Supporting information

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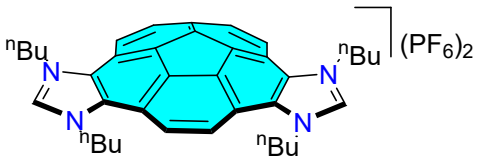
General considerations. The tetraamine corannulene[1] was prepared according to literature methods. All other reagents were used as received from commercial suppliers. NMR spectra were recorded on a Bruker 300 MHz, Bruker 400 MHz or Varian 500 MHz using $CDCl_3$, CD_2Cl_2, toluene-d_8, and tetrachloroethane-d_2 as solvents. Infrared spectra (FTIR) were performed on a FT/IR-6200 (Jasco) spectrometer equipped with a Pro One ATR with a spectral window of 4000-400 cm^{-1}. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulizing gas. Elemental analyses were carried out on a TruSpec Micro Series. Isothermal titration was performed on a TA Nano Isothermal Titration Calorimeter at 25 ˚C. Electrochemical studies were carried out by using an Autolab Potentiostat (Model PGSTAT101) using a three-electrode cell. The cell was equipped with platinum working and counter electrodes, as well as a silver wire reference electrode. In all experiments, $[NBu_4](PF_6)$ (0.1 M in dry CH_2Cl_2) was used as the supporting electrolyte with analyze concentration of approximately 1 mM. Measurements were performed at 50 mVs^{-1} scan rates. All redox potentials were referenced to the Fc/Fc^+ couple as internal standard with $E_{1/2}(Fc/Fc^+)$ *vs*. SCE = +0.44 V.

1. Synthesis and characterization of the compounds.

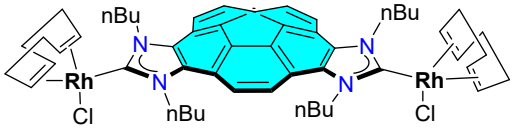


Synthesis of compound $[A](PF_6)_2$.

A Schlenk tube containing a mixture of tetraamine corannulene (150 mg, 0.28 mmol), 4 mL of tributyl orthoformate and NH_4PF_6 (150 mg, 0.92 mmol) was heated at 150 ºC for 12 h. A sticky precipitate crashed out from an orange solution. The solution was discarded and the precipitate was dissolved in copious amount of methanol. The solution was filtrated and removed under vacuum obtained a pale orange solid. The solid was purified by liquid-liquid extraction in H_2O/CH_2Cl_2, then the aqueous phase was removed in vacuum obtained a yellow solid. Yield: 168 mg (71 %). HR-MS (*m/z*): 278.2 $[M]^{2+}$ Elemental analysis calcd (%) for $C_{38}H_{44}N_4P_2F_{12}$: C, 53.90; H, 5.24; N, 6.62. Found C, 53.20; H, 5.46; N, 6.63. ^1H NMR (300 MHz, CD_2Cl_2): δ (ppm) 9.53 (s, 2H, NC*H*N), 8.23 (s, 2H, CH_{cor}), 8.07 (s, 4H, CH_{cor}), 5.01-4.75 (m, 8H, NCH_2CH$_2$CH$_2$CH$_3$), 2.35-2.16 (m, 8H, NCH$_2$CH_2CH$_2$CH$_3$), 1.71-1.53 (m, 8H, NCH$_2$CH$_2$CH_2CH$_3$), 1.12-1.04 (m, 12H, NCH$_2$CH$_2$CH$_2$CH_3). $^{19}F\{^1H\}$ NMR (282 MHz, CD_2Cl_2): -70.53 (d, $^1J_{P\text{-}F}$ = 711 Hz,). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ (ppm) 139.41 (NCHN), 133.66 (C_q), 132.18 (C_q), 132.13 (C_q), 130.38 (C_q), 130.26 (C_q), 129.92 (C_q),

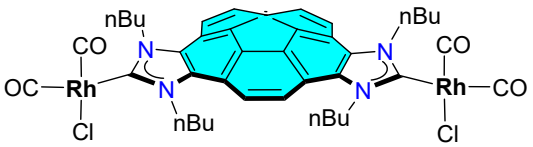
129.27 (CH_{cor}), 125.04 (CH_{cor}), 123.62 (CH_{cor}), 119.25 (C_q), 118.76 (C_q), 50.75 (N$CH_2CH_2CH_2CH_3$), 31.49 (N$CH_2CH_2CH_2CH_3$), 20.14 (N$CH_2CH_2CH_2CH_3$), 13.68 (N$CH_2CH_2CH_2CH_3$).

Synthesis of complex 1.



A Schlenk flask was loaded with **[A](PF$_6$)$_2$** (100 mg, 0.12 mmol), [RhCl(COD)]$_2$ (58 mg, 0.12 mmol) and K_2CO_3 (50 mg, 0.36 mmol). The mixture was suspended in acetone (10 mL) and stirred for 12 h at 60 ºC. The resulting solid was filtered and washed several times with acetone. The crude mixture was dissolved in CH_2Cl_2 and purified by filtration through a pad of Celite. The resulting solution was concentrated to dryness of a yellow solid. Yield: 83.9 mg (68 %). HRMS ESI-TOF-MS (positive mode): 1011.3090 [M-Cl]$^+$. Elemental analysis calcd (%) for $C_{54}H_{66}N_4Cl_2Rh_2$ (1047.828): C, 61.89; H, 6.35; N, 5.35. Found: C, 61.88; H, 6.32; N, 5.33^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.17 (s, 2H, CH_{cor}), 8.07-7.99 (m, 4H, CH_{cor}), 5.53-5.37 (m, 4H, CH_{COD}), 5.30-5.13 (m, 8H, NCH_2CH$_2$CH$_2$CH$_3$), 3.56-3.41 (m, 4H, CH_{COD}), 2.63-2.38 (m, 12H, CH_{2COD}), 2.24-2.12 (m, 4H, CH_{2COD}), 2.12-1.96 (m, 8H, NCH$_2$CH_2CH$_2$CH$_3$), 1.89-1.75 (m, 8H, NCH$_2$CH$_2$CH_2CH$_3$), 1.27-1.22 (m, 12H, NCH$_2$CH$_2$CH$_2$CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 190.24 (d, $^1J_{Rh-C}$ = 52 Hz, Rh-$C_{Carbene}$), 133.20 (C_q), 131.25 (C_q), 131.18 (C_q), 130.37 (C_q), 128.41 (CH_{cor}), 127.80 (C_q), 123.61 (CH_{cor}), 122.50 (CH_{cor}), 119.28 (C_q), 117.67 (C_q), 99.67 (CH_{COD}), 68.91 (CH_{2COD}), 51.32 (CH_{COD}), 33.17 (NCH_2CH$_2$CH$_2$CH$_3$), 31.80 (CH_{2COD}) 29.07 (NCH$_2$CH_2CH$_2$CH$_3$), 20.78 (NCH$_2$CH$_2$CH_2CH$_3$), 14.10 (NCH$_2$CH$_2$CH$_2$CH_3).

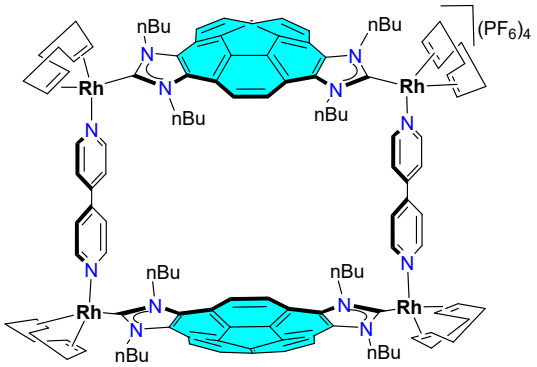
Synthesis of complex 2.



To a solution of **1** (135.5 mg, 0.129 mmol) in dichloromethane (10 mL) in round a bottomed flask, CO gas was bubble through at 0 ºC for 2 h. The solution was concentrated, and hexane was added to precipitate, yielding the desired product as a yelow solid. Yield: 103.7 mg (85 %). Elemental analysis calcd (%) for $C_{42}H_{42}N_4O_4Cl_2Rh_2$ (943.516): C, 53.46; H, 4.49; N, 5.94. Found: C, 53.28; H, 4.42; N, 5.93. ^{1}H NMR (500 MHz, $CDCl_3$): ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.25 (s, 2H, CH_{cor}), 8.15-8.02 (m, 4H, CH_{cor}), 5.34-4.89 (m, 8H, NCH_2CH$_2$CH$_2$CH$_3$),

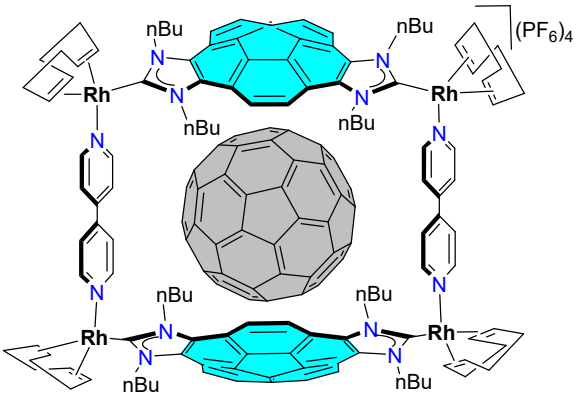
2.40-2.10 (m, 8H, $NCH_2CH_2CH_2CH_3$), 1.81-1.64 (m, 8H, $NCH_2CH_2CH_2CH_3$), 1.16 (t, $^3J_{H-H}$ = 7.5 Hz, 12H, $NCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ (ppm) 185.35 (d, $1J_{Rh-C}$ = 54 Hz, Rh-$C_{Carbene}$), 182.84 (dd, $^1J_{Rh-C}$ = 74 Hz, Rh-C_{CO}), 180.48 (dd, $^1J_{Rh-C}$ = 78 Hz, , $^1J_{Rh-C}$ = 43 Hz, Rh-C_{CO}), 131.23 (C_q), 131.06 (C_q), 130.90 (C_q), 130.72 (C_q), 130.55 (C_q), 129.79 (C_q), 128.80 (C_q), 128.72 (CH_{cor}), 128.08 (C_q), 127.76 (C_q), 123.7 (CH_{cor}), 122.40 (CH_{cor}), 119.09 (C_q), 118.57 (C_q), 117.71 (C_q), 117.27 (C_q), 51.65 ($NCH_2CH_2CH_2CH_3$), 31.89 ($NCH_2CH_2CH_2CH_3$), 20.45 ($NCH_2CH_2CH_2CH_3$), 14.11 ($NCH_2CH_2CH_2CH_3$). IR (cm^{-1}): 2083, 2003; TEP: 2055.

Synthesis of metallobox 3.



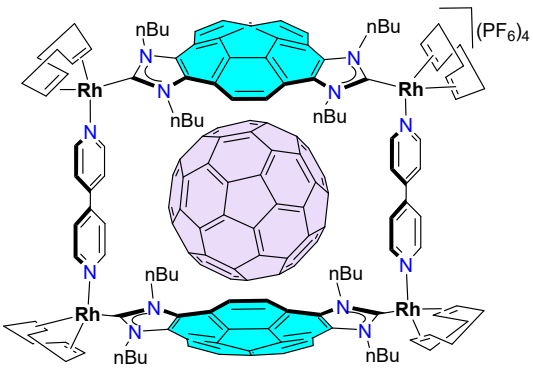
A Schlenk tube containing a mixture of compound **1** (50.5 mg, 0.05 mmol), 4,4'-bipyridine (7.5 mg, 0.05 mmol) and $AgPF_6$ (24.4 mg, 0.10 mmol) were dissolved in dichloromethane (10 mL) and stirred overnight at room temperature. The solution was filtered through a pad of Celite, the resulting solution was concentrated to almost dryness and ether solvent was added to precipitate, yielding the desired product as a yellow solid. Yield: 61.2 mg (89 %). Elemental analysis calcd (%) for $C_{128}H_{148}N_{12}Rh_4P_4F_{24}.2CH_2Cl_2$ (3015.583): C, 51.77; H, 5.08; N, 5.57. Found: C, 51.76; H, 4.96; N, 5.77. ^1H NMR (400 MHz, CD_2Cl_2): δ (ppm) 8.63 (d, $^3J_{H-H}$ = 6 Hz, 4H, CH_{bipy}), 8.52 (d, $^3J_{H-H}$ = 6 Hz, 4H, CH_{bipy}), 8.17 (s, 4H, CH_{cor}), 8.10 (s, 8H, CH_{cor}), 7.41 (d, $^3J_{H-H}$ = 6 Hz, 4H, CH_{bipy}), 7.31 (d, $^3J_{H-H}$ = 6 Hz, 4H, CH_{bipy}), 6.21-5.91 (m, 4H, $NCH_2CH_2CH_2CH_3$), 5.06-4.75 (m, 12H, $NCH_2CH_2CH_2CH_3$), 4.68 (s, 4H, CH_{COD}), 4.47 (s, 6H, CH_{COD}), 4.13 (s, 6H, CH_{COD}), 3.20-2.54 (m, 16H, CH_{2COD}), 2.45-2.15 (m, 16H, CH_{2COD}), 2.15-1.87 (m, 16H, $NCH_2CH_2CH_2CH_3$), 1.82-1.49 (m, 16H, $NCH_2CH_2CH_2CH_3$), 1.48-1.20 (m, 24H, $NCH_2CH_2CH_2CH_3$). $^{19}F\{^1H\}$ NMR (376 MHz, CD_2Cl_2): -72.49 (d, $^1J_{P-F}$ = 714 Hz,). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ (ppm) 185.40 (d, $^1J_{Rh-C}$ = 53 Hz, Rh-$C_{Carbene}$), 152.22 (C_q), 151.51 (CH_{bipy}), 150.95 (CH_{bipy}), 145.47 (C_q), 144.91 (C_q), 131.98 (C_q), 131.68 (C_q), 131.28 (C_q), 129.39 (CH_{cor}),124.15 (CH_{cor}), 123.78 (CH_{Bipy}), 123.73 (CH_{bipy}), 123.26 (CH_{cor}), 119.95 (C_q), 118.77 (C_q), 98.44 (CH_{COD}), 86.19 (CH_{COD}), 78.59 (CH_{COD}), 51.94 ($NCH_2CH_2CH_2CH_3$), 33.02 (CH_{2COD}), 32.59 (CH_{2COD}), 30.88 ($NCH_2CH_2CH_2CH_3$), 29.83 (CH_{2COD}), 29.55 (CH_{2COD}), 20.86 ($NCH_2CH_2CH_2CH_3$), 14.23 ($NCH_2CH_2CH_2CH_3$).

Synthesis of metallobox C_{60}@3.



A solution of the complex **3** (25.00 mg, 0.009 mmol) and C_{60} (6.33 mg, 0.009 mmol) in dichloromethane (10 mL) was stirred overnight at room temperature for 24 h. The solution was concentrated to almost dryness. It was added ether to precipitate a brown solid. Yield: 22.80 mg (73 %). Elemental analysis calcd (%) for $C_{188}H_{148}N_{12}Rh_4P_4F_{24}.3CH_2Cl_2$ (3816.53): C, 60.03; H, 4.06; N, 4.40. Found: C, 60.38; H, 4.09 N, 4.49. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 8.87 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 8H, C*H*$_{bipy}$), 8.14 (s, 4H, C*H*$_{cor}$), 8.07 (d, $^3J_{H\text{-}H}$ = 8.8 Hz, 4H, C*H*$_{cor}$), 7.99 (d, $^3J_{H\text{-}H}$ = 8.8 Hz, 4H, C*H*$_{cor}$), 7.81 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 8H, C*H*$_{bipy}$), 5.86-5.69 (m, 4H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 5.57-5.40 (m, 4H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 5.23-4.94 (m, 8H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 4.63-4.41 (m, 8H, C*H*$_{COD}$), 4.21-4.02 (m, 8H, C*H*$_{COD}$), 2.72-2.57 (m, 16H, C*H*$_{2COD}$), 2.35-2.21 (m, 16H, C*H*$_{2COD}$), 2.01-1.89 (m, 16H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.63-1.52 (m, 16H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.29-1.19 (m, 24H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ (ppm) 185.30 (d, $^1J_{Rh\text{-}C}$ = 53 Hz, Rh-*C*$_{Carbene}$), 152.27 (*C*H$_{bipy}$), 144.64 (*C*$_q$), 143.79 (*C*$_q$), 142.06 (*C*$_q$), 140.89 (*C*$_{C60}$), 131.86 (*C*$_q$), 130.44 (*C*$_q$), 129.90 (*C*H$_{cor}$), 128.97 (*C*$_q$), 124.91 (*C*H$_{cor}$), 123.74 (*C*H$_{bipy}$), 123.55 (*C*H$_{cor}$), 119.41 (*C*$_q$), 117.23 (*C*$_q$), 99.93 (*C*H$_{COD}$), 80.14 (*C*H$_{COD}$), 79.28 (*C*H$_{COD}$), 51.94 (NCH$_2$CH$_2$CH$_2$CH$_3$), 33.77 (*C*H$_{2COD}$), 33.35 (*C*H$_{2COD}$), 32.28 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 29.77 (*C*H$_{2COD}$), 29.48 (*C*H$_{2COD}$), 20.93 (NCH$_2$CH$_2$CH$_2$*C*H$_3$), 14.37 (NCH$_2$CH$_2$CH$_2$*C*H$_3$).

Synthesis of metallobox C_{70}@3.



