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Palladium-catalyzed cross-coupling reactions of arenediazonium tetrafluoroborates with aryl- and alkenylboronic acids

Sylvain Darses[1], Tuyet Jeffery[1], Jean-Louis Brayer[2], Jean-Pierre Demoute[2], Jean-Pierre Genêt[1]*

[1] *Laboratoire de synthèse organique associé au CNRS, École nationale supérieure de chimie de Paris, 11, rue Pierre-et-Marie-Curie, 75231 Paris cedex 05;*
[2] *Centre de recherche Roussel-Uclaf, 102, route de Noisy, 93230 Romainville, France*

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Summary — Arenediazonium tetrafluoroborates undergo a facile and efficient palladium-catalyzed cross-coupling reaction with aryl- and alkenylboronic acids at ambient temperature, without addition of base. The reaction described is characterized by a high chemoselectivity because bromide and triflate functional groups are tolerated.

arenediazonium tetrafluoroborate / arylboronic acid / alkenylboronic acid / cross-coupling reaction / palladium

Résumé — Réactions de couplage des tétrafluoroborates d'arènediazonium avec les acides aryl- et alcénylboroniques catalysées par le palladium. *En présence d'une quantité catalytique d'acétate de palladium, à température ambiante et sans addition de base, les tétrafluoroborates d'arènediazonium constituent des substrats de choix dans les réactions de couplage avec les acides aryl- et alcénylboroniques. Ces réactions sont de plus caractérisées par une grande chimiosélectivité, tolérant des groupements fonctionnels tels que le brome ou le triflate.*

tétrafluoroborate d'arènediazonium / acide arylboronique / acide alcénylboronique / couplage / palladium

Introduction

In the presence of a palladium catalyst, organoboron compounds have been shown to be versatile reagents in cross-coupling reactions [1]. However, since such couplings (Suzuki reactions) are limited to aryl halides [2, 3] and triflates [4], we have attempted to broaden the scope of this reaction by searching for alternatives. Because arenediazonium salts have an excellent nucleofuge (N_2) [5], they were expected to be good candidates. A number of palladium-catalyzed reactions using this type of compound have been described [6], providing a simple method for the transformation of a C-N bond into a C-C bond. In particular, Kikukawa et al [6e] found that arenediazonium salts couple efficiently with tetramethylstannane and vinyltributylstannane, while lower yields are obtained with phenyltributylstannane.

To our knowledge, although various palladium-catalyzed reactions involving arenediazonium salts [6] have been described, the use of these substrates in reactions with organoboron compounds has not been attempted. With our continuing interest in palladium-catalyzed reactions [7], we have recently developed an efficient coupling reaction of arenediazonium tetrafluoroborates with arylboronic acids [8] (fig 1). The main feature of the described reaction is the very mild and simple conditions employed (room temperature, absence of both phosphine ligand and added base). In this paper, we report the scope and limitations of the palladium-catalyzed cross-coupling reaction of arenediazonium tetrafluoroborates with aryl- and alkenylboronic acids.

$$ArN_2BF_4 + Ar'B(OH)_2 \xrightarrow[1,4\text{-Dioxane, } 20\ ^\circ C]{5\%\ Pd(OAc)_2} ArAr'$$

Fig 1. Coupling reaction of arenediazonium tetrafluoroborates with arylboronic acids.

Results and discussion

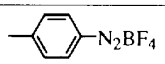
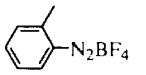
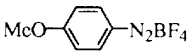
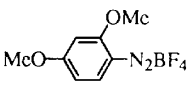
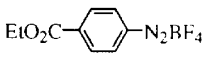
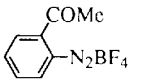
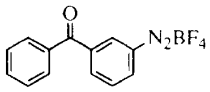
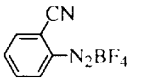
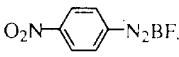
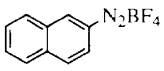
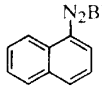
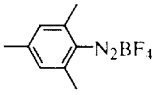
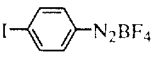
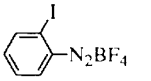
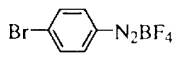
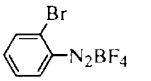
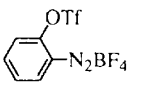
Cross-coupling reactions with arylboronic acids

A series of reactions were performed using 4-methylbenzenediazonium tetrafluoroborate and phenylboronic acid as substrates in order to determine the best reaction conditions. As reported previously [8], good yields of 4-methylbiphenyl were obtained in the presence of

* Correspondence and reprints

5 mol% of $Pd(OAc)_2$ in 1,4-dioxane at room temperature, without the addition of a base.

Table I. Palladium-catalyzed cross-coupling of arenediazonium tetrafluoroborates with phenylboronic acid[a] (fig 1, Ar′ = Ph).

