Journal of Fluorine Chemistry 156 (2013) 164–169

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Microwave-assisted synthesis of substituted fluorophenyl mono- and diazides by S_NAr. A fast methodology to prepare photoaffinity labeling and crosslinking reagents

Elisa Leyva [1],*, Socorro Leyva, Edgar Moctezuma,
Regina M. González-Balderas, Denisse de Loera

Facultad de Ciencias Químicas, Universidad Autónoma de San Luis Potosí, Manuel Nava No. 6, 78210 San Luis Potosí, S.L.P., Mexico

ARTICLE INFO

Article history:
Received 31 May 2013
Received in revised form 25 September 2013
Accepted 2 October 2013
Available online 11 October 2013

Keywords:
Fluoroarylazide
Microwave
Photoaffinity labeling
Diazides

ABSTRACT

The reaction of sodium azide with perfluorobenzene, containing an electron-withdrawing group, under microwave irradiation results in the fast preparation of *p*-substituted tetrafluorophenyl monoazides. Having an excess of sodium azide and a strong electron-withdrawing group like NO_2 or CN, fluorophenyl diazides are also produced upon conventional or microwave heating. A synergic effect between the amount of sodium azide and the electron-withdrawing character of the substituents is observed giving different products. A discussion on the products and reaction mechanism is presented.

1. Introduction

Aryl azides are high-energy molecules with interesting photochemical properties [1]. Their complex photochemistry has fascinated theoretical and experimental chemists for many years. In recent years, they have found many applications in organic chemistry in the synthesis of heterocyclic compounds [2], in polymer chemistry as crosslinking agents [3] and in the biochemical method known as photoaffinity labeling or **PAL** [4].

In a **PAL** experiment, a small light-sensitive moiety is appended to a natural ligand of a biological macromolecule [4]. On photolysis, the modified ligand must generate a short-lived and highly reactive intermediate capable of reacting in an indiscriminating manner with surrounding C–H and N–H bonds present in the macromolecule to produce an adduct. An aryl carbene was utilized in the first **PAL** experiments [4]. However, since this intermediate is long-lived it can migrate out of the binding site and reacts predominantly with water. Based on these experimental results, new reagents for **PAL** are being synthesized.

The use of aromatic azides for **PAL** experiments was first introduced by Bayley and Knowles in 1977 [4]. However, the photolysis of aryl azides gives a variety of products which yields are modified by several factors such as temperature, solvent, and substituents [5]. These reactions are seldom clean with the production of tars and polymers and have limited the application of aryl azides in **PAL**. In a given aryl nitrene, the intermediate generated upon photolysis of an aryl azide, the presence of electron-withdrawing substituents is expected to modify its reactivity. In search of an aryl azide with adequate physicochemical properties like a facile generation of a highly reactive intermediate, we investigated the photochemistry of several fluoro-substituted aryl azides [6]. The experimental observation that pentafluorophenyl azide undergoes photochemical insertion with several solvents led to further investigations about the reactions of this type of azides [7]. It was demonstrated that two fluorine atoms adjacent to the azide group inhibit ring expansion, a secondary nitrene reaction, and favor aryl nitrene (C–H and N–H) insertion reactions [1]. In the case of perfluorophenyl azides, the presence of another electron-withdrawing group (nitro, carbonyl, or cyano) in the *para*-position to the azide group increased C–H insertion reactions since the electrophilicity of the intermediate nitrene, generated upon photolysis, was also increased [8].

In recent years, perfluoro aryl azides are applied in the preparation of bifunctional chelating agents **BFCAs** utilized in

---

* Corresponding author. Present address: Department of Chemistry, UWO, Chemistry Building, London, ON N6A5B7, Canada. Tel.: +1 5196912166; fax: +1 5196613022.

E-mail addresses: eleyvara@uwo.ca, elisa@uaslp.mx (E. Leyva).

[1] On sabbatical leave from UASLP, Mexico.

0022-1139/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jfluchem.2013.10.002

PAL [9]. For these latter **PAL** experiments, an organic compound is prepared with a photoactive moiety (like an aryl azide) and a chelating agent (to chelate a transition metal). **BFCAs** could be useful reagents in nuclear medicinal chemistry to achieve attachment of a radiolabeled molecule to antibodies or antibody fragments which in turn could be attached to specific biological sites for imaging or cancer therapy [1,9].

The application of microwave irradiation as a non-conventional energy source for reactions has become a very popular and useful technique in organic chemistry [10]. In general, the use of this type of energy leads to enhanced conversion rates, higher yields, easier work up and cleaner reactions demonstrating the real advantages of this methodology.

Due to their highly effective and regiospecific reactivity, fluorophenyl azides have gained an important place in the interface between organic chemistry, biology, medicinal and materials science [11]. In the present paper, we report the fast preparation of several fluorophenyl mono and diazides by reaction of the corresponding halogenated compounds with sodium azide under microwave irradiation.

