Comptes Rendus
Chimie
Supplementary material to the article available at:
https://doi.org/10.5802/crchim.144

Supplementary material: Palladium-catalyzed Suzuki–Miyaura cross-coupling with α-aminophosphonates based on 1,3,4-oxadiazole as ligands

Shaima Hkiri [a, b], Soufiane Touil [b], Ali Samarat [b] and David Sémeril [*, a]

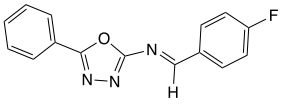
[a] University of Strasbourg, Synthèse Organométallique et Catalyse, UMR-CNRS 7177, 4 rue Blaise Pascal, 67008 Strasbourg, France

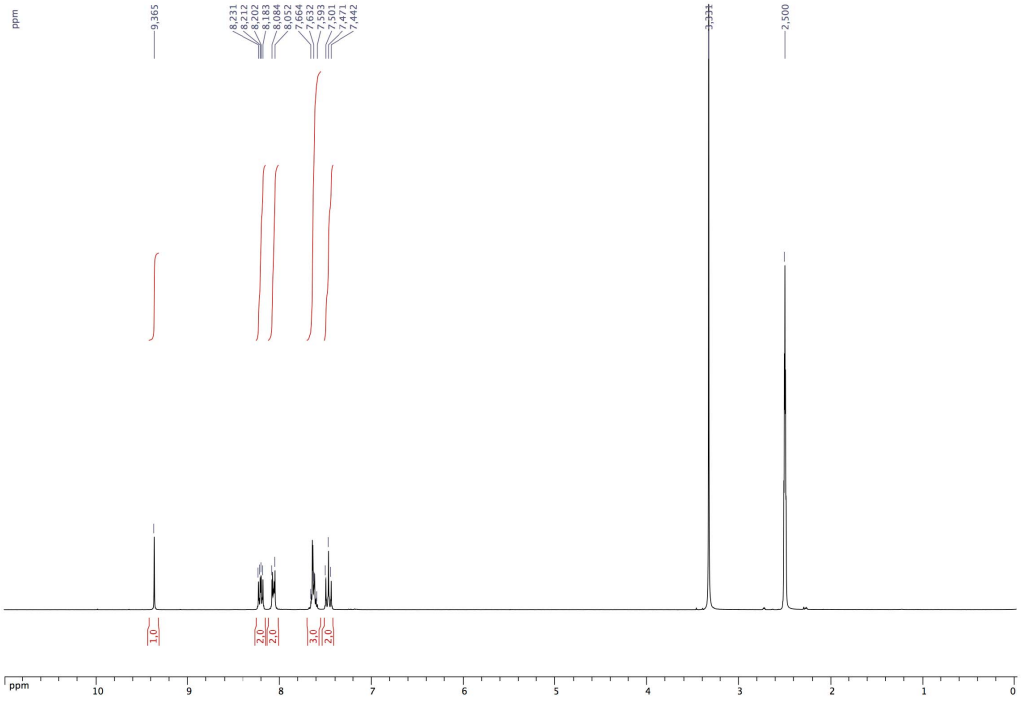
[b] University of Carthage, Faculty of Sciences of Bizerte, LR18ES11, Laboratory of Hetero-Organic Compounds and Nanostructured Materials, 7021, Bizerte, Tunisia

E-mails: hkiri@unistra.fr (S. Hkiri), soufiane.touil@fsb.rnu.tn (S. Touil), ali.samarat@fsb.rnu.tn, ali.samarat@fsb.u-carthage.tn (A. Samarat), dsemeril@unistra.fr (D. Sémeril)

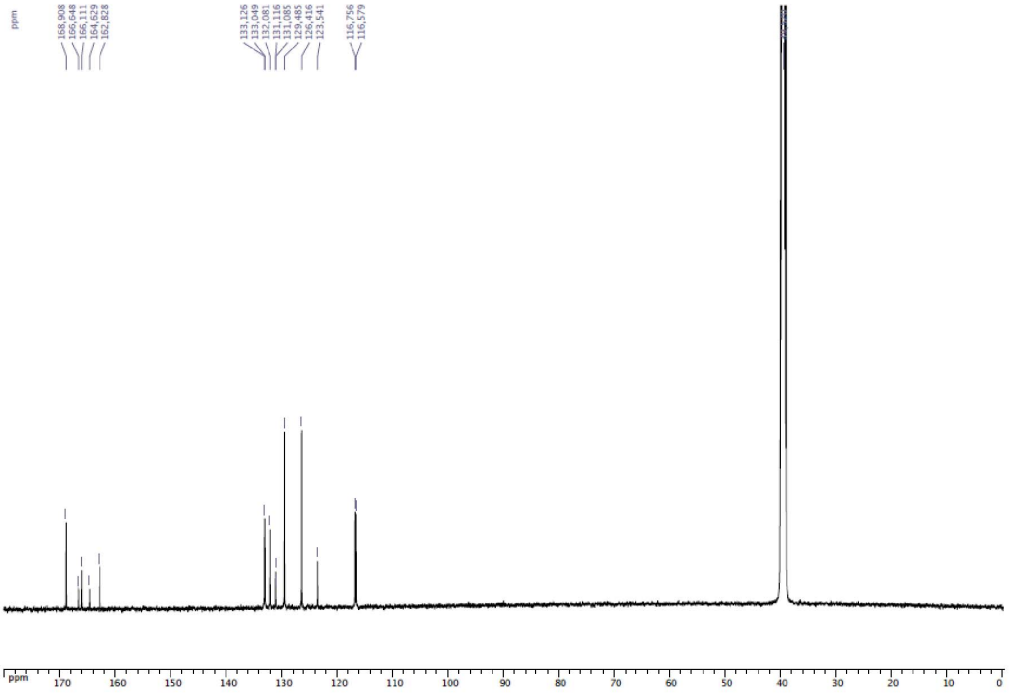
[*] Corresponding author.

