Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

for

Homoleptic complexes of isocyano- and diisocyanobiazulenes with a 12-electron, ligand-based redox capacity

Patrick T. Connelly,[†a] Jason C. Applegate,[†a] David A. Maldonado,[a] Monisola K. Okeowo,[a] Wade C. Henke,[a] Allen G. Oliver,[b] Cindy L. Berrie,*[a] and Mikhail V. Barybin*[a]

[a] *Department of Chemistry, University of Kansas, 1567 Irving Hill Road, Lawrence, KS 66045, USA*

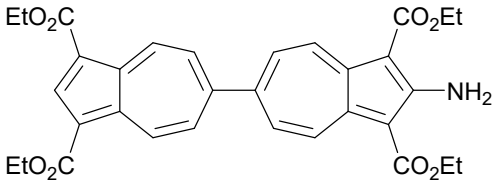
[b] *Department of Chemistry and Biochemistry, University of Notre Dame, 2002 Cavanaugh Drive, Notre Dame, IN 46556, USA*

[†]P.T.C. and J.C.A. contributed equally to this work.

*To whom correspondence should be addressed:
Email: mbarybin@ku.edu, cberrie@ku.edu
Tel: +1-785-864-4106

Table of Contents

A. Synthetic procedures and characterization



4

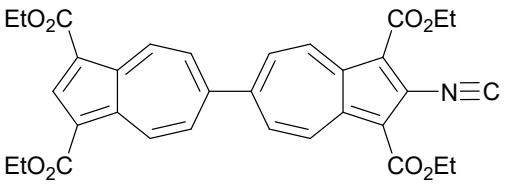
A1. General procedures, starting materials, and equipment. Unless specified otherwise, all operations were performed under an atmosphere of 99.5% argon further purified by passage through columns of activated BASF catalyst and molecular sieves. All connections involving the gas purification systems were made of glass, metal, or other materials impermeable to air. Solutions were transferred via stainless steel needles (cannulas) whenever possible. Standard Schlenk techniques were employed with a double manifold vacuum line. CH_2Cl_2 was distilled over CaH_2. Deuterated chloroform was distilled over P_2O_5. Tetrahydrofuran (THF) and toluene were distilled from Na/benzophenone. Pentane was distilled from Na/benzophenone dissolved in a minimum amount of diglyme. Following purification, all distilled solvents were stored under argon. Other solvents were used as received from commercial sources.

Infrared spectra were recorded on a PerkinElmer Spectrum 100 FTIR spectrometer with liquid samples sealed in 0.1 mm NaCl cells. NMR samples were analyzed on Bruker Avance III HD 400 MHz or Avance III 500 MHz spectrometers. NMR tubes containing air-sensitive samples were sealed under argon atmosphere. ^{1}H and ^{13}C NMR chemical shifts are given with reference to residual solvent resonances relative to $SiMe_4$. Assignments of ^{1}H and ^{13}C resonances were facilitated by 2D ^{1}H COSY and ^{1}H-^{13}C HMBC maps. UV-Vis-NIR spectra were recorded at 22 °C using a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer. Cyclic voltammetry experiments on 0.02 mM solutions of analytes in CH_2Cl_2 were conducted in a dry box at 22 °C using an EPSILON (Bioanalytical Systems Inc. West Lafayette, IN) electrochemical workstation. The supporting electrolyte was 0.1 M [^{n}Bu$_4$N][PF$_6$] in CH_2Cl_2. A three-component system consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and a glass-encased nonaqueous Ag/AgCl reference electrode was used. The reported potentials were determined at a scan rate of 100 mV/s.

Melting points of samples were measured in sealed capillaries. Elemental analyses of samples of **4**, **5**, **6**, **9**, **10**, **11**, **12**, **13**, **14** were carried out by Micro-Analysis, Inc., Wilmington, Delaware. Analytical data for **7** were obtained at the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456. 2,2′-Diisocyano-1,1′,3,3′-tetraethoxycarbonyl-6,6′-biazulene (**1**),[1] 2-amino-1,3-diethoxycarbonyl-6-pinacolatoborylazulene (**2**),[2] 1,3-diethoxycarbonyl-6-bromoazulene (**3**),[3] [(OC)$_5$Cr(2-isocyano-1,3-diethoxycarbonyl-6-bromoazulene)] (**8**),[4] bis(η^6-naphthalene)chromium(0)[5] were prepared according to according to previously published procedures or modified versions thereof. Other reagents were obtained from commercial sources and used as received.

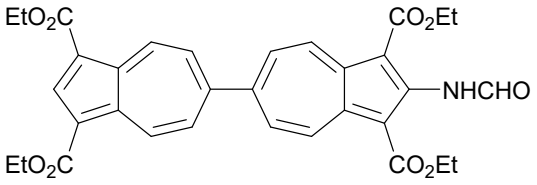
A2. Synthesis of 4. A dark orange-red solution of **2** (0.422 g, 1.02 mmol), **3** (0.332 g, 0.94 mmol), $NaHCO_3$ (0.477 g, 5.67 mmol), and [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) dichloride (dichloromethane adduct, 0.070 g, 0.075 mmol) dissolved in 20.0 mL of toluene was treated with 5.0 mL of reverse osmosed (RO) water and 5.0 mL of ethanol. The resulting mixture was brought to reflux and stirred for 1 hour while acquiring a deep red color. After cooling to room temperature, 100 mL of 5% aqueous NaCl were added, and the organic product was extracted with $CHCl_3$ (2×50 mL). The combined organic extracts were washed with 100 mL of 5% aqueous NaCl, dried over anhydrous Na_2SO_4, and filtered. All solvent was removed from the filtrate under vacuum, and the resultant red-orange residue was recrystallized from 4:1 hexanes:chloroform, affording **4** (0.479 g, 0.859 mmol) as an orange powder in 91% yield. An analogous workup of the mother liquor afforded a second crop of **4** (0.021 g, 0.038 mmol), bringing the total yield of **4** to 95%. MP: 230-232 °C. Anal. calcd for $C_{32}H_{31}NO_8$: C, 68.93; H, 5.60; N, 2.51. Found: C, 68.80; H, 5.64; N, 2.28. IR (CH_2Cl_2): ν_{CO} 1679 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 1.47 (t, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 1.50 (t, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 4.45 (q, $^3J_{HH}$ = 7 Hz, 4H, CH_2), 4.50 (q, $^3J_{HH}$ = 7 Hz, 4H, CH_2), 7.80 (d, $^3J_{HH}$ = 11 Hz, 2H, H^{5,7}/H$^{5',7'}$), 7.95 (d, $^3J_{HH}$ = 11 Hz, 2H, H^{5,7}/H$^{5',7'}$), 7.95 (s, 2H, NH_2), 8.85 (s, 1H, H$^{2'}$), 9.20 (d, $^3J_{HH}$ = 11 Hz, 2H, H^{4,8}/H$^{4',8'}$), 9.83 (d, $^3J_{HH}$ = 11 Hz, 2H, H^{4,8}/H$^{4',8'}$) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C): δ 14.73, 14.83 (CH_3), 60.26, 60.32 (CH_2), 100.9, 117.02, 130.47, 131.53, 133.56, 138.43, 142.9, 143.86, 145.31, 147.62, 156.87, 163.29 (azulenic C atoms), 165.13, 166.56 (ester CO) ppm. UV-Vis (CH_2Cl_2, λ_{max} [ε×10^{-4} M^{-1} cm^{-1}], 25 °C): 331 (5.3), 363 (5.5), 451 (3.1) nm.

A3. Synthesis of 5. Acetic-formic anhydride was prepared by stirring acetic anhydride (39.0 mL) and formic acid (46.0 mL) at 52 °C for 1.5 hours without protection from air. Then a dark red solution of **4** (0.470 g, 0.843 mmol) in 20.0 mL of CH_2Cl_2 was transferred to the acetic-formic anhydride, and the resultant mixture was stirred at 52 °C for 1 hour. After cooling to room temperature, the reaction was quenched with 150 mL of 10% aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (2×50 mL). The combined organic extracts were washed with 10% aqueous $NaHCO_3$ (2×100 mL), and dried over anhydrous Na_2SO_4. The drying agent was filtered off, and the filtrate was concentrated to dryness under vacuum. The brown residue was triturated with boiling *n*-heptane (2×30 mL) and then washed with 30 mL of ice-cold *n*-pentane, affording **5** (0.443 g, 0.757 mmol) as a yellow-brown powder in a 90% yield. MP: 205-207 °C. Anal. calcd for $C_{33}H_{31}NO_9$: C, 67.68; H, 5.34; N, 2.39. Found: C, 67.66; H, 5.46; N, 2.49. IR (CH_2Cl_2): ν_{CO} 1690 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 1.48 (t, $^3J_{HH}$ = 7 Hz, 12H, CH_3), 4.47 (q, $^3J_{HH}$ = 7 Hz, 4H, CH_2), 4.51 (q, $^3J_{HH}$ = 7 Hz, 4H, CH_2), 7.94 (d, $^3J_{HH}$ = 11 Hz, 2H, $H^{5,7}/H^{5',7'}$), 7.95 (d, $^3J_{HH}$ = 11 Hz, 2H, $H^{5,7}/H^{5',7'}$), 8.70 (s, 1H, NH), 8.90 (s, 1H, $H^{2'}$), 9.48 (d, $^3J_{HH}$ = 11 Hz, 2H, $H^{4,8}/H^{4',8'}$), 9.87 (d, $^3J_{HH}$ = 11 Hz, 2H, $H^{4,8}/H^{4',8'}$), 10.39 (s, 1H, CHO) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C): δ 14.56, 14.72 (CH_3), 60.43, 61.19 (CH_2), 77.36, 117.43, 131.37, 132.44, 135.83, 138.52, 143.08, 144.5, 153.37, 155.8, 165.01, 165.56 (azulenic C atoms, formyl CO, ester CO) ppm. UV-Vis (CH_2Cl_2, λ_{max} [ε×10^{-4} M^{-1} cm^{-1}], 25 °C): 352 (8.8), 411 (3.4) nm.



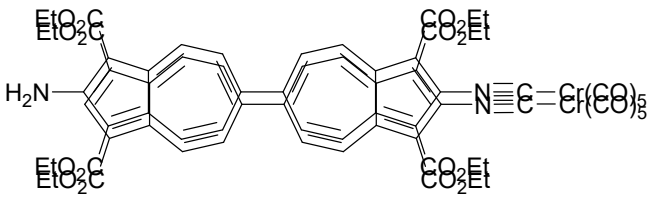
6

A4. Synthesis of 6. $POCl_3$ (0.10 mL, 1.1 mmol) was added slowly via syringe to a dark red solution of **5** (0.404 g, 0.690 mmol) in 20.0 mL THF at 0 °C. After 5 minutes of stirring, triethylamine (0.30 mL, 2.2 mmol) was added dropwise. The reaction was allowed to warm to room temperature over 1 hour while gradually turning purple. All solvent was then removed under vacuum, and the purple-red residue was treated with 100 mL of 10% aqueous $NaHCO_3$. The organic product was extracted with 150 mL CH_2Cl_2, washed with another 100 mL of 10% aqueous $NaHCO_3$, and dried over Na_2SO_4. The drying agent was filtered off, and all solvent was removed from the filtrate under vacuum. The residue was triturated with boiling *n*-heptane (2×20 mL) and filtered. The purple filter cake was washed with *n*-pentane (2×10 mL) and dried at 10^{-2} torr to afford **6** (0.329 g, 0.562 mmol) as a somewhat air-sensitive purple powder in an 84% yield. MP: 200 °C (dec.). Anal. calcd for $C_{33}H_{29}NO_8$: C, 69.83; H, 5.15; N, 2.47. Anal calcd for $C_{33}H_{29}NO_8(CH_2Cl_2)_{0.25}$ Found: C, 67.76; H, 5.05; N, 2.10. IR (CH_2Cl_2): ν_{CO} 1691, ν_{NC} 2128 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 1.48 (t, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 1.53 (t, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 4.47 (q, $^3J_{HH}$ = 7 Hz, 4H, CH_2), 4.54 (q, $^3J_{HH}$ = 7 Hz, 4H, CH_2), 7.93 (d, $^3J_{HH}$ = 11 Hz, 2H, $H^{5,7}/H^{5',7'}$), 8.04 (d, $^3J_{HH}$ = 11 Hz, 2H, $H^{5,7}/H^{5',7'}$), 8.91 (s, 1H, $H^{2'}$), 9.88 (d, $^3J_{HH}$ = 11 Hz, 2H, $H^{4,8}/H^{4',8'}$), 9.90 (d, $^3J_{HH}$ = 11 Hz, 2H, $H^{4,8}/H^{4',8'}$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C): δ 14.36, 14.7 (CH_3), 60.49, 61.36 (CH_2), 113.60, 117.69, 131.13, 132.79, 138.55, 140.35, 140.58, 143.16, 144.91, 154.96, 157.72 (azulenic C atoms), 164.9, 163.33 (ester CO), 178.41 (CNAz), ppm. UV-Vis (CH_2Cl_2, λ_{max} [ε×10^{-4} M^{-1} cm^{-1}], 25 °C): 342 (7.4), 364 (6.2), 535 (0.3) nm.



5

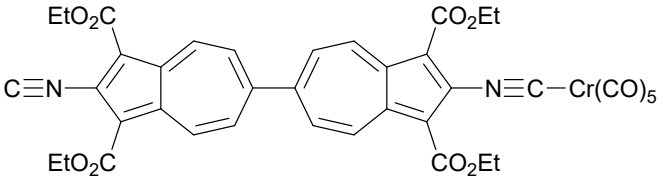
A5. Synthesis of 7. A purple-red mixture of **6** (0.105 g, 0.186 mmol), $Cr(CO)_6$ (0.082 g, 0.373 mmol), and $CoCl_2{\cdot}6H_2O$ (0.009 g, 0.038 mmol) in 40.0 mL of toluene was refluxed for 1.5 hours, acquiring an orange-red color. After cooling to room temperature, all solvent was removed under vacuum, and excess $Cr(CO)_6$ was removed by sublimation *in vacuo* at 50 °C for 2 hours. The resultant residue was dissolved in $CHCl_3$ and eluted through a *ca.* 1 in. plug of celite. All solvent was removed under vacuum to afford **7** (0.123 g, 0.162 mmol) as a red-brown powder in an 87% yield. MP: 155 °C (dec.). Anal. calcd for $C_{38}H_{29}CrNO_{13}$: C, 60.08; H, 3.85; N, 1.84. Found: C, 59.65; H, 4.11; N, 1.78. IR (CH_2Cl_2): ν_{CO} 1961 ($A_1^{(2)}$ + E), 2046 ($A_1^{(1)}$), ν_{NC} 2137 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 1.48 (t, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 1.52 (t, $^3J_{HH}$ = 7 Hz, 6H, CH_3) 4.47 (q, $^3J_{HH}$ = 7 Hz, 4H, CH_2), 4.60 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 7.95 (d, $^3J_{HH}$ = 11 Hz, 2H, $H^{5,7/5',7'}$), 8.05 (d, $^3J_{HH}$ = 11 Hz, 2H, $H^{5,7/5',7'}$), 8.93 (s, 1H, $H^{2'}$), 9.90 (d, $^3J_{HH}$ = 11 Hz, 2H, $H^{4,8/4',8'}$), 9.91 (d, $^3J_{HH}$ = 11 Hz, 2H, $H^{4,8/4',8'}$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C): δ 14.72, 14.85 (CH_3), 60.50, 61.26 (CH_2), 113.45, 117.68, 131.18, 132.50, 133.06, 138.57, 139.66, 141.21, 143.19, 144.88, 155.09, 157.02 (azulenic C atoms), 163.36, 164.95 (ester CO), 184.62 (CNAz), 214.54 (Cr-CO_{cis}), 216.60 (Cr-CO_{trans}) ppm. UV-Vis (CH_2Cl_2, λ_{max} [$\varepsilon\times10^{-4}$ M^{-1} cm^{-1}], 25 °C): 346 (7.0), 477 (2.4) nm.



9$_7$

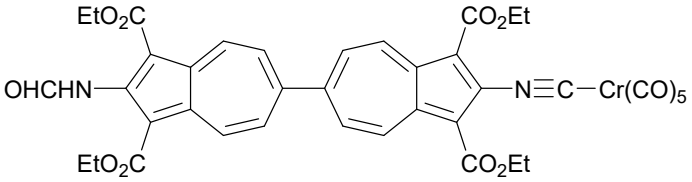
A6. Synthesis of 9. A slurry of **8** (0.090 g, 0.158 mmol), **2** (0.065 g, 0.158 mmol), $Pd(PPh_3)_4$ (0.006 g, 0.005 mmol), and $NaHCO_3$ (0.084 g, 0.998 mmol) in 10.0 mL of toluene and 7.0 mL of 70% ethanol was refluxed for 3 hours without protection from air, acquiring a deep red color. After cooling to room temperature and stirring for another 15 hours, the reaction mixture was treated with 30 mL of RO water and extracted with CH_2Cl_2 (3×20 mL). The combined organic extracts were washed with water (3×50 mL), dried over anhydrous Na_2SO_4, and filtered. All solvent was removed under vacuum, and the residue was subjected to column chromatography on silica gel using neat CH_2Cl_2 as eluent. A deep red band was collected. All solvent was removed under vacuum, and the reddish-brown residue was recrystallized from CH_2Cl_2 layered with *n*-pentane to afford **9** in a 78% yield (0.095 g, 0.123 mmol). MP: 160 °C (dec.) Anal. calcd for $C_{38}H_{30}CrN_2O_{13}$: C, 58.92; H, 3.90; N, 3.62. Found: C, 59.01; H, 4.13; N, 3.65. IR (CH_2Cl_2): ν_{CO} 1679, 1691 (esters), ν_{CO} 1959 ($A_1^{(2)}$ + E), 2047 ($A_1^{(1)}$), ν_{NC} 2138 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.51 (t, $^3J_{HH}$= 7 Hz, 6H, CH_3), 1.52 (t, $^3J_{HH}$= 7 Hz, 6H, CH_3) 4.51 (q, $^3J_{HH}$= 7 Hz, 4H, CH_2), 4.59 (q, $^3J_{HH}$= 7 Hz, 4H, CH_2), 7.80 (d, $^3J_{HH}$= 12 Hz, 2H, $H^{5,7}$), 7.98 (s, 2H, NH_2), 8.04 (d, $^3J_{HH}$= 11 Hz, 2H, $H^{5',7'}$), 9.21 (d, $^3J_{HH}$= 12 Hz, 2H, $H^{4,8}$), 9.85 (d, $^3J_{HH}$= 11 Hz, 2H, $H^{4',8'}$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C): δ 14.83, 14.88 (CH_3), 60.35, 61.14 (CH_2), 101.10, 113.01, 130.35, 131.74, 133.13, 133.41, 139.54, 140.82, 145.44, 146.62, 158.05, 163.41 (azulenic C atoms), 163.50, 166.47 (ester CO), 183.54 (CNAz), 214.59 (Cr-CO_{cis}), 216.69 (Cr-CO_{trans}) ppm. UV-Vis (CH_2Cl_2, λ_{max} [$\varepsilon\times10^{-4}$ M^{-1} cm^{-1}], 25 °C): 329 (5.8), 349 sh (5.2), 364 (4.9), 496 (4.9) nm.

A7. Synthesis of 10. Acetic-formic anhydride was prepared by stirring acetic anhydride (38.0 mL) and formic acid (45.0 mL) at 60 °C for 3 hours without protection from air. Then, a ruby red solution of **9** (0.150 g, 0.194 mmol) dissolved in a minimum volume of CH_2Cl_2 was transferred to the acetic-formic anhydride, and the resultant mixture was stirred at 60 °C for 18 hours. After cooling to room temperature, the reaction was quenched with 10% Na_2CO_3(*aq*) and extracted with CH_2Cl_2 (3×100 mL). The combined organic extracts were washed with 100 mL of RO water, dried over anhydrous Na_2SO_4, and filtered. All solvent was removed from the filtrate under vacuum, and the residue was subjected to column chromatography on silica gel. Neat CH_2Cl_2 eluent was used to remove impurities, followed by 3:1 hexanes:ethyl acetate to elute the product. The eluate containing **10** was concentrated to dryness under vacuum to afford **10** (0.111 g, 0.138 mmol) as a deep brown solid in a 71% yield. MP: 144-145 °C. IR (CH_2Cl_2): ν_{CO} 1666 (formyl), 1693 (esters), ν_{CO} 1960 (E + $A_1^{(2)}$), 2046 ($A_1^{(1)}$), ν_{NC} 2137 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.48 (t, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 1.51 (t, $^3J_{HH}$= 7 Hz, 6H, CH_3), 4.51 (q, $^3J_{HH}$= 7 Hz, 4H, CH_2), 4.60 (q, $^3J_{HH}$= 7 Hz, 4H, CH_2), 7.93 (d, $^3J_{HH}$= 11 Hz, 2H, $H^{5',7'}$), 8.04 (d, $^3J_{HH}$= 11 Hz, 2H, $H^{5,7}$), 8.70 (s, br, 1H, NH), 9.49 (d, $^3J_{HH}$= 11 Hz, 2H, $H^{4',8'}$), 9.90 (d, $^3J_{HH}$= 11 Hz, 2H, $H^{4,8}$), 10.41 (s, br, 1H, CHO) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C): δ 14.53, 14.86 (CH_3), 61.26 (br, CH_2), 113.38, 132.21, 132.37, 133.02, 135.77, 139.60, 141.15, 152.41, 156.86 (azulenic C atoms), 163.39 (ester CO) 165.52 (formyl CO), 184.48 (CNAz), 214.52 (Cr-CO_{cis}), 216.55 (Cr-CO_{trans}) ppm. UV-Vis (CH_2Cl_2, λ_{max} [ε×10^{-4} M^{-1} cm^{-1}], 25 °C): 319 sh (3.7), 354 (6.3), 425 (2.1), 478 (3.0) nm.



