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A New Class of Remote N-Heterocyclic Carbenes with Exceptionally Strong σ-Donor Properties: Introducing Benzo[*c*]quinolin-6-ylidene

Ulrich F. J. Mayer, Elliot Murphy, Mairi F. Haddow, Michael Green, Roger W. Alder, and Duncan F. Wass*[a]

Abstract: We make the case for benzo[*c*]quinolin-6-ylidene (**1**) as a strongly electron-donating carbene ligand. The facile synthesis of 6-trifluoromethanesulfonylbenzo[*c*]quinolizinium trifluoromethanesulfonate (**2**) gives straightforward access to a useful precursor for oxidative addition to low-valent metals, to yield the desired carbene complexes. This concept has been achieved in the case of [Mn(benzo[*c*]quinolin-6-ylidene)$(CO)_5$]$^+$ (**15**) and [Pd(benzo[*c*]quinolin-6-ylidene)$(PPh_3)_2$(L)]$^{2+}$ L = THF (**21**), OTf (**22**) or pyridine (**23**). Attempts to coordinate to nickel result in coupling products from two carbene precursor fragments. The CO IR-stretching-frequency data for the manganese compound suggests benzo[*c*]quinolin-6-ylidene is at least as strong a donor as any heteroatom-stabilised carbene ligand reported.

Keywords: N-heterocyclic carbenes · structure elucidation · transition metals

Introduction

N-Heterocyclic carbenes (NHCs) are now widely studied as examples of relatively stable free-singlet carbenes and as supporting ligands for coordination compounds, especially those with applications in catalysis. With the many variants on the NHC theme that have been developed as ligands for transition metals, it has become clear that the most stable carbenes do not necessarily make the most useful ligands in terms of catalytic applications. The strong σ-donor ability of these ligands makes them pre-eminent in many applications in which an electron-rich catalyst metal centre is important, such as metathesis, cross-coupling and carbon–carbon multiple bond cyclisation reactions.[1a,b,e,2,3] The facile access to a diverse range of structurally different NHCs allows easy fine-tuning of steric and electronic parameters, an attractive feature for such applications.[4]

The stability of such NHC fragments arises both from the steric demand of the substituents on the nitrogen atoms of the heterocyclic ring, which helps to prevent the carbene from dimerising[5–7] and, perhaps more importantly, electronic factors such as the beneficial overlap of the lone pair on the nitrogen atoms with the empty p orbital of the carbene-carbon centre.[1] However, the electronic stabilisation is neither confined to nitrogen atoms nor to their α-position relative to the carbene-carbon atom. Stabilising nitrogen atoms can be replaced with structural elements of appropriate orbital situation and electron density. For example, in amino(ylidene)carbenes (AYCs) stabilisation is induced through a dipolar π system.[8] So-called "remote NHCs" (rNHC) incorporate an enamine π system into a cyclic arrangement to provide the necessary aromatic stabilisation.[9a,10] This stabilising effect of the enamine is not confined to a cyclic arrangement, as demonstrated most recently by Fürstner, who reported remarkably strong electron-donating carbenes stabilised by lateral enamines.[11] Their strong electron-donating properties in connection with the protective encumbrance from the sterically demanding N,N′-substituents result in favorably strong metal–carbene bonds.[12,13] Structures based on "abnormal" carbenes or mesoionic carbenes have also attracted recent attention.[14]

The many synthetic procedures for the generation of NHC–metal complexes often rely on simple ligand exchange and therefore the ability of the carbene ligand to exist in a free or, at least, metastable state in order to react with the transition-metal fragment. By contrast, the isolation of rNHCs in their free form has not yet been achieved, but nickel, palladium and platinum complexes of pyridinylidene, quinolinylidene, isoquinolinylidene and acrylidenylidene by oxidative addition of low-valent transition-metal fragments into the carbon–halogen bond of suitable precursors have been reported.[9b,c,15,16] Some palladium(II) complexes of the type [Pd(carbene)$(PPh_3)_2$(X)][A] (X = Cl or Br; A = BF_4, CF_3SO_3) have been reported to perform as highly efficient catalysts in Heck and Suzuki type C–C coupling reactions,[9c] whereas some nickel(II) complexes of the type [Ni(carbene)$(PPh_3)_2$(Cl)][BF_4] have been reported to exhibit high efficiency in Kumada–Corriu type cross-coupling reactions.[16]

[a] Dr. U. F. J. Mayer, E. Murphy, Dr. M. F. Haddow, Prof. M. Green, Prof. R. W. Alder, Prof. D. F. Wass
School of Chemistry, University of Bristol
Cantock's Close, Bristol, BS8 1TS (UK)
E-mail: Duncan.Wass@bristol.ac.uk

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Manganese pentacarbonyl complexes of an isoquinolin-4-ylidene precursor have also been obtained from the oxidative addition of the corresponding chloride precursors to $Na[Mn(CO)_5]$ in THF.[15] Transmetallation of carbenes first generated by oxidative addition to a late-transition metal is a complementary synthetic approach to deliver transition-metal complexes of rNHCs. For example, the chromium(0)-pentacarbonyl complex of simple rNHC ligand 1-methylpyridine-4(1*H*)-ylidene can be prepared from 4-chloro-1-methylpyridinium triflate and $Na_2[Cr(CO)_5]$ and subsequently used to generate the corresponding gold(I) chloride complex.[17,18] The carbonyl stretching frequencies of such rNHC complexes were found to be significantly lower relative to those of corresponding imidazole-2-ylidene metal complexes,[19,20b] indicating a significantly larger σ_d/π_a ratio for pyridin-4-ylidenes relative to NHCs, which was corroborated by DFT calculations.[10b]

Given the great success of NHCs as ligands, it seems surprising that other carbenes, such as remotely stabilised and carbocyclic carbenes, are underdeveloped, particularly when one considers the experimental and calculated evidence for the extremely strong σ- donor properties of these systems. With this in mind, proton affinities (PAs) and $[Ni(CO)_3(L)]$ CO stretching frequencies were calculated for a selection of known and potentially new carbenes using DFT (see Table 1).[21] As expected, species with higher PAs have lower

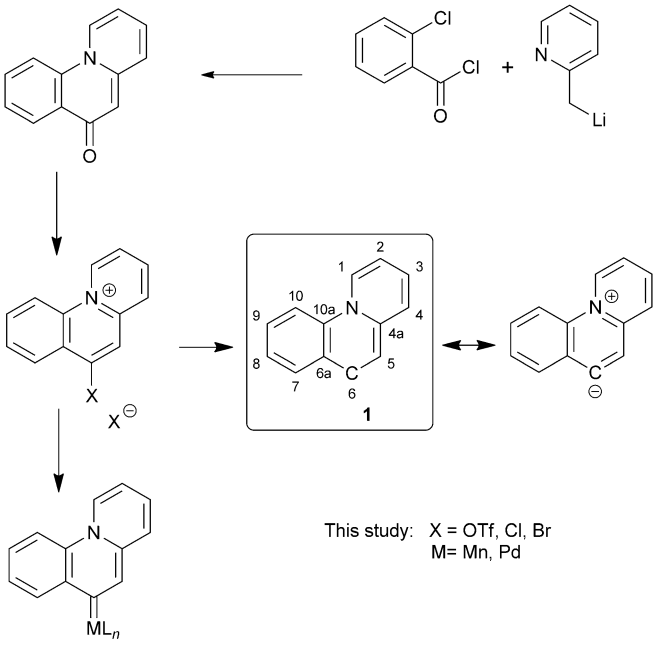
Table 1. DFT-calculated proton affinities (PAs) and $Ni(CO)_3$ C≡O stretching frequencies.

Carbene	PA [kJ mol^{-1}]	ν of $Ni(CO)_3$ [cm^{-1}]
2,3-diphenylcycloprop-2-en-1-ylidene	1104	2068, 2074, 2130
cycloheptatrienylidene	1104	2067, 2069, 2123
dimethyldihydroimidazolidene	1113	2062, 2068, 2129
dimethylimidazolidene	1113	2062, 2066, 2128
N-Me-2-pyridylcarbene	1156	2063, 2066, 2126
bis(dimethylamino)carbene	1150	2060, 2062, 2124
N-Me-4-pyridylcarbene	1225	2056, 2060, 2118
benzo[*c*]quinolin-6-ylidene (**1**)	1258	2052, 2057, 2114

CO stretching frequencies, and these results are very much in line with experimental data where these exist. Of specific interest, the calculations identified carbene **1** as an exceptionally strong electron donor. This seems a doubly attractive target, since general and modular synthetic routes can be envisaged. In particular, the two positions adjacent to the carbene carbon are differently oriented with respect to this carbene centre; substitution at these positions could lead to unique control of reactivity, which is difficult to achieve with more traditional carbene ligands. This report presents the design and synthesis of precursors to and transition-metal complexes of benzo[*c*]quinolin-6-ylidene (**1**). These complexes have allowed us to verify the exceptional donor abilities of this ligand.

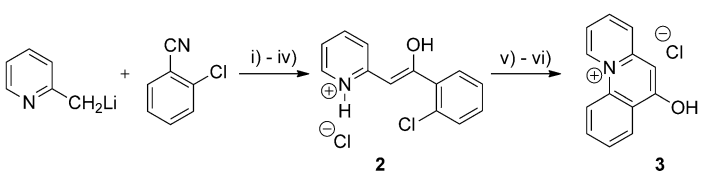
Results and Discussion

Synthesis: Our general strategy to obtain complexes of benzo[*c*]quinolin-6-ylidene was to generate dihalide or dipseudohalide precursor compounds for this carbene of the type illustrated in Scheme 1, which can be used to synthesise the



Scheme 1. Structure of benzo[*c*]quinolin-6-ylidene carbene **1**, synthetic routes, and an example complex.

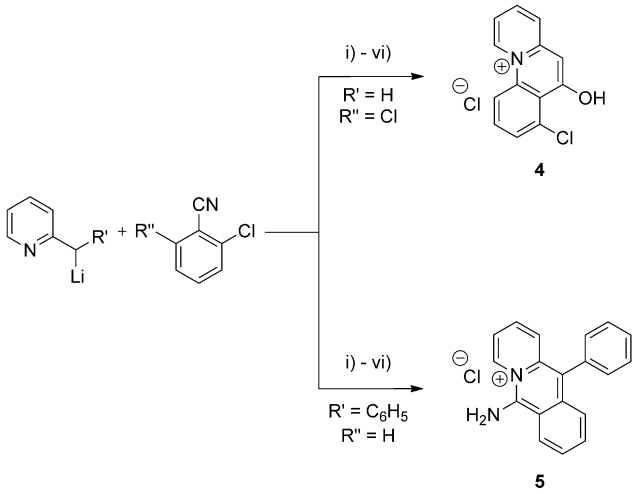
desired metal complexes in a final oxidative addition step. This bypasses the risks associated with trying to isolate "free" carbene species of an unknown type. The synthesis of a variety of 6-hydroxy-benzo[*c*]quinolizinium halide salts has been reported in the literature by the groups of Vierfond,[22,23] Ziegler[24] and Volovenko,[25,26] and the choice of the appropriate method depends on the desired substituent pattern present on the benzo[*c*]quinolizinium frame. Initially, we followed a modification of Vierfond's synthetic protocol (Scheme 2) that enabled us to obtain 2-(2-chlorophenyl)acylpyridinium chloride salt (**2**) in high yield (81%). The condensation reaction of 2-lithiopicoline and 2-chlorobenzonitrile was followed by the abstraction of HCl and a subsequent thermally induced intramolecular ring-closure, to give



Scheme 2. Synthesis of 6-hydroxybenzo[*c*]quinolizinium chloride **3**. Reaction conditions: i) THF, 16 h, −78 °C to RT. ii) H_2SO_4/H_2O (pH 2), 40 °C, 1 h. iii) K_2CO_3 (pH 8). iv) HCl/EtOH (pH 2). v) MeOH/H_2O (1:1 vol%), K_2CO_3 (pH 8). vi) Argon, neat, 180 °C.