2. Results and discussion

Aryl azides are usually prepared by treatment of diazonium salts with sodium azide [12]. Since this method has some limitations several alternative procedures have been investigated. The reaction of *p*-tosyl azide with several compounds like Grignard or lithium reagents and aryl amide salts has been reported [13]. The use of this latter transformation has been limited due to the harsh conditions utilized. The conversion of aromatic amines into the corresponding azides with triflylazide, a potentially explosive reagent, has also been reported [14]. Upon refluxing, pentafluorobenzene containing an electron-withdrawing group (cyano, nitro, or carbonyl) undergoes selective aromatic *para*-substitution with sodium azide [8]. Recently, the nucleophilic aromatic substitution of some aryl halides has been performed in ionic liquid solution using 1-butyl-3-methylimidazolium azide as a nucleophile [15]. However, all of these procedures require long reaction times and either acidic or basic conditions, which are not compatible with many functional groups.

We started by performing the S_NAr reaction under conventional heating (Δ) and reacted several R-pentafluorobenzene derivatives **1a**–**e** with sodium azide by refluxing in acetone/water for 8 h (Table 1). Under these previously reported conditions [8], we obtained the corresponding perfluorophenyl azides **2a**–**e** in good yields. The reaction of sodium azide with pentafluoroacetophenone **1b** was investigated under microwave irradiation (MW, 50 W) at 70 °C for 15 min using a mixture of acetone/water as solvent. The crude product mixture was analyzed by thin layer chromatography, which indicated that the reaction proceeded very fast. The microwave-assisted S_NAr reaction of several pentafluorobenzene derivatives **1a**–**e** was performed and the corresponding aromatic azides **2a**–**e** were obtained in good yields in rather short times (Table 1).

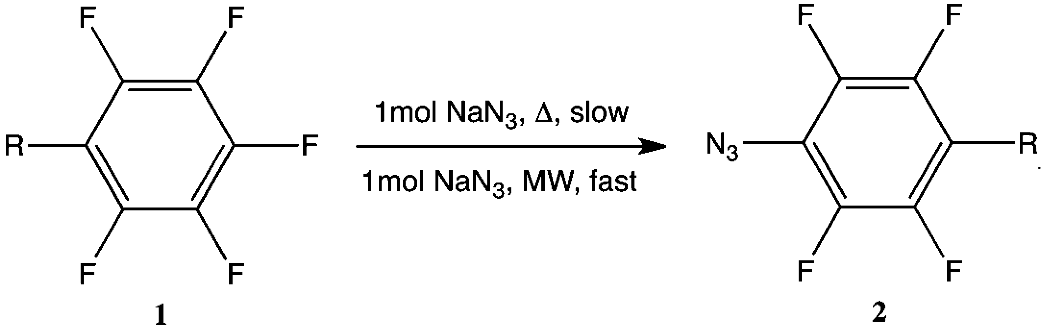
After performing the preparation of several monoazides by S_NAr, we decided to investigate the effect of an excess of the strong nucleophile (NaN_3) under conventional heating or microwave irradiation. When a R-pentafluorobenzene derivative, containing a group like COH or $COCH_3$, was reacted with several equivalents of sodium azide no change in the reaction products was observed (Scheme 1). Even with a large excess of nucleophile only the *para*-substituted fluorophenyl azide was produced.

Performing the reaction of large amounts of sodium azide with a R-pentafluorobenzene, containing an ester group ($COOCH_3$), results in the production of a mixture of two isomeric *ortho*- and *para*-substituted monoazides (Scheme 2). Both positions in the aromatic compound are actually activated by the inductive effect of the substituent, but the *para*-position must be slightly more activated than the *ortho*. Interestingly, two reactions compete under conventional heating or microwave irradiation.

Reacting an equivalent amount of sodium azide with a pentafluorobenzene derivative containing a strong electron-withdrawing group like cyano results in the exclusive formation of a monoazide product (Table 1). In contrast, utilizing a large excess of sodium azide (Scheme 3) results in the production of a mixture of mono and diazide.

Similar results were observed with a pentafluorobenzene derivative containing a very strong electron-withdrawing group like NO_2. A monoazide (Table 1) was obtained with one equivalent

Table 1
Preparation of *p*-substituted fluorophenyl azides **2a**–**e** from R-fluorobenzene **1a**–**e**.