11

A8. Synthesis of 11. Neat $POCl_3$ (0.08 mL, 0.86 mmol) was added dropwise to an orange solution of **10** (0.034 g, 0.043 mmol) in 20 mL THF at −95 °C. After 10 minutes of stirring, triethylamine (0.240 mL, 1.72 mmol) was added to the reaction. The resulting mixture was brought to room temperature and stirred for 2 hours. The solvent was then removed under reduced pressure, and the residue was quenched with 50 mL of 10% aqueous $NaHCO_3$. The organic product was extracted with 50 mL of CH_2Cl_2, washed with additional 10% aqueous $NaHCO_3$ (3×50 mL), and dried over anhydrous Na_2SO_4. The drying agent was filtered off, and all solvent was removed from the filtrate under vacuum. The crude product was purified by elution through a half-inch silica plug using CH_2Cl_2 as eluent. The eluate containing **11** was concentrated under vacuum and layered with *n*-pentane to afford purple microcrystalline **11** (0.026 g, 0.034 mmol) in a 79% yield. MP: 130 °C (dec). Anal. calcd for $C_{39}H_{28}CrN_2O_{13}$: C, 59.70; H, 3.60; N, 3.57. Found: C: 59.39; H: 3.55; N: 3.52. IR (CH_2Cl_2): ν_{CO} 1694 (ester), ν_{CO} 1961 (E + $A_1^{(2)}$), 2045 ($A_1^{(1)}$), ν_{NC} 2127 sh (free), 2136 (complexed) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.48 (t, $^3J_{HH}$ = 7 Hz, 12H, CH_3), 4.55 (q, $^3J_{HH}$= 7 Hz, 4H, CH_2), 4.60 (q, $^3J_{HH}$= 7 Hz, 4H, CH_2), 8.02 (d, $^3J_{HH}$= 11 Hz, 2H, $H^{5,7}$), 8.04 (d, $^3J_{HH}$= 11 Hz, 2H, $H^{5',7'}$), 9.92 (d, $^3J_{HH}$= 11 Hz, 2H, $H^{4,8}$), 9.93 (d,$^3J_{HH}$= 11 Hz, 2H, $H^{4',8'}$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C): δ 14.37, 14.86 (CH_3), 61.33, 61.45 (CH_2), 113.63, 113.78, 132.03, 132.58, 132.78, 132.80, 139.63, 140.40, 140.70, 141.34, 155.92, 156.81 (azulenic C atoms), 163.30, 163.33 (CO), 178.66 (free CNAz), 185.07 (Cr-CNAz), 214.47 (Cr-CO_{cis}), 216.48 (Cr-CO_{trans}) ppm. UV-Vis (CH_2Cl_2, λ_{max} [ε×10^{-4} M^{-1} cm^{-1}], 25 °C): 277 (3.7), 347 (6.2), 372 (5.6), 485 (2.9) nm.

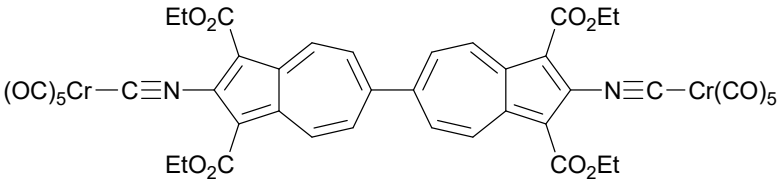


10

Synthesis of **11** from the amino derivative **9** exposed the [(-NC)Cr$(CO)_5$] subunit of **9** to rather harsh conditions. Indeed, conversion of **9** into the corresponding isolable formamide **10** involved acidic formylating conditions. Dehydration of the 2'-formamido group of the orange-colored complex **10** involved treatment of the compound with $POCl_3$. Remarkably, the [(-NC)Cr$(CO)_5$] moiety was unaffected by this harsh reagent. While the product was air- and thermally stable at room temperature, it proved to be difficult to purify. Reversion back to both the formamide **10** and the amine **9** were observed when the mononuclear diisocyanide complex **11** was subjected to column chromatography on silica gel or neutral alumina, respectively. However, if a concentrated solution of crude **11** in CH_2Cl_2 was passed through a short silica gel plug, less than 1 inch in height, a solution of the pure product could be collected from the column prior to its decomposition.

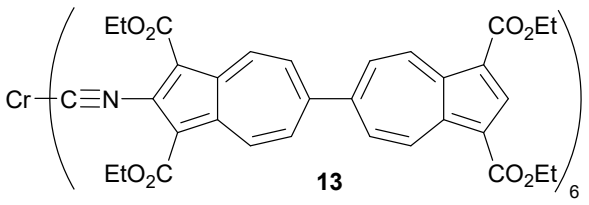
A9. Synthesis of 12. A red-orange solution of Cr$(CO)_5$(THF) was prepared *in situ* by photolysis of Cr$(CO)_6$ (0.033 g, 0.932 mmol) dissolved in 100 mL of THF using a Hanovia Hg 450 W immersion lamp. Upon completion of the

photolysis, a solution of **11** (0.041 g, 0.069 mmol) in 50 mL of THF was added to the $Cr(CO)_5$(THF) solution at ambient temperature. The resulting mixture was stirred for 2 hours. The reactor was then opened to air and its content was concentrated to dryness under vacuum. The residue was passed through a short silica gel column using neat CH_2Cl_2. The first eluted band, deep purple in color, was collected. Solvent removal and drying at 10^{-2} torr afforded **12** as a microcrystalline solid in a 45% yield. MP: 190 °C (dec). Anal. calcd for $C_{44}H_{28}Cr_2N_2O_{18}$: C, 54.11; H, 2.89; N, 2.87. Found: C: 54.14; H: 3.18; N: 2.78. IR (CH_2Cl_2): ν_{CO} 1961 (E + $A_1^{(2)}$), 2043 ($A_1^{(1)}$), ν_{NC} 2136, cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.52 (t, $^3J_{HH}$ = 7 Hz, 12H, CH_3), 4.60 (q, $^3J_{HH}$ = 7 Hz, 8H, CH_2), 8.03 (d, $^3J_{HH}$ = 11 Hz, 4H, $H^{5,5',7,7'}$), 9.92(d, $^3J_{HH}$ = 11 Hz, 4H, $H^{4,4',8,8'}$) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ 14.85 (CH_3), 61.32 (CH_2), 113.62, 132.73, 132.81, 139.61, 141.32, 156.03 (azulenic C atoms), 163.31 (ester CO), 185.06 (CNAz), 214.48 (Cr-CO_{cis}), 216.49 (Cr-CO_{trans}) ppm. UV-Vis (CH_2Cl_2, λ_{max} [$\varepsilon \times 10^{-4}$ M^{-1} cm^{-1}], 25 °C): 281 (4.8) sh, 347 (7.3), 366 (6.5) sh, 507 (4.7) nm.



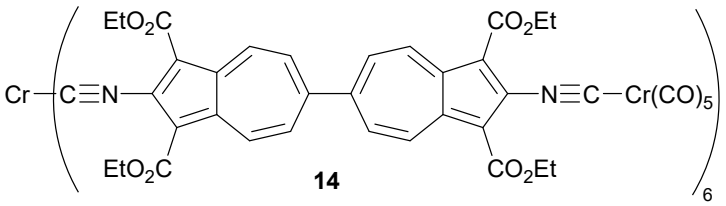
12

A10. Synthesis of 13. A red-purple solution of **6** (0.157 g, 0.277 mmol) in 25.0 mL THF was transferred to a brown solution of bis(η⁶-naphthalene)chromium(0) (0.014 g, 0.045 mmol) in 15.0 mL THF at 0 °C. The reaction mixture turned yellow-brown and was warmed to room temperature while stirring for 3 hours. The reaction mixture was then concentrated to *ca.* 5 mL, and 20.0 mL of *n*-pentane were added to crash out a green-brown solid, which was filtered off in air atmosphere. The filter cake was washed with *n*-pentane (2×5 mL) and dried at 10^{-2} torr to afford somewhat air-sensitive **13** (0.116 g, 0.034 mmol) in a 75% yield. Anal. calcd for $C_{198}H_{174}N_6O_{48}Cr$: C, 68.78; H, 5.07; N, 2.43. Found: C: 65.58; H: 4.79; N: 2.19. While **13** demonstrated excellent spectroscopic purity, three separate elemental analysis attempts invariably resulted in lower than expected %C. IR (CH_2Cl_2): ν_{CO} 1696, ν_{NC} 1973 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 1.08 (t, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 1.47 (t, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 4.21 (q, $^3J_{HH}$ = 7 Hz, 4H, CH_2), 4.46 (q, $^3J_{HH}$ = 7 Hz, 4H, CH_2), 7.86 (d, $^3J_{HH}$ = 11 Hz, 2H, $H^{5,7}$), 7.96 (d, $^3J_{HH}$ = 11 Hz, 2H, $H^{5',7'}$), 8.88 (s, 1H, $H^{2'}$), 9.58 (d, $^3J_{HH}$ = 11 Hz, 2H, $H^{4,8}$), 9.86 (d, $^3J_{HH}$ = 11 Hz, 2H, $H^{4',8'}$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C): δ 14.67, 14.72 (CH_3), 60.40, 60.54 (CH_2), 113.57, 117.35, 131.31, 132.45, 136.31, 138.51, 141.85, 143.05, 144.33, 153.17, 156.10 (azulenic C atoms), 163.65, 165.05 (ester CO) ppm. UV-Vis-NIR (CH_2Cl_2, λ_{max} [$\varepsilon \times 10^{-4}$ M^{-1} cm^{-1}], 25 °C): 480 (41.0), 620 (37.2), 857 (60.1) nm.



13

A11. Synthesis of 14. Bis(η⁶-naphthalene)-chromium(0) (0.008 g, 0.024 mmol) and **11** (0.080 g, 0.103 mmol) were dissolved in 35.0 mL of THF. After 75 minutes of stirring at room temperature, the solution was concentrated to dryness under vacuum. The residue was dissolved in a minimum amount of CH_2Cl_2 and layered with *n*-pentane to crystallize the product overnight. The resulting black crystals were filtered and dried at 10^{-2} torr to afford **14** (0.050 g, 0.001 mmol) in a 64% yield. Anal. calcd for $C_{234}H_{168}Cr_7N_{12}O_{78}$: C, 59.05; H, 3.56; N, 3.53. Found: C, 58.07; H, 3.38; N, 3.42. IR (CH_2Cl_2): ν_{NC} 1960 br (T_{1u}), ν_{CO} 1961 (E + $A_1^{(2)}$), 2043 ($A_1^{(1)}$), ν_{NC} 2134 cm^{-1}.^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.98 (t, $^3J_{HH}$ = 7 Hz, 36H, CH_3), 1.52 (t, $^3J_{HH}$ = 7 Hz, 36H, CH_3), 4.14 (q, $^3J_{HH}$ = 7 Hz, 24H, CH_2), 4.60 (q, $^3J_{HH}$ = 7 Hz, 24H, CH_2), 8.06 (d, $^3J_{HH}$ = 11 Hz, 12H, $H^{5,7}$), 8.32 (d, $^3J_{HH}$ = 11 Hz, 12H, $H^{5',7'}$), 9.71(d, $^3J_{HH}$ = 11 Hz, 12H, $H^{4,8}$), 9.96 (d, $^3J_{HH}$ = 11 Hz, 12H, $H^{4',8'}$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz, 25 °C): δ 14.74, 14.91 (CH_3) 60.74, 61.40 (CH_2) 113.65, 132.40, 132.65, 133.27, 136.48, 139.80, 141.07, 142.16, 152.69, 157.53 (azulenic C atoms), 163.53, 163.74 (ester CO), 184.04 (CNAz), 214.99 (Cr-CO_{cis}), 217.22 (Cr-CO_{trans}) ppm. UV-Vis (CH_2Cl_2, λ_{max} [$\varepsilon \times 10^{-4}$ M^{-1} cm^{-1}], 25 °C): 349 (44.0), 489 (17.8), 650-1700 centered at 1000 (~10) nm.



14

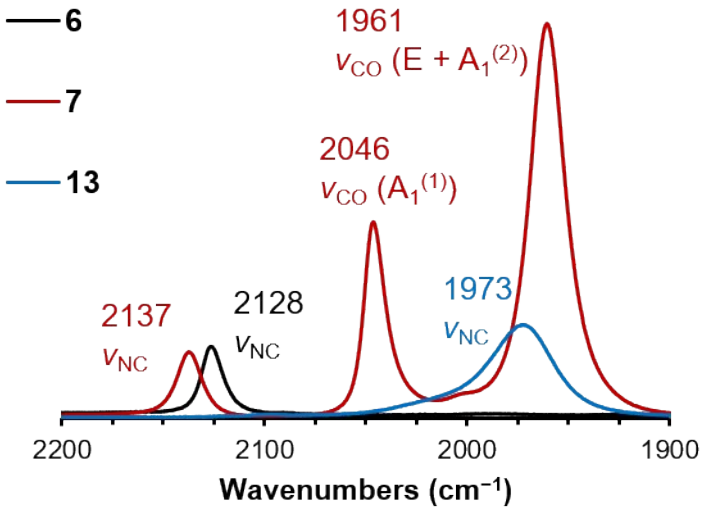


Figure S1: FTIR spectra of **6** (black), **7** (red), and **13** (blue) in CH_2Cl_2 at 22 °C. Vertical axis is absorbance in arbitrary units.

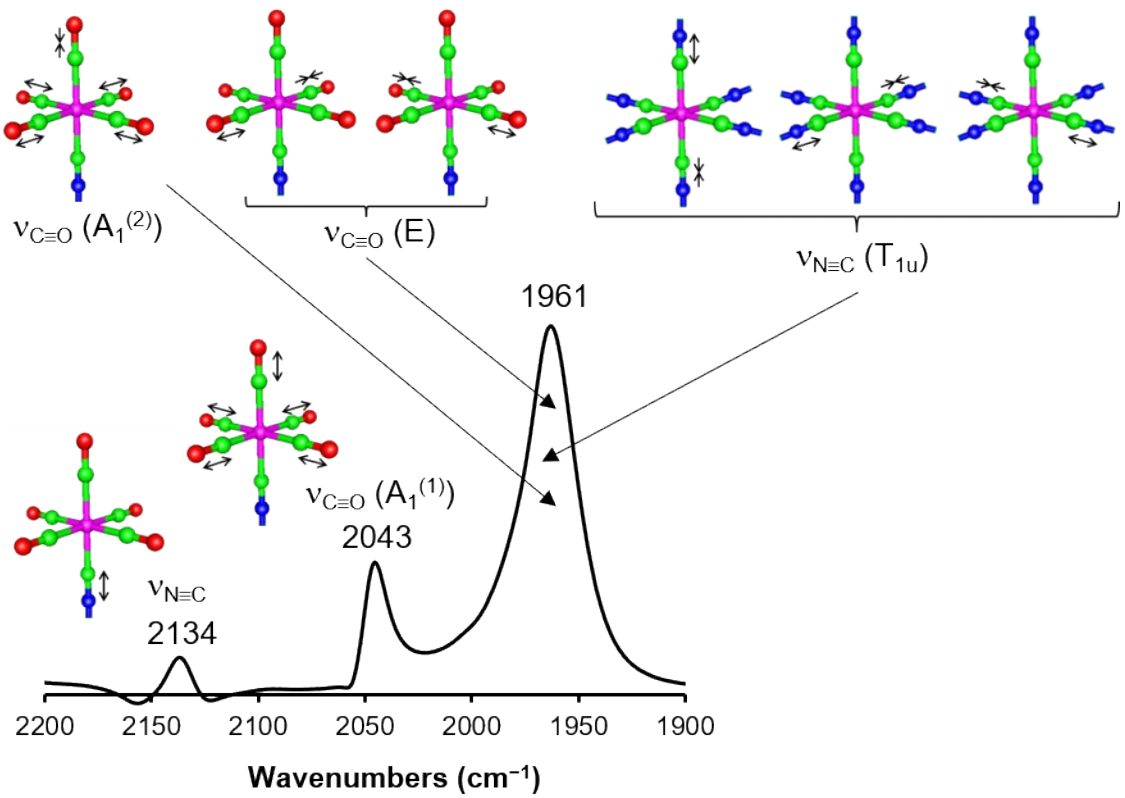


Figure S2: FTIR spectrum of **14** in CH_2Cl_2 at 22 °C. Vertical axis is absorbance in arbitrary units.

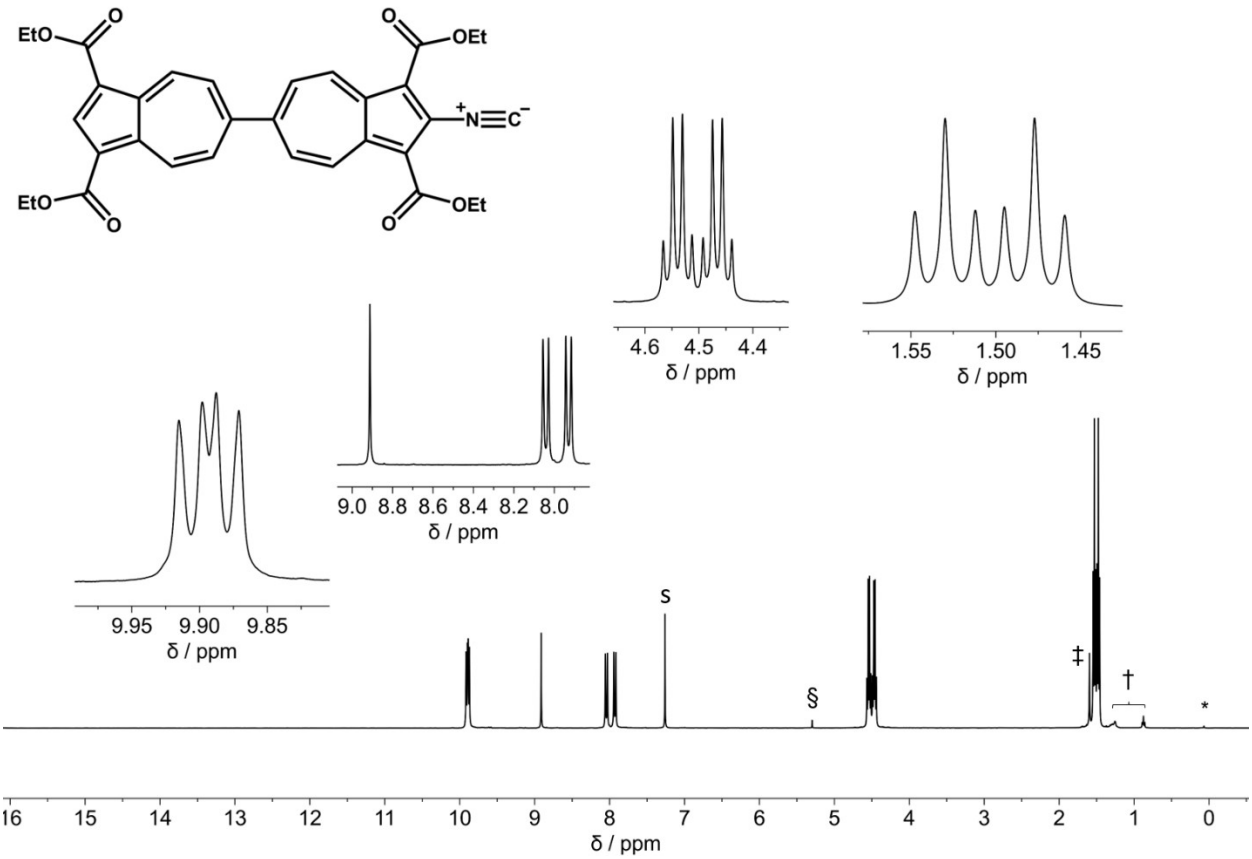


Figure S3: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of **6**. $^{s}CHCl_3$ solvent residual *silicone grease †*n*-pentane impurity $^{\ddagger}H_2O$ impurity in solvent $^{\S}CH_2Cl_2$ impurity.

