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]

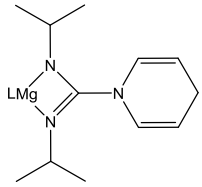
Reactions of Dihydropyridines with Carbodiimides

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.

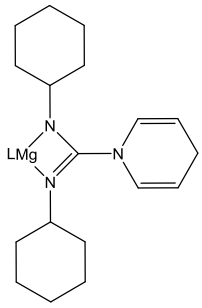
1,4-Dihydropyridide reactions, II

Synthesis of Compound 1



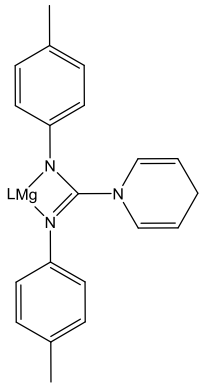
NMR Scale: 30 mg (0.05 mmol) **II** with 5.5 μL (0.05 mmol) of iPrNCNiPr. **Large Scale:** 50 mg (0.083 mmol) of **II** with 12.8 μL (0.083 mmol) of iPrNCNiPr, this was dissolved in toluene and left to stir at room temperature overnight. Solvent was removed *in vacuo* to yield yellow crystals of **1** (35 mg, 67% yield). ^{1}H NMR (300 MHz, d_8-Tol, 300 K) δ_H (ppm): 7.11 – 6.94 (6H, m, Ar-*H*), 5.94 (2H, dt, J_{HH} = 9 Hz, NC*H*), 4.83 (1H, s, NC(CH$_3$)C*H*), 4.38 (2H, dt, ^{3}J = 9 Hz, ^{4}J = 3Hz, NCHC*H*), 3.48 (2H, sept, J_{HH} = 6Hz, NC*H*(CH$_3$)$_2$), 3.41 (4H, sept, J_{HH} = 6 Hz, C*H*(CH$_3$)$_2$), 2.89 (2H, m, NCHCHC*H*$_2$), 1.64 (6H, s, NC(C*H*$_3$)), 1.27 (12H, d, J_{HH} = 6 Hz, CH(C*H*$_3$)$_2$), 1.24 (12H, d, J_{HH} = 6 Hz, CH(C*H*$_3$)$_2$), 0.88 (6H, d, J_{HH} = 6Hz, NCH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, d_8-Tol, 300 K) δ_C (ppm): 169.6 (N*C*(CH$_3$), 164.3 (*C*N$_3$), 145.6 (*ipso*-Ar), 142.6 (*o*-Ar), 129.3 (*p*-Ar), 128.1 (N*C*H), 123.8 (*m*-Ar), 99.0 (NCH*C*H), 94.9 (NC(CH$_3$)*C*H), 45.0 (N*C*H(CH$_3$)$_2$), 28.26 (*C*H(CH$_3$)$_2$), 26.0 (NCH(*C*H$_3$)$_2$), 25.4 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 24.3 (NC(*C*H$_3$)), 22.9 (NCHCH*C*H$_2$). HRMS (ESI) calcd. for hydrolysed product [M$^+$] $C_{12}H_{21}N_3$ *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). ^{1}H NMR (300 MHz, d_8-Tol, 300 K) δ_H (ppm): 7.14 – 6.96 (6H, m, Ar-*H*), 6.00 (2H, dt, J_{HH} = 9 Hz, NC*H*), 4.85 (1H, s, NC(CH$_3$)C*H*), 4.40 (2H, dt, ^{3}J = 9 Hz, ^{4}J = 3 Hz, NCHC*H*), 3.44 (4H, sept, J_{HH} = 6 Hz, C*H*(CH$_3$)$_2$), 3.10 (2H, m, NC*H*(CH$_2$)$_2$), 2.87 (2H, m, NCHCHC*H*$_2$), 1.86 – 0.78 (20H, m, Cy-*H*), 1.65 (6H, s, NC(C*H*$_3$)), 1.33 (12H, d, J_{HH} = 9 Hz, CH(C*H*$_3$)$_2$), 1.26 (12H, d, J_{HH} = 9 Hz, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, d_8-Tol, 300 K) δ_C (ppm): 169.7 (N*C*(CH$_3$), 163.8 (*C*N$_3$), 145.6 (*ipso*-Ar), 142.6 (*o*-Ar), 128.1 (N*C*H), 125.3 (*o*-Ar),123.9 (*m*-Ar), 99.1 (NCH*C*H), 94.8 (NC(CH$_3$)*C*H), 53.5 (N*C*H(CH$_2$)$_2$), 37.0 (CH(*C*H$_2$)$_2$), 28.7 (*C*H(CH$_3$)$_2$), 26.5 (CH(*C*H$_2$)$_2$), 26.0 (CH(*C*H$_3$)$_2$), 25.8 (CH(CH$_2$)$_2$(*C*H$_2$)$_2$), 25.6 (CH(*C*H$_3$)$_2$), 24.5 (NC(*C*H$_3$)), 24.3 (CH(CH$_2$)$_4$*C*H$_2$), 22.8 (NCHCH*C*H$_2$). HRMS (ESI) calcd. for hydrolysed product [M$^+$] $C_{18}H_{29}N_3$ *m/z* 287.45, found 288.2549.

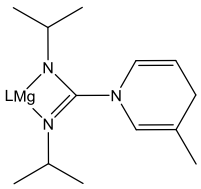
Synthesis of Compound 3



NMR Scale: 30 mg (0.05 mmol) **II** with 11.1 mg (0.05 mmol) of *p*-TolNCN*p*-Tol. ^{1}H 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_{HH} = 9 Hz, NC*H*CH), 4.88 (1H, s, NC(CH_3)C*H*), 4.20 (2H, m, NCHC*H*), 3.64 (4H, m, C*H*(CH_3)$_2$), 2.68 (2H, s, NCHCHCH_2), 2.11 (6H, s, *p*-CH_3), 1.69 (6H, s, NC(CH_3)CH), 1.26 (12H, d, J_{HH} = 6 Hz, CH(CH_3)$_2$), 1.14 – 1.10 (12H, m, CH(CH_3)$_2$. ^{13}C{^{1}H} NMR (75.5 MHz, d_8-Tol, 300 K) δ_C (ppm): 168.3 (N*C*(CH_3)), 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 (N*C*HCH), 100.7 (NCH*C*H), 97.6 (NC(CH_3)*C*H), 32.0 (*C*H(CH_3)$_2$), 27.9 (NCHCH*C*H_2), 25.0 (*p*-*C*H_3), 24.7 (NC(*C*H_3), 21.2 (CH(*C*H_3)$_2$), 20.8 (CH(*C*H_3)$_2$). HRMS (ESI) calcd. for hydrolysed product $[M^+H^+]^+$ $C_{20}H_{21}N_3$ *m/z* 303.41, found 304.1814.

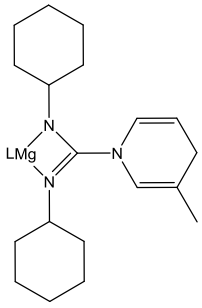
1,4-Dihydro-3-picolide reactions, III

Synthesis of Compound 4



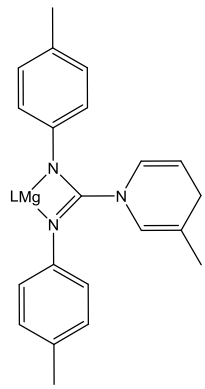
NMR Scale: 30 mg (0.048 mmol) **III** with 4.9 µL (0.048 mmol) of iPrNCNiPr. **Large Scale:** 200 mg (0.32 mmol) of **III** with 49.3 µL (0.32 mmol) of iPrNCNiPr, this was dissolved in toluene and left to stir at room temperature overnight. Solvent was removed *in vacuo* to yield yellow crystals of **4** (140 mg, 66% yield). ^{1}H NMR (300 MHz, d_8-Tol, 300 K) δ_H (ppm): 7.12 – 6.98 (6H, m, Ar), 6.02 (1H, dm, ^{3}J = 6 Hz, ^{4}J = 3Hz, NC*H*CH), 5.87 (1H, m, NC*H*C(CH_3)), 4.85 (1H, s, NC(CH_3)C*H*), 4.46 (1H, dt, ^{3}J = 9 Hz, ^{4}J = 3 Hz, NCHC*H*), 3.43 (2H, sept, J_{HH} = 6 Hz, NC*H*(CH_3)$_2$), 3.33 (4H, sept, J_{HH} = 6 Hz, C*H*(CH_3)$_2$), 2.81 (2H, m, NC- HCHCH_2), 1.87 (3H, s, NCHC(CH_3)), 1.65 (6H, s, NC(CH_3), 1.28 (12H, d, J_{HH} = 6 Hz, CH(CH_3)$_2$), 1.24 (12H, d, J_{HH} = 6 Hz, CH(CH_3)$_2$), 1.05 (12H, d, J_{HH} = 6 Hz, NCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, d_8-Tol, 300 K) δ_C (ppm): 169.5 (N*C*(CH_3)), 164.5 (*C*N_3), 145.8 (*ipso*-Ar), 142.7 (*o*-Ar), 127.5 (N*C*H), 125.3 (*p*-Ar), 123.9 (*m*-Ar), 123.5 (N*C*HC(CH_3)), 107.1 (NCH*C*(CH_3)), 98.0 (NC(CH_3)*C*H), 95.0 (NCH*C*H), 45.0 (N*C*H(CH_3)$_2$), 28.3 (*C*H(CH_3)$_2$), 26.0(NCH(*C*H_3)$_2$), 25.4 (CH(*C*H_3)$_2$), 24.8 (NC(*C*H_3)), 24.3 (CH(*C*H_3)$_2$), 20.9 (NCHCH*C*H_2), 18.0 (NCHC(*C*H_3)).

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). ^{1}H NMR (300 MHz, d_8-Tol, 300 K) δ_H(ppm): 7.15 – 7.07 (6H, m, Ar), 6.07 (1H, dm, J_{HH} = 6 Hz, NC*H*CH), 5.92 (1H, m, NC*H*C(CH$_3$)), 4.86 (1H, s, NC(CH$_3$)C*H*), 4.47 (1H, dt, ^{3}J = 6 Hz, ^{4}J = 3 Hz, NCHC*H*), 3.46 (4H, sept, J_{HH} = 6 Hz, C*H*(CH$_3$)$_2$), 3.12 (2H, m, NC*H*(CH$_2$)$_2$), 2.78 (2H, m, NCHCHC*H*$_2$), 1.83 (3H, s, NCHC(C*H*$_3$)), 1.73 (4H, m, Cy-*H*), 1.55 (4H, m, Cy-*H*), 1.66 (6H, s, NC(C*H*$_3$)), 1.34 (12H, d, J_{HH} = 6Hz, CH(C*H*$_3$)$_2$), 1.26 (12H, d, J_{HH} = 6Hz, CH(C*H*$_3$)$_2$), 1.29 – 0.99 (8H, m, Cy-*H*), 0.85 (4H, m, CH(CH$_2$)$_2$ (CH$_2$)$_2$C*H*$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, d_8-Tol, 300 K) δ_C (ppm): 169.7 (N*C*(CH$_3$)), 164.0 (*C*N$_3$), 145.7 (*ipso*-Ar), 142.7 (*o*-Ar), 127.5 (N*C*H), 125.3 (*p*-Ar), 123.9 (*m*-Ar), 122.8 (N*C*HC(CH$_3$)), 107.3 (NCH*C*(CH$_3$)), 98.1 (NC(CH$_3$)*C*H), 94.9 (NCH*C*H), 53.6 (N*C*H(CH$_2$)$_2$), 37.0 (NCH(*C*H$_2$)$_2$), 28.4 (*C*H(CH$_3$)$_2$), 26.5 (CH(CH$_2$)$_2$(*C*H$_2$)$_2$), 26.1 (CH(*C*H$_3$)$_2$), 25.5 (CH(*C*H$_3$)$_2$), 24.6 (NC(*C*H$_3$)), 24.4 (CH(CH$_2$)$_4$*C*H$_2$), 20.9 (NCHCH*C*H$_2$) 18.0 (NCHC(*C*H$_3$)).

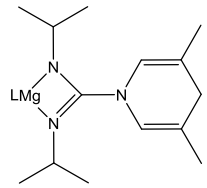
Synthesis of Compound 6



NMR Scale: 30 mg (0.048 mmol) **III** with 10.6 mg (0.048 mmol) of *p*-TolNCN*p*-Tol. ^{1}H 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, NC*H*CH), 5.89 (1H, s, NC*H*C(CH$_3$)), 4.88 (1H, s, NC(CH$_3$)C*H*), 4.30 (1H, m, NCHC*H*), 3.63 (4H, m, C*H*(CH$_3$)$_2$), 2.59 (2H, s, NCHCHC*H*$_2$), 2.07 (6H, s, *p*-C*H*$_3$), 1.70 (6H, s, NC(C*H*$_3$)CH), 1.26 (12H, d, J_{HH} = 6 Hz, CH(C*H*$_3$)$_2$), 1.20 (3H, s, NCHC(C*H*$_3$), 1.11 – 1.08 (12H, m, CH(C*H*$_3$)$_2$. ^{13}C{^{1}H} NMR (75.5 MHz, d_8-Tol, 300 K) δ_C (ppm): 168.2 (N*C*(CH$_3$)), 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 (N*C*HCH), 123.8 (N*C*H(CH$_3$)), 108.9 (NCH*C*H), 100.1 (NCH*C*(CH$_3$), 97.5 (NC(CH$_3$)*C*H), 28.5 (NCHCH*C*H$_2$), 28.0 (CH(*C*H$_3$)$_2$)), 25.1 (*p*-*C*H$_3$), 24.7 (NC(*C*H$_3$), 20.8 (*C*H(CH$_3$)$_2$), 17.7 (NCHC(*C*H$_3$)). HRMS (ESI) calcd. for hydrolysed product [M^{+}H^{+}]$^{+}$ $C_{21}H_{23}N_3$ *m/z* 317.44, found 318.2011.

