Metallocenium Incorporated Charge-Enhanced Thiourea Catalysts

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Experimental section

General. All reaction glassware and NMR tubes were dried at 120 °C and cooled under a flow of argon or in a vacuum desiccator. Volumetric flasks and syringes were stored in a vacuum desiccator for at least 12 h before use. Neutral alumina and molecular sieves were activated in a kiln at 300 °C for at least 24 h. Potassium carbonate was dried at 120 °C for at least 24 h before use. NMR spectra were recorded on 400 and 500 MHz Bruker spectrometers, and chemical shifts are reported in ppm and referenced to solvent residual peaks as follows: δ 7.26 (^{1}H, $CDCl_3$), 5.32 and 53.84 (^{1}H and ^{13}C, CD_2Cl_2), 1.94 (^{1}H, CD_3CN), and -78.5 (^{19}F, external calibrant). A relaxation delay of 10 s was employed for the tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BAr^F_4) salts to obtain more accurate integrations. Due to the paramagnetism of the ferrocenium salt derivatives, their ^{1}H and ^{13}C NMR spectra were not obtained. High-resolution mass spectra were recorded with a Bruker ESI-BioTOF instrument using PEG and PPG standards in methanol. Melting points were obtained in unsealed tubes using an uncalibrated Thomas Hoover Uni-Melt apparatus. Fourier transform-infrared spectra were recorded with a Thermo-Nicollet iS 5 spectrometer equipped with a laminated diamond attenuated total reflection (ATR) attachment.

Chemicals were purchased from Oakwood Chemical and used without further purification. Solvents were acquired from Fischer Scientific. Acetone was used as delivered whereas the tetrahydrofuran, dichloromethane, and diethyl ether were degassed and dried with a Pure Process Technologies solvent purification system. Sodium BAr^F_4 was purchased from AK Scientific as the 2.5 hydrate. It was dried by dissolving the salt in anhydrous methanol and pushing the solution though a plug of activated alumina using a syringe with a 0.45 μm filter, and then removing the solvent under vacuum. The resulting solid was crushed into a fine powder and heated at 150 °C in a nitrogen glovebox for at least 16 h to yield the desired 0.5 hydrate. Deuterated solvents were

purchased from Cambridge Isotope Laboratories. Chloroform-*d* ($CDCl_3$) was purified through a column of K_2CO_3 and activated neutral alumina. Hexanes, dichloromethane-d_2 (CD_2Cl_2), and dimethylsulfoxide-d_6 (DMSO-d_6) were dried over 3Å molecular sieves for 24 h before use.

1-Methyl-3-(3-phenylthioureido)pyridinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (2). This compound was prepared following the literature procedure by Fan and Kass.[11] ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.92 (s, 1H), 8.27 (brs, 1H), 8.16 (d, *J* = 6.0 Hz, 1Hz), 8.08 (d, *J* = 8.4 Hz, 1H), 7.87 (dd, *J* = 8.6, 6.0 Hz, 1H) 7.82 (brs, 1H), 7.72 (brs, 8H), 7.58 – 7.55 (m, 6H), 7.49 (tt, *J* = 2.2, 7.5 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 2H), 4.38 (s, 3H).

Iodoferrocene (7). This compound was prepared according to the literature procedure by Roemer and Nijhuis.[15] At 12 g scale the purification from Kuibiak and coworkers was used in lieu of the sublimation procedure.[16] ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.41 (t, *J* = 1.9 Hz, 2H), 4.19 (s, 5H), 4.16 (t, *J* = 1.9 Hz, 2H).

Aminoferrocene (8a). This compound was prepared using the literature procedure by Gasser and coworkers.[17] ^{1}H NMR (500 MHz, CD_2Cl_2) δ 4.10 (s, 5H), 3.99 (t, *J* = 1.9 Hz), 3.84 (t, *J* = 1.9 Hz, 2H), 2.59 (brs, 2H).

***N*-Ferrocenyl-*N'*-phenylthiourea (9a).** Phenylisothiocyanate (36.4 mg, 0.269 mmol) was added to a solution of aminoferrocene (50.0 mg, 0.249 mmol) in DCM (2.5 mL) under argon atmosphere. The reaction mixture was stirred for 5 hr under argon, and then the solvent was removed under reduced pressure. The residue was purified via silica gel flash chromatography with 5% methanol in methylene chloride to afford 81.9 mg (97%) of the product as a light orange powder (mp 135.3 – 142.5 °C with decomposition). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.37 (s, 1H), 7.48 (d, *J* = 7.9 Hz, 2H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.32 (brs, 1H), 7.26 (t, J = 7.4 Hz, 1H), 4.42 (brs, 2H), 4.31 (s, 5H), 4.23 (brs, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 180.4, 139.8, 129.0, 125.1, 124.0, 95.0, 69.5,

65.5, 55.1. IR-ATR 3348, 3236, 3172, 3080, 3024, 1593, 1555, 1522, 1495, 1469, 1447, 1406, 1374, 1345, 1279, 1217, 1197, 1170, 1104, 820, 743, 693 cm^{-1}. ESI-HRMS calcd for $C_{17}H_{16}FeN_2SNa$ $(M + Na)^+$ 359.0281, found: 359.0279.

***N*-Ferrocenium-*N'*-phenylthiourea tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (4a).** *N*-Ferrocenyl-*N'*-phenylthiourea (50.0 mg, 0.149 mmol) was dissolved in dichloromethane (50 mL), and silver tetrafluoroborate (29.0 mg, 0.149 mmol) in 50 mL of DCM was added dropwise with exclusion of light, under argon. After stirring for 5 min, the reaction mixture was passed through a 0.2 μm syringe filter into a vial and 132 mg (0.149 mmol) of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate was added. The solution was stirred overnight, filtered through a syringe filter, and concentrated under reduced pressure to afford 72 mg (75%) of product as a dark green precipitate (mp 155.2 – 157.5 °C). ^{19}F NMR (471 MHz, CD_2Cl_2) -62.89 (s). ESI-HRMS calcd for $C_{17}H_{16}FeN_2S$ $(M – BAr^F{}_4)^+$ 336.0379, found 336.0396.

Aminomethylferrocene (8b). Ferrocene aldehyde was subjected to the literature procedure by Huikai and coworkers to yield the oxime.[19] This crude intermediate was subjected to the procedure developed by Evans et al. to afford the title compound.[18] ^1H NMR (500 MHz, $CDCl_3$) δ 4.16 (t, *J* = 1.9 Hz, 2H), 4.14 (s, 5H), 4.11 (t, *J* = 1.8 Hz), 3.55 (s, 2H), 1.37 (brs, 2H).

***N*-Methylferrocenyl-*N'*-phenylthiourea (9b).** Aminomethylferrocene (450 mg, 2.09 mmol) was dissolved in 21 mL of dry CH_2Cl_2, and then phenylisothiocyanate (306 mg, 270 μL, 2.25 mmol) was added dropwise with constant stirring. After addition, the reaction mixture was stirred for an additional 4 hrs. The solvent was then removed under reduced pressure, and purification of the residue was accomplished via silica gel column chromatography with hexane (5 min), a ramp to 100% EtOAc (15 min) and a 15 min hold time to elute 592 mg of the orange solid product (81%, mp 152.5 – 153.7°C). ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (brs, 1H), 7.49 (t, *J* = 7.9 Hz, 2H), 7.35

(tt, J = 7.5, 1.3 Hz, 1H), 7.31 (d, J = 7.0 Hz, 2H), 6.26 (brs, 1H), 4.43 (d, J = 4.6 Hz, 2H), 4.11 (t, J = 1.9 Hz, 2H), 4.08 (t, J = 1.9 Hz, 2H), 3.88 (s, 5H). ^{13}C NMR (MHz,) δ 180.2, 136.1, 130.6, 128.0, 126.1, 84.4, 68.4, 68.3, 67.6, 44.9. IR-ATR 3357, 3165, 3096, 3010, 2969, 2923, 2869, 1589, 1526, 1452, 1405, 1386, 1359, 1321, 1306, 1291, 1257, 1192, 1103, 998, 815, 754, 698 cm^{-1}. ESI-HRMS calcd for $C_{18}H_{18}FeN_2NaS$ $(M + Na)^+$ 373.0433, found 373.0456.

Cobaltocenium hexafluorophosphate (11). This compound was prepared according to the literature procedure by Vanicek and coworkers.[20] ^{1}H NMR (400 MHz, CD_3CN) δ 5.67 (s, 10H).

Aminocobaltocenium hexafluorophosphate (12). This compound was prepared following the literature procedure by Jochriem and coworkers.[21] ^{1}H NMR (500 MHz, CD_3CN) δ 5.37 (s, 5H), 5.28 (t, J = 2.2 Hz, 2H), 5.17 (t, J = 2.2 Hz, 2H), 4.93 (brs, 2H).

***N*-Cobaltocenium-*N′*-phenylthiourea hexafluorophosphate (13).** A 60% dispersion of sodium hydride in mineral oil (17.2 mg, 0.430 mmol) was washed with pentane (3 x 2 mL) and cooled to 0 °C. A solution of aminocobaltocenium hexafluorophosphate (100 mg, 0.286 mmol) in THF (2 mL) was added, and the mixture was stirred for 1 hr until hydrogen evolution stopped. Phenylisothiocyanate (42.6 mg, 0.315 mmol) was added, and the solution was warmed to room temperature. A 55% wt/wt aqueous solution (46 µL) of hexafluorophosphoric acid (41.8 mg, 0.286 mmol) was added to the reaction mixture and then the solvent was removed under reduced pressure. The resulting residue was dissolved in minimal dichloromethane and triturated into diethyl ether to afford 87.8 mg (63%) of an orange powder. X-ray crystallographic quality crystals were grown via vapor diffusion of diethyl ether into a solution of *N*-cobaltocenium-*N'*-phenylthiourea hexafluorophosphate in 1,2-dichloroethane (mp 159.8 – 164.9 °C). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.46 (s, 1H), 8.28 (s, 1H), 7.55 (d, J = 7.5 Hz, 2H), 7.41 (t, J = 7.9 Hz, 2H), 7.28 (t, J = 7.4 Hz, 1H), 6.44 (t, J = 2.2 Hz, 2H), 5.63 (s, 5H), 5.39 (t, J = 2.2 Hz, 2H). ^{13}C NMR (101

MHz, DMSO-d_6) δ 179.1, 138.4, 128.9, 125.6, 123.9, 115.4, 84.6, 79.3, 73.9. ^{19}F NMR (376 MHz, CD_2Cl_2) δ -69.95 (s), -71.85 (s). IR-ATR 3648, 3376, 3127, 2928, 2851, 1713, 1582, 1540, 1495, 1370, 1320, 1243, 1200, 837, 742 cm^{-1}. HRMS-ESI calcd for $C_{17}H_{16}CoN_2S$ $(M - PF_6)^+$ 339.0361, found 339.0362.

***N*-Cobaltocenium-*N′*-phenylthiourea tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (5).** *N*-Cobaltocenium-*N'*-phenylthiourea hexafluorophosphate (0.0500 g, 0.103 mmol) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (0.0984 g, 0.114 mmol) were dissolved in 1 mL of anhydrous DCM under argon, and the reaction mixture was stirred overnight. Filtration of the solid precipitate and removal of the solvent under reduced pressure afforded 114 mg (92%) of a yellow solid (mp 141 – 143 °C). ^{1}H NMR (500 MHz, CD_3CN) δ 8.56 (brs, 2H), 7.70 (m, 8H), 7.67 (brs, 4H), 7.46 (t, J = 7.5 Hz, 2H), 7.41 (d, J = 7.0 Hz, 2H), 7.33 (t, J = 7.5 Hz, 1H), 6.23 (t, J = 2.5 Hz, 2H), 5.62 (s, 5H), 5.46 (t, J = 2.5 Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 180.7, 162.6 (q, $^1J_{B\text{-}C}$ = 50 Hz), 135.7, 130.4, 129.9 (qq, $^3J_{B\text{-}C}$ = 15 Hz, $^2J_{F\text{-}C}$ = 125 Hz), 128.1, 126.4, 125.5 (q, $^1J_{F\text{-}C}$ = 272 Hz), 118.7 (septet, J = 3.8 Hz), 116.2, 85.9, 80.4, 75.2 [1 line missing]. ^{19}F NMR (470 MHz, CD_3CN) δ -63.24 (s); IR-ATR 3362, 3194, 3136, 2998, 2955, 1569, 1493, 1354, 1279, 1170, 1136, 891, 753 cm^{-1}. HRMS-ESI calcd for $C_{17}H_{16}CoN_2S$ $(M - BAr^F{}_4)^+$ 339.0361, found 339.0357.

General procedure for Friedel-Crafts kinetics. *N*-Methylindole (6.3 μL, 6.6 mg, 0.050 mmol), *trans*-β-nitrostyrene (74.6 mg, 0.50 mmol), and the appropriate catalyst (0.005 mmol) were added to a 1 mL volumetric flask and filled to the mark with CD_2Cl_2. This solution was mixed and then added to an oven-dried NMR tube, which was sealed with a cap, electrical tape, and parafilm to prevent evaporation of the solvent over the course of the experiment. ^{1}H NMR spectra were collected at intermittent times and the samples were maintained at 27 °C. Temperature was controlled via the NMR spectrometer or when processes were monitored longer than one hour, a

water bath was used. Reaction progress was followed using the signals at δ 6.47 (*N*-methylindole) and 5.17, 5.08, and 4.98 (alkylation product). Rate constants and half-lives were determined from a linear least squares fit of the data using a pseudo-first-order kinetic model.

General procedure for the Friedel-Crafts kinetics with in-situ generated 4a and 4b. *N*-Ferrocenyl-*N'*-phenylthiourea (8.4 mg, 0.025 mmol) or *N*-methylferrocenyl-*N'*-phenylthiourea (5.25 mg, 0.025 mmol), $NaBAr^{F}_{4}$ (22.1 mg, 0.025 mmol), and $AgBF_4$ (4.9 mg, 0.025 mmol) were added to a 6-dram vial charged with a stir bar under an argon atmosphere. Dichloromethane-d_2 (5 mL) was added via syringe, and the reaction mixture was stirred for 5 min with the exclusion of light. *N*-Methylindole (6.3 μL, 6.6 mg, 0.050 mmol) and *trans*-β-nitrostyrene (74.6 mg, 0.500 mmol) were added to a 1 mL volumetric flask under argon, and the dichloromethane solution was filtered through a 0.2 μm syringe filter into the volumetric up to the mark. This mixture was then transferred to an NMR tube, which was sealed with a cap, electrical tape, and parafilm to prevent evaporation of the solvent over the course of the experiment. ^{1}H NMR spectra were collected at intermittent times, and reaction progress was followed using the signals at δ 6.47 (*N*-methylindole) and 5.17, 5.08, and 4.98 (alkylation product). Rate constants and half-lives were determined from a linear least squares fit of the data using a pseudo-first-order kinetic model.