6-hydroxybenzo[*c*]quinolizinium chloride **3** in good overall yield (65%). The structures of compounds **2** and **3**·H_2O have been determined by X-ray crystallography and are very much as expected. The structures are described in the Supporting Information.

In order to increase kinetic protection of the carbene centre, we tried to introduce steric bulk in positions 5 and 7 of the benzo[*c*]quinolizinium moiety.[27] Unfortunately, when applying the same synthetic strategy to 2-lithiopicoline/2,6-dichlorobenzonitrile and 2-lithiobenzylpyridine/2-chlorobenzonitrile, we found the synthetic protocol not to be completely transferrable. The condensation of 2-lithiopicoline and 2,6-dichlorobenzonitrile, resulted in the formation of the desired 6-hydroxy-8-chlorobenzo[*c*]quinolizinium chloride (**4**; Scheme 3). However, when 2-lithiobenzylpyridine and 2-chlorobenzonitrile were subjected to similar reaction conditions, unwanted benzo[*b*]quinolizinium chloride **5** was obtained.



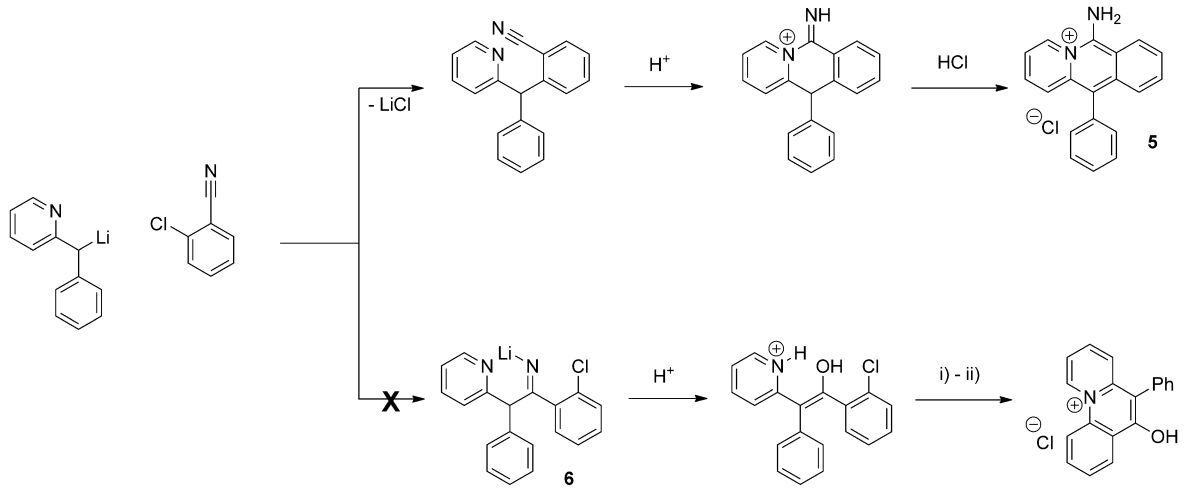
Scheme 3. Reaction products from the addition of 2-lithiopicoline onto 2,6-dichlorobenzonitrile and 2-lithiobenzylpyridine onto 2-chlorobenzonitrile. i) THF, 16 h, −78 °C to RT. ii) H_2SO_4/H_2O (pH 2), 40 °C, 1 h. iii) K_2CO_3 (pH 8). iv) HCl/EtOH (pH 2). v) MeOH/H_2O (1:1 vol%), K_2CO_3 (pH 8). vi) Argon, neat, 180 °C. .

The formation of **5** under the applied reaction conditions suggested that nucleophilic attack of 2-lithiobenzylpyridine at the chloro substituent of the benzene ring is favored almost exclusively with respect to reaction of 2-lithiobenzylpyridine with the nitrile group to form the corresponding lithio–imide **6** (see Scheme 4). The solubility of 2-lithiobenzylpyridine was observed to be poor in THF, especially at temperatures below −5 °C. It is feasible to assume that significant amounts of 2-lithiobenzylpyridine are therefore only available at temperatures above −5 °C, at which temperature formation of **5** is favoured with respect to **6** (Scheme 4). The increased steric encumbrance of this secondary lithium salt or the increased stability of the dibenzyl-type anion, may also have a role.

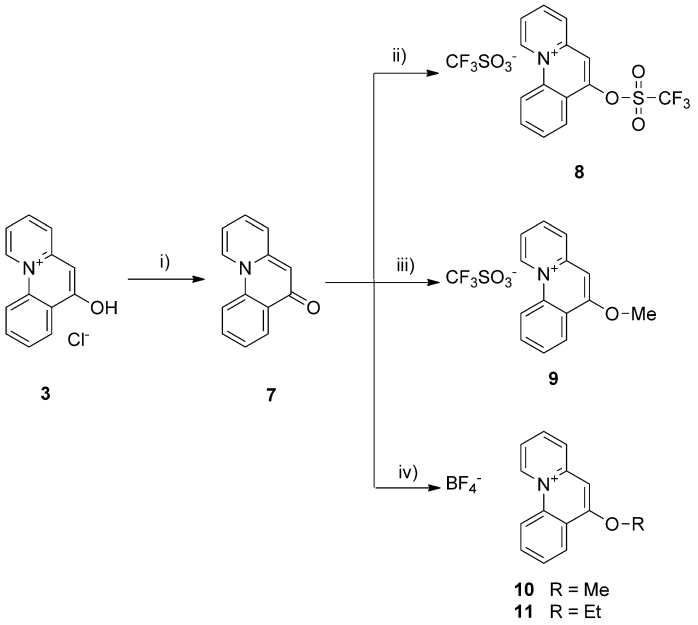
Subsequent reaction of **3** with a saturated aqueous solution of K_2CO_3 resulted in the abstraction of HCl and the formation of benzo[*c*]quinazolinone **7**, which was isolated as a yellow solid in high yields (85%) after vacuum sublimation (Scheme 5).

In order to transform the keto group in **7** into a leaving group, several different synthetic strategies were applied. Firstly, we attempted reactions with either SOX_2 or COX_2 (X = Cl, Br) to form the corresponding 6-halobenzo[*c*]quinolizinium halides. These reactions resulted in the formation of white solids in almost quantitative yields, but the analytical characterisation of the obtained reaction products was severely hampered by their virtual insolubility in all common organic solvents. Furthermore, the extremely low solubility excluded the reaction with transition-metal compounds or attempted anion-exchange reactions.

Secondly, we attempted the transformation of α,β-unsaturated ketone **7** into the corresponding 6-trifluoromethanesulfonylbenzo[*c*]quinolizinium trifluoromethanesulfonate (**8**), which was accomplished by the use of trifluoromethane-



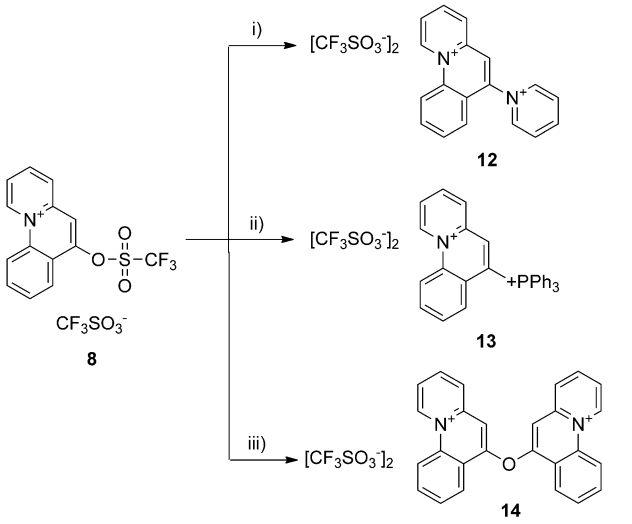
Scheme 4. Mechanistic aspects for the reaction of 2-lithiobenzylpyridine with 2-chlorobenzonitrile. i) MeOH/H_2O (1:1 vol%), K_2CO_3 (pH 8). ii) Argon, neat, 180 °C.



Scheme 5. Synthesis of **7**–**11**. Reaction conditions: i) MeOH/H_2O (1:1 vol%), K_2CO_3 (pH 8). ii) $(CF_3SO_2)_2O/CH_2Cl_2$, −78 to 20 °C, 1 h. iii) $MeOSO_2CF_3$, CH_2Cl_2, −78 to 20 °C, 1 h. iv) $[R_3O][BF_4]/CH_2Cl_2$ (R = Me for **10**, Et for **11**), −78 to 20 °C, 1 h.

sulfonyl anhydride ($(CF_3SO_2)_2O$). The potential of the trifluoromethanesulfonate a good leaving group in subsequent organometallic reactions made this particularly attractive. The conversion of α,β-unsaturated ketones into vinyl trifluoromethanesulfonates using $(CF_3SO_2)_2O$ in the presence of a scavenger base, such as 2,6-di-*tert*-butyl-4-methylpyridine, has been reported by Stang and co-workers, as have similar reactions with simple amides and vinylogous amides.[28,29] The addition of auxiliary base was unnecessary in case of **7**, since a comparable pyridine moiety is already incorporated in the parent ketone. When methyl trifluoromethansulfonate was used instead of $(CF_3SO_2)_2O$, 6-methoxybenzo[*c*]quinolizinium trifluoromethanesulfonate (**9**) was obtained in moderate yield (43%). Alkylation of the keto group in **8** can alternatively be readily accomplished by the use of Meerwein salts $[R_3O][BF_4]$ (R = Me, Et). In this way, 6-alkoxybenzo[*c*]quinolizinium tetrafluoroborates **10** and **11** were obtained from the reaction of **7** and $[R_3O][BF_4]$ (R = Me, Et) in CH_2Cl_2 in very good yields (90 and 77% respectively). The structures of compounds **5**, **7**, **8** and **11** have been determined by X-ray crystallography and are described in the supplementary information.

Solubility of 8 and reactivity towards Lewis bases: Compound **8** was obtained as a white solid after almost quantitative precipitation from CH_2Cl_2 at room temperature. Purification of **8** was achieved by washing with THF and subsequent recrystallisation from diethyl ether and acetonitrile at room temperature. Reaction or decomposition of **8** in acetonitrile at room temperature was not observed. In fact, **8** displayed remarkably high stability towards acetonitrile and even prolonged exposure of **8** in acetonitrile at elevated temperatures did not lead to decomposition. In contrast, reaction of **8** with pyridine resulted in the formation of 6-pyridiniumbenzo[*c*]quinolizinium ditrifluoromethanesulfonate (**12**). Similarly, reaction of **8** with one equivalent of PPh_3 in acetonitrile resulted in the formation of 6-triphenylphosphoniumbenzo[*c*]quinolizinium ditrifluoromethanesulfonate (**13**) and reaction of **8** with one equivalent of **7** in acetonitrile resulted in the almost quantitative formation of **14** (Scheme 6). The structures of compounds **12** and **14** were determined by X-ray crystallography and described in the Supporting Information.

