

Supporting Information

Adducts of Nitrous Oxide and N-Heterocyclic Carbenes: Syntheses, Structures and Reactivity

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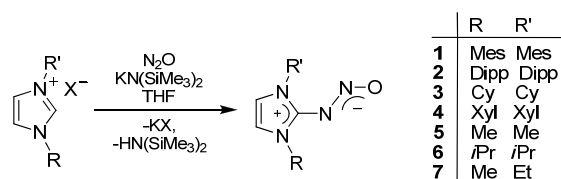
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General remarks

Unless stated otherwise, the reactions were performed under an atmosphere of dry dinitrogen. Solvents were purified and dried according to standard procedures. All the reagents except of dixylylimidazolium chloride were obtained from commercial sources. Dixylylimidazolium chloride was prepared analogously to dimesitylimidazolium chloride.¹ N₂O (99.999%) was purchased from Air-liquide. NMR spectra were measured on a Bruker Avance DPX-400 (¹H: 400 MHz, ¹³C: 100 MHz), Bruker Avance-200 (¹H: 200 MHz) or Bruker DRX-400 (¹⁵N: 40.5 MHz) spectrometer. ¹⁵N spectra were referenced against formamide (112 ppm). Mass spectra were recorded with a Q-TOF Ultima (Waters) instrument. UV-Vis spectra were measured on PerkinElmer Lambda 40 UV-Vis spectrometer. Combustion analysis was performed with a Thermo Scientific Flash 2000 Organic Elemental Analyzer.

General procedure for the synthesis of compounds 1–7



KHMDS (1 equiv.) was added to a suspension of the respective imidazolium salt (1 equiv.) in THF and the resulting mixture was stirred for 24 h. The solution was then filtered and stirred under an atmosphere of N₂O for additional 24 h. The solution or suspension that formed was concentrated to 20 mL (0.5 mL for **2**), and the precipitate was isolated by filtration, washed with hexane (3×10 mL), and dried under vacuum.

1. KHMDS (9.27 mmol, 1.85 g), 1,3-dimesitylimidazolium chloride (9.27 mmol, 3.16 g) and THF (1 L) were used. Yield: 1.45 g (45%). The NMR data of **1** correspond to what has been published.² UV/Vis (CH₂Cl₂): λ_{max} = 302 nm, ε = 1.33×10⁴ M⁻¹cm⁻¹, λ = 448 nm, ε = 205 M⁻¹cm⁻¹. ¹⁵N NMR (CDCl₃): δ 152.0 (NMe_s), 336.9 (CNNO), 617.6 (CNNO).

2. KHMDS (0.47 mmol, 94 mg), 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (0.47 mmol, 200 mg) and THF (5 mL) were used. Yield: 85 mg (42%). The NMR data of **2**

correspond to what has been published.² UV/Vis (CH₂Cl₂): $\lambda_{\text{max}} = 305 \text{ nm}$, $\varepsilon = 0.97 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$, $\lambda = 446 \text{ nm}$, $\varepsilon = 148 \text{ M}^{-1}\text{cm}^{-1}$.

3. KHMDS (1.73 mmol, 346 mg), 1,3-dicyclohexylimidazolium tetrafluoroborate (1.73 mmol, 555 mg) and THF (100 mL) were used. Yield: 271 mg (56%). Elem. anal. calcd for C₁₅H₂₄N₄O: C 65.17; H 8.75; N 20.27. Found: C 65.08; H 9.04; N 20.28. ¹H NMR (400 MHz, CD₂Cl₂): δ 1.17–2.10 (m, 20 H, CH₂), 4.47 (t of t, 11.8 Hz, 3.7 Hz, 2 H, CH from Cy), 6.99 (s, 2 H, CH=CH). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ 25.13, 25.28, 33.09 (CH₂), 56.20 (CH from Cy), 113.92 (CH=CH), 150.63 (CNNO). MS (ESI⁺), found: 277.2029 [M + H]⁺; calcd for C₁₅H₂₅N₄O: 277.2022. UV/Vis (CH₂Cl₂): $\lambda_{\text{max}} = 294 \text{ nm}$, $\varepsilon = 1.20 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$, $\lambda = 431 \text{ nm}$, $\varepsilon = 218 \text{ M}^{-1}\text{cm}^{-1}$. Crystals, suitable for X-ray analysis, were obtained by slow evaporation of a solution of **3** in hexane/CH₂Cl₂ (2:1).

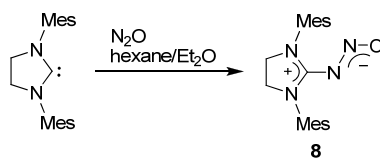
4. KHMDS (352 mg, 1.76 mmol), 1,3-dixylylimidazolium chloride (550 mg, 1.76 mmol) and THF (200 mL) were used. Yield: 293 mg (52%). Elem. anal. calcd for C₁₉H₂₀N₄O: C 71.23; H 6.29; N 17.49. Found: C 71.38; H 6.35; N 17.87. ¹H NMR (400 MHz, CD₂Cl₂): δ 2.20 (s, 12 H, Me), 6.98 (s, 2 H, CH=CH), 7.23 (d, 7.40 Hz, 4 H, *m*-CH from Xyl), 7.35 (t, 7.40 Hz, 2 H, *p*-CH from Xyl). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ 17.62 (Me), 118.67 (CH=CH), 128.49, 129.59, 135.14, 135.33 (arenes), 152.99 (CNNO). MS (ESI⁺), found: 321.1715 [M + H]⁺; calcd for C₁₉H₂₁N₄O: 321.1788. UV/Vis (CH₂Cl₂): $\lambda_{\text{max}} = 303 \text{ nm}$, $\varepsilon = 1.17 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$, $\lambda = 448 \text{ nm}$, $\varepsilon = 158 \text{ M}^{-1}\text{cm}^{-1}$. Crystals, suitable for X-ray analysis, were obtained by slow evaporation of a solution of **4** in THF.

5. KHMDS (3.17 mmol, 634 mg), 1,3-dimethylimidazolium methylsulfate (3.17 mmol, 661 mg) and THF (200 mL) were used. Yield: 180 mg (40%). Elem. anal. calcd for C₅H₈N₄O: C 42.85; H 5.75; N 39.98. Found: C 42.58; H 5.35; N 39.64. ¹H NMR (400 MHz, CD₂Cl₂): δ 3.71 (s, 6 H, Me), 6.81 (s, 2 H, CH=CH). ¹³C{¹H} NMR (100 MHz CD₂Cl₂): δ 35.43 (CH₃), 118.14 (CH=CH), 152.69 (CNNO). MS (ESI⁺), found: 141.0776 [M + H]⁺; calcd for C₅H₉N₄O: 141.0770. UV/Vis (CH₂Cl₂): $\lambda_{\text{max}} = 298 \text{ nm}$, $\varepsilon = 1.2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$, $\lambda = 420 \text{ nm}$, $\varepsilon = 544 \text{ M}^{-1}\text{cm}^{-1}$, $\lambda = 442 \text{ nm}$, $\varepsilon = 461 \text{ M}^{-1}\text{cm}^{-1}$; (H₂O): $\lambda_{\text{max}} = 289 \text{ nm}$, $\varepsilon = 1.1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$. Crystals, suitable for X-ray analysis, were obtained by slow evaporation of a solution of **5** in hexane/CH₂Cl₂ (1:1).

6. KHMDS (1.67 mmol, 334 mg), 1,3-diisopropylimidazolium tetrafluoroborate (1.67 mmol, 316 mg) and THF (100 mL) were used. Yield: 140 mg (43%). Elem. anal. calcd for $C_9H_{16}N_4O$: C 55.08; H 8.21; N 28.54. Found: C 55.23; H 8.40; N 28.80. 1H NMR (400 MHz, $CDCl_3$): δ 1.42 (d, 6.7 Hz, 12 H, $CH(CH_3)_2$), 4.96 (sept, 6.7 Hz, 2 H, $CH(CH_3)_2$), 6.95 (s, 2 H, $CH=CH$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 22.46 ($CH(CH_3)_2$), 49.10 ($CH(CH_3)_2$), 113.38 ($CH=CH$), 150.47 (CNNO). ^{15}N NMR ($CDCl_3$): δ 106 (NiPr), 341.8 (CNNO), 604.6 (CNNO). MS (ESI^+), found: 197.1411 $[M + H]^+$; calcd for $C_9H_{17}N_4O$: 197.1475. UV/Vis (CH_2Cl_2): λ_{max} = 294 nm, ϵ = 1.04×10^4 $M^{-1}cm^{-1}$, λ = 432 nm, ϵ = $167 M^{-1}cm^{-1}$. Crystals, suitable for X-ray analysis, were obtained by slow evaporation of a solution of **6** in hexane/ CH_2Cl_2 (1:2).

7. KHMDS (553 mg, 2.77 mmol), 1-ethyl-3-methylimidazolium bromide (530 mg, 2.77 mmol) and THF (200 mL) were used. Yield: 170 mg (40%). Elem. anal. calcd for $C_6H_{10}N_4O$: C 46.74; H 6.54; N 36.34. Found: C 47.12; H 6.71; N 36.16. 1H NMR (400 MHz, CD_2Cl_2): δ 1.39 (t, 7.2 Hz, 3 H, CH_2CH_3), 4.10 (q, 7.2 Hz, 2 H, CH_2CH_3), 6.82 and 6.86 (two d, 2.3 Hz, 2 H, $CH=CH$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 14.74 (CH_2CH_3), 35.67 (CH_2CH_3), 43.00 (CH_3), 116.23 and 118.49 ($CH=CH$), 152.13 (CNNO). MS (ESI^+), found: 155.0944 $[M + H]^+$; calcd for $C_6H_{11}N_4O$: 155.1005. UV/Vis (CH_2Cl_2): λ_{max} = 297 nm, ϵ = 1.11×10^4 $M^{-1}cm^{-1}$, λ = 437 nm, ϵ = $169 M^{-1}cm^{-1}$. Crystals, suitable for X-ray analysis, were obtained by slow evaporation of a solution of **7** in hexane/ CH_2Cl_2 (1:1).

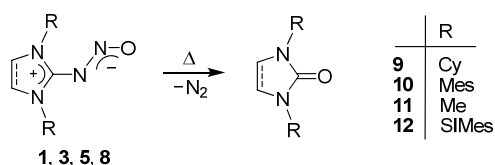
Synthesis of compound **8**



A solution of SIMes (0.33 mmol, 100 mg) in hexane/ Et_2O (1:2, 3 mL) was placed under N_2O , resulting in the precipitation of a yellow solid. After 24 h the precipitate was isolated by filtration, washed with hexane (3×1 mL) and dried under vacuum. Yield: 71 mg (62%). Elem. anal. calcd for $C_{21}H_{26}N_4O$: C 71.97; H 7.48; N 15.99. Found: C 71.90; H 7.92; N 16.36. 1H NMR (400 MHz, CD_2Cl_2): δ 2.29 (s, 12 H, *o*-Me), 2.31 (s, 6 H, *p*-Me), 4.12 (s, 4 H, CH_2-CH_2), 6.96 (s, 4 H, CH from Mes). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 17.46 (*o*-Me),

20.62 (*p*-Me), 47.97 (CH₂-CH₂), 129.21, 133.93, 135.33, 138.40 (Mes), 165.79 (C=N-N=O). MS (ESI⁺), found: 351.2185 [M + H]⁺; calcd for C₂₁H₂₇N₄O: 351.2257. Crystals, suitable for X-ray analysis, were obtained by slow evaporation of a solution of **8** in hexane/Et₂O (1:4).

General procedure for the thermolysis of **1**, **3**, **5** and **8**



A solution of **1**, **3**, **8** (0.021 M) or **5** (saturated solution at RT) in THF-*d*₈ or bromobenzene-*d*₅ was heated at 60 °C. The time course of the decomposition into the corresponding ureas was determined by ¹H NMR spectroscopy.

9. NMR yield: quant. after 36 h. ¹H NMR (400 MHz, THF-*d*₈): δ 0.91–0.99 (m, 20 H, CH₂), 4.11 (m, 2 H, CH from Cy), 5.92 (s, 2 H, CH=CH). ¹³C{¹H} NMR (100 MHz, toluene-*d*₈): δ 25.38, 25.45, 32.41 (CH₂), 51.68 (CH from Cy), 106.24 (CH=CH), 151.96 (C=O). MS (ESI⁺), found: 249.1967 [M + H]⁺; calcd for C₁₅H₂₅N₂O: 249.2039.