General procedure for the Friedel-Crafts substrate scope with catalyst 4a. Indole (6.0 mg, 0.051 mmol), 5-methoxyindole (7.4 mg, 0.050 mmol), 5-chloroindole (7.6 mg, 0.050 mmol) or *N*-methylindole (6.2 μL, 6.5 mg, 0.049 mmol) and *trans*-β-nitrostyrene (14.9 mg, 0.100 mmol), *trans*-2-chloro-β-nitrostyrene (18.4 mg, 0.100 mmol), *trans*-3-bromo-β-nitrostyrene (22.8 mg, 0.100 mmol) or *trans*-4-methoxy-β-nitrostyrene (17.9 mg, 0.100 mmol) were placed in an oven-dried vial which was then sealed, evacuated, and backfilled with argon. In a separate vial under inert atmosphere, 6.7 mg (0.020 mmol) of *N*-ferrocenyl-*N'*-phenylthiourea, 4.3 mg (0.022 mmol)

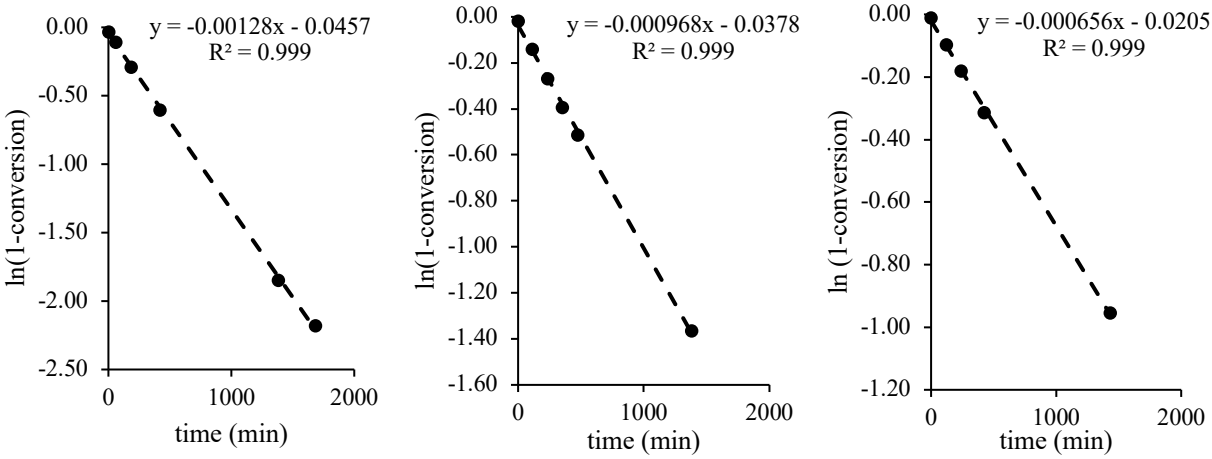
of $AgBF_4$, and 19.7 mg (0.022 mmol) of dried $NaBAr^F_4$ were combined to give a solid precatalyst mixture. Dry dichloromethane (4.0 mL) was added to the vial containing the precatalyst mixture, which was then shaken for 5 min in the absence of light. The resulting green solution was filtered through a 25 mm, 0.2 μm syringe filter and ¼ of the catalyst solution was added to the vial containing indole and *trans*-β-nitrostyrene. It was subsequently shaken for 10 s to dissolve the reactants before being placed in a water bath at 27 °C for 24 h. After the reaction time elapsed, the solvent was removed under reduced pressure with a rotary evaporator, and the residual material was redissolved in a stock solution of mesitylene in 0.6 mL of $CDCl_3$ as an internal standard. Reaction conversions and yields were calculated from NMR integrations of the indole, alkylation product, and mesitylene ratios.[26d]

General procedure for the solvent-free Friedel-Crafts substrate scope with catalyst 5. Indole (6.0 mg, 0.051 mmol), 5-methoxyindole (7.4 mg, 0.050 mmol), 5-chloroindole (7.6 mg, 0.050 mmol) or *N*-methylindole (6.2 μL, 6.5 mg, 0.049 mmol) and *trans*-β-nitrostyrene (14.9 mg, 0.100 mmol), *trans*-2-chloro-β-nitrostyrene (18.4 mg, 0.100 mmol), *trans*-3-bromo-β-nitrostyrene (22.8 mg, 0.100 mmol) or *trans*-4-methoxy-β-nitrostyrene (17.9 mg, 0.100 mmol) were added to an oven-dried vial along with catalyst **5** (6.0 mg, 0.0050 mmol) and the reaction mixture was shaken until the solid material was well combined before being evacuated and backfilled with argon. When *N*-methylindole (6.2 μL, 6.5 mg, 0.049 mmol) was used it was added at this point, and in both instances the vial was transferred to a water bath at 27 °C for 24 h. The contents were then dissolved in $CDCl_3$ and analyzed via ^1H NMR spectroscopy. All of the product spectra can be found in ref. 26d.

Computations. A B3LYP/6-31G(d,p)[S1,S2] transition structure optimization for the Friedel–Crafts alkylation of indole with *trans*-β-nitrostyrene catalyzed by cobaltocenium ion $\mathbf{5}^+$ was carried out

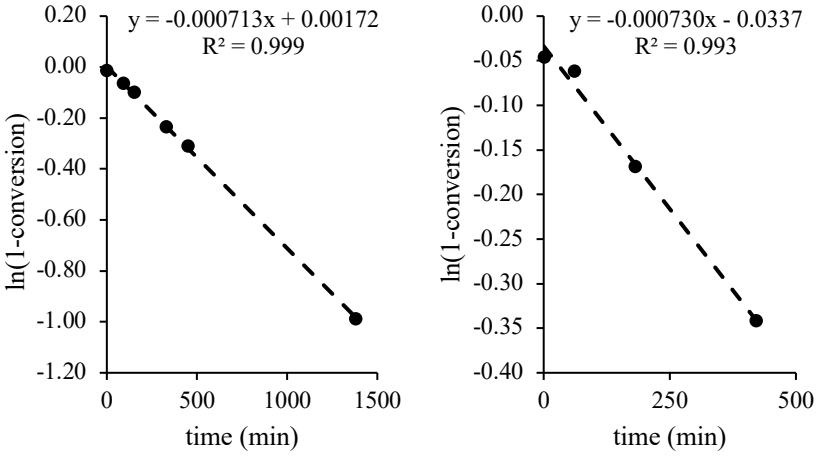
using Gaussian 16 at the Minnesota Supercomputer Institute for Advanced Computational Research.[S3] Vibrational frequencies were subsequently computed, and the resulting structure was found to have one imaginary frequency as required for a stationary point that corresponds to a transition state. All of these calculations were carried out with the default ultrafine integration grid.

Friedel-Crafts kinetic data



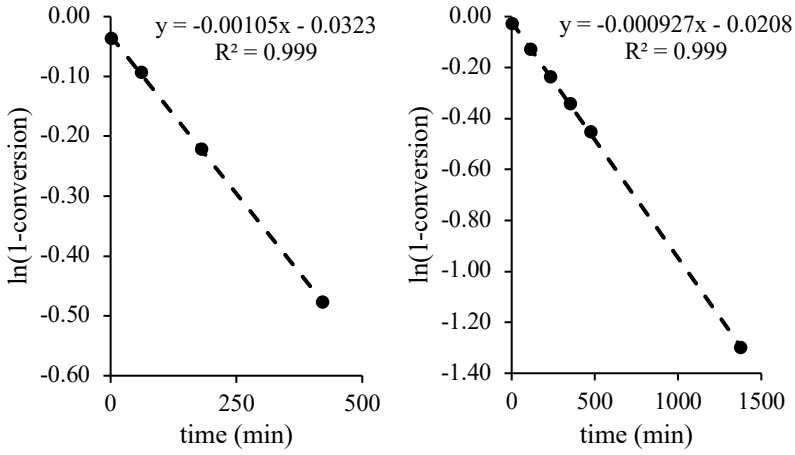
Trial 1			Trial 2			Trial 3		
time (min)	conv.	ln(1-conv.)	time (min)	conv.	ln(1-conv.)	time (min)	conv.	ln(1-conv.)
0.00	0.0323	-0.0328	0.00	0.0164	-0.0165	0.00	0.00990	-0.0100
59.6	0.102	-0.107	112	0.130	-0.140	119	0.0909	-0.0953
180	0.250	-0.288	232	0.235	-0.267	239	0.164	-0.180
419	0.453	-0.602	351	0.324	-0.392	421	0.268	-0.312
1378	0.842	-1.84	472	0.401	-0.513	1430	0.614	-0.953
1680	0.886	-2.18	1379	0.744	-1.36			

Fig. S1 Kinetic plots and data tables for the Friedel-Crafts reaction between *N*-methylindole and *trans*-β-nitrostyrene catalyzed by isolated *N*-ferrocenium-*N'*-phenylthiourea tetrakis-[3,5-bis(trifluoro-methyl)phenyl]borate (BAr^F_4) (**4a**).



Trial 1			Trial 2		
time (min)	conv.	ln(1-conv.)	time (min)	conv.	ln(1-conv.)
0.00	0.0132	-0.0132	0.00	0.0446	-0.0456
88.0	0.0596	-0.0614	60.0	0.0596	-0.061
145	0.0937	-0.0983	181	0.155	-0.168
327	0.208	-0.234	420	0.289	-0.341
446	0.265	-0.307			
1377	0.627	-0.987			

Fig. S2 Kinetic plots of the Friedel-Crafts reaction between *N*-methylindole and *trans*-β-nitrostyrene catalyzed by *N*-cobaltocenium-*N′*-phenylthiourea BAr^F_4 (**5**).



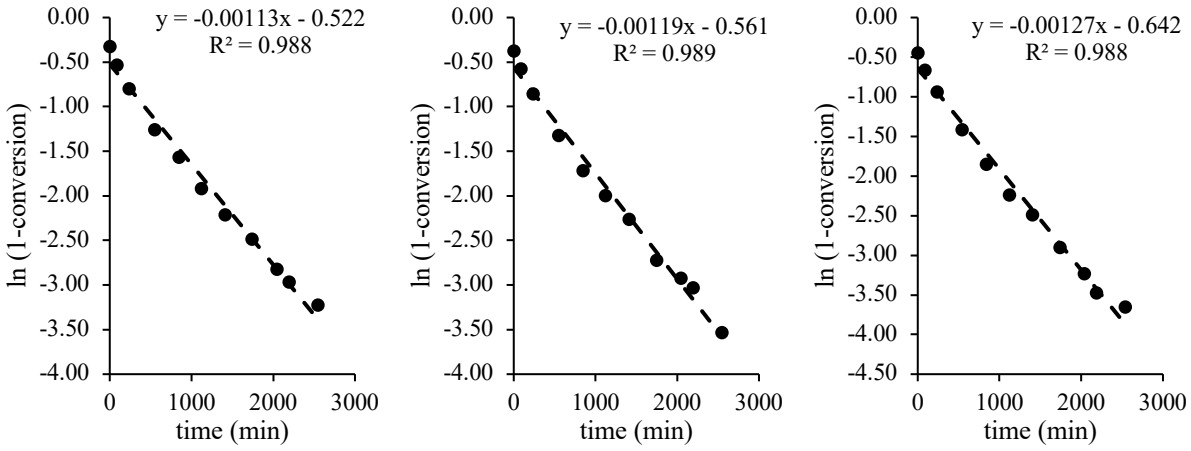
Trial 1

time (min)	conv.	ln(1-conv.)
0.00	0.0354	-0.0360
59.9	0.0881	-0.092
181	0.198	-0.220
420	0.379	-0.476

Trial 2

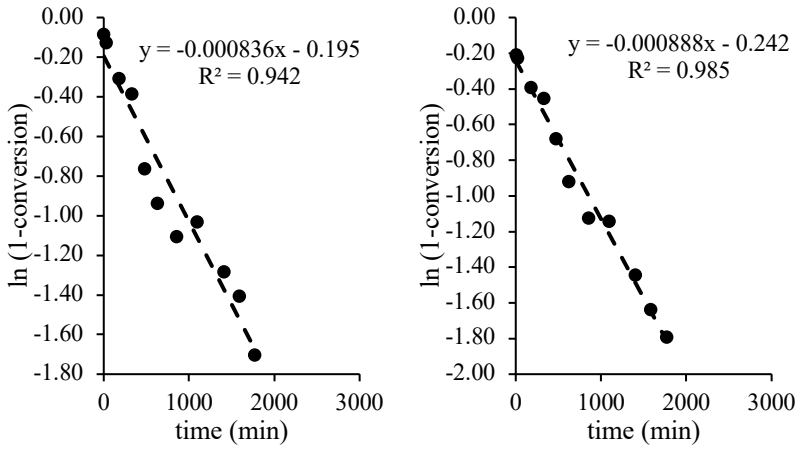
time (min)	conv.	ln(1-conv.)
0.00	0.0260	-0.0263
112	0.120	-0.128
231	0.208	-0.234
351	0.289	-0.341
472	0.363	-0.4511
1373	0.727	-1.30

Fig. S3 Kinetic plots of the Friedel-Crafts reaction between *N*-methylindole and *trans*-β-nitrostyrene catalyzed by *N*-methylpyridinium-*N′*-phenylthiourea BAr^F_4 (**2**).



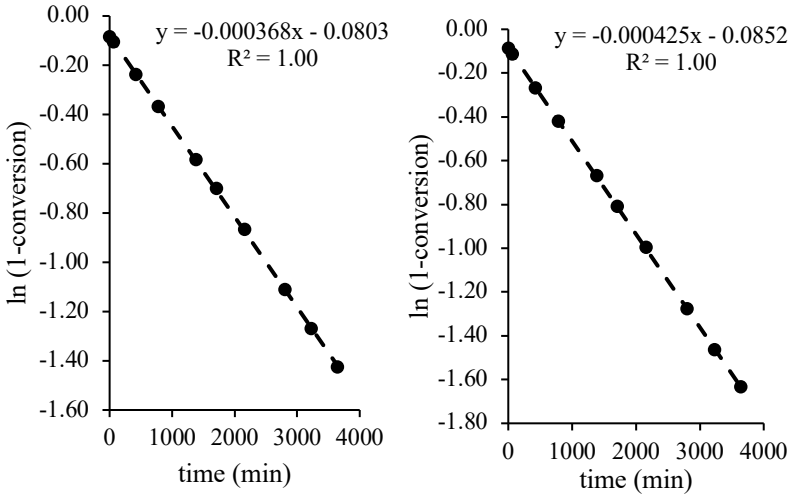
Trial 1			Trial 2			Trial 3		
time (min)	conv.	ln(1-conv.)	time (min)	conv.	ln(1-conv.)	time (min)	conv.	ln(1-conv.)
0.00	0.275	-0.322	0.00	0.309	-0.369	0.00	0.359	-0.445
86.3	0.411	-0.529	86.1	0.438	-0.577	85.4	0.483	-0.659
235	0.550	-0.799	235	0.573	-0.850	234	0.607	-0.935
548	0.714	-1.25	547	0.732	-1.32	546	0.756	-1.41
841	0.791	-1.57	840	0.820	-1.71	839	0.842	-1.84
1121	0.853	-1.91	1120	0.864	-2.00	1119	0.893	-2.24
1405	0.890	-2.21	1406	0.896	-2.26	1406	0.917	-2.48
1740	0.917	-2.48	1740	0.934	-2.72	1739	0.945	-2.90
2041	0.940	-2.82	2041	0.946	-2.92	2040	0.960	-3.23
2190	0.948	-2.97	2190	0.952	-3.03	2189	0.969	-3.47
2543	0.960	-3.22	2543	0.971	-3.53	2542	0.974	-3.64

Fig. S4 Kinetic plots of the Friedel-Crafts reaction between *N*-methylindole and *trans*-β-nitrostyrene catalyzed by in-situ generated *N*-ferrocenium-*N*′-phenylthiourea BAr^{F}_{4} (**4a**).