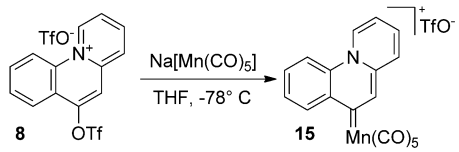


Scheme 6. Reactivity of **8** towards Lewis bases. Reaction conditions: i) C_5H_5N, 20 °C, 16 h. ii) PPh_3 in CH_3CN, 20 °C, 16 h. iii) **7** in CH_3CN, 20 °C, 16 h.

Synthesis of metal complexes by oxidative addition 6-trifluoromethanesulfonyl benzo[*c*]quinolizinium trifluoromethanesulfonate (8) to low valent metals

*Synthesis of [(benzo[c]quinolin-6-ylidene)Mn(CO)$_5$] (**15**)*: Our initial aim of this study was to verify experimentally the strong σ-donor nature of benzo[*c*]quinolin-6-ylidene suggested by our calculations. With this is mind, we targeted a metal–carbonyl complex for which corresponding data for other carbene complexes exists. The usual complexes of the type $[Ni(CO)_3(L)]$ (as in our calculations) or $[Rh(CO)_2(L)]_2$ are inaccessible by the methods we have in hand, since both rely on generating free or metastable carbenes rather than the oxidative-addition route that proved successful for the palladium complex.

However, a modification of the method of Raubenheimer,[15] for the synthesis of a manganese(I)pentacarbonyl(2-methoxy-*N*-methyl,4-dihydroquinolin-4-ylidene) triflate complex, in which $Na[Mn(CO)_5]$ is added to **8** at low (−78 °C) temperature provided a successful route to a com-



Scheme 7. Synthesis of **15**.

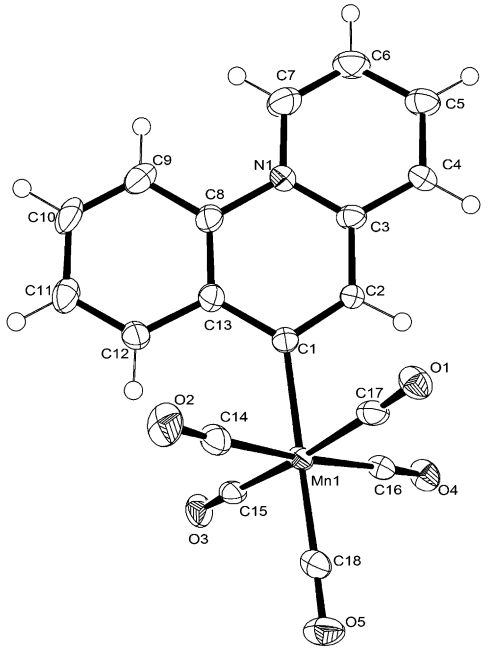


Figure 1. Molecular structure of **15** with thermal ellipsoids drawn at the 30% probability level. Counterion and solvent of crystallisation omitted for clarity. Selected bond lengths [Å] and angles [°]: Mn–C1 2.104, Mn–C18 1.845, C1–C2 1.372, C2–C3 1.423, N1–C3 1.362; C1-Mn-C18 177.58, C14-Mn-C16 175.66, C15-Mn-C17 174.97, Mn-C1-C2 117.32, Mn-C1-C13 128.08.

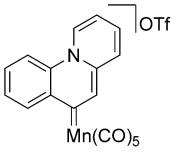
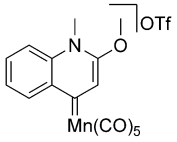
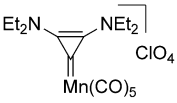
plex of the type [Mn(carbene)$(CO)_5$][OTf] (**15**) (Scheme 7). This route yielded complex **15** as single crystals suitable for X-ray crystallography (Figure 1). As with the palladium complex, (see below, Figure 3) some deviation from planarity is observed in the aromatic rings, due to the loss of aromaticity, resulting from the metal–carbene resonance contribution. Steric crowding between the benzo-fused ring and carbonyl ligands also causes slight rotation of the carbene, in the plane of the rings.

Crucially, the CO bond-stretching frequencies for **15**, when compared to analogous data for related NHC and other carbene complexes (Table 2), prove the benzo[*c*]quinolin-6-ylidene ligand to be at least as strong a donor ligand as the best reported to date.[15,30,31] These data support both the validity of our calculation methodology in this case and also augur well for the further development of these ligands for catalysis.

*Reaction of **8** with [Ni(cod)$_2$] (COD = 1,5-cyclooctadiene)*:

The reaction between **8** and an equimolar amount of [Ni(cod)$_2$] in acetonitrile resulted in the formation of **16**, the product of the reductive dimerisation of two carbene fragments from a Ni^{II} transition-metal centre, that is, [Ni(carbene)$_2$(L)$_2$] (L = MeCN) ;**17**) under formation of [Ni(L)$_n$] (n = 2–4). In order to obtain *cis/trans*-**17**, from which the reductive dimerisation could potentially proceed, a ligand exchange between two molecules of **18** must occur (Scheme 8).[32]

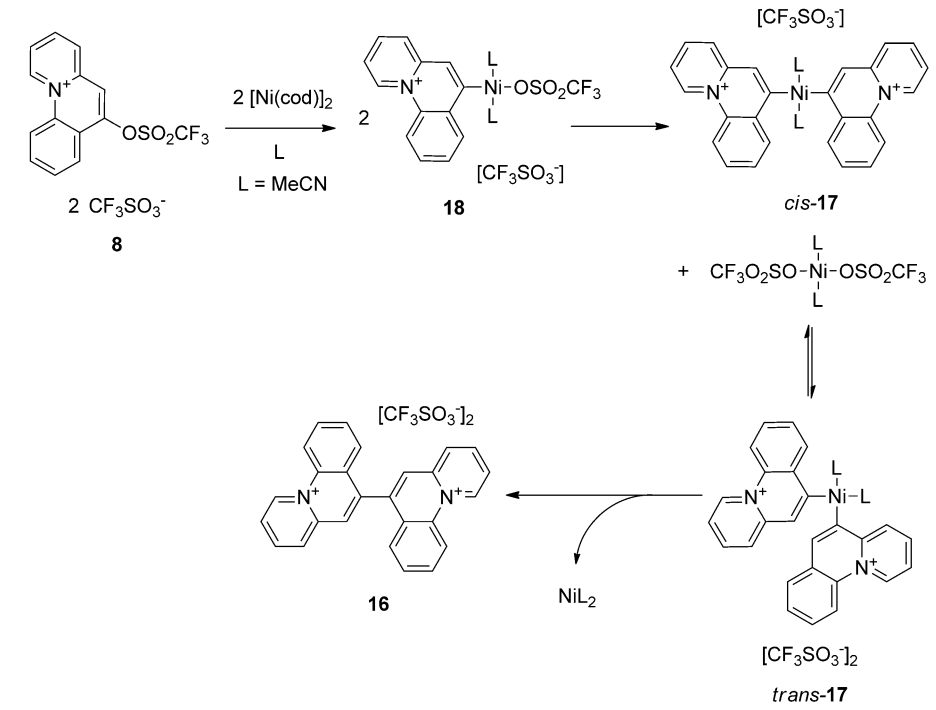
Table 2. C=Mn bond lengths and C≡O stretching frequencies of Mn–NHC complexes.

Complex	C=M Bond length [Å]	C≡O Stretching frequencies [cm^{-1}]			
		1	2	3	mean
	2.104	2128	2069	1997	2065
	no data	2129	2078	2036	2081
	2.090	2134	2049	2045	2076
	no data	2130	2075	2025	2076

Single crystals of **16** suitable for X-ray-diffraction analysis were obtained from diffusion of diethyl ether into a saturated solution of **16** in acetonitrile at ambient temperatures and the molecular structure of **16** is shown in Figure 2.

In order to further probe the transmission effects and the electrochemical reversibility of the dication/radical-cation couple in **16**/**19**, the redox behaviour of **16** was investigated by cyclic voltammetry. Figure 2 shows the cyclic voltammogram of **16** obtained from a 1.0×10^{-3} M^{-1} solution in acetonitrile with 0.1 M^{-1} in [nBu$_4$N][PF$_6$] as the supporting electrolyte. The voltammogram was obtained at room temperature with a scan rate of 50 mV s^{-1} and is referenced to the SCE at 0.00 V. Under these conditions **16** exhibited a reversible (peak–peak separation of 43 mV) reduction at −0.76 V. Interestingly, only half-wave reduction potential was observed for **16** down to reduction potentials of −2.00 V. In order to ascertain a one or two-electron transfer process, simulations for one and two-electron reduction processes were carried out and supported a one-electron reduction process.

Dication **16** could potentially accommodate two electrons, but it is reasonable to assume considerable stability for radical cation **19**, due to the delocalisation of the free radical over the extended conjugated π system. A subsequent secondary reduction of radical cation **19** to form neutral **20** would require substantially stronger reduction potentials, due to the intrinsic strain induced by the steric repulsion be-



Scheme 8. Oxidative addition of $[Ni(cod)_2]$ into the C–O bond in **8**, subsequent ligand exchange in **18** and reductive dimerisation from *trans*-**17** to give **16**.

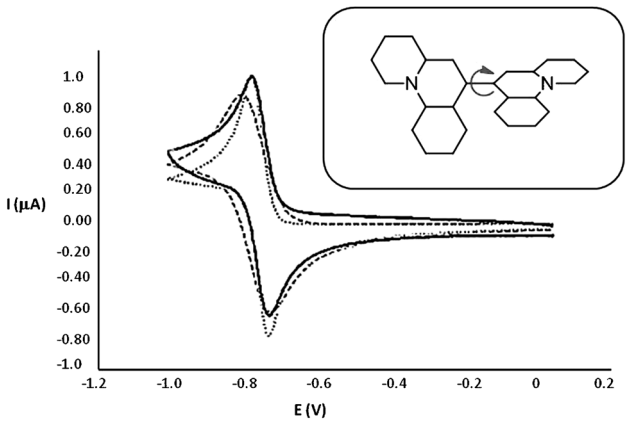


Figure 2. The cyclic voltammogram of a CH_3CN solution of **16** (solid line). Simulated electrochemical one-electron (dotted line) and two-electron reduction processes (dashed line) are shown. Inset: Molecular structure of **16** with thermal ellipsoids drawn at the 30% probability level. Two $CF_3SO_3^-$ ions have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–C1 1.379(2), N1–C5 1.374(2), N1–C13 1.426(2), C1–C2 1.358(2), C2–C3 1.403(2), C3–C4 1.367(2), C4–C5 1.406(2), C5–C6 1.420(2), C6–C7 1.349(2), C7–C8 1.438(2), C7–C7 1.491(2); C5-N1-C13-C8 −4.1(2), C6-C7-C7-C6 −79.0(2).

tween hydrogen atoms in position C6 and C9 of the benzo[*c*]quinon-6-ylidene moiety resulting from the co-planarity of the π system (see Figure 2), supporting the assumption, that only one electron is transferred at the relatively moderate reduction potential of −0.76 V to form **19** (see Scheme 9).

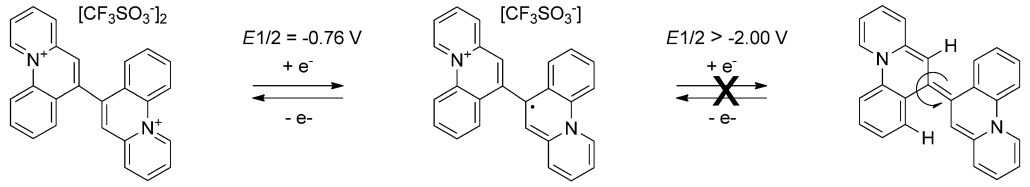
Compound **20** can be synthesised in low yields (ca. 10%) under very forceful conditions and we were able to indirectly prove its existence by coupling two molecules of **7** using low-valent titanium species and subsequently oxidising **20** with two equivalents of ferrocenium hexafluorophosphate (see Scheme 10).

