Formation of Exceptionally Weak C–C Bonds by Metal-Templated Pinacol Coupling.

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Supporting Information

1. Experimental Section

All air-sensitive organic reactions, as well as the handling and synthesis of iron and zinc complexes, were carried out under an inert atmosphere of dry and oxygen-free N_2 using standard Schlenk techniques or were handled in an MBraun labmaster dp glovebox workstation. Dry Et_2O, MeCN, hexane, and toluene were obtained from an MBraun MB SPS-800 solvent purification system. CH_2Cl_2, CD_2Cl_2, and CD_3CN were dried over CaH_2, distilled under N_2. MeOH was dried over Mg^0 turnings and distilled under N_2 prior to use. THF was distilled over sodium/benzophenone under N_2 before use. All dry solvents were degassed by bubbling N_2 through the liquid for ±30 min or by freeze-pump-thaw degassing prior to use and stored over 3 or 4 Å molecular sieves. MeCN and CD_3CN were filtered over activated alumina after storage over 3 Å molecular sieves for one week to remove the molecular sieve dust that has formed. ^1H and $^{13}C\{^1H\}$, ^{19}F, and ^1H-^{13}C HSQC NMR spectra were recorded at 298 K on a Varian VNMRS400 or an Oxford NMR AS400 spectrometer at 400 MHz, 100 MHz, and 376 MHz, respectively. Chemical shifts (δ) are reported in ppm and referenced against residual solvent signal. ATR, KBr pellet, and solution cell (NaCl crystal) infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. EPR analyses were carried on a Bruker EMX Plus 6000 Gauss machine with ER 041 XG X-Band Microwave Bridge. UV-Vis spectra were recorded on an Agilent Cary 50 UV-Vis spectrometer, wavelengths are reported in nm and extinction coefficients (ε) are given in L mol^{-1} cm^{-1}. ESI-MS spectra were recorded on a Waters LCT Premier XE KE317 Micromass Technologies spectrometer. Cyclic voltammetry measurements were performed on a Princeton 263A potentiostat/galvanostat, using a Pt counter electrode, a glassy carbon working electrode, and a $Ag/AgNO_3$ reference electrode. All data are referenced to ferrocene. Analyte concentrations were typically 0.5 to 5 mM in 0.1 M NBu_4PF_6 in MeCN electrolyte. Elemental microanalyses were carried out by the Mikroanalytischen Laboratorium Kolbe, Mulheim a.d. Ruhr, Germany. Solution magnetic moments were determined by Evans' NMR method in CD_2Cl_2/CD_3CN at 298 K.[1] $Fe(OTf)_2.2MeCN$ was synthesized in accordance with a literature procedure.[2] All other chemicals were commercially obtained and used as received.

1-Methyl-4,5-diphenyl-1*H*-imidazole: NaH (60% weight dispersion in mineral oil, 6.13 g, 140 mmol) was suspended in dry THF (200 mL) and 4,5-diphenylimidazole (24.75 g, 112.4 mmol) was added in portions keeping the temperature below 30 °C where the blue suspension turned grey when stirring was continued for 1 h at room temperature. Next, iodomethane (7.35 mL, 118 mmol) was added dropwise keeping the temperature below 35 °C, resulting in an orange cloudy solution. Stirring was continued overnight. All volatiles were evaporated and the residue was taken up in H_2O/CH_2Cl_2 and extraction was performed with CH_2Cl_2 (3 × 40 mL). The combined organic layers were evaporated to dryness to yield a near quantitative yield (27.11 g). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.46 (s, 3H, NCH_3), 7.12 (t, 1H, $^3J_{H,H}$ = 6.9 Hz, Ph*H*), 7.17 (t, 2H, $^3J_{H,H}$ = 7.6 Hz, Ph*H*), 7.30-7.32 (m, 2H, Ph*H*), 7.41-7.48 (m, 5H, Ph*H*), 7.57 (s, 1H, H_{Im}) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 32.15, 126.29, 126.60, 120.12, 128.58, 128.91, 128.98, 130.58, 130.64, 134.69, 137.44, 138.20 ppm. ESI-MS (MeCN/formic acid): *m/z* = 235.1243 {$[M+H]^+$, calc. 235.1235}; 469.2436 {$[2M+H]^+$, calc. 469.2392}.

Bis(1-methyl-4,5-diphenyl-imidazol-2-yl)methanone ($BM^{diPh}IK$, 1): A dry, degassed THF (14 mL) solution of 1-Methyl-4,5-diphenyl-imidazole (1.67 g, 7.12 mmol) under a nitrogen atmosphere was cooled to 0 °C during which a solid formed. Tetramethylethylenediamine (tmeda, 1.07 mL, 7.12 mmol) was added followed by the dropwise addition of *n*-butyllithium (1.6 M in hexanes, 4.9 mL, 7.8 mmol), resulting in a clear dark red solution. After stirring for 1.5 h at 0 °C the mixture was cooled to −78 °C and dimethylcarbamoylchloride (0.31 mL, 3.4 mmol) was added. The mixture was allowed to warm to room temperature overnight resulting in a light yellow suspension and was then quenched with a saturated ammonium chloride solution (3.6 mL) while keeping the temperature below 25 °C. All volatiles were evaporated and the aqueous phase was extracted with CH_2Cl_2 (4 × 4 mL). The combined organic extracts were dried over sodium sulfate, filtered, and concentrated *in vacuo* and the resulting solid was washed with Et_2O (3 × 5 mL), to give the pure product as a yellow powder (1.71 g, 97%). Anal. for $C_{33}H_{26}N_4O$ (494.60), calc. C 80.14, H 5.30, N 11.33; found C 79.70, H 5.29, N 11.22. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.82 (s, 6H, NC*H*$_3$), 7.19-7.29 (m, 6H, Ph*H*), 7.41-7.43 (m, 4H, Ph*H*), 7.50-7.52 (m, 6H, Ph*H*), 7.59 (d, 4H, $^3J_{H,H}$ = 7.1 Hz, *o*-Ph*H*) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ = 33.9, 127.1, 127.7, 128.2, 129.2, 129.4, 129.7, 130.8, 133.9, 135.1, 140.3, 143.6, 175.0 ppm. IR (ATR) ν = 3064.5 (w), 3028.3 (w), 2949.6 (w), 1622.0 (s), 1492.7 (m), 1450.1 (s), 1435.3 (m), 1391.5 (m), 1319.03 (m), 1304.0 (m), 1217.0 (s), 1131.3 (m), 1073.6 (m), 1026.0 (m), 965.89 (m), 909.19 (s), 768.70 (s), 745.00 (s), 690.77 (s) cm^{-1}. ESI-MS (CH_2Cl_2): *m/z* = 495.2124 {[$BM^{diPh}IK$+H]$^+$, calc. 495.2185}. UV-Vis (MeCN, ε [L mol^{-1} cm^{-1}]): λ_{max} = 243 ($2.11\cdot10^4$), 262 ($2.10\cdot10^4$), 370 ($2.18\cdot10^4$) nm.

$BM^{diPh}IK$ reduction: An excess of Na was added to a yellow solution of $BM^{diPh}IK$ (9.7 mg, $2.0\cdot10^{-2}$ mmol) in dry, degassed THF (1 mL), resulting in an immediately color change to clear pink. Within the next 20 min the color changed to dark brown. The solution was filtered over a glass fibre filter and the filtrate was analyzed with EPR.

[Fe($BM^{diPh}IK$)Cl_2] (2): To a light brown suspension of $FeCl_2$ (0.261 g, 2.06 mmol) in dry, degassed CH_2Cl_2 (10 mL) was added a yellow solution of $BM^{diPh}IK$ (1.01 g, 2.04 mmol) in dry, degassed CH_2Cl_2 (15 mL) at room temperature, upon addition the solution colored orange. After 2 h all solids dissolved and the solution was very dark orange. The reaction mixture was stirred overnight, after which Et_2O (60 mL) was added to precipitate the product. The supernatant was removed via a cannula filtration and the product was washed with Et_2O (3 × 2.5 mL), dried *in vacuo*, and obtained as an orange powder (1.37 g, 95%). Crystals suitable for X-ray crystal structure determination were obtained by slow vapor diffusion of CH_2Cl_2/Et_2O. Anal. for $C_{33}H_{26}Cl_2FeN_4O\cdot2CH_2Cl_2$ (621.34+84.93), calc. C 57.82, H 4.00, N 7.93; found C 58.25, H 4.00, N 8.31. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = −7.41 (4H, Ph*H*), 1.93 (4H, Ph*H*), 3.45 (4H, Ph*H*), 4.42 (4H, Ph*H*), 5.61 (2H, *p*-Ph*H*), 5.93 (2H, *p*-Ph*H*), 29.54 (6H, NC*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 25 °C): δ = 120.3, 122.4, 125.4, 126.3, 129.1, 202.5, 229.3, 434.7, 464.2 ppm. IR (ATR) ν = 3058.1 (w), 3031.0 (w), 2957.3 (w), 1647.2 (m), 1496.6 (w), 1468.0 (s), 1448.8 (s), 1437.7 (s), 1409.1 (w), 1393.3 (w), 1306.4 (w), 1225.3 (w), 1137.7 (w), 1073.0 (w), 1026.2 (w), 985.96 (w), 935.57 (s), 919.23 (m), 796.23 (m), 786.09 (m), 772.23 (m), 751.69 (w), 739.8 (w), 701.70 (s), 696.25 (s), 621.04 (w), 543.09 (w), 525.00 (w), 515.69 (w), 489.34 (w) cm^{-1}. ESI-MS (CH_2Cl_2): *m/z* = 495.2071 {[$BM^{diPh}IK$+H]$^+$, calc. 495.2185}; 585.1026 {[Fe($BM^{diPh}IK$)Cl]$^+$, calc. 585.1146}; 989.4304 {[($BM^{diPh}IK$)$_2$+H]$^+$, calc. 989.4291}; 1115.3026 {[Fe($BM^{diPh}IK$)$_2Cl_2$+H]$^+$, calc. 1115.3020}.

Solution magnetic moment (Evans' method): μ_{eff} = 5.2 μ_B. UV-Vis (MeCN): λ_{max} = 240, 263, 373 nm.

[Zn(BM^{diPh}IK)Cl$_2$] (3): A cloudy solution of $ZnCl_2$ (0.273 g, 2.00 mmol) in THF (5 mL) was added dropwise to a yellow suspension of BM^{diPh}IK (0.990 g, 2.00 mmol) in THF (30 mL) upon which first all solids dissolved, after which a yellow precipitate formed. Stirring was continued overnight after which the volume was halved and Et_2O (15 mL) was added to precipitate the product. The supernatant was removed via a cannula filtration and the product was washed with Et_2O (3 × 5 mL), dried *in vacuo*, and obtained as a yellow powder (1.13 g, 90%). Crystals suitable for X-ray crystal structure determination were obtained by slow vapor diffusion of CH_2Cl_2/Et_2O or MeCN/Et_2O. Both crystallizations yielded single crystals suitable for X-ray crystal structure determination, in the case that CH_2Cl_2 was used in crystallization one CH_2Cl_2 molecule co-crystallized. Besides the co-crystallization of a solvent molecule both structures are very similar. Also the geometry is very similar to the corresponding iron complex. Anal. for $C_{33}H_{26}Cl_2N_4OZn$ (630.88), calc. C 62.83, H 4.15, N 8.88; found C 62.88, H 3.95, N 8.71. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 4.05 (s, 6H, NC*H*$_3$), 7.27-7.32 (m, 10H, Ph*H*), 7.45-7.52 (m, 6H, Ph*H*), 7.62 ('d', 4H, $^3J_{H,H}$ = 6.4 Hz, *p*-Ph*H*) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 25 °C): δ = 36.8, 127.1, 128.5, 129.3, 129.5, 130.3, 130.5, 130.8, 131.3, 138.4, 139.6, 141.5, 167.8 ppm. IR (ATR) ν = 3065.5 (w), 3053.7 (w), 2963.3 (w), 1633.0 (m), 1495.1 (w), 1467.4 (m), 1446.4 (s), 1433.1 (s), 1392.6 (m), 1321.9 (w), 1304.5 (m), 1259.9 (w), 1243.5 (w), 1227.0 (m), 1139.4 (m), 1077.0 (w), 1027.2 (w), 983.64 (w), 931.37 (m), 915.48 (s), 780.17 (m), 749.42 (w), 720.20 (m), 706.88 (s), 693.56 (s), 641.28 (m), 606.94 (m), 538.26 (w), 521.86 (w), 513.0 (w), 486.0 (w) cm^{-1}. ESI-MS (CH_2Cl_2): *m/z* = 495.1888 {[BM^{diPh}IK+H]$^+$, calc. 495.2185}; 593.0996 {[Zn(BM^{diPh}IK)Cl]$^+$, calc. 593.1086}.

Complex 4: Naphthalene (24.0 mg, 0.187 mmol) was dissolved in THF (3 mL) followed by the addition of an excess of Na upon which the colorless solution immediately colored dark green due to the formation of sodium naphthalenide. After stirring for 3 h, the solution was filtered and added dropwise over 15 min to a clear orange solution of [Fe(BM^{diPh}IK)Cl$_2$] (105.4 mg, 0.170 mmol) in 6.5 mL THF at −78 °C. Shortly the solution colored dark brown after which quickly a white precipitate formed in a brown solution. The reaction was stirred for 1 h at −78 °C followed by 1 h at room temperature after which the solution was almost colorless. The precipitate was washed 3 times with THF and dried *in vacuo* providing the product as a white powder in quantitative yield (102.8 mg, quant.). The product can be crystallized by slow vapor diffusion of Et_2O into a CH_2Cl_2 solution. Due to the lability of this compound Elemental Analysis as well as ESI-MS measurements were not successful. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = −7.86 (12H, NC*H*$_3$), 1.21 (8H, Ph*H*), 4.22 (4H, *p*-Ph*H*), 5.44 (8H, Ph*H*), 8.13 (8H, Ph*H*), 9.00 (4H, *p*-Ph*H*), 9.57 (8H, Ph*H*) ppm. IR (CH_2Cl_2 solution): ν = 3026.0 (w), 2956.7 (m), 2938.8 (m), 2873.6 (m), 1604.2 (m), 1504.3 (m), 1485.4 (s), 1464.6 (s), 1444.1 (m), 1398.0 (m), 1447.5 (m), 1175.2 (s), 1113.2 (m), 1074.3 (m), 1024.7 (m), 981.87 (m), 863.32 (m), 848.12 (m), 560.27 (s) cm^{-1}. IR (ATR, N_2 flow): ν = 3052.4 (w), 3028.6 (w), 2966.3 (w), 1601.1 (w), 1503.0 (m), 1483.7 (m), 1461.4 (m), 1442.1 (m), 1388.6 (w), 1319.78 (w), 1172.8 (s), 1161.8 (m), 1073.5 (m), 1023.6 (m), 980.30 (m), 860.53 (m), 846.56 (m), 785.50 (s), 771.80 (s), 698.50 (s), 561.42 (s), 500.92 (s) cm^{-1}. Solution magnetic moment (Evans' method): μ_{eff} = 6.4 μ_B.

Complex 5: Naphthalene (34.0 mg, 0.27 mmol) was dissolved in THF (2 mL) followed by the addition of an excess of Na upon which the colorless solution immediately colored dark green due to the formation of sodium naphthalenide. After stirring for 3 h, the solution was filtered and added dropwise over 15 min to an, almost clear, yellow solution of [Zn(BM^{diPh}IK)Cl_2] (151.8 mg, 0.241 mmol) in THF (10 mL) at −78 °C resulting in a clear dark brown solution. The reaction was stirred for 1 h at −78 °C followed by 1 h at room temperature after which the solution was light yellow. Part of the solvent was evaporated and hexane was added to precipitate the product, which was collected by filtration. The residue was washed with hexane, dissolved in CH_2Cl_2 and filtered again. The product was obtained as crystals from the clear yellow CH_2Cl_2 solution by slow vapor diffusion with Et_2O (132.4 mg, 93%). Anal. for $C_{66}H_{52}Cl_2N_8O_2Zn$ (1190.86), calc. C 66.57, H 4.40, N 9.41; found C 66.20, H 4.29, N 9.28. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 3.72 (s, 12H, NC*H*$_3$), 7.14-7.16 (m, 8H, Ph*H*), 7.30-7.35 (m, 12H, Ph*H*), 7.40-7.48 (m, 20H, Ph*H*) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 25 °C): δ = 35.21, 89.81, 128.18, 128.67, 129.24, 129.37, 129.39, 129.60, 131.48, 131.58, 132.14, 135.50, 149.35 ppm. IR (ATR): *ν* = 3051.0 (w), 3035.5 (w), 2965.4 (w), 1601.3 (w), 1577.5 (w), 1504.0 (w), 1483.6 (m), 1460.9 (m), 1443.3 (m), 1387.8 (m), 1322.0 (w), 1235.3 (w), 1178.6 (m), 1074.3 (m), 1024.3 (m), 983.30 (m), 914.43 (m), 858.90 (m), 845.88 (m), 772.98 (s), 697.48 (s), 543.88 (s) cm^{-1}.

Procedure for the chemical oxidation of 4 and 5: A dry, degassed CD_2Cl_2 solution (0.5 mL) of the appropriate complex was mixed with a dark blue suspension containing 2 eq. of [$FeCp_2$][PF_6] and 2.2 eq. of Bu_4NCl in CD_2Cl_2 (0.2 mL). Upon mixing the color instantaneously changed to orange and all solids dissolved. The resulting mixture was analyzed with ^{1}H NMR spectroscopy.

Fe-extraction from 4: Compound **4** (10.3 mg, 0.0088 mmol) was dissolved in dry, degassed CH_2Cl_2 (1.5 mL) followed by the addition of a degassed aqueous solution of EDTA (14.5 mg, 0.0390 mmol) resulting in a yellow organic phase and colorless aqueous phase. After stirring for 1 h under N_2 atmosphere, the organic fraction was removed with a syringe and transferred to a Schlenk flask. The aqueous phase was extracted 2 times with 2 mL CH_2Cl_2, the combined organic phases were dried *in vacuo*. The organic products are isolated as yellow powder (5.3 mg) and based on ^{1}H and ^{13}C NMR measurements the main products are BM^{diPh}IK (51%), H-BM^{diPh}IA (37%), and a third unidentified compound (12%).

Zn-extraction from 5: Compound **5** (18.5 mg, 0.0155 mmol) was dissolved in dry, degassed CH_2Cl_2 (2 mL) followed by the addition of a degassed aqueous solution of EDTA (27.0 mg, 0.0725 mmol) resulting in a yellow organic phase and colorless aqueous phase. After stirring for 1 h under N_2 atmosphere, the organic fraction was removed and transferred with a syringe to a Schlenk flask. The aqueous phase was extracted 2 times with 2 mL CH_2Cl_2, and dried *in vacuo*. The organic products are isolated as yellow powder (16.4 mg) and based on ^{1}H NMR measurements the main products are BM^{diPh}IK (54%), H-BM^{diPh}IA (35%), and a third unidentified compound (11%).

2. Characterisation of the BM^{diPh}IK radical anion

BM^{diPh}IK was chemically reduced by the addition of an excess of metallic sodium to a THF solution of the ligand. This resulted in an intensely colored brown solution containing the corresponding radical anions, as confirmed by EPR spectroscopy (Figure 2). The observed g-value of 2.004 is close to the value for a free electron (g_e = 2.0023), typical for organic radicals, and a complex hyperfine coupling pattern existing of 25 lines is observed. The hyperfine coupling was not assigned to specific coupling constants but likely originates from coupling with the nitrogen atoms in the imidazole rings and hydrogen atoms on the Ph-substituents. Additionally, coupling with the sodium counterion may play a role. Such complex coupling patterns are also observed for structurally related benzophenone derivatives.[3]

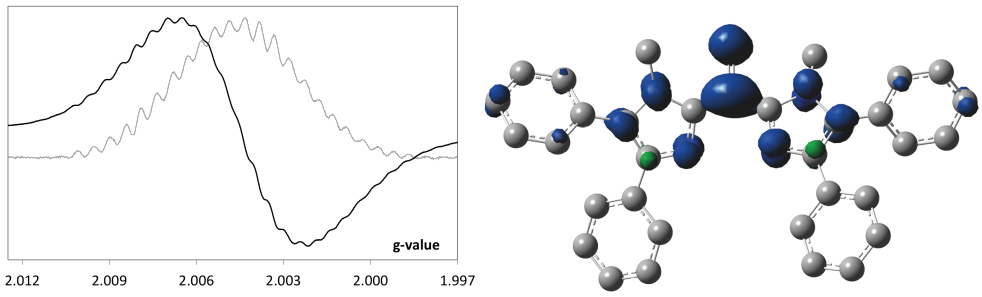

Figure 1. Left: the 1st and 2nd derivative EPR spectra of a THF solution of the reduced ligand measured at rt. Right: isosurface plot of the calculated spin density of the reduced BM^{diPh}IK ligand using B3LYP/6-31g**.

