The design and synthesis of green emissive iridium(III) complexes guided by calculations of the vibrationally-resolved emission spectra

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Supplementary Information

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General Experimental

General Synthetic Considerations. All reactions were performed using standard Schlenk techniques under an inert (N_2) atmosphere. No special precautions were taken to exclude air and moisture during reaction workup and purification. The starting materials 2-bromo-4-trimethylsilyl-pyridine and 2-bromo-5-trimethylsilyl-pyridine were prepared from their respective di-bromo-pyridine precursors according to a literature method.[1] All other chemicals were obtained from commercial suppliers and used as received.

NMR Spectroscopy. ^{1}H, ^{13}C and ^{29}Si spectra were recorded on a Bruker AVANCE II 400 spectrometer equipped with a BBFO probe (400 MHz for ^{1}H; 101 MHz for ^{13}C; 79 MHz for ^{29}Si). ^{13}C and ^{29}Si NMR spectra were recorded with proton decoupling. ^{1}H and ^{13}C NMR spectra were referenced relative to residual solvent peaks, the ^{29}Si spectra were referenced externally to tetramethylsilane (TMS) ($\delta = 0$ ppm). The following abbreviations have been used for multiplicity assignments: "s" for singlet, "d" for doublet, "t" for triplet, "dd" for doublet of doublets, and "m" for multiplet.

Melting Point

Melting points were measured using open-ended capillaries on an Electrothermal 1101D Mel-Temp apparatus and are uncorrected.

HPLC

HPLC traces were recorded on a Shimadzu Nexera LC-40 HPLC system. A Shim-pack GIST 3μm C18 column (3.0 x 150 mm) was used with acetonitrile/water as the mobile phase.

Mass Spectrometry

Mass spectra were measured in positive ion electrospray ionisation (ESI^+) mode on a Thermoscientific LCQ instrument by the St Andrews Mass Spectrometry facility.

Electrochemistry

Cyclic voltammetry (CV) and Differential Pulse Voltammetry were carried out on a CHI620E voltammetric analyser at room temperature with a conventional three-electrode configuration consisting of a platinum disk working electrode, a platinum wire auxiliary electrode and a non-aqueous Ag/AgCl reference electrode. Acetonitrile purged with solvent-saturated nitrogen was used as the solvent, with tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 0.1M) used as the supporting electrolyte. The cyclic voltammograms were obtained at a scan rate of 100 mV s^{-1}. DPV was conducted with an increment potential of 0.01 V and a pulse amplitude, width, and period of 50 mV, 0.06, and 0.5 s, respectively. The redox potentials

are reported relative to a saturated calomel electrode (SCE) with ferrocene/ferricenium (Fc/Fc^+) used as the internal standard (0.38 V vs SCE).[2]

Absorption Spectroscopy

Solutions for absorption spectrometry were prepare in spectroscopic grade toluene (dichloromethane for IrPic) with concentrations in the range 1.39×10^{-4} to 2.78×10^{-5} M. Absorption spectra were recorded at room temperature on a Shimadzu UV-2600 double beam spectrophotometer with a 1 cm quartz cuvette. Molar absorptivity determination was verified by linear regression analysis of values obtained from 4 independent solutions at varying concentrations.

Photophysics

For emission studies, degassed solutions were prepared via three freeze-pump-thaw cycles in a custom made Schlenk cuvette. Steady-state emission, excitation spectra and time-resolved emission spectra were recorded at 298 K using an Edinburgh Instruments FS5. Emission spectra were excited at 400 nm using a Xenon lamp, excitation spectra were recorded while measuring emission at 510 nm. Emission lifetimes were determined using the time correlated single photon counting (TCSPC) technique, the samples were excited at 378 nm by a pulsed laser diode (Picoquant, model PLS 370).

Doped films were prepared from solutions of emitter (10% w/w) and host (90% w/w) in chlorobenzene (chloroform for IrPic) by spin-coating on a quartz substrate. Emission spectra and time-resolved emission spectra were measured at 298 K in a vacuum of $< 2 \times 10^{-4}$ mbar on an Edinburgh Instruments F980. Emission spectra were excited at 340 nm. Emission lifetimes were determined using the time correlated single photon counting (TCSPC) technique, the samples were excited at 378 nm by a pulsed laser diode (Picoquant, model PLS 370). Quantum yields of the thin film samples were measured using an integrating sphere attached to an Edinburgh Instruments FS5 fluorimeter, the samples were purged with nitrogen and excited at 340 nm for the measurement of quantum yields, values are reported to the nearest % with an estimated experimental uncertainty of ± 5%.

Synthesis

Synthesis of Ligands

General Procedure. 2-Bromopyridine (1.00 g, 6.33 mmol, 1.0 equiv.) and 3-trimethylsilyl-phenylboronic acid (1.47 g, 7.59 mmol, 1.2 equiv.) were dissolved in tetrahydrofuran (THF) (50 mL). A solution of 2 M K_2CO_3 (5 mL) was added, and the mixture was degassed by bubbling with nitrogen before the addition of $Pd(PPh_3)_4$ (366 mg, 0.31 mmol, 5 mol%). The reaction mixture was heated to reflux under an inert atmosphere for 16 h. After being cooled, the mixture was quenched with aqueous 1 M HCl (25 mL) before being neutralised with aqueous K_2CO_3 (2M) and extracted with DCM (3 × 25 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure to give a dark yellow oil. The crude oil was purified by column chromatography (2.5% EtOAc in hexane on Silica).

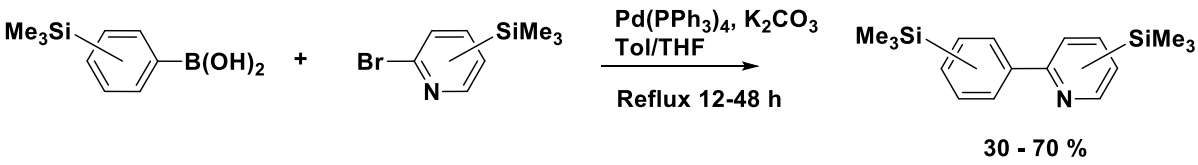


Figure 1. General conditions for the Suzuki coupling to form phenyl-pyridine ligands.

C3Sippy: Product was obtained as a pale-yellow oil. **Yield**: 15%. **^{1}H NMR (400 MHz, $CDCl_3$, δ ppm):** 8.72 (m, 1H), 8.12 (s, 1H), 7.94 (m, 1H), 7.75 (m, 2H), 7.59 (m, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.31 (m, 1H), 7.24 (m, 1H), 0.32 (s, 9H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ ppm):** 158.1, 149.8, 141.2, 138.8, 136.9, 134.1, 131.9, 128.8, 127.7, 122.1, 121.0, -0.9. **^{29}Si{^{1}H} NMR (76 MHz, $CDCl_3$, δ ppm):** -3.5. **HR-MS: $[M+H]^+$ Calculated for $C_{14}H_{18}NSi$,** 228.1209, **Found,** 228.1195.

C4Sippy: Product was obtained as a colourless oil that solidified upon standing to a white solid. **Yield:** 47%. **^{1}H NMR (400 MHz, $CDCl_3$, δ ppm):** 8.70 (m, 1H), 7.97 (d, J = 8.3 Hz, 2H), 7.74 (m, 2H), 7.64 (d, J = 8.3 Hz, 2H), 7.23 (m, 1H), 0.30 (s, 9H) ppm. **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ ppm):** 157.6, 149.8, 141.6, 139.8, 136.9, 133.9, 126.2, 122.3, 120.7, -1.0. **^{29}Si{^{1}H} NMR (76 MHz, $CDCl_3$, δ ppm):** -3.8. **HR-MS: $[M+H]^+$ Calculated for $C_{14}H_{18}NSi$,** 228.1209, **Found,** 228.1195.

N4Sippy: Product was obtained as a colourless oil. **Yield:** 39%. **^{1}H NMR (400 MHz, $CDCl_3$, δ ppm):** 8.66 (dd, J = 4.7 and 1.0 Hz, 1H), 7.98 (m, 2H), 7.81 (*pseudo*-triplet (dd), J = 1.0Hz, 1H), 7.48 (m, 2H), 7.43 (m, 1H), 7.33 (dd, J = 4.6 and 1.0 Hz, 1H), 0.33 (s, 9H). **^{13}C{^{1}H}**

NMR (101 MHz, $CDCl_3$, δ ppm): 156.4, 151.2, 148.7, 140.0, 128.9, 128.8, 127.2, 126.7, 125.2, -1.5. **$^{29}Si\{^1H\}$ NMR (76 MHz, $CDCl_3$, δ ppm):** -2.9. **HR-MS: $[M+H]^+$ Calculated for $C_{14}H_{18}NSi$,** 228.1209, **Found,** 228.1200.

N5Sippy: Product was obtained as a pale-yellow oil. **Yield:** 27%. **^1H NMR (400 MHz, $CDCl_3$, δ ppm):** 8.77 (m, 1H), 8.00 (m, 1H), 7.86 (dd, J = 7.8 and 1.8 Hz, 1H), 7.71 (dd, J = 7.8 and 1.1 Hz, 1H), 7.48 (m, 2H), 7.43 (m, 1H), 0.33 (s, 9H). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ ppm):** 157.6, 154.0, 142.1, 139.6, 133.3, 129.1, 128.9, 127.0, 112.0, -1.1. **$^{29}Si\{^1H\}$ NMR (76 MHz, $CDCl_3$, δ ppm):** -4.0. **HR-MS: $[M+H]^+$ Calculated for $C_{14}H_{18}NSi$,** 228.1209, **Found,** 228.1197.

C3N4Si$_2$ppy: Product was obtained as a colourless oil that solidified upon standing to a white solid. **Yield:** 66%. **^1H NMR (400 MHz, $CDCl_3$, δ ppm):** 8.66 (dd, J = 4.8 and 1.0 Hz, 1H), 8.11 (s, 1H), 7.90 (m, 1H), 7.78 (*pseudo*-triplet (dd), J = 1.0 Hz, 1H), 7.58 (m, 1H), 7.47 (m, 1H), 7.34 (dd, J = 4.8 and 1.0 Hz, 1H), 0.33 (s, 9H), 0.32 (s, 9H). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ ppm):** 157.0, 151.1, 148.7, 141.1, 139.3, 133.9, 132.1, 128.2, 127.8, 126.6, 125.5, -0.9, -1.5. **$^{29}Si\{^1H\}$ NMR (76 MHz, $CDCl_3$, δ ppm):** -2.9, -3.6. **HR-MS: $[M+H]^+$ Calculated for $C_{17}H_{26}NSi_2$,** 300.1604, **Found,** 300.1588.

C3N5Si$_2$ppy: Product was obtained as a pale-yellow oil. **Yield:** 34%. **^1H NMR (400 MHz, $CDCl_3$, δ ppm):** 8.79 (m, 1H), 8.13 (s, 1H), 7.95 (m, 1H), 7.86 (dd, J = 7.8 and 1.8 Hz, 1H), 7.70 (dd, J = 7.8 and 1.0 Hz, 1H), 7.58 (m, 1H), 7.47 (m, 1H), 0.33 (s, 9H), 0.32 (s, 9H). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ ppm):** 158.1, 154.0, 142.0, 141.1, 138.9, 134.1, 133.1, 131.9, 128.2, 127.6, 120.3, -0.9, -1.1. **$^{29}Si\{^1H\}$ NMR (76 MHz, $CDCl_3$, δ ppm):** -3.5, -4.0. **HR-MS: $[M+H]^+$ Calculated for $C_{17}H_{26}NSi_2$,** 300.1604, **Found,** 300.1592.

C4N4Si$_2$ppy: Product was obtained as a colourless oil. **Yield:** 51%. **^1H NMR (400 MHz, $CDCl_3$, δ ppm):** 8.65 (dd, J = 4.7 and 1.1 Hz, 1H), 7.95 (d, J = 8.3 Hz, 2H), 7.85 (*pseudo*-triplet (dd), J = 1.0 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.33 (m, 1H), 0.33 (s, 9H), 0.30 (s, 9H). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ ppm):** 156.5, 151.1, 148.7, 141.3, 140.3, 133.9, 126.7, 126.4, 125.3, -1.0, -1.5. **$^{29}Si\{^1H\}$ NMR (76 MHz, $CDCl_3$, δ ppm):** -2.9, -3.9. **HR-MS: $[M+H]^+$ Calculated for $C_{17}H_{26}NSi_2$,** 300.1604, **Found,** 300.1588.

C4N5Si$_2$ppy: Product was obtained as a colourless oil that solidified upon standing to a white solid. **Yield:** 19%. **^1H NMR (400 MHz, $CDCl_3$, δ ppm):** 8.77 (s, 1H), 7.98 (d, J = 8.4 Hz, 2H), 7.85 (dd, J = 7.9 and 1.9 Hz, 1H), 7.70 (dd, J = 7.9 and 0.9 Hz, 1H), 7.63 (d, J = 8.3 Hz, 2H), 0.33 (s, 9H), 0.30 (s, 9H). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ ppm):** 157.6, 154.1, 142.0, 141.6, 139.9, 133.9, 133.3, 136.2, 126.2, 120.1, -1.0, -1.1. **$^{29}Si\{^1H\}$ NMR (76 MHz,**

$CDCl_3$, δ ppm): -3.8, -4.0. **HR-MS: $[M+H]^+$ Calculated for $C_{17}H_{26}NSi_2$,** 300.1604, **Found,** 300.1596.

Synthesis of Iridium Dimers

General Procedure. $[Ir(COD)Cl]_2$ (200 mg, mmol) and silylated ppyH ligand (4.4 equiv.) were suspended in a mixture of 2-ethoxyethanol and water (3:1, 8 mL). The mixture was degassed by bubbling with nitrogen for 5 minutes, before heating to 120°C for 24 hrs under an inert atmosphere. The mixture was cooled to room temperature before the addition of water (10 mL) and DCM (25 mL). The layers were separated, and the aqueous layer was extracted with DCM (2 × 25 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was removed under vacuum to give a yellow solid. The crude dimer was used as-is for the next reaction without purification.

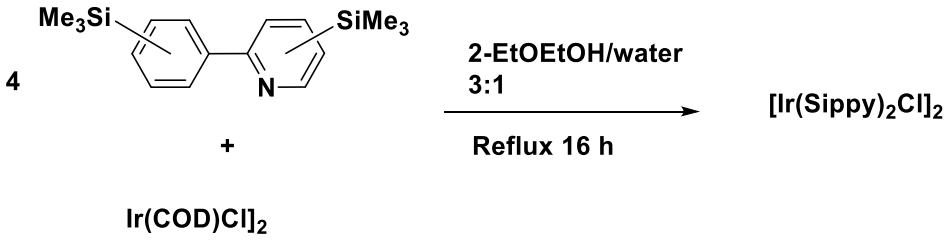


Figure 2. General conditions for the synthesis of the Iridium dimers.

$[Ir(C3Sippy)_2Cl]_2$: The product was obtained as a bright yellow solid in 96% yield.
$[Ir(C4Sippy)_2Cl]_2$: The product was obtained as a bright yellow solid in 90% yield.
$[Ir(N4Sippy)_2Cl]_2$: The product was obtained as a bright yellow solid in 94% yield
$[Ir(N5Sippy)_2Cl]_2$: The product was obtained as a bright yellow solid in 89% yield
$[Ir(C3N4Si_2ppy)_2Cl]_2$: The product was obtained as a bright yellow solid in 74% yield.
$[Ir(C3N5Si_2ppy)_2Cl]_2$: The product was obtained as a bright yellow solid in 45% yield.
$[Ir(C4N4Si_2ppy)_2Cl]_2$: The product was obtained as a bright yellow solid in 83% yield.
$[Ir(C4N5Si_2ppy)_2Cl]_2$: The product was obtained as a bright yellow solid in 54% yield.

Synthesis of Complexes

General Procedure. A schlenk flask was charged with iridium dimer (200 mg), sodium carbonate (10 equiv.), picolinic acid (4.4 equiv.) and 1,2-dimethoxyethane (5 mL). The mixture was purged with nitrogen and heated to reflux overnight and then cooled to room temperature. 10 mL of water and 25 mL of DCM were added, the layers were separated, and the aqueous layer was extracted with DCM (2 × 25 mL). The combined organic layers were dried ($MgSO_4$)

and the solvent removed under vacuum to give a yellow solid. The crude product was purified by column chromatography (EtOAc/MeOH/DCM on Silica) and recrystallised form DCM/hexanes.

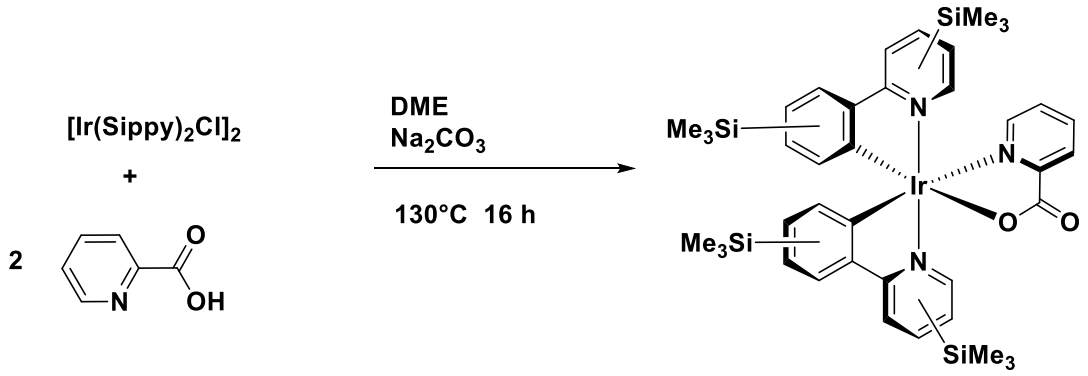


Figure 3. General conditions for the synthesis of the iridium complexes.

[Ir(ppy)$_2$(pic)] (IrPic): The product was obtained using 45% EtOAc and 5% MeOH in DCM as the mobile phase to give a bright yellow solid. The spectroscopic characterisation matches the previously reported data.[3] **Yield:** 87%. **M.p.:** >380 °C. **Rf (5:45:50 MeOH:EtOAc:DCM on silica):** 0.42. **^{1}H NMR (400 MHz, CDCl$_3$, δ):** 8.78 (d, 1H), 8.32 (d, 1H), 7.89-7.82 (m, 3H), 7.77 (d, H), 7.70 (m, 2H), 7.60 (m, 2H), 7.47 (d, 2H), 7.33 (m, 1H), 7.13 (m, 1H), 6.95-6.73 (m, 5H), 6.41 (d, 1H), 6.18 (d, 1H). **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, δ):** 173.0, 169.4, 167.8, 149.3, 149.1, 148.6, 148.2, 147.6, 144.3, 144.2, 137.7, 137.3, 137.2, 132.7, 132.6, 130.2, 129.7, 128.4, 128.1, 124.5, 124.2, 122.3, 122.1, 121.7, 121.2, 119.2, 118.6. **HR-MS: [M+H]$^+$ Calculated for C$_{28}$H$_{21}$IrN$_3$O$_2$,** 624.1263, **Found,** 624.1247.

[Ir(C3Sippy)$_2$(pic)] (C3): The product was obtained using 45% EtOAc and 5% MeOH in DCM as the mobile phase to give a bright yellow solid. **Yield:** 58%. **M.p.:** 239-241 °C. **R$_f$ (5:45:50 MeOH:EtOAc:DCM on silica):** 0.53. **^{1}H NMR (400 MHz, CDCl$_3$, δ):** 8.77 (d, 1H), 8.31 (d, 1H), 7.94 (d, 1H), 7.87 (m, 3H), 7.76 (d, 1H), 7.69 (m, 2H), 7.54 (t, 1H), 7.46 (m, 2H), 7.35 (t, 1H), 7.12 (t, 1H), 6.91 (m, 3H), 6.45 (d, 1H), 6.23 (d, 1H), 0.22 (s, 9H), 0.17 (s, 9H) ppm. **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, δ):** 172.9, 169.4, 167.8, 152.3, 151.1, 149.3, 149.1, 148.6, 148.2, 144.1, 143.9, 137.7, 137.2, 137.1, 135.1, 134.6, 131.5, 131.0, 129.3, 129.1, 128.7, 128.6, 128.3, 128.1, 122.2, 122.0, 119.2, 118.5, -0.8, -0.9 ppm. **^{29}Si{^{1}H} NMR (76 MHz, CDCl$_3$, δ):** -4.5, -4.6 ppm. **HR-MS: [M+H]$^+$ Calculated for C$_{34}$H$_{37}$IrN$_3$O$_2$Si$_2$,** 768.2054, **Found,** 768.2037.

[Ir(C4Sippy)$_2$(pic)] (C4): The product was obtained using 45% EtOAc and 5% MeOH in DCM as the mobile phase to give a bright yellow solid. **Yield:** 66%. **M.p.:** 243-245 °C. **R$_f$ (5:45:50 MeOH:EtOAc:DCM on silica):** 0.50. **^{1}H NMR (400 MHz, CDCl$_3$, δ):** 8.84 3 (d, 1H), 8.32 (d, 1H), 7.85 (m, 3H), 7.70 (m, 3H), 7.52 (m, 3H), 7.32 (m, 1H), 7.14 (m, 1H), 7.05 (d, 1H), 6.96 (d, 1H), 6.93 (m, 1H), 6.55 (s, 1H), 6.34 (s, 1H), 0.36 (s, 9H), 0.35 (s, 9H) ppm. **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, δ):** 173.1, 169.7, 168.2, 152.4, 149.4, 148.4, 148.2, 148.0, 146.6, 144.8, 144.7, 142.7, 141.7, 137.54, 137.47, 13717, 137.15, 137.06, 128.3, 128.1, 126.5, 125.9, 123.3, 123.1, 122.1, 121.9, 119.1, 118.5, -1.1, -1.2 ppm. **^{29}Si{^{1}H} NMR (76 MHz, CDCl$_3$, δ):** -5.1, -5.2 ppm. **HR-MS: [M]$^+$ Calculated for C$_{34}$H$_{36}$IrN$_3$O$_2$Si$_2$,** 767.1975, **Found,** 767.1955.

[Ir(N4Sippy)$_2$(pic)] (N4): The product was obtained using 30% EtOAc in DCM as the mobile phase to give a bright yellow solid. **Yield:** 83%. **M.p.:** 365-367 °C. **R$_f$ (20% EtOAc in DCM on silica):** 0.29. **^{1}H NMR (400 MHz, CDCl$_3$, δ):** 8.71 (d, 1H), 8.31, (d, 1H), 7.96 (s, 1H), 7.91 (s, 1H), 7.85 (m, 1H), 7.76 (d, 1H), 7.65 (m, 2H), 7.36 (d, 1H), 7.30 (m, 1H), 7.17 (d, 1H), 6.98 (d, 1H), 6.93 (m, 1H), 6.85 (m, 1H), 6.80 (m, 1H), 6.74 (m, 1H), 6.45 (d, 1H), 6.18 (d, 1H), 0.22 (s, 9H), 0.17 (s, 9H) ppm. **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, δ):** 173.0, 167.3, 165.8, 152.4, 152.0, 149.4, 148.6, 147.8, 147.6, 146.5, 144.3, 144.2, 137.5, 132.8, 132.6, 129.9, 129.4, 128.3, 128.0, 126.7, 126.5, 124.3, 124.0, 123.5, 122.9, 121.5, 121.0, -1.5, -1.6 ppm. **^{29}Si{^{1}H} NMR (76 MHz, CDCl$_3$, δ):** -2.2 (2Si) ppm. **HR-MS: [M+H]$^+$ Calculated for C$_{34}$H$_{37}$IrN$_3$O$_2$Si$_2$,** 768.2054, **Found,** 768.2017.

[Ir(N5Sippy)$_2$(pic)] (N5): The product was obtained using 20% EtOAc in DCM as the mobile phase to give a bright yellow solid. **Yield:** 65%. **M.p.:** 254-256 °C. **R$_f$ (20% EtOAc in DCM on silica):** 0.47. **^{1}H NMR (400 MHz, CDCl$_3$, δ):** 8.82 (s, 1H), 8.32 (d, 1H), 7.88 (m, 1H), 7.78 (m, 5H), 7.63 (d, 1H), 7.57 (d, 1H), 7.32 (m, 2H), 6.92 (t, 1H), 6.78 (m, 3H), 6.39 (d, 1H), 6.20 (d, 1H), 0.29 (s, 9H), 0.06 (s, 9H) ppm. **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, δ):** 172.7, 169.2, 167.7, 152.7, 151.4, 149.8, 148.7, 148.3, 144.4, 142.0, 137.5, 134.6, 133.4, 132.7, 132.6, 130.1, 129.7, 128.1, 127.8, 124.4, 124.2, 121.6, 121.0, 118.4, 117.9, -1.2, -1.5 ppm. **^{29}Si{^{1}H} NMR (76 MHz, CDCl$_3$, δ):** -3.3, -4.1 ppm. **HR-MS: [M+H]$^+$ Calculated for C$_{34}$H$_{37}$IrN$_3$O$_2$Si$_2$,** 768.2054, **Found,** 768.2024.

[Ir(C3N4Si$_2$ppy)$_2$(pic)] (C3N4): The product was obtained using 20% EtOAc in DCM as the mobile phase to give a bright yellow solid. **Yield:** 44%. **M.p.:** 341-343 °C. **R$_f$ (20% EtOAc in DCM on silica):** 0.44. **^{1}H NMR (400 MHz, CDCl$_3$, δ):** 8.70 (d, 1H), 8.30 (d, 1H), 7.96 (s, 1H), 7.92 (s, 1H), 7.85 (m, 1H), 7.75 (d, 1H), 7.71 (d, 2H), 7.38 (d, 1H), 7.32 (m, 1H), 7.16 (d, 1H), 6.97 (d, 1H), 6.91 (m, 2H), 6.48 (d, 1H), 6.22 (d, 1H), 0.37 (s, 9H), 0.36 (s, 9H), 0.23 (s,

9H), 0.18 (s, 9H) ppm. **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, δ):** 172.9, 167.4, 165.9, 152.4, 152.0, 151.9, 151.4, 149.7, 148.6, 147.6, 146.6, 144.1, 143.9, 137.5, 134.9, 134.4, 132.4, 132.2, 131.3, 130.8, 129.0, 128.8, 128.2, 128.0, 126.5, 123.4, 122.7, -0.8, -0.9, -1.5, -1.6 ppm. **$^{29}Si\{^{1}H\}$ NMR (76 MHz, $CDCl_3$, δ):** -2.2 (2Si), -4.6, -4.7 ppm. **HR-MS: $[M+H]^+$ Calculated for $C_{40}H_{53}IrN_3O_2Si_4$,** 912.2844, **Found,** 912.2828.

[Ir(C3N5Si$_2$ppy)$_2$(pic)] (C3N5): The product was obtained using 15% EtOAc in DCM as the mobile phase to give a bright yellow solid. **Yield:** 37%. **M.p.:** 228-230 °C. **R_f (10% EtOAc in DCM on silica):** 0.24. **^{1}H NMR (400 MHz, $CDCl_3$, δ):** 8.80 (s, 1H), 8.31 (d, 1H), 7.89-7.69 (m, 8H), 7.35 (m, 2H), 6.91 (m, 2H), 6.43 (d, 1H), 6.24 (d, 1H), 0.29 (s, 9H), 0.23 (s, 9H), 0.18 (s, 9H), 0.06 (s, 9H) ppm. **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, δ):** 172.6, 169.2, 167.7, 152.7, 151.6, 151.4, 150.0, 148.7, 144.3, 144.2, 141.9, 137.5, 135.0, 134.7, 134.5, 133.4, 132.4, 132.3, 131.4, 130.7, 129.3, 129.1, 128.2, 127.8, 118.4, 117.9, -0.8, -0.9, -1.1, -1.5 ppm. **$^{29}Si\{^{1}H\}$ NMR (76 MHz, $CDCl_3$, δ):** -3.3, -4.2, -4.6, -4.7 ppm. **HR-MS: $[M+H]^+$ Calculated for $C_{40}H_{53}IrN_3O_2Si_4$,** 912.2844, **Found,** 912.2822.

[Ir(C4N4Si$_2$ppy)$_2$(pic)] (C4N4): The product was obtained using 20% EtOAc in DCM as the mobile phase to give a bright yellow solid. **Yield:** 43%. **M.p.:** 311-313 °C. **R_f (10% EtOAc in DCM on silica):** 0.21. **^{1}H NMR (400 MHz, $CDCl_3$, δ):** 8.77 (d, 1H), 8.32 (d, 1H), 7.94 (s, 1H), 7.90 (s, 1H), 7.85 (m, 1H), 7.74 (d, 1H, 7.54 (m, 2H), 7.47 (d, 1H), 7.21 (dd, 1H), 7.03 (m, 2H), 6.96 (dd, 1H), 6.48 (s, 1H), 6.24 (s, 1H), 0.36 (s, 9H), 0.35 (s, 9H), 0.02 (s, 9H), -0.04 (s, 9H) ppm. **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, δ):** 173.0, 167.8, 166.4, 152.5, 152.1, 152.0, 148.6, 148.2, 147.9, 146.8, 146.7, 144.9, 144.8, 142.3, 141.3, 137.4, 137.3, 128.2, 128.0, 126.5, 126.4, 126.3, 125.7, 123.4, 123.1, 122.9, 122.8, -1.1, -1.2, -1.5, -1.6 ppm. **$^{29}Si\{^{1}H\}$ NMR (76 MHz, $CDCl_3$, δ):** -2.2, -2.3, -5.2, -5.3 ppm. **HR-MS: $[M+H]^+$ Calculated for $C_{40}H_{53}IrN_3O_2Si_4$,** 912.2844, **Found,** 912.2817.

[Ir(C4N5Si$_2$ppy)$_2$(pic)] (C4N5): The product was obtained using 15% EtOAc in DCM as the mobile phase to give a bright yellow solid. **Yield:** 62%. **M.p.:** 362-364 °C. **R_f (10% EtOAc in DCM on silica):** 0.47. **^{1}H NMR (400 MHz, $CDCl_3$, δ):** 8.88 (s, 1H), 8.32 (d, 1H), 7.88 (t, 1H), 7.84-7.72 (m, 5H), 7.55 (d, 1H), 7.52 (d, 1H), 7.41 (s, 1H), 7.35 (t, 1H), 7.04 (d, 1H), 6.99 (d, 1H), 6.54 (s, 1H), 6.35 (s, 1H), 0.31 (s, 9H), 0.07 (s, 9H), 0.03 (s, 9H), -0.02 (s, 9H) ppm. **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, δ):** 172.8, 169.5, 168.0, 153.0, 152.8, 151.5, 148.7, 148.4, 147.3, 145.1, 145.0, 142.6, 141.9, 141.8, 141.7, 137.5, 137.4, 137.2, 134.6, 133.5, 128.2, 127.8, 126.5, 125.7, 123.3, 123.2, 118.4, 117.9, -1.0, -1.1, -1.2, -1.5 ppm. **$^{29}Si\{^{1}H\}$ NMR (76 MHz, $CDCl_3$, δ):** -3.3, -4.1, -5.2, -5.3 ppm. **HR-MS: $[M+H]^+$ Calculated for $C_{40}H_{53}IrN_3O_2Si_4$,** 912.2844, **Found,** 912.2819.

