

Sonogashira Coupling in 3D-Printed NMR Cuvettes: Synthesis and Properties of Arylnaphthylalkynes

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1. Materials and Methods

1.1 General remarks

All operations with air sensitive compounds were carried out at a high-vacuum line ($< 10^{-5}$ mbar) using Schlenk techniques and inside a glove box (*M. Braun, Labmaster 130*) operated under N_2 . If not noted differently, all chemicals were bought from *Sigma–Aldrich* and used as received. CS_2CO_3 (*Acros Organics*), 9-bromoanthracene (*TCI Deutschland GmbH*), 1-bromonaphthalene (*abcr GmbH*) and 1-bromo-5-nitronaphthalene (*abcr GmbH*) and all other solids used for air-sensitive operations were degassed for one night *in vacuo* and transferred *via* flasks equipped with Teflon stopcocks into the glove box. THF and $[D_8]$ THF (*Deutero GmbH*) were degassed and dried with NaK alloy over night and distilled before use. $[D_{18}]$ octane (*Deutero GmbH*) was dried with pure *n*BuLi over night and distilled. DMSO, DBU, bromobenzene (*VWR International GmbH*), 4-bromoanisole (*abcr GmbH*) and 4-bromo-*N,N*-dimethylaniline (*Acros Organics*) were dried over CaH_2 and distilled before use. Propiolic acid (*TCI Deutschland GmbH*) was dried over molecular sieve (4 Å) and distilled before use. Methyl iodide and 1,5-diaminopentane were degassed and distilled in high *vacuo* before use. Silica gel 60 was used for column chromatography (CC).

UV/Vis and fluorescence spectra: *Jasco V 640* spectrophotometer (*Jasco Germany GmbH*). Fluorescence spectra were recorded with a *Jasco FP-8500* fluorescence spectrometer. If not noted differently, spectra were recorded with a speed of 100 nm min⁻¹. **IR spectra:** *Bruker Alpha-T* FT-IR spectrometer (*Bruker Coporation*). For ATR measurements, a Platinum diamond-ATR unit was used. If not noted differently, 16 spectra were accumulated per measurement and a resolution of 1 cm⁻¹ was applied. **NMR spectra:** *Bruker Avance 400* (*Bruker Corporation*) (400 MHz (¹H), 100 MHz (¹³C)) and *Avance III 600* (600 MHz (¹H), 150 MHz (¹³C)) FT-NMR spectrometer. Chemical shifts are given in ppm relative to tetramethylsilane ($\delta = 0.0$) or the residual solvent signal of the deuterated solvent.¹ **Mass spectra:** *Varian 320 MS TQ* mass spectrometer at 20 eV and 70 eV for EI mass spectra (*Agilent Technologies*). *HP 1100 Series* (*Hewlett-Packard*) LC/MS mass spectrometer for ESI mass spectra. A collision energy of 30 V (negative ion mode, **1** and **2**) and 5 V (positive ion mode, **9**) was applied. High-resolution mass spectra were measured by Dr. Gerald Dräger at the Institute of Organic Chemistry of the Leibniz University Hannover.

SEC measurements were performed with a setup equipped with a *Waters 515* HPLC pump (*Waters GmbH, Eschborn, Germany*), *Knauer Smartline* RI detector 2300 (*Knauer Wissenschaftliche Geräte GmbH, Berlin, Germany*) and 2 × 5 µm mixed-C and 1 *PLgel 1000* Å column from *Polymer Laboratories* (*Agilent Technologies, Inc.*). Hexafluoroisopropanol with a flow rate of 1 ml/min at 25 °C was used as eluent. Molecular weights are given relative to PMMA calibration. **Glass transition temperatures** have been measured with a *Mettler-Toledo DSC-1* apparatus under N_2 with a heating speed of 10 K/min (*Mettler-Toledo GmbH, Gießen, Germany*). For elemental analyses a *Vario EL, EAS* (*Elementar Analysensysteme GmbH*) was used. The **residual H₂O content** of the polymer samples was measured *via Karl–Fischer* titration of the condensed residue emitted from molten polymer samples at 150 °C under N_2 flow by the ‘*Mikroanalytisches Labor Pascher*’ in Remagen, Germany. Pressure tests have been performed with a *Gartler 25* bar pressure test pump operated with water and 3D-printed flasks of 3 mm wall thickness and an attached hose nipple.

1.2 DFT calculations

All density-functional theory (DFT) calculations were carried out by using the Jaguar 9.1.013 software² running on Linux 2.6.18-238.el5 SMP (x86_64) on five AMD Phenom II X6 1090T processor workstations (Beowulf-cluster) parallelized with OpenMPI. MM2 optimized structures were used as starting geometries. Complete geometry optimizations were carried out on the LACVP* (Hay-Wadt effective core potential (ECP) basis on heavy atoms, N31G6* for all other atoms) basis set and with the PBE0 hybrid density functional. All calculated structures were proven to be true minima by the absence of imaginary frequencies (with exception of **9**). Plots were obtained using Maestro 10.5.013, the graphical interface of Jaguar. Molecular radii have been calculated from the molecular volume of the optimized geometries (radii of the sphere with the solvent excluded volume) assuming an additional solvent shell of 70 pm. UV/Vis transitions were obtained by time dependent (TD)DFT calculations on the same level of theory. Partial charges were obtained with NBO 6.0³ from the results of the DFT calculations. The geometry optimized structures were aligned along the C-C-triple bond and the first hyperpolarizability tensor β_{CC} was calculated analytically.⁴

1.3 Characterization of the Nylon filament:

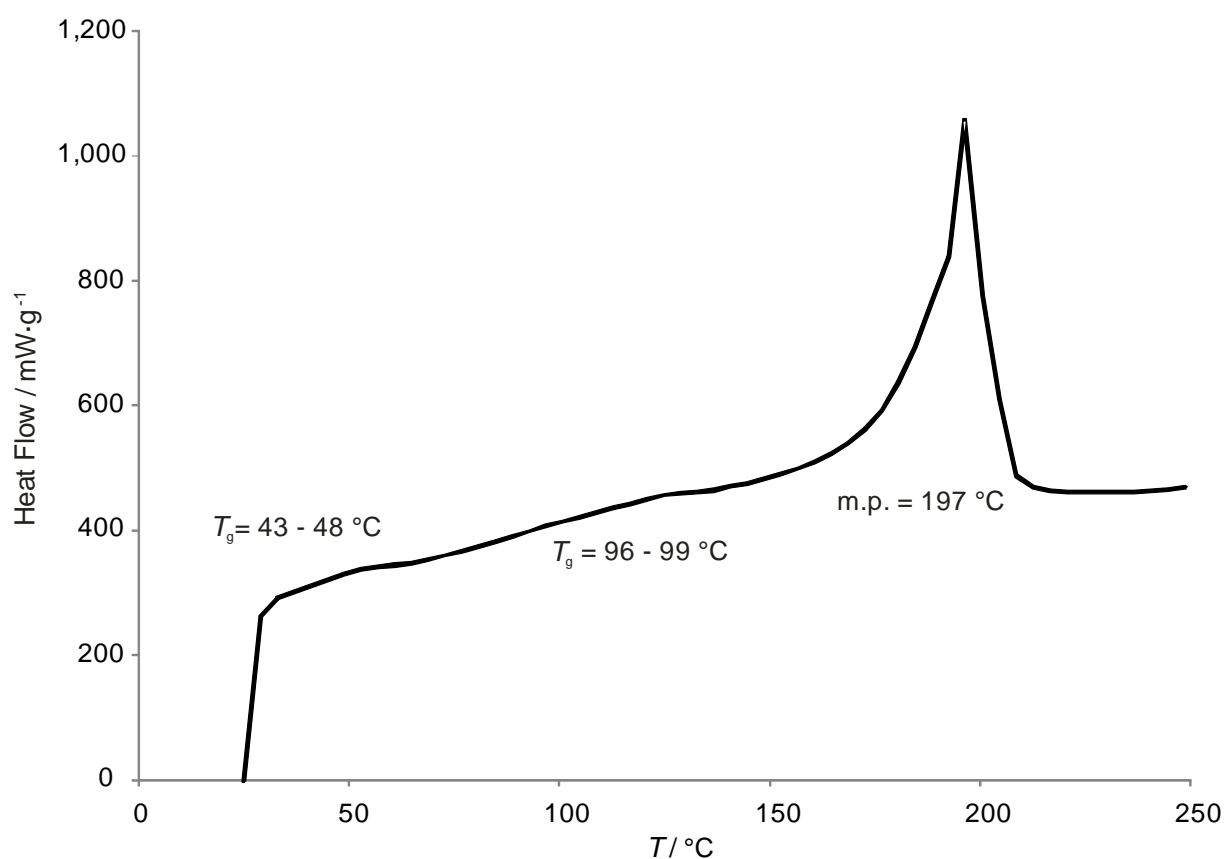


Figure S1. Differential Scanning Calorimetry: First heating curve of Taulman 910.

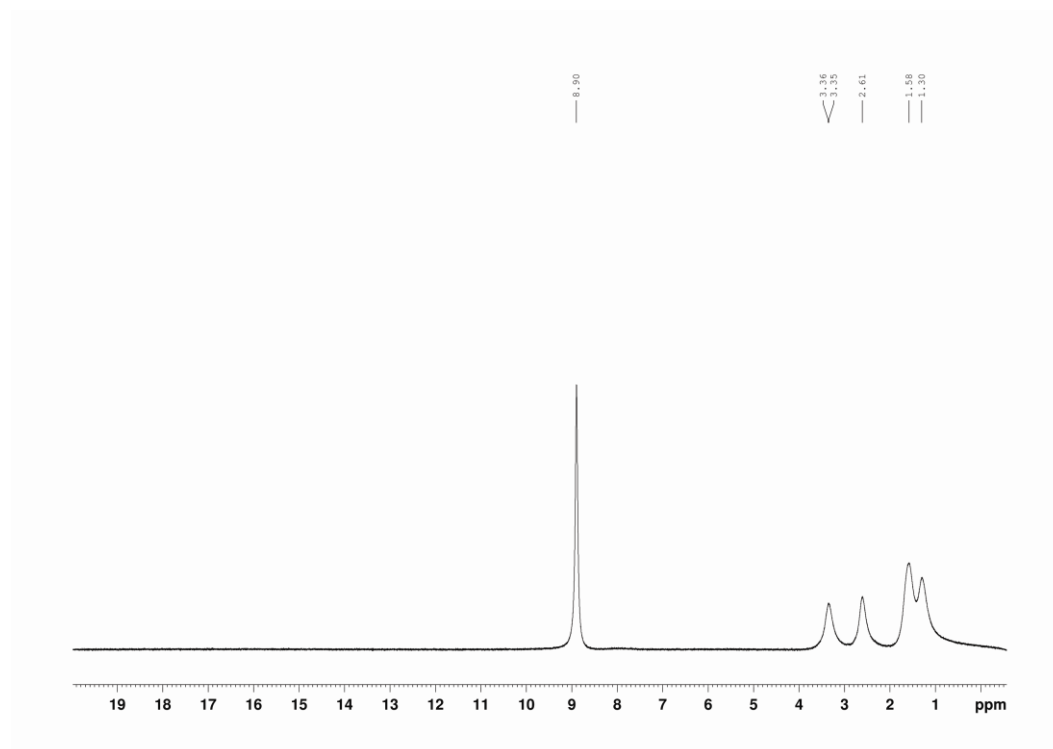


Figure S2. ^1H -NMR spectrum of Taulman 910 in DCl (36 wt-% in D_2O).

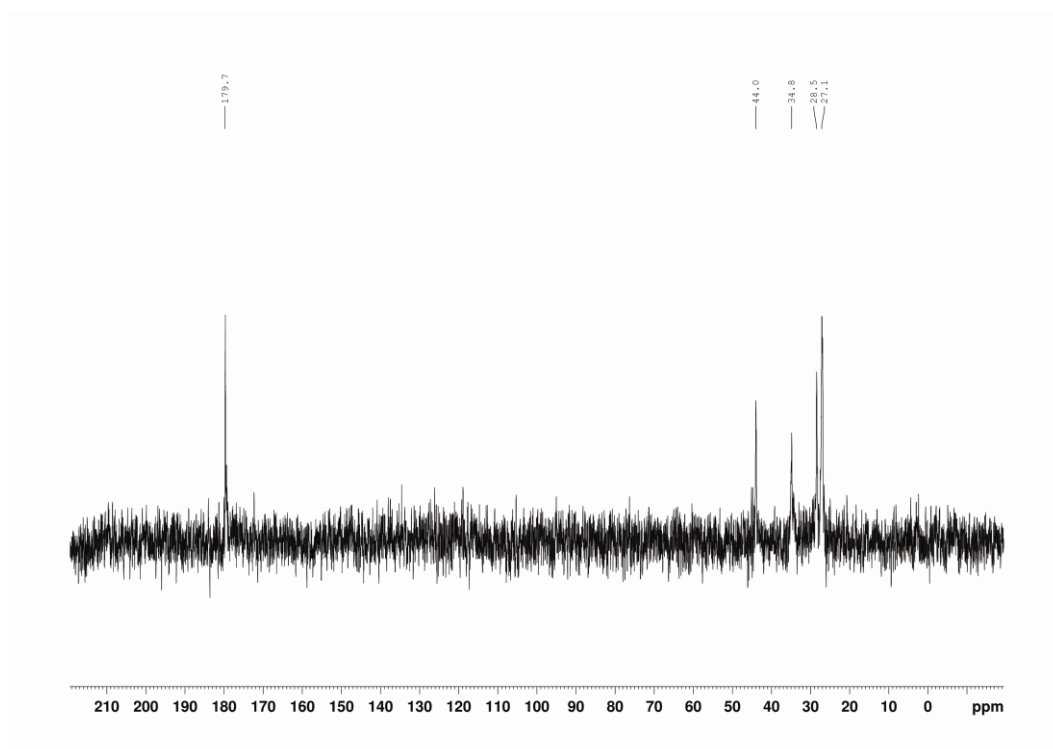


Figure S3. ^{12}C -NMR spectrum of Taulman 910 in DCl (36 wt-% in D_2O).

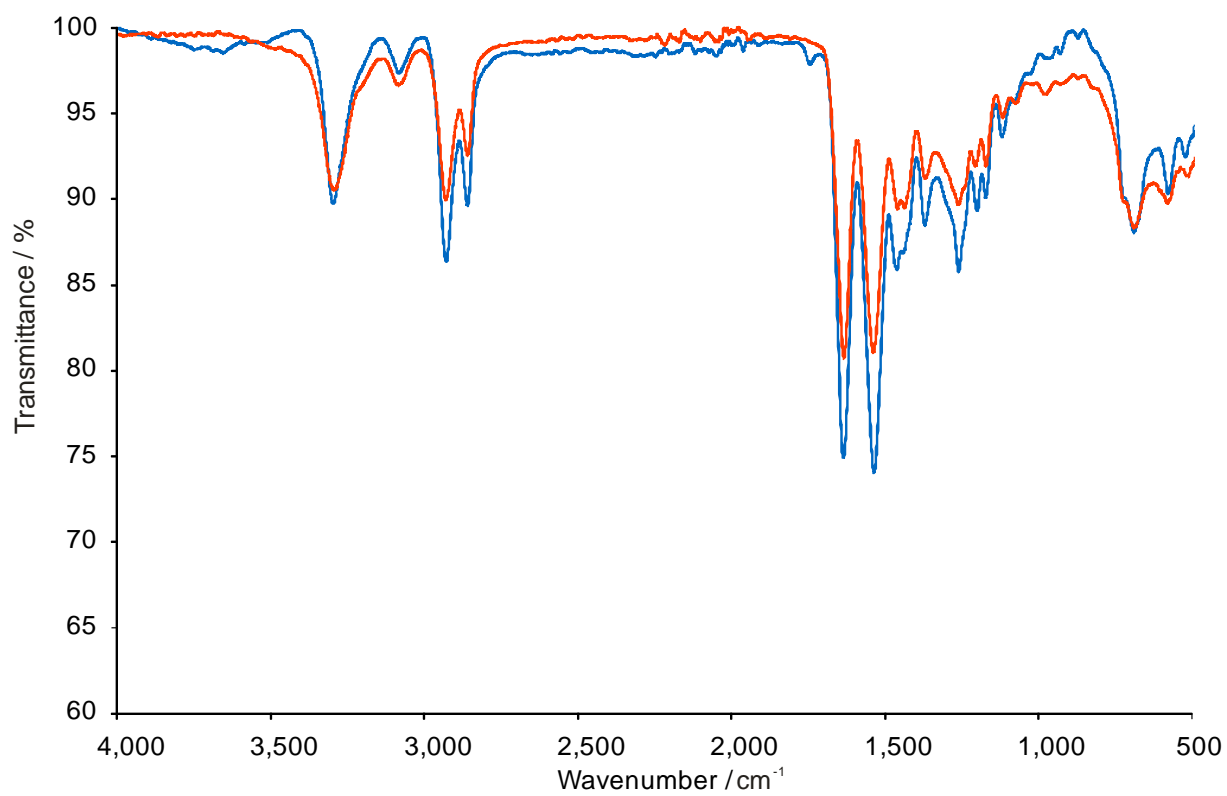


Figure S4. ATR-IR spectra of Taulman 910 before (blue) and after drying (red).

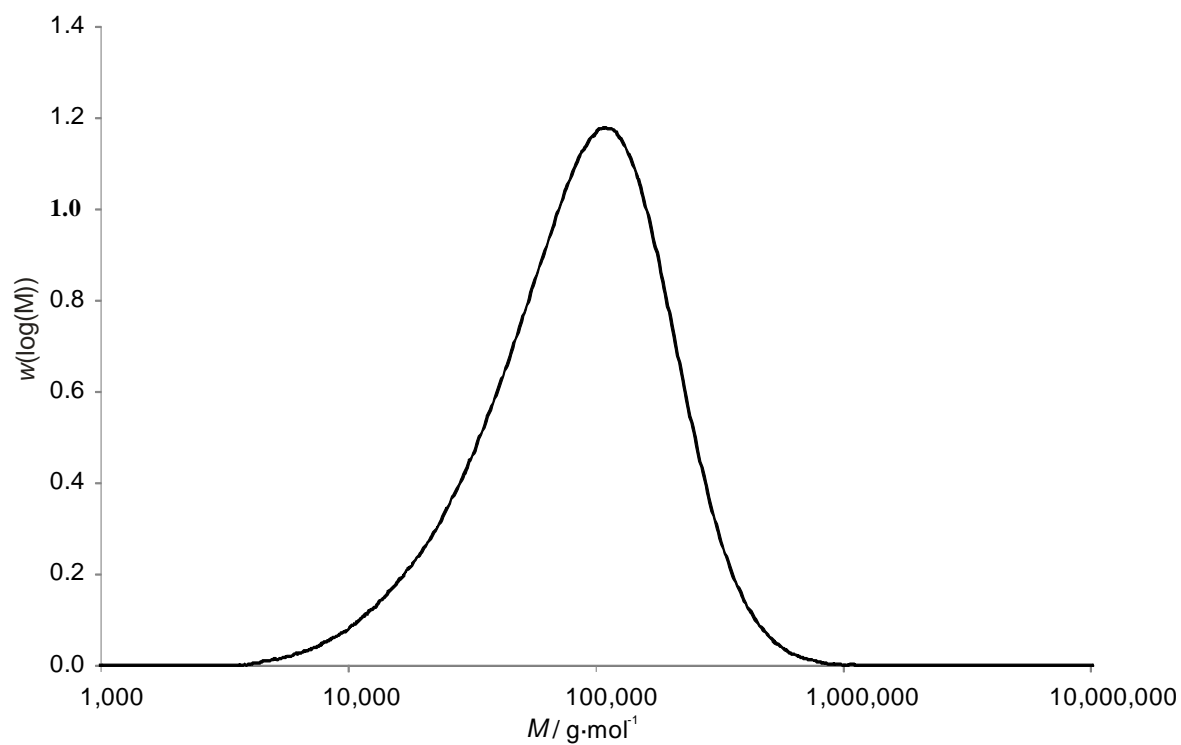


Figure S5. Molecular weight distribution of Taulman 910. SEC calibration relative to PMMA standard. $M_n = 56,000 \text{ g mol}^{-1}$, $M_w = 114,000 \text{ g mol}^{-1}$, $\text{PDI} = 2.02$.

Elemental analysis of Taulman 910 (Nylon Copolymer): **C:** 63.27%, **H:** 9.56%, **N:** 11.71%, **O:** 15.37%.

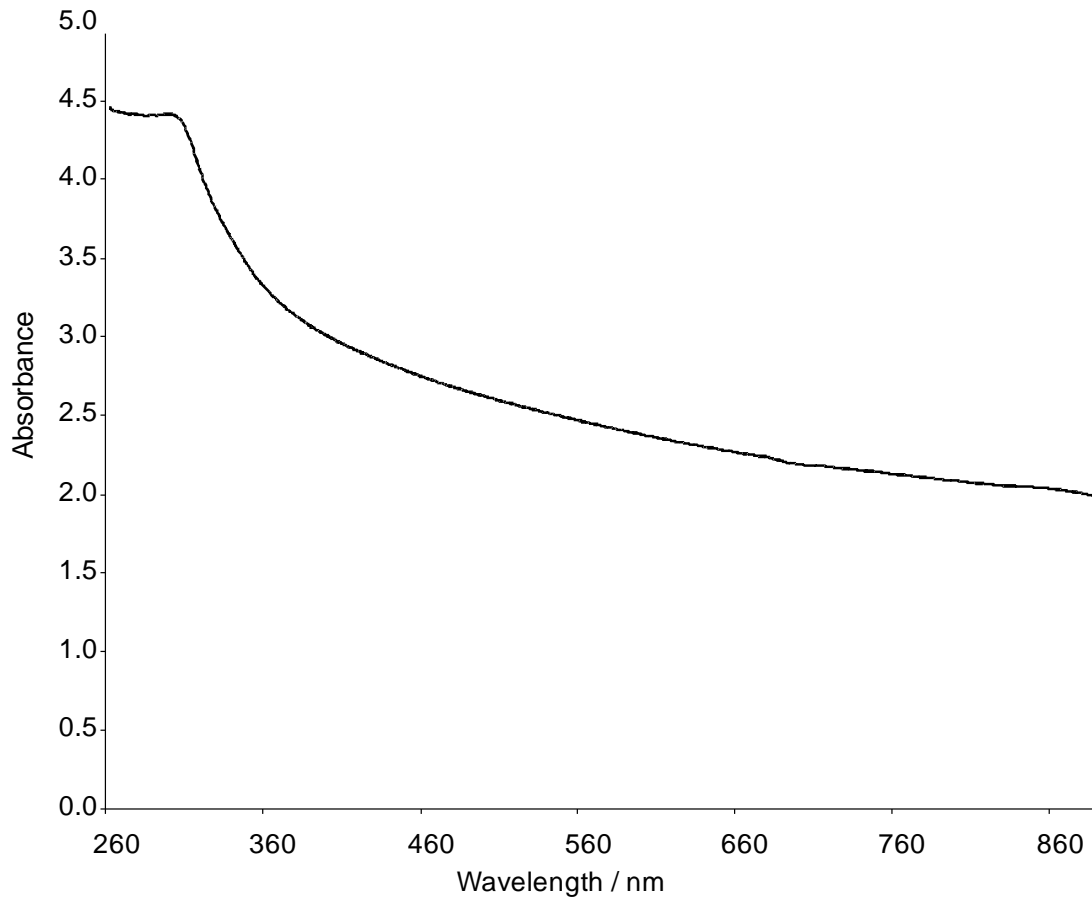


Figure S6. UV/Vis spectrum of Taulman 910 (2 x 1 mm plate) vs air.