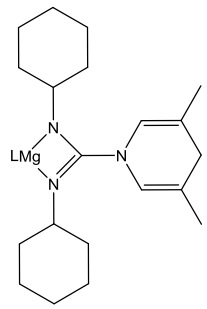
1,4-Dihydro-3,5-Lutidide reactions, IV

Synthesis of Compound 7



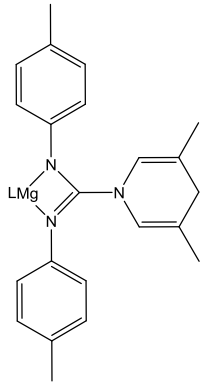
NMR Scale: 30 mg (0.046 mmol) **IV** with 4.7 µL (0.046 mmol) of iPrNCNiPr. **Large Scale:** 50 mg (0.076 mmol) of **IV** with 11.7 µL (0.076 mmol) of iPrNCNiPr, this was dissolved in toluene and left to stir at room temperature overnight. Solvent was removed *in vacuo* to yield yellow crystals of **7** (40 mg, 78% yield). ^{1}H NMR (300 MHz, d_8-Tol, 300 K) δ_H(ppm): 7.15 – 7.08 (6H, m, Ar), 5.94 (2H, s, NC*H*), 4.86 (1H, s, NC(CH$_3$)C*H*), 3.53 (2H, sept, J_{HH} = 6 Hz, NC*H*(CH$_3$)$_2$), 3.45 (4H, sept, J_{HH} = 6 Hz, C*H*(CH$_3$)$_2$), 2.65 (2H, s, NCHC(CH$_3$)C*H*$_2$), 1.53 (6H, s, NCHC(C*H*$_3$)), 1.30 (12H, d, J_{HH} = 9 Hz, CH(C*H*$_3$)$_2$), 1.25 (12H, d, J_{HH} = 6 Hz, CH(C*H*$_3$)$_2$), 0.86 (6H, d, J_{HH} = 6 Hz, NCH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, d_8-Tol, 300 K) δ_C (ppm): 169.4 (N*C*(CH$_3$)), 164.7 (*C*N$_3$), 146.0 (*ipso*-Ar), 142.1 (*o*-Ar), 125.2 (*p*-Ar), 123.9 (*m*-Ar), 122.4 (N*C*H), 106.0 (NCH*C*(CH$_3$)), 95.1 (NC(CH$_3$)*C*H), 45.1 (N*C*H(CH$_3$)$_2$), 34.3 (NCHC(CH$_3$)*C*H$_2$), 28.2 (*C*H(CH$_3$)$_2$), 26.0 (CH(*C*H$_3$)$_2$), 25.3 (CH(*C*H$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 24.4 (NC(*C*H$_3$)), 20.7 (NCHC(*C*H$_3$)). HRMS (ESI) calcd. for hydrolysed product [M$^+$] $C_{14}H_{25}N_3$ *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). ^{1}H NMR (300 MHz, d_8-Tol, 300 K) δ_H(ppm): 7.15 – 7.08 (6H, m, Ar), 6.01 (2H, s, NC*H*), 4.90 (1H, s, NC(CH$_3$)C*H*), 3.51 (2H, sept, J_{HH} = 6 Hz, NC*H*(CH$_3$)$_2$), 3.16 (2H, m, NC*H*(CH$_2$)$_2$), 2.62 (2H, s, NCHC(CH$_3$)C*H*$_2$), 1.89 (6H, s, NCHC(C*H*$_3$), 1.75 – 1.55 (8H, m, Cy-*H*), 1.70 (6H, s, NC(C*H*$_3$)), 1.38 (12H, d, J_{HH} = 6 Hz, CH(C*H*$_3$)$_2$), 1.30 (12H, d, J_{HH} = 6 Hz, CH(C*H*$_3$)$_2$), 1.29 – 1.05 (8H, m, Cy-*H*), 0.90 (4H, m, CH(CH$_2$)$_2$(CH$_2$)$_2$C*H*$_2$).^{13}C{^{1}H} NMR (75.5 MHz, d_8-Tol, 300 K) δ_C (ppm): 169.6 (N*C*(CH$_3$)), 164.1 (*C*N$_3$), 145.8 (*ipso*-Ar), 142.7 (*o*-Ar), 125.2 (*p*-Ar),123.9 (*m*-Ar), 122.4 (N*C*H), 106.3 (NCH*C*(CH$_3$)), 94.9 (NC(CH$_3$)*C*H), 53.7 (N*C*H(CH$_2$)$_2$), 37.0 (NCH(*C*H$_2$)$_2$), 35.4 (NCHC(CH$_3$)*C*H$_2$), 28.4 (*C*H(CH$_3$)$_2$), 26.5 (CH(CH$_2$)$_2$(*C*H$_2$)$_2$), 26.1 (CH(*C*H$_3$)$_2$), 25.5 (CH(*C*H$_3$)$_2$), 24.6 (NC(*C*H$_3$)), 24.4 (CH(CH$_2$)$_4$*C*H$_2$), 17.9 (NCHC(*C*H$_3$)).

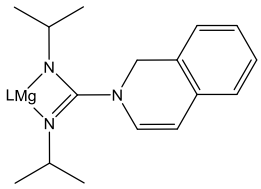
Synthesis of Compound 9



NMR Scale: 30 mg (0.046 mmol) **IV** with 10.1 mg (0.046 mmol) of *p*-TolNCN*p*-Tol. ^{1}H 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, NC*H*C(CH$_3$)), 4.89 (1H, s, NC(CH$_3$)C*H*), 3.69 (4H, m, C*H*(CH$_3$)$_2$), 2.46 (2H, s, NCHC(CH$_3$)C*H*$_2$), 2.06 (6H, s, *p*-C*H*$_3$), 1.73 (6H, s, NC(C*H*$_3$)CH), 1.29 (6H, s, NCHC(C*H*$_3$)) 1.15 – 1.12 (12H, m, CH(C*H*$_3$)$_2$), 0.93 – 0.89 (12H, m, CH(C*H*$_3$)$_2$. ^{13}C{^{1}H} NMR (75.5 MHz, d$_8$-Tol, 300 K) δ_C (ppm): 168.0 (N*C*(CH$_3$)), 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 (N*C*HCH), 108.1 (NCH*C*(CH$_3$), 97.5 (NC(CH$_3$)*C*H), 34.2 (*C*H(CH$_3$)$_2$), 28.0 (NCHC(CH$_3$)*C*H$_2$), 25.2 (*p*-*C*H$_3$), 24.7 (NC(*C*H$_3$), 20.7 (CH(*C*H$_3$)$_2$), 20.6 (CH(*C*H$_3$)$_2$), 17.7 (NCHC(*C*H$_3$)). HRMS (ESI) calcd. for hydrolysed product [M$^+$H$^+$]$^+$ $C_{22}H_{25}N_3$ *m/z* 331.46, found 332.2207, [M$^+$Na$^+$]$^+$ $C_{22}H_{25}N_3Na$ *m/z* 354.45, found 354.2028.

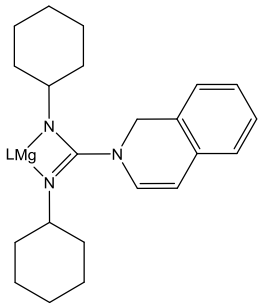
1,2-dihydro-*iso*-quinolide reactions, I

Synthesis of Compound 10



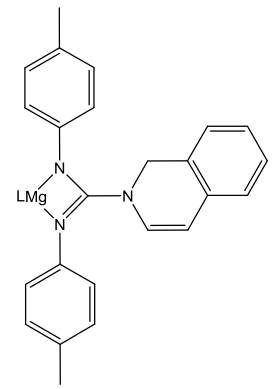
NMR Scale: 30 mg (0.043 mmol) **I** with 4.4 µL (0.043 mmol) of iPrNCNiPr. **Large Scale:** 50 mg (0.071 mmol) of **I** with 11.0 µL (0.071 mmol) of iPrNCNiPr, this was dissolved in toluene and left to stir at room temperature overnight. Solvent was removed *in vacuo* to yield red crystals of **10** (30 mg, 61% yield). ^{1}H NMR (300 MHz, d$_8$-Tol, 300 K) δ_H(ppm): 7.24 – 6.74 (10H, m, Ar-*H*, iQuin-*H*), 6.31 (1H, d, J_{HH} = 6 Hz, NC*H*), 5.50 (1H, d, J_{HH} = 6 Hz, NCHC*H*), 4.84 (1H, s, NC(CH$_3$)C*H*), 4.46 (2H, s, NC*H*$_2$), 3.44 (6H, m, C*H*(CH$_3$)$_2$, NC*H*(CH$_3$)$_2$), 1.65 (6H, s, NC(C*H*$_3$)), 1.30 (12H, d, J_{HH} = 6 Hz, CH(C*H*$_3$)$_2$), 1.25 (12H, d, J_{HH} = 6 Hz, CH(C*H*$_3$)$_2$), 0.79 (12H, d, J_{HH} = 6 Hz, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, d$_8$-Tol, 300 K) δ_C (ppm): 169.6 (N*C*(CH$_3$), 165.4 (*C*N$_3$), 145.6 (*ipso*-Ar), 142.7 (*o*-Ar), 135.5 (iQuin(H)-*C*), 133.6 (iQuin(H)-*C*), 132.9 (N*C*H), 126.4 (iQuin(H)-*C*), 125.8 (iQuin(H)-*C*), 125.3 (*p*-Ar), 123.8 (*m*-Ar), 102.4 (NCHC*H*), 94.8 (NC(CH$_3$)*C*H), 52.4 (N*C*H$_2$), 45.1 (N*C*H(CH$_3$)$_2$), 28.3 (*C*H(CH$_3$)$_2$), 26.1 (CH(*C*H$_3$)$_2$), 25.4 (CH(*C*H$_3$)$_2$), 24.5 (NC(*C*H$_3$)), 24.3 (CH(*C*H$_3$)$_2$), 23.9 (CH(*C*H$_3$)$_2$). HRMS (ESI) calcd. for hydrolysed product [M$^+$] $C_{16}H_{23}N_3$ *m/z* 257.38, found 258.2035.

Synthesis of Compound 11



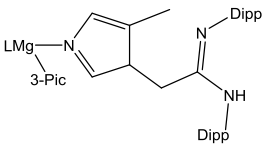
NMR Scale: 30 mg (0.043 mmol) **I** with 5.9 mg (0.043 mmol) of CyNCNCy. **Large Scale:** 50 mg (0.071 mmol) of **I** with 14.6 mg (0.071 mmol) of CyNCNCy, this was dissolved in toluene and left to stir at room temperature overnight. Solvent was removed *in vacuo* to yield red crystals of **11** (37 mg, 67% yield). ^{1}H NMR (300 MHz, d$_8$-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, NC*H*), 5.52 (1H, d, J_{HH} = 9 Hz, NCHC*H*), 4.87 (1H, s, NC(CH$_3$)C*H*), 4.52 (2H, s, NCH_2), 3.47 (4H, sept, J_{HH} = 6 Hz, C*H*(CH$_3$)$_2$), 3.05 (2H, m, NC*H*(CH$_2$)$_2$), 1.66 (6H, s, NC(CH_3), 1.58 – 1.38 (8H, m, Cy-*H*), 1.33 (12H, d, J_{HH} = 6 Hz, CH(CH_3)$_2$), 1.26 (12H, d, J_{HH} = 6 Hz, CH(CH_3)$_2$), 1.14 – 0.76 (12H, m, Cy-*H*). ^{13}C{^{1}H} NMR (75.5 MHz, d$_8$-Tol, 300 K) δ_C (ppm): 169.6 (N*C*(CH$_3$)), 165.2 (*C*N$_3$), 145.8 (*ipso*-Ar), 142.7 (*o*-Ar), 136.0 (iQuin(H)-*C*), 133.7 (iQuin(H)-*C*), 132.9 (N*C*H), 127.7 (iQuin(H)-*C*), 126.4 (iQuin(H)-*C*), 125.3 (*p*-Ar), 123.8 (*m*-Ar), 102.4 (NCH*C*H), 94.9 (NC(CH$_3$)*C*H), 53.9 (N*C*H(CH$_2$)$_2$), 50.8 (N*C*H$_2$), 37.1 (Cy-*C*), 35.4 (Cy-*C*), 28.3 (*C*H(CH$_3$)$_2$), 26.4 (Cy-*C*), 26.0 (CH(*C*H$_3$)$_2$), 25.8 (Cy-*C*), 25.5 (CH(*C*H$_3$)$_2$), 24.6 (NC(*C*H$_3$)), 24.4 (CH(*C*H$_3$)$_2$), 23.9 (CH(*C*H$_3$)$_2$). HRMS (ESI) calcd. for hydrolysed product [M$^+$] C$_{22}$H$_{31}$N$_3$ *m/z* 337.51, found 338.2714.

Synthesis of Compound 12



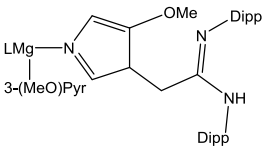
NMR Scale: 30 mg (0.043 mmol) **I** with 9.5 mg (0.043 mmol) of *p*-TolNCN*p*-Tol. ^{1}H NMR (500 MHz, C$_6$D$_6$, 300 K) δ_H (ppm): 7.24 – 6.41 (18H, m, Ar-*H*), 6.07 (1H, d, J_{HH} = 5 Hz, NC*H*CH), 5.32 (1H, d, J_{HH} = 5 Hz, NCHC*H*), 4.94 (1H, s, NC(CH$_3$)C*H*), 4.40 (2H, s, NCH_2), 3.32 (4H, m, C*H*(CH$_3$)$_2$), 1.76 (6H, s, NC(CH_3)CH), 1.67 (6H, s, *p*-CH_3), 1.63 (12H, d, J_{HH} = 5 Hz, CH(CH_3)$_2$), 1.22 (12H, d, J_{HH} = 5 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (125.75 MHz, d$_8$-Tol, 300 K) δ_C (ppm): 168.7 (N*C*(CH$_3$)CH), 161.9 (N$_3$*C*), 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 (N*C*H), 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 (NCH*C*H), 94.6 (NC(CH$_3$)*C*H), 51.5 (N*C*H$_2$), 37.3 (*C*H(CH$_3$)$_2$), 29.0 (NC(*C*H$_3$)CH), 28.4 (*p*-*C*H$_3$ *p*-Tol), 25.5 (CH(*C*H$_3$)$_2$), 25.2 (CH(*C*H$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$), 23.8 (CH(*C*H$_3$)$_2$). HRMS (ESI) calcd. for hydrolysed product [M$^+$H$^+$]$^+$ C$_{24}$H$_{23}$N$_3$ *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). ^{1}H NMR (300 MHz, d$_8$-Tol, 300 K) δ_H (ppm): 7.76 (1H, m, *o*-C*H* 3Pic), 7.13- 6.98 (12H, m, Ar-*H*), 6.67 (1H, s, *o*-C*H*C(CH$_3$) 3Pic), 6.64 (1H, m, *p*-*H*, 3Pic), 6.35 (1H, m, *m*-*H* 3Pic), 6.09 (1H, s, NC*H*), 5.89 (1H, s, NC*H*), 5.83 (1H, s, C*H*$_2$), 4.92 (1H, s, NC(CH$_3$)C*H*), 4.17 (1H, s, C*H*$_2$), 4.01 (1H, s, N*H*), 3.90 (2H, m, C*H*(CH$_3$)$_2$), 3.61 (2H, m, C*H*(CH$_3$)$_2$), 3.41 (4H, m, C*H*(CH$_3$)$_2$), 1.75 (6H, s, NC(C*H*$_3$)CH), 1.73 (3H, s, NCHC(C*H*$_3$), 1.61 (3H, s, *m*-C*H*$_3$ 3Pic), 1.38 – 1.09 (39H, m, CH(C*H*$_3$)$_2$, 3-C*H*$_3$ 3Pic), 1.23 (12H, d, J_{HH} = 6 Hz, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125.75 MHz, d$_8$-Tol, 300 K) δ_C (ppm): 169.7 (N*C*(CH$_3$)CH), 150.5 (N*C*NH), 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*(CH$_3$) Pyr), 126.2 (NCH*C*CH$_2$), 125.9 (NCH*C*(CH$_3$)C), 124.1 (*m*-*C*), 123.9 (*m*-*C* NCN), 123.6 (*m*-*C* NCNH), 120.0 (N*C*HC(CH$_3$)), 117.3 (N*C*H), 94.6 (NC(CH$_3$)*C*H), 70.0 (*C*H$_2$), 29.9 (*C*H(CH$_3$)$_2$), 28.7 (*C*H(CH$_3$)$_2$ NCN), 28.5 (*C*H(CH$_3$)$_2$ NCNH), 28.0 (NC(*C*H$_3$)CH), 26.6 (CH(*C*H$_3$)$_2$), 25.8 (CH(*C*H$_3$)$_2$), 24.6 (CH(*C*H$_3$)$_2$), 24.4 (*C*H$_3$), 23.8 (CH(*C*H$_3$)$_2$), 14.3 (3-*C*H$_3$ 3Pic). Elemental Analysis for C$_{66}$H$_{91}$MgN$_6$ (found): C 79.85 (79.98); H 9.24 (9.38); N 8.47 (8.19). HRMS (ESI) calcd. for hydrolysed product [M$^+$H$^+$]$^+$ C$_{31}$H$_{43}$N$_3$ *m/z* 457.71, found 458.3667.

