Note

A stable carbocation generated via 2,5-cyclohexadien-1-one protonation

Craig Fraser, and Rowan D. Young

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A stable carbocation generated via 2,5-cyclohexadien-1-one protonation

Craig Fraser and Rowan D. Young*
Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543

ABSTRACT: Protonation of a substitututed cyclohexadien-1-one (**1**) leads to the generation of carbocation $[\mathbf{3}]^+$, capable of effecting hydride abstraction and oxidation reactions. The molecular structure of $[\mathbf{3}]^+$ shows it to be structurally similar to $[(p\text{-}MeOC_6H_4)Ph_2C]^+$. The ability to easily access $[\mathbf{3}]^+$ from stable and available precursors, such as **1** and commercially available acids, may allow wider application of the growing number of trityl based reactions in organic syntheses.

Introduction: Protonated oxonium salts play a pivotal role in a range of catalytic cycles. In particular, the Brønsted acid catalyzed reduction of ketones and the Diels Alder reaction utilizing enone substrates invoke protonated keto oxonium intermediates.[1] Although considered highly acidic, many examples of isolated sp^3 oxonium salts exist, however, structures of protonated sp^2 oxonium salts are exceedingly rare. Indeed, structures of non-stablised protonated ketones are not reported. However, stabilised protonated ketones, such as benzophenone, or cyclopropanones, are known.[2]

Valid resonance structures of protonated ketones can be postulated that represent either a protonated sp^2 oxygen atom, or a hydroxyl motif bound to an sp^2 carbocation, this concept is perhaps most ideally exemplified in zwitterionic structures of sulfonefluorescein derivatives.[3] Herein, we report the generation of a stable protonated ketone of the latter form, where aromatic stablisation allowed delocalization of the carbocation to generate a trityl analogue (Figure 1).

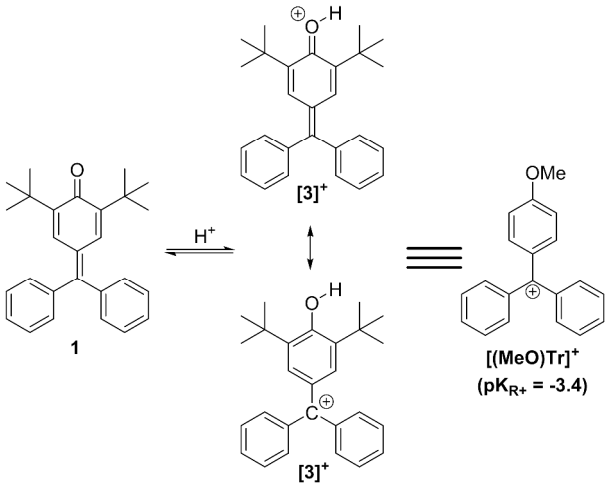


Figure 1. Protonation of **1** generates $[\mathbf{3}]^+$ with possible oxonium and carbocation resonance structures. $[\mathbf{3}]^+$ is analogous to *para*-methoxyphenyl substituted trityl, $[(MeO)Tr]^+$.

Cyclohexadien-1-one **1**, is readily prepared by oxidation of 3,5-di-*tert*-butyl-4-hydroxyphenyl-diphenyl-methane (**2**), which is in turn generated from cheap base materials (*viz*. 2,6-di-*tert*-butyl-phenol and benzophenone).[4] Many studies concerning **1**, or related quinodal ketones (Fuchsones), have been conducted regarding their reactivity, and their ability to act as dyes and stabilize radicals.[5] **1** can be considered a hybrid of a quinone and Thiele's hydrocarbon, with aromatic stabilized resonance forms of di-radical and zwitterion possible.

Indeed, the pK_b of **1** was determined to be significantly lower than that expected for a ketone, with stoichiometric oxonium acid ($[H(OEt_2)_2][BAr^F{}_4]$, $BAr^F{}_4 = [B(C_6F_5)_4]^-$) able to quantitatively protonate **1** to generate the resonance stabilized carbocation $[\mathbf{3}]^+$ (See SI).

Table 1. Selected bond lengths and angles from molecular structures of compounds **1**,[8] **2** and $[\mathbf{3}][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$.

