Microwave-Induced Covalent Functionalization of Few-Layer Graphene with Arynes Under Solvent-Free Conditions

Supporting Information

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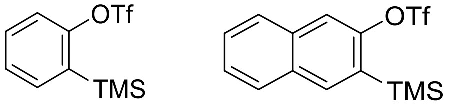
1 General Methods

All reactions were carried out under argon using oven-dried glassware. TLC was performed on Merck silica gel 60 F254; chromatograms were visualized with UV light (254 and 360 nm). Flash column chromatography was performed on Merck silica gel 60 (ASTM 230-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz or 400 and 101 MHz (Varian Mercury 300 or Varian Inova-400 instruments), respectively. Low-resolution electron impact mass spectra were determined at 70 eV on a HP-5988A instrument. High-resolution mass spectra (HRMS) were obtained on a Micromass Autospec spectrometer.

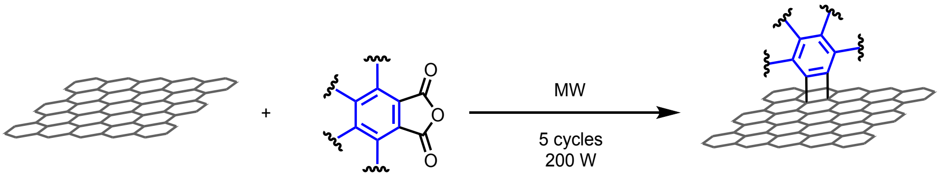
Aryne precursors **16**[1] and **17**[2] were prepared following published procedures (Figure S1). Commercial reagents and anhydrous solvents were purchased from ABCR GmbH, Aldrich Chemical Co., or Strem Chemicals Inc., and were used without further purification.



16 **17**

Figure S1. Chemical structure of aryne precursor **16** and **17**.

1.1. *General method for functionalization of few-layer graphene with arynes*



***f*-G**

All the reactions were carried out under N_2, functionalized graphene (*f*-G) were prepared following the next procedure. Few-layer graphene (FLG, 1 atomic equiv, assuming the sample to be of pure carbon) phthalic anhydride (**1**, 3 equiv) were added to a mortar. The grind of the sample was done until observe a homogeneous mixture. The powder was transfer onto a quartz Vessel. Then, 5 cycles of MW irradiation were applied. In each cycle, the reaction was performed with a fixed power of 200 W until a rise of the temperature of 250 ºC in about 5 seconds. The reaction mixture was cooling down by applying outsider cooling, until the temperature decrease to 175 ºC. Several washes and filtrations in a Millipore system of the resulting *f*-G were performed with: CH_2Cl_2 (3 x 20 mL), H_2O (3 x 20 mL), MeOH (3 x 20 mL), AcOEt (3 x 20 mL) and few drops of Et_2O.

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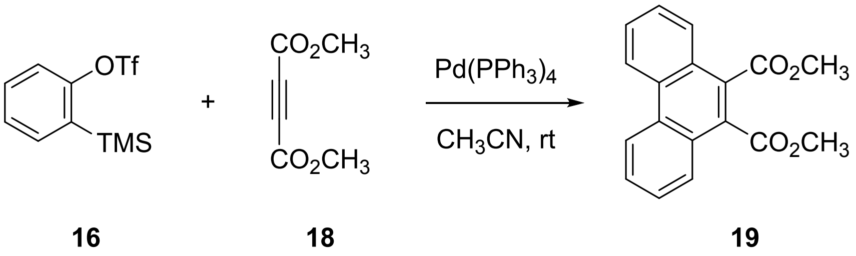
[1] Himeshima, Y.; Sonoda, T.; Kobayashi, H. *Chem. Lett.* **1983**, 1211.

[2] a) Nazuki, N.; Hiroki, M.; Eigo, M.; Itaru, O.; Hayato, K.; Karzuo, T.; Chihaya, A. *Chem. Comun.* **2012**, *48*, 5892. b) Peña, D.; Cobas, A.; Pérez, D.; Guitián, E. *Synthesis* **2002**, 1454.

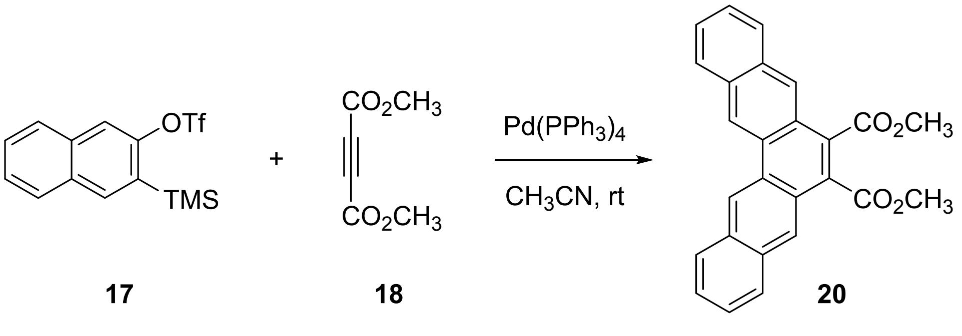
2 Experimental details and spectroscopic data

2.1 Synthesis of dimethyl phenanthrene-9,10-dicarboxylate (19)



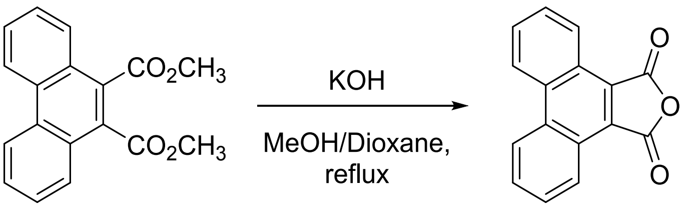
To a deoxygenated solution of triflate **16** (408 mg, 1.37 mmol), dimethyl acetylenedicarboxylate (**18**, 196 µL, 1.92 mmol) and $Pd(PPh_3)_4$ (158 mg, 0.137 mmol) in anhydrous CH_3CN (27 mL) was added CsF (521 mg, 3.43 mmol), and the resulting mixture was stirred at room temperature for 16 h. Then, H_2O (20 mL) and Et_2O (20 mL) were added, the phases separated and the aqueous layer extracted with Et_2O (2 x 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, Hexane/CH_2Cl_2 9:1) to afford dimethyl phenanthrene-9,10-dicarboxylate (**19,** 338 mg, 84% yield) as a white solid. ^{1}H NMR (298 K, 300 MHz, $CDCl_3$) δ: 8.64 (dd, *J* = 7.9, 1.6 Hz, 2H), 8.15 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.76–7.56 (m, 4H), 4.04 (s, 6H) ppm.