(*E*)-1-(4-fluorolphenyl)-*N*-(5-phenyl-1,3,4-oxadiazol-2-yl)methanimine

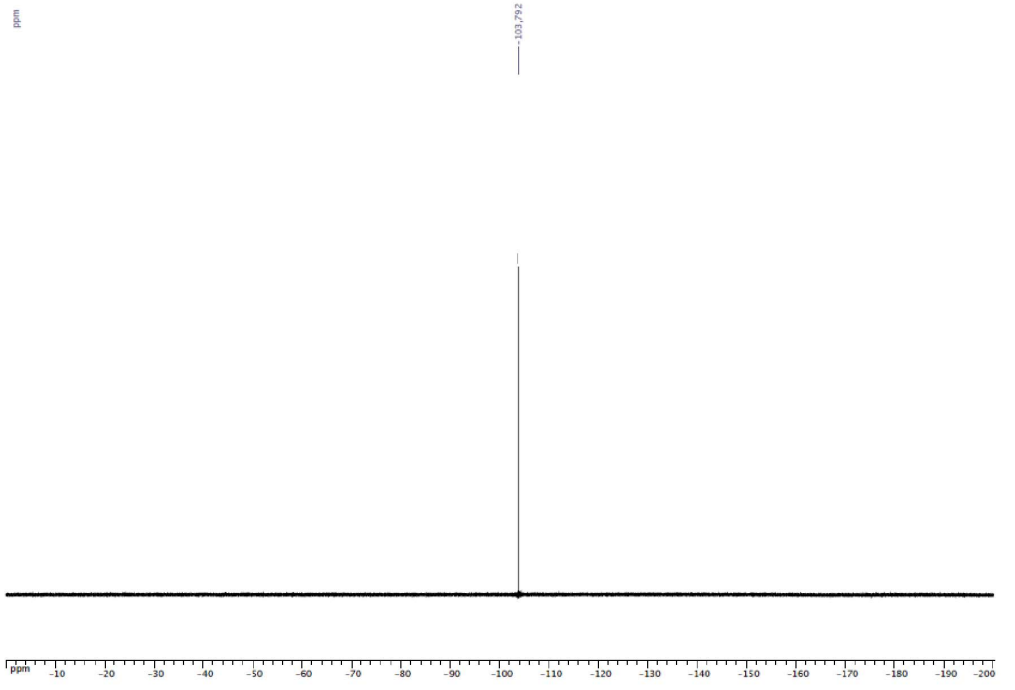




^{1}H NMR spectrum (DMSO-d_6)

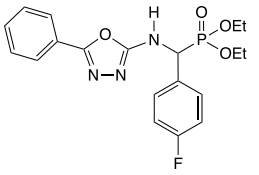


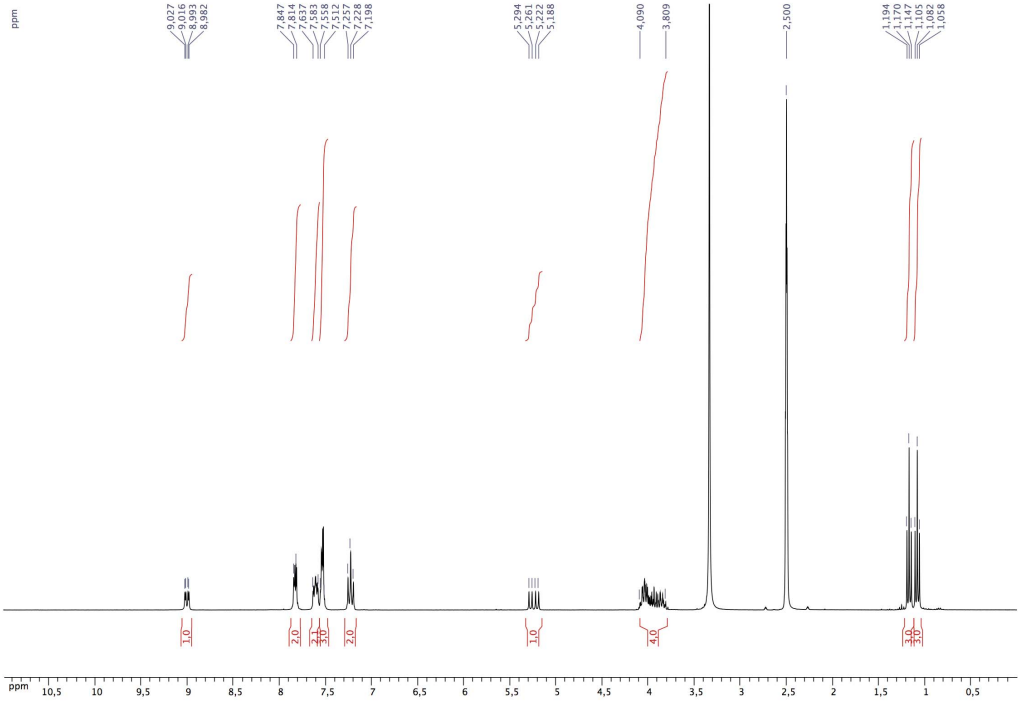
$^{13}C\{^{1}H\}$ NMR spectrum (DMSO-d_6)