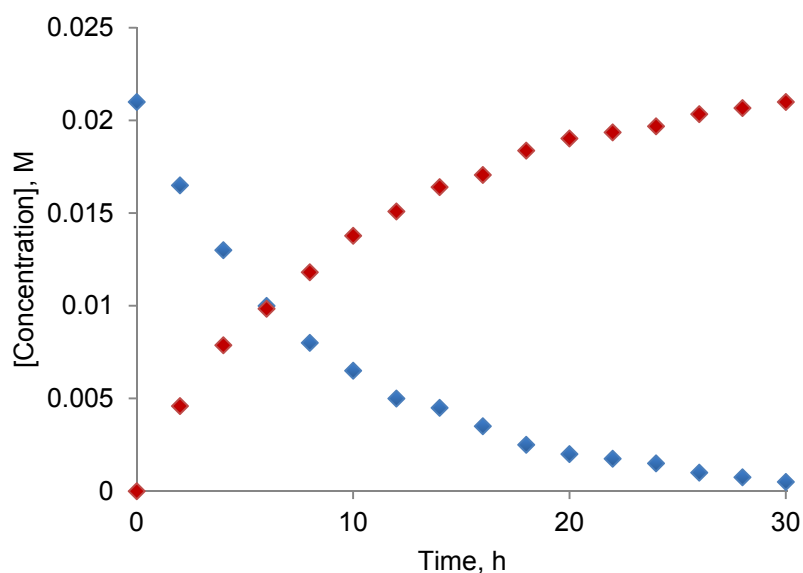


Figure S1. Concentration vs. time for the decomposition of **3** (♦) into **9** (♦) in THF-*d*₈ (0.021 M, 60 °C).

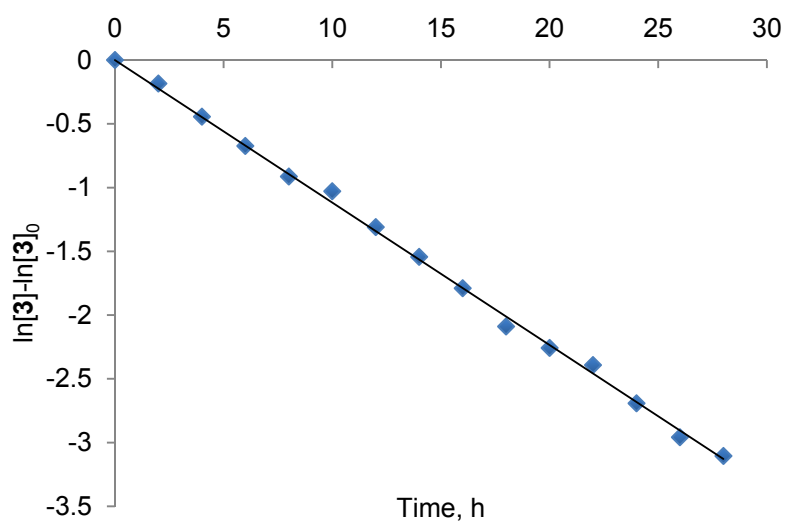


Figure S2. Plot of rate $\ln[3] - \ln[3]_0$ vs. time for the decomposition of **3** into **9** in THF- d_8 (0.021 M, 60 °C). $k = 0.11 \text{ h}^{-1}$, $t_{1/2} = 5.6 \text{ h}$.

10. NMR yield: quant. after 12 h. Analyses were in accord with published data.²

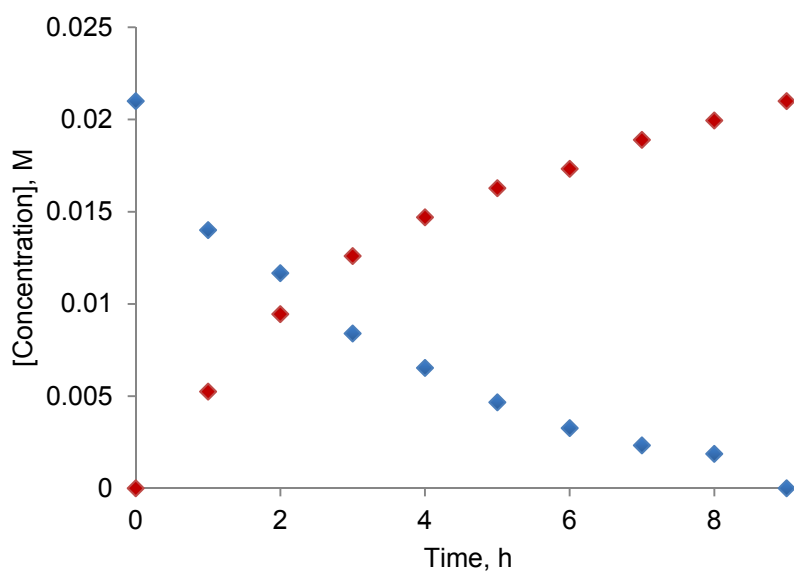


Figure S3. Concentration vs. time for the decomposition of **1** (♦) into **10** (♦) in THF- d_8 (0.021 M, 60 °C).

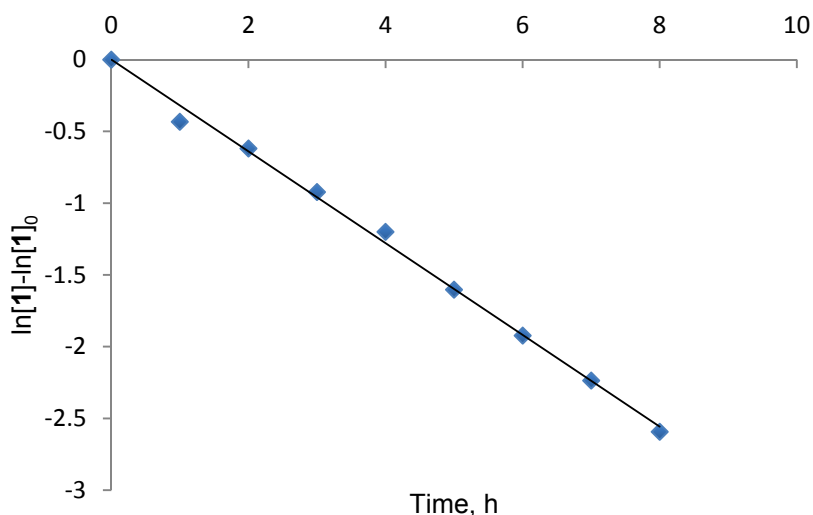


Figure S4. Plot of rate $\ln[1]-\ln[1]_0$ vs. time for the decomposition of **1** into **10** in THF- d_8 (0.021 M, 60 °C). $k = 0.31 \text{ h}^{-1}$, $t_{1/2} = 2.3 \text{ h}$ (for reactions with $[1]_0 = 0.011 \text{ M}$: $k = 0.32 \text{ h}^{-1}$, $t_{1/2} = 2.2 \text{ h}$, for reactions with $[1]_0 = 0.031 \text{ M}$: $k = 0.34 \text{ h}^{-1}$, $t_{1/2} = 2.0 \text{ h}$).

11. NMR yield: quant. after 72 h. ^1H NMR (400 MHz, THF- d_8): δ 0.91 (s, 6 H, CH_3), 4.11 (s, 2 H, $\text{CH}=\text{CH}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, toluene- d_8): δ 25.38 (CH_3), 106.24 ($\text{CH}=\text{CH}$), 151.96 ($\text{C}=\text{O}$). MS (ESI^+), found: 113.0715 $[\text{M} + \text{H}]^+$; calcd for $\text{C}_5\text{H}_9\text{N}_2\text{O}$: 113.0787.

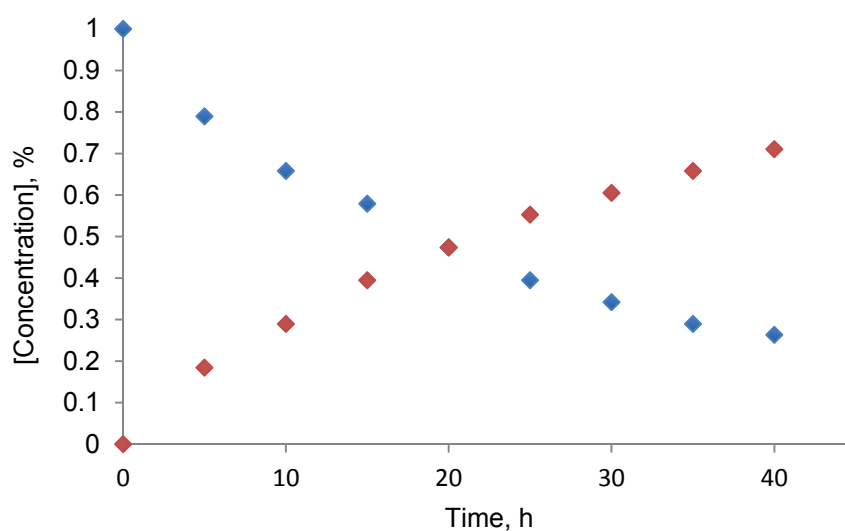


Figure S5. Concentration vs. time for the decomposition of **5** (♦) into **11** (♦) in bromobenzene- d_3 (60 °C).

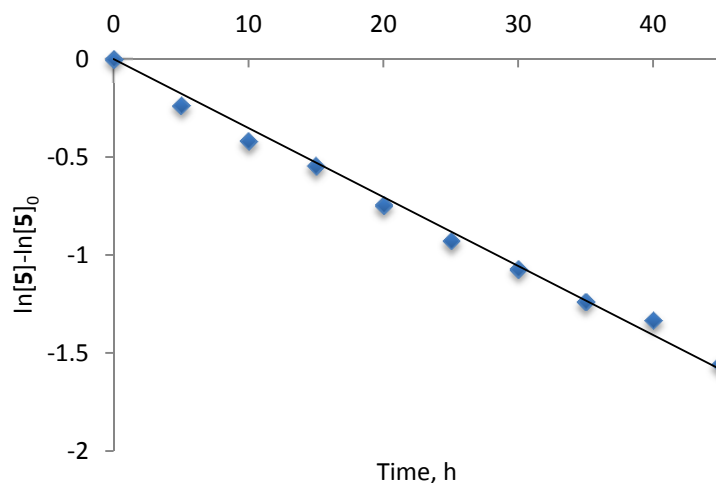


Figure S6. Plot of rate $\ln[5]-\ln[5]_0$ vs. time for the decomposition of **5** into **11** in bromobenzene- d_5 (60 °C). $k = 0.035 \text{ h}^{-1}$, $t_{1/2} = 19.7 \text{ h}$.

12. NMR yield: quant. after 2 h. ^1H NMR (400 MHz, THF- d_8): δ 2.24 (s, 6 H, *o*-Me), 2.26 (s, 12 H, *p*-Me), 3.73 (s, 4 H, $\text{CH}_2\text{-CH}_2$), 6.86 (s, 4 H, CH from Mes). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, THF- d_8): δ 17.08 (*o*-Me), 20.03 (*p*-Me), 43.76 ($\text{CH}_2\text{-CH}_2$), 128.67, 134.48, 136.46, 136.99 (C and CH from Mes), 156.18 (C=O). MS (ESI $^+$), found: 323.2123 $[\text{M} + \text{H}]^+$; calcd for $\text{C}_{21}\text{H}_{27}\text{N}_2\text{O}$: 323.2123.

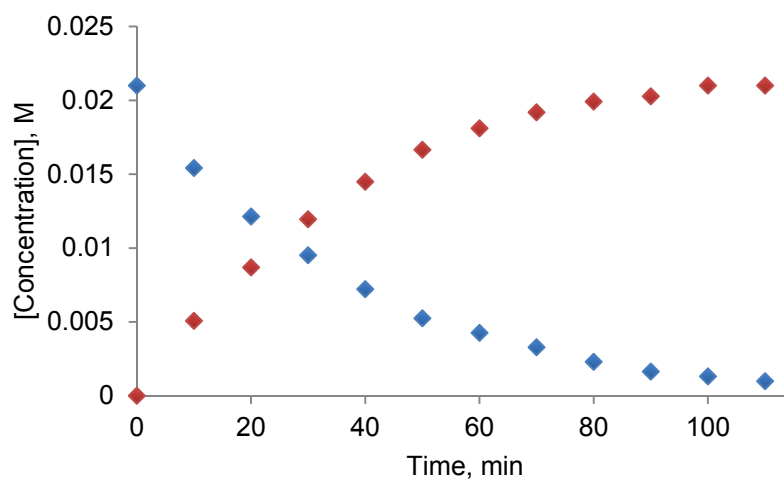


Figure S7. Concentration vs. time for the decomposition of **8** (♦) into **12** (♦) in THF- d_8 (0.021 M, 60 °C).

