Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Reactivity of a T-Shaped Cobalt(I) Pincer-Complex

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Contents

1 NMR Spectra

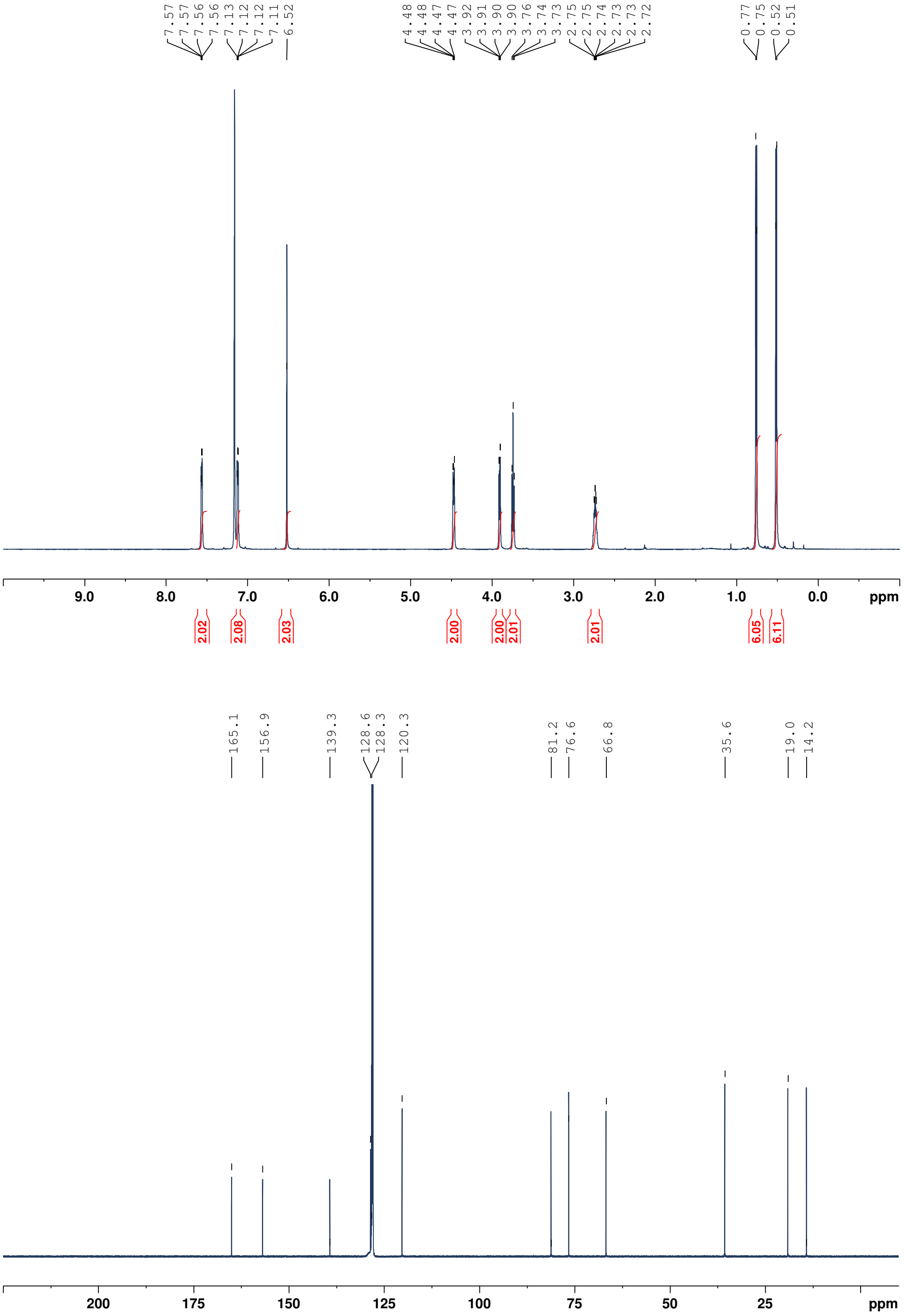

Figure S1: ^{1}H NMR (top, 600.13 MHz, C_6D_6, 295 K) and ^{13}C NMR (bottom, 150.90 MHz, C_6D_6, 295 K) spectra of [(^{iPr}boxmi)Co(CO)] (**2**).

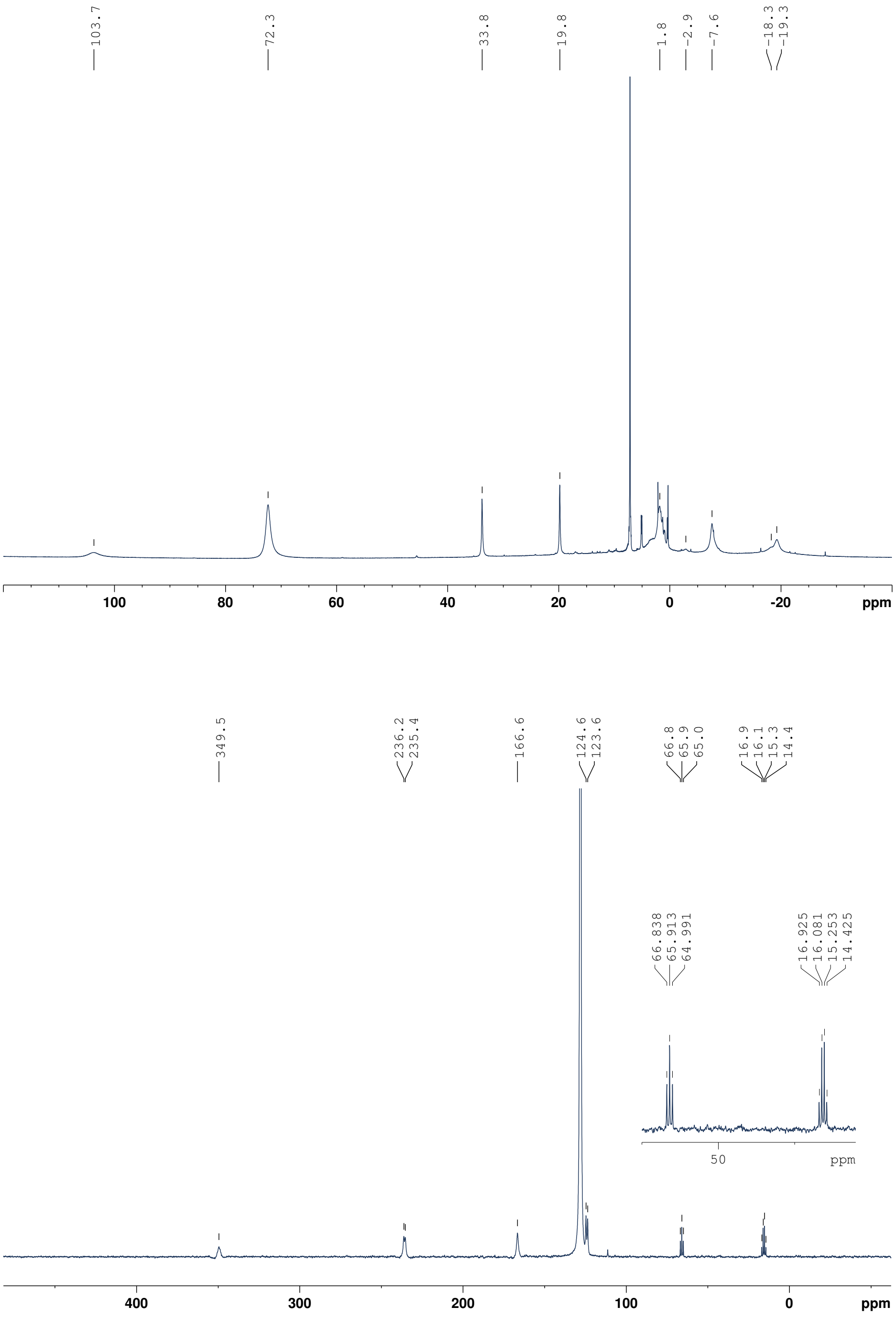

Figure S2: ^{1}H NMR (top, 399.89 MHz, C_6D_6, 295 K) and ^{13}C NMR (bottom, 150.90 MHz, C_6D_6, 295 K) spectra of [(^{iPr}boxmi)Co(PMe_3)] (**3**).