2. 3D-Printing

An *UP Plus 2* 3D-printer from *TierTime Technology Co. Ltd. (PP3DP)* was used for all prints without modifications. The printer fits into the standard vacuum chamber of common glove boxes (39 cm diameter) and was evacuated together with all necessary equipment for one night before insertion into the glove box (*M. Braun, Labmaster 130*). The printing platforms were pasted with *ScotchBlue* tape (*3M*) before insertion into the glove box and several platforms kept on stock inside the box. To enable the USB communication with the printer without additional cable connections leading into the glove box, the USB signal was transmitted *via* ethernet (USB over Ethernet Server *UE204, B&B Electronics*) and the ethernet connection was realized by PowerLAN using the power supply of the glove box for electronic devices inside the box. *UP!* Software 2.13 was used for all prints. 3D-models of all reaction vessels and cuvettes were constructed with *SketchUP Make* 15.3.330. Models were checked with *Netfabb basic* 5.2.1.

The platform was levelled before each print and preheated for 15 min at 50 °C. A nozzle with a diameter of 0.4 mm was used. Nozzle temperature was set to 263 °C (273 °C and 268 °C for the first and second layer). Printing was performed with a layer height of 0.15 mm and “fine” printing settings. In deviation from the standard parameters, a hatch width of 0.32, hatch speed of 30, jump speed of 50 and hatch scale of 1.0 was set to obtain solid walls.⁵

These parameters are only valid for a wall thickness of ~ 3 mm and changes may be necessary for other structures and wall thicknesses.

After the print of a reaction vessel was partly completed, printing was paused shortly and the platform moved to the front to insert solvents and reagent. The pause was kept as short as possible (a few seconds). Printing was continued and if necessary further stops for the addition of subsequent reagents were performed.

Reaction vessels were discharged from the box and checked for irregularities. Extreme careful control of printed NMR tube/spinner combinations should be performed to ensure correct fitting inside the NMR spectrometer. Small protruding residues of printing material were removed by fine emery paper and the NMR tube/spinner combination was cleaned with oil-free compressed air. Additionally, the concentricity was checked by inserting the NMR tube/spinner combination into the NMR sample depth gauge. The tube/spinner combinations were inserted into the NMR spectrometer by the standard air lift. Heating was performed in a heating bath of aluminium beads (*LabArmor*) to prevent contamination of the printed cuvettes. Reaction vessels were opened with a saw after completion of the reaction.

The 3D-printing material *Taulman Alloy 910* (Nylon copolymer, *Taulman 3D*, Saint Peters, MO, USA) was bought as 1.75 mm filament and dried two days at 85 °C and left one day in the vacuum chamber before insertion into the glove box.

3. 3D-Printed Cuvettes and Reaction Vessels

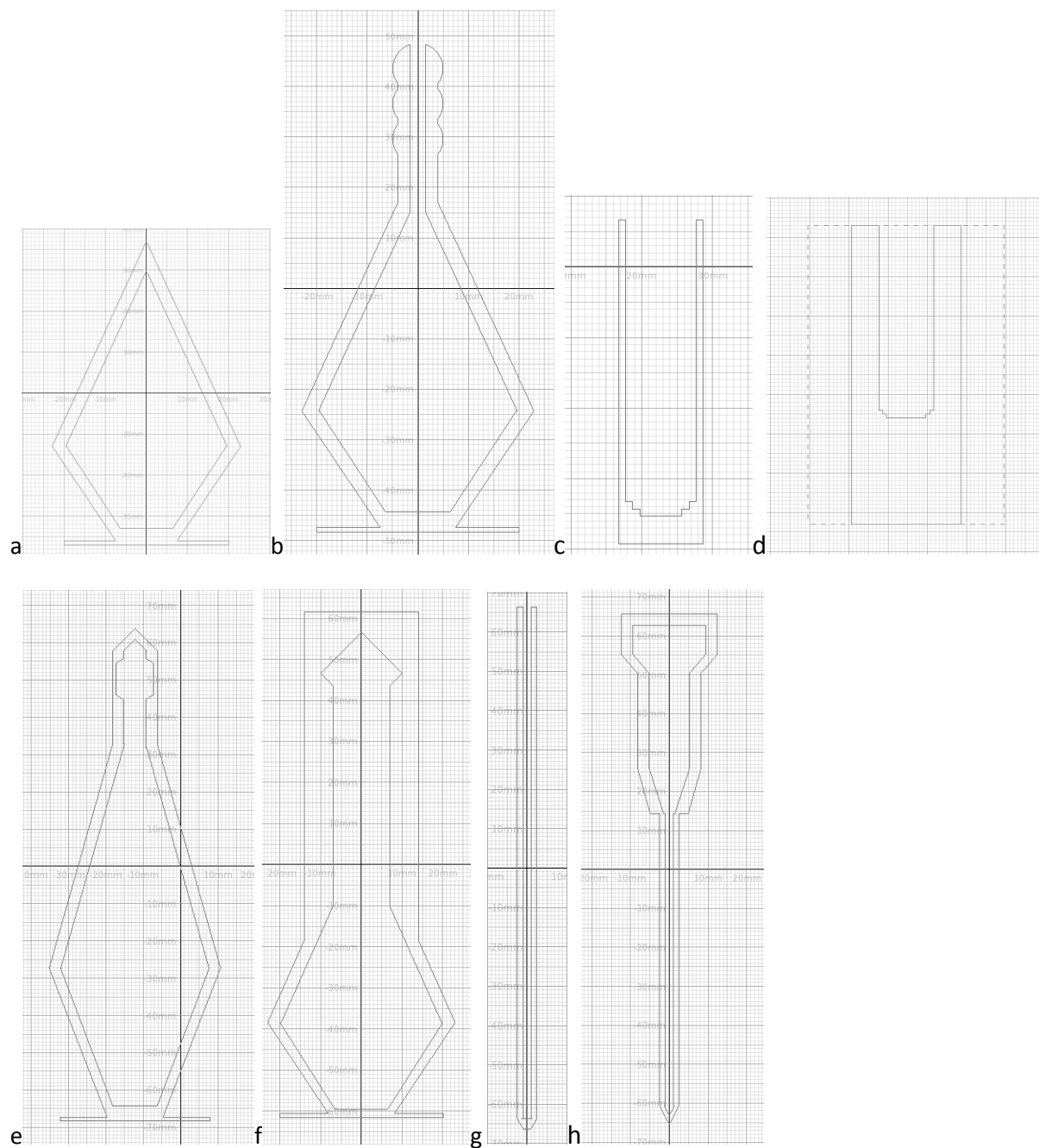


Figure S7. Longitudinal section of 3D-printed objects: a) closed reaction vessel **F1**, b) test vessel with hose nipple **F2**, c) UV cuvette (open) **F3**, d) IR cuvette (open) **F4**, e) reaction vessel with attached UV cuvette (closed) **F5**, f) reaction vessel with attached IR cuvette (closed) **F6**, g) NMR tube (open) **F7**, h) NMR tube/spinner combination **F8**.

4. Test of Analytical Methods

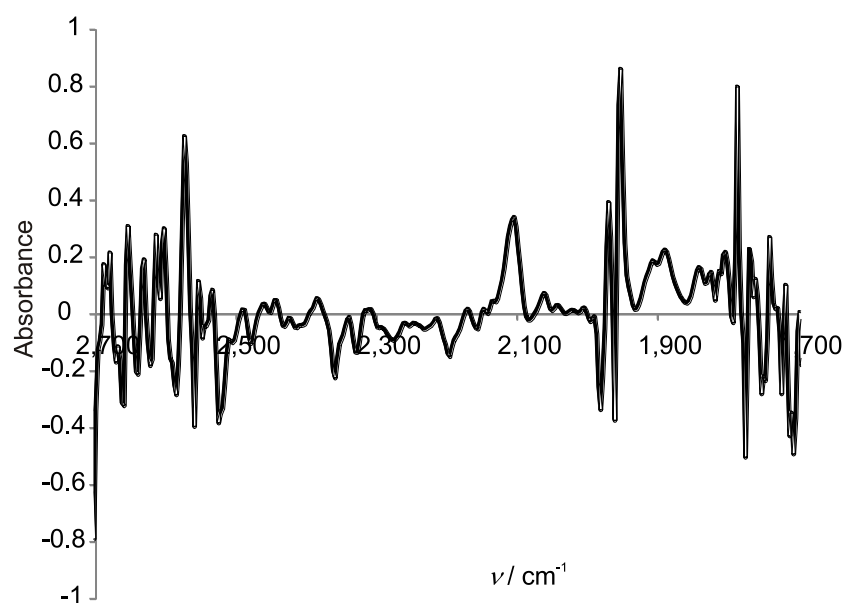


Figure S8. IR spectrum of a solution of phenylacetylene (10 wt-% in THF) vs. THF background in printed IR cuvette **F4**. $\tilde{\nu}_{\text{CC}} = 2110 \text{ cm}^{-1}$.

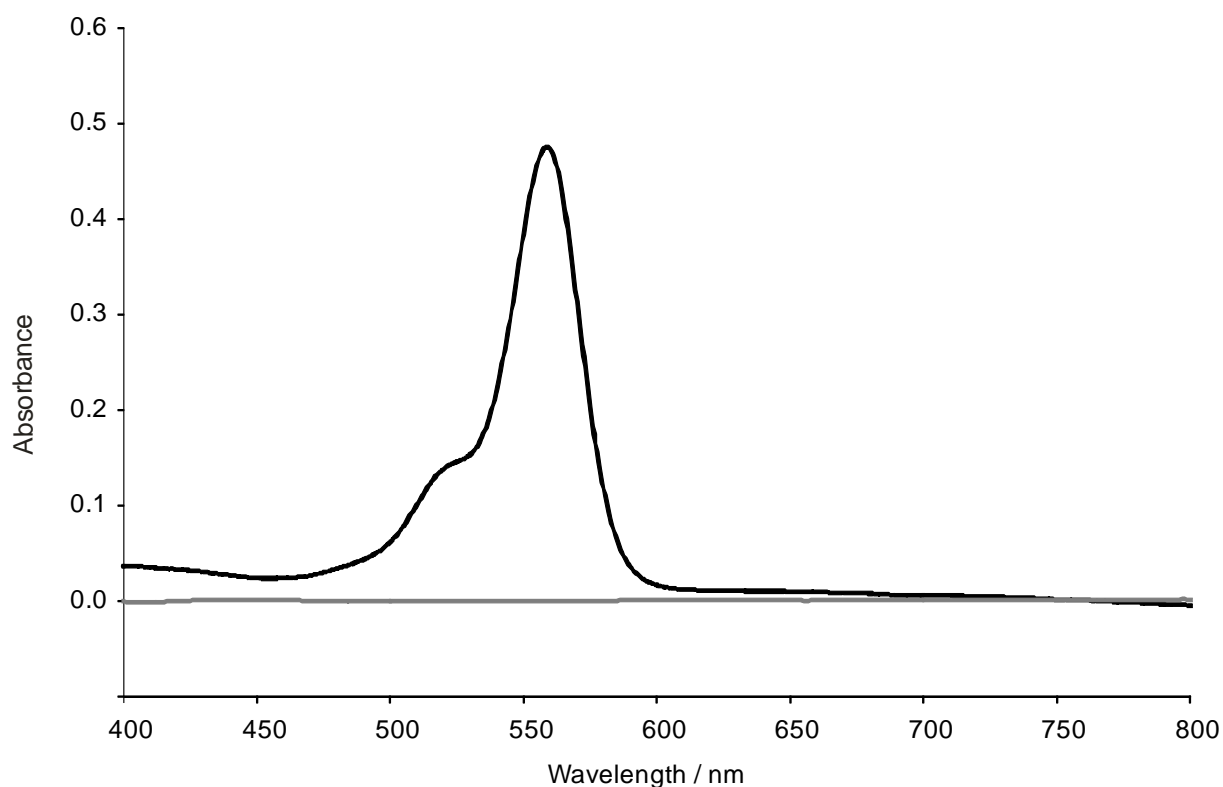


Figure S9. UV/Vis spectra of the printed UV cuvette **F3** (grey) vs. UV cuvette **F3** as background and a 0.01mM solution of rhodamine B in CHCl_3 in cuvette **F3** (black) vs. chloroform background in cuvette **F3**.

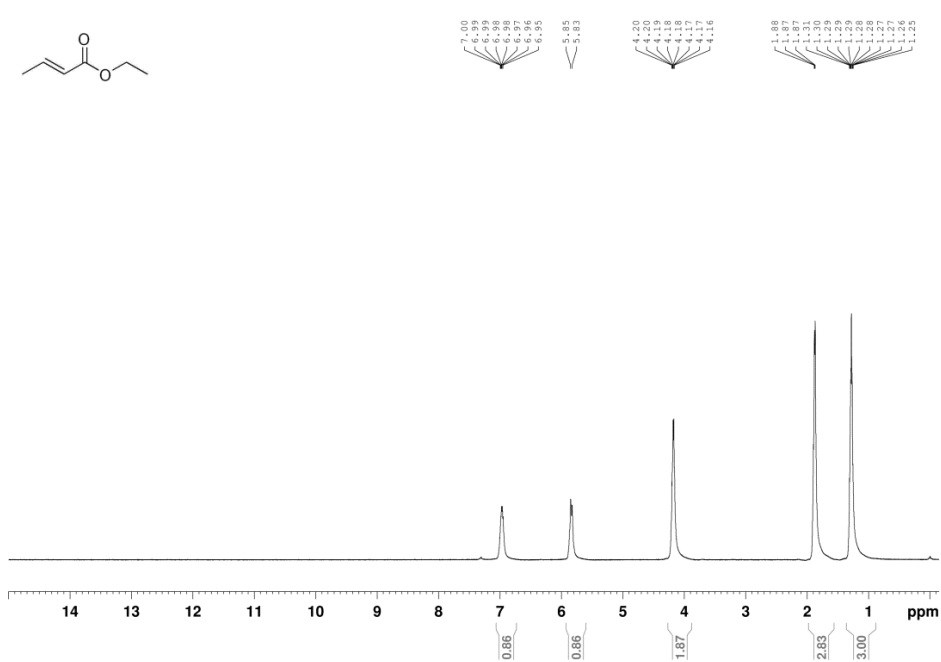


Figure S10. ^1H -NMR spectrum of ethyl crotonate (50 mg) in CDCl_3 measured in printed tube **F7**.

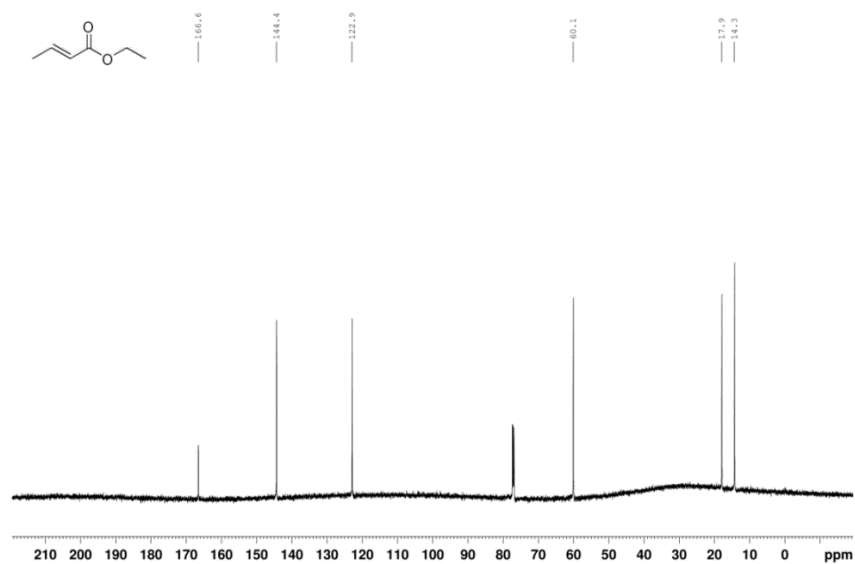


Figure S11. ^{13}C -NMR spectrum of ethyl crotonate (50 mg) in CDCl_3 measured in printed tube **F7**.

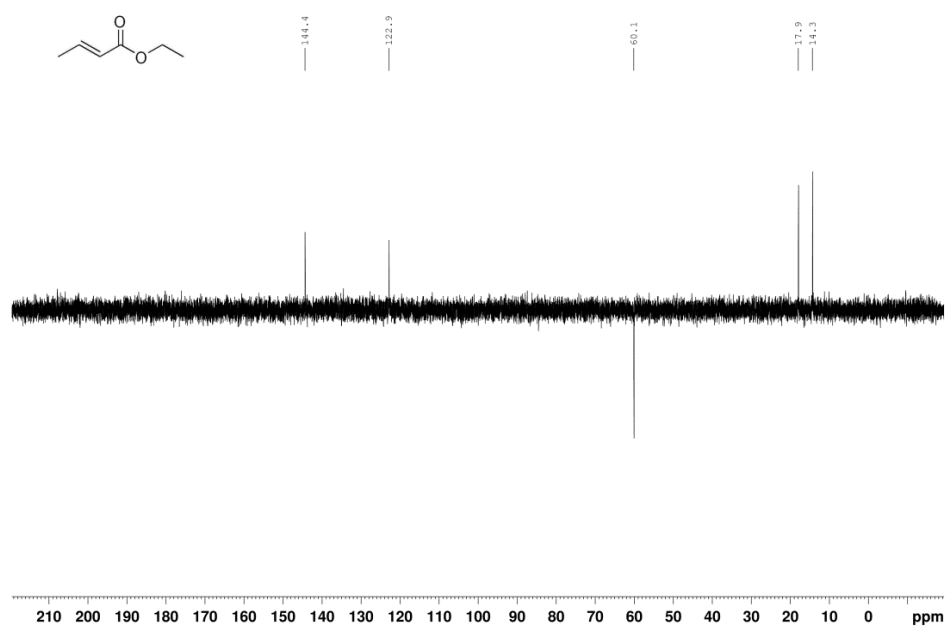


Figure S12. DEPT-135 NMR spectrum of ethyl crotonate (50 mg) in CDCl_3 measured in printed tube F7.

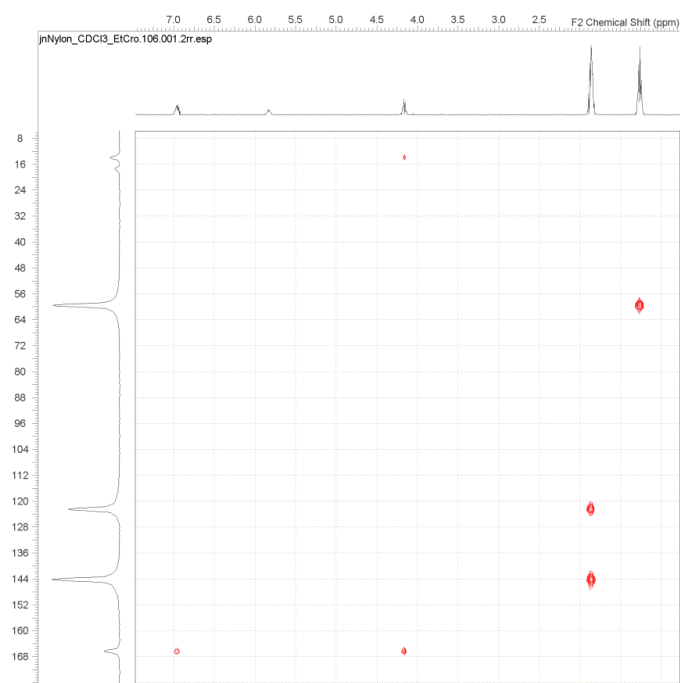


Figure S13. HMBC 2D-NMR spectrum of ethyl crotonate (50 mg) in CDCl_3 measured in printed tube F7.

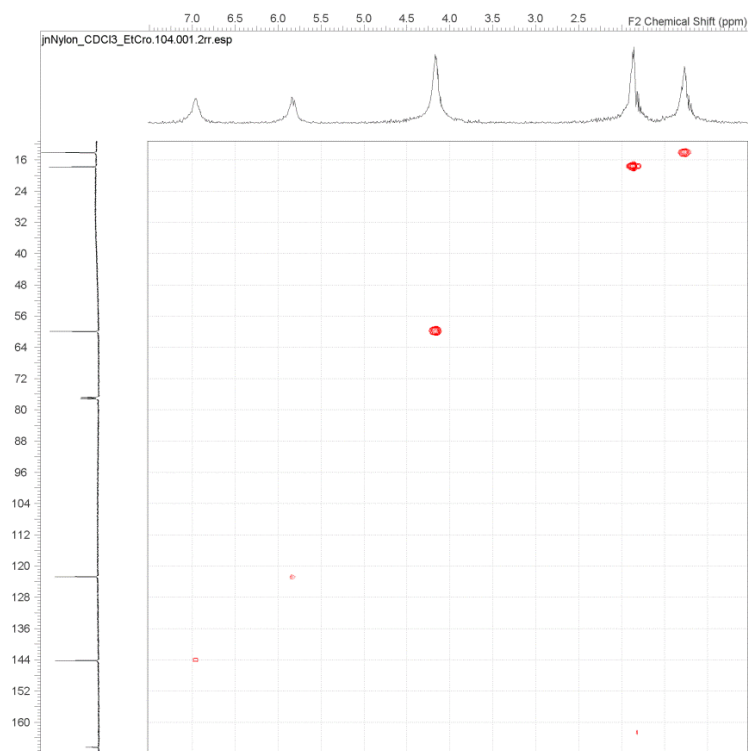


Figure S14. HSQC 2D-NMR spectrum of ethyl crotonate (50 mg) in CDCl_3 measured in printed tube **F7**.

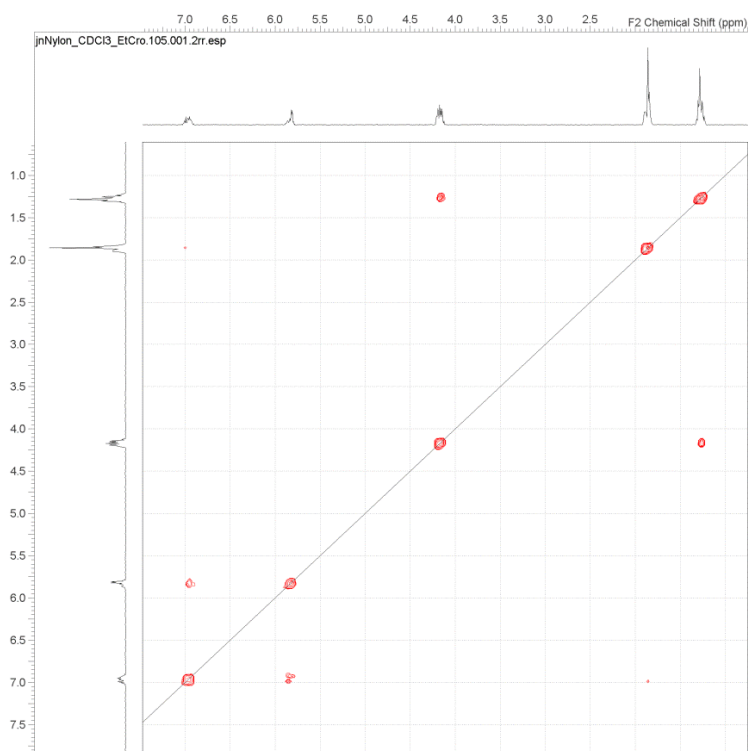


Figure S15. H_1H_2 -COSY 2D-NMR spectrum of ethyl crotonate (50 mg) in CDCl_3 measured in printed tube **F7**.

