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Introduction

The transition metal catalyzed aromatic coupling reactions preceded by oxidative C–H bond activation constitute an extremely valuable synthetic tool in modern chemistry.^{1,2} Most prevalent are the Pd-, Cu-, and FeCl₃-catalyzed reactions which have been successfully used to synthesize a number of fascinating and useful compounds.³ Along with routinely used reagents, new oxidizers have been introduced, such as *e.g.* MoCl₅,⁴ CoF₃,⁵ TiCl₄,⁶ iodonium(III) salts,⁷ (H₃C)ReO₃,⁸ the environmentally friendly H₂O₂/peroxidase-catalyst system,⁹ and highly toxic Hg(II), Tl(III) or Pb(IV) reagents. These methods usually require prefunctionalization

Reconnaissance of reactivity of an Ag(II)SO₄ one-electron oxidizer towards naphthalene derivatives†

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We test divalent silver sulphate, Ag(II)SO₄ as a novel reagent for oxidative coupling of aromatic hydrocarbons under ambient temperature conditions. The applicability of the $C(sp^2)-C(sp^2)$ coupling protocol is illustrated for naphthalene and its 1-substituted derivatives containing either electron donating (e.g. Me, MeO, or Ph) or electron-withdrawing groups (X = F···I), leading to 4,4'-disubstituted-1,1'-binaphthyls. Coupling of 2-bromo-naphthalene yields a mixture of 2,2'-, 2,7'-, and 7,7'-dibromo-1,1'-binaphthyls together with their trimeric and tetrameric analogues. The coupling of strongly electron-withdrawing 1-CF₃-naphthalene provides the 5,5'-disubstituted-1,1'-binaphthyl derivative. The new method does not require the presence of halogen substituents, in contrast to most of the known C-C coupling methods, and it preserves them, if present. Ag(II)SO₄ may be easily electrochemically regenerated from the Ag(I)HSO₄ byproduct. However, the C-C coupling method currently suffers from low yields, up to 17%, and it requires further optimization.

of the organic substrate; also, it is not uncommon to find demanding substrates that are incompatible with the published procedures.¹⁰

The Cu-based reactions are inexpensive and thus attractive for large industrial-scale reactions.¹¹ An interesting example of a recently reported copper-based aromatic coupling protocol without prior functionalization of substrates is the Hirano-Miura reaction;¹² this method has been successfully applied for various substrates,¹³ but it proceeds at elevated temperature, T > 180 °C, as typical for Cu-based methods. Silver, a heavier analogue of copper, has been traditionally used for the coupling reactions involving only the acetylide C(sp) fragment, since Ag(1) readily forms acetylide complexes. Also, the 2-electron Ag(III)/ Ag(1) redox pair has recently been applied for cross-coupling reactions.¹⁴ However, the potential of the 1-electron $Ag(\pi)/Ag(\pi)$ redox pair has not yet been properly explored in organic chemistry¹⁵ and that is mainly due to the very high oxidizing power of Ag(II), which is not compatible with an aqueous environment ($E^0 \approx +2 \text{ V} \nu s$. normal hydrogen electrode).¹⁶ Thus, Ag(II) has only been used as a short-lived redox-intermediate in combination with peroxodisulphate oxidizers, the respective reactions leading to oxidation rather than C-C coupling of reagent molecules.¹⁷ On the other hand, reactions involving AgF_2 and other fluoro $Ag(\pi)$ species lead to partial or exhaustive fluorination of organic compounds.18



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Scheme 1 $Ag(n)SO_4$ -based C-C coupling reactions involving naphthalene and its derivatives.

Here we attempt to expand the family of inorganic substrates used for aromatic coupling reactions by applying a powerful $Ag(\pi)SO_4$ oxidizer as a substrate; $Ag(\pi)SO_4$ is a unique example of a divalent silver compound containing a fluorine-free anion.¹⁹ For reconnaissance of the $Ag(\pi)SO_4$ C–H activation capability and to illustrate the most fundamental features of the method we have initially chosen naphthalene and a set of its 1-substituted derivatives, which contain selected electron donating (MeO, Me, Ph) or withdrawing groups (F, Cl, Br, I, CF₃, CN, NO₂) (Scheme 1). The targeted products – homochiral 1,1'-binaphthyl derivatives – have been utilized in the past as chiral auxiliaries and/or inducers for highly stereoselective reactions because of their axial asymmetry and molecular flexibility.^{20,21}

