

Supporting Information

N-Heterocyclic Carbenes via Abstraction of Ammonia: 'Normal' Carbenes with 'Abnormal' Character

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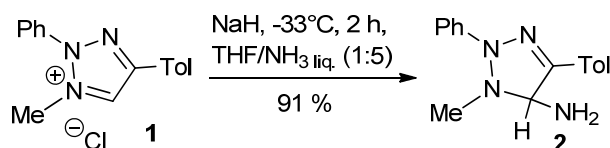
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1. General Information

All manipulations were carried out in an Argon atmosphere by standard Schlenk techniques or in a glovebox. Glassware was dried prior to use by heating it in vacuo. THF was dried with sodium via distillation, all other solvents were dried with a *Grubbs* apparatus and degassed via repeated freeze-pump-thaw cycles. All other commercially available compounds were used without further purification. Compounds *p*-toluoylchloride phenylhydrazine, methylisocyanide und 1-methyl-2-phenyl-4-*p*-tolyl-1,2,3-triazolium-chloride **1** were prepared by following procedures described in literature.^[1] ¹H- and ¹³C-NMR-spectra were recorded on a 400 MHz Bruker Avance III or a 400 MHz Bruker Avance DPX spectrometer at a Temperature of 298 K, if not indicated otherwise. The spectra were referenced in parts per million (ppm) with an internal standard using the residual solvent shifts. Abbreviations for signal multiplicities are: singulett (s), dublett (d), triplett (t), quartet (q), multiplet (m), broad (br). Column chromatography was performed over silica gel (40-63 μm). IR spectra were recorded on a Varian 670 FT-IR Spectrometer. ESI-HRMS analysis was performed on a Thermo Scientific LTQ Orbitrap XL by Thermo Fisher Scientific. Crystallographic data collection were carried out on an area detecting system (APEX II, κ-CCD) at the window of a rotating anode (Bruker AXS, FR591) and graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Elemental Analyses were conducted by the micro-analytical laboratory of the TUM.

2. Synthetic Procedures

2.1. Preparation of 1-methyl-2-phenyl-4-*p*-tolyl-1H-1,2,3-triazol-5-amine (**2**).

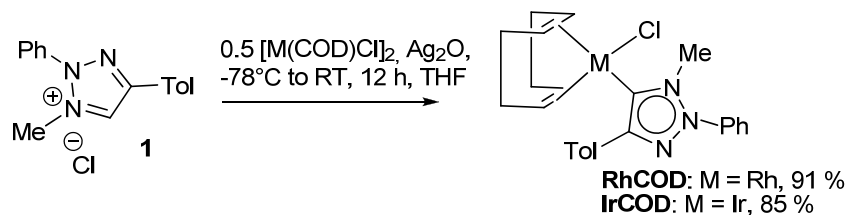


Following a procedure reported by Herrmann and coworkers^[2] this reaction was performed in an apparatus specifically designed for this reaction type: A graduated three-necked Schlenk flask, equipped with a pressure valve, an addition tube, and a magnetic stirrer and connected via a glass tube to another Schlenk flask equipped with an ammonia inlet and a pressure valve, was positioned in a cooling bath with dry ice. The three-necked flask was charged with sodium (5.0 g) before ammonia was condensed at -78 °C. By removing the dry ice bath from the three-necked flask and placing it underneath the second Schlenk flask ammonia was allowed to condense into the second one. 100 mL of dry ammonia were then added to a suspension of 1-methyl-2-phenyl-4-*p*-tolyl-1,2,3-triazolium-chloride **1** (2.00 g, 7.00 mmol) in 20 mL THF. The solution was stirred at reflux of liquid ammonia at -33 °C until **1** was completely dissolved. Via the addition tube NaH (0.185 g, 7.7 mmol) was added under vigorous gas evolution. After stirring under reflux for two hours, liquid ammonia was evaporated and the remaining THF solution was filtered through a cannula. At RT, THF was quickly removed, the remaining oil redissolved in C₆H₆ and lyophilized to yield **2** (1.69 g, 91 %) as a yellow solid, that was stored at -30 °C under Argon.

¹H-NMR (400 MHz, C₆D₆) δ = 8.08 (d, *J* = 8.2 Hz, 2H, *H*_{ar}), 7.61 (dd, *J* = 8.7, 1.1 Hz, 2H, *H*_{ar}), 7.32 – 7.22 (m, 2H, *H*_{ar}), 7.05 (dd, *J* = 8.5, 0.5 Hz, 2H, *H*_{ar}) 6.90 (t, *J* = 7.3 Hz, 1H, *H*_{ar}), 4.41 (t, *J* = 8.7 Hz, 1H, *H*CN), 2.23 (s, 3H, NCH₃), 2.10 (s, 3H, CCH₃), 1.00 (d, *J* = 8.7 Hz, 2H, CNH₂). ¹³C-NMR (101 MHz, THF-d⁸) δ = 147.7, 147.4, 139.3, 129.7, 129.5, 129.4, 128.0, 121.0, 115.1, 82.5, 43.1 (NCH₃), 21.6 (CCH₃). **MS** (ESI) *m/z* (%): 267.2 [M+H]⁺ (15), 250.2 [M-NH₂]⁺ (100). **HR-MS** (ESI) *m/z* calcd. for C₁₆H₁₉N₄ [M+H]⁺ 267.16042, found 267.16009 (5 %); for C₁₆H₁₆N₃ [M+H-NH₃]⁺ 250.13387, found 250.13357 (100 %).

2.2. Synthetic procedure for the preparation of 3 and 4 using silver oxide:

2.2.1. Preparation of (1-Methyl-2-phenyl-4-tolyl-1,2,3-triazol-5-ylidene)(Cyclooctadienyl) Rh(I)Cl (RhCOD) and (1-Methyl-2-phenyl-4-tolyl-1,2,3-triazol-5-ylidene)(Cyclooctadienyl)Ir(I)Cl (IrCOD)



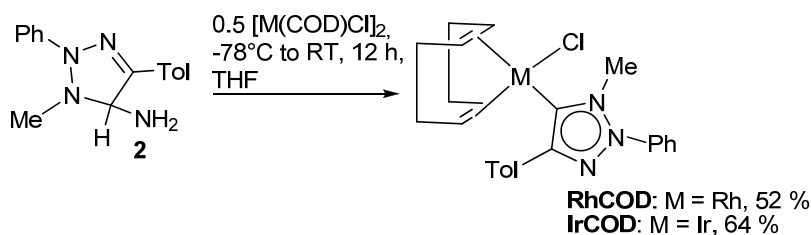
Scheme S2. Synthesis of **RhCOD** and **IrCOD** using **1**.

Silver oxide (68.0 mg, 0.29 mmol), the metal precursor [M(COD)Cl]₂ (0.14 mmol) (M = Rh or Ir) and **1** (85.0 mg, 0.29 mmol) were suspended in 5 mL of THF at -78 °C. The suspension was stirred for 12 h and allowed to slowly warm up to room temperature during that time. The solvent was removed under vacuo and the residue was washed with Et₂O (3 x 3 mL). The raw product was purified by column chromatography (SiO₂, CH₂Cl₂). After removing the solvent **RhCOD** (130 mg, 91 %) or **IrCOD** (144 mg, 85 %) were obtained as bright yellow solids.

For characterization of these compounds see 2.3.

2.3. Synthetic procedure for the preparation of 3 and 4 using 2:

2.3.1. Preparation of (1-Methyl-2-phenyl-4-tolyl-1,2,3-triazol-5-ylidene)(Cyclooctadienyl) Rh(I)Cl (RhCOD) and (1-Methyl-2-phenyl-4-tolyl-1,2,3-triazol-5-ylidene)(Cyclooctadienyl)Ir(I)Cl (IrCOD)



Scheme S3. Synthesis of **RhCOD** and **IrCOD** using **2**.

In a glovebox $[M(\text{COD})\text{Cl}]_2$ (0.10 mmol) and **2** (53.2 mg, 0.20 mmol) were transferred into a Schlenk tube. At -78°C 7 mL DCM were added to the solids. The suspension was stirred for 12 h and allowed to slowly warm up to room temperature during that time. The solvent was removed under vacuo and the residue was washed with Et_2O (3 x 2 mL), extracted with 3 mL of DCM and filtered. Removal of the solvent in vacuo afforded **RhCOD** (51 mg, 52 %) or **IrCOD** (74.8 mg, 64 %).

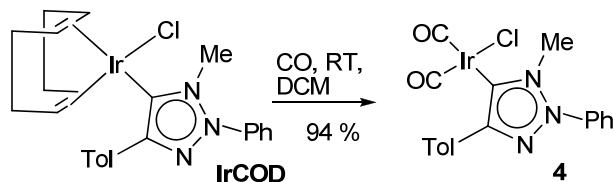
Analytical data for (**RhCOD**):

$^1\text{H-NMR}$ (400 MHz, CD_2Cl_2): δ = 8.81 (d, J = 6.4 Hz, 2 H, CH_{ar}), 7.61-7.56 (m, 3 H, CH_{ar}), 7.39-7.36 (m, 2 H, CH_{ar}), 7.33 (d, J = 6.4 Hz, 2 H, CH_{ar}), 5.17 (*pseudo*-dd, J = 6.3, 11.3 Hz, 1 H, COD), 4.96 (*pseudo*-dd, J = 6.2 Hz, $^2J_{\text{HH}}$ = 13.2 Hz, 1 H, COD), 4.54 (s, 3 H, NCH_3), 3.36-3.31 (m, 1 H, COD), 3.06-2.99 (m, 1 H, COD), 2.61-2.30 (m, 6 H, COD, CCH_3), 2.28-2.15 (m, 1 H, COD), 2.09-1.87 (m, 3 H, COD), 1.82-1.71 (m, 1 H, COD). **$^{13}\text{C-NMR}$** (101 MHz, CD_2Cl_2) δ 182.6 (d, J = 45.9 Hz, Rh- C_{trz}), 155.1 (C_{trz}), 139.3, 136.0, 131.4, 130.3, 129.3, 128.7, 128.3, 126.2 (all C_{ar}), 98.1 (d, J = 7.1 Hz, Rh-COD), 97.5 (d, J = 7.0 Hz, Rh-COD), 69.5 (d, J = 10.6 Hz, Rh-COD), 69.4 (d, J = 10.8 Hz, Rh-COD), 41.3 (NCH_3), 33.8, 32.2, 29.9, 29.0 (all COD), 21.5 (CCH_3). **MS** (FAB) m/z (%): 494.8 [M] (78), 459.8 [M-Cl] (40), 418.8 [M-Ph] (34), 250.0 [triazolium] (100). **EA:** Anal. calcd. for $\text{C}_{24}\text{H}_{27}\text{ClN}_3\text{Rh}$ (495.09): C, 58.13; H, 5.49; N, 8.47. Found: C, 58.13; H, 5.67; N, 8.18.

Analytical data for (**IrCOD**):

$^1\text{H-NMR}$ (400 MHz, CD_2Cl_2): δ = 8.69 (d, J = 8.1 Hz, 2H, CH_{ar}), 7.65 – 7.61 (m, 3H, CH_{ar}), 7.54 – 7.49 (m, 2H, CH_{ar}), 7.32 (d, J = 8.0 Hz, 2H, CH_{ar}), 4.73 (td, J = 7.6, 3.8 Hz, 1H, COD), 4.56 – 4.48 (m, 1H, COD), 4.36 (s, 3H, NCH_3), 2.97 (*pseudo*-dd, J = 6.4, 3.5 Hz, 1H, COD), 2.71 (td, J = 7.2, 3.1 Hz, 1H, COD), 2.43 (s, 3H, CCH_3), 2.40 – 2.30 (m, 1H, COD), 2.27 – 2.18 (m, 2H, COD), 2.13 – 2.01 (m, 1H, COD), 1.87-1.72 (m, 2H, COD), 1.70 – 1.61 (m, 1H, COD), 1.54-1.43 (m, 1H, COD). **$^{13}\text{C-NMR}$** (101 MHz, CD_2Cl_2): δ = 180.3 (Ir- C_{trz}), 155.4 (C_{trz}), 139.2, 135.9, 131.4, 130.4, 129.2, 128.6, 128.3, 126.2 (all C_{ar}), 84.05 (COD), 83.38 (COD), 53.28 (COD), 53.23 (COD), 41.08 (NCH_3), 34.19 (COD), 32.87 (COD), 30.24 (COD), 29.84 (COD), 21.48 (CCH_3). **EA:** Anal. calcd. for $\text{C}_{24}\text{H}_{27}\text{ClIrN}_3$ (585.15): C, 49.26; H, 4.65; N, 7.18. Found: C, 49.09; H, 4.99; N, 6.75.