5. Tests for Impermeability against Oxygen and Water

5.1 Spinner/tube combination F8 with *t*BuLi

A 1.7 M solution of *t*BuLi in pentane (0.7 mL, approx. 1.2 mmol) was transferred into a Schlenk tube equipped with a Teflon stopcock and the pentane was evaporated in high *vacuo*. The Schlenk tube was inserted into the glove box and the solid *t*BuLi (85 mg) was dissolved in dry [D₁₈]octane (1.0 mL, 0.815 g).

The print of the reaction flask **F8** combined with an NMR tube was started inside the glove box with polyamide as printing material. After the print of the spinner section had been completed, the solution of *t*BuLi in [D₁₈]octane was inserted into the spinner *via* a syringe during a short pause of the print. The print was continued until the spinner/tube combination was complete. After finishing the print, flask **F8** was discharged from the glove box and carefully checked for irregularities. An initial ¹³C-NMR spectrum was recorded directly after discharging from the box. The measurement of ¹³C-NMR spectra has been repeated after 1, 4 and 7 days. After 7 days, the flask has been punctured with a hot needle to allow air to enter the spinner and a final ¹³C-NMR spectrum has been recorded. All NMR-spectra have been recorded on the Bruker Avance III 600 spectrometer without spinning the spinner/tube-combination (**F8**). For all acquisitions, a deuterium lock on the [D₁₈]octane signal has been applied. Before each measurement the automatic gradient shimming routine was performed. A flip angle of 30° (¹³C: zgpg30) and a relaxation delay of D1 = 2 s were applied. 256 measurements have been accumulated for each FID. Exponential multiplication with a line broadening (lb) of factor 2 has been applied. Chemical shifts are referenced to the C2-carbon of [D₁₈]octane at 22.0 ppm. Integral values are referenced to the integral of the C1-carbon of [D₁₈]octane at 13.2 ppm.

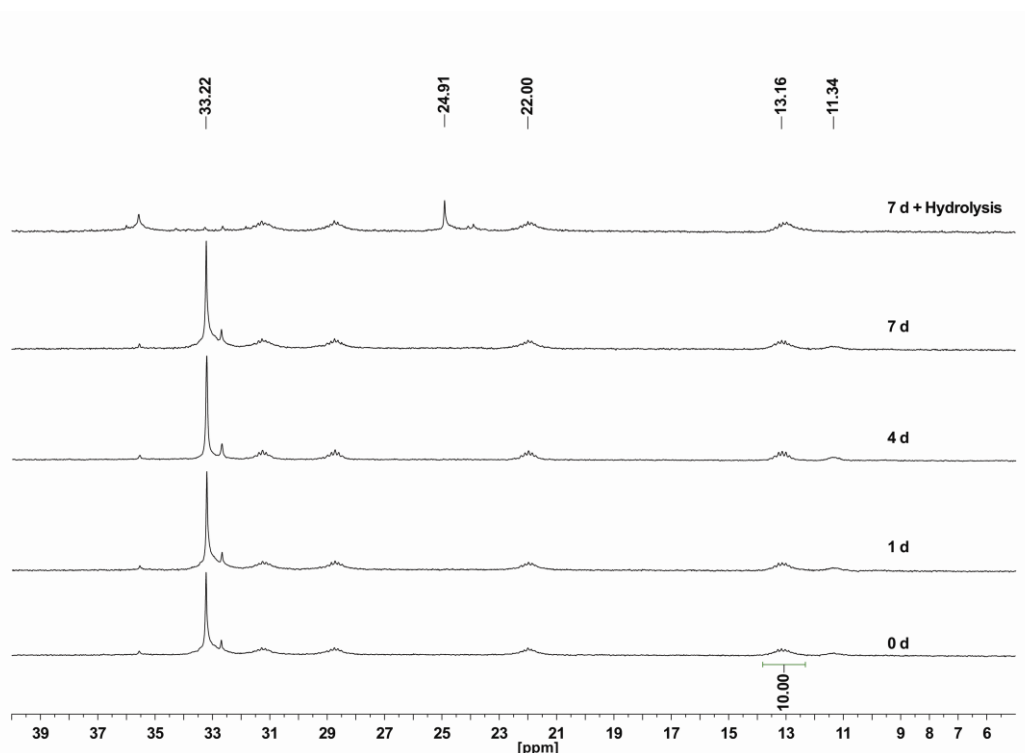


Figure S16. ¹³C-NMR spectra of *t*BuLi in [D₁₈]octane measured in spinner/tube combination **F8** directly after discharging from the glove box, after 1 – 7 days, and after opening of the flask.

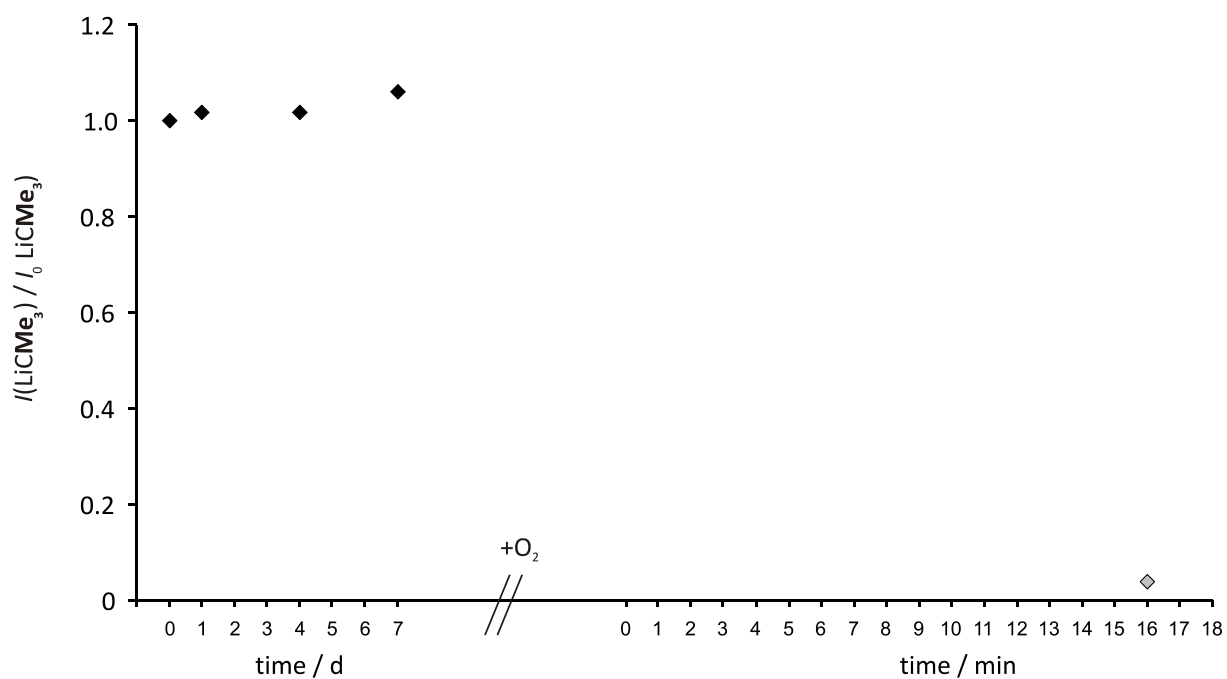


Figure S17. Plot of the integral value (I) of the methyl carbon atoms of $t\text{BuLi}$ / initial integral value (I_0) measured for 7 days after discharging of printed flask **F8** filled with $t\text{BuLi}$ in $[\text{D}_{18}]\text{octane}$ from the glove box (black) and decrease of the integral after puncturing the flask (grey).

5.2 UV cuvette/flask combination F5 with basic pyrogallol solution

The print of the reaction flask combined with an UV/VIS cuvette (**F5**) was started inside the glove box with nylon as printing material. A mixture of pyrogallol (0.377 g, 3.0 mmol) and degassed 1,5-diaminopentane (1.328 g, 13.0 mmol) was dissolved in degassed THF (20.0 mL). Degassed water (0.246 g, 13.7 mmol) was added *via* a syringe and the mixture stirred for 15 min. The solution turned slightly yellow during solvation. As the print of the reaction vessel had nearly completed, 10.0 mL of the solution were transferred into flask **F5** *via* a syringe during a short pause of the 3D-print. After completion of the print, flask **F5** was discharged out of the glove box. UV/Vis spectra were recorded daily after shaking of the reaction vessel and turning flask **F5** upside down. After 10 days, flask **F5** was punctured by a hot needle near the bottom of the turned flask and UV/Vis spectra were recorded approx. every 2 min. The bottle was shaken slightly between the measurements.

For all UV/VIS measurements printed cuvette **F3** filled with deionized water was used as reference cell. Spectra were recorded with a speed of 100 nm min^{-1} (0 – 10 d) or 1000 nm min^{-1} (0 – 24 min). Due to changes in the absorption level in dependence of the exact positioning of flask **F4** all spectra were linearly shifted to an absorption of 0 at 700 nm.

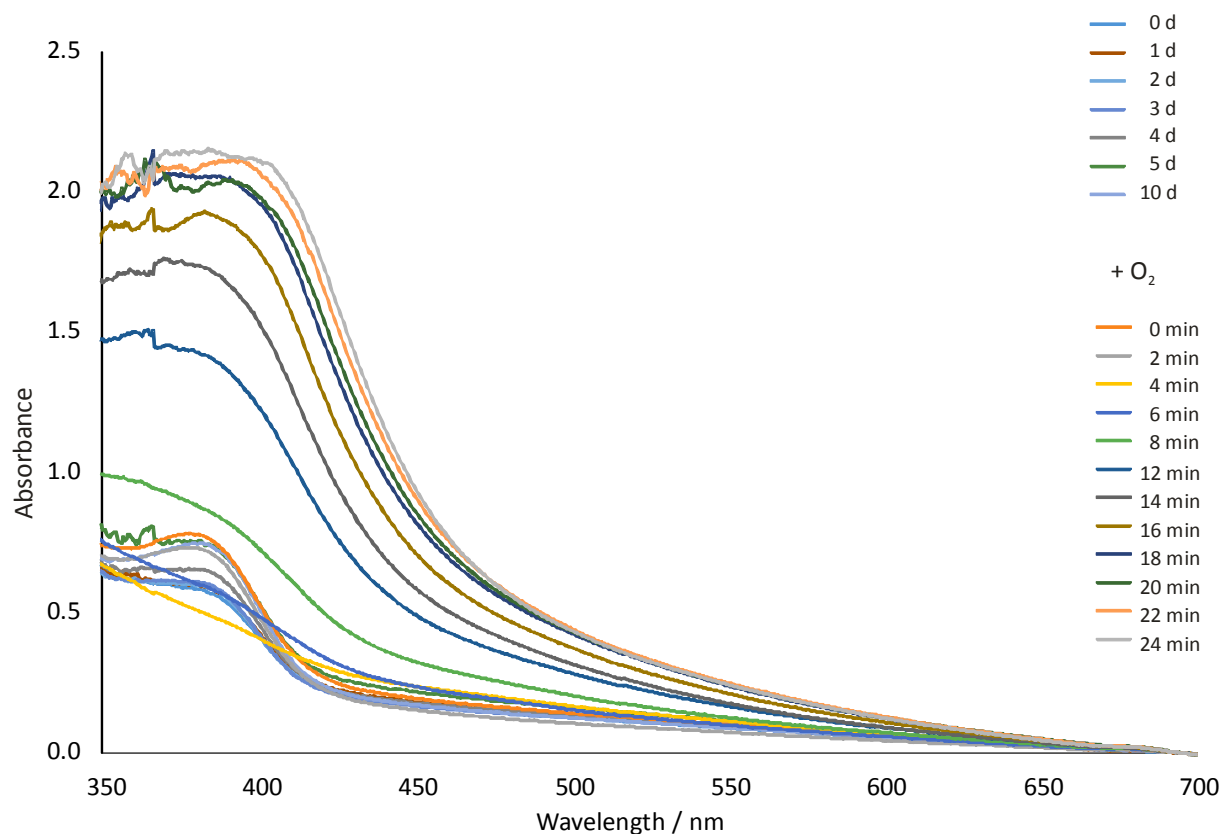


Figure S18. UV/Vis spectra of pyrogallol/diaminopentane in THF measured in flask **F5** directly after discharging from the glove box, after 1 – 10 days, and after opening of the flask.

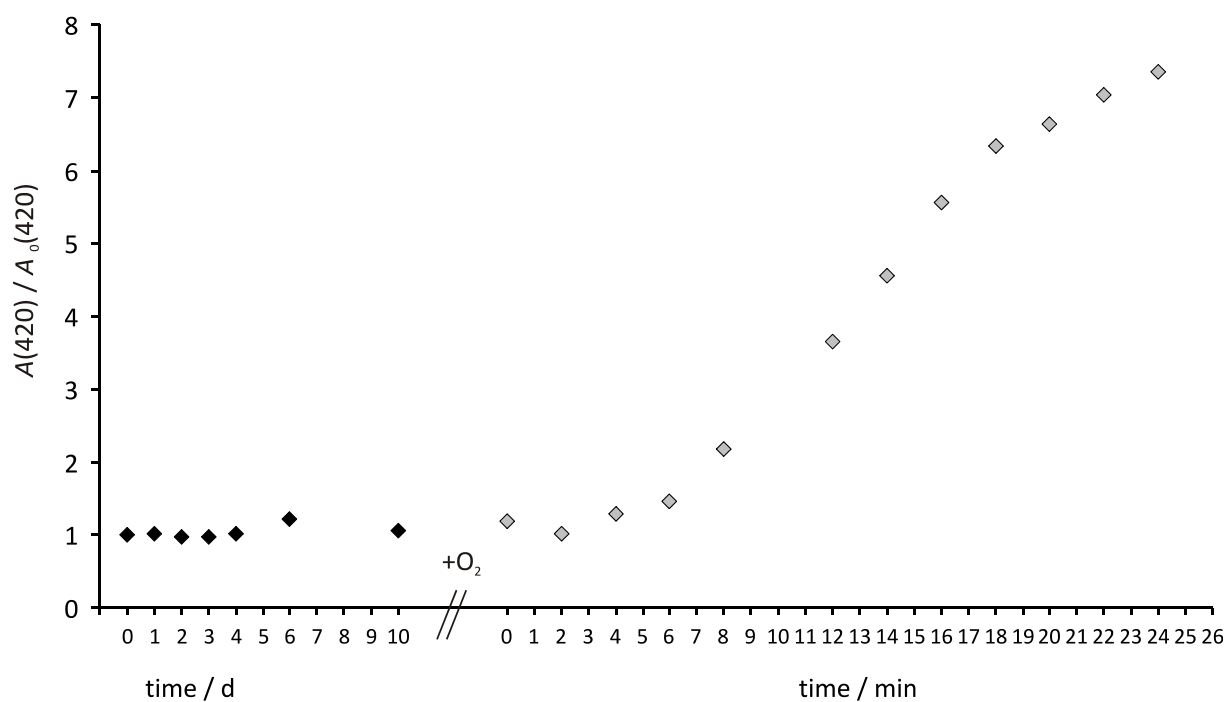
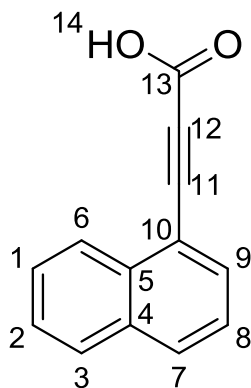


Figure S19. Plot of the absorption (A) at 420 nm / initial absorption (A_0) at 420 nm measured for 10 days after discharging of printed flask **F5** filled with pyrogallol solution from the glove box (black) and immediate increase of the absorption after puncturing the flask (grey).

6. Synthetic Protocols

6.1 3-(Naphthalen-1-yl)propionic acid (1)

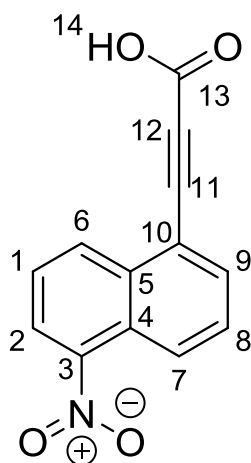
3-(Naphthalene-1-yl)propionic acid (**1**) was synthesized according to literature.⁶



m.p. 129 °C (decomp.); ^1H NMR (600MHz, $[\text{D}_6]\text{DMSO}$, 25°C): δ = 13.95 (b s, 1 H; H-14), 8.22 (dd, $^3J(\text{H,H}) = 8.3$ Hz, $^4J(\text{H,H}) = 1.0$ Hz, 1 H; H-6), 8.14 (d, $^3J(\text{H,H}) = 8.3$ Hz, 1 H; H-7), 8.05 (d, $^3J(\text{H,H}) = 8.1$ Hz, 1 H; H-3), 7.93 (d, $^3J(\text{H,H}) = 7.2$ Hz, 1 H; H-9), 7.73 (dd, $^3J(\text{H,H}) = 8.3$ Hz, $^3J(\text{H,H}) = 6.9$ Hz, 1 H; H-1), 7.65 (ddd, $^3J(\text{H,H}) = 8.1$ Hz, $^3J(\text{H,H}) = 6.9$ Hz, $^4J(\text{H,H}) = 1.0$ Hz, 1 H; H-2), 7.59 ppm (dd, $^3J(\text{H,H}) = 8.3$ Hz, $^3J(\text{H,H}) = 7.2$ Hz, 1 H; H-8); ^{13}C NMR (150 MHz, $[\text{D}_6]\text{DMSO}$, 25°C): δ = 154.3 (q, 1 C; C-13), 132.9 (+, 1 C; C-9); 132.8 (q, 1 C; C-5); 132.7 (q, 1 C; C-4); 131.4 (+, 1 C; C-7); 128.8 (+, 1 C; C-3); 128.1 (+, 1 C; C-1); 127.2 (+, 1 C; C-2); 125.6 (+, 1 C; C-8); 124.8 (+, 1 C; C-6); 116.3 (q, 1 C; C-10); 86.5 (q, 1 C; C-12); 82.4 ppm (q, 1 C; C-11); IR (ATR): $\tilde{\nu}$ = 2956-2803 (wb, COOH), 2666-2507 (w), 2198 (s, C \equiv C), 1667 (s, C=O), 1296 (s), 1261 (s), 1221 (s), 1209 (s), 796 (s), 766 (s), 746 (s), 612 (s), 602 (s), 563 (s), 439 cm^{-1} (s); MS-ESI⁻ (30 eV): m/z (%): 320.9 (8) [$2M^- - 2H - C\equiv C - CO_2H$], 196.1 (12) [M^-], 195.1 (28) [$M^- - H$], 152.1 (14) [$M^- - CO_2$], 151.1 (100) [$M^- - CO_2H$], 149.1 (67) [$M^- - H - CO_2H$].

6.2 3-(5-Nitronaphthalen-1-yl)propionic acid (**2**)

The synthetic protocol is based on the synthesis of 3-(naphthalen-1-yl)propionic acid (**1**).⁶



All operations have been performed inside a glove box. A solution of propionic acid (2.40 mL, 2.700 g, 38.5 mmol) in dry DMSO (21 mL) was prepared. A second flask equipped with Teflon stopcock was filled with Pd(PPh₃)₄ (2.022 g, 1.8 mmol). A solution of 1-bromo-5-nitronaphthalene (8.823 g, 35.0 mmol) and DBU (11.5 mL, 11.722 g, 77.0 mmol) in dry DMSO (50 mL) was added to the palladium catalyst. The solution of propionic acid in DMSO was added to the yellow suspension of the catalyst. The flask was discharged from the glove box and the mixture was stirred at 30 °C for 24 h. Subsequently, the suspension was poured into ethyl acetate (175 mL) and the organic phase was extracted with aqueous NaHCO₃ solution (3 x 150 mL). The combined aqueous phases were acidified with cold 1 M HCl to pH = 2 and extracted with CH₂Cl₂ (3 x 100 mL). The combined DCM phases were dried with MgSO₄ and the solvent removed at reduced pressure. The

resulting brown oil was purified by column chromatography (Pe:EE:HOAc, 4:1:0.05 (v/v/v), *R_f*=0.18) and after removal of the solvent, **2** was received as slightly brown solid. Yield: 1.283 g (15%).

m.p. 154 °C (decomp.); ¹H NMR (600MHz, [D₆]DMSO, 25°C): δ = 14.13 (b s, 1 H; H-14), 8.61 (ddd, ³*J* (H,H) = 8.4 Hz, ⁴*J* (H,H) = 1.2 Hz, ⁵*J* (H,H) = 1.0 Hz, 1 H; H-6), 8.48 (ddd, ³*J* (H,H) = 8.8 Hz, ⁴*J* (H,H) = 0.9 Hz, ⁵*J* (H,H) = 1.0 Hz, 1 H; H-7), 8.42 (dd, ³*J* (H,H) = 7.7 Hz, ⁴*J* (H,H) = 1.2 Hz, 1 H; H-2), 8.13 (dd, ³*J* (H,H) = 7.2 Hz, ⁴*J* (H,H) = 0.9 Hz, 1 H; H-9), 7.92 (dd, ³*J* (H,H) = 8.4 Hz, ³*J* (H,H) = 7.7 Hz, 1 H; H-1), 7.86 (dd, ³*J* (H,H) = 8.8 Hz, ³*J* (H,H) = 7.2 Hz, 1 H; H-8); ¹³C NMR (150 MHz, [D₆]DMSO, 25°C): δ = 154.0 (+, 1 C; C-13), 146.9 (q, 1 C; C-3), 134.1 (+, 1 C; C-9), 133.3 (q, 1 C; C-5), 131.3 (+, 1 C; C-6), 129.0 (+, 1 C; C-8), 127.0 (+, 1 C; C-1), 125.4 (+, 1 C; C-7), 124.9 (+, 1 C; C-2), 124.0 (q, 1 C; C-4), 117.6 (q, 1 C; C-10), 87.4 (q, 1 C; C-12), 81.0 ppm (q, 1 C; C-11); IR (ATR): $\tilde{\nu}$ = 2840-2550 (wb, COOH), 2203-2199 (s, C≡C), 1692 (s, C=O), 1599 (m), 1519 (s), 1462 (m), 1327 (s), 1280 (s), 1232 (s), 872 (m), 813 (m), 785 (s), 738 (s), 620 cm⁻¹ (s); MS-ESI⁻ (30 eV): *m/z* (%): 482.0 (5) [2*M*], 481.0 (19) [2*M*-H], 437.0 (5) [2*M*-CO₂H], 240.1 (12) [*M*-H], 197.1 (17) [*M*-CO₂], 196.1 (100) [*M*-CO₂H], 149.1 (11) [*M*-NO₂-CO₂H-2H]; HRMS-EI⁺ *m/z*: calcd. for C₁₃H₆NO₄ [*M*] 240.0297; found, 240.0297.

6.3 General procedure for the synthesis of Bis(aryl)alkynes in tube/spinner combination F8

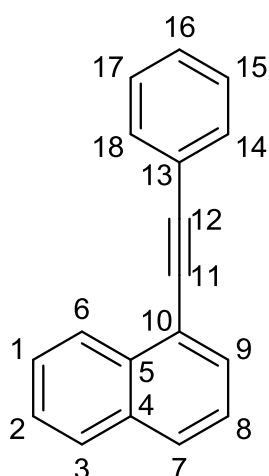
The synthetic protocol is based on a protocol for the palladium-catalyzed decarboxylative coupling of arylpropionic acids with aryl halides.⁷

On a small weighing boat, 1 eq. of the appropriate 3-(naphthalene-1-yl)propionic acid, 1 eq. dry Cs_2CO_3 , 1 mol-% $\text{Pd}(\text{OAc})_2$ and 2 mol-% X-Phos were weighed in with a balance installed in the glove box and mixed thoroughly. In a small flask, a solution of 0.85 eq. of the appropriate dry aryl halide in dry $[\text{D}_8]\text{THF}$ (40 eq.) was prepared separately.

