A Convenient Synthetic Route to Benz[*cd*]azulenes: Versatile Ligands with the Potential To Bind Metals in an η^5, η^6, or η^7 Fashion

Sonya Balduzzi,[a] Helge Müller-Bunz,[b] and Michael J. McGlinchey*[a, b]

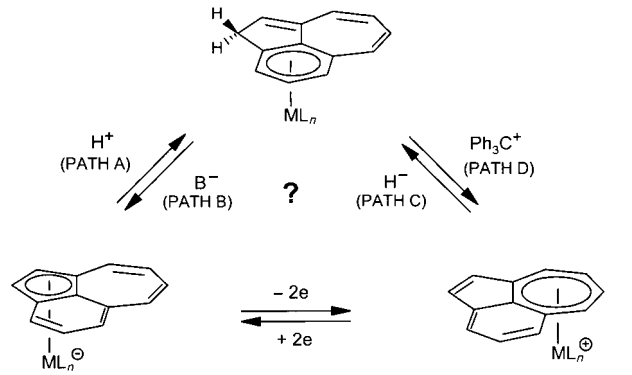
Abstract: A facile method for preparing the 2*H*-benz[*cd*]azulene system, based upon an elaboration of the guaiazulene framework, is presented. Aerial oxidation to the corresponding 8-(2-propylidene)-benz[*cd*]azulene, and also cycloaddition reactions with tetracyanoethylene (TCNE), are described. The first X-ray crystal structure of a 2*H*-benz[*cd*]azulene, as an η^6-coordinated $Cr(CO)_3$ complex, is reported.

Keywords: benzazulenes · chromium · cycloaddition · haptotropic shifts · structure elucidation

Introduction

In continuation of our studies on haptotropic shifts, whereby organometallic moieties, such as $Fe(C_5H_5)$ or $Mn(CO)_3$, migrate over polycyclic surfaces,[1] we sought a system made up of fused five-, six- and seven-membered rings, such that a metal might be able to adopt an η^5, η^6 or η^7 mode of attachment to the ligand. In particular, our goal was to study the organometallic chemistry of a tricyclic system that possessed a single methylene group and so, in principle, could readily be prepared in neutral, cationic and anionic forms. The relatively unexplored, non-alternant[2] hydrocarbon 2*H*-benz[*cd*]azulene was selected as a potentially viable ligand, and a convenient synthetic route was therefore required.

We anticipate that haptotropic shifts of a coordinated metal will be induced through changes in the oxidation state of the polycyclic ligand itself. The potential conversion from η^6 to η^5 bonding of a metal, upon deprotonation of such a ligand, is illustrated in path B of Scheme 1. Likewise, removal of a hydride, as illustrated in path D, could bring about an η^6 to η^7 haptotropic shift. It may even be possible to effect direct interconversion of the η^5-anionic and η^7-cationic isomers of the tricyclic metal complex under appropriate redox conditions. Toward this end, we have prepared such a fused tricyclic system and describe its synthesis and derivatisation herein.



Scheme 1. Possible haptotropic migrations over the benz[*cd*]azulene framework.

Results and Discussion

Synthesis of benz[*cd*]azulenes 3 and 4: The parent molecule, **1**, was prepared by Boekelheide and Smith in 1966 by means of a difficult multistep route based on the carbene-mediated ring expansion of the acenaphthene framework.[3] Unfortunately, the product is obtainable only in very low overall yield, is very susceptible to polymerisation, and can only be handled at low temperatures in dilute solution. Previously, in 1964, Hafner and Schaum had reported the synthesis of 3,4,7,9-tetramethyl-2*H*-benz[*cd*]azulene (**2**), but once again, the yields are low and the product readily decomposes.[4]

Our approach was to extend the guaiazulene carbon framework (**5**) through nucleophilic addition of the reso-

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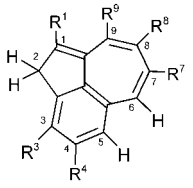


1: $R^1 = R^3 = R^4 = R^7 = R^8 = R^9 = H$
2: $R^3 = R^4 = R^7 = R^9 = CH_3$; $R^1 = R^8 = H$
3: $R^1 = R^3 = R^4 = CH_3$; $R^7 = R^9 = H$; $R^8 = CH(CH_3)_2$
4: $R^1 = CH_3$; $R^4 = C(CH_3)_3$; $R^8 = CH(CH_3)_2$; $R^3 = R^7 = R^9 = H$

nance-stabilized anion **6** to 3-chlorobutanone or 1-chloropinacolone, yielding the alcohols **7a**, **7b** or **9**, respectively, shown in Scheme 2.

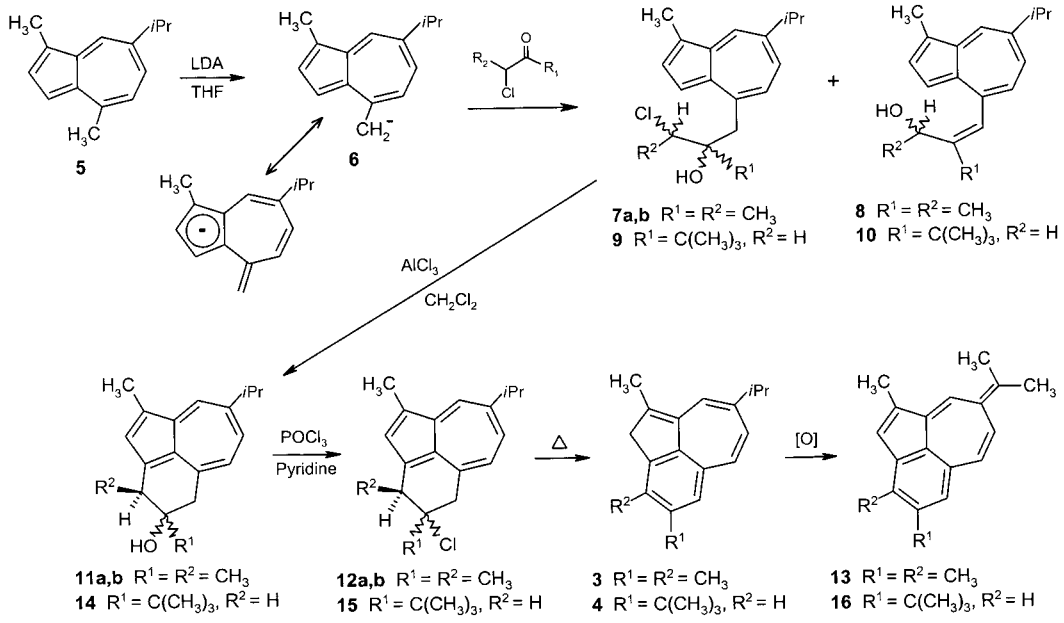
Although the diastereomeric alcohols **7a** and **7b** were separable by column chromatography, they were used as a mixture in the subsequent reaction, whereby formation of the six-membered ring in **11a** and **11b** was accomplished through $AlCl_3$-promoted Friedel–Crafts alkylation. This was made possible by the nucleophilic character of C(3) in the azulene system—C(2*a*) in **3** and **4**—which has been manifested in its reactions with electrophiles,[5] and in molecular orbital calculations that find it to be the site of highest charge density.[6] The *trans* stereochemistry of the two methyl substituents at C(3) and C(4) of the major diastereomer, **11a**, was assigned by using ^1H NMR NOE measurements. Since treatment of the alkenes **8** or **10** with $AlCl_3$ led only to isomerisation about the double bond, one might speculate about the existence of an epoxide-stabilized intermediate rather than a simple secondary cation in the ring closure of **7** or **9**. However, it may simply be the case that **8** and **10** lead to a stable allylic cation with a *syn* (*trans*) configuration that precludes cyclisation.

It was found that treatment of separate solutions of **11a** and **11b** in pyridine, with $POCl_3$, led to **12a** (*cis*-methyl) and **12b** (*trans*-methyl), stereospecifically.[7] Upon warming, both **12a** and **12b** produced a mixture of **3** (the desired benz[*cd*]azulene) and **13**; the latter was generated through oxidation of the former as was evident visually when an orange sample of **3** was transformed into yellow **13** following exposure to air.

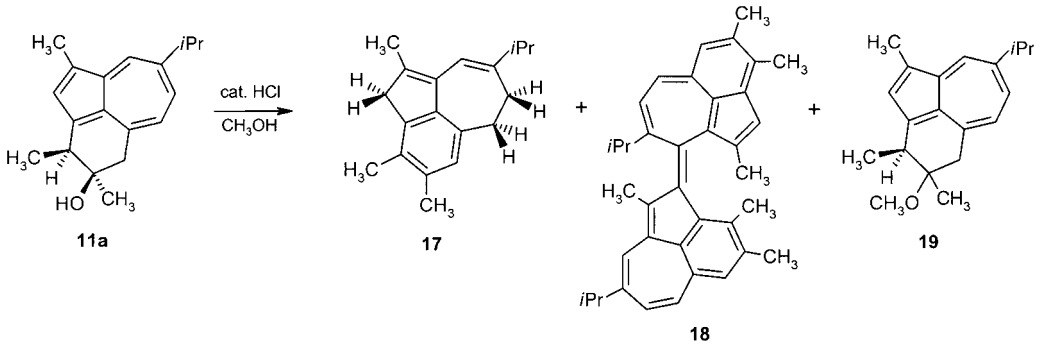
We note that the rate of reaction of **12b** was almost tenfold greater than that of **12a**. One might surmise that the antiperiplanar arrangement of hydrogen and chlorine at C(3) and C(4), respectively, in **12b**, allows E_2 elimination to form the tetrasubstituted double bond. Three consecutive [1,5] sigmatropic rearrangements of a hydrogen initially bonded to C(5) can then give rise to **3**. The vigorous reflux conditions required for the conversion of **12a** to **3** suggest that dehydrohalogenation may have proceeded by an E_1 mechanism.