The electronic structure of the obtained radical anion was studied by DFT calculations. Most of the spin density is found on the C=O moiety, the natural spin density, determined by natural population analysis, on the C=O moiety is 0.5066 (Figure 2). Some delocalization over the imidazole rings is found but no delocalization over the Ph-substituent on the 4-position and hardly on the 5-position takes place according to the calculations. This is probably a consequence of the twisting of the Ph groups out of the ligand plane.

3. NMR Spectra

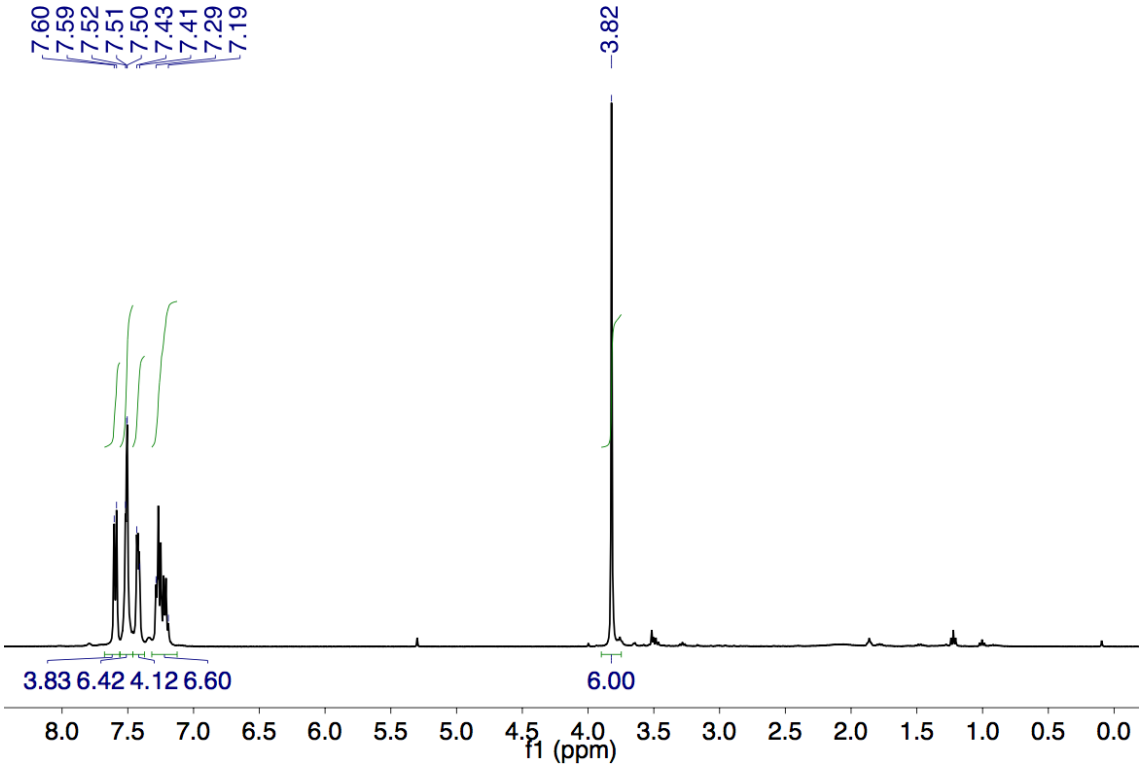

Figure 2. ^{1}H NMR spectrum of BM^{diPh}IK (**1**) in $CDCl_3$.

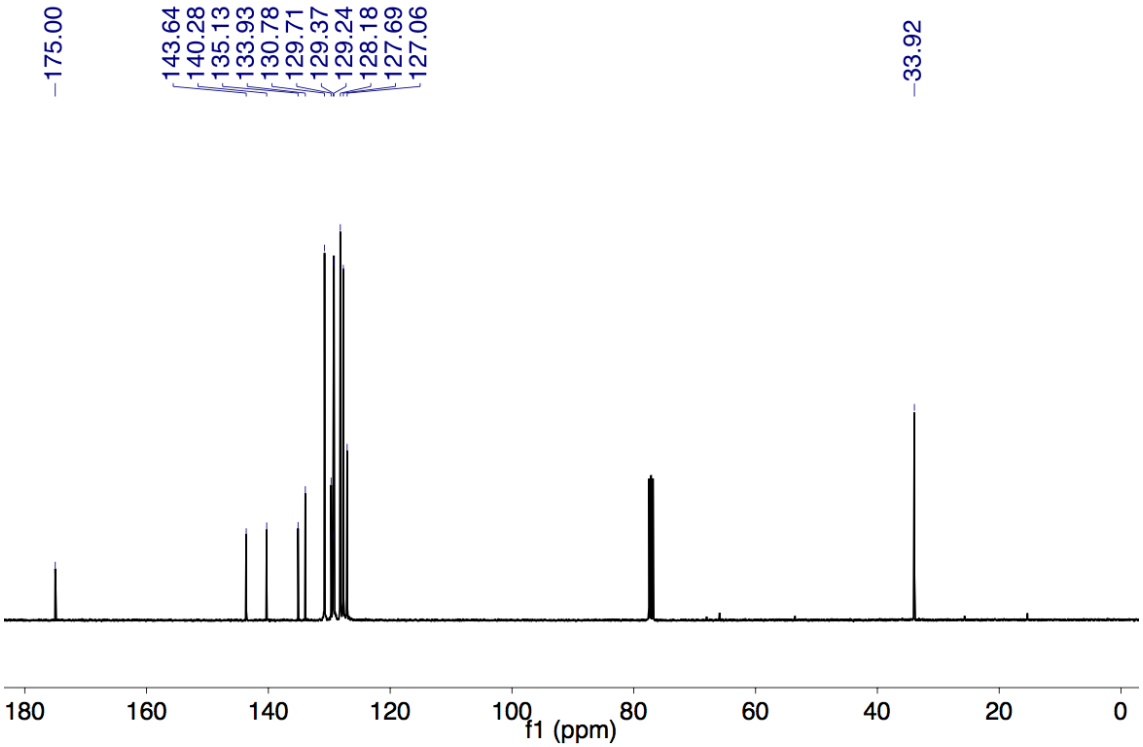

Figure 3. ^{13}C NMR spectrum of BM^{diPh}IK (**1**) in $CDCl_3$.

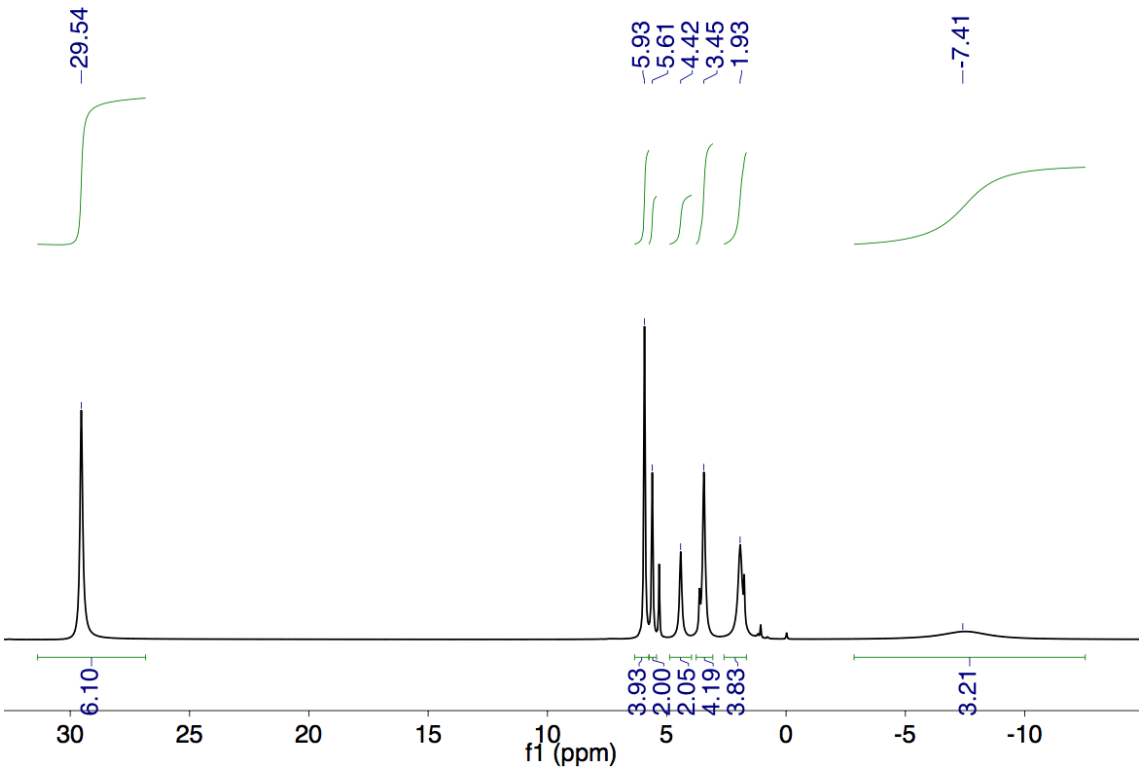

Figure 4. ^{1}H NMR spectrum of [Fe(BM^{diPh}IK)Cl$_2$] (**2**) in CD_2Cl_2.

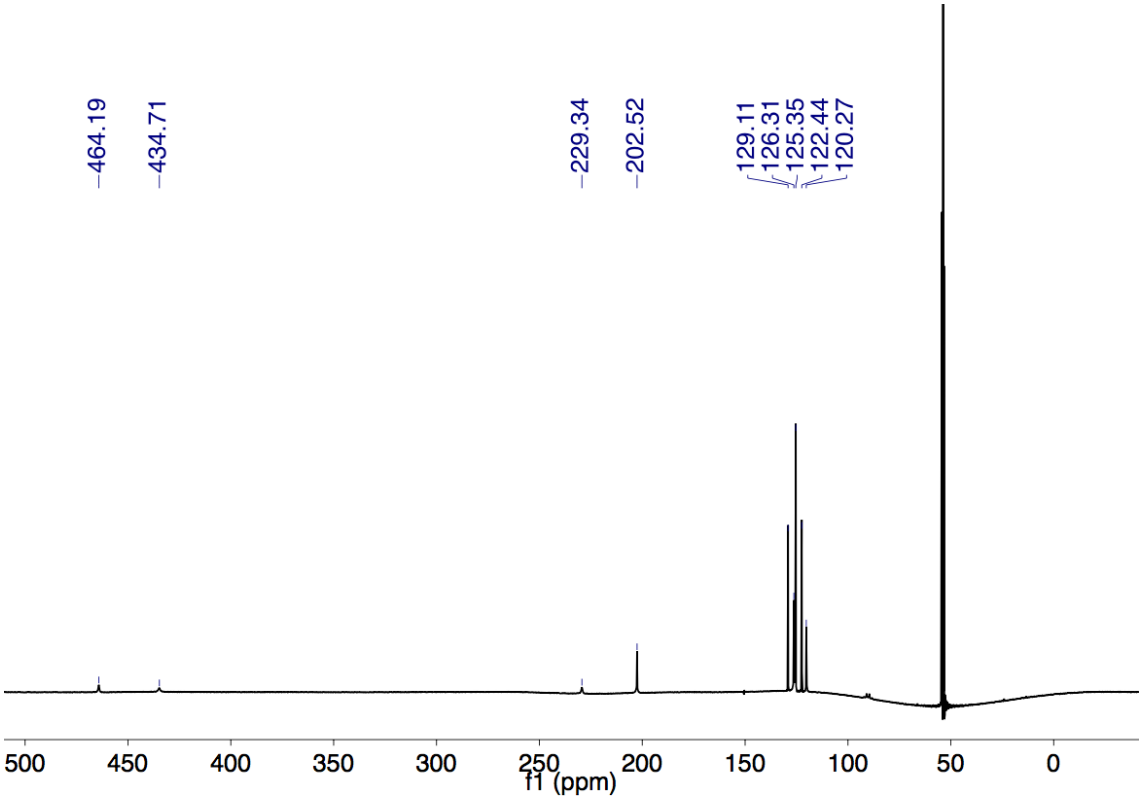

Figure 5. ^{13}C NMR spectrum of [Fe(BM^{diPh}IK)Cl$_2$] (**2**) in CD_2Cl_2.

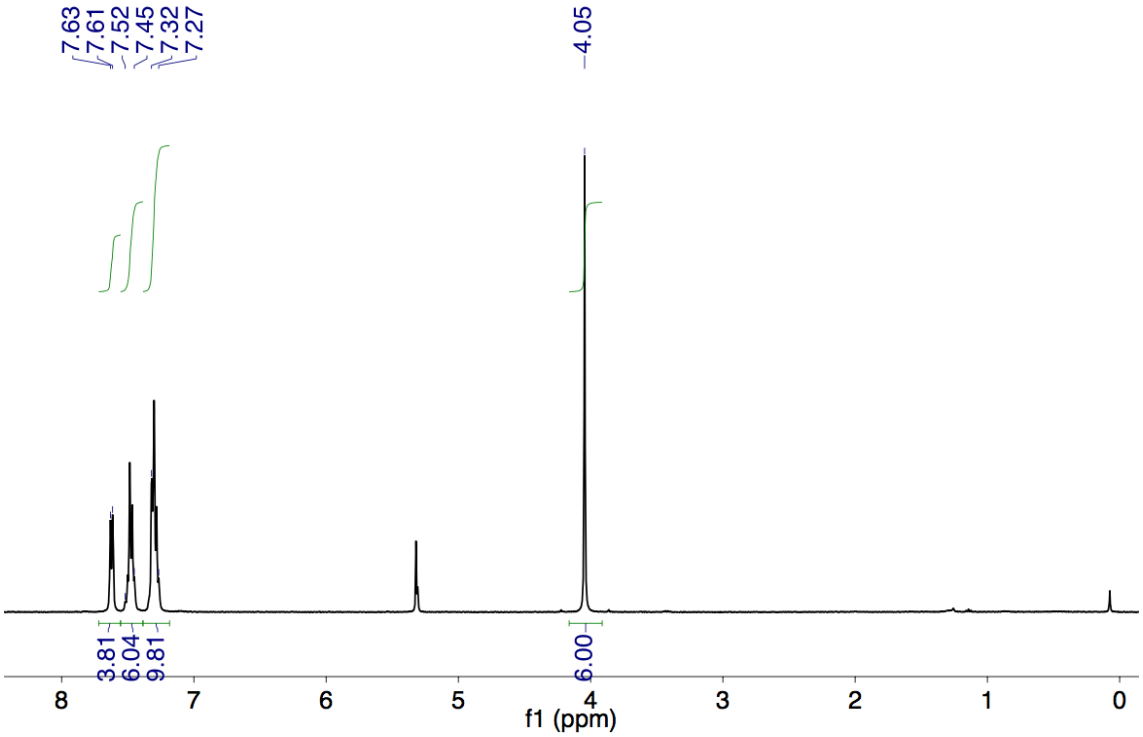

Figure 6. ^{1}H NMR spectrum of [Zn(BM^{diPh}IK)Cl$_2$] (**3**) in CD_2Cl_2.

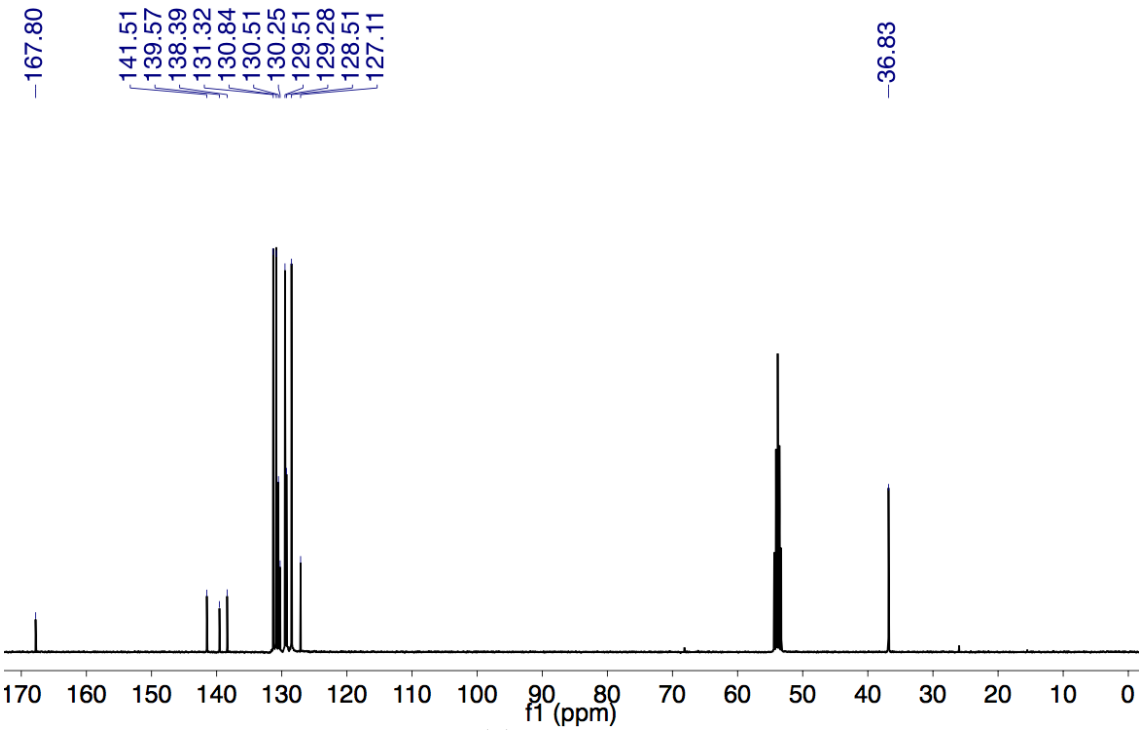

Figure 7. ^{13}C NMR spectrum of [Zn(BM^{diPh}IK)Cl$_2$] (**3**) in CD_2Cl_2.

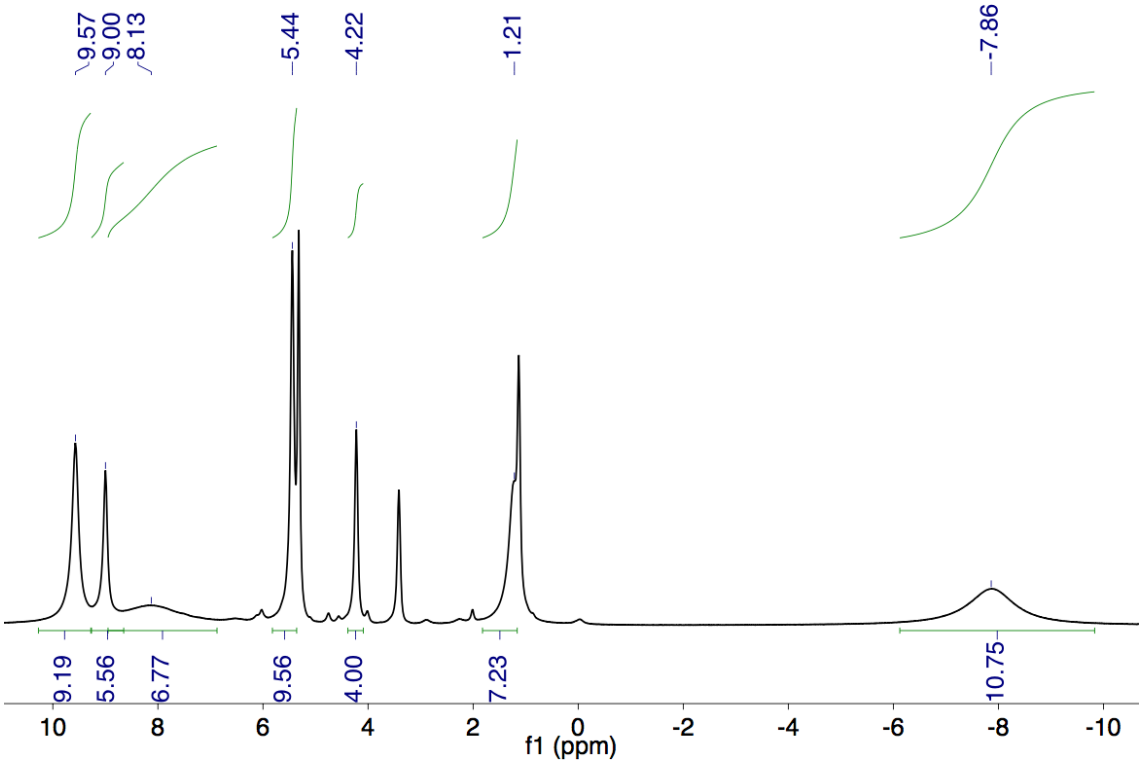

Figure 8. ^{1}H NMR spectrum of complex **4** in CD_2Cl_2.

