ELECTRONIC SUPPORTING INFORMATION

PALLADIUM NANOPARTICLES SUPPORTED ON GRAPHENE ACID: A STABLE AND ECO-FRIENDLY BIFUNCTIONAL C-C HOMO- AND CROSS-COUPLING CATALYST

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Summary

EXTENDED CHARACTERIZATION DATA

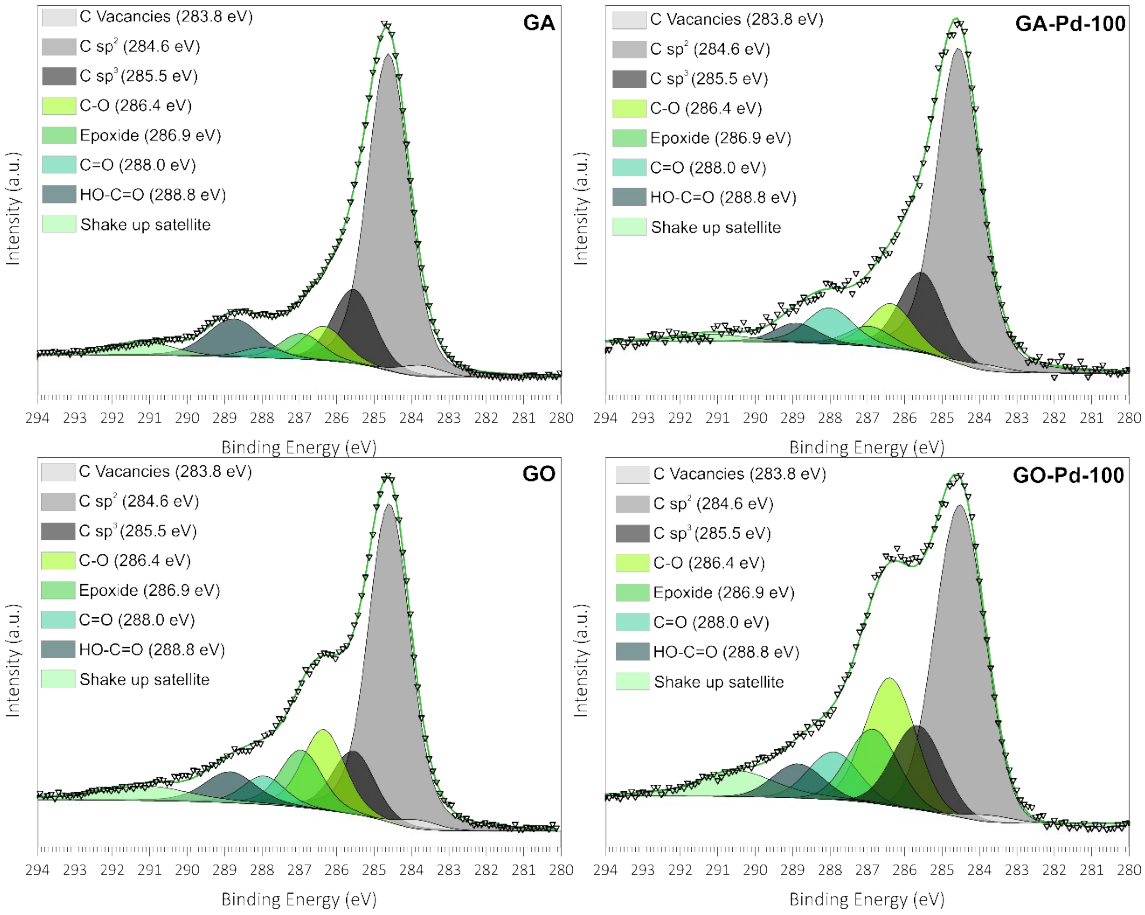


Figure S1. C 1s photoemission lines of pristine (left) and after impregnation (right) materials.

