

Supporting Information

Air-sensitive photoredox catalysis performed under aerobic conditions in gel networks

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1. Devices for irradiation and T_{gel} determination

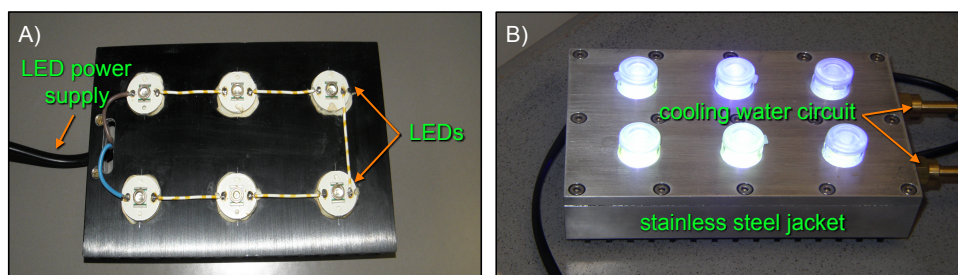


Figure S1. Custom made irradiation device. A) Array of six LEDs connected to a power supply. B) Set-up with a stainless steel jacket to maintain refrigeration of the vials (5 mL). The distance between the LEDs and the reaction vials is adjusted to 0.9 ± 0.1 cm. The apparatus also allows magnetic stirring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

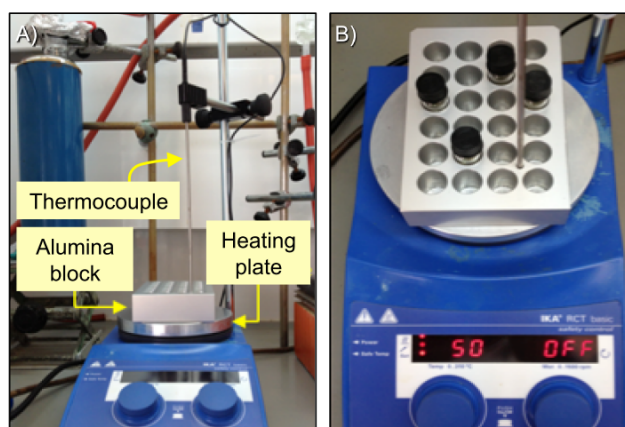


Figure S2. Custom made apparatus for T_{gel} determinations. A) Front view of the set-up. B) Top view of the set-up during a typical experiment. The vials must fit smoothly inside the molds to ensure the optimal transmission of the heat flow.

2. Reactions using Rh-6G

2.1. Control experiments and optimization of reaction conditions

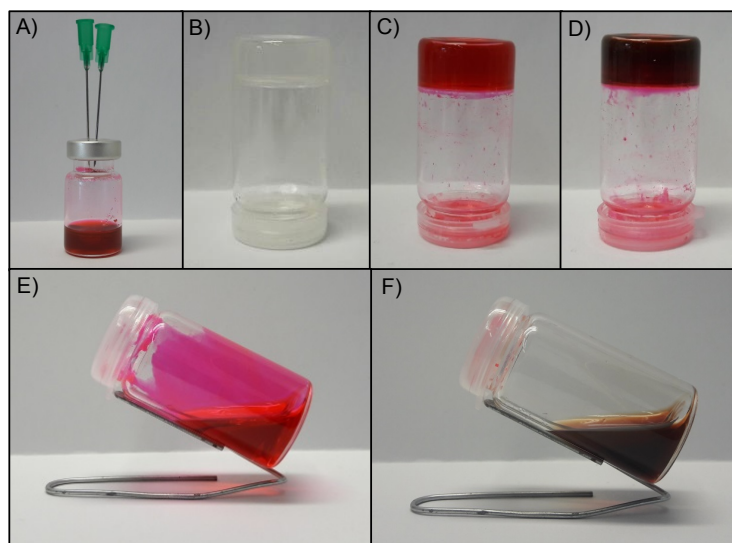
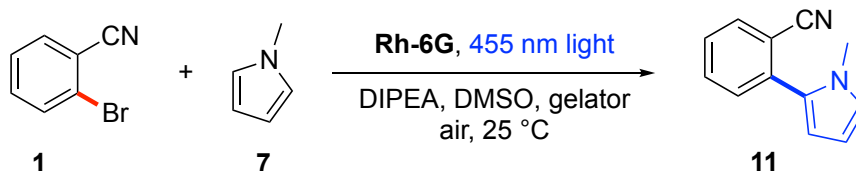


Figure S3. A) Typical set-up of reaction inside gel under constant aerobic conditions. B) Appearance of undoped **G-1**. C) Appearance of doped (with **Rh-6G**, DIPEA, 2-bromobenzonitrile and *N*-methylpyrrole) **G-1** before irradiation. D) Appearance doped **G-1** after irradiation under aerobic conditions. E) Appearance solution before irradiation. F) Appearance solution after irradiation under aerobic conditions.

Table S1. Control experiments for intragel C-H arylation between **1** and **7** as model reaction.^a

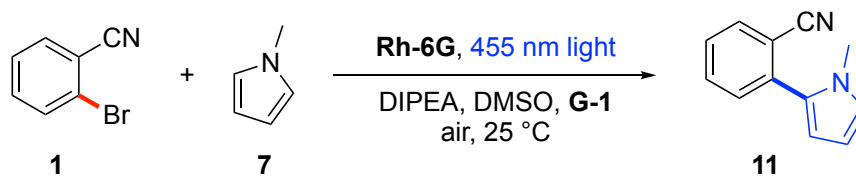
Entry	Rh-6G	DIPEA	Modifications	Yield [%] ^b
1	✓	✓	-	53 ^c
2	X	✓	No photocatalyst	9
3	✓	X	No donor	3
4	X	X	No catalyst, no donor	3
5	✓	✓	530 nm light	12
6	✓	✓	No gelator	5

^a Reactants and conditions: **1** (0.1 mmol), **7** (1.8 mmol), DIPEA (0.15 mmol, 1.5 equiv), **Rh-6G** (10 mol%), **G-1** (10 g L⁻¹), DMSO (1.5 mL), 24 h, 25 °C, reaction flask was equipped with two needles to ensure air flow. ^b Determined by GC-FID with biphenyl as internal standard. ^c Not optimized reaction conditions for reaction inside gel medium.

Table S2. Gelator screening of intragel C-H arylation between **1** and **7** as model reaction.^a

Entry	Gelator	Gelator concentration [g L ⁻¹]	Yield [%] ^c
1	G-1	2	54
2	G-1	5	53
3	G-1	10	57
4	G-1	15	69
5	G-2	15	62
6	G-3	15	49
7 ^b	G-4	120	60

^a Reactants and conditions: **1** (0.1 mmol), **7** (1.8 mmol), DIPEA (0.15 mmol, 1.5 equiv), **Rh-6G** (10 mol%), **G-1** (10 g L⁻¹), DMSO (1.5 mL), 24 h, 25 °C, reaction flask was equipped with two needles to ensure air flow. ^b As solvent 4:6 DMSO/toluene was used instead only DMSO, otherwise no gel state was achieved. ^c Determined by GC-FID with biphenyl as internal standard.

Table S3. Optimization of the reaction conditions for intragel C-H arylation between **1** and **7** as model reaction.^a

Entry	Rh-6G [mol%]	DIPEA [equiv]	G-1 [g L ⁻¹]	Yield [%] ^b
1	10	1.5	15	69
2	15	1.5	15	65
3	15	2.2	15	73

^a Reactants and conditions: **1** (0.1 mmol), **7** (1.8 mmol), DIPEA (0.15 mmol, 1.5 equiv), **Rh-6G** (10 mol%), **G-1** (10 g L⁻¹), DMSO (1.5 mL), 24 h, 25 °C, reaction flask was equipped with two needles to ensure air flow. ^b Determined by GC-FID with biphenyl as internal standard.

2.2. GC-FID analysis

Representative calibration curves are shown in Figure S4 and Figure S5.

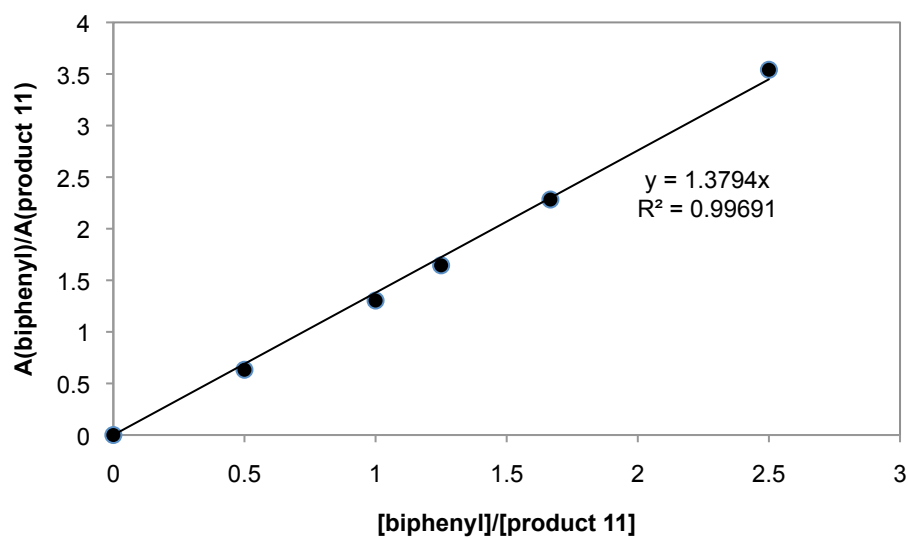


Figure S4. Quantitative GC calibration for product **11** of model reaction with biphenyl as internal standard.

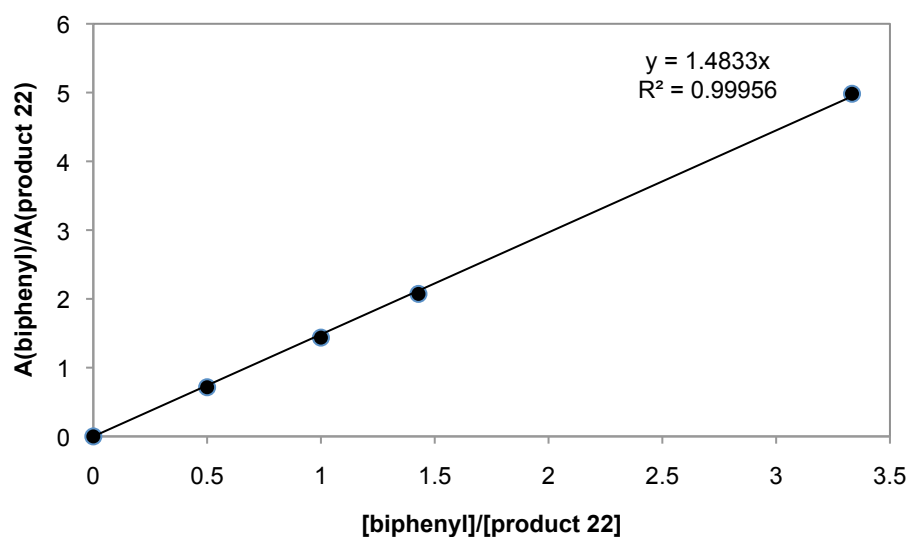


Figure S5. Quantitative GC calibration for **22** with biphenyl as internal standard.

2.3. Oscillatory rheology

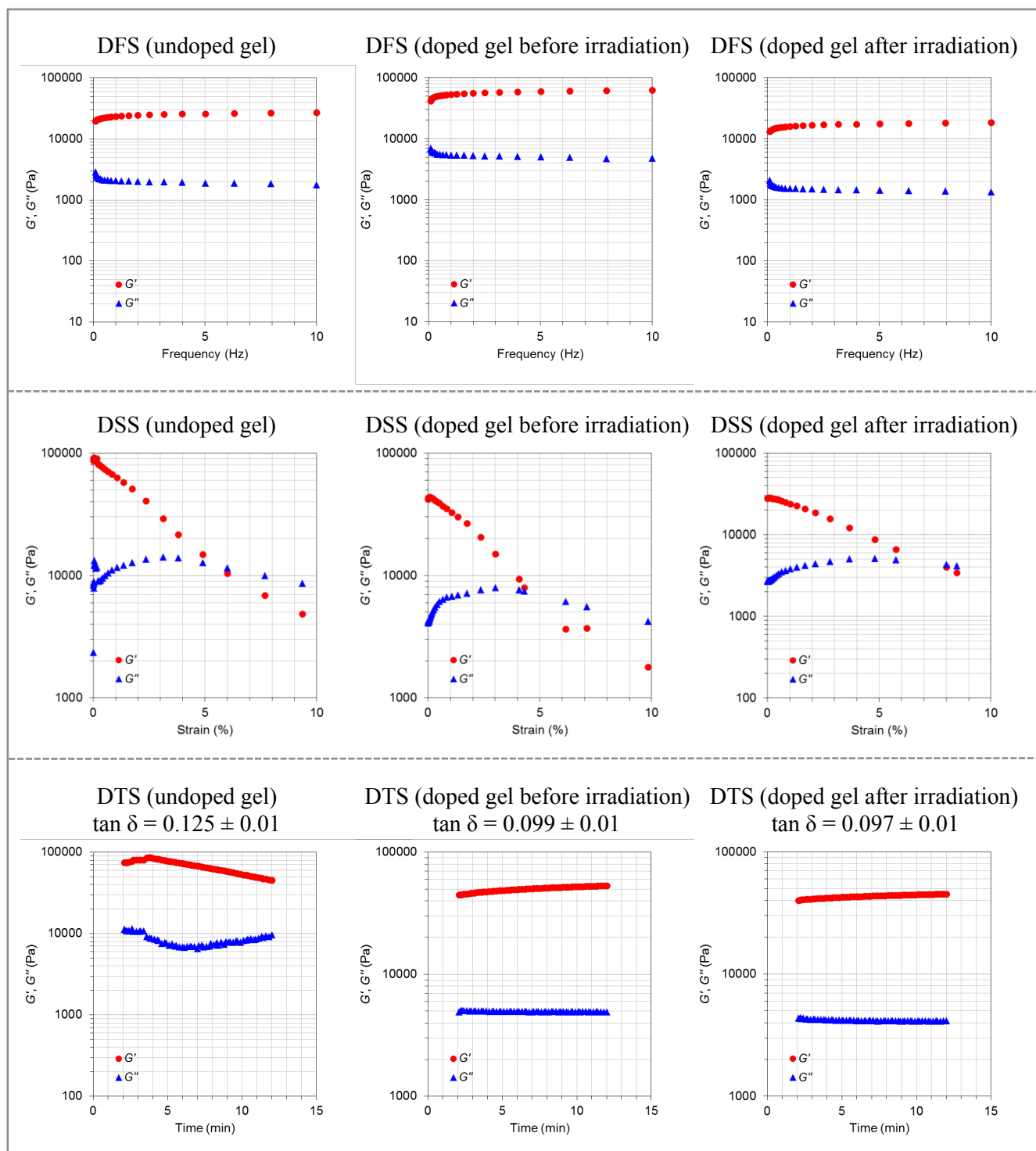
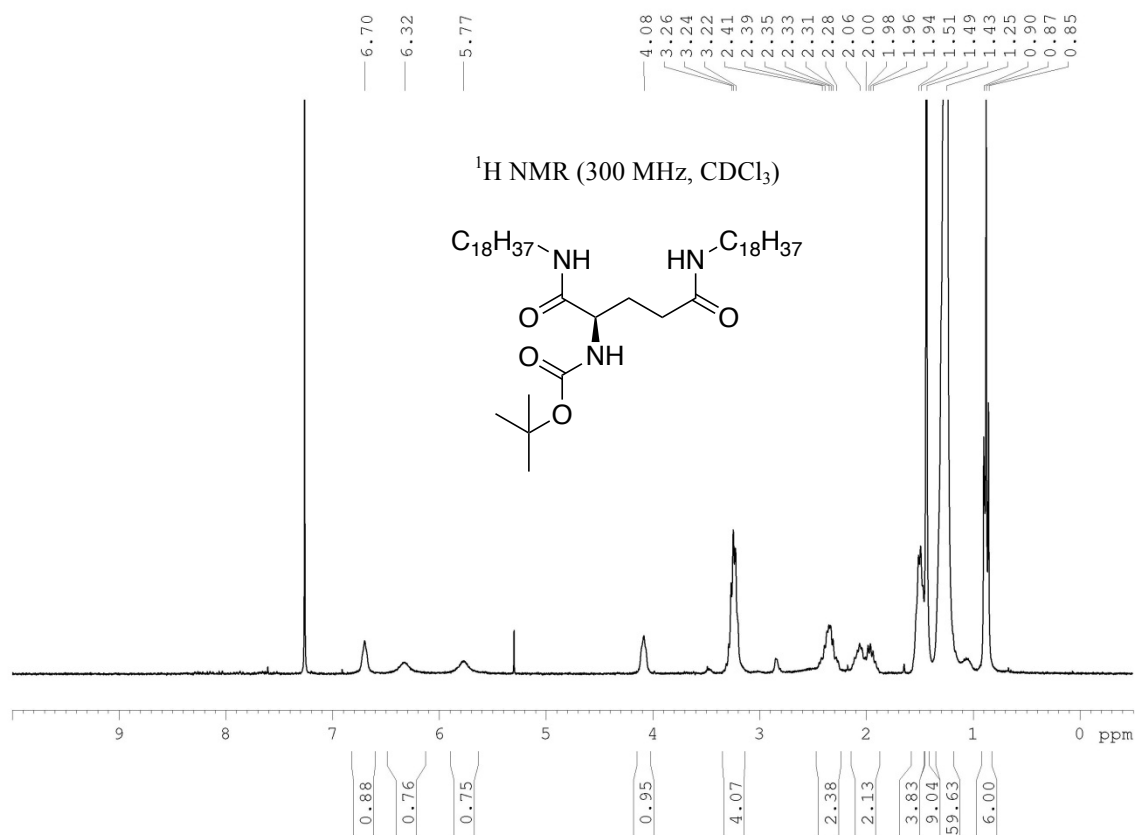


Figure S6. Oscillatory rheological experiments of model undoped and doped brittle gels. Conditions for preparing the doped gel: **1** (0.1 mmol), **7** (1.8 mmol), **Rh-6G** (10 mol%), **DIPEA** (2.2 mmol), **G-1** = 15 g L⁻¹, DMSO (1.5 mL). Irradiation conditions: $\lambda_{\text{ex}} = 455 (\pm 15)$ nm LED, 24 h.

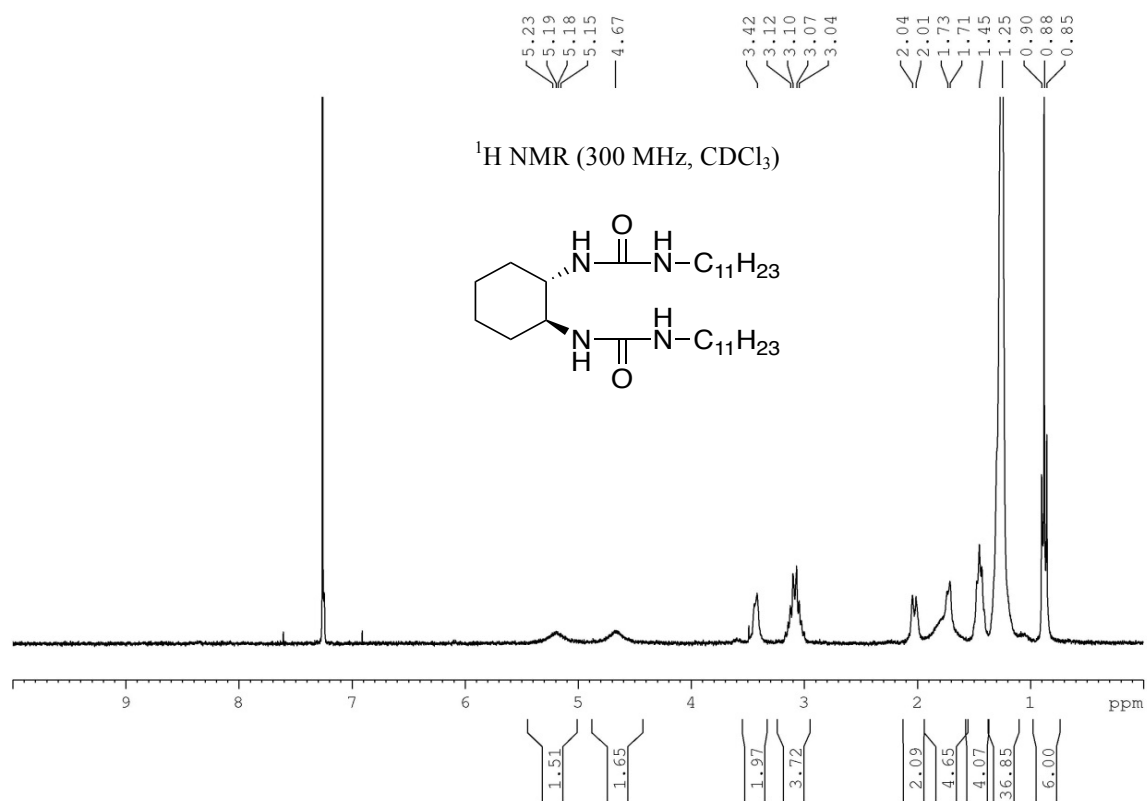
Note: T_{gel} of undoped gel made of **G-1** (61 ± 2 °C) remained practically constant, within the experimental error, upon doping and irradiation, i.e., T_{gel} of doped gel before irradiation = 57 ± 2 °C; T_{gel} of doped gel after irradiation = 59 ± 2 °C.

