

Positive shift in corrole redox potentials leveraged by modest β -CF₃-substitution helps achieve efficient photocatalytic C-H bond functionalization for group 13 complexes

Xuan Zhan ^a, Pinky Yadav ^a, Yael Diskin-Posner ^b, Natalia Fridman ^a, Mahesh Sundararajan ^{c,d}, Zakir Ullah ^{c,d}, Qiu-Cheng Chen ^a, Linda J. W. Shimon ^b, Atif Mahammed ^a, David G. Churchill ^{*a,c,d} Mu-Hyun Baik ^{*c,d} and Zeev Gross ^{*a}

^a Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa 320000, Israel

^b Department of Chemical Research Support, Weizmann Institute of Science, Rehovot, 76100, Israel

^c Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Republic of Korea

^d Center for Catalytic Hydrocarbon Functionalizations, Institute for Basic Science (IBS), Daejeon, Republic of Korea.

Table of contents		Page number
Fig S1	The ¹ H-NMR spectrum of 4CF₃-Ga	S5
Fig S2	The ¹⁹ F-NMR spectrum of 4CF₃-Ga	S5
Fig S3	The ¹ H-NMR spectrum of 3CF₃-Ga	S6
Fig S4	The ¹⁹ F-NMR spectrum of 3CF₃-Ga	S6
Fig S5	The ¹ H-NMR spectrum of 4CF₃-Al	S7
Fig S6	The ¹⁹ F-NMR spectrum of 4CF₃-Al	S7
Fig S7	The ¹ H-NMR spectrum of 3CF₃-Al	S8
Fig S8	The ¹⁹ F-NMR spectrum of 3CF₃-Al	S8
Fig S9	The APCI mass spectrum of 4CF₃-Ga	S9
Fig S10	The APCI mass spectrum of 3CF₃-Ga	S10
Fig S11	The APCI mass spectrum of 4CF₃-Al (negative mode)	S11
Fig S12	The APCI mass spectrum of 4CF₃-Al (positive mode)	S12
Fig S13	The APCI mass spectrum of 3CF₃-Al (negative mode)	S13
Fig S14	The APCI mass spectrum of 3CF₃-Al (positive mode)	S14
Fig S15	CV traces of –CF ₃ substituted compounds in reduction region	S15
Fig S16	H ₂ O ₂ detection by UV-vis method	S15
Table S1	Selected structural data for 3I-Al , 3I-Ga and 3CF₃-Ga .	S16
Table S2	Photophysical properties of investigated corrole complexes	S17
Table S3	Half wave redox potentials of investigated corroles	S18
Table S4	The retention times of involved solvents by GC	S19

Experimental section

Materials: Experimental reagents (Aldrich) and solvents were used without further purification. Silica gel 60 (230–400 mesh) was used for column chromatography.

Synthetic Methods.

Physical Methods: ^1H and ^{19}F NMR spectra were recorded on a Bruker Avance III 400 spectrometer equipped with a 5 mm, automated tuning, and matching broad band probe (BBFO) with z-gradients. Chemical shifts are reported in ppm relative to the peak for residual hydrogen atoms of the deuterated solvent CDCl_3 ($\delta = 7.26$). Absorption spectra of the samples were measured on an Agilent 8454 spectrophotometer. Mass spectra for the compounds were performed on a Bruker Maxis Impact mass spectrometer, using APPI (atmospheric pressure photoionization) direct probe in either positive or negative mode.

Spectroscopy: Steady-state emission spectra were recorded on a Cary Eclipse fluorometer, at room temperature. Quantum yields (QY) of emission were calculated by using tetraphenylporphyrin (TPP) in toluene at room temperature ($\Phi_{\text{F}} = 0.11$) as the standard. The fluorescence lifetimes were measured by the combined spectrometer consisting of the EDINBURCH LIFESPEC II and the picosecond pulsed diode laser: All samples were recorded in toluene at room temperature.

Electrochemistry: Cyclic voltammetry measurements were carried out in acetonitrile (HPLC grade) containing 0.5 mM of the group 13 element Al and Ga complexes and 0.1 M TBAP (Fluka, for electrochemical analysis) as the electrolyte under an argon atmosphere. A conventional three-electrode system consisting of a glassy carbon working electrode, a platinum wire as counter electrode, and silver wire separated from the bulk solution by a sample holder with a porous glass frit in 0.1 M TBAP / 0.01 M AgNO_3 solution. Electrochemical measurements were recorded with an EmStat³⁺ electrochemical system with a scan rate of 100 mVs^{-1} . All the potentials are referenced vs the $\text{Fc}^+/\text{0}$ redox potential added as an internal standard ($E_{1/2} = 0.0975$ V vs. Ag/Ag^+ in 0.1 M TBAP / 0.01 M AgNO_3 solution).

Crystal Structure Determinations: For crystal structure determination of **3I-Al**, data were collected at 100 K on a dual source Rigaku XtaLab PRO diffractometer equipped with PILATUS 200 detector, with [$\lambda(\text{Cu-K}\alpha) = 1.54184$ Å] radiation. Structures were solved with SHELXT and further refined with full matrix least-squares based on F^2 with SHELXL. Hydrogens were calculated in riding mode. For the crystal structural determination of **3CF3-Ga**, the data collection was performed using monochromated Mo $\text{K}\alpha$ radiation, $\lambda = 0.71073$ Å, using φ and ω scans to cover the Ewald sphere. Accurate cell parameters were obtained with the amount of indicated reflections. The structure was solved by direct methods (SHELXS-97) and refined by full matrix least-squares methods against F^2 (SHELXL-97). All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotopically on calculated

positions using a riding model with their Uiso values constrained to 1.5 times the Ueq of their pivot atoms for terminal sp³ carbon atoms and 1.2 times for all other carbon atoms.

