

Supporting Information

for

**Annulated Carbocyclic Gallylene and Bis-Gallylene with
Two-Coordinated Ga(I) Atoms**

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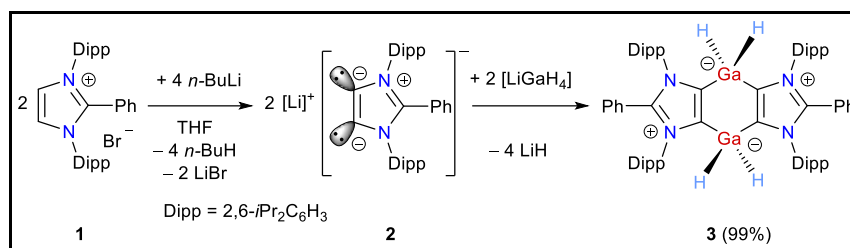
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Materials and Methods

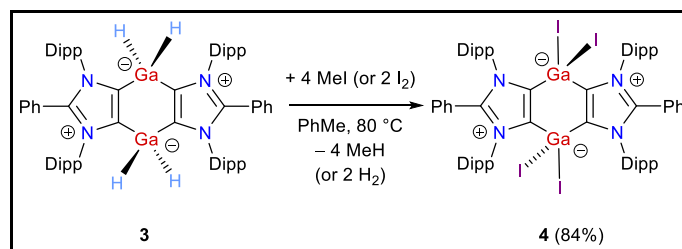
All syntheses and manipulations were carried out under an inert gas atmosphere (Ar or N₂) using standard Schlenk techniques or a glove box (MBraun LABMasterPro). Solvents were dried over appropriate drying agents, distilled, and stored over 4 Å molecular sieve prior to use. Deuterated solvents were dried over appropriate drying agents, distilled, and stored inside a glove box. NMR spectra were recorded on a Bruker Avance III 500 or a Bruker Avance III 500 HD spectrometer. Chemical shifts (in δ , ppm) are referenced to the solvent residual signals [CDCl₃: ¹H, 7.26 and ¹³C, 77.7 ppm, C₆D₆: ¹H, 7.16 and ¹³C, 128.06 ppm, CD₂Cl₂: ¹H, 5.32 and ¹³C, 53.8 ppm].¹ For NMR data, “s” refers to singlet, “d” refers to doublet, “pt” refers to *pseudo*-triplet, “t” refers to triplet, “sept” refers to septet, “m” refers to multiplet, and “br” refers to broad signals. Nano-ESI mass spectra were recorded using an Esquire 3000 ion trap mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a nano-ESI source. Samples were dissolved in a suitable solvent and introduced by static nano-ESI using *in-house* pulled glass emitters. Nitrogen served both as nebulizer as well as dry gas and was generated by a Bruker nitrogen generator NGM 11. Helium served as cooling gas for the ion trap. The mass axis was externally calibrated with ESI-L Tuning Mix (Agilent Technologies, Santa Clara, CA, USA) as a calibration standard. Infrared spectra were recorded using a BrukerAlpha-T FT-IR spectrometer. Melting points were measured with a Büchi B-545 Melting Point apparatus. Elemental analyses were carried out with a EURO EA Element Analyzer. Unless stated otherwise, chemicals from commercial suppliers (Merck, Sigma-Aldrich, or TCI) were used as received. (IPr^{Ph})Br (**1**) (IPr^{Ph} = PhC{N(2,6-*i*Pr₂C₆H₃)CH}₂)₂² and (Me₂S)AuCl³ were prepared according to the reported methods.

Synthesis of [(ADC)GaH₂]₂ (3)



To a 30 mL THF suspension of (IPr^{Ph})Br (**1**) (5.0 g, 9.24 mmol) was added *n*BuLi (8.5 mL, 21.3 mmol, 2.5 M in *n*-hexane) at -30°C . The reaction mixture was brought to room temperature (rt), stirred for 2h, and then added to a THF slurry of a freshly prepared LiGaH₄ (9.70 mmol). [LiGaH₄ was prepared by a slight modification of the literature method: GaCl₃ (1.71 g, 9.70 mmol) was dissolved in 10 mL THF and added to 10 mL THF suspension of LiH (0.34 g, 42.7 mmol) at -50°C . The reaction mixture was slowly brought to rt and stirred for additional 2h].⁴ The reaction mixture was stirred overnight. The volatiles were removed, and the resulting solid was dried *in vacuo* at 150°C for 3h. The residue was extracted with 75 mL toluene and the solvent was removed from the filtrate to obtain **3** as off-white solid in 99% (4.9 g) yield. Single crystals suitable for X-ray diffraction studies were obtained by a slow diffusion of *n*-hexane into a saturated benzene solution of **3**. M.p.: 370°C (dec.). Elemental analysis (%) calculated for C₆₆H₈₂N₄Ga₂ (1071) **3**: C 74.03, H 7.72, N 5.32; found: C 74.46, H 7.83, N 5.23. ¹H NMR (500 MHz, C₆D₆, 298 K): 7.23 (t, *J* = 7.2 Hz, 4H, *p*-C₆H₃), 7.12 (d, *J* = 7.8 Hz, 8H, *m*-C₆H₃), 7.01–6.98 (m, 4H, *o*-C₆H₅), 6.59–6.54 (m, 6H, *m/p*-C₆H₅), 4.16 (s, 4H, GaH₂), 3.22 (sept, *J* = 6.8 Hz, 8H, CHMe₂), 1.44 (d, *J* = 6.8 Hz, 24H, CHMe₂), 0.85 (d, *J* = 6.9 Hz, 24H, CHMe₂) ppm. ¹³C{¹H} NMR (126 MHz, C₆D₆, 298 K): 158.3 (CGa), 145.3 (*i*-C₆H₃), 144.4 (NCN), 136.5, 130.2, 128.9, 128.7, 128.4, 128.0, 125.4, 125.0 (C₆H₃/C₆H₅), 28.8 (CHMe₂), 24.4, 23.6 (CHMe₂) ppm. ESI-MS (*m/z*.): 1069.4 [**3**–H]⁺. FTIR: 1800, 1830 cm⁻¹ (GaH).

Synthesis of [(ADC)GaI₂]₂ (4)

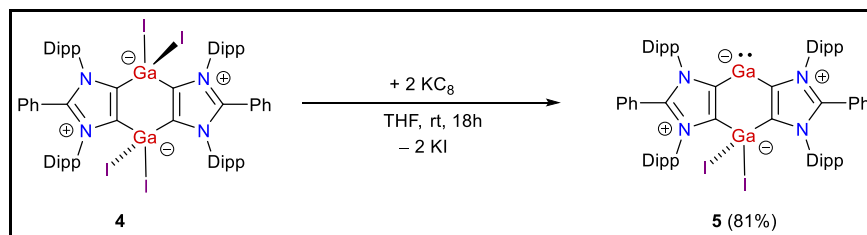


To a 20 mL toluene solution of **3** (0.5 g, 0.47 mmol) was dropwise added MeI (0.14 mL, 2.10 mmol) at rt (*Caution*: Gas evolution). The reaction mixture was stirred at 80°C overnight. Then, the solvent was

reduced to 5 mL and 20 mL of *n*-hexane was added. The precipitate formed was isolated by filtration, washed with 5 mL *n*-hexane twice, and then dried under reduced pressure to obtain compound **4** as an off-white solid in 84% (0.62 g) yield. Single crystals suitable for X-ray diffraction studies were obtained by a slow diffusion of *n*-hexane into a saturated dichloromethane solution of **4**. M.p.: < 410 °C. Elemental analysis (%) calculated for C₆₆H₇₈N₄Ga₂I₄ (1574) **4**: C 50.35, H 4.99, N 3.56; found: C 50.41, H 5.02, N 3.52. ¹H NMR (500 MHz, CDCl₃, 298 K): 7.44 (t, *J* = 7.8 Hz, 4H, *p*-C₆H₃), 7.32 (s, 4H, *m*-C₆H₃), 7.19–7.07 (m, 6H, *m*-C₆H₃/*p*-C₆H₅), 6.97 (t, *J* = 7.8 Hz, 4H, *m*-C₆H₅), 6.73 (d, *J* = 8.2 Hz, 4H, *o*-C₆H₅), 3.11–2.96 (br, 4H, CHMe₂), 2.94–2.78 (br, 4H, CHMe₂), 1.46–1.36 (m, 12H, CHMe₂), 1.33–1.26 (m, 12H, CHMe₂), 1.24–1.14 (m, 12H, CHMe₂), 0.22–0.09 (m, 12H, CHMe₂) ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃, 298 K): 164.0 (CGa), 149.0, 145.3, 132.9, 130.9, 130.4, 129.8, 129.2, 128.1, 125.4, 124.6, 123.7 (C₆H₃/C₆H₅), 28.9, 28.4 (CHMe₂), 26.7, 25.5, 23.9, 23.1 (CHMe₂) ppm. ESI-MS (*m/z*): 1447.0 [**4**-I]⁺.

Alternative Synthesis of 6: I₂ (1.0 g, 3.92 mmol) was dissolved in 10 mL Et₂O and added to a 30 mL toluene solution of **3** (2.0 g, 1.86 mmol) at –20 °C. The reaction mixture was slowly brought to rt and stirred overnight. The solution was reduced to 10 mL and then 50 mL *n*-hexane was added. The precipitate formed was recovered by filtration and dried under reduced pressure to obtain **6** as a pale-yellow solid in 80% (2.3 g) yield.

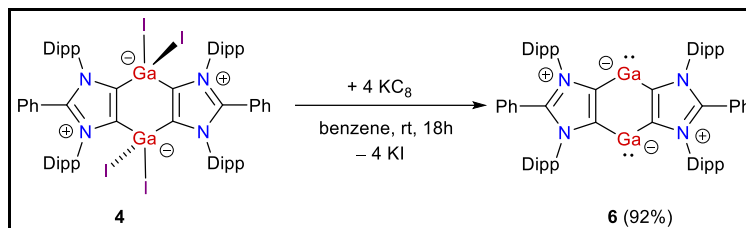
Synthesis of [(ADC)₂Ga(GaI₂)] (**5**)



To a mixture of **6** (0.5 g, 0.32 mmol) and KC₈ (92 mg, 0.68 mmol) was added 10 mL THF (or C₆H₆) and the resulting reaction mixture was stirred overnight at rt. The suspension was filtered through a plug of Celite and the volatiles from the filtrate were removed under vacuum to obtain compound **5** as a brown solid in 81% yield (0.35 g). Elemental analysis (%) calculated for C₆₈H₇₈N₄Ga₂I₂ (1321) **5**: C 60.03, H 5.95, N 4.24; found: C 58.37, H 6.12, N 4.11. ¹H NMR (500 MHz, C₆D₆, 298 K): 7.22 (m, 6H, *p*-C₆H₃/*p*-C₆H₅), 7.13 (d, *J* = 7.8 Hz, 4H, *m*-C₆H₃), 7.08–7.04 (m, 6H, C₆H₅/C₆H₃), 6.60–6.57 (m, 6H, C₆H₅), 3.26 (sept, *J* = 6.8 Hz, 4H, CHMe₂), 3.09 (sept, *J* = 6.8 Hz, 4H, CHMe₂), 1.62 (d, *J* = 6.7 Hz, 12H, CHMe₂), 1.35 (d, *J* = 6.8 Hz, 12H, CHMe₂), 0.92 (d, *J* = 6.9 Hz, 12H, CHMe₂), 0.87 (d, *J* = 6.8 Hz, 12H, CHMe₂) ppm. ¹³C NMR (126 MHz, C₆D₆) 176.4 (CGa), 163.6 (CGaI₂), 145.8, 145.5, 143.7, 136.0, 134.6, 130.7, 130.3, 129.6, 125.2, 125.0, 124.5 (C₆H₃/C₆H₅), 29.1, 29.0 (CHMe₂), 26.1, 25.2, 23.5, 23.2 (CHMe₂) ppm.

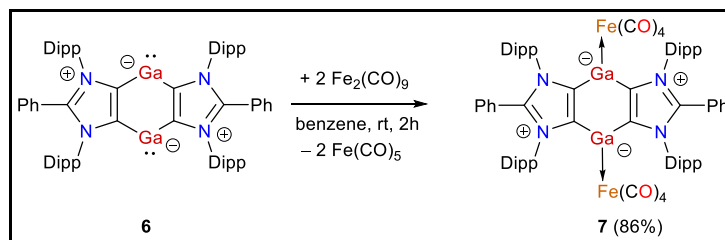
ESI-MS (m/z): 1321.3 $[5+H]^+$. **UV-Vis** [THF, 298 K: $\lambda_{\max}$ (nm) (ϵ ($M^{-1} \text{ cm}^{-1}$))]: 300 (16200), 370 (2150), 500 (600).

Synthesis of [(ADC)Ga]₂ (**6**)



To a solid mixture of **6** (1.50 g, 0.95 mmol) and KC_8 (0.71 g, 5.24 mmol) was added 40 mL benzene at rt and then stirred overnight. The resulting suspension was filtered through a plug of Celite and washed with 20 mL of benzene. The volatiles from the filtrate were removed under reduced pressure to obtain compound **6** as a red-brown solid in 92% yield (0.94 g). Single crystals suitable for X-ray diffraction studies were obtained by storing a saturated toluene solution of **6** at -30°C for two days. M.p.: 150°C (dec.). Elemental analysis (%) calculated for $\text{C}_{68}\text{H}_{78}\text{N}_4\text{Ga}_2$ (1067) **6**: C 74.31, H 7.37, N 4.85; found: C 73.61, H 6.94, N 4.53. ^1H NMR (500 MHz, C_6D_6 , 298 K): 7.23 (t, $J = 7.7$ Hz, 4H, $p\text{-C}_6\text{H}_3$), 7.18–7.16 (m, 4H, $o\text{-C}_6\text{H}_5$), 7.09 (d, $J = 7.8$ Hz, 8H, $m\text{-C}_6\text{H}_3$), 6.71–6.59 (m, 6H, $p/m\text{-C}_6\text{H}_5$), 3.10 (sept, $J = 6.8$ Hz, 8H, CHMe_2), 1.30 (d, $J = 6.7$ Hz, 24H, CHMe_2), 0.97 (d, $J = 6.9$ Hz, 24H, CHMe_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): 173.6 (CGa), 145.5 ($p\text{-C}_6\text{H}_3$), 142.6 (NCN), 137.0, 129.6, 129.5, 128.7, 128.0, 126.4, 124.2 ($\text{C}_6\text{H}_3/\text{C}_6\text{H}_5$), 29.1 (CHMe_2), 25.2, 23.3 (CHMe_2) ppm. **ESI-MS** (m/z): 1067.4 $[6+H]^+$. **UV-Vis** [C_6H_6 , 298 K: $\lambda_{\max}$ (nm) (ϵ ($M^{-1} \text{ cm}^{-1}$))]: 278 (3100), 312 (3720), 330 (3040), 380 (580), 560 (120).

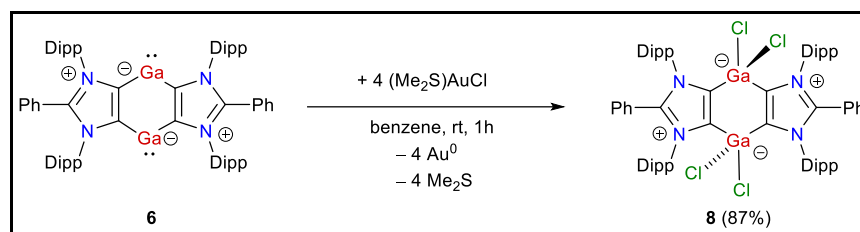
Synthesis of [(ADC)Ga{Fe(CO)₄}]₂ (**7**)



To a mixture of **6** (20 mg, 0.019 mmol) and $\text{Fe}_2(\text{CO})_9$ (13.9 mg, 0.038 mmol) was added 1 mL benzene and stirred for 2h at rt. The suspension was filtered and the volatiles from the filtrate were removed to afford **7** as an orange solid in 86% yield (23.0 mg). Single crystals suitable for X-ray diffraction studies were obtained by a slow diffusion of n -hexane into a saturated benzene solution of **7**. Elemental analysis (%) calculated for $\text{C}_{68}\text{H}_{78}\text{N}_4\text{Ga}_2$ (1403) **7-Fe**: C 63.37, H 5.61, N 3.99; found: C 62.34, H 5.43, N 3.81. ^1H

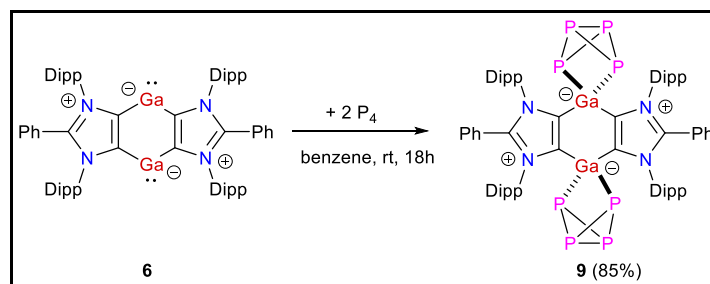
NMR (500 MHz, C₆D₆, 298 K): 7.27 (t, $J = 7.8$ Hz, 4H, p -C₆H₃), 7.07 (d, $J = 7.8$ Hz, 8H, m -C₆H₃), 6.58–6.52 (m, 6H, m/p -C₆H₅), 6.49 (t, $J = 7.7$ Hz, 4H, o -C₆H₅), 2.88–2.75 (br, 8H, CHMe₂), 1.54 (br, 24H, CHMe₂), 0.70 (br, 24H, CHMe₂) ppm. **¹³C{¹H} NMR** (126 MHz, C₆D₆, 298 K): 216.6 (CO), 148.6, 146.0, 132.9, 132.0, 130.6, 130.0, 128.6, 126.0, 124.6 (C₆H₃/C₆H₅), 29.1 (CHMe₂), 26.1, 23.5 (CHMe₂) ppm. **ESI-MS** (m/z): 1409.3 [7-Fe+Li]⁺.

Synthesis of [(ADC)GaCl₂]₂ (**8**)



To a mixture of **6** (20 mg, 0.019 mmol) and (Me₂S)AuCl (23 mg, 0.076 mmol) was added 1 mL benzene and then stirred overnight at rt. The suspension was filtered, and the volatiles were removed from the filtrate under reduced pressure to obtain compound **8** as an off-white solid in 87% (20 mg) yield. Single crystals suitable for X-ray diffraction were obtained by a slow diffusion of *n*-hexane into a saturated benzene solution of **8**. Elemental analysis (%) calculated for C₆₆H₇₈N₄Cl₄Ga₂ (1209) **8**: C 65.59, H 6.51, N 4.64; found: C 65.67, H 6.40, N 4.55. **¹H NMR** (500 MHz, C₆D₆, 298 K): 7.23–7.18 (m, 4H, p -C₆H₃), 7.10 (d, $J = 7.8$ Hz, 8H, m -C₆H₃), 6.98–6.95 (m, 4H, o -C₆H₅), 6.58–6.54 (m, 2H, p -C₆H₅), 6.52–6.48 (m, 4H, m -C₆H₅), 3.17 (sept, $J = 6.7$ Hz, 8H, CHMe₂), 1.58 (d, $J = 6.6$ Hz, 24H, CHMe₂), 0.81 (d, $J = 6.9$ Hz, 24H, CHMe₂) ppm. **¹³C NMR** (126 MHz, C₆D₆) 153.5 (CGa), 145.7, 134.0, 131.0, 130.3, 129.6, 125.1, 124.4 (C₆H₃/C₆H₅), 29.2 (CHMe₂), 25.2, 23.5 (CHMe₂) ppm. **ESI-MS** (m/z): 1315.3 [10-Cl]⁺.

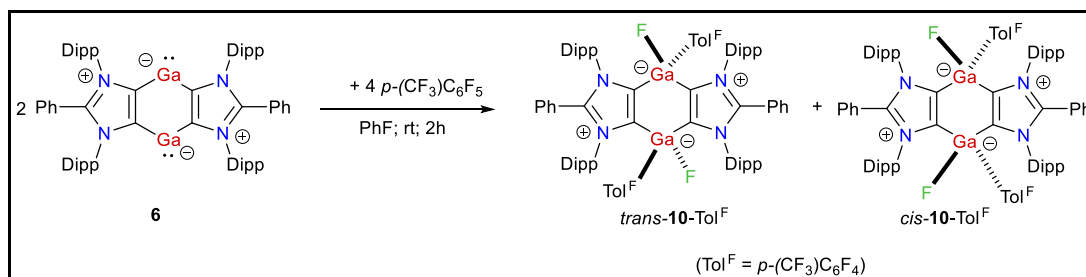
Synthesis of [(ADC)Ga(P₄)]₂ (**9**)



A mixture of **6** (0.10 g, 0.094 mmol) and P₄ (30 mg, 0.24 mmol) was suspended in 5 mL benzene and stirred overnight. The resulting suspension was filtered and the volatiles from the filtrate were removed under vacuum to give **9** as an orange-brown solid in 85% yield (105 mg). Elemental analysis (%) calculated for C₆₈H₇₈N₄Ga₂P₈ (1315) **9**: C 60.30, H 5.98, N 4.26; found: C 59.22, H 5.63, N 4.01. **¹H**

NMR (500 MHz, C₆D₆, 298 K): 7.50–7.40 (m, 12H, C₆H₃), 6.91–6.86 (m, 4H, *o*-C₆H₅), 6.67–6.54 (m, 6H, *m/p*-C₆H₅), 3.23 (sept, *J* = 6.8 Hz, 8H, CHMe₂), 1.70 (d, *J* = 6.7 Hz, 24H, CHMe₂), 0.67 (d, *J* = 6.8 Hz, 24H, CHMe₂) ppm. **¹³C{¹H} NMR** (126 MHz, C₆D₆, 298 K): 157.8 (CGa), 145.1 (NCN), 145.1 (*i*-C₆H₃), 136.0, 131.8, 130.1, 130.1, 130.0, 128.6, 127.3, 125.5 (C₆H₃/C₆H₅), 29.8 (CHMe₂), 24.8, 23.6 (CHMe₂) ppm. **³¹P NMR** (202 MHz, C₆D₆, 298 K) 152.3 (t, *J* = 157 Hz), –298.7 (t, *J* = 157 Hz) ppm. **ESI-MS** (*m/z*.): 1315.3 [8+H]⁺.

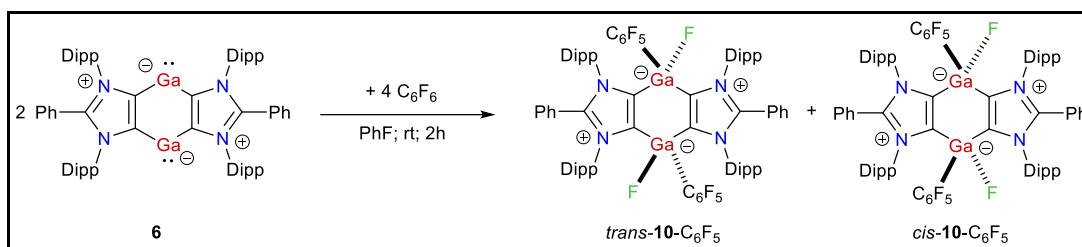
Synthesis of [(ADC)GaF(Tol^F)]₂ (*cis*-/*trans*-10-Tol^F)



To a 5 mL fluorobenzene solution of **6** (0.20 g, 0.187 mmol) was added *p*-(CF₃)C₆F₅ (60 μL, 0.412 mmol) at rt. The reaction mixture was stirred 2h and the volatiles were removed under reduced pressure to obtain a beige solid. NMR analyses indicated complete consumption of **6** and quantitative formation of *cis*-/*trans*-10-Tol^F as a mixture (~1:1 based on ¹H NMR). The residue containing a mixture of *cis*-/*trans*-10-Tol^F was washed with 25 mL *n*-hexane and dried under reduced pressure to obtain a pure sample of *cis*-10-Tol^F as an off-white solid. Elemental analysis (%) calculated for C₈₀H₇₈N₄F₁₆Ga₂ (1539) *cis*-10-Tol^F: C 62.44, H 5.11, N 3.64; found: C 62.67, H 5.20, N 3.55. **¹H NMR** (500 MHz, C₆D₆, 298 K): 7.14 (d, *J* = 4.8 Hz, 8H, *m*-C₆H₃), 6.81 (t, *J* = 4.7 Hz, 4H, *p*-C₆H₃), 6.73 (d, *J* = 8.1 Hz, 4H, *o*-C₆H₅), 6.54 (t, *J* = 7.4 Hz, 2H, *p*-C₆H₅), 6.45 (t, *J* = 8.0 Hz, 4H, *m*-C₆H₅), 3.00 (sept, *J* = 6.7 Hz, 4H, CHMe₂), 2.89 (sept, *J* = 6.7 Hz, 4H, CHMe₂), 1.66 (d, *J* = 6.7 Hz, 12H, CHMe₂), 0.74 (d, *J* = 6.8 Hz, 12H, CHMe₂), 0.52 (pt, *J* = 6.8 Hz, 24H, CHMe₂) ppm. **¹³C{¹H} NMR** (126 MHz, C₆D₆, 298 K): 146.4, 145.9, 143.6, 134.4, 131.2, 130.3, 129.5, 128.3, 128.1, 125.6, 124.6, 124.4 (C₆H₃/C₆H₅/C₇F₇), 29.2, 28.8 (CHMe₂), 24.3, 24.2, 23.7, 23.3 (CHMe₂), 21.8 (CF₃) ppm. **¹⁹F{¹H} NMR** (471 MHz, C₆D₆, 298 K): –56.2 (t, *J* = 21.3 Hz, CF₃), –120.4, –143.3 (C₆F₄), –205.6 (GaF) ppm. **ESI-MS** (*m/z*.): 1561.4 [10-Tol^F+Na]⁺.

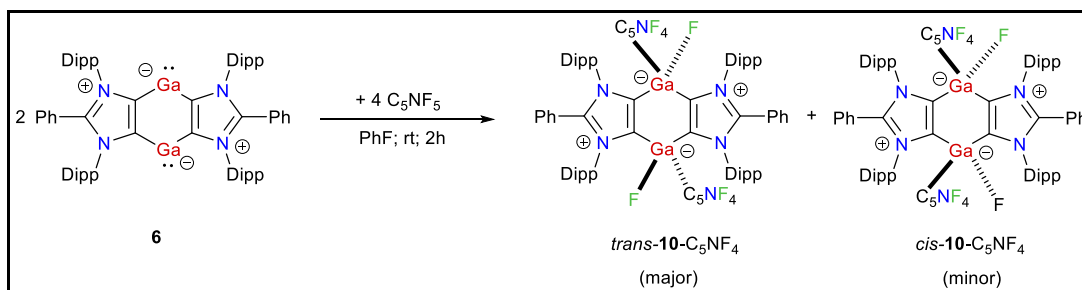
Single crystals suitable of *trans*-10-Tol^F for X-ray diffraction were obtained by a slow diffusion of *n*-hexane into a dichloromethane solution of *cis*-/*trans*-10-Tol^F.

Synthesis of [(ADC)GaF(C₆F₅)]₂ (*cis*-/*trans*-10-C₆F₅)



To a 5 mL fluorobenzene solution of **6** (200 mg, 0.187 mmol) was added C₆F₆ (46 μ L, 0.399 mmol) at rt. The reaction mixture was stirred 2h and then the volatiles were removed under reduced pressure to give a beige solid. NMR analyses showed complete consumption of **6** and quantitative formation of a mixture of *cis*-/*trans*-10-C₆F₅ isomers (in ~4:1 ratio based on ¹H NMR). Compound *trans*-10-C₆F₅ was obtained in a pure form by recrystallization on storing a toluene solution of a mixture of *cis*- and *trans*-10-C₆F₅ at -24 °C. Single crystals suitable for X-ray diffraction were obtained by a slow diffusion of *n*-hexane into a saturated THF solution of *cis*-10-C₆F₅. NMR details are given for *cis*-10-C₆F₅. ¹H NMR (500 MHz, C₆D₆, 298 K): 7.37 (d, *J* = 7.78 Hz, 4H, *m*-C₆H₃), 7.16 (m, 4H, *p*-C₆H₃), 6.80 (d, *J* = 8.07 Hz, 4H, *m*-C₆H₃), 6.71 (d, *J* = 8.07 Hz, 4H, *o*-C₆H₅), 6.49 (t, *J* = 7.17 Hz, 2H, *p*-C₆H₅), 6.41 (t, *J* = 7.65 Hz, 4H, *m*-C₆H₅), 3.85 (m, 4H, CHMe₂), 2.29 (m, 4H, CHMe₂), 1.88 (d, *J* = 6.8 Hz, 12H, CHMe₂), 1.17 (d, *J* = 6.8 Hz, 12H, CHMe₂), 0.32 (d, *J* = 6.8 Hz, 12H, CHMe₂), 0.06 (d, *J* = 6.8 Hz, 12H, CHMe₂) ppm. ¹³C{¹H} NMR (126 MHz, C₆D₆, 298 K): 146.1, 142.7, 133.7, 130.8, 130.2, 129.4, 128.0, 125.3, 124.54 (C₆H₃, C₆H₅, C₆F₅), 29.3, 28.9, 27.9 (CHMe₂), 25.6, 23.3, 22.5, 22.3 (CHMe₂) ppm. ¹⁹F{¹H} NMR (471 MHz, C₆D₆, 298 K): -139.1, -154.1, -158.2, -162.2 (C₆F₅), -207.79 (GaF) ppm.

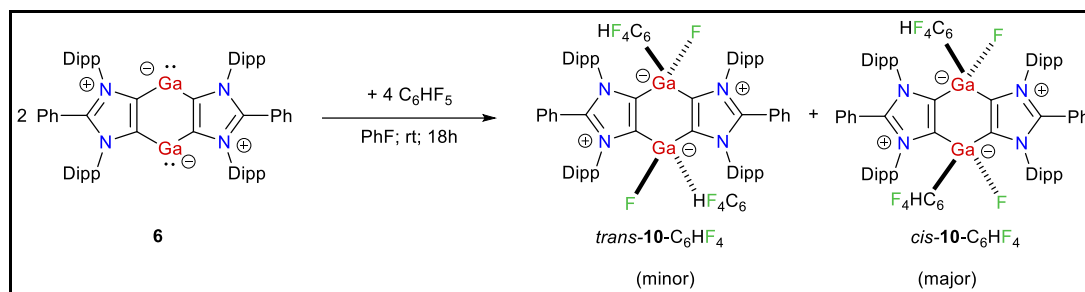
Synthesis of [(ADC)GaF(C₅NF₄)]₂ (*cis*-/*trans*-10-C₅NF₄)



To a 5 mL fluorobenzene solution of **6** (200 mg, 0.187 mmol) was added C₅NF₅ (43 μ L, 0.395 mmol) at rt. The reaction mixture was stirred for 2h and then the volatiles were removed under reduced pressure to afford a beige solid. NMR analyses showed complete consumption of **6** and quantitative formation of a

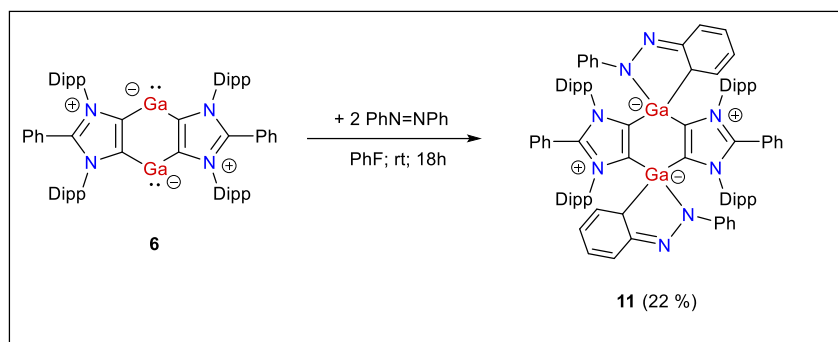
mixture of *cis*-/*trans*-**10**-C₅NF₄ isomers (in ~1:1 ratio based on ¹H NMR). Compounds *trans*-**10**-C₅NF₄ was obtained in a pure form by recrystallization on storing a toluene solution of a mixture of *cis*- and *trans*-**10**-C₅NF₄ at -24 °C. NMR data are given for *trans*-**10**-C₅NF₄. ¹H NMR (500 MHz, CDCl₃, 298 K): 7.40 (m, 8H, *m*-C₆H₃, *p*-C₆H₃), 7.18 (t, *J* = 7.5 Hz, 2H, *p*-C₆H₅), 6.91 (m, 8H, *m*-C₆H₃, *m*-C₆H₅), 6.64 (d, *J* = 7.5 Hz, 4H, *o*-C₆H₅), 3.38 (m, 4H, CHMe₂), 2.06 (m, 4H, CHMe₂), 1.57 (d, *J* = 6.8 Hz, 12H, CHMe₂), 1.04 (d, *J* = 6.8 Hz, 12H CHMe₂), 0.22 (d, *J* = 6.8 Hz, CHMe₂), -0.08 (d, *J* = 6.8 Hz, CHMe₂) ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃, 298 K): 146.0, 145.7, 142.7, 137.9, 134.0, 131.1, 130.5, 129.5, 129.0, 128.2, 128.1, 125.5, 125.3, 124.7, 123.8 (C₆H₃, C₆H₅, C₅NF₄), 29.0, 27.9 (CHMe₂), 23.4, 22.6, 22.4, 21.5 (CHMe₂) ppm. ¹⁹F{¹H} NMR (471 MHz, CDCl₃, 298 K): -96.6, -126.7 (C₅NF₄), -211.8 (GaF) ppm. Single crystals suitable for X-ray diffraction were obtained by a slow diffusion of *n*-hexane into a saturated THF solution of *trans*-**10**-C₅NF₄.