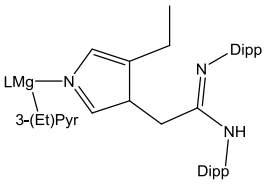
Synthesis of Compound 14



NMR Scale: 50 mg of [HC{(Me)CN(2,6-^{i}Pr$_2$C$_6$H$_3$)}$_2$MgBu] (0.1 mmol), with 2 equivalents of 3-(MeO)pyridine (20.2 µL, 0.2 mmol) and 1 equivalent of PhSiH$_3$ (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. ^{1}H NMR (500 MHz, C$_6$D$_6$, 300 K) δ_H (ppm): 7.48 (1H, m, *o*-C*H* 3Pic), 7.13 – 6.95 (14H, m, Ar-*H*, *o*,*m*-C*H* 3Pic), 6.86 (1H, s, NC*H*), 6.68 (1H, d, J_{HH} = 5 Hz, *p*-C*H* 3Pic), 5.77 (1H, s, NC*H*), 5.47 (1H, s, C*H*$_2$), 4.89 (1H, s, N(CH$_3$)C*H*), 4.18 (1H, s, C*H*$_2$), 4.00 (1H, s, N*H*), 3.88 (2H, m, C*H*(CH$_3$)$_2$), 3.60 (2H, m, C*H*(CH$_3$)$_2$), 3.51 (2H, m, C*H*(CH$_3$)$_2$), 3.34 (3H, s, OC*H*$_3$), 3.28 (C*H*(CH$_3$)$_2$), 2.81 (3H, s, OC*H*$_3$ Pyr), 1.73 (6H, s, NC(C*H*$_3$)CH), 1.33 (12H, m, CH(C*H*$_3$)$_2$), 1.21 (12H, d, J_{HH} = 5 Hz, CH(C*H*$_3$)$_2$), 1.12 (24H, m, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125.75 MHz, d$_8$-Tol, 300 K) δ_C (ppm): 169.7 (N*C*(CH$_3$)CH), 157.1 (N*C*NH), 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*(CH$_3$) Pyr), 125.9 (NCH*C*CH$_2$), 125.8 (NCH*C*(CH$_3$)C) 124.1

(*m*-*C*), 123.9 (*m*-*C*), 123.6 (*m*-*C* NCN), 123.1 (*m*-*C* NCNH), 111.0 (N*C*HC(CH$_3$), 108.3 (N*C*H), 94.5 (NC(CH$_3$)*C*H), 74.4 (*C*H$_2$), 58.0 (O*C*H$_3$), 56.1 (O*C*H$_3$ Pyr), 29.9 (*C*H(CH$_3$)$_2$), 28.7 (*C*H(CH$_3$)$_2$ NCN), 28.6 (*C*H(CH$_3$)$_2$ NCNH), 28.0 (NC(*C*H$_3$)CH), 26.5 (CH(*C*H$_3$)$_2$), 24.6 (CH(*C*H$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$), 23.7 (CH(*C*H$_3$)$_2$), 23.1 (CH(*C*H$_3$)$_2$).

Synthesis of Compound 15



NMR Scale: 50 mg of [HC{(Me)CN(2,6-^{i}Pr$_2$C$_6$H$_3$)}$_2$MgBu] (0.1 mmol), with 2 equivalents of 3-(Et)pyridine (22.4 µL, 0.2 mmol) and 1 equivalent of PhSiH$_3$ (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. ^{1}H NMR (500 MHz, C$_6$D$_6$, 300 K) δ_H (ppm): 7.48 (1H, m, *o*-C*H* Pyr), 7.14 – 7.02 (13H, m, Ar-*H*, *o*-C*H* Pyr), 6.81 (1H, m, *p*-C*H* Pyr), 6.49 (1H, m, *m*-C*H* Pyr), 6.19 (1H, s, NC*H*), 5.86 (1H, s, NC*H*), 5.83 (1H, s, C*H*$_2$), 4.21 (1H, s, C*H*$_2$), 4.03 (1H, s, N*H*), 3.87 (2H, m, C*H*(CH$_3$)$_2$), 3.60 (2H, m, C*H*(CH$_3$)$_2$), 3.40 (2H, m, C*H*(CH$_3$)$_2$), 2.80 (2H, m, C*H*(CH$_3$)$_2$), 2.44 (2H, m, C*H*$_2$CH$_3$), 2.05 (2H, m, 3-C*H*$_2$CH$_3$ Pyr), 1.74 (6H, s, NC(C*H*$_3$)CH), 1.35 (12H, m, CH(C*H*$_3$)$_2$), 1.20 (12H, d, J_{HH} = 5 Hz, CH(C*H*$_3$)$_2$), 1.13 (12H, m, CH(C*H*$_3$)$_2$), 1.08 (3H, t, J_{HH} = 10 Hz, 3-CH$_2$C*H*$_3$), 0.93 (3H, t, J_{HH} = 10 Hz, 3-CH$_2$C*H*$_3$ Pyr), 0.77 (12H, m, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125.75 MHz, d$_8$-Tol, 300 K) δ_C (ppm): 169.7 (N*C*(CH$_3$)CH), 150.2 (N*C*NH), 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*(CH$_3$) Pyr), 126.0 (NCH*C*CH$_2$), 125.2 (N*C*HC(CH$_3$)) 125.9 (NCH*C*(CH$_3$)C), 124.4 (*m*-*C*), 124.1 (*m*-*C*), 123.9 (*m*-*C* NCN), 123.6 (*m*-*C* NCNH), 119.5 (N*C*H), 108.3 (N*C*H), 94.5 (NC(CH$_3$)*C*H), 76.0 (*C*H$_2$), 29.9 (*C*H(CH$_3$)$_2$), 29.3 (*C*H$_2$CH$_3$), 28.9 (3-*C*H$_2$CH$_3$ Pyr), 28.6 (*C*H(CH$_3$)$_2$ NCN), 28.5 (*C*H(CH$_3$)$_2$ NCNH), 28.0 (NC(*C*H$_3$)CH), 26.5 (CH(*C*H$_3$)$_2$), 26.4 (CH(*C*H$_3$)$_2$), 24.6 (CH(*C*H$_3$)$_2$), 24.7 (CH$_2$*C*H$_3$), 24.5 (3-CH$_2$*C*H$_3$ Pyr), 23.7 (CH(*C*H$_3$)$_2$), 23.2 (CH(*C*H$_3$)$_2$).

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

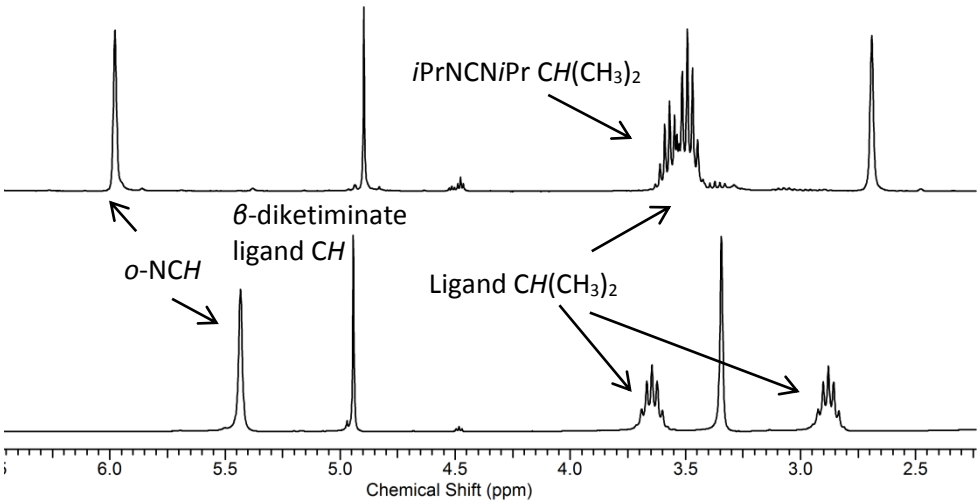


Figure S2: ^{1}H NMR spectrum for compound **13** illustrating the distinctive five (1H) singlet resonances

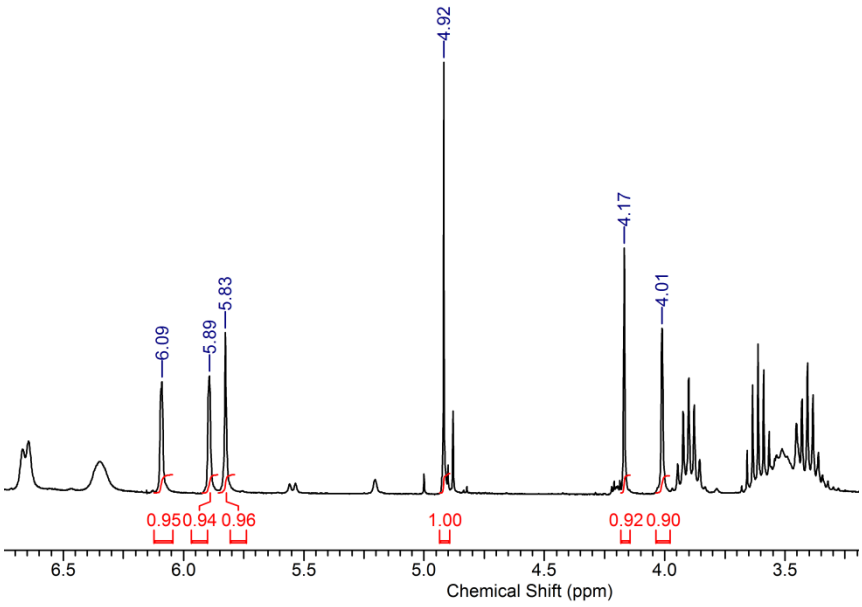


Figure S3: ^{1}H NMR spectrum of the reaction of **III-d$_7$** with DippNCNDipp to form compound **13-d$_7$**

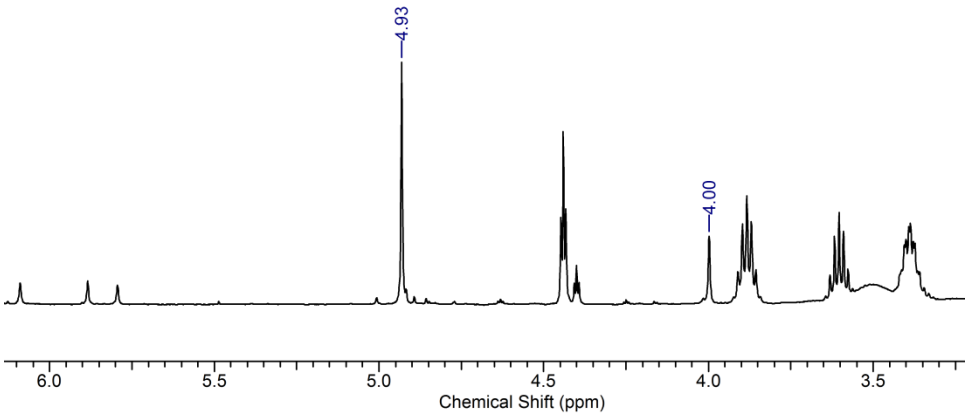
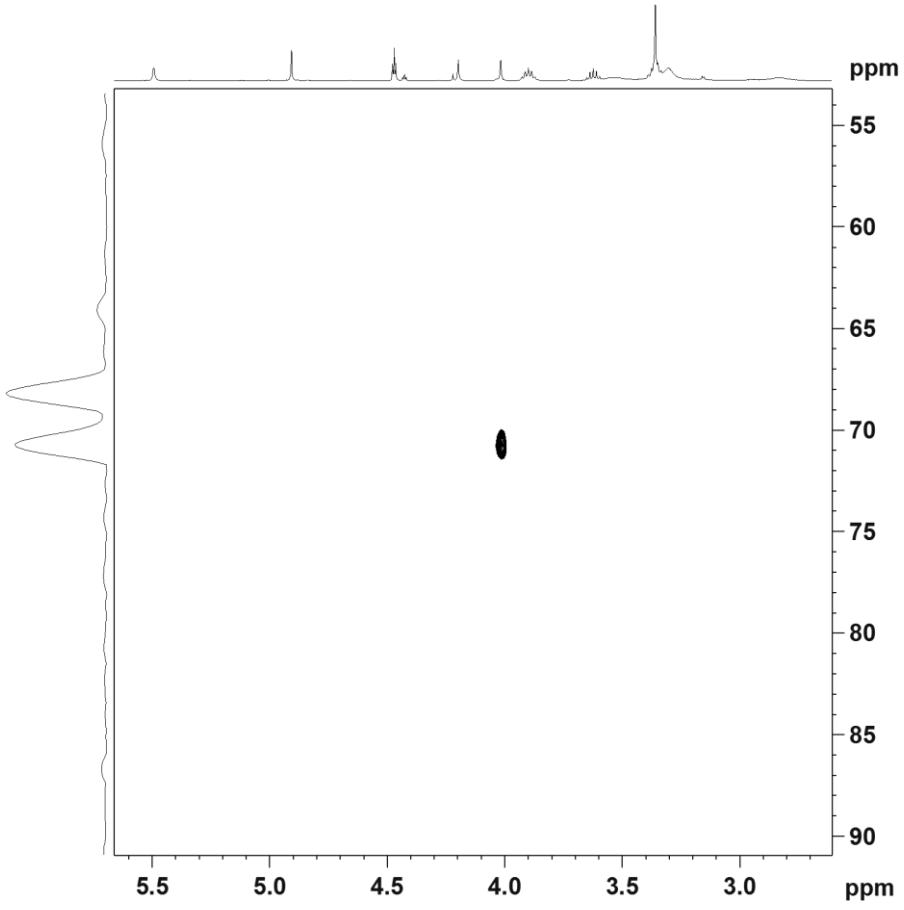
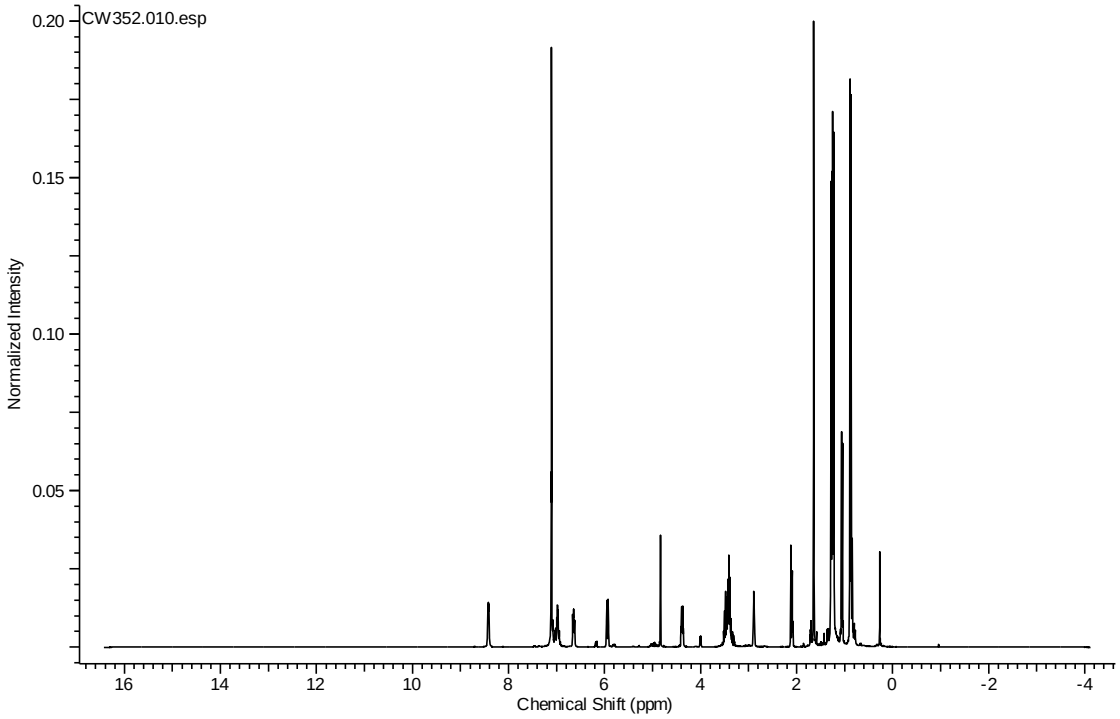