Table S1. XPS surface composition

XPS	C (% at.)	N (% at.)	O (% at.)	Pd (% at.)
GA	81.0	4.5	14.5	-
GA-Pd-25	68.6	4.5	25.3	1.6
GA-Pd-50	71.1	3.8	22.4	2.7
GA-Pd-100	70.4	4.6	20.7	4.3
GA-Pd-200	71.0	4.2	19.7	5.1
GO	74.1	-	25.9	-
GO-Pd-100	63.5	3.1	31.1	2.3

Table S2. Speciation of Pd 3d core level photoemission spectra.

XPS	Pd(0) (% at.)	PdO (% at.)	Pd-MeCN (% at.)
GA-Pd-25	28.8	56.5	14.7
GA-Pd-50	43.1	44.4	12.5
GA-Pd-100	53.4	36.3	10.3
GA-Pd-200	59.3	29.3	11.4

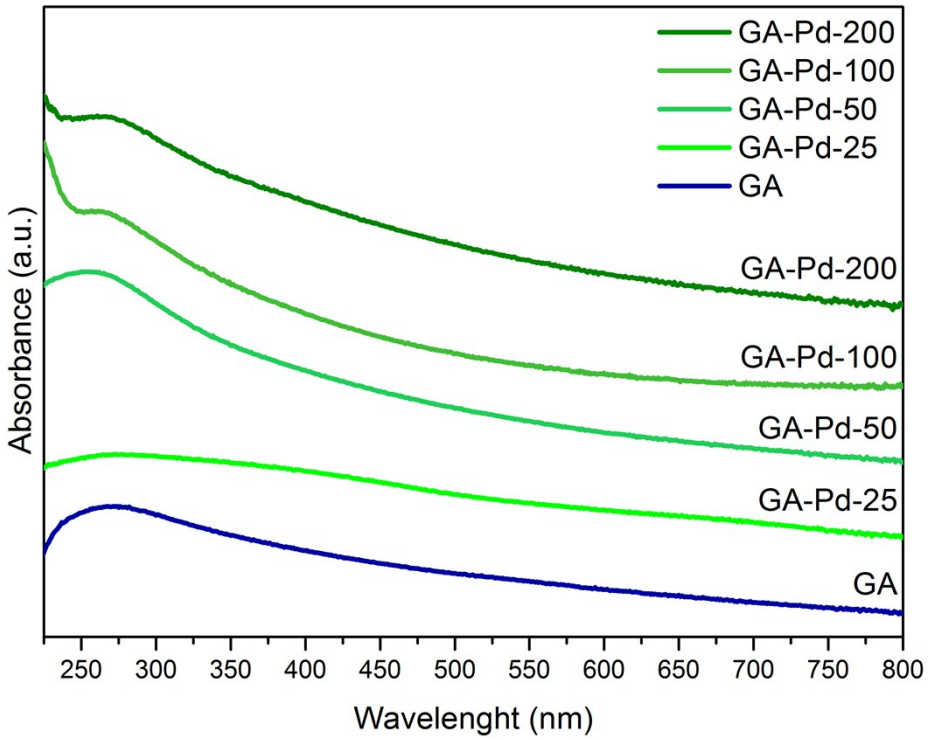


Figure S2. UV-Vis spectra of the different GA-Pd materials.