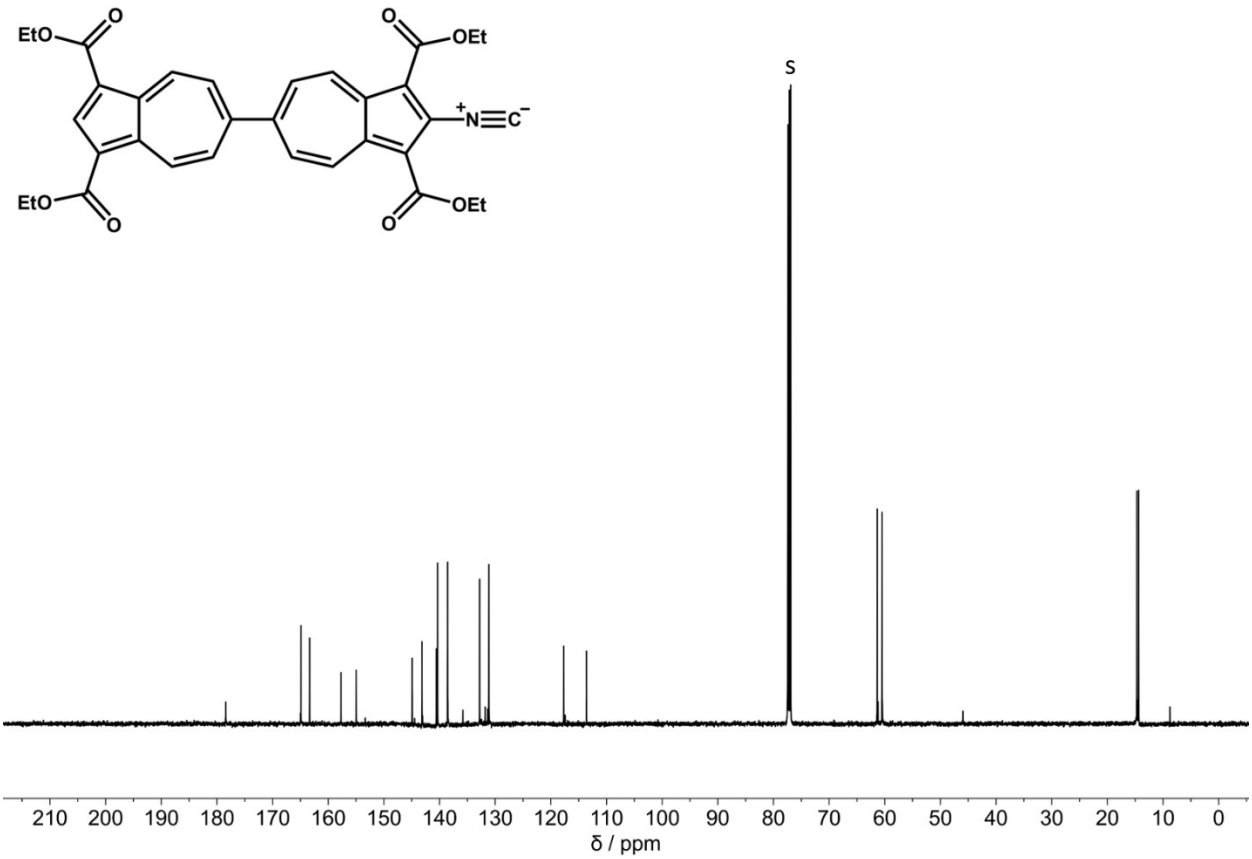


Figure S4: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 25 °C) of **6**. $^{s}CHCl_3$ solvent residual.

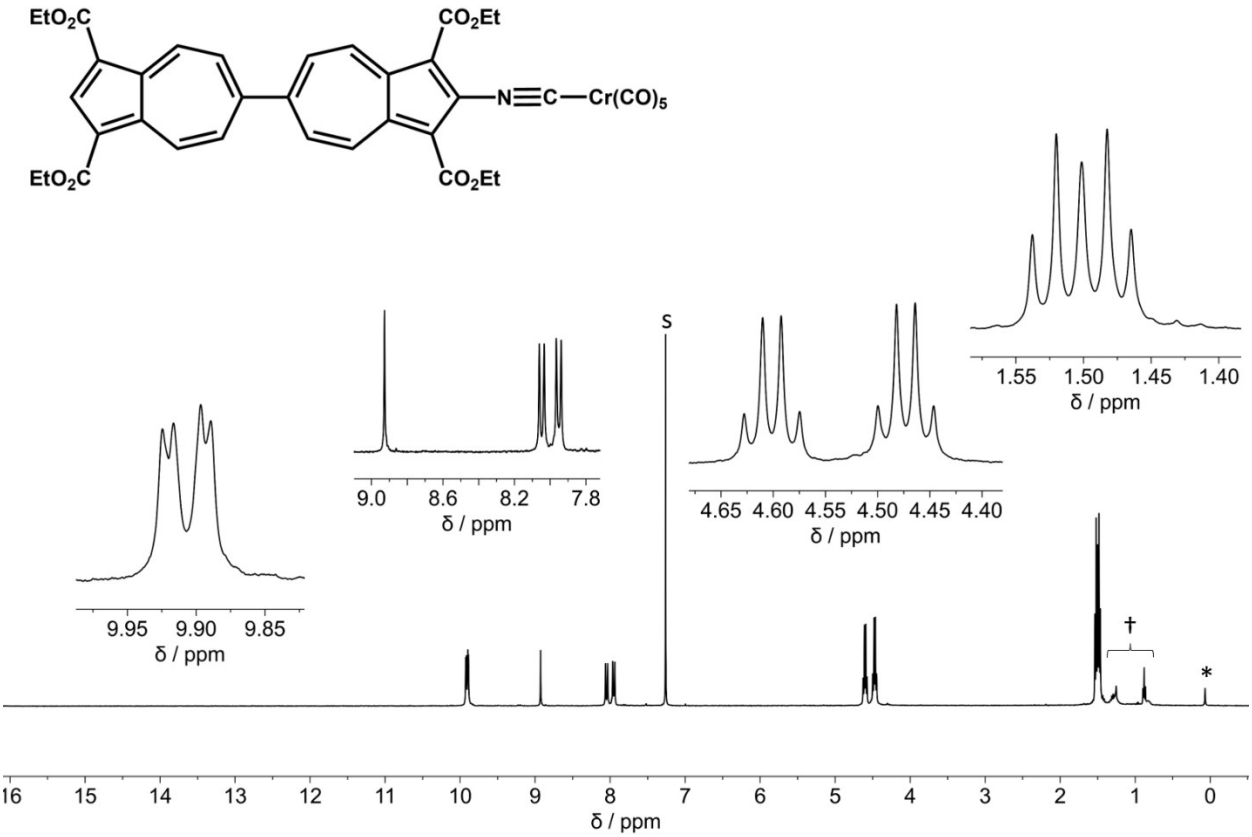


Figure S5: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of **7**. $^{s}CHCl_3$ solvent residual *silicone grease †*n*-pentane impurity.

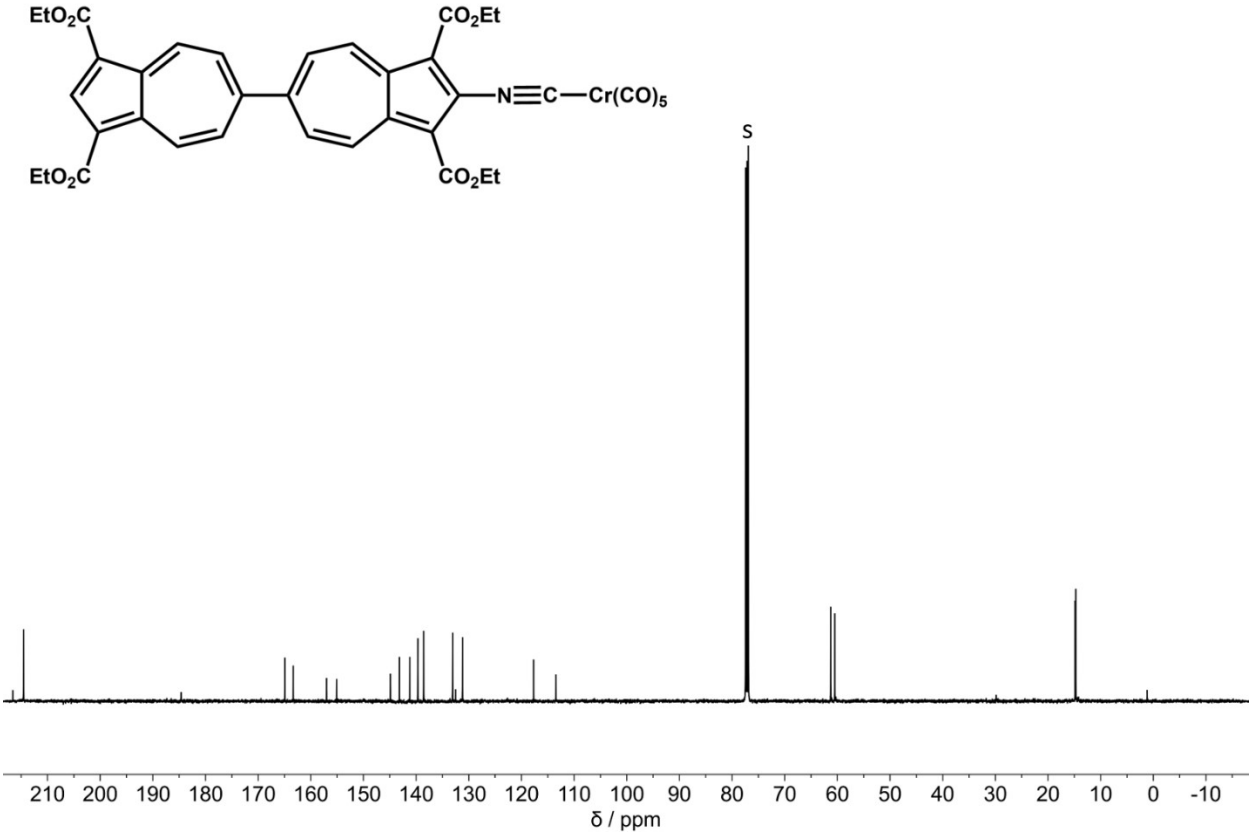


Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 25 °C) of **7**. $^{s}CHCl_3$ solvent residual.

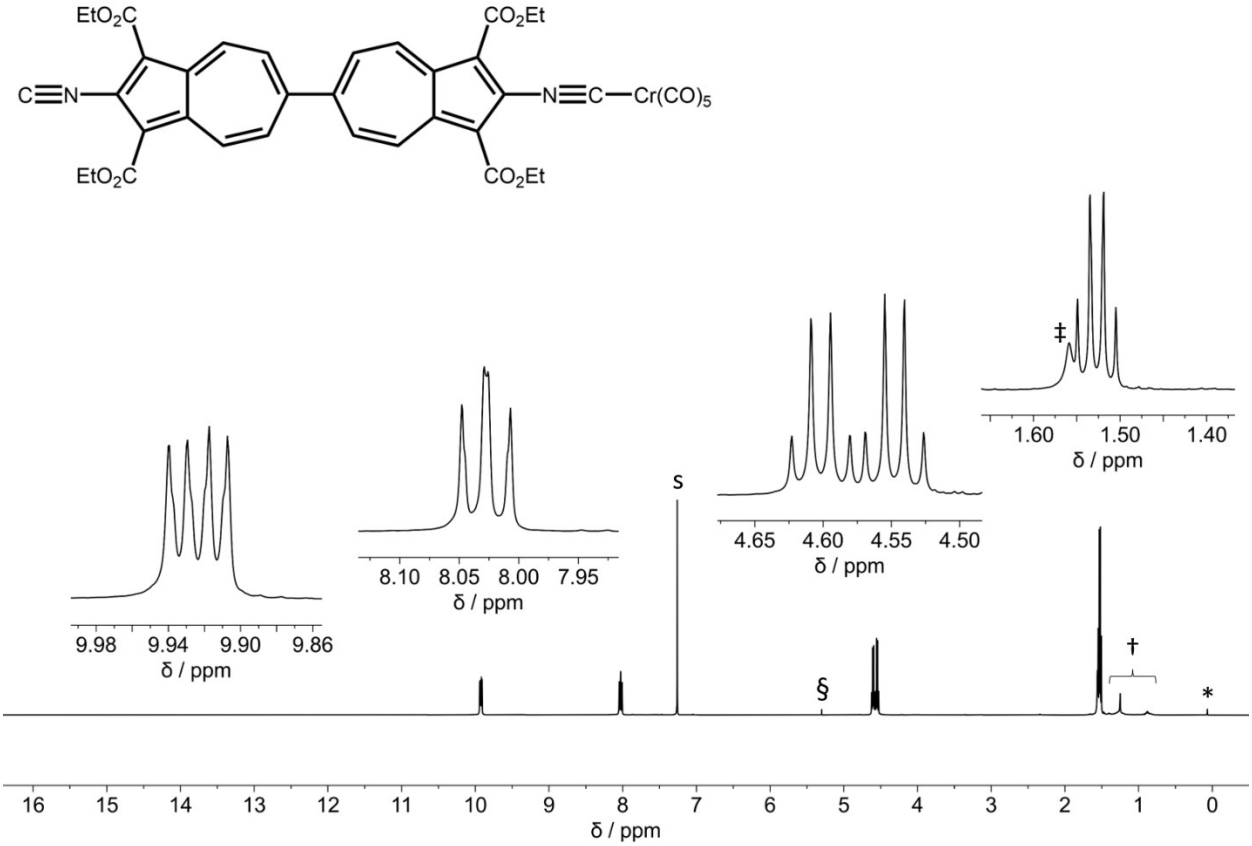


Figure S7: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of **11**. $^{s}CHCl_3$ solvent residual *silicone grease †*n*-pentane impurity $^{\ddagger}H_2O$ impurity in solvent $^{\S}CH_2Cl_2$ impurity.

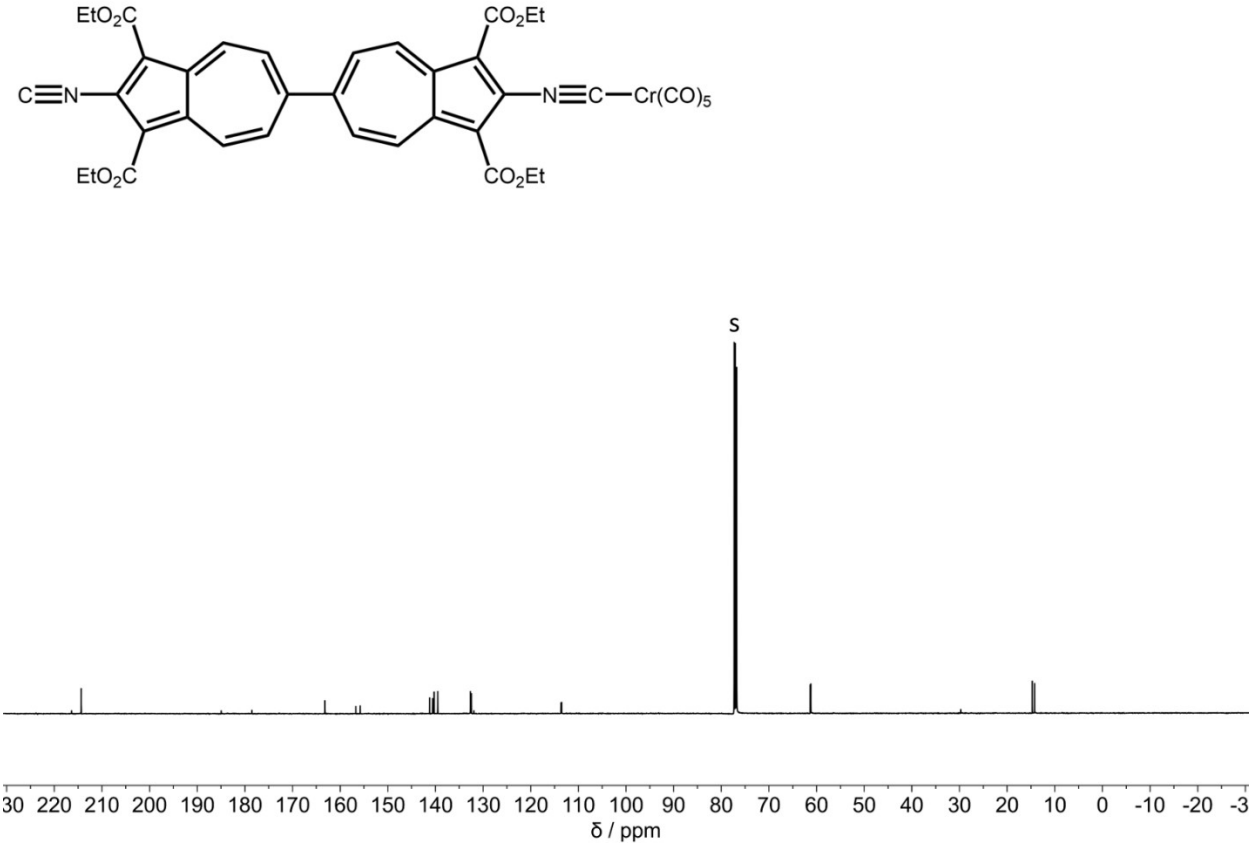


Figure S8: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 25 °C) of **11**. $^{s}CHCl_3$ solvent residual.

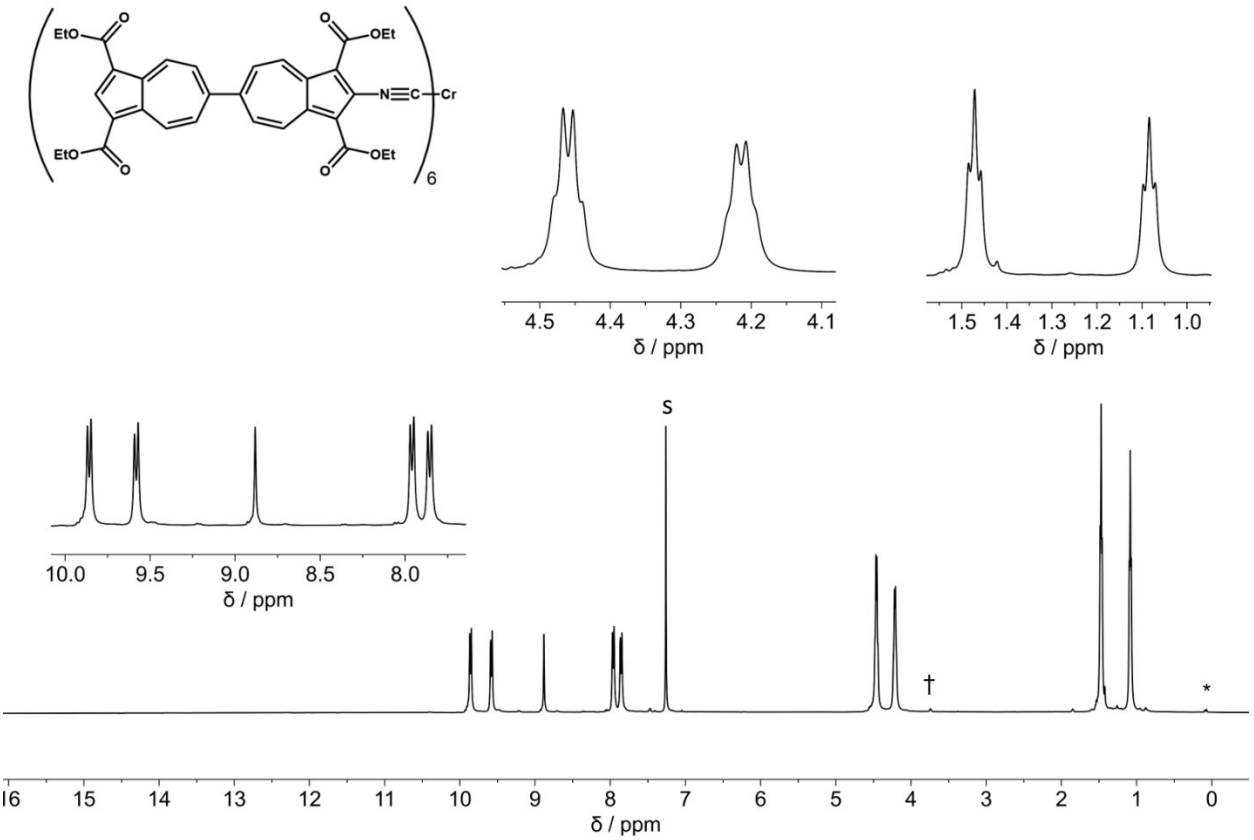


Figure S9: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of **13**. $^{s}CHCl_3$ solvent residual *silicone grease †THF impurity