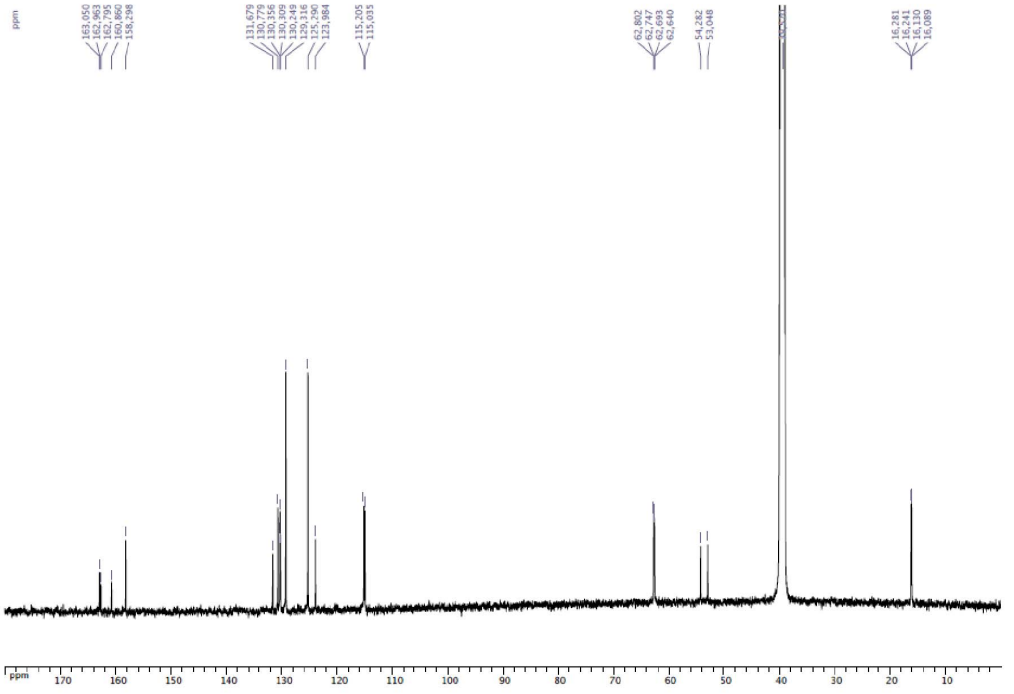
$^{19}F\{^{1}H\}$ NMR spectrum (DMSO-d_6)

Diethyl[(5-phenyl-1,3,4-axodiazol-2-ylamino)(4-fluorophenyl) methyl]phosphonate (4)