The print of the reaction flask **F8** combined with an NMR-tube was started inside the glove box with polyamide as printing material. After half of the print of the spinner section had been completed, the solid mixture prepared before was inserted during a short first pause of the print. The print was continued, until the spinner had been printed completely. The solution of the aryl halide in $[\text{D}_8]\text{THF}$ was inserted into the spinner *via* a syringe during a second short pause of the print. The print was continued until the spinner/tube combination was complete. After finishing the print, flask **F8** was discharged from the glove box and carefully checked for irregularities. An initial ^{13}C -NMR spectrum was recorded directly after discharging from the box. The tube/spinner combination was heated with an aluminium bead bath (*LabArmor*) at 90 °C (bead bath temperature). Regularly, the tube/spinner combination was cooled down and subsequent ^{13}C -NMR spectra were recorded. If necessary, the bead bath temperature was increased to 100 °C. After completion of the reaction, the spinner/tube combination was opened and the dark brown suspension collected in a small flask. The spinner/tube combination was rinsed with diethyl ether (3 x 2.5 mL) and brine (3 x 2.5 mL). The combined solutions were phase-separated in a separating funnel and the aqueous phase extracted with diethyl ether (3 x 5 mL). The combined organic phases were dried with Na_2SO_4 and the solvents were removed at reduced pressure. The remaining dark brown oil was purified by column chromatography.

All ^{13}C -NMR spectra have been recorded on the *Bruker Avance III 600* spectrometer without spinning the spinner/tube-combination (**F8**). For all acquisitions a deuterium lock on the $[\text{D}_8]\text{THF}$ signal has been applied. Before each measurement the automatic shimming routine was performed. A flip angle of 30° (^{13}C : zgpg30) and a relaxation delay of $\text{D1} = 2$ s were applied. 256 measurements have been accumulated for each FID. Exponential multiplication with a line broadening (lb) of factor 2 has been applied. Chemical shifts and integral values are referenced to the α -carbon of $[\text{D}_8]\text{THF}$ at 67.2 ppm.

6.4.1 1-(Phenylethynyl)naphthalene (**3**)

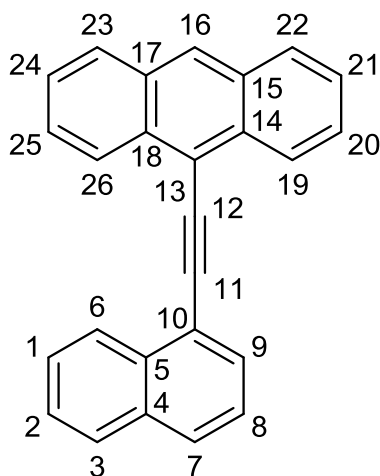


Following the general procedure **6.3**, 3-(naphthalene-1-yl)propionic acid (0.230 g, 1.17 mmol) and bromobenzene (102 μ L, 0.153 g, 0.98 mmol) were used. **3** was received as yellow oil after column chromatography (PE:EE, 20:1 (v/v), R_f =0.67) and removal of the solvent at reduced pressure. Yield: 0.196 g (88%).

^1H NMR (600MHz, $[\text{D}_8]\text{THF}$, 25°C): δ = 8.43 (ddd, $^3J(\text{H,H})$ = 8.3 Hz, $^4J(\text{H,H})$ = 1.6 Hz, $^5J(\text{H,H})$ = 1.0 Hz, 1 H; H-6), 7.89 (dd, $^3J(\text{H,H})$ = 8.7 Hz, $^4J(\text{H,H})$ = 1.1 Hz, 1 H; H-3), 7.88 (ddd, $^3J(\text{H,H})$ = 8.8 Hz, $^4J(\text{H,H})$ = 1.0 Hz, $^5J(\text{H,H})$ = 1.0 Hz, 1 H; H-7), 7.74 (dd, $^3J(\text{H,H})$ = 7.1 Hz, $^4J(\text{H,H})$ = 1.0 Hz, 1 H; H-9), 7.64 (m, 2 H, H-14, H-18), 7.59 (ddd, $^3J(\text{H,H})$ = 8.3 Hz, $^3J(\text{H,H})$ = 6.9 Hz, $^4J(\text{H,H})$ = 1.1 Hz, 1 H; H-1), 7.53 (ddd, $^3J(\text{H,H})$ = 8.7 Hz, $^3J(\text{H,H})$ = 6.9 Hz, $^4J(\text{H,H})$ = 1.6 Hz, 1 H; H-2), 7.47 (dd, $^3J(\text{H,H})$ = 8.8 Hz, $^3J(\text{H,H})$ = 7.1 Hz, 1 H; H-8), 7.41–7.35 ppm (m, 3 H, H-15–H-17); ^{13}C NMR (150 MHz, $[\text{D}_8]\text{THF}$, 25°C): δ = 134.2 (q, 1 C; C-4), 134.0 (q, 1 C; C-5), 132.2 (+, 2 C; C-14, C-18), 130.9 (+, 1 C; C-9), 129.5 (+, 1 C; C-7), 129.1 (+, 2 C; C-15, C-17), 129.1 (+, 1 C; C-16), 129.0 (+, 1 C; C-3), 127.4 (+, 1 C; C-1), 127.1 (+, 1 C; C-2), 126.7 (+, 1 C; C-6), 125.9 (+, 1 C; C-8), 124.20 (q, 1 C; C-13), 121.6 (q, 1 C; C-10), 94.9 (q, 1C; C-12), 88.0 ppm (q, 1 C; C-11); IR (ATR): $\tilde{\nu}$ = 3055 (w, =C-H), 2955–2853 (w, =C-H), 2212 (w, C \equiv C), 1597 (w), 1506 (w), 1506 (m), 1442 (m), 1396 (m), 797 (s), 770 (s), 752 (s), 566 (m), 553 (m), 433 cm^{-1} (m); MS-EI $^+$ (50 eV): m/z (%): 228.2 (100) [M^+], 227.2 (46) [$M^+ - \text{H}$], 226.2 (23) [$M^+ - 2\text{H}$]; UV/Vis (toluene): λ_{max} (ϵ) = 339 (16035), 318 nm (18946 $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$).

The experimental data are in accordance with data given in literature.^{8,9}

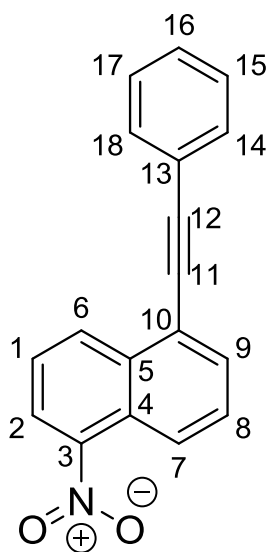
6.4.2 9-(Naphthalen-1-ylethynyl)anthracene (**4**)



Following the general procedure **6.3**, 3-(naphthalene-1-yl)propionic acid (0.230 g, 1.17 mmol) and 9-bromoanthracene (0.251 g, 0.98 mmol) were used. **4** was received as bright yellow powder after column chromatography (PE:EE, 20:1 (v/v), R_f =0.85) and removal of the solvent at reduced pressure. Yield: 0.314 g (98%).

m.p.: 170 °C; ^1H NMR (600MHz, $[\text{D}_8]\text{THF}$, 25°C): δ = 8.79 (ddd, $^3J(\text{H,H})$ = 8.7 Hz, $^4J(\text{H,H})$ = 1.5 Hz, $^5J(\text{H,H})$ = 0.8 Hz, 2 H; H-19, H-26), 8.69 (ddd, $^3J(\text{H,H})$ = 8.3 Hz, $^4J(\text{H,H})$ = 1.6 Hz, $^5J(\text{H,H})$ = 0.9 Hz, 1 H; H-6), 8.58 (b s, 1 H; H-16), 8.10 (ddd, $^3J(\text{H,H})$ = 8.5 Hz, $^4J(\text{H,H})$ = 1.2 Hz, $^5J(\text{H,H})$ = 0.8 Hz, 2 H; H-22, H-23), 8.04 (dd, $^3J(\text{H,H})$ = 7.0 Hz, $^4J(\text{H,H})$ = 1.0 Hz, 1 H; H-9), 7.97 (m, 2 H; H-3, H-7), 7.68 (ddd, $^3J(\text{H,H})$ = 8.3 Hz, $^3J(\text{H,H})$ = 6.3 Hz, $^4J(\text{H,H})$ = 1.9 Hz, 1 H; H-1), 7.65 (ddd, $^3J(\text{H,H})$ = 8.7 Hz, $^3J(\text{H,H})$ = 6.5 Hz, $^4J(\text{H,H})$ = 1.2 Hz, 2 H; H-20 H-25), 7.59 (ddd, $^3J(\text{H,H})$ = 9.0 Hz, $^3J(\text{H,H})$ = 6.3 Hz, $^4J(\text{H,H})$ = 1.6 Hz, 1 H; H-2), 7.58 (dd, $^3J(\text{H,H})$ = 7.0 Hz, $^3J(\text{H,H})$ = 8.3 Hz, 1 H; H-8), 7.55 ppm (ddd, $^3J(\text{H,H})$ = 8.5 Hz, $^3J(\text{H,H})$ = 6.5 Hz, $^4J(\text{H,H})$ = 1.5 Hz, 2 H; H-21, H-24); ^{13}C NMR (150 MHz, $[\text{D}_8]\text{THF}$, 25°C): δ = 134.4 (q, 1 C; C-4), 134.0 (q, 1 C; C-5), 133.5 (q, 2 C; C-14, C-18), 132.2 (q, 2 C; C-15, C-17), 131.4 (+, 1 C; C-9), 129.8 (+, 1 C; C-7), 129.5 (+, 2 C; C-22, C-23), 129.2 (+, 1 C; C-3), 128.73 (+, 1 C; C-16), 127.7 (+, 1 C; C-1), 127.53 (+, 2 C; C-20, C-25), 127.24 (+, 2 C; C-19, C-26), 127.2 (+, 1 C; C-2), 126.8 (+, 1 C; C-6), 126.4 (+, 1 C; C-21, C-24), 126.1 (+, 1 C; C-8), 121.9 (q, 1 C; C-10), 117.8 (q, 1 C; C-13), 99.6 (q, 1 C; C-11), 91.6 ppm (q, 1 C; C-12); IR (ATR): $\tilde{\nu}$ = 3042 (w, =C-H), 2957–2852 (w, =C-H), 1620 (w), 1574 (w), 1417 (w), 1394 (w), 1014 (w), 890 (m), 842 (w), 793 (s), 784 (m), 771 (s), 734 (s), 615 (m), 551 (s), 414 cm^{-1} (s); MS-EI $^+$ (20 eV): m/z (%): 328.2 (100) [M^+]; HRMS-EI $^+$ m/z : calcd. for $\text{C}_{26}\text{H}_{16}$ [M^+] 328.1252; found, 328.1252; UV/Vis (toluene): λ_{max} (ϵ) = 429 (13200), 409 nm (16800 $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$).

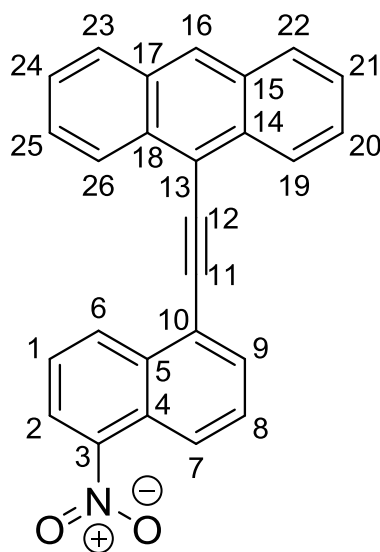
6.4.3 1-Nitro-5-(phenylethynyl)naphthalene (5)



Following the general procedure **6.3**, 3-(5-nitronaphthalene-1-yl)propionic acid (0.170 g, 0.71 mmol) and bromobenzene (61 μ L, 0.092 g, 0.59 mmol) were used. **5** was received as light red oily solid after column chromatography (PE:EE, 20:1 (v/v), R_f =0.34) and removal of the solvent at reduced pressure. Yield: 0.029 g (18%).

^1H NMR (600MHz, $[\text{D}_8]\text{THF}$, 25°C): δ = 8.82 (ddd, $^3J(\text{H,H}) = 7.9$ Hz, $^4J(\text{H,H}) = 1.1$ Hz, $^5J(\text{H,H}) = 0.9$ Hz, 1 H; H-6), 8.46 (ddd, $^3J(\text{H,H}) = 8.1$ Hz, $^4J(\text{H,H}) = 0.9$ Hz, $^5J(\text{H,H}) = 0.9$ Hz, 1 H; H-7), 8.28 (dd, $^3J(\text{H,H}) = 6.7$ Hz, $^4J(\text{H,H}) = 1.1$ Hz, 1 H; H-2), 7.92 (dd, $^3J(\text{H,H}) = 6.7$ Hz, $^4J(\text{H,H}) = 0.9$ Hz, 1 H; H-9), 7.75 (dd, $^3J(\text{H,H}) = 7.9$ Hz, $^3J(\text{H,H}) = 6.7$ Hz, 1 H; H-1), 7.74 (dd, $^3J(\text{H,H}) = 8.1$ Hz, $^3J(\text{H,H}) = 6.7$ Hz, 1 H; H-8), 7.67–7.65 (m, 2 H; H-14, H-18), 7.43–7.41 ppm (m, 3 H; H-15–H-17); ^{13}C NMR (150 MHz, $[\text{D}_8]\text{THF}$, 25°C): δ = 148.3 (q, 1 C; C-3), 134.7 (q, 1 C; C-5), 132.8 (+, 1 C; C-6), 132.3 (+, 2 C; C-14, C-18), 132.3 (+, 1 C; C-9), 129.6 (+, 1 C; C-16), 129.3 (+, 1 C; C-8), 129.2 (+, 2 C; C-15, C-17), 126.1 (+, 1 C; C-1), 125.8 (q, 1 C; C-4), 124.8 (+, 1 C; C-2), 124.1 (+, 1 C; C-7), 123.6 (q, 1 C; C-13), 122.6 (q, 1 C; C-10), 96.4 (q, 1 C; C-12), 86.9 ppm (q, 1 C; C-11); IR (ATR): $\tilde{\nu}$ = 3077–3022 (w, =C-H), 2957–2864 (m), 2219–2197(w; $\text{C}\equiv\text{C}$), 1732 (w), 1572 (w), 1515 (s; C- NO_2), 1490 (s), 1399 (m), 1348 (s), 1326 (s), 1184 (s), 1077 (s), 962 (s), 866 (m), 785 (s), 748 (s), 685 (s), 601 (m), 560 (m), 518 (m), 475 cm^{-1} (m); MS-EI $^+$ (20 eV): m/z (%): 273.2 (100) [M^+], 226.2 (18) [$M^+ - \text{NO}_2 - \text{H}$], 215.3 (34) [$M^+ - \text{CNO}_2\text{H}$]; HRMS-EI $^+$ m/z : calcd. for $\text{C}_{18}\text{H}_{11}\text{NO}_2$ [M^+] 273.0790; found, 273.0790; UV/Vis (toluene): λ_{max} (ϵ) = 355 (5500), 286 nm (9400 $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$).

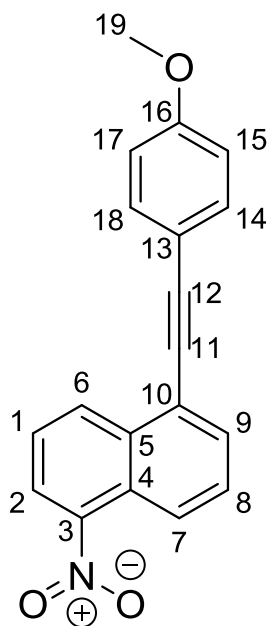
6.4.4 9-((5-Nitronaphthalen-1-yl)ethynyl)anthracene (6)



Following the general procedure **6.3**, 3-(5-nitronaphthalene-1-yl)propionic acid (0.170 g, 0.71 mmol) and 9-bromoanthracene (0.151 g, 0.59 mmol) were used. **6** was received as orange powder after column chromatography (PE:EE, 20:1 (v/v), R_f =0.33) and removal of the solvent at reduced pressure. Yield: 0.064 g (29%).

m.p.: 182 °C; ^1H NMR (600MHz, $[\text{D}_8]\text{THF}$, 25°C): δ = 9.06 (ddd, $^3J(\text{H,H})$ = 7.8 Hz, $^4J(\text{H,H})$ = 1.0 Hz, $^5J(\text{H,H})$ = 0.9 Hz, 1 H; H-2), 8.74 (ddd, $^3J(\text{H,H})$ = 8.7 Hz, $^4J(\text{H,H})$ = 1.5 Hz, $^5J(\text{H,H})$ = 0.8 Hz, 2 H; H-19, H-26), 8.62 (b s, 1 H; H-16), 8.54 (ddd, $^3J(\text{H,H})$ = 8.1 Hz, $^4J(\text{H,H})$ = 0.9 Hz, $^5J(\text{H,H})$ = 0.9 Hz, 1 H; H-7), 8.34 (dd, $^3J(\text{H,H})$ = 7.4 Hz, $^4J(\text{H,H})$ = 1.0 Hz, 1 H; H-6), 8.21 (dd, $^3J(\text{H,H})$ = 7.3 Hz, $^4J(\text{H,H})$ = 0.9 Hz, 1 H; H-9), 8.12 (ddd, $^3J(\text{H,H})$ = 9.0 Hz, $^4J(\text{H,H})$ = 1.1 Hz, $^5J(\text{H,H})$ = 0.8 Hz, 2 H; H-22, H-23), 7.85 (dd, $^3J(\text{H,H})$ = 8.1 Hz, $^3J(\text{H,H})$ = 7.3 Hz, 1 H; H-8), 7.83 (dd, $^3J(\text{H,H})$ = 7.8 Hz, $^3J(\text{H,H})$ = 7.4 Hz, 1 H; H-1), 7.66 (ddd, $^3J(\text{H,H})$ = 8.7 Hz, $^3J(\text{H,H})$ = 6.6 Hz, $^4J(\text{H,H})$ = 1.1 Hz, 2 H; H-20, H-25), 7.56 ppm (ddd, $^3J(\text{H,H})$ = 9.0 Hz, $^3J(\text{H,H})$ = 6.6 Hz, $^4J(\text{H,H})$ = 1.5 Hz, 2 H; H-21, H-24); ^{13}C NMR (150 MHz, $[\text{D}_8]\text{THF}$, 25°C): δ = 148.4 (q, 1 C; C-3), 134.7 (q, 1 C; C-5), 133.6 (q, 2 C; C-14, C-18), 132.9 (+, 1 C; C-2), 132.7 (+, 1 C; C-9), 132.2 (q, 2 C; C-15, C-17), 129.6 (+, 2 C; C-22, C-23), 129.4 (+, 1 C; C-8), 129.3 (+, 1 C; C-16), 127.9 (+, 2 C; C-20, C-25), 127.0 (+, 2 C; C-19, C-26), 126.5 (+, 2 C; C-21, C-24), 126.4 (+, 1 C; C-1), 125.9 (q, 1 C; C-10), 124.9 (+, 1 C; C-6), 124.3 (+, 1 C; C-7), 122.9 (q, 1 C; C-4), 117.0 (q, 1 C; C-13), 98.4 (q, 1 C; C-11), 93.2 (q, 1 C; C-12); IR (ATR): $\tilde{\nu}$ = 3047–3028 (w, =C-H), 2956–2856 (w), 2198 (w; C \equiv C), 1910 (w), 1733 (w), 1621 (w), 1570 (w), 1523 (s), 1410 (m), 1438 (m), 1419 (m), 1338 (s), 1323 (s), 1215 (m), 963 (m), 876 (s), 841(m), 788 (s), 778 (s), 729 (s), 614 (s), 547 (s), 513 cm^{-1} (s); MS-EI $^+$ (20 eV): m/z (%): 373.2 (100) [M^+], 326.2 (15) [$M^+ - \text{NO}_2 - \text{H}$]; HRMS-EI $^+$ m/z : calcd. for $\text{C}_{26}\text{H}_{15}\text{NO}_2$ [M^+] 373.1104; found, 373.1104; UV/Vis (toluene): λ_{max} (ϵ) = 433 (28900), 411 nm (36500 $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$).

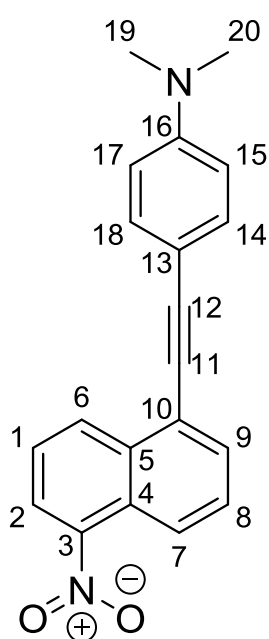
6.4.5 1-((4-Methoxyphenyl)ethynyl)-5-nitronaphthalene (7)



Following the general procedure **6.3**, 3-(5-nitronaphthalene-1-yl)propionic acid (0.220 g, 0.91 mmol) and 4-bromoanisole (0.142 g, 0.76 mmol) were used. **7** was received as yellow powder after column chromatography (PE:EE, 20:1 (v/v), $R_f=0.14$) and removal of the solvent at reduced pressure. Yield: 0.021 g (9%).

m.p. 117 °C; ^1H NMR (600MHz, $[\text{D}_8]\text{THF}$, 25°C): δ = 8.81 (ddd, $^3J(\text{H,H}) = 7.8$ Hz, $^4J(\text{H,H}) = 1.1$ Hz, $^5J(\text{H,H}) = 1.0$ Hz, 1 H; H-6), 8.42 (ddd, $^3J(\text{H,H}) = 8.2$ Hz, $^4J(\text{H,H}) = 1.0$ Hz, $^5J(\text{H,H}) = 1.0$ Hz, 1 H; H-7), 8.26 (dd, $^3J(\text{H,H}) = 7.4$ Hz, $^4J(\text{H,H}) = 1.1$ Hz, 1 H; H-2), 7.87 (dd, $^3J(\text{H,H}) = 7.4$ Hz, $^4J(\text{H,H}) = 1.0$ Hz, 1 H; H-9), 7.73 (dd, $^3J(\text{H,H}) = 7.8$ Hz, $^3J(\text{H,H}) = 7.4$ Hz, 1 H; H-1), 7.72 (dd, $^3J(\text{H,H}) = 8.2$ Hz, $^3J(\text{H,H}) = 7.4$ Hz, 1 H; H-8), 7.59 (m, 2 H; H-14, H-18), 7.98 (m, 2 H; H-15, H-17), 3.82 ppm (s, 3 H, H-19); ^{13}C NMR (150 MHz, $[\text{D}_8]\text{THF}$, 25°C): δ = 161.3 (q, 1 C; C-16), 148.2 (q, 1 C; C-3), 134.6 (q, 1 C; C-5), 133.8 (+, 2 C; C-14, C-18), 132.9 (+, 1 C; C-6), 131.9 (+, 1 C; C-9), 129.3 (+, 1 C; C-8), 125.9 (+, 1 C; C-1), 125.8 (q, 1 C; C-4), 124.8 (+, 1 C; C-2), 123.6 (+, 1 C; C-7), 123.1 (q, 1 C; C-10), 115.4 (q, 1 C; C-13), 114.8 (+, 2 C; C-15, C-17), 96.7 (q, 1 C; C-12), 85.6 (q, 1 C; C-11), 55.4 ppm (+, 1 C; C-19); IR (ATR): $\tilde{\nu}$ = 3360 (w), 3103–3017 (w, =C-H), 2921–2851 (m), 2217–2197(w; C≡C), 1603 (m), 1586 (w), 1570 (m), 1507 (s; C-NO₂), 1459 (m), 1411 (w), 1345 (m), 1326 (m), 1285 (m), 1247 (s), 1173 (m), 1158 (m), 1026 (s), 816 (s), 784 (s), 766 (s), 738 (m), 524 cm⁻¹ (m); MS-EI⁺ (20 eV): m/z (%): 303.2 (100) [M^+], 302.3 (7) [$M^+ - \text{H}$], 245.2 (9) [$M^+ - \text{CNO}_2\text{H}$]; HRMS-EI⁺ m/z : calcd. for C₁₉H₁₃NO₃ [M^+] 303.0895; found, 303.0895; UV/Vis (toluene): λ_{max} (ϵ) = 356 (14500), 296 nm (21800 mol⁻¹ dm³ cm⁻¹).