Bond lengths (Å)	**1**	$[\mathbf{3}]^+$	**2**
O1-C14	1.233(1)	1.339(3)	1.378(3)
C1-C11	1.380(2)	1.423(3)	1.536(3)
C1-C21	1.483(2)	1.457(3)	1.528(3)
C1-C31	1.488(2)	1.455(3)	1.529(3)
Bond angles (°)			
Σ angles around C1	360.0(2)	360.0(4)	337.8(3)

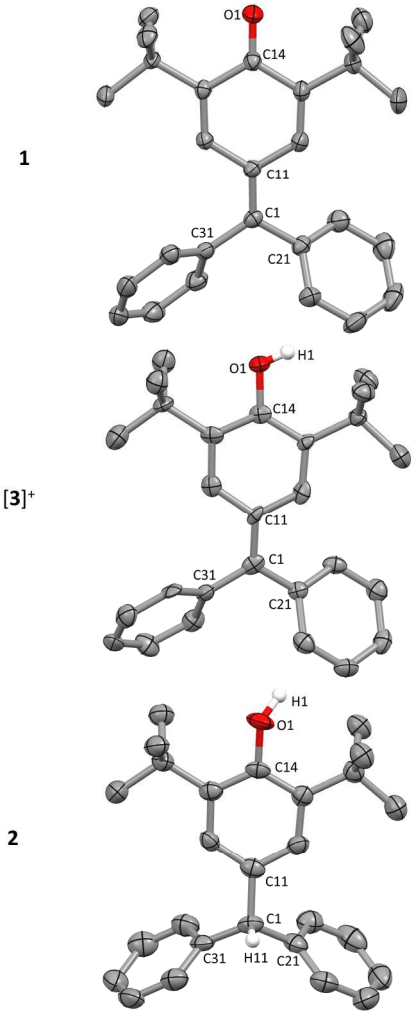
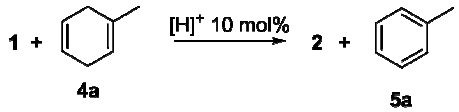


Figure 2. Molecular structures of compounds **1**, **2** and cation fragment of $[\mathbf{3}][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$. Hydrogen atoms except H1 and H11 omitted, 50% thermal ellipsoids. Selected bond lengths and angles given in Table 1.

Table 2. Optimisation of the transfer dehydrogenation of **4a** to generate toluene (**5a**).



Entry	Acid	Solvent	Yield (%)
1	-	DCE	0
2	-	MeCN	0
3	$[H(OEt_2)_2][BAr^F_4]$	DCE	100
4	$[H(OEt_2)_2][BAr^F_4]$	MeCN	100
5	*p*-TsOH	DCE	100
6[b]	*p*-TsOH	MeCN	37
7[b]	TfOH	DCE	81
8	TfOH	MeCN	100
9	MsOH	DCE	100
10[b]	MsOH	MeCN	22
11[b]	CF_3COOH	DCE	10
12[b]	CF_3COOH	MeCN	10
13[c]	$[H(OEt_2)_2][BAr^F_4]$	DCE	0

General conditions: 1 mmol of **1**, 1 mmol of **4a**, 0.1 mmol (10 mol%) of acid and 1 mL solvent heated at 90 °C for 11 h. Yields were determined by GC-MS (decane used as internal standard). [b] Heated for 20 h. DCE = 1,2-dichloroethane. [c] Reaction run in absence of **1**.

In CD_2Cl_2, $[\mathbf{3}]^+$ displays a characteristic methanide ^{13}C NMR resonance at 199.5 ppm (*cf* $[Ph_3C]^+$ 211.3 ppm). Attempts to recrystallize $[\mathbf{3}][BAr^F_4]$ resulted in biphasic mixtures. However, employing the related borate anion $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$, recrystallisation of $[\mathbf{3}][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ was achieved from hexane diffusion into a saturated DCM solution, allowing the structural characterization of $[\mathbf{3}]^+$ (Figure 2). Comparison of the structures of **1**, **2** and $[\mathbf{3}]^+$ in Table 1 shows that $[\mathbf{3}]^+$ maintains a trigonal planar central carbon atom [Σ angles subtending C1 = 360.0(4)°]. Protonation of the quinoidal ketone results in lengthening of the C14-O1 bond in **1** from 1.233(1) Å to 1.339(3) Å in $[\mathbf{3}]^+$ (*cf* 1.378(3) Å in **2**). Structurally, $[\mathbf{3}]^+$ is similar to $[(MeO)Tr]^+$ (Figure 1),[6] which has been reported as an active Lewis acid catalyst for a variety of reactions.[7]