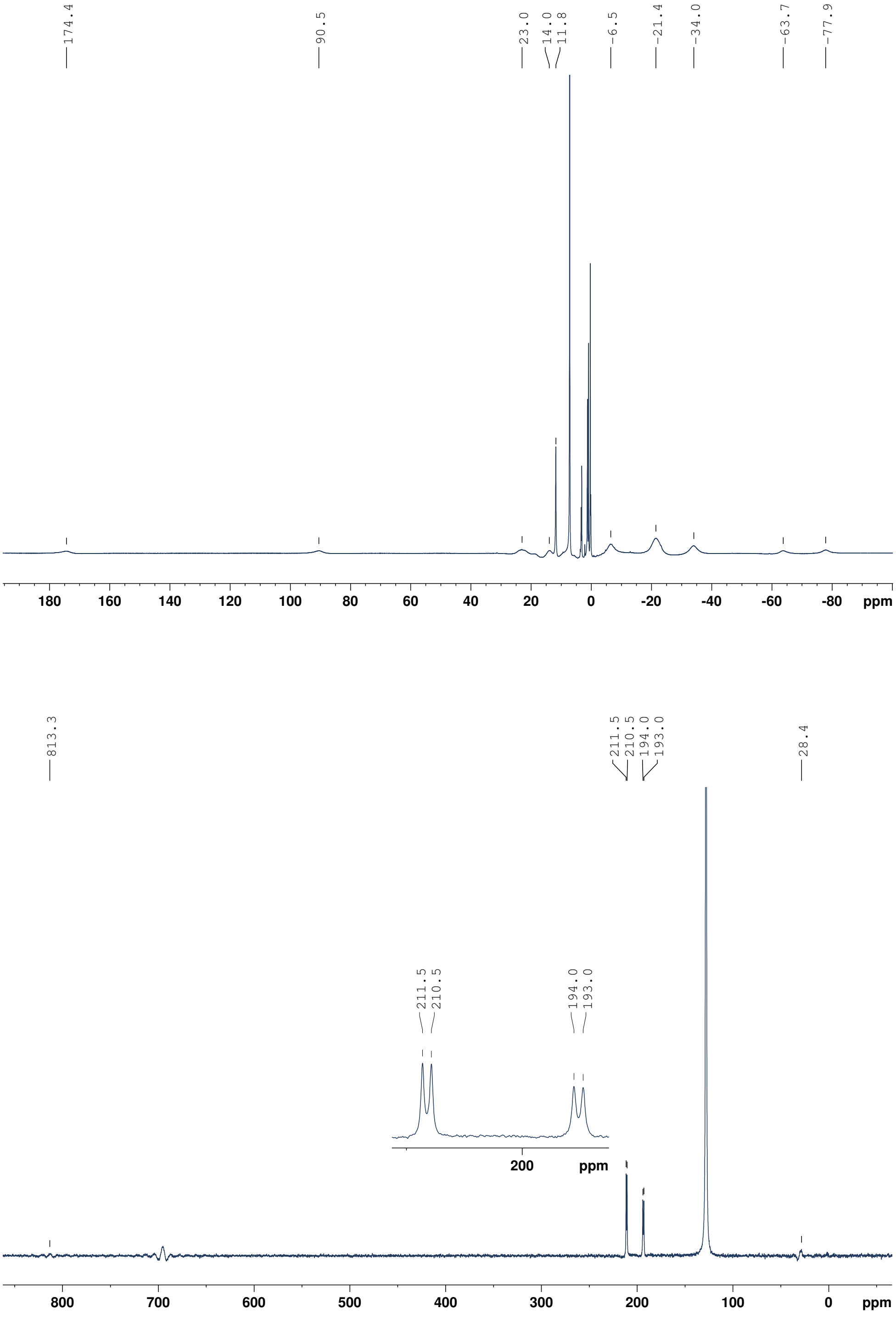

Figure S3: ^{1}H NMR (top, 600.13 MHz, C_6D_6, 295 K) and ^{13}C NMR (bottom, 150.90 MHz, C_6D_6, 295 K) spectra of [(^{iPr}boxmi)Co(I)] (**4**).

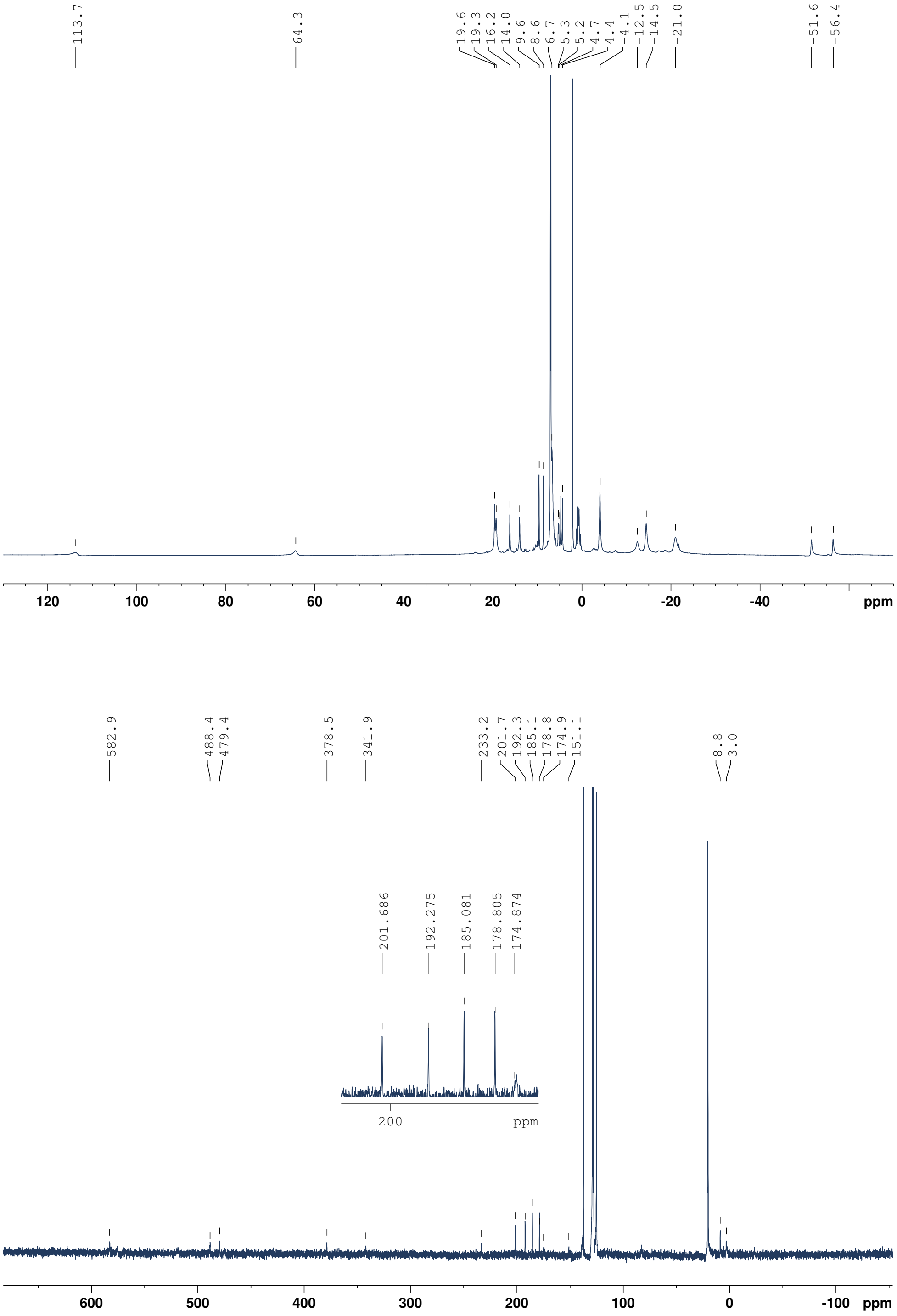

Figure S4: ^{1}H NMR (top, 399.89 MHz, Tol-d_8, 295 K) and ^{13}C{H} NMR (bottom, 150.90 MHz, Tol-d_8, 295 K) spectra of [(^{iPr}boxmi)Co(O^{t}Bu)] (**5a**).