Trial 1			Trial 2		
time (min)	conv.	ln(1-conv.)	time (min)	conv.	ln(1-conv.)
0.00	0.0798	-0.0831	0.00	0.187	-0.207
24.9	0.118	-0.125	15.9	0.202	-0.226
179	0.263	-0.305	171	0.323	-0.390
329	0.320	-0.385	321	0.363	-0.451
477	0.533	-0.761	469	0.492	-0.676
625	0.608	-0.936	617	0.601	-0.919
856	0.669	-1.11	848	0.675	-1.12
1094	0.643	-1.03	1085	0.680	-1.14
1406	0.722	-1.28	1399	0.763	-1.44
1586	0.754	-1.40	1578	0.806	-1.64
1772	0.818	-1.70	1764	0.833	-1.79

Fig. S5 Kinetic plots of the Friedel-Crafts reaction between *N*-methylindole and *trans*-β-nitrostyrene catalyzed by in-situ generated *N*-ferroceniummethyl-*N′*-phenylthiourea BAr^{F}_{4} (**4b**).



Trial 1			Trial 2		
time (min)	conv.	ln(1-conv.)	time (min)	conv.	ln(1-conv.)
0.00	0.0798	-0.0831	0.00	0.0826	-0.0862
56.9	0.0991	-0.104	57.6	0.104	-0.110
418	0.211	-0.236	418	0.233	-0.265
778	0.307	-0.367	777	0.342	-0.419
1376	0.441	-0.582	1376	0.487	-0.668
1704	0.503	-0.700	1704	0.554	-0.806
2154	0.579	-0.866	2154	0.630	-0.994
2799	0.670	-1.11	2798	0.720	-1.27
3226	0.719	-1.27	3225	0.769	-1.46
3636	0.759	-1.42	3636	0.805	-1.63

Fig. S6 Kinetic plots of the Friedel-Crafts reaction between *N*-methylindole and *trans*-β-nitrostyrene catalyzed by Schreiner's Thiourea (**1**).

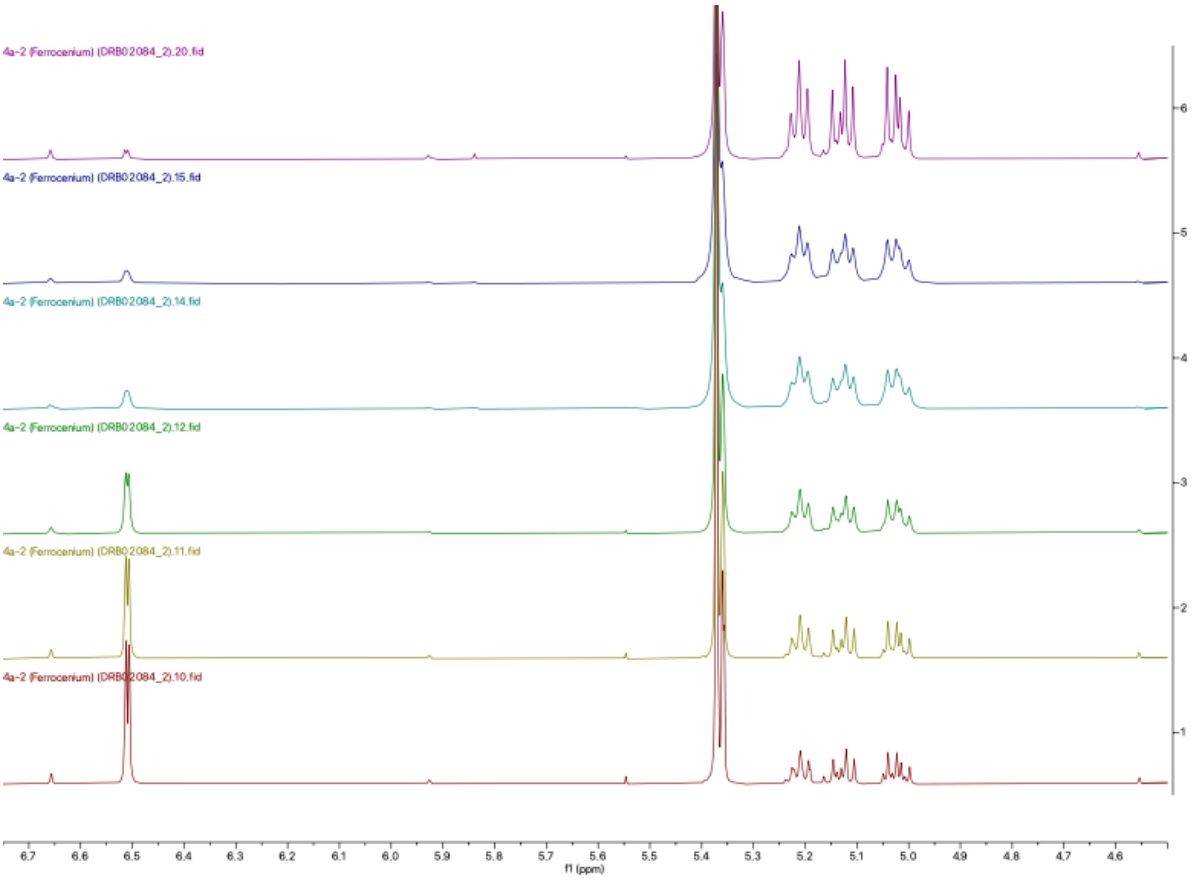


Fig. S7 Stacked spectra for six time points (t = 0, 86.1, 235, 840, 1120, and 1740 min) of the kinetic data for the Friedel-Crafts reaction between *N*-methylindole and *trans*-β-nitrostyrene catalyzed by in-situ generated *N*-ferrocenium-*N*′-phenylthiourea BAr^{F}_{4} (**4a**). The signals at 6.5 and 5.0 - 5.2 δ correspond to *N*-methylindole and the reaction product, respectively.

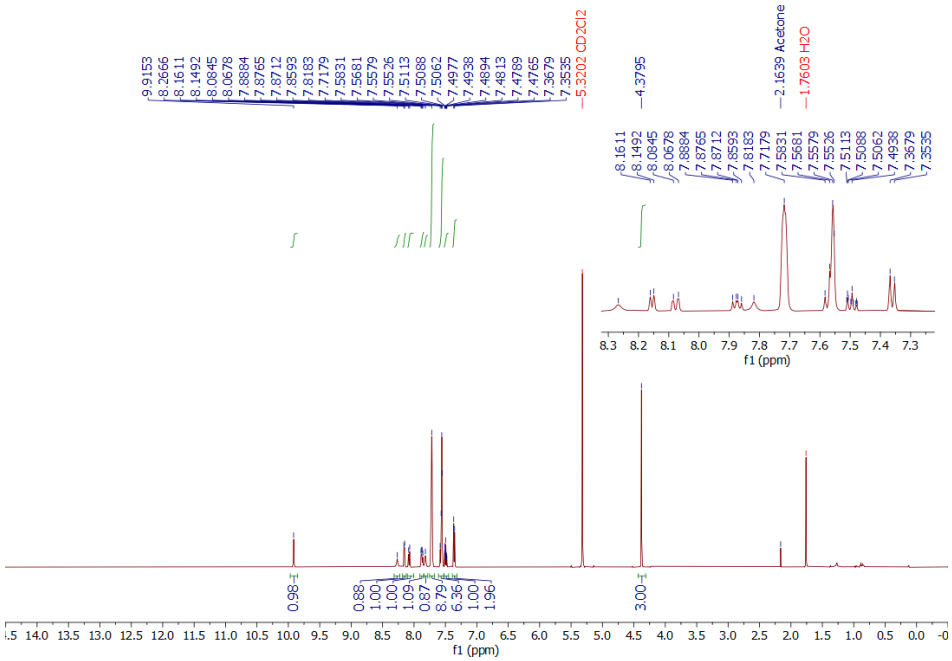


Fig. S8 ^{1}H NMR spectrum of 1-methyl-3-(3-phenylthioureido)pyridinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**2**) in CD_2Cl_2.

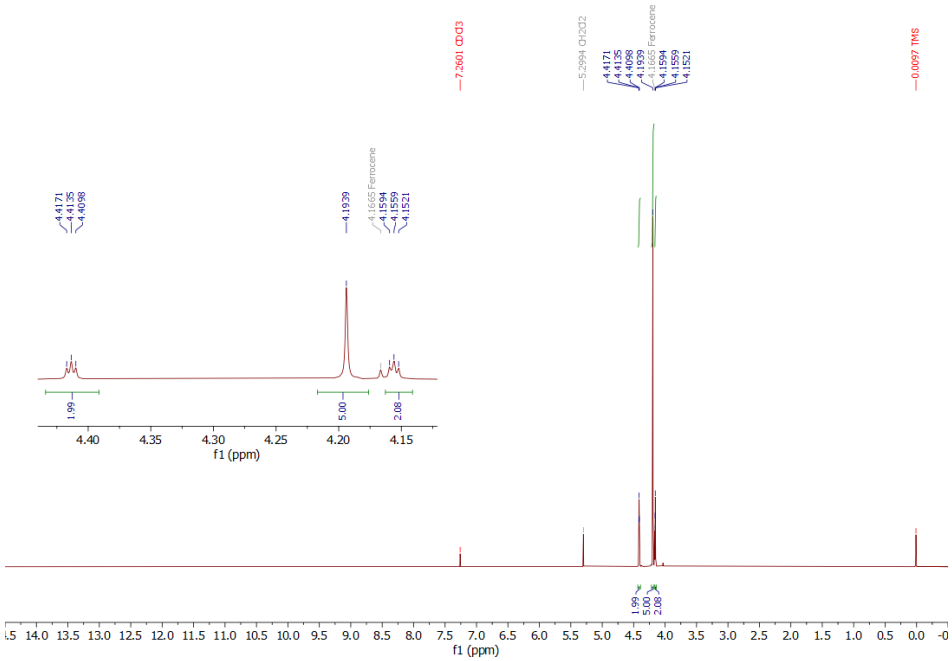


Fig. S9 ^{1}H NMR spectrum of iodoferrocene (**7**) taken in $CDCl_3$.

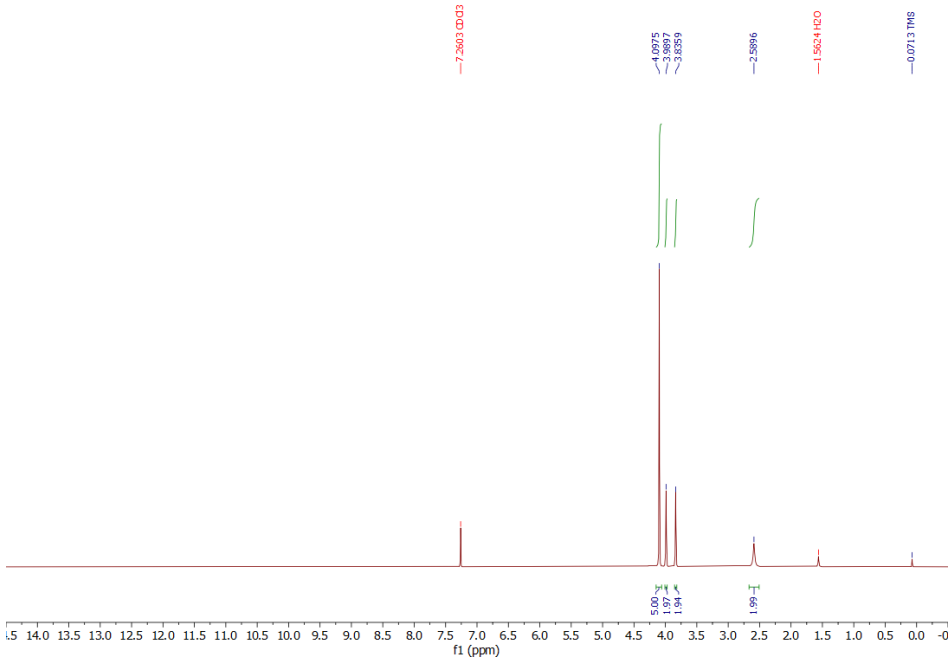


Fig. S10 ^{1}H NMR spectrum of aminoferrocene (**8a**) taken in CD_2Cl_2.

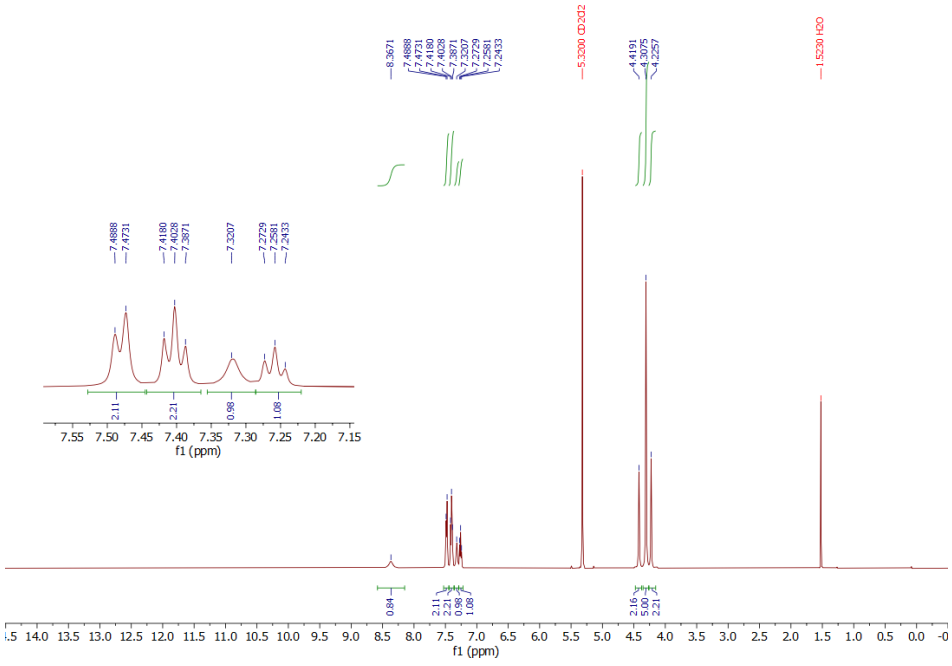


Fig. S11 ^{1}H NMR spectrum of *N*-ferrocenyl-*N*'-phenylthiourea (**9a**) taken in CD_2Cl_2.

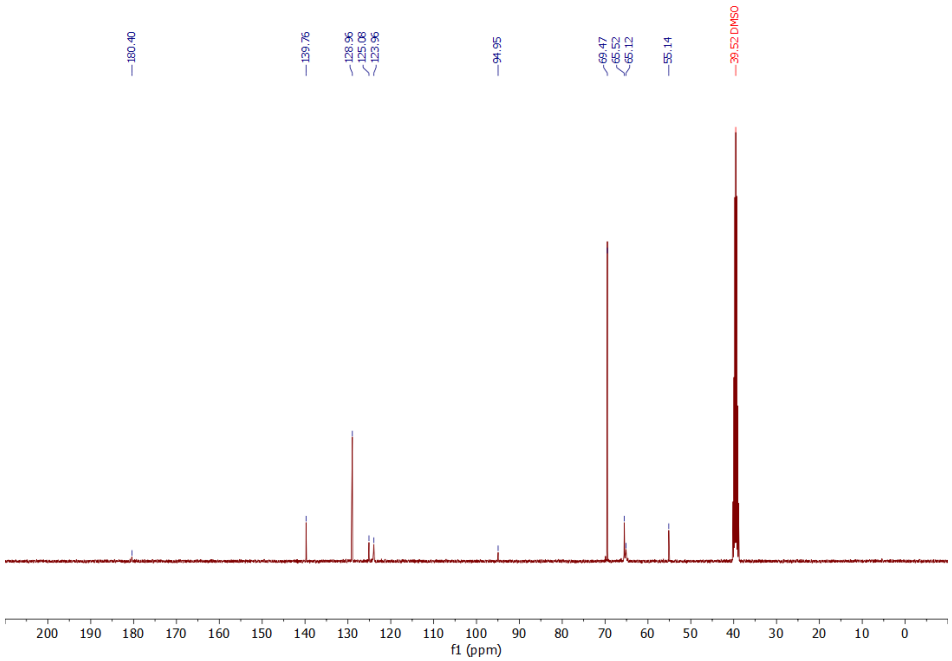


Fig. S12 ^{13}C NMR spectrum of *N*-ferrocenyl-*N*'-phenylthiourea (**9a**) taken in CD_2Cl_2.