Interestingly, an initial attempt to dehydrate the alcohol **11a** by treating it with HCl in methanol, and then warming the solution, yielded two orange solid compounds, **17** and **18**, in addition to the methyl ether **19**, and a small quantity of intractable material. The former was readily identified from its high resolution mass spectrum, and also from the ^1H and ^{13}C 2D-NMR spectra that revealed the presence of adjacent methylene groups, as 6,7-dihydro-2*H*-1,3,4-trimethyl-8-isopropylbenz[*cd*]azulene (**17**) shown in Scheme 3. The most distinguishing features of the ^1H and ^{13}C NMR spectra of **18** include two different sets of "H_6-H_7 environments" with their characteristic 12 Hz doublet coupling patterns, two nonequivalent isopropyl units and six different methyl groups. The data are fully consistent with formation of a bond between two benz[*cd*]azulene units in an unsymmetrical fashion, that is, through the C(2) position of one molecule and the C(9) position of a second molecule (vide infra).

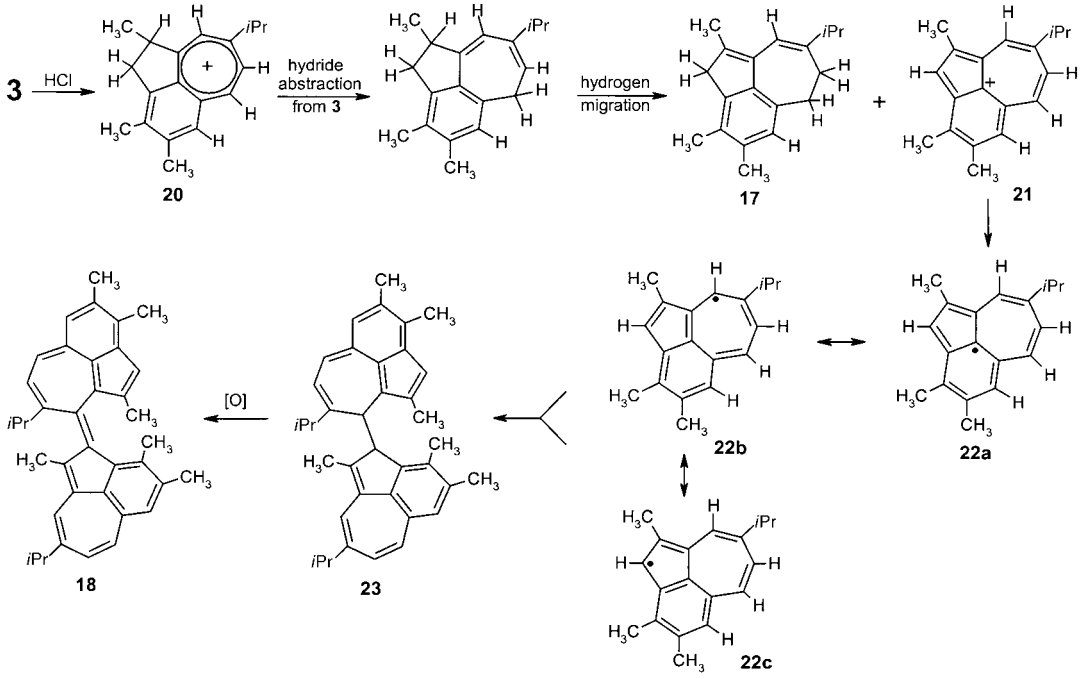
We hypothesize that **17** and **18** arose by protonation of the initially generated dehydration product **3** to produce the tropylium ion **20**. Hydride transfer from **3**, and a subsequent hydrogen migration, yields **17** and the 12π anti-aromatic cation **21**, as shown in Scheme 4. One-electron reduction of **21** can give rise to the benzazulenyl radicals depicted as resonance forms **22a–c**. It follows that compound **23** is pro-



Scheme 2. Formation of the benz[*cd*]azulene skeleton.



Scheme 3. Disproportionation and dimerisation of a benz[*cd*]azulene.



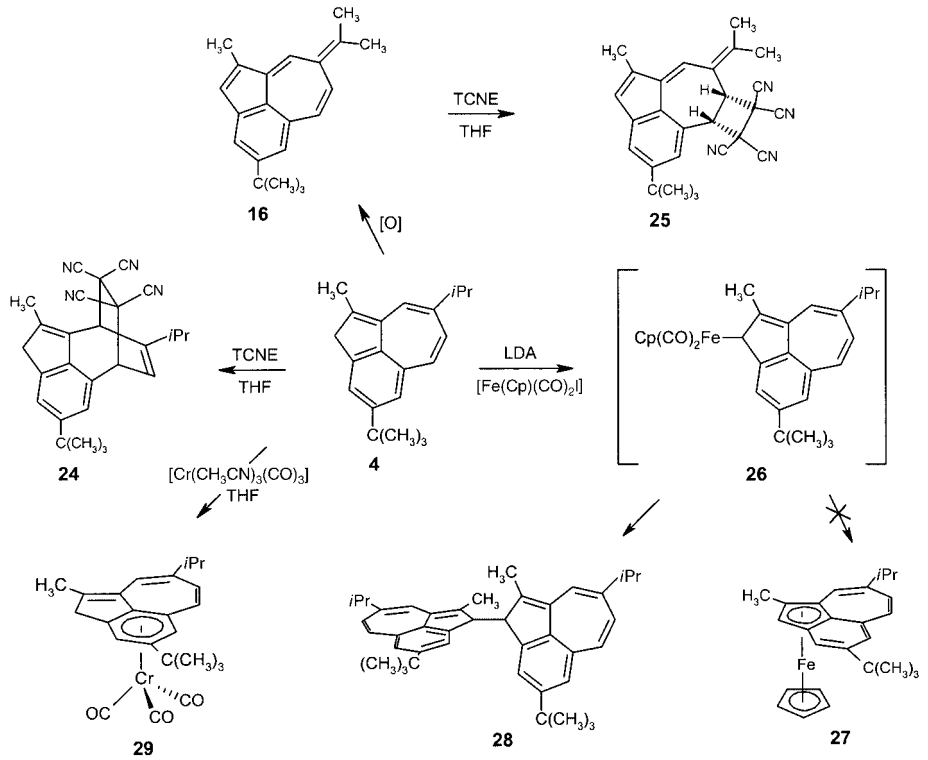
Scheme 4. Proposed mechanism for the formation of **17** and **18**.

duced through coupling of **22b** with **22c**. The ability of the benz[*cd*]azulenyl system to form a cation, anion or radical was anticipated, as it is iso-π-electronic with the odd alternant phenalenyl system, which has been reported to form three redox species.[8] Indeed, substitution at the central carbon C(9*b*) of the benz[*cd*]azulene system has previously been reported by Hafner and co-workers.[9] In this last case, the ^{1}H NMR spectrum of the 9*b*-alkyl-substituted benz[*cd*]-azulene exhibited markedly shielded peripheral protons, entirely characteristic of a 12π system.[10] Radical coupling of **22** is also consistent with the previously reported dimerisation of phenalenyl radicals.[11] Subsequent aerial oxidation of **23** yields the highly conjugated dimer **18**, which is presumably twisted because of steric crowding. Compound **18** proved to be extremely unstable; rapid decomposition to an intractable product is suspected to be the result of additional radical or cationic coupling to form polymeric material.