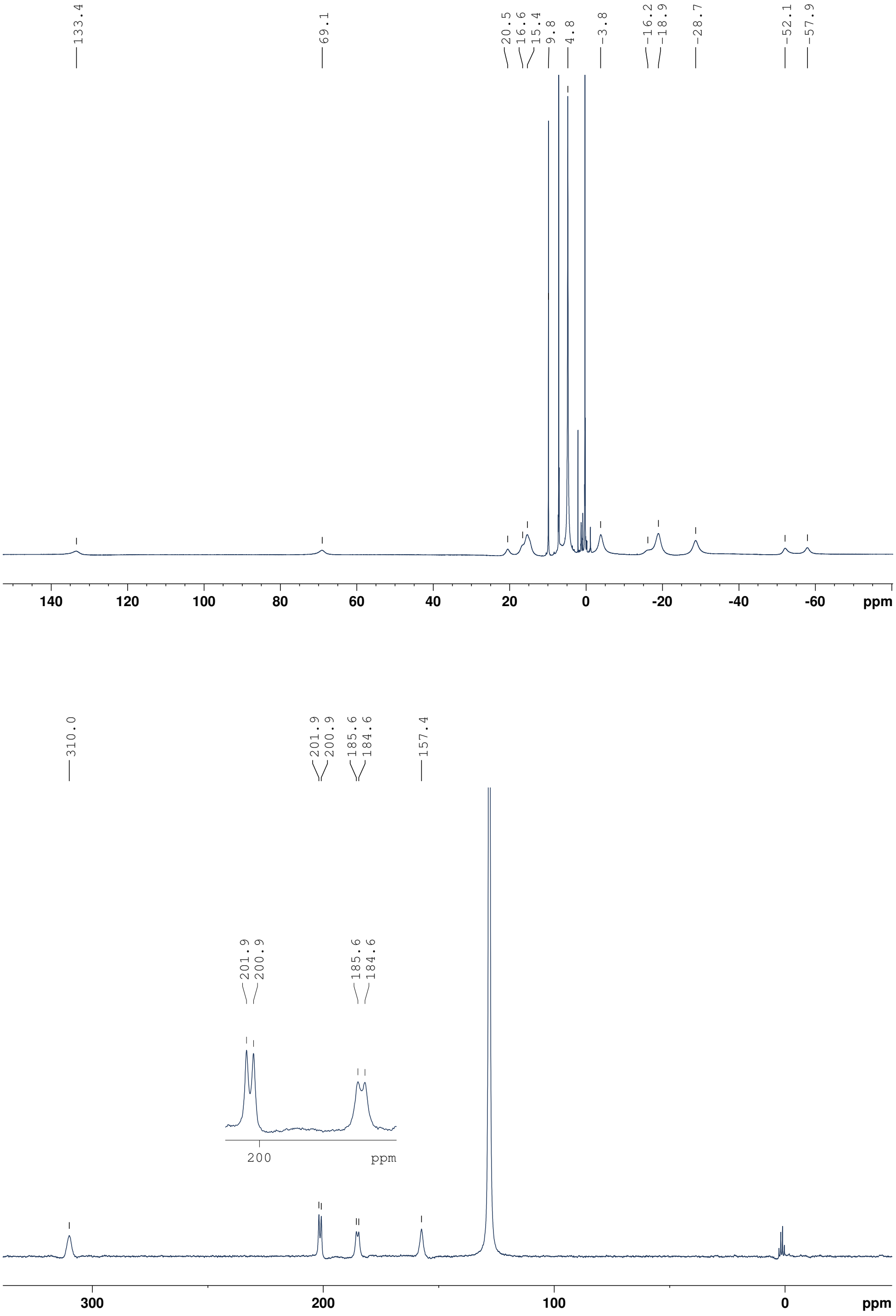

Figure S5: ^{1}H NMR (top, 600.13 MHz, C_6D_6, 295 K) and ^{13}C NMR (bottom, 150.90 MHz, C_6D_6, 295 K) spectra of [(^{iPr}boxmi)Co(OSiMe$_3$)] (**5b**).

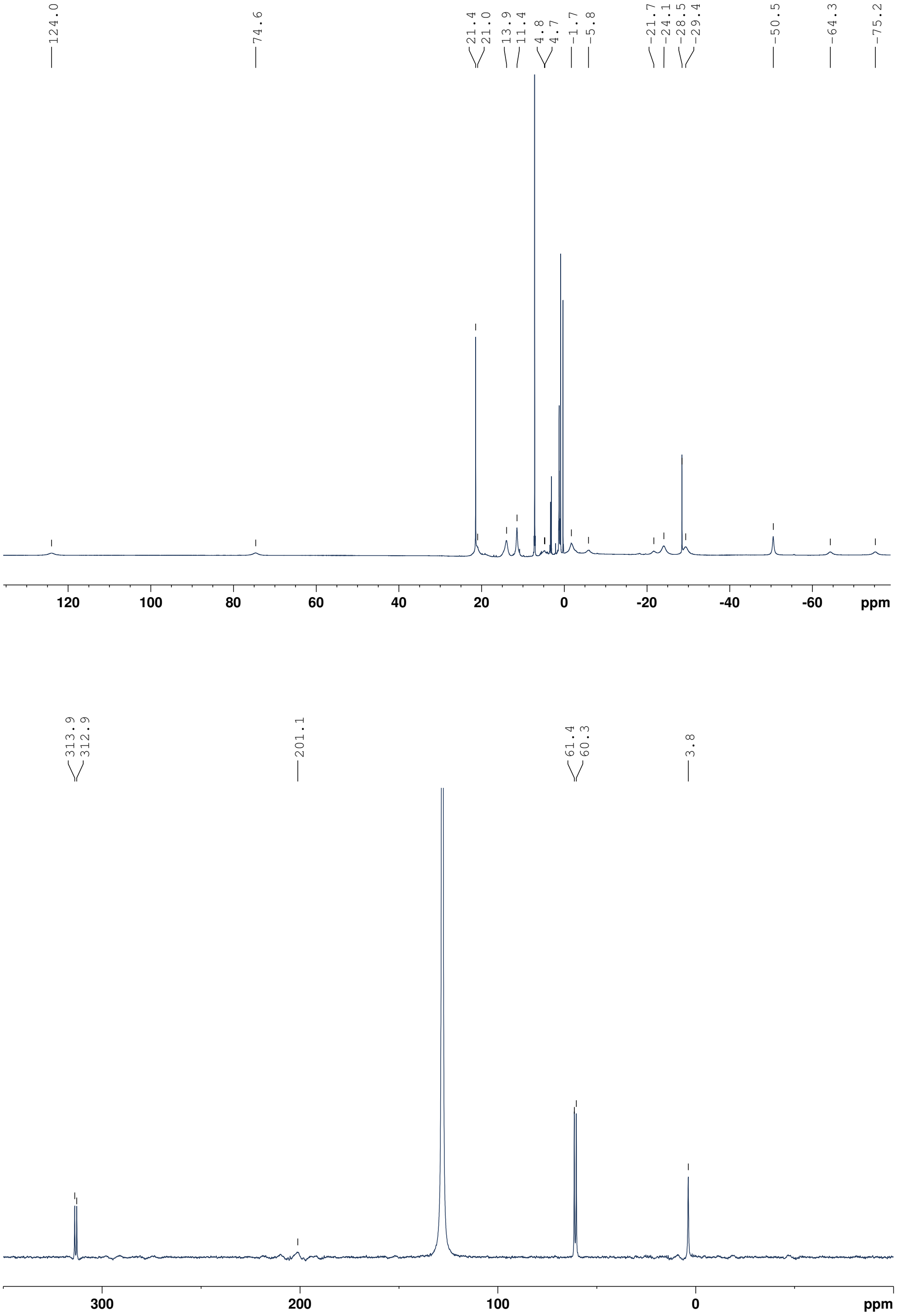

Figure S6: ^{1}H NMR (top, 600.13 MHz, C_6D_6, 295 K) and ^{13}C NMR (bottom, 150.90 MHz, C_6D_6, 295 K) spectra of [(^{iPr}boxmi)Co(SPh)] (**6**).

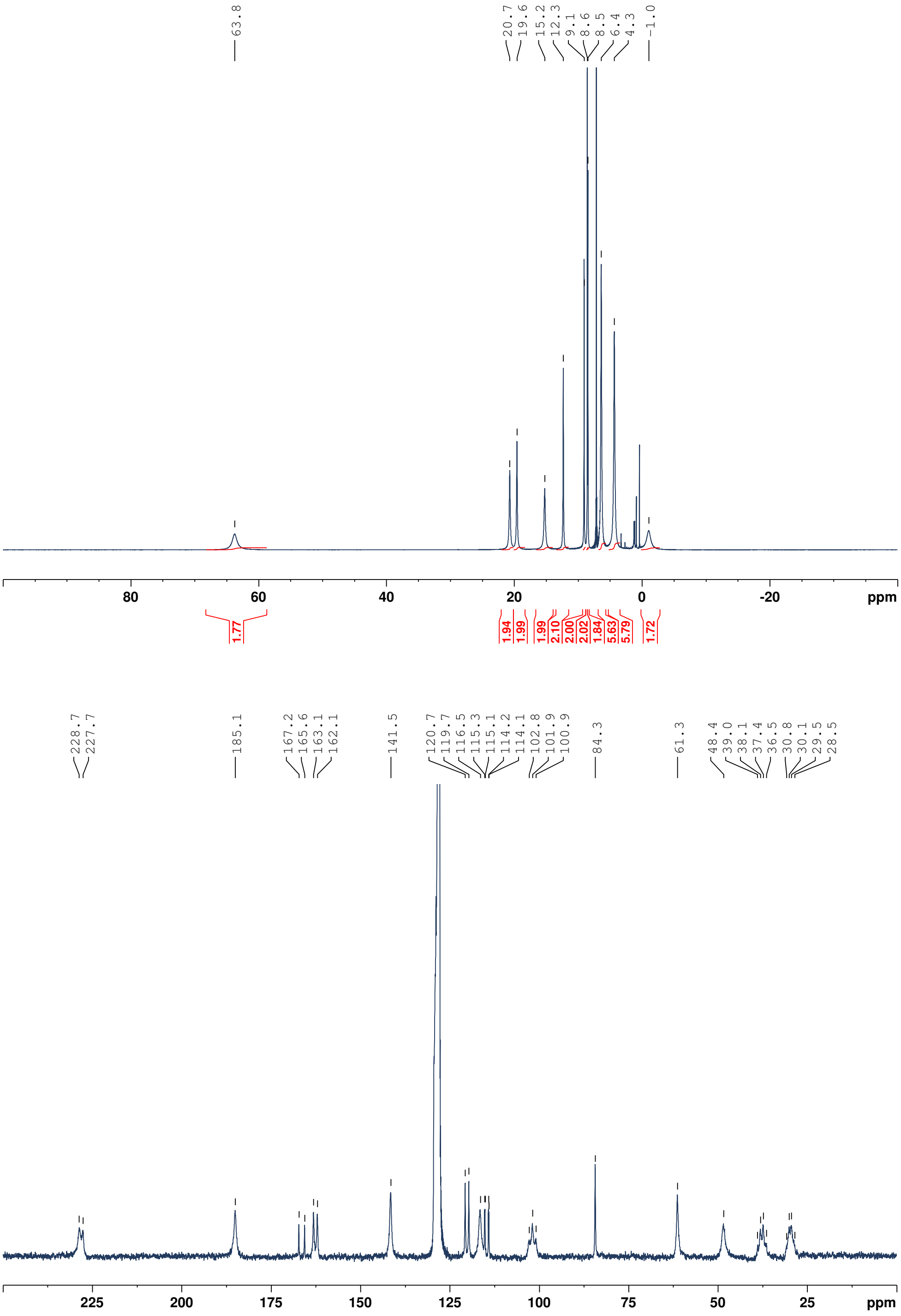

Figure S7: ^{1}H NMR (top, 600.13 MHz, C_6D_6, 295 K) and ^{13}C NMR (bottom, 150.90 MHz, C_6D_6, 295 K) spectra of [(^{iPr}boxmi)Co(CCPh(4-F))] (**7**).