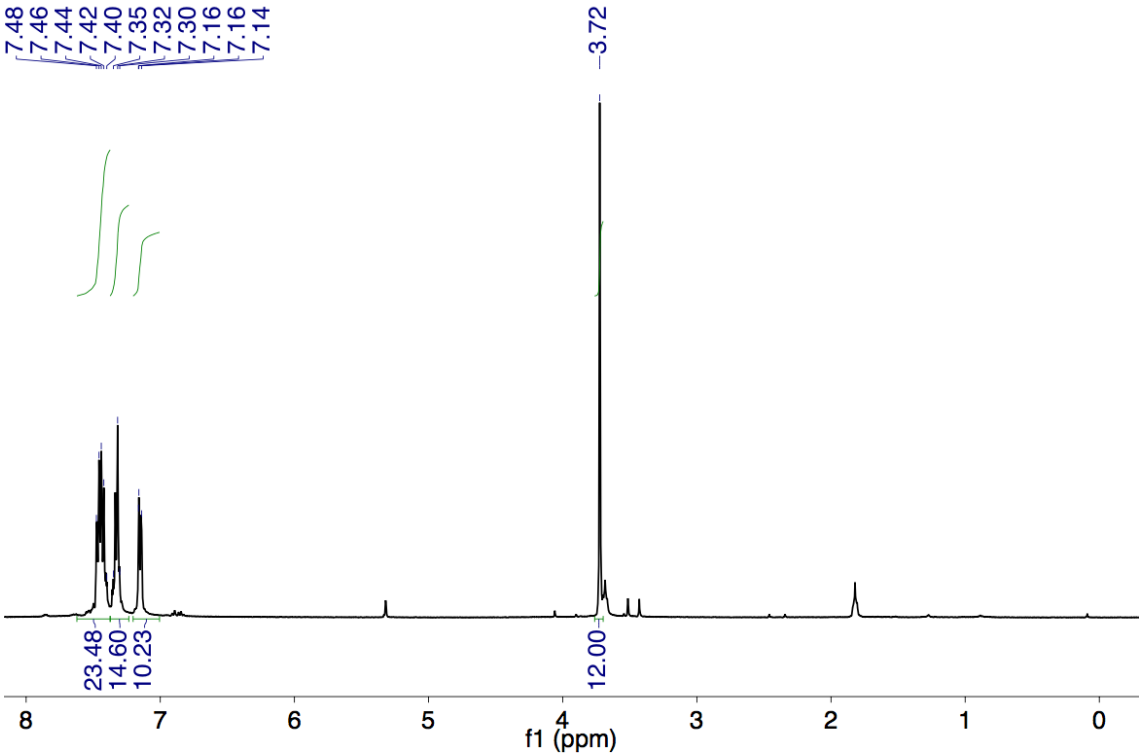

Figure 9. ^{1}H NMR spectrum of complex **5** in CD_2Cl_2.

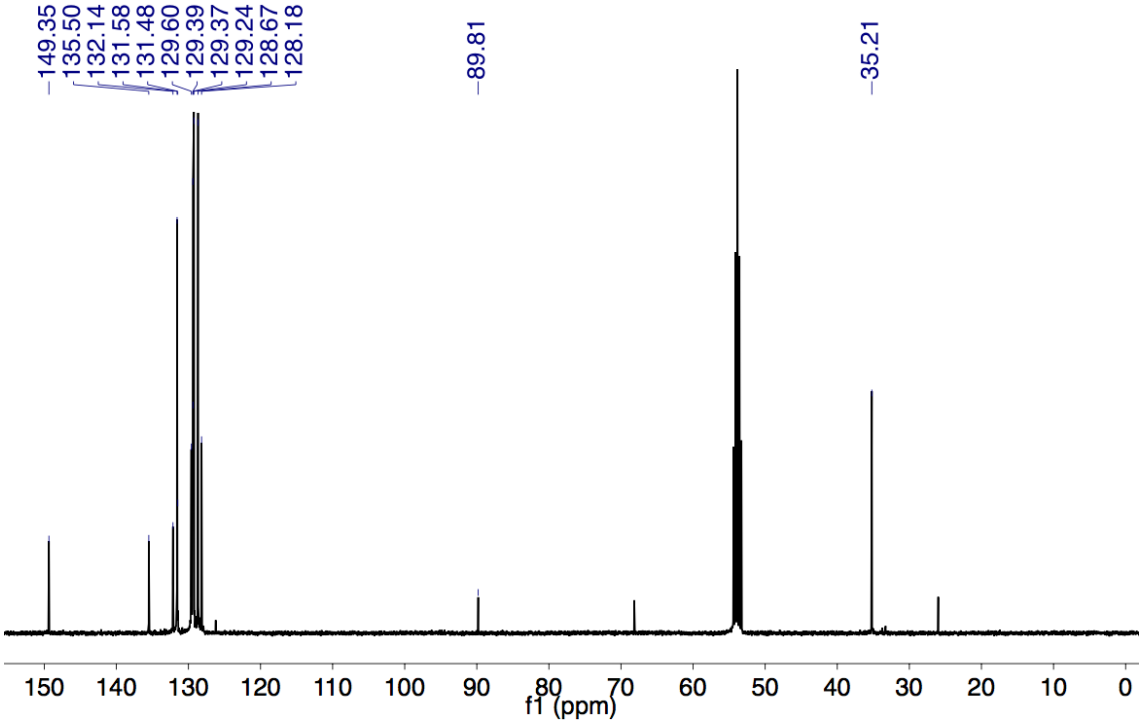

Figure 10. ^{13}C NMR spectrum of complex **5** in CD_2Cl_2.

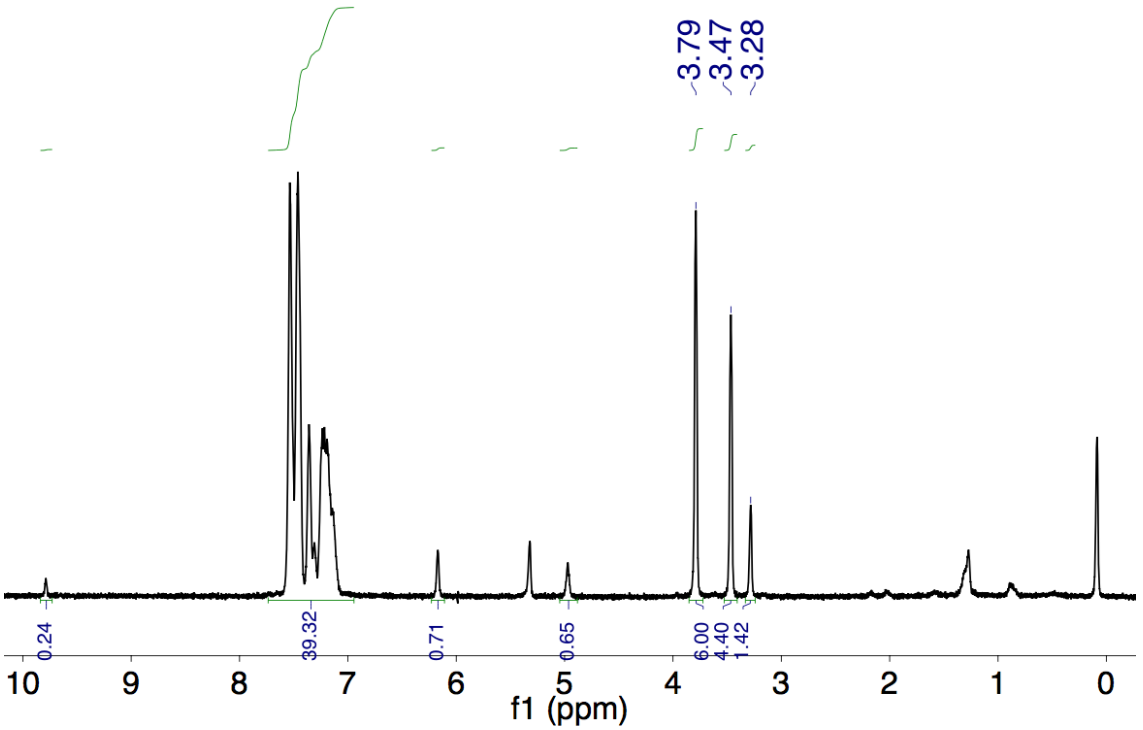

Figure 11. ^{1}H NMR spectrum of the organic fraction resulting from an Fe-extraction attempt of compound **4** in CD_2Cl_2.

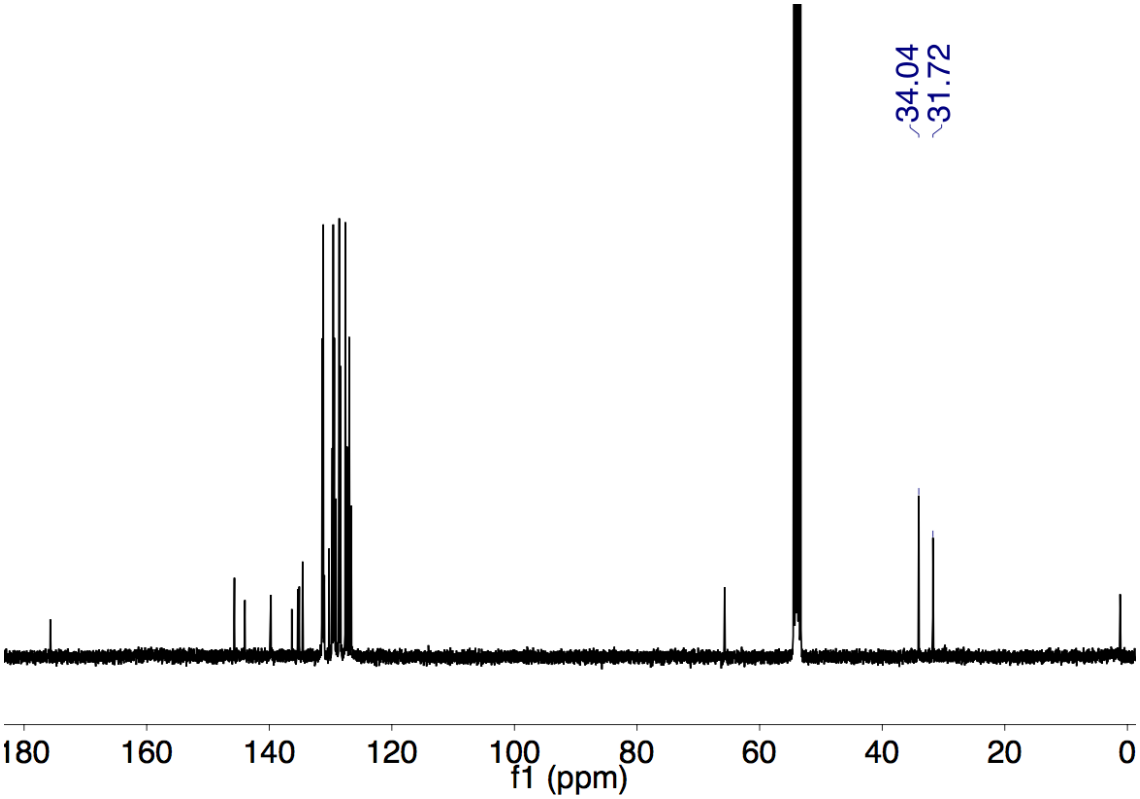

Figure 12. ^{13}C NMR spectrum of the organic fraction resulting from an Fe-extraction attempt of compound **4** in CD_2Cl_2.

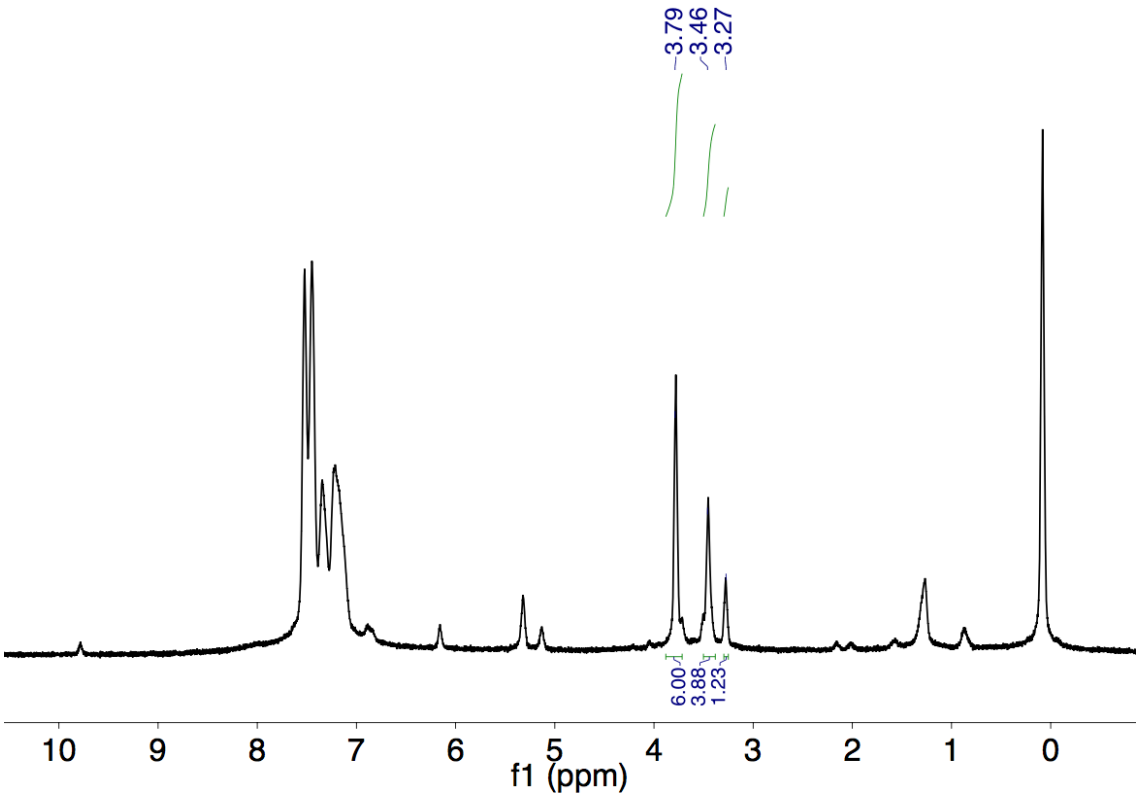

Figure 13. ^{1}H NMR spectrum of the organic fraction resulting from a Zn-extraction attempt of compound **5** in CD_2Cl_2.

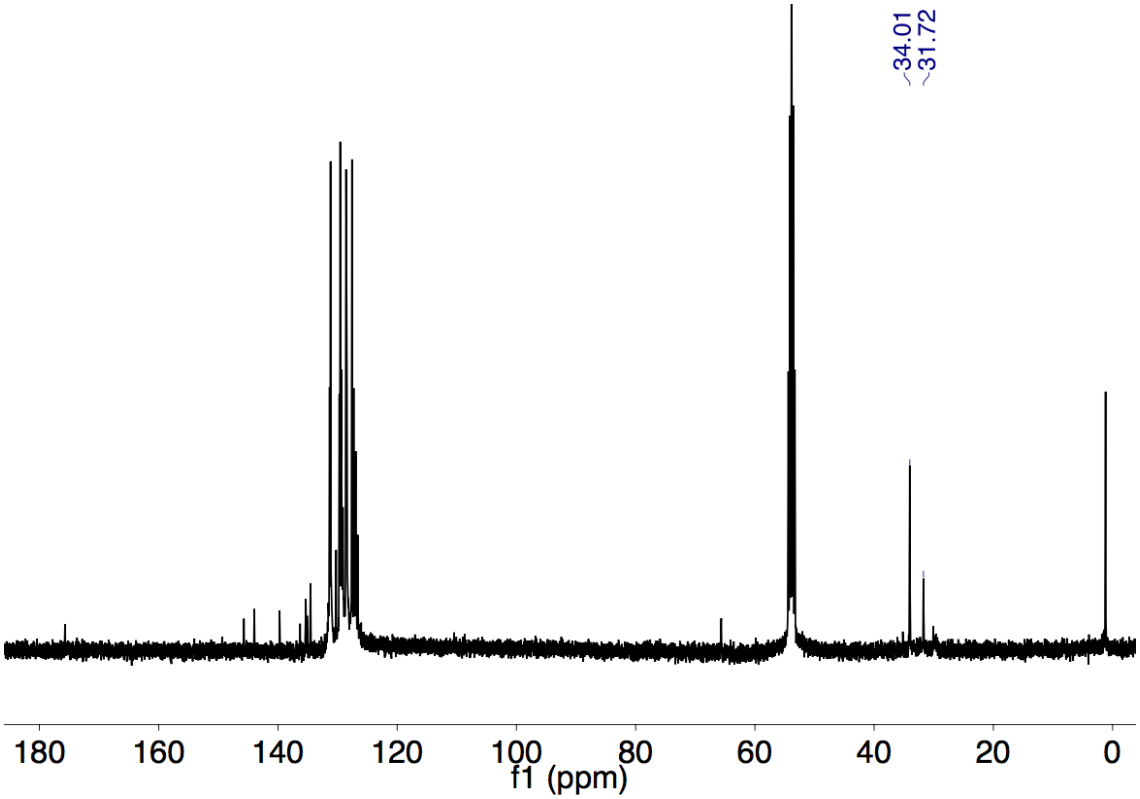

Figure 14. ^{13}C NMR spectrum of the organic fraction resulting from a Zn-extraction attempt of compound **5** in CD_2Cl_2.

4. IR Spectra

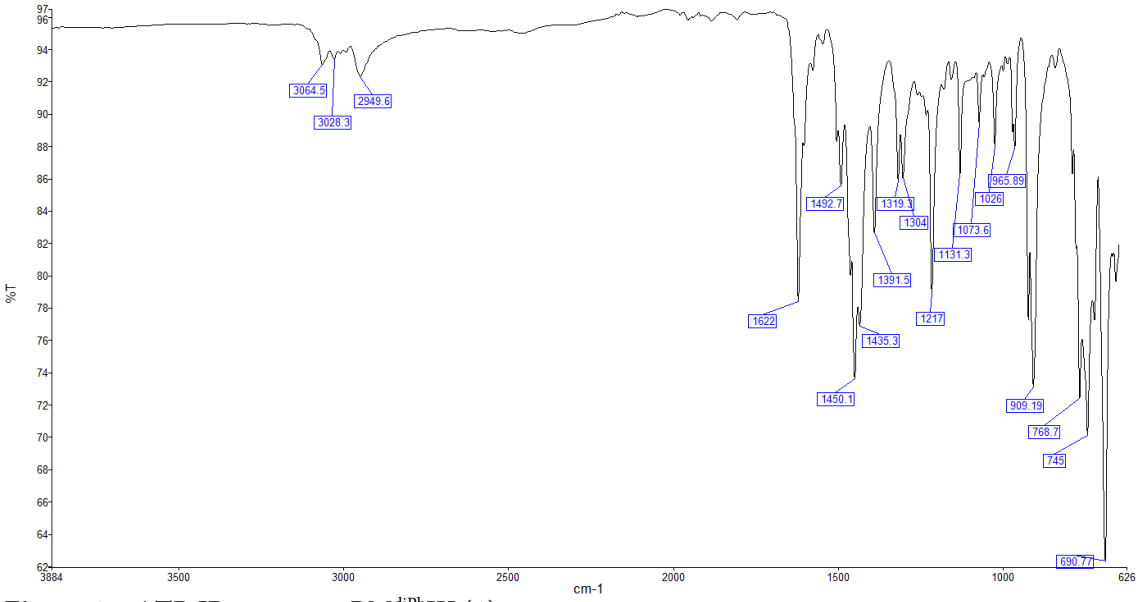

Figure 15. ATR IR spectrum BM^{diPh}IK (**1**).