Reactivity of 1-methyl-8-isopropyl-4-*tert*-butylbenz[*cd*]azulene 4: The benz[*cd*]azulene **4**, and its oxidized analogue **16**, were each treated with tetracyanoethylene to see where cycloaddition might occur. The reaction of TCNE with **4** at room temperature afforded the Diels–Alder adduct **24**, in near quantitative yield. A distinctive feature of the ^{1}H NMR spectrum of **24** is the relatively large chemical shift nonequivalence of the methylene protons at C(2), and also their large geminal coupling constant of 22.7 Hz. This observation contrasts with the corresponding reaction of TCNE with the "oxidized ligand" **16**, which does not possess a *cis*-1,3-diene unit, but which might be considered as a viable participant in a [12+2] cycloaddition involving the exocyclic double bond. However, the reaction of TCNE with **16** merely yields **25**, the [2+2] adduct across the C(6)−C(7) double bond. The cycloaddition chemistry of heptafulvenes and related systems has been comprehensively reviewed.[12]

The *tert*-butyl-substituted compound **4** was selected for incorporation of a metal, since it can be conveniently prepared in high yield. The absence of stereoisomers allows it to be synthesized expediently. We initially decided to prepare a mixed ferrocene (**27**) derived from **4** with the aim of

studying the potential η^5 to η^6 haptotropic shift of the cyclopentadienyliron fragment from the five- to the six-membered ring. In the expectation that the first-formed η^1-bonded complex, depicted as **26** in Scheme 5, could be induced to undergo a conversion to η^5-bonding with concomitant extrusion of both carbonyl groups, either thermally,[13] photochemically,[14] or by the use of trimethylamine-*N*-oxide, $[Fe(C_5H_5)(CO)_2I]$ was added to the lithium anion of **4**. However, in our hands, the symmetrical dimer **28** was recovered, irrespective of the reaction temperature. Whether **28** corresponds to the *meso* compound, or to a *d*,*l* pair of enantiomers, cannot be ascertained from its ^{1}H and ^{13}C NMR spectra, since the protons bonded to C(2) of the two benz[*cd*]azulenyl moieties are chemical-shift equivalent in both cases. A similar situation was previously encountered during reflux of the $Fe(\eta^1\text{-Cp})(CO)_2$ complex of 4*H*-cyclopenta[*def*]phenanthrene, which also yielded a radical coupling product,[1j] presumably generated by thermal homolytic cleavage of the carbon–iron bond.



Scheme 5. Reactions of benz[*cd*]azulenes with TCNE and with organometallic reagents.

For a parallel investigation of the possibility of effecting an η^6 to η^5 haptotropic shift of a metal coordinated to the six-membered ring, the $Cr(CO)_3$ complex of **4** was prepared by warming a solution of **4** and $[Cr(CH_3CN)_3(CO)_3]$ in THF.[15] This reaction afforded the red-orange solid **29**, shown in Scheme 5, in 87% yield. The presence of ν_{CO} stretches at 1951 and 1881 cm^{-1} in the IR spectrum, and a ^{13}C NMR resonance at 234 ppm serve to confirm the presence of the chromium tricarbonyl tripod. Additionally, the ^{1}H NMR chemical shifts of the H(3) and H(5) resonances in **29** are shielded by approximately 0.8 ppm relative to **4**, entirely characteristic of η^6-chromium complexed arenes.[16] Likewise, upon complexation, the ^{13}C nuclei in the six-membered ring of **29** are shielded by 25–30 ppm.[17]

The stability of the chromium complex **29** permitted the isolation of crystals suitable for an X-ray diffraction study, and the resulting structure appears as Figure 1. The ligand is planar, the chromium atom is sited 1.712 Å below the six-membered ring, and the tripod is almost perfectly staggered with respect to the arene carbons. Bond lengths within the benz[*cd*]azulene framework are indicated in Figure 2; it is particularly noteworthy that there is clear bond localisation within the five- and seven-membered rings, but much less so in the chromium-complexed arene ring. It is evident that the C(6)–C(7) and C(8)–C(9) linkages—1.32(1) and 1.31(1) Å, respectively—are double bonds, whereas C(7)–C(8) is a single bond at 1.47(1) Å; this is in accord with the previously mentioned cycloaddition of TCNE and **4** to give the [4+2] adduct **24**.

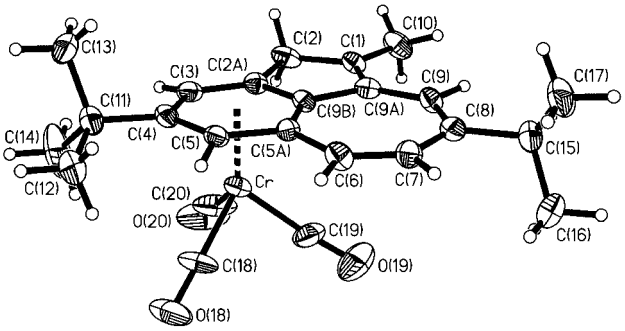


Figure 1. X-ray crystal structure of **29**, showing the atom numbering.

The packing within the unit cell of **29** is also interesting in that the molecules stack in pairs related by a centre of symmetry, such that the five-membered ring of one molecule overlaps substantially with the seven-membered ring of its neighbour, while the six-membered rings are maximally separated as illustrated in Figure 3. We believe this to be the first structural study of a 2*H*-benz[*cd*]azulene; the only relevant previous report of which we are aware describes the palladium-coupled bis(suberene) system, **30**, which, as shown in Figure 4, possesses a benz[*cd*]azulene substructure.[18]

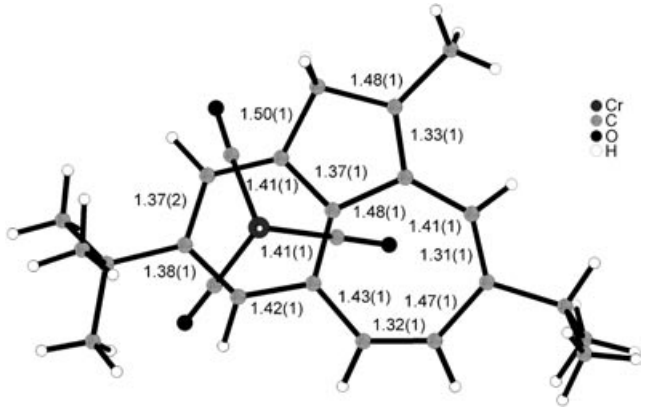


Figure 2. Selected bond lengths in **29**.

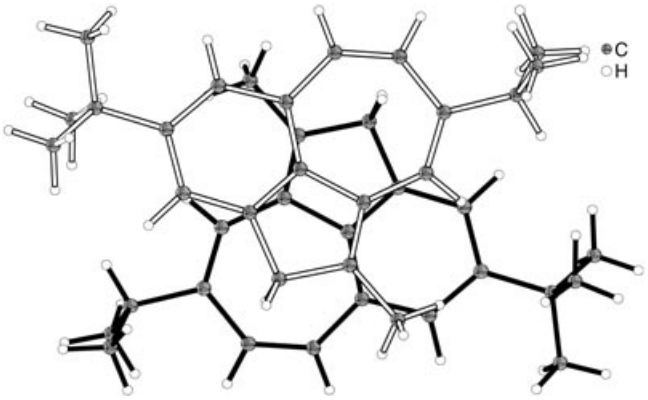


Figure 3. View showing the stacking of neighbouring molecules of **29** within the unit cell; the $Cr(CO)_3$ units have been removed for clarity.

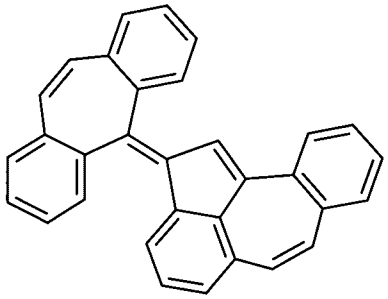


Figure 4. Bis(suberene) coupled product **30**, from reference [18].

To conclude, we describe a convenient route to 8-isopropyl-substituted 2*H*-benz[*cd*]azulenes, **3** and **4**, and note that they undergo ready oxidation to the corresponding 8-(2-propylidene)-benz[*cd*]azulenes, **13** and **16**, respectively. While **4** reacts with TCNE to give the [4+2] adduct in the seven-membered ring, the oxidised benzazulene **16** and TCNE yield the [2+2] product resulting from addition across the C(6)–C(7) bond. Analogous to the known behaviour of the isomeric phenalenyl skeleton, the benz[*cd*]azulene system readily forms radicals that yield both unsymmetrical and symmetrical dimers, **23** and **28**, respectively. The first X-ray crystal structure of a 2*H*-benz[*cd*]azulene reveals bond alternation in the seven-membered ring. A study of the haptotropic behaviour of organometallic derivatives of benz[*cd*]-azulenes will be the topic of a future manuscript.

Experimental Section

^{1}H NMR spectra were recorded on either a Bruker AC-500 spectrometer at 500.13 MHz, a Bruker AC-300 spectrometer at 300.130 MHz or on a Bruker AC-200 spectrometer at 200.20 MHz, with $CDCl_3$ as solvent and internal standard. ^{13}C NMR were recorded on the same instruments at 125.770 MHz, 75.467 MHz or at 50.340 MHz, also with $CDCl_3$ as solvent and internal standard. Assignments were based on standard 2D-NMR techniques. Infrared spectra were recorded on a Bio Rad FTS-40 Fourier transform spectrometer. Liquid samples were used as neat films on NaCl discs and solid samples were prepared as KBr pellets. Chemical ionisation (CI), with ammonia as the reagent gas, and electron impact (EI) mass spectra were recorded at 70 eV with a source temperature of 200 °C on a VG Analytical ZAB-R mass spectrometer equipped with a VG 11–250 data system. Flash chromatography was performed with Merck silica gel 60 (230–400 mesh). Elemental analyses were carried out by the Microanalytical Laboratory at University College Dublin.