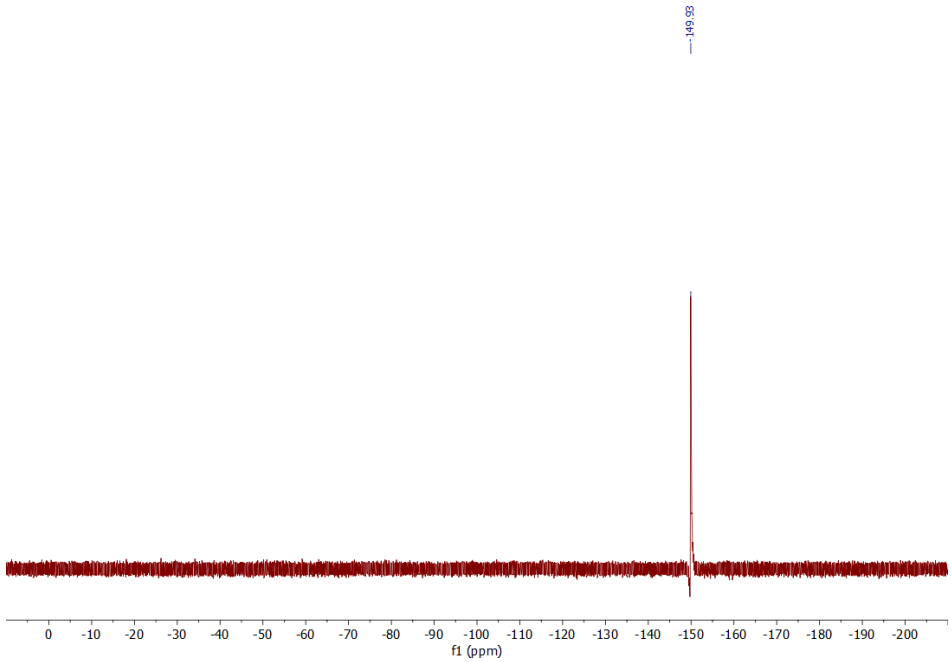


Fig. S13 ^{19}F NMR spectrum of *N*-ferrocenium-*N*'-phenylthiourea tetrafluoroborate (**10**) in CD_2Cl_2.

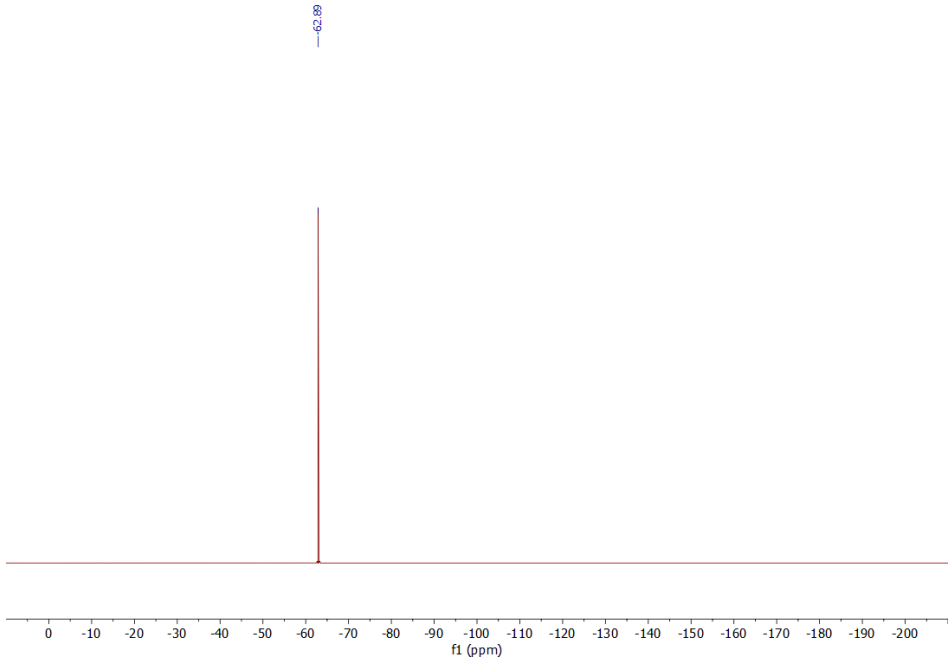


Fig. S14 ^{19}F NMR spectrum of *N*-ferrocenium-*N'*-phenylthiourea tetrakis[3,5-bis(trifluoro-methyl)phenyl]borate (BAr^{F}_{4}) (**4a**) taken in CD_2Cl_2.

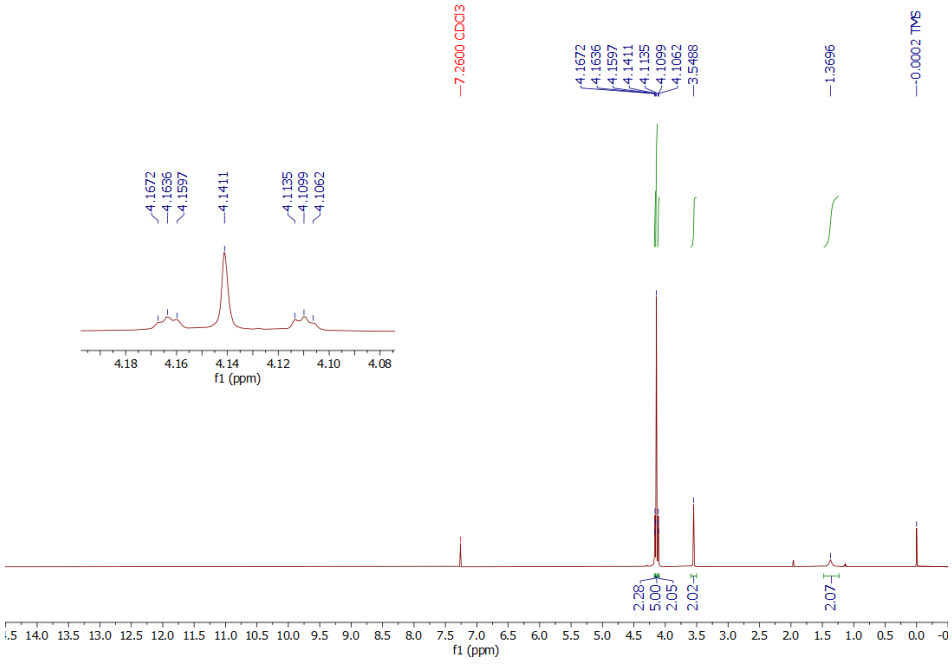


Fig. S15 ^{1}H NMR spectrum of aminomethylferrocene (**8b**) taken in $CDCl_3$.

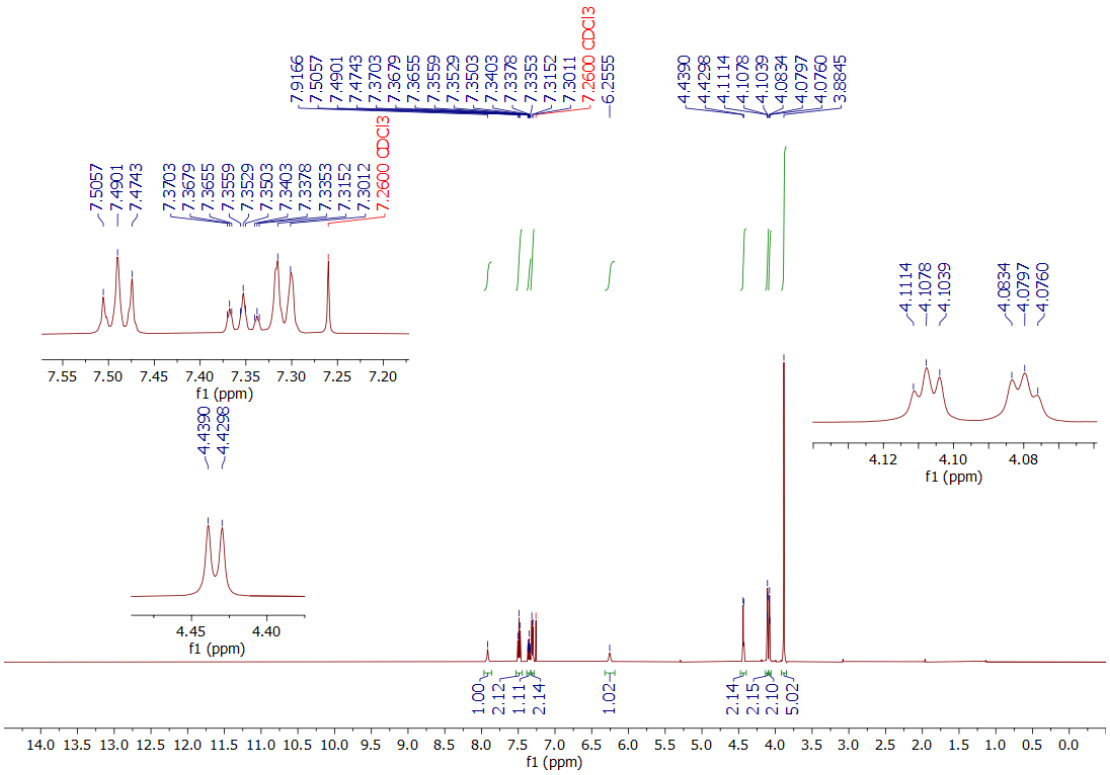


Fig. S16 ^{1}H NMR spectrum of *N*-methylferrocenyl-*N'*-phenylthiourea (**9b**) taken in $CDCl_3$.

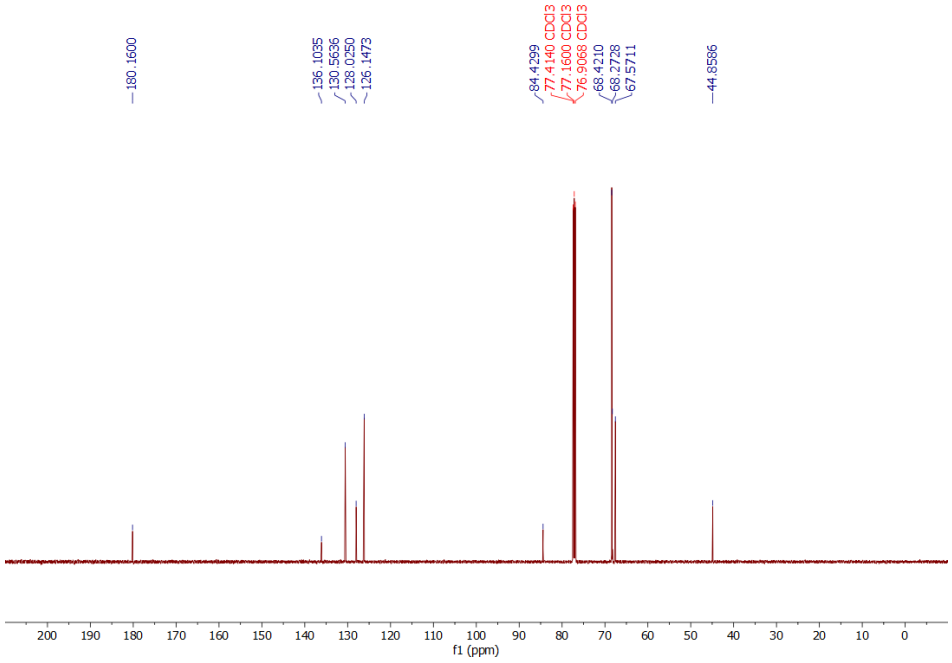


Fig. S17 ^{13}C NMR spectrum of *N*-methylferrocenyl-*N'*-phenylthiourea (**9b**) taken in $CDCl_3$.

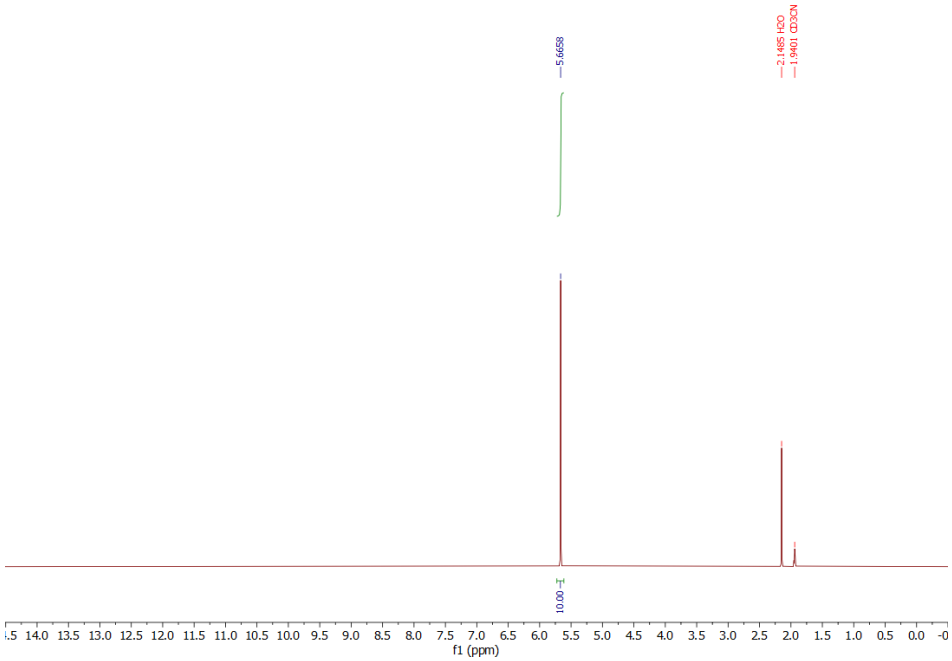


Fig. S18 ^{1}H NMR spectrum of cobaltocenium hexafluorophosphate (**11**) taken in CD_3CN.

