

Dichloro-bis(1-alkyl/styryl-benzimidazole)-cobalt(II) pre-catalyst for ethylene dimerization

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(Z)-1-(2-Fluorostyryl)-benzimidazole (2d)

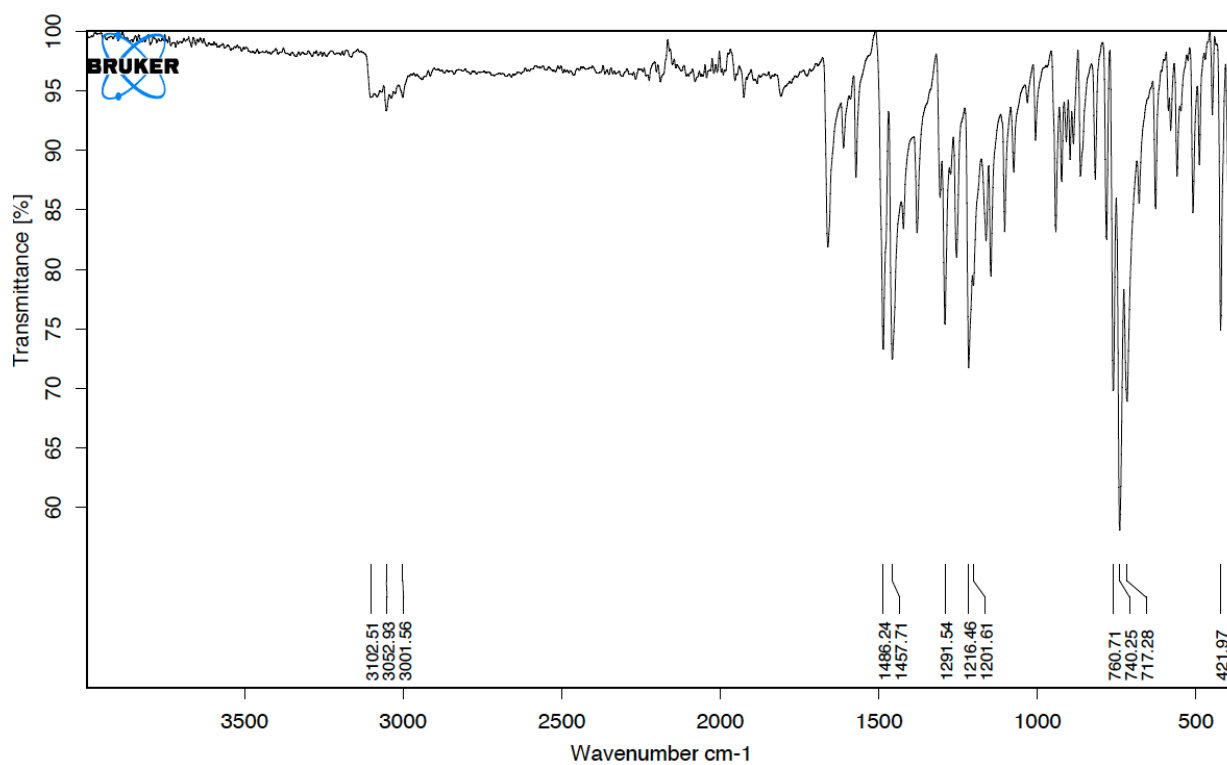
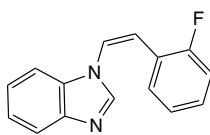


Figure S1. FT-IR spectrum

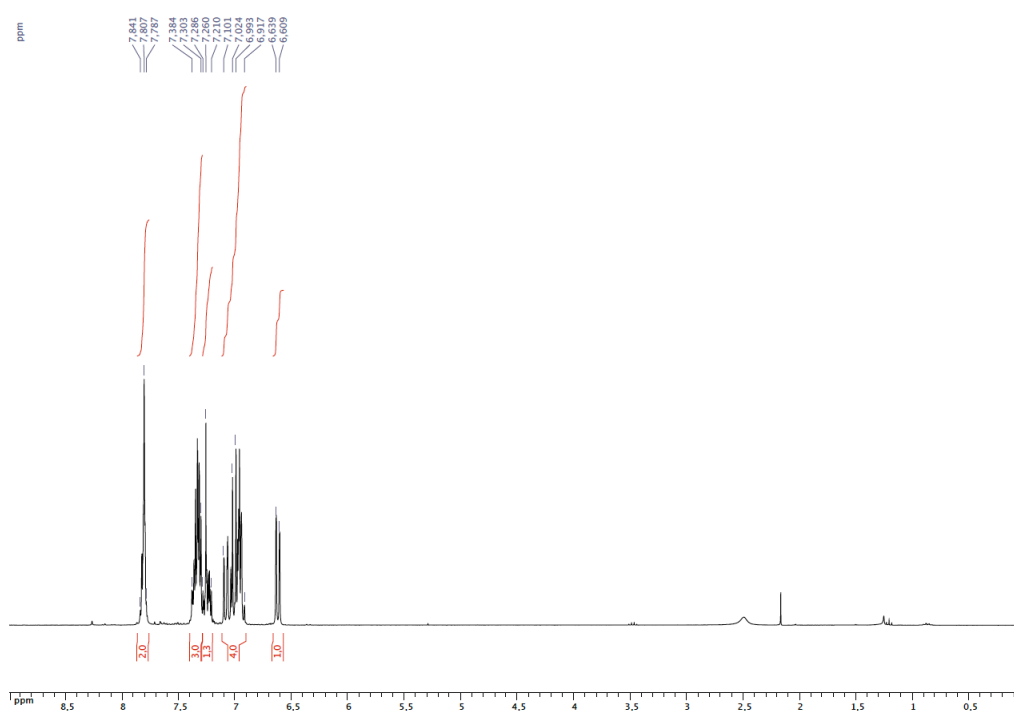


Figure S2. ^1H NMR spectrum (CDCl_3)

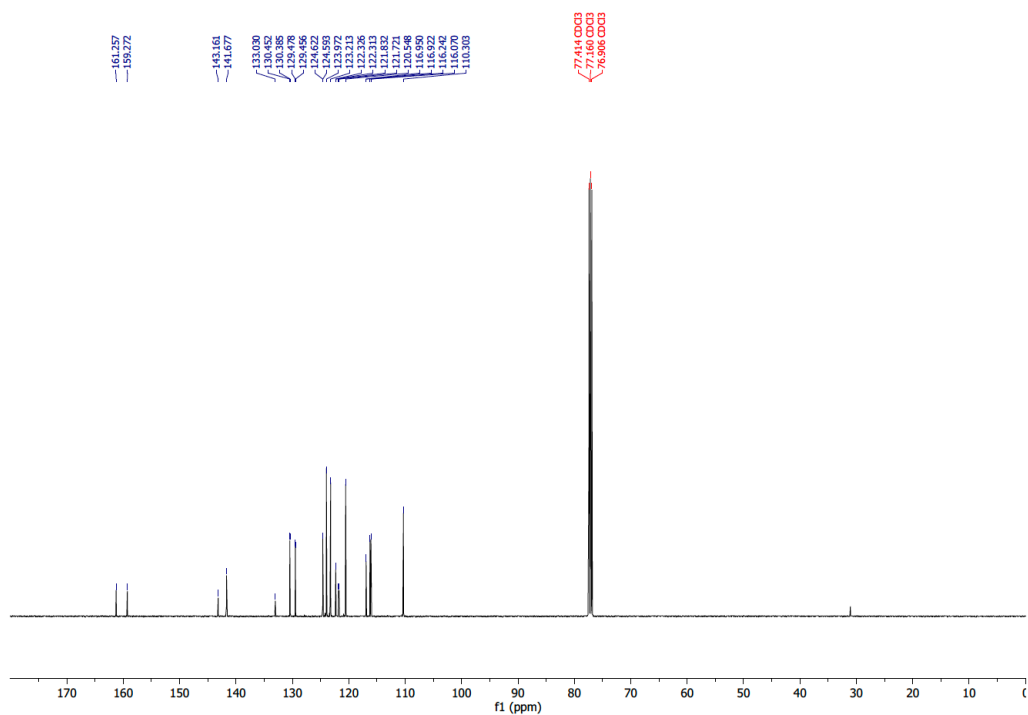


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3)