*Synthesis of palladium complexes [Pd(benzo[c]quinolin-6-ylidene)(PPh$_3$)$_2$(L)]$^{2+}$ L = THF (**21**), OTf (**22**) or pyridine (**23**)*: The wide utility of palladium compounds in catalysis made such complexes attractive targets to evaluate the potential of benzo[*c*]quinoline-6-ylidene as a supporting ligand in catalysis.

Reaction of **8** with $[Pd(PPh_3)_4]$ in THF led to the formation of **21** in good yield (72%; Scheme 11). During the course of the reaction, a clear orange solution is obtained initially at ambient temperatures, followed by an almost immediate precipitation of **21**, which is indicative of a very limited solubility of **21** in THF. The structure of **21** was confirmed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and elemental analysis. The mass spectrum for **21** shows the [Pd(benzo[*c*]quinolin-6-ylidene)$(CF_3SO_3)(PPh_3)_2]^+$ fragment at $m/z = 958$. Attempted crystallisation of **21** from CH_2Cl_2/pentane mixtures at room temperature led to the almost quantitative isolation of **22**·2CH_2Cl_2. The crystals obtained were used to perform single-crystal X-ray diffraction analysis and the solid-state structure of **22**·2CH_2Cl_2 is presented in Figure 3. The carbene moiety is disordered over two positions with relative occupancies of 1:1 and allows only limited conclusions as to estimated carbene–palladium bond lengths. However, the complex connectivity for **22** can be confirmed and supports the proposed mechanism of formation (see Scheme 11).

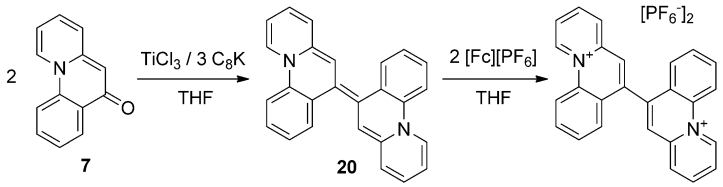
The corresponding reaction of **8** with $[Pd(PPh_3)_4]$ in pyridine generated **23** in good yield (71%). The mass spectrum for **23** showed only the [Pd(benzo[*c*]quinolin-6-ylidene)$(CF_3SO_3)(PPh_3)_2]^+$ and [Pd(benzo[*c*]quinolin-6-ylidene)$(CF_3SO_3)(PPh_3)]^+$ fragments at $m/z = 958$ and 696 respectively. Single crystals suitable for X-ray diffraction analysis were obtained from diffusion of diethyl ether into a saturated solution of **23** in acetonitrile at ambient temperature. The solid-state structure of **23** is shown in Figure 4.

It is interesting that the carbene moiety in **23** shows significant deviation from co-planarity for the three aromatic rings. The dihedral angle C3-N1-C8-C13 in **23** is 12(2)°, rela-



16 19 20

Scheme 9. Electrochemical reduction of dication **16** to generate radical cation **19** and attempted subsequent electrochemical reduction to generate neutral **20**.



7 20

Scheme 10. Reductive dimerisation of **7** to give **20** and subsequent oxidation using $[Fc][PF_6^-]$.

tive to 0.5(3) (**8**), 0.1(3) (**11**), 4.1(2) (**12**), 3.0(2) (**14**) and 4.1(2)° (**16**) in the corresponding benzo[*c*]quinolizinium compounds supporting a carbene-type bond situation with a C=C double bond in **23**.[33]

Two sharp singlets at 20.4 and 22.8 ppm in the $^{31}P\{^1H\}$ NMR spectrum for **23** and **21**, respectively, are characteristic for only one chemically and magnetically distinct phosphorous environment and are indicative of a *trans* coordination for the two molecules of PPh_3. Both compounds appear to be stable in solution with respect to *cis/trans* isomerisation and no evidence for an isomeric exchange can be observed by $^{31}P\{H\}$ NMR spectrum, for example, **23** in CD_2Cl_2 even after one week at ambient temperature. As evident from $^{31}P\{^1H\}$ and ^1H NMR analysis, compound **21** can be transformed quantitatively into **23** by dissolution in pyridine at room temperature.

Preliminary catalyst screening for a range of C<-C>C and C–N coupling reactions and studies to confirm the in-

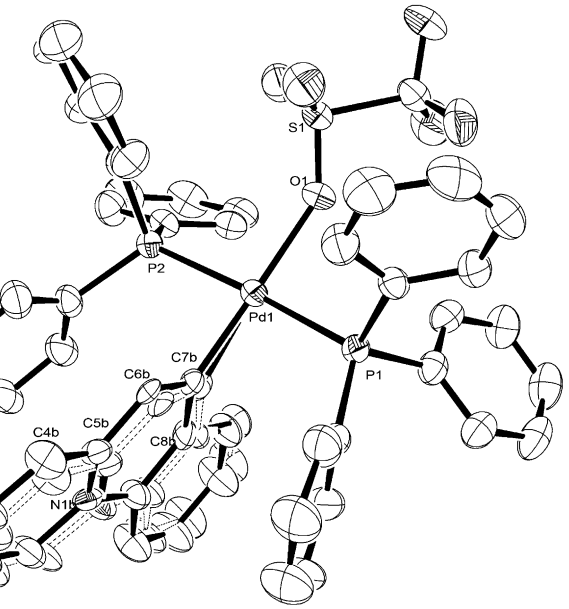
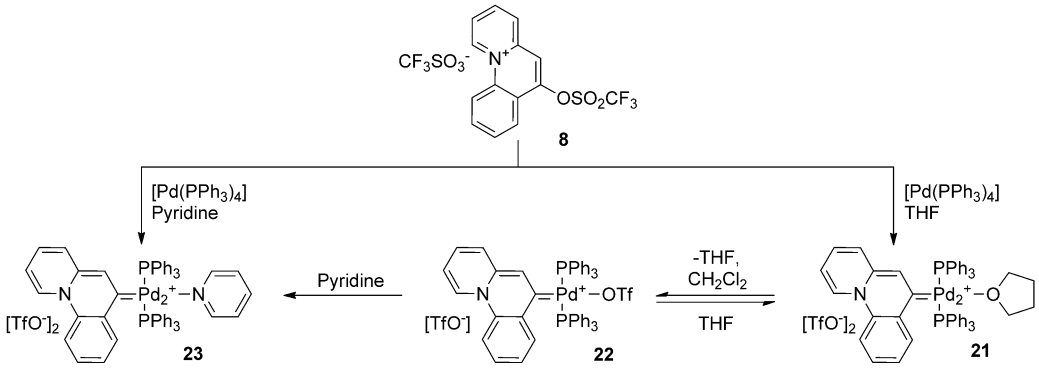


Figure 3. ORTEP representation of **22**·$(CH_2Cl_2)_2$ with thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms and solvent molecules have been omitted for clarity. Only selected atoms have been labelled. Selected bond lengths [Å] and angles [°]: Pd1–O1 2.157(3), Pd1–C7a 1.96(4), Pd1–C7b 1.99(3), Pd1–P1 2.3385(10), Pd1–P2 2.3583(10); C7a-Pd1-P1 88.4(15), C7b-Pd1-P1 90.3(16), P1-Pd1-P2 174.70(4), C7a-Pd1-O1 174.4(9), C7b-Pd1-O1 178.3(10), P1-Pd1-C7a-C8a −100(4), P1-Pd1-C7b-C8b −99(4), C6a-C7a-C8a 119(3), C6b-C7b-C8b 119(2), C5A-N1A-C13A-C8A −4(4), C5B-N1B-C13B-C8B −11(4).



8 23 22 21

Scheme 11. Synthesis of palladium complexes **21**–**23**.

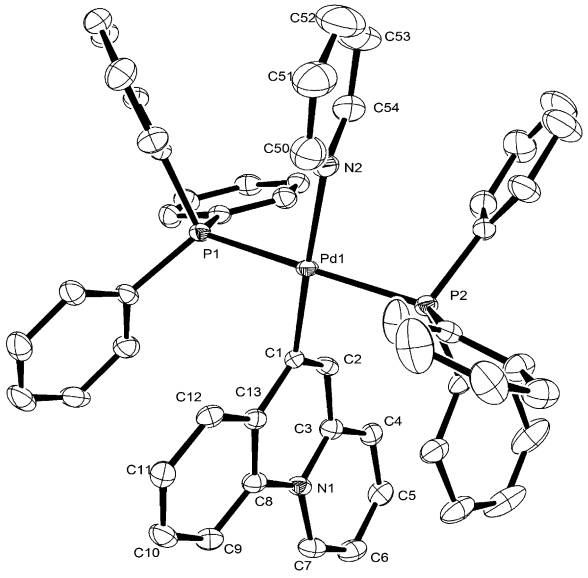


Figure 4. Molecular structure of **23** with thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms have been omitted for clarity and only selected atoms have been labeled. Selected bond lengths [Å] and angles [°]: Pd–N2 2.119(17), Pd–P1 2.348(5), Pd–P2 2.359(5), Pd–C1 1.998(18), C5–C6 1.41(3), C6–C7 1.35(3), N1–C7 1.39(2); C1-Pd1-N2 177.3(7), P1-Pd1-P2 170.2(2), C1-Pd1-P1 87.1(5), N2-Pd1-P1 93.6(5), C1-Pd1-P2 88.9(5), N2-Pd1-P2 90.0(5), C2-C1-C13 117.4(2), P1-Pd1-C1-C2 96.6(14), C3-N1-C8-C13 −12(2).

tegrity of the metal–carbene fragment during catalysis are underway, and will be reported in due course.

Conclusion

We introduce benzo[*c*]quinolin-6-ylidene (**1**) as a new class of strongly electron-donating carbene ligand. Useful precursors to **1** are readily assembled from simple pyridine and benzene components by methods that should permit the introduction of a range of structural diversity. This potentially useful facet is likely to require judicious choice of substituents to avoid complication in some cases by unwanted side reactions. We continue to explore along these lines and progress will be reported in due course. The facile synthesis of 6-trifluoromethanesulfonylbenzo[*c*]quinolizinium trifluoromethanesulfonate (**2**) gives straightforward access to a useful precursor for oxidative addition to low-valent metals, to yield carbene complexes such as [Mn(benzo[*c*]quinolin-6-ylidene)$(CO)_5]^+$ (**15**) and [Pd(benzo[*c*]quinolin-6-ylidene)-$(PPh_3)_2(L)]^{2+}$ L = THF (**21**), OTf (**22**) or pyridine (**23**). CO stretching-frequency data for the manganese compound suggests benzo[*c*]quinolin-6-ylidene is at least as strong a donor as any heteroatom-stabilised carbene ligand reported. With the synthetic organometallic chemistry of this ligand on catalytically relevant metals, such as palladium, in hand, we are now starting to explore its potential in catalysis for reactions in which electron-rich metal centres are believed to be preferred.