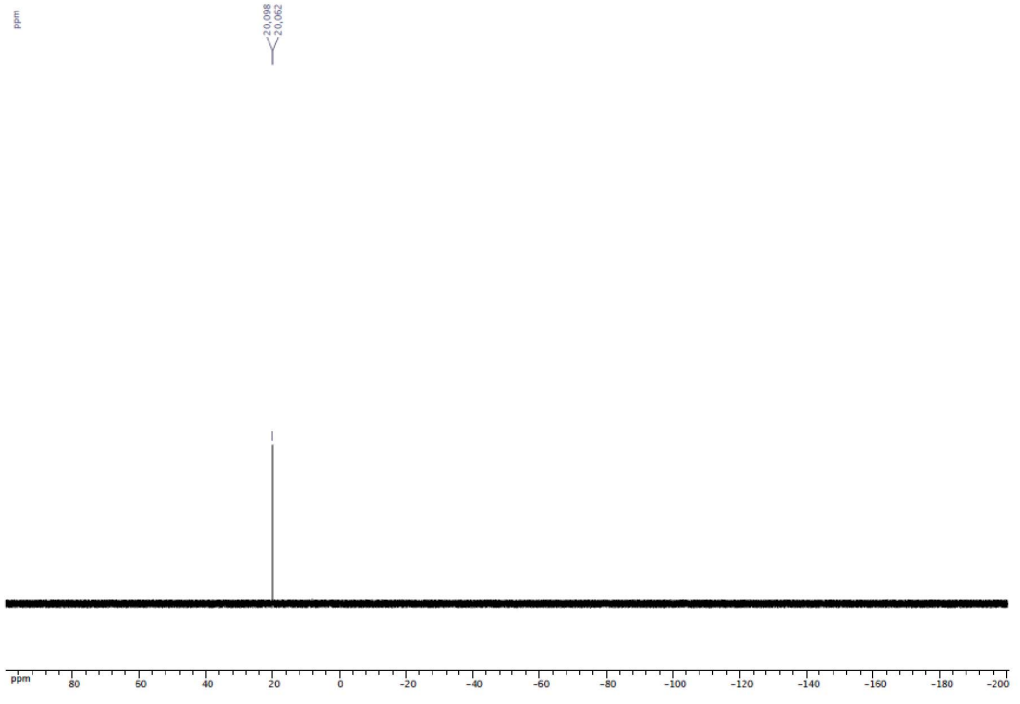




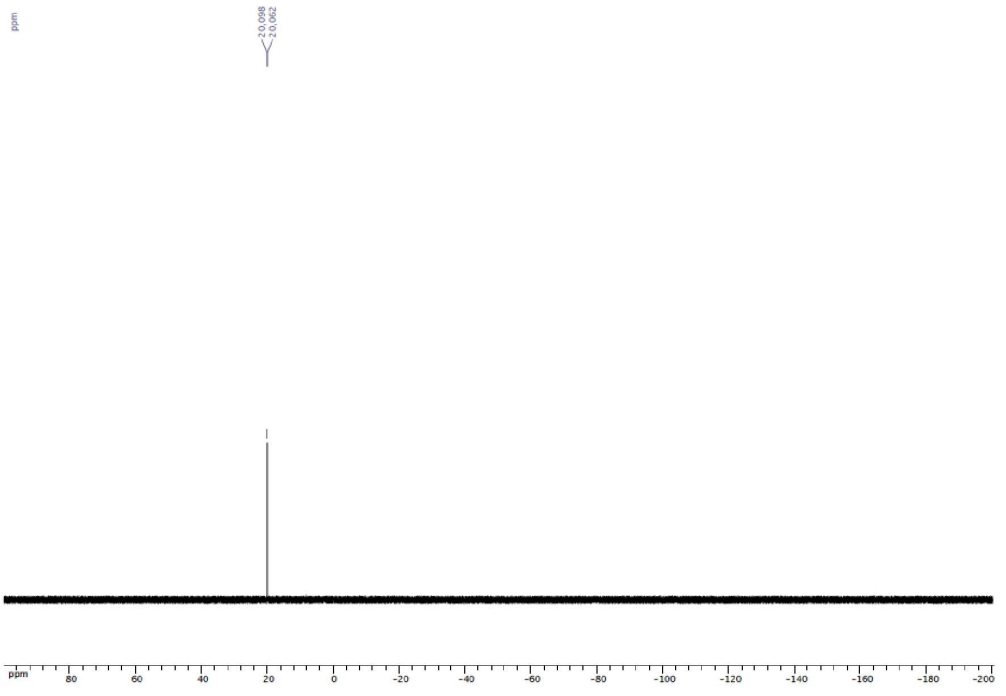
^{1}H NMR spectrum (DMSO-d_6)



$^{13}C\{^{1}H\}$ NMR spectrum (DMSO-d_6)

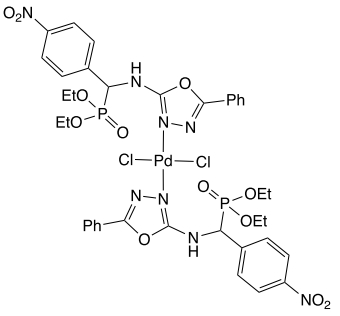


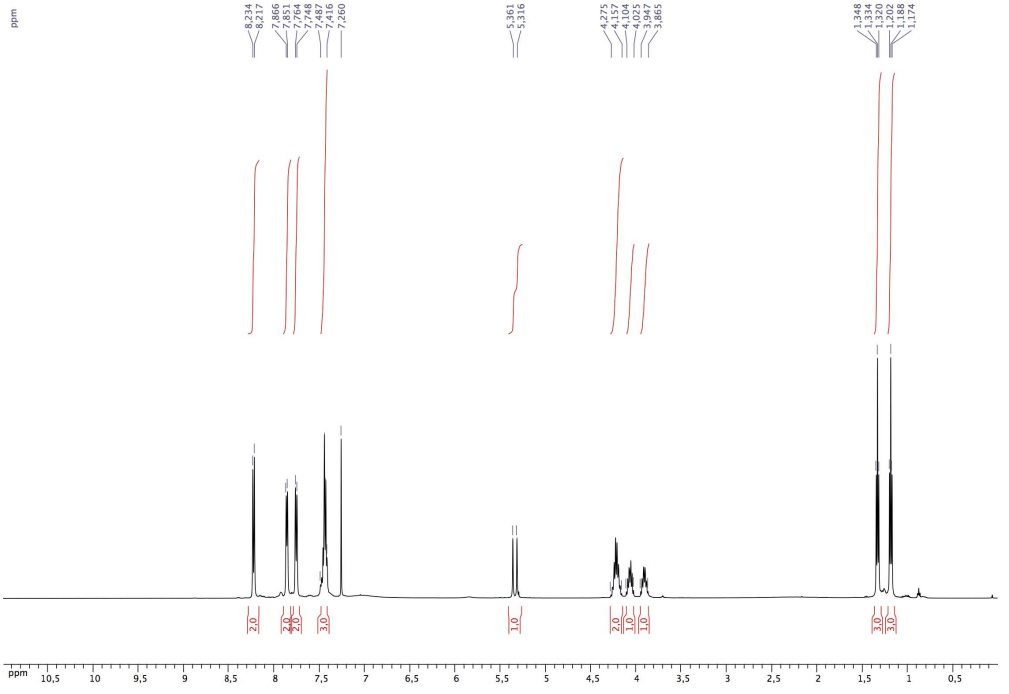
$^{31}P\{^{1}H\}$ NMR spectrum (DMSO-d_6)