6.4.6 *N,N*-Dimethyl-4-((5-nitronaphthalen-1-yl)ethynyl)aniline (**8**)



Following the general procedure **6.3**, 3-(5-nitronaphthalene-1-yl)propionic acid (0.133 g, 0.55 mmol) and 4-bromo-*N,N*-dimethylaniline (0.092 g, 0.46 mmol) were used. **7** was received as dark red powder after column chromatography (PE:EE:NEt₃, 20:1:0.2 (v/v/v), *R_f*=0.27) and removal of the solvent at reduced pressure. Yield: 0.046 g (31%).

m.p. 118 °C; ¹H NMR (600MHz, [D₈]THF, 25°C): δ = 8.82 (ddd, ³*J* (H,H) = 8.4 Hz, ⁴*J* (H,H) = 1.1 Hz, ⁵*J* (H,H) = 1.0 Hz, 1 H; H-6), 8.37 (ddd, ³*J* (H,H) = 8.8 Hz, ⁴*J* (H,H) = 1.0 Hz, ⁵*J* (H,H) = 1.0 Hz, 1 H; H-7), 8.25 (dd, ³*J* (H,H) = 7.6 Hz, ⁴*J* (H,H) = 1.1 Hz, 1 H; H-2), 7.82 (dd, ³*J* (H,H) = 7.2 Hz, ⁴*J* (H,H) = 1.0 Hz, 1 H; H-9), 7.71 (dd, ³*J* (H,H) = 8.4 Hz, ³*J* (H,H) = 7.6 Hz, 1 H; H-1), 7.69 (dd, ³*J* (H,H) = 8.8 Hz, ³*J* (H,H) = 7.2 Hz, 1 H; H-8), 7.48 (m, 2 H; H-14, H-18), 6.74 (m, 2 H; H-15, H-17), 3.01 ppm (s, 6 H; H-19, H-20); ¹³C NMR (150 MHz, [D₈]THF, 25°C): δ = 151.1 (q, 1 C; C-16), 148.2 (q, 1 C; C-3), 134.6 (q, 1 C; C-5), 133.4 (+, 2 C; C-14, C-18), 133.1 (+, 1 C; C-6), 131.3 (+, 1 C; C-9), 129.3 (+, 1 C; C-8), 125.8 (q, 1 C; C-4), 125.6 (+, 1 C; C-1), 124.7 (+, 1 C; C-2), 123.9 (q, 1 C; C-10), 122.9 (+, 1 C; C-7), 112.4 (+, 2 C; C-15, C-17), 109.9 (+, 1 C; C-13), 98.4 (q, 1 C; C-12), 85.0 (q, 1 C; C-11), 39.9 ppm (+, 2 C; C-19, C-20); IR (ATR): $\tilde{\nu}$ = 3067 (wb), 2952–2853 (w, =C-H), 2187 (m; C≡C), 1683 (w), 1606 (s), 1568 (m), 1516 (s; C-NO₂), 1336 (s), 1324 (s), 1186 (s), 1064 (m), 965 (w), 946 (w), 865 (w), 808 (s), 777 (s), 753 (m), 738 (m), 564 (w), 518 cm⁻¹ (w); MS-EI⁺ (20 eV): *m/z* (%): 316.3 (100) [*M*⁺], 315.3 (11) [*M*⁺–H], 270.3 (22) [*M*⁺–NO₂]; HRMS-EI⁺ *m/z*: calcd. for C₂₀H₁₆N₂O₂ [*M*⁺] 316.1212; found, 316.1208; UV/Vis (toluene): λ_{max} (ε) = 389 (8100), 317 nm (16300 mol⁻¹ dm³ cm⁻¹).

6.5 Synthesis of 1-(Phenylethynyl)naphthalene (3) in IR cuvette/flask combination F6

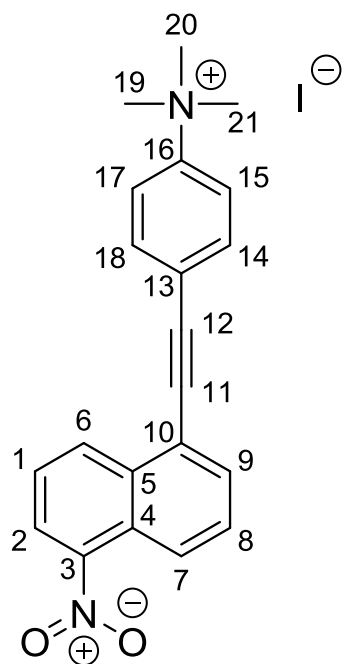
The synthetic protocol is based on the general procedure **6.3**.

On a small weighing boat, 1 eq. 3-(naphthalene-1-yl)propionic acid (0.230 g, 1.17 mmol) , 1 eq. dry Cs_2CO_3 (0.382 g, 1.17 mmol), 1 mol-% $\text{Pd}(\text{OAc})_2$ (2 mg, 0.01 mmol) and 2 mol-% X-Phos (9 mg, 0.02 mmol) were weighed in with a balance installed in the glove box and mixed thoroughly. In a small flask, a solution of 0.85 eq. bromobenzene (102 μL , 0.153 g, 0.98 mmol) in dry THF (40 eq., 3.9 mL) was prepared separately.

The print of the reaction flask **F6** combined with an IR cuvette was started inside the glove box with polyamide as printing material. After half of the print of the reaction vessel had been completed, the solid mixture prepared before was inserted during a short first pause of the print. The print was continued, until the reaction vessel had been nearly printed completely. A magnetic stirring bar was inserted during a second short pause of the print. The print was continued, until the IR cuvette had nearly been printed completely. The solution of the aryl halide in THF was inserted into the upper opening of the IR cuvette *via* a syringe during a third short pause of the print. The print was continued until the IR cuvette/flask combination was complete and closed. After finishing the print, flask **F6** was discharged from the glove box. An initial IR spectrum was recorded directly after discharging from the box. The IR cuvette/flask combination was heated with an aluminium bead bath (*LabArmor*) at 90 °C (bead bath temperature). Regularly, the IR cuvette/flask combination was cooled down and subsequent IR spectra were recorded.

All IR spectra have been recorded on the *Bruker Alpha-T* FT-IR spectrometer. Printed IR cuvette **F4** with pure THF has been used as background. A resolution of 8 cm^{-1} has been applied and 128 scans have been accumulated for each spectrum. Final spectra are averaged over 36 data points. For reaction monitoring, spectra have been baseline corrected and the peak maximum at 2350 cm^{-1} (CO_2) has been used. A control measurement with dry ice dissolved in THF has been performed in printed cuvette **F4**.

6.6 *N,N,N*-Trimethyl-4-((5-nitronaphthalen-1-yl)ethynyl)phenylammonium iodide (**9**)



In a *Schlenk* tube equipped with magnetic stirring bar and Teflon stopcock, *N,N*-Dimethyl-4-((5-nitronaphthalen-1-yl)ethynyl)aniline (**8**) (32 mg, 0.10 mmol) was evacuated at high *vacuo*. Methyl iodide (5.00 g, 35.23 mmol) was directly distilled into the *Schlenk* tube. The mixture was stirred for 5 days at 60 °C. The excess methyl iodide was removed in high *vacuo* and the remaining solid washed with cyclohexane (3 x 1mL) and dried. **9** was received as red solid. Yield: 0.019 g (39%).

m.p: 170 °C; ^1H NMR (600MHz, $[\text{D}_4]\text{MeOH}$, 25°C): δ = 8.80 (ddd, $^3J(\text{H,H})$ = 8.4 Hz, $^4J(\text{H,H})$ = 1.0 Hz, $^5J(\text{H,H})$ = 1.0 Hz, 1 H; H-6), 8.48 (ddd, $^3J(\text{H,H})$ = 8.8 Hz, $^4J(\text{H,H})$ = 1.0 Hz, $^5J(\text{H,H})$ = 1.0 Hz, 1 H; H-7), 8.30 (dd, $^3J(\text{H,H})$ = 7.8 Hz, $^4J(\text{H,H})$ = 1.0 Hz, 1 H; H-2), 8.05–8.02 (m, 2 H; H-15, H-17), 7.99 (dd, $^3J(\text{H,H})$ = 7.2 Hz, $^4J(\text{H,H})$ = 1.0 Hz, 1 H; H-9), 7.97–7.95 (m, 2 H; H-14, H-18), 7.81 (dd, $^3J(\text{H,H})$ = 8.4 Hz, $^3J(\text{H,H})$ = 7.8 Hz, 1 H; H-1), 7.79 (dd, $^3J(\text{H,H})$ = 8.8 Hz, $^3J(\text{H,H})$ = 7.2 Hz, 1 H; H-8), 3.73 ppm (s, 3 H, H-19–H-21); ^{13}C NMR (150 MHz, $[\text{D}_4]\text{MeOH}$, 25°C): δ = 148.8 (q, 1 C; C-3), 148.3 (q, 1 C; C-16), 135.0 (q, 1 C; C-5), 134.6 (+, 2 C; C-14, C-18), 133.4 (+, 1 C; C-9), 133.0 (+, 1 C; C-6), 129.8 (+, 1 C; C-8), 126.9 (+, 1 C; C-1), 126.7 (q, 1 C; C-13), 126.2 (q, 1 C; C-4), 125.4 (+, 1 C; C-2), 125.2(+, 1 C; C-7), 122.2 (q, 1 C; C-10), 121.9 (+, 2 C, C-15, C-17), 94.1 (q, 1 C, C-12), 89.9 (q, 1 C, C-11), 57.8 ppm (+, 3 C, C-19–C-21); IR (ATR): $\tilde{\nu}$ = 3359 (wb), 3099–2853 (w, =C-H), 2209 (w; C \equiv C), 1720 (w), 1603 (w), 1516 (s; C-NO $_2$), 1465 (m), 1410 (m), 1325 (s), 1287 (s), 1027 (s), 956 (s), 936 (s), 845 (s), 783 (s), 564 cm^{-1} (s); MS-ESI $^+$ (5 eV): m/z (%): 331.1 (100) [$M^+ - \text{I}^-$]; HRMS-ESI $^+$ m/z : calcd. for $\text{C}_{21}\text{H}_{13}\text{N}_2\text{O}_2$ [$M^+ - \text{I}^-$] 331.1447; found, 331.1446; UV/VIS (THF): λ_{max} (ϵ) = 360 (4200), 230 nm (13200 $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$).

7. Reaction Monitoring

7.1 Detailed example for the reaction monitoring *via* NMR spectroscopy: Synthesis of 1-nitro-5-(phenylethynyl)naphthalene (5)

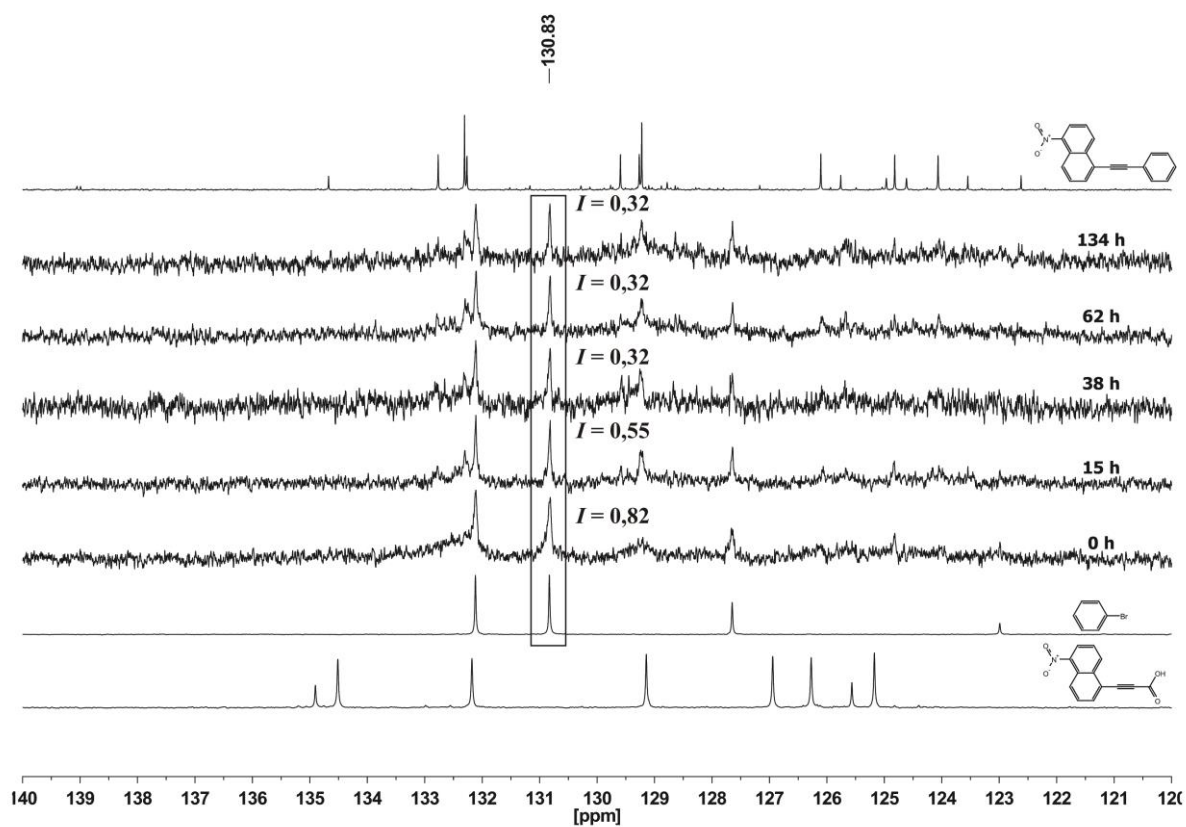


Figure S20. NMR spectra and assigned integral values according to protocol 6.4.3. Progress of the reaction is monitored *via* the consumption of bromobenzene.

7.2 Detailed example for the reaction monitoring *via* IR spectroscopy: Synthesis of 1-(phenylethynyl)naphthalene (3)

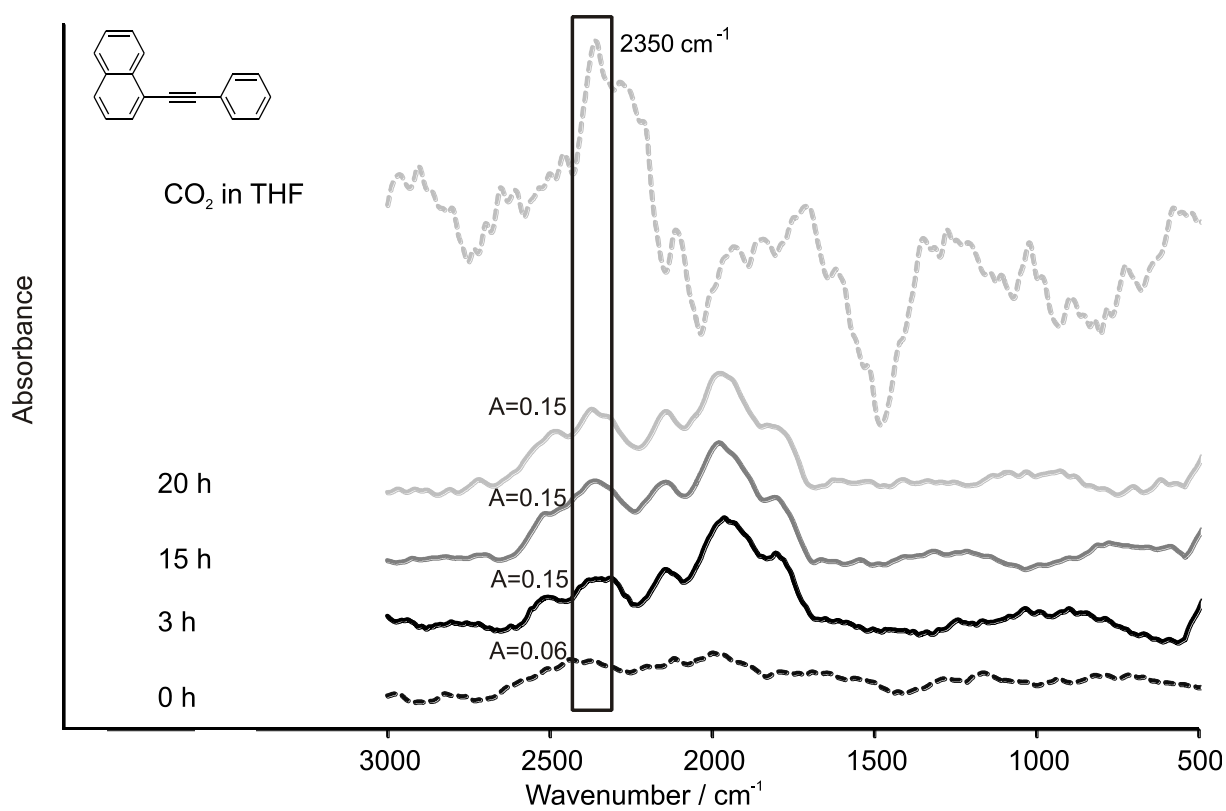
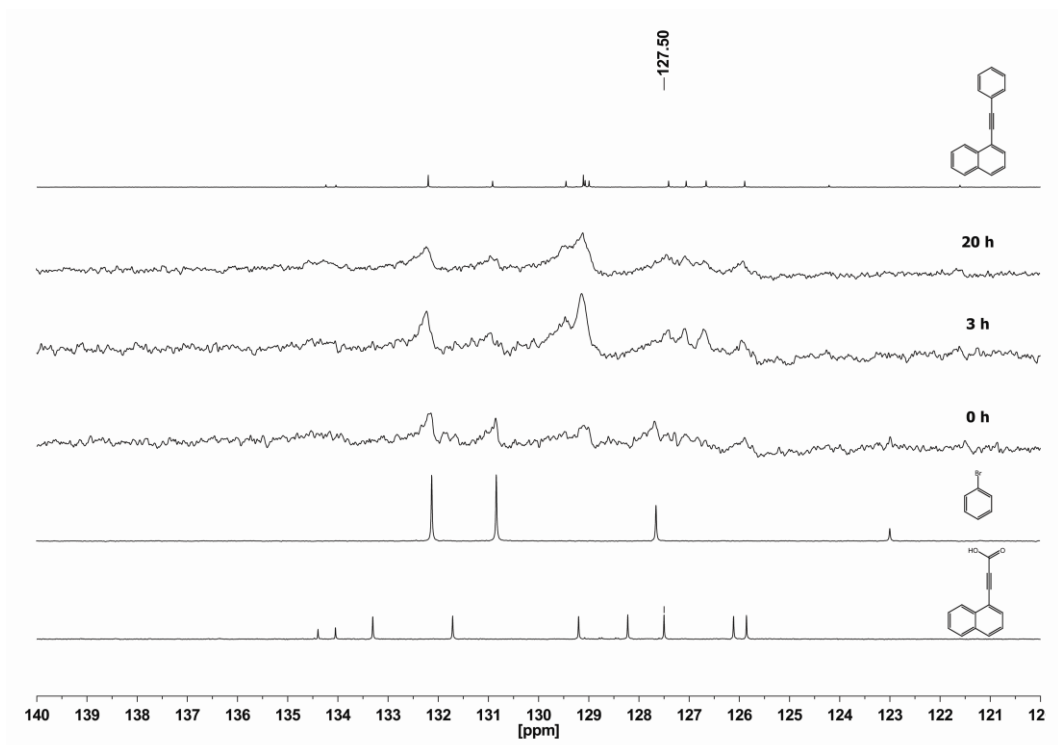


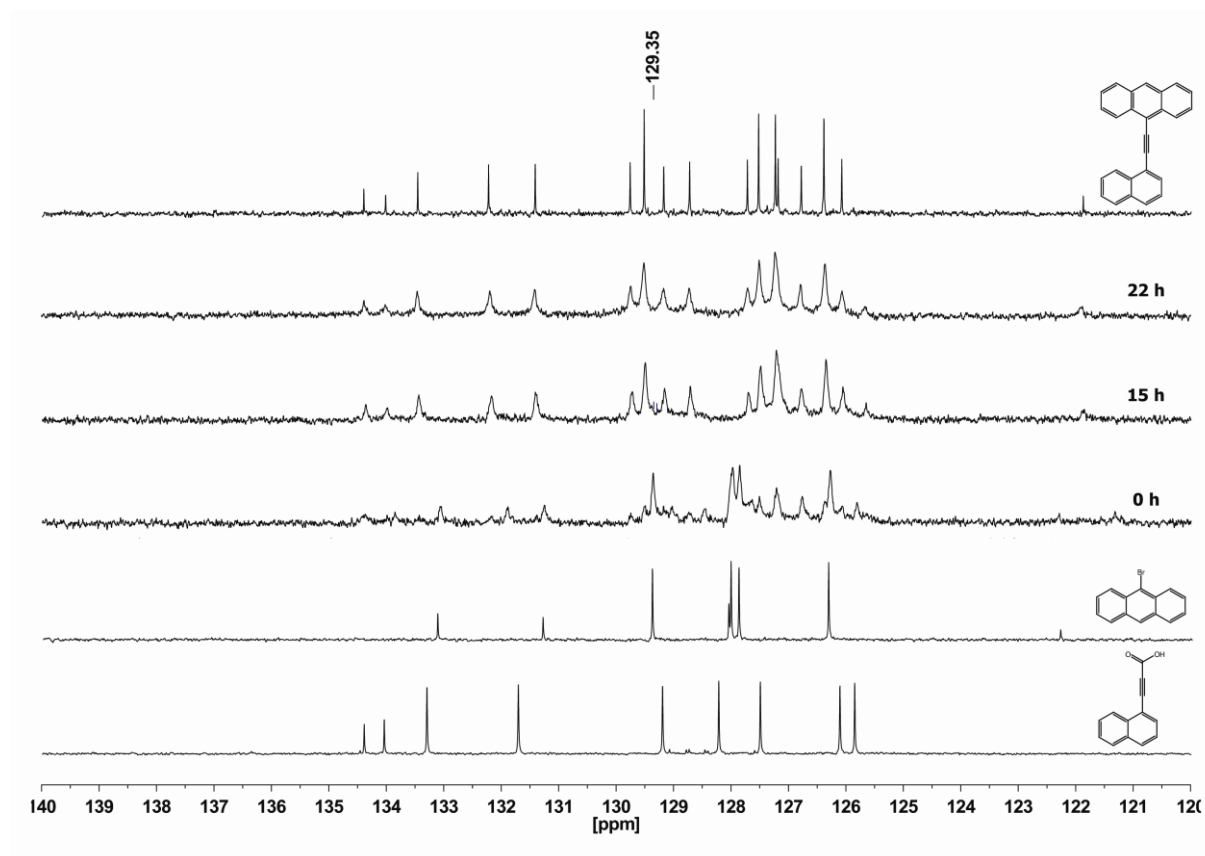
Figure S21. IR spectra according to protocol 6.5. Progress of the reaction is monitored *via* the formation of CO₂.