Experimental Section

Methods and materials: Where necessary, reactions were carried out under an atmosphere of dry argon using either standard Schlenk line techniques or an MBraun Labmaster glove box. NMR spectra were recorded on a Varian 400 (^{1}H: 399.8 MHz, ^{13}C: 100.5 MHz) or a Varian 500 (^{1}H: 499.9 MHz, ^{13}C: 125.7 MHz) spectrometer at ambient temperatures, with all resonances referenced to residual NMR solvent resonances. All elemental analyses were carried out by the Laboratory for Microanalysis of the University of Bristol. All mass spectrometry analyses were carried out on a VG AutoSpec by the Mass Spectrometry Service of the University of Bristol.

Dry N_2-saturated diethyl ether, toluene, hexane, acetonitrile and methylene chloride were collected from a Grubbs-type solvent system using filtration through an alumina column impregnated with deoxygenated catalysts. THF was distilled from freshly cut sodium and benzophenone. Pentane and pyridine were distilled from freshly ground CaH_2 and degassed prior to use. ACS grade methanol and acetone were purchased from Fisher Scientific and used as received.

Silica (60 A, 35–70 μm particle size) and Al_2O_3 (activated, neutral, 507C, 150 μm particle size) were purchased from Fisher Scientific and Sigma–Aldrich respectively and used as received. Potassium carbonate was purchased from Fisher Scientific and used as received.

The compounds 2-chlorobenzonitrile and 2,6-dichlorobenzonitrile were purchased from Sigma-Aldrich and purified prior to use by column chromatography (Silica) with diethyl ether for the former and THF for the latter as eluents. The compounds 2-methylpyridine (2-picoline) and 2-benzylpyridine were purchased from Sigma-Aldrich and distilled from CaH_2 prior to use. A 1.6 M solution of *n*BuLi in hexane was purchased from Acros and used as received, Methyl trifluoromethanesulfonate, trifluoromethanesulfonic anhydride, $[Ni(cod)_2]$, $[Pd(PPh_3)_4]$, $[Pt(PPh_3)_4]$ and PPh_3 were purchased from Sigma-Aldrich and used as received. 2,4,6-Trimethylaniline was purchased from Sigma-Aldrich and distilled from CaH_2 prior to use. Potassium hydride was purchased as a 30 wt% suspension in mineral oil. Prior to use, it was washed with generous portions of dry toluene and pentane before all volatiles were removed under reduced pressure.

The compounds 2-(2-chlorophenacyl)pyridinium chloride (**1**) and 6-hydroxybenzo[*c*]quinolizinium chloride (**2**) were prepared by a modification of the synthetic protocol as described by Vierfond and co-workers.[22] The detailed synthetic procedure we used is outlined below.

Synthesis of 2-(2-chlorophenacyl)pyridinium chloride (2): A solution of 2-picoline (3.95 mL, 40 mmol) in THF (40 mL) was cooled to −78 °C and *n*BuLi (25 mL, 1.6 M in hexane, 40 mmol, 1 equiv) was added in small portions. The reaction mixture was stirred for 10 min at −78 °C until an orange precipitate formed. Warming to 0 °C resulted in the formation of a clear orange solution that was added dropwise to a solution of 2-chlorobenzonitrile (5.5 g, 40 mmol, 1 equiv) in THF (40 mL) at −78 °C. The reaction mixture was stirred for 16 h, whilst being allowed to warm to room temperature. All moisture sensitive compounds were quenched by careful addition of water (100 mL) and all organic volatiles were removed under reduced pressure. After adjusting pH 2 (H_2SO_4/H_2O), the reaction mixture was heated to 40 °C for 1 h. Addition of a saturated aqueous solution of K_2CO_3 until pH 8 resulted in a phase separation between a colourless aqueous phase and an orange oil. The aqueous phase was extracted with pentane (2×100 mL) and the combined organic phases were washed with water (2×100 mL), brine (100 mL) and dried over $MgSO_4$. All solvents were removed under reduced pressure and the viscous orange residue was dissolved in ethanol (10 mL). After addition of 6 M HCl (10 mL) and stirring for 10 min, the reaction mixture was evaporated to dryness to give a white to yellow solid. The solid residue was recrystallised from hot ethanol (ca. 200 mL). Pale beige crystals were obtained at 5 °C and were washed with diethyl ether (2×20 mL), pentane (2×20 mL) and dried in vacuo. The crystals were dissolved in methanol (10 mL) and precipitated by drop-wise addition to rapidly stirred diethyl ether (200 mL) to yield 8.7 g (32.4 mmol, 81.1%) of the target compound as a bright yellow powder. Single crystals suitable for X-ray diffraction

analysis were obtained by diffusion of diethyl ether into a saturated solution of **1** in methanol. ^{1}H NMR: (3.99.8 MHz, [D$_4$]methanol)—this shows a mixture of keto and enol tautomers, in the ratio of 1.4:1 by relative integration; integrations are given relative to the other peaks of that tautomer, with the keto peaks denoted as *: δ=8.92 (ddd, $^5J_{HH}$=0.7 Hz, $^4J_{HH}$=1.5 Hz, $^3J_{HH}$=5.9 Hz, 1H), 8.65 (td, $^4J_{HH}$=1.71 Hz, $^3J_{HH}$=7.8 Hz, 1H), 8.57* (ddd, $^5J_{HH}$=0.7 Hz, $^4J_{HH}$=1.7 Hz, $^3J_{HH}$=6.1 Hz, 1H), 8.40* (ddd, $^5J_{HH}$=1.7 Hz, $^4J_{HH}$=7.6 Hz, $^3J_{HH}$=8.3 Hz, 1H), 8.18–8.09* (m, 2H), 8.09–8.04 (m, 1H), 7.92–7.98 (m, 1H), 7.67 (ddd, $^5J_{HH}$=1.2 Hz, $^4J_{HH}$=6.1 Hz, $^3J_{HH}$=7.6 Hz, 1H), 7.62–7.43 ppm (m, 4H+5H*); ^{13}C NMR (101 MHz, [D$_4$]methanol)—this shows a mixture of keto and enol tautomers: δ=196.11, 164.71, 151.33, 150.09, 146.07, 144.29, 142.26, 140.90, 136.52, 133.76, 131.75, 131.34, 130.74, 130.30, 129.41, 127.85, 125.99, 124.66, 121.69, 96.47, 46.48 ppm; MS (EI, 70 eV): *m/z* (%): 231.1 (35) $[M]^+$, 196.1 (100) $[M-Cl]^+$, 168. 1 (78) $[M-Cl-CO]^+$; elemental analysis calcd (%) for $C_{13}H_{11}Cl_2NO$: C 58.23, H 4.13, N 5.22, found: C 58.06, H 4.05, N 5.33.

Synthesis of 6-hydroxybenzo[*c*]quinolizinium chloride (3): Compound **2** (1.5 g, 5.59 mmol) was dissolved in water (5 mL) to give a clear pale yellow solution and a saturated aqueous solution of K_2CO_3 was added until pH 8 was reached. Phase separation was observed and the yellow to orange organic phase was extracted from the aqueous phase with diethyl ether (3×20 mL). The combined ether fractions were dried over Na_2SO_4, filtered and all solvents were removed under reduced pressure to yield an orange oil. Under an atmosphere of dinitrogen the orange oil was heated for 2 h to 200 °C resulting in the formation of a beige to grey precipitate. After cooling the reaction products to 25 °C, they were dissolved in ethanol (5 mL) and precipitated into large quantities of ethyl acetate (100 mL) to precipitate an off-white powder (crude yield: 0.91 g, 3.92 mmol, 70 %). The powder was dissolved in methanol and slow diffusion of diethyl ether at 5 °C resulted in the formation of pale yellow crystals of **3**·H$_2$O suitable for X-ray diffraction analysis. Analytically pure samples of **3** were obtained from the precipitation of a methanolic solution (5 mL) of these crystals into rapidly stirred diethyl ether (30 mL), filtration of the white solid and subsequent drying under vacuum (0.84 g, 3.64 mmol, 65 %). ^{1}H NMR (399.8 MHz, [D$_6$]DMSO): δ=9.83 (d, $^3J_{HH}$=7.2 Hz, 1H; H^1), 8.87 (d, $^3J_{HH}$=8.9 Hz, 1H; H^{10}), 8.47 (m, 1H; H^7), 8.18 (m, 3H; H^3, H^4, H^9), 7.96 (t, J=8.0 Hz, 1H; H^8), 7.79 (dt, J=7.0, 1.8 Hz, 1H; H^2), 7.35 ppm (s, 1H; H^5); ^{13}C NMR ([D$_6$]DMSO, 100.5 MHz, 20 °C): δ=161.1, 146.4, 137.9 (C^9), 135.8, 133.5 (C^1), 131.8 and 129.6 (C^3 and C^4), 126.2 (C^8), 124.4 (C^7), 121.6, 120.0 (C^{10}), 117.2 (C^2), 101.4 ppm (C^5); MS (EI, 70 eV): *m/z* (%): 195.1 (92) $[M]^+$, 167.1 (100) $[M-CO]^+$; elemental analysis calcd (%) for $C_{13}H_{12}ClNO_2$: C 62.53, H 4.84, N 5.61; found: C 62.60, H 4.76, N 5.60.

Synthesis of 2-(2,4-dichlorophenacyl)pyridinium chloride: An analogous procedure to that employed for synthesis of **2** was followed for synthesis of 2-(2,4-dichlorophenacyl)pyridinium chloride. ^{1}H NMR (399.8 MHz, [D$_6$]DMSO): δ=8.60 (d, J=5.9 Hz, 1H; Ar*H*), 8.37 (t, J=7.5 Hz, 1H; Ar*H*), 8.29 (d, J=8.3 Hz, 1H; Ar*H*), 7.70–7.50 (m, 4H; Ar*H*), 5.87 ppm (s, 1H; C=C*H*); ^{13}C NMR ([D$_6$]DMSO, 100.5 MHz): δ=162.18, 150.74, 144.68, 140.54, 135.75, 133.58, 132.25, 128.82, 128.60, 124.76, 121.74, 96.32 ppm; MS (EI, 70 eV): *m/z* (%): 265.0 (15) $[M]^+$, 230.0 (70) $[M-Cl]^+$, 202.0 (70) $[M-COCl]^+$, 172.9 (100) $[M-PyCH_2]^+$.

Synthesis of 7-chloro-6-hydroxypyrido[1,2-*a*]quinolin-11-ium chloride (4): 2-(2,4-Dichlorophenacyl)pyridinium chloride (4.0 g, 13.4 mmol) was dissolved in methanol (10 mL). This yellow solution was treated with excess saturated aqueous potassium carbonate solution (200 mL), in a separating funnel and the resulting mixture was extracted with THF (5×50 mL). The combined extracts were dried over $MgSO_4$, filtered and the solvents removed in vacuo. Toluene was added and then removed by rotary evaporator, in order to remove remaining traces of water by azeotropic codistillation. The resulting oil was then dried under high vacuum for 30 mins at room temperature before being heated to 200 °C, under nitrogen, for 2.5 h. The oil crystallised upon cooling and the crystals were washed with CH_2Cl_2, to remove any impurities. The resulting product could be recrystallised from hot ethanol to give 1.8 g (45 %) of yellow crystals. ^{1}H NMR (399.8 MHz, [D$_6$]DMSO): δ=9.80 (d, J=7.3 Hz, 1H; Ar*H*), 8.96 (dd, J=8.3, 1.71 Hz, 1H; Ar*H*), 8.13 (m, 2H; Ar*H*), 8.00 (m, 2H; Ar*H*), 7.62 ppm (ddd, J=13.5, 6.36, 2.3 Hz, 1H; Ar*H*); ^{13}C NMR ([D$_6$]DMSO, 100.5 MHz): δ=163.44, 145.90, 139.05, 137.96, 133.07, 132.95, 132.89, 132.15, 125.99, 120.35, 119.26, 118.23, 104.45 ppm; MS (EI, 70 eV): *m/z* (%): 229.0 (80) $[M]^+$, 201.0 (100) $[M-CO]^+$, 166.1 (45) $[M-COCl]^+$.