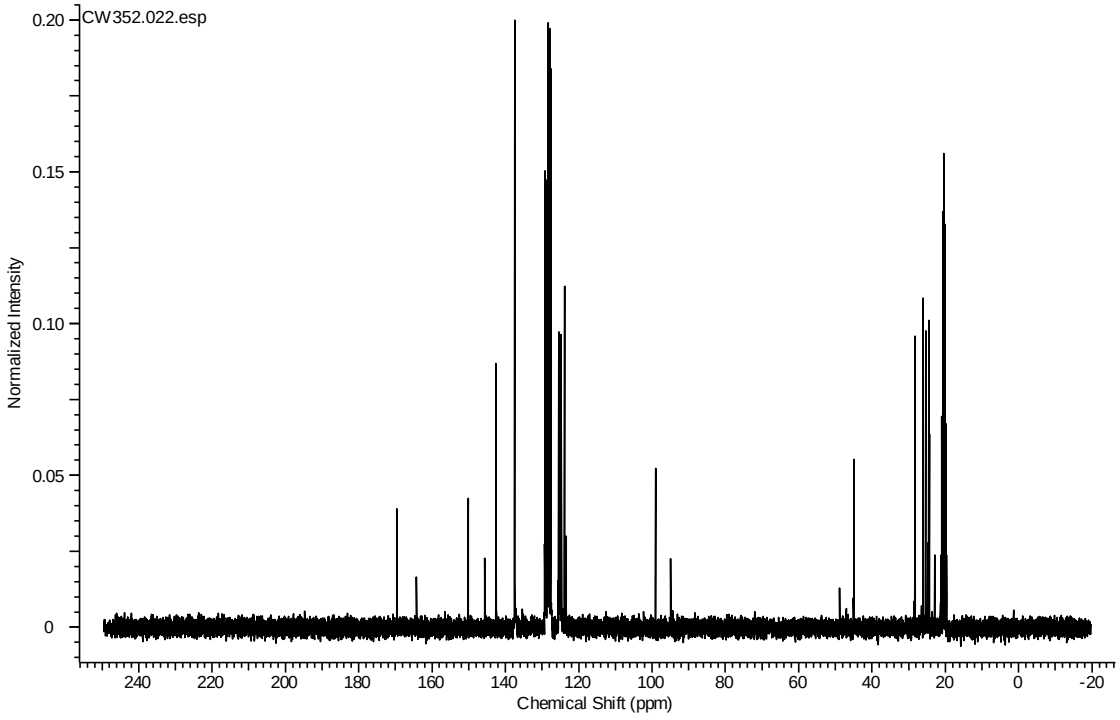
Figure S4: ^{1}H-^{14}N HSQC for compound **13-d$_7$**



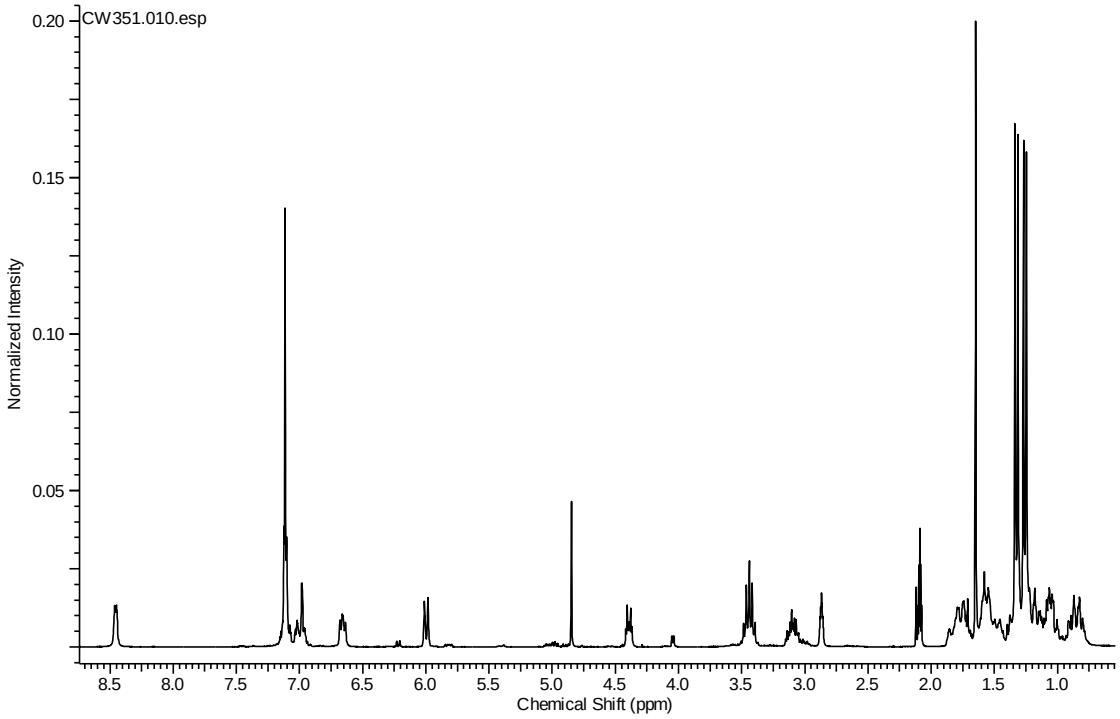
NMR Spectra

Compound 1





Compound 2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4.5
4.0
3.5
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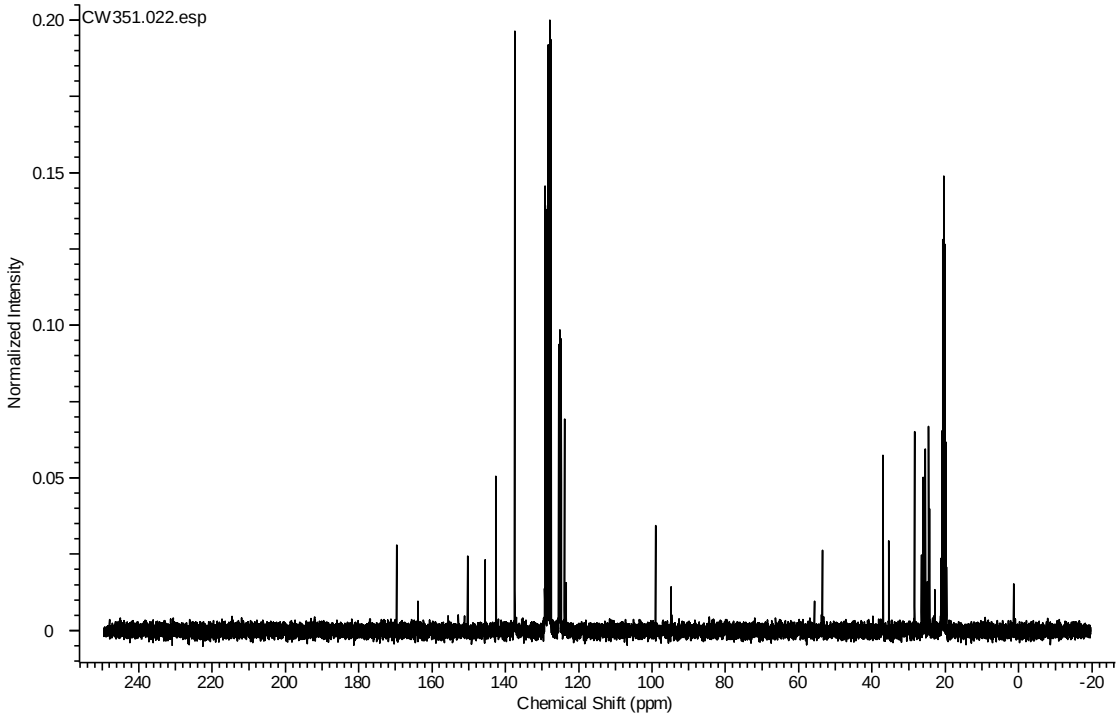
2.5
2.0
1.5
1.0
Chemical Shift (ppm)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80
60
40
20
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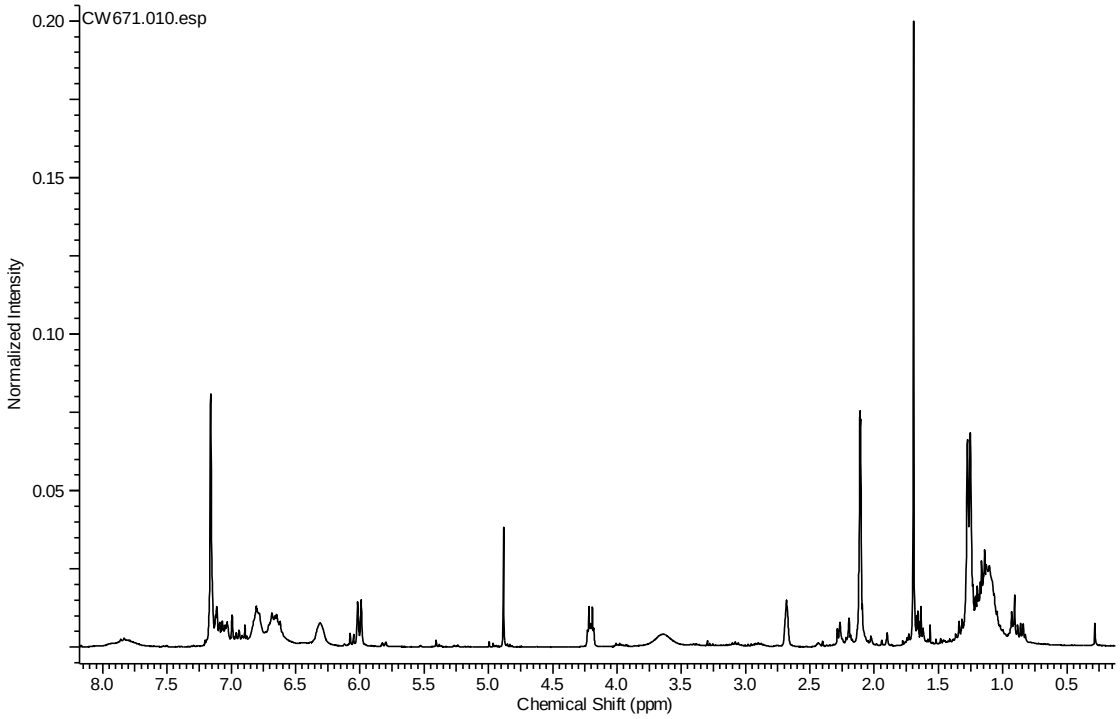
-20
Chemical Shift (ppm)

Compound 3


CW671.010.esp
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0.05
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6.5
6.0
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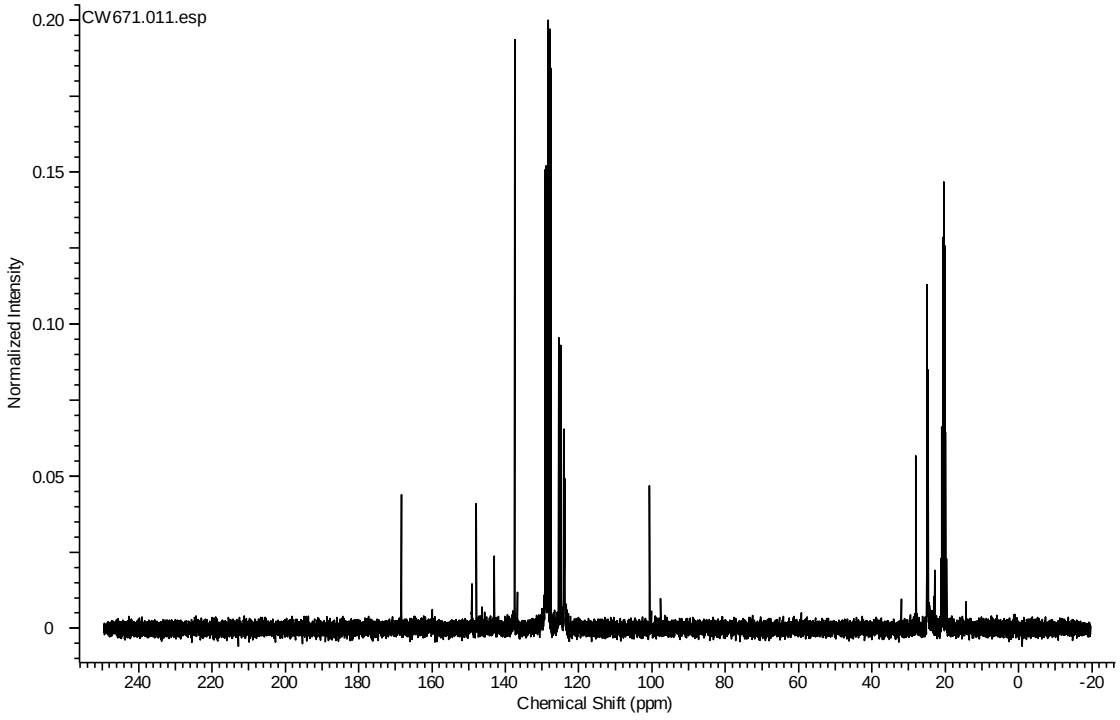
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)