7.3 Spectra of all reactions monitored *via* NMR spectroscopy

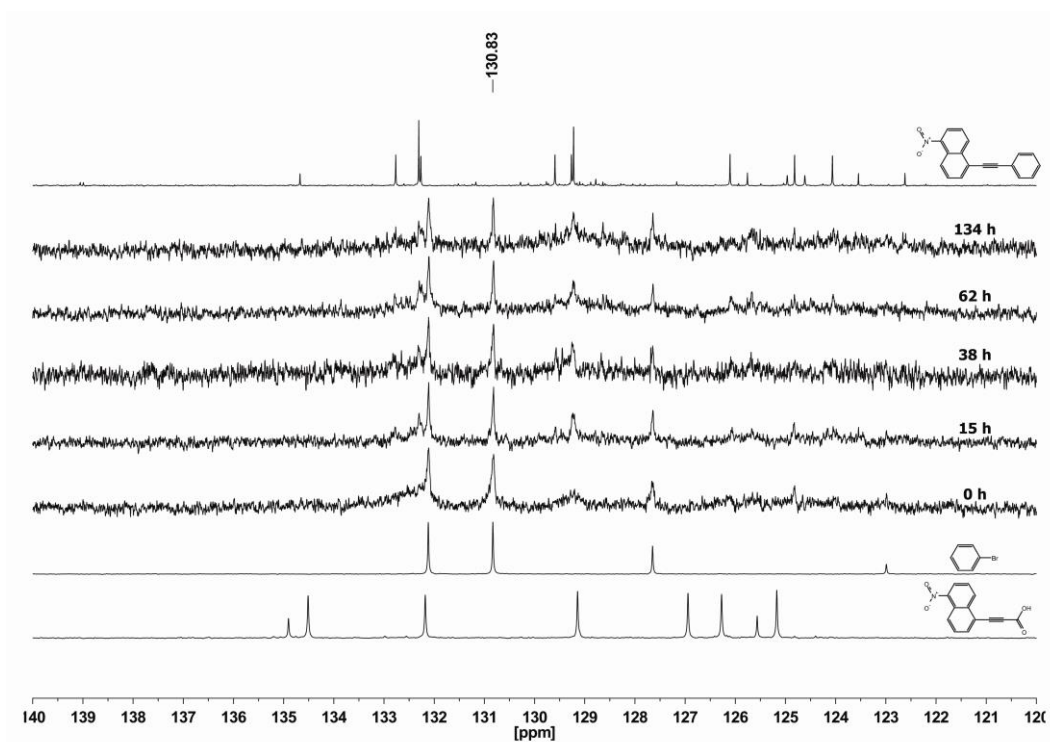
7.3.1 1-(Phenylethynyl)naphthalene (3) (according to 6.4.1)



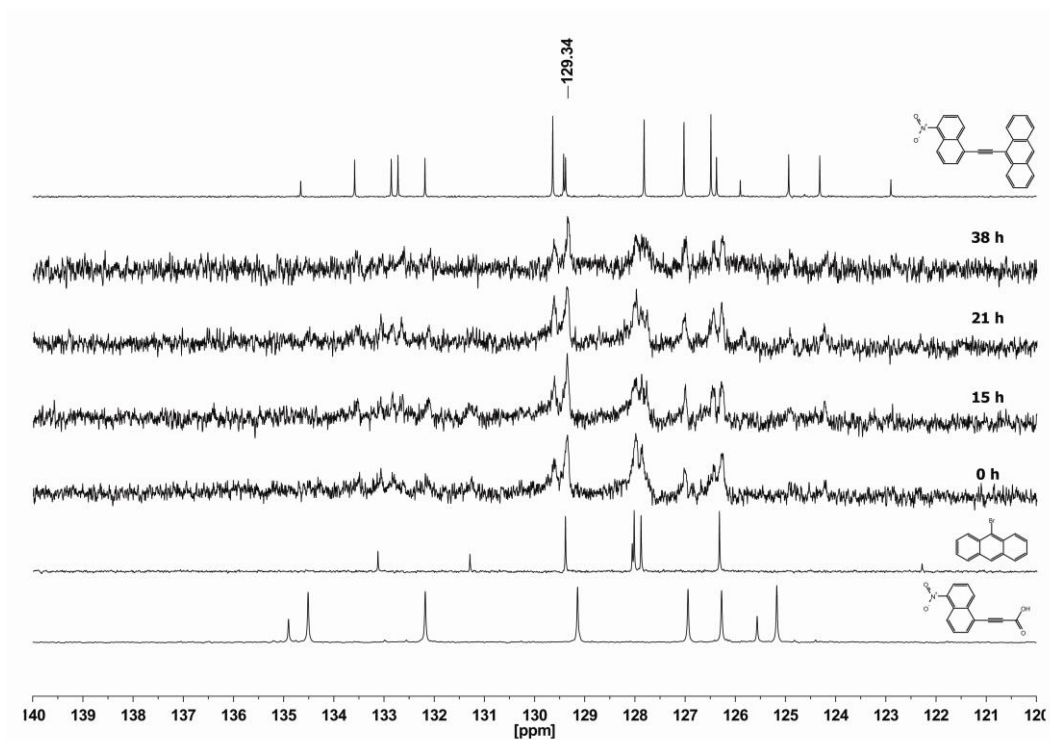
7.3.2 9-(Naphthalen-1-ylethynyl)anthracene (4) (according to 6.4.2)



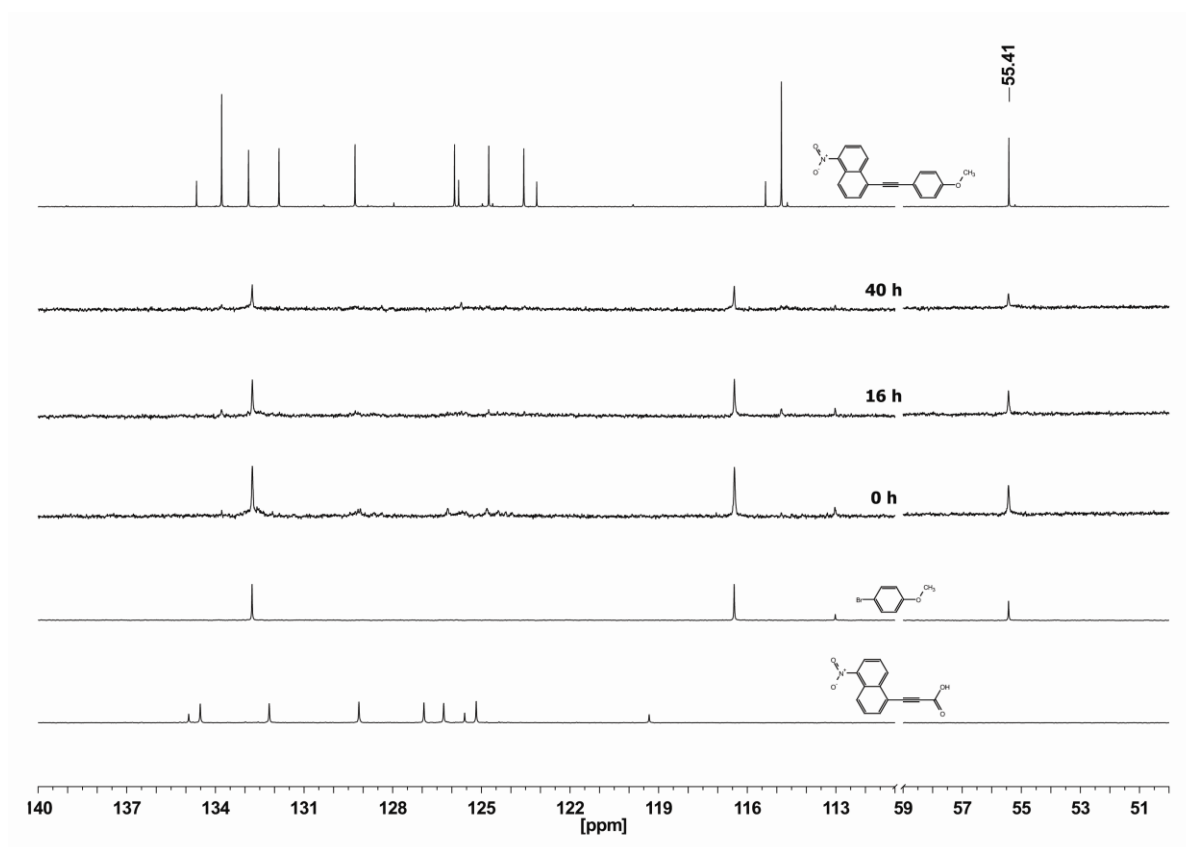
7.3.3 1-Nitro-5-(phenylethynyl)naphthalene (5) according to 6.4.3



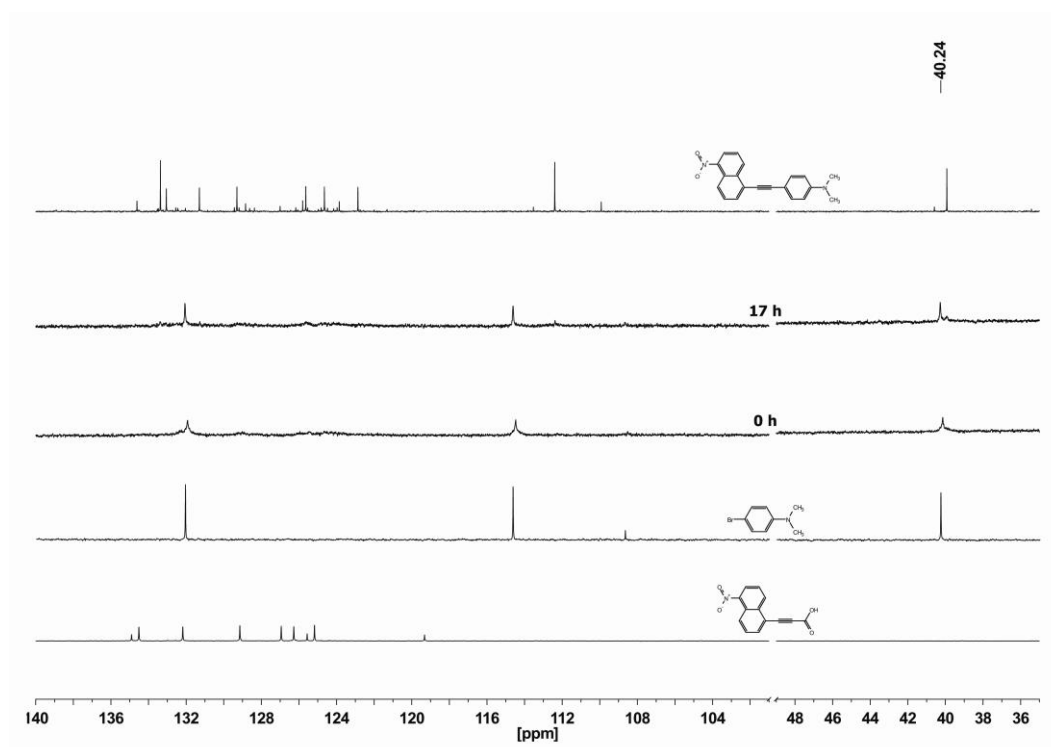
7.3.4 9-((5-Nitronaphthalen-1-yl)ethynyl)anthracene (6) according to 6.4.4



7.3.5 1-((4-Methoxyphenyl)ethynyl)-5-nitronaphthalene (7) according to 6.4.5



7.3.6 *N,N*-Dimethyl-4-((5-nitronaphthalen-1-yl)ethynyl)aniline (8) according to 6.4.6



8. Solvatochromism and Estimation of the First Hyperpolarizability

The static part (β_0) of the first hyperpolarizability β was estimated with help of the solvatochromic method for molecules with a dominant charge-transfer transition (based on the Oudar equation):¹⁰⁻¹²

$$\beta_{CT} = \frac{3}{2h^2 c^2} \cdot \frac{\tilde{\nu}_{eg}^2 |M_{eg}|^2 \Delta\mu_{eg}}{(\tilde{\nu}_{eg}^2 - 4\tilde{\nu}_L^2)(\tilde{\nu}_{eg}^2 - 4\tilde{\nu}_L'^2)}$$

with h = Plank's constant, c = speed of light, $\tilde{\nu}_{eg}$ = wavenumber of the CT absorption band, $\Delta\mu_{eg}$ = difference of dipole moment between ground state and (CT) excited state, M_{eg} = transition dipole moment and $\tilde{\nu}_L$ = wavenumber of laser light.

This equation reduces to the static part ($\tilde{\nu}_L = 0$):

$$\beta_{CT}(\tilde{\nu}_L = 0) = \beta_0 = \frac{3 |M_{eg}|^2 \Delta\mu_{eg}}{2h^2 \nu_{eg}^2}$$

The frequency ν_{eg} of the CT absorption band is taken from the absorption spectra.

The transition dipole moment M_{eg} is calculated from the oscillator strength f of the CT absorption band which is calculated from the integral A_i of the corresponding CT absorption band:¹³

$$|M_{eg}|^2 = \frac{3f\hbar e^2}{8\pi^2 m_e c \tilde{\nu}_{eg}}$$

$$f = \frac{4m_e c^2 \varepsilon_0}{e^2 N_A} \cdot \ln(10) \cdot \int \varepsilon d\tilde{\nu} = 4.319 \cdot 10^{10} \text{ mol} / \text{m} \cdot A_i$$

with e = elementary charge, m_e = mass of an electron, ε_0 = vacuum permittivity and N_A = Avogadro constant.

The difference of dipole moment between ground state and excited state $\Delta\mu_{eg}$ is calculated with help of the *Lippert-Mataga* plot, which is valid due to the absence of hydrogen-bonding and electron pair donor/acceptor interactions between the substances analysed here and the solvents used:^{14,15}

$$\tilde{\nu}_{abs} - \tilde{\nu}_{em} = SS = \frac{2\Delta\mu_{eg}^2}{\hbar c a^3} \left(\frac{\varepsilon_r - 1}{2\varepsilon_r + 1} - \frac{n_D^2 - 1}{2n_D^2 + 1} \right)$$

with SS = Stokes shift in cm^{-1} , a = radius of the molecule (see DFT calculations for details), ε_r = relative permittivity of the solvent and n_D^2 = refractive index of the solvent.

Accordingly, $\Delta\mu_{eg}$ accessible from the plot of the *Stokes* shift vs. the solvent properties $\Delta f(\varepsilon_r, n_D^2)$. Conversion from Gaussian unit system to SI units leads to:

$$\Delta\mu_{eg} = \sqrt{2\pi \varepsilon_0 \hbar c a^3}$$

with m = slope of the *Lippert-Mataga* plot.

UV/Vis absorption spectra for the determination of ν_{eg} and the integral of the CT absorption band have been measured in toluene. Due to the limited solubility, the salt **9** has been measured in THF. For the *Lippert-Mataga* plot, absorption and emission spectra of all substances have been measured in cyclohexane, toluene, diethyl ether, and THF. **9** was measured in DMSO, methanol, ethanol, and THF. Fluorescence intensities have been multiplied with λ^2 for the conversion from I vs. λ to I vs. $\tilde{\nu}$ spectra. The solvent parameters ϵ_r and n_D^2 have been taken from literature.¹⁶

8.1 Examples for absorption/emission spectra

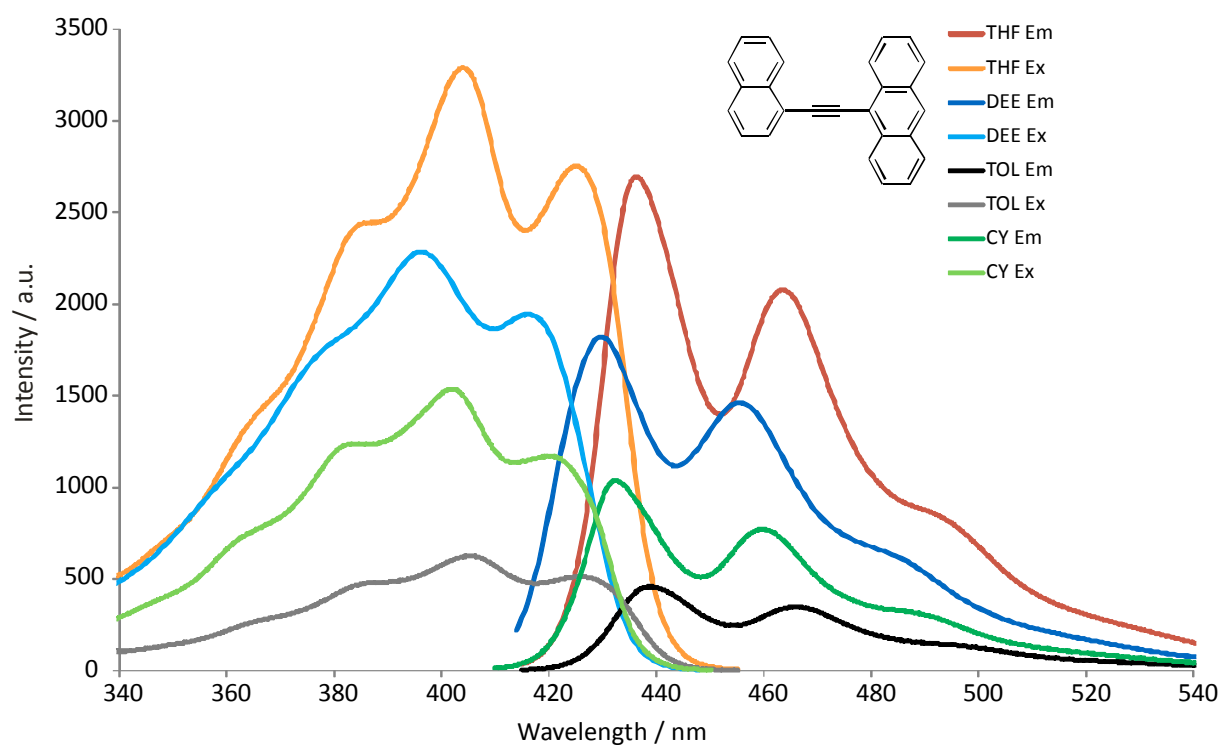


Figure S22. Absorption/emission spectra of **4** in cyclohexane (CY), toluene (TOL), diethyl ether (DEE), and THF. No change of the *Stokes* shift with increasing solvent polarity is noticed.

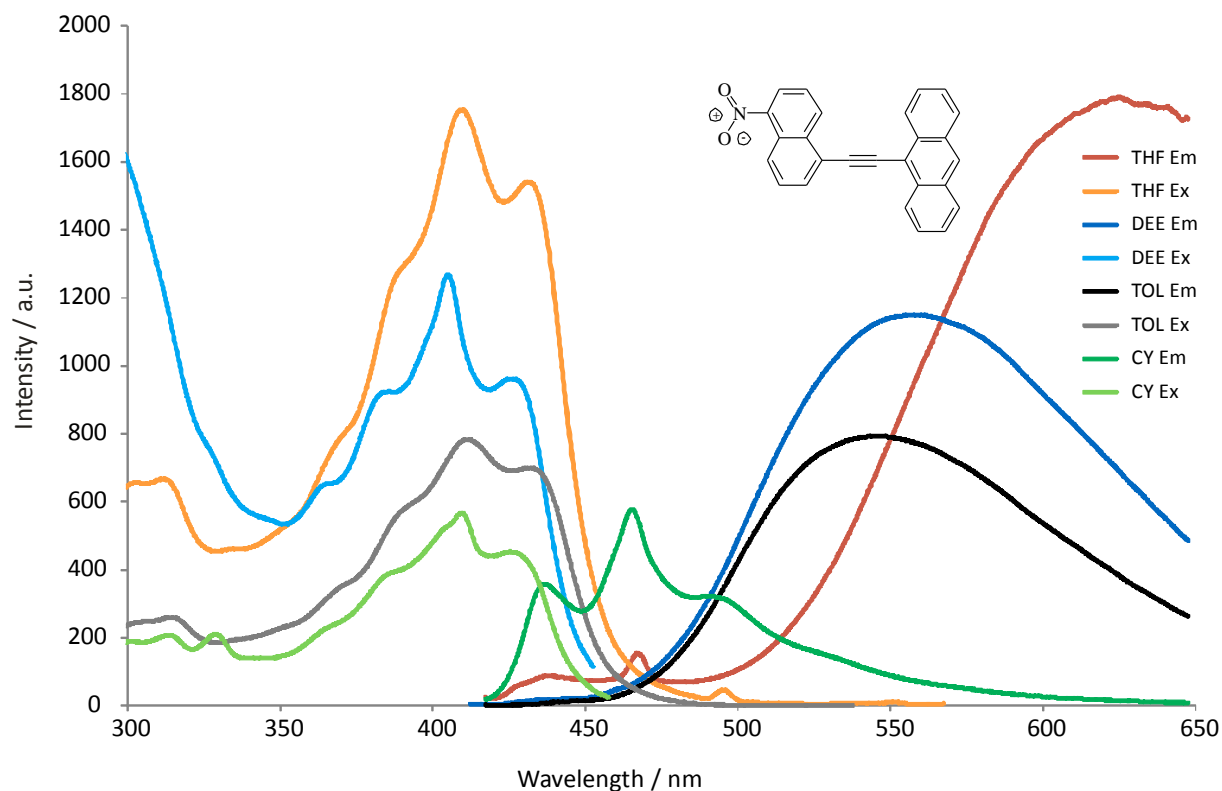


Figure S23. Absorption/emission spectra of **6** in cyclohexane (CY), toluene (TOL), diethyl ether (DEE), and THF. Strong increase of the *Stokes* shift with increasing solvent polarity is noticed.