Synthesis of [(ADC)GaF(C₆HF₄)]₂ (*cis*-/*trans*-**10**-C₆HF₄)



To a 3 mL fluorobenzene solution of **6** (200 mg, 0.187 mmol) was added C₆HF₅ (44 μL, 0.399 mmol) at -30 °C. The reaction mixture was stirred for 2h and then the volatiles were removed under reduced pressure to afford a beige solid. NMR analyses showed complete consumption of **6** and quantitative formation of a mixture of *cis*-/*trans*-**10**-C₆HF₄ isomers (in ~1:1 ratio based on ¹H NMR), which could not be separated. The NMR detail is given for a sample containing a mixture of *cis*-/*trans*-**10**-C₆HF₄. ¹H NMR (500 MHz, CDCl₃, 298 K): 7.40, 7.32, 7.00, 6.91, 6.83, 6.42–6.55 (C₆H₃, C₆H₅, C₆HF₄), 3.94 (m, 4H, CHMe₂), 3.06 (m, 8H, CHMe₂), 2.35 (m, 4H, CHMe₂), 1.92 (d, *J* = 6.8 Hz, 12H, CHMe₂), 1.70 (d, *J* = 6.8 Hz, 12H, CHMe₂), 1.21 (d, *J* = 6.8 Hz, 12H, CHMe₂), 0.77 (d, *J* = 6.8 Hz, 12H, CHMe₂), 0.61 (d, *J* = 6.8 Hz, 24H, CHMe₂), 0.35 (d, *J* = 6.8 Hz, 12H, CHMe₂), 0.01 (d, *J* = 6.8 Hz, 12H, CHMe₂) ppm. ¹⁹F{¹H} NMR (471 MHz, C₆D₆, 298 K): -122.0, -124.4, -141.6 (C₆HF₄), -205.3, -209.0 (GaF) ppm.

Synthesis of [(ADC)GaN(Ph)N=C₆H₅]₂ (**11**)



To a 5 mL fluorobenzene solution of **6** (200 mg, 0.187 mmol) was added 3 mL fluorobenzene solution of PhN=NPh (72 mg, 0.394 mmol) at $-30\text{ }^{\circ}\text{C}$. The reaction mixture was stirred overnight at rt. The volatiles were removed under reduced pressure and the resulting residue was washed with 3 mL *n*-hexane and then with 3 mL toluene. The yellow insoluble solid was dried under vacuum to obtain **11** in 22% (69 mg) yield. **¹H NMR** (500 MHz, CD₂Cl₂, 298 K): 7.43, 7.38, 7.31, 7.22, 7.08, 7.01, 6.92, 6.86, 6.78, 6.69, 6.45 (C₆H₃, C₆H₅), 6.22 (m, 1H, NC₆H₅Ga), 6.03, 5.65 (m, 3H, NC₆H₅Ga), 5.49 (m, 4H, NC₆H₅Ga), 5.43 (m, 2H, NC₆H₅Ga), 3.55 (m, 2H, CHMe₂), 3.45 (m, 2H, CHMe₂), 3.27 (m, 2H, CHMe₂), 3.17 (m, 2H, CHMe₂), 1.70 (m, 3H, CHMe₂), 1.59 (m, 6H, CHMe₂), 1.46 (m, 3H, CHMe₂), 1.06 (m, 3H, CHMe₂), 0.97 (m, 6H, CHMe₂), 0.73 (m, 6H, CHMe₂), 0.56 (m, 6H, CHMe₂), 0.34 (m, 3H, CHMe₂), -0.04 (m, 3H, CHMe₂), -0.18 (m, 3H, CHMe₂), -0.25 (m, 3H, CHMe₂), -0.38 (m, 3H, CHMe₂) ppm. **¹³C{¹H} NMR** (126 MHz, CD₂Cl₂, 298 K): 135.6, 131.0, 130.1, 129.7, 128.1, 126.2, 125.2, 123.3, 120.7, 114.8, 113.9, 108.7, 108.4 (C₆H₃, C₆H₅, NC₆H₅), 24.6, 24.1, 23.5, 23.3, 23.0, 22.9, 22.7, 22.2 (CHMe₂) ppm (due to poor solubility, of **11**, the ¹³C NMR signals were assigned according to a HMQC experiment).

Plots of NMR Spectra

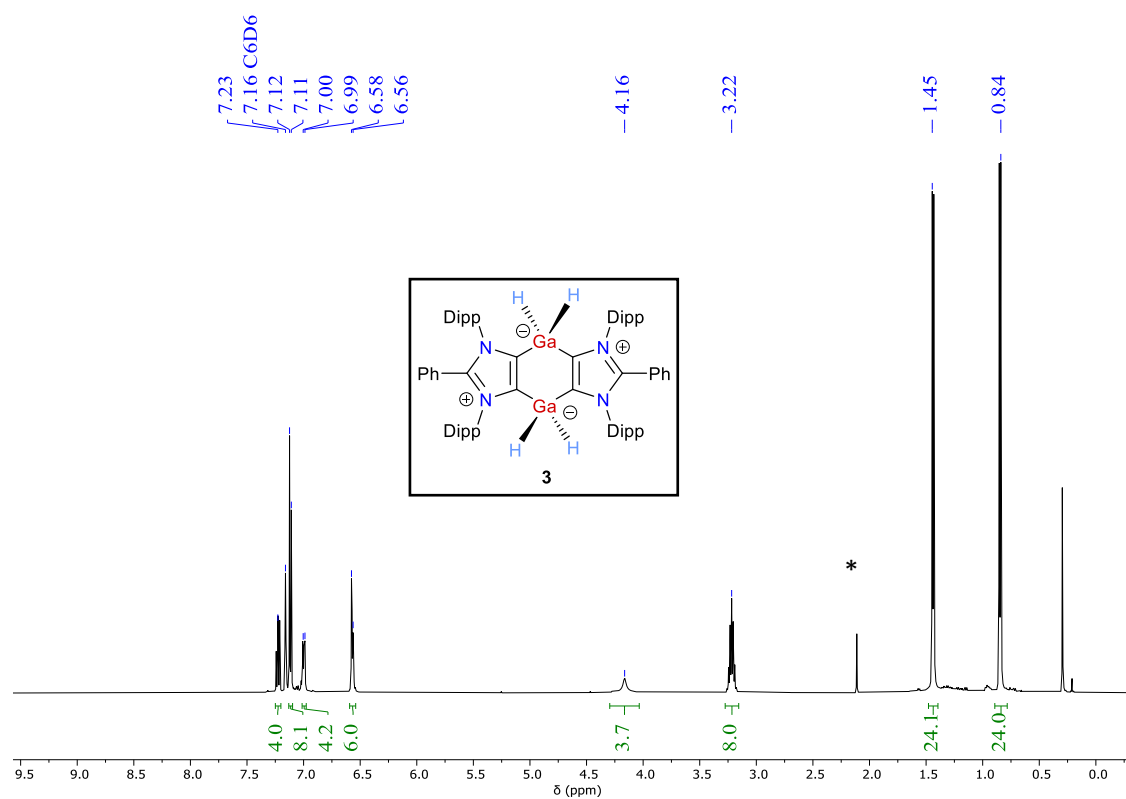


Figure S1. ¹H NMR (500 MHz, C₆D₆, 298 K) spectrum of **3** (*toluene).

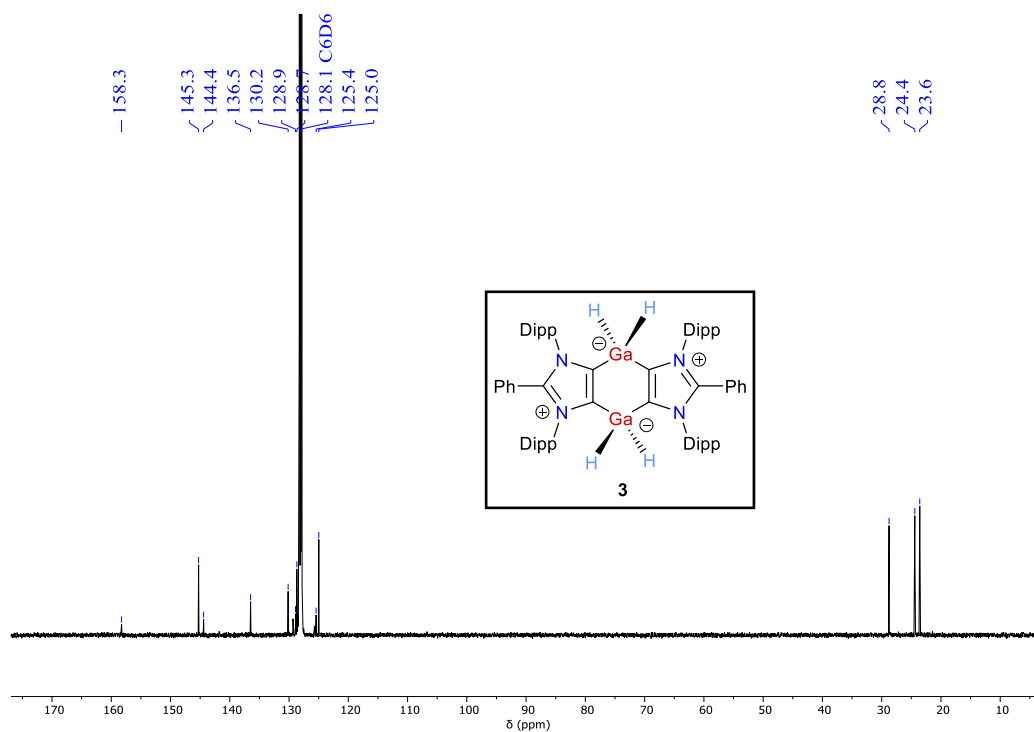


Figure S2. ¹³C{¹H} NMR (126 MHz, C₆D₆, 298 K) spectrum of **3**.

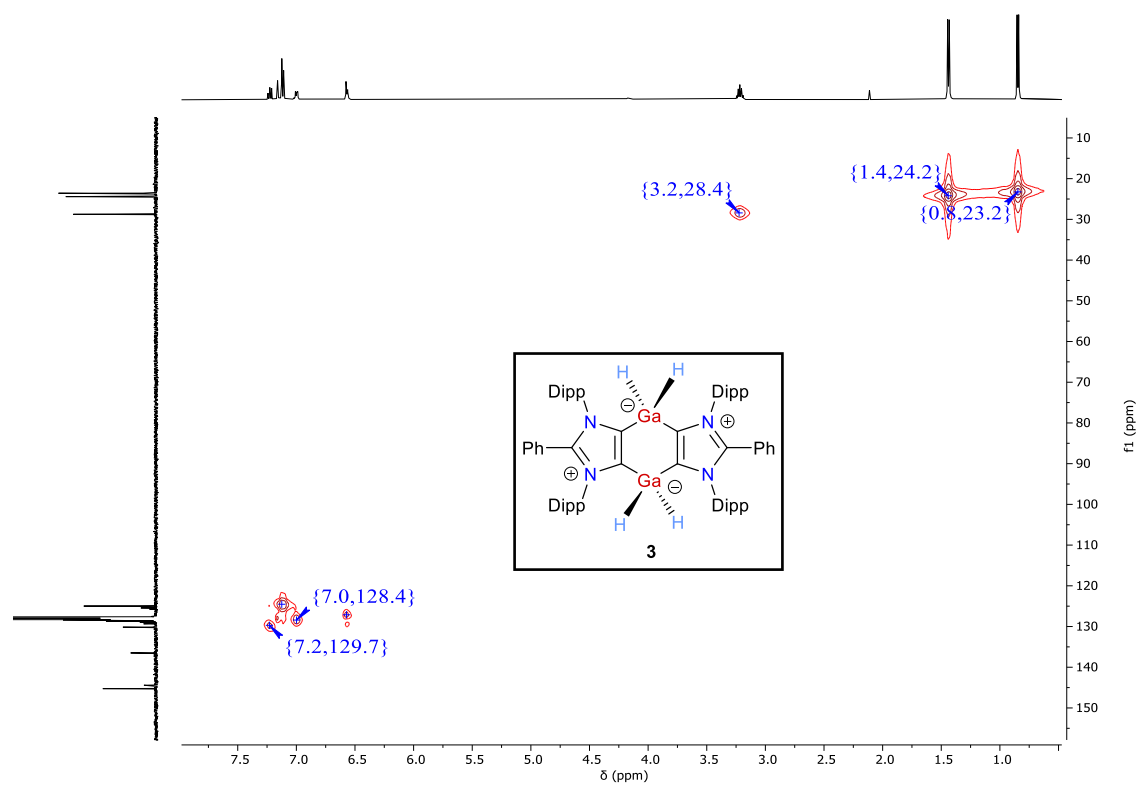


Figure S3. ^1H - $^{13}\text{C}\{^1\text{H}\}$ HMQC (500/126 MHz, C_6D_6 , 298 K) spectrum of **3**.

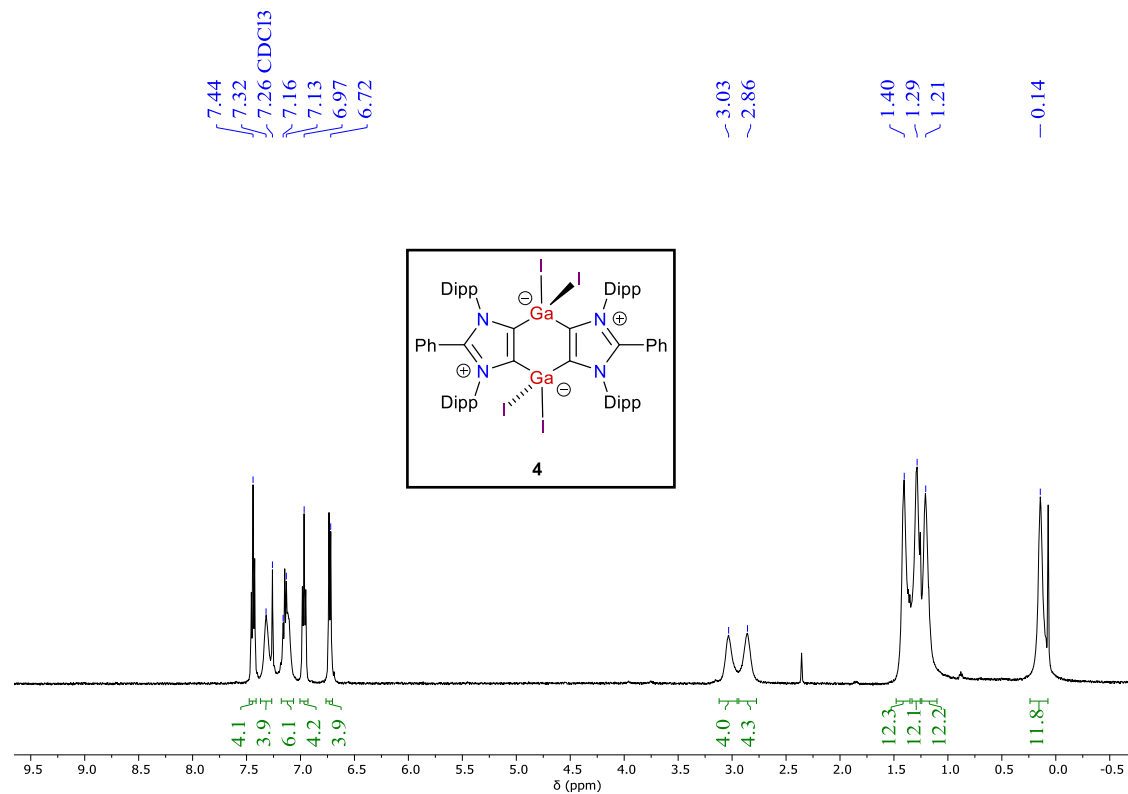


Figure S4. ^1H NMR (500 MHz, CDCl_3 , 298 K) spectrum of **4**.

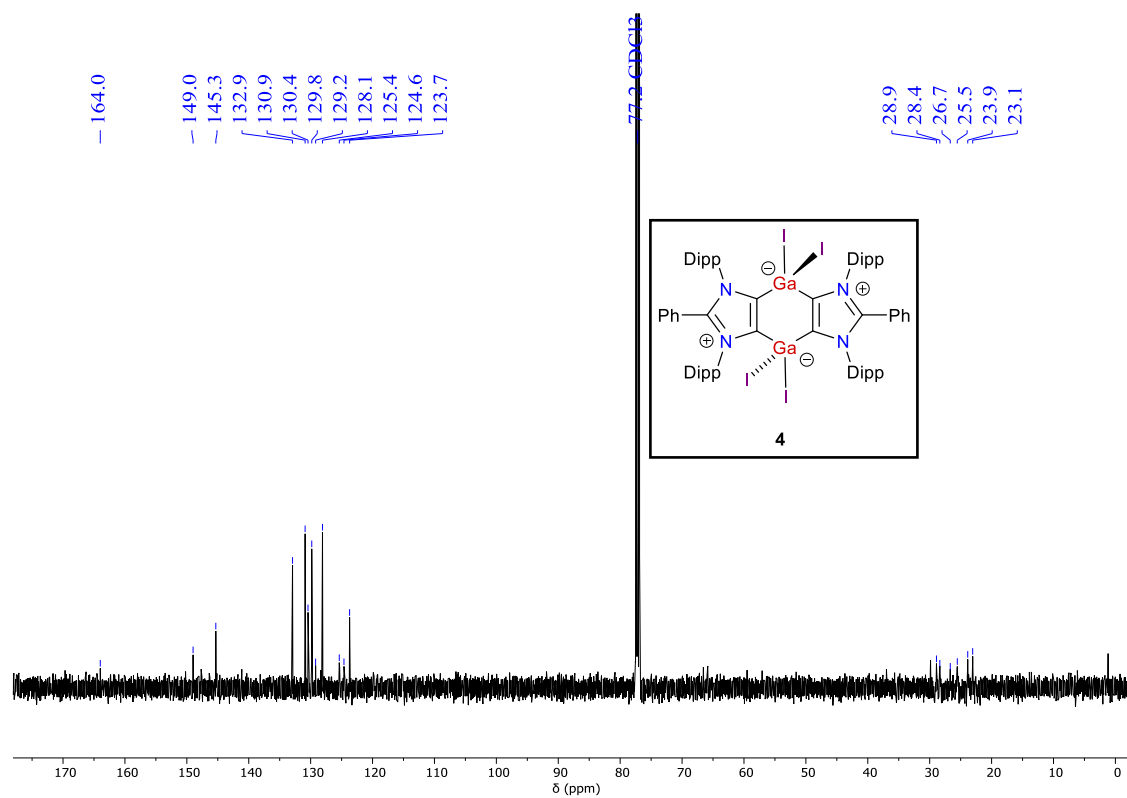


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 298 K) spectrum of **4**.

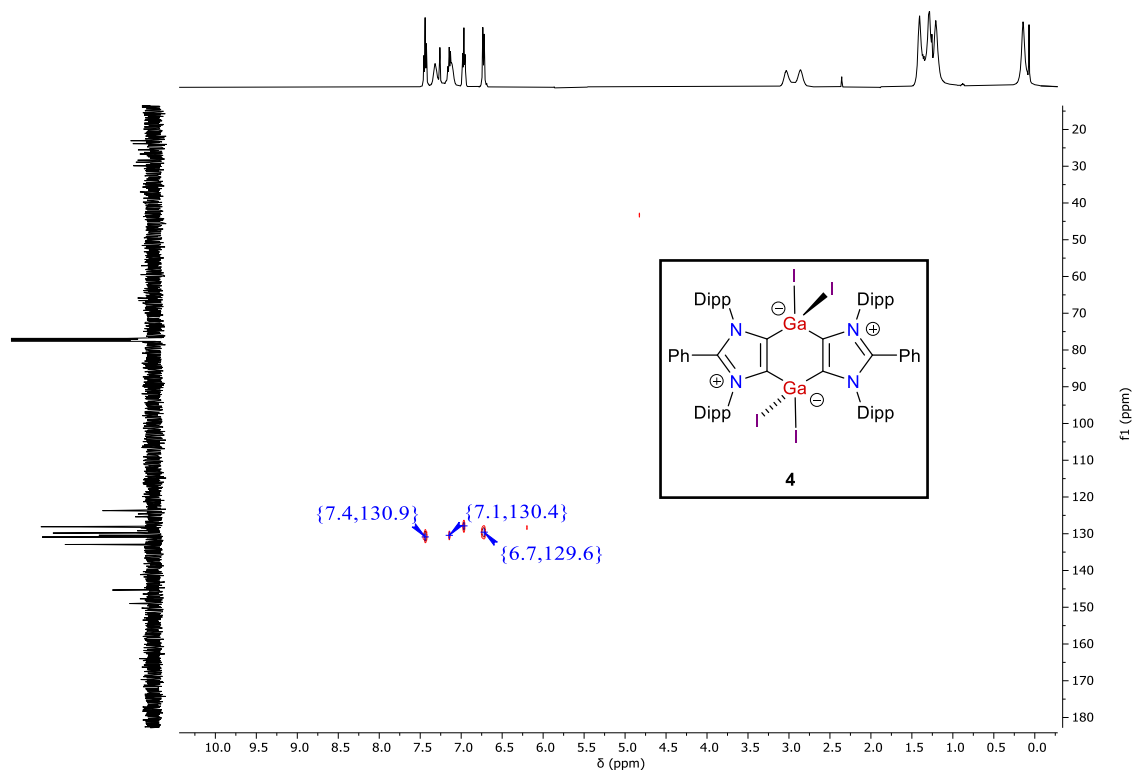


Figure S6. $^1\text{H}-^{13}\text{C}\{^1\text{H}\}$ HMQC (500/126 MHz, CDCl_3 , 298 K) spectrum of **4**.

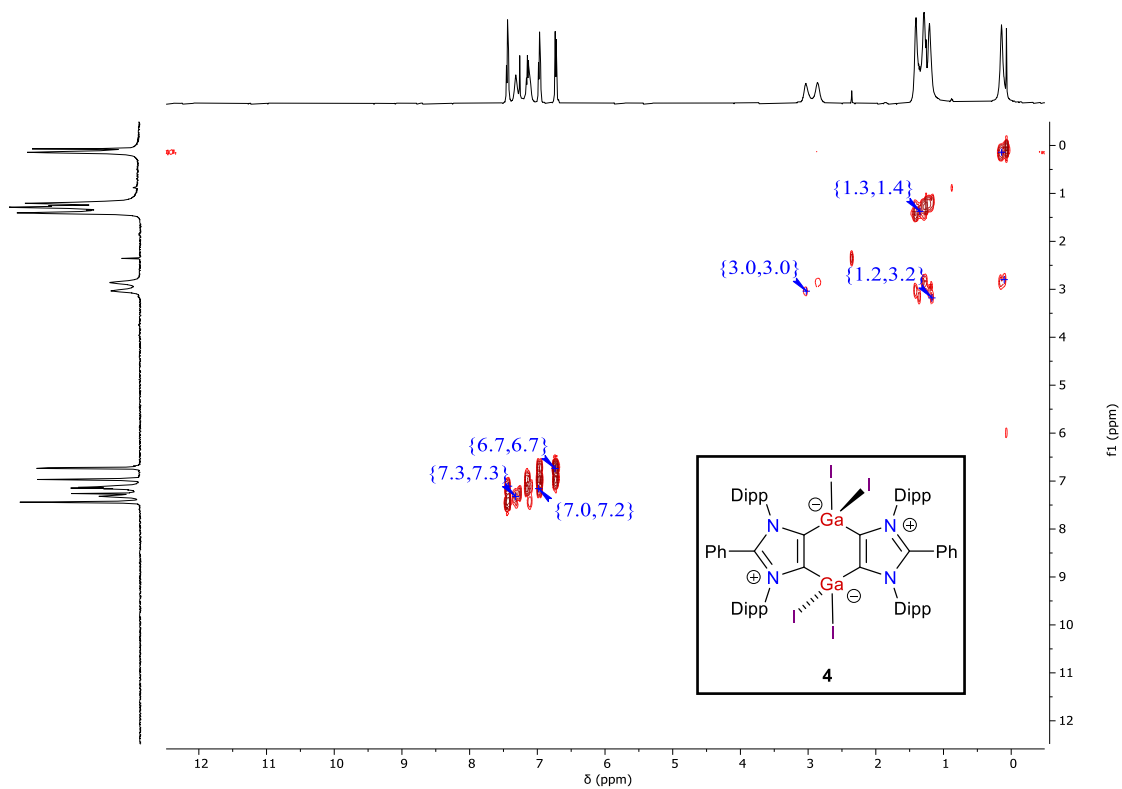


Figure S7. ^1H -COSY (500/500 MHz, CDCl_3 , 298 K) spectrum of **4**.

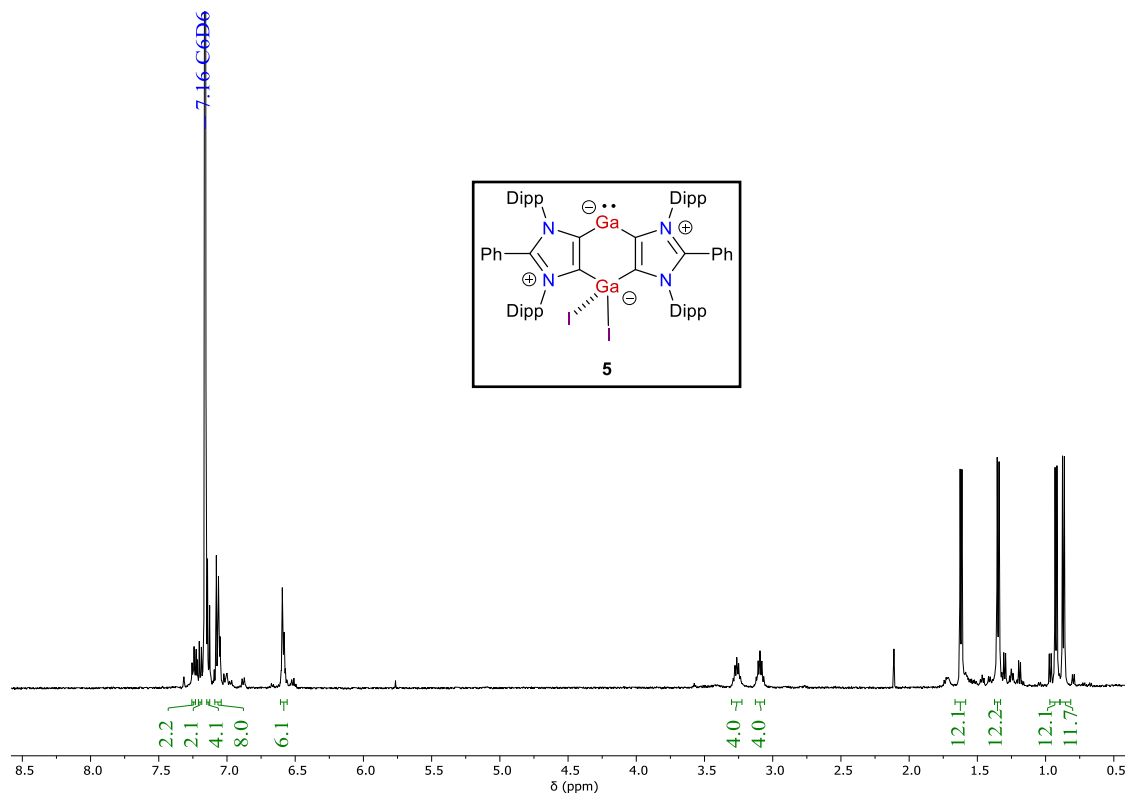


Figure S8. ^1H NMR (500 MHz, C_6D_6 , 298 K) spectrum of **5**.

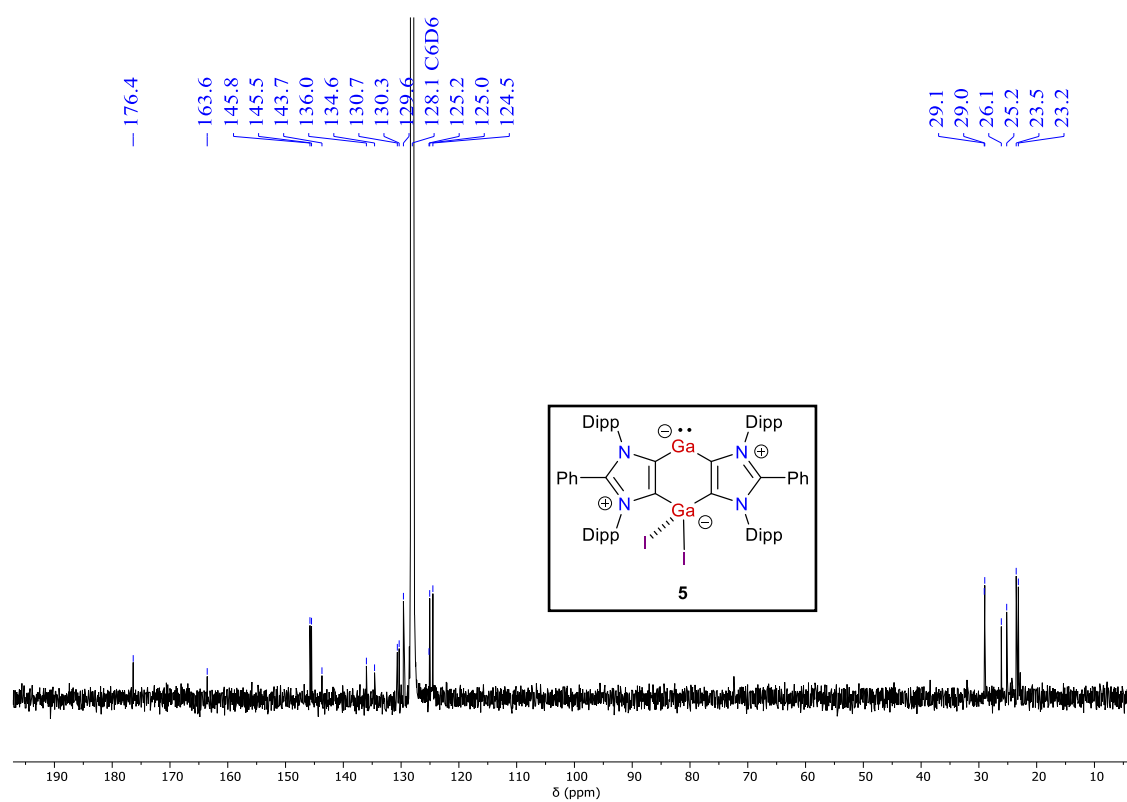


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K) spectrum of 5.