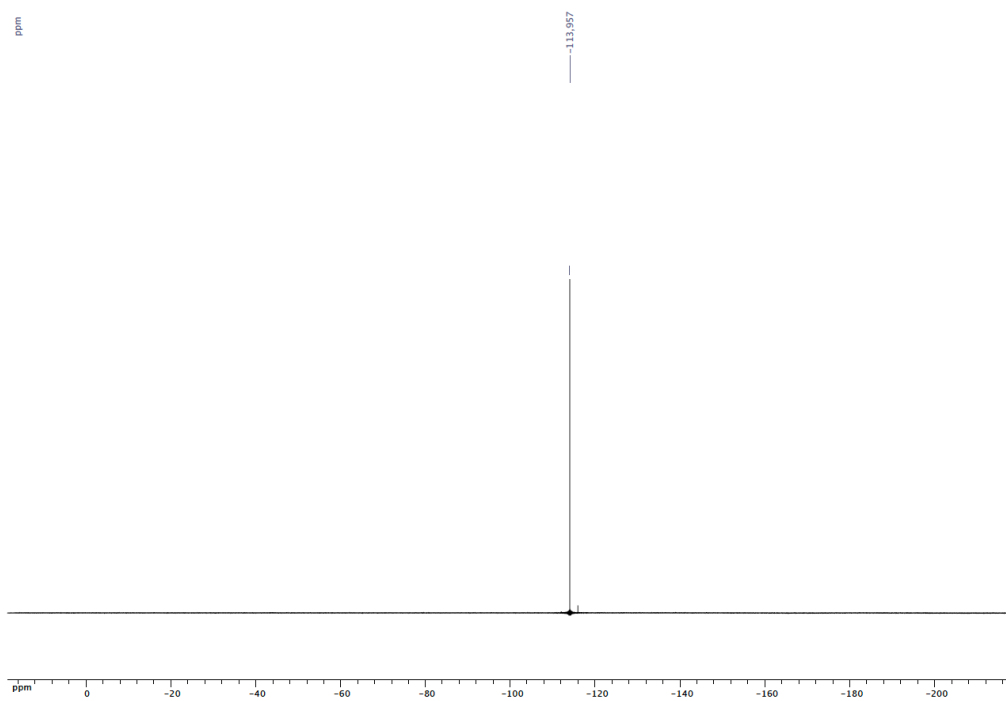


Figure S4. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (CDCl_3)

Dichloro-bis(1-benzyl-benzimidazole)-cobalt(II) (1a)

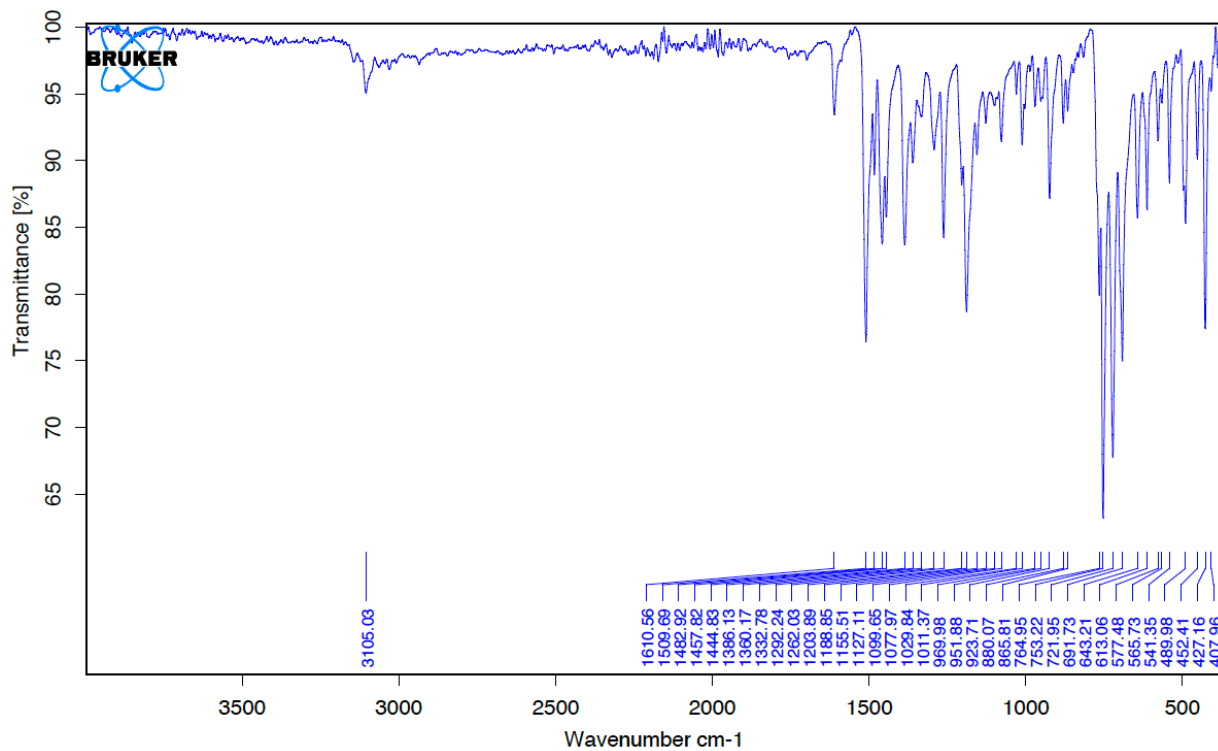
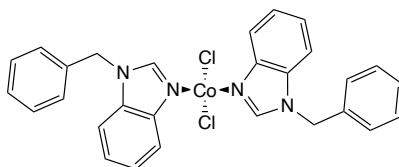


Figure S5. FT-IR spectrum

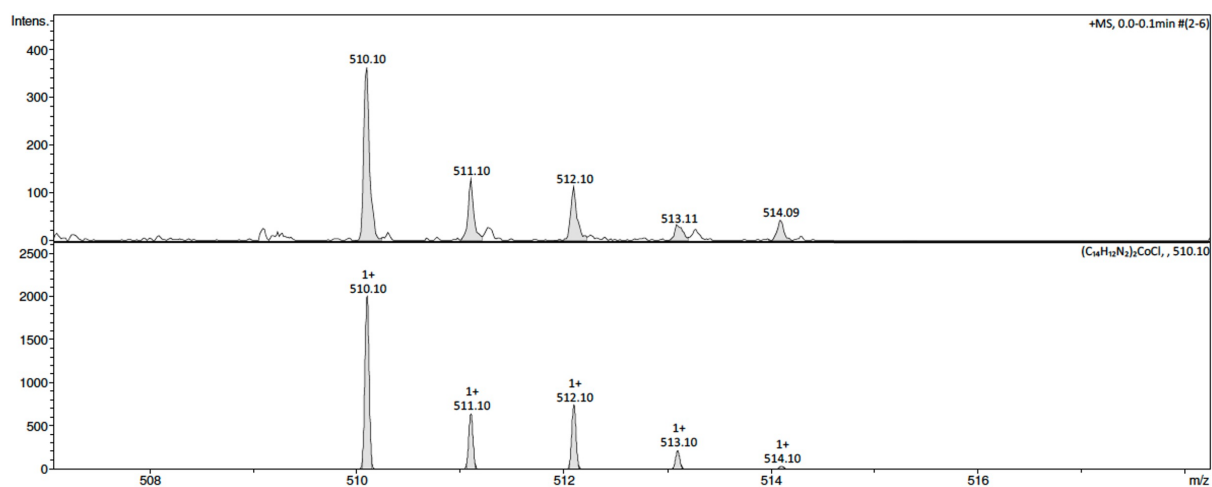


Figure S6. Mass spectrum (ESI-TOF)

exp. spectrum (top); calc. spectrum (bottom) for C₂₈H₂₄N₄ClCo ([M - Cl]⁺)

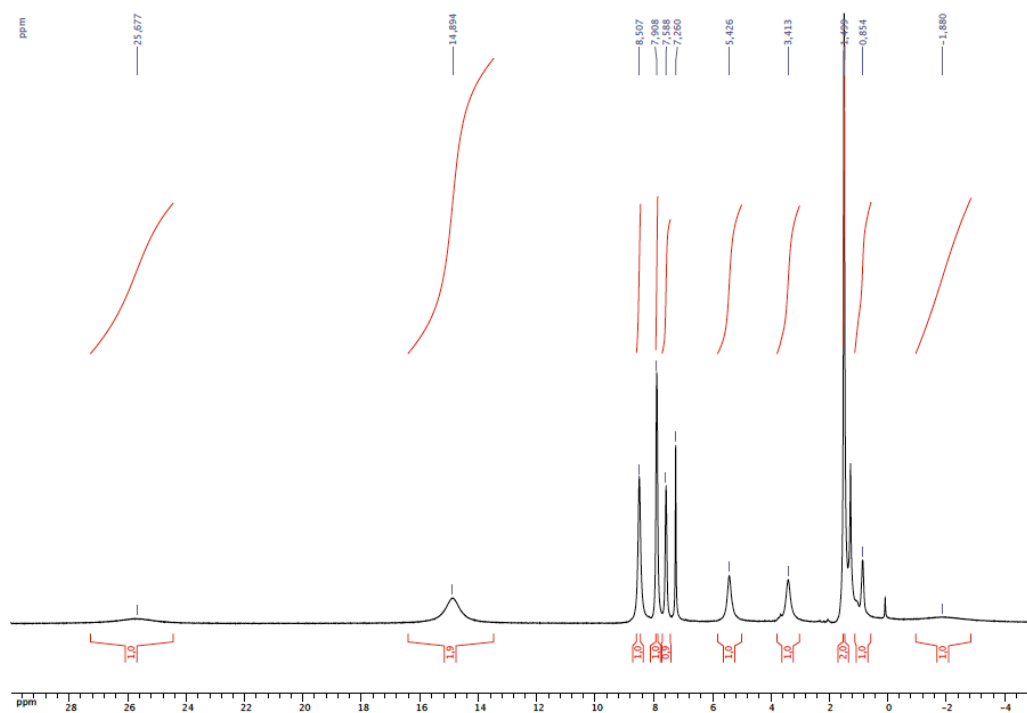


Figure S7. ^1H NMR spectrum (CDCl_3)