Guaiazulene, LDA (2.0 M solution in heptane/tetrahydrofuran/ethylbenzene), 3-chlorobutanone, 1-chloropinacolone, tetracyanoethylene, I_2, $AlCl_3$ and $POCl_3$ were purchased from Aldrich and used without purification. $[Cr(CO)_6]$ and $[\{Fe(C_5H_5Fe)(CO)_2\}_2]$ were purchased from Strem Chemicals and used without further purification. CH_2Cl_2 was distilled from CaH_2 prior to use; THF and diethyl ether were distilled from sodium prior to use.

Synthesis of 7a, 7b and 8: LDA (27.5 mL of a 2.0 M solution) was added to a solution of guaiazulene (5.0 g, 25.0 mmol) and crushed, activated 4 Å molecular sieves (0.1 g) in THF (150 mL) under N_2 at 0 °C, and the mixture was stirred at 0 °C for 30 min. Following the addition of 3-chlorobutanone (2.55 mL, 25.0 mmol) at 0 °C, the mixture was allowed to warm to 25 °C over a period of 3 h, and then quenched by the addition of a solution of brine at 0 °C. Diethyl ether was then added, and the organic layer was extracted with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a blue oil which was separated by flash chromatography.

Data for 7a: Purification by flash chromatography (8:2 pentane/diethyl ether; $R_f = 0.66$) yielded a blue oil (3.88 g, 12.7 mmol, 51 %). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 8.25$ (s, 1H; C(8)H), 7.71 (d, $^3J(H,H) = 3.5$ Hz, 1H; C(2)H), 7.48 (d, $^3J(H,H) = 10.8$ Hz, 1H; C(6)H), 7.40 (d, $^3J(H,H) = 3.5$ Hz, 1H; C(3)H), 7.17 (d, $^3J(H,H) = 10.8$ Hz, 1H; C(5)H), 4.19 (q, $^3J(H,H) = 6.7$ Hz, 1H; C*H*Me), 3.63 (d, $^2J(H,H) = 13.3$ Hz, 1H; CH_2), 3.49 (d, $^2J(H,H) = 13.3$ Hz, 1H; CH_2), 3.12 (septet, $^3J(H,H) = 6.9$ Hz, 1H; C*H*Me_2), 2.70 (s, 3H; C(1)Me), 1.64 (d, $^3J(H,H) = 6.7$ Hz, 3H; CH*Me*), 1.41 (d, $^3J(H,H) = 6.9$ Hz, 6H; CH*Me*$_2$), 1.32 ppm (s, 3H; C*Me*OH); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 142.8$, 140.3, 139.4, 137.0, 136.1, 134.6, 133.5, 126.6, 125.7, 113.0, 76.0, 65.6, 44.5, 38.1, 24.6, 22.6, 19.6, 12.9 ppm; IR (neat): $\tilde{\nu} = 3395$, 3063, 2962, 2927, 2869, 1546, 1459, 1437, 1385, 1070, 1031, 756 cm^{-1}; MS (70 eV, EI): *m/z* (%): 198 (100) [$M^+ - C(CH_3)OHCH(Cl)CH_3$], 304 (32) [$M^+$(^{35}Cl)], 306 (11) [$M^+$(^{37}Cl)]; MS (70 eV, CI, NH_3): *m/z* (%): 198 (34) [$M^+ - C(CH_3)OHCH(Cl)CH_3$], 304 (68) [$M^+$(^{35}Cl)], 305 (100) [$M^+$(^{35}Cl)+H], 306 (31) [$M^+$(^{37}Cl)], 307 (24) [$M^+$(^{37}Cl)+H]; HRMS: *m/z*: calcd for $C_{19}H_{25}OCl$ [M^+]: 304.1594; found: 304.1558.

Data for 7b: Purification by flash chromatography (8:2 pentane/diethyl ether; $R_f = 0.53$) yielded a blue oil (2.66 g, 8.8 mmol, 35 %). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 8.22$ (s, 1H; C(8)H), 7.68 (d, $^3J(H,H) = 3.7$ Hz, 1H; C(2)H), 7.45 (d, $^3J(H,H) = 10.8$ Hz, 1H; C(6)H), 7.35 (d, $^3J(H,H) = 3.7$ Hz, 1H; C(3)H), 7.13 (d, $^3J(H,H) = 10.8$ Hz, 1H; C(5)H), 4.26 (q, $^3J(H,H) = 6.7$ Hz, 1H; C*H*Me), 3.56 (d, $^2J(H,H) = 13.1$ Hz, 1H; CH_2), 3.45 (d, $^2J(H,H) = 13.1$ Hz, 1H; CH_2), 3.10 (septet, $^3J(H,H) = 6.9$ Hz, 1H; C*H*Me_2), 2.68 (s, 3H; C(1)Me), 1.67 (d, $^3J(H,H) = 6.7$ Hz, 3H; CH*Me*), 1.39 (d, $^3J(H,H) = 6.9$ Hz, 6H; CH*Me*$_2$), 1.22 ppm (s, 3H; C*Me*OH); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 143.2$, 140.1, 139.2, 136.9, 136.1, 134.5, 133.4, 126.6, 125.5, 113.2, 75.8, 67.3, 44.8, 38.1, 24.7, 23.6, 19.9, 12.9 ppm; IR (neat): $\tilde{\nu} = 3413$, 3063, 2962, 2927, 2869, 1701, 1545, 1460, 1447, 1386, 1215, 1070, 1032, 756 cm^{-1}; MS (70 eV, EI): *m/z* (%): 198 (100) [$M^+ - C(CH_3)OHCH(Cl)CH_3$], 304 (46) [$M^+$(^{35}Cl)], 306 (15) [$M^+$(^{37}Cl)]; MS (70 eV, CI, NH_3): *m/z* (%): 198 (17) [$M^+ - C(CH_3)OHCH(Cl)CH_3$], 304 (35) [$M^+$(^{35}Cl)], 305 (100) [$M^+$(^{35}Cl)+H], 306 (12) [$M^+$(^{37}Cl)], 307 (26) [$M^+$(^{37}Cl)+H]; HRMS: *m/z*: calcd for $C_{19}H_{25}OCl$ [M^+]: 304.1594; found: 304.1574.

Data for 8: Purification by flash chromatography (8:2 pentane/diethyl ether; $R_f = 0.21$) yielded a blue oil (0.67 g, 2.5 mmol, 10%). ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = 8.27$ (s, 1H; C(8)H), 7.67 (d, $^3J(H,H) = 3.5$ Hz, 1H; C(2)H), 7.49 (d, $^3J(H,H) = 10.6$ Hz, 1H; C(6)H), 7.19 (d, $^3J(H,H) = 3.5$ Hz, 1H; C(3)H), 6.95 (d, $^3J(H,H) = 10.6$ Hz, 1H; C(5)H), 6.83 (s, 1H; =CH), 4.64 (q, $^3J(H,H) = 6.1$ Hz, 1H; C*H*Me), 3.14 (septet, $^3J(H,H) = 6.9$ Hz, 1H; C*H*Me$_2$), 2.73 (s, 3H; C(1)Me), 2.06 (s, 3H; =CMe), 1.43 (d, $^3J(H,H) = 6.9$ Hz, 6H; CH*Me*$_2$), 1.27 ppm (d, $^3J(H,H) = 6.1$ Hz, 3H; CH*Me*); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25°C): $\delta = 143.2$, 141.9, 140.2, 136.9, 136.7, 136.5, 134.6, 133.3, 127.7, 125.3, 123.8, 113.7, 66.4, 38.3, 24.6, 21.0, 16.5, 12.7 ppm; IR (neat): $\tilde{\nu} = 3552$, 3066, 2961, 2934, 2869, 1705, 1552, 1527, 1457, 1384, 1023, 910, 734 cm^{-1}; MS (70 eV, EI): *m/z* (%): 223 (50) [$M^+ - H_3CCH(OH)$], 253 (30) [$M^+ - CH_3$], 268 (100) [M^+]; MS (70 eV, CI, NH_3): *m/z* (%): 268 (11) [M^+], 269 (100) [$M+H^+$]; HRMS: *m/z*: calcd for $C_{19}H_{24}O$ [M^+]: 268.1827; found: 268.1812.

Synthesis of 9 and 10: LDA (27.5 mL of a 2.0 M solution) was added to a solution of guaiazulene (5.0 g, 25.0 mmol) and crushed, activated 4 Å molecular sieves (0.1 g) in dry THF (150 mL) under N_2 at 0°C, and the mixture was stirred at 0°C for 30 min. Following the addition of 1-chloropinacolone (3.3 mL, 25.0 mmol) at 0°C, the mixture was allowed to warm to 25°C over a period of 3 h, and then quenched by the addition of a solution of brine at 0°C. Diethyl ether was added, and the organic layer was extracted with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a blue oil which was separated by flash chromatography.