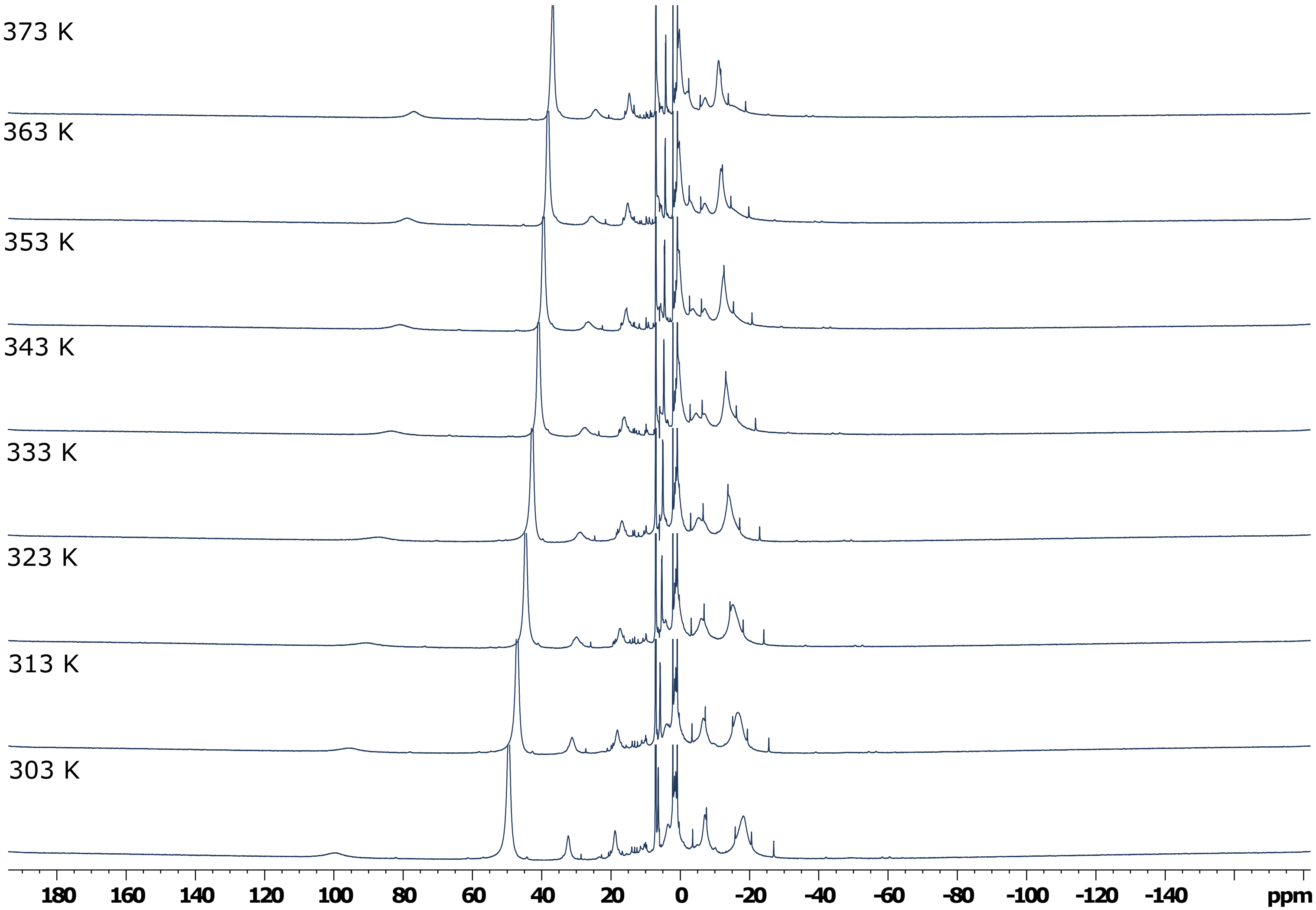

Figure S8: ^{1}H NMR spectra (199.92 MHz, Tol-d_8) of [(^{iPr}boxmi)Co(PMe$_3$)] (**3**) at various temperatures.

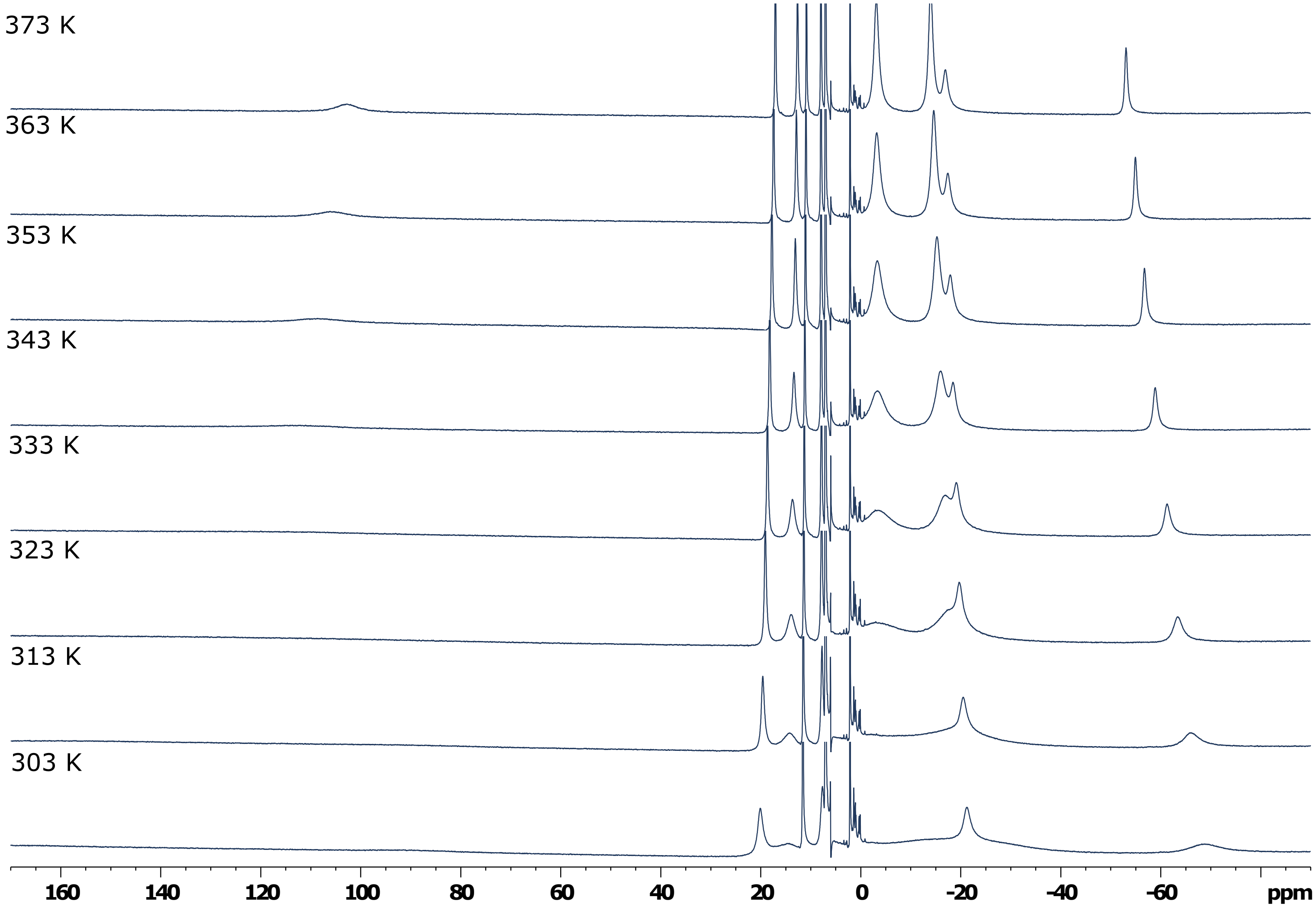

Figure S9: ^{1}H NMR spectra (199.92 MHz, Tol-d_8) of [(^{iPr}boxmi)Co(**I**)] (**4**) at various temperatures.

