

Electronic Supplementary Information (ESI)

A Photoredox Catalyzed Heck Reaction via Hole Transfer From a Ru(II)-bis(terpyridine) Complex to Graphene Oxide

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Fig. S1, Raman Spectroscopy

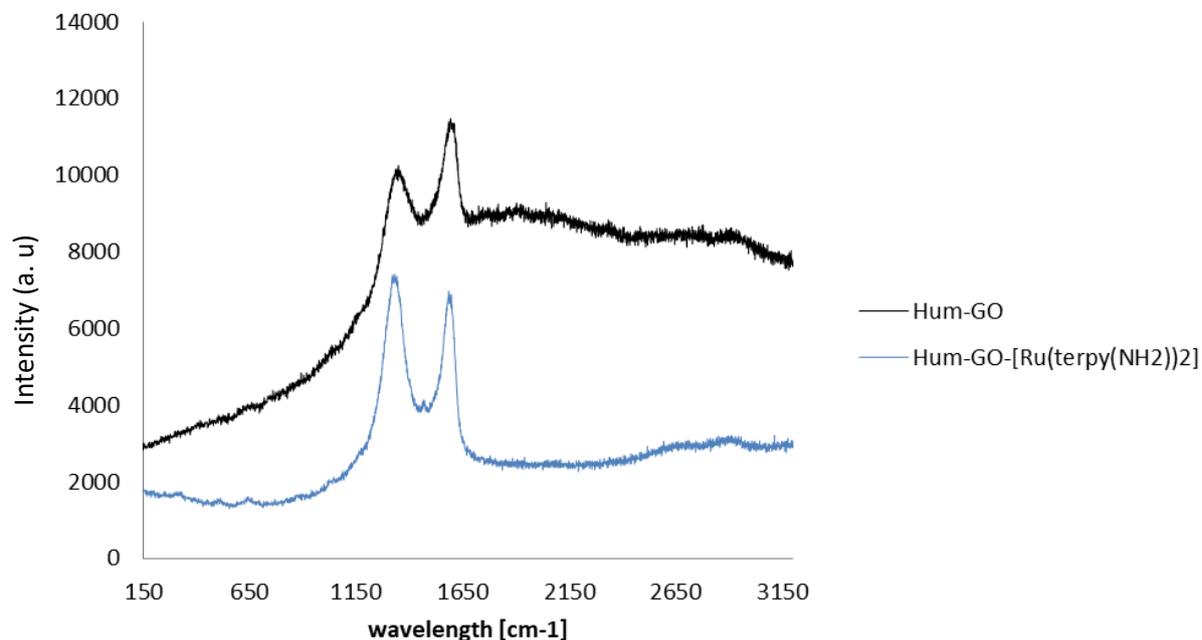


Fig. S1. Raman spectra of GO (black) and **3** (blue) on a Renishaw In Via Raman Spectroscopie.

Fig. S1 shows the Raman spectrum of **3** in comparison to the commercially available GO.¹ Graphitic materials exhibit a significant D-band for sp^3 -centers and a characteristic G-band for sp^2 -centers of carbon atoms. The ratio of the intensities of the D- and G-band allows to postulate the amount of graphene layers present in the material. While the GO consists of 16 layers according to the Raman spectrum the material **3** has a reduced number of 12 layers.

Fig. S2-S4, UV-Vis Spectra

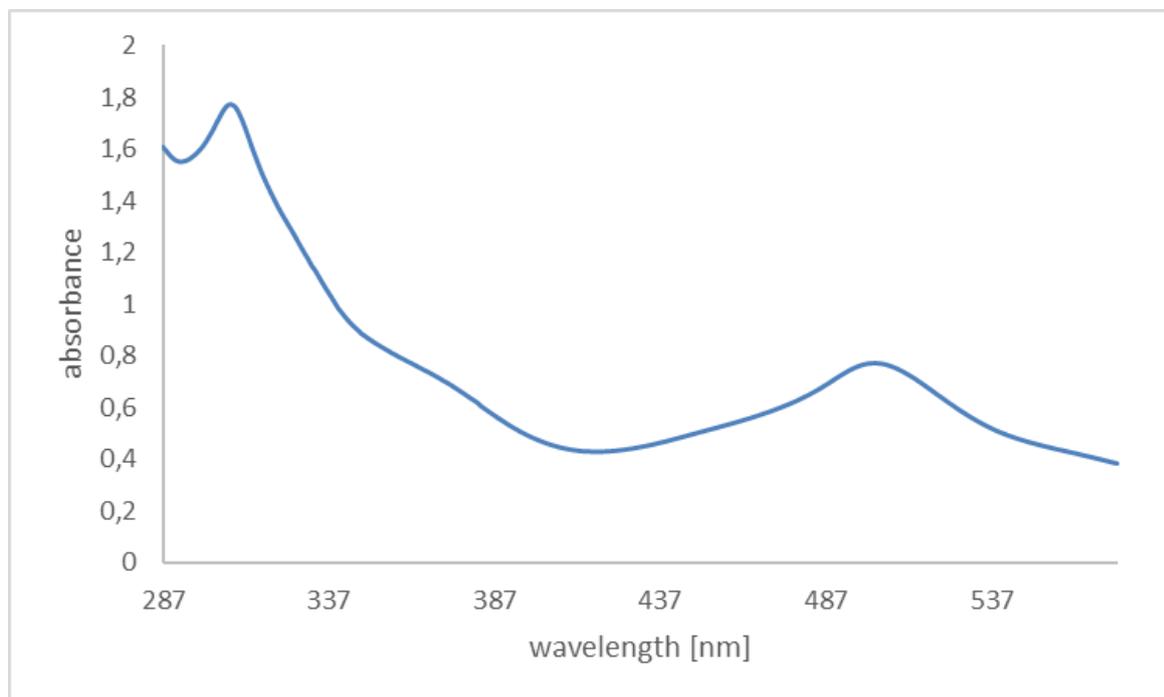


Fig. S2. UV/vis spectrum of **2** in acetonitrile (10^{-4} mol/L)

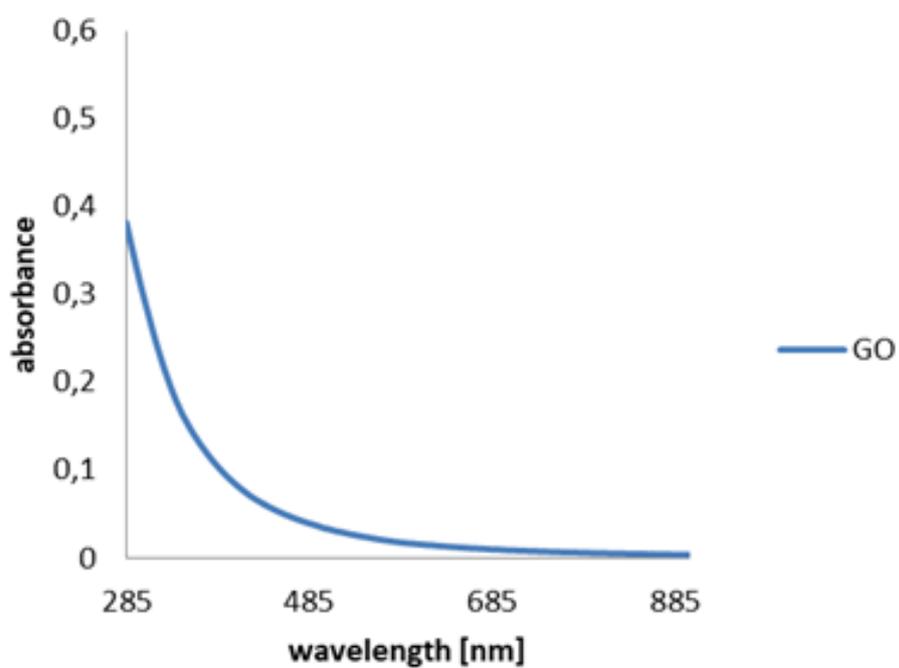


Fig. S3. UV/vis spectrum of GO in DMSO (5^{-4} g/L)

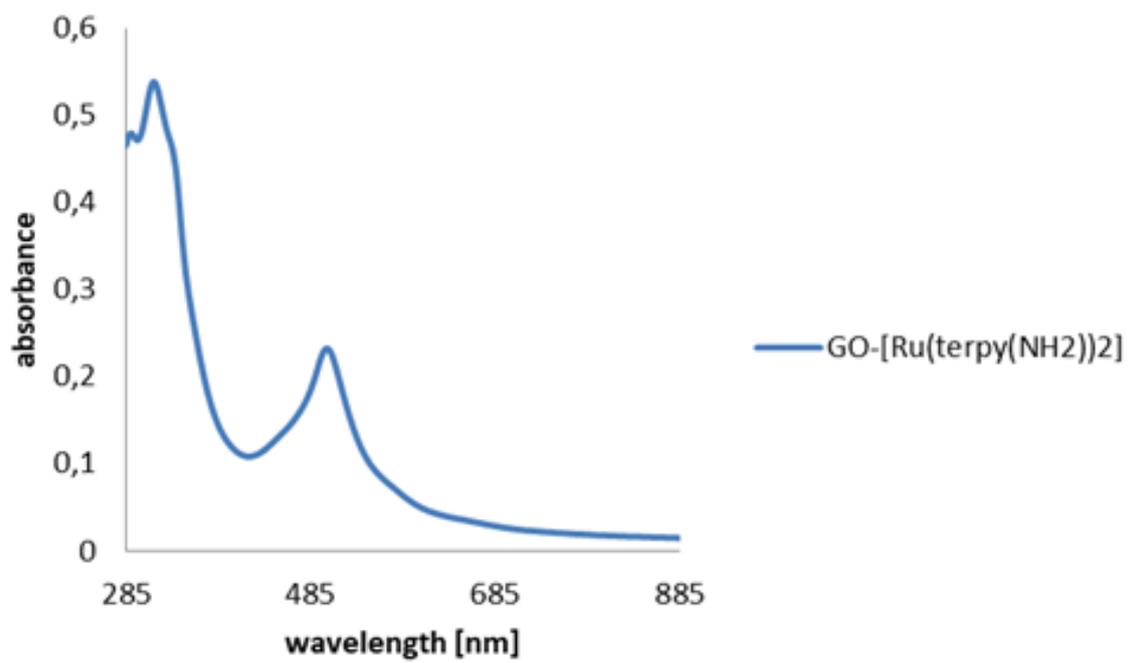


Fig. S4. UV/vis spectrum of **3** in DMSO (5^{-4} g/L)