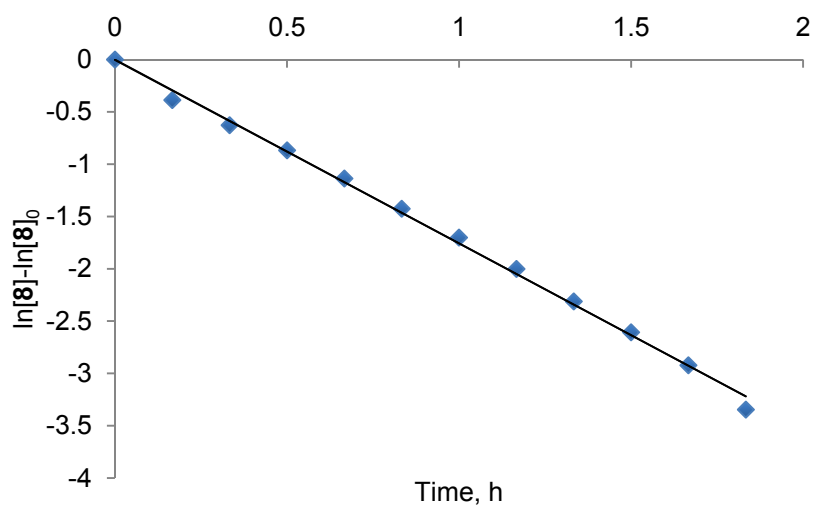
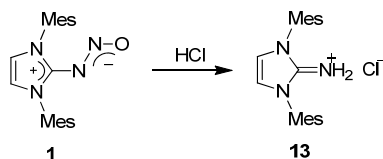


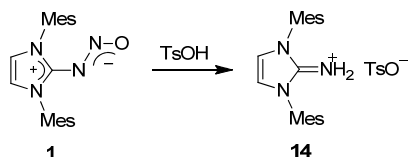
Figure S8. Plot of rate $\ln[8]-\ln[8]_0$ vs. time for the decomposition of **8** into **12** in THF- d_8 (0.021 M, 60 °C). $k = 1.66 \text{ h}^{-1}$, $t_{1/2} = 0.4 \text{ h}$.

Synthesis of compound 13



Excess of HCl, (0.2 mL, 37% in water) was added to a solution of **1** (50 mg, 0.14 mmol) in CH₂Cl₂ (20 mL) and the resulting mixture was stirred for 0.5 h. The solution was subsequently concentrated to ca. 1 mL, Et₂O (10 mL) was added, and the white solid was isolated by filtration and dried under vacuum. Yield: 22 mg (45%). Elem. anal. calcd for C₂₁H₂₆N₃Cl: C 70.86; H 7.36; N 11.81. Found: C 70.49; H 7.30; N 11.94. ¹H NMR (400 MHz, CD₂Cl₂): δ 2.21 (s, 12 H, *o*-Me), 2.40 (s, 6 H, *p*-Me), 6.79 (s, 2 H, CH=CH), 7.12 (s, 4 H, CH, arenes), 7.52 (s, br, 2 H, NH₂). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ 17.26 (*o*-Me), 21.06 (*p*-Me), 116.77, 128.23, 129.97, 135.87, 141.40 (arenes, CH=CH), 145.70 (C=NH₂). MS (ESI⁺), found: 320.2127 [M – Cl]⁺; calcd for C₂₁H₂₆N₃: 320.2199.

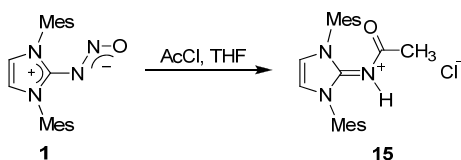
Synthesis of compound 14



TsOH (92 mg, 0.48 mmol) was added to a solution of **1** (84 mg, 0.24 mmol) in THF (5 mL) and the resulting mixture was stirred for 0.5 h. Hexane (10 mL) was added to the solution and the resulting colorless solid was isolated by filtration and dried under vacuum. Yield: 55 mg (47%). Elem. anal. calcd for C₂₈H₃₄N₃O₃S: C 68.26; H 6.96; N 8.53. Found: C 68.06; H 6.74; N 8.38. ¹H NMR (400 MHz, CD₂Cl₂): δ 2.18 (s, 12 H, *o*-Me), 2.38 (s, 3 H, *p*-Me from Ts), 2.39 (s, 6 H, *p*-Me from Mes), 6.79 (s, 2 H, CH=CH), 7.07 (s, br, 2 H, NH₂), 7.09 (s, 4 H, CH from Mes), 7.11 (d, 7.30 Hz, 2 H, CH from Ts), 7.40 (d, 7.30 Hz, 2 H, CH from Ts). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ 17.23 (*o*-Me), 20.92 (*p*-Me from Mes), 20.94 (*p*-Me from Ts), 116.82, 125.66, 128.10, 128.27, 130.05, 135.88, 138.95, 141.52, 143.85, (arenes, CH=CH), 145.83 (C=NH₂). MS (ESI⁺), found: 320.2127 [M – TsO]⁺; calcd for C₂₁H₂₆N₃:

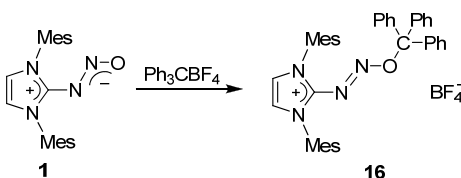
320.2199. Crystals, suitable for X-ray analysis, were obtained by slow evaporation of a solution of **14** in hexane/THF (1:4).

Synthesis of compound 15



AcCl (0.72 mmol, 57 mg) was added to a solution of **1** (0.24 mmol, 85 mg) in THF (5 mL). After 30 min, hexane (5 mL) was added, and the colorless solid was collected, washed with hexane (3×3 mL), and dried under vacuum. Yield: 80 mg (84%). Elem. anal. calcd for C₂₃H₂₈ClN₄O: C 69.42; H 7.09; N 10.56. Found: C 69.22; H 7.08; N 10.46. ¹H NMR, (400 MHz, CD₂Cl₂): δ 1.84 (s, 3 H, C(O)Me), 2.17 (s, 12 H, *p*-Me), 2.29 (s, 6 H, *o*-Me), 6.99 (s, 4 H, CH from Mes), 7.21 (s, 2 H, CH=CH), 13.30 (s, 1 H, NH). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ 17.61 (*o*-Me), 20.90 (*p*-Me), 22.36 (C(O)Me), 121.77, 129.71, 135.31, 141.31 (arenes, CH=CH), 140.90 (C=N), 171.57 (C(O)Me). MS (ESI⁺), found: 362.2232 [M – Cl]⁺; calcd for C₂₃H₂₈N₃O: 362.2305. Crystals, suitable for X-ray analysis, were obtained by the slow evaporation of a solution of **15** in hexane/THF (1:4).

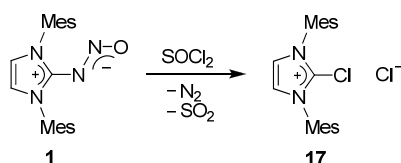
Synthesis of compound 16



Ph₃CBF₄ (0.25 mmol, 83 mg) was added to a solution of **1** (0.25 mmol, 87 mg) in CH₂Cl₂ (5 mL) and the solution was stirred at RT. After 30 min, the solution was evaporated to dryness. The resulting light-yellow solid was washed with Et₂O (3×3 mL) and dried under vacuum. Yield: 140 mg (82%). Elem. anal. calcd for C₄₀H₃₉N₄OBF₄: C 69.16; H 5.79; N 8.25.

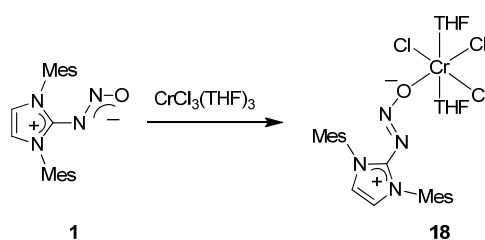
Found: C 69.14; H 6.02; N 8.04. ^1H NMR (400 MHz, CDCl_3): δ 1.89 (s, 12 H, *o*-Me), 2.34 (s, 6 H, *p*-Me), 6.80 (d, $J = 7.5$ Hz, 6 H, *o*-CH from Ph), 6.95 (s, 4 H, CH from Mes), 7.25 (m, 6 H, *m*-CH from Ph), 7.34 (m, 3 H, *p*-CH from Ph), 7.83 (s, 2 H, CH=CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2): δ 17.10 (*o*-Me), 20.94 (*p*-Me), 98.40 (CPh_3), 125.51-142.02 (arenes, CH=CH, CN=NO). MS (ESI^+), found: 592.3202 $[\text{M} - \text{BF}_4]^+$; calcd for $\text{C}_{40}\text{H}_{39}\text{N}_4\text{O}$: 592.3196. Crystals, suitable for X-ray analysis, were obtained by slow evaporation of a solution of **16** in hexane/ CH_2Cl_2 (1:1).

Synthesis of compound 17



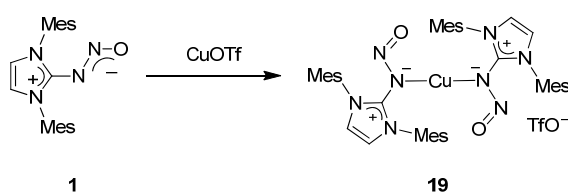
SOCl_2 (0.21 mmol, 25 mg) was added to a solution of **1** (0.18 mmol, 63 mg) in THF (5 mL). The formation of bubbles was observed immediately. After 30 min, a brown-yellow solid was isolated by filtration. Hexane (3 mL) was added to the filtrate, and an additional amount of product was collected. The combined solids were washed with hexane (3×3 mL) and dried under vacuum. Yield: 52 mg (76%). Analyses were in accord with published data.³ *Qualitative detection of SO_2* : The formation of SO_2 was evidenced by the placing of a paper test stripe soaked with a $\text{Na}_2\text{Cr}_2\text{O}_7$ solution over the reaction mixture after the addition of SOCl_2 . The color of the test stripe turned from orange to green.

Synthesis of complex 18



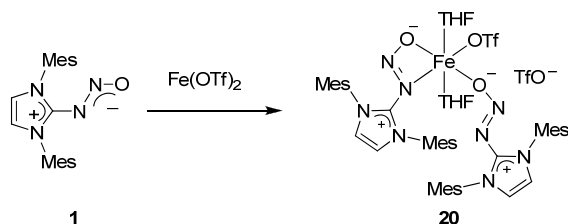
1 (0.11 mmol, 40 mg) was added to a suspension of $\text{CrCl}_3(\text{THF})_3$ (0.11 mmol, 43 mg) in THF (5 mL). After 24 h, the pale purple precipitate was filtered, washed with THF (3×1 mL), and dried under vacuum. Yield: 61 mg (82%). Elem. anal. calcd for $\text{C}_{29}\text{H}_{40}\text{Cl}_3\text{N}_4\text{O}_3\text{Cr}$: C 53.60; H 6.21; N 8.62. Found: C 53.14; H 5.89; N 8.34. Crystals, suitable for X-ray analysis, were obtained by slow evaporation of a solution of **18** in THF.

Synthesis of complex 19



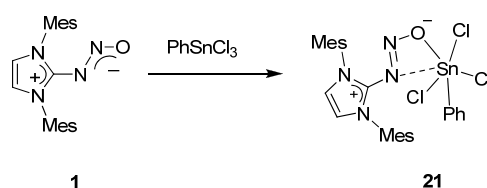
1 (0.46 mmol, 200 mg) was added to a suspension of $[\text{Cu}(\text{OTf})]_2 \cdot \text{toluene}$ (0.14 mmol, 74 mg) in THF (5 mL), and the solution was kept under N_2 resulting in the precipitation of a dark yellow solid. After 24 h, hexane (10 mL) was added under stirring and the precipitate was filtered, washed with hexane (3×1 mL), and dried under vacuum. Yield: 230 mg (84%). Elem. anal. calcd for $\text{C}_{43}\text{H}_{48}\text{CuF}_3\text{N}_8\text{O}_5\text{S}$: C 56.79; H 5.32; N 12.32. Found: C 56.55; H 5.12; N 11.82. ^1H NMR (400 MHz, CDCl_3): δ 2.00 (s, 24 H, *o*-Me), 2.25 (s, 12 H, *p*-Me), 6.89 (s, 8 H, CH, Mes), 7.17 (s, 4 H, CH=CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz CDCl_3): δ 17.75 (*o*-Me), 21.13 (*p*-Me), 121.01, 129.81, 130.40, 134.41, 140.66 (arenes, CH=CH), 146.98 (CNNO). MS (ESI^+), found: 759.3196 $[\text{M} - \text{CF}_3\text{SO}_3]^+$; calcd for $\text{C}_{42}\text{H}_{48}\text{CuN}_8\text{O}_2$: 759.3368. Crystals, suitable for X-ray analysis, were obtained by slow evaporation of a solution of **19** in THF.

Synthesis of complex 20



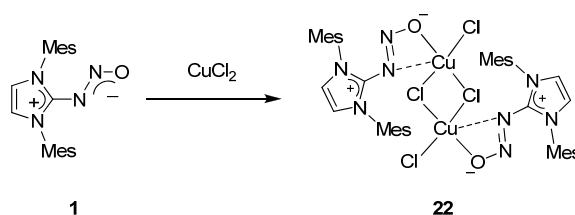
1 (0.13 mmol, 45 mg) was added to a suspension of $\text{Fe}(\text{OTf})_2$ (0.065 mmol, 23 mg) in THF (5 mL) and the suspension was stirred under N_2 . After 24 h, the dark red solution was layered with hexane (10 mL), which resulted in the formation of a red oil and a few crystals of **21**. Due to the low yield, an elemental analysis was not performed.