Results and discussion

Due to the lack of solubility of $Ag(n)SO_4$ in common organic solvents the reactions proceed initially at the solid–liquid interphase. Selection of an appropriate liquid medium is not trivial due to the high reactivity of the inorganic substrate. During a preliminary screening of reaction conditions we have found out that selectivity of reactions as well as their speed and yield increase when lower aliphatic or alicyclic hydrocarbons are substituted by hexafluoroisopropyl alcohol, HFIPA (F₆-i-PrOH). This polar solvent is known to stabilize organic radical cations,²² and also facilitates the 1e⁻ and proton-transfer heterophasic reactions.²³ The herein reported procedure applied to R = H, F,

Cl, Br, I, MeO, Me, and Ph gives the corresponding 4,4'disubstituted-1,1'-binaphthyls (1-8) with rather small yields $(\sim 10\%)$ (Scheme 1 and Table S3 in the ESI[†]) albeit under milder temperature conditions as compared to the relevant Cu(II)-based Hirano-Miura reaction.¹² The 1,1'-binaphthyls formed from pristine naphthalene (X = H), as well as for X = F, Cl, Br, I, Me, OMe, and Ph, trace amounts of ternaphthyl derivatives (unknown isomers, 11, 12) have also been detected in the post-reaction mixture using the GC/MS technique for X = H and F, respectively, thus showing that the formation of oligomeric species using this method is in principle possible. The identity of the products was confirmed using X-ray diffraction on single crystals. In the case of H, MeO, Me and Br substituents, we have confirmed the previously published structures.²⁴ However, for 2, 3, and 5 with electron-withdrawing substituents and for 8, their crystal structures were determined here for the first time (Table 1).

The organic products, formed from $(R-H)^{*+}$, R^{\bullet} in the course of reactions, remain in the solution, and they may be easily separated using extraction and preparative thin-layer chromatography, their chemical identity being confirmed using ¹H, ¹³C, ¹⁹F and ¹H νs . ¹³C HSQC NMR spectra, and IR spectrometry (ESI⁺), as well as single crystal X-ray crystallography – see Table 1. The complete structural and spectroscopic characteristics of all products will be described in a separate contribution.

Cross-coupling compatible with the presence of halogens in the aromatic ring has previously been revealed by Kita and co-workers.⁷ We have also attempted several cross-coupling reactions using mixtures of two different 1-halogenonaphthalenes (**9–10**); GC/MS analysis clearly shows the presence of the cross-coupled products in addition to the homo-di-halogenated ones (ESI†); however, the separation of the products is troublesome due to their similar retention times, and all products co-crystallize while forming mixed crystals (ESI†).

In the case of 1-trifluoromethylnaphthalene, an aromatic system with a very strongly electron withdrawing substituent, C-C coupling proceeds, as expected, with very low yield ($\sim 1.5\%$), but it leads to 5,5'- (13) rather than the 4,4'-disubstituted-1,1'binaphthyl derivative (Fig. 1). This turns out to be the first structurally characterized 5,5'-disubstituted-1,1'-binaphthyl, since the multi-step method published so far leads to the 4,4'-substituted derivative as a side product (26% yield) of Grignard synthesis on the Br-preactivated substrate.²⁵ The ring-deactivating influence of the CF₃ substituent clearly shifts reactivity to the adjacent aromatic ring in the Br-free molecule, as seen in the Ag(II)SO₄-based synthetic protocol. It turns out that the reaction yield may be increased to 17% by using nitromethane as a reaction medium. Despite the still unsatisfactory yield, formation of 13 constitutes an improvement over the previously used methods since 1-trifluoromethylnaphthalene could not so far be activated to form a C-C coupled product. In the case of a 1-cyano substituted substrate, the yield of the C-C coupling was even lower than for the CF₃ one (regardless of the solvent), as evidenced by GC/MS, and the corresponding binaphthyl product (14) could not be isolated. Finally, for $R = NO_2$ the reaction did not proceed to any detectable extent, which shows that even stronger oxidizers may be needed to prepare 15.