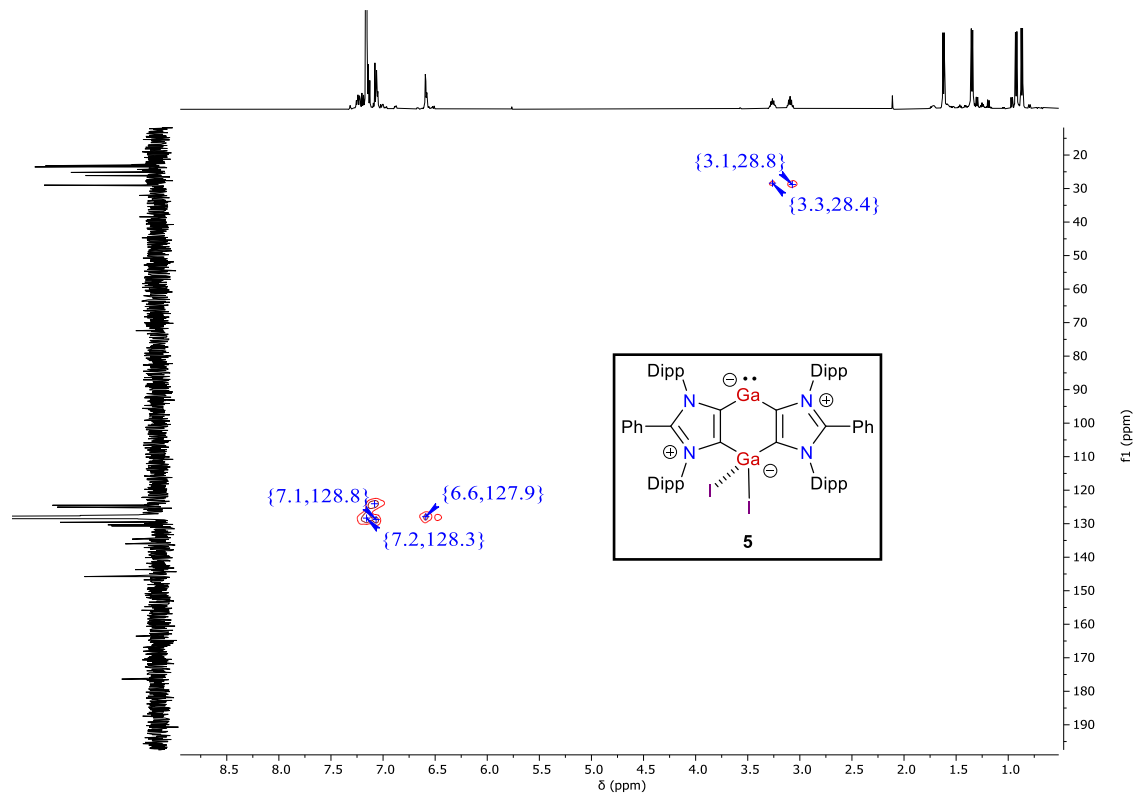


Figure S10. $^1\text{H}-^{13}\text{C}\{^1\text{H}\}$ HMQC (500/126 MHz, C_6D_6 , 298 K) spectrum of 5.

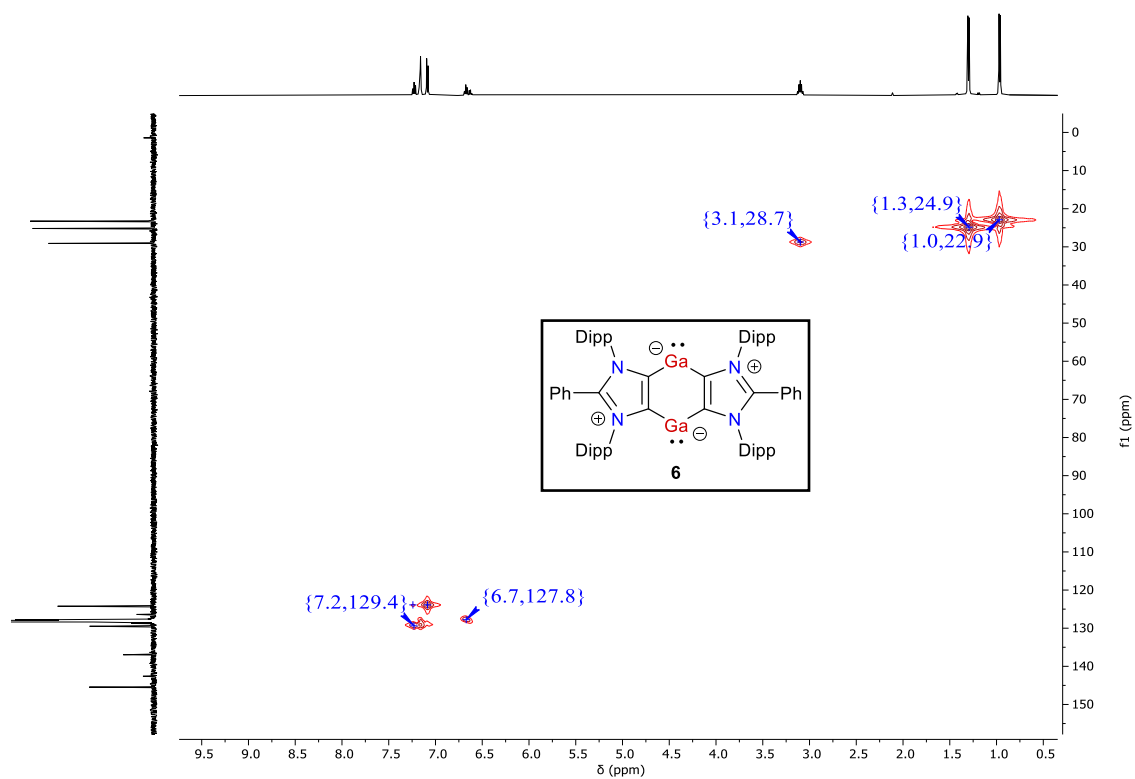


Figure S13. ^1H - $^{13}\text{C}\{^1\text{H}\}$ HMQC (500/126 MHz, C_6D_6 , 298 K) spectrum of **6**.

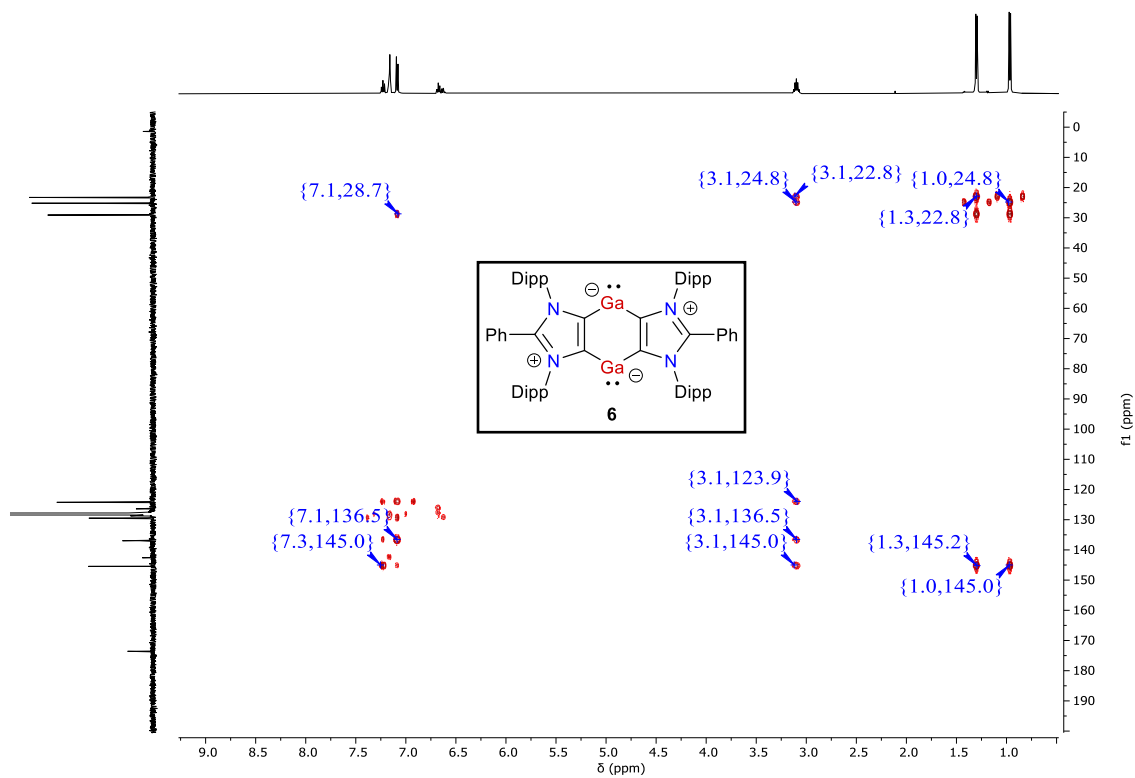


Figure S14. ^1H - $^{13}\text{C}\{^1\text{H}\}$ HMBC (500/126 MHz, C_6D_6 , 298 K) spectrum of **6**.

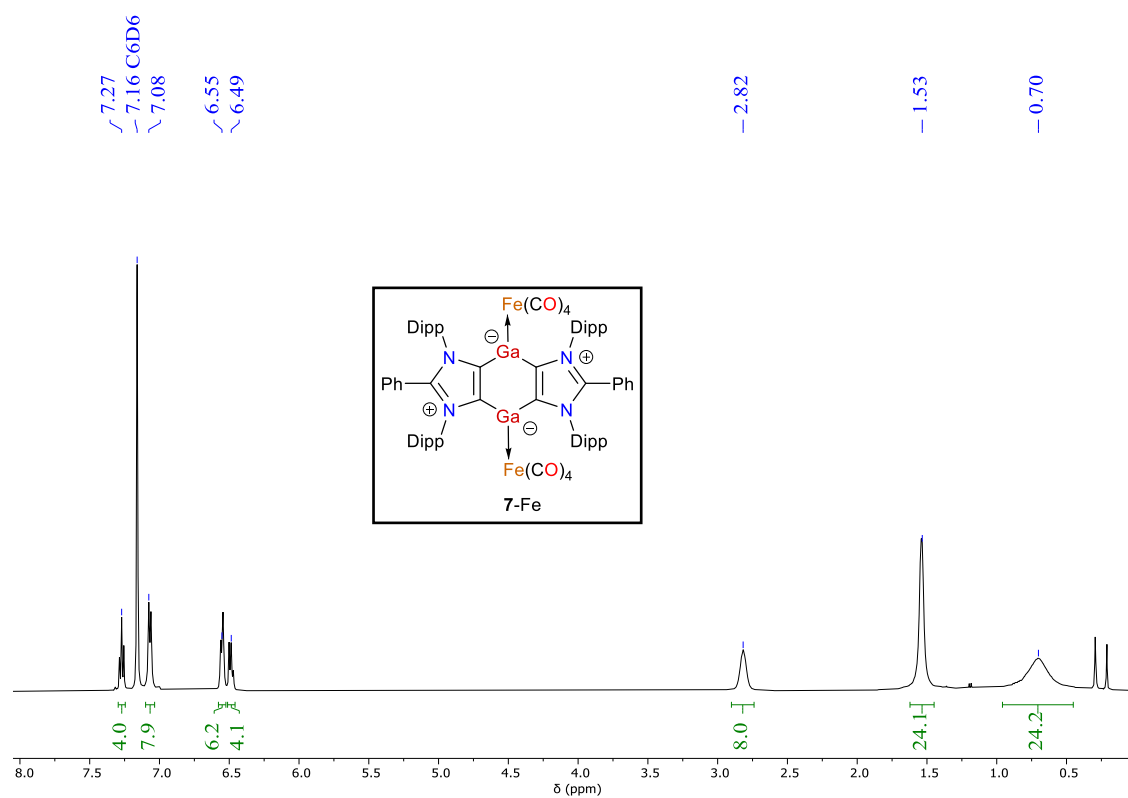


Figure S15. ¹H NMR (500 MHz, C₆D₆, 298 K) spectrum of 7.

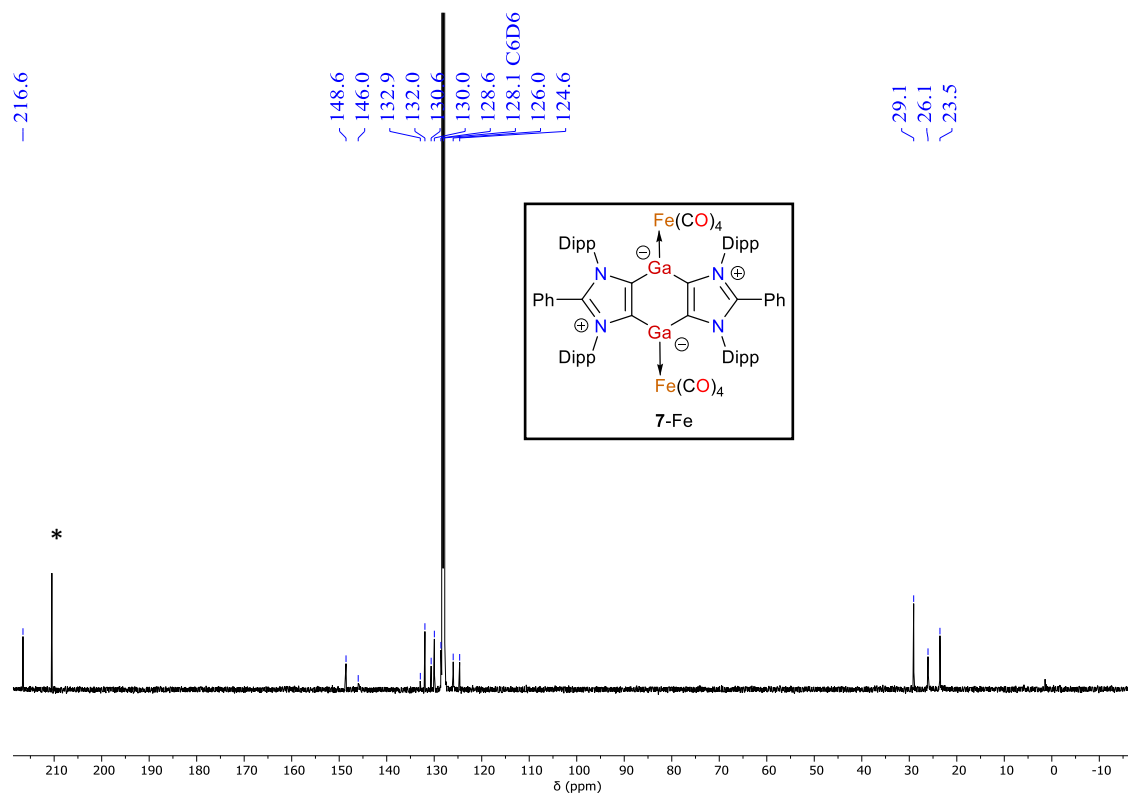


Figure S16. ¹³C{¹H} NMR (126 MHz, C₆D₆, 298 K) spectrum of 7 (*Fe(CO)₅).

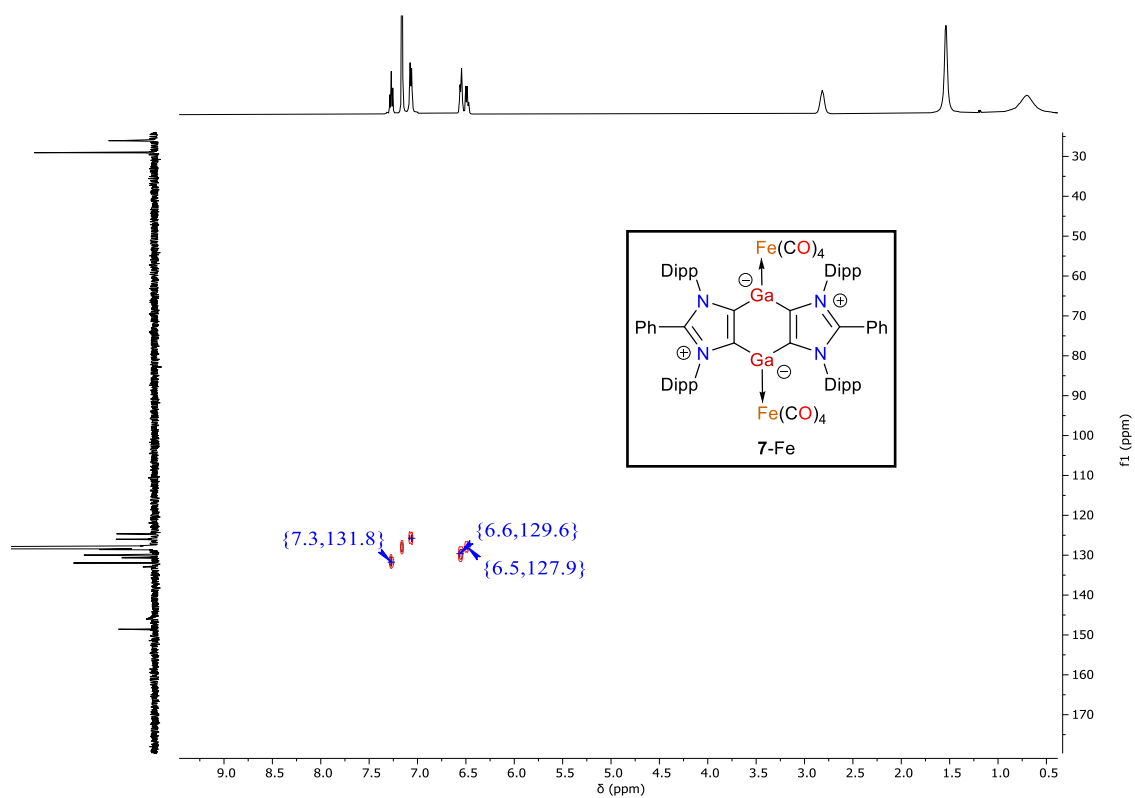


Figure S17. ^1H - $^{13}\text{C}\{^1\text{H}\}$ HMQC (500/126 MHz, C_6D_6 , 298 K) spectrum of **7**.

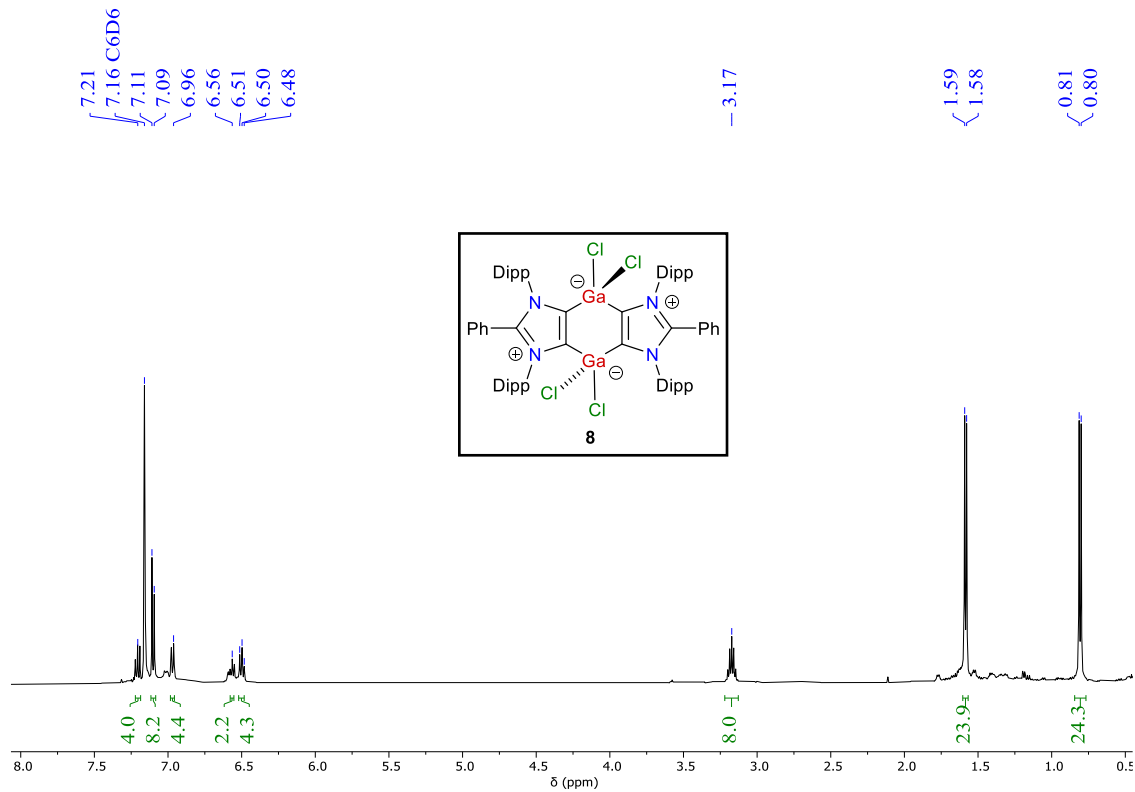


Figure S18. ^1H NMR (500 MHz, C_6D_6 , 298 K) spectrum of **8**.

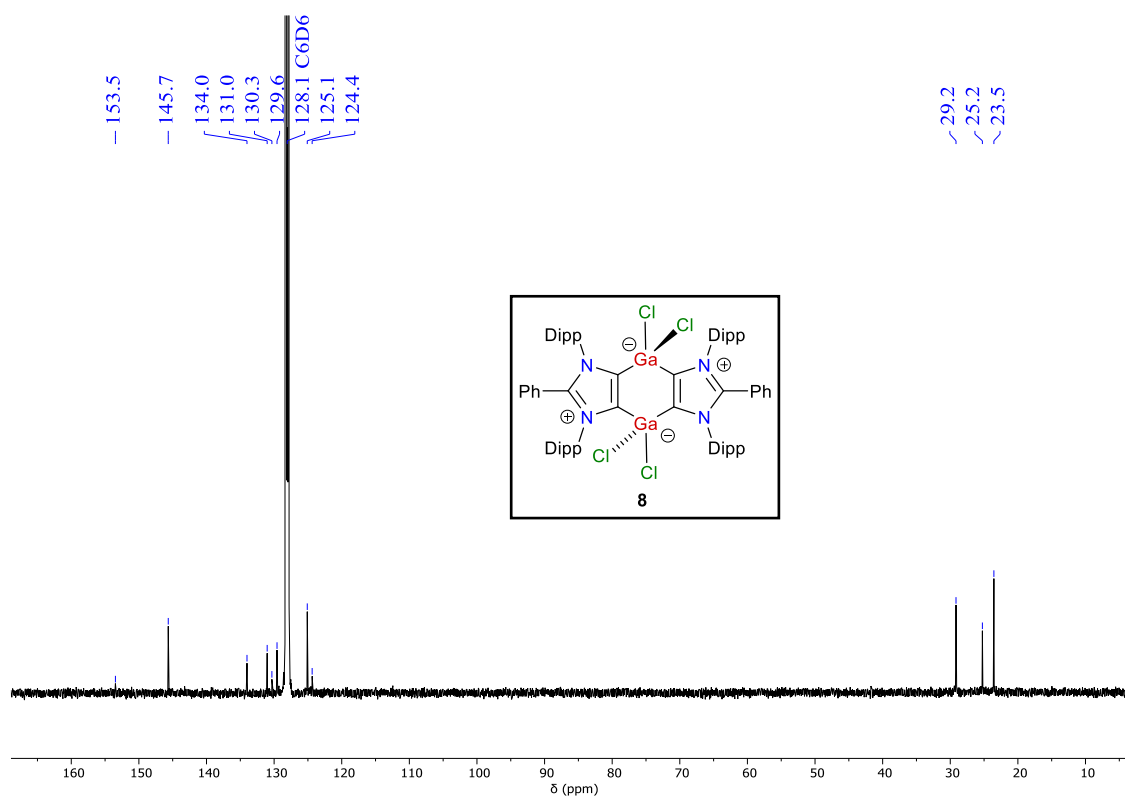


Figure S19. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K) spectrum of **8**.

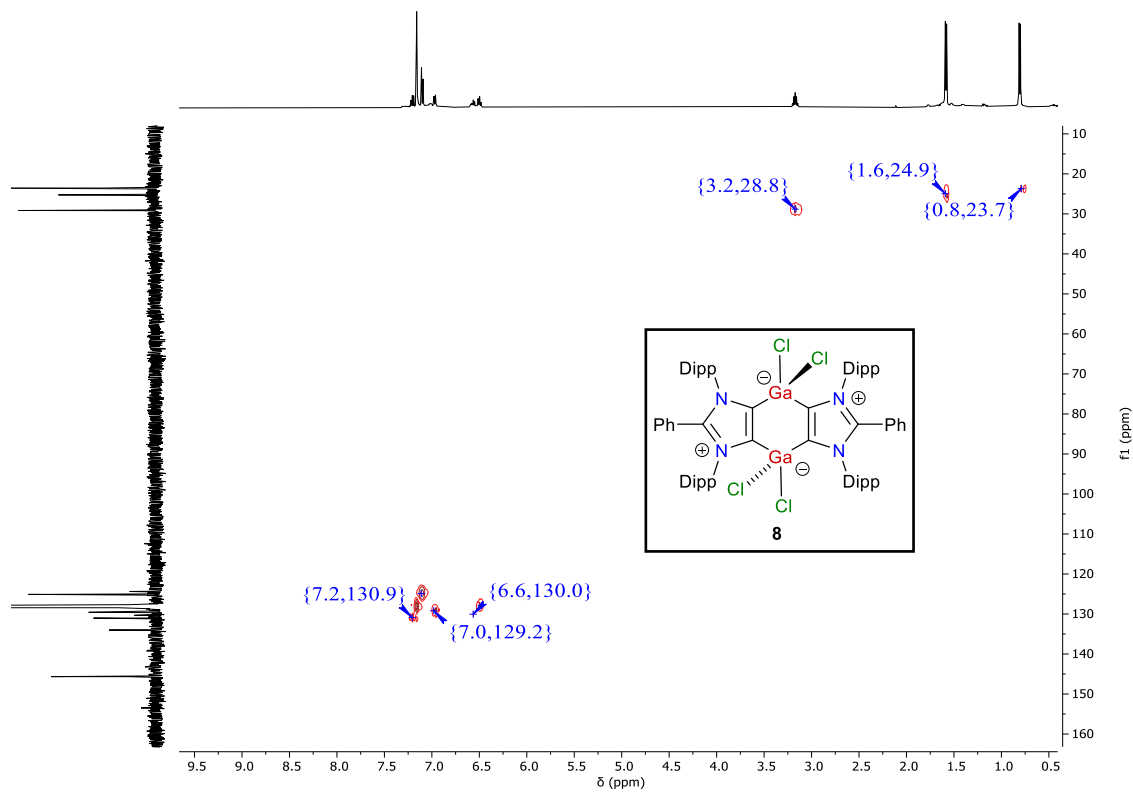


Figure S20. $^1\text{H}-^{13}\text{C}\{^1\text{H}\}$ HMQC (500/126 MHz, C_6D_6 , 298 K) spectrum of **8**.

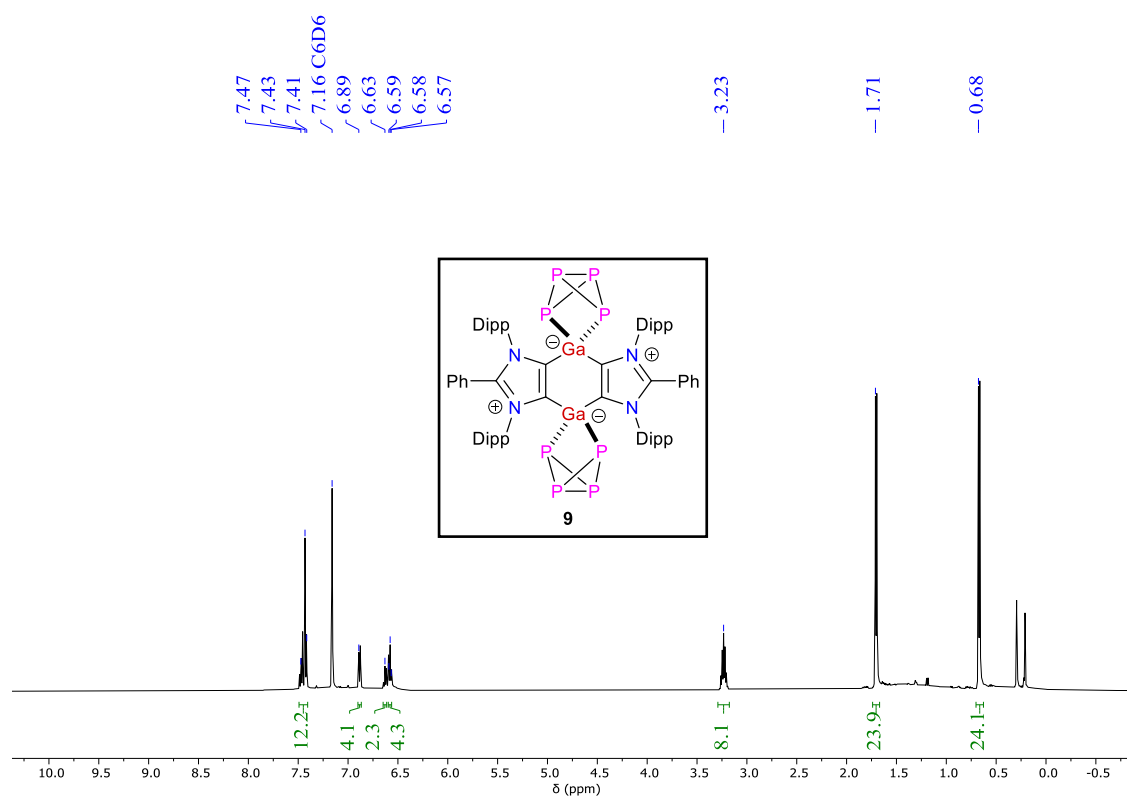


Figure S21. ¹H NMR (500 MHz, C₆D₆, 298 K) spectrum of **9**.

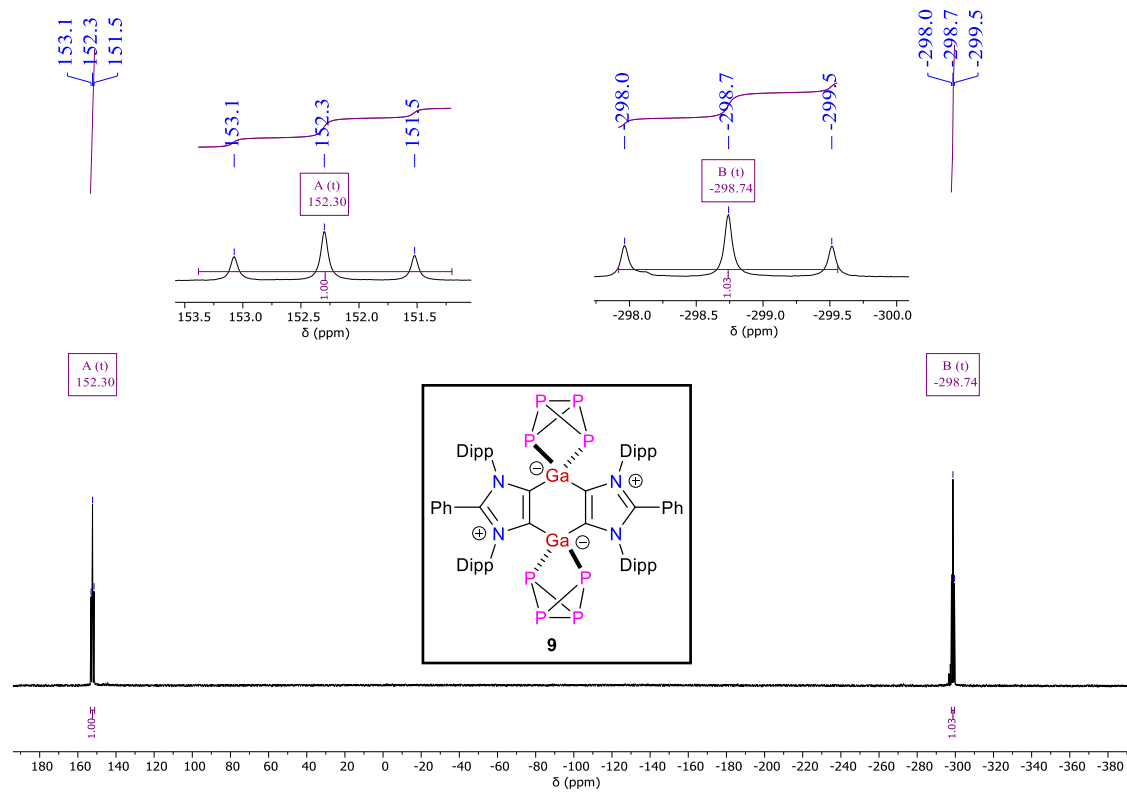


Figure S22. ¹³C NMR (500 MHz, C₆D₆, 298 K) spectrum of **9**.