2.2 Synthesis of dimethyl pentaphene-6,7-dicarboxylate (20)



To a deoxygenated solution of triflate **17** (661 mg, 1.9 mmol), dimethyl acetylenedicarboxylate (**18**, 271.5 µL, 2.66 mmol) and $Pd(PPh_3)_4$ (219 mg, 0.19 mmol) in anhydrous CH_3CN (38 mL) was added CsF (722 mg, 4.75 mmol), and the resulting mixture was stirred at room temperature for 16 h. Then, H_2O (30 mL) and Et_2O (30 mL) were added, the phases separated and the aqueous layer extracted with Et_2O (2 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, Hexane/CH_2Cl_2 9:1) to afford dimethyl pentaphene-6,7-dicarboxylate (**20,** 449 mg, 60% yield) as a yellow solid. ^{1}H NMR (298 K, 300 MHz, $CDCl_3$) δ: 9.18 (s, 2H), 8.52 (s, 2H), 8.10 (d, *J* = 8.1 Hz, 2H), 7.99 (d, *J* = 7.6 Hz, 2H), 7.68–7.48 (m, 4H), 4.11 (s, 6H) ppm. ^{13}C NMR (298 K, 75 MHz, $CDCl_3$) δ: 168.4 (2C), 132.9 (2C), 132.4 (2C), 130.8 (2C), 128.9 (2C), 128.6 (2CH), 128.3 (2CH), 127.3 (2CH), 126.9 (2CH), 126.6 (2CH), 125.4 (2C), 122.3 (2CH), 52.8 (2CH3) ppm. MS (EI), *m/z* (%): 394 (100). HRMS (EI) for $C_{26}H_{18}O_4$, calculated: 394.1205, found: 394.1211.

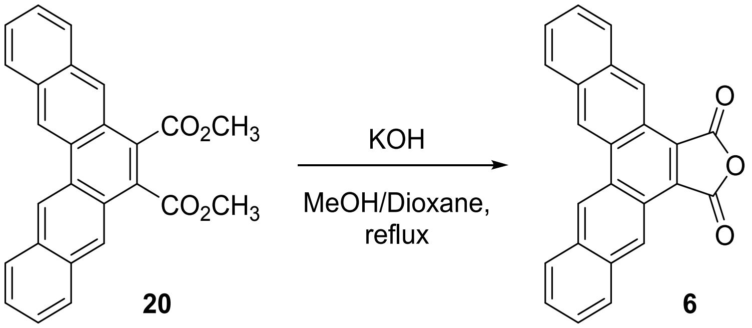
2.3 Synthesis of phenanthro[9,10-c]furan-1,3-dione (5)



19 **21**

In a round bottom flask, a suspension of dimethyl phenanthrene-9,10-dicarboxylate (**19**, 338 mg, 1.15 mmol) in EtOH/dioxane (1:1, 230 mL) was prepared. Then, a solution of KOH (3.79 g, 68 mmol) in EtOH (38 mL) was added, and the mixture refluxed for 2h. After that, aqueous HCl (10%, 20 mL) and Et_2O (30 mL) were added, the phases separated and the aqueous layer extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/AcOEt 49:1) to afford anhydride **5** (291 mg, 98% yield) as a pale-yellow solid. ^1H NMR (298 K, 300 MHz, $CDCl_3$) δ: 9.03 (dd, $J = 8.2$, 1.3 Hz, 2H), 8.80 (d, $J = 8.1$ Hz, 2H), 8.00–7.79 (m, 4H) ppm.[3]

2.4 Synthesis of pentapheno[6,7-c]furan-6,8-dione (6)



In a round bottom flask, a suspension of dimethyl pentaphene-6,7-dicarboxylate (**20**, 449 mg, 1.14 mmol) in EtOH/dioxane (1:1, 228 mL) was prepared. Then, a solution of KOH (3.77 g, 67 mmol) in EtOH (37 mL) was added, and the mixture refluxed for 2h. After that, aqueous HCl (10%, 20 mL) and Et_2O (30 mL) were added, the phases separated and the aqueous layer extracted with CH_2Cl_2 (5 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was subsequently washed with H_2O (2 x 4 mL), Et_2O (3 x 4 mL) and pentane (2 x 4 mL) to afford anhydride **6** (297 mg, 75% yield) as an orange solid. ^1H NMR (388 K, 400 MHz, DMSO-D_6) δ: 9.68 (s, 2H), 9.36 (s, 2H), 8.43 – 8.25 (m, 4H), 7.89 – 7.69 (m, 4H) ppm. ^{13}C NMR (388 K, 101 MHz, DMSO-D_6) δ: 162.96 (2C), 133.13 (2C), 131.55 (2C), 129.91 (2C), 129.57 (2C), 128.22 (2CH), 128.04 (2CH), 127.94 (2CH), 126.98 (2CH), 125.67 (2CH), 123.31 (2CH), 121.36 (2C) ppm. MS (EI), *m/z* (%): 348 (100), 276 (87). HRMS (EI) for $C_{24}H_{12}O_3$, calculated: 348.0786, found: 348.0786.

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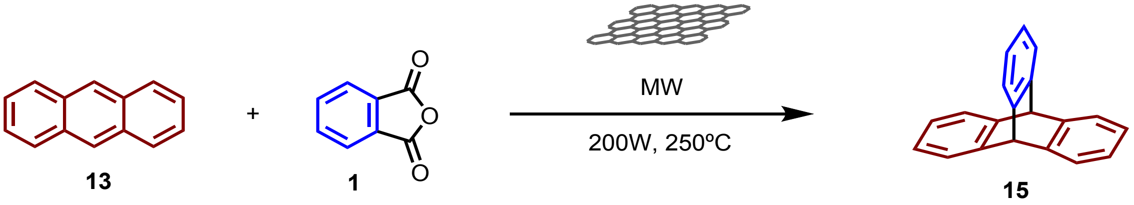
[3] Schonberg, A.; Warren. F. L. *J. Chem Soc.* **1939**, 1838.

2.5 *Synthesis of triptycene (15)*



In a mortar, anthracene (**13**, 104mg, 0.58mmol) phthalic anhydride (**1**, 86mg, 0.58mmol) and FLG (7 mg) were added. The grind of the sample was done until observe a homogeneous mixture. The powder was transfer onto a quartz Vessel. Then, 10 cycles of MW irradiation were applied. In each cycle, the reaction was performed with a fixed power of 200 W until a rise of the temperature of 250 ºC in about 5 seconds. The reaction mixture was cooling down by applying outsider cooling, until the temperature decrease to 175 ºC. The resulting solid mixture was washed with CH_2Cl_2 and filtrated in a Millipore system. The organic layer was dried under reduced pressure. By the analysis of the ^{1}HNMR, **15** was obtained in 13% conversion.