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Identification code Composition	$2 C_{20}H_{12}F_2$	$\frac{3}{\mathrm{C}_{20}\mathrm{H}_{12}\mathrm{Cl}_2}$	$\frac{4}{C_{20}H_{12}Br_2}$	$\frac{5}{C_{20}H_{12}I_2}$	8 C ₃₂ H ₂₂	$13 C_{22}H_{12}F_6$	$22 C_{20}H_{12}Br_2$
M/g 11101 7/K 27Å	290.30 100(2) 0 71073	323.20 100(2) 0.71072	$\frac{412.12}{100(2)}$	306.10 100(2) 0.71073	400.49 100(2) 154170	390.32 100(2) 0.71072	$^{412.12}_{100(2)}$
Ara Size [mm]	0.094	0.086	0.156	0.018	0.014	0.214	0.126
	0.303 0.342	0.129 0.414	0.197 0.477	0.231 0.355	0.243 0.323	0.407 0.422	0.161 0.239
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic _{Di}
Unit cell parameters/å, °	a = 12.4551(9)	a = 13.1656(10)	a = 13.6190(7)	a = 27.406(3)	a = 10.1208(4)	a = 13.6675(11)	a = 7.3184(5)
	b = 10.6234(8) c - 11.1004(9)	b = 10.6206(8) c = 11.2471(0)	b = 10.5374(6) c = 11.4528(6)	b = 6.3564(6) c - 0 = 5554(0)	b = 25.0267(10) c = 22.4207(14)	b = 8.1974(7) c = 14.0821(10)	b = 12.8258(9) c - 18.0770(13)
	$\beta = 115.4835(16)$	$\beta = 115.0519(18)$	$\beta = 115.2950(10)$ $\beta = 115.2950(10)$	$\beta = 106.7452(17)$	$\beta = 92.0165(13)$	$\beta = 90.5433(19)$	$\alpha = 100.369(2)$
							$\beta = 90.011(2)$ $\gamma = 102.874(2)$
$V \left[{ m \AA}^3 ight]$	1336.49(17)	1424.70(19)	1485.99(14)	1594.0(3)	8464.6(6)	1678.6(2)	1551.16(19)
$Z, D_x/g \text{ cm}^{-3}$	4, 1.443	4, 1.507	4, 1.842	4, 2.109	16, 1.276	4, 1.544	4, 1.765
$\mu [\text{mm}^2]$	0.102	0.447 664	5.448 202	3.939 057	0.547 3474	0.136 707	5.219 808
$\theta_{min}, \theta_{max}$	$3.62^{\circ}, 25.49^{\circ}$	$3.42^{\circ}, 26.00^{\circ}$	2.54° , 26.42°	$3.11^{\circ}, 25.05^{\circ}$	$2.21^{\circ}, 64.97^{\circ}$	$2.98^{\circ}, 25.05^{\circ}$	$2.40^{\circ}, 25.42^{\circ}$
Index ranges	$-13 \leq h \leq 15$	$-16 \leq h \leq 16$	$-17 \leq h \leq 15$	$-11 \leq h \leq 11$	$-11 \leq h \leq 11$	$-16 \leq h \leq 16$	$-8 \le h \le 8$
	$-12 \leq k \leq 12$	$-13 \leq k \leq 13$	$0 \leq k \leq 13$	$-7 \leq k \leq 7$	$0 \leq k \leq 29$	$-9 \leq k \leq 9$	$-15 \leq k \leq 14$
Reflections collected/independent	$-13 \le l \le 13$ 5379/1239	$-13 \le l \le 13$ 11706/1403	$0 \le l \le 14$ 16534/1536	$-31 \le l \le 31$ 10 852/1416	$0 \le l \le 39$ 105660/14332	$-1/ \le l \le 1/$ 23 667/2958	$0 \le l \le 21$ 31460/5699
	$[R_{\rm int}=0.0210]$	$[R_{\rm int}=0.0291]$	$[R_{\rm int}=0.0313]^a$	$[R_{\rm int}=0.0379]$	$[R_{\rm int}=0.0762]^b$	$[R_{\rm int}=0.0218]$	$[R_{\rm int}=0.0326]^c$
Completeness/%	99.7	6.66	100.0	99.9	9.66	99.8	8.66
T _{max} , T _{min} Data/restraints/narameters	0.990, 0.966 1239/0/101	0.963, 0.836 1403/0/100	0.484, 0.181 1536/0/100	0.932, 0.335 1416/0/100	0.990, 0.9400 14332/0/1154	0.972, 0.945 2958/0/254	0.559, 0.369 5600/0/308
$Goof on F^2$	1.061	1.077	1.167	1.104	1.087	1.075	1.089
$R\left[I > 2\sigma(I)\right]$	1137 data	1228 data	1400 data	1045 data	8319 data	2651 data	5121 data
	$R_1 = 0.0346$	$R_1 = 0.0331$	$R_1 = 0.0303$	$R_1 = 0.0205$	$R_1 = 0.0694$	$R_1 = 0.0303$	$R_1 = 0.0316$
n (n) doto)	$WR_2 = 0.0979$ $D_2 = 0.0278$	$wR_2 = 0.0786$ $p_1 - 0.0406$	$WR_2 = 0.0791$ $D_2 = 0.0255$	$WR_2 = 0.0476$ $D_2 = 0.0243$	$wR_2 = 0.1648$ $p_1 - 0.1007$	$wR_2 = 0.0746$ $p_1 - 0.0257$	$wR_2 = 0.0631$
A (all uata)	$W_1 = 0.0010$ WR ₂ = 0.1010	$M_1 = 0.031$ WR ₂ = 0.0831	$W_1 = 0.0812$ $WR_2 = 0.0812$	$W_1 = 0.0538$ $WR_2 = 0.0538$	$W_1 = 0.2076$ WR ₂ = 0.2076	$wR_2 = 0.0788$	$w_1 = 0.0664$ $w_2 = 0.0664$
Extinction coefficient	0.0059(16)	a 	a 	a 	0.00019(3)	0.0059(8)	a
$\rho_{\rm max}$, $\rho_{\rm min}/{\rm e}~{ m \AA}^{-3}$	0.353, -0.187	0.288, -0.229	0.600, -0.419	0.538, -0.349	0.318, -0.269	0.228, -0.220	0.751, -0.396