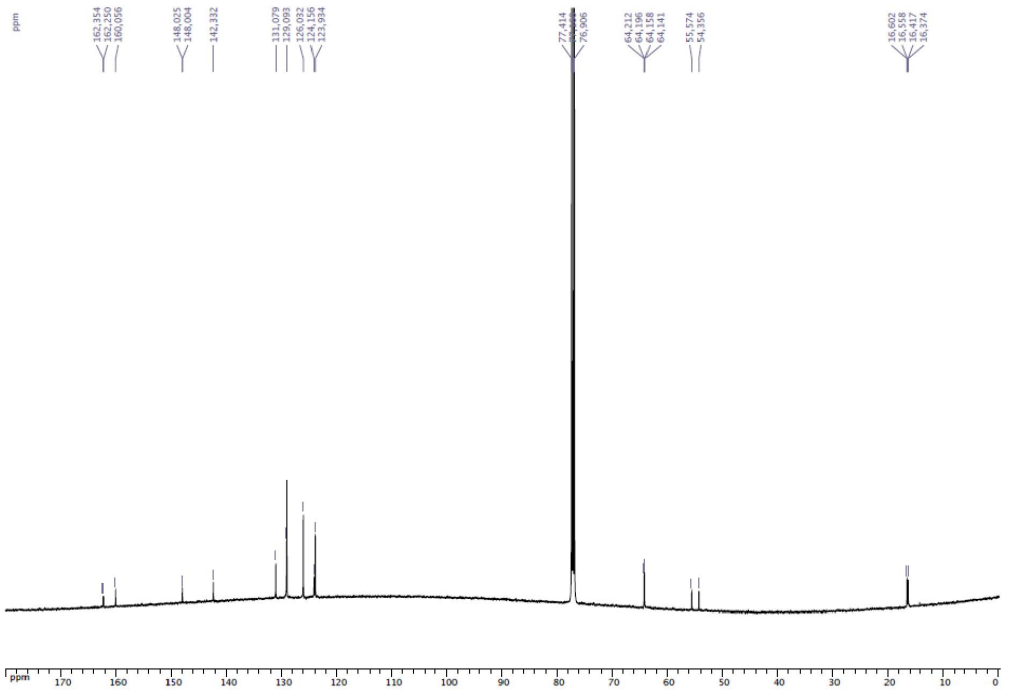
$^{19}F\{^{1}H\}$ NMR spectrum (DMSO-d_6)

Dichloro-bis-{diethyl[(5-phenyl-1,3,4-oxadiazol-2-ylamino)(4-nitrophenyl)methyl]phosphonate} palladium(II) (5)