A solution of the complex **3** (22.20 mg, 0.008 mmol) and C_{70} (14.2 mg, 0.008 mmol) in dichloromethane (10 mL) was stirred overnight at room temperature for 24 h. The solution was concentrated to almost dryness. It was added ether to precipitate a brown solid. Yield: 18.60 mg (65 %). Elemental analysis calcd (%) for $C_{198}H_{148}N_{12}Rh_4P_4F_{24}$ (3686.680): C, 64.50; H, 4.05; N, 4.56. Found: C, 65.11; H, 4.09; N, 4.74. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 8.86 (d, $^3J_{H\text{-}H}$

= 6.0 Hz, 8H, CH_{bipy}), 8.17 (s, 4H, CH_{cor}), 8.13 (d, $^{3}J_{H\text{-}H}$ = 9.0 Hz, 4H, CH_{cor}), 7.98 (d, $^{3}J_{H\text{-}H}$ = 9.0 Hz, 4H, CH_{cor}), 7.82 (d, $^{3}J_{H\text{-}H}$ = 6.0 Hz, 8H, CH_{bipy}), 5.74-5.47 (m, 8H, NCH_2CH$_2$CH$_2$CH$_3$), 5.29-5.10 (m, 8H, NCH_2CH$_2$CH$_2$CH$_3$), 4.58-4.37 (m, 8H, CH_{COD}), 4.18-3.99 (m, 8H, CH_{COD}), 2.77-2.52 (m, 32H, CH_{2COD}), 2.36-2.12 (m, 16H, NCH$_2$CH_2CH$_2$CH$_3$), 2.10-1.86 (m, 16H, NCH$_2$CH$_2$CH_2CH$_3$), 1.39-1.15 (m, 24H, NCH$_2$CH$_2$CH$_2$CH_3). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ (ppm) 185.14 (d, $^{1}J_{Rh\text{-}C}$ = 53 Hz, Rh-$C_{Carbene}$), 152.35 (CH$_{bipy}$), 148.71 (C_{C70}), 146.12 (C_{C70}), 145.35 (C_{C70}), 144.64 (C_q), 143.79 (C_q), 143.33 (C_{C70}), 142.06 (C_q), 131.86 (C_q), 130.50 (C_q), 130.15 (CH$_{cor}$), 128.77 (C_q), 125.12 (CH$_{cor}$), 123.73 (CH$_{bipy}$), 123.73 (CH$_{cor}$), 119.21 (C_q), 117.79 (C_q), 100.12 (CH$_{COD}$), 80.00 (CH$_{COD}$), 52.09 (NCH$_2$CH$_2$CH$_2$CH$_3$), 33.62 (CH$_{2COD}$), 32.40 (NCH$_2$$CH_2CH_2CH_3$), 29.62 ($CH_{2COD}$), 20.90 (NCH$_2CH_2CH_2$$CH_3$), 14.41 (NCH$_2CH_2CH_2$$CH_3$).

2. Spectroscopic data

2.1. ^{1}H, ^{19}F, ^{13}C and ^{1}H-^{13}C HSQC NMR spectra of A.

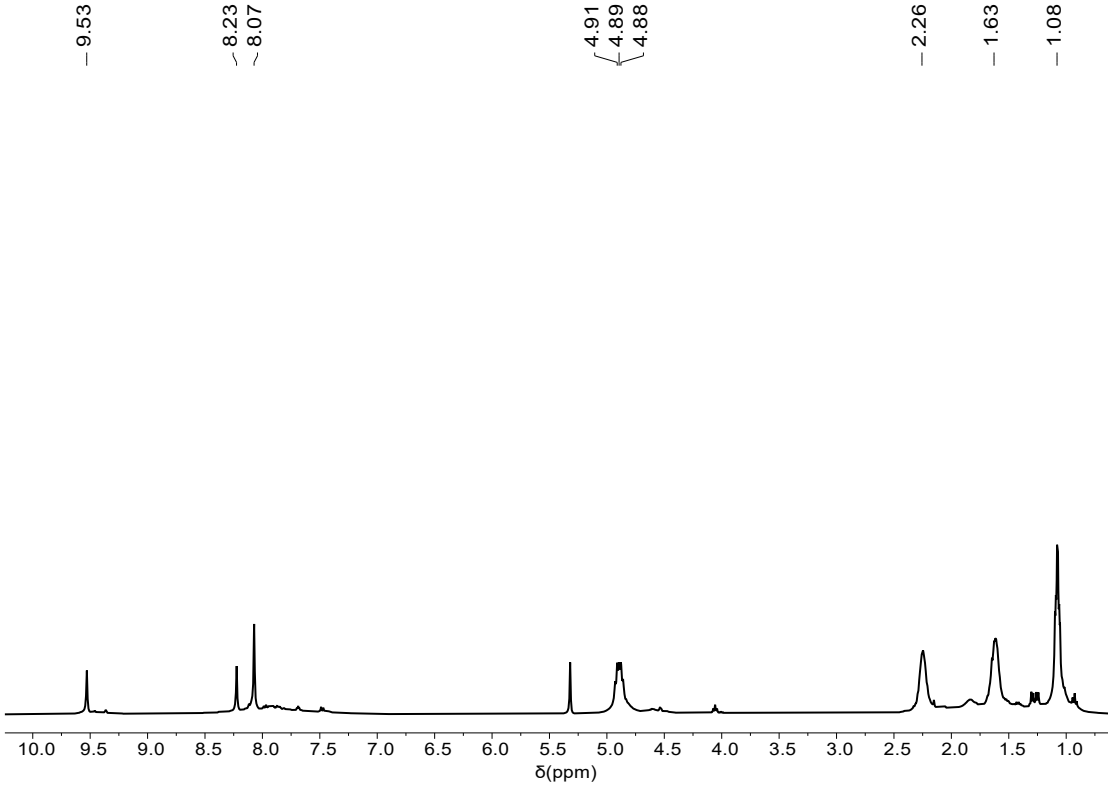


Figure S1. ^{1}H NMR spectrum (300 MHz) of **A** in CD_2Cl_2 at 298 K.

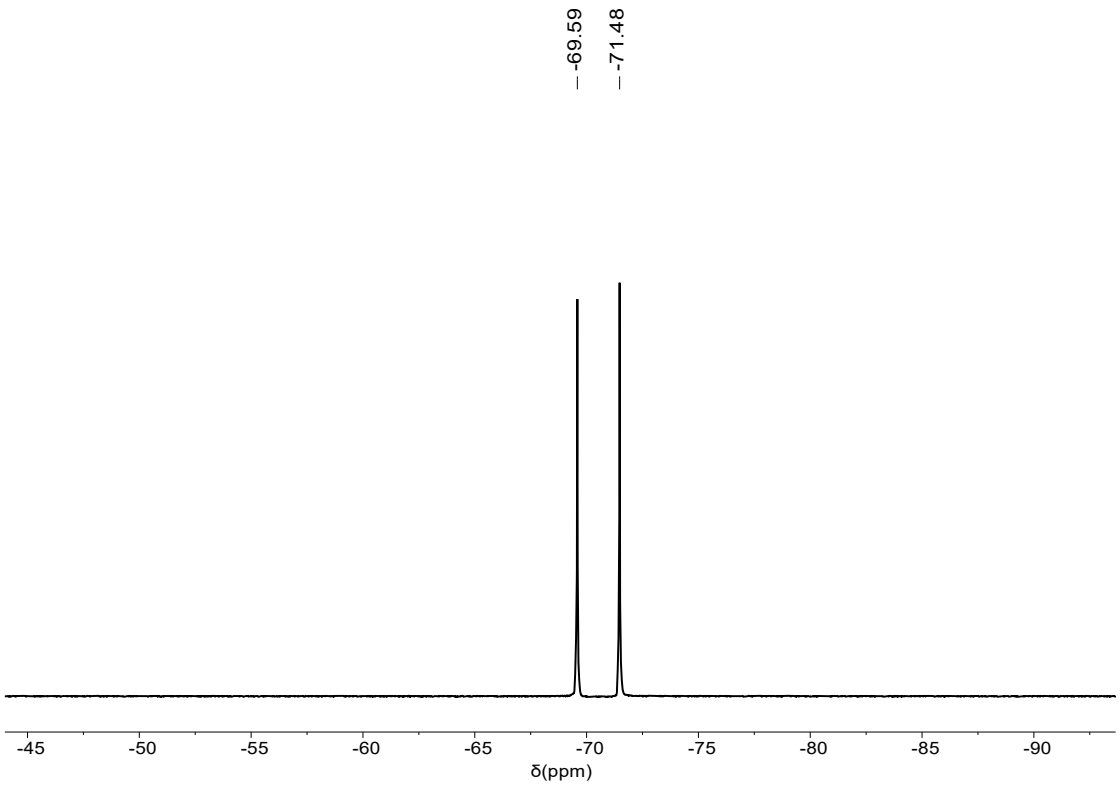


Figure S2. ^{19}F NMR spectrum (282 MHz) of **A** in CD_2Cl_2 at 298 K.

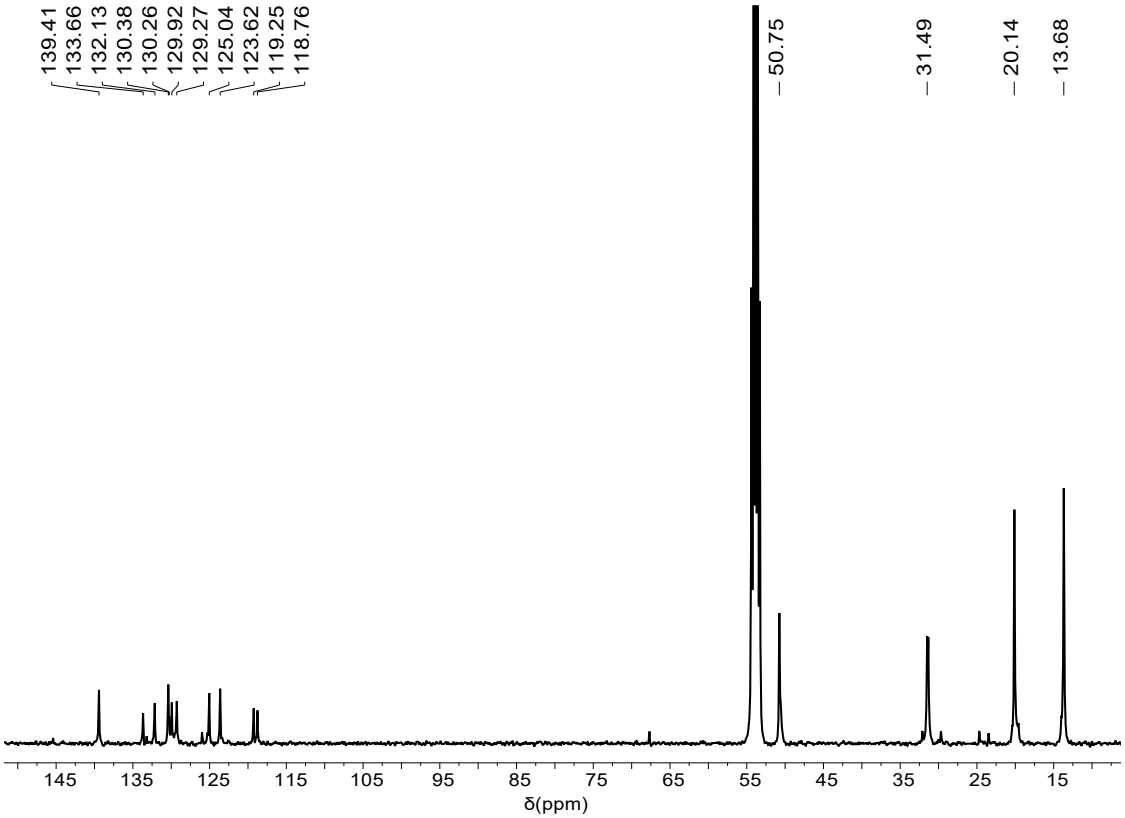


Figure S3. ^{13}C NMR spectrum (75 MHz) of **A** in CD_2Cl_2 at 298 K.

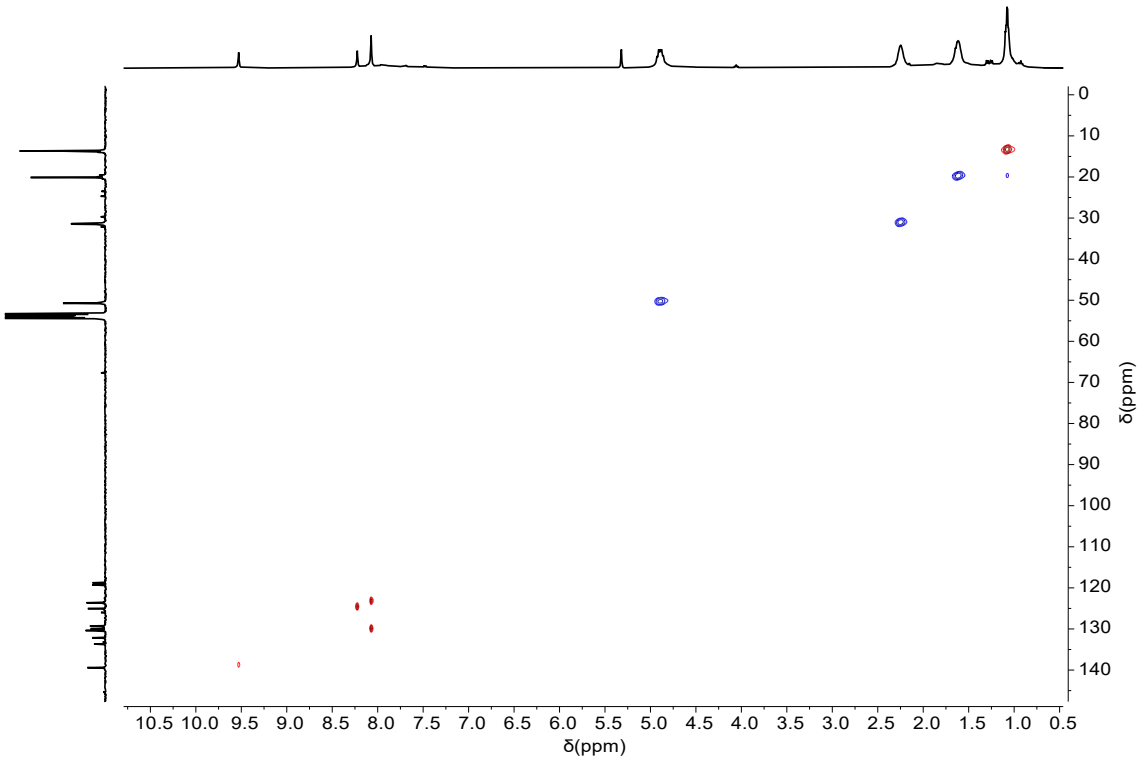


Figure S4. HSQC ^{1}H-^{13}C spectrum of (300 MHz) of **A** in CD_2Cl_2 at 298 K.

2.2. ^{1}H, ^{13}C and ^{1}H-^{13}C HSQC NMR spectra of 1.

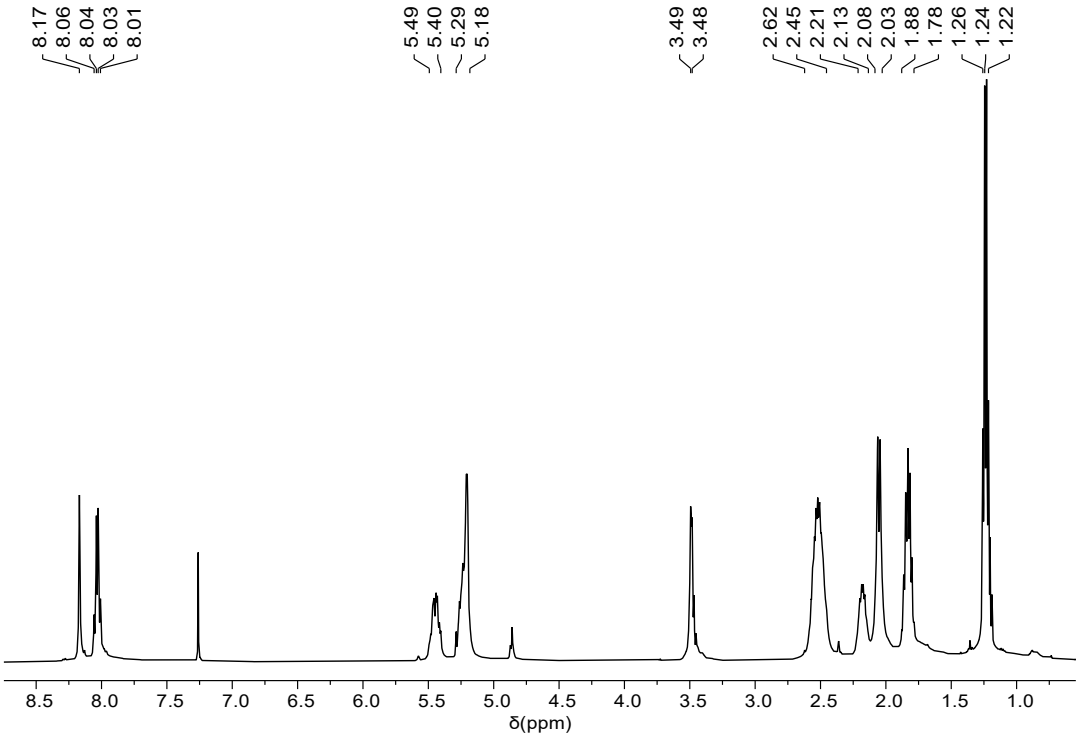


Figure S5. ^{1}H NMR spectrum (300 MHz) of **1** in $CDCl_3$ at 298 K.