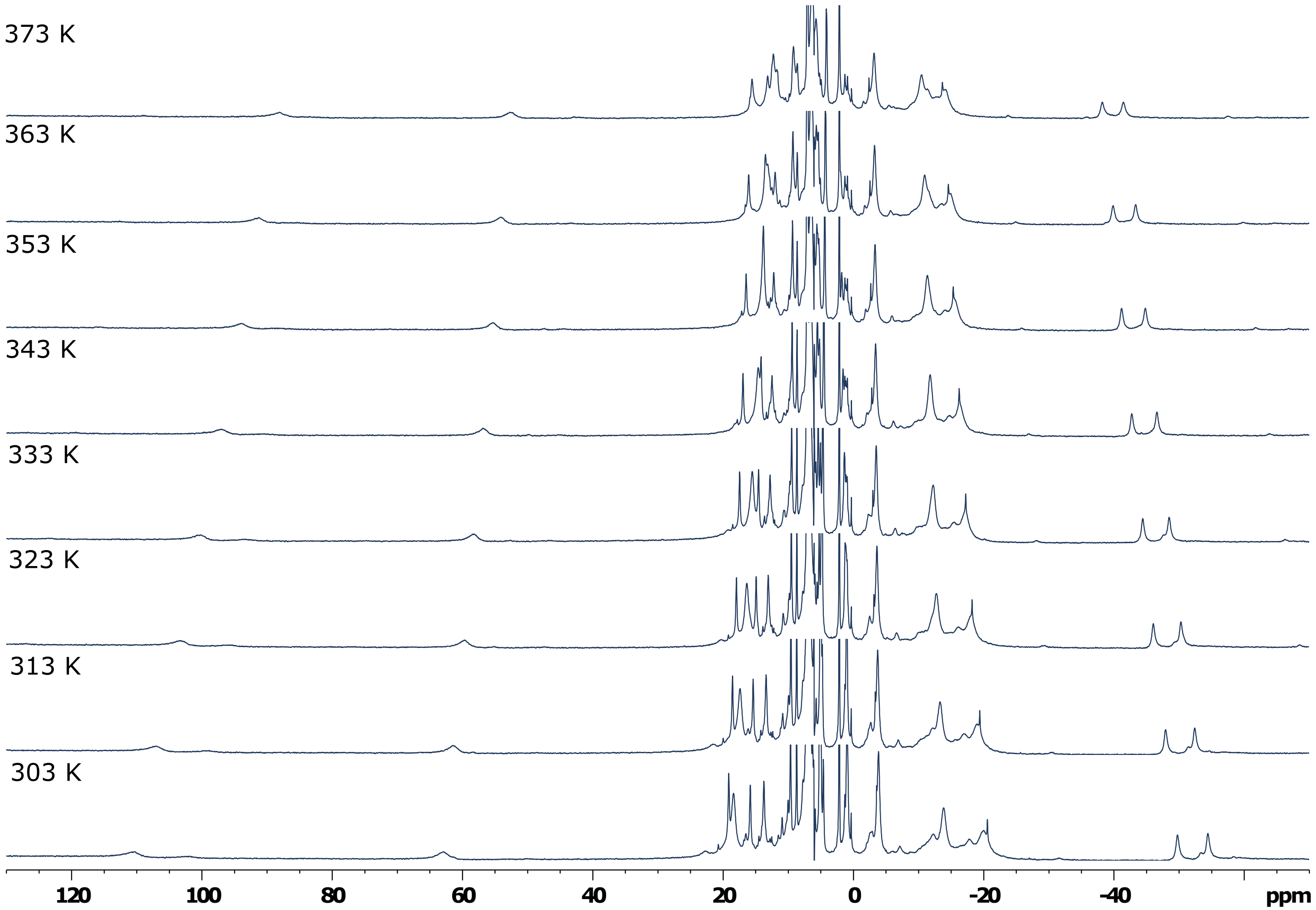

Figure S10: ^{1}H NMR spectra (199.92 MHz, Tol-d_8) of [(^{iPr}boxmi)Co(O^{t}Bu)] (**5a**) at various temperatures.

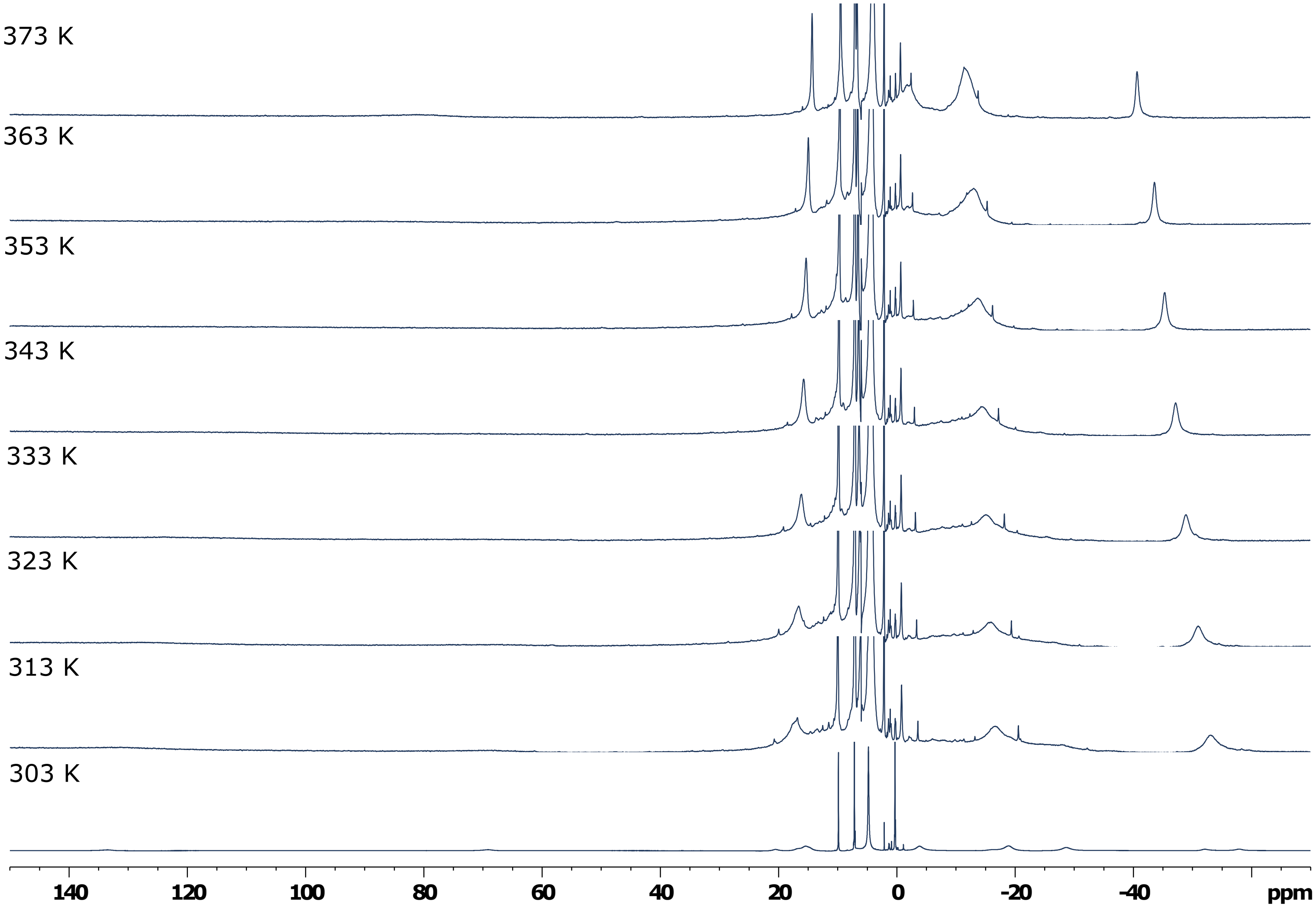

Figure S11: ^{1}H NMR spectra (199.92 MHz, Tol-d_8) of $[(^{iPr}\text{boxmi})\text{Co}(\text{OSiMe}_3)]$ (**5b**) at various temperatures.