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Table 1 Crystal data and structural refinement parameters for obtained crystals

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Table 1 (continued)

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	Br	F/Cl mixture crystal I	F/Cl mixture crystal II	F/Br mixture crystal I in <i>C</i> 2	F/Br mixture crystal I in <i>C</i> 2/ <i>c</i>	F/Br mixture crystal II in <i>C</i> 2	F/Br mixture crystal II in C2/c
Identification code	23	9-1	9-2	10-1 in C2	10-1 in C2/c	10-2 in C2	10-2 in C2/c
Composition	$\mathrm{C_{20}H_{12}Br_2}$	$C_{20}H_{12}Cl_{0.33}F_{1.67}$	$C_{20}H_{12}Cl_{0.33}F_{1.67}$	$\mathrm{C}_{40}\mathrm{H}_{24}\mathrm{Br}_{0.55}\mathrm{F}_{3.45}$	$ m C_{20}H_{12}Br_{0.28}F_{1.72}$	$ m C_{40}H_{24}Br_{0.57}F_{3.43}$	$C_{20}H_{12}Br_{0.29}F_{1.71}$
$M/g/mol^{-1}$	412.12	295.68	295.68	614.09	307.50	615.31	307.96
T/K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
$\lambda/\dot{\mathbf{A}}$	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Size [mm]	0.072	0.128	0.101	0.076	0.076	0.106	0.106
	0.118	0.320	0.215	0.145	0.145	0.278	0.278
	0.377	0.596	0.431	0.395	0.395	0.423	0.423
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$Pca2_1$	C2/c	C2/c	C2	C2/c	C2	C2/c
Unit cell parameters/Å, $^{\circ}$	a = 16.4376(11)	a = 12.6621(9)	a = 12.6399(11)	a = 12.6575(11)	a = 12.6575(11)	a = 12.6657(10)	a = 12.6657(10)
	b = 12.9727(9)	b = 10.6518(8)	b = 10.6517(9)	b = 10.6532(9)	b = 10.6532(9)	b = 10.6594(9)	b = 10.6594(9)
	c = 7.2813(5)	c = 11.1730(8)	c = 11.1760(10)	c = 11.1899(10)	c = 11.1899(10)	c = 11.1921(9)	c = 11.1921(9)
		$\beta = 115.065(2)$	$\beta = 115.128(2)$	$\beta = 115.098(2)$	$\beta=115.098(2)$	$\beta = 115.080(2)$	$\beta=115.080(2)$
$V[\check{A}^3]$	1552.66(18)	1365.04(17)	1362.3(2)	1366.4(2)	1366.4(2)	1368.57(19)	1368.57(19)
Z , $D_x/g \text{ cm}^{-3}$	4, 1.763	4, 1.439	4, 1.442	2, 1.493	4, 1.495	2, 1.493	4, 1.495
$\mu [\mathrm{mm}^{-1}]$	5.214	0.160	0.160	0.901	0.922	0.928	0.943
F(000)	808	610	610	629	629	630	630