Entry	ArN_2BF_4	*Reaction time (h)*	*Yield*[b]
1		4	(87)
2		4.5	(95)
3		5	79
4		7.5	32
5		2	78
6		2	96
7		4	82
8		100	68
9		2	83
10		32	62
11		< 24	67
12		4	traces[c]
13		26	17
14		30	(37)
15		< 24	77[d]
16		< 24	64[d]
17		1	72

[a] See general procedure; [b] isolated yields, yields in parentheses are GLC yields; [c] 25% conversion; [d] The isolated product contains 4–5% biphenyl.

As shown in table I, reactions of phenylboronic acid with various arenediazonium tetrafluoroborates generally afford the cross-coupling product in moderate to good yields. These results clearly show that the nature of the arenediazonium tetrafluoroborate substituents does not exert a significant influence on the reactivity of these substrates. Similar yields are obtained whether the substituent is an electron-withdrawing group (ester, ketone, nitro or cyano) or an electron-donating group (methoxy or methyl).

It is noteworthy that good yields (68–96%) can be obtained with arenediazonium fluoroborates bearing an *ortho*-substituent (entries 2, 6 and 8). However, much lower yields (with rapid precipitation of metallic palladium) are observed when polysubstituted arenediazonium fluoroborates are involved (entries 4 and 12).

The reactivity of the diazonium functional group relative to the halide or triflate groups was investigated, using arenediazonium fluoroborates bearing an iodide, a bromide or a triflate substituent. When iodobenzenediazonium fluoroborate was allowed to react with phenylboronic acid (entries 13 and 14), a rapid precipitation of metallic palladium was observed and the reaction ceased without complete consumption of the diazonium salt. Remarkably, however, 4- and 2-bromobenzenediazonium tetrafluoroborates react with phenylboronic acid to yield exclusively 4- and 2-bromobiphenyl, respectively (entries 15 and 16). Moreover, reaction of 2-(trifluoromethanesulfonyloxy)-benzenediazonium fluoroborate leads to the formation of biphenyl triflate only (entry 17).

The diazonium functional group is thus far more reactive than a bromo or triflate functionality. Owing to this difference in reactivity, the reported reaction offers a very promising pathway to unsymmetrically polysubstituted benzenes by stepwise cross-coupling reactions.

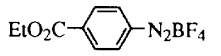
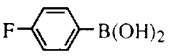
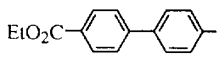
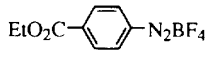
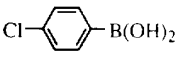
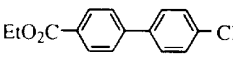
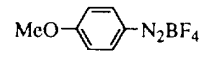
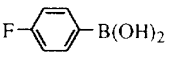
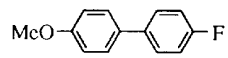
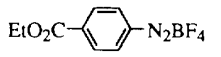
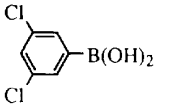
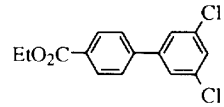
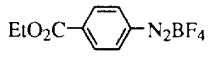
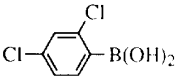
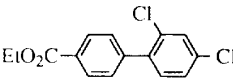
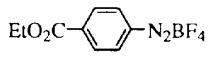
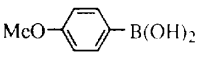
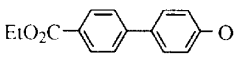
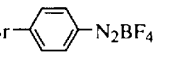
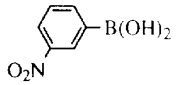
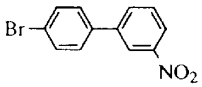
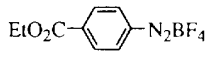
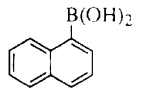
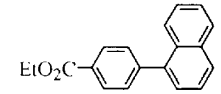
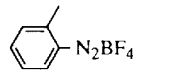
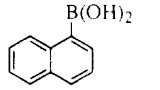
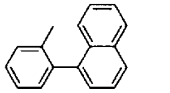
Various arenediazonium tetrafluoroborates were then reacted with different arylboronic acids, under the previously described conditions. In general, good to moderate yields of cross-coupling products are obtained, as shown in table II.

When *ortho*-substituted arylboronic acid is involved (entry 5), a very low reaction yield was observed, even at higher temperature, with formation of reduced products and rapid decomposition of the palladium catalyst. It is worth noting, however, that high yields can be obtained with the very reactive 1-naphthylboronic acid (entries 8 and 9), even when an *ortho*-substituted arenediazonium salt is involved (entry 9).