NMR Spectra

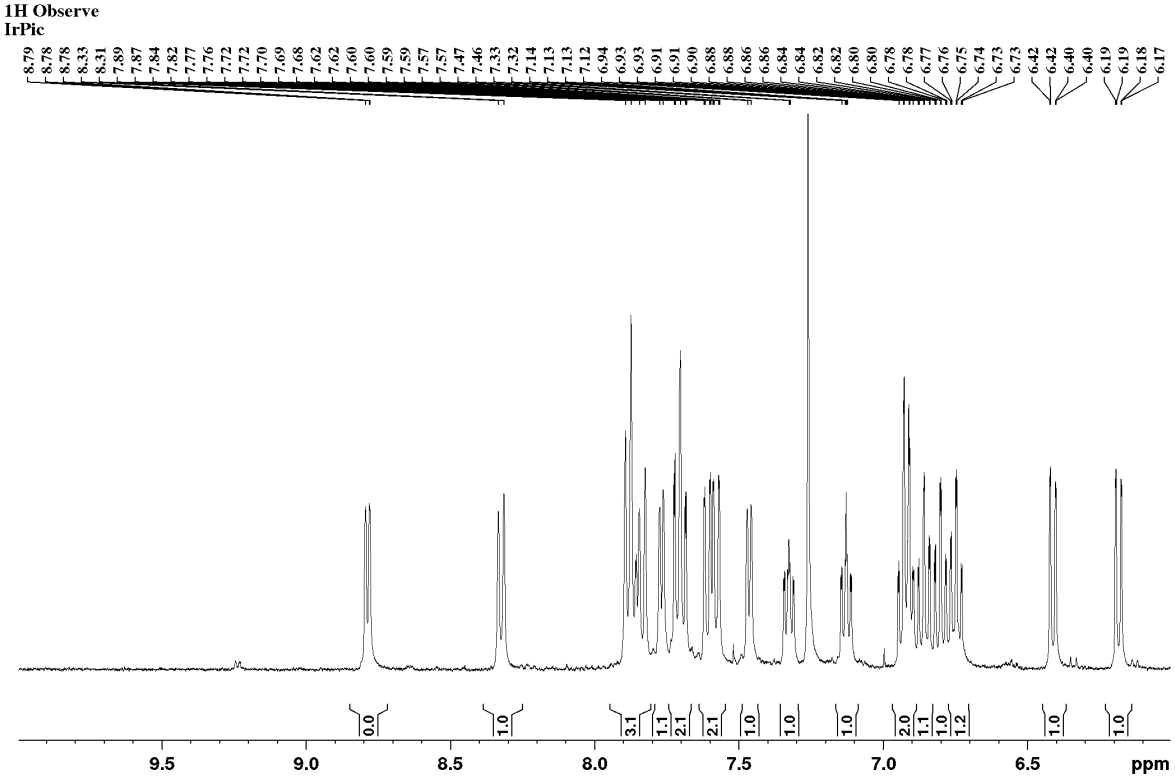


Figure 4. 400 MHz ^{1}H NMR Spectra of **Irpic** in $CDCl_3$.

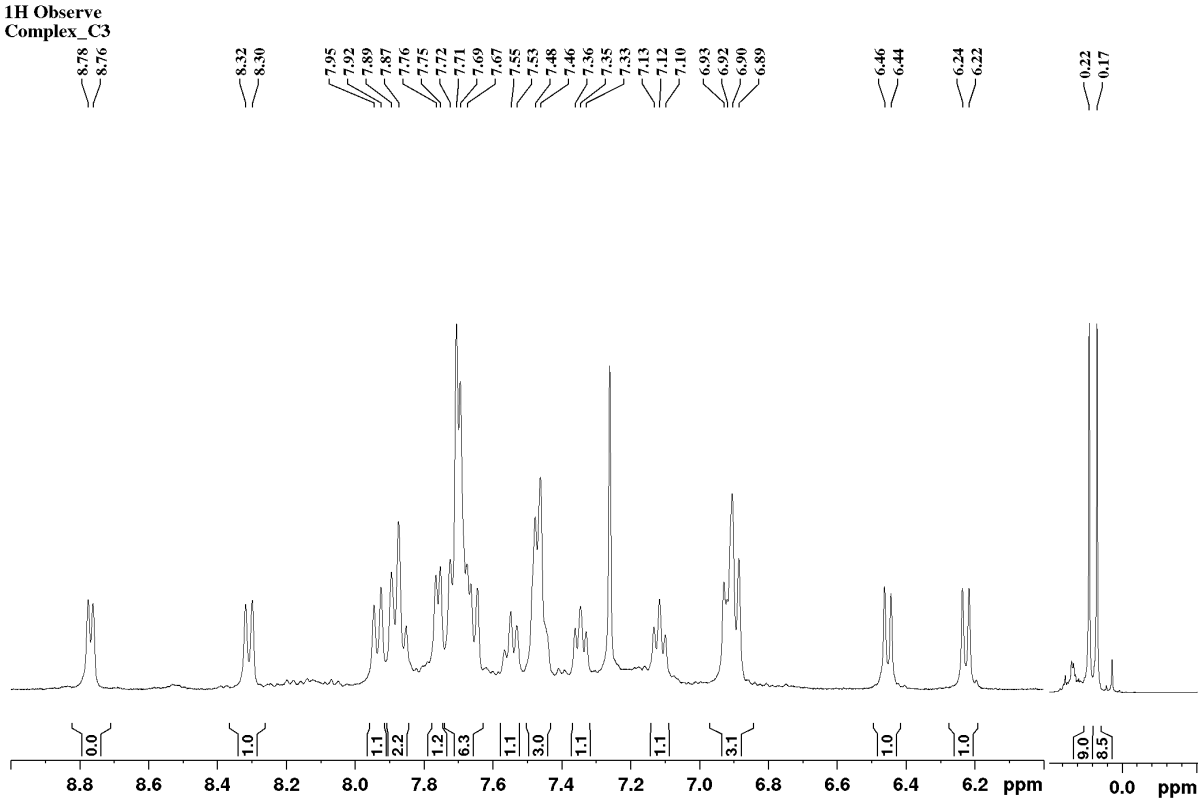


Figure 5. 400 MHz ^{1}H NMR Spectra of **C3** in $CDCl_3$.

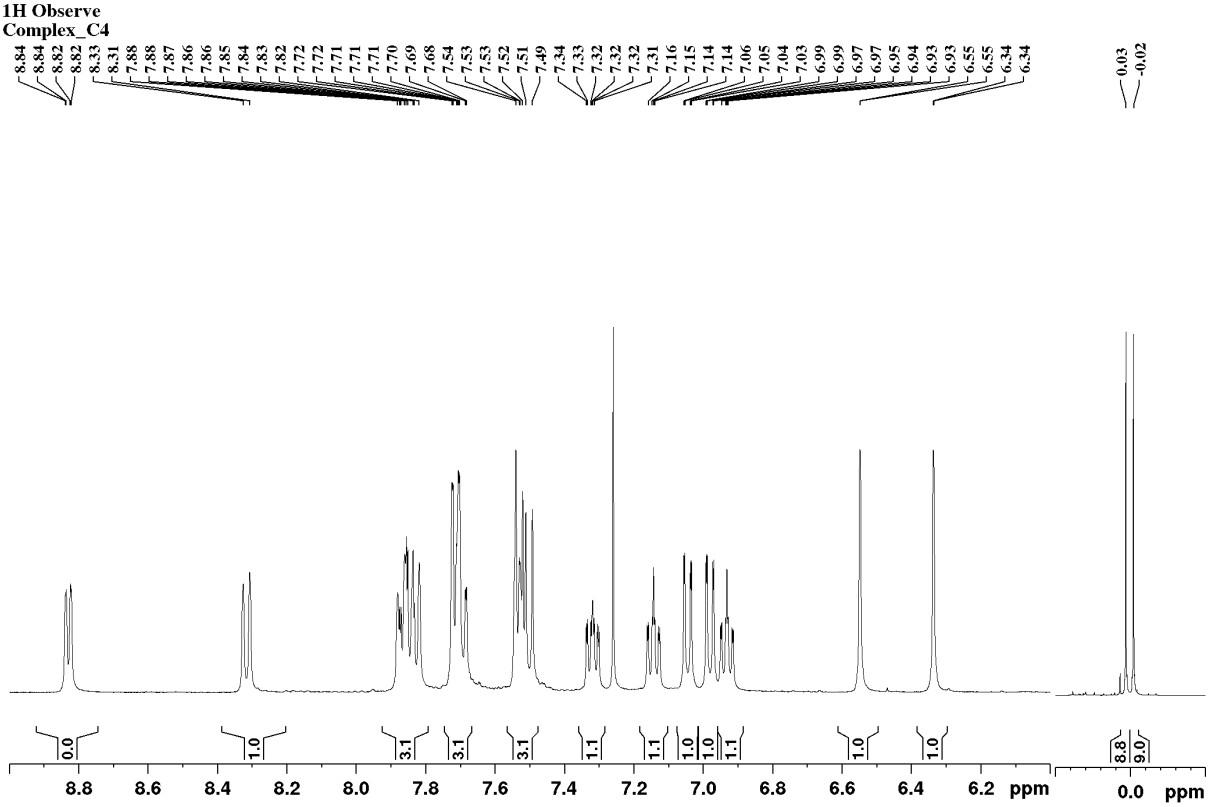


Figure 6. 400 MHz ^{1}H NMR Spectra of **C3** in $CDCl_3$.

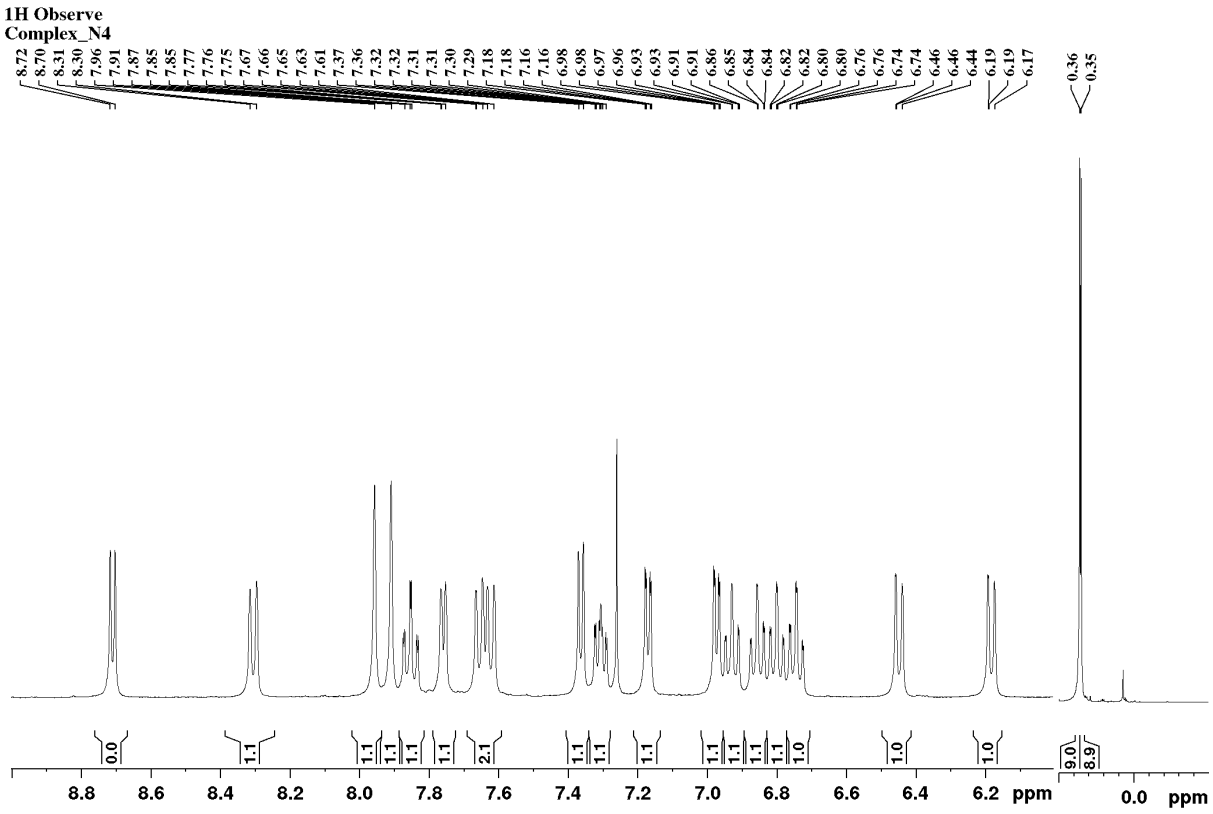


Figure 7. 400 MHz ^{1}H NMR Spectra of **N4** in $CDCl_3$.

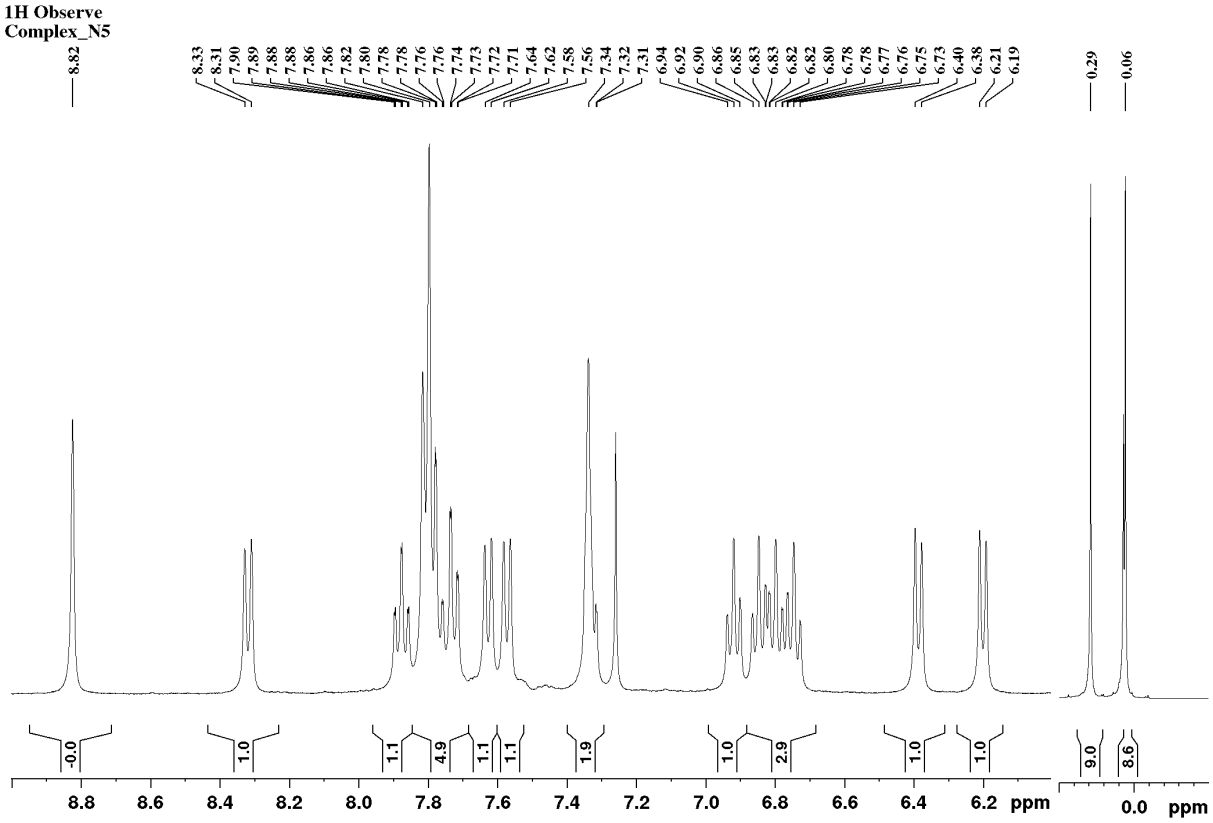


Figure 8. 400 MHz ^{1}H NMR Spectra of **N5** in $CDCl_3$.

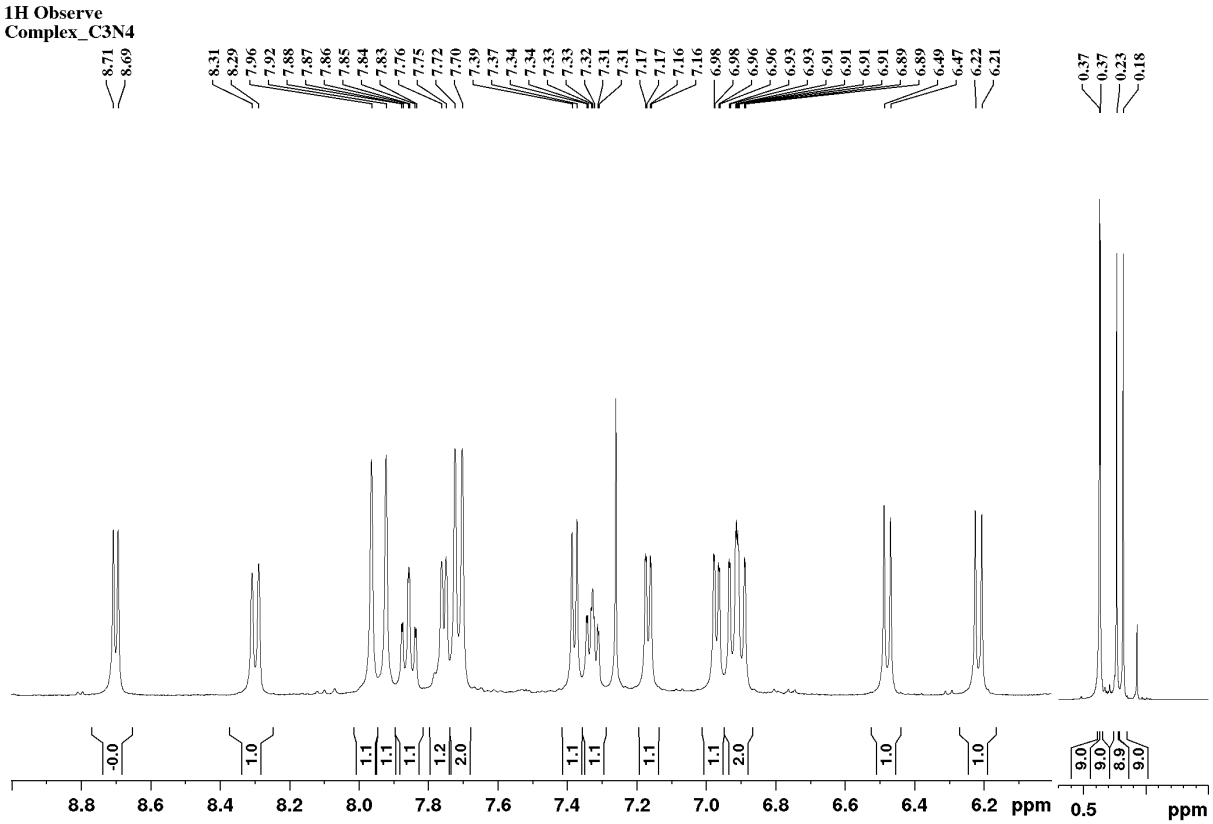


Figure 9. 400 MHz ^{1}H NMR Spectra of **C3N4** in $CDCl_3$.

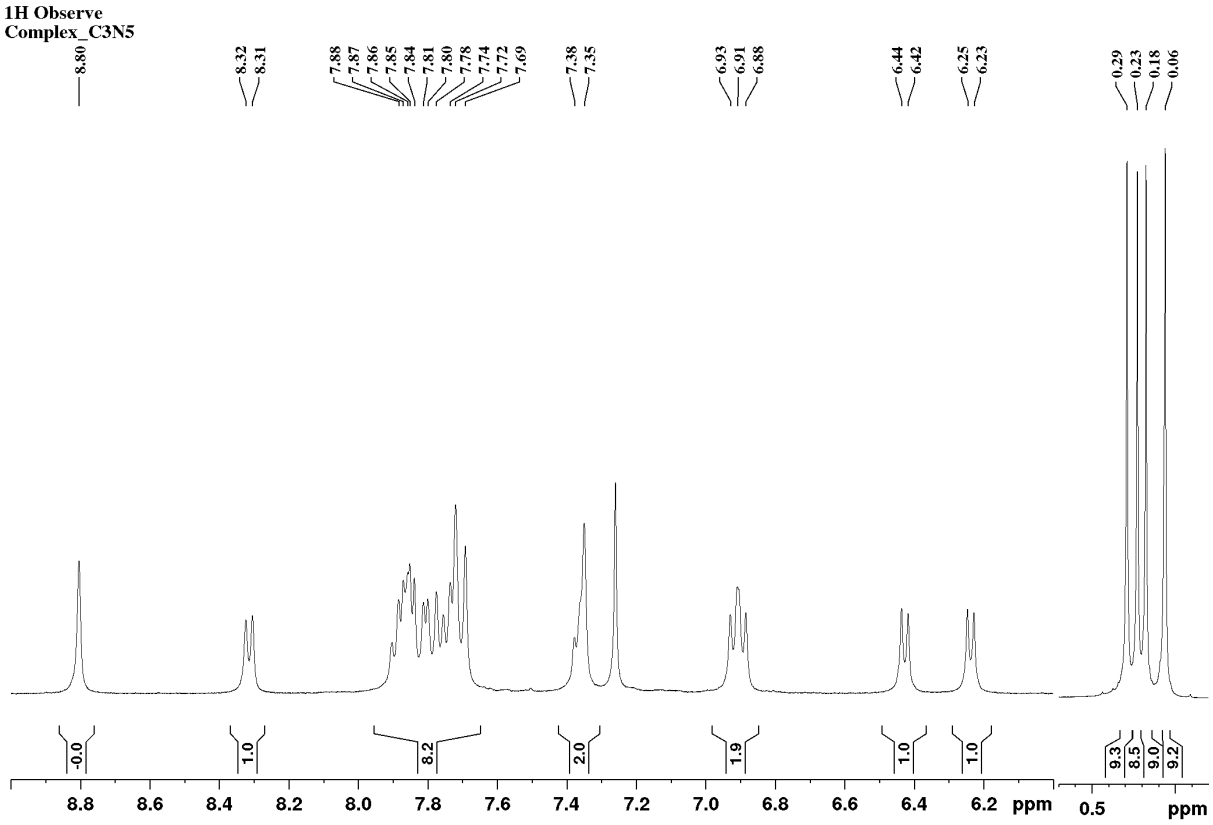


Figure 10. 400 MHz ^{1}H NMR Spectra of **C3N5** in $CDCl_3$.

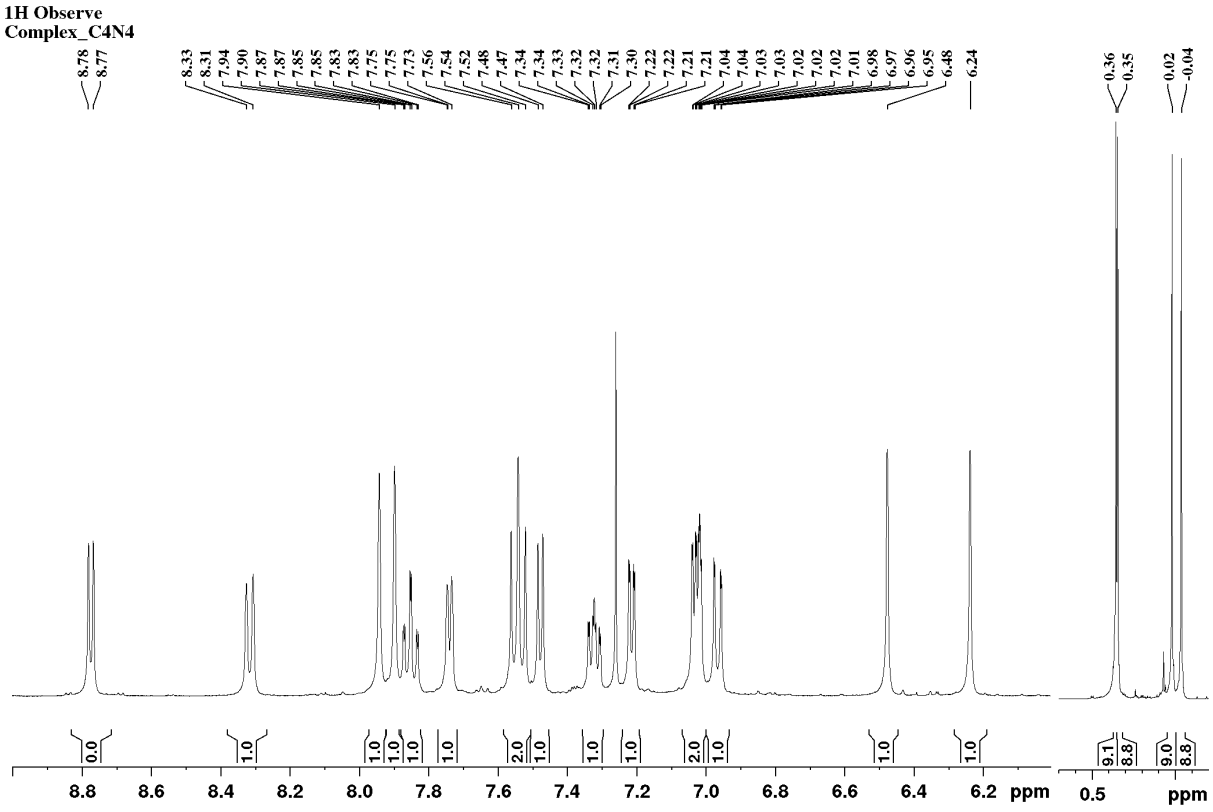


Figure 11. 400 MHz ^{1}H NMR Spectra of **C4N4** in $CDCl_3$.

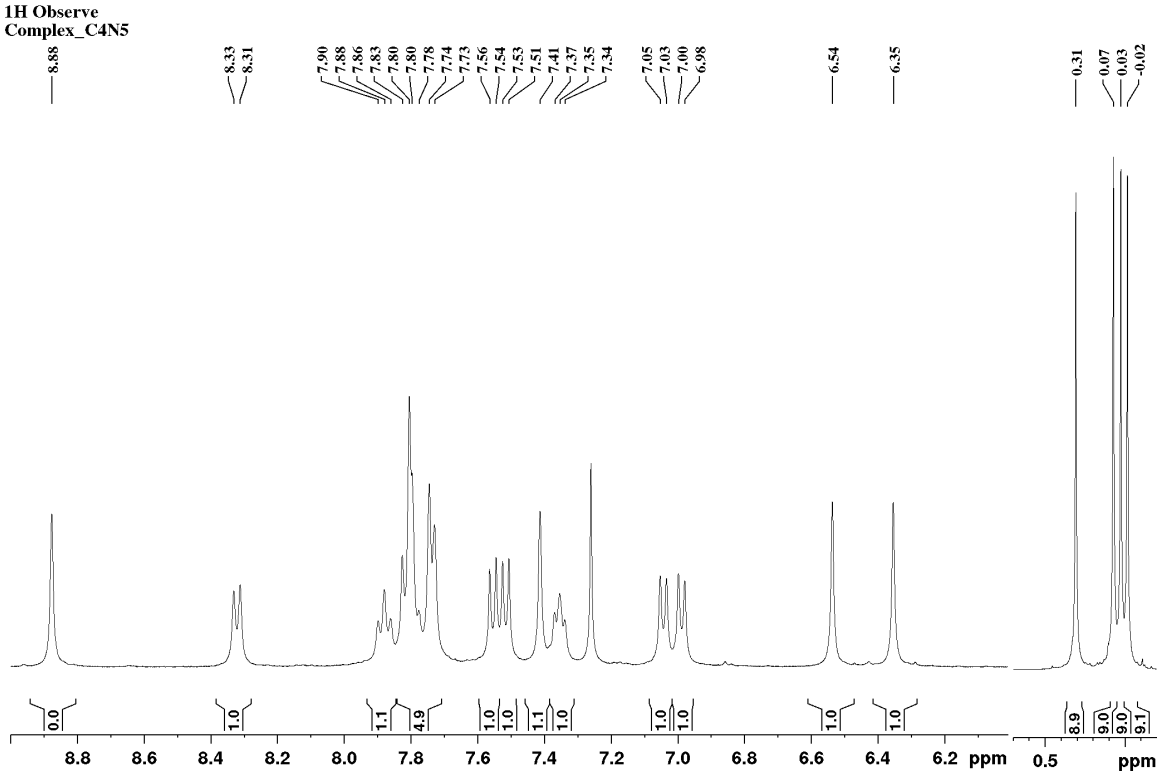


Figure 12. 400 MHz ^{1}H NMR Spectra of **C4N5** in $CDCl_3$.

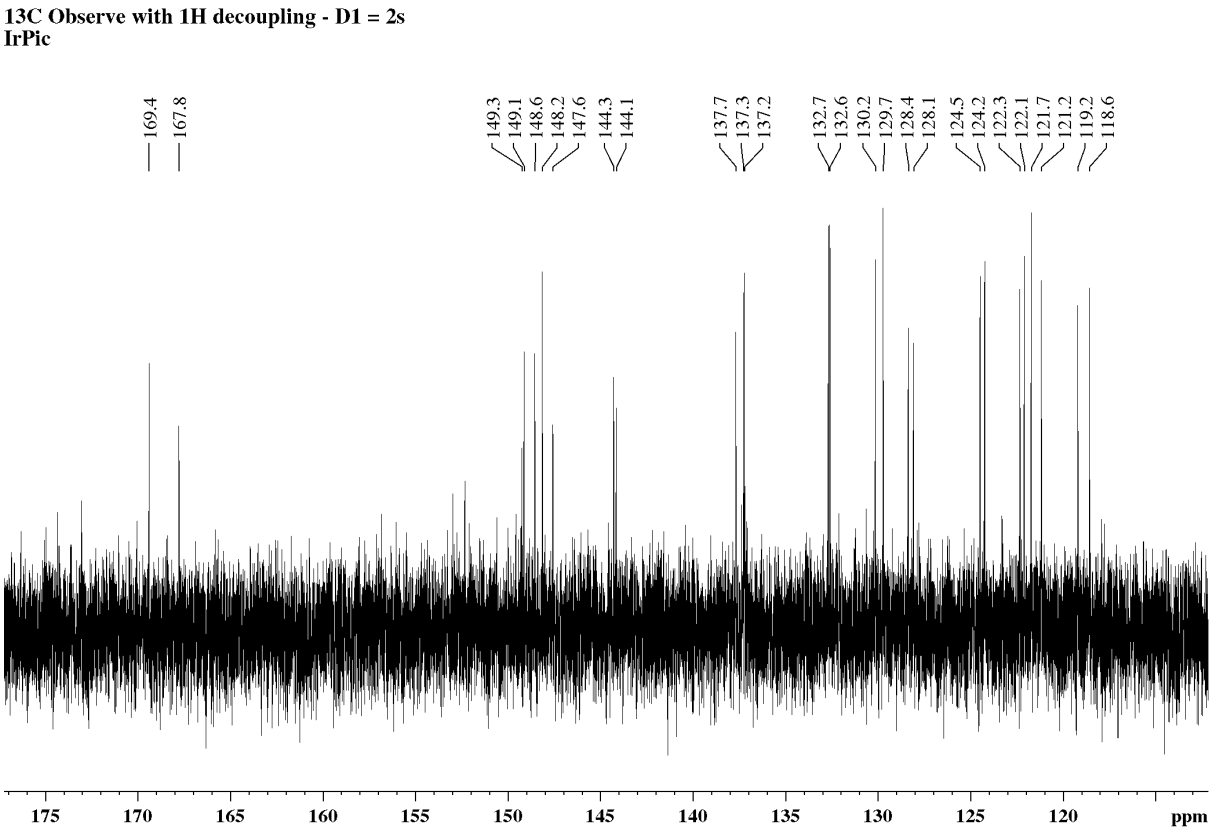


Figure 13. 101 MHz $^{13}C\{^{1}H\}$ NMR Spectra of **Irpic** in $CDCl_3$.

