Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Air-tolerant polymer gel-immobilized iridium photocatalyst with pumping recyclability properties

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1 Experimental Section

1.1 Material and Methods

Chemicals were used without further purification and were purchased from ABCR, Acros, Sigma Aldrich, TCI or Merck. Reactions with oxygen- or moisture-sensitive reagents occurred in dry glassware, which was heated under vacuum and cooled under nitrogen atmosphere for three times. Degassed and dry solvents were used where necessary. For thin-layer chromatography pre-coated TLC-sheets ALUGRAM® Xtra SIL G/UV_{254} were used and the visualization was accomplished with UV (254 nm and 365 nm) lights. Column chromatography was performed using silica gel with particle size 63 – 200 µm and where needed flash chromatography with a particle size of 40–63 µm. High resolution mass spectra (HRMS) were obtained from the central analytic mass spectrometry facilities of the Faculty of Chemistry and Pharmacy, Regensburg University and are reported according to the IUPAC recommendations 2013.

The NMR spectra were measured with a Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{19}F: 376 MHz) or Bruker Avance 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz, ^{19}F: 282 MHz). Chemical shifts δ are reported in the unit parts per million [ppm]. The coupling constant *J* is given in the unit Hertz [Hz]. The definition of the ^{1}H NMR splitting pattern is as follows: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. The integral under a signal displays the relative number of nuclei.

1.2 Measurement of swelling kinetics

The swelling ratio at equilibrium is defined as the ability to absorb solvent into the cavities of the gel matrix in comparison to its dry weight until a constant value. For gravimetric measurements of the swelling ratio values a small piece (50 - 100 mg) of gel was taken in a 50 mL beaker and subjected to DI H_2O at room temperature for 24 h to obtain the maximum swelling ratio value. The swollen piece of gel was taken out from the Water carefully and dabbed with wet tissue paper to remove excess of solvent and weighed on a petri dish. The swelling ratio was calculated from the following equation:

$$Swelling\ ratio\ (\%) = \frac{W_t - W_d}{W_d} \cdot 100$$

where W_t is the weight of the swollen gel at a given time t and W_d is the weight of the dry gel piece.[1]

1.3 Iridium leaching studies

The sample was transferred to a 25 mL NS29 round bottom flask equipped with a magnetic stirrer and heated to 100 °C until all the solvent residues were evaporated under a stream of N_2. The brown residues were treated with 2 mL of 65% nitric acid and boiled for about 5 min until the evolution of nitrous gases stopped. After that 2 mL of conc. sulfuric acid were added and again the solution was boiled at 150 °C for further 5 min until the evaporation of nitrous gases stopped. Afterward, the sample was treated with another 2 mL of 65% nitric acid and boiled for 10 min until a fully homogeneous orange solution was reached. The sample cooled to room temperature and was diluted with distilled water to a total volume of 10.0 mL, filtered with a 0.2 µm PES membrane syringe filter and measured in the ICP-OES apparatus.

1.4 Irradiation device

Photochemical reactions were performed using a custom-made set-up (**Error! Reference source not found.**) with an array of suitable LEDs (3.5 V, 700 mA), i.e. λ_{ex} = 365 ± 15 nm, λ_{ex} = 455 ± 15 nm, λ_{ex} = 530 ± 15 nm. The yields reported are referred to the isolated compounds unless otherwise stated. Oxygen- and moisture-free reactions were carried out with dry and degassed solvents, as well as glassware subjected to several evacuation (vacuum)/refill (nitrogen) cycles.

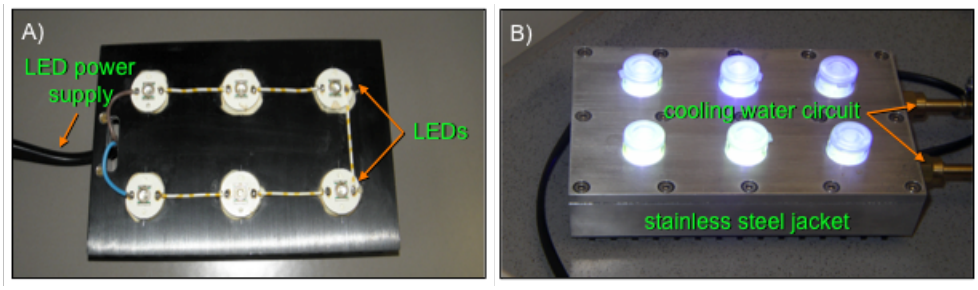
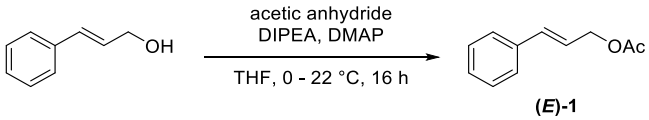


Fig. S1 Custom made irradiation device. A) Array of six LEDs connected to a power supply. B) Set-up with a stainless-steel jacket to maintain refrigeration of the vials (5 mL). The distance between the LEDs and the reaction vials is adjusted to 0.9 ± 0.1 cm. The apparatus also allows magnetic stirring of the reaction mixtures.

1.5 Synthesis of the starting materials

1.5.1 (*E*)-Cinnamyl acetate **(*E*)-1**

The titled compound was synthesized according to the procedure from the literature with minor adaptations.[2]

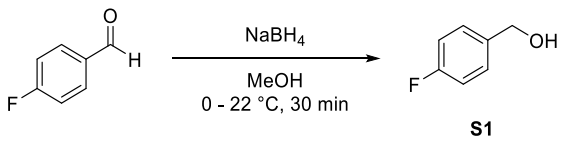


To a 100 mL round bottom flask equipped with magnetic stir bar was added cinnamyl alcohol (3.95 g, 29.44 mmol, 1.0 equiv.), 22 mL THF, acetic anhydride (3.33 m L, 35.33 mmol, 1.2 equiv.), 4-dimethylamino pyridine (DMAP), (18 mg, 147.19 µmol, 0.005 equiv.), and triethylamine (7.4 mL, 53 mmol, 1.8 equiv.). The reaction mixture was stirred at 0 °C for 1 h and then warmed to room temperature and stirred for 16 h. The reaction was monitored by TLC. After the complete consumption of the starting material the solvent was removed under vacuum. The residual oil was diluted with EtOAc. The organic layer was then washed with brine 3x and distilled water 3x and then dried over Na_2SO_4 to obtain the desired cinnamyl acetate **(*E*)-1** as a yellow oil (4.85 g, 93 %) which was used without further purification.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 5H), 6.66 (d, *J* = 15.9 Hz, 1H), 6.29 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.73 (dd, *J* = 6.4, 1.3 Hz, 2H), 2.10 (s, 3H).

1.5.2 4-Fluorobenzyl alcohol **S1**

The titled compound was synthesized according to the procedure from the literature with minor adaptations.[3]

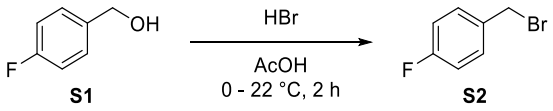


S1

To a round bottom flask equipped with a magnetic stir bar was added 4-fluorobenzaldehyde (4.0 g, 32.2 mmol), MeOH (60 mL) and then the mixture was cooled to 0 °C. Sodium borohydride ($NaBH_4$) (1.34 g, 35.45 mmol) was added portion-wise, and the reaction mixture was allowed to warm to room temperature and stirred for 30 min. The progress of reaction was monitored by TLC. After the complete consumption of the starting material, the reaction mixture was quenched with saturated NH_4Cl, and the solvent volume was reduced under vacuum. The residue left behind was diluted with water (50 mL) and extracted with ethyl acetate (EtOAc) (3 x 100 mL). The organic layer was separated and dried over Na_2SO_4. The solvent was evaporated to yield 4-fluorobenzyl alcohol **S1** (3.95 g, 97 %) which was used without further purification.

1.5.3 4-Fluorobenzyl bromide **S2**

The titled compound was synthesized according to the procedure from the literature with minor adaptations.[3]

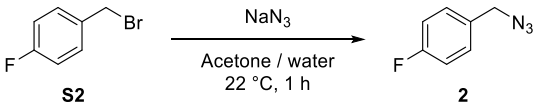


S1 **S2**

To a round bottom flask equipped with a magnetic stir bar was added 4-fluorobenzyl alcohol **S1** (3.95 g, 31.3 mmol), hydrogen bromide (62 %) (50 mL), and acetic acid (100 %) (10 mL) at 0 °C and the reaction mixture was warmed to room temperature and stirred for 2 h. The progress of the reaction was monitored by TLC. After the complete consumption of the starting material the reaction mixture was quenched by sat. Na_2CO_2 and extracted with EtOAc (2 x 100 mL). The organic layer was separated, dried over Na_2SO_4 and the solvent was evaporated to yield 4-fluorobenzyl bromide **S2** (4.22 g, 71 %), which was used without further purification.