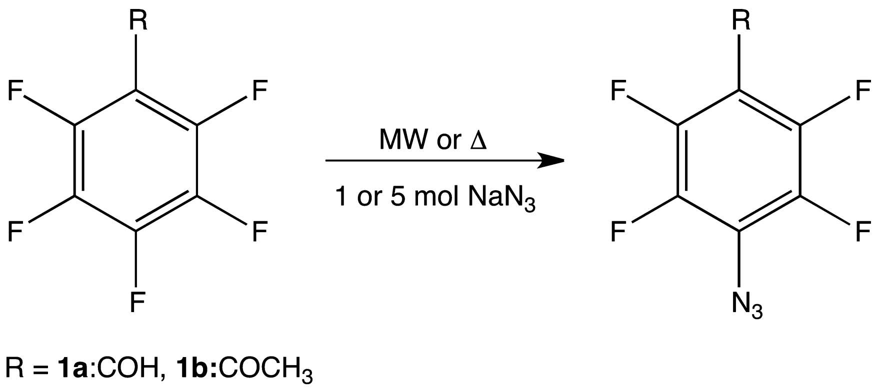


Product	R	Traditional refluxing[a]		Microwave refluxing[b]	
		Time/h	Yield %	Time/min	Yield %
2a	COH	8	90	15	85
2b	$COCH_3$	8	80	15	85
2c	$COOCH_3$	8	80	15	70
2d	CN	8	75	15	90
2e	NO_2	8	70	15	90

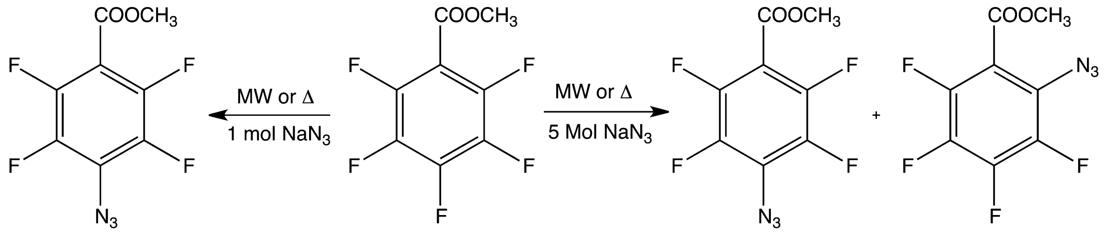
Each *p*-substituted fluorophenyl azide was purified by column chromatography and characterized by UV–vis, IR, NMR and MS.

[a] A solution of R-pentafluorobenzene (1 mol) and NaN_3 (1 mol) in acetone (10 mL) and water (3 mL) was refluxed.

[b] A solution of R-pentafluorobenzene (1 mol) and NaN_3 (1 mol) in acetone (6 mL) and water (2 mL) was irradiated in a microwave reactor (Discover CEM) at 70 °C (50 W).

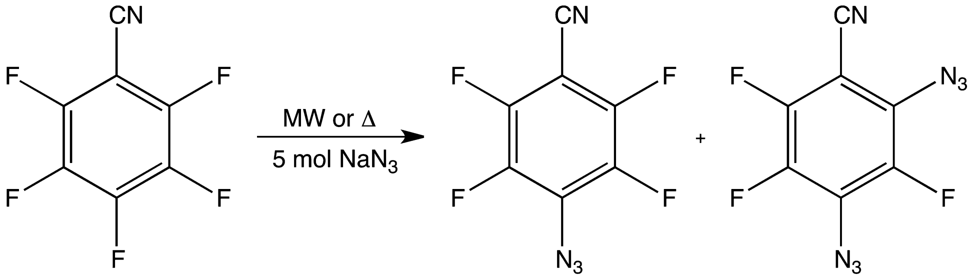


Scheme 1. Reaction of sodium azide with pentafluorobenzaldehyde **1a** and pentafluoroacetophenone **1b**.



1c

Scheme 2. Reaction of sodium azide with methyl pentafluorobenzoate **1c**.

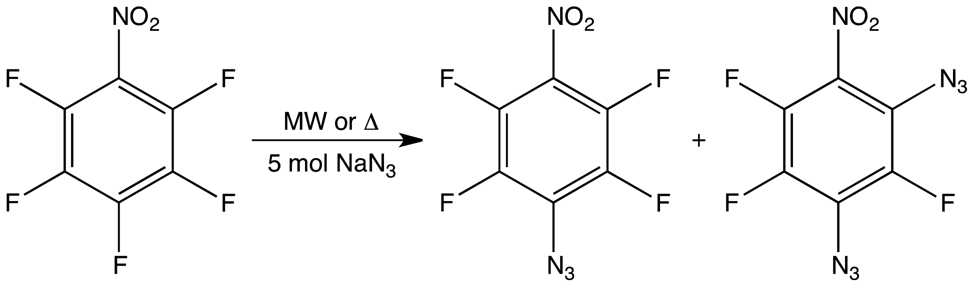


1d 60 % 30 %

Scheme 3. Reaction of sodium azide with pentafluorobenzonitrile **1d**.