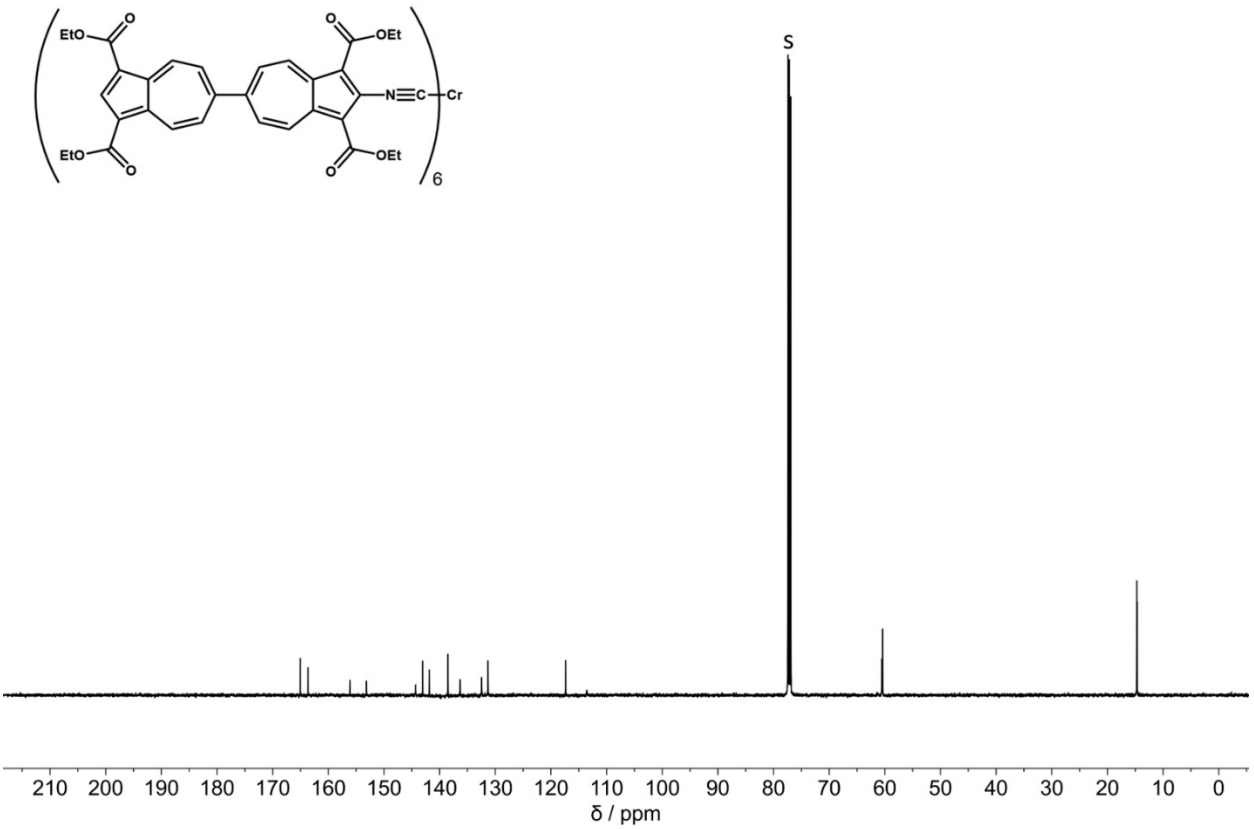


Figure S10: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 25 °C) of **13**. $^{s}CHCl_3$ solvent residual.

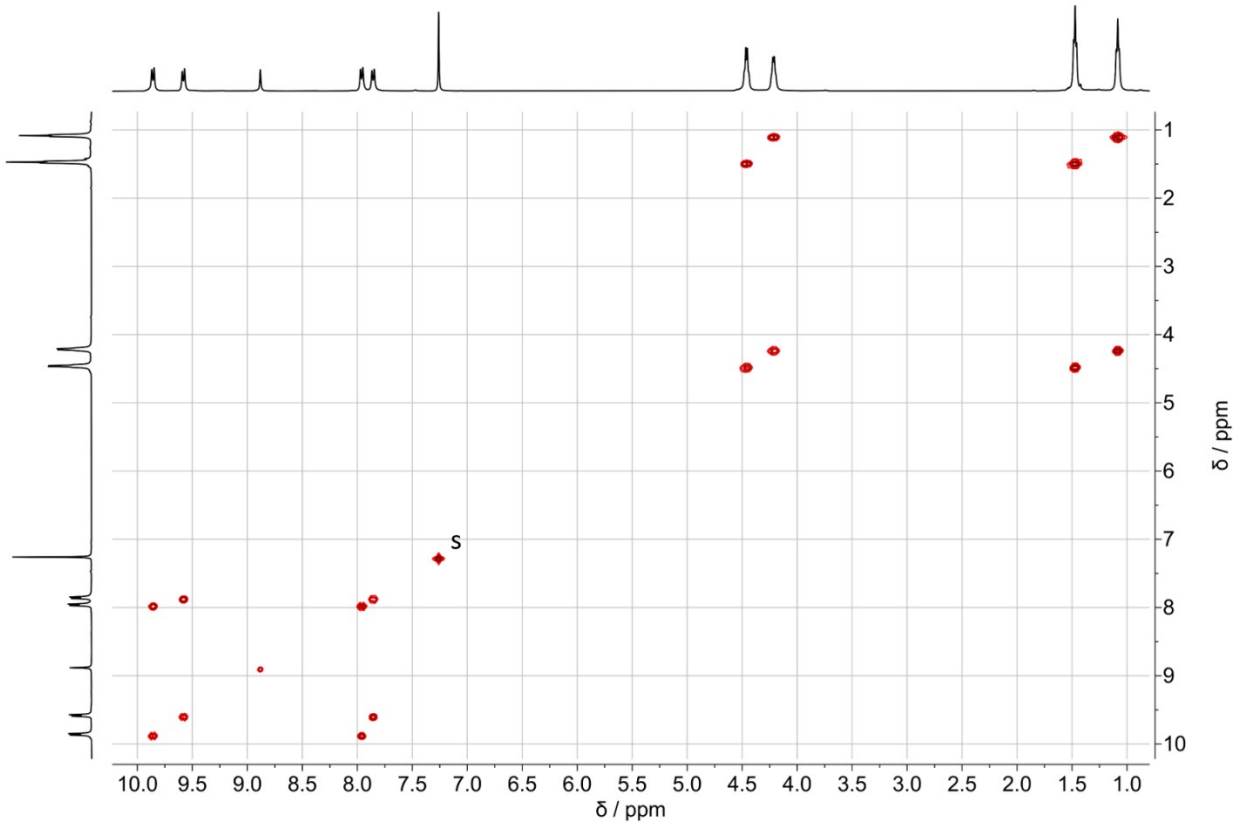


Figure S11: 2D ^{1}H-^{1}H COSY spectrum (126 MHz, $CDCl_3$, 25 °C) of **13**. $^{S}CHCl_3$ solvent residual.

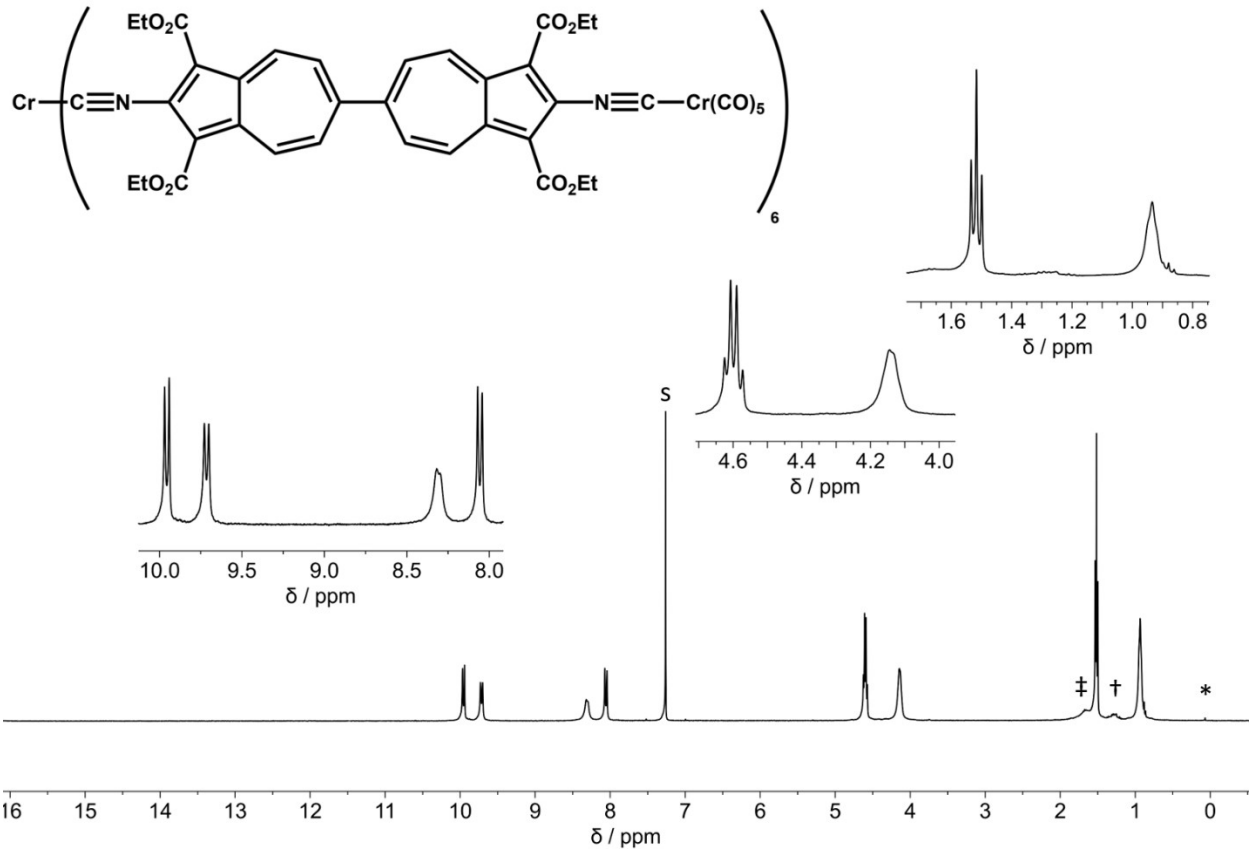


Figure S12: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **14**. $^{s}CHCl_3$ solvent residual *silicone grease †*n*-pentane impurity $^{\ddagger}H_2O$ impurity in solvent.

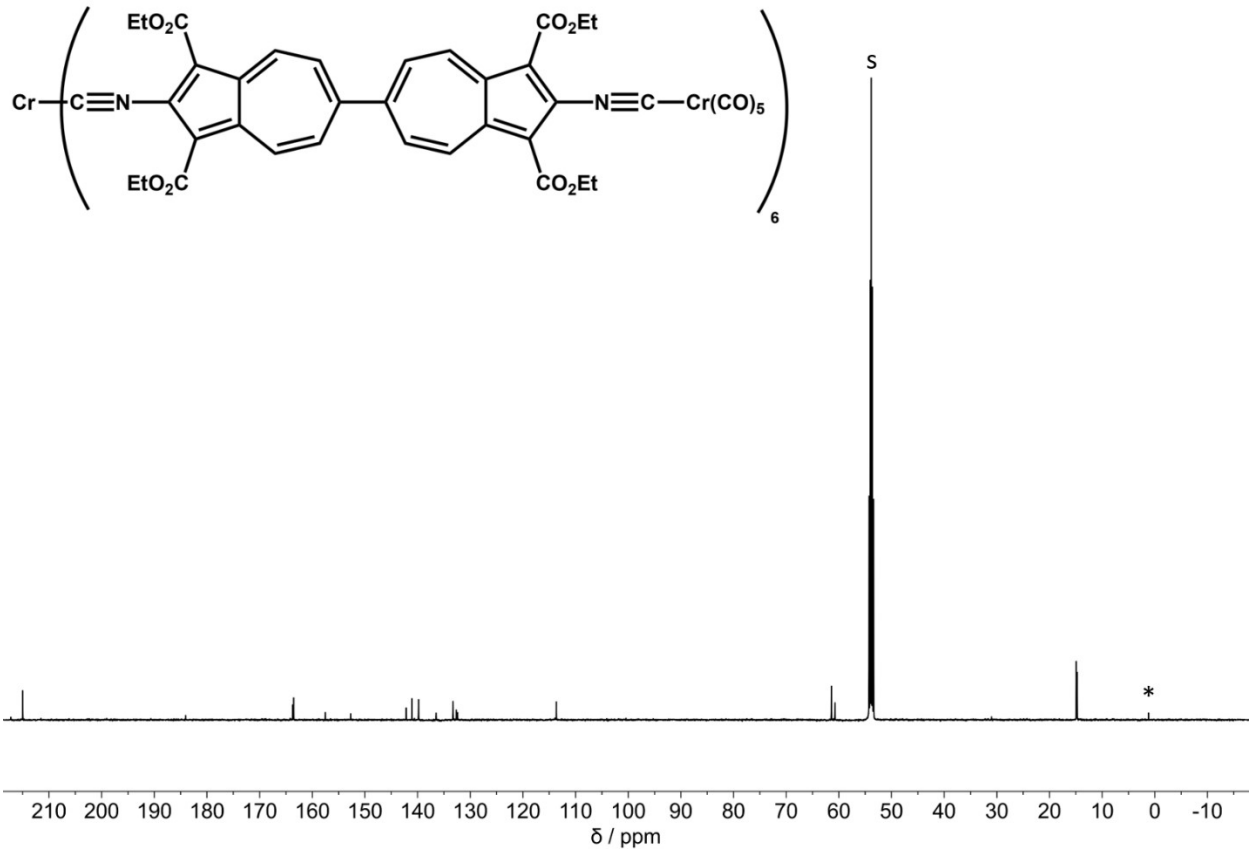


Figure S13: $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, CD_2Cl_2, 25 °C) of **14**. $^{s}CHDCl_2$ solvent residual *silicone grease impurity in solvent.

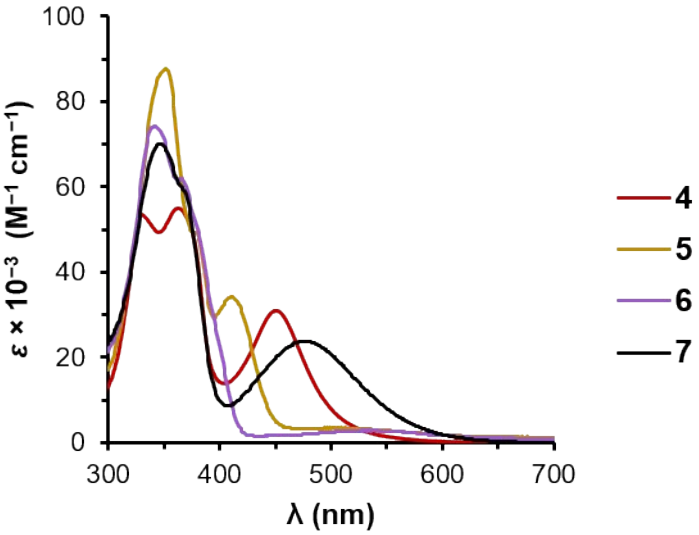


Figure S14: UV-Vis spectra of **4** (red), **5** (gold), **6** (purple), and **7** (black) in CH_2Cl_2 at 22 °C.

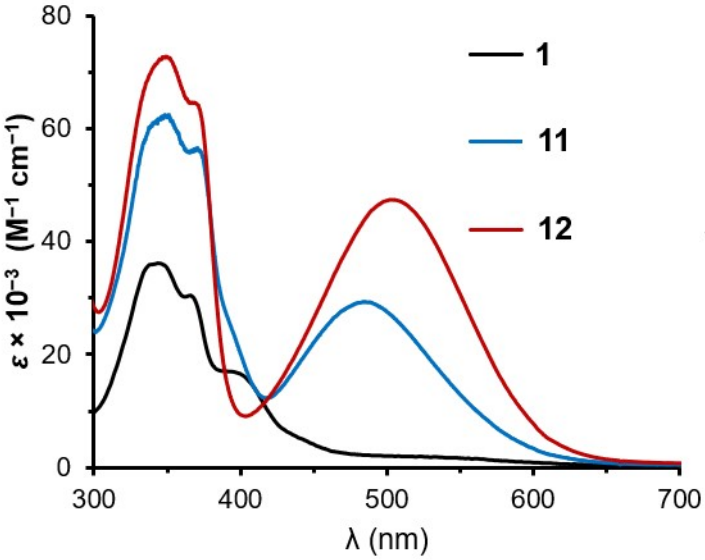


Figure S15: UV-Vis spectra of **1** (black), **11** (blue), and **12** (red) in CH_2Cl_2 at 25 °C.

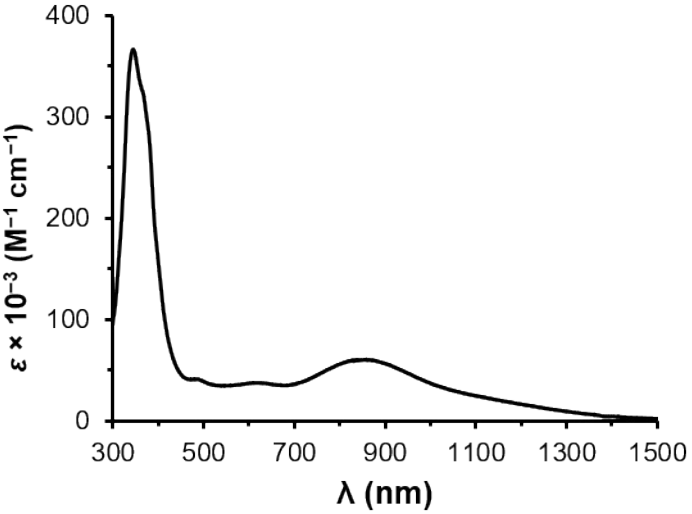


Figure S16: UV-Vis-NIR spectrum of **13** in CH_2Cl_2 at 22 °C.

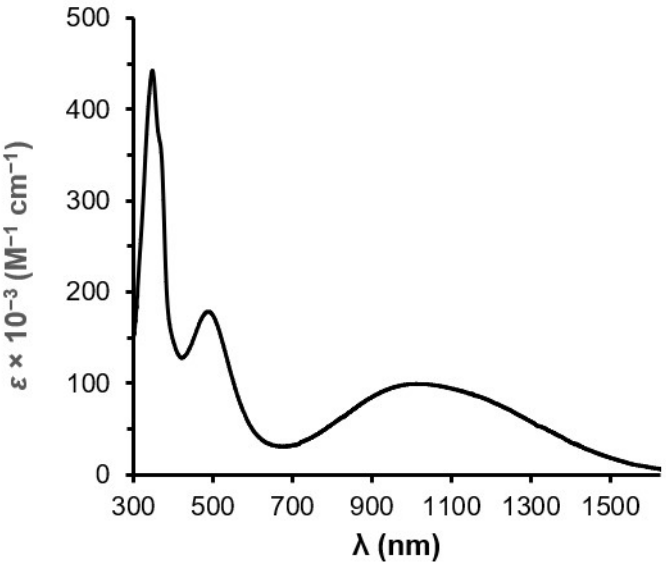


Figure S17: UV-Vis-NIR spectrum of **14** in CH_2Cl_2 at 25 °C.

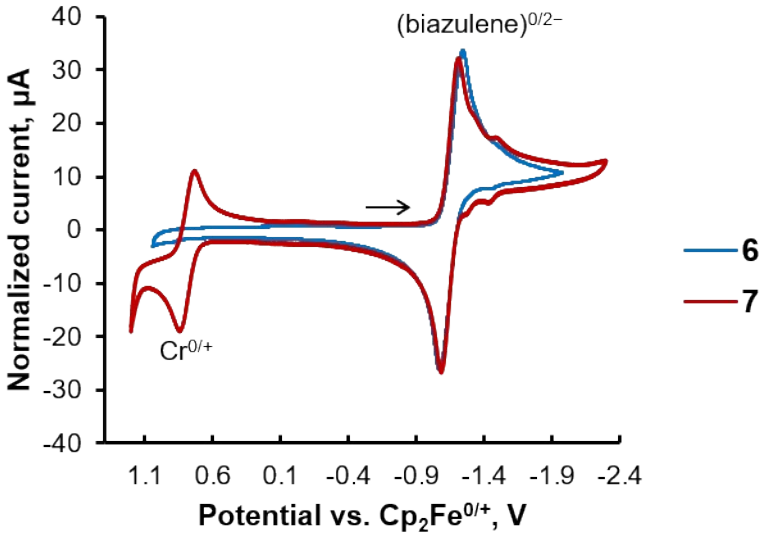


Figure S18: Cyclic voltammograms of solutions of **6** (blue) and **7** (red) in 0.1 M [^{n}Bu$_4$N][PF_6]/CH_2Cl_2 vs. external $Cp_2Fe^{0/+}$ at 22 °C. Scan rate = 50 mV/s.