2.4. NMR spectra

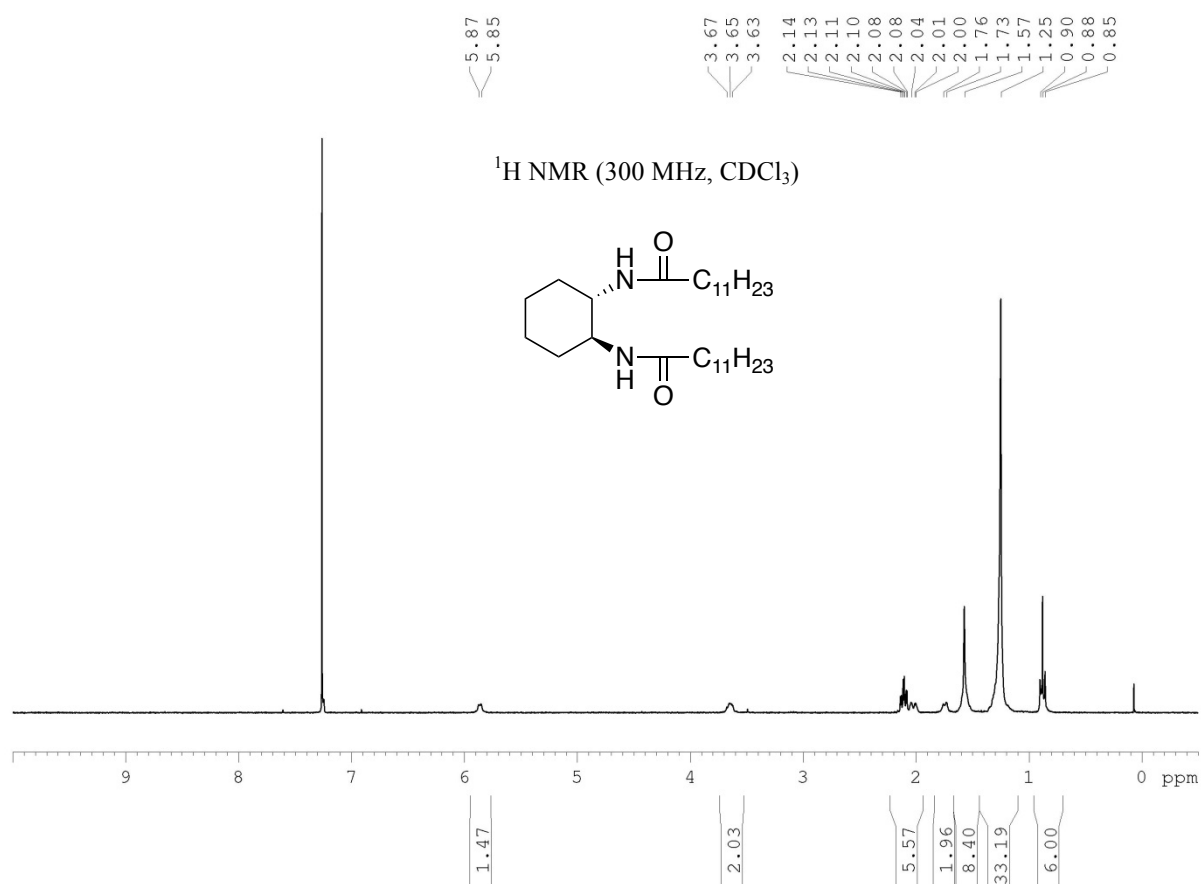
N,N'-Bis(octadecyl)-L-Boc-glutamic diamide (G-1):



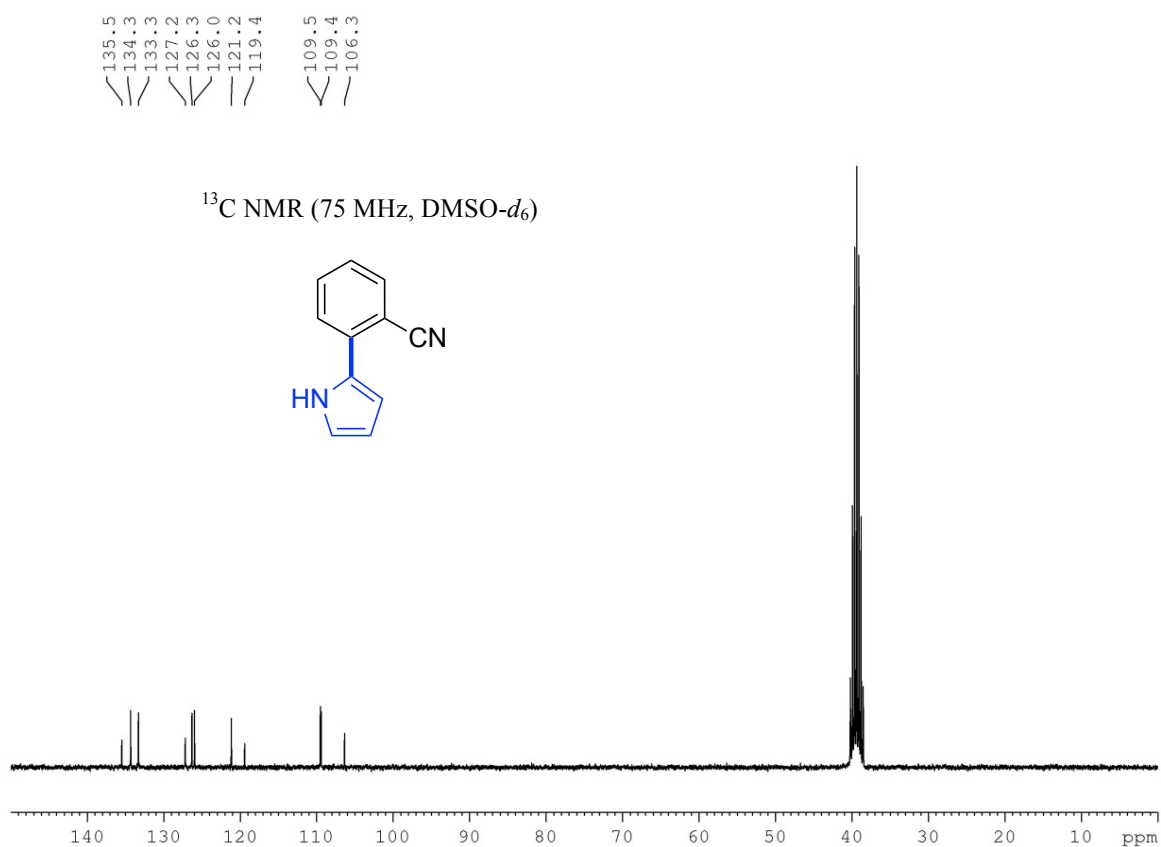
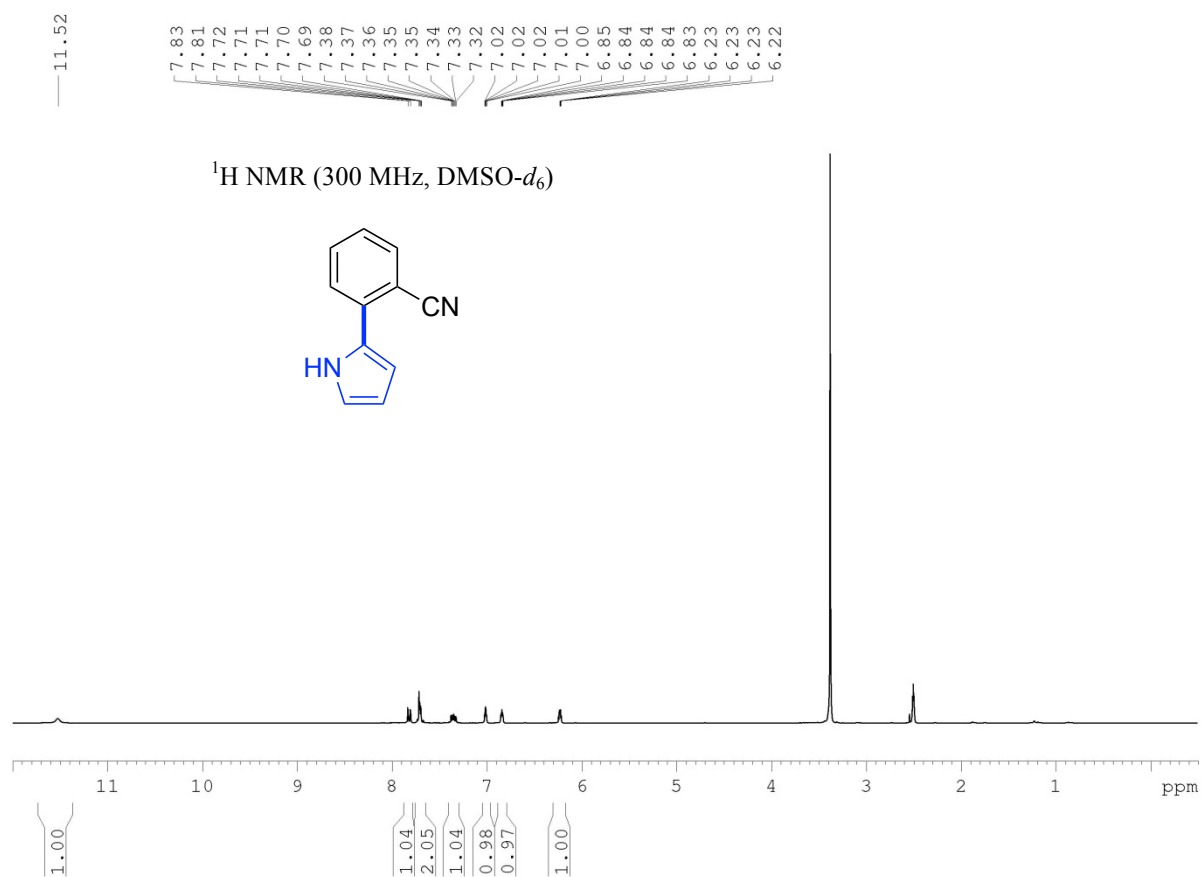
(*S,S*)-Dodecyl-3-[2(3-dodecyl-ureido)cyclohexyl]urea (G-2):



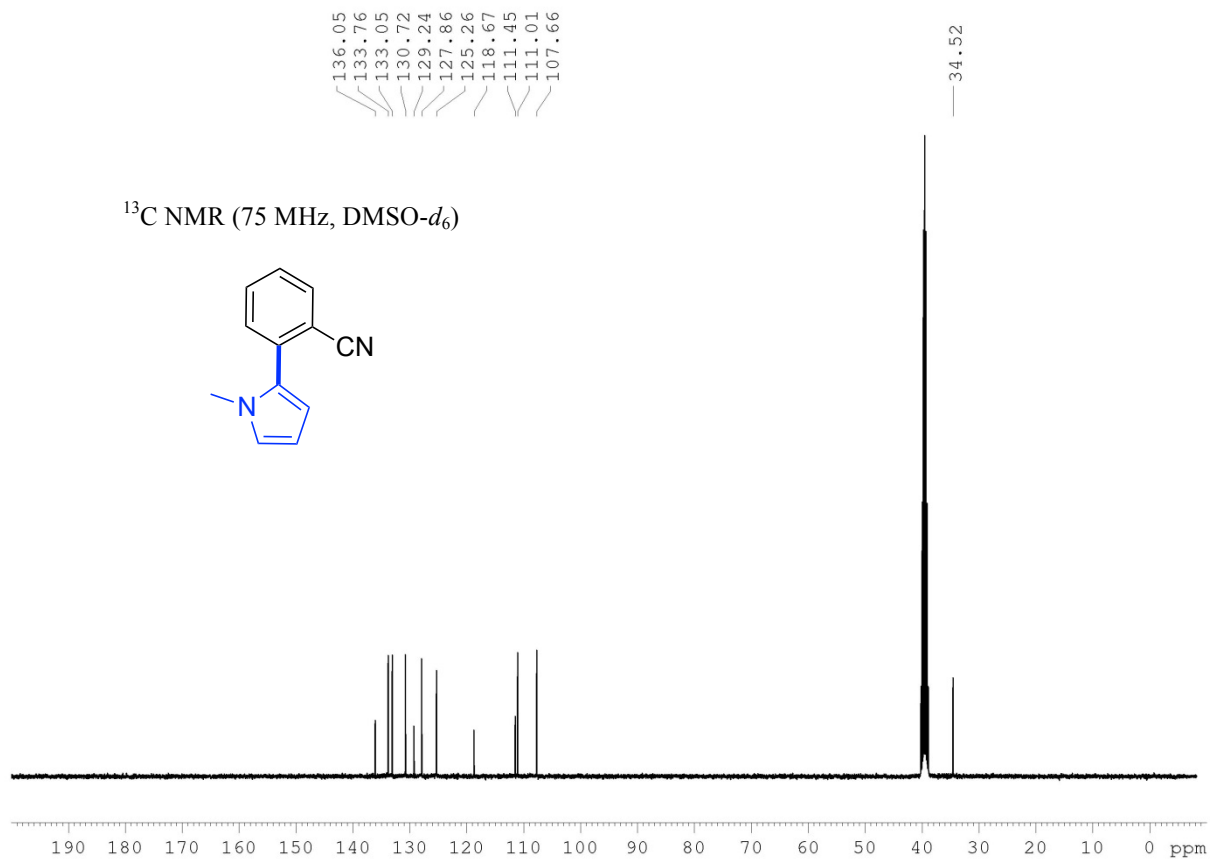
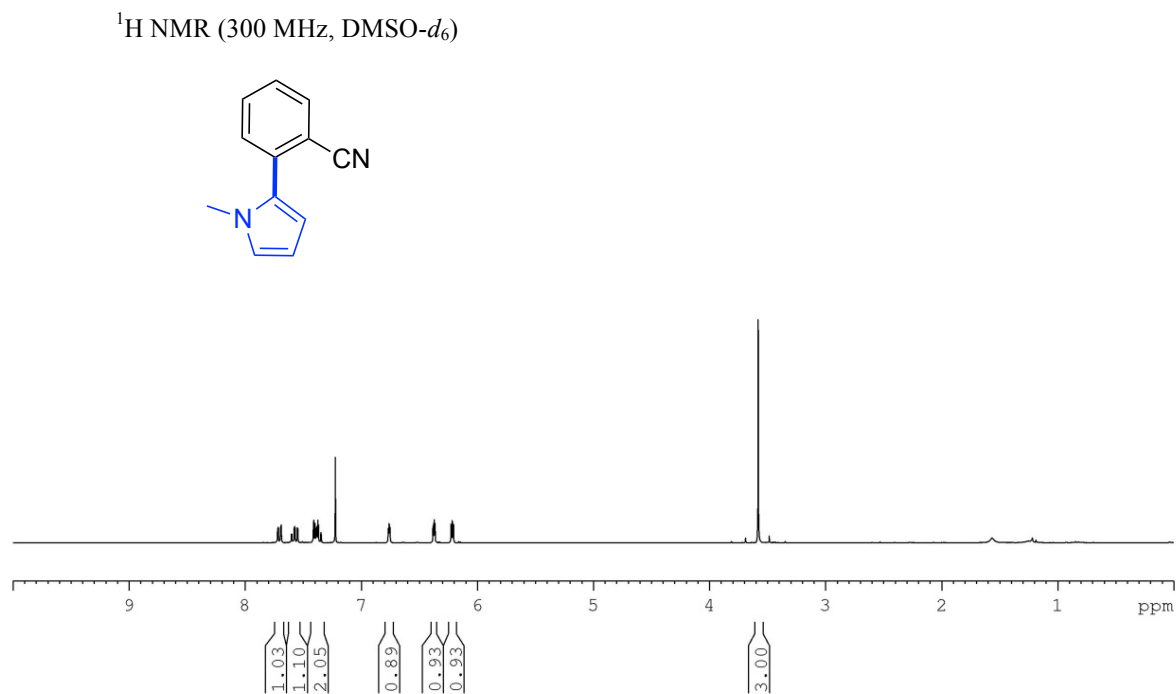
***N,N'*-((1*R*,2*R*)-Cyclohexane-1,2-diyl)didodecanamide (G-3):**