3 ^{1}H and ^{13}C NMR spectra

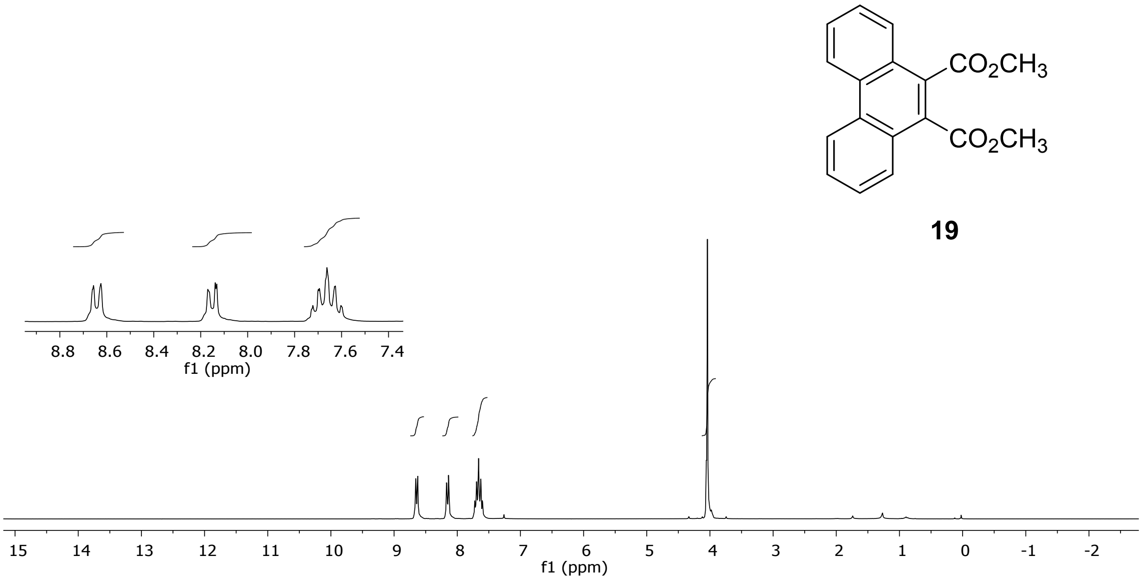


Figure S2. ^{1}HNMR spectrum (300 MHz, $CDCl_3$) of compound **19**.

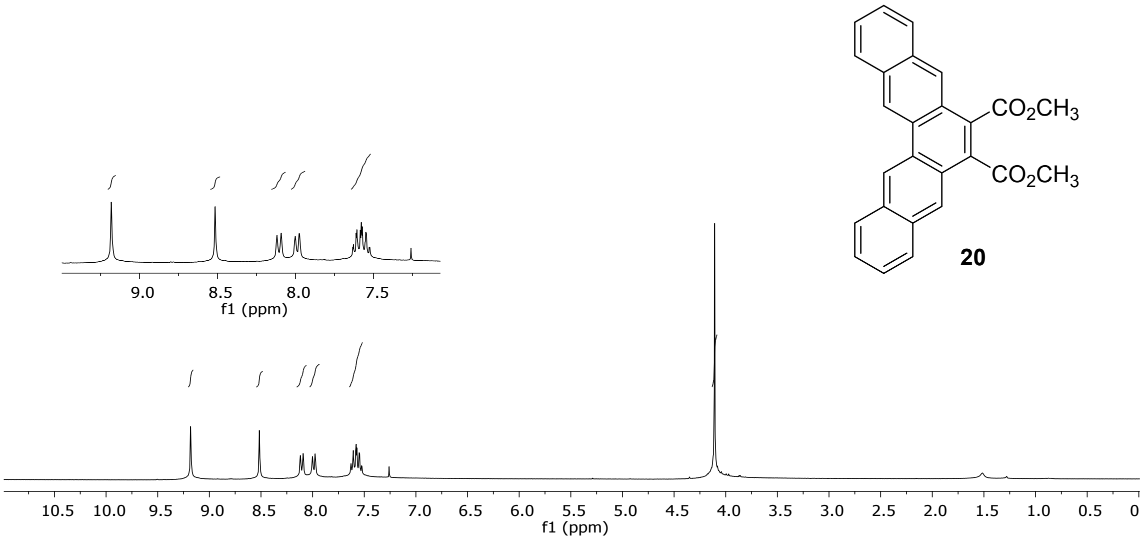


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Figure S3. ^{1}HNMR spectrum (300 MHz, CDCl$_3$) of compound **20**.

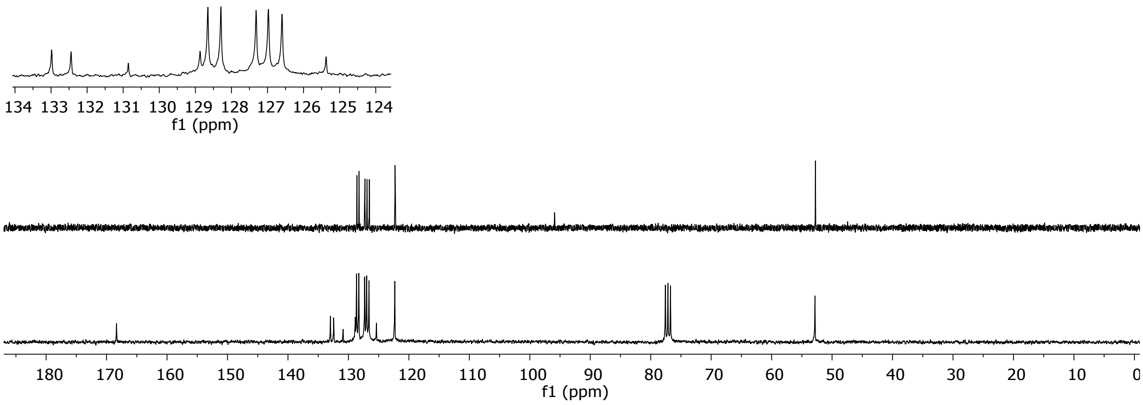

Figure S4. ^{13}CNMR spectrum (75 MHz, CDCl$_3$) of compound **20**.

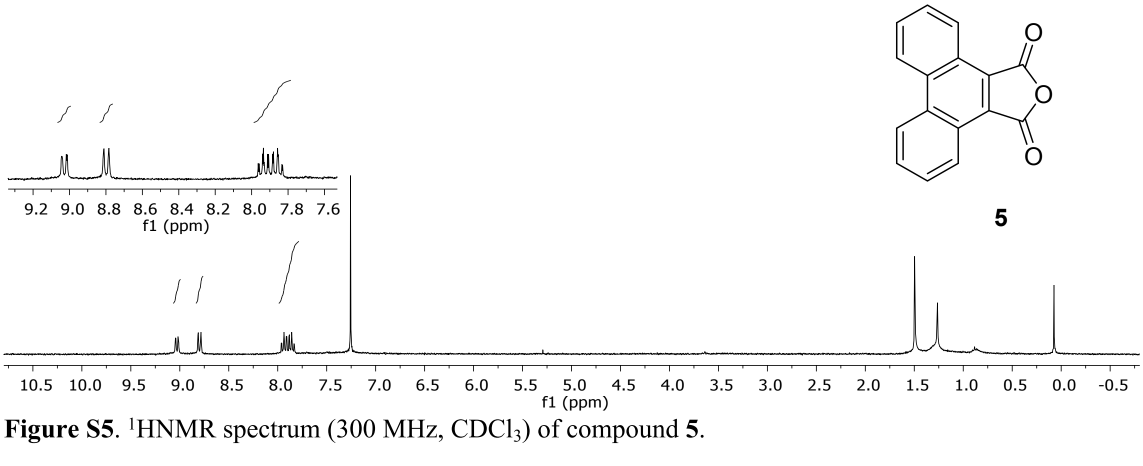

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Figure S5. ^{1}HNMR spectrum (300 MHz, CDCl$_3$) of compound **5**.