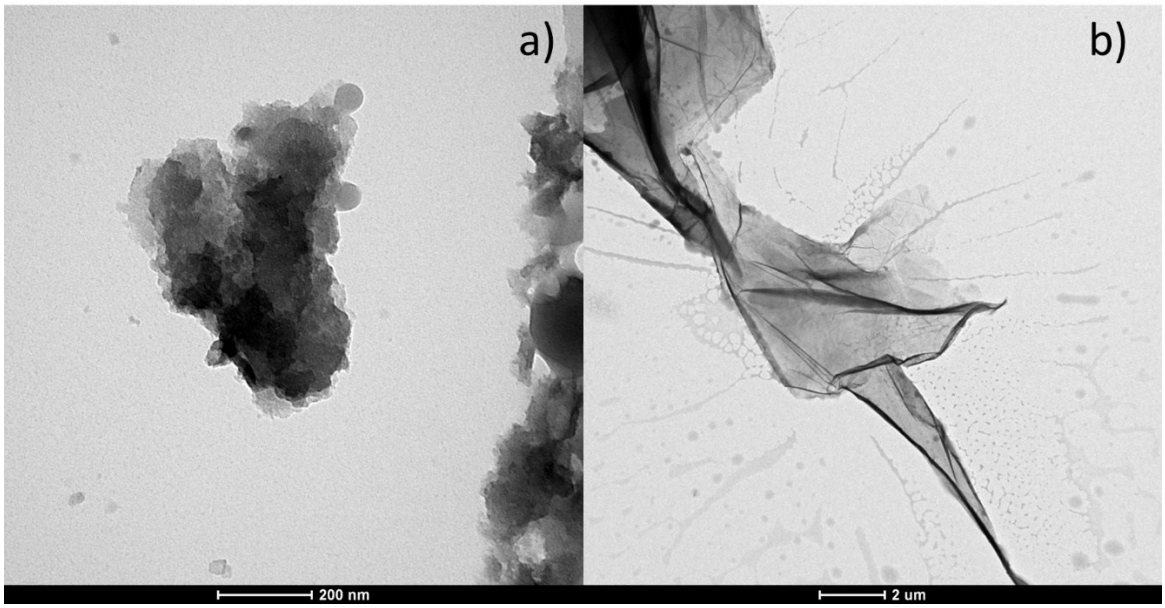


Figure S3. TEM images of pristine a) GA and b) GO

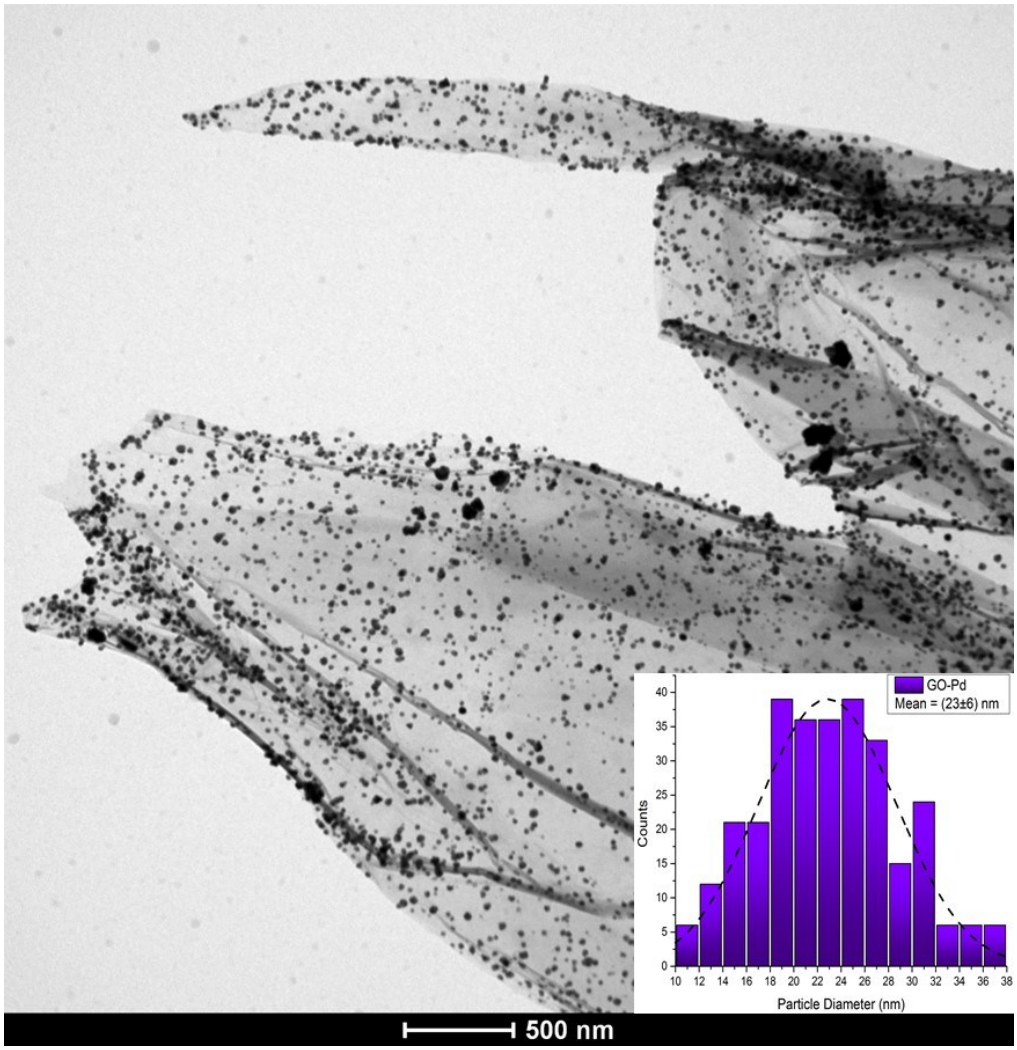


Figure S4. TEM image of GO-Pd-100. Inset: particle size distribution.