Fig. S5, AFM Images

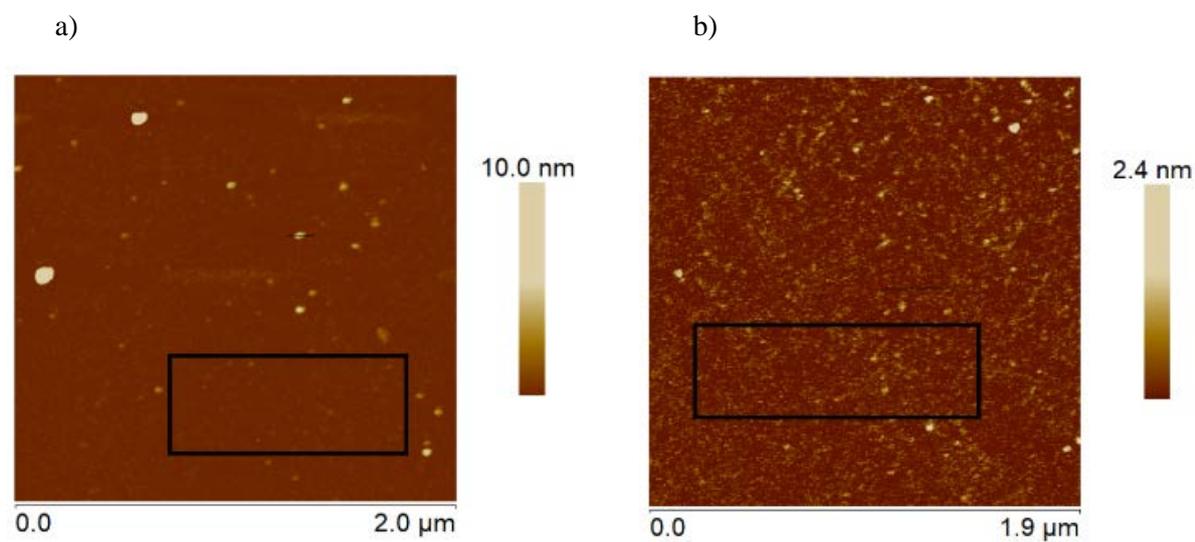
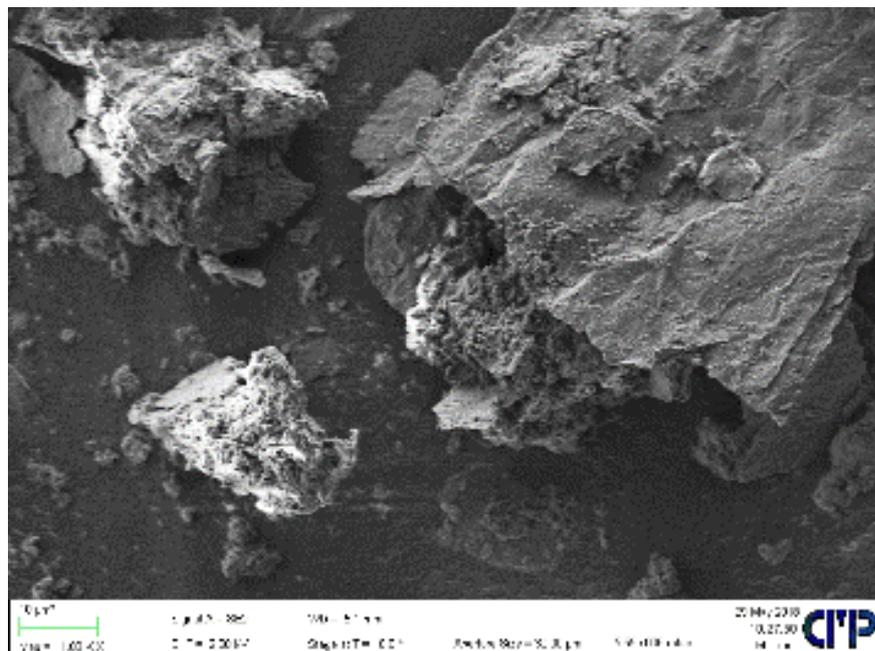


Fig. S5. AFM images a) AFM of GO b) AFM of **3**

AFM measurements of GO and material **3** are presented in Fig. S5. A comparison of the two AFM images shows that the particle size was increased. This can be attributed to the fact, that the bifunctional complex could connect the GO sheets to larger particles. However, the sheets are not forming well defined layers.

Fig. S6, SEM Images

a)



b)

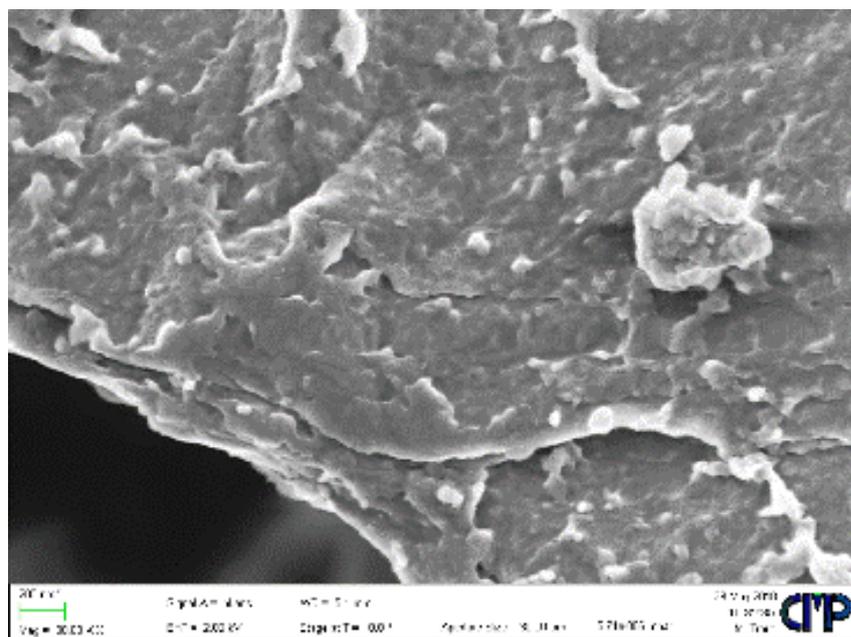
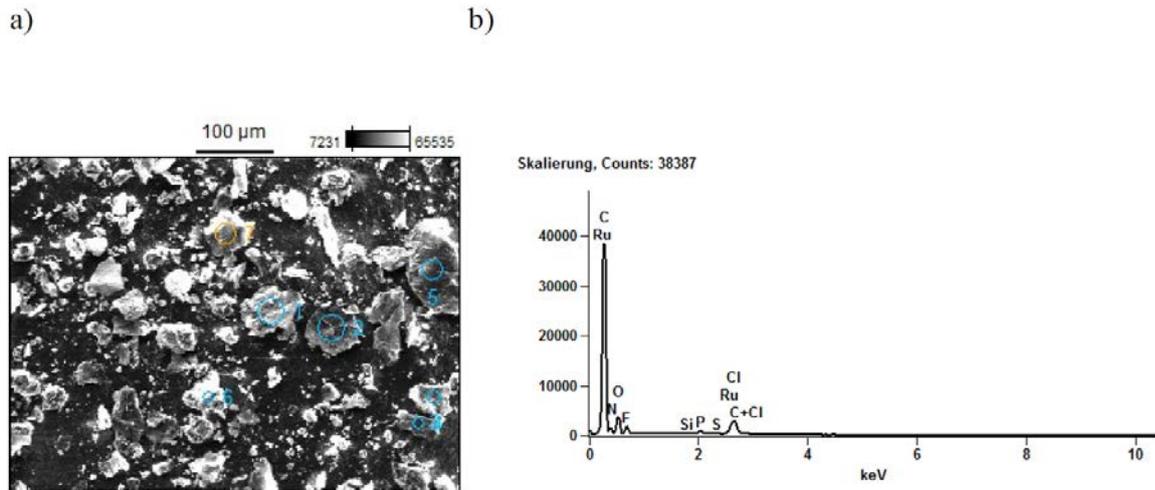


Fig. S6. SEM images of **3**. a) SEM of **3**. Scale bar 10 μm b) Scale bar 200 nm.

The two SEM images of material **3** show no uniform structure (Fig. S6). The edges of the particles are soft and small fiber structures. Hence, the morphology of **3** is different to GO, which can be attributed to the functionalization with complex **2**. An EDX analysis (see Fig. S7-S8) showed that **3** contained ruthenium, nitrogen, fluorine and phosphor from the complex **2** next to carbon and oxygen.

Fig. S7-S8, EDX spectra



c)

126	C-K	N-K	O-K	F-K	Ru-L
Punkt 1	59.45	12.76	20.14	3.33	3.50
Punkt 2	62.08	11.00	20.28	2.49	3.22
Punkt 3	58.80	14.41	16.04	4.41	4.06
Punkt 4	63.00	11.40	17.80	1.96	3.97
Punkt 5	61.12	10.75	20.21	2.61	3.20
Punkt 6	52.90	14.50	20.18	5.77	4.01
Punkt 7	59.54	12.83	20.61	3.16	3.27

Fig. S7. EDX of **3** on a carbon pad. a) SEM, b) EDX spectrum for measuring point 3. c) rel. atom-% of the seven investigated points.

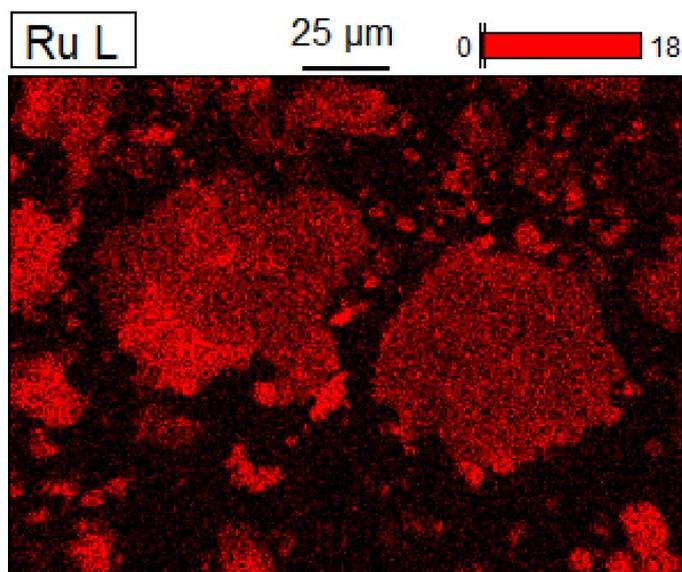


Fig. S8. SEM spectral imaging of **3** for ruthenium.