Cross-coupling reactions with alkenylboronic acids

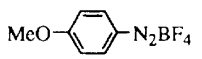
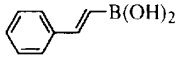
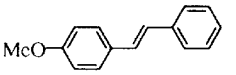
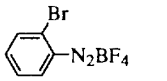
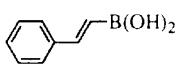
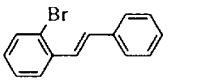
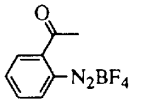
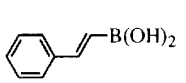
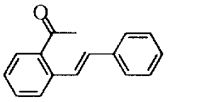
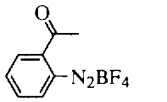
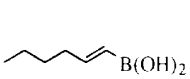
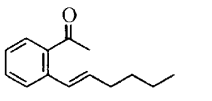
Cross-coupling reactions of arenediazonium tetrafluoroborates with alkenylboronic acids were also investigated. As shown in table III, good to moderate yields (41–91%) of cross-coupled products were obtained when the reactions were performed under the above-described mild conditions. Moreover, the reaction involving 2-bromobenzenediazonium fluoroborate (entry 2) again demonstrates that the diazonium functional group is far more reactive than the bromo functionality and a highly chemoselective coupling with alkenylboronic acids can be achieved.

Table II. Palladium-catalyzed cross-coupling of arenediazonium fluoroborates with arylboronic acids[a].

Entry	*ArN_2BF_4*	*$Ar'B(OH)_2$*	*Reaction time (h)*	*Product*	*Yield*[b]
1			4		49
2			21		58
3			24		60
4			< 20		65
5			5[c]		traces[d]
6			56		57
7			120		34
8			0.5		88
9			5		72

[a] See general procedure; [b] isolated yields; [c] reaction conducted at 40 °C; [d] 1,3-dichlorobenzene and ethyl benzoate are obtained in nearly quantitative yields.

Table III. Palladium-catalyzed cross-coupling of arenediazonium fluoroborates with alkenylboronic acids[a].

Entry	ArN_2BF_4	$R-CH=CH-B(OH)_2$	Reaction time (h)	Product	Yield[b]
1			6		75
2			0.5		91
3			80		63
4			130[c]		41

[a] See general procedure; [b] isolated yields; [c] 75% conversion.

Mechanistic aspects

Although no detailed study has been attempted to elucidate the precise mechanism, the described reaction can be rationalized by a series of several elementary steps, involving: a) formation of zerovalent palladium catalyst; b) oxidative addition; c) transmetalation; and d) reductive elimination, as depicted in figure 2.

The zerovalent palladium catalyst is very probably formed (step a) from reduction of palladium(II) salt by organoboronic acid, via transmetalation followed by reductive elimination (fig 3). Several observations are

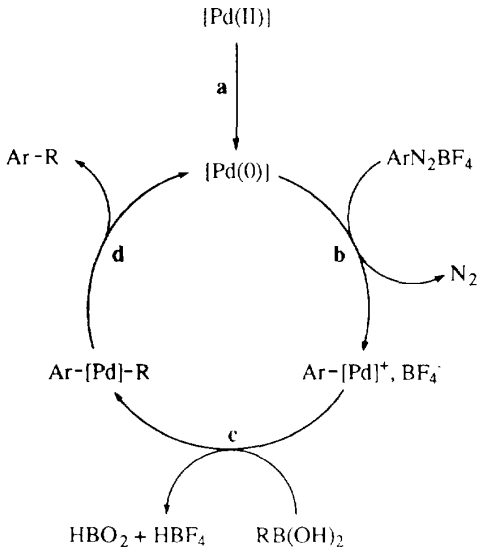


Fig 2. Mechanism of cross-coupling reactions of arene diazonium tetrafluoroborates with organoboronic acids.

in accordance with this hypothesis. An induction period ranging from 1 to 10 min has been observed in all reactions performed in the presence of palladium acetate as catalyst. Formation of metallic palladium [9] and biphenyl [10] has also been evidenced within a few minutes, when phenylboronic acid is reacted with palladium acetate in 1,4-dioxane at room temperature. Similar results have been described by Kikukawa et al [6e] in the cross-coupling reaction between arenediazonium salts and organostannanes in the presence of $Pd(OAc)_2$.

$$Pd(II)X_2 \xrightarrow{2\ RB(OH)_2} R\text{-}[Pd]\text{-}R \longrightarrow [Pd(0)] + R\text{-}R \quad (R = \text{aryl or alkenyl})$$

Fig 3. Formation of the zerovalent palladium catalyst.

Formation of cationic organopalladium complexes (step b) by the oxidative addition of arenediazonium tetrafluoroborates with zerovalent palladium has been described [11], and such intermediates have been suggested in various palladium-catalyzed reactions of arenediazonium salts [6e,g, 12].

By analogy with palladium-catalyzed cross-coupling reactions of organohalides with organoboron compounds [1], the subsequent elementary steps are likely to involve transmetalation (step c) and reductive elimination with regeneration of the zerovalent palladium catalyst (step d).

Conclusion

In conclusion, arenediazonium tetrafluoroborates are effective substrates in palladium-catalyzed cross-coupling reactions with aryl- and alkenylboronic acids, because efficient and chemoselective reactions can be achieved at ambient temperature, without addition of a base. Although the described reaction seems limited to sterically unhindered organoboronic acids, it should be synthetically important as a promising pathway to unsymmetrically polysubstituted benzenes. In addition, from an industrial point of view, arenediazonium tetrafluoroborates, which derive from anilines, are economically more advantageous than aryl bromides or iodides.

