Making Base-Assisted C-H Bond Activation by Cp*Co(III) Effective: A Noncovalent Interaction-Inclusive Theoretical Insight and Experimental Validation.

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Supplementary Material

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1. NMR Spectra of iodocobaltacycles and [Cp*(L-κ^2-*C,N*)CoI][$BArF_{24}$]

*NMR spectra of Iodo(pentamethylcyclopentadienyl)(2-phenylenepyridine-κ^2-C,N) cobalt (III) (**1a**)*

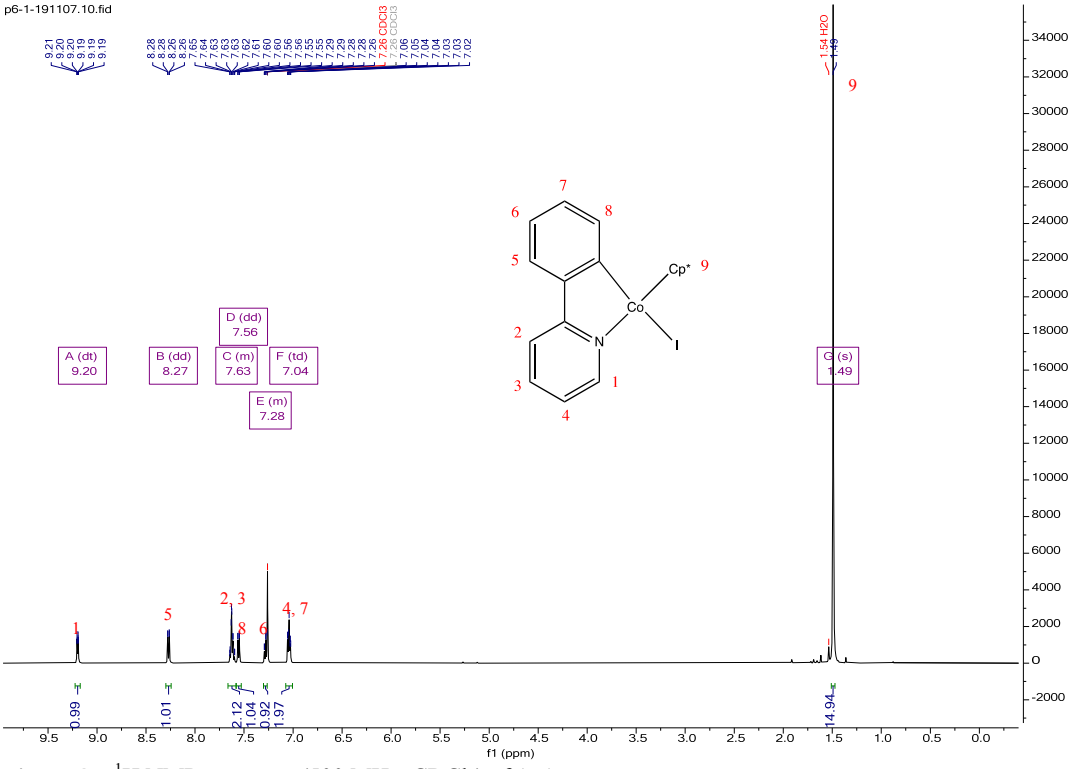


Figure S1. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **(1a)**

Figure S2. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **(1a)**

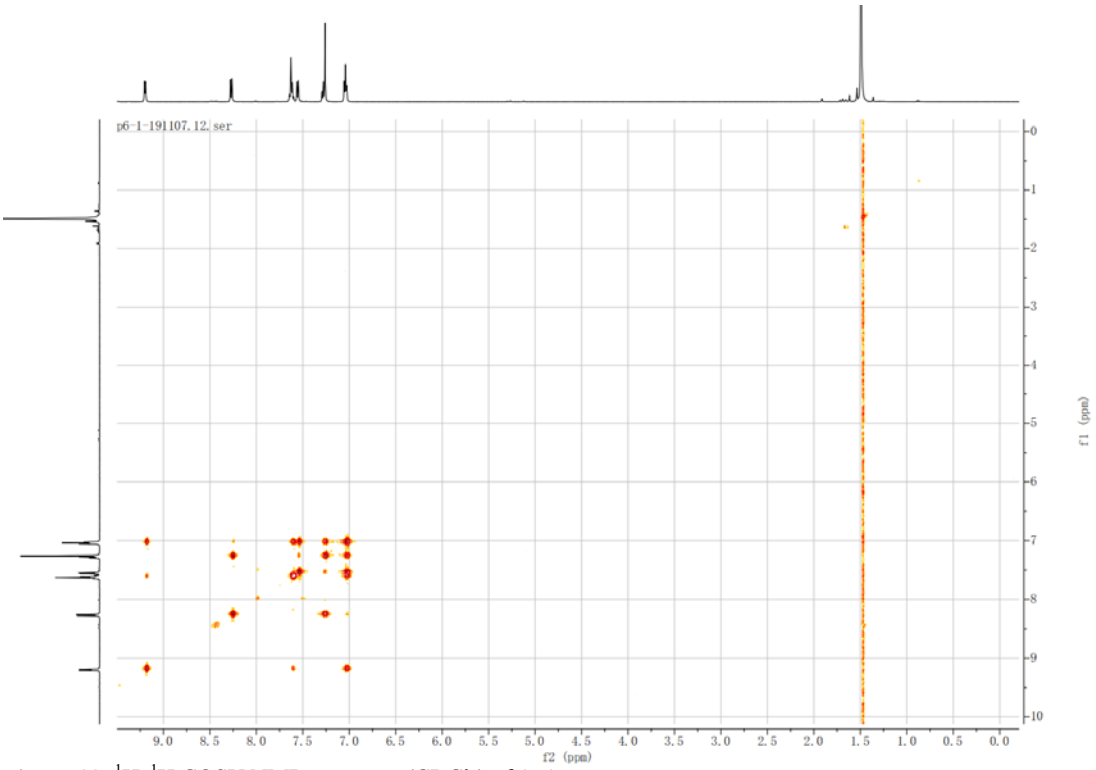


Figure S3. ^{1}H, ^{1}H COSY NMR spectrum ($CDCl_3$) of **(1a)**

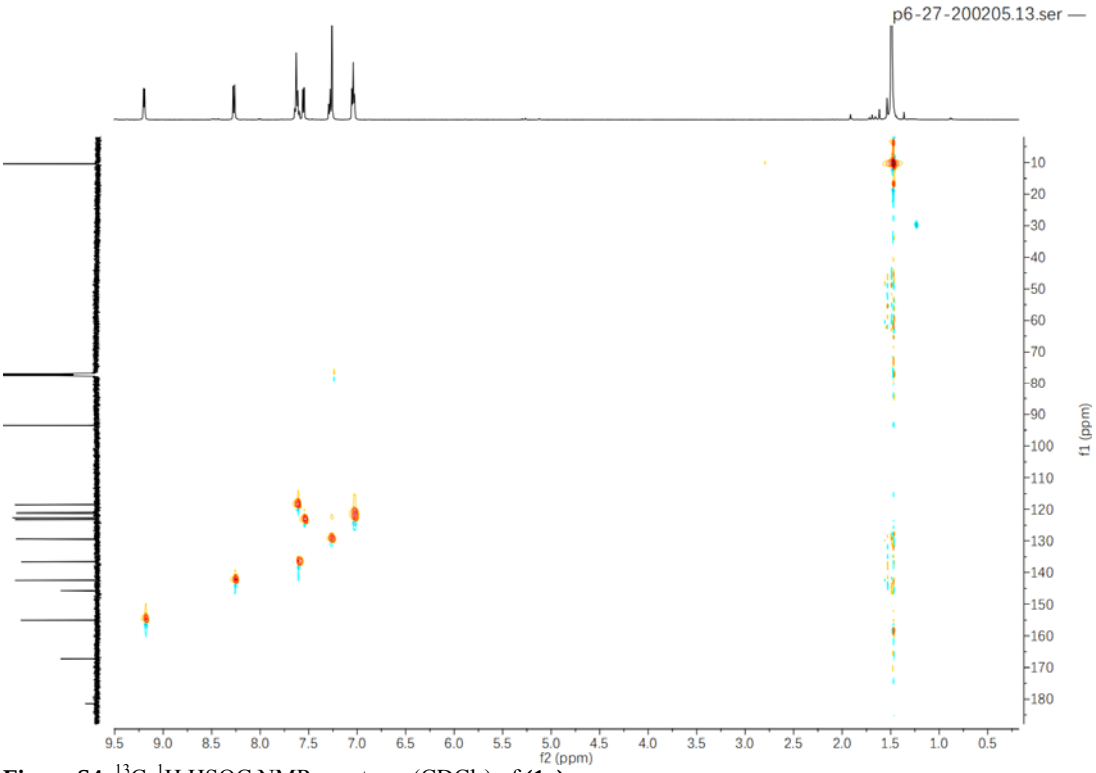


Figure S4. ^{13}C, ^{1}H HSQC NMR spectrum ($CDCl_3$) of **(1a)**

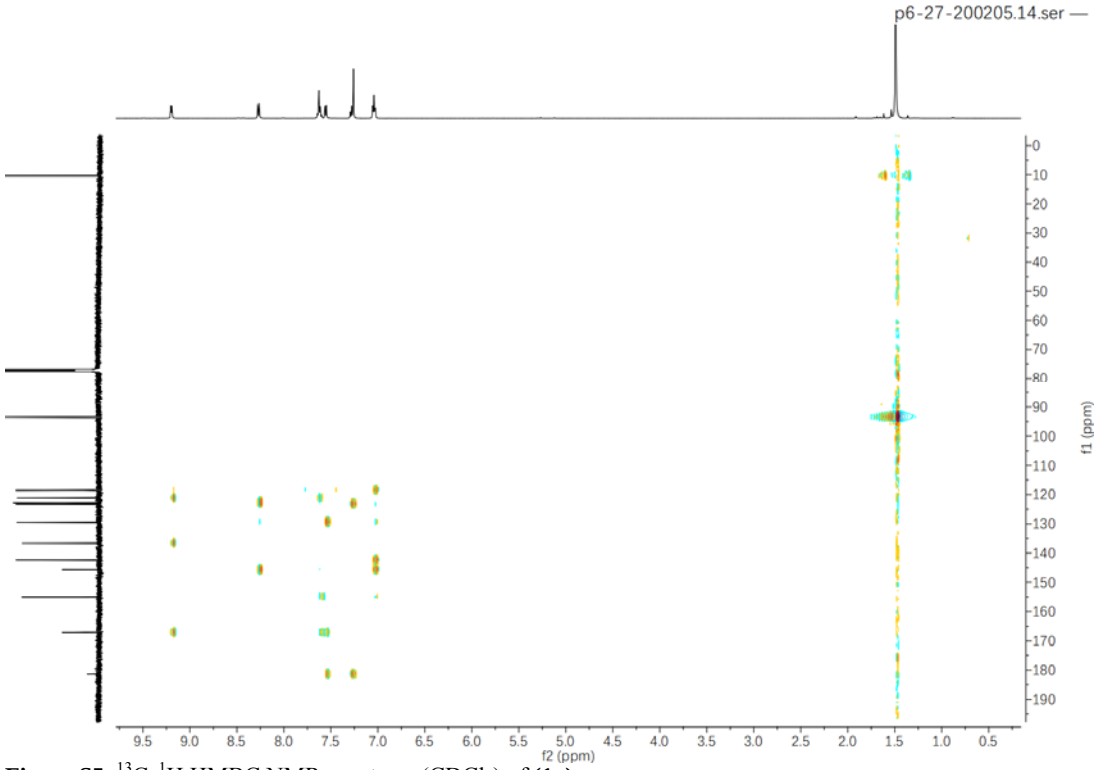


Figure S5. ^{13}C, ^{1}H HMBC NMR spectrum ($CDCl_3$) of **(1a)**

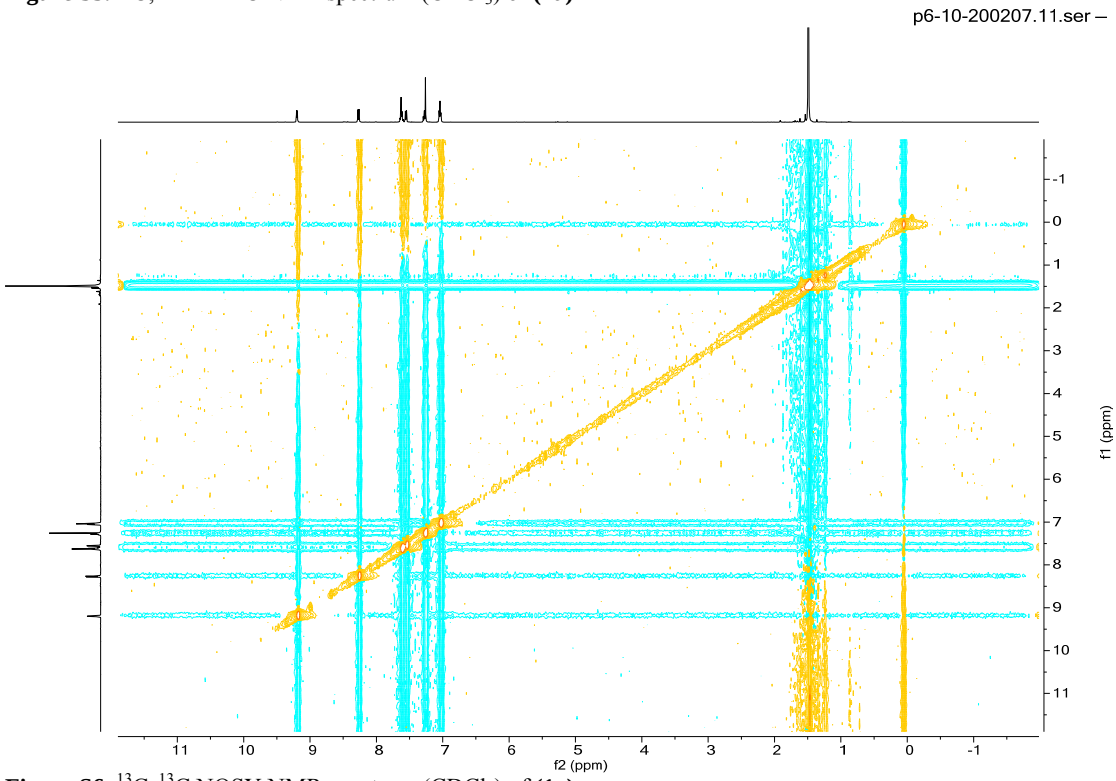


Figure S6. ^{13}C, ^{13}C NOSY NMR spectrum ($CDCl_3$) of **(1a)**

NMR spectra of Iodo[2-(2-methylphenylene)pyridine-κ²-C,N](pentamethylcyclopentadienyl)cobalt (III) (3a)

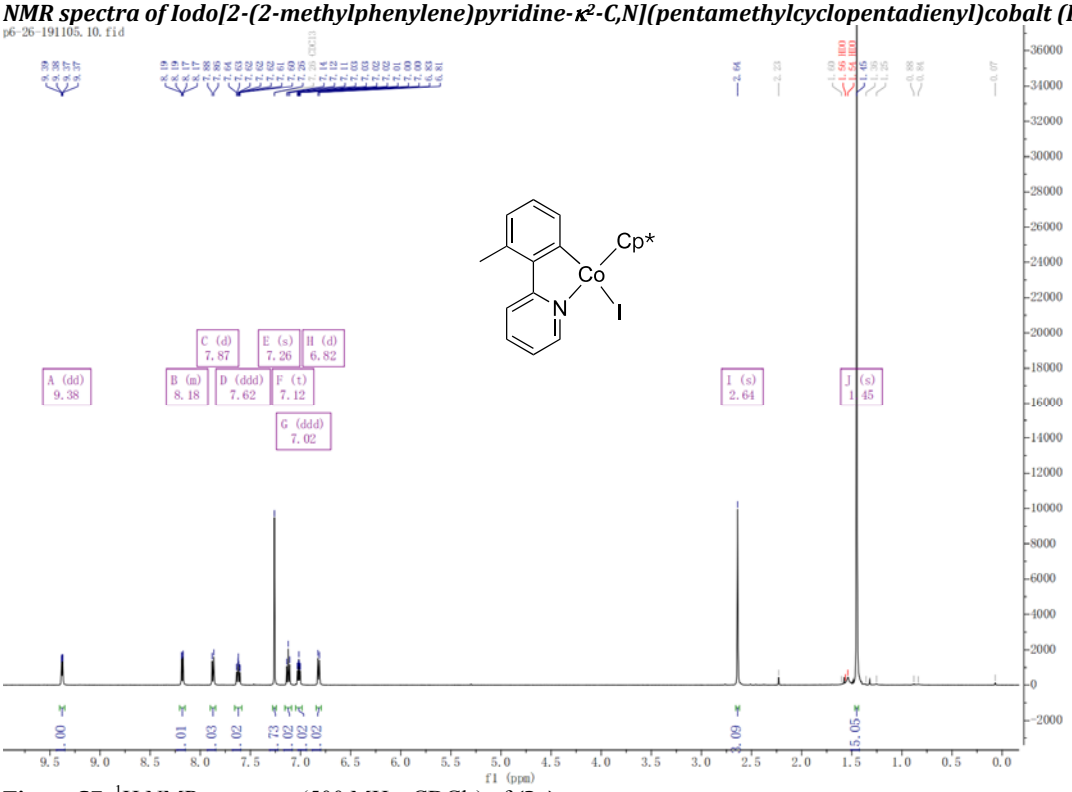


Figure S7. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **(3a)**

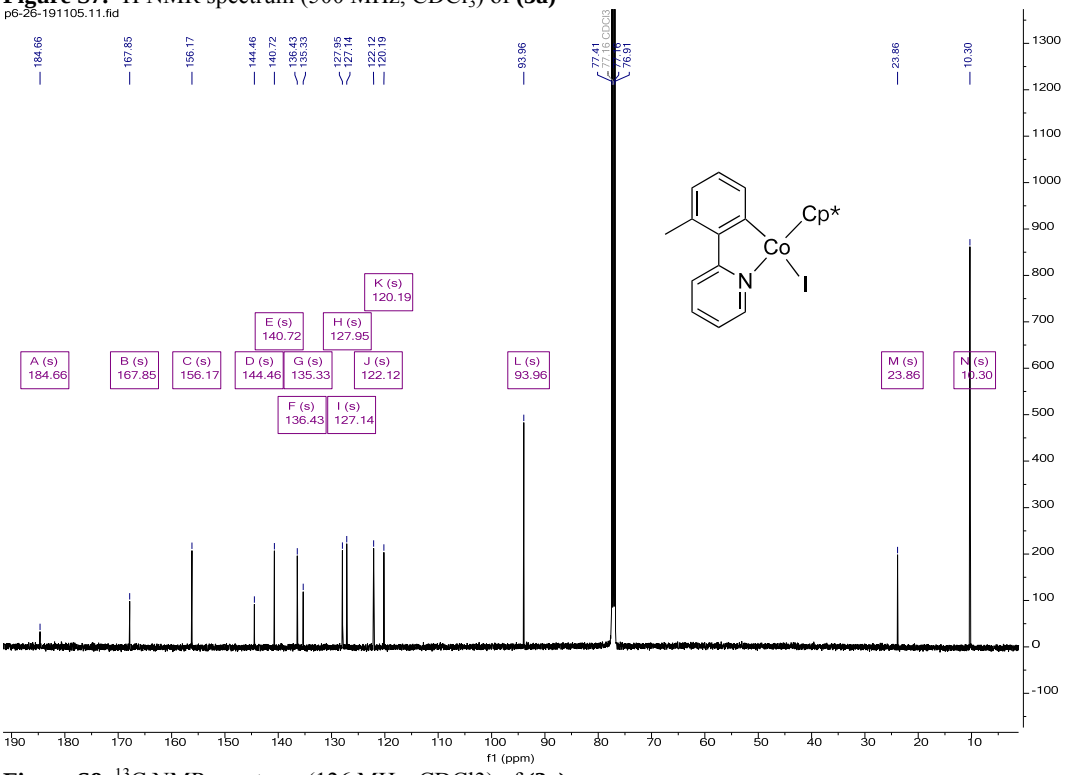


Figure S8. ^{13}C NMR spectrum (126 MHz, CDCl3) of **(3a)**

NMR spectra of Iodo(pentamethylcyclopentadienyl)[4-tertiobutyl,2-(4-N,N-dimethylaminophenylene)pyridine-κ²-C,N]cobalt (III) (4a)

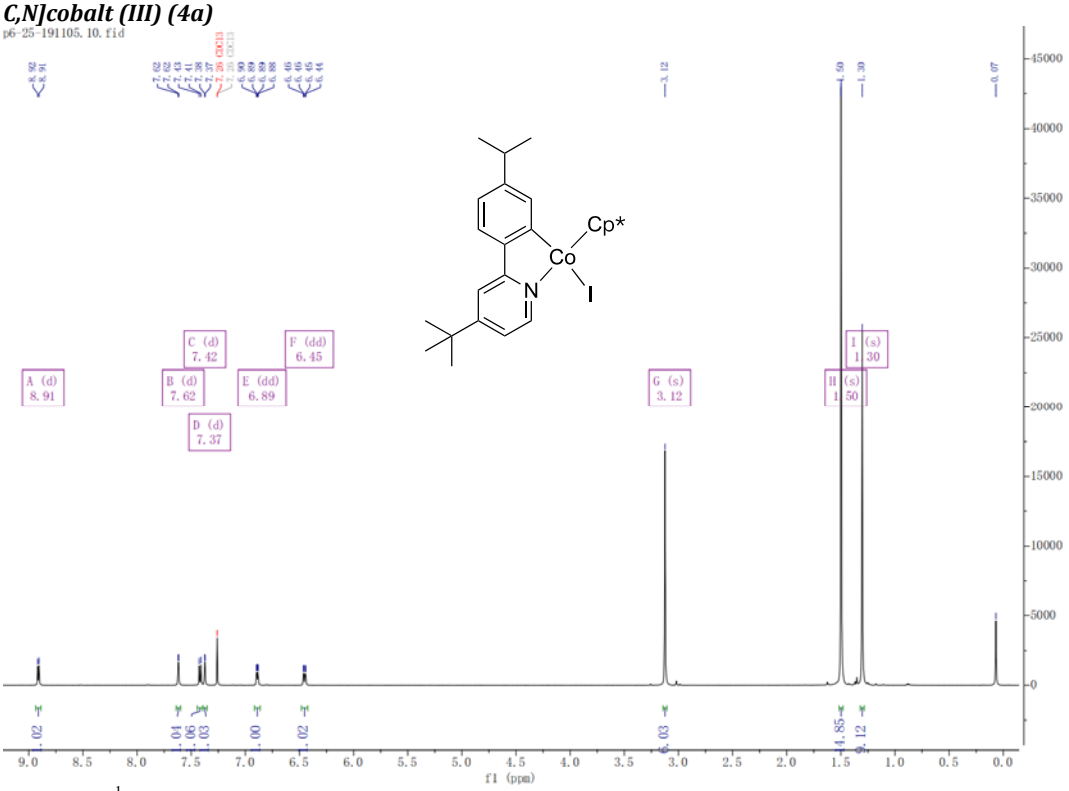


Figure S9. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **(4a)**

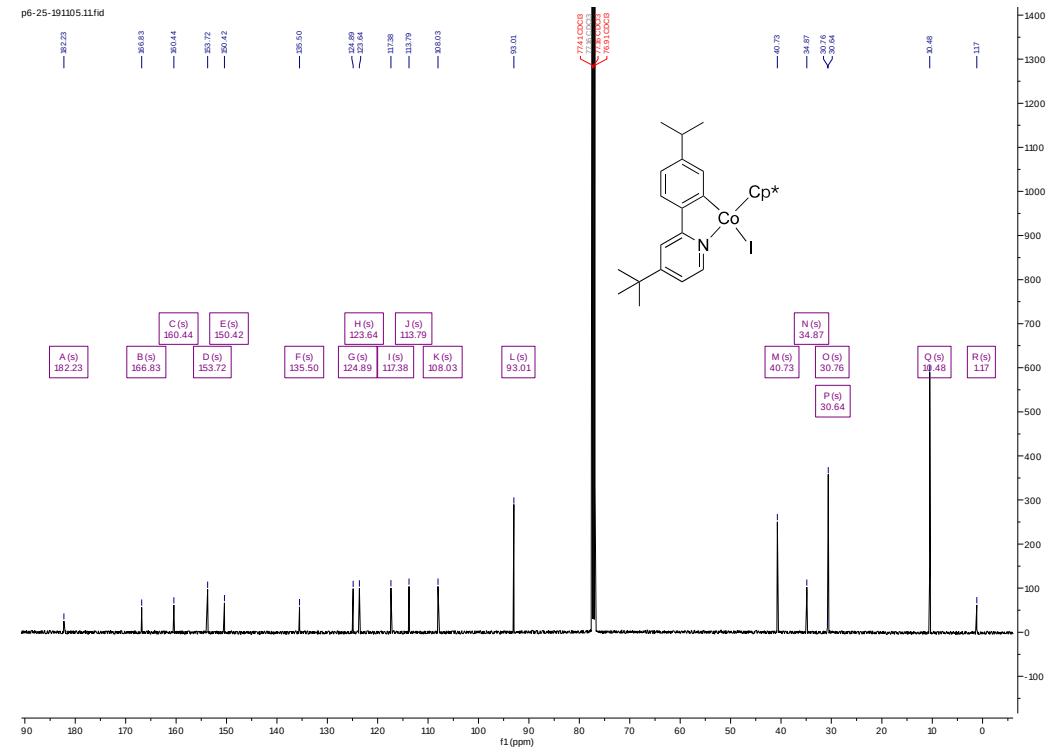


Figure S10. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **(4a)**

NMR spectra of (benzo[h]quinolynyl-κ²-C,N)iodo(pentamethylcyclopentadienyl)cobalt (III) (5a)

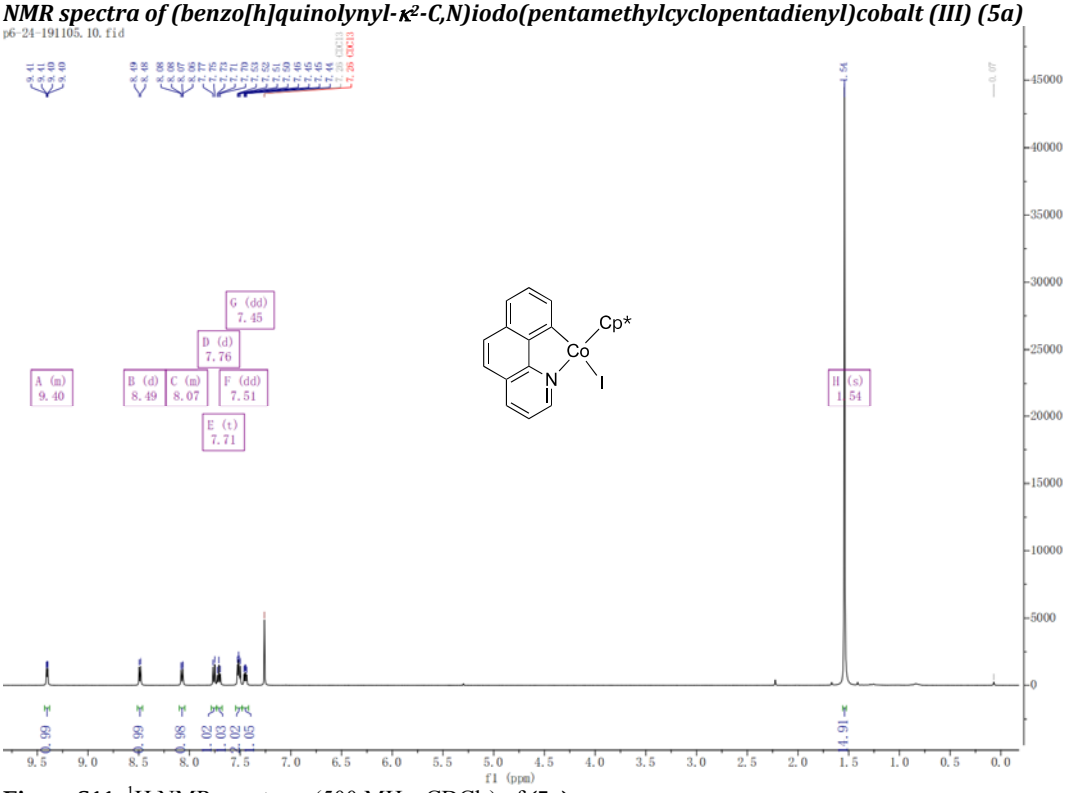


Figure S11. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **(5a)**

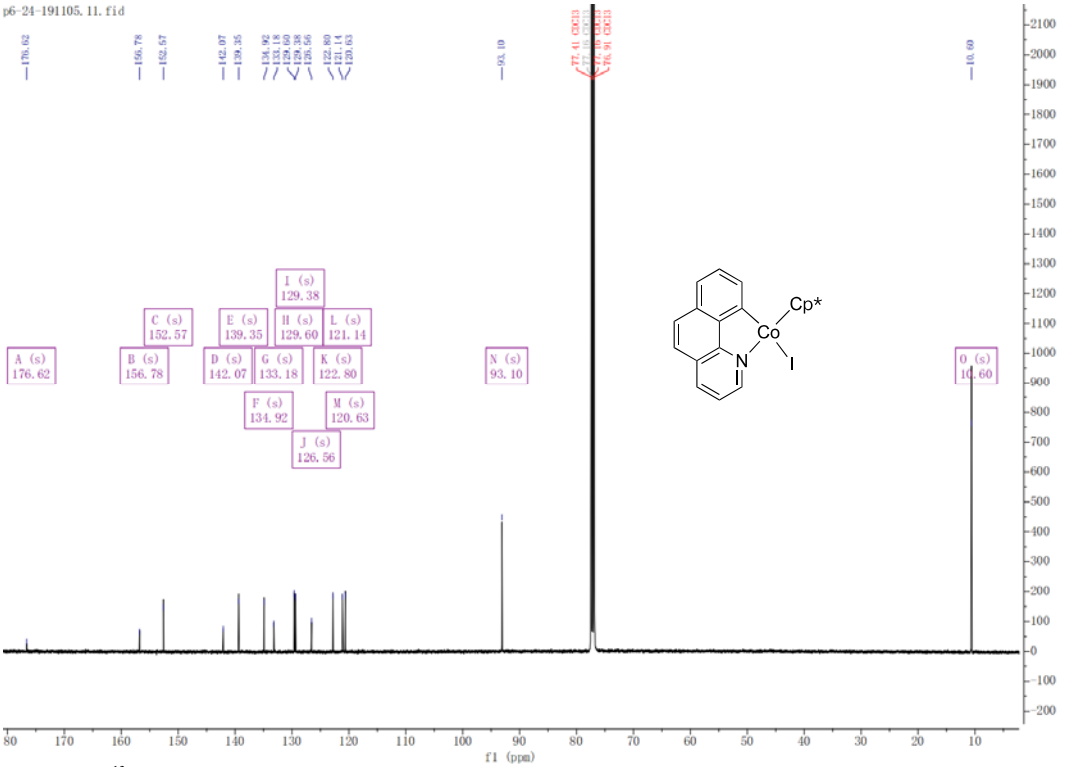


Figure S12. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **(5a)**

NMR spectra of Acetonitrilo(pentamethylcyclopentadienyl)(2-phenylenepyridine-κ²-C,N) cobalt (III) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (1b)

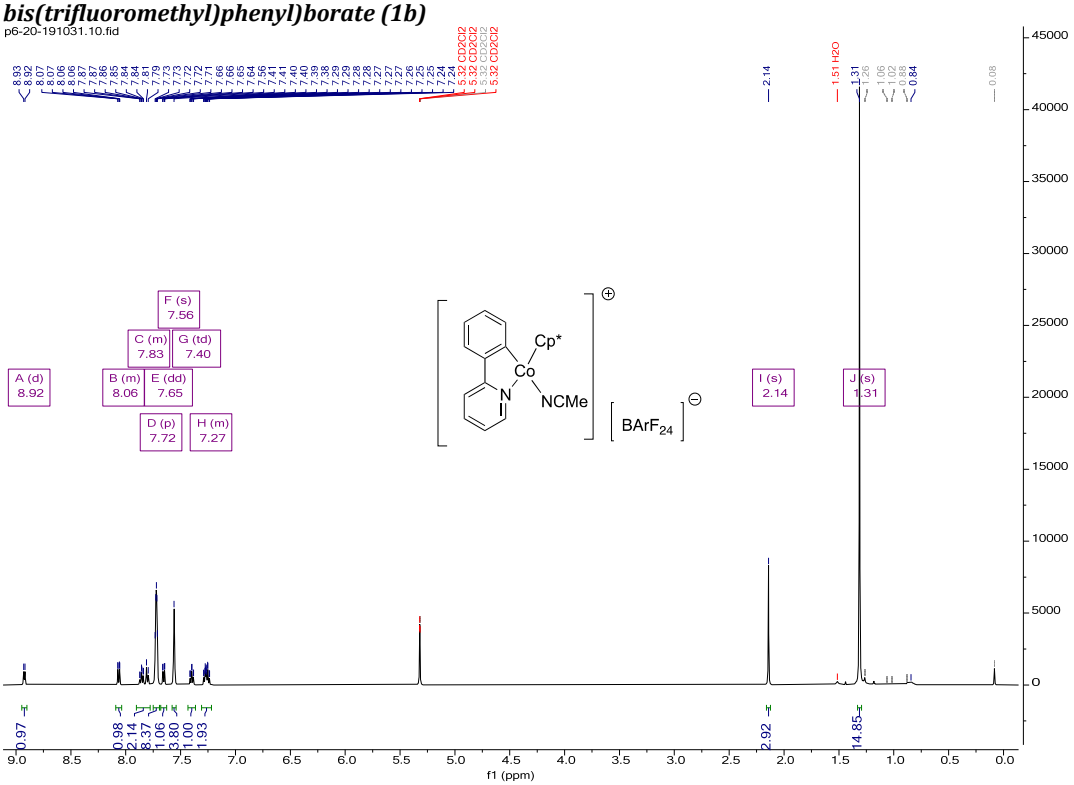


Figure S13. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of **(1b)**

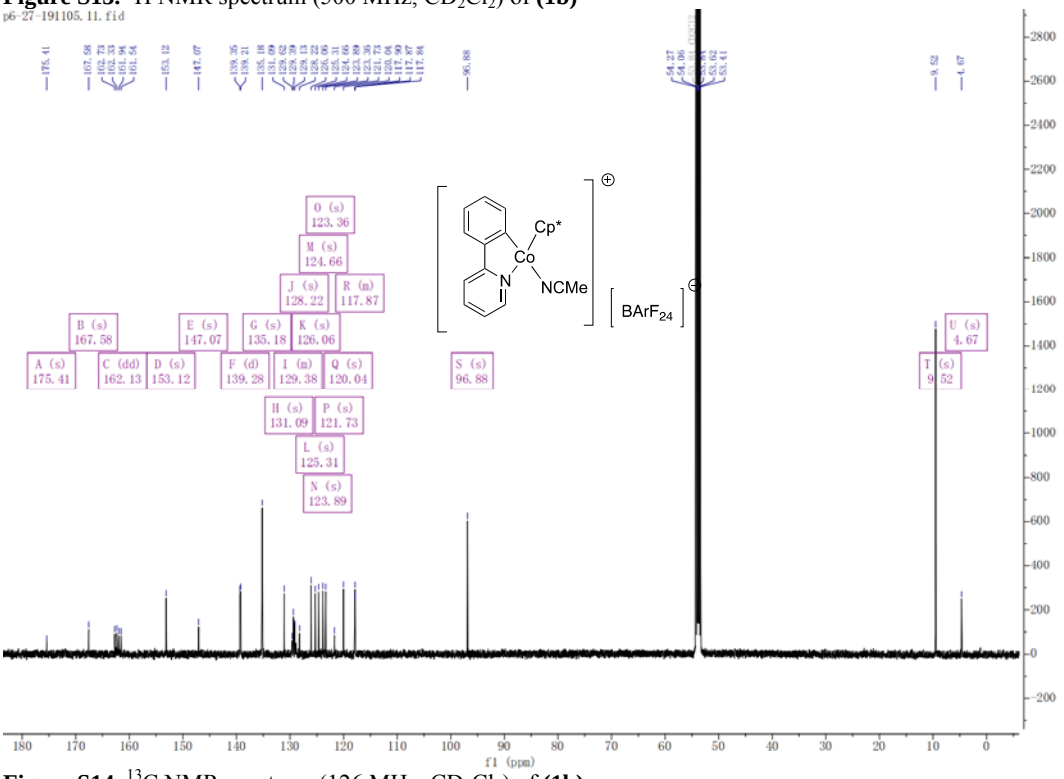


Figure S14. ^{13}C NMR spectrum (126 MHz, CD_2Cl_2) of **(1b)**

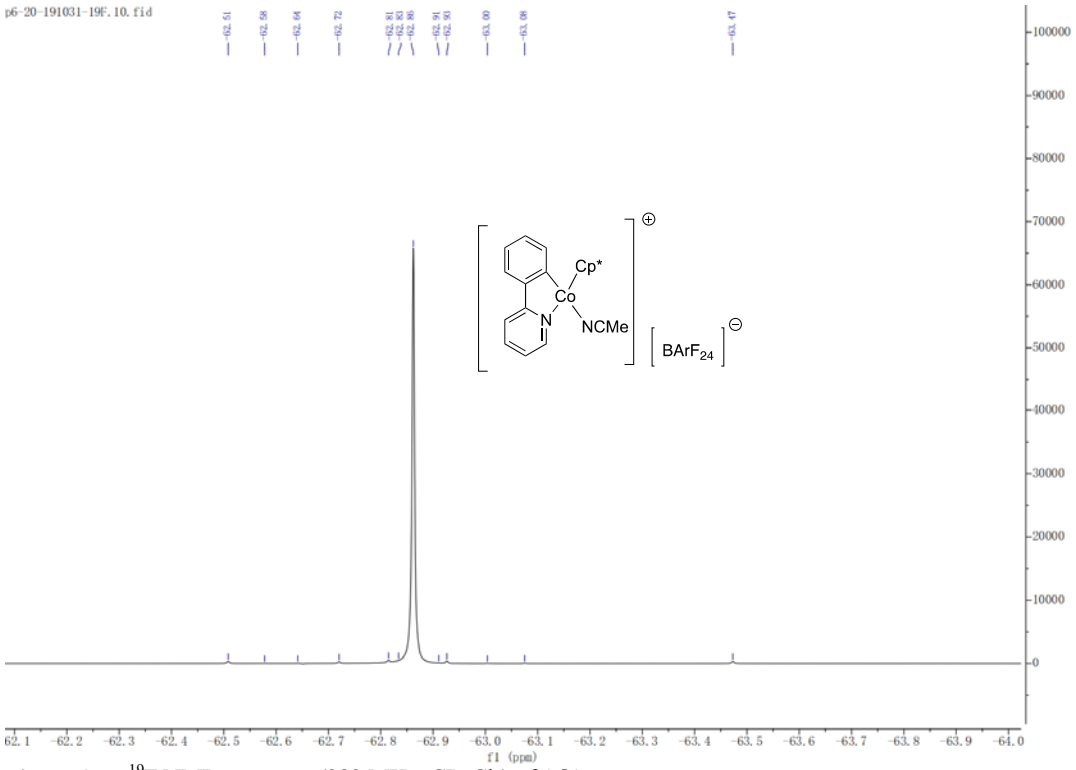


Figure S15. ^{19}F NMR spectrum (282 MHz, CD_2Cl_2) of **(1b)**

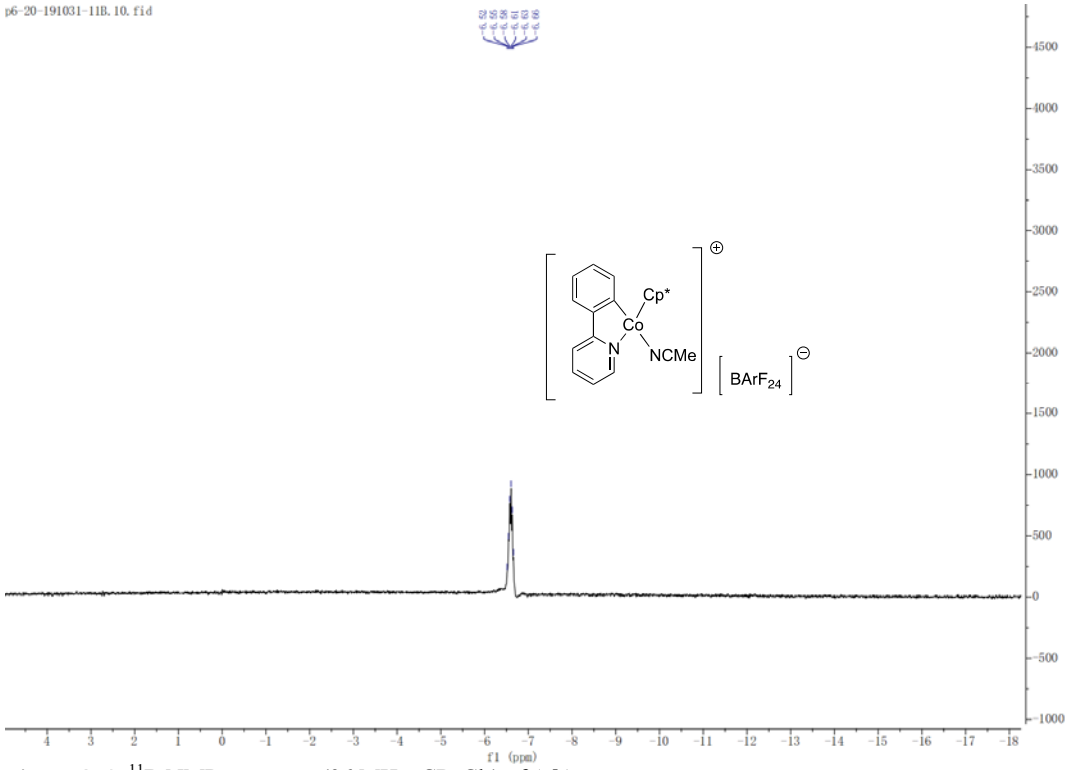


Figure S16. ^{11}B NMR spectrum (96 MHz, CD_2Cl_2) of **(1b)**

NMR spectra of Acetonitrilo[2-(2-methylphenylene)pyridine-κ²-C,N](pentamethylcyclopentadienyl)cobalt (III) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (3b)