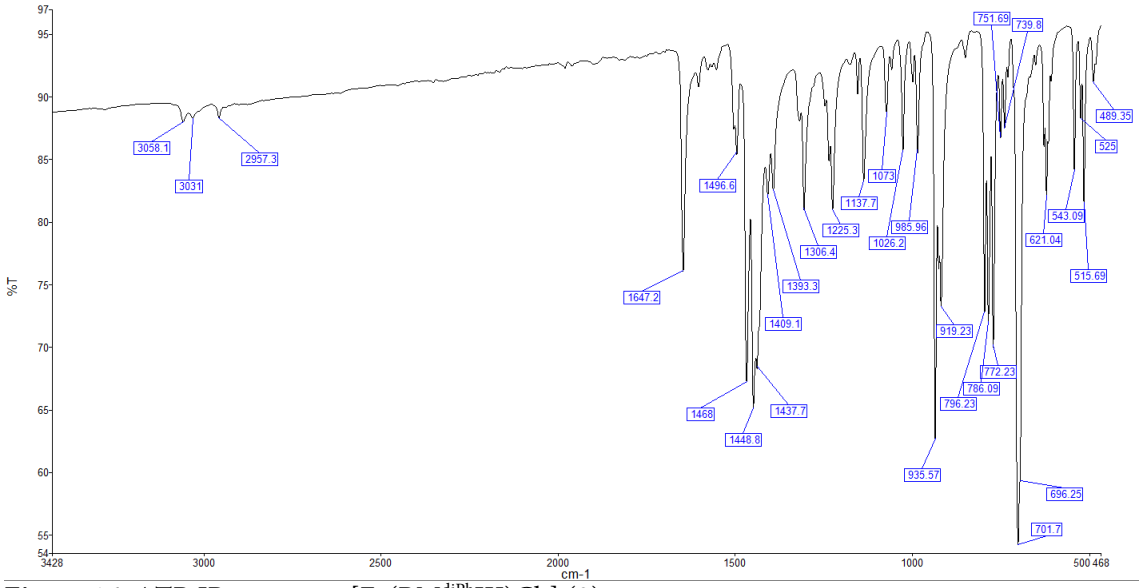

Figure 16. ATR IR spectrum [Fe(BM^{diPh}IK)Cl_2] (**2**).

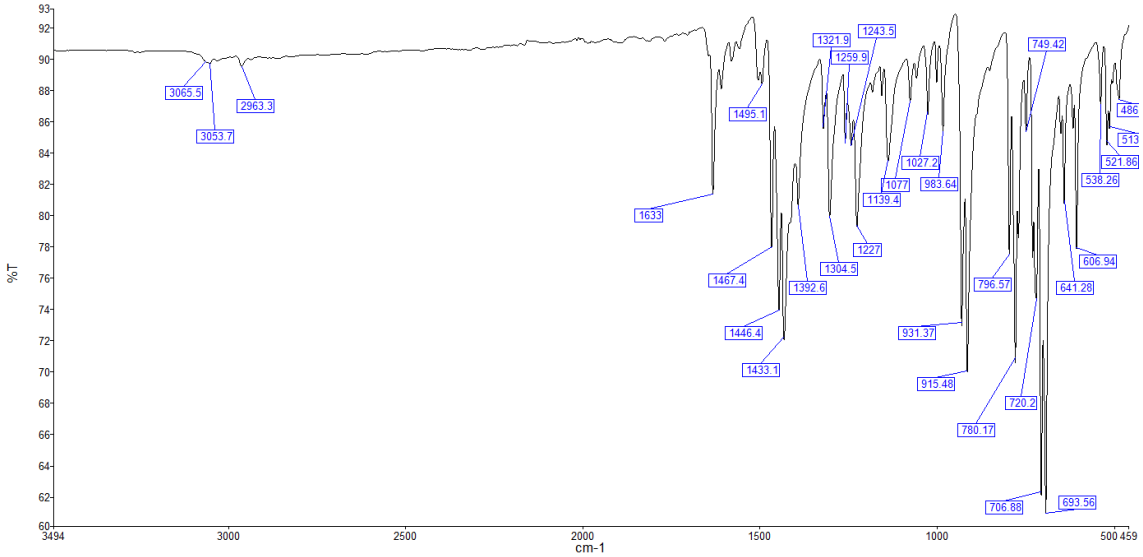

Figure 17. ATR IR spectrum [Zn(BM^{diPh}IK)Cl$_2$] (**3**).

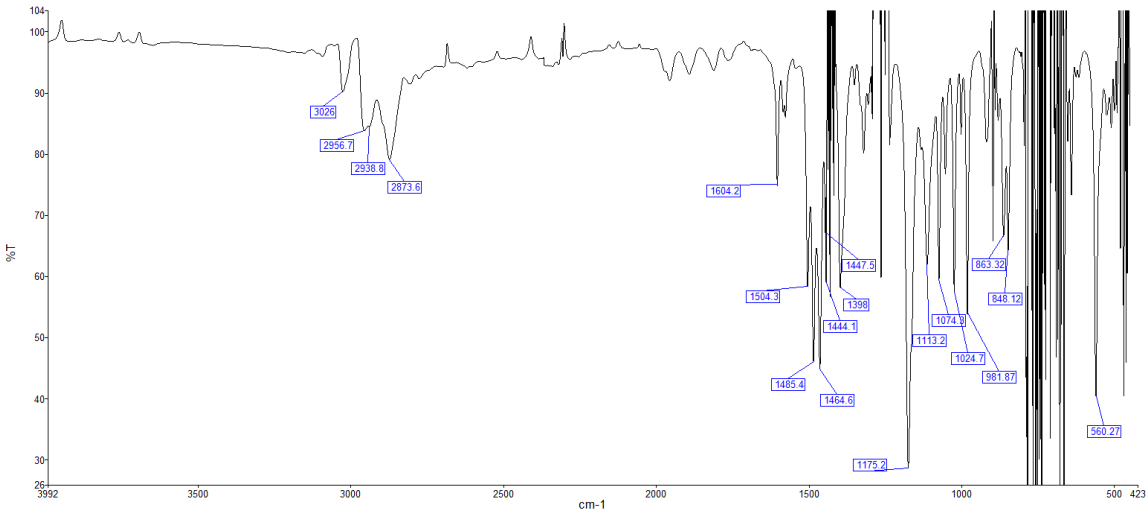

Figure 18. CH_2Cl_2 solution IR spectrum complex **4**.

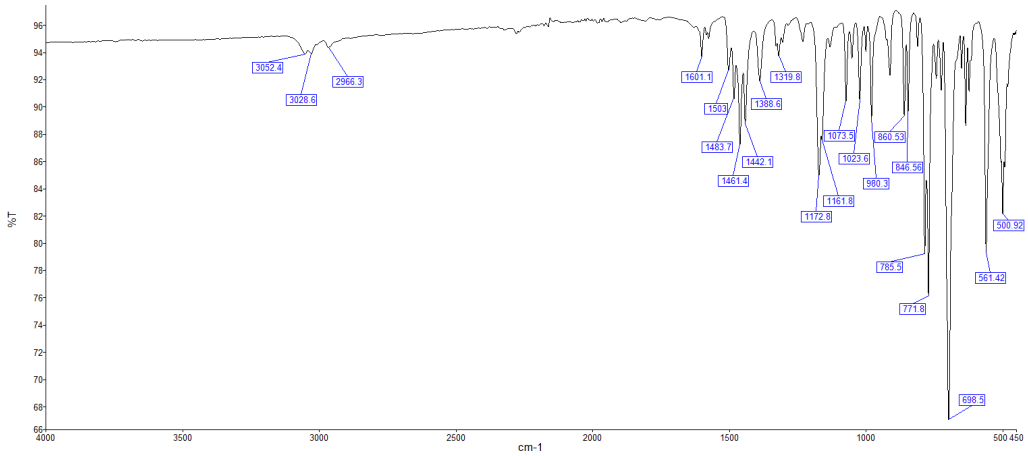

Figure 19. ATR IR spectrum complex **4**.

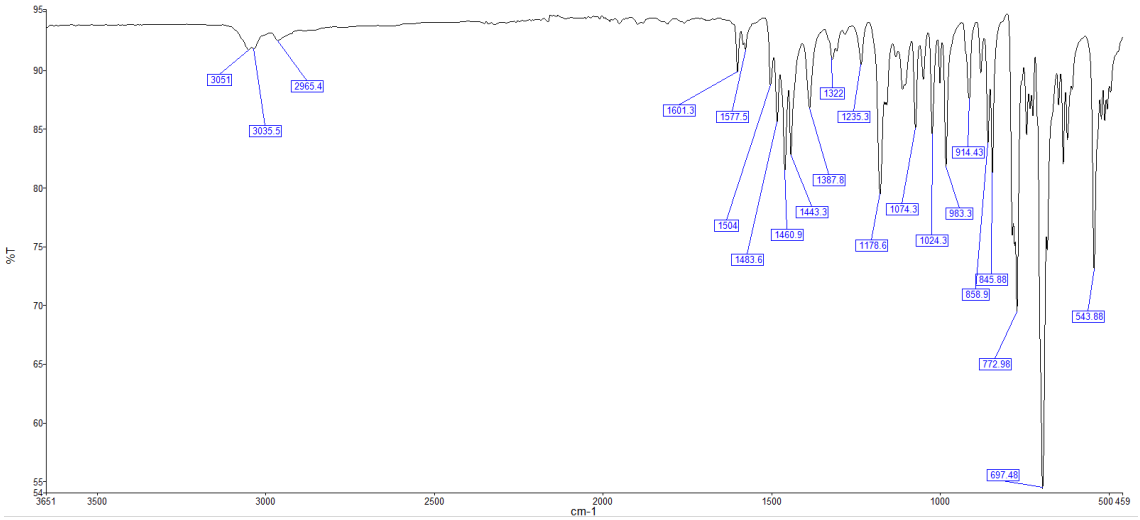

Figure 20. ATR IR spectrum complex **5**.

5. ESI-MS Spectra

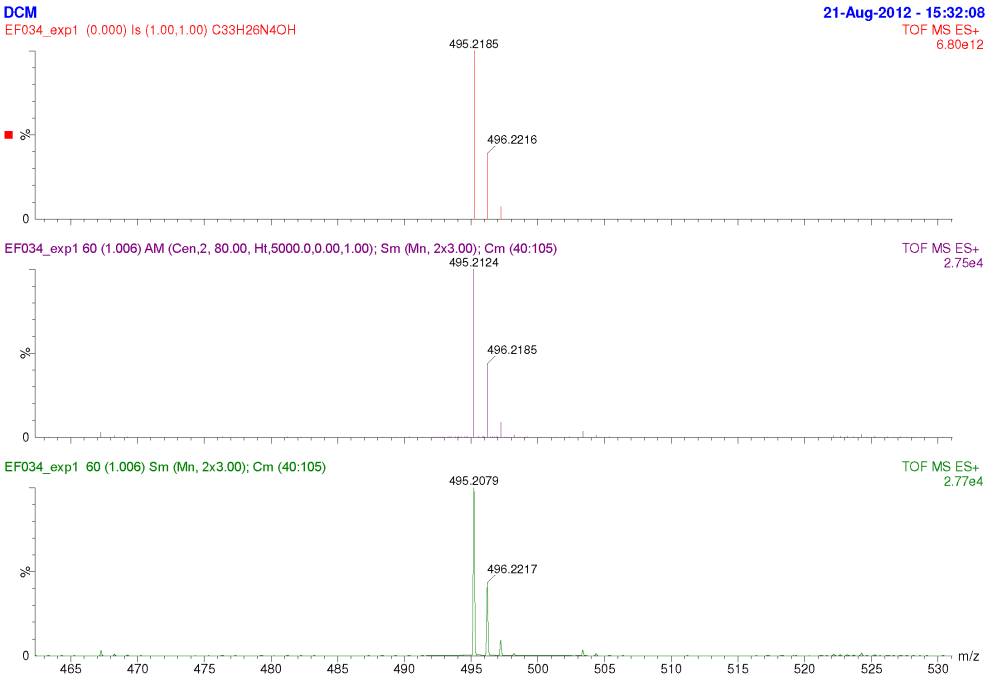

Figure 21. ESI-MS spectrum of BM^{diPh}IK (**1**) in DCM solution. Top: calculated spectrum for $[M+H]^+$; Middle: centroid spectrum; Bottom: continuum spectrum.

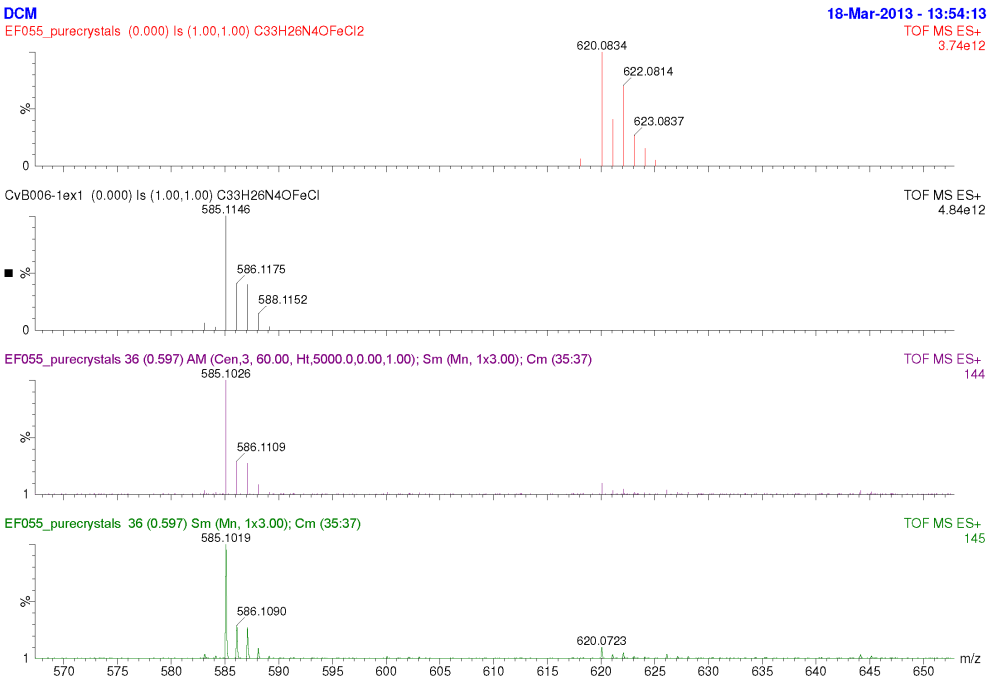

Figure 22. ESI-MS spectrum of [Fe(BM^{diPh}IK)Cl$_2$] (**2**) in DCM solution. Top: calculated spectra for $[M]^+$ (red) and $[M - Cl]^+$ (black); Middle: centroid spectrum; Bottom: continuum spectrum.

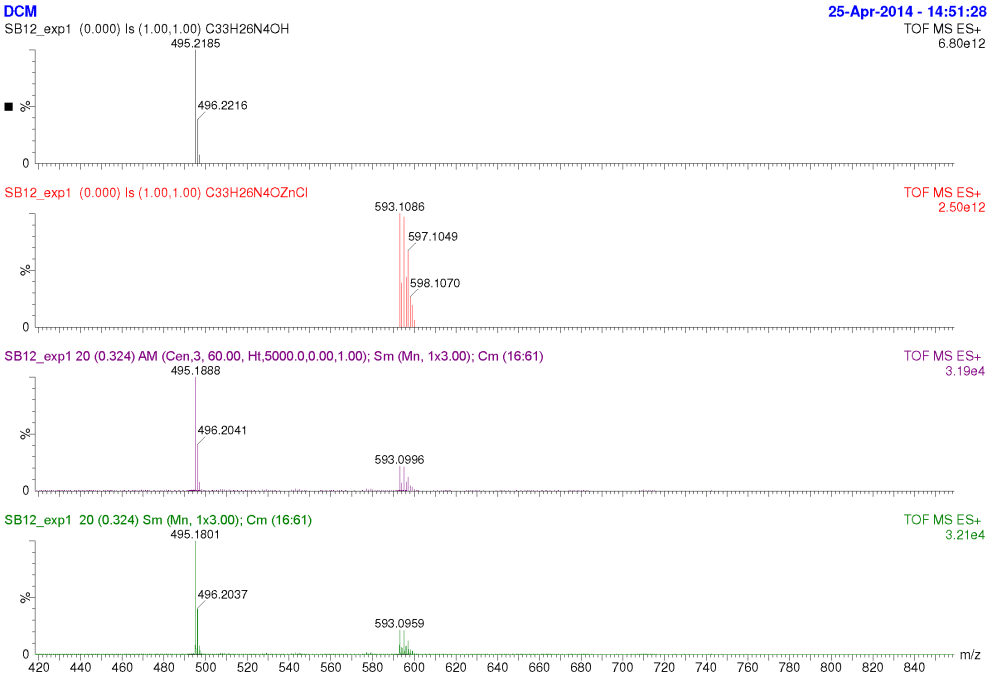

Figure 23. ESI-MS spectrum of [Zn(BM^{diPh}IK)Cl$_2$] (**3**) in DCM solution. Top: calculated spectra for [M – ZnCl2 + H]$^+$ (black) and [M – Cl]$^+$ (red); Middle: centroid spectrum; Bottom: continuum spectrum.

6. X-ray Crystal Structures

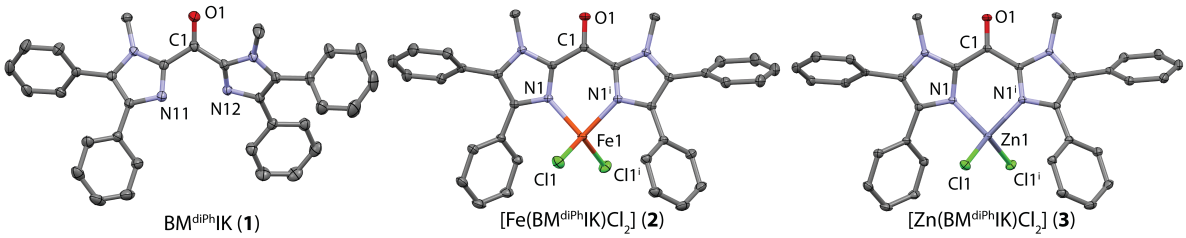

Figure 24. Molecular structures of ligand $BM^{diPh}IK$ (**1**) and complexes **2** and **3**. All hydrogen atoms and disordered solvent molecules have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Symmetry code for **2** and **3** *i*: [-x, y, 0.5−z].

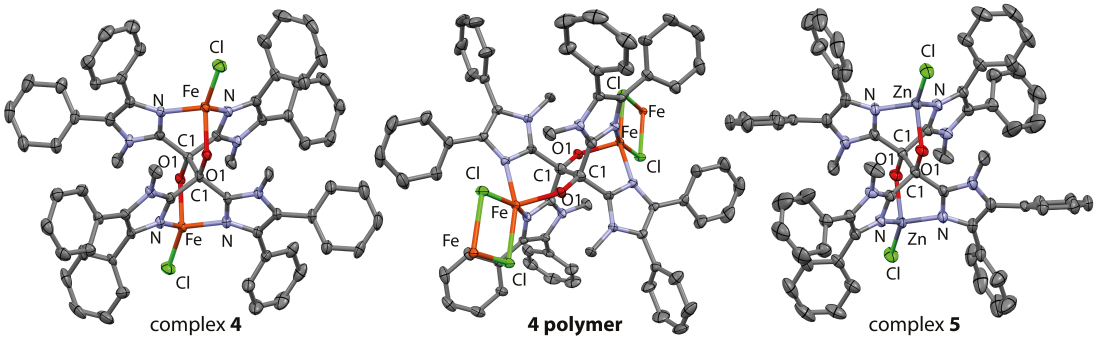

Figure 25. From *left* to *right*: Molecular structures of complex **4**, one monomer out of the **4 polymer**, and **5**. Hydrogen atoms and co-crystallized (solvent) molecules have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

A second independent complex of **4** is present in the asymmetric unit in which there is additionally (partly) coordinated solvent, most likely THF, present, resulting in a 4- and a 5-coordinated Fe center within one structure. This second molecule is severely affected by disorder (not fully resolved) and therefore not further discussed.