Experimental section

^1H NMR spectra were recorded on a Bruker AC 200, AM 250 or ARX 400 respectively at 200, 250 or 400 MHz; chemical shifts (δ) are reported in ppm units, by reference to Me_4Si, and coupling constants (J) are reported in hertz and refer to apparent peak multiplicities. ^{13}C NMR spectra were recorded on a Bruker AC 200, AM 250 or ARX 400 instrument at 50, 63 or 200 MHz. Mass spectra were determined on a Ribermag instrument. Elementary analysis were done at the Regional Service of Microanalysis (Université Pierre-et-Marie-Curie). Thin-layer chromatography was carried out on silica-gel plates (Merck F_{254}) and spots were detected by UV.

1,4-Dioxane (from SDS) was distilled on $LiAlH_4$, stored over 4 Å molecular sieve and carefully degassed before use. $Pd(OAc)_2$ and aromatic amines were purchased from Acros or Aldrich and were used as received, except 2-aminophenol which was recrystallized from ethanol. Arylboronic acids were bought from Lancaster, Acros or Fluka and trifluoromethanesulfonyl chloride from Fluka. Alkenylboronic acids were prepared according to a published procedure [13].

Preparation of arenediazonium tetrafluoroborates

Unless otherwise noted, arenediazonium tetrafluoroborates were generally prepared from commercial aromatic amines according to published method [14]. They were purified, several times if necessary, by precipitation or recrystallization in acetone/diethyl ether or methanol/diethyl ether and could be stored for several months at −20 °C under an argon atmosphere.

2-(Trifluoromethanesulfonyloxy)benzenediazonium tetrafluoroborate

- *2-Aminophenyl trifluoromethanesulfonate*

To a suspension of 2-aminophenol (5 mmol, 0.546 g) in anhydrous dichloromethane (20 mL) was added triethylamine (5 mmol, 0.695 mL) at 25 °C under an argon atmosphere. The mixture was stirred for 30 min at 25 °C, then cooled to −50 °C. Trifluoromethanesulfonyl chloride (5 mmol, 0.529 mL) dissolved in anhydrous dichloromethane (3 mL) was slowly added over 10 min while the temperature was maintained at −50 °C. The resulting orange mixture was stirred while the temperature was allowed to reach 10 °C over a period of 6 h and maintained at 10 °C for 14 h. Diethyl ether (30 mL) and aqueous NaOH (50 mL, pH ≈ 8) were then added. The aqueous layer was separated and extracted with diethyl ether (3 × 15 mL). The organic phases were combined, dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the residue by silica-gel column chromatography using dichloromethane as eluent (R_f = 0.59) gave 1.025 g (85% yield) of the desired product as a light brown oil.

- *2-(Trifluoromethanesulfonyloxy)benzenediazonium tetrafluoroborate*

The title compound (1.367 g, 90% yield) was prepared from 2-aminophenyl trifluoromethanesulfonate according to

the procedure of Doyle and Bruker [15]. When necessary, the product could be purified by rapid precipitation in acetone/diethyl ether. White solid (77% yield from 2-aminophenol). Melting point: 186–188 °C (dec).

^{1}H NMR (CD_3COCD_3, 200 MHz, δ): 9.07 (1H, dd, J = 8.4 and 1.6 Hz), 8.63 (1H, ddd, J = 8.7, 7.8 and 1.7 Hz), 8.26 (1H, dd, J = 8.7 and 0.9 Hz), 8.16 (1H, ddd, J = 8.4, 7.7 and 1.0 Hz).

^{13}C NMR (CD_3COCD_3, 63 MHz, δ): 148.6, 145.3, 136.1, 131.1, 123.5, 119.9 (q, J_{CF} = 320 Hz), 109.6.

General cross-coupling procedure

Arenediazonium tetrafluoroborate (1 mmol), aryl- or alkenylboronic acid (1.2 mmol) and $Pd(OAc)_2$ (5 mol%) were placed in a flask under an argon atmosphere, in the dark. Anhydrous and degassed 1,4-dioxane (2 mL) was then added and the resulting suspension was stirred at 20 °C for the indicated time. The course of the coupling was followed by measuring the evolution of gas with a gas burette. After completion, the catalyst was filtered off on celite and washed with diethyl ether. The organic phase was washed several times with brine and dried over anhydrous magnesium sulfate. The solvent was removed and the crude product was purified by chromatography on silica gel.

- *4-Methoxybiphenyl [613-37-6]*

White solid (79% yield). Melting point: 87 °C.

TLC: R_f = 0.29 (pentane/ether 20:1).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.57 (2H, d, J = 6.9 Hz), 7.54 (2H, d, J = 8.9 Hz), 7.43 (2H, t, J = 7.2 Hz), 7.31 (1H, t, J = 7.2 Hz), 6.99 (2H, d, J = 8.9 Hz), 3.89 (3H, s).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 159.1, 140.8, 133.7, 128.6 (2C), 128.1 (2C), 126.7 (3C), 114.1 (2C), 55.3.

GC/MS (m/z): 184 ($M^{+\cdot}$, 100%), 169, 141, 76, 63.