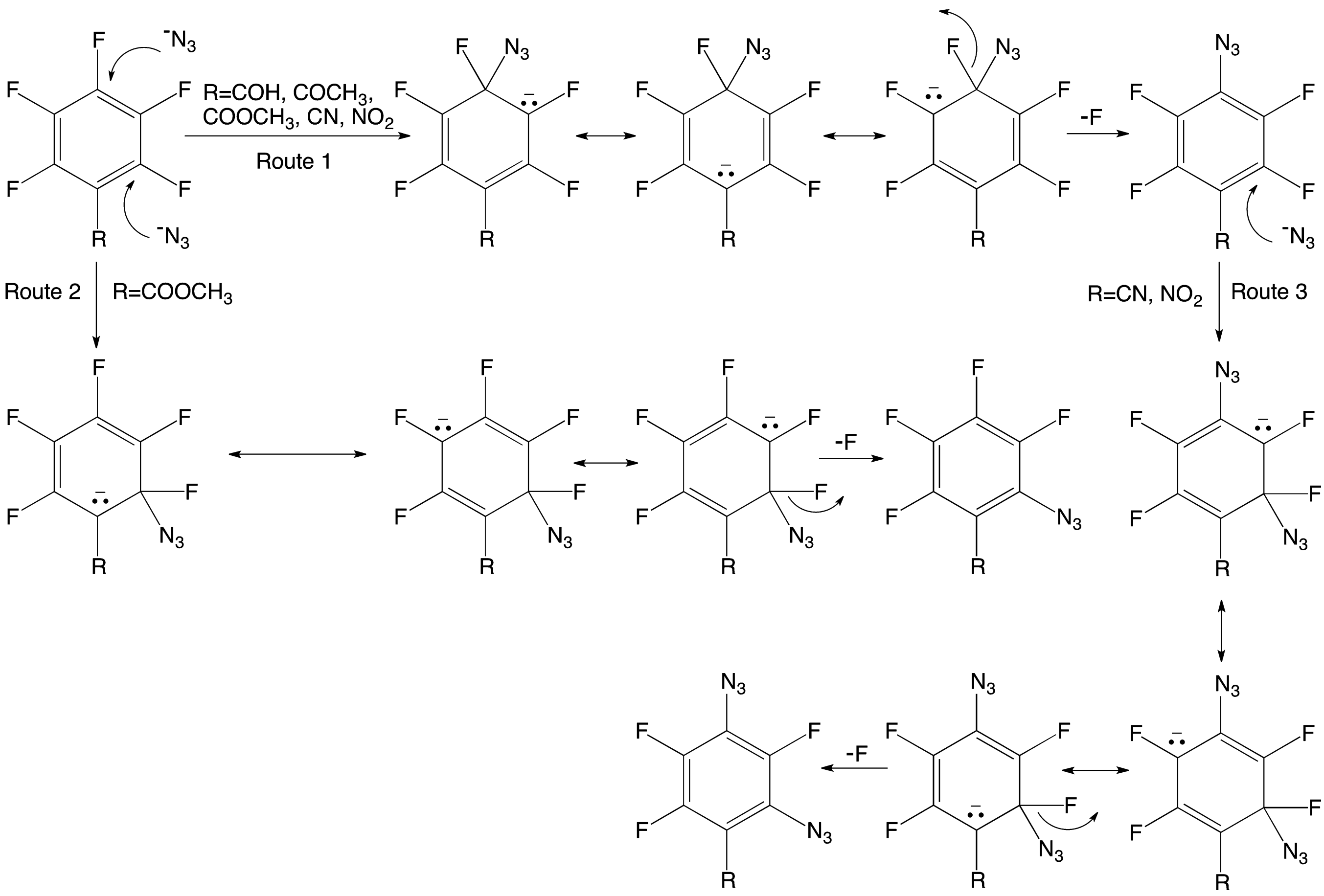
amount of sodium azide and a diazide (Scheme 4) was also produced with a large excess of sodium azide.

Nucleophilic substitution reactions of aryl halides (S_NAr) take place only when an electronic factor makes the carbon bonded to the halogen susceptible to nucleophilic attack [16]. Therefore, these reactions can occur when strong electron-withdrawing groups are *ortho* or *para* to the leaving halogen atom. It is well known that this S_NAr reaction proceeds by an addition-elimination mechanism (Scheme 5) involving the formation of a carbanion with delocalized electrons called a Meisenheimer complex (Fig. 1). This intermediate is strongly stabilized due to the presence of fluorine or other electron-withdrawing group in the several resonance structures.



1e 55 % 35 %

Scheme 4. Reaction of sodium azide with pentafluoronitrobenzene **1e**.