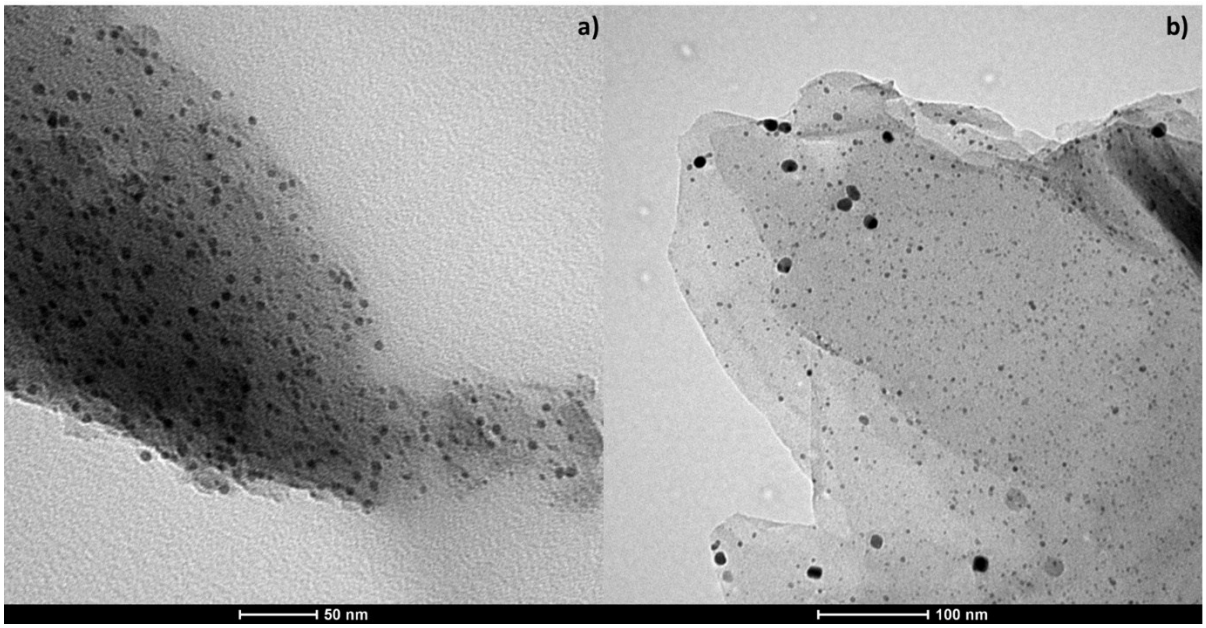


Figure S5. TEM image of a) GA-Pd-100 and b) GO-Pd-100 after 20 min of impregnation

Table S3. Density of nucleation (ρ) of the different hybrid materials.