Photocatalysis

HBr + phenol → *para*-monobrominated phenol + *ortho*-monobrominated phenol: An acetonitrile solution (2.5 mL, with catalyst concentration that leads to OD = 2.0 at 400 nm) was charged with phenol (24 mg, 0.1 M) and aqueous 47% HBr (58 μL, 0.2 M) and placed in a 2.5 mL pyrex vial. The stirred solution was irradiated by a LED lamp with (200 W, λ_{max} = 395 - 405 nm, placed 15 cm from the vial) for 3 h. The internal temperature in the reaction solution was measured to be 36 °C. Prior to injection to the GC for product determination, the mixture was treated with solid K₂CO₃ to neutralize the acid and into dry the solution and nitrobenzene (5 μL, 49 μM) was added as an external reference. Identification of reaction products (see Table S4) and determination of their response factors relative to nitrobenzene was performed by authentic pure products that were either purchased or independently prepared. The retention times checked by the GC for acetonitrile, phenol, nitrobenzene, 2-bromophenol and 4-bromophenol were determined to elute at around 1.3 min, 3.8 min, 6.5 min, 5.8 min and 13.4 min, respectively.

HBr + toluene → **benzyl bromide**: An acetonitrile solution (2.5 mL, with catalyst concentration that leads to OD = 2.0 at 400 nm) was charged with toluene (108 μL, 0.4 M) and aqueous 47% HBr (116 μL, 0.4 M) and placed in a 2.5 mL vial made of Pyrex. The stirred solution was irradiated by a LED lamp with (200 W, λ_{max} = 395 - 405 nm, placed 15 cm from the vial) for 5 h. The internal temperature in the reaction solution was measured to be 36 °C. Prior to injection to the GC for product determination, the mixture was treated with solid K₂CO₃ to neutralize the acid and to dry the solution; nitrobenzene (5 μL, 49 μM) was added as external reference. Identification of reaction products (see Table S4) and determination of their response factors relative to nitrobenzene were performed by using pure products that were either purchased or independently prepared. The retention times checked by the GC for acetonitrile, toluene, nitrobenzene and benzyl bromide were determined around 1.3 min, 1.8 min, 6.5 min and 6.8 min.

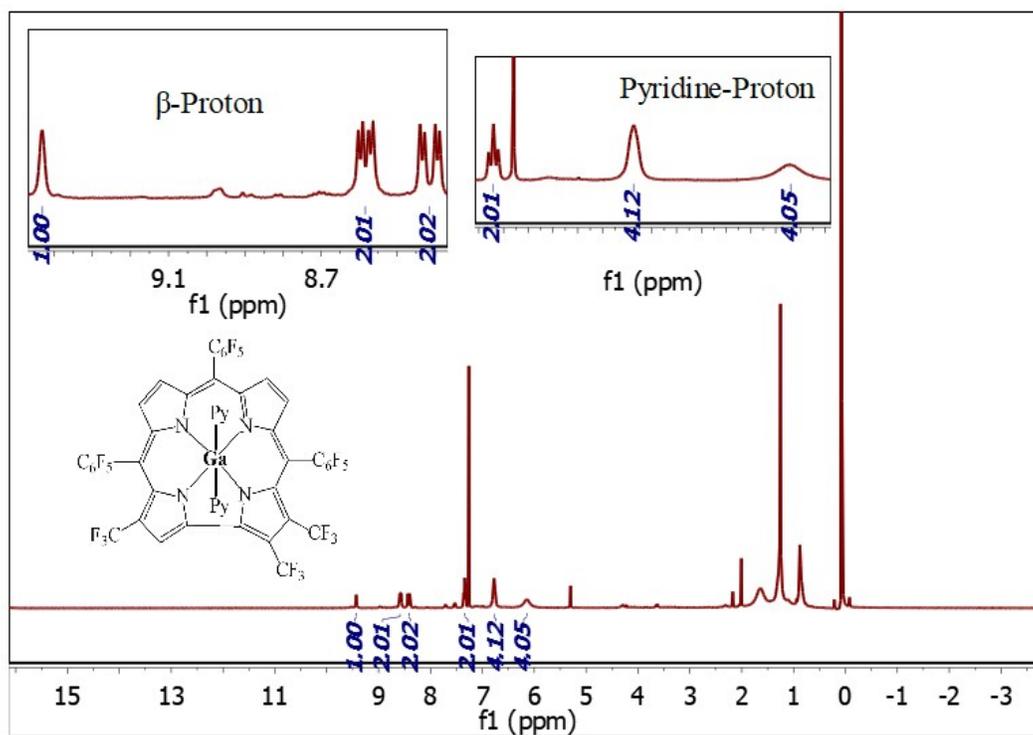


Fig S3. $^1\text{H-NMR}$ spectrum and expanded regions for compound $3\text{CF}_3\text{-Ga}$.

