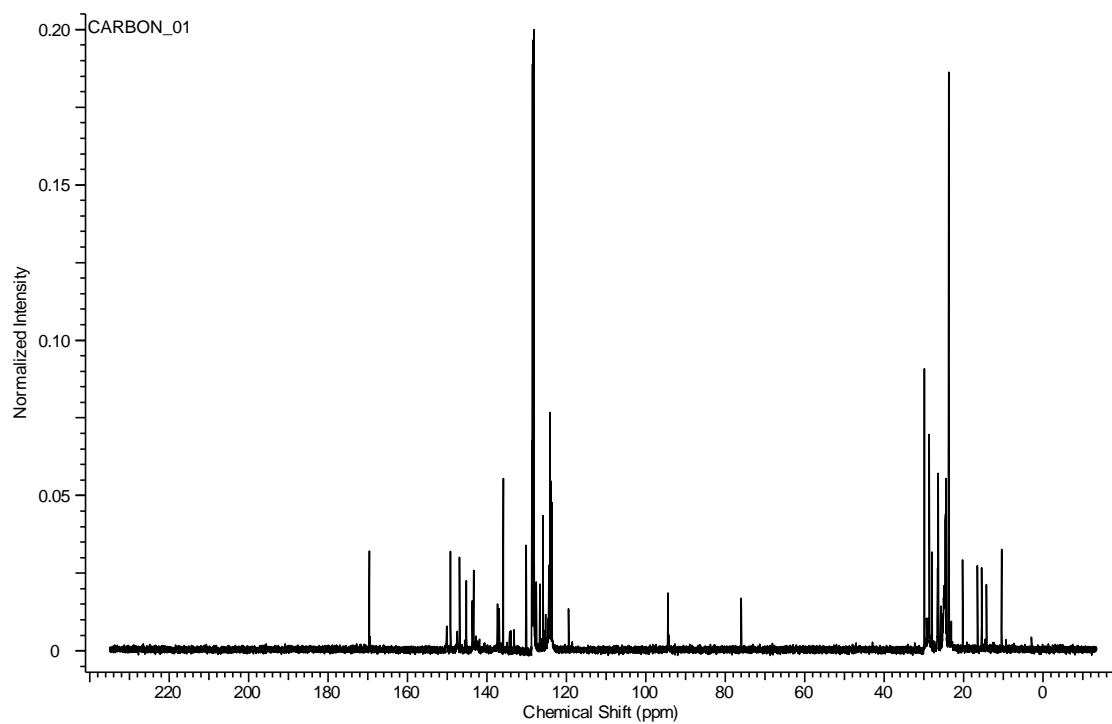
Compound 14





Compound 15





X-ray Diffraction analysis

X-ray diffraction data for compound **13** were collected on a Nonius Kappa CCD with a low temperature device at 150 K, utilizing Mo-K α radiation monochromated with graphite ($\lambda = 0.71070 \text{ \AA}$). Data were processed with the Nonius software,^{2,3} with structure solution and refinement using XSeed, SHELXS and SHELXL⁴ and visualised utilising Ortep 3.⁵ In addition to one molecule of the magnesium complex, the asymmetric unit was noted to contain half of a toluene molecule. This solvent moiety lies close to a crystallographic inversion centre which serves to generate the remainder. As such, the methyl group is present at 50% occupancy, due to symmetry imposed disorder. H5 was located and refined at a distance of 0.98 \AA from N5. The methyl hydrogens attached to C1, C5 and C32 were included as being disordered, at calculated positions. Diffraction was noted to decline at higher Bragg angles and, hence, data were truncated to a theta value of 25 degrees.

Table S1: Crystal data and structure refinement for **13**.

Identification code	k14msh14
Empirical formula	C _{69.50} H ₉₄ Mg N ₆
Formula weight	1037.82
Temperature	150(2) K
Wavelength	0.71073 \AA
Crystal system	Monoclinic
Space group	P21/n
Unit cell dimensions	a = 11.1770(1) \AA $\alpha = 90^\circ$ b = 25.6120(3) \AA $\beta = 96.622(1)^\circ$ c = 22.8890(3) \AA $\gamma = 90^\circ$
Volume	6508.61(13) \AA^3
Z	4
Density (calculated)	1.059 Mg/m ³
Absorption coefficient	0.070 mm ⁻¹
F(000)	2260
Crystal size	0.60 x 0.40 x 0.25 mm
Theta range for data collection	3.76 to 25.02 $^\circ$.
Index ranges	-13 \leq h \leq 13; -30 \leq k \leq 30; -27 \leq l \leq 27
Reflections collected	85482
Independent reflections	11437 [R(int) = 0.0709]
Reflections observed (>2 σ)	8206
Data Completeness	0.995
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.986 and 0.783
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	11437 / 1 / 716
Goodness-of-fit on F ²	1.090
Final R indices [I>2 σ (I)]	R1 = 0.0534 wR2 = 0.1173
R indices (all data)	R1 = 0.0843 wR2 = 0.1339
Largest diff. peak and hole	0.358 and -0.267 e \AA^{-3}

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