Synthesis of complex **21**



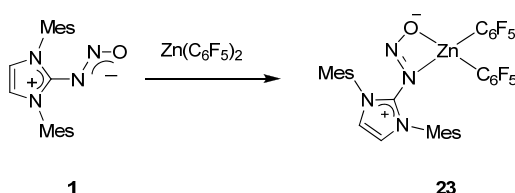
1 (0.23 mmol, 80 mg) was added to a solution of SnCl_3Ph (0.23 mmol, 69 mg) in THF (10 mL), and the colorless solution was kept under N_2 for 24 h resulting in the precipitation of a colorless solid. Hexane (10 mL) was added under stirring and the precipitate was filtered, washed with hexane (3×1 mL), and dried under vacuum. Yield: 140 mg (94%). Elem. anal. calcd for $\text{C}_{27}\text{H}_{29}\text{Cl}_3\text{N}_4\text{OSn}$: C 49.84; H 4.49; N 8.61. Found: C 49.38; H 4.52; N 8.68. ^1H NMR (400 MHz, CD_2Cl_2): δ 2.07 (s, 12 H, *o*-Me), 2.35 (s, 6 H, *p*-Me), 6.91 (s, 4 H, CH, Mes), 7.27 (s, 2 H, CH=CH), 7.38–7.48 (m, 3 H, *m*-CH and *p*-CH from Ph), 7.75 (d, 7.1 Hz, 2 H, *o*-CH from Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2): δ 17.37 (*o*-Me), 20.99 (*p*-Me), 122.32, 128.36, 129.67, 130.16, 134.12, 134.54, 141.52, 141.84 (arenes, CH=CH), 147.39 (CNNO). Crystals, suitable for X-ray analysis, were obtained by slow evaporation of a solution of **21** in THF.

Synthesis of complex **22**



1 (0.23 mmol, 80 mg) was added to a suspension of CuCl₂ (0.23 mmol, 31 mg) in MeOH (2 mL), what led to the formation of brown yellow solution. After 24 h, the solution was concentrated to *ca.* 1 mL. The resulting precipitate was isolated by filtration, washed with methanol (3×0.5 mL), and dried under vacuum. Yield: 52 mg (46%). Elem. anal. calcd for C₄₂H₄₈Cl₄Cu₂N₈O₂: C 52.23; H 5.01; N 11.60. Found: C 51.77; H 5.17; N 11.21. MS (ESI⁺), found: 965.1304 [M + H]⁺; calcd for C₄₂H₄₉Cl₄Cu₂N₈O₂: 965.1597. Crystals, suitable for X-ray analysis, were obtained by slow evaporation of a solution of **22** in MeOH.

Synthesis of complex **23**



1 (0.16 mmol, 57 mg) was added to a solution of Zn(C₆F₅)₂ (0.16 mmol, 65 mg) in CH₂Cl₂ (2 mL). Hexane (2 mL) was added to the colorless solution and the resulting precipitate was isolated by filtration, washed with hexane (3×1 mL), and dried under vacuum. Yield: 85 mg (69%). Elem. anal. calcd for C₃₃H₂₄F₁₀N₄OZn: C 52.99; H 3.23; N 7.49. Found: C 52.76; H 3.16; N 7.49. ¹H NMR (400 MHz, CD₂Cl₂): δ 1.94 (s, 12 H, *o*-Me), 2.18 (s, 6 H, *p*-Me), 6.79 (s, 4 H, CH, Mes), 7.06 (s, 2 H, CH=CH). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ 17.05 (*o*-Me), 20.69 (*p*-Me), 119.23 (m), 135.32 (m), 136.88 (m), 138.83 (m), 140.46 (m), 147.93 (m), 149.44 (m, C₆F₅), 120.80 (CH=CH), 129.38 (CH from Mes), 130.39, 134.57, 141.21 (C from Mes), 145.49 (CNNO). MS (ESI⁺), found: 747.1160 [M + H]⁺; calcd for C₃₃H₂₅F₁₀N₄OZn: 747.1232. Crystals, suitable for X-ray analysis, were obtained by slow evaporation of a solution of **23** in CH₂Cl₂/hexane (1:1).

NMR and UV spectra

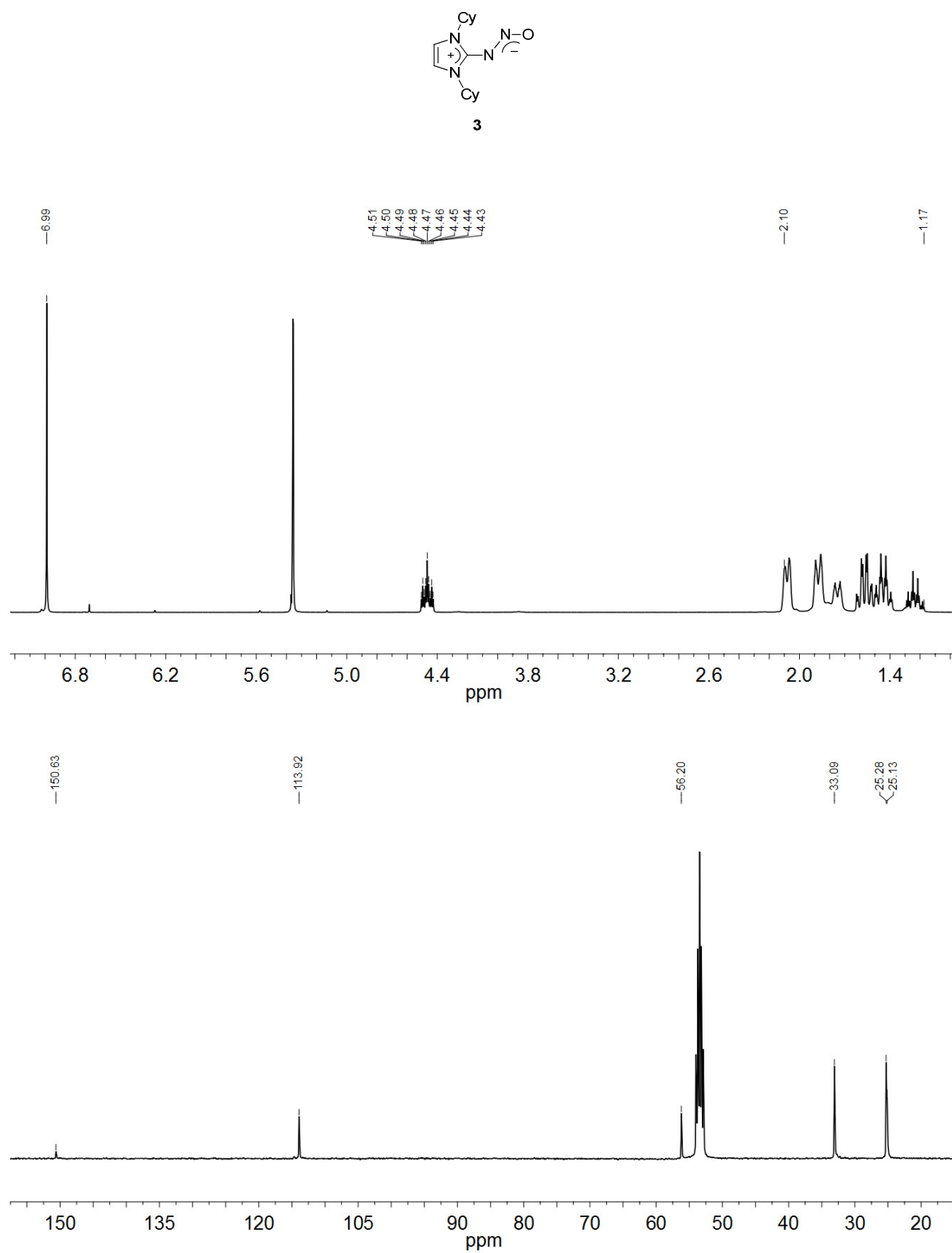


Figure S9. ^1H (top) and ^{13}C (bottom) NMR spectra of **3** in CD_2Cl_2 .

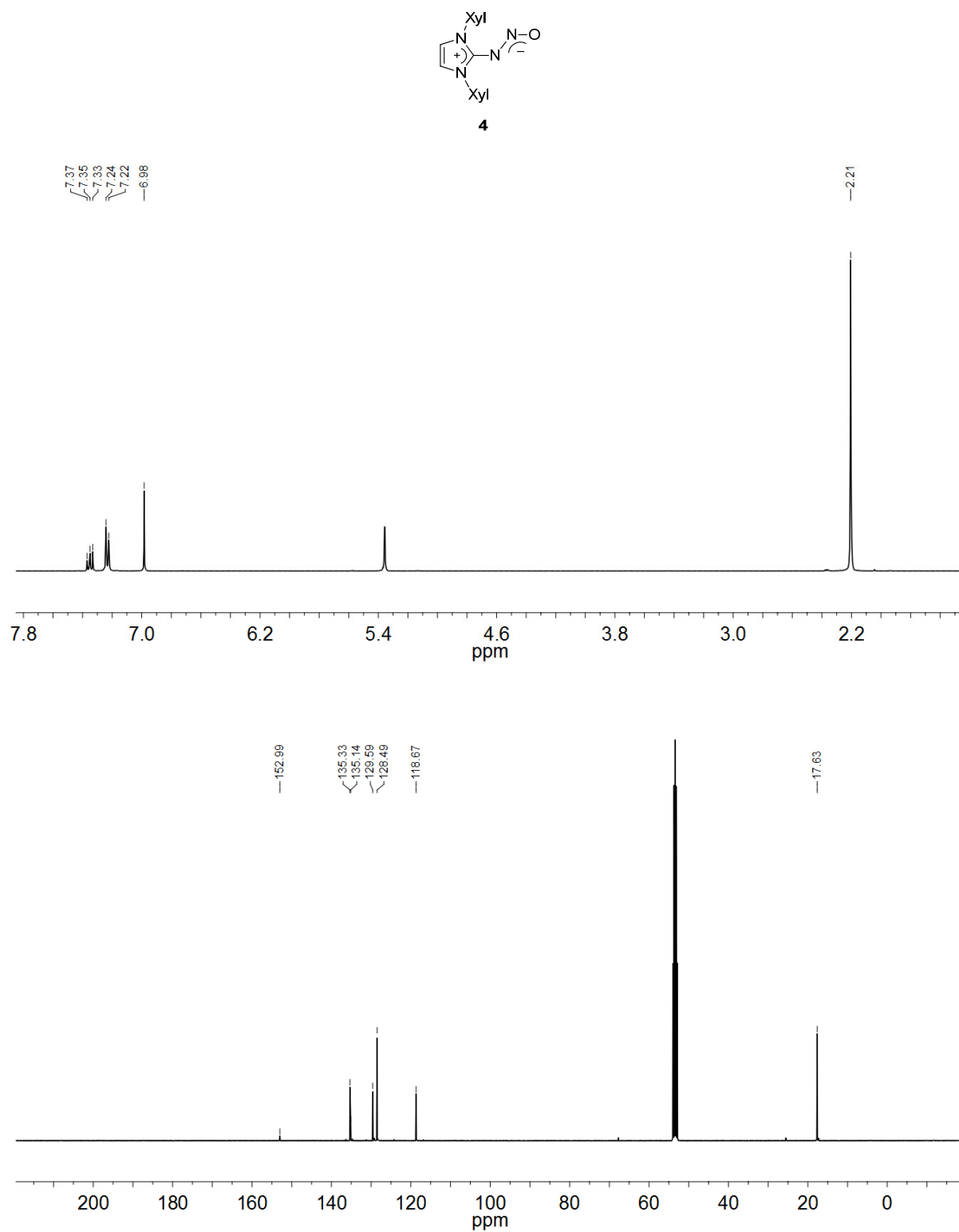


Figure S10. ¹H (top) and ¹³C (bottom) NMR spectra of **4** in CD₂Cl₂.