$\theta_{\min}, \ \theta_{\max}$	$2.48^\circ,25.04^\circ$	$2.61^\circ,25.03^\circ$	$2.61^\circ,25.04^\circ$	$2.61^\circ,26.42^\circ$	$2.61^\circ, 26.42^\circ$	$2.61^\circ,26.43^\circ$	$2.61^\circ, 26.43^\circ$
Index ranges	$-19 \le h \le 19$	$-15 \leq h \leq 15$	$-15 \leq h \leq 14$	$-15 \leq h \leq 15$	$-15 \leq h \leq 15$	$-15 \le h \le 15$	$-15 \le h \le 15$
	$-15 \leq k \leq 15$	$-12 \leq k \leq 12$	$-12 \leq k \leq 12$	$-13 \le k \le 13$	$-13 \leq k \leq 13$	$-13 \le k \le 13$	$-13 \le k \le 13$
	$-8 \le l \le 8$	$-13 \le l \le 13$	$-13 \leq l \leq 13$	$-13 \leq l \leq 13$	$-13 \leq l \leq 13$	$-13 \le l \le 13$	$-13 \le l \le 13$
Reflections collected/independent	20544/2739	8166/1207	7056/1206	10 738/2812	10373/1407	10514/2815	10163/1408
	$[R_{ m int} = 0.0244]$	$[R_{\text{int}} = 0.0190]$	$[R_{\rm int} = 0.0187]$	$[R_{ m int}=0.0242]$	$[R_{ m int} = 0.0256]$	$[R_{\text{int}} = 0.0328]$	$[R_{ m int} = 0.0345]$
Completness/%	99.8	100.0	100.0	6.66	100.0	2.66	99.8
T_{\max}, T_{\min}	0.705, 0.244	0.980, 0.911	0.984, 0.934	0.935, 0.717	0.933, 0.712	0.908, 0.695	0.907, 0.691
Data/restraints/parameters	2739/1/199	1207/0/110	1206/0/110	2812/2/220	1407/0/110	2815/1/220	1408/0/110
GooF on F	1.082	1.100	1.113	1.034	1.325	1.067	1.243
$R \left[I > 2\sigma(I) \right]$	2616 data	1102 data	1099 data	2359 data	1246 data	2382 data	1259 data
	$R_1 = 0.0170$	$R_1 = 0.0318$	$R_1 = 0.0320$	$R_1 = 0.0344$	$R_1 = 0.0515$	$R_1 = 0.0359$	$R_1 = 0.0473$
	$wR_2 = 0.0421$	$WR_2 = 0.0859$	$WR_2 = 0.0852$	$wR_2 = 0.0761$	$WR_2 = 0.1004$	$wR_2 = 0.0901$	$wR_2 = 0.0981$
R (all data)	$R_1 = 0.0182$	$R_1 = 0.0361$	$R_1 = 0.0357$	$R_1 = 0.0474$	$R_1 = 0.0594$	$R_1 = 0.0451$	$R_1 = 0.0529$
	$WR_2 = 0.0426$	$WR_2 = 0.0890$	$WR_2 = 0.0880$	$WR_2 = 0.0815$	$WR_2 = 0.1026$	$WR_2 = 0.0938$	$WR_2 = 0.0997$
Absolute structure parameter	0.010(4)	Ι	Ι	$0.5(0)^{a}$	Ι	$0.2(0)^e$	Ι
$\rho_{\rm max}$, $\rho_{\rm min}/{\rm e}~{\rm \AA}^{-3}$	0.432, -0.179	0.236, -0.145	0.210, -0.129	0.177, -0.152	0.183, -0.175	0.199, -0.162	0.196, -0.178
^a Two component twin with HKLF4 re	efinement with the twi	n fraction during scalin	e heine equal to 0.275	$2:0.7248.^{b}$ Two comp	onent twin with HKLF	5 refinement and subs	equent merging of