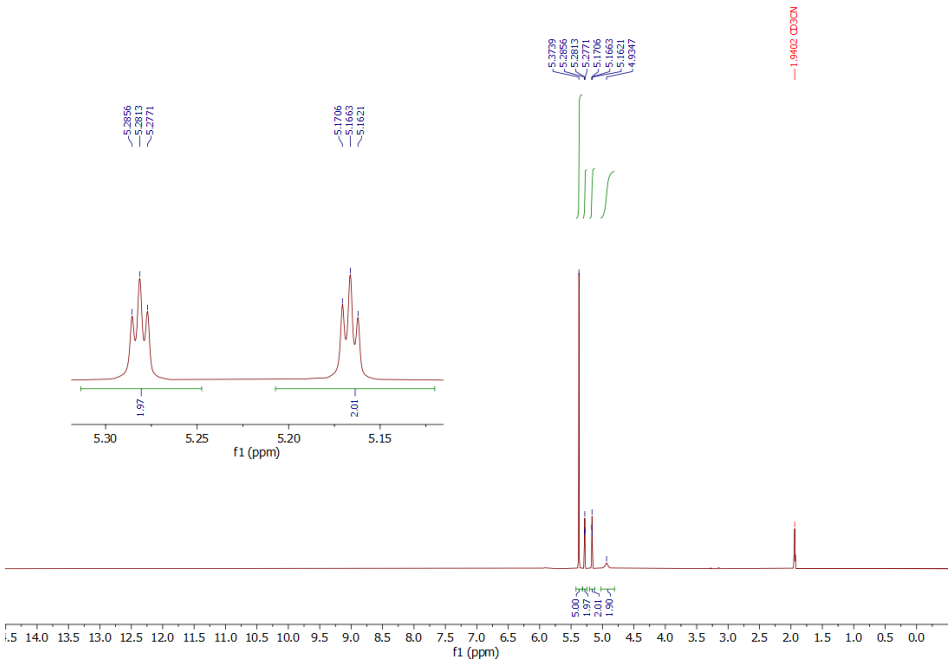


Fig. S19 ^{1}H NMR spectrum of aminocobaltocenium hexafluorophosphate (**12**) in CD_3CN.

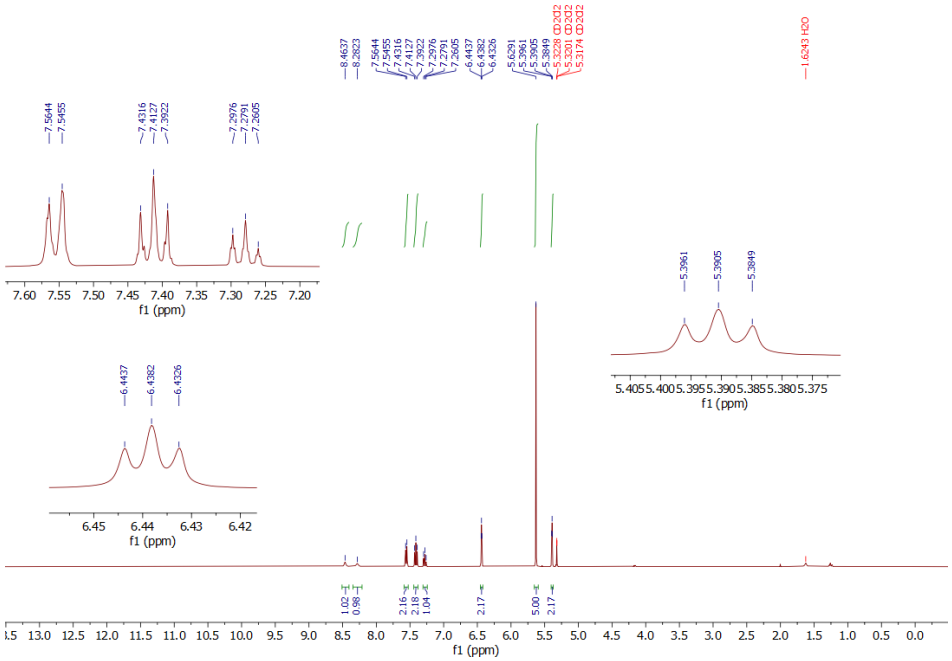


Fig. S20 ^{1}H NMR spectrum of *N*-cobaltocenium-*N*'-phenylthiourea hexafluorophosphate (**13**) in CD_2Cl_2.

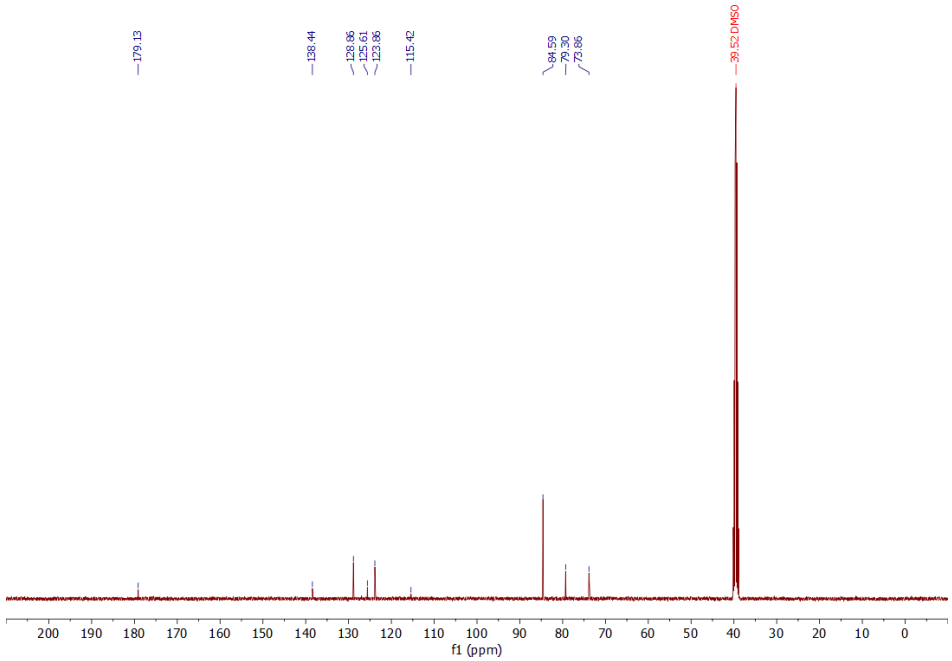


Fig. S21 ^{13}C NMR spectrum of *N*-cobaltocenium-*N*'-phenylthiourea hexafluorophosphate (**13**) in DMSO-d_6.

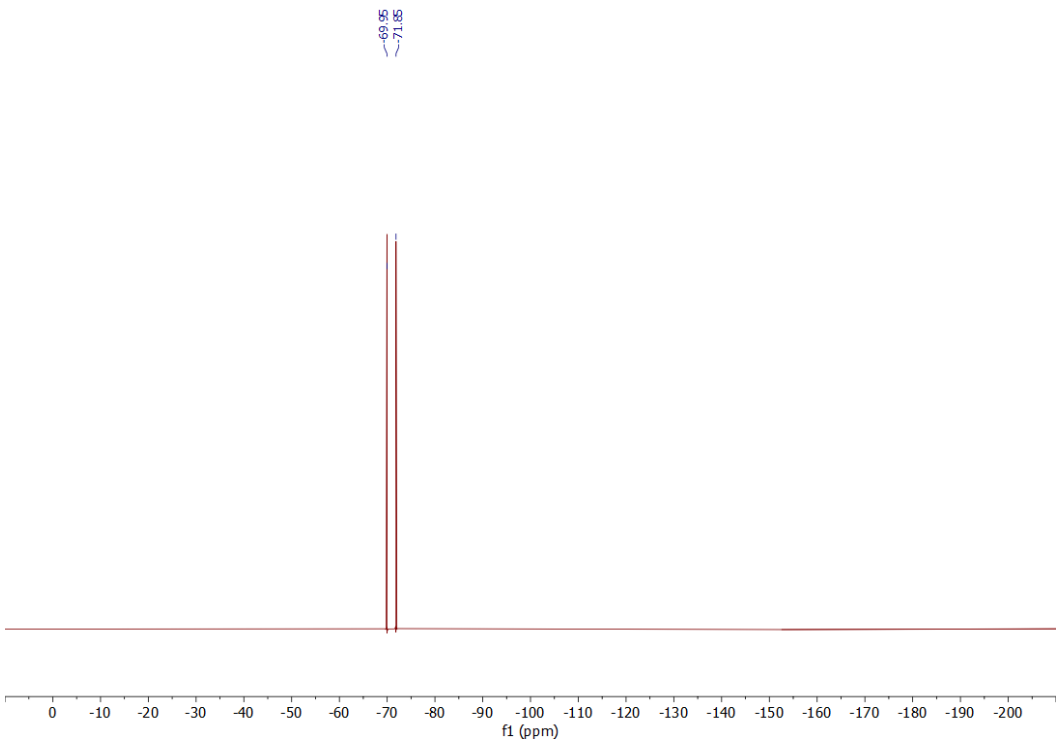


Fig. S22 ^{19}F NMR spectrum of *N*-cobaltocenium-*N'*-phenylthiourea PF_6 (**13**) taken in CD_2Cl_2.

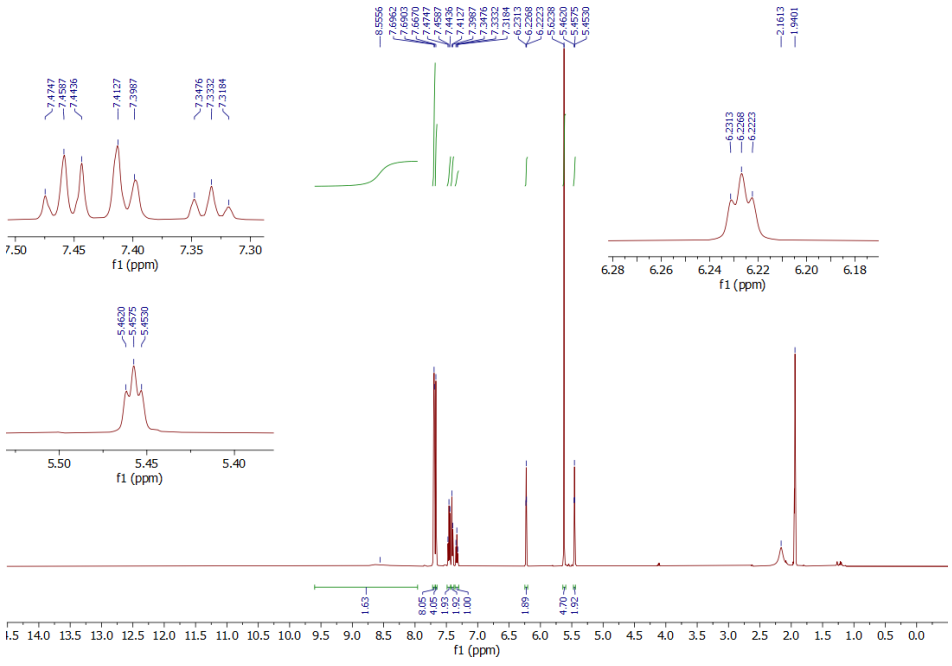


Fig. S23 ^{1}H NMR spectrum of *N*-cobaltocenium-*N'*-phenylthiourea BAr^F_4 (**5**) taken in CD_3CN.

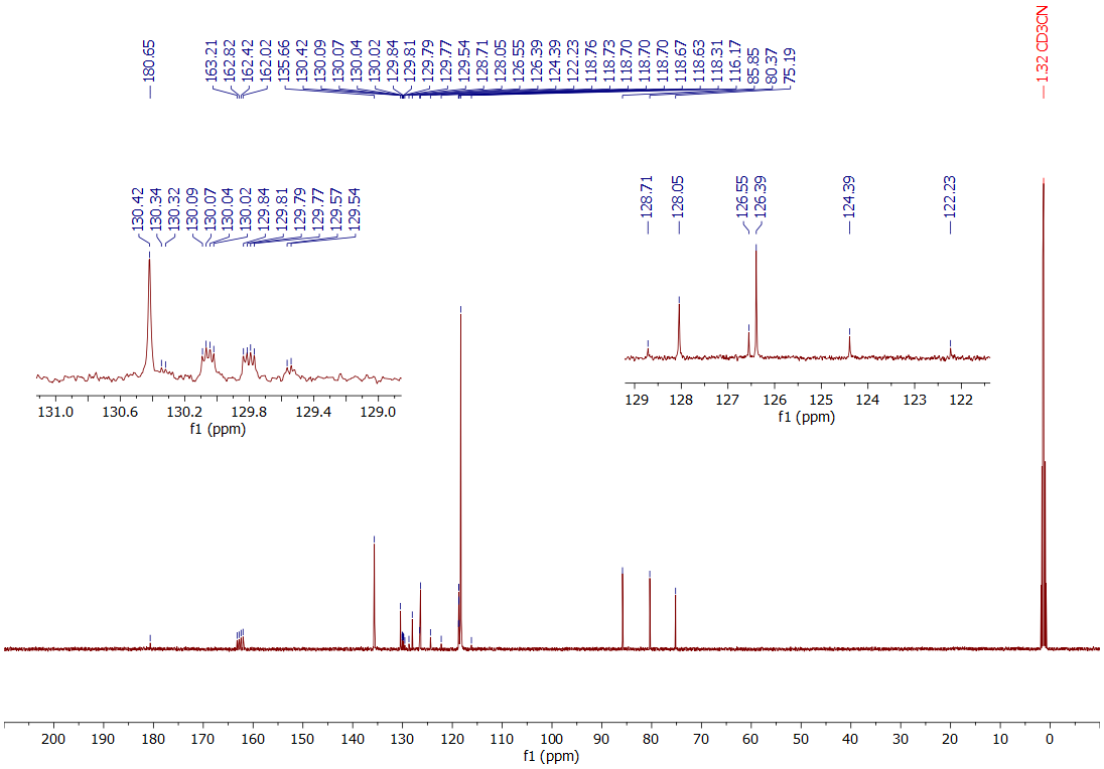


Fig. S24 ^{13}C NMR spectrum of *N*-cobaltocenium-*N*'-phenylthiourea BAr^F_4 (**5**) taken in CD_3CN.

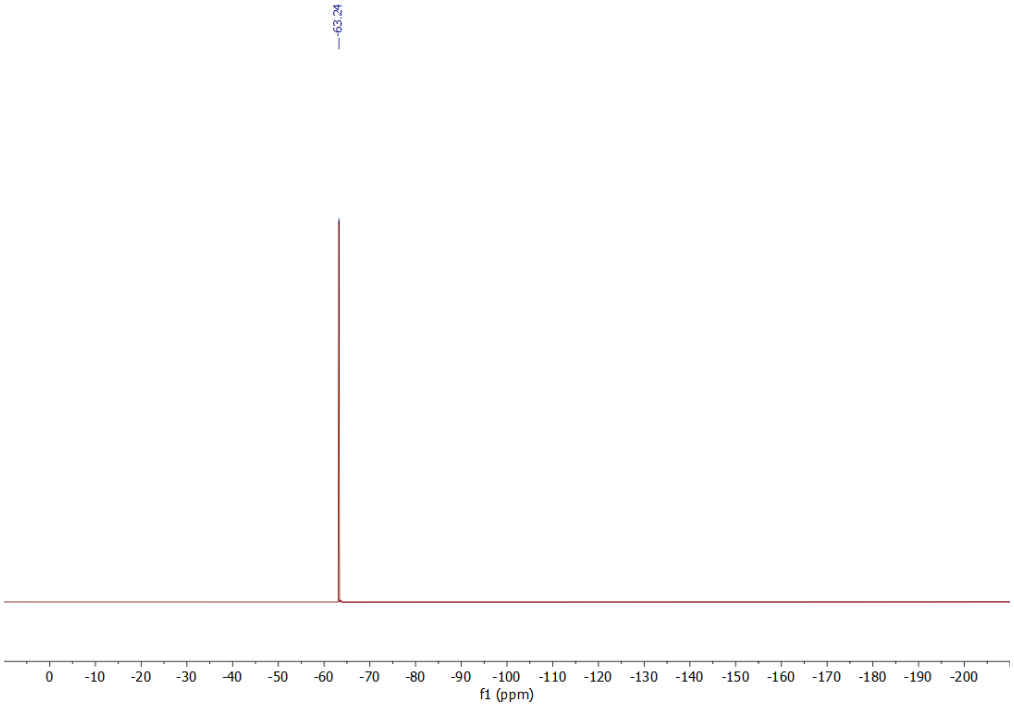


Fig. S25 ^{19}F NMR spectrum of *N*-cobaltocenium-*N*'-phenylthiourea BAr^F_4 (**5**) taken in CD_3CN.