Fig. S9-S10, XRD Spectra

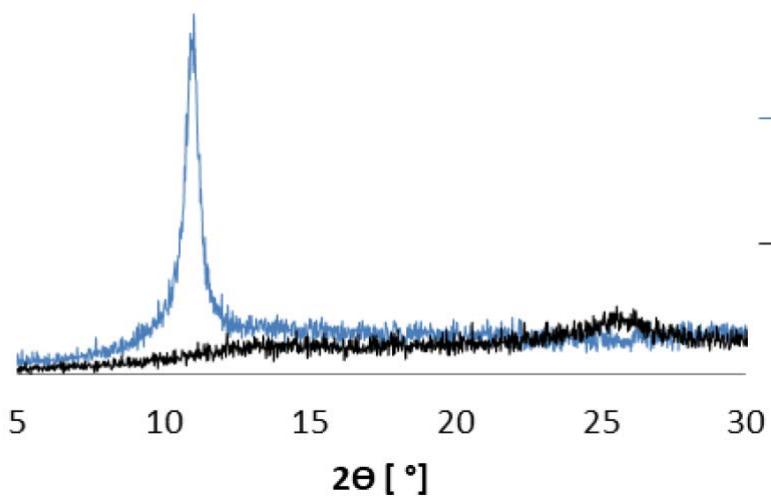


Fig. S9. XRD of GO (blue) and **3** (black)

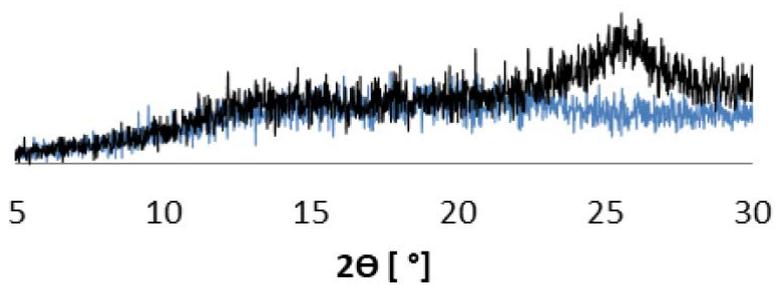


Fig. S10. XRD of **2** (blue) and **3** (black)

XRD spectra showed that the typical peak of GO at 13° disappeared after the functionalization. Instead, a very broad peak between $23\text{-}27^\circ$ appeared, which is specific for graphene material. This change indicated the disappearance of epoxide and carboxylic acid groups in **3**.

Fig. S11, HRTEM Contrast Evaluation of 3

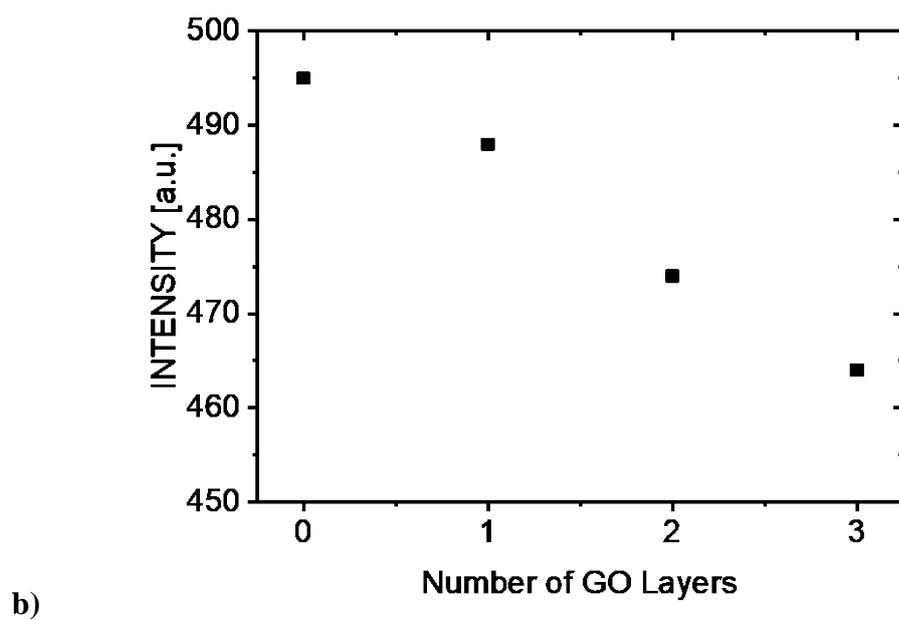
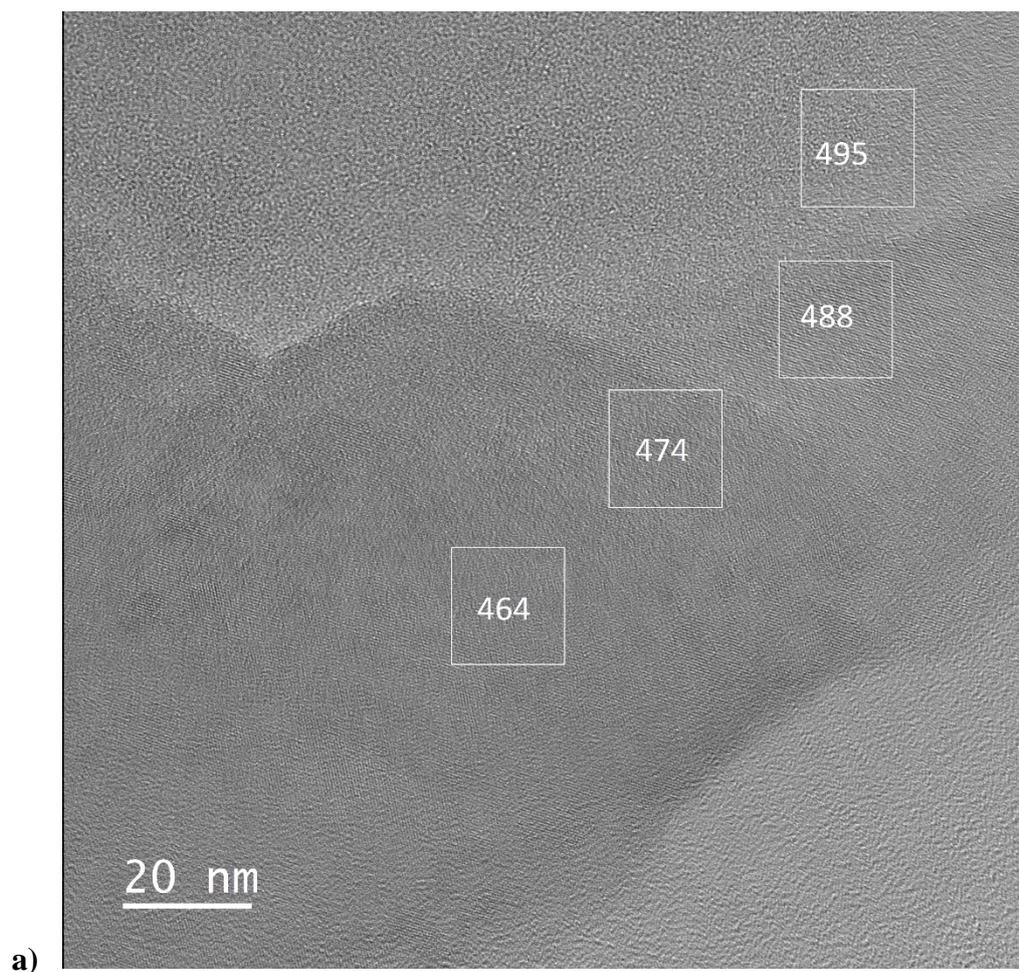


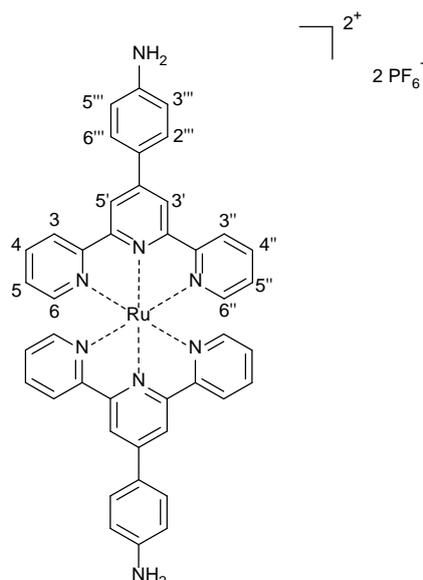
Fig. S11. High-Resolution TEM of **3** and contrast evaluation.

Experimental section

Materials and reagent

All reagents such as NEt_3 (Triethylamine) and DMAP (4-(Dimethylamino)-pyridine) and solvents such as DMF (Dimethylformamide) were purchased from commercial sources like *Fluka AG*, *Merck AG*, *Lancaster*, *Alfa Aesar*, *Riedel de Haën* and *Sigma Aldrich*. Unless specified otherwise the reagents were further purified by standard procedures. GO (Powder, 0.5 – 20 μm , Elemental Analysis: C: 55–65 at%, O: 35-45 at %, S: 0-2 at %, N: 0-1 at %) was purchased from *Graphitene Ltd*. SEM (Scanning Electron Microscope) measurements were performed on a NEON 40 from Zeiss, TEM (Transmission Electron Microscope) measurements were performed on a JEM-ARM200F NEORAM from JOEL. AFM (Atomic Force Microscope) measurements were performed on a Veeco Dimension Icon from Bruker. ^1H NMR spectra were measured at room temperature by Avance 500 and Ascent 700 from *Bruker* using methanol as internal standard. Fourier transform infrared (FTIR) and attenuated total reflection (ATR) spectra were measured with VERTEX 700 by *Bruker* using monocrystalline NaCl or KBr plates. Ligand **1** was prepared according to the literature.²

Synthesis of [(4-([2,2':6',2''-terpyridin]-4'-yl)aniline)Ru(II)](PF₆)₂



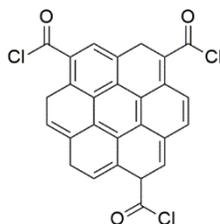
4-([2,2':6',2''-terpyridin]-4'-yl)aniline **1** (0.3 g, 0.93 mmol, 1 eq.) was added to a solution of $\text{Ru(III)Cl}_3 \times 3 \text{H}_2\text{O}$ (0.61 mmol, 0.6 eq.) in a mixture of 50 mL ethanol/water (30 : 20) and refluxed overnight. Excess of NH_4PF_6 (0.1 g, 0.81 mmol, 0.8 eq.) was added to the reaction mixture and stirred for 5 h at room temperature. After evaporation of ethanol, the resulting salt was washed with water (2 x 20 mL), ethanol (2 x 20 mL) and diethyl ether (2 x 20 mL).

Yield: 410 mg (0.39 mmol, 85 %) as black crystalline solid. ^1H -NMR (700 MHz, $\text{CD}_3\text{CN}-d_3$, TMS): δ [ppm] = 4.77 (sbr, 4 H, NH_2), 6.95-6.97 (m, 4 H, $\text{H}3''$, $\text{H}5''$), 7.14-7.16 (m, 4 H, $\text{H}5$, $\text{H}5''$), 7.41-7.42 (m, 4 H, $\text{H}6$, $\text{H}6''$), 7.90-7.93 (m, 4 H, $\text{H}4$, $\text{H}4''$), 8.00-8.02 (m, 4 H, $\text{H}2''$, $\text{H}6''$), 8.61 (d, $J = 8.0$ Hz, 4 H, $\text{H}3$, $\text{H}3''$), 9.91 (s, 4 H, $\text{H}3'$, $\text{H}5'$). ^{13}C -NMR (176 MHz, $\text{CD}_3\text{CN}-d_3$, TMS): δ [ppm] = 115.73 ($\text{C}-3''$, $\text{C}-5''$), 120.76 ($\text{C}-3'$, $\text{C}-5'$), 122.74 ($\text{C}-1''$), 125.16 ($\text{C}-3$, $\text{C}-3''$), 128.17 ($\text{C}-5$, $\text{C}-5''$), 129.77 ($\text{C}-2''$, $\text{C}-6''$), 138.76 ($\text{C}-4$, $\text{C}-4''$), 149.38 ($\text{C}-4''$), 151.78 ($\text{C}-6$,

C-6'''), 153.31 (C-4'), 156.15 (C-2', C-6'), 159.47 (C-2, C-2''). HRMS(ESI): found m/z 375.0907 ($[M]^+$); calc. for $[C_{42}H_{32}N_8Ru]^{+2}$: 375.0907. Raman $\nu = 1991, 1500-3400\text{ cm}^{-1}$. FTIR $\nu = 742, 785, 826, 1186, 1244, 1412, 1466, 1524, 1599, 3369\text{ cm}^{-1}$.