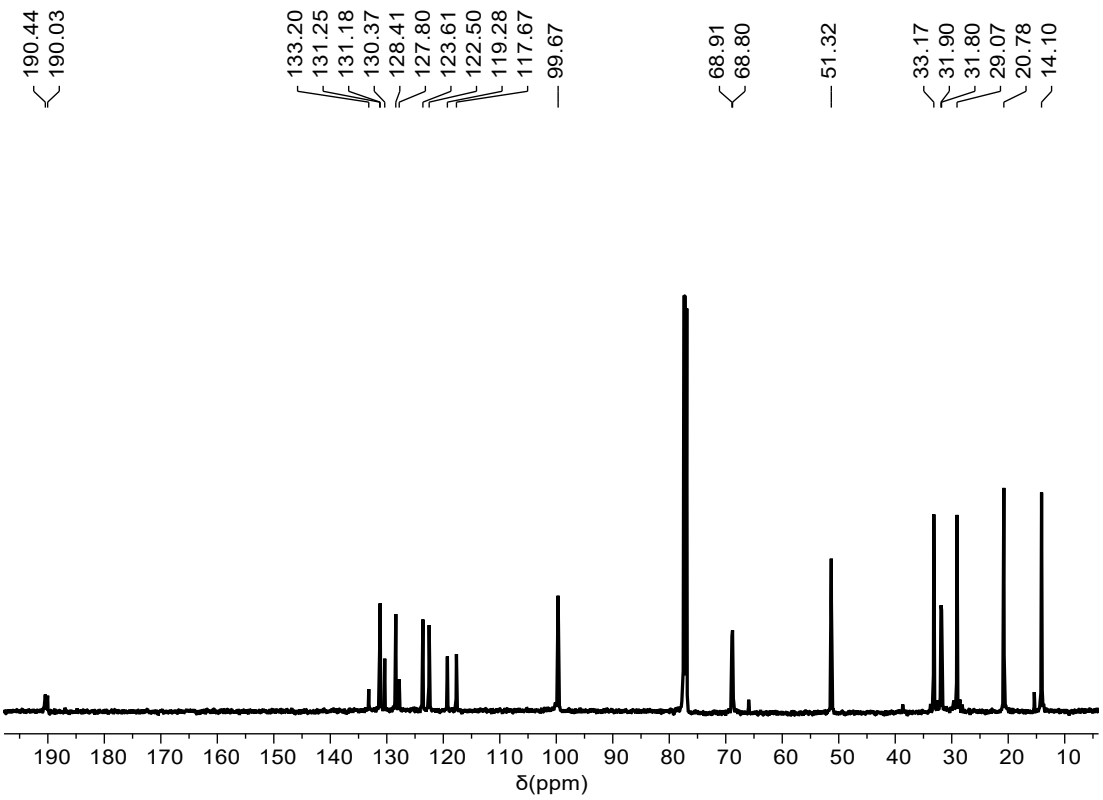


Figure S6. ^{13}C NMR spectrum (75 MHz) of **1** in $CDCl_3$ at 298 K.

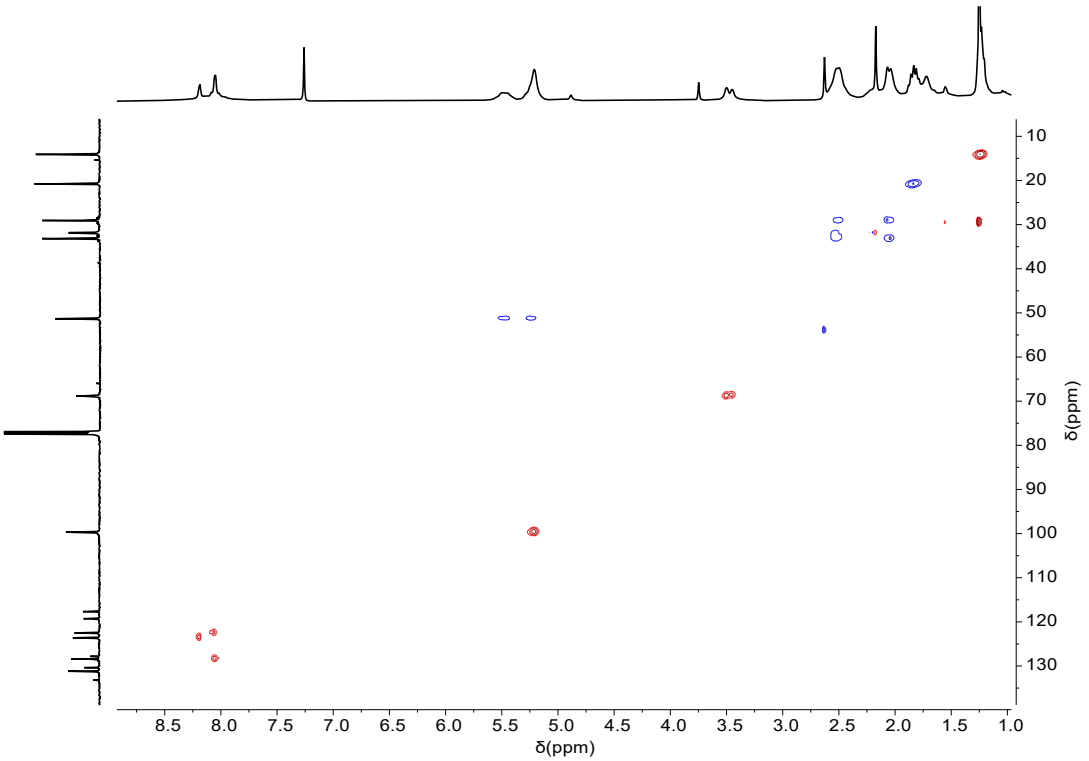


Figure S7. HSQC ^{1}H-^{13}C spectrum (300 MHz) of **1** in $CDCl_3$ at 298 K.

2.3. ^{1}H, ^{13}C and ^{1}H-^{13}C HSQC NMR spectra of 2.

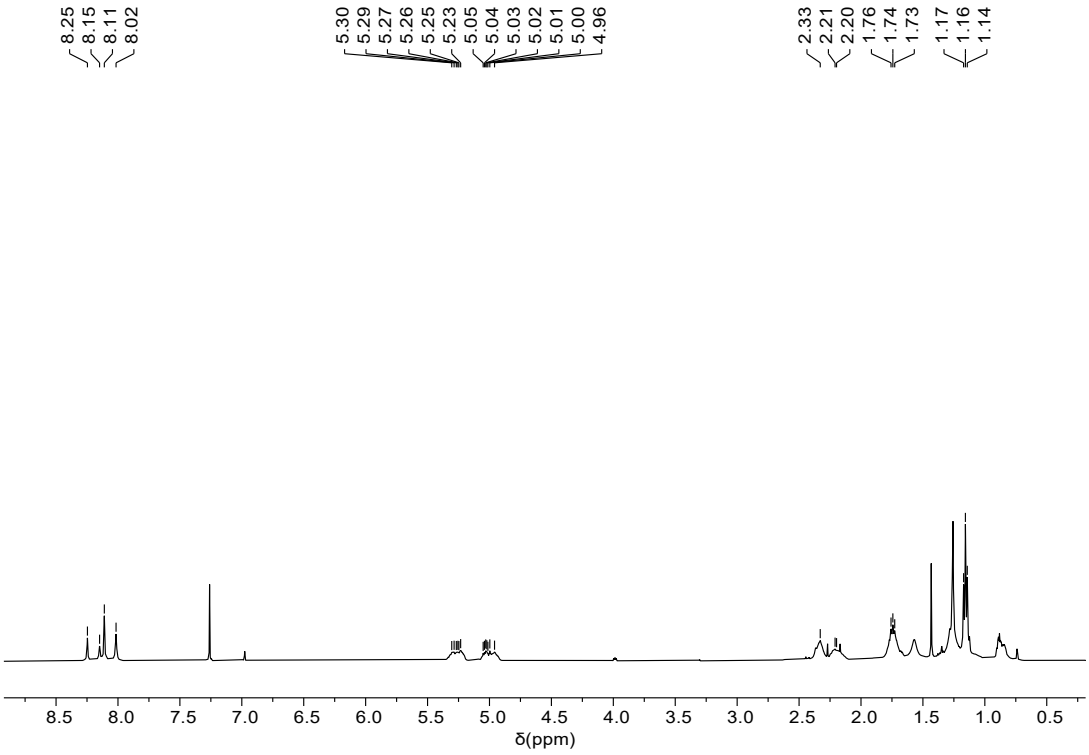


Figure S8. ^{1}H NMR spectrum (500 MHz) of **2** in $CDCl_3$ at 298 K.

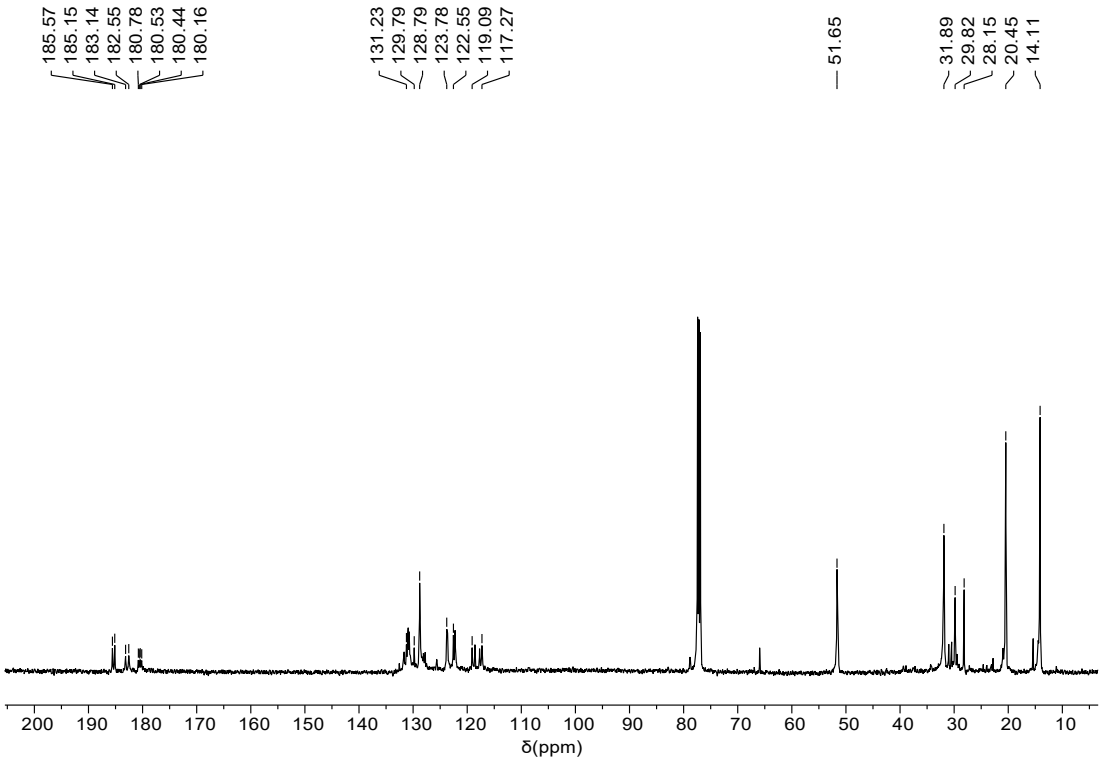


Figure S9. ^{13}C NMR spectrum (126 MHz) of **2** in $CDCl_3$ at 298 K.

2.4. ^{1}H, ^{19}F, ^{13}C, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC NMR spectra of 3.

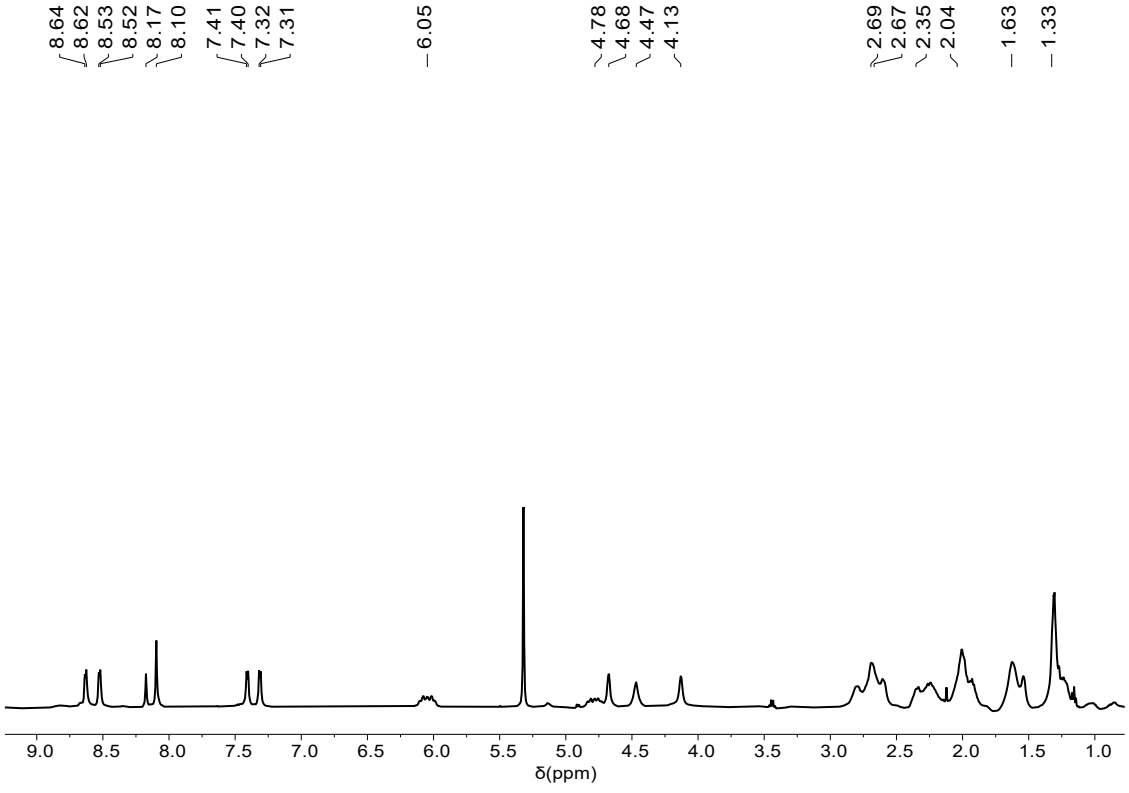


Figure S10. ^{1}H NMR spectrum (400 MHz) of **3** in CD_2Cl_2 at 298 K.

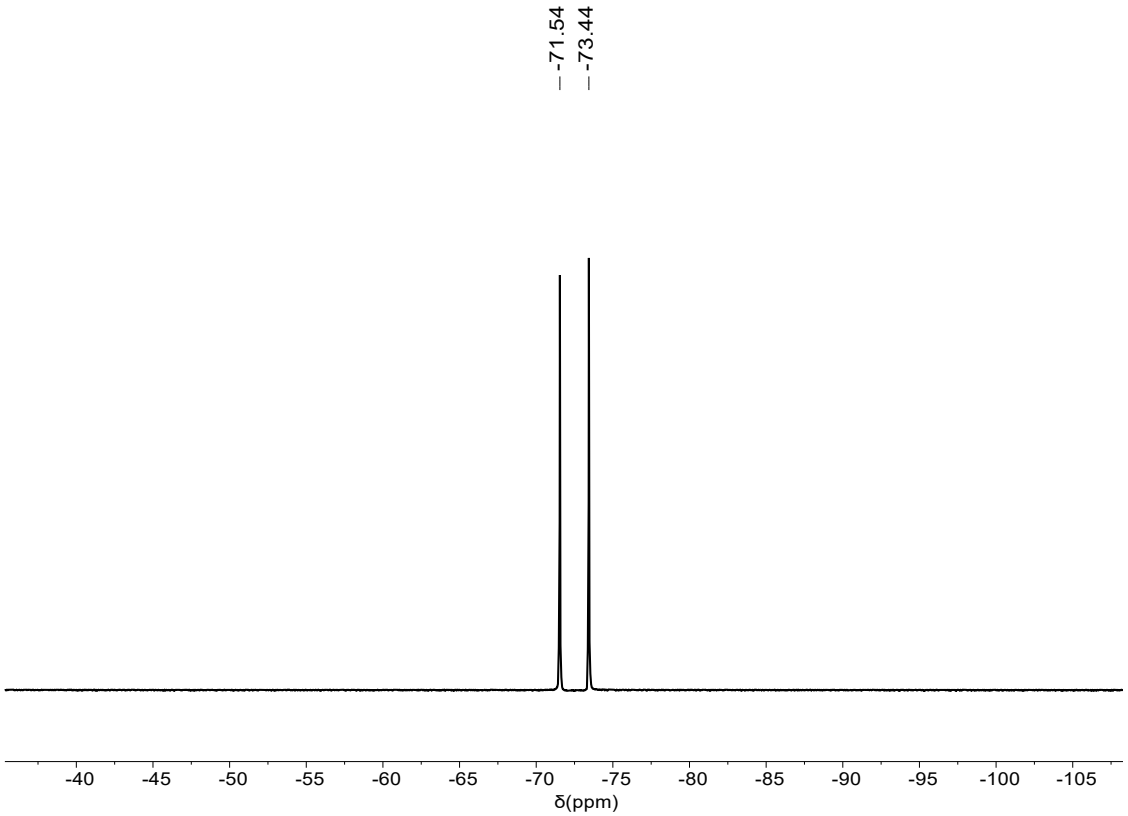


Figure S11. ^{19}F NMR spectrum (376 MHz) of **3** in CD_2Cl_2 at 298 K.