1.5.4 1-(Azidomethyl)-4-fluorobenzene **2**

The titled compound was synthesized according to the procedure from the literature with minor adaptations.[3]



S2 **2**

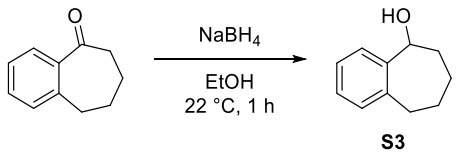
To a round bottom flask equipped with a magnetic stir bar was added 4-fluorobenzyl bromide **S2** (4.22 g, 22.32 mmol), 4:1 acetone/water (88 mL: 22 mL) and sodium azide (2.18 g, 33.49 mmol). The reaction mixture was stirred at room temperature for 1 h and was then diluted with CH_2Cl_2 (200 mL) and washed with dist. water (2 x 50 mL). The organic layer was dried over $MgSO_4$ and concentrated to obtain the product **2** as a slightly yellow liquid (3.1 g, 92 %) which was used without further purification. The ^{1}H NMR data was in accordance with the literature.[5]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 7.14 – 7.01 (m, 2H), 4.32 (s, 2H).

^{19}F NMR (282 MHz, $CDCl_3$) δ -114.04 (ddd, J = 13.9, 8.6, 5.3 Hz).

1.5.5 6,7,8,9-Tetrahydro-5H-benzo[7]annulen-5-ol **S3**

The titled compound was synthesized according to the procedure from the literature with minor adaptations.[3]

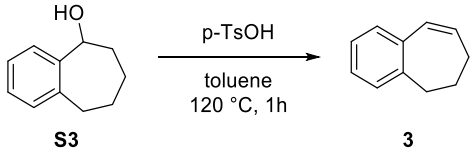


To a round bottom flask equipped with a magnetic stir bar was added 1-benzosuberone (2.0 g, 12.48 mmol) and EtOH (0.25 M). $NaBH_4$ (568 mg, 14.98 mmol) was then added to the reaction mixture portion-wise under an N_2 atmosphere and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was then quenched with 1N HCl (15 mL). The solvent was removed under reduced pressure and the crude material was diluted with CH_2Cl_2 (50 mL) and washed with dist. H_2O (2 x 10 mL). The organic layer was separated, dried over Na_2SO_4, and concentrated to obtain a white solid **S3** (1.97 g, 97 %) which was used without further purification. The ^{1}H NMR data was in accordance with the literature.[6]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 1H), 7.19 (dtd, *J* = 16.3, 7.3, 1.6 Hz, 2H), 7.10 (dd, *J* = 7.2, 1.6 Hz, 1H), 4.97 – 4.90 (m, 1H), 2.93 (dd, *J* = 13.6, 8.6 Hz, 1H), 2.72 (ddd, *J* = 14.2, 10.5, 1.6 Hz, 1H), 2.14 – 1.69 (m, 6H), 1.55 – 1.40 (m, 1H).

1.5.6 6,7-Dihydro-5H-benzo[7]annulene **3**

The titled compound was synthesized according to the procedure from the literature with minor adaptations.[3]

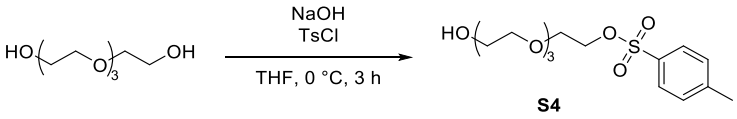


To a round bottom flask equipped with a magnetic stir bar was added 6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ol **S3** (2.0 g, 12.32 mmol), toluene (30 mL) and *p*-toluenesulfonic acid monohydrate (234.4 mg, 1.24 mmol). The reaction mixture was refluxed for 1 h. After reaction completion (monitored by TLC), sat. $NaHCO_3$ (100 mL) was added and the resulting mixture was extracted with ethyl acetate EtOAc (2 x 100 mL). The combined organic layer was washed with brine (100 mL), dried over Na_2SO_4, and concentrated to obtain a brown liquid. This liquid was purified by column chromatography using hexanes as eluent (R_f = 0.51) obtaining the product **3** as a clear liquid (1.3 g, 73 %). The ^{1}H NMR data was in accordance with the literature.[7]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.12 (m, 4H), 6.48 (dt, *J* = 12.2, 2.1 Hz, 1H), 5.96 (dt, *J* = 12.2, 4.5 Hz, 1H), 2.94 – 2.87 (m, 2H), 2.48 (tdd, *J* = 6.6, 4.5, 2.1 Hz, 2H), 2.10 – 1.96 (m, 2H).

1.5.7 Tetraethylene glycol monotosylate (**PEG_4-OTs**) **S4**

The titled compound was synthesized according to the procedure from the literature with minor adaptations.[3]

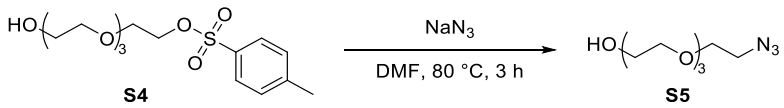


Tetraethylene glycol (36 ml, 206 mmol) was dissolved in THF (40 mL) and cooled to 0 °C. Then, 2 M NaOH aq. (10.3 mL) was slowly added to the solution and stirred for a further 1 h. *p*-TsCl (3.93 g, 20.6 mmol) dissolved in 2 mL THF was added dropwise to the reaction mixture and stirred for further 2 h at 0 °C. After removal of the solvent, the residue was dissolved in CH_2Cl_2, washed with water and brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by silica column chromatography and **S4** was eluted with EtOAc as a slightly yellow oil (7.0 g, 98 %). The ^{1}H NMR data was in accordance with the literature.[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.17 – 4.12 (m, 2H), 3.73 – 3.53 (m, 14H), 2.53 (s, 1H), 2.43 (s, 3H).

1.5.8 11-Azido-3,6,9-trioxaundecanol (**PEG_4-N_3**) **S5**

The titled compound was synthesized according to the procedure from the literature with minor adaptations.[3]

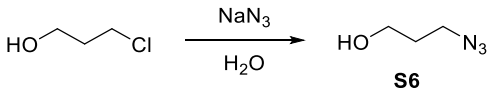


PEG_4-OTs S4 (7.0 g, 20.9 mmol) was dissolved in DMF (50 mL), then sodium azide (6.53 g, 100.5 mmol) was added. The reaction mixture was stirred at 80 °C for 3 h. After filtering, EtOAc and water were added to the mixture. The combined organic phases were washed with water and brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by silica column chromatography and **PEG_4-N_3 S5** was eluted with EtOAc as a slightly yellow oil (2.7 g, 61 %). The ^{1}H NMR data was in accordance with the literature.[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.75 – 3.57 (m, 14H), 3.39 (t, J = 5.2 Hz, 2H), 2.31 (s, 1H).

1.6 Synthesis of the monomer (AzpMA) S7

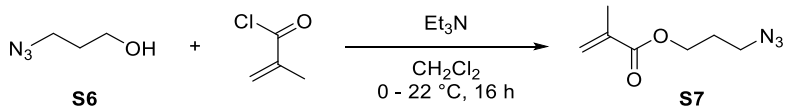
1.6.1 Synthesis of 3-azidopropan-1-ol **S6**



To a solution of NaN_3 (9.33 g, 143.6 mmol, 2 equiv.) containing distilled water (140 mL) was added 3-chloropropan-1-ol (6.79 g, 6 mL, 71.8 mmol, 1 equiv.) slowly by syringe and the mixture was refluxed for 16 h. The mixture was cooled to room temperature and extracted with CH_2Cl_2 (160 mL x 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude product mixture was achieved by silica gel column chromatography using hexanes/EtOAc (7:3, R_f = 0.46) solvent mixtures to obtain the titled compound 3-azidopropan-1-ol **S6** as a colorless liquid (5.96 g, 82 %). The ^{1}H NMR data was in accordance with the literature.[11]

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.75 (t, *J* = 6.0 Hz, 2H), 3.45 (t, *J* = 6.6 Hz, 2H), 1.83 (p, *J* = 6.5 Hz, 2H), 1.72 (s, 1H).