The spectral data were consistent with literature values.³

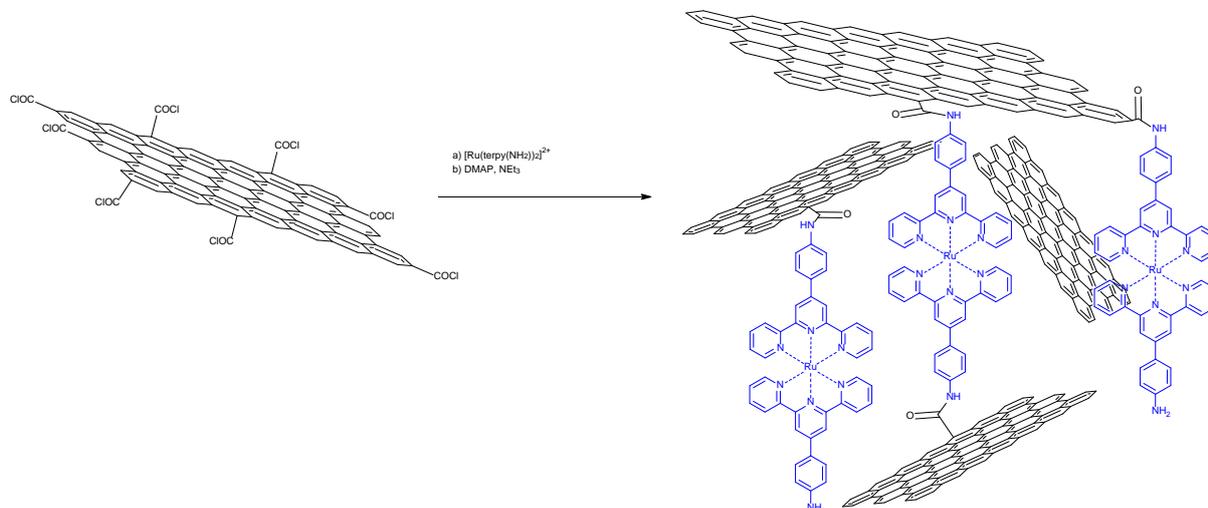
Synthesis of graphene oxide chloride



GO powder (Graphitene Ltd.) (5 g) was solved in dry oxalyl chloride (93.3 g, 0.735 mol, 19.5 eq.). After the addition of anhydrous DMF (25 mL) the reaction mixture was treated with ultrasonic for 3 h to give a homogenous suspension. Afterwards the reaction stirred at 60 °C for 3 d. The residual oxalyl chloride was removed by N_2 -distillation to give the crude product. After drying under *vacuum* GO_{COCl} was directly confirmed in the amidation reaction.

IR (KBr) $\nu = 801, 1024, 1092, 1263, 1406, 1626, 2349, 2926, 2961, 3435\text{ cm}^{-1}$.

Synthesis of 3 ($GO-[Ru(terpy-(C_4H_4NH_2))_2](PF_6)_2$)

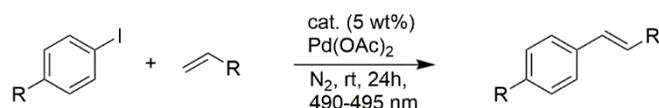


$[Ru(terpy(C_4H_4NH_2))_2](PF_6)_2$ (0.28 g, 0.27 mmol), DMAP (1.48 mg, 0.012 mmol, 0.044 eq.) and NEt_3 (1 mL) were dissolved in a mixture of GO_{Cl} (0.2 g) suspended in anhydrous DMF (6 mL). The reaction mixture was treated with ultrasonic for 3 h to give a homogenous suspension. Afterwards the reaction stirred at 100 °C for 3 d. The reaction was quenched by addition of CH_2Cl_2 (10 mL). Afterwards the reaction mixture was stirred 2 h in the atmosphere of nitrogen.

The crude product was collected by filtration. Afterwards the product was washed with deionized water and chloroform several times. The product was dried under vacuum for 24 h.

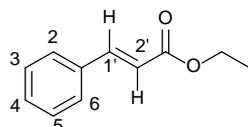
Yield: 0.39 g. Raman $\nu = 1342$ (D), 1594 (G) cm^{-1} . ATR (KBr) $\nu = 748, 785, 837, 1409, 1518, 1602, 1954, 3074, 3386$ cm^{-1} .

Heck-reaction for photocatalytic activity



All reagents were dried and deoxygenated in the present of N_2 -atmosphere. In a general procedure a dry schlenk tube equipped was charged with aryl iodide (0.4 mmol, 1 eq.), $\text{Pd}(\text{OAc})_2$ (0.004 mmol, 1 mol %), NEt_3 (0.8 mmol, 2 eq.) and 5 wt% of the catalyst in DMF (4 ml). The solution was stirred at room temperature under irradiation of cyan blue 3 W power LED cooled with a recirculating cooler to 20°C . After 24 h the reaction was quenched by addition of 1 mL water. The crude product was washed with water (1 x 10 mL) and extracted with chloroform (3 x 10 mL). After that the organic layer was washed with brine (1 x 10 mL), water (3 x 10 mL) and dried over MgSO_4 .

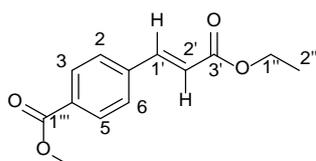
Ethyl cinnamate



Ethyl acrylate (80.10 mg, 0.8 mmol, 2 eq.) was added to a solution of anhydrous DMF (4 ml), iodobenzene (81.6 mg, 0.4 mmol, 1 eq.), $\text{Pd}(\text{OAc})_2$ (0.9 mg, 1 mol%), NEt_3 (0.8 mmol, 2 eq.) and **3** (5 mg).

Yield: 52.8 mg (0.31 mmol, 75 %) as brown liquid. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , TMS): δ [ppm] = 1.34 (t, $J = 7.1, 4.8$ Hz, 3 H, CH_3), 4.27 (q, $J = 7.1$ Hz, 2 H, CH_2), 6.44 (d, $J = 16$ Hz, 1 H, H_2'), 7.37-7.38 (m, 3 H, $\text{H}_3, \text{H}_4, \text{H}_5$), 7.51-7.53 (m, 2 H, H_2, H_6), 7.69 (d, $J = 16$ Hz, 1 H, H_1'). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , TMS): δ [ppm] = 14.44 ($\underline{\text{C}}\text{H}_3$), 60.60 ($\underline{\text{C}}\text{H}_2$), 118.46 ($\text{C-2}'$), 128.16 ($\text{C-2}, \text{C-6}$), 128.99 ($\text{C-3}, \text{C-5}$), 130.32 (C-4), 134.64 (C-1), 144.69 ($\text{C-1}'$), 167.10 (C=O).

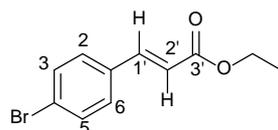
Methyl (E)-4-(3'-ethoxy-3'-oxoprop-1-en-1-yl)benzoate



Ethyl acrylate (104.8 mg, 0.8 mmol, 2 eq.) was added to a solution of anhydrous DMF (4 ml), Methyl 4-iodobenzoate (104.8 mg, 0.4 mmol, 1 eq.), $\text{Pd}(\text{OAc})_2$ (0.9 mg, 1 mol%), NEt_3 (0.8 mmol, 2 eq.) and **3** (5 mg).

Yield: 93.6 mg (0.39 mmol, 99 %) as brown solid. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , TMS): δ [ppm] = 1.35 (t, $J = 7.1$, 4.8 Hz, 3 H, H_2''), 3.93 (s, 3 H, CH_3), 4.28 (q, $J = 7.1$ Hz, 2 H, CH_2), 6.51 (d, $J = 16$ Hz, 1 H, H_2'), 7.58 (d, $J = 8.3$ Hz, 2 H, H_3 , H_5), 7.70 (d, $J = 16$ Hz, 1 H, H_1'), 8.05 (d, $J = 8.3$ Hz, 2 H, H_2 , H_6). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , TMS): δ [ppm] = 14.44 ($\text{C-}2''$), 52.40 (CH_3), 60.88 (CH_2), 120.89 ($\text{C-}2'$), 128.03 ($\text{C-}3$, $\text{C-}5$), 130.26 ($\text{C-}2$, $\text{C-}6$), 131.53 ($\text{C-}1$), 138.89 ($\text{C-}4$), 143.29 ($\text{C-}1'$), 166.61 ($\text{C-}3'$), 166.66 ($\text{C-}1'''$).

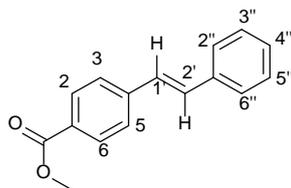
Ethyl (E)-3-(4-bromophenyl)acrylate



Ethyl acrylate (80.10 mg, 0.8 mmol, 2 eq.) was added to a solution of anhydrous DMF (4 ml), 1-Bromo-4-iodobenzene (113.2 mg, 0.4 mmol, 1 eq.), $\text{Pd}(\text{OAc})_2$ (0.9 mg, 1 mol%), NEt_3 (0.8 mmol, 2 eq.) and **3** (5 mg).

Yield: 99 mg (0.39 mmol, 99 %) as brown solid. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , TMS): δ [ppm] = 1.34 (t, $J = 7.1$, 4.8 Hz, 3 H, CH_3), 3.93 (s, 3 H, CH_3), 4.27 (q, $J = 7.1$ Hz, 2 H, CH_2), 6.42 (d, $J = 16$ Hz, 1 H, H_2'), 7.35-7.41 (m, 2 H, H_2 , H_6), 7.748-7.54 (m, 2 H, H_3 , H_5), 7.61 (d, $J = 16$ Hz, 1 H, H_2 , H_1'). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , TMS): δ [ppm] = 14.44 (CH_3), 60.78 (CH_2), 119.21 ($\text{C-}2'$), 124.61 ($\text{C-}4$), 129.56 ($\text{C-}2$, $\text{C-}6$), 132.30 ($\text{C-}3$, $\text{C-}5$), 133.59 ($\text{C-}1$), 143.33 ($\text{C-}1'$), 166.86 ($\text{C-}3'$).

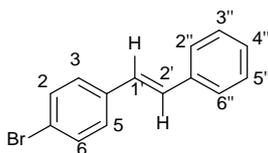
Methyl (E)-4-styrylbenzoate



Styrene (83.32 mg, 0.8 mmol, 2 eq.) was added to a solution of anhydrous DMF (4 ml), Methyl 4-iodobenzoate (104.8 mg, 0.4 mmol, 1 eq.), $\text{Pd}(\text{OAc})_2$ (0.9 mg, 1 mol%), NEt_3 (0.8 mmol, 2 eq.) and **3** (5 mg).