8.2 Summary of data for the evaluation of β_{CT}

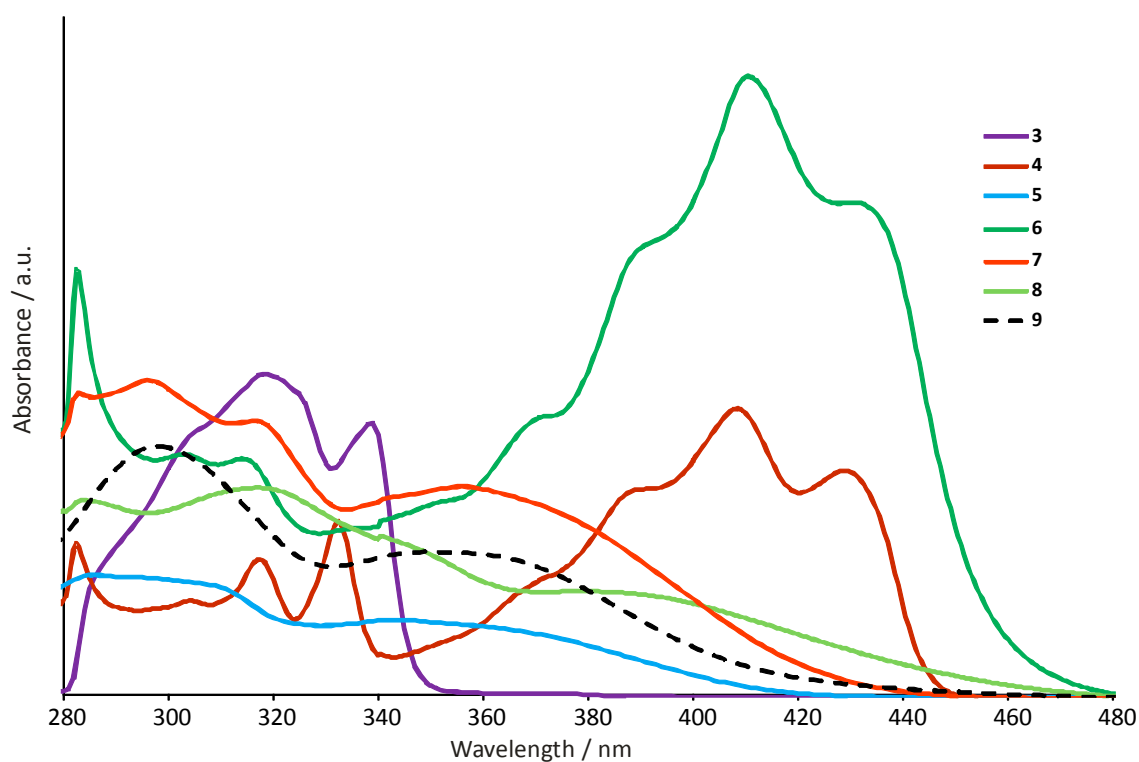


Figure S24. All absorption spectra measured in toluene (**9** measured in THF).

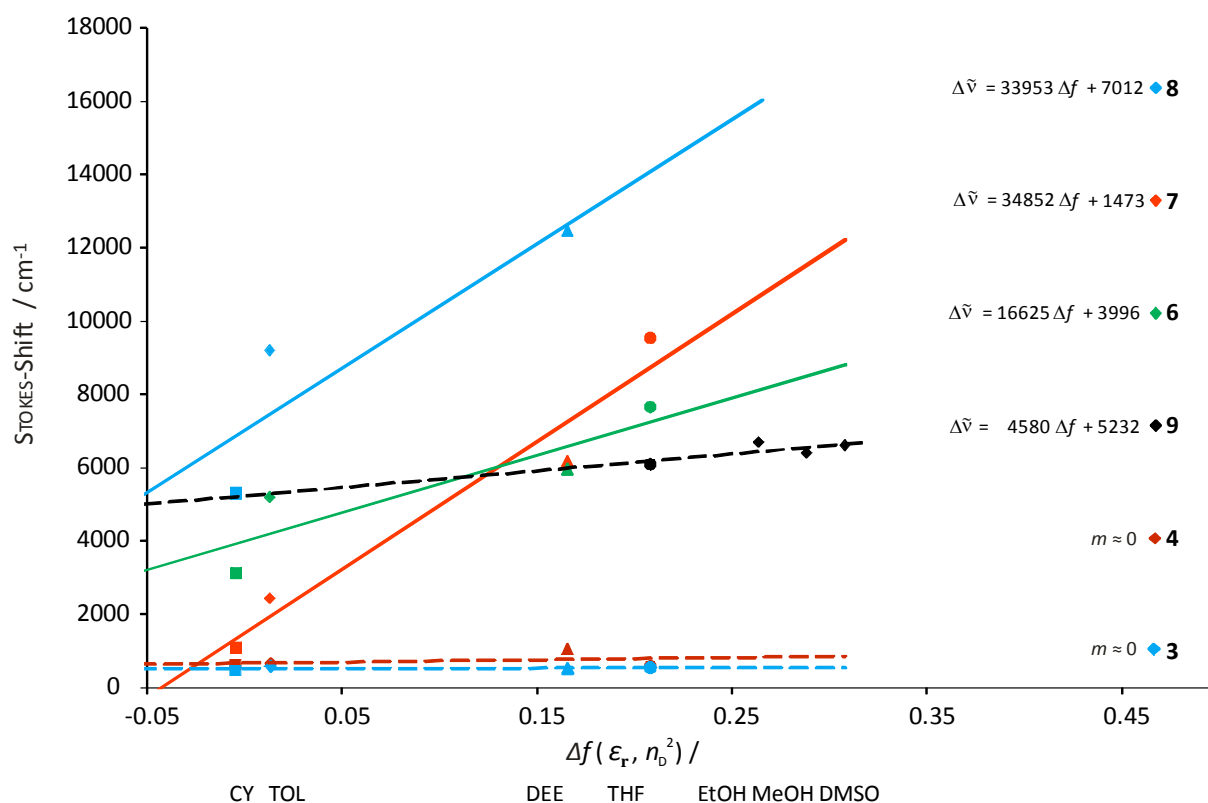
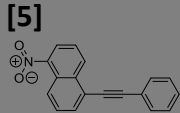
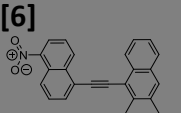
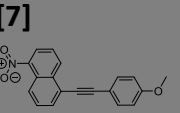
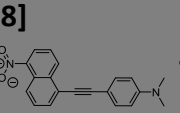
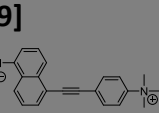


Figure S25. Lippert-Mataga plots for all substances measured in cyclohexane (CY), toluene (TOL), diethyl ether (DEE), and THF. **9** is measured in THF, ethanol (EtOH), methanol (MeOH), and DMSO.

Table 1. Summary of parameters for the calculation of β_{CT} via the solvatochromic method.

Compound					
m [cm ⁻¹]	- ^{*1}	16600	34900	>34000 ^{*2}	4600
r [$\cdot 10^{-10}$ m]	4.39	4.80	4.52	4.63	4.47
$\Delta\mu_{eg}$ [$\cdot 10^{-29}$ C·m]	- ^{*1}	4.5	5.9	>6.1	2.2
A_l [m·mol ⁻¹]	71690000	340354000	457903000	271419000	90323000
f []	0.03	0.15	0.20	0.12	0.04
$\tilde{\nu}_{eg}$ [m ⁻¹]	2816901	2301862	2808989	2574003	2777777
ΔM_{eg} [$\cdot 10^{-29}$ C·m]	0.51	1.23	1.3	1.22	0.6
λ_{eg} [$\cdot 10^{-7}$ m]	3.55	4.34	3.56	3.89	3.60
ΔE_{eg} [$\cdot 10^{-19}$ J]	5.60	4.57	5.58	5.11	5.52
β_{CT} [10^{-30} esu]	- ^{*1}	13	13	>14	1
$\beta_{CC,calc}$ [10^{-30} esu]	15	32	47	104	5

^{*1)} Due to the change from a pure non-CT transition in cyclohexane to a CT transition in THF a useful *Lippert-Mataga* plot could not be created.

^{*2)} In THF, the emission maximum was weak and out of the range of the fluorescence spectrometer. The slope of the *Lippert-Mataga* plot is likely to be larger.

8.3 ATR—IR Spectra

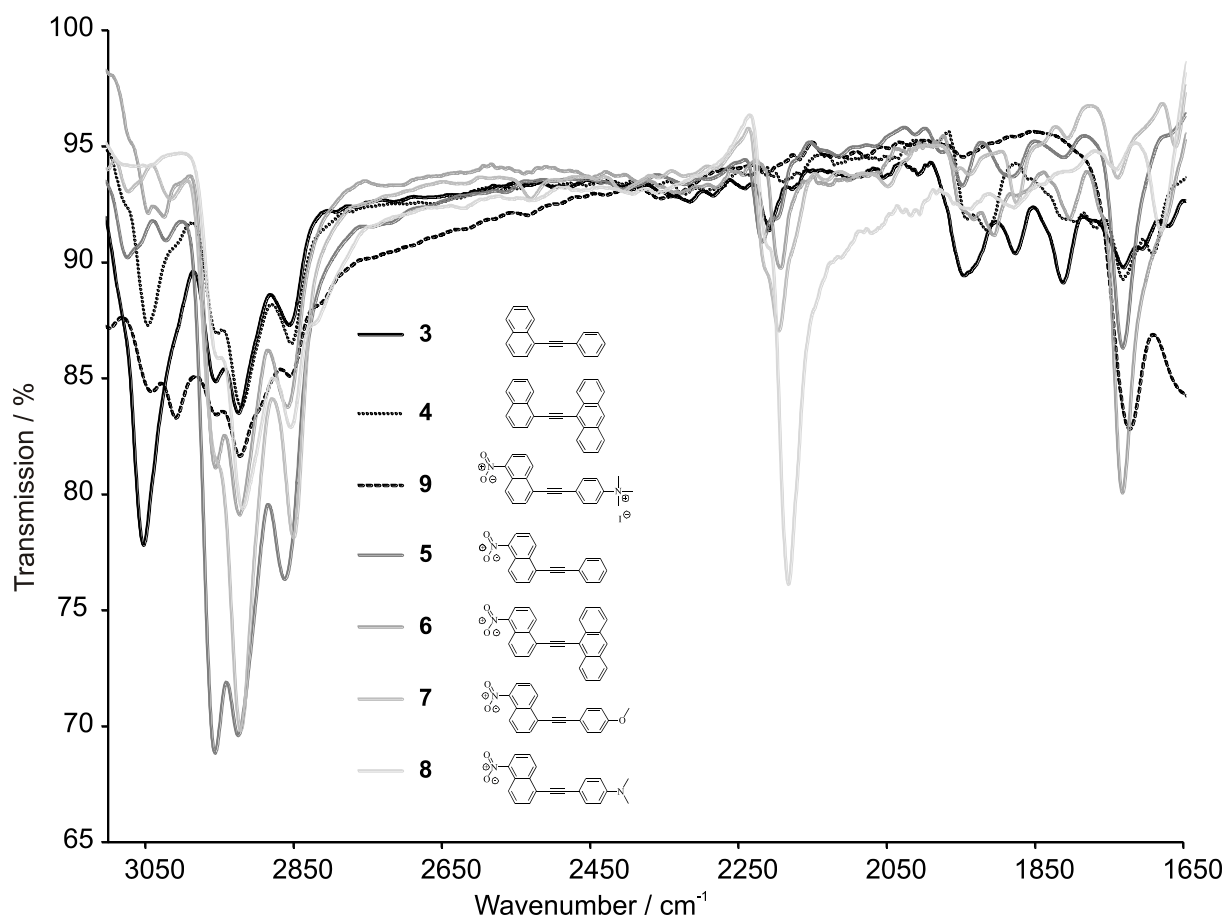
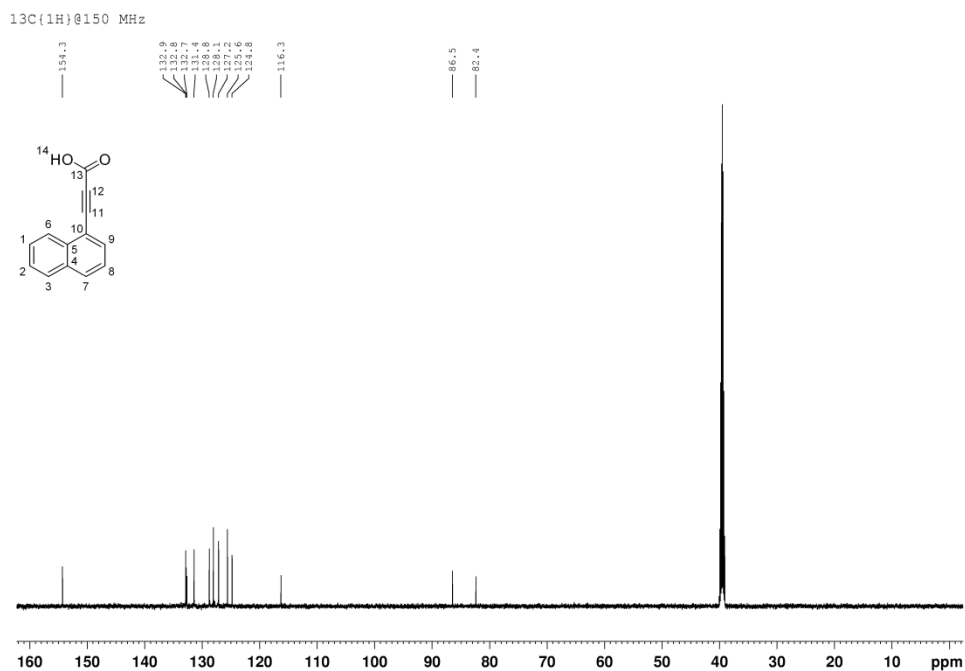
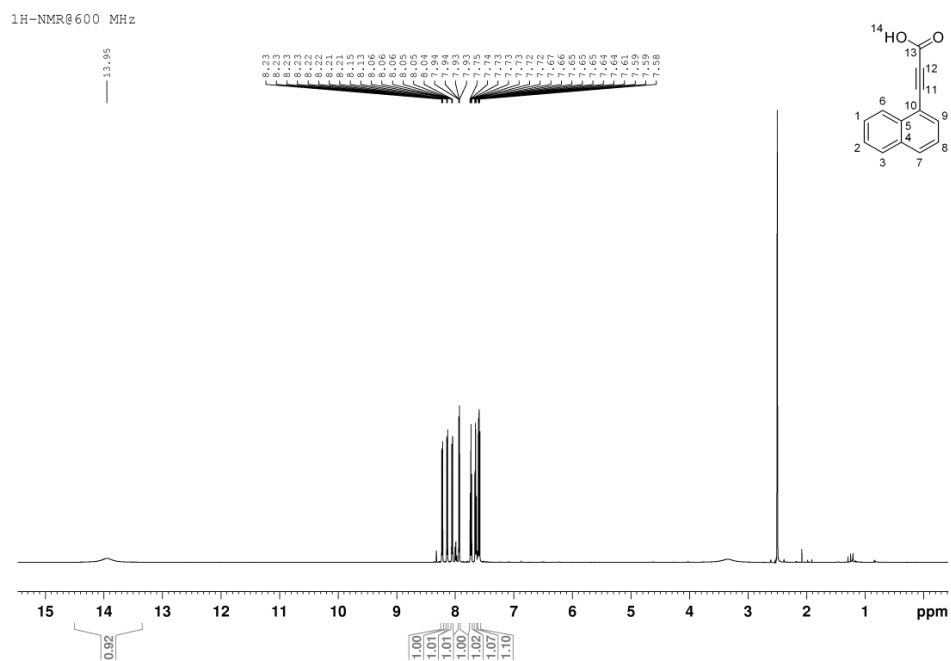


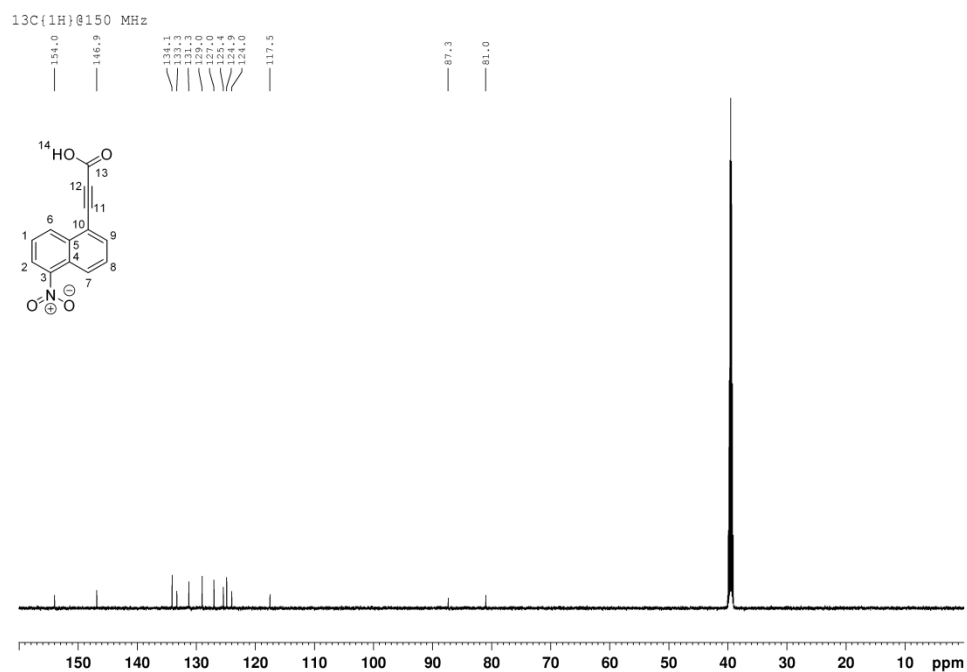
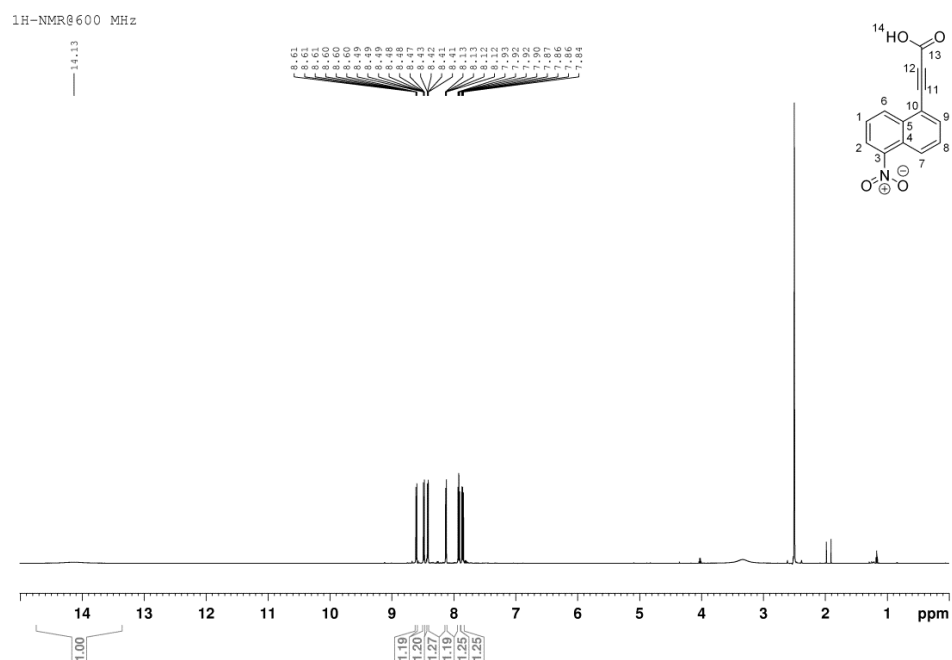
Figure S26. ATR-IR Spectra measured as solid substance. The C-C triple bond stretching vibrational band around 2200 cm⁻¹ has been analyzed and the intensity correlated with the calculated hyperpolarizability.

9. NMR Spectra

9.1. 3-(Naphthalen-1-yl)propionic acid (1)

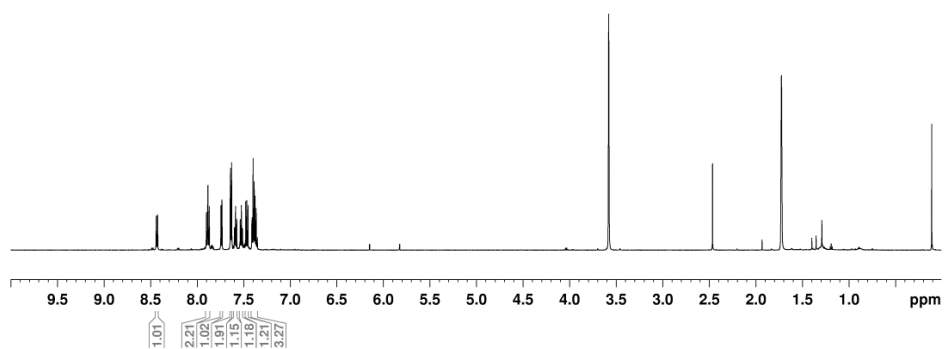


9.2 3-(5-Nitronaphthalen-1-yl)propionic acid (2)

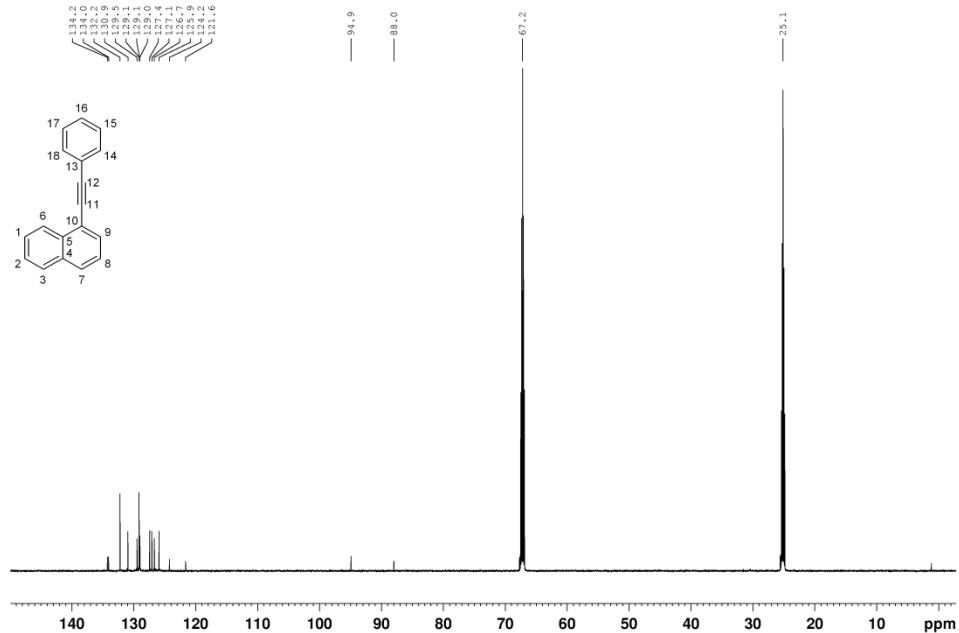
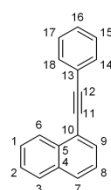
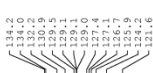


9.3 1-(Phenylethynyl)naphthalene (3)