Dichloro-bis[1-(4-fluorobenzyl)-benzimidazole]-cobalt(II) (1b)

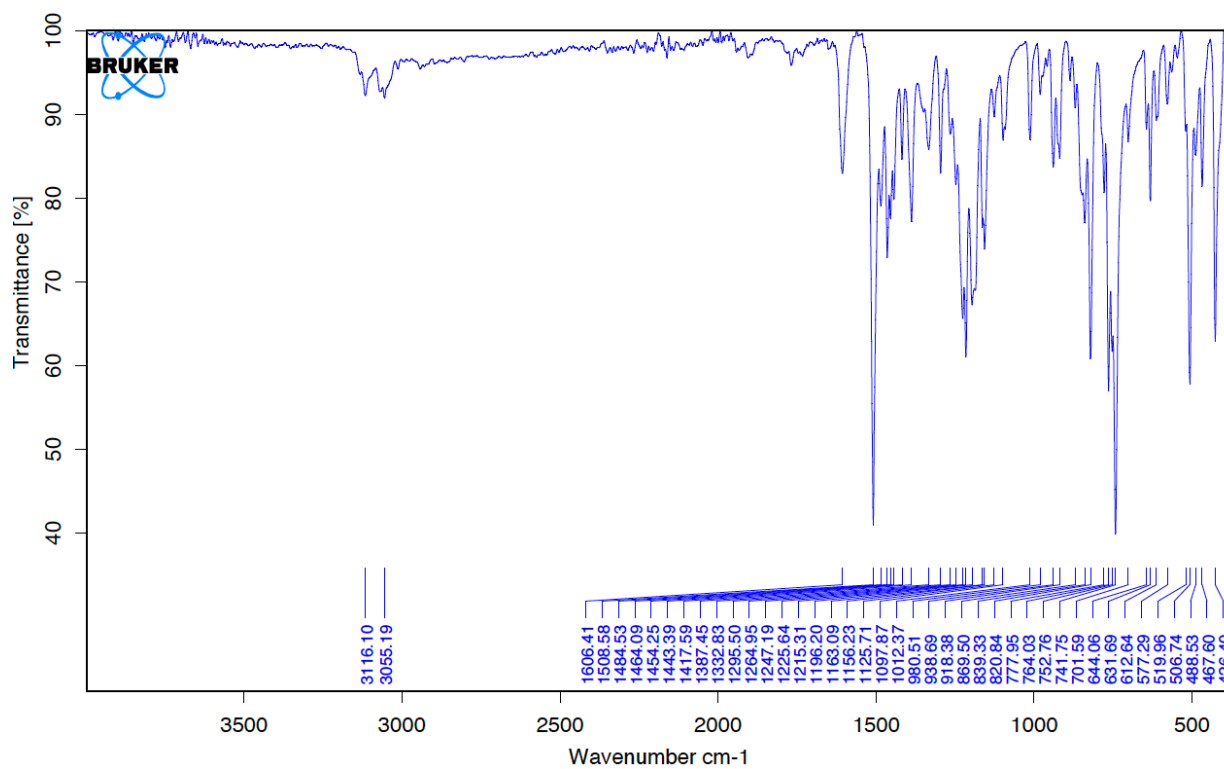
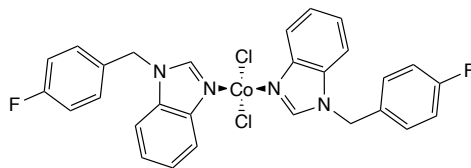


Figure S8. FT-IR spectrum

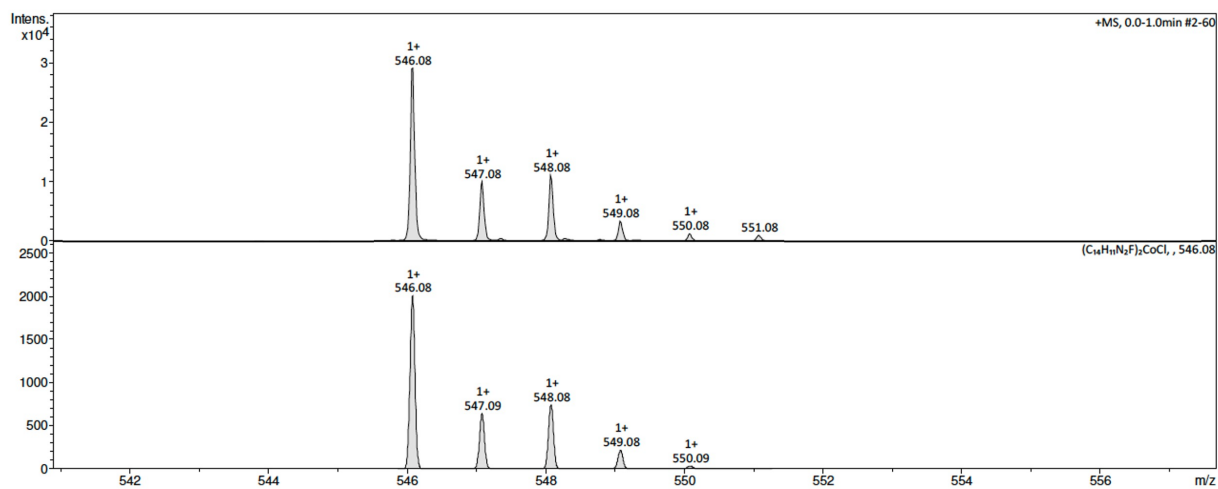


Figure S9. Mass spectrum (ESI-TOF)

exp. spectrum (top); calc. spectrum (bottom) for $C_{24}H_{22}N_4F_2ClCo$ ($[M - Cl]^+$)

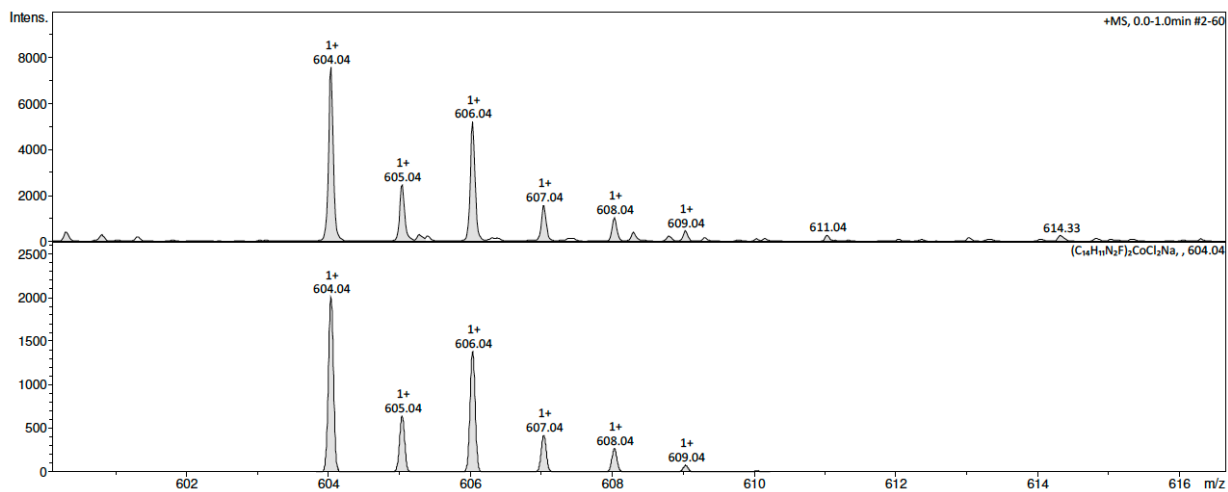


Figure S10. Mass spectrum (ESI-TOF)
exp. spectrum (top); calc. spectrum (bottom) for $C_{28}H_{22}N_4F_2Cl_2CoNa$ ($[M + Na]^+$)

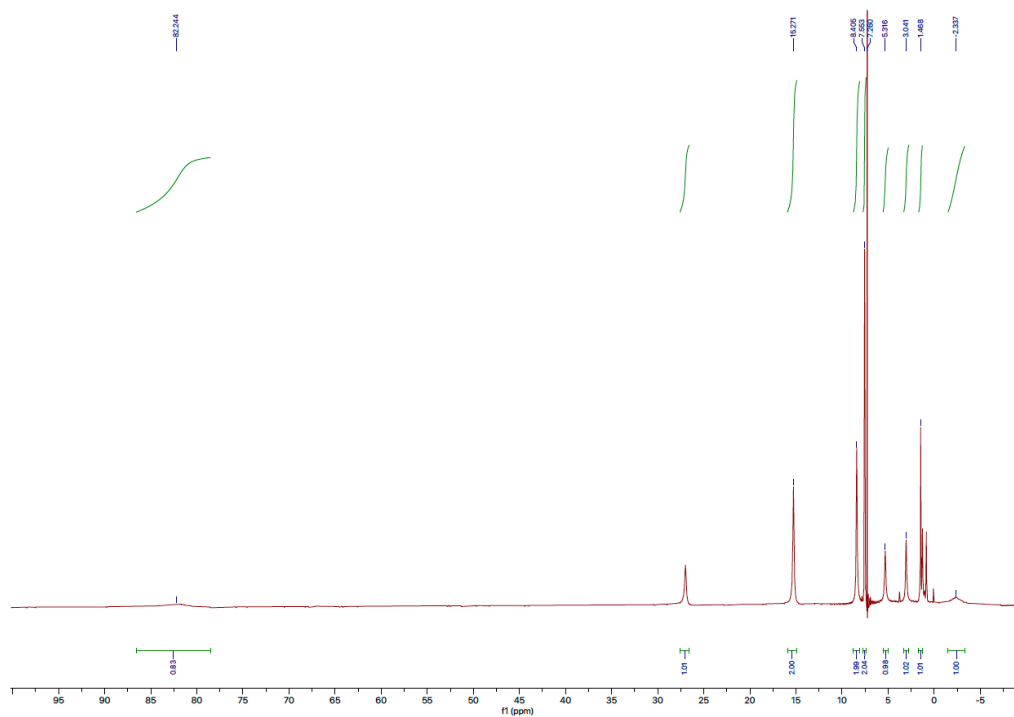


Figure S11. 1H NMR spectrum (CDCl₃)