X-ray Crystallography of *N*-cobaltocenium-*N′*-phenylthiourea hexafluorophosphate (13). Diethyl ether vapor was allowed to diffuse into a saturated solution (2 mL) of *N*-cobaltocenium-*N'*-phenylthiourea hexafluorophosphate in 1,2-dichloroethane at room temperature over three days. A resulting crystal (approximately 0.150 x 0.150 x 0.120 mm) was placed onto the tip of a 0.5 mm MiTeGen loop and mounted on a Bruker PHOTON-III diffractometer for data collection at 125(2) K.[S4] A preliminary set of cell constants was calculated from reflections harvested from three sets of 12 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 9989 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 10 seconds and a detector distance of 6.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.84 Å. Four major sections of frames were collected with 0.30˚ steps in ω at four different f settings and a detector position of -28˚ in 2θ. The intensity data were corrected for absorption and decay.[S5] Final cell constants were calculated from the xyz centroids of 9948 strong reflections from the actual data collection after integration.[S6] For additional crystal and refinement information, see Table S1.

The structure (Fig. S26) was solved using SHELXT 2014/5 (Sheldrick, 2014)[S7,S8] and refined using SHELXL-2018/3 (Sheldrick, 2018).[S9] Its space group $P2_12_12_1$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0443$ and $wR2 = 0.1063$ (F^2, all data).

The structure is the one suggested and is a Z' = 2. There is substantial disorder in one of the PF_6^- anions and it was modelled to make an ideal octahedron using DFIX and EADP functions in conjunction with the more ordered PF_6^- ion. Additionally, to better model the F atoms of the disordered PF_6^-, the ISOR constraint was used.

Table S1. Crystal data and structure refinement for *N*-cobaltocenium-*N*'-phenylthiourea hexafluorophosphate.

Empirical formula	$C_{17}H_{16}CoF_6N_2PS$
Formula weight	484.28
Temperature (K)	125(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	9.9480(4) Å
b (Å)	13.3446(5) Å
c (Å)	27.6271(9) Å
Volume (Å)	3667.6(2) Å
Z	8
Density (calculated)	1.754 Mg/m^3
Absorption coefficient	1.201 mm^{-1}
F(000)	1952
Crystal color, morphology	Orange, block
Crystal size	0.150 x 0.150 x 0.120 mm^3
Theta range for data collection	2.122 to 30.513°
Index ranges	$-13 \leq h \leq 14$, $-16 \leq k \leq 19$, $-31 \leq l \leq 39$
Reflections collected	34402
Independent reflections	11142 [*R*(int) = 0.0416]
Observed reflections	9617
Completeness to theta = 25.242°	99.9%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11142 / 126 / 544
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	*R*1 = 0.0443, *wR*2 = 0.1004
R indices (all data)	*R*1 = 0.0553, *wR*2 = 0.1063
Absolute structure parameter	-0.002(6)
Extinction coefficient	n/a
Largest diff. peak and hole	1.143 and -0.524 e.$Å^{-3}$

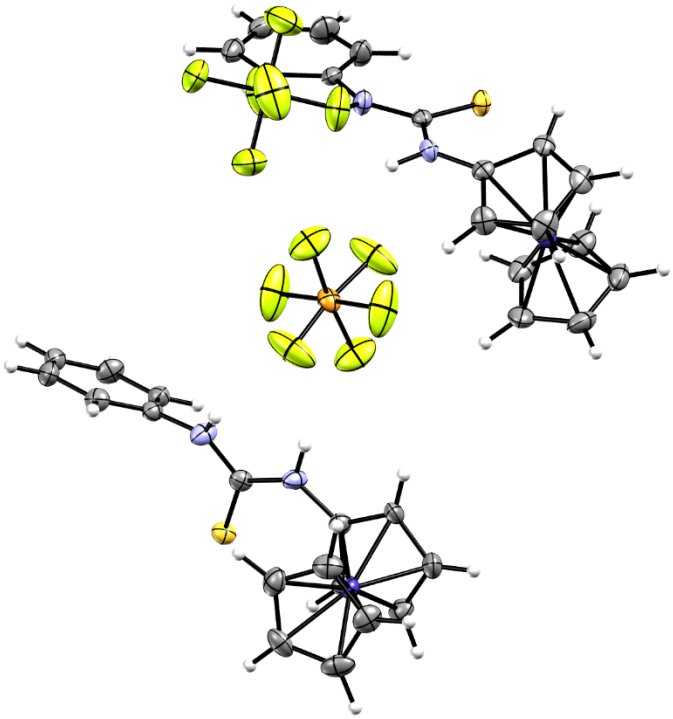


Fig. S26 Structure of *N*-cobaltocenium-*N'*-phenylthiourea hexafluorophosphate as determined by single crystal X-ray diffraction.

Some equations of interest:

$$R_{int} = S\,|F_o^2 - \langle F_o^2 \rangle| \,/\, S|F_o^2|$$

$$R_1 = S||F_o| - |F_c|| \,/\, S|F_o|$$

$$wR2 = [S[w(F_o^2 - F_c^2)^2] \,/\, S\,[w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [s^2(F_o^2) + (a*P)^2 + b*P + d + e*\sin(q)]$$

$$\text{GooF} = S = [S[w(F_o^2 - F_c^2)^2] \,/\, (n-p)]^{1/2}$$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for *N*-cobaltocenium-*N*'-phenylthiourea PF_6^-. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Co1	-339(1)	4723(1)	4693(1)	20(1)
C1	5375(4)	6745(3)	4286(1)	22(1)
N1	4311(4)	6038(3)	4340(2)	29(1)
S1	2320(1)	7279(1)	4105(1)	24(1)
Co2	3560(1)	293(1)	2834(1)	21(1)
C2	5588(4)	7221(3)	3847(2)	26(1)
N2	2354(4)	5269(3)	4183(1)	27(1)
S2	6838(1)	1040(1)	2132(1)	25(1)
P1A	5136(8)	3332(6)	3710(3)	27(1)
F1A	5400(9)	2969(5)	3163(2)	76(2)
F2A	5965(8)	4316(5)	3640(3)	81(2)
F3A	6365(6)	2683(5)	3886(2)	60(1)
F4A	3867(6)	3901(5)	3492(2)	60(1)
F5A	4280(8)	2357(5)	3789(3)	81(2)
F6A	4688(10)	3663(5)	4236(2)	76(2)
P1B	5254(17)	3430(12)	3726(6)	27(1)
F1B	4621(13)	3015(10)	3258(3)	71(3)
F2B	4740(16)	4493(8)	3563(4)	80(3)
F3B	6578(9)	3579(10)	3427(4)	64(3)
F4B	3901(10)	3298(10)	4030(4)	64(3)
F5B	5642(16)	2329(8)	3859(4)	80(3)
F6B	5883(13)	3829(10)	4197(3)	71(3)
P2	9559(1)	955(1)	4274(1)	28(1)
F7	8505(4)	1637(3)	4541(2)	65(1)
C7	3018(4)	6166(3)	4211(1)	22(1)
C6	6235(5)	6915(3)	4670(2)	28(1)
C5	7324(5)	7555(4)	4610(2)	31(1)
N4	6563(4)	866(3)	3089(1)	22(1)
C4	7544(5)	8018(3)	4174(2)	28(1)
F8	9431(6)	146(3)	4688(1)	82(2)

C8	990(4)	5082(3)	4136(2)	25(1)
F9	8376(4)	419(3)	3980(1)	61(1)
C9	-133(4)	5734(3)	4142(2)	27(1)
F10	10619(4)	268(4)	4007(2)	83(1)
C10	-1310(5)	5143(4)	4084(2)	30(1)
F11	9649(5)	1763(3)	3844(1)	72(1)
C11	-915(5)	4114(4)	4059(2)	33(1)
F12	10714(3)	1523(3)	4554(1)	59(1)
C12	494(5)	4077(3)	4100(2)	27(1)
N3	8293(4)	1846(3)	2858(1)	26(1)
C3	6672(5)	7860(4)	3791(2)	30(1)
C19	9990(5)	3092(3)	2894(2)	30(1)
C20	10885(5)	3761(4)	2695(2)	35(1)
C21	10975(5)	3854(4)	2195(2)	37(1)
C22	10153(6)	3274(4)	1911(2)	42(1)
C23	9265(5)	2587(4)	2103(2)	35(1)
C24	7264(4)	1274(3)	2702(1)	20(1)
C25	5525(4)	173(3)	3079(1)	22(1)
C26	5217(4)	-587(3)	2732(2)	25(1)
C27	4115(5)	-1154(3)	2918(2)	32(1)
C28	3724(5)	-733(4)	3368(2)	36(1)
C29	4583(5)	96(3)	3467(2)	30(1)
C30	3348(5)	1660(3)	2514(2)	33(1)
C31	3063(5)	886(4)	2182(2)	35(1)
C32	1975(5)	326(4)	2366(2)	37(1)
C33	1603(5)	727(4)	2821(2)	40(1)
C34	2460(5)	1557(4)	2911(2)	39(1)
C13	685(5)	4875(4)	5323(2)	34(1)
C14	-469(6)	5493(4)	5329(2)	35(1)
C15	-1609(5)	4867(4)	5271(2)	37(1)
C16	-1151(5)	3866(4)	5228(2)	35(1)
C18	9175(4)	2500(3)	2606(2)	24(1)
C17	271(5)	3872(4)	5258(2)	33(1)

Table S3. Bond lengths [Å] and angles [°] for *N*-cobaltocenium-*N*'-phenylthiourea PF_6^-.

Co(1)-C(10)	2.020(4)	P(1A)-F(2A)	1.563(9)
Co(1)-C(11)	2.015(5)	P(1A)-F(3A)	1.575(10)
Co(1)-C(17)	2.024(4)	P(1A)-F(1A)	1.609(10)
Co(1)-C(13)	2.027(4)	P(1B)-F(3B)	1.567(17)
Co(1)-C(12)	2.028(4)	P(1B)-F(5B)	1.563(17)
Co(1)-C(16)	2.035(5)	P(1B)-F(6B)	1.540(17)
Co(1)-C(14)	2.038(4)	P(1B)-F(1B)	1.541(17)
Co(1)-C(9)	2.045(4)	P(1B)-F(2B)	1.574(17)
Co(1)-C(15)	2.046(5)	P(1B)-F(4B)	1.597(17)
Co(1)-C(8)	2.085(4)	P(2)-F(7)	1.572(4)
C(1)-C(6)	1.382(6)	P(2)-F(8)	1.576(4)
C(1)-C(2)	1.385(6)	P(2)-F(10)	1.581(4)
C(1)-N(1)	1.426(5)	P(2)-F(12)	1.579(3)
N(1)-C(7)	1.346(5)	P(2)-F(9)	1.599(4)
N(1)-H(1)	0.87(6)	P(2)-F(11)	1.608(3)
S(1)-C(7)	1.664(4)	C(6)-C(5)	1.390(6)
Co(2)-C(34)	2.022(5)	C(6)-H(6)	0.9500
Co(2)-C(28)	2.020(5)	C(5)-C(4)	1.371(7)
Co(2)-C(27)	2.021(4)	C(5)-H(5)	0.9500
Co(2)-C(31)	2.029(5)	N(4)-C(25)	1.387(5)
Co(2)-C(33)	2.032(5)	N(4)-C(24)	1.388(5)
Co(2)-C(30)	2.038(4)	N(4)-H(4A)	0.91(6)
Co(2)-C(29)	2.039(4)	C(4)-C(3)	1.386(6)
Co(2)-C(26)	2.043(4)	C(4)-H(4)	0.9500
Co(2)-C(32)	2.039(5)	C(8)-C(9)	1.417(6)
Co(2)-C(25)	2.075(4)	C(8)-C(12)	1.432(6)
C(2)-C(3)	1.383(6)	C(9)-C(10)	1.421(6)
C(2)-H(2)	0.9500	C(9)-H(9)	1.0000
N(2)-C(7)	1.369(6)	C(10)-C(11)	1.430(7)
N(2)-C(8)	1.385(5)	C(10)-H(10)	1.0000
N(2)-H(2AA)	0.88(6)	C(11)-C(12)	1.408(7)
S(2)-C(24)	1.659(4)	C(11)-H(11)	1.0000
P(1A)-F(6A)	1.583(9)	C(12)-H(12)	1.0000
P(1A)-F(5A)	1.570(9)	N(3)-C(24)	1.348(5)
P(1A)-F(4A)	1.592(10)	N(3)-C(18)	1.420(6)

N(3)-H(3A)	0.93(4)	C(14)-H(14)	1.0000
C(3)-H(3)	0.9500	C(15)-C(16)	1.417(7)
C(19)-C(20)	1.375(7)	C(15)-H(15)	1.0000
C(19)-C(18)	1.383(6)	C(16)-C(17)	1.417(7)
C(19)-H(19)	0.9500	C(16)-H(16)	1.0000
C(20)-C(21)	1.390(8)	C(17)-H(17)	1.0000
C(20)-H(20)	0.9500	C(10)-Co(1)-C(11)	41.5(2)
C(21)-C(22)	1.372(8)	C(10)-Co(1)-C(17)	160.4(2)
C(21)-H(21)	0.9500	C(11)-Co(1)-C(17)	122.0(2)
C(22)-C(23)	1.380(7)	C(10)-Co(1)-C(13)	158.1(2)
C(22)-H(22)	0.9500	C(11)-Co(1)-C(13)	158.4(2)
C(23)-C(18)	1.398(6)	C(17)-Co(1)-C(13)	40.8(2)
C(23)-H(23)	0.9500	C(10)-Co(1)-C(12)	68.9(2)
C(25)-C(26)	1.428(6)	C(11)-Co(1)-C(12)	40.76(19)
C(25)-C(29)	1.427(6)	C(17)-Co(1)-C(12)	105.18(19)
C(26)-C(27)	1.427(6)	C(13)-Co(1)-C(12)	122.0(2)
C(26)-H(26)	1.0000	C(10)-Co(1)-C(16)	124.8(2)
C(27)-C(28)	1.420(7)	C(11)-Co(1)-C(16)	107.0(2)
C(27)-H(27)	1.0000	C(17)-Co(1)-C(16)	40.9(2)
C(28)-C(29)	1.424(7)	C(13)-Co(1)-C(16)	68.4(2)
C(28)-H(28)	1.0000	C(12)-Co(1)-C(16)	120.6(2)
C(29)-H(29)	1.0000	C(10)-Co(1)-C(14)	123.2(2)
C(30)-C(34)	1.414(8)	C(11)-Co(1)-C(14)	159.1(2)
C(30)-C(31)	1.411(7)	C(17)-Co(1)-C(14)	68.7(2)
C(30)-H(30)	1.0000	C(13)-Co(1)-C(14)	40.7(2)
C(31)-C(32)	1.409(7)	C(12)-Co(1)-C(14)	159.3(2)
C(31)-H(31)	1.0000	C(16)-Co(1)-C(14)	68.5(2)
C(32)-C(33)	1.415(8)	C(10)-Co(1)-C(9)	40.92(18)
C(32)-H(32)	1.0000	C(11)-Co(1)-C(9)	69.3(2)
C(33)-C(34)	1.420(7)	C(17)-Co(1)-C(9)	156.2(2)
C(33)-H(33)	1.0000	C(13)-Co(1)-C(9)	121.53(19)
C(34)-H(34)	1.0000	C(12)-Co(1)-C(9)	68.79(18)
C(13)-C(17)	1.412(7)	C(16)-Co(1)-C(9)	161.99(19)
C(13)-C(14)	1.414(7)	C(14)-Co(1)-C(9)	108.36(18)
C(13)-H(13)	1.0000	C(10)-Co(1)-C(15)	109.22(19)
C(14)-C(15)	1.417(7)	C(11)-Co(1)-C(15)	122.8(2)