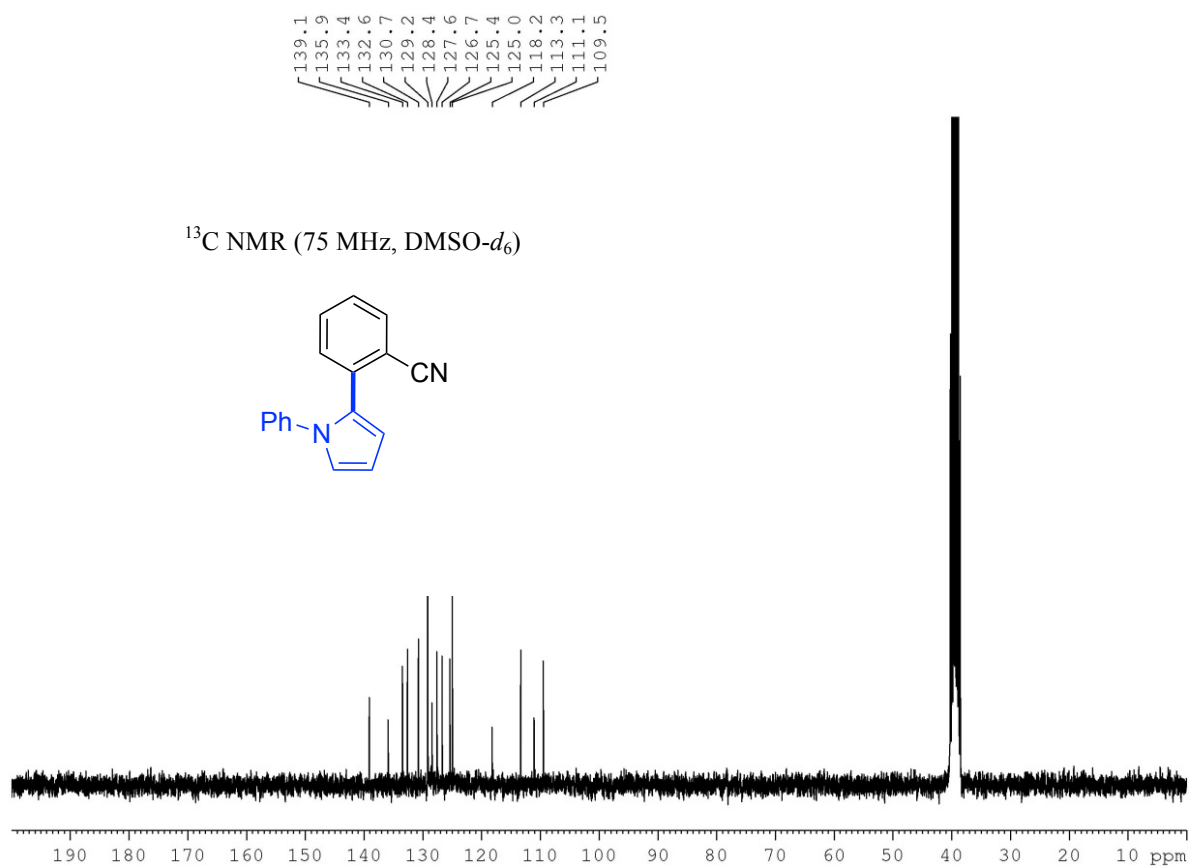
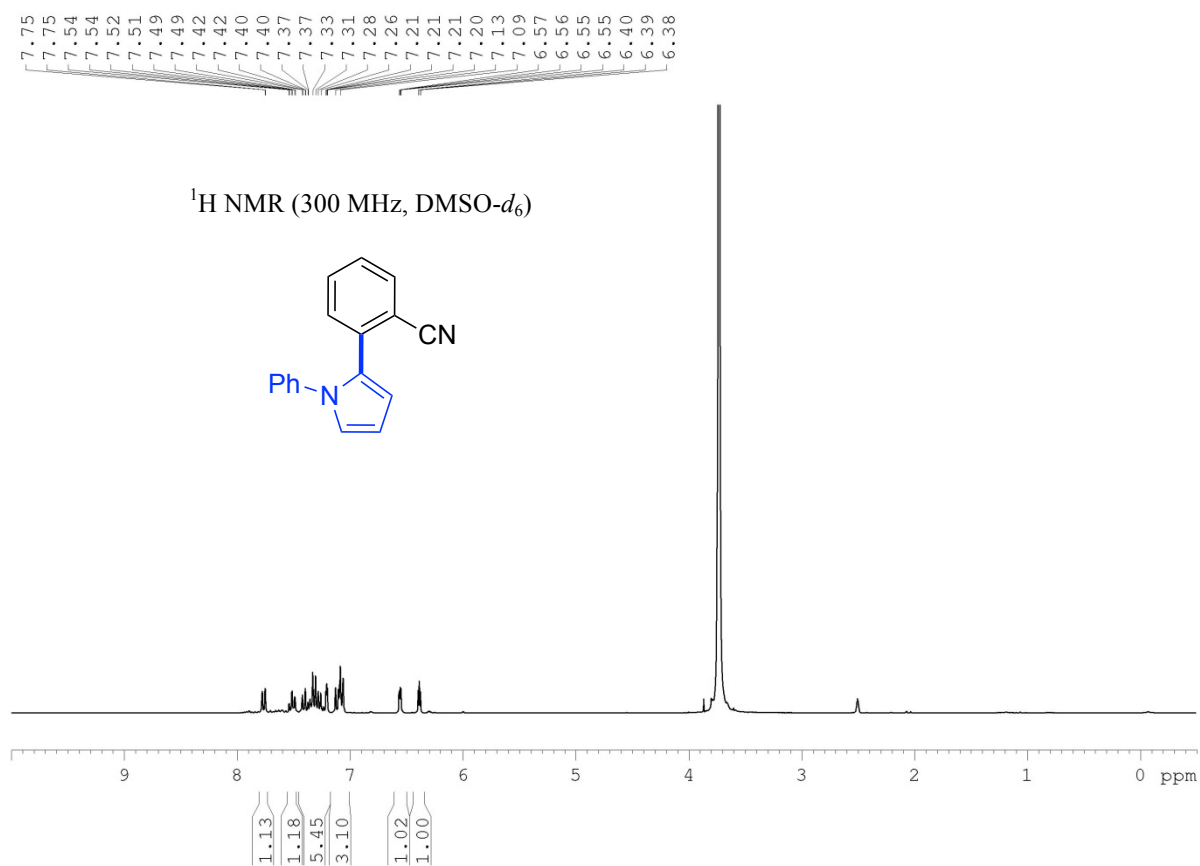
2-(1*H*-Pyrrol-2-yl)benzonitrile (10):



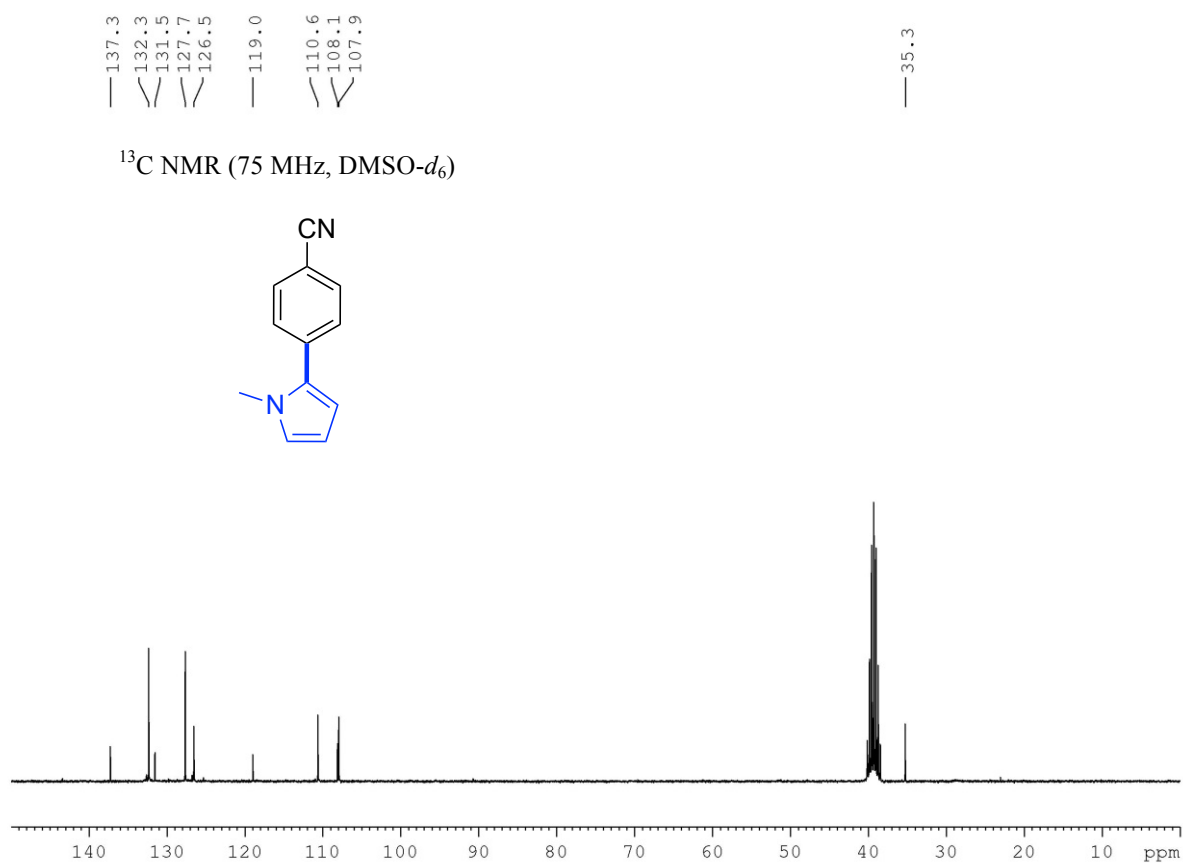
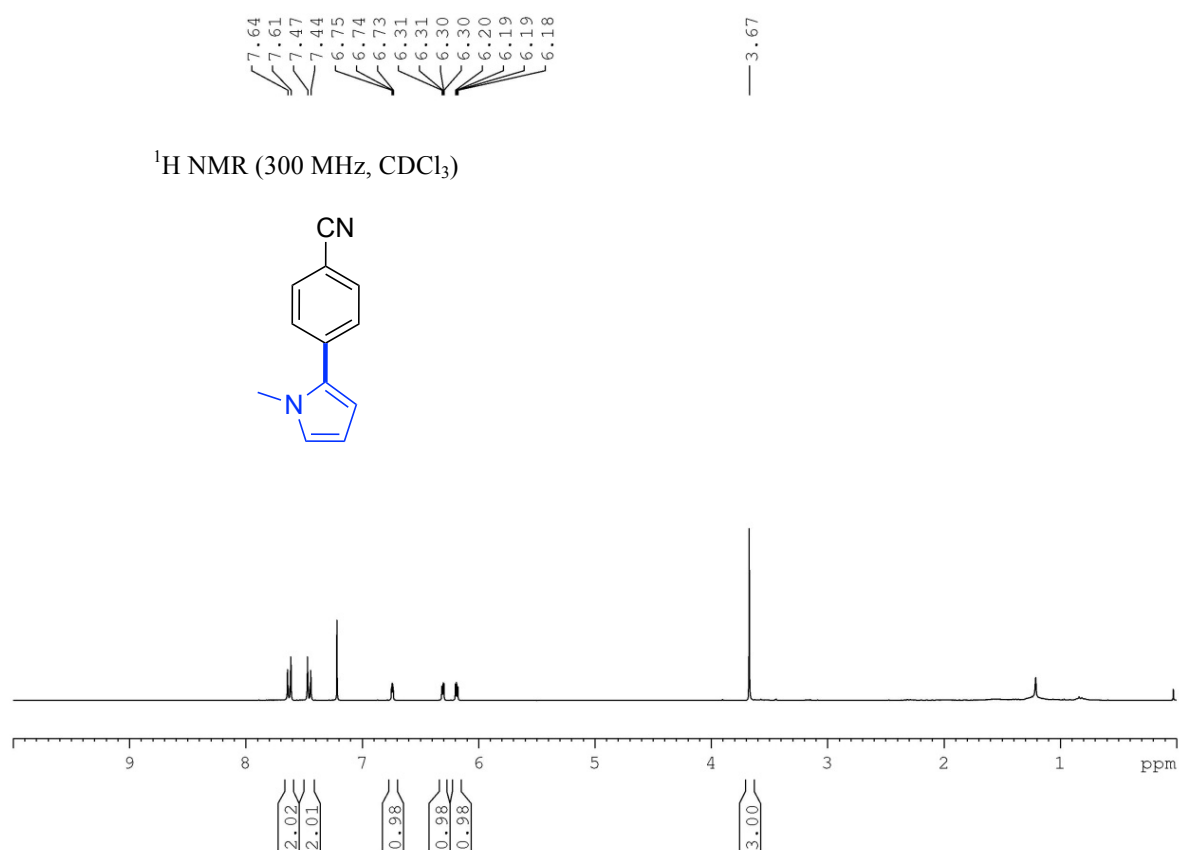
2-(1-Methyl-1*H*-pyrrol-2-yl)benzonitrile (11):



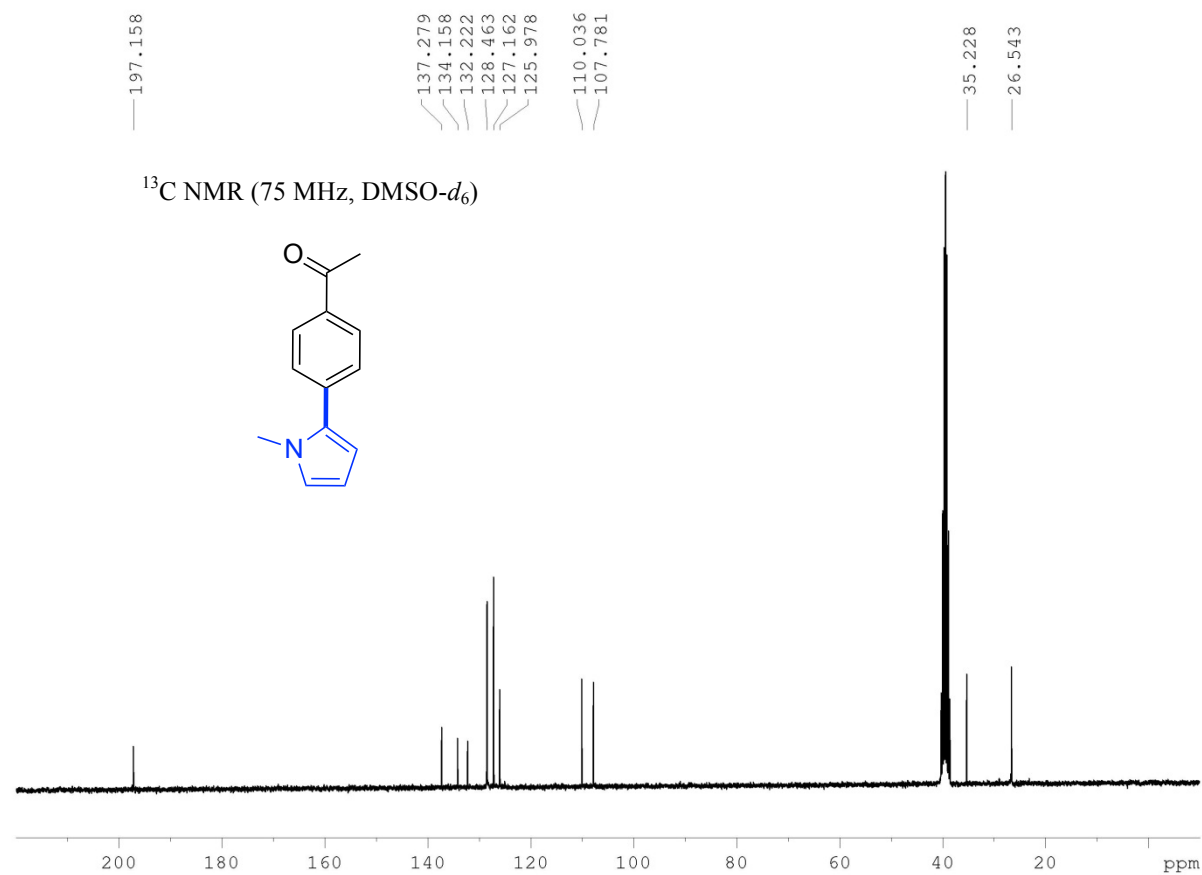
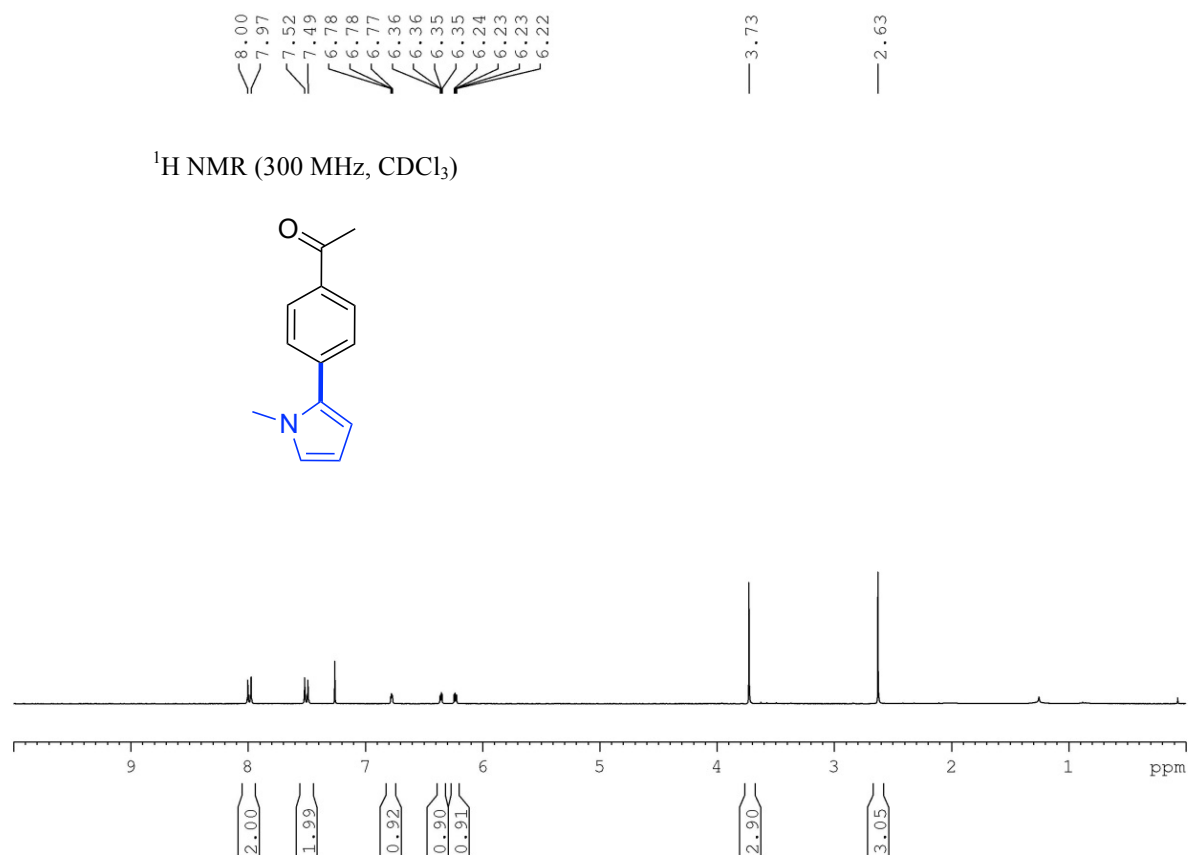
2-(1-Phenyl-1H-pyrrol-2-yl)benzonitrile (12):



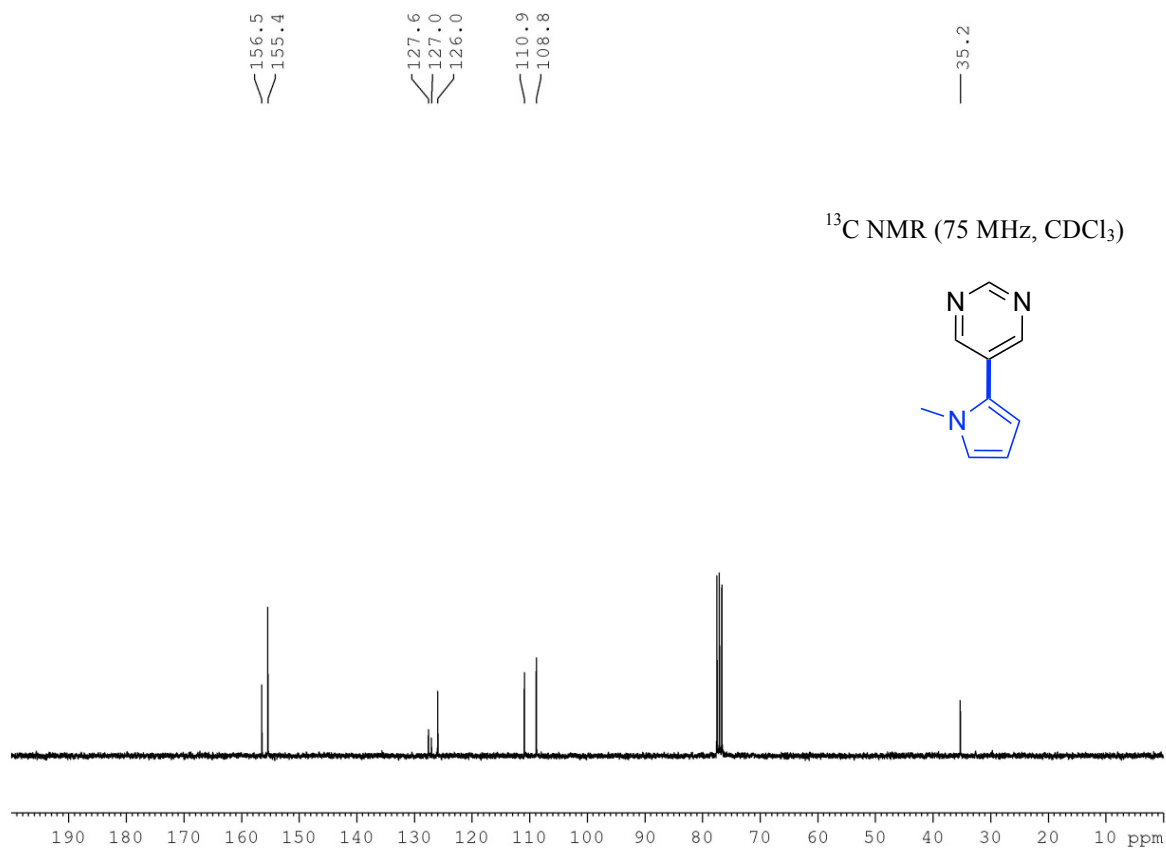
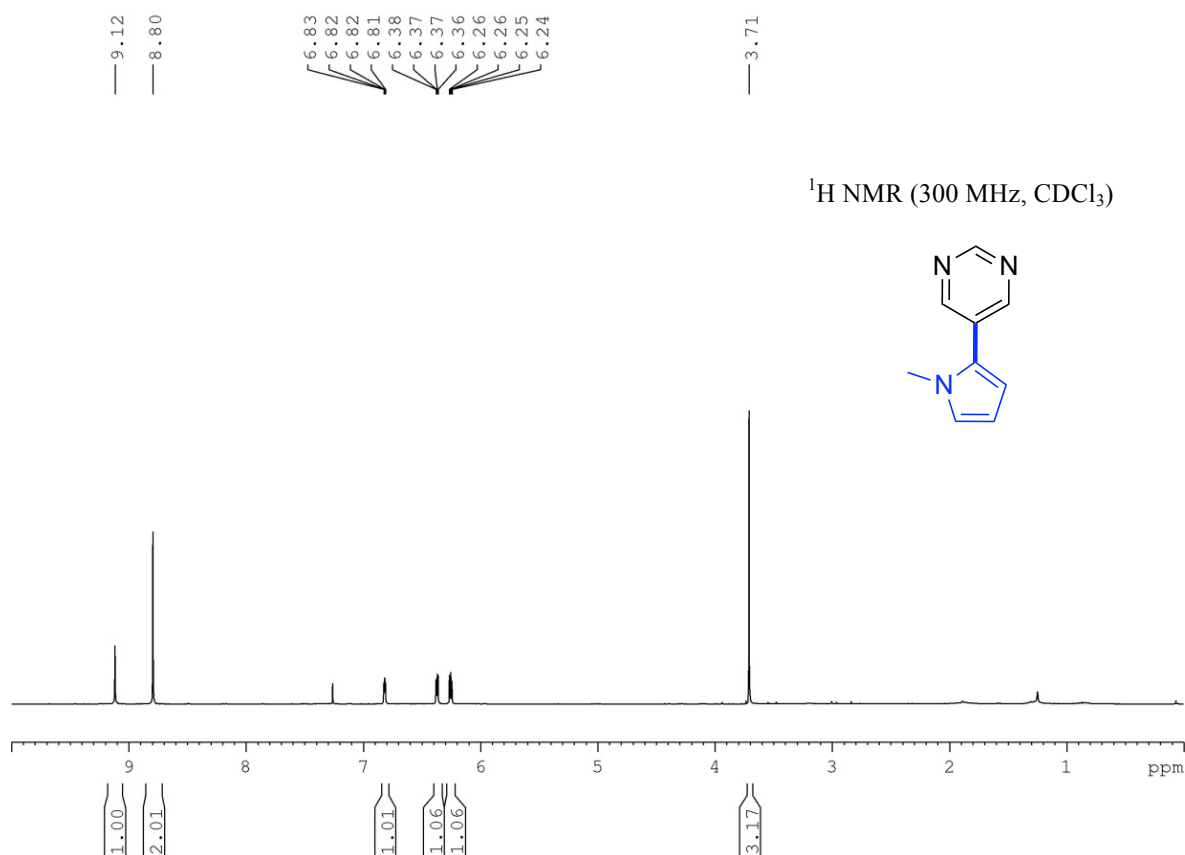
4-(1-Methyl-1H-pyrrol-2-yl)benzonitrile (13):