Sample	Time (min)	ρ (nuclei μm^{-2})
GA-Pd-100	20	221
GO-Pd-100	20	91
GA-Pd-100	240	217
GO-Pd-100	240	41

Table S4. Elemental composition from EDX analysis.

EDX	C + N (% at.)[a]	O (% at.)	Pd (% at.)
GA-Pd-25	79.4	19.2	1.4
GA-Pd-50	71.1	25.6	3.3
GA-Pd-100	75.0	20.6	4.4
GA-Pd-200	75.5	19.4	5.1
GO-Pd-100	70.3	27.4	2.3
a) Due to the proximity of C and N signals, they have been reported as sum of the contributions.			

Table S5. Pd ICP determinations.

Entry	Sample	[Pd][a]
1	GA-Pd-25	9.8
2	GA-Pd-50	12.9
3	GA-Pd-100	24.0
4	GA-Pd-200	31.4
5	GO-Pd-100	11.2
a) %wt.		

Table S6. Pd ICP determinations on the leaching tests.

Entry	Sample	[Pd][a]
1	GA-Pd-100	0.6
2	GO-Pd-100	0.6
3	GA-Pd-100	1.5[b]
4	GA-Pd-100	1.5[c]
a) ppm. b) Leaching test of the hot-filtration experiment in point 1; c) Leaching test of the hot-filtration experiment in point 2.		