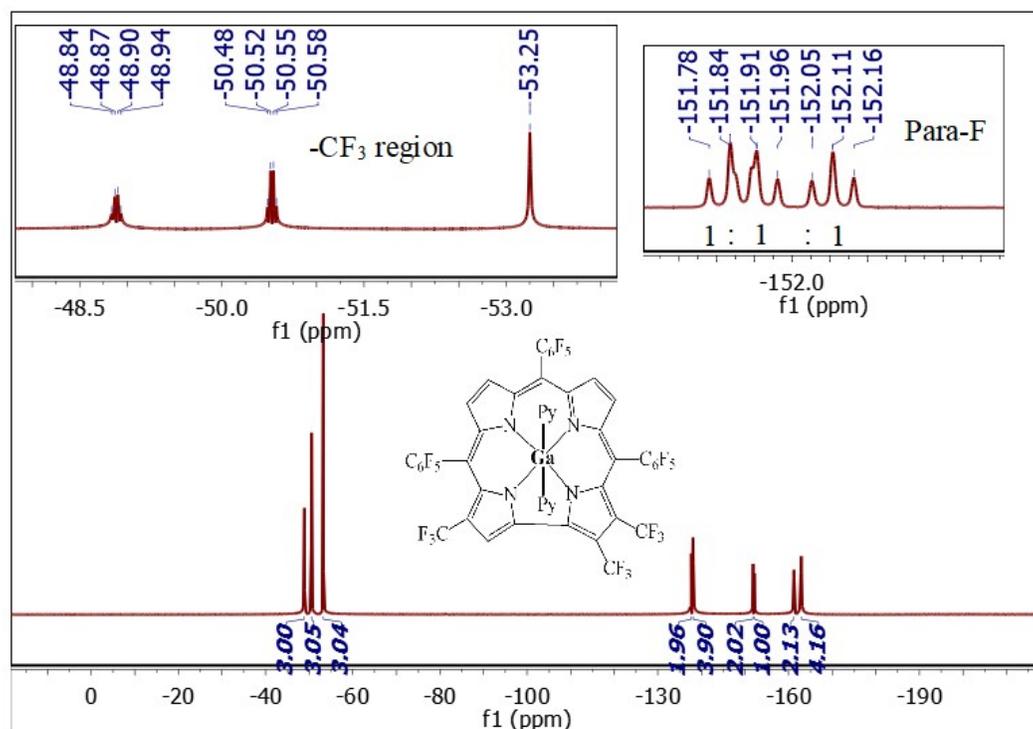


Fig S4. $^{19}\text{F-NMR}$ spectrum and expanded regions for compound $3\text{CF}_3\text{-Ga}$.

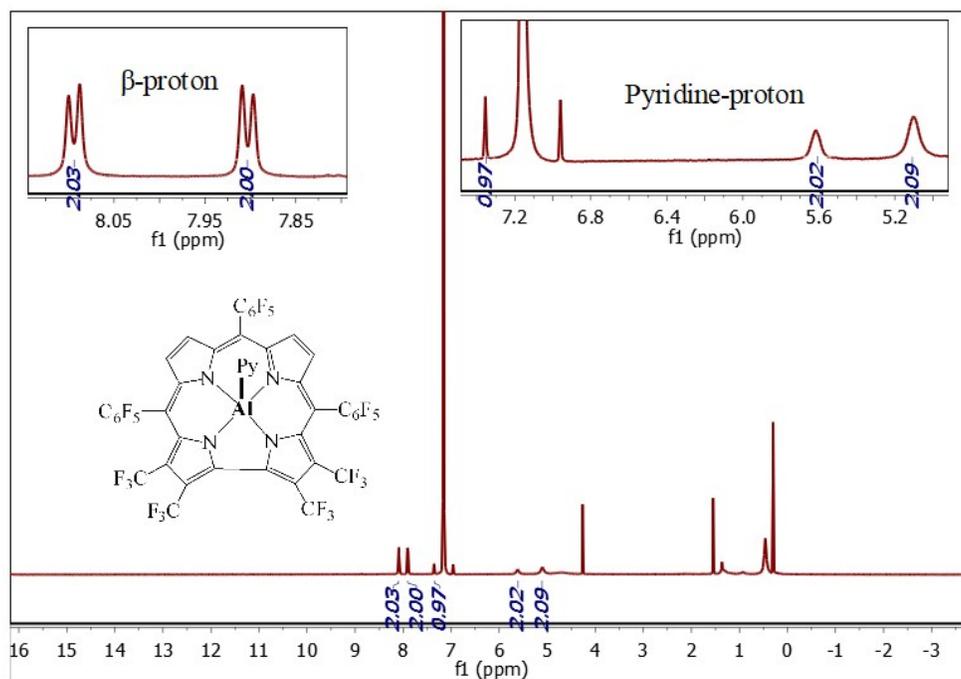


Fig S5. $^1\text{H-NMR}$ spectrum and expanded regions for compound **4CF₃-Al**.

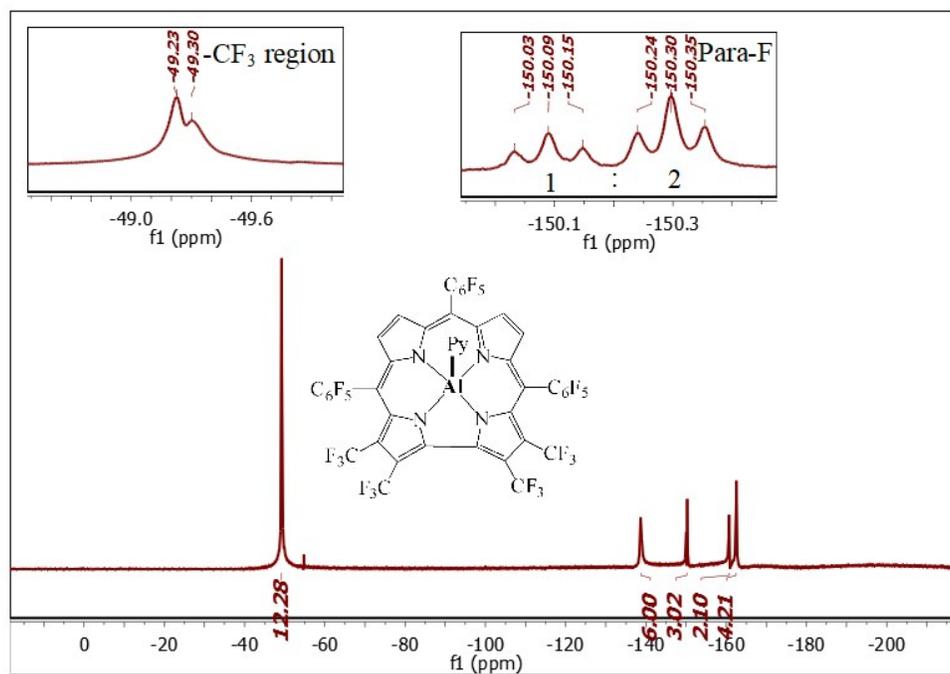


Fig S6. $^{19}\text{F-NMR}$ spectrum and expanded regions for compound **4CF₃-Al**.