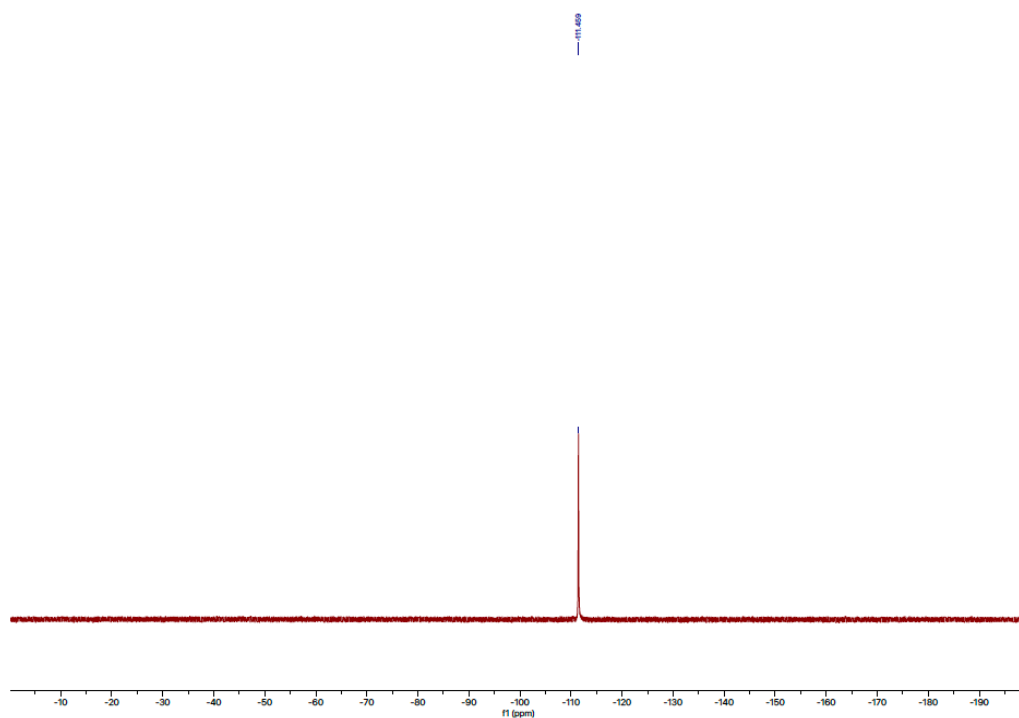


Figure S12. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (CDCl_3)

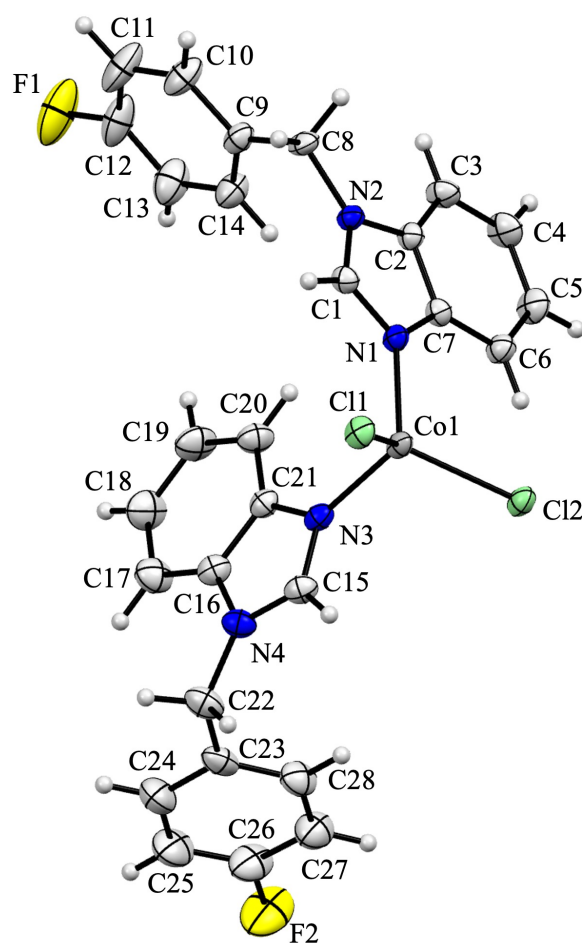


Figure S13. ORTEP drawing of the cobalt(II) complex **1b**
(50% probability thermal ellipsoids)

Table S1. Bond lengths (Å) for the cobalt complex **1b**

Co1-N1	2.0111(17)	Co1-N3	2.0151(19)
Co1-Cl2	2.2429(6)	Co1-Cl1	2.2461(6)
N1-C1	1.323(3)	N1-C7	1.399(3)
C1-N2	1.353(3)	C1-H1	0.9500
N2-C2	1.386(3)	N2-C8	1.466(2)
C2-C3	1.394(3)	C2-C7	1.401(3)
C3-C4	1.379(3)	C3-H3	0.9500
C4-C5	1.399(3)	C4-H4	0.9500
C5-C6	1.384(3)	C5-H5	0.9500
C6-C7	1.395(3)	C6-H6	0.9500
C8-C9	1.516(3)	C8-H8A	0.9900
C8-H8B	0.9900	C9-C14	1.389(3)
C9-C10	1.390(3)	C10-C11	1.387(4)
C10-H10	0.9500	C11-C12	1.370(4)
C11-H11	0.9500	C12-C13	1.366(4)
C12-F1	1.369(3)	C13-C14	1.392(3)
C13-H13	0.9500	C14-H14	0.9500
N3-C15	1.327(3)	N3-C21	1.398(3)
C15-N4	1.342(3)	C15-H15	0.9500
N4-C16	1.390(3)	N4-C22	1.471(3)
C16-C21	1.392(3)	C16-C17	1.393(3)
C17-C18	1.383(4)	C17-H17	0.9500
C18-C19	1.390(4)	C18-H18	0.9500
C19-C20	1.380(3)	C19-H19	0.9500
C20-C21	1.399(3)	C20-H20	0.9500
C22-C23	1.514(3)	C22-H22A	0.9900
C22-H22B	0.9900	C23-C28	1.383(4)
C23-C24	1.385(4)	C24-C25	1.392(4)
C24-H24	0.9500	C25-C26	1.358(5)
C25-H25	0.9500	C26-C27	1.365(4)
C26-F2	1.369(3)	C27-C28	1.384(4)
C27-H27	0.9500	C28-H28	0.9500

Table S2. Angles (°) for the cobalt complex **1b**

N1-Co1-N3	107.68(7)	N1-Co1-Cl2	111.72(5)
N3-Co1-Cl2	108.83(5)	N1-Co1-Cl1	110.37(5)
N3-Co1-Cl1	106.29(6)	Cl2-Co1-Cl1	111.70(2)
C1-N1-C7	105.84(17)	C1-N1-Co1	125.00(15)
C7-N1-Co1	128.93(13)	N1-C1-N2	112.39(19)
N1-C1-H1	123.8	N2-C1-H1	123.8
C1-N2-C2	107.40(16)	C1-N2-C8	125.66(19)
C2-N2-C8	126.89(18)	N2-C2-C3	131.97(19)
N2-C2-C7	105.78(18)	C3-C2-C7	122.2(2)
C4-C3-C2	116.5(2)	C4-C3-H3	121.8
C2-C3-H3	121.8	C3-C4-C5	121.7(2)
C3-C4-H4	119.1	C5-C4-H4	119.1
C6-C5-C4	122.0(2)	C6-C5-H5	119.0
C4-C5-H5	119.0	C5-C6-C7	116.8(2)
C5-C6-H6	121.6	C7-C6-H6	121.6