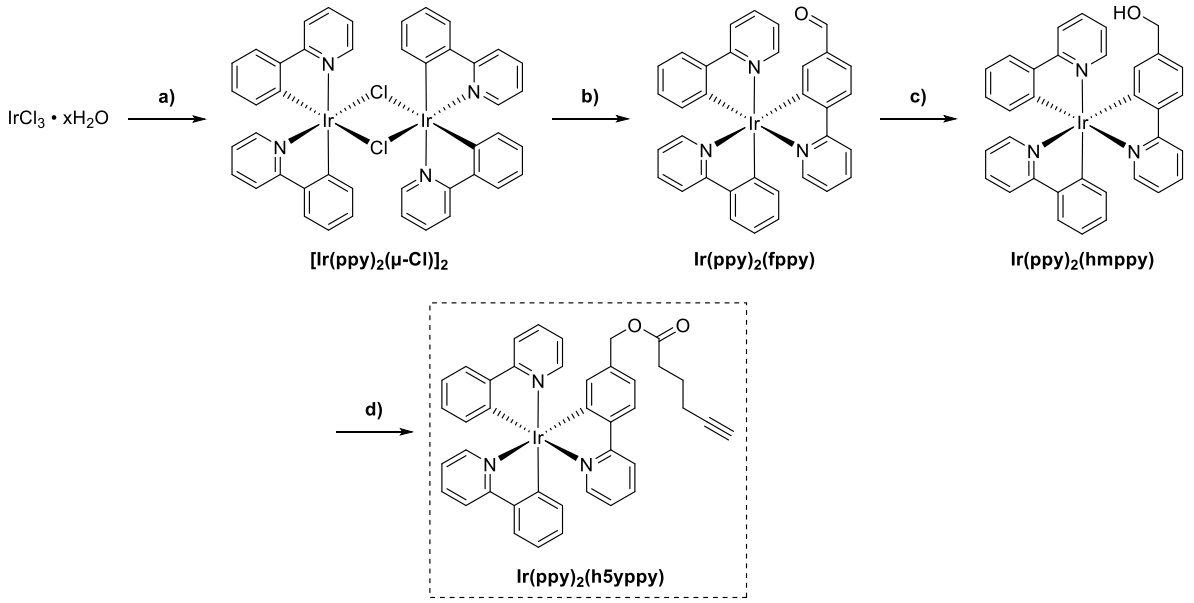
1.6.2 Synthesis of 3-azidopropyl methacrylate (**AzpMA**) **S7**



3-Azidopropan-1-ol (3.0 g, 29.7 mmol, 1.0 equiv.) and hydroquinone (12 mg, 0.4 g/mol) were mixed in anhydrous CH_2Cl_2 (35 mL) under N_2 atmosphere. At 0 °C triethylamine (6.2 mL, 44.6 mmol, 1.5 equiv.) and methacryloyl chloride (3.2 mL, 32.7 mmol, 1.1 equiv.) were added dropwise by syringe and the mixture was stirred for 1 h under 0 °C. The mixture warmed to room temperature and was continued stirring for 16 h. Afterwards all the volatiles were evaporated under reduced pressure and purification of the crude product mixture was achieved by silica gel column chromatography using hexanes /EtOAc (gradient from 10:1 to 3:1, R_f = 0.46) solvent mixtures to obtain the titled compound 3-azidopropyl methacrylate **S7** as a slightly orange/yellow oil (4.95 g, 98 %). The product was stored in freezer. The ^{1}H NMR data was in accordance with the literature.[12]

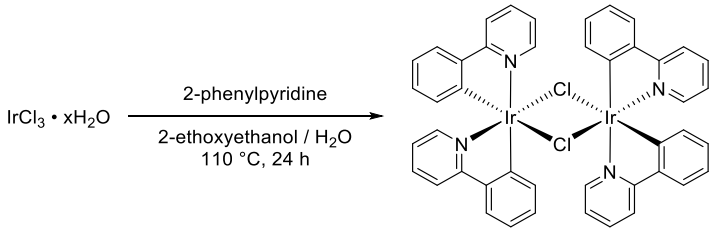
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.10 (dt, *J* = 1.8, 0.9 Hz, 1H), 5.58 (p, *J* = 1.6 Hz, 1H), 4.24 (t, *J* = 6.2 Hz, 2H), 3.41 (t, *J* = 6.7 Hz, 2H), 1.99 – 1.92 (m, 5H).

1.7 Synthesis of the catalyst Ir(ppy)$_2$(h5yppy)



Scheme S1 Reaction conditions: a) 2-Phenylpyridine, 2-ethoxyethanol/water, 110 °C, 24 h. b) $AgCF_3SO_3$, 4-(pyridin-2-yl)benzaldehyde, DMac, 130 °C, 5 h. c) $NaBH_4$, CH_2Cl_2/EtOH, 22 °C, 12 h. d) Hex-5-ynoic acid, DCC, CH_2Cl_2, 50 °C, 48 h.

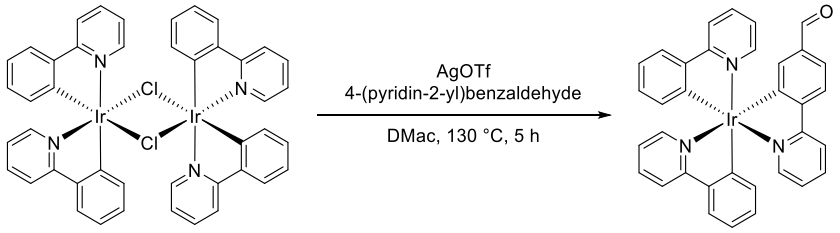
1.7.1 Tetrakis(2-phenylpyridine-$C^2,N^{'}$)(μ-dichloro)diiridium **[Ir(ppy)$_2$(μ-Cl)]$_2$**



Iridium trichloride hydrate (0.78 g, 2.46 mmol) was combined with 2-phenylpyridine (1.55 g, 10 mmol), dissolved in a mixture of 2-ethoxyethanol (50 mL) and water (20 mL) and refluxed for 24 h. The solution was cooled to room temperature and the yellow precipitate was collected on a glass filter frit (P3). The precipitate was washed with ethanol (120 mL) and then dissolved in CH_2Cl_2, filtered and precipitated into hot hexane. The yellow compound was collected and dried in vacuo. The product was obtained as a bright yellow powder (835.9 mg, 63 %). The ^{1}H NMR data was in accordance with the literature.[8]

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.24 (dd, *J* = 5.8, 0.9 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.74 (td, *J* = 7.8, 1.6 Hz, 1H), 7.49 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.81 – 6.71 (m, 2H), 6.56 (td, *J* = 7.5, 1.4 Hz, 1H), 5.93 (dd, *J* = 7.8, 0.9 Hz, 1H).

1.7.2 *fac*-Bis[[2-(2-pyridyl)phenyl]4-(pyridin-2-yl)benzaldehyde]-iridium(III) **Ir(ppy)$_2$(fppy)**

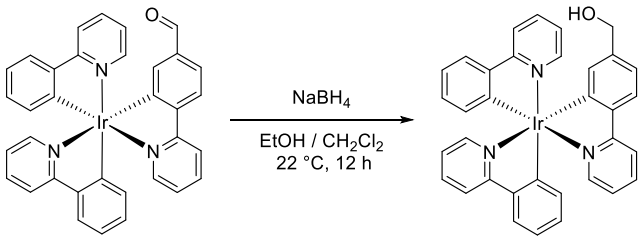


To a 2-neck, 100 mL Schlenk flask equipped with a magnetic stir bar was added Dimer, (1.0 g, 0.93 mmol), AgOTf (1.20 g, 4.66 mmol) and dimethylacetamide (DMac) (40 mL) (dried over CaH_2 and distilled into heated in vacuo MS 4Å). The mixture was degassed with N_2 for 10 minutes, heated to 100 °C for 30 minutes, followed by the addition of 4-(pyridin-2-yl)benzaldehyde (0.43 g, 2.33 mmol) through a stream of N_2. The reaction was then heated to 130 °C for 5 h, cooled to room temperature and filtered and washed with acetonitrile to remove silver salts. The filtrate was added to deionized H_2O (200 mL) and the resulting precipitate was filtered, then dissolved in CH_2Cl_2 (50 mL) and washed with deionized H_2O (3 x 50 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure to yield an orange-brown solid. The crude product was purified by column chromatography on silica-gel, eluting with a gradient starting at 1:1 and ending at 0:1 hexanes / CH_2Cl_2. The solvent was removed by rotary evaporation (and the resulting solid was precipitated from CH_2Cl_2 into hot hexane to provide the desired product after filtration) as a bright red powder (607 mg, 48 % yield). The ^{1}H NMR data was in accordance with the literature.[9]

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.62 (s, 1H), 8.32 (d, *J* = 8.2 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 2H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.88 (td, *J* = 7.9, 1.5 Hz, 1H), 7.79 (q, *J* = 7.4, 6.3 Hz, 4H), 7.57 (d, *J* = 5.5 Hz, 1H), 7.47 (d, *J* =

5.5 Hz, 2H), 7.33 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.26 (ddd, *J* = 7.1, 5.6, 1.0 Hz, 1H), 7.20 – 7.10 (m, 3H), 6.88 – 6.78 (m, 2H), 6.77 – 6.64 (m, 3H), 6.55 (dd, *J* = 7.5, 1.1 Hz, 1H).