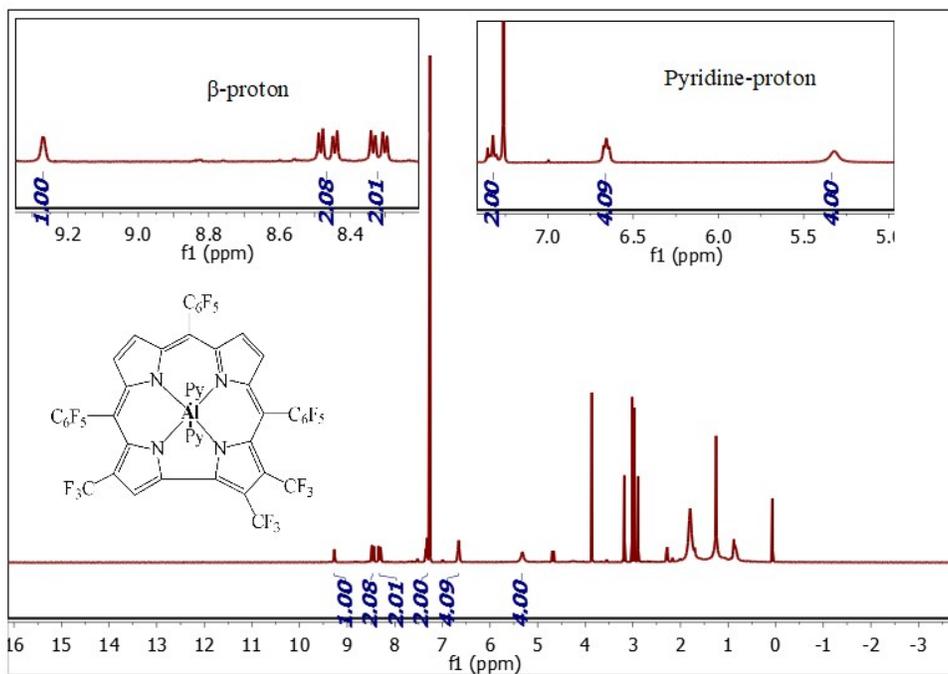


Fig S7. $^1\text{H-NMR}$ spectrum and expanded regions for compound **3CF₃-Al**.

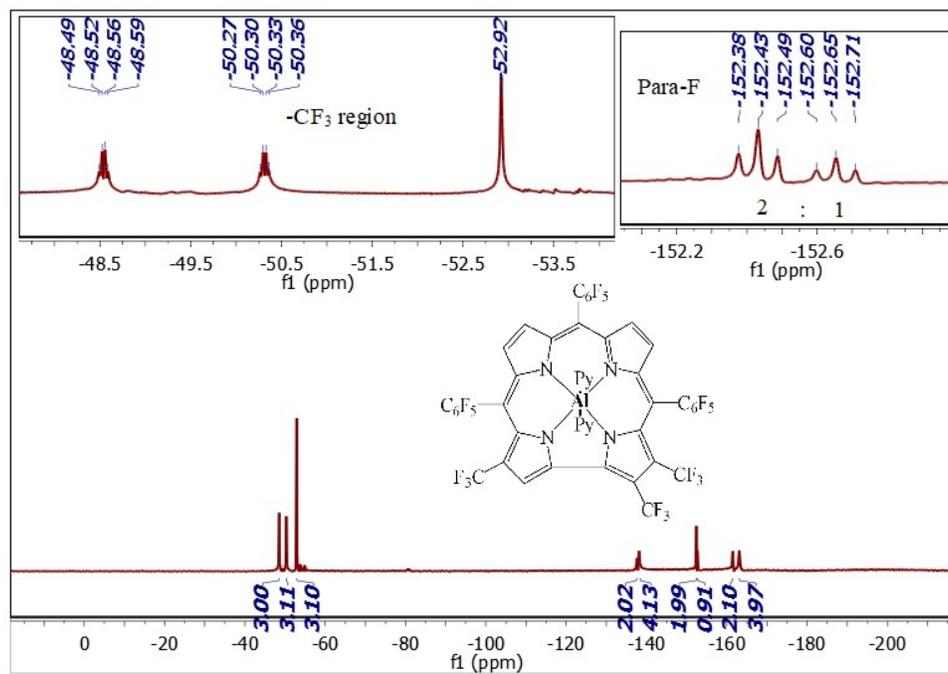


Fig S8. $^{19}\text{F-NMR}$ spectrum and expanded regions for compound **3CF₃-Al**.

Generic Display Report

Analysis Info

Analysis Name D:\Data\Gross\Gr_6282n000001.d
Method APCI_pos_SolidProbe.m
Sample Name 4-Ga-(CF₃)₄
Comment