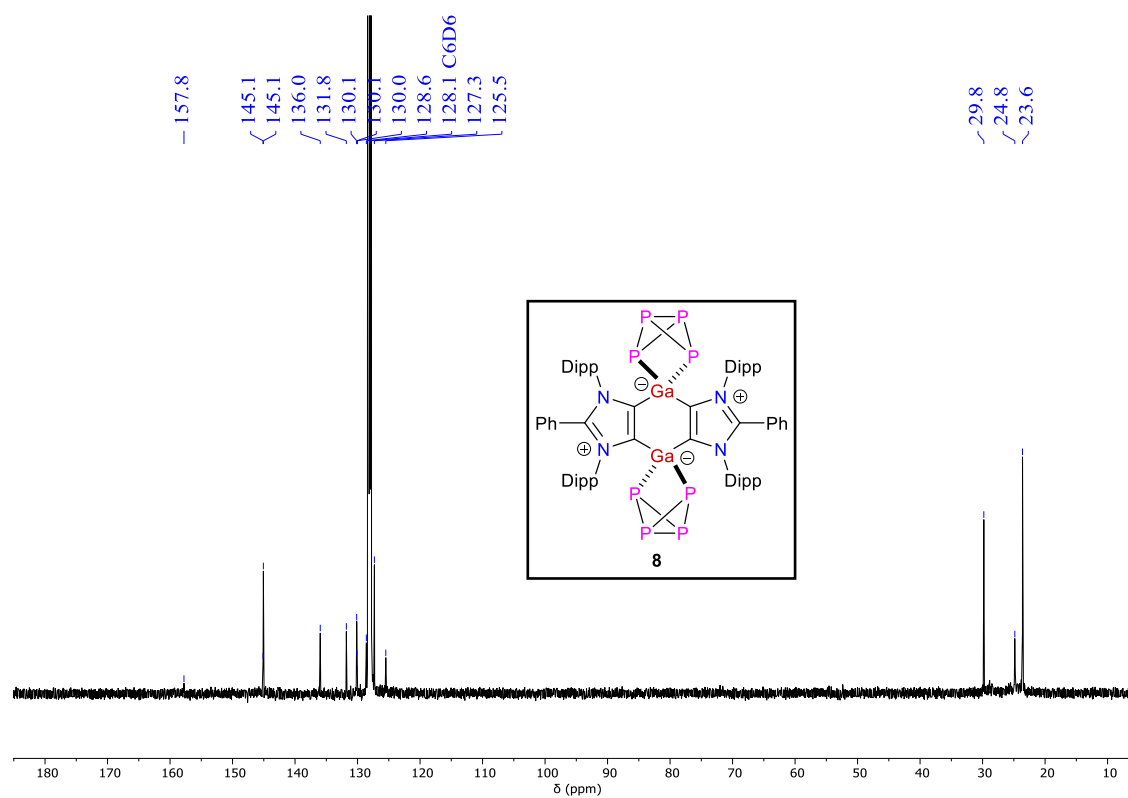


Figure S23. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K) spectrum of **9**.

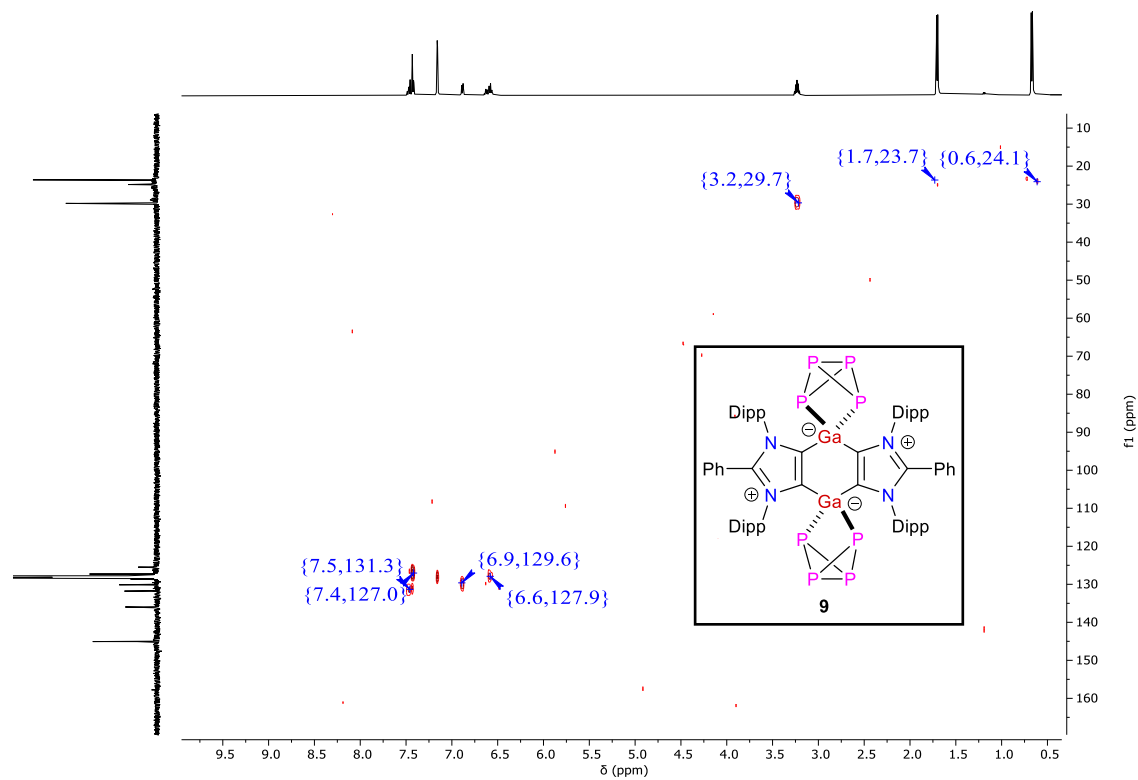


Figure S24. $^1\text{H}-^{13}\text{C}\{^1\text{H}\}$ HMQC (500/126 MHz, C_6D_6 , 298 K) spectrum of **9**.

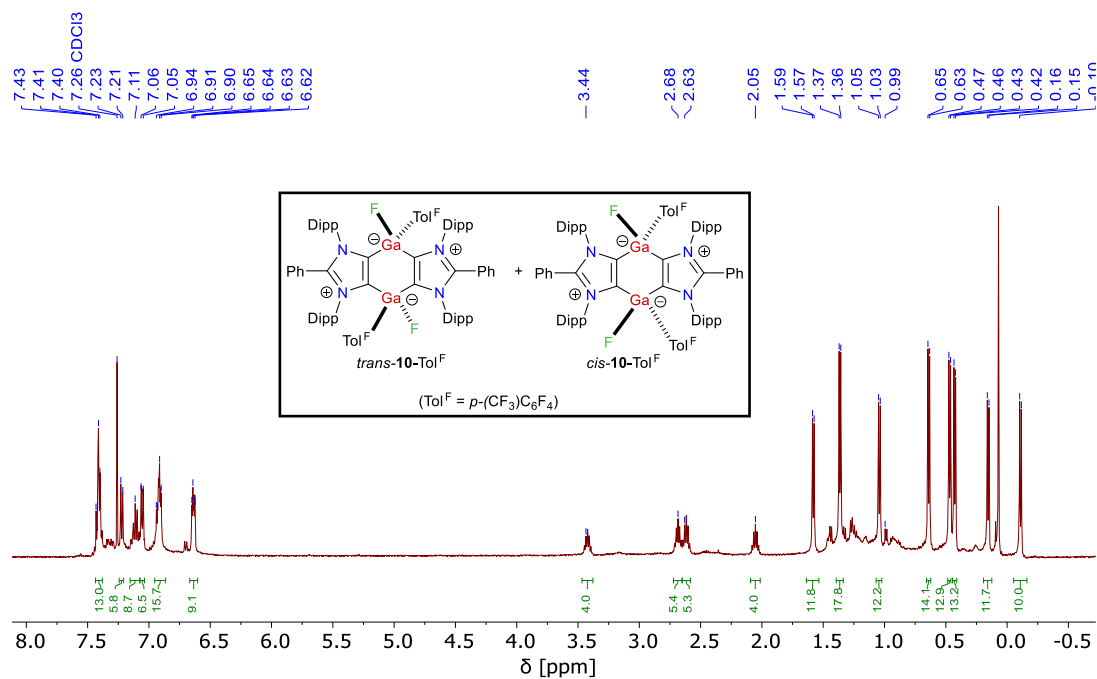


Figure S25. ¹H NMR (500 MHz, CDCl₃, 298 K) spectrum of a sample containing a mixture of *cis*-/*trans*-10-Tol^F.

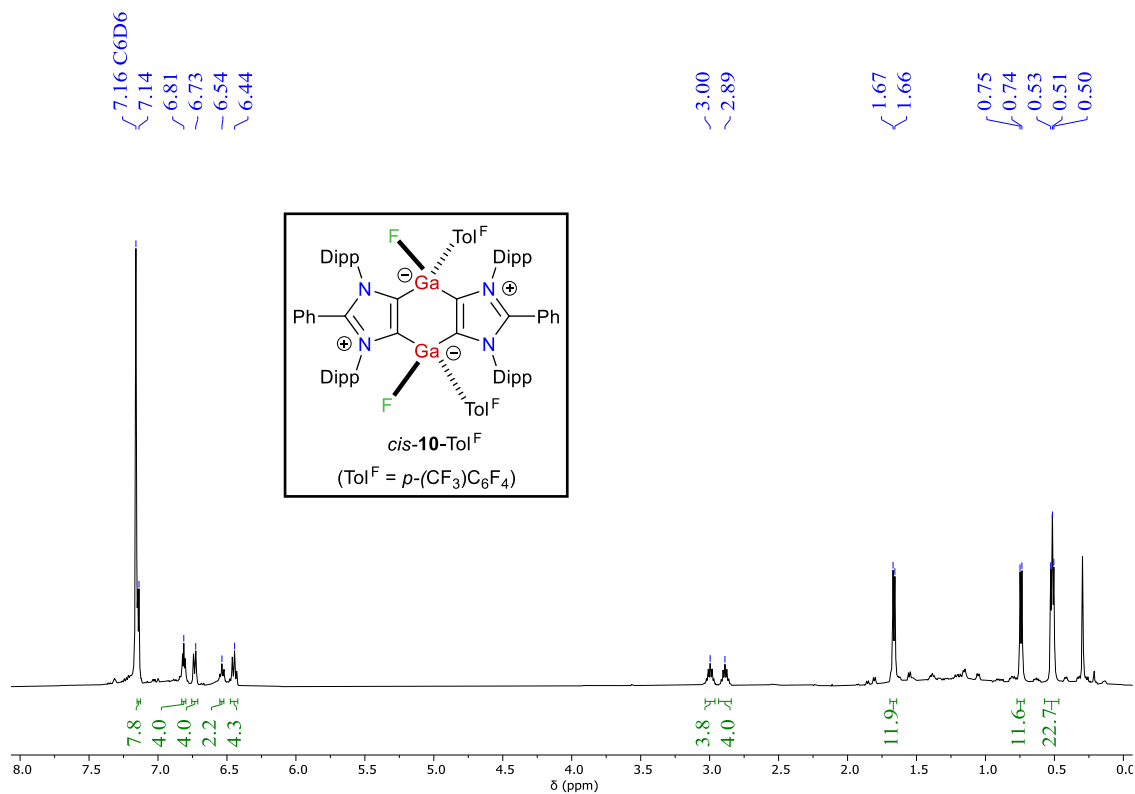


Figure S26. ¹H NMR (500 MHz, C₆D₆, 298 K) spectrum of *cis*-10-Tol^F.

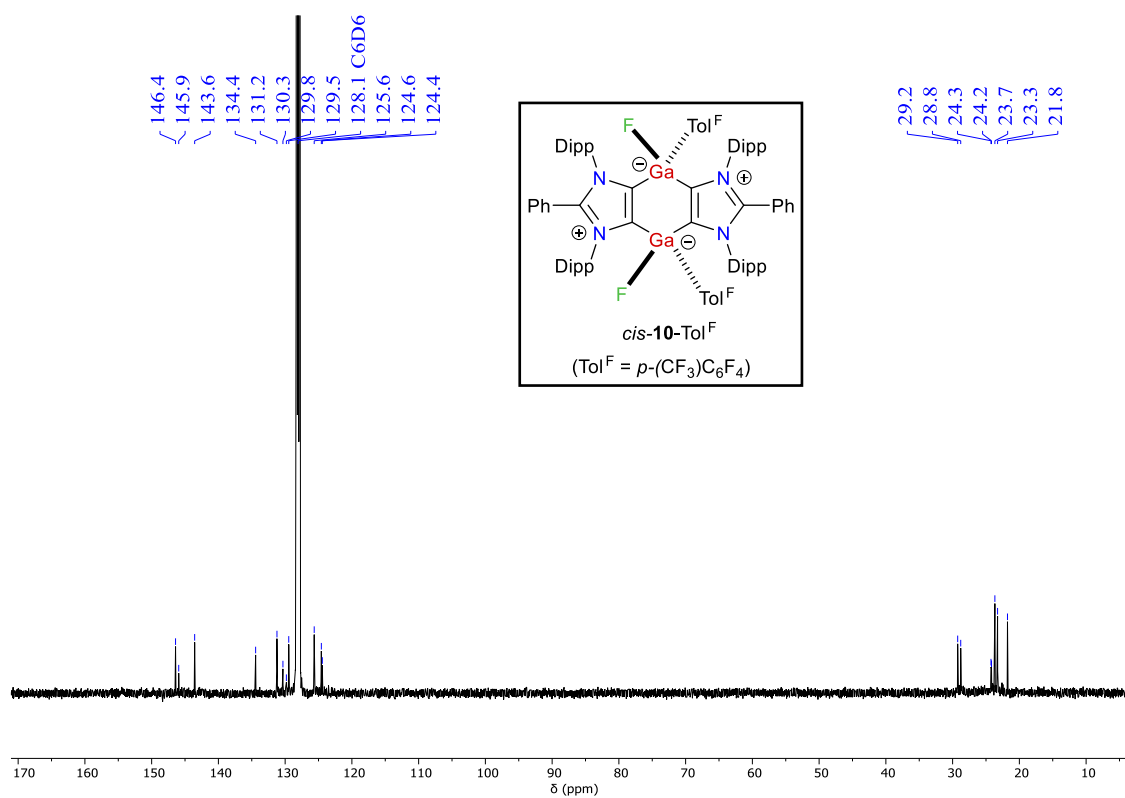


Figure 27 ¹³C{¹H} NMR (471 MHz, C₆D₆, 298 K) spectrum of *cis*-**10**-Tol^F.

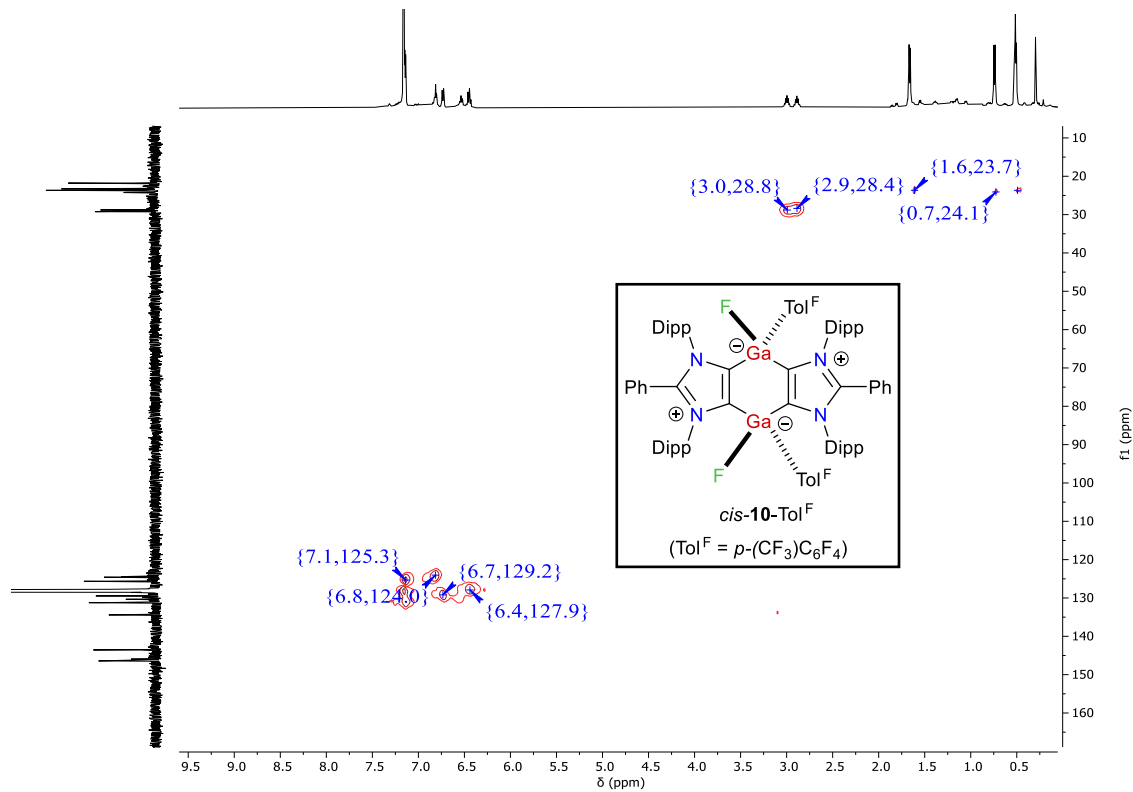


Figure S28. ¹H-¹³C{¹H} HMQC (500/126 MHz, C₆D₆, 298 K) spectrum of *cis*-**10**-Tol^F.

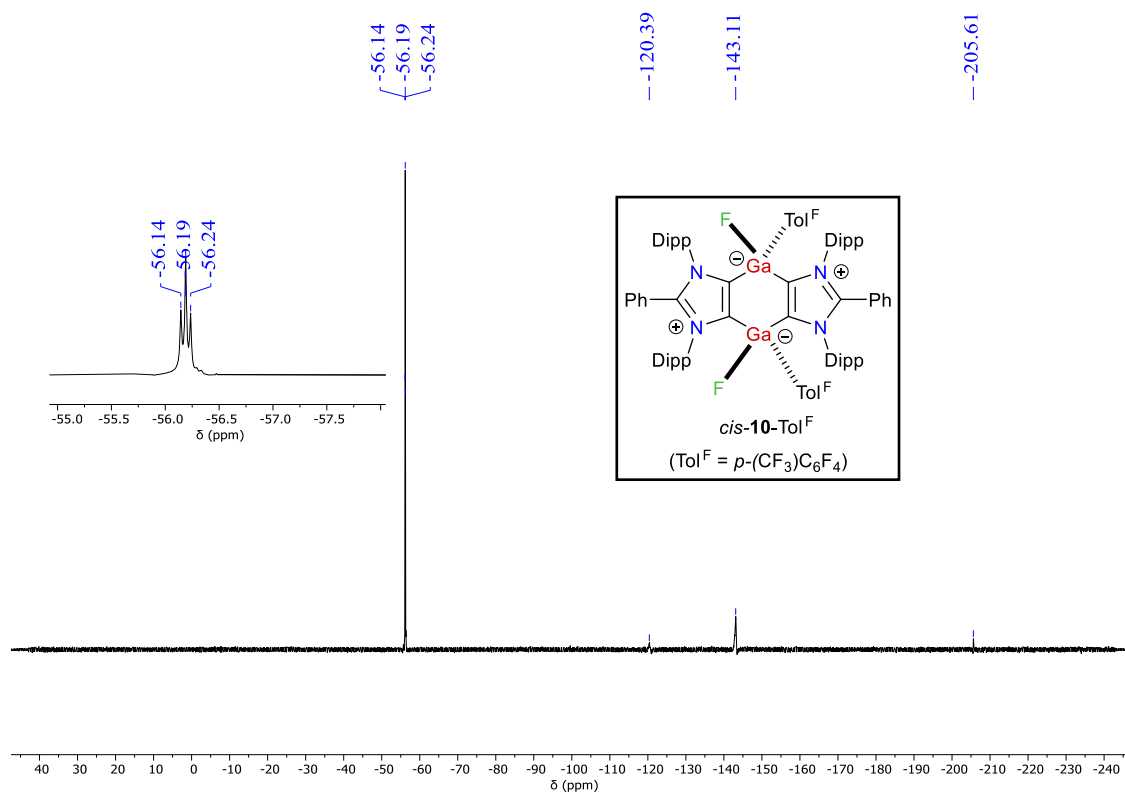


Figure S29. ¹⁹F{¹H} NMR (126 MHz, C₆D₆, 298 K) spectrum of *cis*-**10**-Tol^F.

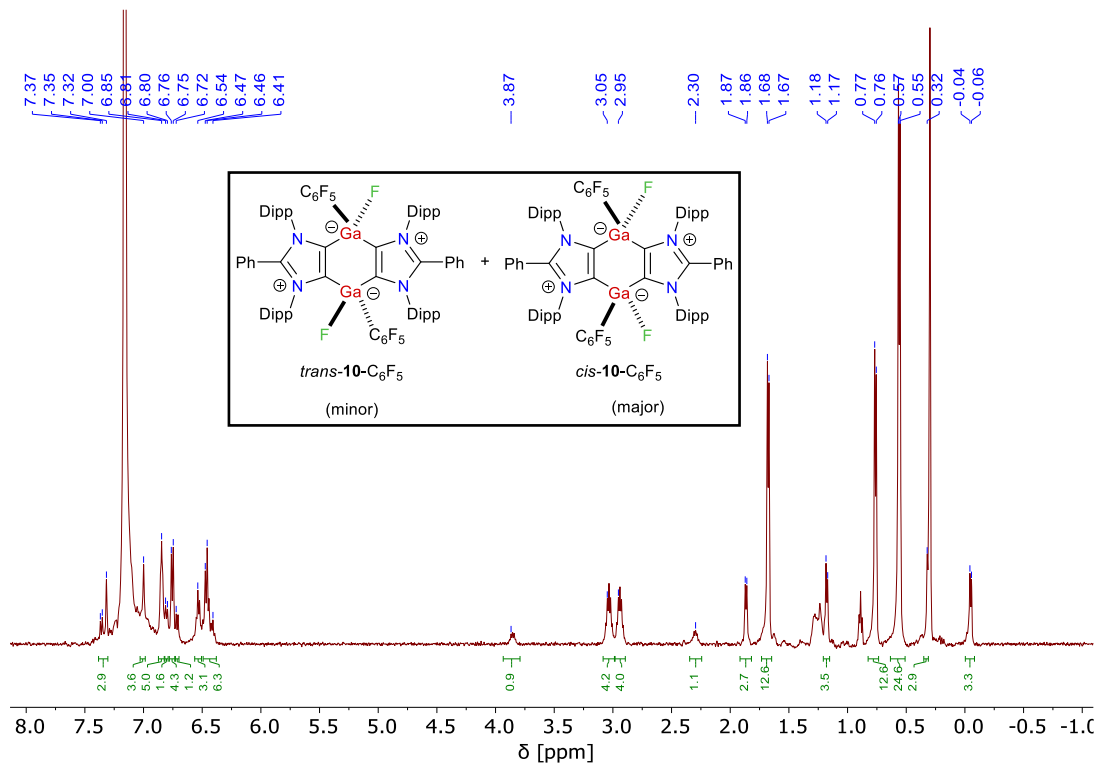


Figure S30. ¹H NMR (500 MHz, C₆D₆, 298 K) spectrum of a sample containing a mixture of *cis*-/*trans*-**10**-C₆F₅.

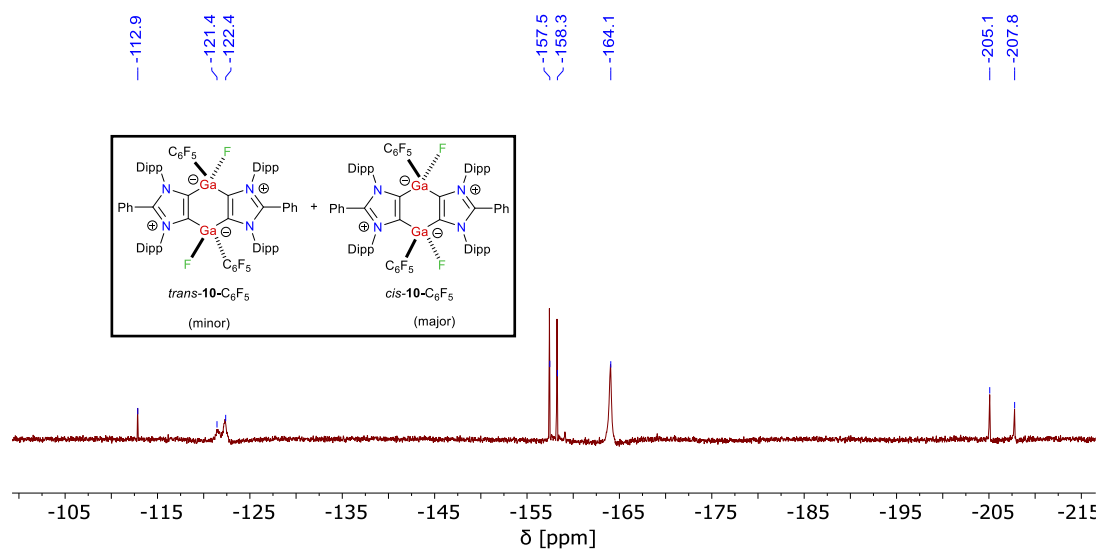


Figure S31. $^{19}\text{F}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K) spectrum of a sample containing a mixture of *cis*-/*trans*-10- C_6F_5 (signal at -112.9 ppm for PhF).

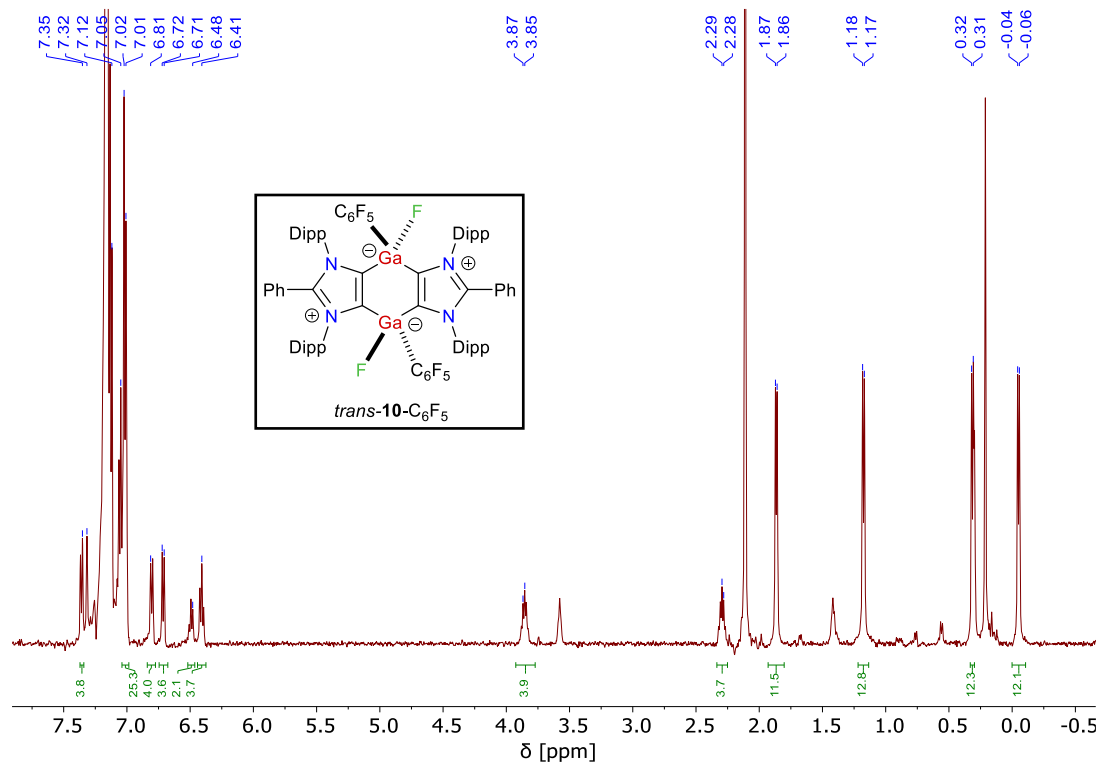


Figure S32. ^1H NMR (500 MHz, C_6D_6 , 298 K) spectrum of *trans*-10- C_6F_5 .

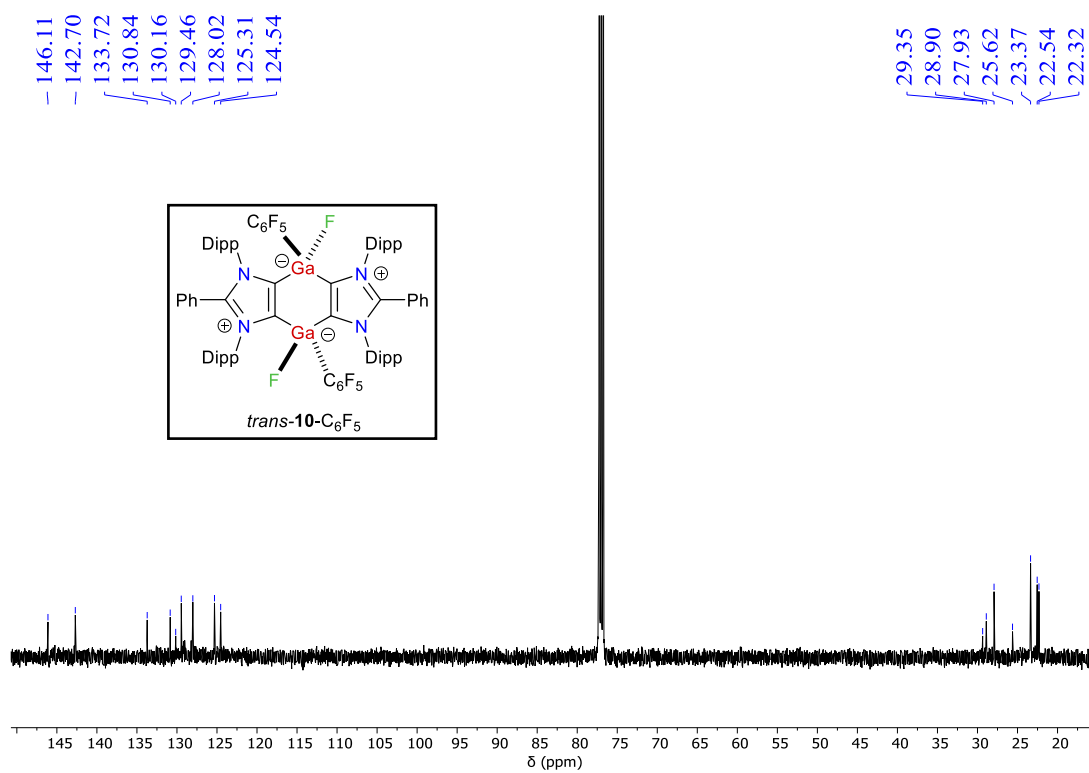


Figure S33. ¹³C{¹H} NMR (471 MHz, C₆D₆, 298 K) spectrum of *trans*-10-C₆F₅.