Scheme 5. Different mechanisms in the reaction of sodium azide with R-pentafluorobenzene (R = COH, $COCH_3$, $COOCH_3$, CN, NO_2).

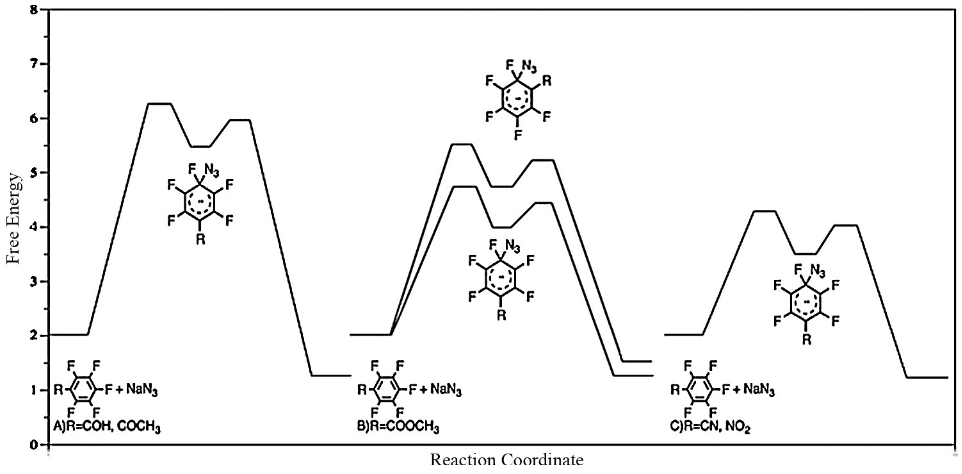


Fig. 1. A free energy diagram for the S_NAr reaction of sodium azide with R-pentafluorobenzene (R = COH, $COCH_3$, $COOCH_3$, CN, NO_2).

In the reaction of pentafluoro benzene with a weak electron-withdrawing substituent (COH, $COCH_3$) only one mechanistic pathway is available (Scheme 5, Route 1). In this case, only the *para*-position is sufficiently activated (Fig. 1A) for substitution under microwave irradiation or conventional heating. Thus the reaction on *ortho*-position must require a larger amount of energy than the one provided. Having an intermediate electron-withdrawing substituent ($COOCH_3$) both mechanisms (Scheme 5, Route 1 and 2) must be close in energy and microwave irradiation or conventional heating provide the energy required for both reactions to occur simultaneously (Fig. 1B). Having a cyano or nitro substituent in the aromatic ring, the *para*-position is actually activated by strong inductive and resonance effects (Fig. 1C) thus making the first substitution a very fast process (Scheme 5, Route 1). In this latter reaction, a *para*-substituted tetrafluorophenyl azide is produced that contains an *ortho*-position strongly activated for a second substitution to take place (Scheme 5, Route 3).

3. Conclusions

In summary, microwave-assisted synthesis of substituted fluorophenyl mono- and diazides by S_NAr represents a fast methodology to prepare photoaffinity labeling and crosslinking reagents. A synergic effect between the amount of sodium azide and the electron-withdrawing character of the substituents is observed in this reaction. In fact, the type of products obtained depends on the electron-withdrawing capacity of the substituents on the fluorophenyl compound. A strong substituent (CN or NO_2) results in the production of a mixture of mono and diazide. A medium strength substituent ($COOCH_3$) results in the production of two mono azides *ortho*- and *para*-substituted while a weak substituent (COH, $COCH_3$) gives exclusively *para*-substituted tetrafluorophenyl azide.

4. Experimental

4.1. General methods

Caution! Organic azides should be considered explosive. They are thermally and frictionally sensitive and all manipulations should take place behind a blast shield. They are light sensitive and all reactions and chromatography procedures should be conducted under diminished light.

Melting points were measured with a Fisher Johns apparatus. UV–vis spectra were obtained on a Shimadzu UV-2401 Spectrophotometer. NMR spectra were obtained on a Varian, Mercury 400 MHz nuclear magnetic resonance spectrometer. ^{1}HNMR spectra were recorded in ppm from tetramethylsilane and ^{19}F NMR spectra were recorded in ppm from hexafluorobenzene. Mass spectra analysis was done on a Finnigan MAT 8200 spectrometer. All the starting compounds were purchased from Aldrich. Reactions under microwave irradiation were performed in a CEM microwave reactor, Discover System DU8756.

4.2. General synthetic methods

4.2.1. Substitution reaction S_NAr under conventional heating (Δ)

A solution of R-pentafluorobenzene (1 mol) and sodium azide (1 or 5 mol) in acetone (10 mL) and water (3 mL) was placed in a flask under reflux for 8 h. After cooling, it was poured in an ice/water mixture and extracted with ether. The organic extract was dried over anhydrous $MgSO_4$, filtered and concentrated. Each fluorophenyl azide was separated and/or purified by column chromatography [6].