Acquisition Date 4/25/2018 6:14:03 PM

Operator Larisa Panz
Instrument maXis impact

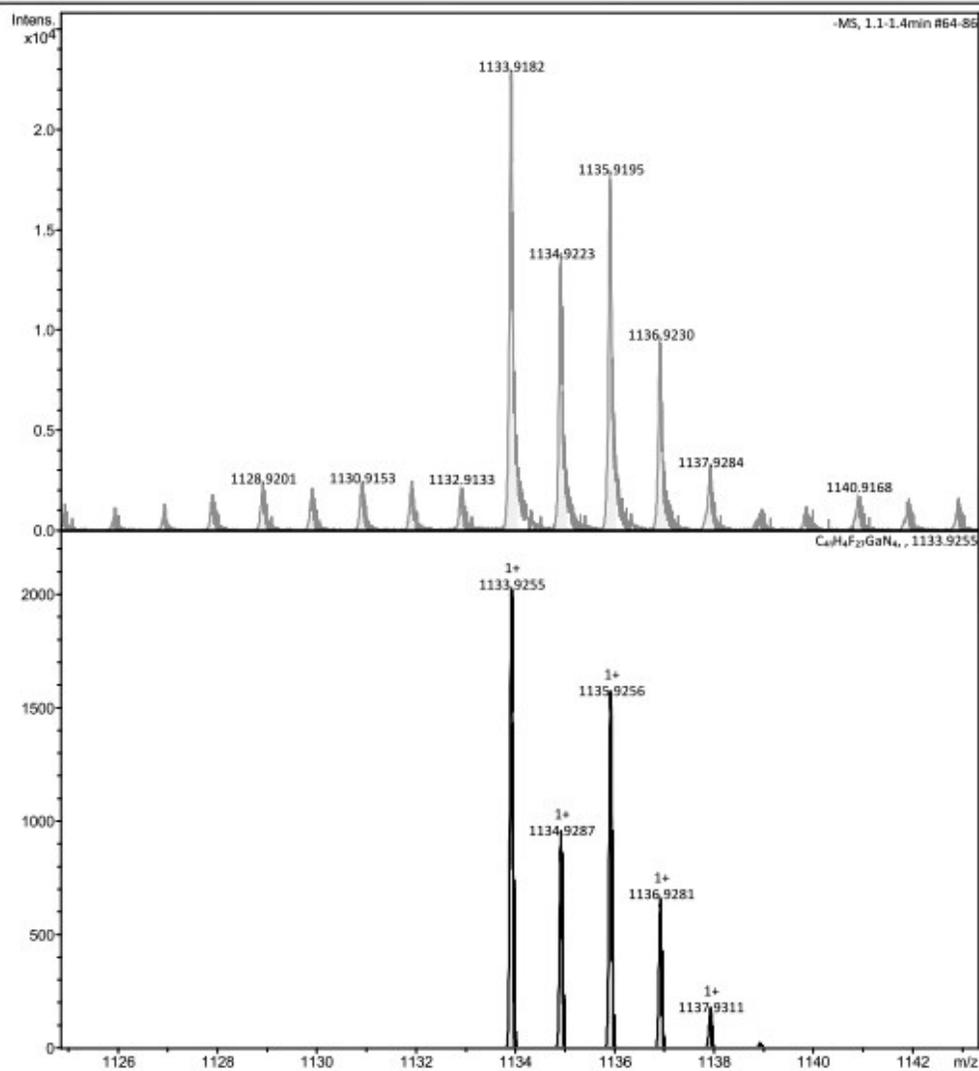


Fig S9. APCI mass spectral data for compound 4CF₃-Ga.

Generic Display Report

Analysis Info

Analysis Name D:\Data\Gross\Gr_6283n000001.d
Method APCI_pos_SolidProbe.m
Sample Name 3-Ga-(CF₃)₃
Comment

Acquisition Date 4/25/2018 5:59:51 PM

Operator Larisa Panz
Instrument maXis impact

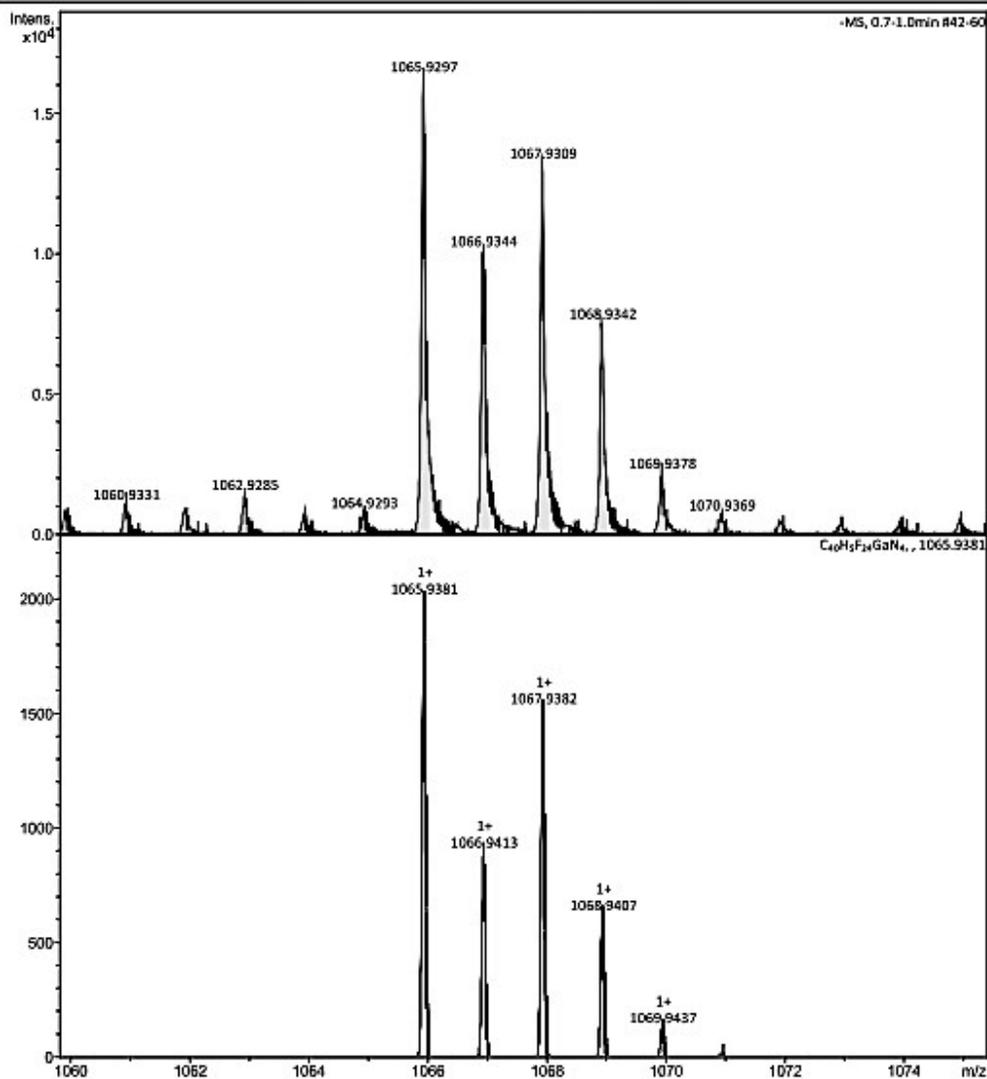


Fig S10. APCI mass spectral data for compound 3CF₃-Ga.