C6-C7-N1	130.66(19)	C6-C7-C2	120.7(2)
N1-C7-C2	108.57(18)	N2-C8-C9	113.82(17)
N2-C8-H8A	108.8	C9-C8-H8A	108.8
N2-C8-H8B	108.8	C9-C8-H8B	108.8
H8A-C8-H8B	107.7	C14-C9-C10	118.3(2)
C14-C9-C8	124.01(19)	C10-C9-C8	117.7(2)
C11-C10-C9	121.1(2)	C11-C10-H10	119.5
C9-C10-H10	119.5	C12-C11-C10	118.4(2)
C12-C11-H11	120.8	C10-C11-H11	120.8
C13-C12-F1	118.5(3)	C13-C12-C11	122.9(2)
F1-C12-C11	118.6(2)	C12-C13-C14	118.1(3)
C12-C13-H13	121.0	C14-C13-H13	121.0
C9-C14-C13	121.3(2)	C9-C14-H14	119.3
C13-C14-H14	119.3	C15-N3-C21	105.13(18)
C15-N3-Co1	122.58(15)	C21-N3-Co1	131.71(14)
N3-C15-N4	113.02(19)	N3-C15-H15	123.5
N4-C15-H15	123.5	C15-N4-C16	107.08(18)
C15-N4-C22	126.52(19)	C16-N4-C22	126.4(2)
N4-C16-C21	105.80(19)	N4-C16-C17	131.2(2)
C21-C16-C17	123.0(2)	C18-C17-C16	115.7(2)
C18-C17-H17	122.2	C16-C17-H17	122.2
C17-C18-C19	122.1(2)	C17-C18-H18	118.9
C19-C18-H18	118.9	C20-C19-C18	122.0(2)
C20-C19-H19	119.0	C18-C19-H19	119.0
C19-C20-C21	117.0(2)	C19-C20-H20	121.5
C21-C20-H20	121.5	C16-C21-N3	108.97(18)
C16-C21-C20	120.2(2)	N3-C21-C20	130.8(2)
N4-C22-C23	111.5(2)	N4-C22-H22A	109.3
C23-C22-H22A	109.3	N4-C22-H22B	109.3
C23-C22-H22B	109.3	H22A-C22-H22B	108.0
C28-C23-C24	119.0(3)	C28-C23-C22	119.7(2)
C24-C23-C22	121.3(3)	C23-C24-C25	120.8(3)
C23-C24-H24	119.6	C25-C24-H24	119.6
C26-C25-C24	117.7(3)	C26-C25-H25	121.2
C24-C25-H25	121.2	C25-C26-C27	123.7(3)
C25-C26-F2	118.6(3)	C27-C26-F2	117.7(3)
C26-C27-C28	118.0(3)	C26-C27-H27	121.0
C28-C27-H27	121.0	C23-C28-C27	120.8(2)
C23-C28-H28	119.	C27-C28-H28	119.6

Dichloro-bis((Z)-1-styryl-benzimidazole)-cobalt(II) (1c)

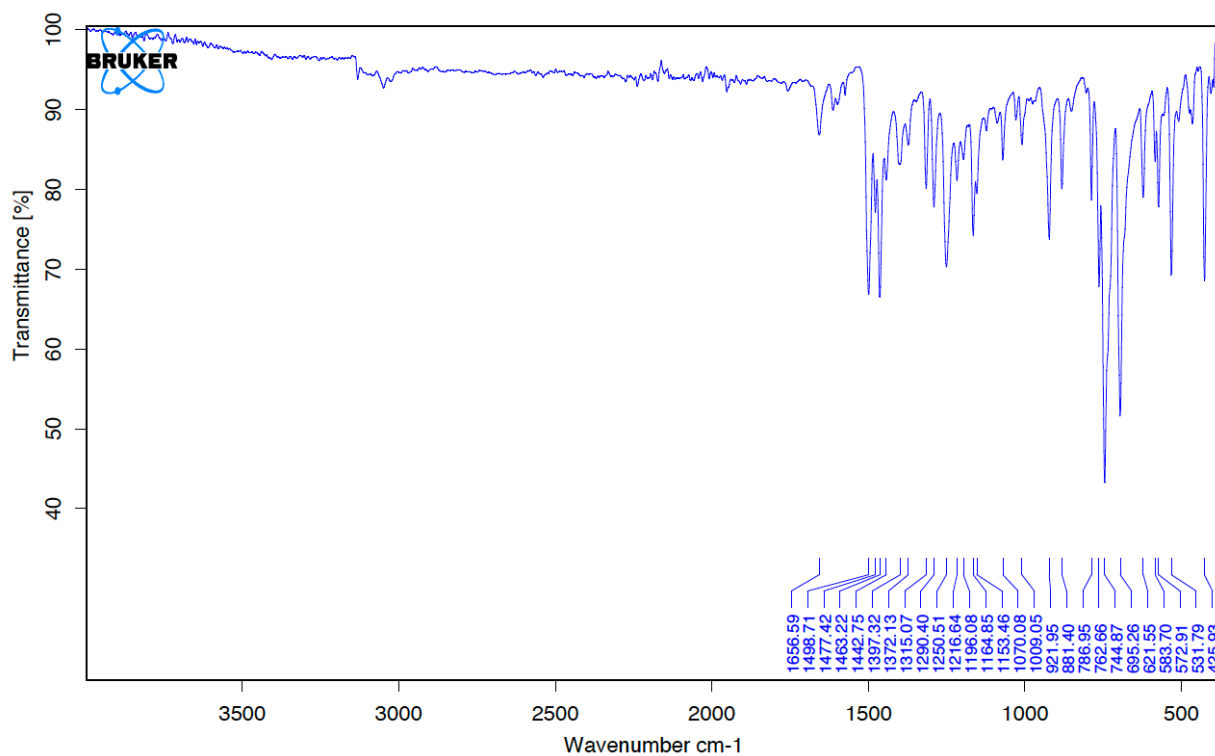
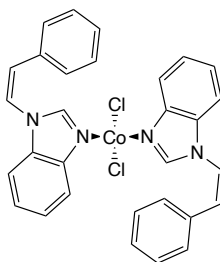


Figure S14. FT-IR spectrum

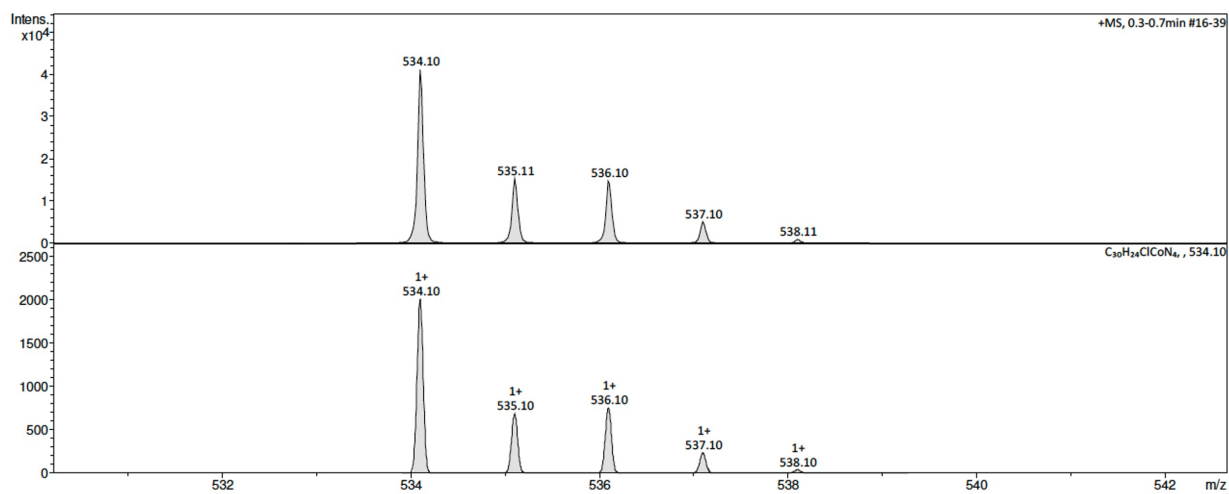


Figure S15. Mass spectrum (ESI-TOF)

exp. spectrum (top); calc. spectrum (bottom) for $C_{30}H_{24}N_4ClCo$ ($[M - Cl]^+$)

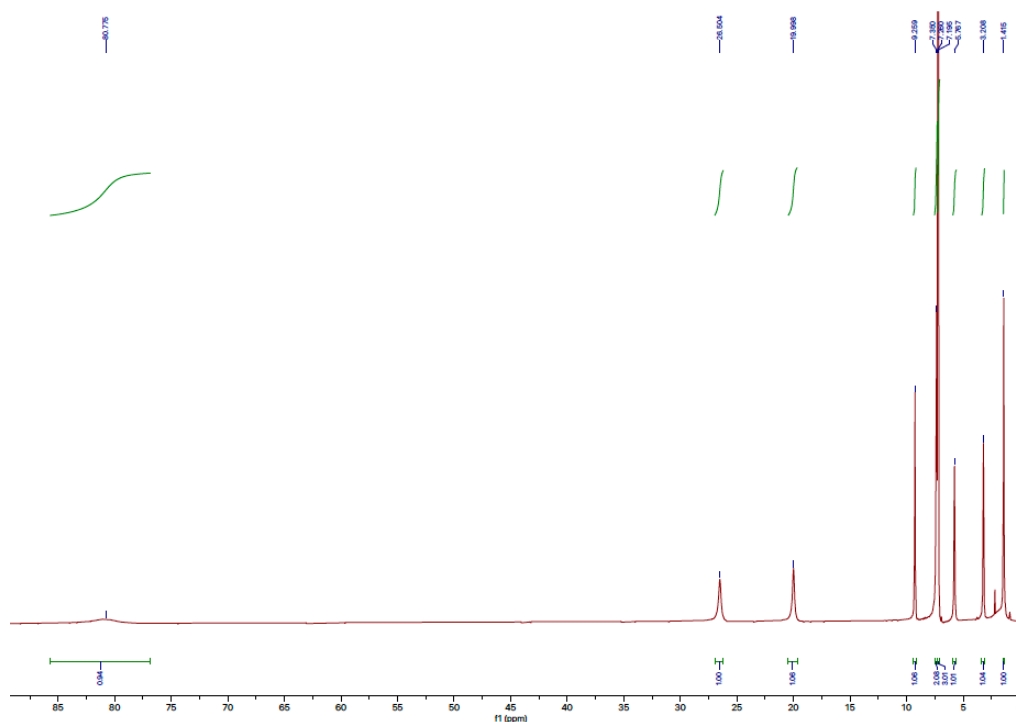


Figure S16. ^1H NMR spectrum (CDCl_3)