Data for 9: Purification by flash chromatography (8:2 pentane/diethyl ether; $R_f = 0.84$) yielded a blue oil (7.14 g, 21.5 mmol, 86%). ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = 8.32$ (s, 1H; C(8)H), 7.78 (d, $^3J(H,H) = 3.3$ Hz, 1H; C(2)H), 7.51 (d, $^3J(H,H) = 10.7$ Hz, 1H; C(6)H), 7.34 (d, $^3J(H,H) = 3.3$ Hz, 1H; C(3)H), 7.08 (d, $^3J(H,H) = 10.7$ Hz, 1H; C(5)H), 3.88 (d, $^2J(H,H) = 14.0$ Hz, 1H; CH_2), 3.51 (d, $^2J(H,H) = 14.0$ Hz, 1H; CH_2), 2.81 (s, 3H; C(1)Me), 2.64 (d, $^2J(H,H) = 3.8$ Hz, 1H; CH_2Cl), 1.99 (d, $^2J(H,H) = 3.8$ Hz, 1H; CH_2Cl), 1.51 (d, $^3J(H,H) = 6.8$ Hz, 6H; CH*Me*$_2$), 1.28 ppm (s, 9H; CMe_3); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25°C): $\delta = 142.7$, 140.0, 138.8, 136.6, 136.0, 134.3, 133.0, 126.4, 124.8, 112.3, 63.7, 47.9, 38.1, 36.8, 34.3, 26.1, 24.6 12.8 ppm; IR (neat): $\tilde{\nu} = 3481$, 3062, 2960, 2872, 1699, 1556, 1464, 1388, 1366, 912, 732 cm^{-1}; MS (70 eV, EI): *m/z* (%): 83 (100) [CH_2=$CC(CH_3)_3^+$], 197 (35) [$M^+ - (CH_3)_3CC(OH)CH_2Cl$], 296 (63) [$M^+$–HCl]; HRMS: *m/z*: calcd for $C_{21}H_{29}OCl$ [M^+]: 332.1907; found: 332.1892.

Data for 10: Purification by flash chromatography (8:2 pentane/diethyl ether; $R_f = 0.50$) yielded a blue oil (0.81 g, 2.8 mmol, 11%). ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = 8.23$ (s, 1H; C(8)H), 7.64 (d, $^3J(H,H) = 3.3$ Hz, 1H; C(2)H), 7.47 (d, $^3J(H,H) = 10.6$ Hz, 1H; C(6)H), 7.09 (d, $^3J(H,H) = 3.3$ Hz, 1H; C(3)H), 7.03 (s, 1H; =CH), 6.98 (d, $^3J(H,H) = 10.6$ Hz, 1H; C(5)H), 4.08 (d, $^3J(H,H) = 5.6$ Hz, 2H; CH_2OH), 3.11 (septet, $^3J(H,H) = 6.8$ Hz, 1H; C*H*Me$_2$), 2.68 (s, 3H; C(1)Me), 1.39 (d, $^3J(H,H) = 6.8$ Hz, 6H; CH*Me*$_2$), 1.33 ppm (s, 9H; CMe_3); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25°C): $\delta = 150.4$, 144.4, 140.5, 137.2, 136.9, 136.6, 134.9, 133.5, 128.2, 125.7, 123.5, 113.3, 59.7, 38.4, 35.9, 29.8, 24.7, 12.8 ppm; IR (neat): $\tilde{\nu} = 3436$, 2962, 2872, 1704, 1464, 1387, 1365, 1217, 1013, 757 cm^{-1}; MS (70 eV, EI): *m/z* (%): 197 (100) [$M^+ - (CH_3)_3CCCH_2OH$], 296 (37) [M^+]; MS (70 eV, CI, NH_3): *m/z* (%): 197 (98) [$M^+ - (CH_3)_3CCCH_2OH$], 296 (55) [M^+], 297 (100) [M^++H]; HRMS: *m/z*: calcd for $C_{21}H_{28}O$ [M^+]: 296.2140; found: 296.2146.

Synthesis of 11a, and 11b: $AlCl_3$ (1.75 g, 13.1 mmol) was added to a solution of **7a**,**7b** (2.0 g, 6.5 mmol) in CH_2Cl_2 (65 mL) under N_2 at 0°C. When the starting material had been consumed (approximately 4 h), as judged by using TLC, the mixture was quenched by the addition of a saturated aqueous solution of $NaHCO_3$ at 0°C. The organic layer was extracted with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield a brown oil which was separated by flash chromatography.

Data for 11a: Purification by flash chromatography (8:2 pentane/diethyl ether; $R_f = 0.25$) yielded a blue oil (1.19 g, 4.4 mmol, 68%). ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = 8.09$ (d, $^4J(H,H) = 1.9$ Hz, 1H; C(9)H), 7.53 (s, 1H; C(2)H), 7.37 (dd, $^4J(H,H) = 1.9$ Hz, $^3J(H,H) = 10.5$ Hz, 1H; C(7)H), 6.76 (d, $^3J(H,H) = 10.5$ Hz, 1H; C(6)H), 3.21 (q, $^3J(H,H) = 6.9$ Hz, 1H; C*H*Me), 3.24 (d, $^2J(H,H) = 16.5$ Hz, 1H; CH_2), 3.13 (d, $^2J(H,H) = 16.5$ Hz, 1H; CH_2), 3.05 (septet, $^3J(H,H) = 6.9$ Hz, 1H; C*H*Me$_2$), 2.66 (s, 3H; C(1)Me), 1.47 (d, $^3J(H,H) = 6.9$ Hz, 6 H: CH*Me*$_2$), 1.46 (s, 3H; C(4)Me), 1.36 ppm (d, $^3J(H,H) = 6.9$ Hz, 3H; CH*Me*); ^{13}C NMR (125 MHz, $CDCl_3$, 25°C): $\delta = 143.3$, 139.2, 135.8, 134.6, 134.3, 133.4, 132.4, 128.2, 124.9, 122.9, 71.3, 48.3, 40.6, 38.6, 26.2, 24.8, 13.7, 12.7 ppm; IR (neat): $\tilde{\nu} = 3428$, 3019, 2966, 2931, 2873, 1707, 1615, 1453, 1380, 1217, 1067, 926, 771 cm^{-1}; MS (70 eV, EI): *m/z* (%): 268 (100) [M^+], 253 (85) [$M^+ - CH_3$]; HRMS: *m/z*: calcd for $C_{19}H_{24}O$ [M^+]: 268.1827; found: 268.1775.

Data for 11b: Purification by flash chromatography (8:2 pentane/diethyl ether; $R_f = 0.15$) yielded a blue oil (0.15 g, 0.5 mmol, 8%). ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = 8.18$ (s, 1H; C(9)H), 7.57 (s, 1H; C(2)H), 7.44 (d, $^3J(H,H) = 10.4$ Hz, 1H; C(7)H), 6.83 (d, $^3J(H,H) = 10.4$ Hz, 1H; C(6)H), 3.30–3.09 (m, 4H; C*H*Me, CH_2 and C*H*Me$_2$), 2.75 (s, 3H; C(1)Me), 1.44 (d, $^3J(H,H) = 6.9$ Hz, 6H; CH*Me*$_2$), 1.38 (d, $^3J(H,H) = 7.4$ Hz, 3H; CH*Me*), 1.36 ppm (s, 3H; C(4)Me); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25°C): $\delta = 143.3$, 138.8, 135.3, 134.5, 133.9, 133.0, 131.4, 129.0, 124.6, 122.4, 72.8, 45.9, 42.1, 38.4, 24.6, 23.6, 18.1, 12.5 ppm; IR (neat): $\tilde{\nu} = 3409$, 2965, 2931, 2875, 1711, 1631, 1570, 1448, 1379, 1109, 756 cm^{-1}; MS (70 eV, CI, NH_3): *m/z* (%): 269 (100) [$M+H^+$]; HRMS: *m/z*: calcd for $C_{19}H_{24}O$ [M^+]: 268.1827; found: 268.1818.

Synthesis of 14: $AlCl_3$ (0.80 g, 6.0 mmol) was added to a solution of **9** (2.0 g, 6.0 mmol) in CH_2Cl_2 (60 mL) under N_2 at 0°C. When the starting material had been consumed (approximately 1 hour), as judged by using TLC, the mixture was quenched by the addition of a saturated aqueous solution of $NaHCO_3$ at 0°C. The organic layer was extracted with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a brown oil. Purification by flash chromatography (8:2 pentane/diethyl ether; $R_f = 0.42$) yielded a blue oil (1.44 g, 4.8 mmol, 81%). ^{1}H NMR (500 MHz, $CDCl_3$, 25°C): $\delta = 7.97$ (s, 1H; C(9)H), 7.37 (d, $^3J(H,H) = 10.3$ Hz, 1H; C(7)H), 7.34 (s, 1H; C(2)H), 6.89 (d, $^3J(H,H) = 10.3$ Hz, 1H; C(6)H), 4.04 (d, $^2J(H,H) = 10.5$ Hz, 1H; C(3)H_2), 3.79 (d, $^2J(H,H) = 10.5$ Hz, 1H; C(3)H_2), 3.69 (d, $^2J(H,H) = 17.9$ Hz, 1H; C(5)H_2), 3.59 (d, $^2J(H,H) = 17.9$ Hz, 1H; C(5)H_2), 3.03 (septet, $^3J(H,H) = 6.8$ Hz, 1H; C*H*Me$_2$), 2.68 (s, 3H; C(1)Me), 1.38 (d, $^3J(H,H) = 6.8$ Hz, 6H; CH*Me*$_2$), 1.0 ppm (s, 9H; CMe_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25°C): $\delta = 153.6$, 149.5, 138.7, 137.4, 133.3, 129.7, 127.4, 127.0, 118.4, 66.8, 58.9, 46.0, 39.5, 35.8, 26.6, 24.9, 12.9 ppm; IR (neat): $\tilde{\nu} = 3421$, 2962, 2873, 1618, 1464, 1365, 1217, 1060, 1029, 756 cm^{-1}; MS (70 eV, EI): *m/z* (%): 197 (52) [$M^+ - CH_2$=$C(OH)C(CH_3)_2$=CH_2], 296 (100) [M^+]; HRMS: *m/z*: calcd for $C_{21}H_{28}O$ [M^+]: 296.2140; found: 296.2109.