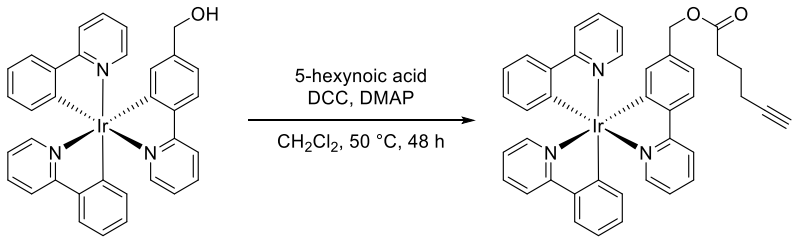
1.7.3 *fac*-Bis[[2-(2-pyridyl)phenyl](4-(pyridin-2-yl)phenyl)methanol]-iridium(III) **Ir(ppy)$_2$(hmppy)**



To a 1-neck 250 mL round-bottom flask equipped with a magnetic stir bar and septum was added Ir(ppy)$_2$fppy (607 mg, 0.879 mmol), dry CH_2Cl_2 and dry EtOH (70 mL each) followed by $NaBH_4$ (44 mg, 1.14 mmol). The mixture was degassed with N_2 for 10 minutes then stirred for 16 h at room temperature. The solvent was removed under reduced pressure and the resulting yellow solid was re-dissolved in CH_2Cl_2 (50 mL) and washed with dist. H_2O (3 x 50 mL). The water phase was extracted with CH_2Cl_2 (2 x 50 ml) and the combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure to yield a yellow solid (566 mg, 826 mmol, 94 %). The ^{1}H NMR data was in accordance with the literature.[9]

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.18 – 8.06 (m, 3H), 7.76 (m, 6H), 7.49 – 7.42 (m, 3H), 7.16 – 7.06 (m, 3H), 6.87 – 6.76 (m, 3H), 6.73 – 6.58 (m, 5H), 4.83 (t, *J* = 5.7 Hz, 1H), 4.23 – 4.06 (m, 2H).

1.7.4 *fac*-Bis[[2-(2-pyridyl(phenyl)]4-(pyridin-2-yl)benzylhex-5-ynoate]-iridium(III) **Ir(ppy)$_2$(h5yppy)**



A mixture of Ir(ppy)$_2$(hmppy) (hmppy = hydroxymethyl-ppy) (0.20 g, 0.29 mmol), 5-hexynoic acid (0.15 g, 1.17 mmol), dicyclohexylcarbodiimide (DCC) (0.28 g, 1.36 mmol), and dimethylaminopyridine (DMAP) (0.02 g, 0.16 mmol) in CH_2Cl_2 (50 mL) was refluxed for 48 h under an N_2 atmosphere. After cooling the reaction to room temperature, the precipitate was filtered off with a glass filter (P3). The filtrate was collected into CH_2Cl_2, concentrated and precipitated into a large volume of cold methanol. The residue was collected by filtration and washed with cold MeOH to give the final compound as a yellow solid (0.18 g, 79 %). The ^{1}H NMR data was in accordance with the literature.[10]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 3H), 7.69 – 7.45 (m, 9H), 6.96 – 6.80 (m, 10H), 6.77 (d, *J* = 1.5 Hz, 1H), 4.92 (s, 2H), 2.40 (t, *J* = 7.5 Hz, 2H), 2.23 (td, *J* = 6.9, 2.6 Hz, 2H), 1.95 (t, *J* = 2.6 Hz, 1H), 1.79 (p, *J* = 7.0 Hz, 2H).

1.8 General procedure of the synthesis of G1(Ir)-G3(Ir)

All cross-linked gels were synthesized in the presence of AIBN as radical source and DEGDMA as cross-linker in a septum sealed 20 mL glass vial. A typical example of gel synthesis is as follows: $PEGMA_{300}$ (896 mg), AzpMA (58 mg), DEGDMA (8.7 mg) and AIBN (0.6 mg) and 0.5 mL of anhydrous DMF were taken into a dry 20 mL septum sealed vial. The reaction vial was purged with nitrogen for 10 min and the gelation reaction was carried out in a preheated reaction block at 70 °C for 16 h.

1.8.1 Purification of **G1-G3**. Procedure I

All gels were collected from the reaction vial by breaking the glass vial carefully and unreacted monomers, cross-linkers and DMF residues were removed by soaking the gel in acetone (150 mL) for 48 h. The acetone was replaced 3 times a day. Finally, all gels were dried under high vacuum for three days.

1.8.2 Immobilization of $Ir(ppy)_2$(h5yppy) into **G1-G3**

In a 20 mL septum sealed vial $Ir(ppy)_2$(h5yppy) (26 mg) and Cu(I)I (5 mg) was dissolved in 3.5 x m_{Gel} mL of DMF a stream of N_2 was passed through the solution. Then under a stream of N_2 the cross-linked gel was placed into the vial, sealed and the gel soaked with that solution and the immobilization click reaction was carried out in a preheated reaction block at 60 °C for 48 h.

1.8.3 Purification of **G1(Ir)-G3(Ir)**. Procedure II

All gels were collected from the reaction vial carefully and unreacted iridium-catalyst and DMF residues were removed by soaking the gel in acetone (150 mL) for 48 h. The acetone was replaced 3 times a day. After that copper was removed by soaking the gel in EDTA solution (0.02 M, 100 mL) for 48 h. The solution was replaced 1 time a day. Finally, all gels were dried under high vacuum for three days. The acetone collected during this process was subjected to a recycling process of $Ir(ppy)_2$(h5yppy). The solvent was evaporated, the residues were collected into the least amount of CH_2Cl_2 (~0.5 mL), centrifuged and the supernatant was precipitated into cold methanol (100 mL) giving back $Ir(ppy)_2$(h5yppy) as a yellow powder after drying in high vacuo.

1.9 General procedure of the reaction in G1(Ir)-G3(Ir)

A piece of **G1(Ir)** (60 mg) was placed into an 8 mL septum sealed vial and a solution containing 0.25 mmol of substrate, 10 mol% DIPEA and 0.2 mL of CH_3CN was dropped by syringe onto the gel. After 15 min the soaking of the gel was finished and it was placed into the irradiation device. After irradiation with LED (λ = 455 nm) the vial was floated with acetone through a syringe (3 x 6 mL) for 24 h to remove the products from the gel. The organic phases were combined, the solvent removed, and the compounds put directly into NMR analysis.

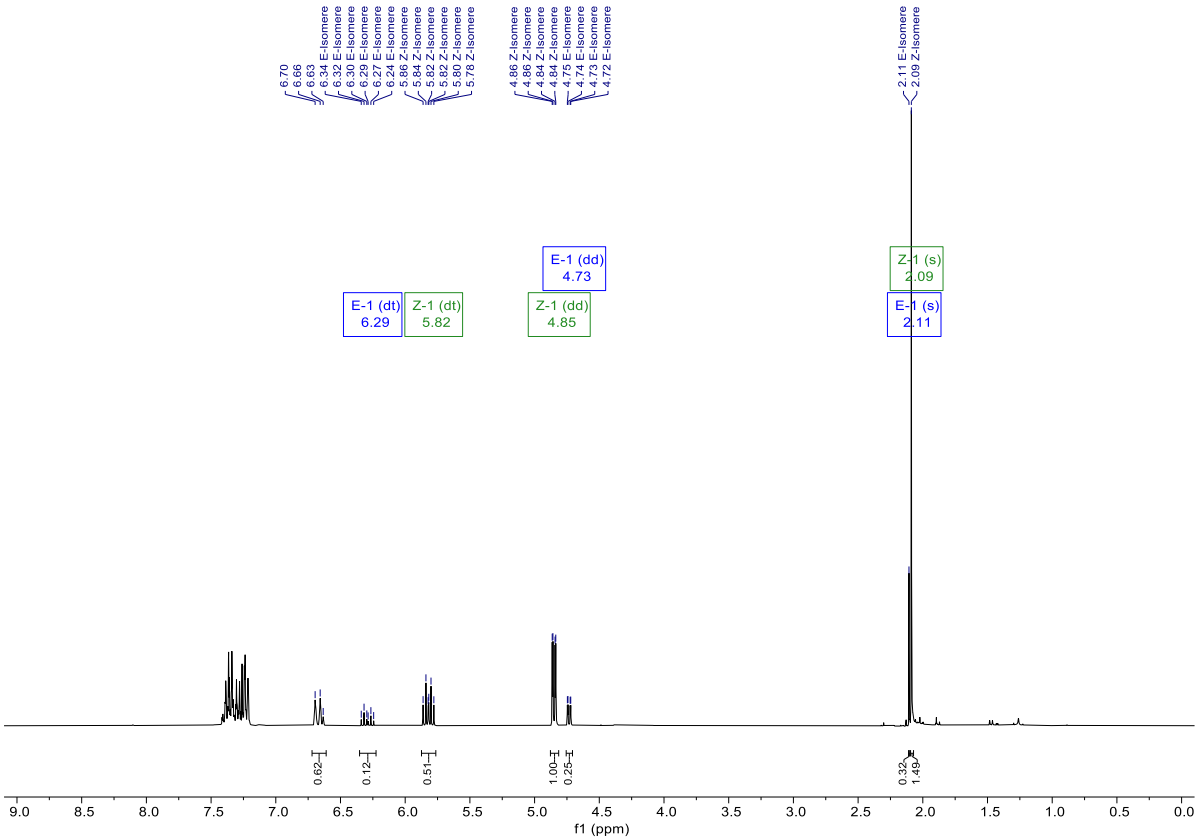


Fig. S2 Example [1]H NMR of one recycling run of the isomerization reaction in **G1(Ir).**