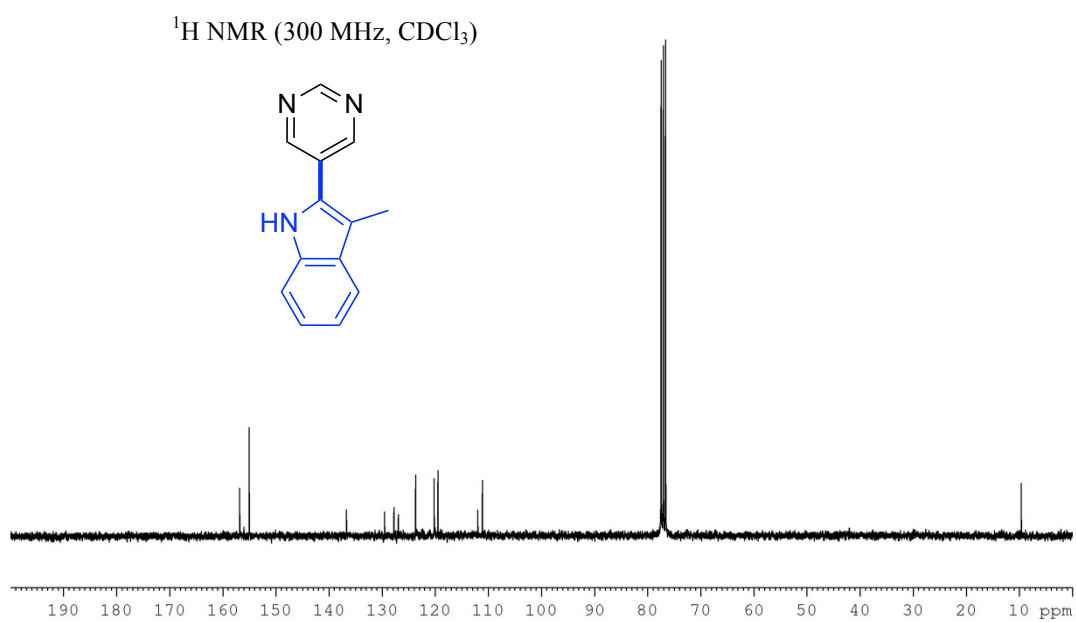
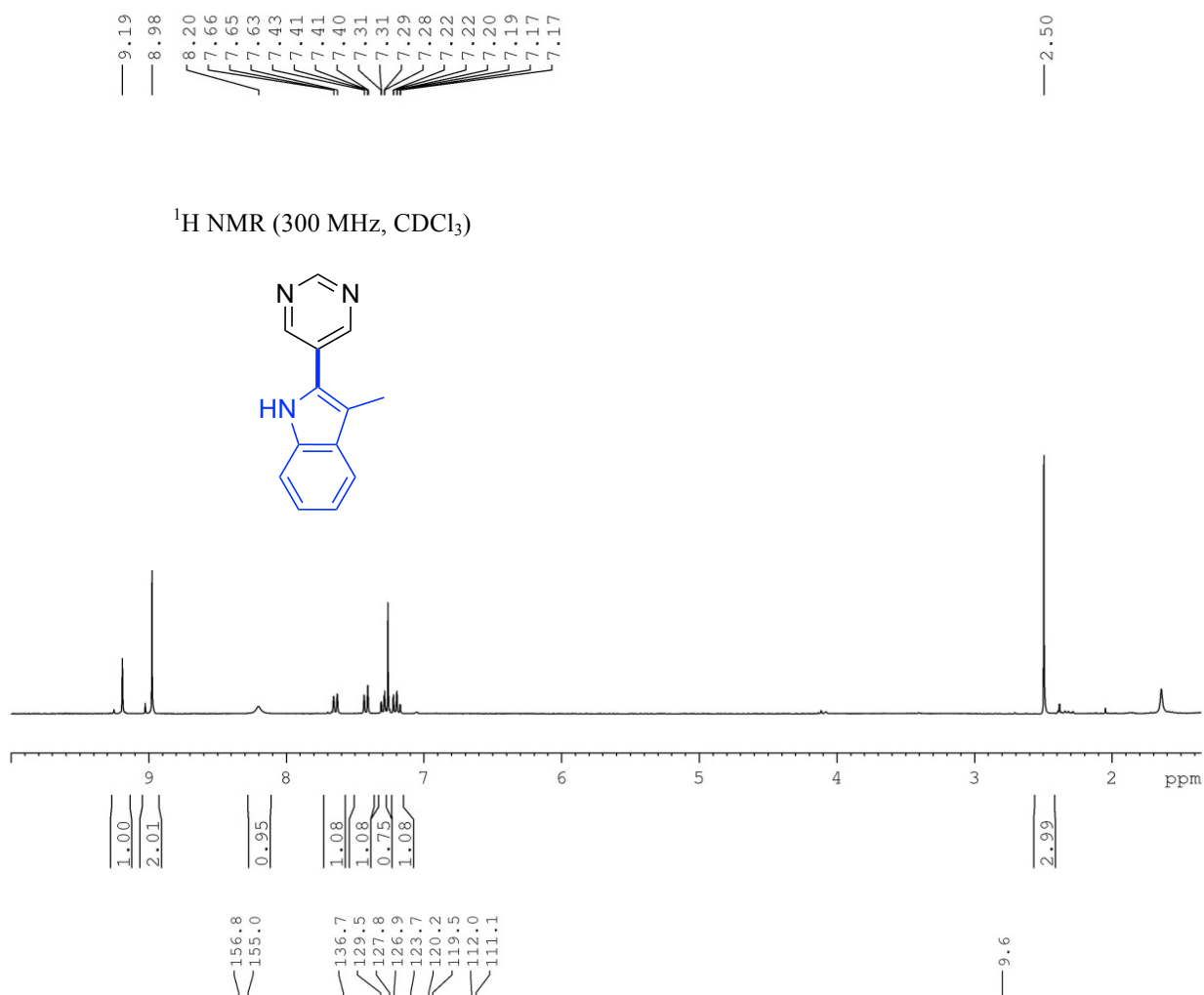
1-(4-(1-Methyl-1*H*-pyrrol-2-yl)phenyl)ethan-1-one (14):



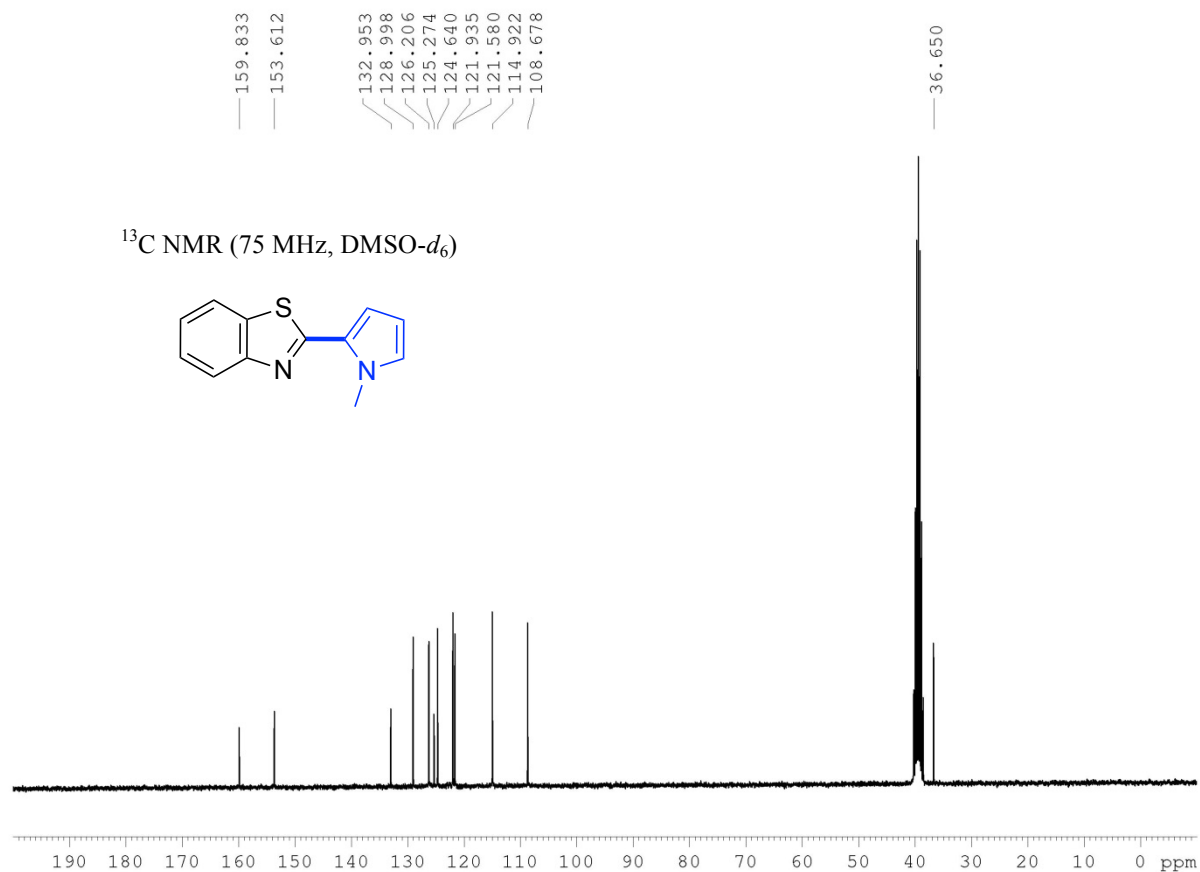
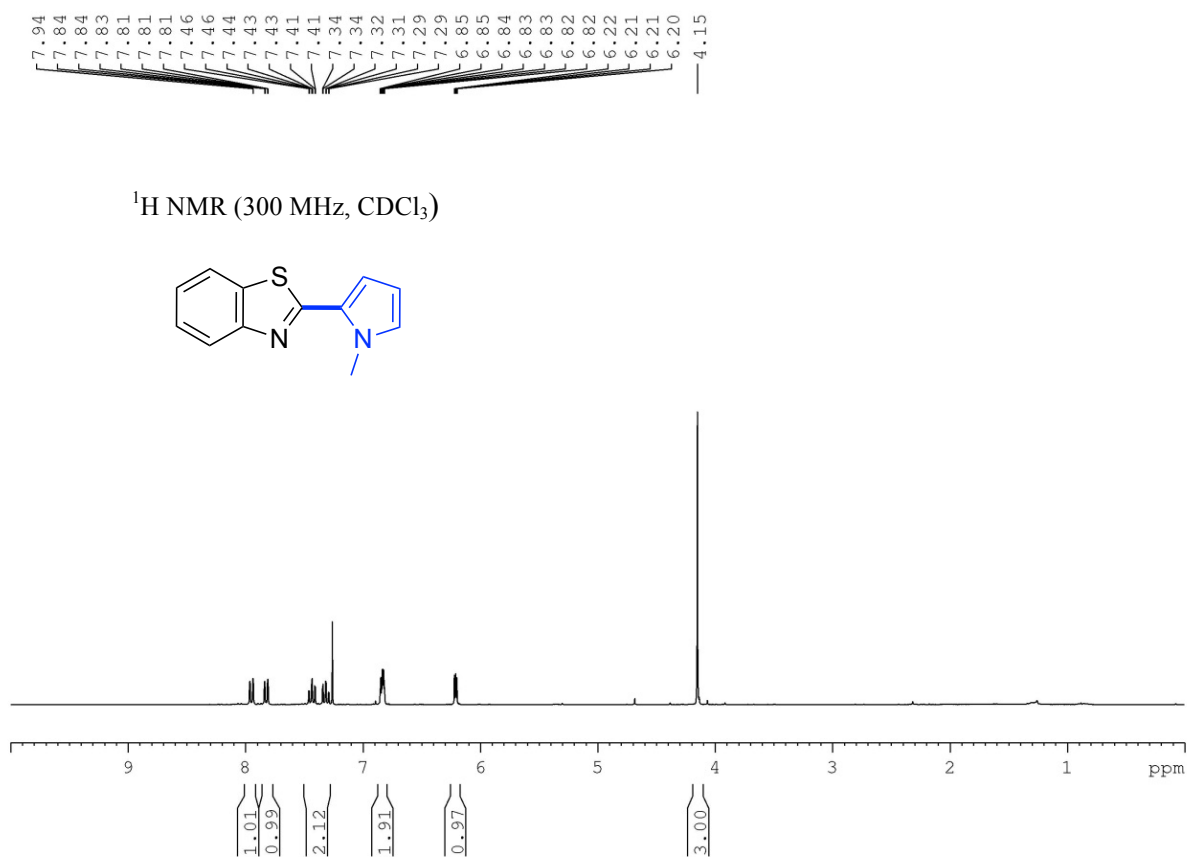
5-(1-Methyl-1*H*-pyrrol-2-yl)pyrimidine (15):



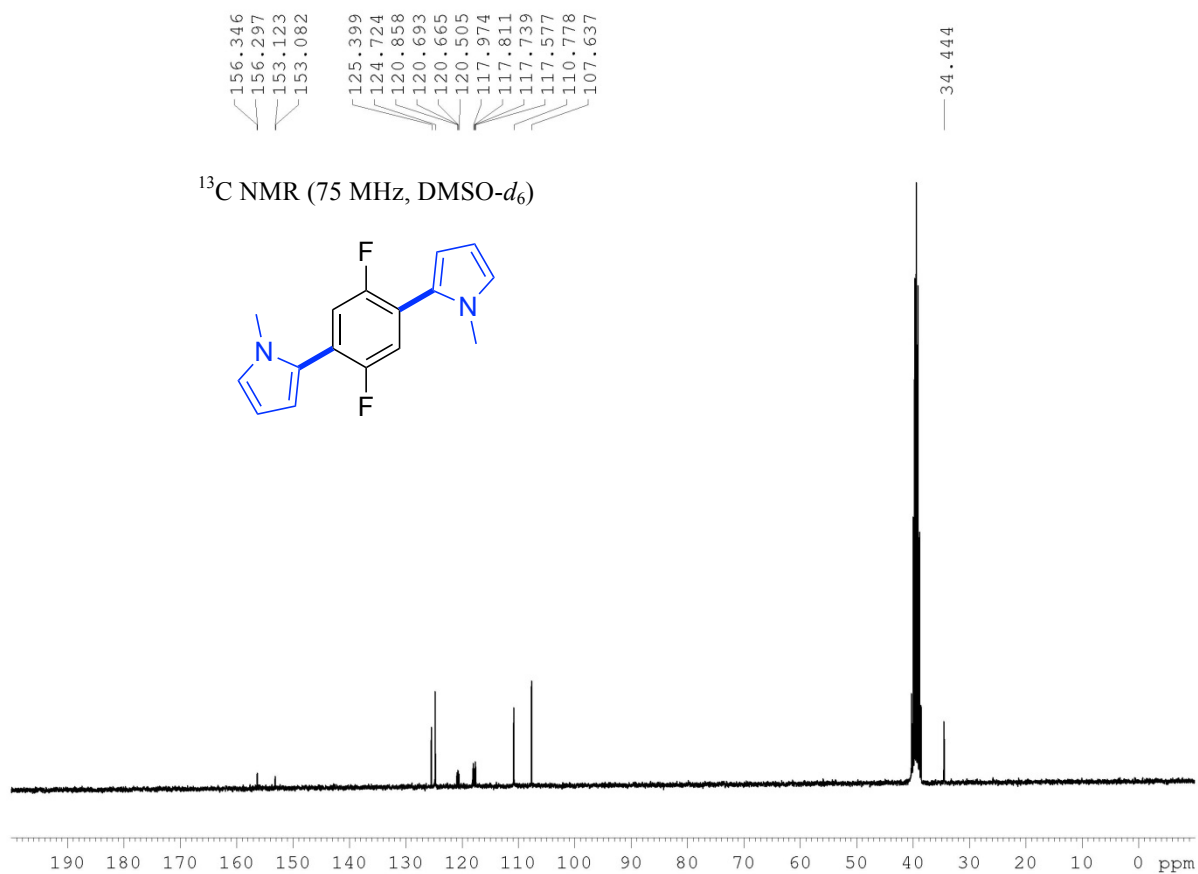
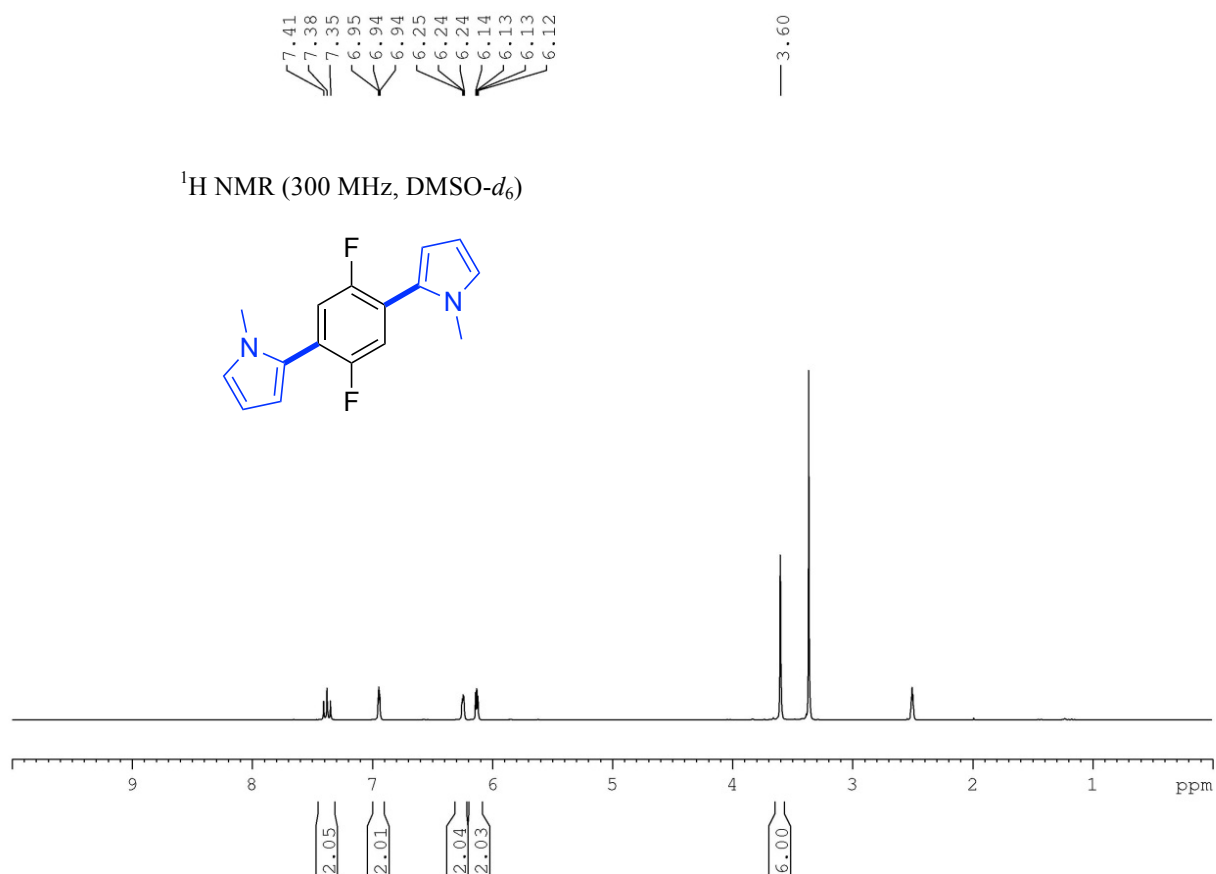
3-Methyl-2-(pyrimidin-5-yl)-1H-indole (16):