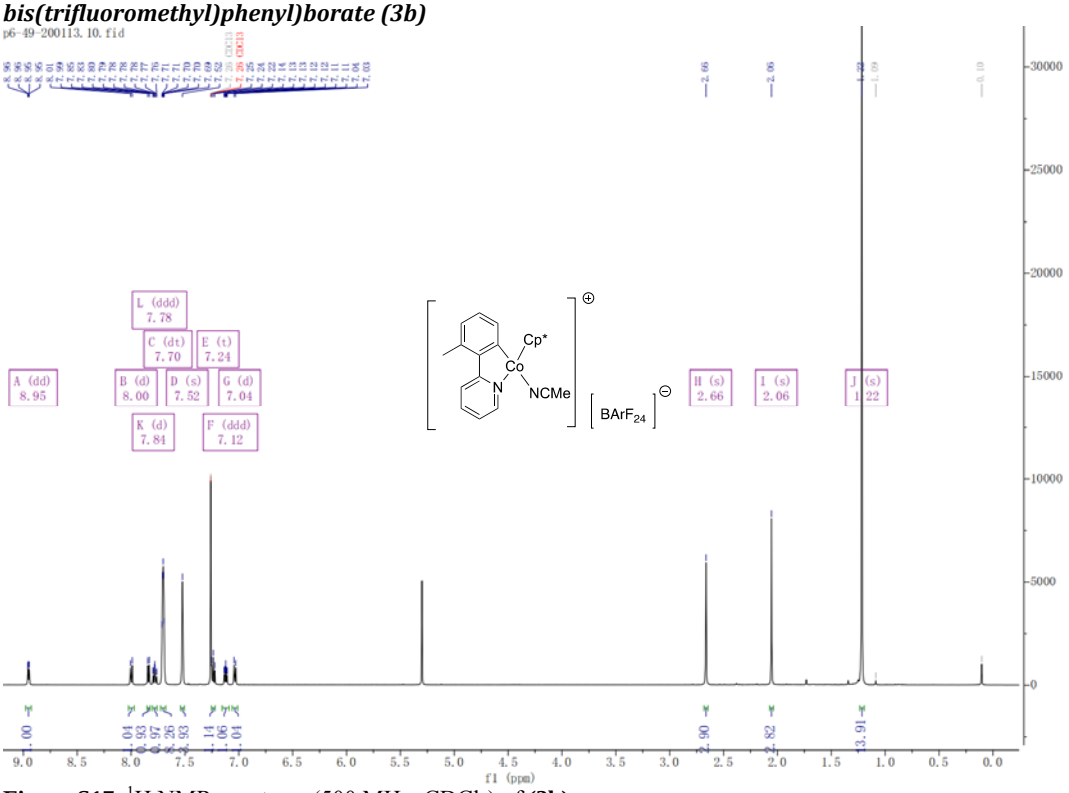


Figure S17. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **(3b)**

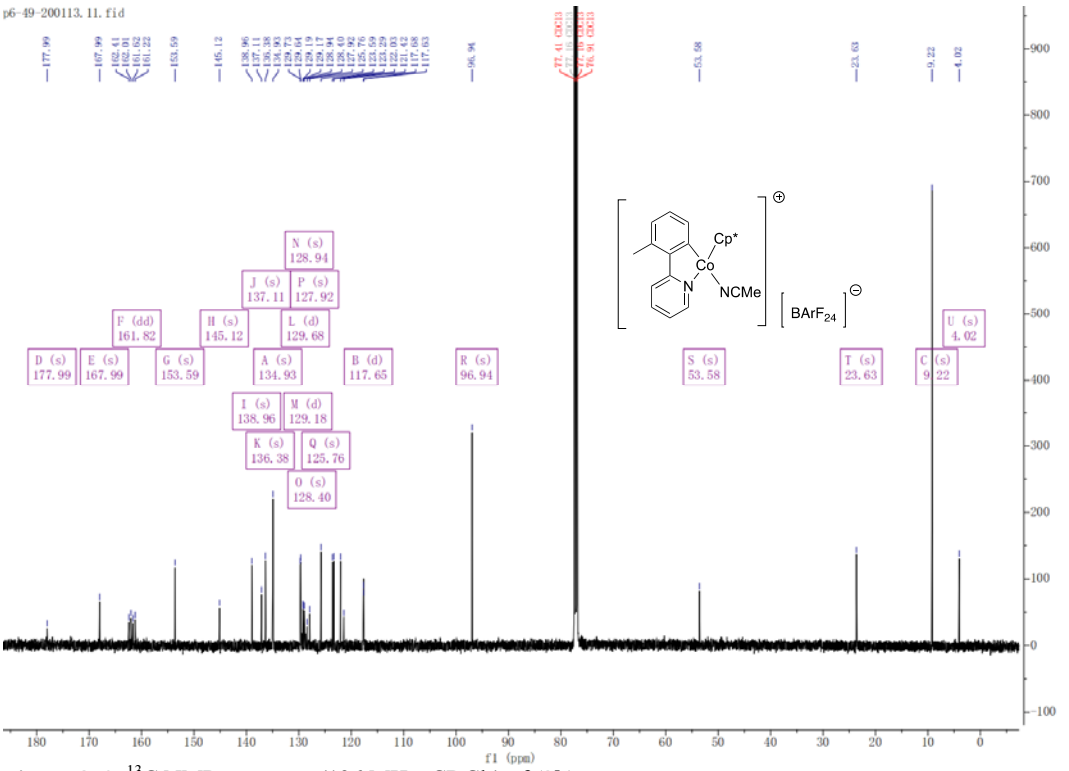


Figure S18. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **(3b)**

Figure S19. ^{19}F NMR spectrum (282 MHz, $CDCl_3$) of **(3b)**

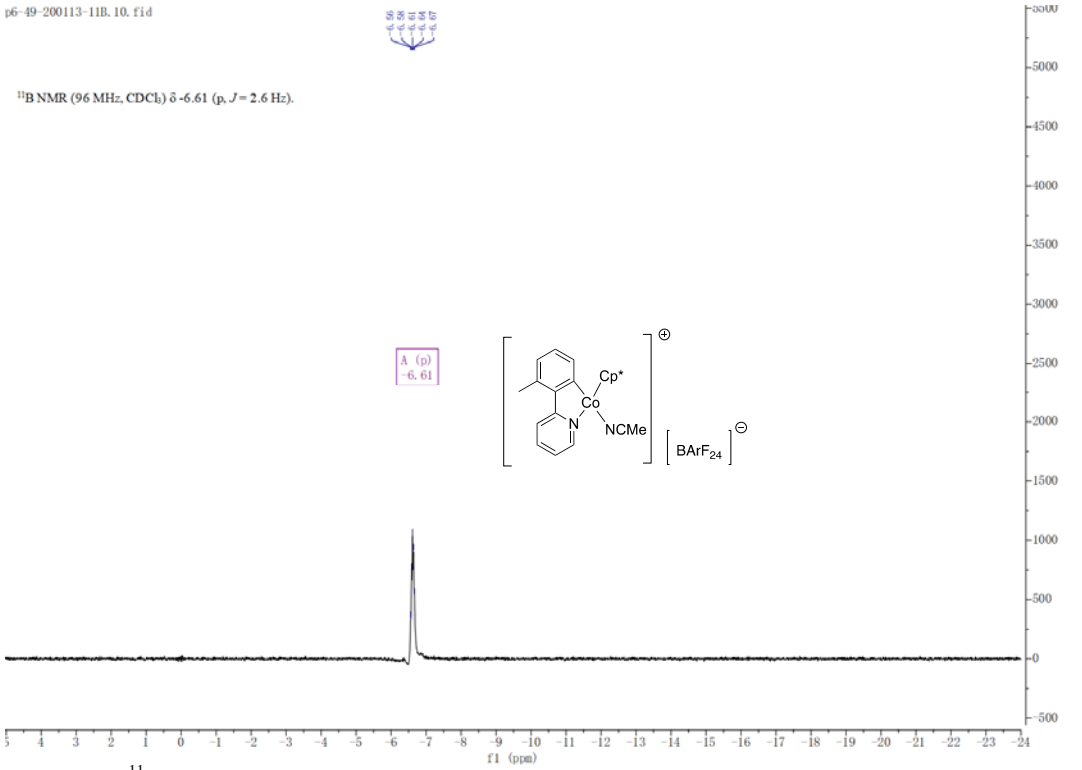


Figure S20. ^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **(3b)**

NMR spectra of Acetonitrilo[4-tertiobutyl,2-(4-N,N-dimethylaminophenylene)pyridine-κ²-C,N](pentamethylcyclopentadienyl)cobalt (III) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (4b)

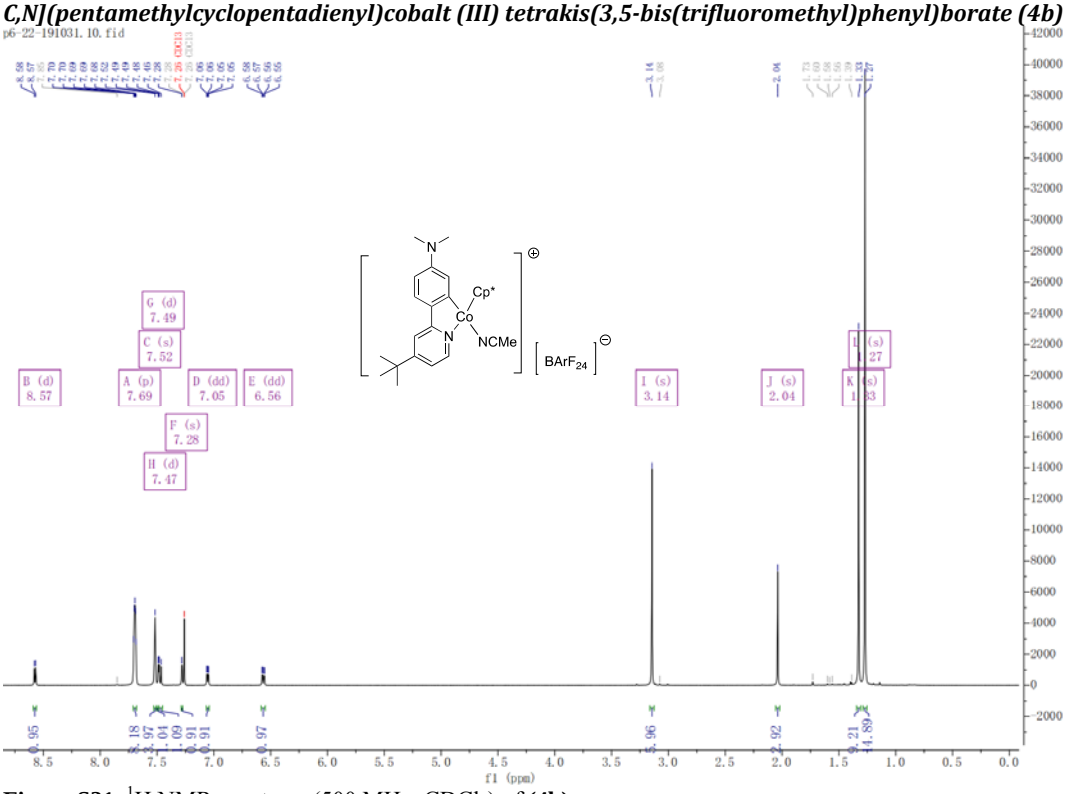


Figure S21. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **(4b)**

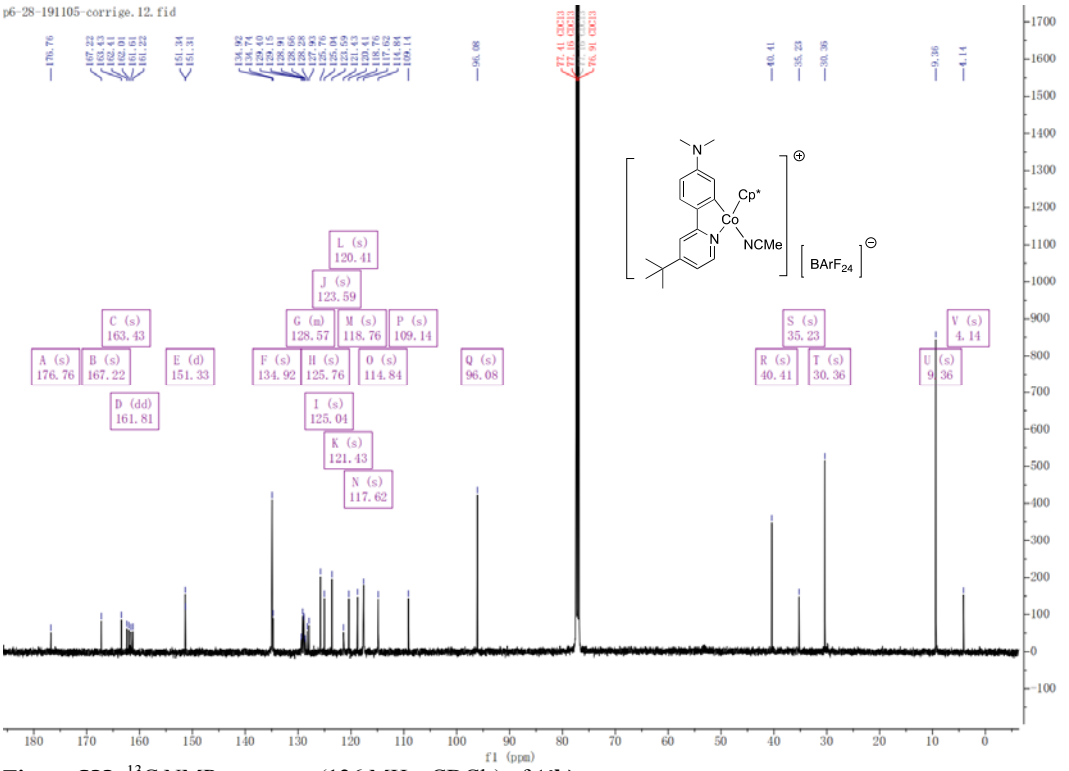


Figure S22. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **(4b)**

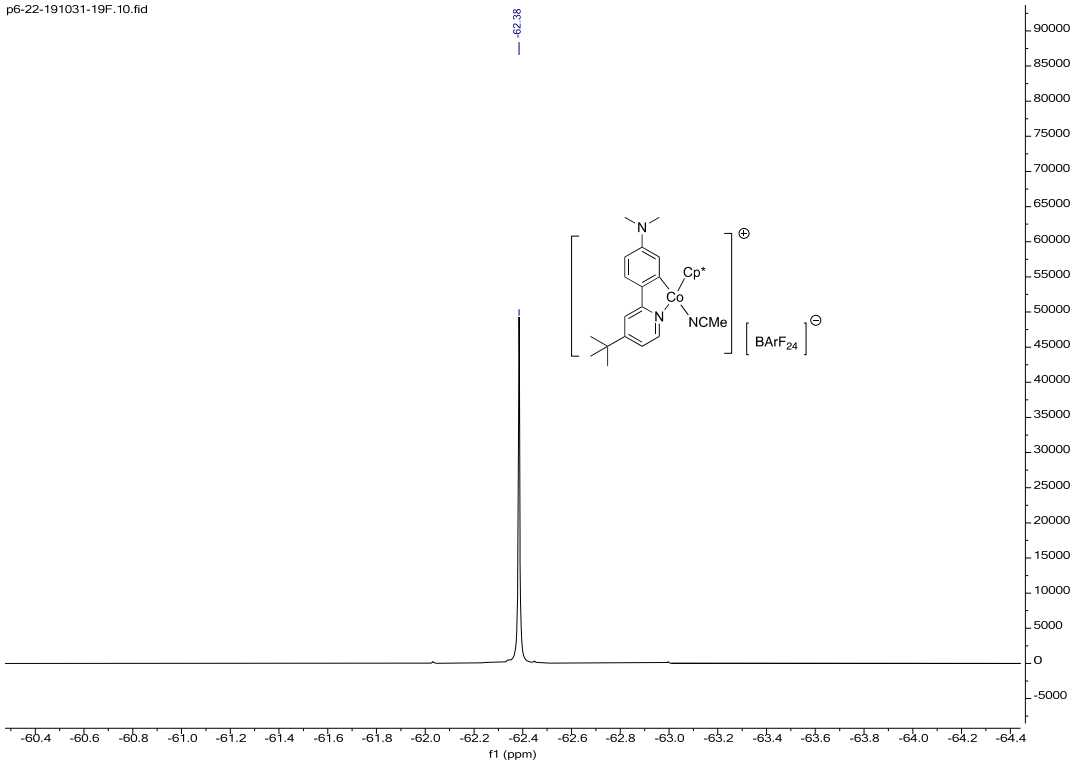


Figure S23. ^{19}F NMR spectrum (282 MHz, $CDCl_3$) of **(4b)**

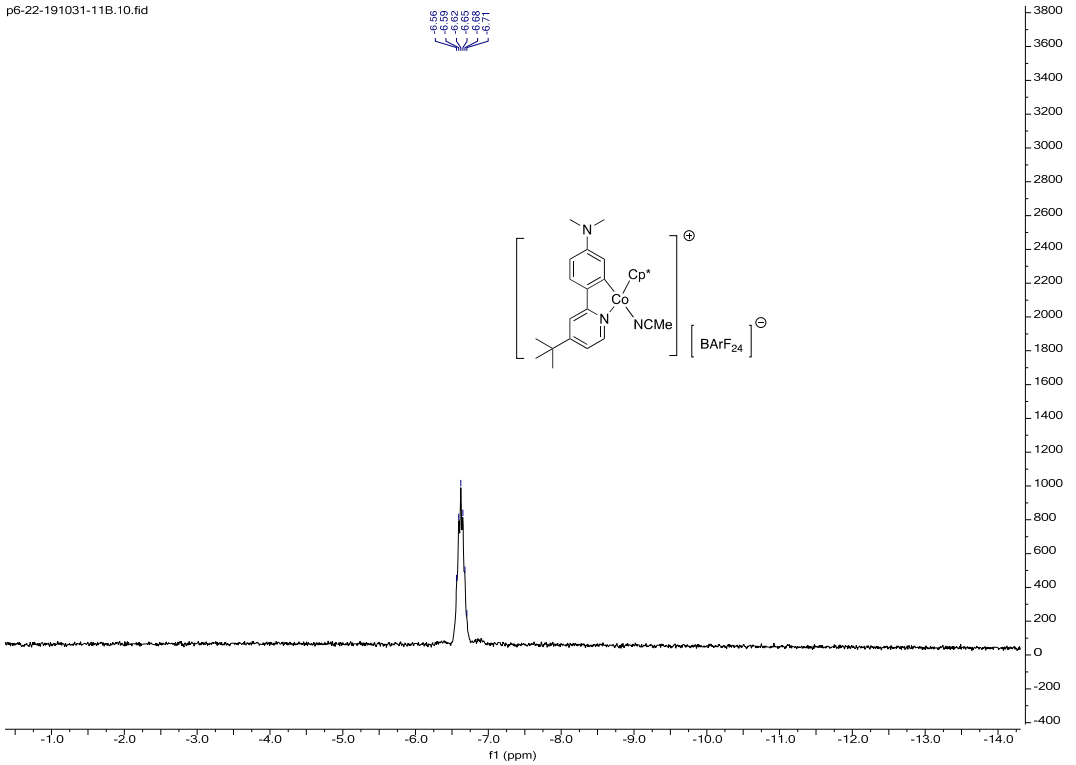


Figure S24. ^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **(4b)**

NMR spectra of Acetonitrilo[benzo[h]quinolynyl-κ²-C,N](pentamethylcyclopentadienyl)cobalt (III) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (5b)

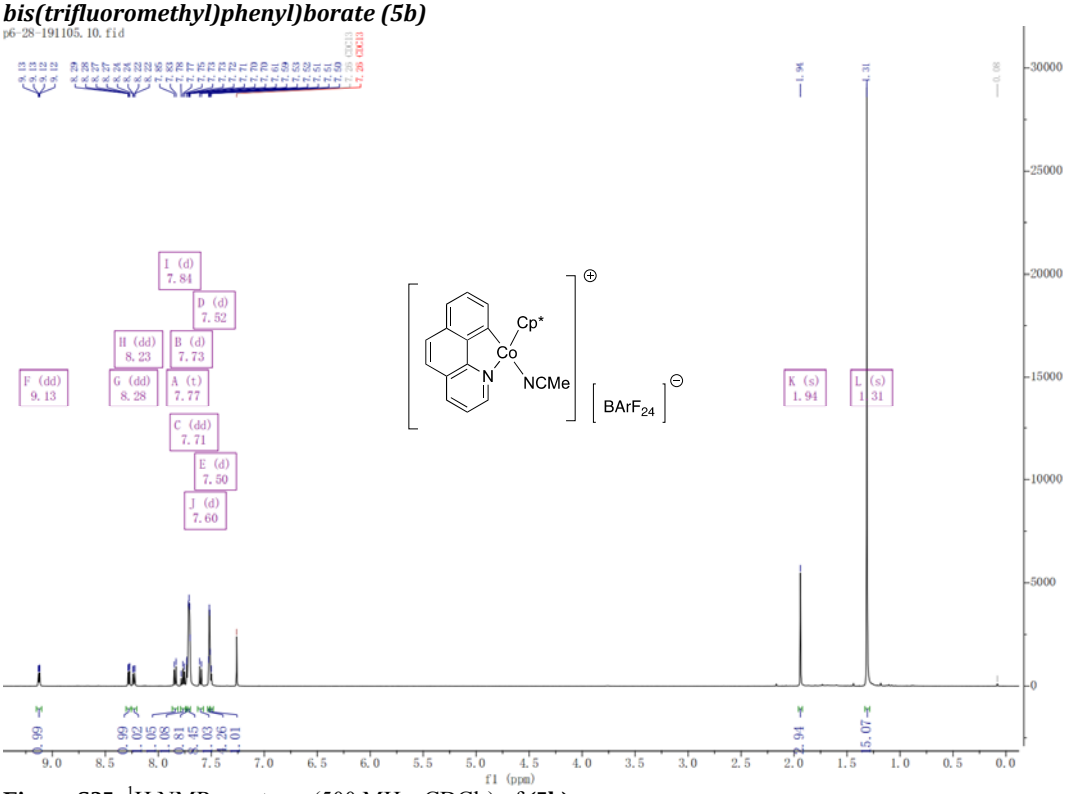


Figure S25. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **(5b)**

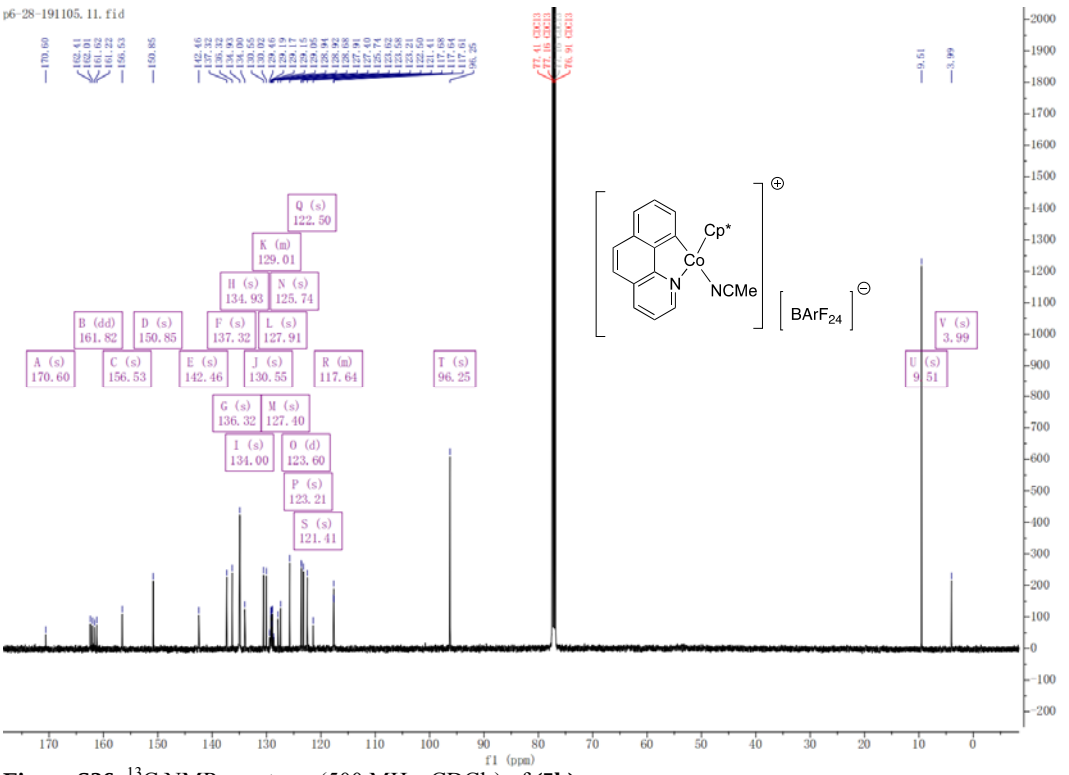


Figure S26. ^{13}C NMR spectrum (500 MHz, $CDCl_3$) of **(5b)**

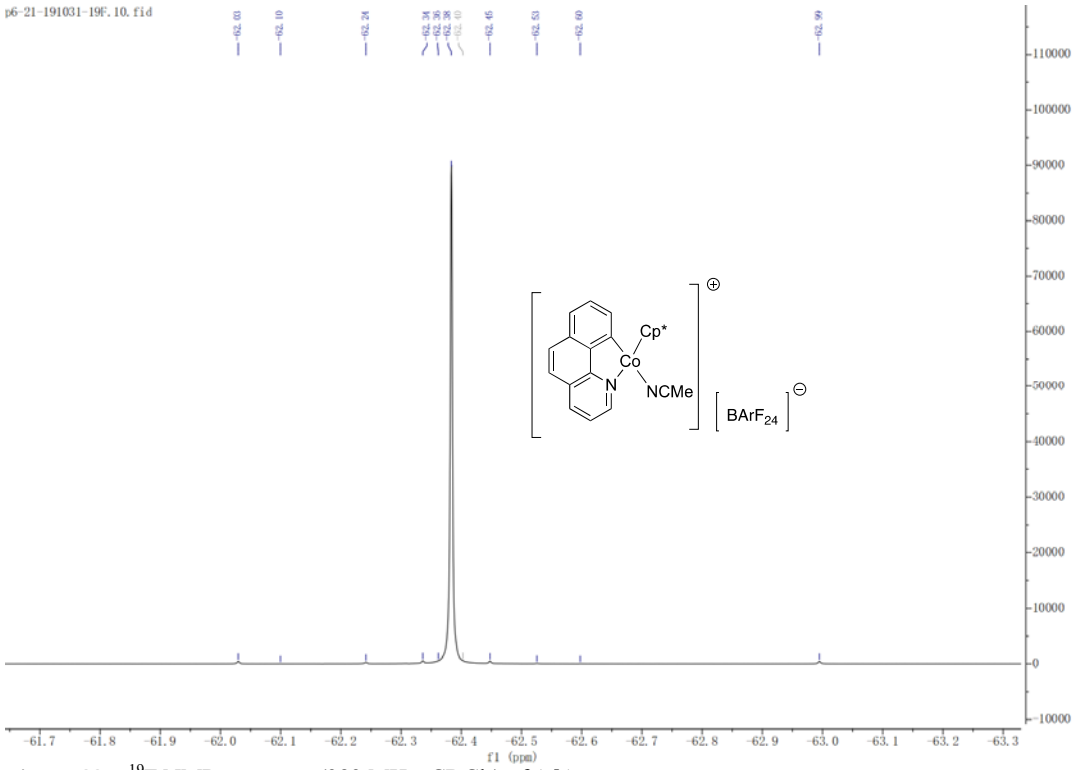


Figure S27. ^{19}F NMR spectrum (282 MHz, $CDCl_3$) of **(5b)**

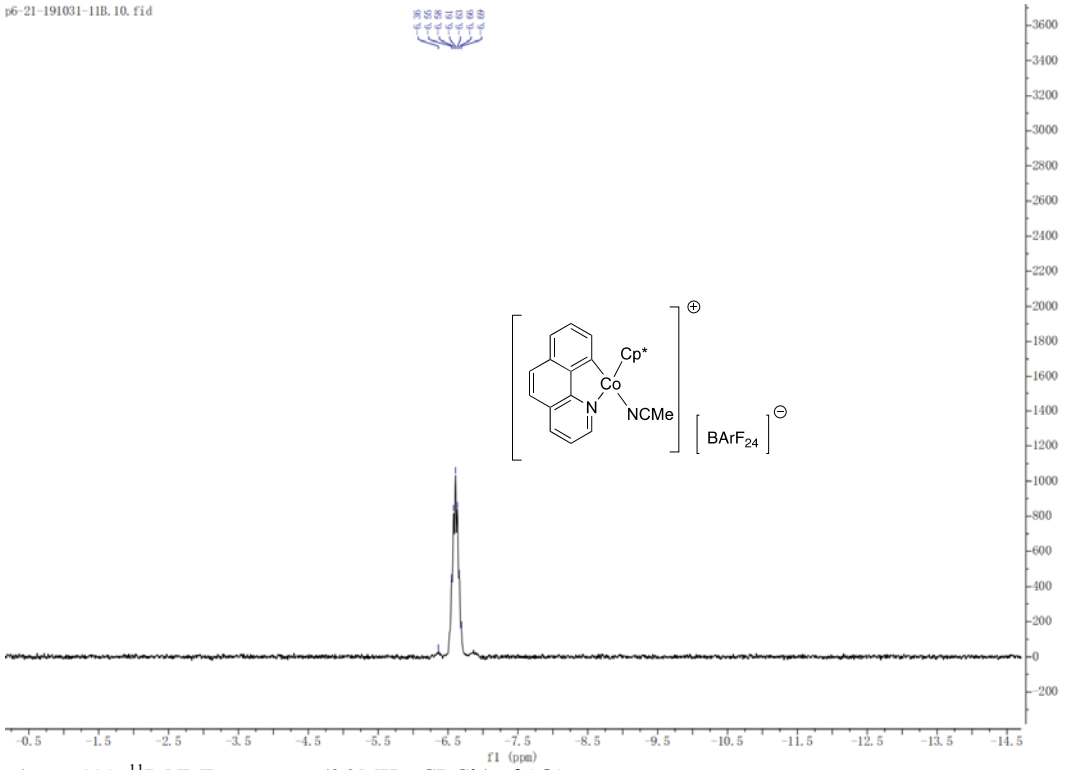


Figure S28. ^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **(5b)**

NMR spectra of Acetamidato[2-phenylenepyridine κ²-(C,N)](pentamethylcyclopentadienyl)cobalt (III) (1f)