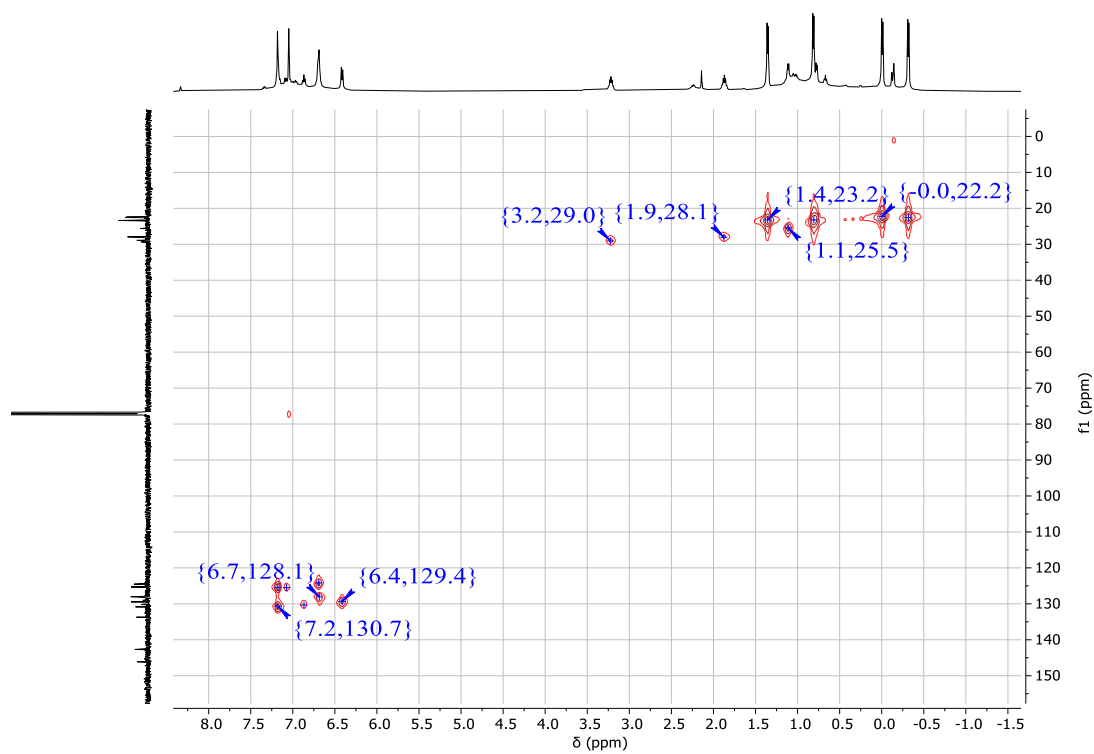


Figure S34. ¹H-¹³C{¹H} HMQC (500/126 MHz, C₆D₆, 298 K) spectrum of *trans*-10-C₆F₅.

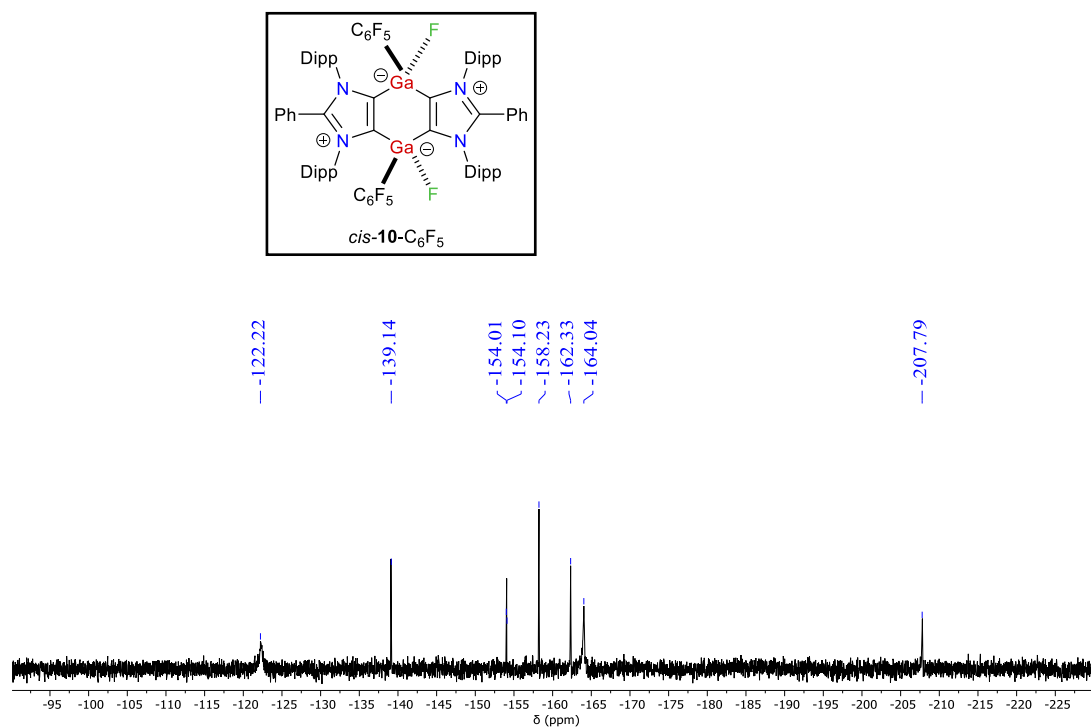


Figure S35. $^{19}\text{F}\{^1\text{H}\}$ NMR (126 MHz, C₆D₆, 298 K) spectrum of *cis*-10-C₆F₅.

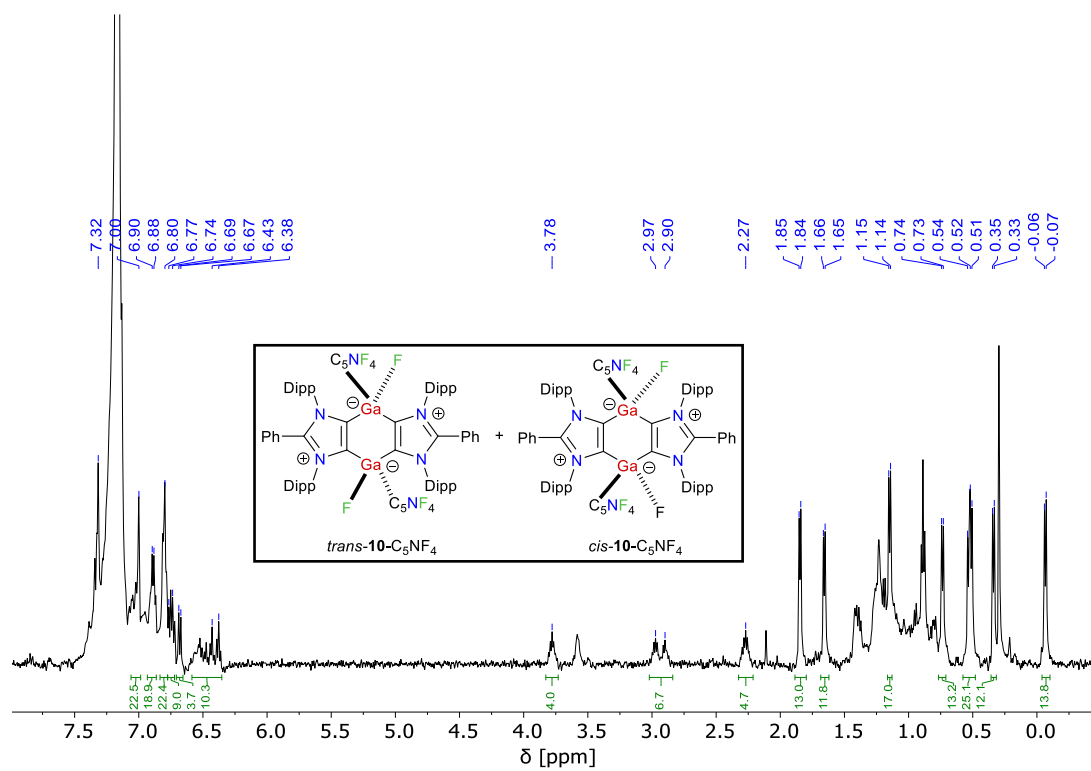


Figure S36. ^1H NMR (500 MHz, C₆D₆, 298 K) spectrum of a sample containing a mixture of *cis*-/*trans*-10-C₅NF₄.

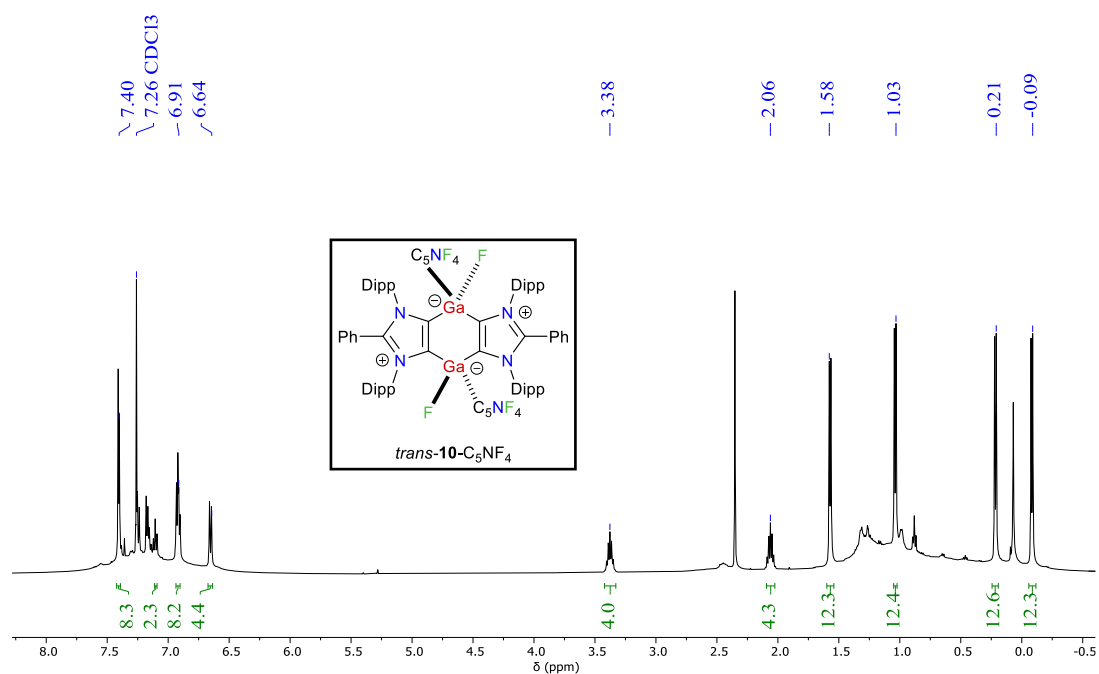


Figure S37. ¹H NMR (500 MHz, CDCl₃, 298 K) spectrum of *trans*-10-C₅NF₄.

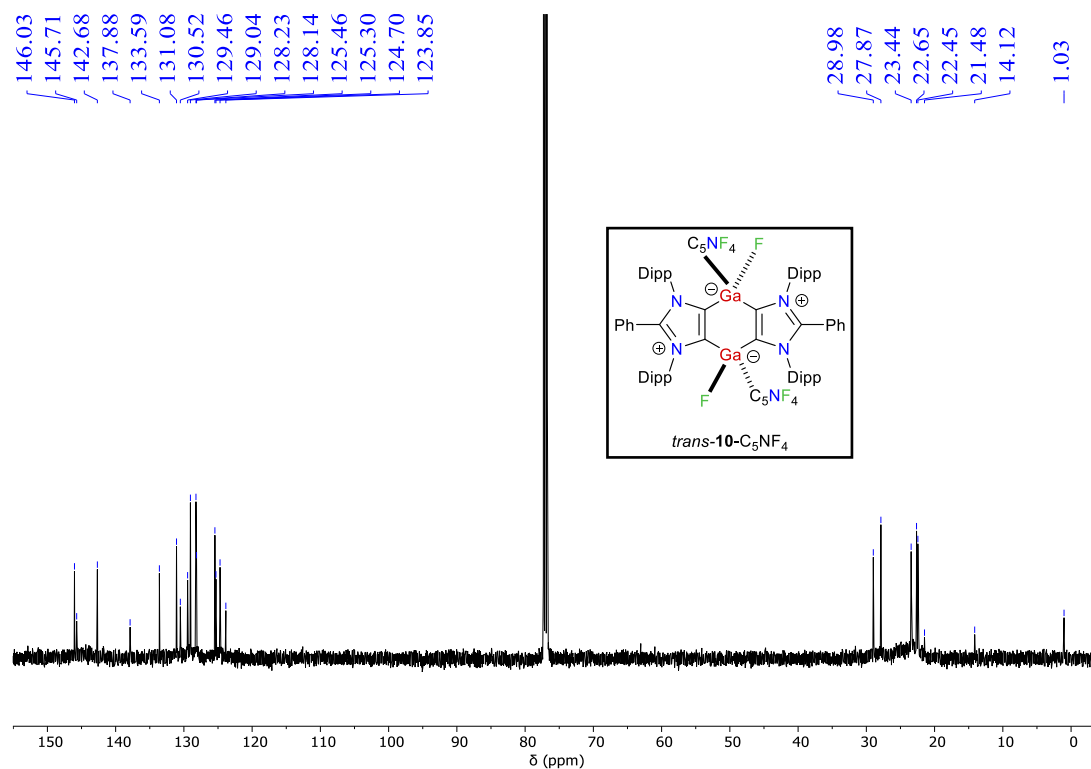


Figure S38. ¹³C{¹H} NMR (471 MHz, CDCl₃, 298 K) spectrum of *trans*-10-C₅NF₄.

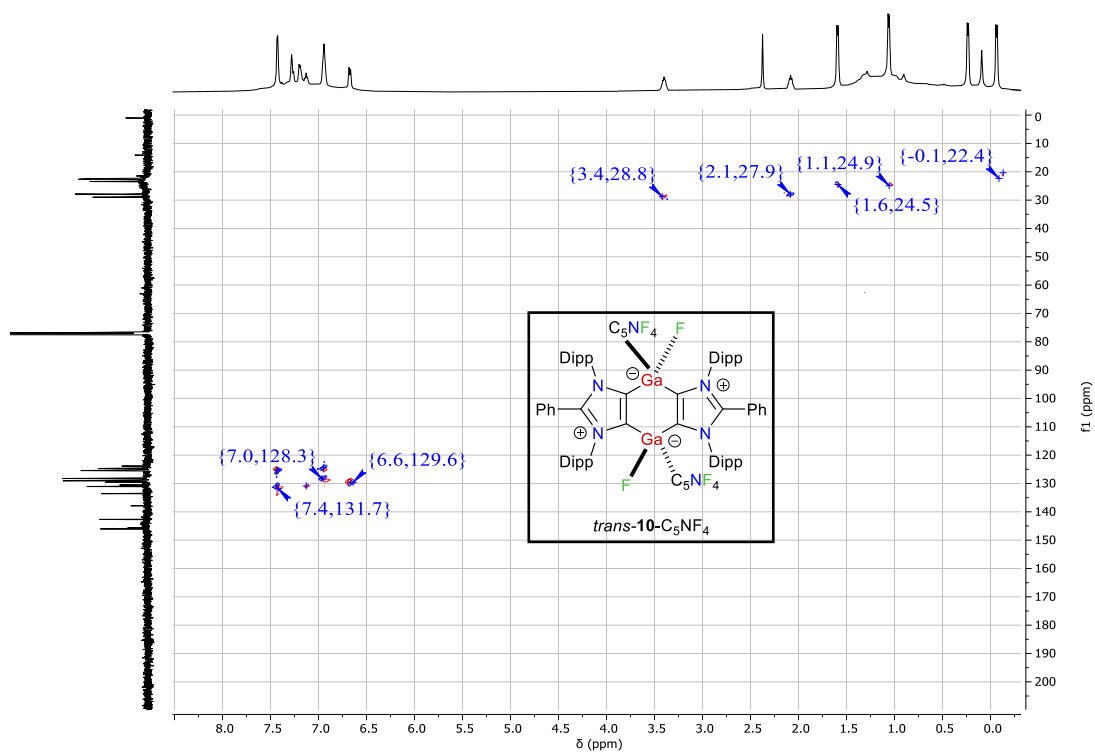


Figure S39. ^1H - $^{13}\text{C}\{^1\text{H}\}$ HMQC (500/126 MHz, CDCl_3 , 298 K) spectrum of *trans*-**10**- C_5NF_4 .

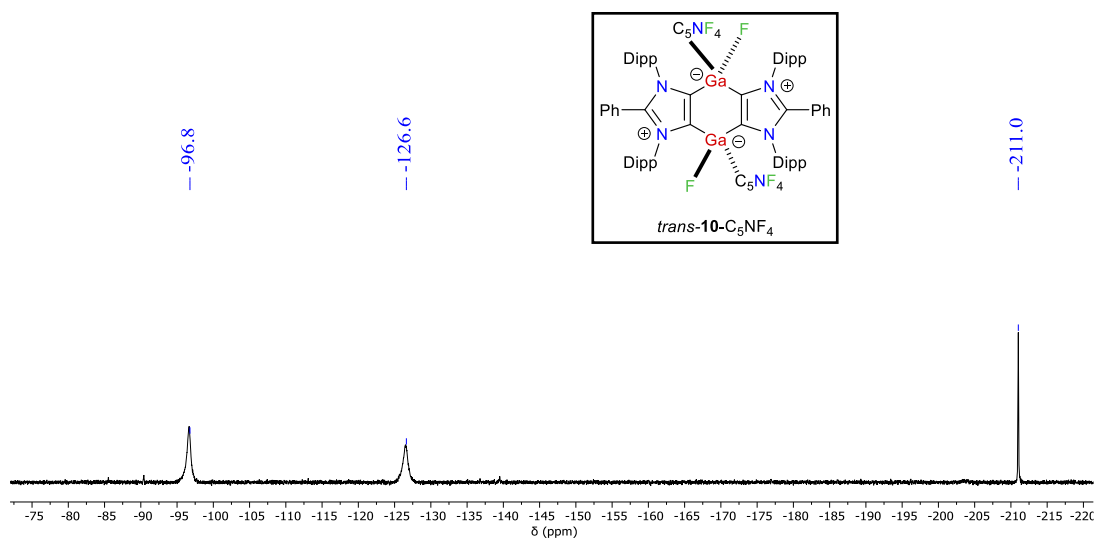


Figure S40. $^{19}\text{F}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 298 K) spectrum of *trans*-**10**- C_5NF_4 .

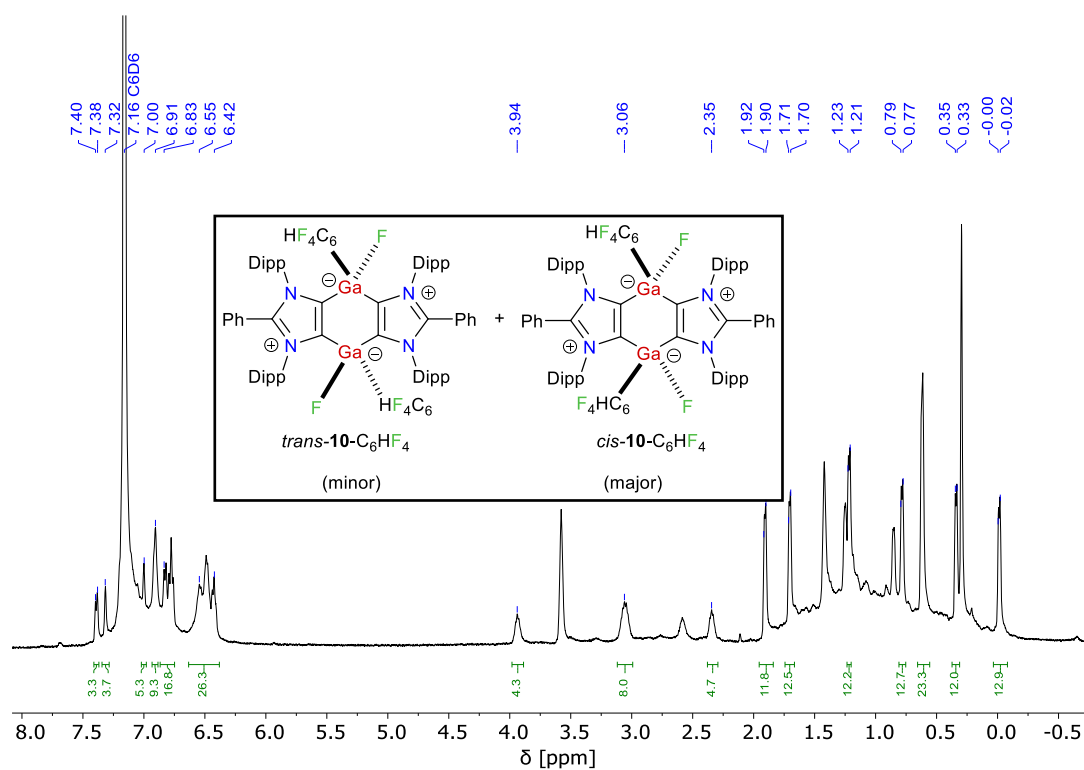


Figure S41a. ¹H NMR (500 MHz, C₆D₆, 298 K) spectrum of a sample containing a mixture of *cis*-/*trans*-10-C₆HF₄.

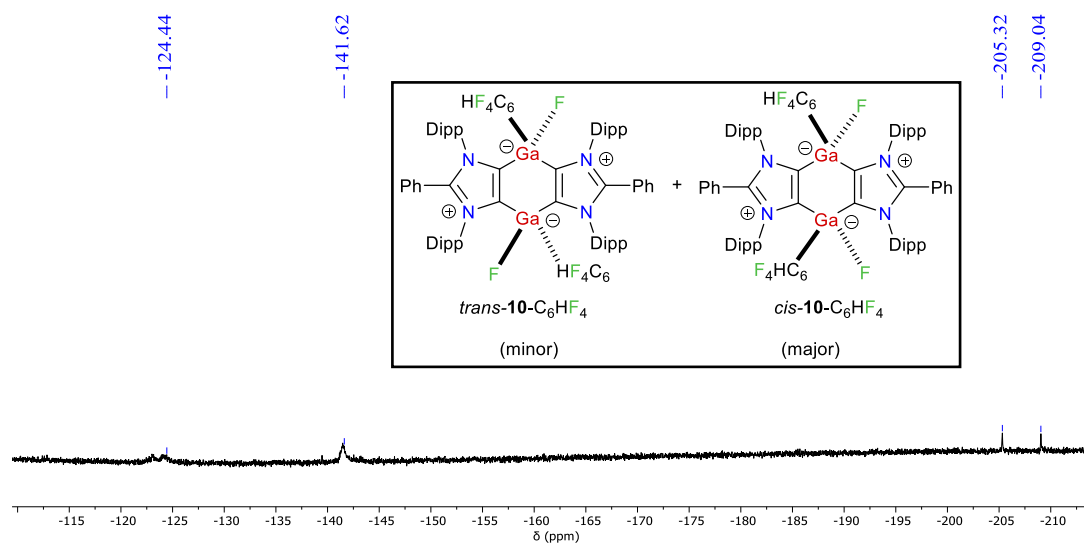


Figure S41b. ¹⁹F{¹H} NMR (126 MHz, C₆D₆, 298 K) spectrum of *cis*-/*trans*-10-C₆HF₄.

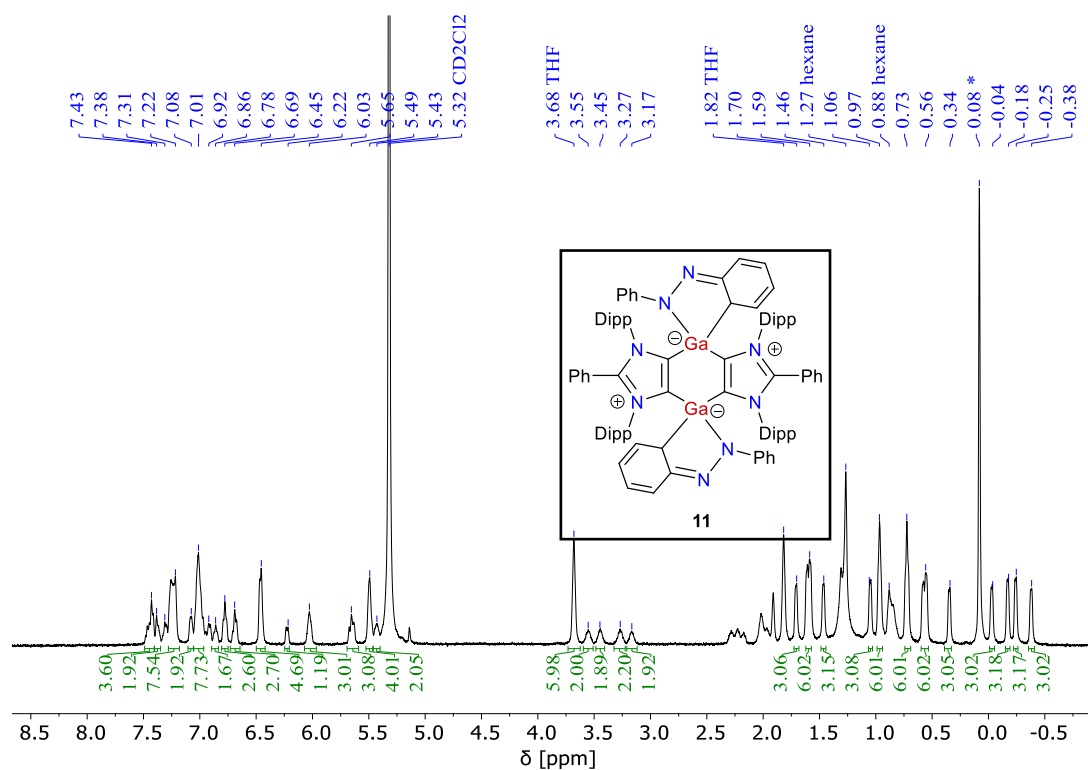


Figure S42. ¹H NMR (500 MHz, CD₂Cl₂, 298 K) spectrum of **11**.

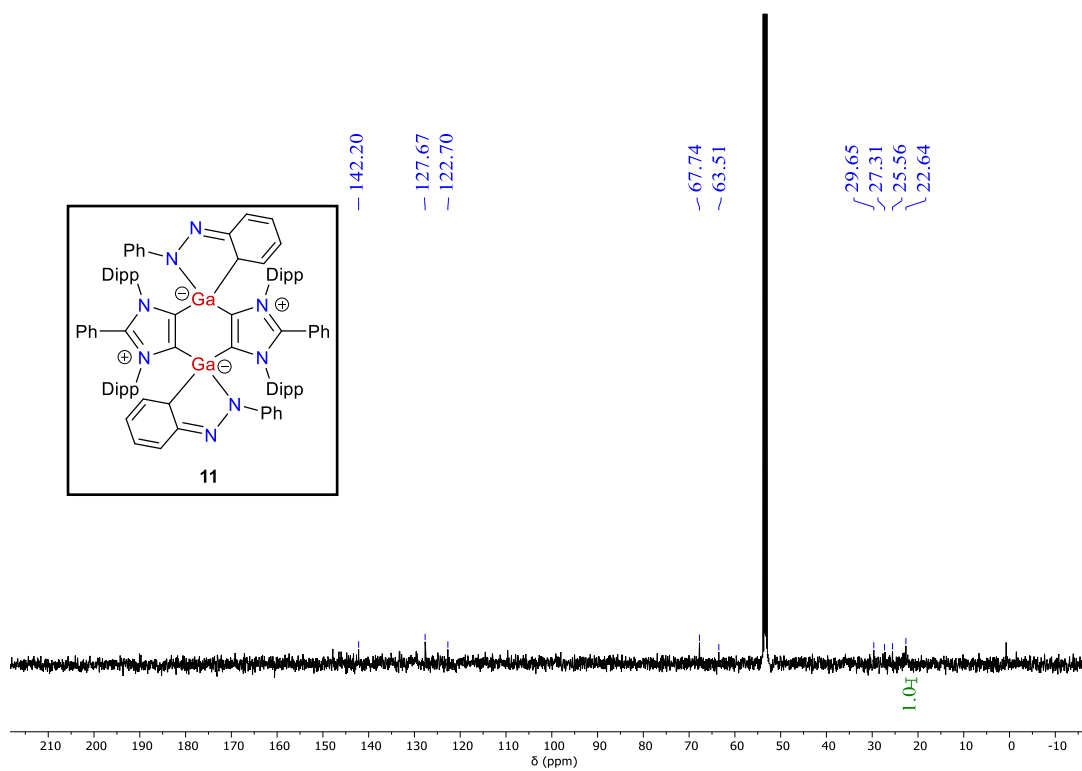


Figure S43. ¹³C{¹H} NMR (471 MHz, CD₂Cl₂, 298 K) spectrum of **11** (almost insoluble).

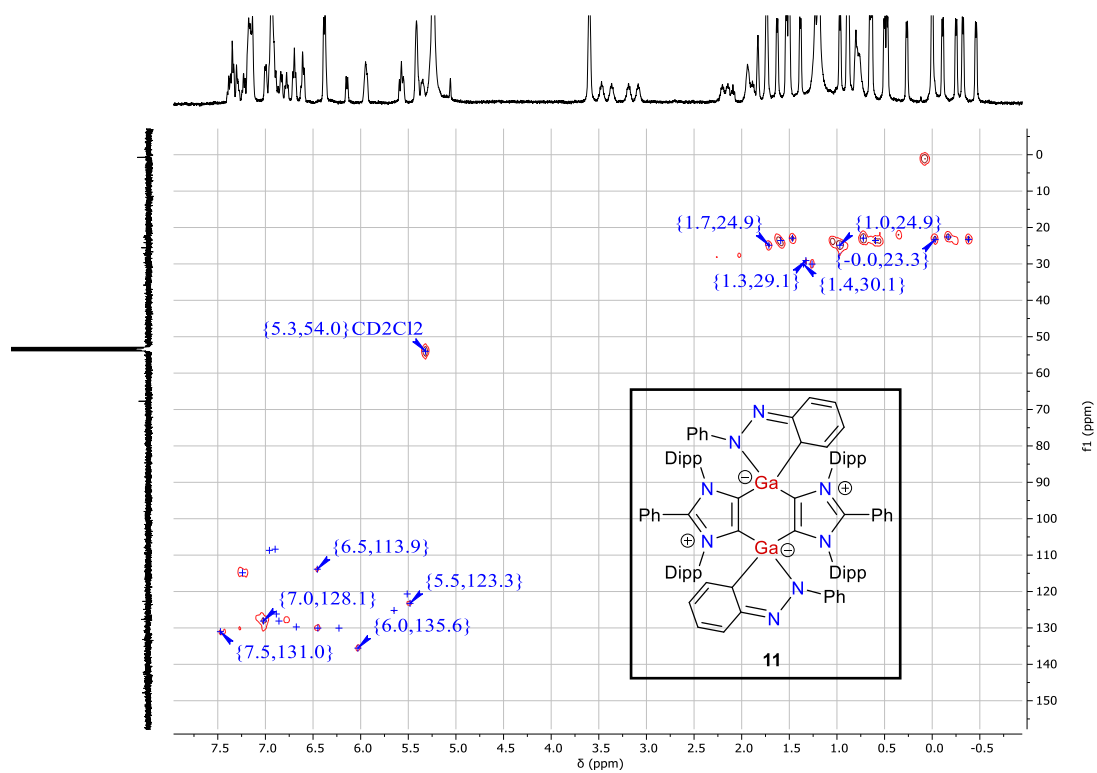


Figure S44. ^1H - $^{13}\text{C}\{^1\text{H}\}$ HMQC (500/126 MHz, CD_2Cl_2 , 298 K) (full) spectrum of **11**.