CW671.011.esp
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0.10
0.05
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240
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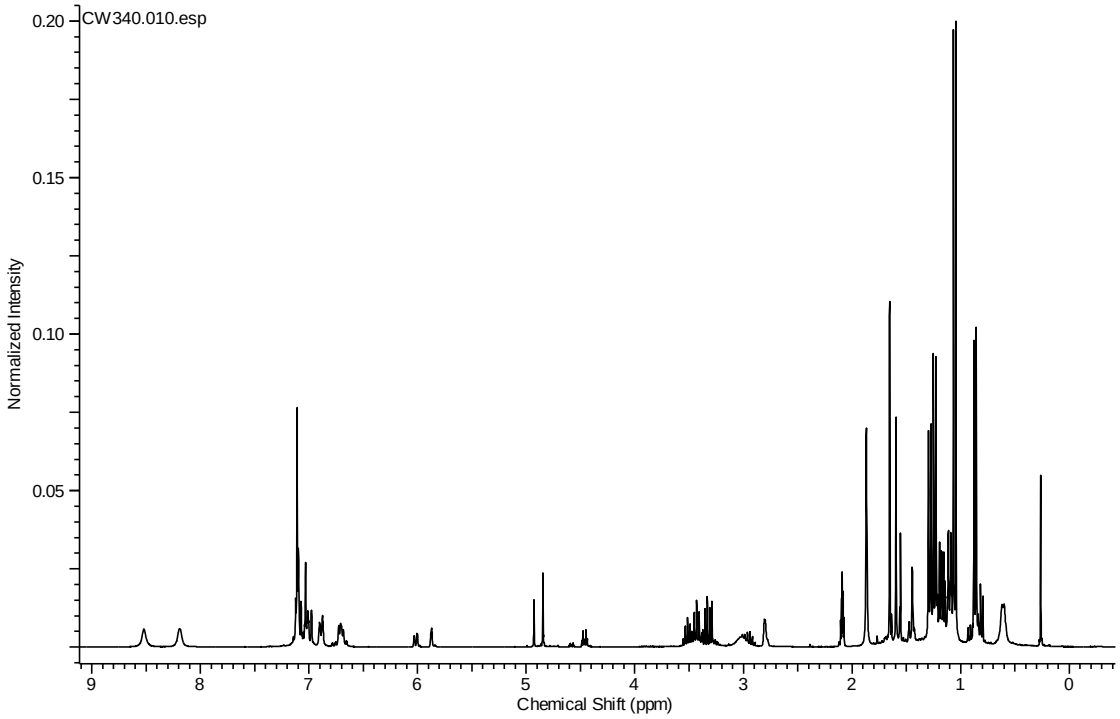
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

Compound 4


CW340.010.esp
Normalized Intensity
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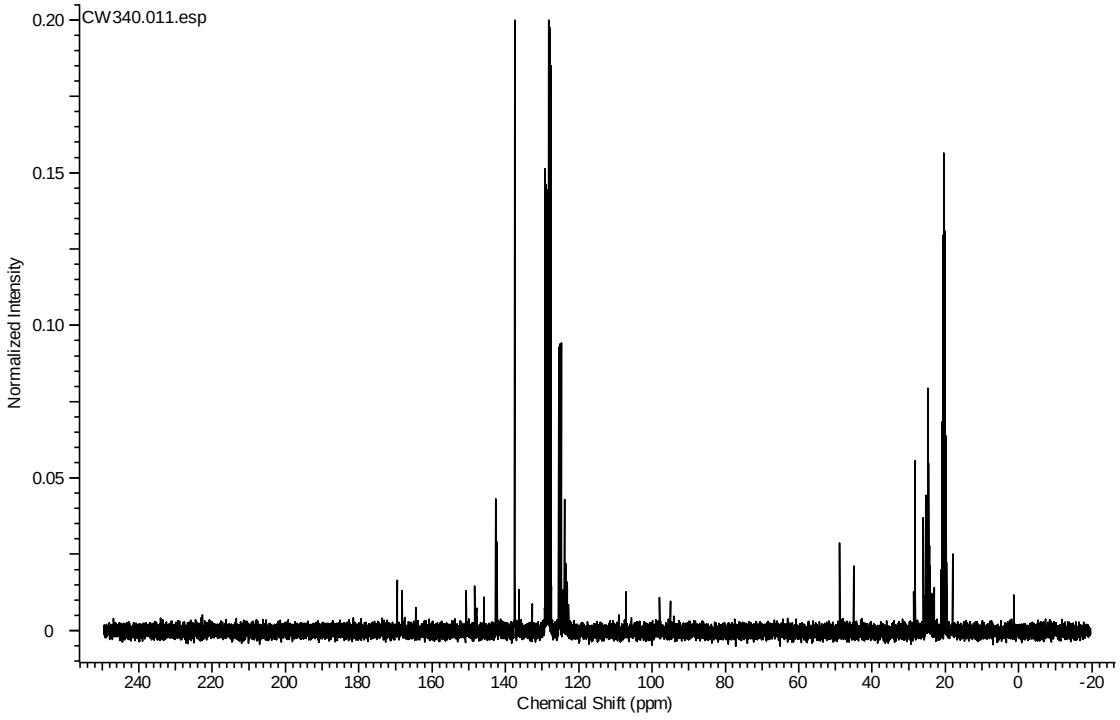
0.10
0.05
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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Normalized Intensity
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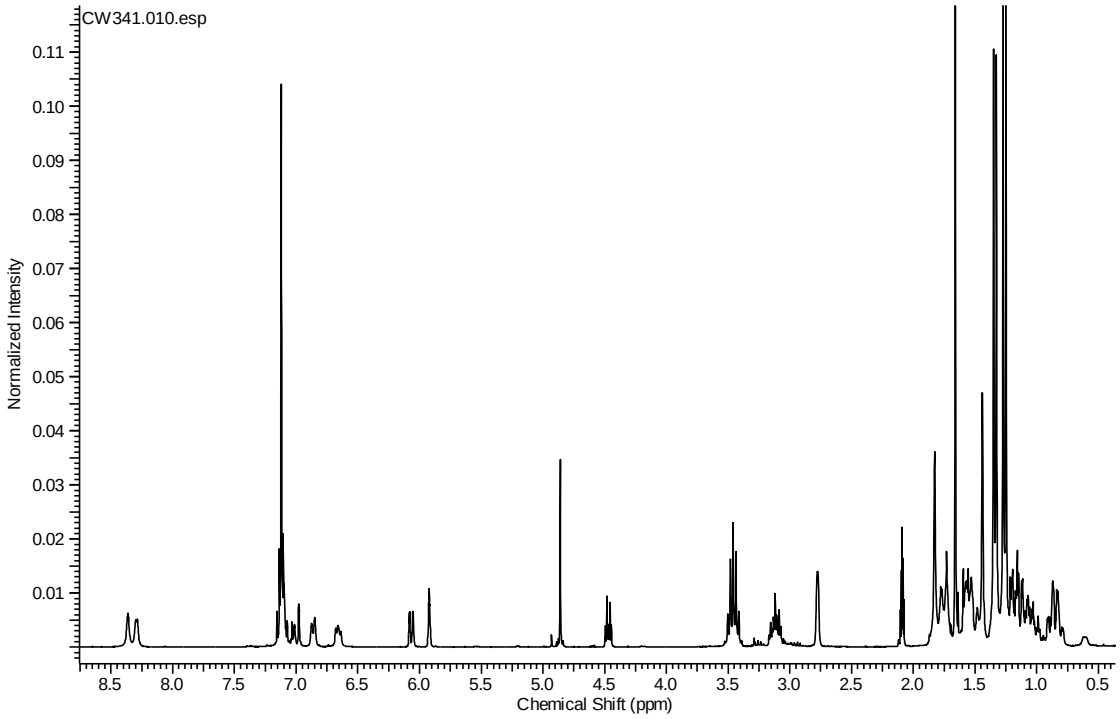
0.10
0.05
0
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

Compound 5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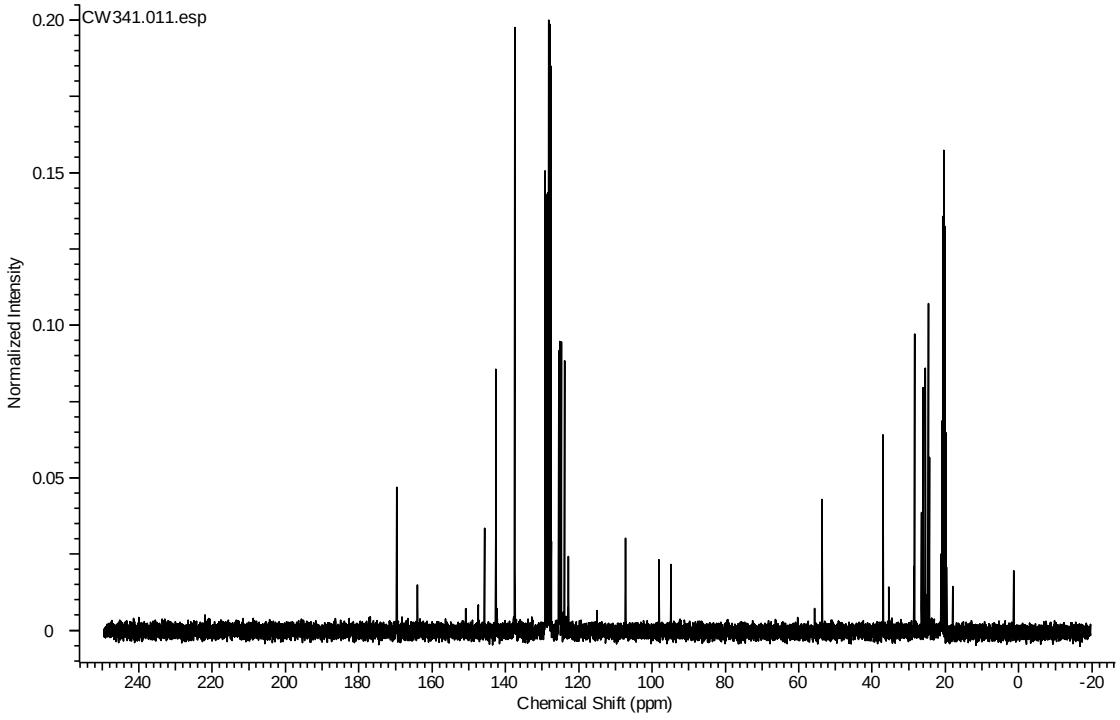
0.04
0.03
0.02
0.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)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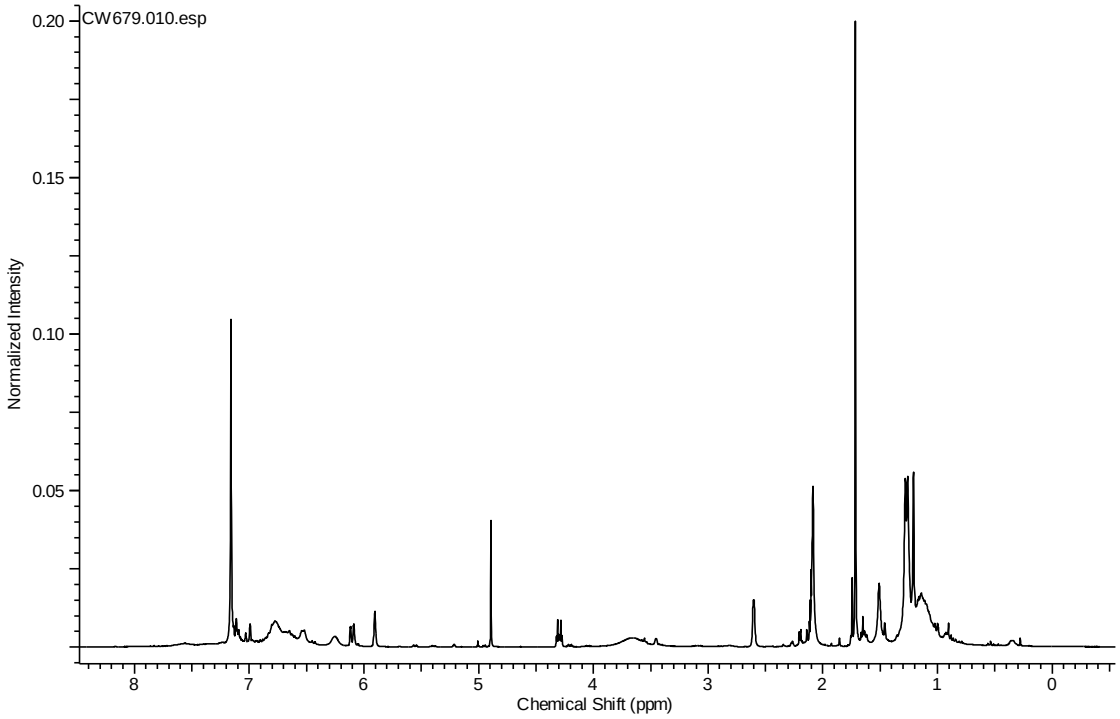
0.10
0.05
0
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

Compound 6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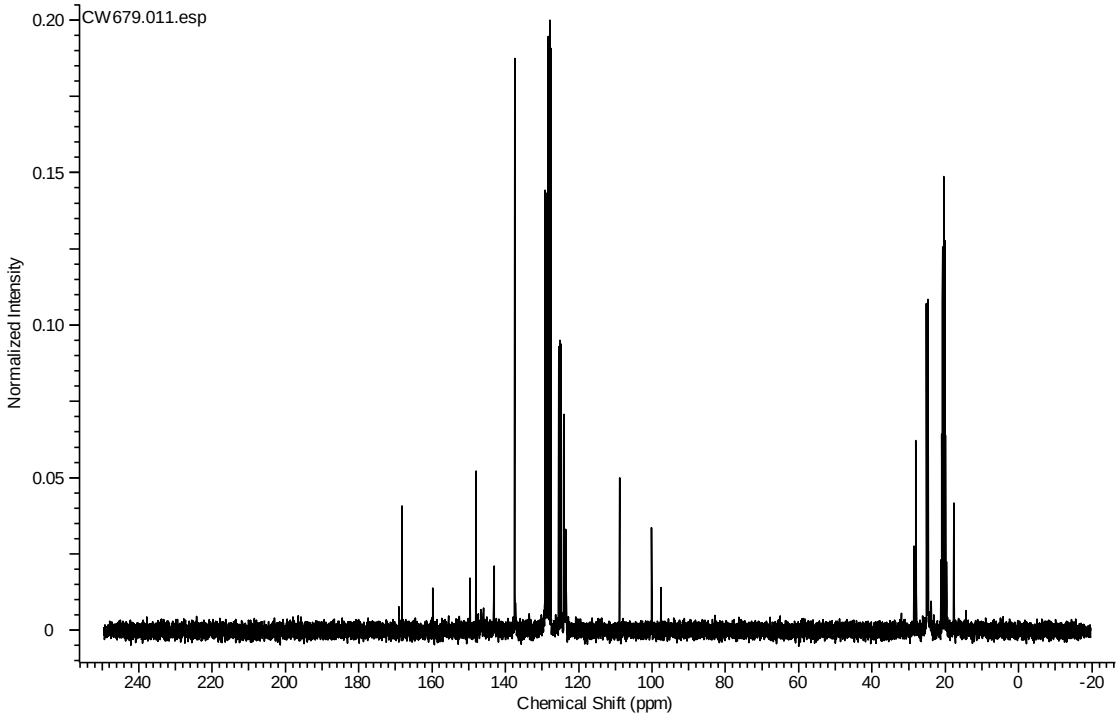
6
5
4
3
2
1
0
Chemical Shift (ppm)