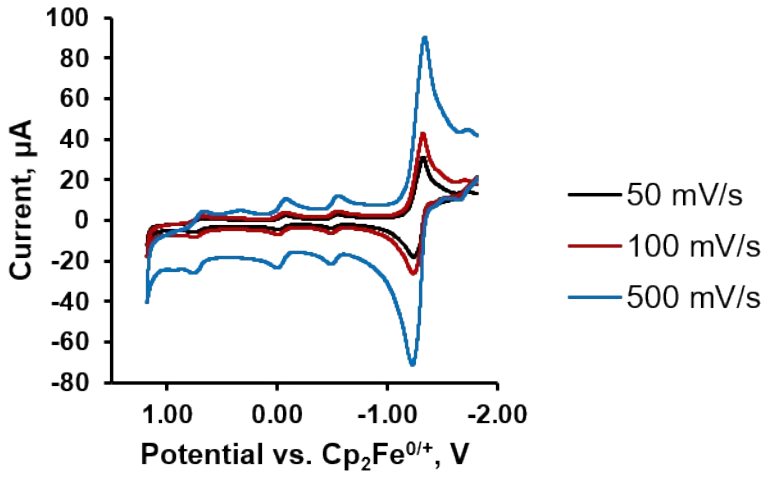


Figure S19: Variable scan rate cyclic voltammograms of **13** in 0.1 M [^{n}Bu$_4$N][PF$_6$]/CH$_2$Cl$_2$ vs. external Cp$_2$Fe$^{0/+}$ at 22 °C.

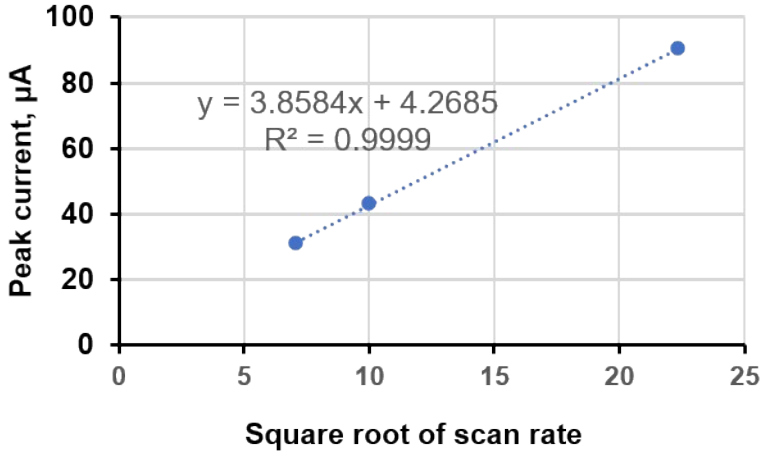


Figure S20: Peak current versus scan rate (50 mV/s, 100 mV/s, 500 mV/s) dependence for the reduction half-wave ($E_{1/2}$ = −1.29 V) for **13** in 0.1 M [^{n}Bu$_4$N][PF$_6$]/CH$_2$Cl$_2$ vs. external Cp$_2$Fe$^{0/+}$ at 22 °C.

B. X-ray crystallographic studies

Crystals were mounted using Paratone oil with MiTeGen loops and placed under a nitrogen stream for data collection. For the selected crystal of compound **7**·$(CH_2Cl_2)_{0.375}$**,** X-ray data were collected at 120 K using 0.5°-wide ω- or ϕ-scans on a Bruker D8 3-circle diffractometer with a PHOTON-II detector. X-rays were provided by a fine-focus Mo-sealed tube running at 50 kV and 35 mA (Mo Kα = 0.71073 Å). All diffractometer manipulations for these structures, including data collection, integration, and scaling, were carried out using the Bruker APEX4 Software Suite.[6, 7] The data set for **7**·$(CH_2Cl_2)_{0.375}$ was corrected for absorption using the multi-scan method by SADABS.[8] OLEX/2 software was used to solve each structure using intrinsic phasing methods.[9] Final stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with OLEX/2 software.[9]

The final structural model for **7**·$(CH_2Cl_2)_{0.375}$ incorporated anisotropic thermal parameters for all ordered full-occupancy and disordered partial-occupancy nonhydrogen atoms. Isotropic thermal parameters were used for all hydrogen atoms. Hydrogen atoms in **7**·$(CH_2Cl_2)_{0.375}$ were fixed at idealized riding model sp^2- or sp^3-hybridized positions with C-H bond lengths of 0.95-0.99 Å. Methyl groups were incorporated into the structural models either as sp^3-hybridized riding model groups with idealized staggered geometry and a C-H bond length of 0.98 Å or as idealized riding model rigid rotors (with a C-H bond length of 0.98 Å) that were allowed to rotate freely about their C-C bonds in least-squares refinement cycles. The isotropic thermal parameters of the hydrogen atoms in **7**·$(CH_2Cl_2)_{0.375}$ were fixed at values 1.2 (non-methyl) or 1.5 (methyl) times the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded. The CCDC entry 2270007 contains the relevant crystallographic data associated with this article. These data can be accessed free of charge from the Cambridge Crystallographic Data Centre. The crystallographic and structure refinement information for **7**·$(CH_2Cl_2)_{0.375}$ is given in Tables S1-S7.

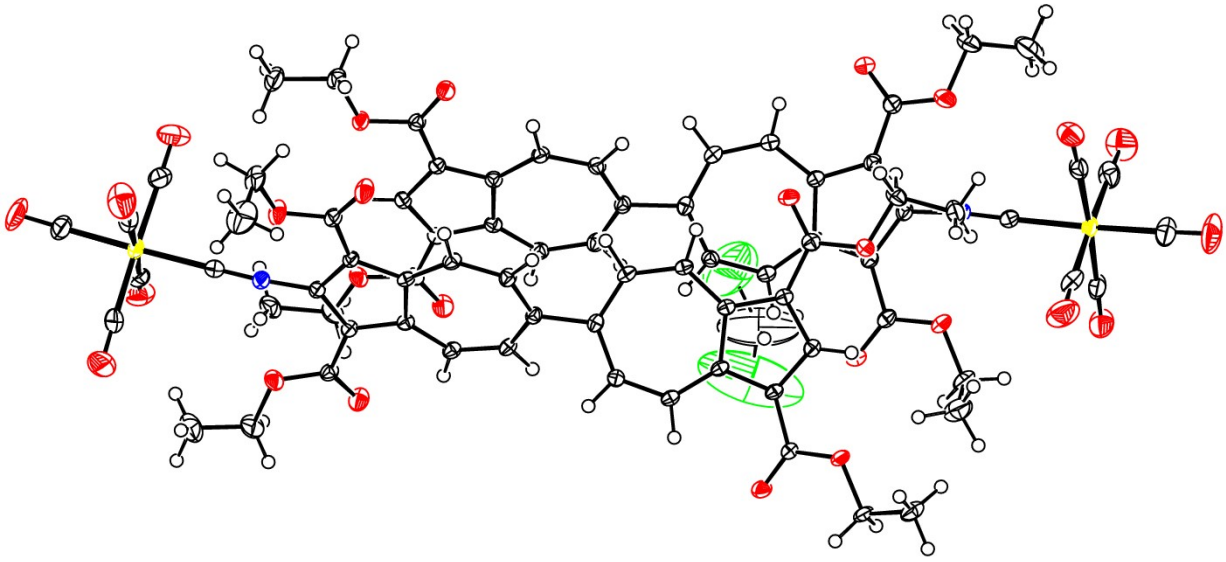


Figure S21: Asymmetric unit incorporating two crystallographically independent molecules of **7**·$(CH_2Cl_2)_{0.375}$.

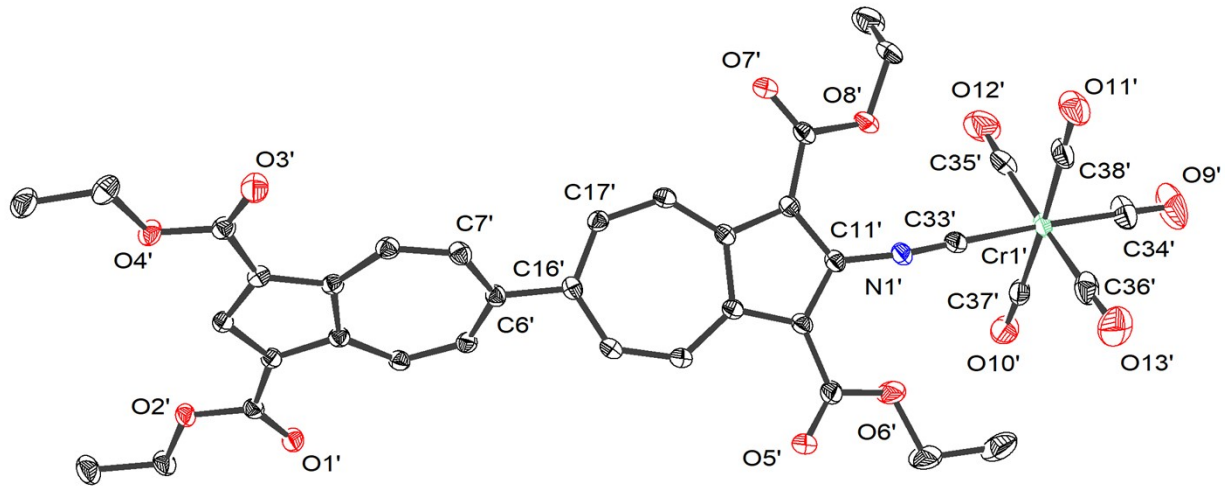


Figure S22: ORTEP diagram (50% thermal ellipsoids) of one of the two crystallographically independent molecules of **7**. Hydrogen atoms and the CH_2Cl_2 solvent of crystallization are omitted for clarity. Selected distances (Å) and angles (deg): Cr1'-C34' 1.892(3), av. Cr1'-CO_{cis} 1.906(3), Cr1'-C33' 1.960(2), C33'-N1' 1.167(3), N1'-C11' 1.373(3), C6'-C16' 1.499(3); Cr1'-C33'-N1' 176.7(2), C11'-N1'-C33' 172.6(2), torsion C7'-C6'-C16'-C17' 46.2(3).

Table S1: Crystal data and structure refinement for **7**·$(CH_2Cl_2)_{0.375}$.

Identification code	**7**
Empirical formula	$C_{38.38}H_{29.75}Cl_{0.75}CrNO_{13}$
Formula weight	791.47
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	P-1
a (Å)	10.7018(5)
b (Å)	16.7383(9)
c (Å)	20.6013(11)
α (°)	90.327(2)
β (°)	92.499(2)
γ (°)	91.085(2)
Volume (Å^3)	3686.1(3)
Z	4
Density (calc; g/cm^3)	1.426
Absorption coefficient (μ mm^{-1})	0.433
F(000)	1630.0
Crystal color, habit	red, plate
Crystal size (mm^3)	0.236×0.190×0.116
θ range for data collection (°)	1.563 to 28.310
Index ranges	−14 ≤ h ≤ 14, −22 ≤ k ≤ 22, −27 ≤ l ≤ 27

Reflections collected	82214
Independent reflections	18286 [R_{int} = 0.0358]
Completeness to θ = 25.242°	100.0%
Absorption correction	Numerical
Max. and min. transmission	0.9753 and 0.9216
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	18286 / 0 / 990
Goodness-of-fit on F^2	1.028
Final R indexes [I>2σ(I)]	R_1 = 0.0503, wR_2 = 0.1292
R indexes (all data)	R_1 = 0.0728, wR_2 = 0.1414
Extinction coefficient	n/a
Largest diff. peak and hole (e^-.Å^{-3})	1.375 and −1.092

Table S2: Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **7**·$(CH_2Cl_2)_{0.375}$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Cr(1)	0.49174(3)	−0.14655(2)	0.13753(2)	0.025(1)
O(1)	0.20989(14)	0.52793(9)	0.64672(8)	0.026(1)
O(2)	0.05578(14)	0.60577(9)	0.68039(7)	0.021(1)
O(3)	−0.40316(14)	0.39968(9)	0.55500(8)	0.024(1)
O(4)	−0.38208(13)	0.52242(9)	0.60034(8)	0.022(1)
O(5)	0.48253(16)	0.22126(10)	0.24636(9)	0.033(1)
O(6)	0.48806(16)	0.10998(10)	0.18603(8)	0.030(1)
O(7)	0.02963(16)	−0.06622(9)	0.33183(8)	0.029(1)
O(8)	0.12353(15)	−0.09677(9)	0.23994(8)	0.024(1)
O(9)	0.6371(2)	−0.26883(15)	0.06464(16)	0.078(1)
O(10)	0.71140(19)	−0.13228(12)	0.23602(11)	0.047(1)
O(11)	0.2654(2)	−0.16091(17)	0.04335(11)	0.062(1)
O(12)	0.38765(18)	−0.28550(12)	0.21453(11)	0.044(1)
O(13)	0.6077(2)	−0.01761(14)	0.05371(11)	0.058(1)
N(1)	0.34904(16)	−0.02111(10)	0.21843(9)	0.019(1)
C(1)	−0.12894(19)	0.51098(12)	0.61992(10)	0.017(1)
C(2)	−0.00181(18)	0.50037(11)	0.61120(10)	0.016(1)
C(3)	0.01072(18)	0.43956(11)	0.56401(10)	0.015(1)
C(4)	0.12279(18)	0.41208(12)	0.54093(10)	0.016(1)
C(5)	0.14195(19)	0.35203(12)	0.49574(10)	0.018(1)
C(6)	0.05535(19)	0.30239(12)	0.46093(10)	0.016(1)
C(7)	−0.07570(19)	0.30364(12)	0.46312(10)	0.017(1)
C(8)	−0.15124(18)	0.35218(12)	0.49911(10)	0.016(1)
C(9)	−0.11705(18)	0.41147(11)	0.54445(10)	0.015(1)
C(10)	−0.20010(18)	0.45790(12)	0.58018(10)	0.016(1)
C(11)	0.29492(19)	0.03504(12)	0.25655(10)	0.017(1)
C(12)	0.34124(18)	0.11384(12)	0.26654(10)	0.017(1)
C(13)	0.26484(18)	0.14980(12)	0.31229(10)	0.016(1)
C(14)	0.27668(19)	0.22864(12)	0.33393(10)	0.018(1)
C(15)	0.20774(19)	0.26926(12)	0.37885(10)	0.019(1)
C(16)	0.10872(19)	0.24255(12)	0.41603(10)	0.017(1)
C(17)	0.05534(19)	0.16531(12)	0.41580(10)	0.018(1)
C(18)	0.08137(19)	0.09922(12)	0.37784(10)	0.018(1)
C(19)	0.17068(18)	0.09036(12)	0.33085(10)	0.016(1)
C(20)	0.18993(19)	0.02018(12)	0.29407(10)	0.016(1)

Atom	*x*	*y*	*z*	U(eq)
C(21)	0.10007(19)	0.54395(12)	0.64667(10)	0.018(1)
C(22)	0.1483(2)	0.65349(13)	0.71751(11)	0.025(1)
C(23)	0.0782(2)	0.71681(15)	0.75184(12)	0.032(1)
C(24)	−0.33728(18)	0.45427(12)	0.57660(10)	0.016(1)
C(25)	−0.51704(19)	0.53026(13)	0.60172(12)	0.023(1)
C(26)	−0.5392(2)	0.61744(13)	0.61431(13)	0.027(1)
C(27)	0.4434(2)	0.15496(13)	0.23354(11)	0.021(1)
C(28)	0.5750(3)	0.14947(16)	0.14345(13)	0.036(1)
C(29)	0.5020(3)	0.1816(2)	0.08527(16)	0.055(1)
C(30)	0.10715(19)	−0.05096(12)	0.29245(10)	0.018(1)
C(31)	0.0362(3)	−0.16380(15)	0.23162(14)	0.036(1)
C(32)	0.0701(3)	−0.21190(19)	0.17568(15)	0.049(1)
C(33)	0.4014(2)	−0.06766(13)	0.18799(11)	0.021(1)
C(34)	0.5817(3)	−0.22253(18)	0.09135(17)	0.045(1)
C(35)	0.5630(3)	−0.06460(17)	0.08594(14)	0.038(1)
C(36)	0.4247(2)	−0.23217(15)	0.18635(13)	0.031(1)
C(37)	0.6288(2)	−0.13695(14)	0.19938(14)	0.032(1)
C(38)	0.3508(3)	−0.15528(18)	0.07801(13)	0.038(1)
Cr(1′)	−0.03893(3)	0.67896(2)	0.96158(2)	0.022(1)
O(1′)	0.64588(14)	0.20698(9)	0.42027(8)	0.023(1)
O(2′)	0.63127(14)	0.09581(9)	0.35824(7)	0.022(1)
O(3′)	0.17631(16)	−0.07300(9)	0.50132(8)	0.028(1)
O(4′)	0.29088(14)	−0.10604(8)	0.41626(7)	0.021(1)
O(5′)	0.44207(15)	0.45848(12)	0.86455(9)	0.034(1)
O(6′)	0.32387(16)	0.55785(11)	0.89765(10)	0.040(1)
O(7′)	−0.18022(14)	0.40338(11)	0.75013(8)	0.029(1)
O(8′)	−0.15847(14)	0.50869(10)	0.81820(8)	0.027(1)
O(9′)	−0.1261(3)	0.82081(13)	1.03849(13)	0.067(1)
O(10′)	0.17547(18)	0.77920(12)	0.91116(9)	0.040(1)
O(11′)	−0.2567(2)	0.57406(12)	1.00294(11)	0.047(1)
O(12′)	−0.2061(2)	0.73111(17)	0.84712(12)	0.060(1)
O(13′)	0.1160(2)	0.62719(15)	1.08117(10)	0.054(1)
N(1′)	0.06741(17)	0.54178(11)	0.87784(9)	0.021(1)
C(1′)	0.43236(19)	0.03300(12)	0.42351(10)	0.016(1)
C(2′)	0.48714(19)	0.10805(12)	0.43865(10)	0.016(1)
C(3′)	0.42288(19)	0.14162(12)	0.49065(10)	0.016(1)
C(4′)	0.44854(19)	0.21590(12)	0.51982(10)	0.018(1)
C(5′)	0.38993(19)	0.25255(12)	0.57078(10)	0.018(1)
C(6′)	0.28982(19)	0.22590(12)	0.60713(10)	0.018(1)
C(7′)	0.2236(2)	0.15307(12)	0.59978(10)	0.020(1)
C(8′)	0.23875(19)	0.09086(12)	0.55598(10)	0.019(1)
C(9′)	0.32466(19)	0.08335(12)	0.50748(10)	0.016(1)
C(10′)	0.33439(19)	0.01745(12)	0.46463(10)	0.017(1)
C(11′)	0.10491(19)	0.48657(12)	0.83348(10)	0.019(1)
C(12′)	0.22996(19)	0.46334(12)	0.82634(10)	0.018(1)
C(13′)	0.22855(19)	0.40664(12)	0.77523(10)	0.017(1)
C(14′)	0.33460(19)	0.37155(13)	0.75036(11)	0.020(1)
C(15′)	0.3427(2)	0.31798(13)	0.69921(11)	0.021(1)
C(16′)	0.24900(19)	0.28181(12)	0.65885(10)	0.017(1)
C(17′)	0.12005(19)	0.29402(12)	0.66166(10)	0.018(1)
C(18′)	0.05426(19)	0.34373(12)	0.70168(10)	0.018(1)
C(19′)	0.09816(19)	0.39433(12)	0.75211(10)	0.016(1)