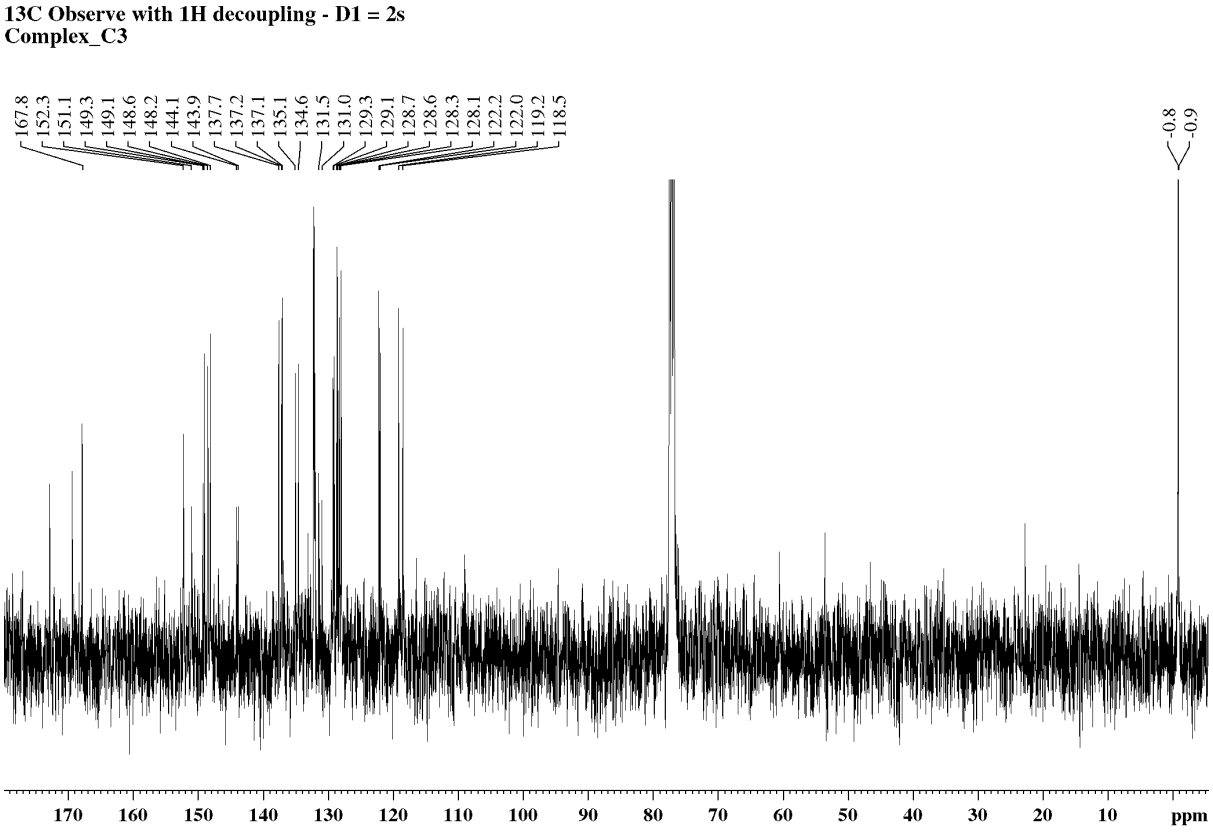


Figure 14. 101 MHz $^{13}C\{^{1}H\}$ NMR Spectra of **C3** in $CDCl_3$.

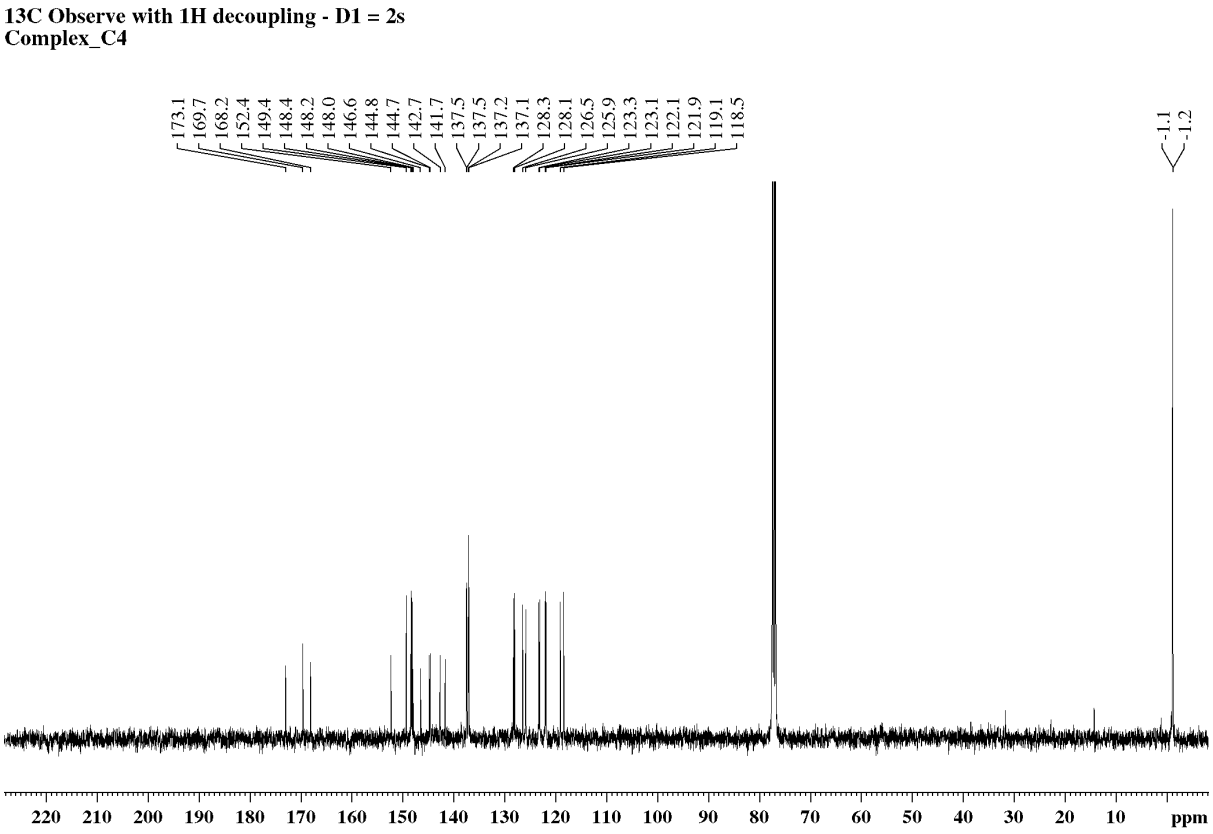


Figure 15. 101 MHz $^{13}C\{^{1}H\}$ NMR Spectra of **Irpic** in $CDCl_3$.

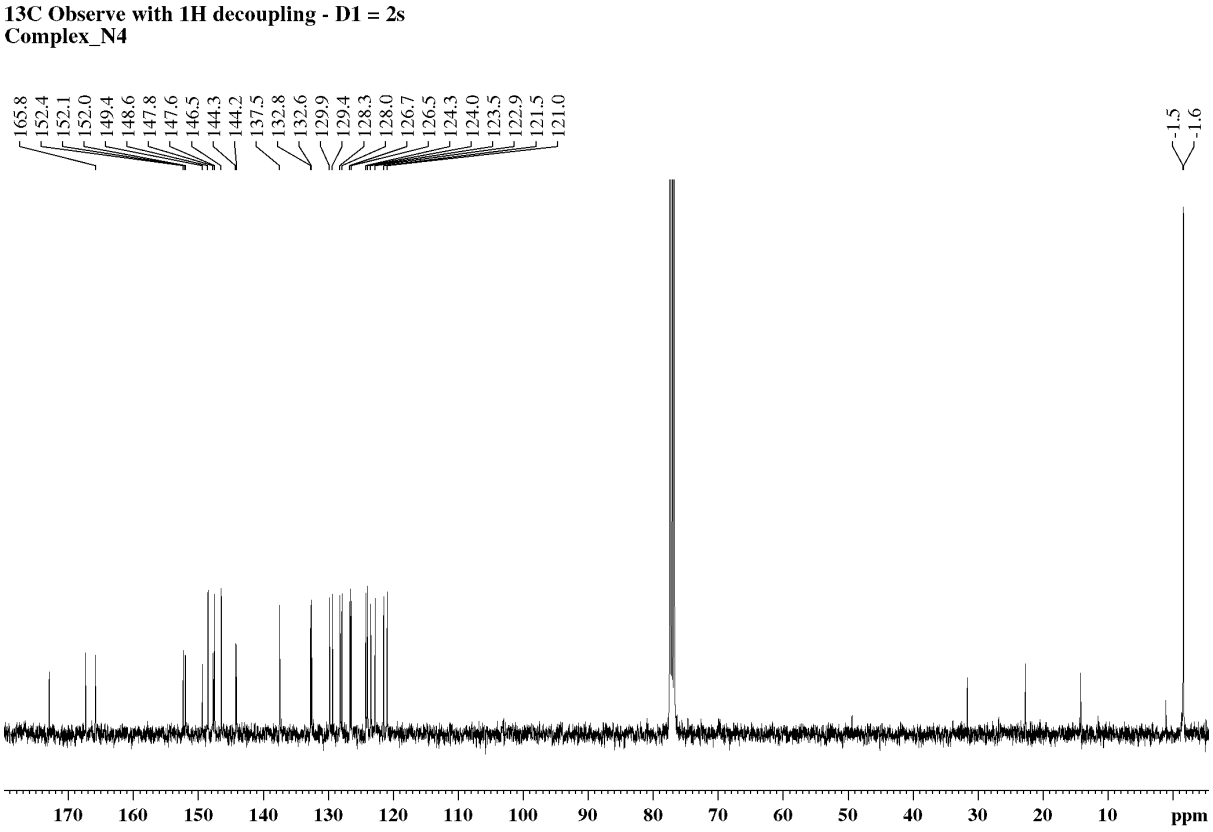


Figure 16. 101 MHz $^{13}C\{^{1}H\}$ NMR Spectra of **N4** in $CDCl_3$.

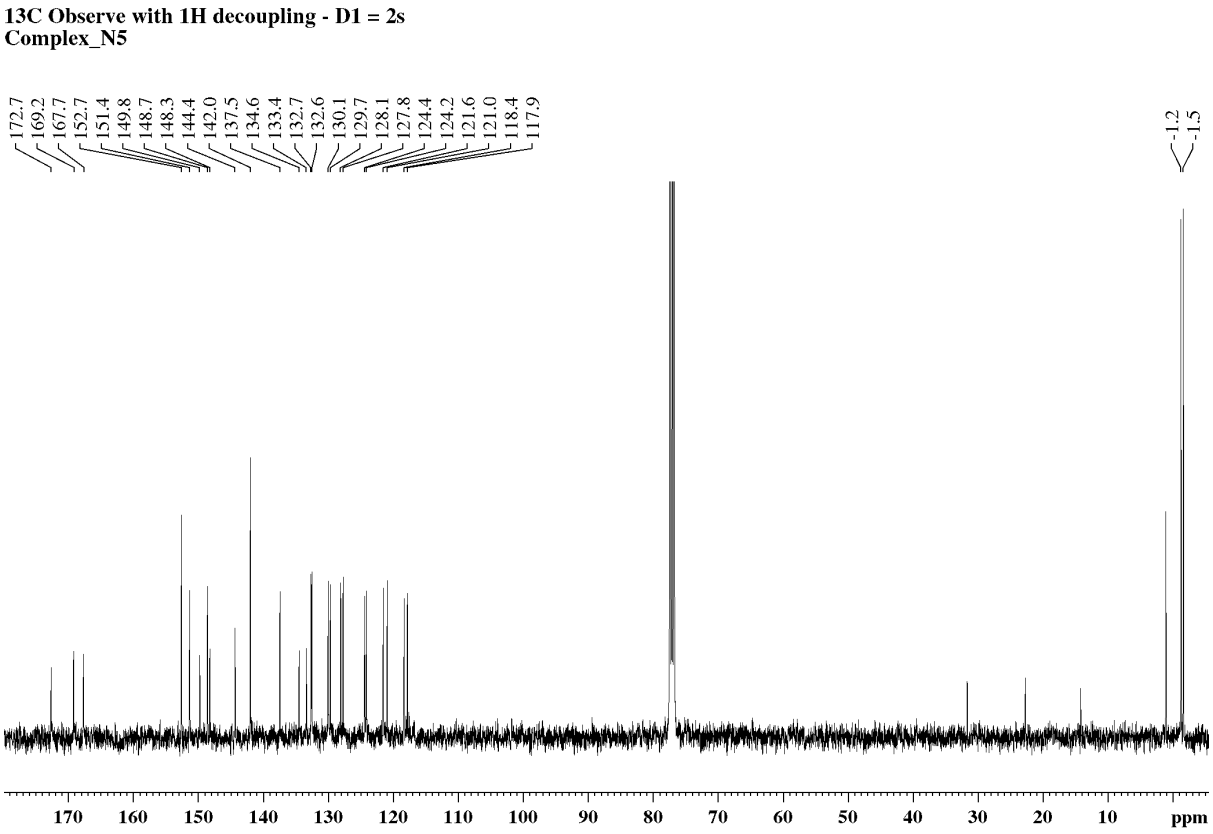


Figure 17. 101 MHz $^{13}C\{^{1}H\}$ NMR Spectra of **N5** in $CDCl_3$.

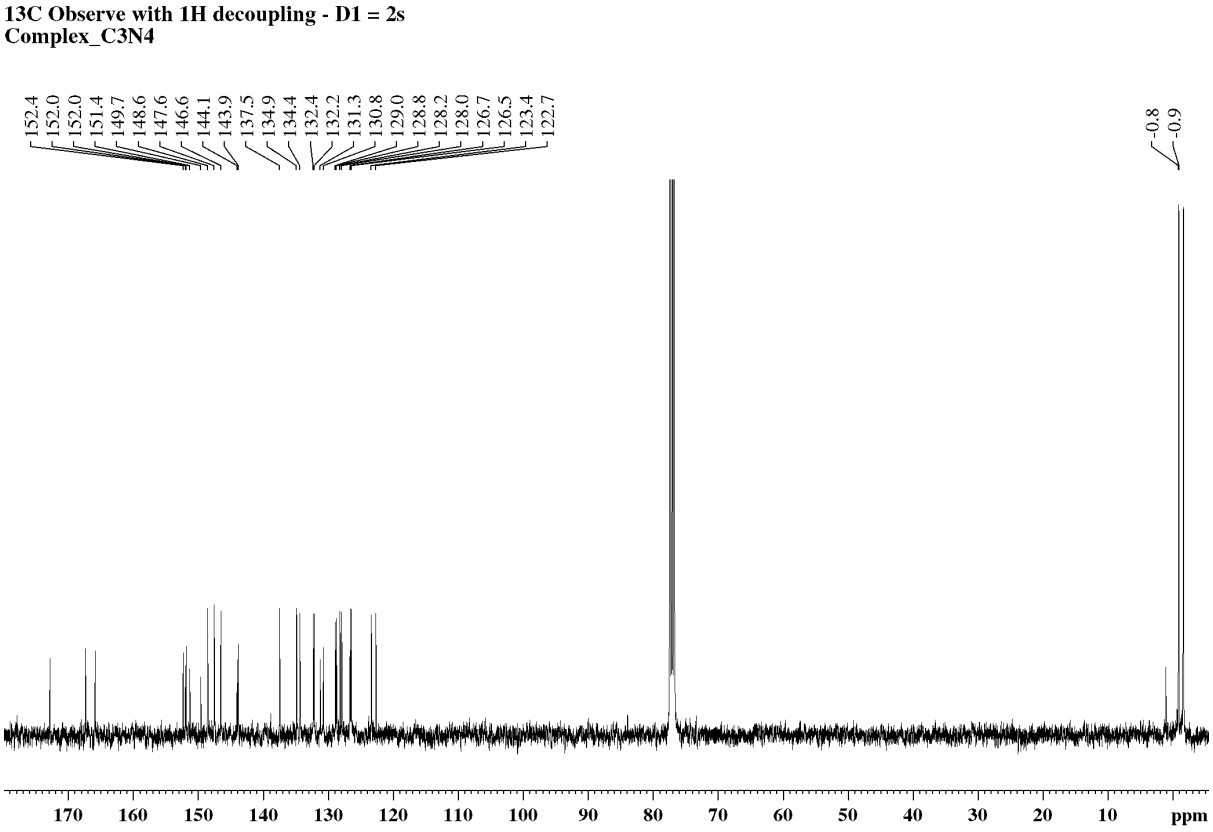


Figure 18. 101 MHz $^{13}C\{^{1}H\}$ NMR Spectra of **C3N4** in $CDCl_3$.

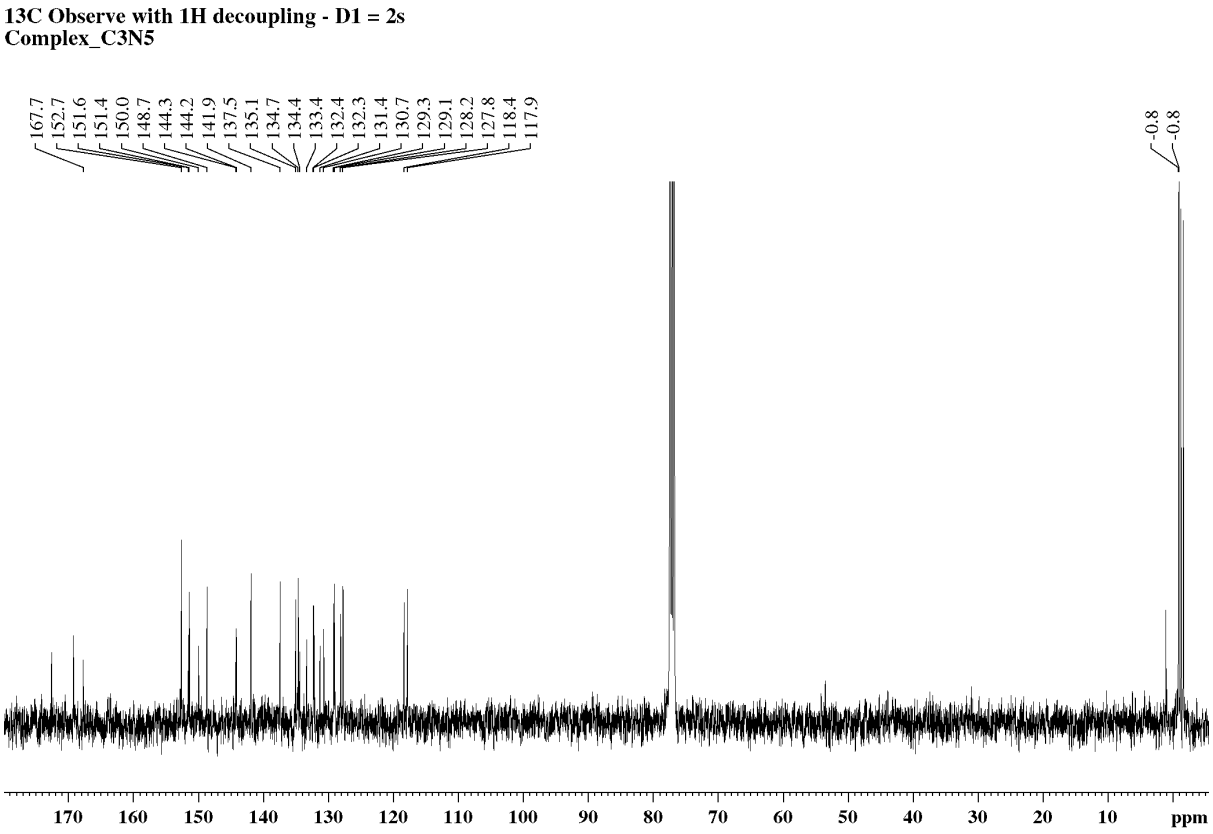


Figure 19. 101 MHz $^{13}C\{^{1}H\}$ NMR Spectra of **C3N5** in $CDCl_3$.

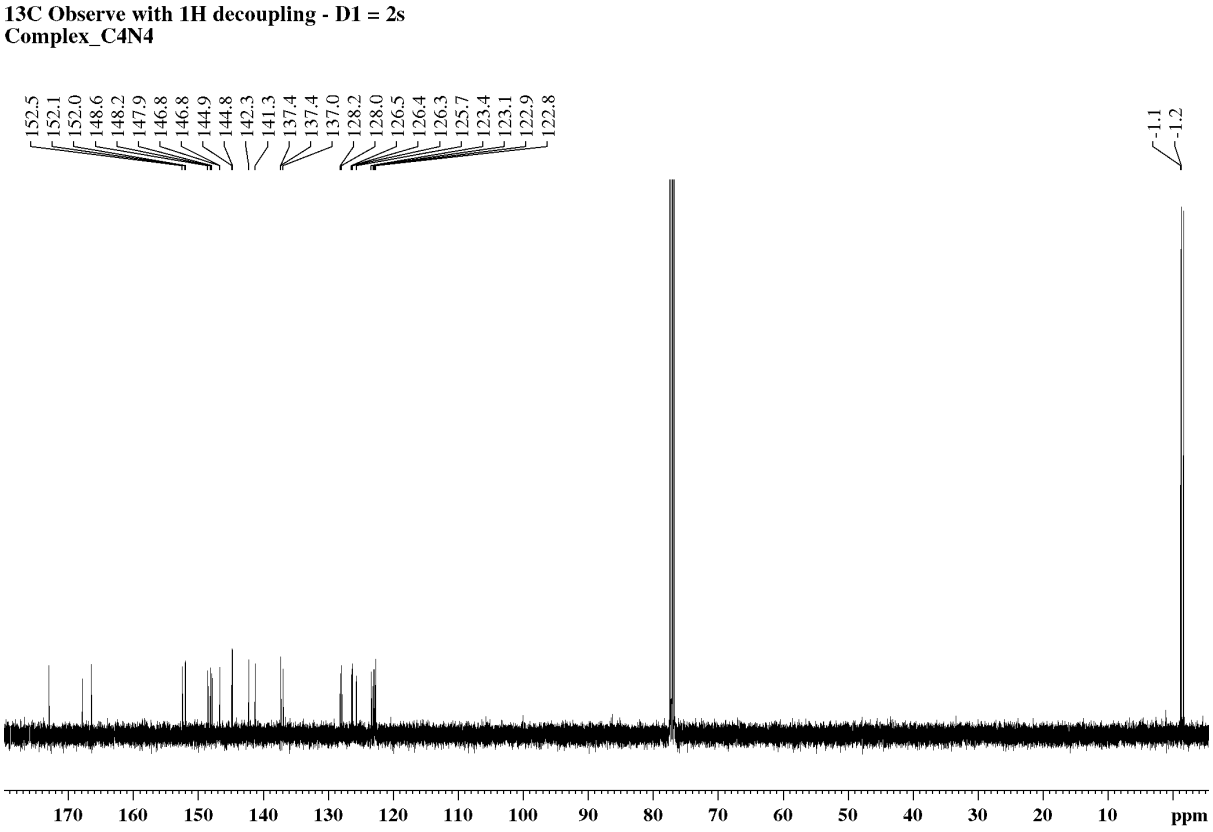


Figure 20. 101 MHz $^{13}C\{^{1}H\}$ NMR Spectra of **C4N4** in $CDCl_3$.

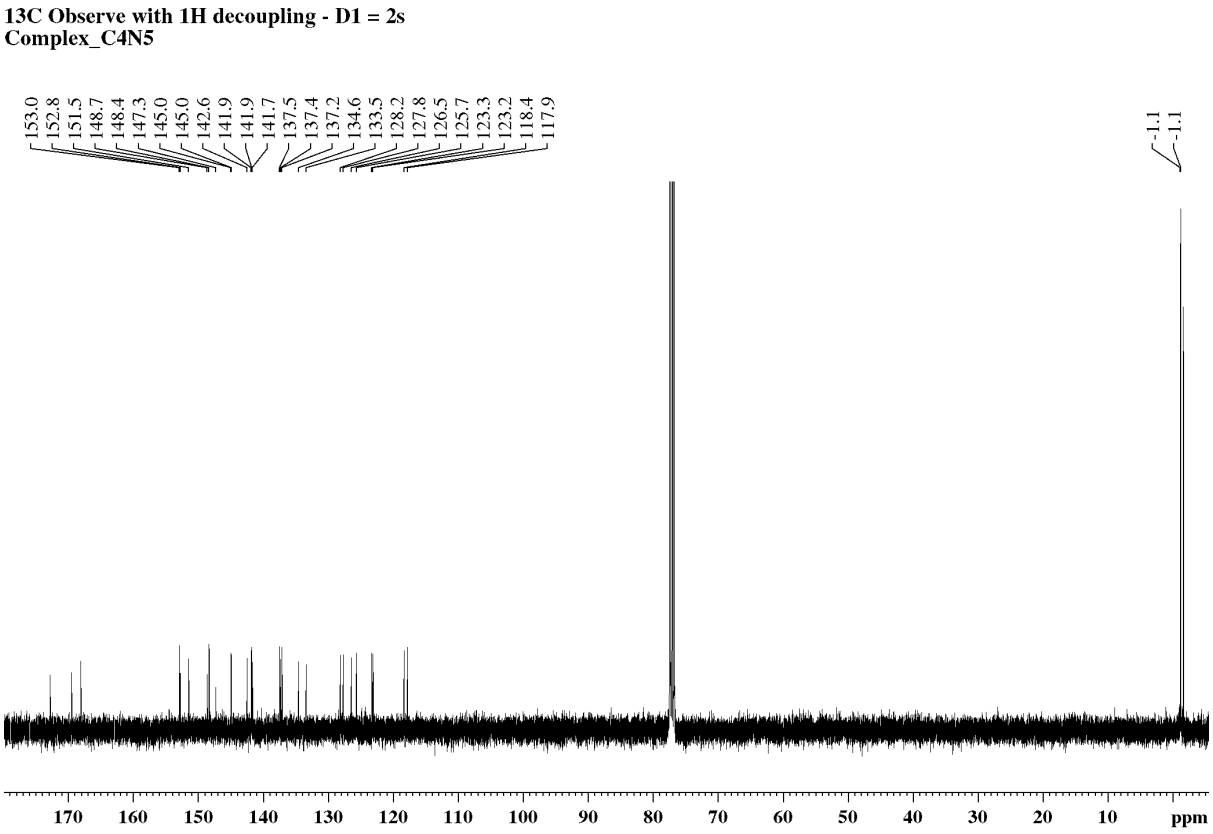


Figure 21. 101 MHz $^{13}C\{^{1}H\}$ NMR Spectra of **C4N5** in $CDCl_3$.

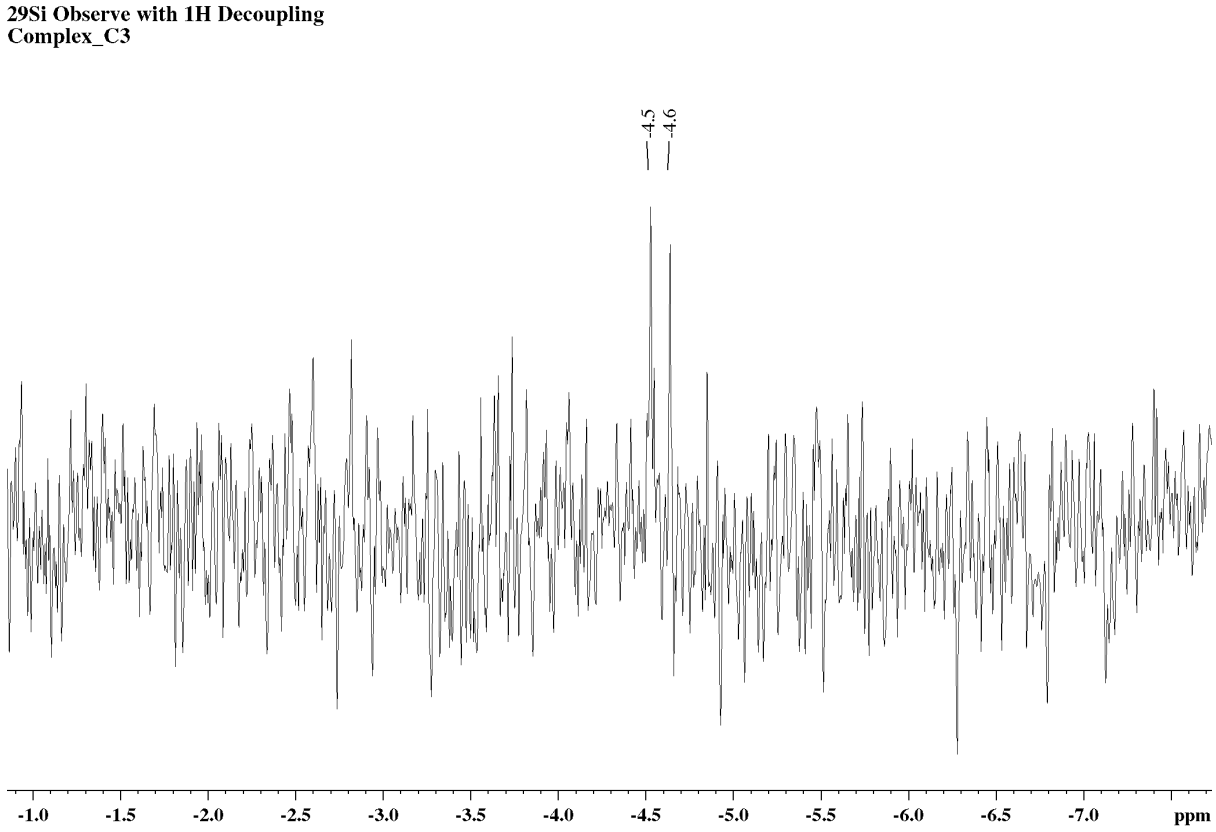


Figure 22. 79 MHz $^{29}Si\{^{1}H\}$ NMR Spectra of **C3** in $CDCl_3$.

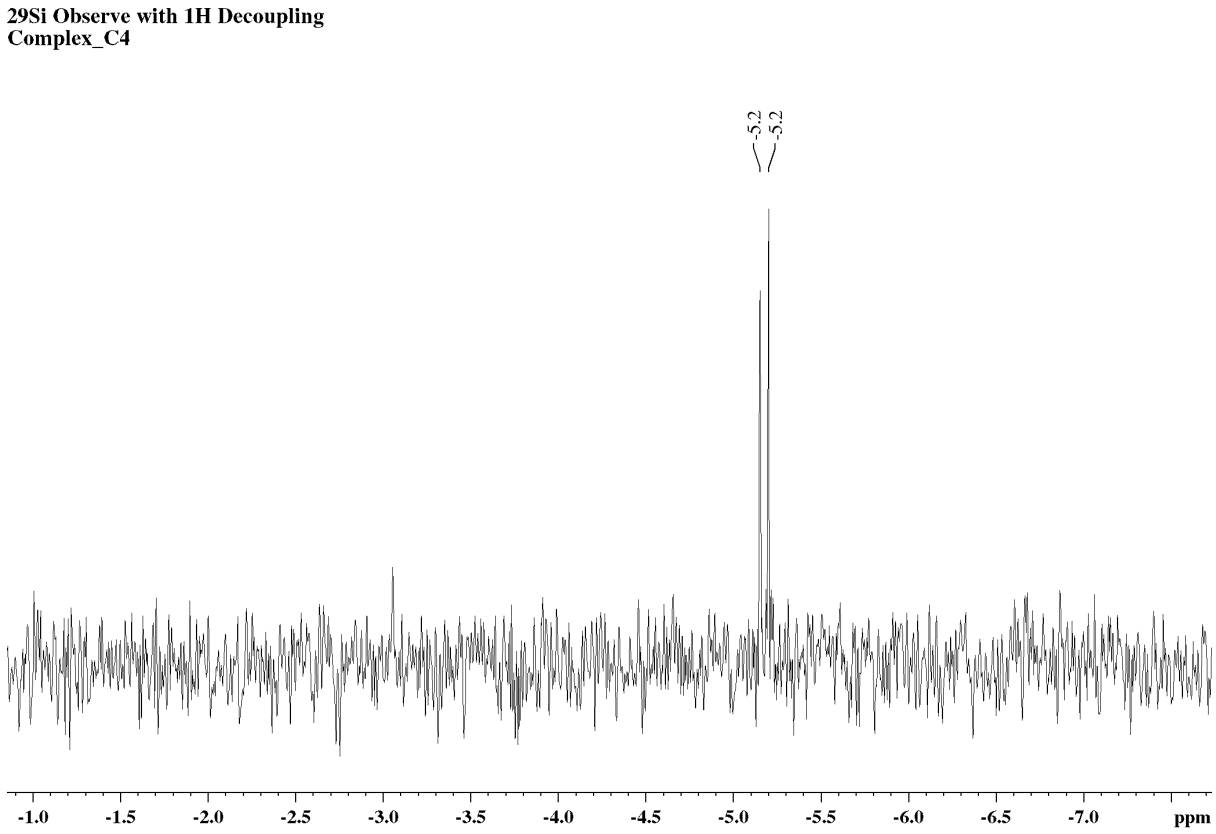


Figure 23. 79 MHz $^{29}Si\{^{1}H\}$ NMR Spectra of **C4** in $CDCl_3$.