Generic Display Report

Analysis Info

Analysis Name D:\Data\Gross\Gr_6370n000001.d
Method APCI_pos_SolidProbe.m
Sample Name 4-CF3-AI
Comment

Acquisition Date 5/3/2018 1:20:56 PM

Operator Larisa Panz
Instrument maXis impact

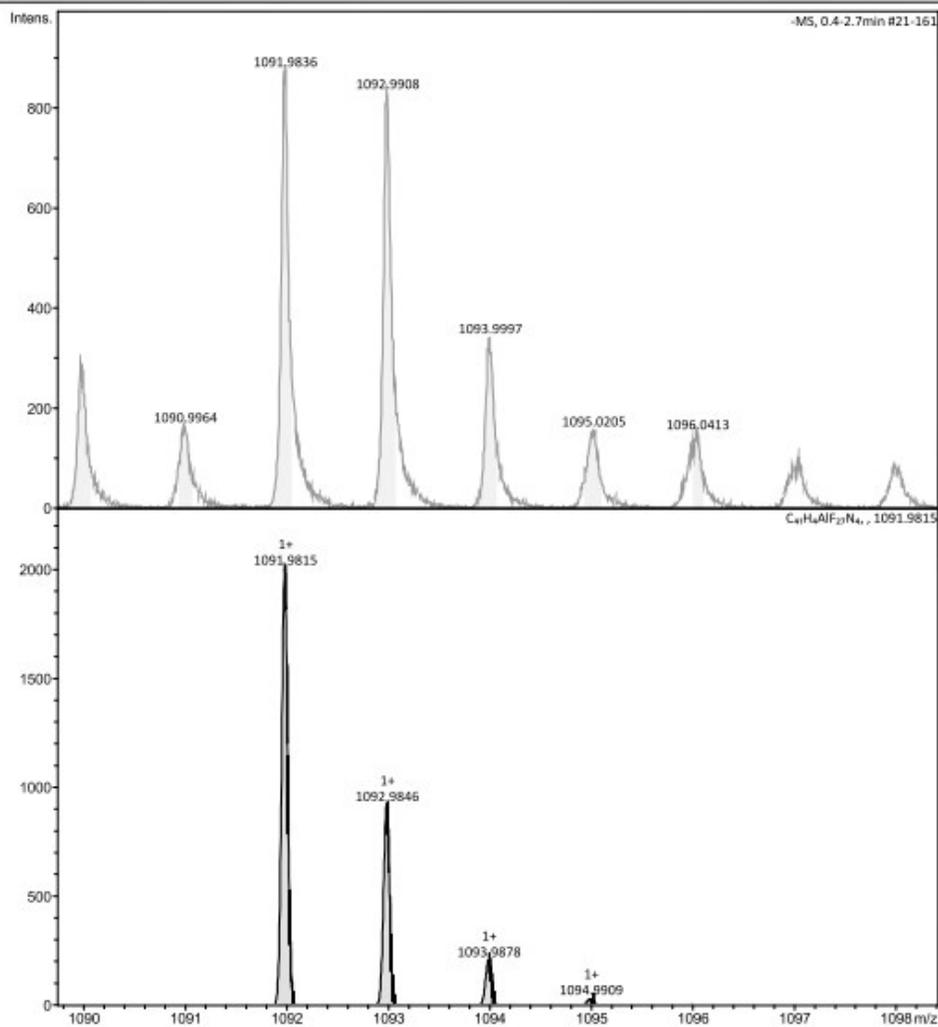


Fig S11. APCI mass spectral data for compound 4CF₃-AI (negative mode).

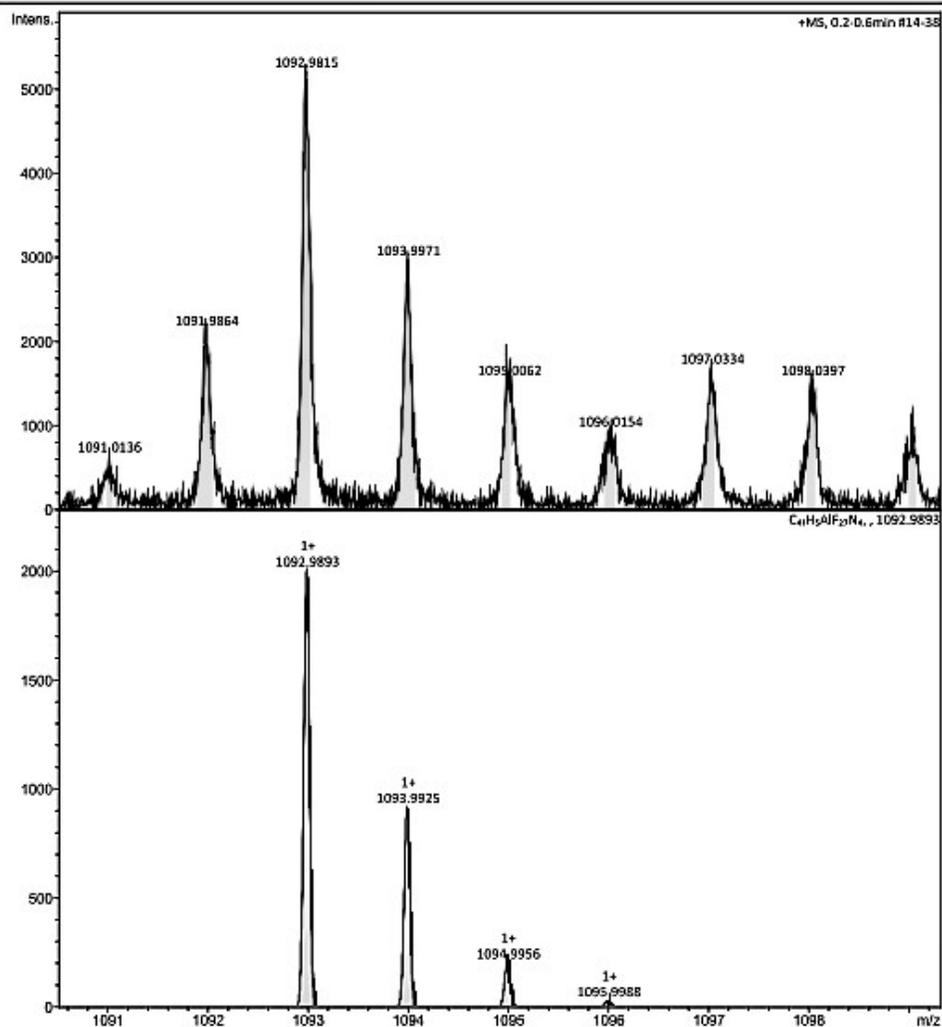
Generic Display Report

Analysis Info

Analysis Name D:\Data\Gross\Gr_6370p000001.d
Method APCI_pos_SolidProbe.m
Sample Name 4-CF3-AI
Comment