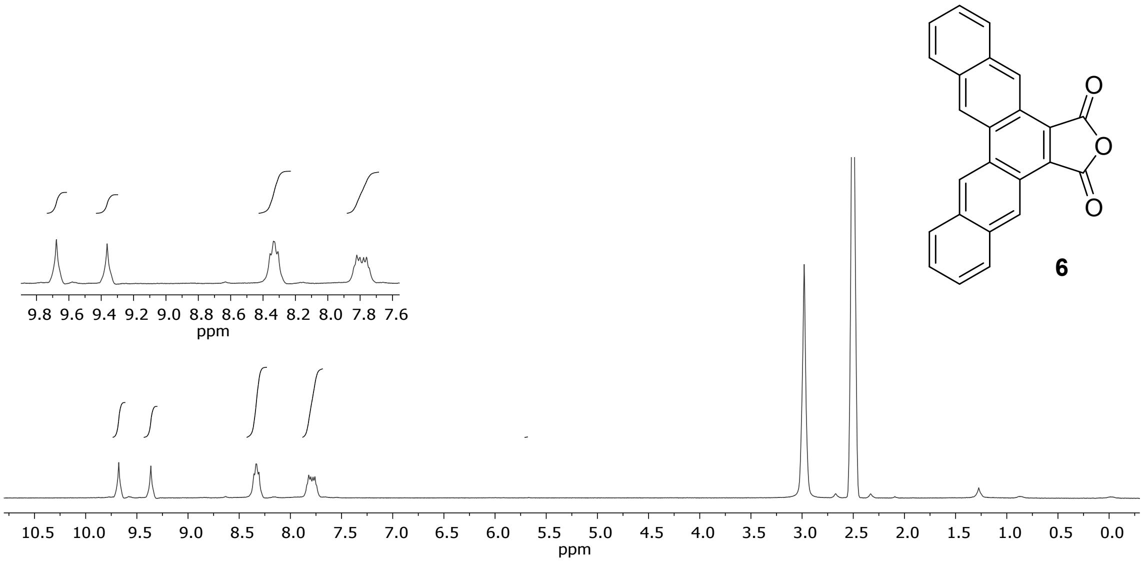

Figure S6. ^{1}HNMR spectrum (400 MHz, DMSO-D$_6$) of compound **6**.

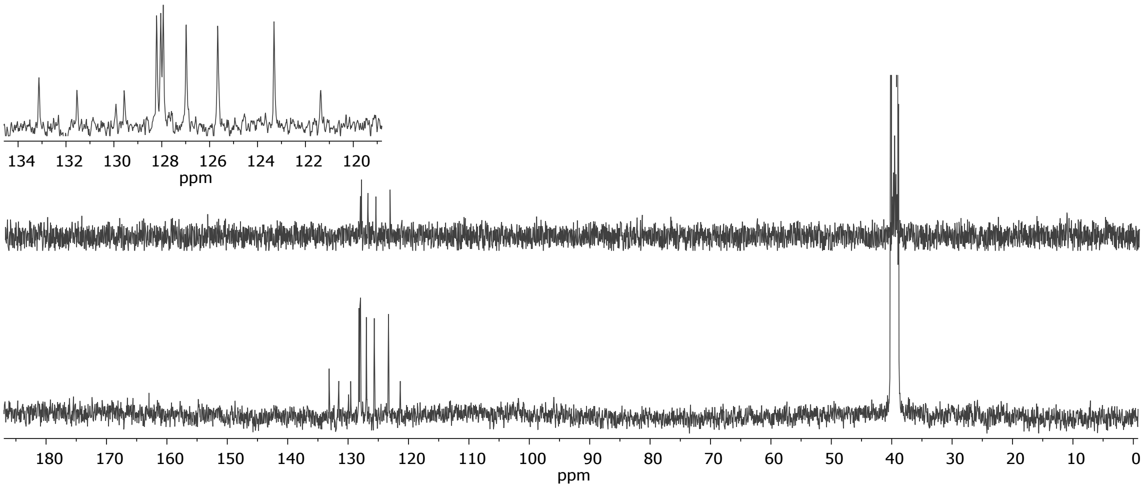

Figure S7. ^{13}CNMR spectrum (101 MHz, DMSO-D$_6$) of compound **6**.

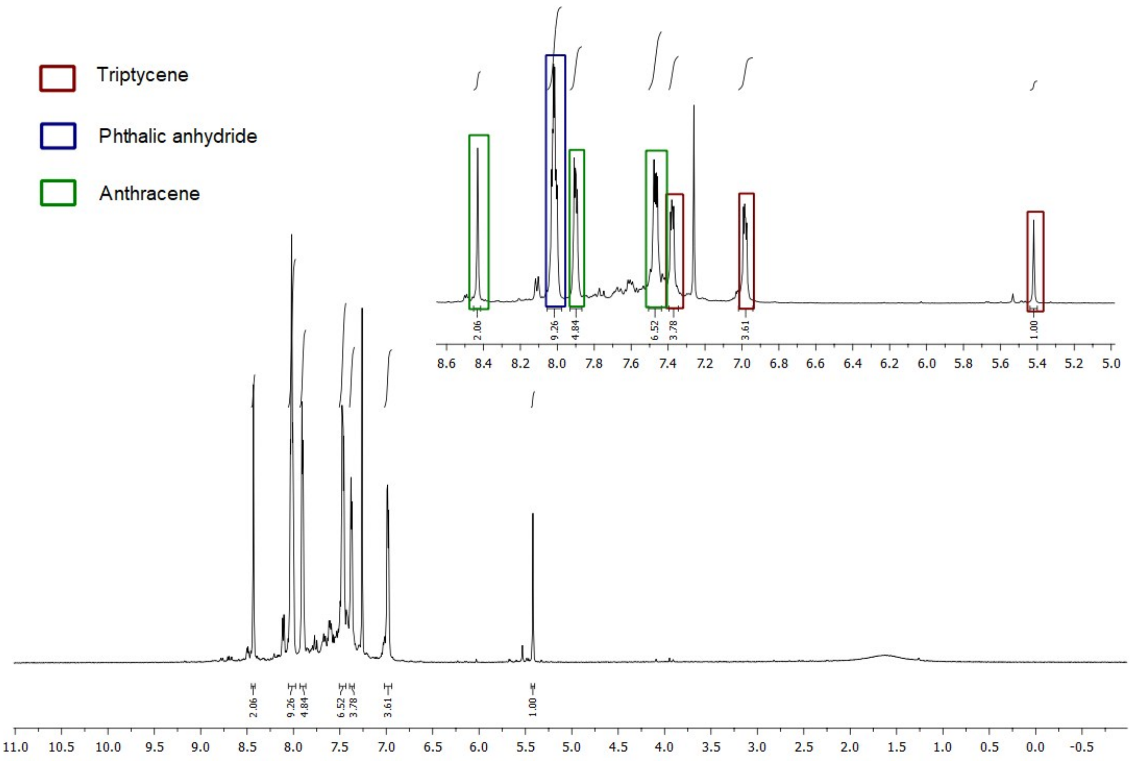

Figure S8. ^{1}HNMR spectrum (300 MHz, $CDCl_3$) of organic layer of the reaction described in Figure 3, mainly composed by anthracene (**13**), phthalic anhydride (**1**) and triptycene (**15**).