EXTENDED CATALYTIC DATA

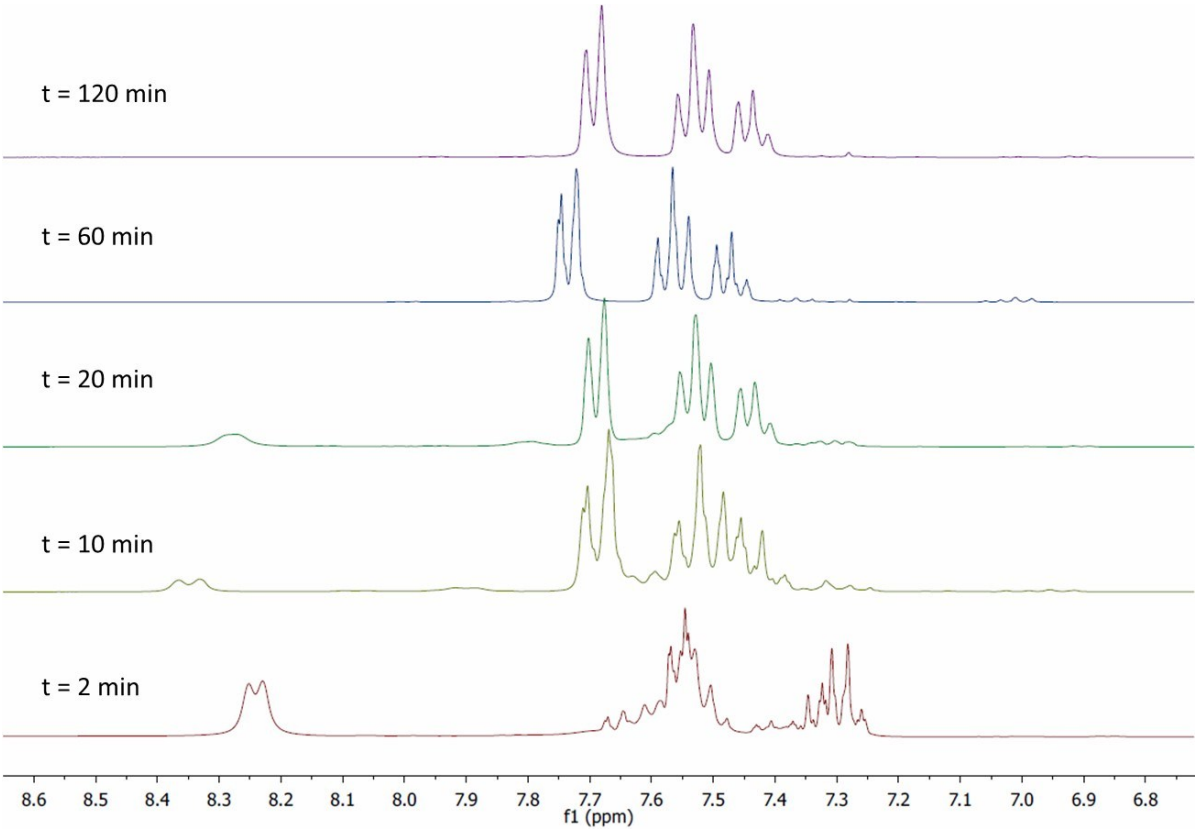


Figure S6. NMR tracking ($CDCl_3$, 300.1 MHz, 298 K) of the SM coupling between bromobenzene and phenylboronic acid (standard conditions) catalysed by GA-Pd-100.

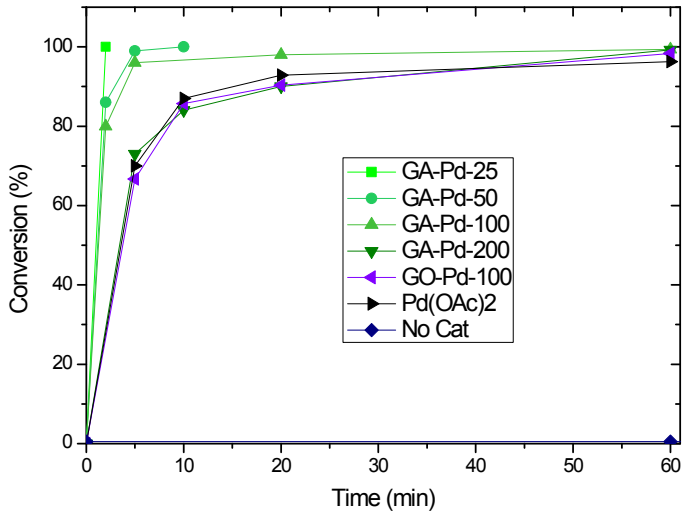


Figure S7. Kinetic profiles of the SM cross-coupling reaction between bromobenzene and phenylboronic acid (standard conditions).

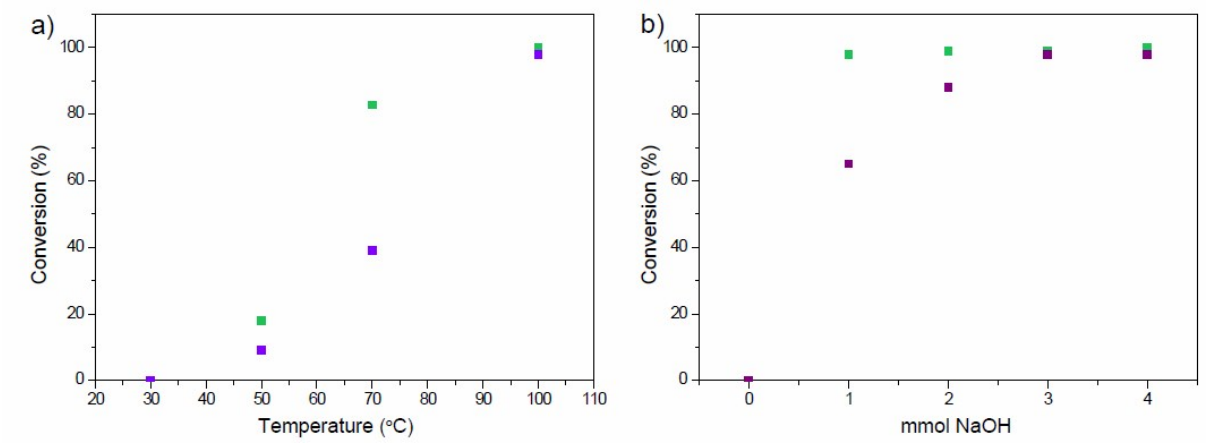


Figure S8. Optimization in a) temperature and b) base amount of the SM cross-coupling reaction for GA-Pd-100 (green) and GO-Pd-100 (purple) between bromobenzene and phenylboronic acid.