Yield: 94.5 mg (0.39 mmol, 99 %) as brown solid. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , TMS): δ [ppm] = 3.99 (s, 3 H, CH_3), 7.18 (d, $J = 16.3$ Hz, 1 H, H_2'), 7.28 (d, $J = 16.3$ Hz, 1 H, H_1'), 7.36 (t, $J = 7.3$ Hz, 1 H, H_4''), 7.44 (t, $J = 7.6$ Hz, 2 H, H_3'' , H_5''), 8.10 (d, $J = 8.4$ Hz, 2 H, H_2 , H_6). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , TMS): δ [ppm] = 52.39 (CH_3), 126.68 ($\text{C-}3$, $\text{C-}5$), 127.16 ($\text{C-}2''$, $\text{C-}6''$), 127.95 ($\text{C-}2'$), 128.59 ($\text{C-}4''$), 129.14 ($\text{C-}3''$, $\text{C-}5''$), 129.32 ($\text{C-}1''$), 130.39 ($\text{C-}2$, $\text{C-}6$), 131.62 ($\text{C-}1'$), 137.15 ($\text{C-}4$), 142.21 ($\text{C-}1$), 167.22 (C=O).

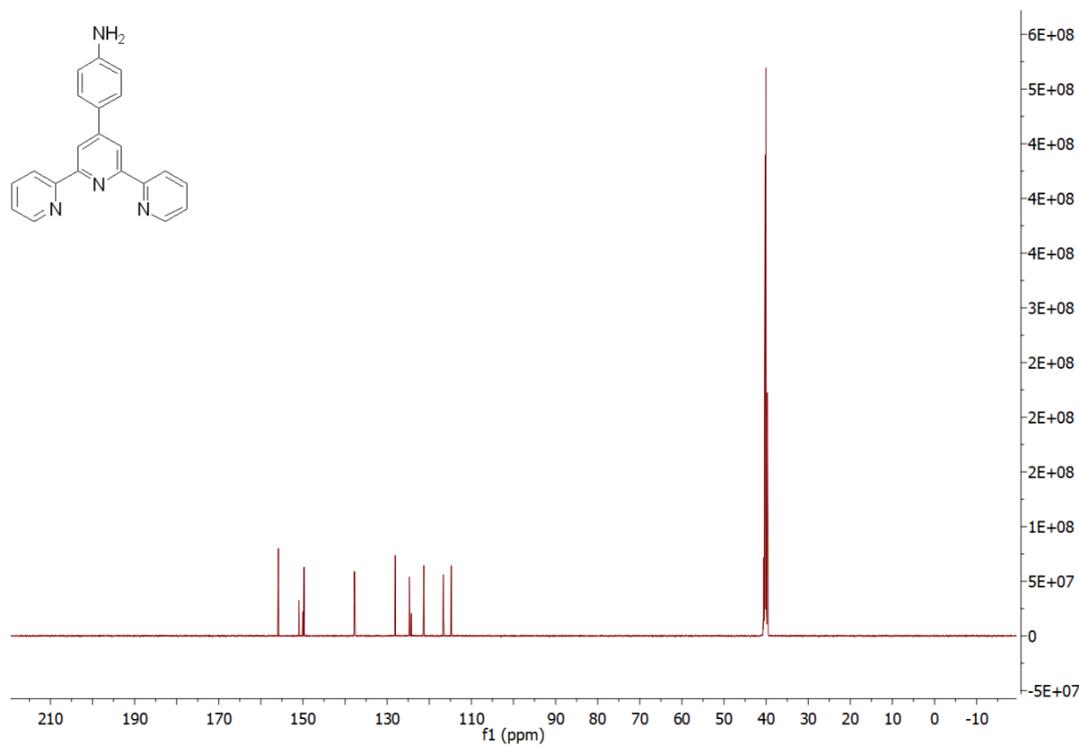
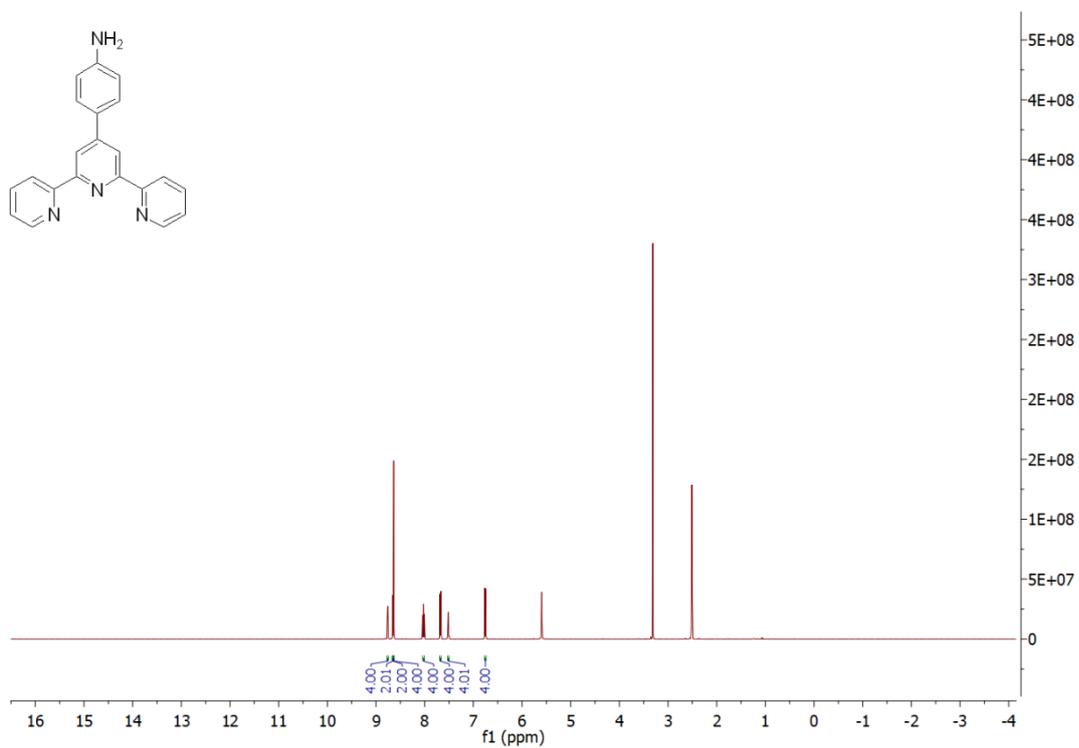
(E)-1-Bromo-4-styrylbenzene

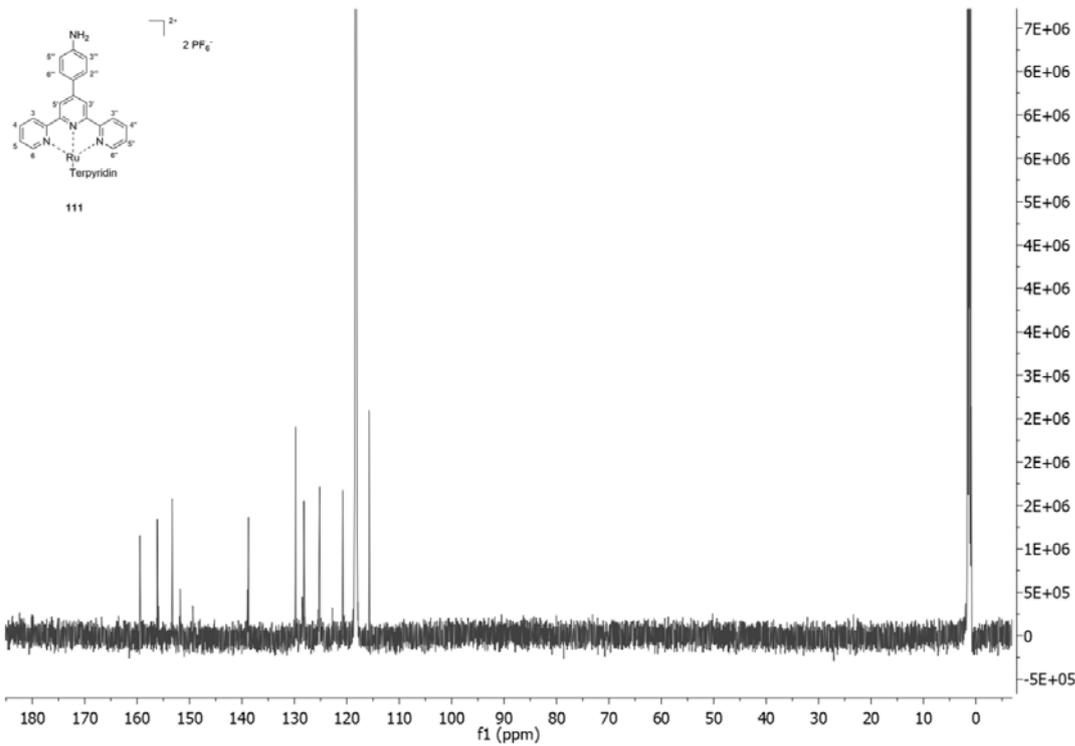
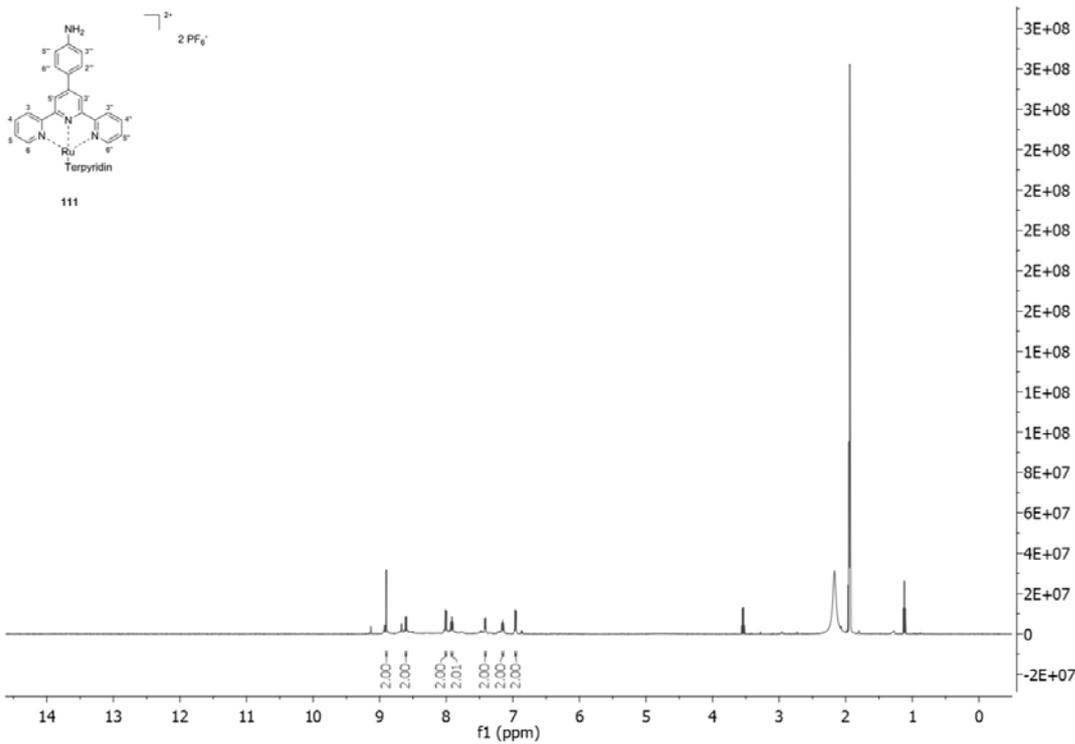