¹ we component with with right are remement with the twin traction during scaling being equal to 0.2752 :0.7248. ^a Two component twin with HKLF5 refinement and subsequent merging of the same index reflections, with the twin fraction during scaling being equal to 0.2038 :0.7962. ^a Two component twin with HKLF5 refinement and subsequent merging of to 0.4562 :0.5438. ^d Crystal refined as the inversion twin with component fractions being equal to 0.530(28) :0.470(28). ^e Crystal refined as the inversion twin with component fractions being equal to 0.630(28) :0.470(28). ^e Crystal refined as the inversion twin with component fractions being equal to 0.630(28) :0.470(28). ^e Crystal refined as the inversion twin with component fractions being equal to 0.630(28) :0.470(28). ^e Crystal refined as the inversion twin with component fractions being equal to 0.630(28) :0.470(28). ^e Crystal refined as the inversion twin with component fractions being equal to 0.630(28) :0.470(28). ^e Crystal refined as the inversion twin with component fractions being equal to 0.630(28) :0.470(28). ^e Crystal refined as the inversion twin with component fractions being equal to 0.630(28) :0.470(28). ^e Crystal refined as the inversion twin with component fractions being equal to 0.600(20) :0.198(29).



Fig. 1 Thermal ellipsoid plot drawn at the 50% probability level for crystal structure of $\mathbf{13}$. CF₃ groups are labelled for clarity.

Interestingly, 2-halogenoaphthalenes react under the same conditions with the formation of a mixture of 2,2'-, 2,7'-, and 7,7'-dihalogeno-1,1'-binaphthyls (16–24) together with trace amounts of their trimeric (25–27) and even tetrameric analogues (28), as evidenced from ESI-TOF spectra (ESI†). The crystal structures of 22 and 23 were determined for the first time and will be focused on elsewhere.

Tentative reaction mechanism and attempts of yield improvement

Given the low yields, we have attempted to gain preliminary insight into the reaction mechanism, so that the reaction conditions could be further judiciously optimized.

It turns out that the first steps of reaction, connected with the formation of deeply-coloured organic radical-cations, and discoloration of black Ag(π)SO₄, proceeds immediately at room temperature and even at -35 °C in most cases, which suggests the presence of an intrinsically low barrier for the electron-transfer reaction, eqn (1):

$$R-H + Ag(II)SO_4 \rightarrow (R-H)^{\bullet^+} + Ag(I)SO_4^-$$
(1)

The small barrier for electron transfer reaction described by eqn (1) is consistent with the large electron affinity of the surface of Ag(II)SO₄ crystallites. Our preliminary screening of organic reagents with diverse ionization potentials (not shown) has indicated that the electron affinity of $Ag(\pi)SO_4$ is at least 9.3 eV, which is quite large as compared to that of common organic electron acceptors, such as TCNQ (4.8 eV), TCNE (2.9-3.2 eV), or F_4 -TCNQ (5.2 eV). This means that the giant electron affinity of the naked Ag(2+) cation in the gas phase (21.5 eV) is reduced to about 43% of its value due to ligation by SO_4^{2-} Lewis bases. Still, what remains suffices for electron transfer reactions with aromatics. It is quite likely that given the large difference of ionization potential of organic molecules studied (e.g. naphthalene 8.14 eV, 1-F-naphthalene 8.15 eV, 2-F-naphthalene 8.23 eV, etc.) and electron affinity of $AgSO_4$ (>9.2 eV) the reaction (eqn (1)) proceeds via the outer sphere mechanism when an organic molecule approaches the surface of AgSO₄. In any case, the radical-cations formed, (R-H)++, are deeply coloured, as observed

previously for the naphthalene derivatives (*e.g.*, orange-brown in nitromethane, purple in $(CF_3)_3COH$, *etc.*; for the $-C \equiv CH$ derivative we have observed a faint green colour of the solution but no product could be isolated).

Given the electron-transfer character of the first step of reaction (eqn (1)), one might try to influence its fate by using solvents of large dielectric constants; HFIPA ($\varepsilon = 17.8$) and NM ($\varepsilon = 35.9$) certainly count as such and the yields in these solvents were much higher than those in nonpolar cyclohexane ($\varepsilon = 2.0$). Further improvement would require the use of *N*-methylacetamide ($\varepsilon = 170$) or *N*-methylformamide ($\varepsilon = 182.4$) but, regretfully, these solvents are readily oxidized by Ag(π)SO₄.