C(17)-Co(1)-C(15)	68.6(2)	C(34)-Co(2)-C(29)	106.7(2)
C(13)-Co(1)-C(15)	68.3(2)	C(28)-Co(2)-C(29)	41.07(19)
C(12)-Co(1)-C(15)	157.4(2)	C(27)-Co(2)-C(29)	69.05(19)
C(16)-Co(1)-C(15)	40.6(2)	C(31)-Co(2)-C(29)	158.9(2)
C(14)-Co(1)-C(15)	40.6(2)	C(33)-Co(2)-C(29)	122.0(2)
C(9)-Co(1)-C(15)	125.54(19)	C(30)-Co(2)-C(29)	122.56(19)
C(10)-Co(1)-C(8)	67.97(18)	C(34)-Co(2)-C(26)	158.5(2)
C(11)-Co(1)-C(8)	68.37(19)	C(28)-Co(2)-C(26)	69.3(2)
C(17)-Co(1)-C(8)	120.53(19)	C(27)-Co(2)-C(26)	41.11(18)
C(13)-Co(1)-C(8)	106.95(19)	C(31)-Co(2)-C(26)	107.39(19)
C(12)-Co(1)-C(8)	40.74(17)	C(33)-Co(2)-C(26)	159.1(2)
C(16)-Co(1)-C(8)	156.43(19)	C(30)-Co(2)-C(26)	122.56(19)
C(14)-Co(1)-C(8)	124.04(19)	C(29)-Co(2)-C(26)	68.98(18)
C(9)-Co(1)-C(8)	40.11(17)	C(34)-Co(2)-C(32)	68.3(2)
C(15)-Co(1)-C(8)	161.2(2)	C(28)-Co(2)-C(32)	122.7(2)
C(6)-C(1)-C(2)	120.2(4)	C(27)-Co(2)-C(32)	107.8(2)
C(6)-C(1)-N(1)	119.2(4)	C(31)-Co(2)-C(32)	40.5(2)
C(2)-C(1)-N(1)	120.6(4)	C(33)-Co(2)-C(32)	40.7(2)
C(7)-N(1)-C(1)	126.7(4)	C(30)-Co(2)-C(32)	68.0(2)
C(7)-N(1)-H(1)	112(4)	C(29)-Co(2)-C(32)	158.7(2)
C(1)-N(1)-H(1)	122(4)	C(26)-Co(2)-C(32)	123.3(2)
C(34)-Co(2)-C(28)	122.1(2)	C(34)-Co(2)-C(25)	122.66(19)
C(34)-Co(2)-C(27)	158.9(2)	C(28)-Co(2)-C(25)	68.50(19)
C(28)-Co(2)-C(27)	41.1(2)	C(27)-Co(2)-C(25)	68.39(18)
C(34)-Co(2)-C(31)	68.6(2)	C(31)-Co(2)-C(25)	123.33(18)
C(28)-Co(2)-C(31)	158.9(2)	C(33)-Co(2)-C(25)	158.6(2)
C(27)-Co(2)-C(31)	122.8(2)	C(30)-Co(2)-C(25)	107.91(18)
C(34)-Co(2)-C(33)	41.0(2)	C(29)-Co(2)-C(25)	40.58(17)
C(28)-Co(2)-C(33)	106.5(2)	C(26)-Co(2)-C(25)	40.57(16)
C(27)-Co(2)-C(33)	122.4(2)	C(32)-Co(2)-C(25)	159.52(19)
C(31)-Co(2)-C(33)	68.8(2)	C(3)-C(2)-C(1)	119.9(4)
C(34)-Co(2)-C(30)	40.8(2)	C(3)-C(2)-H(2)	120.0
C(28)-Co(2)-C(30)	158.7(2)	C(1)-C(2)-H(2)	120.0
C(27)-Co(2)-C(30)	158.9(2)	C(7)-N(2)-C(8)	129.4(4)
C(31)-Co(2)-C(30)	40.6(2)	C(7)-N(2)-H(2AA)	119(4)
C(33)-Co(2)-C(30)	68.8(2)	C(8)-N(2)-H(2AA)	112(4)

F(6A)-P(1A)-F(5A)	87.2(6)	F(7)-P(2)-F(9)	90.4(2)
F(6A)-P(1A)-F(4A)	89.5(6)	F(8)-P(2)-F(9)	90.2(2)
F(5A)-P(1A)-F(4A)	91.0(5)	F(10)-P(2)-F(9)	89.7(2)
F(6A)-P(1A)-F(2A)	91.5(6)	F(12)-P(2)-F(9)	177.7(2)
F(5A)-P(1A)-F(2A)	178.6(8)	F(7)-P(2)-F(11)	89.7(2)
F(4A)-P(1A)-F(2A)	88.3(5)	F(8)-P(2)-F(11)	178.2(2)
F(6A)-P(1A)-F(3A)	95.1(6)	F(10)-P(2)-F(11)	90.3(3)
F(5A)-P(1A)-F(3A)	85.6(5)	F(12)-P(2)-F(11)	89.9(2)
F(4A)-P(1A)-F(3A)	174.1(7)	F(9)-P(2)-F(11)	88.0(2)
F(2A)-P(1A)-F(3A)	95.2(6)	N(1)-C(7)-N(2)	111.3(4)
F(6A)-P(1A)-F(1A)	173.0(8)	N(1)-C(7)-S(1)	124.0(3)
F(5A)-P(1A)-F(1A)	88.2(6)	N(2)-C(7)-S(1)	124.7(3)
F(4A)-P(1A)-F(1A)	85.3(5)	C(1)-C(6)-C(5)	119.5(4)
F(2A)-P(1A)-F(1A)	92.9(6)	C(1)-C(6)-H(6)	120.2
F(3A)-P(1A)-F(1A)	89.8(6)	C(5)-C(6)-H(6)	120.2
F(3B)-P(1B)-F(5B)	92.0(11)	C(4)-C(5)-C(6)	120.3(4)
F(3B)-P(1B)-F(6B)	93.5(10)	C(4)-C(5)-H(5)	119.8
F(5B)-P(1B)-F(6B)	91.4(11)	C(6)-C(5)-H(5)	119.8
F(3B)-P(1B)-F(1B)	86.9(10)	C(25)-N(4)-C(24)	128.2(3)
F(5B)-P(1B)-F(1B)	87.7(11)	C(25)-N(4)-H(4A)	120(4)
F(6B)-P(1B)-F(1B)	179.1(14)	C(24)-N(4)-H(4A)	110(4)
F(3B)-P(1B)-F(2B)	90.5(10)	C(5)-C(4)-C(3)	120.2(4)
F(5B)-P(1B)-F(2B)	174.2(14)	C(5)-C(4)-H(4)	119.9
F(6B)-P(1B)-F(2B)	93.6(11)	C(3)-C(4)-H(4)	119.9
F(1B)-P(1B)-F(2B)	87.2(11)	N(2)-C(8)-C(9)	131.4(4)
F(3B)-P(1B)-F(4B)	179.1(13)	N(2)-C(8)-C(12)	120.8(4)
F(5B)-P(1B)-F(4B)	88.9(10)	C(9)-C(8)-C(12)	107.7(4)
F(6B)-P(1B)-F(4B)	86.3(10)	N(2)-C(8)-Co(1)	126.4(3)
F(1B)-P(1B)-F(4B)	93.3(11)	C(9)-C(8)-Co(1)	68.4(2)
F(2B)-P(1B)-F(4B)	88.6(10)	C(12)-C(8)-Co(1)	67.5(2)
F(7)-P(2)-F(8)	90.2(3)	C(8)-C(9)-C(10)	107.9(4)
F(7)-P(2)-F(10)	180.0(3)	C(8)-C(9)-Co(1)	71.4(2)
F(8)-P(2)-F(10)	89.8(3)	C(10)-C(9)-Co(1)	68.6(2)
F(7)-P(2)-F(12)	88.7(2)	C(8)-C(9)-H(9)	126.0
F(8)-P(2)-F(12)	91.9(2)	C(10)-C(9)-H(9)	126.0
F(10)-P(2)-F(12)	91.3(2)	Co(1)-C(9)-H(9)	126.0

C(9)-C(10)-C(11)	108.2(4)	C(22)-C(23)-C(18)	118.6(4)
C(9)-C(10)-Co(1)	70.5(2)	C(22)-C(23)-H(23)	120.7
C(11)-C(10)-Co(1)	69.0(3)	C(18)-C(23)-H(23)	120.7
C(9)-C(10)-H(10)	125.9	N(3)-C(24)-N(4)	110.9(3)
C(11)-C(10)-H(10)	125.9	N(3)-C(24)-S(2)	127.1(3)
Co(1)-C(10)-H(10)	125.9	N(4)-C(24)-S(2)	121.9(3)
C(12)-C(11)-C(10)	107.7(4)	N(4)-C(25)-C(26)	130.4(4)
C(12)-C(11)-Co(1)	70.1(3)	N(4)-C(25)-C(29)	121.4(4)
C(10)-C(11)-Co(1)	69.4(3)	C(26)-C(25)-C(29)	108.1(4)
C(12)-C(11)-H(11)	126.2	N(4)-C(25)-Co(2)	131.1(3)
C(10)-C(11)-H(11)	126.2	C(26)-C(25)-Co(2)	68.5(2)
Co(1)-C(11)-H(11)	126.2	C(29)-C(25)-Co(2)	68.4(2)
C(11)-C(12)-C(8)	108.4(4)	C(27)-C(26)-C(25)	107.5(4)
C(11)-C(12)-Co(1)	69.1(3)	C(27)-C(26)-Co(2)	68.6(3)
C(8)-C(12)-Co(1)	71.8(2)	C(25)-C(26)-Co(2)	70.9(2)
C(11)-C(12)-H(12)	125.8	C(27)-C(26)-H(26)	126.3
C(8)-C(12)-H(12)	125.8	C(25)-C(26)-H(26)	126.3
Co(1)-C(12)-H(12)	125.8	Co(2)-C(26)-H(26)	126.3
C(24)-N(3)-C(18)	131.4(4)	C(28)-C(27)-C(26)	108.4(4)
C(24)-N(3)-H(3A)	109(3)	C(28)-C(27)-Co(2)	69.4(3)
C(18)-N(3)-H(3A)	120(3)	C(26)-C(27)-Co(2)	70.3(2)
C(2)-C(3)-C(4)	119.8(4)	C(28)-C(27)-H(27)	125.8
C(2)-C(3)-H(3)	120.1	C(26)-C(27)-H(27)	125.8
C(4)-C(3)-H(3)	120.1	Co(2)-C(27)-H(27)	125.8
C(20)-C(19)-C(18)	121.4(5)	C(27)-C(28)-C(29)	108.0(4)
C(20)-C(19)-H(19)	119.3	C(27)-C(28)-Co(2)	69.5(3)
C(18)-C(19)-H(19)	119.3	C(29)-C(28)-Co(2)	70.2(2)
C(19)-C(20)-C(21)	119.8(5)	C(27)-C(28)-H(28)	126.0
C(19)-C(20)-H(20)	120.1	C(29)-C(28)-H(28)	126.0
C(21)-C(20)-H(20)	120.1	Co(2)-C(28)-H(28)	126.0
C(22)-C(21)-C(20)	118.7(5)	C(28)-C(29)-C(25)	107.9(4)
C(22)-C(21)-H(21)	120.7	C(28)-C(29)-Co(2)	68.8(3)
C(20)-C(21)-H(21)	120.7	C(25)-C(29)-Co(2)	71.0(2)
C(21)-C(22)-C(23)	122.4(5)	C(28)-C(29)-H(29)	126.0
C(21)-C(22)-H(22)	118.8	C(25)-C(29)-H(29)	126.0
C(23)-C(22)-H(22)	118.8	Co(2)-C(29)-H(29)	126.0

C(34)-C(30)-C(31)	107.9(4)	C(14)-C(13)-Co(1)	70.1(3)
C(34)-C(30)-Co(2)	69.0(3)	C(17)-C(13)-H(13)	125.7
C(31)-C(30)-Co(2)	69.4(3)	C(14)-C(13)-H(13)	125.7
C(34)-C(30)-H(30)	126.0	Co(1)-C(13)-H(13)	125.7
C(31)-C(30)-H(30)	126.0	C(13)-C(14)-C(15)	107.7(4)
Co(2)-C(30)-H(30)	126.0	C(13)-C(14)-Co(1)	69.2(2)
C(32)-C(31)-C(30)	107.9(5)	C(15)-C(14)-Co(1)	70.0(3)
C(32)-C(31)-Co(2)	70.1(3)	C(13)-C(14)-H(14)	126.1
C(30)-C(31)-Co(2)	70.0(3)	C(15)-C(14)-H(14)	126.1
C(32)-C(31)-H(31)	126.0	Co(1)-C(14)-H(14)	126.1
C(30)-C(31)-H(31)	126.0	C(16)-C(15)-C(14)	107.9(4)
Co(2)-C(31)-H(31)	126.0	C(16)-C(15)-Co(1)	69.3(3)
C(31)-C(32)-C(33)	108.7(5)	C(14)-C(15)-Co(1)	69.4(3)
C(31)-C(32)-Co(2)	69.3(3)	C(16)-C(15)-H(15)	126.0
C(33)-C(32)-Co(2)	69.4(3)	C(14)-C(15)-H(15)	126.0
C(31)-C(32)-H(32)	125.6	Co(1)-C(15)-H(15)	126.0
C(33)-C(32)-H(32)	125.6	C(17)-C(16)-C(15)	108.1(5)
Co(2)-C(32)-H(32)	125.6	C(17)-C(16)-Co(1)	69.1(3)
C(32)-C(33)-C(34)	107.0(5)	C(15)-C(16)-Co(1)	70.1(3)
C(32)-C(33)-Co(2)	69.9(3)	C(17)-C(16)-H(16)	126.0
C(34)-C(33)-Co(2)	69.1(3)	C(15)-C(16)-H(16)	126.0
C(32)-C(33)-H(33)	126.5	Co(1)-C(16)-H(16)	126.0
C(34)-C(33)-H(33)	126.5	C(19)-C(18)-C(23)	119.1(4)
Co(2)-C(33)-H(33)	126.5	C(19)-C(18)-N(3)	115.5(4)
C(30)-C(34)-C(33)	108.4(5)	C(23)-C(18)-N(3)	125.3(4)
C(30)-C(34)-Co(2)	70.2(3)	C(13)-C(17)-C(16)	107.7(5)
C(33)-C(34)-Co(2)	69.9(3)	C(13)-C(17)-Co(1)	69.7(3)
C(30)-C(34)-H(34)	125.8	C(16)-C(17)-Co(1)	70.0(3)
C(33)-C(34)-H(34)	125.8	C(13)-C(17)-H(17)	126.1
Co(2)-C(34)-H(34)	125.8	C(16)-C(17)-H(17)	126.1
C(17)-C(13)-C(14)	108.5(4)	Co(1)-C(17)-H(17)	126.1
C(17)-C(13)-Co(1)	69.5(3)		

Symmetry transformations used to generate equivalent atoms.