NMR DATA FOR ORGANIC COMPOUNDS

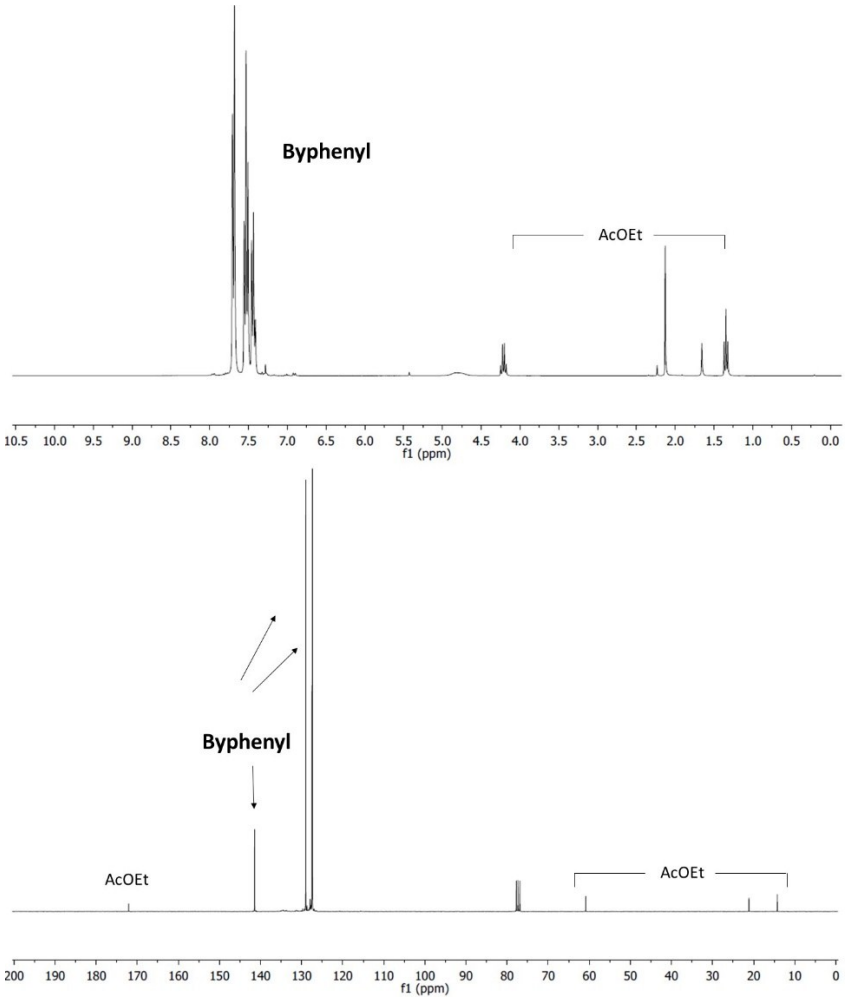
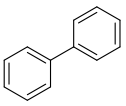
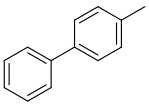


Figure S9. ^{1}H- and ^{13}C-NMR spectrum of the reaction mixture of the Suzuki coupling between bromobenzene and phenylboronic acid after 1 h of reaction employing the optimized conditions. Signals of target molecule and solvent have been highlighted

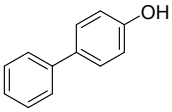
Biphenyl: Prepared according to the general procedure to yield a white solid. ^{1}H-NMR (300.1 MHz, $CDCl_3$, δ ppm): 7.73 (d, J = 8.0 Hz, 4 H), 7.55 (t, J = 7.5 Hz, 4H), 7.46 (d, J = 8.3, 2H).