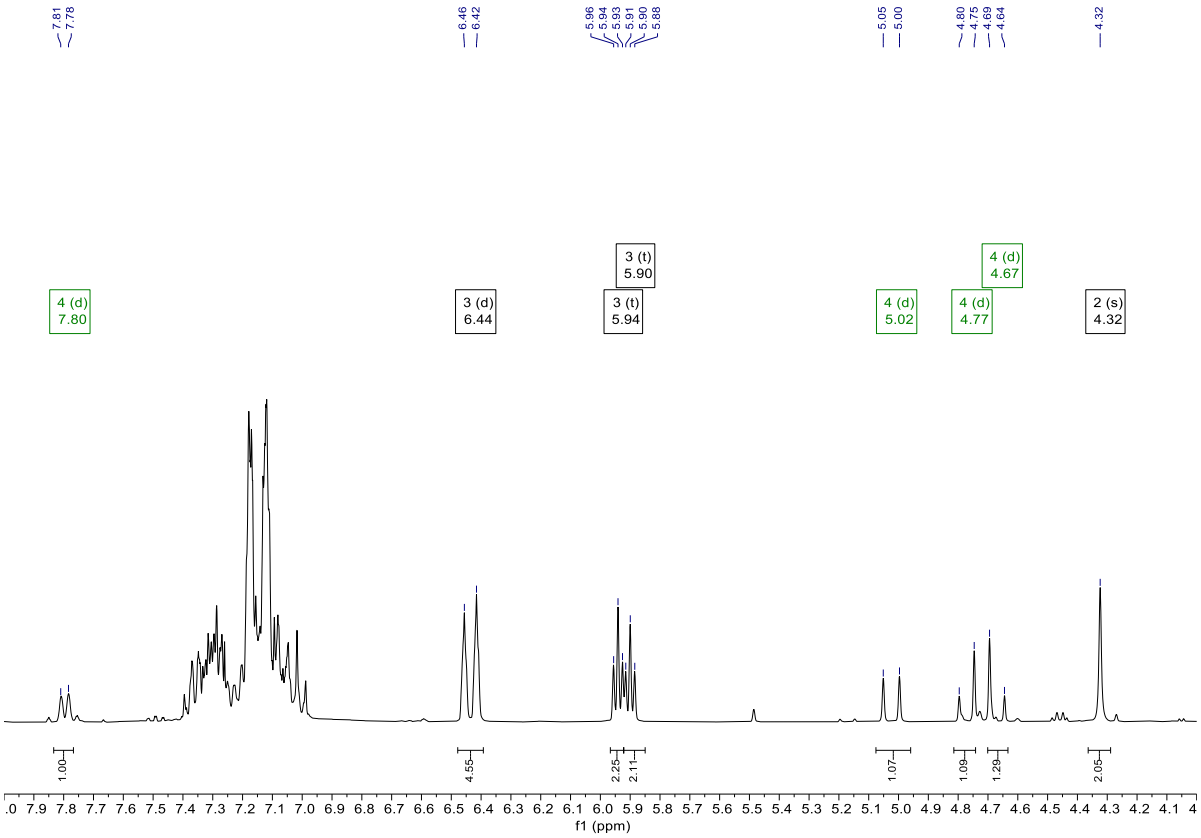


Fig. S3 Example [1]H NMR of the 3rd recycling run of the 2+3 cycloaddition reaction in **G3(Ir)**.

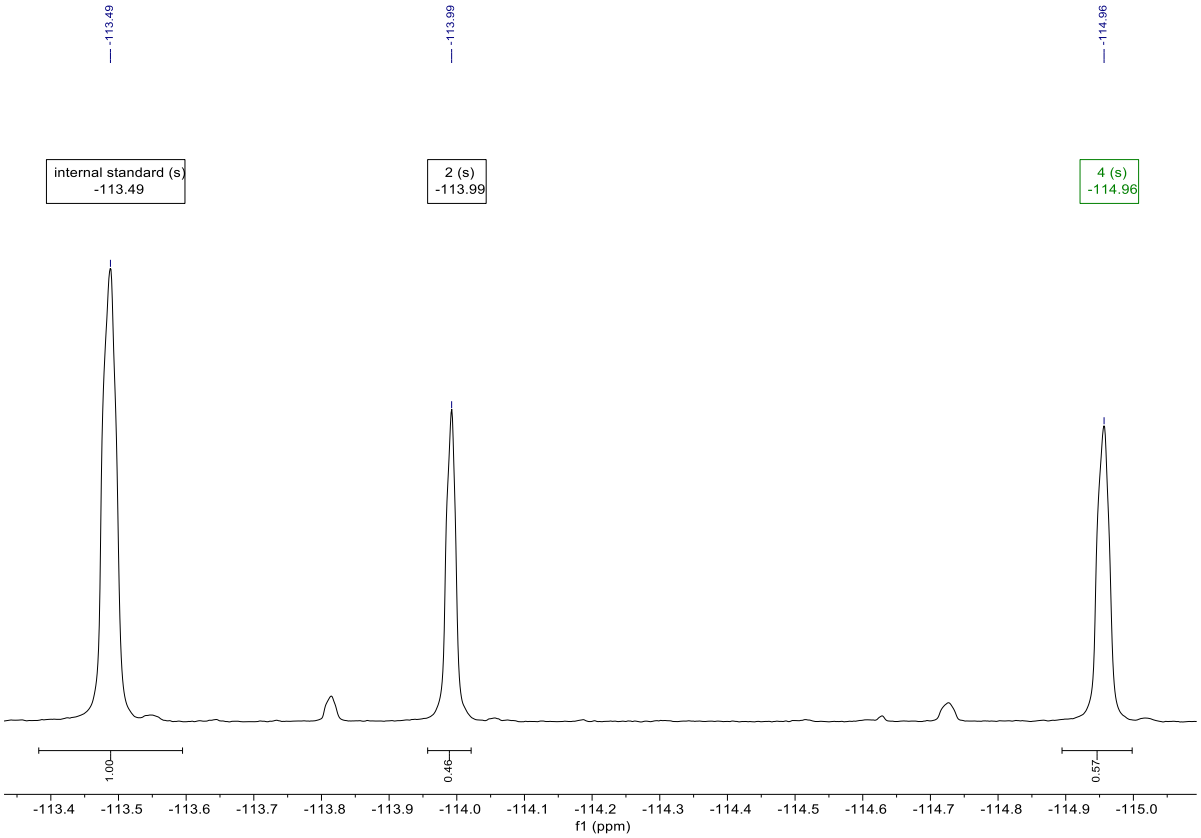


Fig. S4 Example ^{19}F NMR of the 3rd recycling run of the 2+3 cycloaddition reaction in **G3(Ir)** with 0.25 mmol of fluorobenzene as internal standard.

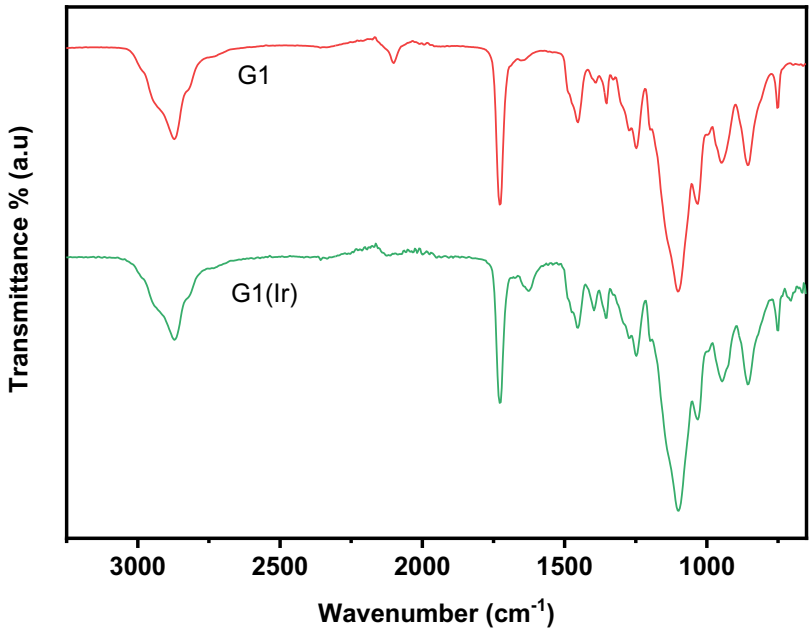


Fig. S5 FTIR spectra of **G1** before immobilization of the photocatalyst (top) and **G1(Ir)** after immobilization of photocatalyst (bottom).