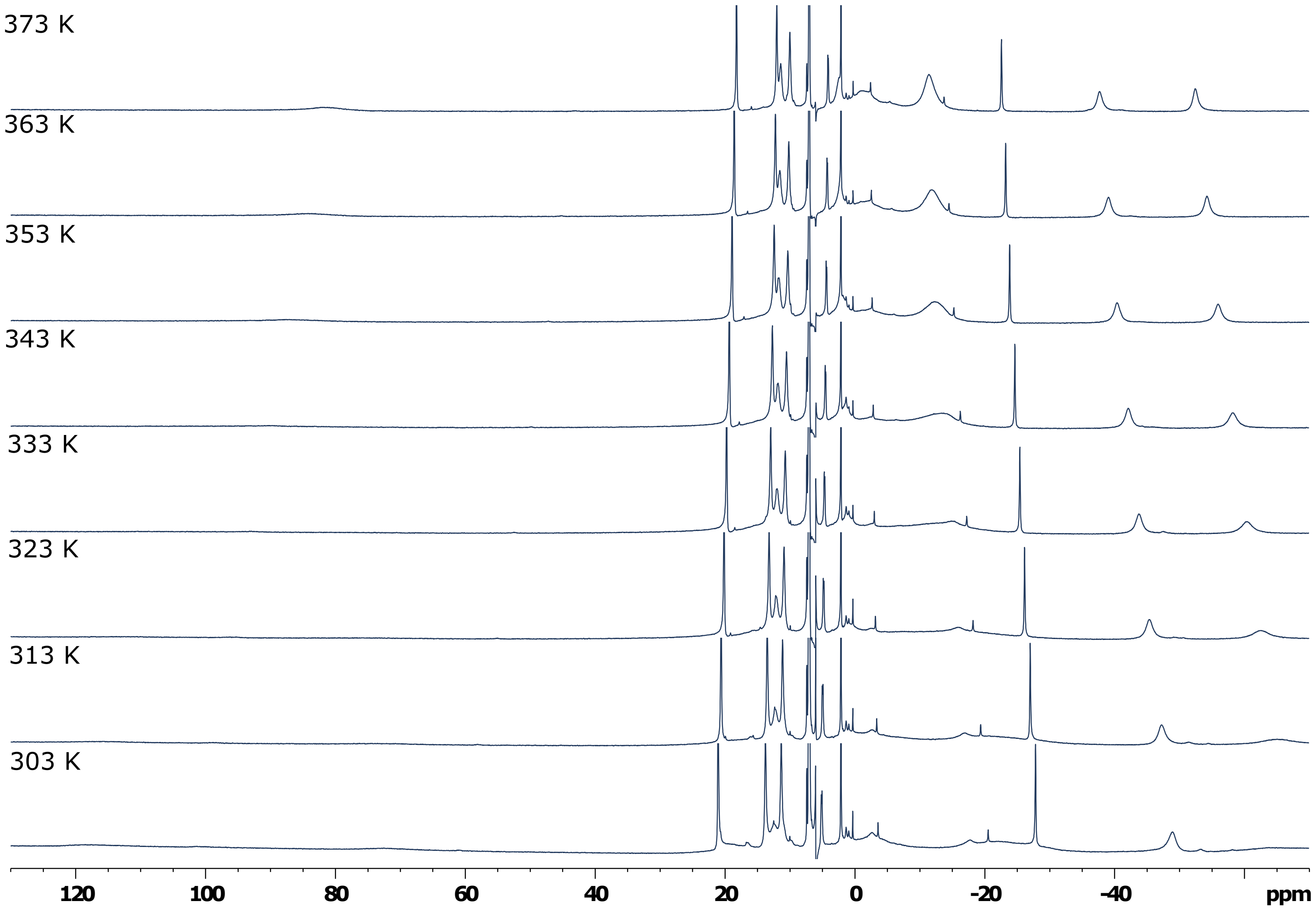

Figure S12: ^{1}H NMR spectra (199.92 MHz, Tol-d_8) of [(^{iPr}boxmi)Co(SPh)] (**6**) at various temperatures.

2 Additional Experiments

Reaction of Cobalt(I) Complex 1 with a terminal alkyne

Cobalt(I) complex $[^{\mathrm{iPr}}\mathrm{boxmiCo}]_2$ (**1**) (9.46 mg, 11.2 µmol, 0.5 eq.) was dissolved in 600 µl C_6D_6 and treated with 1-ethinyl-4-fluorobenzene (2.56 µl, 22.3 µmol, 1.0 eq.). The mixture was then transferred into a J. Young NMR tube and the reaction progress was followed by ^{1}H and ^{19}F NMR spectroscopy. Representative NMR spectra after 15 min reaction time are depicted below, indicating the formation of alkinyl complex **7** as major product. All attempts of recrystallization yielded only complex **7**.

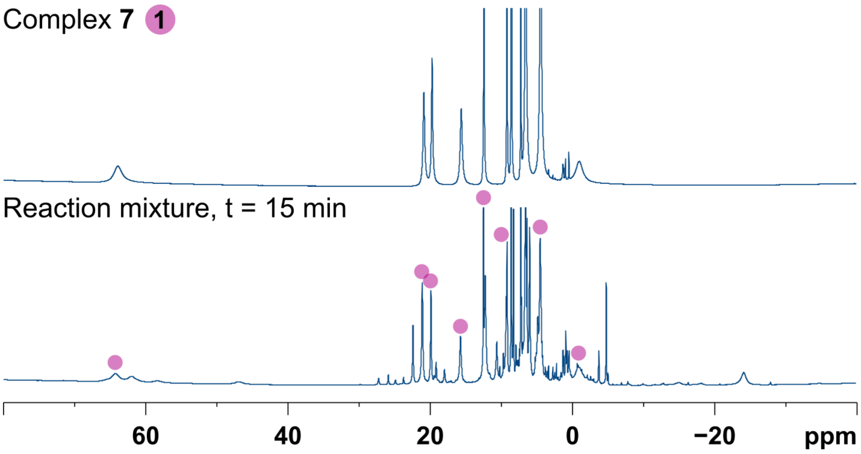

Figure S13: *In situ* ^{1}H NMR (C_6D_6, 399.9 MHz, 295 K) spectrum for the reaction of cobalt(I) complex **1** with 1-ethinyl-4-fluorobenzene after 15 min and reference spectrum for isolated alkinyl complex **7**.

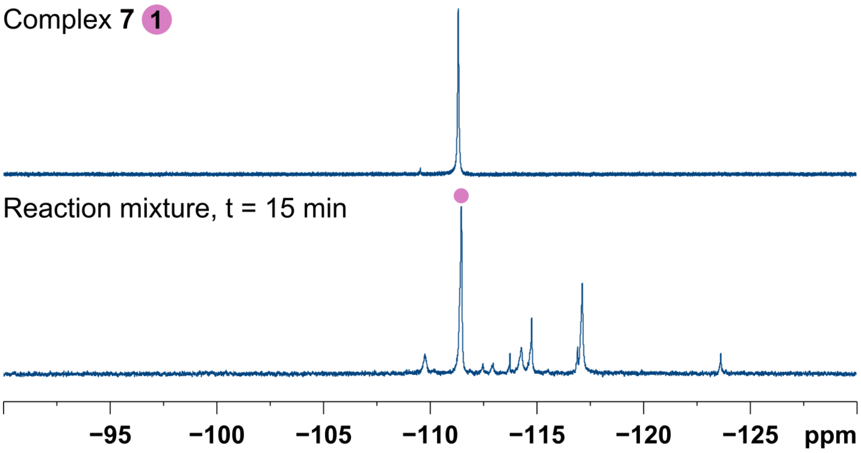

Figure S14: *In situ* ^{19}F NMR (C_6D_6, 376.2 MHz, 295 K) spectrum for the reaction of cobalt(I) complex **1** with 1-ethinyl-4-fluorobenzene after 15 min and reference spectrum for isolated alkinyl complex **7**.

Reaction of Cobalt(II) Alkinyl Complex 7 with HBPin

Complex ^{iPr}boxmiCo(CCAr^F) (**7**) (8.2 mg, 15 µmol, 1.0 eq.) was dissolved in 600 µl C_6D_6 and neat pinacolboran (2.2 µl, 15 µmol, 1.0 eq.) was added. The reaction mixture was then monitored by ^{1}H and ^{19}F NMR spectroscopy. A graphical illustration of the ^{19}F NMR spectra indicating the reaction progress is depicted below.

After 4 h, the reaction mixture was filtered through a plug of silica and eluted with dichloromethane. After removing all volatiles *in vacuo*, the residue was analyzed by ^{1}H and ^{19}F NMR spectroscopy in $CDCl_3$, allowing for the assignment of the organic products. The main products, the β-(*Z*)- and β-(*E*)-isomer, were identified by comparison with literature data.[1,2]