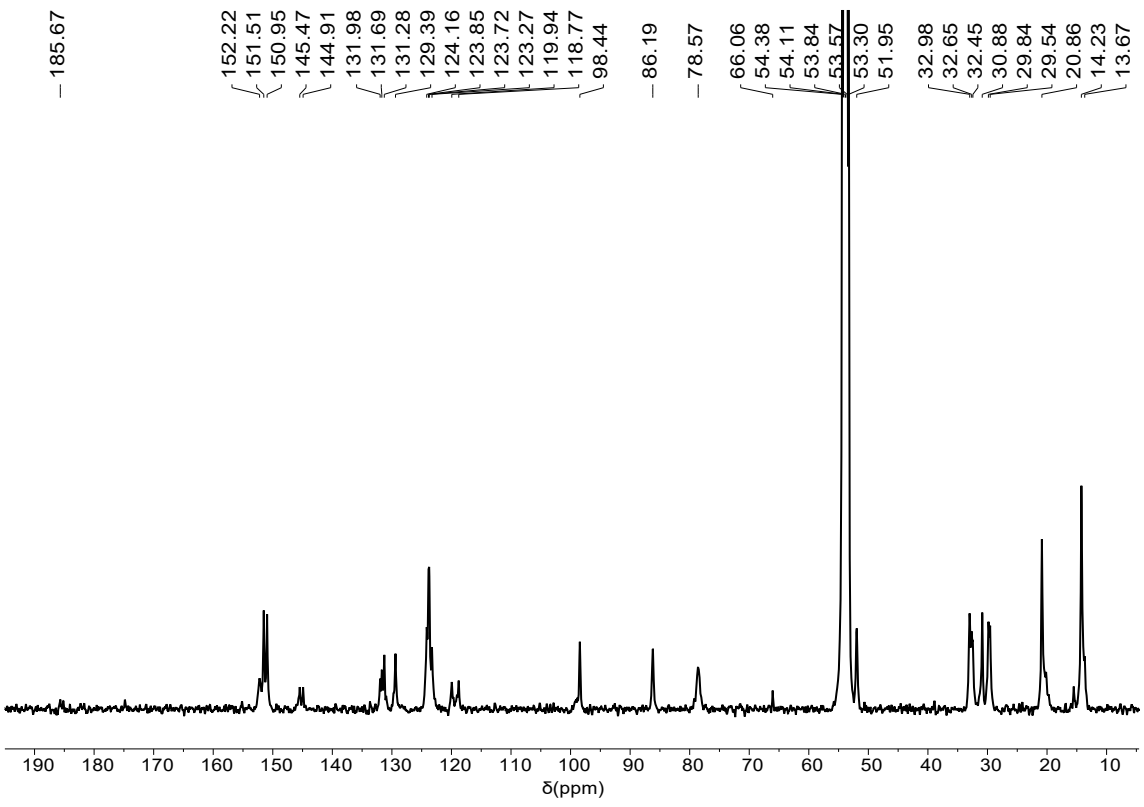


Figure S12. ^{13}C NMR spectrum (100 MHz) of **3** in CD_2Cl_2 at 298 K.

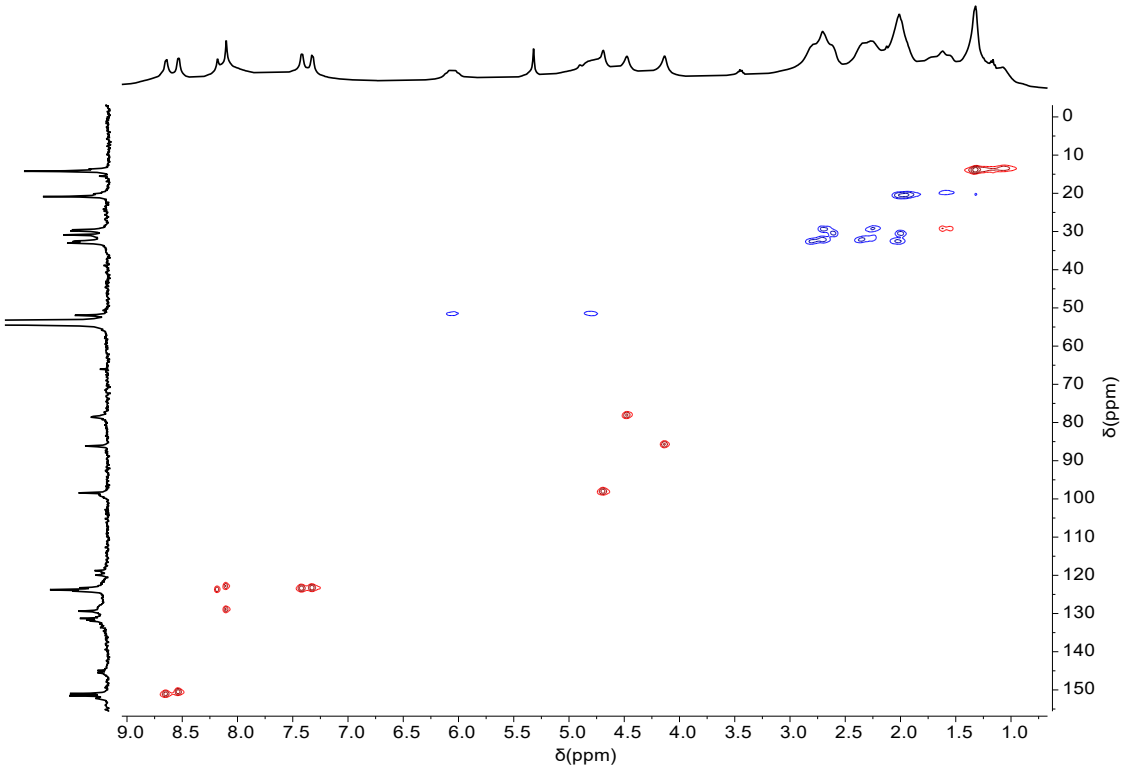


Figure S13. ^{1}H-^{13}C HSQC spectrum (400 MHz) of **3** in CD_2Cl_2 at 298 K.

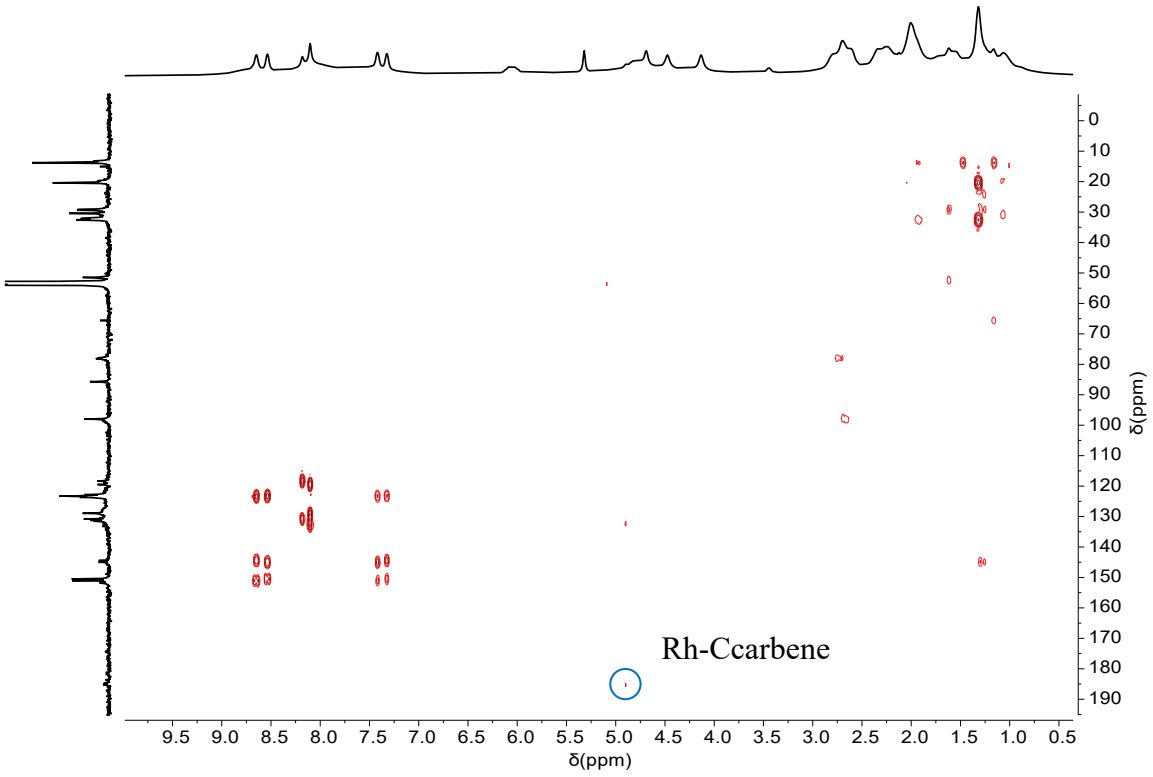


Figure S14. ^{1}H-^{13}C HMBC spectrum (400 MHz) of **3** in CD_2Cl_2 at 298 K.

2.5. ^{1}H, ^{13}C, and ^{1}H-^{13}C HSQC NMR spectra of C_{60}@3.

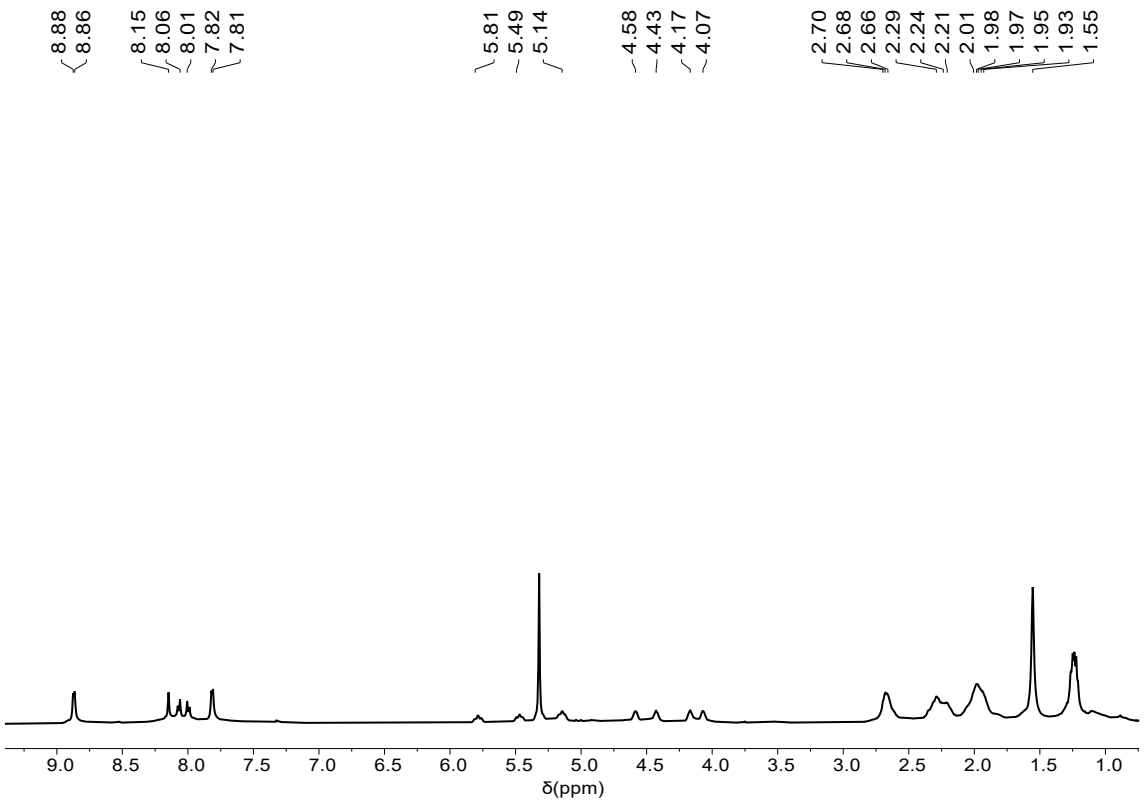


Figure S15. ^{1}H NMR spectrum (300 MHz) of C_{60}@**3** in CD_2Cl_2 at 298 K.

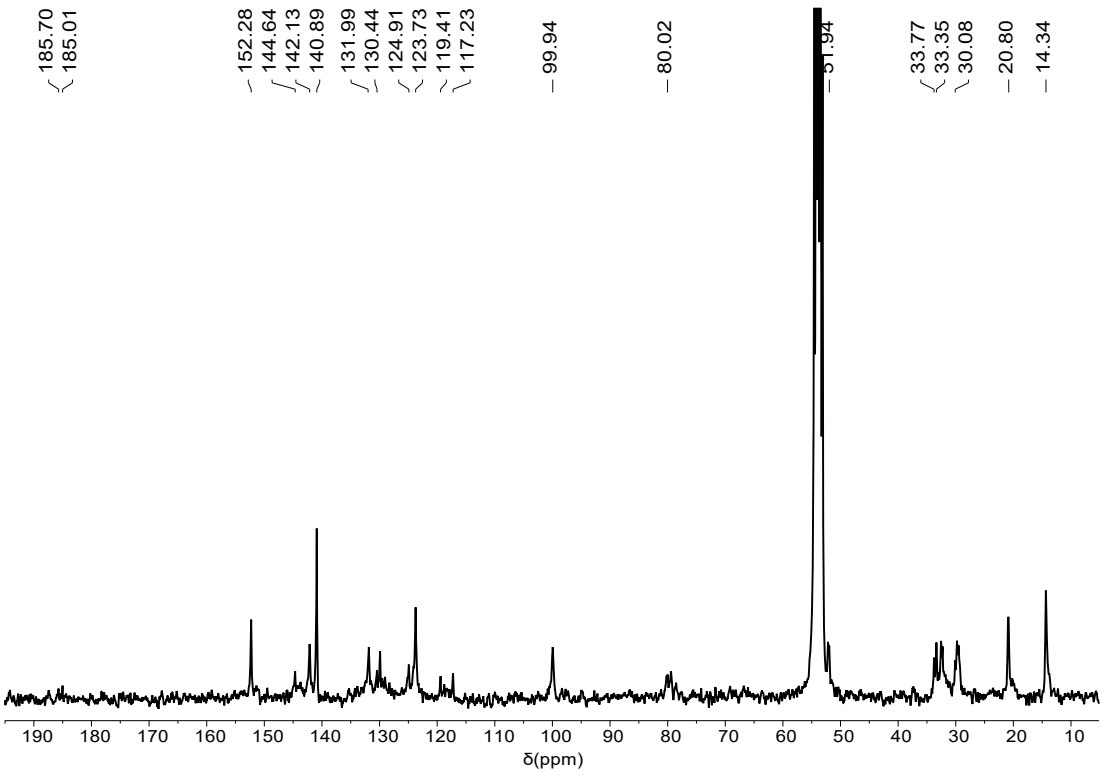


Figure S16. ^{13}C NMR spectrum (75 MHz) of C_{60}@**3** in CD_2Cl_2 at 298 K.

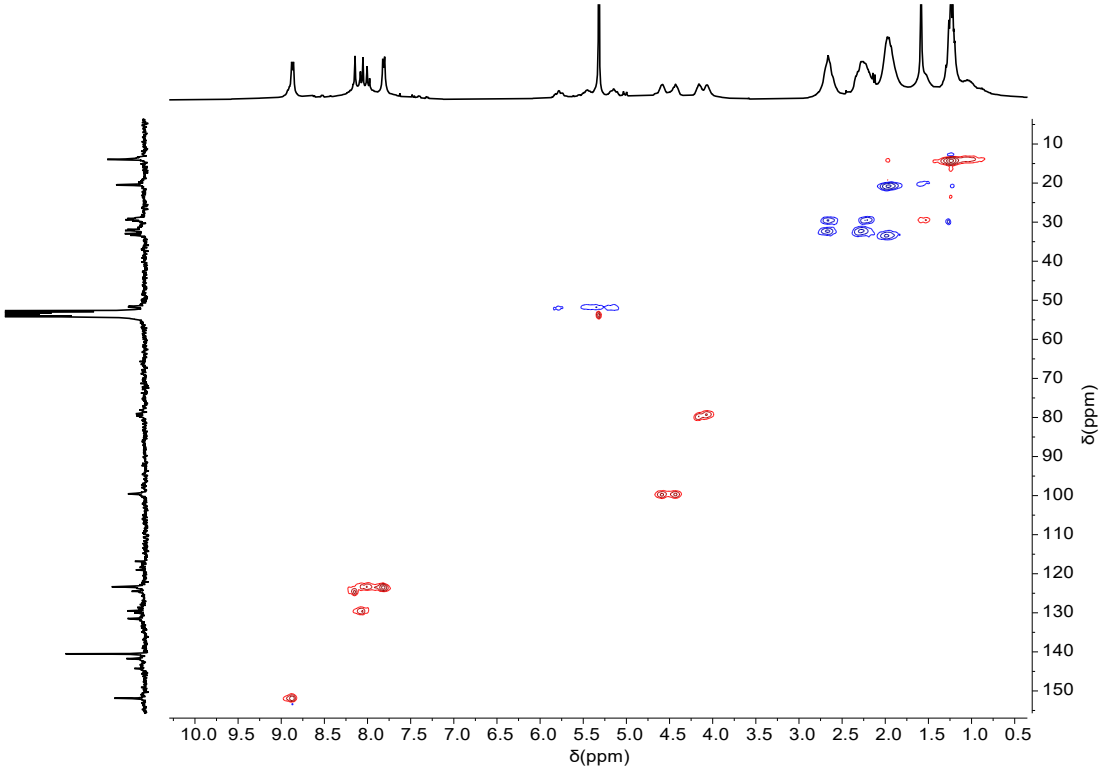


Figure S17. ^{1}H-^{13}C HSQC spectrum (300 MHz) of C_{60}@**3** in CD_2Cl_2 at 298 K.