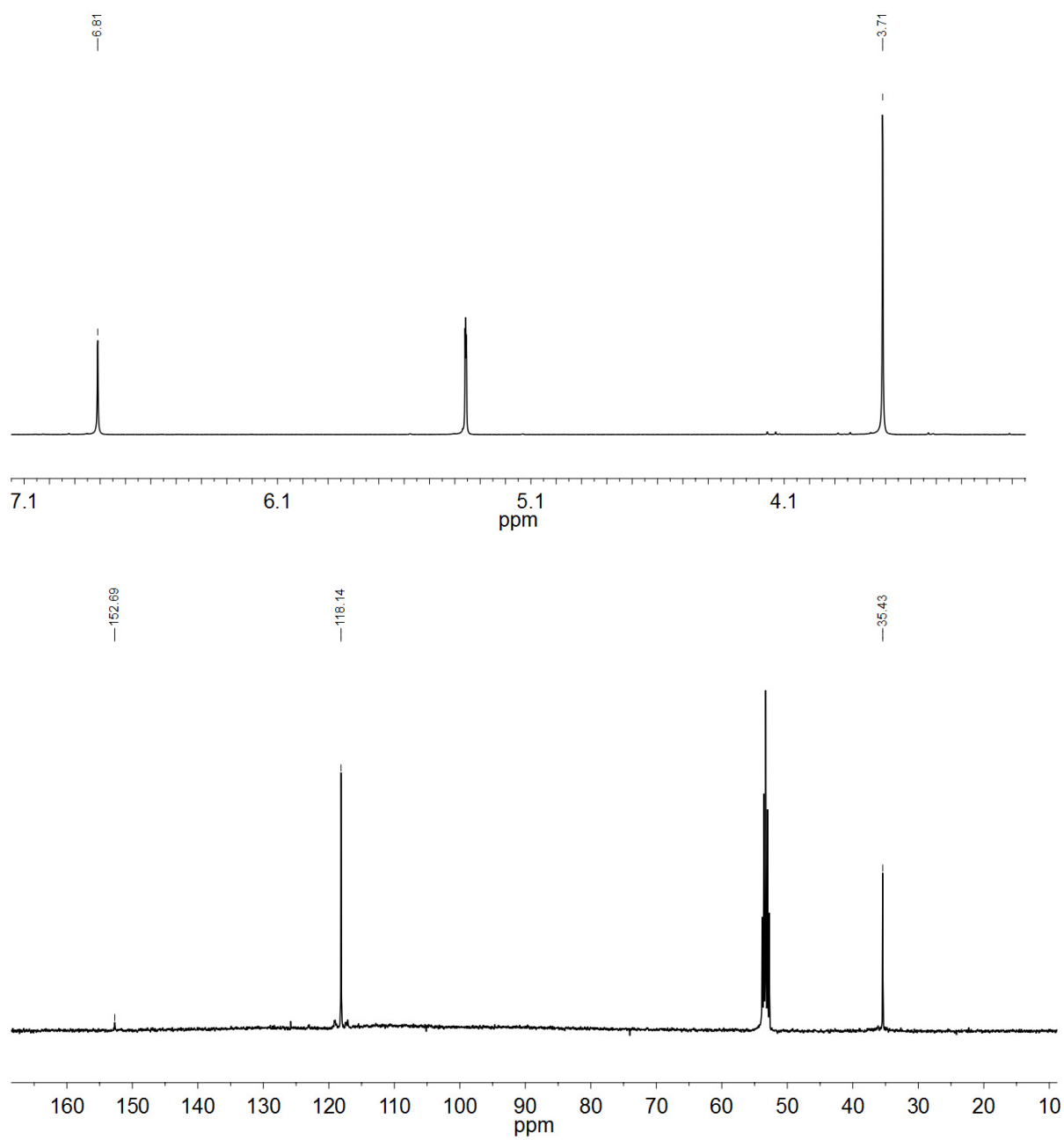
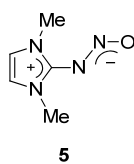


Figure S11. ^1H (top) and ^{13}C NMR spectra of **5** in CD_2Cl_2 .

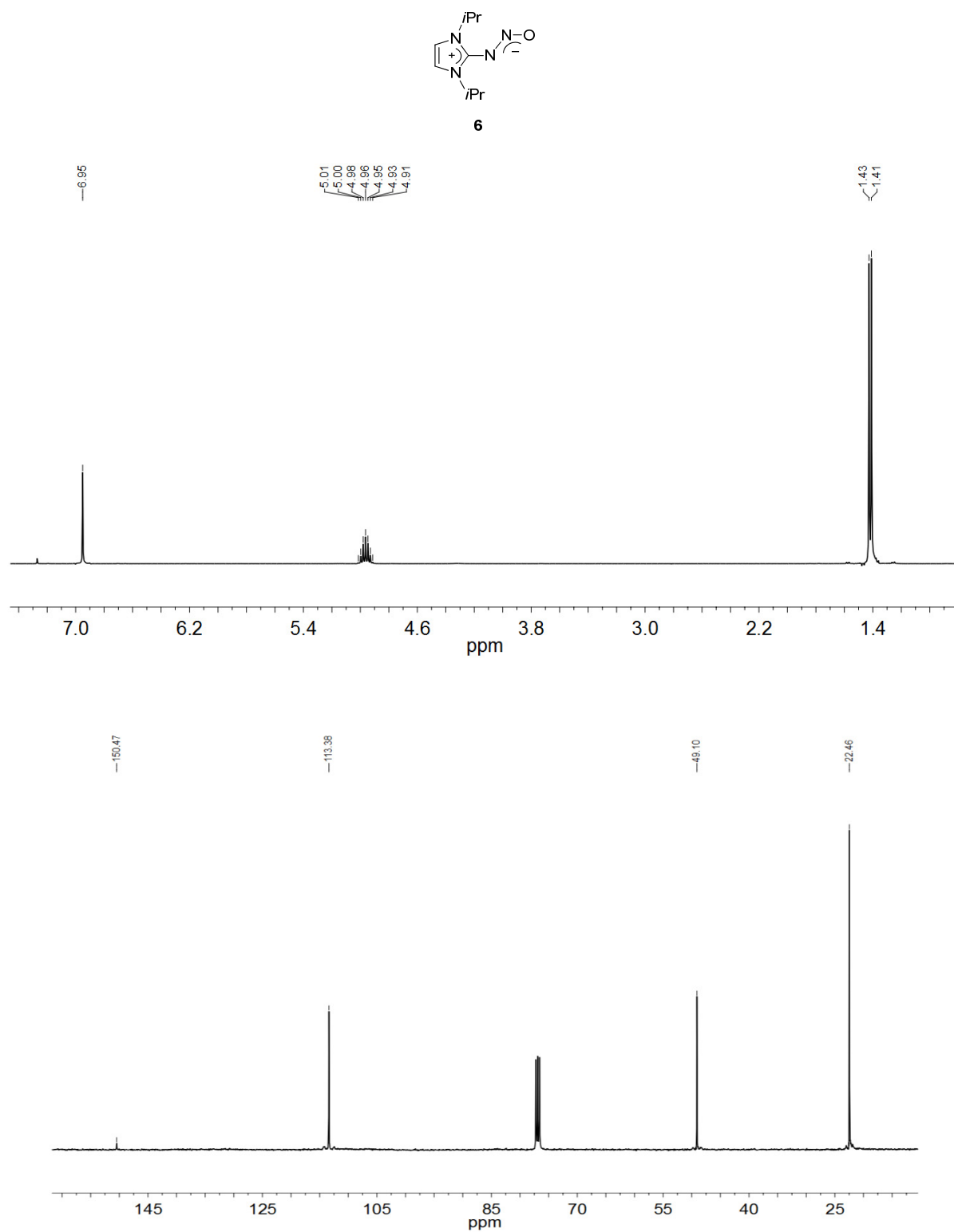


Figure S12. ¹H (top) and ¹³C (bottom) NMR spectra of **6** in CDCl₃.

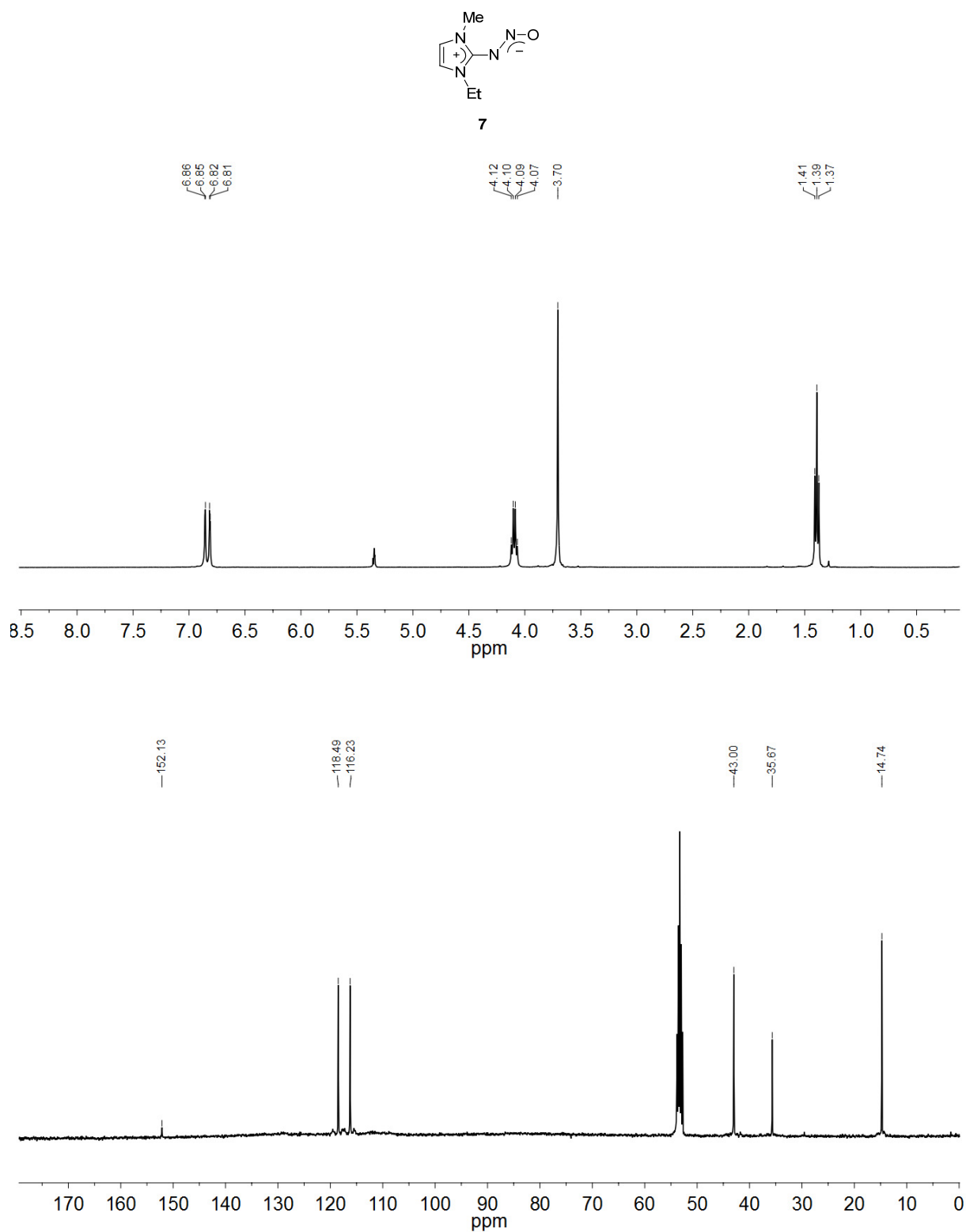


Figure S13. ¹H (top) and ¹³C (bottom) NMR spectra of **7** in CD₂Cl₂.

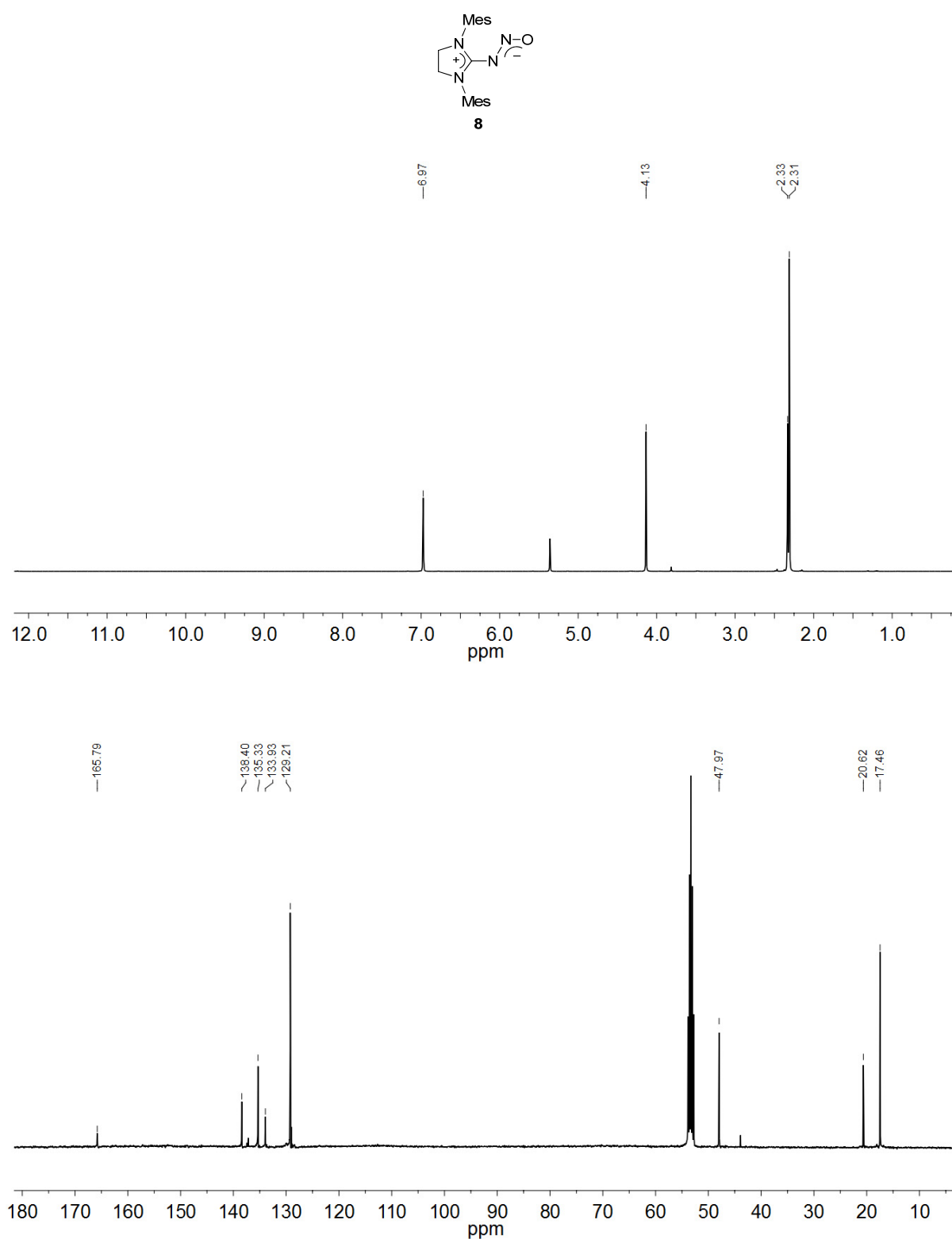


Figure S14. ¹H (top) and ¹³C (bottom) NMR spectra of **8** in CD₂Cl₂.