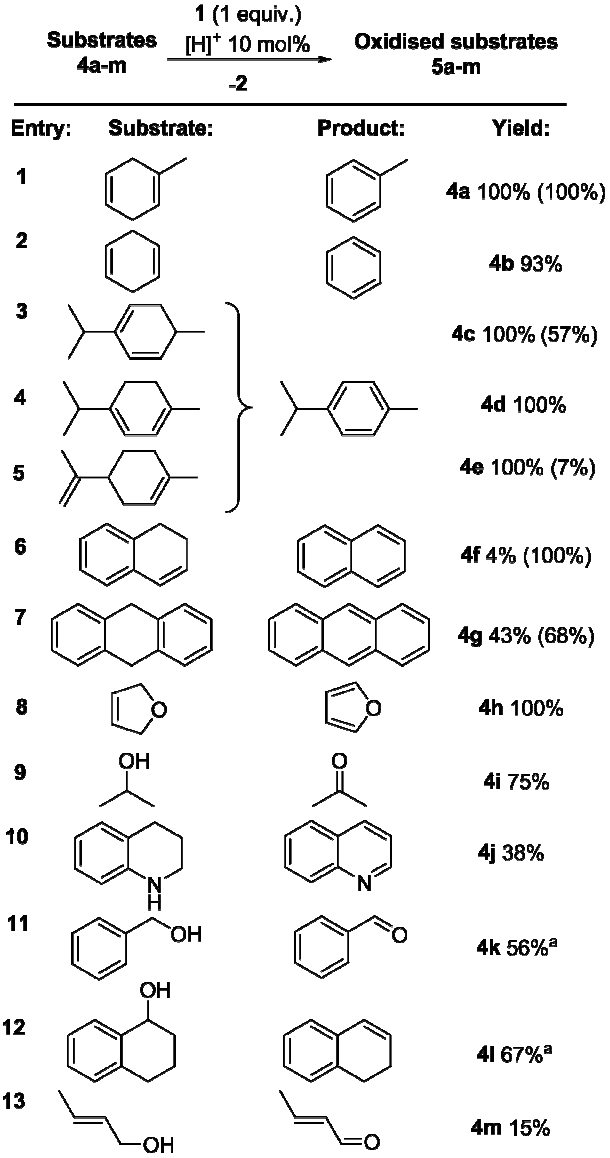
Compound **1** was found to act as a highly protected base, proving resistant to methylation and silylation, with only samples of $[\mathbf{3}][H(OTf)_2]$ (also structurally characterized, see SI) recovered from attempted reactions with MeOTf and TMSOTf (presumably from low concentrations of adventitious water introduced during analysis/attempted isolation).[8]

Addition of an equivalent of PPh_3 to $[\mathbf{3}]^+$ led to a dynamic equilibrium of $[HPPh_3]^+$ and $[\mathbf{3}\text{-}PPh_3]^+$ in a 4:3 ratio. $[\mathbf{3}\text{-}PPh_3]^+$, where the central carbon of $[\mathbf{3}]^+$ is bonded to PPh_3, was identified by spectroscopic comparison to $[Ph_3C\text{-}PPh_3][BAr^F_4]$.[9] The ability of PPh_3 to interact with $[\mathbf{3}]^+$ as a Lewis acid and as a Brønsted acid is also highlighted in this equilibrium. With this in mind, we tested **1** as a H_2 acceptor in a Brønsted acid catalyzed reaction that likely proceeds via $[\mathbf{3}]^+$.

Brønsted acid transfer hydrogenation via carbocation intermediates has been well explored using specific organic H_2 donors such as the Hantzsch ester or 1,4-cyclohexadienes.[10] However, to our knowledge, this is the first exploration of Brønsted acid catalyzed hydrocarbon dehydrogenation (i.e. using a sacrificial H_2 acceptor).[11] In contrast to many organic H_2 donors that gain aromatic stabilization upon loss of H_2 (e.g. Hantzsch ester, 1,4-cyclohexadienes), compound **1** gains aromatic stabilization upon acceptance of H_2 to form **2**.