4.2.2. Substitution reaction S_NAr under microwave irradiation (MW)

A solution of R-pentafluorobenzene (1 mol) and sodium azide (1 or 5 mol) in acetone (6 mL) and water (2 mL) was placed in a flask equipped with a reflux condenser. The reaction mixture was irradiated in a microwave oven (at 50 W and 70 °C) for 15 min. After cooling, it was poured in an ice/water mixture and extracted with ether. The organic extract was dried over anhydrous $MgSO_4$, filtered and concentrated. Each fluorophenyl azide was separated and/or purified by column chromatography [6].

*4.2.2.1. 4-Azido-2,3,5,6-tetrafluorobenzaldehyde (**2a**).* Colorless solid with m.p. 44–45 °C [8]; IR (KBr, cm^{-1}) 2917 (C–H aliphatic), 2860, 2780 (C–H aldehyde), 2116 ($-N_3$), 1703 (C=O), 1642, 1474 (C=C aromatic), 1263, 1238, 1216 (C–F); UV–vis (CH_3OH, nm) 284, 250, 208. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.23 (m, 1H); ^{19}F NMR (400 MHz, $CDCl_3$) δ (ppm) −146.34 (dd, J = 20.11, 7.22 Hz, 2F), −152.40 (dd, J = 20.11, 7.22 Hz, 2F); HRMS calcd for $C_7HF_4N_3O$ was 219.0056, found 219.0052.

*4.2.2.2. 4-Azido-2,3,5,6-tetrafluoroacetophenone (**2b**).* Colorless liquid [8]; IR (neat, cm^{-1}) 2970 (C–H aliphatic) 2127 ($-N_3$), 1642, 1478 (C=C aromatic), 1707 (C=O), 1240, 1196, 1170 (C–F); UV–vis (CH_3OH, nm) 268, 209. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.61 (t, J_{H-F} = 1.77, 3H); ^{19}F NMR (400 MHz, $CDCl_3$) δ (ppm) −140.00 (ddd, J = 20.74, 13.51, 4.83 Hz, 2F), −152.28 (m, J = 20.74, J = 13.51, 4.83 Hz, 2F); HRMS calcd for $C_7H_3F_4N_3O$ was 233.0212, found 233.0210.

*4.2.2.3. Methyl 4-azido-2,3,5,6-tetrafluorobenzoate (**2c**).* Colorless solid with m.p. 54–55 °C [8]; IR (KBr, cm^{-1}) 2960 (C–H aliphatic) 2125 ($-N_3$), 1738 (C=O), 1624, 1485 (C=C aromatic), 1260, 1221, 1000 (C–F); UV–vis (CH_3OH, nm) 264, 207. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.96 (s, 1H); ^{19}F NMR (400 MHz, $CDCl_3$) δ (ppm) −139.45 (ddd, J = 22.80, 13.80, 6.00 Hz, 2F), 161.67 (ddd, J = 22.80, 13.80, 6.00 Hz, 2F); HRMS calcd for $C_8H_3F_4N_3O_2$ was 249.0161, found 249.0155.

*4.2.2.4. 4-Azido-2,3,5,6-tetrafluorobenzonitrile (**2d**).* Pale yellow liquid [8], IR (neat, cm^{-1}) 2239 (CN), 2121 ($-N_3$), 1648, 1475 (C=C aromatic), 1266, 1243, 1215 (C–F); UV–vis (CH_3OH, nm) 284, 258, 208. ^{19}F NMR (400 MHz, $CDCl_3$) δ (ppm) −133.37 (ddd, J = 22.71, 15.51, 7.20 Hz, 2F), −149.97 (ddd, J = 22.71, 15.51, 7.20 Hz, 2F); HRMS calcd for $C_7F_4N_4$ was 216.0059, found 216.0051.

*4.2.2.5. 4-Azido-2,3,5,6-tetrafluoronitrobenzene (**2e**).* Pale yellow liquid [8], IR (neat, cm^{-1}) 2121 ($-N_3$), 1604, 1511, 1489 (C=C aromatic), 1590, 1368 (NO_2), 1129, 1117, 1106 (C–F); UV–vis (CH_3OH, nm) 275, 253, 208. ^{19}F NMR (400 MHz, $CDCl_3$) δ (ppm) −147.05 (ddd, J = 23.50, 15.84, 6.11 Hz, 2F), −150.49 (ddd, J = 23.50, 15.84, 6.11 Hz, 2F); HRMS calcd for $C_6F_4N_4O_2$ was 235.9957, found 235.9942.