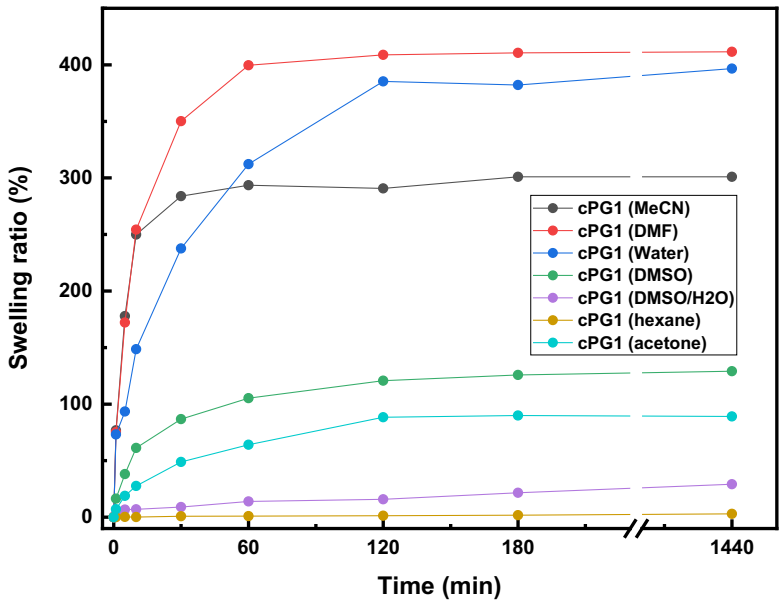
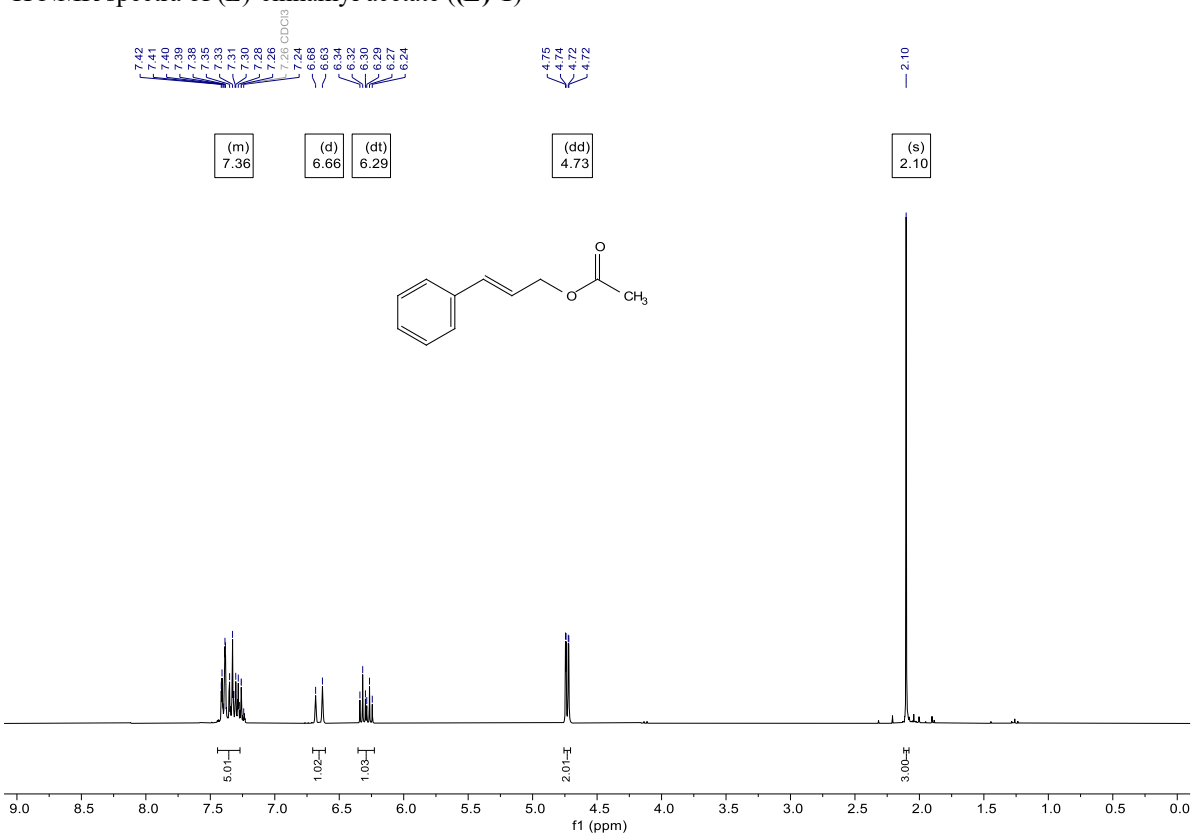


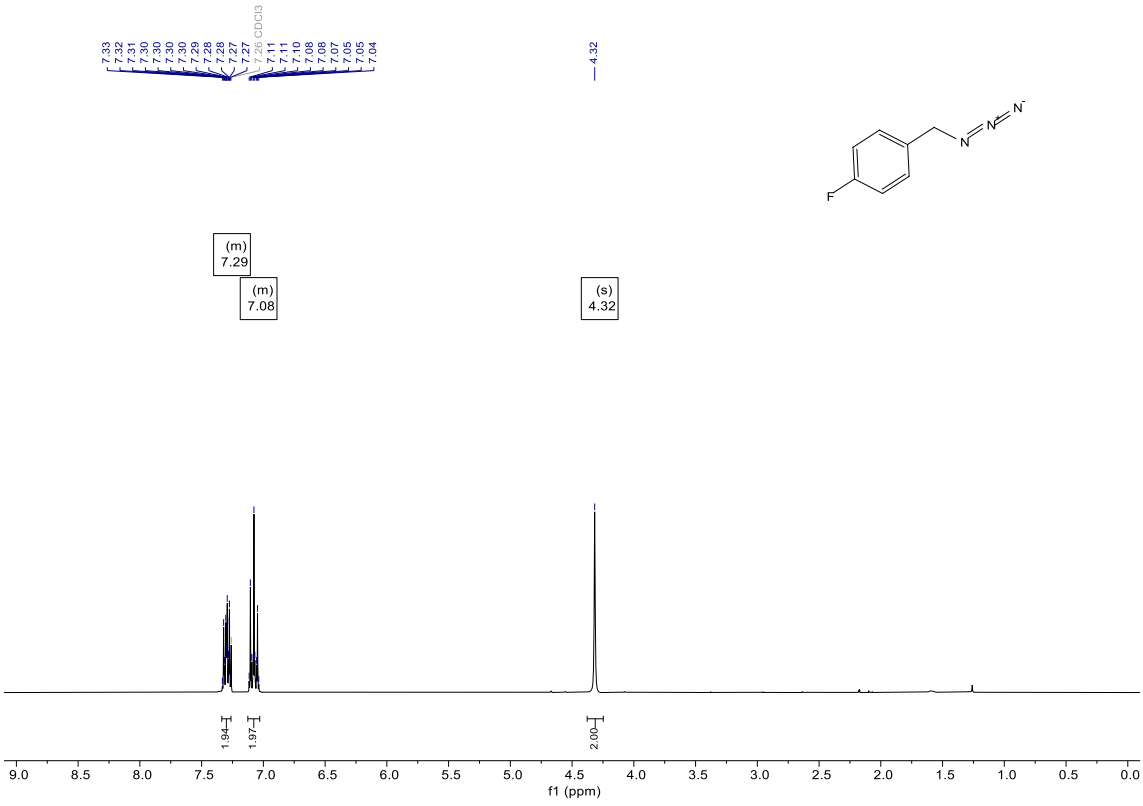
Fig. S6 Swelling properties of **G1(Ir)**.

NMR spectra

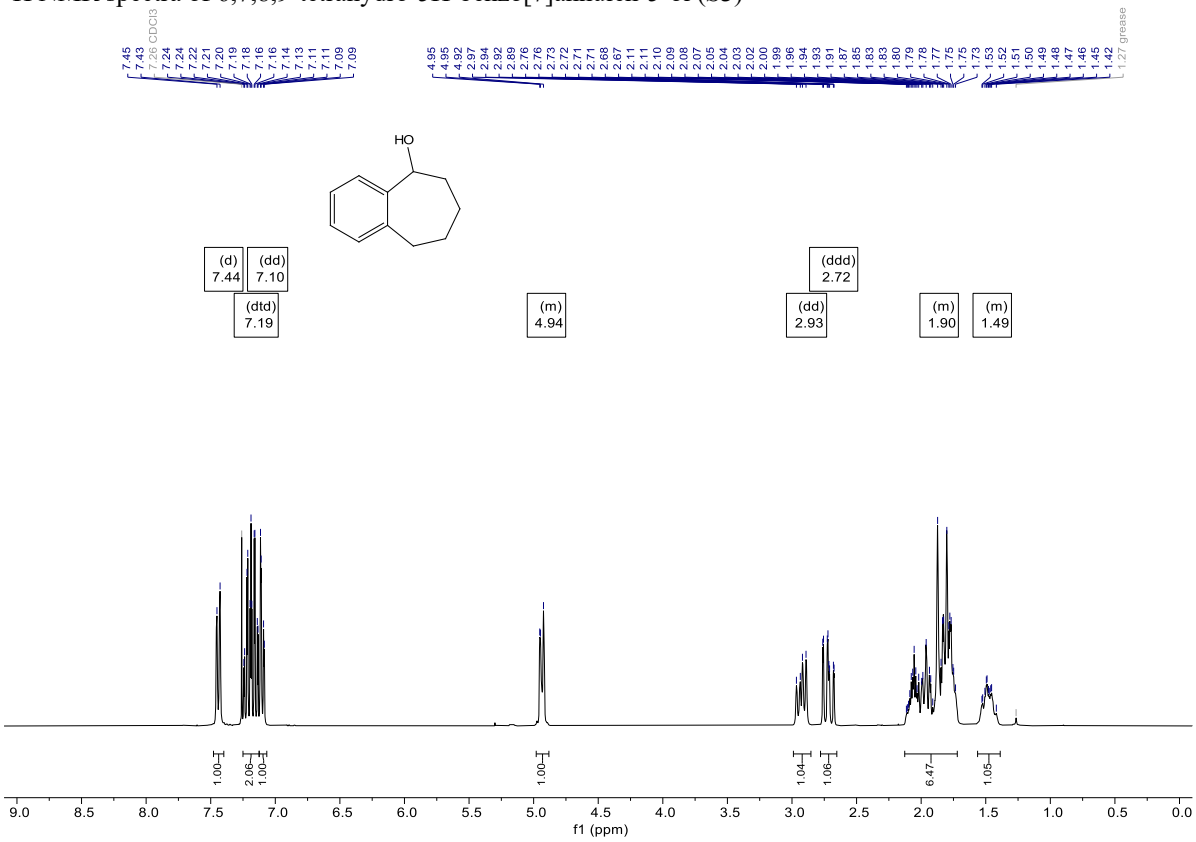
^{1}H NMR spectra of (*E*)-cinnamyl acetate ((***E***)-**1**)