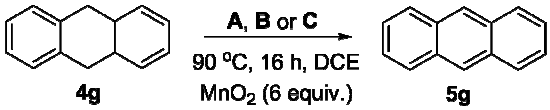
Compound **1** was shown to be an effective stoichiometric dehydrogenation reagent with catalytic amounts of Brønsted acid. A series of Brønsted acid catalysed transfer hydrogenation reactions exemplified the ability of **1** to act as a hydrogen acceptor, generating **2**. Compound **1** was benchmarked against 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as an oxidation reagent. DDQ is an effective stoichiometric oxidation reagent and considered the 'Gold Standard' for chemical oxidants, however, polychlorinated phenol by-products are highly

Table 3. Reaction scope of the oxidation of various substrates using **1** and $[H(OEt_2)_2][BAr^F_4]$.



General conditions: 1 mmol of **1**, 1 mmol of **4**, 10 mol% $[H(OEt_2)_2][BAr^F_4]$ and 1 mL DCE heated at 90 °C for 12 h. Yields (of oxidation products) were determined by GC-MS (decane as internal standard), yields using DDQ as an oxidant are in parentheses for selected substrates. [a] Heated for 48 h.

Table 4. Transfer dehydrogenation of **9g** catalysed by H^+/(**1** or **2**).



Entry	Condition	Yield
1	**A**: 10 mol % **1**, 10 mol % $[H(OEt_2)_2][BAr^F_4]$	45%
2	**B:** 10 mol % **2**, 10 mol % $[H(OEt_2)_2][BAr^F_4]$	44%
3	**C**: No additives	< 1%

General conditions: 1 mmol of **1**, 1 mmol of **4g**, and 1 mL DCE heated at 90 °C for 16 h. Yields of **5g** were determined by GC-MS (decane as internal standard).

toxic, and DDQ is unstable in water, evolving hydrogen cyanide.

Transfer hydrogenation was optimized for the dehydrogenation of 1-methyl-1,4-cyclohexadiene (**4a**) to toluene (Table 2). Acids with pK_a^{aq} *ca* -2 (or lower) were found to be efficient at catalyzing the transfer hydrogenation, while trifluoroacetic acid (pK_a^{aq} = 0.23) performed poorly, with only 10% conversion after 20 h (Table 2, entries 11 and 12). The ability of many acids to catalyse the oxidation was found to be solvent dependent, which is somewhat expected given the solvent dependent nature of pK_a. This may account for the poor performance of sulfonates MsOH and *p*-TsOH in MeCN (Table 2, entries 6 and 10), and of trifluoroacetic acid (Table 2, entry12), given it has a relatively high pK_a in acetonitrile {pK_a^{MeCN} (TFA) = 12.65, *cf* pK_a^{MeCN} ($[HPPh_3]^+$) = 8.0}.[12] The poorer performance of entries 5-12 in Table 2 may also reflect the higher nucleophilicty of the conjugate bases for the acids used in these reactions, which is perhaps exemplified by the poorer performance of TfOH as compared to $[H(OEt_2)_2][BAr^F{}_4]$ (Table 2, entries 3,4,7 and 8) with alkyl triflates generally considered more stable than alkyl etherate oxonium salts.

A control reaction in the absence of acid gave no toluene product (Table 2, entries 1 and 2), ruling out a radical pathway as is seen with quinone type oxidants.

The optimized transfer hydrogenation protocol using **1** was extended to other hydrocarbons, alcohols and heterocycles (Table 3). Generally, **1** was outperformed by DDQ, however, the oxidation of **4c-e** to *para*-cymene was found to be much more effective using **1**. The combination of **1** and $[H(OEt_2)_2][BAr^F{}_4]$ was also able to dehydrogenate alcohols. It was found that this reaction competed with acid catalyzed dehydration of alcohols capable of forming stable carbocations. As such, in the case of substrate **4l**, loss of water led to 1,2-dihydronaphthalene as the dominant product, whereas substrate **4k** formed small amounts of anhydride products in addition to benzaldehyde as the major product.