2.6. ^{1}H, ^{13}C, and ^{1}H-^{13}C HSQC NMR spectra of C_{70}@3.

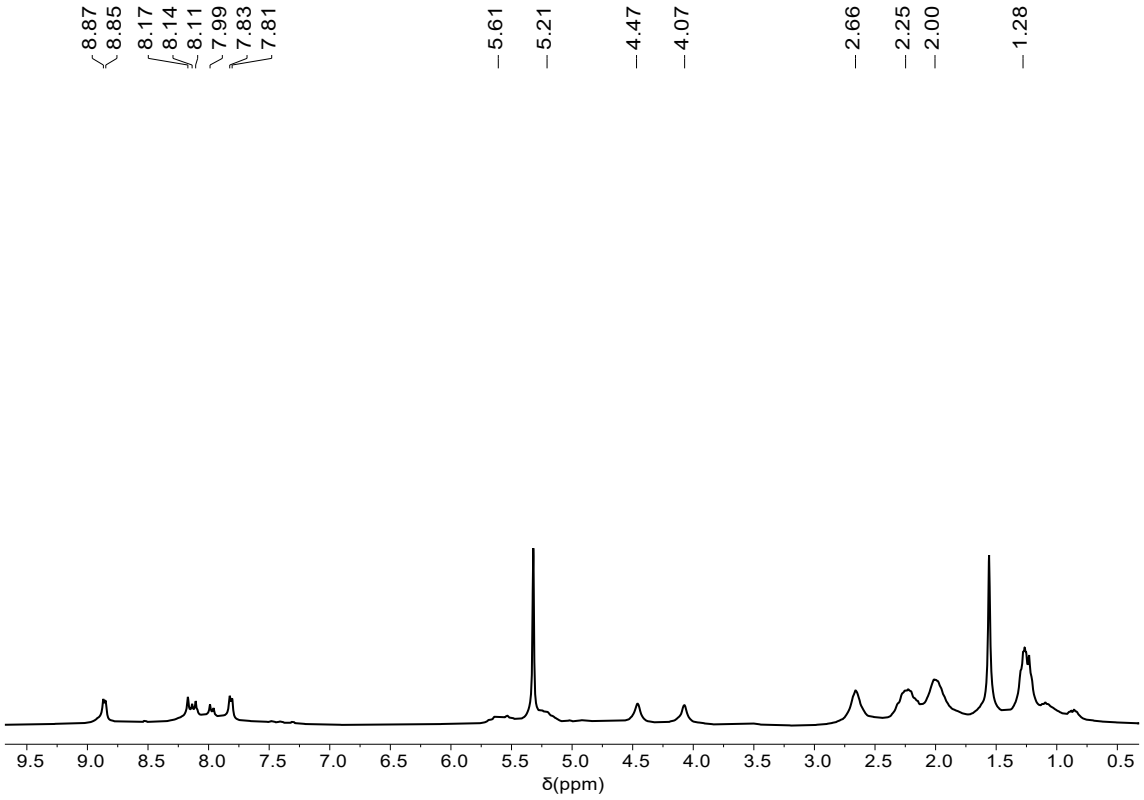


Figure S18. ^{1}H NMR spectrum (300 MHz) of C_{70}@**3** in CD_2Cl_2 at 298 K.

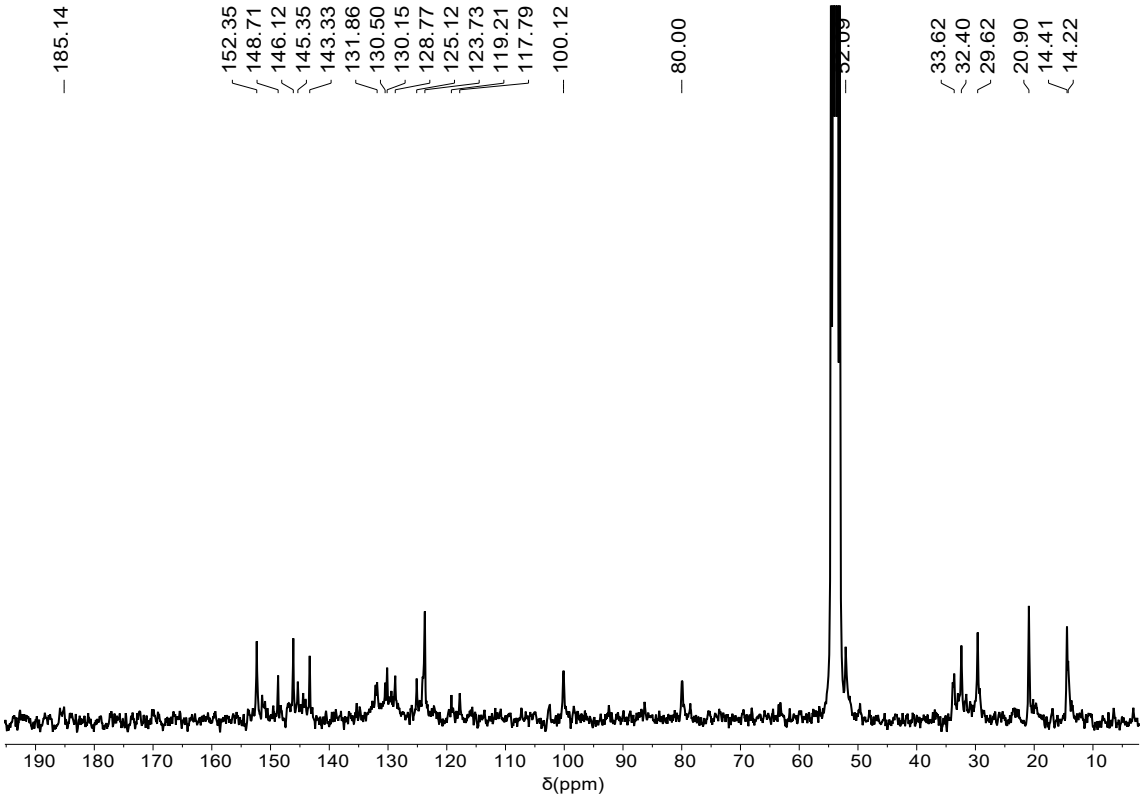


Figure S19. ^{13}C NMR spectrum (75 MHz) of C_{70}@**3** in CD_2Cl_2 at 298 K.

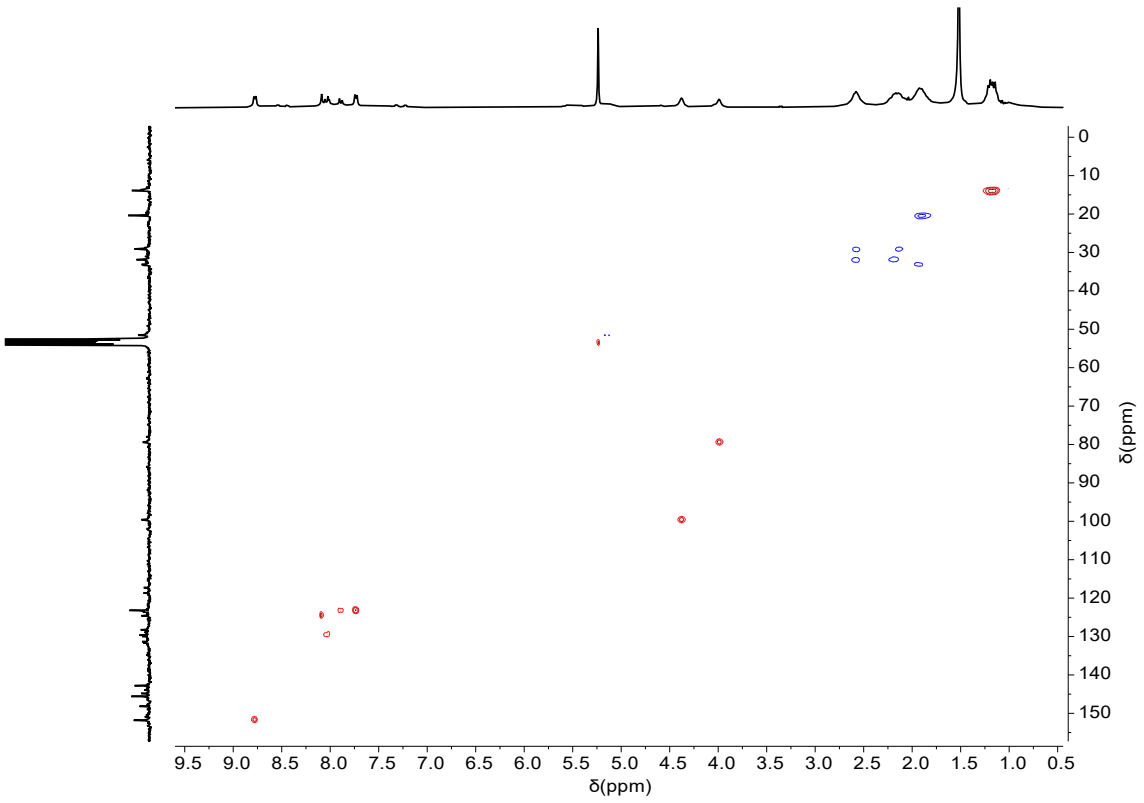


Figure S20. ^{1}H-^{13}C HSQC spectrum (300 MHz) of C_{70}@**3** in CD_2Cl_2 at 298 K.

3. Cyclic voltammetry studies

In all experiments, $[NBu_4](PF_6)$ (0.1 M in dry CH_2Cl_2) was used as the supporting electrolyte with analyze concentration of approximately 1 mM. Measurements were performed at 50 mVs^{-1} scan rates. All redox potentials were referenced to the Fc/Fc^+ couple as internal standard with $E_{1/2}(Fc/Fc^+)$ vs. SCE = +0.44 V.

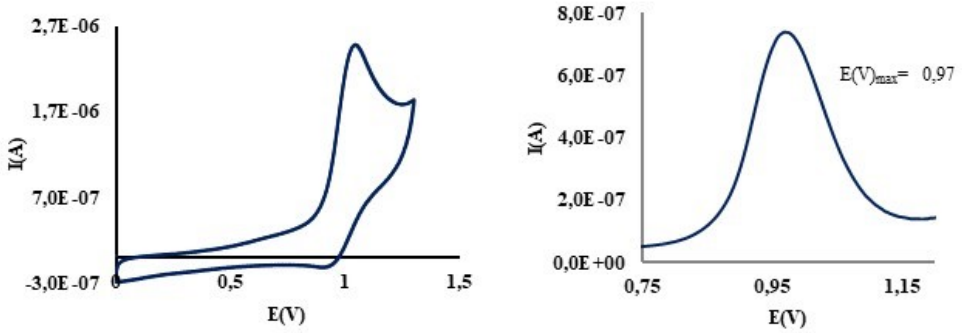


Figure S21. CV plot (left) and relevant DPV section (right) of complex **1**.

4. IR spectroscopy studies

We prepared a solution of the complex **2** at 10 mM of CH_2Cl_2 in FT/IR-6200 (Jasco) spectrometer.

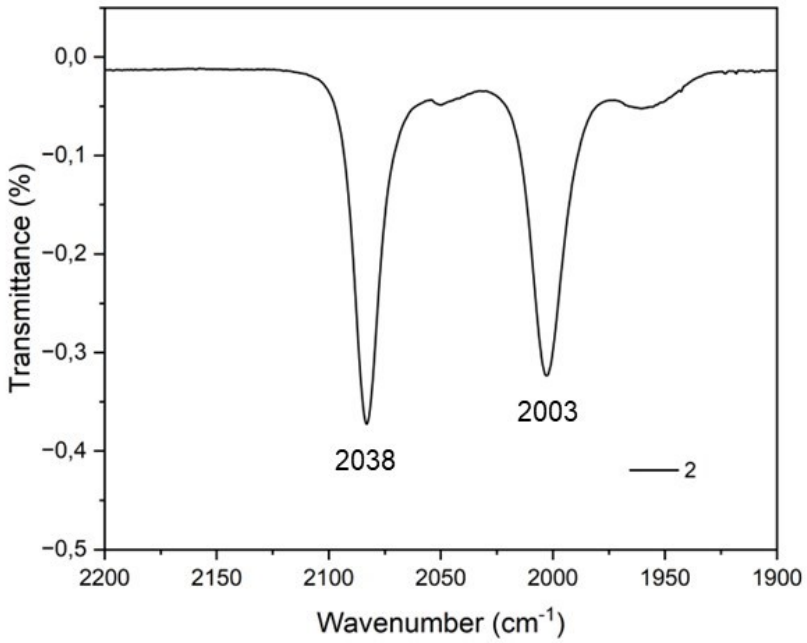


Figure S22. Infrared spectra recorded for complex **2**.

5. X-Ray Crystallography

X-Ray Diffraction studies for complexes C_{60}@3. Crystals suitable for X-ray studies of C_{60}@**3** was obtained by slow diffusion of hexane into a concentrated solution of the complex in acetone. Diffraction data of C_{60}@**3** were recorded at 100(2) K on a Bruker D8 Venture diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Single crystals were mounted on a MiTeGen polymer tip and protected with perfluoropolyether oil. Data were collected using ω- and φ-scans in with narrow oscillation frame strategies. Diffracted intensities were integrated and corrected of absorption effects by using a multi-scan method using SAINT,[2] and SADABS,[3] programs, as included in the APEX4 package. The structure was solved by direct methods with SHELXS[4] and refined by full-matrix least squares on F^2 with SHELXL,[5] and the WinGX system.[6] Hydrogen atoms have been included in the model in calculated positions and refined with a riding model. DFIX restraints were applied to five selected interatomic distances at the end of two butyl groups and in acetone solvent molecules, whereas ISOR instructions were placed on two C-atoms at butyl groups. Key details of the crystal and structure refinement data are summarized in Supplementary Table S1.

The structure model of complex C_{60}@**3** shows the following A alerts after CheckCIF on Platon:

Table S1. Summary of crystal data, data collection, and structure refinement details

	C_{60}@3
Empirical formula	C_{203} H_{178} F_{24} N_{12} O_5 P_4 Rh_4
Formula weight	3857.08
Temperature/K	100(2)
Crystal system	triclinic
Space group	P–1
a/Å	17.8348(14)
b/Å	22.4557(19)
c/Å	25.220(2)
α/°	105.856(3)
β/°	107.732(2)
γ/°	105.180(2)
Volume/Å^3	8573.1(12)
Z	2
ρ_{calcg}/cm^3	1.494
μ/mm^{-1}	0.506
F(000)	3952
Crystal size/mm^3	8573.1(12)
2Θ range for data collection	2.32 – 25.28
Index ranges	$-23 \leq h \leq 23$, $-30 \leq k \leq 29$, $-33 \leq l \leq 33$
Reflections collected	446977
Independent reflections	42939
Data/restraints/ parameters	42939/29/2286
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	0.1129
Final R indexes [all data]	0.3582
Largest diff. peak/hole / e Å^{-3}	2.454 / –1.410

6. Photophysical properties

6.1. UV-visible absorption spectra

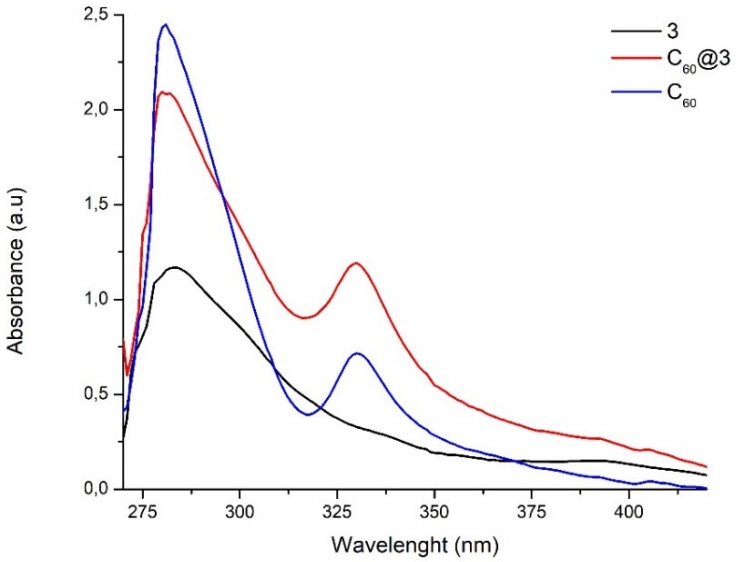


Figure S23. UV-visible absorption spectra of complexes **3**, C_{60} and C_{60}@**3**, recorded in in chloroform-toluene (9:1) at a concentration of 10^{-5} M, under aerobic conditions at room temperature.