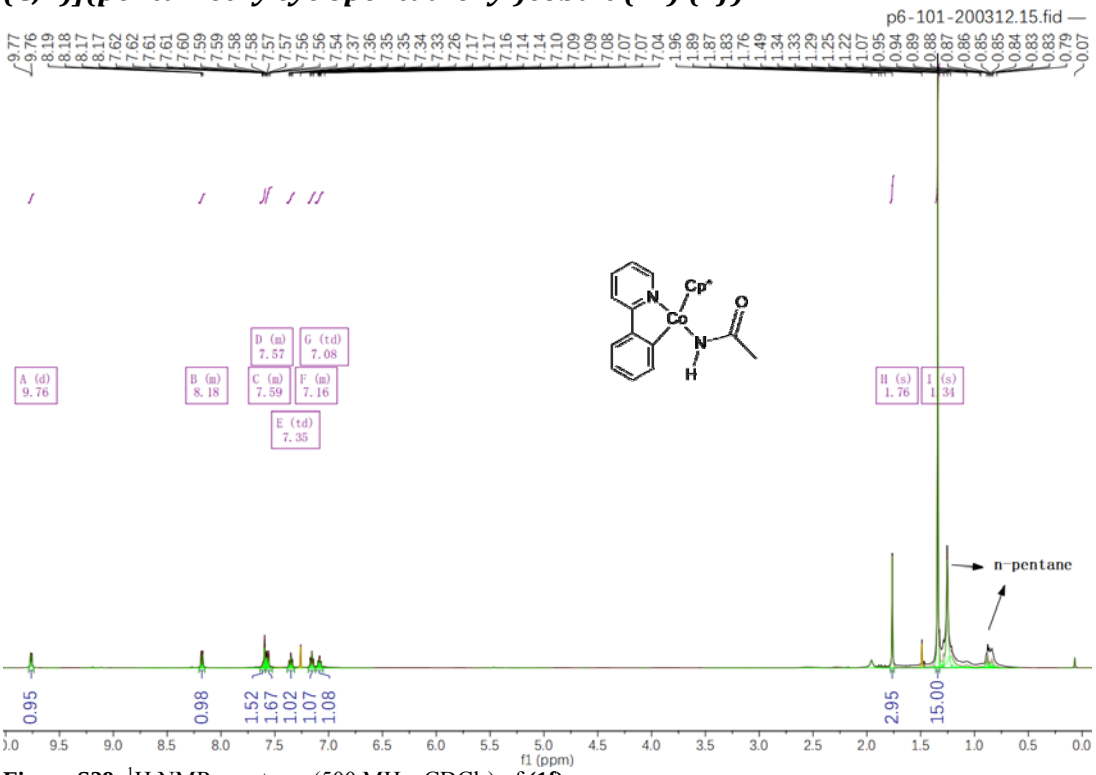


Figure S29. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **(1f)**

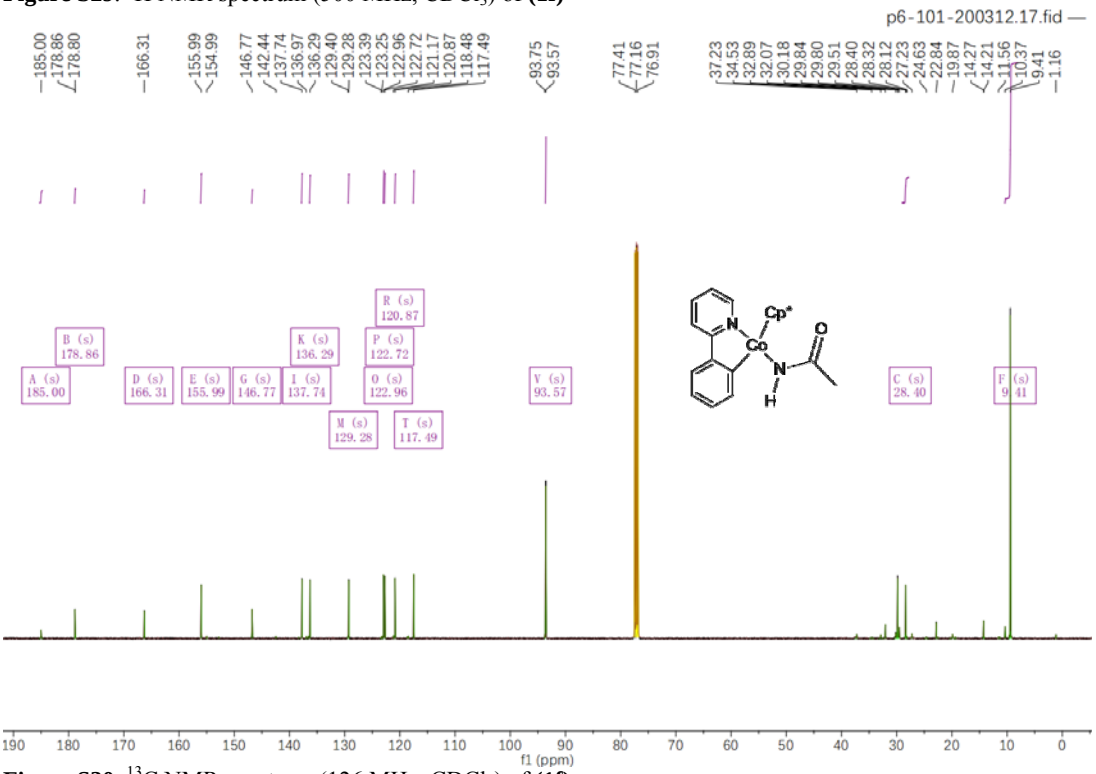


Figure S30. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **(1f)**

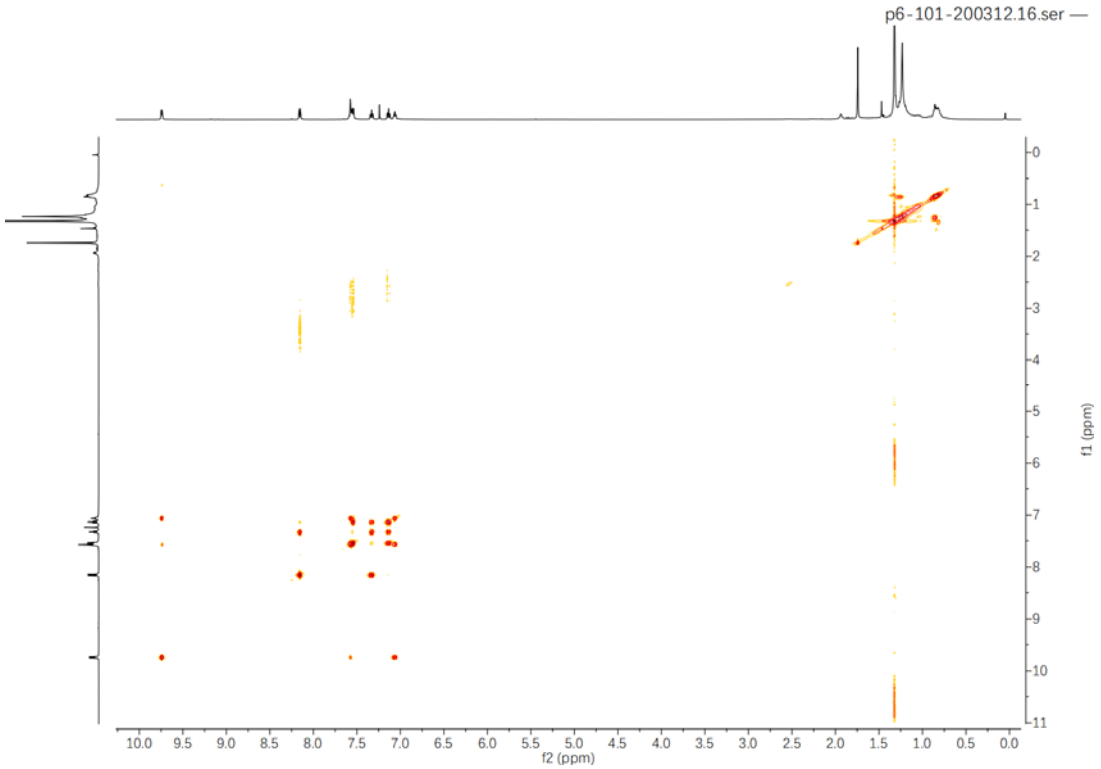


Figure S31. ^{1}H, ^{1}H COSY NMR spectrum ($CDCl_3$) of **(1f)**

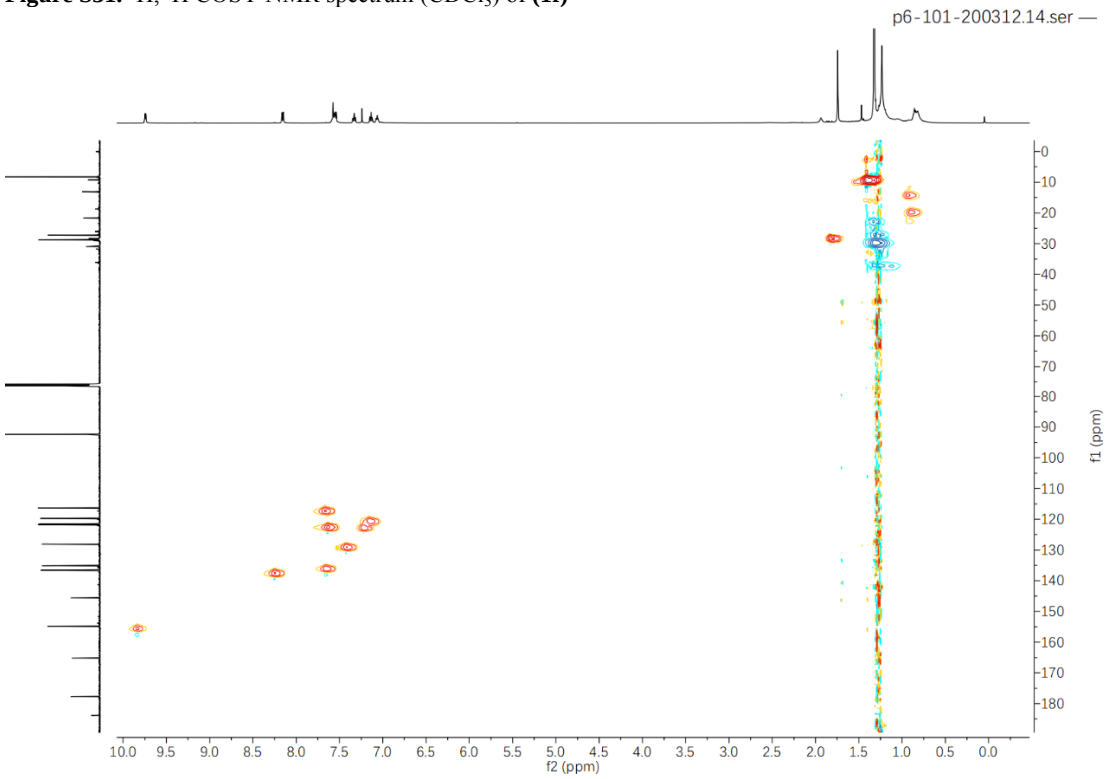


Figure S32. ^{1}H, ^{13}C HSQC NMR spectrum ($CDCl_3$) of **(1f)**

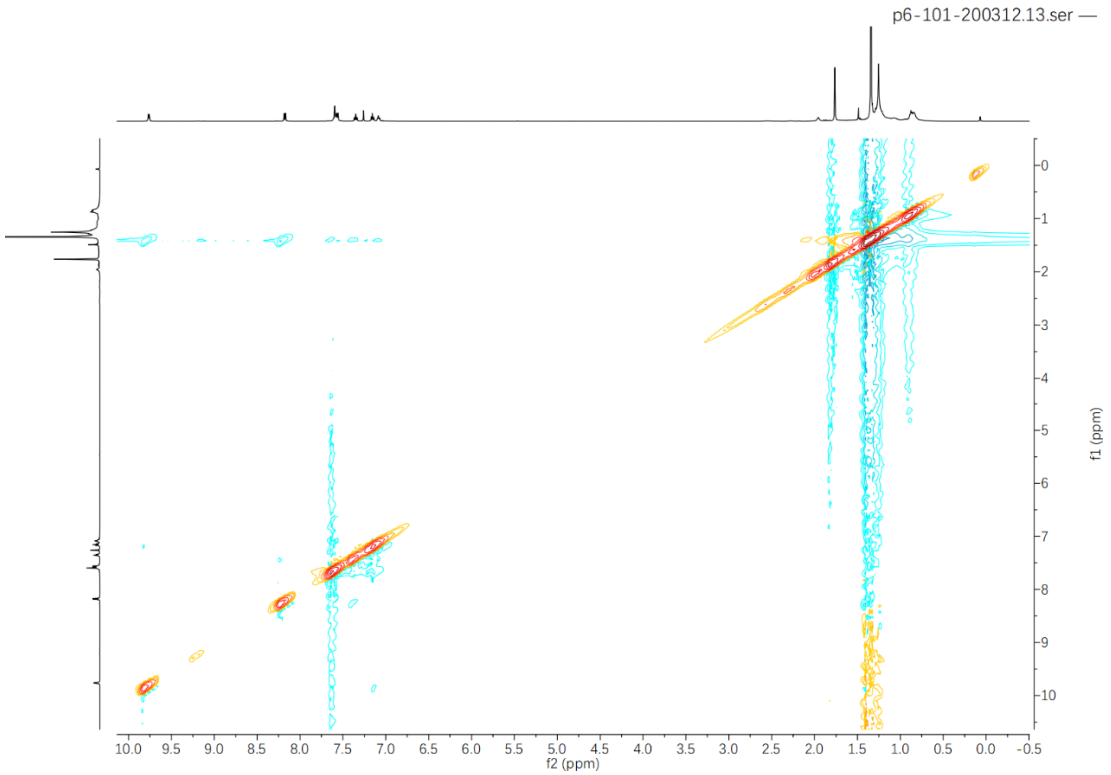


Figure S33. ^{1}H, ^{1}H NOSY NMR spectrum ($CDCl_3$) of **(1f)**

NMR spectra of Acetamidato[2-phenylenepyridine κ²-(C,N)](pentamethylcyclopentadienyl)iridium (III) (2b)

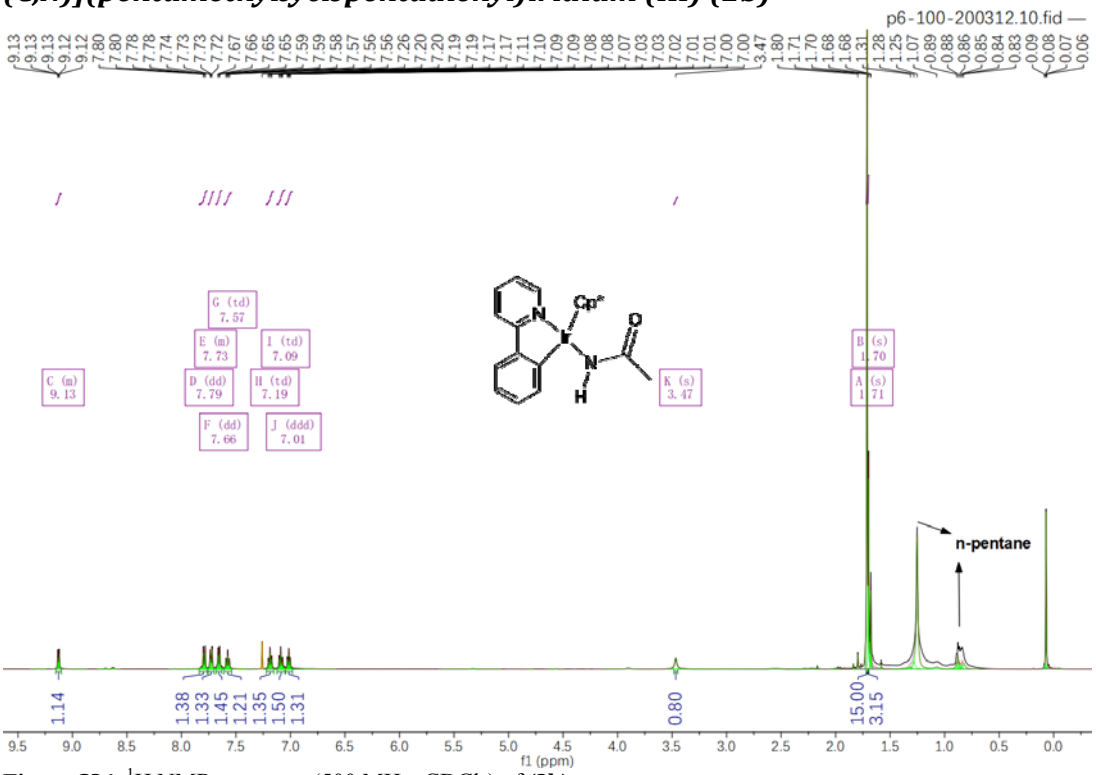


Figure S34. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **(2b)**

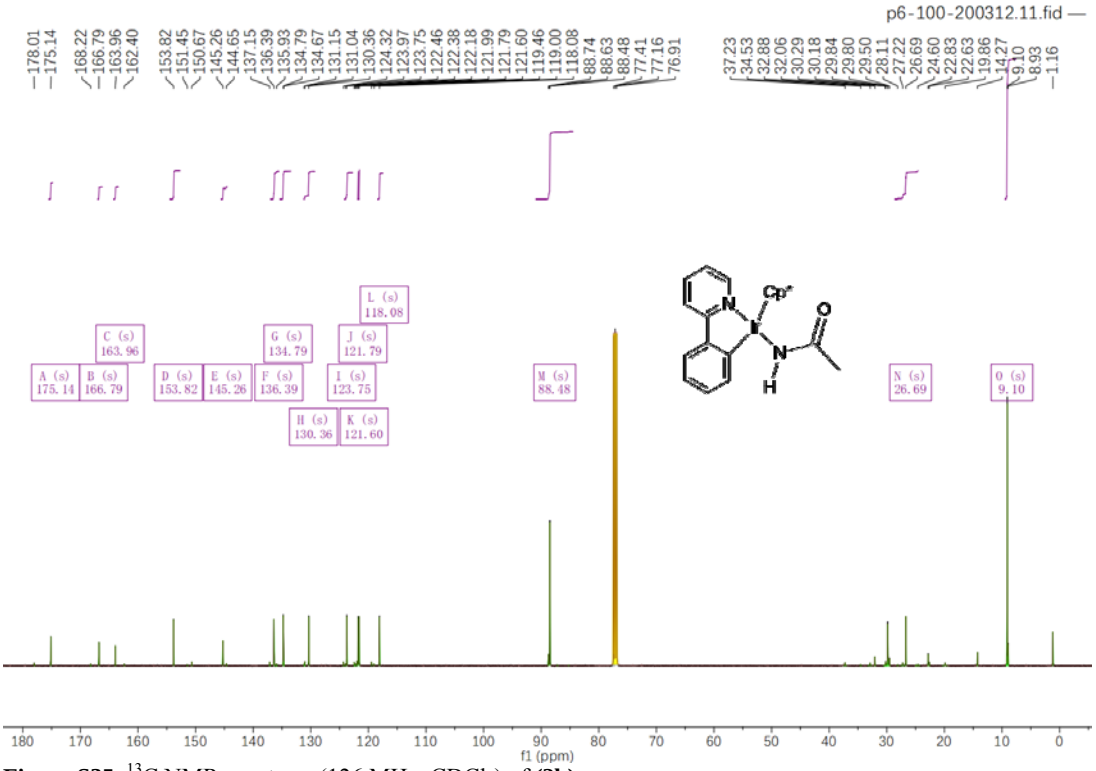


Figure S35. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **(2b)**

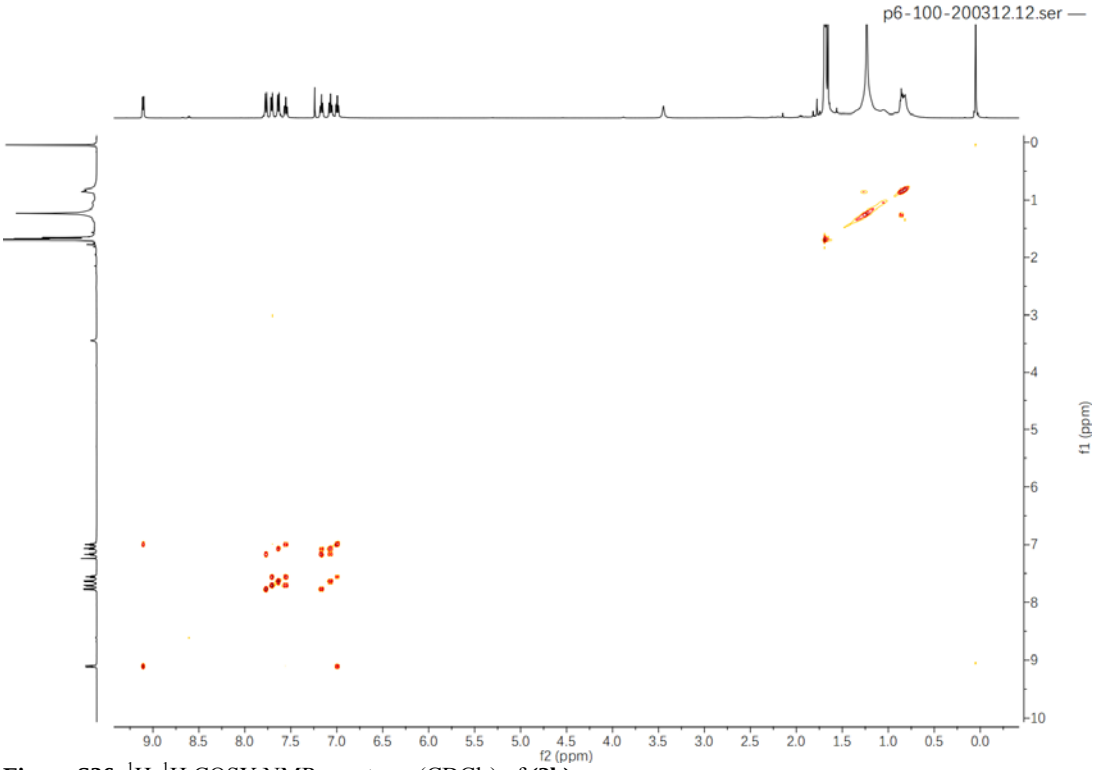


Figure S36. ^{1}H, ^{1}H COSY NMR spectrum ($CDCl_3$) of **(2b)**

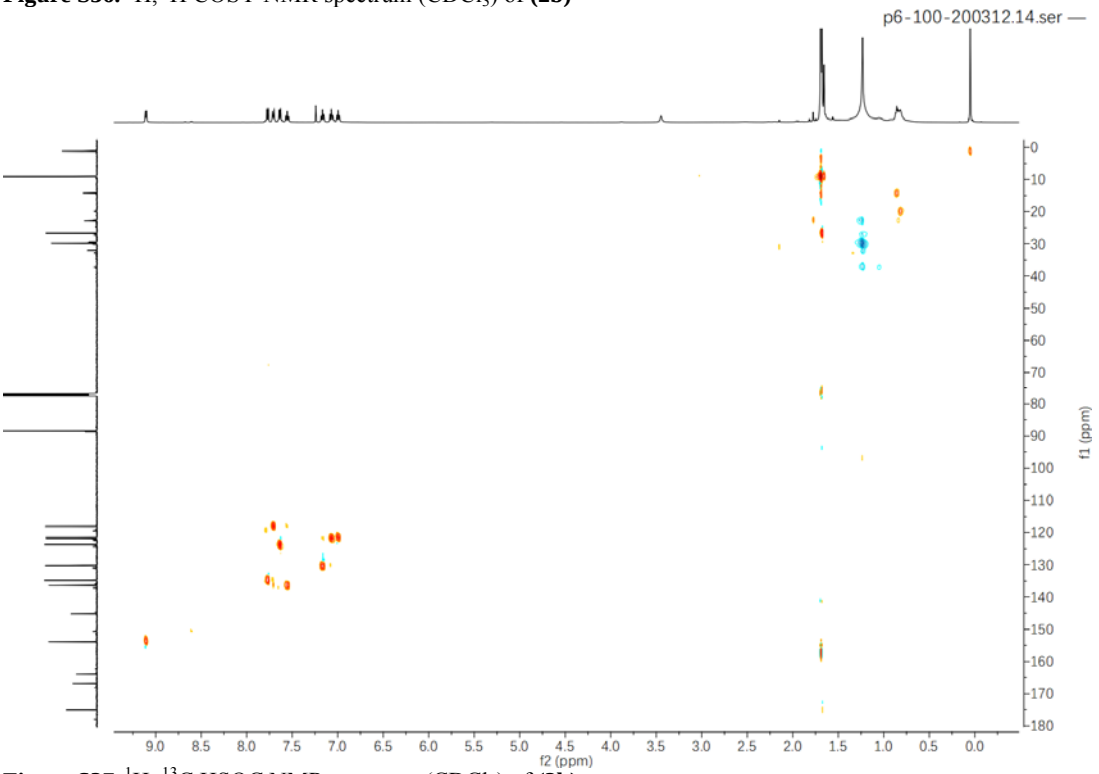


Figure S37. ^{1}H, ^{13}C HSQC NMR spectrum ($CDCl_3$) of **(2b)**

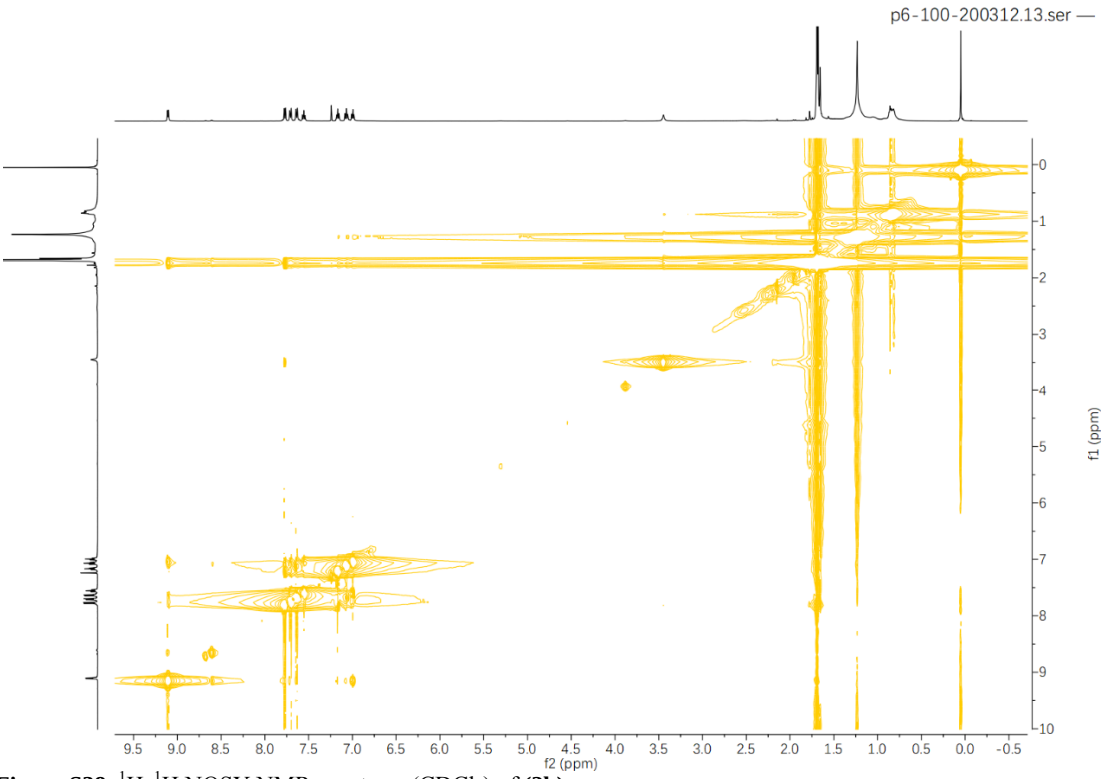
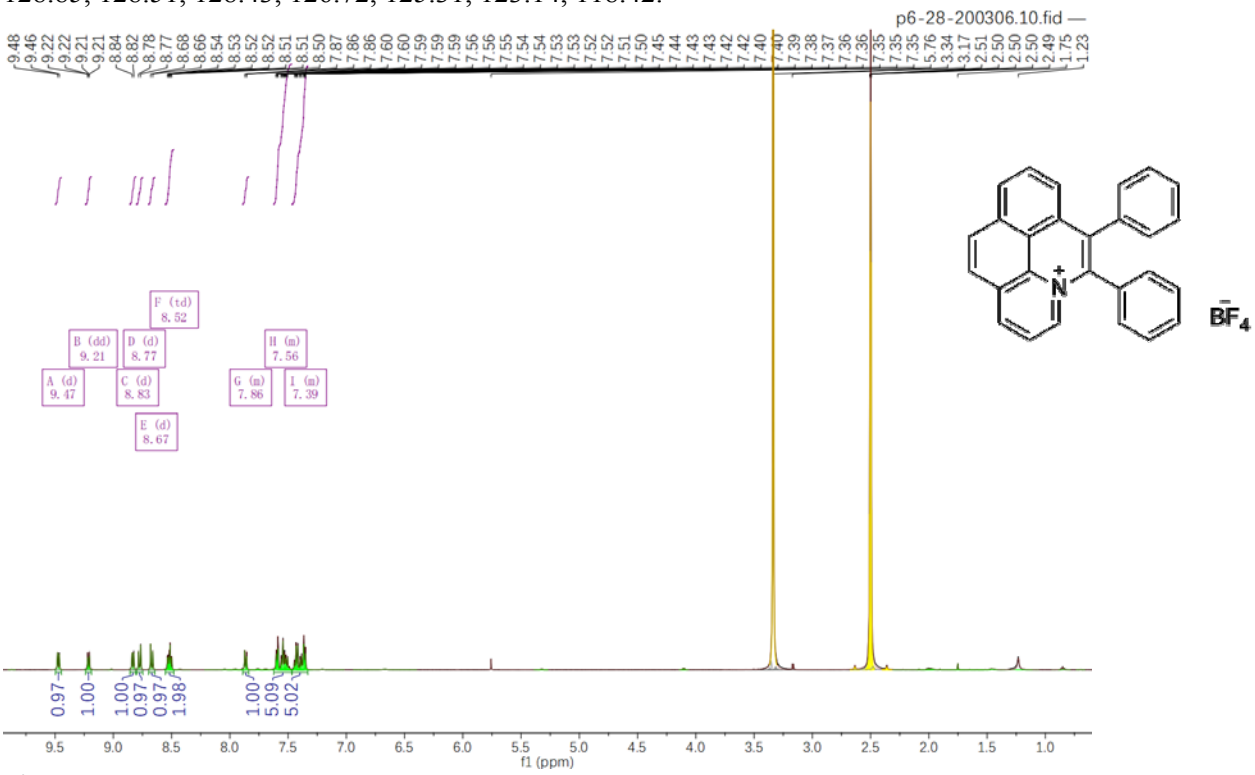


Figure S38. ^{1}H, ^{1}H NOSY NMR spectrum ($CDCl_3$) of **(2b)**

2. NMR spectra of new annulation products

5,6-diphenylbenzo[de]pyrido[3,2,1-ij]quinolin-4-ium tetrafluoroborate

Yellow solid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.47 (d, J = 7.9 Hz, 1H), 9.21 (dd, J = 6.6, 1.0 Hz, 1H), 8.83 (d, J = 7.8 Hz, 1H), 8.77 (d, J = 9.2 Hz, 1H), 8.67 (d, J = 9.2 Hz, 1H), 8.52 (td, J = 7.8, 3.7 Hz, 2H), 7.89 – 7.84 (m, 1H), 7.62 – 7.47 (m, 5H), 7.47 – 7.33 (m, 5H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 140.07, 138.85, 136.48, 135.85, 134.40, 133.32, 132.76, 132.65, 131.17, 131.06, 130.69, 130.27, 130.23, 129.98, 129.60, 129.18, 128.85, 128.51, 128.43, 126.72, 125.31, 123.14, 118.42.



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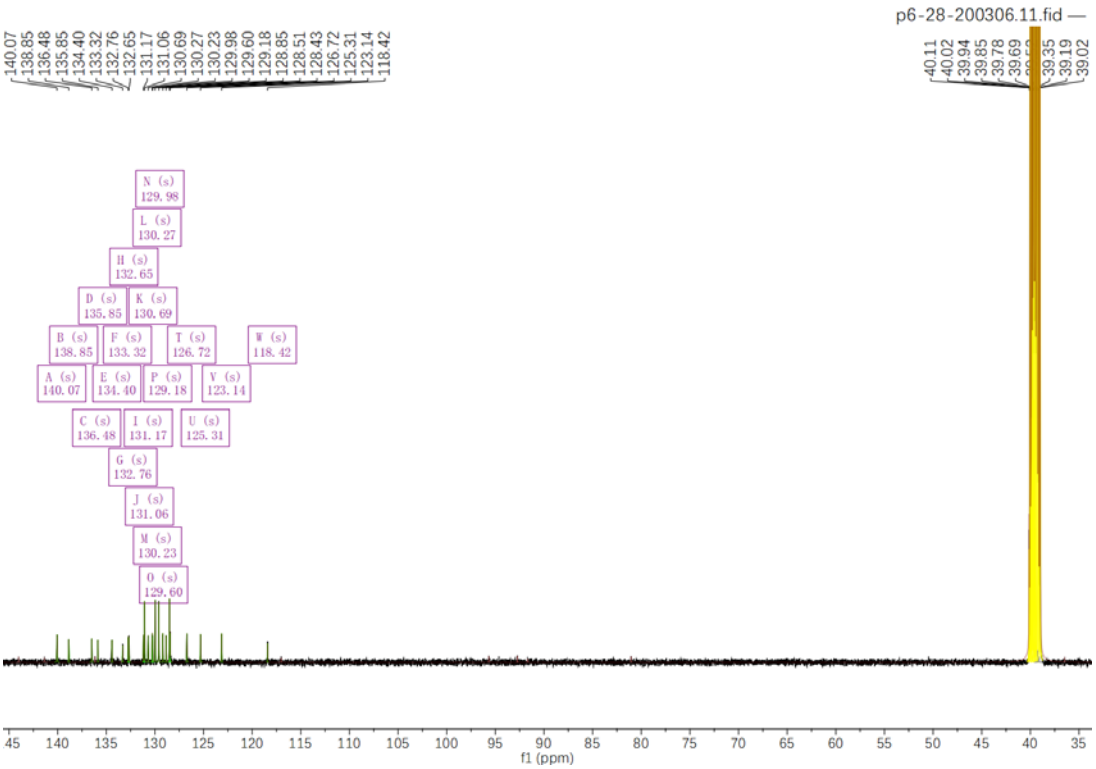
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128.43
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125.31
123.14
118.42
40.11
40.02
39.94
39.85
39.78
39.69
39.35
39.19
39.02
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L (s) 130.27
H (s) 132.65
D (s) 135.85
K (s) 130.69
B (s) 138.85
F (s) 133.32
T (s) 126.72
W (s) 118.42
A (s) 140.07
E (s) 134.40
P (s) 129.18
V (s) 123.14
C (s) 136.48
I (s) 131.17
U (s) 125.31
G (s) 132.76
J (s) 131.06
M (s) 130.23
O (s) 129.60
45 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35
f1 (ppm)

Figure S 40

5,6-diphenyldibenzo[de,g]pyrido[3,2,1-ij]quinolin-4-ium tetrafluoroborate

Yellow solid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.20 (d, J = 7.6 Hz, 1H), 9.56 (d, J = 7.6 Hz, 1H), 9.25 (dt, J = 7.8, 1.7 Hz, 2H), 9.19 (d, J = 6.7 Hz, 1H), 8.57 – 8.49 (m, 2H), 8.15 – 8.05 (m, 2H), 7.83 (d, J = 7.9 Hz, 1H), 7.62 – 7.49 (m, 5H), 7.46 – 7.35 (m, 5H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 138.72, 136.46, 135.76, 135.43, 134.55, 134.48, 133.19, 131.47, 131.16, 131.12, 131.01, 130.96, 130.26, 130.11, 129.99, 129.60, 128.79, 128.50, 128.42, 128.16, 126.50, 125.69, 125.42, 124.89, 124.74, 123.26, 117.97.

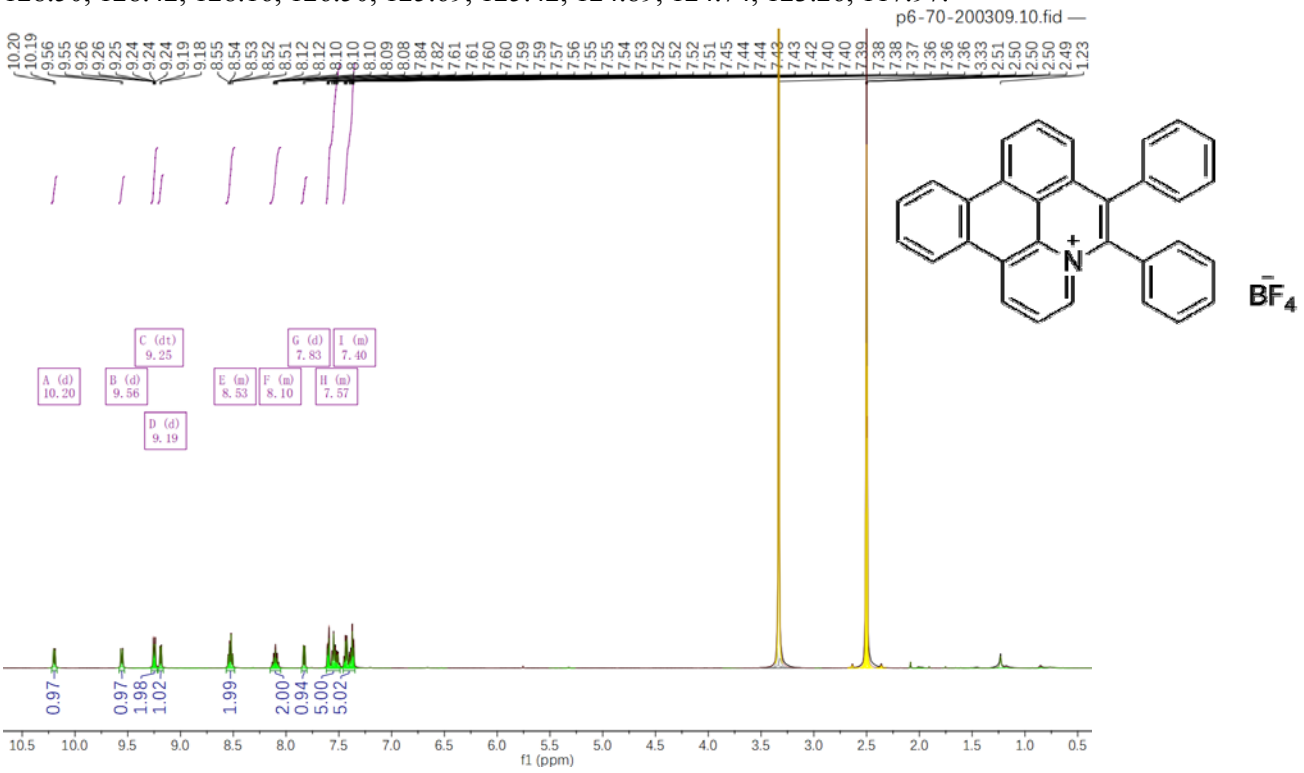


Figure S 41

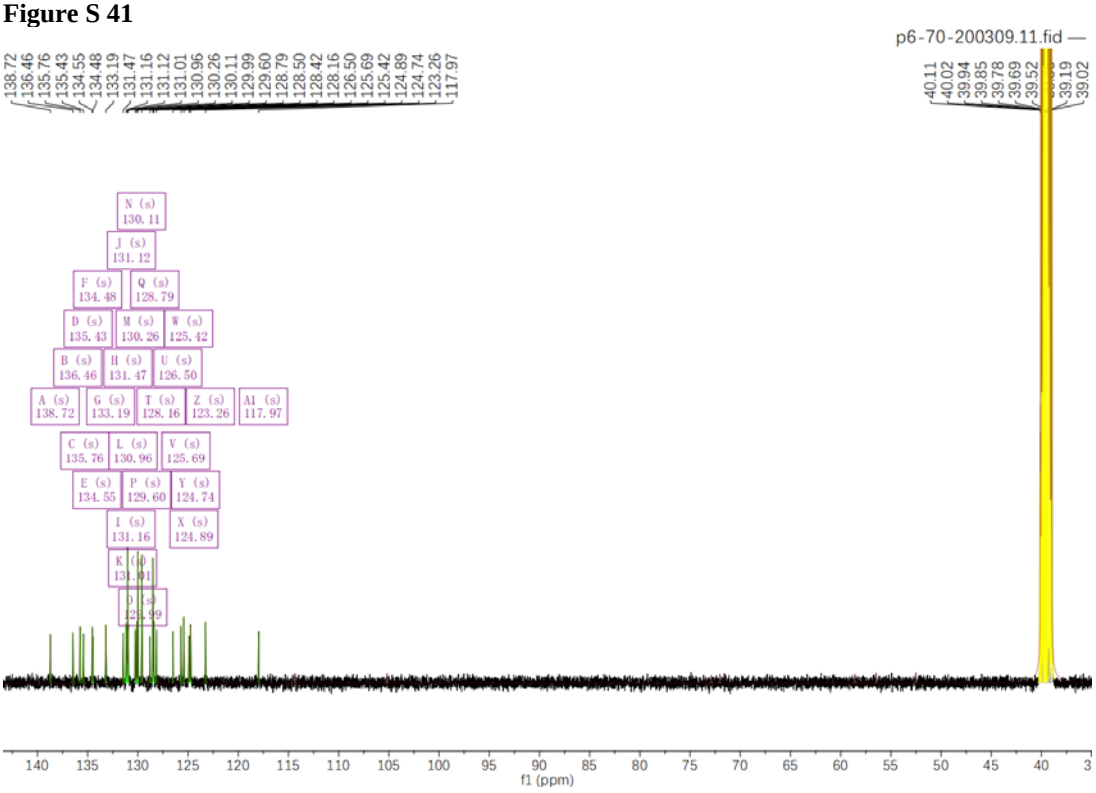


Figure S 42

3. Single Crystal X-Ray Structure Determinations

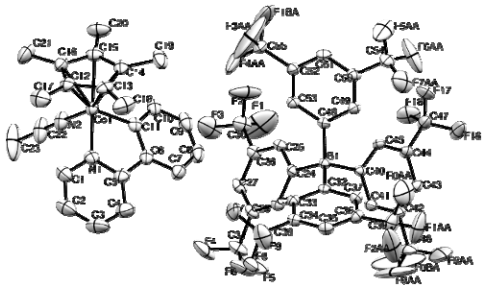


Table S1 Crystal data and structure refinement for (1b).