Under strict exclusion of THF during the crystallization of **4**, a coordination polymer is formed that can be isolated as white snow-like crystals. The structure of the coordination polymer of **4** consists of centrosymmetric binuclear monomers that polymerize by forming an $Fe_2(\mu\text{-}Cl)_2$-bridge. The geometry of the five-coordinate Fe centers is best described as a distorted square pyramidal ($\tau = 0.04$)[4] with the oxygen in the apical position and the two nitrogen atoms and chloride ions in the basal plane. Interestingly, the pinacolate C–C bond in the polymer is found to be significantly shorter (1.597(4) Å) compared to the monomer of **4** (1.729(8) Å), although still quite long.

Table 1: Selected bond lengths (Å) and angles (°) for $BM^{diPh}IK$.

	$BM^{diPh}IK$ *Structure 1*		$BM^{diPh}IK$ *Structure 2*
C1–O1	1.2307(13)	C1–O1	1.2315(13)
N11–C21	1.3284(13)	N1–C2	1.3279(13)
N12–C22	1.3240(14)	N3–C18	1.3236(13)
N11–C41	1.3641(13)	N1–C4	1.3637(13)
N12–C42	1.3674(13)	N3–C20	1.3675(13)
C21–C1–C22	115.83(9)	C2–C1–C18	115.86(9)

Table 2. Selected bond lengths [Å] and angles [°] for complexes **2·CH_2Cl_2**, **3·CH_2Cl_2**, and **3**.

2·CH_2Cl_2[a] [*i*: -x, y, 0.5-z]		**3·CH_2Cl_2**[a] [*i*: -x, y, 0.5-z]		Complex 3	
Fe1-Cl1	2.2563(2)	Zn1-Cl1	2.2270(3)	Zn1-Cl1	2.2190(4)
				Zn1-Cl2	2.2316(4)
Fe1-N1	2.0941(7)	Zn1-N1	2.0487(10)	Zn1-N11	2.0337(11)
				Zn1-N12	2.0395(11)
C1-O1	1.2288(14)	C1-O1	1.225(2)	C1-O1	1.2174(16)
N1-Fe1-N1^{i}	87.36(4)	N1-Zn1-N1^{i}	90.55(6)	N11-Zn1-N12	93.31(5)
Cl1-Fe1-Cl1^{i}	121.072(15)	Cl1-Zn1-Cl1^{i}	117.408(19)	Cl1-Zn1-Cl2	120.057(15)
N1-Fe1-Cl1	120.27(2)	N1-Zn1-Cl1	120.53(3)	N11-Zn1-Cl1	113.54(3)
				N12-Zn1-Cl1	108.03(3)
N1-Fe1-Cl1^{i}	101.97(2)	N1-Zn1-Cl1^{i}	102.89(3)	N11-Zn1-Cl2	104.64(3)
				N12-Zn1-Cl2	114.11(3)
C2-C1-C2^{i}	119.26(10)	C2-C1-C2^{i}	119.29(15)	C21-C1-C22	120.53(12)

[a] **2·CH_2Cl_2** and **3·CH_2Cl_2** are isostructural.

Table 3. Selected bond lengths [Å] and angles [°] for complexes **4**, **4-polymer**, and **5**.

Compound 4[a]				**4-polymer** [*i*: 1-x, 1-y, 1-z; *ii*: 2-x, 1-y, 1-z]		**Compound 5** [*i*: 1-x, 1-y, 1-z]	
Fe1-N11	2.085(5)	Fe2-N12	2.098(5)	Fe1-N11	2.142(2)	Zn1-N1	2.0299(11)
Fe1-N31	2.093(4)	Fe2-N32	2.091(4)	Fe1-N12	2.1648(19)	Zn1-N3	2.0295(11)
Fe1-O12	1.917(4)	Fe2-O11	1.905(4)	Fe1-O1^{i}	1.9368(16)	Zn1-O1^{i}	1.9463(10)
Fe1-Cl1	2.2189(16)	Fe2-Cl2	2.2224(17)	Fe1-Cl1	2.4158(7)	Zn1-Cl1	2.1683(4)
				Fe1-Cl1^{ii}	2.4687(6)		
C11-C12[b]	1.729(5)			C1-C1^{i}[b]	1.597(5)	C1-C1^{i}[b]	1.708(3)
C11-O11	1.354(6)	C12-O12	1.361(6)	C1-O1	1.368(3)	C1-O1	1.3618(16)
Fe1-Fe2	5.7361(11)			Fe1-Fe1^{i}	5.8465(6)	Zn1-Zn1^{i}	5.6471(4)
				Fe1-Fe1^{ii}	3.6484(6)		
N11-Fe1-N31	90.33(18)	N12-Fe2-N32	90.18(18)	N11-Fe1-N12	79.58(8)	N1-Zn1-N3	91.92(5)
N11-Fe1-O12	89.49(18)	N12-Fe2-O11	90.30(17)	N11-Fe1-O1^{i}	93.02(7)	N1-Zn1-O1^{i}	93.44(5)
N11-Fe1-Cl1	119.41(14)	N12-Fe2-Cl2	118.86(14)	N11-Fe1-Cl1	159.32(6)	N1-Zn1-Cl1	125.34(4)
				N11-Fe1-Cl1^{ii}	94.69(6)		
N31-Fe1-O12	89.33(17)	N32-Fe2-O11	89.26(17)	N12-Fe1-O1^{i}	92.37(7)	N3-Zn1-O1^{i}	92.75(4)
N31-Fe1-Cl1	125.15(14)	N32-Fe2-Cl2	125.22(13)	N12-Fe1-Cl1	95.97(6)	N3-Zn1-Cl1	126.69(3)
				N12-Fe1-Cl1^{ii}	162.02(6)		
O12-Fe1-Cl1	131.48(12)	O11-Fe2-Cl1	131.50(13)	O1^{i}-Fe1-Cl1	107.40(5)	O1^{i}-Zn1-Cl1	117.78(3)
				O1^{i}-Fe1-Cl1^{ii}	105.02(5)		
				Cl1-Fe1-Cl1^{ii}	83.35(2)		
C21-C11-C181	111.0(5)	C22-C12-C182	112.5(5)	C21-C1-C22	109.3(2)	C2-C1-C18	111.00(11)

[a] Only one of two independent molecules is described.

[b] Expectation values Csp^3-Csp^3: 1.53 Å; pinacolates 1.56-1.66 Å.[*ref* 5-11]

X-ray Crystal Structure Determinations

$BM^{diPh}IK$ (*structure 1*) (1): $C_{33}H_{26}N_4O$, *Fw* = 494.58, yellow block, 0.34 × 0.19 × 0.19 mm^3, monoclinic, $P2_1/n$ (no. 14), a = 14.9079(3), b = 10.5220(2), c = 16.5128(3) Å, β = 95.862(1)°, V = 2576.66(10) Å^3, Z = 4, D_x = 1.275 g/cm^3, μ = 0.08 mm^{-1}. 45277 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. The Eval15 software[12] as used for the integration of the intensities. Multiscan absorption correction and scaling was performed with SADABS[13] (correction range 0.72-0.75). 5929 Reflections were unique (R_{int} = 0.026), of which 5002 were observed *[I>2σ(I)]*. The structure was solved with Direct Methods using SIR-97.[14] Least-squares refinement was performed with SHELXL-2013[15] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined freely with isotropic displacement parameters. 447 Parameters were refined with no restraints. *R1/wR2 [I > 2σ(I)]*: 0.0369 / 0.0921. *R1/wR2* [all refl.]: 0.0453 / 0.0969. S = 1.045. Residual electron density between −0.21 and 0.26 e/Å^3. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[16]

[Fe($BM^{diPh}IK$)Cl_2] (2): $C_{33}H_{26}Cl_2FeN_4O{\cdot}CH_2Cl_2$, *Fw* = 706.25, orange needle, 0.63 × 0.11 × 0.04 mm^3, monoclinic, C2/c (no. 15), a = 19.4368(5), b = 17.2451(4), c = 10.5985(3) Å, β = 115.884(2)°, V = 3196.14(14) Å^3, Z = 4, D_x = 1.468 g/cm^3, μ = 0.84 mm^{-1}. 40730 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.81 Å^{-1}. The Eval15 software[12] was used for the integration of the intensities. A numerical absorption correction and scaling was performed with SADABS[13] (correction range 0.71-1.00). 7027 Reflections were unique (R_{int} = 0.026), of which 5833 were observed [I>2σ(I)]. The structure was solved with Patterson superposition methods using SHELXT.[18] Least-squares refinement was performed with SHELXL-2012[15] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. The CH_2Cl_2 solvent molecule was refined with a disorder model. Hydrogen atoms of the metal complex were located in difference Fourier maps. The H-atoms of the CH_2Cl_2 were included in calculated positions. All H-atoms were refined with a riding model. 212 Parameters were refined with 14 restraints (distances, angles and displacement parameters of CH_2Cl_2). *R1/wR2 [I > 2σ(I)]*: 0.0298 / 0.0766. *R1/wR2* [all refl.]: 0.0395 / 0.0802. S = 1.041. Residual electron density between −0.53 and 0.47 e/Å^3. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[16]

[Zn($BM^{diPh}IK$)Cl_2]·CH_2Cl_2 (3·CH_2Cl_2): $C_{33}H_{26}Cl_2N_4OZn{\cdot}CH_2Cl_2$, *Fw* = 715.77, yellow needle, 0.47 × 0.10 × 0.06 mm^3, monoclinic, C2/c (no. 15), a = 19.3128(8), b = 17.2091(5), c = 10.5274(4) Å, β = 115.255(2)°, V = 3164.41(19) Å^3, Z = 4, D_x = 1.502 g/cm^3, μ = 1.15 mm^{-1}. 20286 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 110(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. The Eval15 software[12] was used for the integration of the intensities. A numerical absorption correction and scaling was performed with SADABS[13] (correction range 0.67-0.96). 3617 Reflections were unique (R_{int} = 0.018), of which 3379 were observed *[I>2σ(I)]*. Initial coordinates were taken from the isostructural Fe-complex [Fe($BM^{diPh}IK$)Cl_2] (**2**). Least-squares refinement was performed with SHELXL-2013[15] against F^2 of all reflections.

Non-hydrogen atoms were refined freely with anisotropic displacement parameters. The CH_2Cl_2 solvent molecule was refined with a disorder model. Hydrogen atoms were included in calculated positions and refined with a riding model. 212 Parameters were refined with 14 restraints (distances, angles and displacement parameters of CH_2Cl_2). *R1/wR2 [I > 2σ(I)]*: 0.0220 / 0.0551. *R1/wR2* [all refl.]: 0.0242 / 0.0561. *S* = 1.055. Residual electron density between −0.33 and 0.35 e/Å^3. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[16]

[Zn(BM^{diPh}IK)Cl$_2$] (3): $C_{33}H_{26}Cl_2N_4OZn$, *Fw* = 630.85, pale yellow plate, 0.24 × 0.17 × 0.06 mm^3, triclinic, Pī (no. 2), *a* = 9.8959(3), *b* = 10.4838(3), *c* = 14.8613(4) Å, *α* = 85.874(2), *β* = 71.593(2), *γ* = 81.046(2)°, *V* = 1444.66(8) Å^3, *Z* = 2, D_x = 1.450 g/cm^3, *μ* = 1.07 mm^{-1}. 24985 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (*λ* = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. The Eval15 software[12] was used for the integration of the intensities. Multiscan absorption correction and scaling was performed with SADABS[13] (correction range 0.66-0.75). 6622 Reflections were unique (R_{int} = 0.019), of which 5845 were observed *[I>2σ(I)]*. The structure was solved with Patterson superposition methods using SHELXT.[18] Least-squares refinement was performed with SHELXL-2014[15] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined with a riding model. 372 Parameters were refined with no restraints. *R1/wR2 [I > 2σ(I)]*: 0.0236 / 0.0580. *R1/wR2* [all refl.]: 0.0293 / 0.0603. *S* = 1.033. Residual electron density between −0.31 and 0.32 e/Å^3. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[16]

4-polymer: $C_{33}H_{26}ClFeN_4O{\cdot}CH_2Cl_2{\cdot}0.5(C_4H_{10}O)$, *Fw* = 707.86, colorless needle, 0.68 × 0.05 × 0.03 mm^3, triclinic, Pī (no. 2), *a* = 9.1793(4), *b* = 12.1666(5), *c* = 15.4997(6) Å, *α* = 96.363(2), *β* = 102.112(2), *γ* = 100.294(2)°, *V* = 1645.32(12) Å^3, *Z* = 2, D_x = 1.429 g/cm^3, *μ* = 0.74 mm^{-1}. 28465 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (*λ* = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. The Eval15 software[12] was used for the integration of the intensities. A numerical absorption correction and scaling was performed with SADABS[13] (correction range 0.77-1.00). 7527 Reflections were unique (R_{int} = 0.039), of which 5574 were observed *[I>2σ(I)]*. The structure was solved with Patterson superposition methods using SHELXT.[18] Least-squares refinement was performed with SHELXL-2014[15] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. The diethyl ether molecule was disordered on an inversion center. Hydrogen atoms were introduced in calculated positions and refined with a riding model. 435 Parameters were refined with 7 restraints (distances and angles of diethyl ether). *R1/wR2 [I > 2σ(I)]*: 0.0445 / 0.1002. *R1/wR2* [all refl.]: 0.0702 / 0.1112. *S* = 1.023. Residual electron density between −0.40 and 0.68 e/Å^3. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[16]

Complex 4: $[C_{70}H_{60}Cl_2Fe_2N_8O_3][C_{66}H_{52}Cl_2Fe_2N_8O_2]{\cdot}3(CH_2Cl_2)$, *Fw* = 707.86, yellow plate, 0.28 × 0.24 × 0.08 mm^3, monoclinic, P2$_1$ (no. 4), *a* = 14.2435(3), *b* = 17.6941(6), *c* = 25.6720(7) Å, *β* = 103.152(2)°, *V* = 6300.3(3) Å^3, *Z* = 2, D_x = 1.408 g/cm^3, *μ* = 0.73 mm^{-1}. 169375 Reflections were measured on a Bruker Kappa ApexII diffractometer with

sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. The Eval15 software[12] was used for the integration of the intensities. For the prediction of the reflection profiles a large isotropic mosaicity of 1.6° was used. A numerical absorption correction and scaling was performed with SADABS[13] (correction range 0.82-0.98). 28957 Reflections were unique (R_{int} = 0.025), of which 25127 were observed *[I>2σ(I)]*. The structure was solved with Direct Methods using SIR-2011.[19] The crystal structure is *pseudo*-centrosymmetric with only the coordinated solvents at Fe3 and Fe4 violating the symmetry. Least-squares refinement as an inversion twin was performed with SHELXL-2014[15] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. The metal complex containing Fe3 and Fe4 was disordered and the disorder was only partially resolved (mainly in the phenyl rings). Close to Fe4 there is a region of diffuse electron density. The number of electrons in this region was estimated with SQUEEZE[20] to be approximately 39. Concerning the shape and the major distances between the maxima of electron density, the diffuse region was modelled as disordered CH_2Cl_2. Hydrogen atoms were introduced in calculated positions and refined with a riding model. 1718 Parameters were refined with 521 restraints (flatness of phenyl rings; distances, angles and displacement parameters of disordered groups). *R1/wR2 [I > 2σ(I)]*: 0.0537 / 0.1372. *R1/wR2* [all refl.]: 0.0639 / 0.1468. *S* = 1.016. Residual electron density between −0.85 and 1.30 e/Å^3. Batch scale factor of the inversion twinning *BASF* = 0.34(2). Geometry calculations and checking for higher symmetry were performed with the PLATON program.[16]

Complex 5: $C_{66}H_{52}Cl_2N_8O_2Zn_2$ + disordered solvent, *Fw* = 1190.79[21], colorless block, 0.39 × 0.34 × 0.26 mm^3, triclinic, Pī (no. 2), *a* = 10.6545(4), *b* = 12.7083(6), *c* = 15.0735(6) Å, α = 67.700(2), β = 72.709(2), γ = 79.513(2)°, *V* = 1797.44(14) Å^3, *Z* = 1, D_x = 1.100 g/cm$^{3\,21}$, μ = 0.78 mm$^{-1\,21}$. A measurement temperature of 210(2) K was chosen above the temperature of a phase transition. 31525 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. The Eval15 software[12] was used for the integration of the intensities. Multiscan absorption correction and scaling was performed with SADABS[13] (correction range 0.70-0.75). 8256 Reflections were unique (R_{int} = 0.018), of which 7375 were observed *[I>2σ(I)]*. The structure was solved with Patterson superposition methods using SHELXT.[18] Least-squares refinement was performed with SHELXL-2014[15] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. The crystal structure contains severely disordered CH_2Cl_2 solvent molecules. Their contribution to the structure factors was taken into account using the SQUEEZE algorithm.[20] The solvent accessible voids amount to 519 Å^3/unit cell. The contribution of the disordered molecules is 167 electrons / unit cell. One phenyl ring was rotationally disordered over two orientations. Hydrogen atoms were introduced in calculated positions and refined with a riding model. 418 Parameters were refined with 145 restraints (flatness of phenyl rings and distances between phenyl and imidazole rings). *R1/wR2 [I > 2σ(I)]*: 0.0281 / 0.0738. *R1/wR2* [all refl.]: 0.0325 / 0.0757. *S* = 1.056. Residual electron density between −0.44 and 0.47 e/Å^3. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[16]

CCDC 1519042 [**BM^{diPh}IK (*structure 1*)**], 1519043 [**BM^{diPh}IK (*structure 2*)**], 1519044 [**Fe(BM^{diPh}IK)Cl$_2$**], 1519045 ([**Zn(BM^{diPh}IK)Cl$_2$]·CH$_2$Cl$_2$**), 1519046 [**Zn(BM^{diPh}IK)Cl$_2$**], 1519047 (**4-polymer**), 1519048

(Complex 4), 1519049 **(Complex 5)** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

7. DFT Computational Details

DFT results were obtained using the Gaussian 09 software package,[22] using the B3LYP (Becke, three-parameter, Lee-Yang-Parr) functional and the 6-31g** basis set on C, H, N, O, and Cl and LANL2DZ on Zn. If applicable, the structures were optimized with symmetry restraints. Frequency analyses were performed on all calculations. Transition state structures were calculated using the opt=QST2 option. The broken symmetry calculation was forced not to converge to a singlet state by using guess=(mix,NoSymm) keywords. DFT calculation-derived pictures have been generated using the GaussView 5.0.8. software or Jmol and the Jmol-NBO Visualization Helper version 2. For NBO calculations, the NBO6 program up to the NLMO basis set was used.[23]

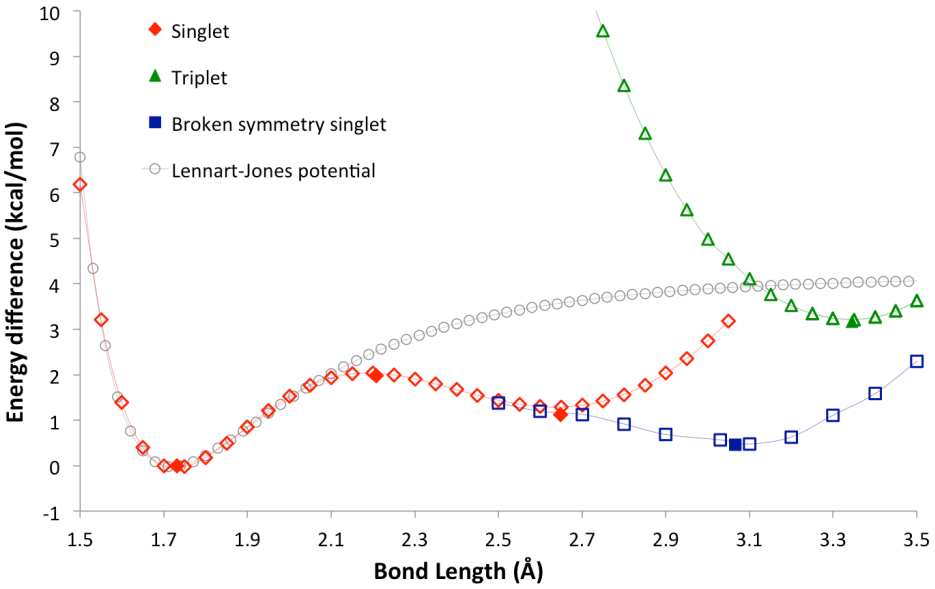

Figure 26. Relaxed potential energy surface scan of the singlet state (diamonds), the broken symmetry singlet state (squares), and the triplet state (triangles) of the single reduced [Zn_2(L-dimer)Cl_2] using (U)B3LYP and 6-31g** for C,H,N,O, and Cl and LANL2DZ for Zn. As a comparison the Lennart-Jones fit for the bound structure is included (circles). The filled symbols indicate local minima or transition state that were optimized without any constrains. A line connecting the data points is added as a guide to the eye. Energy differences are relative to the optimized singlet state (minimum in diamonds).