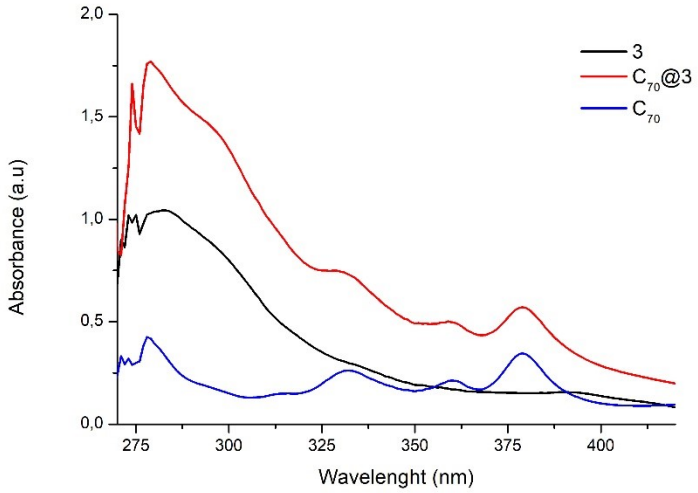


Figure S24. UV-visible absorption spectra of complexes **3**, C_{70} and C_{70}@**3**, recorded in in chloroform-toluene (9:1) at a concentration of 10^{-5} M, under aerobic conditions at room temperature.

6.2. Emission spectra

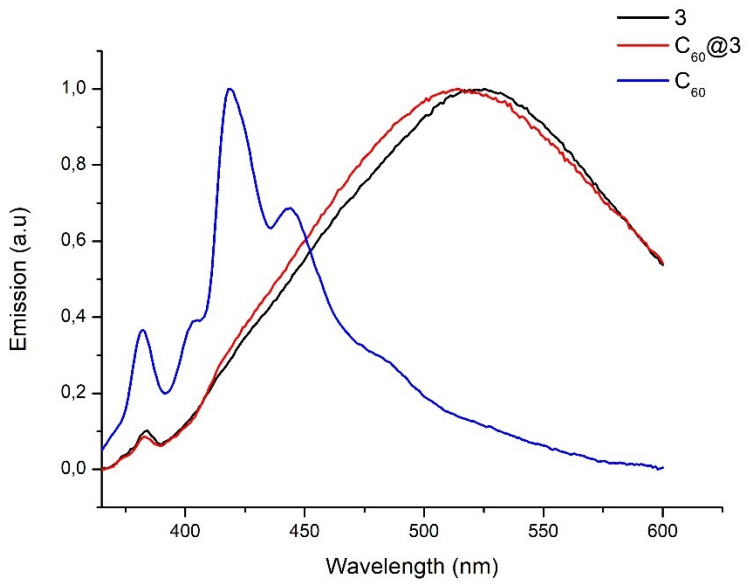


Figure S25. Normalized emission spectra of complexes **3**, C_{60} and C_{60}@**3,** at 345 nm in in chloroform-toluene (9:1) at a concentration of 10^{-5} M, under aerobic conditions at room temperature.

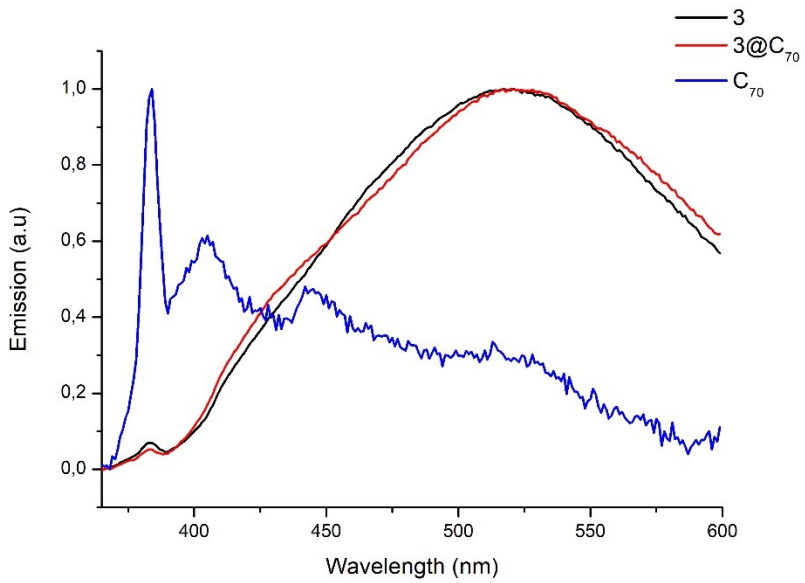


Figure S26. Normalized emission spectra of complexes **3**, C_{70} and C_{70}@**3,** at 345 nm in in chloroform-toluene (9:1) at a concentration of 10^{-5} M, under aerobic conditions at room temperature.

7. Titration experiments

7.1. ^{1}H NMR titration experiments

The recognition capability of complex **1** (host) was studied by ^{1}H NMR titration experiments, by adding increasing amounts of C_{60}, C_{70} and coronene (guest) to a solution of complex **1**. The experiment was carried out in toluene-d_8, at constant concentrations of the host (1.0 mM). Two solutions were prepared: solution A (only containing host at 1.0 mM) and solution B (containing host at 1.0 mM and guest at different mM). The addition of increasing amounts of solution B to solution A produced perturbations on the signal due to the proton of corannulene core of the host. The association constants were calculated by nonlinear least-square analysis, by using the BindFitv0.5 program. The data was fitted to the 2:1 binding model.

Titration of 1 with C_{60}

Table S2. Data values from the titration study of **1** with C_{60}

[1] M	[C_{60}] M	δc_H	δc_H	δc_H	equiv. C_{60}
0,00101798	0	7,98	7,92	7,72	0
0,00101798	0,00031489	8,02	7,93	7,73	0,3
0,00101798	0,00060646	8,06	7,94	7,73	0,6
0,00101798	0,0008772	8,1	7,95	7,74	0,9
0,00101798	0,00112926	8,12	7,96	7,74	1,1
0,00101798	0,00158461	8,14	7,97	7,74	1,6
0,00101798	0,00198477	8,15	7,97	7,74	1,9
0,00101798	0,0026553	8,16	7,98	7,75	2,6
0,00101798	0,00319499	8,17	7,98	7,75	3,1
0,00101798	0,00383229	8,17	7,98	7,75	3,7
0,00101798	0,00446573	8,17	7,98	7,75	4,4
0,00101798	0,00493829	8,17	7,98	7,75	4,8
0,00101798	0,00545811	8,17	7,98	7,75	5,4

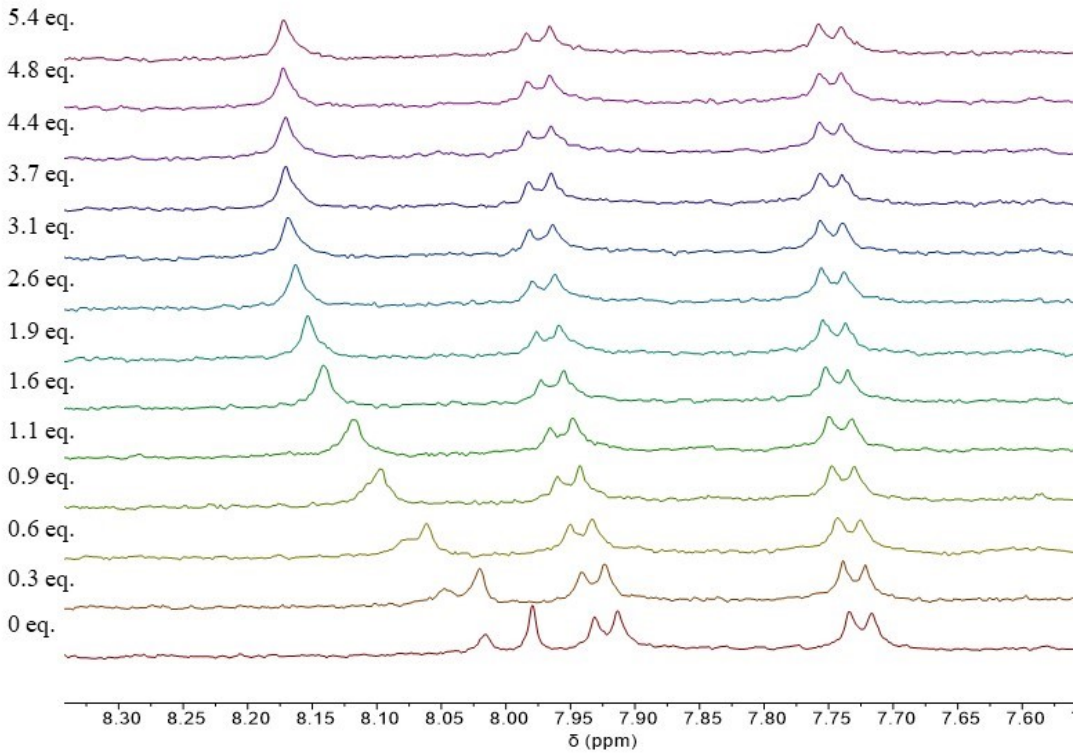


Figure S27. Selected region and spectra (500 MHz, toluene-d_8, 298 K) of the titration of complex **1** with C_{60}.

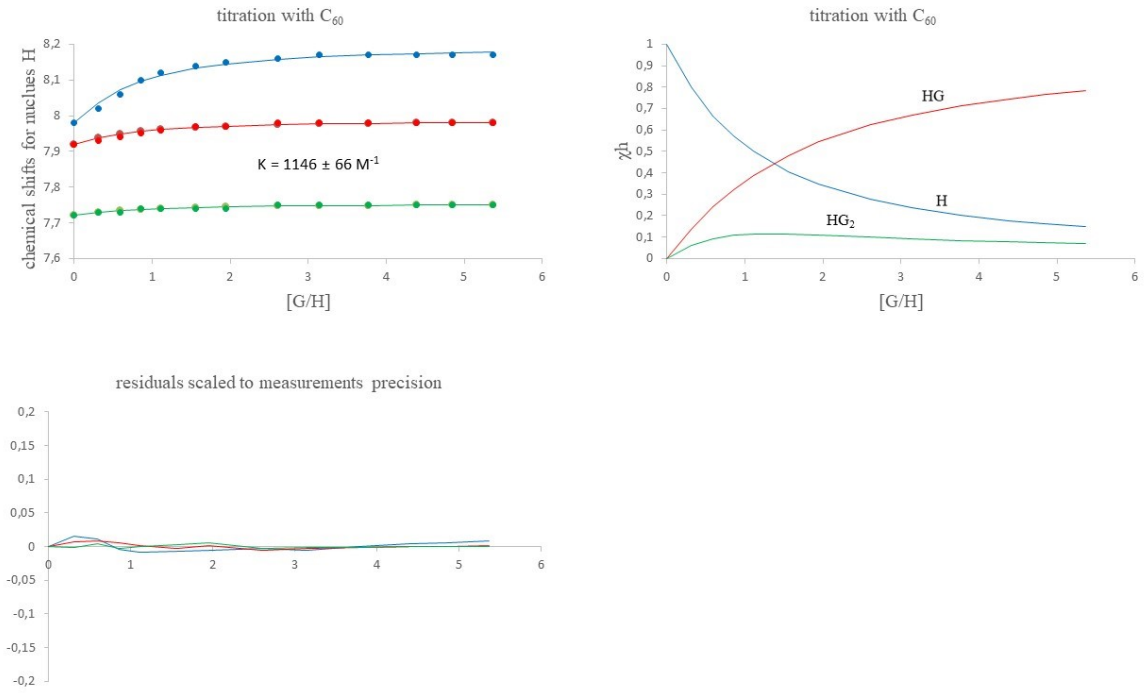


Figure S28. Non-linear least-squares fitting of the chemical shift changes of H during titration experiments of **1** with C_{60}. The Figure on the left represents the speciation profiles.

Titration of 1 with C_{70}

Table S3. Data values from the titration study of **1** with C_{70}

[1] M	$[C_{70}]$ M	δc_H	equiv. C_{70}
0,00114523	0	7,98	0
0,00114523	0,00021501	8	0,2
0,00114523	0,00041409	8,03	0,4
0,00114523	0,00059896	8,05	0,5
0,00114523	0,00077107	8,07	0,7
0,00114523	0,00108198	8,1	0,9
0,00114523	0,00135521	8,11	1,2
0,00114523	0,00181305	8,12	1,6
0,00114523	0,00218156	8,12	1,9
0,00114523	0,00261671	8,13	2,3
0,00114523	0,00304923	8,13	2,7
0,00114523	0,00337189	8,13	2,9
0,00114523	0,00372683	8,13	3,3

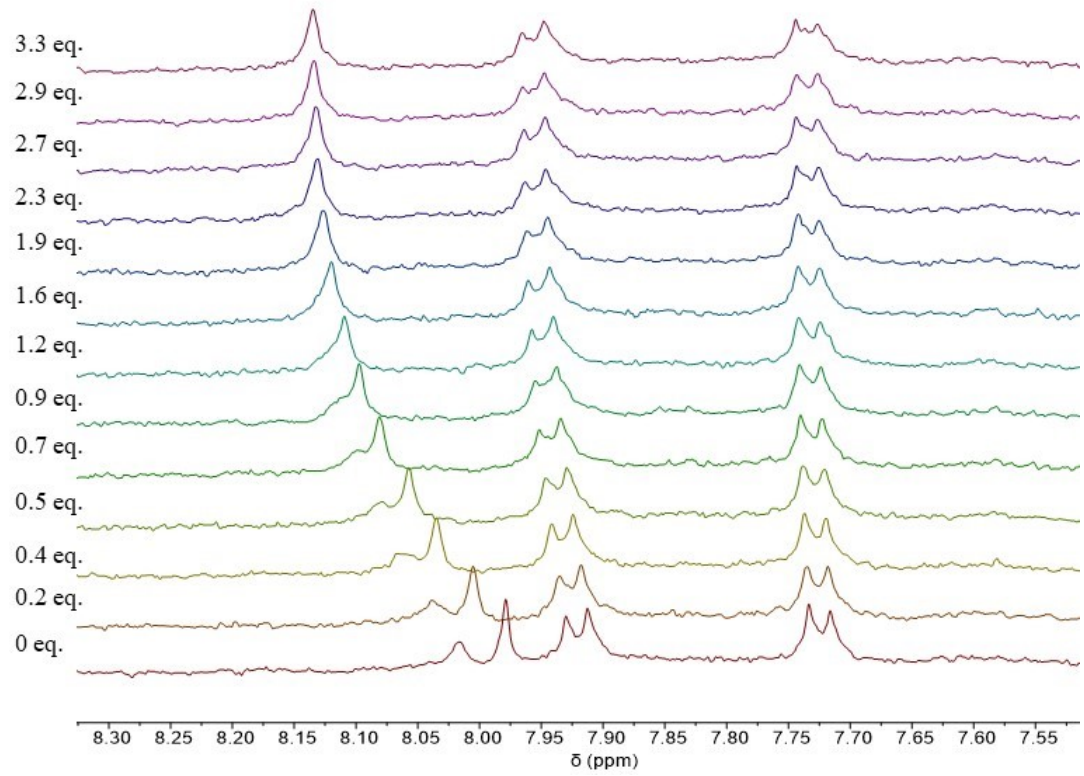


Figure S29. Selected region and spectra (500 MHz, toluene-d_8, 298 K) of the titration of complex **1** with C_{70}.

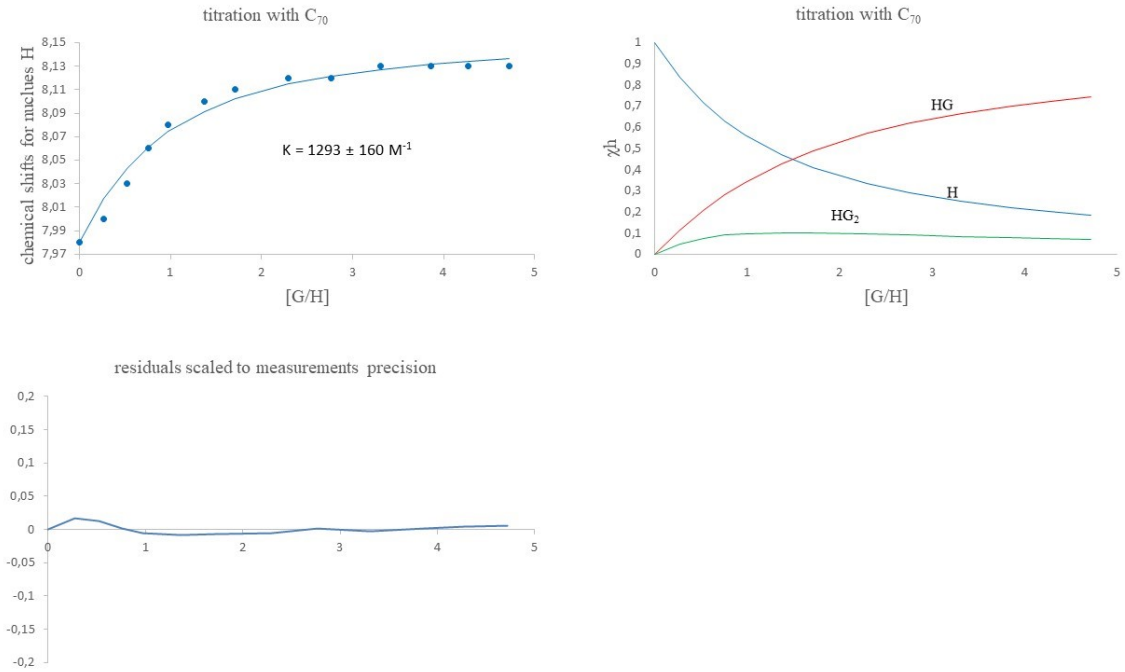


Figure S30. Non-linear least-squares fitting of the chemical shift changes of H during titration experiments of **1** with C_{70}. The Figure on the left represents the speciation profiles.