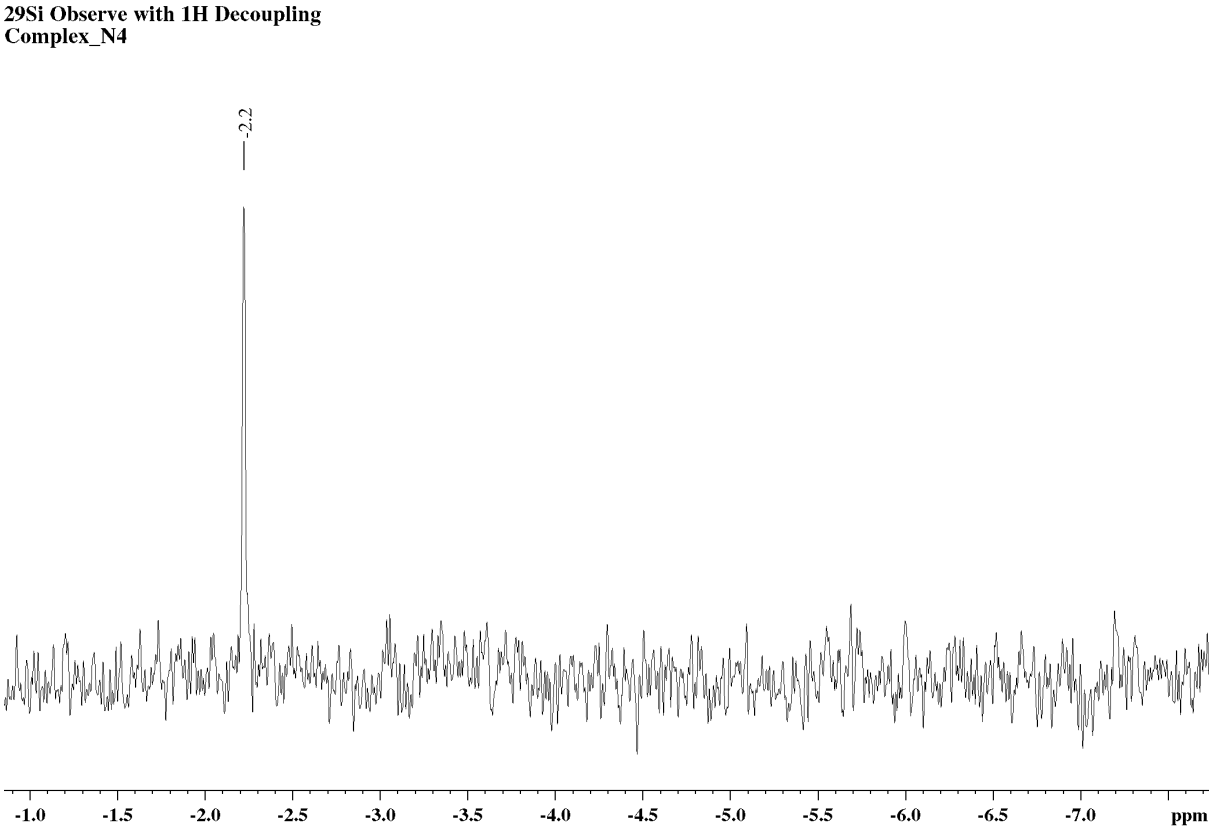


Figure 24. 79 MHz $^{29}Si\{^{1}H\}$ NMR Spectra of **N4** in $CDCl_3$.

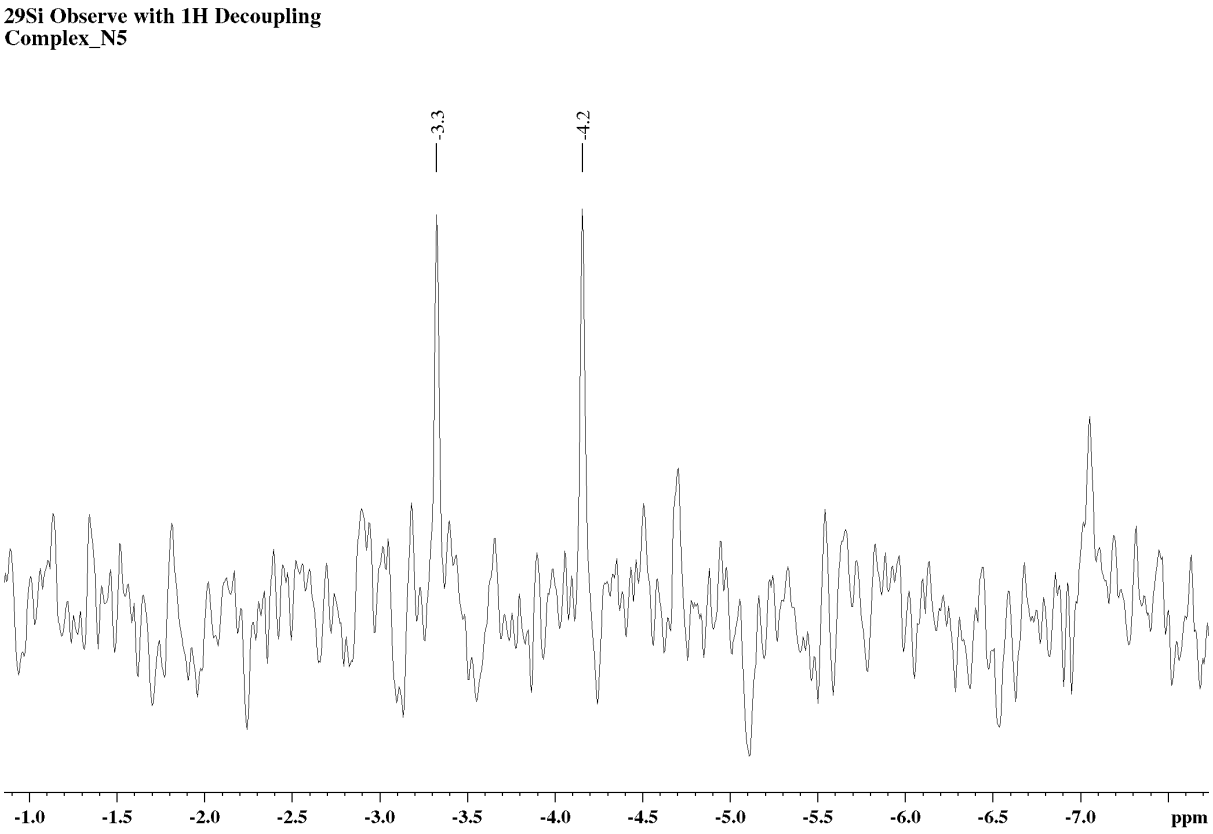


Figure 25. 79 MHz $^{29}Si\{^{1}H\}$ NMR Spectra of **N5** in $CDCl_3$.

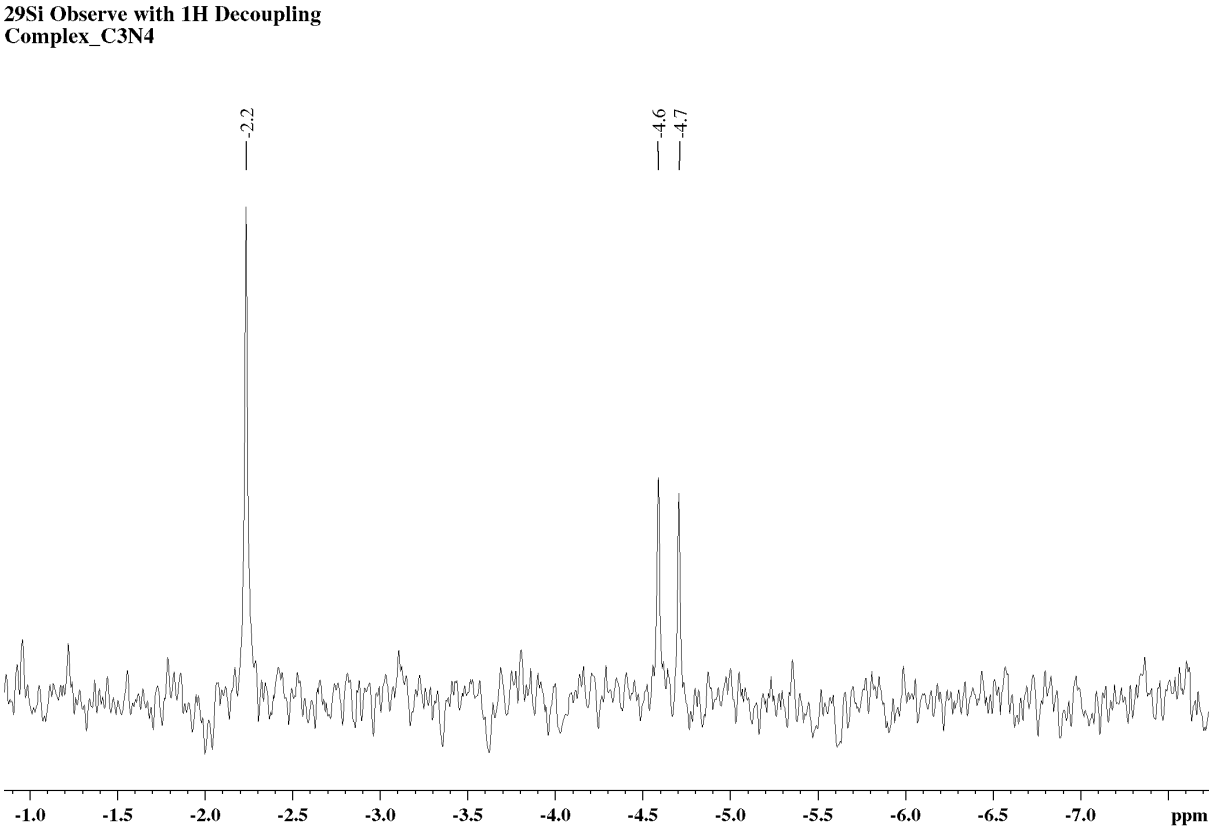


Figure 26. 79 MHz $^{29}Si\{^{1}H\}$ NMR Spectra of **C3N4** in $CDCl_3$.

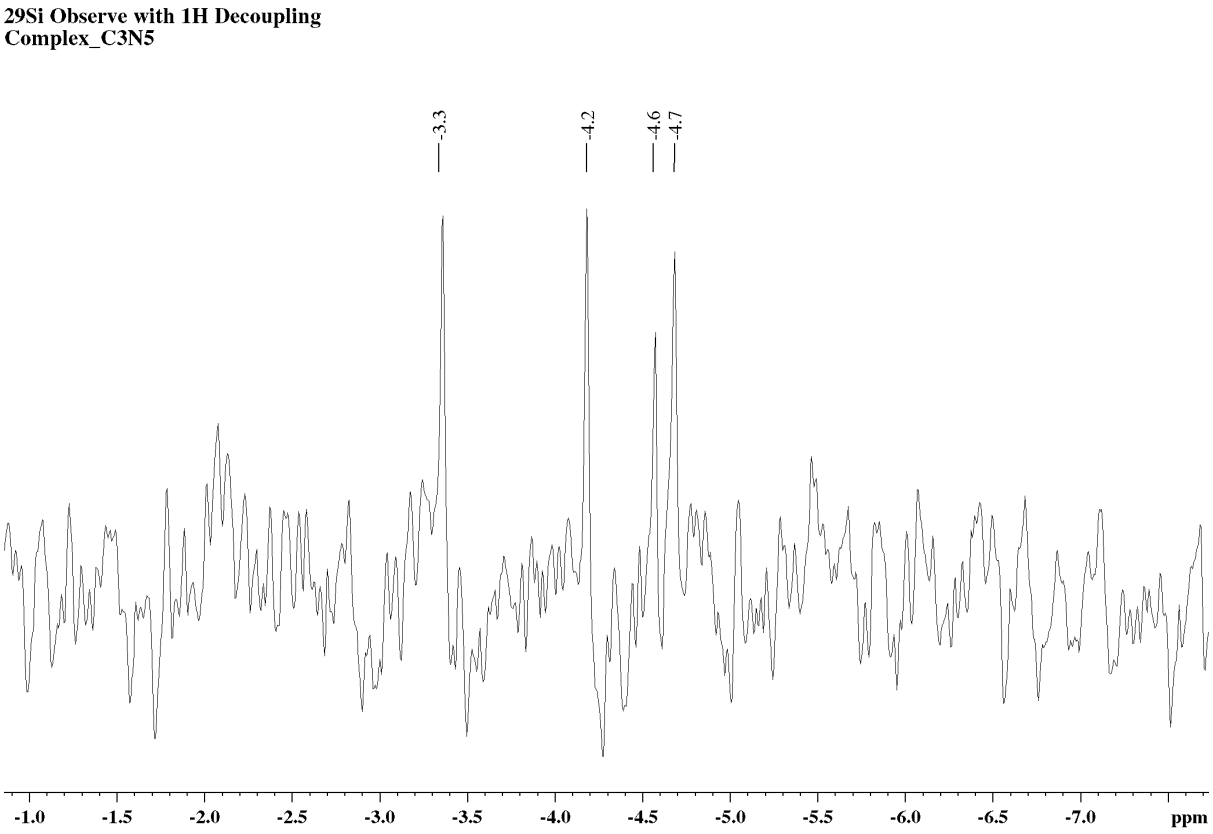


Figure 27. 79 MHz $^{29}Si\{^{1}H\}$ NMR Spectra of **C3N5** in $CDCl_3$.

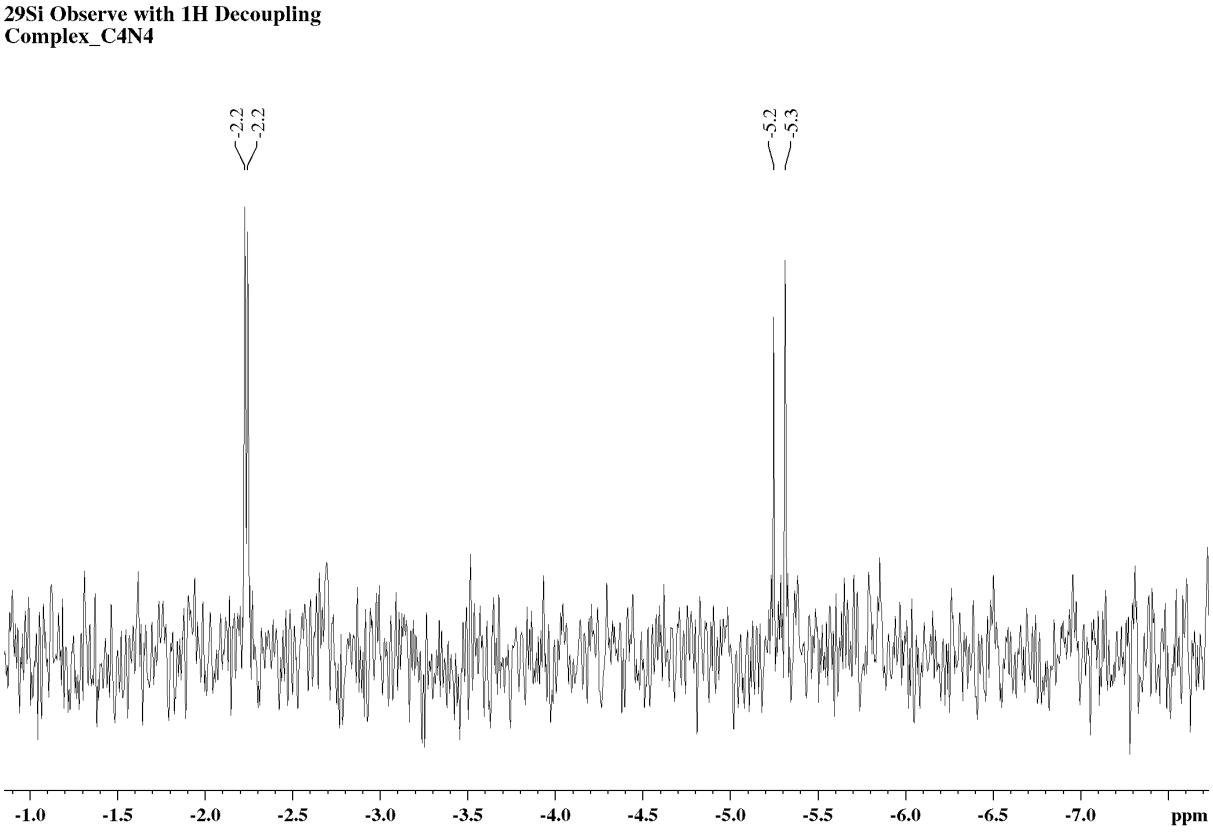


Figure 28. 79 MHz $^{29}Si\{^{1}H\}$ NMR Spectra of **C4N4** in $CDCl_3$.

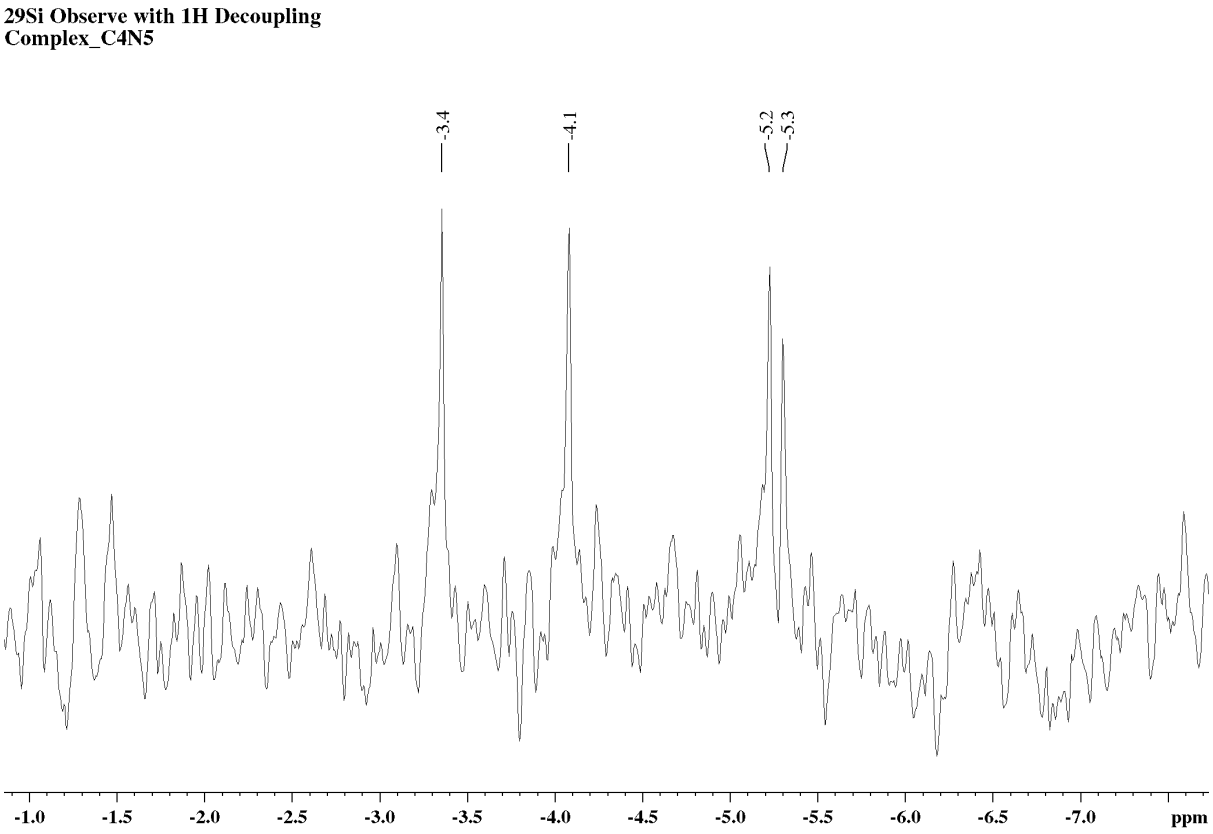


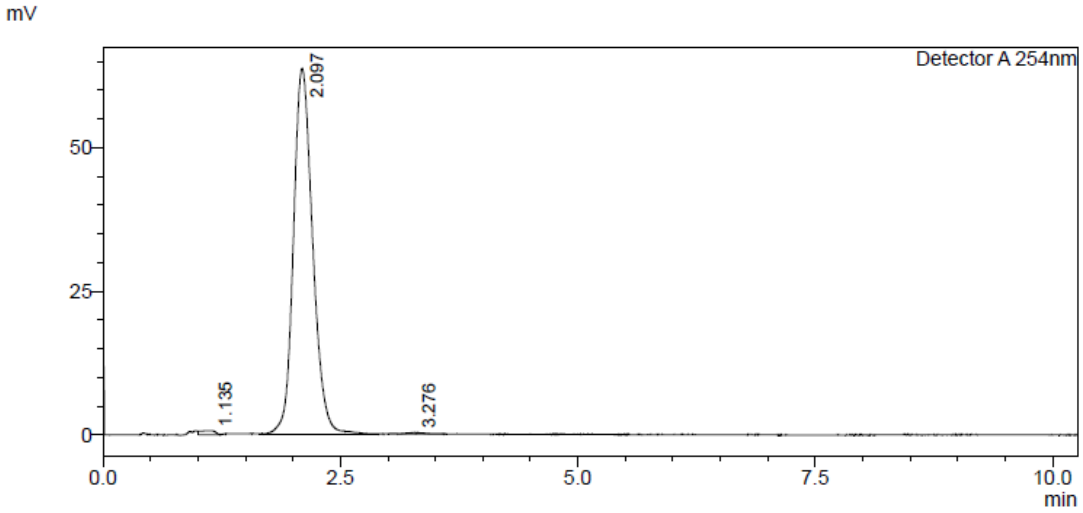
Figure 29. 79 MHz $^{29}Si\{^{1}H\}$ NMR Spectra of **C4N5** in $CDCl_3$.

HPLC Traces

<Sample Information>

Sample Name	: IrPic_55		
Sample ID	: IrPic_55		
Method Filename	: 55% Acetonitrile 45 Water 20 mins.lcm		
Batch Filename	:		
Vial #	: 2-10	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 04/11/2022 16:11:20	Acquired by	: System Administrator
Date Processed	: 04/11/2022 16:21:35	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A 254nm

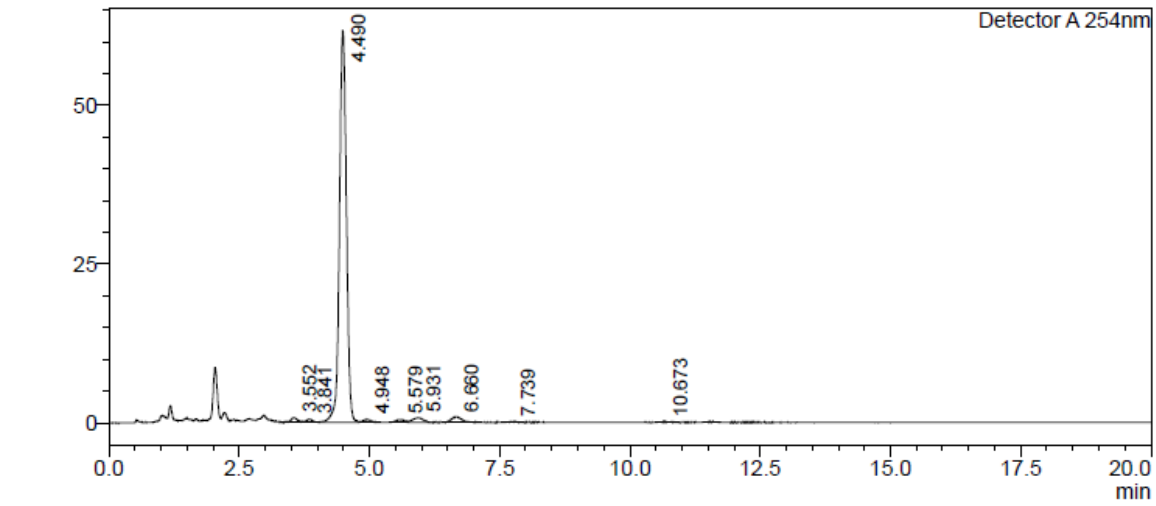
Peak#	Ret. Time	Area	Height	Area%	Area/Height	Width at 5% Height
1	1.135	7373	682	0.815	10.813	--
2	2.097	894148	63593	98.819	14.060	0.478
3	3.276	3309	197	0.366	16.813	0.503
Total		904831	64472	100.000		

Figure 30. HPLC trace of **IrPic**.

<Sample Information>

Sample Name	: C3		
Sample ID	: C3		
Method Filename	: 75% Acetonitrile 25 Water 20 mins.lcm		
Batch Filename	: Green_emitters_MeCN765.lcb		
Vial #	: 2-11	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 04/11/2022 11:25:29	Acquired by	: System Administrator
Date Processed	: 04/11/2022 11:45:31	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Area/Height	Width at 5% Height
1	3.552	7297	773	1.178	9.444	--
2	3.841	4177	502	0.674	8.322	--
3	4.490	573676	61616	92.632	9.311	0.313
4	4.948	4512	454	0.729	9.944	--
5	5.579	4806	433	0.776	11.101	--
6	5.931	10236	735	1.653	13.926	--
7	6.660	12122	845	1.957	14.337	0.541
8	7.739	1287	100	0.208	12.900	0.351
9	10.673	1197	81	0.193	14.738	0.386
Total		619309	65539	100.000		

Figure 31. HPLC trace of **C3.**

<Sample Information>

Sample Name	: C4		
Sample ID	: C4		
Method Filename	: 75% Acetonitrile 25 Water 20 mins.lcm		
Batch Filename	: Green_emitters_MeCN765.lcb		
Vial #	: 2-12	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 04/11/2022 11:56:16	Acquired by	: System Administrator
Date Processed	: 04/11/2022 12:16:19	Processed by	: System Administrator

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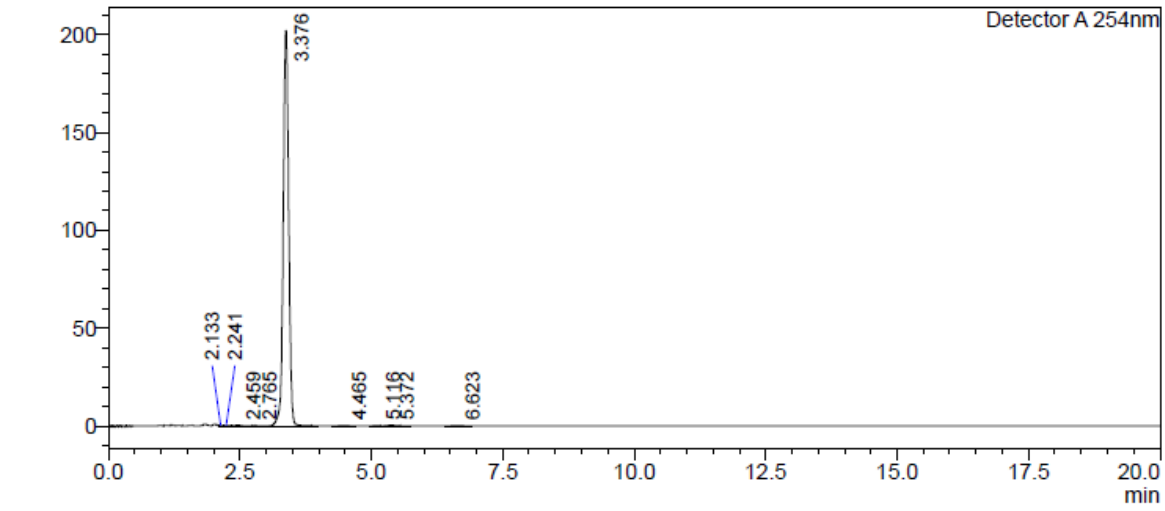

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Area/Height	Width at 5% Height
1	2.133	1617	333	0.109	4.855	--
2	2.241	2456	366	0.165	6.718	--
3	2.459	3865	530	0.260	7.297	--
4	2.765	1729	185	0.116	9.361	--
5	3.376	1464873	201533	98.444	7.269	0.243
6	4.465	2562	214	0.172	11.975	0.347
7	5.116	1196	123	0.080	9.707	--
8	5.372	5732	486	0.385	11.799	--
9	6.623	3993	320	0.268	12.462	0.366
Total		1488023	204089	100.000		

Figure 32. HPLC trace of **C4**.

<Sample Information>

Sample Name	: N4		
Sample ID	: N4		
Method Filename	: 75% Acetonitrile 25 Water 20 mins.lcm		
Batch Filename	: Green_emitters_MeCN765.lcb		
Vial #	: 2-13	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 04/11/2022 12:27:05	Acquired by	: System Administrator
Date Processed	: 04/11/2022 12:47:07	Processed by	: System Administrator

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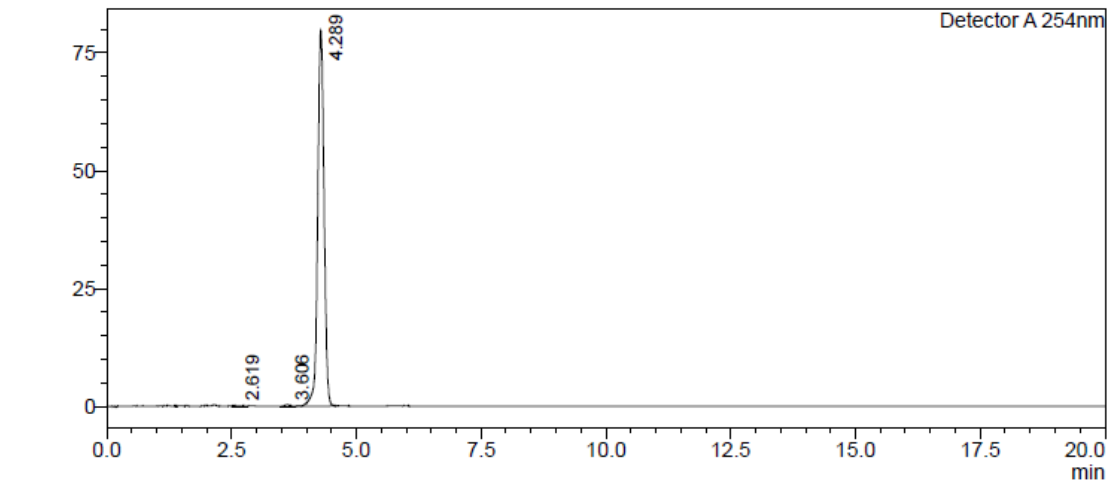


<Peak Table>

Detector A 254nm

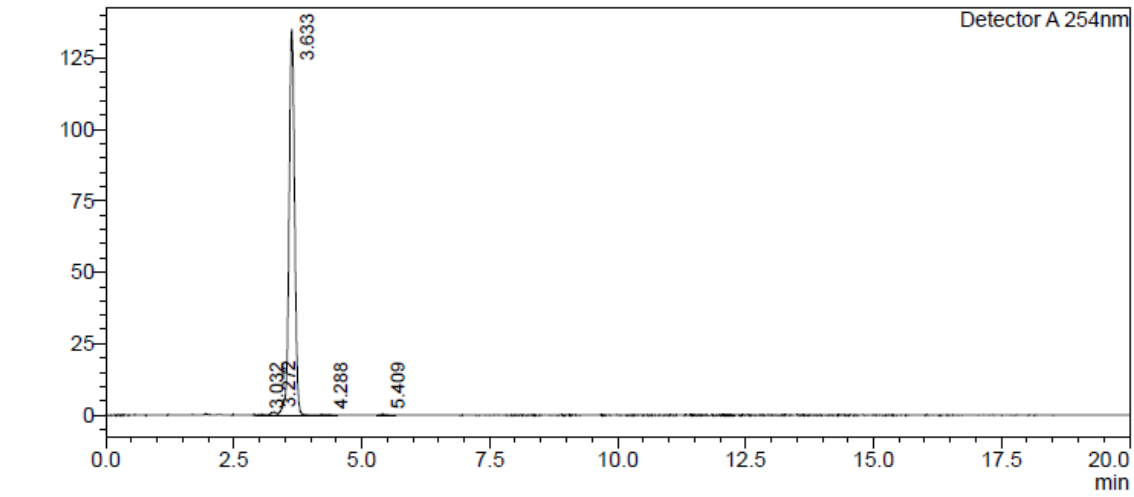
Peak#	Ret. Time	Area	Height	Area%	Area/Height	Width at 5% Height
1	2.619	1021	134	0.143	7.609	--
2	3.606	1980	281	0.277	7.055	0.205
3	4.289	711000	79662	99.580	8.925	0.299
Total		714001	80076	100.000		

Figure 33. HPLC trace of **N4**.