*4.2.2.6. Methyl 2-azido-3,4,5,6-tetrafluorobenzoate (**2f**).* Pale yellow solid with m.p. 66–68 °C, IR (KBr, cm^{-1}) 2970 (C–H aliphatic) 2129 ($-N_3$), 1732 (C=O) 1644, 1479 (C=C aromatic), 1260, 1229, 1216 (C–F); UV–vis (CH_3OH, nm) 208, 270. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.72 (s, 1H); ^{19}F NMR (400 MHz, CDCl3) δ (ppm) −139.98 (ddd, J = 18.31, 12.21, 6.10 Hz, 1F), −149.77 (dd, 20.64, 8.72 Hz, 2F), −152.28 (dd, J = 20.64, 8.72 Hz, 1F). HRMS calcd for $C_8H_3F_4N_3O_2$ was 249.0161, found 249.0155.

*4.2.2.7. 2,4-Diazido-3,5,6-trifluorobenzonitrile (**3a**).* Pale yellow liquid; IR (neat, cm^{-1}) 2230 (CN), 2116 (N_3), 1650, 1631, 1475 (C=C aromatic), 1655, 1243, 1211 (C–F); UV–vis (CH_3OH, nm) 272, 258, 208. ^{19}F NMR (400 MHz, $CDCl_3$) δ (ppm) −140.31 (d, J = 9.11 Hz, 1F), −148.34 (dd, J = 21.26, 9.11 Hz, 1F), −148.94 (d, J = 21.26). HRMS calcd for $C_7F_3N_7$ was 239.0167, found 239.0160.

*4.2.2.8. 2,4-Diazido-3,5,6-trifluoronitrobenzene (**3b**).* Pale yellow liquid; IR (neat, cm^{-1}) 2116 (N_3), 1626, 1579, 1512, 1479 (C=C aromatic), 1599, 1325 (NO_2), 1230, 1198, 1157 (C–F); UV–vis (CH_3OH, nm) 329, 311, 252, 209. ^{19}F NMR (400 MHz, $CDCl_3$) δ (ppm) −133.05 (dd, J = 20.46, 11.05 Hz, 1F), −140.62 (d, J = 11.05 Hz, 1F), −149.43 (d, J = 20.46 Hz, 1F), HRMS calcd for $C_6F_3N_7O_2$ was 259.0066, found 259.0059.

Acknowledgements

We would like to acknowledge financial support by CONACyT (Grant CB-2010-155678). R.M.G.-B. acknowledges financial support by CONACyT (Scholarship No. 290618) for an internship at UCLA.

References

[1] For reviews on aryl azide and aryl nitrene chemistry:
(a) E.F.V. Scriven, Azides and Nitrenes: Reactivity and Utility, Academic Press, New York, 1984;

(b) M.S. Platz, E. Leyva, K. Haider, Selected Topics in the Matrix Photochemistry of Nitrenes, Carbenes and Excited Triplet States, in: A. Padwa (Ed.), Org. Photochem., vol. 11, 1991, pp. 367–429;
(c) M.S. Platz, Nitrenes, in: R.A. Moss, M.S. Platz, M.S. Jones, Jr. (Eds.), Reactive Intermediate Chemistry, John Wiley & Sons Inc., New York, 2004;
(d) D. de Loera, E. Leyva, R. Jiménez-Cataño, Bol. Soc. Quím. Méx 3 (2009) 93–106;
(e) E. Leyva, D. de Loera, S. Leyva, R. Jiménez-Cataño, Fluorinated aryl nitrene precursors, in: D.E. Falvey, A.D. Gudmundsdottir (Eds.), Nitrene and Nitrenium Ions, John Wiley & Sons Inc, New York, 2013.

[2] (a) E.F.V. Scriven, K. Turnbull, Chem. Rev. 88 (1988) 297–368;
(b) S. Leyva, V. Castanedo, E. Leyva, J. Fluorine Chem. 121 (2003) 171–175;
(c) E. Leyva, D. de Loera, R. Jiménez-Cataño, Tetrahedron Lett. 51 (2010) 3978–3979;
(d) E. Leyva, R.-M. González-Balderas, D. de Loera, R. Jiménez-Cataño, Tetrahedron Lett. 53 (2012) 2447–2449;
(e) E. Leyva, S. Leyva, R.M. González-Balderas, D. de Loera, R. Jiménez-Cataño, Mendeleev Commun. 23 (2013) 217–218.

[3] For examples of aryl mono- and diazides as crosslinking reagents:
(a) M. Yan, M.N. Wybourne, J.F.W. Keana, React. Funct. Polym. 43 (2000) 221–225;
(b) T. Hosoya, A. Inoue, T. Hiramatsu, T. Hikemoto, M. Suzuki, Bioorg. Med. Chem. 17 (2009) 2490–2496;
(c) P.J. Crocker, N. Imai, K. Rajagopalan, M.A. Boggess, S. Kwiatkowsky, L.D. Dwyer, T.C. Vanaman, D.S. Watt, Bioconjugate Chem. 1 (1990) 419–424.