2-(1-Methyl-1*H*-pyrrol-2-yl)benzo[d]thiazole (17):



2,2'-(2,5-Difluoro-1,4-phenylene)bis(1-methyl-1*H*-pyrrole) (19):

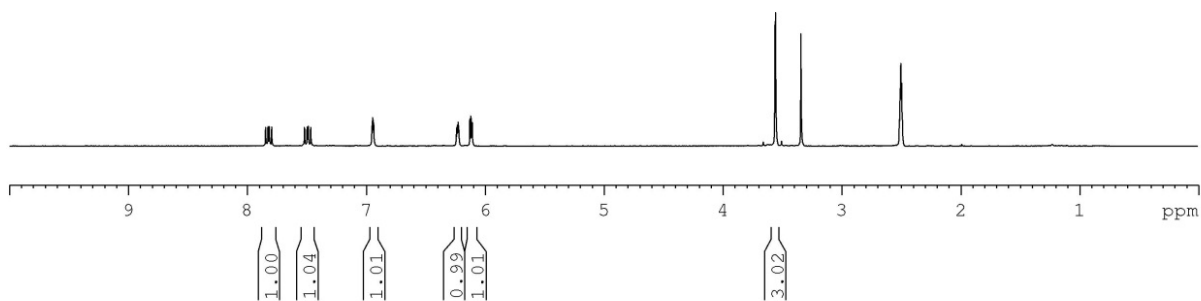
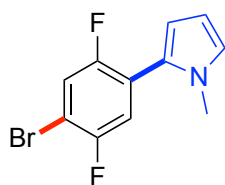


2-(4-Bromo-2,5-difluorophenyl)-1-methyl-1*H*-pyrrole (20):

7.85
7.83
7.81
7.79
7.52
7.50
7.49
7.47
6.94
6.13
6.12
6.12

3.56

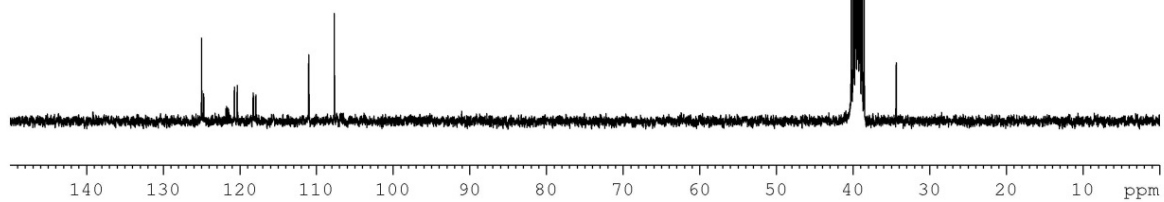
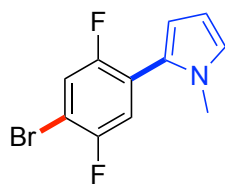
¹H NMR (300 MHz, DMSO-*d*₆)



125.0
124.7
121.8
121.7
121.6
120.7
120.3
118.3
118.2
118.0
117.9
111.0
111.0
107.7

34.4
34.3

¹³C NMR (75 MHz, DMSO-*d*₆)



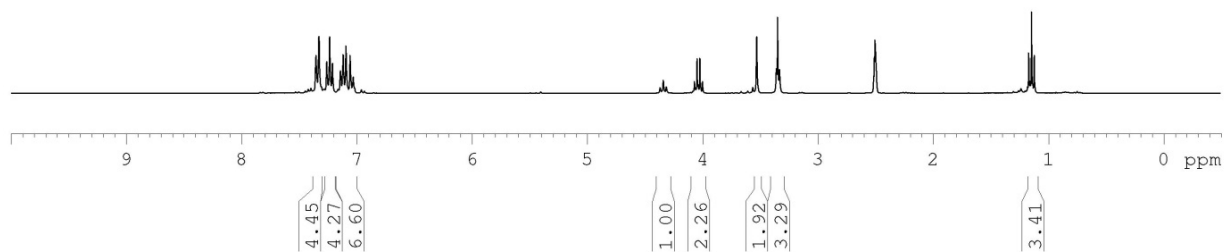
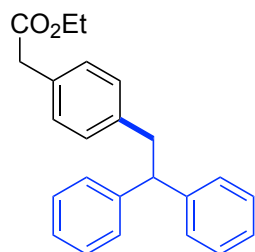
Ethyl 2-(4-(2,2-diphenylethyl)phenyl)acetate (24):

7.35
7.33
7.26
7.24
7.21
7.14
7.12
7.09
7.06
7.03

4.37
4.34
4.31
4.07
4.05
4.02
4.00
3.53
3.36
3.33

1.17
1.14
1.12

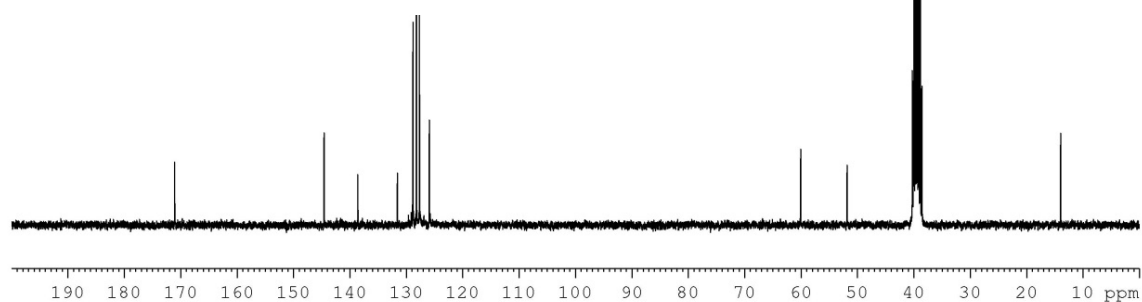
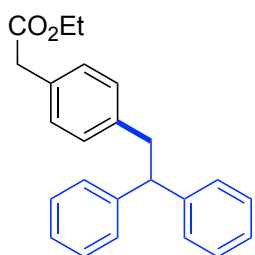
^1H NMR (300 MHz, $\text{DMSO}-d_6$)



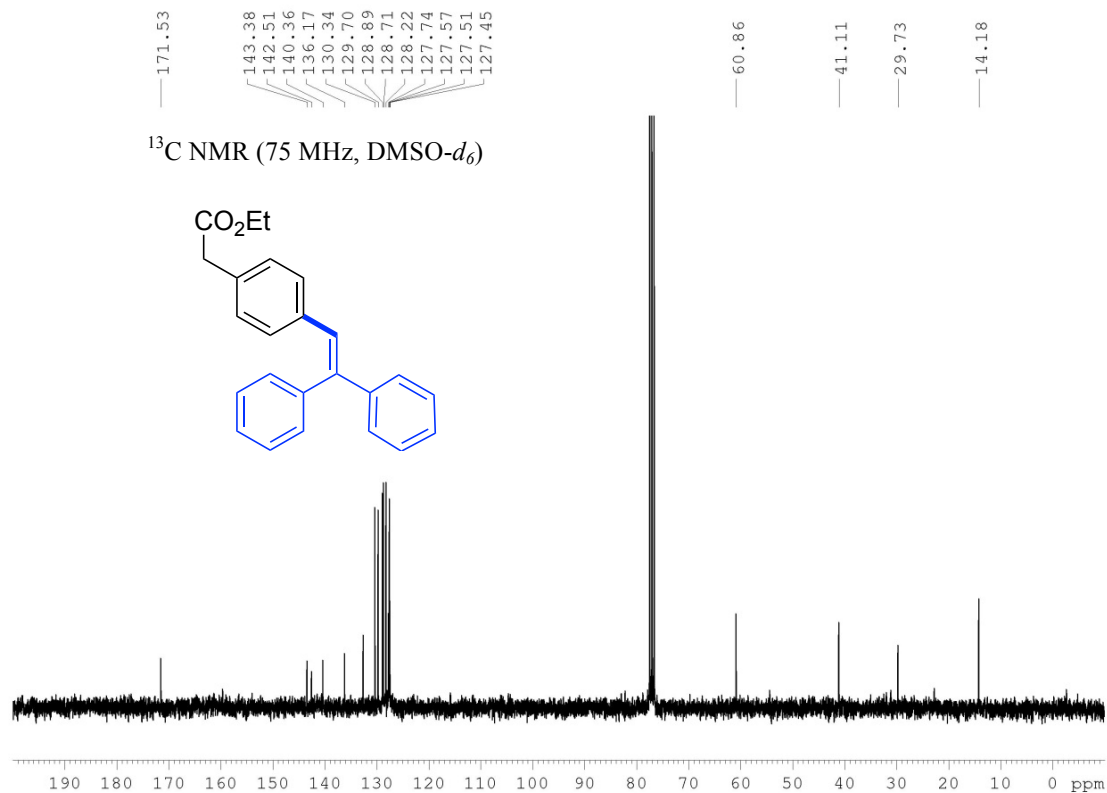
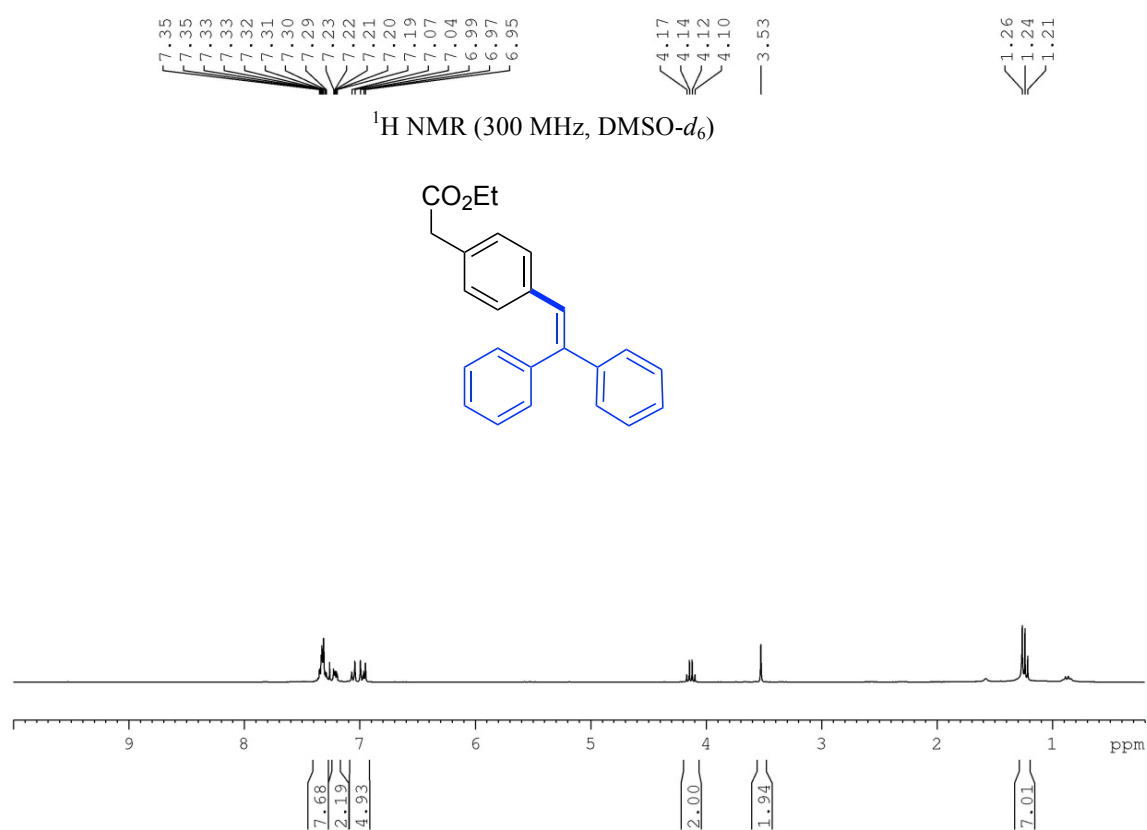
171.1
144.6
138.6
131.6
128.9
128.8
128.2
127.7
125.9
125.7

60.0
51.8
13.9

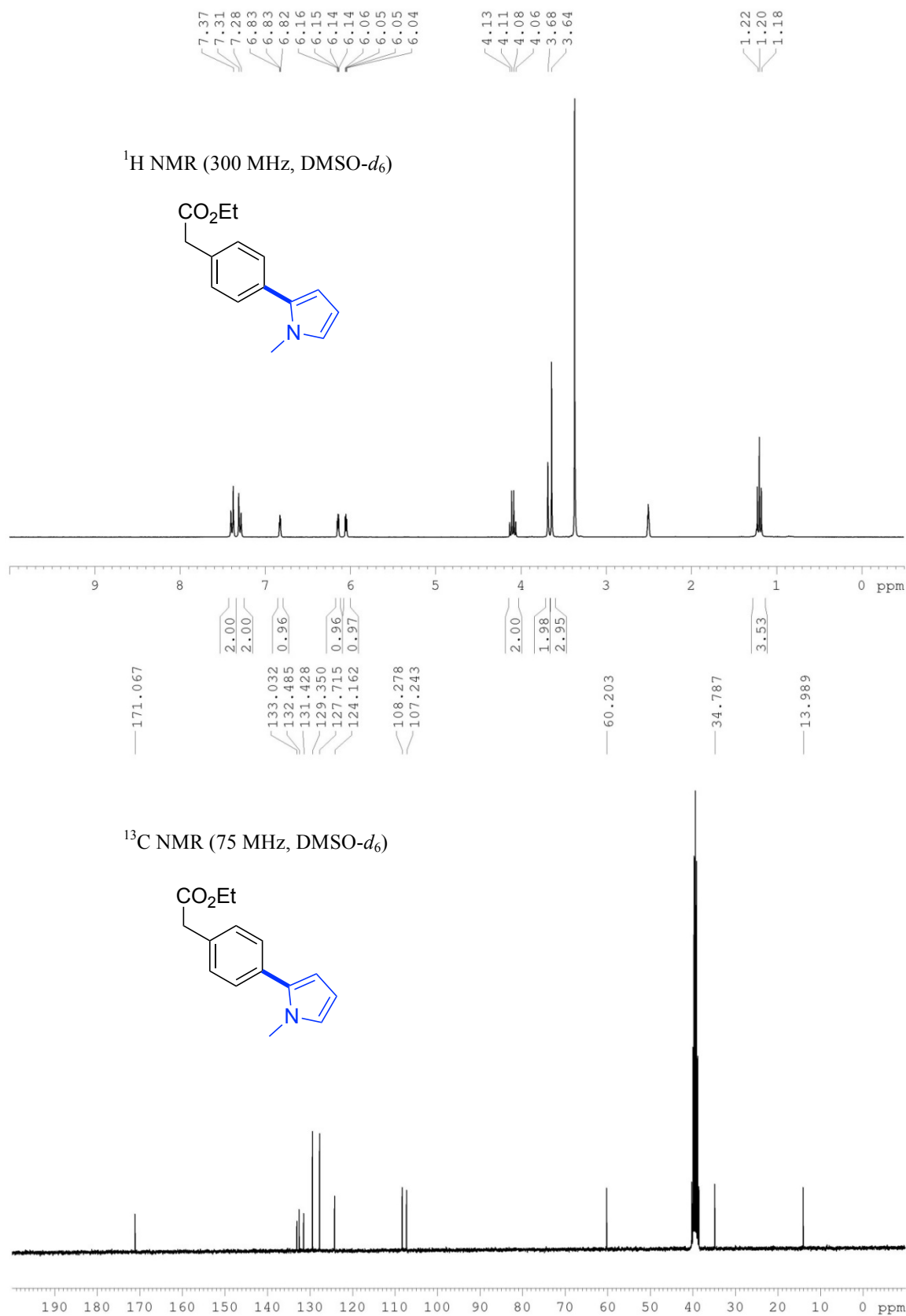
^{13}C NMR (75 MHz, $\text{DMSO}-d_6$)



Ethyl 2-(4-(2,2-diphenylvinyl)phenyl)acetate (24b):



Ethyl 2-(4-(1-methyl-1H-pyrrol-2-yl)phenyl)acetate:



This is an additional compound also synthesized according to the general procedure given in the Experimental Section. The compound was isolated in 19% yield. Conditions: 2-(4-bromophenyl)acetate (**22**) (0.1 mmol, 1.0 equiv), Rh-6G (0.015 mmol, 0.15 equiv), *N*-methylpyrrole (**7**) (1.8 mmol, 18 equiv), DIPEA (0.22 mmol, 2.2 equiv), **G-1** (15 g L⁻¹), DMSO (1.5 mL), 455 nm, 96 h, RT.

3. Reactions using Ru(phen)₃Cl₂ or Ir(Fdppy)₃

3.1. Control experiments and optimization of reaction conditions

Table S4. Control experiments using the trifluoromethylation of *N*-methylpyrrole (**7**) as model reaction.^a

Entry	Ru(phen) ₃ Cl ₂ [mol%]	K ₂ HPO ₄ [mol%]	Yield 37 [%] ^b	Yield 38 [%] ^b
1	-	300	7 ^c	18 ^c
2	1	-	5 ^c	32 ^c
3	-	-	2	0
4 ^d	1	300	0	0
5 ^e	1	300	0	1

^a Reactants and conditions (unless otherwise noted): *N*-methylpyrrole (**7**) (23 μ L, 0.25 mmol), TfCl (53 μ L, 0.5 mmol), Ru(phen)₃Cl₂ (1.8 mg, 0.01 mmol), K₂HPO₄ (131 mg, 0.75 mmol), MeCN (2 mL), **G-1** (15 g L⁻¹), RT, 24 h, irradiation with 455 nm LED. ^b Yields were calculated by ¹⁹F NMR using hexafluorobenzene (29 μ L, 0.25 mmol) as internal standard. ^c Yields are average of three independent experiments (estimated error $\pm$ 2%). ^d The vial was wrapped in aluminum foil. ^e Reaction carried out in solution in aerobic conditions and in the absence of **G-1**. Note: Some background reaction was observed in the absence of photocatalyst although this was found to be substrate-dependent (*vide infra*).

Table S5. Influence of K₂HPO₄ on the gel stability and on the reaction outcome. Trifluoromethylation of *N*-methylpyrrole (**7**) was used as model reaction^a

Entry	K ₂ HPO ₄ [mol%]	Gel behavior	Yield 37 [%] ^b	Yield 38 [%] ^b
1	250	stable	9	41
2	200	stable	2	27
3	150	partially melted	3	35
4	100	melted	1	26
5	50	melted	1	34
6	25	melted	2	40

^a Reactants and conditions (unless otherwise noted): *N*-methylpyrrole (**7**) (22 μ L, 0.25 mmol), TfCl (53 μ L, 0.5 mmol), Ru(phen)₃Cl₂ (1.8 mg, 0.01 mmol), K₂HPO₄, MeCN (2 mL), **G-1** (15 g L⁻¹), RT, 24 h, irradiation with 455 nm LED. ^b Yields were calculated by ¹⁹F NMR using hexafluorobenzene (29 μ L, 0.25 mmol) as internal standard. Note: The poorly soluble base is not only important for the reaction in solution for hygroscopic reasons but it also delays the melting of the gel phase.