2.4. Preparation of (1-Methyl-2-phenyl-4-tolyl-1,2,3-triazol-5-ylidene)Ir(I)Cl (**4**).

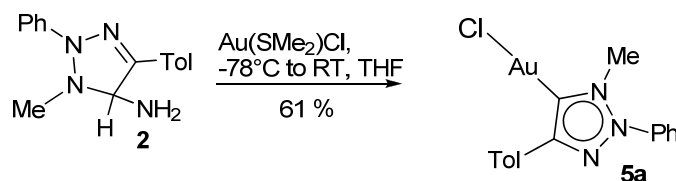


Scheme S4. Synthesis of **4**.

At room temperature CO was bubbled through a solution of **IrCOD** (0.237 g, 0.405 mmol) in 15 mL of dichloromethane for 20 min while stirring. During that time the color of the solution changed from bright to pale yellow. The solvent was removed by evaporation under vacuo and the remaining crude product was purified via column chromatography (SiO₂, CH₂Cl₂), yielding **4** (203 mg, 94 %) as a pale yellow solid.

¹H-NMR (400 MHz, CDCl₃): δ = 8.35 (d, J = 8.1 Hz, 2 H, CH_{ar}), 7.72 – 7.65 (m, 2 H, CH_{ar}), 7.62 – 7.54 (m, 3 H, CH_{ar}), 7.29 (d, J = 8.1 Hz, 2 H, CH_{ar}), 4.34 (s, 3 H, NCH₃), 2.41 (s, 3 H, CCH₃). **¹³C-NMR** (101 MHz, THF-d⁸): δ = 180.1, 167.0, 166.8, 154.3, 136.9, 133.5, 129.5, 127.8, 126.7, 126.3, 125.8, 124.6, 39.2 (NCH₃), 18.4 (CCH₃). **IR** (CH₂Cl₂): ν = 2058, 1975 (ν (CO)) cm⁻¹. **MS** (FAB) m/z (%): 533.7 [M] (58), 497.8 [M-Cl] (100), 469.8 [M-Cl-CO] (72), 440.8 [M-Cl-(CO)₂-H] (28). **EA**: Anal. calcd. for C₁₈H₁₅ClIrN₃O₂ (533.05): C, 40.56; H, 2.84; N, 7.88. Found: C, 40.73; H, 2.80; N, 7.72.

2.5. Preparation of (1-Methyl-2-phenyl-4-tolyl-1,2,3-triazol-5-ylidene)Au(I)Cl (**5a**).

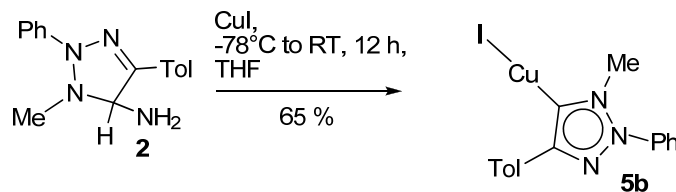


Scheme S5. Synthesis of **5a**.

At – 78 °C a solution of 120 mg **2** (0.451 mmol) in 0.5 mL THF was added to a solution of 125 mg Au(SMe₂)Cl (0.424 mmol) in 2 mL THF. After 10 min the solid CO₂ was removed from the cooling bath. When the temperature of the cooling bath reached 0 °C, the reaction solution was concentrated and 2 mL of diethyl ether were added to precipitate **5a** (125 mg, 259 mmol, 61 %) as a white solid.

¹H NMR (400 MHz, CD₂Cl₂): δ = 8.26 (d, J = 8.2 Hz, 2 H, CH_{ar}), 7.76 – 7.65 (m, 3 H, CH_{ar}), 7.64 – 7.55 (m, 2 H, CH_{ar}), 7.26 (d, J = 7.9 Hz, 2 H, CH_{ar}), 4.22 (s, 3 H, NCH₃), 2.38 (s, 3 H, CCH₃). **¹³C NMR** (101 MHz, CD₂Cl₂): δ = 163.4 (C_{trz}), 155.6, 140.4, 135.6, 132.6, 130.8, 129.9, 127.5, 127.4, 126.9 (all C_{ar}), 42.3 (NCH₃), 21.7 (CCH₃). **MS** (FAB) m/z (%): 445.8 [M-Cl]⁺ (20). **MS** (ESI) m/z (%): 446.3 [M-Cl]⁺ (15). **EA**: Anal. calcd. for C₁₆H₁₅AuClN₃ (481.73): C, 39.89; H, 3.14; N, 8.72; Cl, 7.36. Found: C, 40.34; H, 3.27; N, 8.63; Cl, 7.08.

2.6. Preparation of (1-Methyl-2-phenyl-4-tolyl-1,2,3-triazol-5-ylidene)Cu(I) (5b).

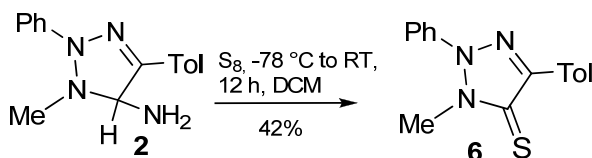


Scheme S6. Synthesis of **5b**.

At $-78\text{ }^{\circ}\text{C}$ a solution of 155 mg **2** (0.582 mmol) in 0.5 mL THF was added to a suspension of 100 mg CuI (0.525 mmol) in 2 mL THF. After stirring for 10 min the dry ice was removed from the cooling bath. As soon as the reaction solution reached $0\text{ }^{\circ}\text{C}$ it was evaporated to dryness. The residue was suspended in 2 mL of DCM and filtered. After concentration of the filtrate, diethyl ether was added to precipitate **5b** (150 mg, 341 μmol , 65 %) as off-white solid.

^1H NMR (400 MHz, CD_2Cl_2): δ = 8.19 (d, J = 8.0 Hz, 2 H, CH_{ar}), 7.67 (*pseudo*-d, J = 7.2 Hz, 3 H, CH_{ar}), 7.54 (*pseudo*-dd, J = 7.7, 1.5 Hz, 2 H, CH_{ar}), 7.27 (d, J = 7.8 Hz, 2 H, CH_{ar}), 4.26 (s, 3 H, NCH_3), 2.39 (s, 3 H, CCH_3). **^{13}C NMR** (101 MHz, CD_2Cl_2): δ = 172.17 (C_{trz}), 157.25, 139.87, 135.87, 132.10, 130.71, 129.93, 128.88, 127.52, 126.87 (all C_{ar}), 42.08 (NCH_3), 21.63 (CCH_3). **MS** (FAB) m/z (%): 311.9 [M-I] (4), 250.2 [triazolium] (100). **EA**: Anal. calcd. for $\text{C}_{16}\text{H}_{15}\text{CuIN}_3$ (439,76): C, 43.70; H, 3.44; N, 9.56. Found: C, 44.09; H, 3.44; N, 9.89.

2.8. Preparation of 1-methyl-2-phenyl-4-p-tolyl-1H-1,2,3-triazol-5-thione (**6**).

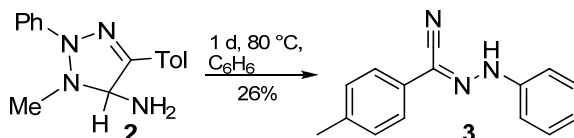


Scheme S8. Synthesis of **6**.

At $-78\text{ }^{\circ}\text{C}$ a solution of **2** (31 mg, 0.11 mmol) in 3 mL of DCM was added to an excess of S_8 (44 mg, 0.17 mmol). Under stirring the solution was allowed to warm up to room temperature overnight. The reaction mixture was directly given on a short pad of silica, washed with 50 mL of DCM and flashed with acetone. Removal of the solvent yielded **6** (13 mg, 42 %) as yellow solid.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 8.44 (d, J = 7.7 Hz, 2H), 7.58 (d, J = 6.0 Hz, 2H), 7.45 (d, J = 7.1 Hz, 1H), 7.32 – 7.21 (m, 2H), 3.91 (s, 2H), 2.40 (s, 2H). **$^{13}\text{C-NMR}$** (101 MHz, CDCl_3): δ = 163.6 ($\text{C}=\text{S}$), 148.4, 139.3, 136.4, 130.5, 130.1, 128.9, 127.3, 126.7, 125.4, 34.8 (NCH_3), 21.4 (CH_3). **HR-MS** (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{16}\text{N}_3\text{S}$ [$\text{M}+\text{H}$]⁺ 282.10594, found 282.10464 (40 %); for $\text{C}_{16}\text{H}_{16}\text{N}_3\text{NaS}$ [$\text{M}+\text{Na}$]⁺ 304.08789, found 304.08685 (100 %).

2.7. Thermal Decomposition Study with Isolation of 4-methyl-N'-phenylbenzohydrazonoyl cyanide (**3**).



Scheme S7. Synthesis of **3**.

At $-78\text{ }^\circ\text{C}$ **2** (150 mg, 0.56 mmol) was solved in 3 mL of benzene and warmed to room temperature. The solution was heated to $80\text{ }^\circ\text{C}$ for one day. Removal of the solvent in vacuo followed by column chromatography (SiO_2 , Et_2O) afforded **3** (highest Rf, 36 mg, 26 %) as yellow solid.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 8.74 (s, 1H), 7.72 (d, J = 7.8 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.27 (*pseudo*-d, J = 8.6 Hz, 4H), 7.08 (t, J = 7.2 Hz, 1H), 2.42 (s, 3H, CH_3). **$^{13}\text{C-NMR}$** (101 MHz, CDCl_3) δ = 142.1, 139.4, 129.6, 129.5, 129.4, 124.8, 122.9, 114.7, 114.2, 111.1, 21.3 (CH_3).

3. Crystallographic data

General: Crystallographic details are summarized in Table 1. X-ray diffraction measurements were performed on single crystals coated with Paratone oil and mounted on Kapton loops. Each crystal was frozen under a stream of dinitrogen while data were collected on an X-ray diffractometer equipped with a CCD detector (APEX II, κ -CCD), a rotating anode (Bruker AXS, FR591) with MoK $_{\alpha}$ radiation ($\lambda = 0.71073 \text{ \AA}$), and a graphite monochromator by using the SMART software package.^[3] A matrix scan using at least 20 centered reflections was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorentz and polarization effects, scan speed, and background using SAINT 4.15.^[4] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.^[5] Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using WinGX^[6] based on SHELXS-97^[7] oder Sir-92.^[8] Hydrogen atoms were either located (in case of **2**) and refined with isotropic replacement parameters or assigned to ideal positions (in case of **3**, **4** and **5a**) and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogens). All non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with SHELXL-97^[9] weighting scheme. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.^[10] All structures were checked for possible problems by using Platon.^[11] Images of the crystal structures were generated by Diamond 3.1^[12] and ORTEP.^[21] Crystallographic data (excluding structure factors) for the **2**, **3**, **4**, and **5a** have been deposited with the Cambridge Structural database at www.ccdc.cam.ac.uk/products/csd/^[13] and are available free of charge: CCDC-788089 (**2**), CCDC-797025 (**4**), CCDC-797026 (**3**), CCDC-849440 (**5a**). **Special:** for **2**: The absolute configuration could not be determined since atoms that cause strong anomalous scattering were absent. Therefore the Friedel pairs were merged for the final refinement; for **4**: Due to the small size of the crystal many weak reflections appear giving rise to poor R-values. To exclude these weak reflections, the data set was cut off at a resolution of 0.93 \AA , resulting in less data, but slightly better R-values.