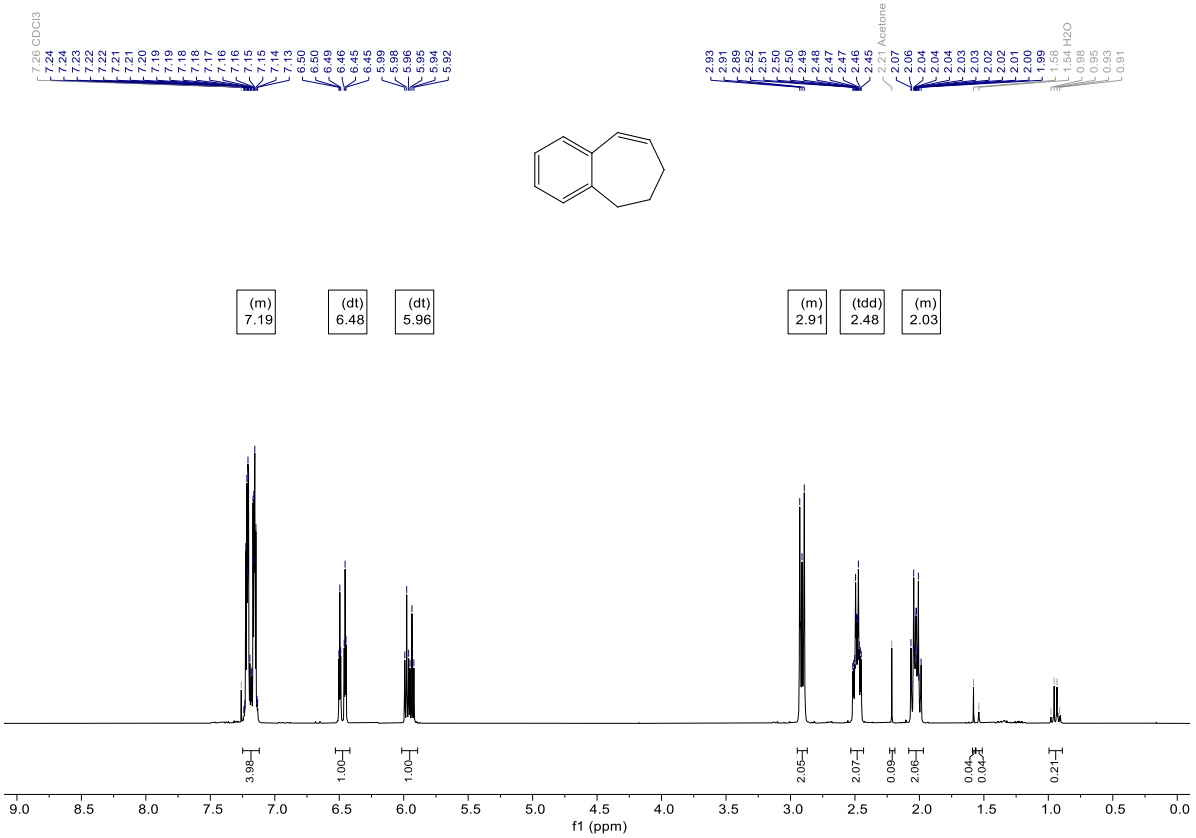
^{1}H NMR spectra of 4-flourobenzyl azide (**2**)



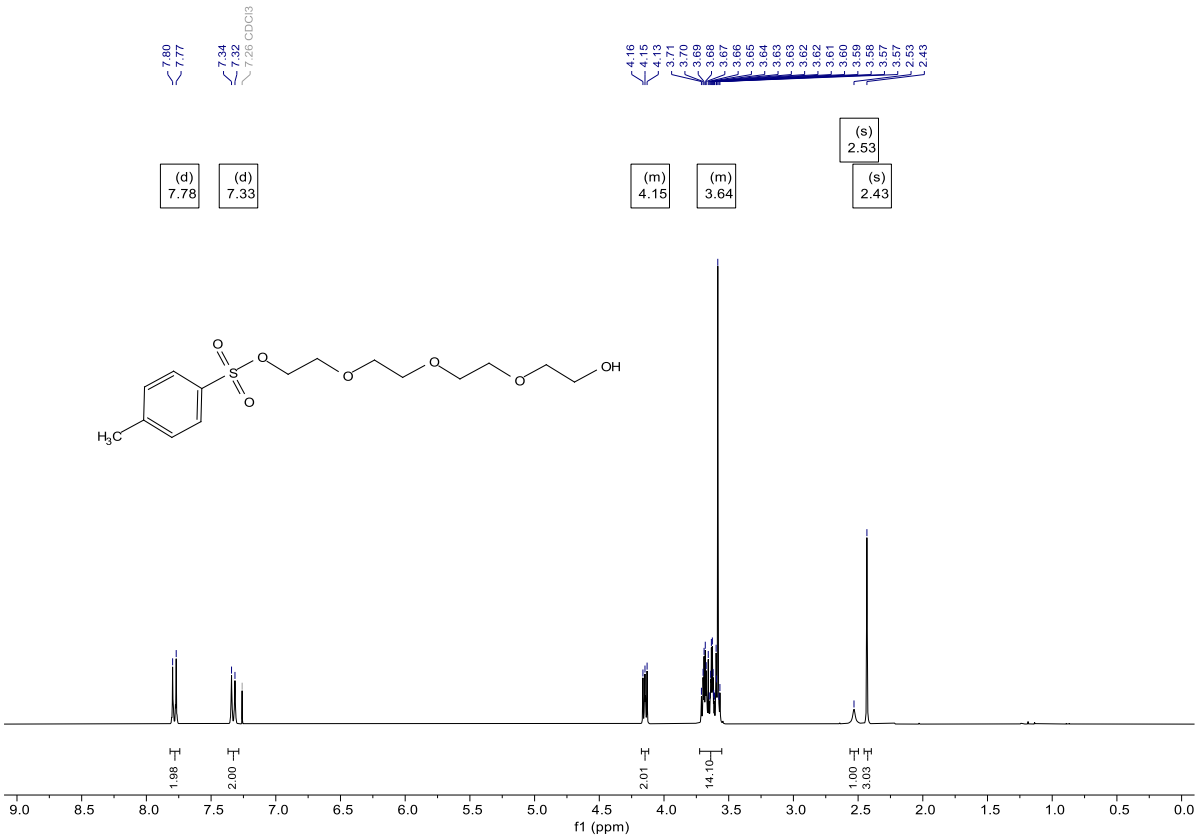
^{1}H NMR spectra of 6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ol (**S3**)