Identification code	**[k^2-(*C,N*)-(2-phpy)CoNCMe][$BArF_{24}$] (1b)**
Empirical formula	$C_{55}H_{38}BCoF_{24}N_2$
Formula weight	1252.61
Temperature/K	173(2)
Crystal system	triclinic
Space group	P-1
a/Å	12.5894(6)
b/Å	13.1911(6)
c/Å	17.0725(8)
α/°	91.818(2)
β/°	97.890(2)
γ/°	107.1210(10)
Volume/Å^3	2676.1(2)
Z	2
ρ_{calc}g/cm^3	1.555
μ/mm^{-1}	0.445
F(000)	1260.0
Crystal size/mm^3	0.35 × 0.25 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.24 to 55.968
Index ranges	-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -22 ≤ l ≤ 22
Reflections collected	114918
Independent reflections	12762 [R_{int} = 0.0643, R_{sigma} = 0.0532]
Data/restraints/parameters	12762/0/751
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0938, wR_2 = 0.1985
Final R indexes [all data]	R_1 = 0.1313, wR_2 = 0.2194
Largest diff. peak/hole / e Å^{-3}	1.47/-1.05

Table S2 Bond Lengths for (1b).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	N1	1.351(5)	C36	C39	1.489(6)
C1	C2	1.366(7)	C38	F8	1.324(5)
C2	C3	1.380(8)	C38	F9	1.332(5)
C3	C4	1.380(8)	C38	F7	1.337(5)
C4	C5	1.392(7)	C39	F10	1.289(8)
C5	N1	1.360(5)	C39	F11B	1.293(15)
C5	C6	1.460(6)	C39	F10B	1.343(11)
C6	C11	1.392(6)	C39	F11	1.356(10)
C6	C7	1.404(6)	C39	F12	1.375(10)
C7	C8	1.381(7)	C39	F12B	1.416(14)
C8	C9	1.368(7)	C40	C45	1.398(5)
C9	C10	1.399(6)	C40	C41	1.401(5)
C10	C11	1.366(6)	C40	B1	1.650(5)
C11	Co1	1.949(4)	C41	C42	1.378(5)
C12	C16	1.401(6)	C42	C43	1.380(5)
C12	C13	1.437(6)	C42	C46	1.483(5)
C12	C17	1.490(6)	C43	C44	1.381(5)
C12	Co1	2.126(4)	C44	C45	1.390(5)
C13	C14	1.413(6)	C44	C47	1.494(5)
C13	C18	1.501(6)	C46	F14B	1.284(13)
C13	Co1	2.056(4)	C46	F15	1.306(10)
C14	C15	1.415(6)	C46	F15B	1.318(14)
C14	C19	1.506(6)	C46	F13	1.321(9)
C14	Co1	2.078(4)	C46	F14	1.392(10)
C15	C16	1.437(6)	C46	F13B	1.429(14)
C15	C20	1.502(6)	C47	F18	1.337(5)
C15	Co1	2.070(4)	C47	F17	1.337(5)
C16	C21	1.498(6)	C47	F16	1.339(5)
C16	Co1	2.125(4)	C48	C49	1.399(5)
C22	N2	1.136(6)	C48	C53	1.404(5)
C22	C23	1.458(8)	C48	B1	1.643(5)
C24	C25	1.402(5)	C49	C50	1.392(5)
C24	C29	1.405(5)	C50	C51	1.386(5)
C24	B1	1.639(5)	C50	C54	1.491(6)
C25	C26	1.392(5)	C51	C52	1.380(6)
C26	C27	1.388(6)	C52	C53	1.392(5)
C26	C30	1.495(6)	C52	C55	1.500(5)
C27	C28	1.383(6)	C54	F20B	1.266(12)
C28	C29	1.388(5)	C54	F21	1.306(7)
C28	C31	1.494(6)	C54	F19	1.326(10)
C30	F1	1.305(7)	C54	F19B	1.365(13)
C30	F3	1.308(6)	C54	F21B	1.389(11)
C30	F2	1.311(6)	C54	F20	1.401(8)
C31	F4	1.326(6)	C55	F23C	1.256(12)
C31	F6	1.328(6)	C55	F22B	1.279(11)
C31	F5	1.329(6)	C55	F23B	1.311(12)
C32	C33	1.403(5)	C55	F24	1.322(9)
C32	C37	1.403(5)	C55	F24C	1.356(12)
C32	B1	1.635(5)	C55	F22C	1.371(12)
C33	C34	1.399(5)	C55	F22	1.374(10)
C34	C35	1.385(6)	C55	F23	1.396(11)
C34	C38	1.494(5)	C55	F24B	1.415(12)
C35	C36	1.386(6)	N1	Co1	1.965(4)

C36	C37	1.387(5)		N2	Co1	1.904(4)	

Table S3 Bond Angles for (1b).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	C1	C2	122.4(5)	C41	C42	C43	121.6(3)
C1	C2	C3	119.2(5)	C41	C42	C46	120.2(4)
C4	C3	C2	119.3(5)	C43	C42	C46	118.2(4)
C3	C4	C5	119.6(5)	C42	C43	C44	117.5(3)
N1	C5	C4	120.4(4)	C43	C44	C45	121.2(3)
N1	C5	C6	113.1(4)	C43	C44	C47	119.0(3)
C4	C5	C6	126.3(4)	C45	C44	C47	119.8(3)
C11	C6	C7	120.5(4)	C44	C45	C40	121.9(3)
C11	C6	C5	114.9(4)	F14B	C46	F15B	114.0(8)
C7	C6	C5	124.4(4)	F15	C46	F13	109.1(6)
C8	C7	C6	119.5(4)	F15	C46	F14	104.7(6)
C9	C8	C7	120.1(4)	F13	C46	F14	98.7(6)
C8	C9	C10	119.9(4)	F14B	C46	F13B	95.4(8)
C11	C10	C9	121.2(4)	F15B	C46	F13B	102.8(8)
C10	C11	C6	118.7(4)	F14B	C46	C42	118.0(6)
C10	C11	Co1	128.4(3)	F15	C46	C42	115.8(5)
C6	C11	Co1	112.9(3)	F15B	C46	C42	114.5(6)
C16	C12	C13	107.1(4)	F13	C46	C42	115.6(5)
C16	C12	C17	127.5(4)	F14	C46	C42	111.0(5)
C13	C12	C17	125.2(4)	F13B	C46	C42	108.8(5)
C16	C12	Co1	70.7(2)	F18	C47	F17	105.7(3)
C13	C12	Co1	67.3(2)	F18	C47	F16	106.5(4)
C17	C12	Co1	131.1(3)	F17	C47	F16	106.5(4)
C14	C13	C12	108.6(4)	F18	C47	C44	111.5(4)
C14	C13	C18	125.0(4)	F17	C47	C44	113.3(4)
C12	C13	C18	126.2(4)	F16	C47	C44	112.8(3)
C14	C13	Co1	70.9(2)	C49	C48	C53	115.7(3)
C12	C13	Co1	72.6(2)	C49	C48	B1	120.7(3)
C18	C13	Co1	126.2(3)	C53	C48	B1	123.5(3)
C13	C14	C15	107.9(4)	C50	C49	C48	122.3(3)
C13	C14	C19	125.6(4)	C51	C50	C49	120.9(3)
C15	C14	C19	126.3(4)	C51	C50	C54	119.3(3)
C13	C14	Co1	69.2(2)	C49	C50	C54	119.9(4)
C15	C14	Co1	69.8(2)	C52	C51	C50	118.0(3)
C19	C14	Co1	130.8(3)	C51	C52	C53	121.2(3)
C14	C15	C16	107.5(4)	C51	C52	C55	118.5(3)
C14	C15	C20	127.5(4)	C53	C52	C55	120.3(4)
C16	C15	C20	124.4(4)	C52	C53	C48	121.9(3)
C14	C15	Co1	70.4(2)	F21	C54	F19	108.7(5)
C16	C15	Co1	72.0(2)	F20B	C54	F19B	107.2(7)
C20	C15	Co1	130.2(3)	F20B	C54	F21B	108.6(6)
C12	C16	C15	108.8(4)	F19B	C54	F21B	103.3(7)
C12	C16	C21	126.4(5)	F21	C54	F20	104.2(5)
C15	C16	C21	124.8(5)	F19	C54	F20	102.8(5)
C12	C16	Co1	70.8(2)	F20B	C54	C50	114.3(6)
C15	C16	Co1	67.9(2)	F21	C54	C50	116.2(4)
C21	C16	Co1	128.0(4)	F19	C54	C50	112.6(5)
N2	C22	C23	178.1(6)	F19B	C54	C50	112.6(6)
C25	C24	C29	115.5(3)	F21B	C54	C50	110.3(5)
C25	C24	B1	122.2(3)	F20	C54	C50	111.2(4)

C29	C24	B1	121.9(3)	F22B	C55	F23B	106.6(8)
C26	C25	C24	122.3(3)	F23C	C55	F24C	112.5(8)
C27	C26	C25	120.8(4)	F23C	C55	F22C	103.7(8)
C27	C26	C30	119.4(4)	F24C	C55	F22C	103.9(8)
C25	C26	C30	119.7(4)	F24	C55	F22	107.1(6)
C28	C27	C26	118.0(4)	F24	C55	F23	106.5(7)
C27	C28	C29	121.1(4)	F22	C55	F23	105.8(6)
C27	C28	C31	119.2(4)	F22B	C55	F24B	105.9(8)
C29	C28	C31	119.6(4)	F23B	C55	F24B	99.7(8)
C28	C29	C24	122.2(4)	F23C	C55	C52	114.0(6)
F1	C30	F3	104.0(5)	F22B	C55	C52	115.8(6)
F1	C30	F2	106.3(5)	F23B	C55	C52	116.5(6)
F3	C30	F2	106.1(5)	F24	C55	C52	115.8(4)
F1	C30	C26	112.3(5)	F24C	C55	C52	110.5(5)
F3	C30	C26	113.6(4)	F22C	C55	C52	111.7(5)
F2	C30	C26	113.8(4)	F22	C55	C52	111.5(5)
F4	C31	F6	106.0(4)	F23	C55	C52	109.7(5)
F4	C31	F5	105.0(4)	F24B	C55	C52	110.7(5)
F6	C31	F5	106.9(5)	C1	N1	C5	119.0(4)
F4	C31	C28	113.1(4)	C1	N1	Co1	126.3(3)
F6	C31	C28	113.1(4)	C5	N1	Co1	114.7(3)
F5	C31	C28	112.2(4)	C22	N2	Co1	172.1(4)
C33	C32	C37	115.5(3)	C32	B1	C24	113.4(3)
C33	C32	B1	123.8(3)	C32	B1	C48	105.0(3)
C37	C32	B1	120.3(3)	C24	B1	C48	112.9(3)
C34	C33	C32	122.2(3)	C32	B1	C40	110.3(3)
C35	C34	C33	120.6(3)	C24	B1	C40	102.8(3)
C35	C34	C38	119.1(3)	C48	B1	C40	112.7(3)
C33	C34	C38	120.2(3)	N2	Co1	C11	94.77(16)
C34	C35	C36	118.2(4)	N2	Co1	N1	90.28(16)
C35	C36	C37	120.9(4)	C11	Co1	N1	82.44(16)
C35	C36	C39	120.1(4)	N2	Co1	C13	154.94(16)
C37	C36	C39	118.9(4)	C11	Co1	C13	110.16(17)
C36	C37	C32	122.5(3)	N1	Co1	C13	95.27(16)
F8	C38	F9	107.3(4)	N2	Co1	C15	104.53(18)
F8	C38	F7	105.9(4)	C11	Co1	C15	105.34(17)
F9	C38	F7	105.0(4)	N1	Co1	C15	162.38(16)
F8	C38	C34	112.7(3)	C13	Co1	C15	67.29(17)
F9	C38	C34	112.4(3)	N2	Co1	C14	143.03(18)
F7	C38	C34	113.0(3)	C11	Co1	C14	88.63(16)
F11B	C39	F10B	120.3(7)	N1	Co1	C14	126.61(16)
F10	C39	F11	107.7(5)	C13	Co1	C14	39.96(17)
F10	C39	F12	109.1(5)	C15	Co1	C14	39.88(17)
F11	C39	F12	97.9(5)	N2	Co1	C16	92.07(17)
F11B	C39	F12B	99.1(7)	C11	Co1	C16	145.11(17)
F10B	C39	F12B	100.6(7)	N1	Co1	C16	131.76(16)
F10	C39	C36	116.2(5)	C13	Co1	C16	66.16(17)
F11B	C39	C36	110.9(6)	C15	Co1	C16	40.04(17)
F10B	C39	C36	113.1(5)	C14	Co1	C16	66.32(16)
F11	C39	C36	114.9(5)	N2	Co1	C12	114.87(16)
F12	C39	C36	109.5(4)	C11	Co1	C12	150.29(17)
F12B	C39	C36	111.1(5)	N1	Co1	C12	98.62(15)
C45	C40	C41	115.7(3)	C13	Co1	C12	40.14(17)
C45	C40	B1	123.3(3)	C15	Co1	C12	66.70(17)
C41	C40	B1	120.7(3)	C14	Co1	C12	66.77(16)

C42	C41	C40	122.0(3)	C16	Co1	C12	38.49(17)

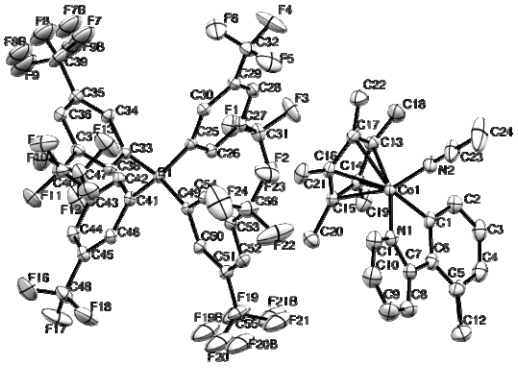


Table S4 Crystal data and structure refinement for (3b).

Identification code	**[k^2-(*C,N*)-(2-*tolpy*)CoNCMe][BArF$_{24}$] (3b)**
Empirical formula	$C_{56}H_{40}BCoF_{24}N_2$
Formula weight	1266.64
Temperature/K	120(2)
Crystal system	triclinic
Space group	P-1
a/Å	12.5987(5)
b/Å	13.3136(5)
c/Å	17.2460(7)
α/°	93.019(2)
β/°	97.6630(10)
γ/°	106.9780(10)
Volume/Å^3	2729.12(19)
Z	2
ρ_{calc}g/cm^3	1.541
μ/mm^{-1}	0.437
F(000)	1276.0
Crystal size/mm^3	0.200 × 0.150 × 0.100
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.858 to 55.86
Index ranges	-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -22 ≤ l ≤ 22
Reflections collected	139336
Independent reflections	13075 [R_{int} = 0.0385, R_{sigma} = 0.0168]
Data/restraints/parameters	13075/0/758
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0700, wR_2 = 0.1824
Final R indexes [all data]	R_1 = 0.0768, wR_2 = 0.1894
Largest diff. peak/hole / e Å^{-3}	2.17/-1.57

Table S5 Bond Lengths for (3b).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.396(4)	C34	C35	1.389(4)
C1	C6	1.405(4)	C35	C36	1.382(4)
C1	Co1	1.927(3)	C35	C39	1.499(4)
C2	C3	1.391(4)	C36	C37	1.385(4)
C3	C4	1.376(5)	C37	C38	1.394(4)
C4	C5	1.390(5)	C37	C40	1.496(4)
C5	C6	1.423(4)	C39	F8B	1.296(12)
C5	C12	1.501(5)	C39	F7	1.307(7)
C6	C7	1.470(4)	C39	F8	1.308(6)
C7	N1	1.371(4)	C39	F9B	1.327(14)
C7	C8	1.398(4)	C39	F9	1.376(6)
C8	C9	1.381(5)	C39	F7B	1.404(13)
C9	C10	1.380(5)	C40	F12	1.337(4)
C10	C11	1.380(5)	C40	F10	1.338(3)
C11	N1	1.342(4)	C40	F11	1.339(4)
C13	C14	1.423(4)	C41	C46	1.402(4)
C13	C17	1.446(4)	C41	C42	1.404(3)
C13	C18	1.497(4)	C41	B1	1.638(4)
C13	Co1	2.077(3)	C42	C43	1.395(4)
C14	C15	1.427(4)	C43	C44	1.389(4)
C14	C19	1.499(4)	C43	C47	1.503(4)
C14	Co1	2.084(3)	C44	C45	1.389(4)
C15	C16	1.440(4)	C45	C46	1.394(4)
C15	C20	1.498(4)	C45	C48	1.501(4)
C15	Co1	2.055(3)	C47	F13	1.331(4)
C16	C17	1.400(4)	C47	F15	1.333(4)
C16	C21	1.497(4)	C47	F14	1.344(4)
C16	Co1	2.137(3)	C48	F18	1.324(4)
C17	C22	1.494(4)	C48	F17	1.327(4)
C17	Co1	2.124(3)	C48	F16	1.334(4)
C23	N2	1.134(4)	C49	C54	1.402(3)
C23	C24	1.456(5)	C49	C50	1.405(3)
C25	C30	1.401(3)	C49	B1	1.639(4)
C25	C26	1.403(3)	C50	C51	1.392(4)
C25	B1	1.637(4)	C51	C52	1.382(4)
C26	C27	1.398(4)	C51	C55	1.501(4)
C27	C28	1.384(4)	C52	C53	1.387(4)
C27	C31	1.494(4)	C53	C54	1.395(4)
C28	C29	1.387(4)	C53	C56	1.495(4)
C29	C30	1.393(4)	C55	F21B	1.282(12)
C29	C32	1.497(4)	C55	F20	1.289(6)
C31	F3	1.337(3)	C55	F19	1.314(6)
C31	F1	1.342(3)	C55	F21	1.356(6)
C31	F2	1.346(4)	C55	F19B	1.381(12)
C32	F4	1.312(4)	C55	F20B	1.413(13)
C32	F6	1.328(4)	C56	F22	1.313(4)
C32	F5	1.346(4)	C56	F23	1.333(4)
C33	C38	1.395(3)	C56	F24	1.336(5)
C33	C34	1.405(3)	N1	Co1	1.942(2)
C33	B1	1.640(4)	N2	Co1	1.906(3)

Table S6 Bond Angles for (3b).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	C1	C6	119.8(3)	F12	C40	F10	106.6(3)
C2	C1	Co1	125.7(2)	F12	C40	F11	105.7(2)
C6	C1	Co1	114.4(2)	F10	C40	F11	107.0(3)
C3	C2	C1	120.0(3)	F12	C40	C37	113.0(2)
C4	C3	C2	119.7(3)	F10	C40	C37	112.9(2)
C3	C4	C5	122.5(3)	F11	C40	C37	111.1(3)
C4	C5	C6	117.7(3)	C46	C41	C42	115.8(2)
C4	C5	C12	117.8(3)	C46	C41	B1	121.6(2)
C6	C5	C12	124.5(3)	C42	C41	B1	122.0(2)
C1	C6	C5	120.1(3)	C43	C42	C41	122.0(2)
C1	C6	C7	113.1(2)	C44	C43	C42	121.1(2)
C5	C6	C7	126.6(3)	C44	C43	C47	119.3(3)
N1	C7	C8	118.6(3)	C42	C43	C47	119.6(3)
N1	C7	C6	112.2(2)	C45	C44	C43	117.8(2)
C8	C7	C6	129.0(3)	C44	C45	C46	121.0(3)
C9	C8	C7	120.4(3)	C44	C45	C48	119.4(2)
C10	C9	C8	119.9(3)	C46	C45	C48	119.6(2)
C9	C10	C11	118.0(3)	C45	C46	C41	122.2(2)
N1	C11	C10	122.7(3)	F13	C47	F15	106.0(3)
C14	C13	C17	107.5(2)	F13	C47	F14	107.7(3)
C14	C13	C18	127.5(3)	F15	C47	F14	106.0(3)
C17	C13	C18	124.4(3)	F13	C47	C43	112.7(3)
C14	C13	Co1	70.26(16)	F15	C47	C43	112.4(3)
C17	C13	Co1	71.60(16)	F14	C47	C43	111.6(3)
C18	C13	Co1	130.2(2)	F18	C48	F17	106.3(3)
C13	C14	C15	107.4(2)	F18	C48	F16	107.2(3)
C13	C14	C19	127.2(3)	F17	C48	F16	105.3(3)
C15	C14	C19	125.3(3)	F18	C48	C45	113.1(2)
C13	C14	Co1	69.76(16)	F17	C48	C45	112.6(3)
C15	C14	Co1	68.76(16)	F16	C48	C45	111.8(3)
C19	C14	Co1	130.2(2)	C54	C49	C50	115.9(2)
C14	C15	C16	108.7(2)	C54	C49	B1	120.3(2)
C14	C15	C20	125.3(3)	C50	C49	B1	123.5(2)
C16	C15	C20	125.8(3)	C51	C50	C49	121.6(2)
C14	C15	Co1	70.90(16)	C52	C51	C50	121.7(2)
C16	C15	Co1	72.99(16)	C52	C51	C55	118.1(3)
C20	C15	Co1	125.6(2)	C50	C51	C55	120.2(3)
C17	C16	C15	107.2(2)	C51	C52	C53	117.7(2)
C17	C16	C21	126.9(3)	C52	C53	C54	121.0(2)
C15	C16	C21	125.7(3)	C52	C53	C56	120.0(3)
C17	C16	Co1	70.31(16)	C54	C53	C56	118.9(3)

C15	C16	Co1	66.89(15)	C53	C54	C49	122.1(2)
C21	C16	Co1	131.6(2)	F20	C55	F19	114.9(4)
C16	C17	C13	109.0(3)	F20	C55	F21	103.5(4)
C16	C17	C22	127.0(3)	F19	C55	F21	100.7(4)
C13	C17	C22	124.0(3)	F21B	C55	F19B	112.4(7)
C16	C17	Co1	71.33(16)	F21B	C55	F20B	103.0(7)
C13	C17	Co1	68.15(16)	F19B	C55	F20B	94.5(7)
C22	C17	Co1	127.7(2)	F21B	C55	C51	118.4(5)
N2	C23	C24	178.6(5)	F20	C55	C51	113.0(3)
C30	C25	C26	115.8(2)	F19	C55	C51	112.4(3)
C30	C25	B1	121.0(2)	F21	C55	C51	111.3(3)
C26	C25	B1	122.8(2)	F19B	C55	C51	112.5(4)
C27	C26	C25	121.9(2)	F20B	C55	C51	113.0(4)
C28	C27	C26	121.3(2)	F22	C56	F23	105.8(3)
C28	C27	C31	120.6(2)	F22	C56	F24	107.8(4)
C26	C27	C31	118.0(2)	F23	C56	F24	103.6(3)
C27	C28	C29	117.6(2)	F22	C56	C53	113.7(3)
C28	C29	C30	121.3(2)	F23	C56	C53	112.6(3)
C28	C29	C32	120.5(2)	F24	C56	C53	112.6(3)
C30	C29	C32	118.2(3)	C11	N1	C7	120.2(3)
C29	C30	C25	122.1(2)	C11	N1	Co1	123.9(2)
F3	C31	F1	107.6(2)	C7	N1	Co1	115.91(19)
F3	C31	F2	106.5(2)	C23	N2	Co1	172.8(3)
F1	C31	F2	105.3(2)	C25	B1	C41	113.1(2)
F3	C31	C27	112.9(2)	C25	B1	C49	104.21(19)
F1	C31	C27	111.6(2)	C41	B1	C49	112.8(2)
F2	C31	C27	112.4(2)	C25	B1	C33	110.7(2)
F4	C32	F6	110.1(3)	C41	B1	C33	102.70(19)
F4	C32	F5	105.4(3)	C49	B1	C33	113.6(2)
F6	C32	F5	103.1(3)	N2	Co1	C1	94.30(11)
F4	C32	C29	113.8(3)	N2	Co1	N1	90.85(11)
F6	C32	C29	112.4(3)	C1	Co1	N1	82.06(12)
F5	C32	C29	111.3(3)	N2	Co1	C15	155.15(11)
C38	C33	C34	116.0(2)	C1	Co1	C15	110.42(12)
C38	C33	B1	123.2(2)	N1	Co1	C15	94.91(11)
C34	C33	B1	120.5(2)	N2	Co1	C13	104.99(12)
C35	C34	C33	121.9(2)	C1	Co1	C13	103.87(12)
C36	C35	C34	121.2(2)	N1	Co1	C13	162.43(11)
C36	C35	C39	118.8(3)	C15	Co1	C13	67.52(11)
C34	C35	C39	120.0(3)	N2	Co1	C14	143.48(12)
C35	C36	C37	117.8(2)	C1	Co1	C14	87.65(11)
C36	C37	C38	121.2(2)	N1	Co1	C14	125.44(11)
C36	C37	C40	119.2(2)	C15	Co1	C14	40.34(11)
C38	C37	C40	119.5(2)	C13	Co1	C14	39.98(12)
C37	C38	C33	121.9(2)	N2	Co1	C17	92.39(11)

F7	C39	F8	111.1(4)	C1	Co1	C17	143.79(12)
F8B	C39	F9B	113.5(7)	N1	Co1	C17	133.42(11)
F7	C39	F9	104.3(4)	C15	Co1	C17	66.31(11)
F8	C39	F9	99.2(4)	C13	Co1	C17	40.26(11)
F8B	C39	F7B	96.2(8)	C14	Co1	C17	66.72(11)
F9B	C39	F7B	106.5(8)	N2	Co1	C16	115.06(11)
F8B	C39	C35	115.4(5)	C1	Co1	C16	150.44(11)
F7	C39	C35	114.9(3)	N1	Co1	C16	99.95(11)
F8	C39	C35	114.9(3)	C15	Co1	C16	40.12(11)
F9B	C39	C35	114.4(6)	C13	Co1	C16	66.68(11)
F9	C39	C35	110.8(3)	C14	Co1	C16	67.00(11)
F7B	C39	C35	108.7(4)	C17	Co1	C16	38.35(11)

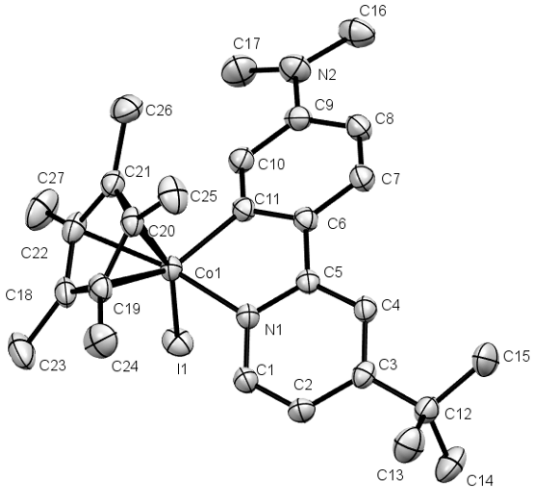


Table S7 Crystal data and structure refinement for (4a).

Identification code	**[*k*^{2}-(C,N)-(2-*anpy*)CoI] (4a)**
Empirical formula	$C_{27}H_{36}CoIN_2$
Formula weight	574.41
Temperature/K	173(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.6481(3)
b/Å	11.3372(5)
c/Å	13.9563(6)
α/°	78.3310(10)
β/°	75.4490(10)
γ/°	84.3210(10)
Volume/Å^3	1295.41(9)
Z	2
ρ_{calc}g/cm^3	1.473
μ/mm^{-1}	1.870
F(000)	584.0
Crystal size/mm^3	0.16 × 0.1 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.674 to 60.392
Index ranges	-12 ≤ h ≤ 12, -16 ≤ k ≤ 16, -19 ≤ l ≤ 19
Reflections collected	39425
Independent reflections	7644 [R_{int} = 0.0342, R_{sigma} = 0.0293]
Data/restraints/parameters	7644/0/290
Goodness-of-fit on F^2	1.005
Final R indexes [I>=2σ (I)]	R_1 = 0.0275, wR_2 = 0.0548
Final R indexes [all data]	R_1 = 0.0455, wR_2 = 0.0600
Largest diff. peak/hole / e Å^{-3}	0.79/-0.42

Table S8 Bond Lengths for (4a).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	N1	1.345(2)	C16	N2	1.453(3)
C1	C2	1.374(3)	C17	N2	1.438(3)
C2	C3	1.406(3)	C18	C19	1.395(3)
C3	C4	1.386(3)	C18	C22	1.449(3)
C3	C12	1.526(3)	C18	C23	1.505(3)
C4	C5	1.399(3)	C18	Co1	2.1524(19)
C5	N1	1.360(2)	C19	C20	1.444(3)
C5	C6	1.450(3)	C19	C24	1.497(3)
C6	C7	1.399(3)	C19	Co1	2.149(2)
C6	C11	1.406(3)	C20	C21	1.425(3)
C7	C8	1.379(3)	C20	C25	1.498(3)
C8	C9	1.411(3)	C20	Co1	2.0546(19)
C9	N2	1.388(3)	C21	C22	1.419(3)
C9	C10	1.413(3)	C21	C26	1.499(3)
C10	C11	1.391(3)	C21	Co1	2.080(2)
C11	Co1	1.9311(18)	C22	C27	1.500(3)
C12	C14	1.531(3)	C22	Co1	2.080(2)
C12	C15	1.534(3)	N1	Co1	1.9440(16)
C12	C13	1.536(3)	Co1	I1	2.5738(3)

Table S9 Bond Angles for (4a).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	C1	C2	122.55(18)	C22	C21	C26	127.7(2)
C1	C2	C3	120.43(18)	C20	C21	C26	124.43(19)
C4	C3	C2	116.30(18)	C22	C21	Co1	70.05(11)
C4	C3	C12	123.42(18)	C20	C21	Co1	68.88(11)
C2	C3	C12	120.08(18)	C26	C21	Co1	130.34(15)
C3	C4	C5	121.37(18)	C21	C22	C18	107.78(18)
N1	C5	C4	120.47(17)	C21	C22	C27	126.6(2)
N1	C5	C6	112.39(16)	C18	C22	C27	125.3(2)
C4	C5	C6	126.78(17)	C21	C22	Co1	70.07(11)
C7	C6	C11	119.85(18)	C18	C22	Co1	72.68(12)
C7	C6	C5	124.76(18)	C27	C22	Co1	127.60(17)
C11	C6	C5	114.55(16)	C1	N1	C5	118.74(16)
C8	C7	C6	121.08(19)	C1	N1	Co1	125.81(13)
C7	C8	C9	120.25(18)	C5	N1	Co1	115.44(13)
N2	C9	C8	120.71(18)	C9	N2	C17	118.89(19)
N2	C9	C10	121.11(19)	C9	N2	C16	119.2(2)
C8	C9	C10	118.17(18)	C17	N2	C16	118.08(19)
C11	C10	C9	121.75(19)	C11	Co1	N1	82.44(7)
C10	C11	C6	118.79(17)	C11	Co1	C20	105.61(8)
C10	C11	Co1	128.73(15)	N1	Co1	C20	98.67(7)
C6	C11	Co1	112.49(14)	C11	Co1	C22	112.65(9)
C3	C12	C14	107.82(18)	N1	Co1	C22	161.32(8)
C3	C12	C15	112.20(18)	C20	Co1	C22	67.43(8)
C14	C12	C15	109.1(2)	C11	Co1	C21	90.20(8)
C3	C12	C13	110.61(17)	N1	Co1	C21	134.21(7)
C14	C12	C13	108.7(2)	C20	Co1	C21	40.30(8)
C15	C12	C13	108.3(2)	C22	Co1	C21	39.88(8)
C19	C18	C22	108.34(18)	C11	Co1	C19	145.16(8)
C19	C18	C23	126.1(2)	N1	Co1	C19	95.26(7)

C22	C18	C23	125.4(2)	C20	Co1	C19	40.11(8)
C19	C18	Co1	70.96(11)	C22	Co1	C19	66.06(8)
C22	C18	Co1	67.31(11)	C21	Co1	C19	66.58(8)
C23	C18	Co1	130.88(16)	C11	Co1	C18	152.58(9)
C18	C19	C20	107.91(19)	N1	Co1	C18	123.88(8)
C18	C19	C24	127.1(2)	C20	Co1	C18	66.10(8)
C20	C19	C24	124.9(2)	C22	Co1	C18	40.01(9)
C18	C19	Co1	71.20(12)	C21	Co1	C18	66.36(8)
C20	C19	Co1	66.41(11)	C19	Co1	C18	37.84(8)
C24	C19	Co1	131.23(16)	C11	Co1	I1	91.70(6)
C21	C20	C19	108.10(17)	N1	Co1	I1	92.97(5)
C21	C20	C25	125.8(2)	C20	Co1	I1	160.21(5)
C19	C20	C25	125.8(2)	C22	Co1	I1	97.33(6)
C21	C20	Co1	70.82(11)	C21	Co1	I1	132.53(6)
C19	C20	Co1	73.48(11)	C19	Co1	I1	123.13(6)
C25	C20	Co1	126.10(15)	C18	Co1	I1	94.12(6)
C22	C21	C20	107.64(18)				

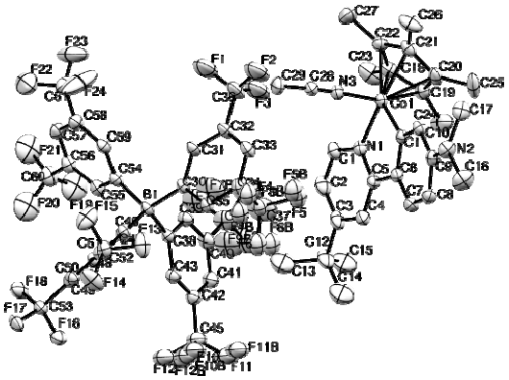


Table S10 Crystal data and structure refinement for (4b).