The dehydrogenation could be performed catalytically in **1** or **2** when excess manganese oxide was employed (Table 4). No conversion was observed when **1** or **2** were absent (i.e. MnO_2 could not independently oxidise **4g** under these conditions). Such an approach has been previously reported using catalytic DDQ.[13] Under such conditions, it was found that yields were similar to when stoichiometric **1** was used. Given that $[\mathbf{3}]^+$ is suspected as the active catalyst, a more favorable comparison can be made when employing DDQ in catalytic amounts, with similar turn-over rates reported for the oxidation of hydrocarbons as is observed in Table 4.[13]

In conclusion, we have demonstrated the concept of formation of a stable, persistent Lewis acid from the combination of **1** and suitable Brønsted acids. The resultant Lewis acid $[\mathbf{3}]^+$ was found to facilitate oxidation reactions with a variety of hydrocarbons and alcohols.

Given the diverse reactions that trityl cations are known to partake in, it is hoped that in situ generated $[\mathbf{3}]^+$ may be employed as an easy to prepare trityl substitute for a range of catalyzed or stoichiometric reactions. This concept may also be extended to a range of other highly available precursors that are bench stable and able to form carbocation Lewis acids upon protonation (e.g. phenolphthalein, Fluorescein).

Experimental

All manipulations of air-sensitive compounds were carried out under a dry and oxygen-free nitrogen atmosphere using standard Schlenk and glove box techniques. Reactions were performed in a J. Young NMR tube or in a 4mL reaction vial with septum cap in a nitrogen atmosphere glovebox. Glassware were flame-dried under vacuum prior to use. All solvents, including deuterated NMR solvents were distilled, degassed and dried with calcium hydride before use. NMR spectra were recorded at 25 °C on Bruker Avance 400 MHz or Bruker AMX 500 MHz spectrometers. The chemical shifts (δ) for ^{1}H NMR and ^{13}C NMR spectra are given in ppm relative to residual signals of the solvent. All GC-MS studies were performed on an Agilent GC/MS (Agilent 7890A GC/Agilent 5975C MS) system. HRMS (ESI-TOF) spectra were obtained using an Agilent Technologies 6230 TOF. Commercially available chemicals were used as purchased. $[H(OEt_2)_2][BAr^F{}_4]$ ($[BAr^F{}_4]$ = $[B(C_6F_5)_4]$) was synthesised according to literature procedures.[14]

Synthesis of compound 1

1 was synthesised according to the literature procedure.[15] Data for **1** matched those reported. Yield 0.71 g, 72%. ^{1}H NMR (CD_2Cl_2): δ 7.43 (d, 4 H, *J* = 2.0 Hz), 7.41 (d, 2 H, *J* = 2.0 Hz), 7.25- 7.23 (m, 4 H), 7.19 (s, 2 H), 1.22 (s, 18 H). ^{13}C NMR (CD_2Cl_2): δ 186.6 (s, 1 C), 156.6 (s, 1 C), 147.9 (s, 2 C), 141.5 (s, 2 C), 132.5 (s, 2 C), 132.4 (s, 4 C), 130.4 (s, 1 C), 129.7 (s, 2 C), 128.6 (s, 4 C), 35.8 (s, 2 C), 29.8 (s, 6 C).

Synthesis of compound 2

2 was synthesised according to the literature procedure.[2] Data for **2** matched those reported. Yield 1.33 g, 70%. ^{1}H NMR (CD_2Cl_2): δ 7.30-7.26 (m, 4 H), 7.21-7.17 (m, 2 H) 7.14-7.12 (m, 4 H), 6.95 (s, 2 H), 5.43 (s, 1 H), 5.11 (s, 1 H), 1.36 (s, 18 H); ^{13}C NMR ($CDCl_3$): δ 152.1 (s, 1 C), 144.8 (s, 2 C), 135.4 (s, 2 C), 134.1 (s, 1 C), 129.4 (s, 4 C), 128.1 (s, 2 C), 126.1 (s, 4 C), 126.0 (s, 2 C), 56.8 (s, 1 C), 34.3 (s, 2 C), 30.3 (s, 6 C). *Crystal data for* $C_{27}H_{32}O_1$, *M* = 372.55, monoclinic, *C 2/c* (No. 15), *a* = 19.8182(11), *b* = 5.9878(3), *c* = 36.1268(17) Å, α = 90, β = 96.953(4), γ = 90°, *V* = 4255.5(2) Å^3, *Z* = 8, δ_{calc} = 1.163 Mgm^{-3}, μ(Cu Kα) = 0.517 mm^{-1}, *T* = 100(2) K, colourless block, 0.1 x 0.1 x 0.1 mm, 21,810 reflections collected, 3,766 unique data (2θ ≤ 133.4°), R_1 = 0.0557 [for 2,514 reflections with $I > 2\sigma(I)$], wR_2 = 0.1333 (all data), 253 parameters, S = 1.01.