From the Lennart-Jones potential we could read an estimate for the bond dissociation energy (BDE) of ±4 kcal/mol. The Lennart-Jones potential ($V(R_{(CC)}) = \varepsilon\left[\left(\frac{r_m}{R_{(CC)}}\right)^{12} - 2\left(\frac{r_m}{R_{(CC)}}\right)^{6}\right]$) is fitted by adjusting the parameters manually. The best fit was obtained with values for the equilibrium distance (r_m) of 1.72 Å and the depth of the potential well (ε) of 4.2 kcal/mol. This last value can be used as an approximate measure of the BDE, not taking into account other interactions within the molecule like Zn–O interaction.

The geometry optimization starting from the X-ray crystal structure geometry resulted in a line parallel to the singlet state but slightly higher in energy as a consequence of a different rotation of the phenyl groups. It is decided to use the global minimum in our discussion instead of the local minimum obtained from the X-ray crystal structure geometry.

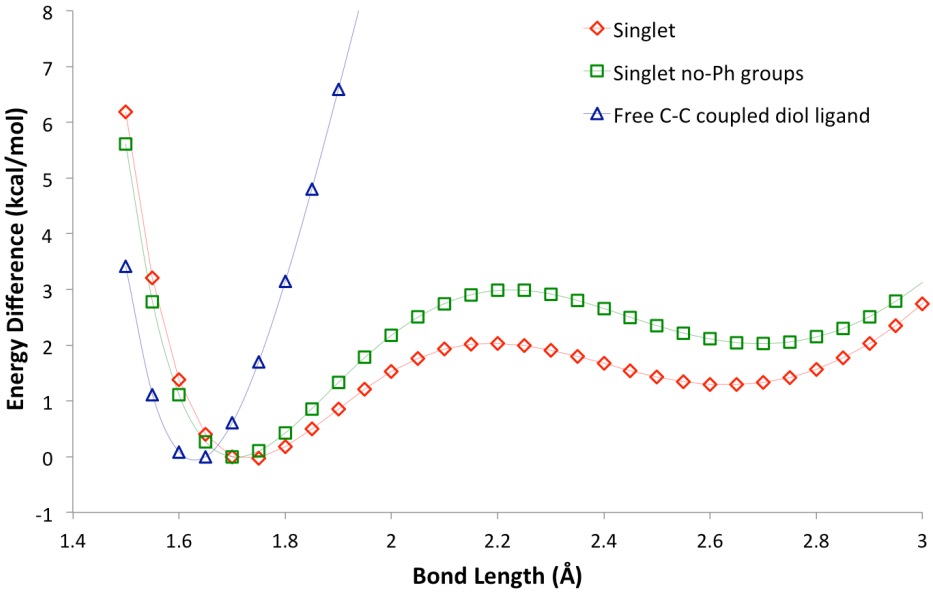

Figure 27. Relaxed potential energy surface scan of the singlet state (diamonds), the singlet state without phenyl-groups (squares), and the free L-dimer (triangles) of the single reduced [Zn_2(L-dimer)Cl_2] using (U)B3LYP and 6-31g** for C,H,N,O, and Cl and LANL2DZ for Zn. The smooth line connecting the separate data points is added to clarify the trends. The energy differences are relative to the minimum of the corresponding scan.

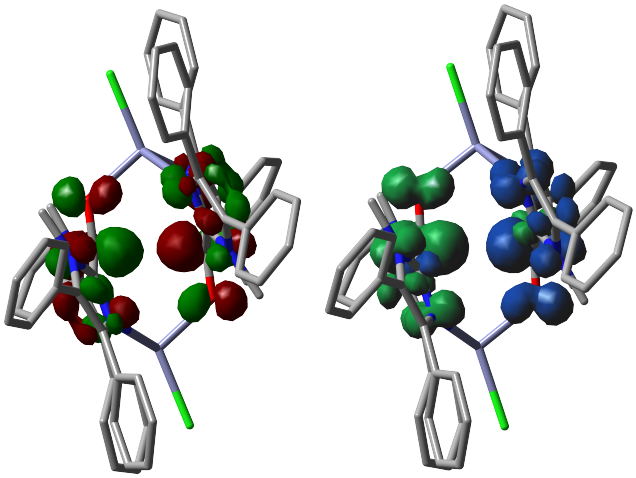

Figure 28. The α and β spin SOMO (left) and spin density plot (right) for the broken symmetry singlet structure. Hydrogen atoms are omitted for clarity.

Table 4. Overview of the DFT results. Functional: (U)B3LYP Basis set: 6-31** for C, H, N, O, and Cl and LANL2DZ for Zn

Entry		Electronic energy (Hartree/Particle)	Gibbs free energy (Hartree/Particle)	C–C length (Å)	ν(C–C) (cm^{-1})	ν(C–O) (cm^{-1})	ν(Zn–O) (cm^{-1})
1	Experimental **5**	-	-	1.712(3)	-	1180	546
2	$BM^{diPh}IK$	−1567.49572442	−1567.055154	-	-	1558	-
3	$BE^{Ph}IK$	−1184.00948823	−1183.663465	-	-	1566	-
4	BMBIK	−950.549427533	−950.317814	-	-	1571	-
5	Short singlet	−4186.70411567	−4185.789854	1.73085	831.45	1223/1241	554/568
6	Long singlet	−4186.7023231	−4185.787206	2.64857	-	1337/1348	553/566
7	Transition State	−4186.70095494	−4185.785424	2.20727	-118	1297	553
8	Broken symmetry singlet	−4186.70337231	−4185.789538	3.06645	-	1365	541
9	Long triplet	−4186.69907835	−4185.782616	3.34418	-	1347/1360	565
10	Isolated radical	−2093.31453736	−2092.87403	-	-	1397.89	-
11	Short singlet no Ph-substituents	−2338.24113853	−2337.917951	1.70765	719.69/ 856.48	1199/1218	589
12	Free pinacol	−3136.14804021	−3135.204746	1.62966	986.37	1127	-

Entry		Wiberg bond index C–C	Wiberg bond index C–O	Wiberg bond index Zn–O	^{13}C chemical shift (ppm)
1	Experimental **5**	-	-	-	89.81
2	Experimental $BM^{diPh}IK$	-	-	-	175
3	Experimental $BE^{Ph}IK$	-	-	-	174
4	Experimental BMBIK	-	-	-	179
5	Short singlet	0.7714	1.0679	0.1166	101.83
6	Long singlet	0.1896	1.1929	0.1057	128.70
7	Transition State	-	-	-	-
8	Broken symmetry singlet	0.0467	1.2423	0.1102	134.30
9	Long triplet	0.0015	1.2584	0.1152	140.36
10	Isolated radical	-	1.4327	-	145.17
11	Short singlet no Ph-substituents	0.7943	1.0627	0.1214	99.59
12	Free pinacol	0.8871	0.9571	-	91.580

Optimized coordinates for the BM^{diPh}IK radical

Functional: (U)B3LYP Basis set: 6-31**

	X	Y	Z
C	0.00001200	1.92884900	0.00021000
C	1.25928900	1.18116400	−0.02269600
C	−1.25925600	1.18113000	0.02293100
O	−0.00002600	3.21625300	0.00028400
N	−2.49119900	1.78601000	−0.27282900
N	−1.44703600	−0.09911400	0.39570000
N	1.44701100	−0.09906000	−0.39556500
N	2.49128300	1.78603600	0.27287900
C	−3.49129100	0.81944000	−0.09227200
C	−2.79345300	−0.33798500	0.33391900
C	2.79342400	−0.33797800	−0.33386600
C	3.49132400	0.81942600	0.09227300
C	−2.68296300	3.08275200	−0.91901100
C	2.68315800	3.08277500	0.91903400
H	−3.43626400	2.98345300	−1.71981200
H	−1.71393800	3.41626300	−1.30960500
H	−3.02867500	3.84899600	−0.20081200
H	1.71401400	3.41660600	1.30906800
H	3.02949800	3.84883000	0.20093500
H	3.43603400	2.98333100	1.72022100
C	−4.90463400	1.06853400	−0.37173900
C	−5.68465400	0.10878800	−1.08048900
C	−5.56223700	2.26556000	0.03543800
C	−7.03839500	0.32896500	−1.35044400
H	−5.19983900	−0.81165500	−1.42248800
C	−6.91428000	2.48670200	−0.25098400
H	−5.00312700	3.01244600	0.60895300
C	−7.66928300	1.52238800	−0.94474600
H	−7.60673400	−0.43153800	−1.90085900
H	−7.38904000	3.41788600	0.08400700
H	−8.72860700	1.69684700	−1.16651300
C	−3.30141200	−1.65187700	0.77709900
C	−2.41952400	−2.76009200	0.75053400
C	−4.60883300	−1.85581800	1.27930200
C	−2.83702100	−4.02483500	1.18297900
H	−1.39941000	−2.58888000	0.39241400
C	−5.02439700	−3.12457900	1.70916300
H	−5.29915900	−1.00949900	1.34524500
C	−4.14522400	−4.21911100	1.66024700
H	−2.13458000	−4.86713800	1.14813700
H	−6.04297300	−3.25453900	2.09639300
H	−4.47296800	−5.21026700	1.99736800
C	3.30132300	−1.65187900	−0.77707800
C	4.60874500	−1.85587000	−1.27925900
C	2.41938500	−2.76005700	−0.75054400
C	5.02425900	−3.12464200	−1.70913600
H	5.29911200	−1.00958100	−1.34516800
C	2.83683400	−4.02480900	−1.18300400
H	1.39927500	−2.58880300	−0.39243300
C	4.14503500	−4.21913500	−1.66025600
H	6.04283700	−3.25464100	−2.09634800
H	2.13435500	−4.86708200	−1.14818800
H	4.47274100	−5.21029900	−1.99738900
C	4.90469500	1.06847700	0.37165200
C	5.56232100	2.26546300	−0.03559900
C	5.68471300	0.10871900	1.08038400
C	6.91438500	2.48656500	0.25075400
H	5.00321400	3.01234600	−0.60912300
C	7.03847800	0.32885200	1.35026600
H	5.19987800	−0.81169700	1.42242700
C	7.66938500	1.52224300	0.94450700
H	7.38916500	3.41772100	−0.08428900
H	7.60681700	−0.43165800	1.90066900
H	8.72872600	1.69667200	1.16621800

E_{total} = −1567.49572442 Hartree/Particle
G = −1567.055154 Hartree/Particle

Optimized coordinates for compound 5 (bound singlet)

Functional: B3LYP Basis set: 6-31** for C, H, N, O, and Cl and LANL2DZ for Zn

	X	Y	Z
Zn	−1.69447800	2.35304500	0.00000000
Cl	−3.56292000	3.60273400	0.00000000
O	1.83098800	−0.38146800	0.00000000
N	−0.16391900	2.29477800	1.47722200
N	−0.16391900	2.29477800	−1.47722200
N	1.53645700	1.18199100	2.34502300
N	1.53645700	1.18199100	−2.34502300
C	0.75094300	0.43016900	0.00000000
C	0.72101700	1.31773700	1.25738200
C	0.72101700	1.31773700	−1.25738200
C	1.13004000	2.11714200	3.29805800
C	1.13004000	2.11714200	−3.29805800
C	0.06750700	2.80380400	2.73993200
C	0.06750700	2.80380400	−2.73993200
C	2.72144500	0.32478900	2.51068500
C	2.72144500	0.32478900	−2.51068500
C	1.80284900	2.30125300	4.59954500
C	1.80284900	2.30125300	−4.59954500
C	1.92572400	1.24233900	5.51644500
C	1.92572400	1.24233900	−5.51644500
C	2.54922700	1.43802100	6.74860500
C	2.54922700	1.43802100	−6.74860500
C	3.05230700	2.69527900	7.08856100
C	3.05230700	2.69527900	−7.08856100
C	2.93027700	3.75611200	6.18852600
C	2.93027700	3.75611200	−6.18852600
C	2.31467100	3.56112400	4.95317500
C	2.31467100	3.56112400	−4.95317500
C	−0.74295200	3.89422800	3.31228700
C	−0.74295200	3.89422800	−3.31228700
C	−1.13004400	3.87752700	4.66368000
C	−1.13004400	3.87752700	−4.66368000
C	−1.89490100	4.91366000	5.19552300
C	−1.89490100	4.91366000	−5.19552300
C	−2.29455400	5.98028200	4.38721100

C	−2.29455400	5.98028200	−4.38721100
C	−1.92226000	6.00352800	3.04263900
C	−1.92226000	6.00352800	−3.04263900
C	−1.15047600	4.97204600	2.51048500
C	−1.15047600	4.97204600	−2.51048500
H	2.43328400	−0.66905500	2.86030600
H	3.37100000	0.79084500	3.25044100
H	3.22223800	0.22347800	1.55487800
H	3.22223800	0.22347800	−1.55487800
H	3.37100000	0.79084500	−3.25044100
H	2.43328400	−0.66905500	−2.86030600
H	1.52215100	0.26558400	5.26503200
H	1.52215100	0.26558400	−5.26503200
H	2.63649900	0.60896400	7.44484500
H	2.63649900	0.60896400	−7.44484500
H	3.53625000	2.84725900	8.04890700
H	3.53625000	2.84725900	−8.04890700
H	3.32096600	4.73639800	6.44544500
H	3.32096600	4.73639800	−6.44544500
H	2.22479800	4.38442000	4.25185600
H	2.22479800	4.38442000	−4.25185600
H	−0.83552000	3.04538100	5.29489800
H	−0.83552000	3.04538100	−5.29489800
H	−2.18809000	4.88258000	6.24113300
H	−2.18809000	4.88258000	−6.24113300
H	−2.89684600	6.78372700	4.80117700
H	−2.89684600	6.78372700	−4.80117700
H	−2.23496400	6.82302200	2.40282900
H	−2.23496400	6.82302200	−2.40282900
H	−0.85573200	5.00368500	1.46699100
H	−0.85573200	5.00368500	−1.46699100
O	−1.83098800	0.38146800	0.00000000
N	0.16391900	−2.29477800	−1.47722200
N	0.16391900	−2.29477800	1.47722200
N	−1.53645700	−1.18199100	−2.34502300
N	−1.53645700	−1.18199100	2.34502300
C	−0.75094300	−0.43016900	0.00000000
C	−0.72101700	−1.31773700	−1.25738200
C	−0.72101700	−1.31773700	1.25738200
C	−1.13004000	−2.11714200	−3.29805800
C	−1.13004000	−2.11714200	3.29805800
C	−0.06750700	−2.80380400	−2.73993200
C	−0.06750700	−2.80380400	2.73993200
C	−2.72144500	−0.32478900	−2.51068500
C	−2.72144500	−0.32478900	2.51068500
C	−1.80284900	−2.30125300	−4.59954500
C	−1.80284900	−2.30125300	4.59954500
C	−1.92572400	−1.24233900	−5.51644500
C	−1.92572400	−1.24233900	5.51644500
C	−2.54922700	−1.43802100	−6.74860500
C	−2.54922700	−1.43802100	6.74860500
C	−3.05230700	−2.69527900	−7.08856100
C	−3.05230700	−2.69527900	7.08856100
C	−2.93027700	−3.75611200	−6.18852600
C	−2.93027700	−3.75611200	6.18852600
C	−2.31467100	−3.56112400	−4.95317500
C	−2.31467100	−3.56112400	4.95317500
C	0.74295200	−3.89422800	−3.31228700
C	0.74295200	−3.89422800	3.31228700
C	1.13004400	−3.87752700	−4.66368000
C	1.13004400	−3.87752700	4.66368000
C	1.89490100	−4.91366000	−5.19552300
C	1.89490100	−4.91366000	5.19552300
C	2.29455400	−5.98028200	−4.38721100
C	2.29455400	−5.98028200	4.38721100
C	1.92226000	−6.00352800	−3.04263900
C	1.92226000	−6.00352800	3.04263900
C	1.15047600	−4.97204600	−2.51048500
C	1.15047600	−4.97204600	2.51048500
H	−2.43328400	0.66905500	−2.86030600
H	−3.37100000	−0.79084500	−3.25044100
H	−3.22223800	−0.22347800	−1.55487800
H	−3.22223800	−0.22347800	1.55487800
H	−3.37100000	−0.79084500	3.25044100
H	−2.43328400	0.66905500	2.86030600
H	−1.52215100	−0.26558400	−5.26503200
H	−1.52215100	−0.26558400	5.26503200
H	−2.63649900	−0.60896400	−7.44484500
H	−2.63649900	−0.60896400	7.44484500
H	−3.53625000	−2.84725900	−8.04890700
H	−3.53625000	−2.84725900	8.04890700
H	−3.32096600	−4.73639800	−6.44544500
H	−3.32096600	−4.73639800	6.44544500
H	−2.22479800	−4.38442000	−4.25185600
H	−2.22479800	−4.38442000	4.25185600
H	0.83552000	−3.04538100	−5.29489800
H	0.83552000	−3.04538100	5.29489800
H	2.18809000	−4.88258000	−6.24113300
H	2.18809000	−4.88258000	6.24113300
H	2.89684600	−6.78372700	−4.80117700
H	2.89684600	−6.78372700	4.80117700
H	2.23496400	−6.82302200	−2.40282900
H	2.23496400	−6.82302200	2.40282900
H	0.85573200	−5.00368500	−1.46699100
H	0.85573200	−5.00368500	1.46699100
Zn	1.69447800	−2.35304500	0.00000000
Cl	3.56292000	−3.60273400	0.00000000

E_{total} = −4186.70411567 Hartree/Particle
G = −4185.789854 Hartree/Particle

Optimized coordinates for compound 5, elongated closed-shell singlet

Functional: B3LYP Basis set: 6-31** for C, H, N, O, and Cl and LANL2DZ for Zn

	X	Y	Z
Zn	2.81091900	0.04748500	0.00000000
Cl	4.94853200	−0.66469900	0.00000000
O	−1.47824600	1.46799900	0.00000000
N	1.85920100	1.23673600	−1.46195500
N	1.85920100	1.23673600	1.46195500
N	−0.02515400	1.91147700	−2.43166300
N	−0.02515400	1.91147700	2.43166300
C	−0.17834700	1.31222200	0.00000000