Identification code	**[k^2-(*C,N*)-(2-*anpy*)CoNCMe][BArF$_{24}$] (4b)**
Empirical formula	$C_{61}H_{51}BCoF_{24}N_3$
Formula weight	1351.79
Temperature/K	120(2)
Crystal system	triclinic
Space group	P-1
a/Å	14.6865(7)
b/Å	15.3384(8)
c/Å	16.6795(8)
α/°	99.496(2)
β/°	98.116(2)
γ/°	109.430(2)
Volume/Å^3	3416.3(3)
Z	2
ρ_{calc}g/cm^3	1.314
μ/mm^{-1}	0.354
F(000)	1372.0
Crystal size/mm^3	0.180 × 0.100 × 0.080
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.168 to 64.096
Index ranges	-21 ≤ h ≤ 21, -22 ≤ k ≤ 22, -24 ≤ l ≤ 24
Reflections collected	143751
Independent reflections	23751 [R_{int} = 0.0473, R_{sigma} = 0.0363]
Data/restraints/parameters	23751/0/777
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0823, wR_2 = 0.2268
Final R indexes [all data]	R_1 = 0.1100, wR_2 = 0.2521
Largest diff. peak/hole / e Å^{-3}	1.71/-1.95

Table S11 Bond Lengths for (4b).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	N1	1.350(3)	C37	F6B	1.406(7)
C1	C2	1.377(4)	C38	C39	1.393(3)
C2	C3	1.405(5)	C38	C43	1.404(4)
C3	C4	1.389(4)	C38	B1	1.640(4)
C3	C12	1.529(4)	C39	C40	1.398(4)
C4	C5	1.398(4)	C40	C41	1.375(4)
C5	N1	1.358(4)	C40	C44	1.484(4)
C5	C6	1.452(4)	C41	C42	1.388(4)
C6	C7	1.399(4)	C42	C43	1.388(4)
C6	C11	1.405(3)	C42	C45	1.490(4)
C7	C8	1.386(4)	C44	F7B	1.268(12)
C8	C9	1.405(4)	C44	F9	1.275(8)
C9	N2	1.384(3)	C44	F8	1.344(8)
C9	C10	1.414(4)	C44	F9B	1.368(12)
C10	C11	1.385(3)	C44	F8B	1.377(11)
C11	Co1	1.944(2)	C44	F7	1.410(9)
C12	C15	1.498(8)	C45	F10B	1.289(13)
C12	C13	1.508(7)	C45	F11	1.292(6)
C12	C14	1.546(8)	C45	F12B	1.309(8)
C16	N2	1.452(4)	C45	F10	1.361(9)
C17	N2	1.451(4)	C45	F12	1.380(6)
C18	C22	1.398(4)	C45	F11B	1.464(9)
C18	C19	1.450(4)	C46	C47	1.401(3)
C18	C23	1.491(4)	C46	C51	1.403(3)
C18	Co1	2.146(3)	C46	B1	1.638(3)
C19	C20	1.423(4)	C47	C48	1.394(3)
C19	C24	1.487(4)	C48	C49	1.384(3)
C19	Co1	2.048(3)	C48	C52	1.506(3)
C20	C21	1.408(4)	C49	C50	1.393(3)
C20	C25	1.500(4)	C50	C51	1.389(3)
C20	Co1	2.072(3)	C50	C53	1.505(3)
C21	C22	1.448(4)	C52	F14	1.328(3)
C21	C26	1.499(4)	C52	F15	1.333(3)
C21	Co1	2.062(3)	C52	F13	1.341(3)
C22	C27	1.495(4)	C53	F18	1.335(3)
C22	Co1	2.129(3)	C53	F17	1.336(3)
C28	N3	1.138(3)	C53	F16	1.347(3)
C28	C29	1.454(4)	C54	C55	1.402(3)
C30	C31	1.400(3)	C54	C59	1.407(4)
C30	C35	1.403(3)	C54	B1	1.636(4)
C30	B1	1.637(3)	C55	C56	1.392(4)
C31	C32	1.396(3)	C56	C57	1.381(4)
C32	C33	1.387(4)	C56	C60	1.495(4)
C32	C36	1.495(4)	C57	C58	1.395(4)
C33	C34	1.383(4)	C58	C59	1.381(4)
C34	C35	1.392(3)	C58	C61	1.504(4)
C34	C37	1.497(4)	C60	F21	1.319(5)
C36	F1	1.316(5)	C60	F19	1.327(5)
C36	F2	1.328(4)	C60	F20	1.328(5)
C36	F3	1.339(5)	C61	F23	1.292(4)
C37	F6	1.288(6)	C61	F24	1.324(4)

C37	F4B	1.316(6)	C61	F22	1.328(4)
C37	F5B	1.327(8)	N1	Co1	1.974(2)
C37	F5	1.345(6)	N3	Co1	1.907(2)
C37	F4	1.386(5)			

Table S12 Bond Angles for (4b).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N1	C1	C2	123.1(3)	F9	C44	C40	117.3(4)
C1	C2	C3	120.2(3)	F8	C44	C40	112.8(4)
C4	C3	C2	116.3(3)	F9B	C44	C40	111.8(5)
C4	C3	C12	122.4(3)	F8B	C44	C40	109.7(4)
C2	C3	C12	121.3(3)	F7	C44	C40	108.3(4)
C3	C4	C5	121.2(3)	F10B	C45	F12B	109.6(5)
N1	C5	C4	121.3(2)	F11	C45	F10	107.6(5)
N1	C5	C6	113.2(2)	F11	C45	F12	108.4(4)
C4	C5	C6	125.5(3)	F10	C45	F12	102.1(4)
C7	C6	C11	119.5(2)	F10B	C45	F11B	100.8(7)
C7	C6	C5	124.6(2)	F12B	C45	F11B	103.6(5)
C11	C6	C5	115.7(2)	F10B	C45	C42	118.4(5)
C8	C7	C6	120.9(2)	F11	C45	C42	116.4(3)
C7	C8	C9	120.4(2)	F12B	C45	C42	114.7(4)
N2	C9	C8	120.9(2)	F10	C45	C42	111.0(4)
N2	C9	C10	121.1(2)	F12	C45	C42	110.2(3)
C8	C9	C10	118.0(2)	F11B	C45	C42	107.5(4)
C11	C10	C9	121.8(2)	C47	C46	C51	115.7(2)
C10	C11	C6	119.2(2)	C47	C46	B1	124.9(2)
C10	C11	Co1	128.28(19)	C51	C46	B1	119.3(2)
C6	C11	Co1	112.47(17)	C48	C47	C46	121.9(2)
C15	C12	C13	114.0(4)	C49	C48	C47	121.5(2)
C15	C12	C3	108.1(3)	C49	C48	C52	120.1(2)
C13	C12	C3	109.7(3)	C47	C48	C52	118.3(2)
C15	C12	C14	106.3(4)	C48	C49	C50	117.3(2)
C13	C12	C14	107.1(4)	C51	C50	C49	121.3(2)
C3	C12	C14	111.7(3)	C51	C50	C53	118.1(2)
C22	C18	C19	107.5(2)	C49	C50	C53	120.7(2)
C22	C18	C23	127.9(3)	C50	C51	C46	122.2(2)
C19	C18	C23	124.3(3)	F14	C52	F15	106.8(2)
C22	C18	Co1	70.26(15)	F14	C52	F13	106.5(2)
C19	C18	Co1	66.15(14)	F15	C52	F13	105.5(2)
C23	C18	Co1	132.8(2)	F14	C52	C48	112.7(2)
C20	C19	C18	107.8(2)	F15	C52	C48	112.8(2)
C20	C19	C24	125.8(3)	F13	C52	C48	112.1(2)

C18	C19	C24	126.2(3)	F18	C53	F17	107.1(2)
C20	C19	Co1	70.74(15)	F18	C53	F16	105.8(2)
C18	C19	Co1	73.47(16)	F17	C53	F16	106.7(2)
C24	C19	Co1	124.7(2)	F18	C53	C50	112.8(2)
C21	C20	C19	108.1(2)	F17	C53	C50	112.8(2)
C21	C20	C25	126.4(3)	F16	C53	C50	111.3(2)
C19	C20	C25	125.3(3)	C55	C54	C59	115.4(2)
C21	C20	Co1	69.69(15)	C55	C54	B1	122.7(2)
C19	C20	Co1	68.86(15)	C59	C54	B1	121.6(2)
C25	C20	Co1	131.4(2)	C56	C55	C54	122.2(2)
C20	C21	C22	107.9(2)	C57	C56	C55	121.3(2)
C20	C21	C26	127.4(3)	C57	C56	C60	120.0(3)
C22	C21	C26	124.3(3)	C55	C56	C60	118.7(3)
C20	C21	Co1	70.50(16)	C56	C57	C58	117.5(2)
C22	C21	Co1	72.31(15)	C59	C58	C57	121.3(3)
C26	C21	Co1	128.4(2)	C59	C58	C61	120.6(3)
C18	C22	C21	108.3(2)	C57	C58	C61	118.2(3)
C18	C22	C27	126.6(3)	C58	C59	C54	122.3(2)
C21	C22	C27	125.0(3)	F21	C60	F19	104.8(3)
C18	C22	Co1	71.57(16)	F21	C60	F20	106.4(3)
C21	C22	Co1	67.30(15)	F19	C60	F20	104.9(3)
C27	C22	Co1	128.1(2)	F21	C60	C56	114.4(3)
N3	C28	C29	177.2(3)	F19	C60	C56	113.2(3)
C31	C30	C35	115.9(2)	F20	C60	C56	112.4(3)
C31	C30	B1	122.8(2)	F23	C61	F24	109.3(4)
C35	C30	B1	121.1(2)	F23	C61	F22	105.3(3)
C32	C31	C30	121.9(2)	F24	C61	F22	102.7(4)
C33	C32	C31	121.1(2)	F23	C61	C58	113.6(3)
C33	C32	C36	119.6(2)	F24	C61	C58	112.8(3)
C31	C32	C36	119.3(3)	F22	C61	C58	112.4(3)
C34	C33	C32	117.9(2)	C1	N1	C5	117.8(2)
C33	C34	C35	121.0(2)	C1	N1	Co1	127.4(2)
C33	C34	C37	119.0(2)	C5	N1	Co1	114.74(17)
C35	C34	C37	119.8(2)	C9	N2	C17	119.9(2)
C34	C35	C30	122.1(2)	C9	N2	C16	119.7(3)
F1	C36	F2	107.0(3)	C17	N2	C16	115.2(3)
F1	C36	F3	105.8(3)	C28	N3	Co1	177.6(2)
F2	C36	F3	105.5(3)	C54	B1	C30	112.9(2)
F1	C36	C32	113.4(3)	C54	B1	C46	104.78(19)
F2	C36	C32	112.9(3)	C30	B1	C46	112.60(18)
F3	C36	C32	111.6(3)	C54	B1	C38	111.09(19)
F4B	C37	F5B	109.6(4)	C30	B1	C38	104.15(19)
F6	C37	F5	108.5(4)	C46	B1	C38	111.5(2)
F6	C37	F4	107.5(3)	N3	Co1	C11	90.03(10)
F5	C37	F4	103.3(3)	N3	Co1	N1	93.72(9)

F4B	C37	F6B	104.5(4)	C11	Co1	N1	82.94(10)
F5B	C37	F6B	103.5(4)	N3	Co1	C19	160.72(11)
F6	C37	C34	115.4(3)	C11	Co1	C19	107.64(11)
F4B	C37	C34	113.0(3)	N1	Co1	C19	96.00(11)
F5B	C37	C34	114.6(4)	N3	Co1	C21	99.80(10)
F5	C37	C34	111.3(3)	C11	Co1	C21	108.55(11)
F4	C37	C34	110.1(3)	N1	Co1	C21	162.10(10)
F6B	C37	C34	110.7(3)	C19	Co1	C21	67.77(11)
C39	C38	C43	116.0(2)	N3	Co1	C20	135.70(11)
C39	C38	B1	119.8(2)	C11	Co1	C20	89.09(10)
C43	C38	B1	124.0(2)	N1	Co1	C20	130.02(11)
C38	C39	C40	122.1(2)	C19	Co1	C20	40.40(12)
C41	C40	C39	120.9(2)	C21	Co1	C20	39.82(12)
C41	C40	C44	119.9(3)	N3	Co1	C22	94.20(10)
C39	C40	C44	119.2(3)	C11	Co1	C22	148.91(10)
C40	C41	C42	118.0(3)	N1	Co1	C22	127.35(10)
C43	C42	C41	121.2(2)	C19	Co1	C22	66.71(11)
C43	C42	C45	119.9(3)	C21	Co1	C22	40.39(11)
C41	C42	C45	118.8(3)	C20	Co1	C22	66.67(11)
C42	C43	C38	121.7(2)	N3	Co1	C18	121.91(11)
F9	C44	F8	110.0(5)	C11	Co1	C18	147.95(11)
F7B	C44	F9B	104.7(7)	N1	Co1	C18	96.40(10)
F7B	C44	F8B	102.8(6)	C19	Co1	C18	40.38(12)
F9B	C44	F8B	107.2(6)	C21	Co1	C18	66.49(10)
F9	C44	F7	108.4(5)	C20	Co1	C18	66.76(11)
F8	C44	F7	98.1(4)	C22	Co1	C18	38.17(11)
F7B	C44	C40	119.7(5)				

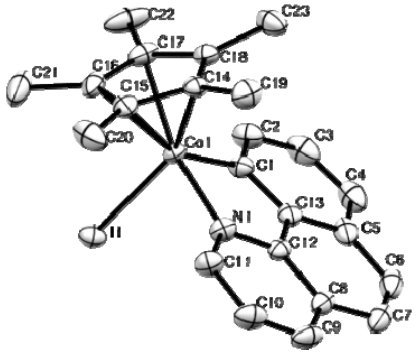


Table S13 Crystal data and structure refinement for (5a).

Identification code	**[k^2-(*C,N*)-(*bzq*)CoI] (5a)**
Empirical formula	$C_{23}H_{23}CoIN$
Formula weight	499.25
Temperature/K	173(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.2480(5)
b/Å	14.5894(9)
c/Å	16.1813(10)
α/°	90
β/°	99.481(2)
γ/°	90
Volume/Å^3	1920.6(2)
Z	4
ρ_{calc}g/cm^3	1.727
μ/mm^{-1}	2.507
F(000)	992.0
Crystal size/mm^3	0.350 × 0.200 × 0.150
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.782 to 60.118
Index ranges	$-10 \le h \le 11$, $-20 \le k \le 20$, $-22 \le l \le 22$
Reflections collected	49203
Independent reflections	5625 [R_{int} = 0.0170, R_{sigma} = 0.0085]
Data/restraints/parameters	5625/0/240
Goodness-of-fit on F^2	1.257
Final R indexes [I>=2σ (I)]	R_1 = 0.0238, wR_2 = 0.0555
Final R indexes [all data]	R_1 = 0.0252, wR_2 = 0.0560
Largest diff. peak/hole / e Å^{-3}	0.54/-0.46

Table S14 Bond Lengths for (5a).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.372(3)	C14	C15	1.430(3)
C1	C13	1.396(3)	C14	C18	1.431(3)
C1	Co1	1.9631(18)	C14	C19	1.494(3)
C2	C3	1.409(3)	C14	Co1	2.0850(18)
C3	C4	1.381(4)	C15	C16	1.414(3)
C4	C5	1.405(3)	C15	C20	1.502(3)
C5	C13	1.413(3)	C15	Co1	2.1278(19)
C5	C6	1.441(3)	C16	C17	1.427(3)
C6	C7	1.355(4)	C16	C21	1.497(3)
C7	C8	1.440(3)	C16	Co1	2.142(2)
C8	C9	1.404(3)	C17	C18	1.433(3)
C8	C12	1.413(3)	C17	C22	1.501(3)
C9	C10	1.374(4)	C17	Co1	2.087(2)
C10	C11	1.406(3)	C18	C23	1.496(3)
C11	N1	1.352(3)	C18	Co1	2.0659(19)
C12	N1	1.376(3)	N1	Co1	1.9703(17)
C12	C13	1.422(3)	Co1	I1	2.5730(3)

Table S15 Bond Angles for (5a).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	C1	C13	116.49(18)	C16	C17	C22	124.7(2)
C2	C1	Co1	131.62(16)	C18	C17	C22	127.2(2)
C13	C1	Co1	111.86(13)	C16	C17	Co1	72.35(12)
C1	C2	C3	121.6(2)	C18	C17	Co1	69.02(11)
C4	C3	C2	121.2(2)	C22	C17	Co1	130.27(16)
C3	C4	C5	119.1(2)	C14	C18	C17	107.62(17)
C4	C5	C13	117.6(2)	C14	C18	C23	125.4(2)
C4	C5	C6	124.5(2)	C17	C18	C23	126.9(2)
C13	C5	C6	117.8(2)	C14	C18	Co1	70.55(11)
C7	C6	C5	121.7(2)	C17	C18	Co1	70.61(11)
C6	C7	C8	121.5(2)	C23	C18	Co1	127.32(15)
C9	C8	C12	117.6(2)	C11	N1	C12	117.53(17)
C9	C8	C7	125.0(2)	C11	N1	Co1	129.72(15)
C12	C8	C7	117.5(2)	C12	N1	Co1	112.75(13)
C10	C9	C8	118.97(19)	C1	Co1	N1	83.65(7)
C9	C10	C11	121.0(2)	C1	Co1	C18	91.85(8)
N1	C11	C10	121.5(2)	N1	Co1	C18	120.61(8)
N1	C12	C8	123.38(19)	C1	Co1	C14	120.38(8)
N1	C12	C13	115.43(17)	N1	Co1	C14	93.63(7)
C8	C12	C13	121.15(18)	C18	Co1	C14	40.33(7)

C1	C13	C5	123.83(19)	C1	Co1	C17	100.61(8)
C1	C13	C12	115.89(17)	N1	Co1	C17	160.05(8)
C5	C13	C12	120.24(19)	C18	Co1	C17	40.37(8)
C15	C14	C18	108.20(17)	C14	Co1	C17	67.29(8)
C15	C14	C19	125.86(19)	C1	Co1	C15	158.51(8)
C18	C14	C19	125.78(19)	N1	Co1	C15	102.94(8)
C15	C14	Co1	71.77(11)	C18	Co1	C15	67.09(8)
C18	C14	Co1	69.11(11)	C14	Co1	C15	39.68(8)
C19	C14	Co1	128.43(14)	C17	Co1	C15	66.52(8)
C16	C15	C14	107.70(18)	C1	Co1	C16	137.48(9)
C16	C15	C20	125.7(2)	N1	Co1	C16	138.79(9)
C14	C15	C20	126.3(2)	C18	Co1	C16	66.48(8)
C16	C15	Co1	71.20(12)	C14	Co1	C16	65.81(8)
C14	C15	Co1	68.55(11)	C17	Co1	C16	39.43(9)
C20	C15	Co1	131.11(16)	C15	Co1	C16	38.68(9)
C15	C16	C17	108.91(18)	C1	Co1	I1	90.66(5)
C15	C16	C21	124.9(3)	N1	Co1	I1	90.79(5)
C17	C16	C21	126.0(2)	C18	Co1	I1	148.58(6)
C15	C16	Co1	70.13(11)	C14	Co1	I1	148.94(5)
C17	C16	Co1	68.22(11)	C17	Co1	I1	108.52(6)
C21	C16	Co1	132.03(16)	C15	Co1	I1	109.47(6)
C16	C17	C18	107.54(18)	C16	Co1	I1	91.15(6)

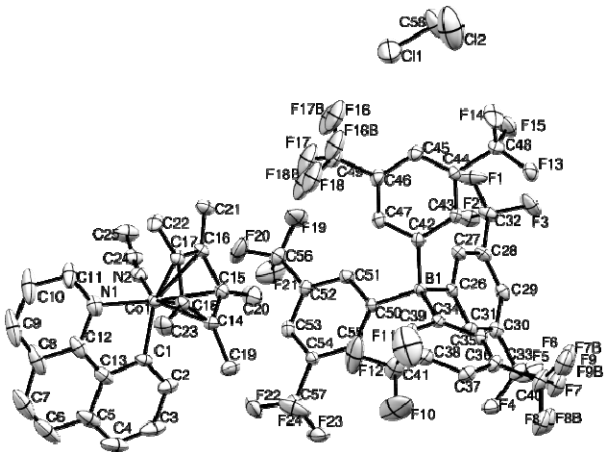


Table S16 Crystal data and structure refinement for (5b).

Identification code	**[*k*^{2}-(*C,N*)-(*bzq*)CoNCMe][BArF$_{24}$] (5b)**
Empirical formula	$C_{58}H_{40}BCl_2CoF_{24}N_2$
Formula weight	1361.56
Temperature/K	120(2)
Crystal system	triclinic
Space group	P-1
a/Å	12.3000(7)
b/Å	12.8438(8)
c/Å	18.7707(11)
α/°	87.846(2)
β/°	81.776(2)
γ/°	74.818(2)
Volume/Å^3	2832.4(3)
Z	2
ρ_{calc}g/cm^3	1.596
μ/mm^{-1}	0.518
F(000)	1368.0
Crystal size/mm^3	0.200 × 0.150 × 0.120
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.836 to 55.856
Index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -24 ≤ l ≤ 24
Reflections collected	199456
Independent reflections	13555 [R_{int} = 0.0499, R_{sigma} = 0.0183]
Data/restraints/parameters	13555/0/793
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0715, wR_2 = 0.1967
Final R indexes [all data]	R_1 = 0.0798, wR_2 = 0.2062
Largest diff. peak/hole / e Å^{-3}	1.99/-1.88

Table S17 Bond Lengths for (5b).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.371(4)	C35	C36	1.394(4)
C1	C13	1.402(4)	C36	C37	1.381(4)
C1	Co1	1.958(3)	C36	C40	1.501(4)
C2	C3	1.411(5)	C37	C38	1.386(4)
C3	C4	1.362(7)	C38	C39	1.390(4)
C4	C5	1.407(7)	C38	C41	1.503(4)
C5	C13	1.417(5)	C40	F8B	1.246(10)
C5	C6	1.442(7)	C40	F9	1.311(9)
C6	C7	1.330(9)	C40	F7	1.313(6)
C7	C8	1.447(7)	C40	F8	1.395(7)
C8	C9	1.387(8)	C40	F7B	1.418(8)
C8	C12	1.421(5)	C40	F9B	1.420(12)
C9	C10	1.363(8)	C41	F10	1.287(5)
C10	C11	1.404(6)	C41	F12	1.305(5)
C11	N1	1.335(5)	C41	F11	1.357(6)
C12	N1	1.378(5)	C42	C47	1.402(4)
C12	C13	1.408(5)	C42	C43	1.406(4)
C14	C15	1.422(4)	C42	B1	1.645(4)
C14	C18	1.428(4)	C43	C44	1.390(4)
C14	C19	1.494(4)	C44	C45	1.394(4)
C14	Co1	2.076(3)	C44	C48	1.497(4)
C15	C16	1.443(4)	C45	C46	1.377(4)
C15	C20	1.492(4)	C46	C47	1.390(4)
C15	Co1	2.071(3)	C46	C49	1.500(4)
C16	C17	1.400(4)	C48	F14	1.331(4)
C16	C21	1.495(4)	C48	F13	1.333(4)
C16	Co1	2.115(3)	C48	F15	1.344(4)
C17	C18	1.444(4)	C49	F17B	1.259(10)
C17	C22	1.495(4)	C49	F18B	1.297(11)
C17	Co1	2.125(3)	C49	F18	1.306(7)
C18	C23	1.496(4)	C49	F16	1.319(7)
C18	Co1	2.055(3)	C49	F17	1.375(7)
C24	N2	1.135(4)	C49	F16B	1.463(10)
C24	C25	1.460(5)	C50	C55	1.397(4)
C26	C27	1.401(4)	C50	C51	1.411(4)
C26	C31	1.405(4)	C50	B1	1.645(4)
C26	B1	1.639(4)	C51	C52	1.388(4)
C27	C28	1.394(4)	C52	C53	1.391(4)
C28	C29	1.383(4)	C52	C56	1.496(4)
C28	C32	1.497(4)	C53	C54	1.380(4)
C29	C30	1.387(4)	C54	C55	1.399(4)
C30	C31	1.394(4)	C54	C57	1.495(4)
C30	C33	1.497(4)	C56	F19	1.326(4)

C32	F1	1.330(4)	C56	F21	1.328(4)
C32	F3	1.341(4)	C56	F20	1.337(4)
C32	F2	1.341(4)	C57	F23	1.312(4)
C33	F5	1.336(4)	C57	F22	1.322(4)
C33	F4	1.336(4)	C57	F24	1.349(4)
C33	F6	1.343(4)	C58	Cl1	1.710(5)
C34	C35	1.400(4)	C58	Cl2	1.757(6)
C34	C39	1.405(4)	N1	Co1	1.977(3)
C34	B1	1.643(4)	N2	Co1	1.910(3)

Table S18 Bond Angles for (5b).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	C1	C13	117.4(3)	F9B	C40	C36	109.6(4)
C2	C1	Co1	131.5(3)	F10	C41	F12	111.4(4)
C13	C1	Co1	111.1(2)	F10	C41	F11	102.2(4)
C1	C2	C3	120.7(4)	F12	C41	F11	103.3(4)
C4	C3	C2	121.8(4)	F10	C41	C38	113.5(3)
C3	C4	C5	119.7(3)	F12	C41	C38	114.2(3)
C4	C5	C13	117.5(4)	F11	C41	C38	111.0(3)
C4	C5	C6	125.6(4)	C47	C42	C43	115.9(3)
C13	C5	C6	116.8(5)	C47	C42	B1	122.9(2)
C7	C6	C5	122.4(4)	C43	C42	B1	121.2(2)
C6	C7	C8	122.3(4)	C44	C43	C42	122.1(3)
C9	C8	C12	117.5(4)	C43	C44	C45	120.8(3)
C9	C8	C7	126.5(4)	C43	C44	C48	120.5(3)
C12	C8	C7	115.9(5)	C45	C44	C48	118.6(3)
C10	C9	C8	119.5(4)	C46	C45	C44	117.7(3)
C9	C10	C11	120.7(5)	C45	C46	C47	121.7(3)
N1	C11	C10	121.8(4)	C45	C46	C49	120.2(3)
N1	C12	C13	115.6(3)	C47	C46	C49	118.1(3)
N1	C12	C8	122.5(4)	C46	C47	C42	121.7(3)
C13	C12	C8	121.8(4)	F14	C48	F13	106.9(3)
C1	C13	C12	116.6(3)	F14	C48	F15	106.2(3)
C1	C13	C5	122.9(4)	F13	C48	F15	105.3(3)
C12	C13	C5	120.5(3)	F14	C48	C44	112.9(3)
C15	C14	C18	107.9(2)	F13	C48	C44	112.9(3)
C15	C14	C19	126.6(3)	F15	C48	C44	112.2(3)
C18	C14	C19	125.3(3)	F17B	C49	F18B	123.9(6)
C15	C14	Co1	69.76(17)	F18	C49	F16	105.9(5)
C18	C14	Co1	68.99(17)	F18	C49	F17	103.9(5)
C19	C14	Co1	131.1(2)	F16	C49	F17	106.4(5)
C14	C15	C16	107.4(2)	F17	C49	F16	98.5(6)

				B		B	
C14	C15	C20	127.3(3)	F18 B	C49	F16 B	92.6(6)
C16	C15	C20	124.9(3)	F17 B	C49	C46	114.2(4)
C14	C15	Co1	70.14(17)	F18 B	C49	C46	114.8(4)
C16	C15	Co1	71.47(16)	F18	C49	C46	113.8(4)
C20	C15	Co1	128.8(2)	F16	C49	C46	115.2(4)
C17	C16	C15	109.0(2)	F17	C49	C46	110.7(3)
C17	C16	C21	125.1(3)	F16 B	C49	C46	106.0(4)
C15	C16	C21	125.9(3)	C55	C50	C51	115.8(2)
C17	C16	Co1	71.10(16)	C55	C50	B1	124.2(2)
C15	C16	Co1	68.23(16)	C51	C50	B1	119.9(2)
C21	C16	Co1	127.5(2)	C52	C51	C50	122.0(3)
C16	C17	C18	107.5(2)	C51	C52	C53	120.8(3)
C16	C17	C22	125.8(3)	C51	C52	C56	121.3(3)
C18	C17	C22	126.4(3)	C53	C52	C56	118.0(3)
C16	C17	Co1	70.33(16)	C54	C53	C52	118.3(3)
C18	C17	Co1	67.22(16)	C53	C54	C55	120.9(3)
C22	C17	Co1	132.3(2)	C53	C54	C57	120.3(3)
C14	C18	C17	108.0(2)	C55	C54	C57	118.8(3)
C14	C18	C23	125.5(3)	C50	C55	C54	122.1(2)
C17	C18	C23	126.2(3)	F19	C56	F21	107.7(3)
C14	C18	Co1	70.57(17)	F19	C56	F20	105.6(3)
C17	C18	Co1	72.39(16)	F21	C56	F20	105.6(3)
C23	C18	Co1	126.7(2)	F19	C56	C52	113.5(3)
N2	C24	C25	178.3(4)	F21	C56	C52	112.2(3)
C27	C26	C31	115.8(2)	F20	C56	C52	111.7(3)
C27	C26	B1	121.8(2)	F23	C57	F22	108.9(3)
C31	C26	B1	122.2(2)	F23	C57	F24	104.9(3)
C28	C27	C26	121.9(3)	F22	C57	F24	104.6(3)
C29	C28	C27	121.3(3)	F23	C57	C54	113.1(3)
C29	C28	C32	117.8(3)	F22	C57	C54	113.5(3)
C27	C28	C32	120.9(3)	F24	C57	C54	111.0(3)
C28	C29	C30	118.1(3)	Cl1	C58	Cl2	114.6(3)
C29	C30	C31	120.7(3)	C11	N1	C12	117.8(3)
C29	C30	C33	119.9(3)	C11	N1	Co1	130.3(3)
C31	C30	C33	119.4(3)	C12	N1	Co1	111.8(2)
C30	C31	C26	122.3(2)	C24	N2	Co1	173.6(3)
F1	C32	F3	105.9(3)	C26	B1	C34	113.0(2)
F1	C32	F2	107.6(3)	C26	B1	C42	110.6(2)
F3	C32	F2	105.9(2)	C34	B1	C42	105.6(2)
F1	C32	C28	113.3(2)	C26	B1	C50	105.1(2)
F3	C32	C28	112.2(3)	C34	B1	C50	111.6(2)

F2	C32	C28	111.6(2)	C42	B1	C50	111.0(2)
F5	C33	F4	106.1(3)	N2	Co1	C1	91.92(11)
F5	C33	F6	107.6(3)	N2	Co1	N1	95.47(12)
F4	C33	F6	105.4(3)	C1	Co1	N1	83.89(13)
F5	C33	C30	113.0(3)	N2	Co1	C18	156.42(11)
F4	C33	C30	112.5(3)	C1	Co1	C18	110.53(12)
F6	C33	C30	111.7(3)	N1	Co1	C18	94.07(12)
C35	C34	C39	115.8(2)	N2	Co1	C15	99.42(12)
C35	C34	B1	123.7(2)	C1	Co1	C15	106.96(12)
C39	C34	B1	120.4(2)	N1	Co1	C15	161.16(12)
C36	C35	C34	121.7(3)	C18	Co1	C15	67.89(12)
C37	C36	C35	121.6(3)	N2	Co1	C14	137.17(12)
C37	C36	C40	119.3(3)	C1	Co1	C14	89.70(12)
C35	C36	C40	119.1(3)	N1	Co1	C14	127.22(12)
C36	C37	C38	117.6(3)	C18	Co1	C14	40.44(12)
C37	C38	C39	121.2(3)	C15	Co1	C14	40.10(11)
C37	C38	C41	118.6(3)	N2	Co1	C16	90.60(11)
C39	C38	C41	120.2(3)	C1	Co1	C16	146.97(12)
C38	C39	C34	122.1(3)	N1	Co1	C16	128.60(12)
F9	C40	F7	110.4(4)	C18	Co1	C16	66.73(11)
F9	C40	F8	105.9(4)	C15	Co1	C16	40.30(11)
F7	C40	F8	105.4(4)	C14	Co1	C16	66.84(11)
F8B	C40	F7B	108.7(5)	N2	Co1	C17	116.96(11)
F8B	C40	F9B	104.8(7)	C1	Co1	C17	150.91(12)
F7B	C40	F9B	100.3(5)	N1	Co1	C17	95.99(11)
F8B	C40	C36	119.0(5)	C18	Co1	C17	40.38(11)
F9	C40	C36	113.3(4)	C15	Co1	C17	66.94(11)
F7	C40	C36	112.0(3)	C14	Co1	C17	67.17(11)
F8	C40	C36	109.3(3)	C16	Co1	C17	38.57(11)
F7B	C40	C36	112.4(4)				

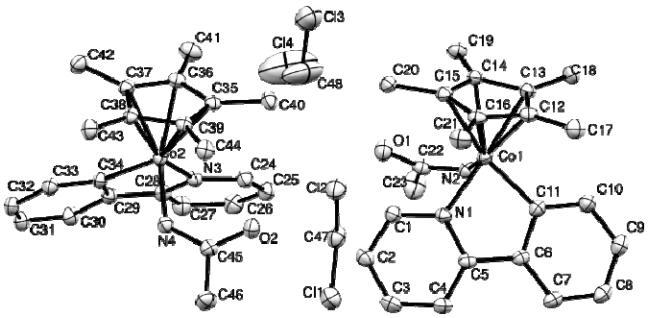


Table S19 Crystal data and structure refinement for (1f).