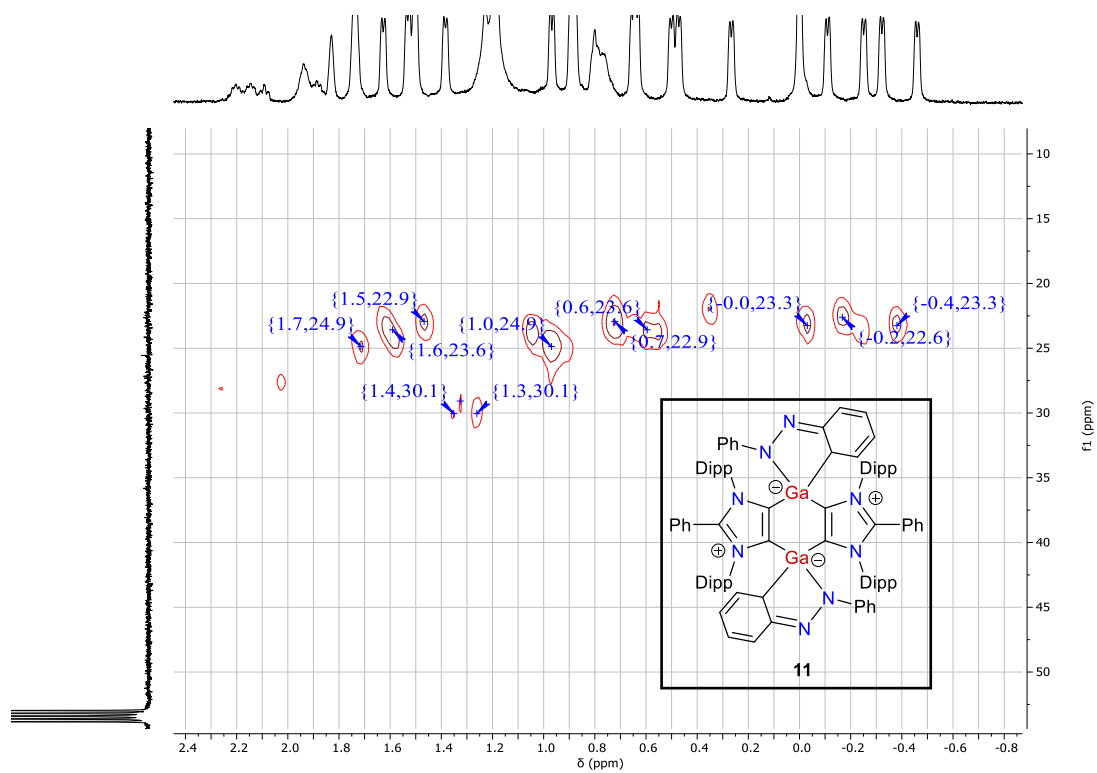


Figure S45. ^1H - $^{13}\text{C}\{^1\text{H}\}$ HMQC (500/126 MHz, CD_2Cl_2 , 298 K) (aliphatic region) spectrum of **11**.

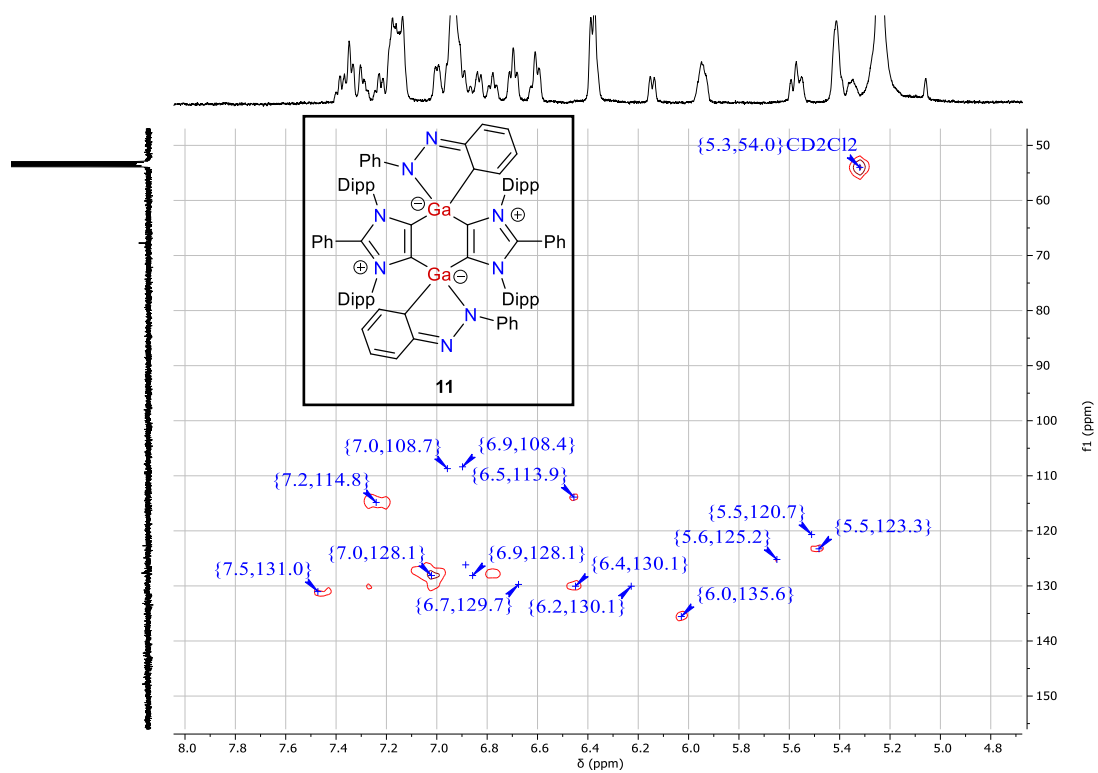


Figure S46. ¹H-¹³C{¹H} HMQC (500/126 MHz, CD₂Cl₂, 298 K) (aromatic region) spectrum of **11**.

Plots of FT-IR Spectra

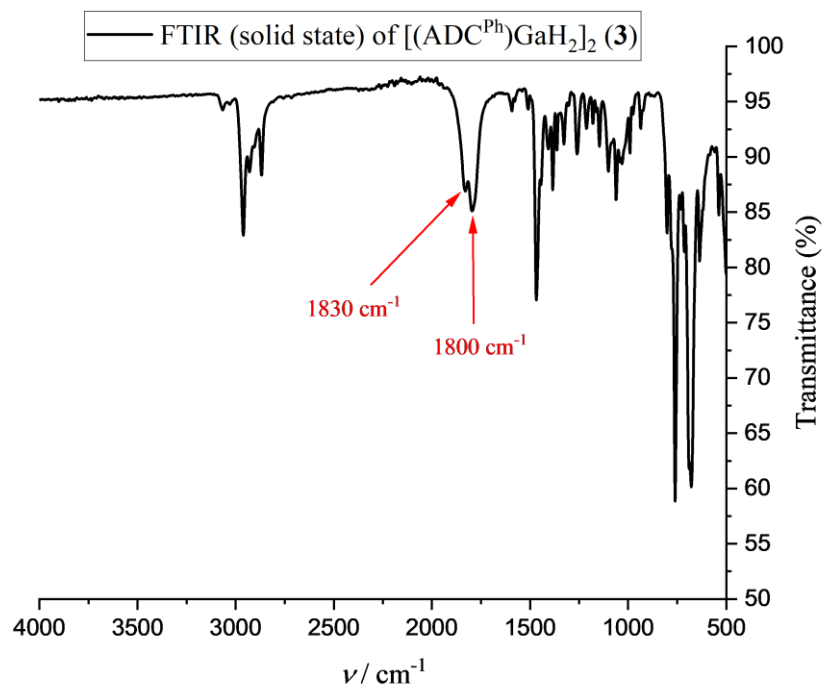


Figure S47. FT-IR spectrum of **3** in the solid state at 298 K.

Plots of UV-Vis Spectra

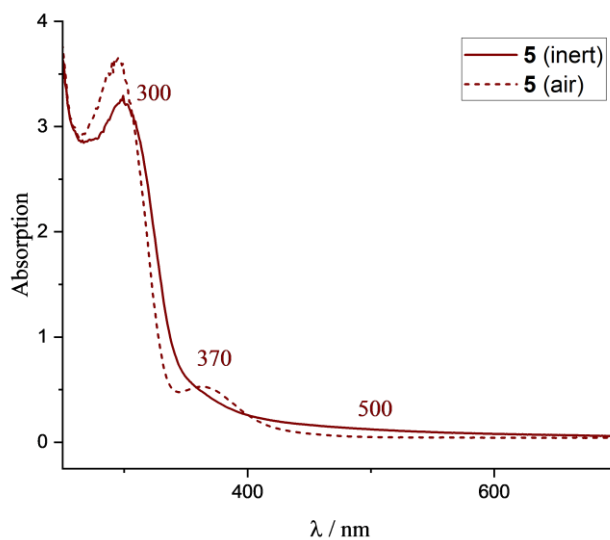


Figure S48. UV-Vis (THF, 2.5×10^{-4} M) spectrum of **5** under inert conditions (solid) and under air (dashed).

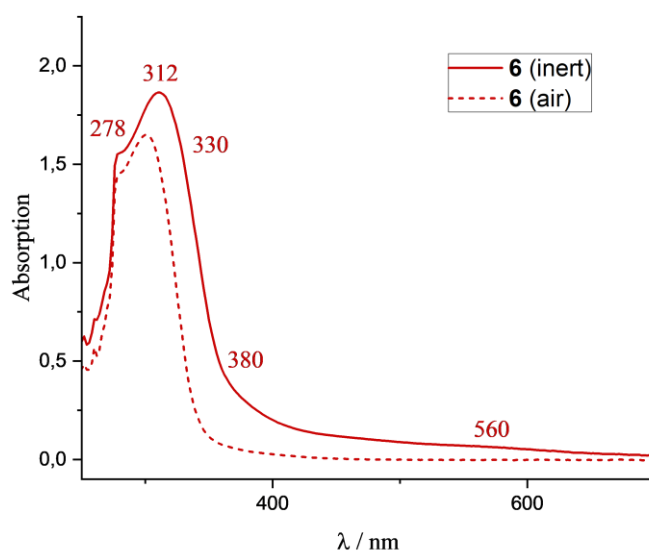


Figure S49. UV-Vis (C_6H_6 , 5×10^{-4} M) spectrum of **6** under inert conditions (solid) and under air (dashed).

Crystallographic Details

Single crystals were examined on a Rigaku Supernova diffractometer using Cu K α ($\lambda = 1.54184$ Å) or Mo K α ($\lambda = 0.71073$ Å) radiation. Using Olex2,⁵ the structures were solved with the ShelXT⁶ (**3**, **4**, **7**, **8**, *trans*-**10**-Tol^F) structure solution program using Intrinsic Phasing and refined with the ShelXL⁷ (**3**, **4**, **7**, **8**, *trans*-**10**-Tol^F) refinement package using Least Squares minimization. **4** was refined with the olex2.refine refinement package⁸ using Gauss-Newton minimization using NoSpherA2, an implementation of NON-SPHERical Atom-form-factors in Olex2.⁹ For **3**, the hydrogen atoms bonded to Ga1 were refined isotropically, the other hydrogen atoms were taken into account using a riding model. For **6**, phase transition was observed below 220 K. Ga1 (91:9) and Ga2 (57:43) are disordered over two sites. C37, C38, C41, C42, C44-C54, and C56-C66 are disordered over two sites (57:43). Anisotropic displacement parameters of disordered atoms were constrained pair wisely to be same. Suitable restraints and constraints were applied for the disordered atoms. A solvent mask was calculated, 90 electrons were found in a volume of 424 Å³ in 3 voids per unit cell. This is consistent with the presence of one toluene per asymmetric unit, which accounts for 100 electrons per unit cell. For **7**, a mixed crystal was measured with different atoms at the Ga2 atom. The Ga2 bound Fe(CO)₄ moiety has an occupancy of 96.9 % and the iodides an occupancy of 3.1%. For **8**, a solvent mask was calculated, 152 electrons were found in a volume of 952 Å³ in one void per unit cell. This is consistent with the presence of two benzene molecules per asymmetric unit, which accounts for 168 electrons per unit cell. *cis*-**10**-C₆F₅ contains highly disordered benzene near an inversion center, a solvent mask was calculated and 84 electrons were found in a volume of 936 Å³ in 3 voids per unit cell. This is consistent with the presence of 0.5[C₆H₆] per Asymmetric Unit, which account for 84 electrons per unit cell. For *trans*-**10**-C₅NF₄, highly disordered solvent could not be refined reliably, therefore a solvent mask was calculated and 426 electrons were found in a volume of 1735 Å³ in 1 void per unit cell. This is consistent with the presence of 2[C₆H₅F] per formula unit, which account for 400 electrons per unit cell. Disorder of C26, C27 over two sites (ratio 89:11), and disorder of C35, C36, C37, C38, F2, F3, F4, and F5 over two sites (ratio 54:46).

Details of the X-ray investigation are given in Table S1 and S2. CCDC 2334945, 2334948–2334953, 2379059, and 2379060 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html.

Table S1. Crystallographic details of **3**, **4**, and **6**.

	3 x 2 C ₆ H ₆	4	6
Empirical formula	C ₈₄ H ₁₀₀ Ga ₂ N ₄	C ₆₆ H ₇₈ Ga ₂ I ₄ N ₄	C ₇₃ Ga ₂ H ₈₆ N ₄
Formula weight	1305.11	1574.446	1158.89
Temperature/K	100.0(1)	100.0(1)	220.0(1)
Crystal system	tetragonal	triclinic	triclinic
Space group	I4 ₁ cd	P-1	P-1
a/Å	17.2516(2)	10.5694(1)	12.7988(7)
b/Å	17.2516(2)	12.1801(1)	14.6243(7)
c/Å	47.4743(8)	13.6704(1)	18.1282(9)
α /°	90	101.963(1)	80.487(4)
β /°	90	98.911(1)	79.632(4)
γ /°	90	107.530(1)	85.811(4)
Volume/Å ³	14129.1(4)	1596.52(3)	3288.5(3)
Z	8	1	2
ρ_{calc} /cm ³	1.227	1.638	1.170
μ /mm ⁻¹	0.810	2.819	0.862
F(000)	5552.0	775.164	1228.0
Crystal size/mm ³	0.07 × 0.069 × 0.026	0.36 × 0.14 × 0.13	0.28 × 0.24 × 0.15
Radiation/Å	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)
2 Θ range for data collection/°	5.35 to 60.058	6.4 to 75.58	6.434 to 51.364
Index ranges	-24 ≤ h ≤ 24, -24 ≤ k ≤ 24, -66 ≤ l ≤ 66	-18 ≤ h ≤ 18, -20 ≤ k ≤ 20, -23 ≤ l ≤ 23	-15 ≤ h ≤ 15, -17 ≤ k ≤ 17, -22 ≤ l ≤ 22
Reflections collected	222973	157579	64721
Independent reflections	10335 [R _{int} = 0.0863, R _{sigma} = 0.0288]	16604 [R _{int} = 0.0310, R _{sigma} = 0.0165]	12461 [R _{int} = 0.0486, R _{sigma} = 0.0402]
Reflections with $I > 2\sigma(I)$	9117	14979	8211
Data/restraints/parameters	10335/1/426	16604/0/460	12461/648/897
Goodness-of-fit on F ²	1.109	1.051	1.031
Final R indexes [$I > 2\sigma(I)$]	R ₁ = 0.0336, wR ₂ = 0.0780	R ₁ = 0.0180, wR ₂ = 0.0365	R ₁ = 0.0645, wR ₂ = 0.1573
Final R indexes [all data]	R ₁ = 0.0442, wR ₂ = 0.0826	R ₁ = 0.0228, wR ₂ = 0.0385	R ₁ = 0.1001, wR ₂ = 0.1789
Largest diff. peak/hole / e Å ⁻³	0.37/-0.26	1.33/-1.39	0.95/-0.72
Flack parameter	0.484(11)	–	–
CCDC number	2334945	2334948	2334949

Table S2. Crystallographic details of **7**, **8**, and *trans*-**10**-Tol^F.

	7	8	<i>trans</i> - 10 -Tol ^F
Empirical formula	C _{82.88} H ₈₇ Fe _{1.97} Ga ₂ I _{0.07} N ₄ O _{7.88}	C ₆₆ H ₇₈ Cl ₄ Ga ₂ N ₄ 2[C ₆ H ₆]	C ₈₀ H ₇₈ N ₄ F ₁₆ Ga ₂
Formula weight	1522.77	1364.77	1538.90
Temperature/K	100.0(1)	173.0(1)	100.0(1)
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	P2 ₁ /n	P2 ₁ /c
a/Å	10.8571(2)	10.3023(8)	19.4377(4)
b/Å	14.3020(3)	18.4534(13)	19.6182(4)
c/Å	25.6182(5)	20.0384(16)	19.7964(5)
α /°	98.115(2)	90	90
β /°	96.616(2)	103.039(7)	100.679(2)
γ /°	102.807(2)	90	90
Volume/Å ³	3795.66(13)	3711.3(5)	7418.3(3)
Z	2	2	4
ρ_{calc} /cm ³	1.332	1.221	1.378
μ /mm ⁻¹	4.430	0.913	1.633
F(000)	1584.0	1432	3168.0
Crystal size/mm ³	0.36 × 0.21 × 0.1	0.302 × 0.26 × 0.137	0.19 × 0.07 × 0.06
Radiation/Å	Cu K α (λ = 1.54184)	Mo K α (λ = 0.71073)	Cu K α (λ = 1.54184)
2 Θ range for data collection/°	6.784 to 152.846	6.64 to 52.042	6.398 to 143.758
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 17, -32 ≤ l ≤ 32	-12 ≤ h ≤ 12, -22 ≤ k ≤ 22, -21 ≤ l ≤ 24	-10 ≤ h ≤ 23, -23 ≤ k ≤ 21, -24 ≤ l ≤ 23
Reflections collected	34577	28520	29275
Independent reflections	15591 [R _{int} = 0.0297, R _{sigma} = 0.0346]	7104 [R _{int} = 0.0431, R _{sigma} = 0.0439]	14048 [R _{int} = 0.0450, R _{sigma} = 0.0618]
Reflections with $I > 2\sigma(I)$	14480	5704	10814
Data/restraints/parameters	15591/0/927	7104/0/351	14048/0/935
Goodness-of-fit on F ²	1.021	1.044	1.026
Final R indexes [$I > 2\sigma(I)$]	R ₁ = 0.0373, wR ₂ = 0.0994	R ₁ = 0.0447, wR ₂ = 0.1139	R ₁ = 0.0522, wR ₂ = 0.1232
Final R indexes [all data]	R ₁ = 0.0405, wR ₂ = 0.1027	R ₁ = 0.0577, wR ₂ = 0.1219	R ₁ = 0.0728, wR ₂ = 0.1350
Largest diff. peak/hole / e Å ⁻³	0.87/-0.73	1.09/-0.54	1.67/-0.47
CCDC number	23349450	23349452	23349451

Table S3. Crystallographic details of *cis*-**10**-C₆F₅, *trans*-**10**-C₅NF₄, and **11**.

	<i>cis</i> - 10 -C ₆ F ₅	<i>trans</i> - 10 -C ₅ NF ₄	11 (CHCl ₃)
Empirical formula	C ₈₁ H ₈₁ F ₁₂ Ga ₂ N ₄	C ₈₈ H ₈₈ F ₁₂ Ga ₂ N ₆	C ₉₃ H ₁₀₁ Cl ₉ Ga ₂ N ₈
Formula weight	1478.000	1597.08	1789.30
Temperature/K	100.00(1)	100.0(1)	100.0(1)
Crystal system	monoclinic	monoclinic	triclinic
Space group	P2 ₁ /c	C2/c	P-1
a/Å	26.58465(18)	21.1589(5)	12.9660(4)
b/Å	12.30259(7)	19.2641(4)	13.2339(5)
c/Å	23.64645(14)	19.4975(4)	15.4127(4)
α/°	90	90	110.468(3)
β/°	106.0431(7)	91.4975(4)	90.678(2)
γ/°	90	90	117.109(3)
Volume/Å ³	7432.61(8)	7945.0(3)	2158.55(14)
Z	4	4	1
ρ _{calc} /g/cm ³	1.321	1.335	1.376
μ/mm ⁻¹	1.527	0.755	3.722
F(000)	3060.2	3312.0	930.0
Crystal size/mm ³	0.59 × 0.08 × 0.07	0.39 × 0.26 × 0.13	0.21 × 0.14 × 0.07
Radiation/Å	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.6 to 151.96	6.544 to 60.16	7.826 to 152.008
Index ranges	−33 ≤ h ≤ 33 −15 ≤ k ≤ 15 −29 ≤ l ≤ 29	−29 ≤ h ≤ 29 −27 ≤ k ≤ 27 −27 ≤ l ≤ 27	−15 ≤ h ≤ 16, −15 ≤ k ≤ 16, −19 ≤ l ≤ 15
Reflections collected	216854	139259	17814
Independent reflections	15470 [R _{int} = 0.0284, R _{sigma} = 0.0099]	11652 [R _{int} = 0.1053, R _{sigma} = 0.0387]	8769 [R _{int} = 0.0430, R _{sigma} = 0.0479]
Reflections with I > 2σ(I)	14587	10743	7850
Data/restraints/parameters	15470/0/881	11652/474/524	8769/0/495
Goodness-of-fit on F ²	1.041	1.174	1.039
Final R indexes [I > 2σ(I)]	R ₁ = 0.0297, wR ₂ = 0.0804	R ₁ = 0.0675, wR ₂ = 0.1644	R ₁ = 0.0492, wR ₂ = 0.1270
Final R indexes [all data]	R ₁ = 0.0313, wR ₂ = 0.0818	R ₁ = 0.0712, wR ₂ = 0.1664	R ₁ = 0.0541, wR ₂ = 0.1318
Largest diff. peak/hole / e Å ⁻³	0.81/−0.46	0.54/−0.92	0.84/-1.16
CCDC number	2379059	2379060	2334953

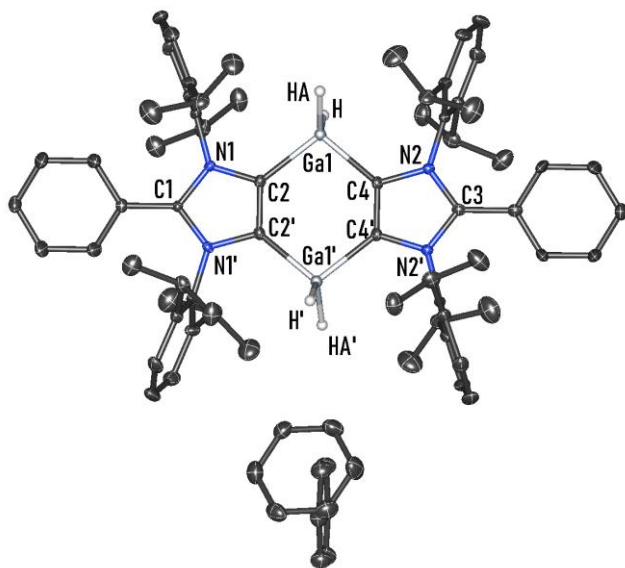


Figure S50. Solid state molecular structure of **3**. Hydrogen atoms (except bound to gallium) were omitted for clarity. Selected bond lengths (Å) and angles (°) for **3**: C2–Ga1 2.016(3), C4–Ga1 2.015(3), C2–C2' 1.377(6), C4–C4' 1.368(6), C2–Ga1–C4 101.2(1), C2'–C2–Ga1 128.9(1), C2'–C2–N1 105.9(2), C2–Ga1–H 108.1(2), C2–Ga1–Ha 113.7(2).

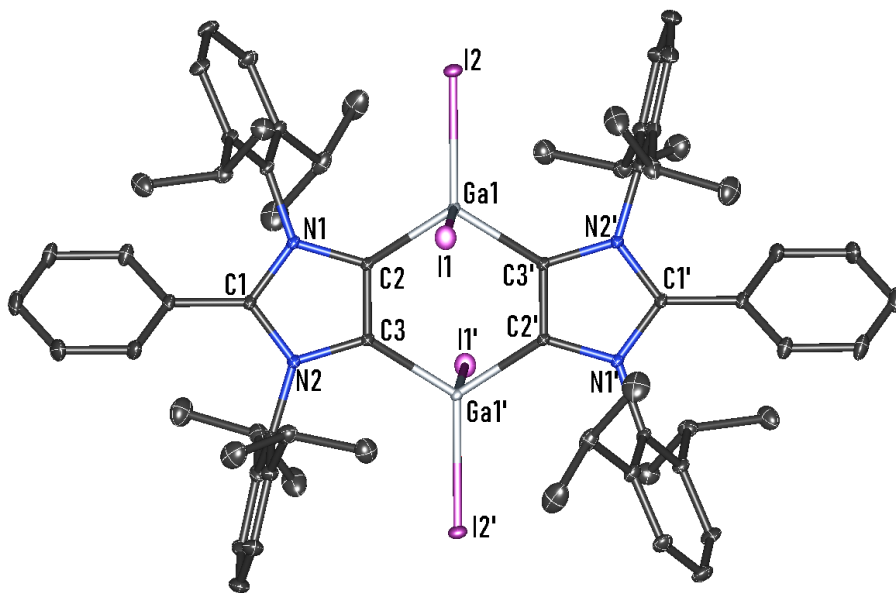


Figure S51. Solid state molecular structure of **4**. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°) for **4**: C2–Ga1 1.993(1), C3'–Ga1 1.993(1), Ga1–I1 2.6117(1), Ga1–I2 2.5230(1), C2–C3 1.378(1), I1–Ga1–I2 107.47(1), C2–Ga1–I1 100.14(2), C2–Ga1–I2 117.85(2), C2–Ga1–C3' 107.36(3), C3–C2–N1 106.5(1), C3–C2–Ga1 122.2(1).

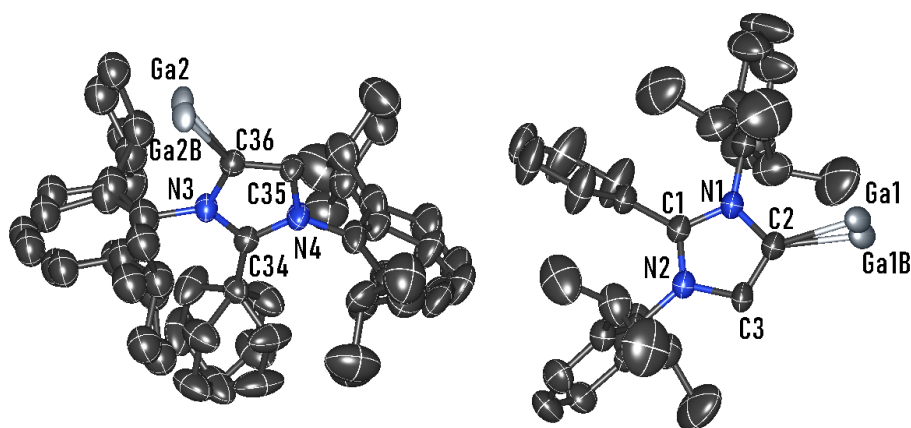


Figure S52. Solid state molecular structure of **6**. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°) for **6**: C2–Ga1 2.092(4), C2–Ga1b 2.043(9), C3'–Ga1 2.107(4), C3'–Ga1b 1.994(9), C36'–Ga2 2.089(6), C36'–Ga2b 2.127(7), C35–Ga2 2.090(5), C35–Ga2b 2.092(7), C2–C3 1.388(5), C35–C36 1.382(5), C2–Ga1–C3' 92.6(1), C2–Ga1b–C3' 97.5(4), C35–Ga2–C36' 93.2(2), C35–Ga2b–C36' 92.0(3) C3–C2–Ga1 132.6(3), C3–C2–Ga1b 127.5(4), C3–C2–N1 105.2(3), C2–C3–N2 105.8(3).

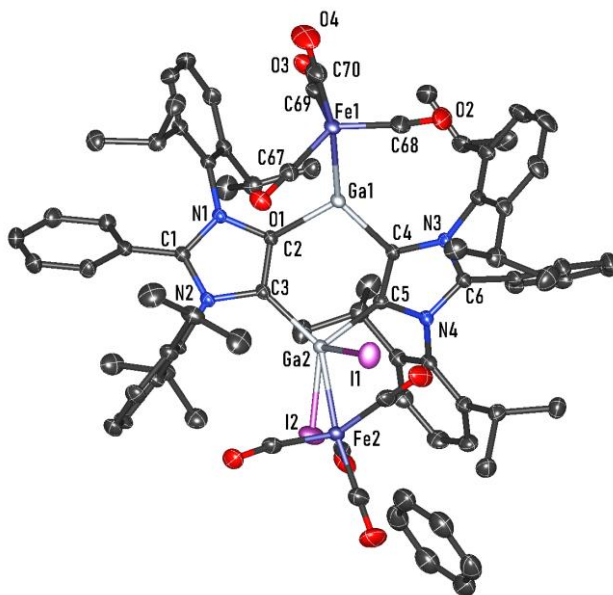


Figure S53. Solid state molecular structure of **7**. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°) for **7**: C2–Ga1 2.021(2), C4–Ga1 2.010(2), C3–Ga2 2.009(2), C5–Ga2 2.028(2), Ga1–Fe1 2.327(1), Ga2–Fe2 2.320(1), Ga2–I1 2.772(4), Ga2–I2 2.313(5), C2–C3 1.383(2), C4–C5 1.376(2), C3–C2–N1 106.0(1), C2–C3–N2 106.2(2), C5–C4–N3 106.6(2), C4–C5–N4 106.1(2), C2–Ga1–C4 99.9(1), C2–Ga1–Fe1 119.6(1), C4–Ga1–Fe1 139.7(1), C3–Ga2–C5 99.8(1), C3–Ga2–Fe2 139.2(1), C5–Ga2–Fe2 120.3(1).

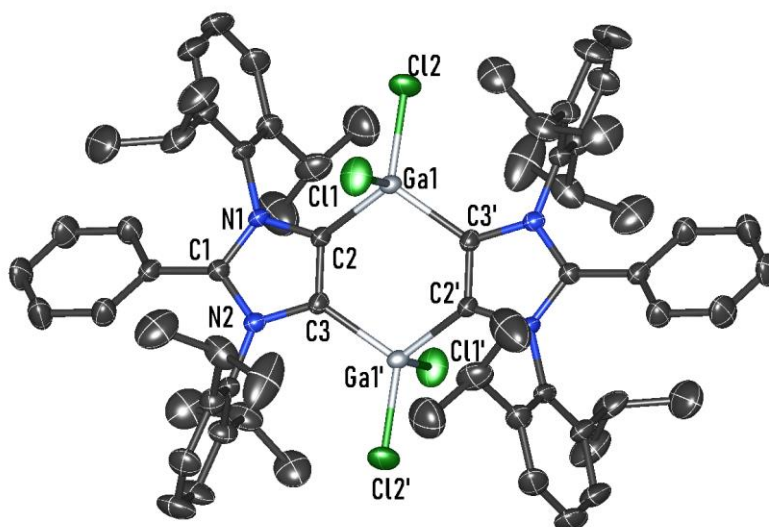


Figure S54. Solid state molecular structure of **8**. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°) for **8**: C2–Ga1 1.981(3), C3'–Ga1 1.992(2), Ga1–Cl1 2.225(1), Ga1–Cl2 2.159(1), C2–C3 1.359(4), C3–C2–N1 106.2(2), C2–C3–N2 106.9(2), C2–Ga1–C3' 107.5(1), Cl1–Ga1–Cl2 106.4(1), C2–Ga1–Cl1 103.5(1), C2–Ga1–Cl2 117.5(1).