Table S1. Crystallographic details

Compound name	2	4	3	5a
formula	C ₁₆ H ₁₈ N ₄	C ₁₈ H ₁₅ ClIrN ₃ O ₂	C ₁₅ H ₁₃ N ₃	C ₁₆ H ₁₅ AuClN ₃
CCDC number	788089	797025	797026	849440
M _r (g/mol)	266.34	532.98	235.28	481.73
Crystal description	yellow fragment	colorless fragment	yellow needle	yellow needle
Crystal dimensions (mm ³)	0.18x0.19x0.21	0.05x0.05x0.08	0.02x0.05x0.33	0.05x0.05x0.46
Temperature (K)	150(2)	123(2)	123(2)	173(2)
crystal system, space group	orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁	monoclinic, <i>P</i> 2 ₁ / <i>c</i>	monoclinic, <i>P</i> 2 ₁ / <i>c</i>	triclinic, <i>P</i> $\bar{1}$
<i>a</i> (Å)	7.441(2)	7.527(1)	13.034(4)	5.7486(4)
<i>b</i> (Å)	10.655(2)	22.640(3)	5.507(2)	11.6907(8)
<i>c</i> (Å)	17.446(4)	11.656(2)	18.643(6)	12.9093(9)
α (°)	90	90	90	67.988(3)
β (°)	90	114.72(1)	106.30(2)	87.564(3)
γ (°)	90	90	90	78.131(3)
<i>V</i> (Å ³)	1383.2(5)	1804.2(4)	1284.4(7)	786.56(9)
<i>Z</i>	4	4	4	2
<i>d</i> _{calc} (g/cm ³)	1.279	1.962	1.217	2.034
<i>F</i> ₀₀₀	568	1016	496	456
μ (mm ⁻¹)	0.079	7.564	0.075	9.517
θ ranges (°)	2.24-25.42	1.80-25.44	1.63-22.35	1.70-25.33
Collected reflections	20485	18809	12071	12020
Unique reflections [all data]	1484	3247	1538	2833
<i>R</i> _{int} / <i>R</i> _{σ}	0.0573/0.0241	0.0792/0.0667	0.1064/0.1068	0.0340/0.0293
Unique reflections [<i>I</i> ₀ >2 σ (<i>I</i> ₀)]	1425	2545	973	2571
Data/Restraints/Parameter	1484/0/253	3247/0/228	1538/0/164	2833/0/192
GoF (on <i>F</i> ²)	1.190	1.074	1.047	1.074
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> ₀ >2 σ (<i>I</i> ₀)]	0.0302/0.0747	0.0469/0.1089	0.0605/0.1082	0.0281/0.0745
<i>R</i> ₁ / <i>wR</i> ₂ [all data]	0.0318/0.0759	0.0424/0.1161	0.1521/0.1311	0.0336/0.0777
Max./Min. residual electron density	0.14/-0.15	2.40/-1.97	0.18/-0.21	2.09/-1.18

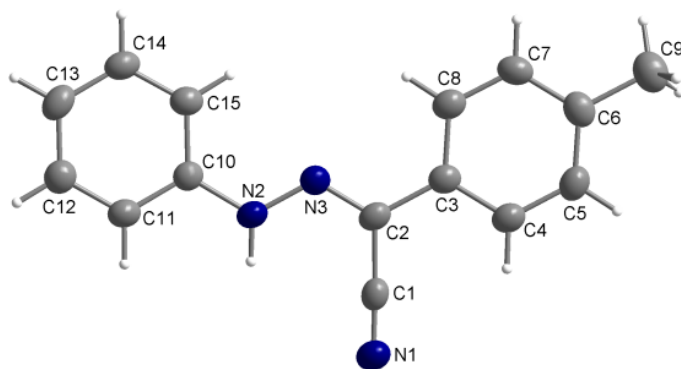


Figure S1. Molecular structure of **3**. Thermal Ellipsoids are displayed at the 50% probability level. Selected bond lengths [Å] and angles [°]: N1-C1 1.157(4), C1-C2 1.459(5), C2-N3 1.307(3), N2-N3 1.345(3); C10-N2-N3 120.1(2), N2-N3-C2 120.1(3), N3-C2-C3 120.6(3), C3-C2-C1 118.0(3), N3-C2-C1 121.4(3), C2-C1-N1 178.1(3).

4. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra

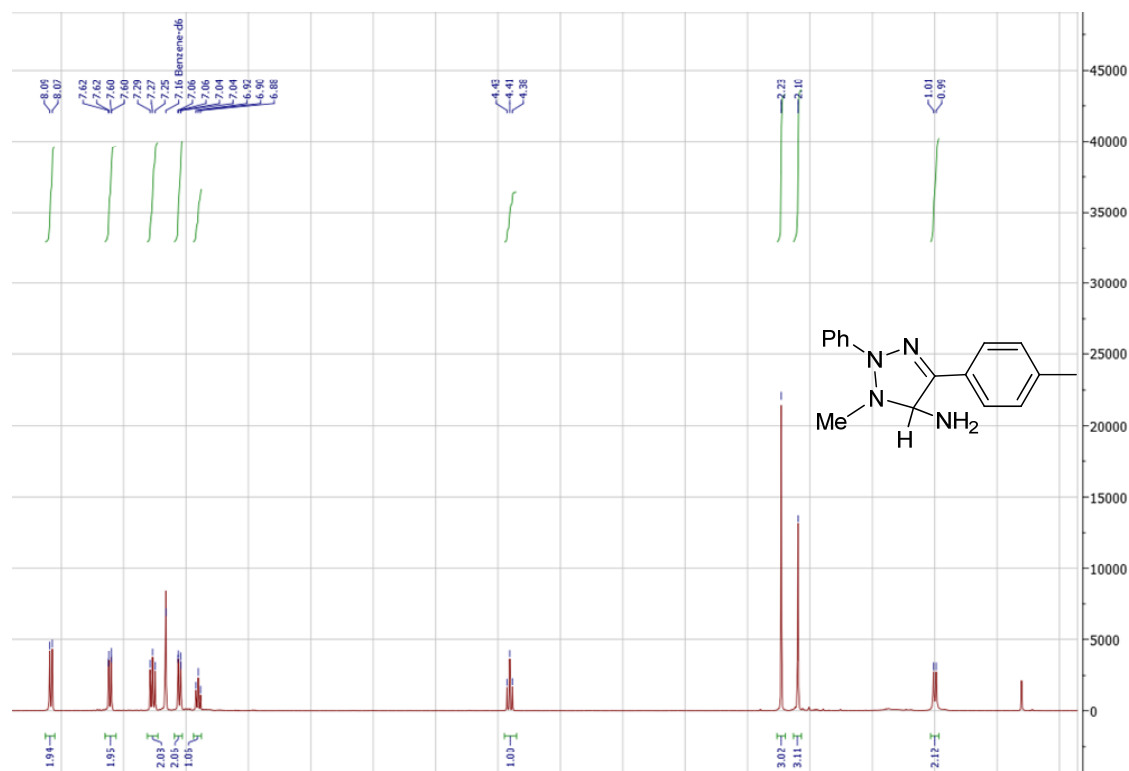


Figure S2. $^1\text{H-NMR}$ spectrum of **2**

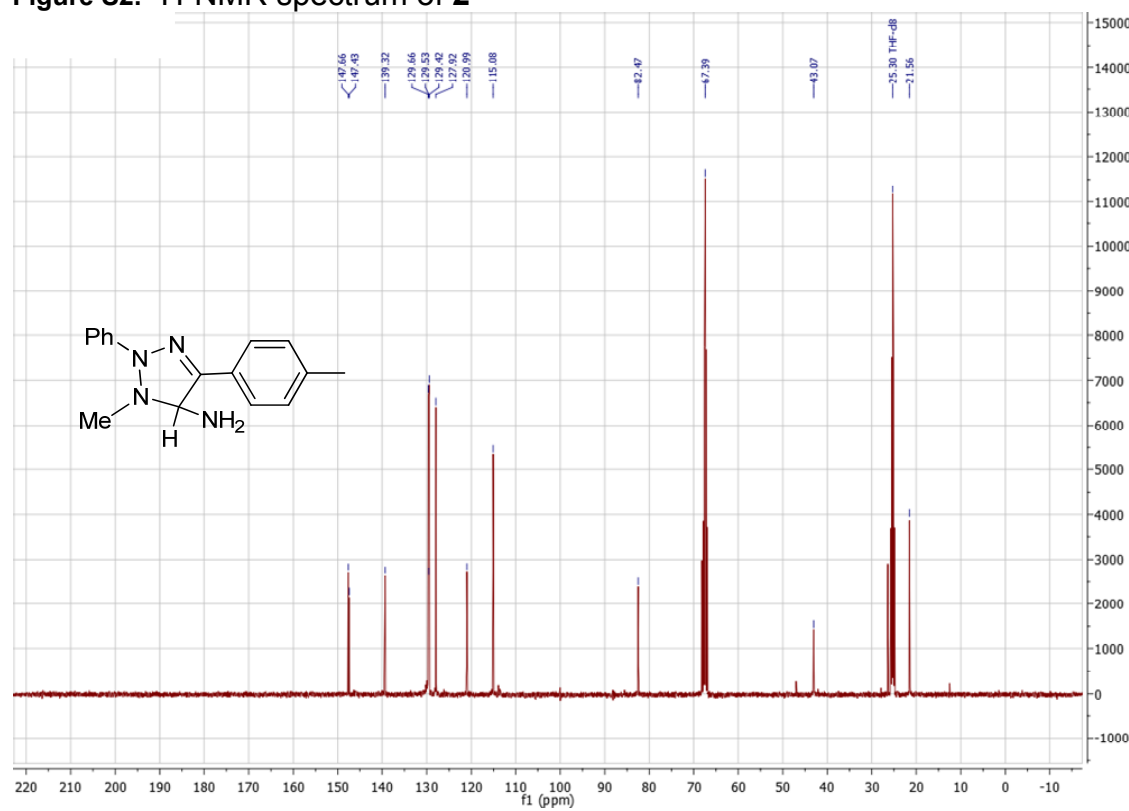


Figure S3. $^{13}\text{C-NMR}$ spectrum of **2**

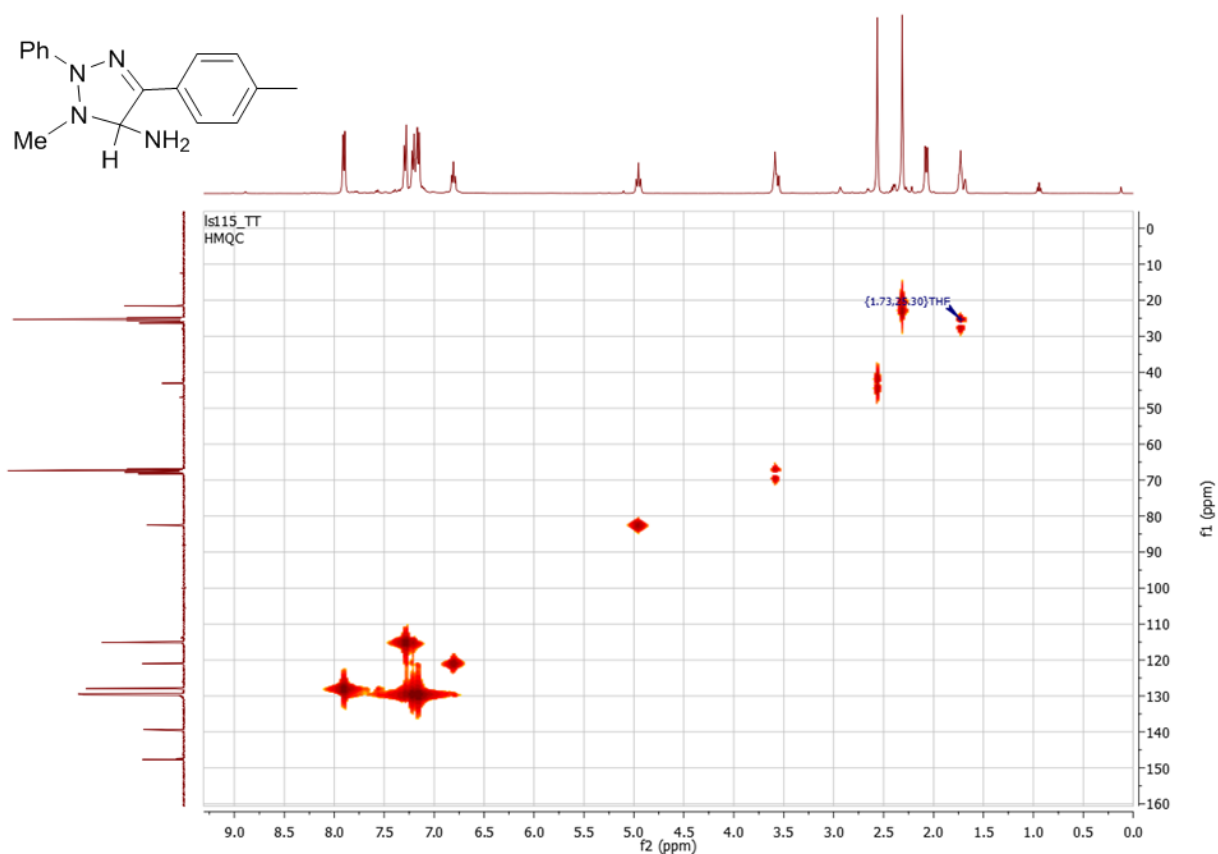


Figure S4. HMQC spectrum of **2**.