- *2,4-Dimethoxybiphenyl [17715-56-9]*

Colorless oil (32% yield).

TLC: R_f = 0.17 (pentane/ether 20:1).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.51 (2H, d, J = 6.8 Hz), 7.37–7.44 (2H, m), 7.26–7.34 (1H, m), 7.26 (1H, d, J = 9.0 Hz), 6.59 (1H, dd, J = 9.0 and 2.4 Hz), 6.58 (1H, d, J = 2.2 Hz), 3.90 (3H, s), 3.84 (3H, s).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 160.3, 157.4, 138.3, 131.2, 129.4 (2C), 127.9 (2C), 126.4, 123.6, 104.5, 98.9, 55.5, 55.3.

Anal calc for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.37; H, 6.68.

- *Ethyl 4-phenylbenzoate [6301-56-0]*

White solid (78% yield). Melting point ≈ 50 °C (lit [16]: 49–53 °C).

TLC: R_f = 0.18 (pentane/ether 20:1).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 8.14 (2H, td, J = 8.6 and 1.9 Hz), 7.68 (2H, td, J = 8.6 and 1.9 Hz), 7.61–7.67 (2H, m), 7.36–7.53 (3H, m), 4.43 (2H, q, J = 7.1 Hz), 1.44 (3H, t, J = 7.1 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 166.4, 145.4, 140.0, 130.0 (2C), 129.2, 128.8 (2C), 128.0, 127.2 (2C), 126.9 (2C), 60.9, 14.3.

GC/MS (m/z): 226 ($M^{+\cdot}$), 198, 181 (100%), 127, 76.

- *2-Acetylbiphenyl [451-40-1]*

Colorless oil (96% yield).

TLC: R_f = 0.19 (pentane/ether 10:1).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.49–7.60 (2H, m), 7.33–7.47 (7H, m), 2.02 (3H, s).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 204.8, 140.8, 140.6, 140.4, 130.6, 130.1, 128.8 (2C), 128.6 (2C), 127.8 (2C), 127.4, 30.3.

GC/MS (m/z): 196 ($M^{+\cdot}$), 181 (100%), 152, 76, 43.

Anal calc for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 84.98; H, 6.31.

- *3-Benzoylbiphenyl [3378-09-4]*

White solid (82% yield). Melting point: 78 °C (ether/pentane).

TLC: R_f = 0.16 (pentane/ether 20:1).

^{1}H NMR ($CDCl_3$, 400 MHz, δ): 8.04 (1H, t, J = 1.6 Hz), 7.87 (2H, d, J = 7.4 Hz), 7.83 (1H, td, J = 7.7 and 0.8 Hz), 7.78 (1H, td, J = 7.6 and 0.8 Hz), 7.63 (2H, d, J = 7.3 Hz), 7.62 (1H, t, J = 7.4 Hz), 7.57 (1H, t, J = 7.7 Hz), 7.51 (2H, t, J = 7.8 Hz), 7.47 (2H, t, J = 7.8 Hz), 7.39 (1H, t, J = 7.5 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 196.6, 141.3, 140.1, 138.1, 137.5, 132.5, 131.0, 130.0 (2C), 128.9 (3C), 128.7, 128.5, 128.3 (2C), 127.7, 127.1 (2C).

GC/MS (m/z): 258 ($M^{+\cdot}$), 181 (100%), 152, 105, 77, 51.

- *2-Cyanobiphenyl [24973-49-7]*

Colorless oil (68% yield).

TLC: R_f = 0.18 (light petroleum/ether 10:1).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.78 (1H, ddd, J = 7.7, 1.2 and 0.5 Hz), 7.66 (1H, td, J = 7.6 and 1.4 Hz), 7.59 (2H, d, J = 7.1 Hz), 7.53 (1H, ddd, J = 7.7, 1.4 and 0.5 Hz), 7.48–7.52 (3H, m), 7.45 (1H, t, J = 7.5 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 145.4, 138.1, 133.7, 132.8, 130.0, 128.68 (2C), 128.66 (3C), 127.5, 118.7, 111.2.

Anal calc for $C_{13}H_9N$: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.01; H, 5.08; N, 7.75.

- *4-Nitrobiphenyl [92-93-3]*

Pale yellow solid (83% yield). Melting point: 114–115 °C (lit [17]: 113–115 °C, MeOH).

TLC: R_f = 0.21 (pentane/ether 20:1).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 8.31 (2H, td, J = 9.2 and 2.2 Hz), 7.75 (2H, td, J = 9.2 and 2.2 Hz), 7.62–7.66 (2H, m), 7.41–7.56 (3H, m).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 147.5, 147.0, 138.7, 129.1 (2C), 128.8, 127.7 (2C), 127.3 (2C), 124.0 (2C).

GC/MS (m/z): 199 ($M^{+\cdot}$, 100%), 152, 141, 76, 63.

- *2-Phenylnaphthalene [612-94-2]*

White solid (62% yield). Melting point: 101 °C (lit [18]: 101–102 °C).