7.2 ITC titration experiments

Titration of the host **1** with **C_{60}** or **C_{70}** was carried out in toluene by the addition of small aliquots of C_{60} (8 µL) of a solution of the guest (2.7 mM) into a solution of the host (0.6 mM). The solutions were prepared in spectroscopic grade solvents and equilibrated for 24 h at room temperature before use. The titrations were duplicated independently, and isotherm fittings were used to calculate the average Ka and ΔH with relevant standard errors. Isothermal titration was performed on a TA Nano Isothermal Titration Calorimeter at 25 ˚C. A hastelloy cell was used with an active cell volume 182 µL. The stirring speed was set at 150 rpm. The association constant was obtained from the fit of the titration data to a 1:2 binding model using the TA Nano Isothermal Titration Calorimeter indicating the C_{60} or C_{70} were placed in the syringe. The two sites are assumed to be non-cooperative.

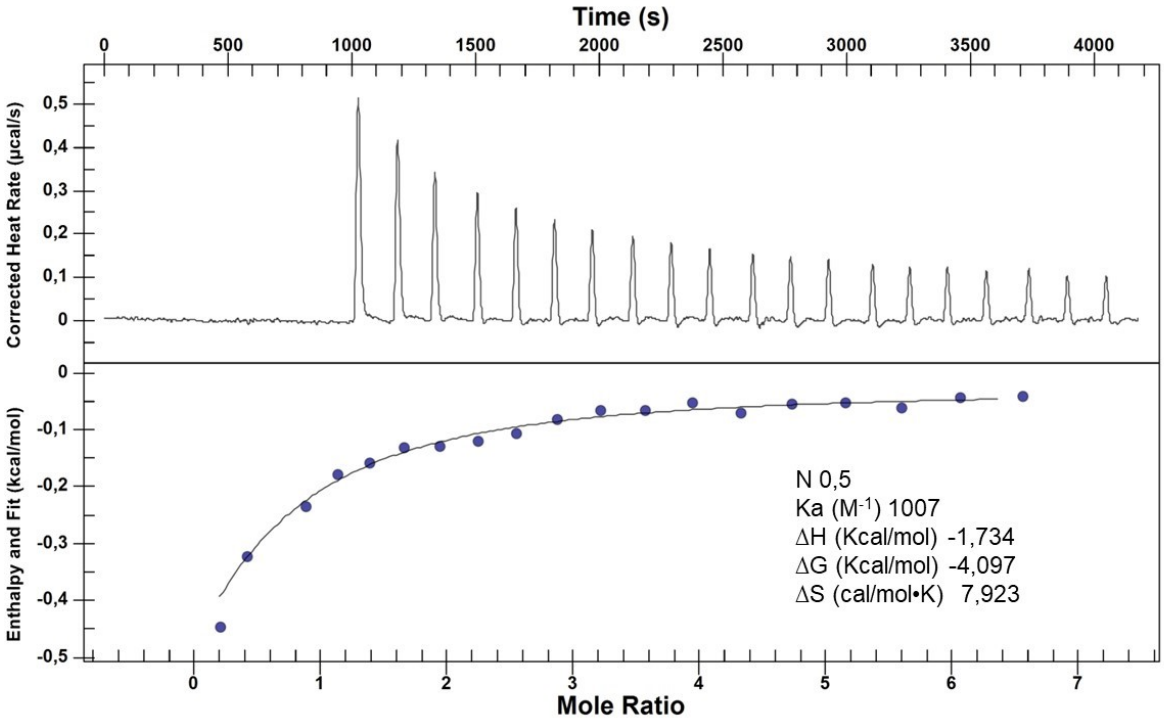


Figure S31. Heat *vs*. time plot for the titration of guest C_{60} into host **1.** One set of site binding isotherm (blank line) fit to the experimental data if the complex of higher stoichiometry formed by the two binding partners is C_{60}@**1**.

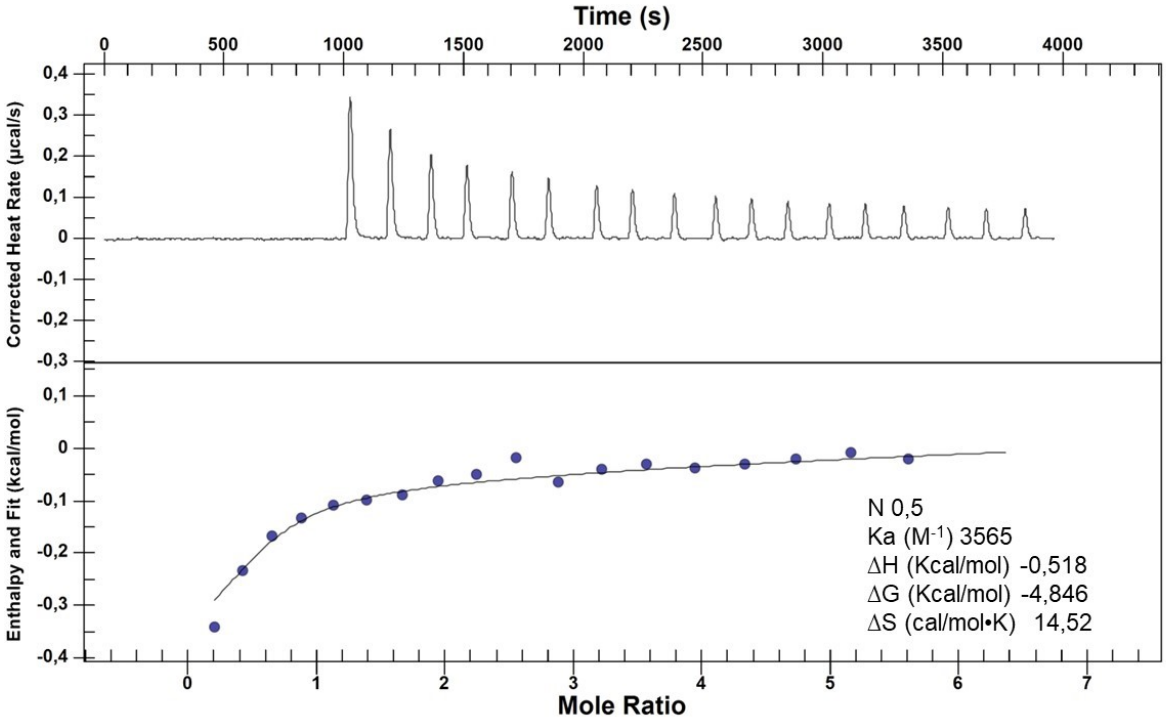


Figure S32. Heat *vs.* time plot for the titration of guest C_{70} into host **1.** One set of site binding isotherm (blank line) fit to the experimental data if the complex of higher stoichiometry formed by the two binding partners is C_{70}@**1**.

8. Encapsulation experiments with fullerenes.

A solution of **3** in CD_2Cl_2 (17.22 mM) was placed in an NMR tube. Then, the corresponding fullerene (C_{60} or C_{70}) was added (17.22 mM), and the suspension was placed in an ultrasonic bath. NMR spectra were recorded after different hours of sonication. After 24 hours, the formation of the host-guest adducts (fullerene@**3**) was complete.

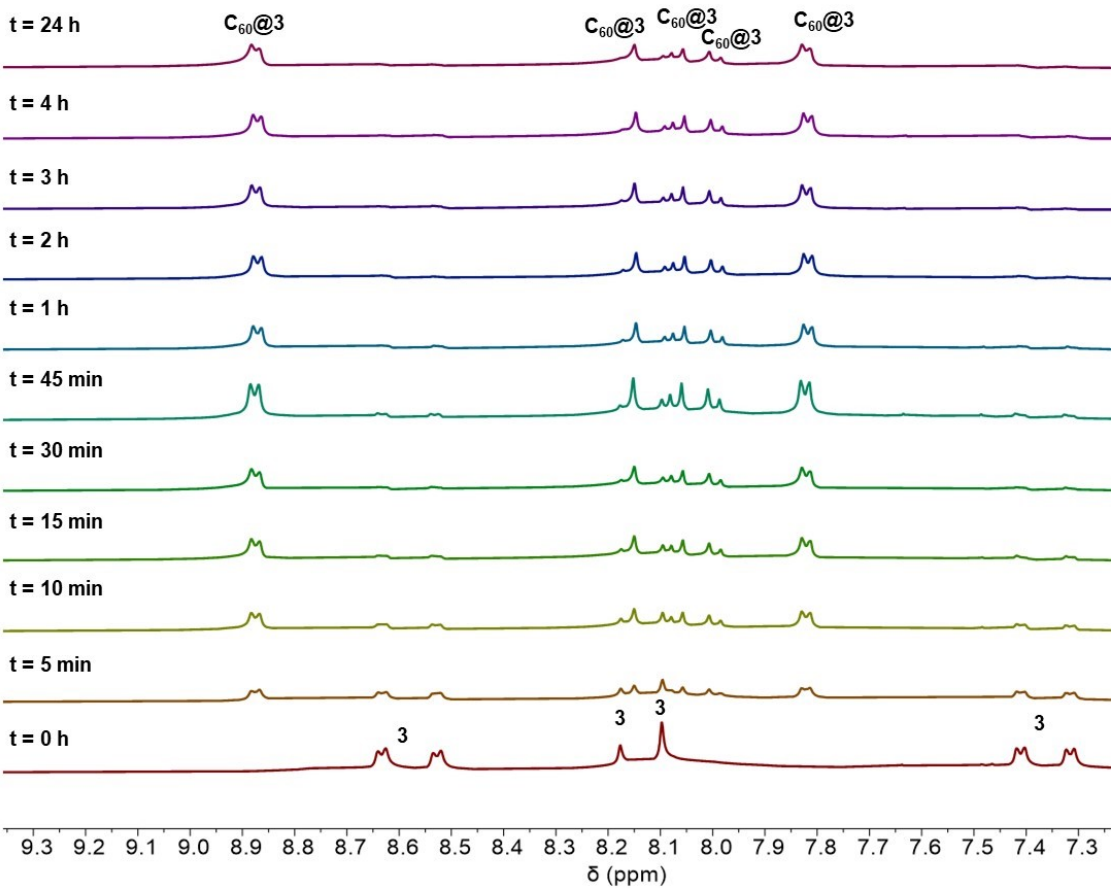


Figure S33. Selected region of the ^{1}H NMR spectra (400 MHz) of the encapsulation of C_{60} in metallobox **3**, in CD_2Cl_2, at different times.

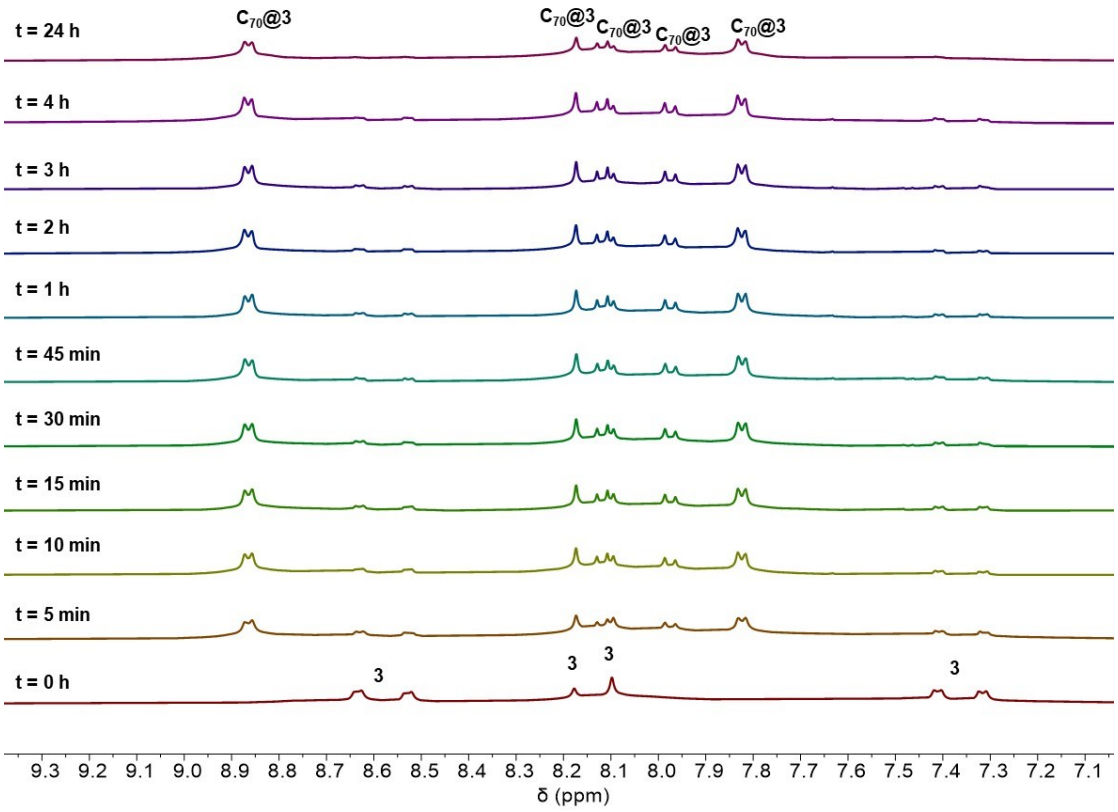


Figure S34. Selected region of the ^{1}H NMR spectra (400 MHz) of the encapsulation of C_{70} in metallobox **3**, in CD_2Cl_2, at different times.

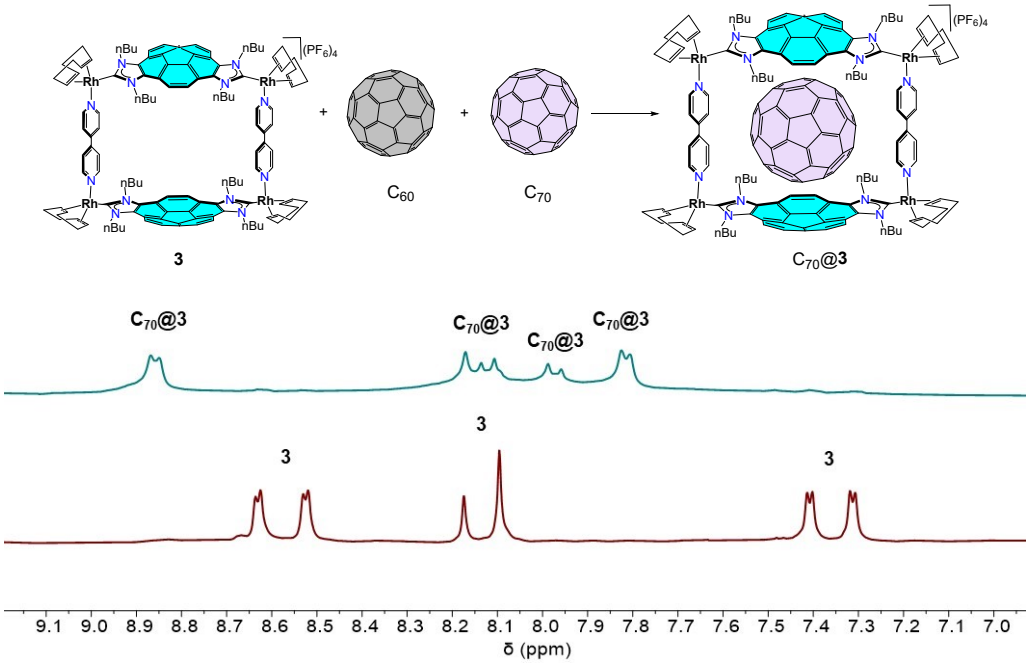


Figure S35. Selected region of the ^{1}H NMR spectra (300 MHz) of the competitive experiment encapsulation between **3**, C_{60}, and C_{70} in CD_2Cl_2.

9. Variable-temperature ^{1}H NMR experiments

A solution of **3** in $C_2D_2Cl_4$ (6.75 mM) was placed in an NMR tube. Then, the corresponding fullerene (C_{60}) was added (6.75 mM), and the suspension was placed in an ultrasonic bath. NMR spectra were recorded after different temperatures.