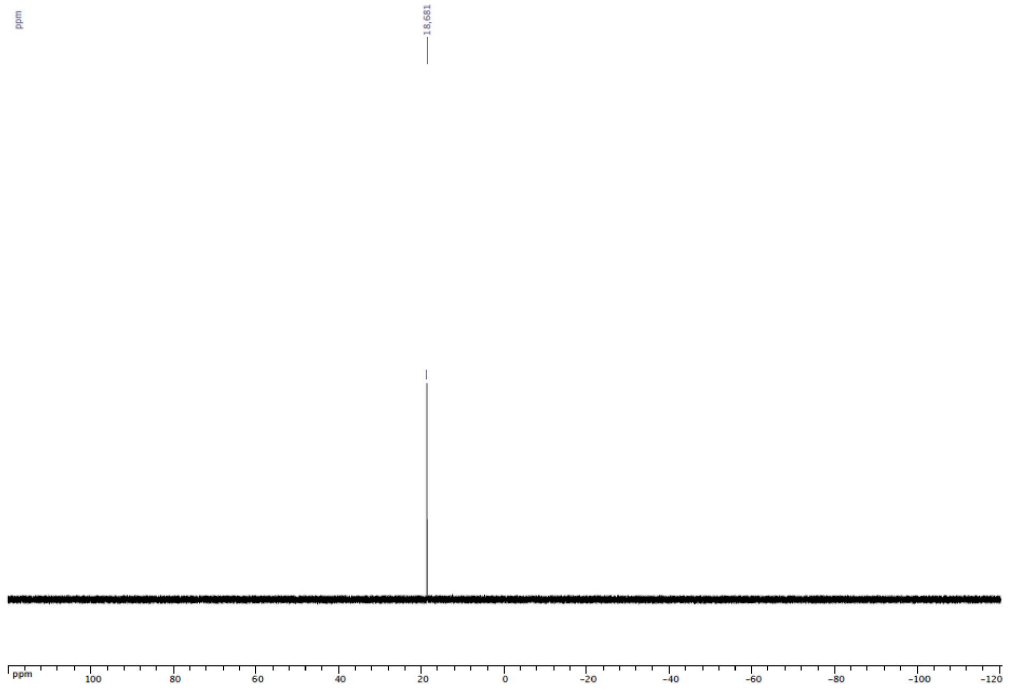




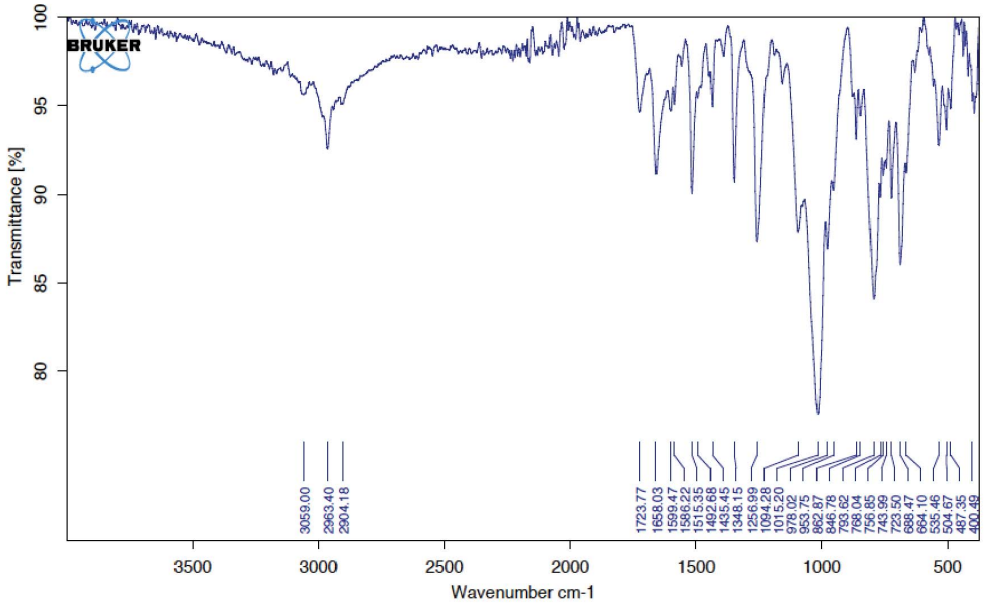
^{1}H NMR spectrum ($CDCl_3$)



$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



$^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



FT-IR spectrum

Typical procedure for the palladium-catalyzed Suzuki–Miyaura cross-coupling reactions

In a Schlenk tube in an inert atmosphere a solution of $[Pd(OAc)_2]$ in 1,4-dioxane, a solution of the ligand **1** (ratio Pd/**1** = 1/1) in 1,4-dioxane, aryl halide (0.5 mmol), aryl boronic acid (0.75 mmol), Cs_2CO_3 (0.325 g, 0. 75 mmol), decane (0.025 mL, internal reference) and a complementary amount of 1,4-dioxane, so that the total reaction volume was 2.0 mL, were introduced. The reaction mixture was then heated at 100 °C. After cooling to room temperature, a small amount (0.5 mL) of the resulting solution was passed through a Millipore filter and analyzed by GC.

Some homocoupling product (Ar′–Ar′ coming from $Ar'B(OH)_2$) was detected in each run, but the Ar′–Ar′:Ar–Ar′ ratio did never exceed 5%. The products were unambiguously identified by ^{1}H NMR after their isolation. Their NMR spectra were compared to those reported in the literature.

In this study the following products were prepared:

4-Methoxybiphenyl [1] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.56–7.51 (m, 4H, arom. CH), 7.41 (t, 2H, arom. CH, $^3J_{HH}$ = 7.4 Hz), 7.29 (t, 1H, arom. CH, $^3J_{HH}$ = 7.4 Hz), 6.97 (d, 2H, arom. CH, $^3J_{HH}$ = 7.5 Hz), 3.85 (s, 3H, OCH_3) ppm.

2-Methoxybiphenyl [1] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.54 (d, 1H, arom. CH, $^3J_{HH}$ = 7.5 Hz), 7.42–7.26 (m, 6H, arom. CH), 7.05–6.95 (m, 2H, arom. CH), 3.78 (s, 3H, OCH_3) ppm.

2-Methoxy-6-phenylnaphthalene [2] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.96 (s, 1H, arom. CH), 7.76–7.12 (m, 10H, arom. CH), 3.89 (s, 3H, OCH_3) ppm.

4-Methylbiphenyl [2] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.57 (d, 2H, arom. CH, $^3J_{HH}$ = 7.3 Hz), 7.50 (d, 2H, arom. CH, $^3J_{HH}$ = 7.4 Hz), 7.42 (t, 2H, arom. CH, $^3J_{HH}$ = 7.4 Hz), 7.32 (t, 1H, arom. CH, $^3J_{HH}$ = 7.4 Hz), 7.25 (d, 2H, arom. CH, $^3J_{HH}$ = 7.4 Hz), 2.40 (s, 3H, CH_3) ppm.

3-Methylbiphenyl [2] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.59–7.24 (m, 8H, arom. CH), 7.15 (d, 1H, arom. CH, $^3J_{HH}$ = 7.5 Hz), 2.39 (s, 3H, CH_3) ppm.

2-Methylbiphenyl [2] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.59 (d, 1H, arom. CH, $^3J_{HH}$ = 7.4 Hz), 7.41–7.20 (m, 8H, arom. CH), 2.30 (s, 3H, CH_3) ppm.

1-Phenylnaphthalene [1] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.93 (d, 2H, arom. CH, $^3J_{HH}$ = 8.1 Hz), 7.89 (d, 1H, arom. CH, $^3J_{HH}$ = 8.0 Hz), 7.58–7.40 (m, 9H, arom. CH) ppm.

4-Methoxy-2′-methylbiphenyl [3] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.37–7.12 (m, 6H, arom. CH), 6.95 (d, 2H, arom. CH, $^3J_{HH}$ = 7.3 Hz), 3.87 (s, 3H, OCH_3), 2.31 (s, 3H, CH_3) ppm.