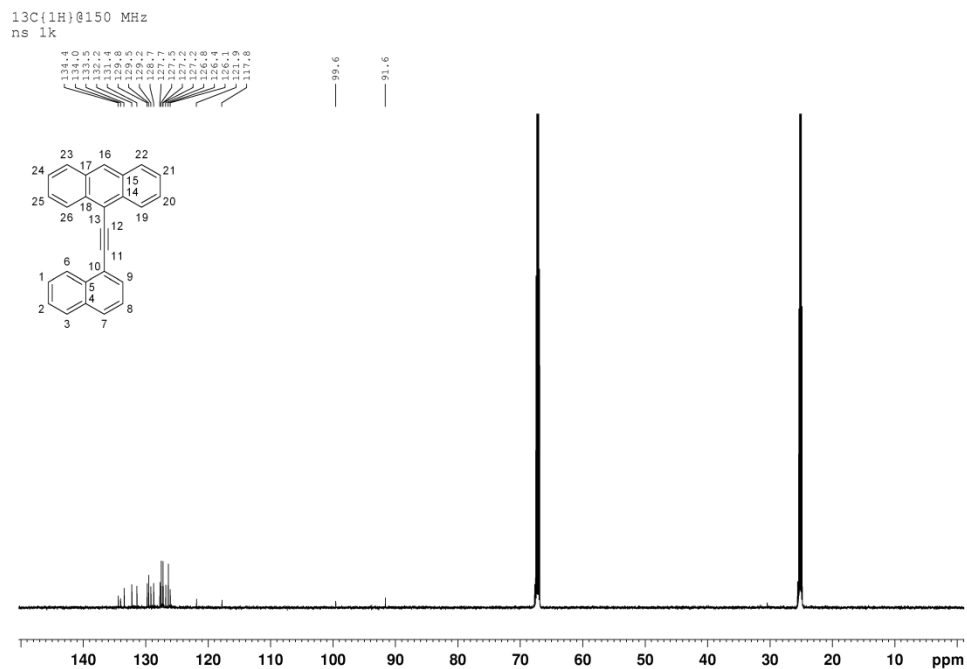
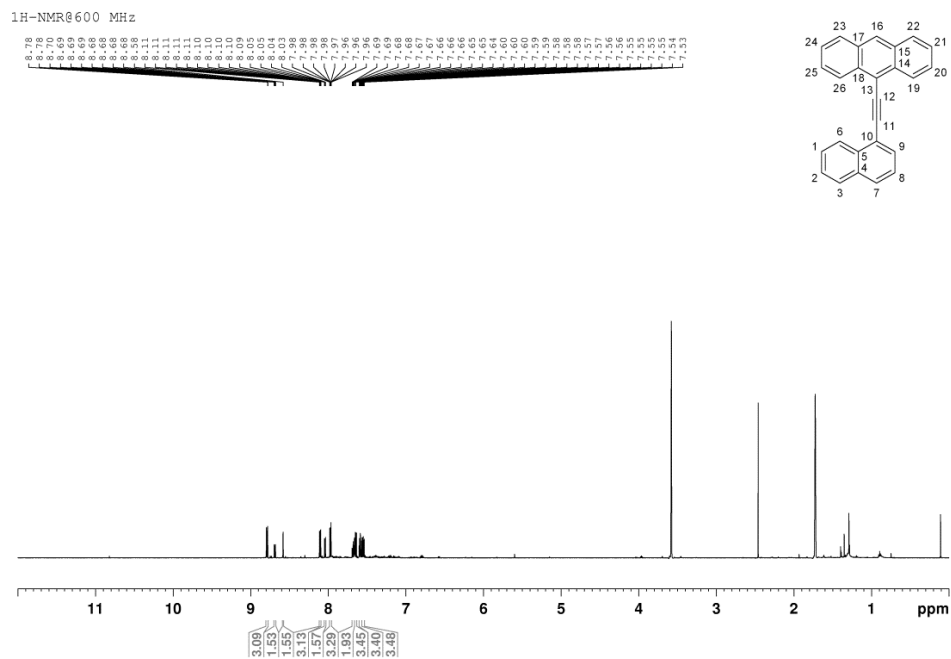
¹H-NMR@600 MHz



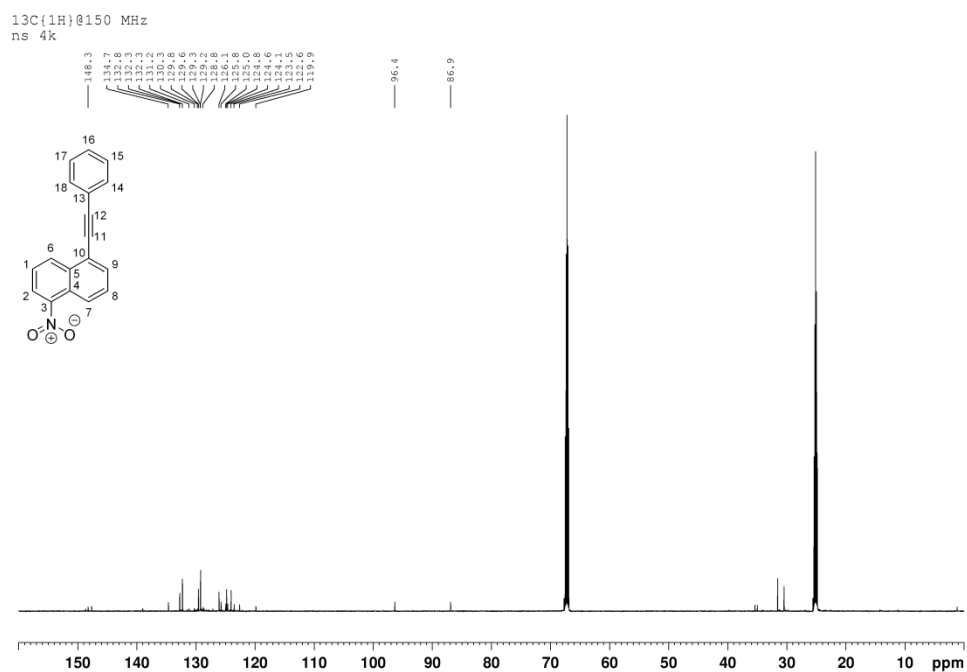
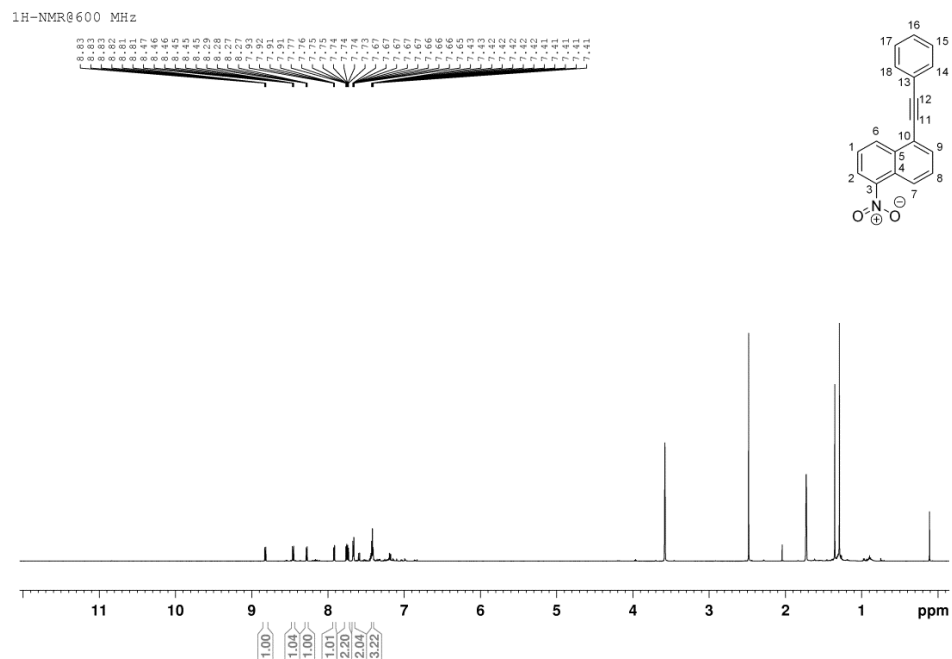
¹³C{¹H}@150 MHz



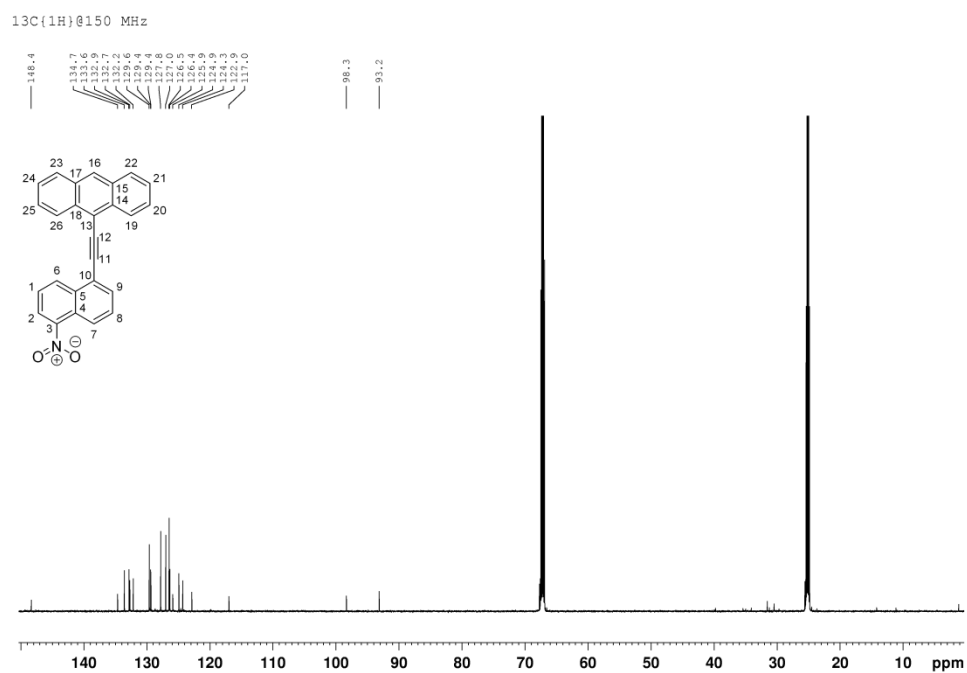
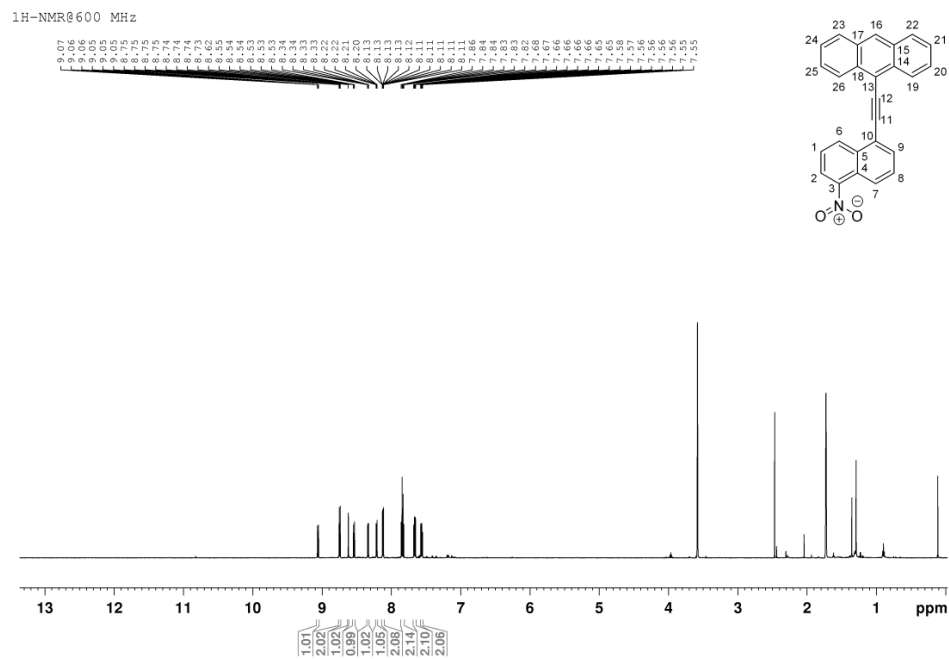
9.4 9-(Naphthalen-1-ylethynyl)anthracene (4)



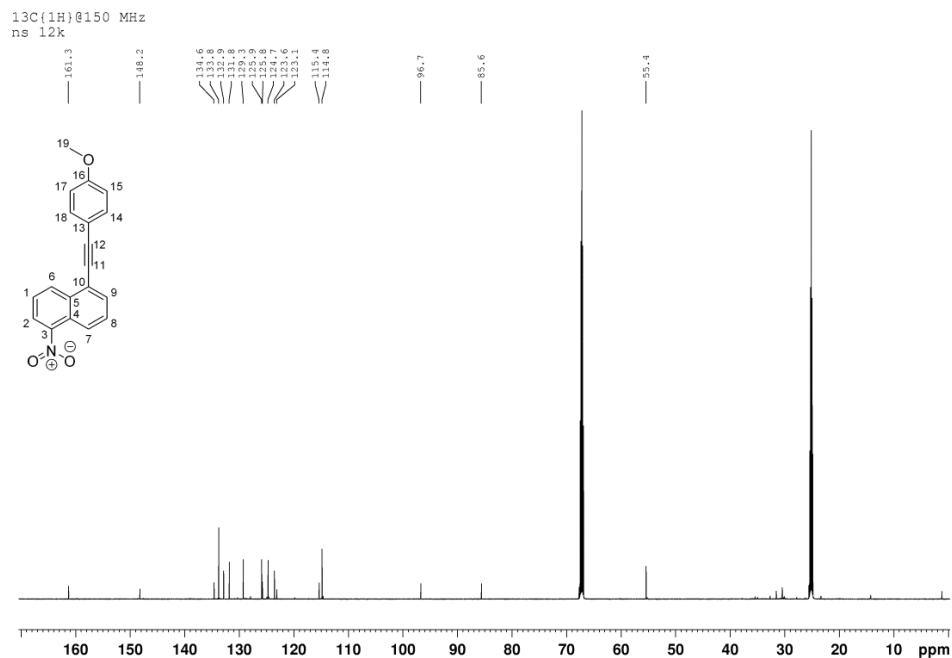
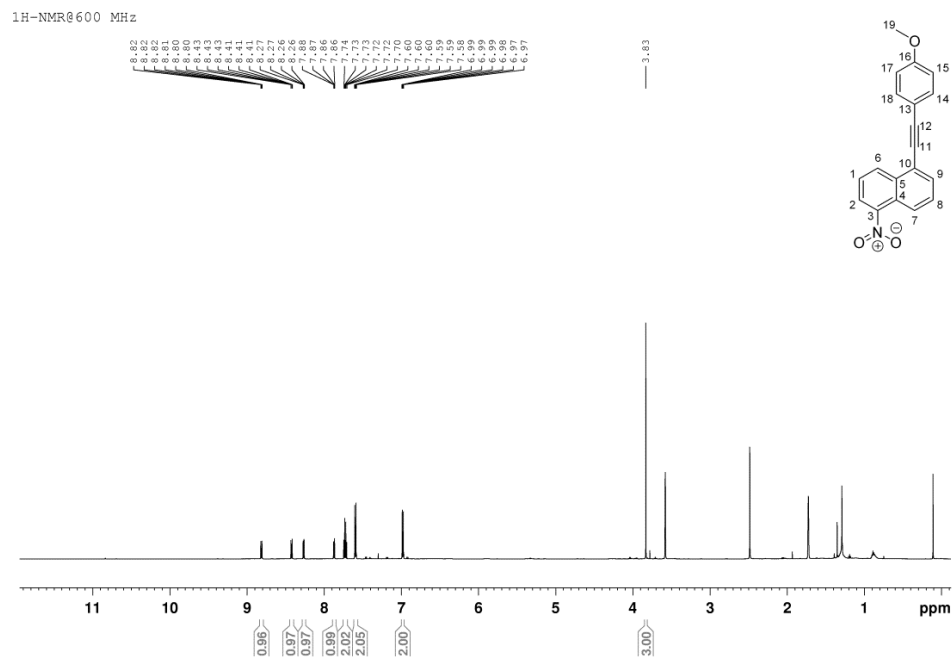
9.5 1-Nitro-5-(phenylethynyl)naphthalene (5)



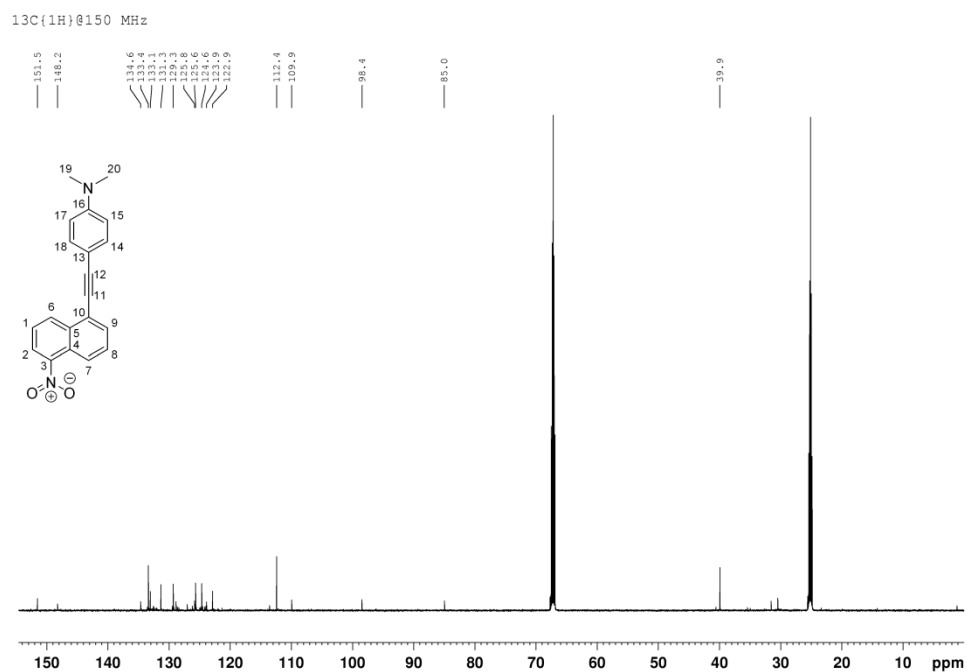
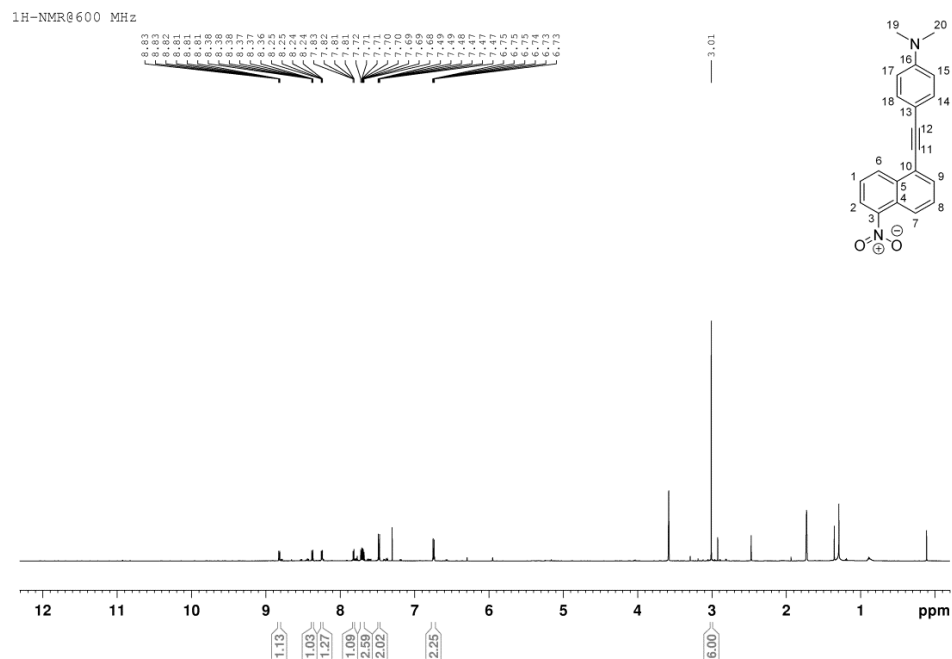
9.6 9-((5-Nitronaphthalen-1-yl)ethynyl)anthracene (6)



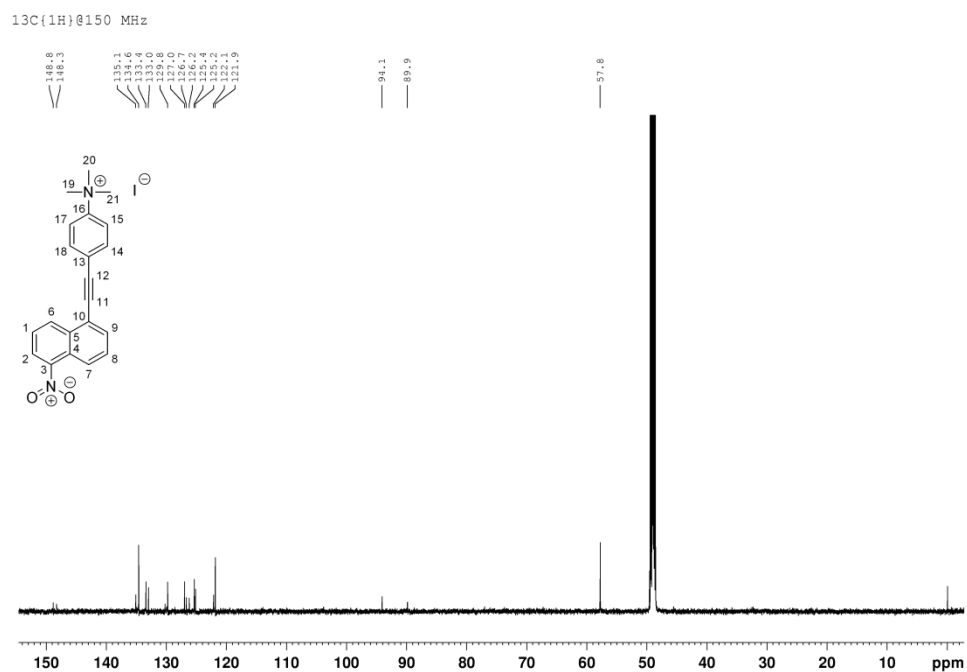
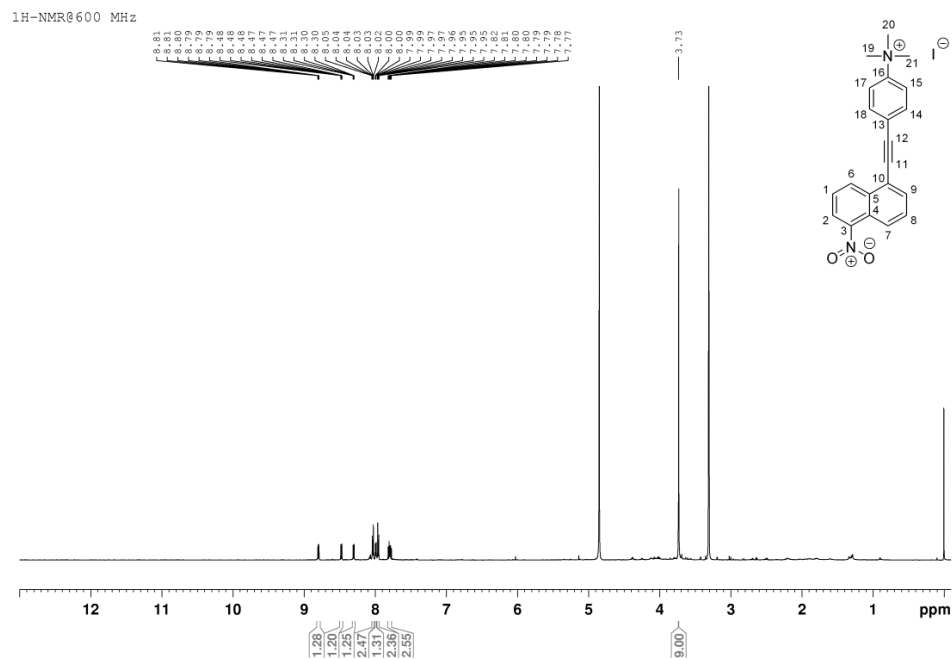
9.7 1-((4-Methoxyphenyl)ethynyl)-5-nitronaphthalene (7)



9.8 *N,N*-Dimethyl-4-((5-nitronaphthalen-1-yl)ethynyl)aniline (8)



9.9 *N,N,N*-Trimethyl-4-((5-nitronaphthalen-1-yl)ethynyl)phenylammonium iodide (9)



10. References

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