<Sample Information>

Sample Name	: N5		
Sample ID	: N5		
Method Filename	: 75% Acetonitrile 25 Water 20 mins.lcm		
Batch Filename	: Green_emitters_MeCN765.lcb		
Vial #	: 2-14	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 04/11/2022 12:57:53	Acquired by	: System Administrator
Date Processed	: 04/11/2022 13:17:55	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A 254nm

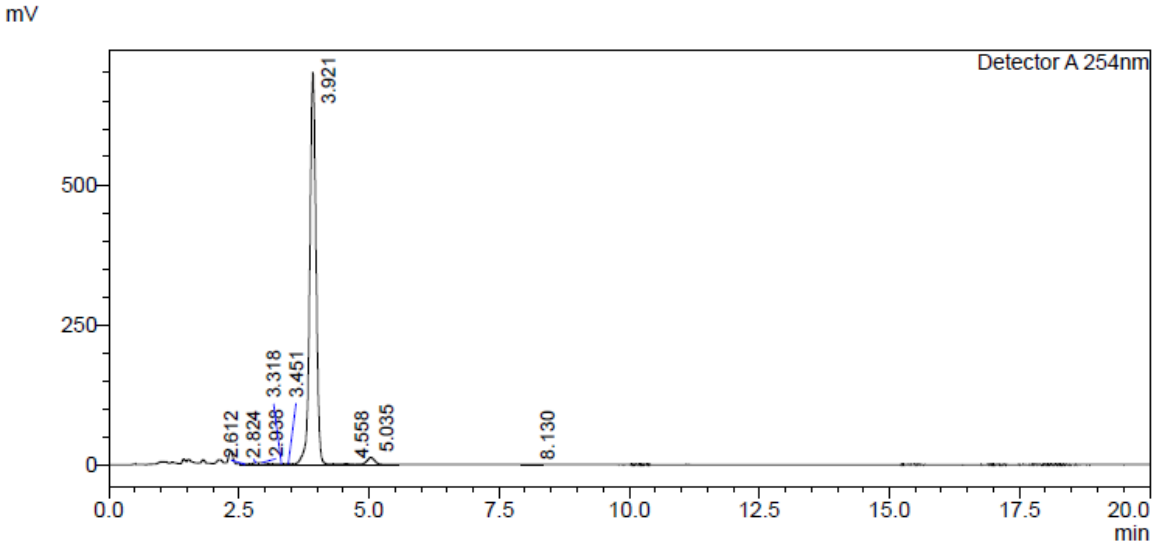
Peak#	Ret. Time	Area	Height	Area%	Area/Height	Width at 5% Height
1	3.032	1289	183	0.124	7.041	--
2	3.272	7396	1054	0.713	7.019	--
3	3.633	1025515	134376	98.816	7.632	0.257
4	4.288	1691	109	0.163	15.488	--
5	5.409	1911	186	0.184	10.250	--
Total		1037802	135909	100.000		

Figure 34. HPLC Trace of **N5**.

<Sample Information>

Sample Name	: C3N4_90		
Sample ID	: C3N4_90		
Method Filename	: 90% Acetonitrile 10 Water 20 mins.lcm		
Batch Filename	: Green_emitters_MeCN765.lcb		
Vial #	: 2-15	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 04/11/2022 16:42:09	Acquired by	: System Administrator
Date Processed	: 04/11/2022 17:02:12	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Area/Height	Width at 5% Height
1	2.612	7526	991	0.123	7.594	--
2	2.824	22184	2943	0.363	7.537	--
3	2.938	36639	3402	0.600	10.771	--
4	3.318	10296	971	0.168	10.607	--
5	3.451	13022	1598	0.213	8.151	--
6	3.921	5864119	699749	95.956	8.380	0.290
7	4.558	21724	1626	0.355	13.363	--
8	5.035	134073	12470	2.194	10.752	0.394
9	8.130	1705	145	0.028	11.754	0.330
Total		6111289	723894	100.000		

Figure 35. HPLC Trace of **C3N4**.

<Sample Information>

Sample Name	: C3N5_90		
Sample ID	: C3N5_90		
Method Filename	: 90% Acetonitrile 10 Water 20 mins.lcm		
Batch Filename	: Green_emitters_MeCN765.lcb		
Vial #	: 2-16	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 04/11/2022 17:13:00	Acquired by	: System Administrator
Date Processed	: 04/11/2022 17:33:01	Processed by	: System Administrator

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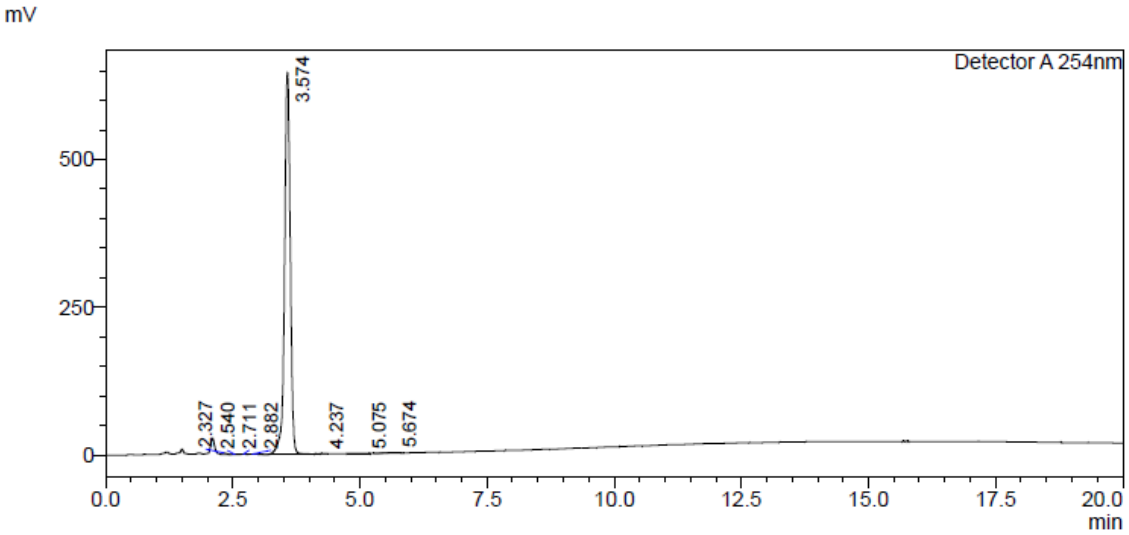


<Peak Table>

Detector A 254nm

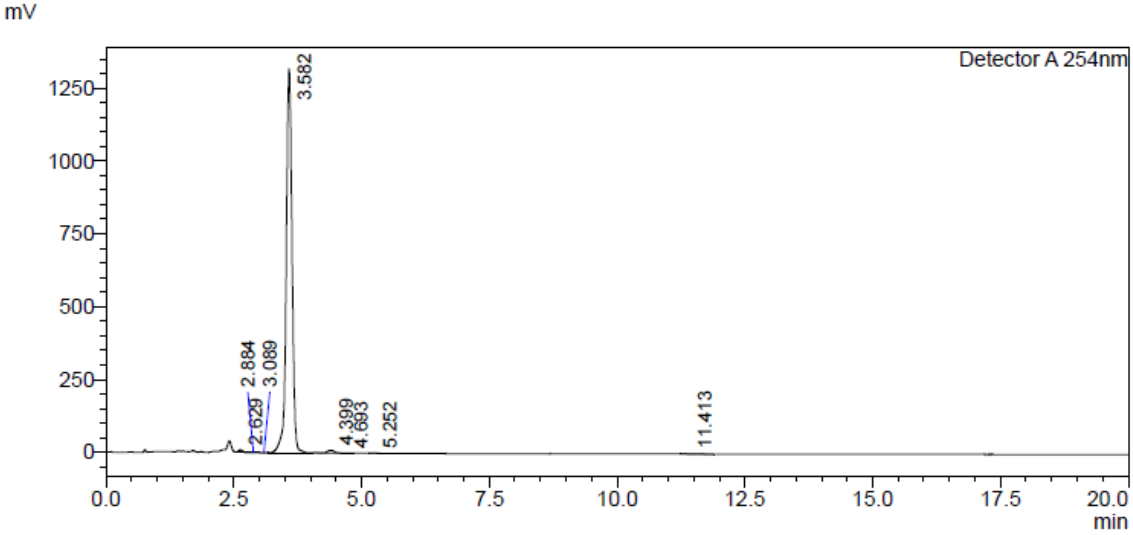
Peak#	Ret. Time	Area	Height	Area%	Area/Height	Width at 5% Height
1	2.327	18190	2505	0.358	7.263	--
2	2.540	2466	350	0.049	7.052	--
3	2.711	4144	535	0.082	7.745	--
4	2.882	5749	610	0.113	9.427	--
5	3.574	5034789	644443	99.081	7.813	0.277
6	4.237	3307	440	0.065	7.521	0.227
7	5.075	1271	101	0.025	12.642	0.334
8	5.674	11586	678	0.228	17.098	0.500
Total		5081502	649660	100.000		

Figure 36. HPLC Trace of **C3N5**.

<Sample Information>

Sample Name	: C4N4_90		
Sample ID	: C4N4_90		
Method Filename	: 90% Acetonitrile 10 Water 20 mins.lcm		
Batch Filename	: Green_emitters_MeCN765.lcb		
Vial #	: 2-17	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 04/11/2022 17:43:48	Acquired by	: System Administrator
Date Processed	: 04/11/2022 18:03:50	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A 254nm

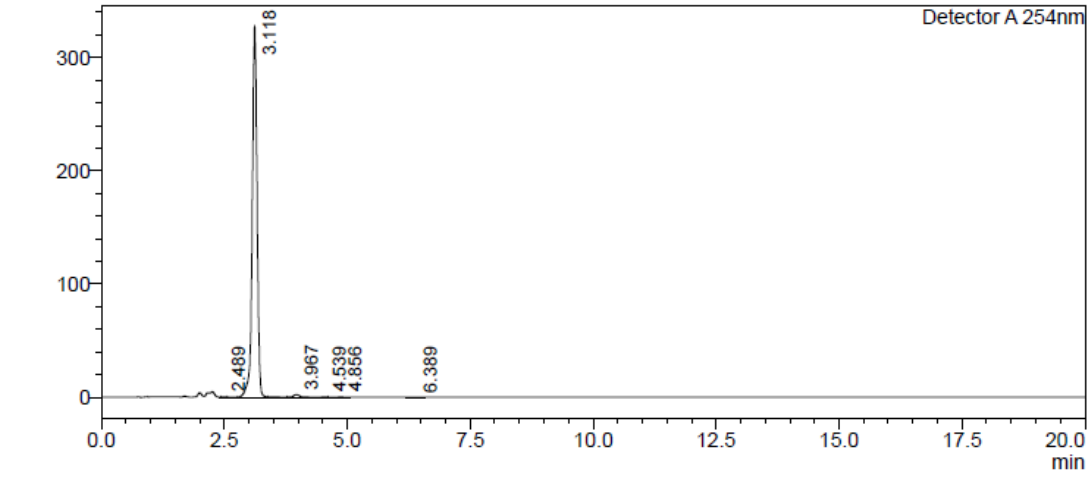
Peak#	Ret. Time	Area	Height	Area%	Area/Height	Width at 5% Height
1	2.629	57089	9398	0.542	6.075	--
2	2.884	3426	671	0.033	5.110	0.155
3	3.089	3960	638	0.038	6.205	--
4	3.582	10378155	1313188	98.520	7.903	0.278
5	4.399	84762	9366	0.805	9.050	0.311
6	4.693	2078	293	0.020	7.093	0.188
7	5.252	2041	218	0.019	9.357	0.264
8	11.413	2536	128	0.024	19.745	0.487
Total		10534048	1333900	100.000		

Figure 37. HPLC Trace of **C4N4**.

<Sample Information>

Sample Name	: C4N5_90		
Sample ID	: C4N5_90		
Method Filename	: 90% Acetonitrile 10 Water 20 mins.lcm		
Batch Filename	: Green_emitters_MeCN765.lcb		
Vial #	: 2-18	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 04/11/2022 18:14:38	Acquired by	: System Administrator
Date Processed	: 04/11/2022 18:34:40	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Area/Height	Width at 5% Height
1	2.489	3850	426	0.168	9.030	--
2	3.118	2268528	325893	98.812	6.961	0.246
3	3.967	18782	2148	0.818	8.744	0.377
4	4.539	1914	214	0.083	8.957	0.275
5	4.856	1450	166	0.063	8.753	0.249
6	6.389	1286	116	0.056	11.092	0.301
Total		2295809	328962	100.000		

Figure 38. HPLC Trace of **C4N5**.

HRMS

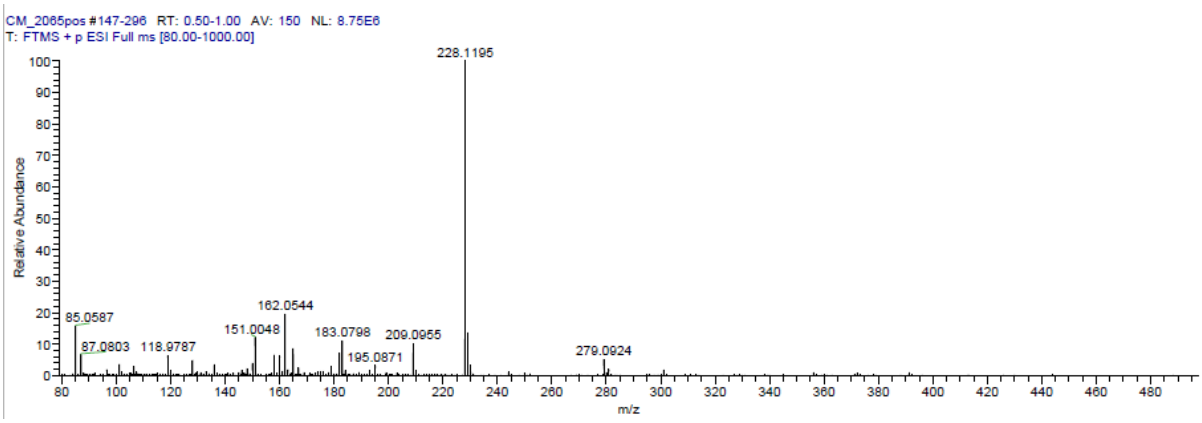


Figure 39. HR-MS of **C3Sippy** ligand.

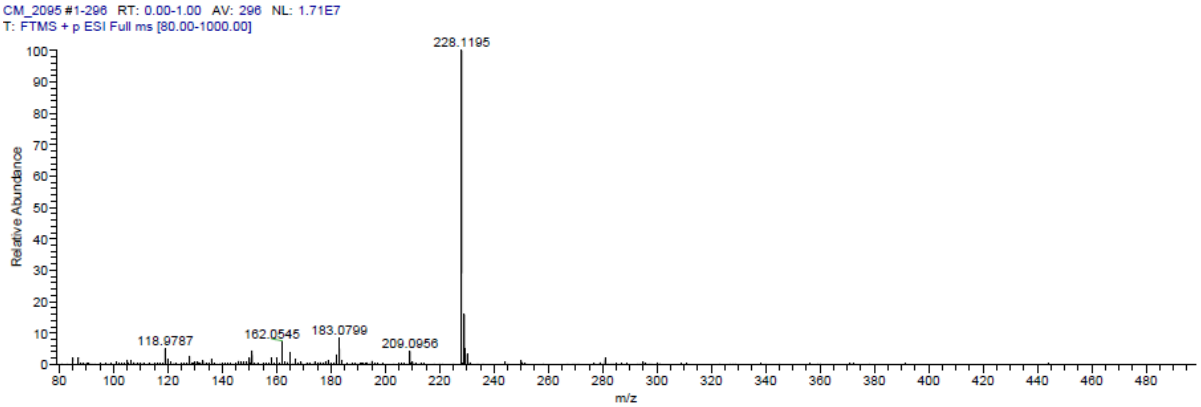


Figure 40. HR-MS of **C4Sippy** ligand.

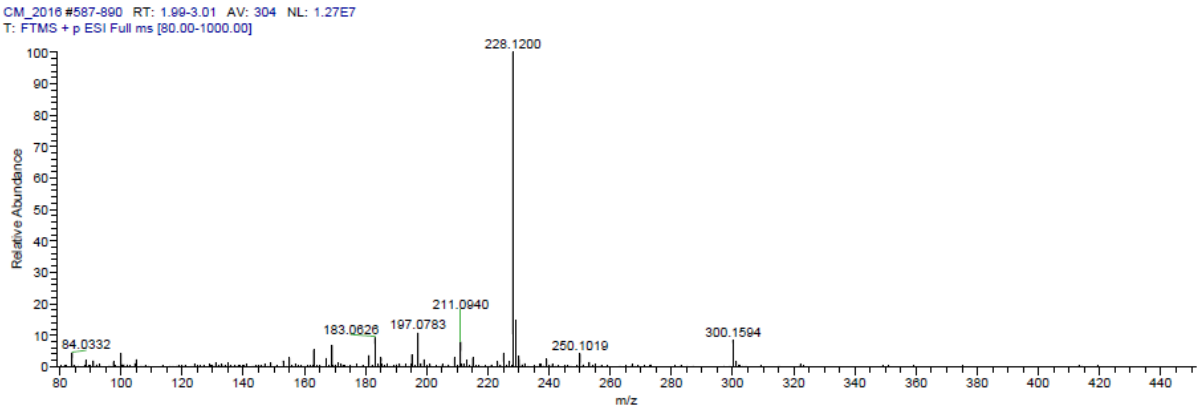


Figure 41. HR-MS of **N4Sippy** ligand.

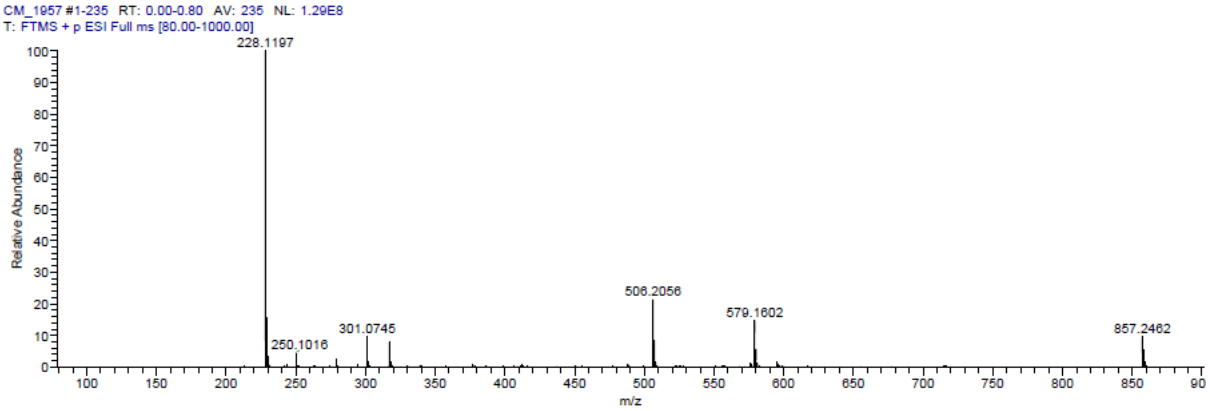


Figure 42. HR-MS of **N5Sippy** ligand.

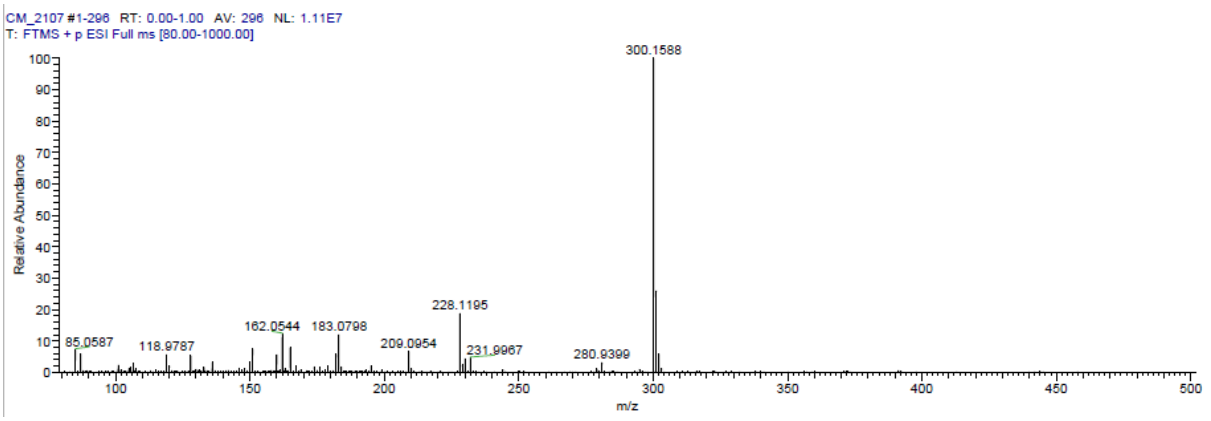


Figure 43. HR-MS of **C3N4Sippy** ligand.

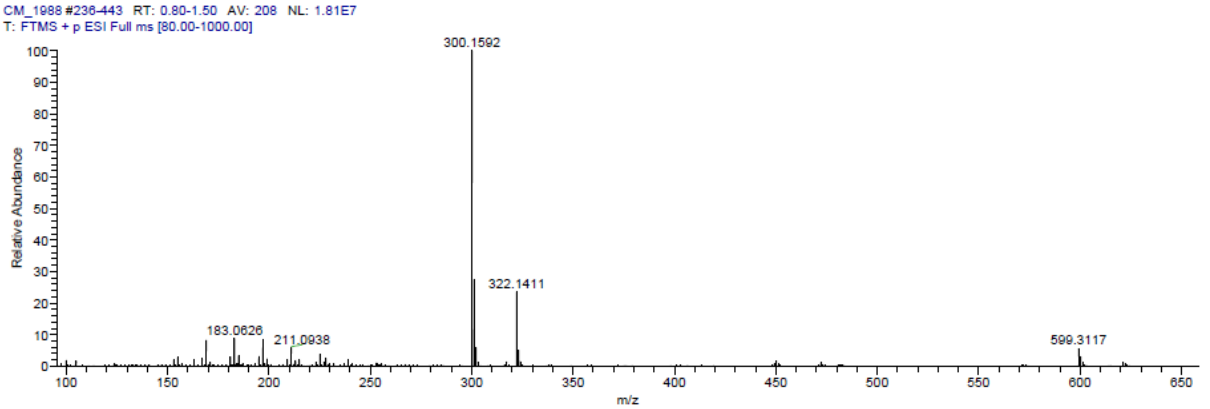


Figure 44. HR-MS of **C3N5Sippy** ligand.

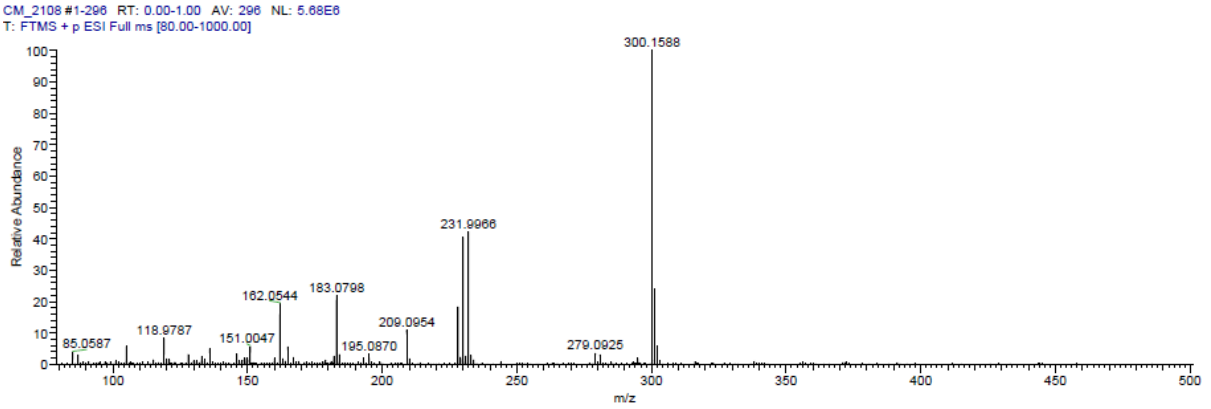


Figure 45. HR-MS of **C4N4Sippy** ligand.

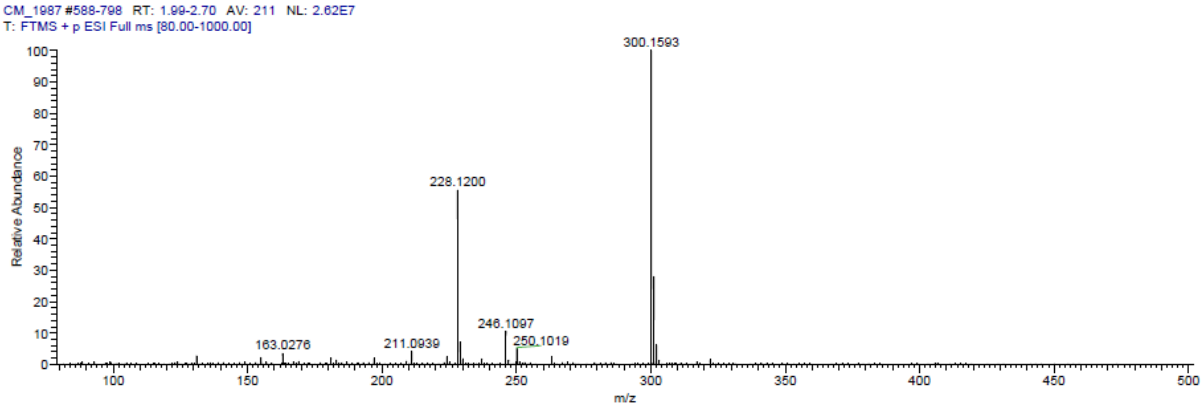


Figure 46. HR-MS of **C4N5Sippy** ligand.

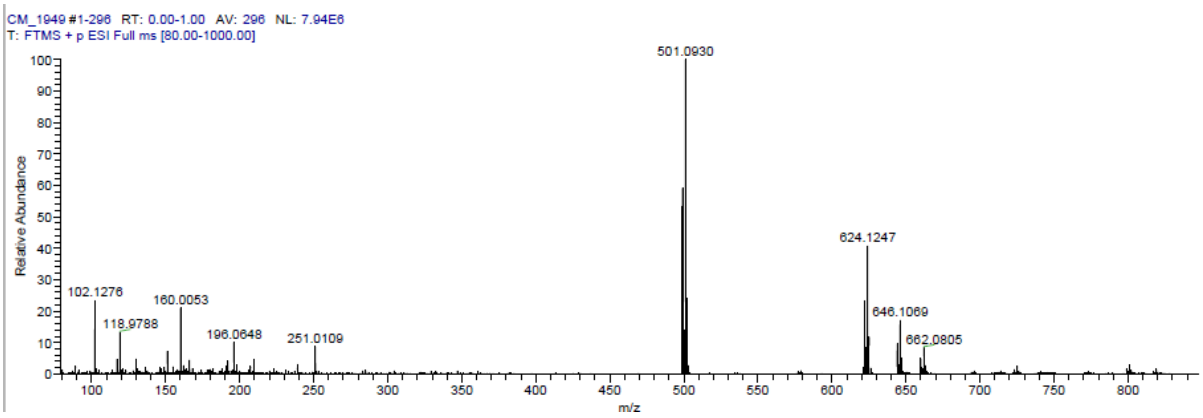


Figure 47. HR-MS of **IrPic**.

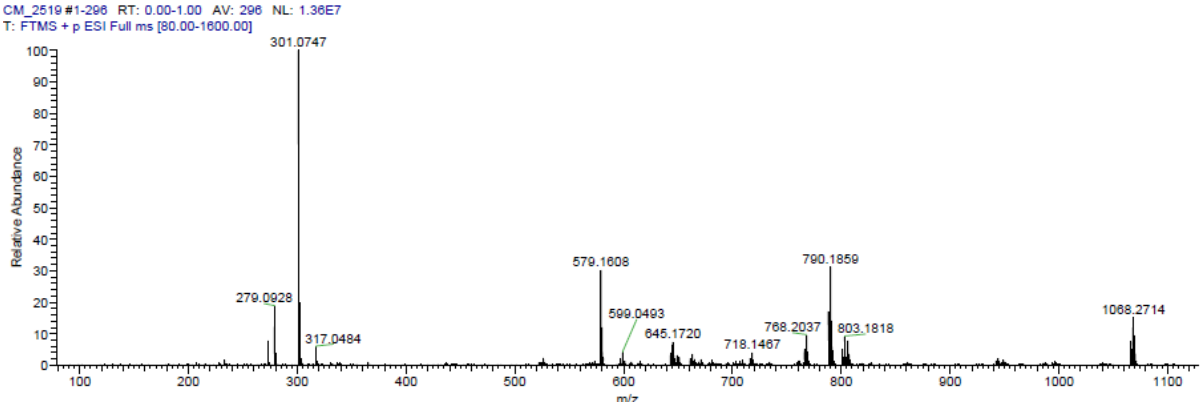


Figure 48. HR-MS of **C3**.

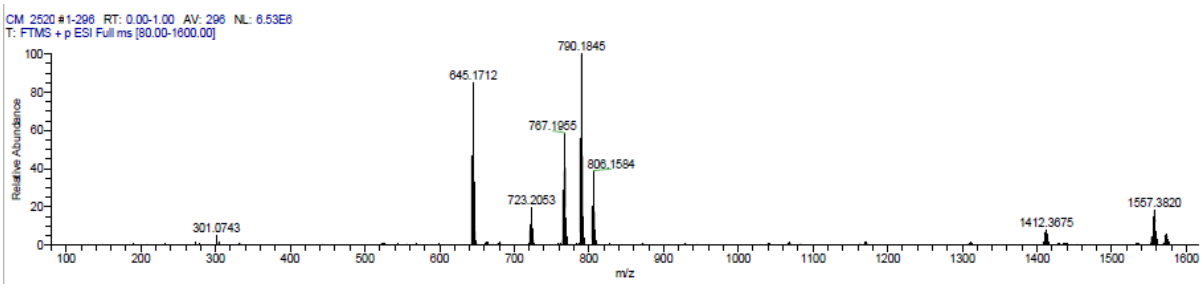


Figure 49. HR-MS of **C4**.