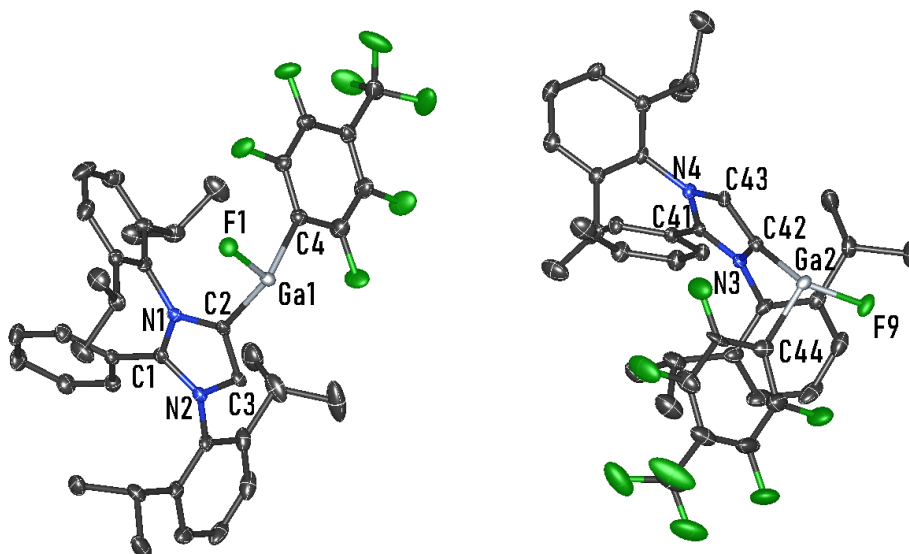


Figure S55. Solid state molecular structure of *trans*-**10-Tol^F**. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°) for **10-Tol^F**: C2–Ga1 1.997(3), C3'–Ga1 1.997(3), C4–Ga1 2.017(3), Ga1–F1 1.795(2), C2–C3 1.375(4), C42–Ga2 1.992(3), C43'–Ga2 1.991(3), C44–Ga2 2.030(3), Ga2–F9 1.787(2), C42–C43 1.375(4), C3–C2–N1 106.5(3), C2–C3–N2 106.2(3), C2–Ga1–C3' 106.5(1), C2–Ga1–C4 109.9(1), C2–Ga1–F1 112.9(1).

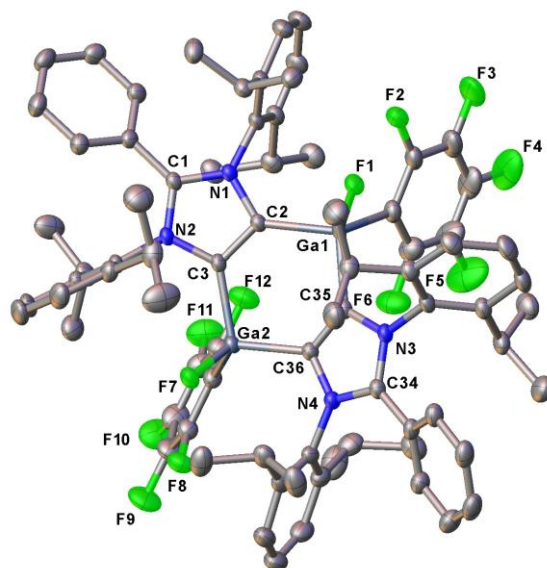


Figure S56. Solid state molecular structure of *cis*-**10**-C₆F₅. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°) for *cis*-**10**-C₆F₅: C2–Ga1 1.999(1), C35–Ga1 2.003(1), C67–Ga1 2.010(1), Ga1–F1 1.800(1), C2–C3 1.369(2), C3–Ga2 1.982(1), C36–Ga2 1.984(1), C73–Ga2 2.005(1), Ga2–F7 1.798(1), C35–C36 1.370(2), C3–C2–N1 105.9(1), C2–C3–N2 106.9(1), C2–Ga1–C35 103.8(1), C2–Ga1–C67 115.6(1), C2–Ga1–F1 107.4(1).

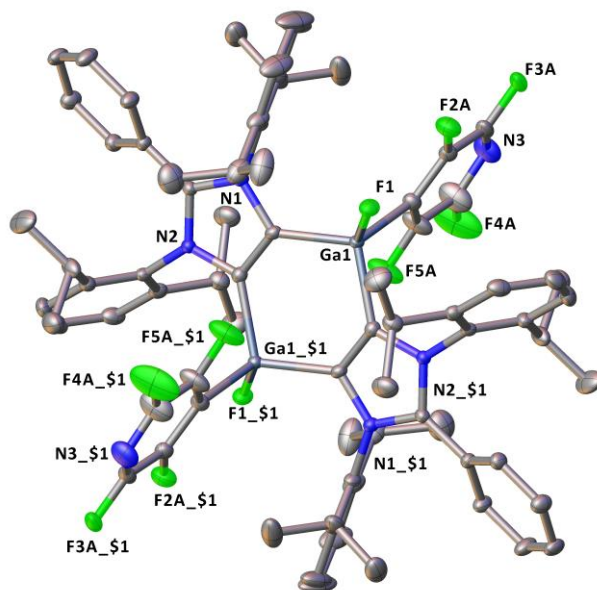


Figure S57. Solid state molecular structure of *trans*-**10**-C₅NF₄. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°) for *trans*-**10**-C₅NF₄: C2–Ga1 1.990(3), C3'–Ga1 1.997(3), C34–Ga1 2.023(3), Ga1–F1 1.792(2), C2–C3 1.374(4), C3–C2–N1 106.1(2), C2–C3–N2 106.8(2), C2–Ga1–C3' 106.4(1), C2–Ga1–C34 109.7(1), C2–Ga1–F1 112.3(1).

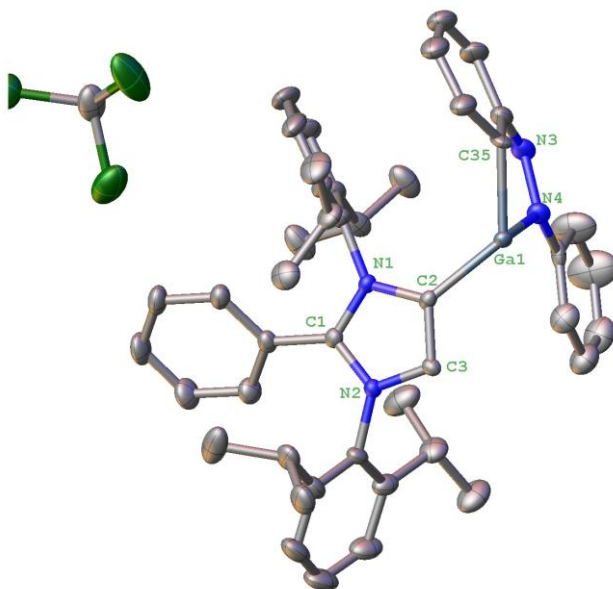


Figure S58. Solid state molecular structure of **11**. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°) for **11**: C2–Ga1 2.009(2), C3'–Ga1 2.008(2), Ga1–C35 2.052(2), Ga1–N4 1.969(2), N3–N4 1.394(3), N3–C34 1.294(4), C34–C35 1.472(4), C2–Ga1–C3' 103.8(1), N4–Ga1–C35 82.4(1).

Computational Details

The molecular structure of compound **6** was optimized at the r²SCAN-3c level of theory.¹⁰ Additionally, energies were calculated using the PBE0-D3BJ/def2-TZVPP approximation.¹¹ For this, the Orca 5.0.4 software package was utilized.¹² As the starting approximation, the solid-state molecular structure from the sc-XRD was taken. The convergence for optimization was set to TightOpt. In all Orca calculations, we used the settings TightSCF and DefGrid3, as well as the RIJCOSX accelerating approximation.¹³ The electronic structure solutions, namely closed shell singlet (**CS**, using RKS), open shell singlet diradical (**OS**, UKS), and open shell triplet (**T**, UKS) were tested. To obtain a singlet diradical solution, the triplet solution was taken and the electron spin at one of the Ga atoms was flipped. All these calculations converged effectively to RKS singlet (**CS**) solutions. The results are summarized in Table S4. Thus, compound **6** has a **CS** ground state. The optimized molecular structure is shown in Figure S62.

To investigate the electron correlation, we performed fractional occupation weighted density (FOD) analyses¹⁴ at the PBE0/def2-TZVPP ($T_{el} = 10000$ K) level of theory. The calculation produced $N_{FOD} = 2.85 e$ for **6**, suggesting a moderate level of electron correlation. The FOD plot (Figure S66) shows that the respective (HOT) electron density is mainly located at the Ga and the adjacent C atoms.

The UV-Vis spectrum for **6** was modeled using TD-DFT calculations with TDA approximation at the PBE0/def2-TZVPP level of theory, and applying the CPCM scheme for taking into account THF solvent. Selected transitions are summarized in Table S6. The TD-DFT plot of the modeled spectrum is shown in Figure S68. Frontier molecular orbitals (FMOs) are depicted in Figure S64. Natural bond orbital (NBO) analyses¹⁵ were performed using NBO 6.0.18a program¹⁶ within Gaussian 16 package.¹⁷ The wavefunction in this analysis was calculated at the RKS-PBE0/def2-TZVPP level for the optimized molecular geometry. The NBO charges and Wiberg Bond Indices (WBIs) for selected atoms and atom pairs, respectively, are collected in Table S7.

In addition to compound **6** (Figure S62), we also computationally investigated compounds **4** (Figure S59) and **5** (Figure S60) as well as the isomer **5'** (Figure S61) using the similar approximations (see above). In the isomer **5'**, each three-coordinated Ga(II) atom has an iodide substituent and an unpaired electron. Compound **5'** has the lowest energy for the **T** electronic state, while the **CS** is energetically only 0.26 kcal/mol high-lying. The other two molecules **4** and **5** have **CS** ground states. The mixed-valent Ga^I/Ga^{III} compound **5** was calculated to be energetically more stable by 17.6 kcal/mol in comparison to **5'** with formally Ga^{II} atoms. FOD calculations for **5** produced $N_{FOD} = 2.50 e$ with large localization at the two-coordinated Ga(I) atom (Figure S65). On the basis of TD-DFT calculations, the UV-Vis spectrum for **5** was simulated (Figure S67). Selected transitions are listed in Table S5. Selected frontier molecular orbitals (FMOs) of **5** are shown in Figure S63. Moreover, the NBO analyses were performed for **4** and **5**. The results are summarized in Table S7.

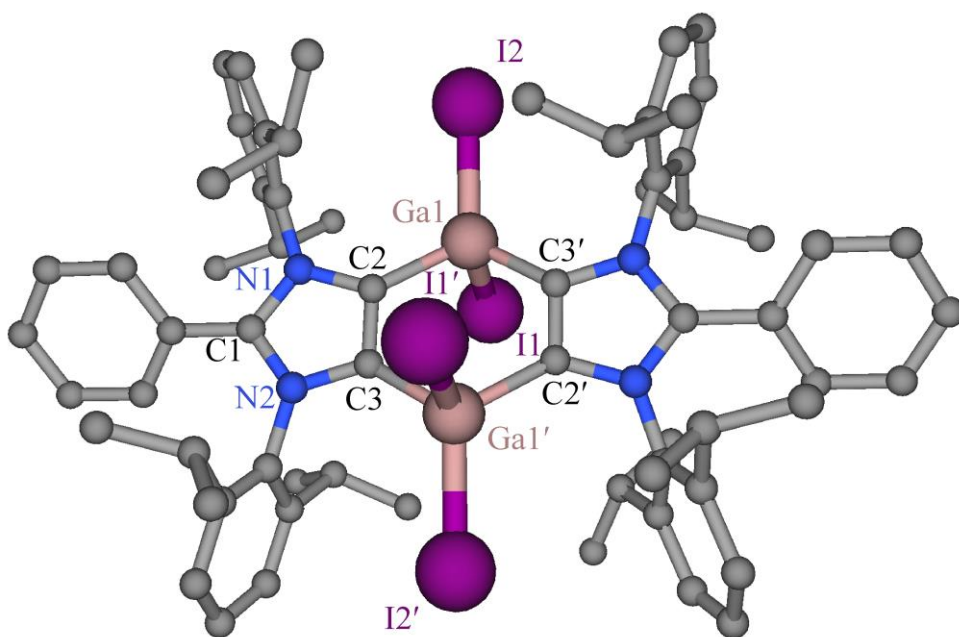


Figure S59. Optimized molecular structure of **4** (C_i symmetry) at the r^2 SCAN-3c level. Hydrogen atoms are omitted for clarity. Selected equilibrium parameters ($\text{\AA}$, $^\circ$) are: Ga1–I2 2.553, Ga1–I1 2.639, C2–Ga1 2.000, C1–N1 1.357, C1–N2 1.355, C2–N1 1.392, C2–C3 1.378, I1–Ga1–I2 108.8, C2–Ga1–I2 101.0, C2–Ga1–I1 117.6, C3–C2–Ga1 121.7, Ga1–C2–C3–N2 160.7.

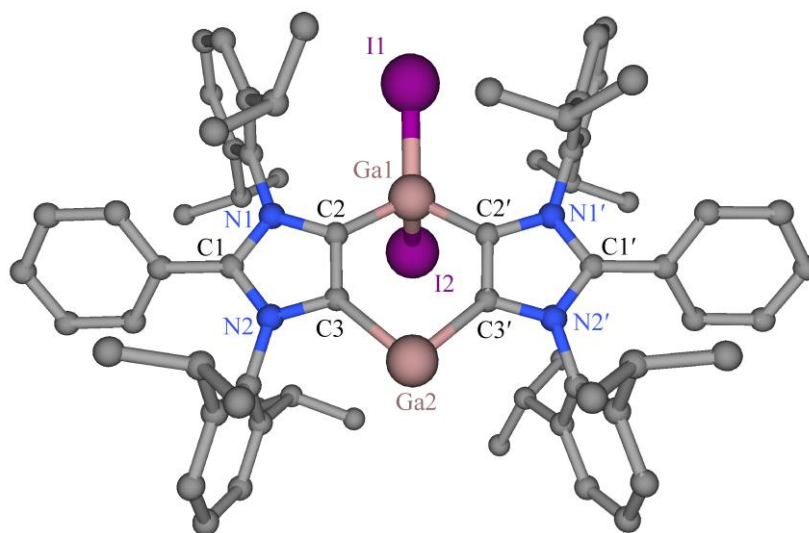


Figure S60. Optimized molecular structure of **5** (C_1 symmetry) at the r^2 SCAN-3c level. Hydrogen atoms are omitted for clarity. Ga1–I2 bond is approximately in the plane of the image; Ga1–I1 bond is oriented approximately in the direction away from the reader. Selected equilibrium parameters ($\text{\AA}$, $^\circ$) are: C3–Ga2 2.133, C2–Ga1 1.990, C2–C3 1.384, Ga1–I2 2.566, Ga1–I1 2.646, C2–C3–Ga2 129.8, C3–C2–Ga1 119.3, I1–Ga1–I2 109.1, N2–C2–C3–Ga1 160.2, N1–C2–C3–Ga2 153.4.

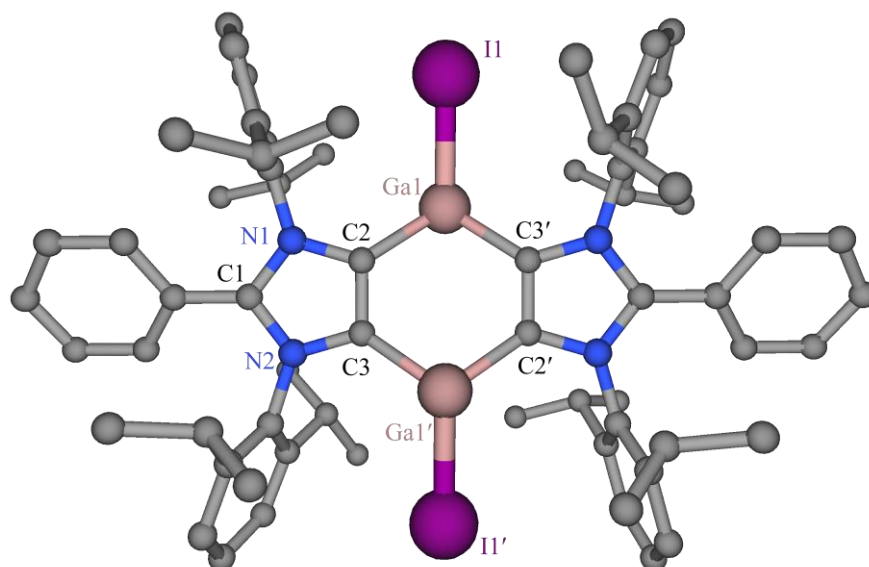


Figure S61. Optimized molecular structure of **5'** (C_i symmetry) at the r^2 SCAN-3c level. Hydrogen atoms are omitted for clarity. Selected equilibrium parameters ($\text{\AA}$, $^\circ$) are: C2–Ga1 1.968, C3'–Ga1 1.987, Ga1–I1 2.575, C2–C3 1.395, C2–Ga1–I1 120.3, C3–C2–Ga1 121.8, N2–C3–C2–Ga1 160.9.

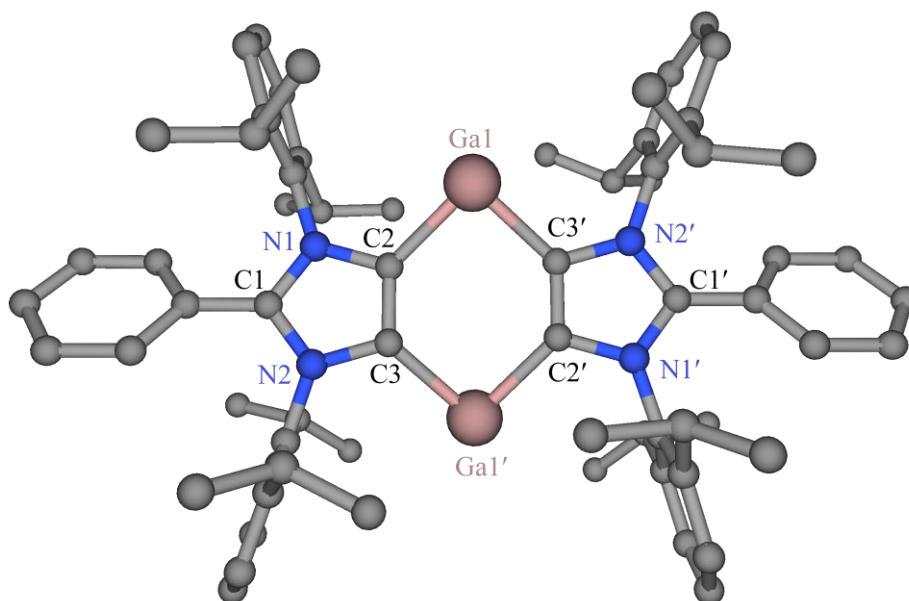


Figure S62. Optimized molecular structure of **6** (C_i symmetry) at the r^2 SCAN-3c level. Hydrogen atoms are omitted for clarity. Selected equilibrium parameters ($\text{\AA}$, $^\circ$) are: Ga1–C2 = 2.128, Ga1–C3' = 2.113, C2–C3 = 1.393, N1–C2 = 1.408, C1–N1 = 1.352, C2–Ga1–C3' = 91.8, C3–C2–Ga1 = 131.3, C2–C3–Ga1' = 127.9, Ga1'–C3–C2–Ga1 = -42.5 , C3–C2–Ga1–C3' = 32.2.

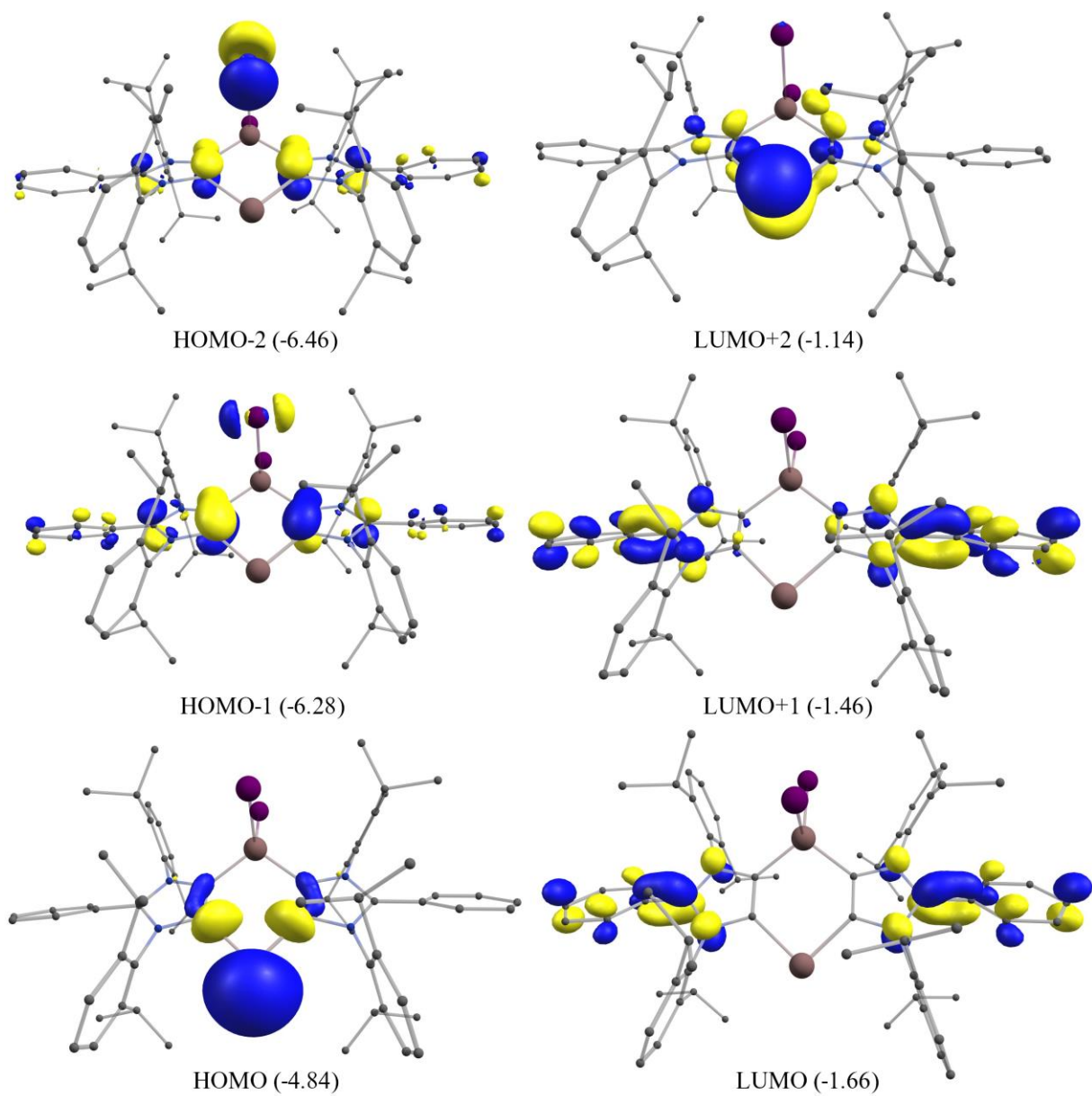


Figure S63. Frontier molecular orbitals (0.05 a.u. isosurfaces) with respective energies (in eV) of **5** in RKS-PBE0/def2-TZVPP calculation.

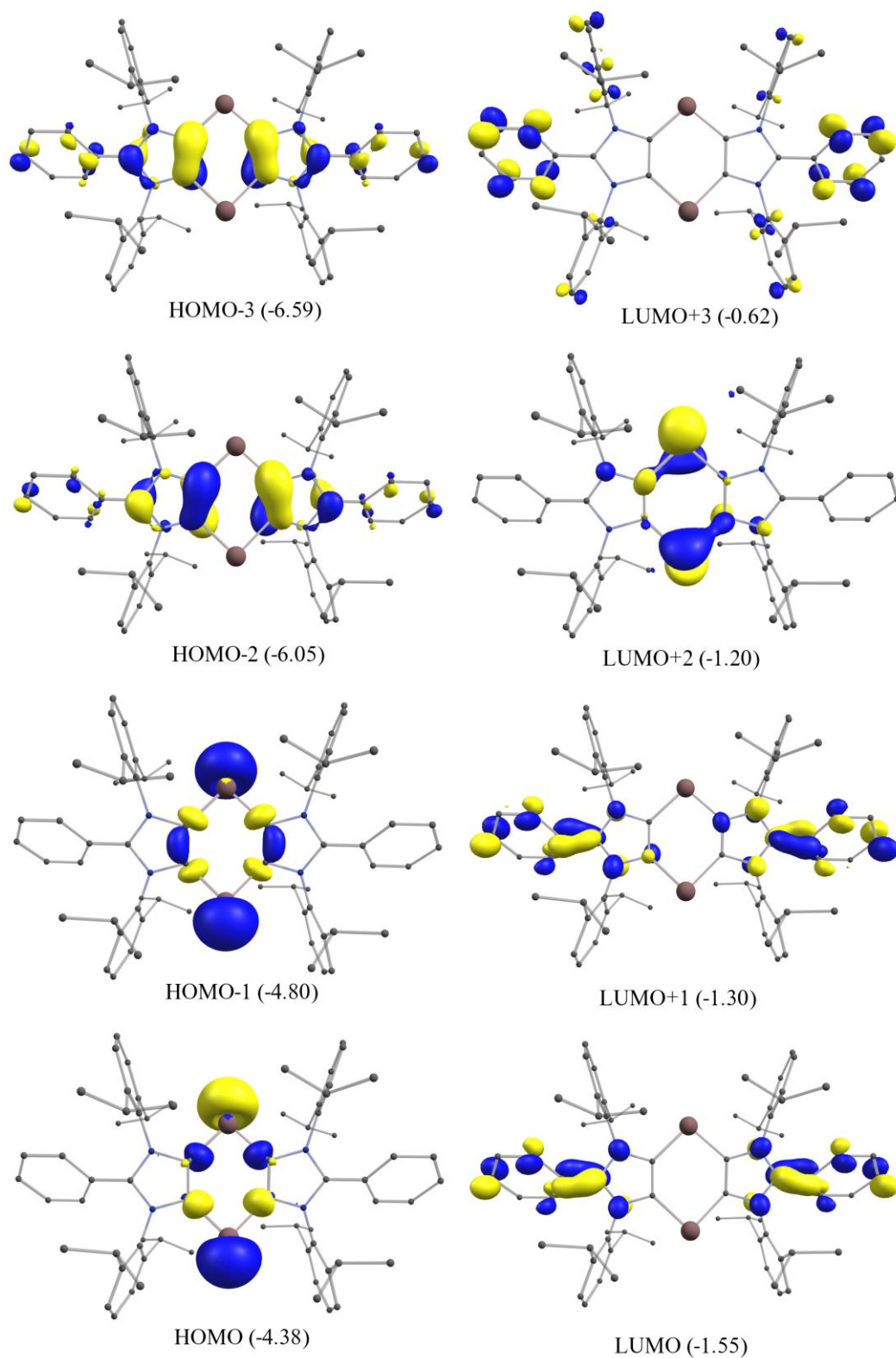


Figure S64. Frontier molecular orbitals (0.05 a.u. isosurfaces) with respective energies (in eV) of **6** in RKS-PBE0/def2-TZVPP calculation.

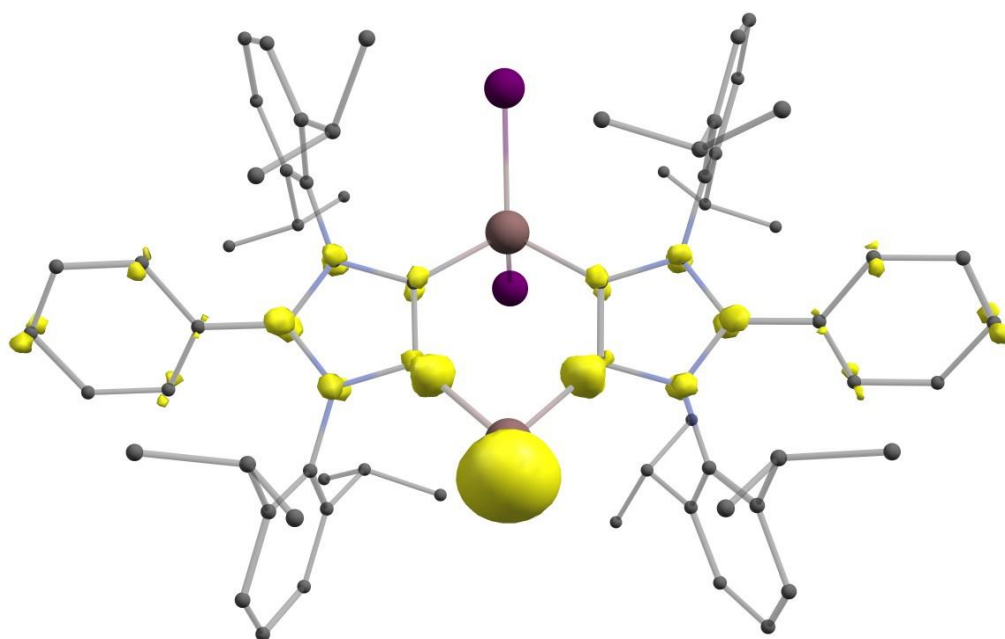


Figure S65. FOD plot (isosurfaces 0.005 a.e. in yellow) of **5**. Hydrogen atoms are omitted for clarity.

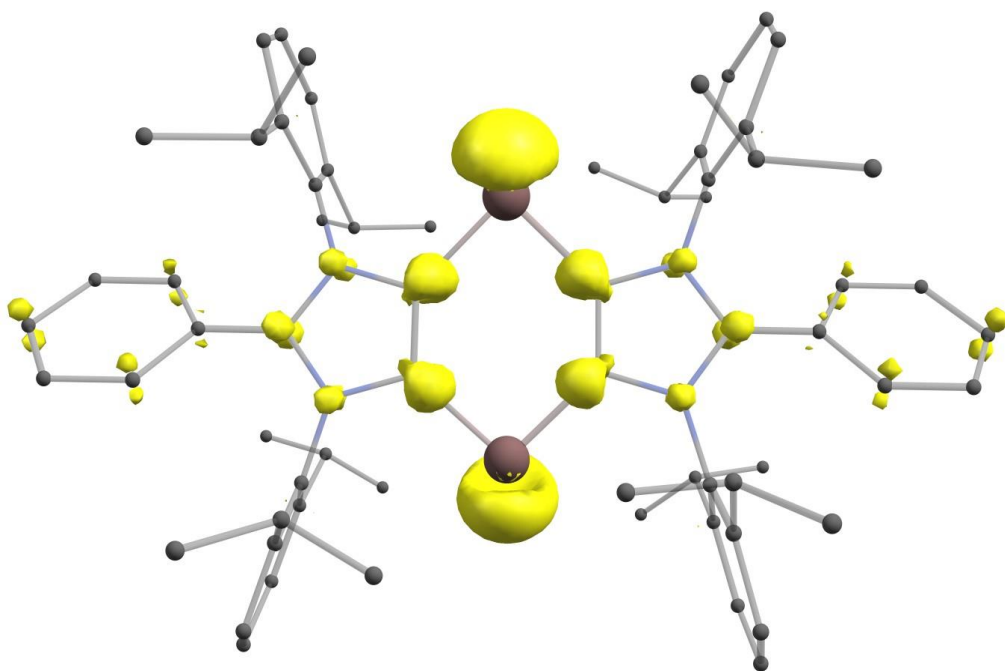


Figure S66. FOD plot (isosurfaces 0.005 a.e. in yellow) of **6**. Hydrogen atoms are omitted for clarity.