4 Raman spectroscopy

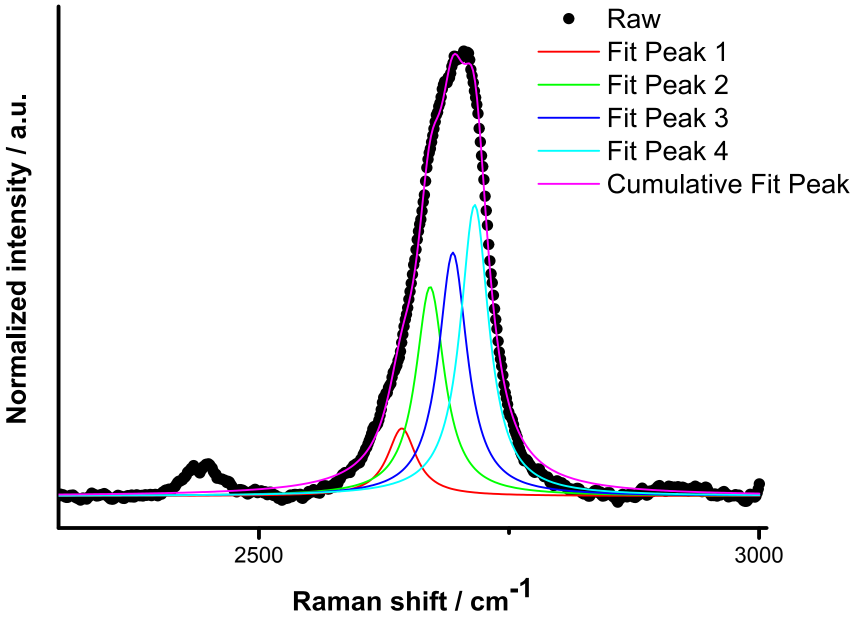

Figure S9. Deconvolution of 2D band for FLG.

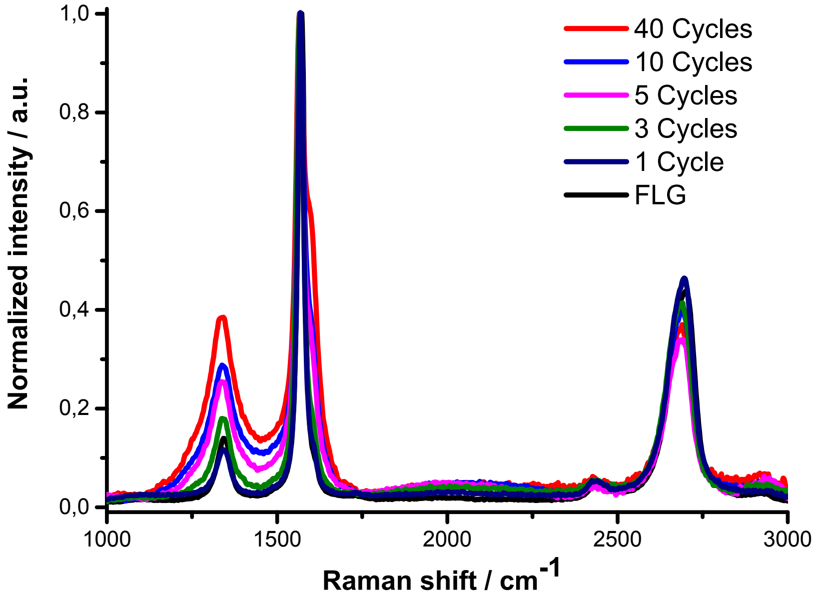

Figure S10. Raman spectra of *f*-G(**7**) at different cycles of MW irradiation.

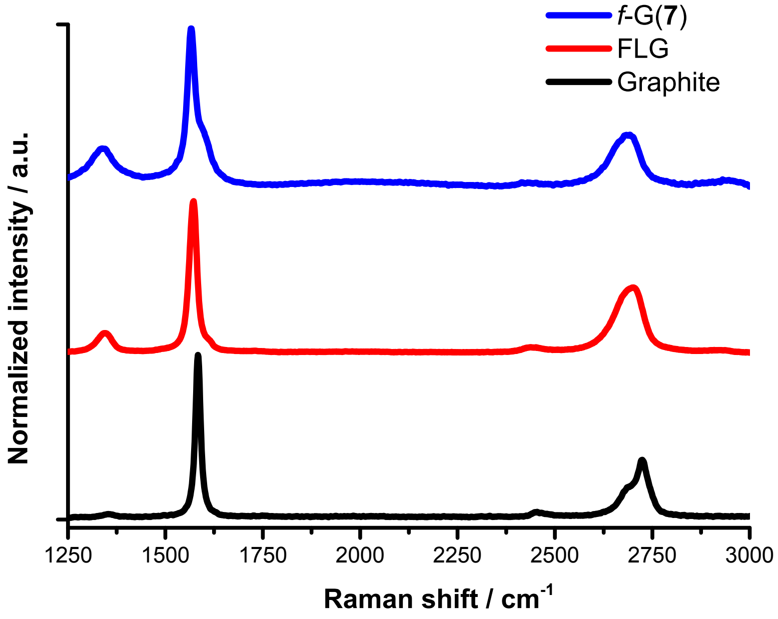

Figure S11. Average spectra for Graphite (dark line), FLG (red line) and *f*-G(**7**) (blue line).

5 Microwave Irradiation

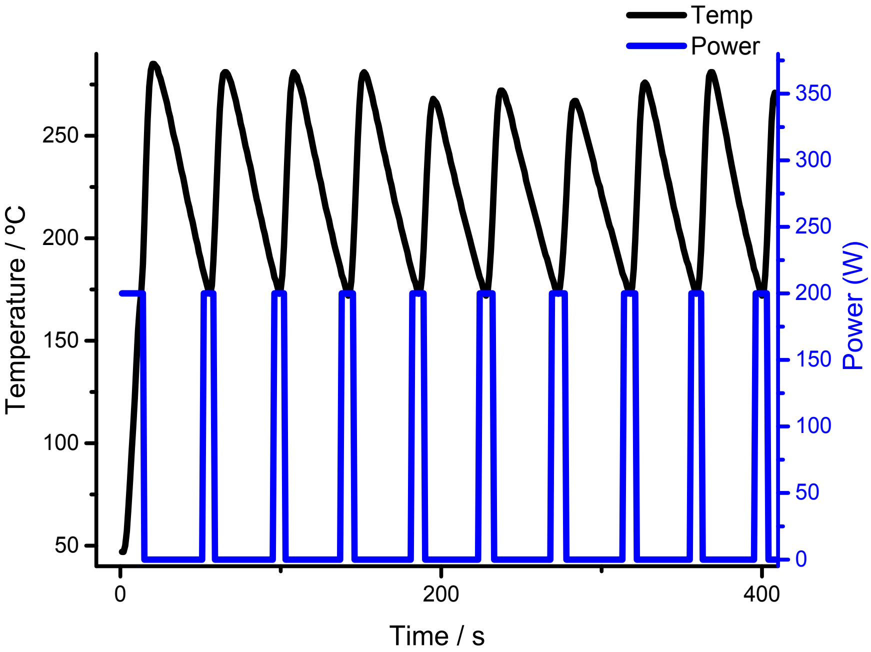

Figure S12. Temperature (blue line) and power evolution of microwave irradiation (black line) against the time.