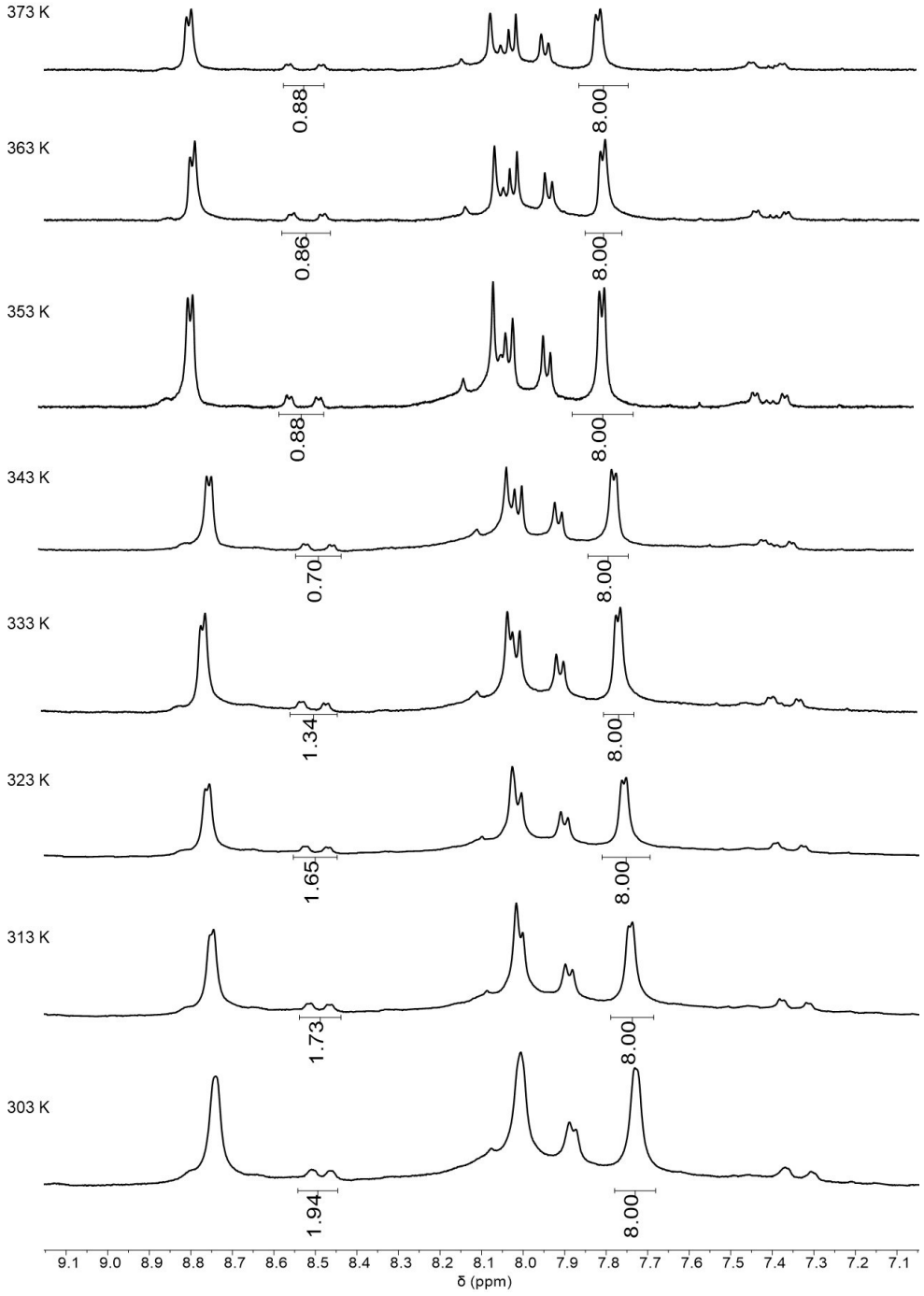


Figure S36. Selected region of the ^{1}H NMR spectra (500 MHz) of complex **C_{60}@3** in $C_2D_2Cl_4$ at different temperatures.

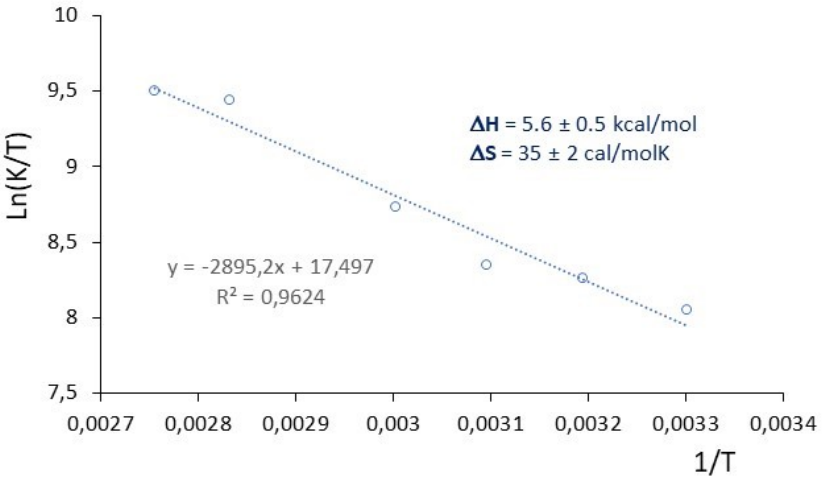


Figure S37. Van't Hoff plot resulting from the calculation of the equilibrium constants between **3** and C_{60} obtained from the ^{1}H NMR spectra ($C_2D_2Cl_4$) in a temperature range between 303-373 K.

10. DOSY experiments

The experiments were carried out in CD_2Cl_2, at constant concentrations of 5 mM on a Varian Innova 500 MHz.

Complexes	G (m^2/s)
1	$8.30\ 10^{-10}$
3	$7.04\ 10^{-10}$
C_{60}@**3**	$6.64\ 10^{-10}$
C_{70}@**3**	$6.05\ 10^{-10}$

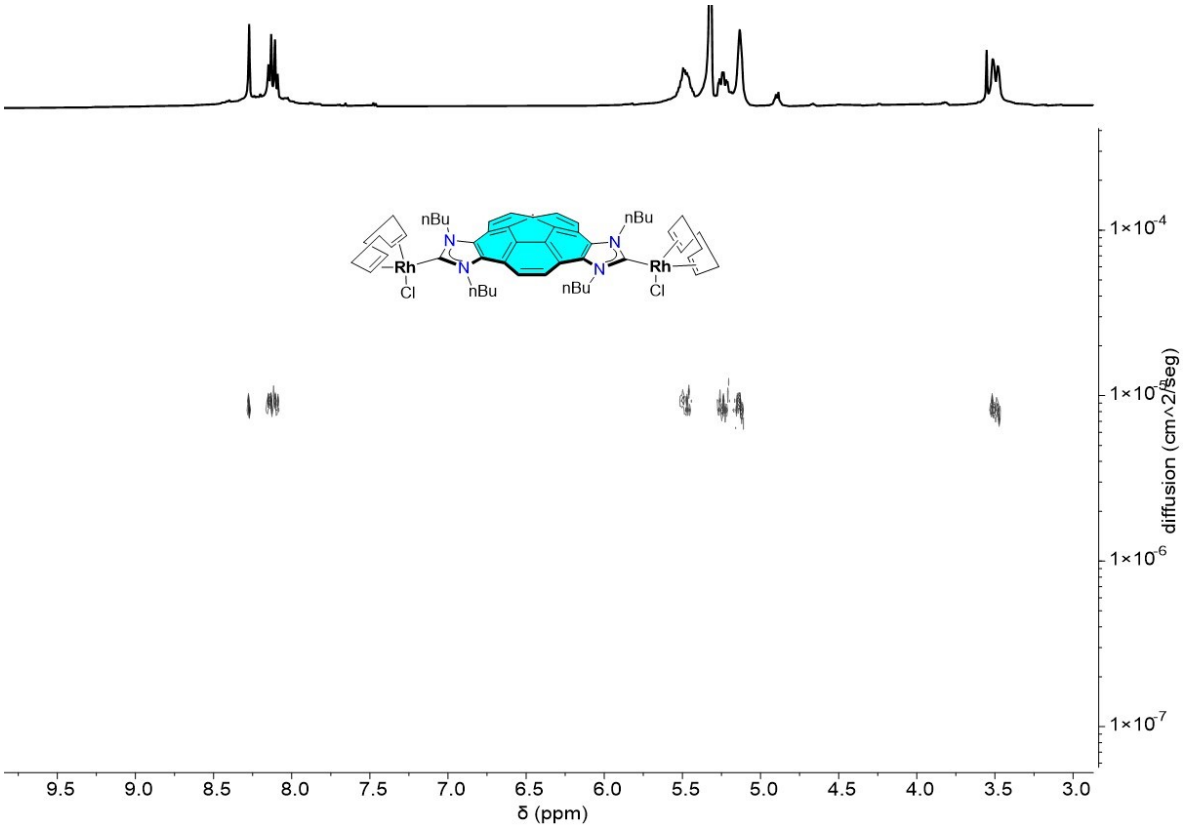


Figure S38. DOSY NMR spectrum (500 MHz) of **1** in CD_2Cl_2.

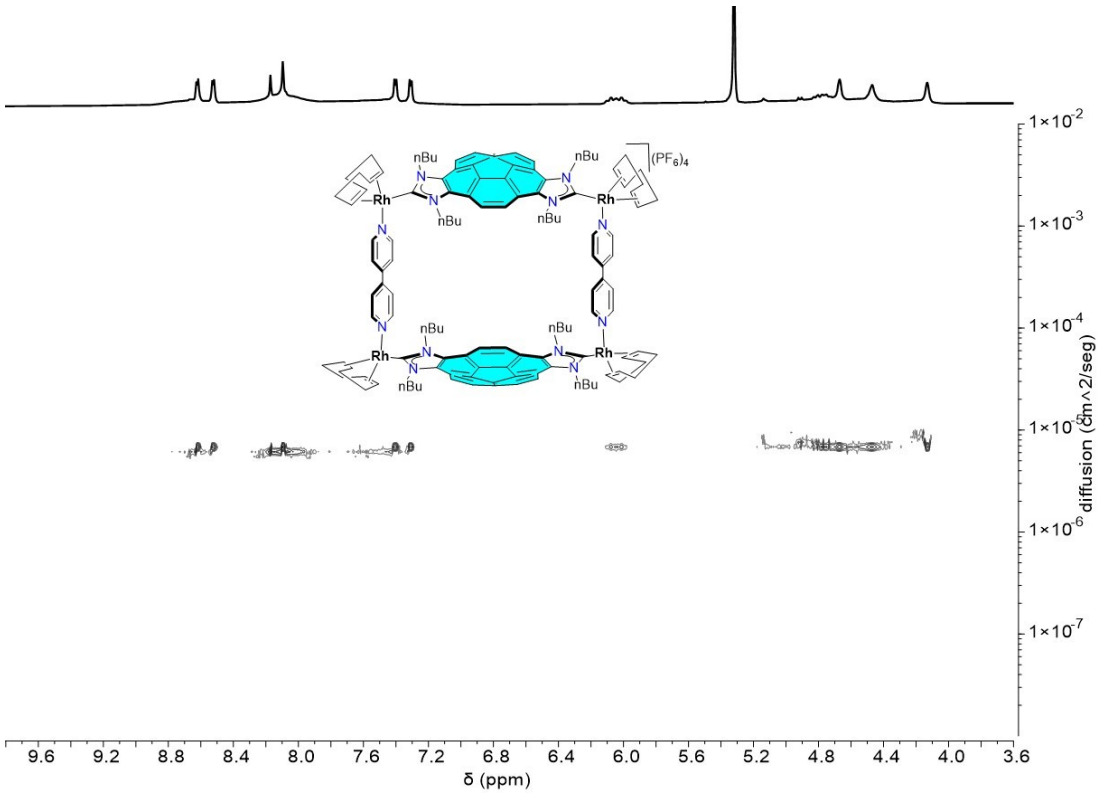


Figure S39. DOSY NMR spectrum (500 MHz) of **3** in CD_2Cl_2.

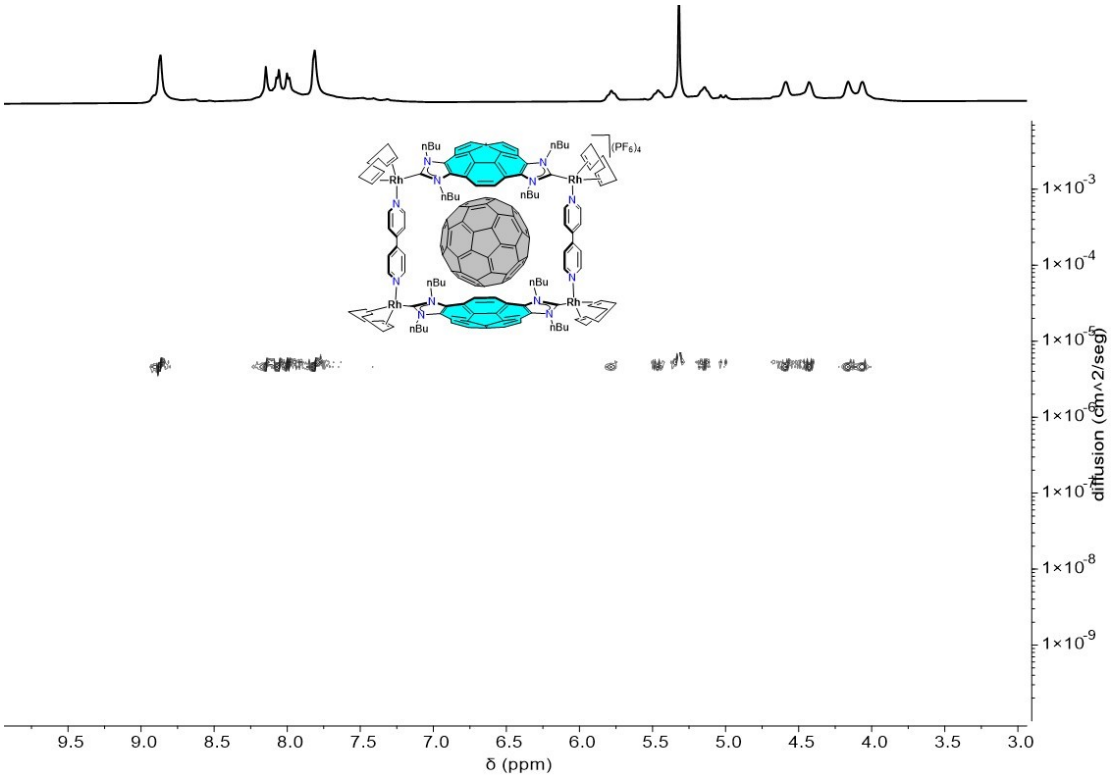


Figure S40. DOSY NMR spectrum (500 MHz) of C_{60}@**3** in CD_2Cl_2.

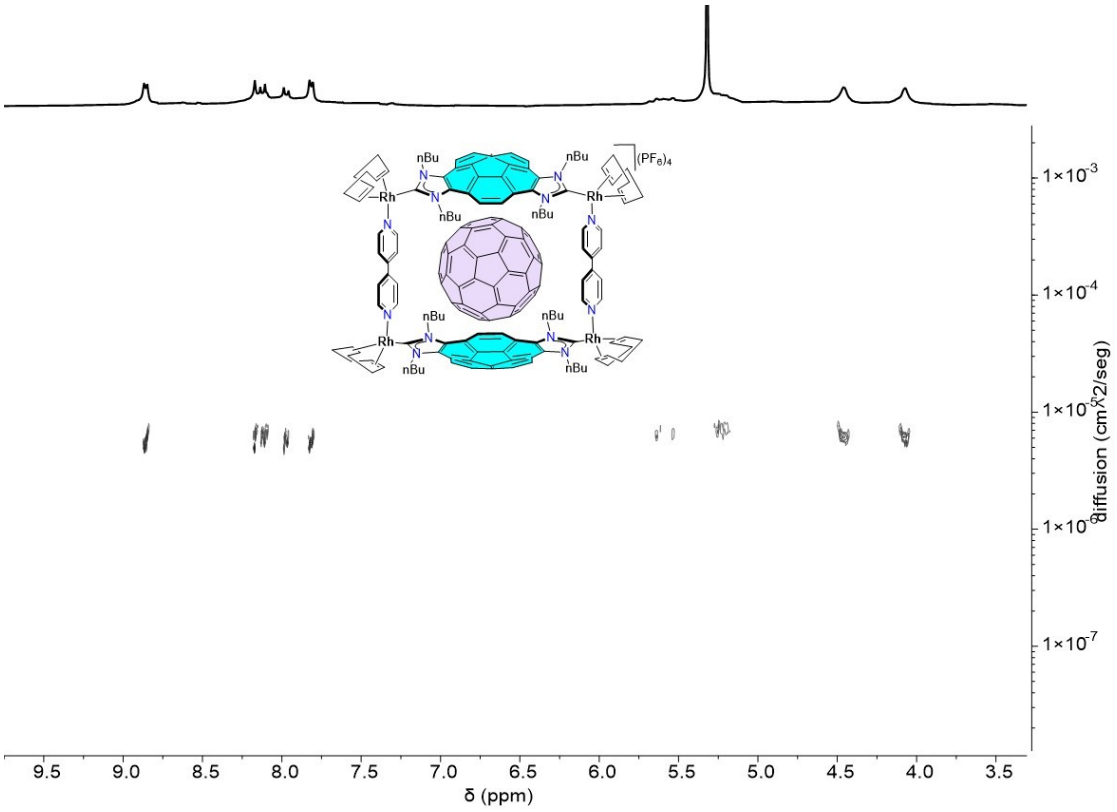


Figure 41. DOSY NMR spectrum (500 MHz) of C_{70}@**3** in CD_2Cl_2.

11. References

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