TLC: R_f = 0.22 (pentane).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 8.06 (1H, d, J = 1.7 Hz), 7.93 (1H, d, J = 8.6 Hz), 7.91 (1H, d, J = 7.4 Hz), 7.88 (1H, dd, J = 7.2 and 2.0 Hz), 7.77 (1H, dd, J = 8.7 and 1.8 Hz), 7.75 (2H, d, J = 7.5 Hz), 7.49–7.55 (4H, m), 7.40 (1H, t, J = 7.4 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 141.0, 138.5, 133.6, 132.5, 128.8 (2C), 128.3, 128.1, 127.5, 127.3 (2C), 127.2, 126.2, 125.8, 125.7, 125.5.

GC/MS (m/z): 204 ($M^{+\cdot}$, 100%), 150, 101, 76.

- *1-Phenylnaphthalene [605-02-7]*

Colorless oil (67% yield).

TLC: R_f = 0.24 (pentane).

^{1}H NMR ($CDCl_3$, 250 MHz, δ): 7.87–7.95 (3H, m), 7.42–7.58 (9H, m).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 140.7, 140.2, 133.7, 131.6, 130.0 (2C), 128.2 (3C), 127.6, 127.2, 126.9, 126.0 (2C), 125.7, 125.3.

GC/MS (m/z): 204 ($M^{+\bullet}$, 100%), 101, 63.

• *4-Iodobiphenyl [1591-31-7]*

White solid (17% yield). Melting point: 109 °C (ether/pentane).

TLC: R_f = 0.34 (pentane).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.78 (2H, d, J = 8.6 Hz), 7.56 (2H, d, J = 6.5 Hz), 7.38–7.50 (3H, m), 7.34 (2H, d, J = 8.5 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 140.7, 140.0, 137.8 (2C), 129.0 (2C), 128.9 (2C), 127.7, 126.9 (2C), 93.0.

GC/MS (m/z): 280 ($M^{+\bullet}$, 100%), 152, 126, 76.

Anal calc for $C_{12}H_9I$: C, 51.46; H, 3.24. Found: C, 51.31; H, 3.19.

• *4-Bromobiphenyl [92-66-0]*

White solid (77% yield). Melting point: 89–90 °C (lit [19]: 88–90 °C).

TLC: R_f = 0.32 (pentane).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.60 (2H, d, J = 8.5 Hz), 7.59 (2H, d, J = 6.8 Hz), 7.49 (2H, d, J = 8.5 Hz), 7.48 (2H, d, J = 7.2 Hz), 7.40 (1H, t, J = 7.0 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 140.0, 139.8, 131.7 (2C), 128.7 (2C), 128.6 (2C), 127.5, 126.8 (2C), 121.4.

GC/MS (m/z): 234 and 232 ($M^{+\bullet}$, 100%), 152, 76, 63.

• *2-Bromobiphenyl [2052-07-5]*

Light yellow oil (64% yield).

TLC: R_f = 0.30 (pentane).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.68 (1H, d, J = 7.9 Hz), 7.42–7.48 (5H, m), 7.35 (1H, t, J = 7.5 Hz), 7.35 (1H, dd, J = 6.4 and 1.2 Hz), 7.20 (1H, ddd, J = 7.9, 6.0 and 3.3 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 142.6, 141.1, 133.1, 131.3, 129.4 (2C), 128.7, 127.9 (2C), 127.6, 127.3, 122.6.

GC/MS (m/z): 234 and 232 ($M^{+\bullet}$, 100%), 152, 126, 76, 63.

• *2-(Trifluoromethanesulfonyloxy)biphenyl [17763-65-4]*

Colorless oil (72% yield).

TLC: R_f = 0.19 (pentane/ether 100:1).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.39–7.72 (9H, m).

^{13}C NMR ($CDCl_3$, 63 MHz, δ): 147.0, 135.7, 132.1 (2C), 129.5 (2C), 129.1, 128.65, 128.62 (2C), 128.4, 122.2, 118.3 (q, J_{C-F} = 320 Hz).

GC/MS (m/z): 302 ($M^{+\bullet}$), 169 (100%), 141, 115, 89, 69.

Anal calc for $C_{13}H_9F_3O_3S$: C, 51.66; H, 3.00. Found: C, 51.76; H, 2.93.

• *Ethyl 4-(4-fluorophenyl)benzoate*

White solid (49% yield). Melting point: 64 °C (ether/pentane).

TLC: R_f = 0.17 (pentane/ether 20:1).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 8.16 (2H, d, J = 8.6 Hz), 7.62 (2H, d, J = 8.6 Hz), 7.58 (2H, m), 7.16 (2H, tt, J_{AX} = 8.7 Hz, J_{HF} = 2.0 Hz), 4.43 (2H, q, J = 7.1 Hz), 1.45 (3H, t, J = 7.1 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 166.5, 163.0 (d, J_{CF} = 246 Hz), 144.5, 136.2, 130.2 (2C), 129.3, 129.0 (2C, d, J_{CF} = 8.1 Hz), 126.9 (2C), 115.9 (2C, d, J_{CF} = 21 Hz), 61.1, 14.4.