Table S6. Control reactions in the absence of photocatalyst and with different substrates.^a

Entry	Substrate	Yield [%] ^b
1		8
2		4
3		0
4		0

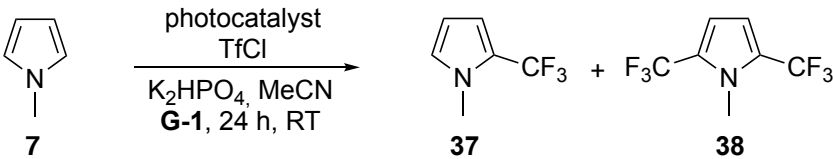
^a Reactants and conditions: Heteroarene (0.25 mmol), TfCl (0.5-1 mmol, 2-4 equiv), K₂HPO₄ (131 mg, 0.75 mmol), MeCN (2.5 mL), **G-1** (10 g L⁻¹), RT, 24 h, irradiation with 365 nm LED. ^b Yields were calculated by ¹⁹F NMR using hexafluorobenzene (29 μL, 0.25 mmol) as internal standard. Name of substrates: 2-Isopropyl-3-methoxypyrazine (entry 1), 2,6-dimethyl-γ-pyrone (entry 2), *p*-xylene (entry 3), 1,3-dimethyluracil (entry 4).

Table S7. Effect of gelator concentration on the trifluoromethylation of *N*-methylpyrrole as model reaction.^a

Entry	Gelator concentration (g L ⁻¹)	Yield 37 [%] ^b	Yield 38 [%] ^b
1	5	4	44
2	10	2	37
3	15	0	46
4	20	1	46

^a Reactants and conditions: *N*-methylpyrrole (**7**) (22 μL, 0.25 mmol), TfCl (53 μL, 0.5 mmol), Ru(phen)₃Cl₂ (1.8 mg, 0.01 mmol), K₂HPO₄ (131 mg, 0.75 mmol), MeCN (2 mL), **G-1**, RT, 24 h, irradiation with 455 nm LED. ^b Yields were calculated by ¹⁹F NMR using hexafluorobenzene (29 μL, 0.25 mmol) as internal standard. Note: Although all gels remained stable during the reaction, the gel prepared at 5 g L⁻¹ was slightly melted at the end of irradiation.

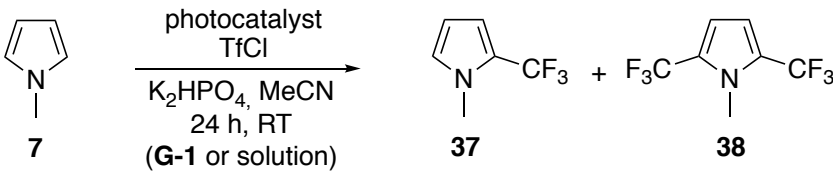
Table S8. Effect of total volume on the trifluoromethylation of *N*-methylpyrrole (**7**) as model reaction in gel phase.^a



Entry	MeCN (mL)	Yield 37 [%] ^b	Yield 38 [%] ^b
1	1	1	31
2	1.5	2	40
3	2	0	46
4	2.5	5	44
5	3	6	30

^a Reactants and conditions: *N*-methylpyrrole (**7**) (22 μ L, 0.25 mmol), TfCl (53 μ L, 0.5 mmol), Ru(phen)₃Cl₂ (1.8 mg, 0.01 mmol), K₂HPO₄ (131 mg, 0.75 mmol), MeCN, **G-1** (15 g L⁻¹), RT, 24 h, irradiation with 455 nm LED. ^b Yields were calculated by ¹⁹F NMR using hexafluorobenzene (29 μ L, 0.25 mmol) as internal standard.

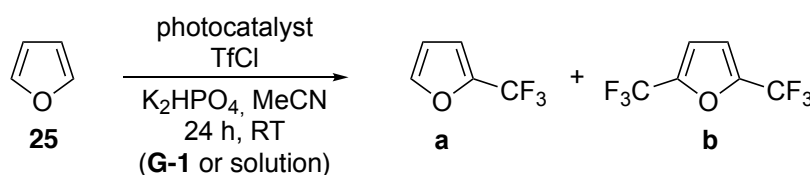
Table S9. Comparison of reactivity of *N*-methylpyrrole (**7**) under different conditions.^a



Entry	Conditions	TfCl (equiv)	Yield 37 [%] ^b	Yield 38 [%] ^b
1	Gel, bulb	1	35	1
2	Gel, bulb	2	4	26
3 ^c	Solution, bulb	1	58	2
4 ^c	Solution, bulb	2	9	38
5	Gel, 455 nm LEDs	1	36	1
6	Gel, 455 nm LEDs	2	5	44
7 ^c	Solution, 455 nm LEDs	1	58	2
8 ^c	Solution, 455 nm LEDs	2	1	45

^a Reactants and conditions: *N*-methylpyrrole (**7**) (22 μ L, 0.25 mmol), TfCl (22.5-53 μ L, 0.25-0.5 mmol), Ru(phen)₃Cl₂ (1.8 mg, 0.01 mmol), K₂HPO₄ (131 mg, 0.75 mmol), MeCN (2.5 mL), for reactions in gel phase **G-1** (20 g L⁻¹) was used as gelator, RT, 24 h, irradiation with 455 nm LED. ^b Yields were calculated by ¹⁹F NMR using hexafluorobenzene (29 μ L, 0.25 mmol) as internal standard. ^c Degassing via three freeze-pump-thaw cycles and then backfilled with nitrogen. Note: Interestingly, the formation of the corresponding disubstituted product **b** as major product was only significant when 2 equiv of TfCl were used regardless the solvent phase and irradiation source. Note: These values were initially obtained under non-optimized conditions with the only aim to compare bulb and LED irradiation. The yields provided in Figure 2 in the main text correspond to those obtained under optimized conditions.

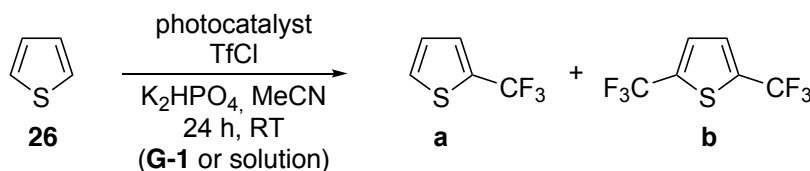
Table S10. Comparison of reactivity of furan (**25**) under different conditions comparing solvent phase and irradiation source.^a



Entry	Conditions	TfCl (equiv)	Yield a [%] ^b	Yield b [%] ^b
1	Gel, bulb	1	24	0
2	Gel, bulb	2	31	0
3 ^c	Solution, bulb	1	37	0
4 ^c	Solution, bulb	2	50	0
5	Gel, 455 nm LEDs	1	42	0
6	Gel, 455 nm LEDs	2	22	17
7 ^c	Solution, 455 nm LEDs	1	53	0
8 ^c	Solution, 455 nm LEDs	2	28	16

^a Reactants and conditions: Furan (**25**) (18 μL , 0.25 mmol), TfCl (22.5-53 μL , 0.25-0.5 mmol), Ru(phen)₃Cl₂ (1.8 mg, 0.01 mmol), K₂HPO₄ (131 mg, 0.75 mmol), MeCN (2 mL), for reactions in gel phase **G-1** (15 g L⁻¹) was used as gelator, RT, 24 h, irradiation with 455 nm LED or bulb light as indicated. ^b Yields were calculated by ¹⁹F NMR using hexafluorobenzene (29 μL , 0.25 mmol) as internal standard. ^c Degassing via three freeze-pump-thaw cycles and then backfilled with nitrogen. Note: In contrast to the behavior observed with *N*-methylpyrrole (**7**), the disubstituted product **b** in the case of less reactive furan (**25**) was only observed when 2 equiv of TfCl when LEDs were used regardless the solvent phase.

Table S11. Comparison of reactivity of thiophene (**26**) under different conditions.^a



Entry	Conditions	TfCl (equiv)	Yield a [%] ^b	Yield b [%] ^b
1	Gel, bulb	1	10	0
2	Gel, bulb	2	19	0
3 ^c	Solution, bulb	1	37	0
4 ^c	Solution, bulb	2	38	0
5	Gel, 455 nm LEDs	1	30	0
6	Gel, 455 nm LEDs	2	47	4
7 ^c	Solution, 455 nm LEDs	1	49	0
8 ^c	Solution, 455 nm LEDs	2	45	13

^a Reactants and conditions: Thiophene (**26**) (20 μL , 0.25 mmol), TfCl (22.5-53 μL , 0.25-0.5 mmol), Ru(phen)₃Cl₂ (1.8 mg, 0.01 mmol), K₂HPO₄ (131 mg, 0.75 mmol), MeCN (2 mL), for reactions in gel phase **G-1** (15 g L⁻¹) was used as gelator, RT, 24 h, irradiation with 455 nm LED or bulb light as indicated. ^b Yields were calculated by ¹⁹F NMR using hexafluorobenzene (29 μL , 0.25 mmol) as internal standard. ^c Degassing via three freeze-pump-thaw cycles and then backfilled with nitrogen. Note 1: It is worth to emphasize that for less reactive 5-membered heteroarenes such as **26** the use of LEDs was found to be superior than bulb irradiation. Note 2: Disubstituted product **b** was only observed with the use of LEDs and 2 equiv of TfCl.

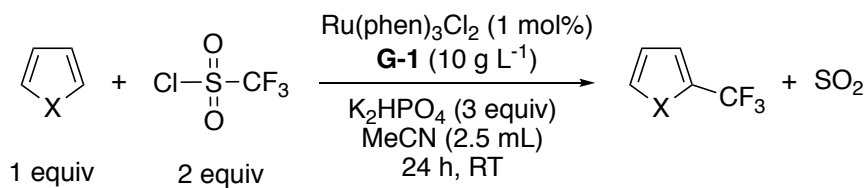
Table S12. Influence of the gelator on the reaction outcome.^a

<chem>CN1C=CC=C1</chem> 7 photocatalyst TfCl $\xrightarrow{\text{K}_2\text{HPO}_4, \text{MeCN}}$ <chem>CN1C=CC(=C1)C(F)(F)F</chem> 37 + <chem>CN1C=CC(=C1)C(F)(F)F</chem> 38 G-1, 24 h, RT				
Entry	Gelator	Gelator concentration (g L ⁻¹)	Yield 37 [%] ^b	Yield 38 [%] ^b
1	G-1	10	5	44
2 ^c	G-3	15	1	46
3 ^c	Fmoc-Lys(Fmoc)-OH ^d	20	36	29

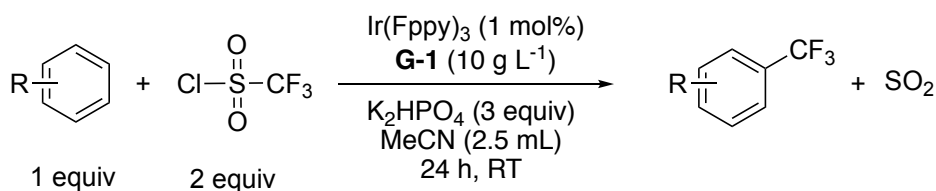
^a Reactants and conditions (unless otherwise noted): *N*-methylpyrrole (**7**) (22 μ L, 0.25 mmol), TfCl (53 μ L, 0.5 mmol), Ru(phen)₃Cl₂ (1.8 mg, 0.01 mmol), K₂HPO₄ (131 mg, 0.75 mmol), MeCN (2.5 mL), gelator, RT, 24 h, irradiation with 455 nm LED. ^b Yields were calculated by ¹⁹F NMR using hexafluorobenzene (29 μ L, 0.25 mmol) as internal standard. ^c 2 mL MeCN was used. Note: Gelator **G-2** was not tested due to difficulties to obtain an isotropic solution at high temperature. ^d **Fmoc-Lys(Fmoc)-OH** was purchased from Sigma-Aldrich (catalog number 47317). Note: Although a higher concentration was needed to form a stable gel with **Fmoc-Lys(Fmoc)-OH** compared to the other gelators, it demonstrated that the use of different gelators (and therefore different gel network structures) should be always taken into account for the optimization of intragel photo-induced processes in a similar way that different solvents are tested to optimized a given chemical reaction.

3.2. Schemes for general procedures and representative TLC analyses

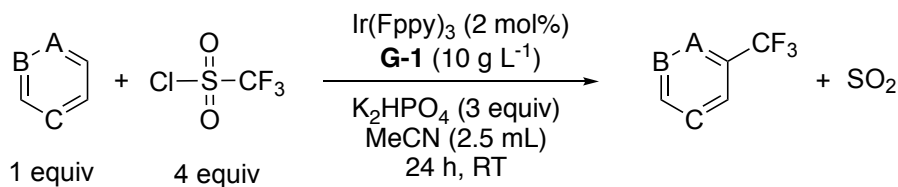
- General procedure A:



- General procedure B:



- General procedure C:



- General procedure D:

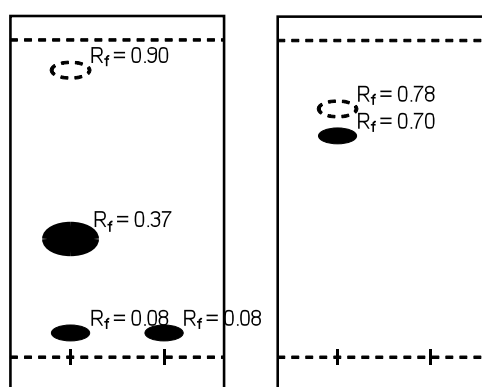
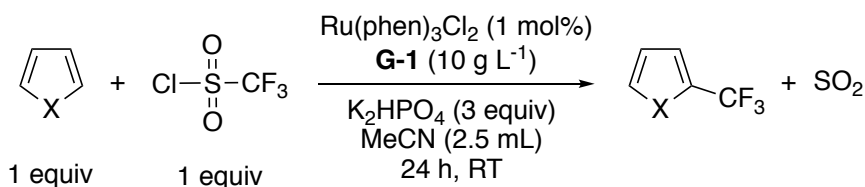


Figure S7. TLC analysis during the synthesis of compound **48**. *Left:* TLC (50% EtAc/PE). Di-substituted product: $R_f = 0.90$. (Monosubstituted) product: $R_f = 0.37$. Educt: $R_f = 0.08$. *Right:* TLC (4:4:1 PE:EtAc:MeOH). Product: $R_f = 0.70$.

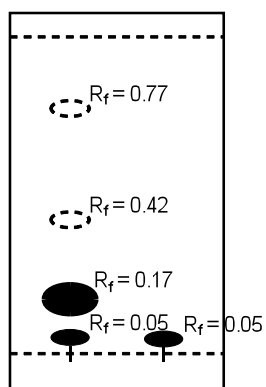


Figure S8. TLC analysis during the synthesis of compound **49**. TLC (25% EtAc/PE). Product: R_f = 0.17. Educt: R_f = 0.05.

3.3. Oscillatory rheology

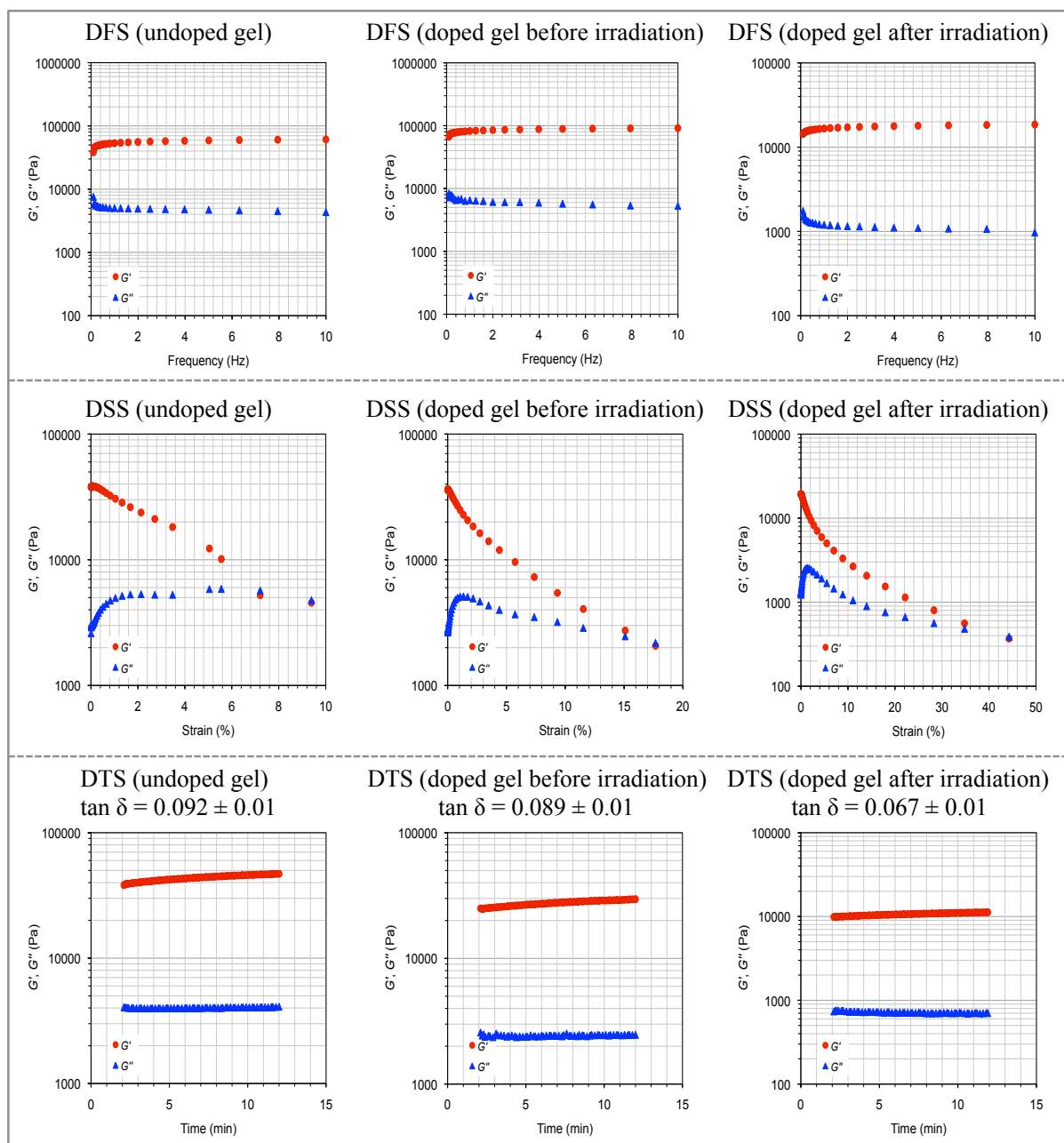


Figure S9. Typical oscillatory rheological experiments of model undoped and doped brittle gels. Conditions for preparing the doped gel: 2-Methylfuran (18 μL , 0.25 mmol), $\text{Ru}(\text{phen})_3\text{Cl}_2$ (1.8 mg, 0.01 mmol), TfCl (53 μL , 0.5 mmol), **G-1** = 10 g L^{-1} , K_2HPO_4 (131 mg, 0.75 mmol), MeCN (2.5 mL). Irradiation conditions: λ_{ex} = 455 ($\pm$ 15) nm LED, 24 h. Product yield = 55%.

Note: T_{gel} of undoped gel made remained practically constant within the experimental error upon doping and irradiation, i.e., T_{gel} of doped gel before irradiation = 67 ± 2 $^{\circ}\text{C}$; T_{gel} of doped gel after irradiation = 65 ± 2 $^{\circ}\text{C}$.