2-Methoxy-6-(2-methylphenyl)naphthalene [4] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.73 (t, 2H, arom. CH, $^3J_{HH}$ = 7.4 Hz), 7.68 (s, 1H, arom. CH), 7.42 (d, 1H, arom. CH, $^3J_{HH}$ = 7.5 Hz), 7.30–7.25 (m, 4H, arom. CH), 7.20–7.14 (m, 2H, arom. CH), 3.89 (s, 3H, OCH_3), 2.30 (s, 3H, CH_3) ppm.

2,4′-Dimethylbiphenyl [5] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.30–7.14 (m, 8H, arom. CH), 2.42 (s, 3H, CH_3), 2.30 (s, 3H, CH_3) ppm.

2,3′-Dimethylbiphenyl [6] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.35–7.21 (m, 8H, arom. CH), 2.42 (s, 3H, CH_3), 2.29 (s, 3H, CH_3) ppm.

2,4′-Dimethoxybiphenyl [7] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.62–7.55 (m, 2H, arom. CH), 7.43–7.36 (m, 2H, arom. CH), 7.20–7.03 (m, 4H, arom. CH), 3.93 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3) ppm.

2-Methoxy-6-(2-methoxyphenyl)-naphthalene [8] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.95 (s, 1H, arom. CH), 7.82–7.77 (m, 2H, arom. CH), 7.69 (d, 1H, arom. CH, $^3J_{HH}$ = 8.2 Hz), 7.37 (t, 1H, arom. CH, $^3J_{HH}$ = 7.7 Hz), 7.26 (d, 1H, arom. CH, $^3J_{HH}$ = 8.0 Hz), 7.22 (t, 1H, arom. CH, $^3J_{HH}$ = 7.4 Hz), 7.15 (d, 1H, arom. CH, $^3J_{HH}$ = 7.5 Hz), 7.14 (s, 1H, arom. CH), 6.90 (d, 1H, arom. CH, $^3J_{HH}$ = 8.2 Hz), 3.94 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3) ppm.

2-Methoxy-4′-methylbiphenyl [9] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.62–7.55 (m, 2H, arom. CH), 7.48–7.40 (m, 2H, arom. CH), 7.37 (d, 2H, arom. CH, $^3J_{HH}$ = 7.5 Hz), 7.19–7.10 (m, 2H, arom. CH), 3.91 (s, 3H, OCH_3), 2.53 (s, 3H, CH_3) ppm.

2-Methoxy-3′-methylbiphenyl [6] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.45–7.31 (m, 5H, arom. CH), 7.16 (d, 1H, arom. CH, $^3J_{HH}$ = 7.5 Hz), 7.08–6.99 (m, 2H, arom. CH), 3.83 (s, 3H, OCH_3), 2.42 (s, 3H, CH_3) ppm.

2-Methoxy-2′-methylbiphenyl [10] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.35–7.30 (m, 1H, arom. CH), 7.25–7.11 (m, 5H, arom. CH), 7.02–6.91 (m, 2H, arom. CH), 3.73 (s, 3H, OCH_3), 2.12 (s, 3H, CH_3) ppm.

2,6-Dimethyl-4′-methoxybiphenyl [6] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.22–7.18 (m, 5H, arom. CH), 7.12–7.01 (m, 2H, arom. CH), 3.92 (s, 3H, OCH_3), 2.09 (s, 6H, CH_3) ppm.

2,6-Dimethyl-2′-methoxybiphenyl [11] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.43–7.38 (m, 1H, arom. CH), 7.25–7.00 (m, 6H, arom. CH), 3.78 (s, 3H, OCH_3), 2.07 (s, 6H, CH_3) ppm.

2-Methoxy-6-(2,6-dimethyphenyl)-naphthalene [12] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.80 (d, 1H, arom. CH, $^3J_{HH}$ = 8.5 Hz), 7.74 (d, 1H, arom. CH, $^3J_{HH}$ = 8.5 Hz), 7.55 (br s, 1H, arom. CH), 7.26–7.23 (m, 1H, arom. CH), 7.22–7.14 (m, 3H, arom. CH), 7.14–7.10 (m, 2H, arom. CH), 3.94 (s, 3H, OCH_3), 2.05 (s, 6H, CH_3) ppm.

2,6,4′-Trimethylbiphenyl [10] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.31–7.24 (m, 3H, arom. CH), 7.20–7.14 (m, 2H, arom. CH), 7.13–7.03 (m, 2H, arom. CH), 2.43 (s, 3H, CH_3), 2.07 (s, 6H, CH_3) ppm.

2,6,3′-Trimethylbiphenyl [6] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.39–7.31 (m, 1H, arom. CH), 7.19–7.08 (m, 4H, arom. CH), 6.95 (d, 2H, arom. CH, $^3J_{HH}$ = 7.0 Hz), 2.40 (s, 3H, CH_3), 2.06 (s, 6H, CH_3) ppm.

2,6,2′-Trimethylbiphenyl [6] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.35–7.31 (m, 1H, arom. CH), 7.20–7.14 (m, 2H, arom. CH), 7.12–7.09 (m, 2H, arom. CH), 6.98–6.93 (m, 2H, arom. CH), 2.41 (s, 3H, CH_3), 2.05 (s, 6H, CH_3) ppm.