Analysis of the white solid residue using powder X-ray diffraction and IR spectroscopy has showed that $Ag(I)HSO_4$ is the solid by-product of the reaction; this suggests that a subsequent proton transfer reaction must take place, eqn (2):

$$(\mathbf{R}-\mathbf{H})^{\bullet^+} + \mathrm{Ag}(\mathbf{I})\mathrm{SO}_4^- \to \mathbf{R}^{\bullet} + \mathrm{Ag}(\mathbf{I})\mathrm{HSO}_4$$
(2)

Indeed, we have observed that if reactions are conducted in $(CF_3)_3COH$ (which is more (Brønsted) acidic than $(CF_3)_2C(H)OH$, by 4 orders of magnitude in pK_a values) the reaction yields are usually even smaller than for $(CF_3)_2C(H)OH$ solvent. On the other hand, some improvement of the reaction yield may be achieved in selected cases when using nitromethane (NM) as a solvent; note that NM is 2 orders of magnitude less acidic than $(CF_3)_2C(H)OH$. Taken together this suggests that proton transfer is an important step in the overall reaction cycle. Consequently, we have attempted to influence the equilibrium of this reaction stage by adding Lewis bases (such as amines or fluorinated amines) to the reaction mixture; regretfully, most Lewis bases are not capable of withstanding the presence of $Ag(n)SO_4$ and the reaction yields could not be improved.

Given the chemical nature of the main reaction products, the simplified overall reaction of the oxidative dehydrodimerization may be written as:

$$2R-H + 2Ag(II)SO_4 \rightarrow R-R + 2Ag(I)HSO_4$$
(3)

Importantly, $Ag(II)SO_4$ may be easily regenerated from $Ag(I)HSO_4$ via electrolysis with ~70% current yield:^{26,27}

$$2Ag(I)HSO_4 \rightarrow H_2 + 2Ag(II)SO_4 \tag{4}$$

Eqn (1) might suggest that Ag(n) is a substrate of the reaction; however, since it may be regenerated (eqn (3)) it rather becomes a redox mediator, and the overall reaction cycle ((3) + (4)) corresponds jointly to:

$$2R-H \rightarrow R-R + H-H \tag{5}$$

The process described by eqn (5) is thermodynamically uphill for naphthalene ($\Delta H^{\circ} \approx +280 \text{ kJ mol}^{-1}$, $\Delta G^{\circ} \approx +240 \text{ kJ mol}^{-1}$), and its derivatives, but reactions (1)–(3) are jointly downhill in free energy, while only eqn (4) requires energy input.

Synthetic procedures

 $AgSO_4$ was obtained as described in the literature.^{19,27} A typical synthetic procedure is as follows: 2 mmol of $Ag(II)SO_4$

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(2-fold excess) was added to 1 mmol of naphthalene dissolved in 10 ml of HFIPA at room temperature. After 72 h the resulting dark mixture was evaporated using a rotary evaporator. The residue was washed with hexane (2 × 5 ml) and methylene chloride (2 × 5 ml) and evaporated again. The crude product was then dissolved in 2 ml of methylene chloride and purified on a preparative silica gel TLC plate using hexane as the eluent. The products were obtained by collecting the appropriate phases and subsequent removal of the solvent under reduced pressure. The purity and physicochemical properties of the product were investigated using the tandem GC/MS technique, and ¹H, ¹³C, ¹⁹F and ¹H ν s. ¹³C HSQC NMR & IR spectra (ESI†). The crystal structures of the products were determined using single-crystal XRD, with the help of the software and procedures described in ref. 28.