Synthesis of 12a: $POCl_3$ (0.08 mL, 0.8 mmol) was added to a solution of **11a** (0.2 g, 0.7 mmol) in dry pyridine (7 mL) at 0°C. The mixture was stirred at 0°C until complete consumption of the starting material (approximately 30 min). H_2O and diethyl ether were added and the organic layer was extracted with H_2O, a dilute solution of HCl, brine, and then dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography (8:2 pentane/diethyl ether; $R_f = 0.93$) yielded a blue oil (0.19 g, 0.66 mmol, 94%). ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = 8.09$ (s, 1H; C(9)H), 7.50 (s, 1H; C(2)H), 7.38 (d, $^3J(H,H) = 10.5$ Hz, 1H; C(7)H), 6.75 (d, $^3J(H,H) = 10.5$ Hz, 1H; C(6)H), 3.66 (d, $^2J(H,H) = 16.1$ Hz, 1H; CH_2), 3.39 (d, $^2J(H,H) = 16.1$ Hz, 1H; CH_2), 3.65 (q, $^3J(H,H) = 7.0$ Hz, 1H; C*H*Me), 3.04 (septet, $^3J(H,H) = 6.9$ Hz, 1H; C*H*Me$_2$), 2.64 (s, 3H; C(1)Me), 1.51 (d, $^3J(H,H) = 7.0$ Hz, 3H; CH*Me*), 1.47 (s, 3H; C(4)Me), 1.35 ppm (d, $^3J(H,H) = 6.9$ Hz, 6H; CH*Me*$_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25°C): $\delta = 142.8$, 139.2, 135.5, 134.1, 133.9, 133.4, 131.6, 128.3, 124.5, 121.6, 72.7, 50.2, 43.6, 38.5, 25.0, 24.7, 15.9, 12.6 ppm; IR (neat): $\tilde{\nu} = 2962$, 2933, 2869, 1573, 1460, 1448, 1377, 1074, 1062, 756 cm^{-1}; MS (70 eV, EI): *m/z* (%): 235 (100) [$M^+ - HCl - CH_3$], 271 (52) [$M^+ - CH_3$], 286 (87) [$M^+(^{35}Cl)$], 288 (29) [$M^+(^{37}Cl)$]; MS (70 eV, CI, NH_3): *m/z* (%): 286 (45) [$M^+(^{35}Cl)$], 287 (100) [$M^+(^{35}Cl)$+H], 288 (27) [$M^+(^{37}Cl)$], 289 (26) [$M^+(^{37}Cl)$+H], 251 (92) [M^+–Cl]; HRMS: *m/z*: calcd for $C_{19}H_{23}Cl$ [M^+]: 286.1488; found: 286.1471.

Synthesis of 15: The procedure as described for the preparation of **12a** was followed. Purification by flash chromatography (8:2 pentane/diethyl ether; $R_f = 0.43$) yielded a blue oil (0.20 g, 0.64 mmol, 95%). ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = 8.08$ (s, 1H; C(9)H), 7.45 (s, 1H; C(2)H), 7.36 (d, $^3J(H,H) = 10.4$ Hz, 1H; C(7)H), 6.73 (d, $^3J(H,H) = 10.4$ Hz, 1H; C(6)H), 3.53 (d, $^2J(H,H) = 8.2$ Hz, 1H; C(3)H_2), 3.51 (d, $^2J(H,H) = 16.5$ Hz, 1H; C(5)H_2), 3.49 (d, $^2J(H,H) = 8.2$ Hz, 1H; C(3)H_2), 3.35 (d, $^2J(H,H) = 16.5$ Hz, 1H; C(5)H_2), 3.03 (septet, $^3J(H,H) = 6.8$ Hz, 1H;

C*H*Me$_2$), 2.65 (s, 3H; C(1)Me), 1.35 (d, ^3J(H,H) = 6.8 Hz, 6H; CH*Me*$_2$), 1.29 ppm (s, 9H; CMe$_3$).

Synthesis of 3 and 13: POCl$_3$ (0.19 mL, 2.1 mmol) was added to a solution of **11a** (0.5 g, 1.9 mmol) in pyridine (3.5 mL) at 0 °C. The mixture was stirred at 0 °C for 30 min, followed by refluxing until the starting material had been nearly completely consumed (approximately 8 h), as judged by using TLC. The mixture was then cooled to 0 °C and quenched by the addition of H_2O and diethyl ether. The organic layer was extracted with H_2O, a dilute solution of HCl, brine, and then dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a brown oil that was separated by flash chromatography. Compounds **3** and **13** can also be obtained from **12b**, in which case warming the reaction mixture to 30 °C for approximately 1 h is sufficient for complete conversion.

Data for 3: Purification by flash chromatography (49:1 pentane/diethyl ether; R_f = 0.84) yielded an orange solid (0.28 g, 1.12 mmol, 59 %). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 6.49 (s, 1H; C(5)H), 5.94 (s, 1H; C(9)H), 5.87 (d, ^3J(H,H) = 12.4 Hz, 1H; C(6)H), 5.36 (d, ^3J(H,H) = 12.4 Hz, 1H; C(7)H), 3.10 (br s, 2H; CH$_2$), 2.20 (septet, ^3J(H,H) = 6.8 Hz, 1H; C*H*Me$_2$), 2.15 (s, 3H; C(4)Me), 2.04 (s, 3H; C(3)Me), 1.89 (s, 3H; C(1)Me), 1.05 ppm (d, ^3J(H,H) = 6.8 Hz, 6H; CH*Me*$_2$); ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C): δ = 143.7, 141.9, 141.4, 137.7, 133.2, 133.0, 131.8, 130.1, 129.3, 127.2, 126.8, 122.5, 42.0, 37.8, 21.8, 19.0, 15.3, 13.4 ppm; IR (neat): $\tilde{\nu}$ = 3013, 2964, 2923, 2860, 1687, 1642, 1594, 1452, 1381, 1213, 757 cm^{-1}; MS (70 eV, EI): *m/z* (%): 235 (100) [M^+−CH$_3$], 250 (55) [M^+]; HRMS: *m/z*: calcd for $C_{19}H_{22}$ [M^+]: 250.1721; found: 250.1691.

Data for 13: Purification by flash chromatography (49:1 pentane/diethyl ether; R_f = 0.78) yielded a yellow solid (0.04 g, 0.17 mmol, 9 %). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 6.82 (s, 1H; C(9)H), 6.50 (s, 1H; C(2)H), 6.46 (s, 1H; C(5)H), 6.19 (d, ^3J(H,H) = 12.8 Hz, 1H; C(7)H), 5.93 (d, ^3J(H,H) = 12.8 Hz, 1H; C(6)H), 2.18 (s, 3H; C(3)Me), 2.16 (s, 3H; C(4)Me), 2.13 (s, 3H; C(1)Me), 1.95 (s, 3H; =CMe$_2$), 1.89 ppm (s, 3H; =CMe$_2$); ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C): δ = 141.3, 139.7, 137.9, 136.5, 135.5, 132.4, 131.2, 131.1, 129.6, 128.1, 127.9, 127.5, 126.7, 126.2, 22.0, 21.8, 19.6, 14.8, 12.6 ppm; IR (neat): $\tilde{\nu}$ = 2965, 2923, 2859, 1446, 1261, 1092, 1021, 800 cm^{-1}; MS (70 eV, EI): *m/z* (%): 83 (100) [CH$_3$C(O)C(CH$_3$)CH$_2^+$], 233 (37) [M^+−CH$_3$], 248 (28) [M^+], 252 (23) [M^++4H], 266 (5) [M^++2H]; HRMS: *m/z*: calcd for $C_{19}H_{20}$ [M^+]: 248.1565; found: 248.1560.

Synthesis of 4 and 16: The procedure described above, but with **14** instead of **11a** was utilised. Complete conversion required approximately 3 h at 30 °C. The brown oil obtained was separated by flash chromatography.