1-(2,6-Dimethylphenyl)-naphthalene [13] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.90 (d, 1H, arom. CH, $^3J_{HH}$ = 8.0 Hz), 7.87 (d, 1H, arom. CH, $^3J_{HH}$ = 7.8 Hz), 7.55 (t, 1H, arom. CH, $^3J_{HH}$ = 8.0 Hz), 7.51–7.47 (m, 1H, arom. CH), 7.37–7.33 (m, 2H, arom. CH), 7.29–7.23 (m, 3H, arom. CH), 7.19–7.17 (m, 1H, arom. CH), 1.99 (s, 6H, CH_3) ppm.

1-(2-Methoxyphenyl)naphthalene [14] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.93–7.85 (m, 2H, arom. CH), 7.59 (d, 1H, arom. CH, $^3J_{HH}$ = 6.2 Hz), 7.57–7.53 (m, 1H, arom. CH), 7.47–7.38 (m, 4H, arom. CH), 7.29 (d, 1H, arom. CH, $^3J_{HH}$ = 5.5 Hz), 7.13–7.05 (m, 2H, arom. CH), 3.72 (s, 3H, OCH_3) ppm.

1-(2-Methylphenyl)-naphthalene [13] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.10 (d, 1H, arom. CH, $^3J_{HH}$ = 7.5 Hz), 8.07 (d, 1H, arom. CH, $^3J_{HH}$ = 7.7 Hz), 7.74 8.10 (t, 1H, arom. CH, $^3J_{HH}$ = 7.8 Hz), 7.77–7.65 (m, 2H, arom. CH), 7.58–7.52 (m, 4H, arom. CH), 7.48–7.43 (m, 2H, arom. CH), 2.24 (s, 3H, CH_3) ppm.

1-(4-Methoxyphenyl)naphthalene [14] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.01–7.92 (m, 2H, arom. CH), 7.87 (d, 1H, arom. CH, $^3J_{HH}$ = 8.0 Hz), 7.62–7.40 (m, 6H, arom. CH), 7.14–7.02 (m, 2H, arom. CH), 3.93 (s, 3H, OCH_3) ppm.

1-(4-Methylphenyl)naphthalene [15] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.96 (d, 1H, arom. CH,

$^3J_{HH}$ = 8.5 Hz), 7.93 (d, 1H, arom. CH, $^3J_{HH}$ = 8.5 Hz), 7.88 (d, 1H, arom. CH, $^3J_{HH}$ = 8.0 Hz), 7.56–7.41 (m, 6H, arom. CH), 7.34 (d, 2H, arom. CH, $^3J_{HH}$ = 8.0 Hz), 2.47 (s, 3H, CH_3) ppm.

References

[1] X.-H. Fan, L.-M. Yang, *Eur. J. Org. Chem.*, 2010, 2457-2460.

[2] W. Liu, H. Cao, A. Lei, *Angew. Chem. Int. Ed.*, 2010, **49**, 2004-2008.

[3] B. Tao, D. Woykin, *J. Org. Chem.*, 2004, **69**, 4330-4335.

[4] J. Zhang, J. Xu, Y. Xu, H. Sun, Q. Shen, Y. Zhang, *Organometallics*, 2015, **34**, 5792-5800.

[5] V. Vece, K. C. Szeto, M. O. Charlin, P. Rouge, A. De Mallmann, M. Taam, P.-Y. Dugas, M. Lansalot, F. D'Agosto, M. Taoufik, *Catal. Commun.*, 2019, **129**, article no. 105715.

[6] M.-T. Chen, B.-Y. Hsieh, Y.-H. Liu, K.-H. Wu, N. Lussari, A. A. C. Braga, *Appl. Organomet. Chem.*, 2020, **34**, article no. 5870.

[7] J. Yang, *Appl. Organometal. Chem.*, 2017, **31**, article no. 734.

[8] R. Hartmann, M. Frotscher, S. Oberwinkler, E. Ziegler, J. Messinger, H.-H. Thole, 2008, Universität des Saarlandes, WO 2008116920 A2.

[9] S. M. Wong, C. M. So, K. H. Chung, C. P. Lau, F. Y. Kwong, *Eur. J. Org. Chem.*, 2012, 4172-4177.

[10] H. Ke, X. Chen, G. Zou, *J. Org. Chem.*, 2014, **79**, 7132-7140.

[11] J.-Y. Lee, D. Ghosh, J.-Y. Lee, S.-S. Wu, C.-H. Hu, S.-D. Liu, H. M. Lee, *Organometallics*, 2014, **33**, 6481-6492.

[12] A. Berezin, N. Biot, T. Battisti, D. Bonifazi, *Angew. Chem. Int. Ed.*, 2018, **57**, 8942-8946.

[13] M. M. Beromi, A. Nova, D. Balcells, A. M. Brasacchio, G. W. Brudvig, L. M. Guard, N. Hazari, D. J. Vinyard, *J. Am. Chem. Soc.*, 2017, **139**, 922-936.

[14] X.-B. Lan, F.-M. Chen, B.-B. Ma, D.-S. Shen, F.-S. Liu, *Organometallics*, 2016, **35**, 3852-3860.

[15] H. Zhang, J.-H. Zhu, F. Hou, Z.-J. Quan, X.-C. Wang, *Appl. Organomet. Chem.*, 2020, **34**, article no. 5495.