Synthesis of 5: Identical synthetic protocol as for synthesis of **2**, from 2-benzylpyridine (10.54 g, 60.2 mmol) and 2-chlorobenzonitrile (8.28 g, 60.2 mmol). Purified by crystallisation from either, hot ethanol or slow diffusion of diethyl ether into a solution of **5** in methanol. Yield after crystallisation from hot ethanol: 2.86 g (15 %); yellow solid. ^{1}H NMR (399.8 MHz, [D$_6$]DMSO): δ=10.31 (s, 1H; NH_2), 9.17–9.10 (m, 1H; N=C*H*), 9.07 (d, J=8.56 Hz, 1H), 7.93–7.86 (m, 1H), 7.84–7.76 (m, 1H), 7.67–7.54 (m, 3H), 7.44–7.22 ppm (m, 6H); ^{13}C NMR ([D$_6$]DMSO, 100.5 MHz, 20 °C): δ=150.24, 134.56, 134.50, 133.63, 131.66, 129.84, 129.25, 128.42, 127.09, 126.95, 126.17, 126.04, 125.31, 121.12, 118.05, 114.62 ppm; MS (EI, 70 eV): *m/z* (%): 270.1 (100) $[M-HCl]^+$.

Synthesis of benzo[*c*]quinazolinon(pyrido[1,2-*a*]quinolin-6-one) (7): 6-Hydroxybenzo[*c*]quinolizinium chloride **3** (1.5 g, 6.45 mmol) was dissolved in a mixture of methanol and water (30 mL, 1:1 vol %). A saturated aqueous solution of K_2CO_3 was added dropwise until the aqueous phase was almost discoloured and an orange oil was separated. The aqueous phase was extracted with methylene chloride (6×100 mL) and the combined organic fractions were dried over $MgSO_4$. All volatiles were removed under reduced pressure to leave a bright yellow solid (1.13 g, 5.81 mmol, 90 %). Satisfactory elemental analysis for the yellow solid was obtained after recrystallisation from hot acetone, followed by vacuum sublimation (150 °C, 5.0×10^{-3} mbar). Crystals suitable for single-crystal X-ray diffraction analysis were obtained by crystallisation of **7** from hot acetone. ^{1}H NMR ([D$_6$]DMSO, 399.8 MHz, 20 °C): δ=8.97 (d, $^3J_{HH}$=7.5 Hz, 1H; H^1), 8.49 (d, $^3J_{HH}$=9.0 Hz, 1H; H^{10}), 8.36 (dd, $^4J_{HH}$=1.7 Hz, $^3J_{HH}$=8.0 Hz, 1H; H^7), 7.81 (m, 1H; H^9), 7.62 (t, $^3J_{HH}$=7.2 Hz, 1H; H^8), 7.29 (m, 2H; H^3 and H^4), 6.74 (m, 1H; H^2), 6.28 ppm (s, 1H; H^5); ^{13}C NMR ([D$_6$]DMSO, 125.7 MHz, 20 °C): δ=172.6, 146.3, 137.1, 132.6 (C^9), 130.4 (C^1), 132.1 and 125.3 (C^3 and C^4), 130.4 (C^1), 127.2 (C^8), 126.8 (C^7), 117.7 (C^{10}), 112.3 (C^2), 104.5 ppm (C^5); MS (EI, 70 eV): *m/z* (%): 195.1 (92) $[M]^+$, 167.1 (100 %) $[M-CO]^+$; elemental analysis calcd (%) for $C_{13}H_9NO$: C 79.98; H 4.65; N 7.17; found: C 79.70, H 4.80, N 7.20.

Synthesis of 6-trifluoromethanesulfonylbenzo[*c*]quinolizinium trifluoromethanesulfonate (8) A stirred solution of **7** (0.300 g, 1.54 mmol) in CH_2Cl_2 (10 mL) was cooled to −78 °C. At this temperature, $(CF_3SO_2)_2O$ (0.280 mL, 1.69 mmol, 1.1 equiv) was added dropwise by syringe and stirring was continued for 1 h at −78 °C. The cooling bath was removed and the reaction mixture was allowed to warm to room temperature while stirring was continued for 16 h. The formation of a white precipitate in a clear pink supernatant was observed. All volatiles were removed under reduced pressure and the remaining white solid was washed with THF (3×10 mL). After drying in vacuo, analytically pure **8** (0.700 mg, 1.46 mmol, 95 %) was obtained. Single crystals of **8** were obtained from the slow diffusion of diethyl ether into a saturated solution of **8** in acetonitrile at 20 °C. ^{1}H NMR ([D$_3$]acetonitrile, 399.8 MHz, 20 °C): δ=10.14 (d, $^3J_{HH}$=7.0 Hz, 1H), 9.03 (d, $^3J_{HH}$=9.1 Hz, 1H), 8.69–8.67 (m, 2H), 8.43–8.40 (m, 2H), 8.35–8.30 (m, 2H), 8.22–8.18 ppm (m, 1H); ^{13}C NMR ([D$_3$]acetonitrile, 125.7 MHz, 20 °C): δ=149.6, 144.3, 142.3, 136.7, 135.3, 135.1, 132.2, 129.7, 126.0, 123.8, 121.2, 120.5, 119.0, 117.3, 114.1 ppm; MS (EI, 70 eV): *m/z* (%): 328 (18) $[M]^+$, 195 (80) $[M-CF_3SO_3]^+$, 167 (100) [195−CO]; HRMS (ESI): *m/z* calcd for $C_{14}H_9N_2O_3F_3S$: 328.0255 $[M]^+$; found: 328.0242; elemental analysis calcd (%) for $C_{15}H_9F_6NO_6S_2$: C 37.74, H 1.90, N 2.93; found: C 37.76, H 1.96, N 3.04.

Synthesis of 6-methoxybenzo[*c*]quinolizinium trifluoromethanesulfonate (9): Ketone **7** (0.200 g, 1.02 mmol) was dissolved in CH_2Cl_2 (10 mL) and cooled to −78 °C, before $CH_3OSO_2CF_3$ (0.128 mL, 1.13 mmol) was added dropwise by syringe. The reaction mixture was stirred for 15 min at −78 °C, after which the cooling bath was removed and the reaction mixture was allowed to warm slowly to room temperature. Stirring was continued at this temperature for 15 min. The yellow precipitate obtained was filtered, washed with CH_2Cl_2 (3×5 mL) and dried in vacuo (0.156 g, 43 %). ^{1}H NMR ([D$_3$]acetonitrile, 399.8 MHz, 20 °C): δ=9.68–9.65 (m, 1H), 8.75–8.72 (m, 1H), 8.51 (ddd, $^3J_{HH}$=0.5 Hz, J_{HH}=1.6 Hz, J_{HH}=8.2 Hz, 1H), 8.31–8.22 (m, 2H), 8.18–8.14 (m, 1H), 8.02–7.98 (m, 1H),

7.85 (dt, J_{HH} = 1.9 Hz, J_{HH} = 14.1 Hz, 1H), 7.54 (s, 1H), 4.28 ppm (s, 3H); ^{13}C NMR ([D$_3$]acetonitrile, 125.7 MHz, 20 °C): δ = 162.0, 140.4, 134.6, 133.6, 131.5, 128.1, 125.3, 123.8, 122.7, 122.3, 118.7, 100.7, 58.8 ppm; MS (EI, 70 eV): *m/z* (%): 210 (10) $[M]^+$, 195 (90) $[M-CH_3]^+$, 167 (100) $[M-COMe]^+$; elemental analysis calcd (%) for $C_{15}H_{12}F_3NO_4S$: C 50.14, H 3.37, N 3.90; found: C 50.25, H 3.56, N 3.91.

Synthesis of 6-methoxybenzo[*c*]quinolizinium tetrafluoroborate (10): Ketone **7** (0.233 g, 1.19 mmol) and $[Me_3O][BF_4]$ (0.206 g, 1.40 mmol) were mixed in the absence of solvent and cooled to −78 °C before CH_2Cl_2 (10 mL) was added. The reaction mixture was allowed to slowly warm to ambient temperature over the course of 16 h. All volatiles were removed under reduced pressure, and the white residue was washed with MeOH (2×5 mL) and dried in vacuo (0.320 g, 1.08 mmol, 90% yield). ^{1}H NMR ([D$_6$]DMSO, 400.2 MHz, 22 °C): δ = 10.12 (d, $^3J_{HH}$ = 7.0 Hz, 1H,), 9.11 (d, $^3J_{HH}$ = 9.0 Hz, 1H), 8.50 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.5 Hz, 1H), 8.46–8.42 (m, 1H), 8.25–8.20 (m, 1H), 8.08–8.04 (m, 1H), 7.99–7.95 (m, 1H), 7.92 (s, 1H), 4.29 ppm (s, 3H); ^{13}C NMR ([D$_6$]DMSO, 100.6 MHz, 23 °C): δ = 160.5, 146.6, 140.0, 139.2, 135.8, 133.9, 130.8, 127.5, 124.3, 121.8, 121.6, 118.9, 100.6, 58.5 ppm; MS (EI, 70 eV): *m/z* (%): 210 (10) $[M]^+$, 195 (70) $[M-CH_3]^+$, 167 (100) $[M-COCH_3]^+$; HRMS (EI): *m/z* calcd for $C_{14}H_{12}NO$: 210.0919 $[M]^+$; found: 210.0916; elemental analysis calcd (%) for $C_{14}H_{12}BF_4NO$: C 56.61, H 4.07, N 4.72; found: C 56.48, H 4.32, N 4.59.

Synthesis of 6-ethoxybenzo[*c*]quinolizinium tetrafluoroborate (11): Ketone **7** (0.233 g, 1.19 mmol) and $[Et_3O][BF_4]$ (0.265 g, 1.40 mmol) were mixed in the absence of solvent and cooled to −78 °C before CH_2Cl_2 (10 mL) was added. The reaction mixture was allowed to slowly warm to ambient temperature over the course of 16 h. All volatiles were removed under reduced pressure, and the white residue was dissolved in CH_3CN (5 mL), filtered and precipitated by dropwise addition into rapidly stirred diethyl ether (25 mL) to give a white powder (0.285 g, 0.916 mmol, 77%). ^{1}H NMR ([D$_3$]acetonitrile, 399.8 MHz, 25 °C): δ = 9.61(d, $^3J_{HH}$ = 7.1 Hz, 1H), 8.69 (d, $^3J_{HH}$ = 8.6 Hz, 1H), 8.51 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.7 Hz, 1H), 8.29–8.25 (m, 1H), 8.21–8.18 (m, 1H), 8.15–8.11 (m, 1H), 8.00–7.96 (m, 1H), 7.83 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.7 Hz, 1H), 7.47 (s, 1H), 4.53 (q, $^3J_{HH}$ = 7.1 Hz, 2H), 1.62 ppm (t, $^3J_{HH}$ = 7.1 Hz, 3H); ^{13}C NMR ([D$_3$]acetonitrile, 125.7 MHz, 25 °C): δ = 161.5, 147.9, 140.5, 136.7, 134.9, 133.6, 131.7, 128.4, 125.6, 123.0, 122.5, 118.8 (overlapping with NMR solvent at 118.7), 101.4, 101.3, 68.3, 14.8 ppm; MS (EI, 70 eV): *m/z* (%): 224 (80) $[M]^+$, 195 (95) $[M-C_2H_5]^+$, 167 (100) $[M-COC_2H_5]^+$; HRMS (EI): *m/z* calcd for $C_{15}H_{14}NO$: 224.1075 $[M]^+$; found: 224.1073; elemental analysis calcd (%) for $C_{15}H_{12}F_3NO_4S$: C 50.14, H 3.37, N 3.90; found: C 50.25, H 3.56, N 3.91.