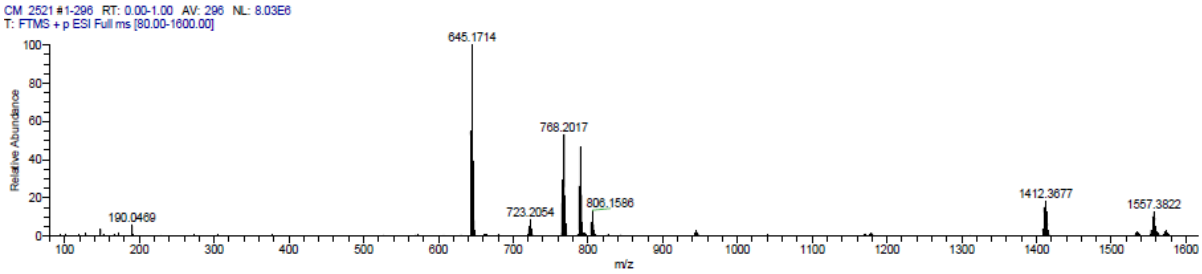


Figure 50. HR-MS of **N4**.

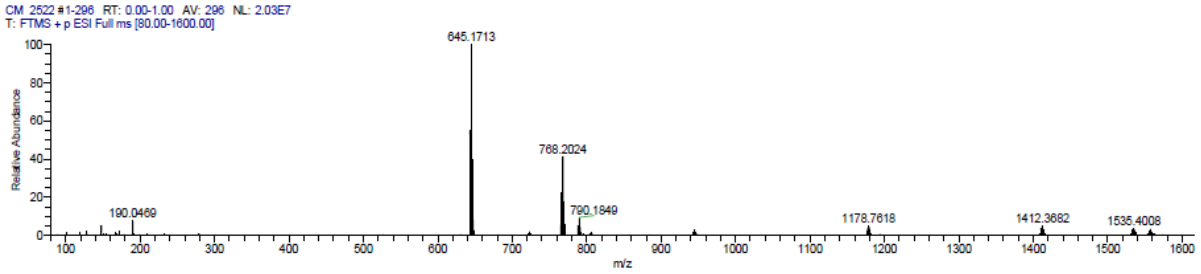


Figure 51. HR-MS of **N5**.

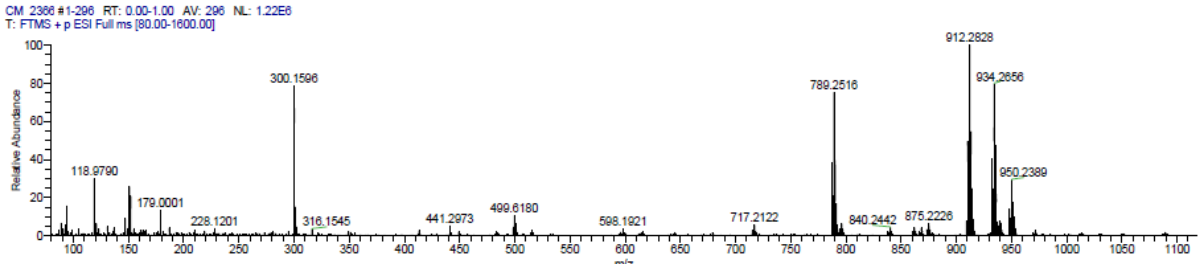


Figure 52. HR-MS of **C3N4**.

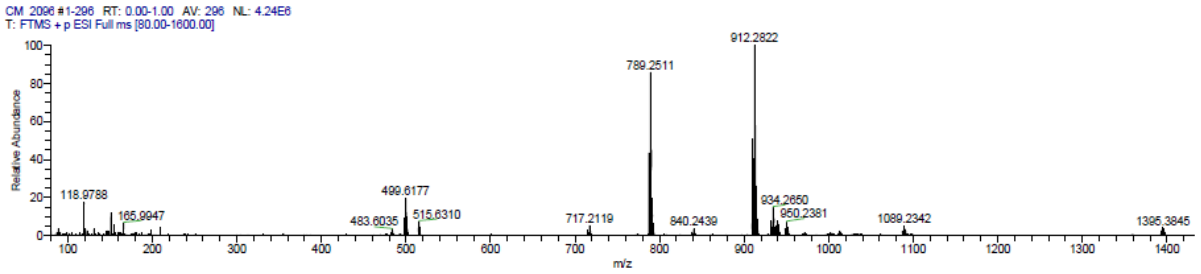


Figure 53. HR-MS of **C3N5**.

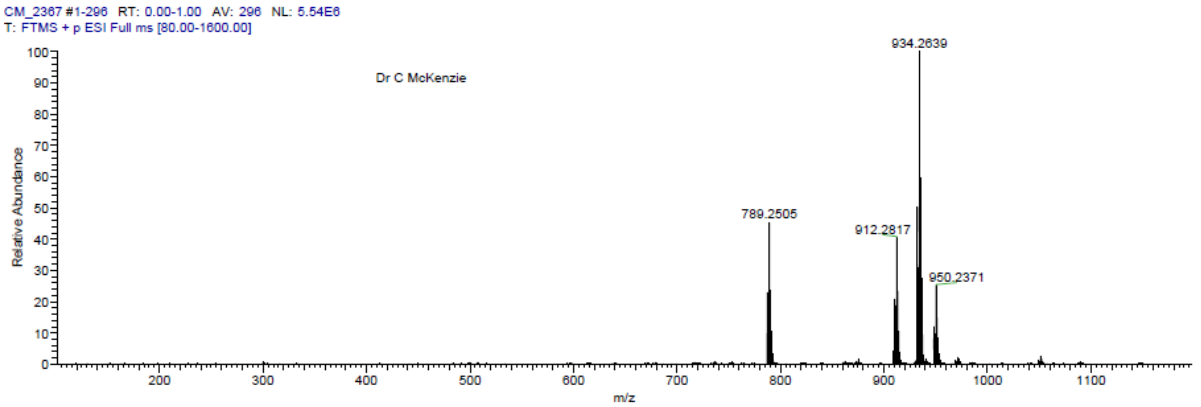


Figure 54. HR-MS of **C4N4**.

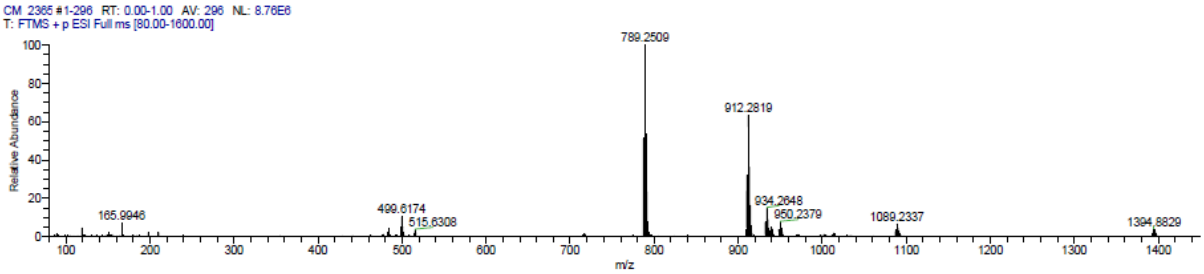


Figure 55. HR-MS of **C4N5**.

Photophysics

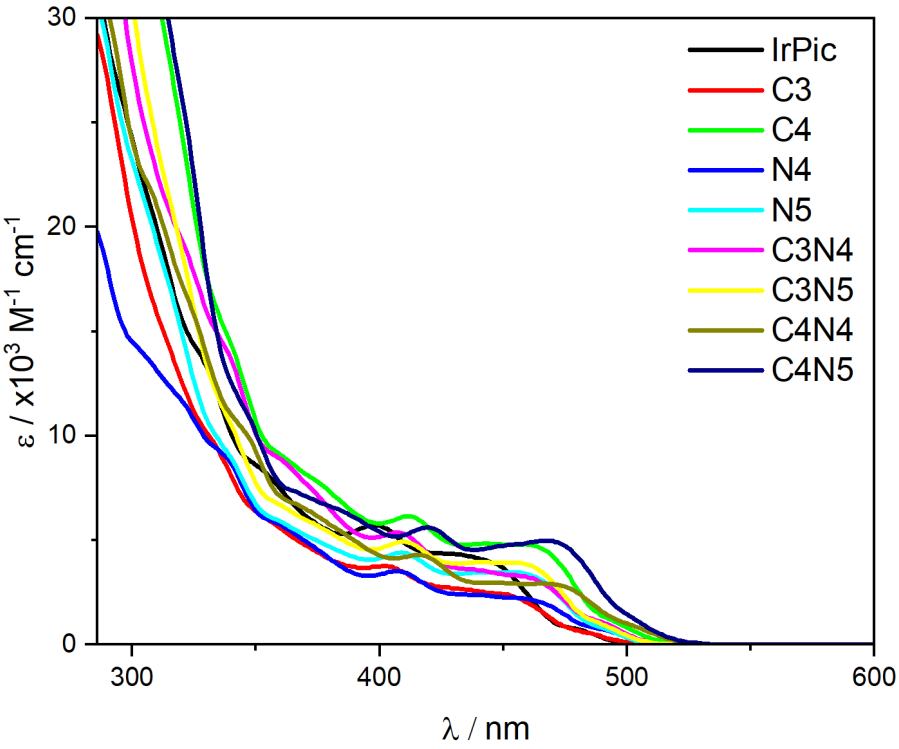


Figure S56. Absorption spectra of the 8 trimethylsilyl-substituted complexes and **IrPic** in toluene solution.

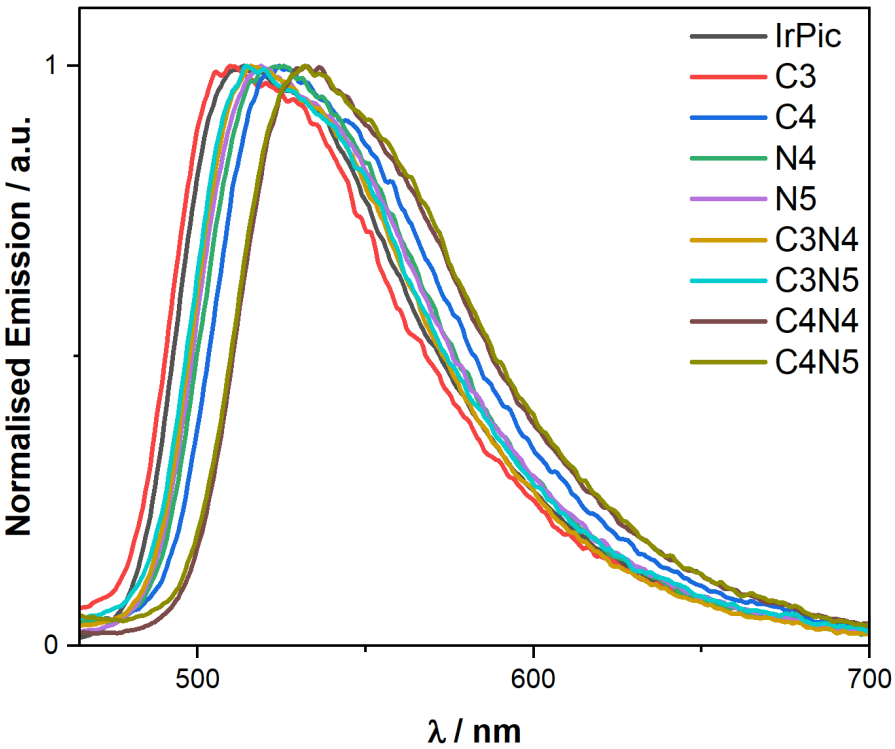


Figure S57. PL spectra of in 10 wt% doped films of the iridium complexes in mCBP (spin-coated from chlorobenzene), λexc = 340 nm.

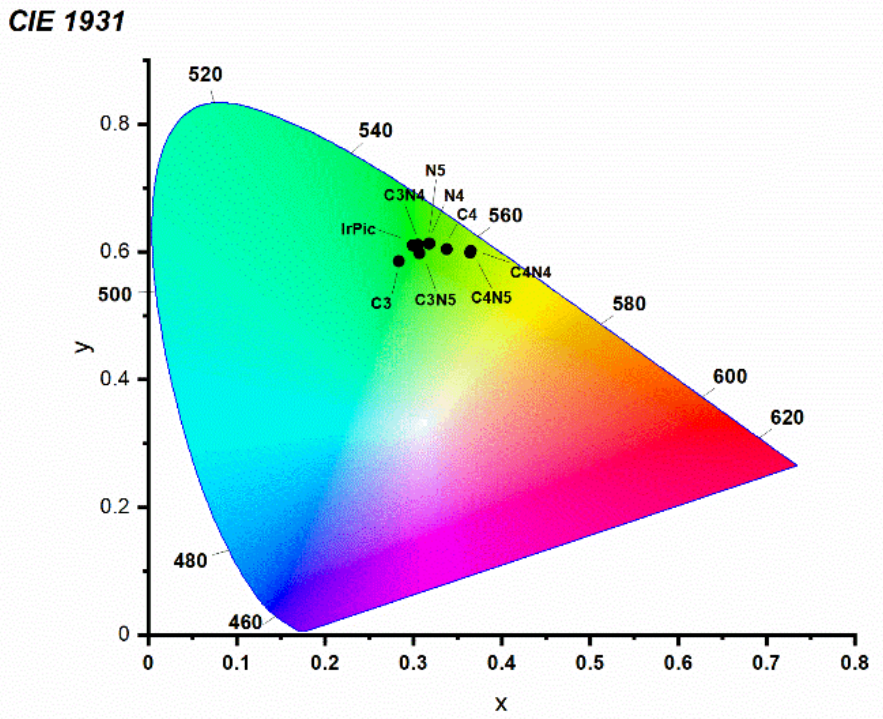


Figure S58. CIE diagram for the emission of the complexes in doped films (10 wt% in *m*CBP, spin-coated from chlorobenzene), (λ_{exc} = 340 nm).

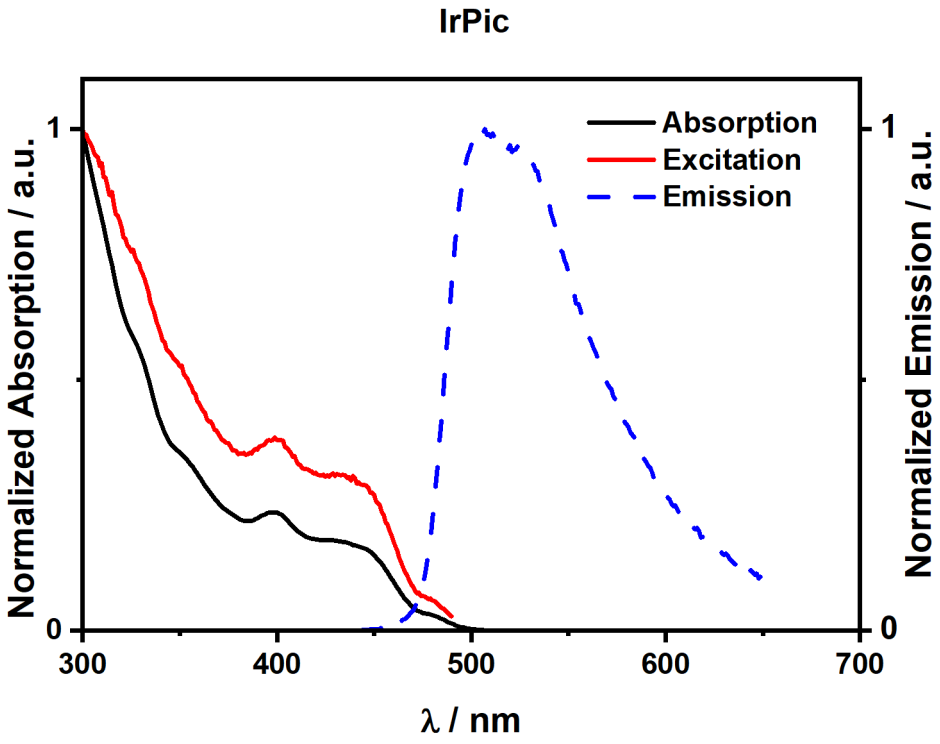


Figure 59. Plots of the normalised absorption, excitation (λ_{em} = 510 nm) and emission (λ_{exc} = 400 nm) of **IrPic** in dichloromethane solution.

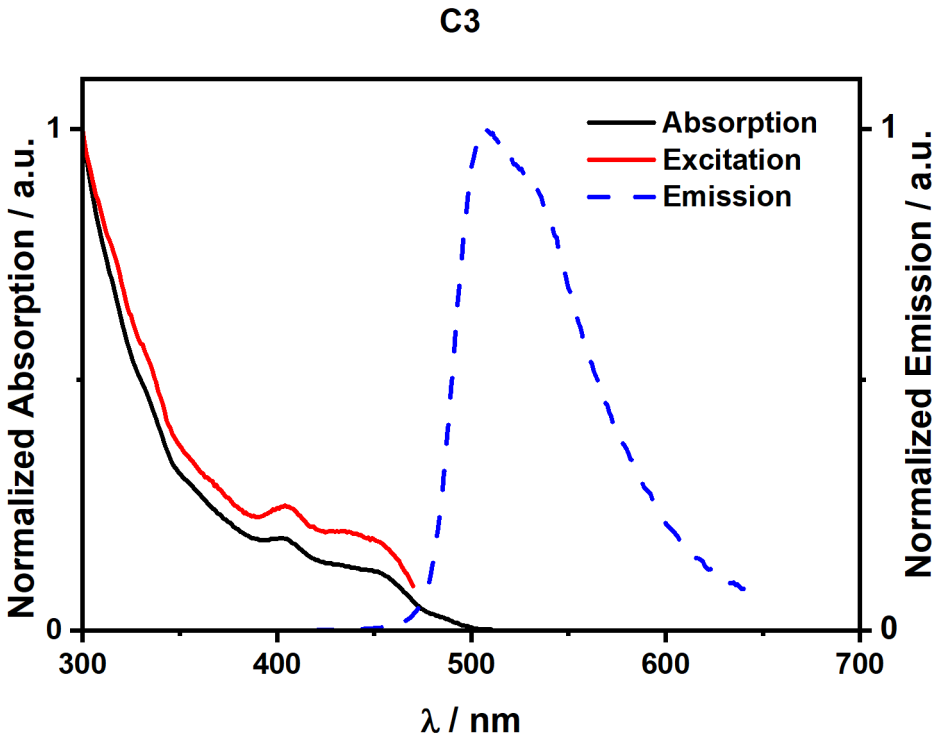


Figure 60. Plots of the normalised absorption, excitation (λ_{em} = 510 nm) and emission (λ_{exc} = 400 nm) of **C3** in toluene solution.

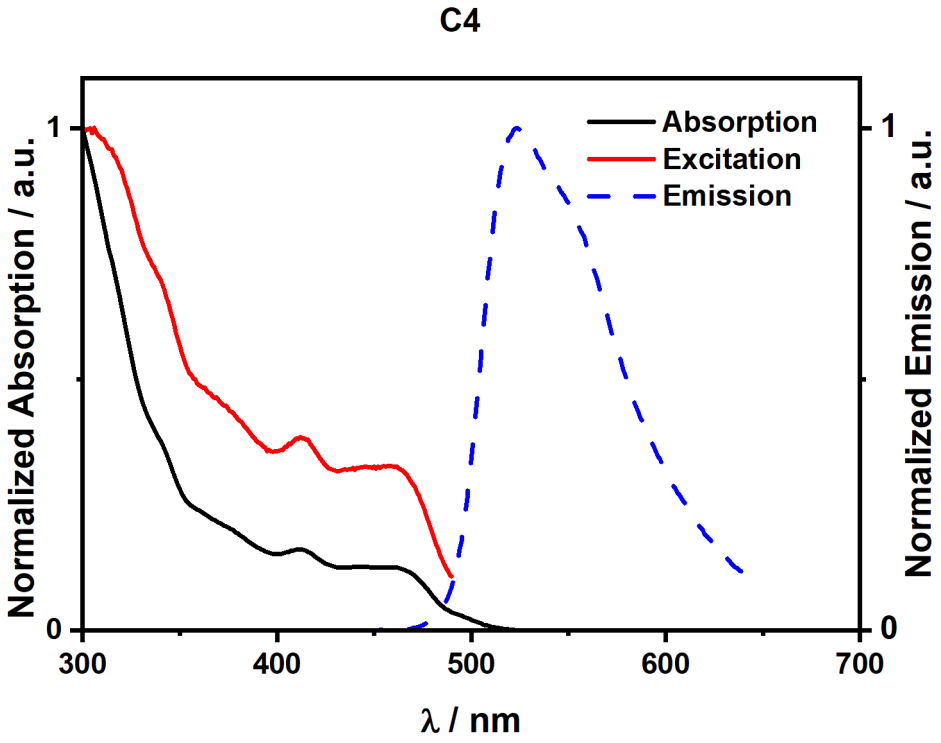


Figure 61. Plots of the normalised absorption, excitation (λ_{em} = 510 nm) and emission (λ_{exc} = 400 nm) of **C4** in toluene solution.

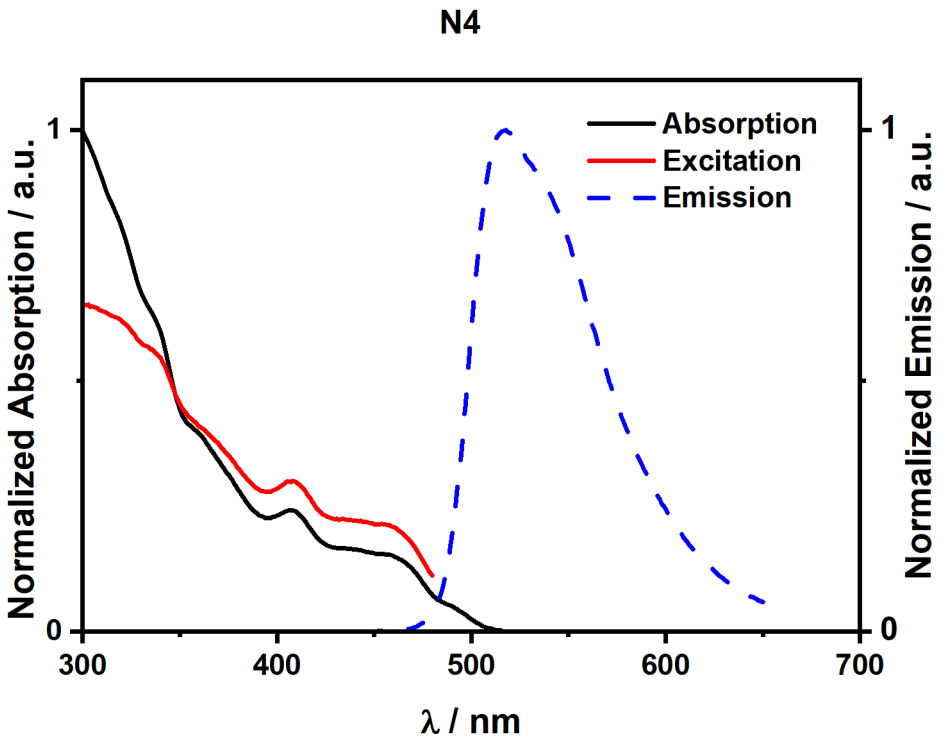


Figure 62. Plots of the normalised absorption, excitation (λ_{em} = 510 nm) and emission (λ_{exc} = 400 nm) of **N4** in toluene solution.

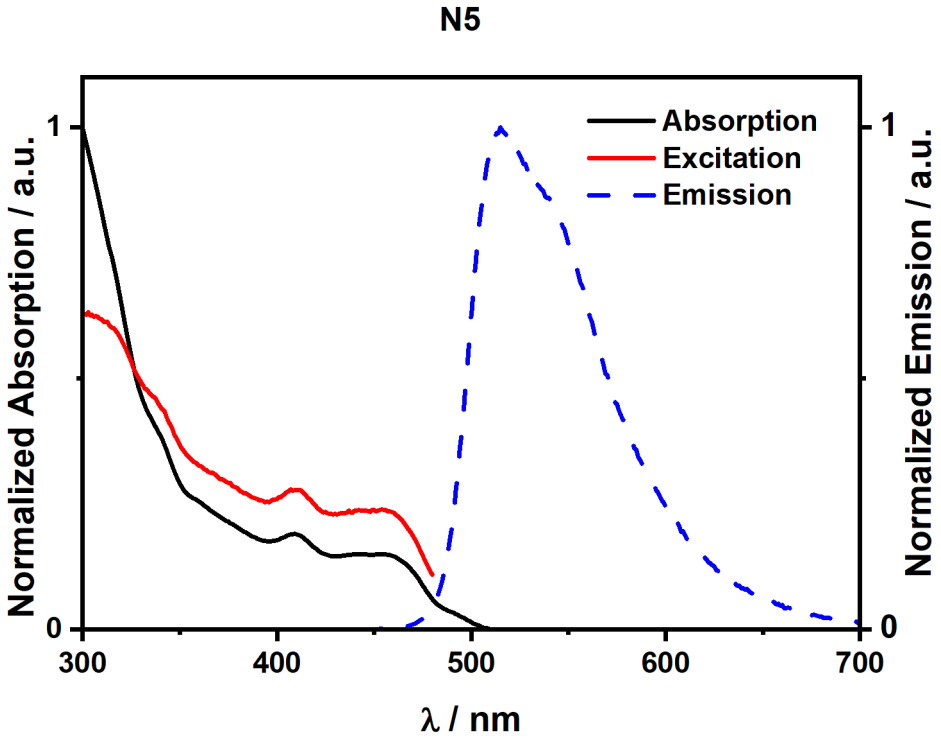


Figure 63. Plots of the normalised absorption, excitation (λ_{em} = 510 nm) and emission (λ_{exc} = 400 nm) of **N5** in toluene solution.

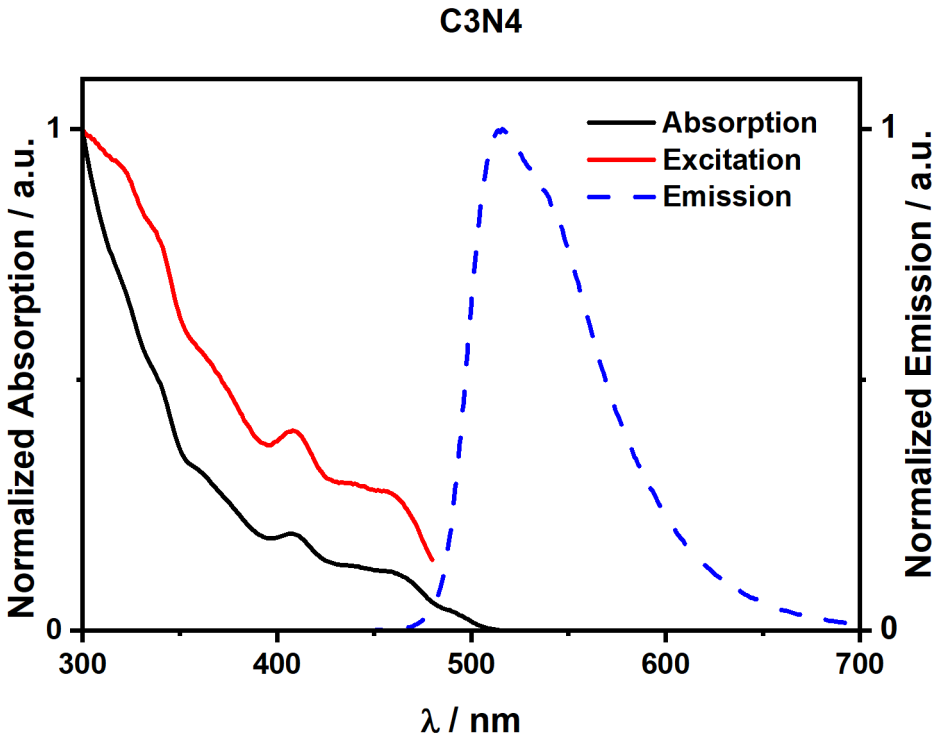


Figure 64. Plots of the normalised absorption, excitation (λ_{em} = 510 nm) and emission (λ_{exc} = 400 nm) of **C3N4** in toluene solution.

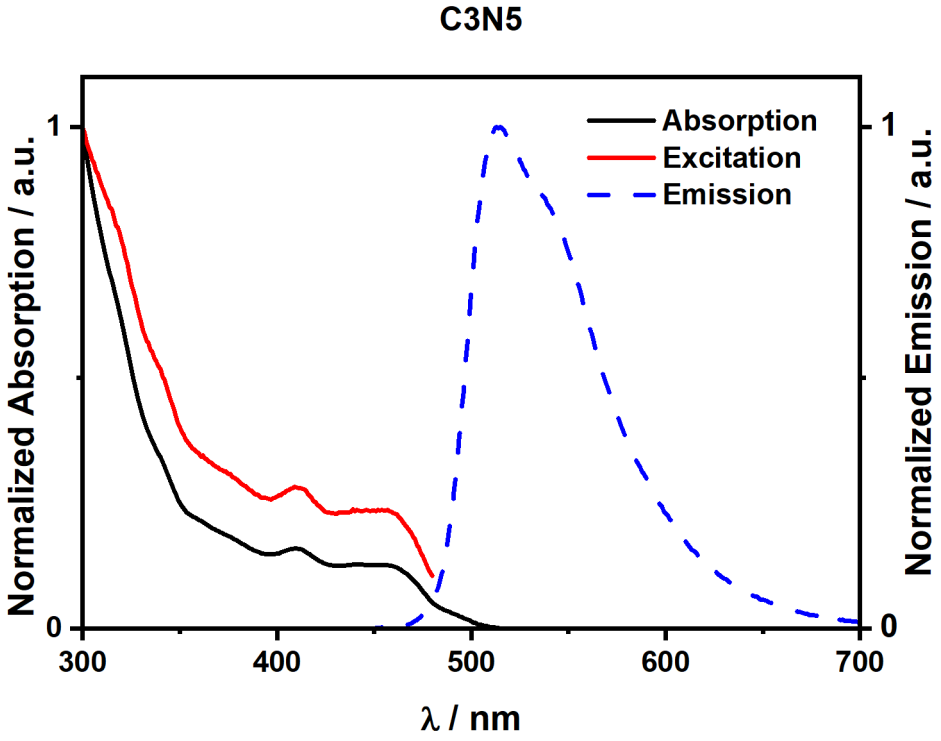


Figure 65. Plots of the normalised absorption, excitation (λ_{em} = 510 nm) and emission (λ_{exc} = 400 nm) of **C3N5** in toluene solution.

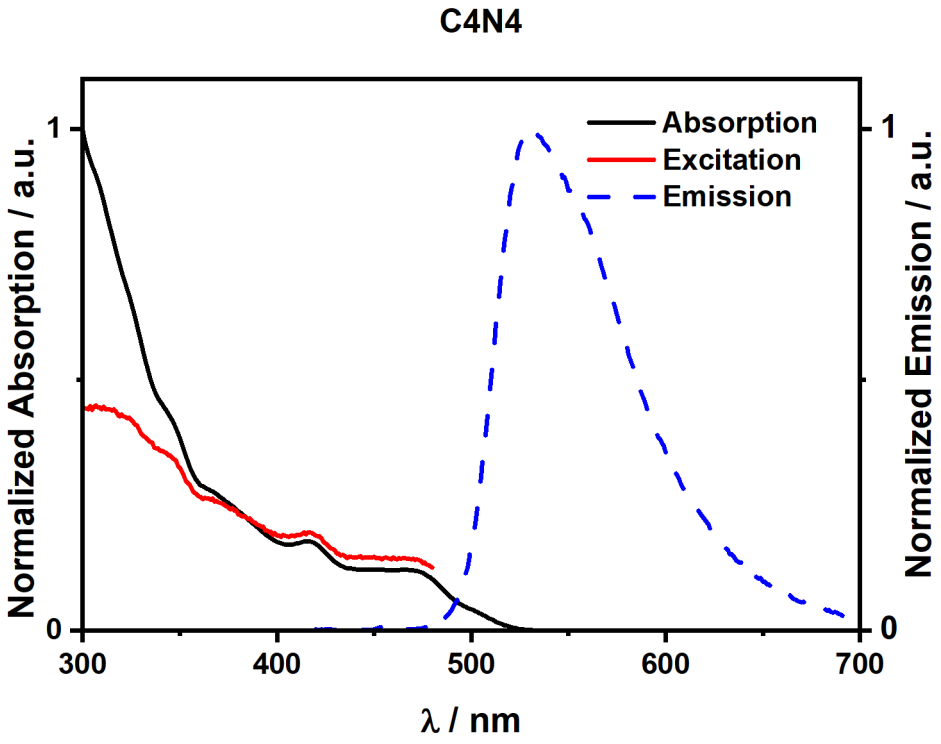


Figure 66. Plots of the normalised absorption, excitation (λ_{em} = 510 nm) and emission (λ_{exc} = 400 nm) of **C4N4** in toluene solution.