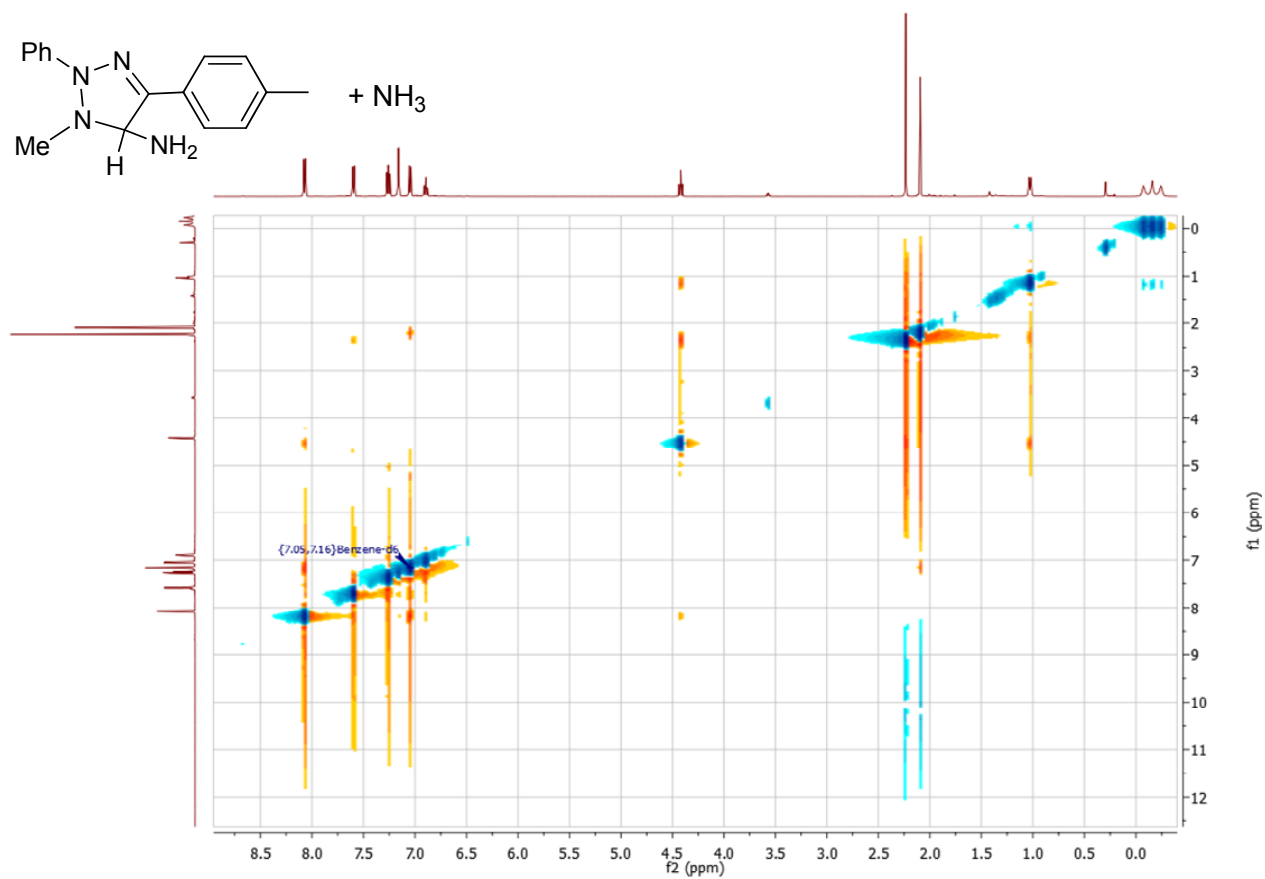


Figure S5. EXSY spectrum of **2** + NH₃.

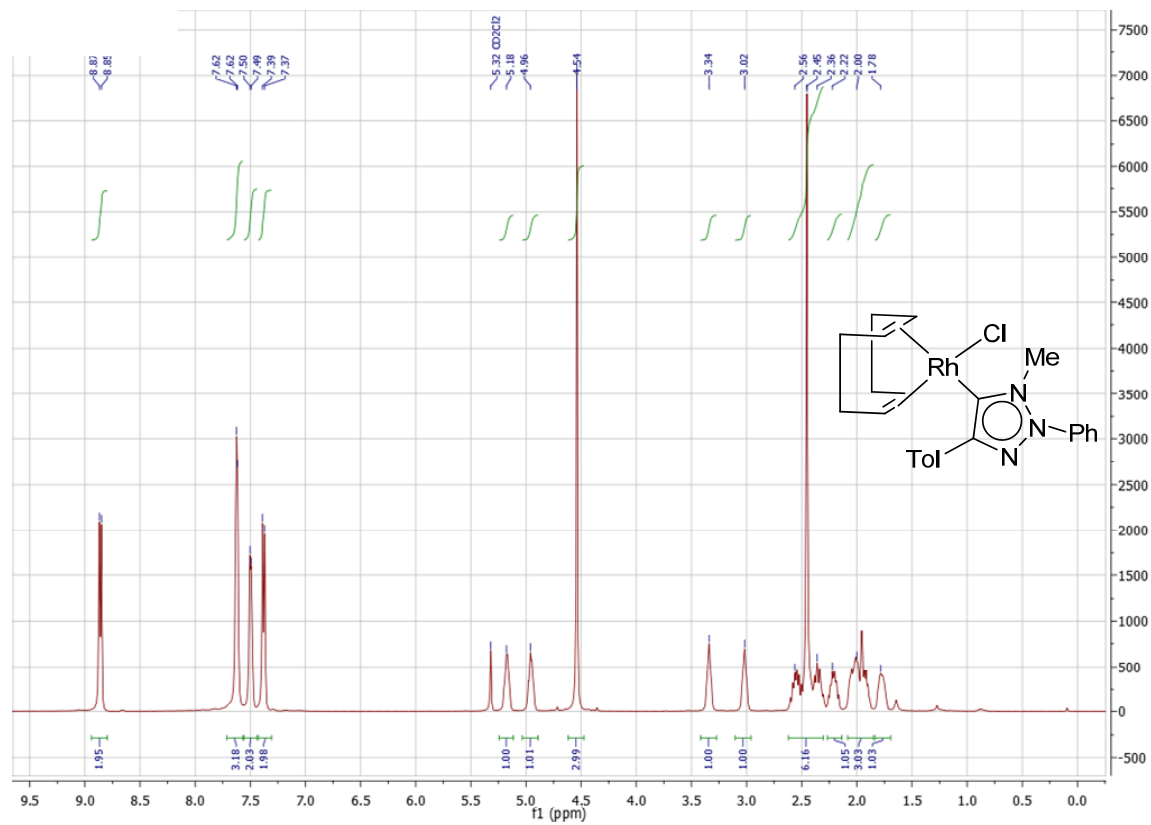


Figure S6. $^1\text{H-NMR}$ spectrum of RhCOD.

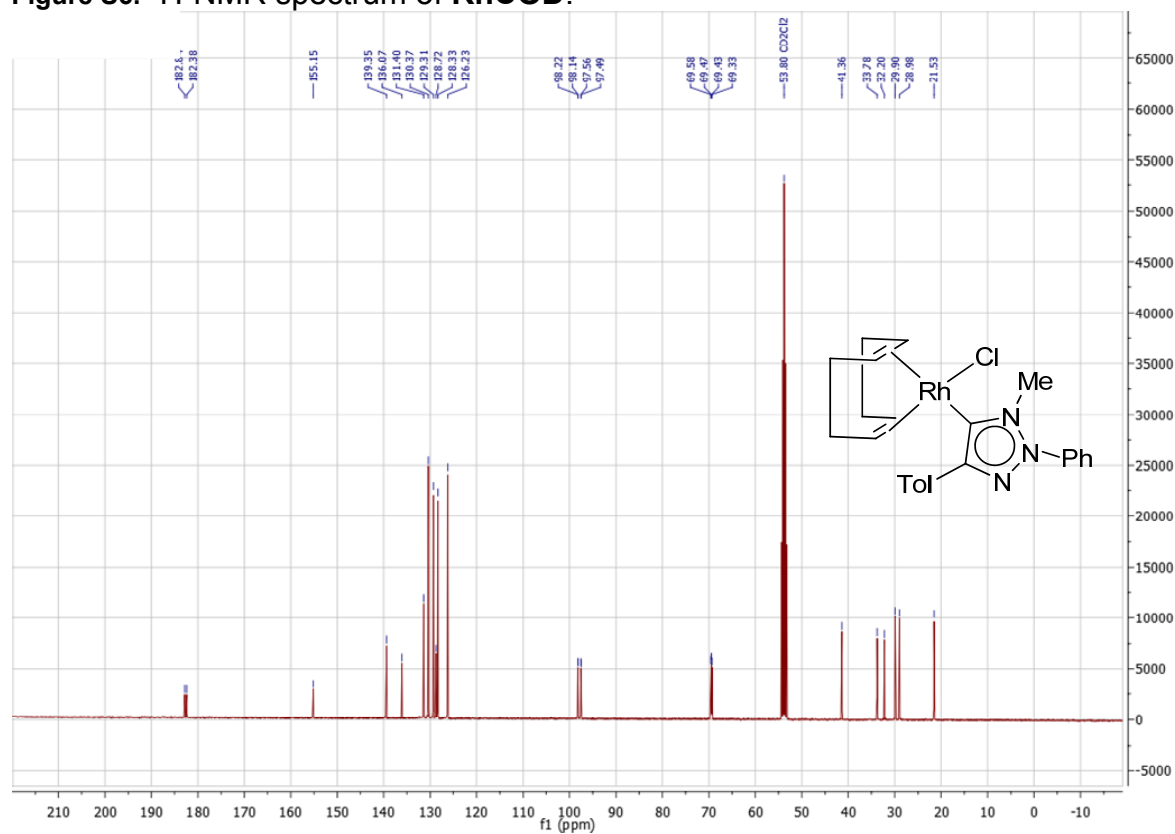


Figure S7. $^{13}\text{C-NMR}$ spectrum of RhCOD.

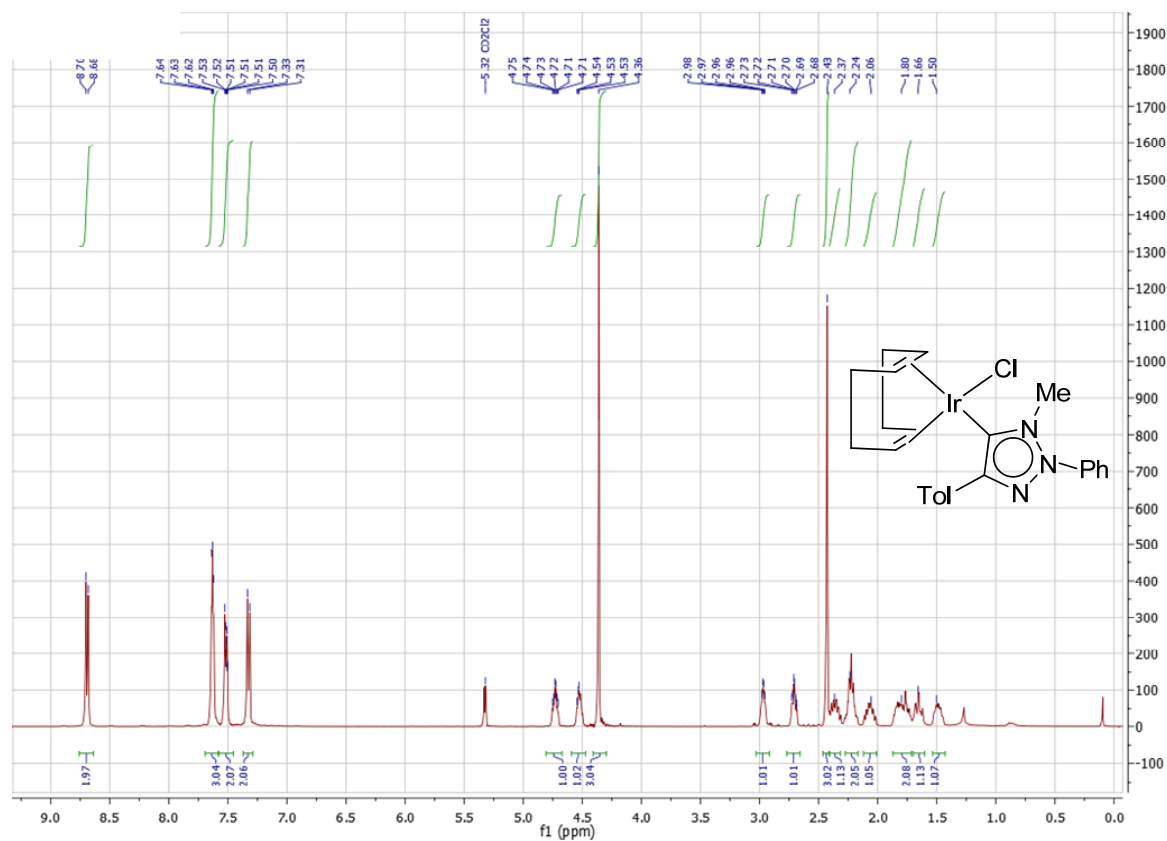


Figure S8. $^1\text{H-NMR}$ spectrum of IrCOD.