Atom	*x*	*y*	*z*	U(eq)
C(20′)	0.02319(19)	0.44453(12)	0.78905(10)	0.017(1)
C(21′)	0.59453(19)	0.14365(12)	0.40646(10)	0.018(1)
C(22′)	0.7382(2)	0.12504(14)	0.32410(12)	0.026(1)
C(23′)	0.7745(2)	0.05982(16)	0.27838(13)	0.033(1)
C(24′)	0.2580(2)	−0.05635(12)	0.46407(10)	0.019(1)
C(25′)	0.2291(2)	−0.18390(13)	0.41433(12)	0.026(1)
C(26′)	0.2789(2)	−0.22852(14)	0.35774(13)	0.030(1)
C(27′)	0.3429(2)	0.49145(14)	0.86375(11)	0.023(1)
C(28′)	0.4289(3)	0.5868(2)	0.93933(18)	0.056(1)
C(29′)	0.3800(3)	0.62102(17)	0.99906(16)	0.046(1)
C(30′)	−0.11465(19)	0.44859(13)	0.78267(10)	0.020(1)
C(31′)	−0.2941(2)	0.51075(16)	0.82255(13)	0.031(1)
C(32′)	−0.3523(3)	0.5581(2)	0.76810(14)	0.043(1)
C(33′)	0.0261(2)	0.59121(13)	0.91031(11)	0.022(1)
C(34′)	−0.0946(3)	0.76717(16)	1.00950(14)	0.038(1)
C(35′)	−0.1425(2)	0.71120(17)	0.88948(14)	0.035(1)
C(36′)	0.0593(3)	0.64640(16)	1.03600(13)	0.034(1)
C(37′)	0.0960(2)	0.74243(14)	0.93103(11)	0.026(1)
C(38′)	−0.1742(2)	0.61307(15)	0.98812(13)	0.032(1)
C(1S)	0.0666(9)	0.0182(7)	0.0924(7)	0.195(6)
Cl(1S)	0.1745(5)	0.0677(3)	0.0956(3)	0.315(4)
Cl(2S)	−0.0757(3)	0.0204(2)	0.1044(2)	0.213(2)
H(1)	−0.16229	0.54881	0.64870	0.020
H(4)	0.19644	0.43806	0.55857	0.020
H(5)	0.22706	0.34320	0.48706	0.021
H(7)	−0.11931	0.26551	0.43585	0.020
H(8)	−0.23872	0.34365	0.49168	0.020
H(14)	0.34144	0.25922	0.31524	0.022
H(15)	0.23153	0.32378	0.38539	0.022
H(17)	−0.00800	0.15693	0.44608	0.022
H(18)	0.03082	0.05308	0.38489	0.022
H(22C)	0.20884	0.67821	0.68831	0.029
H(22D)	0.19454	0.61983	0.74937	0.029
H(23D)	0.03580	0.75104	0.71970	0.047
H(23E)	0.13695	0.74923	0.77919	0.047
H(23F)	0.01602	0.69149	0.77903	0.047
H(25C)	−0.55115	0.49706	0.63666	0.027
H(25D)	−0.55765	0.51322	0.55968	0.027
H(26D)	−0.49848	0.64968	0.58145	0.041
H(26E)	−0.50420	0.63223	0.65757	0.041
H(26F)	−0.62929	0.62714	0.61212	0.041
H(28C)	0.63745	0.11095	0.12913	0.043
H(28D)	0.62005	0.19375	0.16708	0.043
H(29D)	0.56011	0.20434	0.05453	0.083
H(29E)	0.44583	0.22317	0.09944	0.083
H(29F)	0.45278	0.13810	0.06406	0.083
H(31C)	−0.04987	−0.14401	0.22452	0.043
H(31D)	0.03870	−0.19698	0.27126	0.043
H(32D)	0.07281	−0.17796	0.13715	0.073
H(32E)	0.00776	−0.25492	0.16798	0.073
H(32F)	0.15256	−0.23502	0.18450	0.073
H(1′)	0.45800	−0.00195	0.39033	0.020

Atom	*x*	*y*	*z*	U(eq)
H(4′)	0.51556	0.24569	0.50242	0.021
H(5′)	0.42308	0.30382	0.58285	0.022
H(7′)	0.15854	0.14503	0.62914	0.024
H(8′)	0.18208	0.04691	0.55966	0.023
H(14′)	0.41206	0.38669	0.77163	0.024
H(15′)	0.42546	0.30338	0.69002	0.025
H(17′)	0.06951	0.26338	0.63133	0.021
H(18′)	−0.03380	0.34319	0.69348	0.021
H(22A)	0.80862	0.13824	0.35534	0.031
H(22B)	0.71642	0.17384	0.29951	0.031
H(23A)	0.70323	0.04605	0.24868	0.049
H(23B)	0.79888	0.01255	0.30339	0.049
H(23C)	0.84504	0.07841	0.25329	0.049
H(25A)	0.13741	−0.17817	0.40855	0.031
H(25B)	0.24743	−0.21291	0.45529	0.031
H(26A)	0.26028	−0.19911	0.31759	0.045
H(26B)	0.23933	−0.28176	0.35463	0.045
H(26C)	0.36968	−0.23379	0.36413	0.045
H(28A)	0.47715	0.62814	0.91636	0.068
H(28B)	0.48527	0.54228	0.95043	0.068
H(29A)	0.32695	0.66645	0.98784	0.069
H(29B)	0.44993	0.63911	1.02809	0.069
H(29C)	0.33052	0.58021	1.02093	0.069
H(31A)	−0.31489	0.53496	0.86459	0.037
H(31B)	−0.32896	0.45553	0.82092	0.037
H(32A)	−0.34388	0.52938	0.72698	0.065
H(32B)	−0.30988	0.61036	0.76604	0.065
H(32C)	−0.44110	0.56549	0.77565	0.065
H(1SA)	0.09339	−0.02748	0.11964	0.234
H(1SB)	0.06667	−0.00226	0.04727	0.234

Table S3: Anisotropic displacement parameters (Å^2) for **7**·$(CH_2Cl_2)_{0.375}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+\ldots+2hka^*b^*U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cr(1)	0.0197(2)	0.0259(2)	0.0311(2)	−0.0123(2)	0.0065(2)	0.0007(1)
O(1)	0.0146(7)	0.0257(8)	0.0373(9)	−0.0066(7)	−0.0002(7)	−0.0016(6)
O(2)	0.0183(7)	0.0203(7)	0.0233(8)	−0.0054(6)	0.0000(6)	−0.0016(6)
O(3)	0.0164(7)	0.0208(8)	0.0358(9)	−0.0046(7)	0.0040(6)	−0.0025(6)
O(4)	0.0115(7)	0.0210(7)	0.0342(9)	−0.0067(6)	0.0025(6)	0.0027(6)
O(5)	0.0312(9)	0.0265(9)	0.0436(11)	−0.0111(7)	0.0215(8)	−0.0106(7)
O(6)	0.0328(9)	0.0269(8)	0.0314(9)	−0.0068(7)	0.0218(7)	−0.0095(7)
O(7)	0.0283(9)	0.0212(8)	0.0370(10)	−0.0030(7)	0.0140(7)	−0.0062(6)
O(8)	0.0255(8)	0.0205(7)	0.0262(8)	−0.0052(6)	0.0051(6)	−0.0082(6)
O(9)	0.0448(13)	0.0598(15)	0.131(2)	−0.0575(16)	0.0454(15)	−0.0076(11)
O(10)	0.0323(10)	0.0400(11)	0.0674(15)	0.0019(10)	−0.0158(10)	−0.0039(9)
O(11)	0.0424(13)	0.106(2)	0.0374(12)	−0.0238(13)	−0.0073(10)	−0.0009(13)
O(12)	0.0321(10)	0.0354(11)	0.0645(14)	0.0027(10)	0.0018(9)	−0.0024(8)
O(13)	0.0748(17)	0.0518(13)	0.0479(13)	−0.0008(11)	0.0231(12)	−0.0137(12)
N(1)	0.0177(8)	0.0195(8)	0.0204(9)	−0.0018(7)	0.0032(7)	−0.0005(7)
C(1)	0.0169(9)	0.0143(9)	0.0189(10)	0.0013(7)	0.0030(8)	0.0009(7)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(2)	0.0150(9)	0.0146(9)	0.0176(10)	0.0028(7)	0.0013(7)	−0.0005(7)
C(3)	0.0139(9)	0.0141(9)	0.0172(10)	0.0036(7)	0.0018(7)	−0.0006(7)
C(4)	0.0131(9)	0.0185(9)	0.0177(10)	0.0024(8)	0.0017(7)	−0.0004(7)
C(5)	0.0127(9)	0.0215(10)	0.0193(10)	0.0032(8)	0.0033(8)	0.0022(7)
C(6)	0.0176(9)	0.0151(9)	0.0157(9)	0.0022(7)	0.0039(7)	0.0016(7)
C(7)	0.0174(9)	0.0153(9)	0.0176(10)	0.0007(7)	0.0017(8)	−0.0008(7)
C(8)	0.0132(9)	0.0169(9)	0.0192(10)	0.0035(8)	0.0026(7)	0.0003(7)
C(9)	0.0126(9)	0.0151(9)	0.0177(10)	0.0041(7)	0.0024(7)	0.0009(7)
C(10)	0.0130(9)	0.0154(9)	0.0196(10)	0.0028(7)	0.0031(7)	−0.0001(7)
C(11)	0.0159(9)	0.0178(9)	0.0160(9)	0.0000(7)	0.0013(8)	0.0014(7)
C(12)	0.0147(9)	0.0177(9)	0.0176(10)	−0.0009(7)	0.0034(8)	0.0002(7)
C(13)	0.0119(9)	0.0183(9)	0.0173(10)	0.0021(7)	0.0027(7)	−0.0003(7)
C(14)	0.0157(9)	0.0179(9)	0.0212(10)	0.0023(8)	0.0042(8)	−0.0018(8)
C(15)	0.0190(10)	0.0148(9)	0.0226(11)	−0.0004(8)	0.0044(8)	0.0001(8)
C(16)	0.0162(9)	0.0175(9)	0.0168(10)	0.0004(8)	0.0010(8)	0.0034(7)
C(17)	0.0153(9)	0.0202(10)	0.0198(10)	0.0016(8)	0.0056(8)	0.0016(8)
C(18)	0.0156(9)	0.0170(9)	0.0215(10)	0.0020(8)	0.0031(8)	0.0001(7)
C(19)	0.0149(9)	0.0146(9)	0.0185(10)	0.0015(7)	0.0015(8)	0.0002(7)
C(20)	0.0157(9)	0.0156(9)	0.0177(10)	0.0004(7)	0.0025(8)	0.0008(7)
C(21)	0.0185(10)	0.0158(9)	0.0199(10)	0.0023(8)	0.0021(8)	−0.0019(8)
C(22)	0.0249(11)	0.0230(11)	0.0252(11)	−0.0032(9)	−0.0021(9)	−0.0058(9)
C(23)	0.0363(13)	0.0328(13)	0.0253(12)	−0.0107(10)	0.0061(10)	−0.0067(10)
C(24)	0.0143(9)	0.0167(9)	0.0182(10)	0.0009(7)	0.0028(7)	0.0016(7)
C(25)	0.0102(9)	0.0233(11)	0.0353(13)	−0.0034(9)	0.0040(8)	0.0021(8)
C(26)	0.0180(10)	0.0227(11)	0.0417(14)	0.0022(10)	0.0053(10)	0.0044(8)
C(27)	0.0182(10)	0.0231(10)	0.0205(10)	−0.0016(8)	0.0056(8)	−0.0008(8)
C(28)	0.0368(14)	0.0348(13)	0.0365(14)	−0.0062(11)	0.0250(12)	−0.0119(11)
C(29)	0.057(2)	0.063(2)	0.0479(19)	0.0121(16)	0.0273(16)	−0.0062(16)
C(30)	0.0160(9)	0.0152(9)	0.0242(11)	0.0009(8)	0.0029(8)	0.0013(7)
C(31)	0.0344(14)	0.0272(12)	0.0450(16)	−0.0095(11)	0.0082(12)	−0.0148(10)
C(32)	0.0539(19)	0.0478(17)	0.0441(17)	−0.0205(14)	0.0129(14)	−0.0216(14)
C(33)	0.0182(10)	0.0223(10)	0.0229(11)	−0.0010(8)	0.0001(8)	−0.0017(8)
C(34)	0.0290(13)	0.0397(15)	0.068(2)	−0.0259(14)	0.0202(13)	−0.0084(11)
C(35)	0.0406(15)	0.0416(15)	0.0333(14)	−0.0118(12)	0.0114(12)	−0.0018(12)
C(36)	0.0187(11)	0.0293(12)	0.0446(15)	−0.0111(11)	0.0020(10)	0.0034(9)
C(37)	0.0232(12)	0.0216(11)	0.0512(16)	−0.0049(11)	0.0036(11)	−0.0001(9)
C(38)	0.0336(14)	0.0519(17)	0.0297(14)	−0.0175(12)	0.0072(11)	−0.0005(12)
Cr(1′)	0.0230(2)	0.0211(2)	0.0224(2)	−0.0054(1)	0.0094(1)	−0.0020(1)
O(1′)	0.0219(8)	0.0191(7)	0.0286(8)	−0.0044(6)	0.0057(6)	−0.0038(6)
O(2′)	0.0191(7)	0.0218(7)	0.0240(8)	−0.0058(6)	0.0077(6)	−0.0034(6)
O(3′)	0.0301(9)	0.0239(8)	0.0300(9)	−0.0025(7)	0.0099(7)	−0.0090(7)
O(4′)	0.0246(8)	0.0151(7)	0.0241(8)	−0.0027(6)	0.0025(6)	−0.0050(6)
O(5′)	0.0163(8)	0.0496(11)	0.0370(10)	−0.0180(8)	−0.0014(7)	0.0020(7)
O(6′)	0.0229(9)	0.0348(10)	0.0602(13)	−0.0259(9)	−0.0076(8)	0.0003(7)
O(7′)	0.0160(7)	0.0382(9)	0.0333(9)	−0.0097(7)	0.0031(7)	−0.0020(7)
O(8′)	0.0155(7)	0.0310(9)	0.0347(9)	−0.0065(7)	0.0044(7)	0.0050(6)
O(9′)	0.0832(18)	0.0352(12)	0.0844(18)	−0.0265(12)	0.0424(15)	−0.0013(11)
O(10′)	0.0368(10)	0.0516(12)	0.0305(10)	−0.0004(8)	0.0073(8)	−0.0186(9)
O(11′)	0.0442(12)	0.0420(11)	0.0547(13)	−0.0109(9)	0.0245(10)	−0.0159(9)
O(12′)	0.0381(12)	0.0882(18)	0.0527(14)	0.0062(13)	−0.0029(11)	0.0197(12)
O(13′)	0.0637(15)	0.0686(15)	0.0280(11)	0.0126(10)	0.0006(10)	−0.0008(12)
N(1′)	0.0184(9)	0.0236(9)	0.0221(9)	−0.0029(7)	0.0054(7)	−0.0004(7)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1′)	0.0174(9)	0.0155(9)	0.0165(10)	−0.0001(7)	−0.0008(8)	0.0009(7)
C(2′)	0.0164(9)	0.0154(9)	0.0167(10)	0.0008(7)	−0.0005(8)	0.0015(7)
C(3′)	0.0162(9)	0.0170(9)	0.0164(10)	0.0008(7)	−0.0006(8)	0.0011(7)
C(4′)	0.0152(9)	0.0177(9)	0.0203(10)	0.0005(8)	0.0020(8)	−0.0001(7)
C(5′)	0.0172(10)	0.0154(9)	0.0216(10)	−0.0016(8)	−0.0003(8)	−0.0002(7)
C(6′)	0.0181(10)	0.0168(9)	0.0178(10)	−0.0006(8)	0.0005(8)	0.0030(8)
C(7′)	0.0189(10)	0.0204(10)	0.0205(10)	0.0015(8)	0.0055(8)	−0.0009(8)
C(8′)	0.0175(10)	0.0172(9)	0.0222(11)	0.0005(8)	0.0012(8)	−0.0021(8)
C(9′)	0.0159(9)	0.0153(9)	0.0174(10)	0.0015(7)	−0.0019(8)	0.0010(7)
C(10′)	0.0178(10)	0.0167(9)	0.0172(10)	0.0011(8)	−0.0004(8)	−0.0007(8)
C(11′)	0.0182(10)	0.0170(9)	0.0207(10)	−0.0009(8)	0.0050(8)	−0.0004(8)
C(12′)	0.0157(9)	0.0194(10)	0.0202(10)	−0.0001(8)	0.0041(8)	−0.0004(8)
C(13′)	0.0154(9)	0.0178(9)	0.0179(10)	0.0012(8)	0.0022(8)	−0.0003(7)
C(14′)	0.0148(9)	0.0225(10)	0.0227(11)	−0.0019(8)	0.0000(8)	0.0005(8)
C(15′)	0.0149(9)	0.0233(10)	0.0234(11)	−0.0015(8)	0.0027(8)	0.0033(8)
C(16′)	0.0192(10)	0.0152(9)	0.0182(10)	0.0011(7)	0.0041(8)	0.0014(7)
C(17′)	0.0172(10)	0.0188(9)	0.0165(10)	−0.0001(8)	0.0011(8)	−0.0024(8)
C(18′)	0.0150(9)	0.0180(9)	0.0196(10)	0.0026(8)	0.0018(8)	−0.0004(7)
C(19′)	0.0160(9)	0.0168(9)	0.0158(9)	0.0034(7)	0.0037(7)	0.0013(7)
C(20′)	0.0168(10)	0.0178(9)	0.0176(10)	0.0014(8)	0.0032(8)	−0.0001(8)
C(21′)	0.0165(10)	0.0168(9)	0.0199(10)	−0.0002(8)	0.0009(8)	0.0021(7)
C(22′)	0.0208(11)	0.0259(11)	0.0315(12)	−0.0051(9)	0.0117(9)	−0.0042(9)
C(23′)	0.0292(13)	0.0340(13)	0.0365(14)	−0.0074(11)	0.0147(11)	0.0005(10)
C(24′)	0.0195(10)	0.0171(9)	0.0196(10)	0.0005(8)	−0.0015(8)	−0.0001(8)
C(25′)	0.0316(12)	0.0164(10)	0.0302(12)	−0.0009(9)	−0.0011(10)	−0.0067(9)
C(26′)	0.0333(13)	0.0202(11)	0.0356(14)	−0.0072(9)	−0.0057(11)	−0.0005(9)
C(27′)	0.0203(11)	0.0266(11)	0.0226(11)	−0.0040(9)	0.0050(8)	−0.0037(9)
C(28′)	0.0258(14)	0.0578(19)	0.084(3)	−0.0451(18)	−0.0118(15)	−0.0014(13)
C(29′)	0.0443(16)	0.0344(14)	0.0570(19)	−0.0132(13)	−0.0217(14)	−0.0003(12)
C(30′)	0.0172(10)	0.0228(10)	0.0189(10)	0.0030(8)	0.0054(8)	0.0018(8)
C(31′)	0.0160(11)	0.0434(14)	0.0336(13)	−0.0040(11)	0.0062(9)	0.0068(10)
C(32′)	0.0265(13)	0.064(2)	0.0396(16)	0.0052(14)	0.0019(12)	0.0093(13)
C(33′)	0.0171(10)	0.0245(11)	0.0233(11)	−0.0021(9)	0.0045(8)	−0.0027(8)
C(34′)	0.0446(16)	0.0288(13)	0.0424(16)	−0.0063(11)	0.0196(13)	−0.0036(11)
C(35′)	0.0235(12)	0.0429(15)	0.0393(15)	−0.0040(12)	0.0105(11)	0.0060(11)
C(36′)	0.0418(15)	0.0341(13)	0.0253(13)	−0.0010(10)	0.0126(11)	−0.0066(11)
C(37′)	0.0298(12)	0.0293(12)	0.0200(11)	−0.0042(9)	0.0036(9)	−0.0020(10)
C(38′)	0.0331(13)	0.0281(12)	0.0351(14)	−0.0108(10)	0.0152(11)	−0.0027(10)
C(1S)	0.110(7)	0.198(11)	0.271(14)	0.142(11)	−0.039(8)	−0.080(8)
Cl(1S)	0.319(6)	0.228(4)	0.374(6)	0.214(4)	−0.238(5)	−0.113(4)
Cl(2S)	0.146(3)	0.179(3)	0.318(5)	−0.050(3)	0.006(3)	0.078(2)

Table S4: Bond lengths (Å) for **7**·$(CH_2Cl_2)_{0.375}$.