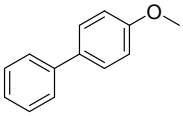
4-methyl-1,1'-biphenyl: prepared according to the general procedure to yield a white solid. ^{1}H-NMR (300.1 MHz, $CDCl_3$, δ ppm): 7.72 (m, 2H), 7.63 (d, J = 8.1 Hz, 2H), 7.55 (t, J = 7.9 Hz, 2H), 7.46 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 8.2 Hz, 2H), 2.52 (s, 3H).

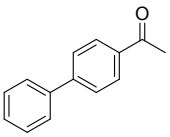


[1,1'-biphenyl]-4-ol: Prepared according to the general procedure to yield a white solid. ^{1}H-NMR (300.1 MHz, $CDCl_3$, δ ppm): 7.75 (d, J = 8.2 Hz, 2 H), 7.55-7.38 (m, 5H), 6.83 (d, J = 8.3, 2H), 5.0 (bs, 1H).



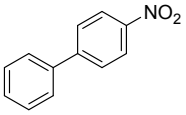
4-methoxy-1,1'-biphenyl: Prepared according to the general procedure to yield a white solid. ^{1}H-NMR (300.1 MHz, $CDCl_3$, δ ppm): 7.77 (d, J = 8.2 Hz, 2 H), 7.55-7.38 (m, 5H), 7.07 (d, J = 8.1, 2H), 3.91 (s, 3H).



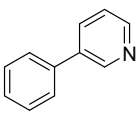


4-phenylacetophenone: prepared according to the general procedure to yield a white solid. ^{1}H-NMR (300.1 MHz, $CDCl_3$, δ ppm): 8.05 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H), 7.61 (t, J = 8.3 Hz, 2H), 7.46 (m, 3H), 2.65 (s, 3H).

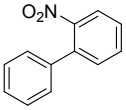
4-nitro-1,1'-biphenyl: prepared according to the general procedure to yield a yellow solid. ^{1}H-NMR (300.1 MHz, $CDCl_3$, δ ppm): 8.10 (d, J = 8.1 Hz, 1H), 7.68 (d, J = 8.1 Hz 2H), 7.56 – 7.25 (m, 5H).



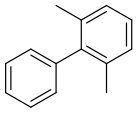
3-phenylpyridine: prepared according to the general procedure to yield a pale-yellow oil. ^{1}H-NMR (300.1 MHz, $CDCl_3$, δ ppm): 8.87 (d, J = 2.0 Hz, 1H), 8.72 (dd, J = 5.1, 1.2 Hz, 1H), 8.13 (m, 2H), 7.92 (ddd, J = 8.2, 2.1, 1.4 Hz, 1H), 7.43 (m, 4H), 7.30 (dt, J = 13.7, 6.7 Hz, 1H).



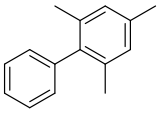
2-nitro-1,1'-biphenyl: prepared according to the general procedure to yield a pale-yellow solid. ^{1}H-NMR (300.1 MHz, $CDCl_3$, δ ppm): 8.00 (m, 2H), 7.82 (dd, J = 6.0, 2.2 Hz, 1H), 7.70 (dd, J = 5.7, 2.1 Hz, 1H), 7.45-7.30 (m, 5H).



2,6-dimethyl-1,1'-biphenyl: prepared according to the general procedure to yield a white solid. ^{1}H-NMR (300.1 MHz, $CDCl_3$, δ ppm): 7.75-7.40 (m, 5H), 7.32-7.05 (m, 3H), 2.51 (s, 6H).



2,4,6-trimethyl-1,1'-biphenyl: prepared according to the general procedure to yield a white solid. ^{1}H-NMR (300.1 MHz, $CDCl_3$, δ ppm): 7.77-7.35 (m, 5H), 6.94 (s, 2H), 2.44 (s, 6H), 2.10 (s, 3H).



Phenol: found as byproduct applying the general procedure. ^{1}H-NMR (300.1 MHz, $CDCl_3$, δ ppm): 7.28 (t, J = 7.9 Hz, 2H), 6.98 (t, J = 7.4 Hz, 1H), 6.89 (d, J = 7.9 Hz, 2H).