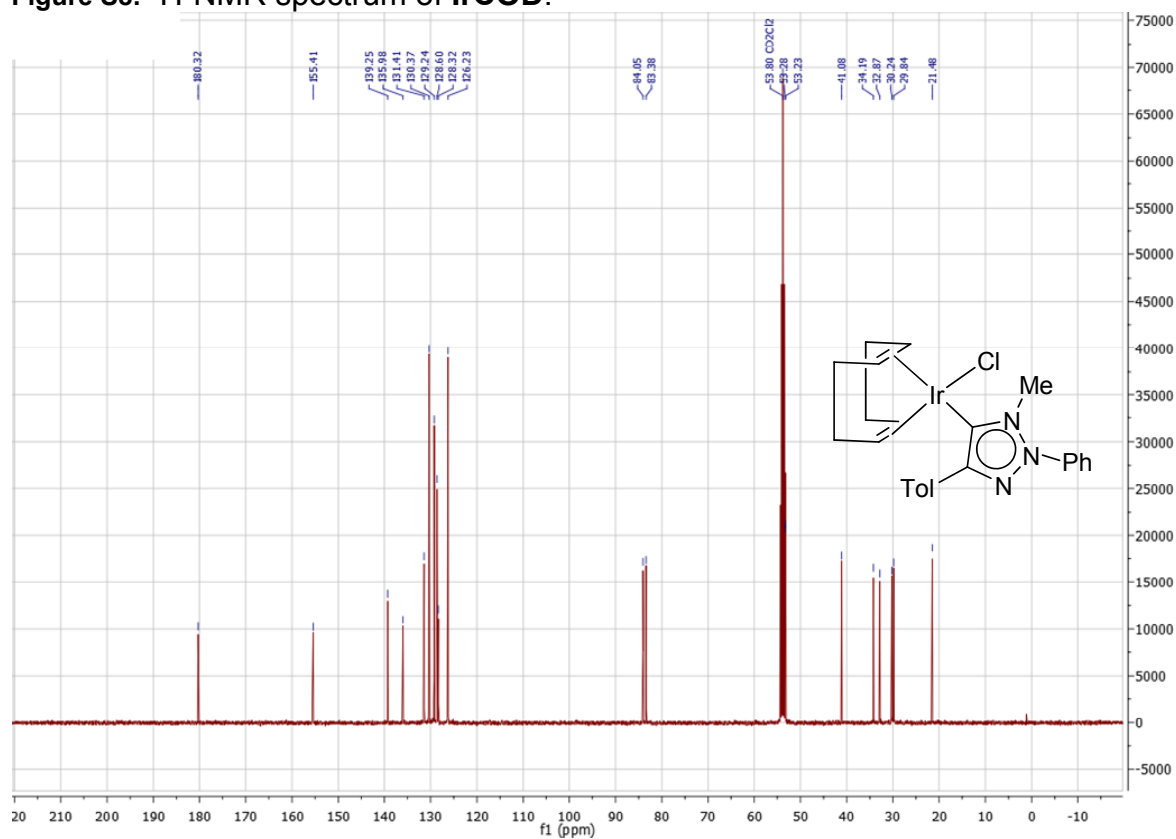


Figure S9. $^{13}\text{C-NMR}$ spectrum of IrCOD.

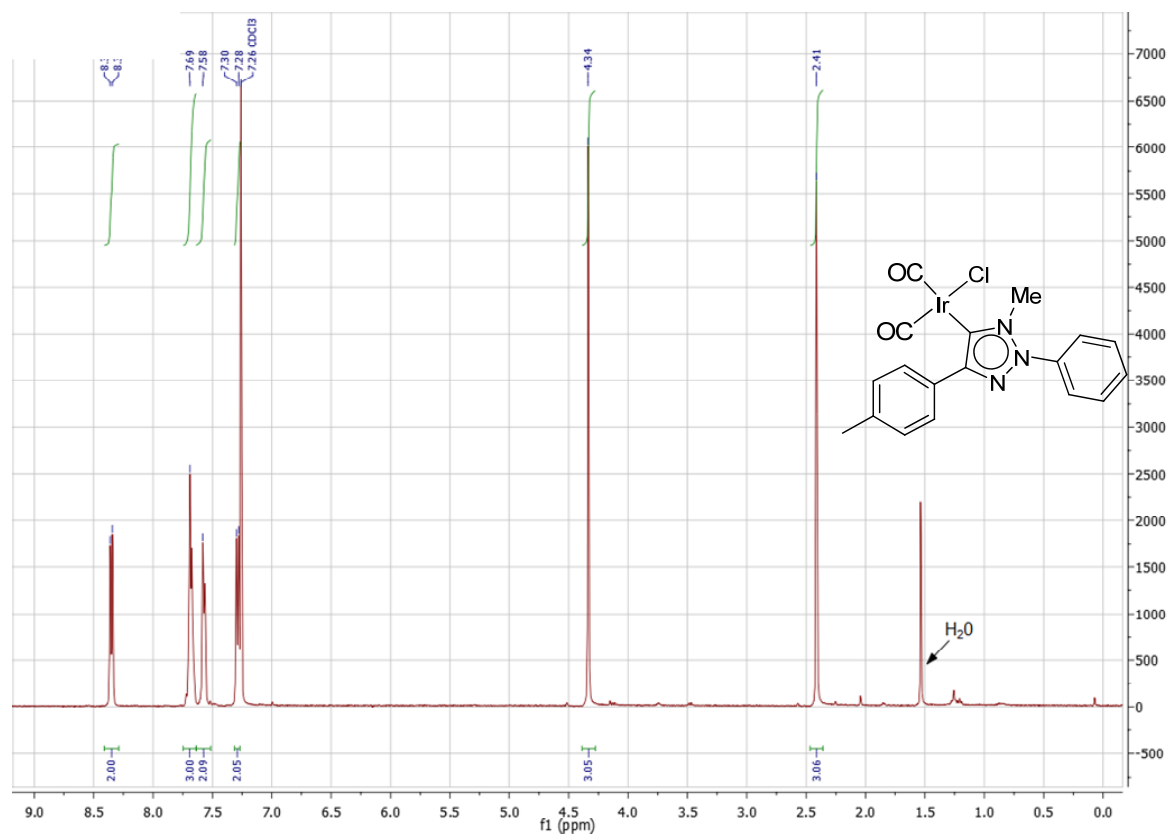


Figure S10. ¹H-NMR spectrum of 4.

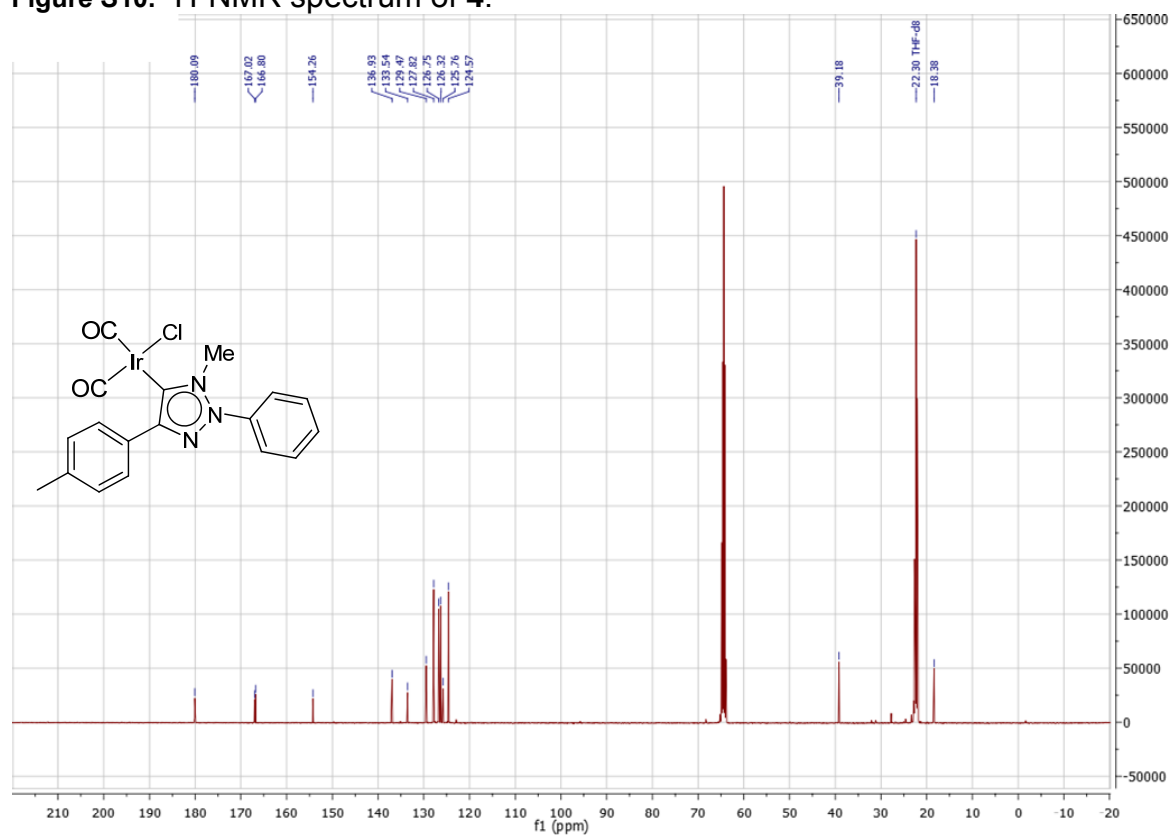


Figure S11. ¹³C-NMR spectrum of 4.

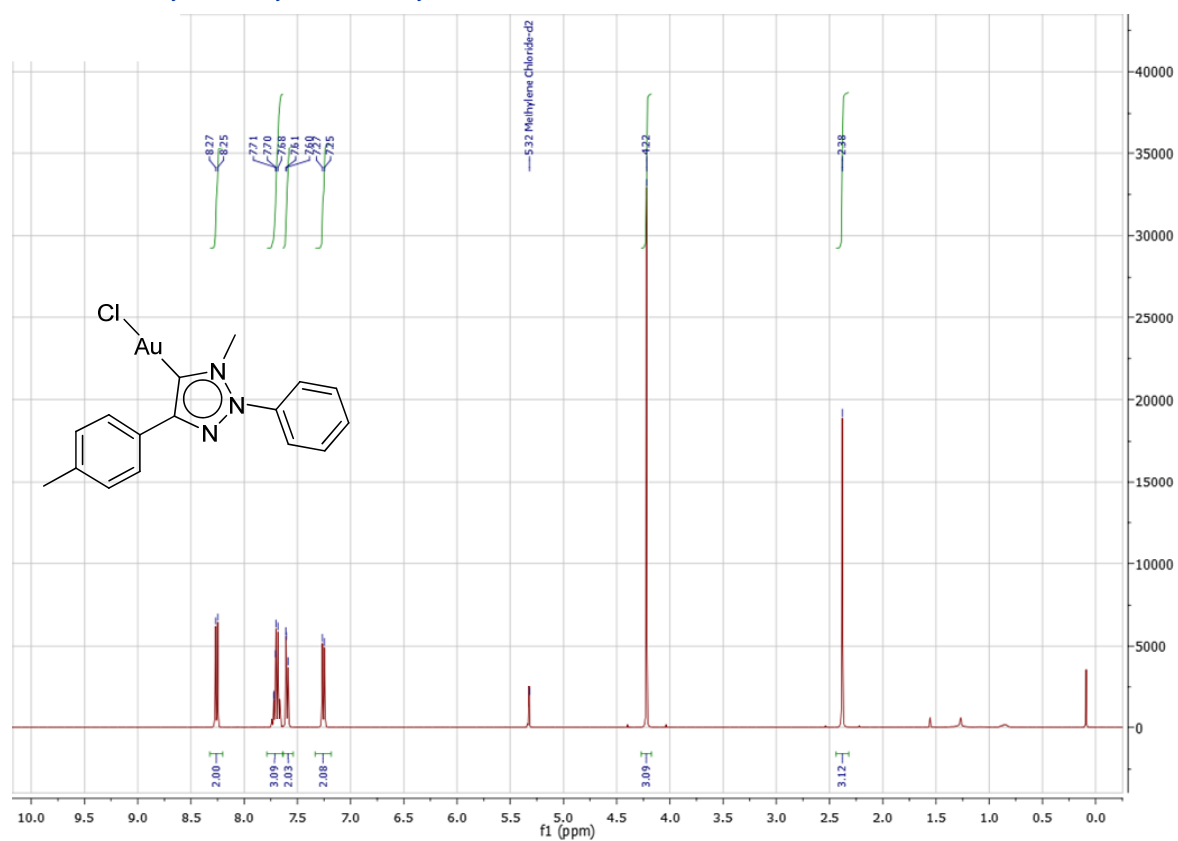


Figure S12. ¹H-NMR spectrum of 5a.