atom-atom	distance	atom-atom	distance
Cr(1)-C(34)	1.887(3)	Cr(1)-C(36)	1.903(3)
Cr(1)-C(37)	1.904(3)	Cr(1)-C(38)	1.905(3)
Cr(1)-C(35)	1.908(3)	Cr(1)-C(33)	1.970(2)
O(1)-C(21)	1.210(3)	O(2)-C(21)	1.348(2)
O(2)-C(22)	1.449(3)	O(3)-C(24)	1.214(2)
O(4)-C(24)	1.344(2)	O(4)-C(25)	1.454(2)

atom-atom	distance	atom-atom	distance
O(5)-C(27)	1.202(3)	O(6)-C(27)	1.341(3)
O(6)-C(28)	1.459(3)	O(7)-C(30)	1.210(3)
O(8)-C(30)	1.342(3)	O(8)-C(31)	1.451(3)
O(9)-C(34)	1.138(3)	O(10)-C(37)	1.139(3)
O(11)-C(38)	1.137(3)	O(12)-C(36)	1.142(3)
O(13)-C(35)	1.143(4)	N(1)-C(33)	1.164(3)
N(1)-C(11)	1.374(3)	C(1)-C(2)	1.395(3)
C(1)-C(10)	1.397(3)	C(1)-H(1)	0.9500
C(2)-C(3)	1.416(3)	C(2)-C(21)	1.466(3)
C(3)-C(4)	1.394(3)	C(3)-C(9)	1.476(3)
C(4)-C(5)	1.390(3)	C(4)-H(4)	0.9500
C(5)-C(6)	1.403(3)	C(5)-H(5)	0.9500
C(6)-C(7)	1.406(3)	C(6)-C(16)	1.497(3)
C(7)-C(8)	1.391(3)	C(7)-H(7)	0.9500
C(8)-C(9)	1.392(3)	C(8)-H(8)	0.9500
C(9)-C(10)	1.419(3)	C(10)-C(24)	1.467(3)
C(11)-C(20)	1.410(3)	C(11)-C(12)	1.411(3)
C(12)-C(13)	1.414(3)	C(12)-C(27)	1.474(3)
C(13)-C(14)	1.392(3)	C(13)-C(19)	1.467(3)
C(14)-C(15)	1.391(3)	C(14)-H(14)	0.9500
C(15)-C(16)	1.402(3)	C(15)-H(15)	0.9500
C(16)-C(17)	1.404(3)	C(17)-C(18)	1.391(3)
C(17)-H(17)	0.9500	C(18)-C(19)	1.399(3)
C(18)-H(18)	0.9500	C(19)-C(20)	1.417(3)
C(20)-C(30)	1.470(3)	C(22)-C(23)	1.501(3)
C(22)-H(22C)	0.9900	C(22)-H(22D)	0.9900
C(23)-H(23D)	0.9800	C(23)-H(23E)	0.9800
C(23)-H(23F)	0.9800	C(25)-C(26)	1.506(3)
C(25)-H(25C)	0.9900	C(25)-H(25D)	0.9900
C(26)-H(26D)	0.9800	C(26)-H(26E)	0.9800
C(26)-H(26F)	0.9800	C(28)-C(29)	1.509(5)
C(28)-H(28C)	0.9900	C(28)-H(28D)	0.9900
C(29)-H(29D)	0.9800	C(29)-H(29E)	0.9800
C(29)-H(29F)	0.9800	C(31)-C(32)	1.465(4)
C(31)-H(31C)	0.9900	C(31)-H(31D)	0.9900
C(32)-H(32D)	0.9800	C(32)-H(32E)	0.9800
C(32)-H(32F)	0.9800	Cr(1')-C(34')	1.891(3)
Cr(1')-C(35')	1.901(3)	Cr(1')-C(38')	1.905(3)
Cr(1')-C(37')	1.908(2)	Cr(1')-C(36')	1.909(3)
Cr(1')-C(33')	1.960(2)	O(1')-C(21')	1.211(2)
O(2')-C(21')	1.349(2)	O(2')-C(22')	1.448(3)
O(3')-C(24')	1.218(3)	O(4')-C(24')	1.348(3)
O(4')-C(25')	1.450(2)	O(5')-C(27')	1.205(3)
O(6')-C(27')	1.333(3)	O(6')-C(28')	1.458(3)
O(7')-C(30')	1.203(3)	O(8')-C(30')	1.344(3)
O(8')-C(31')	1.460(3)	O(9')-C(34')	1.140(3)
O(10')-C(37')	1.133(3)	O(11')-C(38')	1.142(3)
O(12')-C(35')	1.138(3)	O(13')-C(36')	1.140(3)
N(1')-C(33')	1.166(3)	N(1')-C(11')	1.374(3)
C(1')-C(10')	1.398(3)	C(1')-C(2')	1.404(3)
C(1')-H(1')	0.9500	C(2')-C(3')	1.417(3)
C(2')-C(21')	1.470(3)	C(3')-C(4')	1.395(3)

atom-atom	distance	atom-atom	distance
C(3')-C(9')	1.474(3)	C(4')-C(5')	1.392(3)
C(4')-H(4')	0.9500	C(5')-C(6')	1.401(3)
C(5')-H(5')	0.9500	C(6')-C(7')	1.403(3)
C(6')-C(16')	1.499(3)	C(7')-C(8')	1.390(3)
C(7')-H(7')	0.9500	C(8')-C(9')	1.394(3)
C(8')-H(8')	0.9500	C(9')-C(10')	1.417(3)
C(10')-C(24')	1.468(3)	C(11')-C(20')	1.413(3)
C(11')-C(12')	1.414(3)	C(12')-C(13')	1.413(3)
C(12')-C(27')	1.473(3)	C(13')-C(14')	1.403(3)
C(13')-C(19')	1.465(3)	C(14')-C(15')	1.386(3)
C(14')-H(14')	0.9500	C(15')-C(16')	1.401(3)
C(15')-H(15')	0.9500	C(16')-C(17')	1.403(3)
C(17')-C(18')	1.390(3)	C(17')-H(17')	0.9500
C(18')-C(19')	1.396(3)	C(18')-H(18')	0.9500
C(19')-C(20')	1.414(3)	C(20')-C(30')	1.478(3)
C(22')-C(23')	1.505(3)	C(22')-H(22A)	0.9900
C(22')-H(22B)	0.9900	C(23')-H(23A)	0.9800
C(23')-H(23B)	0.9800	C(23')-H(23C)	0.9800
C(25')-C(26')	1.504(3)	C(25')-H(25A)	0.9900
C(25')-H(25B)	0.9900	C(26')-H(26A)	0.9800
C(26')-H(26B)	0.9800	C(26')-H(26C)	0.9800
C(28')-C(29')	1.475(4)	C(28')-H(28A)	0.9900
C(28')-H(28B)	0.9900	C(29')-H(29A)	0.9800
C(29')-H(29B)	0.9800	C(29')-H(29C)	0.9800
C(31')-C(32')	1.497(4)	C(31')-H(31A)	0.9900
C(31')-H(31B)	0.9900	C(32')-H(32A)	0.9800
C(32')-H(32B)	0.9800	C(32')-H(32C)	0.9800
C(1S)-Cl(1S)	1.408(8)	C(1S)-Cl(2S)	1.555(10)
C(1S)-H(1SA)	0.9900	C(1S)-H(1SB)	0.9900

Table S5: Bond angles (°) for **7**·$(CH_2Cl_2)_{0.375}$.

atom-atom-atom	angle	atom-atom-atom	angle
C(34)-Cr(1)-C(36)	88.22(12)	C(34)-Cr(1)-C(37)	89.28(12)
C(36)-Cr(1)-C(37)	89.59(11)	C(34)-Cr(1)-C(38)	92.46(13)
C(36)-Cr(1)-C(38)	89.46(12)	C(37)-Cr(1)-C(38)	177.99(11)
C(34)-Cr(1)-C(35)	88.88(13)	C(36)-Cr(1)-C(35)	177.09(11)
C(37)-Cr(1)-C(35)	90.61(12)	C(38)-Cr(1)-C(35)	90.43(13)
C(34)-Cr(1)-C(33)	178.26(13)	C(36)-Cr(1)-C(33)	91.30(10)
C(37)-Cr(1)-C(33)	89.05(10)	C(38)-Cr(1)-C(33)	89.21(10)
C(35)-Cr(1)-C(33)	91.60(10)	C(21)-O(2)-C(22)	115.95(16)
C(24)-O(4)-C(25)	118.06(16)	C(27)-O(6)-C(28)	116.43(18)
C(30)-O(8)-C(31)	114.95(17)	C(33)-N(1)-C(11)	176.1(2)
C(2)-C(1)-C(10)	110.12(18)	C(2)-C(1)-H(1)	124.9
C(10)-C(1)-H(1)	124.9	C(1)-C(2)-C(3)	108.34(17)
C(1)-C(2)-C(21)	125.05(18)	C(3)-C(2)-C(21)	126.59(18)
C(4)-C(3)-C(2)	126.13(18)	C(4)-C(3)-C(9)	127.16(18)
C(2)-C(3)-C(9)	106.72(17)	C(5)-C(4)-C(3)	129.12(19)
C(5)-C(4)-H(4)	115.4	C(3)-C(4)-H(4)	115.4
C(4)-C(5)-C(6)	130.17(19)	C(4)-C(5)-H(5)	114.9
C(6)-C(5)-H(5)	114.9	C(5)-C(6)-C(7)	126.98(18)

atom-atom-atom	angle	atom-atom-atom	angle
C(5)-C(6)-C(16)	116.25(18)	C(7)-C(6)-C(16)	116.76(18)
C(8)-C(7)-C(6)	129.85(19)	C(8)-C(7)-H(7)	115.1
C(6)-C(7)-H(7)	115.1	C(7)-C(8)-C(9)	129.28(19)
C(7)-C(8)-H(8)	115.4	C(9)-C(8)-H(8)	115.4
C(8)-C(9)-C(10)	126.03(18)	C(8)-C(9)-C(3)	127.38(18)
C(10)-C(9)-C(3)	106.58(17)	C(1)-C(10)-C(9)	108.23(17)
C(1)-C(10)-C(24)	124.19(18)	C(9)-C(10)-C(24)	127.56(18)
N(1)-C(11)-C(20)	124.45(18)	N(1)-C(11)-C(12)	124.61(18)
C(20)-C(11)-C(12)	110.84(17)	C(11)-C(12)-C(13)	106.80(17)
C(11)-C(12)-C(27)	128.17(18)	C(13)-C(12)-C(27)	124.92(18)
C(14)-C(13)-C(12)	125.11(18)	C(14)-C(13)-C(19)	126.88(18)
C(12)-C(13)-C(19)	107.99(17)	C(15)-C(14)-C(13)	129.57(19)
C(15)-C(14)-H(14)	115.2	C(13)-C(14)-H(14)	115.2
C(14)-C(15)-C(16)	130.28(19)	C(14)-C(15)-H(15)	114.9
C(16)-C(15)-H(15)	114.9	C(15)-C(16)-C(17)	126.61(19)
C(15)-C(16)-C(6)	116.63(18)	C(17)-C(16)-C(6)	116.76(18)
C(18)-C(17)-C(16)	129.62(19)	C(18)-C(17)-H(17)	115.2
C(16)-C(17)-H(17)	115.2	C(17)-C(18)-C(19)	129.82(19)
C(17)-C(18)-H(18)	115.1	C(19)-C(18)-H(18)	115.1
C(18)-C(19)-C(20)	125.79(18)	C(18)-C(19)-C(13)	126.97(18)
C(20)-C(19)-C(13)	107.19(17)	C(11)-C(20)-C(19)	107.13(17)
C(11)-C(20)-C(30)	127.77(18)	C(19)-C(20)-C(30)	124.90(18)
O(1)-C(21)-O(2)	123.22(19)	O(1)-C(21)-C(2)	125.86(19)
O(2)-C(21)-C(2)	110.92(17)	O(2)-C(22)-C(23)	106.65(18)
O(2)-C(22)-H(22C)	110.4	C(23)-C(22)-H(22C)	110.4
O(2)-C(22)-H(22D)	110.4	C(23)-C(22)-H(22D)	110.4
H(22C)-C(22)-H(22D)	108.6	C(22)-C(23)-H(23D)	109.5
C(22)-C(23)-H(23E)	109.5	H(23D)-C(23)-H(23E)	109.5
C(22)-C(23)-H(23F)	109.5	H(23D)-C(23)-H(23F)	109.5
H(23E)-C(23)-H(23F)	109.5	O(3)-C(24)-O(4)	123.66(18)
O(3)-C(24)-C(10)	126.78(18)	O(4)-C(24)-C(10)	109.56(17)
O(4)-C(25)-C(26)	105.84(17)	O(4)-C(25)-H(25C)	110.6
C(26)-C(25)-H(25C)	110.6	O(4)-C(25)-H(25D)	110.6
C(26)-C(25)-H(25D)	110.6	H(25C)-C(25)-H(25D)	108.7
C(25)-C(26)-H(26D)	109.5	C(25)-C(26)-H(26E)	109.5
H(26D)-C(26)-H(26E)	109.5	C(25)-C(26)-H(26F)	109.5
H(26D)-C(26)-H(26F)	109.5	H(26E)-C(26)-H(26F)	109.5
O(5)-C(27)-O(6)	123.01(19)	O(5)-C(27)-C(12)	124.99(19)
O(6)-C(27)-C(12)	112.00(18)	O(6)-C(28)-C(29)	108.7(2)
O(6)-C(28)-H(28C)	110.0	C(29)-C(28)-H(28C)	110.0
O(6)-C(28)-H(28D)	110.0	C(29)-C(28)-H(28D)	110.0
H(28C)-C(28)-H(28D)	108.3	C(28)-C(29)-H(29D)	109.5
C(28)-C(29)-H(29E)	109.5	H(29D)-C(29)-H(29E)	109.5
C(28)-C(29)-H(29F)	109.5	H(29D)-C(29)-H(29F)	109.5
H(29E)-C(29)-H(29F)	109.5	O(7)-C(30)-O(8)	122.88(19)
O(7)-C(30)-C(20)	125.17(19)	O(8)-C(30)-C(20)	111.89(17)
O(8)-C(31)-C(32)	109.3(2)	O(8)-C(31)-H(31C)	109.8
C(32)-C(31)-H(31C)	109.8	O(8)-C(31)-H(31D)	109.8
C(32)-C(31)-H(31D)	109.8	H(31C)-C(31)-H(31D)	108.3
C(31)-C(32)-H(32D)	109.5	C(31)-C(32)-H(32E)	109.5
H(32D)-C(32)-H(32E)	109.5	C(31)-C(32)-H(32F)	109.5
H(32D)-C(32)-H(32F)	109.5	H(32E)-C(32)-H(32F)	109.5

atom-atom-atom	angle	atom-atom-atom	angle
N(1)-C(33)-Cr(1)	179.2(2)	O(9)-C(34)-Cr(1)	178.6(4)
O(13)-C(35)-Cr(1)	177.5(2)	O(12)-C(36)-Cr(1)	177.3(2)
O(10)-C(37)-Cr(1)	178.9(2)	O(11)-C(38)-Cr(1)	178.8(3)
C(34')-Cr(1')-C(35')	89.25(13)	C(34')-Cr(1')-C(38')	91.90(11)
C(35')-Cr(1')-C(38')	88.24(12)	C(34')-Cr(1')-C(37')	90.33(11)
C(35')-Cr(1')-C(37')	90.18(11)	C(38')-Cr(1')-C(37')	177.25(10)
C(34')-Cr(1')-C(36')	89.50(13)	C(35')-Cr(1')-C(36')	177.71(11)
C(38')-Cr(1')-C(36')	89.88(12)	C(37')-Cr(1')-C(36')	91.75(11)
C(34')-Cr(1')-C(33')	176.92(11)	C(35')-Cr(1')-C(33')	90.74(10)
C(38')-Cr(1')-C(33')	91.18(9)	C(37')-Cr(1')-C(33')	86.59(9)
C(36')-Cr(1')-C(33')	90.60(10)	C(21')-O(2')-C(22')	115.20(16)
C(24')-O(4')-C(25')	115.90(17)	C(27')-O(6')-C(28')	116.1(2)
C(30')-O(8')-C(31')	115.89(18)	C(33')-N(1')-C(11')	172.6(2)
C(10')-C(1')-C(2')	109.73(18)	C(10')-C(1')-H(1')	125.1
C(2')-C(1')-H(1')	125.1	C(1')-C(2')-C(3')	108.17(18)
C(1')-C(2')-C(21')	125.09(18)	C(3')-C(2')-C(21')	126.72(18)
C(4')-C(3')-C(2')	126.01(19)	C(4')-C(3')-C(9')	127.03(18)
C(2')-C(3')-C(9')	106.96(17)	C(5')-C(4')-C(3')	129.21(19)
C(5')-C(4')-H(4')	115.4	C(3')-C(4')-H(4')	115.4
C(4')-C(5')-C(6')	130.30(19)	C(4')-C(5')-H(5')	114.8
C(6')-C(5')-H(5')	114.8	C(5')-C(6')-C(7')	126.90(19)
C(5')-C(6')-C(16')	116.17(18)	C(7')-C(6')-C(16')	116.92(18)
C(8')-C(7')-C(6')	129.7(2)	C(8')-C(7')-H(7')	115.1
C(6')-C(7')-H(7')	115.1	C(7')-C(8')-C(9')	129.67(19)
C(7')-C(8')-H(8')	115.2	C(9')-C(8')-H(8')	115.2
C(8')-C(9')-C(10')	126.29(19)	C(8')-C(9')-C(3')	127.15(18)
C(10')-C(9')-C(3')	106.56(17)	C(1')-C(10')-C(9')	108.59(17)
C(1')-C(10')-C(24')	124.96(19)	C(9')-C(10')-C(24')	126.42(19)
N(1')-C(11')-C(20')	124.47(19)	N(1')-C(11')-C(12')	124.86(19)
C(20')-C(11')-C(12')	110.67(18)	C(13')-C(12')-C(11')	107.05(18)
C(13')-C(12')-C(27')	124.93(19)	C(11')-C(12')-C(27')	128.02(19)
C(14')-C(13')-C(12')	125.31(19)	C(14')-C(13')-C(19')	127.08(19)
C(12')-C(13')-C(19')	107.57(17)	C(15')-C(14')-C(13')	129.3(2)
C(15')-C(14')-H(14')	115.3	C(13')-C(14')-H(14')	115.3
C(14')-C(15')-C(16')	130.7(2)	C(14')-C(15')-H(15')	114.7
C(16')-C(15')-H(15')	114.7	C(15')-C(16')-C(17')	125.95(19)
C(15')-C(16')-C(6')	117.30(18)	C(17')-C(16')-C(6')	116.74(18)
C(18')-C(17')-C(16')	130.42(19)	C(18')-C(17')-H(17')	114.8
C(16')-C(17')-H(17')	114.8	C(17')-C(18')-C(19')	129.71(19)
C(17')-C(18')-H(18')	115.1	C(19')-C(18')-H(18')	115.1
C(18')-C(19')-C(20')	125.36(19)	C(18')-C(19')-C(13')	126.76(18)
C(20')-C(19')-C(13')	107.87(17)	C(11')-C(20')-C(19')	106.83(18)
C(11')-C(20')-C(30')	127.78(19)	C(19')-C(20')-C(30')	125.36(19)
O(1')-C(21')-O(2')	122.95(19)	O(1')-C(21')-C(2')	126.13(19)
O(2')-C(21')-C(2')	110.92(17)	O(2')-C(22')-C(23')	107.35(18)
O(2')-C(22')-H(22A)	110.2	C(23')-C(22')-H(22A)	110.2
O(2')-C(22')-H(22B)	110.2	C(23')-C(22')-H(22B)	110.2
H(22A)-C(22')-H(22B)	108.5	C(22')-C(23')-H(23A)	109.5
C(22')-C(23')-H(23B)	109.5	H(23A)-C(23')-H(23B)	109.5
C(22')-C(23')-H(23C)	109.5	H(23A)-C(23')-H(23C)	109.5
H(23B)-C(23')-H(23C)	109.5	O(3')-C(24')-O(4')	122.86(19)
O(3')-C(24')-C(10')	126.3(2)	O(4')-C(24')-C(10')	110.85(18)

atom-atom-atom	angle	atom-atom-atom	angle
O(4')-C(25')-C(26')	106.79(19)	O(4')-C(25')-H(25A)	110.4
C(26')-C(25')-H(25A)	110.4	O(4')-C(25')-H(25B)	110.4
C(26')-C(25')-H(25B)	110.4	H(25A)-C(25')-H(25B)	108.6
C(25')-C(26')-H(26A)	109.5	C(25')-C(26')-H(26B)	109.5
H(26A)-C(26')-H(26B)	109.5	C(25')-C(26')-H(26C)	109.5
H(26A)-C(26')-H(26C)	109.5	H(26B)-C(26')-H(26C)	109.5
O(5')-C(27')-O(6')	122.9(2)	O(5')-C(27')-C(12')	124.5(2)
O(6')-C(27')-C(12')	112.62(19)	O(6')-C(28')-C(29')	108.8(2)
O(6')-C(28')-H(28A)	109.9	C(29')-C(28')-H(28A)	109.9
O(6')-C(28')-H(28B)	109.9	C(29')-C(28')-H(28B)	109.9
H(28A)-C(28')-H(28B)	108.3	C(28')-C(29')-H(29A)	109.5
C(28')-C(29')-H(29B)	109.5	H(29A)-C(29')-H(29B)	109.5
C(28')-C(29')-H(29C)	109.5	H(29A)-C(29')-H(29C)	109.5
H(29B)-C(29')-H(29C)	109.5	O(7')-C(30')-O(8')	123.83(19)
O(7')-C(30')-C(20')	124.37(19)	O(8')-C(30')-C(20')	111.79(18)
O(8')-C(31')-C(32')	111.0(2)	O(8')-C(31')-H(31A)	109.4
C(32')-C(31')-H(31A)	109.4	O(8')-C(31')-H(31B)	109.4
C(32')-C(31')-H(31B)	109.4	H(31A)-C(31')-H(31B)	108.0
C(31')-C(32')-H(32A)	109.5	C(31')-C(32')-H(32B)	109.5
H(32A)-C(32')-H(32B)	109.5	C(31')-C(32')-H(32C)	109.5
H(32A)-C(32')-H(32C)	109.5	H(32B)-C(32')-H(32C)	109.5
N(1')-C(33')-Cr(1')	176.7(2)	O(9')-C(34')-Cr(1')	178.8(3)
O(12')-C(35')-Cr(1')	178.7(2)	O(13')-C(36')-Cr(1')	178.7(2)
O(10')-C(37')-Cr(1')	178.0(2)	O(11')-C(38')-Cr(1')	178.6(3)
Cl(1S)-C(1S)-Cl(2S)	140.9(11)	Cl(1S)-C(1S)-H(1SA)	101.8
Cl(2S)-C(1S)-H(1SA)	101.8	Cl(1S)-C(1S)-H(1SB)	101.8
Cl(2S)-C(1S)-H(1SB)	101.8	H(1SA)-C(1S)-H(1SB)	104.7