Identification code	**[k^2-(*C,N*)-(2-phpy)CoNHAc] (1f)**
Empirical formula	$C_{24}H_{29}Cl_2CoN_2O$
Formula weight	491.32
Temperature/K	120(2)
Crystal system	triclinic
Space group	P-1
a/Å	13.0238(6)
b/Å	13.1444(6)
c/Å	15.2024(8)
α/°	88.651(2)
β/°	71.961(2)
γ/°	71.357(2)
Volume/Å^3	2336.5(2)
Z	4
ρ_{calc}g/cm^3	1.397
μ/mm^{-1}	0.981
F(000)	1024.0
Crystal size/mm^3	0.220 × 0.180 × 0.150
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.922 to 58.364
Index ranges	-17 ≤ h ≤ 17, -17 ≤ k ≤ 18, -20 ≤ l ≤ 20
Reflections collected	177479
Independent reflections	12596 [R_{int} = 0.0378, R_{sigma} = 0.0151]
Data/restraints/parameters	12596/0/561
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.0959
Final R indexes [all data]	R_1 = 0.0459, wR_2 = 0.1016
Largest diff. peak/hole / e Å^{-3}	1.67/-2.06

Table S20 Bond Lengths for (1f).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	N1	1.345(2)	C27	C28	1.398(3)
C1	C2	1.388(3)	C28	N3	1.359(2)
C2	C3	1.390(3)	C28	C29	1.464(2)
C3	C4	1.384(3)	C29	C30	1.401(2)
C4	C5	1.396(3)	C29	C34	1.409(2)
C5	N1	1.360(2)	C30	C31	1.390(3)
C5	C6	1.463(3)	C31	C32	1.391(3)
C6	C7	1.403(2)	C32	C33	1.395(3)
C6	C11	1.410(3)	C33	C34	1.399(2)
C7	C8	1.387(3)	C34	Co2	1.9215(17)
C8	C9	1.390(3)	C35	C39	1.408(2)
C9	C10	1.397(3)	C35	C36	1.447(3)
C10	C11	1.399(3)	C35	C40	1.496(3)
C11	Co1	1.9319(18)	C35	Co2	2.1463(17)
C12	C16	1.427(3)	C36	C37	1.423(3)
C12	C13	1.435(3)	C36	C41	1.497(3)
C12	C17	1.499(3)	C36	Co2	2.0887(18)
C12	Co1	2.0780(18)	C37	C38	1.434(3)
C13	C14	1.437(3)	C37	C42	1.497(3)
C13	C18	1.499(3)	C37	Co2	2.0831(18)
C13	Co1	2.0701(18)	C38	C39	1.441(2)
C14	C15	1.413(2)	C38	C43	1.497(3)
C14	C19	1.495(3)	C38	Co2	2.0650(17)
C14	Co1	2.1203(17)	C39	C44	1.490(2)
C15	C16	1.441(3)	C39	Co2	2.1313(17)
C15	C20	1.497(3)	C45	O2	1.253(2)
C15	Co1	2.1442(17)	C45	N4	1.328(2)
C16	C21	1.500(3)	C45	C46	1.520(3)
C16	Co1	2.0897(18)	C47	Cl2	1.771(2)
C22	O1	1.254(2)	C47	Cl1	1.771(2)
C22	N2	1.323(2)	C48	Cl4	1.718(5)
C22	C23	1.518(3)	C48	Cl3	1.720(4)
C24	N3	1.348(2)	N1	Co1	1.9590(15)
C24	C25	1.386(3)	N2	Co1	1.9276(16)
C25	C26	1.390(3)	N3	Co2	1.9673(15)
C26	C27	1.385(3)	N4	Co2	1.9286(16)

Table S21 Bond Angles for (1f).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N1	C1	C2	122.97(18)	C38	C37	Co2	69.10(10)
C1	C2	C3	118.44(18)	C42	C37	Co2	129.95(13)
C4	C3	C2	119.14(18)	C37	C38	C39	107.53(16)
C3	C4	C5	119.75(18)	C37	C38	C43	127.90(17)
N1	C5	C4	120.97(17)	C39	C38	C43	124.02(16)
N1	C5	C6	113.27(15)	C37	C38	Co2	70.46(10)
C4	C5	C6	125.74(17)	C39	C38	Co2	72.42(10)
C7	C6	C11	121.64(17)	C43	C38	Co2	129.18(13)
C7	C6	C5	123.55(17)	C35	C39	C38	108.73(16)
C11	C6	C5	114.76(15)	C35	C39	C44	127.20(16)
C8	C7	C6	119.74(18)	C38	C39	C44	124.06(16)
C7	C8	C9	119.60(18)	C35	C39	Co2	71.37(10)
C8	C9	C10	120.53(19)	C38	C39	Co2	67.47(10)
C9	C10	C11	121.34(19)	C44	C39	Co2	128.11(13)
C10	C11	C6	117.12(17)	O2	C45	N4	123.26(18)
C10	C11	Co1	129.51(14)	O2	C45	C46	118.41(17)
C6	C11	Co1	113.23(13)	N4	C45	C46	118.31(17)
C16	C12	C13	107.55(16)	Cl2	C47	Cl1	111.50(12)
C16	C12	C17	125.76(17)	Cl4	C48	Cl3	117.3(2)
C13	C12	C17	126.49(18)	C1	N1	C5	118.68(16)
C16	C12	Co1	70.42(10)	C1	N1	Co1	126.06(13)
C13	C12	Co1	69.47(10)	C5	N1	Co1	115.20(12)
C17	C12	Co1	129.40(14)	C22	N2	Co1	126.05(14)
C12	C13	C14	107.65(16)	C24	N3	C28	118.60(15)
C12	C13	C18	127.41(17)	C24	N3	Co2	126.23(12)
C14	C13	C18	124.44(17)	C28	N3	Co2	115.17(12)
C12	C13	Co1	70.06(10)	C45	N4	Co2	125.48(13)
C14	C13	Co1	71.83(10)	N2	Co1	C11	88.06(7)
C18	C13	Co1	129.88(13)	N2	Co1	N1	90.12(7)
C15	C14	C13	108.78(16)	C11	Co1	N1	83.51(7)
C15	C14	C19	126.30(17)	N2	Co1	C13	106.21(7)
C13	C14	C19	124.92(16)	C11	Co1	C13	101.78(8)
C15	C14	Co1	71.57(10)	N1	Co1	C13	162.89(7)
C13	C14	Co1	68.07(10)	N2	Co1	C12	145.83(7)
C19	C14	Co1	126.87(13)	C11	Co1	C12	92.14(7)
C14	C15	C16	107.47(16)	N1	Co1	C12	123.87(7)
C14	C15	C20	125.38(17)	C13	Co1	C12	40.47(7)
C16	C15	C20	127.00(17)	N2	Co1	C16	152.38(7)
C14	C15	Co1	69.74(10)	C11	Co1	C16	119.38(8)
C16	C15	Co1	68.08(10)	N1	Co1	C16	95.75(7)
C20	C15	Co1	130.76(13)	C13	Co1	C16	67.41(7)
C12	C16	C15	108.51(16)	C12	Co1	C16	40.04(7)

C12	C16	C21	126.02(18)	N2	Co1	C14	91.28(7)
C15	C16	C21	125.39(18)	C11	Co1	C14	139.51(8)
C12	C16	Co1	69.54(10)	N1	Co1	C14	136.99(7)
C15	C16	Co1	72.16(10)	C13	Co1	C14	40.10(7)
C21	C16	Co1	126.75(13)	C12	Co1	C14	67.03(7)
O1	C22	N2	123.93(18)	C16	Co1	C14	66.26(7)
O1	C22	C23	117.59(18)	N2	Co1	C15	112.62(7)
N2	C22	C23	118.48(18)	C11	Co1	C15	158.14(7)
N3	C24	C25	122.91(17)	N1	Co1	C15	102.66(7)
C24	C25	C26	118.48(18)	C13	Co1	C15	66.69(7)
C27	C26	C25	119.30(18)	C12	Co1	C15	66.89(7)
C26	C27	C28	119.44(18)	C16	Co1	C15	39.77(7)
N3	C28	C27	121.17(17)	C14	Co1	C15	38.69(7)
N3	C28	C29	112.86(15)	C34	Co2	N4	88.64(7)
C27	C28	C29	125.92(16)	C34	Co2	N3	83.11(7)
C30	C29	C34	121.78(17)	N4	Co2	N3	92.85(7)
C30	C29	C28	123.47(17)	C34	Co2	C38	103.61(7)
C34	C29	C28	114.58(15)	N4	Co2	C38	102.02(7)
C31	C30	C29	119.55(18)	N3	Co2	C38	163.72(7)
C30	C31	C32	119.58(17)	C34	Co2	C37	91.13(7)
C31	C32	C33	120.60(18)	N4	Co2	C37	140.93(7)
C32	C33	C34	121.27(18)	N3	Co2	C37	125.90(7)
C33	C34	C29	117.21(16)	C38	Co2	C37	40.44(7)
C33	C34	Co2	128.82(14)	C34	Co2	C36	115.94(7)
C29	C34	Co2	113.84(13)	N4	Co2	C36	154.60(7)
C39	C35	C36	107.60(16)	N3	Co2	C36	96.22(7)
C39	C35	C40	125.83(17)	C38	Co2	C36	67.50(7)
C36	C35	C40	126.46(17)	C37	Co2	C36	39.89(7)
C39	C35	Co2	70.21(10)	C34	Co2	C39	142.43(7)
C36	C35	Co2	67.90(10)	N4	Co2	C39	90.71(7)
C40	C35	Co2	130.13(13)	N3	Co2	C39	134.42(7)
C37	C36	C35	108.25(16)	C38	Co2	C39	40.12(7)
C37	C36	C41	126.05(17)	C37	Co2	C39	66.74(7)
C35	C36	C41	125.53(17)	C36	Co2	C39	66.15(7)
C37	C36	Co2	69.84(10)	C34	Co2	C35	155.52(7)
C35	C36	Co2	72.19(10)	N4	Co2	C35	114.97(7)
C41	C36	Co2	127.28(14)	N3	Co2	C35	101.15(7)
C36	C37	C38	107.77(15)	C38	Co2	C35	66.66(7)
C36	C37	C42	125.63(17)	C37	Co2	C35	66.69(7)
C38	C37	C42	126.41(17)	C36	Co2	C35	39.92(7)
C36	C37	Co2	70.27(10)	C39	Co2	C35	38.42(7)

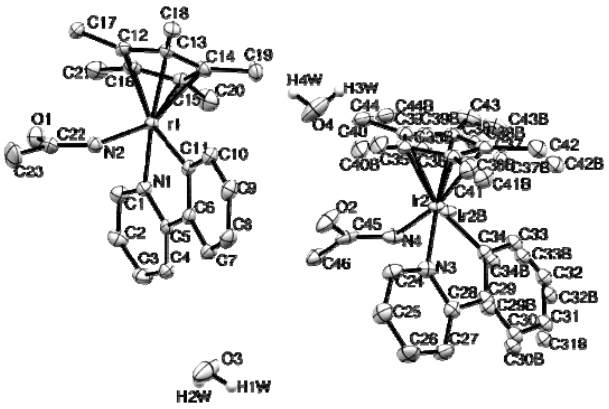


Table S22 Crystal data and structure refinement for (2b).

Identification code	**[k^2-(*C*,*N*)-(2-phpy)IrNHAc] (2b)**
Empirical formula	$C_{23}H_{29}IrN_2O_2$
Formula weight	557.68
Temperature/K	120(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.9189(5)
b/Å	12.9178(5)
c/Å	16.1472(7)
α/°	98.7820(10)
β/°	107.051(2)
γ/°	93.859(2)
Volume/Å^3	2136.70(16)
Z	4
ρ_{calc}g/cm^3	1.734
μ/mm^{-1}	6.269
F(000)	1096.0
Crystal size/mm^3	0.120 × 0.100 × 0.080
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.542 to 60.112
Index ranges	$-15 \le h \le 15$, $-18 \le k \le 15$, $-22 \le l \le 22$
Reflections collected	81688
Independent reflections	12491 [R_{int} = 0.0345, R_{sigma} = 0.0220]
Data/restraints/parameters	12491/0/543
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0197, wR_2 = 0.0341
Final R indexes [all data]	R_1 = 0.0260, wR_2 = 0.0364
Largest diff. peak/hole / e Å^{-3}	1.51/-1.90

Table S23 Bond Lengths for (2b).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	N1	1.348(3)	C29B	C30B	1.408(10)
C1	C2	1.378(3)	C29B	C34B	1.416(10)
C2	C3	1.387(3)	C30B	C31B	1.382(8)
C3	C4	1.381(3)	C31B	C32B	1.374(7)
C4	C5	1.397(3)	C32B	C33B	1.391(7)
C5	N1	1.359(3)	C33B	C34B	1.416(9)
C5	C6	1.460(3)	C34B	Ir2B	2.005(7)
C6	C7	1.402(3)	C35	C39	1.401(6)
C6	C11	1.409(3)	C35	C36	1.456(6)
C7	C8	1.386(3)	C35	C40	1.507(6)
C8	C9	1.392(3)	C35	Ir2	2.264(5)
C9	C10	1.393(3)	C36	C37	1.442(6)
C10	C11	1.399(3)	C36	C41	1.473(10)
C11	Ir1	2.033(2)	C36	Ir2	2.178(5)
C12	C16	1.408(3)	C37	C38	1.445(6)
C12	C13	1.447(3)	C37	C42	1.501(7)
C12	C17	1.496(3)	C37	Ir2	2.170(4)
C12	Ir1	2.245(2)	C38	C39	1.437(6)
C13	C14	1.443(3)	C38	C43	1.508(7)
C13	C18	1.501(3)	C38	Ir2	2.158(4)
C13	Ir1	2.156(2)	C39	C44	1.499(7)
C14	C15	1.434(3)	C39	Ir2	2.234(4)
C14	C19	1.502(3)	C35B	C36B	1.448(7)
C14	Ir1	2.172(2)	C35B	C39B	1.451(8)
C15	C16	1.460(3)	C35B	C40B	1.488(8)
C15	C20	1.500(3)	C35B	Ir2B	2.267(6)
C15	Ir1	2.177(2)	C36B	C37B	1.435(8)
C16	C21	1.499(3)	C36B	C41B	1.539(14)
C16	Ir1	2.267(2)	C36B	Ir2B	2.190(6)
C22	O1	1.255(3)	C37B	C38B	1.442(7)
C22	N2	1.314(3)	C37B	C42B	1.496(8)
C22	C23	1.514(4)	C37B	Ir2B	2.178(5)
C24	N3	1.347(3)	C38B	C39B	1.417(7)
C24	C25	1.372(3)	C38B	C43B	1.523(8)
C25	C26	1.381(4)	C38B	Ir2B	2.168(5)
C26	C27	1.379(3)	C39B	C44B	1.492(9)
C27	C28	1.393(3)	C39B	Ir2B	2.249(5)
C28	N3	1.358(3)	C45	O2	1.267(3)
C28	C29	1.465(10)	C45	N4	1.299(3)
C28	C29B	1.467(12)	C45	C46	1.513(3)
C29	C30	1.392(8)	N1	Ir1	2.0868(17)
C29	C34	1.400(8)	N2	Ir1	2.0656(18)
C30	C31	1.404(7)	N3	Ir2	2.0789(19)
C31	C32	1.385(6)	N3	Ir2B	2.094(2)
C32	C33	1.382(6)	N4	Ir2	2.040(2)
C33	C34	1.397(8)	N4	Ir2B	2.122(2)
C34	Ir2	2.066(6)			

Table S24 Bond Angles for (2b).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N1	C1	C2	122.5(2)	C35B	C36B	Ir2B	74.0(3)
C1	C2	C3	118.8(2)	C41B	C36B	Ir2B	126.2(6)
C4	C3	C2	119.3(2)	C36B	C37B	C38B	107.3(5)
C3	C4	C5	119.7(2)	C36B	C37B	C42B	126.9(5)
N1	C5	C4	120.6(2)	C38B	C37B	C42B	125.7(5)
N1	C5	C6	113.35(18)	C36B	C37B	Ir2B	71.3(3)
C4	C5	C6	126.1(2)	C38B	C37B	Ir2B	70.2(3)
C7	C6	C11	121.9(2)	C42B	C37B	Ir2B	127.0(4)
C7	C6	C5	123.1(2)	C39B	C38B	C37B	108.7(5)
C11	C6	C5	115.01(18)	C39B	C38B	C43B	125.6(5)
C8	C7	C6	119.2(2)	C37B	C38B	C43B	124.8(5)
C7	C8	C9	120.2(2)	C39B	C38B	Ir2B	74.5(3)
C8	C9	C10	120.1(2)	C37B	C38B	Ir2B	71.0(3)
C9	C10	C11	121.6(2)	C43B	C38B	Ir2B	129.0(4)
C10	C11	C6	117.04(19)	C38B	C39B	C35B	108.6(5)
C10	C11	Ir1	126.62(16)	C38B	C39B	C44B	126.5(6)
C6	C11	Ir1	115.96(15)	C35B	C39B	C44B	124.9(6)
C16	C12	C13	109.30(19)	C38B	C39B	Ir2B	68.2(3)
C16	C12	C17	126.3(2)	C35B	C39B	Ir2B	71.9(3)
C13	C12	C17	124.4(2)	C44B	C39B	Ir2B	125.6(4)
C16	C12	Ir1	72.68(12)	O2	C45	N4	123.2(2)
C13	C12	Ir1	67.52(11)	O2	C45	C46	117.3(2)
C17	C12	Ir1	126.41(15)	N4	C45	C46	119.5(2)
C14	C13	C12	107.51(18)	C1	N1	C5	119.09(19)
C14	C13	C18	127.25(19)	C1	N1	Ir1	123.81(15)
C12	C13	C18	124.45(19)	C5	N1	Ir1	117.08(14)
C14	C13	Ir1	71.13(12)	C22	N2	Ir1	125.66(16)
C12	C13	Ir1	74.16(12)	C24	N3	C28	119.32(19)
C18	C13	Ir1	128.22(15)	C24	N3	Ir2	118.96(15)
C15	C14	C13	107.35(19)	C28	N3	Ir2	121.60(15)
C15	C14	C19	127.1(2)	C24	N3	Ir2B	128.67(16)
C13	C14	C19	125.5(2)	C28	N3	Ir2B	112.00(15)
C15	C14	Ir1	70.94(12)	C45	N4	Ir2	120.07(17)
C13	C14	Ir1	69.91(11)	C45	N4	Ir2B	129.46(17)
C19	C14	Ir1	126.53(16)	C11	Ir1	N2	82.72(8)
C14	C15	C16	108.46(19)	C11	Ir1	N1	78.22(8)
C14	C15	C20	126.5(2)	N2	Ir1	N1	87.45(7)
C16	C15	C20	124.8(2)	C11	Ir1	C13	108.88(8)
C14	C15	Ir1	70.57(12)	N2	Ir1	C13	106.15(8)
C16	C15	Ir1	74.19(12)	N1	Ir1	C13	165.15(7)
C20	C15	Ir1	124.97(16)	C11	Ir1	C14	99.55(8)
C12	C16	C15	107.20(19)	N2	Ir1	C14	144.09(8)

C12	C16	C21	125.3(2)	N1	Ir1	C14	128.29(8)
C15	C16	C21	127.4(2)	C13	Ir1	C14	38.95(8)
C12	C16	Ir1	70.95(12)	C11	Ir1	C15	123.89(8)
C15	C16	Ir1	67.53(12)	N2	Ir1	C15	153.17(8)
C21	C16	Ir1	128.93(15)	N1	Ir1	C15	100.49(8)
O1	C22	N2	123.0(2)	C13	Ir1	C15	64.68(8)
O1	C22	C23	118.8(2)	C14	Ir1	C15	38.50(8)
N2	C22	C23	118.2(2)	C11	Ir1	C12	144.58(8)
N3	C24	C25	122.3(2)	N2	Ir1	C12	93.84(8)
C24	C25	C26	118.9(2)	N1	Ir1	C12	137.03(7)
C27	C26	C25	119.5(2)	C13	Ir1	C12	38.33(8)
C26	C27	C28	119.6(2)	C14	Ir1	C12	63.68(8)
N3	C28	C27	120.4(2)	C15	Ir1	C12	62.92(8)
N3	C28	C29	109.7(4)	C11	Ir1	C16	161.82(8)
C27	C28	C29	129.9(4)	N2	Ir1	C16	114.91(8)
N3	C28	C29B	118.4(5)	N1	Ir1	C16	105.71(7)
C27	C28	C29B	121.2(5)	C13	Ir1	C16	63.48(8)
C30	C29	C34	122.0(7)	C14	Ir1	C16	63.82(8)
C30	C29	C28	121.5(6)	C15	Ir1	C16	38.29(8)
C34	C29	C28	116.4(6)	C12	Ir1	C16	36.37(8)
C29	C30	C31	119.4(5)	N4	Ir2	C34	81.1(2)
C32	C31	C30	119.0(4)	N4	Ir2	N3	84.68(8)
C33	C32	C31	121.0(4)	C34	Ir2	N3	75.8(3)
C32	C33	C34	121.5(4)	N4	Ir2	C38	107.91(13)
C33	C34	C29	117.1(5)	C34	Ir2	C38	109.0(3)
C33	C34	Ir2	126.3(5)	N3	Ir2	C38	166.91(13)
C29	C34	Ir2	116.5(6)	N4	Ir2	C37	145.81(14)
C30B	C29B	C34B	123.0(8)	C34	Ir2	C37	100.1(3)
C30B	C29B	C28	124.2(8)	N3	Ir2	C37	129.05(14)
C34B	C29B	C28	112.8(8)	C38	Ir2	C37	39.02(16)
C31B	C30B	C29B	118.4(6)	N4	Ir2	C36	153.32(14)
C32B	C31B	C30B	120.7(5)	C34	Ir2	C36	125.5(2)
C31B	C32B	C33B	120.8(5)	N3	Ir2	C36	102.72(14)
C32B	C33B	C34B	121.6(5)	C38	Ir2	C36	64.42(17)
C29B	C34B	C33B	115.5(6)	C37	Ir2	C36	38.74(17)
C29B	C34B	Ir2B	115.7(7)	N4	Ir2	C39	95.17(13)
C33B	C34B	Ir2B	128.7(6)	C34	Ir2	C39	144.1(3)
C39	C35	C36	106.6(4)	N3	Ir2	C39	139.71(13)
C39	C35	C40	125.7(5)	C38	Ir2	C39	38.14(16)
C36	C35	C40	127.7(5)	C37	Ir2	C39	63.80(17)
C39	C35	Ir2	70.7(3)	C36	Ir2	C39	62.53(16)
C36	C35	Ir2	67.7(2)	N4	Ir2	C35	115.11(13)
C40	C35	Ir2	127.7(4)	C34	Ir2	C35	163.2(3)
C37	C36	C35	109.1(4)	N3	Ir2	C35	108.44(14)
C37	C36	C41	126.2(5)	C38	Ir2	C35	63.44(17)

C35	C36	C41	124.6(5)	C37	Ir2	C35	64.31(17)
C37	C36	Ir2	70.3(2)	C36	Ir2	C35	38.21(16)
C35	C36	Ir2	74.1(2)	C39	Ir2	C35	36.29(16)
C41	C36	Ir2	125.0(4)	C34B	Ir2B	N3	81.0(3)
C36	C37	C38	106.4(4)	C34B	Ir2B	N4	88.3(3)
C36	C37	C42	127.1(4)	N3	Ir2B	N4	82.28(8)
C38	C37	C42	126.5(4)	C34B	Ir2B	C38B	108.1(3)
C36	C37	Ir2	71.0(2)	N3	Ir2B	C38B	163.03(16)
C38	C37	Ir2	70.1(2)	N4	Ir2B	C38B	111.67(16)
C42	C37	Ir2	126.2(3)	C34B	Ir2B	C37B	99.0(3)
C39	C38	C37	107.7(4)	N3	Ir2B	C37B	127.14(17)
C39	C38	C43	124.5(4)	N4	Ir2B	C37B	150.35(17)
C37	C38	C43	127.2(5)	C38B	Ir2B	C37B	38.8(2)
C39	C38	Ir2	73.8(2)	C34B	Ir2B	C36B	123.8(3)
C37	C38	Ir2	70.9(2)	N3	Ir2B	C36B	98.77(18)
C43	C38	Ir2	127.6(3)	N4	Ir2B	C36B	147.74(16)
C35	C39	C38	110.1(4)	C38B	Ir2B	C36B	64.3(2)
C35	C39	C44	126.3(5)	C37B	Ir2B	C36B	38.3(2)
C38	C39	C44	123.5(4)	C34B	Ir2B	C39B	142.7(4)
C35	C39	Ir2	73.0(3)	N3	Ir2B	C39B	136.23(17)
C38	C39	Ir2	68.1(2)	N4	Ir2B	C39B	93.78(15)
C44	C39	Ir2	126.0(3)	C38B	Ir2B	C39B	37.36(19)
C36B	C35B	C39B	106.7(5)	C37B	Ir2B	C39B	63.3(2)
C36B	C35B	C40B	126.7(6)	C36B	Ir2B	C39B	63.1(2)
C39B	C35B	C40B	126.6(6)	C34B	Ir2B	C35B	161.2(3)
C36B	C35B	Ir2B	68.2(3)	N3	Ir2B	C35B	103.51(16)
C39B	C35B	Ir2B	70.6(3)	N4	Ir2B	C35B	110.28(16)
C40B	C35B	Ir2B	128.3(5)	C38B	Ir2B	C35B	63.3(2)
C37B	C36B	C35B	108.6(5)	C37B	Ir2B	C35B	63.5(2)
C37B	C36B	C41B	125.6(6)	C36B	Ir2B	C35B	37.85(19)
C35B	C36B	C41B	125.5(6)	C39B	Ir2B	C35B	37.5(2)
C37B	C36B	Ir2B	70.4(3)				

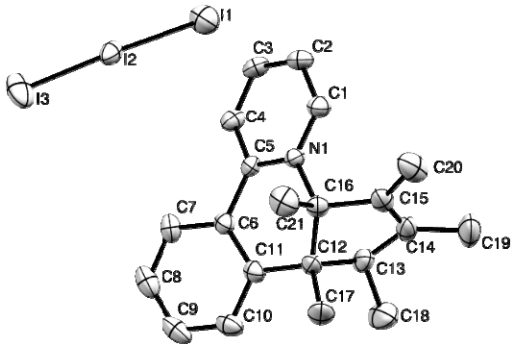


Table S25 Crystal data and structure refinement for [1c][I_3].

Identification code	**[1c][I_3]**
Empirical formula	$C_{21}H_{24}I_3N$
Formula weight	671.11
Temperature/K	173(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.3746(4)
b/Å	13.0748(6)
c/Å	16.9157(7)
α/°	90.00
β/°	95.694(2)
γ/°	90.00
Volume/Å^3	2283.22(17)
Z	4
ρ_{calc}g/cm^3	1.952
μ/mm^{-1}	4.111
F(000)	1264.0
Crystal size/mm^3	0.2 × 0.16 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.94 to 60.1
Index ranges	$-12 \le h \le 14$, $-18 \le k \le 18$, $-23 \le l \le 23$
Reflections collected	42452
Independent reflections	6692 [R_{int} = 0.0374, R_{sigma} = 0.0231]
Data/restraints/parameters	6692/0/231
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0435, wR_2 = 0.0834
Final R indexes [all data]	R_1 = 0.0652, wR_2 = 0.0938
Largest diff. peak/hole / e Å^{-3}	3.06/-2.25

Table S26 Bond Lengths for [1c][I_3].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.374(6)	C12	C13	1.560(6)
C1	N1	1.352(5)	C12	C16	1.557(6)
C2	C3	1.382(7)	C12	C17	1.546(6)
C3	C4	1.367(6)	C13	C14	1.500(7)
C4	C5	1.394(5)	C13	C18	1.508(7)
C5	C6	1.470(6)	C14	C15	1.338(7)
C5	N1	1.359(5)	C14	C19	1.502(6)
C6	C7	1.401(6)	C15	C16	1.522(6)
C6	C11	1.399(6)	C15	C20	1.510(7)
C7	C8	1.382(7)	C16	C21	1.522(6)
C8	C9	1.383(8)	C16	N1	1.544(5)
C9	C10	1.384(7)	I1	I2	2.9389(5)
C10	C11	1.401(6)	I2	I3	2.8802(5)
C11	C12	1.513(6)			

Table S27 Bond Angles for [1c][I_3].

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N1	C1	C2	122.1(4)	C17	C12	C13	110.7(3)
C1	C2	C3	118.5(4)	C17	C12	C16	107.7(4)
C4	C3	C2	119.1(4)	C14	C13	C12	102.2(4)
C3	C4	C5	121.7(4)	C14	C13	C18	115.9(4)
C4	C5	C6	122.5(4)	C18	C13	C12	116.2(4)
N1	C5	C4	118.1(4)	C13	C14	C19	121.7(5)
N1	C5	C6	119.5(3)	C15	C14	C13	111.7(4)
C7	C6	C5	119.2(4)	C15	C14	C19	126.6(5)
C11	C6	C5	120.0(4)	C14	C15	C16	109.1(4)
C11	C6	C7	120.8(4)	C14	C15	C20	127.1(4)
C8	C7	C6	120.0(5)	C20	C15	C16	123.7(5)
C7	C8	C9	119.9(5)	C15	C16	C12	102.0(3)
C8	C9	C10	120.2(4)	C15	C16	C21	116.6(4)
C9	C10	C11	121.4(5)	C15	C16	N1	107.6(3)
C6	C11	C10	117.6(4)	C21	C16	C12	115.9(4)
C6	C11	C12	119.8(4)	C21	C16	N1	105.4(3)
C10	C11	C12	122.5(4)	N1	C16	C12	109.0(3)
C11	C12	C13	113.8(4)	C1	N1	C5	120.5(3)
C11	C12	C16	113.1(3)	C1	N1	C16	117.5(3)
C11	C12	C17	110.6(3)	C5	N1	C16	122.0(3)
C16	C12	C13	100.3(3)	I3	I2	I1	177.604(16)

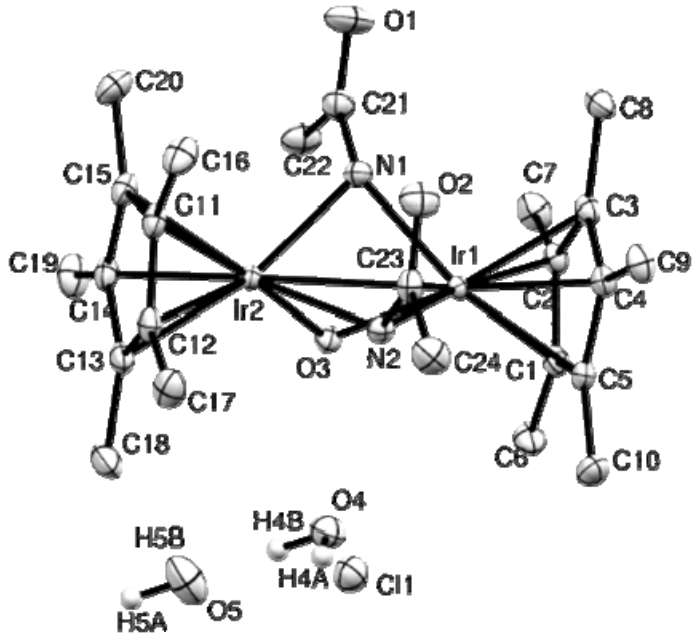


Table S28 Crystal data and structure refinement for (2c).

Identification code	**2C**
Empirical formula	$C_{24}H_{43}ClIr_2N_2O_5$
Formula weight	859.45
Temperature/K	120(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.4469(4)
b/Å	10.0791(4)
c/Å	17.3569(8)
α/°	93.5250(10)
β/°	95.071(2)
γ/°	111.9100(10)
Volume/Å^3	1358.46(11)
Z	2
ρ_{calc}g/cm^3	2.101
μ/mm^{-1}	9.920
F(000)	824.0
Crystal size/mm^3	0.250 × 0.200 × 0.120
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.378 to 64.142
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 15, -25 ≤ l ≤ 25
Reflections collected	100357
Independent reflections	9439 [R_{int} = 0.0331, R_{sigma} = 0.0168]
Data/restraints/parameters	9439/0/347
Goodness-of-fit on F^2	1.118
Final R indexes [I>=2σ (I)]	R_1 = 0.0150, wR_2 = 0.0379
Final R indexes [all data]	R_1 = 0.0158, wR_2 = 0.0384
Largest diff. peak/hole / e Å^{-3}	1.29/-1.46

Table S29 Bond Lengths for (2c).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C5	1.435(3)	C13	C14	1.454(3)
C1	C2	1.446(3)	C13	C18	1.496(3)
C1	C6	1.495(3)	C13	Ir2	2.1462(19)
C1	Ir1	2.1575(18)	C14	C15	1.435(3)
C2	C3	1.450(3)	C14	C19	1.496(3)
C2	C7	1.496(3)	C14	Ir2	2.1490(18)
C2	Ir1	2.1469(18)	C15	C20	1.496(3)
C3	C4	1.434(3)	C15	Ir2	2.1648(19)
C3	C8	1.496(3)	C21	O1	1.222(3)
C3	Ir1	2.1555(18)	C21	N1	1.399(2)
C4	C5	1.455(3)	C21	C22	1.507(3)
C4	C9	1.496(3)	C23	O2	1.220(3)
C4	Ir1	2.1485(18)	C23	N2	1.412(2)
C5	C10	1.496(3)	C23	C24	1.501(3)
C5	Ir1	2.1430(18)	N1	Ir2	2.1508(16)
C11	C12	1.441(3)	N1	Ir1	2.1525(16)
C11	C15	1.451(3)	N2	Ir1	2.1530(16)
C11	C16	1.504(3)	N2	Ir2	2.1536(15)
C11	Ir2	2.1348(18)	O3	Ir1	2.0856(13)
C12	C13	1.436(3)	O3	Ir2	2.1035(13)
C12	C17	1.497(3)	Ir1	Ir2	3.05985(13)
C12	Ir2	2.1524(19)			

Table S30 Bond Angles for (2c).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C5	C1	C2	108.63(16)	O3	Ir1	C5	122.97(6)
C5	C1	C6	125.06(18)	O3	Ir1	C2	112.45(6)
C2	C1	C6	126.30(17)	C5	Ir1	C2	66.13(7)
C5	C1	Ir1	69.96(10)	O3	Ir1	C4	162.47(7)
C2	C1	Ir1	69.97(10)	C5	Ir1	C4	39.62(7)
C6	C1	Ir1	125.06(13)	C2	Ir1	C4	65.99(7)
C1	C2	C3	107.28(16)	O3	Ir1	N1	74.04(6)
C1	C2	C7	126.49(17)	C5	Ir1	N1	162.37(7)
C3	C2	C7	126.07(17)	C2	Ir1	N1	113.99(7)
C1	C2	Ir1	70.76(10)	C4	Ir1	N1	123.13(7)
C3	C2	Ir1	70.62(10)	O3	Ir1	N2	75.02(6)
C7	C2	Ir1	127.44(14)	C5	Ir1	N2	104.44(7)
C4	C3	C2	108.40(16)	C2	Ir1	N2	170.02(7)
C4	C3	C8	126.31(17)	C4	Ir1	N2	104.82(6)
C2	C3	C8	125.29(17)	N1	Ir1	N2	73.89(6)
C4	C3	Ir1	70.28(10)	O3	Ir1	C3	148.58(6)
C2	C3	Ir1	69.98(10)	C5	Ir1	C3	65.85(7)
C8	C3	Ir1	125.47(13)	C2	Ir1	C3	39.40(7)
C3	C4	C5	107.98(16)	C4	Ir1	C3	38.91(7)
C3	C4	C9	126.22(17)	N1	Ir1	C3	102.48(7)
C5	C4	C9	125.73(17)	N2	Ir1	C3	135.00(6)
C3	C4	Ir1	70.81(10)	O3	Ir1	C1	101.63(6)
C5	C4	Ir1	69.99(10)	C5	Ir1	C1	38.98(7)
C9	C4	Ir1	127.13(13)	C2	Ir1	C1	39.27(7)
C1	C5	C4	107.67(16)	C4	Ir1	C1	65.61(7)
C1	C5	C10	125.98(18)	N1	Ir1	C1	150.06(7)
C4	C5	C10	126.33(18)	N2	Ir1	C1	134.58(7)
C1	C5	Ir1	71.05(10)	C3	Ir1	C1	65.49(7)
C4	C5	Ir1	70.39(10)	O3	Ir1	Ir2	43.31(4)
C10	C5	Ir1	125.51(14)	C5	Ir1	Ir2	143.88(5)
C12	C11	C15	107.30(17)	C2	Ir1	Ir2	145.23(5)
C12	C11	C16	126.86(19)	C4	Ir1	Ir2	145.71(5)
C15	C11	C16	125.75(19)	N1	Ir1	Ir2	44.66(4)
C12	C11	Ir2	71.01(10)	N2	Ir1	Ir2	44.73(4)
C15	C11	Ir2	71.40(11)	C3	Ir1	Ir2	146.77(5)
C16	C11	Ir2	125.65(14)	C1	Ir1	Ir2	144.18(5)
C13	C12	C11	108.80(17)	O3	Ir2	C11	171.38(6)
C13	C12	C17	124.5(2)	O3	Ir2	C13	106.79(6)
C11	C12	C17	126.68(19)	C11	Ir2	C13	66.24(8)
C13	C12	Ir2	70.26(11)	O3	Ir2	C14	105.24(6)
C11	C12	Ir2	69.70(11)	C11	Ir2	C14	66.19(7)
C17	C12	Ir2	126.08(14)	C13	Ir2	C14	39.58(8)

C12	C13	C14	107.55(17)	O3	Ir2	N1	73.72(6)
C12	C13	C18	126.2(2)	C11	Ir2	N1	111.54(7)
C14	C13	C18	126.15(19)	C13	Ir2	N1	164.55(7)
C12	C13	Ir2	70.72(11)	C14	Ir2	N1	125.00(7)
C14	C13	Ir2	70.31(11)	O3	Ir2	C12	137.61(7)
C18	C13	Ir2	126.79(14)	C11	Ir2	C12	39.29(8)
C15	C14	C13	107.96(17)	C13	Ir2	C12	39.02(8)
C15	C14	C19	126.7(2)	C14	Ir2	C12	65.64(8)
C13	C14	C19	125.29(19)	N1	Ir2	C12	146.87(7)
C15	C14	Ir2	71.17(10)	O3	Ir2	N2	74.64(6)
C13	C14	Ir2	70.11(10)	C11	Ir2	N2	113.06(7)
C19	C14	Ir2	126.44(14)	C13	Ir2	N2	121.40(7)
C14	C15	C11	108.30(18)	C14	Ir2	N2	160.71(7)
C14	C15	C20	127.01(18)	N1	Ir2	N2	73.91(6)
C11	C15	C20	124.68(18)	C12	Ir2	N2	101.02(7)
C14	C15	Ir2	69.98(11)	O3	Ir2	C15	133.94(6)
C11	C15	Ir2	69.17(10)	C11	Ir2	C15	39.44(7)
C20	C15	Ir2	127.09(15)	C13	Ir2	C15	65.64(8)
O1	C21	N1	121.09(19)	C14	Ir2	C15	38.85(7)
O1	C21	C22	121.10(19)	N1	Ir2	C15	102.49(7)
N1	C21	C22	117.79(18)	C12	Ir2	C15	65.31(8)
O2	C23	N2	122.40(18)	N2	Ir2	C15	149.96(7)
O2	C23	C24	121.64(18)	O3	Ir2	Ir1	42.85(4)
N2	C23	C24	115.96(18)	C11	Ir2	Ir1	145.54(5)
C21	N1	Ir2	119.58(13)	C13	Ir2	Ir1	144.13(5)
C21	N1	Ir1	121.14(13)	C14	Ir2	Ir1	144.75(5)
Ir2	N1	Ir1	90.64(6)	N1	Ir2	Ir1	44.70(4)
C23	N2	Ir1	116.86(12)	C12	Ir2	Ir1	145.25(5)
C23	N2	Ir2	117.43(12)	N2	Ir2	Ir1	44.72(4)
Ir1	N2	Ir2	90.55(6)	C15	Ir2	Ir1	146.16(6)
Ir1	O3	Ir2	93.84(5)				

4. Mass Spectra

*Iodo(pentamethylcyclopentadienyl)(2-phenylenepyridine-κ²-C,N) cobalt (III) (**1a**)*

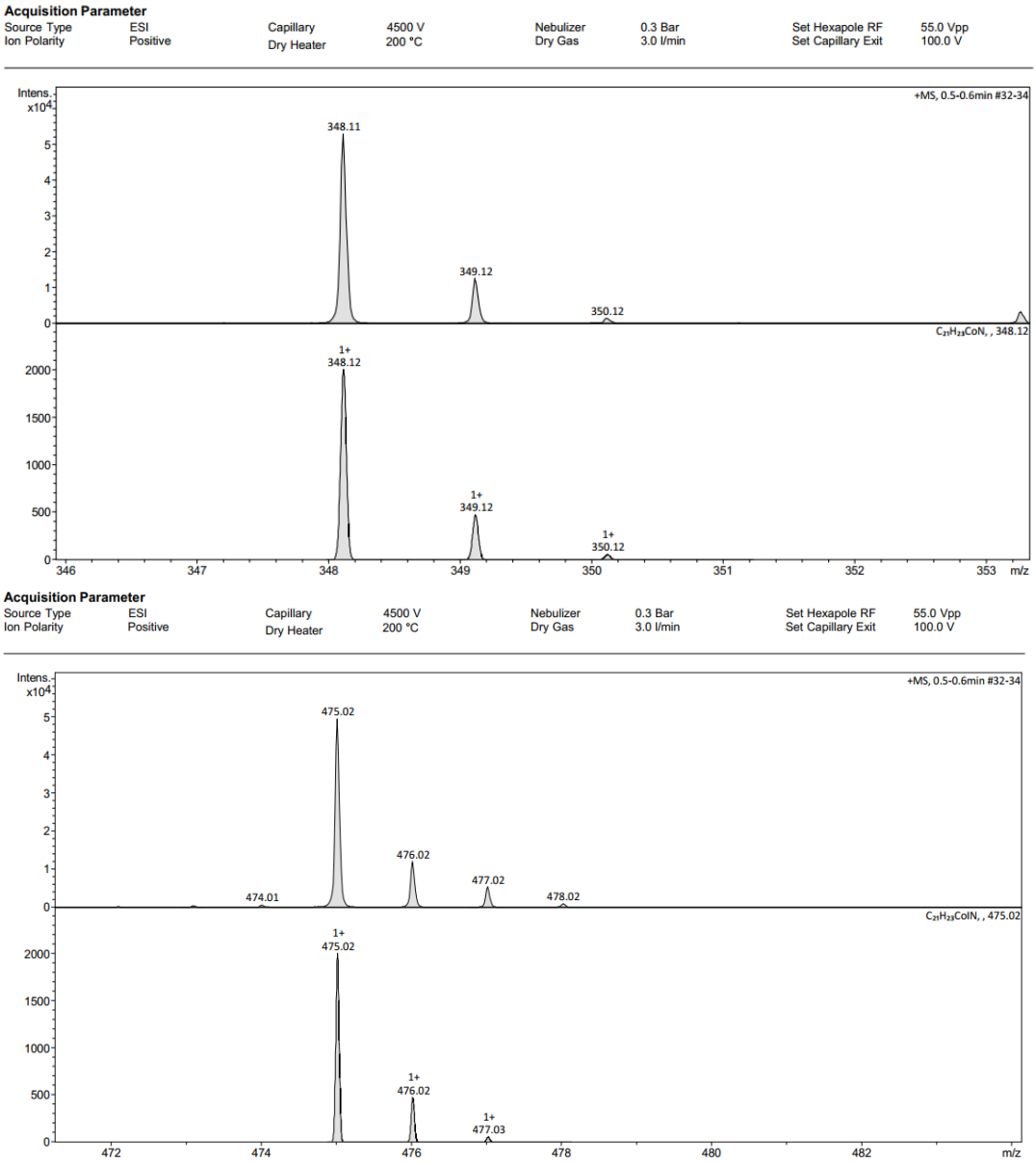


Figure S 43

*Iodo[2-(2-methylphenylene)pyridine-κ²-C,N](pentamethylcyclopentadienyl)cobalt (III) (**3a**)*