Synthesis of compound $[\mathbf{3}][BAr^F{}_4]$

To a solution of compound **1** (0.020 g) in DCM or MeCN (0.5 mL) was added $[H(OEt_2)_2][BAr^F{}_4]$ (0.055 g). The orange solution turned red immediately. ^{1}H NMR showed the generation of $[\mathbf{3}]^+$ to be quantitative. Characterisation was performed directly on the DCM and MeCN solutions. Attempts to crystallise the title compound resulted only in biphasic solutions. ^{1}H NMR (CD_3CN): δ 9.23 (s (br), 1 H), 8.01 (t, 2 H, *J* = 7.0 Hz), 7.74 (t, 4 H, *J* = 7.0 Hz), 7.63 (s, 2 H), 7.52 (d, 4 H, *J* = 7.0 Hz), 1.40 (s, 18 H); ^{1}H NMR (CD_2Cl_2): δ 7.59 (t, 2 H, *J* = 7.3 Hz), 7.50 (t, 4 H, *J* = 7.3 Hz), 7.31 (d, 4 H, *J* = 7.3 Hz), 7.30 (s, 2 H), 6.40 (s, (br, 1 H), 1.28 (s, 18 H); ^{13}C NMR (CD_3CN): δ 199.1 (s, 1 C), 174.5 (s, 1 C), 149.1 (d (br), 8 C, *J* = 237.7 Hz), 145.0 (s, 2 C), 141.8 (s, 1 C), 140.6 (s, 2 C), 139.9 (s, 4 C), 139.3 (d (br), 4 C, *J* = 241.3 Hz), 139.1 (s, 2 C), 137.3 (d (br), 8 C, *J* = 244.7 Hz), 134.4 (s, 1 C), 130.3 (s, 4 C), 35.6 (s, 2 C), 29.7 (s, 6 C); ESI-TOF-MS (*m/z*): 371.2362 (calc. for $C_{27}H_{31}O$, 371.2375).

Preparation of [3][B(3,5-$(CF_3)_2C_6H_3)_4$] for crystallographic study

To a solution of [**3**][B(3,5-$(CF_3)_2C_6H_3)_4$] in DCM, prepared as above for [**3**][BAr^F_4], hexane was added slowly to form a layered sample. Slow diffusion at room temperature afforded crystals suitable for an X-ray diffraction study. ^{1}H NMR (CD_2Cl_2): δ 8.03 (t, 2 H, J = 7.5 Hz), 7.76 (t, 4 H, J = 7.5 Hz), 7.74 (s, 8 H), 7.63 (s, 2 H), 7.57 (s, 4 H), 7.51 (d, 4 H, J = 7.5 Hz), 5.34 (s, 1 H – shoulder on DCM signal), 1.48 (s, 18 H); ^{13}C NMR (CD_2Cl_2): δ 199.5 (s, 1 C), 173.6 (s, 1 C), 162.4 (q, 4 C, J_{BC} = 50.0 Hz), 144.0 (s, 4 C), 141.6 (s, 2 C), 139.9 (s, 2 C), 139.6 (s, 4 C), 139.5 (s, 8 C), 135.4 (s (br), 8 C), 134.1 (s, 1 C), 130.3 (s, 8 C), 129.5 (q, 8 C, J_{FC} = 50.0 Hz), 126.3 (s, 2 C), 124.1 (s, 2 C), 118.1 (s, 4 C), 35.4 (s, 2 C), 30.0 (s, 6 C). *Crystal data for* $C_{60}H_{45}B_1Cl_2F_{24}O_1$, M =1319.68, triclinic, P-1 (No. 2), a = 13.181(3), b = 13.877(3), c = 16.365(4) Å, α = 101.985(7), β = 96.122(7), γ = 90.289(8)°, V = 2910.5(6) Å^3, Z = 2, δ_{calc} = 1.506 Mgm^{-3}, μ(Mo Kα) = 0.230 mm^{-1}, T = 100(2) K, orange block, 0.1 x 0.1 x 0.1 mm, 56,248 reflections collected, 12,872 unique data (2θ ≤ 55°), R_1 = 0.0543 [for 8,005 reflections with $I > 2\sigma(I)$], wR_2 = 0.1388 (all data), 793 parameters, S = 0.94.