Acquisition Date 5/3/2018 1:39:37 PM

Operator Larisa Panz
Instrument maXis impact



Bruker Compass DataAnalysis 4.2

printed: 5/3/2018 1:41:53 PM

by: Larisa Panz

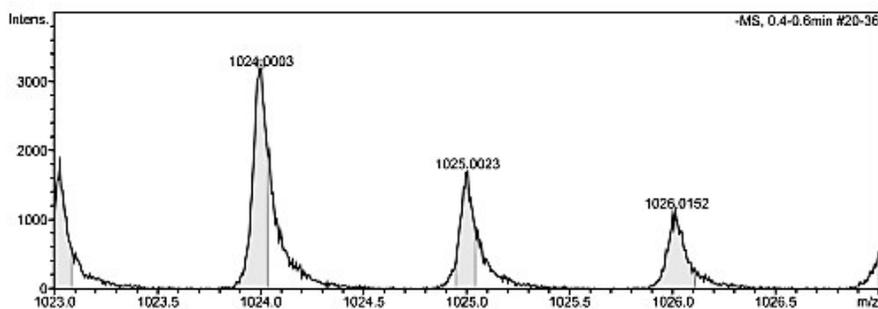
Page 1 of 1

Fig S12. APCI mass spectral data for compound 4CF₃-AI (positive mode).

Compound Spectrum SmartFormula Report

Analysis Info		Acquisition Date 4/25/2018 5:50:39 PM			
Analysis Name	D:\Data\Gross\Gr_6285n000001.d	Operator	Larisa Panz		
Method	APCI_pos_SolidProbe.m	Instrument	maXis impact 282001.00128		
Sample Name	3-Al-(CF ₃) ₃	Comment			
Acquisition Parameter					
Source Type	APCI	Ion Polarity	Negative	Set Nebulizer	1.2 Bar
Focus	Active	Sel Capillary	4000 V	Set Dry Heater	120 °C
Scan Begin	50 m/z	Sel End Plate Offset	-500 V	Set Dry Gas	1.5 l/min
Scan End	2500 m/z	Sel Charging Voltage	2000 V	Set Divert Valve	Source
		Sel Corona	2000 nA	Set APCI Heater	300 °C

-MS, 0.4-0.6min #20-36



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e ⁻ Conf	N-Rule	[err] [mDa]
1024.0003	1	C40H4AlF24N4	1022.9868	-10.1	447.0	1	100.00	29.5	even	ok	10.3
	2	C40H2AlF24N4	1020.9712	-19.3	697.9	2	0.00	30.5	even	ok	19.7

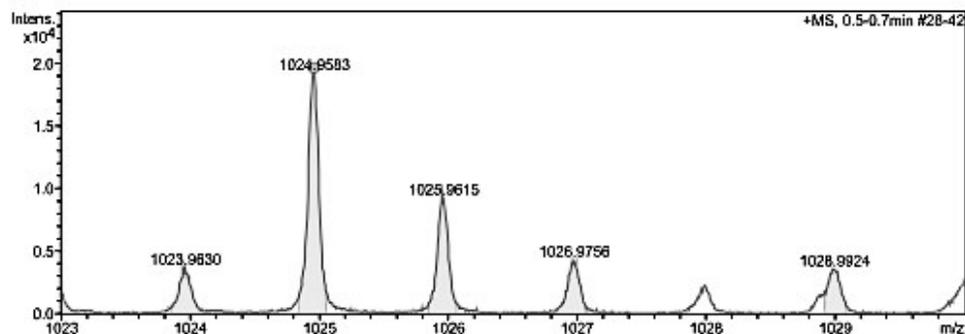
Fig S13. APCI mass spectral data for compound **3CF₃-Al** (negative mode).

Compound Spectrum SmartFormula Report

Analysis Info		Acquisition Date	4/24/2018 12:00:00 PM	
Analysis Name	D:\Data\Gross\Gr_6285000001.d		Operator	Larisa Panz
Method	APCI_pos_SolidProbe.m		Instrument	maXis impact
Sample Name	3-Al-CF3			282001.00128
Comment				

Acquisition Parameter					
Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	3000 V	Set Dry Heater	120 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.5 l/min
Scan End	2500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	5000 nA	Set APCI Heater	300 °C

+MS, 0.5-0.7min #28-42



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	c ⁻	Conf	N-Rule	err [mDa]
1024.9583	1	C4O116AlF24N4	1025.0019	42.5	66.0	1	0.00	28.5	even		ok	43.6
	2	C36H6AlF24N4O3	1024.9867	27.7	79.0	2	100.00	24.5	even		ok	28.3

Gr_6285000001.d

Bruker Compass DataAnalysis 4.2

printed: 4/24/2018 12:06:23 PM

by: Larisa Panz

Page 1 of 1

Fig S14. APCI mass spectral data for compound **3CF₃-Al** (positive mode).