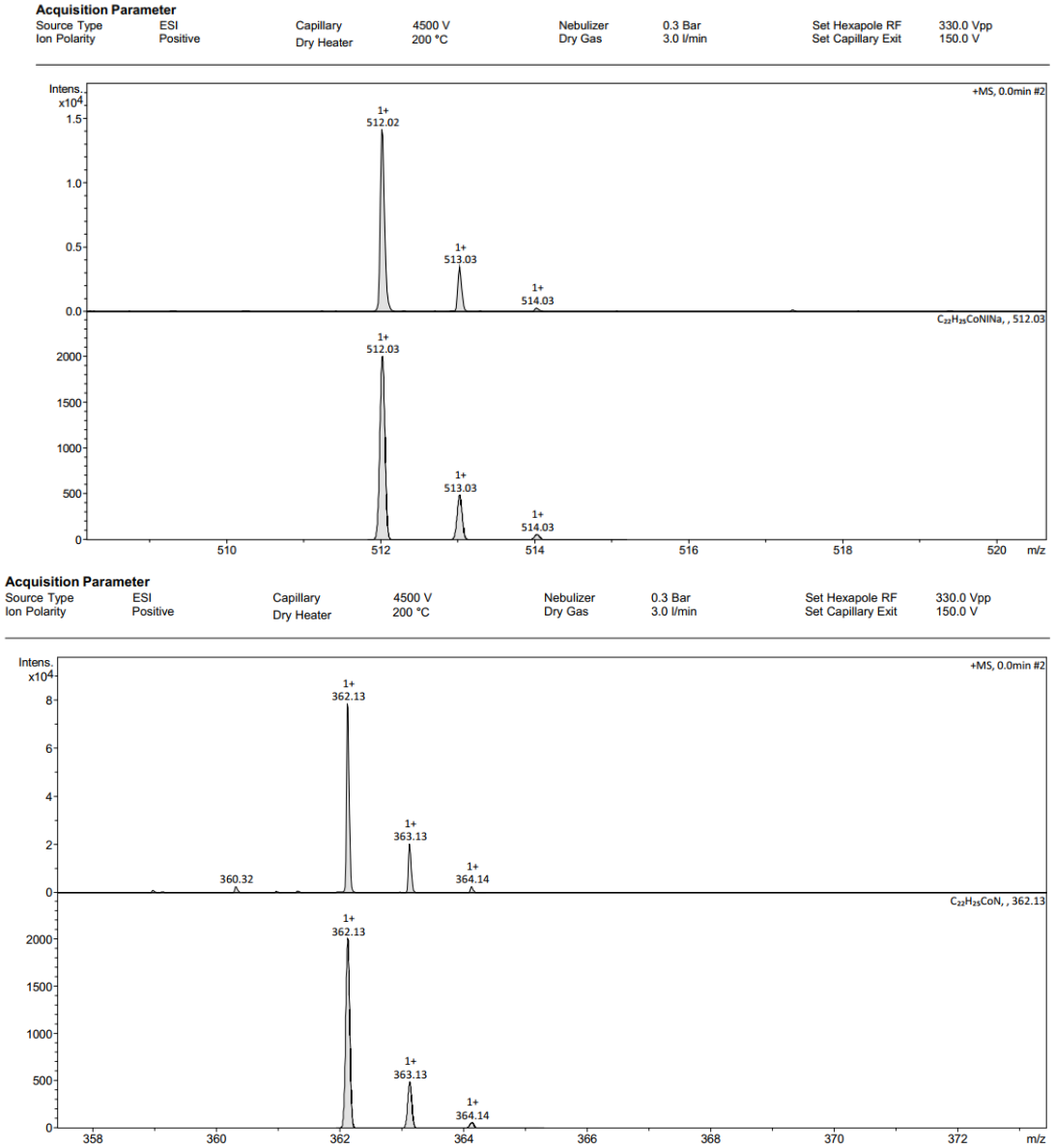


Figure S 44

Iodo(pentamethylcyclopentadienyl)[4-tertiobutyl,2-(4-N,N-dimethylaminophenylene)pyridine-κ²-C,N]cobalt (III) (4a)

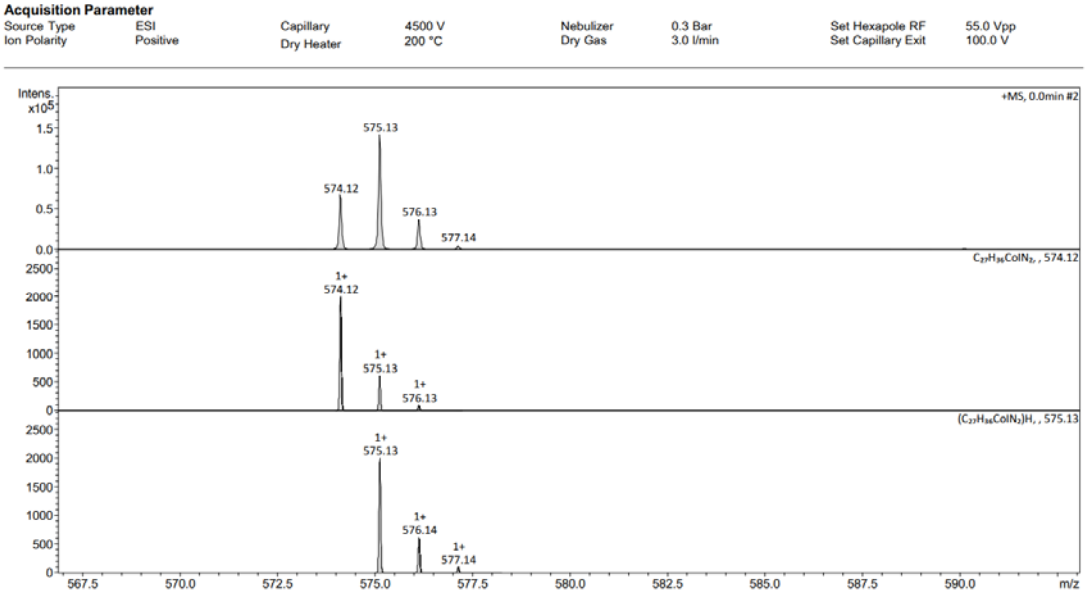


Figure S 45

*(benzo[h]quinolynyl-κ²-C,N)iodo(pentamethylcyclopentadienyl)cobalt (III) (**5a**)*

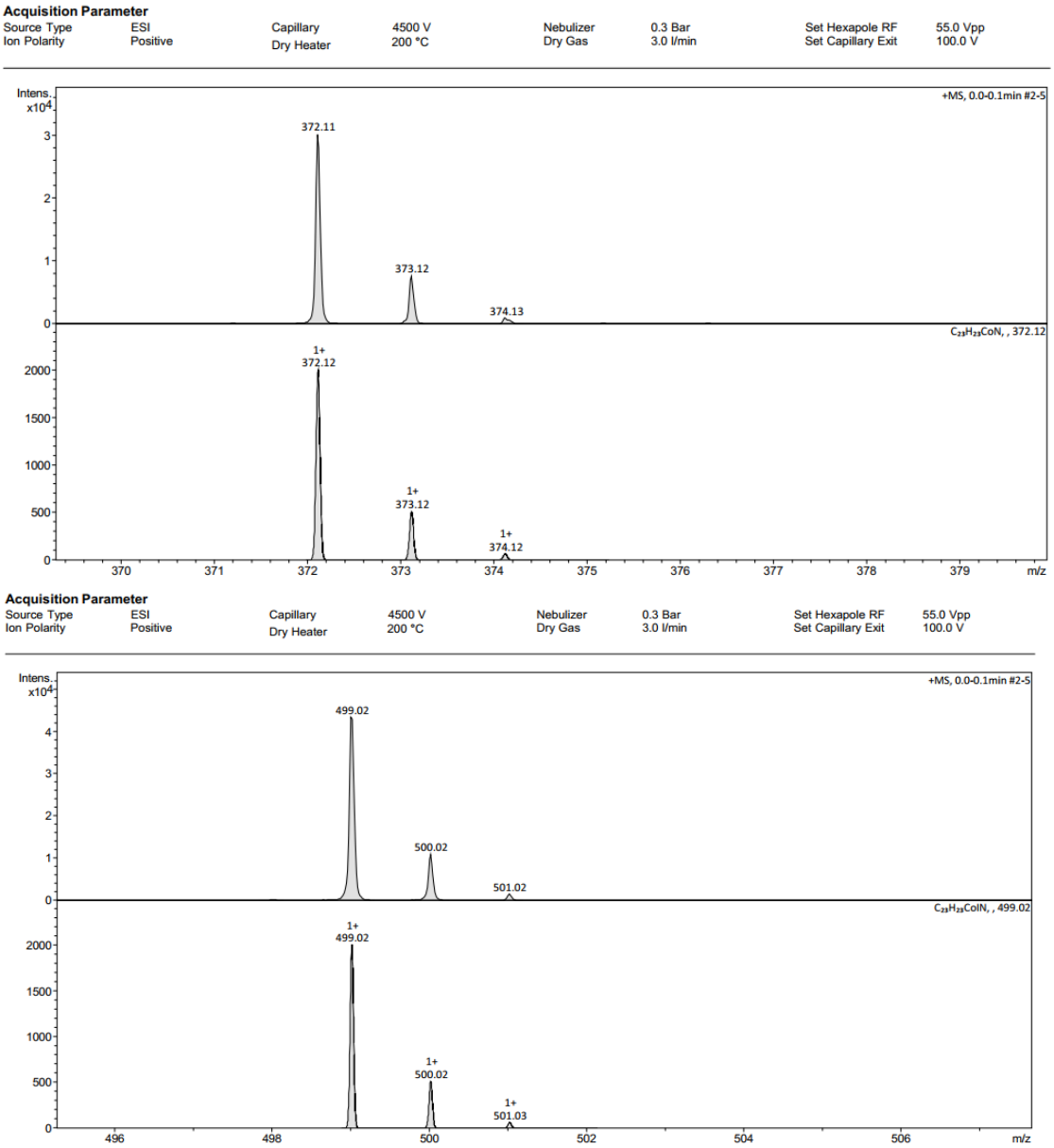


Figure S 46

*Acetonitrilo(pentamethylcyclopentadienyl)(2-phenylenepyridine-κ²-C,N) cobalt (III) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**1b**)*

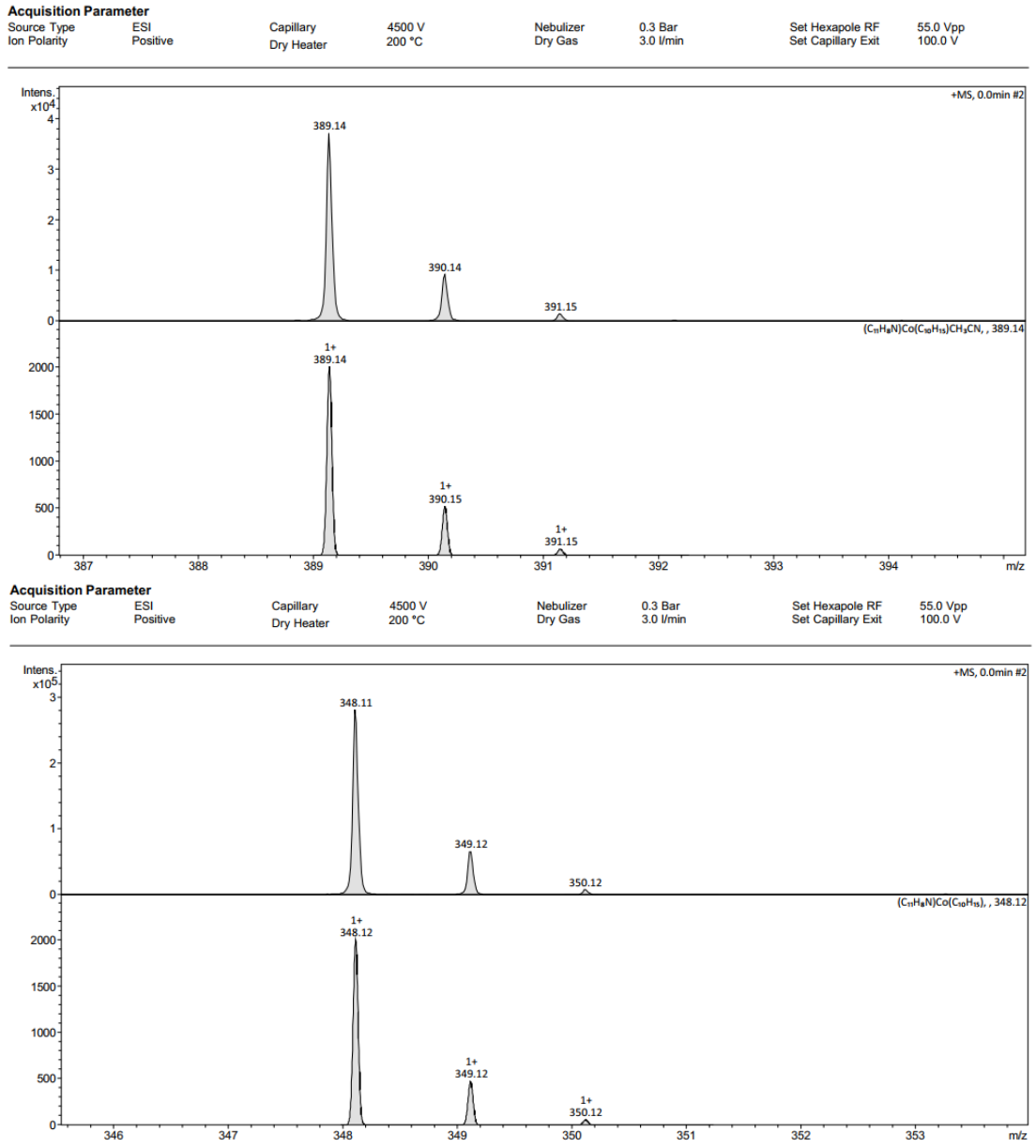


Figure S 47

*Acetonitrilo[2-(2-methylphenylene)pyridine-κ²-C,N](pentamethylcyclopentadienyl)cobalt (III) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**3b**)*

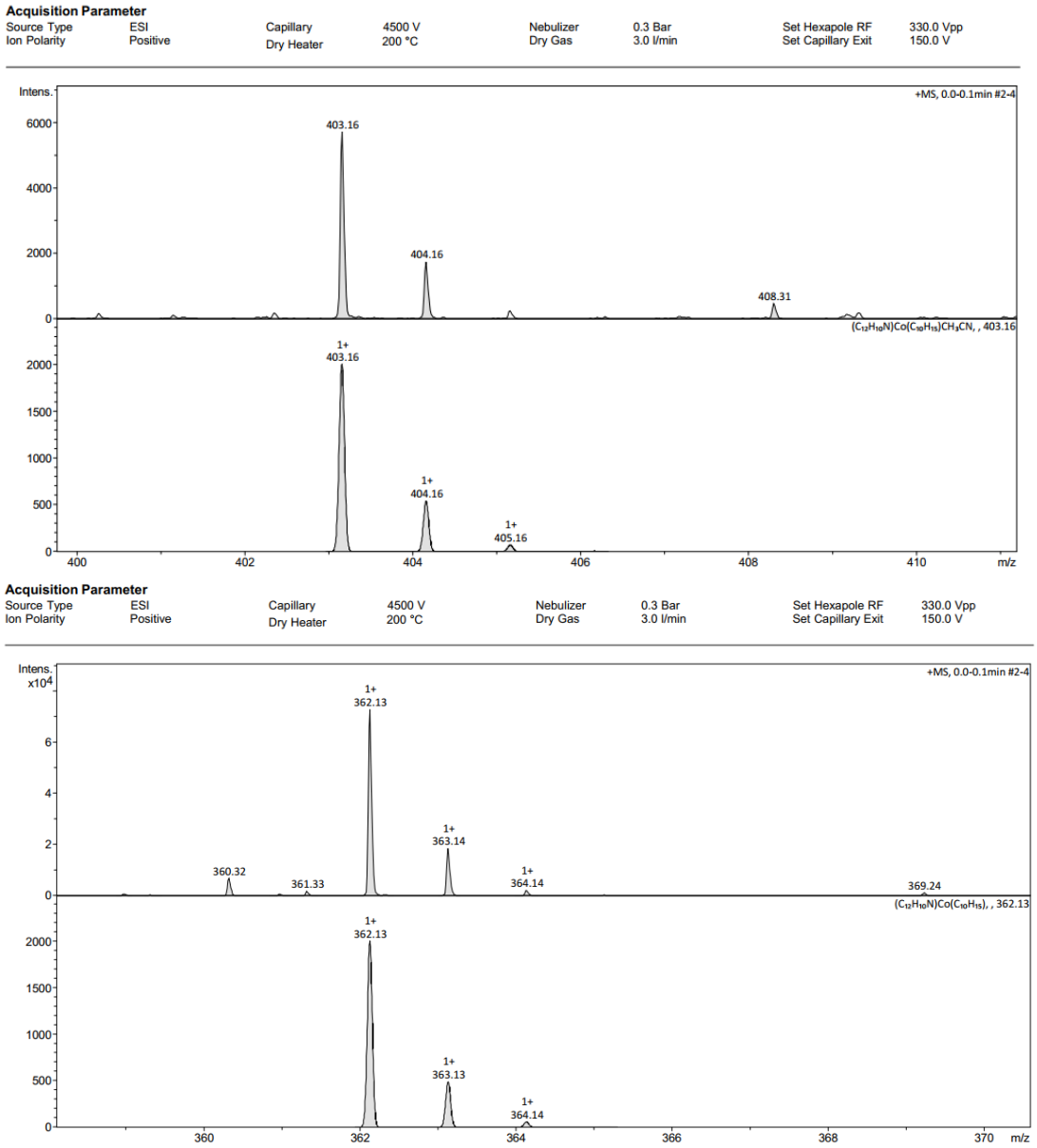


Figure S 48

Acetonitrilo[4-tertiobutyl,2-(4-N,N-dimethylaminophenylene)pyridine-κ²-C,N](pentamethylcyclopentadienyl)cobalt (III) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (4b)

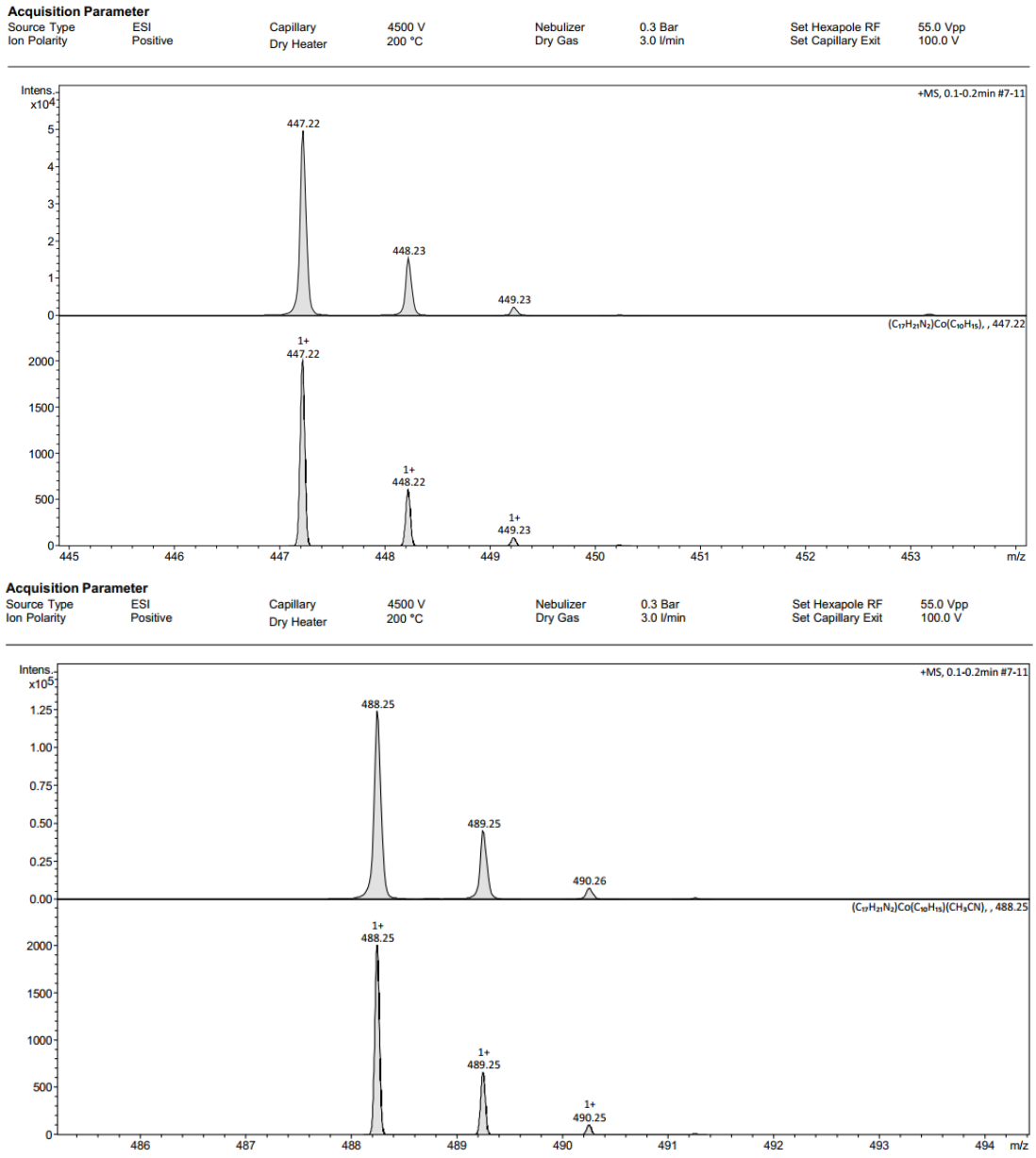


Figure S 49

Acetonitrilo[benzo[h]quinolynyl-κ²-C,N](pentamethylcyclopentadienyl)cobalt (III) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (5b)

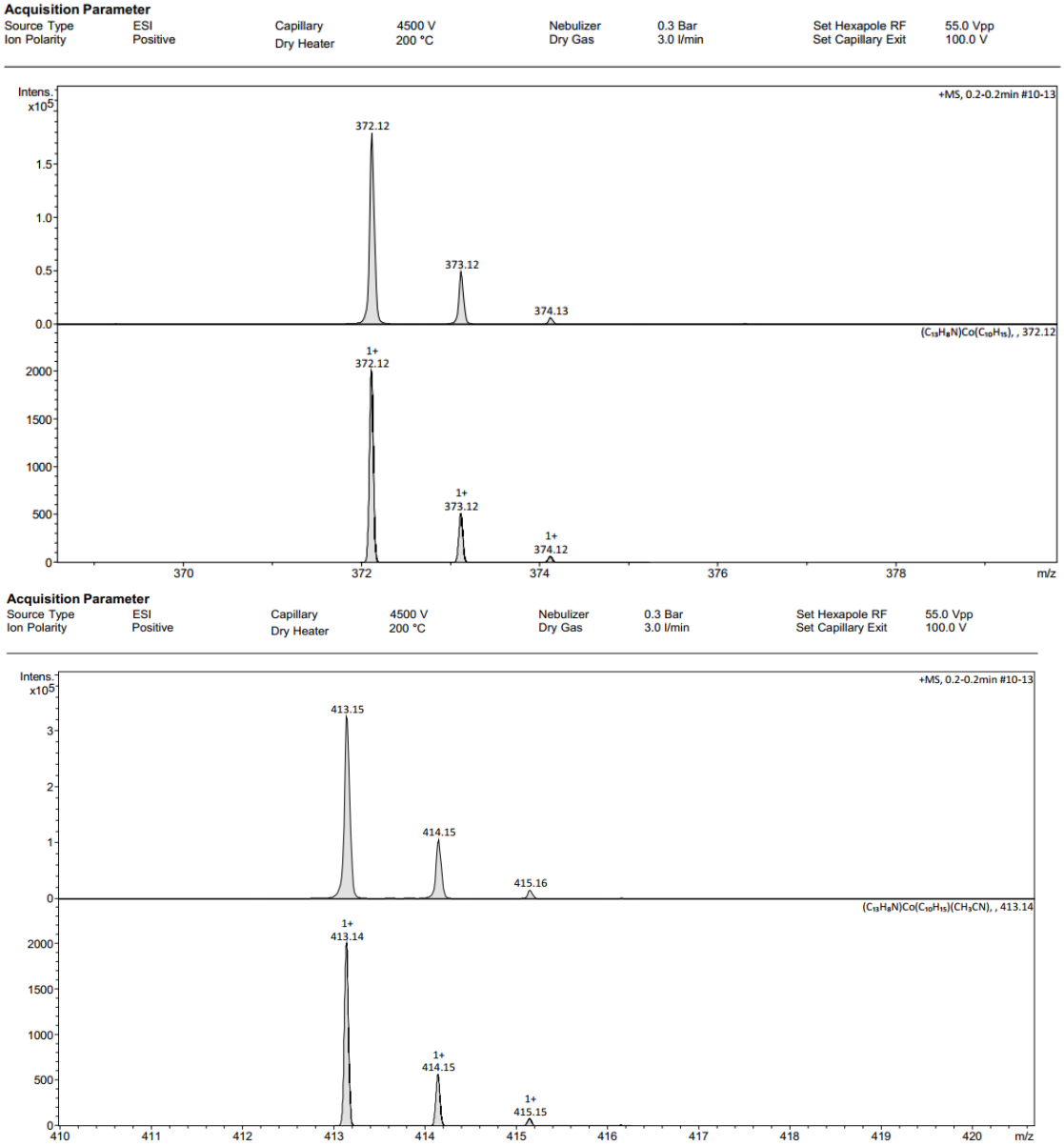


Figure S 50

*Acetamidato[2-phenylenepyridine κ²-(C,N)](pentamethylcyclopentadienyl)cobalt (III) (**1f**)*

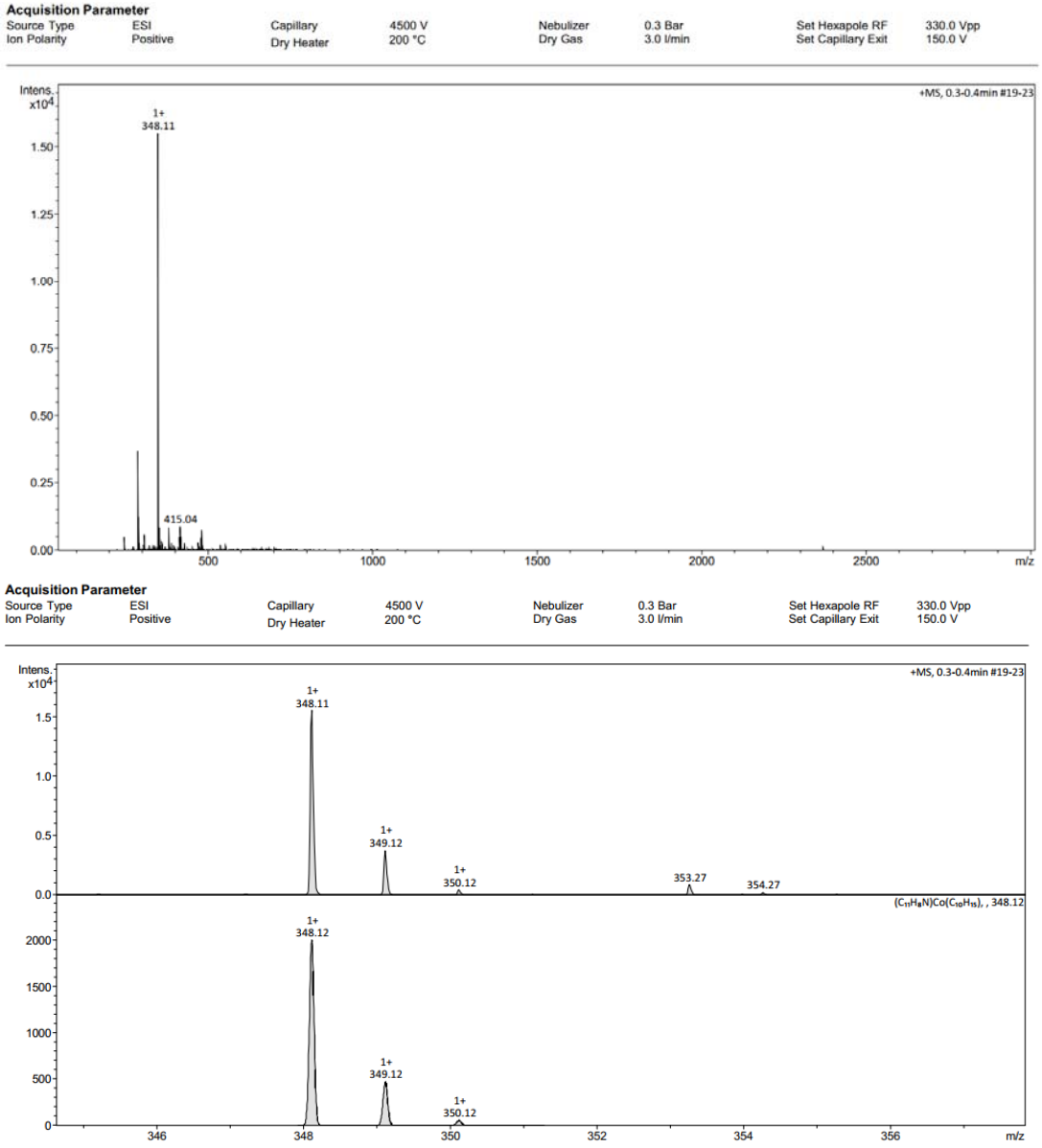


Figure S 51

Acetamidato[2-phenylenepyridine κ²-(C,N)](pentamethylcyclopentadienyl)iridium (III) (2b)

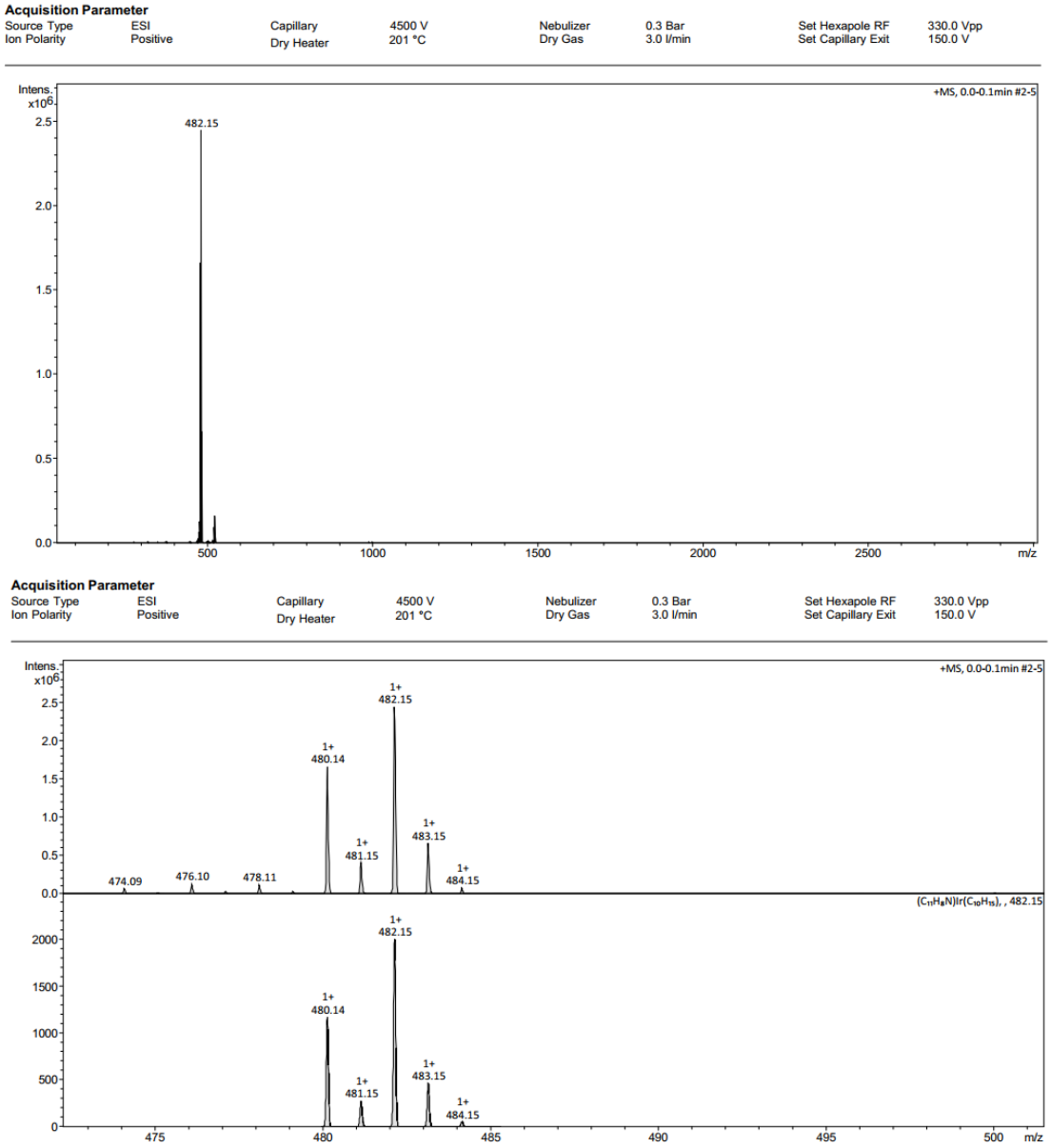


Figure S 52

5. DFT Calculations: Energies of Stationary points (COSMO(CH_2Cl_2)-ZORA-PBE-D3(BJ)/all electron TZP)

Co-OAc

anag

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.910	34.952	104.651	183.514
	Internal Energy (Kcal/mole):	0.889	0.889	288.003	289.781
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	103.700	109.662

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.271991518394209	-333.9379	-7700.79	-32220.11
Internal Energy:	0.461794652277326	12.5661	289.78	1212.44
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-11.809252680103397	-321.3461	-7410.42	-31005.19
-T*S:	-0.087193311636014	-2.3727	-54.71	-228.93
Gibbs free energy:	-11.896445991739411	-323.7188	-7465.13	-31234.11

TS-ag

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.910	34.910	94.150	172.970
	Internal Energy (Kcal/mole):	0.889	0.889	286.065	287.842
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	98.287	104.248

Contributions from frequencies below 20 1/cm

Frequency (1/cm):	16.358
Entropy (cal/mole-K):	7.033
Internal Energy (Kcal/mole):	0.593
Constant Volume Heat Capacity (cal/mole-K):	1.986

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.252814575632121	-333.4160	-7688.76	-32169.76
Internal Energy:	0.458706109496748	12.4820	287.84	1204.33
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-11.793164280121886	-320.9083	-7400.32	-30962.95
-T*S:	-0.082183500545028	-2.2363	-51.57	-215.77
Gibbs free energy:	-11.875347780666914	-323.1447	-7451.89	-31178.72

ag

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.910	34.874	105.392	184.176
	Internal Energy (Kcal/mole):	0.889	0.889	287.370	289.147
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	103.909	109.871

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.260285986099655	-333.6194	-7693.45	-32189.38
Internal Energy:	0.460785123862548	12.5386	289.15	1209.79
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-11.798556676223621	-321.0551	-7403.71	-30977.11
-T*S:	-0.087507897391291	-2.3812	-54.91	-229.75
Gibbs free energy:	-11.886064573614911	-323.4363	-7458.62	-31206.86

TS-CH

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.910	34.816	95.474	174.200
	Internal Energy (Kcal/mole):	0.889	0.889	284.068	285.846
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	100.599	106.560

Contributions from frequencies below 20 1/cm

Frequency (1/cm):	19.107
Entropy (cal/mole-K):	6.725
Internal Energy (Kcal/mole):	0.593
Constant Volume Heat Capacity (cal/mole-K):	1.986

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.251200923488641	-333.3721	-7687.75	-32165.52
Internal Energy:	0.455524386533448	12.3954	285.85	1195.98
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-11.794732350941707	-320.9510	-7401.31	-30967.07
-T*S:	-0.082767880663257	-2.2522	-51.94	-217.31
Gibbs free energy:	-11.877500231604964	-323.2032	-7453.24	-31184.37

MCH

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.910	34.854	104.695	183.460
	Internal Energy (Kcal/mole):	0.889	0.889	287.574	289.352
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	103.762	109.724