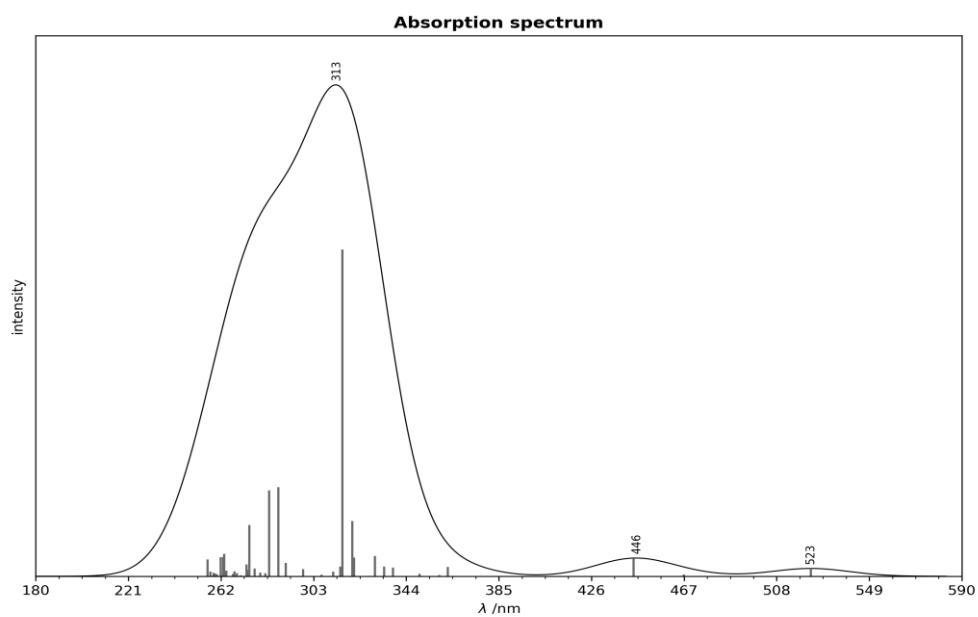


Figure S67. Plot of UV-Vis spectrum of **5** obtained from TD-DFT calculations.

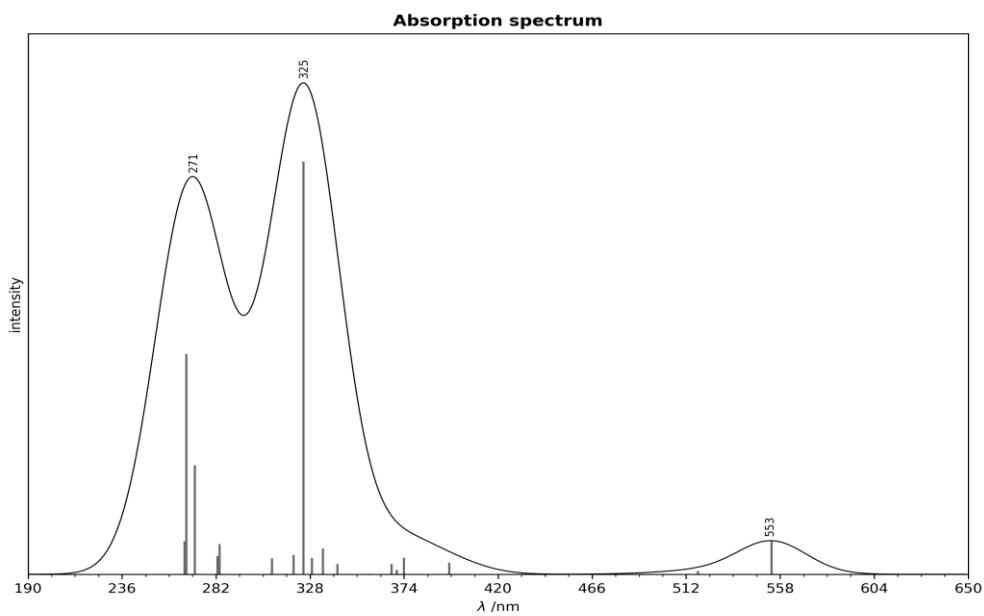


Figure S68. Plot of UV-Vis spectrum of **6** obtained from TD-DFT calculations.

Table S4. Relative energies [in kcal/mol] of **6** for different electronic solutions.

Electronic solution	6	
	PBE0-D3BJ/def2-TZVPP ^a	r ² SCAN-3c ^b
CS	0.0	0.0
OS	— ^c	— ^c
T	37.4	12.8

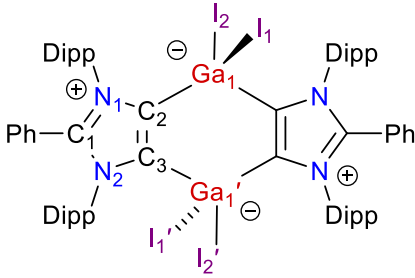
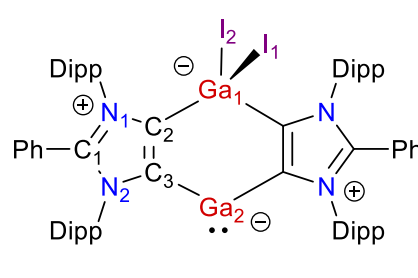
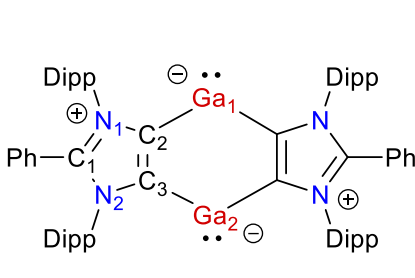
^a Vertical energies calculated for structures optimized at the r²SCAN-3c level.^b Adiabatic energies.^c SCF has converged to the CS solution.**Table S5.** Most important transitions in the TD-DFT absorption spectrum of **5**. Wavelengths λ in nm, oscillator strengths f via transition electric dipole moments and assignments are listed.

λ , nm	f	Assignment
523	0.02	91 % HOMO $\rightarrow$ LUMO
445	0.04	90 % HOMO $\rightarrow$ LUMO+2
316	0.81	82 % HOMO-1 $\rightarrow$ LUMO

Table S6. Most important transitions in the TD-DFT absorption spectrum of **6**. Wavelengths λ in nm, oscillator strengths f via transition electric dipole moments and assignments are listed.

λ , nm	f	Assignment
553	0.09	76 % HOMO $\rightarrow$ LUMO+2; 17 % HOMO $\rightarrow$ LUMO+1
325	1.11	94 % HOMO-2 $\rightarrow$ LUMO
271	0.29	72 % HOMO-3 $\rightarrow$ LUMO+2; 17 % HOMO-3 $\rightarrow$ LUMO+1
267	0.59	42 % HOMO-3 $\rightarrow$ LUMO+1; 21 % HOMO-1 $\rightarrow$ LUMO+17

Table S7. NBO charges and WBIs for compounds **4**, **5**, and **6** (all in C_i symmetry).

					
NBO (PBE0/def2-TZVPP) Charges					
Atom	q	Atom	q	Atom	q
Ga1	1.02	Ga1	1.02	Ga1	0.48
		Ga2	0.52		
I1	−0.41	I1	−0.43	C2	−0.33
I2	−0.34	I2	−0.36		
C1	0.42	C1	0.40	C1	0.38
C3	−0.31	C3	−0.30	C3	−0.34
-	-	C2	−0.35		
-	-	N1	−0.35	N1	−0.37
N2	−0.34	N2	−0.36	N2	−0.36
WBIs (PBE0/def2-TZVPP) for Selected Atom Pairs					
Atom pair	WBI	Atom pair	WBI	Atom pair	WBI
Ga1–I1	0.75	Ga1–I1	0.74	-	-
Ga1–I2	0.89	Ga1–I2	0.86	-	-
Ga1–C2	0.54	Ga1–C2	0.56	Ga1–C2	0.47
-	-	Ga2–C3	0.45	Ga1–C3'	0.47
N1–C1	1.25	N1–C1	1.25	N1–C1	1.25
C2–N1	1.12	C2–N1	1.10	N1–C2	1.09
C1–N2	1.26	C1–N2	1.24	N2–C1	1.25
N2–C3	1.11	N2–C3	1.10	N2–C3	1.09
C2–C3	1.58	C2–C3	1.57	C2–C3	1.57

Cartesian Coordinates

Optimized Cartesian coordinates of **4** (RKS singlet) at the r²SCAN-3c level.

I	1.204319337	0.024829215	-3.202244917
I	1.319907462	-3.795839496	-1.413265618
Ga	0.674440612	-1.357599099	-1.018101593
N	-2.376197912	-1.574973520	-1.313882754
N	-3.036478118	0.393757198	-0.686331345
C	-3.454555716	-0.751471760	-1.277915896
C	-1.265482913	-0.942581879	-0.762960176
C	-1.691393939	0.297448718	-0.338755080
C	-4.799897211	-1.046778422	-1.777244587
C	-5.353713857	-2.330148487	-1.639007011
H	-4.796142131	-3.119546829	-1.152866224
C	-6.627448558	-2.603528225	-2.117325734
H	-7.034466053	-3.602740517	-1.995603154
C	-7.377347921	-1.612097368	-2.741847195
H	-8.373249520	-1.831251496	-3.115298025
C	-6.838799929	-0.337565622	-2.882802158
H	-7.408617943	0.447452637	-3.370758333
C	-5.565994622	-0.053828409	-2.407720855
H	-5.169448605	0.944350572	-2.533142329
C	-2.407470390	-2.948492483	-1.753206236
C	-2.474041144	-3.223838555	-3.122187886
C	-2.611535544	-4.563193420	-3.496690300
H	-2.670156829	-4.816933791	-4.550820305
C	-2.662370049	-5.567669372	-2.545469924
H	-2.771640754	-6.602811106	-2.856427779
C	-2.541392429	-5.263705271	-1.193766561
H	-2.539878056	-6.069178998	-0.468003070

C	-2.401280706	-3.947581165	-0.760452385
C	-2.369938548	-2.155333162	-4.193425526
H	-2.183480229	-1.189576895	-3.707598025
C	-1.173854904	-2.438522561	-5.114722535
H	-0.254446903	-2.578050468	-4.540048106
H	-1.346349520	-3.336526887	-5.718434147
H	-1.020552168	-1.596049701	-5.797132313
C	-3.663328110	-2.041635429	-5.014152203
H	-3.850951649	-2.965675787	-5.572684739
H	-4.533992752	-1.846987265	-4.381804061
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H	-1.551734623	-2.784505896	0.809096577
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H	-3.979138647	-2.251582838	0.868386628
H	-4.344762517	-3.940961816	1.271000429
H	-3.429575892	-2.918423943	2.402662842
C	-1.685896462	-4.779990430	1.534956483
H	-2.404595677	-5.601526910	1.635358828
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H	-1.452172374	-4.427574741	2.544208744
C	-3.776867207	1.630633777	-0.635464811
C	-3.540326645	2.553550791	-1.667944084
C	-4.266255326	3.742731861	-1.633034948
H	-4.107242084	4.487244115	-2.407682309
C	-5.186932739	3.988538731	-0.622381821
H	-5.744392721	4.920901985	-0.615289658
C	-5.387471537	3.058023587	0.386270802
H	-6.097177890	3.271902311	1.179409273
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C	-2.546588904	2.301445647	-2.791146083

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C	-4.888184959	0.862914275	1.535901175
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H	-3.887710682	2.125265444	3.008594215
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H	-4.803888309	0.776235904	3.696095504
C	-6.227061373	0.125697537	1.376592684
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I	-1.204319337	-0.024829215	3.202244917
I	-1.319907462	3.795839496	1.413265618
Ga	-0.674440612	1.357599099	1.018101593
N	2.376197912	1.574973520	1.313882754
N	3.036478118	-0.393757198	0.686331345
C	3.454555716	0.751471760	1.277915896
C	1.265482913	0.942581879	0.762960176
C	1.691393939	-0.297448718	0.338755080
C	4.799897211	1.046778422	1.777244587
C	5.353713857	2.330148487	1.639007011
H	4.796142131	3.119546829	1.152866224
C	6.627448558	2.603528225	2.117325734

H	7.034466053	3.602740517	1.995603154
C	7.377347921	1.612097368	2.741847195
H	8.373249520	1.831251496	3.115298025
C	6.838799929	0.337565622	2.882802158
H	7.408617943	-0.447452637	3.370758333
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H	5.169448605	-0.944350572	2.533142329
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C	2.474041144	3.223838555	3.122187886
C	2.611535544	4.563193420	3.496690300
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C	1.173854904	2.438522561	5.114722535
H	0.254446903	2.578050468	4.540048106
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H	6.344557427	0.616342309	-2.174205414
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Optimized Cartesian coordinates of 5 (RKS singlet) at the r²SCAN-3c level.

```
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N -2.38045685826612 -1.60774006651531 -1.12648549062545  
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C -1.70374902561820 0.29766150113461 -0.24157783612418  
C -4.73730616877915 -1.05518409622315 -1.82503617399316  
C -5.33139832526624 -2.31732238149366 -1.65940631455217  
H -4.83546642780118 -3.08257730696195 -1.07641081376714  
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H -7.00503592753229 -3.57859364252463 -2.08661686205167  
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H -8.19664763032008 -1.85628838033706 -3.42694935452096  
C -6.65209847906431 -0.38015844749221 -3.15205181814390  
H -7.15837060496701 0.38241962015324 -3.73641534206808  
C -5.41871664520813 -0.09177064419355 -2.58397607305366  
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H	-4.47542467318317	-3.90924084707828	1.34138564694533
H	-3.62709612253465	-2.87509310273957	2.51438336867911
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H	-2.59410748884243	-5.58791003956312	1.86796542696900
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C	-3.52819459728127	2.55987056139917	-1.72237756156749
C	-4.22683129141084	3.76444935219870	-1.68975392831562
H	-4.06414710027046	4.50034964458450	-2.47138009772682
C	-5.13033600882120	4.03634477040532	-0.66982661149327
H	-5.66665720107315	4.98096909501911	-0.66172833960798
C	-5.34235711256980	3.11427365300454	0.34329150927788
H	-6.04100591003966	3.34628008358143	1.14097934519887
C	-4.65233123806623	1.90038073104102	0.37094114754276
C	-2.55227105524250	2.26313747179598	-2.84904741688950
H	-2.34262845688766	1.18617153645714	-2.84731104522273
C	-3.11380529630764	2.61804377807141	-4.23238752599316
H	-3.22787577725773	3.69987825382375	-4.35635839520886

H	-2.42429739739706	2.27210999796201	-5.00982234807056
H	-4.08847814476678	2.15306598840950	-4.41375166186036
C	-1.22132969574351	2.98974780490842	-2.61647867908922
H	-1.37267909488145	4.07494026435293	-2.60819318984763
H	-0.78156093368893	2.71225408467464	-1.65492920664661
H	-0.50887825704599	2.74322453118689	-3.41222989488019
C	-4.87883650112880	0.91373481152773	1.49940627700317
H	-4.05832730228368	0.18597797502092	1.48687734514466
C	-4.84722514852775	1.59505086175557	2.87275996984041
H	-3.94445451319764	2.20059229160333	2.99299668633786
H	-5.72323136347582	2.23563193356542	3.02488471460869
H	-4.84878458281487	0.83440698917148	3.65979157609047
C	-6.20128970862744	0.15586738553435	1.30270298571815
H	-6.33045545194922	-0.58912603150006	2.09591430848421
H	-7.04925692184295	0.84953087015095	1.34647117902319
H	-6.23865325465825	-0.35813900014149	0.33727436038857
I	-1.26194299220090	0.02941666887214	3.33590840656928
I	-1.35185011943510	3.83129680832301	1.44564602533509
Ga	-0.71838845450988	1.36603116482552	1.11740833267855
N	2.34824911791094	1.60807023389506	1.30940741022091
N	2.94521111689455	-0.40027222370132	0.76460848363113
C	3.40959151106787	0.76340360750216	1.27904225186589
C	1.20634159610054	0.95703834353981	0.83722670610920
C	1.57996612685355	-0.32198341577495	0.46571506431323
C	4.76988357821798	1.03804656359300	1.74248206635922
C	5.36130492204350	2.30098501481259	1.57843307346356
H	4.81774958432793	3.10294057810634	1.09636240587429
C	6.65019684726876	2.54031997691673	2.03532563607448
H	7.08650629034627	3.52485163830120	1.89589516891738
C	7.37750343906831	1.53459771022228	2.66373755323948
H	8.38540361862552	1.72712430336411	3.01922755253761

C	6.79836142384755	0.28141141686804	2.83774605083175
H	7.34771773448379	-0.51145558586380	3.33650118103290
C	5.51009492031782	0.03325938215214	2.38621340214524
H	5.07436099268291	-0.94473147445566	2.54481051873300
C	2.41173026692924	2.98037515363057	1.74630797452770
C	2.50093865361853	3.25363705373857	3.11561288590240
C	2.66359456812047	4.58939470051573	3.49239649397583
H	2.74085447023536	4.83774932546423	4.54664501607634
C	2.71439149691455	5.59794069048331	2.54549643731124
H	2.84226368581551	6.63017570746815	2.85892631921709
C	2.56762653182414	5.29988061701761	1.19546890820741
H	2.56487370240054	6.10773927333752	0.47208062424350
C	2.40331156518364	3.98667683236974	0.76229375165382
C	2.39410729222843	2.18595336260326	4.18738630099524
H	2.18782047956120	1.22337084034913	3.70362682795652
C	1.21306326862449	2.48626977748489	5.12260684639470
H	0.28880786356314	2.63715950849996	4.55868502532108
H	1.40494835945478	3.38263500838128	5.72306115305470
H	1.05570698606273	1.64647624678061	5.80727949099456
C	3.69571598093649	2.05492975529330	4.99250834281497
H	3.89915693278487	2.97456746736064	5.55286485606644
H	4.55687742371153	1.85463064641561	4.34897642481280
H	3.60737563865533	1.23692964077693	5.71610600436658
C	2.23354745754058	3.66699750680035	-0.71535496208638
H	1.55954759540035	2.80460578703908	-0.78680862777144
C	3.56463639580756	3.26999250532967	-1.37467882182245
H	4.01287184207224	2.38743210409402	-0.90950668878271
H	4.28794038653347	4.09188006454562	-1.30865456972741
H	3.40550722765159	3.04199169280002	-2.43454648995478
C	1.58830983699820	4.81244450705950	-1.49922673952950
H	2.26530490518691	5.66806921211376	-1.60168613496051

H	0.66399653985944	5.14852966598670	-1.01918695628022
H	1.34629125473062	4.47063010791550	-2.51039031651709
C	3.70007069235062	-1.61392002524829	0.60386143514837
C	3.50347652330855	-2.62978608383164	1.55225733369901
C	4.23688911957450	-3.80476955486407	1.39195103720858
H	4.10962332332036	-4.61532825262604	2.10362540469415
C	5.12921468175313	-3.95163649193537	0.33712778795548
H	5.69575703149485	-4.87266316265844	0.23287645385745
C	5.29047723171811	-2.93284054619457	-0.59081372240101
H	5.97821727682723	-3.06698864890902	-1.42079613032305
C	4.56824832728170	-1.74297809136100	-0.48532121137521
C	2.52671872017406	-2.48278049408650	2.70577426135469
H	2.18821881933236	-1.44162902917918	2.75182644412235
C	3.15757350142294	-2.82122725064026	4.06264305623140
H	3.43933769807842	-3.87754268834330	4.12877211368576
H	2.43686524626292	-2.62016093950405	4.86224186526104
H	4.05230358052367	-2.21968632504058	4.25580811450134
C	1.28228084319422	-3.34417835449602	2.46062719485668
H	1.53709644179838	-4.41051088537198	2.45850310802377
H	0.82678228487789	-3.10898710395123	1.49077537971657
H	0.53379081742258	-3.15804468500208	3.23716611406773
C	4.72244974963532	-0.66086791489633	-1.53496735292333
H	4.00013477804045	0.13212953069260	-1.31165939601503
C	4.38013903606852	-1.19607069468764	-2.93229387205151
H	3.38395192239904	-1.65069545119336	-2.93804379661577
H	5.10544539775958	-1.94888032232788	-3.26021076365366
H	4.39747009647657	-0.37800445833775	-3.66103024854036
C	6.12896971590510	-0.04630943071558	-1.50431087991301
H	6.19807344047413	0.77770578856498	-2.22353197144661
H	6.88552888406190	-0.79178010803876	-1.77455862156231
H	6.37677838925763	0.34156153954313	-0.51103381718865

Optimized Cartesian coordinates of 5' (UKS triplet) at the r²SCAN-3c level.

I	2.281208763	-0.713755901	3.593556010
Ga	0.574585490	-0.397054478	1.692171615
N	0.390588611	2.653497013	1.601359081
N	-0.905996508	2.987066882	-0.110050947
C	-0.329932118	3.621889685	0.954516298
C	0.259207713	1.424517696	0.967729030
C	-0.552525794	1.643583718	-0.145458137
C	-0.470802263	5.014019397	1.340555984
C	0.555269252	5.692442758	2.033986723
H	1.480272053	5.187450815	2.276663104
C	0.404002240	7.018002105	2.409175255
H	1.214647618	7.509878178	2.938978201
C	-0.762138048	7.718165256	2.108766079
H	-0.874228913	8.756413504	2.405398462
C	-1.781267089	7.064197385	1.420680016
H	-2.701356919	7.588531692	1.178857792
C	-1.644986513	5.737666534	1.043258854
H	-2.460382150	5.259465111	0.518774963
C	1.133443649	2.854466103	2.814228380
C	0.428713877	3.011448470	4.011596668
C	1.173642405	3.274814775	5.163252917
H	0.661618375	3.402325253	6.112642163
C	2.554811834	3.368445704	5.110536110
H	3.117782130	3.577240571	6.015808531
C	3.229470779	3.165813714	3.911357211
H	4.313296951	3.201639820	3.900572528
C	2.536687473	2.891067958	2.734952693
C	-1.079194082	2.873545770	4.100578308
H	-1.472599875	2.703670942	3.092121914

C	-1.452891513	1.646763218	4.946006525
H	-0.987202280	0.739038781	4.548338000
H	-1.123155005	1.767897035	5.983770663
H	-2.539846728	1.508352840	4.950618374
C	-1.739699235	4.146845694	4.646513285
H	-1.445994913	4.331036019	5.685873773
H	-1.464353876	5.024752865	4.053846381
H	-2.830321661	4.043725442	4.622774952
C	3.265341125	2.648345206	1.421716397
H	2.706553818	1.873248996	0.881499360
C	3.284380575	3.905099915	0.535839552
H	2.277787127	4.251673477	0.283948897
H	3.808568272	4.725462313	1.040695637
H	3.808520982	3.693375799	-0.402731710
C	4.689266911	2.122463702	1.616379005
H	5.357544803	2.893246903	2.017231039
H	4.704154429	1.258334582	2.288035789
H	5.097344255	1.811219608	0.649263966
C	-1.798778928	3.573918512	-1.070185131
C	-3.177683118	3.393543092	-0.879046432
C	-4.030550685	3.950189122	-1.830039616
H	-5.104254020	3.824871857	-1.725052270
C	-3.526384264	4.662685132	-2.911097649
H	-4.208425950	5.089474400	-3.640903696
C	-2.157886138	4.821545060	-3.071029093
H	-1.778078769	5.370508917	-3.927627540
C	-1.259246965	4.268032259	-2.157535326
C	-3.740751662	2.641102111	0.315551466
H	-2.922718851	2.458192651	1.022206192
C	-4.815760401	3.448063503	1.057284835
H	-5.706949237	3.596553353	0.438520335

H	-5.127680214	2.907821706	1.957660202
H	-4.447790474	4.432205897	1.365138746
C	-4.293944609	1.272405706	-0.104825558
H	-5.112990315	1.385622997	-0.824255861
H	-3.521039704	0.662540749	-0.580340064
H	-4.674892198	0.734290436	0.770514078
C	0.235754909	4.428332493	-2.354213076
H	0.744873153	3.783321159	-1.628583388
C	0.674496558	3.967898562	-3.750684836
H	0.324080980	2.951997970	-3.958153270
H	0.285917542	4.629469848	-4.532557110
H	1.767649711	3.980709678	-3.819985676
C	0.672663474	5.876688359	-2.088168187
H	1.760005225	5.969415983	-2.188845969
H	0.206824839	6.559331641	-2.808204702
H	0.390073022	6.203202650	-1.082233185
I	-2.281208763	0.713755901	-3.593556010
Ga	-0.574585490	0.397054478	-1.692171615
N	-0.390588611	-2.653497013	-1.601359081
N	0.905996508	-2.987066882	0.110050947
C	0.329932118	-3.621889685	-0.954516298
C	-0.259207713	-1.424517696	-0.967729030
C	0.552525794	-1.643583718	0.145458137
C	0.470802263	-5.014019397	-1.340555984
C	-0.555269252	-5.692442758	-2.033986723
H	-1.480272053	-5.187450815	-2.276663104
C	-0.404002240	-7.018002105	-2.409175255
H	-1.214647618	-7.509878178	-2.938978201
C	0.762138048	-7.718165256	-2.108766079
H	0.874228913	-8.756413504	-2.405398462
C	1.781267089	-7.064197385	-1.420680016

H	2.701356919	-7.588531692	-1.178857792
C	1.644986513	-5.737666534	-1.043258854
H	2.460382150	-5.259465111	-0.518774963
C	-1.133443649	-2.854466103	-2.814228380
C	-0.428713877	-3.011448470	-4.011596668
C	-1.173642405	-3.274814775	-5.163252917
H	-0.661618375	-3.402325253	-6.112642163
C	-2.554811834	-3.368445704	-5.110536110
H	-3.117782130	-3.577240571	-6.015808531
C	-3.229470779	-3.165813714	-3.911357211
H	-4.313296951	-3.201639820	-3.900572528
C	-2.536687473	-2.891067958	-2.734952693
C	1.079194082	-2.873545770	-4.100578308
H	1.472599875	-2.703670942	-3.092121914
C	1.452891513	-1.646763218	-4.946006525
H	0.987202280	-0.739038781	-4.548338000
H	1.123155005	-1.767897035	-5.983770663
H	2.539846728	-1.508352840	-4.950618374
C	1.739699235	-4.146845694	-4.646513285
H	1.445994913	-4.331036019	-5.685873773
H	1.464353876	-5.024752865	-4.053846381
H	2.830321661	-4.043725442	-4.622774952
C	-3.265341125	-2.648345206	-1.421716397
H	-2.706553818	-1.873248996	-0.881499360
C	-3.284380575	-3.905099915	-0.535839552
H	-2.277787127	-4.251673477	-0.283948897
H	-3.808568272	-4.725462313	-1.040695637
H	-3.808520982	-3.693375799	0.402731710
C	-4.689266911	-2.122463702	-1.616379005
H	-5.357544803	-2.893246903	-2.017231039
H	-4.704154429	-1.258334582	-2.288035789

H	-5.097344255	-1.811219608	-0.649263966
C	1.798778928	-3.573918512	1.070185131
C	3.177683118	-3.393543092	0.879046432
C	4.030550685	-3.950189122	1.830039616
H	5.104254020	-3.824871857	1.725052270
C	3.526384264	-4.662685132	2.911097649
H	4.208425950	-5.089474400	3.640903696
C	2.157886138	-4.821545060	3.071029093
H	1.778078769	-5.370508917	3.927627540
C	1.259246965	-4.268032259	2.157535326
C	3.740751662	-2.641102111	-0.315551466
H	2.922718851	-2.458192651	-1.022206192
C	4.815760401	-3.448063503	-1.057284835
H	5.706949237	-3.596553353	-0.438520335
H	5.127680214	-2.907821706	-1.957660202
H	4.447790474	-4.432205897	-1.365138746
C	4.293944609	-1.272405706	0.104825558
H	5.112990315	-1.385622997	0.824255861
H	3.521039704	-0.662540749	0.580340064
H	4.674892198	-0.734290436	-0.770514078
C	-0.235754909	-4.428332493	2.354213076
H	-0.744873153	-3.783321159	1.628583388
C	-0.674496558	-3.967898562	3.750684836
H	-0.324080980	-2.951997970	3.958153270
H	-0.285917542	-4.629469848	4.532557110
H	-1.767649711	-3.980709678	3.819985676
C	-0.672663474	-5.876688359	2.088168187
H	-1.760005225	-5.969415983	2.188845969
H	-0.206824839	-6.559331641	2.808204702
H	-0.390073022	-6.203202650	1.082233185

Optimized Cartesian coordinates of **6** (RKS singlet) at the r²SCAN-3c level.

N	2.464306777	1.591524621	0.848897050
N	2.249933166	1.677976913	-1.300164649
C	3.030818720	2.090319502	-0.272925942
C	1.294993471	0.865919639	0.552446704
C	1.164968771	0.907619231	-0.834163660
C	4.210839243	2.946962908	-0.356241607
C	5.325142523	2.746281949	0.472239947
H	5.336493121	1.927452768	1.179576738
C	6.426564250	3.587376319	0.389351022
H	7.278578623	3.412542232	1.039708560
C	6.445588368	4.639705739	-0.521020477
H	7.309689357	5.294491628	-0.583496438
C	5.346609767	4.845833089	-1.349913675
H	5.344234369	5.666164764	-2.061667219
C	4.240302635	4.012747119	-1.267280402
H	3.385703590	4.193465996	-1.905615339
C	2.942764412	1.810057815	2.187221477
C	3.771286179	0.833827183	2.763966266
C	4.176878884	1.031965726	4.082482330
H	4.814329008	0.298005493	4.565444630
C	3.787363165	2.166116004	4.785504871
H	4.115020383	2.303545570	5.812086570
C	2.990041708	3.125518326	4.180251068
H	2.698904734	4.010717009	4.738078825
C	2.542829196	2.965514429	2.867501178
C	4.220780684	-0.387715732	1.979702868
H	4.189712013	-0.130053754	0.912707428
C	5.657488404	-0.813593610	2.303600404
H	6.360498927	0.023707747	2.234316142

H	5.979186977	-1.587433325	1.598921695
H	5.737054622	-1.238990459	3.309608167
C	3.255766823	-1.559895722	2.192879207
H	3.202516659	-1.822121759	3.255422891
H	3.591814429	-2.441057224	1.633773070
H	2.249727617	-1.303598492	1.848761803
C	1.678184150	4.030490997	2.221895159
H	1.330616737	3.647492907	1.255064957
C	0.431772101	4.335525859	3.062776061
H	-0.120891324	3.414633966	3.277705034
H	-0.226613759	5.022479482	2.519524588
H	0.696191976	4.813566140	4.012612162
C	2.496966969	5.304970066	1.963475144
H	2.828923443	5.749884013	2.908589555
H	1.887213258	6.048328880	1.437395590
H	3.385503254	5.096236482	1.358916043
C	2.622183794	1.802861221	-2.686392508
C	1.999966309	2.773898155	-3.484405136
C	2.405542489	2.876310000	-4.814721486
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C	3.392419834	2.045232701	-5.327510002
H	3.698865504	2.144200747	-6.364987068
C	3.976756146	1.079151556	-4.521685411
H	4.733490226	0.420046355	-4.937482127
C	3.597858870	0.928831428	-3.187407473
C	0.882572812	3.654992079	-2.959318813
H	0.845895642	3.548001238	-1.868250337
C	1.073291713	5.142085781	-3.285983136
H	2.031899169	5.529306771	-2.925505519
H	0.276248724	5.729240492	-2.817359716
H	1.023473029	5.325923904	-4.364261607

C	-0.455954170	3.157449801	-3.520684156
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H	-1.293661594	3.689587445	-3.056912231
H	-0.577499312	2.083662731	-3.342647217
C	4.222360886	-0.169474619	-2.347615972
H	3.737285308	-0.166411612	-1.364970102
C	5.724394281	0.069669735	-2.139216179
H	6.139056955	-0.686448148	-1.462297923
H	5.918046751	1.058640925	-1.712360018
H	6.266428418	0.000018375	-3.089157632
C	3.962000348	-1.550047081	-2.966424764
H	4.476781026	-1.659974541	-3.927398496
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H	-3.385503254	-5.096236482	-1.358916043
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C	-1.999966309	-2.773898155	3.484405136

C	-2.405542489	-2.876310000	4.814721486
H	-1.940827086	-3.616131004	5.459935897
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C	-0.882572812	-3.654992079	2.959318813
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C	0.455954170	-3.157449801	3.520684156
H	0.501224155	-3.317117586	4.604389929
H	1.293661594	-3.689587445	3.056912231
H	0.577499312	-2.083662731	3.342647217
C	-4.222360886	0.169474619	2.347615972
H	-3.737285308	0.166411612	1.364970102
C	-5.724394281	-0.069669735	2.139216179
H	-6.139056955	0.686448148	1.462297923
H	-5.918046751	-1.058640925	1.712360018
H	-6.266428418	-0.000018375	3.089157632
C	-3.962000348	1.550047081	2.966424764
H	-4.476781026	1.659974541	3.927398496
H	-2.889380832	1.702880355	3.128848788
H	-4.331320071	2.336015980	2.297922205
Ga	0.121320222	-0.440674385	-2.082708648

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