Table S6: Torsion angles (°) for **7**·$(CH_2Cl_2)_{0.375}$.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
C(10)-C(1)-C(2)-C(3)	0.7(2)	C(10)-C(1)-C(2)-C(21)	−177.78(19)
C(1)-C(2)-C(3)-C(4)	178.98(19)	C(21)-C(2)-C(3)-C(4)	−2.5(3)
C(1)-C(2)-C(3)-C(9)	−1.1(2)	C(21)-C(2)-C(3)-C(9)	177.45(19)
C(2)-C(3)-C(4)-C(5)	178.8(2)	C(9)-C(3)-C(4)-C(5)	−1.2(4)
C(3)-C(4)-C(5)-C(6)	−0.1(4)	C(4)-C(5)-C(6)-C(7)	1.5(4)
C(4)-C(5)-C(6)-C(16)	−179.4(2)	C(5)-C(6)-C(7)-C(8)	−0.3(4)
C(16)-C(6)-C(7)-C(8)	−179.4(2)	C(6)-C(7)-C(8)-C(9)	−2.1(4)
C(7)-C(8)-C(9)-C(10)	−178.9(2)	C(7)-C(8)-C(9)-C(3)	2.3(4)
C(4)-C(3)-C(9)-C(8)	−0.1(3)	C(2)-C(3)-C(9)-C(8)	179.92(19)
C(4)-C(3)-C(9)-C(10)	−179.1(2)	C(2)-C(3)-C(9)-C(10)	1.0(2)
C(2)-C(1)-C(10)-C(9)	−0.1(2)	C(2)-C(1)-C(10)-C(24)	−178.86(19)
C(8)-C(9)-C(10)-C(1)	−179.50(19)	C(3)-C(9)-C(10)-C(1)	−0.5(2)
C(8)-C(9)-C(10)-C(24)	−0.8(3)	C(3)-C(9)-C(10)-C(24)	178.16(19)
N(1)-C(11)-C(12)-C(13)	−175.65(19)	C(20)-C(11)-C(12)-C(13)	0.8(2)
N(1)-C(11)-C(12)-C(27)	8.2(4)	C(20)-C(11)-C(12)-C(27)	−175.3(2)
C(11)-C(12)-C(13)-C(14)	−177.8(2)	C(27)-C(12)-C(13)-C(14)	−1.5(3)
C(11)-C(12)-C(13)-C(19)	0.7(2)	C(27)-C(12)-C(13)-C(19)	176.96(19)
C(12)-C(13)-C(14)-C(15)	−179.3(2)	C(19)-C(13)-C(14)-C(15)	2.5(4)
C(13)-C(14)-C(15)-C(16)	1.4(4)	C(14)-C(15)-C(16)-C(17)	0.0(4)

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
C(14)-C(15)-C(16)-C(6)	179.4(2)	C(5)-C(6)-C(16)-C(15)	−42.2(3)
C(7)-C(6)-C(16)-C(15)	137.0(2)	C(5)-C(6)-C(16)-C(17)	137.3(2)
C(7)-C(6)-C(16)-C(17)	−43.5(3)	C(15)-C(16)-C(17)-C(18)	−3.6(4)
C(6)-C(16)-C(17)-C(18)	177.0(2)	C(16)-C(17)-C(18)-C(19)	2.4(4)
C(17)-C(18)-C(19)-C(20)	−179.6(2)	C(17)-C(18)-C(19)-C(13)	3.2(4)
C(14)-C(13)-C(19)-C(18)	−5.8(4)	C(12)-C(13)-C(19)-C(18)	175.7(2)
C(14)-C(13)-C(19)-C(20)	176.6(2)	C(12)-C(13)-C(19)-C(20)	−1.9(2)
N(1)-C(11)-C(20)-C(19)	174.47(19)	C(12)-C(11)-C(20)-C(19)	−2.0(2)
N(1)-C(11)-C(20)-C(30)	−10.5(3)	C(12)-C(11)-C(20)-C(30)	173.0(2)
C(18)-C(19)-C(20)-C(11)	−175.3(2)	C(13)-C(19)-C(20)-C(11)	2.3(2)
C(18)-C(19)-C(20)-C(30)	9.5(3)	C(13)-C(19)-C(20)-C(30)	−172.89(19)
C(22)-O(2)-C(21)-O(1)	0.2(3)	C(22)-O(2)-C(21)-C(2)	−179.97(17)
C(1)-C(2)-C(21)-O(1)	168.7(2)	C(3)-C(2)-C(21)-O(1)	−9.6(3)
C(1)-C(2)-C(21)-O(2)	−11.1(3)	C(3)-C(2)-C(21)-O(2)	170.60(18)
C(21)-O(2)-C(22)-C(23)	−178.73(18)	C(25)-O(4)-C(24)-O(3)	1.6(3)
C(25)-O(4)-C(24)-C(10)	−179.33(18)	C(1)-C(10)-C(24)-O(3)	−162.4(2)
C(9)-C(10)-C(24)-O(3)	19.1(4)	C(1)-C(10)-C(24)-O(4)	18.6(3)
C(9)-C(10)-C(24)-O(4)	−159.94(19)	C(24)-O(4)-C(25)-C(26)	−166.29(19)
C(28)-O(6)-C(27)-O(5)	−8.7(3)	C(28)-O(6)-C(27)-C(12)	170.4(2)
C(11)-C(12)-C(27)-O(5)	−176.4(2)	C(13)-C(12)-C(27)-O(5)	8.1(4)
C(11)-C(12)-C(27)-O(6)	4.5(3)	C(13)-C(12)-C(27)-O(6)	−171.0(2)
C(27)-O(6)-C(28)-C(29)	−92.7(3)	C(31)-O(8)-C(30)-O(7)	3.5(3)
C(31)-O(8)-C(30)-C(20)	−174.0(2)	C(11)-C(20)-C(30)-O(7)	168.6(2)
C(19)-C(20)-C(30)-O(7)	−17.2(3)	C(11)-C(20)-C(30)-O(8)	−14.0(3)
C(19)-C(20)-C(30)-O(8)	160.25(19)	C(30)-O(8)-C(31)-C(32)	−175.8(2)
C(10′)-C(1′)-C(2′)-C(3′)	−0.1(2)	C(10′)-C(1′)-C(2′)-C(21′)	178.63(19)
C(1′)-C(2′)-C(3′)-C(4′)	−179.8(2)	C(21′)-C(2′)-C(3′)-C(4′)	1.6(3)
C(1′)-C(2′)-C(3′)-C(9′)	0.1(2)	C(21′)-C(2′)-C(3′)-C(9′)	−178.56(19)
C(2′)-C(3′)-C(4′)-C(5′)	−179.9(2)	C(9′)-C(3′)-C(4′)-C(5′)	0.2(4)
C(3′)-C(4′)-C(5′)-C(6′)	0.1(4)	C(4′)-C(5′)-C(6′)-C(7′)	0.0(4)
C(4′)-C(5′)-C(6′)-C(16′)	−179.4(2)	C(5′)-C(6′)-C(7′)-C(8′)	−0.4(4)
C(16′)-C(6′)-C(7′)-C(8′)	179.0(2)	C(6′)-C(7′)-C(8′)-C(9′)	0.5(4)
C(7′)-C(8′)-C(9′)-C(10′)	179.8(2)	C(7′)-C(8′)-C(9′)-C(3′)	−0.1(4)
C(4′)-C(3′)-C(9′)-C(8′)	−0.3(3)	C(2′)-C(3′)-C(9′)-C(8′)	179.8(2)
C(4′)-C(3′)-C(9′)-C(10′)	179.8(2)	C(2′)-C(3′)-C(9′)-C(10′)	−0.1(2)
C(2′)-C(1′)-C(10′)-C(9′)	0.0(2)	C(2′)-C(1′)-C(10′)-C(24′)	−178.26(19)
C(8′)-C(9′)-C(10′)-C(1′)	−179.8(2)	C(3′)-C(9′)-C(10′)-C(1′)	0.1(2)
C(8′)-C(9′)-C(10′)-C(24′)	−1.6(3)	C(3′)-C(9′)-C(10′)-C(24′)	178.30(19)
N(1′)-C(11′)-C(12′)-C(13′)	−179.2(2)	C(20′)-C(11′)-C(12′)-C(13′)	1.4(2)
N(1′)-C(11′)-C(12′)-C(27′)	0.6(4)	C(20′)-C(11′)-C(12′)-C(27′)	−178.8(2)
C(11′)-C(12′)-C(13′)-C(14′)	176.6(2)	C(27′)-C(12′)-C(13′)-C(14′)	−3.3(3)
C(11′)-C(12′)-C(13′)-C(19′)	−1.3(2)	C(27′)-C(12′)-C(13′)-C(19′)	178.9(2)
C(12′)-C(13′)-C(14′)-C(15′)	−177.5(2)	C(19′)-C(13′)-C(14′)-C(15′)	0.0(4)
C(13′)-C(14′)-C(15′)-C(16′)	−1.9(4)	C(14′)-C(15′)-C(16′)-C(17′)	0.9(4)
C(14′)-C(15′)-C(16′)-C(6′)	179.9(2)	C(5′)-C(6′)-C(16′)-C(15′)	−45.7(3)
C(7′)-C(6′)-C(16′)-C(15′)	134.8(2)	C(5′)-C(6′)-C(16′)-C(17′)	133.3(2)
C(7′)-C(6′)-C(16′)-C(17′)	−46.1(3)	C(15′)-C(16′)-C(17′)-C(18′)	1.7(4)
C(6′)-C(16′)-C(17′)-C(18′)	−177.2(2)	C(16′)-C(17′)-C(18′)-C(19′)	−2.1(4)
C(17′)-C(18′)-C(19′)-C(20′)	178.2(2)	C(17′)-C(18′)-C(19′)-C(13′)	−0.3(4)
C(14′)-C(13′)-C(19′)-C(18′)	1.6(3)	C(12′)-C(13′)-C(19′)-C(18′)	179.4(2)
C(14′)-C(13′)-C(19′)-C(20′)	−177.1(2)	C(12′)-C(13′)-C(19′)-C(20′)	0.7(2)
N(1′)-C(11′)-C(20′)-C(19′)	179.67(19)	C(12′)-C(11′)-C(20′)-C(19′)	−0.9(2)

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
N(1')-C(11')-C(20')-C(30')	−2.3(3)	C(12')-C(11')-C(20')-C(30')	177.1(2)
C(18')-C(19')-C(20')-C(11')	−178.57(19)	C(13')-C(19')-C(20')-C(11')	0.1(2)
C(18')-C(19')-C(20')-C(30')	3.4(3)	C(13')-C(19')-C(20')-C(30')	−177.95(19)
C(22')-O(2')-C(21')-O(1')	0.6(3)	C(22')-O(2')-C(21')-C(2')	−179.00(18)
C(1')-C(2')-C(21')-O(1')	−177.3(2)	C(3')-C(2')-C(21')-O(1')	1.2(4)
C(1')-C(2')-C(21')-O(2')	2.4(3)	C(3')-C(2')-C(21')-O(2')	−179.17(19)
C(21')-O(2')-C(22')-C(23')	173.18(19)	C(25')-O(4')-C(24')-O(3')	−4.3(3)
C(25')-O(4')-C(24')-C(10')	174.95(18)	C(1')-C(10')-C(24')-O(3')	176.2(2)
C(9')-C(10')-C(24')-O(3')	−1.7(4)	C(1')-C(10')-C(24')-O(4')	−3.0(3)
C(9')-C(10')-C(24')-O(4')	179.07(19)	C(24')-O(4')-C(25')-C(26')	179.73(18)
C(28')-O(6')-C(27')-O(5')	−3.3(4)	C(28')-O(6')-C(27')-C(12')	176.2(3)
C(13')-C(12')-C(27')-O(5')	−15.9(4)	C(11')-C(12')-C(27')-O(5')	164.3(2)
C(13')-C(12')-C(27')-O(6')	164.6(2)	C(11')-C(12')-C(27')-O(6')	−15.2(3)
C(27')-O(6')-C(28')-C(29')	−144.1(3)	C(31')-O(8')-C(30')-O(7')	7.8(3)
C(31')-O(8')-C(30')-C(20')	−171.59(19)	C(11')-C(20')-C(30')-O(7')	−169.2(2)
C(19')-C(20')-C(30')-O(7')	8.5(3)	C(11')-C(20')-C(30')-O(8')	10.2(3)
C(19')-C(20')-C(30')-O(8')	−172.12(19)	C(30')-O(8')-C(31')-C(32')	−89.0(3)

Table S7: Hydrogen atom coordinates and isotropic displacement parameters (Å^2) for **7**·$(CH_2Cl_2)_{0.375}$.

Atom	*x*	*y*	*z*	U(eq)
H8	7612.72	3436.54	−83.38	20
H18'	9661.93	3431.83	1934.81	21
H4	11964.58	4380.63	585.48	20
H1	8376.91	5487.98	1487.12	20
H5'	14230.72	3038.12	828.62	22
H4'	15155.16	2456.99	24.14	21
H7	8807.1	2655.03	−641.46	20
H14	13414.56	2592.15	−1847.37	22
H17	9920.13	1569.2	−539.18	22
H15	12314.89	3237.85	−1146.19	22
H1'	14580.25	−19.53	−1096.68	20
H18	10308.37	530.77	−1151.02	22
H15'	14254.73	3034.02	1900.13	25
H7'	11585.59	1450.2	1291.52	24
H14'	14120.61	3866.98	2716.41	24
H5	12270.69	3431.76	−129.29	21
H8'	11820.53	469.2	596.5	23
H25C	4487.94	4969.4	1365.89	27
H25D	4423.24	5133.99	596.44	27
H25A	11374.02	−1781.47	−914.49	31
H25B	12474.17	−2129.18	−447.21	31
H22A	18086.39	1382.07	−1446.53	31
H22B	17164.5	1738.16	−2004.84	31
H22C	12088.14	6782.35	1883.17	29

Atom	*x*	*y*	*z*	U(eq)
H22D	11945.48	6198.36	2493.66	29
H23D	10357.04	7509.86	2197.14	47
H23E	11369.5	7492.36	2791.71	47
H23F	10160.83	6914.5	2790.75	47
H26D	5016.56	6498.05	817.34	41
H26E	4961.21	6321	1578.21	41
H26F	3709.1	6272.54	1124.65	41
H26A	12606.26	−1989.61	−1823.89	45
H26B	12389.62	−2816.44	−1455.26	45
H26C	13695.87	−2340.34	−1357.82	45
H28C	16374.75	1109.77	−3708.64	43
H28D	16199.97	1937.92	−3329.46	43
H31A	6850.91	5349.06	3646.05	37
H31B	6710.6	4554.82	3209.14	37
H31C	9500.78	−1440.02	−2755.06	43
H31D	10386.32	−1969.86	−2287.53	43
H23A	17032.34	460.06	−2513.11	49
H23B	17988.94	125.1	−1966.01	49
H23C	18450.41	783.59	−2467.06	49
H32A	6563.4	5294.8	2269.24	65
H32B	6898.4	6104.44	2661.23	65
H32C	5587.68	5653.14	2755.36	65
H28A	14771.62	6280.99	4163.84	68
H28B	14852.32	5422.32	4504.45	68
H29A	13270.66	6664.95	4878.75	69
H29B	14499.12	6389.94	5281.58	69
H29C	13303.55	5802.22	5209.21	69
H29D	15601.29	2043.29	−4454.6	83
H29E	14457.8	2230.91	−4005.77	83
H29F	14528.76	1380.32	−4359.54	83
H32D	10725.33	−1779.82	−3628.93	73
H32E	10078.88	−2550.09	−3319.6	73
H32F	11526.48	−2348.67	−3155.62	73
H17’	10695.08	2633.91	1313.17	21
H1SA	9326.94	33.27	4521.52	235
H1SB	9063.74	271.5	3794.27	235

Table S8: Atomic occupancy for CH_2Cl_2 solvent of crystallization in **7**·$(CH_2Cl_2)_{0.375}$.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
H26E	0.5	Cl2S	0.75	Cl1S	0.75
C1S	0.75	H1SA	0.75	H1SB	0.75

C. Surface studies

C1. Self-assembled monolayer films (SAMs) of 11 on Au(111) surfaces. Commercial gold-coated silicon substrates (Platypus Technologies) featuring (111) preferred orientation normal to the substrate[10] were soaked sequentially in distilled chloroform, acetone, and 200-proof ethanol for two hours in each solvent. The bare gold substrates were thoroughly dried under a stream of N_2 gas, and their ellipsometric physical constants *n* and *k* were measured. SAM films of **11** were formed by placing a freshly cleaned ~1×1 cm^2 gold substrate into a 2 mM solution of **11** in CH_2Cl_2 for *ca.* 24 hrs. Prior to their analysis, the SAM-coated substrates were rinsed thoroughly with CH_2Cl_2 and dried in a flow of N_2 gas. No precautions to exclude air or ambient laboratory lighting were exercised during these SAM preparation experiments.

C2. Surface IR measurements. The grazing incidence Reflection Absorption Fourier Transform Infrared Spectroscopy spectra for the SAMs of **11** on gold were recorded using a Thermo Nicolet Nexus 670 FTIR spectrometer with a VeeMax grazing angle accessory set at an angle of 70°. A background spectrum was collected using a freshly cleaned bare gold substrate before acquiring the spectrum of each sample. Ten thousand scans from 600 to 4000 cm^{-1} at 4 cm^{-1} resolution were collected for each background/sample combination.

C3. Optical ellipsometry. The film thicknesses were determined using an Auto EL III ellipsometer (Rudolph Research). All measurements were conducted with a HeNe laser at a wavelength of 632.8 nm and an incident angle of 70° to the surface normal. The optical constants *n* and *k* were obtained for each sample individually by measuring these parameters for the corresponding freshly cleaned bare gold substrates prior to the SAM formation. These optical constants were used as input in determining thicknesses of the adsorbed thin layers of **11**. A refractive index of 1.45 was assumed[11-13] for all organic thin films described herein. Several SAM-on-Au(111) samples were subjected to ellipsometric thickness measurements. On each sample, five measurements were taken, and the reported thickness values constitute averages across all SAM samples.

D. References

1. T. R. Maher, A. D. Spaeth, B. M. Neal, C. L. Berrie, W. H. Thompson, V. W. Day and M. V. Barybin, *J. Am. Chem. Soc.*, 2010, **132**, 15924-15926.
2. L. C. Murfin, M. Weber, S. J. Park, W. T. Kim, C. M. Lopez-Alled, C. L. McMullin, F. Pradaux-Caggiano, C. L. Lyall, G. Kociok-Köhn, J. Wenk, S. D. Bull, J. Yoon, H. M. Kim, T. D. James and S. E. Lewis, *J. Am. Chem. Soc.*, 2019, **141**, 19389-19396.
3. R. N. McDonald, J. M. Richmond, J. R. Curtis, H. E. Petty and T. L. Hoskins, *J. Org. Chem.*, 1976, **41**, 1811-1821.
4. J. C. Applegate, M. K. Okeowo, N. R. Erickson, B. M. Neal, C. L. Berrie, N. N. Gerasimchuk and M. V. Barybin, *Chem. Sci.*, 2016, **7**, 1422-1429.
5. M. K. Pomije, C. J. Kurth, J. E. Ellis and M. V. Barybin, *Organometallics*, 1997, **16**, 3582-3587.
6. *Apex2, Version 2 User Manual, M86-E01078*, Bruker Analytical X-ray Systems, Inc., Madison, WI, USA, 2006.
7. SAINT (8.40A), Brucker Analytical X-ray Systems: Inc., Madison, WI, USA, 2022.
8. G. M. Sheldrick. SADABS: Program for Absorption Correction for Data from Area Detector Frames (2008/1), University of Göttingen, 2008.
9. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.
10. M. Aguilar, E. Anguiano, J. A. Aznárez and J. L. Sacedón, *Surf. Sci.*, 2001, **482-485**, 935-939.
11. S. C. Clear and P. F. Nealey, *Langmuir*, 2001, **17**, 720-732.
12. J. D. Le Grange, J. L. Markham and C. R. Kurkjian, *Langmuir*, 1993, **9**, 1749-1753.
13. S. R. Wasserman, G. M. Whitesides, I. M. Tidswell, B. M. Ocko, P. S. Pershan and J. D. Axe, *J. Am. Chem. Soc.*, 1989, **111**, 5852-5861.