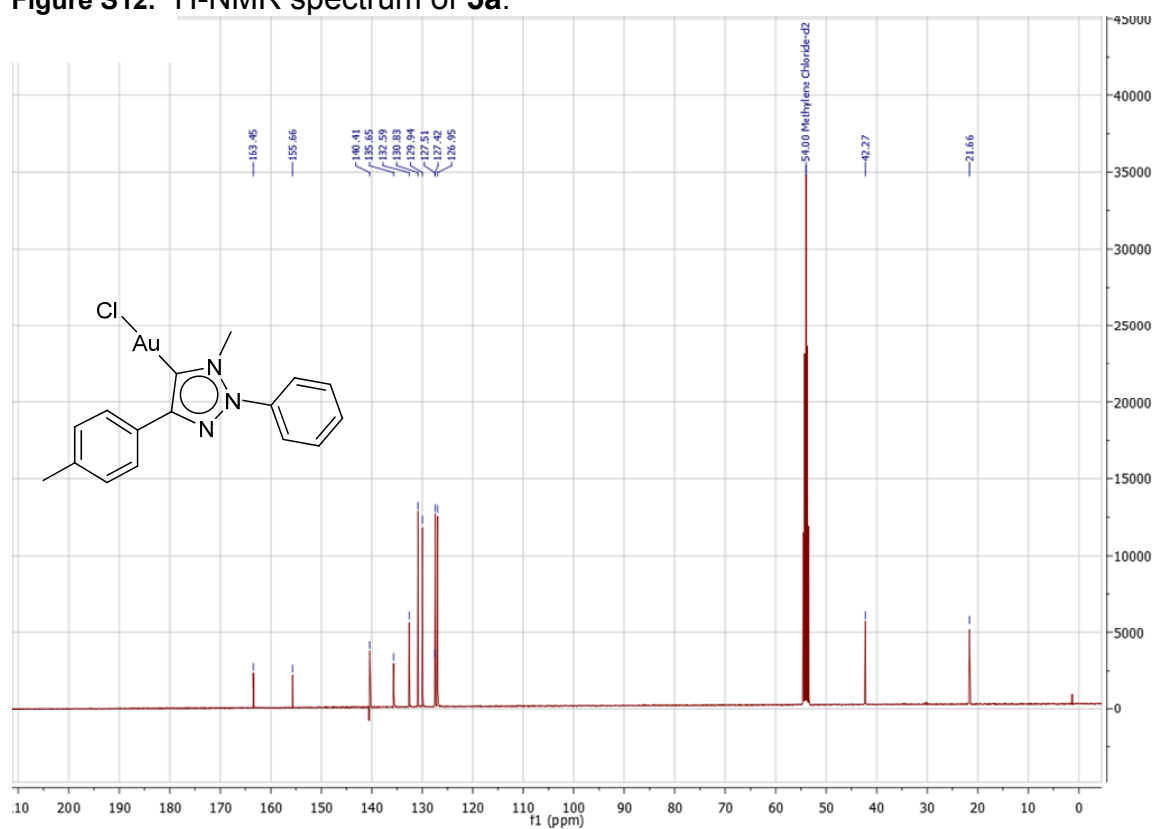


Figure S13. ¹³C-NMR spectrum of 5a.

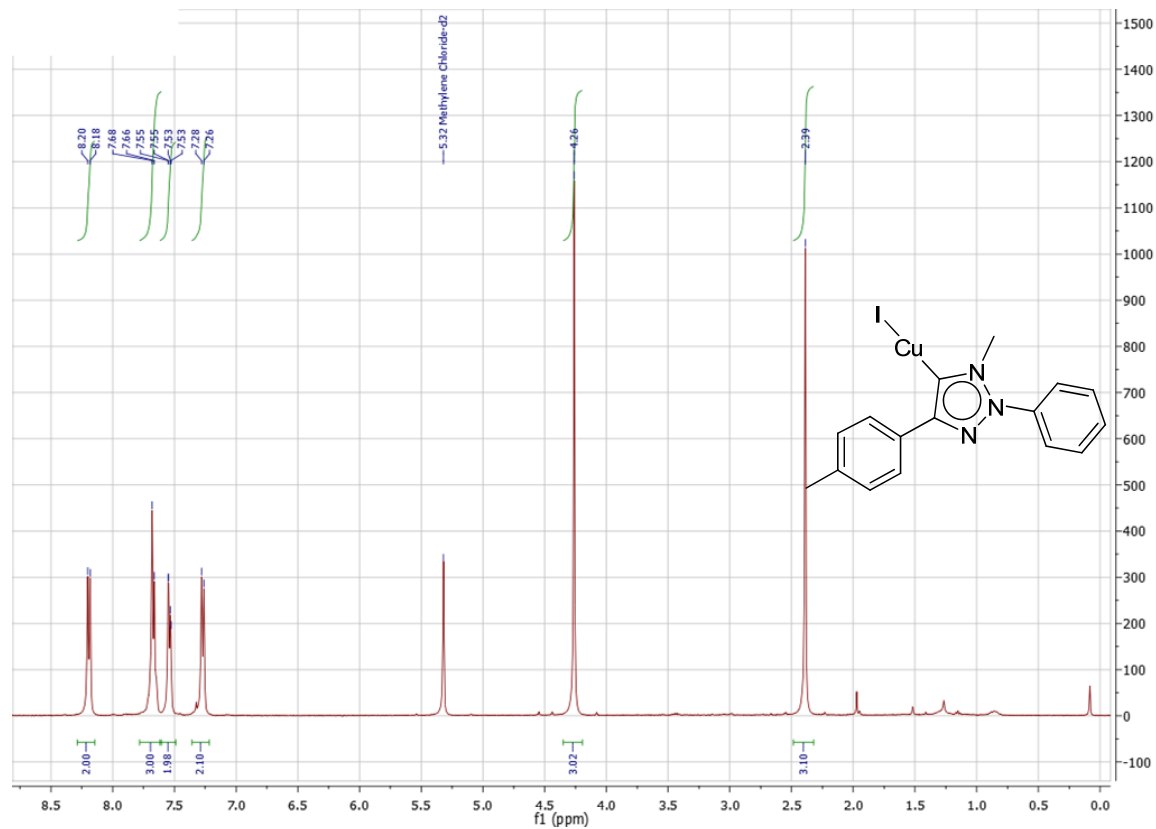


Figure S14. $^1\text{H-NMR}$ spectrum of **5b**.

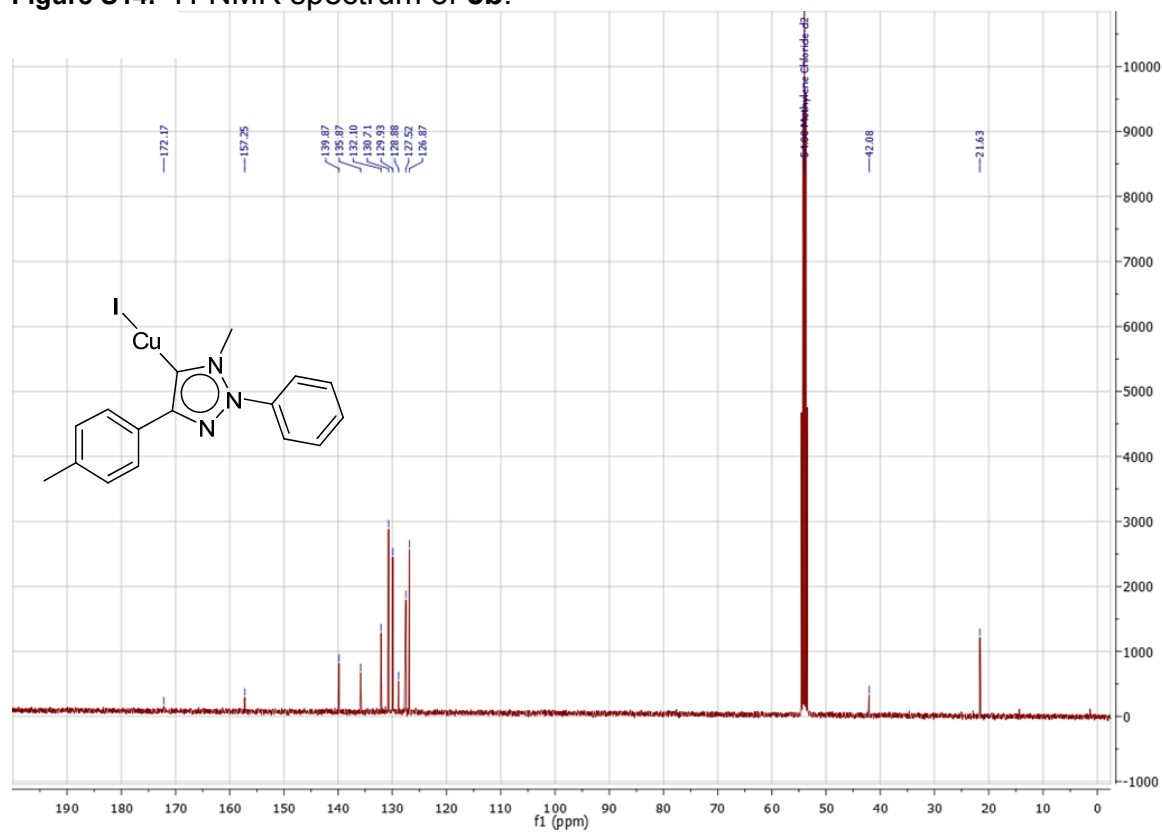


Figure S15. $^{13}\text{C-NMR}$ spectrum of **5b**.

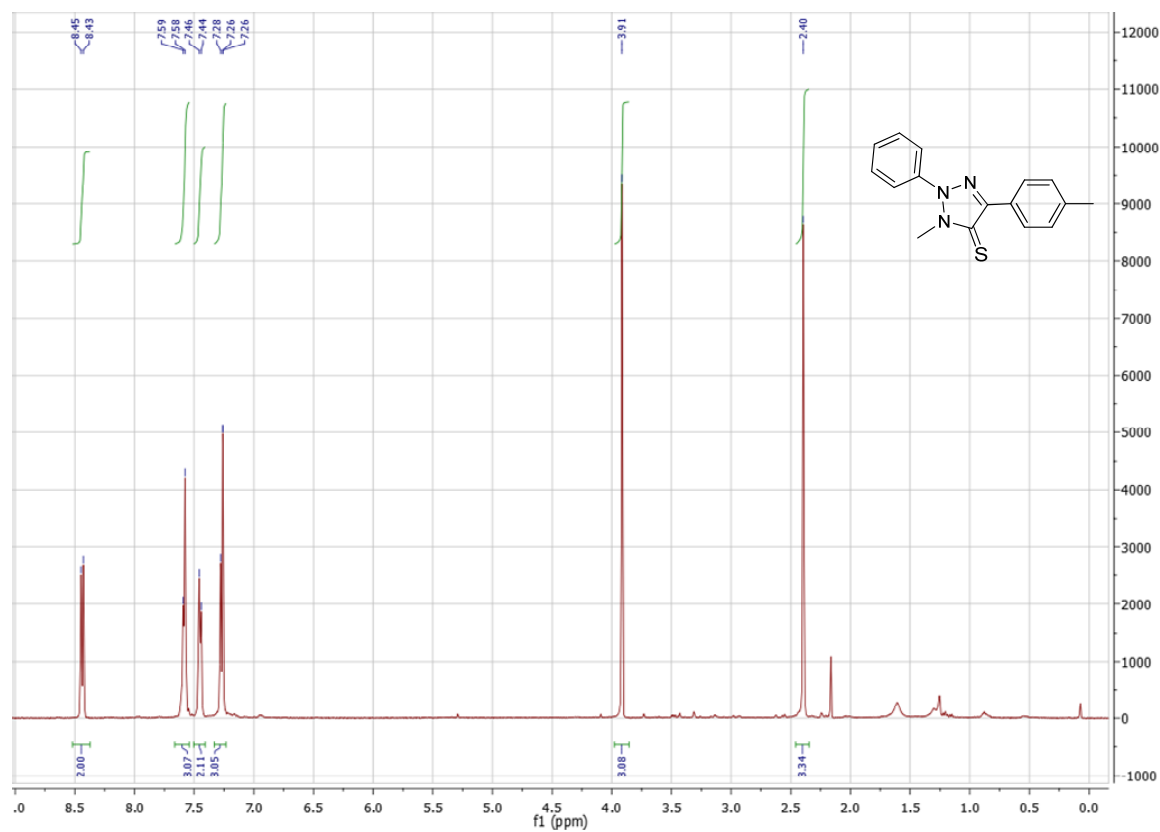


Figure S16. $^1\text{H-NMR}$ spectrum of **6**.