3.4. NMR spectra

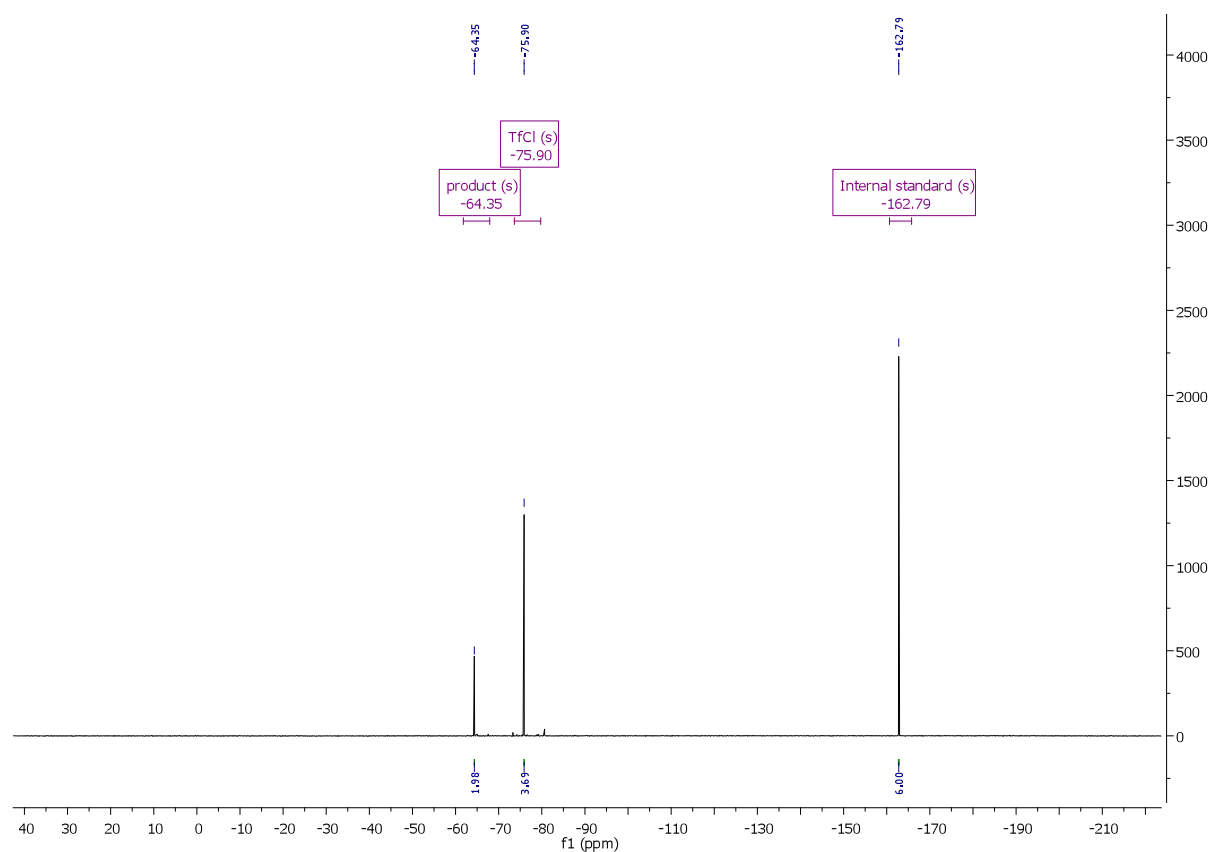
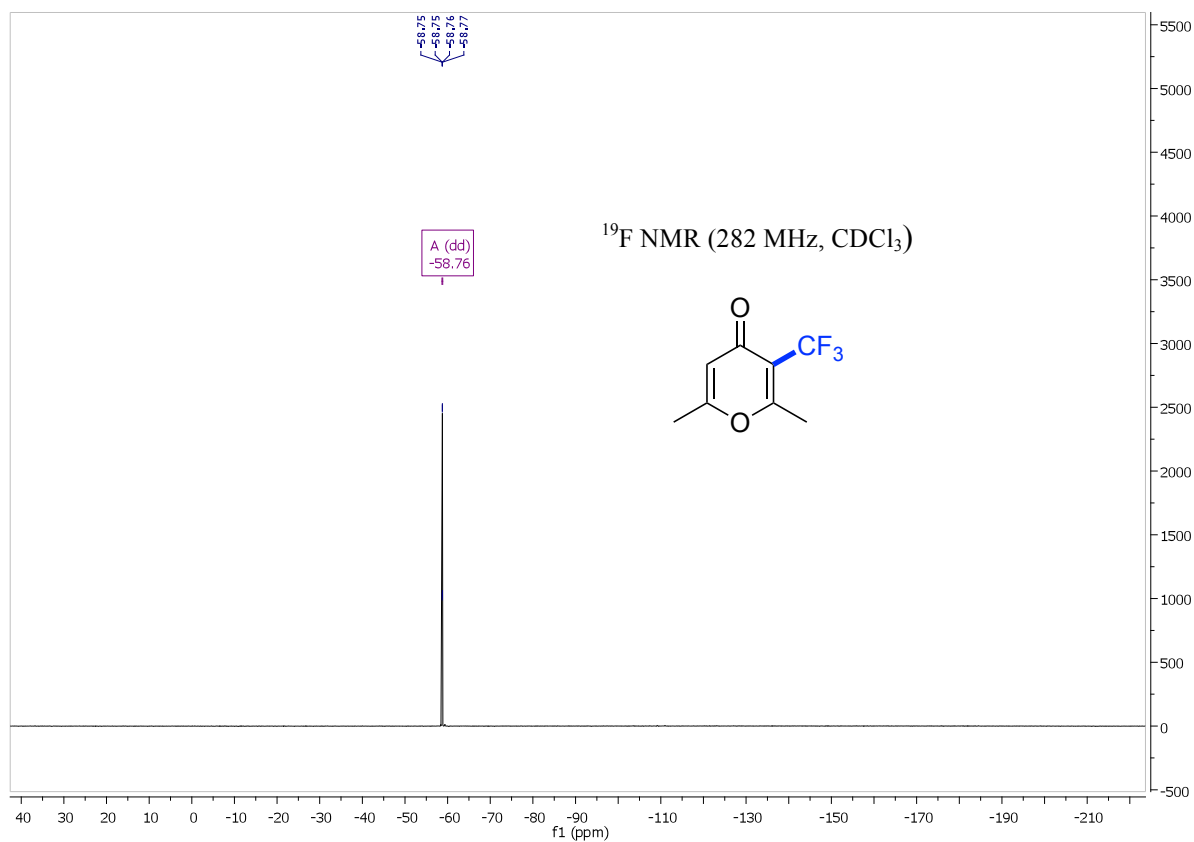
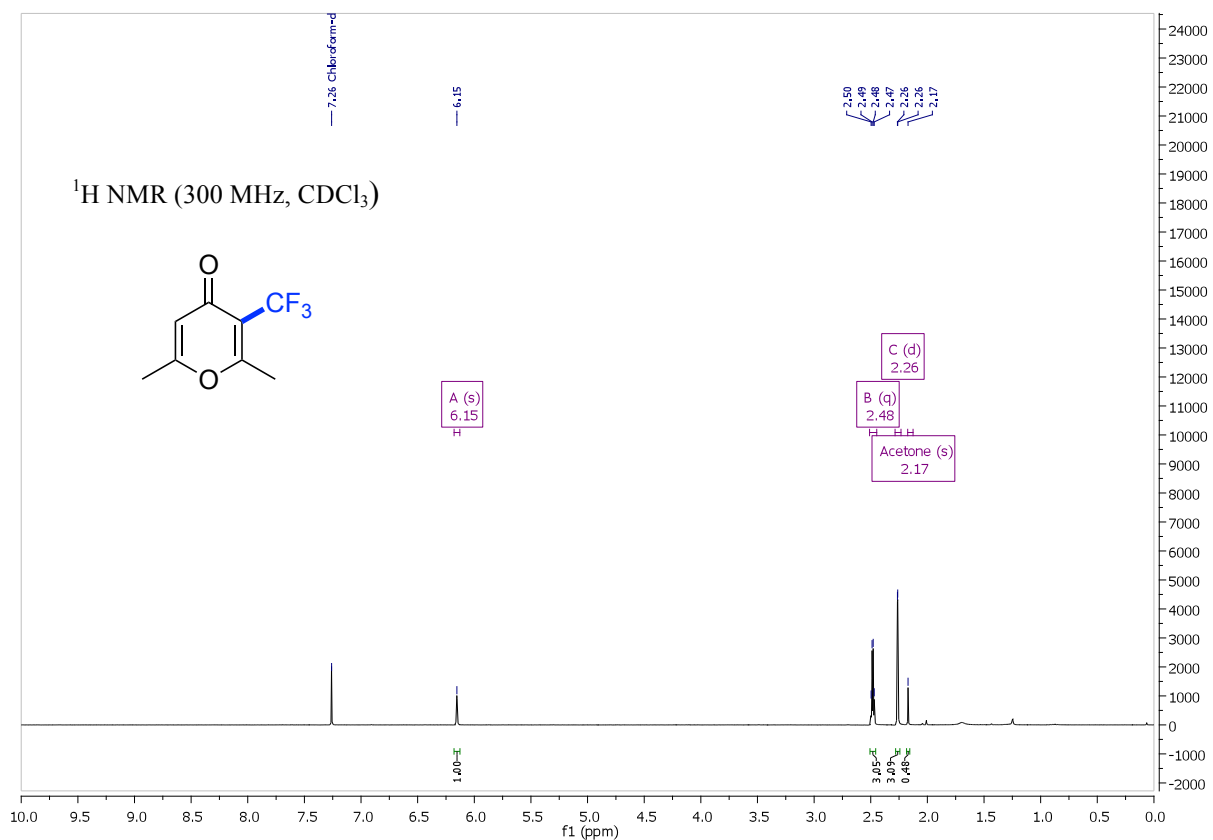
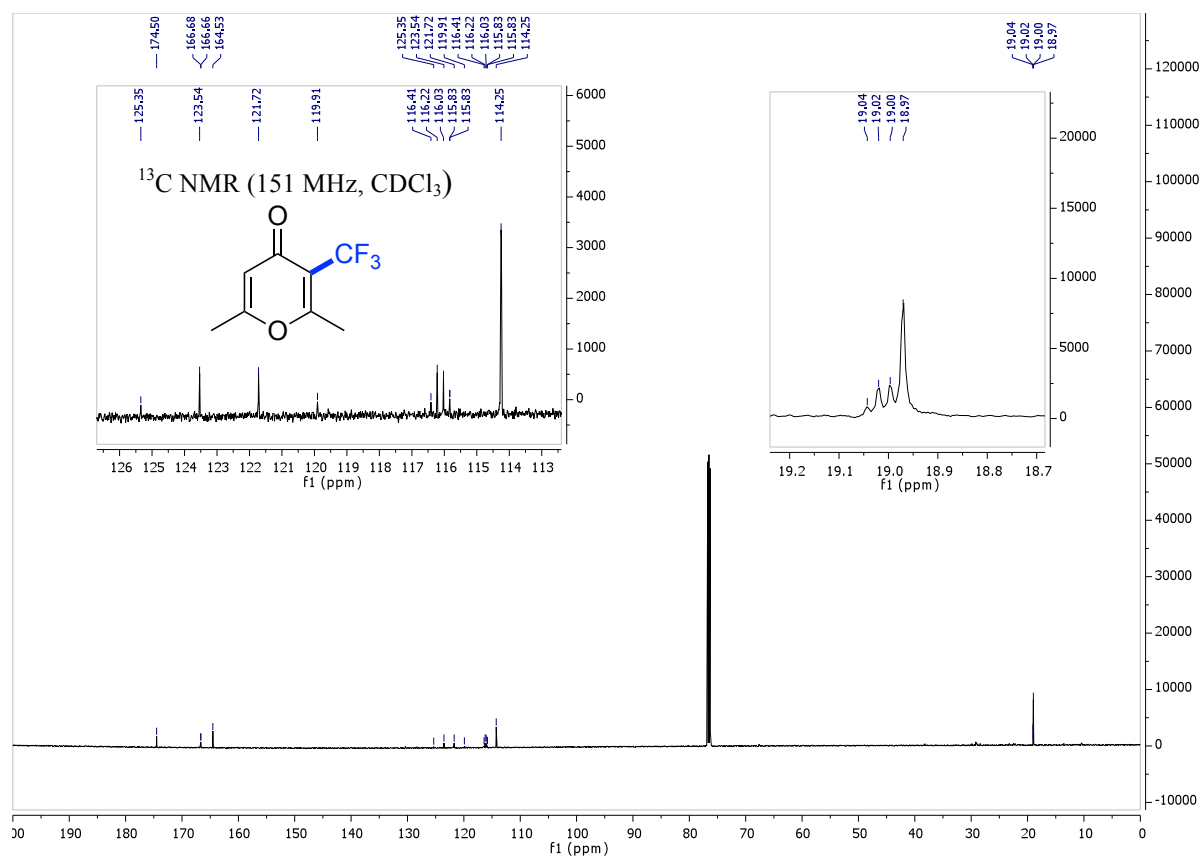


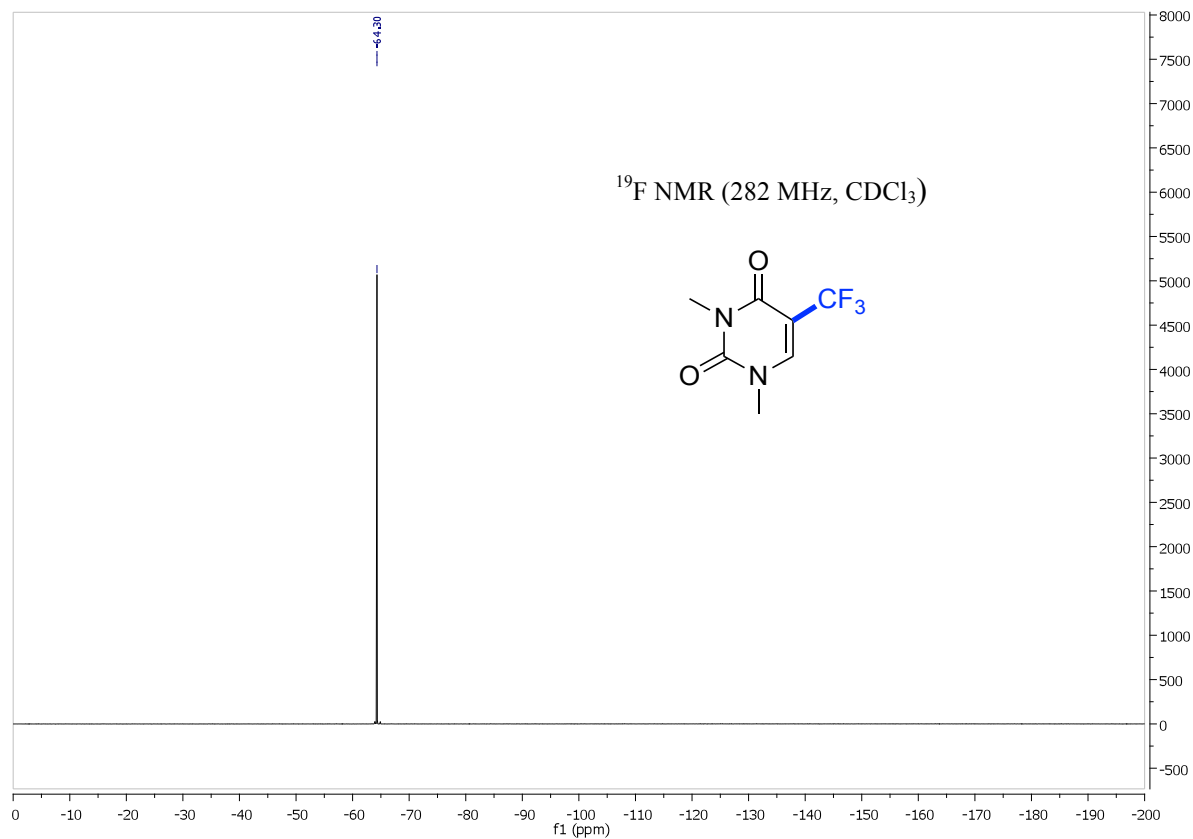
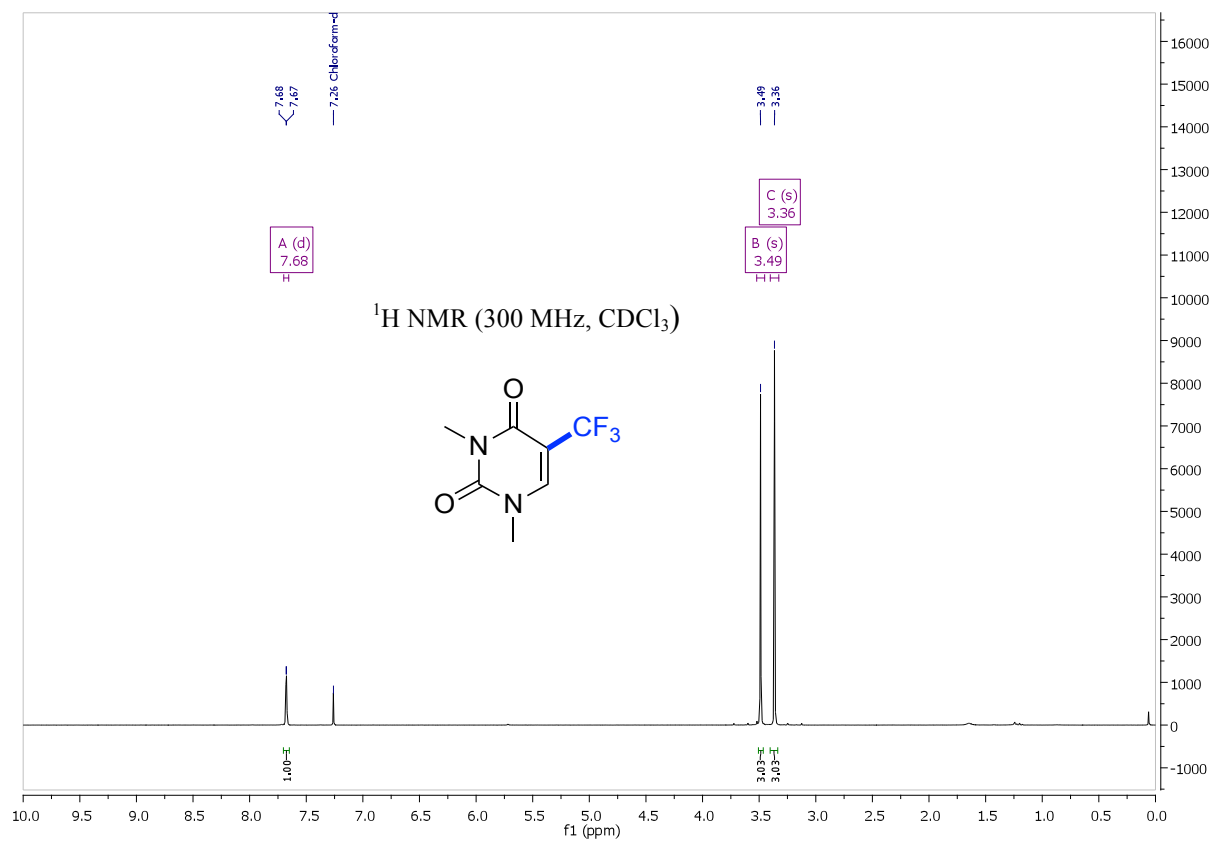
Figure S10. ^{19}F NMR spectrum of CF_3 - γ -pyranone with hexafluorobenzene as internal standard (0.25 mmol) and TfCl residues.