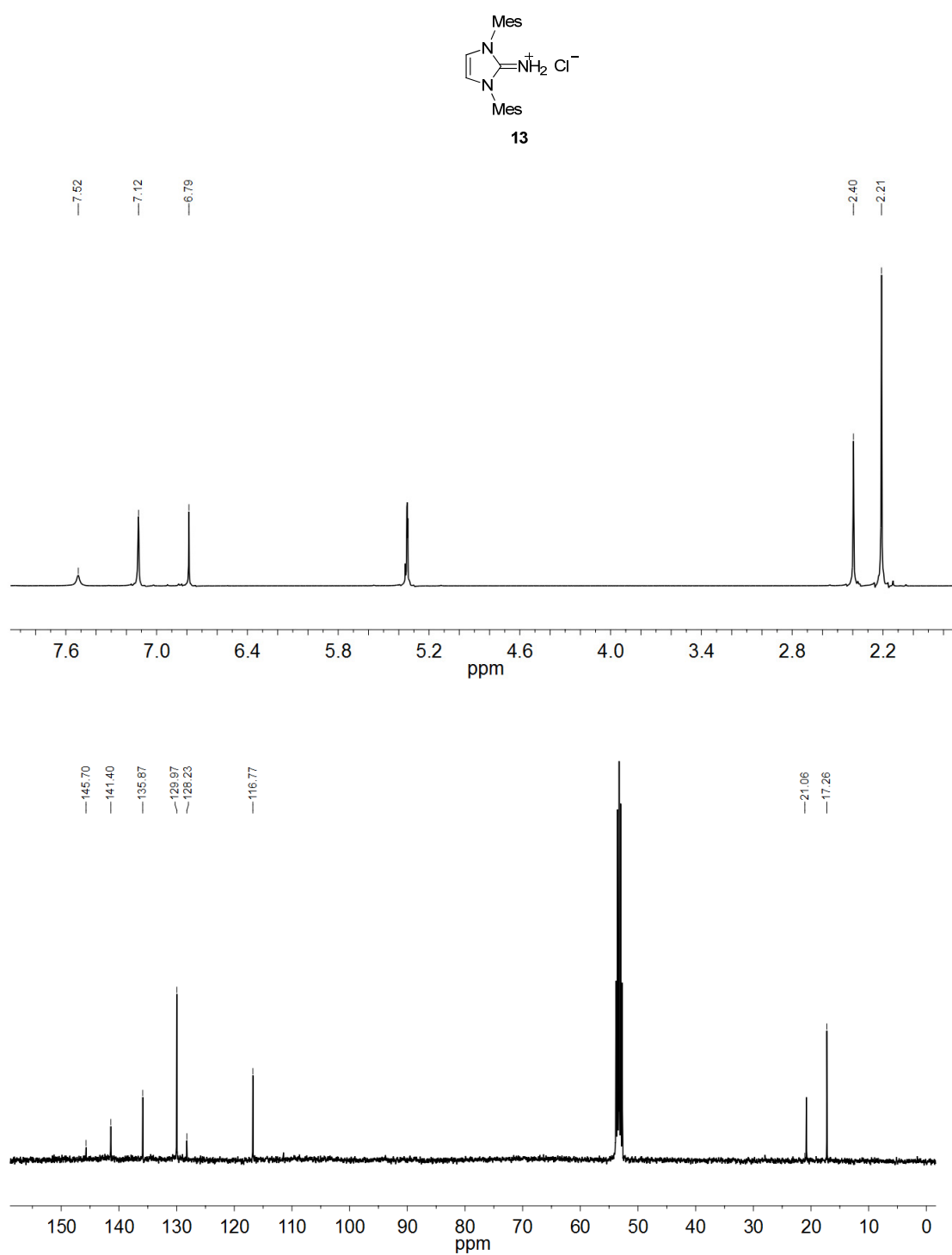


Figure S15. ¹H (top) and ¹³C (bottom) NMR spectra of **13** in CD₂Cl₂.

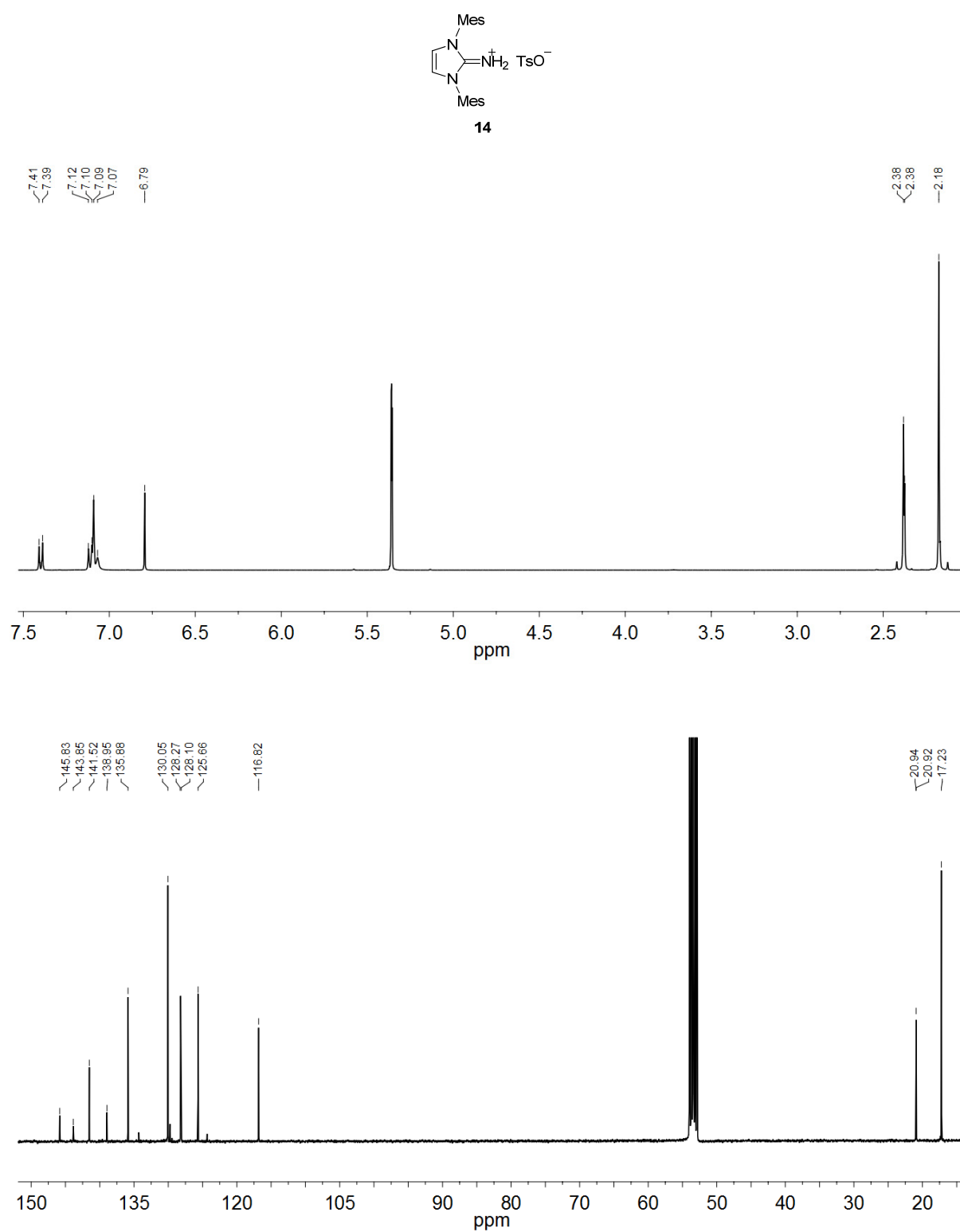


Figure S16. ¹H (top) and ¹³C (bottom) NMR spectra of **14** in CD₂Cl₂.

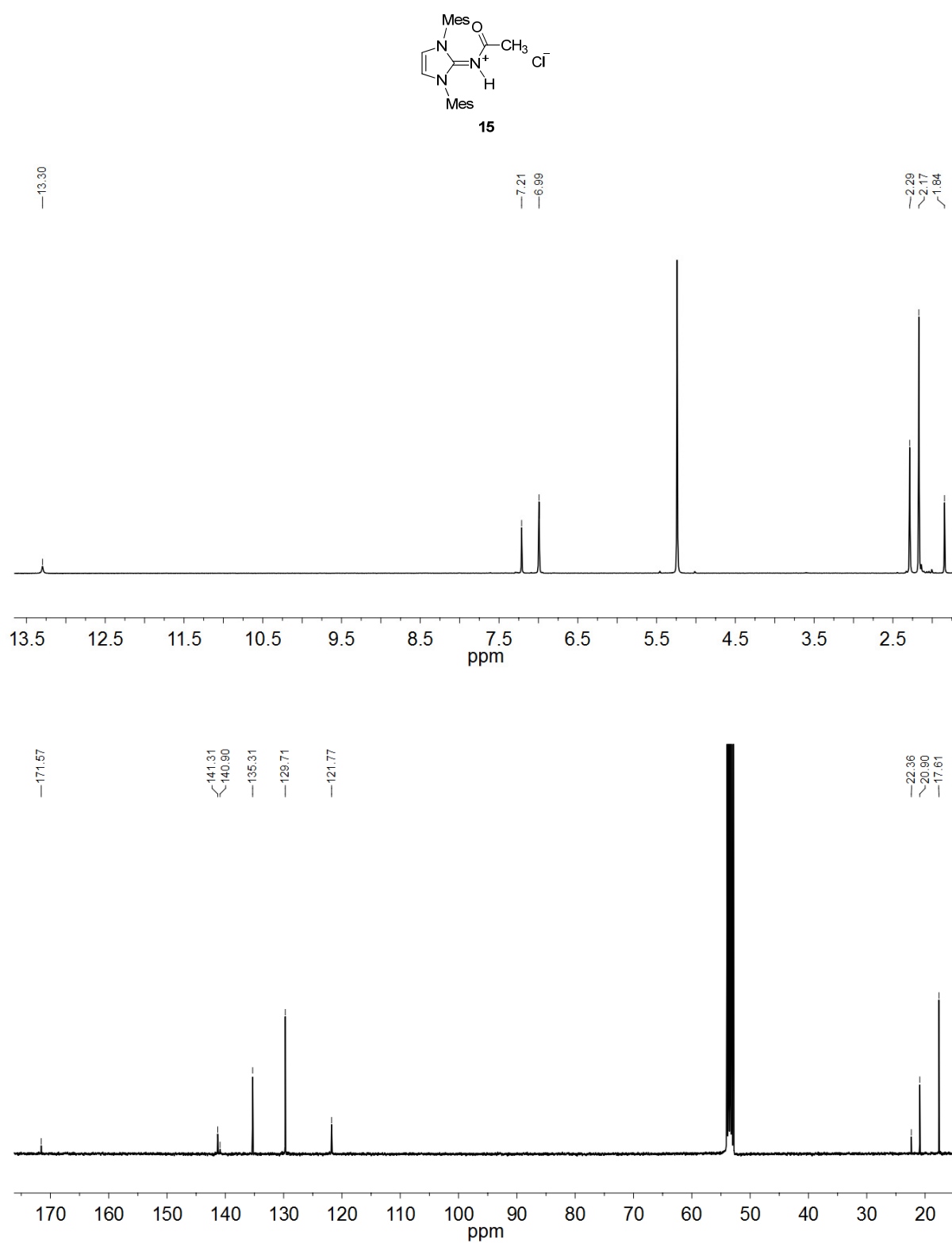


Figure S17. ¹H (top) and ¹³C (bottom) NMR spectra of **15** in CD₂Cl₂.