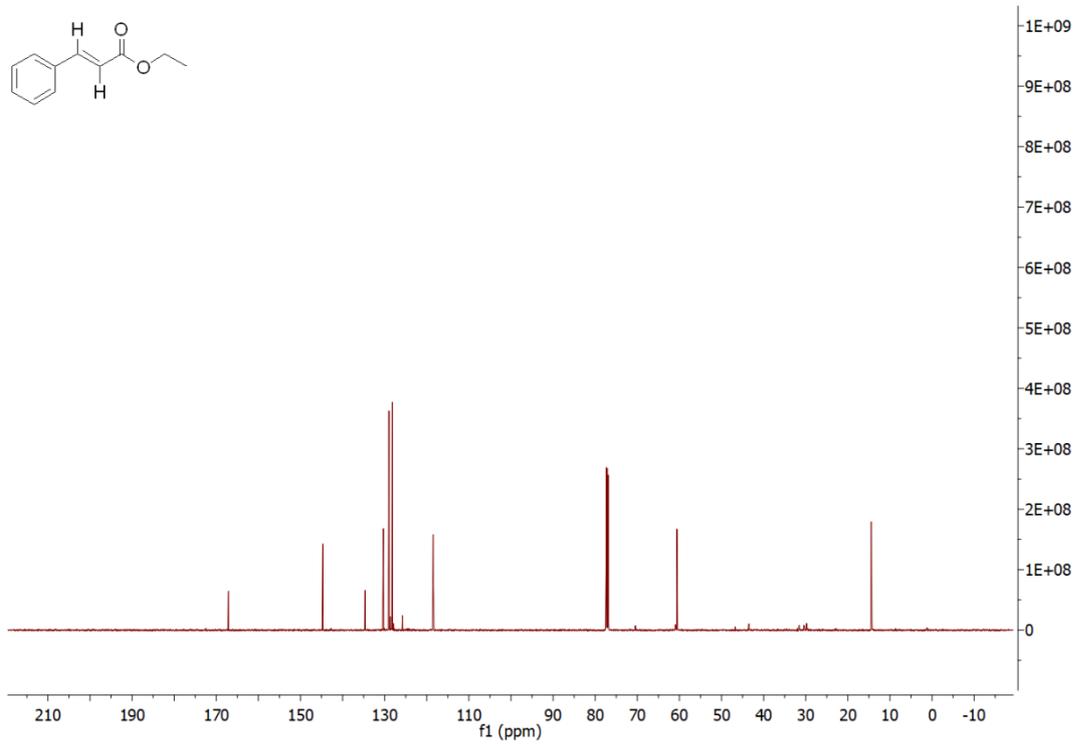
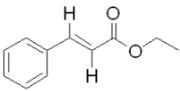
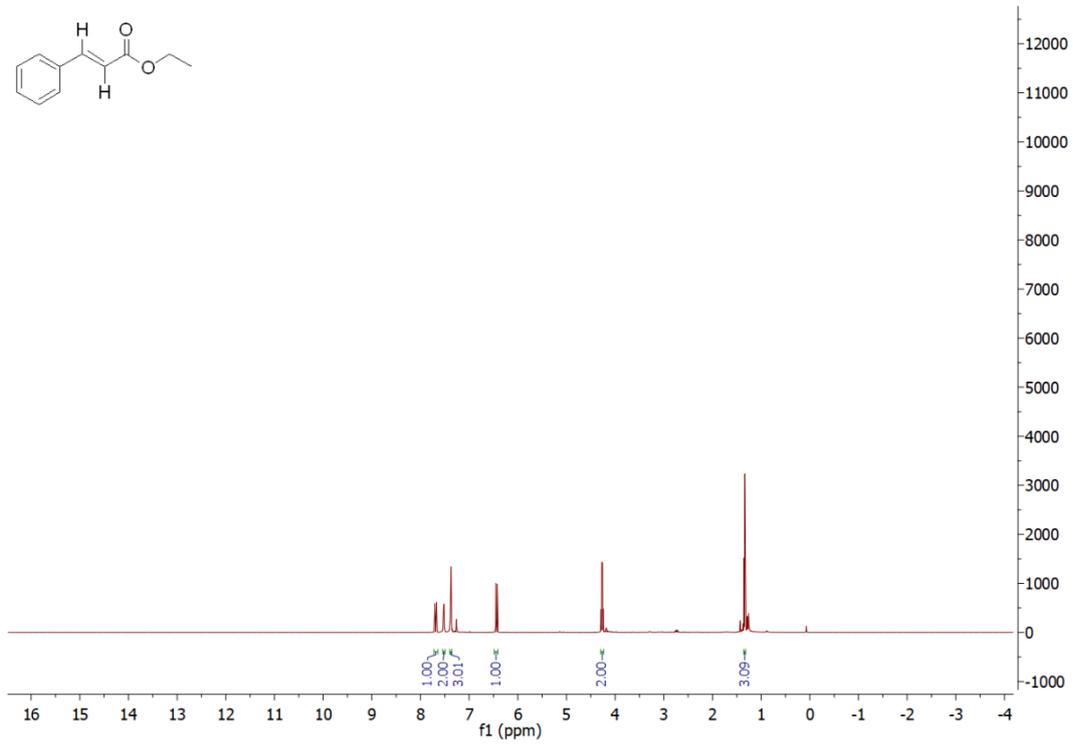
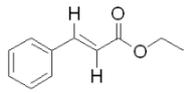
Styrene (83.30 mg, 0.8 mmol, 2 eq.) was added to a solution of anhydrous DMF (4 ml), 1-Bromo-4-iodobenzene (113.2 mg, 0.4 mmol, 1 eq.), Pd(OAc)₂ (0.9 mg, 1 mol%), NEt₃ (0.8 mmol, 2 eq.) and **3** (5 mg).

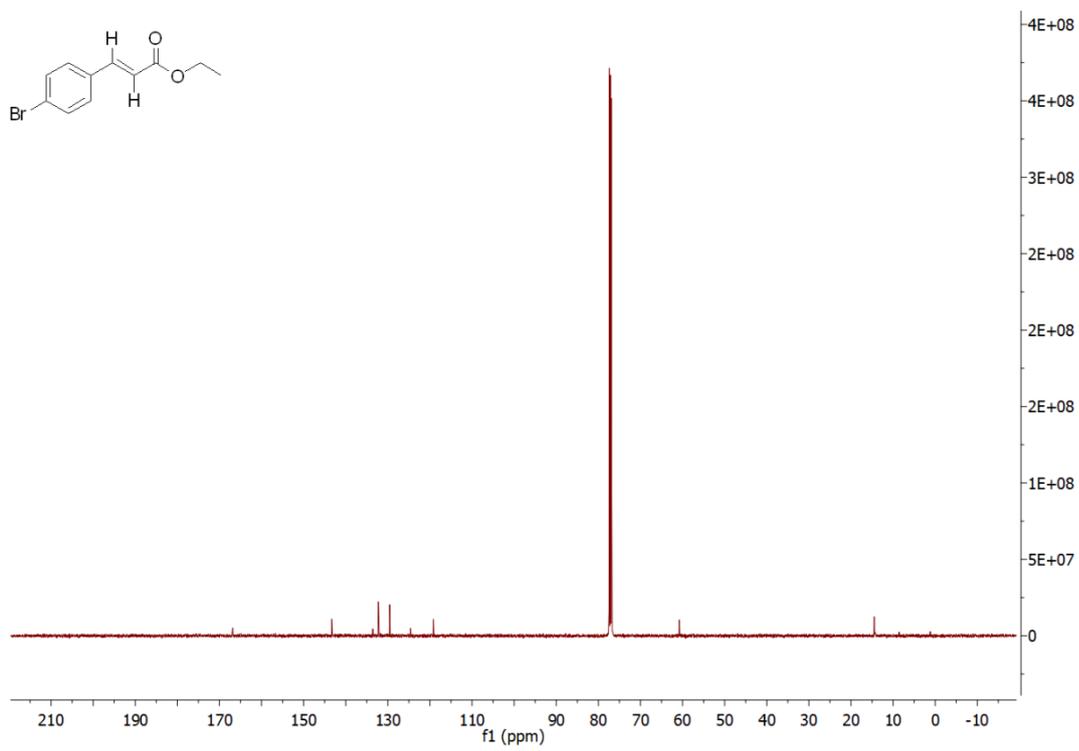
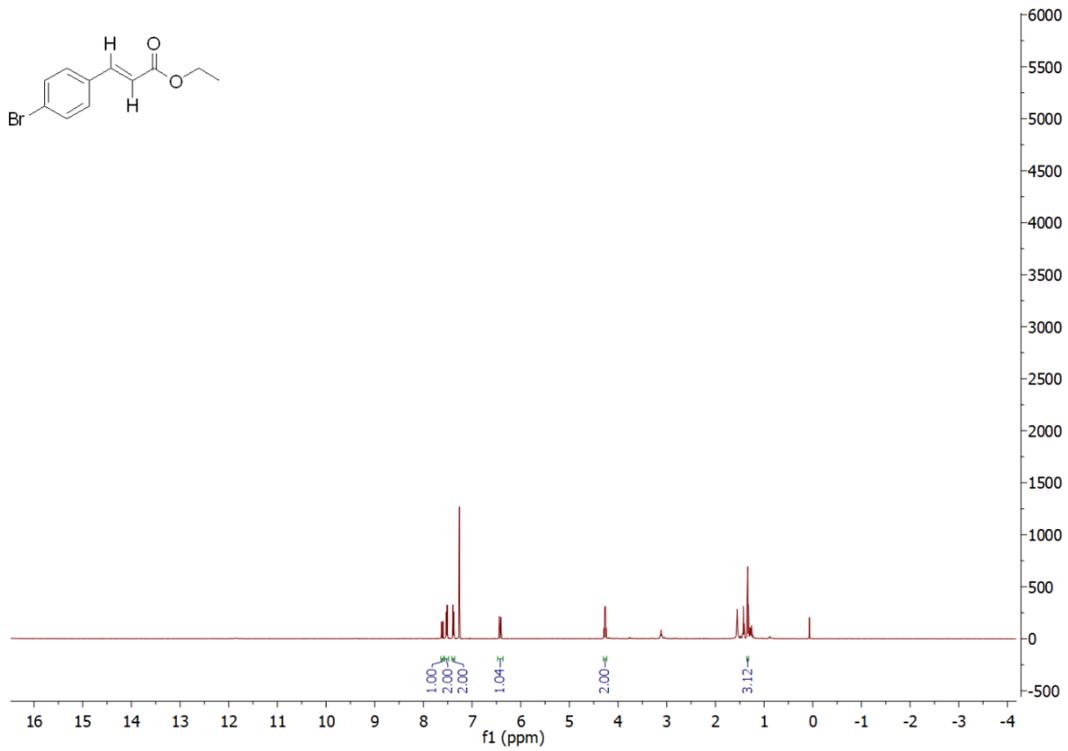
Yield: 96.7 mg (0.37 mmol, 93 %) as brown solid. ¹H-NMR (500 MHz, CDCl₃, TMS): δ [ppm] = 7.06 (d, *J* = 16.3 Hz, 1 H, H1'), 7.12 (d, *J* = 16.3 Hz, 1 H, H2'), 7.31 (d, *J* = 7.3 Hz, 1 H, H4''), 7.38 (d, *J* = 7.7 Hz, 2 H, H3'', H5''), 7.40 (d, *J* = 8.2 Hz, 2 H, H3, H5), 7.50 (d, *J* = 8.4 Hz, 2 H, H2, H6), 7.53 (d, *J* = 7.7 Hz, 2 H, H2', H6'). ¹³C-NMR (125 MHz, CDCl₃, TMS): δ [ppm] = 121.69 (C-1), 126.94 (C-2'', C-6''), 127.78 (C-1'), 128.29 (C-4''), 128.36 (C-3, C-5), 129.13 (C-3'', C-5''), 129.81 (C-2'), 132.16 (C-2, C-6), 136.67(C-4), 137.33 (C1').