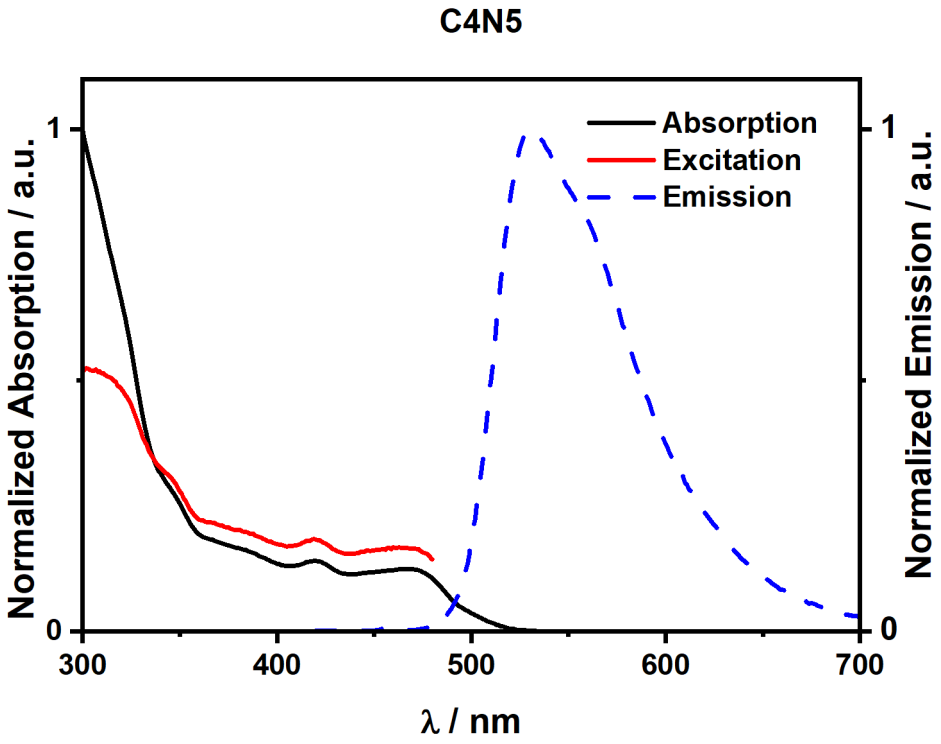
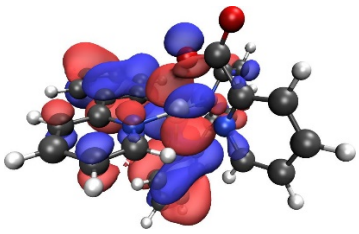
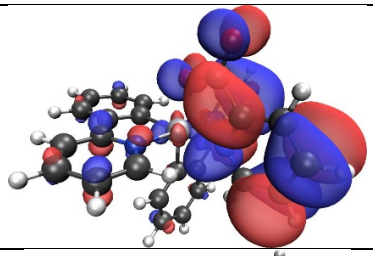
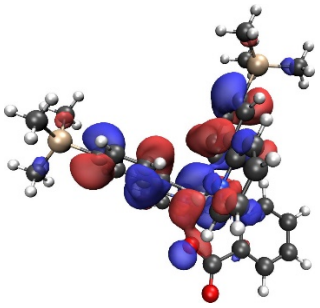
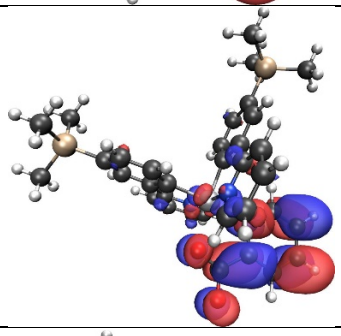
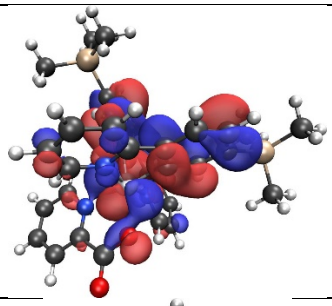
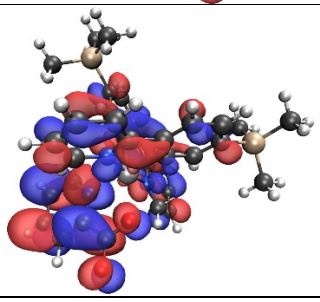
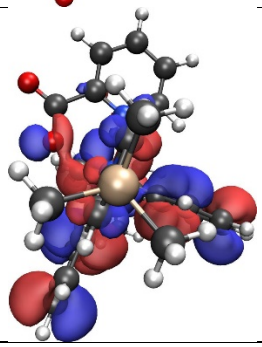
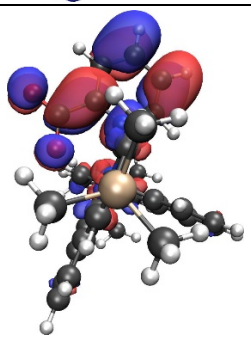
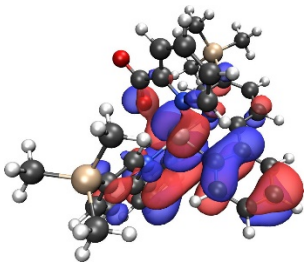
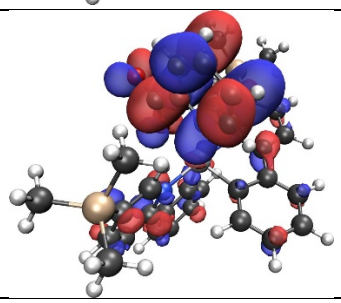


Figure 67. Plots of the normalised absorption, excitation (λ_{em} = 510 nm) and emission (λ_{exc} = 400 nm) of **C4N5** in toluene solution.

DFT Calculations

Table S1. Plots of the HOMO and LUMO orbitals for each of the complexes.

Complex	HOMO	LUMO
IrPic		
C3		
C4		
N4		
N5		

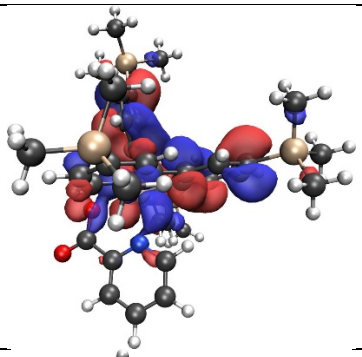
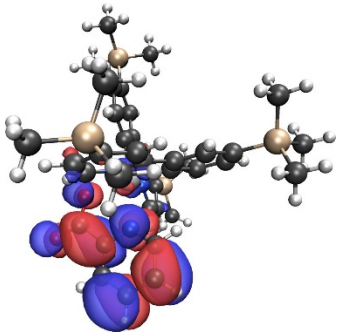
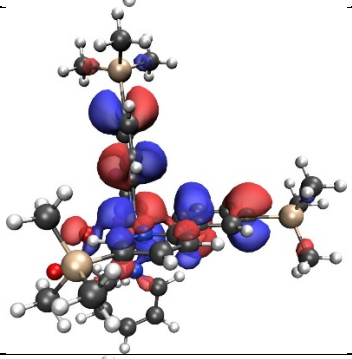
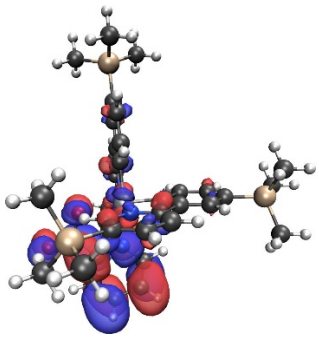
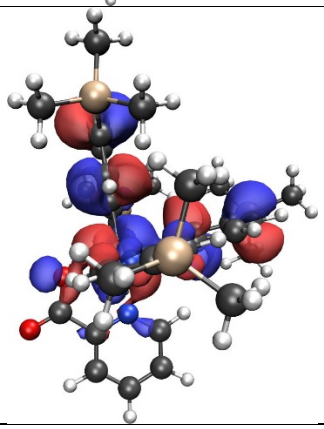
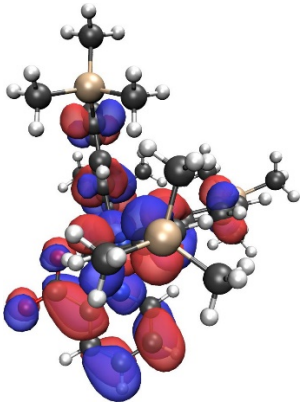
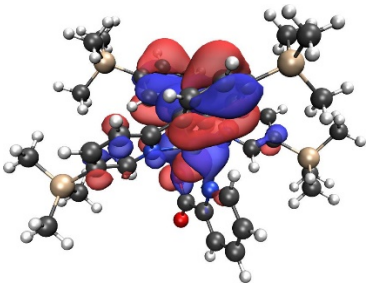
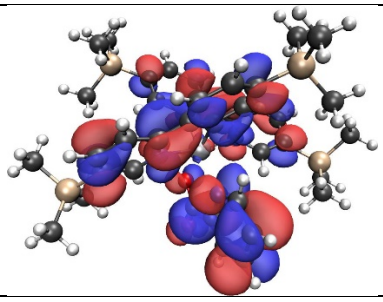
C3N4		
C3N5		
C4N4		
C4N5		

Table S2. Excited state transitions for each of the complexes from TD-DFT calculations.

Complex	State	Energy / eV	Wavelength / nm	Oscillator strength (*f*)	Transition	Contribution / %
IrPic	T_1	2.6522	467.48	0	HOMO→LUMO+1	69
	T_2	2.7141	456.82	0	HOMO→LUMO+2	69
	T_3	2.8636	432.97	0	HOMO→LUMO	86
	S_1	2.8932	428.54	0.013	HOMO→LUMO	98
	S_2	2.9265	423.66	0.1086	HOMO→LUMO+1	97
	S_3	3.0471	406.89	0.0023	HOMO→LUMO+2	97
C3	T_1	2.6591	466.26	0	HOMO→LUMO+1	71
	T_2	2.7208	455.69	0	HOMO→LUMO+2	68
	T_3	2.8454	435.74	0	HOMO→LUMO	89
	S_1	2.8743	431.35	0.0082	HOMO→LUMO	98
	S_2	2.9234	424.11	0.1078	HOMO→LUMO+1	97
	S_3	3.0427	407.48	0.0024	HOMO→LUMO+2	97
C4	T_1	2.5939	477.98	0	HOMO→LUMO+1 HOMO→LUMO	52 27
	T_2	2.6661	465.04	0	HOMO→LUMO+2	68
	T_3	2.8494	435.12	0	HOMO→LUMO HOMO→LUMO+1	64 34
	S_1	2.858	433.81	0.1146	HOMO→LUMO HOMO→LUMO+1	67 31
	S_2	2.8849	429.77	0.0144	HOMO→LUMO+1 HOMO→LUMO	67 31
	S_3	3.0023	412.96	0.0028	HOMO→LUMO+2	97
N4	T_1	2.6522	467.48	0	HOMO→LUMO+1	71
	T_2	2.7125	457.08	0	HOMO→LUMO+2	68
	T_3	2.845	435.8	0	HOMO→LUMO	89
	S_1	2.8766	431.01	0.0053	HOMO→LUMO	96
	S_2	2.9138	425.51	0.1128	HOMO→LUMO+1	95
	S_3	3.0266	409.65	0.0026	HOMO→LUMO+2	97
N5	T_1	2.6294	471.53	0	HOMO→LUMO+1	62
	T_2	2.6936	460.29	0	HOMO→LUMO+2	68
	T_3	2.8396	436.63	0	HOMO→LUMO	79
	S_1	2.8625	433.13	0.0278	HOMO→LUMO	98
	S_2	2.9158	425.22	0.1236	HOMO→LUMO+1	97
	S_3	3.0369	408.26	0.0082	HOMO→LUMO+2	97
C3N4	T_1	2.6581	466.44	0	HOMO→LUMO+1	72
	T_2	2.7191	455.98	0	HOMO→LUMO+2	68
	T_3	2.8283	438.37	0	HOMO→LUMO	90
	S_1	2.8587	433.71	0.0052	HOMO→LUMO	97
	S_2	2.9097	426.11	0.1075	HOMO→LUMO+1	96
	S_3	3.021	410.41	0.0024	HOMO→LUMO+2	97
C3N5	T_1	2.6427	469.16	0	HOMO→LUMO+1	62
	T_2	2.7053	458.3	0	HOMO→LUMO+2	66
	T_3	2.821	439.5	0	HOMO→LUMO	81

	S_1	2.8428	436.13	0.0182	HOMO→LUMO	98
	S_2	2.9219	424.33	0.1293	HOMO→LUMO+1	97
	S_3	3.0399	407.86	0.0058	HOMO→LUMO+2	97
C4N4	T_1	2.5824	480.11	0	HOMO→LUMO HOMO→LUMO+1	42 37
	T_2	2.6745	463.58	0	HOMO→LUMO+2	62
	S_1	2.8358	437.21	0.1237	HOMO→LUMO HOMO→LUMO+1	70 28
	T_3	2.8488	435.22	0	HOMO→LUMO+1 HOMO→LUMO	52 45
	S_2	2.8831	430.04	0.0043	HOMO→LUMO+1 HOMO→LUMO	70 28
	S_3	3.0026	412.92	0.0016	HOMO→LUMO+2	97
C4N5	T_1	2.5577	484.75	0	HOMO→LUMO HOMO→LUMO+1	46 35
	T_2	2.6242	472.46	0	HOMO→LUMO+2	71
	S_1	2.8024	442.42	0.1229	HOMO→LUMO	94
	T_3	2.8188	439.85	0	HOMO→LUMO+1 HOMO→LUMO	53 45
	S_2	2.8676	432.36	0.0529	HOMO→LUMO+1	93
	S_3	2.9459	420.87	0.0031	HOMO→LUMO+2	97

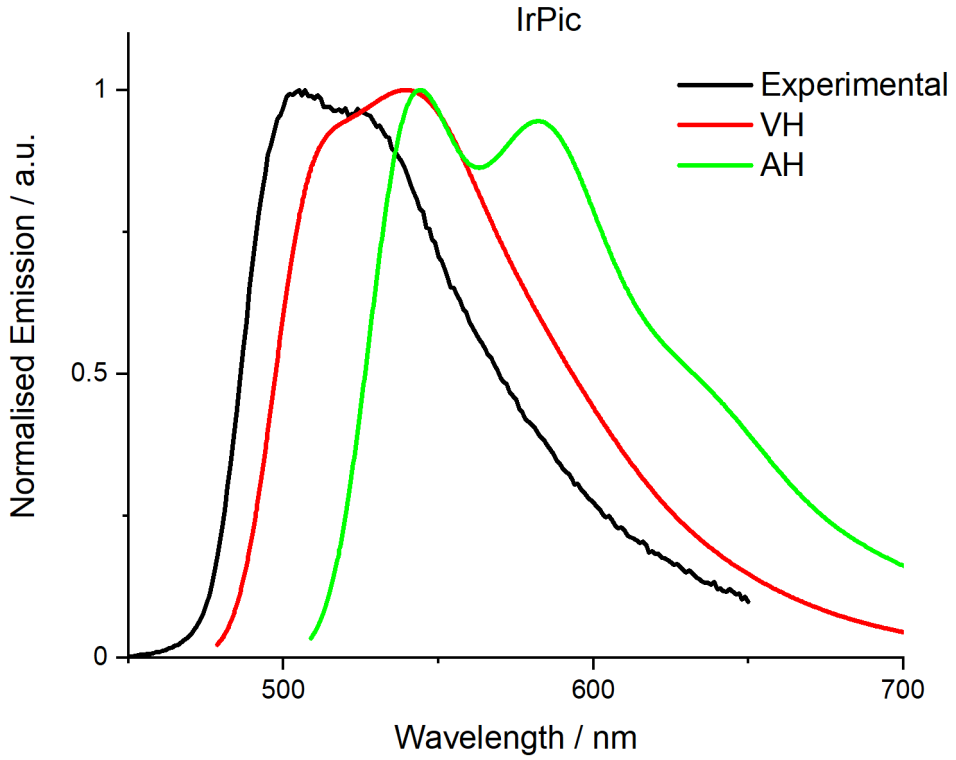


Figure S68. Comparison of experimental (degassed toluene solution) and calculated emission spectra (VH and AH methods) for **IrPic**.

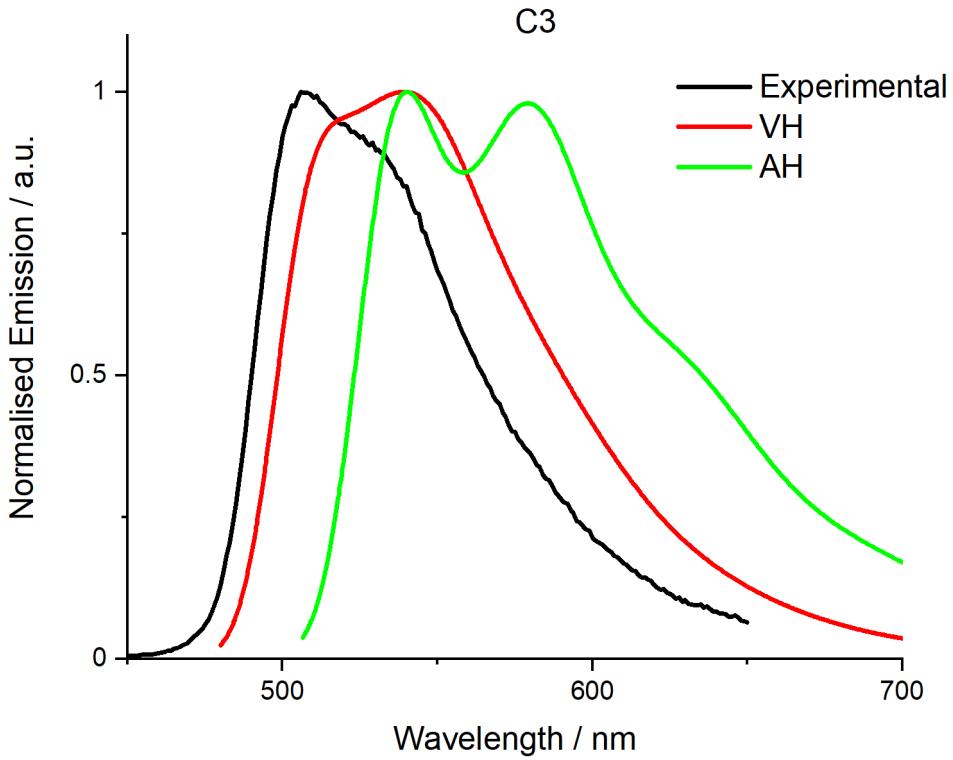


Figure S69. Comparison of experimental (degassed toluene solution) and calculated emission spectra (VH and AH, using silane model complex, methods) for **C3**.

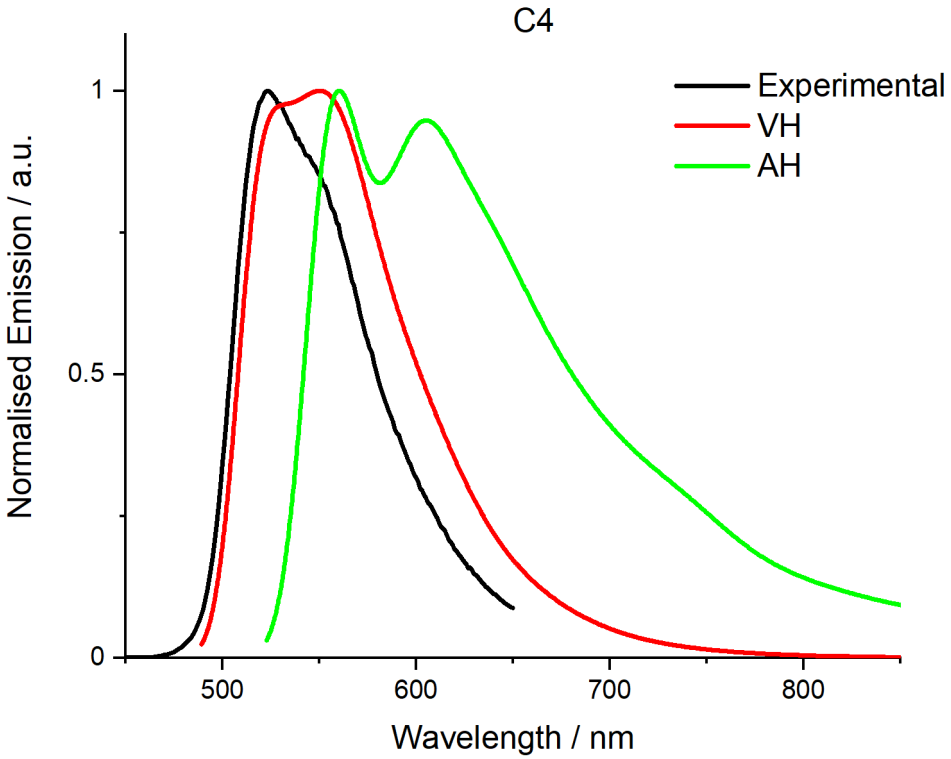


Figure S70. Comparison of experimental (degassed toluene solution) and calculated emission spectra (VH and AH, using silane model complex, methods) for **C4**.

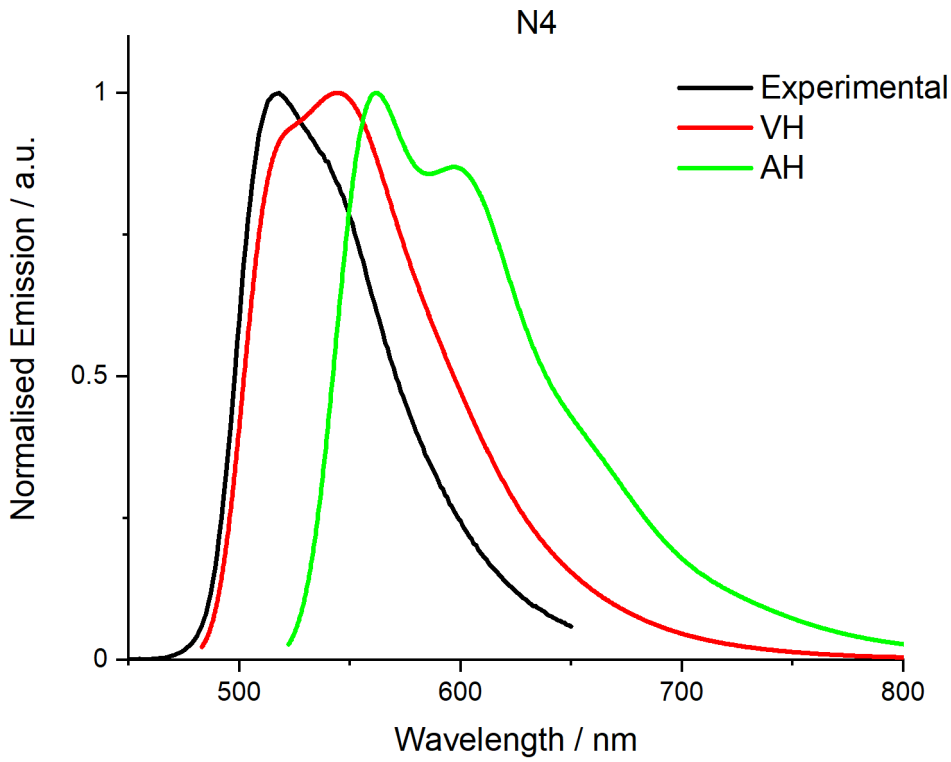


Figure S71. Comparison of experimental (degassed toluene solution) and calculated emission spectra (VH and AH, using silane model complex, methods) for **N4**.

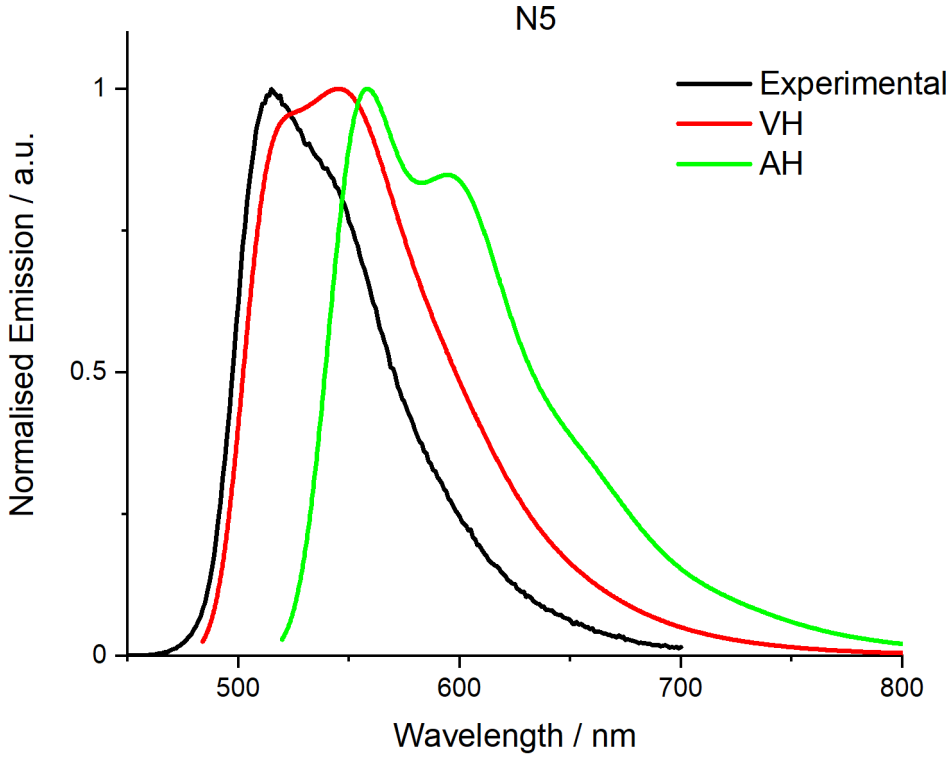


Figure S72. Comparison of experimental (degassed toluene solution) and calculated emission spectra (VH and AH, using silane model complex, methods) for **N5**.

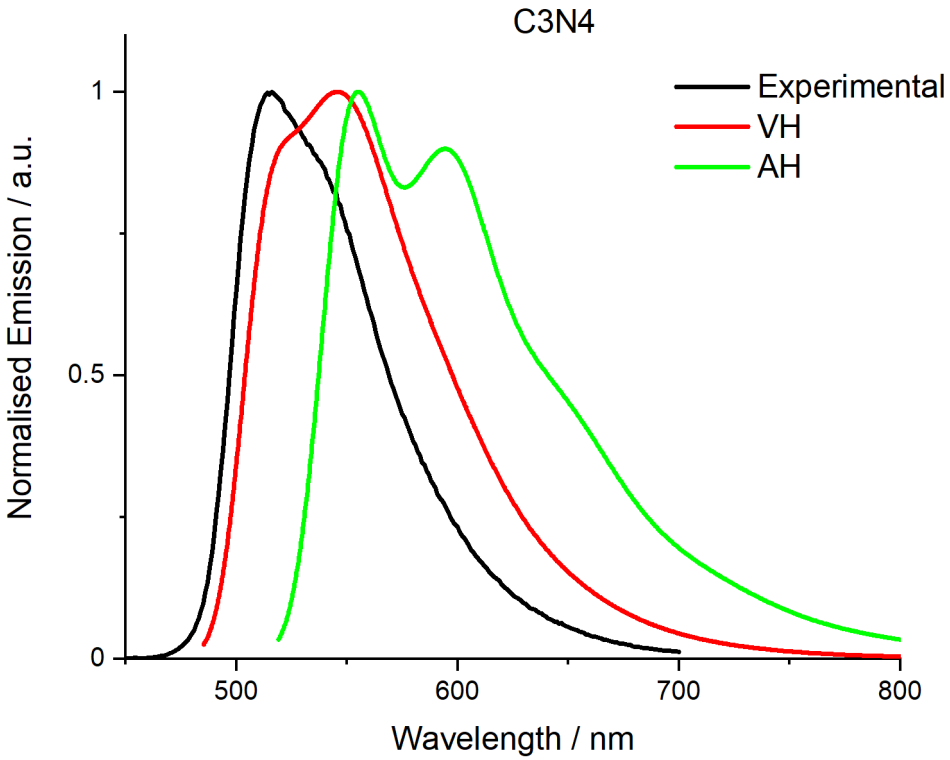


Figure S73. Comparison of experimental (degassed toluene solution) and calculated emission spectra (VH and AH, using silane model complex, methods) for **C3N4**.

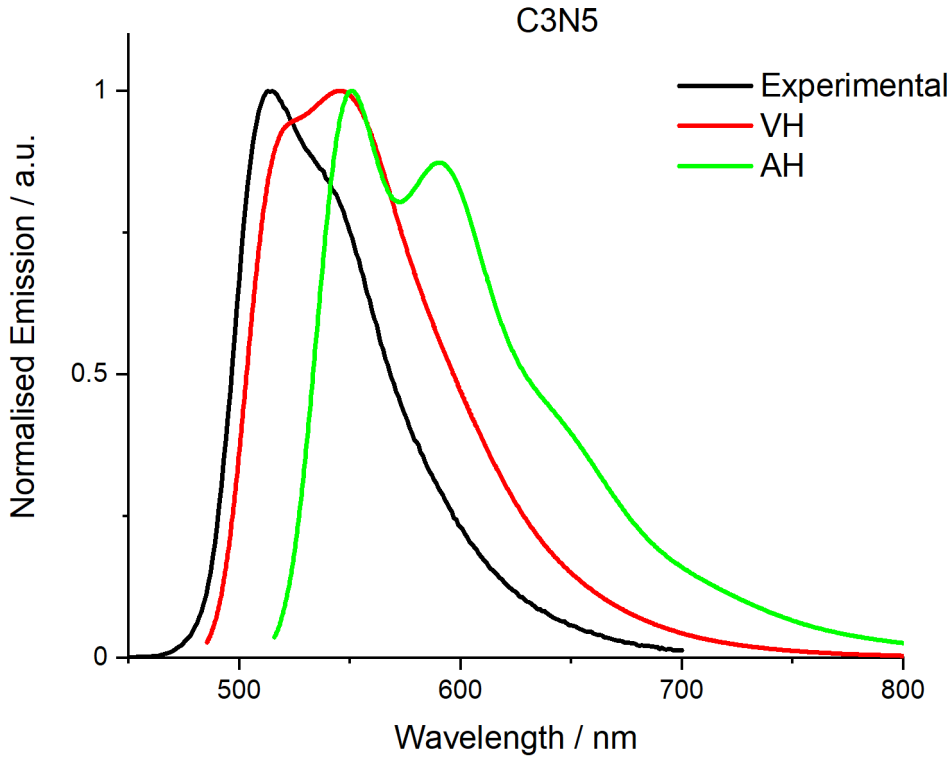


Figure S74. Comparison of experimental (degassed toluene solution) and calculated emission spectra (VH and AH, using silane model complex, methods) for **C3N5**.