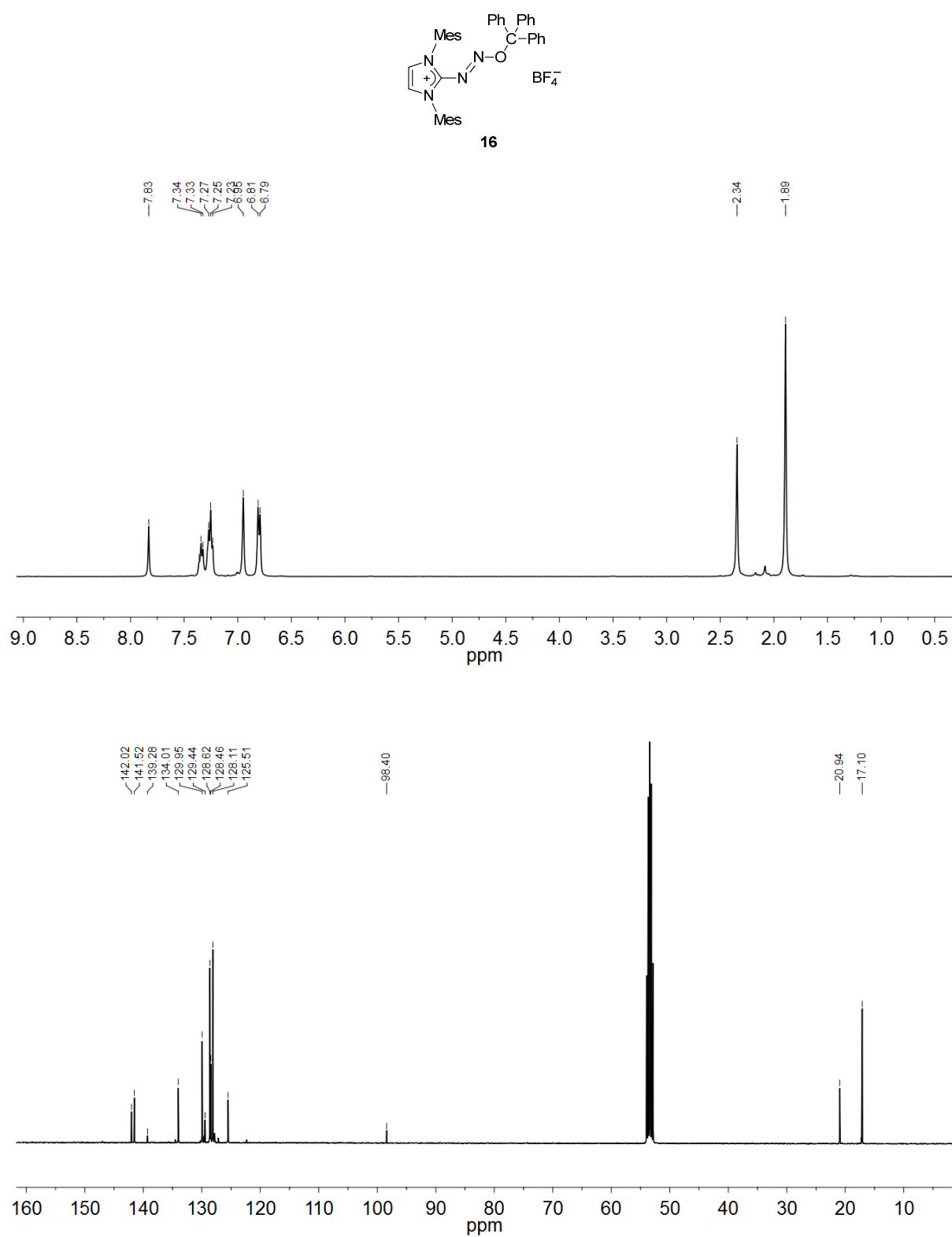
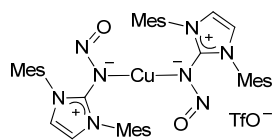


Figure S18. ¹H (top) and ¹³C (bottom) NMR spectra of **16** in CD₂Cl₂.



19

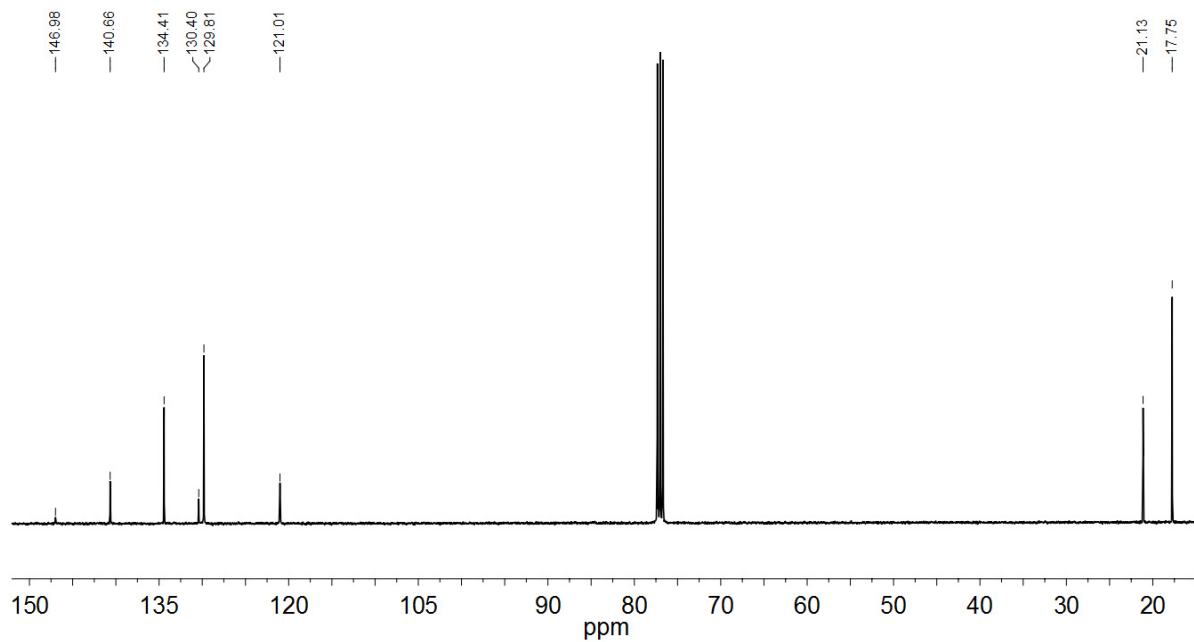
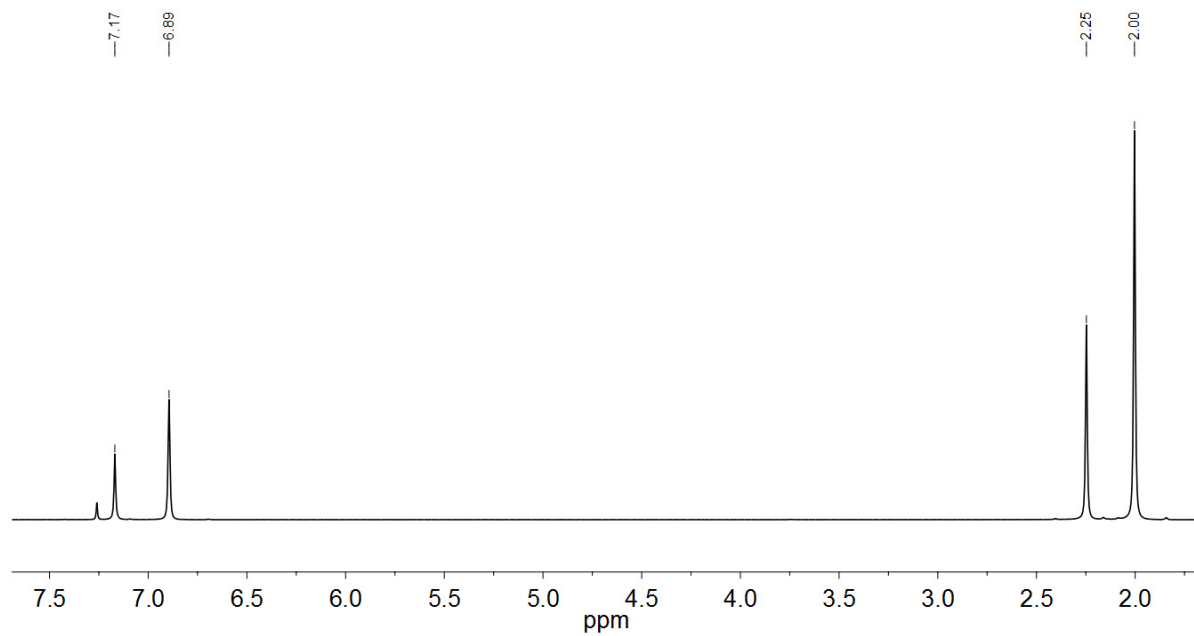


Figure S19. ¹H (top) and ¹³C (bottom) NMR spectra of **19** in CDCl₃.

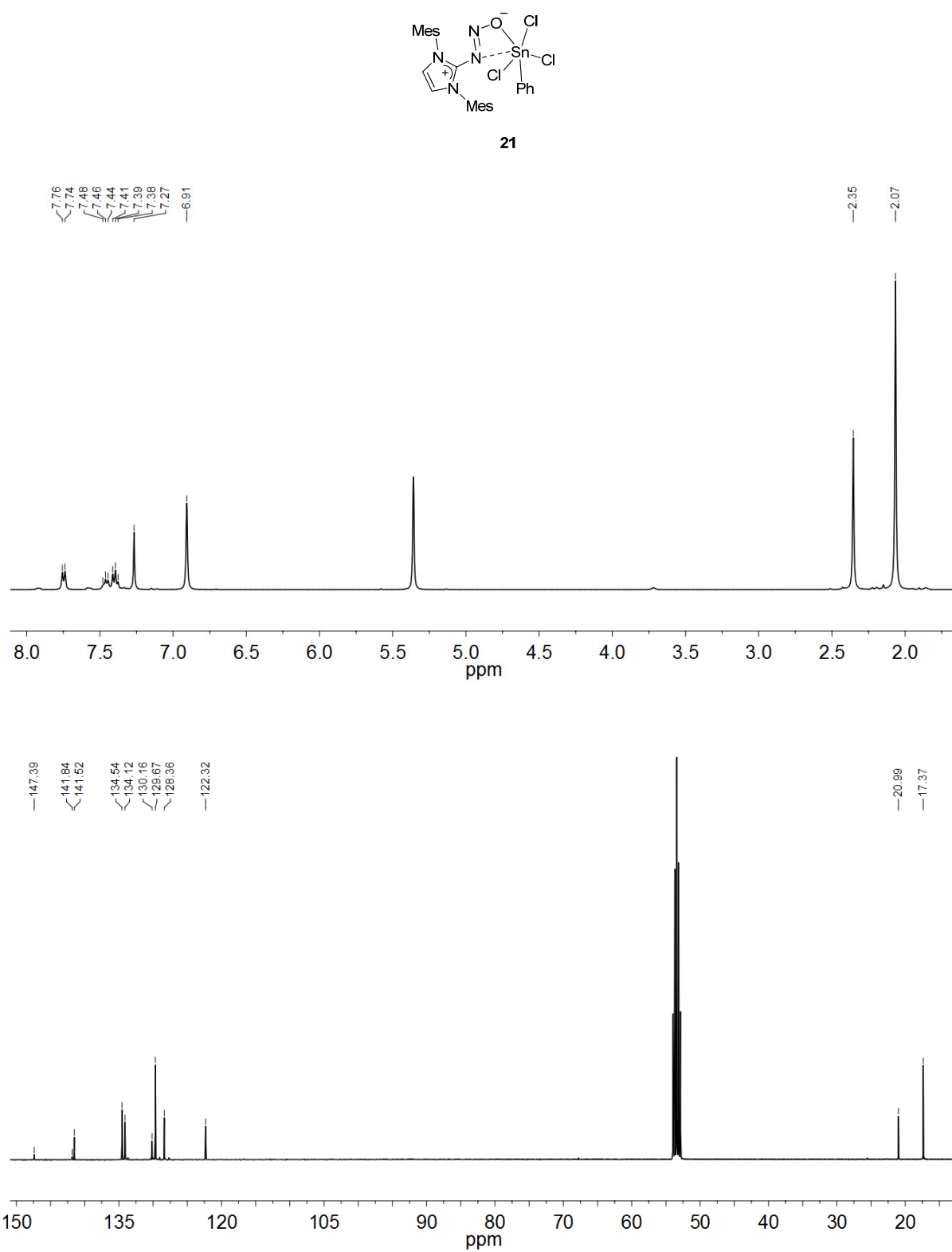
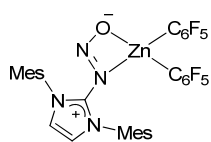


Figure S20. ¹H (top) and ¹³C (bottom) NMR spectra of **21** in CDCl₃.