6 TGA Analysis

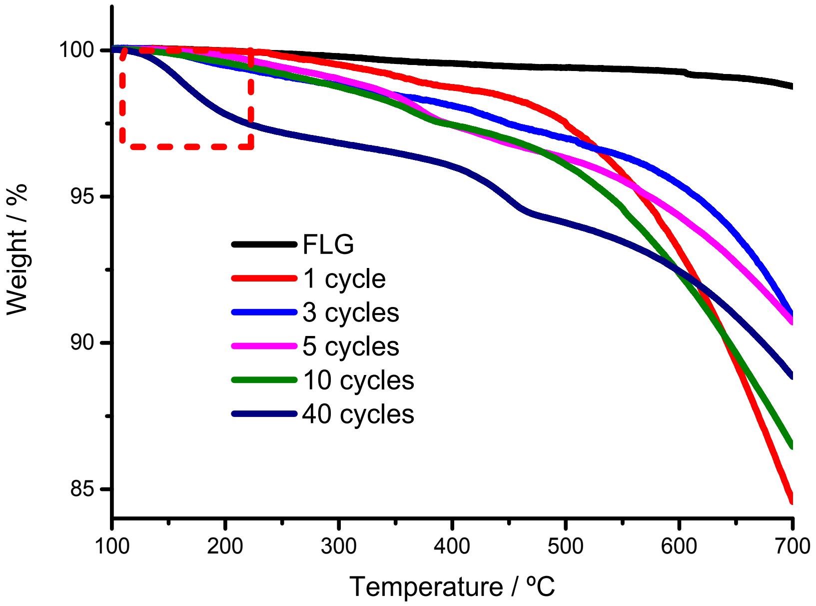

Figure S13. TGA profiles under N_2 atmosphere for *f*-G(**7**) at different cycles.

In order to draw quantitative information from thermogravimetric plots, we performed the following calculation to obtain functionalization degree (FD); where L corresponds to the weight loss observed at 500ºC (in %), after having subtracted the analogous loss from the pristine material. The molecular weight (Mw) is set for the expected desorbed moiety. The conversion factor (10^4) provides data in the desired unities (µmol/g)

$$\frac{L(\%)\cdot 10^4}{Mw(g/mol)} = FD\ (\mu mol/g) \qquad \text{Equation (S1)}$$

Table S1. Average I_D/I_G ratio and functionalization degree by TGA for *f*-G(**7**).

Nº of cycles	Δ I_D/I_G	FD (µmol FG / g G)[a]
1	0.14	264
3	0.19	357
5	0.29	699
10	0.30	514
40	0.35	672

[a] TGA-determined weight loss at 500 ° C.

Table S2. Average I_D/I_G ratio and functionalization degree by TGA for modified graphene derivatives.

Aryne precursor	*f*-G	Δ I_D/I_G	FD (µmol/g)	Functionalization Yield (%)[a]	Production Yield (%)[b]
1	*f*-G(**7**)	0.16	699	114	3
2	*f*-G(**8**)	0.18	380	178	5
3	*f*-G(**9**)	0.14	366	190	5
4	*f*-G(**10**)	0.17	751	100	3
5	*f*-G(**11**)	0.52	239	134	4
6	*f*-G(**12**)	0.26	301	188	5

a) (mg *f*-G/mg FLG)·100; b) (mg *f*-G/mg Graphite)·100

7 XPS analysis

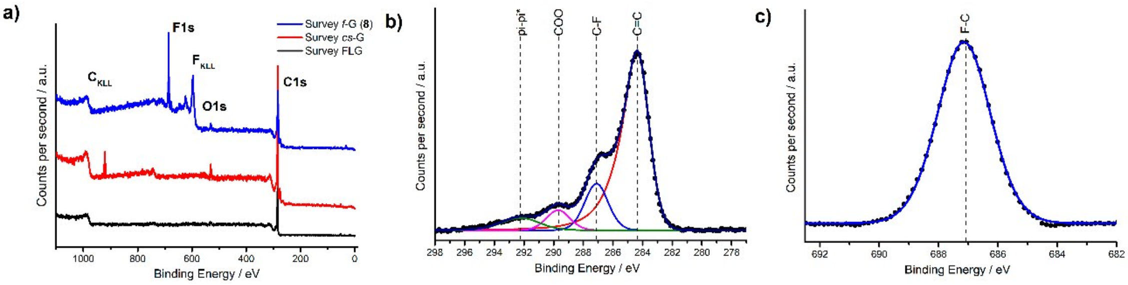

Figure S14. Survey spectra (a), C1s (b) and F1s core level (c) for *f*-G(**8**).

Table S3. Atomic ratios of graphene derivatives determined from the XPS survey spectra

Graphene material	Core	BE (eV)	Atomic %
FLG	C1s	284.71	98.1
	O1s	532.56	1.9
cs-G[a]	C1s	284.37	93.8
	O1s	531.46	6.2
f-G(**7**)	C1s	284.39	87.4
	O1s	531.80	12.6
f-G(**8**)	C1s	284.31	79.7
	O1s	532.76	2.8
	F1s	687.01	17.5
f-G(**9**)	C1s	531.92	73.5
	O1s	284.37	26.5
f-G(**10**)	C1s	531.80	67.8
	O1s	284.40	32.2
f-G(**11**)	C1s	531.56	80.3
	O1s	284.31	19.7
f-G(**12**)	C1s	531.54	89.0
	O1s	284.59	10.0

Table S4. Core-level spectra of GBMs.

Sample	C1s /eV						O1s / eV		F1s / eV
	sp^2 C	C-F	C-O	C=O	COO	π-π*	O-C	O=C	F-C
FLG	284.37	-	286.31	287.71	-	290.72	533.14	531.19	-
cs-G	284.37	-	287.05	288.22	-	290.68	531.78	529.99	-
f-G(**7**)	284.37	-	285.66	-	-	291.48	533.11	531.93	-
f-G(**8**)	284.37	286.11	-	-	289.69	292.23	533.59	531.92	687.15
f-G(**9**)	284.37	-	287.44	-	289.85	292.33	532.11	530.8	-
f-G(**10**)	284.37	-	286.55	288.44	-	-	532.83	531.50	-
f-G(**11**)	284.37	-	286.61	288.6	-	-	532.48	530.83	-