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for *N*-cobaltocenium-*N'*-phenyl-

thiourea PF_6^-. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co1	18(1)	20(1)	23(1)	-1(1)	1(1)	-3(1)
C1	21(2)	17(2)	28(2)	0(2)	2(2)	1(2)
N1	23(2)	20(2)	43(2)	10(2)	0(2)	2(1)
S1	28(1)	20(1)	26(1)	4(1)	2(1)	2(1)
Co2	21(1)	16(1)	26(1)	2(1)	1(1)	-2(1)
C2	23(2)	29(2)	25(2)	-2(2)	0(2)	-2(2)
N2	21(2)	18(2)	41(2)	1(2)	6(2)	2(2)
S2	29(1)	27(1)	19(1)	-1(1)	-3(1)	-6(1)
P1A	34(2)	18(2)	29(1)	1(1)	-3(1)	2(1)
F1A	139(5)	56(3)	34(2)	0(2)	10(3)	41(3)
F2A	100(4)	52(3)	92(3)	38(2)	-40(3)	-48(3)
F3A	45(2)	70(3)	66(2)	33(2)	-12(2)	12(2)
F4A	45(2)	70(3)	66(2)	33(2)	-12(2)	12(2)
F5A	100(4)	52(3)	92(3)	38(2)	-40(3)	-48(3)
F6A	139(5)	56(3)	34(2)	0(2)	10(3)	41(3)
P1B	34(2)	18(2)	29(1)	1(1)	-3(1)	2(1)
F1B	78(5)	102(6)	34(3)	-9(4)	-14(4)	-38(5)
F2B	114(7)	57(5)	70(5)	16(4)	33(5)	39(5)
F3B	39(4)	99(6)	53(4)	22(4)	12(3)	1(4)
F4B	39(4)	99(6)	53(4)	22(4)	12(3)	1(4)
F5B	114(7)	57(5)	70(5)	16(4)	33(5)	39(5)
F6B	78(5)	102(6)	34(3)	-9(4)	-14(4)	-38(5)
P2	30(1)	24(1)	31(1)	4(1)	-5(1)	-2(1)
F7	42(2)	77(3)	75(3)	-22(2)	0(2)	15(2)
C7	24(2)	20(2)	21(2)	4(2)	5(2)	-1(2)
C6	29(2)	31(2)	24(2)	2(2)	0(2)	3(2)
C5	24(2)	35(2)	33(2)	-8(2)	-5(2)	-1(2)
N4	26(2)	23(2)	18(1)	-2(1)	-4(1)	-1(1)
C4	24(2)	24(2)	36(2)	-6(2)	2(2)	-1(2)
F8	153(4)	45(2)	48(2)	22(2)	-26(3)	-16(3)
C8	24(2)	26(2)	24(2)	-1(2)	4(2)	-3(2)

F9	69(2)	61(2)	54(2)	4(2)	-25(2)	-27(2)
C9	25(2)	28(2)	27(2)	3(2)	3(2)	1(2)
F10	74(3)	99(3)	77(3)	-43(3)	-4(2)	33(3)
C10	23(2)	41(3)	27(2)	1(2)	-5(2)	2(2)
F11	119(4)	51(2)	46(2)	16(2)	-12(2)	-29(2)
C11	29(2)	37(3)	34(2)	-13(2)	-4(2)	-5(2)
F12	34(2)	72(2)	71(2)	-19(2)	-15(2)	-5(2)
C12	27(2)	27(2)	28(2)	-12(2)	3(2)	-3(2)
N3	26(2)	30(2)	22(2)	-3(2)	-4(2)	-6(1)
C3	28(2)	33(2)	30(2)	9(2)	6(2)	-4(2)
C19	27(2)	25(2)	37(2)	-6(2)	-5(2)	1(2)
C20	24(2)	25(2)	55(3)	-5(2)	-3(2)	-2(2)
C21	22(2)	34(3)	55(3)	0(2)	7(2)	-1(2)
C22	35(3)	51(3)	41(3)	1(2)	13(2)	-12(2)
C23	29(2)	46(3)	31(2)	-9(2)	4(2)	-12(2)
C24	19(2)	19(2)	21(2)	-1(1)	-2(1)	4(1)
C25	21(2)	22(2)	22(2)	5(2)	-3(1)	3(2)
C26	25(2)	16(2)	34(2)	1(2)	-6(2)	4(2)
C27	37(2)	12(2)	48(3)	8(2)	-4(2)	-3(2)
C28	38(3)	31(2)	38(2)	16(2)	0(2)	-11(2)
C29	39(2)	30(2)	22(2)	7(2)	0(2)	-4(2)
C30	27(2)	18(2)	55(3)	13(2)	-10(2)	0(2)
C31	33(2)	38(3)	35(2)	11(2)	-6(2)	3(2)
C32	29(2)	30(2)	52(3)	-4(2)	-15(2)	0(2)
C33	20(2)	38(3)	61(3)	3(3)	5(2)	2(2)
C34	31(3)	30(2)	55(3)	-11(2)	-4(2)	10(2)
C13	33(2)	45(3)	25(2)	-1(2)	-6(2)	-5(2)
C14	52(3)	29(2)	23(2)	-5(2)	6(2)	0(2)
C15	31(2)	53(3)	27(2)	9(2)	9(2)	10(2)
C16	35(3)	34(3)	35(2)	11(2)	7(2)	-7(2)
C18	15(2)	24(2)	33(2)	-4(2)	1(2)	1(2)
C17	36(2)	33(2)	30(2)	9(2)	4(2)	7(2)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for *N*-cobaltocenium-*N*'-phenylthiourea PF_6^-.

	x	y	z	U(eq)
H1	4450(60)	5440(50)	4460(20)	44(16)
H2AA	2830(50)	4710(50)	4170(20)	37(14)
H2	4989	7110	3584	31
H6	6082	6597	4973	34
H5	7920	7673	4873	37
H4A	6750(60)	1210(40)	3370(20)	39(15)
H4	8296	8449	4135	34
H9	-103	6480	4177	32
H10	-2253	5402	4066	36
H11	-1529	3527	4017	40
H12	1056	3455	4098	33
H3A	8410(50)	1740(30)	3189(16)	14(11)
H3	6818	8188	3491	36
H19	9930	3035	3236	36
H20	11440	4158	2899	42
H21	11592	4310	2053	44
H22	10198	3349	1569	51
H23	8726	2181	1897	42
H26	5693	-704	2419	30
H27	3687	-1744	2757	39
H28	2977	-977	3580	43
H29	4538	542	3757	36
H30	4067	2179	2479	40
H31	3539	763	1869	42
H32	1558	-270	2207	44
H33	868	477	3036	48
H34	2438	1995	3205	47
H13	1635	5109	5355	41
H14	-479	6238	5365	42
H15	-2567	5093	5258	45
H16	-1730	3261	5180	42
H17	872	3272	5240	40

Table S6. Torsion angles [°] for *N*-cobaltocenium-*N'*-phenylthiourea PF_6^-.

C6-C1-N1-C7	133.6(5)
C2-C1-N1-C7	-49.5(6)
C6-C1-C2-C3	0.7(7)
N1-C1-C2-C3	-176.1(4)
C1-N1-C7-N2	162.8(4)
C1-N1-C7-S1	-18.0(6)
C8-N2-C7-N1	169.1(4)
C8-N2-C7-S1	-10.1(6)
C2-C1-C6-C5	-0.9(7)
N1-C1-C6-C5	175.9(4)
C1-C6-C5-C4	0.2(7)
C6-C5-C4-C3	0.7(7)
C7-N2-C8-C9	-6.0(8)
C7-N2-C8-C12	178.2(4)
C7-N2-C8-Co1	-98.3(5)
N2-C8-C9-C10	-179.2(5)
C12-C8-C9-C10	-3.0(5)
Co1-C8-C9-C10	-59.1(3)
N2-C8-C9-Co1	-120.1(5)
C12-C8-C9-Co1	56.1(3)
C8-C9-C10-C11	1.9(5)
Co1-C9-C10-C11	-59.0(3)
C8-C9-C10-Co1	60.9(3)
C9-C10-C11-C12	-0.1(6)
Co1-C10-C11-C12	-60.0(3)
C9-C10-C11-Co1	59.9(3)
C10-C11-C12-C8	-1.8(6)
Co1-C11-C12-C8	-61.3(3)
C10-C11-C12-Co1	59.5(3)
N2-C8-C12-C11	179.7(4)
C9-C8-C12-C11	3.0(5)
Co1-C8-C12-C11	59.6(3)
N2-C8-C12-Co1	120.0(4)
C9-C8-C12-Co1	-56.7(3)

C1-C2-C3-C4	0.2(7)
C5-C4-C3-C2	-0.9(7)
C18-C19-C20-C21	0.3(7)
C19-C20-C21-C22	0.4(7)
C20-C21-C22-C23	-1.5(8)
C21-C22-C23-C18	1.8(8)
C18-N3-C24-N4	-171.3(4)
C18-N3-C24-S2	9.3(7)
C25-N4-C24-N3	-173.8(4)
C25-N4-C24-S2	5.6(6)
C24-N4-C25-C26	27.3(7)
C24-N4-C25-C29	-156.4(4)
C24-N4-C25-Co2	-68.7(6)
N4-C25-C26-C27	174.5(4)
C29-C25-C26-C27	-2.2(5)
Co2-C25-C26-C27	-59.1(3)
N4-C25-C26-Co2	-126.3(4)
C29-C25-C26-Co2	56.9(3)
C25-C26-C27-C28	1.5(5)
Co2-C26-C27-C28	-59.1(3)
C25-C26-C27-Co2	60.6(3)
C26-C27-C28-C29	-0.2(5)
Co2-C27-C28-C29	-59.8(3)
C26-C27-C28-Co2	59.6(3)
C27-C28-C29-C25	-1.2(5)
Co2-C28-C29-C25	-60.5(3)
C27-C28-C29-Co2	59.4(3)
N4-C25-C29-C28	-175.0(4)
C26-C25-C29-C28	2.1(5)
Co2-C25-C29-C28	59.1(3)
N4-C25-C29-Co2	125.9(4)
C26-C25-C29-Co2	-57.0(3)
C34-C30-C31-C32	1.8(5)
Co2-C30-C31-C32	60.2(3)
C34-C30-C31-Co2	-58.4(3)
C30-C31-C32-C33	-1.8(6)

Co2-C31-C32-C33	58.3(4)
C30-C31-C32-Co2	-60.1(3)
C31-C32-C33-C34	1.1(6)
Co2-C32-C33-C34	59.4(4)
C31-C32-C33-Co2	-58.3(3)
C31-C30-C34-C33	-1.1(5)
Co2-C30-C34-C33	-59.7(4)
C31-C30-C34-Co2	58.6(3)
C32-C33-C34-C30	0.0(6)
Co2-C33-C34-C30	59.9(3)
C32-C33-C34-Co2	-59.9(3)
C17-C13-C14-C15	0.5(5)
Co1-C13-C14-C15	59.6(3)
C17-C13-C14-Co1	-59.1(3)
C13-C14-C15-C16	-0.4(5)
Co1-C14-C15-C16	58.8(3)
C13-C14-C15-Co1	-59.1(3)
C14-C15-C16-C17	0.0(5)
Co1-C15-C16-C17	58.9(3)
C14-C15-C16-Co1	-58.8(3)
C20-C19-C18-C23	0.0(7)
C20-C19-C18-N3	-179.7(4)
C22-C23-C18-C19	-1.0(7)
C22-C23-C18-N3	178.6(5)
C24-N3-C18-C19	170.3(4)
C24-N3-C18-C23	-9.4(7)
C14-C13-C17-C16	-0.5(5)
Co1-C13-C17-C16	-59.9(3)
C14-C13-C17-Co1	59.4(3)
C15-C16-C17-C13	0.3(5)
Co1-C16-C17-C13	59.8(3)
C15-C16-C17-Co1	-59.5(3)

Computed transition structure

B3LYP/6-31G(d,p) = -3194.566046, zero-point energy (unscaled) = 0.483081, imaginary frequency = 266i

1	6	0	4.795616	-0.565510	-1.742611
2	6	0	3.835369	0.444864	-1.433278
3	6	0	2.590039	-0.200941	-1.121306
4	6	0	2.844464	-1.620210	-1.126830
5	6	0	4.184526	-1.840564	-1.555831
6	1	0	5.819464	-0.384599	-2.039907
7	1	0	3.992092	1.511267	-1.433889
8	1	0	2.103669	-2.371176	-0.886484
9	1	0	4.657794	-2.803837	-1.686388
10	6	0	4.502273	-1.950905	1.817990
11	6	0	3.514354	-0.953665	2.095076
12	6	0	5.710813	-1.286246	1.455339
13	1	0	4.353653	-3.021139	1.860635
14	6	0	4.106820	0.323488	1.890724
15	1	0	2.484054	-1.139403	2.365750
16	6	0	5.463081	0.117181	1.486063
17	1	0	6.638088	-1.763578	1.169705
18	1	0	3.601181	1.278133	1.946877
19	1	0	6.168888	0.894081	1.226270
20	6	0	0.967167	1.616540	-0.570790
21	16	0	2.041153	2.858693	-0.219324
22	7	0	-0.380777	1.715891	-0.635977
23	1	0	-0.882533	0.891437	-0.993117
24	6	0	-1.211687	2.843159	-0.400787
25	6	0	-2.308640	3.010044	-1.257891
26	6	0	-1.024728	3.723107	0.671425
27	6	0	-3.208835	4.053329	-1.047388
28	1	0	-2.439905	2.327607	-2.092505
29	6	0	-1.928917	4.766140	0.869497
30	1	0	-0.181789	3.594152	1.336849
31	6	0	-3.021605	4.937546	0.017142
32	1	0	-4.047973	4.182669	-1.724327
33	1	0	-1.776093	5.448822	1.699774
34	1	0	-3.716190	5.756219	0.176699
35	7	0	1.356457	0.297971	-0.829599
36	1	0	0.626452	-0.435510	-0.732976
37	7	0	-1.480614	-1.727687	-1.068971
38	8	0	-0.364884	-1.857595	-0.459699
39	8	0	-1.808574	-0.609044	-1.573308
40	6	0	-2.292718	-2.809081	-1.184295
41	1	0	-1.914376	-3.705583	-0.717044
42	6	0	-3.536209	-2.703397	-1.868458
43	1	0	-3.587030	-1.841706	-2.529165
44	1	0	-3.878635	-3.618666	-2.345974
45	27	0	4.184924	-0.785215	0.168631
46	6	0	-5.042016	-2.295784	-0.839516
47	1	0	-5.738609	-2.127996	-1.656247
48	6	0	-4.738979	-1.221050	0.133818
49	6	0	-4.563159	-1.830125	1.389195
50	6	0	-4.568970	0.159153	0.025718
51	6	0	-4.222846	-1.133822	2.545445
52	6	0	-4.241987	0.881817	1.172968
53	1	0	-4.679162	0.663430	-0.927721
54	6	0	-4.067894	0.244393	2.412853
55	1	0	-4.094534	-1.631123	3.501341
56	1	0	-4.110447	1.956193	1.102801
57	1	0	-3.810947	0.836282	3.285050
58	7	0	-4.844082	-3.203416	1.223412
59	6	0	-5.219378	-3.464036	-0.024843
60	1	0	-5.501233	-4.462901	-0.330646
61	1	0	-4.802225	-3.890105	1.966192

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