23

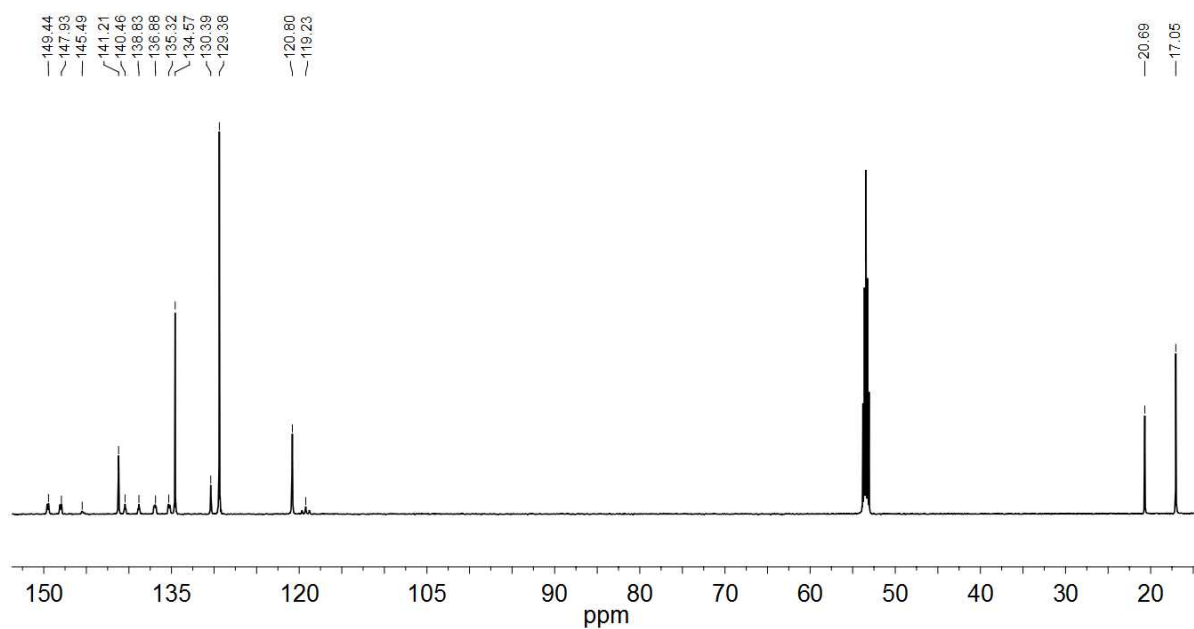
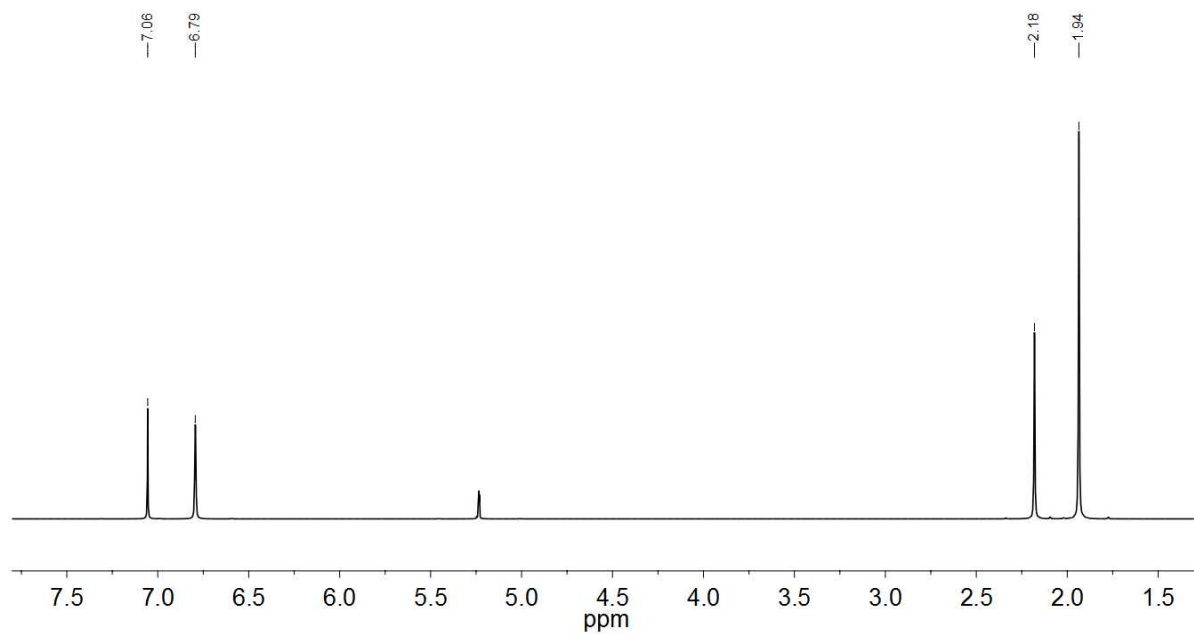


Figure S21. ^1H (top) and ^{13}C (bottom) NMR spectra of **23** in CDCl_3 .

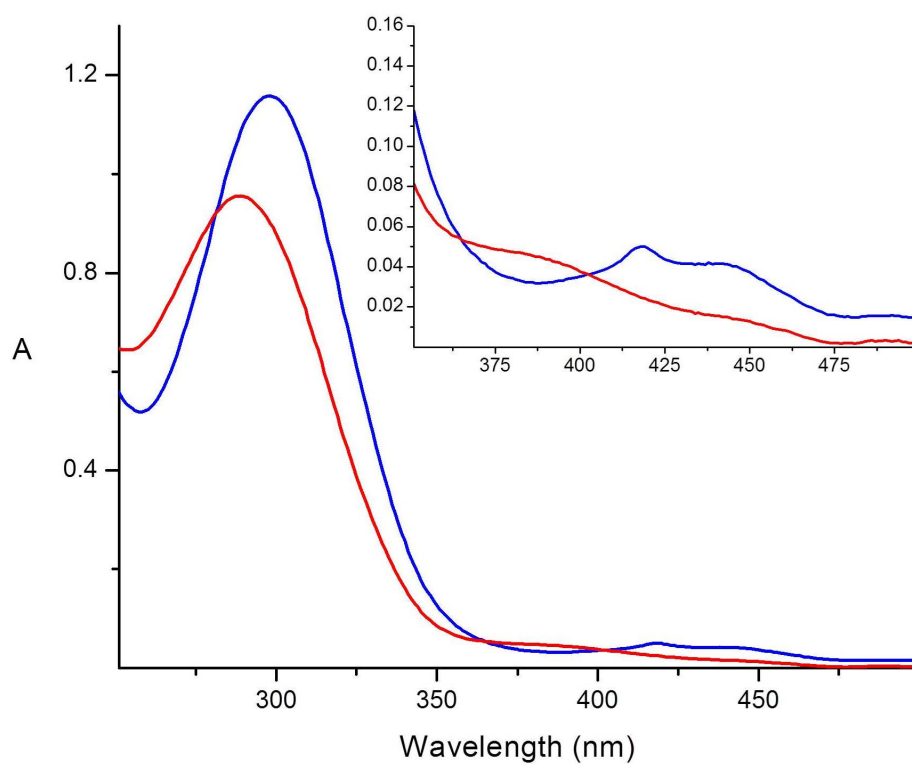


Figure S22. UV spectra of **5** in H₂O (red) and CH₂Cl₂ (blue).

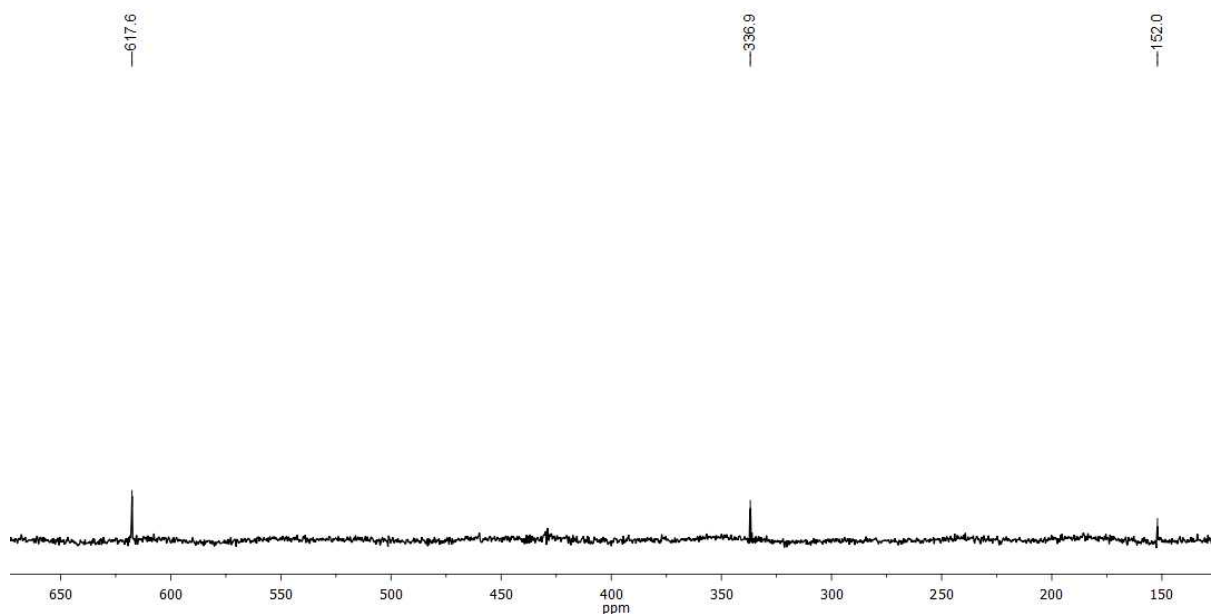


Figure S23. ^{15}N NMR spectrum of **1** in CDCl_3 .

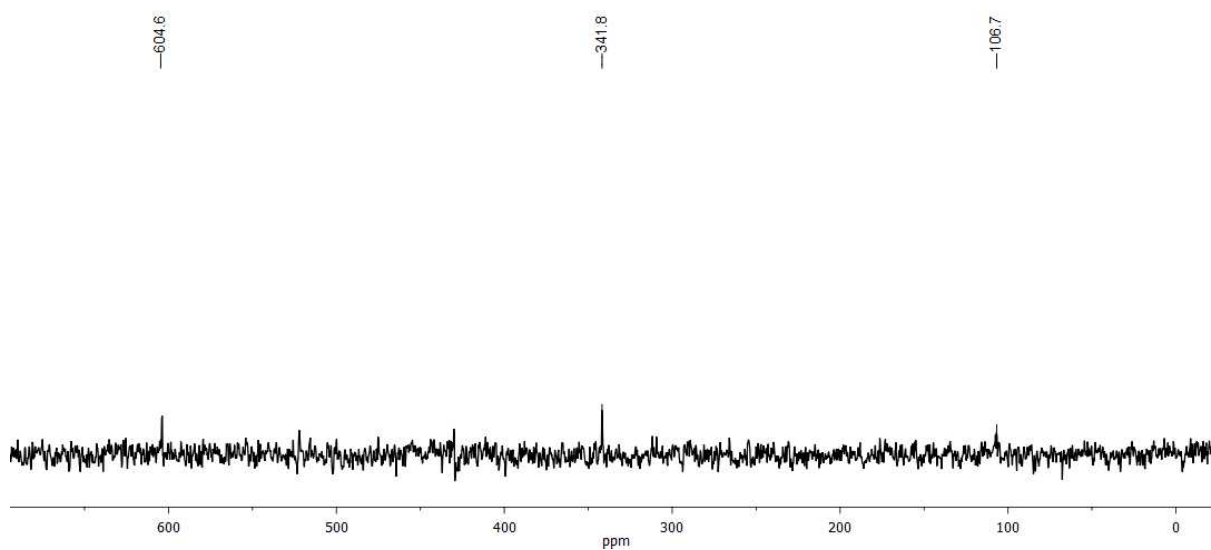


Figure S24. ^{15}N NMR spectrum of **6** in CDCl_3 .

X-ray crystallography

The diffraction data (except compounds **1.H₂O**, **4**, **15**, **22** and **23**) were measured at low temperature [100(2) K] using Mo K_α radiation on a Bruker APEX II CCD diffractometer equipped with a kappa geometry goniometer. The datasets were reduced by EvalCCD⁴ and then corrected for absorption.⁵ The data collections of compounds **1.H₂O**, **4** and **22** were collected at low temperature [140(2) K] using Mo K_α radiation on a mar345dtb system in

combination with a Genix Hi-Flux small focus generator (*mar μ X* system). The data reduction was carried out by *automar*.⁶ The data collections of compounds **15** and **23** were performed at room temperature using Cu (**23**) or Mo (**15**) K_{α} radiation on an Agilent Technologies SuperNova dual system in combination with an Atlas CCD detector. The data reduction was carried out by Crysalis PRO.⁷

The solutions and refinements were performed by SHELX.⁸ The crystal structures were refined using full-matrix least-squares based on F^2 with all non hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the “riding” model. Additional electron density found in the difference Fourier map of compound **16** was treated by the SQUEEZE algorithm of PLATON.⁹ Pseudo merohedral twinning was found for compound **19** and treated by the TWINROT MAT algorithm of PLATON,⁹ obtaining two BASF values: 0.239(4), 0.013(4).

References

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