X-Ray Crystal Structure Analysis of complex **1c**

Single crystals of cobalt(II) complex **1c**, suitable for X-ray analysis, were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of the complex. The crystal structures was determined using a Bruker APEX-II CCD with Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at $T = 173(2) \text{ K}$. The structures were solved with SHELXT-2018/2 [1], which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, all of the hydrogen atoms were found with a Fourier difference map. The structure was refined with SHELXL-2019/3 [2] by the full-matrix least-square techniques (use of F square magnitude; x, y, z, β_{ij} for C, Cl, N and Co atoms; x, y, z in riding mode for H atoms). CCDC contain the supplementary crystallographic data for the structures. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

[1] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *A71*, 3-8

[2] G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *C71*, 3-8.

Table S3. Selected crystallographic data for complex **1c**.

CCDC depository	2487683	Chemical formula	C ₃₀ H ₂₄ Cl ₂ CoN ₄	
Molar mass (g mol ⁻¹)	570.36	Temperature	173(2)	
Crystal system	Triclinic	Space group	<i>P</i> $\bar{1}$	
Unit cell parameters	<i>a</i> (Å)	10.329(2)	Unit cell <i>α</i> (°)	98.220(6)
	<i>b</i> (Å)	10.4787(19)	Unit cell <i>β</i> (°)	107.274(7)
	<i>c</i> (Å)	14.116(3)	Unit cell <i>γ</i> (°)	109.036(6)
Volume (Å ³)	1329.6(4)	<i>Z</i>	2	
<i>ρ</i> _{calc.} (g.cm ⁻³)	1.425	<i>μ</i> (mm ⁻¹)	0.873	
<i>F</i> (000)	586	Crystal size (mm)	0.140 x 0.100 x 0.060	
Index ranges	$-13 \leq h \leq 13$		<i>θ</i> range for data collection (°)	$1.567 \leq \theta \leq 28.161$
	$-13 \leq k \leq 13$		Reflections collected	18108
	$-13 \leq l \leq 13$		Independent / observed	6132 / 2823
<i>R</i> _{int}	0.1284	Data	6132	
Restraints	0	Parameters	334	
Goodness-of-fit on <i>F</i> ²	1.191	<i>T</i> _{min} , <i>T</i> _{max}	0.888, 0.949	
Final <i>R</i> indices (<i>I</i> > 2.0 <i>σ</i> (<i>I</i>))	<i>R</i> ₁ = 0.1127	<i>R</i> indices (all data)	<i>R</i> ₁ = 0.22369	
	w <i>R</i> ₂ = 0.1127		w <i>R</i> ₂ = 0.1401	
<i>Δρ</i> _{max} , <i>Δρ</i> _{min} (e Å ⁻³)	0.615, -0.858			

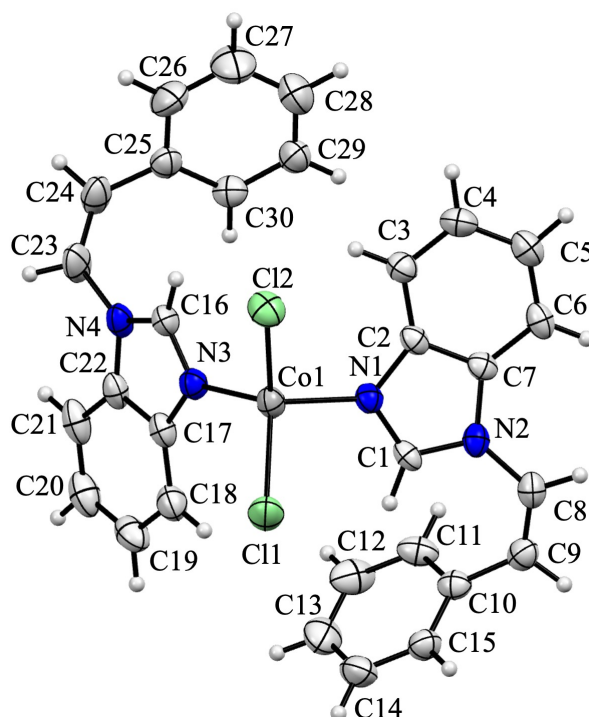
**Figure S17.** ORTEP drawing of the cobalt(II) complex **1c** (50% probability thermal ellipsoids)

Table S4. Bond lengths (Å) for the cobalt complex **1c**

C1-N1	1.306(6)	C1-N2	1.362(6)
C1-H1	0.9500	C2-C3	1.378(7)
C2-N1	1.396(6)	C2-C7	1.396(7)
C3-C4	1.371(7)	C3-H3	0.9500
C4-C5	1.399(7)	C4-H4	0.9500
C5-C6	1.373(7)	C5-H5	0.9500
C6-C7	1.385(7)	C6-H6	0.9500
C7-N2	1.382(6)	C8-C9	1.304(7)
C8-N2	1.419(6)	C8-H8	0.9500
C9-C10	1.476(7)	C9-H9	0.9500
C10-C15	1.372(7)	C10-C11	1.389(7)
C11-C12	1.372(7)	C11-H11	0.9500
C12-C13	1.363(8)	C12-H12	0.9500
C13-C14	1.380(8)	C13-H13	0.9500
C14-C15	1.389(7)	C14-H14	0.9500
C15-H15	0.9500	C16-N3	1.312(6)
C16-N4	1.357(6)	C16-H16	0.9500
C17-C18	1.383(7)	C17-N3	1.391(6)
C17-C22	1.393(7)	C18-C19	1.375(7)
C18-H18	0.9500	C19-C20	1.398(8)
C19-H19	0.9500	C20-C21	1.370(8)
C20-H20	0.9500	C21-C22	1.382(7)
C21-H21	0.9500	C22-N4	1.382(7)
C23-C24	1.312(8)	C23-N4	1.410(7)
C23-H23	0.9500	C24-C25	1.462(8)
C24-H24	0.9500	C25-C26	1.374(8)
C25-C30	1.394(7)	C26-C27	1.369(8)
C26-H26	0.9500	C27-C28	1.366(8)
C27-H27	0.9500	C28-C29	1.358(8)
C28-H28	0.9500	C29-C30	1.385(7)
C29-H29	0.9500	C30-H30	0.9500
N1-Co1	2.027(4)	N3-Co1	2.009(4)
Cl1-Co1	2.2312(17)	Cl2-Co1	2.2301(17)

Table S5. Angles (°) for the cobalt complex **1c**

N1-C1-N2	113.0(5)	N1-C1-H1	123.5
N2-C1-H1	123.5	C3-C2-N1	130.2(5)
C3-C2-C7	120.9(5)	N1-C2-C7	108.9(5)
C4-C3-C2	117.3(6)	C4-C3-H3	121.4
C2-C3-H3	121.4	C3-C4-C5	121.7(6)
C3-C4-H4	119.1	C5-C4-H4	119.1
C6-C5-C4	121.5(6)	C6-C5-H5	119.2
C4-C5-H5	119.2	C5-C6-C7	116.5(6)
C5-C6-H6	121.7	C7-C6-H6	121.7