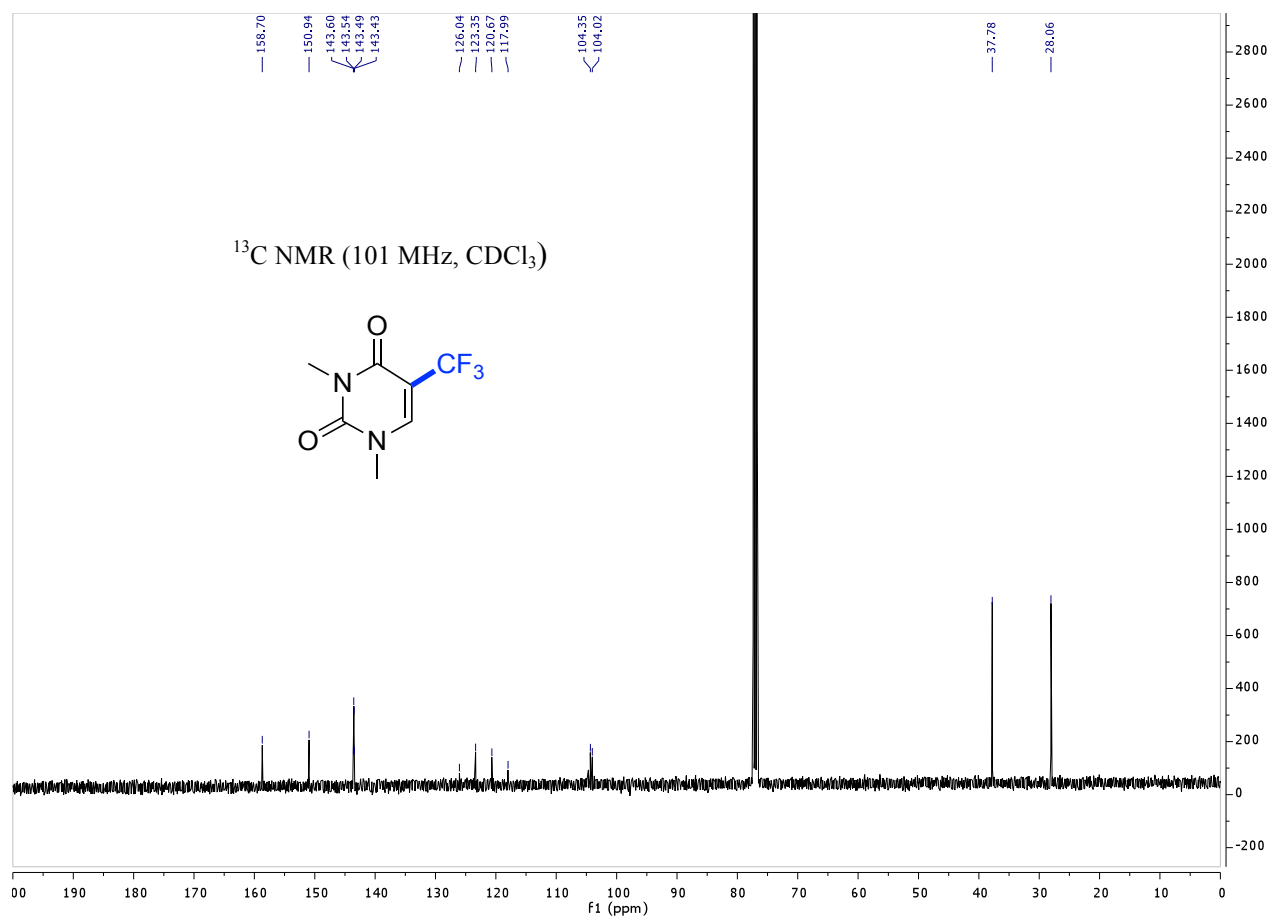
2,6-Dimethyl-3-trifluoromethyl- γ -pyranone (48):





1,3-Dimethyl-5-trifluoromethyluracil (49):





4. Additional supporting experiments and information

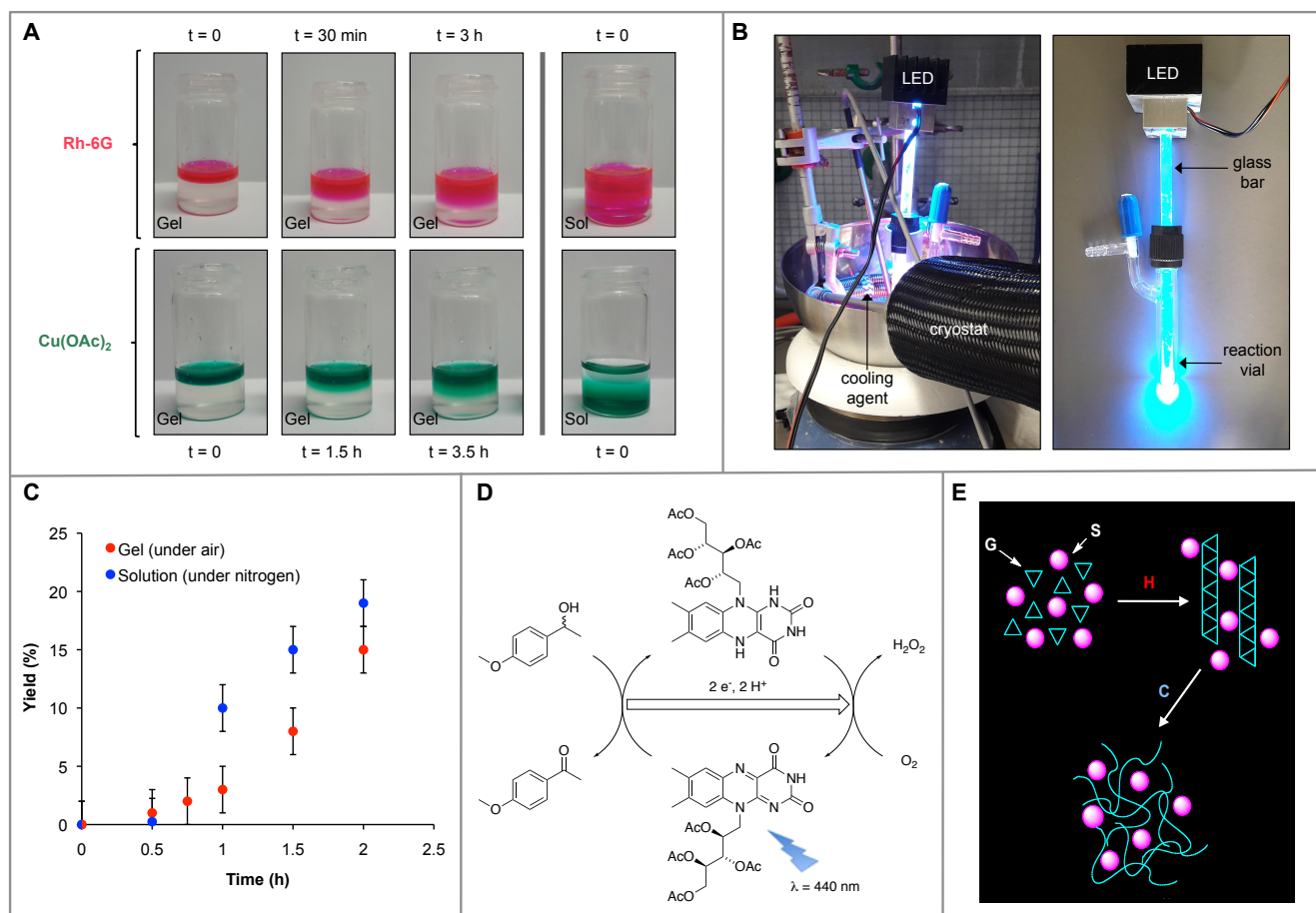


Figure S11. Additional supporting figures. A) Qualitative visualization of the slow diffusion of small molecules such as **Rh-6G** or $\text{Cu}(\text{OAc})_2$ through the interface liquid-gel at RT. A DMSO-solution of the corresponding dye was slowly poured on top of the preformed gel made of gelator **G-1** (15 mg L^{-1}) in DMSO. In contrast, diffusion of the dyes in solution was almost instantaneous (liquid-liquid diffusion). Note: Diameter of $\text{O}_2 \approx 3.5 \text{ \AA}$; diameter of $\text{Cu}(\text{OAc})_2 \approx 7 \text{ \AA}$. It should be considered that the diffusion of small molecules into the supramolecular gel network depends on multiple factors including, among others, the molecular size and physical state of the diffusant, the morphology of the network, the compatibility or solubility limit of the solute within the gel matrix, the volatility of the solute, and the interfacial energies.¹ B) Typical set-up used to perform individual reactions at low temperature using 2-propanol as cooling agent. At low temperature the viscosity of the medium increases and molecular diffusion decreases. In solution, small amounts of O_2 that may stay even after the degassing step can be consumed via an electron transfer event (i.e., molecular oxygen takes an electron from the reduced **Rh-6G**).² C) Kinetics profile within the first two hours of the model reaction between **1** and **7** in solution under nitrogen and in gel under air as described in the experimental section. Conditions: **1** (0.1 mmol), **Rh-6G** (0.015 mmol), **7** (1.8 mmol), DIPEA (0.22 mmol), **G-1** (15 g L^{-1}), DMSO (1.5 mL). No significant differences were observed between the two curves after 2 h. The apparent induction period within the first hour was observed for both solution and gel, being not conclusive as the data points obtained by GC lie within the experimental error. D) Mechanistic cycle of riboflavin tetraacetate (RFT)-catalyzed aerobic photooxidation of 1-(4-methoxyphenyl)ethanol. The reaction was successfully carried out inside the gel made of **G-1** (15 g L^{-1}) in MeCN leading to the formation of the corresponding ketone in 63% yield. The result is in agreement with our previous observations³ and demonstrates that the oxygen present in aerated gels can be active for other processes. Experimental procedure: RFT ($50 \text{ }\mu\text{L}$ from a 0.01 M in CH_2Cl_2) and the alcohol ($50 \text{ }\mu\text{L}$ from a 0.1 M in CH_2Cl_2) were added to a 5 mL vial containing 10 mg of **G-1**. The solvent was then allowed to evaporate and then 1 mL MeCN was added. The mixture was gently heated until everything was dissolved. The mixture was allowed to cool to RT leading to gel formation. After an equilibration period (12 h), the samples were subjected to LED irradiation (440 nm). After 1 h the gel was dissolved by dilution, heating, and mechanical agitation. 1 mL water was added and extracted with ethyl acetate ($5 \times 5 \text{ mL}$). The combined organic layers were dried over Na_2SO_4 , filtered, and evaporated. The residue was redissolved in CDCl_3 for NMR analysis. Yield was determined by the ratio between starting alcohol and formed ketone. E) General illustration showing the gelation mechanism of LMW gelators. Abbreviations: G = gelator molecules; S = solvent molecules; H = heating; C = cooling. The photoinduced reactions described in this paper most likely take place within the solvent pools immobilized between the gel fibers without incorporation of the reactants in the fibers. Note: Homogeneous distribution of reactants and products through the supramolecular gel matrix was previously demonstrated using different gelators.³

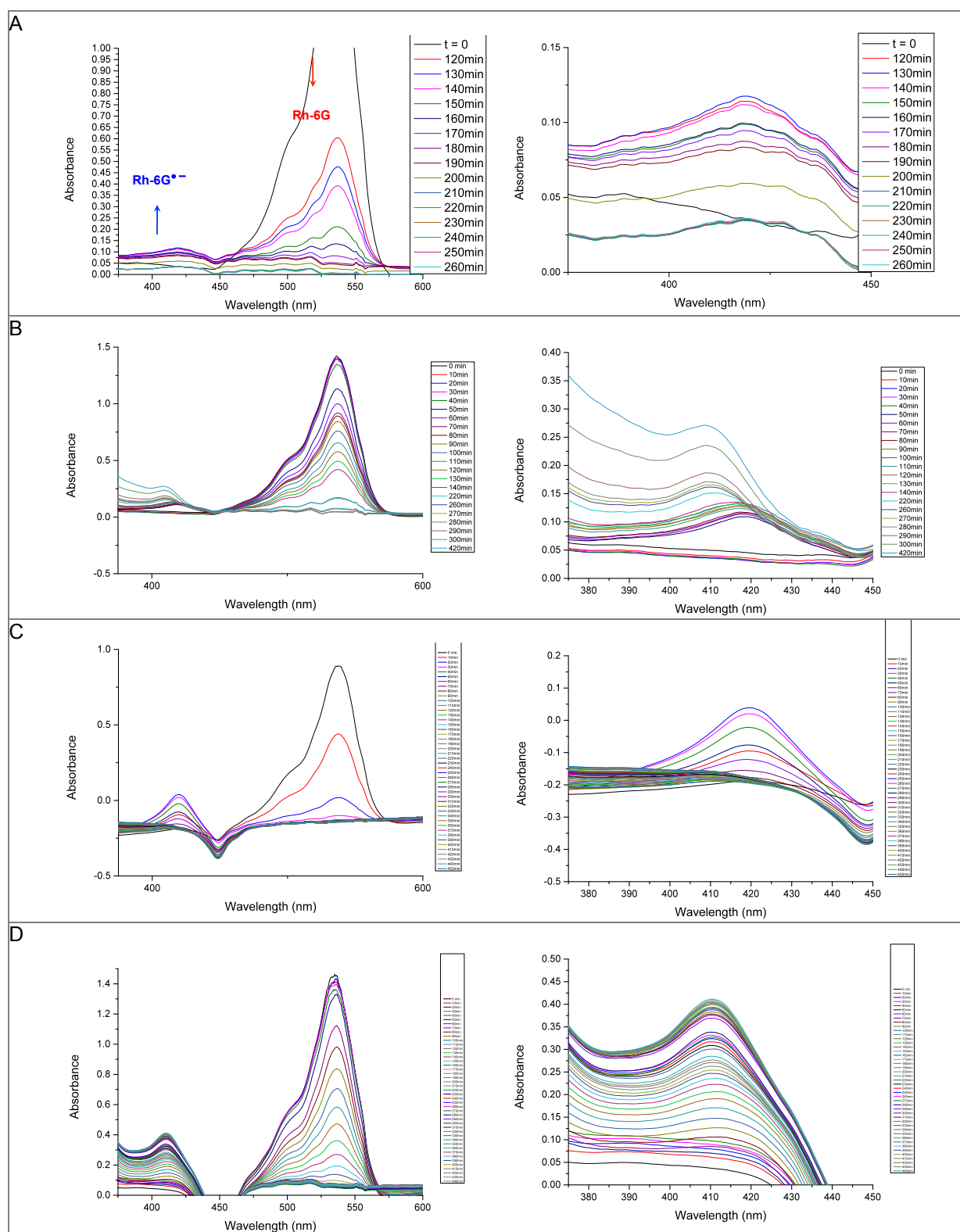


Figure S12. Selected UV-Vis spectra recorded during irradiation of rhodamine-based photocatalytic system under different conditions as described in the Experimental Section. Constant parameters: **Rh-6G** (16.7 mM), DIPEA (50 mL), DMSO (3.0 mL), irradiation at $\lambda_{\text{ex}} = 455$ nm. For reactions in gel medium, gelator **G-1** (10 g L^{-1}) was used. Variables: A) Solution under N_2 atmosphere. B) Solution in air. C) Gel under N_2 atmosphere. D) Gel in air. Plots on the right side correspond to zoomed zone of the radical anion $[\text{Rh-6G}^{\bullet-}]$. The deactivation pathway of the radical anion in aerated media is clearly different to that under inert conditions. The protection offered by the gel matrix against aerobic deactivation of photocatalytic species most likely involves excited species generated after the first step of the catalytic cycle, which is in agreement with the phosphorescence measurements (see below).

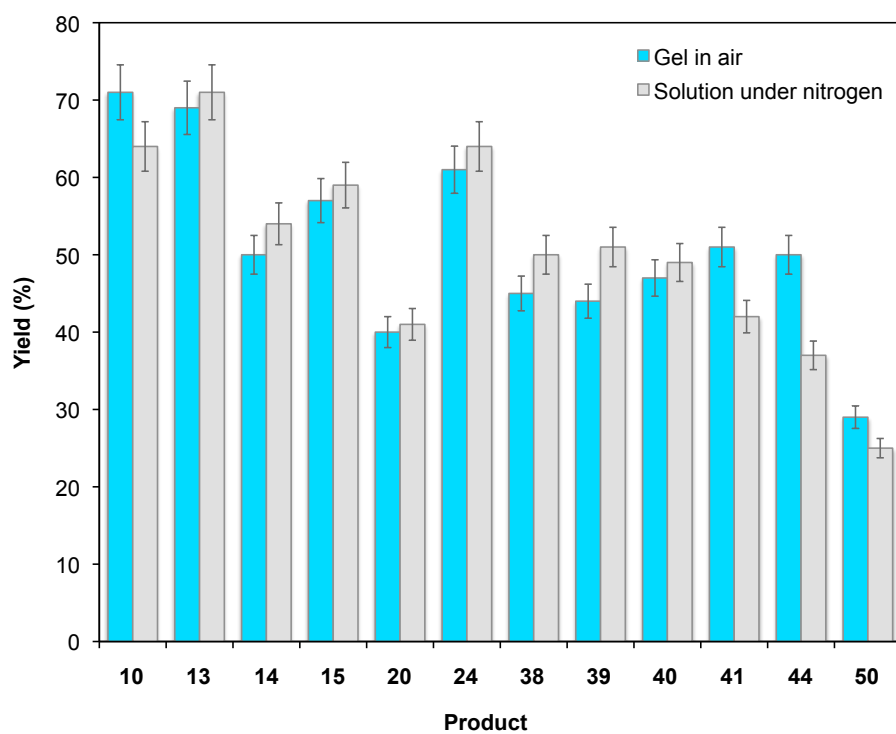


Figure S13. Comparative yields obtained from representative reactions carried out in solution under N₂ atmosphere (in the absence of gelator) and in gel in air under comparable conditions (see Figures 1-2 in main text). Product numbers as given in the main text are indicated in each case in the X-axis.

5. Phosphorescence measurements

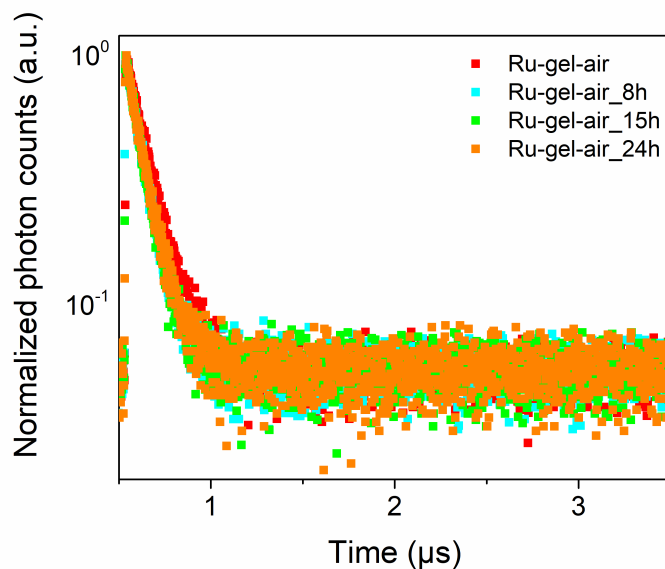


Figure S14. Photoluminescence decays at 605 nm ($\lambda_{\text{ex}} = 405$ nm) of Ru(phen)₃Cl₂ in aerated **G-1** gel before and after photoirradiation (xenon lamp with 450 nm band-pass filter) for 8 h, 15 h and 24 h.

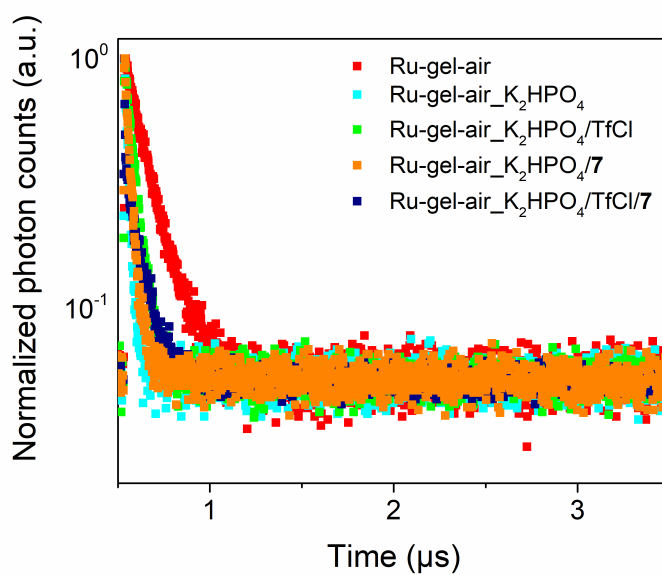


Figure S15. Photoluminescence decays at 605 nm ($\lambda_{\text{ex}} = 405$ nm) of Ru(phen)₃Cl₂ in aerated **G-1** gel with additives such as K₂HPO₄, TfCl and **7**.

7. References

- (1) Oxygen solubility (mM/cm^3) in DMSO is 2.10, whereas in MeCN is 8.1. See, Sawyer, D. T.; Chiericato, G.; Angelis, C. T.; Nanni, E. J.; Tsuchiya, T. Effects of media and electrode materials on the electrochemical reduction of dioxygen. *Anal. Chem.* **1982**, *54*, 1720–1724.
- (2) Ghosh, I.; König, B. Chromoselective photocatalysis: Controlled bond activation through light-color regulation of redox potentials. *Angew. Chem. Int. Ed.* **2016**, *55*, 7676–7679.
- (3) Bachl, J.; Hohenleutner, A.; Dhar, B. B.; Cativiela, C.; Maitra, U.; König, B.; Díaz, D. D. Organophotocatalysis in nanostructured soft gel materials as tunable reaction vessels: comparison with homogeneous and micellar solutions. *J. Mater. Chem. A* **2013**, *1*, 4577–4588.