Anal calc for $C_{15}H_{13}FO_2$: C, 73.76; H, 5.36. Found: C, 73.67; H, 5.38.

• *Ethyl 4-(4-chlorophenyl)benzoate*

White solid (58% yield). Melting point: 73 °C (ether/pentane).

TLC: R_f = 0.17 (pentane/ether 20:1).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 8.12 (2H, d, J = 8.6 Hz), 7.63 (2H, d, J = 8.6 Hz), 7.57 (2H, d, J = 8.7 Hz), 7.44 (2H, d, J = 8.7 Hz), 4.43 (2H, q, J = 7.1 Hz), 1.45 (3H, t, J = 7.1 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 166.3, 144.1, 138.4, 134.2, 130.1 (2C), 129.5, 129.0 (2C), 128.4 (2C), 126.7 (2C), 61.0, 14.3.

Anal calc for $C_{15}H_{13}ClO_2$: C, 69.10; H, 5.03. Found: C, 69.00; H, 5.05.

• *4-Fluoro-4′-methoxybiphenyl [450-39-5]*

White solid (60% yield). Melting point: 92 °C (ether/pentane) (lit [20]: 90–91 °C, ethanol).

TLC: R_f = 0.21 (pentane/ether 50:1).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.44–7.56 (4H, m), 7.11 (2H, t, J_{HF} = J_{AX} = 8.7 Hz), 6.98 (2H, d, J = 8.8 Hz), 3.86 (3H, s).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 162.1 (d, J_{CF} = 240 Hz), 159.0, 136.9, 132.7, 128.1 (2C, d, J_{CF} = 8.0 Hz), 127.9 (2C), 115.4 (2C, d, J_{CF} = 21 Hz), 114.2 (2C), 55.2.

GC/MS (m/z): 202 ($M^{+\bullet}$, 100%), 187, 159, 133, 101, 63.

• *Ethyl 4-(3,5-dichlorophenyl)benzoate*

White solid (65% yield). Melting point: 85 °C (ether/pentane).

TLC: R_f = 0.27 (pentane/ether 20:1).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 8.13 (2H, d, J = 8.6 Hz), 7.60 (2H, d, J = 8.6 Hz), 7.49 (2H, d, J = 1.9 Hz), 7.39 (1H, t, J = 1.9 Hz), 4.44 (2H, q, J = 7.1 Hz), 1.45 (3H, t, J = 7.1 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 166.0, 142.9, 142.6, 135.4 (2C), 130.3, 130.2 (2C), 127.8, 126.9 (2C), 125.7 (2C), 61.1, 14.2.

Anal calc for $C_{15}H_{12}Cl_2O_2$: C, 61.04; H, 4.10. Found: C, 60.89; H, 4.03.

• *Ethyl 4-(4-methoxyphenyl)benzoate*

White solid (57% yield). Melting point: 105 °C (ether/pentane).

TLC: R_f = 0.12 (pentane/ether 20:1).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 8.10 (2H, d, J = 8.5 Hz), 7.63 (2H, d, J = 8.1 Hz), 7.59 (2H, d, J = 8.7 Hz), 7.01 (2H, d, J = 8.8 Hz), 4.42 (2H, q, J = 7.1 Hz), 3.89 (3H, s), 1.44 (3H, t, J = 7.1 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 166.5, 159.7, 145.0, 132.4, 130.0 (2C), 128.4, 128.3 (2C), 126.3 (2C), 114.3 (2C), 60.8, 55.3, 14.3.

GC/MS (m/z): 256 ($M^{+\bullet}$, 100%), 228, 211, 168, 139, 105, 63.

Anal calc for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.83; H, 6.36.

• *4′-Bromo-3-nitrobiphenyl [32858-99-4]*

White solid (34% yield). Melting point: 94 °C (ether/pentane) (lit [16]: 87–91 °C, light petroleum).

TLC: R_f = 0.17 (pentane/ether 20:1).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 8.43 (1H, t, J = 1.9 Hz), 8.23 (1H, ddd, J = 8.2, 2.2, and 1.0 Hz), 7.89 (1H, ddd, J = 7.8, 1.7 and 1.1 Hz), 7.64 (2H, d, J = 8.7 Hz), 7.63 (1H, t, J = 8.0 Hz), 7.50 (2H, d, J = 8.7 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 149.3, 141.6, 138.8, 132.7, 132.2 (2C), 129.8, 128.6 (2C), 122.9, 122.3, 121.7.

Anal calc for $C_{12}H_8BrNO_2$: C, 51.83; H, 2.90. Found: C, 51.96; H, 2.86.

- *Ethyl 4-(1-naphthyl)benzoate*

White solid (88% yield). Melting point: 55 °C (ether/pentane).

TLC: R_f = 0.19 (pentane/ether 20:1).