N2-C7-C6	132.1(5)	N2-C7-C2	105.8(5)
C6-C7-C2	122.0(5)	C9-C8-N2	125.4(5)
C9-C8-H8	117.3	N2-C8-H8	117.3
C8-C9-C10	126.0(6)	C8-C9-H9	117.0
C10-C9-H9	117.0	C15-C10-C11	118.7(5)
C15-C10-C9	121.7(5)	C11-C10-C9	119.6(5)
C12-C11-C10	120.4(6)	C12-C11-H11	119.8
C10-C11-H11	119.8	C13-C12-C11	120.5(6)
C13-C12-H12	119.8	C11-C12-H12	119.8
C12-C13-C14	120.3(6)	C12-C13-H13	119.8
C14-C13-H13	119.8	C13-C14-C15	119.0(6)
C13-C14-H14	120.5	C15-C14-H14	120.5
C10-C15-C14	121.1(6)	C10-C15-H15	119.4
C14-C15-H15	119.4	N3-C16-N4	112.4(5)
N3-C16-H16	123.8	N4-C16-H16	123.8
C18-C17-N3	131.0(5)	C18-C17-C22	120.6(5)
N3-C17-C22	108.4(5)	C19-C18-C17	116.9(6)
C19-C18-H18	121.5	C17-C18-H18	121.5
C18-C19-C20	122.3(6)	C18-C19-H19	118.9
C20-C19-H19	118.9	C21-C20-C19	120.9(6)
C21-C20-H20	119.5	C19-C20-H20	119.5
C20-C21-C22	117.0(6)	C20-C21-H21	121.5
C22-C21-H21	121.5	C21-C22-N4	131.6(6)
C21-C22-C17	122.2(6)	N4-C22-C17	106.2(5)
C24-C23-N4	125.8(5)	C24-C23-H23	117.1
N4-C23-H23	117.1	C23-C24-C25	129.5(6)
C23-C24-H24	115.2	C25-C24-H24	115.2
C26-C25-C30	118.2(6)	C26-C25-C24	119.8(6)
C30-C25-C24	121.9(6)	C27-C26-C25	121.2(6)
C27-C26-H26	119.4	C25-C26-H26	119.4
C28-C27-C26	120.1(7)	C28-C27-H27	119.9
C26-C27-H27	119.9	C29-C28-C27	120.2(6)
C29-C28-H28	119.9	C27-C28-H28	119.9
C28-C29-C30	120.2(6)	C28-C29-H29	119.9
C30-C29-H29	119.9	C29-C30-C25	120.0(6)
C29-C30-H30	120.0	C25-C30-H30	120.0
C1-N1-C2	105.6(4)	C1-N1-Co1	122.8(4)
C2-N1-Co1	130.6(4)	C1-N2-C7	106.6(5)
C1-N2-C8	126.8(5)	C7-N2-C8	126.4(5)
C16-N3-C17	106.2(4)	C16-N3-Co1	123.6(4)
C17-N3-Co1	130.1(4)	C16-N4-C22	106.7(5)
C16-N4-C23	126.8(5)	C22-N4-C23	125.9(5)
N3-Co1-N1	109.99(17)	N3-Co1-Cl2	105.54(14)
N1-Co1-Cl2	106.31(13)	N3-Co1-Cl1	112.09(14)
N1-Co1-Cl1	103.40(14)	Cl2-Co1-Cl1	119.23(7)

Dichloro-bis[(Z)-1-(2-fluorostyryl)-benzimidazole]-cobalt(II) (1d)

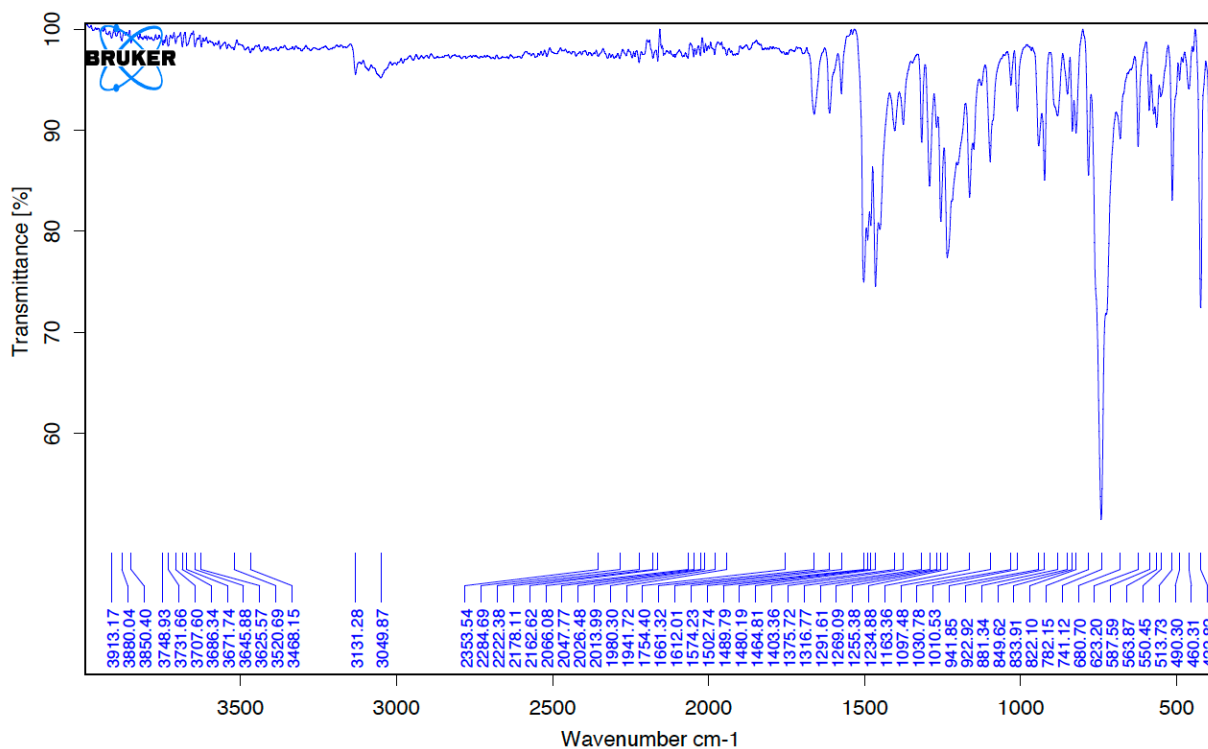
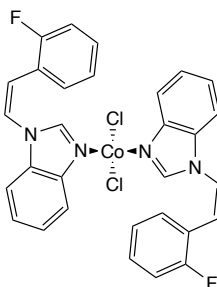


Figure S18. FT-IR spectrum

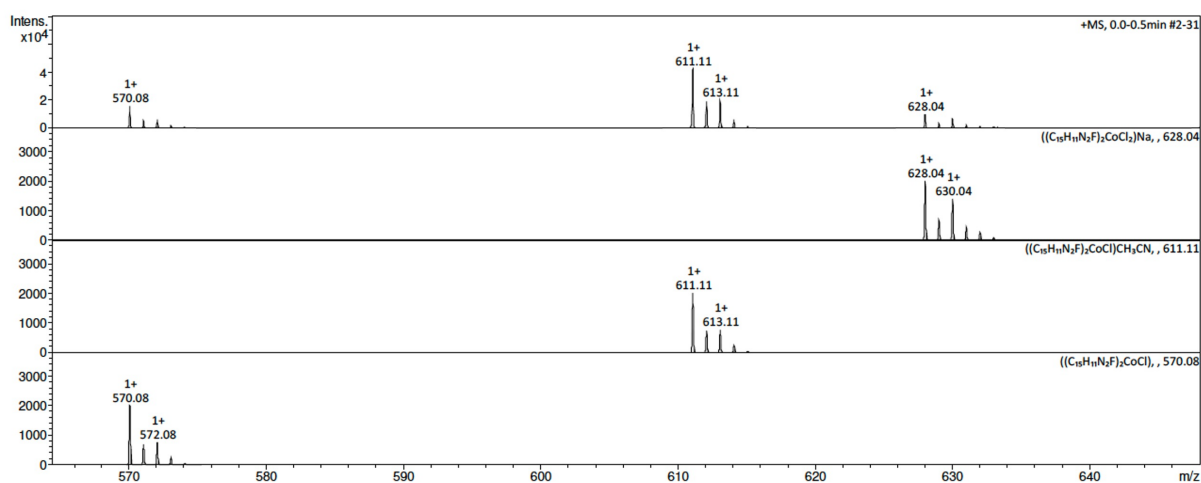


Figure S19. Mass spectrum (ESI-TOF)

exp. spectrum (top); calc. spectrum (second) for $C_{30}H_{22}N_4F_2Cl_2CoNa$ ($[M + Na]^+$); calc. spectrum (third) for $C_{32}H_{25}N_5F_2ClCo$ ($[M - Cl + CH_3CN]^+$); calc. spectrum (bottom) for $C_{30}H_{22}N_4F_2ClCo$ ($[M - Cl]^+$)



Dichloro-bis(1-cinnamyl-benzimidazole)-cobalt(II) (1e)