Data for 4: Purification by flash chromatography (pentane; R_f = 0.51) yielded an orange solid (0.32 g, 1.15 mmol, 61 %). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 7.07 (s, 1H; C(3)H), 6.64 (s, 1H; C(5)H), 5.89 (s, 1H; C(9)H), 5.88 (d, ^3J(H,H) = 12.3 Hz, 1H; C(6)H), 5.36 (d, ^3J(H,H) = 12.3 Hz, 1H; C(7)H), 3.17 (broad s, 2H; CH$_2$), 2.18 (septet, ^3J(H,H) = 6.8 Hz, 1H; C*H*Me$_2$), 1.86 (s, 3H; C(1)Me), 1.25 (s, 9H; CMe$_3$), 1.04 ppm (d, ^3J(H,H) = 6.8 Hz, 6H; CH*Me*$_2$); ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C): δ = 148.2, 144.2, 143.0, 141.3, 137.3, 133.7, 132.4, 131.2, 128.0, 125.3, 122.8, 122.1, 42.7, 37.7, 34.1, 31.2, 21.7, 13.3 ppm; IR (neat): $\tilde{\nu}$ = 3031, 2960, 2901, 2867, 1605, 1463, 1359, 1217, 754 cm^{-1}; MS (70 eV, EI): *m/z* (%): 235 (100) [M^+−CH(CH$_3$)$_2$], 278 (4) [M^+], 280 (15) [M^++2H]; HRMS: *m/z*: calcd for $C_{21}H_{26}$ [M^+]: 278.2035; found: 278.2018.

Data for 16: Purification by flash chromatography (pentane; R_f = 0.38) yielded a yellow solid (0.12 g, 0.44 mmol, 23 %). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 6.81 (d, ^4J(H,H) = 1.9 Hz, 1H; C(9)H), 6.91 (d, ^4J(H,H) = 1.4 Hz, 1H; C(3)H), 6.64 (d, ^4J(H,H) = 1.4 Hz, 1H; C(5)H), 6.37 (broad s, 1H; C(2)H), 6.22 (dd, ^4J(H,H) = 1.9 Hz, ^3J(H,H) = 12.7 Hz, 1H; C(7)H), 5.97 (d, ^3J(H,H) = 12.7 Hz, 1H; C(6)H), 2.10 (d, ^4J(H,H) = 1.4 Hz, 3H; C(1)Me), 1.93 (s, 3H; =CMe$_2$), 1.88 (s, 3H; =CMe$_2$), 1.27 ppm (s, 9H; CMe$_3$); ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C): δ = 151.6, 142.3, 139.2, 138.6, 136.1, 133.1, 132.4, 131.0, 129.5, 128.8, 128.3, 127.8, 122.3, 116.7, 34.6, 31.3, 21.9, 21.8, 12.4 ppm; IR (neat): $\tilde{\nu}$ = 2965, 2927, 2870, 1714, 1582, 1462, 1366, 1218, 757 cm^{-1}; MS (70 eV, EI): *m/z* (%): 235 (100) [M^+−H$_3$CC=CH$_2$], 278 (6) [M^++2H]; HRMS: *m/z*: calcd for $C_{21}H_{24}$ [M^+]: 276.1878; found: 276.1869.

Synthesis of 17, 18 and 19: Three drops of concentrated HCl was added to a solution of **11a**,**11b** (1.0 g, 3.7 mmol) in CH$_3$OH (40 mL) at 25 °C, and the solution was refluxed for 6 h. After cooling to 25 °C, H_2O and diethyl ether were added and the organic layer was extracted with H_2O, dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a brown oil which was separated by flash chromatography.

Data for 17: Purification by flash chromatography (49:1 pentane/diethyl ether; R_f = 0.65) yielded an orange solid (0.14 g, 0.56 mmol, 15 %). ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 6.83 (s, 1H; C(5)H), 6.31 (s, 1H; C(9)H), 3.26 (broad s, 2H; C(2)H$_2$), 2.90 (m, 2H; C(6)H$_2$), 2.49 (m, 2H; C(7)H$_2$), 2.48 (septet, ^3J(H,H) = 6.8 Hz, 1H; C*H*Me$_2$), 2.30 (s, 3H; C(4)Me), 2.23 (s, 3H; C(3)Me), 2.16 (s, 3H; C(1)Me), 1.13 ppm (d, ^3J(H,H) = 6.8 Hz, 6H; CH*Me*$_2$); ^{13}C NMR (50.3 MHz, CDCl$_3$, 25 °C): δ = 148.9, 141.4, 140.2, 138.4, 135.6, 133.0, 131.6, 128.5, 128.3, 116.3, 42.1, 38.5, 33.5, 30.6, 21.1, 19.3, 15.1, 14.2 ppm; IR (neat): $\tilde{\nu}$ = 3007, 2959, 2928, 2866, 1719, 1447, 1383, 1157, 865, 755 cm^{-1}; MS (70 eV, EI): *m/z* (%): 209 (48) [M^+−CH(CH$_3$)$_2$], 237 (41) [M^+ - CH$_3$], 252 (100) [M^+]; MS (70 eV, CI, NH$_3$): *m/z* (%): 252 (55) [M^+]; 253 (100) [M+H$^+$], 254 (15) [M^++2H]; HRMS: *m/z*: calcd for $C_{19}H_{24}$ [M^+]: 252.1878; found: 252.1858.

Data for 18: Purification by flash chromatography (49:1 pentane/diethyl ether; R_f = 0.42) yielded an orange solid (0.07 g, 0.14 mmol, 4 %). ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 6.54 (s, 1H; CH), 6.39 (s, 1H; CH), 6.07 (s, 1H; CH), 6.04 (d, ^3J(H,H) = 12.3 Hz, 1H; CH), 5.93 (d, ^3J(H,H) = 12.3 Hz, 1H; CH), 5.87 (s, 1H; CH), 5.78 (d, ^3J(H,H) = 12.3 Hz, 1H; CH), 5.39 (d, ^3J(H,H) = 12.3 Hz, 1H; CH), 3.20 (septet, ^3J(H,H) = 6.9 Hz, 1H; C*H*Me$_2$), 3.11 (septet, ^3J(H,H) = 6.7 Hz, 1H; C*H*Me$_2$), 2.22 (d, ^3J(H,H) = 6.9 Hz, 6H; CH*Me*$_2$), 2.18 (s, 3H; Me), 2.17 (s, 3H; Me), 1.96 (s, 3H; Me), 1.77 (s, 3H; Me), 1.68 (s, 3H; Me), 1.58 (s, 3H; Me), 1.06 ppm (d, ^3J(H,H) = 6.7 Hz, 6H; CH*Me*$_2$); ^{13}C NMR (50.3 MHz, CDCl$_3$, 25 °C): δ = 147.2, 146.0, 144.0, 142.4, 140.2, 139.9, 136.9, 136.5, 133.5, 133.3, 132.9, 132.1, 132.0, 131.5, 130.1, 129.8, 129.6, 129.5, 129.4, 129.1, 127.2, 126.6, 122.7, 121.8, 30.5, 29.8, 22.0, 21.9, 21.7, 20.9, 19.6, 17.6, 15.6, 14.7 ppm; MS (70 eV, CI, NH$_3$): *m/z*: (%): 249 (34) [M^+−C$_{19}$H$_{21}$], 253 (100) [M^++4H−C$_{19}$H$_{21}$].

Data for 19: Purification by flash chromatography (19:1 pentane/diethyl ether; R_f = 0.36) yielded a blue oil (0.29 g, 1.04 mmol, 28 %). ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 8.05 (s, 1H; C(9)H), 7.48 (s, 1H; C(2)H), 7.33 (d, ^3J(H,H) = 10.5 Hz, 1H; C(7)H), 6.74 (d, ^3J(H,H) = 10.5 Hz, 1H; C(6)H), 3.40 (q, ^3J(H,H) = 6.3 Hz, 1H; C*H*Me), 3.32 (s, 3H; OMe), 3.27 (d, ^2J(H,H) = 15.7 Hz, 1H; CH$_2$), 3.06 (d, ^2J(H,H) = 15.7 Hz, 1H; CH$_2$), 3.02 (septet, ^3J(H,H) = 6.3 Hz, 1H; C*H*Me$_2$), 2.65 (s, 3H; C(1)Me), 1.35 (d, ^3J(H,H) = 6.3 Hz, 3H; C(3)Me), 1.34 (d, ^3J(H,H) = 6.3 Hz, 6H; CH*Me*$_2$), 1.12 ppm (s, 3H; C(4)Me); ^{13}C NMR (50.3 MHz, CDCl$_3$, 25 °C): δ = 143.9, 143.9, 138.5, 135.3, 133.7, 133.1, 131.8, 130.0, 124.3, 121.9, 77.2, 49.3, 42.8, 38.5, 38.2, 24.7, 18.8, 15.5, 12.6 ppm; MS (70 eV, EI): *m/z* (%): 235 (100) [M^+−CH$_3$OH−CH$_3$], 267 (42) [M^+−CH$_3$], 282 (48) [M^+]; MS (70 eV, CI, NH$_3$): *m/z* (%): 283 (100) [M^++H].