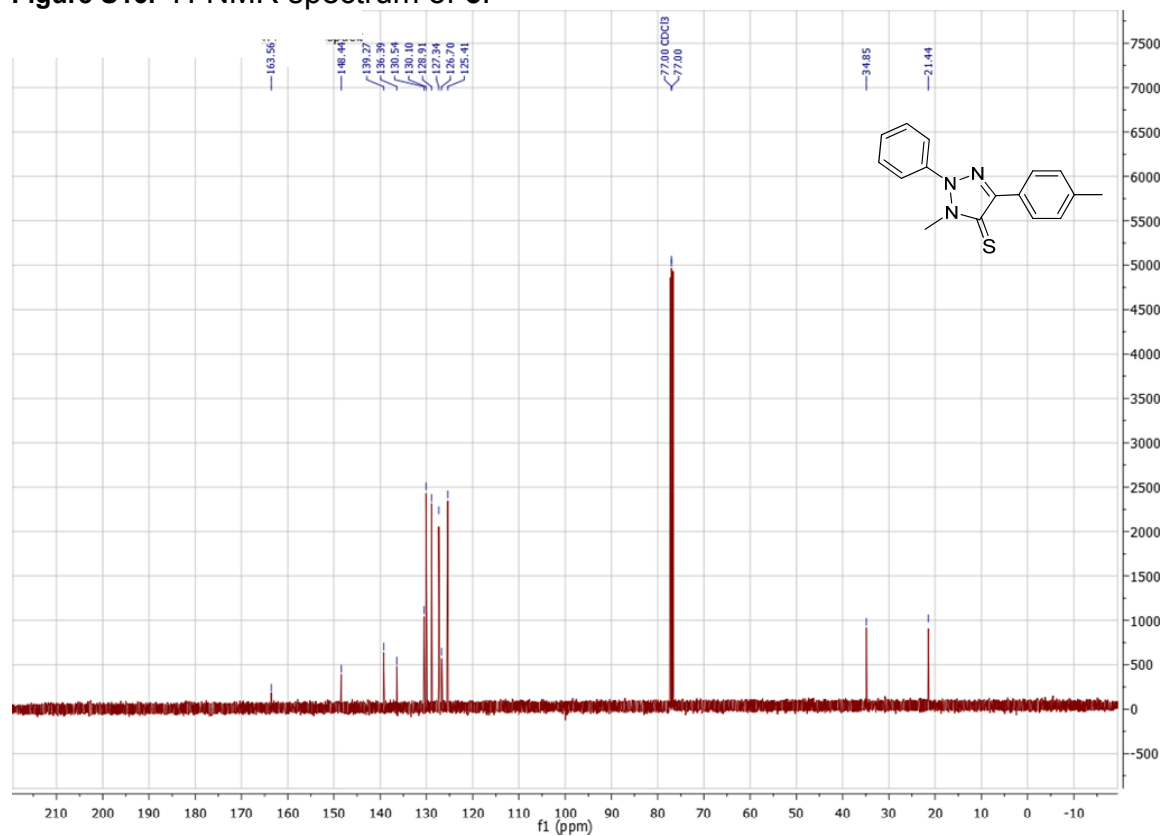


Figure S17. $^{13}\text{C-NMR}$ spectrum of **6**.

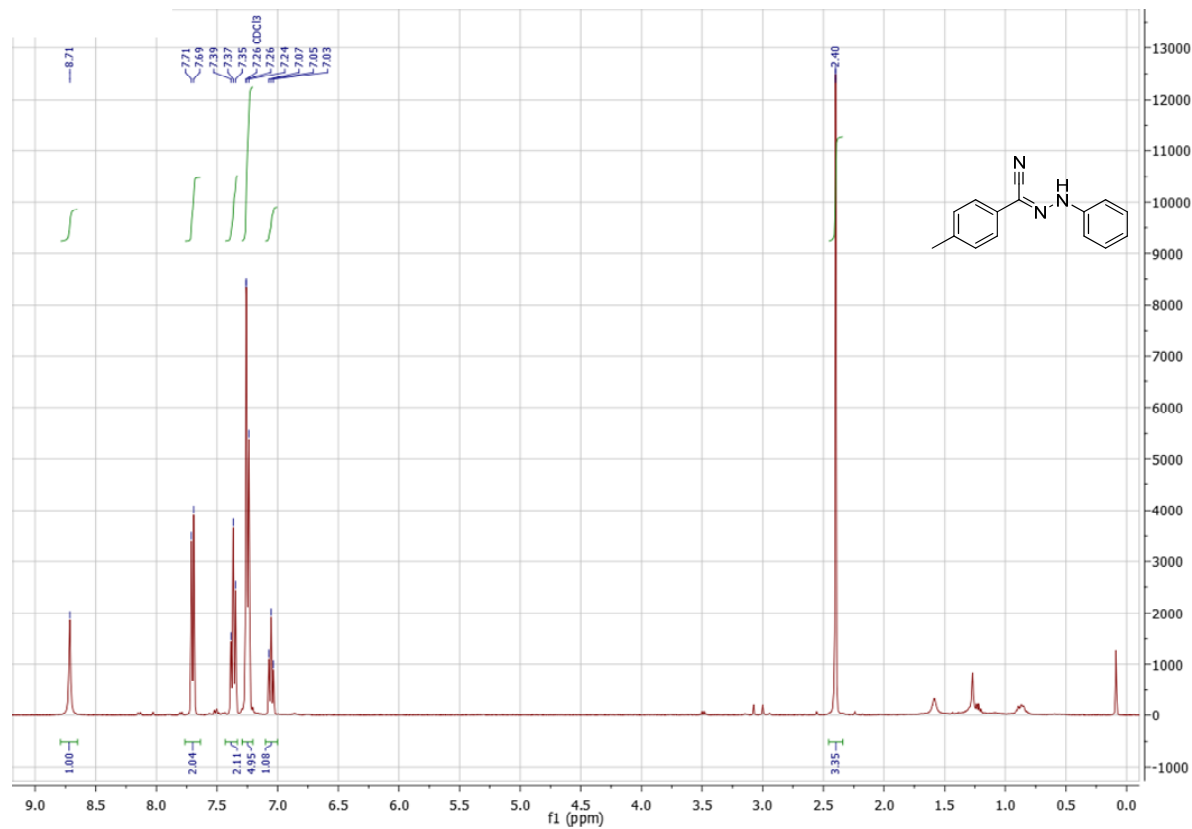


Figure S18. $^1\text{H-NMR}$ spectrum of **3**.

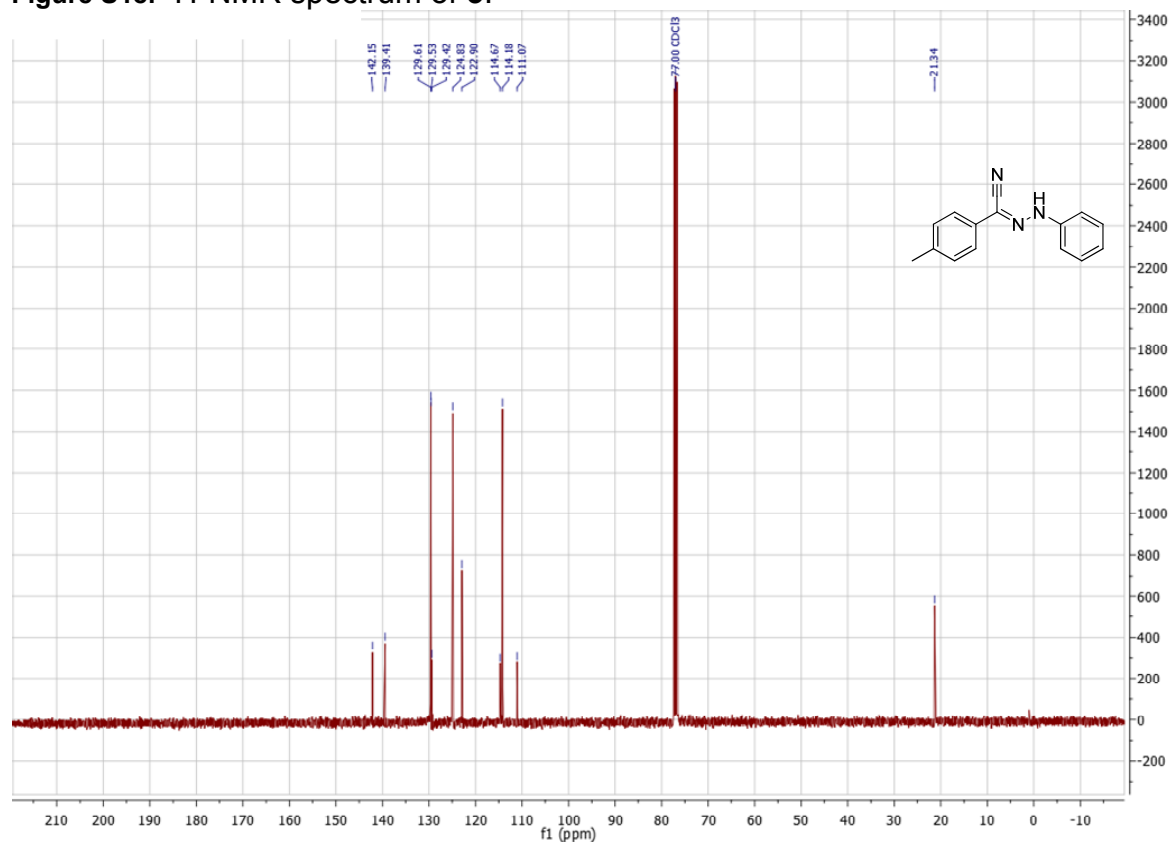


Figure S19. $^{13}\text{C-NMR}$ spectrum of **3**.

5. ESI-Mass Spectra

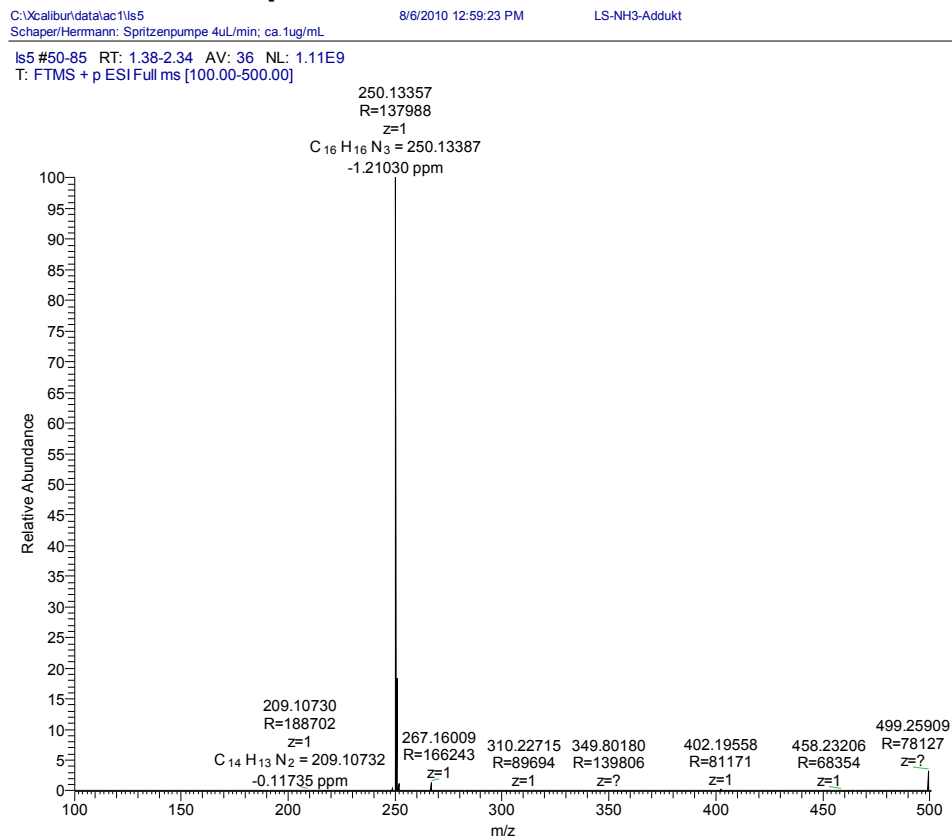


Figure S20. ESI-mass spectrum of **2** (wide range).