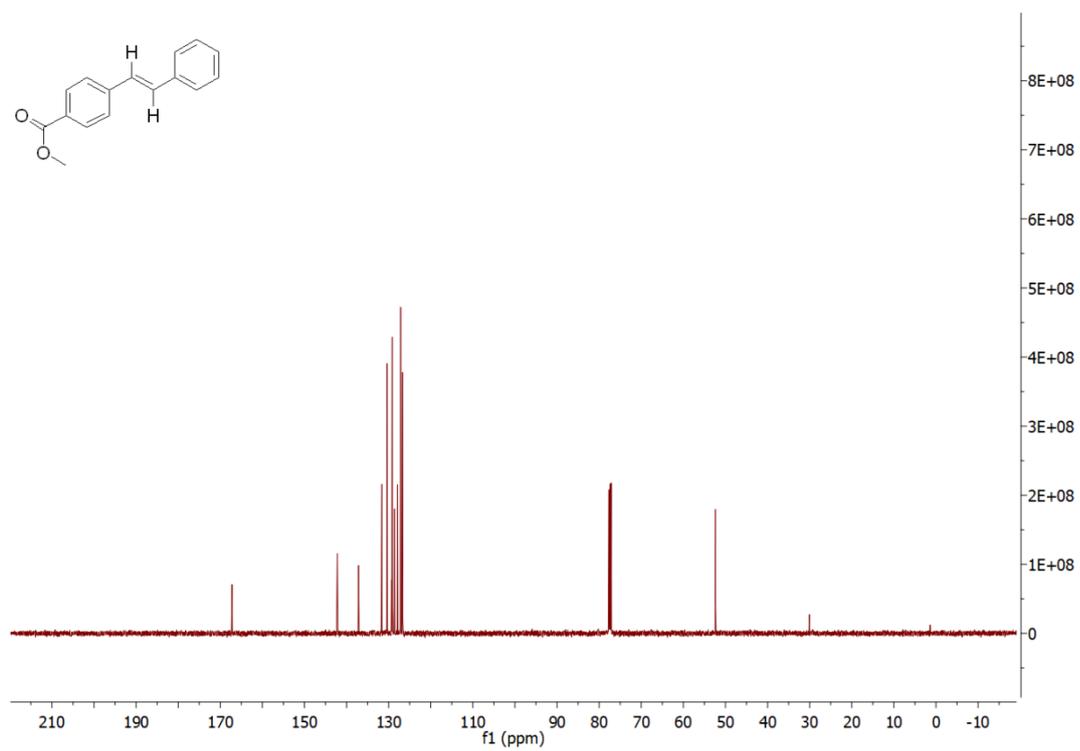
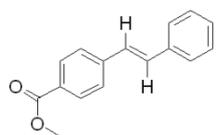
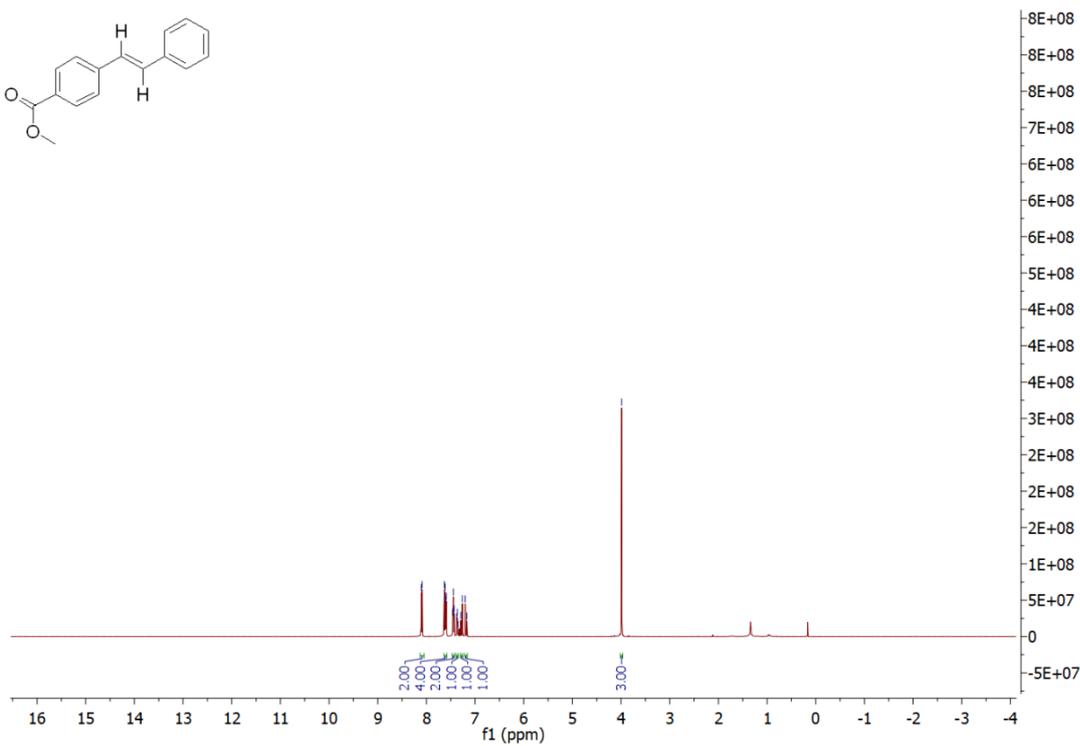
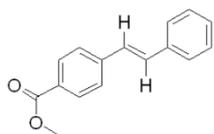
NMR-Spectra

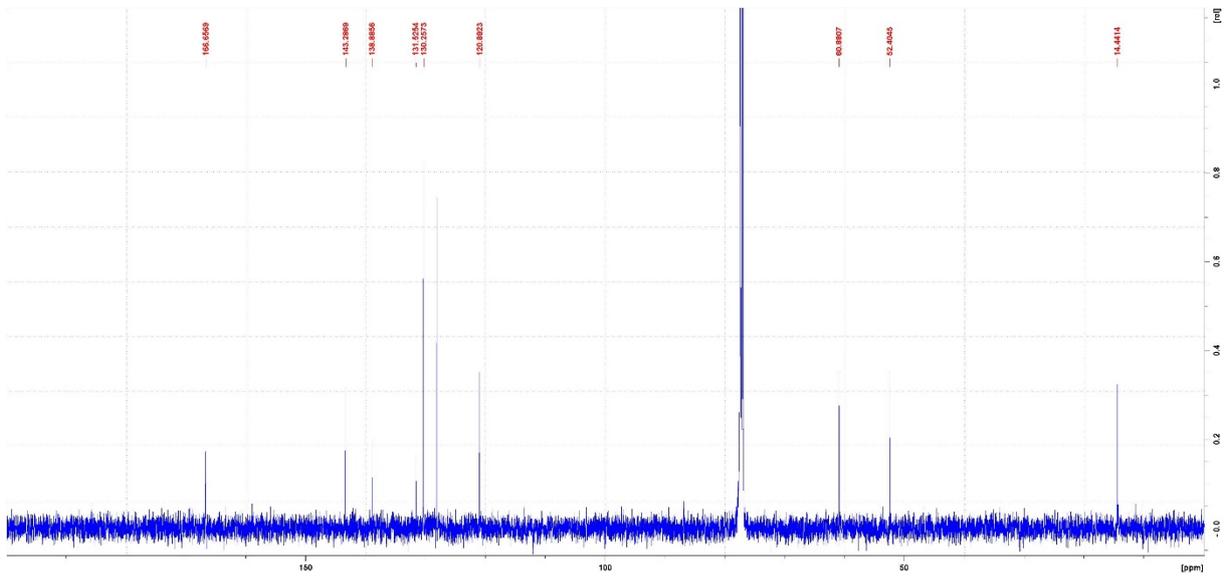
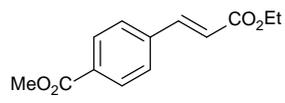
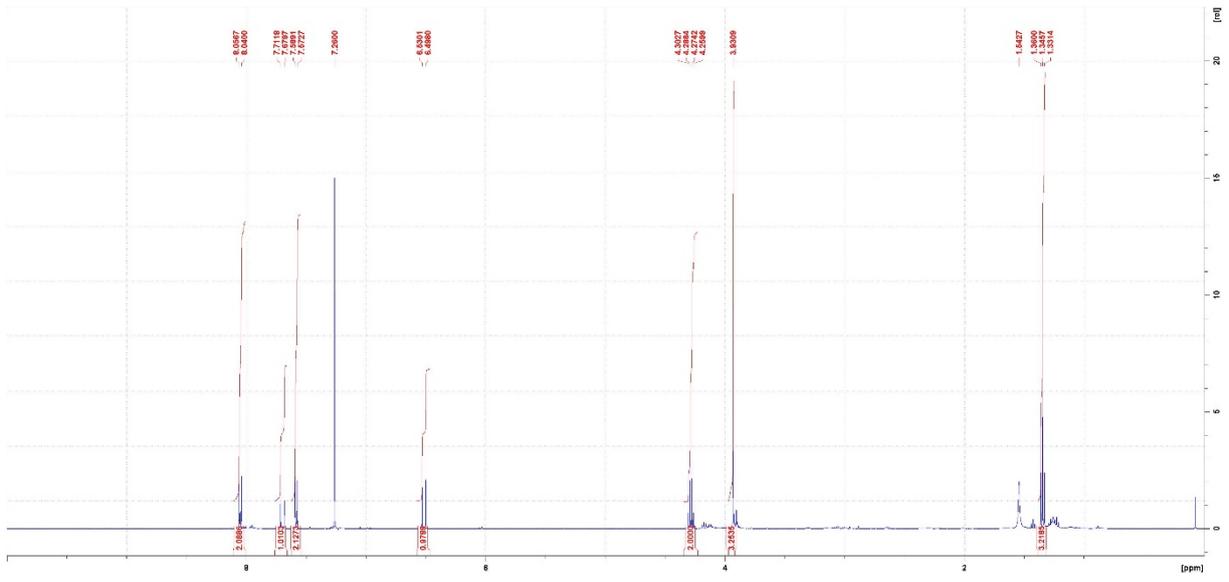
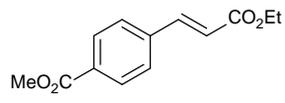