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.267019303421160	-333.8026	-7697.67	-32207.05
Internal Energy:	0.461111169430714	12.5475	289.35	1210.65
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-11.804963947976960	-321.2294	-7407.73	-30993.93
-T*S:	-0.087167647900566	-2.3720	-54.70	-228.86
Gibbs free energy:	-11.892131595877526	-323.6014	-7462.43	-31222.79

Co-NHAc

anag

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.903	34.968	98.913	177.785
	Internal Energy (Kcal/mole):	0.889	0.889	294.883	296.660
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	103.229	109.191

Contributions from frequencies below 20 1/cm

Frequency (1/cm):	18.519
Entropy (cal/mole-K):	6.787
Internal Energy (Kcal/mole):	0.593
Constant Volume Heat Capacity (cal/mole-K):	1.986

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.454835339909538	-338.9133	-7815.53	-32700.17
Internal Energy:	0.472758137644034	12.8644	296.66	1241.23
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-11.981133016252018	-326.0232	-7518.28	-31456.46
-T*S:	-0.084471227633381	-2.2986	-53.01	-221.78
Gibbs free energy:	-12.065604243885399	-328.3218	-7571.28	-31678.24

TS-ag

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.903	34.946	98.760	177.609
	Internal Energy (Kcal/mole):	0.889	0.889	294.110	295.887
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	101.765	107.727

Contributions from frequencies below 20 1/cm

Frequency (1/cm):	19.309
Entropy (cal/mole-K):	6.704
Internal Energy (Kcal/mole):	0.593
Constant Volume Heat Capacity (cal/mole-K):	1.986

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.442851033285256	-338.5872	-7808.01	-32668.70
Internal Energy:	0.471526326835612	12.8309	295.89	1237.99
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-11.970380520436159	-325.7306	-7511.53	-31428.23
-T*S:	-0.084387920613332	-2.2963	-52.95	-221.56
Gibbs free energy:	-12.054768441049491	-328.0269	-7564.48	-31649.79

ag

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.903	34.904	104.010	182.818
	Internal Energy (Kcal/mole):	0.889	0.889	295.072	296.849
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	105.199	111.160

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.448415727849707	-338.7386	-7811.50	-32683.31
Internal Energy:	0.473059626211084	12.8726	296.85	1242.02
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-11.974411915625137	-325.8403	-7514.06	-31438.81
-T*S:	-0.086862576230690	-2.3637	-54.51	-228.06
Gibbs free energy:	-12.061274491855826	-328.2040	-7568.56	-31666.87

TS-CH

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.903	34.829	93.850	172.582
	Internal Energy (Kcal/mole):	0.889	0.889	292.153	293.931
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	101.450	107.412

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.448519930733772	-338.7415	-7811.57	-32683.58
Internal Energy:	0.468408489464901	12.7460	293.93	1229.81
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-11.979167255255385	-325.9697	-7517.04	-31451.30
-T*S:	-0.081999408451539	-2.2313	-51.46	-215.29
Gibbs free energy:	-12.061166663706924	-328.2010	-7568.50	-31666.59

MCH

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	43.903	34.861	102.055	180.819
	Internal Energy (Kcal/mole):	0.889	0.889	295.678	297.455
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	104.530	110.492

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.465924197660872	-339.2151	-7822.49	-32729.28
Internal Energy:	0.474024981342458	12.8989	297.46	1244.55
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-11.990955030304928	-326.2905	-7524.44	-31482.25
-T*S:	-0.085912767688622	-2.3378	-53.91	-225.56
Gibbs free energy:	-12.076867797993550	-328.6283	-7578.35	-31707.81

Ir-OAc

anag

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	44.757	35.170	96.338	176.264
	Internal Energy (Kcal/mole):	0.889	0.889	286.637	288.414
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	100.322	106.284

Contributions from frequencies below 20 1/cm

Frequency (1/cm):	17.773
Entropy (cal/mole-K):	6.869
Internal Energy (Kcal/mole):	0.593
Constant Volume Heat Capacity (cal/mole-K):	1.986

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.272063483265541	-333.9398	-7700.84	-32220.30
Internal Energy:	0.459617324747465	12.5068	288.41	1206.73
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-11.811501972504590	-321.4073	-7411.83	-31011.09
-T*S:	-0.083748891613994	-2.2789	-52.55	-219.88
Gibbs free energy:	-11.895250864118584	-323.6862	-7464.38	-31230.98

TS-ag

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	44.757	35.066	111.648	191.470
	Internal Energy (Kcal/mole):	0.889	0.889	287.238	289.015
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	104.796	110.757

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.261529612357618	-333.6532	-7694.23	-32192.64
Internal Energy:	0.460574723809572	12.5329	289.02	1209.24
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-11.800010702534561	-321.0946	-7404.62	-30980.92
-T*S:	-0.090973753245572	-2.4755	-57.09	-238.85
Gibbs free energy:	-11.890984455780133	-323.5702	-7461.71	-31219.78

ag

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	44.757	35.109	97.917	177.783
	Internal Energy (Kcal/mole):	0.889	0.889	285.859	287.636
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	98.800	104.762

Contributions from frequencies below 20 1/cm

Frequency (1/cm):	13.659
Entropy (cal/mole-K):	7.392
Internal Energy (Kcal/mole):	0.593
Constant Volume Heat Capacity (cal/mole-K):	1.986

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.254329787130294	-333.4573	-7689.71	-32173.74
Internal Energy:	0.458377563718904	12.4731	287.64	1203.47
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-11.795008037397904	-320.9585	-7401.48	-30967.79
-T*S:	-0.084470250189199	-2.2986	-53.01	-221.78
Gibbs free energy:	-11.879478287587103	-323.2571	-7454.49	-31189.57

TS-CH

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	44.757	35.040	93.471	173.267
	Internal Energy (Kcal/mole):	0.889	0.889	283.069	284.847
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	99.164	105.126

Contributions from frequencies below 20 1/cm

Frequency (1/cm):	15.980
Entropy (cal/mole-K):	7.080
Internal Energy (Kcal/mole):	0.593
Constant Volume Heat Capacity (cal/mole-K):	1.986

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.261525728176252	-333.6531	-7694.22	-32192.63
Internal Energy:	0.453932088844508	12.3521	284.85	1191.80
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-11.806649453318260	-321.2753	-7408.79	-30998.35
-T*S:	-0.082324772165576	-2.2402	-51.66	-216.14
Gibbs free energy:	-11.888974225483835	-323.5154	-7460.44	-31214.50

MCH

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	44.757	35.106	100.665	180.527
	Internal Energy (Kcal/mole):	0.889	0.889	286.844	288.622
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	102.384	108.346

Contributions from frequencies below 20 1/cm

Frequency (1/cm):	8.616
Entropy (cal/mole-K):	8.307
Internal Energy (Kcal/mole):	0.593
Constant Volume Heat Capacity (cal/mole-K):	1.987

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.276810490819294	-334.0690	-7703.82	-32232.76
Internal Energy:	0.459947897582999	12.5158	288.62	1207.59
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-11.815918407222808	-321.5275	-7414.60	-31022.69
-T*S:	-0.085774414904061	-2.3340	-53.82	-225.20
Gibbs free energy:	-11.901692822126870	-323.8615	-7468.43	-31247.89

Ir-NHAc

anag

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	44.751	35.181	100.160	180.092
	Internal Energy (Kcal/mole):	0.889	0.889	294.790	296.567
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	103.655	109.617

Contributions from frequencies below 20 1/cm

Frequency (1/cm):	17.927
Entropy (cal/mole-K):	6.851
Internal Energy (Kcal/mole):	0.593
Constant Volume Heat Capacity (cal/mole-K):	1.986

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.459391046387385	-339.0373	-7818.39	-32712.13
Internal Energy:	0.472610024719462	12.8604	296.57	1240.84
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-11.985836835654437	-326.1512	-7521.23	-31468.81
-T*S:	-0.085567641407969	-2.3284	-53.69	-224.66
Gibbs free energy:	-12.071404477062407	-328.4796	-7574.92	-31693.47

TS-ag

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	44.751	35.204	99.792	179.747
	Internal Energy (Kcal/mole):	0.889	0.889	294.205	295.982
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	101.859	107.821

Contributions from frequencies below 20 1/cm

Frequency (1/cm):	16.155
Entropy (cal/mole-K):	7.058
Internal Energy (Kcal/mole):	0.593
Constant Volume Heat Capacity (cal/mole-K):	1.986

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.450385564392356	-338.7922	-7812.74	-32688.48
Internal Energy:	0.471677461860631	12.8350	295.98	1238.39
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-11.977763916518239	-325.9315	-7516.16	-31447.61
-T*S:	-0.085403588367597	-2.3239	-53.59	-224.23
Gibbs free energy:	-12.063167504885836	-328.2555	-7569.75	-31671.84

ag

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	44.751	35.275	104.344	184.370
	Internal Energy (Kcal/mole):	0.889	0.889	294.816	296.593
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	103.510	109.472

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.460736208900574	-339.0739	-7819.23	-32715.66
Internal Energy:	0.472650937403440	12.8615	296.59	1240.94
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-11.987141085483648	-326.1867	-7522.05	-31472.23
-T*S:	-0.087600065012271	-2.3837	-54.97	-229.99
Gibbs free energy:	-12.074741150495919	-328.5704	-7577.02	-31702.23

ag-col

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	44.751	35.056	99.940	179.748
	Internal Energy (Kcal/mole):	0.889	0.889	293.773	295.551
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	103.495	109.456

Contributions from frequencies below 20 1/cm

Frequency (1/cm):	17.312
Entropy (cal/mole-K):	6.921
Internal Energy (Kcal/mole):	0.593
Constant Volume Heat Capacity (cal/mole-K):	1.986

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.458727508376384	-339.0192	-7817.97	-32710.38
Internal Energy:	0.470990251892357	12.8163	295.55	1236.58
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-11.986793070470542	-326.1772	-7521.83	-31471.32
-T*S:	-0.085404080454200	-2.3240	-53.59	-224.23
Gibbs free energy:	-12.072197150924742	-328.5012	-7575.42	-31695.55

TS-CH

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	44.751	35.047	96.900	176.699
	Internal Energy (Kcal/mole):	0.889	0.889	292.478	294.256
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	101.609	107.571

Contributions from frequencies below 20 1/cm

Frequency (1/cm):	10.991
Entropy (cal/mole-K):	7.823
Internal Energy (Kcal/mole):	0.593
Constant Volume Heat Capacity (cal/mole-K):	1.987

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.453523203496044	-338.8776	-7814.70	-32696.72
Internal Energy:	0.468925979823461	12.7601	294.26	1231.16
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-11.983653037659098	-326.0918	-7519.86	-31463.08
-T*S:	-0.083955222176349	-2.2845	-52.68	-220.42
Gibbs free energy:	-12.067608259835445	-328.3763	-7572.54	-31683.50

MCH

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	44.751	35.105	100.025	179.882
	Internal Energy (Kcal/mole):	0.889	0.889	294.912	296.689
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	103.159	109.120

Contributions from frequencies below 20 1/cm

Frequency (1/cm):	17.666
Entropy (cal/mole-K):	6.881
Internal Energy (Kcal/mole):	0.593
Constant Volume Heat Capacity (cal/mole-K):	1.986

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-12.480775538673159	-339.6192	-7831.81	-32768.27
Internal Energy:	0.472804221259592	12.8657	296.69	1241.35
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-12.007027131400081	-326.7278	-7534.52	-31524.45
-T*S:	-0.085467684508398	-2.3257	-53.63	-224.40
Gibbs free energy:	-12.092494815908479	-329.0535	-7588.16	-31748.84

6. DFT Calculations: QTAIM-IQA data

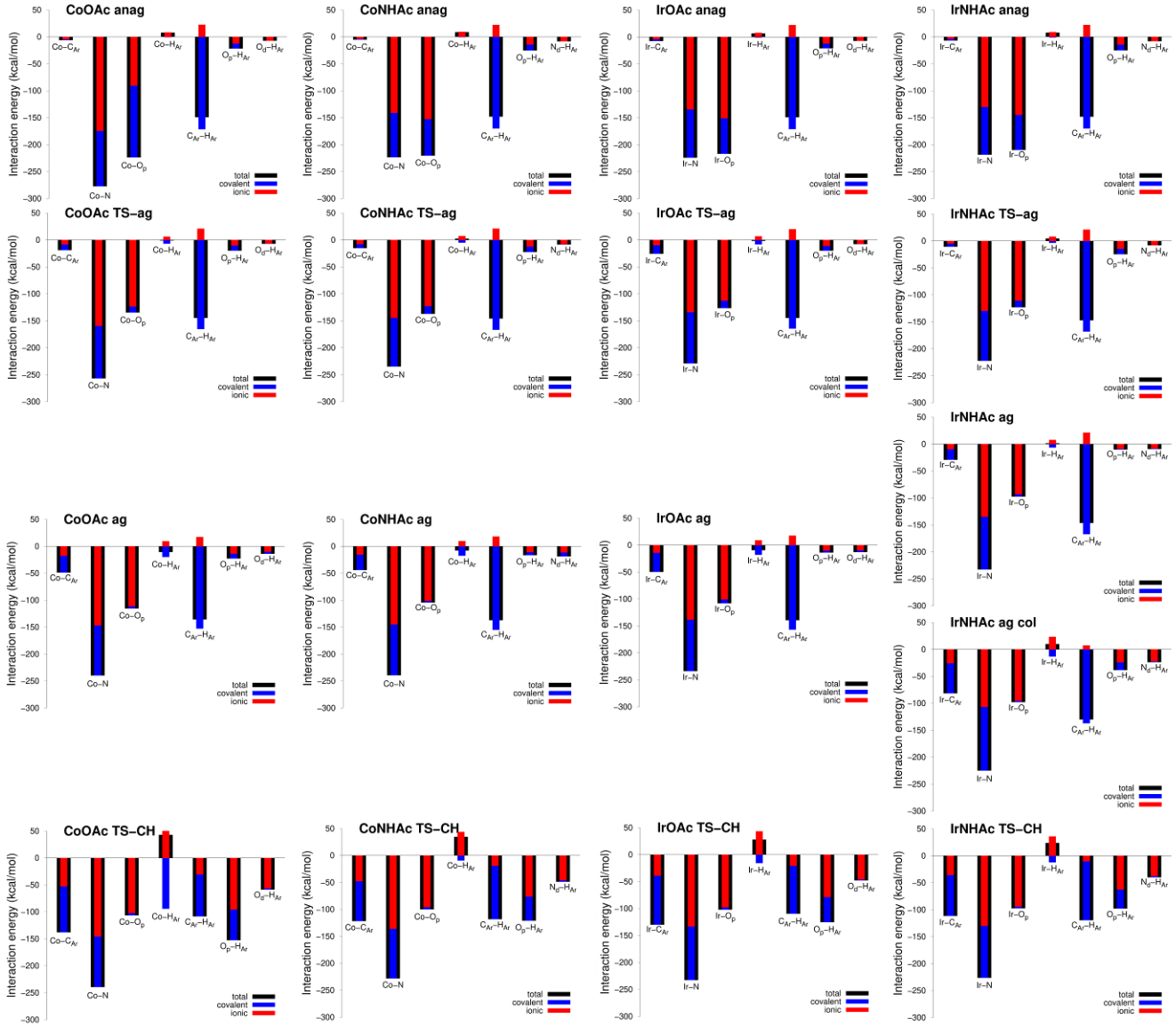


Figure S 53. IQA analysis of **anag**, **TS-ag**, **ag** and **TS-CH** in **CoOAc**, **CoNHAc**, **IrOAc** and **IrNHAc** systems (and **ag-col** in **IrNHAc**). Histograms of atom-pair interaction energies within the reactive site (black coloured, total E_{int} in kcal/mol) are decomposed into their covalent component (blue colored bars) and ionic component (red coloured bars).

7. LED analysis of the DLPNO-CCS(D)T computations

Table S31: DLPNO-CCSD(T)/LED results for **Co-OAc** (All energies in kcal/mol)

	anag	**TS-ag**	**ag**	**TS-CH**	**MCH**
Etot	-1554789	-1554777	-1554776	-1554766	-1554780
E_{2-1}	334	438	527	482	377
E_{3-1}	-1346	-1103	-1077	-988	-792
E_{4-1}	-1015	-1272	-1589	-2096	-2731
E_{5-1}	-4296	-4575	-4373	-3901	-3511
E_{3-2}	-140	-157	-176	-343	-555
E_{4-2}	-701	-726	-741	-499	-214
E_{5-2}	-120	-160	-187	-164	-124
E_{4-3}	143	162	184	137	162
E_{5-3}	220	194	184	179	157
E_{5-4}	163	218	255	247	250

Table S32: DLPNO-CCSD(T)/LED results for **Co-NHAc** (All energies in kcal/mol)

	anag	**TS-ag**	**ag**	**TS-CH**	**MCH**
Etot	-1542315	-1542303	-1542304	-1542296	-1542315
E_{2-1}	334	418	520	481	366
E_{3-1}	-1616	-1383	-1357	-1315	-1041
E_{4-1}	-981	-1201	-1542	-1922	-2761
E_{5-1}	-4063	-4356	-4203	-3749	-3287
E_{3-2}	-154	-167	-185	-296	-573
E_{4-2}	-695	-715	-739	-573	-202
E_{5-2}	-118	-149	-180	-160	-119
E_{4-3}	-159	-177	-201	-166	-179
E_{5-3}	237	210	192	195	161
E_{5-4}	153	199	242	230	237

Table S33: DLPNO-CCSD(T)/LED results for **Ir-OAc** (All energies in kcal/mol)

	anag	**TS-ag**	**ag**	**TS-CH**	**MCH**
Etot	-752850	-752829	-752839	-752833	-7528551
E_{2-1}	333	426	487	481	365
E_{3-1}	-1036	-880	-868	-838	-661
E_{4-1}	-849	-1051	-12552	-1631	-2011
E_{5-1}	-3347	-3512	-3341	-3001	-27883
E_{3-2}	-139	-153	-159	-296	-557
E_{4-2}	-699	-717	-731	--540	-198
E_{5-2}	-126	-165	184	-175	-131
E_{4-3}	141	159	177	145	153
E_{5-3}	206	196	180	177	154
E_{5-4}	169	221	248	251	261

Table S34: DLPNO-CCSD(T)/LED results for **Ir-NHAc** (All energies in kcal/mol)

	anag	**TS-ag**	**ag**	**ag-col**	**TS-CH**	**MCH**
Etot	-740380	-740369	-740378	-740371	-740369	-740390
E_{2-1}	333	362	341	473	472	354
E_{3-1}	-1242	-1113	-1195	-1074	-1060	-867
E_{4-1}	-830	-908	-885	-1355	-1492	-2021
E_{5-1}	-3167	-3440	-3443	-3062	-2938	-2575
E_{3-2}	-153	-156	-115	-211	-260	-571
E_{4-2}	-693	-696	-713	-673	-603	-191
E_{5-2}	-123	-140	-130	-171	-168	-122
E_{4-3}	156	152	143	184	172	171
E_{5-3}	227	226	201	203	197	161
E_{5-4}	157	183	181	228	231	242

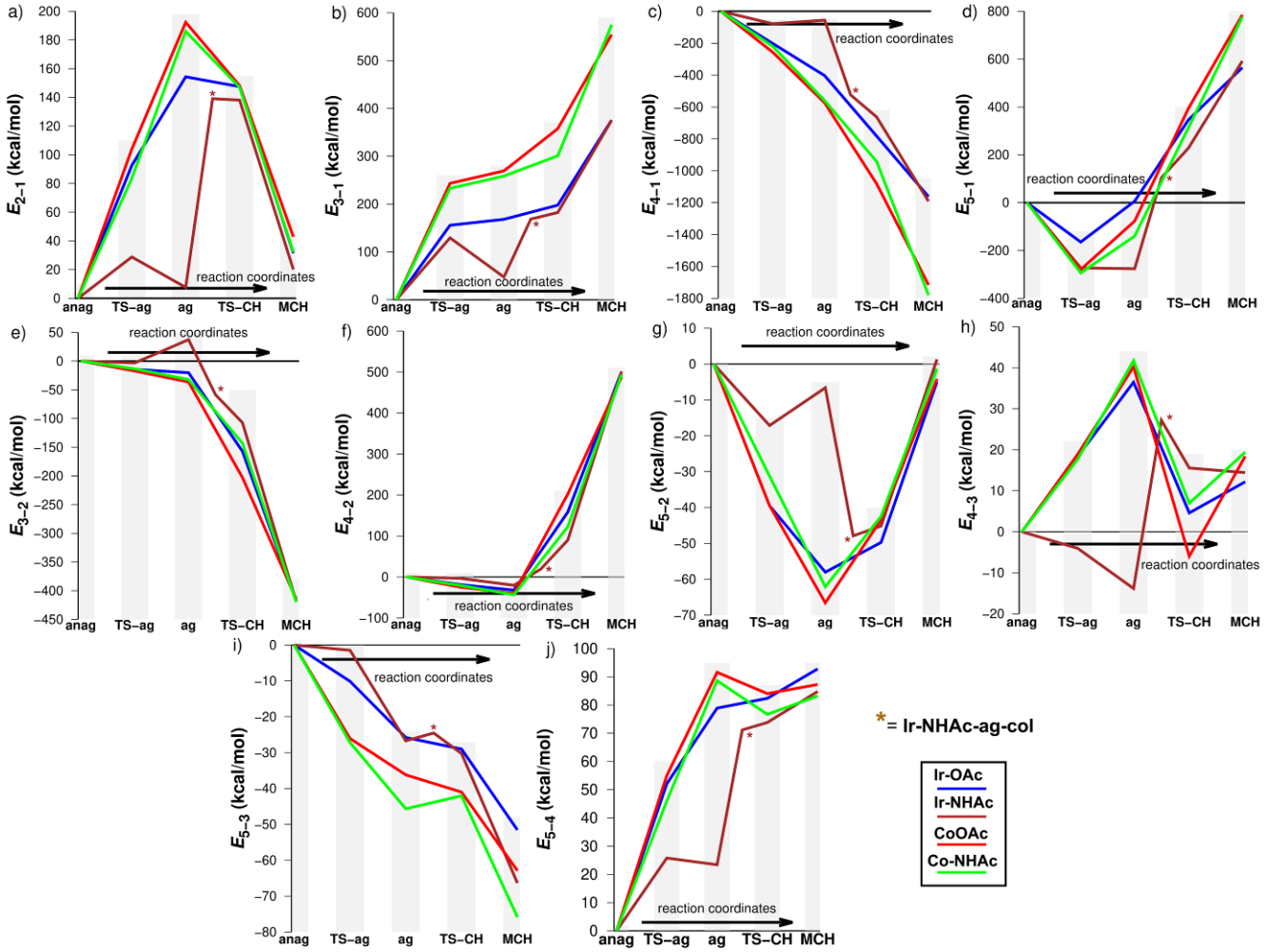
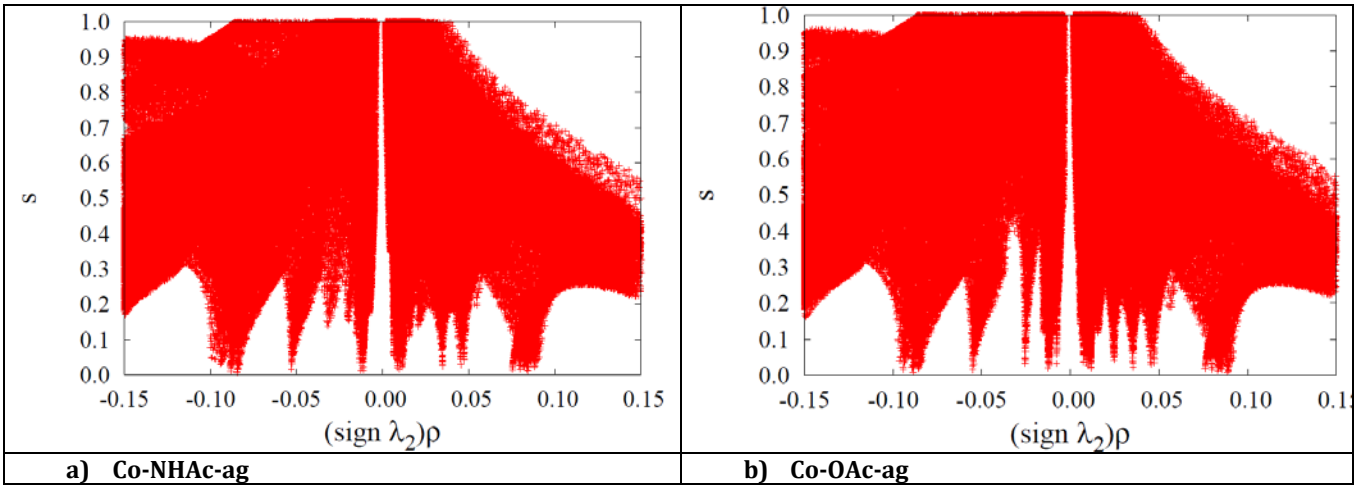
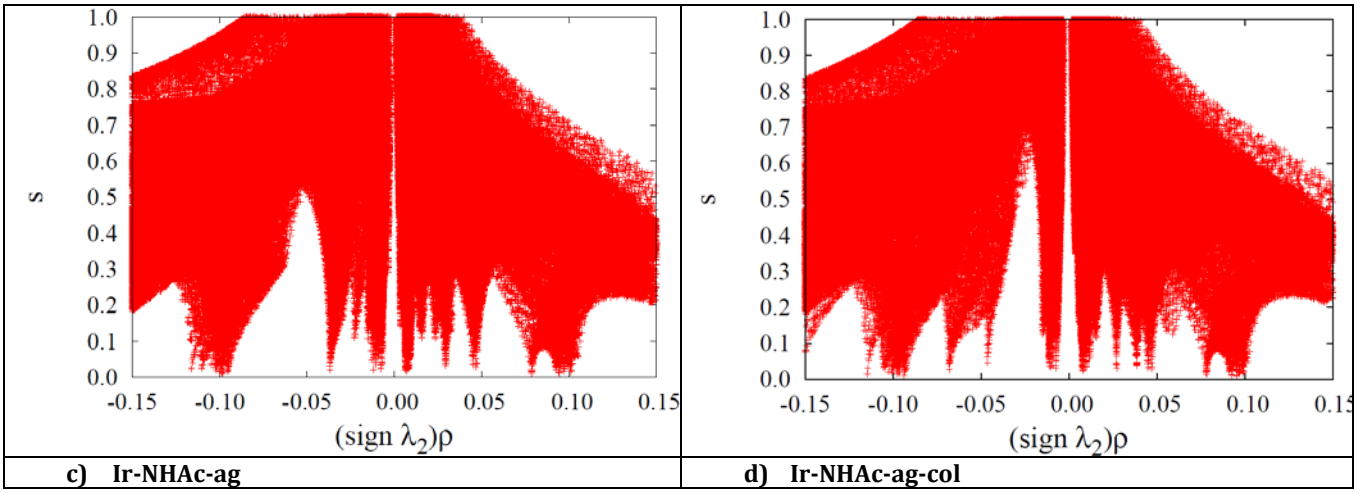


Figure S 54. LED analysis for **Co-OAc** (red lines), **Co-NHAc** (green lines), **Ir-OAc** (blue lines) and **Ir-NHAc** (brown lines) systems along the reaction coordinates of the CMD mechanism with plots of inter-fragment interaction energies E_{i-j}, where i and j are the considered molecular fragment numbers : a) interaction energy between fragments 2 (H^+) and 1 (metal), b) interaction energy between fragments 3 (auxiliary basis) and 1 (metal), c) interaction energy between fragments 4 (2-*phpy*$^-$) and 1 (metal), d) interation energy between fragments 5 (Cp* ligand) and 1 (metal), e) interaction energy between fragments 3 (auxiliary basis) and 2 (H^+), f) interaction energy between fragments 4 (2-*phpy*$^-$) and 2 (H^+), g) interaction energy between fragments 5 (Cp* ligand) and 2 (H^+), h) interaction energy between fragments 4 (2-*phpy*$^-$) and 3 (auxiliary basis), i) interaction energy between fragments 5 (Cp* ligand) and 3 (auxiliary basis), j) interaction energy between fragments 5 (Cp* ligand) and 4 (2-*phpy*$^-$).

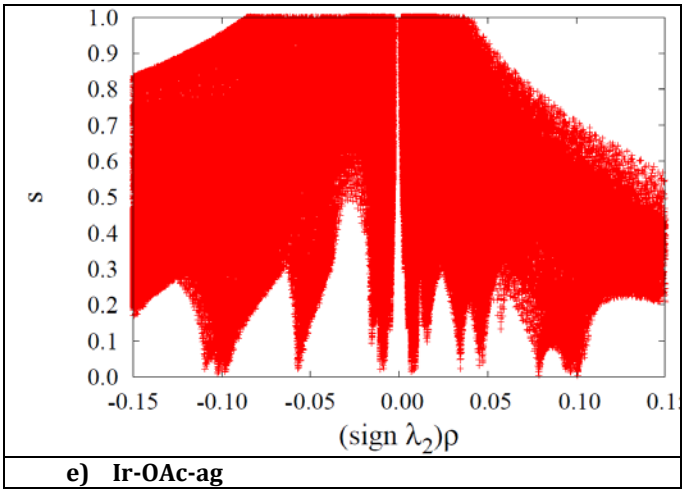
8. NCI index analysis



a) **Co-NHAc-ag** b) **Co-OAc-ag**



c) **Ir-NHAc-ag** d) **Ir-NHAc-ag-col**



e) **Ir-OAc-ag**

Figure S55. s(ρ) diagrams for **ag** and **Ir-NHAc-ag-col** compounds.

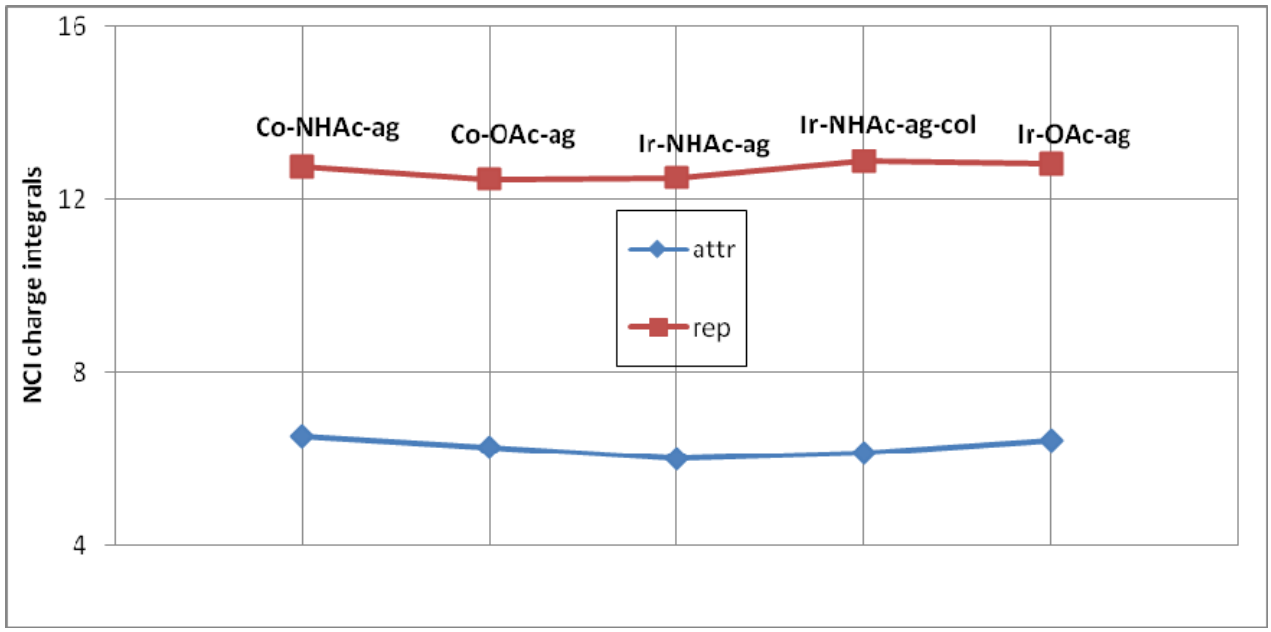


Figure S56. NCI integrals for **ag** and **Ir-NHAc-ag-col** compounds.

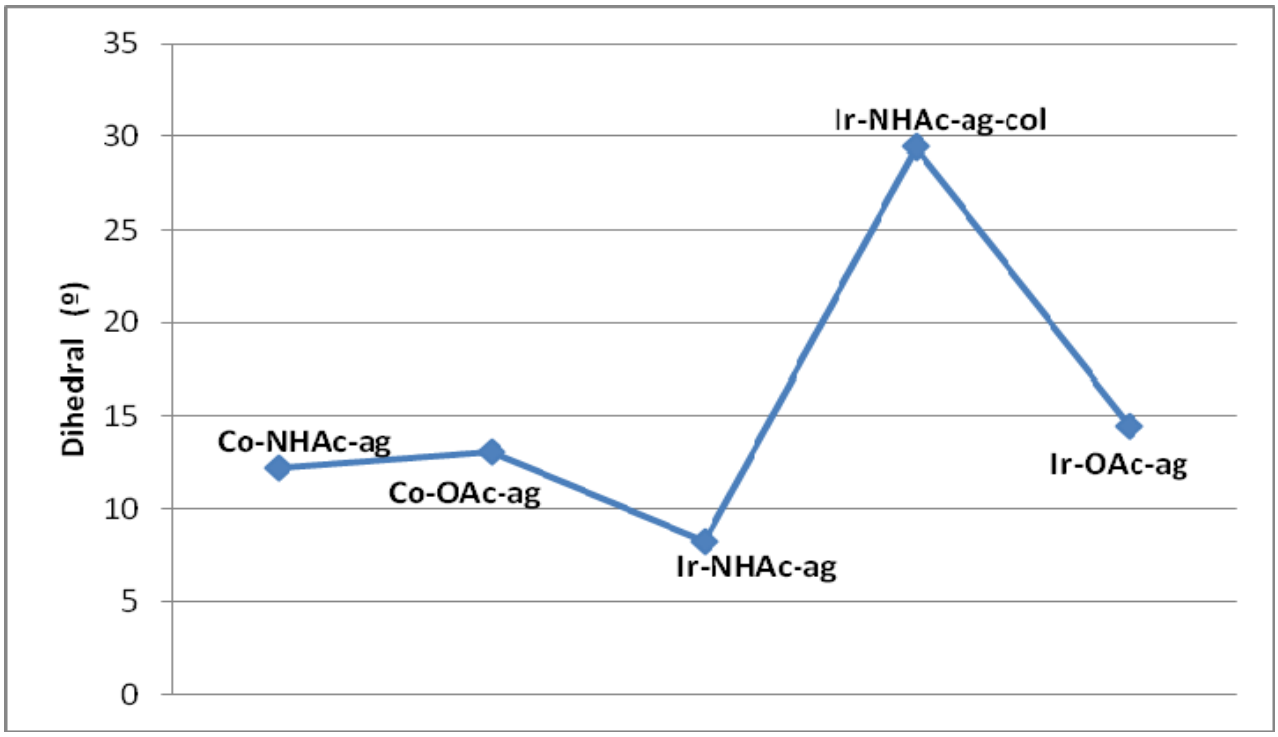


Figure S57. H_{ag}-C_{ag}-C_{β}-H_{β} dihedral for **ag** and **ag-col** compounds.

9. Electrophilic C-H activation profile , energies (COSMO (CH_2Cl_2) - ZORA - PBE-D3(BJ) / all electron TZP)

$[Cp^*Co]^{2+}$

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-5.193480509846736	-141.3218	-3258.96	-13635.48
Internal Energy:	0.226576047255176	6.1654	142.18	594.88
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-4.965960276578073	-135.1307	-3116.19	-13038.13
-T*S:	-0.054711611543022	-1.4888	-34.33	-143.65
Gibbs free energy:	-5.020671888121095	-136.6194	-3150.52	-13181.77

2-*phpyH*

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-5.148539652192721	-140.0989	-3230.76	-13517.49
Internal Energy:	0.173169979936746	4.7122	108.67	454.66
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-4.974425486242488	-135.3610	-3121.50	-13060.35
-T*S:	-0.044859292856173	-1.2207	-28.15	-117.78
Gibbs free energy:	-5.019284779098661	-136.5817	-3149.65	-13178.13

EA-π (2+)

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-10.462359766787859	-284.6953	-6565.23	-27468.92
Internal Energy:	0.404317609803391	11.0020	253.71	1061.54
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-10.057097970970982	-273.6676	-6310.92	-26404.91
-T*S:	-0.074224259503733	-2.0197	-46.58	-194.88
Gibbs free energy:	-10.131322230474716	-275.6873	-6357.50	-26599.78

EA-pre-TS (2+)

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-15.634413983919819	-425.4341	-9810.74	-41048.15
Internal Energy:	0.580363622440300	15.7925	364.18	1523.74
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-15.053106175466032	-409.6159	-9445.97	-39521.92
-T*S:	-0.099572324699498	-2.7095	-62.48	-261.43
Gibbs free energy:	-15.152678500165530	-412.3254	-9508.45	-39783.35

EA-TS-CH (2+)

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-15.628210571346047	-425.2652	-9806.85	-41031.86
Internal Energy:	0.575121170229745	15.6498	360.89	1509.98
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-15.052145215102817	-409.5897	-9445.36	-39519.40
-T*S:	-0.094260050190373	-2.5649	-59.15	-247.48
Gibbs free energy:	-15.146405265293190	-412.1547	-9504.51	-39766.88

EA-MCH (2+)

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-15.649161782477812	-425.8354	-9820.00	-41086.87
Internal Energy:	0.581024366988613	15.8105	364.60	1525.48
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-15.067193229475713	-409.9992	-9454.81	-39558.91
-T*S:	-0.093412647094798	-2.5419	-58.62	-245.25
Gibbs free energy:	-15.160605876570511	-412.5411	-9513.42	-39804.17