Synthesis of 6-pyridiniumbenzo[*c*]quinolizinium ditriflate (12): A sample of **8** (0.100 g, 0.210 mmol) was dissolved in pyridine (5 mL) and stirred at 20 °C for 16 h. All volatiles were removed under reduced pressure to yield a colourless crystalline solid. Purification was achieved by recrystallisation from the slow diffusion of diethyl ether into a saturated solution of the product in CH_3CN at 20 °C. Colorless crystals (0.115 g, 0.207 mmol, 99% yield) suitable for single crystal X-ray diffraction analysis were obtained. ^{1}H NMR ([D$_3$]acetonitrile, 399.8 MHz, 20 °C): δ = 10.24 (d, $^3J_{HH}$ = 7.0 Hz, 1H), 9.07–9.10 (m, 3H), 8.69–8.67 (tt, $^4J_{HH}$ = 2.5 Hz, $^3J_{HH}$ = 16.0 Hz, 1H), 8.82–8.73 (m, 2H), 8.66 (s, 1H), 8.48–8.45 (m, 3H), 8.39–8.34 (m, 1H), 8.11 (t, $^3J_{HH}$ = 15.5 Hz, 1H), 7.70 ppm (dd, $^4J_{HH}$ = 1.3 Hz, $^3J_{HH}$ = 8.3 Hz, 1H); ^{13}C NMR ([D$_3$]acetonitrile, 125.7 MHz, 20 °C): δ = 150.0, 146.1, 143.3, 136.0, 135.2, 132.5, 130.6, 129.8, 127.3, 124.9, 122.7, 122.4, 119.2 ppm.

Synthesis of 6-triphenylphosphoniumbenzo[*c*]quinolizinium ditriflate (13): Triphenylphosphine (0.100 g, 0.210 mmol) and **8** (54.9 mg, 0.210 mmol) were mixed in the absence of solvent. Acetonitrile (2 mL) was added and a clear yellowish solution was obtained instantly. After stirring for 16 h, all volatiles were removed under reduced pressure. The foamy yellow residue was washed consecutively with CH_2Cl_2 (2×3 mL) and THF (3×5 mL) to precipitate a white solid, which was filtered and dried under reduced pressure to yield the target compound (0.140 g, 0.189 mmol, 90%). ^{1}H NMR ([D$_3$]acetonitrile, 399.8 MHz, 20 °C): δ = 10.24 (d, $^3J_{HH}$ = 6.9 Hz, 1H), 9.01 (d, $^3J_{HH}$ = 8.9 Hz, 1H), 8.77 (t, $^3J_{HH}$ = 15.6 Hz, 1H), 8.62 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 8.51–8.47 (m, 1H), 8.20–8.16 (m, 2H), 8.00–7.95 (m, 3H), 7.87–7.69 ppm (m, 14H); ^{13}C NMR ([D$_3$]acetonitrile, 125.7 MHz, 20 °C): δ = 150.0, 146.1, 143.3, 136.0, 135.2, 132.5, 130.6, 129.8, 127.3, 124.9, 122.7, 122.4, 119.2 ppm; ^{31}P NMR (299.9 MHz, [D$_3$]acetonitrile): δ = 23.0 ppm (s); MS (ESI): *m/z* (%): 590.1 (100) $[M+CF_3SO_3]^+$, 220.6 (30) $[M]^{2+}$; HRMS (EI): *m/z* calcd for $C_{31}H_{24}N_1P_1^{+}$: 220.5818 $[M]^{2+}$; found: 220.5820; elemental analysis calcd (%) for $C_{33}H_{24}F_6NO_6PS_2$: C 53.59, H 3.27, N 1.89; found: C 54.03, H 3.61, N 2.28.

Synthesis of 14: A solution of triflate **8** (0.100 g, 0.210 mmol) in acetonitrile (2 mL) was treated dropwise with a solution of ketone **7** (41.0 mg, 0.210 mmol) in acetonitrile (2 mL). The clear yellow solution was stirred for 16 h at ambient temperature to precipitate a pale beige solid. The reaction mixture was warmed briefly to 60 °C until all the residue was dissolved, filtered and allowed to cool slowly to room temperature. Colorless crystals (0.131 g, 0.195 mmol, 93%) of the target compound were obtained after cooling to 5 °C. ^{1}H NMR ([D$_3$]acetonitrile, 399.8 MHz, 25 °C): δ = 9.98 (d, $^3J_{HH}$ = 6.6 Hz, 1H), 8.97 (d, $^3J_{HH}$ = 9.3 Hz, 1H), 8.68 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.5 Hz, 1H), 8.50–8.46 (m, 1H), 8.35–8.29 (m, 2H), 8.16–8.12 (m, 2H), 7.94 ppm (s, 1H); ^{13}C NMR ([D$_3$]acetonitrile, 100.5 MHz, 25 °C): δ = 157.3, 146.3, 141.7, 135.4, 134.8, 132.2, 129.2, 125.2, 124.7, 122.3, 119.2, 110.2, 100.9 ppm; MS (ESI): *m/z* (%): 523.1 (100) $[M-CF_3SO_3]^+$, 373.1 (20) $[M-H]^{2+}$; HRMS (ESI): *m/z* calcd for $C_{27}H_{18}F_3N_2O_4S^+$: 523.0934 $[M-CF_3SO_3]^+$; found: 523.0924; elemental analysis calcd (%) for $C_{28}H_{18}F_6N_2O_7S_2$: C 50.00, H 2.70, N 4.17; found: C 49.96, H 2.61, N 4.25.

Synthesis of 15: Sodium metal (20 mg, 0.89 mmol) was added to mercury (0.37 mL) in small pieces and stirred for approximately 15 mins, until all amalgamated. $[Mn_2(CO)_{10}]$ (137 mg, 0.35 mmol) was added to the resulting amalgam in THF (6 mL). This mixture was stirred for 2 h before filtering through celite, directly into a flask containing solid bis triflate **8** (200 mg, 0.42 mmol). The resulting red suspension was stirred overnight and an off-white solid filtered off. This solid was dried under vacuum and extracted with CH_2Cl_2 (3×2 mL). The resulting solution was concentrated to approximately 2 mL and cooled to −20 °C to give **15** as very pale yellow prisms (22 mg, 0.044 mmol, 10% yield). ^{1}H NMR ([D$_6$]DMSO, 399.8 MHz): δ = 10.12 (d, J = 7.1 Hz, 1H), 9.08 (d, J = 8.1 Hz, 1H), 8.76 (s, 1H), 8.61 (dd, J = 7.3, 1.96 Hz, 1H), 8.43–8.52 (m, 2H), 8.13–8.06 (m, 2H) 8.03–7.96 ppm (m, 1H); ^{13}C NMR ([D$_6$]DMSO, 100.4 MHz): δ = 209.79, 179.08, 140.60, 139.64, 137.37, 137.22, 136.20, 133.21, 132.37, 132.25, 130.21, 126.80, 122.89, 119.60 ppm; FTIR (solid state): $\tilde{\nu}$ = 2127.9 (C≡O stretch), 2069.2 (C≡O stretch), 1997.0 (C≡O stretch), 1634.3, 1604.0, 1579.3, 1570.8, 1524.6, 1488.9, 1453.4, 1438.8, 1422.7, 1256.3, 1225.3, 1210.8, 1150.2, 1028.0, 914.0, 902.1, 842.7, 770.9, 732.9, 649.5 cm^{-1}; MS (ESI): *m/z* (%): 345.99 (100) $[M-CO]^+$, 373.98 (55) $[M]^+$.

Synthesis of 16: In the absence of solvent, **8** (0.100 g, 0.210 mmol) and $[Ni(cod)_2]$ (0.057 g, 0.207 mmol) were mixed in the absence of solvent. Acetonitrile (2.0 mL) was added slowly at 20 °C and stirring was continued for 16 h, after which a yellow solution was obtained. All volatiles were removed under reduced pressure and the grey residues were dissolved in acetonitrile (1 mL) and filtered. Diffusion of diethyl ether vapour into this solution resulted in the formation of colorless crystals (0.065 g, 0.099 mmol, 94%). An analytically pure sample of **16** was obtained after column chromatography (Al_2O_3, MeCN) and crystallisation from an acetonitrile/diethyl ether mixture. ^{1}H NMR ([D$_3$]acetonitrile, 399.8 MHz, 20 °C): δ = 10.18 (d, $^3J_{HH}$ = 7.2 Hz, 2H), 9.04 (d, $^3J_{HH}$ = 9.0 Hz, 2H,), 8.73–8.69 (m, 2H), 8.64 (dd, $^4J_{HH}$ = 1.8 Hz, $^3J_{HH}$ = 8.3 Hz, 2H), 8.39–8.35 (m, 4H), 8.28–8.24 (m, 2H), 7.93–7.89 (m, 2H), 7.79–7.76 ppm (dd, $^4J_{HH}$ = 1.47 Hz, $^3J_{HH}$ = 8.19 Hz, 2H); ^{13}C NMR ([D$_3$]acetonitrile, 125.7 MHz, 20 °C): δ = 143.3, 142.2, 141.9, 135.0, 134.7, 134.1, 131.5, 129.6, 128.7, 126.6, 125.8, 124.8, 118.6 ppm; MS (ESI): *m/z* (%): 507.1 (100) $[(C_{13}H_9N)_2(CF_3SO_3)]^+$, 179.1 (36) $[(C_{13}H_9N)_2]^{2+}$; HRMS (ESI): *m/z* calcd for $C_{27}H_{18}N_2F_3O_3S$: 507.0985 $[(C_{13}H_9N)_2(CF_3SO_3)]^+$; found: 507.0977; elemental analysis calcd (%) for $C_{13}H_9NO$: C 79.98, H 4.65, N 7.17; found: C 79.70, H 4.80, N 7.20.