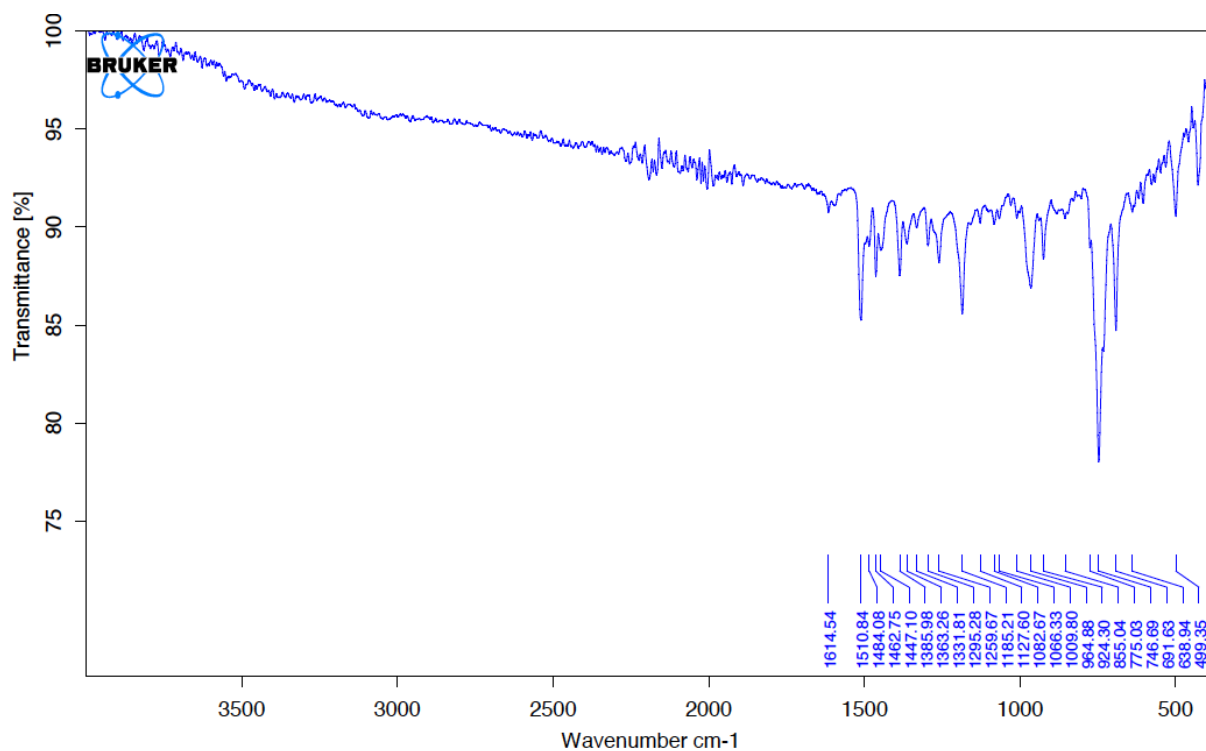
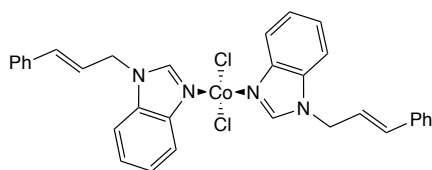


Figure S22. FT-IR spectrum

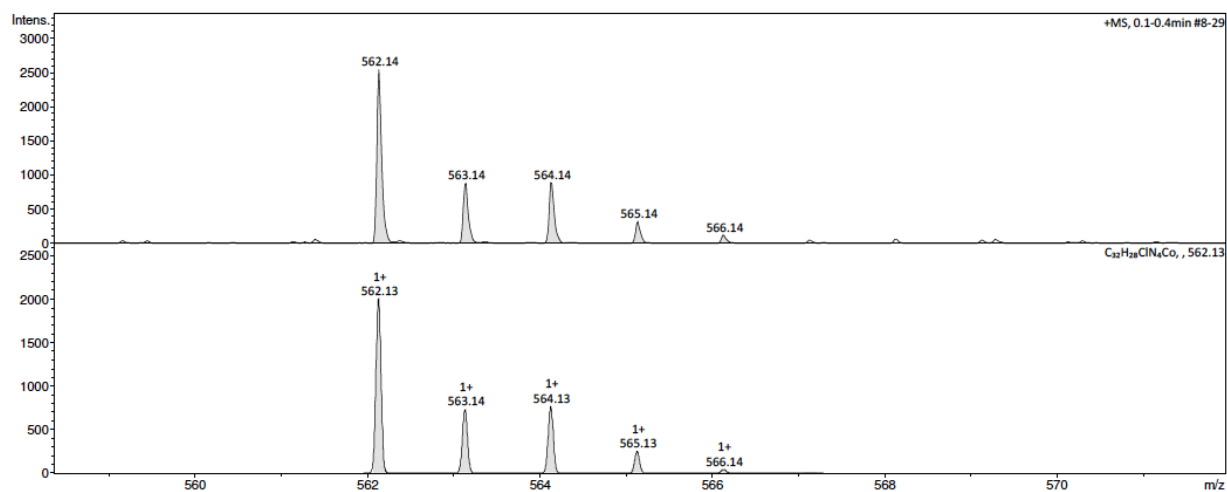


Figure S23. Mass spectrum (ESI-TOF)

exp. spectrum (top); calc. spectrum (bottom) for C₃₂H₂₈N₄ClCo ([M - Cl]⁺)

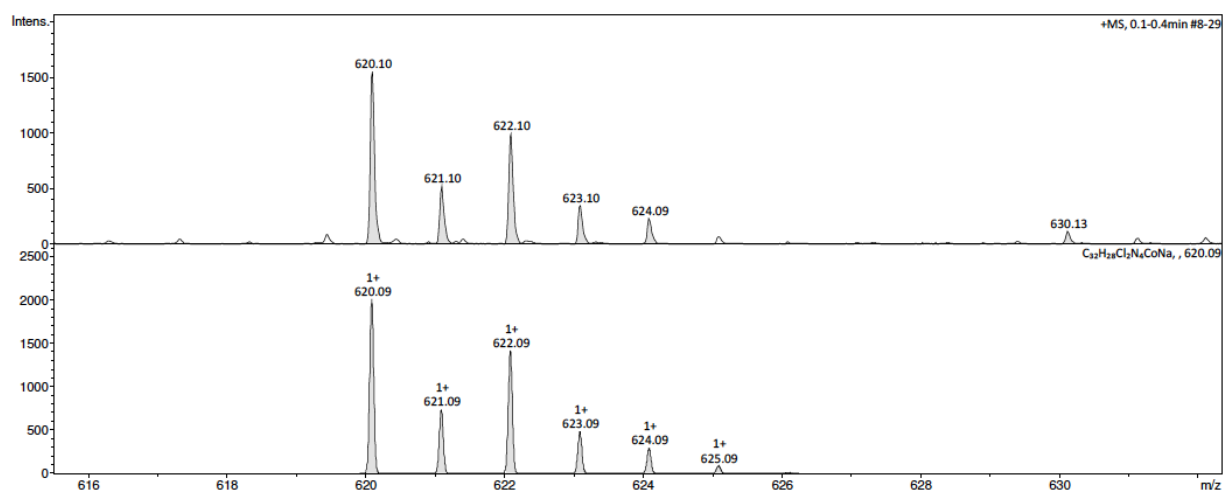


Figure S24. Mass spectrum (ESI-TOF)
exp. spectrum (top); calc. spectrum (bottom) for $C_{32}H_{28}N_4Cl_2CoNa$ ($[M + Na]^+$)

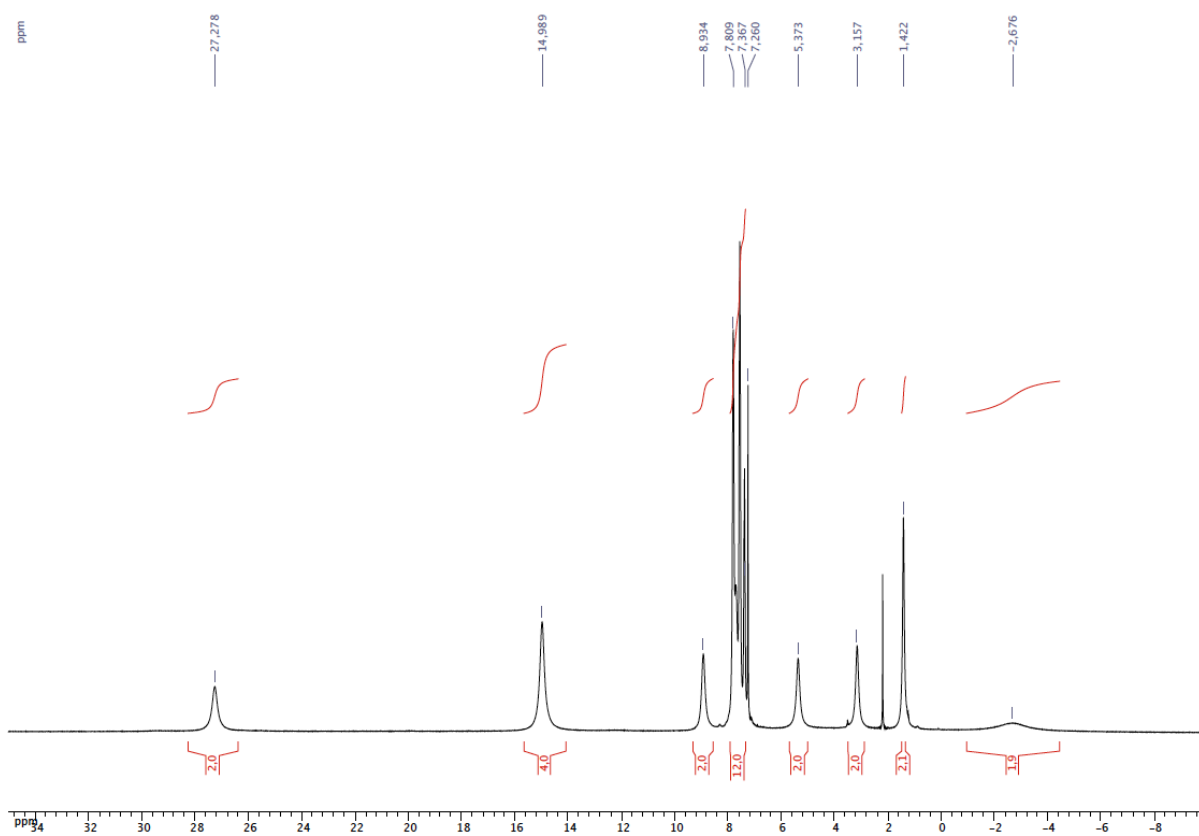


Figure S25. 1H NMR spectrum ($CDCl_3$)