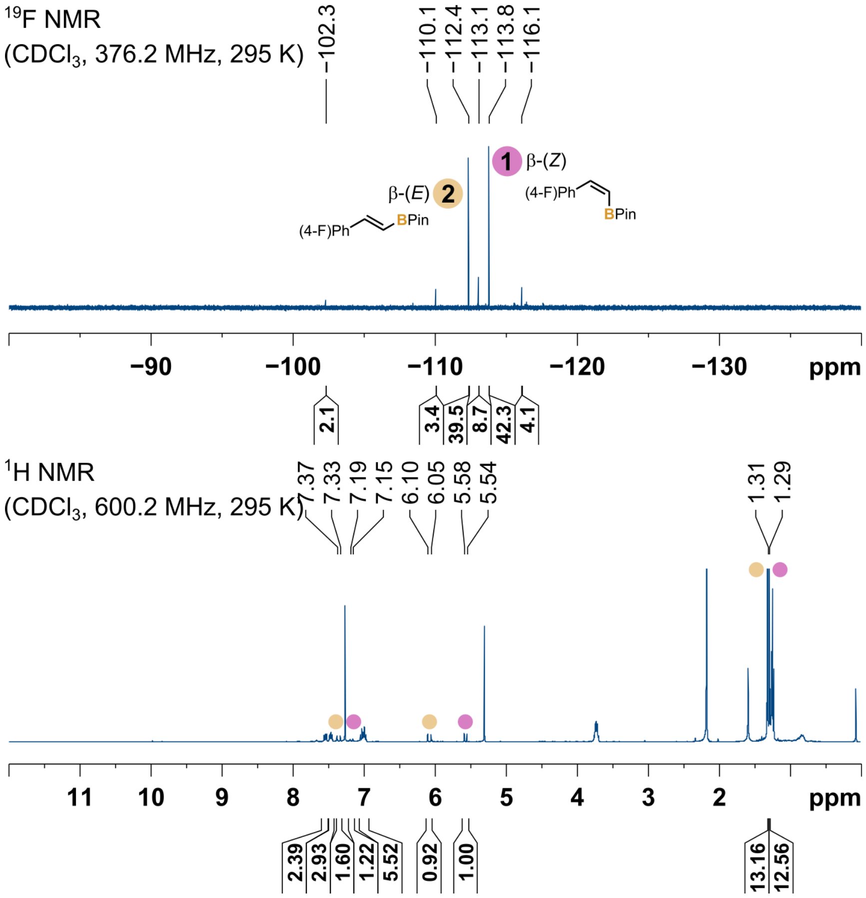

Figure S15: NMR spectra after work-up for the reaction of complex **7** with pinacolborane.

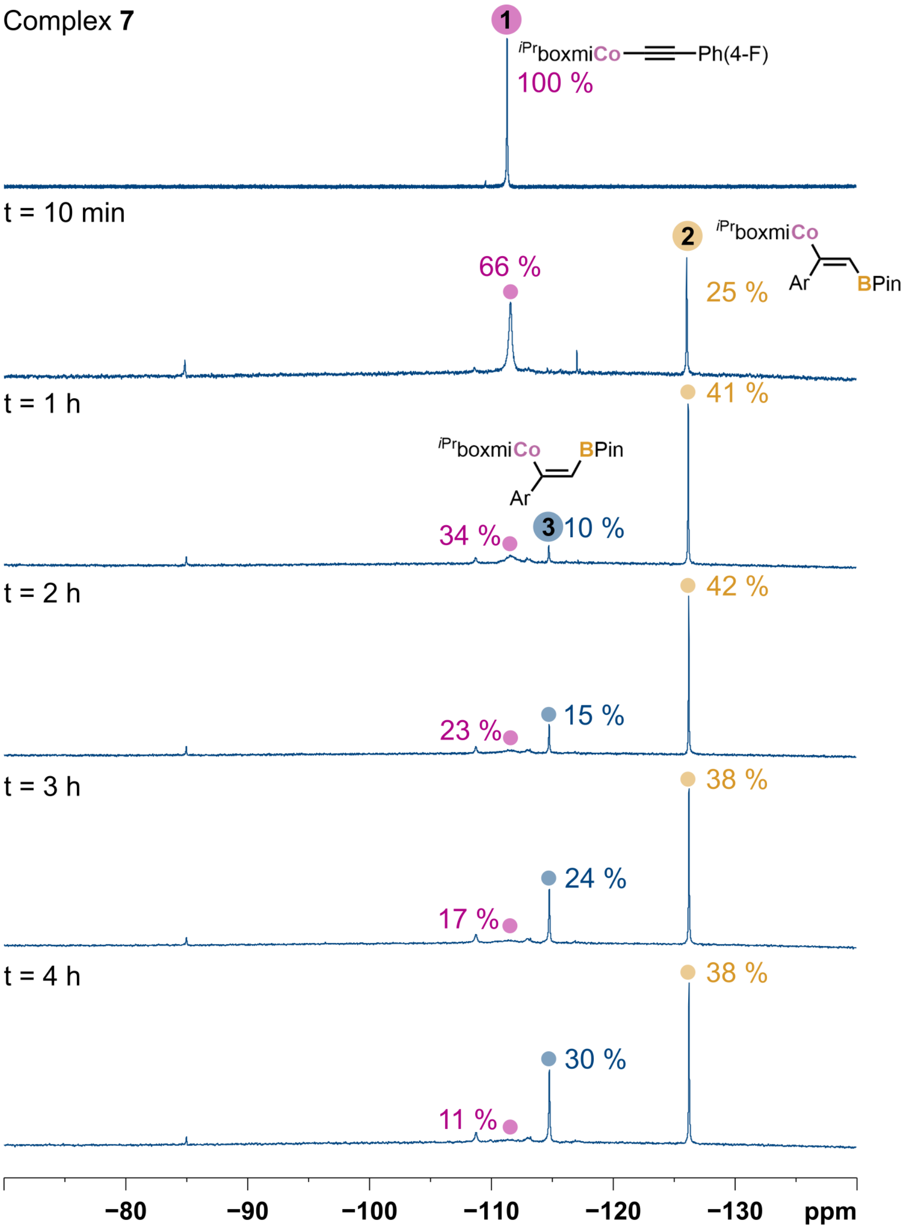

Figure S16: *In situ* ^{19}F NMR (C_6D_6, 376.2 MHz, 295 K) spectra for the reaction of complex **7** with pinacolborane.

3 UV/Vis Spectra

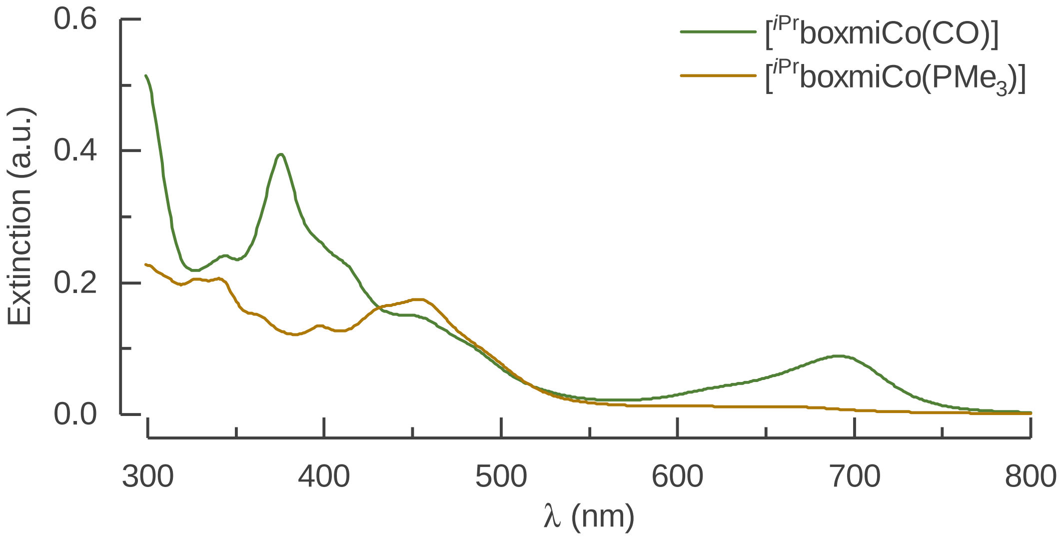

Figure S17: UV/Vis spectra of complexes [($^{i\mathrm{Pr}}$boxmi)Co(CO)] (**2**, 50.1 μM) and [($^{i\mathrm{Pr}}$boxmi)Co(PMe$_3$)] (**3**, 49.7 μM) in toluene.

4 DFT Calculations

Computational Details

All geometry optimizations and calculations were performed at the DFT level of theory using the Gaussian 09[3] program without any symmetry restrictions. The B3LYP exchange-correlation functional[4–6] combined with Ahlrichs def2-TZVP (for cobalt and nitrogen) and def2-SVP basis set[7,8] was employed. Frequency calculations at the same level of theory were performed to identify the optimized structures as stationary points.

Coordinates of optimized structures

63
(S,S)-[$^{i\mathrm{Pr}}$boxmiCo(CCPh(4-F))]

Co	0.49124	0.00006	0.00002
F	-8.23296	-0.00045	0.00178
O	1.20845	-3.90225	1.18446
O	1.20944	3.90179	-1.18573
N	0.46459	-1.92547	0.42181
N	2.48761	-0.00012	0.00029
N	0.46500	1.92543	-0.42256
C	-0.71232	-2.83507	0.36780
H	-1.56380	-2.33750	0.84403
C	-0.22574	-4.02851	1.20330
H	-0.56000	-3.97741	2.25294
H	-0.48977	-5.01225	0.79286
C	1.49025	-2.64409	0.80332
C	2.85854	-2.26757	0.82580
H	3.57209	-3.02283	1.14926
C	3.29395	-1.04144	0.39453
C	4.70878	-0.65213	0.26030
C	5.90428	-1.31976	0.52764
H	5.91188	-2.33451	0.93221
C	7.10578	-0.65203	0.26236
H	8.05697	-1.15118	0.46296
C	7.10599	0.65116	-0.25961
H	8.05734	1.15015	-0.45983
C	5.90471	1.31908	-0.52542
H	5.91264	2.33382	-0.92999
C	4.70900	0.65164	-0.25855
C	3.29428	1.04110	-0.39355
C	2.85922	2.26722	-0.82519
H	3.57302	3.02240	-1.14832
C	1.49094	2.64381	-0.80374
C	-0.22473	4.02803	-1.20569
H	-0.55827	3.97622	-2.25552
H	-0.48907	5.01204	-0.79609
C	-0.71188	2.83516	-0.36970
H	-1.56318	2.33736	-0.84601
C	-1.11281	-3.17231	-1.08908
H	-1.27450	-2.19387	-1.56893
C	-2.44929	-3.92549	-1.11549
H	-2.37573	-4.91438	-0.62986
H	-2.77756	-4.09932	-2.15250
H	-3.24152	-3.35508	-0.60536
C	-0.02692	-3.91505	-1.87718
H	0.92204	-3.35727	-1.89397
H	-0.34375	-4.05304	-2.92336
H	0.17594	-4.91899	-1.46701
C	-1.11300	3.17346	1.08677
H	-1.27495	2.19538	1.56726
C	-0.02742	3.91671	1.87481