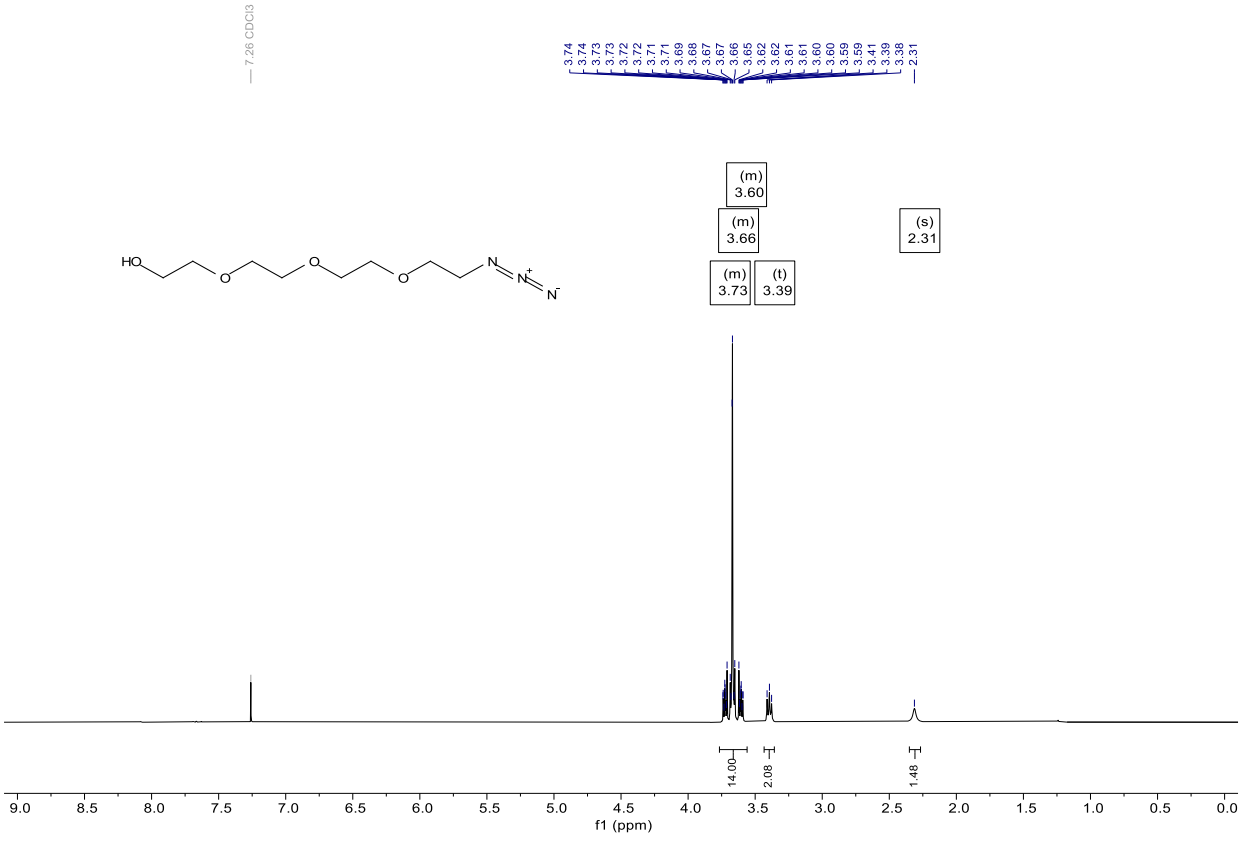
^{1}H NMR spectra of 6,7-dihydro-5H-benzo[7]annulene (**3**)



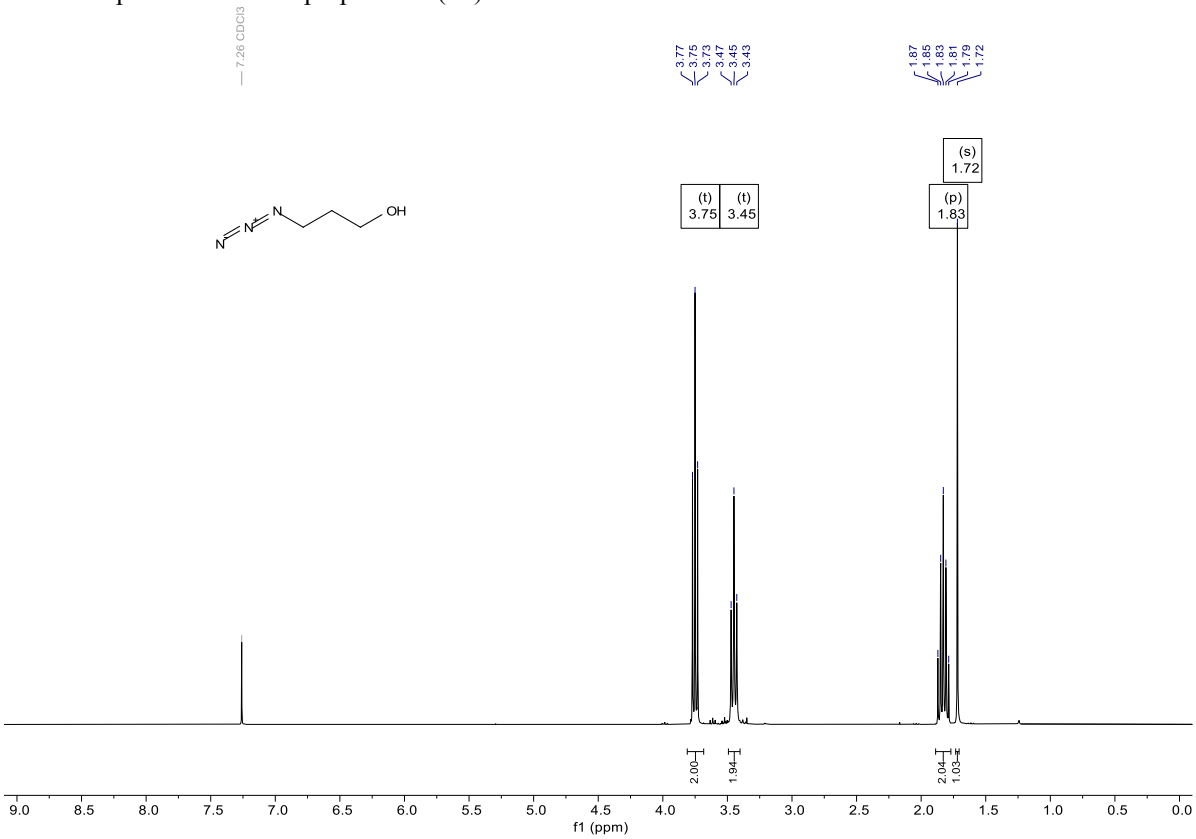
^{1}H NMR spectra of tetraethylene glycol monotosylate (**S4**)



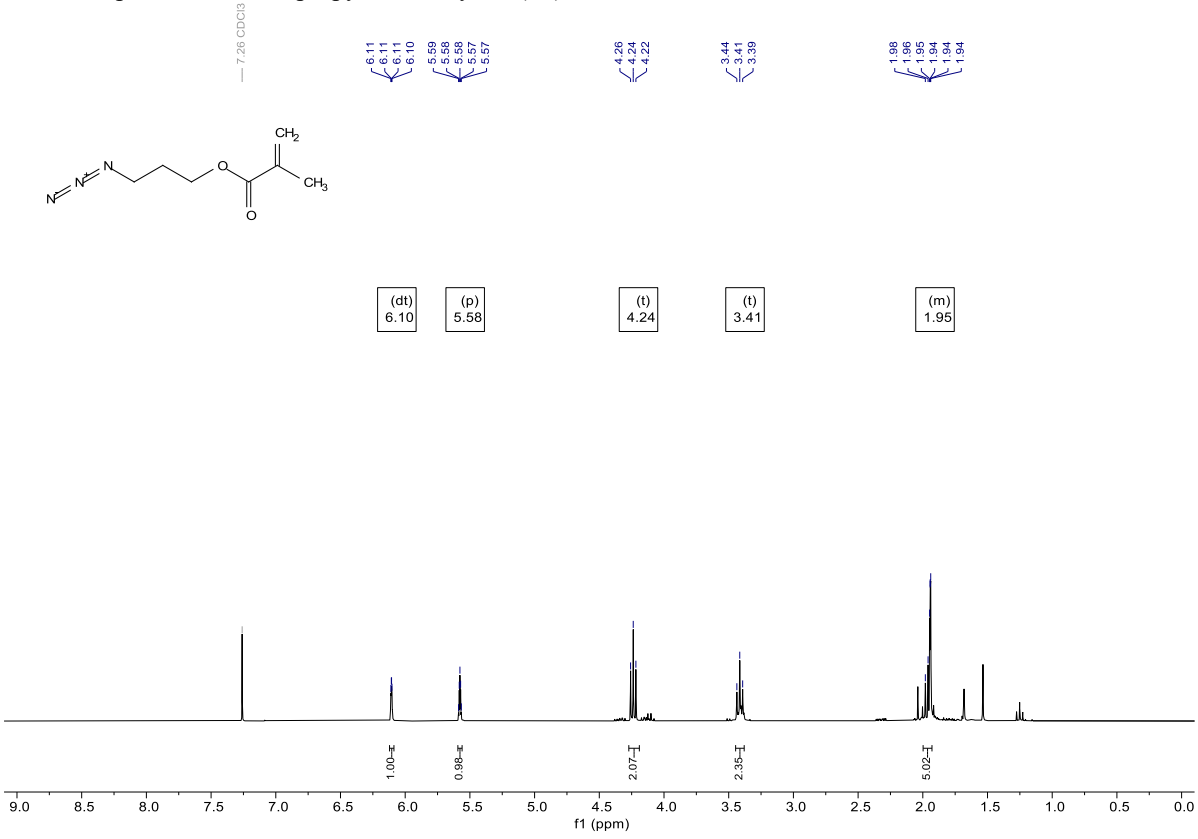
^{1}H NMR spectra of 11-azido-3,6,9-trioxaundecanol (**S5**)



^{1}H NMR spectra of 3-Azidopropan-1-ol (**S6**)



^{1}H NMR spectra of 3-azidopropyl methacrylate (**S7**)



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