CW679.011.esp
Normalized Intensity
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0.10
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240
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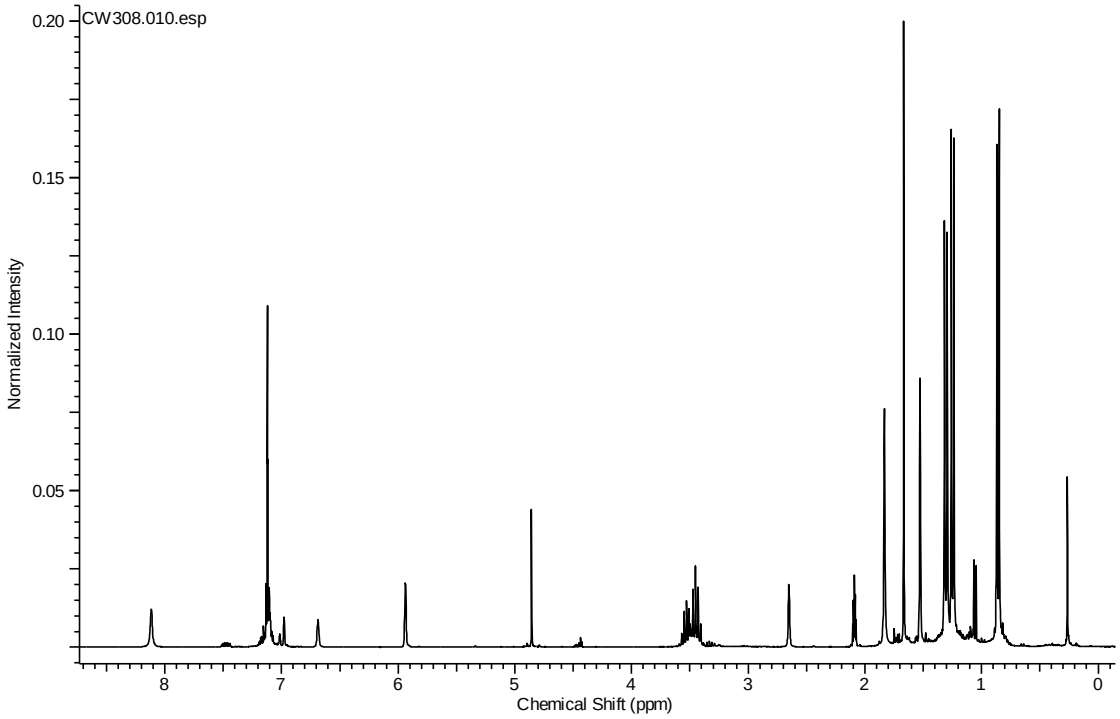
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

Compound 7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6
5
4
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2
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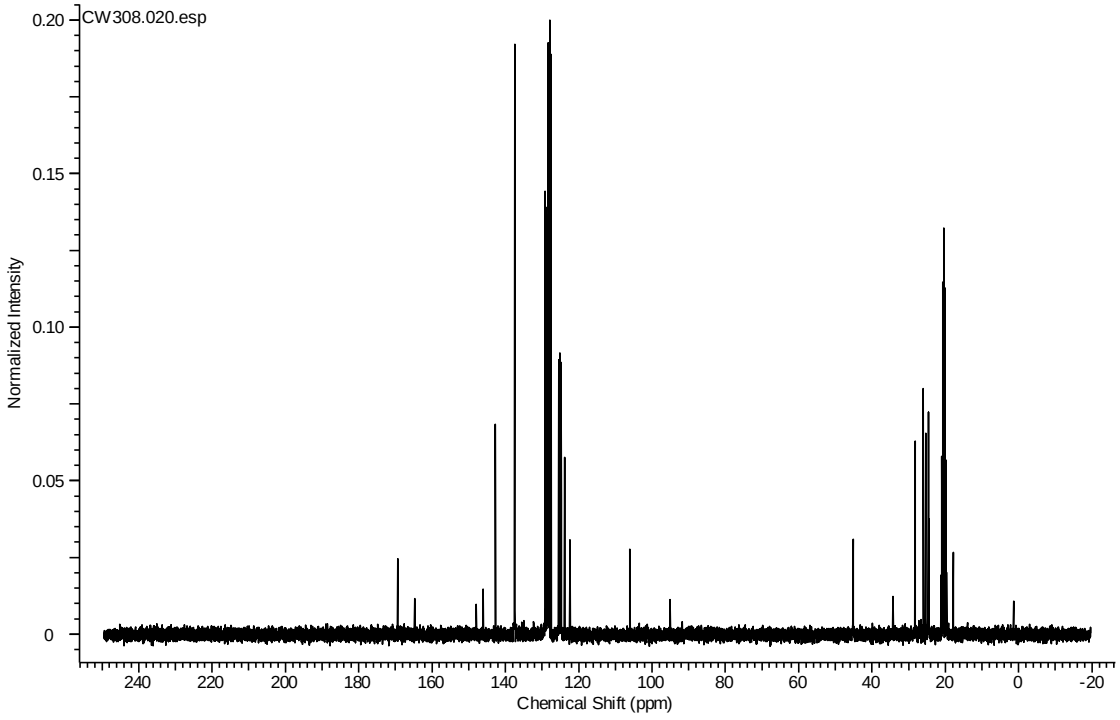
0
Chemical Shift (ppm)


CW308.020.esp
Normalized Intensity
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200
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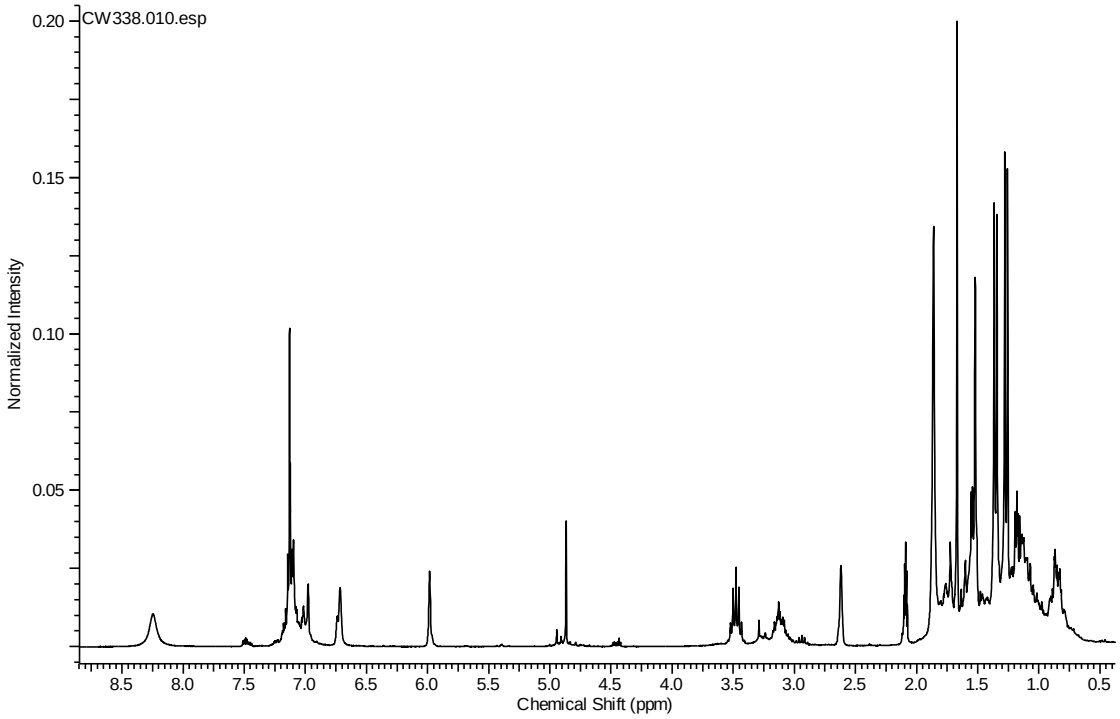
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

Compound 8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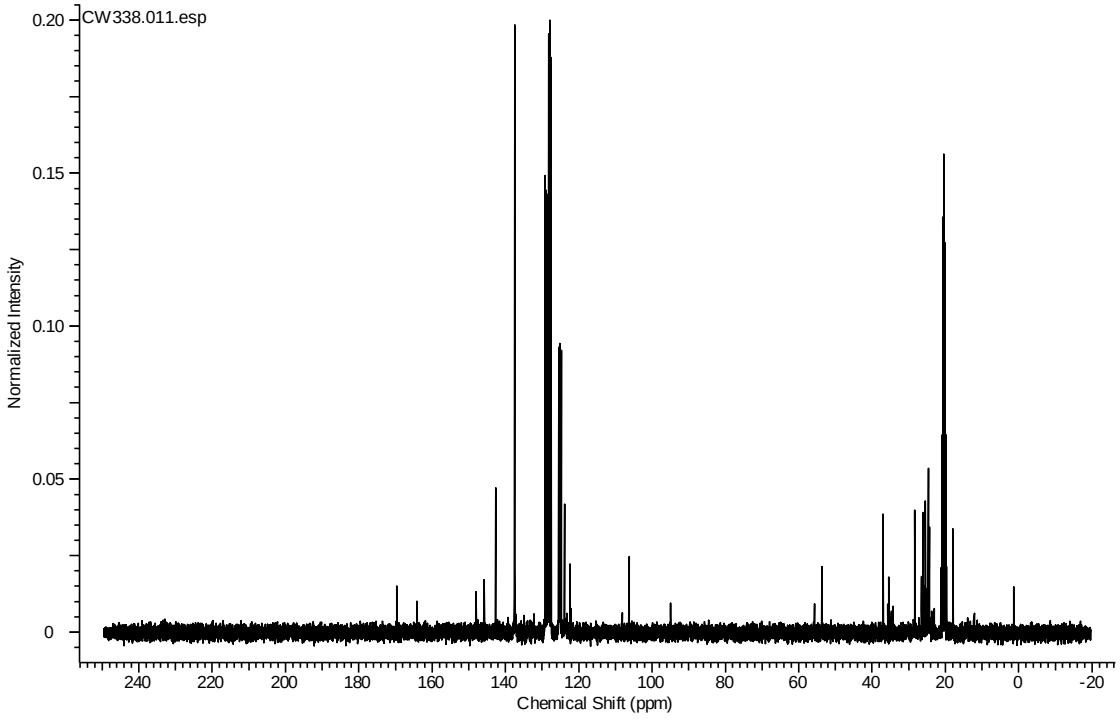
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)


CW338.011.esp
Normalized Intensity
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0.10
0.05
0
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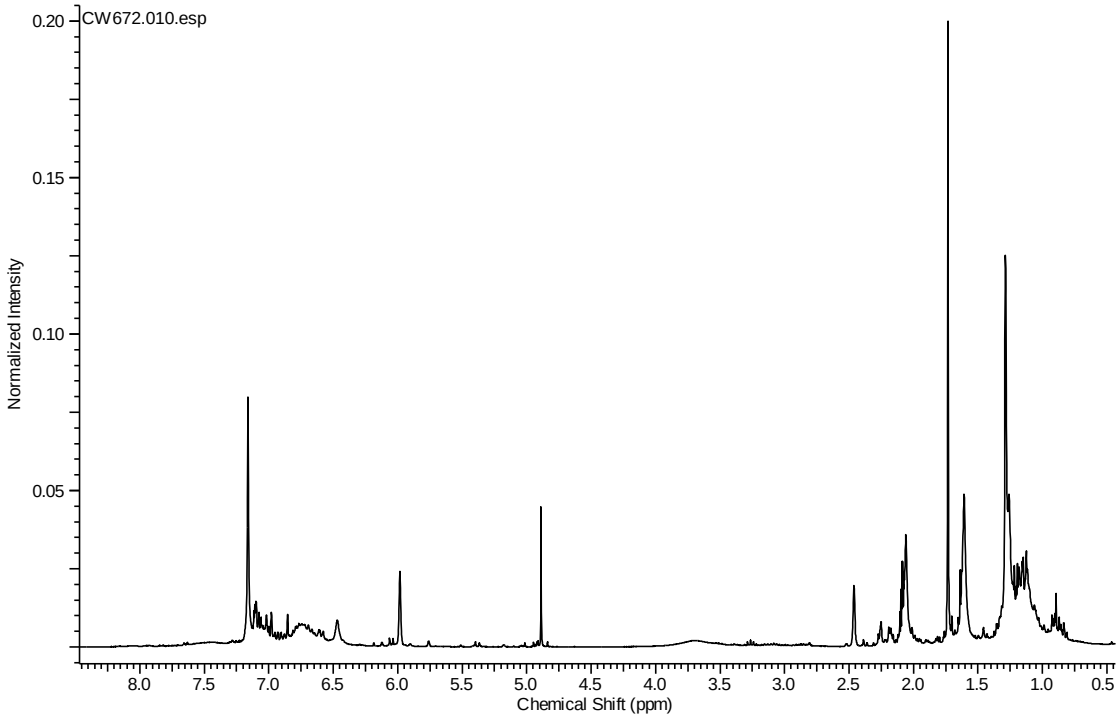
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

Compound 9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Normalized Intensity
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5.5
5.0
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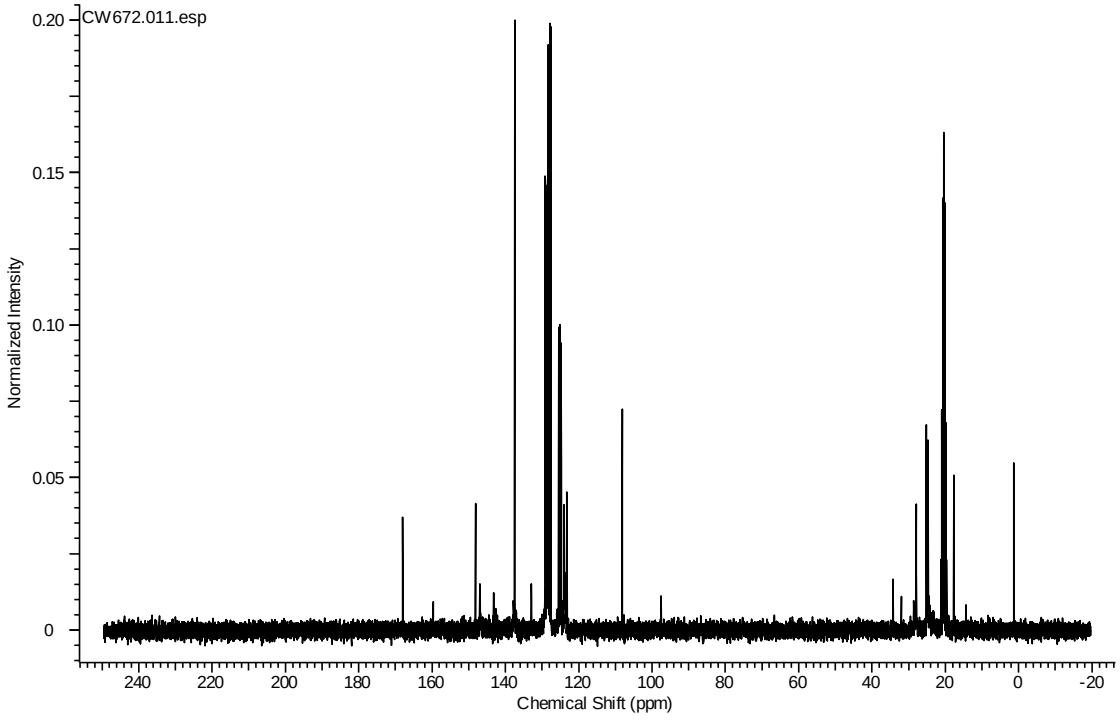
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)