f-G(**12**)	284.37	-	-	288.07	290.15	292.24	532.32	531.39	-

8 TEM characterization

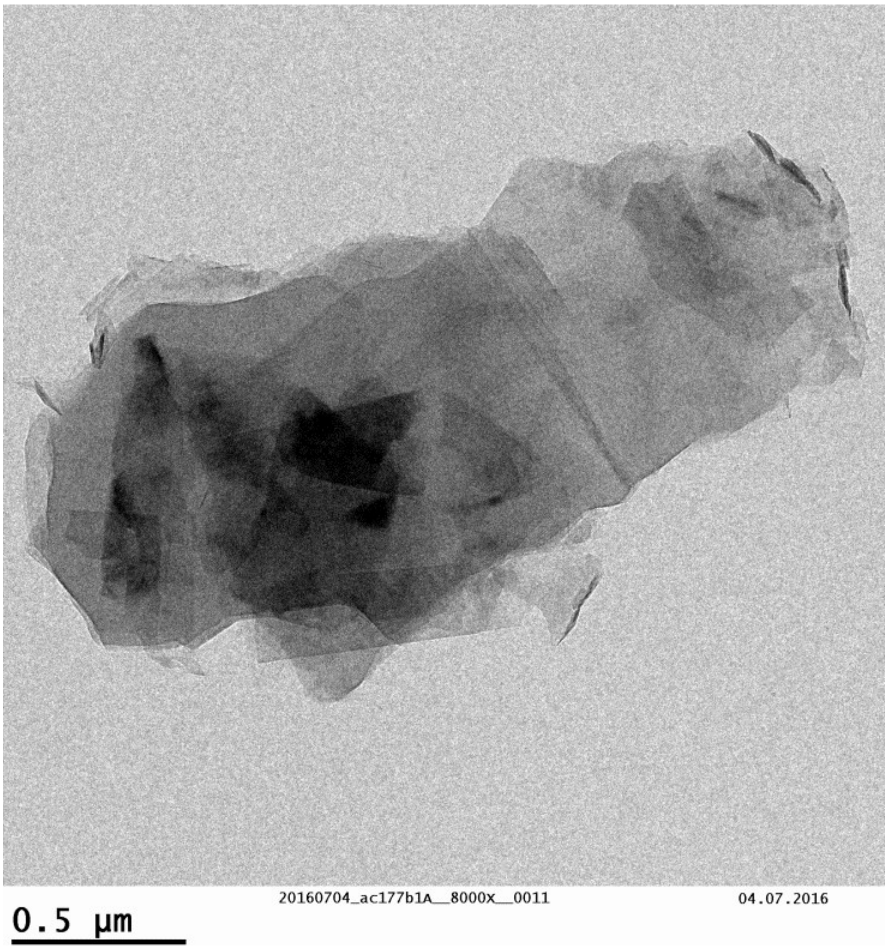

Figure S15. TEM image of FLG.

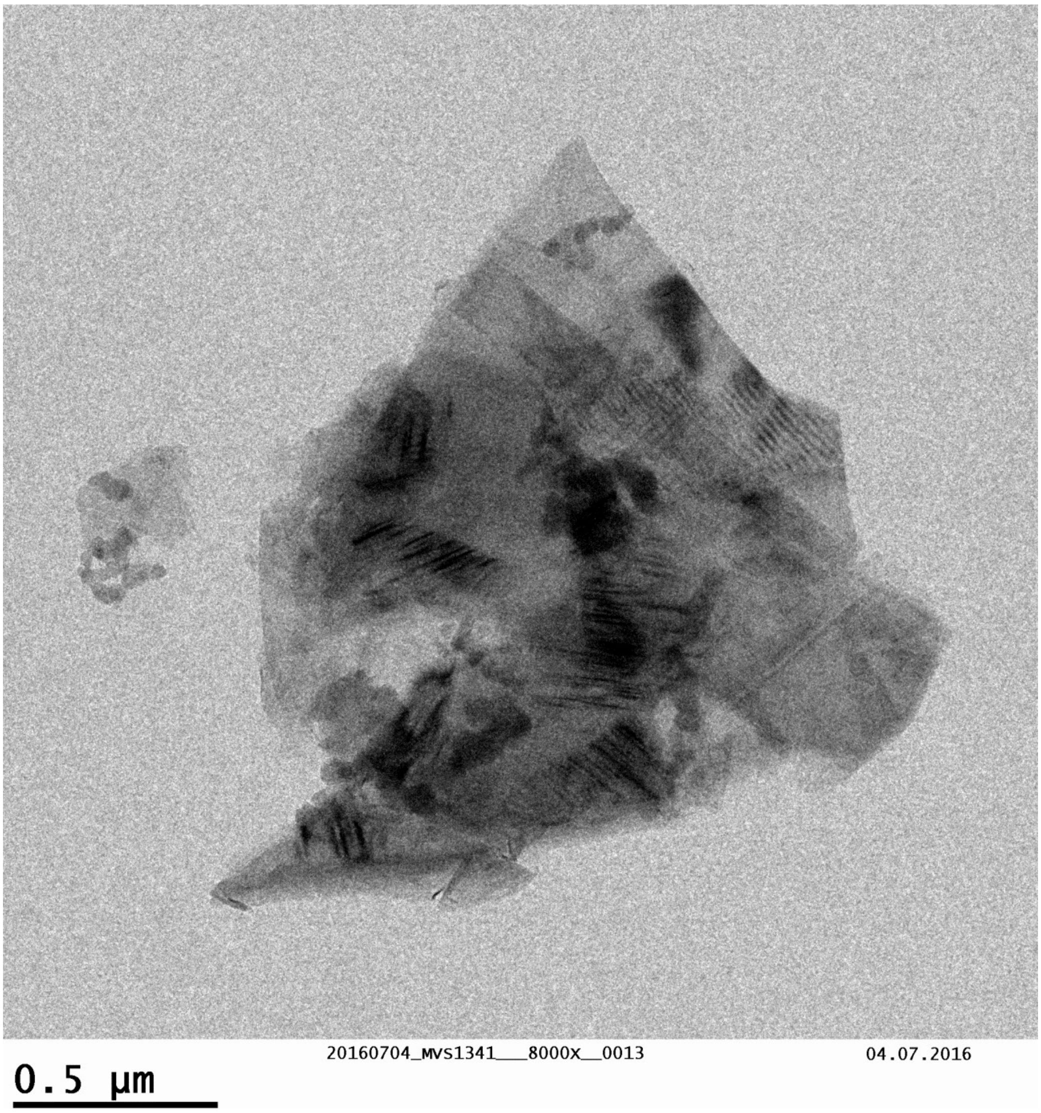

Figure S16. TEM image of *f*-G(**7**).