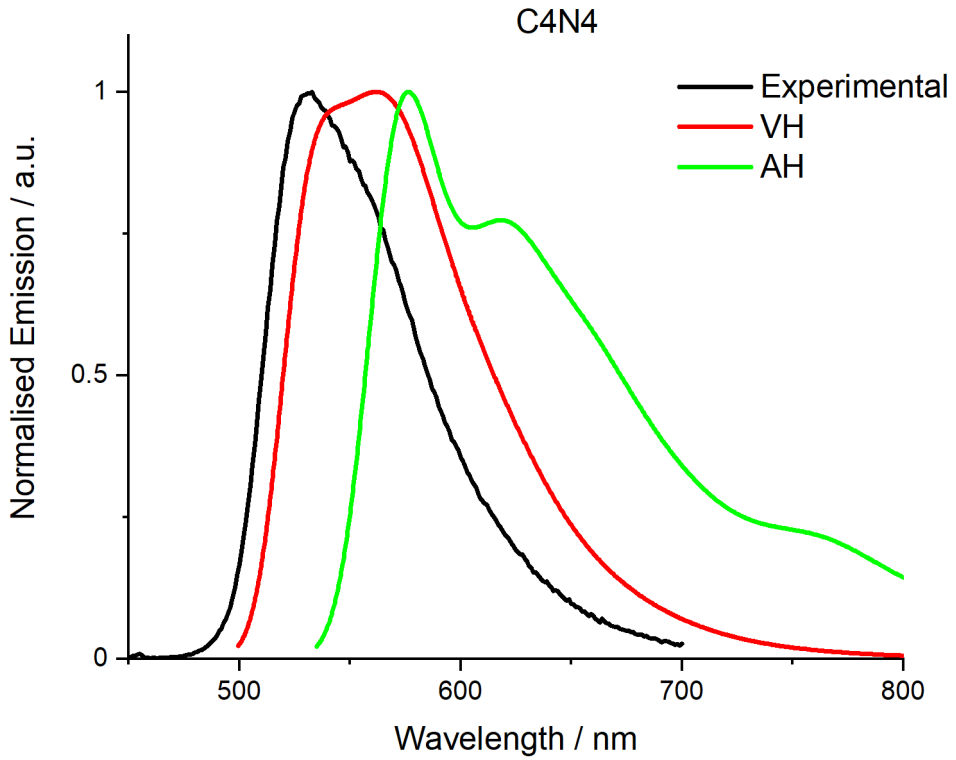


Figure S75. Comparison of experimental (degassed toluene solution) and calculated emission spectra (VH and AH, using silane model complex, methods) for **C4N4**.

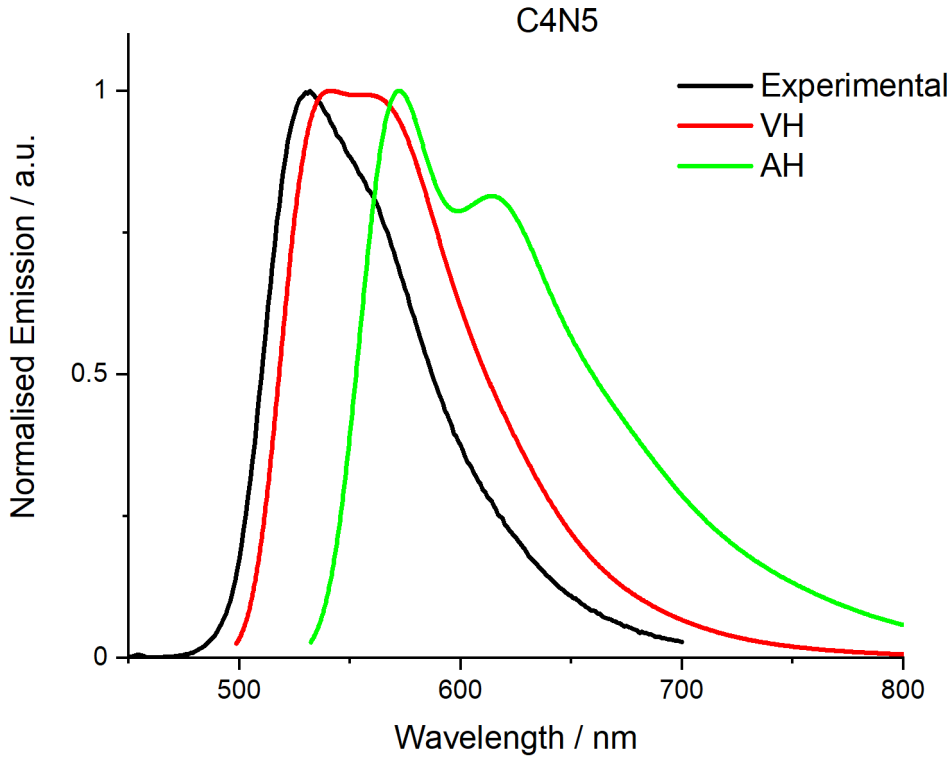


Figure S76. Comparison of experimental (degassed toluene solution) and calculated emission spectra (VH and AH, using silane model complex, methods) for **C4N5**.

Table S3. Information on the dipole transitions in the vibrational spectra of the reference complexes (***fac*-Ir(ppy)$_3$**, **Ir(ppy)$_2$(pic)** and **Ir(ppy)$_2$(acac)**) calculated by the AH method, a dipole strength of 0.002 was used as a cut-off for the reported transitions.

Complex	Energy / cm^{-1}	Transition	Intensity	Dipolar Strength
***fac*-Ir(ppy)$_3$**	-1648	|0>->|153^1>->	0.4514	0.00346
	-1629	|0>->|150^1>->	0.3101	0.00237
	-1626	|0>->|148^1>->	0.4979	0.00380
	-1588	|0>->|144^1>->	0.3651	0.00276
	-1588	|0>->|143^1>->	0.5455	0.00412
	-1588	|0>->|142^1>->	0.2872	0.00217
	-1512	|0>->|141^1>->	1.256	0.00933
	-1509	|0>->|139^1>->	0.5961	0.00442
	-1486	|0>->|137^1>->	0.4514	0.00333
	-1486	|0>->|136^1>->	0.405	0.00299
	-1344	|0>->|128^1>->	0.4746	0.00339
	-1333	|0>->|126^1>->	0.3173	0.00226
	-1332	|0>->|125^1>->	0.3655	0.00260
	-1331	|0>->|124^1>->	0.439	0.00313
	-1185	|0>->|113^1>->	0.4777	0.00329
	-1059	|0>->|96^1>->	0.4346	0.00291
	-1048	|0>->|95^1>->	1.11	0.00742
	-1042	|0>->|92^1>->	0.3852	0.00257
	-1041	|0>->|91^1>->	0.3478	0.00232
	-1030	|0>->|90^1>->	0.6846	0.00455
	-776	|0>->|65^1>->	0.8078	0.00507
	-687	|0>->|54^1>->	0.6257	0.00385
	-680	|0>->|53^1>->	0.4281	0.00263
	-309	|0>->|27^1>->	0.5928	0.00336
	-277	|0>->|22^1>->	0.7306	0.00411
	-263	|0>->|21^1>->	0.9719	0.00545
	-231	|0>->|19^1>->	0.3892	0.00217
	-125	|0>->|12^1>->	0.4897	0.00267
	-46	|0>->|6^1>->	0.4695	0.00252
	-40	|0>->|5^1>->	1.98	0.01059
	-39	|0>->|4^1>->	1.815	0.00971
	-29	|0>->|3^1>->	1.346	0.00718
	0	|0>->|0>->	13.81	0.07321
Ir(ppy)$_2$(pic) (IrPic)	-1654	|0> -> |134^1> ->	0.4304	0.003364
	-1631	|0> -> |132^1> ->	0.4101	0.003188
	-1628	|0> -> |131^1> ->	0.3525	0.002738
	-1593	|0> -> |126^1> ->	1.193	0.009191
	-1518	|0> -> |125^1> ->	0.9161	0.006935
	-1515	|0> -> |124^1> ->	0.7846	0.005937
	-1490	|0> -> |121^1> ->	0.4273	0.003214

	-1347	|0> -> |113^1> ->	0.3457	0.002516
	-1339	|0> -> |112^1> ->	0.7636	0.005546
	-1186	|0> -> |100^1> ->	0.5479	0.003842
	-1062	|0> -> |86^1> ->	0.8052	0.005488
	-1053	|0> -> |85^1> ->	0.6411	0.004361
	-1049	|0> -> |83^1> ->	0.3412	0.002319
	-779	|0> -> |60^1> ->	0.3207	0.002051
	-777	|0> -> |59^1> ->	0.4974	0.003180
	-691	|0> -> |49^1> ->	0.7451	0.004672
	-310	|0> -> |25^1> ->	1.329	0.007662
	-295	|0> -> |24^1> ->	0.5675	0.003261
	-259	|0> -> |20^1> ->	1.061	0.006052
	-223	|0> -> |19^1> ->	0.7834	0.004432
	-83	|0> -> |7^1> ->	1.468	0.008057
	-42	|0> -> |5^1> ->	1.95	0.010610
	-38	|0> -> |4^1> ->	0.6205	0.003373
	-34	|0> -> |3^1> ->	0.8908	0.004838
	-33	|0> -> |2^1> ->	0.3969	0.002155
	0	|0> -> |0> ->	11.8	0.063610
Ir(ppy)$_2$(acac)	-1632	|0>->|134^1>->	0.3193	0.00266
	-1627	|0>->|133^1>->	0.2937	0.00244
	-1592	|0>->|129^1>->	0.5346	0.00441
	-1592	|0>->|128^1>->	0.4795	0.00395
	-1544	|0>->|126^1;1^1>->	0.257	0.00210
	-1543	|0>->|125^1;1^1>->	0.2591	0.00211
	-1516	|0>->|126^1>->	0.7279	0.00589
	-1515	|0>->|125^1>->	0.727	0.00589
	-1492	|0>->|123^1>->	0.2953	0.00238
	-1338	|0>->|109^1>->	0.425	0.00330
	-1338	|0>->|108^1>->	0.3925	0.00305
	-1185	|0>->|99^1>->	0.2999	0.00225
	-1184	|0>->|98^1>->	0.3087	0.00231
	-1061	|0>->|87^1>->	0.5676	0.00413
	-1052	|0>->|85^1>->	0.7147	0.00519
	-1049	|0>->|83^1>->	0.3949	0.00287
	-777	|0>->|59^1>->	0.4039	0.00276
	-691	|0>->|52^1>->	0.6384	0.00427
	-307	|0>->|27^1>->	0.8621	0.00529
	-289	|0>->|26^1>->	0.3832	0.00234
	-288	|0>->|23^1;1^1>->	0.447	0.00273
	-260	|0>->|23^1>->	1.366	0.00830
	-107	|0>->|8^1;1^1>->	0.475	0.00279
	-79	|0>->|8^1>->	1.341	0.00783
	-76	|0>->|5^1;1^1>->	0.4746	0.00277

	-63	|0>->|3^1;1^1>->	0.5228	0.00304
	-56	|0>->|1^2>->	0.7668	0.00445
	-48	|0>->|5^1>->	1.251	0.00725
	-35	|0>->|3^1>->	1.475	0.00853
	-28	|0>->|1^1>->	3.837	0.02215
	0	|0>->|0>->	10.76	0.06171

Table S4. Information on the dipole transitions in the vibrational spectra of the complexes calculated by the VH method, a dipole strength of 0.002 was used as a cut-off for the reported transitions.

Complex	Energy / cm^{-1}	Transition	Intensity	Dipolar Strength
IrPic	-1660	|0> -> |135^1> ->	0.6501	0.003845
	-1508	|0> -> |124^1> ->	0.3853	0.002205
	-1507	|0> -> |123^1> ->	0.4104	0.002347
	-1071	|0> -> |84^1;3^1> ->	0.4279	0.002228
	-1037	|0> -> |84^1> ->	0.8824	0.004562
	-1032	|0> -> |83^1> ->	0.7486	0.003867
	-797	|0> -> |57^1;3^1> ->	0.451	0.002217
	-763	|0> -> |57^1> ->	0.9561	0.004666
	-711	|0> -> |48^1;3^1> ->	0.6512	0.003144
	-677	|0> -> |48^1> ->	1.341	0.006427
	-311	|0> -> |25^1> ->	0.4567	0.002030
	-260	|0> -> |20^1> ->	0.846	0.003721
	-74	|0> -> |4^1;3^1> ->	0.8346	0.003535
	-68	|0> -> |3^2> ->	0.7522	0.003183
	-60	|0> -> |3^1;1^1> ->	0.5844	0.002468
	-39	|0> -> |4^1> ->	1.627	0.006845
	-34	|0> -> |3^1> ->	3.05	0.012820
	-25	|0> -> |1^1> ->	1.482	0.006216
	0	|0> -> |0> ->	6.24	0.026040
C3	-1049	|0> -> |122^1;1^2> ->	0.5572	0.002923
	-1040	|0> -> |122^1;1^1> ->	0.6421	0.003363
	-720	|0> -> |80^1;1^2> ->	0.8301	0.004064
	-711	|0> -> |80^1;1^1> ->	0.9584	0.004682
	-702	|0> -> |80^1> ->	0.467	0.002277
	-75	|0> -> |10^1;1^1> ->	0.53	0.002272
	-48	|0> -> |5^1;1^2> ->	0.5667	0.002416
	-39	|0> -> |5^1;1^1> ->	0.583	0.002481
	-28	|0> -> |1^3> ->	1.286	0.005457
	-18	|0> -> |1^2> ->	2.761	0.011700
	-9	|0> -> |1^1> ->	3.177	0.013440
	0	|0> -> |0> ->	1.544	0.006519
C4	-61	|0> -> |3^4> ->	0.5022	0.002324

	-46	|0> -> |3^3> ->	0.7343	0.003387
	-31	|0> -> |3^2> ->	1.015	0.004667
	-24	|0> -> |3^1;1^1> ->	0.6216	0.002855
	-22	|0> -> |2^1;1^1> ->	0.4845	0.002224
	-15	|0> -> |3^1> ->	1.178	0.005400
	-12	|0> -> |2^1> ->	0.452	0.002070
	-9	|0> -> |1^1> ->	1.103	0.005050
	0	|0> -> |0> ->	1.344	0.006140
N4	-1651	|0> -> |191^1> ->	0.5296	0.003263
	-1509	|0> -> |180^1> ->	0.5347	0.003193
	-1352	|0> -> |158^1> ->	0.367	0.002118
	-1069	|0> -> |122^1;6^1> ->	0.4521	0.002453
	-1036	|0> -> |122^1> ->	0.8215	0.004427
	-812	|0> -> |95^1> ->	0.6271	0.003222
	-679	|0> -> |72^1> ->	0.6082	0.003038
	-65	|0> -> |6^2> ->	0.6062	0.002667
	-46	|0> -> |6^1;1^1> ->	0.662	0.002901
	-46	|0> -> |8^1> ->	0.4607	0.002019
	-33	|0> -> |6^1> ->	2.358	0.010310
	-30	|0> -> |5^1> ->	0.6016	0.002627
	-17	|0> -> |2^1> ->	0.4887	0.002129
	-14	|0> -> |1^1> ->	1.596	0.006949
	0	|0> -> |0> ->	4.267	0.018530
N5	-1652	|0> -> |191^1> ->	0.8155	0.005056
	-1450	|0> -> |162^1> ->	0.5668	0.003361
	-1417	|0> -> |161^1> ->	0.3771	0.002220
	-1135	|0> -> |132^1> ->	0.3933	0.002177
	-1118	|0> -> |131^1> ->	0.3935	0.002171
	-1038	|0> -> |124^1> ->	0.5632	0.003054
	-831	|0> -> |93^1;8^1> ->	0.3914	0.002030
	-785	|0> -> |93^1> ->	1.378	0.007081
	-687	|0> -> |72^1> ->	0.7155	0.003600
	-646	|0> -> |69^1> ->	0.5063	0.002526
	-328	|0> -> |47^1> ->	0.4357	0.002034
	-258	|0> -> |40^1> ->	0.5342	0.002458
	-46	|0> -> |8^1> ->	1.783	0.007856
	-38	|0> -> |7^1> ->	1.002	0.004407
	-33	|0> -> |6^1> ->	1.381	0.006070
	-26	|0> -> |5^1> ->	1.045	0.004585
	-21	|0> -> |3^1> ->	0.9852	0.004318
	0	|0> -> |0> ->	6.197	0.027050
C3N4	-1522	|0> -> |237^1;2^1> ->	0.3311	0.002023
	-1355	|0> -> |202^1;2^1> ->	0.3614	0.002129
	-1051	|0> -> |161^1;2^2> ->	0.4157	0.002292

	-1042	|0> -> |161^1;2^1> ->	0.6476	0.003564
	-1032	|0> -> |161^1> ->	0.398	0.002186
	-847	|0> -> |132^1;2^1> ->	0.4101	0.002164
	-723	|0> -> |111^1;2^2> ->	0.659	0.003387
	-714	|0> -> |111^1;2^1> ->	1.028	0.005272
	-705	|0> -> |111^1> ->	0.6321	0.003237
	-28	|0> -> |2^3> ->	0.7161	0.003185
	-19	|0> -> |2^2> ->	2.348	0.010420
	-18	|0> -> |2^1;1^1> ->	0.4697	0.002085
	-9	|0> -> |2^1> ->	3.648	0.016170
	0	|0> -> |0> ->	2.237	0.009895
C3N5	-1651	|0> -> |247^1> ->	0.4324	0.002720
	-1631	|0> -> |244^1> ->	0.3553	0.002224
	-1450	|0> -> |207^1> ->	0.3665	0.002205
	-1141	|0> -> |172^1> ->	0.4582	0.002576
	-1038	|0> -> |161^1;2^1> ->	0.3955	0.002175
	-1029	|0> -> |161^1> ->	0.6153	0.003377
	-825	|0> -> |129^1;2^1> ->	0.4289	0.002253
	-816	|0> -> |129^1> ->	0.6709	0.003518
	-741	|0> -> |114^1> ->	0.4528	0.002337
	-19	|0> -> |2^2> ->	0.6849	0.003041
	-18	|0> -> |2^1;1^1> ->	0.8111	0.003601
	-9	|0> -> |2^1> ->	2.595	0.011500
	-9	|0> -> |1^1> ->	1.522	0.006746
	0	|0> -> |0> ->	4.03	0.017830
C4N4	-1651	|0> -> |247^1> ->	0.2979	0.002138
	-1636	|0> -> |244^1> ->	0.2811	0.002011
	-1468	|0> -> |232^1> ->	0.2989	0.002057
	-991	|0> -> |157^1> ->	0.3912	0.002419
	-822	|0> -> |129^1> ->	0.5598	0.003334
	-707	|0> -> |111^1> ->	0.9409	0.005465
	-39	|0> -> |10^1> ->	1.024	0.005157
	-26	|0> -> |7^1> ->	0.9292	0.004664
	-12	|0> -> |1^1> ->	0.7627	0.003817
	0	|0> -> |0> ->	4.464	0.022280
C4N5	-1652	|0> -> |244^1;1^1> ->	0.283	0.002014
	-1650	|0> -> |247^1> ->	0.4583	0.003261
	-1637	|0> -> |244^1> ->	0.4684	0.003323
	-1445	|0> -> |207^1;1^1> ->	0.5139	0.003489
	-1430	|0> -> |207^1> ->	0.8444	0.005713
	-1155	|0> -> |172^1;1^1> ->	0.4596	0.002923
	-1140	|0> -> |172^1> ->	0.7535	0.004776
	-1139	|0> -> |171^1> ->	0.3328	0.002109
	-819	|0> -> |129^1;1^1> ->	0.4303	0.002540

	-804	|0> -> |129^1> ->	0.7112	0.004185
	-321	|0> -> |67^1> ->	0.5871	0.003113
	-244	|0> -> |58^1> ->	0.4828	0.002517
	-147	|0> -> |26^1> ->	0.5895	0.003012
	-36	|0> -> |9^1> ->	0.5417	0.002703
	-30	|0> -> |1^2> ->	0.8778	0.004375
	-15	|0> -> |1^1> ->	3.17	0.015750
	0	|0> -> |0> ->	5.183	0.025670

Table S5. Selected vibrational modes for the ground state complexes in the vibrational calculations by the VH method, a vibrational intensity of 200 KM/mol is used as a cut-off for the reported vibrations.

Complex	Mode	Frequency / cm^{-1}	IR intensity / $KMmol^{-1}$
IrPic	71	935.49	200.2499
	79	1008.26	314.4454
	94	1127.48	322.5319
	103	1205.28	331.7055
	114	1374.17	382.188
	116	1418.56	251.7772
	117	1440.76	437.4632
	126	1514.9	209.3839
	127	1529.33	262.0755
	128	1561.81	645.1789
	129	1562.68	255.1247
	134	1642.25	530.3205
	136	1667.7	1168.156
C3	104	861.66	224.6866
	107	865.75	478.8404
	108	874.63	557.5119
	113	958	303.7302
	119	1013.17	306.017
	159	1374.45	384.3191
	160	1413.18	281.2341
	163	1442.99	475.1171
	182	1514.08	211.4045
	184	1541.13	637.5692
	190	1641.62	583.4166
	192	1666.38	1149.637
C4	93	773.42	200.1132
	106	865.9	646.2393
	107	872.75	381.3585
	130	1104.83	795.8017
	141	1201.94	356.3131
	158	1367.6	222.0828

	159	1374.28	410.8153
	162	1427.2	410.624
	183	1530.24	378.2906
	184	1548.58	702.2495
	190	1641.92	593.8492
	192	1665.35	1003.753
N4	106	874.83	677.6044
	159	1374	383.375
	168	1458.23	218.5795
	188	1640.59	237.7836
	189	1643.62	279.2531
	191	1650.8	316.7414
	192	1669.9	973.256
N5	103	861.51	668.7448
	104	862.3	489.7969
	107	873.1	398.3428
	111	948.33	291.0672
	134	1150	250.4396
	141	1197.7	579.4761
	158	1375.01	379.1891
	162	1427.25	210.1452
	180	1492.83	258.1653
	183	1529.96	447.1626
	185	1564.82	996.7995
	191	1641.96	516.5704
	192	1667.41	1115.184
C3N4	131	816.05	370.5343
	138	856.84	231.3734
	141	861.79	241.7848
	142	862.04	315.3436
	143	862.27	740.1618
	145	867.03	230.3165
	146	870.23	319.0033
	148	875.59	703.4691
	149	890.49	432.2064
	155	956.76	288.7763
	160	1018.17	530.8604
	168	1091.3	414.4068
	173	1152	668.4637
	204	1375.37	458.8432
	205	1416.42	390.9619
	208	1446.25	463.9173
	240	1530.22	855.5427
	246	1641.71	594.0887

	248	1665.06	946.3764
C3N5	139	858.03	216.9392
	140	859.17	1138.051
	141	861.23	244.3628
	142	861.42	202.9777
	146	867.68	467.6328
	149	877.84	677.3524
	160	1019.17	300.6022
	174	1168.07	267.7923
	177	1186.29	227.5513
	203	1374.14	439.2699
	206	1416.77	223.9956
	236	1484.49	349.9674
	239	1523.55	209.16
	240	1540.81	718.2158
	246	1639.65	222.0842
	247	1641.42	534.5761
	248	1664.62	908.6639
C4N4	130	800.56	252.7033
	144	866.4	583.3293
	146	871.19	1073.887
	147	873.46	273.5808
	148	879.19	490.072
	154	948.78	238.4885
	167	1079.05	1282.784
	179	1196.26	398.4768
	203	1372.7	531.5166
	204	1375.54	229.3786
	207	1429.47	402.4787
	239	1515.78	412.7118
	240	1525.69	883.4048
	242	1564.11	201.317
	246	1641.56	662.9512
	248	1664.29	1010.157
C4N5	142	862.25	410.3133
	143	863.6	319.3598
	144	866.15	259.9975
	145	866.9	734.345
	147	870.16	885.2174
	153	964.47	270.4406
	168	1106.55	715.0987
	179	1203.03	625.7837
	198	1323.08	240.4224
	204	1376.07	260.0901

	208	1441.33	230.6644
	239	1529.11	840.812
	240	1549.99	681.6393
	246	1638.8	250.1828
	247	1641.68	593.8704
	248	1664.9	959.3727

Table S6. Information on the dipole transitions in the vibrational spectra of the complexes with methyl groups replaced by hydrogen atoms calculated by the AH method, a dipole strength of 0.002 was used as a cut-off for the reported transitions.

Complex	Energy / cm^{-1}	Transition	Intensity	Dipole Strength
IrPic	-1654	|0> -> |134^1> ->	0.4304	0.003364
	-1631	|0> -> |132^1> ->	0.4101	0.003188
	-1628	|0> -> |131^1> ->	0.3525	0.002738
	-1593	|0> -> |126^1> ->	1.193	0.009191
	-1518	|0> -> |125^1> ->	0.9161	0.006935
	-1515	|0> -> |124^1> ->	0.7846	0.005937
	-1490	|0> -> |121^1> ->	0.4273	0.003214
	-1347	|0> -> |113^1> ->	0.3457	0.002516
	-1339	|0> -> |112^1> ->	0.7636	0.005546
	-1186	|0> -> |100^1> ->	0.5479	0.003842
	-1062	|0> -> |86^1> ->	0.8052	0.005488
	-1053	|0> -> |85^1> ->	0.6411	0.004361
	-1049	|0> -> |83^1> ->	0.3412	0.002319
	-779	|0> -> |60^1> ->	0.3207	0.002051
	-777	|0> -> |59^1> ->	0.4974	0.003180
	-691	|0> -> |49^1> ->	0.7451	0.004672
	-310	|0> -> |25^1> ->	1.329	0.007662
	-295	|0> -> |24^1> ->	0.5675	0.003261
	-259	|0> -> |20^1> ->	1.061	0.006052
	-223	|0> -> |19^1> ->	0.7834	0.004432
	-83	|0> -> |7^1> ->	1.468	0.008057
	-42	|0> -> |5^1> ->	1.95	0.010610
	-38	|0> -> |4^1> ->	0.6205	0.003373
	-34	|0> -> |3^1> ->	0.8908	0.004838
	-33	|0> -> |2^1> ->	0.3969	0.002155
	0	|0> -> |0> ->	11.8	0.063610
C3	-1560	|0> -> |140^1> ->	1.777	0.013310
	-1346	|0> -> |127^1> ->	1.003	0.007151
	-1044	|0> -> |96^1> ->	0.8789	0.005848
	-722	|0> -> |63^1> ->	1.418	0.008775
	-309	|0> -> |31^1> ->	0.9349	0.005286
	-92	|0> -> |12^1> ->	1.132	0.006106

	-39	|0> -> |7^1> ->	1.573	0.008389
	-29	|0> -> |3^1> ->	0.9522	0.005069
	0	|0> -> |0> ->	12.05	0.063730
C4	0	|0> -> |0> ->	1.427	0.008632
N4	-1565	|0> -> |141^1> ->	1.103	0.009521
	-1336	|0> -> |126^1> ->	0.7785	0.006365
	-79	|0> -> |9^1> ->	1.052	0.006442
	-34	|0> -> |5^1> ->	3.208	0.019460
	0	|0> -> |0> ->	6.218	0.037430
N5	-321	|0> -> |33^1> ->	1.539	0.009755
	-54	|0> -> |9^1> ->	2.075	0.012400
	-31	|0> -> |3^1> ->	2.989	0.017760
	0	|0> -> |0> ->	8.082	0.047710
C3N4	-1558	|0> -> |155^1> ->	0.844	0.007079
	-1558	|0> -> |154^1> ->	0.6588	0.005525
	-1340	|0> -> |142^1> ->	0.7148	0.005693
	-79	|0> -> |12^1> ->	1.057	0.006313
	-21	|0> -> |3^1> ->	1.08	0.006373
	-19	|0> -> |2^1> ->	1.869	0.011020
	0	|0> -> |0> ->	6.658	0.039090
C3N5	-1559	|0> -> |155^1> ->	1.375	0.011210
	-1520	|0> -> |152^1> ->	0.8472	0.006845
	-1483	|0> -> |150^1> ->	0.8959	0.007175
	-92	|0> -> |16^1> ->	1.012	0.005907
	-50	|0> -> |11^1> ->	2.953	0.017070
	0	|0> -> |0> ->	12.03	0.068790
C4N4	0	|0> -> |0> ->	4.67E-02	0.000312
C4N5	-32	|0> -> |7^1> ->	1.311	0.008621
	0	|0> -> |0> ->	2.829	0.018460

Table S7. Selected vibrational modes for the ground state complexes with methyl groups replaced by hydrogen atoms calculated by the AH method, a vibrational intensity of 200 KM/mol is used as a cut-off for the reported vibrations.

Complex	**Mode**	**Frequency / cm^{-1}**	**IR intensity / $KMmol^{-1}$**
IrPic	115	1374.78	380.3607
	124	1515.35	301.4648
	132	1631.24	224.7082
	133	1641.43	402.7128
	136	1665.91	882.3079
C3	79	919.58	894.076
	81	922.3	728.8396
	129	1374.24	384.5786
	138	1514.69	253.4634

	145	1621.59	220.7478
	146	1626.2	294.6527
	147	1642.13	420.5083
	150	1666.7	895.6113
	151	2209.25	262.6201
	152	2210.04	256.4958
	153	2219.26	322.1661
	154	2220.04	302.711
	155	2233.18	241.3029
	156	2234.26	212.4437
C4	79	917.96	1161.7461
	80	918.78	364.551
	129	1374.23	383.1111
	138	1509.81	289.869
	147	1641.73	472.2918
	150	1666.53	940.4743
	151	2213.06	236.2249
	152	2213.36	265.9622
	153	2221.34	324.1569
	154	2224.5	290.5834
	155	2236.99	216.3094
	156	2237.66	212.686
N4	79	911.45	1485.028
	129	1375.31	385.9434
	146	1631.24	227.7983
	147	1642.01	407.558
	150	1666.69	905.2827
	151	2240.85	205.8418
	152	2240.97	206.7587
	153	2243.6	411.2721
N5	79	914.26	1065.1422
	80	915.57	461.4642
	129	1374.84	375.0039
	138	1521.1	258.7699
	146	1630.67	290.4187
	147	1640.25	310.2636
	149	1641.81	354.759
	150	1666.44	874.1672
	151	2235.27	217.6027
	152	2236.12	215.4129
	153	2240.03	319.802
	154	2240.72	213.753
C3N4	89	910.72	946.5077
	90	912.48	434.9295

	91	920.19	1065.6968
	94	924.21	665.569
	143	1375.08	388.8649
	159	1621.43	238.142
	160	1626.07	293.8925
	161	1642.33	406.0744
	164	1667.37	934.0178
	165	2209.74	259.1041
	166	2210.58	254.5405
	167	2219.61	327.0957
	168	2220.38	301.1945
	169	2233.74	237.6718
	170	2234.68	208.8511
	171	2241.52	205.0479
	172	2242.12	204.5007
	173	2244.23	322.5924
C3N5	67	676.41	212.9857
	69	677.6	204.1776
	89	913.56	1039.5225
	90	914.94	702.7834
	91	919.84	891.4996
	92	922.73	519.4236
	143	1373.77	376.6482
	159	1621.33	271.1875
	160	1625.82	346.5887
	161	1640.36	326.1027
	163	1642.16	349.9718
	164	1667.2	905.2433
	165	2210.12	258.1127
	166	2211.26	255.1067
	167	2219.92	329.0375
	168	2221.07	310.2469
	169	2234.08	234.7018
	170	2235.18	208.9493
	171	2236.34	216.2802
	172	2237.1	213.9512
	173	2241.17	354.378
C4N4	68	690.65	216.7252
	89	911.32	1550.9041
	91	917.93	730.9214
	92	919.11	338.617
	93	919.43	334.8885
	143	1374.58	384.3943
	161	1641.77	469.2848

	164	1666.79	960.5006
	165	2211.95	235.2165
	166	2212.66	276.6705
	167	2224.53	317.9918
	168	2226.8	278.707
	169	2236.25	225.0185
	170	2236.82	221.149
	171	2241.76	203.2658
	172	2242.35	202.9785
	173	2244.46	310.8429
C4N5	89	911.82	1529.9419
	90	912.44	1478.4276
	143	1374.56	379.7296
	152	1514.85	212.7886
	161	1639.86	293.2622
	163	1641.99	387.4216
	164	1667.12	941.7029
	165	2213.87	257.0214
	166	2214.9	244.8895
	167	2222.57	308.3432
	168	2223.57	325.6336
	169	2236.11	226.5392
	170	2237.37	209.8032
	171	2237.62	219.9327
	172	2238.6	230.4077
	173	2240.99	280.7904
	174	2241.93	211.9456

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