C	0.54771200	1.48273100	−1.25730800
C	0.54771200	1.48273100	1.25730800
C	0.97119700	1.93955400	−3.40574800
C	0.97119700	1.93955400	3.40574800
C	2.13451200	1.51496400	−2.78613400
C	2.13451200	1.51496400	2.78613400
C	−1.37442800	2.45570100	−2.63181800
C	−1.37442800	2.45570100	2.63181800
C	0.74735600	2.43318800	−4.77741700
C	0.74735600	2.43318800	4.77741700
C	−0.26936200	1.90277600	−5.59124700
C	−0.26936200	1.90277600	5.59124700
C	−0.46302500	2.37725700	−6.88825600
C	−0.46302500	2.37725700	6.88825600
C	0.35873600	3.38419800	−7.39768000
C	0.35873600	3.38419800	7.39768000
C	1.37442300	3.91666500	−6.60008900
C	1.37442300	3.91666500	6.60008900
C	1.56553500	3.45005200	−5.30096200
C	1.56553500	3.45005200	5.30096200
C	3.48635800	1.37412500	−3.35763900
C	3.48635800	1.37412500	3.35763900
C	3.68048100	0.85525800	−4.65037400
C	3.68048100	0.85525800	4.65037400
C	4.96223900	0.73675600	−5.18295900
C	4.96223900	0.73675600	5.18295900
C	6.07428400	1.12815500	−4.43355200
C	6.07428400	1.12815500	4.43355200
C	5.89401700	1.64058100	−3.14854000
C	5.89401700	1.64058100	3.14854000
C	4.61210200	1.76543100	−2.61579400
C	4.61210200	1.76543100	2.61579400
H	−2.05807000	1.68225300	−2.99075800
H	−1.31564500	3.25107300	−3.37494300
H	−1.75118900	2.83572700	−1.68827700
H	−1.75118900	2.83572700	1.68827700
H	−1.31564500	3.25107300	3.37494300
H	−2.05807000	1.68225300	2.99075800
H	−0.90014500	1.10653500	−5.20862900
H	−0.90014500	1.10653500	5.20862900
H	−1.25241400	1.95386700	−7.50248100
H	−1.25241400	1.95386700	7.50248100
H	0.20852600	3.75208900	−8.40843800
H	0.20852600	3.75208900	8.40843800
H	2.01534700	4.70341400	−6.98729600
H	2.01534700	4.70341400	6.98729600
H	2.34987000	3.87127900	−4.68064800
H	2.34987000	3.87127900	4.68064800
H	2.82195800	0.54668100	−5.23809700
H	2.82195800	0.54668100	5.23809700
H	5.09369300	0.33007500	−6.18170500
H	5.09369300	0.33007500	6.18170500
H	7.07375300	1.02890600	−4.84684500
H	7.07375300	1.02890600	4.84684500
H	6.75166400	1.93929700	−2.55380400
H	6.75166400	1.93929700	2.55380400
H	4.47979300	2.17515500	−1.62040400
H	4.47979300	2.17515500	1.62040400
O	1.47824600	−1.46799900	0.00000000
N	−1.85920100	−1.23673600	1.46195500
N	−1.85920100	−1.23673600	−1.46195500
N	0.02515400	−1.91147700	2.43166300
N	0.02515400	−1.91147700	−2.43166300
C	0.17834700	−1.31222200	0.00000000
C	−0.54771200	−1.48273100	1.25730800
C	−0.54771200	−1.48273100	−1.25730800
C	−0.97119700	−1.93955400	3.40574800
C	−0.97119700	−1.93955400	−3.40574800
C	−2.13451200	−1.51496400	2.78613400
C	−2.13451200	−1.51496400	−2.78613400
C	1.37442800	−2.45570100	2.63181800
C	1.37442800	−2.45570100	−2.63181800
C	−0.74735600	−2.43318800	4.77741700
C	−0.74735600	−2.43318800	−4.77741700
C	0.26936200	−1.90277600	5.59124700
C	0.26936200	−1.90277600	−5.59124700
C	0.46302500	−2.37725700	6.88825600
C	0.46302500	−2.37725700	−6.88825600
C	−0.35873600	−3.38419800	7.39768000
C	−0.35873600	−3.38419800	−7.39768000
C	−1.37442300	−3.91666500	6.60008900
C	−1.37442300	−3.91666500	−6.60008900
C	−1.56553500	−3.45005200	5.30096200
C	−1.56553500	−3.45005200	−5.30096200
C	−3.48635800	−1.37412500	3.35763900
C	−3.48635800	−1.37412500	−3.35763900
C	−3.68048100	−0.85525800	4.65037400
C	−3.68048100	−0.85525800	−4.65037400
C	−4.96223900	−0.73675600	5.18295900
C	−4.96223900	−0.73675600	−5.18295900
C	−6.07428400	−1.12815500	4.43355200
C	−6.07428400	−1.12815500	−4.43355200
C	−5.89401700	−1.64058100	3.14854000
C	−5.89401700	−1.64058100	−3.14854000
C	−4.61210200	−1.76543100	2.61579400
C	−4.61210200	−1.76543100	−2.61579400
H	2.05807000	−1.68225300	2.99075800
H	1.31564500	−3.25107300	3.37494300
H	1.75118900	−2.83572700	1.68827700
H	1.75118900	−2.83572700	−1.68827700
H	1.31564500	−3.25107300	−3.37494300
H	2.05807000	−1.68225300	−2.99075800
H	0.90014500	−1.10653500	5.20862900
H	0.90014500	−1.10653500	−5.20862900
H	1.25241400	−1.95386700	7.50248100
H	1.25241400	−1.95386700	−7.50248100
H	−0.20852600	−3.75208900	8.40843800
H	−0.20852600	−3.75208900	−8.40843800
H	−2.01534700	−4.70341400	6.98729600
H	−2.01534700	−4.70341400	−6.98729600
H	−2.34987000	−3.87127900	4.68064800
H	−2.34987000	−3.87127900	−4.68064800
H	−2.82195800	−0.54668100	5.23809700
H	−2.82195800	−0.54668100	−5.23809700
H	−5.09369300	−0.33007500	6.18170500
H	−5.09369300	−0.33007500	−6.18170500
H	−7.07375300	−1.02890600	4.84684500
H	−7.07375300	−1.02890600	−4.84684500

H	−6.75166400	−1.93929700	2.55380400
H	−6.75166400	−1.93929700	−2.55380400
H	−4.47979300	−2.17515500	1.62040400
H	−4.47979300	−2.17515500	−1.62040400
Zn	−2.81091900	−0.04748500	0.00000000
Cl	−4.94853200	0.66469900	0.00000000

E_{total} = −4186.70232310 Hartree/Particle
G = −4185.787206 Hartree/Particle

Optimized coordinates for the transition state

Functional: (U)B3LYP Basis set: 6-31** for C, H, N, O, and Cl and LANL2DZ for Zn

	X	Y	Z
Zn	−0.02239800	−2.67270600	−0.96359200
Cl	−0.14110100	−4.41138900	−2.38979000
O	0.25334000	0.87087200	1.77913100
N	1.46610800	−2.31717700	0.49621700
N	−1.48373100	−2.04661100	0.44131400
N	2.57149200	−0.80646800	1.68445200
N	−2.19255000	−0.57043000	1.93463300
C	0.17079100	−0.24627200	1.07588600
C	1.37164400	−1.12323700	1.10355700
C	−1.13569000	−0.96834900	1.16090100
C	3.45705700	−1.85522800	1.42897000
C	−3.25575500	−1.43564000	1.68071100
C	2.75170900	−2.78462300	0.68448300
C	−2.80021000	−2.34535400	0.74294700
C	2.88228300	0.33024700	2.56222900
C	−2.21033400	0.44575700	2.99699600
C	4.82840500	−1.91609200	1.96941300
C	−4.54572100	−1.36428500	2.39330400
C	5.74492100	−0.86589900	1.78116800
C	−5.29638500	−0.17617700	2.44181300
C	7.04103200	−0.95119800	2.28955100
C	−6.51496400	−0.13354200	3.11897600
C	7.44734400	−2.08829200	2.98973400
C	−7.00908600	−1.27600500	3.75092100
C	6.54754500	−3.13939500	3.18090600
C	−6.27436700	−2.46306000	3.70551900
C	5.24991500	−3.05387100	2.68025800
C	−5.05191300	−2.50673200	3.03816100
C	3.20130400	−4.08187900	0.14752200
C	−3.53722700	−3.44842400	0.09926600
C	4.47066400	−4.22473200	−0.43892800
C	−4.88400900	−3.28716000	−0.27653500
C	4.88595200	−5.45653000	−0.94015600
C	−5.58054900	−4.32670500	−0.88920900
C	4.03983900	−6.56567000	−0.87066900
C	−4.94525500	−5.54427200	−1.14573800
C	2.77544800	−6.43385800	−0.29554900
C	−3.60963200	−5.71404100	−0.78055900
C	2.35966800	−5.20364400	0.21101800
C	−2.91296700	−4.67837600	−0.15883600
H	3.27245300	1.17132300	1.98298400
H	3.63605400	0.00993000	3.28109400
H	1.97496900	0.64955200	3.06257200
H	−1.20471100	0.58018600	3.37871700
H	−2.88382700	0.10365400	3.78271300
H	−2.56708000	1.40436900	2.61345100
H	5.44488400	0.01697700	1.22538700
H	−4.92938800	0.71480800	1.94180800
H	7.73406200	−0.12974000	2.13243600
H	−7.08011800	0.79354300	3.14728300
H	8.45701200	−2.15482500	3.38424200
H	−7.95904400	−1.24146100	4.27627400
H	6.85392300	−4.02615400	3.72811900
H	−6.64927200	−3.35546100	4.19825400
H	4.55126000	−3.86906500	2.83702900
H	−4.47822500	−3.42748000	3.01183900
H	5.12868700	−3.36433900	−0.50668000
H	−5.38250400	−2.34275600	−0.08387700
H	5.86829300	−5.54791700	−1.39489700
H	−6.61928200	−4.18286700	−1.17333500
H	4.36177900	−7.52381200	−1.26806100
H	−5.48628700	−6.35167200	−1.63058900
H	2.10696400	−7.28786400	−0.24452200
H	−3.10114700	−6.65145800	−0.98322800
H	1.37912700	−5.10956200	0.66608400
H	−1.87772900	−4.82830100	0.12526800
O	0.25323000	−0.87086000	−1.77896600
N	−1.48386600	2.04653900	−0.44106700
N	1.46606200	2.31722500	−0.49617100
N	−2.19243000	0.57053600	−1.93469100
N	2.57150800	0.80644900	−1.68428000
C	0.17078300	0.24628000	−1.07572200
C	−1.13569700	0.96838400	−1.16075100
C	1.37165000	1.12322900	−1.10341900
C	−3.25568400	1.43569600	−1.68081700
C	3.45704100	1.85524900	−1.42885500
C	−2.80031700	2.34528500	−0.74284500
C	2.75165800	2.78468200	−0.68444500
C	−2.21002900	−0.44556100	−2.99714600
C	2.88236100	−0.33033500	−2.56194500
C	−4.54557200	1.36437200	−2.39355300
C	4.82837300	1.91611900	−1.96933700
C	−5.29618300	0.17623700	−2.44226000
C	5.74492200	0.86596000	−1.78106900
C	−6.51470800	0.13363600	−3.11951900
C	7.04101300	0.95126500	−2.28950100
C	−7.00882600	1.27615700	−3.75136400
C	7.44727200	2.08833400	−2.98975600
C	−6.27416000	2.46323800	−3.70576200
C	6.54744400	3.13940900	−3.18094000
C	−5.05176100	2.50687900	−3.03830100
C	5.24983400	3.05388000	−2.68024000
C	−3.53753000	3.44816900	−0.09906000
C	3.20123100	4.08200100	−0.14761200
C	−4.88440400	3.28674500	0.27635500
C	4.47058600	4.22492000	0.43883400
C	−5.58114900	4.32608600	0.88914200
C	4.88587700	5.45677900	0.93990900
C	−4.94597500	5.54361000	1.14617500
C	4.03977300	6.56591500	0.87027000

C	−3.61026900	5.71353800	0.78137900
C	2.77538700	6.43403600	0.29515300
C	−2.91339900	4.67808200	0.15953400
C	2.35960200	5.20376000	−0.21125900
H	−2.56609200	−1.40441300	−2.61357600
H	−2.88399100	−0.10373800	−3.78257700
H	−1.20448500	−0.57941500	−3.37928100
H	1.97493100	−0.65007900	−3.06179700
H	3.63570200	−0.00991200	−3.28121700
H	3.27310700	−1.17112700	−1.98267000
H	−4.92918400	−0.71479100	−1.94233000
H	5.44493100	−0.01689100	−1.22522400
H	−7.07982900	−0.79346400	−3.14797900
H	7.73406900	0.12983300	−2.13236700
H	−7.95874500	1.24164000	−4.27678900
H	8.45692400	2.15487200	−3.38430400
H	−6.64906300	3.35568200	−4.19841900
H	6.85378200	4.02615100	−3.72820300
H	−4.47811100	3.42764600	−3.01182100
H	4.55115900	3.86905400	−2.83701800
H	−5.38281500	2.34237800	0.08330400
H	5.12860100	3.36453200	0.50670500
H	−6.61994800	4.18212100	1.17295800
H	5.86821500	5.54821700	1.39464800
H	−5.48716600	6.35085000	1.63111500
H	4.36171400	7.52410700	1.26753900
H	−3.10186900	6.65091700	0.98443700
H	2.10690800	7.28804000	0.24401300
H	−1.87809900	4.82815700	−0.12424500
H	1.37906200	5.10962200	−0.66631500
Zn	−0.02240500	2.67266100	0.96372400
Cl	−0.14071100	4.41163600	2.38961900

E_{total} = −4186.70095494 Hartree/Particle
G = −4185.785424 Hartree/Particle

Optimized coordinates for compound 5, broken symmetry singlet

Functional: (U)B3LYP Basis set: 6-31** for C, H, N, O, and Cl and LANL2DZ for Zn

	X	Y	Z
Zn	0.82529200	2.59192000	−0.03551400
Cl	2.13292000	4.43176600	−0.11558100
O	−1.96172900	−0.92245300	0.12816400
N	−0.62194000	2.04545200	−1.49561300
N	−0.62310800	2.19693000	1.46079300
N	−2.06802200	0.56704100	−2.32233100
N	−1.86920000	0.68624900	2.52356000
C	−1.50283800	0.30392200	0.08548600
C	−1.38751200	0.97260000	−1.19936400
C	−1.32705300	1.05149400	1.31298000
C	−1.72623700	1.42766200	−3.36148300
C	−1.50170900	1.64891300	3.46176600
C	−0.82043300	2.33457900	−2.83278700
C	−0.72562600	2.57612700	2.78439500
C	−3.13729000	−0.43491900	−2.38821600
C	−2.84099000	−0.38415100	2.76941300
C	−2.33946700	1.36219700	−4.70029800
C	−1.97053300	1.63774500	4.85900400
C	−2.39188500	0.16097300	−5.42997300
C	−1.82158100	0.50138700	5.67433000
C	−2.97862700	0.12236400	−6.69466800
C	−2.26490300	0.51031200	6.99658300
C	−3.51681300	1.28128500	−7.25651900
C	−2.85918100	1.65511500	7.53027400
C	−3.46845200	2.48086500	−6.54230300
C	−3.01007000	2.79118600	6.73143400
C	−2.89133100	2.52144700	−5.27496500
C	−2.57498200	2.78308800	5.40778000
C	−0.13058000	3.43831500	−3.52529200
C	−0.08742300	3.79707500	3.30961500
C	0.36534700	3.26842200	−4.83147000
C	0.56082700	3.79941200	4.55753900
C	1.00874700	4.31439700	−5.48932900
C	1.14786700	4.96258400	5.05067700
C	1.17488600	5.54793800	−4.85444900
C	1.10240700	6.14315700	4.30525000
C	0.68928500	5.72652000	−3.55906300
C	0.46653600	6.15089900	3.06348100
C	0.03825000	4.68362400	−2.90099700
C	−0.12459300	4.98926300	2.56951900
H	−2.74138000	−1.41521600	−2.66336100
H	−3.86121500	−0.11559100	−3.13780200
H	−3.61024700	−0.52327800	−1.41488200
H	−3.38803900	−0.59155300	1.85493700
H	−3.51950400	−0.05884900	3.55824300
H	−2.34131700	−1.30447800	3.08191400
H	−1.96529900	−0.74395100	−5.00932400
H	−1.34092900	−0.38564300	5.27385100
H	−3.00955400	−0.81502700	−7.24249500
H	−2.13784200	−0.37625900	7.61101300
H	−3.97208400	1.24999100	−8.24205800
H	−3.20291600	1.66218000	8.56048600
H	−3.88991400	3.38650800	−6.96882500
H	−3.47544100	3.68467300	7.13742600
H	−2.86501600	3.45258900	−4.71873600
H	−2.70151200	3.66429600	4.78757800
H	0.23811200	2.31333400	−5.33058200
H	0.60163900	2.88527100	5.14130400
H	1.38551800	4.16443300	−6.49728100
H	1.64855700	4.94520300	6.01462000
H	1.68263800	6.36119700	−5.36484200
H	1.56529900	7.04829800	4.68747900
H	0.82103200	6.67665800	−3.05093100
H	0.43500900	7.06028500	2.47138300
H	−0.33872700	4.83767600	−1.89662700
H	−0.62207000	5.00428400	1.60595200
O	1.96165400	0.92247500	0.12875600
N	0.62287600	−2.19736600	1.46014800
N	0.62209200	−2.04490100	−1.49618900
N	1.86889600	−0.68708300	2.52356100
N	2.06822700	−0.56618400	−2.32227000
C	1.50276700	−0.30388600	0.08558700
C	1.32684800	−1.05188700	1.31280300

C	1.38759700	−0.97212000	−1.19950800
C	1.50128800	−1.65006000	3.46139800
C	1.72658400	−1.42648400	−3.36173500
C	0.72527100	−2.57703500	2.78362500
C	0.82073400	−2.33358600	−2.83343400
C	2.84067100	0.38322300	2.76989000
C	3.13746600	0.43583300	−2.38772800
C	1.96997500	−1.63938800	4.85868700
C	2.33999900	−1.36061200	−4.70044500
C	1.82091400	−0.50333100	5.67441300
C	2.39253100	−0.15916900	−5.42974900
C	2.26410600	−0.51272600	6.99670600
C	2.97945500	−0.12018000	−6.69434800
C	2.85836100	−1.65771000	7.53003700
C	3.51771500	−1.27893400	−7.25647400
C	3.00935500	−2.79348700	6.73079800
C	3.46924200	−2.47873000	−6.54262700
C	2.57439600	−2.78491600	5.40710400
C	2.89194000	−2.51969100	−5.27538400
C	0.08702400	−3.79816500	3.30836400
C	0.13098500	−3.43712300	−3.52636100
C	−0.56128100	−3.80094800	4.55625900
C	−0.36483100	−3.26682800	−4.83252800
C	−1.14834600	−4.96429400	5.04895600
C	−1.00813900	−4.31261500	−5.49077600
C	−1.10286100	−6.14460100	4.30310900
C	−1.17429100	−5.54636400	−4.85630300
C	−0.46693900	−6.15189900	3.06136400
C	−0.68880100	−5.72534400	−3.56093100
C	0.12421700	−4.99008900	2.56784400
C	−0.03786200	−4.68263400	−2.90247400
H	2.34096800	1.30344700	3.08264400
H	3.51909100	0.05764900	3.55868900
H	3.38782700	0.59092800	1.85554800
H	3.61016800	0.52405100	−1.41426000
H	3.86159100	0.11667400	−3.13719400
H	2.74157200	1.41615700	−2.66280400
H	1.34027600	0.38383300	5.27421100
H	1.96589700	0.74563400	−5.00888900
H	2.13696300	0.37361700	7.61144700
H	3.01046800	0.81737600	−7.24188600
H	3.20199500	−1.66514200	8.56028000
H	3.97313000	−1.24734600	−8.24193700
H	3.47470700	−3.68711000	7.13651100
H	3.89076000	−3.38424600	−6.96936200
H	2.70100500	−3.66589600	4.78659500
H	2.86554000	−3.45100100	−4.71944100
H	−0.60211300	−2.88701800	5.14035300
H	−0.23758400	−2.31157300	−5.33131900
H	−1.64907600	−4.94725500	6.01288500
H	−1.38482800	−4.16234400	−6.49871300
H	−1.56577100	−7.04987700	4.68499500
H	−1.68197000	−6.35947700	−5.36700100
H	−0.43538900	−7.06107300	2.46894100
H	−0.82056100	−6.67564900	−3.05311500
H	0.62173200	−5.00476900	1.60429200
H	0.33903000	−4.83698800	−1.89811800
Zn	−0.82534400	−2.59184500	−0.03647700
Cl	−2.13297500	−4.43165600	−0.11727400