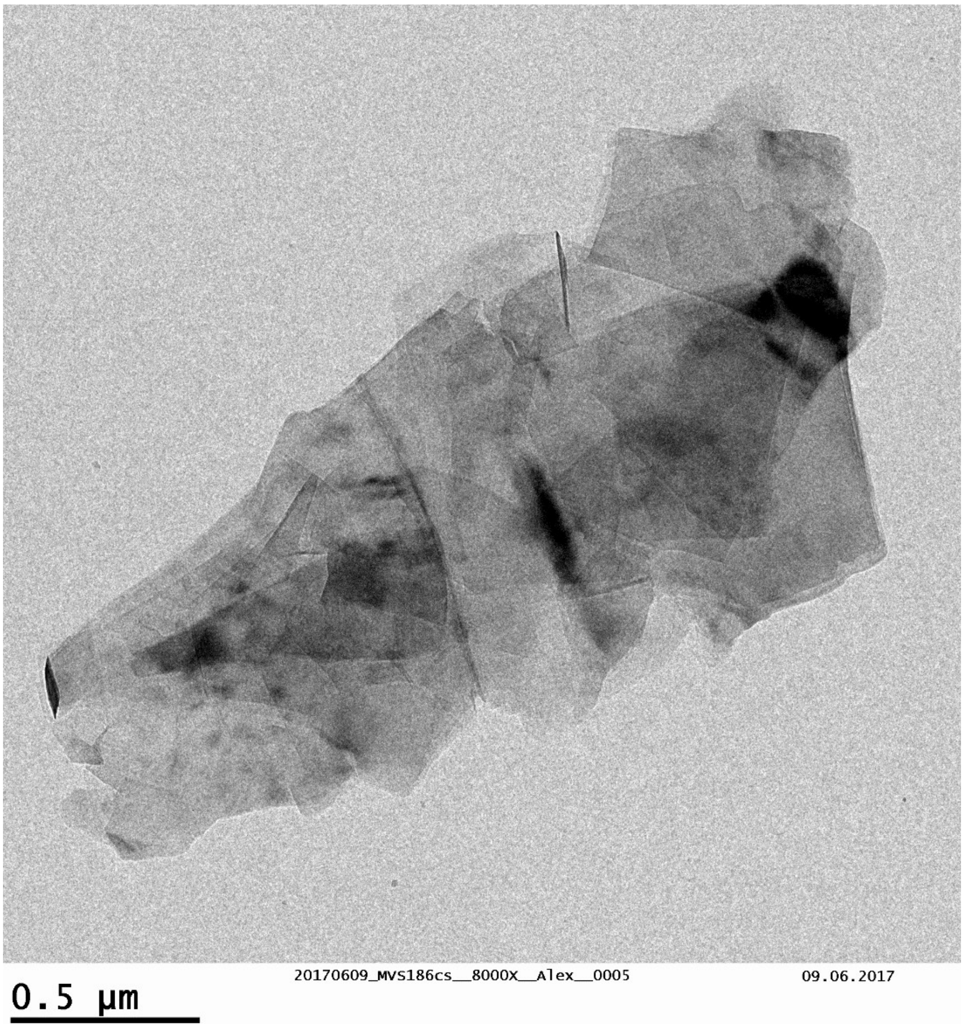

Figure S17. TEM image of *cs*-G.

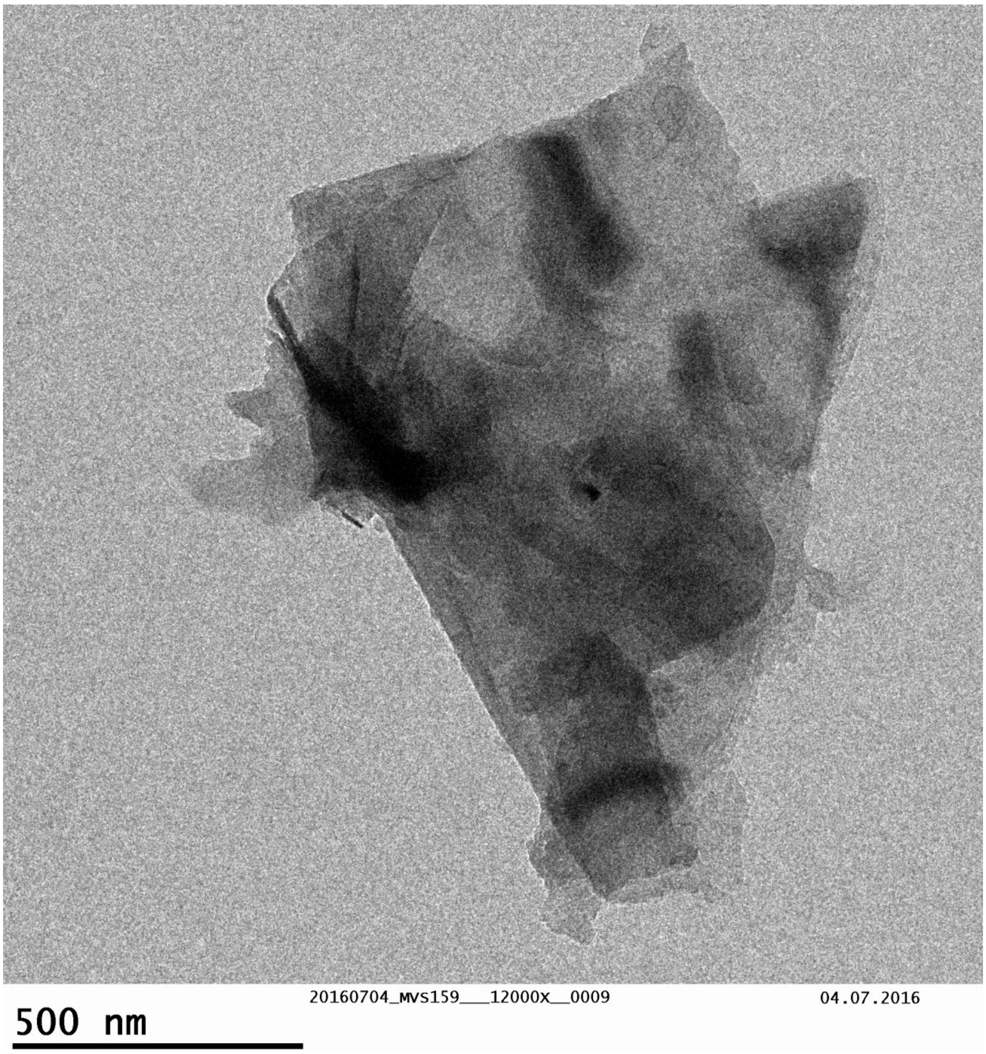

Figure S18. TEM image of *f*-G(**8**).

9 Graphene Suspensions

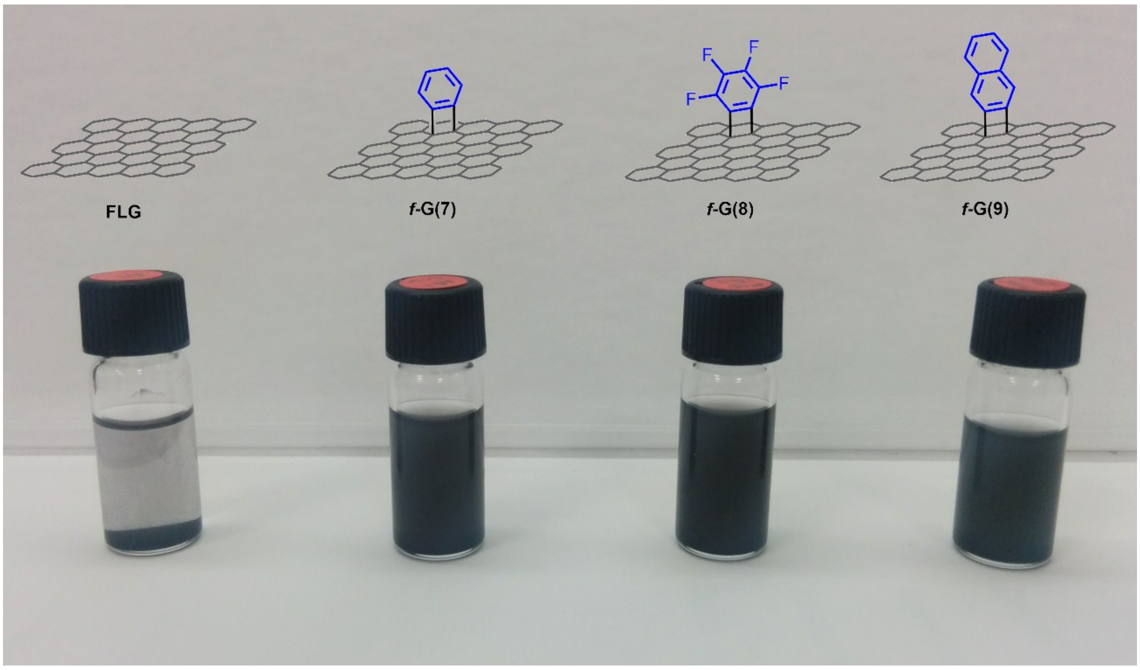

Figure S19. Suspensions of FLG and *f*-G(**7**-**9**) (from the left to the right) in EtOH (0.2 mg/mL) after 24 h.

Figure S20. Image of the quartz Vessel during the reaction process for the functionalization of FLG.