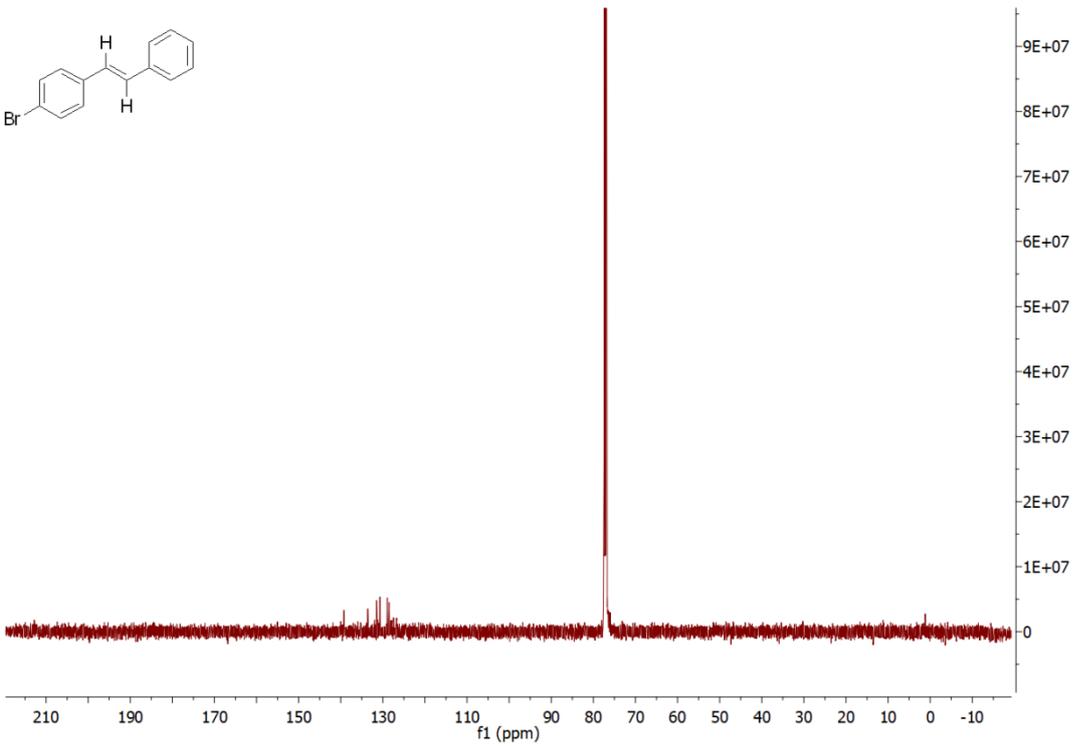
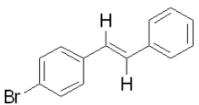
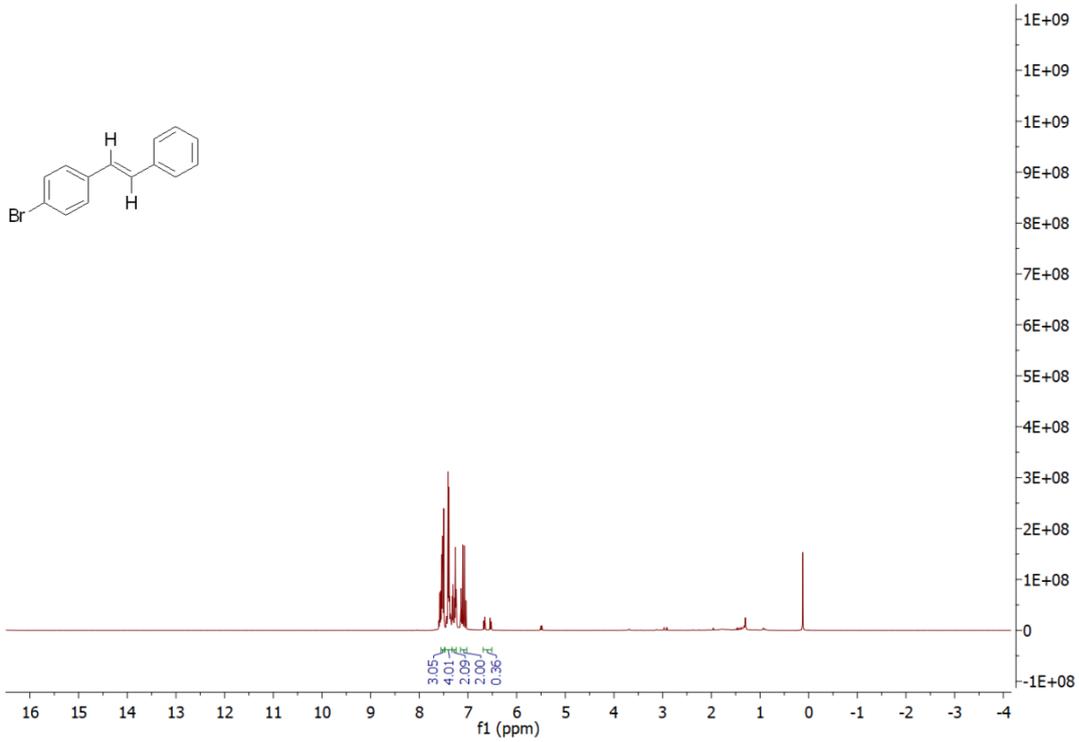
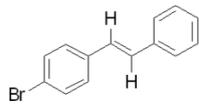












DFT modeling: GO-functionalized Ru-units

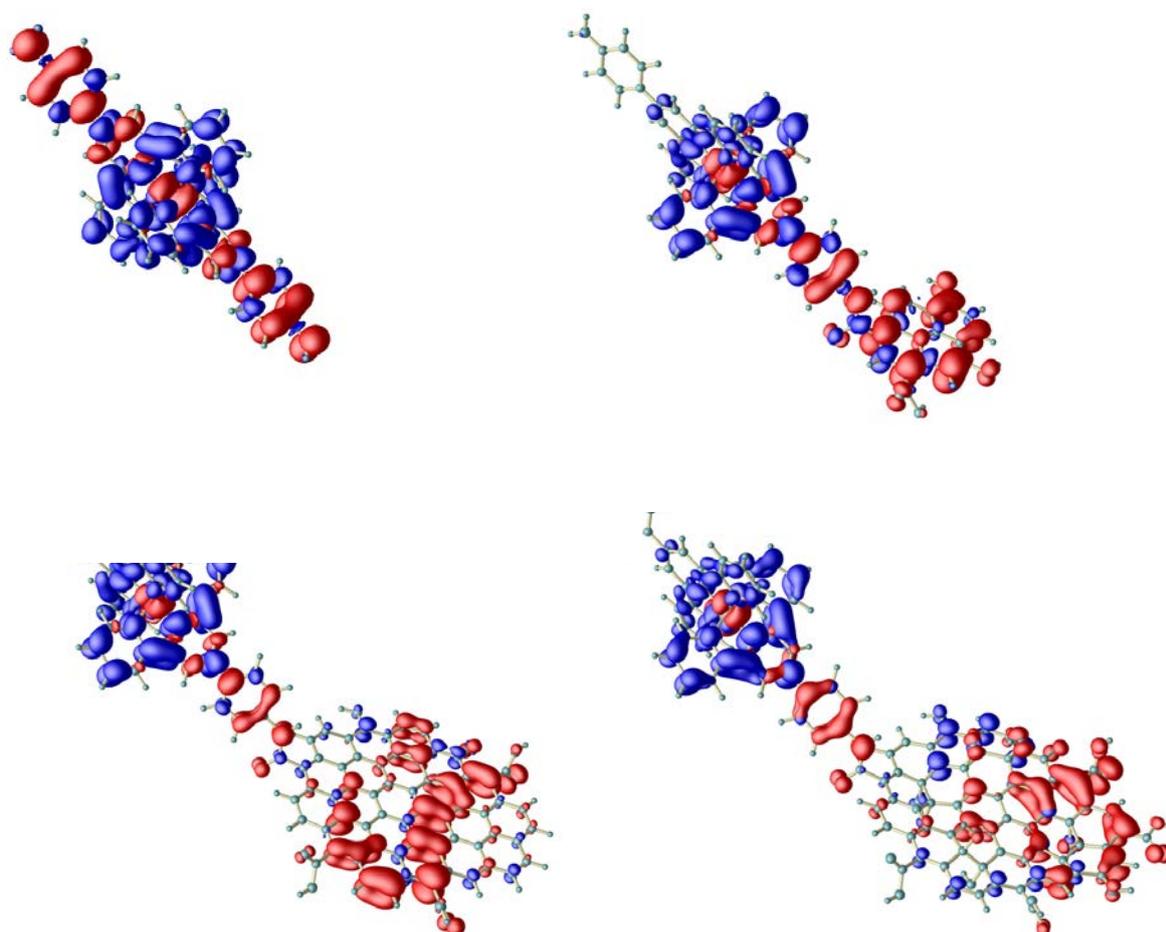


Fig. S12. Ru-complex, pure and functionalized with graphene-flakes of different size and different O-content. *Top, left:* pure Ru-complex; *bottom, left:* Ru-unit with purely H-terminated graphene flake (88 atoms, no O attached). *Top, right:* Ru-unit with minimum size graphene oxide (GO)-flake (32 atoms, O/C ratio = 0.30); *bottom, right:* Ru-unit with larger GO-flake (104 atoms), again with similar O/C ratio of about 0.32. Shown are the orbitals involved in the molecular HOMO-LUMO transition (intra Ru-4d excitation). The electron is always ‘pumped’ from the HOMO (*red*) into the LUMO (*blue*). The latter remains almost unaffected from details of the attached GO-flake. The basic results of the DFT calculations appear, thus, to be robust against details of the structural modeling:

Total energy density functional theory (DFT) calculations have been performed with the Quantum ESPRESSO code.⁴ Exchange and correlation interactions have been modeled by employing the gradient-corrected PBE functional⁵ complemented with a dispersion correction (DFT-D).⁶ The electron-ion interaction was described by using scalar relativistic norm-conserving pseudo-potentials. As basis set we use plane waves with kinetic energies up to 800 eV. All atoms of the entire structure (Ru-unit with attached GO-flake) have been freely relaxed with convergence criteria of 0.005 eV/Å for forces and 10⁻⁶eV for total energies.

For the modeling of the GO, the edges of irregularly shaped graphene flakes have been terminated with hydrogen (-H), hydroxyl (-OH), and carboxyl (-COOH) groups. Both sides of the graphene lattice have been further decorated with hydroxyl and epoxy bridges. As a consequence of this attachment the structurally relax GO lattice becomes locally bended. The HOMO (*red* in Fig. S12) is found in almost flat regions (with still *sp*²-coordinated carbon atoms).

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