Synthesis of 21: Compound **8** (0.100 g, 0.210 mmol) and $[Pd(PPh_3)_4]$ (0.242 g, 0.210 mmol) were mixed in the absence of solvent before THF (3 mL) was added at −78 °C. Stirring was continued for 1 h, before the reaction mixture was allowed to warm to 0 °C, after which stirring was

continued for 2 h. A pale beige precipitate formed rapidly, which was isolated by filtration, washed with toluene (3×5 mL), pentane (3×5 mL) and dried in vaccuo (0.178 g, 0.151 mmol, 72% yield). ^{1}H NMR ([D$_2$]methylenechloride, 399.8 MHz, 25 °C): δ = 9.65 (d, $^3J_{HH}$ = 7.1 Hz, 1H), 9.02 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.2 Hz, 1H), 8.44 (d, $^3J_{HH}$ = 8.8 Hz, 1H,), 8.12 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.90–7.85 (m, 2H), 7.72 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.52–7.47 (m, 14H), 7.35–7.31 (m, 6H), 7.24–7.21 (m, 13H), 3.70–3.65 (m, 4H), 1.84–1.80 ppm (m, 4H); ^{13}C NMR ([D$_2$]methylenechloride, 75.6 MHz, 21 °C): δ = 139.3, 139.0, 134.8, 134.7, 134.6, 133.9, 132.8, 132.0, 131.8, 131.7, 131.6, 130.4, 129.5, 129.1, 129.0, 128.9, 128.7, 128.6, 128.2, 127.9, 126.0, 123.1, 118.1, 68.3, 26.1 ppm; ^{31}P{H} NMR ([D$_2$]methylene chloride, 121.4 MHz, 21 °C): δ = 22.8 ppm (s); MS (ESI): *m/z* (%): 958.1 (100) $[(C_{13}H_9N)(PPh_3)_2Pd(CF_3SO_3)]^+$, 846.1 (44) $[(C_{13}H_9N)(PPh_3)Pd(CF_3SO_3)_2]^+$, 696.0 (20) $[(C_{13}H_9N)(PPh_3)Pd(CF_3SO_3)]^+$; HRMS (ESI): *m/z* calcd for $C_{50}H_{39}F_3NO_3P_2PdS$: 958.1107 $[(C_{13}H_9N)(PPh_3)_2Pd(CF_3SO_3)]^+$; found: 958.1131; elemental analysis calcd (%) for $C_{55}H_{47}F_6NO_7P_2PdS_2$: C 55.96, H 4.01, N 1.19; found: C 56.53, H 4.25, N 1.29.

Synthesis of 22: Pentane vapor was allowed to slowly diffuse into a solution of **21** in CH_2Cl_2, to give single crystals of **22**. NMR data was identical to that of **21** as both were recorded in [D$_2$]methylene chloride, in which the triflate counterion displaces the previously coordinated THF molecule. Elemental analysis calcd (%) for $C_{51}H_{39}F_6NO_6P_2PdS_2$: C 55.27, H 3.55, N 1.26; found: C 56.49, H 4.26, N 1.29.

Synthesis of 23: In the absence of solvent, $[Pd(PPh_3)_4]$ (0.210 mmol, 0.242 g) and **8** (0.100 g, 0.210 mmol) were mixed, before dry pyridine (5 mL) was added at 0 °C. The resulting dark brown solution was stirred for 16 h. After removal of all volatiles under reduced pressure and washing with THF (3×5 mL), toluene (3×5 mL) and pentane (5 mL), the target compound was isolated as a grey solid and dried in vacuo (0.255 g, 0.150 mmol, 71% yield). Single crystals suitable for X-ray diffraction analysis were obtained from a diffusion of diethyl ether into a saturated solution of the target compound in acetonitrile. ^{1}H NMR ([D$_2$]methylenechloride, 399.8 MHz, 25 °C): δ = 9.36 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.5 Hz, 1H), 9.30 (d, $^3J_{HH}$ = 7.1 Hz, 1H), 8.22–8.18 (m, 2H), 8.10–8.09 (m, 2H), 8.08–7.97 (m, 3H), 7.83–7.79 (m, 1H), 7.69 (dt, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 2.0 Hz, 1H), 7.39–7.34 (m, 12H), 7.24–7.13 (m, 19H), 6.69–6.65 (m, 2H), 2.28 (s, 3H), 2.02 ppm (s, 6H); ^{13}C NMR ([D$_2$]methylenechloride, 100.5 MHz, 25 °C): δ = 178.2, 151.3, 138.6, 137.9, 137.8, 136.5, 133.8, 133.7, 133.6, 133.0, 132.4, 131.2, 130.9, 130.6, 130.3, 129.7, 129.0, 128.9, 128.8, 127.5, 127.2, 126.9, 126.7, 125.2, 122.9, 121.9, 119.7, 116.0 ppm; ^{31}P NMR ([D$_2$]methylene chloride, 121.4 MHz, 25 °C): δ = 20.4 ppm (s); MS (ESI): *m/z* (%): 958.1 (2) $[Pd(C_{13}H_9N)(PPh_3)_2(CF_3SO_3)]^+$, 696.0 (100) $[Pd(C_{13}H_9N)(PPh_3)(CF_3SO_3)]^+$; elemental analysis calcd (%) for $C_{56}H_{44}F_6N_2O_6P_2PdS_2$: C 56.64, H 3.73, N 2.36; found: C 56.81, H 4.00, N 2.57.

Crystallographic data

*X-ray crystal structure analysis for **33***: The nitrogen atom N2 in the pyridinium moiety in **33** is disordered over two positions C2/N2 with relative occupancies approximating 1:1. X-ray Crystal Structure Analysis for **33**: $C_{19}H_{15}ClN_2$, M_w = 306.78 g mol^{-1}, yellow blocks, crystal size 0.22×0.18×0.18 mm, monoclinic, space group *C2/c*, *a* = 15.6994(4), *b* = 10.2109(2), *c* = 20.7769(6) Å, $\alpha=\gamma$ = 90.00, β = 111.2620(10)°, *V* = 3103.93(13) Å^3, *T* = 100 K, *Z* = 8, $\lambda(Mo_{K\alpha})$ = 0.71073 Å, empirical absorption correction (min/max transmission = 0.68/0.75), Bruker Apex II CCD diffractometer, 2.43 < θ < 27.52, 13578 measured reflections, 3576 independent reflections, 3104 reflections with $I > 2\sigma(I)$. Structure solved by direct methods and refined by full-matrix least squares against F^2 to R_1 = 0.036 [$I > 2\sigma(I)$], wR_2 = 0.087, *S* = 1.043. All esds (except the esd in the dihedral angle between two least squares. planes) are estimated using the full covariance matrix.

*X-ray crystal structure analysis for **7***: $C_{13}H_9N_2O$, M_w = 195.21 g mol^{-1}, brown laths, crystal size 0.35×0.12×0.06 mm, orthorhombic, space group *Pbca*, *a* = 9.6438(2), *b* = 14.2266(4), *c* = 26.8589(7) Å, $\alpha=\beta=\gamma$ = 90.00°, *V* = 3685.00(16) Å^3, *T* = 100 K, *Z* = 16, $\lambda(Mo_{K\alpha})$ = 0.71073 Å, empirical absorption correction (min/max transmission = 0.89/1.00), Bruker Apex II CCD diffractometer, 2.60 < θ < 27.51, 30616 measured reflections, 4237 independent reflections, 3445 reflections with $I > 2\sigma(I)$. Structure solved by direct methods and refined by full-matrix least squares against F^2 to R_1 = 0.060 [$I > 2\sigma(I)$], wR_2 = 0.156, *S* = 1.107. All esds (except the esd in the dihedral angle between two least squares. planes) are estimated using the full covariance matrix.

*X-ray crystal structure analysis for **16***: Only half a molecule of **16** is contained in the asymmetric *C2/c* unit cell. The full molecule is generated by a crystallographic *XYZ element*; $C_{53}H_{43}Cl_4F_6NO_6P_2PdS_2$, M_w = 656.56 g mol^{-1}, pale yellow blocks, crystal size 0.17×0.17×0.08 mm, monoclinic, space group *C2/c*, *a* = 21.4143(5), *b* = 11.2527(3), *c* = 12.2863(3) Å, $\alpha=\gamma$ = 90.00, β = 110.8520(10)°, *V* = 2766.70(12) Å^3, *T* = 100 K, *Z* = 4, $\lambda(Mo_{K\alpha})$ = 0.71073 Å, empirical absorption correction (min/max transmission = 0.68/0.75), Bruker Apex II CCD diffractometer, 2.04 < θ < 27.59, 24192 measured reflections, 3205 independent reflections, 2801 reflections with $I > 2\sigma(I)$. Structure solved by direct methods and refined by full-matrix least squares against F^2 to R_1 = 0.037 [$I > 2\sigma(I)$], wR_2 = 0.086, *S* = 1.044. All esds (except the esd in the dihedral angle between two least squares. planes) are estimated using the full covariance matrix.

*X-ray crystal structure analysis for **23***: $C_{56}H_{44}F_6N_2O_6P_2PdS_2$, M_w = 1187.39 g mol^{-1}, colorless blocks, crystal size 0.07×0.08×0.08 mm, monoclinic, space group *C2/c*, *a* = 33.0544(12), *b* = 14.1897(5), *c* = 22.5278(8) Å, $\alpha=\gamma$ = 90.00, β = 99.418(2)°, *V* = 10423.8(6) Å^3, *T* = 100 K, *Z* = 8, $\lambda(Mo_{K\alpha})$ = 0.71073 Å, empirical absorption correction (min/max transmission = 0.64/0.75), Bruker Apex II CCD diffractometer, 1.86 < θ < 27.50, 80172 measured reflections, 11954 independent reflections, 8826 reflections with $I > 2\sigma(I)$. Structure solved by direct methods and refined by full-matrix least squares against F^2 to R_1 = 0.071 [$I > 2\sigma(I)$], wR_2 = 0.119, *S* = 5.934. All esds (except the esd in the dihedral angle between two least squares. planes) are estimated using the full covariance matrix.

*X-ray crystal structure analysis for **22**:* $C_{53}H_{43}Cl_4F_6NO_6P_2PdS_2$, M_w = 1278.14 g mol^{-1}, yellow blocks, crystal size 0.32×0.18×0.12 mm, monoclinic, space group $P2_1/c$, *a* = 13.1041(4), *b* = 19.4984(5), *c* = 22.3558(6) Å, $\alpha=\gamma$ = 90.00, β = 97.688(2)°, *V* = 5660.8(3) Å^3, *T* = 200 K, *Z* = 4, $\lambda(Mo_{K\alpha})$ = 0.71073 Å, empirical absorption correction ((min/max transmission = 0.60/0.75), Bruker Apex II CCD diffractometer, 1.39 < θ < 27.48, 92844 measured reflections, 12984 independent reflections, 9837 reflections with $I > 2\sigma(I)$. Structure solved by direct methods and refined by full-matrix least squares against F^2 to R_1 = 0.087 [$I > 2\sigma(I)$], wR_2 = 0.145, *S* = 1.163. All esds (except the esd in the dihedral angle between two least squares. planes) are estimated using the full covariance matrix.

*X-ray crystal structure analysis for **15**:* $C_{20}H_{11}Cl_2F_3MnNO_8S$, M_w = 608.21 g mol^{-1}, pale yellow prisms, crystal size 0.28×0.20×0.15 mm, monoclinic, space group $P2_1/n$, *a* = 12.1911, *b* = 16.2847, *c* = 12.6143 Å, $\alpha=\gamma$ = 90.00, β = 103.410°, *V* = 2436.02 Å^3, *T* = 200 K, *Z* = 6, $\lambda(Mo_{K\alpha})$ = 0.71073 Å, empirical absorption correction (min/max transmission = 0.60/0.75), Bruker Apex II CCD diffractometer, 2.08 < θ < 27.56, 92844 measured reflections, 5602 independent reflections, 4545 reflections with $I > 2\sigma(I)$. Structure solved by direct methods and refined by full-matrix least squares against F^2 to R_1 = 0.1308 [$I > 2\sigma(I)$], wR_2 = 0.4166, *S* = 2.110. All esds (except the esd in the dihedral angle between two least squares. planes) are estimated using the full covariance matrix.

Theoretical methods: All structures were optimised with Gaussian 03,[34] using the standard B3LYP density functional as implemented in Gaussian[35] and the standard 6–31G(d,p) basis set with 5 d functions on all atoms except for the metal centre, where the Stuttgart/Dresden effective core potential (SDD) was used, specifying the default number of core electrons (MDF10 for Ni).[36] After geometry optimisation with default settings, minima were verified by frequency calculations.

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