E_{total} = −4186.70337231 Hartree/Particle
G = −4185.789538 Hartree/Particle

Optimized coordinates for compound 5, triplet state

Functional: (U)B3LYP Basis set: 6-31** for C, H, N, O, and Cl and LANL2DZ for Zn

	X	Y	Z
Zn	2.60078800	−0.48975600	0.00000000
Cl	4.62087800	−1.51349900	0.00000000
O	−1.15267000	1.90976400	0.00000000
N	1.99174200	0.89973000	−1.50250400
N	1.99174200	0.89973000	1.50250400
N	0.40798200	2.17481400	−2.41339500
N	0.40798200	2.17481400	2.41339500
C	0.13799800	1.66638700	0.00000000
C	0.84720900	1.57565800	−1.25847000
C	0.84720900	1.57565800	1.25847000
C	1.32154200	1.87902000	−3.42120600
C	1.32154200	1.87902000	3.42120600
C	2.29411700	1.07909000	−2.84002200
C	2.29411700	1.07909000	2.84002200
C	−0.69062800	3.13773300	−2.52666800
C	−0.69062800	3.13773300	2.52666800
C	1.22542000	2.42665700	−4.78551700
C	1.22542000	2.42665700	4.78551700
C	0.03489800	2.34475500	−5.53012200
C	0.03489800	2.34475500	5.53012200
C	−0.03487800	2.87024100	−6.82014300
C	−0.03487800	2.87024100	6.82014300
C	1.08257100	3.48013600	−7.39267500
C	1.08257100	3.48013600	7.39267500
C	2.27138400	3.56507200	−6.66393500
C	2.27138400	3.56507200	6.66393500
C	2.34231000	3.04929600	−5.37179200
C	2.34231000	3.04929600	5.37179200
C	3.46396500	0.46094700	−3.49078600
C	3.46396500	0.46094700	3.49078600
C	3.35020800	−0.11493300	−4.76999500
C	3.35020800	−0.11493300	4.76999500
C	4.45640600	−0.68942200	−5.39202800
C	4.45640600	−0.68942200	5.39202800
C	5.69550700	−0.70561300	−4.74660500
C	5.69550700	−0.70561300	4.74660500
C	5.81849300	−0.14067100	−3.47714900
C	5.81849300	−0.14067100	3.47714900
C	4.71453100	0.44158300	−2.85504400
C	4.71453100	0.44158300	2.85504400
H	−1.62676600	2.63938800	−2.78868200
H	−0.43605100	3.86176200	−3.30066700
H	−0.83195800	3.63767900	−1.57238700
H	−0.83195800	3.63767900	1.57238700
H	−0.43605100	3.86176200	3.30066700
H	−1.62676600	2.63938800	2.78868200
H	−0.83591700	1.86011200	−5.10018400

H	−0.83591700	1.86011200	5.10018400
H	−0.96290600	2.79647000	−7.37968700
H	−0.96290600	2.79647000	7.37968700
H	1.02753900	3.88743800	−8.39796300
H	1.02753900	3.88743800	8.39796300
H	3.14439100	4.04274400	−7.09918900
H	3.14439100	4.04274400	7.09918900
H	3.26423300	3.12615200	−4.80502400
H	3.26423300	3.12615200	4.80502400
H	2.39088300	−0.10247600	−5.27732600
H	2.39088300	−0.10247600	5.27732600
H	4.34968300	−1.13019500	−6.37932300
H	4.34968300	−1.13019500	6.37932300
H	6.55651100	−1.15978300	−5.22845500
H	6.55651100	−1.15978300	5.22845500
H	6.77307100	−0.15728600	−2.96058800
H	6.77307100	−0.15728600	2.96058800
H	4.82377700	0.87820300	−1.86922700
H	4.82377700	0.87820300	1.86922700
O	1.15267000	−1.90976400	0.00000000
N	−1.99174200	−0.89973000	1.50250400
N	−1.99174200	−0.89973000	−1.50250400
N	−0.40798200	−2.17481400	2.41339500
N	−0.40798200	−2.17481400	−2.41339500
C	−0.13799800	−1.66638700	0.00000000
C	−0.84720900	−1.57565800	1.25847000
C	−0.84720900	−1.57565800	−1.25847000
C	−1.32154200	−1.87902000	3.42120600
C	−1.32154200	−1.87902000	−3.42120600
C	−2.29411700	−1.07909000	2.84002200
C	−2.29411700	−1.07909000	−2.84002200
C	0.69062800	−3.13773300	2.52666800
C	0.69062800	−3.13773300	−2.52666800
C	−1.22542000	−2.42665700	4.78551700
C	−1.22542000	−2.42665700	−4.78551700
C	−0.03489800	−2.34475500	5.53012200
C	−0.03489800	−2.34475500	−5.53012200
C	0.03487800	−2.87024100	6.82014300
C	0.03487800	−2.87024100	−6.82014300
C	−1.08257100	−3.48013600	7.39267500
C	−1.08257100	−3.48013600	−7.39267500
C	−2.27138400	−3.56507200	6.66393500
C	−2.27138400	−3.56507200	−6.66393500
C	−2.34231000	−3.04929600	5.37179200
C	−2.34231000	−3.04929600	−5.37179200
C	−3.46396500	−0.46094700	3.49078600
C	−3.46396500	−0.46094700	−3.49078600
C	−3.35020800	0.11493300	4.76999500
C	−3.35020800	0.11493300	−4.76999500
C	−4.45640600	0.68942200	5.39202800
C	−4.45640600	0.68942200	−5.39202800
C	−5.69550700	0.70561300	4.74660500
C	−5.69550700	0.70561300	−4.74660500
C	−5.81849300	0.14067100	3.47714900
C	−5.81849300	0.14067100	−3.47714900
C	−4.71453100	−0.44158300	2.85504400
C	−4.71453100	−0.44158300	−2.85504400
H	1.62676600	−2.63938800	2.78868200
H	0.43605100	−3.86176200	3.30066700
H	0.83195800	−3.63767900	1.57238700
H	0.83195800	−3.63767900	−1.57238700
H	0.43605100	−3.86176200	−3.30066700
H	1.62676600	−2.63938800	−2.78868200
H	0.83591700	−1.86011200	5.10018400
H	0.83591700	−1.86011200	−5.10018400
H	0.96290600	−2.79647000	7.37968700
H	0.96290600	−2.79647000	−7.37968700
H	−1.02753900	−3.88743800	8.39796300
H	−1.02753900	−3.88743800	−8.39796300
H	−3.14439100	−4.04274400	7.09918900
H	−3.14439100	−4.04274400	−7.09918900
H	−3.26423300	−3.12615200	4.80502400
H	−3.26423300	−3.12615200	−4.80502400
H	−2.39088300	0.10247600	5.27732600
H	−2.39088300	0.10247600	−5.27732600
H	−4.34968300	1.13019500	6.37932300
H	−4.34968300	1.13019500	−6.37932300
H	−6.55651100	1.15978300	5.22845500
H	−6.55651100	1.15978300	−5.22845500
H	−6.77307100	0.15728600	2.96058800
H	−6.77307100	0.15728600	−2.96058800
H	−4.82377700	−0.87820300	1.86922700
H	−4.82377700	−0.87820300	−1.86922700
Zn	−2.60078800	0.48975600	0.00000000
Cl	−4.62087800	1.51349900	0.00000000

E_{total} = −4186.68747171 Hartree/Particle
G = −4185.782616 Hartree/Particle

Optimized coordinates for the isolated radical [Zn(BM^{diPh}IK)Cl$_2$]$^{\bullet-}$

Functional: (U)B3LYP Basis set: 6-31** for C, H, N, O, and Cl and LANL2DZ for Zn

	X	Y	Z
O	−3.48028100	−0.41404900	0.00000000
N	−0.15852900	−0.02993600	1.46860600
N	−0.15852900	−0.02993600	−1.46860600
N	−2.13484600	−0.02409700	2.47945500
N	−2.13484600	−0.02409700	−2.47945500
C	−2.21602400	−0.21444400	0.00000000
C	−1.50179000	−0.08763600	1.25953000
C	−1.50179000	−0.08763600	−1.25953000
C	−1.16100100	0.07653600	3.47699400
C	−1.16100100	0.07653600	−3.47699400
C	0.05735400	0.07748700	2.83261800
C	0.05735400	0.07748700	−2.83261800
C	−3.57694000	0.09513700	2.70823000
C	−3.57694000	0.09513700	−2.70823000
C	−1.46947800	0.18241800	4.91422000
C	−1.46947800	0.18241800	−4.91422000
C	−2.28947000	−0.76362000	5.55606700
C	−2.28947000	−0.76362000	−5.55606700
C	−2.55931600	−0.66198900	6.92016200
C	−2.55931600	−0.66198900	−6.92016200
C	−2.00920700	0.37988400	7.66962100

C	−2.00920700	0.37988400	−7.66962100
C	−1.18870700	1.32167500	7.04487900
C	−1.18870700	1.32167500	−7.04487900
C	−0.92482700	1.22834400	5.67945000
C	−0.92482700	1.22834400	−5.67945000
C	1.41825200	0.18040700	3.38555500
C	1.41825200	0.18040700	−3.38555500
C	1.81426900	−0.57144500	4.50424800
C	1.81426900	−0.57144500	−4.50424800
C	3.11119100	−0.46736000	5.00254400
C	3.11119100	−0.46736000	−5.00254400
C	4.03718400	0.38156700	4.39140200
C	4.03718400	0.38156700	−4.39140200
C	3.65587000	1.13264100	3.27904200
C	3.65587000	1.13264100	−3.27904200
C	2.35654500	1.03555100	2.78258200
C	2.35654500	1.03555100	−2.78258200
H	−4.06187600	−0.88244600	2.66002800
H	−3.72878600	0.53367700	3.69430500
H	−4.01614600	0.71816200	1.93419300
H	−4.01614600	0.71816200	−1.93419300
H	−3.72878600	0.53367700	−3.69430500
H	−4.06187600	−0.88244600	−2.66002800
H	−2.70239300	−1.58979100	4.98473100
H	−2.70239300	−1.58979100	−4.98473100
H	−3.19280900	−1.40299200	7.39918900
H	−3.19280900	−1.40299200	−7.39918900
H	−2.21795300	0.45681900	8.73265800
H	−2.21795300	0.45681900	−8.73265800
H	−0.75901100	2.13670200	7.62010500
H	−0.75901100	2.13670200	−7.62010500
H	−0.29545200	1.96727900	5.19425200
H	−0.29545200	1.96727900	−5.19425200
H	1.10485500	−1.24692900	4.97081300
H	1.10485500	−1.24692900	−4.97081300
H	3.40388800	−1.06135500	5.86356200
H	3.40388800	−1.06135500	−5.86356200
H	5.04956100	0.45377300	4.77762900
H	5.04956100	0.45377300	−4.77762900
H	4.36776700	1.79763700	2.79905900
H	4.36776700	1.79763700	−2.79905900
H	2.05322800	1.65066600	1.93887800
H	2.05322800	1.65066600	−1.93887800
Zn	1.14240900	−0.52745900	0.00000000
Cl	3.04261700	−1.66813400	0.00000000

E_{total} = −2093.31453736 Hartree/Particle
G = −2092.874030 Hartree/Particle

Optimized coordinates for compound 5 with Ph-groups substituted for H

Functional: (U)B3LYP Basis set: 6-31** for C, H, N, O, and Cl and LANL2DZ for Zn

	X	Y	Z
Zn	−0.07398300	2.89898800	0.00000000
Cl	−0.69251100	5.05699000	0.00000000
O	1.30968200	−1.34565600	0.00000000
N	1.12523300	1.98735900	1.47807100
N	1.12523300	1.98735900	−1.47807100
N	2.02854200	0.14742200	2.29482300
N	2.02854200	0.14742200	−2.29482300
C	0.85104600	−0.06884700	0.00000000
C	1.33573100	0.68677400	1.24923900
C	1.33573100	0.68677400	−1.24923900
C	2.24733200	1.15987600	3.21157900
C	2.24733200	1.15987600	−3.21157900
C	1.68503400	2.29252700	2.69479100
C	1.68503400	2.29252700	−2.69479100
C	2.48078800	−1.23143300	2.51830200
C	2.48078800	−1.23143300	−2.51830200
H	1.64300800	−1.86396800	2.81762400
H	3.22168800	−1.20919500	3.31964200
H	2.91072200	−1.63127900	1.60556300
H	2.91072200	−1.63127900	−1.60556300
H	3.22168800	−1.20919500	−3.31964200
H	1.64300800	−1.86396800	−2.81762400
O	−1.30968200	1.34565600	0.00000000
N	−1.12523300	−1.98735900	−1.47807100
N	−1.12523300	−1.98735900	1.47807100
N	−2.02854200	−0.14742200	−2.29482300
N	−2.02854200	−0.14742200	2.29482300
C	−0.85104600	0.06884700	0.00000000
C	−1.33573100	−0.68677400	−1.24923900
C	−1.33573100	−0.68677400	1.24923900
C	−2.24733200	−1.15987600	−3.21157900
C	−2.24733200	−1.15987600	3.21157900
C	−1.68503400	−2.29252700	−2.69479100
C	−1.68503400	−2.29252700	2.69479100
C	−2.48078800	1.23143300	−2.51830200
C	−2.48078800	1.23143300	2.51830200
H	−1.64300800	1.86396800	−2.81762400
H	−3.22168800	1.20919500	−3.31964200
H	−2.91072200	1.63127900	−1.60556300
H	−2.91072200	1.63127900	1.60556300
H	−3.22168800	1.20919500	3.31964200
H	−1.64300800	1.86396800	2.81762400
Zn	0.07398300	−2.89898800	0.00000000
Cl	0.69251100	−5.05699000	0.00000000
H	1.65521300	3.29220600	−3.10152200
H	2.78696100	0.97863700	−4.12783700
H	1.65521300	3.29220600	3.10152200
H	2.78696100	0.97863700	4.12783700
H	−2.78696100	−0.97863700	4.12783700
H	−1.65521300	−3.29220600	3.10152200
H	−1.65521300	−3.29220600	−3.10152200
H	−2.78696100	−0.97863700	−4.12783700

E_{total} = −2338.24113853 Hartree/Particle
G = −2337.917951 Hartree/Particle

Optimized coordinates for the free pinacol

Functional: (U)B3LYP Basis set: 6-31**

	X	Y	Z
O	0.33832100	−0.04560400	−1.85899200
N	−1.31563800	−2.33695800	0.34152000
N	2.04353700	−1.63774600	0.84285400
N	−2.18490100	−1.16031300	−1.34044500
N	1.87144100	−2.41099800	−1.22177700
C	0.21010100	−0.58610000	−0.56600000
C	−1.09502400	−1.36874300	−0.52537300
C	1.37233800	−1.54544100	−0.28990100
C	−3.15258800	−2.08338100	−0.94787200
C	2.93371000	−3.09011100	−0.62634500
C	−2.59171200	−2.79533800	0.10702400
C	3.02463900	−2.58775200	0.66349800
C	−2.30694200	−0.25910700	−2.49482800
C	1.31816200	−2.68282700	−2.54666700
C	−4.45016100	−2.23874300	−1.64043200
C	3.70287000	−4.14146000	−1.31819500
C	−5.40078900	−1.20329800	−1.67100100
C	4.35414500	−3.88824900	−2.53820800
C	−6.62362100	−1.37626100	−2.31989800
C	5.07895500	−4.89208200	−3.18002000
C	−6.92196900	−2.58890700	−2.94289000
C	5.17393300	−6.16263900	−2.61031900
C	−5.98874100	−3.62708300	−2.91564100
C	4.53771900	−6.42427400	−1.39498800
C	−4.76310600	−3.45270200	−2.27499300
C	3.80481100	−5.42580400	−0.75660900
C	−3.14918700	−3.87273800	0.94473300
C	3.96740900	−2.90767100	1.74878200
C	−4.53044900	−4.07893600	1.10393100
C	5.29665000	−3.28576400	1.49523200
C	−5.00821000	−5.10786800	1.91429400
C	6.16709400	−3.57146900	2.54561700
C	−4.12077400	−5.94646000	2.59031800
C	5.73259300	−3.47722500	3.86890900
C	−2.74633500	−5.74058000	2.45282300
C	4.41698100	−3.09132200	4.13296900
C	−2.26523000	−4.71594600	1.64184000
C	3.54331000	−2.80933900	3.08513600
H	−1.98376500	0.74254100	−2.22211300
H	−3.34867200	−0.24618000	−2.80759000
H	−1.68464000	−0.61351300	−3.31764300
H	0.23009900	−2.67702900	−2.49318500
H	1.65630600	−3.66703600	−2.86881500
H	1.63464700	−1.92739200	−3.26761800
H	−5.18083100	−0.26041900	−1.17902600
H	4.30449500	−2.89477200	−2.97427500
H	−7.34444400	−0.56397000	−2.33302100
H	5.57721800	−4.67750800	−4.12095000
H	−7.87506700	−2.72431700	−3.44554800
H	5.74110100	−6.94312100	−3.10886200
H	−6.21262600	−4.57349100	−3.39922500
H	4.60547400	−7.41093400	−0.94614000
H	−4.03717700	−4.25934400	−2.25651500
H	3.30365200	−5.63203600	0.18348700
H	−5.23538900	−3.42611200	0.60198000
H	5.65262700	−3.34092500	0.47234700
H	−6.08014200	−5.24793300	2.02385000
H	7.19212700	−3.85839000	2.32828100
H	−4.49572500	−6.74677500	3.22180900
H	6.41325900	−3.69856700	4.68588200
H	−2.04486800	−6.38184300	2.97956000
H	4.06765000	−3.01431800	5.15889100
H	−1.19924000	−4.54565100	1.53850800
H	2.51845500	−2.51849000	3.29087200
O	0.33836300	0.04572100	1.85902100
N	2.04368000	1.63769500	−0.84278200
N	−1.31563000	2.33703200	−0.34151900
N	1.87140700	2.41117400	1.22174800
N	−2.18488600	1.16039000	1.34044900
C	0.21012300	0.58620800	0.56603000
C	1.37236700	1.54553300	0.28991000
C	−1.09499300	1.36885100	0.52540900
C	2.93374500	3.09020300	0.62634200
C	−3.15259200	2.08342300	0.94785000
C	3.02479400	2.58769400	−0.66343300
C	−2.59171600	2.79538800	−0.10704400
C	1.31802300	2.68310200	2.54657200
C	−2.30691000	0.25917800	2.49483400
C	3.70286400	4.14160100	1.31816600
C	−4.45017600	2.23876500	1.64039100
C	4.35398600	3.88849600	2.53828300
C	−5.40074000	1.20326200	1.67104100
C	5.07874900	4.89237600	3.18007600
C	−6.62358600	1.37620000	2.31991900
C	5.17383100	6.16287000	2.61025400
C	−6.92201300	2.58887800	2.94281000
C	4.53776900	6.42439800	1.39482000
C	−5.98884900	3.62710900	2.91548200
C	3.80490700	5.42588300	0.75645800
C	−4.76320000	3.45275400	2.27485500
C	3.96768500	2.90746200	−1.74865300
C	−3.14921800	3.87274600	−0.94478800
C	5.29690800	3.28555700	−1.49501000
C	−4.53048700	4.07885600	−1.10404700
C	6.16746900	3.57111600	−2.54533700
C	−5.00827800	5.10774800	−1.91444100
C	5.73310800	3.47672200	−3.86866500
C	−4.12086500	5.94638800	−2.59043700
C	4.41751500	3.09081600	−4.13281600
C	−2.74641900	5.74059300	−2.45288300
C	3.54372800	2.80897900	−3.08504200
C	−2.26528300	4.71599700	−1.64186900
H	1.63439700	1.92768200	3.26758700
H	1.65619100	3.66730800	2.86870600
H	0.22996400	2.67736800	2.49299000
H	−1.68452900	0.61354300	3.31760400
H	−3.34862200	0.24631100	2.80765600
H	−1.98380300	−0.74248700	2.22209200
H	4.30425600	2.89506500	2.97444600
H	−5.18072100	0.26035400	1.17914800
H	5.57689600	4.67788700	4.12108800
H	−7.34435700	0.56386400	2.33310500
H	5.74096000	6.94338900	3.10878400
H	−7.87512400	2.72427000	3.44545100
H	4.60560700	7.41101000	0.94588000
H	−6.21279400	4.57354200	3.39899100

H	3.30386800	5.63202800	−0.18372100
H	−4.03732100	4.25944000	2.25631900
H	5.65278200	3.34083400	−0.47209500
H	−5.23540400	3.42599200	−0.60211700
H	7.19248500	3.85804300	−2.32792400
H	−6.08021400	5.24774600	−2.02404400
H	6.41386600	3.69795300	−4.68559100
H	−4.49583700	6.74667300	−3.22195300
H	4.06829000	3.01369400	−5.15876500
H	−2.04497100	6.38189500	−2.97959800
H	2.51888800	2.51813100	−3.29085400
H	−1.19928800	4.54576800	−1.53849300
H	1.08820900	0.60529900	−1.80737400
H	1.08826600	−0.60517000	1.80737800

E_{total} = −3136.14804021 Hartree/Particle
G = −3135.204746 Hartree/Particle

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