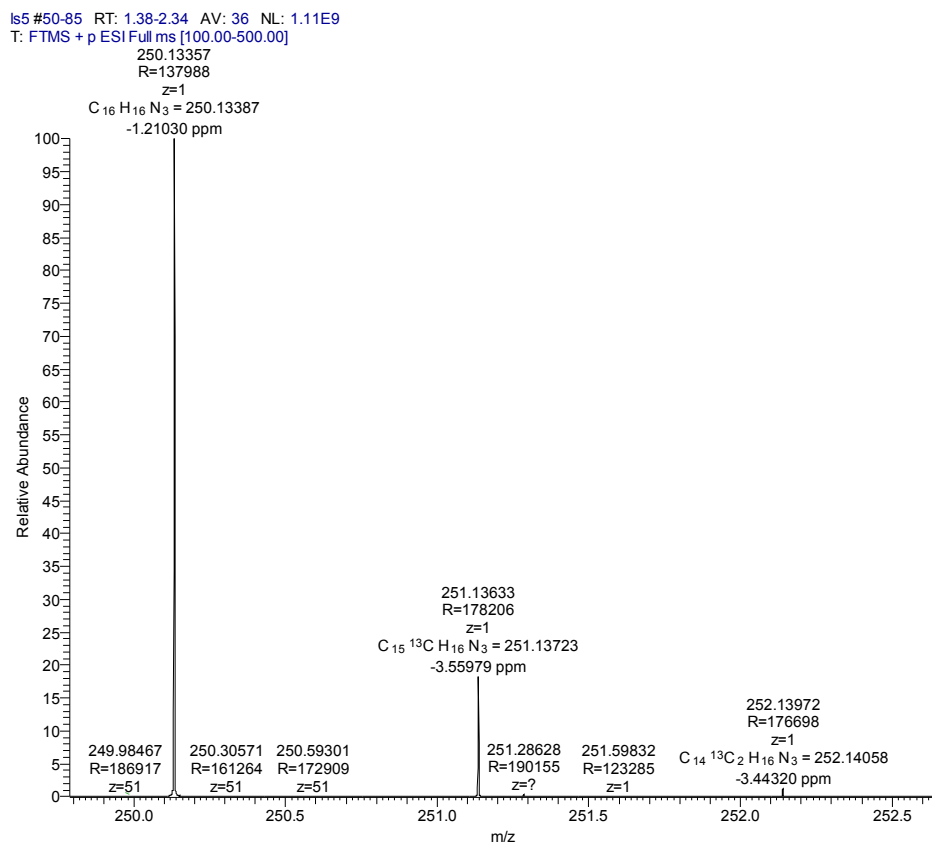


Figure S21. ESI-mass spectrum of **2** ([M+H⁺-NH₃] fragment).

Is5 #50-85 RT: 1.38-2.34 AV: 36 NL: 1.46E7
T: FTMS + p ESI Full ms [100.00-500.00]

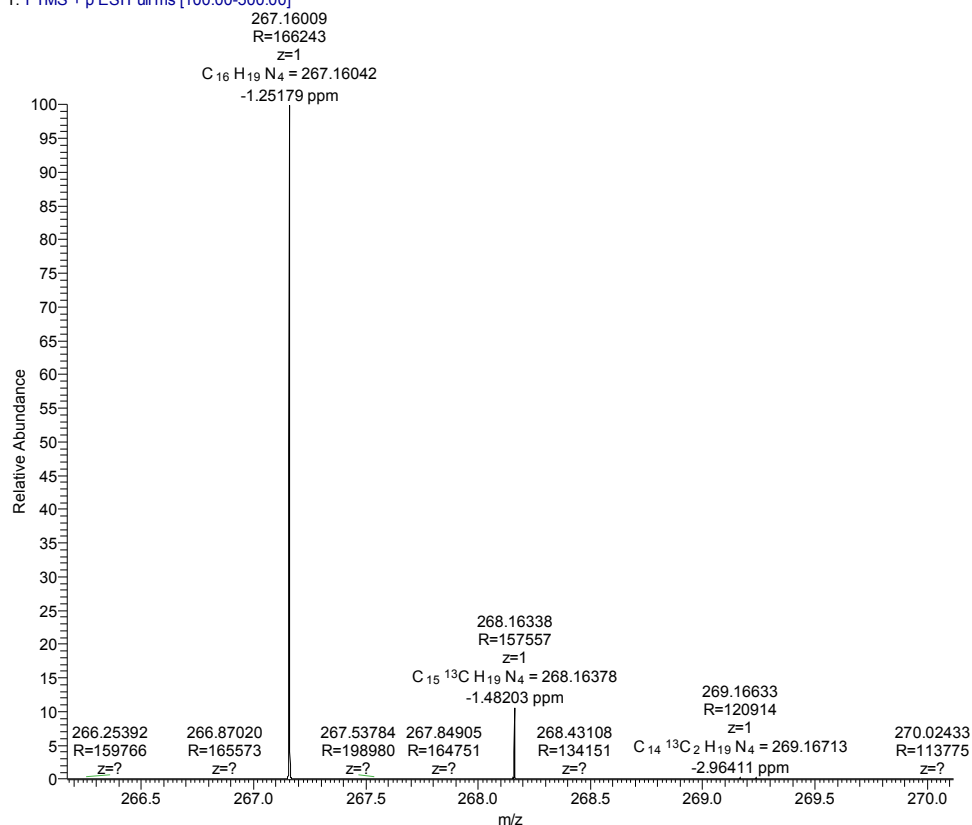


Figure S22. ESI-mass spectrum of **2** ([M+H⁺]).

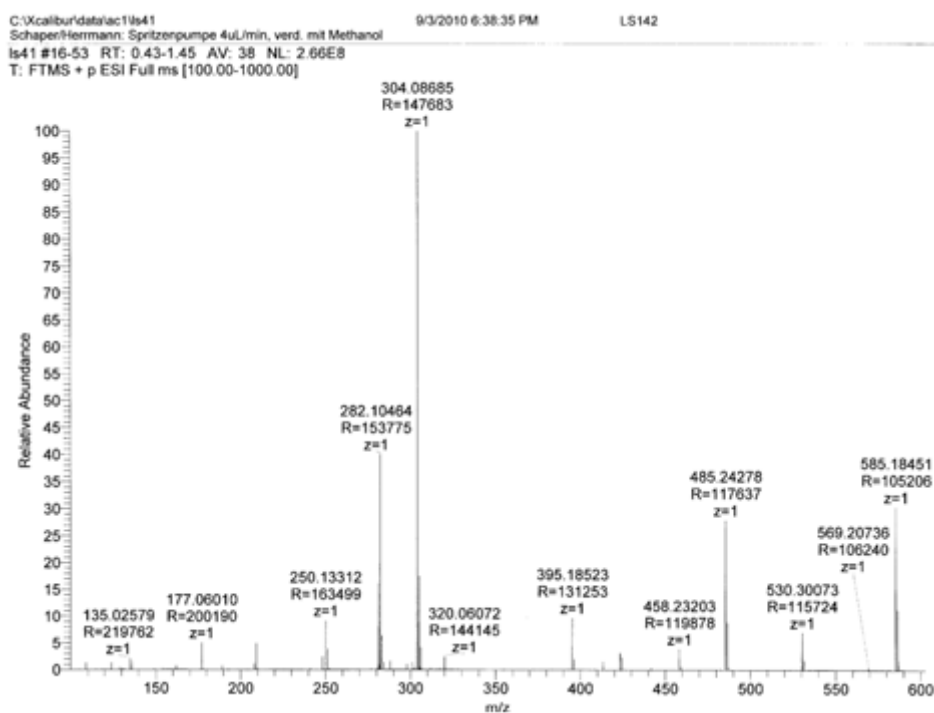


Figure S23. ESI-mass spectrum of **S2** ([M+H⁺]).

6. Computational Details

All calculations were performed with GAUSSIAN-03^[14] using the density functional / Hartree-Fock hybrid model Becke3LYP^[15] and the split valence double- ζ (DZ) basis set 6-31G*^[16]. No symmetry or internal coordinate constraints were applied during optimizations. All reported intermediates were verified as being true minima by the absence of negative eigenvalues in the vibrational frequency analysis, while transition states were located according to the Berny algorithm. Transition-state structures (indicated by TS) were located using the Berny algorithm^[17] until the Hessian matrix had only one imaginary eigenvalue. The identities of all transition states were confirmed by IRC calculations, and by animating the negative eigenvector coordinate with MOLDEN^[18] and GaussView^[19]. Approximate free energies (ΔG) and enthalpies ΔH were obtained through thermochemical analysis of frequency calculations, using the thermal correction to Gibbs free energy as reported by GAUSSIAN-03. This takes into account zero-point effects, thermal enthalpy corrections, and entropy. All energies reported in this paper, unless otherwise noted, are free energies at 298 K, using unscaled frequencies. All optimizations are PCM calculations^[20] to include solvation effects with THF ($\epsilon = 7.4257$) as solvent.

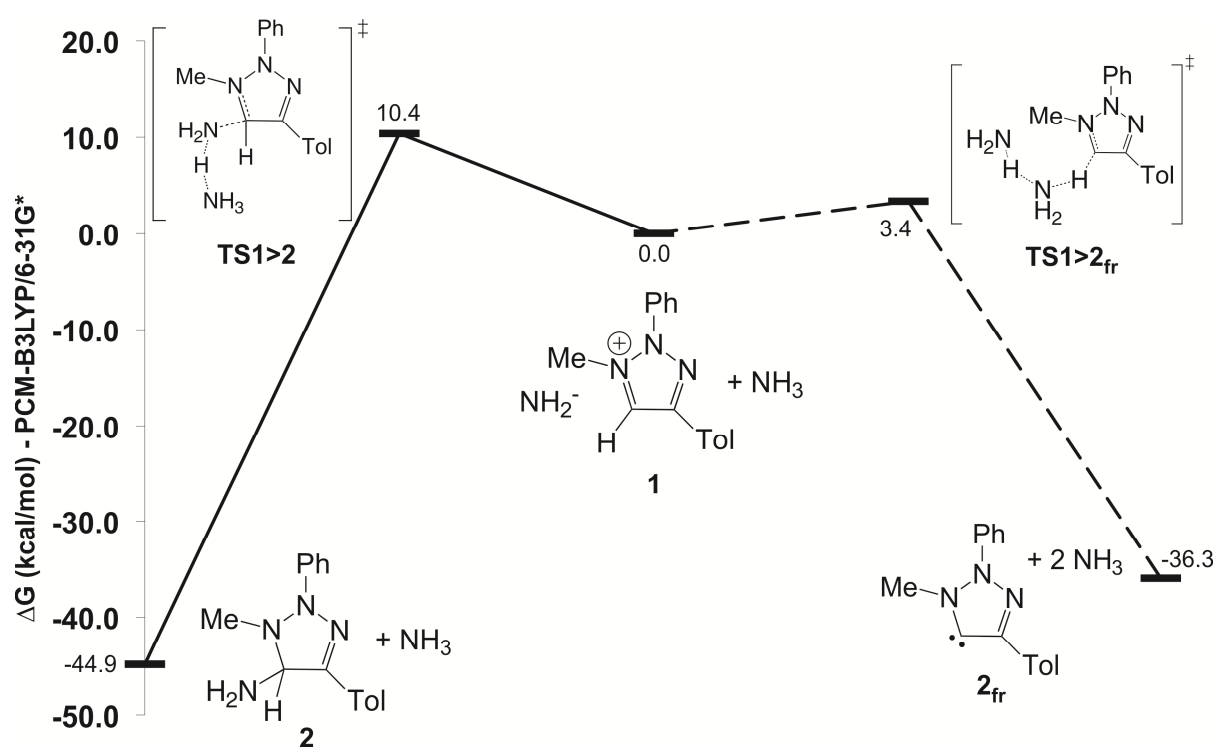


Figure S24. Calculated energy profile (free reaction enthalpy) for the formation of **2** and **2_{fr}** from reaction of **1** with NH_2^- and NH_3 .

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