H	0.92153	3.35895	1.89233
H	-0.34467	4.05533	2.92078
H	0.17559	4.92040	1.46411
C	-2.44946	3.92670	1.11202
H	-2.37572	4.91513	0.62546
H	-2.77807	4.10155	2.14875
H	-3.24152	3.35582	0.60217
C	-1.41528	0.00021	0.00014
C	-2.64722	0.00015	0.00035
C	-4.07938	0.00002	0.00070
C	-4.81154	-0.09053	1.20778
H	-4.26716	-0.15978	2.15183
C	-6.20624	-0.09079	1.21262
H	-6.77388	-0.15982	2.14300
C	-6.88891	-0.00029	0.00143
C	-6.20689	0.09035	-1.21011
H	-6.77503	0.15924	-2.14020
C	-4.81219	0.09040	-1.20600
H	-4.26832	0.15977	-2.15033

5 X-ray Crystal Structure Determinations

Crystal data and details of the structure determinations are compiled in Tables S1 and S2. Full shells of intensity data were collected at low temperature with an Agilent Technologies Supernova-E CCD diffractometer (Mo- or Cu-K_α radiation, microfocus X-ray tubes, multilayer mirror optics). Detector frames (typically ω-, occasionally φ-scans, scan width 0.5 or 1°) were integrated by profile fitting.[9,10] Data were corrected for air and detector absorption, Lorentz and polarization effects[10] and scaled essentially by application of appropriate spherical harmonic functions.[10,11,12] Absorption by the crystal was treated numerically (Gaussian grid).[13] An illumination correction was performed as part of the numerical absorption correction.[12] The structures were solved by ab initio dual space methods involving difference Fourier syntheses (VLD procedure, complex 6)[14] or by the charge flip procedure (all other complexes)[15] and refined by full-matrix least squares methods based on F^2 against all unique reflections.[16]

All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were input at calculated positions and refined with a riding model.[17] Split atom models were used to refine disordered groups and/or solvent molecules. When found necessary, suitable geometry and adp restraints were applied.[17,18]

CCDC 2056218-2056224 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre's and FIZ Karlsruhes joint Access Service *via*:

https://www.ccdc.cam.ac.uk/structures/?.

Table S1: Details of the crystal structure determinations of compounds **2**, **3**, **4** and **5a**.

Compound	**2**	**3**	**4**	**5a**
Deposition number, CCDC	2056218	2056219	2056220	2056221
Empirical formula	$C_{23}H_{26}CoN_3O_3$	$C_{25}H_{35}CoN_3O_2P$	$C_{22}H_{26}CoIN_3O_2$	$C_{26}H_{35}CoN_3O_3$
Formula weight M_r /g·mol^{-1}	451.40	499.46	550.29	496.50
Crystal system	orthorombic	monoclinic	monoclinic	monoclinic
Space group	$P\,2_1\,2_1\,2_1$ (IT Nr. 19)	$P\,2_1$ (IT Nr. 4)	$P\,2_1$ (IT Nr. 4)	$P\,2_1$ (IT Nr. 4)
a /Å	6.15132(13)	9.30263(12)	11.83518(11)	10.37052(17)
b /Å	19.7189(3)	8.28334(8)	11.45668(12)	14.5624(2)
c /Å	52.8650(9)	16.9709(2)	16.88113(15)	16.5891(4)
β /°		103.2244(13)	102.3353(9)	90.6321(17)
V /Å^3	6412.4(2)	1273.05(3)	2236.10(4)	2505.12(8)
Z	12	2	4	4
F_{000}	2832	528	1100	1052
d_c /Mg·m^{-3}	1.403	1.303	1.635	1.316
X-radiation, λ /Å	Cu-K_α, 1.54184	Mo-K_α, 0.71073	Mo-K_α, 0.71073	Cu-K_α, 1.54184
μ /mm^{-1}	6.534	0.762	2.170	5.619
Transmissions factors: max, min	0.969, 0.579	1.000, 0.618	1.000, 0.811	0.875, 0.555
Data collect. temp. /K	120 (1)	120(1)	120(1)	120(1)
θ range for data collection /°	2.4 to 71.4	2.2 to 34.2	2.2 to 34.2	2.7 to 71.8
Index ranges h, k, l	$-7\ldots7$, $-24\ldots23$, $-64\ldots64$	$-14\ldots14$, $-13\ldots13$, $-26\ldots26$	$-18\ldots18$, $-17\ldots17$, $-26\ldots26$	$-12\ldots12$, $-17\ldots17$, $-19\ldots20$
Reflections measured	214059	83617	120221	74573
Independent refl. [R_{int}]	12326 [0.127]	10215 [0.052]	17938 [0.049]	9574 [0.047]
Observed refl. [$I \geq 2\sigma(I)$]	9951	9672	16530	8483
Data / restraints / parameters	12326 / 0 / 823	10215 / 1 / 296	17938 / 1 / 531	9574 / 179 / 684
GooF on F^2	1.098	1.044	1.043	1.016
R [$F > 4\sigma(F)$], $R(F)$, $wR(F^2)$	0.0611, 0.1108	0.0281, 0.0650	0.0271, 0.0505	0.0367, 0.0836
R (all data) $R(F)$, $wR(F^2)$	0.0818, 0.1190	0.0309, 0.0662	0.0318, 0.0522	0.0448, 0.0879
Absolute structure parameter	$-0.0274(19)$	$-0.009(3)$	$-0.024(5)$	$-0.0316(14)$
Diff. density: rms, max, min / $e \cdot$ Å^{-3}	0.077, 0.642, -0.645	0.050, 0.402, -0.265	0.074, 0.745, -0.442	0.039, 0.314, -0.322

Table S2: Details of the crystal structure determinations of compounds **5b**, **6** and **7**.

Compound	**5b**	**6**	**7**
Deposition number, CCDC	2056222	2056223	2056224
Empirical formula	$C_{25}H_{35}CoN_3O_3Si$	$C_{28}H_{31}CoN_3O_2S$	$C_{30}H_{30}CoFN_3O_2$
Formula weight M_r /g·mol^{-1}	512.58	532.55	542.50
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P\,2_1$ (IT Nr. 4)	$P\,2_1$ (IT Nr. 4)	$P\,2_1$ (IT Nr. 4)
a /Å	10.4793(2)	10.46816(18)	12.2841(2)
b /Å	14.5506(3)	10.86892(15)	6.01267(11)
c /Å	16.9441(4)	11.73210(18)	17.8300(3)
β /°	91.139(2)	91.3805(16)	100.4658(19)
V /Å^3	2583.14(11)	1334.46(4)	1295.02(4)
Z	4	2	2
F_{000}	1084	558	566
d_c /Mg·m^{-3}	1.318	1.325	1.391
X-radiation, λ /Å	Cu-K_α, 1.54184	Cu-K_α, 1.54184	Mo-K_α 0.71073
μ /mm^{-1}	5.895	6.000	0.703
Transmissions factors: max, min	1.000, 0.548	1.000, 0.513	1.000, 0.667
Data collect. temp. /K	120 (1)	120(1)	120 (1)
θ range for data collection /°	2.6 to 71.1	3.8 to 71.3	2.2 to 34.2
Index ranges h, k, l	−12...12, −17...17, −20...20	−12...10, −13...13, −14...14	−19...19, −9...9, −27...27
Reflections measured	60453	56927	44394
Independent refl. [R_{int}]	9887 [0.078]	5132 [0.069]	10195 [0.053]
Observed refl. [$I \geq 2\sigma(I)$]	7831	4614	8776
Data / restraints / parameters	9887 / 1 / 609	5132 / 1 / 320	10195 / 1 / 338
GooF on F^2	1.028	1.038	1.046
R [$F > 4\sigma(F)$], $R(F)$, $wR(F^2)$	0.0470, 0.1033	0.0328, 0.0730	0.0403, 0.0748
R (all data) $R(F)$, $wR(F^2)$	0.0674, 0.1131	0.0410, 0.0764	0.0532, 0.0801
Absolute structure parameter	−0.029(2)	−0.030(2)	−0.013(6)
Diff. density: rms, max, min / $e \cdot$ Å^{-3}	0.053, 0.476, -0.538	0.045, 0.349, −0.451	0.065, 0.506, −0.402

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