^{1}H NMR ($CDCl_3$, 250 MHz, δ): 8.17 (2H, d, J = 8.4 Hz), 7.84 (1H, d, J = 8.5 Hz), 7.83–7.94 (2H, m), 7.58 (2H, td, J = 8.2 and 1.6 Hz), 7.41–7.57 (4H, m), 4.44 (2H, q, J = 7.1 Hz), 1.44 (3H, t, J = 7.1 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 166.5, 145.4, 139.1, 133.7, 131.2, 130.0 (2C), 129.5 (2C), 129.3, 128.3, 128.2, 126.9, 126.3, 125.9, 125.6, 125.3, 61.0, 14.4.

Anal calc for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.41; H, 5.92.

- *1-(2-Methylphenyl)naphthalene [14476-01-8]*

White solid (72% yield). Melting point: 67 °C.

TLC: R_f = 0.26 (pentane).

^{1}H NMR ($CDCl_3$, 250 MHz, δ): 7.92 (1H, d, J = 8.1 Hz), 7.88 (1H, d, J = 8.4 Hz), 7.46–7.57 (3H, m), 7.28–7.42 (6H, m), 2.04 (3H, s).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 140.2, 139.7, 136.7, 133.5, 131.9, 130.3, 129.8, 128.1, 127.5, 127.4, 126.6, 126.0, 125.9, 125.7, 125.5, 125.3, 20.0.

GC/MS (m/z): 218 ($M^{+\bullet}$, 100%), 203, 108, 101, 63.

Anal calc for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.47; H, 6.57.

- *(E)-4-Methoxystilbene [1694-19-5]*

White solid (75% yield). Melting point: 136 °C (ether/pentane) (lit [6c]: 134.7–136.4 °C).

TLC: R_f = 0.34 (pentane/ether 20:1).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.43–7.56 (2H, m), 7.47 (2H, d, J = 8.7 Hz), 7.3–7.4 (2H, m), 7.2–7.3 (1H, m), 7.10 (1H, d, J = 16.3 Hz), 6.98 (1H, d, J = 16.3 Hz), 6.92 (2H, d, J = 8.8 Hz), 3.87 (3H, s).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 159.4, 137.6, 130.1, 128.5 (2C), 128.1, 127.6 (2C), 127.1, 126.5, 126.1 (2C), 114.0 (2C), 55.2.

GC/MS (m/z): 210 ($M^{+\bullet}$, 100%), 165, 115, 89, 63.

- *(E)-2-Bromostilbene*

Colorless oil (91% yield).

TLC: R_f = 0.27 (pentane).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.70 (1H, dd, J = 7.8 and 1.6 Hz), 7.61 (1H, dd, J = 7.9 and 1.3 Hz), 7.58 (2H, d, J = 7.1 Hz), 7.50 (1H, d, J = 16.3 Hz), 7.41 (2H, t, J = 7.1 Hz), 7.34 (1H, t, J = 7.8 Hz), 7.31 (1H, t, J = 7.0 Hz), 7.16 (1H, td, J = 7.8 and 1.6 Hz), 7.06 (1H, d, J = 16.3 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 137.1, 136.9, 133.0, 131.4, 128.7 (3C), 128.0, 127.5, 127.4, 126.8 (2C), 126.6, 124.1.

Anal calc for $C_{14}H_{11}Br$: C, 64.89; H, 4.28. Found: C, 64.77; H, 4.36.

- *(E)-2-Acetylstilbene*

Yellow oil (63% yield).

TLC: R_f = 0.19 (pentane/ether 20:3).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.72 (1H, d, J = 7.7 Hz), 7.70 (1H, d, J = 16.2 Hz), 7.70 (1H, dd, J = 7.6 and 1.4 Hz), 7.55 (2H, d, J = 7.7 Hz), 7.51 (1H, t, J = 7.7 Hz), 7.38 (2H, t, J = 7.7 Hz), 7.35 (1H, t, J = 7.6 Hz), 7.28 (1H, t, J = 7.2 Hz), 7.00 (1H, d, J = 16.2 Hz), 2.63 (3H, s).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 202.0, 137.2 (3C), 131.5 (2C), 129.0, 128.6 (2C), 127.8, 127.3 (2C), 127.1, 126.7 (2C), 29.8.

Anal calc for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.47; H, 6.48.

- *(E)-1-[2-(Hex-1-enyl)phenyl]ethanone*

Colorless oil (41% yield).

TLC: R_f = 0.26 (pentane/ether 20:1).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.58 (1H, dd, J = 7.6 and 1.4 Hz), 7.52 (1H, dd, J = 7.8 and 1.4 Hz), 7.41 (1H, td, J = 7.5 and 1.4 Hz), 7.27 (1H, td, J = 7.4 and 1.4 Hz), 6.85 (1H, d, J = 15.7 Hz), 6.12 (1H, td, J = 15.7 and 6.9 Hz), 2.57 (3H, s), 2.25 (2H, q, J = 6.9 Hz), 1.36–1.55 (4H, m), 0.94 (3H, t, J = 7.0 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 202.6, 137.5, 137.3, 134.4, 131.2, 128.4, 128.2, 127.4, 126.4, 32.8, 31.2, 30.0, 22.2, 13.8.

Anal calc for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.92; H, 9.02.

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