CW672.011.esp
Normalized Intensity
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0.10
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220
200
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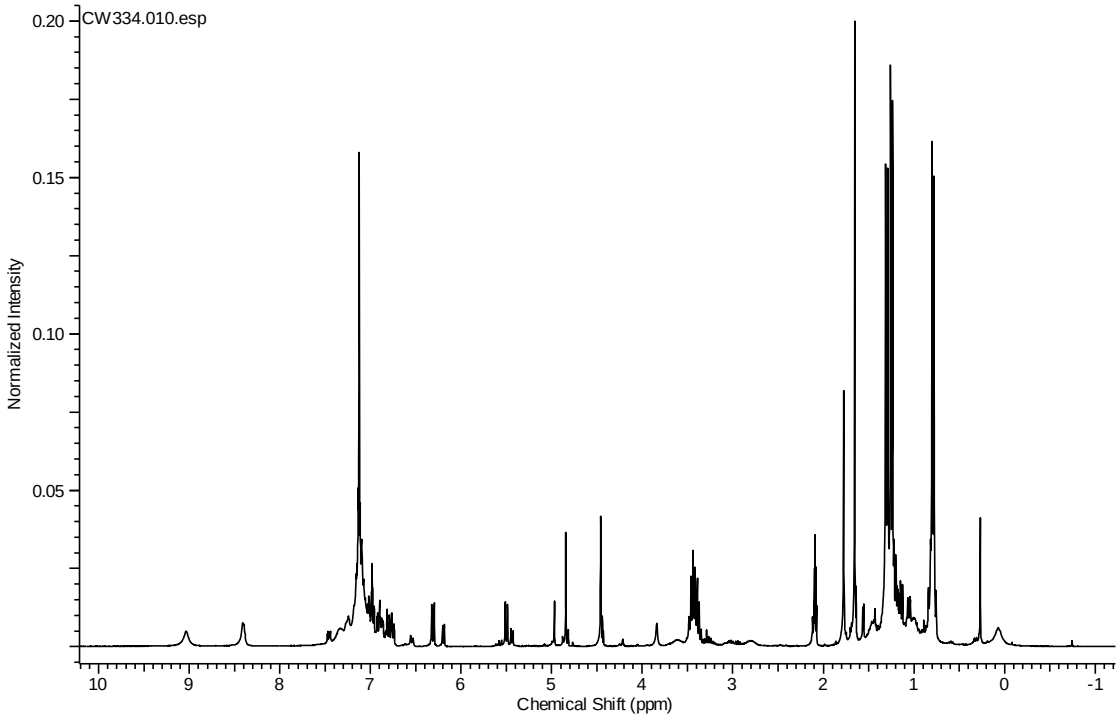
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

Compound 10


CW334.010.esp
Normalized Intensity
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10
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7
6
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4
3
2
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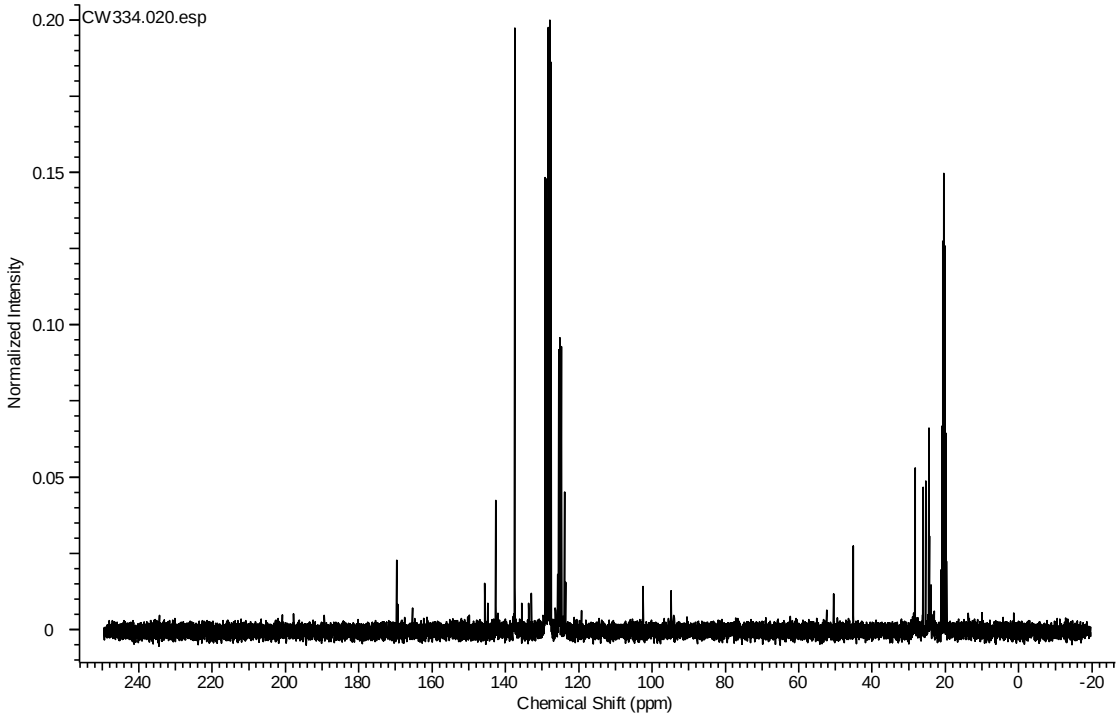
0
-1
Chemical Shift (ppm)


CW334.020.esp
Normalized Intensity
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0.10
0.05
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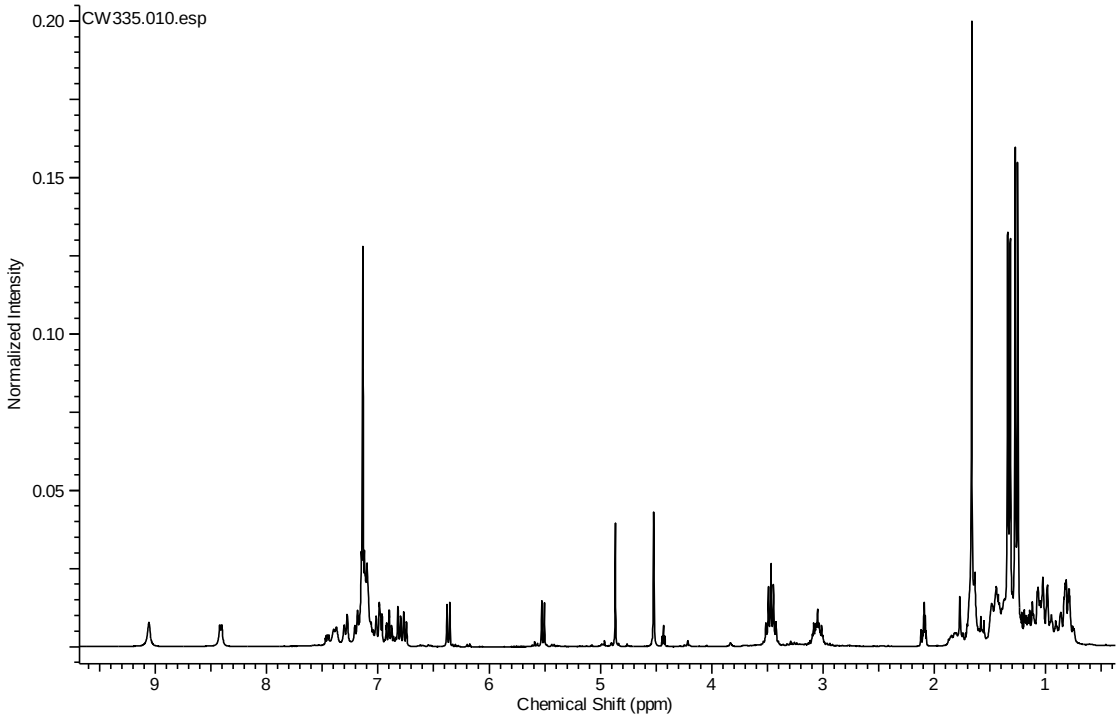
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

Compound 11


CW335.010.esp
Normalized Intensity
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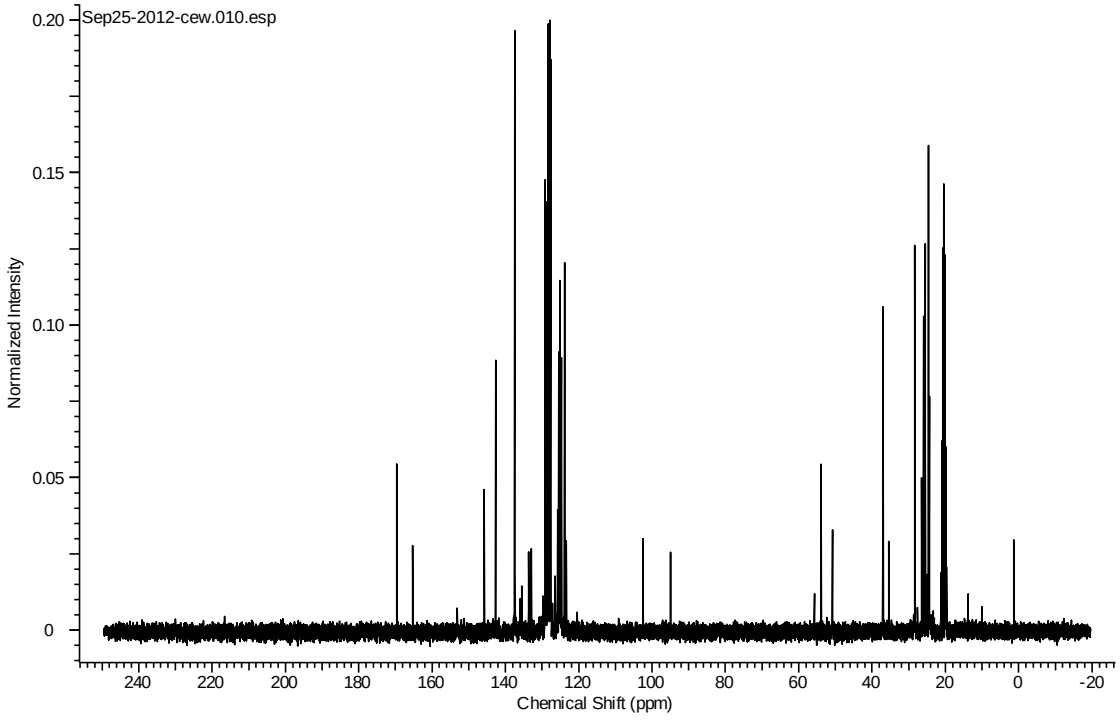
0.05
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)


Sep25-2012-cew.010.esp
Normalized Intensity
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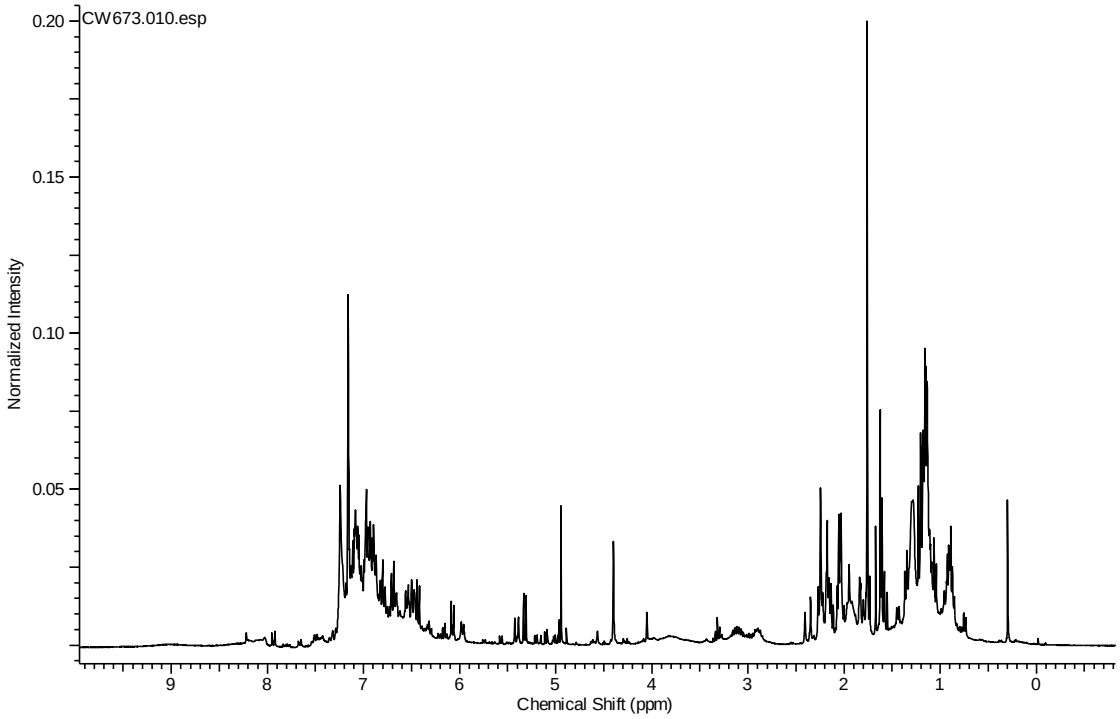
40
20
0
-20
Chemical Shift (ppm)

Compound 12


CW673.010.esp
Normalized Intensity
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0.05
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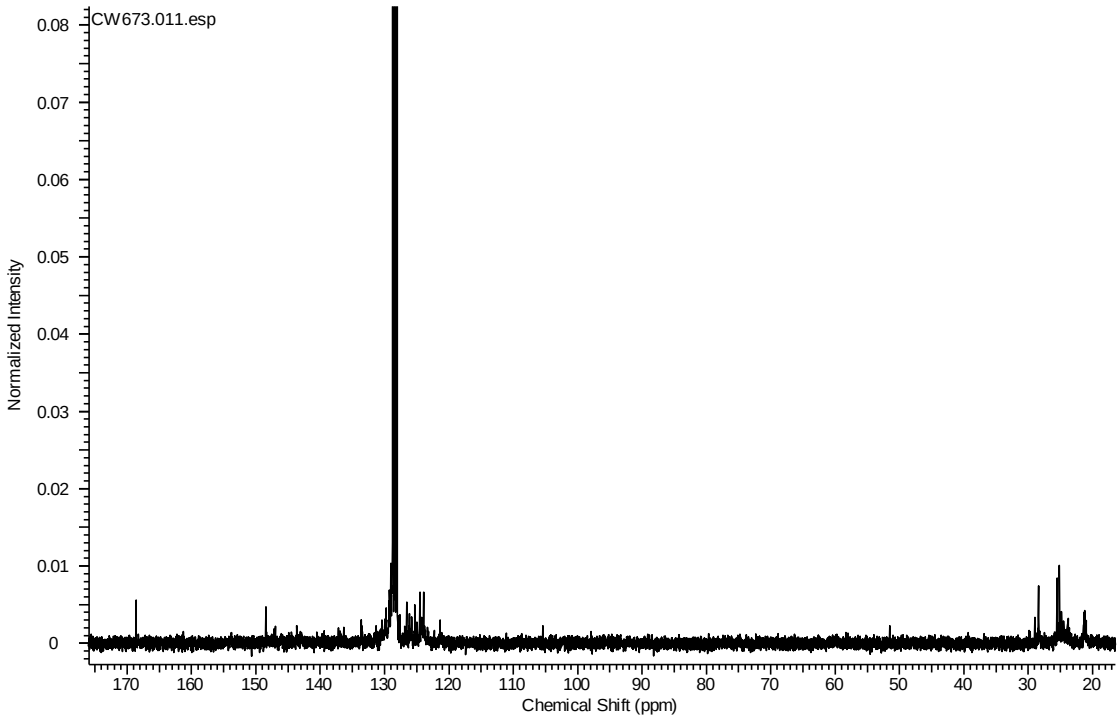
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