Preparation of [3][H(OTf)$_2$] for crystallographic study

To a solution of **1** (0.10 g) in DCM (3 mL) was added TfOH (0.2 mL). Hexane (6 mL) was added to the resulting solution to precipitate the product. Excess solvent was cannula decanted and the resulting red solid was dissolved in DCM (2 mL) and layered with hexane. Slow diffusion at room temperature afforded crystals of [**3**][H(OTf)$_2$] suitable for a X-ray diffraction study. Yield 0.05 g, 28%. *Crystal data for* $C_{29}H_{32}F_6O_7S_2$, M = 670.69, triclinic, P-1 (No. 2), a = 9.7072(15), b = 9.9398(16), c = 18.474(3) Å, α = 79.874(5), β = 83.488(5), γ = 61.399(4)°, V = 1539.7(2) Å^3, Z = 2, δ_{calc} = 1.447 Mgm^{-3}, μ(Mo Kα) = 0.254 mm^{-1}, T = 100(2) K, red block, 0.1 x 0.1 x 0.1 mm, 21,729 reflections collected, 5,422 unique data (2θ ≤ 50°), R_1 = 0.0663 [for 3,121 reflections with $I > 2\sigma(I)$], wR_2 = 0.1300 (all data), 397 parameters, S = 1.00.

General Procedure for optimisation of oxidation reactions with various acids

To an oven-dried 4 mL glass vial in a glove box was added solvent (1 mL), **4a** (1 mmol), **1** (1 mmol) and acid (10 mol %). The reaction was heated for 11-20 hours. The reaction mixture was then washed with CH_2Cl_2 to a 5 mL volumetric flask, followed by extraction of a 1 mL aliquot for GCMS analysis. The conversion of **4a** was determined by the integral ratio of **4a** and the product (**5a**) relative to the internal standard.

General Procedure for the oxidation reactions

To an oven-dried 4 mL glass vial in a glove box was added 1,2-dichloroethane (1 mL), substrate (**4a-l**) (1 mmol), **1** (1 mmol) and [$H(OEt_2)_2$][BAr^F_4] (10 mol %). The reaction was heated for 12 hours. The reaction mixture was then washed with CH_2Cl_2 to a 5 mL volumetric flask, followed by extraction of a 1 mL aliquot for GCMS analysis. The conversion of substrate was determined by the integral ratio of substrate and the product relative to the internal standard.

General Procedure for the oxidation of dihydroanthracene with MnO_2 and catalytic acid, and 1 or 2.

To an oven-dried 4 mL glass vial in a glove box was added 1,2-dichloroethane (1 mL), substrate (**4g**) (1 mmol), MnO_2 (6 equiv.), and additives according to conditions **A**-**C** (see below). The reaction was heated for 16 hours. The reaction mixture was then washed with CH_2Cl_2 to a 5 mL volumetric flask, followed by extraction of a 1 mL aliquot for GCMS analysis. The conversion of substrate was determined by the integral ratio of substrate and the product relative to the internal standard.

Condition **A**: 10 mol % **1**, 10 mol % [$H(OEt_2)_2$][BAr^F_4]
Condition **B**: 10 mol % **2**, 10 mol % [$H(OEt_2)_2$][BAr^F_4]
Condition **C**: No additives

Procedure for the reaction of [3][BAr^F_4] with PPh_3

To an oven-dried J. Young's NMR tube in a glove box was added dichloromethane-d2 (0.5 mL), **1** (0.03 mmol) and [$H(OEt_2)_2$][BAr^F_4] (0.03 mmol). The reaction NMR tube was first subjected to screening of the initial ^{1}H spectrum. One equivalent of PPh_3 was then added to the NMR tube, the tube was shaken repeatedly over a few minutes, and then the samples were analysed by ^{1}H and ^{31}P NMR spectroscopy. Excess 2,6-lutidine was added to the tube to regenerate PPh_3 and **1**.

ASSOCIATED CONTENT

The Supporting Information, including NMR spectra and molecular structures of **2**, [**3**][BAr^F_4] and [**3**][H(OTf)$_2$], is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

Corresponding Author

*rowan.young@nus.edu.sg

Note: The authors declare no competing financial interest.

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