[4] For reviews on aryl azides as photoaffinity labels:
(a) H. Bayley, Photogenerated Reagents in Biochemistry and Molecular Biology, Elsevier, New York, 1983;
(b) S.A. Fleming, Tetrahedron 51 (1995) 12479–12520;
(c) E. Leyva, S. Leyva-Ramos, C. Cortés-García, Rev. Mex. Cienc. Farm. 44 (2013) 7–23.

[5] (a) E. Leyva, M.S. Platz, G. Persy, J. Wirz, J. Am. Chem. Soc. 108 (1986) 3783–3790;
(b) E. Leyva, M.S. Platz, Tetrahedron Lett. 26 (1985) 2147–2150;
(c) E. Leyva, M.S. Platz, Tetrahedron Lett. 28 (1987) 11–14.

[6] (a) E. Leyva, M.J.T. Young, M.S. Platz, J. Am. Chem. Soc. 108 (1986) 8307–8309;
(b) E. Leyva, D. Munoz, M.S. Platz, J. Org. Chem. 54 (1989) 5938–5945;
(c) R. Poe, M.J.T. Young, E. Leyva, M.S. Platz, J. Am. Chem. Soc. 113 (1991) 3209–3211;
(d) K. Schnapp, R. Poe, E. Leyva, N. Saudararajan, M.S. Platz, Bioconjugate Chem. 4 (1993) 172–177.

[7] (a) E. Leyva, R. Sagredo, Tetrahedron 54 (1998) 7367–7374;
(b) E. Leyva, R. Sagredo, E. Moctezuma, J. Fluorine Chem. 125 (2004) 741–747;
(c) W.L. Karney, W.T. Borden, J. Am. Chem. Soc. 119 (1997) 3347–3350;
(d) N.P. Gritsan, A.D. Gudmunsdottir, D. Tigelaar, Z. Zhu, W.L. Karney, C.M. Haddad, M.S. Platz, J. Am. Chem. Soc. 123 (2001) 1951–1962.

[8] (a) F.W. Keana, S.X. Cai, J. Org. Chem. 55 (1990) 3640–3650;
(b) J.F.W. Keana, S.X. Cai, J. Fluorine Chem. 43 (1989) 151–154;
(c) M. Yang, S.X. Cai, J.F.W. Keana, J. Org. Chem. 59 (1994) 5951–5954;
(d) K.A.H. Chehade, H.P. Spielmann, J. Org. Chem. 65 (2000) 4949–4953.

[9] (a) R.S. Pandurangi, S.R. Karra, R.R. Kuntz, W.A. Volkert, Photochem. Photobiol. 65 (1997) 208–221;
(b) R.S. Pandurangi, K.V. Katti, L. Stilwell, C.L. Barnes, J. Am. Chem. Soc. 20 (1998) 11364–11373;
(c) R.S. Pandurangi, P. Lusiak, R.R. Kuntz, W.A. Volkert, J. Rogowski, M.S. Platz, J. Org. Chem. 63 (1998) 9019–9020.

[10] (a) B.L. Hayes, Microwave Synthesis: Chemistry at the Speed of Light, CEM Publishing, USA, 2002;
(b) J.P. Tierney, P. Lidström, Microwave Assisted Organic Synthesis, Blackwell Publishing, Oxford, UK, 2005;
(c) A. de la Hoz, A. Díaz-Ortiz, A. Moreno, Chem. Soc. Rev. 34 (2005) 164–178.

[11] For a review in new applications of perfluoroarylazides: L.-H. Liu, M. Yang, Accounts Chem. Res. 43 (2010) 1434–1443.

[12] (a) P.A.S. Smith, J.H. Boyer, J. Am. Chem. Soc. 73 (1951) 2626–2629;
(b) P.A.S. Smith, C.D. Rowe, L.B. Bruner, J. Org. Chem. 34 (1969) 3430–3433;
(c) P.A.S. Smith, G.F. Budde, S.P. Chou, J. Org. Chem. 50 (1985) 2062–2064.

[13] (a) W. Fisher, J.-P. Anselme, J. Am. Chem. Soc. 89 (1967) 5284–5287.

[14] Q. Liu, Y. Tor, Org. Lett. 5 (2003) 2571–2572.

[15] (a) F. D'Anna, S. Marullo, R. Noto, J. Org. Chem. 73 (2008) 6224–6228;
(b) F. D'Anna, S. Marullo, P. Vitale, R. Noto, Ultrason. Sonochem. 19 (2012) 136–142.

[16] T.W.G. Solomons, C.B. Fryhle, Organic Chemistry, John Wiley & Sons, Inc., New York, U.S.A., 2004.