CW673.011.esp
Normalized Intensity
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0.02
0.01
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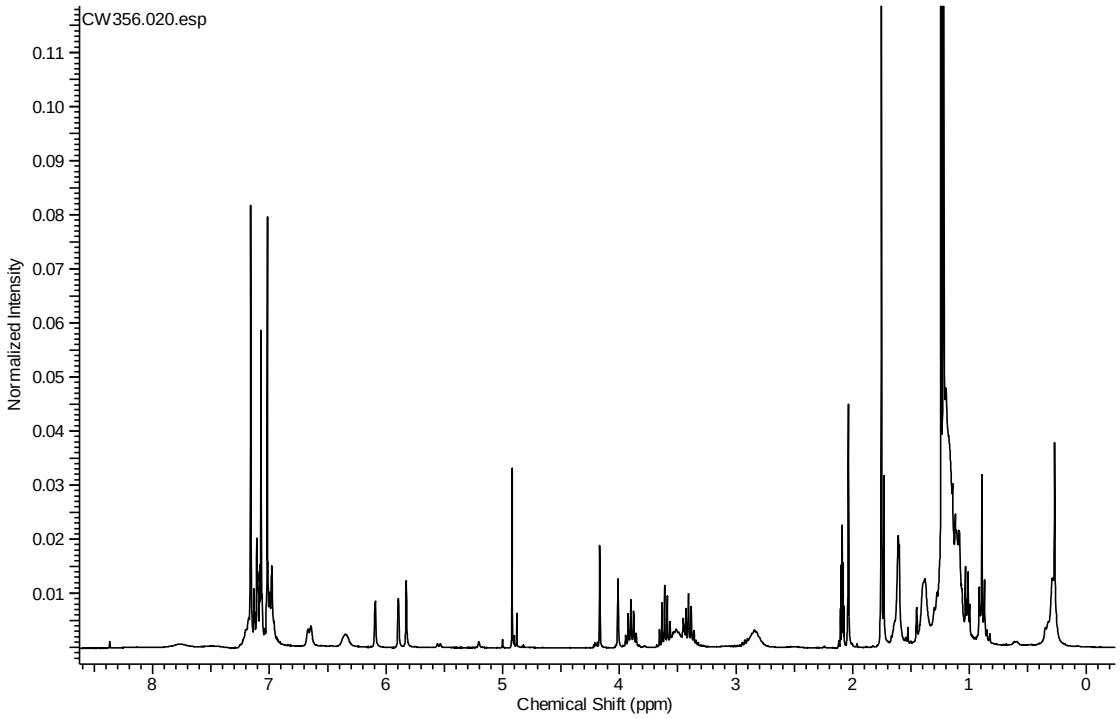
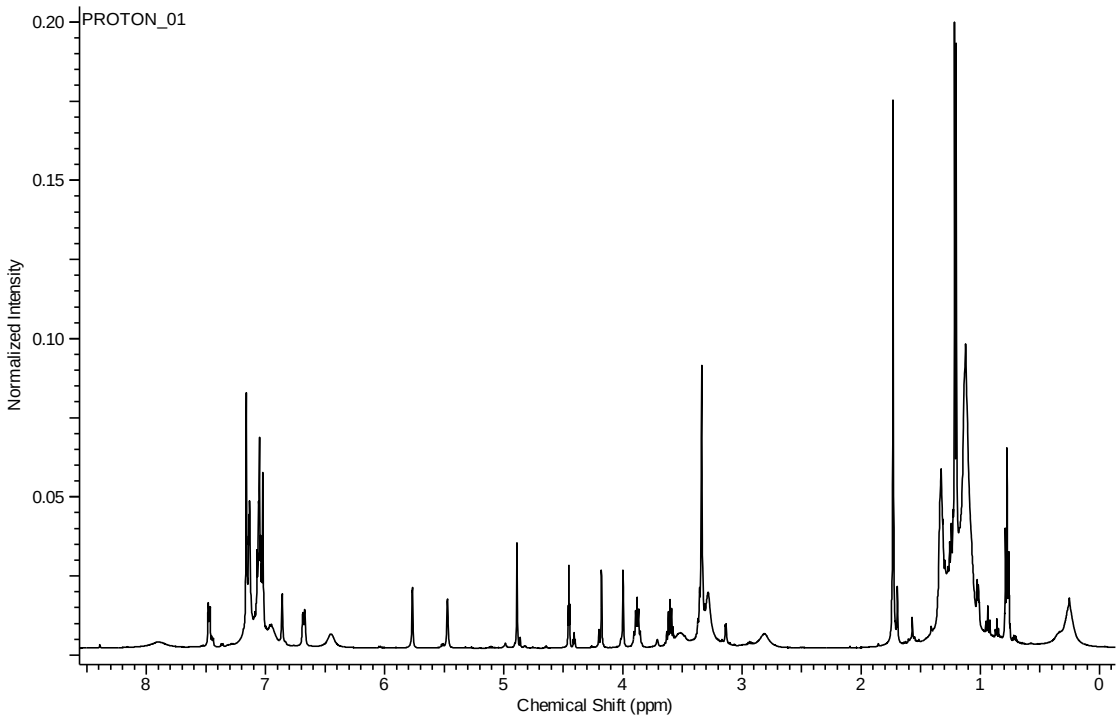
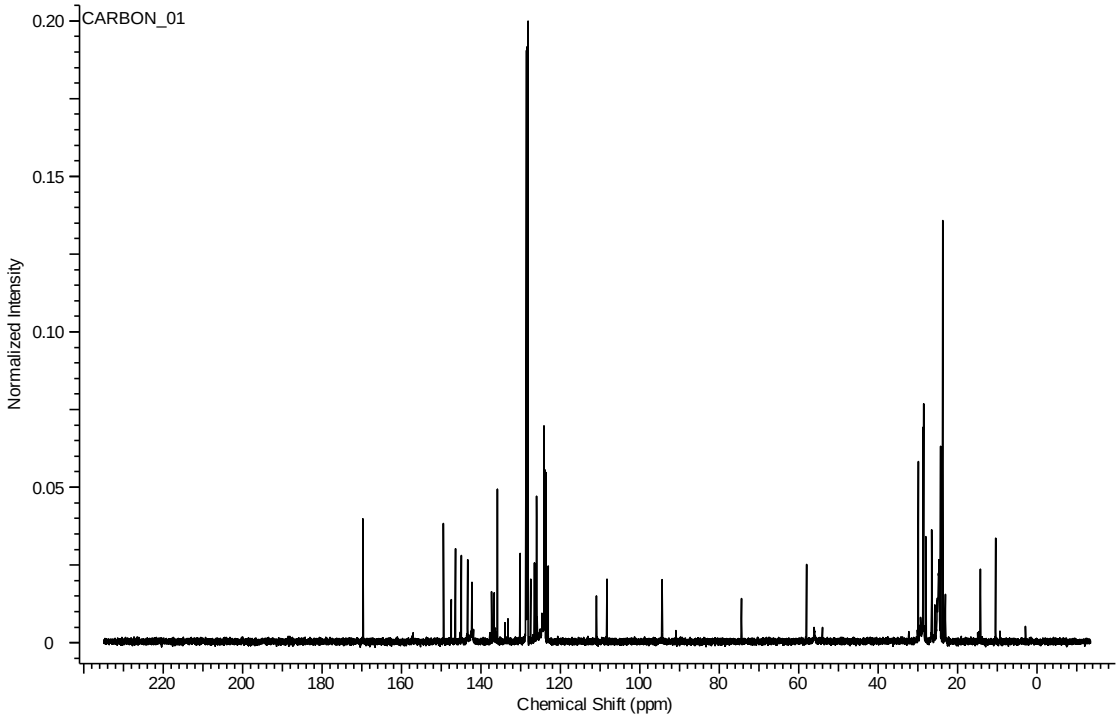
150
140
130
120
110
100
90
80
70
60
50
40
30
20
Chemical Shift (ppm)

Compound 13



Compound 14




CARBON_01
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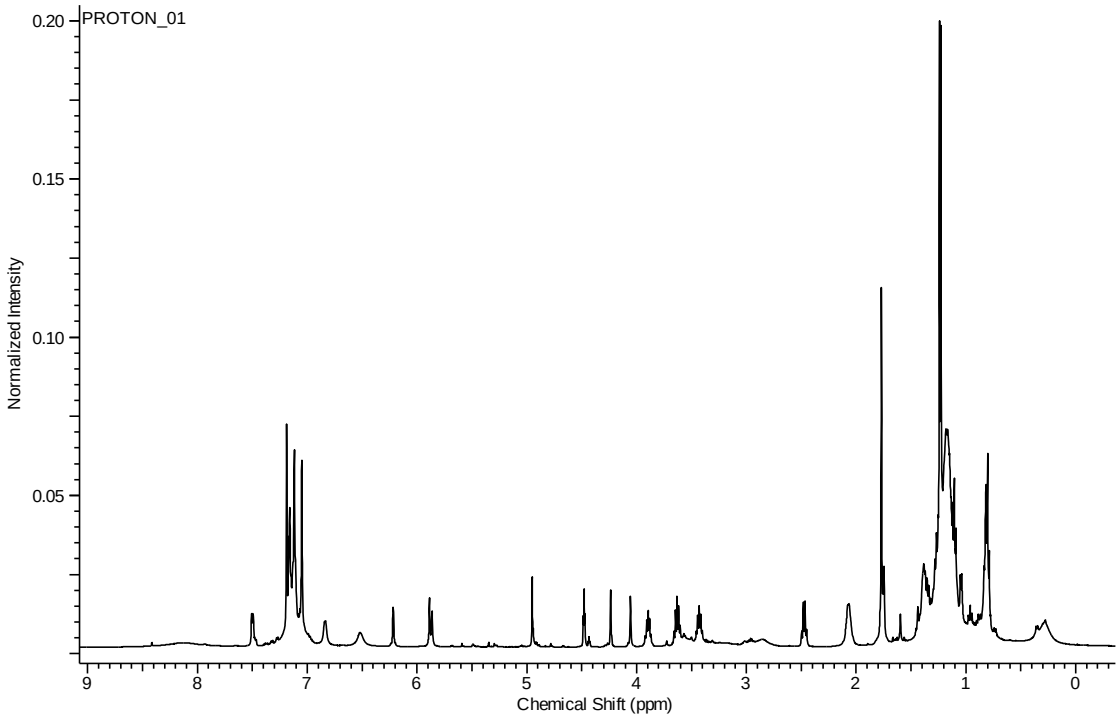
0.10
0.05
0
220
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

Compound 15


PROTON_01
Normalized Intensity
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0.05
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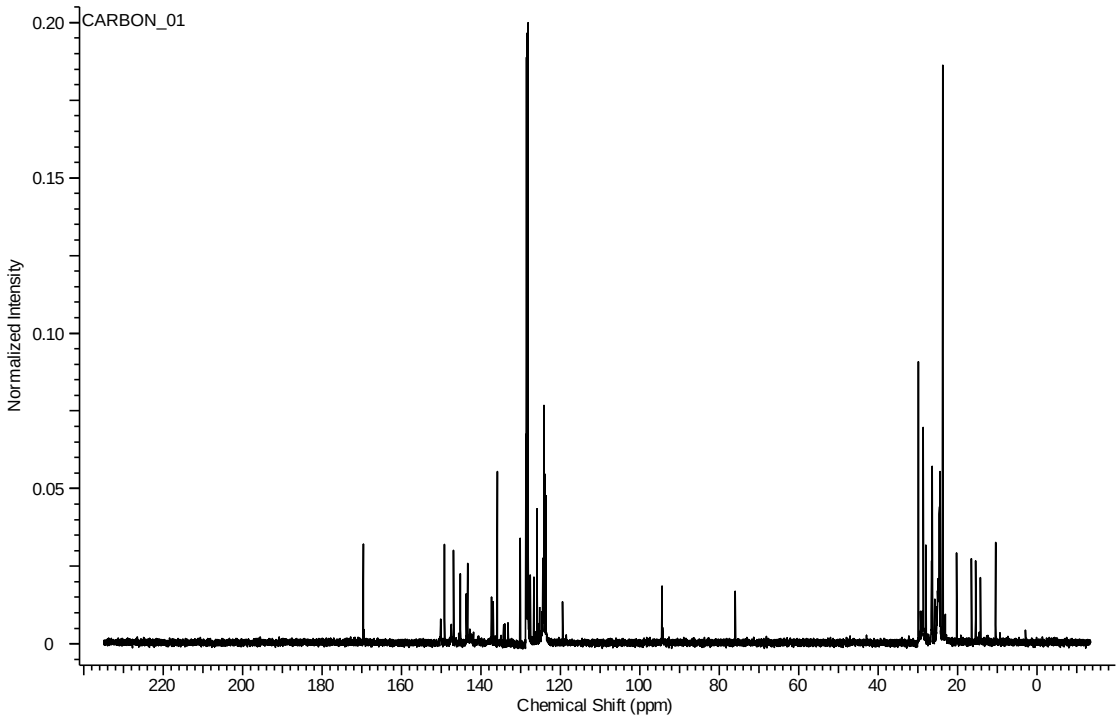
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


CARBON_01
Normalized Intensity
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0.15
0.10
0.05
0
220
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

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-Kα radiation monochromated with graphite (λ = 0.71070 Å). Data were processed with the Nonius software,[2,3] with structure solution and refinement using XSeed, SHELXS and SHELXL[4] 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 0.98Å 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	C69.50 H94 Mg N6
Formula weight	1037.82
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/n
Unit cell dimensions	a = 11.1770(1)Å alpha = 90°
	b = 25.6120(3)Å beta = 96.622(1)°
	c = 22.8890(3)Å gamma = 90°
Volume	6508.61(13) $Å^3$
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 °.
Index ranges	-13<=h<=13; -30<=k<=30; -27<=l<=27
Reflections collected	85482
Independent reflections	11437 [R(int) = 0.0709]
Reflections observed (>2sigma)	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>2sigma(I)]	R1 = 0.0534 *wR*2 = 0.1173
R indices (all data)	R1 = 0.0843 *wR*2 = 0.1339
Largest diff. peak and hole	0.358 and -0.267 $eÅ^{-3}$

References

1. V. C. Gibson, J. A. Segal, A. J. P. White, D. J. Williams,*J. A. Chem. Soc.* **2000**, *122*, 7120.

2. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *Journal of Applied Crystallography*, **1999**, *32*, 115-119.

3. Z. Otwinowski and W. Minor, *DENZO-SMN Manual*, University of Texas Southwestern Medical Center, Dallas, USA, **1996**.

4. G. M. Sheldrick, *SHELXL97-2, Program for Crystal Structure Refinement*, Universität Göttingen, Göttingen, Germany, **1998**.

5. C. Barnes, *Journal of Applied Crystallography*, **1997**, *30*, 568.