Four investigated crystals obtained after cross-coupling reactions involving F/Cl and F/Br substituted naphthalene derivatives are disordered and contain non-integer numbers of halogen atoms. This is due to the co-crystallization of F/Cl and F/Br reaction products in a non-stoichiometric ratio to form mixed crystals. During the structural refinement of the mixed crystals the position and anisotropic temperature factors for all non-H atoms were refined. The occupancy ratio of F/Cl or F/Br atoms was free to refine. To check if this ratio was preserved in the solid phase we measured two different crystals for both cross-coupling reactions. Crystals (9) and (10) correspond to F/Cl and F/Br samples respectively. In the case of F/Br mixed crystals we observed possible lowering of the space group symmetry from C2/c to chiral C2. For a better comparison we present both refinements for each crystal of (10) [(10-1 in C2), (10-1 in C2/c), (10-2 in C2) and (10-2 in C2/c)]. When applying the chiral C2 symmetry the crystals appeared to be twinned by inversion. The twin component ratios were refined to be 0.53(3) and 0.47(3) and 0.80(3) and 0.20(3) for (10-1 in C2) and (10-2 in C2) crystals respectively. Indeed, better structural refinement parameters in the chiral space group comparable to the centrosymmetric C2/c choice and the statistically significant component ratio definitely far from 0.5 for (10-2 in C2) suggests the lowering of the symmetry in mixed F/Br crystals. All the mixed crystals can be considered as isostructural with (2), (3), and (4) with molecules located on a 2-fold axis. In the F/Br crystals refined in the C2 space group the asymmetric part of the unit cell contains, however, two halves of the organic molecule. The presence of the binaphthyl derivative on the special symmetry suggests that the reaction products are homo-halogens. One should have in mind, however, that mixed coupling products in the solid state may imitate higher symmetry using substitutional disorder. Larger and elongated thermal ellipsoids of C atoms in mixed crystals compared to their single-component analogues suggest that whole molecules in (9) and (10) exhibit positional disorder.

Further details of the crystal structures may be obtained from Cambridge Crystallographic Data Centre on quoting the CCDC 1476385, 1476386, 1476387, 1476388, 1476389, 1476392, 1476393, 1476394, 1476395, 1476396, 1476397, 1476390, 1528855 and 1528856 for 2, 3, 4, 5, 8, (9-1), (9-2), (10-1 in *C*2), (10-1 in C2/c), (10-2 in C2) and (10-2 in C2/c), 13, 22, and 23, respectively.

Conclusions

In conclusion, we have described the application of a divalent silver compound, $Ag(n)SO_4$, for CH activation and oxidative coupling of naphthalene derivatives. A novel regioselective single-pot protocol leads to the formation of 1,1'-coupled binaphthyls when corresponding substrates contain the electron donating groups or mildly electron withdrawing groups; oligomerization and cross-coupling have also been observed. For very strongly electron withdrawing and ring-deactivating substituents 5,5'-coupled products are formed. $Ag(n)SO_4$ turns out to be the only oxidizer currently known which enables direct oxidative aromatic coupling of electron-poor CF₃-substituted naphthalene, albeit with low yield up to 17%. Despite their rather low yields, the syntheses on the 2 mmol scale followed by preparative thin layer chromatography allowed us to prepare about a dozen novel binaphthyl derivatives.

The Ag(II)-based protocol does not require any prefunctionalization of the organic substrate (similarly to the Hirano-Miura method¹² and to the cross-dehydrogenative coupling of the C(sp³)-H bonds, which has been recently reviewed²⁹), and it even preserves the halogen substituent, if present. The reactions proceed without the formation of substituted naphthoquinones or phthalic acids, as would be typical for Ag(II)-mediated reactions using peroxodisulphate reagents in the aqueous environment; on the other hand, this method does not tolerate functional groups, which may easily be oxidized (NH2, OH, CHO, etc.). The inorganic Ag(I) intermediate (Ag(I)HSO4) may easily be separated from organic products, and recycled back to Ag(II)SO4;30 minor Ag(I)containing impurities are considered to be biocompatible, unlike many other transition metal traces. The low yields, currently up to 17% at room temperature, are difficult to be improved by the judicious choice of the reaction medium due to constraints imposed by the very potent one-electron oxidizer, $Ag(II)SO_4$.

In forthcoming contributions we will describe the applicability of $Ag(II)SO_4$ and other Ag(II) salts in the formation of $C(sp^2)$ – $C(sp^3)$ and $C(sp^3)$ – $C(sp^3)$ coupled products including phenyl derivatives,²³ novel reactivity patterns, more detailed mechanistic studies of the reaction mechanism and further attempts of reaction optimization.³¹

Conflicts of interest

There are no conflicts of interest to declare.

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- 31 Achieving homogeneous rather than heterogeneous reaction conditions as well as catalytic action rather than 1:1 reactivity, would constitute most desirable improvements.