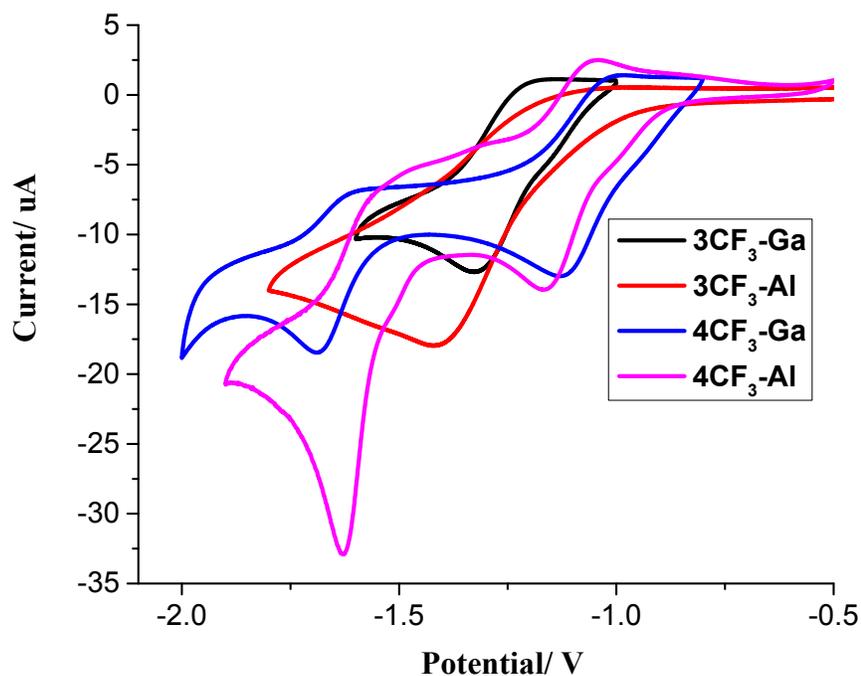


Fig S15. CV traces in the reduction region for all $-\text{CF}_3$ substituted compounds studied herein (room temperature, argon atmosphere, glassy carbon working electrode, ferrocene standard, 100 mVs^{-1} scan rate, 0.5 mm complex, 0.1 M TBAP, in CH_3CN , V vs Ag/ AgNO_3).

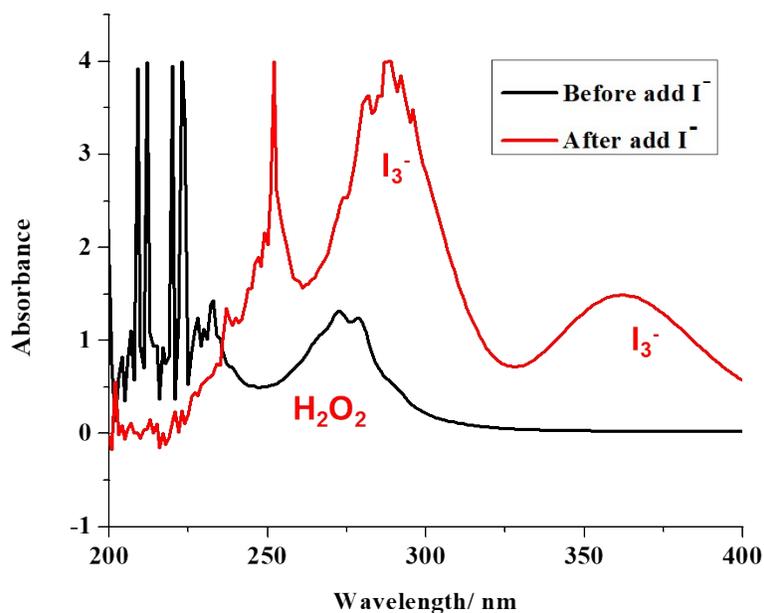


Fig S16. The UV-vis spectra of a reaction mixture ($3\text{CF}_3\text{-Ga}$ ($25 \mu\text{M}$) + $58 \mu\text{L}$ HBr (0.2 M) + 24 mg phenol (0.1 M) in 2.5 mL MeCN , after irradiation (400 nm) for 2 h) before and after adding excess TBAI (tetrabutylammonium iodide).

Complex	Ga deviation [Å] from the N4 corrole plane	Ga-pyridine bond length [Å]	Ga-N(pyrrole)bond length ranges [Å]	Table S1. Select ed struct ural data for comp ounds 3I-Al, 3I-Ga and
3I-Al	0.00025	2.153, 2.155	1.895-1.904	
3I-Ga	0.018	2.292, 2.230	1.912-1.952	
3CF₃-Ga	0.023	-	1.918-1.971	

3CF₃-Ga.

Table S2. Photophysical properties of investigated corrole complexes recorded in toluene.

Complex	Soret band (nm) (ϵ, 10^4)	Q band (nm) (ϵ, 10^4)	λ_{em} (nm)	Φ_f	τ (ns)	Kr (10^8 S⁻¹)	Knr (10^8 S⁻¹)
1-Ga	402	571	602	0.28	2.61	1.07	2.75
	424 (28.3)	597 (2.4)	657				
1-Al	401	572	627	0.76	6.32	1.20	0.38
	422 (29.4)	593	689				
3CF₃-Ga	405(2.96), 427 (7.16)	590(1.479),	623,	0.57	2.49	2.29	1.73
		615 (2.024)	677				
3CF₃-Al	403(2.98), 424 (7.77)	590 (1.808),	618,	0.71	3.30	2.37	0.88
		612 (2.203)	672				
4CF₃-Ga	360 (1.66), 416(4.67), 430 (6.36)	574(1.559),	634,	0.55	4.54	1.21	4.02
		596(2.033),	689				
		627 (3.386)					
4CF₃-Al	360(1.36), 426 (4.21)	572 (1.08),	635,	0.66	4.58	1.44	0.74
		595 (1.56),	687				
		620 (2.26)					

Table S3. Half wave redox potentials of investigated corroles.

Complex	1st oxidation (V)	reduction (V)	ΔE^a (V)
1-Ga	0.37	-	-
3CF₃-Ga	0.77	-1.26	2.02
4CF₃-Ga	0.83	-1.07, -1.64	1.90
1-Al	0.23	-	-
3CF₃-Al	0.62	-1.24	1.87
4CF₃-Al	0.74	-1.11, -1.59	1.85

Table S4. Retention times of involved solvents recorded by our GC.

Solvent	Retention time in GC (min)
Acetonitrile	~1.3
Benzaldehyde	~3.4
Phenol	~3.8
Nitrobenzene	~6.5
2-bromophenol	~5.8
4-bromophenol	~13.4
Benzyl bromide	~6.8

END OF SUPPORTING INFORMATION