Synthesis of 24: TCNE (0.05 g, 0.39 mmol) was added to a solution of **4** (0.10 g, 0.36 mmol) in THF (1.5 mL) at 0 °C. After stirring at 25 °C for 4 h, the solvent was evaporated and the brown residue was purified by flash chromatography (8:2 pentane/diethyl ether; R_f = 0.40), yielding a yellow solid (0.14 g, 0.35 mmol, 96 %). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 7.46 (s, 1H; C(5)H), 7.17 (s, 1H; C(3)H), 6.37 (d, ^3J(H,H) = 7.7 Hz, 1H; C(7)H), 4.31 (s, 1H; C(9)H), 4.21 (d, ^3J(H,H) = 7.7 Hz, 1H; C(6)H), 3.52 (d, ^2J(H,H) = 22.7 Hz, 1H; CH$_2$), 3.38 (d, ^2J(H,H) = 22.7 Hz, 1H; CH$_2$), 2.58 (septet, ^3J(H,H) = 6.8 Hz, 1H; C*H*Me$_2$), 2.24 (s, 3H; C(1)Me), 1.36 (s, 9H; CMe$_3$), 1.16 ppm (d, ^3J(H,H) = 6.8 Hz, 6H; CH*Me*$_2$); ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C): δ = 149.6, 145.9, 144.5, 142.4, 138.2, 127.2, 125.8, 123.2, 122.3, 122.3, 112.9, 112.9, 111.0, 111.0, 49.3, 47.5, 46.6, 46.2, 43.2, 35.0, 34.5, 31.7, 20.7, 20.5, 14.0 ppm; IR (neat): $\tilde{\nu}$ = 3030, 2965, 2872, 2252, 1626, 1478, 1464, 1263, 1217, 1097, 1012, 758 cm^{-1}; MS (70 eV, EI): *m/z* (%): 278 (100) [M^+−C$_2$(CN)$_4$], 406 (10) [M^+]; MS (70 eV, CI, NH$_3$): *m/z* (%): 278 (100) [M^+−C$_2$(CN)$_4$], 406 (15) [M^+], 424 (53) [M^++NH$_4$]; HRMS: *m/z*: calcd for $C_{27}H_{26}N_4$ [M^+]: 406.2157; found: 406.2162.

Synthesis of 25: TCNE (0.05 g, 0.39 mmol) was added to a solution of **16** (0.10 g, 0.36 mmol) in THF (1.5 mL) at 0 °C. After stirring at 25 °C for 4 h, the solvent was evaporated and the brown residue was purified by flash chromatography (8:2 pentane/diethyl ether; R_f = 0.38), yielding a yellow solid (0.13 g, 0.32 mmol, 89 %). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 7.23 (s, 1H; C(5)H), 7.19 (s, 1H; C(3)H), 6.61 (s, 1H; C(2)H), 6.40 (s, 1H; C(9)H), 3.43 (d, ^3J(H,H) = 3.7 Hz, 1H; C(7)H), 2.16 (s, 3H;

C(1)Me), 1.97 (s, 3H; =CMe), 1.66 (d, ^3J(H,H) = 3.7 Hz, 1H; C(6)H), 1.55 (s, 3H; =CMe), 1.35 ppm (s, 9H; CMe_3); IR (neat): $\tilde{\nu}$ = 3028, 2965, 2923, 2872, 2216, 1716, 1604, 1464, 1064, 758 cm^{-1}.

Synthesis of 28: LDA (0.2 mL of a 2.0 M solution) was added to a solution of **4** (0.10 g, 0.36 mmol) in THF (3.5 mL) at −78 °C under N_2. Stirring was continued at −78 °C for 20 min, followed by addition of a solution of $C_5H_5Fe(CO)_2I$ (0.12 g, 0.39 mmol) in THF (3.5 mL) by cannula. After stirring at −78 °C for 1 h, the mixture was allowed to warm to 25 °C and allowed to stir for an additional hour. The mixture was then quenched by the addition of H_2O and diethyl ether at 0 °C, and the organic layer was extracted with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The black oil was purified by flash chromatography (19:1 pentane/diethyl ether; R_f = 0.82), yielding an orange solid (0.16 g, 0.30 mmol, 84 %). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.78 (s, 1H; C(3)H), 6.45 (s, 1H; C(5)H), 6.08 (s, 1H; C(9)H), 5.78 (d, ^3J(H,H) = 12.3 Hz, 1H; C(6)H), 5.33 (d, ^3J(H,H) = 12.3 Hz, 1H; C(7)H), 3.56 (s, 1H; C(2)H), 2.25 (septet, ^3J(H,H) = 6.8 Hz, 1H; C*H*Me_2), 2.06 (s, 3H; C(1)Me), 1.19 (s, 9H; CMe_3), 1.07 ppm (d, ^3J(H,H) = 6.8 Hz, 6H; CH*Me*$_2$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 147.7, 142.9, 142.6, 142.2, 139.3, 134.1, 131.6, 130.3, 127.0, 125.7, 125.4, 122.3, 121.9, 52.1, 38.0, 34.0, 31.2, 21.8, 21.7, 12.0 ppm; IR (neat): $\tilde{\nu}$ = 3021, 2960, 2869, 1637, 1599, 1464, 1363, 1217, 1028, 878, 758 cm^{-1}; MS (70 eV, EI): *m/z*: (%): 276 (100) [$M^+ - C_{21}H_{26}$], 277 (56) [$M^+ - C_{21}H_{25}$]; HRMS: *m/z*: calcd for $C_{42}H_{50}$ [M^+]: 554.3913; found: 554.3908.

Synthesis of 29: A solution of freshly prepared [$Cr(CH_3CN)_3(CO)_3$] in THF (3.5 mL) was added, using a cannula, to a solution of **4** (0.10 g, 0.36 mmol) in THF (3.5 mL) at 25 °C under N_2. The mixture was then refluxed for 8 h. After cooling, the solvent was evaporated and the brown residue was purified by flash chromatography (9:1 pentane/diethyl ether; R_f = 0.65), yielding a red-orange solid (0.13 g, 0.31 mmol, 87 %). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.01 (s, 1H; C(9)H), 5.81 (s, 1H; C(3)H), 5.67 (d, ^3J(H,H) = 12.3 Hz, 1H; C(7)H), 5.60 (d, ^3J(H,H) = 12.3 Hz, 1H; C(6)H), 5.11 (s, 1H; C(5)H), 3.42 (broad s, 2H; CH_2), 2.29 (septet, ^3J(H,H) = 6.8 Hz, 1H; C*H*Me_2), 1.94 (s, 3H; C(1)Me), 1.28 (s, 9H; CMe_3), 1.07 ppm (d, ^3J(H,H) = 6.8 Hz, 6H; CH*Me*$_2$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 234.2, 141.0, 138.9, 134.0, 129.4, 129.2, 120.7, 120.3, 116.7, 109.2, 98.0, 92.5, 89.4, 42.9, 38.0, 33.8, 31.2, 21.9, 21.8, 13.9 ppm; IR (neat): $\tilde{\nu}$ = 3026, 2965, 2911, 2873, 1951, 1881, 1465, 1395, 1368, 1097, 1017, 909, 735 cm^{-1}; MS (70 eV, EI): *m/z* (%): 278 (44) [$M^+ - Cr(CO)_3$], 279 (100) [$M^+ + H - Cr(CO)_3$], 330 (21) [$M^+ - 3(CO)$], 414 (4) [M^+]; HRMS: *m/z*: calcd for $C_{24}H_{26}O_3Cr$ [M^+]: 414.1287; found: 414.1234; elemental analysis calcd (%) for $C_{24}H_{26}O_3Cr$: C 69.55, H 6.32, Cr 12.55; found: C 69.83, H 6.27, Cr 12.97.

X-ray measurement for 29: X-ray crystallographic data for **29** were collected on a suitable sample mounted with grease on the end of a thin glass fiber. Data were collected on a D8 Bruker diffractometer equipped with a Bruker SMART APEX CCD area detector (employing the program SMART[19]) and an X-ray tube utilizing graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Data processing was carried out by the use of the program SAINT,[20] while the program SADABS[21] was utilised for the scaling of diffraction data and an empirical absorption correction based on redundant reflections. The structure was solved by using the direct-methods procedure in the Bruker SHELXTL[22] program library and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were added as fixed contributors at calculated positions with isotropic thermal parameters based on the carbon atom to which they are attached.

Crystal data for 29: $C_{24}H_{26}O_3Cr$, M_r = 414.45, monoclinic, space group $P2_1/n$, a = 9.560(9), b = 18.78(1), c = 12.07(1) Å, β = 97.30(2)°, V = 2150(3) Å^3, Z = 4, ρ_{calcd} = 1.280 g cm^{-3}, $F(000)$ = 872, T = 293(2) K, μ = 0.552 mm^{-1}. Data were collected over the range $2.02° < \theta < 22.5°$, index ranges $-9 \le h \le 9$; $-19 \le k \le 18$; $-7 \le l \le 2$. Of a total of 11277 reflections, 2468 were independent and 1346 observed [$F_o > 4\sigma(F)$], the largest difference peak and hole were 0.58 and −0.48 e Å^{-3}, respectively; $R1$ = 0.078, $wR2$ = 0.181.

CCDC-236711 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

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